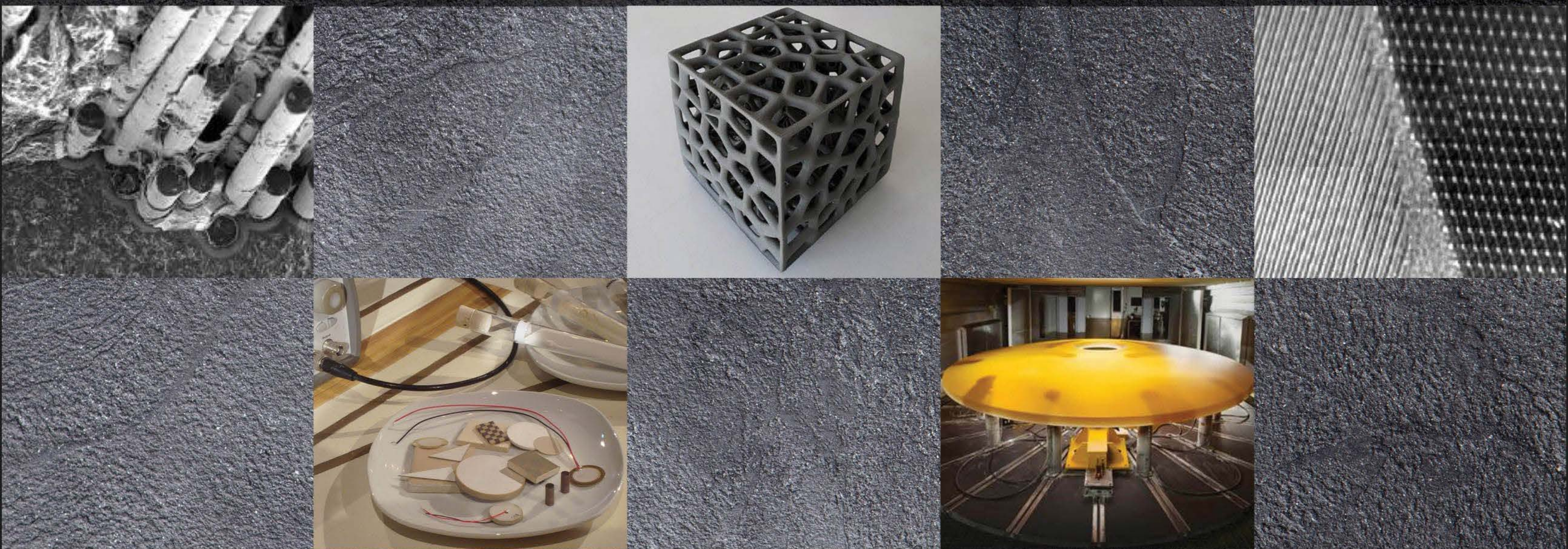


ENCYCLOPEDIA OF MATERIALS

TECHNICAL CERAMICS AND GLASSES



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ENCYCLOPEDIA OF MATERIALS TECHNICAL CERAMICS AND GLASSES

Volume 1

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Volume 1



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CONTENT OF VOLUME 1

List of Contributors for Volume 1	ix
Content of All Volumes	xiii
Editor Biographies	xxiii
Preface	xxv

VOLUME 1

Overview: Manufacture of Ceramics and Microstructural Developments in Ceramics <i>Francis Cambier and Anne Leriche</i>	1
Synthesis of Oxide and Non-Oxide Advanced Ceramics <i>Prashant N Kumta</i>	2
Synthesis of Ceramic Powders by Wet Chemical Routes <i>Paola Palmero</i>	27
Self-Propagating High-Temperature Synthesis <i>Jerzy Lis</i>	40
Hydrothermal Synthesis <i>Ender Suvaci and Emel Özel</i>	59
Ultrasonic Sprayed Aerosol for Ultrafine Ceramic Powder Synthesis <i>Sylvie Foucaud and Yann Leconte</i>	69
Calcination and Phase Transformations <i>Gary L Messing</i>	83
Preceramic Polymers as Precursors of Advanced Ceramics: The Polymer-Derived Ceramics (PDCs) Route <i>Yuji Iwamoto, Günter Motz, Emanuel Ionescu, and Samuel Bernard</i>	93
Organic Additives in Ceramic Processing <i>Anne Aimable and Thierry Chartier</i>	103
Powder Mixing and Grinding Processes for Ceramics <i>David Houivet and Jérôme Bernard</i>	112
Powder Granulation and Compaction <i>Michele Dondi</i>	136
Colloid Casting Processes: Slip Casting, Centrifugal Casting, and Gel Casting <i>Nur S Yüzbaşı and Thomas Graule</i>	146
Processing of Ceramics by Direct Coagulation Casting <i>Margarida Almeida and Joaquim M Vieira</i>	154
Extrusion <i>Stuart Blackburn and Marcin Szymiczek</i>	162

Ceramic Injection Molding <i>Moritz v Witzleben and Tassilo Moritz</i>	179
Tape Casting and Lamination <i>Eric R Twiname</i>	189
Freeze Casting <i>Dominique Hautcoeur</i>	195
Additive Manufacturing <i>Andrea Zocca, Giorgia Franchin, Paolo Colombo, and Jens Günster</i>	203
Green Machining of Ceramics <i>Fabrice Petit</i>	222
Screen Printing <i>Danjela Kuscer</i>	227
Sintering of Ceramics: An Overview <i>Anne Leriche, Francis Cambier, and Stuart Hampshire</i>	233
Solid-State Sintering <i>John E Blendell and Wolfgang Rheinheimer</i>	249
Liquid Phase Sintering: Fundamentals <i>Suk-Joong L Kang</i>	258
Viscous Sintering <i>George W Scherer</i>	265
Hot Pressing and Hot Isostatic Pressing <i>Mathias Herrmann and Jan Räthel</i>	270
Reaction Sintering <i>Carmen Baudin</i>	278
Flash Sintering and Other Rapid Sintering Techniques <i>David Salamon</i>	286
Spark Plasma Sintering <i>Umberto Anselmi-Tamburini</i>	294
Cold Sintering and Hydrothermal Sintering <i>Graziella Goglio, Arnaud Ndayishimiye, Catherine Elissalde, and Clive A Randall</i>	311
Microwave Sintering of Ceramics <i>Jean-Marc Chaix</i>	327
Porous Ceramics Processing <i>Manabu Fukushima, Akihiro Shimamura, Paolo Colombo, Hideki Hyuga, Tatsuki Ohji, and Yu-ichi Yoshizawa</i>	342
Porous Ceramics Including Fibrous Insulation, Structure and Properties of <i>M Fukushima, T Ohji, P Colombo, and Y-I Yoshizawa</i>	346
Control of the Microstructure in Ceramics <i>Anne Leriche, Stuart Hampshire, and Francis Cambier</i>	349
Templated Grain Growth of Textured Ceramics <i>Gary L Messing</i>	367
Functionally Graded Ceramics <i>Omer Van der Biest and Achim Neubrand</i>	374
Transparent Ceramics: Materials, Processing, Properties and Applications <i>Marc Rubat du Merac</i>	399

Geopolymers and Geopolymer-Derived Composites <i>Waltraud M Kriven</i>	424
Overview: Characterization and Modelling of Ceramics and Glasses <i>Michael Pomeroy and Stuart Hampshire</i>	439
Ceramic Genomics: Total Bond Order Density <i>Wai-Yim Ching</i>	441
Predictive Modeling of Ceramic Materials <i>Sarah Guerin, Syed AM Tofail, and Damien Thompson</i>	475
Molecular Dynamics Simulations of Glass Structure <i>Mattias Edén</i>	481
Computation of Phase Diagrams for Ceramics <i>Sara Serena, Angel Caballero, Antonio H de Aza, and Maria A Sainz</i>	498
Characterization of Ceramic Powders <i>Martin J Murtagh and Navin Venugopal</i>	517
Amorphous Materials: Vibrational Spectroscopy <i>PF McMillan</i>	530
MAS NMR Analysis of Ceramics and Glasses <i>Yajie Gao</i>	536
X-Ray Powder Diffraction <i>Scott T Misture</i>	549
Case Studies in the X-ray Diffraction of Ceramics <i>Maurice Gonon</i>	560
Introduction to Transmission Electron Microscopy; The Basics <i>Ann-Katrin Fetzter, Maximilian Trapp, Stefan Lauterbach, and Hans-Joachim Kleebe</i>	578
High Resolution Analytical Electron Microscopy of Ceramics and Glasses <i>Jennifer Cookman, Michele Conroy, and Ursel Bangert</i>	600
Introduction to Three Dimensional Electron Crystallography <i>Andrew Stewart and Ute Kolb</i>	618
Preparation of Ceramic, Glass-Ceramic and Glasses for Microstructural Examination <i>Michael J Pomeroy</i>	634
Scanning Electron Microscopy for Ceramics and Glasses <i>Michael J Pomeroy</i>	651
Fractography: Brittle Materials <i>John J Mecholsky, Jr.</i>	662
Thermal Analysis Techniques for Technical Ceramics and Glasses <i>Michael J Pomeroy</i>	676
High-Temperature Characterization of Glasses and Melts <i>Sohei Sukenaga and Hiroyuki Shibata</i>	689
Overview: Mechanical and Physical Properties and Property Testing of Ceramics and Glasses <i>Anne Leriche and Francis Cambier</i>	704
Elastic and Inelastic Behavior of Ceramics <i>Daniele Mari and Robert Schaller</i>	705
Indentation of Ceramics <i>Emilio Jiménez-Piqué</i>	718

Contact Damage Resistance and Tribological Behavior of Ceramic/Carbon Nanostructure Composites <i>Manuel Belmonte</i>	733
Methods of Determination of Young's Modulus and Tensile, Flexural and Compressive Strength <i>Sylvain Meille</i>	745
Fracture Toughness Measurement <i>Tanja Lube</i>	762
R-Curve Behavior of Ceramics <i>Marc J Anglada</i>	775
Subcritical Crack Growth: Basic Relations and Experimental Evaluation <i>Malika Saâdaoui</i>	797
Subcritical Crack Growth: Modeling of the v-K Curve in Different Environments <i>Raul Bermejo</i>	811
Ceramics: Transformation Toughening <i>DB Marshall and RHJ Hannink</i>	818
Mixed-Mode Fracture and Microstructural Aspects of Crack Propagation <i>Delia Gutiérrez-Campos and Yuk Ming X Hung-Hung</i>	823
R-Ratio and Microstructure Effects <i>Delia Gutiérrez-Campos, Eliana Pinto-González, and Elvira Saab-Llatas</i>	841
Thermal Properties of Ceramic Materials <i>David S Smith and Benoît Naït-Ali</i>	855
Thermal Shock Behavior of Ceramics: Fundamentals and Thermal Shock Resistance Parameters <i>Carmen Baudín</i>	867
Thermal Shock and Thermal Fatigue Behavior of Ceramics: Microstructural Effects <i>Gilbert Fantozzi and Malika Saâdaoui</i>	879
Creep Behavior of Ceramics <i>Gilbert Fantozzi and Arturo Dominguez-Rodriguez</i>	891
Nonoxide Ceramics, Creep and Creep Rupture of: Silicon Nitrides and Silicon Carbides <i>SM Wiederhorn</i>	908
Dislocations in Ceramic Materials <i>Jacques Rabier</i>	911
Corrosion of Ceramics in Aqueous Environments <i>Mathias Herrmann</i>	921
Corrosion and Degradation of Glass <i>Dagmar Galusková and Dušan Galusek</i>	932

LIST OF CONTRIBUTORS FOR VOLUME 1

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CONTENT OF ALL VOLUMES

List of Contributors for Volume	ix
Editor Biographies	xxiii
Preface	xxv

VOLUME 1

Overview: Manufacture of Ceramics and Microstructural Developments in Ceramics <i>Francis Cambier and Anne Leriche</i>	1
Synthesis of Oxide and Non-Oxide Advanced Ceramics <i>Prashant N Kumta</i>	2
Synthesis of Ceramic Powders by Wet Chemical Routes <i>Paola Palmero</i>	27
Self-Propagating High-Temperature Synthesis <i>Jerzy Lis</i>	40
Hydrothermal Synthesis <i>Ender Suvaci and Emel Özel</i>	59
Ultrasonic Sprayed Aerosol for Ultrafine Ceramic Powder Synthesis <i>Sylvie Foucaud and Yann Leconte</i>	69
Calcination and Phase Transformations <i>Gary L Messing</i>	83
Preceramic Polymers as Precursors of Advanced Ceramics: The Polymer-Derived Ceramics (PDCs) Route <i>Yuji Iwamoto, Günter Motz, Emanuel Ionescu, and Samuel Bernard</i>	93
Organic Additives in Ceramic Processing <i>Anne Aimable and Thierry Chartier</i>	103
Powder Mixing and Grinding Processes for Ceramics <i>David Houivet and Jérôme Bernard</i>	112
Powder Granulation and Compaction <i>Michele Dondi</i>	136
Colloid Casting Processes: Slip Casting, Centrifugal Casting, and Gel Casting <i>Nur S Yüzbaşı and Thomas Graule</i>	146
Processing of Ceramics by Direct Coagulation Casting <i>Margarida Almeida and Joaquim M Vieira</i>	154
Extrusion <i>Stuart Blackburn and Marcin Szymiczek</i>	162
Ceramic Injection Molding <i>Moritz v Witzleben and Tassilo Moritz</i>	179

Tape Casting and Lamination <i>Eric R Twiname</i>	189
Freeze Casting <i>Dominique Hautcoeur</i>	195
Additive Manufacturing <i>Andrea Zocca, Giorgia Franchin, Paolo Colombo, and Jens Günster</i>	203
Green Machining of Ceramics <i>Fabrice Petit</i>	222
Screen Printing <i>Danjela Kuscser</i>	227
Sintering of Ceramics: An Overview <i>Anne Leriche, Francis Cambier, and Stuart Hampshire</i>	233
Solid-State Sintering <i>John E Blendell and Wolfgang Rheinheimer</i>	249
Liquid Phase Sintering: Fundamentals <i>Suk-Joong L Kang</i>	258
Viscous Sintering <i>George W Scherer</i>	265
Hot Pressing and Hot Isostatic Pressing <i>Mathias Herrmann and Jan Räthel</i>	270
Reaction Sintering <i>Carmen Baudín</i>	278
Flash Sintering and Other Rapid Sintering Techniques <i>David Salamon</i>	286
Spark Plasma Sintering <i>Umberto Anselmi-Tamburini</i>	294
Cold Sintering and Hydrothermal Sintering <i>Graziella Goglio, Arnaud Ndayishimiye, Catherine Elissalde, and Clive A Randall</i>	311
Microwave Sintering of Ceramics <i>Jean-Marc Chaix</i>	327
Porous Ceramics Processing <i>Manabu Fukushima, Akihiro Shimamura, Paolo Colombo, Hideki Hyuga, Tatsuki Ohji, and Yu-ichi Yoshizawa</i>	342
Porous Ceramics Including Fibrous Insulation, Structure and Properties of <i>M Fukushima, T Ohji, P Colombo, and Y-I Yoshizawa</i>	346
Control of the Microstructure in Ceramics <i>Anne Leriche, Stuart Hampshire, and Francis Cambier</i>	349
Templated Grain Growth of Textured Ceramics <i>Gary L Messing</i>	367
Functionally Graded Ceramics <i>Omer Van der Biest and Achim Neubrand</i>	374
Transparent Ceramics: Materials, Processing, Properties and Applications <i>Marc Rubat du Merac</i>	399
Geopolymers and Geopolymer-Derived Composites <i>Waltraud M Kriven</i>	424

Overview: Characterization and Modelling of Ceramics and Glasses <i>Michael Pomeroy and Stuart Hampshire</i>	439
Ceramic Genomics: Total Bond Order Density <i>Wai-Yim Ching</i>	441
Predictive Modeling of Ceramic Materials <i>Sarah Guerin, Syed AM Tofail, and Damien Thompson</i>	475
Molecular Dynamics Simulations of Glass Structure <i>Mattias Edén</i>	481
Computation of Phase Diagrams for Ceramics <i>Sara Serena, Angel Caballero, Antonio H de Aza, and Maria A Sainz</i>	498
Characterization of Ceramic Powders <i>Martin J Murtagh and Navin Venugopal</i>	517
Amorphous Materials: Vibrational Spectroscopy <i>PF McMillan</i>	530
MAS NMR Analysis of Ceramics and Glasses <i>Yajie Gao</i>	536
X-Ray Powder Diffraction <i>Scott T Mixture</i>	549
Case Studies in the X-ray Diffraction of Ceramics <i>Maurice Gonon</i>	560
Introduction to Transmission Electron Microscopy; The Basics <i>Ann-Katrin Fetzer, Maximilian Trapp, Stefan Lauterbach, and Hans-Joachim Kleebe</i>	578
High Resolution Analytical Electron Microscopy of Ceramics and Glasses <i>Jennifer Cookman, Michele Conroy, and Ursel Bangert</i>	600
Introduction to Three Dimensional Electron Crystallography <i>Andrew Stewart and Ute Kolb</i>	618
Preparation of Ceramic, Glass-Ceramic and Glasses for Microstructural Examination <i>Michael J Pomeroy</i>	634
Scanning Electron Microscopy for Ceramics and Glasses <i>Michael J Pomeroy</i>	651
Fractography: Brittle Materials <i>John J Mecholsky, Jr.</i>	662
Thermal Analysis Techniques for Technical Ceramics and Glasses <i>Michael J Pomeroy</i>	676
High-Temperature Characterization of Glasses and Melts <i>Sohei Sukenaga and Hiroyuki Shibata</i>	689
Overview: Mechanical and Physical Properties and Property Testing of Ceramics and Glasses <i>Anne Leriche and Francis Cambier</i>	704
Elastic and Inelastic Behavior of Ceramics <i>Daniele Mari and Robert Schaller</i>	705
Indentation of Ceramics <i>Emilio Jiménez-Piqué</i>	718
Contact Damage Resistance and Tribological Behavior of Ceramic/Carbon Nanostructure Composites <i>Manuel Belmonte</i>	733

Methods of Determination of Young's Modulus and Tensile, Flexural and Compressive Strength <i>Sylvain Meille</i>	745
Fracture Toughness Measurement <i>Tanja Lube</i>	762
R-Curve Behavior of Ceramics <i>Marc J Anglada</i>	775
Subcritical Crack Growth: Basic Relations and Experimental Evaluation <i>Malika Saâdaoui</i>	797
Subcritical Crack Growth: Modeling of the v-K Curve in Different Environments <i>Raul Bermejo</i>	811
Ceramics: Transformation Toughening <i>DB Marshall and RHJ Hannink</i>	818
Mixed-Mode Fracture and Microstructural Aspects of Crack Propagation <i>Delia Gutiérrez-Campos and Yuk Ming X Hung-Hung</i>	823
R-Ratio and Microstructure Effects <i>Delia Gutiérrez-Campos, Eliana Pinto-González, and Elvira Saab-Llatas</i>	841
Thermal Properties of Ceramic Materials <i>David S Smith and Benoît Naït-Ali</i>	855
Thermal Shock Behavior of Ceramics: Fundamentals and Thermal Shock Resistance Parameters <i>Carmen Baudín</i>	867
Thermal Shock and Thermal Fatigue Behavior of Ceramics: Microstructural Effects <i>Gilbert Fantozzi and Malika Saâdaoui</i>	879
Creep Behavior of Ceramics <i>Gilbert Fantozzi and Arturo Dominguez-Rodriguez</i>	891
Nonoxide Ceramics, Creep and Creep Rupture of: Silicon Nitrides and Silicon Carbides <i>SM Wiederhorn</i>	908
Dislocations in Ceramic Materials <i>Jacques Rabier</i>	911
Corrosion of Ceramics in Aqueous Environments <i>Mathias Herrmann</i>	921
Corrosion and Degradation of Glass <i>Dagmar Galusková and Dušan Galusek</i>	932

VOLUME 2

Overview: Oxide Ceramics and Non-oxide Ceramics <i>Stuart Hampshire and Michael Pomeroy</i>	1
Structural and Thermostructural Ceramics <i>Jon Binner and Tammana SRC Murthy</i>	3
Alumina, Structure and Properties <i>Carmen Baudín</i>	25
Low Thermal Expansion Ceramic and Glass-Ceramic Materials <i>Pascal Pilate and Florimond Delobel</i>	47

Mullite: Structure and Properties <i>Gi��le L Lecomte-Nana and Aghiles Hammas</i>	59
Aluminum Titanate, Structure and Properties <i>Salvador Bueno and Carmen Baud��n</i>	76
Zirconia Ceramics, Structure and Properties <i>Anne Leriche, Francis Cambier, and Helen Reveron</i>	93
Si ₃ N ₄ -Ceramics: An Introduction <i>MJ Hoffmann</i>	105
Si ₃ N ₄ Ceramics, Structure and Properties <i>Monika Tatarkov��, Peter Tatarko, and Pavol ��ajgal��k</i>	109
SiALONs and the Representation of Phase Relationships <i>Stuart Hampshire</i>	119
Si-Al-O-N Ceramics, Structure and Properties <i>Ali ��elik and Servet Turan</i>	128
Aluminum Nitride and ALON Ceramics, Structure and Properties of <i>JW McCauley</i>	144
SiC Ceramics, Structure, Processing and Properties <i>Young-Wook Kim and Rohit Malik</i>	150
High Thermal Conductivity Ceramics <i>Mikito Kitayama</i>	165
MAX Phases, Structure, Processing, and Properties <i>Nick Goossens, Bensu Tunca, Thomas Lapauw, Konstantina Lambrinou, and Jozef Vleugels</i>	182
ZrB ₂ , HfB ₂ , OsB ₂ and IrB ₂ Boride Ceramics: Processing, Structure, and Properties <i>Nina Orlovskaya, Holden Hyer, Yongho Sohn, Mykola Lugovy, Gurdial Blugan, Thomas Graule, Jakob Kuebler, Sergey Yarmolenko, Jagannathan Sankar, and Michael J Reece</i>	200
Directionally-Solidified Eutectic Oxide Ceramics <i>VM Orera[†] and J Llorca</i>	216
Overview: High-Performance Ceramics and Ceramic Composites <i>Michael Pomeroy</i>	225
Ceramic Matrix Composites With Roughly Equiaxed Reinforcements: Microstructure and Mechanical Behavior <i>Gilbert Fantozzi and J��r��me Chevalier</i>	227
Nanoscale Ceramic Composites <i>GS Thompson and MP Harmer</i>	240
Ceramic Matrix Graphene and Carbon Nanotube Composites <i>Katalin Bal��zsi, M��nika Furk��, and Csaba Bal��zsi</i>	243
Short Fiber Ceramic Matrix Composites (SF-CMCs) <i>Walter Krenkel, Stefan Flauder, and Georg Puchas</i>	260
Glass and Glass-Ceramic Matrix Composites for Advanced Applications: Part I: Properties and Manufacturing Technologies <i>Dino Boccaccini, Maria Cannio, Enrico Bernardo, and Aldo R Boccaccini</i>	277
Glass and Glass-Ceramic Matrix Composites for Advanced Applications: Part II: Applications <i>Dino Boccaccini, Maria Cannio, Enrico Bernardo, and Aldo R Boccaccini</i>	288

[†]Deceased.

High Performance Fibers <i>AR Bunsell</i>	304
Spun (Slurry and Sol–Gel) Ceramic Fibers <i>DM Wilson</i>	314
Ceramic Matrix Fiber Composites <i>Francis Rebillat</i>	317
Ultra-High Temperature Ceramic Matrix Composites <i>Luca Zoli, Diletta Sciti, Antonio Vinci, Pietro Galizia, Frédéric Monteverde, Simone Failla, and Laura Silvestroni</i>	340
Carbon-Matrix Composites <i>Deborah DL Chung</i>	353
Ceramics in Space Applications <i>Barry Twomey, Daithi de Faoite, Kevin AJ Doherty, and Kenneth T Stanton</i>	359
Porous Ceramics for Energy Applications <i>Andreas Kaiser, Bhaskar R Sudireddy, and Farid Akhtar</i>	380
Joining of Advanced Ceramics <i>John A Fernie and Kevin M Knowles</i>	393
Abrasives <i>Jean-André Alary</i>	406
Wear and Erosion Resistant Ceramic Materials <i>Pavol Hvizdoš</i>	416
Wear and Erosion Resistant Ceramic Coatings <i>František Lofaj and Marián Mikula</i>	425
Oxidation and Corrosion of Non-oxide Ceramics <i>NS Jacobson and EJ Opila</i>	440
Overview: Glass and Glass Ceramics <i>Stuart Hampshire</i>	445
The Glassy State <i>Maziar Montazerian and Edgar D Zanutto</i>	448
Glasses: Alkali and Alkaline-Earth Silicates <i>Benjamin JA Moulton and Grant S Henderson</i>	462
Soda-Lime-Silica Glasses <i>Russell J Hand</i>	483
Glasses: Aluminosilicates <i>Laurent Cormier</i>	496
Borosilicate Glasses <i>Yuanzheng Yue, Manzila I Tuheen, and Jincheng Du</i>	519
Glasses: Chalcogenides <i>Myungkoo Kang and Kathleen A Richardson</i>	540
Glasses: Oxynitride Glass Formation and Structure <i>Stuart Hampshire</i>	555
Glasses: Oxynitride Glass Properties and Crystallization <i>Stuart Hampshire</i>	569
Glasses: Phosphates <i>Andrea Moguš-Milanković, Ana Šantić, and Luka Pavić</i>	580

Halide Glasses <i>Marcel Poulain</i>	591
Glass: Annealing and Tempering <i>Mathieu Hubert and Peter J Lezzi</i>	623
Glass: Chemical and Thermal Strengthening <i>Ali Talimian and Vincenzo M Sglavo</i>	632
Properties of Glass Materials <i>M Hasanuzzaman, A Rafferty, M Sajjia, and A-G Olabi</i>	647
Optical Glass: Challenges From Optical Design <i>Ulrich Fotheringham, Martin Letz, Uwe Petzold, Simone Ritter, and Yvonne Menke-Berg</i>	658
Glass Fibers <i>KK Chawla</i>	676
Glass: Optical Fibers – Manufacture and Properties <i>Conleth D Hussey</i>	681
Glasses: Sol–Gel Methods: An Introduction <i>T Woignier and J Phalippou</i>	689
Glasses and Glass-Ceramics Prepared by Sol–Gel <i>María E Cruz, Yolanda Castro, and Alicia Durán</i>	695
Glass-Ceramics and Their Applications <i>Maurice Gonon and Florian Dupla</i>	709
Glass Reactive Sintering <i>Acacio Rincon Romero, Hamada Elsayed, Jozef Kraxner, and Enrico Bernardo</i>	728
Glasses and Glass-Ceramics as Sealing Materials <i>María J Pascual</i>	746
Glasses and Glass-Ceramics for Nuclear Waste Immobilization <i>Daniel Caurant and Odile Majerus</i>	762

VOLUME 3

Overview: Electroceramics and Ceramics and Glasses in Energy Generation and Storage <i>Carmen Galassi</i>	1
Photovoltaics: Advanced Inorganic Materials <i>Abdelilah Slaoui and Reuben T Collins</i>	5
Ion Conducting Materials: Superionic Conductors and Solid-State Ionics <i>Junichi Kawamura</i>	17
Development, Structure, and Mechanical Properties of Sulfide Solid Electrolytes <i>Koji Ohara, Atsushi Sakuda, and Akitoshi Hayashi</i>	38
Solid Oxide Fuel Cells <i>Alessandra Sanson and Angela Gondolini</i>	49
Laser Processing of Energy Storage Materials <i>Heungsoo Kim and Alberto Piqué</i>	59
Aluminum, Gallium, and Indium Nitrides <i>Qilin Hua, Bei Ma, and Weiguo Hu</i>	74
Novel Nitride Phosphors <i>M Bettinelli</i>	84

Phosphors: VUV Excitation <i>Jean-Claude Krupa and AZMS Rahman</i>	89
Silicon Carbide Electronic Devices <i>PG Neudeck and GK Sujan</i>	93
Scintillator Crystals <i>D Klimm</i>	103
Ceramics for Laser Technologies <i>Jan Hostaša</i>	110
Ceramic Sensors for Industrial Applications <i>David Degler, Frank Allmendinger, and Nicolae Barsan</i>	125
Pyroelectric Crystals, Ceramics, and Thin Films for IR Sensors <i>Roger W Whatmore</i>	139
Superconducting Materials <i>Peter Majewski</i>	151
Superconductors: Borocarbides <i>Günter Fuchs, Karl-Hartmut Müller, and Vladimir N Narozhnyi</i>	162
The RABiTS Approach for Second Generation (2G) High Temperature Superconductors <i>Martin W Rupich</i>	174
Ferrite Ceramics at Microwave Frequencies: Applications and Characterization <i>Jean-Luc Mattei, Alexis Chevalier, and Vincent Laur</i>	183
Ferrite Magnets: Properties and Applications <i>Jean-Marie Le Breton</i>	206
Ferrites <i>PJ van der Zaag</i>	217
Multiferroic Composites <i>Xianfeng Liang, Huaihao Chen, Cheng Tu, Zhaoqiang Chu, Cunzheng Dong, Yifan He, Yuyi Wei, Yuan Gao, Hwaider Lin, and Nian X Sun</i>	225
Zinc-Oxide-Based Electronics and Photonics <i>David J Rogers, Ferechteh H Teherani, Eric V Sandana, and Philippe Bove</i>	241
Varistor Electrical Properties: Microstructural Effects <i>Zumret Topcagic and Thomas E Tsovilis</i>	254
Latest Trend of ZnO Multilayer Ceramic Varistors <i>Eiichi Koga, Yoshiko Higashi, and Michio Matsuoka</i>	272
Dielectric, Ferroelectric, Antiferroelectric, Relaxor, Piezoelectric Ceramics: Definitions and Main Applications <i>Floriana Craciun</i>	281
Electroceramics: Modeling of Sintering, Microstructure Evolution and Functional Properties <i>Constantin Hutanu, Vlad Alexandru Lukacs, and Liliana Mitoseriu</i>	295
BaTiO ₃ -Based Ceramics: Fundamentals, Properties and Applications <i>Vincenzo Buscaglia, Maria Teresa Buscaglia, and Giovanna Canu</i>	311
The PZT System <i>Florian Jean and Christian Courtois</i>	345
Lead-Free Piezoelectric Ceramics <i>Barbara Malič, Mojca Otoničar, Kristian Radan, and Jurij Koruza</i>	358

Electrostrictive Ceramics and Their Applications <i>Simone Santucci and Vincenzo Esposito</i>	369
Low-Loss Ceramics in Mobile Communications <i>K Wakino, H Tamura, and GK Sujan</i>	375
Small-Scale Energy Harvesting Devices for Smart Electronics <i>Sumanta Kumar Karan, Rammohan Sriramdas, Min-Gyu Kang, Yongke Yan, and Shashank Priya</i>	391
Multilayer Ceramic Actuators <i>K Uchino</i>	426
Multilayer Glass–Ceramic/Ceramic Composite Substrates <i>Jobin Varghese, Nina Joseph, and Heli Jantunen</i>	437
Functional Ceramics through Novel Chemical Approaches <i>K Kato, Y Torii, and G Majumdar</i>	452
Overview: Bioceramics and Bioreactive Glasses <i>Anne Leriche and Francis Cambier</i>	458
Bone as a Material: Lessons From Nature <i>Laura M O'Sullivan and Laoise M McNamara</i>	459
Overview of Substitutes for Bone Replacement: Natural and Synthetic Products <i>Nicolas Somers and Marie Lasgorceix</i>	473
New Trends in Ceramics for Orthopedics <i>Laurent Gremillard and Jérôme Chevalier</i>	493
New Trends in Ceramics for Dentistry <i>Paola Palmero</i>	501
Oxide Ceramics for Biomedical Applications <i>Corrado Piconi and Anna Tampieri</i>	511
Non-Oxide Ceramics as Biomaterials <i>Stuart Hampshire</i>	526
Carbon in Biomedical Engineering <i>Jill S Kawalec</i>	533
Yttria-Stabilized Zirconia as a Biomaterial: From Orthopedic Towards Dental Applications <i>Helen Reveron and Jérôme Chevalier</i>	540
ZTA Ceramics for Biomedical Applications <i>Frank Kern, Paola Palmero, and Wolfgang Burger</i>	553
Phosphates <i>David Grossin</i>	567
Apatitic and Tricalcic Calcium Phosphate-Based Bioceramics: Overview and Perspectives <i>Christophe Drouet and Christèle Combes</i>	575
Calcium Phosphates in Biomedical Engineering <i>Maria Canillas, Antonio H de Aza, and Miguel A Rodríguez</i>	595
Bioceramics in Regenerative Medicine <i>Simone Sprio, Anna Tampieri, Massimiliano Dapporto, Michele Iafisco, and Monica Montesi</i>	601
Bioactive Glasses and Glass-Ceramics <i>Francesco Baino</i>	614
Calcium Phosphate Cements <i>Aoife Culliton and Eamonn De Barra</i>	624

Bone Regeneration With Ceramics Scaffold <i>Vida Strasser and Maja Dutour Sikirić</i>	646
Advanced Processes for the Design of Customized Ceramic Medical Devices <i>Eric Champion and Patricia Pascaud-Mathieu</i>	662
Bioactive and Biodegradable Polymer-Based Composites <i>Lukas Gritsch and Aldo R Boccaccini</i>	674
Surface Treatment of Bioceramics <i>Nicolas Somers and Marie Lasgorceix</i>	701
Chemical Functionalization of Calcium Phosphate Bioceramic Surfaces <i>Chantal Damia, Amandine Magnaudeix, and Betty Laverdet</i>	716
Thermally Sprayed Materials for Biomedical Applications <i>Andreas Killinger and Rainer Gadow</i>	732
Design of Tissue Engineering Scaffold by Means of Mathematical Modeling <i>Stefan Scheiner</i>	750
Unconventional, Nature-Inspired Approaches to Develop Bioceramics for Regenerative Medicine <i>Anna Tampieri, Simone Sprio, Monica Sandri, Elisabetta Campodoni, Andrea Ruffini, Laura Mengozzi, and Silvia Panseri</i>	758
Assessment of Mechanical Properties of Bioceramics <i>Gilbert Fantozzi</i>	772
Mechanical Properties of Dental Ceramics <i>Fei Zhang and Jozef Vleugels</i>	784
Biological Assessment of Bioceramics: In Vitro and In Vivo Tests <i>Maria H Fernandes and Pedro de Sousa Gomes</i>	798
Zirconia Ceramics: Clinical and Biological Aspects in Dentistry <i>Andraž Kocjan, Tadej Mirt, Ralf-Joachim Kohal, Zhijian Shen, and Peter Jevnikar</i>	817
Subject Index	832

EDITOR BIOGRAPHIES

Editor In Chief



Michael J. Pomeroy, is Emeritus Professor of Materials Science & Technology at the University of Limerick, Ireland. His education comprised: B. Sc. Chemistry and Materials Science at the University of Wolverhampton, M.Sc. Surface Technology and Management Techniques at the University of Aston and Ph.D. "Corrosion of Alloys in Fluidized Bed Combustion Systems" at the University of Wolverhampton. Following four years as a Researcher in fluidized bed combustion at the University of Limerick, Michael took up a Research position in Silicon Nitride Ceramics. He became an academic at the University of Limerick in 1985. Since then he has carried out research on the oxidation and corrosion of high temperature alloys, metallic coatings and ceramics as well as in the development of silicon nitride and sialon ceramics and related glasses. His more recent research work was related to aluminosilicate glasses containing fluorine and nitrogen, determining how glass structure and properties are affected by cation and anion substitutions. Michael has worked with many

collaborators in Europe, the US and Japan and has collaborated throughout his career with University of Limerick colleague Prof. S. Hampshire. He still collaborates with University and international colleagues on research on glass ceramics and additive manufacturing. Before retirement, Michael developed very successful Masters programs in Biomedical Materials and Advanced Engineering Materials as well as modules in advanced characterization techniques for PhD programs with a taught element. Michael has edited 2 books and was sub-editor of the Reference Module in Materials Science and Materials Engineering (Ceramics section). He has published nearly 200 papers in journals and conference proceedings. He was conferred as a Fellow of the European Ceramic Society in 2017. His spare time is devoted to ringing church bells.

Section Editors



Anne L. Leriche is a ceramist specialising in technical ceramic processing and their microstructure control. She is Professor at Polytechnic University Hauts-de-France. Born in Belgium, she studied at University of Mons (Belgium). She obtained a Masters in Chemistry with honors in 1981. A Post-Graduate grant from Industrial Research Council allowed her to complete her doctorate with honors in 1986 from the State University of Mons, Belgium on "Reactive Sintering of Mullite-Zirconia Composites". During her PhD thesis, she spent time at the Ceramics Department of Leeds University, UK. After a few years as researcher at Belgian Ceramics Research Centre in Mons, she became responsible for R&D in a SME involved in the fabrication of advanced oxide ceramics. In 1990, Anne joined the Ceramic Materials and Processing Lab (LMCPA) at Polytechnic University Hauts-de-France, Maubeuge. In 1994, she was promoted to Professor (full Professor in 2005) and was Director of LMCPA leading 30 researchers from 1999 to 2016. She has supervised 26 PhD

students, managed numerous European projects, published 220 journal or proceedings papers and presented 40 invited lectures. She has served as Board Member of the Belgian Ceramic Society, President of the French Ceramic Society, President of the European Ceramic Society and of the JECS Trust. She is member of the World Academy of Ceramics. In her spare time, Anne likes travelling and takes care of her donkeys and other animals sharing her life in countryside



Carmen Galassi received the degree of Dottore in Industrial Chemistry (*summa cum laude*), Bologna University, 1981. She is Research Fellow at the Politecnico di Milano, Department of Mechanical Engineering and Senior Research Associate at CNR-ISTEC Faenza. Since 1984 she has been a member of the permanent staff at ISTEC, as Researcher, Senior Researcher and Research Director. Her main research interests and expertise are in the development and characterization of ceramic materials with emphasis on ferroelectrics, piezoelectrics and multiferroics. Her main activity was research projects coordination and dissemination, and scientific responsibility of several contracts with industry. She was Coordinator of a network of 11 Laboratories within the EU Program HCM (1995–1997), and two national projects and scientific coordinator of the research Unit ISTEC in several national and EU projects. She participated to the Spin-off Action to establish IPECC srl. Dr Galassi tutored 20 MSC and five PhD students, and has got the National Scientific Qualification as full Professor of Materials Science and Technology in Italian Universities. Out of more than 250 papers co-authored, 185 are published in international, refereed journals and received more than 3000 citations (full list on <https://orcid.org/0000-0002-7892-2836>). She lives in the countryside and likes walking, cooking and travelling.



Francis Cambier received a Masters degree in 1971 and a DSc in 1978, from the University of Mons (Belgium), both in applied chemistry. In 1979 he moved to the Belgian Ceramic Research Centre (BCRC) becoming a research group leader in 1981, Director of Research in 1983 and Director General in 1996. He officially retired from BCRC in July 2017, staying on the board to help his successor. Over 40 years he had the opportunity to develop a broad range of applied research topics in close collaboration with universities and companies all over Europe. His main areas of interest are the manufacturing processes of oxides and non-oxides, their mechanical and microstructural characterization, the application of ceramics in traditional, refractory, structural and biomedical fields. Francis is author or co-author of more than 300 papers, most of them in peer reviewed Journals, has presented more than 350 oral or poster communications, among which about 60 invited. He has always been strongly involved in relations with companies and societies and was board member of several companies and received various awards and distinctions (in Belgium, Germany, Poland, Sweden). A member of the Belgian Ceramic Society, he was its President from 2001–2006. He is a fellow of the American Ceramic Society, and of the European Ceramic Society (ECerS). During many years he oversaw the secretariat of ECerS (2001–2019).

Francis is now president-elect of ECerS (he will be president from 2021–2023) and vice-president of the advisory board of the World Academy of Ceramics. Outside of work he has the very important job of lovingly caring for six grandchildren and 20 vintage cars.



Professor Stuart Hampshire is Professor Emeritus of Materials Science at the University of Limerick, Ireland. Following a first degree from the University of Sheffield in Ceramics Technology, he worked in industry on nitride-bonded refractories before undertaking a PhD at the University of Newcastle on Sintering of Nitride Ceramics. Stuart stayed on as a post-doctoral fellow carrying out research on Oxynitride Glasses which he continued after his appointment at Limerick. He developed the first degree programme in Materials Science, established a research group on ceramics and glasses, collaborating on European-funded projects with other laboratories, and, throughout his career, working with Editor-in-Chief, Professor Mike Pomeroy Stuart was subsequently promoted to full professor in 1996. At that time Stuart was Director of the Materials Ireland Research Centre working with Enterprise Ireland to support Irish industry in areas of Materials Technology. In 1999 he was a founding member of the Materials and Surface Science Institute (now the Bernal Institute) and successfully led the University's proposals for government infrastructure funding of €16 million for new labs and analytical facilities. Stuart has published over 250 papers and given 70 invited

lectures. He is a Fellow of both the American and European Ceramic Societies and a member of the European Ceramic Society Council. He has received various honours including European Ceramic Society Stuijts Award (2007), American Ceramic Society International Bridge Building Award (2008) and an Honorary Doctorate from the University of Limoges, France (2009). The American Ceramic Society Engineering Ceramics Division held a symposium in his honour in 2014. Stuart enjoys classical music and is a member of the Limerick Choral Union.

PREFACE

The Encyclopedia of Materials: Science and Technology was published in 2001 when technical ceramics and glasses were under active development. Since then these materials have seen exponential development and become very important in Industrial sectors related to medical devices, electrical and electronic devices, green energy, automobiles and aerospace. The need for ceramic and glass researchers increased accordingly and will do so in the future. The Encyclopedia of Materials: Technical Ceramics and Glasses (EM-TCG) was therefore conceived to update ceramic and glass related knowledge from the 2001 Encyclopedia and to include chapters covering new materials, processes and applications since that time. The EM-TCG was designed to be, as far as possible, the ultimate source for background knowledge for undergraduate students and early career researchers in ceramics and glasses, written by leaders in the field for the advancement of ceramic and glass science & engineering. A secondary, but equally important objective of EM-TCG was to provide background information for parties interested in the processing, properties and applications of technical ceramics and glasses from a policy or product / process development standpoint. EM-TCG was thus designed to be a solid background information source for a relatively wide audience requiring specialized knowledge in a readily accessible format.

Each of the chapters should help readers readily develop their knowledge base in their specific area. To this end, EM-TCG users should be able to readily access comprehensive, organized, detailed, quality information to support their educational and professional development. This means that in some ways, the encyclopedia could be thought of as a virtual mentor. It is also hoped that early stage researchers and industrial researchers will use EM-TCG as a solid background information source to widen their interest in technical ceramic and glass materials. This can be very important as there are frequent parallels between research areas which appear at face value to be unique and very different.

The subject matter for the Encyclopedia follows a broad schema of processing, materials modeling & characterization, mechanical properties, oxide & non-oxide ceramics, ceramic matrix composites, glasses & glass ceramics, electrical & electronic ceramics and bioceramics & bioglasses. Each of these broad sections has an introductory article which the reader is advised to peruse to get a feel for the section's contents. Whilst not absolutely comprehensive, EM-TCG will thus provide an excellent reference tome. All effort has been made to ensure that the content is wide ranging and detailed. This has been made possible by all of those authors who have made contributions to the encyclopedia. In a few instances, it was decided that some fundamental articles from the original 2001 Encyclopedia should be included as well as some articles more recently contributed to the Reference Module in Materials Science and Materials Engineering.

It must be said that persuading people to write for reference works is not easy because of the reward recognition afforded in terms of career deliverables. This difficulty was further compounded by the Coronavirus outbreak which required many of the authors who had agreed to write having to totally reorganize their day jobs. I am particularly grateful to those authors who had to write and record whole semesters of lecture notes as well as develop new ways of assessing students. To do this as well as contribute to the encyclopedia is highly laudable. I and the Editorial team most heartily thank the nearly 300 authors from across the world who contributed to the 197 chapters in EM-TCG.

I am indebted to the members of the Editorial team whose untiring work beyond the call of duty led to the completion of the Encyclopedia. The Editorial team had as its origins a European Project on Silicon Nitride which began in 1983. Since that time, Prof. Anne Leriche, Prof. Francis Cambier, Prof. Stuart Hampshire and I have collaborated in one form or another. Dr. Carmen Galassi visited Limerick in 1985 for a Conference on Non-Oxide Ceramics and has become well known to the rest of the group since that time. I also thank the people at Elsevier who have helped along the way. Particular thanks must go to Sean Simms and Richard Berryman for their help in smoothing the way from start to finish. Sajana, who seemed able to keep the chapters, authors and editors under control and always be at a computer, deserves very special thanks.

To good ceramic and glass science, good fellowship, fine dining and fine wine - all inseparable!

Michael J. Pomeroy
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Overview: Manufacture of Ceramics and Microstructural Developments in Ceramics

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Ceramics and glass are arguably the oldest materials that man has made. Objects dating back to more than 25,000 years BC have been found. The oldest object is a small statue made of ceramics (fired clay) discovered in 1925 in Moravia (Czech Republic). It is called the “Venus of Dolní Věstonice”. It is a small figurine, representing a nude female. It is remarkable that the Venus de Dolní Věstonice was found broken in two parts, in the middle of ashes. This statue would therefore have been produced using the classical powder → shaping → firing sequence. It was found on the site where it was produced (close to an artisanal oven) and where it was abandoned, it is perhaps also the first witness to the fragility of an incompletely densified ceramics produced from clay.

The processing of ceramics following the classical sequence was continuously improved over time. For many centuries, the use of ceramics has been confined to domestic applications (dishes, containers, etc.) or to luxury and religious objects (jewelry, statuettes, for example). In the nineteenth century, industrialization, the discovery of electricity gradually led to the manufacture of new materials such as refractories, insulators, abrasives. Very quickly the natural source of raw materials revealed flaws and the ceramists realized the need to create advanced raw materials, to imagine innovative manufacturing techniques, to find more efficient consolidation means, and finally to control more strictly every stage of the ceramic materials production process that we call today “technical ceramics”. Empiricism turned into scientific knowledge when the observed phenomena were gradually understood.

This first section of the Encyclopedia of Materials: Technical Ceramics and Glasses is specifically devoted to “*Ceramics Manufacturing and Ceramic Microstructural Development*”. It includes different subsections:

- A. The first part concerns the description of different ways of synthesizing the raw materials developed specifically for the manufacture of technical ceramics. Indeed, such materials must have, on the one hand, an adequate chemical composition with a controlled content of impurities, possibly with specific chemical additions modifying its sintering behavior and the good development of its microstructure and, on the other hand, they must be composed of particles of size, shape, particle size distribution, surface finish, etc. chosen to adapt the raw material to the type of shaping chosen for the industrial manufacture of the green parts and for its subsequent densification.

Seven chapters make up this subsection, the first chapter introduces the various synthesis techniques. Some more specific chapters follow on wet methods, sol gel, SHS technique, hydrothermal synthesis and synthesis with the help of ultrasounds. Most of the methods result in chemical intermediates which must be transformed to obtain the desired composition. A chapter therefore concerns the stages of calcination and phase transformation of raw materials. Finally, some ceramics can be obtained directly from the chemical compound to the finished product: the last chapter of this subsection concerns this type of ceramics.

- B. The second part looks at the steps necessary to obtain the desired shapes in industrial production. In the majority of cases, organic (including polymers) or organo-metallic additives are mixed with the powder raw materials in order to give them an adequate aptitude for shaping. A grinding step may be necessary and/or a granulation step, in particular when the shaping is obtained by compaction. Specific chapters are devoted to forming processes involving dispersion in a solvent (slip, centrifugal, gel casting, direct coagulation process), to those using a viscous paste (extrusion, injection molding, tape casting). Two chapters deal with innovative freeze casting and additive manufacturing techniques. Of course, whenever possible, shaping techniques are tending to achieve a near to net shape object, however, corrections are often necessary, by machining, preferably at the green stage. Finally, some components must be prepared in layers, which is why a chapter is devoted to screen printing.
- C. When the desired shape is achieved, the component must be densified to enhance its integrity. After an introductory chapter describing the principles of the different sintering techniques, three specific chapters give more details on the behavior when no (solid state), a little (liquid phase) or a lot of liquid phase (viscous) is involved in the process. Two other chapters examine the influence of the added pressure and that of the simultaneity of a reaction during densification.

Sintering is a very time consuming and energy intensive process. The objective of a series of recent developments is the reduction of sintering time and therefore of energy consumption. After an introductory chapter giving a brief description of new rapid sintering techniques, more details are given on “Spark Plasma Sintering”, cold, hydrothermal and microwave sintering.

Not all components need full densification. It is particularly the case for ceramics used in a series of applications as catalysts, filters, bioceramic scaffolds, etc., where controlled porosity must be achieved. Two chapters are therefore devoted to porous ceramics.

- D. During the densification process, there is a competition between the disappearance of pores and the unwanted growth of grains. Techniques exist to control the development of the microstructure. They are the subject of a detailed specific chapter.

Two other chapters concern the obtaining of textured and functionally calibrated ceramics. Finally, good examples illustrating the techniques described in the previous chapters for controlling raw materials, shaping, processing, sintering and microstructure are given in the manufacture of transparent ceramics and in the fabrication of geopolymers.

Synthesis of Oxide and Non-Oxide Advanced Ceramics

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Introduction

Oxide and non-oxide are universal classifications of ceramics. Oxide or “traditional” ceramics are formed by the reaction of metals with oxygen. These compounds comprise almost 90% of the ceramic materials known today ([Table 1](#)) and constitute a majority of the advanced electronic, structural, optical, magnetic, electrochemical, and biological materials ([Barsoum, 1997](#); [Julien and Nazri, 1994](#); [Lee et al., 2012](#); [Ghadge et al., 2018](#)). Non-oxide ceramics are obtained by reacting a metal, or a semimetal in some cases, with oxygen-free elements such as, S, N, C, B, P, As, Sb, Se, and Te. Unlike oxides, barring diamond and graphitic as well as many of the amorphous carbons, these compounds of non-oxide ceramic systems constitute some of the largest manmade substances. Development of non-oxides have always been slow in progression in comparison to the ubiquitous oxide systems. As a result, the implementation as well as translation to commercially viable products has also been sluggish. The primary barriers to rapid and escalated developments have primarily been due to challenges involved in synthesis and processing of dense structures due to the covalent nature of these systems and also the inherent reactivity of the non-oxygen species particularly, S, Se, Te, P and N to oxygen and moisture even under ambient conditions. The meticulous care needed to process these systems also make it a challenge to develop easily scalable methods to translate the technology from laboratory scale to commercially viable large kilogram scale quantities preserving the purity, microstructure and other attributes to reproduce the desired functionality. Most laboratory scale approaches result in only demonstrating the feasibility of creating a unique configuration or nanoscale architecture such as nanowires, nanotubes, hollow nanotubes, nanodots, nanodroplets, nanoflakes, nanowhiskers etc. At the laboratory scale, these systems demonstrate some very unique and unprecedented properties that has advanced the field of nanotechnology. However, the task of converting these features into the commercial landscape has always proven to be an enormous challenge. Research and advances in manufacturing science has come a long way to overcome many of these hurdles. Nevertheless, striking the right balance between cost and salability while also keeping in mind the attainment of desired microstructure, phase and surface properties to attain the desired functionality is still a challenge requiring more advances to be made. Most of the currently researched non-oxide ceramics belong to the carbide, boride, nitride, and sulfide families whose applications are shown in [Table 1](#) ([Kumta and Risbud, 1994](#); [Srinivasan and Rafaniello, 1997](#); [Jampani et al., 2010](#); [Choi et al., 2006](#); [Kadokia et al., 2014a,b,c](#); [Ghadge et al., 2018](#); [Jampani et al., 2013](#)).

Synthesis of Oxide Ceramics

Oxides as mentioned above are generally stable under normal ambient conditions of atmospheric pressure and temperature, possessing complex structures and exhibiting unusual properties. Several methods described below can and are typically used to synthesize these materials by and large.

Solid-State Approach

This is the conventional and most ubiquitously used method for synthesizing various ceramic materials and consists of mixing and grinding raw materials in a ball-mill or a mortar and pestle. The mixture is then heat-treated at high temperatures to yield the desired ceramic. It is by definition a very convenient and preferred method for synthesizing ceramics, but it suffers from several major limitations. Prolonged high-temperature treatments required to achieve complete conversion and stabilization of the desired phases and microstructure preclude the generation of metastable structures with precise control of grain size, stoichiometry, phase purity, crystal structure, defects and microstructure. Hence the method cannot be used to completely exploit microstructure related properties of the materials. Incomplete conversion and the incorporation of process related contaminants are other factors limiting the methods. The past several years since the original article was published in late 1990 have however witnessed a plethora of efforts to identify alternative approaches for synthesizing oxide ceramics. These approaches and their attributes for various emerging technologies are discussed in the sections to follow.

Chemical-Based Solution Approaches

These methods by definition involve executing chemical reactions conducted at low temperatures (25–100°C) in the presence of a liquid solvent. Inorganic or organometallic salts are generally selected as the primary reactants. The reactions conducted in solution

Table 1 Selected properties and applications of common oxide and non-oxide advanced ceramics

Property	Material class
Electrical and dielectric	SiC, ZrO ₂ , MoSi ₂ , BaTiO ₃ , SrTiO ₃ , etc.; PbZr _{0.5} Ti _{0.5} O ₃ , AlN, Al ₂ O ₃ , β -Al ₂ O ₃ , doped ZrO ₂ , etc.; oxides of Fe, Mn, Co, Bi-doped ZnO, SiC, SnO ₂ , ZnO, etc; ABX ₃ (A = CH ₃ NH ₃ , B = Pb, X = Br, I) Bi ₂ Te ₃ , SnSe; NaPb _m SbSe _{m+2} ; WS ₂ ; MoS ₂
Thermal	SiO ₂ , Al ₂ O ₃ , ZrO ₂ , Al ₂ O ₃ – SiO ₂ , AlN, SiC, diamond
Magnetic	(Ba, Sr)O.6Fe ₂ O ₃ , RE ₂ Fe ₁₇ (Nx (RE = rare earth)), (Zn, M)Fe ₂ O ₃ (M = MnCo, Mg), rare earth garnets, YBa ₂ Cu ₃ O _{7-x} ; MgB ₂
Optical	Soda-lime glass, SiO ₂ , CaLa ₂ S ₄ , ZnS, γ -La ₂ S ₃ , BaF ₂ , GeS ₂ , Al ₂ O ₃ , MgO, Y ₂ O ₃ , Mn:ZnS, CaWO ₄ Zn ₂ SiO ₄ :Mn, LiNbO ₃ , As ₂ S ₃ , Ge – Sb – S; GeS ₂ – La ₂ S ₃
Chemical	Cordierite (2MgO.2Al ₂ O ₃ .5SiO ₂), Mo ₂ N, W ₂ N, TiS ₂ , SiC
Biological	Bioglass (CaO–P ₂ O ₅ –SiO ₂), Al ₂ O ₃ , Hydroxyapatite [Ca ₁₀ (PO ₄) ₆ (OH) ₂]; Mg ₃ (PO ₄) ₂ ; α -Ca ₃ (PO ₄) ₂ ; β -Ca ₃ (PO ₄) ₂ ; Ca ₈ H ₂ (PO ₄) ₆ · 5H ₂ O
Mechanical	SiC whisker – reinforced, Al ₂ O ₃ , Si ₃ N ₄ ; BN; BCN
Electrochemical	LiCoO ₂ , LiMn ₂ O ₄ ; LiNiO ₂ ; LiNi _{0.33} Mn _{0.33} Co _{0.33} O ₂ ; LiNi _{0.8} Mn _{0.1} Co _{0.1} O ₂ ; RuO ₂ ; RuO ₂ ·xH ₂ O; IrO ₂ ; F-doped I ₂ O ₂ ; (Sn _{0.8} Ir _{0.2})O ₂ :10F; (Sn _{0.8} Ru _{0.2})O ₂ :10F; Cu _{1.5} Mn _{1.5} O ₄ :10F; Ir _{0.2} Mn _{0.8} O ₂ :10F; VN; W _{0.7} Ir _{0.3} O ₃ ; NaMnO ₂ ; Mg _x Mo ₆ S ₈ ; etc.

phase result in excellent molecular-level mixing of the various components an aspect not attainable in solid-state techniques. In addition, selection of the appropriate precursors and control of the reaction chemistry can help to generate amorphous precursors containing molecular level coordination and composition similar to those observed and desired in the final ceramic. Good control of the structure, phase, and microstructure of the particles can thus be achieved. Excellent mixing at the molecular level also promotes diffusion at scales of ≈ 100 Å enabling high-temperature materials to form at moderate ($< 1000^\circ\text{C}$) temperatures, hence enabling preservation of many microstructural and phase related features including stabilization of metastable phases critical for achieving certain functionality. There are several chemical-based methods.

- (1) *The sol – gel method.* This is the most popular method for synthesizing oxide ceramics and glasses with the ability to achieve varying degrees of control of stoichiometry, phase purity, and microstructure. Since its applicability for ceramics was first demonstrated by Roy (1956), it has become the hallmark method for synthesizing a variety of oxides and soon emerging for generating non-oxide as well. The approach is based on hydrolyzing metal alkoxides followed by polymerization and condensation to yield amorphous metal oxides. The use of myriad catalysts, complexing agents, drying control additives, and different types of solvents alter the kinetics of these reactions leading to the generation of extremely fine nanostructured particles of equilibrium and non-equilibrium phases exhibiting unique morphologies. Common complexing agents include acetic acid and β -diketonates including other electron donating chelating agents. These complexing agents control the reactions, thereby increasing the gel time and controlling the particle size while also varying the extent of the polymerized chains in the gel solution, rendering it amenable for dip and spin-coating to form oxide films. At the solution level by controlling and delaying the reaction kinetics, the technique also makes it amenable for spraying and vaporizing to generate epitaxial growth via exploitation of thin film techniques such as metal-organic chemical vapor deposition (MOCVD). The approach over the years in particular, since the emergence and dominance of nanotechnology has clearly emerged as the most viable method of choice for synthesizing a vast range of ceramics and glasses for electronic, optical, magnetic, and electrochemical applications. Several articles and texts provide an exhaustive description of the process and its applications (Brinker and Scherer, 1990; Thomas, 1988; Wood and Dislich, 1995). While traditional sol – gel approaches involve the use of metal alkoxides, factors of cost, polymeric nature, reactivity, and moisture sensitivity of alkoxides have led to the identification of alternative non-alkoxide-based approaches for synthesizing materials without losing the characteristic favorable and desirable sol – gel attributes. In this vein, development of the particulate sol – gel (PSG) approach for synthesizing LiNiO₂, a lithium-ion electrode (Chang et al., 1998) is a good example of a nonalkoxide process. The oxide is obtained by the reaction of LiOH and Ni(CH₃COO)₂ in the presence of water and methanol. A gel is formed by the presence of Ni(OH)(CH₃COO) species undergoing OH – OCH₃ exchange. Fig. 1 shows the SEM images of the PSG derived precursor, the transformed, nanosized (≈ 100 nm) LiNiO₂, and the solid state-derived Li₂CO₃. The reaction between the large-grained solid-state derived Li₂CO₃ and NiO is kinetically hindered yielding a defective and an incompletely transformed, electrochemically inferior LiNiO₂, whereas excellent mixing of the intermediate nanocrystalline Li₂CO₃ and NiO (Fig. 2) products formed by virtue of the molecular level mixing in the PSG process results in the formation of defect-free stoichiometric LiNiO₂ with good and desirable electrochemical properties of specific capacity and cycle life. This approach indeed has the potential for generating high Ni containing high energy density lithium transition metal oxide cathodes extensively researched at present. While the approach demonstrates retention of many of the attributes of typical metal alkoxide derived sol-gel process, there have been attempts to explore non-hydrolytic approaches. Thus, in 1992 Goel et al. (1992) showed that oxides can be made by non-hydrolytic sol-gel process using acetone as the condensation agent via an aldol-condensation-elimination reaction sequence. They demonstrated this approach by reacting Zn alkoxides with acetone in benzene resulting in mesityl oxide and ZnO. The mesityl oxide is formed via the aldol condensation mechanism where in carbonyl compounds dimerize forming β -hydroxyketones that dehydrate resulting in α , β – unsaturated carbonyl compounds. The stability of the gels is however, limited

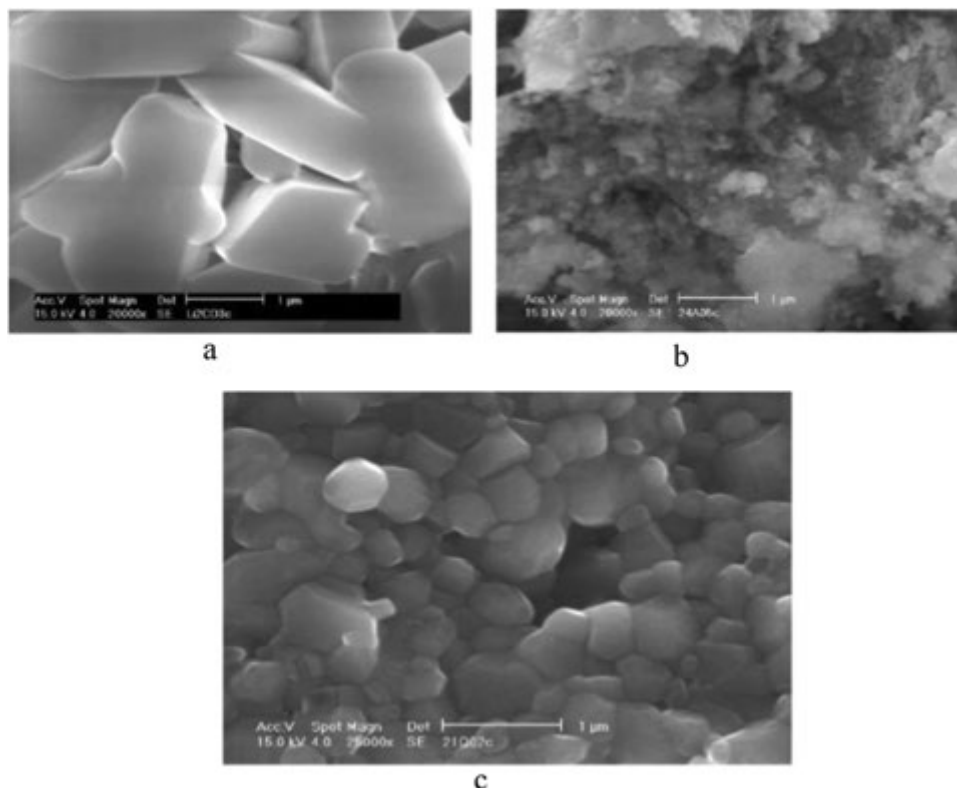


Fig. 1 SEM micrographs showing the morphology of commercial lithium carbonate: (a) decomposed PSG-derived xerogel sample; (b) at a magnification of 20 kX; (c) LiNO_2 obtained after heat treatment at 750°C for 5 h.

shrinking with time to form precipitates. Subsequent to this approach, [Acosta et al. \(1994\)](#) demonstrated formation of oxide gels via a non-hydrolytic sol-gel process through the reaction of an aluminum alkoxide with corresponding halide salt to form the oxide gel releasing alkyl halide. Alumina gels were obtained by conducting the reaction in the $70\text{--}110^\circ\text{C}$ temperature range. Calcination in air at 600°C resulted in alumina with loss of the volatile hydrocarbons showing another approach to generating oxides without the normal hydrolysis and condensation of metal alkoxides.

- (2) *Colloidal precipitation.* This is a classical method for synthesizing several crystalline and amorphous metal oxides. The procedure consists of solubilizing the inorganic or organometallic salts of any desired metal in an aqueous or non-aqueous solvent followed by hydrolysis using strong inorganic hydrolyzing agents that tend to be strong electrophiles as well as alkaline bases such as NH_4OH or NaOH . In most cases, the immediately generated precipitated hydroxides depending on the concentration are heat-treated to yield the oxides. In some cases such as barium titanate, oxalate precipitates derived from a solution of chlorides or nitrates are decomposed to form the oxide ([Reed, 1988](#)). Precipitation is induced when the solubility product, K_{sp} is exceeded. The precipitation approach has been exploited extensively earlier on by Matijevic as reported by [Ellis and McNamara \(1989\)](#) for synthesizing a vast array of uniform dispersions of homogeneous and monosized particles of oxide and nonoxides that could be isolated or even self-assembled into unique colloidal architectures. The kinetics of the reactions are controlled to induce uniform growth of a single burst of nuclei yielding spherical particles with a narrow size distribution in the range of $0.5\text{ }\mu\text{m}$.
- (3) *Intercalation and ion exchange.* These are important approaches that have evolved over the years and has become synonymous with generation of high surface area layered structures by exfoliation for synthesizing several layered compounds and involve hosting a variety of guest molecules in the cavities, channels, or interlayer spaces of host oxides and sulfides ([Rao, 1994](#)). Many of these reactions are topochemical governed by orientation relationships rather than involving major changes in crystal structures. The unique feature of ion-exchange and intercalation would be to preserve the host crystal structure. Characteristic intercalation reactions are those popularized in the Li-ion battery field dominated by lithiated transition metal oxides LiMO_2 ($\text{M} = \text{Ni}, \text{Co}, \text{V}, \text{and Mn}$). Insertion and removal of Li^+ results in alteration of the oxidation state of the transition metal leading to an electrochemical potential which is the basis for lithium-ion batteries. Ion exchange is also effective in yielding new oxides as seen in $\beta\text{-Al}_2\text{O}_3$ ($\text{Na}_2\text{O} \cdot n\text{Al}_2\text{O}_3$, $n = 5\text{--}11$) and NaMnO_2 where other cations in the former and lithium in the latter can exchange sodium. The approach has also been used to insert Li^+ into graphitic anodes for Li-ion batteries.
- (4) *Hydrothermal and solvothermal processes.* These are powerful methods for synthesizing oxides and involve reactions that occur in the presence of a solvent under supercritical conditions or close to such temperature – pressure domains ([Demazeau, 1999](#)).

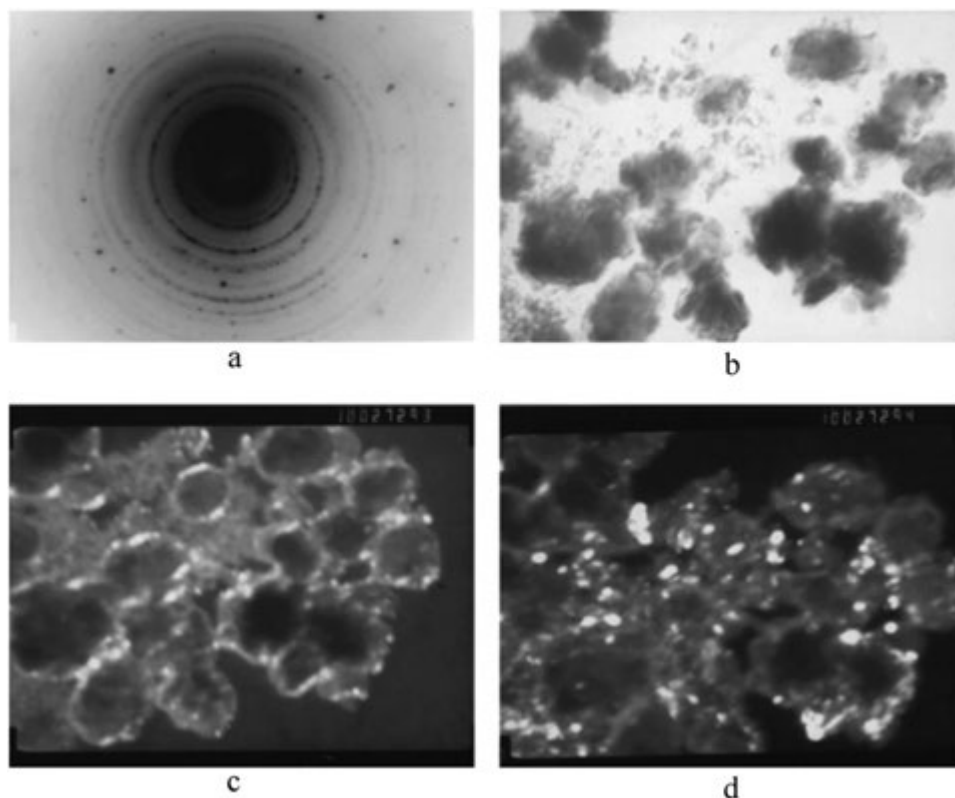


Fig. 2 (a) Diffraction pattern of the decomposed PSG-derived xerogel sample corresponding to Li_2CO_3 and NiO ; (b) corresponding bright field image; (c) dark field image of lithium carbonate taken at the same region as shown in the bright field image; (d) dark field image corresponding to nickel oxide.

The physicochemical properties of the solvent under varying temperature and pressure can be used to alter diffusion of chemical species resulting in the stabilization of novel structures that are difficult or not obtained via standard techniques. The term “hydrothermal” is given to reactions performed in the presence of water (Lencka and Riman, 1993). A variety of ferroelectric oxides [$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$], spinels (LiMn_2O_4), giant magnetoresistant oxides ($\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$), and phyllosiloxides ($\text{KMg}_2\text{AlSi}_4\text{O}_{12}$), a new class of bi-dimensional oxides, has been obtained by this method. The approach has grown over the years and used now routinely to generate unique metastable microstructures such as nanotubes and nanowires of a variety of oxides (Ghadge *et al.*, 2018; Patel *et al.*, 2016)

- (5) *Topochemical methods.* These methods are based on executing reduction and oxidation reactions conducted on the parent system leading to a homologous series of compounds (Rao, 1994). The reactions are governed by inducing orientation changes in the parent oxide. Examples can be seen in LaNiO_3 and LaCoO_3 wherein the formation of the homologous series $\text{La}_n\text{B}_n\text{O}_{3n-1}$ ($\text{B} = \text{Ni, Co}$) is observed by reduction of the parent oxide LaBO_3 ($\text{B} = \text{Ni, Co}$) in hydrogen. The parent oxide is recovered by oxidation. The high-temperature superconductor phase, $\text{YBa}_2\text{Cu}_3\text{O}_7$ can be reduced to $\text{YBa}_2\text{Cu}_3\text{O}_6$ by a similar topochemical reaction. A similar topochemically induced relationship is observed in the transformation of the perovskite-like phases of various manganites $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_{6-y}$ ($y < 1$), belonging to the homologous series $\text{A}_n\text{B}_n\text{O}_{3n-1}$ ($n = 3$; $\text{A} = \text{Ca, Fe}$; $\text{B} = \text{Mn}$), to the brownmillerite structures. Similar approaches are popular in the catalysis field.
- (6) *Thermal decomposition of precursors.* This approach is suitable for synthesizing mixed metal oxides by decomposition of a single solid precursor containing all the individual components (Rao, 1994). A major advantage is the reduced diffusion distances of the multiple ions due to the generation of the solid precursor via solution approaches. Thus thermal decomposition of $\text{LaCo}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$ and $\text{LaFe}(\text{CN})_6 \cdot \text{H}_2\text{O}$ in air readily yields LaCoO_3 and LaFeO_3 . Similarly, BaTiO_3 and LiCrO_2 can be obtained by decomposing the precipitated oxalates $\text{Ba}[\text{TiO}(\text{C}_2\text{O}_4)_2]$ and $\text{Li}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$. Single-phase solid solutions of the monoxides $\text{Mn}_{1-x}\text{M}_x\text{O}$ ($\text{M} = \text{Mg, Ca, Co, or Cd}$) possessing the rock-salt structure are also obtained by decomposition of the isostructural carbonates of the metals. Similarly, ternary and quaternary oxides of the perovskite and the brownmillerite families can be obtained. Perovskite and related oxide structures containing mixed metals can also be obtained by decomposing hydroxide, nitrate, and cyanide solid solutions.
- (7) *Pechini process.* This method has been exploited over the years by several researchers and is as popular as the sol-gel process and has been used for synthesizing over 100 mixed metal oxides including lanthanum manganite for solid oxide fuel cells and BaTiO_3 that was first popularized by Lessing (1989). Unlike the sol – gel process in which the metal alkoxide creates alkoxy moieties participating in the gel forming reactions, this process is also based on a gelation reaction primarily induced

by a polymeric esterification reaction between the alcohol and acid used as solvents. A polymeric resin containing a good distribution of cations is thus obtained which yields the oxide upon calcination. The use of polyacrylic acid with higher functionality results in highly cross-linked resins containing a more uniform distribution of the reacting cations. The gel structures can be easily and conveniently varied depending on the acid-to-alcohol ratio. A low organic content is however preferred to decrease the calcination time and temperature in order to obtain fine-grained materials with low carbon contents and high purity. The presence of carbon can also be tailored depending on the application requiring improved transport of surface charges especially in the field of supercapacitors discussed later.

- (8) *Microemulsion techniques.* The approach is based on the immiscibility of organic liquids (oils) and water resulting in droplets. An oil-in-water emulsion is generated if the first liquid is oil and the second is water, and water-in-oil if the sequence is reversed. Macroemulsions are turbid due to the large droplet size ($> 1 \mu\text{m}$). Microemulsions on the other hand, are thermodynamically stable and are transparent, created by modifying the oil and water interface using surfactants. The droplets are smaller than $0.15 \mu\text{m}$. A water-in-oil microemulsion or a reverse micelle microemulsion contains hydrocarbon chains with their polar heads pointing inwards. The central portion is the aqueous phase in which inorganic reactions can be conducted to yield several oxides (Osseo-Assare and Arriagada, 1990). Alteration of the pH can result in folding of the micellar regions to form microtubules. Sol – gel reactions conducted around the cylindrical micelles after calcination lead to oxide tubules. Mesoporous SiO_2 (MCM-41) has been obtained in this fashion which has been popularized over the years for catalytic applications (Kresge *et al.*, 1992).
- (9) *Other techniques.* Several modified approaches have emerged, some of which include spray pyrolysis and aerosol decomposition. In these methods the clear sol containing colloidal particles or a clear solution of metal salts can be easily atomized to form droplets through an atomizer that can be then pyrolyzed by leading the aerosol droplets into a furnace to yield metal oxides. Nebulization leads to a mist or an aerosol containing fine-sized droplets that are decomposed to form oxides. Transparent conducting oxides (e.g., SnO_2) (Chawla *et al.*, 1983) and other oxides have been obtained in this fashion. The approach has also been universally adopted for a variety of oxides.

Other techniques include mechanochemical approaches (Gaffet *et al.*, 1999) based on high-energy mechanical milling of oxide precursors to yield nanostructured solid solutions. A variety of oxides such as mullite, calcia and yttria-doped ZrO_2 , zircon and Al_2O_3 , ZrO_2 , $\text{ZrO}_2 - \text{MgO}$ solid solutions, and LiMO_2 ($\text{M} = \text{Ni, Co}$) has been obtained. Other methods include self-propagating high-temperature combustion and flame synthesis methods to yield oxides. The former involves sustained use of an exothermic oxidation reaction typically initiated by an ignition step which sets up instantaneously, a combustion front that assists in the reaction. The latter is an extension of combustion involving the oxidation of SiCl_4 and AlCl_3 to yield oxides (Lin *et al.*, 1999; Chung *et al.*, 1990). The approach received significant attention due to the ability to create extremely fine particles in the nanometer range.

Emergent techniques

Over the years, since 2000, there have been improvised methods of chemical and solution based approaches to generate various oxide systems for a variety of applications. These range from electrodes for supercapacitors to framework materials for rechargeable lithium ion batteries, electrocatalysts for proton exchange membrane (PEM) based fuel cells (PEMFCs) utilizing hydrogen derived from electrolysis of water as well as the recently emerging field of perovskite based solar cells including biomaterials and delivery systems for tissue engineering and regenerative medicine. These advances have also stemmed from the emergence and growing developments in the field of nanotechnology.

Supercapacitors: The field of supercapacitors until 2000 was largely dominated by the concept of double layers and surface adsorption of electric charges. Thus, carbon based systems demonstrating the ubiquitous electrical double layer was the primary phenomenon behind the electric double layer capacitors (EDLC) wherein the ability of protons and hydroxyl ions as well as other cations and anions present in electrolytes to adsorb to high surface area electrodes was the primary source for charge storage. However, with the emergence and the recognition of lithium-ion intercalation and ability to cycle Li-ions in host systems, the concept of incorporating ions exhibiting multi-valence states and the accompanying oxidation and reduction (redox) of the cations contributing to charge storage in addition to surface active states presented by the high surface area substrate gave rise to the field of pseudo-capacitors and the coining of the term, supercapacitors for systems exhibiting very high ability to store charge capitalizing on the system undergoing Faradaic redox reactions combined with high surface area. Thus, the system driven largely by noble metal based oxides such as high surface area RuO_2 as well as transition metal non-oxides became immensely popular in the mid-2000 and beyond (Jampani *et al.*, 2010; Choi *et al.*, 2006). Crystalline RuO_2 and amorphous $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ are well-known pseudocapacitors that are well-studied exhibiting specific capacitance as high as 350 F/g and 720 F/g, respectively. The high capacitance follows from the redox activity presented by Ru via proton adsorption in acidic electrolyte. Despite the high cost of RuO_2 , it has been studied extensively since Ru presents the ability to undergo a variety of oxidation states (II-IV) while also exhibiting very good electronic conductivity ($\sigma_{\text{bulk}} = 2.8 \times 10^6 \text{ S/m}$). Crystalline and amorphous RuO_2 are largely synthesized by chemical approaches involving mixing aqueous solutions of NaOH and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$. The base, NaOH was added to mainly adjust the pH to a value of ~ 7 , to initiate controlled precipitation. Crystallinity was controlled by annealing the precipitated hydrous oxide at elevated temperatures (Hu *et al.*, 2004; Zheng and Jow, 1995).

Beginning in 2000 and beyond until the resurgence of lithium ion systems, supercapacitor systems utilizing multiple oxidation states of transition metals was a targeted focus. In this connection to combat the cost of precious group metals, effort was directed to vanadium. Accordingly, VN and V_2O_5 were explored as charge storage systems. In the latter case, the approach was to exploit the

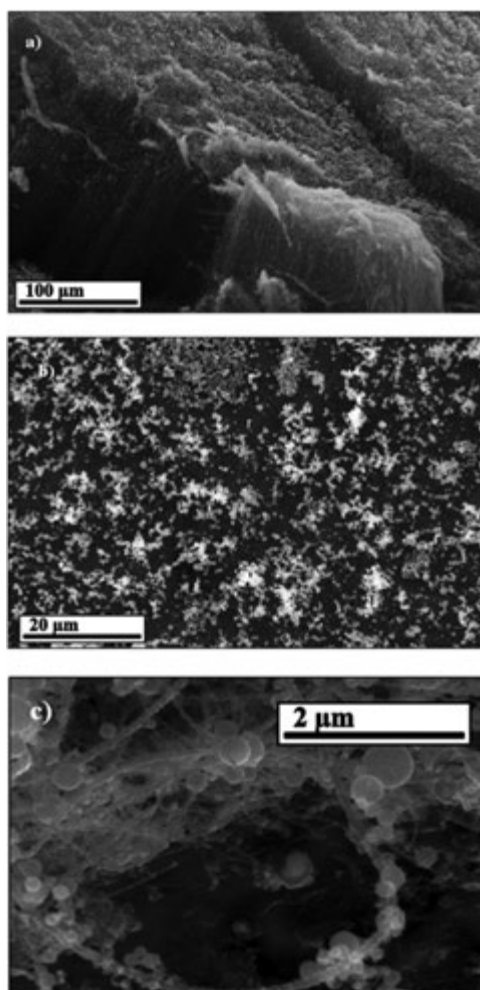


Fig. 3 Scanning electron microscope images of (a) VACNT; (b) Vanadium oxide thin film; (c) CVD deposited vanadium oxide – VACNT architectures.

electronic conductivity of a substrate to serve as the carrier to house the nanoparticles of the transition metal oxide. In this regard, the well-known electronic and mechanical compliance characteristics of carbon nanotubes was heavily exploited. For example, [Jampani et al. \(2013\)](#) utilized a facile two-step chemical vapor deposition (CVD) approach to synthesize carbon nanotube (CNT) supported vanadium oxide nanoparticles as a heterostructured composite architecture to serve as electrochemical supercapacitors. The high electronic conductivity of CNTs was exploited to provide a facile 3-D electron transport channel on which the vanadium oxide nanoparticles interact with the electrolyte to demonstrate superior supercapacitor response in aqueous media. They have shown that nanoparticulate droplets of vanadium oxide deposited on CNTs exhibit excellent capacitance values as high as 1400 F/g with acceptable rate capability and excellent charge retention up to 200 cycles. They used nickel disks on which vertically aligned carbon nanotubes (VACNTs) were deposited following an approach wherein a mixture of ferrocene in m-xylene was used as the carbon source with ferrocene acting as the catalyst for CNT nucleation and growth. The mixture following vaporization was led into a hot wall CVD reactor maintained at 700°C. A low temperature atmospheric pressure CVD (APCVD) setup was used to generate vanadium oxide nanoparticles directly on the vertically aligned carbon nanotubes. To generate the vanadium oxide nanoscale droplets, vanadium chloride, VCl_4 and distilled water were used as precursors that were evaporated and carried into the hot wall CVD reactor wherein the CNT coated Ni disks were placed. Deposition to generate the vanadium oxide nanoparticles on the vertically aligned CNT was conducted at 450°C for 45 min. **Fig. 3** shows the scanning electron microscope collected image of vertically aligned CNTs deposited by chemical vapor deposition on Ni substrate. The oxide deposited is in the form of 0.2–0.5 μm diameter spheres which cover the length of the CNT at regular spacing between each spherical particle allowing for maximum electron transport through the CNT-oxide interface minimizing transport through the oxide grain boundaries enabling fast charge transfer of the stored charge. The nanospherical morphology also affords increased surface exposure of the oxide to the electrolyte thus maximizing the electrochemical surface area resulting in optimal capacitance response.

[Jampani et al. \(2015\)](#) further studied the influence of doping of Ti into the VACNT derived vanadium oxide nanoscale droplets in a subsequent publication showing the improved electronic conductivity of the Ti-doped vanadium oxide nanospheres on

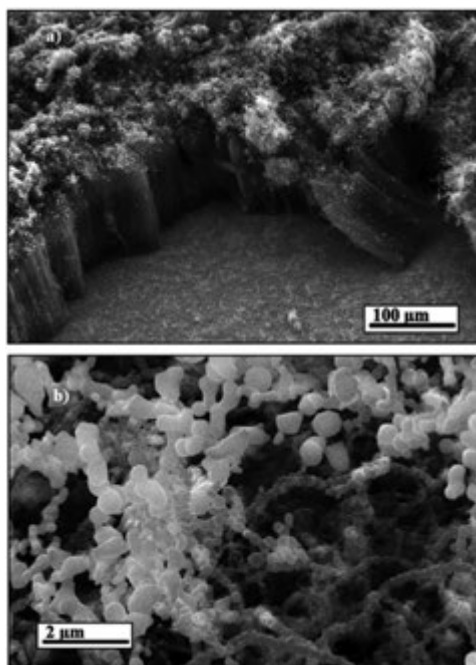


Fig. 4 SEM image of (a) CVD derived VACNTs coated with Ti doped vanadium oxide showing VACNT forests and (b) Ti-doped vanadium oxide coated CNTs grown by CVD.

VACNT in the form of a semi-contiguous film comprising of ~ 250 nm diameter amorphous Ti-doped vanadium oxide ($V_{1.6}Ti_{0.4}O_{5-x}$ with $x \sim 0.4$) globules (Fig. 4) similar in morphology to those seen in Fig. 3. The doping of Ti was achieved by using $TiCl_4$ and VCl_4 dissolved in an aprotic solvent of chloroform recovered in a sealed stainless steel evaporator bottle. The doped vanadium oxide nanospheres were deposited on the VACNTs using a hot wall tubular atmospheric pressure CVD similar to undoped vanadium oxide. Deposition was carried out at 250°C for 20 min. The Ti-doped vanadium oxides results in an order of magnitude improvements in electronic conductivity compared to the undoped counterparts. The increase in electronic conductivity induced by the introduction of the dopant via the CVD process coupled with the anchoring of the doped oxide nanoparticles to the carbon nanotube is expected to increase the electron transport and hence, result in enhanced supercapacitor performance (Jampani *et al.*, 2015).

Electrocatalysts: Over the last decade or so, there has been intense activity in the area of electrocatalysts for acid mediated proton exchange membrane (PEM) based fuel cells and water electrolysis for generating hydrogen to drive the PEM-based hydrogen fuel cells. Iridium oxide (IrO_2) has been the gold standard platinum group metals (PGM) metals based electrocatalyst. The standard method for generating IrO_2 has been the Adams catalyst synthesis approach based on the oxidative reduction of the salts of platinum group metals. Modification of the Adams synthesis approach has been attempted to generate high specific surface area IrO_2 ($\sim 191\text{ m}^2/\text{g}$) electrocatalyst followed by doping with fluorine. Fluorine contents of 5, 10, 15 and 20 wt% were incorporated into the oxide to improve the electronic conductivity. The approach consisted of reacting iridium tetrachloride [$IrCl_4$] and ammonium fluoride [NH_4F] in stoichiometric amounts dissolved in deionized water (D.I.). The solution containing these dissolved salts were then reacted with excess sodium nitrate also in D.I. water to generate the corresponding nitrate precursors with vigorous stirring for 2 h followed by evaporation to remove the water at 60°C and then subsequently, heat treating the nitrate mixture to 500°C for 1 h to generate the high specific surface area F-doped IrO_2 powders. The F-doped IrO_2 nanoparticles generated by Kadakia *et al.* (Fig. 5) show the $\sim 5\text{--}10$ nm sized particles of $IrO_2:10\text{ wt\% F}$ electrocatalyst of specific surface area $\sim 157\text{ m}^2/\text{g}$ (Kadakia *et al.*, 2014a,b,c).

Following the demonstration of F-doped IrO_2 , there have been several studies to generate reduced PGM containing electrocatalysts and also PGM-free oxide electrocatalysts. Accordingly, tin oxide containing reduced amount of Ir maintaining the solid solution of tin oxide and the same lattice registry was generated. Similarly, manganese oxide containing reduced amount of Ir also maintaining solid solution of manganese oxide and iridium oxide were synthesized to demonstrate similar electrocatalytic performance as the parent IrO_2 . Keeping in line with the hypothesis of reducing the noble metal content while preserving the crystal structure of the parent oxide and thereby result in a solid solution, first attempted to generate solid solutions of IrO_2 containing tin oxide accompanied by fluorine doping. Correspondingly, they synthesized $SnO_2:10\text{ at\%F}$ containing only 20 at% IrO_2 to form $(Sn_{0.80}Ir_{0.20})O_2:10F$ to demonstrate robust electrocatalytic performance of acid mediated proton exchange membrane based oxygen evolution reaction (OER) electrocatalysts. They generated the solid solution oxide electrocatalyst by dissolving the respective chloride salts of Ir and Sn along with NH_4F as the source for fluorine. Stock solutions corresponding to $IrCl_4$ and $SnCl_2 \cdot 2H_2O$ of the desired compositions were dissolved in absolute ethanol. Ammonium fluoride was dissolved in an ethanol-water mixture. The stock

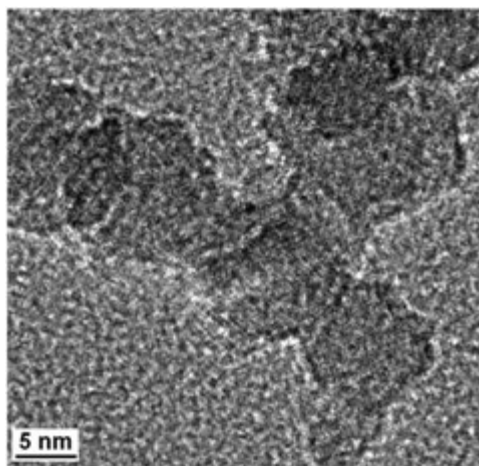


Fig. 5 High resolution TEM image of $\text{IrO}_2:10 \text{ wt\% F}$ particles showing the nanostructured nature of the electrocatalysts.

solutions of the fluoride and the oxide were mixed to generate the $(\text{Sn}_{0.80}\text{Ir}_{0.20})\text{O}_2:10\text{F}$ electrocatalyst by spin coating on pretreated titanium substrates at a rotating speed of 500 rpm for 10 s. The spin coated films were dried at 60°C for 2 h and then thermally treated at 400°C for 4 h in air to decompose the precursors and form the solid solution oxide electrocatalyst composition containing fluorine as the doped anion. **Fig. 6** shows the SEM micrograph along with X-ray mapping of Ir, Sn, and O (**Fig. 6(a)**) and EDAX (**Fig. 6(b)**) of the $(\text{Sn}_{0.8}\text{Ir}_{0.2})\text{O}_2:10\text{F}$ film. The SEM image along with the elemental x-ray mapping (**Fig. 6(a)**) combined with EDAX (**Fig. 6(b)**) of the representative area of the $(\text{Sn}_{0.8}\text{Ir}_{0.2})\text{O}_2:10\text{F}$ film containing 10 wt%F indicates the presence of the typical “mud crack” features of the oxide coated film on the Ti foil (**Fig. 6(a)**) confirming the presence of Ir, Sn and O homogeneously distributed within the oxide film particles. The bright field TEM image of the film (**Fig. 6(c)**) shows presence of fine nanometer size ($\sim 10\text{--}15 \text{ nm}$) particles corresponding to the solid solution composition of $(\text{Sn}_{0.8}\text{Ir}_{0.2})\text{O}_2:10\text{F}$.

Subsequent to the successful demonstration of the excellent electrocatalytic activity for OER of the solid solution thin film generated of composition of $(\text{Sn}_{0.8}\text{Ir}_{0.2})\text{O}_2:10\text{F}$ that is indeed comparable or even better than pure IrO_2 OER catalyst considered as the gold standard, the group also followed by generating nanostructured powders of the same solid solution composition. They observed that $(\text{Ir}_{0.3}\text{Sn}_{0.7})\text{O}_2:10 \text{ wt\% F}$ displayed electrochemical activity for oxygen evolution reaction in acid mediated PEM based conditions comparable to commercially obtained pure IrO_2 demonstrating a reduction of $\sim 70 \text{ mol\%}$ in the noble metal content (*Kadakia et al., 2014a,b,c*). The powders were generated by using a surfactant based template approach. A mixed amphiphilic surfactant cetyl trimethylammonium bromide (CTAB) is dissolved in de-ionized (D.I.) water to which 6 wt% ammonium hydroxide is added. After homogenization, a solution of tin chloride hydrate dissolved in D.I. water is added which results in a white slurry. To introduce fluorine, NH_4F dissolved in D.I. water is added after the addition of the tin chloride. The resultant solution is aged at room temperature for 48 h after vigorous stirring for 4 h. The precipitate obtained is filtered and dried in an oven at 50°C followed by heat treatment in air at 300°C resulting in fluorine doped SnO_2 . To prepare the iridium tin oxide solid solution, IrCl_4 was dissolved in ethanol along with the required amounts of the as-prepared F-doped SnO_2 . The solution was dried in an alumina crucible in an oven for 60°C for 3 h and then subjected to heat treatment in air at 400°C for 4 h to form the $(\text{Ir}, \text{Sn})\text{O}_2:\text{F}$ solid solutions. **Fig. 7** shows the bright field TEM image of the undoped and 10 wt% F doped $(\text{Ir}_{0.3}\text{Sn}_{0.7})\text{O}_2$ nanoparticles.

In line with synthesis of the solid solution of Sn containing iridium oxide, the researchers also explored solid solution of RuO_2 with 80 at% SnO_2 [e.g., $(\text{Sn}_{0.8}\text{Ru}_{0.2})\text{O}_2:10\text{F}$] synthesized by a very similar approach displaying remarkably similar electrochemical activity and moreover, even comparable or much improved electrochemical stability and durability compared to the undoped and pure noble metal equivalent oxide, RuO_2 . They prepared the solid solution oxide using ruthenium chloride, RuCl_3 and tin chloride, SnCl_2 dihydrate with ammonium fluoride as the starting precursors (*Kadakia et al., 2014a,b,c*). Stock solutions corresponding to RuCl_3 and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ of the desired composition were dissolved in absolute ethanol along with use of NH_4F dissolved in ethanol-deionized water mixture of 5:1 vol ratios. They spin coated the mixture of the chlorides and the fluoride at a speed of 500 rpm for 10 s followed by drying at 60°C for 2 h after which they were thermally heat treated at 450°C for 4 h in air to decompose the precursors and generate the solid solution electrocatalyst. **Fig. 8** shows the SEM image with x-ray mapping of the Ru, Sn and O in the $(\text{Sn}_{0.8}\text{Ru}_{0.2})\text{O}_2:10\text{F}$ film. The TEM image also similar to the Ir system shows the presence of fine nanoparticles.

Efforts were also focused on generating vertically aligned nanorods of the reduced precious group metal containing electrocatalysts. Keeping in line with this theme and trying to exploit the nanoscale aspects to achieve improved electron and ion transport, the team of *Chadge et al. (2018)* explored and first reported the synthesis of vertically aligned $(\text{Sn}_{0.8}\text{Ir}_{0.2})\text{O}_2:10\text{F}$ nanotubes showing excellent electrocatalytic activity for acid mediated oxygen evolution reaction (OER) superior to IrO_2 thin film. They generated the nanotubes by first generating ZnO nanowires as a sacrificial template on Ti foils by the hydrothermal method. Zinc acetate solution in ethanol was spin coated on cleaned Ti substrates at 500 rpm for 40 s and then heated to dry at 125°C . The Ti foil containing the zinc acetate layer was then subjected to heat treatment in air at 340°C for 20 min which resulted in the seed layer of ZnO on the Ti foil. To grow the ZnO nanowire template, the Ti foiled containing the ZnO seed layer was placed in a sealed container- enclosing the growth solution of zinc nitrate hexahydrate,

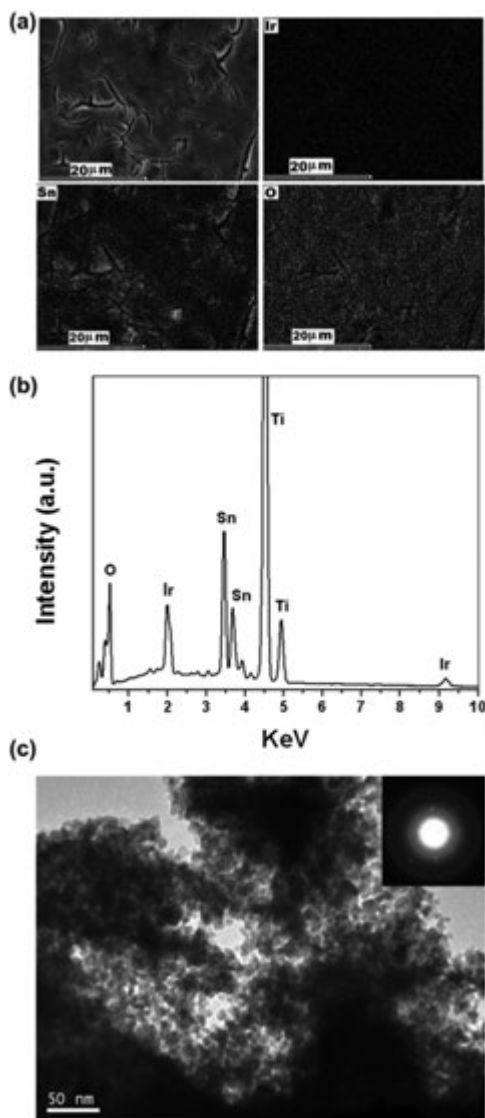


Fig. 6 SEM micrograph and x-ray mapping of Ir, Sn and O (a) and EDAX (b) of the $(\text{Sn}_{0.8}\text{Ir}_{0.2})\text{O}_2\cdot 10\text{F}$ film. (c) Bright field TEM image of film showing nanoparticles in the film.

hexamethylenetetramine, polyethyleneimine and ammonium hydroxide. The sealed container was placed in a water bath, preheated to 90°C for 6 h. The formed nanowires were then carefully washed with ethanol and D.I. water followed by drying at 50°C for 6 h.

The tin oxide nanotubes, SnO_2 NTs were generated using the ZnO nanowires template by placing the ZnO nanowires grown Ti substrate in an aqueous solution of 3 ml of 0.15 M ammonium hexafluorostannate with 1 ml of 0.5 M boric acid and 1 ml of D.I. water at 26°C for 30 min. In this process, the ZnO nanowire template on Ti substrate is replaced with the SnO_2 nanotubes retaining the pre-formed vertically aligned morphology of ZnO. Following the generation of the SnO_2 NTs, the Ti substrate containing the SnO_2 NTs were placed in a solution of IrCl_4 and ammonium fluoride in DI water corresponding to the composition of $(\text{Sn}_{0.8}\text{Ir}_{0.2})\text{O}_2\cdot 10\text{ wt}\% \text{F}$. The Ti substrate containing the SnO_2 NTs infiltrated with IrCl_4 and NH_4F solution was then subjected to heat treatment at 400°C for 4 h to form the $(\text{Sn}_{1-x}\text{Ir}_x)\text{O}_2\cdot 10\text{F}$ vertically aligned nanotubes (VANTs) on Ti foil. The entire synthesis scheme is shown in Figs. 9 and 10 shows the morphology and elemental mapping analysis of the synthesized $(\text{Sn}_{0.8}\text{Ir}_{0.2})\text{O}_2\cdot 10\text{ wt}\% \text{F}$ VANTs.

The above is a demonstration of how chemical synthesis approaches were utilized to generate solid solutions of mixed oxide elements to generate effective electrocatalysts for OER in acid mediated PEM based water electrolysis. In line with the overall aims to reduce the precious group metal contents, efforts have also been directed to synthesize highly efficient and robust electrocatalysts that are completely devoid of any noble or precious metal contents. The group embarked on exploiting spinel oxides containing the base structure of manganese oxides with incorporation of copper to generate the spinel oxides along with doping the oxide solid solution with fluorine to induce improvements in electrical conductivity needed to match these systems with precious group metals such as Pt and IrO_2 . Exploiting density functional theory (DFT) as with the other systems discussed above, Patel *et al.* (2016) identified and synthesized $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4\cdot 10\text{F}$ as an effective spinel electrocatalyst showing excellent activity for OER as well as oxygen reduction

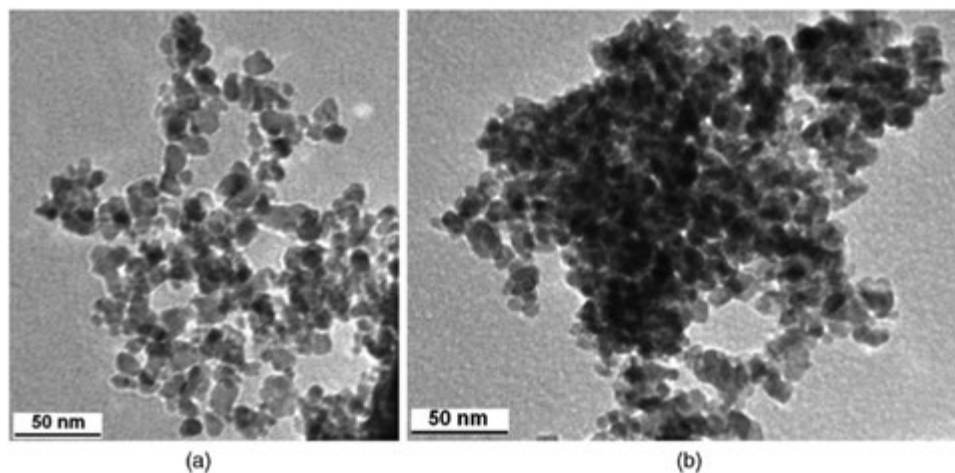


Fig. 7 Bright field TEM image of (a) $(\text{Ir}_{0.3}\text{Sn}_{0.7})\text{O}_2:10 \text{ wt\% F}$, and (b) undoped $(\text{Ir}_{0.3}\text{Sn}_{0.7})\text{O}_2$ showing the nanometer sized fine particles generated by the template approach.

reaction (ORR) in acid mediated PEM based systems. They synthesized the high surface area nanoparticles of $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4:10\text{F}$ by exploiting a template approach. First, they synthesized nanoparticles (NPs) of MnO_2 by taking manganese acetate tetrahydrate dissolved in 25 ml of DI water. To this solution, KMnO_4 was added with vigorous stirring immediately resulting in the formation of a brown precipitated slurry. The precipitate was collected by filtration and then thoroughly washed by DI water followed by drying at 60°C for 2 h which formed amorphous MnO_2 nanoparticles which gave a specific surface area of $\sim 150 \text{ m}^2/\text{g}$. The $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4:10\text{F}$ NPs were generated by soaking the as-synthesized MnO_2 NPs in stoichiometric amounts of copper chloride dehydrate achieved by dissolving $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 25 ml of DI water followed by addition of as-synthesized MnO_2 NPs. To generate the F doped oxide, $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4:10\text{F}$, again stoichiometric amount of ammonium fluoride (NH_4F) was dissolved in 5 ml of DI water to which was added stoichiometric amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (20 ml) solution with stoichiometric amount of as synthesized MnO_2 NPs. The solution of the MnO_2 NPs along with the solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and NH_4F was dried in an alumina crucible in a drying oven at 60°C for 2 h followed by heat treatment in air at 500°C for 4 h. They generated $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4: x \text{ wt\% F}$ with different F contents ($x = 0, 5, 10, 15$) with $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4:10\text{F}$ exhibiting the best OER and oxygen reduction reaction (ORR) response under acid mediated PEM conditions. **Fig. 11** shows the schematic of the synthesis approach and morphology of the synthesized spinel NPs.

Synthesis of electrocatalyst systems discussed thus far has focused on acid mediated PEM based electrolysis and fuel cells. However, there has also been sufficient interest in identifying, developing and synthesizing electrocatalysts in the neutral and alkaline conditions as well. [Kanan and Nocera \(2008\)](#) for example demonstrated that by electrodepositing cobalt phosphate on indium tin oxide, they were able to demonstrate good electrocatalytic activity for water splitting under neutral conditions. The electrodeposited electrocatalyst film of potassium containing amorphous cobalt phosphate ($\text{Co}_3(\text{PO}_4)_2$) in **Fig. 12** shows the typical mud-crack morphology similar to that seen under spin coating discussed above.

Similarly, [Suntivich et al. \(2011\)](#) showed that $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) catalyzes the OER reaction with intrinsic electrochemical activity that is at least an order of magnitude higher than the state of the art iridium oxide electrocatalyst in alkaline media. They prepared the BSCF electrocatalyst using glycine nitrate combustion approach wherein alkaline earth and transition metal nitrates were prepared in water to which glycine was added at 0.1 M concentration. The mixture was heated with vigorous evaporation followed by calcining at 1100°C in air for 24 h to generate the BSCF electrocatalyst. **Fig. 13** shows the XRD pattern of the BSCF electrocatalyst.

Biomaterials: The field of biomaterials has been largely dominated by biodegradable polymers with the approval granted by Food & Drug Administration (FDA) to the use of biodegradable polymers, such as polycaprolactone (PCL), poly-L-lactic acid (PLLA) and polyglycolic acid (PGA) as well as co-polymers of PLLA and PGA, namely poly-L-lactic-co-glycolic acid (PLGA). The use of calcium phosphates (CaPs) is well documented in the literature ([Lee et al., 2012](#)) primarily for use as scaffolds and delivery systems. In fact, one of the earliest uses of CaPs in the form of particulates has been as a control system for non-viral gene delivery. However, in early 2000 and even later on, [Olton et al. \(2007\)](#) showed for the first time that with control of the concentration of the reactants without the use of any toxic surfactants, it is possible to generate uniform, nano-sized, mono-dispersed CaP nanoparticles complexed with plasmid DNA (pDNA) under physiological conditions. They generated the CaP nanoparticles which they appropriately called nanostructured calcium phosphates also abbreviated and termed as NanoCaPs by reacting the Ca-salt, CaCl_2 with a phosphate precursor, Na_3PO_4 along with the base such as NaOH chosen suitably to ensure that the pH during the whole process remains above neutral to ensure hydroxyapatite formation but stable at physiological pH of 7.4 critical to cellular function and viability. As a result the process was executed thus maintaining the pH greater than 7 to consistently generate stoichiometric hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ under physiological conditions. Moreover, when they synthesized NanoCaPs by adding pDNA to $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and then adding the pDNA complexed $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ to an equal volume of phosphate precursor solution at pH 7.5 in a controlled manner using a syringe pump at a set flow rate of $13.4 \mu\text{l/s}$, the resultant precipitation reaction leads to condensation of the plasmid DNA forming condensed and complexed form of NanoCaPs-pDNA complexes. These NanoCaPs-pDNA nanoparticulate complexes in the range of 25–50 nm in size (**Fig. 14**)

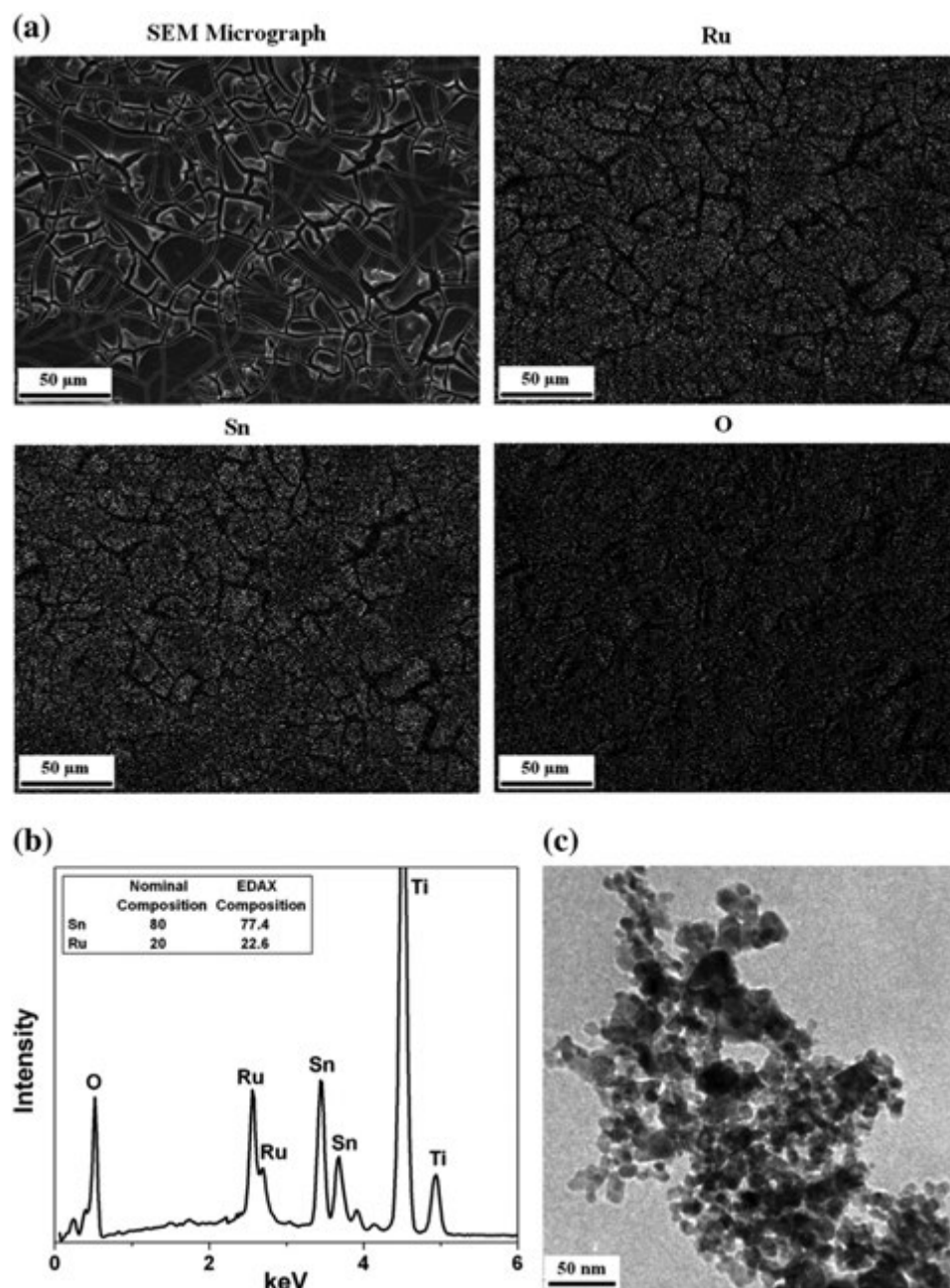


Fig. 8 SEM micrograph combined with x-ray mapping of elements (a), and EDAX (b) of $(\text{Sn}_{0.8}\text{Ru}_{0.2})\text{O}_2:10\text{F}$ film. (c) TEM bright field image of $(\text{Sn}_{0.8}\text{Ru}_{0.2})\text{O}_2:10\text{F}$ film indicating clearly the presence of nanoparticles in the thin films.

could serve as efficient carriers of pDNA for non-viral gene transfection. Following this demonstration, there have been several developments of use of CaPs as scaffolds in mineralized tissue engineering. The development of injectable bone cements using NanoCaPs as well as CaP systems combined with biodegradable polymers has demonstrated efficacy for releasing growth factors and antibiotics (Roy *et al.*, 2016). Roy *et al.* prepared the cements by mixing the CaP cement precursor with NanoCaPs solution in a polystyrene pour boat. The cements would set at 25°C and 37°C with an initial set time of 9 min and final setting time of 25 min at 25°C. At physiological temperature of 37°C, the initial setting time would reduce to 7 min with a final setting time of 19 min. With the addition of PLGA polymer of particle size 40 µm, the initial and final setting times were measured to be 10 min at 28 min at 37°C. The PLGA-CaP cement made by adding a resorbable calcium phosphate (ReCaPP) cement to PLGA serves as an effective delivery systems as well as forms a porous cement (Fig. 15) that will undergo resorption when implanted thus serving as an effective drug, growth factor as well as an efficient and very safe non-viral gene delivery systems capable of delivering the required payloads and dosage while also acting as promising resorbable scaffolds for mineralized tissue engineering applications. The synthesis of this composite is a demonstration of how effectively a composite cement can be made using an oxide ceramic such as CaP along with a degradable polymeric

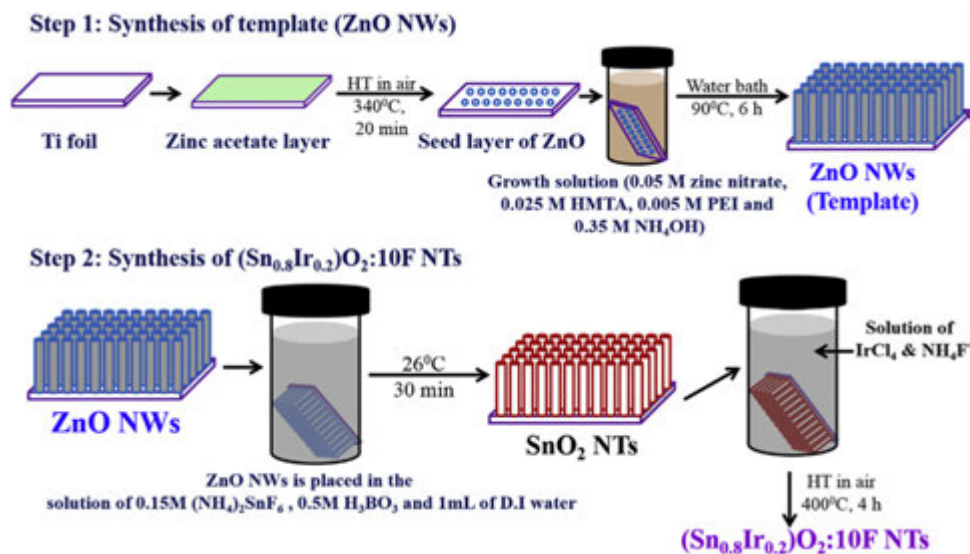


Fig. 9 Schematic of the synthesis of (Sn_{0.8}Ir_{0.2})O₂:10F VANTs using the template approach.

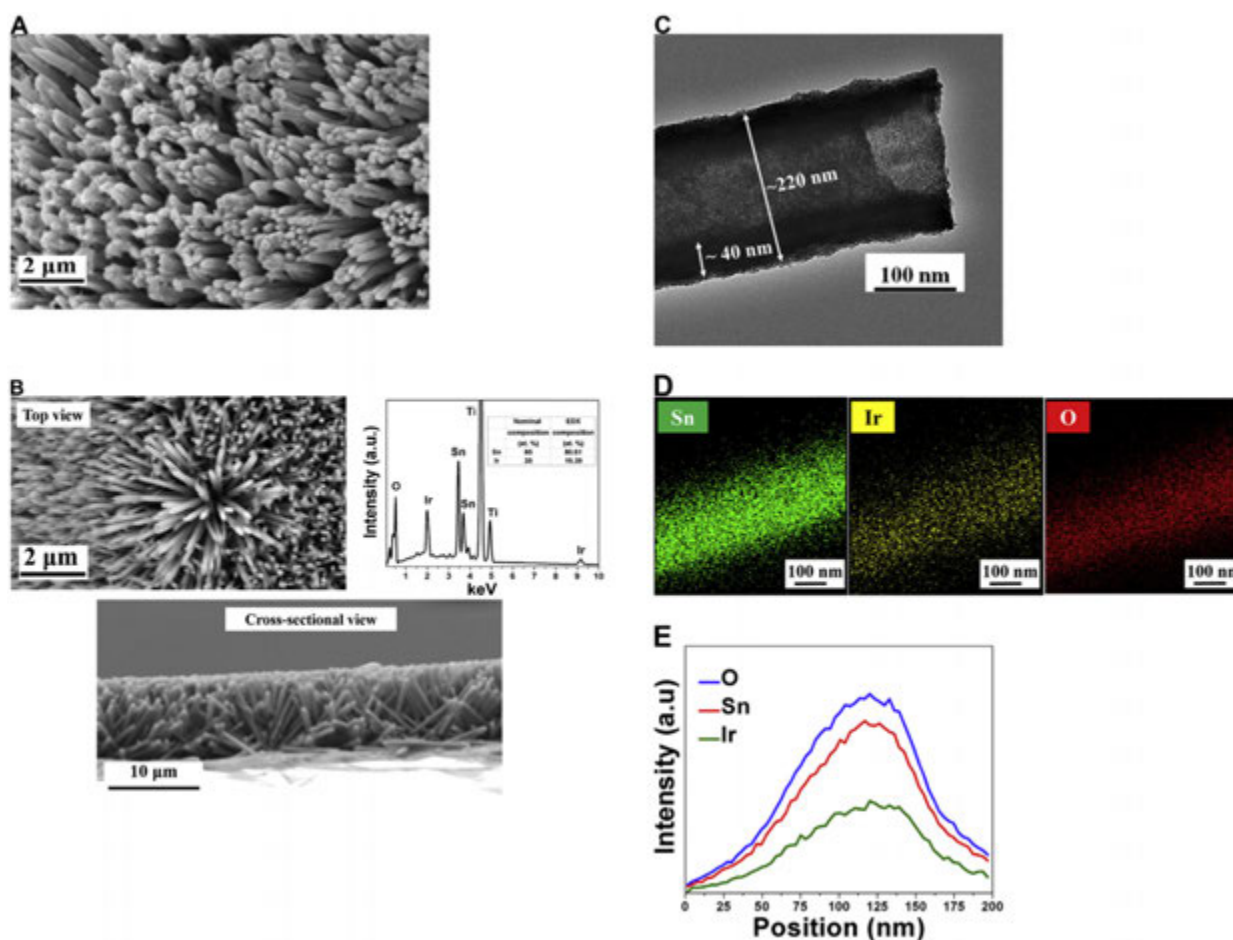


Fig. 10 (A) SEM micrograph showing top view of SnO₂NTs, (B) SEM micrograph showing top view, cross-sectional view and EDAX spectrum collected on (Sn_{0.8}Ir_{0.2})O₂:10F NTs, (C) Bright field TEM image of (Sn_{0.8}Ir_{0.2})O₂:10F NT, (D) EDS elemental mapping of Sn, Ir and O of the (Sn_{0.8}Ir_{0.2})O₂:10F NT, and (E) line scan analysis taken across the (Sn_{0.8}Ir_{0.2})O₂:10F NT.

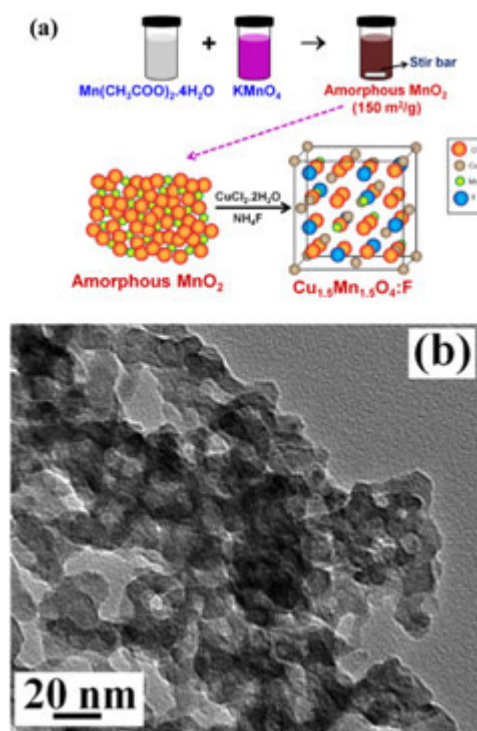


Fig. 11 (a) Schematic illustration showing the synthesis process of high surface area $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4:10\text{F}$ nanoparticles (NPs); (b) Bright field TEM image of $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4:10\text{F}$ showing the presence of fine ($\sim 8\text{--}10\text{ nm}$) nanoparticles.

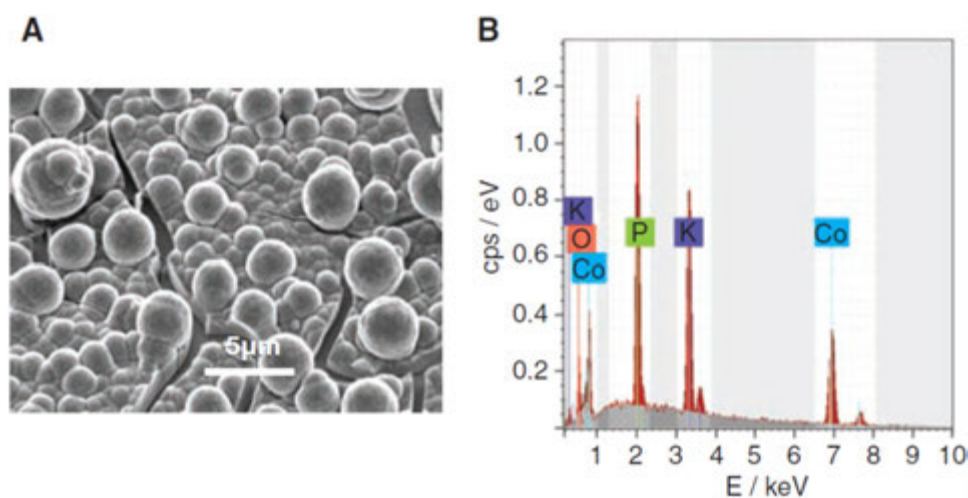


Fig. 12 SEM image of electrodeposited catalyst showing 'mud-crack' features. EDX spectrum showing the elemental contents.

sphere that can together serve to bind and contain various antibiotics, growth factors as well as plasmid DNA for controlled release of the bound growth factor, DNA and drug. At the same time, the resorbable nature of the entire composite makes it also an effective scaffold with and without the polymer for mineralized tissue engineering particularly for growing and regenerating bone for patients afflicted with traumatic orthopedic bone injuries requiring a scaffold to fill a segmental bone defect exceeding the critical size beyond which the body loses its inherent ability to heal and regenerate bone.

Synthesis of Non-Oxide Advanced Ceramics

Synthetic efforts have thus far been directed at few popular systems such as SiC , TiN , AlN , Si_3N_4 , TiC , Mo_2C , ZnS , CaLa_2S_4 , Mo_2N , $\gamma\text{-La}_2\text{S}_3$ and TiB_2 . There has been some unique interest in ternary nitrides (DiSalvo, 1990) due to their novel electronic and

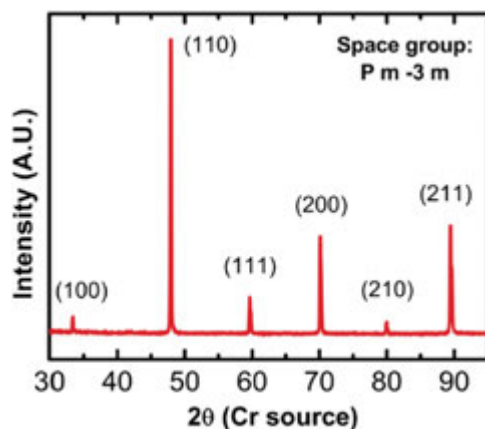


Fig. 13 XRD pattern of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) electrocatalyst.

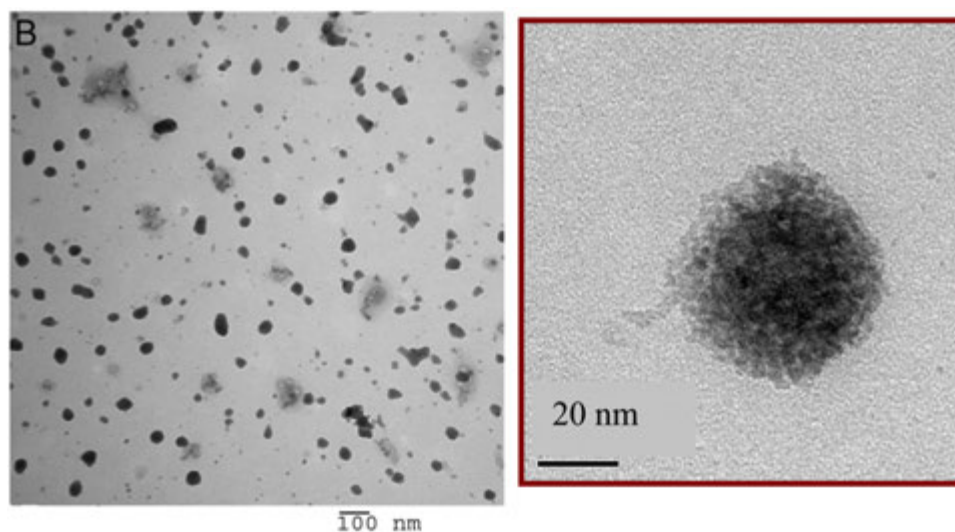


Fig. 14 TEM images showing the NanoCaPs-pDNA complexes synthesized using Ca/P ratio of 130 displaying uniform size in the 25–50 nm range.

magnetic properties. Over the years there has been significant interest in transition metal carbides, nitrides and sulfides including borides as well as composites of B, C, and N for a variety of insulating, electronically conducting, electromagnetic shielding, unique electronic switches as well as semiconducting properties particularly of layered systems as discussed in the sections to follow. Common and nonconventional methods used to obtain non-oxides are also discussed below.

Solid-State Approach

This is the most common method used to synthesize non-oxides ([Srinivasan and Rafaniello, 1997](#)) very similar to oxides and involves carbothermal reduction at high temperatures in excess of 1500°C in the presence of nitrogen to form compounds such as AlN , Si_3N_4 , TiN , NbN , SiC , TaC , NbC , B_4C , TiC , WC , and ZrC . Borides, TiB_2 , TaB_2 , and ZrB_2 are also synthesized by the reaction of the corresponding oxides of transition metal and boron with carbon acting as a reducing agent. As noticed, the reactions are requiring of very high temperatures owing to the inertness of nitrogen and carbon, much higher than that typically needed for oxides. Direct reaction of sulfur with metals has also been used traditionally to obtain sulfides (e.g., TiS_2) ([Sriram and Kumta, 1998](#)). The solid-state process has been used to explore several ternary nitrides (LiMoN_2 , $\text{Co}_3\text{Mo}_3\text{N}$, $\text{Fe}_3\text{Mo}_3\text{N}$, FeWN_2 , etc.) due to their interesting properties. Alkali metals, being electropositive, help to stabilize the transition metal and the higher oxidation state of nitrogen in the solid-state reaction of alkali metal nitrides and transition metal nitrides as outlined by DiSalvo. Ternary nitrides have also been obtained by ammonolysis of the mixed metal oxides or the mixed metal powders as well as nitridation of sulfides ([Marchand et al., 1999](#)).

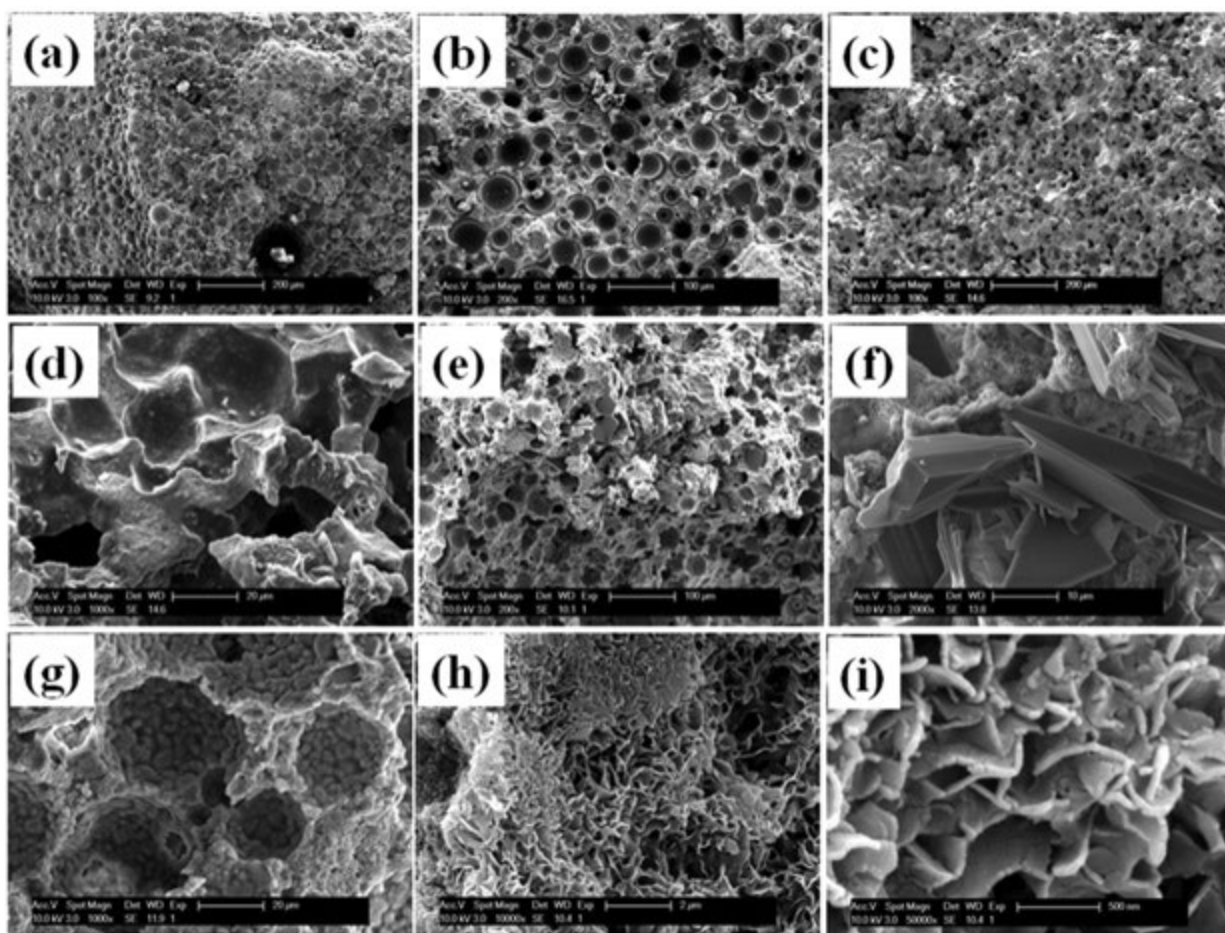


Fig. 15 The SEM images at different magnifications of PLGA-ReCaPP-40 cement aging at 37°C for different time periods (a) 0 day, (b) 6 days, (c) 15 days, (d) 15 days at high magnification showing the PLGA film on the cement, (e) 30 days and (f) 30 days at high magnification showing CaP crystals formation, (g) 30 days showing interconnected porosity of macropores, (h) 30 days at high magnification showing the presence of platelet like morphology and (i) 30 days at high magnification showing formation of nanostructured CaP. The scale bar in (a and c) is 200 μm, in (b and e) 100 μm, in (d and g) 20 μm, in (f) 10 μm, in (h) 2 μm and in (i) 500 nm.

Solution-Based Wet Chemistry Techniques

The advantages of chemical techniques as articulated for the case of the oxide ceramics earlier have also led to extensive studies in the area of non-oxide ceramics of which many have involved the heat treatment of sol – gel-derived oxides in ammonia, carburizing, or sulfidizing atmospheres to generate metal nitrides, carbides, or sulfides. These methods using the pre-synthesized oxide provide the advantages inherent to chemical techniques at least for generating the oxides favoring the rapid conversion to the non-oxide due to the higher chemical reactivity afforded by the high surface area nature of the pre-synthesized oxide precursor, although complete conversion to the non-oxide still entails prolonged annealing at elevated temperatures. In parallel, studies have also focused on pyrolysis of organometallics or polymers to synthesize a variety of nitrides and carbides. In the case of transition metals, these methods entail the reaction of tetrakisdiakylamido compounds of transition metals with amine reagents such as ethylenediamine (Seyferth and Mignani, 1988) to yield polymeric complexes, resulting in the metal nitride, carbide, or carbonitride after pyrolysis in NH_3 . Thermolysis of borazine, and other variations of the compound, has been used to obtain BN (Rüssel and Seibold, 1994; Gonsalves and Xiao, 1994). Methods have also been improvised to generate soluble polysilazane precursors, which are converted to the desired nitride by spray pyrolysis in the presence of ammonia (Mizutani and Liu, 1990). Solid and liquid polysilazanes of differing hydrocarbon content are synthesized by reacting chlorosilanes with ammonia. The sol – gel process has also been applied to synthesize directly sulfides and nitrides. This involves direct replacement of the alkoxy groups of alkoxides by thiol and amino groups in solution using sulfidizing and nitriding agents. The approaches have been called the thio-sol-gel and hydrazide sol-gel processes (Sriram and Kumta, 1998; Kumta *et al.*, 1999). The advantage is the ability to form metal-sulfur and metal-nitrogen bonds directly in the solution level by the direct replacement of the alkoxy groups by hydrosulfide and hydrazide species in the solution stage itself. The direct replacement results in gels depending on the alkoxide and the solvent, although complete replacement is difficult due to the polymeric nature of the alkoxide and the lower electronegativity of the hydrosulfide, amine and hydrazide species compared to the hydroxyl ions. Nevertheless, the gels have significant amounts of the non-oxide anions, and hence conversion of the alkoxy-non-

oxide precursor to the corresponding non-oxide occurs at moderate temperatures while also inheriting the advantages of molecular level mixing and nanoscale porosity to result in porous high surface area materials. The method has been used successively to synthesize non-oxides of reactive group IIIA, transition, and rare-earth metals. The incomplete replacement is advantageous since unique nano-crystalline microstructures can be achieved exhibiting interesting electrochemical properties. Alkoxides have also been used to synthesize silicon oxycarbide glasses, called "black glass", by sol – gel reactions of alkyltrialkoxysilanes (Zhang and Pantano, 1990). Metal – alkyl links create metal – carbon bonds in these glasses when pyrolyzed resulting in metal oxycarbides which are refractory exhibiting high temperature insulating properties for use in thermally resistant composites. These very same approaches to create the metal-non-oxygen linkages in the precursor stage via alkoxy-thiol or alkoxy-hydrazide or creating a polymeric precursor containing the metal-carbon or metal – nitrogen or metal-boron linkages to convert to the desired non-oxide at moderate temperatures has also been utilized to create mesoporous ordered structures by incorporating templates. These approaches are discussed below and consequently, such structures have tremendous applications in variety of areas of electrocatalysis, energy storage, conversion as well as electromagnetic shields and emerging fields of sensing etc.

Other Approaches

Other vapor-phase related approaches exist particularly for synthesizing silicon nitride via plasma and aerosol decomposition (Anderson *et al.*, 1989). The process consists of initiating a reaction between SiH_4 and NH_3 in a high-frequency plasma. The resulting amorphous powders containing largely silicon diimide and hydrogen yield the nitride upon calcination providing the thermal energy in appropriate environments. Improved processes using low temperatures and low pressure assisted plasma have also been developed for controlling the stoichiometry and purity of the nitride. Solvothermal reaction has also emerged as an attractive process for synthesizing nitrides and sulfides by executing reactions between metal or metal salts and sulfidizing or nitriding agents in non-aqueous solvents at modified temperatures and pressures in an autoclave (Demazeau, 1999). Several nitrides Mo_2N , GaN, TiN, and C_3N_4 , sulfides In_2S_3 , CdS, PbS, etc., and selenides and tellurides of Pb and Bi (Yu *et al.*, 1998) have been obtained in this fashion.

Metal salts and nitriding or sulfidizing agents in polar solvents directly precipitate nitrides and sulfides. The reaction can be controlled to generate a homogeneous distribution of uniform particles in the case of ZnS (Guiton *et al.*, 1988) or to yield nanostructured nitrides (Sriram *et al.*, 1995). Metathetic reactions of metal chlorides or organometallics and various nitriding agents such as liquid ammonia, hydrazine, hexamethyldisilazane, and amines or sulfidizing agents in suitable solvents result in nanostructured nitrides (Narula and Allard, 1998) or sulfides. Thus AlN, Si_3N_4 , GaN, TiN, ZrN, TiS_2 , CdS, ZnS, BN, etc. have all been successfully obtained in this manner. Mechanochemical milling, a direct extension of the well-known high energy mechanical milling approach, by milling metals with carbon and NH_3 yields nanostructured SiC (Yang and Shaw, 1996), Si_3N_4 , and GaN (Li *et al.*, 1998; Millet and Calka, 1995). Borides (e.g., TiB_2), and $\text{Sn}_2\text{Fe}/\text{SnFe}_3\text{C}$ (Mao *et al.*, 1999) and Si/TiN (Kim *et al.*, 2000) nanocomposite anodes for Li-ion cells have also been obtained. The success of this approach has been extensively utilized in subsequent years by various researchers to also generate other nanoscale composites of Si with inert non-oxide ceramics such as SiC, TiB_2 including carbon as alternative anodes to traditionally used carbon in lithium ion batteries.

Chemical complexation (Weil and Kumta, 1997) and electrochemical reactions (Rüssel and Seibold, 1994) are other methods to generate nitrides. The former are effective for obtaining powders and films, and are based on use of chelating metal chlorides in organic solvents initially which helps to shield the precursors from attack by moisture which would normally occur. The direct consequence of this shielding effectively provided by use of various low and high molecular weight chelating agents as well as the control of concentration of chelating agents is the ability to form stable complexes that yield unique ternary nitrides (CrWN_2 , $\text{Ni}_3\text{Mo}_3\text{N}$, $\text{Ni}_2\text{Mo}_3\text{N}$) after pyrolysis in NH_3 . The latter yield metal nitrides (AlN, TiN, Ti(C,N) , ZrN) by anodic dissolution and oxidation of metals while reducing organic electrolytes such as propylamine or acetonitrile to obtain polymers, which after pyrolysis yield nitrides or carbides. Similar to solution based approaches, these methods above can also be used to generate mesoporous ordered structures by executing the above reactions in the presence of a template as discussed in the section to follow.

Emergent techniques

Since 2000, there has been significant developments in the field of non-oxide ceramics as well similar to the advances witnessed in the field of oxide ceramics. These developments have been commensurate with advanced technologies and applications requiring the use of next generation non-oxide ceramics. The developments have come into vogue primarily with the intense research and evolution of the field of nanotechnology very similar to the area of oxide ceramics discussed above. Some of these advances in processing arises from the exploitation of chemistry principles to generate non oxide ceramics via oxide free sol-gel processes.

As outlined in the nice review by Hector (2007), is the oxide free sol-gel approach, an approach that has gained much notoriety especially in the field of silicon nitrides different from the use of alkoxides to form sulfides via the thio-sol-gel and the hydrazide sol-gel process used in principle for synthesizing transition metal sulfides and nitrides discussed above. One of the common approaches was the straightforward approach of ammonolysis of dialkyl aminosilanes with ammonia followed by condensation to make the imide ($-\text{NH}-$) linkages very similar to the hydrolysis and condensation reaction observed in alkoxides. A problem with use of non-oxygenated species is the extreme reactivity to moisture and air requiring the process to be handled under extreme care and under inert conditions. In relation to this, the common and well established approach was that developed by Bradley by condensation of metal dialkyl amides by first forming an amide precursor that would undergo condensation without the need for ammonolysis in the beginning to generate

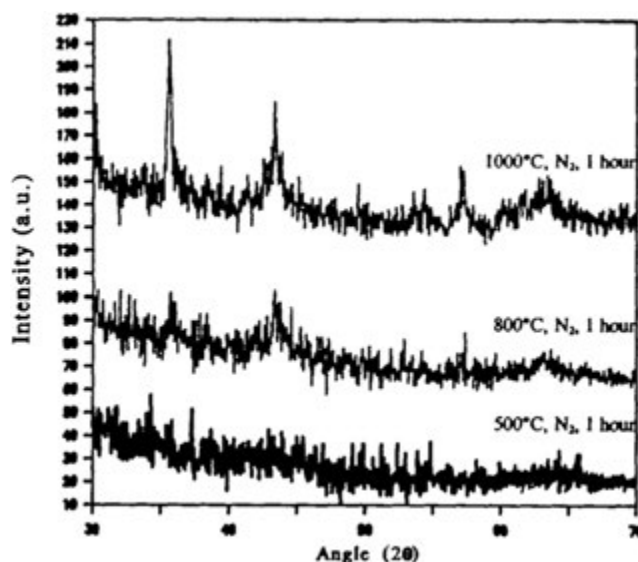
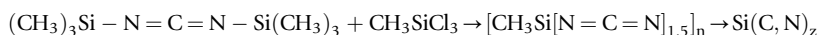


Fig. 16 X-ray diffraction pattern of Ti(C, N) coatings heat treated at different temperatures.

the nitrides. Zheng *et al.* with Mackenzie later exploited this approach for metal dialkyl amides to undergo aminolysis and polymerization reaction with primary amines to form metal nitrides (Zheng *et al.*, 1992). They used this approach to generate coatings of titanium carbonitride as well as TiN. They would take the soluble precursors formed via the reaction of metal dialkyl amides with primary amines to dip coat suitable substrates such as silicon followed by heat treatment in nitrogen at 500°C prior to each dip to generate the coatings before firing at elevated temperatures up to 1000°C in N₂ for 1 h to generate the metal carbonitride coatings (Fig. 16). Another approach popularized for silicon carbide and carbonitride was the approach by Kroke and Riedel (Balan *et al.*, 2000). They generated silicon carbodiimide gels via the reaction of bis(trimethyl silyl)carbodiimide with chloro(organo)silanes as shown below resulting in polymeric silicon based carbodiimide gels which can be pyrolyzed to generate silicon carbonitride. The approach is quite flexible and can be used to link other metals via the use of metal halides to react with the bis(trimethyl silyl)carbodiimide.



Similar approaches were used to generate hexagonal boron nitride by reacting cyclic chloroborazines with hexamethyl disilazane as shown in Fig. 17 to form gels that transformed to glassy solids on solvent removal. Pyrolysis of these solids in ammonia would form hexagonal boron nitride (*h*-BN). Similar approaches have been used to generate B/C/N materials with composition close to B₄CN₄ when pyrolyzed at 1200°C giving pure B₄C at 1800°C.

Many of the advances in the field of non-oxide ceramics can also be discussed in connection with the relevant technologies similar to the advanced oxide ceramics earlier as under.

Supercapacitors: As in the case of oxide ceramics above, transition metal non-oxides were identified as emergent materials in 2006 for advancing the field of supercapacitors. This was primarily by virtue of exploiting the variable oxidation states afforded by transition metals allowing the ability to harness multiple redox couples with various electronic transitions akin to ruthenium oxide discussed in the oxide ceramics. One notable example here is the work by Choi *et al.* (2006) wherein they showed that nanostructured VN synthesized by a two-step ammonolysis approach would have promising supercapacitor response matching and even exceeding that of the precious metal group counterpart of RuO₂·xH₂O. They generated the nanostructured nitride by reacting the dissolved chloride salt in anhydrous chloroform with anhydrous ammonia to generate chloroamide precursors that were then heat treated in anhydrous ammonia to 400°C then passivated with flowing 0.1% oxygen containing ultra-high purity Ar at room temperature for 4 h to generate oxygen passivated nitrides. The resultant nanocrystalline nitrides of specific surface area ~38.8 m²/g shown in Fig. 18 exhibit excellent supercapacitor response with capacitance as high as 1340 F/g for the first time which exceeded that of ruthenium oxides.

Thermoelectrics: In a recent article by Slade *et al.* (2019) they have shown that alloys of PbSe and NaSbSe₂ represented as NaPb_mSbSe_{m+2} or NaSbSe₂ + mPbSe are a new class of materials for thermoelectric applications exhibiting a maximum figure of merit, ZT of 1.4 near 900K when properly doped. These compounds were however, synthesized by normal solid state approaches, the novelty being the generation of a new class of systems. The approach involved batching elemental Pb wire, Se shot, Sb shot, and Na cubes in stoichiometric amounts after removing oxide layers on the surface of Pb and Na into carbon coated fused silica tubes which were flame sealed at ~2 × 10⁻³ Torr. The tubes were heated in a box furnace to 773K over 12 h, held for 2 h, and then heated to 1473K for over 7 h and then held for 5 h. The tubes were then quenched in ice water with annealing at 773K for 12 h. After these treatments, the ingots were recovered, ground to a fine powder and then sintered into dense pellets by spark plasma sintering. Fig. 19 shows the TEM and EDS analysis of the Na_{1.15}Pb_{0.85}SbSe₁₂ synthesized by the above approach.

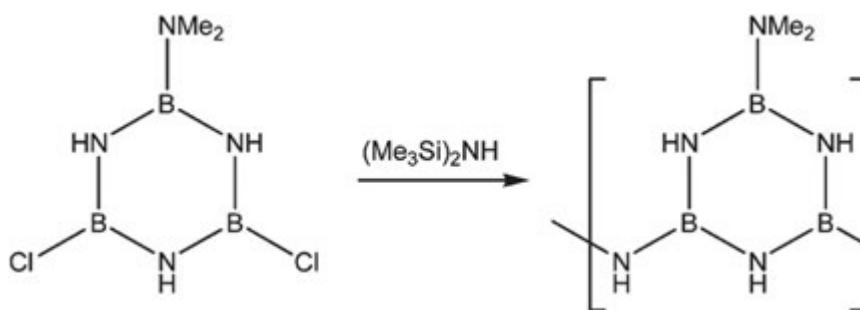


Fig. 17 Chloroborazine cross-linking induced by reaction with hexamethyldisilazane.

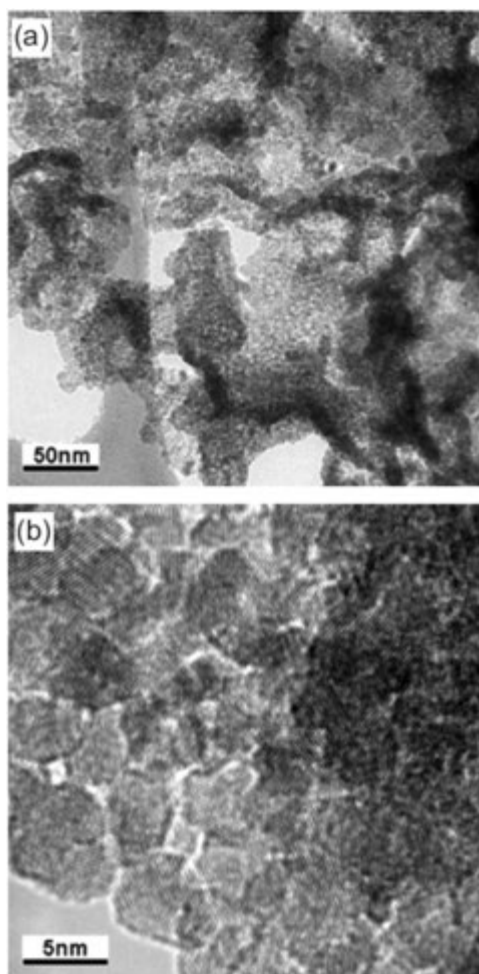


Fig. 18 High resolution TEM images of (a) nanocrystalline VN agglomerates and (b) VN nanocrystals obtained at 400°C in NH₃.

Solar cells: Since 2009, there has been extensive interest in perovskite solar cells based on methyl ammonium lead triiodide (CH₃NH₃PbI₃) and phenomenal progress has been documented (Nazeeruddin and Snaith, 2015). The systems have been synthesized using various techniques of precursor solution deposition, two-step sequential deposition, dual-source vapor deposition, and vapor-assisted solution processed techniques. In particular, Zhou *et al.* (2015) synthesized the CH₃NH₃PbI₃ material by vapor assisted solution process (VASP) technique. This includes first deposition of the inorganic framework by a solution approach and subsequently, the in-situ reaction of the inorganic species of PbI₂ with the desired organic vapor of CH₃NH₃I at 150°C with time scaling up to 4 h as shown in Fig. 20. The perovskite film obtained using this VASP technique and the characteristics of the film obtained are shown in Figs. 21 and 22.

Layered carbides sulfides and nitrides: Layered transition metal dichalcogenides (TMDs) have been studied (Chhowalla *et al.*, 2013) recently for their technological interest as electrocatalysts for hydrogen evolution, hydrosulfurization as well as electrically active materials for opto-electronics. Some of these systems include MoS₂, WS₂, TiS₂, TaS₂, ZrS₂ and NbSe₂. These systems are synthesized

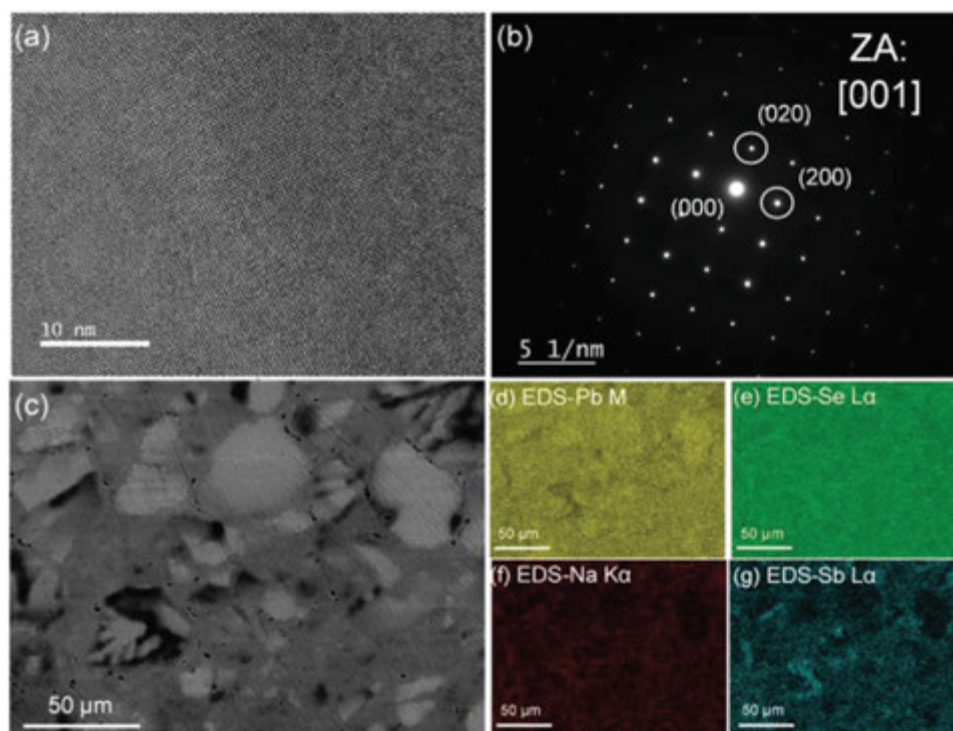


Fig. 19 (a) Characteristic high-resolution TEM image of a $\text{Na}_{1.15}\text{Pb}_{9.85}\text{SbSe}_{12}$ and (b) selected area electron diffraction pattern, confirming a clean rocksalt structure with no evidence of any nanoscale precipitates. (c) Backscattered electron image showing noticeable Z contrast and (d) – (g) EDS elemental maps over the region shown in (c). The EDS maps confirm that there were minor elemental segregation into Pb rich and Na/Sb rich regions.

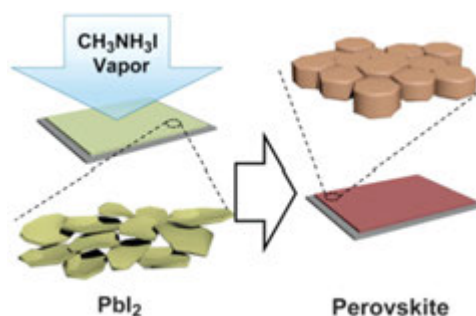


Fig. 20 Schematic of the two-step vapor treatment approach for generation of dense, continuous perovskite thin film.

by chemical vapor deposition (CVD) and chemical exfoliation of the bulk material by top-down and bottom-up approaches (Wang *et al.*, 2012). Top-down methods involve peeling of atomically thin layers of TMDs from parent bulk crystals by micromechanical cleavage using adhesive tape. The method is however, not scalable. Exfoliated nanosheets by liquid phase separation is promising. Intercalation of lithium ions into TMDs by n-butyl lithium for more than a day to allow Li ions to intercalate followed by exposing the intercalated TMDs to water causing removing of Li between the layers evolving hydrogen gas rapidly separating the layers. Another approach is ultrasonication in appropriate liquids including organic solvents, aqueous surfactant solutions or solutions of polymers in solvents. Bottom up approaches involve the use of CVD to generate wafer scale synthesis of TMDs in the form of large area single crystals via epitaxy. TMDs have also been generated by hydrothermal synthesis in an autoclave or reaction of molybdic or tungstic acid with thiourea or selenourea at elevated temperatures to form the corresponding TMD material. These approaches are shown in Fig. 23. As shown in the figure, are described methods for synthesizing TMD layers (a) Stable suspensions of layered materials from liquid-phase exfoliation in solvents (top) and thin films derived from vacuum filtration of the suspensions (bottom), (b) suspension of Li-intercalated and exfoliated MoS_2 in water (left). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of MoS_2 (middle) from suspensions in the left panel and atomic force microscopy (AFM) image of MoS_2 flakes deposited on SiO_2 (right). White line is a height profile taken at the red line position. Inset in the middle panel is magnified view of HAADF-STEM image showing honeycomb arrangement of MoS_2 . Green and yellow dots represent Mo and S. Scale

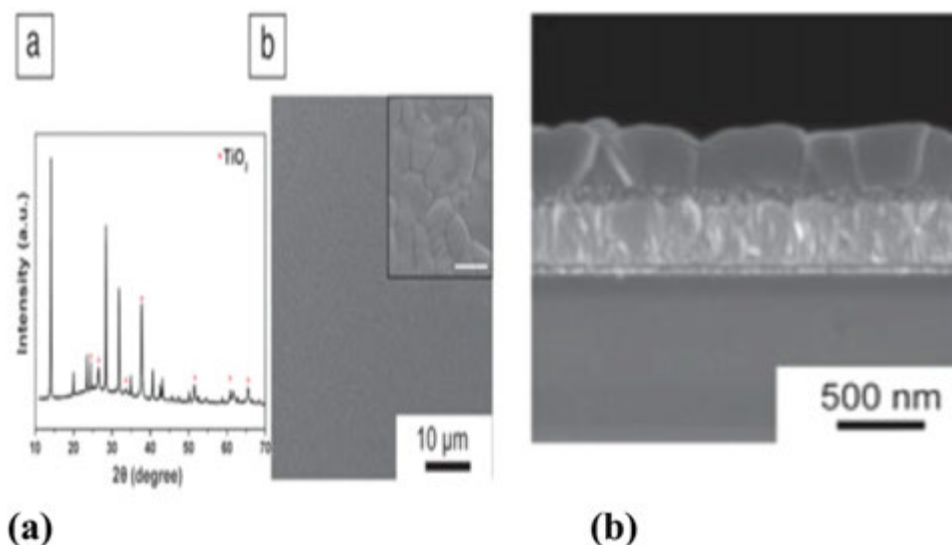


Fig. 21 Perovskite film on fluorine doped tin oxide substrate by VASP: (a) top-view SEM image (inset: higher resolution image scale bar = 1 μm); (b) cross-sectional SEM image of the film.

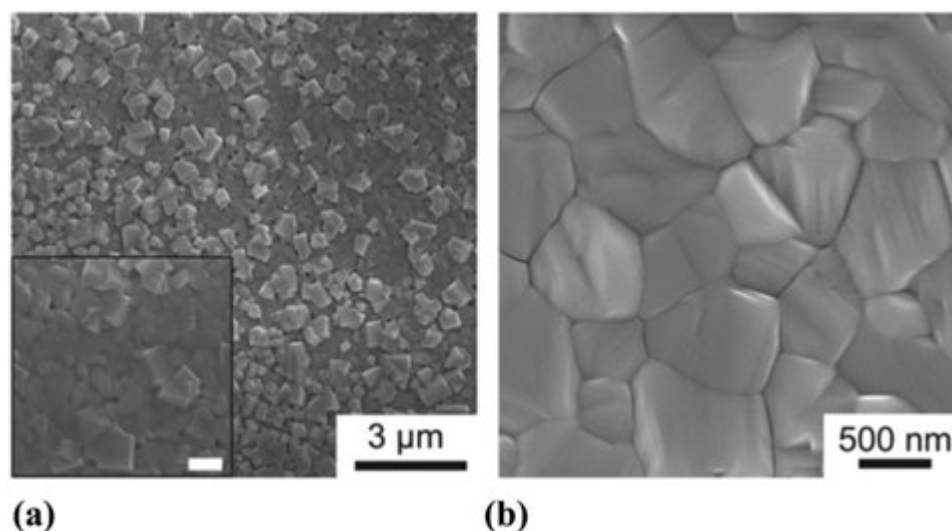


Fig. 22 (a) The $\text{PbI}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ film at the intermediate stage at 0.5 h (inset: wider view, scale bar = 3 μm) and (b) the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film at the post-stage at 4 h.

bar 0.5 nm. (c) CVD schematic of MoS_2 from S and MoO_3 (left) forming MoS_2 films on SiO_2 (right). Red dots are furnace heating elements. Optical microscopy image show MoS_2 in lighter regions and darker regions are silica. (d) CVD of MoS_2 from solid Mo on SiO_2 exposed to S vapor (top left) giving MoS_2 layers visible in optical microscopy (right). Bottom left: side-view schematic of an MoS_2 layer on Si/SiO_2 substrate. (5) CVD of MoS_2 from dip-coated precursor on substrate and growth in Ar gas and S vapor.

Similar to TMDs, another system that has gained popularity since its identification in late 1990s are transition metal containing silicon and aluminum nitrides and carbides. In 2011, Barsoum *et al.* identified a new class of 2D transition metal carbides and nitrides, they labeled as MXenes (Anasori *et al.*, 2015). The term was given due to the ability to selectively etch the A layers from the 3D layered parent compounds, the $\text{M}_{n+1}\text{AX}_n$ or MAX phases where M is an early transition metal, A is an A group element such as Al or Si and X is carbon and/or nitrogen and $n = 1-3$. To date, MXenes synthesized are $\text{Ti}_3\text{C}_2\text{T}_x$, Ti_2CT_x , V_2CT_x , Nb_2CT_x , $\text{Nb}_4\text{C}_3\text{T}_x$. Here, T_x represents surface groups of O, OH, and F. Other MXenes with other M elements such as Sc, Zr, Hf and Mo have also been predicted by the team. They synthesized the MAX phases by ball milling of Mo, Ti, Al and graphite powders for 18 h using zirconia balls in plastic jars to form $\text{Mo}_2\text{TiAlC}_2$ and $\text{Mo}_2\text{Ti}_2\text{AlC}_3$, respectively with molar ratios of Mo/Ti/Al/C of 2:1:1:2 for the former and 2:2:1.3:2.7 for the latter. Powder mixtures were then heated in covered alumina crucibles at $5^\circ\text{C}/\text{min}$ to 1600°C and held for 4 h under flowing argon. After cooling the porous structures were milled using a TiN coated milling bit producing powders of $\text{Mo}_2\text{Ti}_2\text{AlC}_3$ phase. $\text{Cr}_2\text{TiAlC}_2$ was synthesized by heating elemental mixtures of Cr, Ti, Al and C at 1500°C for 1 h under Ar flow. To

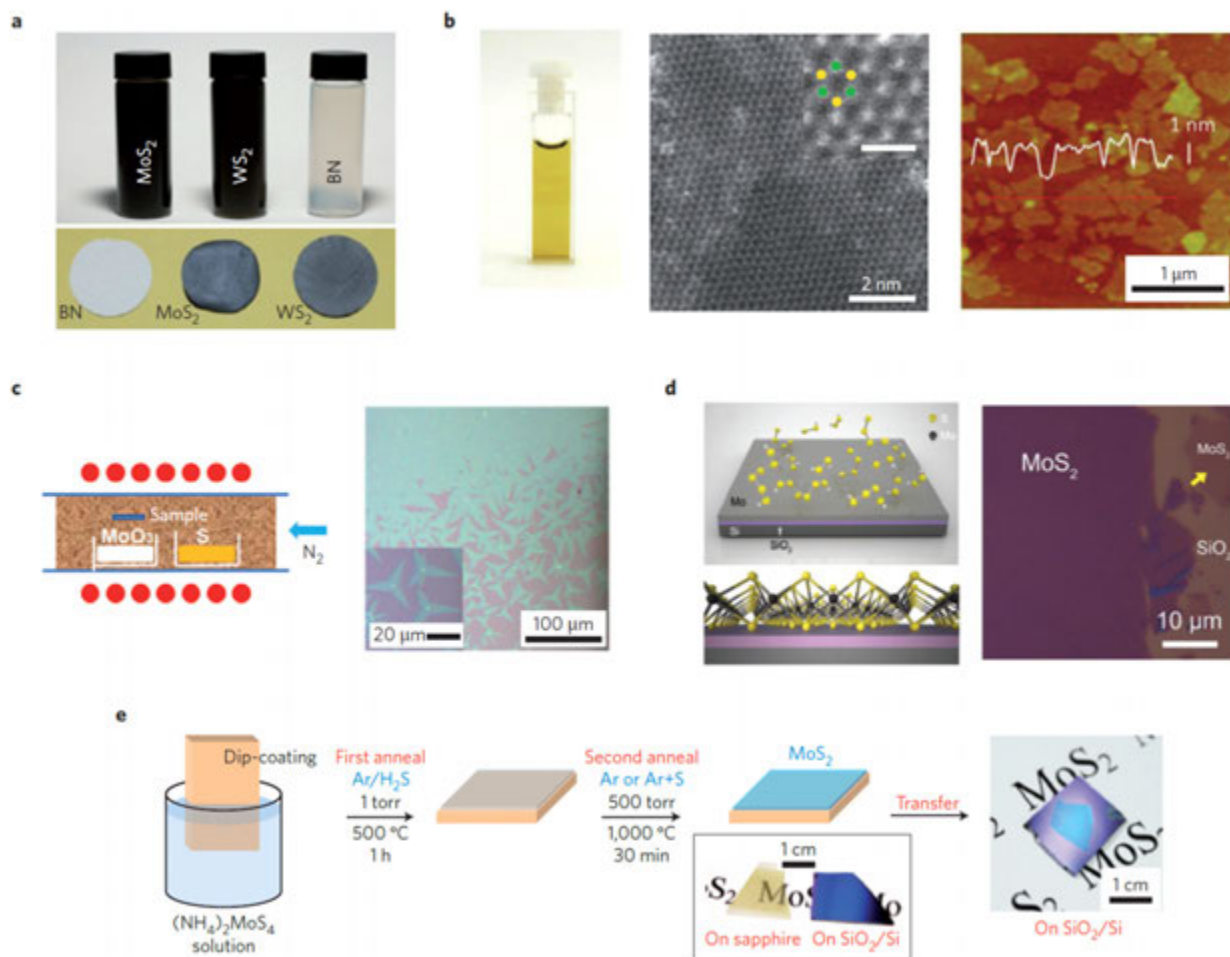


Fig. 23 Methods for generating TMD layers (a) Stable suspension by liquid phase exfoliation. (b) Suspension of Li intercalated and exfoliated MoS₂ in water. HAADF-STEM image of MoS₂. AFM image of MoS₂ flakes on SiO₂. White light is height profile. Inset is magnified HAADF-STEM image. (c) Schematic of CVD of MoS₂ (d) CVD growth of MoS₂ from S vapor and Mo on SiO₂. (e) CVD of MoS₂ from dip-coated precursor on substrate and growth in Ar gas and S vapor.

generate the MXene phases, 2 g of Mo₂TiAlC₂ or Mo₂Ti₂AlC₃ powders was added over ~60 s, to 20 ml of 48%–51% aqueous HF solution and held at ambient temperature (55 °C for Mo₂Ti₂AlC₃) for 48 h (90 °C for Mo₂TiAlC₂) with stirring followed by washing 5 times with distilled water and then centrifuging at 3500 rpm for 120 s with final decantation. The pH of the supernatant was maintained greater than 6. The final product was then mixed with distilled water and filtered on a membrane to generate the layered carbide structures. Fig. 24 shows the synthesis and structure of Mo₂TiC₂ and Mo₂Ti₂C₃. (a) Shows the XRD patterns of the Mo₂TiAlC₂ phase before (red) and after (green) HF treatment and after delamination (blue). In the delaminated state, only the c-direction peaks, (00l) peaks are seen corresponding to a, c – lattice parameter of 30.44 Å; the (110) peak is not observed, thus showing loss of order in non-basal direction. (b) XRD patterns of Mo₂Ti₂AlC₃ before (pink) and after (purple) HF treatment and after delamination (black). (c) and (d) show the schematics of Mo₂TiAlC₂ to Mo₂TiC₂T_x and Mo₂Ti₂AlC₃ to Mo₂Ti₂C₃T_x transformations, respectively; the red and green, blue and black circles correspondingly represent Mo, Ti, Al and C atoms, respectively. (e) and (f) are SEM images of Mo₂TiAlC₂ and Mo₂TiC₂T_x, respectively. Note the layers become more open after etching in Mo₂TiC₂T_x (g) and (h) show the HRSTEM images of Mo₂TiAlC₂ and Mo₂TiC₂T_x, respectively. Atoms are shown with the same colors as in (c). Atomic ordering is confirmed by EDAX mapping. No Al is observed in the EDAX analysis of Mo₂TiC₂T_x (i) Lower magnification TEM image of (f) showing the layered structure throughout the sample. (j) and (k) are SEM images of Mo₂Ti₂AlC₃ and Mo₂Ti₂C₃T_x, respectively. HRSTEM images of (l) Mo₂Ti₂AlC₃ and (m) and (n) Mo₂Ti₂C₃. Atoms are shown with the same colors as in (d).

Mesoporous Non-Oxides: Similar to the oxide field, there has been considerable activity in the area of synthesis of ordered mesoporous non-oxide materials (Shi *et al.*, 2011). Shi *et al.* have reviewed and discussed various approaches outlined by reviewers in generating ordered mesoporous inorganic non-oxide materials having interest in a variety of applications in catalysis, energy conversion, storage, electronic transport, shielding, etc. due to their unique properties. Most of the approaches are very similar to those followed in oxide ceramics and those outlined above. These include hard-templating (nanocasting) and soft-templating (surfactant assembly) methods. The major issues in these approaches involve template composition, mesostructured, pore surface

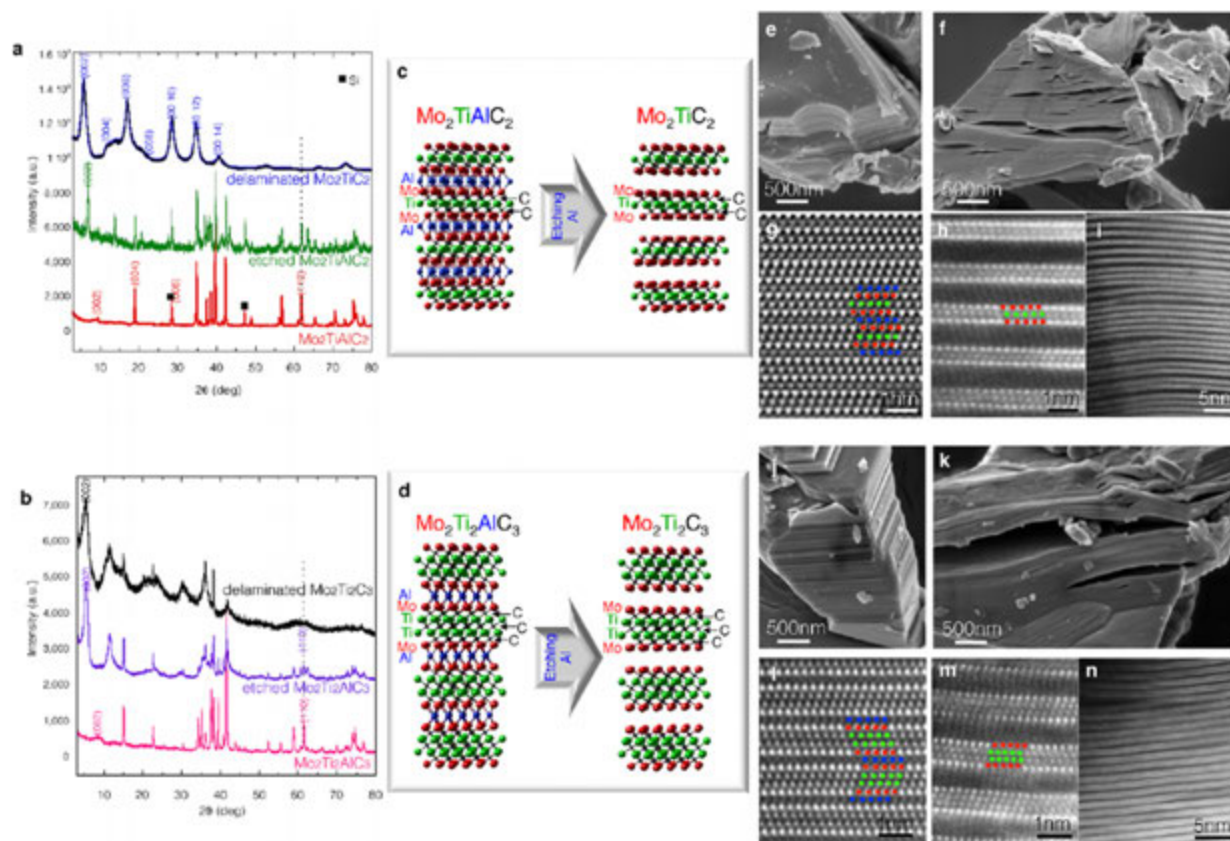


Fig. 24 Synthesis and structure of Mo_2TiC_2 and $\text{Mo}_2\text{Ti}_2\text{C}_3$ systems. (a) XRD patterns of $\text{Mo}_2\text{TiAlC}_2$ before and after HF etching and after delamination. (b) XRD patterns of $\text{Mo}_2\text{Ti}_2\text{AlC}_3$ before and after HF treatment and after delamination. (c) and (d) show the schematics of the transformation from $\text{Mo}_2\text{TiAlC}_2$ to Mo_2TiC_2 and $\text{Mo}_2\text{Ti}_2\text{AlC}_3$ to $\text{Mo}_2\text{Ti}_2\text{C}_3$, respectively. (e) and (f) are SEM images of $\text{Mo}_2\text{TiAlC}_2$ and Mo_2TiC_2 , respectively. (g) and (h) are HRSTEM images of $\text{Mo}_2\text{TiAlC}_2$ and Mo_2TiC_2 , respectively. (i) Lower magnification TEM image of (f) showing the layered structure throughout the sample. (j) and (k) are SEM images of $\text{Mo}_2\text{Ti}_2\text{AlC}_3$ and $\text{Mo}_2\text{Ti}_2\text{C}_3$, respectively. HRSTEM images of (l) $\text{Mo}_2\text{Ti}_2\text{AlC}_3$ and (m) and (n) are $\text{Mo}_2\text{Ti}_2\text{C}_3$.

chemistry, precursor selection processing and template removal. With regards to the soft templating methods, most of the issues relate to choice of surfactant such as CTAB or cetylpyridinium bromide (CPBr) or even the use of long chain *N*-eicosane-*N,N*-dimethyl-*N*-(2-hydroxyethyl) ammonium bromide (EDMHEAB) and creating the surfactant assisted liquid-crystal mesophases while studying their stability to generate mesostructured non-oxide ceramics. Both approaches utilize exploiting a framework mesoporous structures of aluminosilicate, silica (SBA-15 or SBA-16) that serves as a template for conducting the polymerization, pyrolysis and other related chemical reactions as a structure directing agent (SDA) which result in the final product assuming the configuration and microstructure of the underlying template. The template is then removed leaving behind the final material assuming the morphology of the template akin to the topotactic mechanism well-known described earlier. Intrinsic porosity can in most cases be achieved by pyrolysis of the related polymers with removal of excess carbon, nitrogen and sulfur typically present in the polymer backbone contributing to the porosity. **Fig. 25** is an example of synthesis of ordered mesostructured BN or BCN from self-assembly and pyrolysis of a block copolymer of laboratory created polymer such as polynorbomene-*b*-polynorbornedecaborane (PNB-*b*-PDB) with microstructure that can be tailored by choice of a suitable organic solvent and the composition controlled by the pyrolysis atmosphere: nitrogen to give BCN and ammonia to yield BN, thus generating mesoporous ordered boron nitride (BN) or boron carbonitride (BCN). Another example in **Fig. 26** is that of mesoporous WS_2 generated by high temperature reductive sulfuration or sulfuration of phosphotungstic acid with H_2S and H_2 showing the orientation correlation between the resulting WS_2 crystal layers and the mesochannels afforded by the silica template of SBA-15 and KIT-6: the *c*-axis of the WS_2 layered crystals being always perpendicular to the original mesopore long direction as shown in the inset of **Fig. 26(a)**.

Summary

The above techniques describe the various approaches used to generate advanced ceramics over the period spanning almost three decades. These novel approaches not only enable generation of interesting systems for various applications but also demonstrate

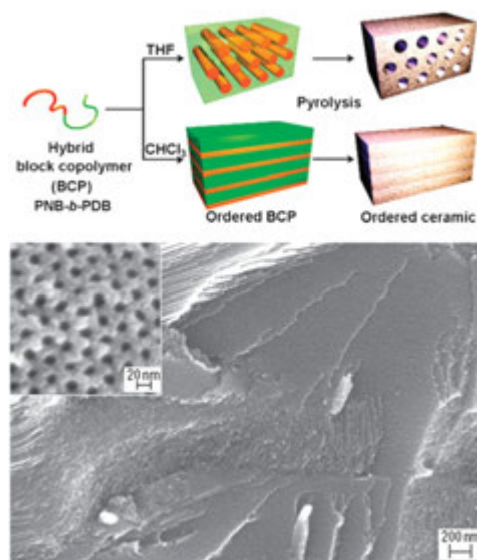


Fig. 25 (Top) synthesis of ordered mesoporous BN or BCN from self-assembly and pyrolysis of block copolymer (PNB-*b*-PDB). (Bottom) SEM image and high magnification image (inset) of the resulting mesoporous BCN.

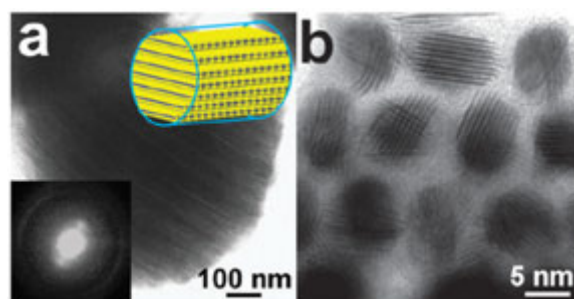


Fig. 26 TEM images (a), (b) and SAED pattern (inset of (a)) of mesoporous WS_2 synthesized by high temperature reductive sulfurization approach. The inset of (a) also shows the orientation correlation between the WS_2 crystal layers and the mesochannels of the silica template: the *c*-axis of the WS_2 layered crystals is always seen to be perpendicular to the length direction of the original mesopore of the silica template.

the ability of the process and the system to exhibit different morphologies depending on the approach adopted for a given system ranging from spherical particles to nanorods, fibers, whiskers, and platelets including aligned structures depending on the system and the process. The possibility of achieving new nanostructured materials with novel microstructures exhibiting remarkable properties has led to the identification of novel non-equilibrium techniques and template based approaches which enable the systems to be created in unique nanostructured morphologies that were never before possible under equilibrium conventional methods. The continuing advances in theory and fundamental aspects of materials processing will no doubt continue to lead to further advances in the synthesis of novel advanced ceramic materials. Thus the new millennium will continue to witness further advances in the area of synthesis of nanoscale and new materials under the materials genome initiative coupled with advanced computational tools including the fusion of machine learning algorithms data mining and various evolving artificial intelligence platforms which will enable not only identification of new and advanced systems but will also help identify the configuration and morphology needed to deliver the optimal and best performance. This will allow the experimentalists to continue to aspire to come up and invent newer techniques for realizing the potential of systems identified by theoretical calculations for a number of applications ranging from electronics, optics, electrochemical, magnetics, stem cells, organ engineering, and biomaterials to the growing field of tissue engineering.

Acknowledgment

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References

- Acosta, S., Corriu, R.J.P., Leclercq, D., *et al.*, 1994. Preparation of alumina gels by a non-hydrolytic sol-gel processing method. *Journal of Non-Crystalline Solids* 170, 234–242.
- Anasori, B., Xie, Y., Beidaghi, M., *et al.*, 2015. Two-dimensional, ordered, double transition metals carbides (MXenes). *ACS Nano* 9 (10), 9507–9516.
- Anderson, H., Kodas, T.T., Smith, D.M., 1989. Vapor-phase processing of powders: Plasma synthesis and aerosol decomposition. *Ceramic Bulletin* 68, 996–1000.
- Balan, C., Völger, K.W., Kroke, E., Riedle, R., 2000. Viscoelastic properties of novel silicon carbodiimide gels. *Macromolecules* 33, 3404–3408.
- Barsoum, M.W., 1997. *Fundamentals of Ceramics*. New York: McGraw-Hill.
- Brinker, C.J., Scherer, G.W., 1990. *Sol – Gel Science*. Boston, MA: Academic Press.
- Chang, C.C., Scarr, N., Kumta, P.N., 1998. Synthesis and electrochemical characterization of LiMO_2 ($M = \text{Ni}, \text{Ni}_{0.75}\text{Co}_{0.25}$) for rechargeable lithium ion batteries. *Solid State Ionics* 112, 329–344.
- Chawla, K.L., Major, S., Pandya, D.K., 1983. Transparent conductors – A status review. *Thin Solid Films* 102, 1–46.
- Chhowalla, M., Shin, H.S., Eda, G., *et al.*, 2013. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nature Chemistry* 5 (April 2013), 263–275.
- Choi, D., Blomgren, G.E., Kumta, P.N., 2006. Fast and reversible surface redox reaction in nanocrystalline vanadium nitride supercapacitors. *Advanced Materials* 18, 1178–1182.
- Chung, S.L., Sheu, Y.C., Tsai, M.S., 1990. In: Messing, G.L., Hirano, S., Hausner, H. (Eds.), *Ceramic Powder Science III*. Westerville, OH: The American Ceramic Society.
- Demazeau, G., 1999. Solvothermal processes: A route to the stabilization of new materials. *Journal of Materials Chemistry* 9, 15–18.
- DiSalvo, F.J., 1990. Solid-state chemistry: A rediscovered chemical frontier. *Science* 247, 649–655.
- Ellis, S.K., McNamara Jr, E.P., 1989. Powder synthesis research at CAMP. *Ceramic Bulletin* 68, 988–994.
- Gaffet, E., Bernard, F., Niepce, J.C., *et al.*, 1999. Some recent developments in mechanical activation and mechanochemistry. *Journal of Materials Chemistry* 9, 305–314.
- Ghadge, S.D., Patel, P.P., Datta, M.K., *et al.*, 2018. First report of vertically aligned $(\text{Sn}, \text{Ir})\text{O}_2/\text{F}$ solid solution nanotubes: Highly efficient and robust oxygen evolution electrocatalysts for proton exchange membrane based water electrolysis. *Journal of Power Sources* 392, 139–149.
- Goel, S.C., Chiang, M.Y., Gibbons, P.C., Buhro, W.E., 1992. New chemistry for the Sol-gel process: Acetone as a new condensation reagent. *Materials Research Society Symposium Proceedings* 271, 3–13.
- Gonsalves, K.E., Xiao, T.D., 1994. In: Lee, B.I., Pope, J.A. (Eds.), *Chemical Processing of Ceramics*. New York: Dekker, pp. 359–373.
- Guiton, T.A., Czekaj, C.L., RauM, S., Geoffroy, G.L., Pantano, C.G., 1988. In: Brinker, C.J., Clark, D.E., Ulrich, D.R. (Eds.), *Better Ceramics Through Chemistry III*. Pittsburgh, PA: Materials Research Society, pp. 503–508.
- Hector, A.L., 2007. Materials synthesis using oxide free sol-gel systems. *Chemical Society Reviews* 36, 1745–1753.
- Hu, C.-C., Chen, W.-C., Chang, K.-H., 2004. How to achieve maximum utilization of hydrous ruthenium oxide for supercapacitors. *Journal of The Electrochemical Society* 151 (2), A281–A290.
- Jampani, P., Manivannan, A., Kumta, P.N., 2010. Advancing the supercapacitor materials and technology frontier for improving power quality. *The Electrochemical Society Interface* 19 (3), 57–62.
- Jampani, P.H., Kadakia, K., Hong, D.H., *et al.*, 2013. CVD derived vanadium oxide nano-sphere-carbon nanotube (CNT) nano-composite hetero-structures: High energy supercapacitors. *Journal of The Electrochemical Society* 160 (8), A1118–A1127.
- Jampani, P.H., Velikokhatnyi, O., Kadakia, K., *et al.*, 2015. High energy density titanium doped-vanadium oxide-vertically aligned CNT composite electrodes for supercapacitor applications. *Journal of Materials Chemistry A* 3, 8413–8432.
- Julien, C., Nazri, G.A. (Eds.), 1994. *Solid State Batteries: Materials Design and Optimization*. Boston, MA: Kluwer Academic Press.
- Kadakia, K., Datta, M.K., Velikokhatnyi, O.I., *et al.*, 2014a. High performance fluorine doped $(\text{Sn}, \text{Ru})\text{O}_2$ oxygen evolution reaction electro-catalysts for proton exchange membrane based water electrolysis. *Journal of Power Sources* 245, 362–370.
- Kadakia, K.S., Jampani, P., Velikokhatnyi, O.I., *et al.*, 2014b. Nanostructured $(\text{Ir}, \text{Sn})\text{O}_2/\text{F}$ – Oxygen evolution reaction anode electro-catalyst powders for PEM based water electrolysis. *Journal of The Electrochemical Society* 161 (9), F868–F875.
- Kadakia, K.S., Jampani, P.H., Velikokhatnyi, O.I., *et al.*, 2014c. Nanostructured F doped IrO_2 electro-catalyst powders for PEM based water electrolysis. *Journal of Power Sources* 269, 855–865.
- Kanan, M.W., Nocera, D.G., 2008. In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co^{2+} . *Science* 321, 1072–1075.
- Kim, I.S., Kumta, P.N., Blomgren, G.E., 2000. Si/TiN nanocomposites: Novel anode materials for Li-ion batteries. *Electrochemical and Solid-State Letters* 3, 493–496.
- Kresge, C.T., Leonowicz, M.E., Roth, W.J., Vartuli, J.C., Beck, J.S., 1992. Ordered mesoporous molecular sieves synthesized by a liquid crystal template mechanism. *Nature* 359, 710–712.
- Kumta, P.N., Risbud, S.H., 1994. Rare earth chalcogenides – A new class of emerging optical materials. *Journal of Materials Science* 29, 1135–1158.
- Kumta, P.N., Kim, J.Y., Sriram, M.A., 1999. In: Bansal, N.P., Singh, J.P. (Eds.), *Innovative Processing and Synthesis of Ceramics, Glasses, and Composites II*. Westerville, OH: The American Ceramic Society, pp. 163–183.
- Lee, D., Upadhye, K., Kumta, P.N., 2012. Nano-sized calcium phosphate (CaP) carriers for non-viral gene delivery. *Materials Science and Engineering B* 177, 289–302.
- Lencka, M.M., Riman, R.E., 1993. Synthesis of lead titanate: Thermodynamic modeling and experimental verification. *Journal of The American Ceramic Society* 76, 2649–2659.
- Lessing, P.A., 1989. Mixed-cation oxide powders via polymeric precursors. *Ceramic Bulletin* 68, 1002–1007.
- Li, Z.L., Williams, J.S., Calka, A., 1998. Temperature effects of Si milling in NH_3 . *Materials Science Forum* 269–72, 485–490.
- Lin, S.C., Wilkins, R., Nersisyan, M., Luss, D., 1999. In: Bansal, N.P., Singh, J.P. (Eds.), *Innovative Processing and Synthesis of Ceramics, Glasses, and Composites II*. Westerville, OH: The American Ceramic Society, pp. 23–33.
- Mao, O., Turner, R.L., Courtney, I.A., *et al.*, 1999. Active/inactive nanocomposites as anodes for Li-ion batteries. *Electrochemical and Solid-State Letters* 2, 3–5.
- Marchand, R., Tessier, F., DiSalvo, F.J., 1999. New routes to transition metal nitrides: Preparation and characterization of new phases. *Journal of Materials Chemistry A* 9, 297–304.
- Millet, P., Calka, A., 1995. Ball milling of soft metals: The formation of gallium nitride. *Materials Science Forum* 179–181, 321–324.
- Mizutani, N., Liu, T., 1990. In: Messing, G.L., Hirano, S., Hausner, H. (Eds.), *Ceramic Powder Science III*. Westerville, OH: The American Ceramic Society, pp. 59–73.
- Narula, C.K., Allard, L.F., 1998. Novel zirconium nitride precursor: Synthesis, decomposition pathway, and pyrolysis of $[(\text{CH}_3)\text{Si}_2\text{NH}]\text{ZrCl}_4$. *Journal of Materials Chemistry* 8, 1881–1884.
- Nazeeruddin, M.K., Snaith, H., 2015. Methylammonium lead triiodide perovskite solar cells: A new paradigm in photovoltaics. *MRS Bulletin* 40 (8), 641–645.

- Olton, D., Li, J., Wilson, M.E., *et al.*, 2007. Nanostructured calcium phosphates (NanoCaPs) for non-viral gene delivery: Influence of the synthesis parameters on transfection efficiency. *Biomaterials* 28, 1267–1279.
- Osseo-Assare, K., Arriagada, F.J., 1990. In: Messing, G.L., Hirano, S., Hausner, H. (Eds.), *Ceramic Powder Science III*. Westerville, OH: The American Ceramic Society, pp. 3–16.
- Patel, P.P., Datta, M.K., Velikokhatnyi, O.I., *et al.*, 2016. Noble metal-free bifunctional oxygen evolution and oxygen reduction acidic media electro-catalysts. *Nature Scientific Reports*, 1–14.
- Rao, C.N.R., 1994. In: Lee, B.I., Pope, J.A. (Eds.), *Chemical Processing of Ceramics*. New York: Dekker, pp. 61–74.
- Reed, J.S., 1988. *Introduction to the Principles of Ceramic Processing*. New York: Wiley.
- Roy, A., Jhunjhunwala, S., Bayer, E., *et al.*, 2016. Porous calcium phosphate-poly (lactic-co-glycolic) acid composite bone cement: A viable tunable drug delivery system. *Materials Science and Engineering C* 59, 92–101.
- Roy, R., 1956. Aids in hydrothermal experimentation: II. Methods of making mixtures for both “dry” and “wet” phase equilibrium studies. *Journal of the American Ceramic Society* 39, 145–146.
- Rüssel, C., Seibold, M., 1994. In: Lee, B.I., Pope, J.A. (Eds.), *Chemical Processing of Ceramics*. New York: Dekker, pp. 105–127.
- Seyferth, D., Mignani, G., 1988. Preparation of titanium nitride and titanium carbonitride by the preceramic polymer route. *Journal of Materials Science Letters* 7, 487–488.
- Shi, Y., Wan, Y., Zhao, D., 2011. Ordered mesoporous non-oxide materials. *Chemical Society Reviews* 40, 3854–3878.
- Slade, T.J., Bailey, T.P., Grovogui, J.A., *et al.*, 2019. High thermoelectric performance in PbSe-NaSbSe₂ alloys from valence band convergence and low thermal conductivity. *Advanced Energy Materials* 9, 1–12. (1901377).
- Srinivasan, M., Rafaniello, W., 1997. In: Weimer, A.W. (Ed.), *Carbide, Nitride and Boride Materials Synthesis and Processing*. London: Chapman & Hall, pp. 3–42.
- Sriram, M.A., Kumta, P.N., 1998. The thio-sol-gel synthesis of titanium disulfide and niobium disulfide. Part 1. Materials chemistry. *Journal of Materials Chemistry* 8, 2441–2451.
- Sriram, M.A., Kumta, P.N., Ko, E.I., 1995. Interaction of solvent and the nature of adducts on the chemical synthesis of molybdenum nitride powders. *Chemistry of Materials* 7, 859–864.
- Suntivich, J., May, K.J., Gasteiger, H.A., Goodenough, J.B., Shao-Horn, Y., 2011. A perovskite oxide optimized for oxygen evolution catalysis from molecular orbital principles. *Science* 334, 1383–1385.
- Thomas, I.M., 1988. In: Klein, L.C. (Ed.), *Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics, and Specialty Shapes*. Park Ridge, NJ: Noyes Publications, pp. 2–15.
- Wang, Q.H., Zadeh, K.K., Kis, A., Coleman, J.N., Strano, M.S., 2012. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nature Nanotechnology* 7, 699–712.
- Weil, K.S., Kumta, P.N., 1997. Chemical synthesis and structural investigation of a new ternary nitride, CrWN₂. *Journal of Solid State Chemistry* 128, 185–190.
- Wood, T.E., Dislich, H., 1995. In: Pope, J.A., Sakka, S., Klein, L.C. (Eds.), *Sol – Gel Science and Technology*. Westerville, OH: American Ceramic Society, pp. 3–23.
- Yang, Z.G., Shaw, L.L., 1996. Synthesis of nanocrystalline SiC at ambient temperature through high energy reaction milling. *Nanostructured Materials* 7, 873–886.
- Yu, S.H., Yang, J., Wu, Y.S., *et al.*, 1998. A new low temperature one-step route to metal chalcogenide semiconductors: PbE, Bi₂E₃ (E = S, Se, Te). *Journal of Materials Chemistry* 8, 1949–1951.
- Zhang, H., Pantano, C.G., 1990. Synthesis and characterization of silicon oxycarbide glasses. *Journal of the American Ceramic Society* 73, 958–963.
- Zheng, H., Oka, K., Mackenzie, J.D., 1992. Preparation of titanium carbonitride coatings by the sol-gel process. *Materials Research Society Proceedings* 271, 893–898.
- Zheng, J.P., Jow, T.R., 1995. A new charge storage mechanism for electrochemical capacitors. *Journal of the Electrochemical Society* 142 (1), L6–L8.
- Zhou, H., Chen, Q., Yang, Y., 2015. Vapor-assisted solution process for perovskite materials and solar cells. *MRS Bulletin* 40 (8), 667–673.

Synthesis of Ceramic Powders by Wet Chemical Routes

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Introduction

Aim of this chapter is to describe wet-chemical routes of both oxide and non-oxide ceramic particles. The main solution-based technologies are described, focusing on the process, providing some examples and highlighting both advantages and drawbacks in controlling the final particle features. For the manufacturing of advanced ceramics, in fact, primary particles with suitable physicochemical characteristics should be used, where these characteristics include the purity, the homogeneity, the density, the particle size, the particle size distribution, the shape and morphology, the specific surface area and the surface chemistry.

Although wet-chemical routes are effective in controlling the aforementioned characteristics, each synthesis is more suitable than the others in controlling some specific parameter, also considering the wide range of ceramic particles type nowadays required in ceramic processing, which include single-phase, multi-cationic, complex phases and composite powders, either in the oxide and non-oxide systems.

While single-phase ceramic particles with the desired characteristics are relatively easy to prepare, the synthesis of multi-cation or composite powders is more challenging. In fact, the conventional powder technologies for these types of powders requires three consecutive steps, namely mixing, solid-state reaction, and milling. The overall process can produce undesirable characteristics, which include phase and stoichiometric heterogeneities, poor control of size and morphology, significant particles aggregation. In many cases, to improve the characteristics of conventional powders, repeated calcination and milling steps are performed, with a consequent increased risk of pollution from the milling media. The limitations of the mixing-and-milling route drove the research towards the development of chemical synthesis methods for producing ceramic powders.

Wet-chemical syntheses include several technologies. The ones discussed in this chapter all use a liquid phase to solubilize one or more components in the process. In particular way, the routes described in this contribution are classified into three types, depending on where the chemical supersaturation (which produces the particle phase) takes place: (1) in the bulk liquid phase (includes sol-gel and precipitation); (2) between heterogeneous phases (includes solvothermal synthesis and molten salt synthesis); (3) in a droplet (includes microemulsions and spray syntheses).

Chemistry in the Bulk Liquid Phase

Sol-Gel Synthesis

Overview of the process

Sol-gel process can be described as the formation of an oxidic network through the polycondensation reaction of a molecular precursor in a liquid (Gonzalo-Juan and Riedel, 2016). This technique is suitable for both oxide and not-oxide ceramics, in the form of bulk materials, films, coatings, particles and fibers.

The term *sol* refers to a dispersion of colloidal particles in a liquid medium, where the stability of the colloids, at room temperature, is due to both Brownian motion and small particle size, which is usually less than 1 μm . As an alternative to *sol*, *solutions* can also be used, where the latter is thermodynamically stable, contrary to the former. The term *gel* refers to a three-dimensional network of a solid phase interwoven with an entrapped and immobilized continuous liquid phase.

The sol-gel process involves the preparation of a precursor mix (a *sol* or a solution), which transforms into a more solid-like material as a result of evaporation of the solvent, dehydration, and chemical cross-linking between the solid particles or dissolved precursors. The transformation of a *sol* or solution into ceramic material, via a gel-like intermediate, can be often accomplished at temperatures that are significantly lower than those necessary in “traditional” processing. This is because the precursors used are intermixed at a molecular level and can react through chemical pathways to form a network of chemical bonds that are characteristic of ceramic materials.

Precursors for the process can be either inorganic metal salts and metal alkoxides, $\text{M}(\text{OR})_n$. Alkoxide molecules exist as low molecular weight species, usually monomers or small oligomers, depending on the particular alkoxides used, the solvent, and other factors. The polymerization of these species occurs via hydrolysis of the M-OR species and polycondensation reactions involving the resulting M-OH group. Water acts as the “initiator” and is usually externally added. Water can also be generated in-situ by condensation reactions such as the formation of esters by the condensation of carboxylic acids and alcohols. Acids or bases are used as catalysts for these reactions.

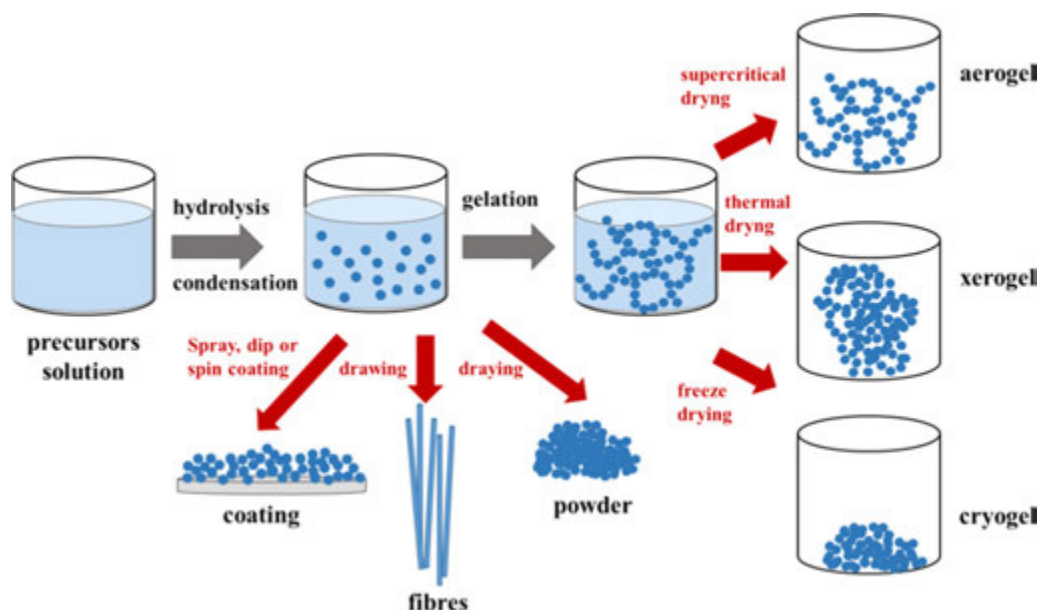


Fig. 1 Main reactions, processes and products involved in the sol-gel synthesis route.

The (complete) reaction of metal alkoxides with water provides the hydrolysis reaction:



In this process, proper care must be taken in handling, packaging, and using metal alkoxides. Even traces of moisture are often sufficient to cause pre-hydrolysis and undesirable precipitation of hydroxides.

The synthesis proceeds through the following condensation reactions:



The products of condensation reactions may be alcohol, water, or both, depending on the alkoxide used. Thus M-O-M bonds can form during the condensation reactions that occur using either alkoxide or colloidal oxide precursors. As an example, the overall reaction to synthesize silica is shown in the following:



It should be specified that sol-gel is referred to as hydrolytic process when water, used as the solvent or generated in-situ during by the condensation reactions, is the oxygen donor. On the opposite, non-hydrolytic (i.e., non-aqueous) sol-gel occurs under organic solvents, where the precursors (alkoxides, acetylacetonates, etc.) react with oxygen donors (metal alkoxides, ethers, alcohols, acetates, aldehydes, ketones, etc.). While hydrolytic sol-gel allows the production of only metal oxide ceramic particles, in the case of non-aqueous process, both oxide and non-oxide ceramic particles (such as silicon carbonitride, $Si_xC_2N_y$, GaN, CdSe, CdTe) can be produced (Gonzalo-Juan and Riedel, 2016).

After the polycondensation reactions and the gel formation, a further critical step is the solvent removal. The most traditional process implies the evaporation of the solvent, which induces a capillary pressure and consequent shrinkage of the gel, which is referred to as *xerogel*. A second possibility implies the extraction of the solvent under supercritical conditions: in an autoclave, the removal of the solvent is carried out at pressure and temperature higher than the solvent critical point. Under these conditions, the lack of liquid-vapor interface impedes the formation of capillary pressure, and therefore drying occurs with little shrinkage. The product is named *aerogel*, and is normally characterized by a very high porosity in the nanometer scale and large surface area. Finally, the gel can be freeze dried, meaning that the pore liquid is frozen and then sublimed, producing a material named *cryogel*. In Fig. 1, a scheme of the sol-gel process is proposed, within the different dried products.

Advantages, issues, applications

The main advantage of this process lies in the low temperatures involved. In fact, through the polycondensation reactions shown in Eqs. (2) and (3), a network of metal-oxygen bonds is created at very low temperatures, typically lower than 100°C. Here, the choice of suitable precursors is one key, justifying the preferred choice of metal alkoxides and colloidal oxides as precursors. Other advantages include the high purity of the products and the ability to synthesize oxide ceramics in different product forms. The versatility of the process towards the development of different products (i.e., powders, thin films and coatings, fibers, bulk ceramics) is still depicted in Fig. 1.

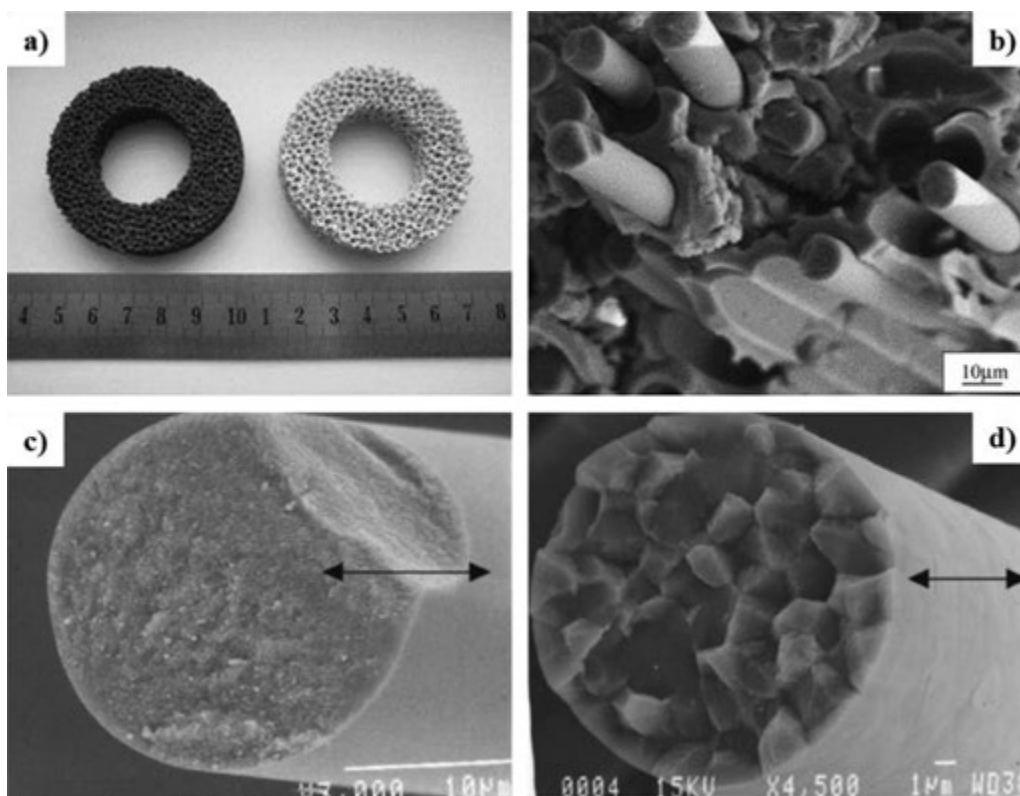
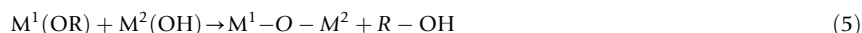


Fig. 2 (a) Digital photos of the uncoated and sol-gel derived TiO_2 -coated SiC foams; (b) morphology of Nextel 720 fibers within a fiber-reinforced SiC composite; Microstructure of sol-gel-derived α -alumina ceramic fibers: (c) superfine-microstructure, dense alumina fiber after sintering with nucleating agent and (d) coarse-microstructure, porous alumina fiber after sintering with no nucleating agent. (a) Modified from Hao, D., Yang, Z., Jiang, C., Zhang, J., 2014. Synergistic photocatalytic effect of TiO_2 coatings and p-type semiconductive SiC foam supports for degradation of organic contaminant. *Applied Catalysis B: Environmental* 144, 196–202 with the permission of Elsevier under the license no. 4900191225167; (b) reprinted from (Chen *et al.*, 2005) with the permission of Elsevier under the license no. 4900730728115.

Among the disadvantages, it should be mentioned the high cost of the precursor alkoxides. As a second, important issue, the preparation of composites or multiphase ceramics is still a complex issue. To produce two phase materials, for instance, cross-condensation reactions should occur, i.e., reactions between species from two or more cations:



In principle, these reactions are possible, and solution containing different alkoxides could be used to construct a network of many cations. In practice, however, differential hydrolysis and polycondensation rates of different alkoxides pose a problem. Also, certain metals may be introduced in the form of other precursors that do not exhibit hydrolysis and polycondensation reactions. Different approaches including pre-hydrolysis of the more slowly reacting metal alkoxides as well as stabilization of highly reactive metal alkoxides by a molecular modification process have been developed to tackle this important problem (Phulé and Khairulla, 1990).

Commercial applications of sol-gel technology include the areas of optical fibers, refractory and reinforcing ceramic fibers, abrasive minerals, aerogels, coatings. An example of sol-gel derived TiO_2 coating on a SiC foam is depicted in Fig. 2(a) (Hao *et al.*, 2014). The first practicable sol-gel process for making high-quality silica optical fibers was reported by researchers at Lucent Technology (MacChesney *et al.*, 1999). More specifically, the sol-gel process is used for the production of silica tubes which serve as overcladding material of the optical fibers. Very high silica purity and dimensional control are the key requirements, which justify the choice of a colloidal sol-gel route. In fact, the high cost of the organometallic precursors and the large drying shrinkage make unfeasible the alkoxide route. As a precursor, largely available and low cost silica fume was used, and tetramethylammonium hydroxide was added to stabilize the suspension and decrease the viscosity. Then, addition of an ester (methyl formate) decreased the pH and induced gelation, which occurred within 10 min, allowing casting in a precision mold, demolding and drying. Purification was carried out at 1000°C in a chlorine-containing atmosphere to remove residual water and volatile organics. Finally, highly pure and transparent silica was obtained after sintering at $1500\text{--}1550^\circ\text{C}$. Optical fiber preforms are then fabricated by collapsing the tube over a vapor-deposited core rod, and high-quality optical fibers are then drawn from such optical fiber preforms.

Other examples of commercial applications of the sol-gel process include the development of the Nextel fibers by 3M Company. Nextel fibers are prepared by extruding, drying, and firing a concentrated sol containing a basic aluminum salt mixture

along with additives such as colloidal silica, organic polymers, and, in some cases, a boron oxide precursor. In general, the Nextel fibers are polycrystalline, transparent, and can be woven or braided for different engineering applications. Nextel 312 fibers based on a ceramic consisting of 62% Al_2O_3 , 14% B_2O_3 , and 24% SiO_2 , are processed using a colloidal sol-gel process. Nextel 720 is another grade of 3M fibers, composed by 85% Al_2O_3 and 15% SiO_2 , which gives rise to an alumina/mullite composite. (Tariq *et al.*, 2011). The morphology of this fiber, within a SiC-based composite, is depicted in Fig. 2(b). Nextel 610 fibers are high-modulus, α -alumina ceramic fibers having an exceedingly fine grain size (average grain size less than 2 μm). In the production of these fibers nucleating agents are used to reduce the sintering temperature, and therefore the average grain size. In Fig. 2(c), a sol-gel derived α -alumina fiber, characterized by a dense and ultrafine microstructure – due to sintering with nucleating agent – is depicted. In Fig. 2(d), the same fiber, but with a coarsened microstructure is shown: in this case, no nucleating agent has been added before sintering. Such sol-gel-derived ceramic fibers and materials find applications in insulation products, ceramic fiber-reinforced metal matrix composites and in reinforced ceramics and plastics.

Since 1970s, researchers at 3M Company began to develop sol-gel derived dense and tough ceramic materials, developing a number of abrasive minerals, including materials based on α -alumina/spinel mixtures, superfine-grained aluminas, and alumina/rare earth aluminates. The synthesis of these materials involves first forming a concentrated sol of boehmite (aluminum oxy-hydroxide) which is gelled either by raising the ionic strength of the sol or by heating. To form the ceramic abrasive grain, the boehmite gel is dried, crushed to size, calcined, and fired to full density.

In many familiar applications, sol-gel-derived products play an important role that is often not readily recognized. For example, precipitated silicas are used as a filler material in the manufacture of automobile tires. Other products such as paints and toothpastes also often make use of colloidal silica particles. Some of the other applications of sol-gel-derived products include antireflective coatings, abrasion resistant coatings for ophthalmic products such as eyeglasses and contact lenses, spin-on glasses for dielectric planarization, ferroelectric thin films, electrochromic coatings, and thin layers of transparent oxide conductors.

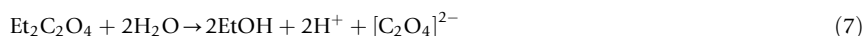
Precipitation

Overview of the process

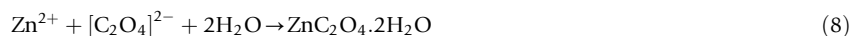
Precipitation can be performed either under direct- and reverse-strike mode. In *direct strike precipitation*, the most commonly employed method, a precipitating agent or solution is dropwise added to a metal salts solution. Upon addition of the precipitant, the salts solution pH increases, leading to hydroxides precipitation. On the opposite, in *reverse strike precipitation*, a soluble salts solution is slowly added to a solution containing the precipitating agent, inducing a progressive pH decrease of the precipitating solution. When two or more chemical species have to be simultaneously precipitated (process referred to as *co-precipitation*) the salts solution and an extra-precipitation solution are added at the same time. In such a way, the pH is kept to a constant value, corresponding to the hydroxide formation of both species (Palmero *et al.*, 2005; Palermo and Traverso, 2014), thus assuring the simultaneous and quantitative precipitation of both. As respect to direct strike precipitation, this last route allows a higher homogeneity of distribution of the different elements, providing lower crystallization temperature of the multi-cationic oxide material. Precipitation is a suitable route for preparing both oxide and non-oxide ceramic particles. In the case of oxide ceramics, the precipitation of lanthanum-modified lead zirconate titanate is shortly described here: lead and lanthanum nitrates, zirconium oxychloride, titanium tetrachloride, and hydrogen peroxide are used as precursors, and dissolved in water at 40°C. Upon addition of ammonium hydroxide till the achievement of a pH of 9, the precipitation of mixed hydroxides occurred. After washing, drying and calcination at 650°C, the complex oxide formed. Concerning non-oxide ceramic particles, silicon nitride was produced starting from silicon chloride (SiCl_4) which was precipitated under ammonia addition, providing silicon diimide $[(-\text{Si}(\text{NH})_2)_x]$, which was then converted to Si_3N_4 by pyrolysis at 1200–1700°C.

Direct precipitation method can be assisted by the addition of a non-solvent. First, an aqueous solution is prepared and then precipitation is induced by dilution with a hydrophilic non-solvent. Soluble salts employed include sulfates, citrates, and nitrates, while alcohol (ethanol, isopropanol, etc.) or acetone are typically employed as the non-solvent. Proper choice of the salt concentration, solution environment (pH, addition of complexing agents) and non-solvent is essential to achieve the proper stoichiometry and satisfactory homogeneity. Materials such as barium titanate, lead zirconate, magnesium aluminate, and manganese ferrites can be prepared.

The conventional precipitation processes, where the precipitant solution is added to the reaction medium, often produces localized concentration effects. To overcome such an issue, *precipitation from homogeneous solutions* can be performed, where the precipitant is generated over a long period of time and uniformly throughout the entire reaction region. Here, the level of supersaturation remains low, providing the precipitation of compact crystals instead of coagulated colloids, completely avoiding concentration gradients. In order to control particle size, size distribution and morphology, special attention must be given to concentration, pH, heating rate, temperature, corresponding anion of the soluble metal salt, choice of precipitating reaction, and aging conditions. The most commonly used precipitation from homogeneous solution technique uses a soluble salt co-dissolved with a precursor that decomposes upon heating, releasing an anion that quantitatively precipitates the dissolved cation. As an example, the synthesis of zinc oxalate dihydrate is here reported, starting from an aqueous solution of oxalic acid-zinc nitrate, via anion release:



The release of the oxalate anion is being regulated by the rate of diethyl oxalate decomposition in a solution of dissociated Zn^{2+} to precipitate $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, as shown below:



This technique can also be used to prepare multicomponent powders with controlled stoichiometry and phase homogeneity, such as strontium-titanium hydrous oxides and yttria-doped zirconium hydrous oxide. In order to obtain a phase-homogeneous powder with the intended cation stoichiometry, careful attention must be paid to the preparation of the homogeneous solution and the types of multicomponent complexes that form. Finally, the feasibility to prepare not-oxide powders was demonstrated as well: submicron diborides of titanium, zirconium, and hafnium are prepared by refluxing metal borohydrides in xylene at 140°C:



Silicon and titanium carbides were produced from chlorides, by dehalogenation and carburization in n-heptane at 130°C, as shown in the following reaction:



Advantages, issues, applications

Precipitation and co-precipitation offer advantages in terms of fine particles size, controlled stoichiometry and purity of the final powders. As in other wet-chemical synthesis methods, agglomeration of the particles is one of the major issues. In addition, the common ion effect can induce heterogeneities in the system. This could happen in multi-component precursor solutions, when the anion of a soluble salt makes insoluble the cation of another salt. Such a heterogeneous precursor system is unlikely to produce a physically and chemically uniform powder. To avoid this issue, the solubility of all salts included in the system must be carefully taken into account.

A further undesirable effect relates to the anionic by-products (e.g., chlorides and sulfates) which can be co-precipitated within the primary products. These impurities can be incorporated into the particles as lattice defects or can adsorb onto powder surfaces. In addition, soluble species in solution can become occluded within particle agglomerates. Proper choice of the soluble anions in solution is important in order to minimize the above problems. Anions which decompose at low temperatures are preferred, since they can be eliminated from the powder during calcination. For examples, nitrates should be preferred to chlorides, due to the lower decomposition temperature of the related by-products.

One of the most important industrial example of precipitated powder is $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (gibbsite), which is precipitated from a sodium aluminate solution (Bayer process). Subsequent calcination produces transition or α -alumina, which finds several commercial applications for abrasive materials, fire-retardants, adsorbents, catalysts, ceramics and fillers for polymeric composites (Denigres Filho *et al.*, 2016). A second example is provided by the precipitation of $\text{Mg}(\text{OH})_2$ that form a brine solution, which is again calcined to give the 'dead burnt' magnesia (Ring, 1996), the main raw material for basic refractory products. As an example, companies like Martin Marietta Magnesia Specialties, LLC (US) and Terna Mag (Greece) supply these kinds of product.

Co-precipitated yttrium aluminum garnet (YAG) powders can be used for the production of polycrystalline sintered transparent ceramics. To achieve optical transparency, the starting powders should satisfy some strict requirements, consisting in extreme purity, controlled stoichiometry, ultrafine particle size, and narrow particle size distribution, allowing to produce fully dense ceramics. As an example, a transmission electron microscopy micrograph of a co-precipitated YAG powder (after calcination at 1350°C) is depicted in Fig. 3 (left), where the nanometric size of the primary particles can be observed (Palmero *et al.*, 2005). Moreover, the formation of a well-crystallized and pure YAG phase was confirmed by comparing the experimental interplanar distances (d_{hkl} values) measured from the electron diffraction pattern with the nominal ones, as reported in the Table at the center of Fig. 3. Such a fine, homogenous, pure powder was suitable for the production of transparent sintered ceramic, as depicted in Fig. 3 (right) (Spina *et al.*, 2012; Palmero *et al.*, 2013). Polycrystalline transparent ceramics can be used as high-energy laser windows: for example, a 1.46 kW Nd: YAG laser has been demonstrated by Konoshima Chemical Co. in Japan, while transparent ceramics (YAG and yttria) are currently commercialized by CoorsTek (see "Relevant Website section").

Chemistry Between Heterogeneous Phases

Solvothermal Synthesis

Overview of the process

Starting from the '70s, the direct precipitation of crystalline oxide structures become feasible thanks to the introduction of the hydrothermal syntheses. Solutions, gels and suspensions are used to precipitate anhydrous oxides, being the reactants placed in closed vessels and processed under high pressure and temperature conditions, allowing solubilization reactions which are not allowed under ordinary temperature and pressure ($< 100^\circ\text{C}$, < 1 atm).

More precisely, solvothermal synthesis can be carried out either under mild or extreme conditions. In the former case, reactions are carried out below $\sim 300^\circ\text{C}$, due to the fact that the ionic products have typical values in the range 250–300°C (Hayashi and Hakuta, 2010), avoiding reaching the critical water pressure and temperature (22.1 MPa and 374°C, respectively). In the second case, such values are overcome, causing a significant change of some physical properties such as dielectric constant and solubility, affecting reaction rate and providing favorable conditions for particle formation (Hayashi and Hakuta, 2010).

Even though mild conditions ($T < 350^\circ\text{C}$ and $P < 50$ MPa) are preferred, in order to lower the process cost and extend the durability of the reactions vessels (Suchanek and Riman, 2006), supercritical conditions (up to $T \sim 1000^\circ\text{C}$ and $P \sim 500$ MPa)

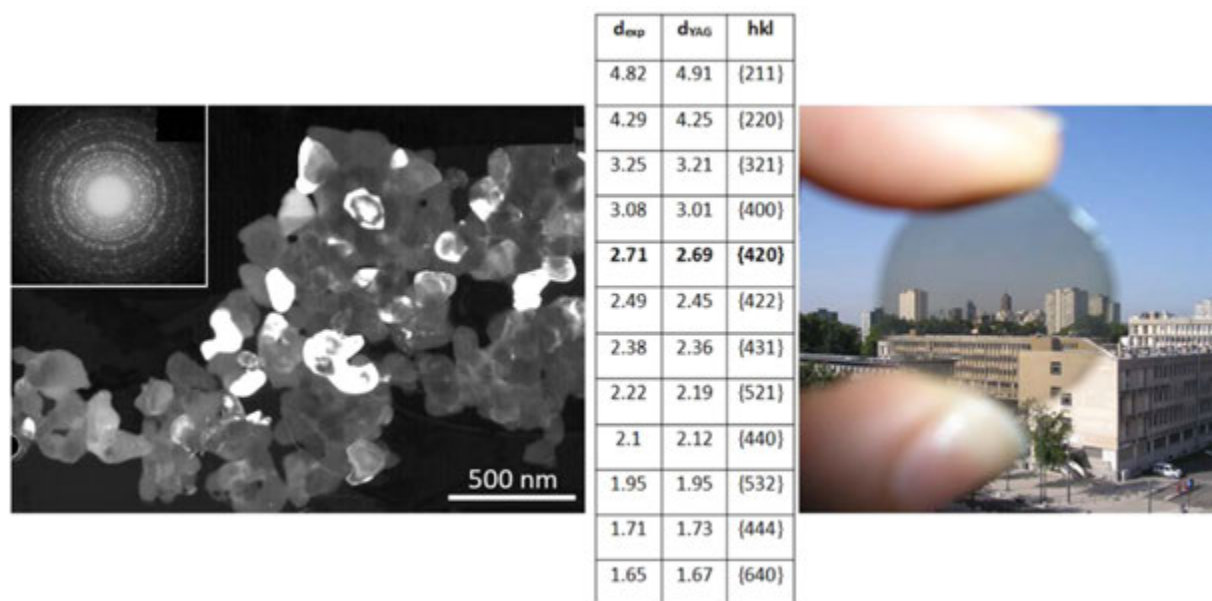


Fig. 3 (left): Transmission electron microscopy micrograph of co-precipitated yttrium aluminum garnet (YAG), after calcination at 1350°C. Inset to the figure, the electron diffraction pattern to derive the interplanar distances, reported in the table (center); (right): digital photo of polycrystalline sintered YAG, showing high optical transparency.

(Roy, 1994) allows faster reactions (reaction rate $> 10^3$ times compared to conventional hydrothermal conditions) and higher degree of crystallinity in the products.

Mild hydrothermal synthesis can proceed either by in situ transformation or dissolution/re-precipitation mechanisms. In the former case, the dispersed particles undergo a polymorphic or chemical phase transformation. For example, titanium hydrous oxide can be chemically transformed into polycrystalline anhydrous anatase phase by refluxing the powder for 12 h in an ammonium hydroxide-water solution, at pH 10, atmospheric pressure and temperature of 100°C. In the case of dissolution-reprecipitation mechanism, the dispersed particles dissolve into solution, supersaturate the solution phase and then reprecipitate. In most cases, the solubility needs to be improved by proper solubilizing components. For example, a hydrothermal reaction at low pH (< 3.5) dissolves the zirconium hydrous oxide precursor in soluble species, that subsequently reprecipitates the zirconium oxide.

Hydrothermal synthesis has been successfully used for the preparation of a number of ceramic particles, including single-phase, complex oxides as well as non-oxide ceramics (Suchanek and Riman, 2006). Among the single phases, numerous studies relate to the hydrothermal preparation of silica, alumina, zirconia (stabilized by calcia, yttria, scandia, ceria, etc.) (Sato *et al.*, 2015; Kim *et al.*, 2012; Rizzuti *et al.*, 2009), titania, zinc and iron oxide. A number of complex oxides were synthesized as well: perovskites, such as titanates ($ATiO_3$, with $A = Ba, Ca, Sr, Pb$, etc.) (Walton, 2020) zirconates ($BZrO_3$, $B = Ba, Ca, Sr$) and their mixed oxides like $Pb(Ti_{1-x}Zr_x)O_3$ (PZT); niobates (such as $KNbO_3$ and $LiNbO_3$); cobalt and nickel ferrites (such as $CoFe_2O_4$ and $NiFe_2O_4$) (Zalite *et al.*, 2015; Bućko and Haberko, 2007); apatites; zeolites, etc. In addition, nanocomposite powders, such as alumina-hydroxyapatite (Sivaperumal *et al.*, 2017), alumina-yttria stabilized zirconia (Geuzens *et al.*, 2008), magnetite-hydroxyapatite (Murakami *et al.*, 2008), titania-hydroxyapatite and titania-silica (Suchanek and Riman, 2006) as well as core-shell structures particles (CdS/ZnO , $CoAl_2O_4/ZnAl_2O_4$) (Suchanek and Riman, 2006) have been also successfully prepared. The process also allows the preparation of non-oxides ceramics, such as nickel or cobalt selenides, lead or cadmium tellurides, cobalt, tin, or molybdenum sulfides, vanadium nitrides, rare-earth fluorides, (cubic BN, hexagonal BN), arsenides ($InAs$, $GaAs$), etc (Suchanek and Riman, 2006; Huang *et al.*, 2014; Wang *et al.*, 2006).

Crystalline products can be in a variety of forms, such as equiaxed (for example cubes, spherical), elongated (fibers, whiskers, nanorods, nanotubes), plates, nanoribbons, nanobelts, etc. Fig. 4 depicts the transmission electron microscope images of different ceramic particles produced under supercritical water conditions (Hayashi and Hakuta, 2010), showing the effectiveness of the method in producing different powder morphologies.

Advantages, issues, applications

Compared to conventional wet-chemical routes, hydrothermal synthesis offers numerous and significant advantages. First, all types of ceramic can be synthesized, such as powders and fibers, single crystals and polycrystalline ceramics, bulk materials and coatings. Then, the precipitation of already crystallized phases is a unique feature, while the control of particle size, shape and agglomeration degree is improved as respect to traditional processes. The synthesis of metastable compounds is possible as well, which is not feasible under the conventional high temperatures processing methods. A poorly agglomerated powder, characterized

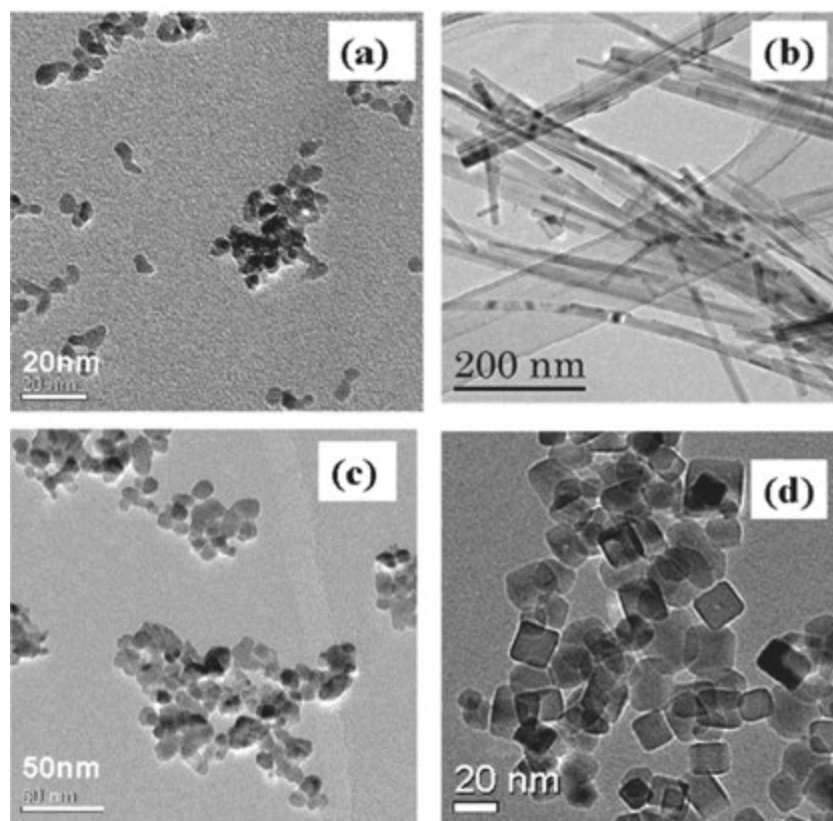


Fig. 4 Transmission electron microscopy (TEM) images of metal oxide nano-particles synthesized by the supercritical hydrothermal flow system. (a) $\text{Y}_x\text{Zr}_{1-x}\text{O}_2$, (b) $\text{K}_2\text{Ti}_6\text{O}_{13}$, (c) BaTiO_3 , (d) $\text{Ca}_{0.7}\text{Sr}_{0.3}\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$. Reproduced from Hayashi, H., Hakuta, Y., 2010. Hydrothermal synthesis of metal oxide nanoparticles in supercritical water. *Materials* 3, 3794–3817, under the Creative Commons Attribution License.

by a narrow particle size distribution leads to higher fired densities and more microstructural homogeneity, which leads to more controlled final properties. Finally, in spite the application of temperature and pressure during synthesis, the following steps of calcination, mixing and milling are minimized, and therefore the whole process is a less time- and energy-consuming method respect to other wet synthesis technologies.

Only few disadvantages characterize the hydrothermal synthesis, such as the safety issues during the reaction process and the high cost of the autoclaves.

Starting from the 20th century, hydrothermal synthesis was clearly identified as an important technology for materials synthesis, predominantly in the fields of hydrometallurgy and single crystal growth. However, the severe (supercritical) reaction conditions required for growing single crystals have discouraged extensive research and commercialization for many materials. Currently, single crystals of α -quartz for frequency control and optical applications, ZnO for UV- and blue light-emitting devices, and KTiOPO_4 for nonlinear optical applications, are commercially available (Suchanek and Riman, 2006). In recent years, the commercial interest in solvothermal synthesis increased, and specifically in the field of primary ceramic particles, which can be processed under mild hydrothermal conditions (Suchanek and Riman, 2006). The widely used Bayer process uses hydrothermal methods to dissolve bauxite and subsequently precipitate aluminum hydroxide, which is later heat-treated at high temperature to crystallize as α -alumina. Sawyer Technical Materials, LLC recently developed hydrothermal production of high-purity α - Al_2O_3 particles, and powders characterized by different size and morphologies (equiaxed, needles, nano-sheets) are currently available on the market (see “Relevant Websites section”). The production of perovskite-based dielectrics and zirconia-based structural ceramics is a promising growth area for hydrothermal methods. Corporations such as Cabot Corporation, Sakai Chemical Company, Murata Industries, Ferro Corporation and others have established commercial hydrothermal production processes for making dielectric ceramic powder compositions for capacitors.

Molten Salt Synthesis

Overview of the process

Ceramic powders are solubilized into molten inorganic salts, which are used as high-temperature solvents, mimicking the crystal nucleation and growth processes which typically occur in conventional solvents. The procedure implies (1) the mixing of the reactants with a salt; (2) their heating above the salt melting temperature; (3) the dissolution of the reactants, their reaction and

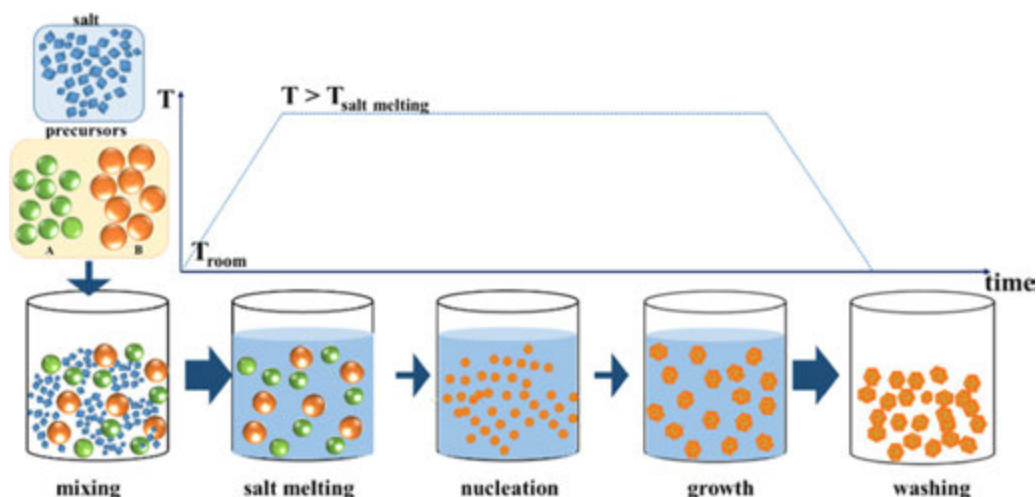


Fig. 5 Scheme of the salt melt synthesis.

formation of the product that precipitate from the solution through nucleation and growth processes; finally, (4) the cooling down and final washing to remove the residual salt. A scheme of the process, showing the main above steps, is depicted in Fig. 5.

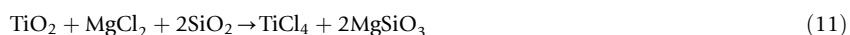
The product is formed through two stages. The former is the reaction, where the constituents (typically single-oxide phases) dissolve in the molten liquid and form the product. Here, under high saturation degree, two conditions can occur: (1) solution-precipitation, where both constituents dissolve in the molten liquid and the product is formed by precipitation; (2) solution-diffusion, where just one constituent dissolves, then diffuses in the melt and react with the second solid constituent, providing the product. In these stages, the particles shape is similar to that of one of the reactive. Then, upon further heating, the growth stage of the product starts, following an Ostwald ripening mechanism which determines the size distribution of the product particles. Here, the particle shape approaches the equilibrium one. It should be mentioned that the solubility of metal oxide in molten salts varies from less than 1×10^{-10} mol fraction to more than 1×10^{-3} mol fraction (Gonzalo-Juan and Riedel, 2016): the difference from typical solvent-based synthesis, where the solubilization of the reactants is almost complete and the precipitation occurs from homogeneous solution, is evident.

Molten salt synthesis has been successfully used to prepare both single crystals and polycrystalline ceramic powders. In the case of single crystals, the cooling conditions have to be controlled thus to generate a limited number of nuclei; on the opposite, for powders, an elevated nuclei number is required, which also affects the particles final grain size, that can range from a few tens nanometer to few tens micrometers.

The presence of molten salts play some key roles in this process, since they increase the reaction rate, decrease the reaction temperature compared to solid state synthesis (due to the increased mobility of the reactive phases), control the particle size, shape and agglomeration degree of the final product. Salts are required to be stable under the used conditions, readily available, inexpensive, and they have to be easily washed away with water (Kimura, 2011). Typical salts used in molten salt synthesis are chlorides and sulfates, while in many cases eutectic mixtures of salts are used, in order to decrease the liquid formation temperature.

As an example, the synthesis of lead zirconate titanate is here reported, where TiO_2 , ZrO_2 , PbO are mixed together in an aqueous slurry. A KCl-NaCl molten salt eutectic is mixed into the slurry, causing the system to gel. Upon drying, the mixture is heated at $\sim 1000^\circ\text{C}$ to form the lead zirconate titanate, which is subsequently washed, to eliminate both molten salts and any excess unreacted ions. Sodium iron titanate has been also successfully synthesized by molten salt procedure (Zhang *et al.*, 2019). As raw materials, Na_2CO_3 and FeTiO_3 were used, while NaCl, at the optimal molar ratio α of 4 (where α = moles of the molten salt respect to the moles of the raw materials) was added to generate the molten liquid medium at temperatures between 600 and 1000°C . Under these conditions, needle-like NaFeTiO_4 particles were obtained, while when extra Fe_2O_3 powder was added as raw material, a different morphology and composition was produced, yielding $\text{Na}_{0.75}\text{Fe}_{0.75}\text{Ti}_{0.25}\text{O}_2$ platelets, as shown in Fig. 6.

In some cases, the salt can participate to the reaction, as in the following example, where the salt cation directly contributes to the formation of the final product:



Here, the high volatility of TiCl_4 favors the elimination of the synthesis by-product.

Advantages, issues, applications

The main advantages of the molten salt synthesis are the simplicity, the versatility and the cost-effectiveness. In addition, compared to the traditional solid state reaction, where sintering implies neck formation and thus particles agglomeration, here the molten salt covers the surfaces of the reactive particles and prevents the formation of necks between the produced compounds, limiting the agglomeration degree.

In addition, this synthesis route is particularly suitable for covalent-bond based ceramic particles, such as borides, carbide and nitrides. For such non-oxide ceramics, mild synthetic conditions yield amorphous or poorly crystallized materials, since the high

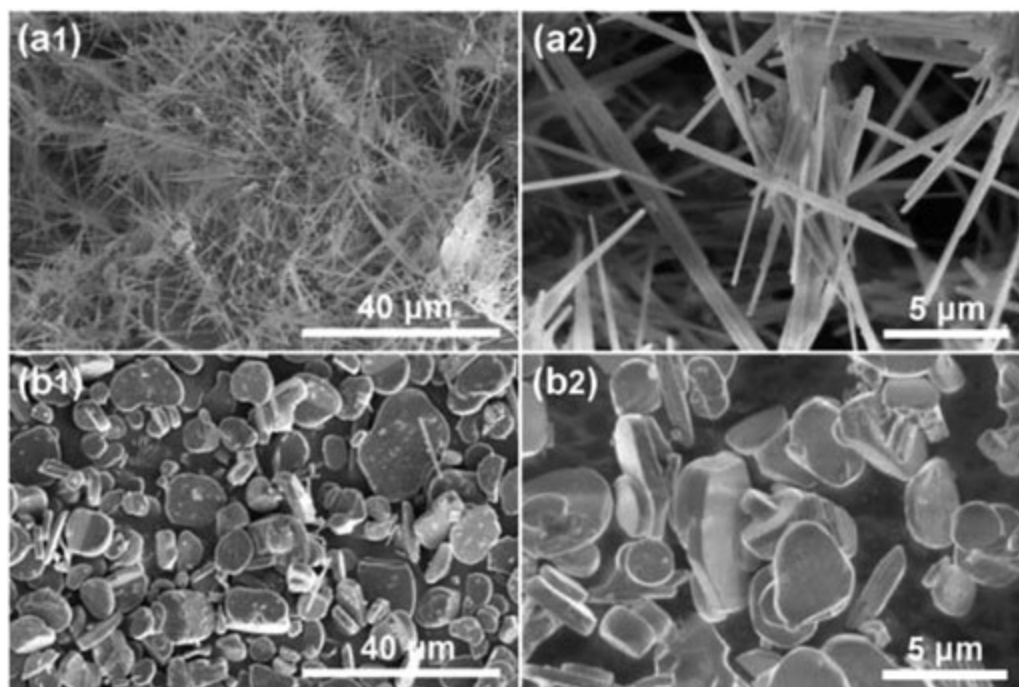


Fig. 6 SEM images of (a1, a2) NaFeTiO_4 needles (formed at $\alpha = 4$, $T = 900^\circ\text{C}$, and $t = 4$ h), and (b1, b2) $\text{Na}_{0.75}\text{Fe}_{0.75}\text{Ti}_{0.25}\text{O}_2$ platelets (formed at $\alpha = 4$, $T = 1000^\circ\text{C}$, and $t = 4$ h). Reprinted from Zhang, H., Li, M., Zhou, Z., Shen, L., Bao, N., 2019. Microstructure and morphology control of potassium magnesium titanates and sodium iron titanates by molten salt synthesis. *Materials* 12, 1577, under the Creative Commons Attribution License.

temperatures required to crystallize these powders normally exceed the operational temperatures allowed with organic solvents. This drawback can be overcome by the molten salt synthesis, thanks to the wide operational temperature (from 100 to 1000°C), the high mass transfer and high thermal conductivity of the system, which make feasible the synthesis of crystallized not-oxide ceramics (Gonzalo-Juan and Riedel, 2016).

The most important disadvantage relies to the numerous washing steps necessary to eliminate the residual salts, especially in the case they adsorb on the particle surface, and of the other synthesis by-products.

During the last 15 years, the interest towards molten salt synthesis significantly increased, especially for the preparation of multi-cationic materials such as ferroelectric and ferromagnetic ceramics, materials for Li-ion batteries (Santhanam and Rambabu, 2010), semiconductors (Huang *et al.*, 2010), phosphors (Yan and Lei, 2010), and photocatalysts (Arney *et al.*, 2008), especially when nano-sized materials are required (Mao *et al.*, 2007). In spite salt melts have been widely used as solvent, even at the industrial level, due to their low toxicity, low cost, low vapor pressure and large availability, no ceramic products based on molten salt synthesis (to the best of the authors' knowledge) are currently commercially available.

Chemistry in a Droplet

In this approach, the synthesis is confined within a solvent droplet, which controls the physical characteristics of the resulting powder and limits chemical segregation to the droplet scale. The syntheses included in this category involve the use of either liquid phase system (such as emulsions or microemulsions) or liquid-gas phase systems (such as aerosols and spray pyrolysis).

Emulsion and Microemulsion Synthesis

Overview of the process

An emulsion is a mixture of two immiscible liquids in which one liquid is dispersed into the other with the aid of a surfactant. A single or a mixture of surfactants stabilizes the emulsion by reducing interfacial tension, reinforcing the interfacial film, preventing coalescence of the droplets.

Surfactants as amphiphilic molecules made by hydrophilic head and a hydrophobic tail, which tend to adsorb at the water/organic phase interface and decrease their surface energy. This generates a dispersed phase confined in nanometer regimes, in which the synthesis of nanoparticles can be carried out (Sadat-Shojai *et al.*, 2013). Three types of emulsions can be prepared: water-in-oil, oil-in-water and water-in-oil-in-water double emulsion (Sadat-Shojai *et al.*, 2013), being the former one the mostly used for

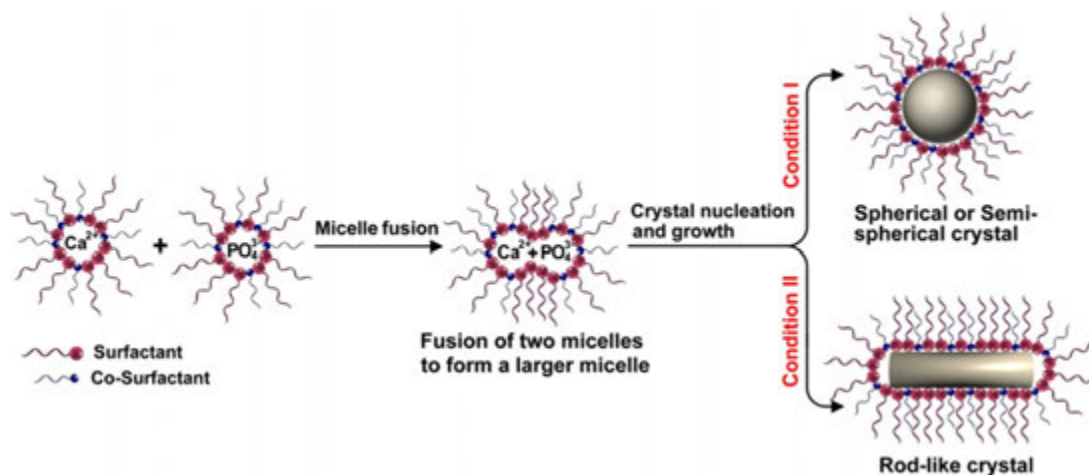


Fig. 7 Fusion process of the reverse micelles containing different ions to form hydroxyapatite nanoparticles of spherical morphology (condition I) or rod-like morphology (condition II). Reprinted from Sadat-Shojai, M., Khorasani, M.-T., Dinpanah-Khoshdargi, E., Jamshidi, A., 2013. Synthesis methods for nanosized hydroxyapatite with diverse structures. *Acta Biomaterialia* 9, 7591–7621, with the permission of Elsevier under the license no. 4901260452701.

the synthesis of single-phase oxides (TiO_2 , ZrO_2 , SiO_2 , GeO_2 and Fe_2O_3), multicomponent oxides (such as MnFe_2O_4 and other ferrite materials) (Malik *et al.*, 2012) and non-oxide ceramics such as the carbides of thorium or uranium.

Water-in-oil emulsion consists on the preparation of a stable colloidal sol, emulsified in an oil medium to form spherical droplets. Then, two methods can be used to induce the gelation of the droplets. In one case, dehydration or evaporation of the liquid is used. In the case of dehydration, an organic phase such as a long-chain alcohol (2-ethylhexanol) is used to concentrate the sol by dehydrating the droplets, through flocculation of the sol (with possible precipitation reaction) inside the droplets. In the second case, gel can be formed upon pH variation inside the sol, for instance by adding urea which decomposes and releases ammonia in the aqueous phase during heating of the emulsion.

Emulsions typically show a milky appearance. They are kinetically stable but thermodynamically unstable, and therefore tend to separate into the constituent phases, causing the merging of the droplets and the separation of the second liquid phase.

Microemulsions allow to overcome this drawback, since they are stable by a thermodynamic point of view. Here, droplets with size lower than $0.15\ \mu\text{m}$ make the emulsion transparent, while for sizes larger than $1\ \mu\text{m}$, the appearance is turbid. In principle, the smaller the droplet size, the smaller the synthesized particles. Mixing conditions, surfactant types and concentration are the keys to control the size of the droplet.

Water-in-oil microemulsion are also known as reverse micelles, characterized by the ability to solubilize both hydrophilic and hydrophobic species. Even though the mechanism of nanoparticles synthesis is not completely understood, it seems to proceed in the following way: when reactants are included in a microemulsion and mixed together, intramicellar collisions promote the reactants exchanges, and consequently the occurrence of precipitation reactions, followed by nucleation and growth, resulting in the formation of the final nanoparticles surrounded by water and/or stabilized by the surfactants.

An example of multi-cationic ceramic phase produced by the microemulsion technique is provided by the synthesis of hydroxyapatite (Sadat-Shojai *et al.*, 2013). Specifically, the synthesis is carried out in a water-in-oil system, where a transparent microemulsion is made of reverse micelles dispersed in a continuous oil phase. Each micelle contains a droplet of solution in which the first precursor (e.g., calcium ions) is solubilized. Upon the addition of the second microemulsion, containing the other reagent (phosphate ions), collision and fusion between the reverse micelles occur, allowing the reaction between Ca^{2+} and PO_4^{3-} ions, followed by nucleation and growth of the hydroxyapatite crystals, as illustrated in Fig. 6. Considering that each reverse micelle acts as a nano- or micro-reactor, the same micelles also play a role as a templating agent, affecting the morphology and the size of the hydroxyapatite particles. A further key role in affecting particle size, morphology and crystallinity of the final particles is played by the surfactants, where the above features can be tuned by adjusting the electrostatic interaction between the ionic surfactants and oppositely charged groups on the hydroxyapatite surface. Therefore, by changing surfactant type, the electrostatic interactions change, and thus the particle features, which can move from spherical to rod-like, as schematically shown in Fig. 7.

Advantages, issues, applications

The main advantage of the microemulsion technique lies in the possibility to synthesize nanosized particles, where the droplets/micelles act as a template to tune the size and the morphology of the final particles, and the surfactant prevent their agglomeration (Sadat-Shojai *et al.*, 2013).

However, the formation of microemulsions generally requires large amounts of surfactants and/or co-surfactants, which are generally irritating when used at high concentrations (Gupta *et al.*, 2013). In addition, the microemulsion stability is affected by temperature, pH and other external factors.

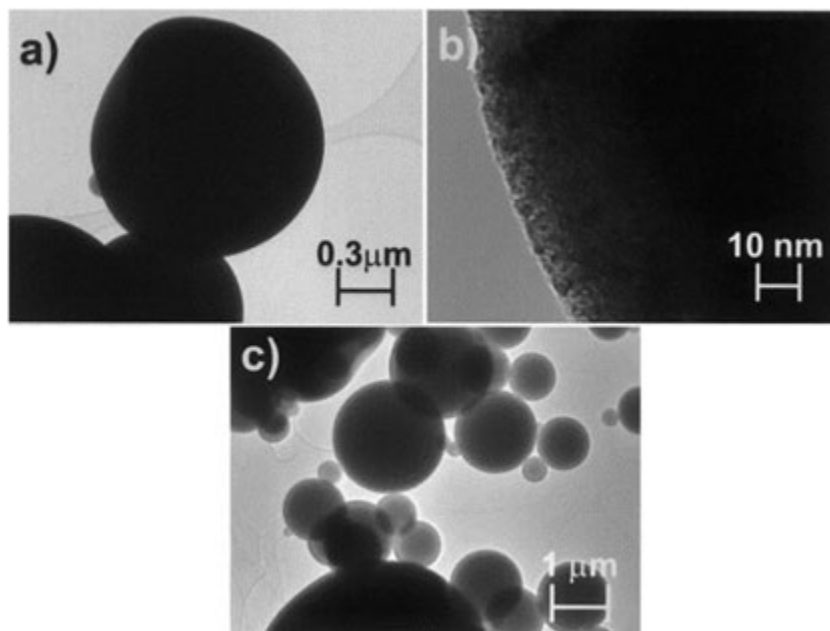


Fig. 8 TEM images of the as-synthesized titania powders, at different hydrolysis water: titania precursor molar ratio: (a–b) $[\text{H}_2\text{O}]:[\text{Ti}] = 2$; (c) $[\text{H}_2\text{O}]:[\text{Ti}] = 4$. Reprinted from Ahonen, P.P., Tapper, U., Kauppinen, E.I., Joubert, J.-C., Deschanvres, J.-L., 2001. Aerosol synthesis of Ti–O powders via in-droplet hydrolysis of titanium alkoxide. *Materials Science and Engineering A* 315, 113–121 with the permission of Elsevier under the license no. 4905940125317.

As mentioned before, this synthesis route has been successfully used to prepare single-phase and multi-cation oxide, non-oxides, nanowires, nanocomposite ceramics. Concerning the applications, magnetic ceramic particles are successfully synthesized by the microemulsion technique (Wang *et al.*, 1997; Malik *et al.*, 2012) even though not yet at a marketable level. New applications arise from the development of 3D printing technologies for ceramic materials, namely concerning ceramic pigments (Chang *et al.*, 2018). A suitable ink for 3D printing should be prepared by fine powders and pigments, with size smaller than 1/100 that of the nozzle, to avoid clogging. Microemulsion is able to provide nanoparticles with size in the range ~ 0.2 – $1.0 \mu\text{m}$, thus meeting the demands of ink-jet printing. In addition, microemulsions can incorporate both hydrophilic and lipophilic species (like therapeutic agents and drugs) with application in medicine (Malik *et al.*, 2012).

Spray-Based Syntheses

Overview of the process

Aerosols or sprays are liquids dispersed in the gas phase. As with microemulsions (see section “Emulsion and Microemulsion Synthesis”), the droplet size directly affects the particle size, while droplet dimension is determined the precursor types and the method of aerosol generation.

Aerosols can be generated either by vapor condensation and mechanical condensation. Vapor condensation has been used primarily in low-temperature reactions, where the precursors contained in the droplets react with the species in the vapor phase, to form the particles, which have normally submicron size. For instance, titania and alumina ultrafine powders ($\sim 0.2 \mu\text{m}$), characterized by narrow size distribution, can be precipitated from monodisperse $0.4 \mu\text{m}$ aerosols of alkoxides (such as $\text{Ti}(\text{OR})_4$ and $\text{Al}(\text{O-sec-Bu})_3$) or metal tetrachlorides (such as SiCl_4 and TiCl_4) by seeding the vapor phase with silver chloride and subsequently hydrolyzing the droplets with water vapor at temperatures higher than 0°C , while the completion of the hydrolysis reactions occurred at aerosol temperature $\geq 100^\circ\text{C}$. The same route was used to prepare TiO_2 - SiO_2 composite powders, by diffusing SiCl_4 vapor into monodisperse $\text{Ti}(\text{OEt})_4$ droplets and subsequently hydrolyzing the multicomponent droplet. Here the major issue is the chlorine contamination, which could affect the following ceramic processing. A modified method was employed by Ahonen *et al.* (2001) to produce TiO_2 nanoparticles, where in-drop hydrolysis is carried out. $\text{Ti}(\text{OBu})_4$, hydrolysis water, and acetic acid were added to ethanol, and the solution was atomized. The spray was transferred to a tubular flow reactor (operating at 200°C , under N_2 /air atmosphere, at ordinary pressure): upon alcohol evaporation, polycondensation reactions and formation of titania particles occurred. As-synthesized particles were amorphous, and characterized by spherical morphology of few microns in size, as shown in Fig. 8. Crystallization of the anatase phase and rutile phase occurred at temperatures higher than 500 and 900°C , respectively.

The second route implies the mechanical condensation, where sols are sprayed into immiscible liquids, to form “gel-microspheres”, by a subsequent dehydration or pH change. An ultrasonic spray atomizer has been used to react aqueous zirconium nitrate with ammonia gas to precipitate a hydrous oxide. Electrostatic aerosols of aqueous solutions of zirconium acetate and

polyethylene oxide yielded 0.1–5.0 μm diameter acetate particles, which were subsequently calcined at 1100°C to form zirconia. In this system, varying concentrations of polyethylene oxide (<0.06 wt%) served as a means to control the particle size. Salts can be spray-dried as well; however, significantly larger particle sizes result. Iron oxides spray dried as various salts typically have particle sizes of 3–20 μm . Recently, the spray drying technique was used to develop alumina and zirconia-based nanocomposite powders (Palmero *et al.*, 2011; Palermo and Esnouf, 2011; Palermo *et al.*, 2014). Within this approach, a commercial and well dispersed alumina or zirconia powder is mixed with an aqueous salts solution, being the salts the precursors of the second phases. During atomization, instantaneous water evaporation occurs, thus to induce the quick and homogeneous precipitation of the salts on the particles surface, thus avoiding segregation phenomena which can occur during conventional drying procedure. During subsequent calcination, salts decomposition and reaction provide the formation of the desired second-phases. As compared to the traditional mixing and milling procedure, this process allows an optimal distribution of the second-phases within the composites, as well as a careful control of particle size, morphology, and composition of all the phases. The procedure applies to both reactive and not-reactive systems; in the former case, the salts react with the matrix material to produce the second-phase, as in the case of yttrium-doped alumina to produce $\text{Al}_2\text{O}_3\text{-Y}_3\text{Al}_5\text{O}_{12}$ composites; in the second-one, the salts just crystalize on the surface of the matrix material, as in the case of zirconium-doped alumina, to provide $\text{Al}_2\text{O}_3\text{-ZrO}_2$ composites.

Ceramic powders have been prepared by freeze drying, in which multicomponent liquid solutions are sprayed into a cold liquid to freeze the droplets which are then separated from the liquid and subsequently sublimed. Spherical alumina, magnesium oxide, and spinel powders with submillimeter particle sizes have been prepared from calcined sulfate salts by pneumatically spraying aluminum sulfate solutions into hexane solutions chilled with a dry ice-acetone bath.

Powders can also be precipitated in spray droplets by solvent replacement. This technique involves the addition of an aerosol of an aqueous solution of metal salts to a non-solvent that solubilizes water but not the dissolved salts.

In spray pyrolysis, liquid droplets are sprayed into a reactor that has a low-temperature chamber for precipitating salts and a high-temperature chamber for subsequent pyrolysis. Powders range from micrometer-sized shell-like aggregates to narrow size distribution submicron solid spheres. A broad range of oxide, non-oxide, and composite powders (e.g., WC/Co) are prepared using this approach. The problems inherent in spray pyrolysis are magnified due to the fact that reactor and precursor systems must incorporate the ideal attributes of both spray-drying and calcination processes. During drying, the kinetics of both solvent evaporation and salt precipitation propagating inwards from the surface of the droplet should be optimized while maintaining the spherical morphology. During pyrolysis, attention must be paid to the large amounts of volatile products that are associated with rate-limiting processes such as heat transfer, diffusion through a product layer, and crust formation. In addition, in each case it must be determined whether or not spray pyrolysis is a liquid-gas phase reaction or a vapor-phase process using a liquid precursor. If the latter process is occurring, particle size will not be controlled by droplet size.

Advantages, issues, applications

Aerosol synthesis, and particularly spray pyrolysis, offers several advantages, being the main one the high purity of the produced powder. Moreover, spray pyrolysis allows producing particles with a narrow size distribution and homogeneous composition, due to the reaction being confined to the droplet dimension. In addition, each droplet contains precursors in the correct amount, making stoichiometry well controlled in the final product. A further key of spray synthesis is the relative simplicity of the process, which allows easy scale-up to pre-industrial or industrial scale.

The main challenges for spray-based synthesis relate to the stoichiometric control, the difficulty arising from the different solubility of the precursors. This can lead to segregation phenomena, which is – however- limited to the droplet dimension. In addition, the droplet output from the spray source significantly affects the features of the products, being larger and less homogeneous particles those generated at higher atomizer output rate. A further issue is related to the formation of crashed or hallow particles, which is undesirable especially for ready-to-press powder production. More in general, the morphology control of the synthesized powders is still a challenge.

Summary

Advanced ceramics are designed and developed to satisfy a number of functional and mechanical properties, for applications which spread from structural, to biomedical, environmental, electronic, optical, thermal, and magnetic areas. To achieve the expected performance, a key role is played by the starting ceramics particles. For instance, the starting particle size, the size distribution, the agglomeration degree, the shape and the specific surface area play an important role on the compact sinterability, and thus on the final density, microstructure and physical-mechanical properties. At the same time, particle size, morphology, aspect ratio, chemical surface are important features to control the electrical or magnetic properties. As respect to traditional preparation routes, were precursors are typically submitted to long and repeated mixing, milling and calcination steps, with disadvantages related to lack of homogeneity, purity, compositional and morphological control, current wet-chemical routes offer many alternative approaches for preparing powders with ideal or near-ideal characteristics. This contribution explores some of these wet-preparation routes, with the aim of highlighting the potential in achieving the desired physical and chemical characteristics, the application field and – in some cases – the commercial availability of the powders or related ceramic products, but also the main issues. Final aim of this contribution is not only to revise the main synthesis routes belonging to the wide ‘wet-chemical route’ class, but also to provide readers some guidelines to choice the most appropriate technology, and to scientifically approach them.

References

- Ahonen, P.P., Tapper, U., Kauppinen, E.I., Joubert, J.-C., Deschanvres, J.-L., 2001. Aerosol synthesis of Ti-O powders via in-droplet hydrolysis of titanium alkoxide. *Materials Science and Engineering A* 315, 113–121.
- Arney, D., Porter, B., Greve, B., Maggard, P.A., 2008. New molten-salt synthesis and photocatalytic properties of $\text{La}_2\text{Ti}_2\text{O}_7$ particles. *Journal of Photochemistry and Photobiology A: Chemistry* 199, 230–235.
- Bučko, M.M., Haberk, K., 2007. Hydrothermal synthesis of nickel ferrite powders, their properties and sintering. *Journal of the European Ceramic Society* 27, 723–727.
- Chang, Y., Feng, T., Wu, C., *et al.*, 2018. Controlled synthesis of blue spherical CoAl_2O_4 pigment powder in Pickering emulsion assisted with a hydrothermal process. *Advanced Powder Technology* 29, 1222–1229.
- Chen, Z., Zhang, L., Cheng, L., Xu, Y., 2005. Properties and microstructure of Nextel 720/ SiC composites. *Ceramics International* 5, 573–575.
- Denigres Filho, R.W.N., de Araujo Rocha, G., Regina Montes, C., Carlos Vieira-Coelho, A., 2016. Synthesis and characterization of boehmites obtained from gibbsite in presence of different environments. *Materials Research* 19, 659–668.
- Geuzens, E., Mullens, S., Coymans, J., *et al.*, 2008. Synthesis and mechanical and tribological characterization of alumina–yttria stabilized zirconia (YSZ) nanocomposites with YSZ synthesized by means of an aqueous solution–gel method or a hydrothermal route. *Ceramics International* 34, 1315–1325.
- Gonzalo-Juan, I., Riedel, R., 2016. Ceramic synthesis from condensed phases. *ChemTexts*. 2–6.
- Gupta, S., Kesarla, R., Omri, A., 2013. Formulation strategies to improve the bioavailability of poorly absorbed drugs with special emphasis on self-emulsifying systems. *ISRN Pharmaceutics*. 848043.
- Hayashi, H., Hakuta, Y., 2010. Hydrothermal synthesis of metal oxide nanoparticles in supercritical water. *Materials* 3, 3794–3817.
- Hao, D., Yang, Z., Jiang, C., Zhang, J., 2014. Synergistic photocatalytic effect of TiO_2 coatings and p-type semiconductive SiC foam supports for degradation of organic contaminant. *Applied Catalysis B: Environmental* 144, 196–202.
- Huang, T., Mao, S., Zhou, G., *et al.*, 2014. Hydrothermal synthesis of vanadium nitride and modulation of its catalytic performance for oxygen reduction reaction. *Nanoscale* 6, 9608–9613.
- Huang, Z., Li, B., Liu, J., 2010. Molten-salt synthesis of oxyapatite $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ powders as electrolytes for intermediate temperature solid oxide fuel cells. *Physica Status Solidi A – Application and Materials Science* 207, 2247–2251.
- Kim, J.-R., Lee, K.-Y., Suh, M.-J., Ihm, S.-K., 2012. Ceria–zirconia mixed oxide prepared by continuous hydrothermal synthesis in supercritical water as catalyst support. *Catalysis Today* 185, 25–34.
- Kimura, T., 2011. Molten salt synthesis of ceramic powders. In: Sikalidis, C. (Ed.), *Advances in Ceramics – Synthesis and Characterization, Processing and Specific Applications*. IntechOpen. Available from: <http://www.intechopen.com/books/advances-in-ceramics-synthesis-and-characterization-processing-and-specific-applications/molten-salt-synthesis-of-ceramic-powders>.
- MacChesney, J.B., Johnson Jr., D.W., Bhandarkar, S., *et al.*, 1999. Sol-gel process for optical fiber manufacture. *American Ceramic Society, Ceramic Transactions* 95, 65–72.
- Mao, Y., Park, T.-J., Zhang, F., Zhou, H., Wong, S.S., 2007. Environmentally friendly methodologies of nanostructure synthesis. *Small* 3, 1122–1139.
- Malik, M.A., Wani, M.Y., Hashim, M.A., 2012. Microemulsion method: A novel route to synthesize organic and inorganic nanomaterials. *Arabian Journal of Chemistry* 5, 397–417.
- Murakami, S., Hosono, T., Jeyadevan, B., Kamitakahara, M., Ioku, K., 2008. Hydrothermal synthesis of magnetite/hydroxyapatite composite material for hyperthermia therapy for bone cancer. *Journal of the Ceramic Society of Japan* 116, 950–954.
- Palmero, P., Esnouf, C., 2011. Phase and microstructural evolution of yttrium-doped nanocrystalline alumina: A contribution of advanced microscopy techniques. *Journal of the European Ceramic Society* 31, 507–516.
- Palmero, P., Traverso, R., 2014. Co-precipitation of YAG powders for transparent materials: Effect of the synthesis parameters on processing and microstructure. *Materials* 7, 7145–7156.
- Palmero, P., Esnouf, L., Montanaro, L., Fantozzi, G., 2005. Influence of the co-precipitation temperature on phase evolution in yttrium–aluminium oxide materials. *Journal of the European Ceramic Society* 25, 1565–1573.
- Palmero, P., Naglieri, V., Spina, M., Lombardi, M., 2011. Microstructural design and elaboration of multiphase ultra-fine ceramics. *Ceramics International* 37, 139–144.
- Palmero, P., Montanaro, L., Reveron, H., Chevalier, J., 2014. Surface coating of oxide powders: A new synthesis method to process biomedical grade nano-composites. *Materials* 7, 5012–5037.
- Palmero, P., Bonelli, B., Fantozzi, G., *et al.*, 2013. Surface and mechanical properties of transparent polycrystalline YAG fabricated by SPS. *Materials Research Bulletin* 48, 2589–2597.
- Phulé, P.P., Khairulla, F., 1990. Molecularly modified alkoxide precursors for chemical synthesis of dielectric ceramics. In: Zelinski, B.J., Brinker, C.J., Clark, D.E., Ulrich, D.R. (Eds.), *Better Ceramics Through Chemistry IV* 180. *Materials Research Society*, pp. 527–532.
- Ring, T., 1996. Chapter 6: Liquid phase synthesis by precipitation. In *Fundamentals of Ceramic Powder Processing and Synthesis*. Academic press.
- Rizzuti, A., Corradi, A., Leonelli, C., *et al.*, 2009. Microwave technique applied to the hydrothermal synthesis and sintering of calcia stabilized zirconia nanoparticles. *Journal of Nanoparticle Research* 12, 327–335.
- Roy, R., 1994. Accelerating the kinetics of low-temperature inorganic syntheses. *Journal of Solid State Chemistry* 111, 11–17.
- Sadat-Shojai, M., Khorasani, M.-T., Dinpanah-Khoshdargi, E., Jamshidi, A., 2013. Synthesis methods for nanosized hydroxyapatite with diverse structures. *Acta Biomaterialia* 9, 7591–7621.
- Santhanam, R., Rambabu, B., 2010. Research Progress in High Voltage Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Material. *Journal of Power Sources* 195, 5442–5451.
- Sato, K., Hriguchi, K., Nishikawa, T., *et al.*, 2015. Hydrothermal synthesis of yttria-stabilized zirconia nanocrystals with controlled yttria content. *Inorganic Chemistry* 54, 7976–7984.
- Sivaperumal, V.R., Mani, R., Nachiappan, M.S., Arumugam, K., 2017. Direct hydrothermal synthesis of hydroxyapatite/alumina nanocomposite. *Materials Characterization* 134, 416–421.
- Spina, G., Bonnefont, G., Palermo, P., *et al.*, 2012. Transparent YAG obtained by spark plasma sintering of co-precipitated powder. Influence of dispersion route and sintering parameters on optical and microstructural characteristics. *Journal of the European Ceramic Society* 32, 2957–2964.
- Suchanek, W.L., Riman, R.E., 2006. Hydrothermal synthesis of advanced ceramic powders. *Advances in Science and Technology* 45, 184–193.
- Tariq, M., Hanif, F., Ashraf, A., 2011. Overview of Nextel™ based structures for space applications. *Journal of Space Technology* 1, 88–94.
- Walton, R.I., 2020. Perovskite oxides prepared by hydrothermal and solvothermal synthesis: A review of crystallisation, chemistry, and compositions. *Chemistry – A European Journal* 26, 9041–9069.
- Wang, J., Chong, P.F., Ng, S.C., Gan, L.M., 1997. Microemulsion processing of manganese zinc ferrites. *Materials Letters* 30, 217–221.
- Wang, X., Zhuang, J., Peng, Q., Li, Y., 2006. Hydrothermal synthesis of rare-earth fluoride nanocrystals. *Inorganic Chemistry* 45, 6661–6665.
- Yan, B., Lei, F., 2010. Molten salt synthesis, characterization and luminescence of $\text{ZnWO}_4\text{Eu}^{3+}$ nanoparticles. *Journal of Alloys and Compounds* 507, 460–464.
- Zalite, I., Heidemane, G., Kuznetsova, L., Maiorov, M., 2015. Hydrothermal synthesis of cobalt ferrite nanosized powders. *IOP Conference Series: Materials Science and Engineering* 77, 012011.
- Zhang, H., Li, M., Zhou, Z., Shen, L., Bao, N., 2019. Microstructure and morphology control of potassium magnesium titanates and sodium iron titanates by molten salt synthesis. *Materials* 12, 1577.

Relevant Websites

www.SawyerLLC.com
 Sawyer Technical Materials.
http://www.coorstek.co.jp/eng/rd/detail_04.html
 Transparent Ceramics.

Self-Propagating High-Temperature Synthesis

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Introduction

The material presented in this chapter is assumed to be a basic lecture and it is addressed to those interested in materials and their technologies but not familiar with the SHS technique, especially for high school and university students as well as technologists working in industry. The text was prepared on the basis of the author's lectures for students of materials engineering, chemical technology and ceramics at the Faculty of Materials Science and Ceramics, AGH University of Science and Technology in Krakow, Poland. An advanced reader can find full information about SHS in numerous monographic studies, especially recently published "*Concise Encyclopedia of Self-Propagating High-Temperature Synthesis; History, Theory, technology and Products*" edited by Borovinskaya I.P., Gromov A.G., Levashov E.A., Maksimov Y.M., Mukasyan A.S., Rogachev A.S. and printed by Elsevier Inc. 2017 (Borovinskaya *et al.*, 2017) and a book written by Rogachev A.S. and Mukasyan A.S., "*Combustion for Material Synthesis*" published by CRC Press in 2014 (Rogachev and Mukasyan, 2014).

Basic Features of SHS

General Approach

SHS reactions join two important phenomena: (1) combustion occurring in the system due to an exothermic chemical reaction and (2) simultaneous/sequential formation of the final product. To describe the basic features of the SHS reaction from the combustion point of view, we can use a simple cybernetic scheme treating SHS as a thermal system (Figs. 1 and 2).

Let there be an exothermic reaction (I) which proceeds with the release of heat (II). The reaction is carried out in a thermal system consisting of an external heat source (III) supplying heat and a heat removal system (dissipating) (IV) (Lis, 1994).

If the rate of heat removal from the system is greater than the rate of heat transfer outside from the reaction, then the thermal conditions of the reaction are determined by the relationship between the heat supplied from the outside and the heat that is released and removed. Under thermal equilibrium, the reaction proceeds at a constant temperature. By controlling the outside temperature, we can control the course of the reaction, and so its speed, degree of conversion, etc. This is a typical case for most of the chemical reactions.

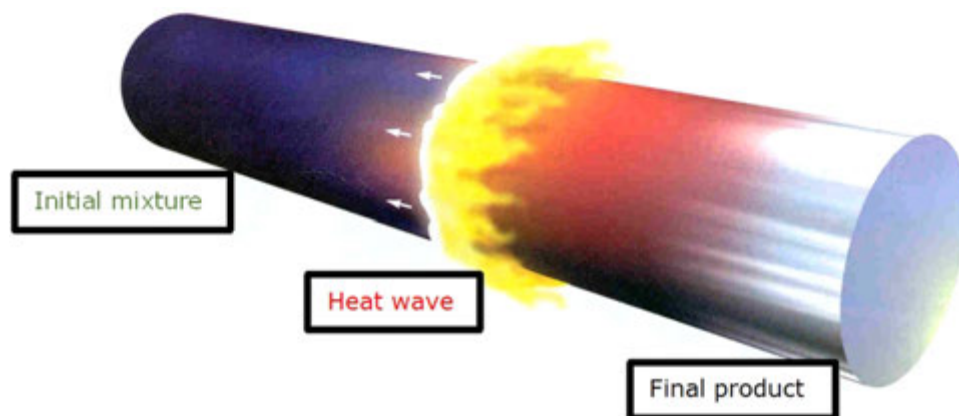


Fig. 1 A schematic picture of self-propagating high-temperature synthesis (SHS).

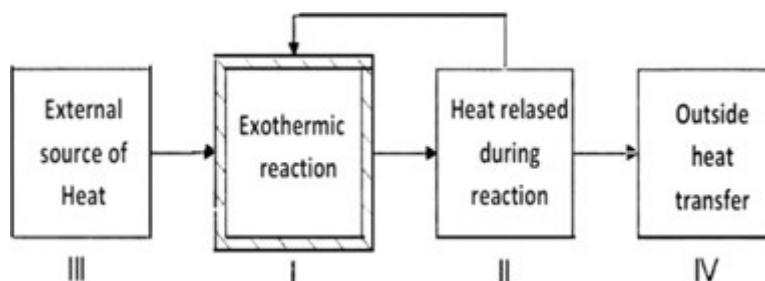


Fig. 2 The idea of SHS as a thermal system.

However, if the rate of internal heat generated is greater than the rate of heat dissipated, then the heat can be accumulated in the system causing a temperature increase. In the case of a thermally activated reaction, this increases the reaction rate and, consequently, further increases the rate of heat release. There is therefore positive feedback causing a gradual acceleration of the reaction rate. This moment is called “ignition”. The reaction continues until the raw substrates are completely worn out in the reacting system. The degree of positive feedback is determined by the dependence of the reaction rate on the temperature, which in the case of chemical reactions can be taken as the relationship of the Arrhenius type. The parameter controlling the process is reaction activation energy. The higher the activation energy, the greater the self-heating capacity of the system. At the same time, it is necessary for the reaction to proceed under conditions as close to adiabatic as possible.

A characteristic feature of the SHS reaction is the need for thermal initiation, i.e., ignition, for which an external heat source is used. Before the ignition, the process has a traditional character: it is slow and is controlled by heat supplied from an external source. From the moment of ignition, the combustion process runs rapidly and spontaneously and is practically not controlled by external factors (Fig. 3) (ISMAN, 2020, Munir, 2001).

Two different ignition techniques are possible to start combustion during the SHS, as illustrated schematically in Fig. 4. The first, more typical, case is if the SHS is initiated in one place of the reacting system by using of a high-temperature heat source, i.e., an igniter. As shown in Fig. 4(a), the reaction “ignites” when in contact with a high-temperature igniter and then the high-temperature reaction front is formed, propagating through the entire system. Different high-temperature heat emitters, like resistant wire, termite reaction, laser beam, etc., can be used as the “igniter”.

The second type of ignition is schematically shown in Fig. 4(b). With the use of an external heat source will bring the whole reacting system to a high temperature, which can lead to spontaneous ignition in the entire volume. Such a case is called “thermal explosion”. In each of the two described cases, the end result is a completely reacted system.

After ignition, the reaction spreads from the ignited site over the whole volume of the reaction system. This characteristic of self-propagation is recognized as the next most important and defining feature of the SHS reaction. The propagating reaction front has

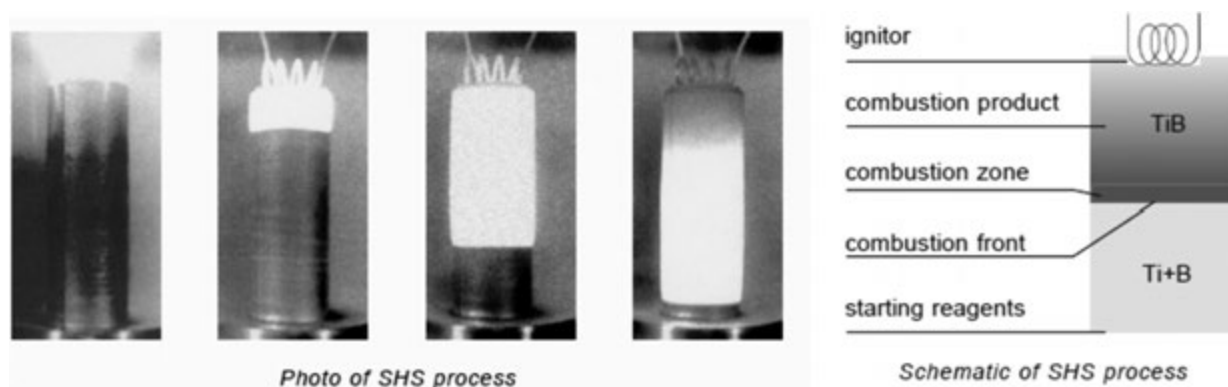


Fig. 3 The ignition and propagation of the reaction zone in the SHS process. Reproduced from (ISMAN 2020).

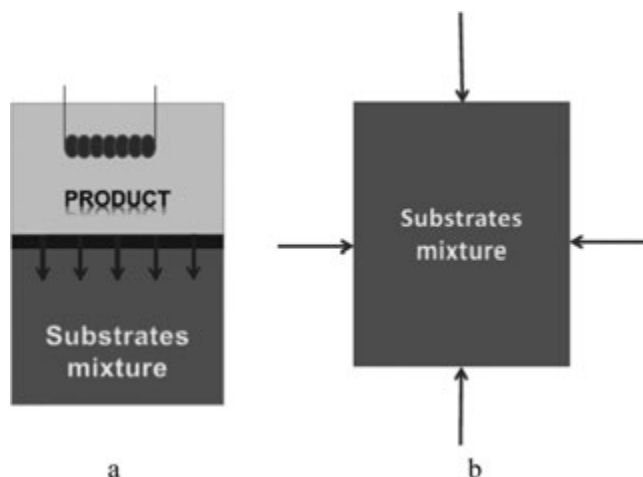


Fig. 4 The ignition types in SHS processes: (a) local ignition by a thermal igniter. (b) ignition in the volume of “thermal explosion”.

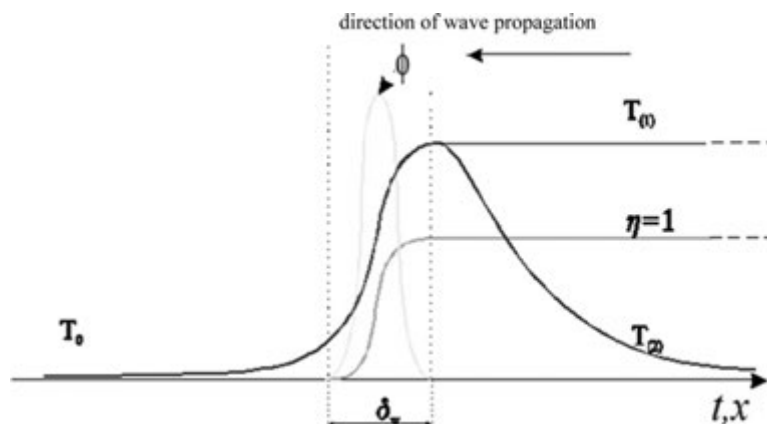


Fig. 5 A schematic image of the heat wave in the SHS process: (t, x) time/distance axis; T_0 – initial temperature; $T_{(1)}$ – maximum temperature; $T_{(2)}$ – reaction front real temperature; δ_w – width of the SHS propagating front, η – yield of the reaction; f – heat release rate.

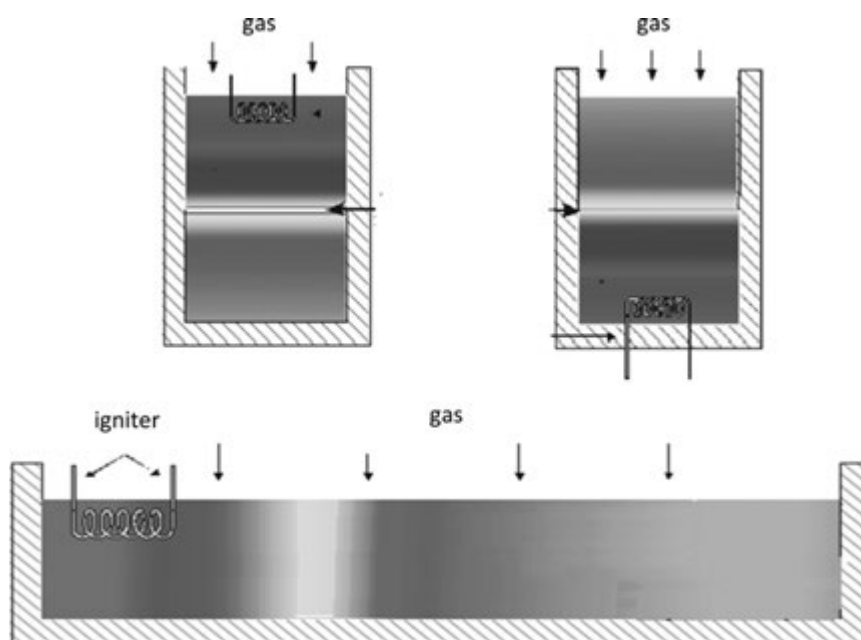


Fig. 6 The types of reactors in SHS with the participation of the gas phase, the so-called “filtration combustion”.

the character of a heat wave. A schematic picture of the reaction front is shown in [Fig. 5](#) ([Munir, 2001](#); [Merzhanov, 1990](#); [Merzhanov, 2005](#)).

The picture presents the profile of the temperature changes, the yield of conversion and the rate of heat release in the volume element of the system through which the reaction front passes. A characteristic feature for SHS processes is a narrow reaction zone, which practically has a dimension of the order of millimeters. At high rates of wave propagation, the process has a very intense nature with very high reaction rates, high temperatures, high temperature gradients and close to adiabatic nature. In real-world SHS processes, the reaction front propagation rates reach an additive, the temperature increase rates up to 100°C/s , and the temperatures rise up to 4000°C . At the same time, it is rather safe because the amount of heat emitted by the whole system in a unit of time is small.

The main task in implementing each SHS process is to ensure stable wave propagation. Wave parameters such as propagation speed, front width, maximum temperature and temperature distribution are determined by the physicochemical characteristics of the system and have a decisive impact on the resulting product. It should be noted that the conditions of “thermal explosion” can also be treated as a process in which heat wave propagation occurs, but the place of its initiation and the way of its course are more difficult to control.

A typical reaction system in the case of SHS is a mixture of powders in a solid state – “solid state combustion”. A combustion reaction with the participation of a gaseous reactant (oxygen, hydrogen or nitrogen) of the “filtration combustion” type is also

possible, which is schematically shown in Fig. 6. One solution in which one of the reactants is in a liquid state (“liquid combustion”) as well as a whole range of mixed systems are also possible.

In summary, it can be stated, that the SHS reaction can be carried out in a system in which a strongly exothermic chemical reaction takes place with high activation energy; the thermal conditions should ensure that the entire system or part of it is heated to the temperature at which the combustion type reaction will be initiated; the reaction front formed during combustion must be able to spread throughout the entire system, in addition it is preferred that the combustion takes place in an adiabatic-closed system.

Obtaining the Final Products by Structural Transformation

SHS technologies use the combustion effect to obtain a material, so the main problem is to learn and control the mechanism of structural transformation phenomena occurring in the system and causing the formation of the final product. There are two main mechanisms of the final product formation during the SHS process: equilibrium and nonequilibrium mechanisms (Maksimov, 2017).

For the equilibrium mechanism, the chemical changes of a green mixture in the combustion wave and the structure formation of a final product are considered to occur simultaneously. In this case, combustion and structure formation are strongly dependent on each other. The non-equilibrium mechanism corresponding to the condition describes a more complex structure and the processes can proceed one after the other. Here the combustion process does not directly influence the structure formation in the reaction products and the formation occurs far behind the front of the exothermic reaction. It can happen that the mechanism is mixed and the mechanism of combustion was equilibrium for one of the intermediate products and non-equilibrium for another product.

The study of the details of the reaction mechanism can be carried out using many techniques, also used in situ, such as: video recording, thermocouple measurement, thermography, XRD, SEM, TEM, neutronography, etc. (Rogachev and Mukasyan, 2017). A schematic diagram of the experimental SHS study in laboratory conditions is given in Fig. 7.

To learn and identify the mechanism of a reaction, the techniques of “freezing” the reaction front using different quenching techniques are very useful. They are followed by a *post-mortem* analysis of the microstructure of this area of the front including its chemical and phase composition. This allows the analysis of the phenomena occurring during SHS and the formation of the final product. Such phenomena are usually very complex and consist of, for example, parallel or sequential processes like chemical reactions occurring on contacts of grains, melting, evaporation, dissolution or crystallization phenomena.

An example of the complexity of the process is the mechanism identified by the authors which is close to those observed during the SHS preparation of SiC (Pampuch *et al.*, 1990; Pampuch *et al.*, 1991) during the SHS preparation of Ti_3SiC_2 , i.e., one of the so-called “MAX phases”, triple carbides with interesting properties (Barsoum and El-Raghy, 2000). This synthesis is possible (Lis *et al.*, 1993) by the SHS reaction in the $\text{Ti} + \text{Si} + \text{C}$ powder system according to the equation:



This process was carried out in the reactor whose diagram is shown in Fig. 8(a), and the temperature profile obtained as a result of the exothermic reaction is shown in Fig. 8(b). The self-heating of the system leads to a temperature in the reaction front up to a

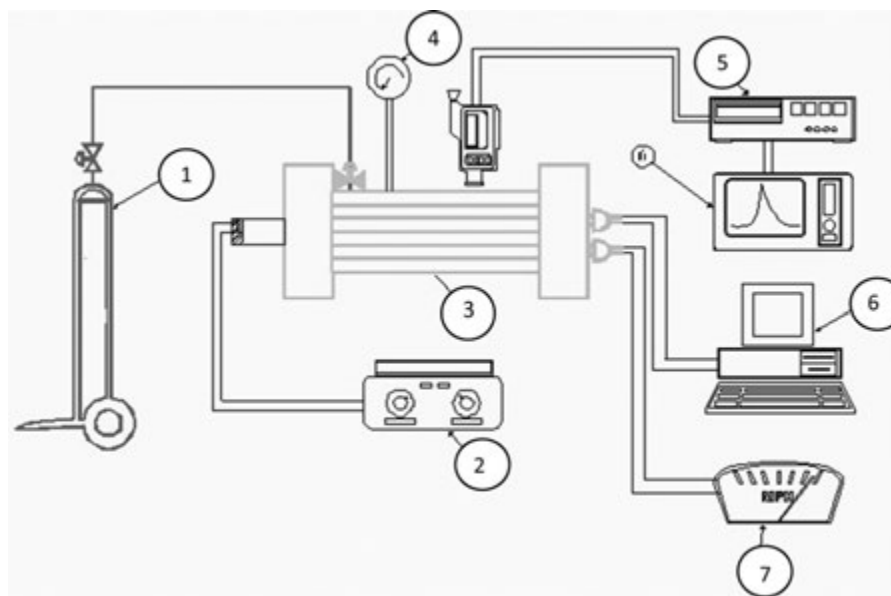


Fig. 7 A schematics of an SHS experimental system: (1) gas supply; (2) vacuum pump; (3) SHS reactor; (4) pressure measuring; (5) video recording; (6) thermocouple with temperature recording; (7) igniter supply.

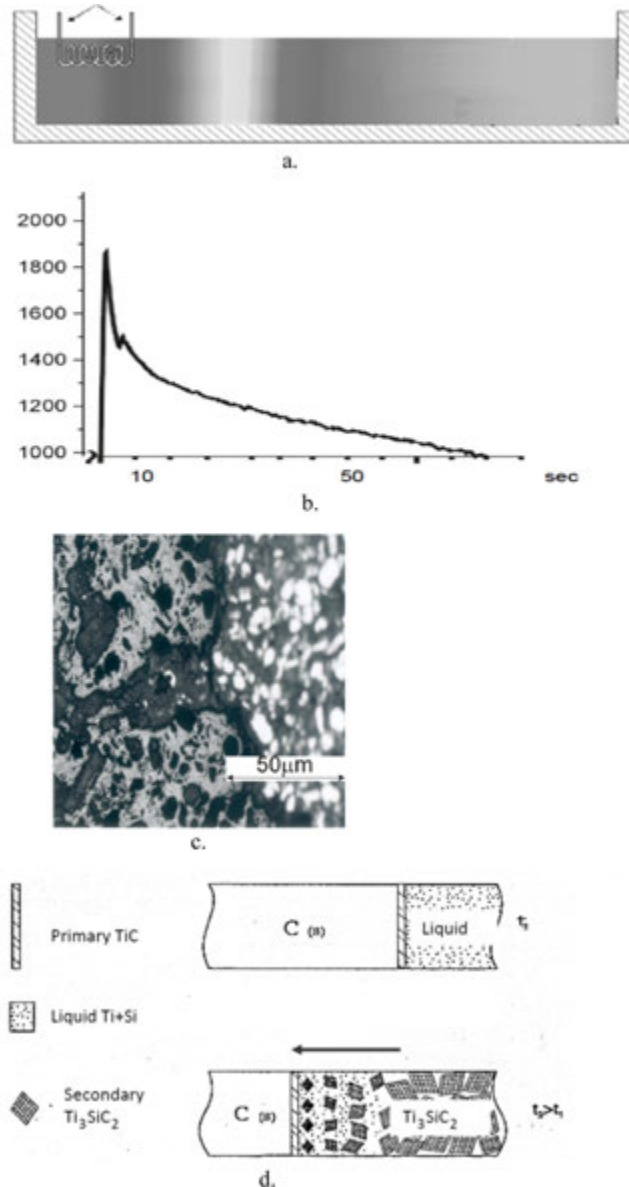


Fig. 8 The SHS synthesis of Ti_3SiC_2 ; (a) using an SHS reactor; (b) the measured temperature profile; (c) a SEM picture of the frozen SHS propagating front; (d) the identified SHS mechanism.

level of 1800°C. The cross section of the frozen reaction front is shown in Fig. 8(c). The analysis of the phenomena occurring in the course of the reaction led to the identification of the reaction mechanism. It was detected, that SHS starts with a primary reaction between Ti + C particles which rapidly increase the temperature in the front. Then metallic reactants melt rapidly and form a Ti–Si liquid which dissolves the carbon. The formation of the SHS Ti_3SiC_2 product occurs by crystallization from the molten alloys. Ti_3SiC_2 + TiC mixture is found in the final SHS product. It is shown in Fig. 8(d). By controlling the SHS parameters, the optimum conditions for a formation product with more than 95% of Ti_3SiC_2 in the product with the rest of TiC can be achieved.

SHS Classification

The SHS system is a broad concept encompassing various synthesis techniques but having common characteristics as combustion. Different SHS phenomena can be classified taking into account various process features, for example with regard to (ISMAN, 2020):

- Method of ignition (thermal explosion, local ignition, mixing method).
- Reagent type (solid phase combustion, gas + solid phase combustion, liquid phase combustion, mixed combustion).

- Chemical reaction type (synthesis from elements according to the scheme: $A + B = AB$, exchange reactions: $AB + C = A + BC$ (e.g., thermite reactions), synthesis from compounds: $AB + CD = ABCD$, decomposition reactions: $AB = A + B$, etc.).
- Type of the obtained compounds (carbides, nitrides, oxides, borides, composites, ...).
- Type of the resulting product: (powders, sintered porous matter, dense polycrystals, layers, single crystals).
- Way of carrying out the process (free combustion, SHS + hot pressing, SHS + isostatic hot pressing, SHS + centrifugal forces, SHS + SPS, SHS + laser synthesis etc.).
- Ignition method (membrane heating, resistance spirals, electric arc, laser, chemical igniter, detonation energy).
- Nature of wave propagation: (stationary, oscillating, spin, spontaneous).
- Products application (alloys, structure ceramics, functional ceramics, refractories, abrasives, biomaterials, ...).

Modeling of SHS

Due to the very well-developed mathematical apparatus enabling the description of physicochemical phenomena occurring during SHS, there are many possibilities for their simulation and modeling. Such works were the basis of the initial research on SHS and are currently being developed, in particular thanks to the development of computer techniques. Modeling allows, among other things, to determine the potential possibility of a process in the SHS mode, the nature and conditions of ignition, the thermal waveform including the temperature and time changes, the nature and stability of combustion, etc. With the development of knowledge about physicochemical phenomena occurring during combustion, these models in addition to the phenomenological approach increasingly more frequently take into account such processes as chemical reactions and their sequence, evaporation, melting and dissolution, gas filtration and transport, crystallization and recrystallization or sintering. There are many works in this area summarized in the encyclopedic literature (Borovinskaya *et al.*, 2017; Rogachev and Mukasyan, 2014).

For applications of the models in the design of material technologies, three basic approaches are presented:

- (1) Determination of the “adiabatic temperature”, i.e., the maximum temperature to which the SHS system can heat up,
- (2) Models of the “thermal ignition” type of SHS,
- (3) Models of the self-propagating SHS “thermal wave”.

Adiabatic Temperature of SHS

The simplest model analysis of the SHS phenomenon can be the calculation of the reaction temperature based on the thermochemical approach. This type of analysis allows to determine the potential possibilities of the system to achieve high temperatures by self-heating and, at the same time, allows to analyze the influence of some parameters on this course. The analysis of the model temperature course in the SHS reaction can be carried out by means of thermochemical calculations starting from the balance of the heat released and absorbed in the system, assuming the adiabatic nature of the process (Lis, 1994).

The SHS-type exothermic chemical reaction begins at T_0 . If we assume adiabatic conditions, due to the self-heating of the system, the temperature of the system gradually increases. The amount of the heat released from the beginning of the reaction can be presented by the following Eq. (2):

$$Q_1^T = \int_{x=0}^x |\Delta H_T^r| dx \quad (2)$$

where:

x – the degree of reaction over time t at temperature T ,

ΔH_T^r – change in reaction enthalpy at temperature T .

If the process is adiabatic, the heat is completely absorbed by the system and heated to the temperature T of the whole system, i.e., substrates, products and possibly inert substances, as well as covers the endothermic phenomena that can occur during the process, such as melting, phase transformations, etc. The total heat absorbed in the system until (x, T) is equal to:

$$Q_2^T = \int_{x=0}^x \int_{T=T_0}^T \left(\sum_i n_i c_{pi} + \sum_k \int_{l=0}^l [\Delta H_k^m] dl \right) dT dx \quad (3)$$

where:

c_{pi} – molar heat of the i -th component,

n_i – the amount of moles of the i -th component,

ΔH_k^m – enthalpy of melting (transformation) of the k -th component,

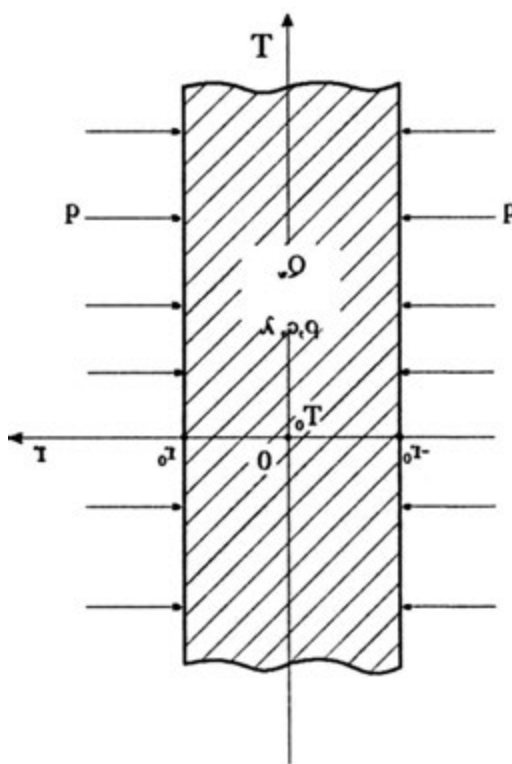
l – the degree of melting (transformation) of the k -th component at the moment (x, T) .

Assuming that at the temperature T :

$$Q_1^T = Q_2^T \quad (4)$$

Table 1 Adiabatic temperatures of selected chemical reactions

SHS reaction	Adiabatic temperature $T_o = 25^\circ\text{C}$
$\text{Si} + \text{C} = \text{SiC}$	1690
$\text{Si} + 4\text{B} = \text{B}_4\text{C}$	980
$\text{Ti} + \text{C} = \text{TiC}$	3020
$\text{Ti} + 2\text{B} = \text{TiB}_2$	3150
$\text{Ti} + 2\text{Si} = \text{TiSi}_2$	1690
$\text{Ti} + \text{Si} = \text{TiSi}$	1720
$3\text{Si} + 2\text{N}_2 = \text{S}_3\text{N}_4$	4980
$\text{Al} + 1/2\text{N}_2 = \text{AlN}$	2900
$3\text{Ti} + \text{B}_4\text{C} = \text{TiC} + 2\text{TiB}_2$	2680
$4\text{Si} + \text{C} + 2\text{N}_2 = \text{SiC} + \text{S}_3\text{N}_4$	2850
$3\text{Ti} + \text{Si} + 2\text{C} = \text{T}_3\text{SiC}_2$	1930

**Fig. 9** A model schema for the thermal explosion mode of SHS.

and knowing all thermodynamic data, we can calculate the relationship between x , T and l at a given stage of reaction. If the system has reacted completely, i.e., $x=1$ and $l=1$, we can calculate the maximum attained temperature T of the system called the “adiabatic temperature T_a ”.

Selected results of such calculations are presented in [Table 1](#).

SHS Reaction in the “Thermal Explosion” Mode

Thermal explosion models can be derived from the analysis of combustion phenomena and can be used for SHS reactions initiated both by the method of thermal explosion and under self-propagation conditions. The analysis usually starts with a very simplified geometric model of the system, such as the one presented in [Fig. 9](#) ([Lis, 1994](#)).

The basic geometry is usually taken as an infinite cylinder with a radius r_0 . It is assumed that the system is homogeneous and has a density ρ , specific heat δ and thermal conductivity of λ , and is held at an initial temperature T_o .

The system is exposed to an external heat source under the assumed heating conditions, as well as to heat transfer with the environment (p). The thermal behavior of the model in these conditions can be described based on the Fourier equation type (5).

We assume that the system heats up as a result of heat release from the exothermic chemical reaction Q_w (Eqs. (6) and (7)) and by means of other internal heat sources. In general, this gives the heat balance of the equation type (8).

$$c\rho \frac{\partial T}{\partial t} = \lambda \nabla^2 T \quad (5)$$

$$Q_w = k(T, \eta) \quad (6)$$

$$\frac{\partial \eta}{\partial t} = k(T, \lambda) = k_0(1 - \lambda)^n = \exp\left(-\frac{E}{RT}\right) \quad (7)$$

$$c\rho \frac{\partial T}{\partial t} = \lambda \nabla^2 T + Qk(T, \eta) + f(t) \quad (8)$$

where:

T – temperature, c – specific heat, ρ – density, t – time, k – chemical reaction rate, η – reaction progress rate, Q reaction heat, $f(t)$ efficiency of internal non-chemical heat sources, k_0 – pre-exponential factor, n – reaction order, E – activation energy.

By solving the above system, assuming specific initial and boundary conditions, it is possible to simulate most cases of the macroscopic behavior of systems in which SHS occurs. Typical solutions look for relationships describing the temperature changes and the degree of reaction progress as a function of time. The system of the above equations has no analytical solution, but many numerical solutions or simplified analytical methods are used.

As an example of the description of the behavior of the system in the method of thermal explosion, let us give a model developed by the author and used to describe the SHS reaction of obtaining silicon carbide by synthesis from elements (Lis, 1994). The theoretical calculation is presented in Fig. 10 and, for comparison, the actual measured temperatures obtained during the SHS synthesis of SiC powders using the “thermal explosion” mode are presented in Fig. 11.

SHS “Thermal Wave” Modeling

Heat wave models are derived in many studies on the propagation of flames in burning gases (Borovinskaya *et al.*, 2017; Zeldovich, 1948). In the combustion process in a homogeneous system, a stationary wave propagates at a velocity u described by the general equation type (9). This wave is the result of an exothermic chemical reaction occurring in the system, whose thermal efficiency W can be determined by the relationship (9):

$$u = A(T, \eta) \exp\left(-\frac{E}{RT}\right) \quad (9)$$

where:

u – velocity of combustion front, T – temperature, η – degree of reaction conversion at temperature T , A – parameter dependent on T and η , E – activation energy, R – gas constant.

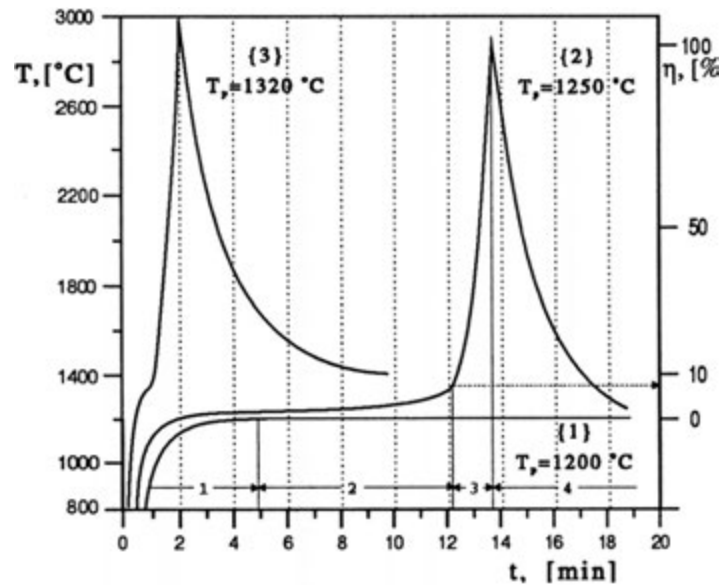


Fig. 10 The theoretical combustion temperatures in the Si + C system ignited by “thermal explosion”.

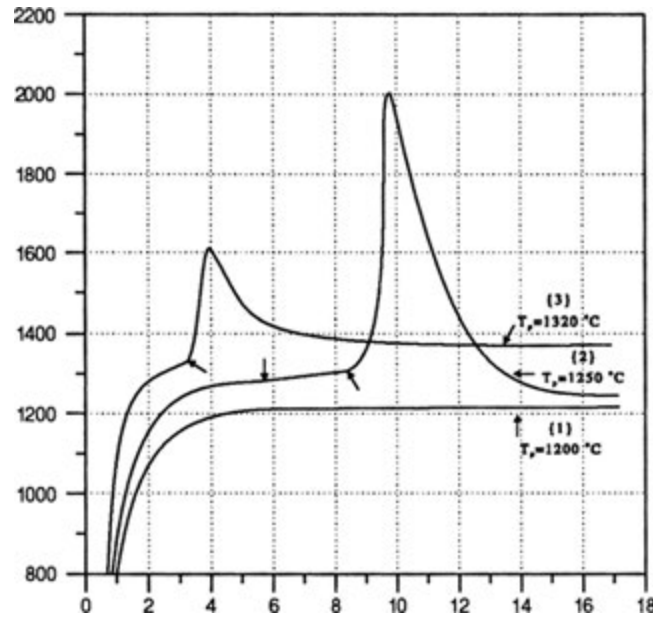


Fig. 11 The experimental measured combustion temperatures in an Si + C system ignited by “thermal explosion”.

This wave is the result of an exothermic chemical reaction occurring in the system, whose thermal efficiency W can be determined by the relationship (10), where n is a concentration of substance:

$$W = Qnpk_0 \exp\left(-\frac{E}{RT}\right) \quad (10)$$

If a reference system moving with a reaction front is adopted, such a process can be described by the equations:

$$\lambda \nabla^2 T - c\rho u \nabla T + Qnpk_0 \exp\left(-\frac{E}{RT}\right) = 0 \quad (11)$$

$$D \nabla^2 n - u \nabla n - k_0 n \exp\left(-\frac{E}{RT}\right) = 0 \quad (12)$$

Depending on the of the adopted procedure, the above system has several forms of solutions (Borovinskaya *et al.*, 2017; Maksomov *et al.*, 1984; Degreve *et al.*, 1987), so numerical methods are commonly used to solve it. The functions of temperature distribution are obtained, which take simple form as in Fig. 4 or more complex profiles (Merzhanov, 1990).

By solving the system of equations analytically, a relationship describing the speed of heat wave propagation can be obtained, e.g., for a one-dimensional medium it has the form of (Khakin and Merzchanov, 1966):

$$u^2 = f(n) \left(\frac{ck}{\rho}\right) \left(\frac{RT^2}{E}\right) k_0 \exp\left(-\frac{E}{RT}\right) \quad (13)$$

One of the basic theoretical problems for SHS is the determination conditions of heat wave propagation stability (Bayliss and Matkowsky, 1990). The propagation of the wave can: (1) take place in stationary conditions with a constant speed, (2) be of the oscillatory type with different oscillation frequencies, whereby the oscillations may be of a pulsating or spin nature, (3) be unstable of the dying type.

Analytical work determines such cases, depending on the adopted models and process parameters. Newly developed works in this field introduce additional parameters to models such as more complex geometric shapes, various equations describing reaction kinetics, complex thermal conditions, etc. What is particularly interesting are the solutions departing from the assumption of homogeneity of the system and introducing elements of the actual structure of the system to models such as system dispersion, melting, evaporation or crystallization phenomena. The theoretical simulations are verified in practical SHS experiments, which allows the possibility of checking the SHS models and improving the SHS process control.

SHS State of the Art

Starting a brief review of the history of the SHS development, it should be stated that SHS techniques are based on violent exothermic chemical reactions, the most spectacular example of which are explosive reactions. The history of the development of

explosives begins in ancient China around 2000 BCE with the invention of gunpowder, leads through nitroglycerin, TNT and ends with fusion reactions (Anderson, 1989).

SHS reactions, however, have more in common with less violent combustion-like phenomena. In the combustion process itself, the theoretical foundations of SHS can be found. The theories of combustion, especially the combustion of homogeneous systems (gaseous fuels), were developed based on the fundamental works of Zeldovich, Siemionov and Frank-Kameniecki (Degreve *et al.*, 1987; Zeldovich and Frank-Kameniecki, 1938; Semionov, 1961) from the 1930s. They were continued in the works on the combustion of condensed systems in Russia (Novoshilov, 1962), from which Merzhanov work on the theory of solids combustion (Merzhanov, 1990) and the thermal wave theory originated. These works focused on the analysis of the thermal effects of processes were based on a phenomenological approach and mainly concerned mathematical modeling.

In the cited fundamental work by Merzhanov *et al.* (1967), for the first time attention was drawn not to the use of heat or light from the combustion process but to the waste product ("ash") resulting from combustion. It was shown that the compounds formed during combustion can be treated as the final product of the process.

It should be noted, however, that this approach involving the use of the effect of the exothermic reaction and the phenomenon of self-propagation in chemical synthesis processes is found in the chemical literature of the nineteenth century. The review of these works was carried out by Hlavacek (1991). First at all, we should consider the nineteenth-century works of Berzelius (1825) and Moissan (1979) in which the preparation of oxides and nitrides by methods of metal combustion in gases was described. However, the historical creator of the combustion method of material synthesis was in fact Goldschmidt (Goldschmidt, 1895), who in 1895 for the first time described the so-called aluminothermy method, which consists in obtaining metals or alloys by reducing their oxides with the help of powder metallic aluminum. He characterized the phenomenon of self-propagation occurring in this case in condensed systems, based on the fact that after initiating the reaction in one place, it propagated spontaneously throughout the entire system. The temperatures achieved by the self-heating of the reacting substances were very high, i.e., on the order of 3000°C. The aluminum-thermic and similar magnesia-thermal methods in various variants were used in chemical technology and technique (incendiary substances, photography). Other exothermic reactions occurring in condensed systems described in the literature were the reactions of metals with sulfur and phosphorus studied in France (Fonze-Diacon, 1900). The work on obtaining hydrides by burning metals in hydrogen conducted in Germany (Kellenberg and Kraft, 1902) and the United States (Alexander, 1941) should also be mentioned here. The use of exothermic reactions as heat sources in the processes of obtaining materials was proposed for applying ceramic layers, in processes of the type of chemical hot-pressing, reaction-pressing or in various so-called variants chemical ovens.

The undeniable merit of Russian scientists (Merzhanov, Borovinskaya and others) was combining the rich scientific achievements of the theoretical direction of the study of combustion phenomena with the formation of structure products. It should be noted that in the 1980s SHS technologies were recognized as one of the priority achievements of the Soviet Union materials science, which was demonstrated by allocating corresponding funds for the synthesis of materials by SHS. They are mainly concentrated at the Institute of Structural Macrokinetics and Materials Science of the Russian Academy of Sciences (ISMAN) in Chernogolovka near Moscow (ISMAN, 2020). The main research was concentrated on synthesis of: refractory borides, nitrides and carbides (Borovinskaya, Mukasyan, Amosov, Prokudina, Levashov), casting alloys (Sanin, Yukhvid), ceramic-metal and ceramic-ceramic composites (Amosov, Levashov), MAX phases (Rogachev, Sytchev), complex oxides (Balashov, Barinova), organic materials (Klimchuk), and others materials.

The research centers founded in the former Soviet Union are still the leading research centers in the field of SHS globally. Since the collapse of the Soviet Union, the following SHS centers have remained active in Russia, namely: Institute of Structural Macrokinetics and Materials Science, ISMAN RAS; National University of Science and Technology MISIS Moscow, The Scientific-Educational Center of SHS; Tomsk Scientific Center of RAS and Samara State Technical University. SHS is also very explored in Armenia (Kharatyan, 2017), Kazakhstan (Ksandopulo *et al.*, 2017), Belorussia (Khina, 2017), and Georgia (Onashvili, 2017). A detailed description of the achievements in this area can be found on the ISMAN web-page (ISMAN, 2020), where information about appropriate monographs (Merzhanov, 2005) and others are available.

The information on SHS in the USA can be found in the review by Puszynski (2017). In the United States, the first reported research utilizing the self-sustaining character of thermite condensed-phase reactions was conducted by Walton and Poulos (1959) in the mid- and late-1950s. More significant research efforts were undertaken in the United States from the early 1980s. In 1982, McCauley *et al.* (1982) and Holt and Kingman (1982) published new results in the area of combustion synthesis, which generated interest at several universities and US government laboratories. The scope of research in American centers covers a whole range of problems in the field of SHS, from basic model considerations to technological studies. In the field of modeling, the works of Matkowsky (Bayliss and Matkowsky, 1990) and the group led by Hlavacek and Puszynski (Degreve *et al.*, 1987) deserve to be emphasized. In California (Los Alamos, Davis), the work led by Holt and Munir is focused on nitride systems with emphasis on studying nitriding phenomena and process mechanisms (Munir, 1993). Nitride systems are also studied at SUNY Buffalo, where the focus is on using SHS to obtain powders and ceramic products on an industrial scale (Hlavacek, Puszynski, Majorowski, Agrafiotis, Lis) (Agrafiotis *et al.*, 1990). These works are currently being continued and developed by Puszynski at the School of Mines and Technology, S. Dakota. A strong research center for SHS was established at the University of Alfred in 1989, which brought together scholars from other centers (Spriggs, McCauley, Stangle). Other significant centers in this field include the University of Notre Dame (Varma, Mukasyan), the University of Texas, Brausville (Rogahov), Anny Materials Research Lab, Watertown (McCauley, Croft); RPI, Troye (German); Ceramtec, Saint Lake City (Cutler); General Sc. Inc. (Rilcy); ART Buffalo (Blakely) and others.

Japanese research activities on the SHS process were started in 1979 by research and development studies on ceramic linings with thermite reactions performed inside a centrifuged hollow pipe (centrifugalthermite process). The Japanese SHS-oriented investigations accelerated in 1982 under the influence of J.F. Crider's review paper published in *Ceramic Engineering and Science Proceedings* (Crider, 1982). The works on SHS in Japan have been conducted since 1984 in several centers. The most interesting research seems to be carried out at Osaka University on the synthesis of nitride powders (Hirao *et al.*, 1987a) and the synthesis of materials using an original technique combining SHS synthesis, "chemical furnace" and hot isostatic pressing (SHS-HIP) (Miyamoto) (Lis *et al.*, 1995). The latter solution allows obtaining dense materials such as TiB₂, TiC, SiC and composites in one technological cycle. The next achievement in this field is the successful application of this method to obtaining the so-called "functionally gradient materials" (FGM), which are layered materials with a continuous transition from metal to ceramics (Koizumi, Miyamoto). The Japan Research Association of Combustion Synthesis (ORACS) was established in 1987 with members from 5 universities, 4 national laboratories, and 29 industries. For the Japanese achievements in SHS, see the review prepared by Odawara (2017).

Apart from Japanese works, several centers in Asia are involved in working on SHS, mainly in China, Turkey, South Korea, India and Taiwan. The SHS research in China began in the late 1980s at Wuhan University and the Beijing University of Science and Technology. In WUT (Fu), the main research directions are SHS-based fast synthesis and sintering materials, and SHS for thermoelectric materials. At the Beijing University of Science and Technology (Ge), the main specialization is SHS FGM for tube coatings, and the combination of sol-gel and SHS. At the Harbin Institute of Technology, the research activity is focused on SHS for high-temperature multiphase ceramics. SHS is also developed in Shijiazhuang Mechanical Engineering College, Technical Institute of Physics and Chemistry. More detailed information can be found in the Fu review (Fu, 2017).

The beginning of metallothermic reduction-based studies in Turkey was a result of studies on the carbothermal synthesis of advanced ceramics (e.g., B₄C) and ferroalloys (e.g., FeB) at Istanbul Technical University (ITU) in the late 1980s. In the SHS field, the first study was on the determination of the optimum SHS parameters for the synthesis of TiB₂ in 2004. Many SHS studies have been conducted at ITU concerning the SHS of borides and carbides, such as TiB₂, B₄C, and ZrB₂, and the metallothermic reduction of iron and its alloys, such as carbon-free Cr-Ni-Mo-Ti-containing alloys and shape memory alloys. Middle East Technical University (METU) in Turkey has also contributed to the literature on volume combustion synthesis (VCS) (Yucel review (Yucel, 2017)).

SHS processes were introduced in Korea in the early 1995. A number of universities and organizations were involved in the research activity focused on the production of various compact and porous inorganic materials. The list of organizations involved in the SHS activity and their main fields of interest is as follows (Nersisyan *et al.*, 2017): Chungnam National University (nanostructured materials and LED phosphor powders), Korea Institute of Machinery & Materials (porous MoSi₂), Korean Atomic Energy Research Institute (TiC, SiC, and ZrC powders and C/SiC/C multilayer composite), Chonbuk National University (Mo-Si-SiC composite), Ulsan University (porous TiNi alloy), Hong Ik University (MoSi₂ and AlN); Pusan National University (AlN and ZrB₂), the Korea Institute of Geoscience and Mineral Resources (AlN powder), Changwon National University (SiAlON), Hanbat University (MoSi₂, SiO₂), Kyungnam University (TiC, SiC, WC, and composites), Sun-Moon University (TiC nanofibers) and Dong-A University (Ba-Zn ferrites).

The SHS methods are spreading in Europe, mainly in Italy, France, Spain, Poland Greece and Israel. The scientific output of the seven research groups that have been active in Italy over the past 20 years cover diverse classical topics in SHS, i.e., the combustion theory and modeling, structural macrokinetics and the synthesis of ceramics, intermetallics and composites. The main centers are: the University of Cagliari (Cao, Orru) (the SHS and field-activated combustion synthesis processes or their combination with ball milling or mechanical activation to synthesize various materials), the University Of Genoa (Ferretti) (combustion synthesis of various metal nitrides), National Research Council Ieni, Milan, Ing. (Zanotti) (SHS of Ti-Al, Ti-Ni and functionally graded materials (FGM)), the University of Pavia (Anselmi Tamburini) (SHS of various systems such as Ni-Al foils, Y₂O₃-ZrO₂, Ni/YSZ, ZrO₂, Zr-Si, Fe-ZrO₂, Cr-Si, metastable solid solutions, Ta-Si, Ti-Si, Co-Al, Nb-Al, metal-metal oxides, Ti-Al, Ti-Ni, and FGM) and the University of Sassari (Copcco, Mariani) (combustion of dioxins, herbicides, and hexachlorobenzene). A review of the Italian SHS activity was presented by Cao and Orru (2017).

In France, the major scientific SHS center is the University of Bourgogne in Dijon (Bernard). What is very interesting are in situ simultaneous infrared and time-resolved X-ray diffraction measurements conducted in order to study the self-sustained reactions. The other research included: (1) heat generation where the SHS reaction is used to generate heat as a "chemical oven"; (2) SHS of composites such as the dense NiAl-ZrO₂ composite, which can be produced by combining thermal explosion with a post thermal cycle and dense MoSi₂-Al₂O₃-based functionally graded materials (FGM) with different alumina contents, (3) repairing and coatings used to simultaneously repair and coat the Ni-based superalloy and (4) production of fully dense nano-intermetallics by reactive sintering in an SPS machine, testing of mechanical properties of the MAX phases prepared by SHS (Kozak *et al.*, 2019). More details can be found in the Bernard review (Bernard, 2017).

In Spain, the research on SHS began in 1991 with a joint project of ISMAN, Russia, United Technologies Corp. (UTC), and Tecnologia del Grupo INI (TGI, INI group). The Institute of Ceramics and Glass IGV-CSIC (Bernard) and the INASMET Technology Center also collaborated in this project as support centers. The aim was to produce a pilot plant for the production of powders by SHS: Si₃N₄, AlN, TiC, and Cr₂C. The goal was successfully accomplished and led to the creation of SHS Ceramics, S. A., the first Spanish company to obtain raw SHS materials. Currently, the work on combustion synthesis is ongoing in several new different directions, including field-assisted combustion synthesis and solution combustion synthesis. The obtained materials were meant for use in different fields, i.e., for structural applications, functional applications, and biomaterials. More details are contained in the review by Rodrigues (2017).

SHS was introduced to Poland in the 1970s at the AGH – University of Science and Technology, Faculty of Materials Science and Ceramics, in Kraków by Pampuch *et al.* (1989). A majority of their works confirmed the applicability of SHS to the preparation

of sinterable non-oxide ceramic powders like SiC, B₄C, Si₃N₄, Sialons, Alons, MAXs, etc. The aim of the AGH-UST work was to prepare single-phase sintered polycrystals as well as multiphase ceramic composite materials from SHS derived powders. Dense polycrystals with interesting properties were synthesized for materials in numerous explored systems: Si–C–B, Si–C–N, Si–Al–O–N, Si–Al–N–C, Al–O–N, Ti–B–C, Ti–Si–C, Ti–Si, Ti–Al–C, Ti–Si–C–N and Ti–Al–C–N. The second SHS research effort took place at the Center of High Pressures UNIPRESS of the Polish Academy of Sciences in Warsaw (Skibaska). These investigations, performed from the 1980s, were focused on the preparation of silicon nitride powders by the SHS method. The next research line opened at the Laboratory of Nanomaterials Physics and Chemistry. The Department of Chemistry, Warsaw University (WU) (Huczko) has conducted studies on SHS and solution combustion synthesis (SCS) applications, including the discovery of SHS of SiC nanofibers. The work on the application of combustion effects and explosive phenomena to the synthesis of materials is a subject of research at the Faculty of Advanced Technology and Chemistry, the Military University of Technology (WAT), in Warsaw (Cudziło, Jużwik). More details are available in the review by Lis (2017).

There is extensive factual literature on the work on SHS. The following works, besides the cited ones (Borovinskaya *et al.*, 2017; Rogachev and Mukasyan, 2014), can be recommended as the most important studies in this field: (Pampuch and Stobierski, 1991; McCauley, 1990; Merzchanov, 1990; ISMAN, 2020).

Review of the Materials Prepared Using the SHS Methods

The advantage of SHS as a technique for obtaining materials that is often brought to the fore is its energy-saving nature. The maximum use of the heat of internal exothermic reactions allows to save approx. 50%–98% of the total energy necessary for synthesis (Borovinskaya, 2017). As regards this aspect, the SHS reactions can be classified into the most energetic explosive reactions and typical ceramic technology processes, such as sintering, which require the supply of large amounts of energy (Pampuch *et al.*, 1993).

The attractiveness of SHS techniques for the production of different materials, however, primarily results from a large variety of obtainable compounds and material forms. Examples of chemical compounds obtained by the SHS techniques presented in the literature are summarized in Table 2. The presented list contains more than 200 compounds and is still open. An analysis of the literature indicates that currently the list of various materials obtained using SHS far exceeds 1000 examples. The amount of compounds synthesized by SHS is still being expanded, especially by increasingly complex multiphase materials.

In the SHS method, chemical compounds can be obtained as materials in various forms, depending on the type of material and the SHS technique used. One of the possible classifications of materials obtained by the SHS method is as follows:

(1) Powders

The basic SHS process of the free combustion method produces materials in the form of powders. The SHS powder products are in more or less agglomerated form with different chemical purity. They usually require further processing, such

Table 2 A list of chemical compounds obtained by self-developing high-temperature SHS synthesis methods

Groups of materials	Compounds prepared by SHS
Carbides	TiC, SiC, ZrC, TaC, NbC, WC, B ₄ C, HfC, Cr ₃ C ₂ , Mo ₂ C, SiC–B ₄ C, TiC–WC, W–Fe–C, TiC–Cr ₃ C ₂ , TiC–Mo ₂ C, Ti ₃ SiC ₂ , TiAl ₂ C
Borides	TiB, TiB ₂ , ZrB ₂ , NbB ₂ , TaB ₂ , CoB, HfB ₂ , V ₃ B ₂ , VB, VB ₂ , CrB, CrB ₂ , MoB, MoB ₂ , Mo ₂ B, Mo ₂ B ₅ , WB, W ₂ B, MoB ₄ , HfB ₂ , WB ₄ , ZrB ₂ –CrB ₂ , NiB, FeB, LaB ₆ , TiB ₂ –CrB ₂
Nitrides	Si ₃ N ₄ , α, β, γ sialons, AlN, TiN, TaN, ZrN, NbN, HfN, VN, BN, NbN, LaN, ScN, ErN, PrN, NdN, SmN, GdN, DyN, TbN, Si ₃ N ₄ –AlN, TiN–AlN
Silicides	MoSi ₂ , MoSi, Ti ₅ Si ₃ , ZrSi, TiSi ₂ , VSi, NbSi ₂ , TaSi ₂
Intermetallics	TiAl, ZrAl, NiAl, Ni ₃ Al, Ni ₂ Al ₃ , NdAl, CuAl, TiFe, TiNi, TiCo, VAl, NbGe, Nb ₃ Al, TiNi, WAl, ZrPT ₃
Hydrides	TiH ₂ , ZrH ₂ , NbH ₂ , SeH ₂ , VH ₂ , VH ₃ , LaH ₂ , PrH ₂ , NdH ₂ , SmH ₂ , SmH ₃ , GdH ₂ , TbH ₂ , TbH ₃ , DyH ₂ , DyH ₃ , MoH ₂ , MoH ₃ , TiZrH ₂ , ZrCoH ₃ , ZrCoH ₅ , ZrNbH ₅ , TiCoH ₃
Sulphides	WS ₂ , MoS ₂ , TaS ₂ , NbS ₂ , La ₂ S ₃ , WNbS ₂ , LaTaS ₃ , LaNbS ₃ , PrNbS ₃ , NbNdS ₃ , TbNbS ₃ , DyNbS ₃ , YNbS ₃ , PrTaS ₃ , NdTaS ₃ , TbTaS ₃ , DyTaS ₃ , ErTaS ₃ , EuTaS ₂ , EuNbS ₂ , MoS ₂ , MoS ₂
Selenides	WSe ₂ , MoSe ₂ , TaSe ₂ , NbSe ₂ , WNbSe ₂ , MoNiSe ₂
Phosphides	AlP, CuP, NbP, FeP, MnP, TiP, CrP, Co ₂ P, Fe–Mo–P, Fe–Mn–P
Oxides	BaTiO ₃ , PbTiO ₃ , PbZrO ₃ , BaZrO ₃ , YAlO ₃ , LiTaO ₃ , MrAl ₂ O ₄ , NaTaO ₃ , KTaO ₃ , BaNaTa ₅ O ₁₅ , Bi ₄ V ₄ O ₁₁ , Bi ₄ Fe ₂ O ₃ , Bi ₄ Ti ₃ O ₁₂ , Bi ₃ TiNbO ₉ , Bi ₃ TiTaO ₉ , BaBiNbO ₉ , PbBi ₂ Ta ₂ O ₉ , BiCu ₃ O ₁₂ , Bi ₂ MoO ₆ , LiNd(MoO ₄) ₂ , PbMoO ₄ , PbWO ₄ , Li(MO ₃) ₂ , Cd ₂ Mo ₃ O ₁₂ , Ba ₂ NaNb ₅ O ₁₅ , Ba ₂ KNb ₅ O ₁₅ , BaNb ₄ O ₆ , YBa ₂ Cu ₃ O ₇ , CoFe ₂ O ₄ , BaFe ₂ O ₄ , BaFe ₁₂ O ₉ , Li ₂ Fe ₂ O ₄
Alloys	Cr–Ti, Cr–Zr, Mo–Ti, W–Mo, Ti–Zr, Mo–Nb, W–Nb, Zr–Co–Ni, Hf–Nb–Ti, Ti–Cr–Sc–W
Triple compounds	MAX phases: Ti ₃ SiC ₂ , TiAlC ₂ , TiSiC, TiAlN, TiAl ₂ N, TiAlN, TiC _x N _{1–x} , ZrCrN, NbC _x N _{1–x} , TaC _x N _{1–x} , Ti–C–H, Ti–N–H, Zr–N–H
Composites	WC–Co, VN–Fe, Ti–TiB ₂ , Ti–SiC, TiC–Ni, ZrB ₂ –Fe, TiC–MnNi, TiC–Mo–Re, (Cr–Ti–C)NiMo, (W–Ti–Cr–C)NiCo, Al ₂ O ₃ –TiC–Fe, SiC–Si, SiC–B ₄ C, TiC–TiB ₂ , SiC–Al ₂ O ₃ , Al ₂ O ₃ –B ₄ C, Al ₂ O ₃ –MoB, Al ₂ O ₃ –AlN, AlN–AlON, AlN–Al ₂ O ₃ –AlON, Al ₂ O ₃ –TiN, Al ₂ O ₃ –VN, Al ₂ O ₃ –CrB ₂ , Al ₂ O ₃ –MoB ₂ , Al ₂ O ₃ –MoSi ₂ , MgO–MoSi ₂ , TiC–Cr ₂ O ₃ , TiC–MgO, Cr ₂ C ₃ –Al ₂ O ₃ –Ni, SiC–TiB ₂ –Al ₂ O ₃ , TiC–SiC, SiC–B ₄ C, TiC–Ti ₃ SiC ₂

as grinding and milling in the case of powders, which is aimed at obtaining materials by sintering or chemical treatment for powders using thermite methods. However, there are SHS solutions that allow obtaining fine powders and even nano-powders by using additives to prevent agglomeration and junction of particles (Borovinskaya, 2017).

Powders from the SHS synthesis can be used mainly:

- As starting powders for obtaining ceramic polycrystals by sintering, HP, etc. (Pampuch *et al.*, 1993),
- As abrasive powders (Merzhanov *et al.*, 1981; Prokudina, 2017),
- For the production of cemented carbides (Konyashin, 2014).

(2) Porous materials

The high temperatures at which SHS processes take place mean that the synthesis can occur simultaneously with the consolidation processes. At the same time, the chemical reactions occurring during sintering generally make full compaction difficult and prevent achieving high densities of materials. The additional factors limiting the achievement of high densities of synthesis products are: short process times, gas evolution and large temperature gradients. Typically, polycrystalline porous materials with a porosity of 5%–70% are obtained with the SHS method. It is promising as regards producing materials with controlled porosity for applications as filters, catalyst substrates, biomaterials etc. (Agnote *et al.*, 2017; Xanthopoulou, 2017; Potanin *et al.*, 2015).

(3) Dense materials

There are some solutions that increase the final densities during SHS, for example, running the process in a vacuum, introducing additives that increase the amount of the liquid phase during the synthesis or using external additional mechanical pressing. Such a combination of the SHS process and force pressing which allows for obtaining dense materials in one stage is currently a well-developed field of the SHS applications. The SHS process can be carried out in a matrix under mechanical pressure HP or isostatic pressure HIP (Hirao *et al.*, 1987b) and Spark Plasma Sintering SPS solution (Ortu *et al.*, 2014; Koshiyama *et al.*, 2016). Examples of materials obtained by this method include dense polycrystals, superalloys, gradient materials FGM and ceramic composites.

(4) Thin foils, deposited and layers

Materials in the form of layers are obtained using SHS by both solid and gas phase combustion. In Japan, India, China, and Russia (Odawara and Ikeuchi, 1986; Kachin and Yukvid, 1992), technologies have been developed for the application of SHS using ceramic layers on metal pipes under centrifugal forces. SHS is also tested for the preparation of deposits in the form of thin foils and layers from superalloys, ceramics, gradient FGM, etc. (Rogachev, 2008; Kumar *et al.*, 2012). Powders obtained by SHS methods used as substrates in plasma deposition techniques are also of particular interest from the point of view of technology (Aruna *et al.*, 2013).

(5) Monocrystals

SHS conditions can be combined with zonal melting to produce a single crystal product. In more developed solutions, single monocrystals (Ohtani *et al.*, 1987) or single-crystallite form of powders, whiskers, nanotubes and fibers are obtained in this way (Wang *et al.*, 2010; Borovinskaya *et al.*, 2010).

(6) Joining and welding

SHS proved to be an effective and economically competitive method of joining various materials such as metal-metal, metal-ceramics, ceramics-ceramics using different “chemical welding” reactions (Mukasyan, 2017) and laser supported SHS (Rutkowski *et al.*, 2018).

SHS Technique Used for Ceramic Materials Technologies

Advantages of the SHS Method for Ceramics

Generally, the distinctive features recognized as the basic advantages of the SHS method are:

- (1) Energy saving based on the use of internal reaction heat,
- (2) High temperatures achieved by self-heating,
- (3) High heat wave propagation speeds enabling processes of very short duration time in seconds with high efficiency,
- (4) Relatively simple apparatus

Some limitations of the SHS method can be related to the problem of prices and the availability of raw materials. In SHS methods, processed powders, mainly metallic, are used as raw materials, which in some cases are relatively cheap and available in large quantities (e.g., silicon, aluminum, etc.). Hence, other methods of holding covalent powders, e.g., carbothermal methods, plasma synthesis, etc. using more easily available oxide or organic raw materials have undeniable advantages from this point of view. As regards the other reported SHS weakness, it is undoubtedly the difficulty of process control, especially during the scaling-up stage.

It can generally be said that the SHS technique can be particularly beneficial in ceramic production technologies. With the exception of carbon materials, ceramic materials in both conventional and advanced ceramics are in the form of chemical compounds. Both ionic and covalent bonds in ceramic materials have a high enthalpy of formation. Therefore, the reactions of the synthesis of ceramic compounds from elements are exothermic and have high activation energies. The transport processes, such as diffusion, are difficult in these materials as sintering causes problems, especially in the case of covalent compounds. Moreover, these processes require high temperatures as well as special technical treatment, e.g., HP, HIP, SPS, etc.

If the synthesis process and sintering take place simultaneously, as it occurs in the course of SHS, then the heat of reaction can be used to simultaneously heat the system to temperatures enabling consolidation. These processes are therefore highly energy-efficient. At the same time, the short duration of the phenomena associated with rapid heating and cooling of the system causes the whole process to acquire the character of “fast sintering, fast firing”, close to other flash methods of consolidation, such as Spark Plasma Synthesis SPS, Laser Manufacturing LM or Plasma Sintering PS. In addition, self-purification occurs under combustion conditions as a result of the evaporation of volatile impurities or the selection of admixtures in the liquid phase, which makes SHS attractive for ceramic processing.

Numerous studies have found that because of the rapid high-temperature reaction conditions with ultrafast heating and cooling rates, the specific mechanisms of the reaction can occur, which results in solid solutions, multiphase composition, non-equilibrium phases, etc. Due to this, in some cases, it is not easy to obtain the possibility of preparing unique phase compositions by other more conventional methods. SHS can be a method for obtaining sintered nano and micro ceramic powders, active catalysts, biomaterials, thin layers, layered materials, etc. (Xanthopoulou, 2017; Pampuch *et al.*, 1993).

Potential advantages of SHS processes as methods of obtaining ceramic materials are associated with specific conditions under which the reaction takes place. These are:

- High temperature increase rates,
- High cooling rates,
- Specific reaction mechanisms,
- Processes of self-cleaning of the system from impurities

The special possibilities are:

- Obtaining ceramic materials with high chemical purity,
- Obtaining non-equilibrium phases and systems,
- Obtaining systems with high homogeneity,
- Obtaining composite multiphase materials, e.g., granular composites and such unique materials as gradient materials (FGM).

Principles in the Processing of Ceramics Using SHS

The goal of ceramic technology is to obtain products with particular properties, including appropriate dimensions and shape, surface state as well as mechanical, thermal, electrical, optical properties, etc. Considering the current state of knowledge and the development of SHS techniques, it can be stated that the technologies for obtaining ceramic materials can be divided into two basic types (Fig. 12(a) and (b)).

The best and most cost-effective solution is to obtain the finished product directly in a one-stage SHS process (Fig. 1(a); Lis, 1994; Amosov, 2017). In such a solution, as a result of SHS, powders, porous sinters, layers, coatings, single monocrystals and other forms of materials can be obtained, which, after any kind of mechanical processing, can be the used as the final product. The real problems are sometimes related to obtaining dense materials with a controlled microstructure. Generally, due to the rapid combustion phenomena and short process times as well as the potential for the evaporation of reagents, a typical SHS product is porous.

More dense materials also full compaction can be achieved by using a combination of SHS with simultaneous mechanical pressure, e.g., hot mechanical and isostatic pressing (HP/HIP SHS, reactive forging) (Hirao *et al.*, 1987a; Gutmanas and Gotman, 1999), high mechanical force (Forced SHS) (Levashov *et al.*, 2014), explosion detonation (Thadhani, 1993) or SPS (Ortu *et al.*, 2014). Techniques using other methods of applying various mechanical forces, such as centrifugal SHS casting (Yukhvid, 1992; Odawara, 1990), rolling SHS (Chernyshov *et al.*, 1993) or controlled gravitational field (Odawara, 1997), are also interesting. Also, conscious sintering support by using a controlled liquid phase can lead to the thickening of the synthesized material (Yukhvid, 1992).

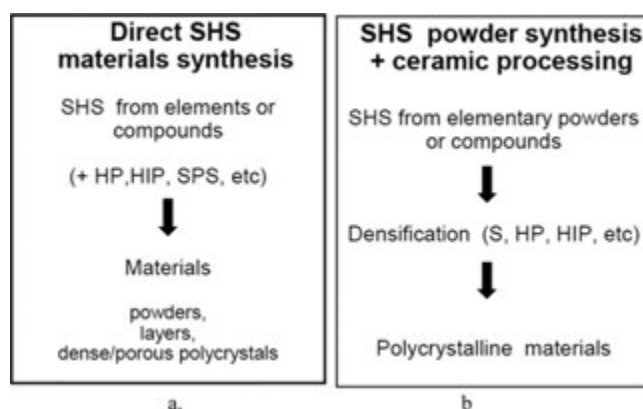


Fig. 12 The preparation of materials by SHS: (a) one-step process, (b) two or multi step treatment.

Another approach is to use SHS-obtained ceramic powders as precursors to sintered products in a multistep technological treatment (**Fig. 14(b)**). On the one hand, SHS allows for relatively easy and cheap obtaining of simple and complex powders of such compounds as carbides, nitrides or borides in different forms, including nanopowders, whiskers or nanotubes (*Borovinskaya et al., 2010*). Secondly, these powders are characterized by high chemical and phase purity, and at the same time, they are active in sintering due to their non-equilibrium nature. In technology, they sometimes require an additional de-agglomeration stage in the milling process (*Pampuch et al., 1993*).

Because of the development of SHS, the synthesis of SHS powders is often combined with other techniques that support the processes of obtaining materials and controlling their properties. Interesting solutions include the so-called “chemically assisted combustion synthesis” (CACS) (*Kharatyan and Nersisyan, 2002; Amosov et al., 1992*), consisting in adding materials that cause additional chemical reactions thermally activating SHS or control the morphology of the final product to the synthesis. The same effect can be obtained by using additional reaction catalysts (*Kim and Wooldroge, 2001*). Recently, techniques combining SHS with mechanical activation processes and milling (mechanically activated SHS MS-SHS) have been developing, especially those used to obtain powders with thermite methods or powders of metal alloys (*Takacs, 2002; Kubatkina et al., 2008; Bernard and Gaffet, 2001*). To additionally support SHS, field-activated SHS, which is close to SPS and ultrasound (*Khina and Kulak, 2013*), are also used. SHS phenomena are used to obtain so-called energetic materials, which in the form of nanopowders can cause extreme changes in temperature or pressure in the course of violent reactions (*Puszynski et al., 2007*).

One of typical examples of a multi-steps SHS approach is schematically shown in **Fig. 13** in the laboratory process for obtaining ceramics based on the MAX phase Ti_2AlN for a structural application (ceramic armor). The basic chemical reactions used in a two-step SHS are as follows (*Chlubny et al., 2012*):



The presented developed process has the following unit operations:

- (1) Preparation of TiAl powder by the SHS method,
- (2) Mixing the TiAl powder with Ti powder,
- (3) SHS filtration combustion of the TiAl powder in nitrogen in a pressure reactor,
- (4) Milling the SHS product
- (5) Sintering in an HP press
- (6) Final machining of the product

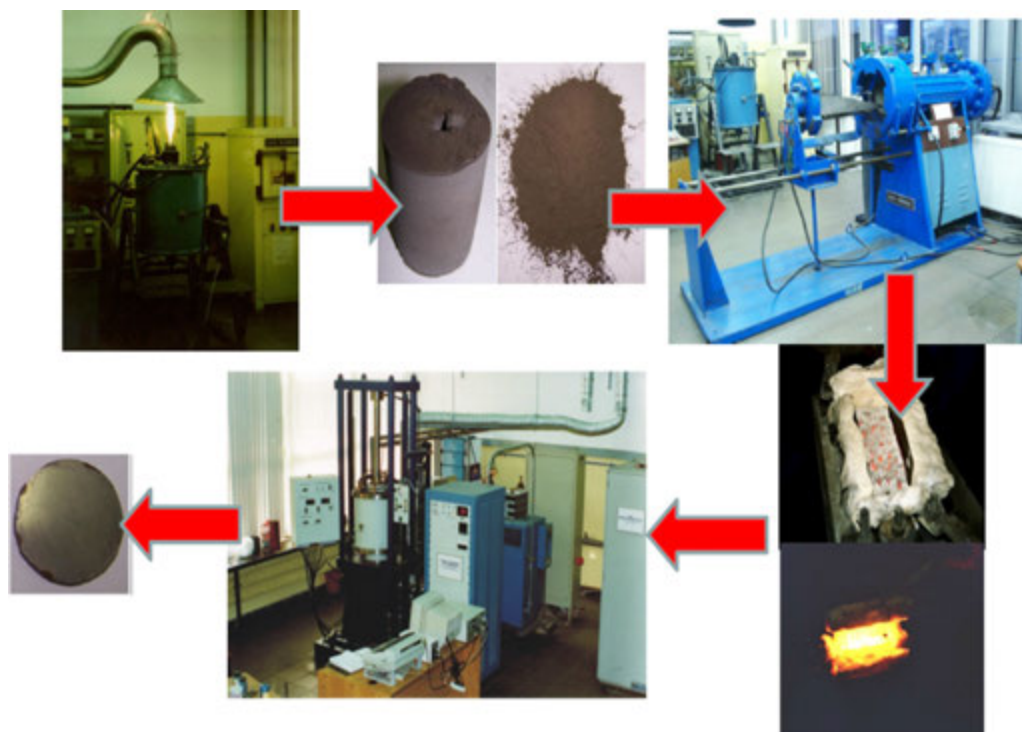


Fig. 13 The multi-step process of obtaining the TiAl_2N product using SHS.

Table 3 SHS-based technologies as an alternative to conventional ones

<i>SHS as alternative technology</i>	<i>Alternative SHS technology</i>
<i>Conventional technology</i>	
Synthesis in furnace	SHS powder technology
Plasma-chemical synthesis	
Spark plasma sintering SPS	
Sintering	
Hot pressing HP	SHS sintering
Hot isostatic pressing	SHS force compaction
Casting, centrifugal casting	SHS casting
Plasma and detonation spraying	SHS technology of gas-transport coating
Gas-phase precipitation	Induction SHS surfacing
CVD- processes	SHS technology of gas-transport coating
Electric arc and induction surfacing	SHS surfacing
	Induction SHS surfacing
Electric welding	SHS welding

Note: (ISMAN, 2020).

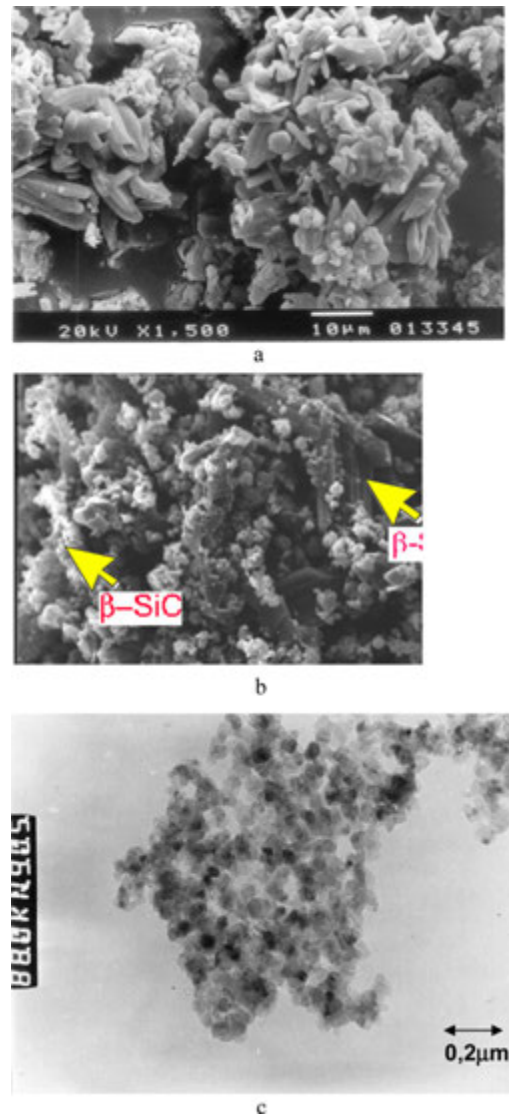


Fig. 14 Ceramic powders: Si_3N_4 (a), $\text{Si}_3\text{N}_4\text{-SiC}$ (b), and SiC nanopowders (c) prepared by SHS filtration combustion. Reproduced from (Kata et al., 1995).



Fig. 15 Structure ceramics from SHS prepared from SiC–B₄C powders. Reproduced from (AGH UST, 2020).

Application of SHS Methods in Technological Scale

The application of the SHS technique to obtaining materials has been used in many developed, patented and implemented technological solutions (Pampuch, 1999). There are three types of SHS production: pilot-scale, semi-industrial, and industrial-scale (Borovinskaya, 2017). The first pilot-scale and semi-industrial facilities appeared in Russia for obtaining of powders of carbides, borides, nitrides and composites i.e., consolidated materials from refractory compounds (ISMAN, 2020). Semi-industrial production appeared also in different countries: Japan, Kazakhstan, United States, China, and Poland. Based on semi-industrial production, industrial SHS facilities were developed. One of these was set up in Armenia for the manufacturing of high temperature heating elements based on molybdenum disilicide. The SHS production of nitrided ferroalloys and alloying additives was organized in Russia. One of the most significant achievements of the industrial application of SHS technologies is the production of ceramic powders in Spain and Russia, hard-alloyed tungsten carbide powders in Russia and pipes with corrosion-resistant internal ceramic coatings in China (Borovinskaya, 2017).

The broadest technology list is offered by ISMAN (Chernogolovka, Russia). (ISMAN, 2020). They classify SHS technologies divided into six categories:

- (1) SHS Powder Technology
- (2) SHS Sintering
- (3) SHS Force Compaction
- (4) SHS Metallurgy and SHS Technology of High-Temperature Melts
- (5) SHS Welding
- (6) SHS Technology of Gas-transport Coatings

These technological types are characterized by the following features:

- Low energy consumption (in most cases an additional energy is only necessary for initiating an SHS process,
- Simple technological equipment, its high productive capacity and ecological parameters;
- Decreased number of technological stages in comparison with conventional technologies;
- Feasibility of production lines adaptable to the production of different materials and items and amenable to mechanization and automation;
- Possible substitution of raw materials with cheaper ones for producing one and the same product;
- High technical and economical parameters of a great number of valuable materials and items for up-to-date engineering.

According to the information of authors from the ISMAN (ISMAN, 2020), more than 700 various inorganic compounds and materials have been obtained by the SHS methods and these technologies can be alternative to many traditional materials technologies, as shown in Table 3.

In conclusion, examples of ceramic materials obtained in the AGH UST using SHS technologies are presented in Figs. 14 and 15.

References

- AGH UST, 2020. Products of the Department of Ceramics and Refractories. Poland: Faculty of Materials Science and Ceramics AGH UST.
- Agnote, I., Lagos, M.A., Gutierrez, M., Sargysyan, A., 2017. Foams. In: Borovinskaya, I., Gromov, A., Levashov, E., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*, first ed. Elsevier Inc., pp. 1–466.
- Agrafiotis, C.C., Lis, J., Puszynski, J.A., Hlavacek, V., 1990. *J. Am. Ceram. Soc.* 73, 3514–3517.
- Alexander, P.P., Production of Metal Hydrides, U.S. Patent 2372168, 1941; No. 2378368 1943 and 2425711, 1944.
- Amosov, A.P., 2017. Composite materials. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc.
- Amosov, A.P., Bichurov, G.V., Bolshova, N.F., *et al.*, 1992. *Int. J. SHS* 1 (2), 239–245.

- Anderson, J., 1989. *Mater. Res. Bull.* 14, 84–85.
- Aruna, S.T., Sanjeeviraja, C., Bajali, N., Manikandanath, N.T., 2013. *Surf. Cat. Tech.* 219, 131–138.
- Barsoum, M.W., El-Raghy, A.M., 2000. *Metall. Mater. Trans. Phys. Metall. Mater. Sci.* 31 (7), 1857–1865.
- Bayliss, A., Matkowsky, B.J., 1990. Modeling and numerical computation of nonsteady SHS processes. In: Munir, Z.A., Holt, J.B. (Eds.), *Combustion and Plasma Synthesis of High-Temperature Materials*. NY: VCH Publishers, pp. 61–72.
- Bernard, F., 2017. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *SHS in France in Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 288–290.
- Bernard, F., Gaffet, E., 2001. *Int. J. SHS* 10 (2), 109–132.
- Berzelius, J.J., 1825. *Pogg. Ann.* 126–132.
- Borovinskaya, I.P., 2017. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Industrialization of SHS in Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 168–169.
- Borovinskaya, I.P., 2017. Nitrides and nitride ceramics. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 214–217.
- Borovinskaya, I.P., Gromov, A.G., Levashov, E.A., *et al.*, 2017. *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis; History, Theory, Technology, and Products*. Elsevier Inc.
- Borovinskaya, I.P., Barinova, T.V., Vershininrov, V.I., Ignatieva, T.I., 2010. *Int. J. SHS* 19 (2), 114–119.
- Cao, G., Orru, R., 2017. SHS in Italy. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 296–297.
- Chernyshov, V.N., Osipov, E.E., Levashov, E.A., Merzhanov, A.G., Biyachi, L., 1993. *Int. J. SHS* 2 (3), 315–321.
- Chlubny, L., Lis, J., Bucko, M.M., Kata, D., 2012. *Ceram. Eng. Sci. Proc.* 9, 171–177.
- Crider, J.F., 1982. *Ceram. Eng. Sci. Proc.* 3 (9–10), 519–528.
- Degreve, J., Dimitriou, P., Puszyński, J.A., Hlavacek, V., 1987. *Chem. Eng. Comm.* 58, 105–118.
- Fonze-Diacon, H., 1900. *Compt. Rend.* 130, 1314.
- Fu, Z., 2017. SHS in China. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 284–287.
- Goldsmidt, H., 1895. *Ger. Pat. No. DRP 96317*.
- Gutmanas, E.Y., Gotman, I., 1999. *J. Eur. Ceram. Soc.* 19, 2381–2393.
- Hirao, K., Miyamoto, Y., Koizumi, M., 1987a. *Adv. Ceram. Mater.* 2 (4), 780.
- Hirao, K., Miyamoto, Y., Koizumi, M., 1987b. *Adv. Ceram. Mater. Sci.* 2, 780–791.
- Hlavacek, V., 1991. *Am. Ceram. Soc. Bull.* 70 (2), 240–243.
- Holt, J.B., Kingman, D.D., 1982. In: Rayley, N.C. (Ed.), *Proceedings of the University Conference on Ceramic Science*. Nord Carolina State University.
- ISMAN, 2020. *Virtual Textbook on SHS*, The Institute of Structural Macrokinetics and Materials Science Russia Academy of Sciences, Chernogolovka n. Moscow. Available at: www.ism.ac.ru.
- Kachin, A.R., Yukvid, V.I., 1992. *Int. J. SHS* 1 (1), 168–171.
- Kata, D., Lis, J., Pampuch, R., 1995. In: Bellosi, A. (Ed.), *Proceedings of the Fourth Euroceramics*, vol. 4, pp. 437–442. Faenza, Italy: C.N.R.-IRTEC.
- Kellenberg, F., Kraft, K., 1902. *Liebings Ann. Re.* 325, 279.
- Khakin, B.I., Merzchanov, A.G., 1966. *Comb. Expl. Shock Waves* 2, 22.
- Kharatyan, S.L., 2017. SHS in Armenia. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 279–281.
- Kharatyan, S.L., Nersisyan, H.H., 2002. *Key Eng. Mater.* 217, 83–93.
- Khina, B.B., 2017. SHS in Belorussia. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 282–283.
- Khina, B.B., Kulak, M.M., 2013. *J. Alloys Comp.* 358, 595–601.
- Kim, T., Wooldroge, M.S., 2001. *J. Am. Ceram. Soc.* 84, 976–982.
- Konyashin, I.Y., 2014. In: Sarin, V. (Ed.), *Cemented Carbides for Mining, Construction and Wear Parts in Comprehensive Hard Materials*. Elsevier Science and Technology, pp. 425–451.
- Koshiyama, M., Sako, H., Ohno, M., Matsuura, K., 2016. *Mater. Trans.* 57 (9), 1593–1596.
- Kozak, K., Bucko, M., Chlubny, L., *et al.*, 2019. *Mater. Sci. Eng. A* 74, 114–122.
- Ksanderpulo, G.I., Mansurov, Z.A., Mofa, N.N., Fomenko, S.M., Abdulkarimova, R.G., 2017. SHS in Kazakhstan. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 301–303.
- Kubatkina, V.V., Levashov, E.A., Patsera, E.I., Kochetov, N.A., Rogachev, A.S., 2008. *Int. J. SHS* 17 (3), 1–6.
- Kumar, A., Mukasyan, A.S., Wolf, E.E., 2012. *Appl. Katal. A Gen.* 372, 175–183.
- Levashov, E.A., Pogoshev, Y.F., Potanin, A.Y., 2014. *Ceram. Int.* 40, 6541–6542.
- Lis, J., 1994. Sinterable powders of covalent compounds prepared by SHS. In: Pampuch, R. (Ed.), *Ceramics 44*. Polish Ceramic Society. (in Polish).
- Lis, J., 2017. SHS in Poland. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 306–308.
- Lis, J., Pampuch, R., Piekarczyk, J., Stobierski, L., 1993. *Ceram. Int.* 19, 91–96.
- Lis, J., Miyamoto, Y., Pampuch, R., Tanihata, K., 1995. *Mater. Lett.* 22, 163–168.
- Maksimov, Y.M., 2017. Combustion mechanism. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 72–73.
- Maksomov, Y.M., Ziaditov, M.X., Merzhanov, A.G., Raskolenko, L.G., Lepiatova, O.K., 1984. *Fiz. Gor. Vzryva* 5, 16–21.
- McCauley, J.W., 1990. *Ceram. Eng. Sci. Proc.* 11, 1137–1142.
- McCauley, J.W., Corbin, N.D., Resetas, T.M., Wong, P., 1982. *Ceram. Eng. Sci. Proc.* 3 (9–10), 538–554.
- Merzchanov, A.G., 2012. Self-Propagating High-Temperature Synthesis in ISMAN web-page. Available at: www.ism.ac.ru.
- Merzhanov, A.G., 2005. Who is Who in SHS Chernogolovka: ISMAN.
- Merzhanov, A.G., 1990. Self propagation high-temperature synthesis: Twenty years of search and finding. In: Munir, Z.A., Holt, J.B. (Eds.), *Combustion and Plasma Synthesis of High-Temperature Materials*. NY: VCH Publishers, pp. 1–54.
- Merzhanov, A.G., Borovinskaya, I.P., Sharvker, S.Y., *et al.*, 1981. *Powder Metall.* 10, 50–55.
- Merzhanov, A.G., Shkuro, V.M., Borovinskaya, I.P., 1967. *USSR Inventor Certificate*, 255221.
- Moissan, H., 1979. *C R Hebd. Seances Acad. Sci.* 14, 1017–1025.
- Mukasyan, A.S., 2017. Joining of refractory and dissimilar materials. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 179–181.
- Munir, Z.A., 1993. *J. Mater. Synth. Proc.* 1, 387–394.

- Munir, Z.A., 2001. Self-Propagating High-Temperature Synthesis, *Encyclopedia of Materials: Science and Technology*. Elsevier Science Ltd., 8322–8327.
- Nersisyan, H., Won II, H., Won, C.W., Lee, J.H., 2017. SHS in South Korea. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 311–313.
- Novoshilov, B.V., 1962. *Dokl. Akad. Nauk SSSR* 144, 1328–1339.
- Odawara, O., 1990. *J. Am. Ceram. Soc.* 629–633.
- Odawara, O., 1997. *Ceram. Int.* 23, 273–278.
- Odawara, O., 2017. SHS in Japan. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 298–300.
- Odawara, O., Ikeuchi, J., 1986. *J. Am. Ceram. Soc.* 69 (4), C80–C81.
- Ohtani, S., Tanaka, T., Ishizawa, J., 1987. *J. Cryst. Growth* 83, 481.
- Onashvilli, G., 2017. SHS in Georgia. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 291–292.
- Orru, R., Licheri, R., Musa, C., Cao, G., 2014. *Adv. Sci. Tech.* 88, 111–120.
- Pampuch, R., 1999. *J. Eur. Ceram Soc.* 19, 2395–2404.
- Pampuch, R., Stobierski, L., 1991. *Ceram. Int.* 17, 1–6.
- Pampuch, R., Pampuch, L., Stobierski, J., 1989. *J. Am. Ceram. Soc.* 72, 645–647.
- Pampuch, R., Lis, J., Stobierski, L., 1990. Heterogeneous reaction mechanisms in Si-C system under conditions of solid combustion. In: Munir, Z.A., Holt, J.B. (Eds.), *Combustion and Plasma Synthesis of High-Temperature Materials*. NY: VCH Publishers, pp. 211–218.
- Pampuch, R., Rączka, M., Lis, J., 1991. *Int. J. Mater. Prod. Tech.* 2, 132–138.
- Pampuch, R., Lis, J., Stobierski, L., Ermer, E., 1993. *Int. J. SHS* 2 (1), 49–55.
- Potani, A.Y., Levashov, E.A., Pogozhev, Y.S., Shvindina, N.V., Kovalev, D.Y., 2015. *Ceram. Int.* 14, 8177–8185.
- Prokudina, V.K., 2017. Abrasives. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 2–5.
- Puszynski, J.A., 2017. SHS in United States of America. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 320–322.
- Puszynski, J.A., Bulian, C.A., Swiatkiewicz, J.J., 2007. *J. Propuls Power* 23, 698.
- Rodrigues, M.A., 2017. SHS in Spain. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 314–316.
- Rogachev, A.S., 2008. *Russ. Chem. Rev.* 77, 22–38.
- Rogachev, A.S., Mukasyan, A.S., 2014. *Combustion for Material Synthesis*. CRC Press.
- Rogachev, A.S., Mukasyan, A.S., 2017. Dynamic methods of experimental diagnostics. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 96–97.
- Rutkowski, P., Huebner, J., Kata, D., *et al.*, 2018. *Ceram. Int.* 44, 10883–10890.
- Semionov, N.N., 1961. In: Fahigkelt, E. (Ed.), *Einige Probleme der Chemischen Kinetik und Reaction*. Akademie Verlag Berlin.
- Takacs, L., 2002. *Prog. Mater. Sci.* 47, 355–414.
- Thadhani, N.N., 1993. *Proc. Mater. Sci.* 37, 117–226.
- Walton, J.D., Poulos, N.E., 1959. *J. Am. Ceram. Soc.* 42 (1), 40–49.
- Wang, J., Gu, Y., Zhang, L., Zhang, Z., 2010. *J. Nanomater.* 6.
- Xanthopoulou, G.G., 2017. Catalysts. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 50–51.
- Yucel, O., 2017. SHS in Turkey. In: Borovinskaya, I.P., Gromov, A., Levashov, E.A., *et al.* (Eds.), *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*. Elsevier Inc., pp. 317–319.
- Yukhvid, V.I., 1992. *Pure Appl. Chem.* 64, 977–988.
- Zeldovich, Y.B., 1948. *Zh. Fiz. Khimii* 22, 22–28.
- Zeldovich, Y.B., Frank-Kamenecky, D.A., 1938. *Dokl. Akad. Nauk SSSR* 19, 693–699.

Hydrothermal Synthesis

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Powder Synthesis Methods

Particulate materials play significant roles in technological developments and subsequently impact our daily lives. Their physical and chemical characteristics significantly affect their functionality properties and performance (Adair and Suvaci, 2000). Therefore, it is critical to control particle characteristics to fulfill the expectations of future technologies. Moreover, such particulate materials can exhibit novel properties by tailoring its physical characteristics. For example, when their size goes down to nanoscale then they demonstrate unique properties or particles with anisometric (plates, rods, etc.) morphology enable researchers to have access to novel anisotropic properties via texture development in advanced ceramics (Messing *et al.*, 2004; Suvaci and Ozer, 2005). Therefore, the powder synthesis methods should enable one to tailor the physical properties of particles.

The most widely utilized nonmetallic inorganic powder synthesis methods are mixed oxide solid-state reaction, liquid phase based methods such as coprecipitation and hydrothermal synthesis, and gas phase based methods such as vapor-phase reaction. Although the solid-state method is commonly used for powder synthesis, this method has many drawbacks such as low purity, large particle size, and broad particle size distribution. The vapor phase methods provide high purity powders but stoichiometry of the resultant particles can be poor and they exhibit usually high degree of aggregation. On the other hand, the liquid based methods can lead to improved control of the thermodynamics and kinetics involved in nucleation and growth processes. Therefore, growing particles of varied morphologies in those methods can be achieved by altering thermodynamic and kinetic parameters such as temperature, concentration of reactants, duration of crystal growth, and additives (Ring, 1996). High purity and better stoichiometry control are provided with the coprecipitation method; however, wide particle size distribution can be formed from submicron to micron size (Adair and Suvaci, 2001). Since the precipitation phase in aqueous media is usually not oxides but its hydrates, it should be calcined to achieve the final form prior to use of such particles and unfortunately this calcination step results in aggregation of fine particles. As a result, most of such powders should be milled to achieve fine particle size. Among the synthesis methods, hydrothermal synthesis has been widely utilized because it leads to powder with superior properties such as high purity, phase stability (stoichiometry), tailorable particle size, and narrow size distribution, and controllable morphologies depending on technological developments and hence demands in particle technologies. Hydrothermal synthesis involves direct formation of crystals from solutions in aqueous media at elevated temperature ($T > 25^{\circ}\text{C}$) and pressure ($> 100\text{ kPa}$). In this method, powders nucleate and grow in a controlled manner and subsequently result in crystallized particles with controlled size and morphology as well as low degree of aggregation/agglomeration. As an example, Fig. 1 shows various oxide particles with various morphologies spanning from cubes to rods synthesized by hydrothermal methods. In addition, coating of particles can be achieved by using hydrothermal synthesis to improve particle characteristics or to add new functionality to the substrate particle as shown in Fig. 2 where PbTiO_3 platelet is coated with BaTiO_3 particles. Besides allowing controllable material characteristics with stoichiometry, hydrothermal synthesis offers additional substantial benefits such as operating at low synthesis temperature, fast and flexible continuous or batch processing, large scale industrial production, cleaner processing routes, and not involving harmful organic solvents. In addition, energy consuming steps such as high temperature calcination and milling are not needed in this process. Consequently, hydrothermal synthesis can be considered as a green and energy efficient process. The assessment of the powder synthesis methods according to obtained particle characteristics are presented in Table 1.

Recent Activities in Hydrothermal Synthesis

Recently, various synthesis strategies for precise control of the hydrothermal synthesis conditions have been developed in order to tailor synthesised product characteristics in terms of size, shape and composition (Feng and Li, 2017). These strategies consist of internal factors related to the reaction system such as use of organic additives, templates, and substrates and the external environment's effects including but not limited to utilization of microwaves, electric field, or magnetic field during hydrothermal synthesis to get desired materials structure forms (Yang and Park, 2019). Such developments also contributed to earlier hydrothermal-based synthesis types and now hydrothermal synthesis has been used in many different forms as depicted as hydrothermal synthesis tree in Fig. 3.

During the last two decades, hydrothermal synthesis has become the key synthesis method for powder materials to obtain unique properties by tailoring their physical characteristics. Fig. 4 shows the number of publications on the hydrothermal synthesis for each year beginning from 2000. The data were collected from the Web of Science by using the key words *hydrothermal* and *synthesis*. As shown in Fig. 4, the number of published papers steadily increased to 2014; since then there has been a slight decrease but the numbers are still high. Accordingly, the total number of publications on hydrothermal synthesis since 2000 to date exceeds 11,000.

Among those published papers, an increasing number about continuous hydrothermal synthesis is very remarkable. More recently, scientists have worked diligently to demonstrate potential use of rapid continuous hydrothermal methods for production of inorganic materials. With continuous hydrothermal synthesis, manufacture of various nanomaterials can be scaled up for

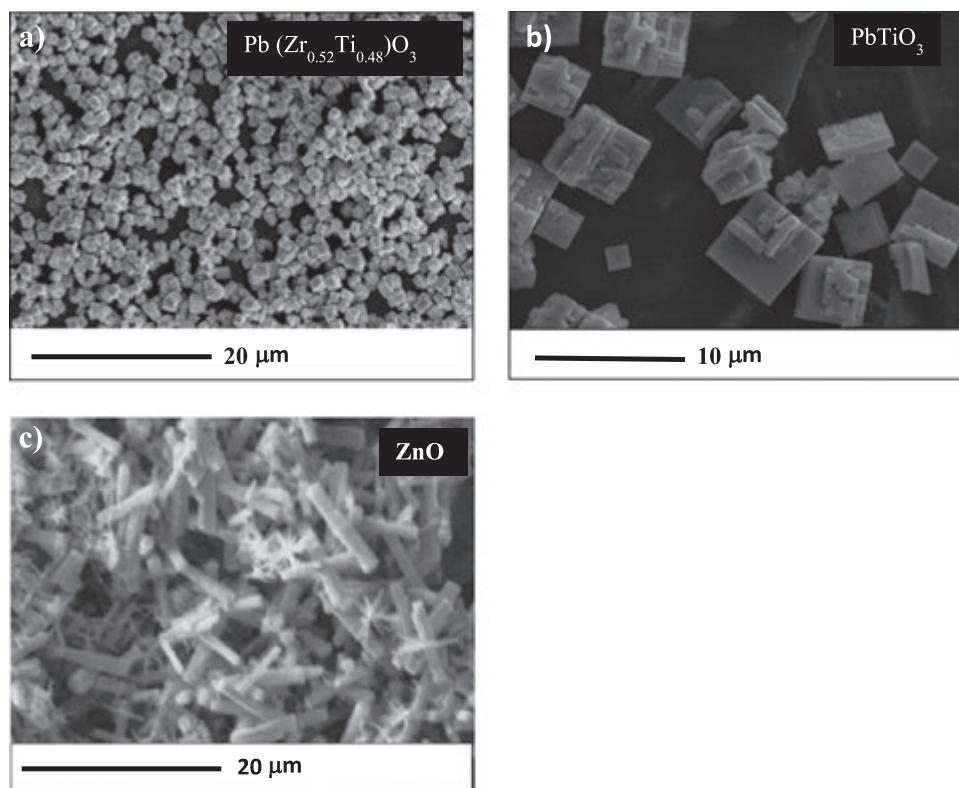


Fig. 1 Scanning electron microscopy images of various oxide particles with various morphologies synthesized by hydrothermal method: (a) Cubic $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ particles, (b) plate-like PbTiO_3 particles, and (c) rod-like ZnO particles.

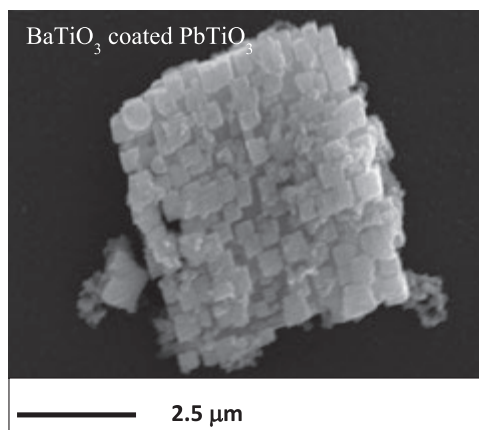


Fig. 2 Scanning electron microscopy image of BaTiO_3 coated PbTiO_3 platelets.

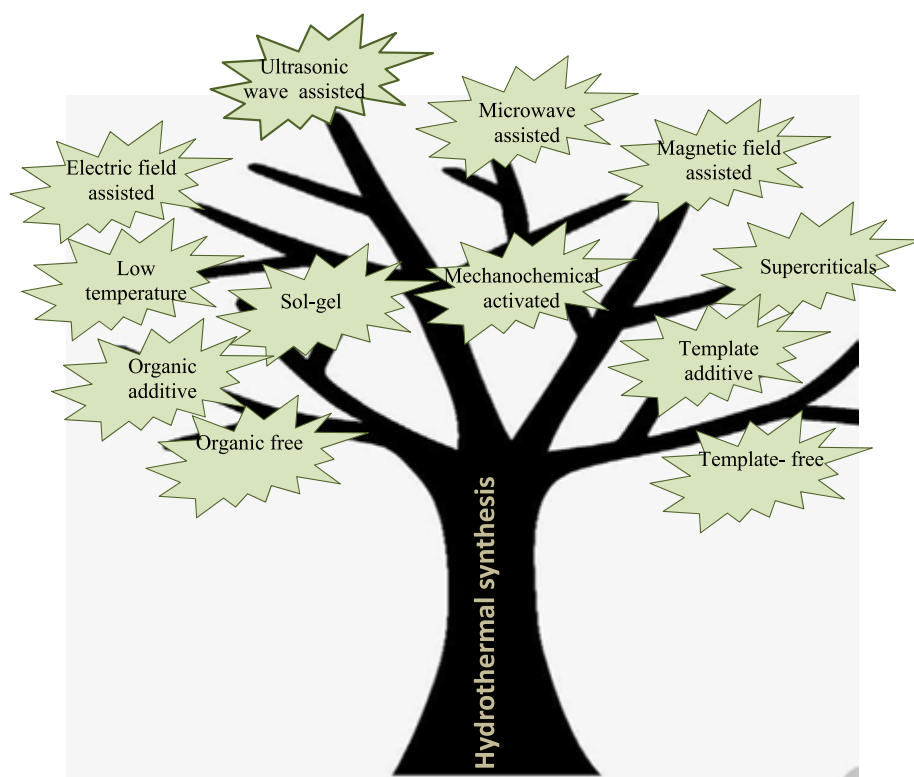
commercial applications with controllable particle properties (stoichiometry, size, shape, porosity, etc.). The latest progress in continuous hydrothermal techniques was presented recently by some research groups (Dunne *et al.*, 2015; Darr *et al.*, 2017).

To investigate the impact of the external environment's effects on the synthesis and the properties of the nanomaterials such as semiconducting nanomaterials, scientists have designed and developed microwave, electric field, and magnetic field assisted hydrothermal methods. The increase in number of the published papers on microwave assisted hydrothermal synthesis sorted by year is shown in the inset in Fig. 4. Although there are a limited number of papers (<15) on magnetic and electric field assisted hydrothermal synthesis, the number of publications on microwave assisted hydrothermal synthesis exceeds 115 in 2019 alone. Similar to the publication numbers of papers, 141 patents on microwave assisted hydrothermal synthesis, 37 patents on continuous hydrothermal synthesis, 9 patents on magnetic field assisted, 1 patent on electric field assisted hydrothermal synthesis have been published since 2000. Consequently, large numbers of published papers and patents on hybrid hydrothermal synthesis have been issued by companies and scientists to improve both powder properties and process efficiency.

Table 1 Particle characteristics depending on the powder synthesis methods

Powder Synthesis methods	Size	Morphology control	Stoichiometry	Purity	Aggregation
Solid-state reaction (mixed-oxide)	Coarse (micron)	Poor	Poor	Low	Yes
Coprecipitation	Coarse (submicron–micron)	Medium	Good	Medium	Yes
Sol–gel	Fine (nanosubmicron)	Medium	Good	High	Yes
Molten flux	Coarse (micron)	Medium	Medium	Low	No
Vapor phase	Fine (nanomicon)	Medium	Poor	High	Yes
Hydrothermal	Fine (nanosubmicron)	Good	Good	High	No

Note: Compiled from Adair, J.H., Suvaci, E., 2001. Submicron electroceramics powder by hydrothermal synthesis. In: Buschow, K.H.J., Cahn, R.W., Flemings, M.C., *et al.* (Eds.), *Encyclopedia of Materials: Science and Technology*, second ed. Amsterdam: Elsevier. Phanichphant, S., Heimann, R.B., 2004. Hydrothermal synthesis of submicron- to nano-sized ferroelectric powders: Properties and characterization. *CMU Journal* 3 (2), 113–132. Yoshimura, M., Byrappa, K., 2008. Hydrothermal processing of materials: Past, present and future. *Journal of Materials Science* 43, 2085–2103. Shandilya, M., Rai, R., Singh, J., 2016. Review: Hydrothermal technology for smart materials. *Advances in Applied Ceramics* 115 (6), 354–376.

**Fig. 3** The hydrothermal synthesis tree, which shows branches of hydrothermal synthesis reported in the literature to date.

Among these hybrid hydrothermal methods, the microwave assisted hydrothermal synthesis has had high research interest in recent years. Compared with the traditional hydrothermal method that performed in relatively high reaction temperature differences and long reaction time, the microwave hydrothermal method gives ultrafine nanoparticles with narrow particle size distribution and uniform morphology by applying a fast and uniform heating system. Recently, hydrothermal powder synthesis and its applications for smart materials were reviewed by [Shandilya *et al.* \(2016\)](#) where they focused on process definitions, technological merits, and current applications. In another study, [Yang and Park \(2019\)](#) reviewed the developments on the conventional and microwave hydrothermal methods, their reaction mechanisms, and practical applications of the two methods.

General Principles and Equipment

In hydrothermal synthesis, chemical reactions of substances take place in a sealed and heated aqueous solution at elevated temperatures ($T > 25^{\circ}\text{C}$) and pressures ($P > 100 \text{ kPa}$) to form crystalline materials directly from solution. In this method, pressures as high as 500 MPa and temperatures up to 1000°C can be utilized to enhance dissolution of reactants and subsequently the nucleation and growth of certain types of materials such as single crystals of oxides, diamond, or carbon nanotubes ([Suchanek *et al.*, 2004](#)). If the

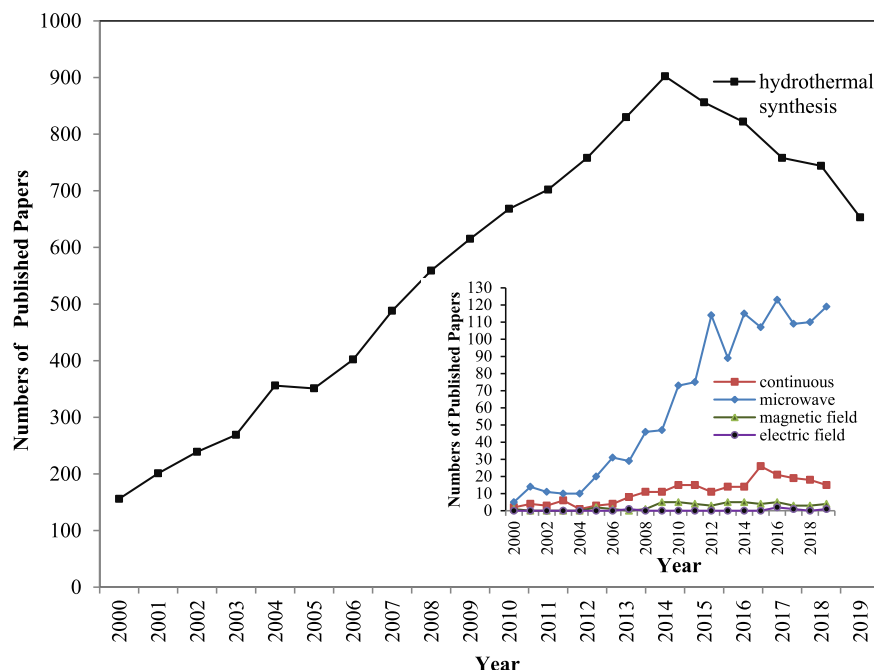


Fig. 4 The number of publications on hydrothermal synthesis for each year beginning in 2000. The data were collected from the Web of Science by using key words *hydrothermal* and *synthesis*.

synthesis takes place in a nonaqueous solution with organic solvents at relatively high temperature, it is called solvothermal synthesis. There are different forms of solvothermal synthesis based on the solvent type, such as alcohols, glycols (i.e., ethylene glycol, diethylene glycol, triethylene glycol) or oleylamine (OAm). For example, the solvothermal method is called glycolthermal synthesis when glycols such as ethylene glycol or 1,4-butanediol are used as solvents (Adair and Suvaci, 2001) whereas it is called alcohothermal synthesis when alcohols (e.g., ethanol) are used.

In hydrothermal and solvothermal systems, sealed container (reactor or autoclave) or high-pressure autoclave is used under subcritical or supercritical conditions of the solvent. The pressure developed in an autoclave is related with the filling volume (typically maximum filling volume is 70% of the autoclave capacity to assure the process safety). In most cases, reactors are metal autoclaves such as stainless steel or high-strength alloys with Teflon or alloy linings. Teflon inserts are commonly used in autoclaves up to 200°C and 20 MPa synthesis conditions because they are inert to both acidic and alkaline media compared with glass and quartz inserts. In the case of Teflon uses at $T > 200^{\circ}\text{C}$, Teflon can creep and this can cause undesired problems. In such cases, other alternative materials such as high-strength alloy autoclaves with tubes made from platinum, gold, or silver are utilized to protect the autoclave body from the corrosive solvents or ingredients (Li et al., 2015).

Approaches for Hydrothermal Synthesis

There are several steps that should be considered for achieving desired powder characteristics in hydrothermal synthesis process. The algorithm for a hydrothermal synthesis shown in Fig. 5 demonstrates a general perspective for hydrothermal synthesis application to achieve target material properties.

What is the Nature of the Material?

Before starting synthesis of any materials, the nature of the materials to be synthesized should be known and their expected properties should be identified or listed. It is essential to understand the materials properties to optimize or control their particle features. Material properties can be classified as chemical properties, physical properties, colloidal properties, electronic properties, and optical properties (Adair et al., 1988, 1998). The critical chemical properties such as phase equilibria and solubility are necessary to control phase purity. The physical properties such as crystal structure and equilibrium crystal shape, dictated by surface energies of crystallographic plane, are important to control the morphology of particles. The colloidal properties include surface groups, hydrophilicity, isoelectric point, Hamaker constant, etc., and they are useful to control to dispersion of particles in solutions or preventing agglomeration of particles. Since the attractive van der Waals forces among the particles result in agglomerated particles, they can also affect electrical properties (e.g., dielectric constant, dielectric dispersion, ferroelectricity, piezoelectricity, ferromagnetism) and optical properties (e.g., band gap, absorption spectra) (Adair et al., 1988, 1998).

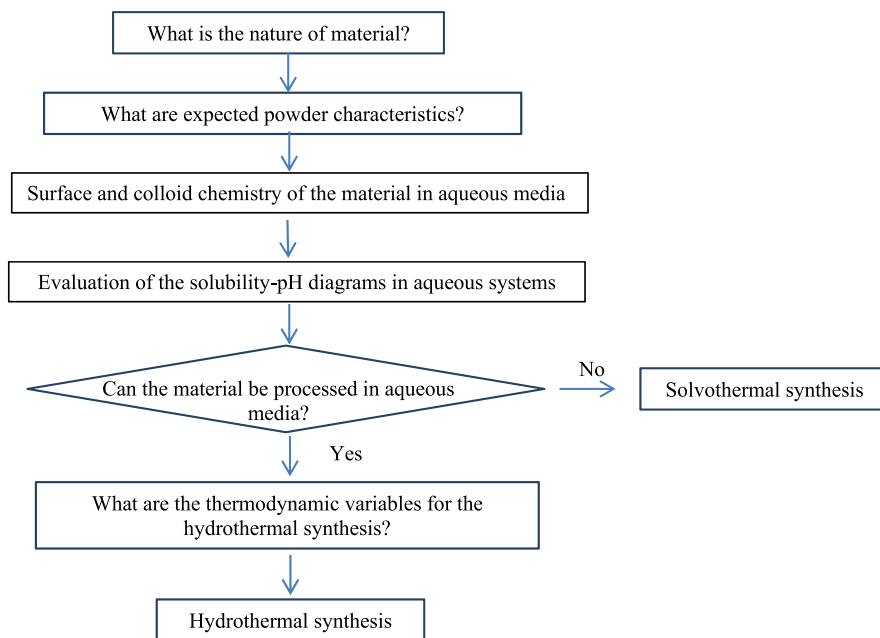


Fig. 5 Algorithm for a hydrothermal synthesis.

What are the Expected Powder Characteristics?

The powder characteristics that can control properties and performances of particulate materials are stoichiometry, phase stability, size, size distribution, morphology, purity, and degree of agglomeration. To establish phase stability, combinatorial routes for phase development can be applied, dissolution and phase changes are evaluated, and process variables such as degree of supersaturation, solution pH, and temperature should be employed. The control over size of the particles can be achieved by degree of supersaturation control, nuclei concentration, homogeneity of solution, and solution properties such as viscosity, ionic strength, etc., as described in the mechanism section below. In the case of the morphological control for particles, surface equilibria, complexing agent, and surface electrostatic features play important role during hydrothermal synthesis. To prevent aggregation, surface charge of particles must be controlled and interaction energies, van der Waals and polarization forces and organic adsorbates should be considered (Adair *et al.*, 1988, 1998).

The hydrothermal method allows controlling of material characteristics with stoichiometry. Therefore, this method is often chosen to synthesize or produce different types of nanomaterials such as silicates, zeolites, oxides, ceramics, metals, alloys, composites, and so on. These materials can be in variety of forms such as equiaxed (e.g., cubes, spherical), elongated (fibers, whiskers, nanorods, nanotubes), plates, etc., as shown in Fig. 1. With hydrothermal synthesis, particle size and morphology characteristics can be manipulated over a wide range. For example, whiskers, plates, or cubes can be oriented to form materials with single crystallite like properties, such as textured ceramic-ceramic composites with anisotropic properties (Suchanek and Riman, 2006). Recently, much effort has been devoted to improve physical, chemical, and electrical properties of nanomaterials by designing of these material characteristics. For example, as anode material, Zn_2SnO_4 particles with high purity, smaller particle size, and uniform morphology have the best properties for Li ion batteries. With improving physical properties and morphological structures of Zn_2SnO_4 materials, battery performance and the electrochemical performance can be enhanced with hollow cube structure compared with dispersed single crystal cubes (Zhao *et al.*, 2016).

Surface and Colloid Chemistry of the Material in Aqueous Media

Water is an environmentally safe material and cheaper than other organic solvents and thus it is much more widely utilized in hydrothermal synthesis compared with organic solvents. Frank (1978) summarized the physical and chemical properties of water dependent pressure and temperature (PT) data under hydrothermal conditions. These data and other physical properties for water up to 1000°C and 1000 MPa are well known (Byrappa and Yoshimura, 2001). Under high temperature and pressure conditions in an autoclave, the density, surface tension, and viscosity of water will be lower resulting in significantly higher ionic and molecular mobility than at ambient conditions (Feng and Li, 2017). Therefore, since solvent properties of water under high temperature and pressure can be considerably changed, using of pressure and temperature diagram of the water effectively is very important for understanding the hydrothermal synthesis better. Because of the increased ionization of water caused by increased temperature, the ionic or chemical reactions of the indissoluble inorganic materials can be promoted under hydrothermal condition at the high temperature and pressure.

Another important issue of hydrothermal synthesis is to understand the surface and colloid chemistry of materials in an aqueous reaction medium. When metal oxide based powders are immersed into water, surface charge develops on the particles. The most important charging mechanism for these systems are (1) the dissociation of the surface to yield an ion (usually a proton) to the solution; (2) Nernstian charging through specific adsorption or desorption of lattice ions; (3) metal hydrolysis via ionization of the

particle surface due to protonation or deprotonation of acid or basic surface groups; and (4) incongruent dissolution (leaching). Mechanism 3 is commonly observed for all metal oxides (except silica) and metal hydroxides. Solution pH is the most critical solution feature, which can be used to change surface charge. Mechanism 4 involves metal hydrolysis with incongruent dissolution of the at least one of the cationic species (Adair *et al.*, 2001). Especially, final mechanism is critical to mixed metal (multication) oxide systems. Therefore, during in situ transformation of powder from precursor solution or precipitation–recrystallization in aqueous media, cation concentration must be under control to conserve stoichiometry of each component because of the such colloidal interactions between particles and water molecules. This has been shown by Tuncolu *et al.* (2015) where excessive Zn^{2+} dissolution during washing of the precipitated Zn_2SnO_4 phase results in difficulty in stoichiometry control.

Evaluation of the Solubility–pH Diagrams in Aqueous System

Evaluation of the solubility–pH diagram is another important issue for understanding dissolution–reprecipitation behavior of metal salts depending on concentration, pH of solution, and temperature. When suspended particles dissolve into solution, they supersaturate the solution and then dissolution–recrystallization is observed and consequently particles precipitate in the solution. Solubility limits of starting metal oxide salts and solubility behavior of materials will change depending on pH and concentration in reaction solution and subsequently they will affect. Thus, assessment of the solubility–pH diagram will help to choose appropriate initial concentration of cations and pH of the reaction medium. For example, Since Zn^{2+} solubility is greater than Sn^{4+} solubility; in our earlier studies, to achieve stoichiometric Zn_2SnO_4 particles, excess Zn^{2+} (i.e., $\text{Zn}^{2+}/\text{Sn}^{4+} = 2.4$ instead of $\text{Zn}^{2+}/\text{Sn}^{4+} = 2.0$) should have been added to system prior to hydrothermal synthesis at pH 8.0 (Tuncolu *et al.*, 2015). In the case of the limiting solubility in water, mineralizers such as pH adjusting agents (e.g., acids or bases) or the complexing agents can be added to enhance the solubility in water. When starting materials have higher solubility and difficulties in the control of dissolution–recrystallization in aqueous media, solvothermal synthesis can be considered with organic solvents. On the other hand, in hydrothermal synthesis, some materials such as barium titanate or hydroxyapatite often can exhibit water related lattice defects or poor stoichiometry. For example, in barium titanate synthesis, hydroxyl ions substituted for oxygen ions generate barium ion vacancies, which degrade the dielectric properties; in hydroxyapatite synthesis, poor control of its calcium stoichiometry can be observed at presence of residual water (Suchanek *et al.*, 2004). In such cases, the problem of water incorporation can be overcome by either adjusting synthesis conditions or by using of solvothermal processing with nonaqueous solvents.

What are the Thermodynamics and Kinetic Variables for the Hydrothermal Synthesis?

Thermodynamics and kinetic variables are the key parameters that control the hydrothermal synthesis and hence final product characteristics. Therefore, these variables should be evaluated for the materials system in detail prior to hydrothermal synthesis. The thermodynamic process variables are concentration of reactants and additives, temperature and pH of solution (Suchanek and Riman, 2006). These parameters influence both reactor and crystallization kinetics. Crystal morphology and size can be modified by surfactants that can adsorb on specific crystallographic faces (Ring, 1996). Size of the crystals and phase purity can be controlled by varying temperature and concentration (Tuncolu *et al.*, 2015). Mass transport process and kinetics of chemical reactions generally increase in magnitude with increasing temperature. Mass transport process and chemical reaction rates generally increase in magnitude with increasing temperature. Since the kinematic viscosity for hydrothermal solution is approximately one order of magnitude lower in aqueous media than that for the gas phase. As a result, the hydrothermal synthesis conditions allow fast transport and high dissolution rates. Since the effect of pressure on the viscosity is significant only above the critical points of temperature and pressure, mass transport process and chemical reaction rates do not change with pressure during typical hydrothermal synthesis where usually temperature and pressure are below the critical values. The influence of pressure on the process is observed when the pressures exceeds 100 MPa and only at $T > 300^\circ\text{C}$ (Suchanek and Riman, 2012).

If the thermodynamic variables are limited to achieve the desired morphology and size control, nonthermodynamic variables such as stirring can be employed to enhance uniformity and the control over the particle formation process. Previous studies showed that the stirring speed can be varied to change morphology of the particles during the hydrothermal synthesis. Potential segregation problems that can be caused by concentration and temperature gradients or low heating rates can be prevented by stirring (Suchanek and Riman, 2012).

Powder Synthesis via Hydrothermal Method

In practice, a typical powder synthesis via hydrothermal method usually involves four important stages including selection of precursor, precipitation and gel formation, removal of undesired species, and hydrothermal reactions. Fig. 6 shows the steps of hydrothermal synthesis as a flow chart.

Selection of Precursors

In hydrothermal synthesis, many types of precursor such as aqueous solution of dissolved salts, aqueous dispersion of solids (suspensions), or precipitated colloidal dispersion (gel precursors) are used. Metal salts such as nitrates, chlorides, sulfates,

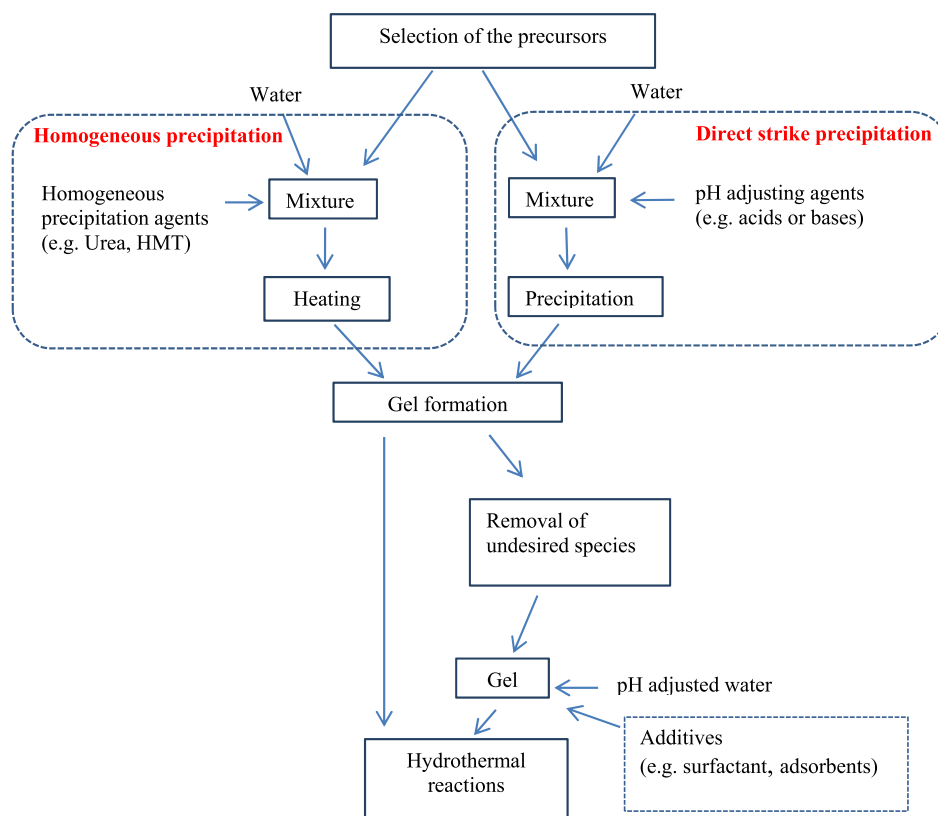


Fig. 6 Stages of the hydrothermal synthesis.

acetates, etc., have solubility in aqueous media and are generally used as a starting material. Inexpensive precursor compounds, easy to handle chemicals, and compounds that react cleanly to form the product are desired. When choosing metal salts as a starting material, the role of released ions on the purity, size, and morphology of synthesized powders should be considered. Detailed recommended features for different type of precursors to provide reasonable yields of product were already reported in previous studies (Adair *et al.*, 1988, 1998). In one of the earlier studies, the effect of the precursor type on the morphology of the hydrothermally synthesized ZnO particles was evaluated by using ZnCl_2 and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursors (Ozel *et al.*, 2016). It has been shown that during hydrothermal synthesis of ZnO particles, particle size and morphology of ZnO crystals were affected from precursor type and initial concentration that result in change in growth mechanisms such as classical nucleation growth or Ostwald ripening. When ZnCl_2 was used as precursor, agglomerated ellipsoidal rod like morphology was formed with classical nucleation growth mechanism whereas flower like morphology was obtained by using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor via Ostwald ripening for the initial concentration range between 0.25 and 1 M.

Preparation of Gels

In addition to solutions and dispersions, precipitated intermediate forms such as gels or sols are frequently used as precursors in hydrothermal synthesis. Gel formation can be achieved by either homogeneous precipitation or direct strike precipitation methods. In the homogeneous precipitation technique, the precipitation occurs homogeneously due to uniform pH change in the solution, where homogeneous precipitation agents such as urea and hexamethylenetetramine are activated by heating or using enzymes. On the other hand, in the direct strike precipitation method, direct addition of acids or bases into the solution results in precipitation. Since the pH change in the solution is much more uniform, the gel structure is usually more homogeneous in the homogeneous precipitation with respect to that of the direct strike precipitation. However, the direct strike precipitation is readily applicable and can be used at high molarity levels while the homogeneous precipitation is only suitable at relatively low concentrations.

Removal of Undesired Species

In hydrothermal synthesis, the chemical purity of the powder materials is higher due to starting with high purity precursors. During crystallization processes, growing crystals/crystallites tend to reject impurities present in the growth environment. Therefore, it is expected that impurities such as ions come from metal salts or pH adjusting agents remove from the system together with

the crystallization solution. However, some of them can be adsorbed to particle surface due to the colloidal interactions between particles and present ions. If high purity in the synthesis powder is the target to obtain excellent physical properties and high material performance, two steps hydrothermal synthesis must be considered to removing of undesired species comes from metal salts by washing with pH adjusted water rather than using one step hydrothermal synthesis that involves direct feeding of the gel prepared above and its supernatant to the autoclave without separating the gel and supernatant (Tuncolu *et al.*, 2015). For example, high purity Zn_2SnO_4 powder via hydrothermal method was synthesized by removing anions with pH adjusted water to obtain better ceramic target performance to develop thin film for transistor channels.

Additives

The varieties of synthesis precursors, mineralizers, and additives such as organics, complexing agents, surfactants, or adsorbates offer more room for design the material characteristics. Mineralizers are either inorganic or organic additives and are often used to adjust pH and improve solubility. In addition, there are other additives that are used to promote particle dispersion or control crystal morphology. Complexing agents can establish morphological control for particles. Surfactants and organic adsorbates prevent aggregation of particles (Adair *et al.*, 1988, 1998). Recently, in a review article, Shi *et al.* (2013) demonstrated utilization of four hydrothermal synthesis approaches (i.e., organic additive-assisted, organic additive and template free, template assisted, and substrate assisted hydrothermal syntheses) to control particle size and morphology effectively during the hydrothermal synthesis of inorganic semiconducting nanoparticles.

Mechanisms

Powder synthesis during hydrothermal process involves utilization of precursors. Such precursors can be sols, gels, or suspensions. Conversion of such precursors to powder can occur via either in situ transformation or dissolution-precipitation mechanisms. In the former, characteristics of the precursor can dictate the powder characteristics, whereas, in the latter mechanism, precursor is completely dissolved and then precipitates in powder form. Therefore, precursor characteristics are not transferred directly to the powder during this mechanism. It should also be noted that as mentioned above regardless of mechanisms, powder formation can still be kinetically controlled by chemical characteristics of the precursor such as ion release rate, formation of less soluble intermediate phases, etc. Besides precursor type and concentration, the morphology of the ZnO crystals is also influenced by pH of the solution and used alkaline solutions such as KOH, NaOH, or NH_4OH . For example, Podlogar *et al.* (2016) showed that the resulting morphology of the ZnO with different shapes and crystal sizes can be achieved by altering the pH of the suspension with NaOH solution after the precipitation. Depending on the ratio of $\text{Zn}^{2+}/\text{OH}^-$ ions in the starting solutions, rods or branched clusters composed of rod-like crystals were observed after the hydrothermal treatment of pure $\text{Zn}(\text{OH})_2$ at the highest ratio of $\text{Zn}^{2+}/\text{OH}^-$ ions of 2.5 whereas petal-like ZnO crystals precipitated from the solution and only coarsened at the expense of dissolved $\text{Zn}(\text{OH})_2$ by lowering the $\text{Zn}^{2+}/\text{OH}^-$ ion concentration and sphalerites-like ZnO precipitated at the lowest $\text{Zn}^{2+}/\text{OH}^-$ ratio of 0.1.

Final powder characteristics, particularly size and morphology, are directly determined by nucleation and growth kinetics during hydrothermal synthesis. According to the classical nucleation and growth theory, as cation concentration increases number of nuclei increases due to higher saturation and nucleation frequency and hence particle size decreases. However, if some of the nuclei are too small to survive, they dissolve and increase the saturation level so that other relatively larger nuclei grow at the expense of those fine nuclei. Such growth process is called Ostwald ripening. In such systems, particle size increases as cation concentration increases. It has been shown that there is a critical cation concentration (CCC) for the hydrothermal systems at which nucleation and growth mechanism changes. While the mechanism described by Ostwald ripening is effective at concentrations below the CCC, classical nucleation and growth theory is effective at concentrations greater than the CCC (Fig. 7). The CCC is a function of temperature, pH, pressure, concentrations of other ions and all other processing parameters that can affect solubility of the powder constituents in particular cations. Aciksari *et al.* (2016) showed that for hydrothermal synthesis of SnO_2 , the CCC was 0.1 M.

The growth process determines the final particle size during hydrothermal synthesis. The growth rate is controlled by either diffusion or interface reaction. The growth mechanism can be determined by using LSW (Lifshitz, Slyozov, and Wagner) theory where

$$r^n - r_0^n = kt$$

where, r is the average particle size at time t ; r_0 is the average initial particle radius; k is rate constant; t is the allowed time for the growth; and n is the constant describing the mechanism. If $n = 2$, the growth is controlled by interface reaction whereas if $n = 3$ then diffusion is the rate controlling mechanism. Since determination of the mechanism enables one to tailor the processing parameters to achieve the targeted particle characteristics, such understanding can also enhance the predictability of the final powder characteristics.

Modeling

Like all well-developed industrial processes, to make hydrothermal synthesis one of the most preferred and widely used powder synthesis methods by the industry, it should be possible to predict the product and its characteristics as a function of critical

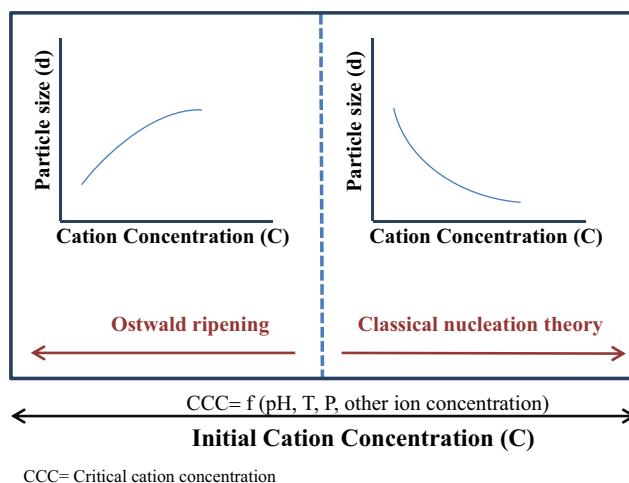


Fig. 7 Effect of the initial cation concentration on the growth mechanism during the hydrothermal systems.

processing parameters without requiring many trial and error type experiments. This can only be achieved by modeling hydrothermal processes where thermodynamic and kinetic effects play critical roles on the powder characteristics. Therefore, many researchers have involved in modeling hydrothermal synthesis so that it will be one of the mainstream particle synthesis technologies.

In early attempts, hydrothermal synthesis was modeled based on the thermodynamic criteria for ideal solutions to predict phase stability diagrams for the systems under investigation (Baes and Mesmer, 1976; Adair *et al.*, 1988, 1998). However, since the precursor concentrations and corresponding powder yields are not specified by such phase stability diagrams, it was proposed to use of yield diagrams that demonstrate specific synthesis conditions to achieve precipitation of the phase of interest, quantitatively (Lencka and Riman, 1993). Phase stability and yield diagrams are calculated based on a thermodynamic model that follows the Helgeson–Kirkham–Flowers–Tanger equation. This equation uses activity coefficients to predict standard state properties of aqueous species with a nonideal solution model. Methodology for generating phase stability and yield diagrams was discussed by Suchanek *et al.* (2004) in an earlier publication.

Although thermodynamically derived phase stability and yield diagrams are very critical to understand the roles of concentration, temperature, and pressure on the final phase, as well as effects of precursor type on final powder characteristics and the cost, there are other phenomena such as hydrothermal reaction rate, particle size, and morphology development that are controlled by kinetic factors. Therefore, in addition to thermodynamic modeling, kinetic models that can predict the reaction rate, particle size, and morphology should be developed. Although the thermodynamic models are mature and their high prediction capability for some specific systems has been successfully shown, the kinetic models are not mature enough yet and hence they still need to be improved. Accordingly, to engineer hydrothermal reactions after the phase stability and the yield diagrams are established for the materials of interest, hydrothermal experiments should be designed to test and validate the calculated diagrams and after the validation experiments the processing variable-phase maps can be generated and they can be used to predict hydrothermal reaction and crystallization kinetics (Suchanek and Riman, 2012).

References

- Aciksari, C., Tuncolu, İ.G., Suvaci, E., *et al.*, 2016. The role of cation concentration on particle formation mechanism during hydrothermal synthesis of nanosized tin oxide (SnO₂). *Journal of the Australian Ceramic Society* 52 (1), 60–71.
- Adair, J.H., Suvaci, E., 2000. Morphological control of particles. *Current Opinion in Colloid & Interface Science* 5 (1–2), 160–167.
- Adair, J.H., Suvaci, E., 2001. Submicron electroceramics powder by hydrothermal synthesis. In: Buschow, K.H.J., Cahn, R.W., Flemings, M.C., *et al.* (Eds.), *Encyclopedia of Materials: Science and Technology*, second ed. Amsterdam: Elsevier.
- Adair, J.H., Suvaci, E., Sindel, J., 2001. Surface and colloid chemistry. In: Buschow, K.H.J., Cahn, R.W., Flemings, M.C., *et al.* (Eds.), *Encyclopedia of Materials: Science and Technology*, second ed. Amsterdam: Elsevier.
- Adair, J.H., Denkwicz, R.P., Arriagada, F.J., Osseo-Asare, K., 1988. Precipitation and in-situ transformation in the hydrothermal synthesis of crystalline zirconium dioxide. In: Messing, G.L., Fuller, E.R., Hausner, H. (Eds.), *Ceramic transactions* 21. Ohio: American Ceramic Society Inc., pp. 135–145.
- Adair, J.H., Kerchner, J.A., Bell, N.S., Carasso, M.L., 1998. Application of chemical principles in the solution synthesis and processing of ceramic and metal particles. In: Serio, M.A., Gruen, D.M., Malhotra, R. (Eds.), *Synthesis and characterization of advanced materials*, ACS Symposium Series. Washington, D.C.: American Chemical Society, pp. 82–94.
- Baes, C.F., Mesmer, R.S., 1976. *The Hydrolysis of Cations*. New York: John Wiley & Sons.
- Byrappa, K., Yoshimura, M., 2001. *Handbook of Hydrothermal Technology*. Norwich, NY: William Andrew Inc.
- Darr, J.A., Zhang, J., Makwana, N.M., Weng, X., 2017. Continuous hydrothermal synthesis of inorganic nanoparticles: Applications and future directions. *Chemical Reviews* 117, 11125–11238.
- Dunne, P.W., Munn, A.S., Starkey, C.L., Huddle, T.A., Lester, E.H., 2015. Continuous-flow hydrothermal synthesis for the production of inorganic nanomaterials. *Philosophical Transactions of the Royal Society A* 373. (20150015).

- Feng, S.H., Li, G.H., 2017. *Modern Inorganic Synthetic Chemistry: Hydrothermal and Solvothermal Syntheses*. Amsterdam: Elsevier.
- Frank, E.U., 1978. Experimental investigations of fluids at high pressures and elevated temperatures. *High Pressure Chemistry* 221–257.
- Lencka, M.M., Riman, R.E., 1993. Synthesis of lead titanate: Thermodynamic modelling and experimental verification. *Journal of the American Ceramic Society* 76 (10), 2649–2659.
- Li, J., Wu, Q., Wu, J., 2015. Synthesis of nanoparticles via solvothermal and hydrothermal methods. In: Aliofkhazraei, M. (Ed.), *Handbook of Nanoparticles*. Springer International Publishing.
- Messing, G.L., Trolter-McKinstry, S., Sabolsky, E.M., *et al.*, 2004. Templated grain growth of textured piezoelectric ceramics. *Critical Reviews in Solid State and Materials Sciences* 29 (2), 45–96.
- Ozel, E., Tuncolu, I.G., Açikarı, C., Suvacı, E., 2016. Effect of precursor type on zinc oxide formation and morphology development during hydrothermal synthesis. *Hittite Journal of Science & Engineering* 3 (2), 73–80.
- Podlogar, M., Rečnik, A., Yilmazoglu, G., *et al.*, 2016. The role of hydrothermal pathways in the evolution of the morphology of ZnO crystals. *Ceramics International* 42, 15358–15366.
- Ring, T., 1996. *Fundamentals of Ceramic Powder Processing and Synthesis*. Academic Press.
- Shandilya, M., Rai, R., Singh, J., 2016. Review: Hydrothermal technology for smart materials. *Advances in Applied Ceramics* 115 (6), 354–376.
- Shi, W., Song, S., Zhang, H., 2013. Hydrothermal synthetic strategies of inorganic semiconducting nanostructures. *Chemical Society Reviews* 42, 5714.
- Suchanek, W.L., Riman, R.E., 2006. Hydrothermal synthesis of advanced ceramic powders. *Advances in Science and Technology* 45, 184–193.
- Suchanek, W.L., Riman, R.E., 2012. Hydrothermal routes to advanced ceramic powders and materials. In: Riedel, R., Chen, I.W. (Eds.), *Ceramics Science and Technology: Synthesis and Processing*, first ed. Wiley-VCH Verlag GmbH & Co. KGaA.
- Suchanek, W.L., Lencka, M.M., Riman, R.E., 2004. Hydrothermal synthesis of ceramic materials. In: Palmer, D.A., Fernández-Prini, R., Harvey, A.H. (Eds.), *Aqueous Systems at Elevated Temperatures and Pressures: Physical Chemistry in Water, Steam and Hydrothermal Solutions*. Amsterdam: Elsevier, pp. 717–744.
- Suvacı, E., Ozer, I.O., 2005. Processing of textured zinc oxide varistors via templated grain growth. *Journal of the European Ceramic Society* 25 (9), 1663–1673.
- Tuncolu, I.G., Acikarı, C., Suvacı, E., *et al.*, 2015. Synthesis of Zn₂SnO₄ powders via hydrothermal method for ceramic targets. *Journal of the European Ceramic Society* 35, 3885–3892.
- Yang, G., Park, S.J., 2019. Conventional and microwave hydrothermal synthesis and application of functional materials: A Review. *Materials* 12, 1177.
- Zhao, Y., Li, X., Yan, B., *et al.*, 2016. Recent developments and understanding of novel mixed transition-metal oxides as anodes in lithium ion batteries. *Advanced Energy Materials* 6, 1502175.

Ultrasonic Sprayed Aerosol for Ultrafine Ceramic Powder Synthesis

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Introduction

The control of the final ceramic microstructure depends strongly on the characteristics of starting powders like chemical composition and particle size distribution. To favor the multi-functional ceramics rise, development of new composite powders with high chemical purity and controlled particle size distribution is necessary. For areas such as biomedical, electronics, catalysis, energy storage etc., the morphology of the powder should be designed with different properties in the core or at the surface of the grain. In this case, the synthesis processes must be able to lead to original architectures such as core-shell structures.

To reach high chemical purity and ultrafine particle size, numerous dedicated synthesis methods have been developed. These processes can be classified into three categories (Ring, 1996): solid, liquid and gaseous routes. In the case of solid phase reaction synthesis, three types of chemical reaction are referenced; oxidation or reduction of a solid, thermal decomposition of a solid, and solid state reaction between two types of solid, and in particular, mechanical alloying methods. Gaseous phase ceramic powder synthesis routes consist in evaporation-condensation and chemical reactions in the gas phase. Concerning liquid phase synthesis, six different methods can be cited: drying of a liquid, precipitation, reactions of a liquid metal melt with a gas, hydrothermal treatment, sol-gel synthesis (for synthesis of oxide ceramics), and Polymer Derived Ceramics route (PDC, for non-oxide ceramics). Solid state syntheses of ceramic powders are known for the difficulty to obtain in the same time pure powders without residual species and ultrafine particle size. For gas phase synthesis, the major disadvantage lies in the use of expensive and sometimes dangerous gaseous species. Moreover, for some materials it is not always possible to find a gaseous precursor, which narrows the range of achievable compositions.

Liquid routes allow overcoming these drawbacks: there is a huge number of available precursors, whether they are liquids themselves or they consist in a solution (salts, organometallics). Liquid phase mixing ensures the homogeneity of the precursor media, and as most liquid processes do not induce pollution, the purity of final products is generally the consequence of the initial purity of the precursors. Dedicated precursors can also be synthesized by chemical engineering: the PDC or sol-gel routes rely on the synthesis of organometallic precursors (sol or polymer), with accurate composition and viscosity, which are then heat-treated to form oxide or non-oxide ceramics with tunable properties according to the operating conditions (synthesis and/or thermal treatment). Furthermore, the possibility to obtain multi-element powders and original architectures such as core-shell structures by liquid state processes paves the way to the development of novel materials with tailored original properties. Beyond powders, the versatility of PDC and sol-gel routes has been demonstrated through numerous investigations showing their ability to synthesize films, fibers, monoliths and composites.

The direct thermal treatment (pyrolysis) of the liquid precursor cannot lead to a homogenous and ultrafine powder. To maintain the initial homogeneity of the precursor mixture in the final product, and to obtain small particles, the liquid phase has to be divided in small droplets that can be further heat treated separately (the droplet is the reactor) or vaporized (similarly to gas phase processes). In this context, the spray pyrolysis process, also called aerosol decomposition, is a technique in which a precursor solution (e.g., salt or mixed salts solution, organometallics, liquid polymers, colloidal suspension) is dispersed, via an atomizer or a nebulizer, into fine droplets (aerosol), which further undergo in-flight thermal treatment and experience physical/chemical phenomena including evaporation, precipitation, drying, thermolysis or decomposition into inorganic phases (oxides or non-oxides), sometimes in-flight sintering, to produce ultrafine or nanometric powders in one single step. The resulting solid particles form a dry aerosol carried by the process gas to collectors downstream where filters can separate the powders from the gaseous phase. These powders can then be collected directly in dry route, or solvent can be added in order to form a slurry for nanoparticles safety issues. These flow processes operate continuously and are very suitable for upscaling to industrial level. Some of them are already used to produce tons of materials per year (Ulrich, 1984; Gutsch *et al.*, 2002). Laboratory-scale processes can easily produce several tens of grams per hour of nanopowders.

Spray pyrolysis processes, also called aerosol-assisted vapor phase syntheses, are known to lead to powder grain size lower than 1 μm as it was demonstrated for TiO_2 , Al_2O_3 , TaC or GaN for example (Janik *et al.*, 2006; Baseta and Biscans, 2007; Cheng *et al.*, 2017). Spray pyrolysis processes differ in the energy source used for the in-flight thermal treatment step of the aerosol. The most used ones are the combustion flame and the furnace, secondarily the laser and the plasma (Baseta and Biscans, 2007; Cauchetier *et al.*, 1991). Fewer studies are also devoted to microwave assisted spray pyrolysis (Li *et al.*, 2016). The ceramization behavior of many precursors was studied intensively for each experimental set-up aiming to a detailed description of the chemical reactions involved. However, the comparison between the different methods is difficult because most often, different sets of precursors were used when different techniques were applied.

The combustion flame (flame spray pyrolysis process) is very widely used for oxide nanoparticles synthesis, even if this process can be used for metallic nanoparticles as well (Athanassiou *et al.*, 2010). Most of the time the spray is generated by pneumatic nebulizer rather than with ultrasonic device and this process is very rarely used for non-oxide ceramics. Several interesting review

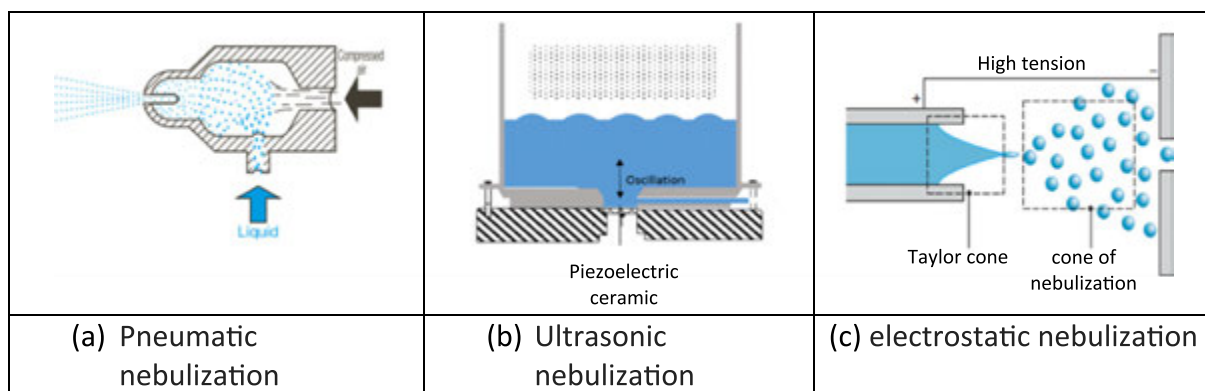


Fig. 1 Principle of operation of different methods of nebulization. Reproduced from Le Moyne, L., 2010. Atomization, Pulvérisation et Aérosols. Techniques Ingénieur.

papers can be found in the literature (Strobel and Pratsinis, 2007; Teoh *et al.*, 2010). Plasma source can be operated at very high temperatures that enable the use of cheap solid precursors. The liquid route, though existing (Arita *et al.*, 2017), is thus less extensively documented in the literature where most of papers dedicated to nanopowders synthesis deal with inductively coupled plasma torch used to vaporize raw powders furtherly condensed into nanoparticles (Leparoux *et al.*, 2005). Furnace (thermal spray pyrolysis) and laser (laser spray pyrolysis) processes, operating at lower temperatures and/or with shorter residence times, are more suitable to highlight the use of ultrasonic generated aerosol because they take advantage of the small droplet size. Thus these two processes were chosen to be presented in this paper.

Nebulization Techniques

Aerosol Generation

In the spray pyrolysis process, different atomization systems can be used. One of the best known is the pneumatic nebulization which consists in destabilizing the liquid jet with a flow of gas under pressure (Fig. 1(a)), thus forming droplets. In the ultrasonic nebulization process, the aerosol results from the vibrations imparted to a liquid layer by a piezoelectric material (Fig. 1(b)): the waves formed by this vibration become unstable and produce the ejection of drops. Finally, the electrostatic nebulization (Fig. 1(c)) consists in applying a constant electric field to a jet of liquid so as to reduce the effective surface tension of the liquid and cause the detachment of the drops. These methods differ in the size distribution of the drops formed, the rate at which the drops are ejected from the liquid volume and the nebulization rate (Messing *et al.*, 1993).

One of the main disadvantages of atomizing a liquid by conventional means such as pneumatic atomization is the difficulty to obtain narrow droplet size distributions. In many case, when large droplets issues is critical, a cyclone has to be used at the outlet of the nebulizer to cut the larger part of the size distribution. The consequence is a decrease in production rate. The other drawback of pneumatic nebulizer is the resulting carrier gas flow. Indeed, the inlet gas pressure cannot be decreased too low as the gas is the driving force for nebulization. Such high carrier gas flow rates induce shorter residence time in the reaction zone, which can impede the precursor decomposition yield in fast processes as laser spray pyrolysis for example. On the other hand, ultrasonic nebulization appears as an alternative for the production of very small drops which size can be tuned by adapting mainly the ultrasound frequency. These generators produce generally narrower size distributions (Mwakikunga, 2014; Barba *et al.*, 2009; Blandenet *et al.*, 1981). As the aerosol is produced by the piezoelectric transducer, the carrier gas flow can be tuned independently from the droplet production rate, and thus can be set to lower values when compared to pneumatic nebulization. Finally electrostatic nebulization consists of applying a constant electric field to a liquid jet and causing the production of drops. This latter process is rarely used for powders synthesis and thus will not be detailed here.

In the case of ultrasonic nebulization, ultrasound waves are applied to a film or a volume of liquid by a piezoelectric actuator in order to cause liquid fragmentation into fine droplets. The formation of a spray from a liquid by ultrasound waves is supposed to be caused by two principal mechanisms: the capillary wave instability development at the liquid surface and the cavitation phenomenon. The droplet formation due to capillary waves is based on Taylor's instability theory which explains the instability apparition and development at the interface between two fluids with different densities: this phenomenon appears at relatively low frequency of ultrasound (20–100 kHz) and is identified by the formation of a well-structured wave pattern on the liquid surface, observed by some authors (Lang, 1962; Yule and Al-Suleimani, 2000; Avvaru *et al.*, 2006; Ramisetty *et al.*, 2013). The waves produce drops from the ejection of their peaks when they are destabilized (Rajan and Pandit, 2001). The cavitation phenomenon appears at higher frequencies (0.1–5 MHz), and is caused by local changes in pressure, due to high frequency waves through the liquid, that forms vapor cavities in the liquid volume until their implosion causes liquid rupture with droplet ejection (Franc and Michel, 2004).

Modelization

To understand the spray pyrolysis process, the understanding of each step is important and in particular, the relationship between the size distribution of the aerosol produced by the nebulizer device and the synthesized powder characteristics. The first step of the spray pyrolysis process is the generation of the used liquid precursor aerosol. This step consists in ultrasonic nebulization of a volume of liquid, forming a mist which is then transported by a gas to the pyrolysis reactor. The size of the drops that constitute the fog varies depending on the characteristics of the liquid to be sprayed, including its viscosity and surface tension, and the frequency and power of the ultrasound delivered by the generator. The aerosol droplet size distributions can be estimated experimentally with a shadowgraph imaging device. All size distributions show a bimodal shape (around 3 and 9 μm) that evolves between the different measurements locations, but remains present until the reactor entrance.

An empiric modeling of the mean particle diameter depending on the precursor physical properties and nebulizer device can then be carried out by adapting correlations laws proposed in the literature to the specific device and liquids used in the study of Munoz *et al.* (2018). It allowed defining an initial state of the precursor before entering in the reaction zone corresponding to the decomposition and recombination steps, establishing a clearer relationship between the aerosol and final powders characteristics and contributing to understand the mechanisms involved in the process.

To improve the agreement of the average diameter obtained by correlation laws with experimental values, dimensionless numbers have been adapted to the system and used to obtain the coefficients for the proposed correlation. The Ohnesorge number was considered in its original expression (noted Oh' , Eq. (1)). The Weber number (noted We') and the intensity number (noted In') were also reformulated (Eqs. (2) and (4)) including parameters like the thickness and volume of liquid and the power applied to the aerosol generator:

$$Oh' = \frac{\eta}{(\rho \sigma e)^{\frac{1}{2}}} \quad (1)$$

$$We' = \frac{\rho A m^2 f^2 e}{\sigma} \quad (2)$$

$$In' = \frac{P}{\rho V A m^2 f^3} \quad (3)$$

where e is the liquid thickness (m), P the power applied to the aerosol generator (W), V the liquid volume (m^3), λ the wavelength (m), σ the surface tension (N m^{-1}), ρ the density (kg m^{-3}), f the ultrasound frequency f (s^{-1}), η the viscosity of the liquid (Pa s), $A m$ the amplitude of the surface waves (m).

The selected dimensionless numbers expressions were then used to calculate the new exponents of the correlation law still considering the structure of Avvaru's one. The obtained expression is shown in Eq. (4).

$$d = 1.2765 \left[\left(\frac{\pi \sigma}{\rho f^2} \right)^{\frac{1}{3}} + 9.48 \exp^{-7} (We')^{0.347} (Oh')^{0.435} (In')^{-1.65} \right] \quad (4)$$

Observing both terms of the expression 4 separately, the first one, that only considers the term of capillary waves, describes the bigger drops population. The second one, that represents the cavitation term through the association of dimensionless numbers, describes the smaller population of the bimodal distribution of formed droplets. This equation is valid for density ranging between 774 and 998 kg m^{-3} , the surface tension between 0.018 and 0.073 mN m^{-1} and the viscosity in the range 0.62–1.2 mPa s .

The curves of droplets size distribution obtained in this part of the study (evaporation, drops-wall interaction, coalescence) are shown in Fig. 2. Its comparison to experimental results in three positions of measure was also traced. The experimental evolution of drops size distributions for the liquid shows a slight variation between three positions of measure, result that is reproduced by simulated curves. Otherwise, the width of distributions matches between experimental and simulated results and different populations of drops are well identified in both cases.

Description of a Generic Spray Pyrolysis Set-Up

The generic set-up detailed in this part was developed in order to work under inert or reactive atmosphere to reach non-oxide or oxide compositions. This process can be divided into three main parts (Fig. 3):

- (1) Precursor aerosol generation,
- (2) Conversion of the precursor into ceramic (pyrolysis),
- (3) Powders collection (filtration).

Aerosol Generator Device

The generator used is composed of a glass chamber seated on a metallic support containing an ultrasonic transducer. A water circulation between the transducer and a plastic membrane allows regulating the temperature of the precursor solution filled over the membrane, especially to ensure the reproducibility of the experiments since the surface tension and the viscosity of liquids

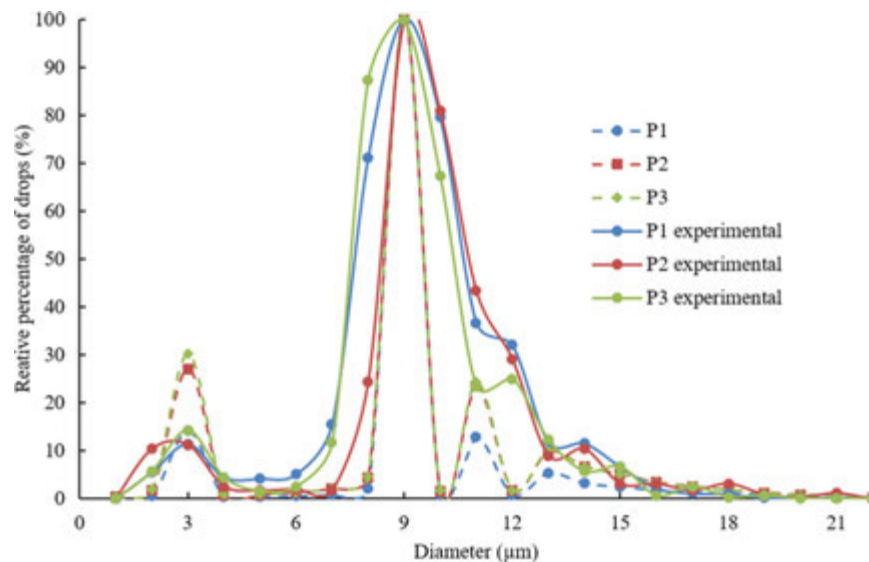


Fig. 2 Drop size distributions considering all phenomena and compared to experimental results in each position of measure.

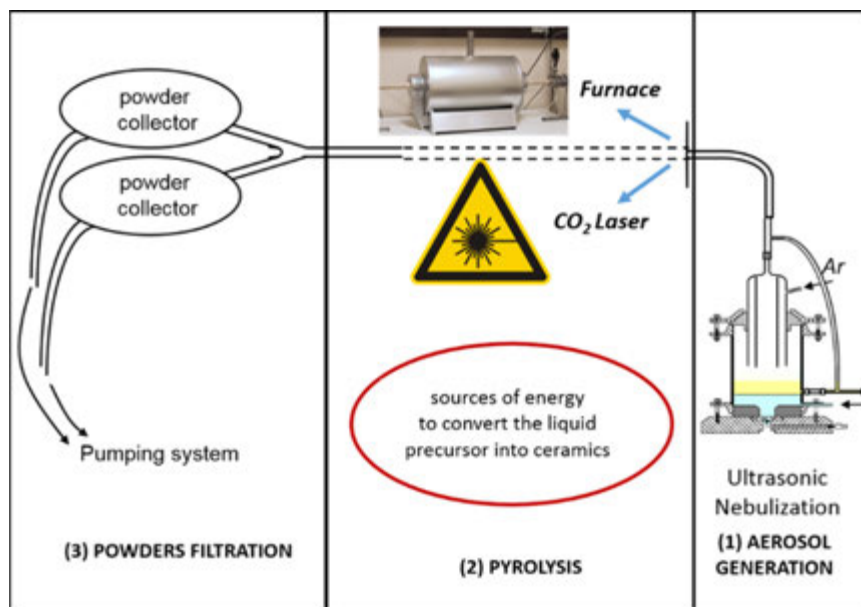


Fig. 3 Schematic representation of spray pyrolysis process.

strongly evolve with the temperature. The transducer is a barium titanate ceramic. The frequency and power alimentations are in the order of a few hundred kHz and in the 0–170 W range respectively. These values have to be adjusted according to the precursor rheological properties and to the required precursor feeding rate. There are many commercially available aerosol generators with different operating frequencies and powers. The continuous precursor feeding is controlled by a peristaltic pump to keep the liquid level constant into the aerosol chamber. The aerosol chamber is directly connected to the pyrolysis set-up. Once the aerosol formed at the surface of the liquid, it can be carried to the reaction chamber by a neutral or reactive gas flow. This carrier gas flow rate as well as ultrasound power enables the control of the precursor feeding rate.

Pyrolysis Set-Up

As discussed before, two different pyrolysis techniques are preferred, namely thermal spray pyrolysis (using a furnace as energy source for the reaction) and laser spray pyrolysis (using a laser as energy source).

The thermal spray pyrolysis process (Zhang *et al.*, 1990; Song *et al.*, 2004; Salles *et al.*, 2007) is a versatile and simple method for the production of oxide powders and also adaptable to the production of non-oxide powders. Almost any kind of liquid precursor can be

Table 1 Comparison between laser and furnace pyrolysis

	Laser Pyrolysis	Furnace Pyrolysis
Source of energy	CO ₂ laser	Furnace
Temperature control	500–2000°C ^a	800–1500°C
Residence time of the species in the reaction zone	<70 ms	Between 0.5 and 1.5 s

^aThe temperature is not regulated but results from the absorption of the beam by the reaction medium.

used, as long as it can be nebulized. The basic principle is the evaporation/reaction of the aerosol liquid droplets by in-flight heat treatment in an oven, aiming at the formation of ceramic powders through different phenomena that will be described in the next section.

In a conventional thermal spray pyrolysis set-up, the furnace consists in a ceramic tube where the precursor solution can be sprayed with a neutral or reactive carrier gas. The precursor micro-droplets are mainly heated by radiation transfers from the walls (Salles *et al.*, 2007). Typical reaction temperatures are in the 800–1500°C range, with residence time in the order of magnitude of 1 s depending on the carrier gas flow and the length of the isothermal zone of the furnace.

The Laser spray pyrolysis process (Cannon *et al.*, 1982; Cauchetier *et al.*, 1987) is based on the interaction between a CO₂ laser beam emitting at 10.6 µm and the precursor, or with a sensitizer when the precursor does not absorb the laser wavelength itself. Because of the low-energy photons, there is no photodissociation but the temperature upon absorption raises high enough to decompose the molecules: it is actually a pyrolysis effect. This process can be seen as very versatile, but its efficiency strongly depends on the precursor. When this latter does not absorb the laser, which is the case for the majority of materials, a sensitizer such as NH₃, C₂H₄ or SF₆ has to be added, leading to low decomposition yield and possible powder contamination. Moreover, the short residence time, which is an advantage when small nanoparticles are wanted, requires small droplets in the aerosol to ensure complete precursor decomposition. In that case ultrasonic aerosol generator is almost mandatory, and as will be discussed in the aerosol generation section, this means low concentration solutions for precursors and thus low production rates. For example, production rate at the lab scale for SiC nanopowders can easily reach several tens of grams per hour because the precursors are gaseous and at least one of them (SiH₄) absorbs directly the laser radiation. On the opposite, some compositions requiring liquid media with low solubility of the salts hardly reach few hundreds of milligrams per hour.

Despite of these drawbacks, laser pyrolysis enables an accurate control over the nanoparticles size under 10 nm and over the crystallinity of the materials. Residence time for the precursor is indeed very short due to the limited interaction region with the beam. This latter can be focused to decrease the interaction zone dimension down to a few µm, leading to residence times as short as few milliseconds. This residence time can also be tuned through total gas flow rate and aerosol inlet nozzle diameter. Moreover, the laser can be operated continuously (aiming at high production rate) or in a pulsed mode that enables the control of the amount of energy delivered to the reaction. Together with other conventional spray process parameters, it allows producing either amorphous particles or single-crystalline ones (Sublemontier *et al.*, 2011).

A typical laser pyrolysis reactor consists in a vacuum-type chamber with two KCl or ZnSe windows (transparent at 10.6 µm) that allow the laser beam to cross the chamber. At the center of this chamber, the precursor aerosol is introduced through a nozzle perpendicularly to the laser beam. The reaction is confined in the center of the reactor by a flow of inert gas (argon) concentric to the precursor nozzle. The laser power is usually in the 100–2000 W range. The reaction temperatures depend on laser parameters, but also on the absorption properties of the reaction zone (concentration and absorption coefficient of the absorbing species). The resulting temperatures are typically in the 600–2000°C range.

In conclusion, thermal spray pyrolysis and laser spray pyrolysis appear as complementary methods, each of them being able to synthesize oxide or non-oxide complex nanomaterials in weighable amounts. When the very small sizes are not mandatory, when no absorbing precursor is available, or when this latter requires long residence time to be completely reacted (PDC routes for example), use of a furnace should be selected. When the final grain size should be smaller than 50 nm and more generally for silicon bases non oxide ceramics, laser pyrolysis is a process of choice.

Table 1 summarizes the characteristics of the laser and the furnace pyrolysis.

Powder Traps

The aerosol pyrolysis can lead to powders with primary particles size much smaller than 100 nm. They can nevertheless efficiently be trapped using a micro-porous filters (fiber fabrics, porous metallic or ceramic tubes...) because these primary particles are agglomerated and form larger objects.

Fig. 4 resumes the properties which can be changed by varying parameters during the ceramic synthesis by spray pyrolysis. The impact of these parameters will be treated in different examples in the last paragraph of this document.

Particles Growth Phenomena

Several mechanisms can be experienced by the droplets when they enter the heated zone of the reactor, leading to the formation of solid particles. Depending on these mechanisms, the morphology of the obtained products will be strongly affected. When properly controlled, aerosol processes actually offer the possibility to tune the shape and structure of the obtained products from

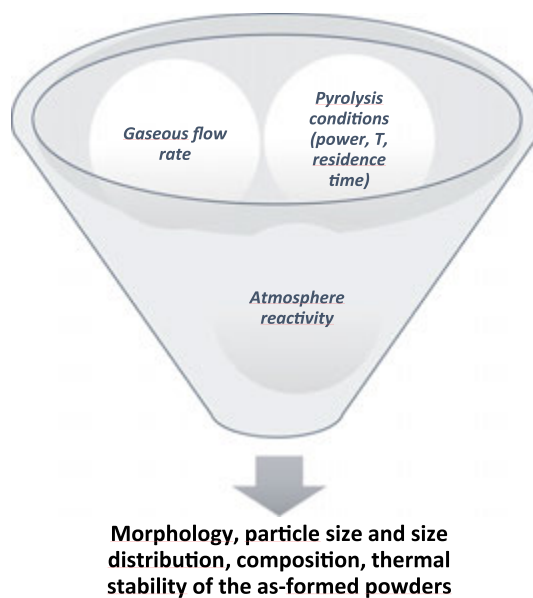


Fig. 4 Evolution of materials features (at the bottom part) with the parameters adjusted (at the top of the diagram) during pyrolysis.

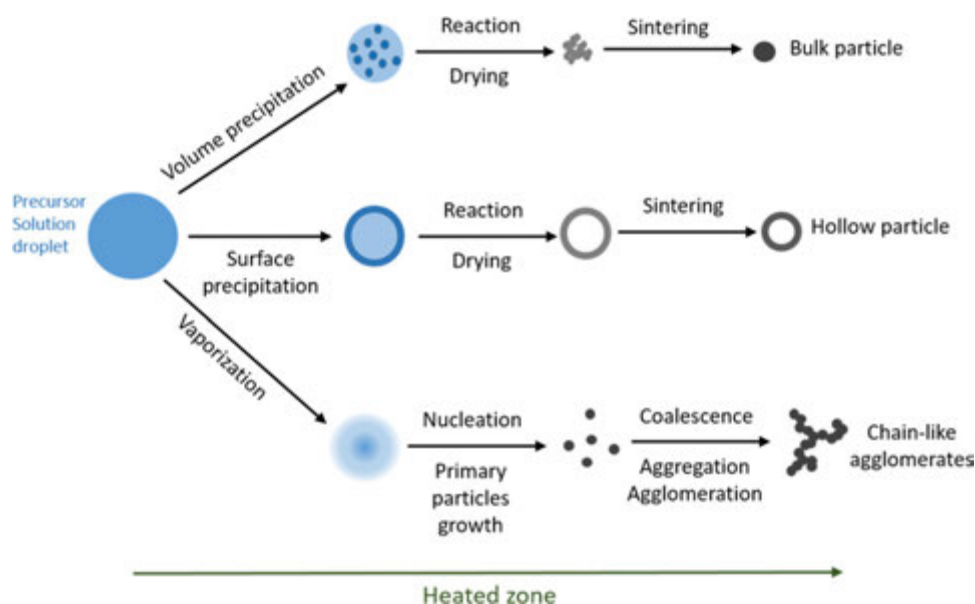


Fig. 5 Main particles formation mechanisms encountered in spray pyrolysis.

chain-like type agglomerated nanoparticles to nanostructured micron-sized objects showing different morphologies (dense, porous, hollow).

The most generic and versatile approach concerns the use of a solution prepared from one or several metal salts or metalorganic dissolved in water or in an organic solvent. In this case, one considers the formation of one particle per droplet following mechanisms well described by [Messing *et al.* \(1993\)](#). As depicted in [Fig. 5](#), when entering the hot zone, the solvent vaporizes and the solute starts to condensate. Depending on solvent and salt properties or process parameters, this condensation can take place in volume or at the surface of the droplet. In the first case, the precipitate forms a relatively dense solid where the thermal reaction can take place and lead to the novel phase. A sintering phenomenon allows decreasing the porosity in this solid and leads to the final particle with a size within the micron range. In the second case, the vaporized solvent flows through the porous precipitate at the surface of the droplet, leading to a hollow solid particle at the end of the drying stage. Thermal reaction takes place in this shell, leading to hollow final particles. When the heating rate of the solvent is too high or the permeability of the shell is too low, an increase in pressure inside the drying droplet can break the shell and lead to irregular morphology of particles. In both cases the final particle size depends on the initial droplet size and the solution concentration.

Table 2 Spray pyrolysis parameters

<i>Solution conc. C (mol L⁻¹)</i>	<i>Atomizing frequency f (kHz)</i>	<i>Gas flow rate Q (L min⁻¹)</i>	<i>Furnace temperature T (°C)</i>
0.0025	850	3	400
0.025	2500	6	1000

When two different species are mixed in the solution, the precipitation step can be homogeneous (both precursors precipitate in volume or at the surface at the same time), or heterogeneous. In this latter case, core-shell structures can be obtained with a core constituted by the material that condensates first. More advanced structures (for example with controlled porosity) can be achieved using surfactants, as will be presented later in the examples section.

Nevertheless, the “one particle per droplet” or droplet-to-particle rule is no longer relevant when the precursor is completely vaporized. This happens when a liquid precursor is employed (for example titanium isopropoxide or tetrachloride for titanium based compounds), or when the process temperature and the heating rate are high enough to vaporize the precursor together with solvent before the pyrolysis reaction takes place in a condensed solute. Such conditions are frequently met in laser, plasma or flame spray processes, and lead to the formation of small nanoparticles agglomerated in poorly dense chain-like structures. In this case, the growth mechanisms are similar to the ones encountered in gas-phase processes and rely on nucleation and growth phenomena (Flagan and Lunden, 2007): condensation of the supersaturated gaseous phase upon fast cooling, growth by coagulation, aggregation and finally agglomeration during the temperature drop. Depending on the nucleation rate and on the residence time in the hottest reaction zone (coagulation phenomenon), the primary particles size in the agglomerates can be as small as few nanometers or reach several hundreds of nanometers. When very small nanoparticles are required, this reaction path should be favored versus droplet-to-particle mechanisms.

Combined or different mechanisms are reported in the literature for more specific aerosol processes using for example solid particles suspensions as precursors, combined liquid and gaseous precursors or sol-gel derivated processes (Debecker *et al.*, 2018). These more specific approaches will not be presented here.

The next section will present several examples taking advantage of these multiple growth phenomena to obtain advanced ceramic powders.

Examples

Control of Nanopowders Size and Composition

In this part, several examples are presented to illustrate the effect of experimental parameters of the spray pyrolysis processes (nature of precursors, pyrolysis temperature, nature of the pyrolysis atmosphere etc.) on the particle size and size distribution, and to demonstrate the ability of these processes to produce nanopowders with homogeneous complex compositions and controlled crystalline phases.

Nanopowders synthesis in the GdCeO system (Goulart and Djurado, 2013)

In this study, the authors are interested in synthesizing gadolinia-doped ceria nanostructured particles $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (CGO), with a control of the morphology of the as-formed powders. These materials are quite useful in the field of fuel cells (SOFC).

Spray pyrolysis of nitrate-based precursors was used to fabricate fine and polycrystalline $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (CGO) powders with controlled microstructure in a one-step process varying four spray-pyrolysis parameters: precursor solution concentration, atomizing frequency, carrier gas flow rate, and pyrolysis temperature, as shown in the Table 2.

The authors have shown that the particle morphology is mainly affected by the concentration of the precursor solution and the furnace temperature, and it is not dependent on the frequency of the ultrasonic atomizer and the carrier gas flow rate. All the powders obtained are generally composed of ovoid and/or spherical shaped and smooth particles, as shown in Fig. 6. In fact these submicron size particles have a hard-aggregated structure of primary particles with nanometer size that will be referred as crystallites.

The authors have performed an interesting statistical analysis to quantify the influences of the main process parameters and their interactions on the particle size, particle size distribution and crystallite size. Ovoid, dense and monodispersed particles with a peak diameter < 150 nm are obtained in one step at only 400°C by reducing the precursor solution concentration to 0.0025 mol L⁻¹ for a high atomizing frequency of 2500 kHz whatever is the flow rate. In these conditions, particles are found to be smaller with a narrower distribution. Porous and uneven particles are obtained when the pyrolysis temperature and concentration of precursor solution are increased whatever the flow rate and the frequency. The combination of both low pyrolysis temperature and low precursor solution concentration strongly affects the synthesis towards a smaller mean particle size, narrower particle size distribution and smaller mean size of the primary particles. Single phase cubic fluorite CGO was detected by XRD. The mean size of the primary particles decreased from 21.2 to 3.7 nm as the pyrolysis temperature changed from 1000 to 400°C while the precursor solution concentration was ten times smaller for the same atomizing frequency and flow rate.

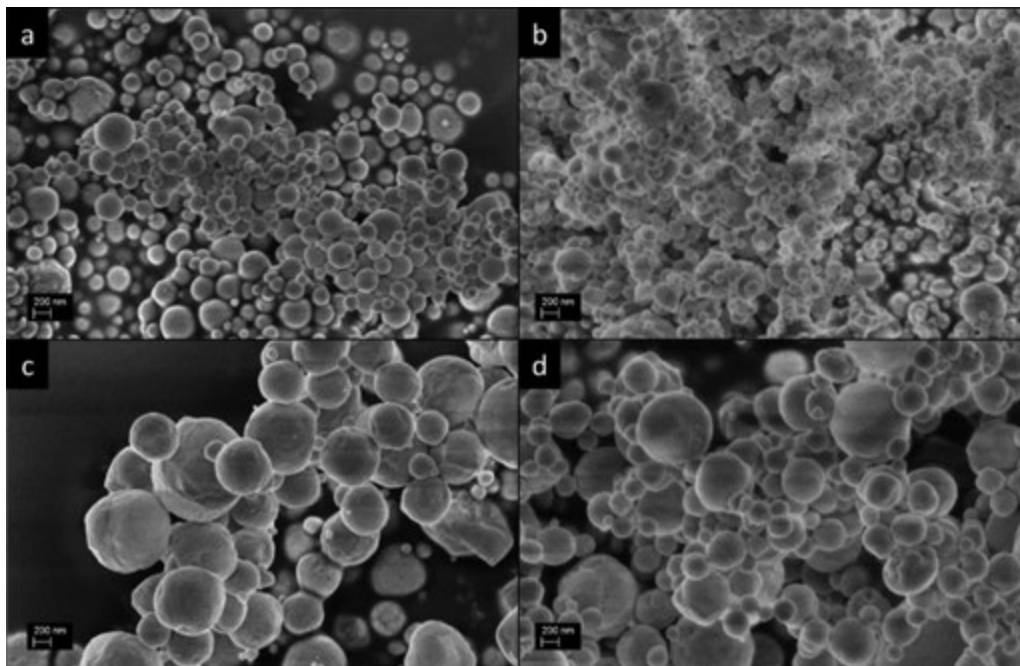


Fig. 6 FE-SEM images of GdO powders (a) $C = 0.0025 \text{ mol L}^{-1}$, $F = 850 \text{ kHz}$, $T = 400^\circ\text{C}$, $Q = 3 \text{ L min}^{-1}$; (b) $C = 0.0025 \text{ mol L}^{-1}$, $F = 2500 \text{ kHz}$, $T = 400^\circ\text{C}$, $Q = 6 \text{ L min}^{-1}$; (c) $C = 0.025 \text{ mol L}^{-1}$, $F = 850 \text{ kHz}$, $T = 1000^\circ\text{C}$, $Q = 6 \text{ L min}^{-1}$; (d) $C = 0.025 \text{ mol L}^{-1}$, $F = 2500 \text{ kHz}$, $T = 1000^\circ\text{C}$, $Q = 6 \text{ L min}^{-1}$. Reproduced from Goulart, C., Djurado, E., 2013. Synthesis and sintering of Gd-doped CeO_2 nanopowders prepared by ultrasonic spray pyrolysis. *Journal of the European Ceramic Society* 33 (4), 769–778.

Grain morphology control through the precursor solution in laser spray pyrolysis: Example of C/N/Fe nanoparticles

Growing interest for proton-exchange membrane fuel cells (PEMFC) motivates the development of new catalysts for the oxygen reduction reaction (ORR) without noble metals such as Pt. In this context, recent work was published dealing with C/N/Fe nanoparticles synthesis by laser spray pyrolysis (Perez *et al.*, 2018). Indeed, peculiar structures of carbon containing nitrogen in specific configuration show relevant activity towards ORR. Moreover, the presence of Fe during the synthesis of these C/N materials appears to favor the formation of the nitrogen sites with ORR activity.

In this paper, two different types of liquid solutions were used, both being sprayed to the reactor by ultrasonic device, with a strong effect on the final morphology of the obtained particles. The first type is a mixture of pyridine ($\text{C}_5\text{H}_5\text{N}$, acting as C and N source) with a suspension of goethite (FeOOH) nanoparticles in ethanol as Fe source. The second type is a solution of Fe acetylacetonate ($\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$) in pyridine. In both case precursors were sprayed using an ultrasonic device and the resulting aerosol was carried to the reaction chamber by a gaseous flow made of a mixture of argon and NH_3 . This carrier gas flow ratio $\text{NH}_3/(\text{Ar} + \text{NH}_3)$ was found to strongly influence the electronic structure of the products as probed by XPS, and consequently the ORR performance as well. Indeed, in such synthesis NH_3 has several roles: laser absorbent (thus effect on reaction temperature), N source, nitriding effect on Fe favoring nitride phases, and corrosive effect on C generating porosity. The nature of the solution appears to have its influence on the final performance too: an important effect on the powder morphology is observed (see Fig. 7). Goethite based suspension seems to favor droplet-to-particle mechanisms with the formation of large spherical objects, while the solution approach seems to lead to vapor phase growth phenomena with a main population of small nanoparticles forming fractal-like poorly dense agglomerates.

Towards complex crystalline structures: Nasicon nanopowders

Development of post-Lithium batteries such as Sodium-ion batteries requires research activity on electrodes materials able to withstand the rapid insertion of the “large” Na^+ ion. In this context, large interstitial space structures such as the ones encountered in layered transition sodium oxides materials are of great interest. Among these materials, sodium super ionic conductors (Nasicon) with generic formula $\text{Na}_x\text{M}_2(\text{PO}_4)_3$ ($M = \text{Ti}, \text{V}, \dots$) draw peculiar interest. In a 2015 article, promising electrochemical performances were recorded with $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanocomposites prepared by thermal spray pyrolysis (Mao *et al.*, 2015).

To synthesize these particles, the authors used a solution of NH_4VO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, Na_2CO_3 in water and citric acid sprayed into the furnace at $50 \mu\text{L min}^{-1}$ with argon carrier gas at 3 L min^{-1} . The pyrolysis temperature was 600°C . Crystalline powders were obtained after 3 h annealing of the collected particles at 800°C under argon. These particles were compared to other ones prepared by a more conventional sol-gel process.

SEM pictures of the obtained particles show typical structures of droplet-to-particle conversion (see Fig. 8). The large spherical and hollow particles ($2\text{--}10 \mu\text{m}$) are constituted by smaller sintered grains (tens to hundreds nanometers) forming a porous wall

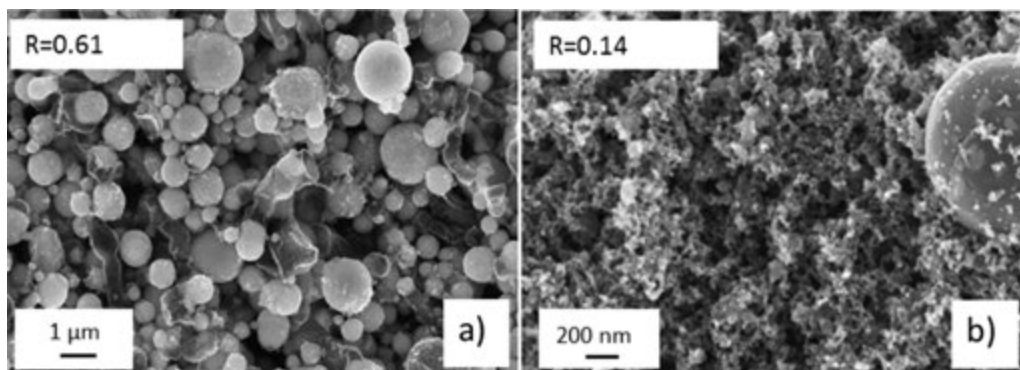


Fig. 7 SEM pictures of C/N/Fe particles obtained for different values of the carrier gas ratio R from goethite suspension in ethanol/pyridine (a), and (b) from Fe acetylacetonate solution in pyridine. Reproduced from Perez, H., Jorda, V., Bonville, P., *et al.*, 2018. Synthesis and characterization of Carbon/Nitrogen/Iron based nanoparticles by laser pyrolysis as non-noble metal electrocatalysts for oxygen reduction. *Journal of Carbon Research* 4, 43.

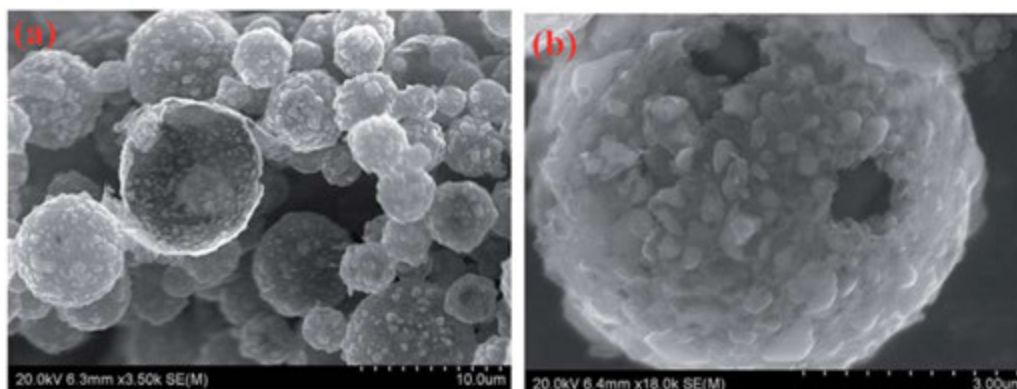


Fig. 8 SEM pictures of $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanocomposites obtained by spray pyrolysis showing large hollow spherical particles with nanometric substructure. Reproduced from Mao, J., Luo, C., Gao, T., Fan, X., Wang, C., 2015. Scalable synthesis of $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ porous hollow spheres as a cathode for Na-ion batteries. *Journal of Materials Chemistry A* 3, 10378–10385.

together with a carbon layer. This structure contrasts with the one obtained by the sol-gel process showing aggregated irregular shapes of 1–8 μm objects.

Both types of particles show the same crystalline $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ phase (see XRD in [Fig. 9](#)), but differ in their specific surface: $55.5 \text{ m}^2 \text{ g}^{-1}$ for sprayed particles versus $21.0 \text{ m}^2 \text{ g}^{-1}$ for sol-gel derivative ones. The difference on obtained porosity is clearly seen on adsorption curves (see [Fig. 9](#)), and appears as the direct consequence of the hierarchical porous structure observed in the sprayed particles.

Nanopowders synthesis in the SiCN system (Chehaidi *et al.*, 2011a)

Processing of dense silicon nitride-based materials needs sintering aids introduction such Al_2O_3 , Y_2O_3 , MgO , etc. A new route to produce dense silicon nitride-based materials, from nanopowder synthesis followed by a sintering step, seems to be more promising. An original approach is to favor an atomic scale distribution of sintering aids ($\text{Al}_2\text{Y}_2\text{O}_3$) which should lead to an homogeneous microstructure after densification. This work deals with the elaboration of SiCN_{YO} ultrafine powders by spray pyrolysis from a hybrid precursor. An yttrium organometallic (silylated yttrium acetate) was synthesized and mixed in a liquid silazane (hexamethyldisilazane) and the SiCN_{YO} powder synthesis was undertaken by spray-pyrolysis process. The pyrolysis conditions are: carrier total gas flow rate = 3 L min^{-1} and furnace temperature = 1400°C . In order to explore the influence of the nature of the reactive atmosphere on the powders characteristics two kinds of atmosphere with variable gas content were considered: Ar/NH_3 (75/25)% and $\text{Ar}/\text{H}_2/\text{NH}_3$ (65/10/25) %.

The morphology and the grain size distribution of the resulting particles were observed by the FEG-SEM image ([Fig. 10](#)). Spherical and solid particles with a grain size comprised between 30 and 100 nm have been obtained.

As shown [Fig. 10](#), a bimodal particles size distribution is observed whatever pyrolysis atmosphere is used. As shown in [Fig. 10\(a\)](#), the diameter of the largest grains is between 70 and 100 nm and the smallest ones is centered on 50 nm. During aerosol generation, two different mechanisms could be at the origin of this phenomenon as explained by [Chen *et al.* \(2008\)](#): one-particle-per-drop

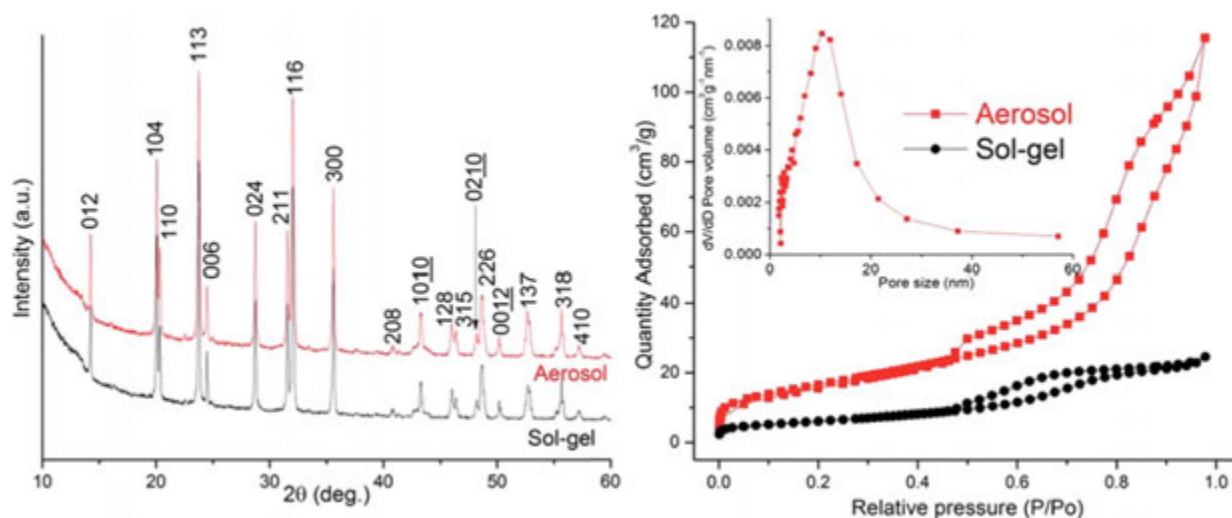


Fig. 9 XRD diagrams recorded on aerosol (sprayed) particles and sol-gel derivate ones showing $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ structure (left); and (right) adsorption curves recorded for these materials. Reproduced from Mao, J., Luo, C., Gao, T., Fan, X., Wang, C., 2015. Scalable synthesis of $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ porous hollow spheres as a cathode for Na-ion batteries. *Journal of Materials Chemistry A* 3, 10378–10385.

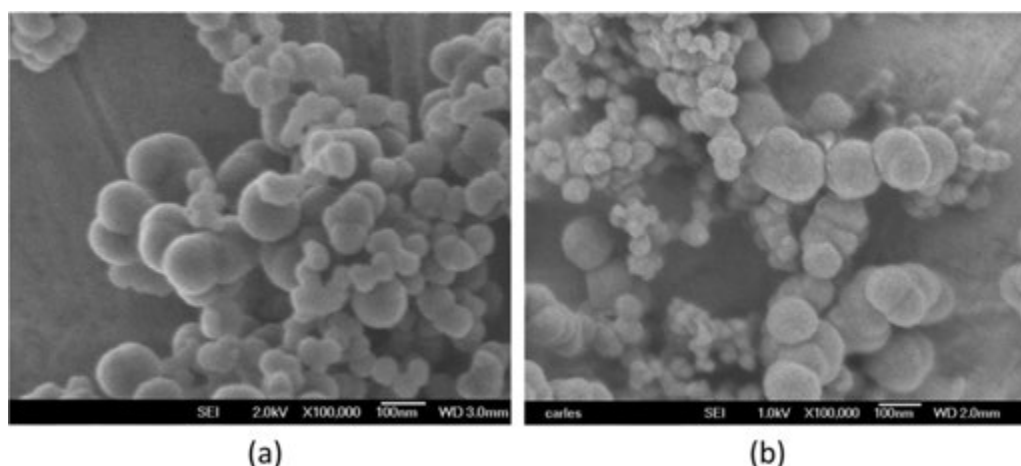


Fig. 10 FEG-SEM micrographs of powders synthesized at 1400°C with 3 L min^{-1} flow rate of (a) $\text{Ar}/\text{H}_2/\text{NH}_3$ (65%–10%–25%) and (b) Ar/NH_3 (75%–25%).

mechanism for the larger particles and gas-to-particle conversion mechanism for the smaller ones. In addition to these two proposed mechanisms, the carrier gas composition seems to have a significant effect on the particle size distribution. Whatever the spraying atmosphere, two particle distributions are observed. In one hand, under Ar/H_2 spraying, (Fig. 10(a)), the average diameters are around 80 nm and 50 nm for the larger and the smaller particles, respectively. In the other hand, under Ar spraying, (Fig. 10(b)), the size of the larger particles is still the same whereas, for smaller particles, the diameter is reduced to 30 nm. Under a reactive carrier gas (Ar/H_2) the reactivity between particles and gas phase should promote the growing of the individual particles. In return, under an inert carrier gas (Ar), the particles-gas exchange seems to be limited and prevent the smaller particles from enlarging.

Complementary work was also achieved by the same group with aluminum based sintering additive following the same precursor engineering successful approach (Chehaidi *et al.*, 2011b).

A similar pathway was followed using laser spray pyrolysis with the same objective of preparing $\text{SiCN}/\text{Al}/\text{Y}/\text{O}$ nanopowders (Cauchetier *et al.*, 1999). HMDS was also used as $\text{Si}/\text{C}/\text{N}$ precursor because it shows an efficient absorption band of the laser wavelength, and was simply mixed with different Al and/or Y alkoxides with varying ratios. The obtained liquid was used as prepared or heated and/or diluted with isopropanol in order to decrease its viscosity, and was subsequently sprayed by an ultrasonic device towards the reactor, carried by an argon flow. Obtained powders were amorphous with sizes in the 20–30 nm range and specific surfaces ranging from 66 to $110 \text{ m}^2 \text{ g}^{-1}$. Production rate varies from 30 to 67 g h^{-1} depending on feeding parameters (precursor nature, solution heating or dilution, argon carrier gas flowrate). Interestingly, the ratio of the Al or Y

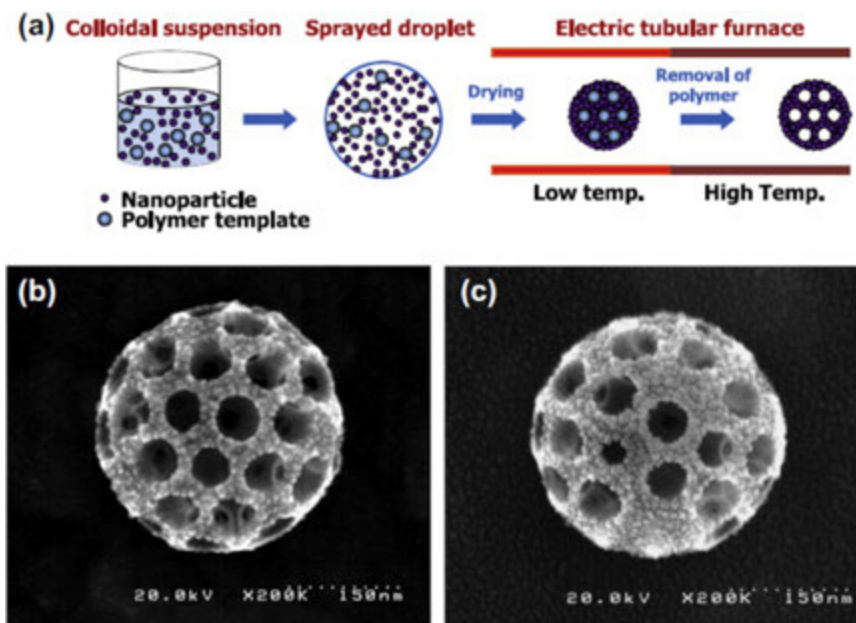


Fig. 11 (a) Schematic diagrams for the preparation of porous particles with ordered pores using organic template particles. (b and c) SEM images of self-assembled porous SiO_2 particles prepared from colloidal mixtures of silica nanoparticles and PSL. Reproduced from Chang, H., Okuyama, K., 2002. Optical properties of dense and porous spheroids consisting of primary silica nanoparticles. *Journal of Aerosol Science* 33, 1701–1720.

additives atoms over Si atoms in the starting solution (0.05–0.07) was generally found close to the same ratio measured in the obtained products. Additional work by the same group dealt with the study of the electronic structure of these materials by XPS, and concluded on the presence of a YSiAlON layer at the surface of the grains after annealing at 1600°C during 1 h under N_2 (Ténégal *et al.*, 2000), which was assumed to be favorable for liquid phase sintering process. While the introduction of sintering additives during the particle growth appeared successful, the poor thermal stability of the powders was pointed out with relative weight losses as high as 30% upon annealing at 1500°C under N_2 . Addition of silane to the reaction (SiH_4 acts both as laser absorber and Si source), together with the use of NH_3 (laser absorber and N source), allowed a better control of the powders composition and was found to enhance the thermal stability of the products but also lead to a more expensive process (Dez *et al.*, 2002).

Core-Shell Particles and Advanced Structures

Porous particles

The synthesis of porous powders can be undertaken by spray pyrolysis. Chang and Jang (2014) have produced an excellent and comprehensive review on the preparation and application of porous particles prepared using aerosol methods. The typical experimental setups as well as general experimental procedures for the preparation of porous particles have been presented and the various routes for the controlled synthesis of porous particles (including self-assembled porous particles made using organic templating, and pore size- and porosity-controlled particles from aggregated nanoparticles) have been discussed. The general experimental procedure for the preparation of porous particles is as follows: (1). Preparation of the colloidal precursor. (2). Spraying of the colloidal precursor into droplets. (3). Droplet-to-particle conversion by evaporation of the solvent and/or pyrolysis of the precursor in the furnace. (4). Removal of organic templates in the furnace. (5). Collection of porous particles. Fig. 11 shows a schematic diagram for the preparation of porous particles with ordered pores using organic template particles.

This approach is also illustrated in the work of Hyodo *et al.* which deals with the synthesis of porous In_2O_3 powders (Hyodo *et al.*, 2017).

For a cost-effective process, it is necessary to produce pore size controlled particles without organic templates. As mentioned before, the aggregated nanoparticles suspended in the starting colloid affect the pore size of the final porous particles. The preparation of porous particles can be managed from different colloidal suspensions composed of well-dispersed nanoparticles and aggregated nanoparticles. SEM images and pore size distributions of (1) the meso-porous and (2) the macro-porous SiO_2 particles prepared from the above different colloidal suspensions are shown in Fig. 12. Pore size-controlled particles were successfully prepared without any organic templates. The porosity of porous particles can be easily controlled by manipulating the size of the primary nanoparticles contained in the starting colloidal suspension.

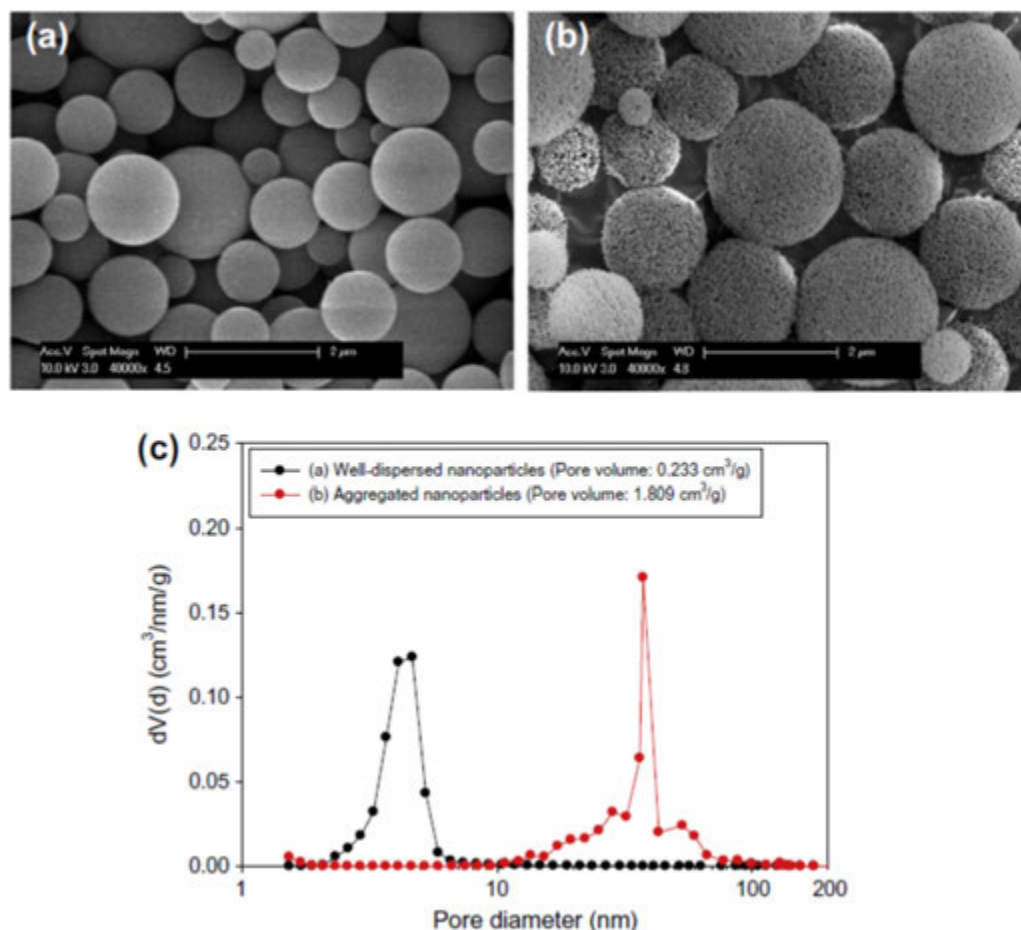


Fig. 12 (a and b) SEM images and (c) pore size distributions of pore size-controlled SiO₂ particles prepared from different colloidal suspensions composed of (a) well-dispersed nanoparticles and (b) aggregated nanoparticles. Reproduced from Jang, H.D., Kil, D.S., Chang, H., *et al.*, 2011. Preparation of nanoporous SiO₂ particles and their application in drug release control. *Journal of Nanoscience and Nanotechnology* 11, 4169–4173.

Advanced morphology of particles obtained by spray pyrolysis: Core-shell and yolk-shell structures

Spray pyrolysis offers the possibility to control the final morphology of the particles thanks to the droplet-to-particle mechanisms where decomposition/reaction and growth phenomena take place inside a spherical micro-reactor (i.e., the droplet). This possibility provides a decisive advantage when it comes to produce core-shell (a core-particle at the center with its surface protected by a shell) or yolk-shell (a particle with a “free” surface placed inside a larger hollow shell) particles. Such structures draw particular interest for Li-ion battery applications where performances and durability of the electrodes materials are governed by their tolerance to volume changes upon Li insertion and surface reactions with electrolyte.

Core-shell structures can be obtained with single-step spray pyrolysis process from solutions containing the different precursors for both core and shell. In many case the process takes advantage of the difference in physical properties between the selected precursors to ensure the initial precipitation of the core within the droplet while the shell precursor is expelled towards its surface. Carbon shells are among the most common coatings that can be encountered in the literature; a relevant example is the one step synthesis of tin oxide cores coated by carbon for energy storage applications (Hong and Kang, 2015). In this work, authors used an aqueous solution of Sn oxalate (C₂O₄Sn) and polyvinylpyrrolidone that was subsequently sprayed by an ultrasonic device into a furnace heated at 650°C. The obtained objects show a mean diameter of 770 nm with a C shell of about 30 nm in thickness (see Fig. 13(a)). Following the same approach, magnetic iron-based cores coated by C were synthesized by single-step laser spray pyrolysis for medical imaging applications (Leconte *et al.*, 2007). Other type of shell was also addressed by the same group using laser spray pyrolysis, still for the same magnetic contrast agent application, replacing carbon by silica as coating layer (Bomati-Miguel *et al.*, 2005). Nevertheless, when the shell material precursor does not “naturally” migrate towards the droplet surface upon heating versus the core precursor, alternate strategy can be followed. As an example, a sequential thermal spray pyrolysis reactor was developed to synthesize TiO₂-RuO₂ core-shell particles (Stopic *et al.*, 2013). The core precursor (Tetra-n-butyl orthotitanate (C₁₆H₃₆O₄Ti)) is sprayed in a first furnace, enabling the growth of the TiO₂ particles which are subsequently conveyed as a dry aerosol to a second furnace where they meet a second aerosol stream coming from another ultrasonic device spraying the shell precursor (ruthenium chloride (RuCl₃)). This latter precursor reacts around the solid TiO₂ particles and forms a continuous RuO₂

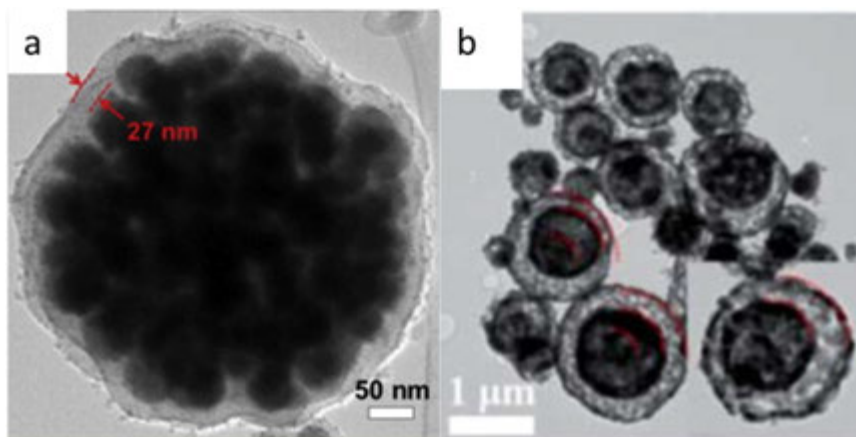


Fig. 13 (a) TEM pictures of SnO_x/C core-shell particles; (b) TEM picture of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ yolk-shell particles. Reproduced from (a) Hong, Y.J., Kang, Y.C., 2015. One-pot synthesis of core-shell-structured tin oxide-carbon composite powders by spray pyrolysis for use as anode materials in Li-ion batteries. *Carbon* 88, 262–269. (b) Choi, S.H., Hong, Y.J., Kang, Y.C., 2013. Yolk-shelled cathode materials with extremely high electrochemical performances prepared by spray pyrolysis. *Nanoscale* 5, 7867–7871.

shell. In this case, syntheses of core and shell materials are independent, and thus almost any core-shell couple can be achieved. Similar strategy was followed using gas phase laser pyrolysis with a two stage reactor for the synthesis of Si cores coated by C (Sourice *et al.*, 2013), that could also be used with liquid precursors. At the first stage, the Si precursor (SiH_4) crosses the laser beam to form the Si cores which are carried as a dry aerosol to a second nozzle where they are mixed with a C precursor (C_2H_4). This latter nozzle introduces the mixture to the second stage, crossed by the laser beam using a set of mirrors, leading to the growth of the C shell around the Si cores by heterogeneous nucleation (gas phase process). Such two-steps approaches, using furnace or laser, appear very versatile but still show limitations. The precursor's decomposition products coming from the core growth at the first step are introduced in the second step together with the solid particles, which can lead to contamination of the materials. Moreover, when an oxide core has to be coupled to a non-oxide shell, oxygen coming from first step constitutes an issue for the second step.

Yolk-shell structures are the matter of huge interest from the scientific community, especially for energy storage applications. When compared to core-shell structures, their elaboration process is generally more complex. Organic buffer layer (citrate for example) is sometimes used to fill the space between the inner particle and the shell, and has to be removed afterwards (heat treatment, washing, etching...). A suspension of nanoparticles previously synthesized can also be used, mixed with the shell precursor and subsequently sprayed to the reaction zone (see for example the elaboration of $\text{MnFe}_2\text{O}_4 - \text{SnO}_2$ yolk-shell particles) (Li *et al.*, 2017). Nevertheless, some yolk-shell structures were obtained using single step spray pyrolysis. Relevant example is shown in Fig. 13(b) for the synthesis of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ yolk-shell powders (Choi *et al.*, 2013). The authors used an aqueous solution of lithium nitrate (LiNO_3), nickel nitrate ($\text{Ni}(\text{NO}_3)_2$), and manganese nitrate ($\text{Mn}(\text{NO}_3)_2$). This solution was mixed with sucrose which acts as a carbon source useful for the formation of the specific structure. Indeed, according to the authors, the final structure results from a succession of contraction and combustion steps after the first formation of a metal oxide and carbon composite upon droplet heating, the center of the composite particle being incompletely burnt because of insufficient oxygen diffusion.

As it has been seen in the case of yolk-shell structures, suspensions of pre-synthesized objects can be mixed with other precursors and jointly be sprayed to the pyrolysis set up. Using such an approach, composite powders can easily be obtained with efficient contact between the different components of the composite as their association takes place at high temperature. A very popular application is the elaboration of composites with carbon structures such as nanotubes or graphene that are known for their mechanical and transport properties. These numerous approaches will not be addressed here but interesting review papers can be found in the literature (Zhao *et al.*, 2016; Jung *et al.*, 2014).

References

- Arita, S., Aoyagi, N., Ohshita, K., Tsubota, Y., Ogohara, T., 2017. Synthesis and characterization of spherical alumina nanoparticles by spray pyrolysis using radiofrequency plasma. *Journal of the Ceramic Society of Japan* 125 (6), 539–542.
- Athanassiou, E.K., Grass, R.N., Stark, W.J., 2010. Chemical aerosol engineering as a novel tool for material science: From oxides to salt and metal nanoparticles. *Aerosol Science Technology* 44 (2), 161–172.
- Avvaru, B., Patil, M.N., Gogate, P.R., Pandit, A.B., 2006. Ultrasonic atomization: Effect of liquid phase properties. *Ultrasonics* 44, 146–158.
- Barba, A.A., D'Amore, M., Cascone, S., Lamberti, S.G., Titomanlio, G., 2009. Intensification of biopolymeric microparticles production by ultrasonic assisted atomization. *Chemical Engineering* 48, 1477–1483.
- Baseta, N., Biscans, B., 2007. *Kona* 25, 190.
- Blandenet, G., Court, M., Lagarde, Y., 1981. Thin layers deposited by the pyrosol process. *Thin Solid Films* 77, 81–90.

- Bomati-Miguel, O., Leconte, Y., Morales, M.P., Herlin-Boime, N., Veintemillas-Verdaguer, S., 2005. Laser pyrolysis preparation of SiO_2 coated magnetic nanoparticles for biomedical applications. *Journal of Magnetism and Magnetic Materials* 290–291, 272–275.
- Cannon, W.R., Danforth, S.C., Flint, J.H., Haggerty, J.S., Marra, R.A., 1982. Sinterable ceramic powders from laser-driven reactions. I. Process description and modeling. *Journal of American Ceramic Society* 65, 324–330.
- Cauchetier, M., Armand, X., Herlin, N., *et al.*, 1999. Si/C/N nanocomposite powders with Al (and Y) additives obtained by laser spray pyrolysis of organometallic compounds. *Journal of Material Science* 34, 5257–5264.
- Cauchetier, M., Croix, O., Luce, M., Michon, M., 1987. Laser synthesis of ultrafine powders. *Ceramics International* 13, 13–17.
- Cauchetier, M., Croix, O., Herlin, N., *et al.*, 1991. Nanometric Si/C/N powders: Laser synthesis and IR characterization. *Journal of the European Ceramic Society* 8, 215–219.
- Chang, H., Jang, H.D., 2014. Controlled synthesis of porous particles via aerosol processing and their applications. *Advanced Powder Technology* 25, 32–42.
- Chehaidi, S., Foucaud, S., Maître, A., Goursat, P., 2011a. Synthesis of SiCNYO nanopowders by spray pyrolysis. *Powder Technology* 208, 343–350.
- Chehaidi, S., Salles, V., Foucaud, S., Maître, A., Goursat, P., 2011b. Influence of H_2/NH_3 mixtures on the composition of SiCNYO and SiCNAI(O) nanopowders. *Journal of European Ceramic Society* 31, 1113–1122.
- Chen, C.Y., Tseng, T.K., Tsai, S.C., Lin, C.K., Lin, H.M., 2008. Effect of precursor characteristics on zirconia and ceria particle morphology in spray pyrolysis. *Ceramics International* 34, 409–416.
- Cheng, Z., Foroughi, P., Behrens, A., 2017. Synthesis of nanocrystalline TaC powders via single-step high temperature spray pyrolysis from solution precursors. *Ceramics International* 43, 3431–3434.
- Choi, S.H., Hong, Y.J., Kang, Y.C., 2013. Yolk-shelled cathode materials with extremely high electrochemical performances prepared by spray pyrolysis. *Nanoscale* 5, 7867–7871.
- Debecker, D.P., Le Bras, S., Boissiere, C., Chaumonnot, A., Sanchez, C., 2018. Aerosol processing: A wind of innovation in the field of advanced heterogeneous catalysts. *Chemical Society Reviews* 47, 4112–4155.
- Dez, R., Tenegal, F., Reynaud, C., *et al.*, 2002. Laser synthesis of silicon carbonitride nanopowders; structure and thermal stability. *Journal of European Ceramic Society* 22, 2969–2979.
- Flagan, R.C., Lunden, M.M., 2007. Particle structure control in nanoparticle synthesis from the vapor phase. *Materials Science and Engineering A204*, 113–124.
- Franc, J.-P., Michel, J.-M., 2004. *Fundamentals of Cavitation*. Dordrecht; Boston: Kluwer Academic Publishers.
- Goulart, C., Djurado, E., 2013. Synthesis and sintering of Gd-doped CeO_2 nanopowders prepared by ultrasonic spray pyrolysis. *Journal of the European Ceramic Society* 33 (4), 769–778.
- Gutsch, A., Krämer, M., Michael, G., *et al.*, 2002. Gas phase production of nanoparticles. *Kona* 20, 24–37.
- Hong, Y.J., Kang, Y.C., 2015. One-pot synthesis of core-shell-structured tin oxide-carbon composite powders by spray pyrolysis for use as anode materials in Li-ion batteries. *Carbon* 88, 262–269.
- Hyodo, T., Fujii, E., Ishida, K., Ueda, T., Shimizu, Y., 2017. Microstructural control of porous In_2O_3 powders prepared by ultrasonic-spray pyrolysis employing self-synthesized polymethylmethacrylate microspheres as a template and their NO_2 -sensing properties. *Sensors and Actuators B* 244, 992–1003.
- Janik, J.F., Drygaś, M., Stelmach, S., *et al.*, 2006. Tuning aerosol-assisted vapor phase processing towards low oxygen GaN powders. *Physica Status Solidi A* 203 (6), 1301–1306.
- Jung, D.S., Ko, Y.N., Kang, Y.C., Park, S.B., 2014. Recent progress in electrode materials produced by spray pyrolysis for next-generation lithium ion batteries. *Advanced Powder Technology* 25, 18–31.
- Lang, R., 1962. Ultrasonic atomization of liquids. *Journal of Acoustical Society of America* 34, 6–8.
- Leconte, Y., Veintemillas-Verdaguer, S., Morales, M.P., *et al.*, 2007. Continuous production of water dispersible carbon coated iron based nanoparticles for biomedical applications. *Journal of Colloid and Interface Science* 313, 511–518.
- Leparoux, M., Schreuders, C., Shin, J.W., Siegmann, S., 2005. Induction plasma synthesis of carbide nanopowders. *Advanced Engineering Materials* 7 (5), 349–353.
- Li, S., Wang, F., Dai, H., *et al.*, 2016. Self-assembly of silica nanoparticles into hollow spheres via a microwave-assisted aerosol process. *Materials Research Bulletin* 74, 459–464.
- Li, Y., Li, L., Hu, J., Yan, L., 2017. A spray pyrolysis synthesis of $\text{MnFe}_2\text{O}_4/\text{SnO}_2$ yolk/shell composites for magnetically recyclable photocatalyst. *Materials Letters* 199, 135–138.
- Mao, J., Luo, C., Gao, T., Fan, X., Wang, C., 2015. Scalable synthesis of $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ porous hollow spheres as a cathode for Na-ion batteries. *Journal of Materials Chemistry A* 3, 10378–10385.
- Messing, G., Zhang, S.-C., Jayanthi, G., 1993. Ceramic powder synthesis by spray pyrolysis. *Journal of American Ceramic Society* 76, 2707.
- Munoz, M., Goutier, S., Foucaud, S., Mariaux, G., Poirier, T., 2018. Droplet size prediction in ultrasonic nebulization for non-oxide ceramic powder synthesis. *Ultrasonics* 84, 25–33.
- Mwakikunga, B.W., 2014. Progress in Ultrasonic Spray pyrolysis for condensed matter sciences developed from ultrasonic nebulization theories since Michael Faraday. *Critical Reviews in Solid State and Materials Science* 39, 46–80.
- Perez, H., Jorda, V., Bonville, P., *et al.*, 2018. Synthesis and characterization of Carbon/Nitrogen/Iron based nanoparticles by laser pyrolysis as non-noble metal electrocatalysts for oxygen reduction. *Journal of Carbon Research* 4, 43.
- Rajan, R., Pandit, A.B., 2001. Correlations to predict droplet size in ultrasonic atomization. *Ultrasonics* 39, 235–255.
- Ramisetty, K.A., Pandit, A.B., Gogate, P.R., 2013. Investigations into ultrasound induced atomization. *Ultrasonics Sonochemistry* 20, 254–264.
- Ring, T.A., 1996. *Fundamentals of Ceramic Processing and Synthesis*. Elsevier. (ISBN 978-0-12-588930-8).
- Salles, V., Foucaud, S., Laborde, E., Champion, E., Goursat, P., 2007. Synthesis of SiCNAI(O) pre-alloyed nanopowders by pyrolysis of an aluminosilazane aerosol. *Journal of European Ceramic Society* 27, 357–366.
- Song, Y.L., Tsai, S.C., Chen, C.Y., *et al.*, 2004. Ultrasonic spray pyrolysis for synthesis of spherical zirconia particles. *Journal of American Ceramic Society* 87, 1864–1871.
- Sourice, J., Quinsac, A., Leconte, Y., *et al.*, 2013. One step synthesis of Si@C nanoparticles by laser pyrolysis: High capacity anode material for lithium ion batteries. *Applied Materials Interfaces* 7, 6637–6644.
- Stopic, S., Friedrich, B., Schroeder, M., Weirich, T.E., 2013. Synthesis of TiO_2 core/ RuO_2 shell particles using multistep ultrasonic spray pyrolysis. *Materials Research Bulletin* 48 (9), 3633–3635.
- Strobel, R., Pratsinis, S.E., 2007. Flame aerosol synthesis of smart nanostructured materials. *Journal of Materials Chemistry* 17, 4743–4756.
- Sublemontier, O., Kintz, H., Lacour, F., *et al.*, 2011. Synthesis and on-line size control of silicon quantum dots. *Kona* 29, 236–250.
- Ténégal, F., Gheorghiu de la Rocque, A., Dufour, G., *et al.*, 2000. Local order determination in SiCN(AlY) laser-synthesized nanopowders by x-ray photoemission spectroscopy. *Journal of Applied Physics* 87 (11), 7864–7870.
- Teoh, W.Y., Amal, R., Mädler, L., 2010. Flame spray pyrolysis: An enabling technology for nanoparticles design and fabrication. *Nanoscale* 2, 1324–1347.
- Ulrich, G.D., 1984. Flame synthesis of fine particles. *Chemical Engineering News Archive* 62 (32), 22–29.
- Yule, A., Al-Suleimani, Y., 2000. On droplet formation from capillary waves on a vibrating surface. *Proceedings of the Royal Society of London A* 456, 1069–1085.
- Zhang, S.-C., Messing, G.L., Borden, M., 1990. Synthesis of solid, spherical zirconia particles by spray pyrolysis. *Journal of American Ceramic Society* 73, 61–67.
- Zhao, Y., Wang, L.P., Sougrati, M.T., *et al.*, 2016. A review on design strategies for carbon based metal oxides and sulfides nanocomposites for high performance Li and Na ion battery anodes. *Advanced Energy Materials*. 1601424.

Calcination and Phase Transformations

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Industrial scale powder synthesis involves mixing tonnage-scale lots of metal carbonate, hydroxide and oxalate precursor powders, and/or metal oxide powders to produce complex, or mixed metal, oxide powders by calcination (e.g., $\text{MgCO}_3 + \gamma\text{-Al}(\text{OH})_3 \rightarrow \text{MgAl}_2\text{O}_4$). In this case calcination involves a lower temperature step to first decompose the MgCO_3 to form MgO and $\gamma\text{-Al}(\text{OH})_3$ decomposition to form $\gamma\text{-Al}_2\text{O}_3$, at higher temperature $\gamma\text{-Al}_2\text{O}_3$ is transformed to $\alpha\text{-Al}_2\text{O}_3$, and at even higher temperature the calcination process involves the solid-state reaction between MgO and $\alpha\text{-Al}_2\text{O}_3$ particles to form MgAl_2O_4 spinel. Small batch synthesis may involve mixing highly water-soluble metal salts like acetates, chlorides and nitrates to achieve homogeneous solutions of the metal cations. These solutions are rapidly co-precipitated to preserve the atomic-scale homogeneity of the metal ions by forming a mixture of the respective sparingly soluble carbonate, hydroxides or oxalates. In contrast to the micrometer-scale powders used in large-scale industrial processes, co-precipitated particles are submicrometer in size as a result of the rapid co-precipitation step. The scale and uniformity of mixing of the co-precipitated powder is finer and more uniform than possible by dry mixing coarser powders.

A metal salt solution can also be rapidly dried to precipitate a homogeneous mixture of the metal salts. For example, PLZT $[(\text{Pb}_{0.85}\text{La}_{0.15})(\text{Zr}_{0.8}\text{Ti}_{0.2})\text{O}_3]$ can be synthesized by dissolving $\text{Pb}(\text{NO}_3)_2$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{ZrO}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ and $\text{Ti}(\text{i-OC}_3\text{H}_7)_4$ in water to achieve atomic scale mixing of the cations. Drying the solution results in the co-precipitation of the metal salts. In this case calcination involves a low temperature (e.g., $< 200^\circ\text{C}$) step to remove the structural water of hydration, decomposition of the anhydrous metal nitrates at $550\text{--}600^\circ\text{C}$, and formation of PLZT powder by the solid state reaction between PbO , La_2O_3 , ZrO_2 and TiO_2 by heating to $950\text{--}1000^\circ\text{C}$.

The objective of calcination is to produce a thermodynamically stable form of a powder so that the above decomposition processes and shrinkage from phase formation do not occur during sintering the ceramic part, and the particles formed are not aggregated by partial sintering prior to dispersion and forming. Table 1 lists examples of calcination processes and ceramic powders that are commonly produced by calcination. Calcination is used mainly for thermal decomposition reactions, phase transformation and solid-state reactions. Another objective may be to remove impurities remaining from a vapor synthesis process like removal of adsorbed HCl in Si_3N_4 powder derived from nitridation of SiCl_4 gas.

Decomposition Reactions

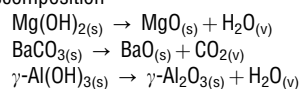
Thermodynamics has a major impact on decomposition reactions because the rate of decomposition is directly related to the reaction temperature and product gas concentration required for reaction. The free energy of the decomposition reaction is given by

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (1)$$

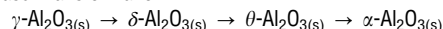
where G^0 is the Gibbs free energy for the reaction, ΔH^0 is the enthalpy of the reaction and $T\Delta S^0$ is the entropy of the system; all at standard state. The equilibrium temperature for the reaction can be determined by calculating the free energy of formation from standard reference tables. Plots of ΔG^0 versus temperature, as shown in Fig. 1 (referred to as an Ellingham, or standard free energy

Table 1 Examples of calcination processes for producing ceramic powders

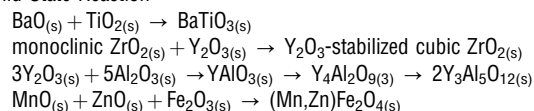
Decomposition



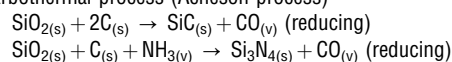
Phase Transformation



Solid State Reaction



Carbothermal process (Acheson process)



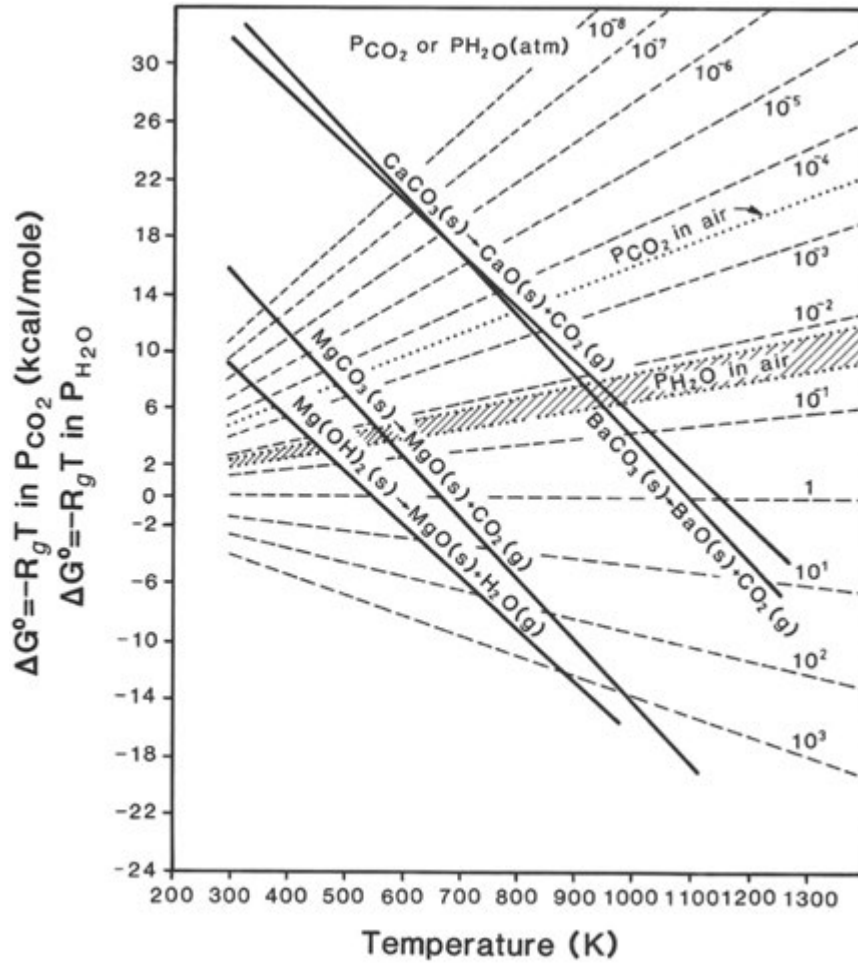


Fig. 1 Standard free energy of reaction as a function of temperature and equilibrium gas pressure for decomposition of metal carbonates and magnesium hydroxide. Reproduced from Ring, T.A., 1996. Fundamentals of Ceramic Processing and Synthesis. Boston, MA: Academic Press.

of formation, plot) provide practical insights about how product gas pressure and temperature affect the relative thermal stability of materials (Gaskell, 1995). To illustrate the importance of thermodynamics, consider the decomposition of $\text{CaCO}_3(\text{s})$ to form $\text{CaO}(\text{s})$ and $\text{CO}_2(\text{v})$. For solids at standard conditions, the activity is assumed to be one. Thus, the equilibrium constant $K_{\text{eq}} = (\text{CO}_2)$ and for a gas, $(\text{CO}_2) = P_{\text{CO}_2}$. Thus,

$$\Delta G_{\text{rx}} = \Delta G_{\text{rx}}^0 + RT \ln (K_{\text{eq}}) \quad (2)$$

At equilibrium, the free energy of the reaction ΔG_{rx} is zero and

$$\Delta G_{\text{rx}}^0 = -RT \ln (P_{\text{CO}_2\text{eq}})$$

In general, we can write

$$\Delta G_{\text{rx}}^0 = -RT \ln \left(\frac{P_{\text{CO}_2}}{P_{\text{CO}_2\text{eq}}} \right)$$

If ΔG_{rx}^0 is positive, then decomposition does not occur at that temperature and product gas pressure and when ΔG_{rx}^0 is negative decomposition takes place.

Note that for metal hydroxides, like $\text{Mg}(\text{OH})_2$, the free energy equation takes the form

$$\Delta G_{\text{rx}}^0 = -RT \ln \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{Oeq}}} \right) \quad (3)$$

Because the product gases of carbonates and hydroxides exist in the atmosphere at low concentrations, atmospheric conditions play more of a role during decomposition of these types of precursors as well as metal oxalates $[\text{C}_2\text{O}_4^{-2}]$, acetates $[\text{CH}_3\text{COO}^-]$, and citrates $[\text{C}_6\text{H}_5\text{O}_7^-]$, which decompose into gaseous H_2O , CO , and CO_2 . From Fig. 1 the equilibrium temperature for one atmosphere of product gas occurs at $\Delta G_{\text{rx}} = 0$. At the equilibrium condition, $T_{\text{eq}} = 1156\text{K}$ (883°C) for CaCO_3 , 672K (399°C) for MgCO_3 and 550K (277°C) for $\text{Mg}(\text{OH})_2$. $P_{\text{CO}_2} = 5 \times 10^{-3}$ atm and $P_{\text{H}_2\text{O}} = 0.05$ atm in air, and thus, when calcined in air T_{eq}

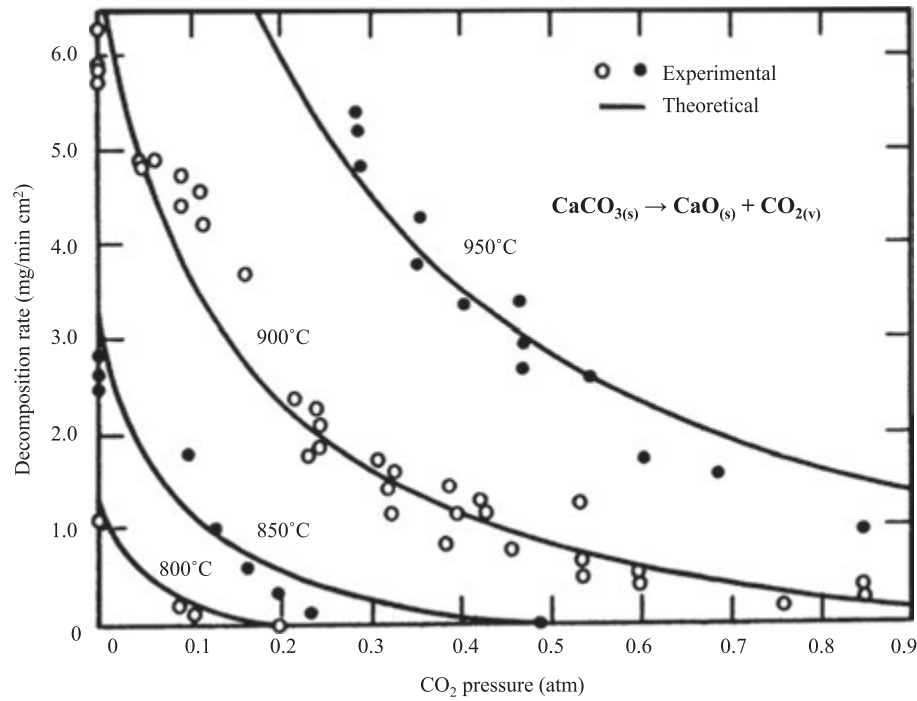


Fig. 2 Rate of decomposition of CaCO_3 in CO_2 atmosphere. Reproduced from Hyatt, E.P., Cutler, I.B., Wadsworth, M.E., 1958. Calcium carbonate decomposition in carbon dioxide atmosphere. *J. Am. Ceram. Soc.* 41, 70–74.

decreases to 810K for CaCO_3 , to 480K for MgCO_3 , and to 445–465K for $\text{Mg}(\text{OH})_2$. For practical reasons, decomposition reactions are carried out at a higher temperature than the minimum temperature/pressure conditions predicted by thermodynamics. [Mu and Perlmutter \(1981\)](#) is a useful reference for decomposition reactions and decomposition temperatures of commonly used metal carbonates, metal acetates, metal oxalates and metal hydroxides.

The kinetics of decomposition reactions are governed by a variety of factors that fundamentally determine whether the reaction is controlled by (1) nucleation (interface reaction), (2) mass transfer of the product gas, or (3) heat transfer. During decomposition nucleation is less important because the powder mass is nearly all interfaces and nucleation readily occurs at elevated temperature. As noted above, the reaction gas pressure plays a critical role during decomposition reactions. [Fig. 2](#) illustrates the effect of product gas pressure on the decomposition of CaCO_3 . Recall from [Fig. 1](#) that T_{eq} in air is 810K (537°C) but T_{eq} increases to 1123K (850°C) at a CO_2 pressure of 0.4 atm. The temperature at which decomposition begins decreases as the product gas pressure in the system decreases. For a single particle, the gas pressure controlling the rate of decomposition is the pressure adjacent to the decomposition front inside the particle since that is the site of highest product gas concentration and thus controls the equilibrium temperature of decomposition.

The rate of powder decomposition in a saggar (i.e. a ceramic vessel used for calcination) can be controlled by the rate of gas diffusion through the reacted powder and thus depends significantly on powder bed depth in the saggar, and powder size, pore size and packing density. So that reactions are not rate-limited by gas diffusion through the powder bed, the powder is often fluidized, or the bed is continuously stirred in a rotary calciner. Likewise, any method to remove the product gas accelerates the process, such as with a vacuum or the use of a sweep gas. Using the above approaches ensures heat transfer controls the kinetics of decomposition.

The shrinking core model in [Fig. 3](#) has been used to model decomposition reactions. The model is characterized by a solid unreacted core, and a sharp interface between the unreacted core and decomposed metal oxide layer. The model accounts for gas flow from the particle surface to the furnace ([Eq. 6](#)) and from the reaction interface through the porous metal oxide shell ([Eq. 5](#)). The product of the decomposition reaction is nanocrystalline and thus the unreacted core is surrounded by a shell of <100 nm nanopores. The nanoporosity of the reaction product decreases the rate of mass transport of the product gas relative to in the furnace and thus mass transport through the nanoporous shell surrounding the solid unreacted core can be rate-limiting because the internal gas pressure is higher than the ambient gas pressure. The nanoporosity of the new oxide decreases the thermal conductivity relative to the unreacted solid particles. [Eq. \(8\)](#) shows the heat transfer from the furnace to the particle surface and thermal conductivity ([Eq. 9](#)) through the porous metal oxide product layer ([Kingery et al., 1975](#)).

$$J_{\text{reaction interface}} = kr4\pi r^2(P_e - P_r), \text{ where } P_e = e^{-\Delta G^0/RT_f} \quad (4)$$

$$J_{\text{porous layer}} = 4\pi \frac{D'_{\text{CO}_2}(P_r - P_s)r_s}{r_s - r} \quad (5)$$

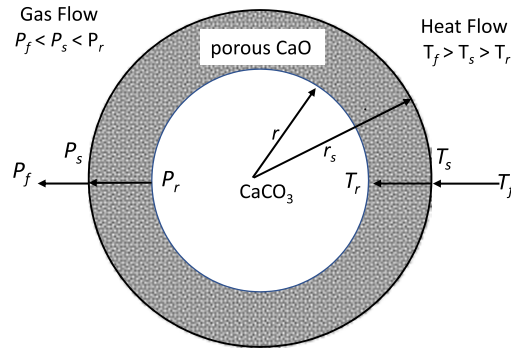


Fig. 3 Schematic of the partial decomposition of a spherical particle (e.g., CaCO_3) showing the solid unreacted core surrounded by a shell of porous, nanocrystalline metal oxide (e.g., CaO). The reaction is endothermic, requiring heat transfer to the reaction interface. The driving forces for heat transfer and mass transport for steady-state decomposition are expressed as temperatures and pressures in the furnace (T_f , P_f), at the particle surface (T_s , P_s), and at the reaction interface (T_r , P_r).

$$J_{\text{furnace}} = 4\pi r_s^2 \frac{D_{\text{CO}_2}}{\delta} (P_s - P_f) \quad (6)$$

where δ is the boundary layer thickness at the interface between the furnace and outside surface of the particle and D'_{CO_2} is the CO_2 diffusion rate through the porous metal oxide layer.

Heat transfer to the reacting particle is given by

$$q_{\text{reaction interface}} = \frac{4\pi r^2 \rho}{M} \Delta H_{T_f}^o \frac{dr}{dt} \quad (7)$$

$$q_{\text{furnace}} = h_s 4\pi r_s^2 (T_f - T_s) \quad (8)$$

$$q_{\text{porous layer}} = \frac{4\pi k (T_s - T_r) r r_s}{r_s - r} \quad (9)$$

where ρ is density of CaCO_3 , M is molecular weight, h_s is the heat transfer coefficient at the solid CaCO_3 surface, and k is the thermal conductivity of the porous CaO shell.

Fig. 4 illustrates how the center temperature of a large CaCO_3 crystal changes relative to the surface temperature when heated at 1332°C . The center of the crystal is about 450°C less than the surface temperature during most of the calcination process because the heat is absorbed at the reaction interface to sustain the endothermic decomposition reaction (Eq. 4). Only after 2 h does the center temperature start to increase. To increase the rate of reaction for a single particle, it is important to decrease particle size to reduce the distance between the heat source and particle core.

In powder beds the reaction front recedes from the powder bed surface into the reacting powder bed with time. The temperature at the reaction front is governed by the amount of heat required to sustain the typically endothermic reaction. The above example underscores the importance of heat transfer for bulk powder calcination because the powder bed depth in a saggar is orders of magnitude greater than the particle size. Shallow saggar fill depths, rotary calciners or fluidized beds are used to decrease the effects of powder bed depth on gas transport and heat transfer and to limit the effects of non-uniform heating and reaction during calcination. The mathematics underlying the rates of heat and mass transfer on decomposition reactions has been extensively reported for a wide variety of process conditions and calcination reaction types, including decomposition (Levenspiel, 1972; Turkdogan, 1980; Ring, 1996).

The overall reaction rate is controlled by the relative rates of heat transfer and mass transport. These processes are in series and thus the rate of the reaction is controlled by the slower rate process. In general, surface reaction control occurs at low temperatures since this is when the new phase is nucleated. The reaction is heat transfer controlled at intermediate reaction temperatures whereas mass transport of the product gas is rate-controlling at the highest temperatures. One means to accelerate the reaction is to increase the temperature. However, increasing temperature to $> \sim 50\%$ of T_m (K) (i.e., the Tammann temperature) of the product metal oxides increases the rate of solid state diffusion and causes coarsening (i.e., size enlargement of the nanoscale product phase), and sintering of the fine crystallite particles leading to formation of a hard, porous product phase referred to as an aggregate. Such multiparticle aggregates must be milled to break them into separate particles because multiparticle aggregates adversely affect subsequent densification of the shaped ceramic.

Solid-State Reactions

Most multicomponent ceramic materials (i.e., mixed metal oxides) are synthesized via a solid-state process. The uniformity of mixing and the length scale between the particle reactants have major influences on the time and temperature required to complete the reaction. Thus, to decrease diffusion distances most mixed metal oxides are synthesized by a solution approach in which the cations

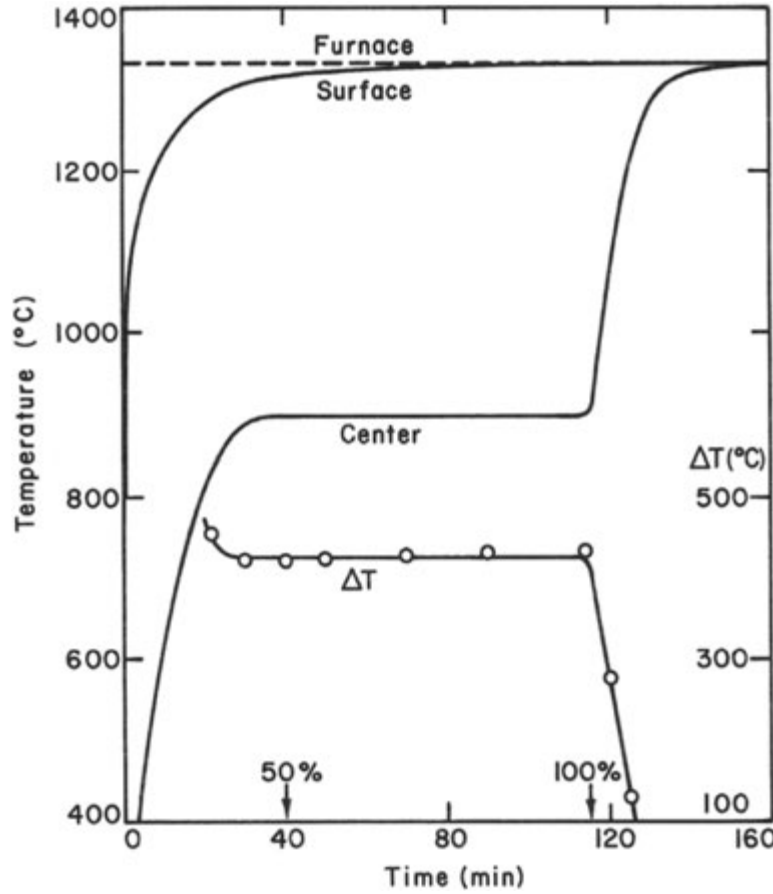


Fig. 4 Variation of surface and center temperatures of an 8.3 cm diameter CaCO_3 sphere heated at 1332°C in 1 atm argon. Reproduced from Turkdogan, E.T., 1980. *Physical Chemistry of High Temperature Technology*. Boston, MA: Academic Press.

are intimately mixed in a liquid and co-precipitated or co-hydrolyzed to form a homogeneous mixture of the individual, sparingly soluble metal hydroxides, oxalates, or carbonates. It is important to note that the uniformity of the co-precipitated powder has a major influence on the path and kinetics of phase formation during subsequent heating (Narendar and Messing, 1997).

The degree of phase transformation versus time follows the typical S-shaped kinetics plot. The plot is characterized by an incubation period, a period of rapid reaction kinetics, and a period of decelerating kinetics. The incubation period is interpreted as the time required for the growth of nuclei of critical size. Once this size is achieved, the energetically favored growth or transformation of a new phase begins. The nucleation period can be reduced by increasing temperature, adding a flux, or by adding seed particles (see below).

Analysis of Transformation Kinetics

There are two approaches for analyzing phase transformation kinetics: (1) measurement of phase formation as a function of time at isothermal temperatures and (2) measuring the effect of heating rate on exothermic temperature. The first approach, called an Arrhenius analysis, uses quantitative x-ray analysis of the degree of phase development as a function of time for three or more isothermal temperatures. The data is then analyzed to extract the rate constants and activation energies at various degrees of reaction to determine rate-controlling processes. In this case many samples are needed to obtain an accurate activation energy for the transformation. Kissinger (1956) developed an alternative method using either differential scanning calorimetry or differential thermal analysis to obtain the activation energy for a phase transformation. The Kissinger analysis only requires the peak temperature of the exothermic phase transformation at various heating rates. The Kissinger equation is:

$$\ln \left[\frac{dT/dt}{T_m^2} \right] = - \frac{E_a}{R} \left(\frac{1}{T_m} \right) + B \quad (10)$$

$$B = \ln \left(\frac{AR}{E_a} \right) = \text{constant}$$

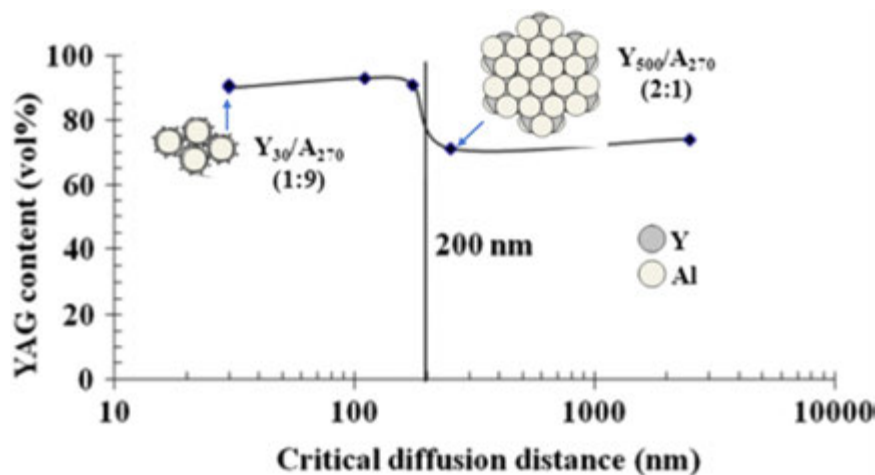


Fig. 5 YAG content at 1450°C as a function of critical diffusion distance. Schematics illustrate the influence of size and size ratio on completion of YAG phase formation. Reproduced from Kupp, E., Kochawattana, S., Lee, S., Mixture, S., Messing, G.L., 2014. Particle size effects on yttrium aluminum garnet (YAG) phase formation by solid-state reaction. *J. Mater. Res.* 29, 2303–2311.

where T is temperature in K , t is time, T_m is the peak temperature of the phase transformation, E_a is activation energy, A is the Arrhenius constant, and R is the gas constant. By plotting $\ln \left[\frac{dT/dt}{T_m^2} \right]$ versus $(1/T_m)$ for various heating rates one can obtain the activation energy from the slope, $-E_a/R$. The Kissinger approach has its limitations but is useful for limited study of irreversible single step reactions but fails for many reasons in complex systems (Vyazovkin, 2020).

There have been many attempts to model the kinetics of phase formation. In all approaches a linear fit of the degree of reaction to time and/or temperature is interpreted as representative of a single reaction mechanism. However, the analysis of the kinetics of reactions is complicated by non-spherical particle shapes, a distribution of number of contacts from particle to particle, mixing heterogeneity, and differences in particle sizes. Activation energies and rate constants obtained by curve fitting are useful for comparisons as a function of various parameters within the same study but often lack any fundamental meaning. To appreciate the complexity of these analyses see Ring (1996) and Khawam and Flanagan (2006).

Analysis of phase formation kinetics is particularly complicated by differences in particle size between reactant powders. Kupp *et al.* (2014) showed that the size ratio between Al_2O_3 and Y_2O_3 particles during formation of $\text{Y}_3\text{Al}_5\text{O}_{12}$ dramatically affects the reaction pathway and kinetics. It is known that Al^{3+} diffusion into Y_2O_3 particles is the rate-controlling process for YAG formation. Thus, the Y_2O_3 particle size establishes the critical diffusion distance affecting the degree of YAG formation. Fig. 5 shows that the reaction was near complete only when the Y_2O_3 particle size was less than 110 nm diameter and the number of Al_2O_3 particles in contact with Y_2O_3 was approximately 10 and the Al_2O_3 and Y_2O_3 particles have a size ratio near 1. This example illustrates that it is important to tailor the powder system for solid-state calcination by matching the particle sizes and size ratio of the reactant particles.

Seeding of Ceramic Reactions

Phase formation during calcination plays a major role in microstructure and property development in ceramic systems. Common to most ceramic reactions, variations in nucleation and growth determine the process temperature and time, product particle size, and chemical phase development. Seeding to direct ceramic transformations has been demonstrated in a variety of systems (Messing *et al.*, 1986). Homoepitaxy, in which the seed and desired phase have identical lattice parameters and crystal structures, is the most likely prospect for nucleation manipulation by seeding in ceramic systems. Besides selection by seed crystal structure and lattice parameter, it is important to determine the intrinsic nucleation frequency of the system being seeded. The intrinsic nucleation frequencies in transition alumina (e.g., γ - Al_2O_3 or θ - Al_2O_3) phase transformations to α - Al_2O_3 ranges from 10^9 to 10^{12} nuclei cm^{-1} . To nucleate a reaction and achieve smaller particle size after transformation, it is necessary to exceed the intrinsic nucleation frequency. Seed particle surfaces typically act as sites for multiple nucleation, making exact estimations of extrinsic nucleation frequency from seeding imprecise. However, we can calculate transformed particle size if the seed size and number frequency per volume are known.

An example of a seeded transformation is the introduction of α - Al_2O_3 particles to an γ - AlOOH gel (boehmite) that transforms to γ - Al_2O_3 at 500°C, to θ - Al_2O_3 at 900°C and to α - Al_2O_3 at 1200°C. Fig. 6 shows the unseeded phase transformation has an incubation period of ~ 16 min and takes over 6 h to completely transform to α - Al_2O_3 when heated at 1050°C. However, when 2.7×10^{13} α - Al_2O_3 seed particles cm^{-3} are introduced to the initial boehmite gel, the initiation of the θ to α - Al_2O_3 phase transformation is almost instantaneous, and the total time for complete transformation is decreased to ~ 16 min. The graph shows that increasing the seeding (nucleation) frequency increases the transformation rate in proportion to the number of transformation

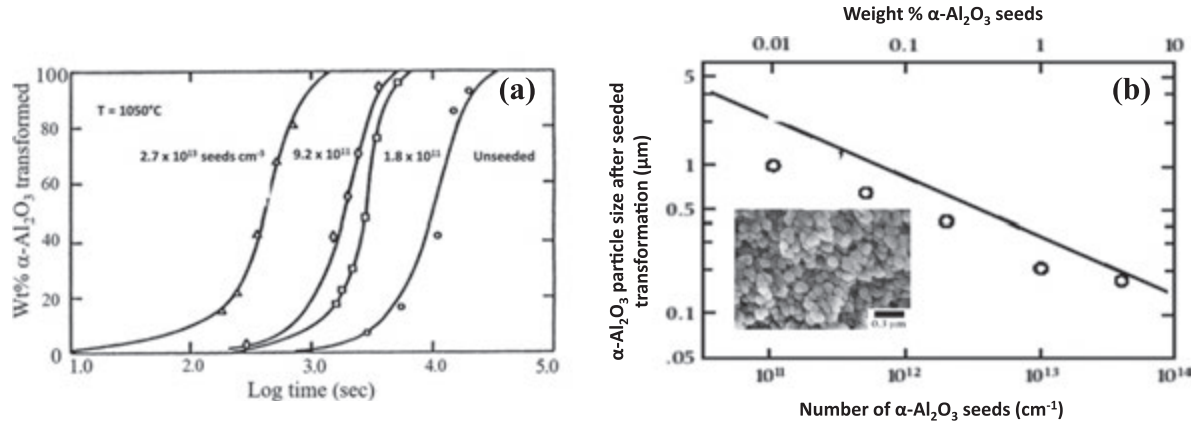


Fig. 6 Alpha alumina phase formation (a) kinetics at 1050°C and (b) theoretical (Eq. 11) and experimental α -Al₂O₃ particle size as a function of α -Al₂O₃ seed number concentration (inset seeded alumina particles).

growth centers (i.e., seed particles). In this manner the nucleation-limited, solid-state transformation of θ -Al₂O₃ to α -Al₂O₃ was lowered by as much as 200°C relative to the unseeded α -Al₂O₃ phase transformation (Kumagai and Messing, 1985). The temperature for the intrinsic solid-state diffusional processes of the system limits further calcination temperature reduction. However, increasing the rate of transport by using “mineralizers” that react to form a liquid (V₂O₅) or vapor (HF, H₂O) with alumina has been shown to lower the alpha alumina transformation temperature by an additional 200–300°C. (Shelleman and Messing, 1988; Shaklee and Messing, 1994; Bagwell and Messing, 1999).

Assuming a single particle develops from each seed and the seeds are uniformly distributed in the transforming matrix, the particle size (PS) of the transformed material after seeding at a frequency f_s is

$$PS = kf_s^{-1/3} \quad (11)$$

where k is a correction factor for particle shape and the molar volume difference between the untransformed and transformed materials. Assuming no volume contribution from the seed particle, the predicted α -Al₂O₃ particle size obtained by seeding γ -AlOOH with 2.4×10^{14} α -Al₂O₃ seed particles cm⁻³ is 0.16 μm (Fig. 6(b) and (c)). This example illustrates that significantly smaller particles can be obtained by seeding a phase transformation.

Epitaxy

The principles governing seed characteristics are related to the ability of the seed crystal to favor oriented overgrowth (i.e., epitaxy) in the reacting system because of crystallographic matching. Solid-phase epitaxy, or the introduction of solid seed particles to a system undergoing a solid-state reaction as a means of controlling ceramic reactions, has been demonstrated to be an effective means to control solid-state kinetics, microstructure development and phase development (Messing *et al.*, 1986).

Epitaxy concerns the degree of lattice parameter matching (δ) during growth at the interface between a reacting system or matrix (a_α) and the seed crystal or substrate (a_β)

$$\delta = \frac{a_\alpha - a_\beta}{a_\beta} \quad (12)$$

The nucleation effectiveness of a seed crystal is related to the seed-matrix interfacial energy ($\gamma_{\alpha\beta}$) and the seed-matrix contact angle (θ).

$$\cos \theta = \frac{\gamma_\alpha - \gamma_\beta}{\gamma_{\alpha\beta}} \quad (13)$$

For low values of δ the seed and host matrix are coherently oriented at the interface and $\gamma_{\alpha\beta}$ ranges from 1 to 200 mJ m⁻². For larger degrees of lattice mismatch, the strained, incoherent interface is accommodated by dislocations and $\gamma_{\alpha\beta}$ is 200–500 mJ m⁻² (Porter and Easterling, 1992). For values of δ greater than $\pm 15\%$, the incoherent interphase interface energy is 1000 mJ m⁻² and there is no effect of the seed particle on nucleation (i.e., epitaxy does not occur). Seed crystals with a lattice parameter mismatch with the transformed product of less than $\pm 15\%$ are typically effective nucleation “catalysts”.

The addition of seed crystals lowers the free energy for nucleation (ΔG_{heter}) to less than that required for homogeneous nucleation (ΔG_{hom}) through its effect on the interphase interfacial energy and the seed-matrix contact angle:

$$\Delta G_{\text{heter}} = \Delta G_{\text{hom}} \{ (2 + \cos \theta)(1 - \cos \theta)^2 \} / 4 \quad (14)$$

For example, when $\theta = 10^\circ$, $\Delta G_{\text{heter}} \sim 10^{-4} \Delta G_{\text{hom}}$, demonstrating the significant reduction in nucleation energy afforded by seeding (Porter and Easterling, 1992).

Applying the principles of epitaxy, McArdle and Messing (1993) showed that $\alpha\text{-Fe}_2\text{O}_3$ with a 5.5% lattice parameter mismatch with $\alpha\text{-Al}_2\text{O}_3$, is an equally effective substrate for seeding the $\alpha\text{-Al}_2\text{O}_3$ transformation as $\alpha\text{-Al}_2\text{O}_3$ particles. An added benefit of $\alpha\text{-Fe}_2\text{O}_3$ seeds is <100 nm size particles can be chemically synthesized and thus it is easier to achieve 10^{14} seeds cm^{-3} number concentrations. It should be noted that as heteroepitactic seed particles like $\alpha\text{-Fe}_2\text{O}_3$ become smaller (e.g., $\alpha\text{-Fe}_2\text{O}_3$ seeding of $\alpha\text{-Al}_2\text{O}_3$), their reactivity and propensity for solid solution with the matrix increases. If there is a solid solution before the particle seeds the phase transformation then the seed particles may not be present to act as an effective seed.

Seeding Strategy

It has been shown that the seed number density, not the seed weight addition, is the more useful variable for understanding how seeding affects the transformation kinetics and particle size control during the θ to $\alpha\text{-Al}_2\text{O}_3$ phase transformation (Kumagai and Messing, 1985). The seed number density, f_s , depends on the seed size, d , according to

$$f_s = \frac{N_s}{V_{\text{tot}}} = \frac{6m_x}{\pi\rho_o V_{\text{tot}}} \sum_{i=1}^n \frac{wf_i}{d_i^3} \quad (15)$$

where N_s is the number of seeds, V_{tot} is the total volume of the powder, m_x is the weight of the seeds added, ρ_o is the theoretical density of the seed material, and d_i is the seed size for a given weight fraction, wf_i .

Seeding by addition of solid seed particles is limited by the availability of sufficiently small particles ($< 0.1 \mu\text{m}$) to achieve high nucleation number frequencies (i.e., N_s of $> 10^{14} \text{ cm}^{-3}$). Therefore, an important prospect is the development of in-situ chemical processes for nucleation control. Huling and Messing (1990) mixed molecular and colloidal gels to form a hybrid gel for the in-situ nucleation and transformation of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). Upon heating, the molecular gel transformed to mullite crystallites in the colloidal gel matrix, providing nuclei for the bulk transformation of the colloidal gel to mullite. This example illustrates the potential for the control of solid-state transformations by controlling the original chemistry of the system to produce in-situ growth of seed crystals as a means of controlling nucleation of the bulk material.

Phase Separation

Despite homogeneous cation distribution in a precipitate or gel, phase separation is commonly observed during oxide formation in a variety of heterometallic systems. The difference in the crystallization behavior of seemingly homogeneous systems and the influence of processing and impurities on crystallization can be understood from nucleation theory. The classical steady-state homogeneous nucleation rate is given by J_s^* .

$$J_s^* = z\beta N \left(\exp \frac{\Delta G_{\text{hom}}^*}{kT} \right) \quad (16)$$

where z is the Zeldovich factor, β is the rate of single atoms joining a cluster, N is the number of nucleation sites per unit volume (for homogeneous nucleation N = the number of atoms per unit volume), T is temperature, k is the Boltzmann constant and ΔG_{hom}^* is the activation energy for homogeneous nucleation (Porter and Easterling, 1992).

$$\Delta G_{\text{hom}}^* = \frac{16\pi\gamma_{\alpha\beta}^3}{3(\Delta G_v + \Delta G_e)^2} \quad (17)$$

where ΔG_v is the thermodynamic driving force for crystallization, ΔG_e is the strain energy associated with the transformation, and $\gamma_{\alpha\beta}$ is the surface energy of the nucleus-precursor interface.

In general, the activation energy for homogeneous nucleation is high, owing to a high nucleus-matrix surface energy. Consequently, nucleation from homogeneous systems is usually observed at heterogeneous sites such as interfaces or surface heterogeneities. Heterogeneities replace part of the high-energy nucleus-precursor interface with a lower energy heterogeneity-nucleus interface, thus lowering the overall activation barrier. The number of nucleation sites in heterogeneous nucleation is limited by the number of heterogeneities per unit or volume, N_{heter} or N_s . During crystallization, the phase with the highest nucleation rate controls phase formation. The criteria for a high nucleation rate are a high negative free energy of formation (ΔG_v), a low strain energy (ΔG_e), a low nucleus to matrix interfacial energy ($\gamma_{\alpha\beta}$) and a large heterogeneous nucleation site density (N_{heter}). Based only on the free energy of formation, the equilibrium phase has the largest $-\Delta G_v$ and the maximum driving force. However, strain energy differences, surface energy and nucleation site density also affect the nucleation rate and such kinetic factors can lead to the nucleation of nonequilibrium phases. The factors that influence the nucleation rate can be divided into intrinsic and extrinsic processes. Some factors are intrinsic to the equilibrium and competing metastable phases such as the respective free energies of formation, crystal density, surface energy or compositional stability range. Extrinsic factors are usually processing related, such as stoichiometry of heterometallic complexes, heating rate differences during oxide crystallization, incongruent vaporization, and the presence of dissolved impurities or second-phase impurities.

Differences in heterogeneous site density are also responsible for the formation of intermediates with a large compositional stability or for the formation of disordered intermediates before formation of ordered phases. The most common examples of

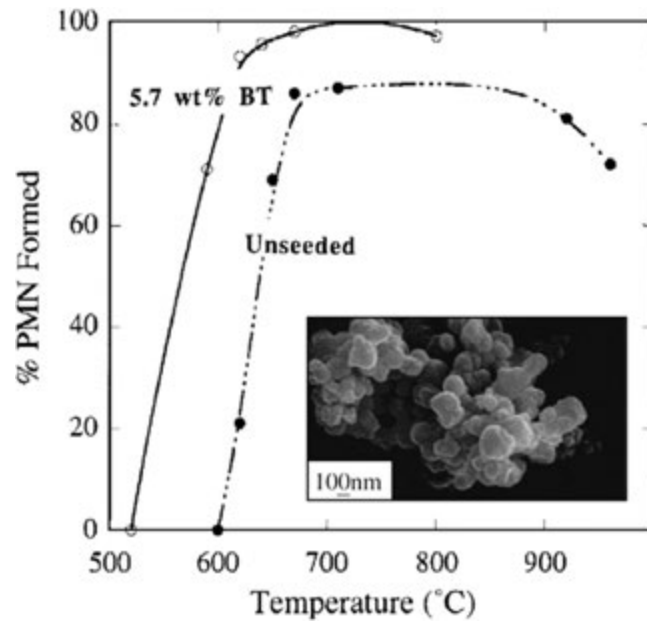


Fig. 7 Effect of BaTiO_3 seeding on perovskite $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ phase formation temperature and PMN particles seeded in a PMN-EDTA precursor. Seed concentration = $1.2 \times 10^{14} \text{ cm}^{-3}$ 100 nm BaTiO_3 particles Reproduced from Narendar, Y., Messing, G.L., 1999. Seeding of perovskite lead magnesium niobate crystallization from Pb-Mg-Nb-EDTA gels. *J. Am. Ceram. Soc* 82, 1659–1664.

undesirable second phase formation in ceramics are observed during synthesis of lead-based perovskite phases. Swartz and Shrout (1982) showed that formation of phase pure $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ from a mixture of PbO , MgO and Nb_2O_5 was impeded by the formation of an intermediate pyrochlore phase. Once the pyrochlore phase formed it was not possible to produce phase pure perovskite powder at higher temperature processing. They developed the so-called “columbite” process in which they used MgNb_2O_6 columbite powders as one of the reactants and completely avoided the formation of the intermediate pyrochlore phase. This process is used routinely for synthesizing many phase-pure lead-based perovskite powders. Incongruent volatilization during calcination is particularly a problem during synthesis of lead-based compounds like $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$. Narendar and Messing (1997) demonstrated the lowering of the synthesis temperature for $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ in a metal carboxylate gel (Fig. 7) by seeding the reaction with 100 nm BaTiO_3 particles (lattice mismatch of $<2\%$ with PMN). Lower synthesis temperature avoided PbO volatilization, and formation of the undesirable pyrochlore phase. The seeding also resulted in fine, equiaxed PMN particles like achieved in the above seeded alumina case.

Summary

Calcination and phase transformations are of critical importance for ceramics, since almost all ceramic powders are produced by such processes. The formation of phase pure ceramic powders of sub-micrometer particle size and without hard multiparticle aggregates is a primary goal of powder synthesis before firing. Seeding of ceramic transformations offers tremendous control over reaction temperatures, rates, and phase development of single and mixed oxide powders. The inherent benefits and technological simplicity of in-situ chemical seeding promises to provide a variety of new seeded ceramic materials and to establish epitaxy as an important tool for process control, as it already is in other advanced materials applications such as single crystal growth and thin film processing.

References

- Bagwell, R.B., Messing, G.L., 1999. Effect of seeding and water vapor on the nucleation and growth of $\alpha\text{-Al}_2\text{O}_3$ from $\gamma\text{-Al}_2\text{O}_3$. *J. Am. Ceram. Soc* 82, 825–832.
- Gaskell, D.R., 1995. *Introduction to the Thermodynamics of Materials*, third ed. Washington, DC: Taylor and Francis.
- Huling, J.C., Messing, G.L., 1990. Hybrid gels for homoepitactic nucleation of mullite. *J. Am. Ceram. Soc.* 72, 1725–1729.
- Khawam, A., Flanagan, D.R., 2006. Solid-state kinetic models: Basics and mathematical fundamentals. *J. Phys. Chem. B* 110, 17315–17328.
- Kingery, W.D., Bowen, H.K., Uhlmann, D.R., 1975. *Introduction to Ceramics*, second ed. New York: Wiley.
- Kissinger, H.E., 1956. Variation of peak temperature with heating rate in differential thermal analysis. *J. Res. Natl. Bur. Stand.* 57, 217–221.
- Kumagai, M., Messing, G.L., 1985. Controlled transformation and sintering of a boehmite sol gel by alpha alumina seeding. *J. Am. Ceram. Soc.* 68, 500–505.
- Kupp, E., Kochawattana, S., Lee, S., Misture, S., Messing, G.L., 2014. Particle size effects on yttrium aluminum garnet (YAG) phase formation by solid-state reaction. *J. Mater. Res.* 29, 2303–2311.
- Levenspiel, O., 1972. *Chemical Reaction Engineering*. New York: Wiley.

- McArdle, J.L., Messing, G.L., 1993. Transformation, microstructure development, and densification in α -Fe₂O₃-seeded boehmite-derived alumina. *J. Am. Ceram. Soc.* 76, 214–222.
- Messing, G.L., McArdle, J.L., Shelleman, R.A., 1986. The need for controlled heterogeneous nucleation in ceramic processing. In: Brinker, C.J., Clark, D.E., Ulrich, D.R. (Eds.), *Better Ceramics Through Chemistry*. Pittsburgh: Materials Research Society, pp. 471–480.
- Mu, J., Perlmutter, D.D., 1981. Thermal decomposition of carbonates, carboxylates, oxalates, acetates, formates and hydroxides. *Thermochim Acta* 49, 207–218.
- Narendar, Y., Messing, G.L., 1997. Mechanisms of phase separation in gel-based synthesis of multicomponent metal oxides. *Catal. Today* 35, 247–268.
- Porter, D.A., Easterling, K.E., 1992. *Phase Transformations in Metals and Alloys*, second ed. UK: Chapman and Hall.
- Ring, T.A., 1996. *Fundamentals of Ceramic Processing and Synthesis*. Boston, MA: Academic Press.
- Shaklee, C.A., Messing, G.L., 1994. Growth of α -Al₂O₃ platelets in the HF- γ -Al₂O₃ System. *J. Am. Ceram. Soc.* 77, 2977–2984.
- Shelleman, R.A., Messing, G.L., 1988. Liquid phase assisted transformation of seeded α -alumina. *J. Am. Ceram. Soc.* 71, 317–322.
- Swartz, S.L., Shrout, T.R., 1982. Fabrication of perovskite lead magnesium niobate. *Mater. Res. Bull.* 17, 1245–1250.
- Turkdogan, E.T., 1980. *Physical Chemistry of High Temperature Technology*. Boston, MA: Academic Press.
- Vyazovkin, S., 2020. Kissinger method in kinetics of materials: Things to beware and be aware of. *Molecules* 25, 2813–2831.

Preceramic Polymers as Precursors of Advanced Ceramics: The Polymer-Derived Ceramics (PDCs) Route

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Introduction

Designing matter from atomistic to macroscopic scale is a unique attribute of chemical materials technologies, such as those based on well-defined molecular and polymeric precursors, to solve the problems arising from ceramic manufacturing with traditional powder-based technologies. They allow a precise control over the chemical compositions and microstructure of advanced ceramics and provide various possibilities towards (more or less complex) shape design that cannot be generated through conventional processes.

The Polymer-Derived Ceramics (PDCs) route represents such a chemical approach to design ceramic materials. This is typically achieved through the pyrolysis of inorganic/organometallic polymers, denoted as “preceramic polymers”, which are prepared from well-defined molecular precursors.

The main benefits of using molecular precursors and synthesizing preceramic polymers (Ionescu *et al.*, 2019) are:

- highest purity of the PDCs compared with those obtained by traditional powder technology. This is attributed to the use of precursors and polymers which allows easy purification of the reacting species by distillation or crystallization,
- high control of the homogeneity, atomic distribution and microstructure of ceramics,
- possibility to produce multi-component and hybrid (organic-inorganic) materials,
- high versatility in terms of processability because of the possibility to precisely control the physical state and rheological properties of preceramic polymers to be shaped using the same methods as for organic polymers or plastics. Alternatively, the ceramic powders (especially those with a complex composition difficult to prepare using the conventional preparative methods) derived from the preceramic polymers can be used in forming processes as performed through the conventional way of processing ceramics, *e.g.*, sintering.

A flow diagram of the single steps involved in the design of advanced ceramics from molecular precursors and preceramic polymers is shown in Fig. 1. Processing ceramics *via* preceramic polymers involves the synthesis (from molecular precursors as monomers), crosslinking (to form an infusible network) and transformation, *i.e.*, ceramization, *via* pyrolysis of these precursors at moderate temperature, typically at 800–1200°C, into amorphous covalently bound ceramics. Subsequently, an optional heat-treatment at higher temperature will achieve the crystallization of the amorphous ceramics.

The first conversion of molecular precursors into ceramics has been reported in the 1950s by Fritz and Raabe (1956) who investigated the thermal decomposition of alkyl silanes, although the initial purpose of this pioneering work was not the synthesis of SiC precursors. During the 1960s, Si-based non-oxide ceramics derived from molecular precursors and preceramic polymers (although the terms ‘preceramic polymers’ was not employed at that time) was reported by Ainger and Herbert (1960) as well as by Chantrell and Popper (1965). These works are usually considered as the pioneer studies performed in the field of PDCs. All these fundamental works led a decade later to the production of silicon carbonitride (Si–C–N) fibers by Verbeek (1974) and silicon carbide (SiC) fibers by Yajima *et al.* (1976) from polysilazanes and polycarbosilanes, respectively. These works nicely marked the beginning of the new field of PDCs and illustrated the contribution of organosilicon precursor chemistry to the preparation of non-oxide ceramics. In the intervening years, there has been much activity worldwide in the PDCs field; especially by extending the potentialities of the PDCs route toward the production of ceramics in compositions other than those containing silicon and in particular shapes, structures and textures in a way not known from other techniques.

Synthesis of Preceramic Polymers and Modification of Pre-Formed Polymers

Synthesis of Preceramic Polymers

Because of their commercial availability and low cost, chlorosilanes of the type $R_{4-x}SiCl_x$ ($1 \leq x \leq 4$) have been largely investigated as monomers for the synthesis of polysiloxanes by hydrolysis of Si–Cl bonds followed by subsequent condensation of the Si–OH intermediates to form Si–O–Si groups in polysiloxanes (Fig. 2) (Moretto *et al.*, 2000). If ammonia is used instead of water, a similar reaction – known as ammonolysis – takes place and silylamines are formed, which can condense to give polysilazanes (Fig. 2) (Kroke *et al.*, 2000). It should be mentioned that chlorosilanes can be mixed together to form blended

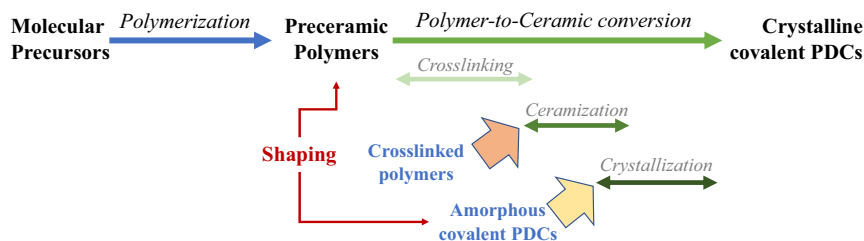


Fig. 1 Flow diagram for the processing of PDCs.

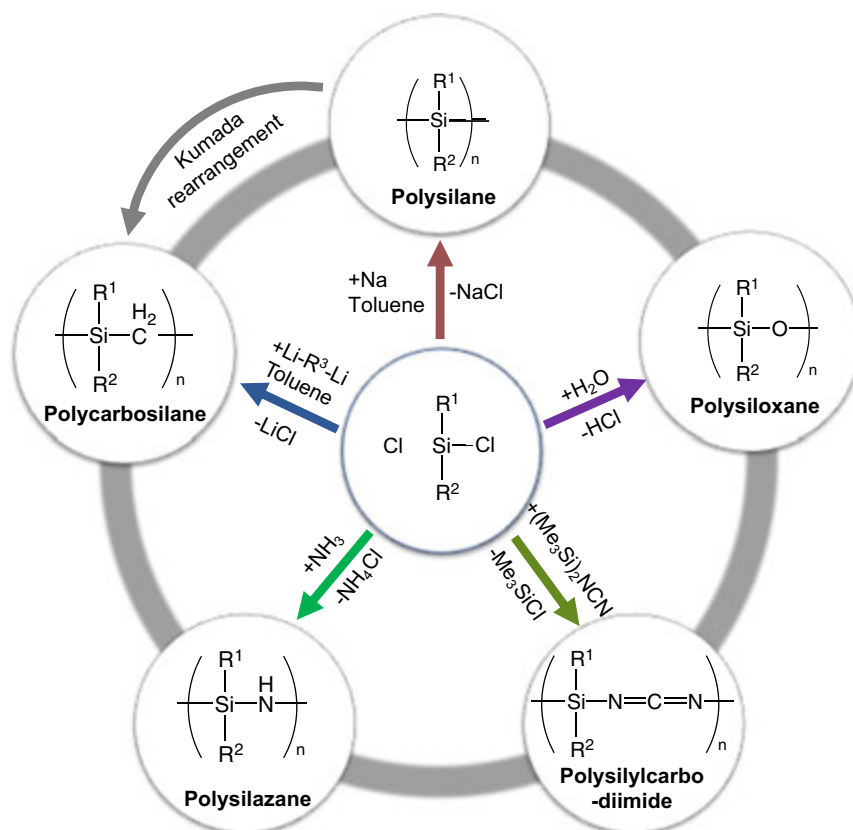
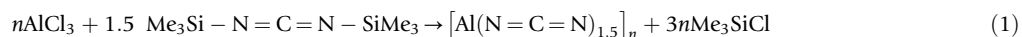


Fig. 2 Organosilicon precursors in the Si-C-N-O system ($R^1 = R^2 = \text{H, CH}_3, \text{CH} = \text{CH}_2$, etc.).

precursors or co-polymers (Weinmann *et al.*, 2001). In addition, they can be modified before their reaction to add specific elements to the future polymer network such as boron using, for instance, borane dimethyl sulfide as a Lewis acid-base complex (Viard *et al.*, 2018; Nguyen *et al.*, 2014). Concerning the synthesis of SiC precursors, the common approach, extensively developed by Yajima *et al.* (1976), consists of the synthesis of polysilanes (PS) *via* the Wurtz coupling method using chlorosilanes and alkali metals. The polysilanes are further converted into polycarbosilanes (PCS, $(-\text{SiR}^1\text{R}^2\text{CH}_2-)_n$) and more precisely $[-\text{SiH}(\text{CH}_3)\text{CH}_2-]_n$ upon thermolysis through the Kumada rearrangement (Fig. 2) (Yajima *et al.*, 1976; Birot *et al.*, 1995). More complex structures containing Si, C, N, and/or O in the three-dimensional polymeric network such as polysilylcarbodiimides can also be produced by non-oxidic sol-gel condensation reaction of chlorosilanes with bis(trimethylsilyl)carbodiimide $(\text{Me}_3\text{Si})_2\text{NCN}$ as illustrated in Fig. 2 (Mera *et al.*, 2013).

These reactions are not limited to organosilicon compounds. Other polymeric compositions can be envisioned by taking advantages of the reactivity of chlorine-containing precursors as molecular precursors including metal chlorides with low molecular weight compounds such as ammonia, amines, hexadimethylsilazane, hydrazines or bis(trimethylsilyl)carbodiimide to form after pyrolysis nitrides and carbonitrides. As an illustration, Eqs. (1) and (2) report specific reactions leading to metal (aluminum or titanium)-organic precursors as preceramic polymers that form aluminum nitride (Eq. (1), (Shimokawa *et al.*, 2015)) and titanium carbonitride (Eq. (2), (Lichtenberger *et al.*, 2003)) after pyrolysis.



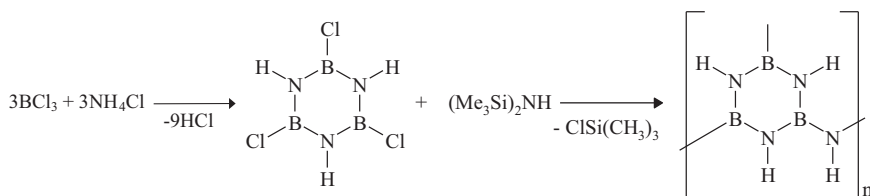
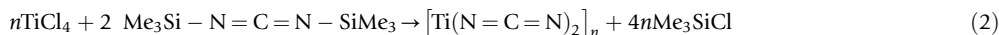


Fig. 3 Formation of boron nitride (BN) precursors starting from boron trichloride (BCl_3) via the synthesis of trichloroborazine (TCB).



An intermediate step can be eventually included as represented in Fig. 3 with the synthesis of boron nitride (BN) precursors starting from boron trichloride (BCl_3) (Narula *et al.*, 1987).

These reactions can be assisted with catalysts and/or a low temperature treatment. However, a problem which always arises when chlorine-containing precursors are transformed into preceramic polymers using the above described strategies is the formation of HCl, liquid by-products or even salts (especially using ammonia and amine) that have to be separated from the polymer, usually by distillation (liquid by-products) or filtration (solid by-products). An elegant way to overcome this problem is to enable polymerization using reactive sites bearing by the molecular precursors such as N-H, M-H, M-C=C (M = cation such as B, Al, Si, *etc.*) by elimination, substitution or addition reactions. Such reactions can be activated by thermolysis and/or use of catalysts such as transition metal-containing compounds. These reactions represent alternative methods for the synthesis of polysilanes, polycarbosilanes, polysilazanes using hydridosilanes as molecular precursors or using chlorine-free molecules to prepare ceramics other than those produced from organosilicon precursors (Bernard and Miele, 2014a,b, Fig. 4).

Once the preceramic polymer structure is established and the synthesis done (pre-formed polymer), the process to design ceramics can be continued through the different steps detailed in Fig. 1. However, the pre-formed polymer can be further modified, chemically and/or at micro-/nanoscale, before its conversion into ceramics. This is presented in the next sections of the present chapter.

Reaction of Pre-Formed Polymers With Low Molecular Weight Species

The reactive sites, if still present in the pre-formed polymer, can be used to (1) attach low molecular weight species to the polymer backbone in order to incorporate additional elements or offer functionality to the pre-formed polymer, *e.g.*, photoresistivity and (2) perform the reaction with a second polymer (at the polymer level or during the first stages of the pyrolysis). It should be pointed out that the chemical modification of preceramic polymers (point (1)) and reaction with a second polymer (point (2)) also help to the crosslinking of preceramic polymers.

The first approach uses low molecular weight species such as Lewis acid-base complex or metal-organic species that contain one or more reactive ends capable of forming bonds by reaction with the reactive sites present in the pre-formed preceramic network. The molecules are selected on the basis of:

- (1) the nature of the element (*e.g.*, metal or metalloid) which should be added to the polymer network to form the targeted ceramics with a homogeneous distribution of the elements at atomic scale,
- (2) their supposed chemical reactivities mainly determined by the nature of the ligands they incorporate.

Most conventional structural ceramics such as binary ceramics (SiC , Si_3N_4 , BN, AlN, *etc.*) have a number of favorable performance characteristics appropriate for high-end applications. This approach that consists to chemically modify pre-formed polymers is in general investigated to access to more complex systems made of three or more elements such as highly stable amorphous structures of PDCs, *e.g.*, Si-B-C-N ceramics (Birod *et al.*, 1995; Viard *et al.*, 2017; Riedel *et al.*, 1996), ceramic nanocomposites (Bechelany *et al.*, 2014; Lale *et al.*, 2017; Bechelany *et al.*, 2017; Ionescu *et al.*, 2012; Papendorf *et al.*, 2011) and mixed crystalline solid solutions of two or more pure phases (*e.g.*, AlN/SiC (Fonblanc *et al.*, 2018)). These complex systems often exhibit dramatically enhanced properties compared to more conventional ceramics. As an illustration, using Lewis acid-base complexes based on borane (or alane) to introduce boron (or aluminum) at molecular scale via vinyl/allyl sites (*i.e.*, hydrometallation) as well as NH units (*i.e.*, dehydrocoupling) as reactive sites present in the pre-formed polymer, Si-B-C-N ceramics as highly stable amorphous ceramics and Si-Al-C-N ceramics as mixed crystalline solid solutions made of AlN and SiC phases can be generated (Fig. 5).

Using metal-organic species such as MX_z (X = ligand, z being the number of ligands attached to M) to introduce metal in the polymer network via reactive sites such as MH (M = B, Si, Al, ...) and NH groups, metal-modified silicon carbide (Cheng *et al.*, 2017; Wen *et al.*, 2014), silicon nitride (Bechelany *et al.*, 2014; Lale *et al.*, 2017; Bechelany *et al.*, 2017; Zhou *et al.*, 2015) or silicon carbonitride (Yuan *et al.*, 2014), mostly as nanocomposites can be synthesized. This can be extended to PDCs other than Si-based compositions.

Beside the addition of elements at molecular scale, this approach can be used to offer functionality to the preceramic polymer. For instance, the reaction of UV-sensitive molecules with the preceramic polymers can lead to photosensitive preceramic polymers with high ceramic yield (Nghiem *et al.*, 2007).

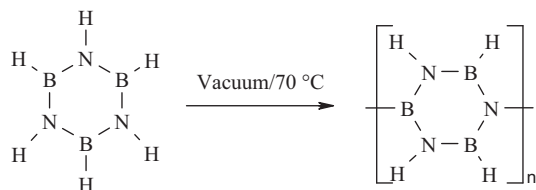


Fig. 4 Self-condensation of borazine leading to polyborazylene as a preceramic polymer through dehydrocoupling reactions between NH and BH reactive groups.

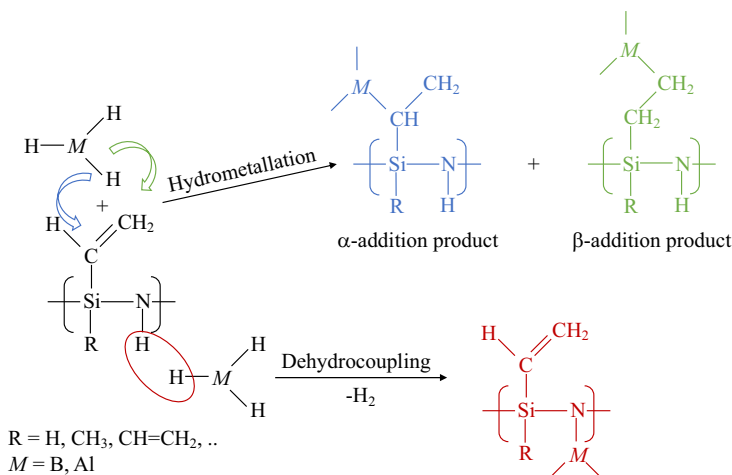


Fig. 5 Addition of elements to pre-formed polymers via hydrometallation (= hydroboration via the addition of B and hydroalumination via the addition of Al) and dehydrocoupling.

Blended Precursors

The second approach consists to mix different polymers. The use of polymer blends as a mixture of at least two polymers leads to the formation of composite materials (by mixing only preceramic polymers together). It should be mentioned that preceramic polymers can be also mixed with organic polymers or resin to offer functionality, *e.g.*, UV-sensitive compounds (De Hazan and Penner, 2017; Eckel *et al.*, 2016; Zanchetta *et al.*, 2016), to form hybrid organic-inorganic compounds (Augustinho *et al.*, 2016), to design porous ceramics by mixing preceramic polymers with organic polymers as sacrificial agents (*e.g.*, PMMA, polyethylene, polystyrene, ...) or nanostructured ceramics by mixing preceramic polymers with block copolymers (Lale *et al.*, 2018). Such approaches are not the subject of the present section; they will be more developed in the section devoted to processability.

This blended precursor approach has been first focused on the design of C/SiC composite materials based on the pioneering work of Interrante *et al.* (1998) from a mixture of a preceramic polymer as SiC precursor (allyl hydrido polycarbosilane, AHPCS) with pitch as C precursor. Then, it has been extended to the preparation of composites such as AlN/SiC, B₄C/SiC, and BN/SiC by simply mixing two single-component precursors (= preceramic polymers) of the desired composition (Interrante *et al.*, 2002; Paine *et al.*, 1994; Guron *et al.*, 2008, 2009; Mori *et al.*, 2006). If single-component precursors are miscible with each other or soluble in organic solvents, a molecular-level homogeneity can be achieved in blended precursors. In general, the two polymers are interacting chemically, *i.e.*, they crosslink *via* condensation or addition reactions of reactive sites present in each individual polymer at the polymer level but better during the first stages of the pyrolysis, thereby limiting the loss of the low-molecular-weight, volatile byproducts that are typically evolved during the pyrolysis of the individual polymers. This induces an increase of the ceramic yield of the pre-formed polymer. In order to increase the ceramic yield of polymers while volume shrinkage is reduced, preceramic polymers including pre-formed polymers and chemically modified polymers can be mixed with fillers at micro-/nanoscale before the conversion into ceramics.

Modification of Preceramic Polymers at Micro-/Nanoscale

As mentioned above, preceramic polymers can be modified at microscale using ceramic powders as passive fillers or metallic powders as active fillers (Francis *et al.*, 2009; Günthner *et al.*, 2012) as deeply investigated by Greil and Seibold (1992), Greil (1995, 1998, 2000) and pioneered by Seyferth (1988) and Seyferth *et al.* (1991). The first purpose of Greil's works was to investigate the limitations when producing polymer-derived bulk components. Indeed, the polymer-to-ceramic conversion (*i.e.*, polymer pyrolysis) involves a complex sequence of structural and chemical changes based on molecular rearrangements

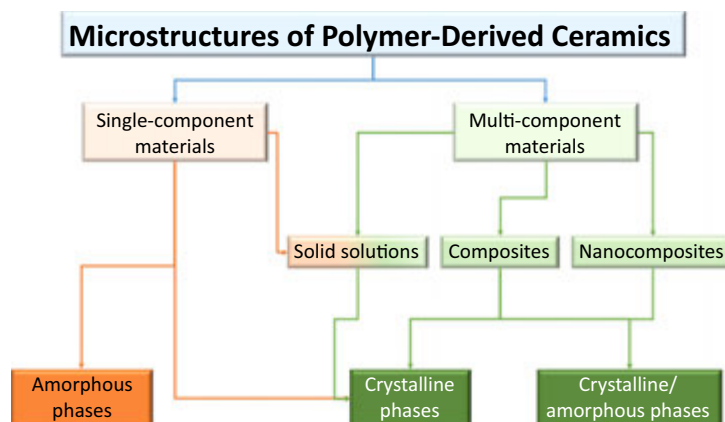


Fig. 6 Various microstructures identified in PDCs.

associated with the release of gaseous by-products inherently inducing both weight loss and a pronounced density increase from the polymers to the targeted ceramics. The resulting high-volume shrinkage leads, if not controlled, to the collapse of the work piece that is produced. Through these reports, it has been suggested that the addition of active fillers such as metal powders to the polymers might significantly minimize the volume shrinkage (and porosity) that is developed upon pyrolysis of a polymeric green body. This is due to the reaction of fillers with the gaseous and solid decomposition products and the gases from the atmosphere (Scheffler *et al.*, 2003). Near net shape manufacturing becomes possible while the reactions allow influencing the ceramic composition by producing new phases; thus, forming in general multi-component ceramics (Torrey and Bordia, 2009). The modification of preceramic polymers at nanoscale using nanoscaled metallic powders such as titanium nanoparticles (Ti NPs) allowed nanostructuring these composites and form nanocomposites (Proust *et al.*, 2016).

After the preparation of preceramic polymers as precursors of ceramics, a heat-treatment under a controlled atmosphere at an appropriate temperature is required to achieve the conversion of preceramic polymers into ceramics.

Thermo-Chemical Conversion of Preceramic Polymers Into Ceramics

Once the synthesis of preceramic polymers has been achieved, a thermo-chemical conversion is needed to deliver ceramics in the targeted phase composition and microstructure. The conversion of the preceramic polymers into ceramics usually consists of two steps: (1) cross-linking processes at low temperatures (100–400°C) leading to infusible hybrids, *i.e.*, organic-inorganic networks; and (2) ceramization at higher temperatures by pyrolysis up to 800–1200°C leading to amorphous ceramics. Subsequent annealing at high temperatures involves the crystallization of the amorphous ceramic network and leads to (poly)crystalline ceramics. Cross-linking reduces the loss of low molecular weight components of the preceramic polymer, *i.e.*, oligomers, as well as their fragmentation processes during the further pyrolysis achieving the ceramization; thus, it increases the ceramic yield of the preceramic polymer. Cross-linking is usually thermally activated *via* addition, substitution or condensation reactions using the reactive groups that did not react at the polymer level, *i.e.*, reactive groups with latent reactivity. In addition to this classical way, it can be assisted by the reactivity of the atmosphere, *e.g.*, ammonia, chlorine, *etc.*, with functional groups, or activated by an external process, *e.g.*, electron beam, UV, plasma, The ceramization process of the cross-linked precursors involves a complex sequence of chemical and physical changes in which polymers evolve toward amorphous covalent ceramics. This occurs through various types of reactions mainly associated with the release of gaseous by-products from the reaction between the different functional groups present in the polymeric network. The evolution of gaseous byproducts involves a weight loss upon the heat treatment. The ceramic yield, represented by $(m_{\text{ceramic}}/m_{\text{polymer}}) \times 100\%$, is a subject of major importance as it decides the general applicability of preceramic polymers as ceramic precursors. The reactions which occur during pyrolysis can be investigated by means of *in-situ* characterization, *e.g.*, gas chromatography-mass spectroscopy coupled with thermogravimetric analyses and *ex-situ* methods such as solid-state NMR, FTIR, X-ray diffraction, Raman spectroscopy and elemental analyses of pyrolysis intermediates isolated at different temperatures during the conversion process. This combined characterization approach allows learning more about the mechanisms involved in the polymer-to-ceramic conversion.

Microstructural Feature of PDCs

The thermo-chemical conversion of preceramic polymers leads to amorphous, covalently bound ceramics. The amorphous character of the covalent ceramics forms a specific state which can be “isolated” or occurs as an intermediate step toward the formation of the desired crystalline ceramics composed of thermodynamically stable phases corresponding to the overall

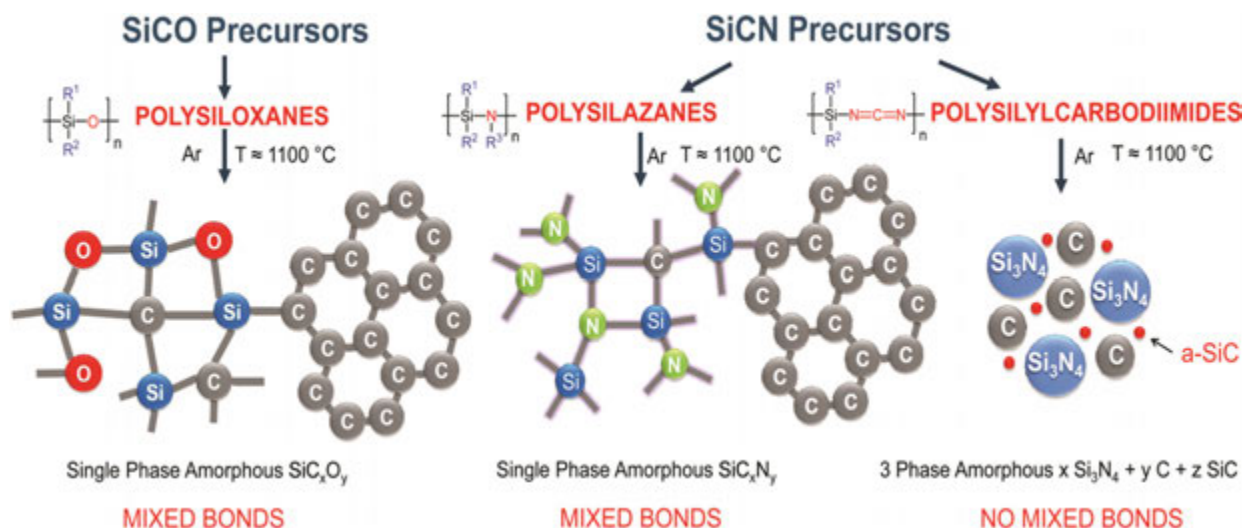


Fig. 7 Precursors used for the synthesis of polymer-derived Si-O-C and Si-C-N ceramics and sketches of the microstructure of their derived ceramics when pyrolyzed at 1100°C in an argon atmosphere.

composition of the amorphous network. Thus, the microstructural feature of PDCs is complex and they can consist of one chemical component, *i.e.*, with a uniquely-defined chemical composition, or as a multi-component material composed of two or more chemical compounds, including solid solutions, composites and nanocomposites. Multi-component PDCs mainly consist of different phases separated from one another by distinct boundaries and represent a means to obtain novel materials with new properties. However, a multi-component material can also exist as a single phase if the different chemical components are intimately mixed (*i.e.*, miscible) at the atomic length scale forming a solid solution in the solid state. Fig. 6 reports the various microstructures accessible for PDCs.

The structures which are generated in PDCs are closely related to the temperature at which polymers have been heat-treated, to the nature of the atmosphere and to the polymer composition and structure. The pioneered works of Yajima on SiC fibers (1976) touched off a rapid development of preceramic polymers that first led to thermodynamic stable crystalline forms of ceramics made of a unique crystalline phase such as boron nitride (BN) and aluminum nitride (AlN) (Bernard and Miele, 2014a,b; Termoss *et al.*, 2009; Penckert *et al.*, 1990; Paine and Narula, 1990). Although such single-component ceramics can display differences in terms of crystallinity and crystalline quality compared to their counterparts prepared by more conventional approaches (this is particularly true for polymer-derived BN which usually displays a “meso-hexagonal” structure as defined by Hubacek *et al.* (1996)), they have a number of favorable performance characteristics appropriate for advanced component applications. However, an inherent weakness is their brittleness: they cleave along the lattice planes. A promising approach to solve this problem consists to prepare single-component ceramics composed of an amorphous inorganic network although such materials can be outside the global thermodynamic equilibrium state. Thus, by selecting element combinations for which the binding energies are derived predominantly from local covalent bonds, polymer-derived amorphous ceramics, as single-component materials, of high kinetic stability, and thus durability, can be formed. These requirements have been met by combining silicon, boron, carbon, nitrogen and/or oxygen in the same material. As an illustration, polymer-derived Si-O-C glasses, composed of a network of $\text{SiO}_x\text{C}_{4-x}$ tetrahedra (*i.e.*, SiO_4 , SiO_3C , SiO_2C_2 , SiOC_3 , and SiC_4) incorporating both Si-C and Si-O but no C-O bonds, are X-ray amorphous after pyrolysis and represent a typical example of a single-component PDC with an amorphous structure that persists up to very high temperatures (Widgeon *et al.*, 2010; Stabler *et al.*, 2018). The small amount of crystallization observed at $>1500^\circ\text{C}$ produces SiC as a result of a carbothermal reaction between SiO_2 and C (Renlund *et al.*, 1991; Bois *et al.*, 1995; Saha and Raj, 2007).

Similar observations can be made with Si-C-N materials as a second typical example of a single-component PDC with an amorphous structure that persists up to very high temperatures. The microstructure of polysilazanes-derived Si-C-N ceramics (prepared at $800\text{--}1200^\circ\text{C}$) consists of an amorphous Si-C-N matrix with tetrahedrally coordinated Si atoms bonded to either nitrogen or carbon or a mixture of carbon and nitrogen and can be therefore designated as $\text{SiC}_x\text{N}_{4-x}$ and referred to a network of mixed bond tetrahedra as for Si-O-C systems (Fig. 7). Upon further heat-treatment, Si-C-N materials remain stable up to $1400\text{--}1500^\circ\text{C}$; before starting to crystallize into Si_3N_4 that react with free carbon to form SiC. It should be pointed out that Si-C-N ceramics derived from polysilylcarbodiimides do not contain any significant concentration of mixed bond tetrahedra (Iwamoto *et al.*, 2001) as previously described for polysilazane-derived Si-C-N ceramics. Their microstructure is rather composed of nanodomains (1–3 nm in size) of amorphous Si_3N_4 and amorphous carbon (a-C) which is responsible for stability against crystallization at temperatures higher than that characteristic of the polysilazanes-derived ceramics (Fig. 7 – Widgeon *et al.*, 2012).

The incorporation of additional elements into the Si-O-C and Si-C-N (or even Si-N) systems, *i.e.*, chemical modification of polysiloxanes and polysilazanes, can lead to a further modification of their microstructure. This can first stabilize the amorphous



Fig. 8 Preparation of ceramic materials by precursor processing.

network as observed with the addition of boron to the Si–O–C and Si–C–N systems. For instance, the quaternary compositions of Si–B–C–N are found to crystallize only at temperatures as high as 1750–1800°C. This can also lead to ceramic composites (and nanocomposites) and solid solutions of two or more pure phases, especially through the modification of preceramic polymers with metal-organic species containing alkaline earth metals (Gonzalo-Juan *et al.*, 2016), first-row metals (Zaheer *et al.*, 2012a,b), transition metals as well as main group semi-metals and metals (Hojamberdiev *et al.*, 2013; Kaspar *et al.*, 2014). The incorporation of metals into Si–O–C, Si–C–N, and Si–N systems affects the phase composition and network architecture of the ceramics as well as their high-temperature evolution. Because of the different ways of incorporating metals into such systems, a large variety of materials can be synthesized from metal nanoclusters distributed in a Si–C–N matrix (Glatz *et al.*, 2010; Bazarjani *et al.*, 2011; Zaheer *et al.*, 2012a,b; Kamperman *et al.*, 2009; Schwarz *et al.*, 2015) to transition metal carbides (TMC), transition metal nitrides (TMN) and/or transition metal silicides (TMS) nanocrystals growing in a SiC, Si₃N₄, Si–C–N, or Si–C–O matrix.

Preceramic polymers do not only provide single- and multi-component ceramics as powders with excellent properties. More importantly, the polymers may be processed before their thermo-chemical conversion into advanced ceramics in more complex shapes in ways not realizable/compatible with other ceramic preparative methods. Thus, there has been intense interest by many research groups on the development of highly processable preceramic polymers as detailed in the following section.

Processability of Preceramic Polymers-Functional PDCs

Because of the possibility of controlling the cross-linking degree, the type of bonds linking monomeric units and the nature of functional groups or substituents attached to the polymer network, preceramic polymers with tailored rheological properties can be synthesized (Duperrier *et al.*, 2007; Ouyang *et al.*, 2013). Thus, the chemistry behind the synthesis of preceramic polymers can be well tailored in order to form, in a next step, as-synthesized preceramic polymers (that can contain active or passive fillers) into a desired shape. This is accomplished by a shape forming process. Thus, polymers can be highly processable as, *e.g.*, thermoset liquid compounds (thermoset because containing reactive groups with latent reactivity, *e.g.*, Si–H, CH=CH₂, B–H, N–H, ... that will react after shaping as explained above) or solid-state materials which can display thermoplasticity when heated at low temperature for applications requiring melt-processing, *e.g.*, melt-spinning.

Polymer shaping allows to produce thin parts or complex architectures such as fibers, matrices, coatings, or dense monoliths (Colombo *et al.*, 2010; Barroso *et al.*, 2019; Viard *et al.*, 2016) using common forming methods such as extrusion-based processing, impregnation/injection-based processes, dip-/spin-coating, slip-/tape-casting and pressing-based processes, *etc.* (Fig. 8). Using additive manufacturing, highly complex 3D architectures can be designed. These forming techniques can be coupled with methods for generating pore networks such as foaming processes and template-based approaches (including the use of sacrificial agents, the hard-template approaches and the self/co-assembly processing using block copolymers) to develop the porosity at various length scales (Colombo, 2008; Borchardt *et al.*, 2012; Vakifahmetoglu *et al.*, 2016) leading to micro-, meso- and/or macroporous components (Fig. 8).

After the polymers are formed, these "green" parts undergo a heat-treatment to produce a rigid, finished product. As ceramics, final materials may undergo a machining and/or polishing step in order to meet specific engineering design criteria for advanced applications. Alternatively, polymers can be directly heat-treated to form powders that can be shaped and/or sintered (Fig. 8). This

approach is very convenient to design dense ceramics when the powders exhibit a complex and tailored composition (*e.g.*, made of three or four elements) which cannot be prepared by the conventional ceramic powder technology (Bechelany *et al.*, 2015; Yuan *et al.*, 2017).

This combined approach coupling chemistry and engineering allows developing the functionality of PDCs. Thus, as-prepared PDCs can fulfill certain functions for applications requiring particular physical-chemical properties such as controlled thermal, electric, optical, magnetic, catalytic properties. As an illustration, PDCs offer a panel of applications such as reinforcing agent, thermal barrier coating systems (Barroso *et al.*, 2015), membranes (Sandra *et al.*, 2016), catalysts, electrocatalysts (de Almeida e Silva *et al.*, 2019; Swain *et al.*, 2019), solar receivers (Mazo *et al.*, 2018), or thermoelectric materials (Kousaalayla *et al.*, 2018), *etc.*

Conclusion

The present chapter has been systematically structured to give clear and detailed insights on the chemistry of polymeric precursors and transformation mechanisms for converting precursors into the solid-state polymer-derived ceramics (PDCs) structures. The PDCs route based on well-defined precursors represents a unique preparative access to ceramics with precise control over phase compositions and microstructures according to the fact that the chemical composition of the materials is controlled at molecular scale. Its main purpose is to produce ceramic materials, often non-oxidic, through the thermo-chemical conversion of suitable preceramic polymers *via* shaping (as a way of forming PDCs), curing (to further crosslink the polymer), pyrolysis (to transform the cured polymer into an amorphous ceramic) and optionally annealing (to crystallize the amorphous ceramics). The PDCs method has provided access to a vast number of Si-based ceramics including SiC and Si₃N₄ and more complex systems made of three or more elements homogeneously distributed on the atomic level (difficult to realize by conventional methods) that provide additional and improved properties as compared to those of binary systems, *e.g.*, higher stability of the amorphous network, better mechanical properties with nanocomposites consisting of ceramic nanoclusters distributed in an amorphous ceramic matrix, *etc.* Besides, the PDCs route allows accessing to conventional Si-free binary systems such as BN and AlN as well as to homogeneously mixed crystalline ceramic solid solutions and (nano)composites in various carbide, nitride, boride and silicide systems.

The industrial potential of PDCs is evident; this has been well demonstrated with the production of SiC fibers in Japan. However, to extend this potential, the process needs to be analyzed, discussed towards simplicity, scalability and cost-effectiveness. Functional properties should be also deeply investigated. With such objectives in mind, it is anticipated that there will be new opportunities for scientists in the practical use of this class of exciting materials.

References

- Ainger, F., Herbert, J., 1960. The preparation of phosphorus-nitrogen compounds as non-porous solids. In: Popper, P. (Ed.), *Special Ceramics*. New York: Academic Press, pp. 168–182.
- Augustinho, T.R., Motz, G., Ihlow, S., Machado, R.A.F., 2016. Application of hybrid organic/inorganic polymers as coatings on metallic substrates. *Materials Research Express* 3, 095301.
- Barroso, G., Krenkel, W., Motz, G., 2015. Low thermal conductivity coating system for application up to 1000°C by simple PDC processing with active and passive fillers. *Journal of the European Ceramic Society* 35, 3339–3348.
- Barroso, G., Li, Q., Bordia, R.K., Motz, G., 2019. Polymeric and ceramic silicon-based coatings – A review. *Journal of Materials Chemistry A* 7, 1936–1963.
- Bazarjani, M.S., Kleebe, H.-J., Müller, M.M., *et al.*, 2011. Nanoporous silicon oxycarbonitride ceramics derived from polysilazanes in situ modified with nickel nanoparticles. *Chemistry of Materials* 23, 4112–4123.
- Bechelany, M.C., Proust, V., Gervais, C., *et al.*, 2014. In situ controlled growth of titanium nitride in amorphous silicon nitride: A general route toward bulk nitride nanocomposites with very high hardness. *Advanced Materials* 26, 6548–6553.
- Bernard, S., Miele, P., 2014a. Polymer-derived boron nitride: A review on the chemistry, shaping and ceramic conversion of borazine derivatives. *Materials* 7, 7436–7459.
- Bernard, S., Miele, P., 2014b. Nanostructured and architected boron nitride. *Materials Today* 17, 443–450.
- Bechelany, M.C., Salameh, C., Viard, A., *et al.*, 2015. Preparation of polymer-derived Si-B-C-N monoliths by spark plasma sintering technique. *Journal of the European Ceramic Society* 35, 1361–1374.
- Bechelany, M.C., Proust, V., Lale, A., *et al.*, 2017. Nanocomposites through the chemistry of single-source precursors: Understanding the role of chemistry behind the design of monolith-type nanostructured titanium nitride/silicon nitride. *Chemistry: A European Journal* 23, 832–845.
- Biro, M., Pillot, J.-P., Dunogues, J., 1995. Comprehensive chemistry of polycarbosilanes, polysilazanes and polycarbosilazanes as precursors of ceramics. *Chemical Reviews* 95, 1443–1477.
- Bois, L., Maquet, J., Babonneau, F., Mutin, H., Lahlou, D., 1995. Structural characterization of sol-gel derived oxycarbide glasses. 1. Study of the thermal stability of the silicon oxycarbide phase. *Chemistry of Materials* 7, 975–981.
- Borchardt, L., Hoffmann, C., Oschatz, M., *et al.*, 2012. Preparation and application of cellular and nanoporous carbides. *Chemical Society Reviews* 41, 5053–5067.
- Chantrell, P., Popper, P., 1965. Inorganic polymers and ceramics. In: Popper, P. (Ed.), *Special Ceramics*. New York: Academic Press, pp. 87–103.
- Cheng, J., Wang, X., Wang, H., Shao, C., Wang, J., 2017. Preparation and high-temperature behavior of HfC-SiC nanocomposites derived from a non-oxygen single-source-precursor. *Journal of the American Ceramic Society* 100, 5044–5055.
- Colombo, P., 2008. Engineering porosity in polymer-derived ceramics. *Journal of the European Ceramic Society* 28, 1389–1395.
- Colombo, P., Mera, G., Riedel, R., Soraru, G.D., 2010. Polymer-derived ceramics: 40 Years of research and innovation in advanced ceramics. *Journal of the American Ceramic Society* 93, 1805–1837.
- de Almeida e Silva, T.C., Mooste, M., Kibena-Poldsepp, E., *et al.*, 2019. Polymer-derived Co/Ni-SiOC(N) ceramic electrocatalysts for oxygen reduction reaction in fuel cells. *Catalysis Science and Technology* 9, 854–866.

- de Hazan, Y., Penner, D., 2017. SiC and SiOC ceramic articles produced by stereolithography of acrylate modified polycarbosilane systems. *Journal of the European Ceramic Society* 37, 5205–5212.
- Duperrier, S., Bernard, S., Calin, A., *et al.*, 2007. Design of a series of preceramic B-tri(methylamino)borazine-based polymers as fiber precursors: Shear rheology investigations. *Macromolecules* 40, 1028–1034.
- Eckel, Z.C., Zhou, C., Martin, J.H., *et al.*, 2016. Additive manufacturing of polymer-derived ceramics. *Science* 351, 58–62.
- Fonblanc, D., Lopez-Ferber, D., Wynn, M., *et al.*, 2018. Crosslinking chemistry of poly(vinylmethyl-co-methyl)silazanes toward low-temperature formable preceramic polymers as precursors of functional aluminium-modified Si-C-N ceramics. *Dalton Transactions* 47, 14580–14593.
- Francis, A., Ionescu, E., Fasel, C., Riedel, R., 2009. Crystallization behavior and controlling mechanism of iron-containing Si – C – N Ceramics. *Inorganic Chemistry* 48, 10078–10083.
- Fritz, G., Raabe, B., 1956. Bildung siliciumorganischer verbindungen. Die thermische zersetzung von $\text{Si}(\text{CH}_3)_4$ und $\text{Si}(\text{C}_2\text{H}_5)_4$. *Zeitschrift für anorganische und allgemeine Chemie* 286, 149–167.
- Glatz, G., Schmalz, T., Kraus, T., *et al.*, 2010. Copper-containing SiCN precursor ceramics (Cu@SiCN) as selective hydrocarbon oxidation catalysts using air as an oxidant. *Chemistry-A European Journal* 16, 4231–4238.
- Gonzalo-Juan, I., Deutsch, R., Mathur, S., *et al.*, 2016. Synthesis and in vitro activity assessment of novel silicon oxycarbide-based bioactive glasses. *Materials* 9, 959.
- Greil, P., Seibold, M., 1992. Modelling of dimensional changes during polymer-ceramic conversion for bulk component fabrication. *Journal of Materials Science* 27, 1053–1060.
- Greil, P., 1995. Active-filler-controlled pyrolysis of preceramic polymers. *Journal of the American Ceramic Society* 78, 835–848.
- Greil, P., 1998. Near net shape manufacturing of polymer derived ceramics. *Journal of the European Ceramic Society* 18, 1905–1914.
- Greil, P., 2000. Polymer-derived engineering ceramics. *Advanced Engineering Materials* 2, 339–348.
- Guron, M.M., Kim, M.J., Sneddon, L.G., 2008. A simple polymeric precursor strategy for the synthesis of complex zirconium and hafnium-based ultra-high-temperature silicon carbide composites ceramics. *Journal of the American Ceramic Society* 91, 1412–1415.
- Guron, M.M., Wei, X., Welna, D., *et al.*, 2009. Preceramic polymer blends as precursors for boron-carbide/silicon-carbide composite ceramics and ceramic fibers. *Chemistry of Materials* 21, 1708–1715.
- Günthner, M., Wang, K., Bordia, R.K., Motz, G., 2012. Conversion behavior and resulting mechanical properties of polysilazane-based coatings. *Journal of the European Ceramic Society* 32, 1883–1892.
- Hojamberdiev, M., Prasad, R.M., Fasel, C., Riedel, R., Ionescu, E., 2013. Single-source-precursor synthesis of soft magnetic Fe_3Si - and Fe_3Si_3 -containing SiOC ceramic nanocomposites. *Journal of the European Ceramic Society* 33, 2465–2472.
- Hubacek, M., Uekii, M., Sato, T., Brozek, V., 1996. High-temperature behaviour of hexagonal boron nitride. *Thermochimica Acta* 282–283, 359–367.
- Interrante, L.V., Moraes, K., Sherwood, W., Jacobs, J., Whitmarsh, C.W., 1998. Low-cost, near-net shape ceramic composites by polymer infiltration and pyrolysis. In: *Proceedings of the 8th Japan-U.S. Conference on Composite Materials*, pp. 506–515. Lancaster, PA: Technomic Publishing.
- Interrante, L.V., Moraes, K., Liu, Q., *et al.*, 2002. Silicon-based ceramics from polymer precursors. *Pure and Applied Chemistry* 74, 2111–2117.
- Ionescu, E., Kleebe, H.-J., Riedel, R., 2012. Silicon-containing polymer-derived ceramic nanocomposites (PDC-NCs): Preparative approaches and properties. *Chemical Society Reviews* 41, 5032–5052.
- Ionescu, E., Bernard, S., Lucas, R., *et al.*, 2019. Ultrahigh temperature ceramics (UHTCs) and related materials – Syntheses from polymeric precursors and energetics. *Advanced Engineering Materials* 21. doi:10.1002/adem.201900269.
- Iwamoto, Y., Matsunaga, K., Saito, T., *et al.*, 2001. Crystallization behaviors of amorphous Si-C-N ceramics derived from organometallic precursors. *Journal of the American Ceramic Society* 84, 2170–2178.
- Kamperman, M., Burns, A., Weissgraeber, R., *et al.*, 2009. Integrating structure control over multiple length scales in porous high temperature ceramics with functional platinum nanoparticles. *Nano Letters* 9, 2756–2762.
- Kaspar, J., Terzioglu, C., Ionescu, E., *et al.*, 2014. Stable SiOC/Sn nanocomposite anodes for lithium-ion batteries with outstanding cycling stability. *Advanced Functional Materials* 24, 4097–4104.
- Kousaalya, A.B., Zeng, X., Karakaya, M., *et al.*, 2018. Polymer-derived silicon oxycarbide ceramics as promising next generation sustainable thermoelectrics. *ACS Applied Materials and Interfaces* 10, 2236–2241.
- Kroke, E., Li, Y.-L., Konetschny, C., *et al.*, 2000. Silazane derived ceramics and related materials. *Materials Science and Engineering* 26, 97–199.
- Lale, A., Proust, V., Bechelany, M.C., *et al.*, 2017. A comprehensive study on the influence of the polyorganosilazane chemistry and material shape on the high temperature behavior of titanium nitride/silicon nitride nanocomposites. *Journal of the European Ceramic Society* 37, 5167–5175.
- Lale, A., Schmidt, M., Mallmann, M.D., *et al.*, 2018. Polymer-derived ceramics with engineered mesoporosity: From design to application in catalysis. *Surface and Coatings Technology* 350, 569–586.
- Lichtenberger, O., Pippel, E., Woltersdorf, J., Riedel, R., 2003. Formation of nanocrystalline titanium carbonitride by pyrolysis of poly(titanylcarbodiimide). *Materials Chemistry and Physics* 81, 195–201.
- Mazo, M.A., Padilla, I., Tamayo, A., *et al.*, 2018. Evaluation of thermal shock resistance of silicon oxycarbide materials for high-temperature receiver applications. *Solar Energy* 173, 256–267.
- Mera, G., Navrotsky, A., Sen, S., Kleebe, H.-J., Riedel, R., 2013. Polymer-derived SiCN and SiOC ceramics-structure and energetics at the nanoscale. *Journal of Materials Chemistry A* 1, 3826–3836.
- Moretto, H.-H., Schulze, M., Wagner, G., 2000. Silicenes. In: *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA.
- Mori, Y., Ueda, T., Kitaoka, S., Sugahara, Y., 2006. Preparation of Si-Al-N-C ceramic composites by pyrolysis of blended precursors. *Journal of the Ceramic Society of Japan* 114, 497–501.
- Narula, C.K., Schaeffer, R., Paine, R.T., Datye, A., Hammett, W.F., 1987. Synthesis of boron nitride ceramics from poly(borazylamine) precursors. *Journal of the American Chemical Society* 109, 5556–5557.
- Nguyen, V.L., Proust, V., Quievryn, C., *et al.*, 2014. Processing, mechanical characterization and alkali resistance of siliconboronoxycarbide (SiBOC) glass fibers. *Journal of the American Ceramic Society* 97, 3143–3149.
- Nghiem, Q.D., Kim, D., Kim, D.-P., 2007. Synthesis of inorganic-organic deblock copolymers as a precursor of ordered mesoporous SiCN ceramic. *Advanced Materials* 19, 2351–2354.
- Ouyang, T., Gottardo, L., Bernard, S., Balan, C., Miele, P., 2013. Tuning of the viscoelastic properties of melt-spinnable boron- and silicon-based preceramic polymers. *Journal of Applied Polymer Science* 128, 248–257.
- Paine, R.T., Narula, C.K., 1990. Synthetic routes to boron nitride. *Chemical Reviews* 90, 73–91.
- Paine, R.T., Janik, J.F., Fan, M., 1994. Some recent developments in precursor routes to ceramic nanocomposites. *Polyhedron* 13, 1225–1232.
- Papendorf, B., Nonnemacher, K., Ionescu, E., Kleebe, H.-J., Riedel, R., 2011. Strong influence of polymer architecture on the microstructural evolution of hafnium-alkoxide-modified silazanes upon ceramization. *Small* 7, 970–978.
- Penckert, M., Vaahs, T., Bruck, M., 1990. Ceramics from organometallic polymers. *Advanced Materials* 2, 398–404.
- Proust, V., Bechelany, M.C., Ghisleni, R., *et al.*, 2016. Polymer-derived Si-C-Ti systems: From titanium nanoparticle-filled polycarbosilanes to dense monolithic multi-phase components with high hardness. *Journal of the European Ceramic Society* 36, 3671–3679.
- Renlund, G.M., Prochazka, S., Doremus, R.H., 1991. Silicon oxycarbide glasses: Part II. Structure and properties. *Journal of Materials Research* 6, 2723–2734.

- Riedel, R., Kienzie, A., Dressler, W., *et al.*, 1996. A silicoboron carbonitride ceramic stable to 2000°C. *Nature* 382, 796–798.
- Saha, A., Raj, R., 2007. Crystallization maps for SiCO amorphous ceramics. *Journal of the American Ceramic Society* 90, 578–583.
- Sandra, F., Ballestero, A., NGuyen, V.L., *et al.*, 2016. Silicon carbide-based membranes with high filtration efficiency, durability and catalytic activity for CO/HC oxidation and soot combustion. *Journal of Membrane Science* 501, 79–92.
- Scheffler, M., Dernovsek, O., Schwarze, D., *et al.*, 2003. Polymer/filler derived NbC composite ceramics. *Journal of Materials Science* 38, 4925–4931.
- Schwarz, S., Friedrich, M., Motz, G., Kempe, R., 2015. Synthesis of hierarchically porous SiCN materials and Pd catalysts based on it for the oxidation of methane. *Zeitschrift für anorganische und allgemeine Chemie* 641, 2266–2271.
- Seyferth, D., 1988. Organosilicon polymers as precursors for silicon-containing ceramics. In: Laine, R.M. (Ed.), *Transformation of Organometallics Into Common and Exotic Materials: Design and Activation*. The Netherlands: Springer, pp. 133–154.
- Seyferth, D., Bryson, N., Workman, D.P., Sobon, C.A., 1991. Preceramic polymers as “reagents” in the preparation of ceramics. *Journal of the American Ceramic Society* 74, 2687–2689.
- Shimokawa, Y., Fujiwara, A., Ionescu, E., *et al.*, 2015. Formation of aluminium nitride from metal-organic precursors synthesized by reacting aluminium tri-chloride with bis (trimethylsilyl)carbodiimide. *Journal of the Ceramic Society of Japan* 123, 106–113.
- Stabler, C., Ionescu, E., Graczyk-Zajac, M., Gonzalo-Juan, I., Riedel, R., 2018. Silicon oxycarbide glasses and glass-ceramics: “all-rounder” materials for advanced structural and functional applications. *Journal of the American Ceramic Society* 101, 4817–4856.
- Swain, I.P., Pati, S., Behera, S.K., 2019. A preceramic polymer derived nanoporous carbon hybrid for supercapacitors. *Chemical Communications* 55, 8631–8634.
- Termoss, H., Bechelany, M., Toury, B., *et al.*, 2009. Shaping potentialities of aluminum nitride polymeric precursors. Preparation of thin coatings and nanostructures in liquid phase. *Journal of the European Ceramic Society* 29, 857–861.
- Torrey, J.D., Bordia, R.K., 2009. Filler systems (bulk components and nanocomposites). In: Colombo, P., Riedel, R., Soraru, G.D., Kleebe, H.-J. (Eds.), *Polymer-Derived Ceramics: From Nano-Structure to Applications*. Lancaster, PA: DEStech, pp. 329–341.
- Vakifahmetoglu, C., Zeydanli, D., Colombo, P., 2016. Porous polymer derived ceramics. *Materials Science and Engineering R* 106, 1–30.
- Verbeek, W., 1974. Production of shaped articles of homogeneous mixtures of silicon carbide and nitride. U.S. Patent 3,853,567.
- Viard, A., Miele, P., Bernard, S., 2016. Polymer-derived ceramics route toward SiCN and SiBCN fibers: From chemistry of polycarbosilazanes to the design and characterization of ceramic fibers. *Journal of the Ceramic Society of Japan* 124, 967–980.
- Viard, A., Fonblanc, D., Schmidt, M., *et al.*, 2017. Molecular chemistry and engineering of boron-modified polyorganosilazanes as new processable and functional SiBCN precursors. *Chemistry: A European Journal* 23, 9076–9090.
- Viard, A., Fonblanc, D., Lopez-Ferber, D., *et al.*, 2018. Polymer derived Si-B-C-N ceramics: 30 years of research. *Advanced Engineering Materials* 20, 1800360–1800371.
- Weinmann, M., Zern, A., Aldinger, F., 2001. Stoichiometric silicon nitride/silicon carbide composites from polymeric precursors. *Advanced Materials* 13, 1704–1708.
- Wen, Q., Xu, Y., Xu, B., *et al.*, 2014. Single-source-precursor synthesis of dense SiC/HfC_xN_{1-x}-based ultrahigh-temperature ceramic nanocomposites. *Nanoscale* 6, 13678–13689.
- Widgeon, S.J., Sen, S., Mera, G., *et al.*, 2010. ²⁹Si and ¹³C solid-state nmr spectroscopic study of nanometer-scale structure and mass fractal characteristics of amorphous polymer derived silicon oxycarbide ceramics. *Chemistry of Materials* 22, 6221–6228.
- Widgeon, S., Mera, G., Gao, Y., *et al.*, 2012. Nanostructure and energetics of carbon-rich sicn ceramics derived from polysilylcarbodiimides: Role of the nanodomain interfaces. *Chemistry of Materials* 24, 1181–1191.
- Yajima, S., Hayashi, J., Omori, M., Okamura, K., 1976. Development of a silicon carbide fibre with high tensile strength. *Nature* 261, 683–685.
- Yuan, J., Li, D., Johans, K.E., *et al.*, 2017. Preparation of dense SiHf(B)CN-based ceramic nanocomposites via rapid spark plasma sintering. *Journal of the European Ceramic Society* 37, 5157–5165.
- Yuan, J., Hapis, S., Breitzke, H., *et al.*, 2014. Single-source-precursor synthesis of hafnium-containing ultrahigh-temperature ceramic nanocomposites (UHTC-NCs). *Inorganic Chemistry* 53, 10443–10455.
- Zaheer, M., Keenan, C.D., Hermannsdörfer, J., *et al.*, 2012a. Robust microporous monoliths with integrated catalytically active metal sites investigated by hyperpolarized ¹²⁹Xe NMR. *Chemistry of Materials* 24, 3952–3963.
- Zaheer, M., Schmalz, T., Motz, G., Kempe, R., 2012b. Polymer derived non-oxide ceramics modified with late transition metals. *Chemical Society Reviews* 41, 5102–5116.
- Zanchetta, E., Cattaldo, M., Franchin, G., *et al.*, 2016. Stereolithography of SiOC ceramic microcomponents. *Advanced Materials* 28, 370–376.
- Zhou, C., Gao, X., Xu, Y., *et al.*, 2015. Synthesis and high-temperature evolution of single-phase amorphous Si–Hf–N ceramics. *Journal of the European Ceramic Society* 35, 2007–2015.

Organic Additives in Ceramic Processing

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Introduction

The twentieth century saw the development of new technical ceramics and has profoundly transformed the traditional techniques of fabrication. Ceramics are no-longer only clay-based materials with a natural plasticity when mixed with water, but are also based on metal oxides (such as alumina, titania, zirconia, etc.), or non-oxides (such as nitrides, carbides, borides), which are difficult to shape. Multiple ceramic processes appeared thus, using these raw materials in the form of powders, pastes and suspensions to transform them into functional ceramic products. To control their homogeneity, stability, and rheological properties, and to adjust the formulations to the process specifications, organic processing aids, such as dispersants, polymers, or surfactants, are necessarily added to ceramic powders (Lange, 1989).

The twenty first century is the one of industry 4.0, which makes the convergence of industrial production and information and communication technologies. The industry 4.0 is a new concept based on principles that are still not completely defined. One consequence is the advent of product customization and highly flexible production in smart factories. The ceramic industry is engaged in this revolution. It has already started with the arrival of innovative processing techniques such as additive manufacturing, opening new perspectives to get on-demand materials, finer resolution, original shapes and more versatility (Zocca *et al.*, 2015). The current challenge concerns the discrete nature of raw materials, ceramic powders being heterogeneous, often with agglomerates, abrasive, and with a high melting temperature.

This chapter presents the basis of ceramic formulations emphasizing the specific actions of organics to adapt the raw powder properties to ceramic processing requirements. More attention is paid to the triptych dispersant, binder and plasticizer, which confers fundamental properties, i.e., stability, adapted rheology with low viscosity at high solid loadings, and green cohesion. The new developments done this last decade are emphasized, either on new formulas, or on a better understanding of the organics action and interactions. Finally some challenges are stated for the future of ceramic formulations, which will come along the developments of new manufacturing methods, in a century where new rules will be imposed by a higher environmental awareness.

Formulation Concepts for Ceramic Processing

Traditional ceramics, as potteries manufactured thousand years ago, are made up of clays, because these materials are naturally plastic when mixed with water. Actually most ceramic powders are inherently difficult to handle and shape, because of a lack of cohesiveness and plasticity. Forming techniques commonly employed for metals and polymers, e.g., deformation methods, melt casting, or machining operations, are unsuitable. In order to develop technical and advanced ceramics, the strategy consists in employing organic processing aids in order to adapt the raw material to the forming technique specifications (Reed, 1995). Organics are necessary to provide to ceramic mixtures optimal properties for the forming process chosen, generally in terms of stability and rheology (Shanefield, 1999).

In a classical approach (Lange, 1989; Haussonne *et al.*, 2005), a ceramic material is the result of five processing steps, which all affect its final properties (Chartier, 2007):

- (1) Powder selection: ceramic powders can be prepared by different synthesis methods, or obtained by chemical treatments of natural ores. Their properties are adapted to the process or the final application by chemical or physical treatments, generally classification, grinding, milling, and dispersion.
- (2) Formulation: this step consists in the definition of the nature and amount of solvent and organics added to the powder, in order to confer to the ceramic mixture the required properties to the shaping process. This step most often requires an optimization.
- (3) Shaping process: this step allows to give a shape to a ceramic powder, feedstock or slurry through the use of a specific technique.
- (4) Low temperature consolidation: drying.
- (5) High temperature consolidation: organics removal (debinding) and sintering.

Shaping processes can be classified according to the nature of the ceramic mixture that can be in a dry state (e.g., for uniaxial or isostatic pressing), in a plastic state (for extrusion or injection), or in a liquid state (e.g., for slip casting or granulation). The nature and amount of organics differ drastically between the different processes, from only a few percent of the volume of the final mixture (e.g., for uniaxial pressing), to 50% of the volume (e.g., for injection), as summarized in Table 1.

The role of these additives is also to confer the desired cohesion and plasticity to the green body. Drying is a critical step which can reveal problems present in the formulation such as inhomogeneity, segregation, sedimentation, or lead to cracks due to capillary stresses associated to the inherent fragility of ceramics, which may be partially solved by an appropriate use of organics.

Table 1 Classification of ceramic formulations depending on the forming process

Formulation			Ceramic forming process	
Ceramic mixture	%vol of powder	%vol of solvent and organics	Classical	Additive manufacturing
Powder	>90	<10	Pressing (uniaxial, isostatic, etc.)	SLS (selective laser sintering)...
Paste or feedstock	50–70	30–50	Extrusion, injection molding	Robocasting,...
Colloidal suspension	15–50	50–85	Slip/gel/coagulation casting, tape casting, granulation...	Ink jet printing, stereolithography, etc.

Table 2 List of nature and functions of organic additives used for ceramic processing

Nature of organic additives	Function
Dispersants	Improve stability, state of dispersion and adjust rheological behavior of suspensions
Binders	Improve green strength
Plasticizers	Improve flexibility and handling of green bodies
Lubricants	Decrease frictions and improve mold release
Wetting agents	Decrease surface tension of liquids and improve wettability
Humectants	Slow down drying
Antifoaming agents	Prevent foam formation or destroy foam
Fungicides, bactericides	Improve stability with aging

Finally, these organics, which are necessary during the formulation and the shaping steps, must be completely removed before the sintering step. They are usually released by pyrolysis at moderate temperature (200–600°C), below the temperature of densification of the material. The debinding remains a critical step in the elaboration of a ceramic part. Therefore the choice of the nature and amount of organics also depend of parameters such as the temperature and time of pyrolysis, the chemical elements remaining after calcination which may affect the densification and the final properties (such as alkali, sulfur, carbon, etc.) and cost.

General Use of Organics for Ceramic Processing

Types of Organic Additives

Organic additives for ceramic processing provide multiple functions (Pugh and Bergström, 1993), most of them being reported in Table 2.

The stability of the ceramic base system and a satisfactory state of dispersion are generally difficult to obtain without the use of a dispersant, which is compulsory in most ceramic formulations. Dispersants avoid particle agglomeration, and improve rheological behavior of suspensions (Lewis, 2000; Bergstrom, 2001).

Binders and plasticizers are also present in most ceramic formulations, as it is very difficult to give cohesion, avoid cracks together with a good handling of green bodies from ceramic powders only.

The other additives listed are less common and really depend on the processing method and the powder. For example, ink-jet printing imposes drastic specifications to the formulation of ceramic suspensions in terms of surface tension for instance, in order to be ejected through very fine nozzles below 50 µm in diameter, and in terms of drying of the deposited droplet. Therefore formulations include dispersant, binder, plasticizer, humectant and surfactant (Magdassi, 2010). Extrusion process will impose the use of a lubricant to limit the frictions with the metallic parts of the machine, as well as a defoaming agent to eliminate air bubbles introduced during the aqueous feedstock preparation.

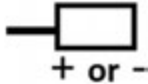
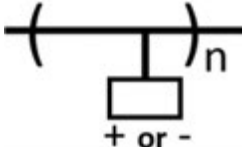
A focus on the action of dispersant, binder and plasticizer, and the main molecules used for these functions, is presented in the following.

Dispersants

The role of dispersants is to maintain a high degree of stability of ceramic powders in liquid or organic medium, i.e., to avoid their agglomeration, coagulation or flocculation, and finally their sedimentation.

Dispersion of ceramic powders in liquids is the result of three stages. The first one is wetting, in which the liquid phase wets and spreads on the powder external surface, and where solid/gas interfaces are replaced by solid/liquid interfaces. The second stage consists in deagglomeration, by breaking up aggregates and agglomerates, in order to form primary particles, using a mechanical action such as dispersion or milling. The last stage is the stabilization when the primary units remain dispersed through the liquid medium.

Table 3 Dispersant stabilization

<i>Dispersant stabilization</i>		
<i>Electrostatic</i>	<i>Steric</i>	<i>Electrosteric</i>
		
Carboxylic acid, sulfate, sulfonate, phosphate, etc.	Non-ionic polymer, oil, fatty acid, ester phosphate, etc.	Polyelectrolyte (polyacrylate, polymetacrylate, polysulfonate, etc.), polyimine, etc.

In the last stage, particles are subject to different interactions: attractive forces of Van der Waals, repulsive forces resulting from their surface charge, Brownian motion, gravitational effects. For colloidal particles, the problem of the stabilization is treated by the DLVO theory (Derjaguin and Landau, 1993).

Dispersants are surface-active chemical agents allowing either electrostatic and/or steric repulsions between primary particles. The selection of appropriate dispersants depends on the nature of the chemical surface of particles, and the nature of the solvent (Table 3).

Steric stabilization

Steric dispersants are oligomers, long-chain polymers or block copolymers, which adsorb at the surface of ceramic particles and create a physical barrier avoiding particles to approach at a distance where Van der Waals forces are influent (a few nanometers) (Napper, 1983). To be efficient, such species should contain anchoring groups to adsorb on the particle surface, and have a good solubility in the solvent to form the largest layer of repulsion. However, if the polymer can adsorb to more than one particle at the same time, the polymer will hold the particles together, and give rise to the so-called bridging flocculation. This effect is generally observed with a strong adsorption from the polymer of high molecular weight. In the case of non-adsorbed polymer, an attractive force is created if the polymer is evicted from the region between two approaching surfaces. A high concentration of polymer creates an osmotic pressure difference resulting in the so-called depletion flocculation. With a good solvent compatibility, polymers will extend their chains and form long tails, whereas with lower compatibility, they will roll and form loops to minimize solvent interactions, and thus their effect. Therefore, non-charged polymers are used in organic solvents (polyethylene glycol...), as well as organic molecules of smaller size such as phosphate esters, fatty acid esters, oils (Menhaden fish oil), etc., whereas polyelectrolytes are used in aqueous solvent.

Electrostatic and electrosteric stabilization

All materials spontaneously acquire an electrical surface charge when they are in contact with a polar medium like water. In the case of ceramics, which present a metal oxide surface (M–OH), surface charges are the result of an ionization of surface groups and is very dependent of pH and electrolyte concentration (James and Parks, 1982).

The role of electrostatic dispersants is to enhance particles surface charge by adsorbing charged molecules. Electrostatic stability is generally correlated to a high zeta potential value (Vallar *et al.*, 1999). Acidic molecules stabilize basic surfaces (such as alumina), and basic molecules stabilize acidic surfaces (such as silica). For example, alumina or zirconia suspension is stabilized with inorganic acids such as nitric acid, and organic acids such as acetic acid which adds a small steric barrier (Bowen *et al.*, 2002; Hanaor *et al.*, 2012). Silica or silicon carbide suspension is stabilized by inorganic bases such as ammonia, or by organic bases such as TMAH (tetramethylammonium hydroxide) (Li *et al.*, 2004).

Polyelectrolyte dispersants are widely used in aqueous-based formulations. These are polymers which contain ionizable groups such as carboxylic acids, sulfates or sulfonic acids. Polyanions are much more widely used, whereas positive charges are almost essentially obtained with polyethylene imine (PEI) which contains amino groups (Baklouti *et al.*, 1997b; Boufi *et al.*, 2002). The most employed polyelectrolytes are the derivatives of polyacrylic acid such as Darvan C–N from Vanderbilt Minerals, and Dolapix from Zschimmer & Schwarz. Polyelectrolytes combine both steric and electrostatic effects, sometimes called electrosteric effect, leading to very high performances at low concentration of polymer. Their adsorption and conformation are correlated to the chemical and physical properties of the powder and the solvent (pH and ionic strength). Adsorption is favored when polyelectrolyte species and particle surface carry opposite charges. For example, polyacrylate (PAA) adsorption onto alumina surfaces is doubled at pH 6 compared to pH 10, and saturation is observed very rapidly at pH 10 (Bowen *et al.*, 2005). Moreover PAA conformation is very different at pH 6 and pH 10: many adsorption sites are present at pH 6 leading to a flat conformation, whereas at pH 10, the number of adsorption sites is few leading to a brush-like conformation.

Dispersants of lower molecular weight may have advantages over such polyelectrolytes thanks to a lower cost, higher adsorption capacities, or by avoiding bridging effects. Small carboxylic acids such as citric acid, oxalic acid, formic acid, etc., are very effective electrostatic dispersants for aqueous suspensions of Al₂O₃, TiO₂, or ZrO₂. More recently, new molecules proved a very high efficiency for the dispersion of alumina nanopowders, allowing high solid loadings at low concentration of dispersant. This is the case of 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA), introduced in the form of a sodium salt (PBTCA), and which presents an “umbrella” structure with three functional –COO[–] groups (Penard *et al.*, 2005). This molecule can be grafted at the oxide surface thanks to the phosphonate group. Its performance is close to 4,5-dihydroxy-1,3-benzenedisulfonic acid (Tiron)

added as a disodium salt. This last molecule adsorption is due to the formation of an inner sphere complex between the alcohol groups and the metal ion of the alumina surface, while the two functional $-\text{SO}_3^-$ groups bring a high negative charge.

Clays were traditionally stabilized with inorganic salts such as sodium metasilicate (Na_2SiO_3), sodium orthosilicate (Na_4SiO_4), sodium carbonate (Na_2CO_3), or some mixtures of those salts (like Dolaflux Zschimmer & Schwarz). Some new defloculants have recently appeared showing a higher efficiency, by coupling a better understanding of the stabilization mechanisms and the physico-chemical properties of the raw powders (Carty *et al.*, 2000). Actually, these materials are phyllosilicates, presenting both silica-like and alumina-like surfaces. The efficient dispersants are the same as those used for alumina in technical applications, despite the dual nature of these materials. Therefore, polyelectrolytes such as polyacrylic acid (PAA), polymetacrylic acid (PMAA) or polyphosphates like sodium hexametaphosphate (HMP) are now classically used in clay formulations (Carty *et al.*, 2000). Another class of dispersant for these materials are block copolymers, with a block bearing anionic groups such as acrylates, and another block inducing steric hindrance.

Finally, even if electrostatic stabilization is closely associated to aqueous solvents, electrostatic effects should not be neglected in non-polar media. In electrolyte with moderate dielectric constant such as low molecular weight alcohols, amines, aldehydes or ketones, there is a low degree of ionization leading to charging mechanisms similar to those present in water, with a lower charge density. For solvents with a very low dielectric constant (alkanes, alkenes, aromatics, etc.) some dispersing agents are able to give a particle surface charge through an electron-donor or acid-base mechanism (Pugh and Bergström, 1993). Therefore acidic polymers (e.g., PVC) or basic polymers (e.g., PMMA) are very effective dispersants in non-aqueous media.

Binders and Plasticizers

The role of binders is to enhance the strength of green ceramic bodies, whereas plasticizers bring flexibility and malleability. These additives are generally polymers. Binders often present a higher molecular weight than plasticizers (generally 10^4 – 10^5 g/mol for binders, and 10^2 – 10^3 g/mol for plasticizers). Plasticizers have generally a high degree of solvent power for the binder. Their action results from an adsorption on the polymer chains to reduce the valence forces between them. This leads to a softened polymer, with enhanced flexibility and a lower glass transition temperature (T_g) (Baklouti *et al.*, 1997a).

The binding action is the result of a physical adsorption on the surface of ceramic particles. These polymers must present a good affinity for ceramic surfaces through electrostatic interactions or hydrogen bonding. As a consequence, their adsorption can compete with dispersant, leading sometimes to a desorption of the dispersant in time, and a loss of stability in the final formulation. That is why the protocols of formulation have to be carefully defined. For example, the order the additives are introduced with the ceramic powder is crucial: if the binder is present first, all adsorption sites may be occupied and no dispersant may adsorb (Marie *et al.*, 2017). The successive treatments applied to the suspensions or pastes have to be carefully considered. If a milling treatment is applied, desorption of the dispersant may occur. Moreover, the milling treatments in general may break the chains of the polymers and modify their action.

Binders and plasticizers must be soluble in the solvent. To be water soluble, organic binders have to contain polar groups. These chemical functions develop intermolecular bonds that often make them insoluble. To avoid this effect, they present side groups to inhibit intermolecular interactions. This is the case with poly(vinyl alcohol) (PVA), which is a classical binder for ceramic systems in aqueous solvent. PVA is insoluble in water and presents 12%–20% of acetate groups to render it soluble. Cellulose is modified in the same way by replacing $-\text{OH}$ groups by methyl, hydroxyethyl, carboxymethyl or hydroxypropyl side groups. In non aqueous systems, the most common binders used are poly(vinyl butyral), poly(methyl methacrylate), polystyrene, ethylcellulose, paraffin, wax, etc. Phthalates are excellent plasticizers in organic solvents.

Binders have a significant effect on viscosity, depending on their concentration. Examples of low-viscosity polymers are Arabic gum, lignosulfonates and dextrin. Low to medium-viscosity polymers include poly(vinyl alcohol), poly(vinylpyrrolidone), poly(ethylene oxide), acrylic and poly(ethylene imine). Medium to high-viscosity polymers include modified cellulose and alginate. The viscosity is also impacted by molecular weight, as well as polymer conformation. If the chains of the molecule are deployed and extended, it will confer a higher viscosity to the formulation than if they are curved and rolled. Furthermore a solution of binder can gel, by physical or chemical bonding between the polymer molecules. The formation of the gel can be induced by a thermal action (heating or cooling), or through the addition of a chemical agent.

Organic binders that are insoluble in water can be added as emulsions or latexes. For example, waxes can be used in aqueous systems through the use of an emulsifying agent. A latex consists of a stable concentrated polymer colloidal dispersion in water. In ceramic formulations, acrylic latexes are predominant (Pagnoux *et al.*, 1998). Their great advantage is that the viscosity remains low even at high solid loadings, reducing the amount of solvent to be removed during drying. The action of this type of binder is based on a different mechanism than classical polymers. When water evaporates during the drying stage, polymer colloids coalesce to yield a binding film that encapsulate ceramic particles to give cohesion and strength (Kiennemann *et al.*, 2005). With a high T_g , the latex will give strength to the ceramic material, whereas with a low T_g (below ambient), it will provide flexibility. Therefore, some different latexes can be combined to obtain the required green strength.

Other Additives

Dispersant, binder and plasticizer constitute the compulsory triptych of the organics used in ceramic formulations to get an adapted behavior of a suspension, a paste or a ceramic powder. However some other additives can be added to address specific requirements.

Wetting agents may be added to ceramic formulations in order to lower the surface tension of the suspension, leading to a better spreading on surfaces during the processing steps or in the molds. These are generally surfactants possessing a hydrophilic head and a hydrophobic tail.

The presence of many organics and especially surfactants may cause the stabilization of air bubbles, in the form of micro-bubbles or surface foam, which cause residual porosity in the final material. Defoamers are chemicals that prevent foaming, or destroy any foam produced during the processing steps. Generally a defoamer is insoluble in the foaming medium and has surface active properties. Its action results from an affinity to the air-liquid surface to destabilize the foam lamellas, leading to the rupture of the air bubbles. A large variety of defoaming agent exists. The main products are oil-based defoamers containing waxes such as paraffin, esters or fatty alcohols, and silicone based defoamers, which can be found as oils or water-based emulsions. The last generation are molecular defoaming agents, which interact with the other surfactants in the formulation to prevent them from stabilizing the foam.

Lubricants are used to minimize the friction, heat and wear of mechanical parts in contact with the ceramic system, which can lead to pollution of the ceramic material. Lubricating oil is the most commonly used lubricant because of its wide range of applications. Mineral oils are refined from naturally occurring petroleum. Synthetic oils are manufactured polyalphaolefins, which are hydrocarbon-based polyglycols or ester oils.

Humectants are hygroscopic substances used to keep moisture, and slow down drying. Their hygroscopic power comes from the presence of hydroxyl groups ($-OH$) or other hydrophilic sites (amines...) that can interact through hydrogen bonding with water molecules. Common humectants are glycerol, propylene glycol or sugars such as sorbitol.

Fungicides or bactericides may be used to kill parasitic fungi or their spores and bacteria, or at least limit their development, in order to increase the shelf life of formulas, especially for water-based systems.

Therefore ceramic formulations may contain many different organic additives. Some of them present sometimes a dual effect: dispersant and wetting agent, plasticizer and lubricant, etc. However ceramists and formulators are well encouraged to limit their number and their amount as much as possible, to limit the cost, the potential unfavorable interactions between them and problems during debinding.

New Challenges for Organics in Ceramic Formulations

The bases of ceramic formulations are now well-established. Current researches are performed on the introduction of new products, with more efficiency at lower cost, with a lower environmental impact, or with specific functions addressed by the arrival of new shaping processes.

Copolymers Acting as Dispersant and Binder

Polymeric binders used in aqueous formulations generally present interactions of lower intensity compared to the electrostatic interactions typically encountered for dispersants, mainly polyelectrolytes. This induces an increase of the viscosity of the suspension due to a large amount of binder remaining in solution, and a heterogeneous distribution of the organics in the green material, for instance in dry pressing of spray-dried granules. The use of a copolymer acting both as a dispersant and as a binder constitutes an attractive solution. Copolymers of sodium acrylate and of vinyl hydroxide have been synthesized with different contents of acrylate groups corresponding to the dispersing block. They were used for the spray drying of alumina suspension (Romdhane *et al.*, 2004, 2007). Adsorption takes place due to carboxylic groups that anchor the polymer chain on specific surface sites, namely $Al-(OH_2)^+$. On one hand, the amount of carboxylic groups controls the effective charge density of the particle surface and thus the dispersing effect. In another hand, the hydroxyl vinyl groups promote a loop-like adsorbed configuration, the thickness of loops increasing with the content of such groups, and thus the binding effect. Many advantages are obtained from these organics. These copolymers have a low T_g , and thus no plasticizer is needed. Because they are adsorbed at the particle surface, no migration is observed during the spray-drying, leading to a more homogeneous distribution in the final granule. As a consequence a higher density is measured on pressed pellets prepared from these granules, as well as a more homogeneous microstructure and much higher mechanical properties.

Organic Templates for Porous Ceramics

The highest density is the general target for most ceramic applications and porosity is generally avoided. However, an increasing demand of porous ceramics have appeared in the last decades, especially for environments where high temperatures, extensive wear and corrosive media are involved. Different strategies exist to produce porous ceramics, depending on the pore morphology, the porous volume fraction, and the pore size, which were reviewed by several authors in the last years (Imhof and Pine, 1997; Studart *et al.*, 2006; Holzwarth and Ma, 2011). "Large templating objects such as colloids, microspheres and emulsions are exploited to create macroporosity at different length scales, from submicron to several hundred micrometers and millimeters, whereas mesopores are obtained via supramolecular structures formed from self-assembly of surfactants, and micropores can be generated by the templating effect of single molecules", cited from (Colombo *et al.*, 2010).

One strategy to create macroporosity is the replica method, based on the impregnation of a cellular structure with a ceramic suspension or a precursor solution, in order to produce a ceramic exhibiting the same morphology as the original porous material. Synthetic templates, such as polyurethane foams, are the most widely used, whereas some natural templates can also be found (wood or coral...) (Studart *et al.*, 2006). Another technique is the use of a sacrificial phase, also called porogen or pore-former agent, which is dispersed into the ceramic matrix, and leads to porosity after pyrolysis. Many different organics can be found in the literature, such as synthetic polymers (PVC, polystyrene, PMMA beads, etc.) (Tang *et al.*, 2004) or natural products (cellulose, starch, gelatin, etc.).

Mesoporosity concerns pores below 50 nm, and is obtained through the condensation of ceramic precursors around a molecular template made of surfactants or block copolymers (Wan and Zhao, 2007; Cai *et al.*, 2011). Surfactants are interesting molecules which form micelles by self-assembly leading to original architectures. The mesoporous material is obtained via the EISA effect (Evaporation Induced Self-Assembly), after elimination of the solvent and the organic template (surfactant or polymer). The mesoporosity is determined by the nature of the organic, its concentration, and its interaction with the ceramic precursor. This strategy, by using a strong coupling between inorganic and organic chemistry, is falling into the field of hybrid materials, which represents also a novel branch of developments for ingeniously designed ceramic materials (Judeinstein and Sanchez, 1996; Sanchez *et al.*, 2005).

Organics for Innovative Processing Methods

In the last twenty years, some new shaping processes have been developed in the domain of traditional and technical ceramics. It is first explained by the arrival in mass of powders with finer particle sizes, in the colloidal domain ($< 1 \mu\text{m}$), along with a better understanding of the fundamental mechanisms underlying particle–particle interactions. The “colloidal processing” concept appeared, which is based on the manipulation and control of the interparticle forces in suspensions, in order to remove heterogeneities and to optimize the suspension properties (Lewis, 2000; Bergstrom, 2001). At the same time, there has been a growing interest for additive manufacturing techniques to produce 3D ceramic parts with complex architectures. Specific organics accompanied these evolutions, with some examples reported below.

Colloidal granulation

Colloidal granulation is an original shaping process leading to spherical granules of millimetric size directly in suspension from a diluted system of colloids. It was obtained first by heterocoagulation of two materials, e.g., alumina and silica, to produce dense spheres (Garcia-Perez *et al.*, 2007). These primary systems contained no organics, and thus many defects were observed, attributed to a low compaction of the green material and a high migration rate of the particles during the drying step (Pagnoux *et al.*, 2009). Another system studied was made of titania nanoparticles dispersed with a polyelectrolyte, the poly(sodium 4-styrenesulfonate) (PSS). In a very small range of conditions, some primary agglomerates could be formed thanks to an attractive interaction between Ti-OH_2^+ surface groups and $-\text{SO}_3^-$ functions of the adsorbed polymer, and then inducing a coalescence through a bonding effect (Pringuet *et al.*, 2008). By adding a second polyelectrolyte of opposite charge, the chitosan (cationic, whereas PSS is anionic), an electrostatic interaction between the two polymers occurred in situ, leading to the formation of submicronic organic filaments binding titania agglomerates to each other, and extending the experimental range of conditions to form the millimetric spheres (Pringuet *et al.*, 2011b). The use of these organics also present the advantage of adding plasticity inside the spheres, improving the drying step by allowing colloidal particles to move and rearrange when water is removed. Finally, some organic colloids such as a latex of polystyrene could also be added leading to the formation of porous granules presenting a very well-ordered microstructure, with multi-scale porosity (Pringuet *et al.*, 2011a).

Direct casting forming methods

Direct casting forming methods are able to create near-net-shape products and components with more complex shapes. The concept is to transform a fluid suspension to a stiff gel, in order to retain the homogeneous state of the dense slurry (Sigmund *et al.*, 2000). The great advantage of these methods, compared to more classical shaping processes, is the minimization of heterogeneities and density gradients. The physical or chemical processes responsible for the formation of a solid green body may vary, but all methods require a well-dispersed suspension with very high solids loading and a low viscosity to facilitate the mold-filling process. The preliminary step of powder dispersion must be particularly optimized with an appropriate use of dispersants. In a second step, the green body formation is obtained through the formation of either physical or chemical bonds between the particles or some species introduced in the dispersion.

Physical gels rely on the formation of physical bonds which is mainly achieved by manipulating the interparticle forces between the particles in suspension to become attractive (Gauckler *et al.*, 1999). This can be achieved by changing pH or increasing salt content, whereas sterically stabilized systems can be flocculated by changing the solvency of the adsorbed polymer (Bergström and Sjöström, 1999). pH may be modified by addition of an electrolyte (HCl, or $(\text{C}_2\text{H}_5)_4\text{NOH}$), but a better approach is to use a reaction that produces the desired pH or salt change in-situ. Examples of such reactions are thermally activated decomposition of urea, formamide, acetamide, or hexamethylene tetramine, which change the pH from acidic toward neutral by slowly forming NH_3 at 60–80°C (Sigmund *et al.*, 2000). Hydrolysis of esters or lactones yields carboxylic acids, changing pH from alkaline toward neutral. An increase in salt concentration is induced by the decomposition of urea, which can also be catalyzed by an enzyme,

urease (Gauckler *et al.*, 1999). Hydroxylaluminum diacetate decomposes as the temperature increases to release acetate and aluminum ions (Laucournet *et al.*, 2000).

Chemical gels are obtained by the formation of permanent chemical bonds between either the particles or some species in the dispersion. Typical examples are the formation of a percolating polymer network by polymerizing a monomer in the slurry, or the gelation of dissolved polymers. Vinylmonomers and cross-linking agents are mainly used in this process (Young *et al.*, 1991; Omatete *et al.*, 1997). Because they undergo a free-radical chain polymerization reaction, the setting is very rapid. Natural gels can also be used such as gelatin or alginates (Yang *et al.*, 2011), with much lower toxicity (Janney *et al.*, 1998). Cross-linking of polymers or proteins is also reported, for example cross-linking of PVA with Ti^{4+} (Morissette and Lewis, 1999).

Additive manufacturing of ceramics

Additive Manufacturing (AM) processes are numerical technologies used to fabricate 3D parts directly from their 3D Computer Aided Design (CAD), without specific tooling. AM involves the addition and/or bonding of materials to form objects, and is based on a manufacturing procedure with a construction layer upon layer.

These technologies offer advantages such as a reduced cost for the fabrication of prototypes or of short-run production, a reduced time to market, the process of complex shapes and specific architectures impossible to obtain by conventional routes, to be able to improve properties or to introduce new functions. AM is more and more used to directly fabricate useful functional parts or functional prototypes to test forms, fit and function. Another important application is the concept modeling and prototyping (Chartier and Badev, 2013).

Several processes have been developed for the additive manufacturing of ceramic parts, based on powder, suspension, paste, or tapes systems. The majority of these processes require the use of organic additives.

Stereolithography involves the selective photopolymerization of a reactive system. The reactive system consists in a dispersion of ceramic particles in a curable monomer/oligomer (e.g., acrylates) with the help of a dispersant. A photoinitiator (benzophenone derivative) allows to cure the system and a diluent (e.g., 1,6-hexane diol diacrylate (HDDA)) is used to decrease the viscosity (Badev *et al.*, 2011).

Robocasting or Fused Deposition Modeling processes consists in the extrusion of a filaments through a nozzle. FDM used a thermoplastic (e.g., waxes) ceramic system that immediately hardens after being extruded from the nozzle and bonds to the layer below. Robocasting consists in extrusion of a filament through a nozzle. The feedstock contains, as for the extrusion process, a dispersant, a solvent, a binder and a plasticizer (Cesarano, 1998; Lewis *et al.*, 2006).

Inkjet printing consists in the deposition of small droplets (typically about 50 μm diameter) of a ceramic suspension or of precursors, generally by means of piezoelectric nozzle. The ejection of the droplet (viscosity, surface tension, etc.) and its drying just after deposition require low concentrated suspensions of ceramic particles containing a dispersant, a binder, a plasticizer, a surfactant and a humectant (Lejeune *et al.*, 2009).

Binder jetting involves the jetting of binder (aqueous solution of PAA, PVA, or PEG) to selectively consolidate a deposited layer of powder. A jetting head deposits a binder to bond ceramic particles in the defined pattern (Sachs *et al.*, 1990).

Towards Low Environmental Impact (“Green”) Formulations

Most of the organics introduced in ceramic formulations are chemical products coming from the petroleum industry, which may present risks for the operator health or the environment. From a more general point of view, there is today a growing manifest conscience of the negative impact of some human activities on the energetic and raw materials resources, as well as the pollution. Therefore there is a tremendous demand for low-impact and sustainable chemicals and processes, in order to preserve living and energetic resources.

In this context, researchers propose some substitutes to the traditional organic additives coming from petrochemicals via the use of biosourced additives, which present less risks for the operator's health, and are renewable products.

Lignosulfonates have been identified as renewable alternatives to classical polyelectrolytes used as dispersants in ceramic formulations. Lignosulfonate macromolecules are negatively charged when dissolved in water. It has been shown that ammonium lignosulfonate extracted from the maritime pine of Landes (France) is an effective alternative to polymethacrylate for alumina dispersion, leading to similar performances in terms of zeta potential and rheological behavior (Marie *et al.*, 2017). Few other organics have been reported as ceramic powder dispersant in the literature, such as cellulose derivatives (methylcellulose, ethyl hydroxyethyl cellulose (Schlordt *et al.*, 2013)).

Naturally occurring polysaccharides are biopolymers and a wide variety of them have been employed for various material applications (Kamel *et al.*, 2008; Umoren and Eduok, 2016), especially as binders: gums, carboxymethyl and hydroxyethyl cellulose, starch, pectin, substituted or modified chitosans, carrageenan, dextrin and cyclodextrins, alginates, etc. Different biosourced binders have been recently used in alumina formulations: a pectin gel for tape casting (Marie *et al.*, 2017), and a psyllium gel for micro extrusion (Bouret *et al.*, 2018) which showed high performances.

One limitation to the use of these biopolymers is that they are often subjected to preliminary treatments which may impact the environment. For example cellulose is not water-soluble, therefore cellulose derivatives are synthesized by chemical transformations such as substitution of hydroxyl groups by methoxyl groups using caustic soda solution. Chitosan is obtained by a reaction of deacetylation in strong alkaline conditions of crustacean shells. Another limitation is the reliability and the reproducibility of

these products in term of purity, and intrinsic properties such as concentration of active matter, rheology, etc. But the diversity of such products and their high modulation capacity open very large perspectives for a more environmental-friendly approach of ceramic formulations.

References

- Badev, A., Abouliatim, Y., Chartier, T., *et al.*, 2011. Photopolymerization kinetics of a polyether acrylate in the presence of ceramic fillers used in stereolithography. *Journal of Photochemistry and Photobiology A: Chemistry* 222 (1), 117–122. doi:10.1016/j.jphotochem.2011.05.010.
- Baklouti, S., Chartier, T., Baumard, J.-F., 1997a. Mechanical properties of dry-pressed ceramic green products: The effect of the binder. *Journal of the American Ceramic Society* 80 (8), 1992–1996. doi:10.1111/j.1151-2916.1997.tb03082.x.
- Baklouti, S., Chartier, T., Baumard, J.-F., 1997b. Processing of aqueous α - Al_2O_3 , α - SiO_2 and α - SiC suspensions with polyelectrolytes. *Journal of the European Ceramic Society* 17 (12), 1387–1392. doi:10.1016/S0955-2219(97)00010-1.
- Romdhane, M.R.B., Chartier, T., Baklouti, S., *et al.*, 2007. A new processing aid for dry-pressing: A copolymer acting as dispersant and binder. *Journal of the European Ceramic Society* 27 (7), 2687–2695. doi:10.1016/j.jeurceramsoc.2006.11.076.
- Bergstrom, L., 2001. Colloidal processing of ceramics. In: Holmberg, K. (Ed.), *Handbook of Applied Surface and Colloidal Chemistry*. John Wiley & Sons, Ltd., pp. 201–218. Available at: <https://fr.scribd.com/document/259254918/Colloidal-Processing-of-Ceramics> (accessed 16.12.16).
- Bergström, L., Sjöström, E., 1999. Temperature induced gelation of concentrated ceramic suspensions: Rheological properties. *Journal of the European Ceramic Society* 19 (12), 2117–2123. doi:10.1016/S0955-2219(99)00021-7.
- Boufi, S., Baklouti, S., Pagnoux, C., Baumard, J.-F., 2002. Interaction of cationic and anionic polyelectrolyte with SiO_2 and Al_2O_3 powders. *Journal of the European Ceramic Society* 22 (9), 1493–1500. doi:10.1016/S0955-2219(01)00459-9.
- Bourret, J., El Younsi, I., Blenia, M., *et al.*, 2018. Micro extrusion of innovative alumina pastes based on aqueous solvent and eco-friendly binder. *Journal of the European Ceramic Society* 38 (7), 2802–2807. doi:10.1016/j.jeurceramsoc.2018.02.018.
- Bowen, P., Carry, C., Luxembourg, D., Hofmann, H., 2005. Colloidal processing and sintering of nanosized transition aluminas. *Powder Technology* 157 (1–3), 100–107. doi:10.1016/j.powtec.2005.05.015.
- Bowen, P., Hofmann, H., Staiger, M., *et al.*, 2002. Colloidal processing of nanoceramic powders for porous ceramic film applications. *Key Engineering Materials* 206–213, 1977–1980. doi:10.4028/www.scientific.net/KEM.206-213.1977.
- Cai, W., Yu, J., Anand, C., Vinu, A., Jaroniec, M., 2011. Facile synthesis of ordered mesoporous alumina and alumina-supported metal oxides with tailored adsorption and framework properties. *Chemistry of Materials* 23 (5), 1147–1157. doi:10.1021/cm102512v.
- Carty, W.M., Rossington, K.R., Kupinski, P., Sundlof, B.R., 2000. Rheology of aqueous suspensions of clay and porcelain bodies. *Qualicer* 2000, 369–378.
- Cesarano, J., 1998. A review of robocasting technology. *MRS Online Proceedings Library Archive* 542. Available at: <https://www.cambridge.org/core/journals/mrs-online-proceedings-library-archive/article/review-of-robocasting-technology/5A182C696B3BCAC9F05644FD5DB5E122> (accessed 18.07.19).
- Chartier, T., 2007. Ceramic forming processes. In: Boch, P., Niepce, J.-C. (Eds.), *Ceramic Materials: Processes, Properties and Applications*. John Wiley & Sons, Ltd, pp. 123–197. Available at: <https://onlinelibrary.wiley.com/doi/abs/10.1002/9780470612415.ch5> (accessed 18.07.19).
- Chartier, T., Badev, A., 2013. Chapter 6.5 – Rapid prototyping of ceramics. In: Somiya, S. (Ed.), *Handbook of Advanced Ceramics*, second ed. Oxford: Academic Press, pp. 489–524. Available at: <http://www.sciencedirect.com/science/article/pii/B9780123854698000289> (accessed 18.07.19).
- Colombo, P., Vakifahmetoglu, C., Costacurra, S., 2010. Fabrication of ceramic components with hierarchical porosity. *Journal of Materials Science* 45 (20), 5425–5455. doi:10.1007/s10853-010-4708-9.
- Derjaguin, B., Landau, L., 1993. Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes. *Progress in Surface Science* 43 (1–4), 30–59. doi:10.1016/0079-6816(93)90013-L.
- Garcia-Perez, P., Pagnoux, C., Pringuet, A., Videcoq, A., Baumard, J.-F., 2007. Agglomeration of alumina submicronparticles by silica nanoparticles: Application to processing spheres by colloidal route. *Journal of Colloid and Interface Science* 313 (2), 527–536. doi:10.1016/j.jcis.2007.04.050.
- Gauckler, L.J., Graule, T., Baader, F., 1999. Ceramic forming using enzyme catalyzed reactions. *Materials Chemistry and Physics* 61 (1), 78–102. doi:10.1016/S0254-0584(99)00117-0.
- Hanaor, D., Michelazzi, M., Leonelli, C., Sorrell, C., 2012. The effects of carboxylic acids on the aqueous dispersion and electrophoretic deposition of ZrO_2 . *Journal of the European Ceramic Society* 32 (1), 235–244. doi:10.1016/j.jeurceramsoc.2011.08.015.
- Haussonne, J.-M., Carry, C., Bowen, P., Barton, J., 2005. *Céramiques et verres: Principes et techniques d'élaboration*. Presses Polytechniques Universitaires Romandes.
- Holzwarth, J.M., Ma, P.X., 2011. Biomimetic nanofibrous scaffolds for bone tissue engineering. *Biomaterials* 32 (36), 9622–9629. doi:10.1016/j.biomaterials.2011.09.009.
- Imhof, A., Pine, D.J., 1997. Ordered macroporous materials by emulsion templating. *Nature* 389 (6654), 948. doi:10.1038/40105.
- James, R.O., Parks, G.A., 1982. Characterization of aqueous colloids by their electrical double-layer and intrinsic surface chemical properties. In: Matijević, E. (Ed.), *Surface and Colloid Science*. Boston, MA: Springer, pp. 119–216. doi:10.1007/978-1-4613-3204-6_2.
- Janney, M.A., Omatete, O.O., Walls, C.A., 1998. Development of low-toxicity gelcasting systems. *Journal of the American Ceramic Society* 81 (3), 581–591. doi:10.1111/j.1151-2916.1998.tb02377.x.
- Judeinstein, P., Sanchez, C., 1996. Hybrid organic-inorganic materials: A land of multidisciplinary. *Journal of Materials Chemistry* 6 (4), 511. doi:10.1039/jm9960600511.
- Kamel, S., Ali, N., Jahangir, K., Shah, S.M., El-Gendy, A.A., 2008. Pharmaceutical significance of cellulose: A review. *eXPRESS Polymer Letters* 2 (11), 758–778.
- Kienemann, J., Chartier, T., Pagnoux, C., *et al.*, 2005. Drying mechanisms and stress development in aqueous alumina tape casting. *Journal of the European Ceramic Society* 25 (9), 1551–1564. doi:10.1016/j.jeurceramsoc.2004.05.028.
- Lange, F.F., 1989. Powder processing science and technology for increased reliability. *Journal of the American Ceramic Society* 72 (1), 3–15. doi:10.1111/j.1151-2916.1989.tb05945.x.
- Laucournet, R., Pagnoux, C., Chartier, T., Baumard, J.-F., 2000. Coagulation method of aqueous concentrated alumina suspensions by thermal decomposition of hydroxylaluminum diacetate. *Journal of the American Ceramic Society* 83 (11), 2661–2667. doi:10.1111/j.1151-2916.2000.tb01611.x.
- Lejeune, M., Chartier, T., Dossou-Yovo, C., Noguera, R., 2009. Ink-jet printing of ceramic micro-pillar arrays. *Journal of the European Ceramic Society* 29 (5), 905–911. doi:10.1016/j.jeurceramsoc.2008.07.040.
- Lewis, J.A., 2000. Colloidal processing of ceramics. *Journal of the American Ceramic Society* 83 (10), 2341–2359. doi:10.1111/j.1151-2916.2000.tb01560.x.
- Lewis, J.A., Smay, J.E., Stuecker, J., Cesarano III, J., 2006. Direct ink writing of three-dimensional ceramic structures. *Journal of the American Ceramic Society* 89 (12), 3599–3609. doi:10.1111/j.1151-2916.2006.01382.x.
- Li, W., Chen, P., Gu, M., Jin, Y., 2004. Effect of TMAH on rheological behavior of SiC aqueous suspension. *Journal of the European Ceramic Society* 24 (14), 3679–3684. doi:10.1016/j.jeurceramsoc.2003.12.023.
- Magdassi, S., 2010. *The Chemistry of Inkjet Inks*. Singapore: World Scientific Publishing Company.
- Marie, J., Bourret, J., Geffroy, P.-M., *et al.*, 2017. Eco-friendly alumina suspensions for tape-casting process. *Journal of the European Ceramic Society* 37 (16), 5239–5248. doi:10.1016/j.jeurceramsoc.2017.04.033.

- Morisette, S.L., Lewis, J.A., 1999. Chemorheology of aqueous-based alumina-poly(vinyl alcohol) gelcasting suspensions. *Journal of the American Ceramic Society* 82 (3), 521–528. doi:10.1111/j.1151-2916.1999.tb01796.x.
- Napper, D.H., 1983. *Polymeric Stabilization of Colloidal Dispersions*. London, New York: Academic Press.
- Omatete, O.O., Janney, M.A., Nunn, S.D., 1997. Gelcasting: From laboratory development toward industrial production. *Journal of the European Ceramic Society* 17 (2), 407–413. doi:10.1016/S0955-2219(96)00147-1.
- Pagnoux, C., Chartier, T., de F. Granja, F., *et al.*, 1998. Aqueous suspensions for tape-casting based on acrylic binders. *Journal of the European Ceramic Society* 18 (3), 241–247. doi:10.1016/S0955-2219(97)00115-5.
- Pagnoux, C., Tessier-Doyen, N., Pringuet, A., Cerbelaud, M., Garcia-Perez, P., 2009. Influence of the suspension flocculated state on the microstructure of alumina spheres elaborated by colloidal granulation. *Journal of the European Ceramic Society* 29 (8), 1379–1385. doi:10.1016/j.jeurceramsoc.2008.09.007.
- Penard, A.-L., Rossignol, F., Hasakoppa, N., Pagnoux, C., Chartier, T., 2005. Dispersion of alpha-alumina ultrafine powders using 2-phosphonobutane-1,2,4-tricarboxylic acid for the implementation of a DCC process. *Journal of the European Ceramic Society* 25 (7), 1109–1118. doi:10.1016/j.jeurceramsoc.2004.05.006.
- Pringuet, A., Belounis, F., Pagnoux, C., 2011b. Use of polyelectrolyte complexes as a binding agent in the granulation process of titania particles. *Journal of the American Ceramic Society* 94 (3), 729–735. doi:10.1111/j.1551-2916.2010.04169.x.
- Pringuet, A., Pagnoux, C., Videcoq, A., Baumard, J.-F., 2008. Granulating titania powder by colloidal route using polyelectrolytes. *Langmuir* 24, 10702–10708. doi:10.1021/la8009578.
- Pringuet, A., Pagnoux, C., Videcoq, A., Baumard, J.-F., 2011a. Granulating fine powders into millimetric spheres with a multiscale porosity: The case of titania. *Microporous and Mesoporous Materials* 140 (1), 17–24. doi:10.1016/j.micromeso.2010.09.005.
- Pugh, R.J., Bergström, L., 1993. *Surface and Colloid Chemistry in Advanced Ceramics Processing*. CRC Press.
- Romdhane, M.R.B., Baklouti, S., Bouaziz, J., Chartier, T., Baumard, J.-F., 2004. Dispersion of Al_2O_3 concentrated suspensions with new molecules able to act as binder. *Journal of the European Ceramic Society* 24 (9), 2723–2731. doi:10.1016/j.jeurceramsoc.2003.09.014.
- Reed, J.S., 1995. *Principles of Ceramics Processing*. Wiley.
- Sachs, E., Cima, M., Cornie, J., 1990. Three-dimensional printing: Rapid tooling and prototypes directly from a CAD model. *CIRP Annals* 39 (1), 201–204. doi:10.1016/S0007-8506(07)61035-X.
- Sanchez, C., Julian-Lopez, B., Belleville, P., Popall, M., 2005. Applications of hybrid organic–inorganic nanocomposites. *Journal of Materials Chemistry* 15 (35–36), 3559–3592. doi:10.1039/B509097K.
- Schlödt, T., Schwankel, S., Keppner, F., *et al.*, 2013. Robocasting of alumina hollow filament lattice structures. *Journal of the European Ceramic Society* 33 (15), 3243–3248. doi:10.1016/j.jeurceramsoc.2013.06.001.
- Shanefield, D.J., 1999. *Organic Additives and Ceramic Processing: With Applications in Powder Metallurgy, Ink, and Paint*, 1999. Springer-Verlag New York Inc. (Softcover reprint of the original).
- Sigmund, W.M., Bell, N.S., Bergström, L., 2000. Novel powder-processing methods for advanced ceramics. *Journal of the American Ceramic Society* 83 (7), 1557–1574. doi:10.1111/j.1151-2916.2000.tb01432.x.
- Stuart, A.R., Gonzenbach, U.T., Tervoort, E., Gauckler, L.J., 2006. Processing routes to macroporous ceramics: A review. *Journal of the American Ceramic Society* 89 (6), 1771–1789. doi:10.1111/j.1551-2916.2006.01044.x.
- Tang, F., Fudouzi, H., Uchikoshi, T., Sakka, Y., 2004. Preparation of porous materials with controlled pore size and porosity. *Journal of the European Ceramic Society* 24 (2), 341–344. doi:10.1016/S0955-2219(03)00223-1.
- Umoren, S.A., Eduok, U.M., 2016. Application of carbohydrate polymers as corrosion inhibitors for metal substrates in different media: A review. *Carbohydrate Polymers* 140, 314–341. doi:10.1016/j.carbpol.2015.12.038.
- Vallar, S., Houivet, D., El Fallah, J., Kervadec, D., Haussonne, J.-M., 1999. Oxide slurries stability and powders dispersion: Optimization with zeta potential and rheological measurements. *Journal of the European Ceramic Society* 19 (6), 1017–1021. doi:10.1016/S0955-2219(98)00365-3.
- Wan, Y., Zhao, D., 2007. On the controllable soft-templating approach to mesoporous silicates. *Chemical Reviews* 107 (7), 2821–2860. doi:10.1021/cr068020s.
- Yang, J., Yu, J., Huang, Y., 2011. Recent developments in gelcasting of ceramics. *Journal of the European Ceramic Society* 31 (14), 2569–2591. doi:10.1016/j.jeurceramsoc.2010.12.035.
- Young, A.C., Omatete, O.O., Janney, M.A., Menchhofer, P.A., 1991. Gelcasting of Alumina. *Journal of the American Ceramic Society* 74 (3), 612–618. doi:10.1111/j.1151-2916.1991.tb04068.x.
- Zocca, A., Colombo, P., Gomes, C.M., Günster, J., 2015. Additive manufacturing of ceramics: Issues, potentialities, and opportunities. *Journal of the American Ceramic Society* 98 (7), 1983–2001. doi:10.1111/jace.13700.

Powder Mixing and Grinding Processes for Ceramics

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Introduction

Ceramics are prepared from inorganic raw materials in the form of powder grains. During sintering, due to the action of diffusion mechanisms, grains weld together and porosity between grains is eliminated leading to material densification. The raw materials have therefore a direct influence on the final properties of ceramics. In order to control these properties, a selection of the raw powders with adequate characteristics is required and some post-treatments can be applied to obtain the desired characteristics.

It is commonly accepted that the initial powders used for technical ceramics, both in the laboratory and in industry, should:

- (1) Possess a high chemical purity, often exceeding 99%. Care must be taken to limit the pollution generated by the adaptation processes, particularly grinding;
- (2) Be fine. Indeed, the reactivity of powders in the solid process is directly linked to the size and particle size distribution. The finer is the powder, the higher the specific surface area, which increases the energy of the system and promotes diffusion reactions in the solid sintering process, and which leads to a reduction of sintering temperature and time. As a result, micron- and sub-micron sized powders will be sought. The classic grain diameter range is from 10 μm to 10 nm, corresponding to specific surface areas between 0.1 and 100 m^2/g ;
- (3) Be homogeneous and well dispersed, without presence of aggregates or agglomerates. In the case of a mixture of powders of different natures, it must be intimate and as homogeneous as possible to reduce the diffusion distances during solid state reactions or during reactive sintering. In addition to the gain of energy, it is wished that the formation of secondary phases resulting from a localized stoichiometry different from the rest of the mixture can be avoided and a well controlled and homogeneous microstructure of the ceramic can be obtained.

A first major technological step in the manufacture of a ceramic is the mixing and grinding of raw materials, or calcined powders, in order to adapt the powders to the desired characteristics. This stage can be carried out in a dry or wet environment.

At the beginning of the 19th century, Brongniart (1844) pointed out the difficulty of working "pastes", such as siliceous materials "which were difficult to work into the bottom of the water". Empirical solutions included adding vinegar, "rot" or even swampy water. The porcelain and earthenware treaty of the 1950s (Haussonne, 1954) is more pragmatic and recommended adding acetic acid or ammonia to keep the powder in suspension. Finally, more scientific considerations (Jouenne, 1980) were published with first studies of the dispersion of the slurries considering the pH value.

It appears therefore that in order to master this mixing and grinding stage, it is necessary to have a good understanding of slurry dispersion. Some notions are essential such as knowledge of the physico-chemistry of powder surfaces, of the dispersion behavior, of the additives which allow to control both the attractive or repulsive forces arising between particles and which will modify the rheological behavior of these suspensions. This will be the first part of this chapter.

As the electronic properties of ceramics are often very sensitive to dopants, special attention must be paid to the contamination that may be brought about by the grinding process. As it will be seen in the various applications described below, a compromise will often have to be made between the positive effects of grinding, which makes it easier to achieve better densification, more homogeneous microstructures, or the formation of pure phases, and a negative aspect brought about by polluting elements. These aspects will be discussed in the second part of the chapter through a short description of two major studies.

State of the Art

This chapter is devoted to the necessary knowledge to understand the phenomena occurring during slurry dispersion and mixing and grinding steps occurring in ceramic processing. It presents a synthesis of several books and review articles (Haussonne *et al.*, 2005; Funk and Dinger, 1994; Parfitt, 1981; Dinger, 2002; He *et al.*, 2004; Vallar *et al.*, 1999).

Properties of Slurries and Pastes

In order to adapt the characteristics of powders to the desired parameters (in particular average diameter, or specific surface area), a cycle of mixing and grinding of the powders is necessary. The most efficient methods require this operation to be carried out in a liquid medium, in the form of slurry. The aim is to mix different constituents, in powder form, which are intended to react in a solid form in a subsequent thermal cycle. They must therefore be mixed as carefully as possible in order to limit the diffusion distances, which will result in a reduction of the calcination temperature, and avoid the formation of intermediate phases or obtain better physical properties. It is therefore essential to work with stable, deflocculated slurries before, during and after the grinding step.

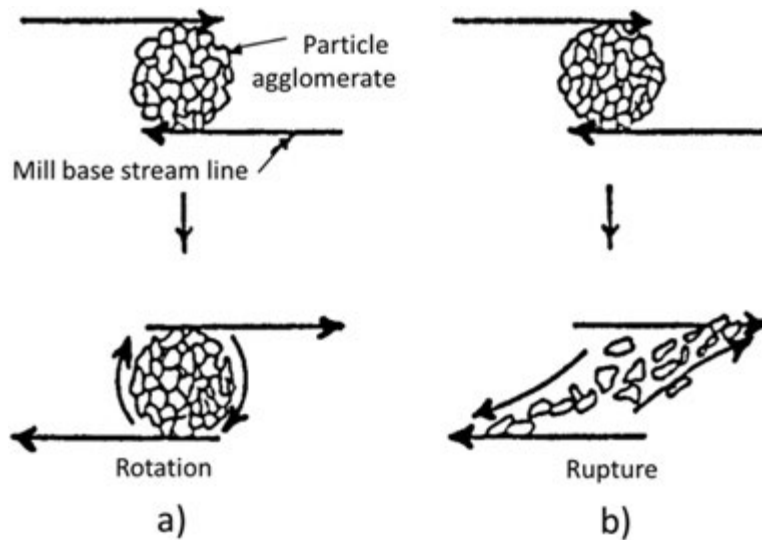


Fig. 1 Influence of the viscosity of the grinding medium on the breakage of agglomerates in laminar shear layers: (a) in non-viscous media, the agglomerates are rotated by the displacement of the liquid; (b) in viscous media, a laminar flow can be established and cause the agglomerates to break up.

The fundamental aspects on the dispersion of powders in liquids and the experimental techniques allowing to characterize this state of dispersion, such as zetametry and rheology are presented below.

The Various Stages of Dispersion

The process of dispersing solid particles in a liquid can be broken down into elementary operations (Parfitt, 1981). These are in practice closely linked: the mechanical breaking of agglomerates or aggregates, the wetting, the distribution and stabilization of the slurry obtained.

Mechanical Breakage or Comminution

Mechanical grain breakage of a powdery solid refers to the disintegration or reduction of large particles which are usually aggregates (hard agglomerates: clusters of grains with strong bonds, the grains often being associated by faces) or soft agglomerates (clusters of grains with weak bonds, the grains often being associated by edges or corners). Disagglomeration can be achieved by mechanical grinding treatment. Rumpf considers three types of mechanical stress (Rumpf, 1962):

- (1) Those that can be subjected to crushed and/or sheared particles between two surfaces. In this case, the shape of the mill elements and their speed of rotation must be considered. This is for example the case of attrition grinding or laboratory grinding in a "Pulverisette Fritch".
- (2) Those associated with the impact of moving particles, either to a surface or to other particles. This is the case, for example, with impact grinding of ball mills or particles impacting against each other in a jet mill.
- (3) Those imposed by the surrounding environment: in this case, the viscosity of the dispersing medium has some influence on the comminution of agglomerates as shown in Fig. 1. It affects as well as surface strength, the penetration of the liquid into the channels of the agglomerate, which can provide sufficient pressure to disintegrate the cluster.

The nature of the dominant mechanism during a particular grinding stage or for a particular product will depend on the microstructure of the particles, i.e., the type and concentration of defects in single crystals, grain boundaries in polycrystalline materials and the nature of the bridging in agglomerates. The value of the impact fracture stress of a particle tends to increase as the particle size decreases and approaches dense single crystal materials. As a result, there is a size limit for a perfect single crystal which is, for example, in the order of 1 μm for quartz and 4 μm for calcite. Below these limit values, it is no longer possible to accumulate sufficient elastic energy in a particle, which can then only deform plastically. The attrition (shear) fracture mechanism, which is a consequence of the high stresses produced during friction between the particles, is, for sizes below these limit sizes, the mechanism for further size reduction. When the submicron range which is often desired for technical ceramics is reached, the large forces involved can deform the mesh of the crystals constituting the particles, which induces residual stresses. For a Bayer alumina, this can be a stress range of around 40 nm with dislocation densities of around 10^{11} cm^{-2} .

During grinding, very high local temperatures can be reached due to the high amount of energy released which is converted into heat at the crack propagation front or due to friction between the particles and the grinding balls during attrition. This can

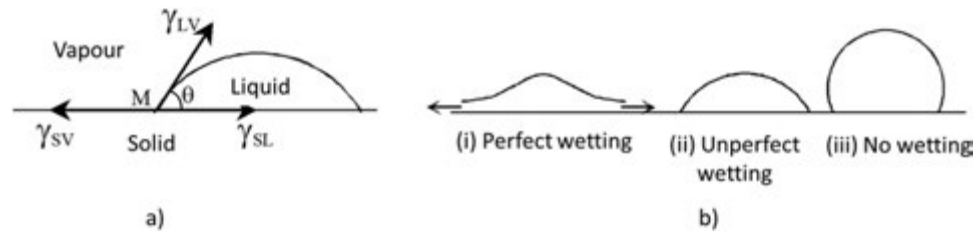


Fig. 2 (a) Vector representation of the “drop model”. (b) Wetting characteristics of a solid surface.

result in a softening of the material and lead to a more plastic behavior. This heat can also result in local changes in the material, producing an amorphous layer or even a phase transformation. Mechanochemistry techniques, including the use of planetary mills with decoupled high-energy movements (pulverisette), have been widely used for metal alloys since the 1970s and in the ceramic field. (Suryanarayana, 2001; Nachbaur *et al.*, 2009).

Defects that remain in the powders after grinding can also have a positive influence on sintering by facilitating the diffusion of material components at grain boundaries or in volume. However, in all cases, the transmission of mechanical energy to the particles requires that they be thoroughly wetted beforehand in a humid environment.

Wetting

Wetting corresponds to the spreading of the dispersing liquid on the surface of the solid; it results in replacing the solid-air interface with a new solid-liquid interface. Wetting is, therefore, an interfacial phenomenon which is influenced by the thermodynamic characteristics of the interfaces of the two phases concerned (free surface energy of the solid and surface tension of the liquid). These parameters were established from the “drop model”. When a drop of liquid is deposited on a solid interface, it adopts a particular configuration that reflects the nature of the interactions between the solid and the liquid. The drop takes the form of an equilibrium that minimizes the free energy of the system.

Young proposed for this state of equilibrium the vector representation shown in Fig. 2. At point M, there is equilibrium of tensions, which is expressed by the relation:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

with

γ_{SV} : Free surface energy of the solid in the presence of the vapor of the liquid; γ_{LS} : Interfacial free energy between solid and liquid; γ_{LV} : Free interfacial energy of the liquid in the presence of its vapor; θ angle of contact of the liquid on the solid, or wetting angle

The ability of the liquid to wet the solid is defined as follows:

$\theta = 0^\circ$, i.e., $\gamma_{SV} = \gamma_{LS}$, wetting is spontaneous;

$0^\circ < \theta < 90^\circ$, i.e., $\gamma_{SV} > \gamma_{LS}$, the liquid wets the solid but not perfectly (case of water on glass);

$\theta > 90^\circ$, i.e., $\gamma_{SV} < \gamma_{LS}$, the liquid does not get wet, but rather curls on the surface of the solid (case of mercury on glass).

A decrease in γ_{LS} through the use of surface active agents (dispersant or surfactant), which can adsorb to the surface, will result in a decrease of θ , therefore in increase of wetting.

The reduction of γ_{LV} can be obtained with a liquid such as ethanol whose surface tension at 20°C (23 mN m^{-1}) is about three times lower than that of water (73 mN m^{-1}).

The work required to change from a dry powder (with all surfaces exposed to the vapor phase, e.g., air) to a fully immersed powder wetted by a liquid (with only solid-liquid interfaces remaining) is described by the equation:

$$W_D = -(\gamma_{SV} - \gamma_{SL})$$

When the dispersion work is negative, then the dispersion of the powder in the liquid is a spontaneous process.

Powders of ionic materials with polar surfaces, such as oxides, can be easily dispersed in polar liquids such as water. The use of water as the main component of the dispersing liquid represents a great advantage in terms of both economic and environmental cost. Materials with more covalent bonds, such as silicon nitride or carbide, are less easily dispersed in water and the use of organic solvents is often used. Another factor to consider when selecting the liquid is the solubility of the ceramic powder in the liquid. A good wetting of the surface should not be correlated with a solubilization which would alter the composition of the powder.

Dispersion

Dispersion refers to the process by which finely divided, wetted solid particles occupy the entire dispersing medium in a very homogeneous manner. This dispersion is achieved by hydrodynamic processes. This dispersion starts with an operation involving mechanical, vibrating or ultrasonic agitation mixers. These mixers are often not enough powerful to have a disagglomeration or

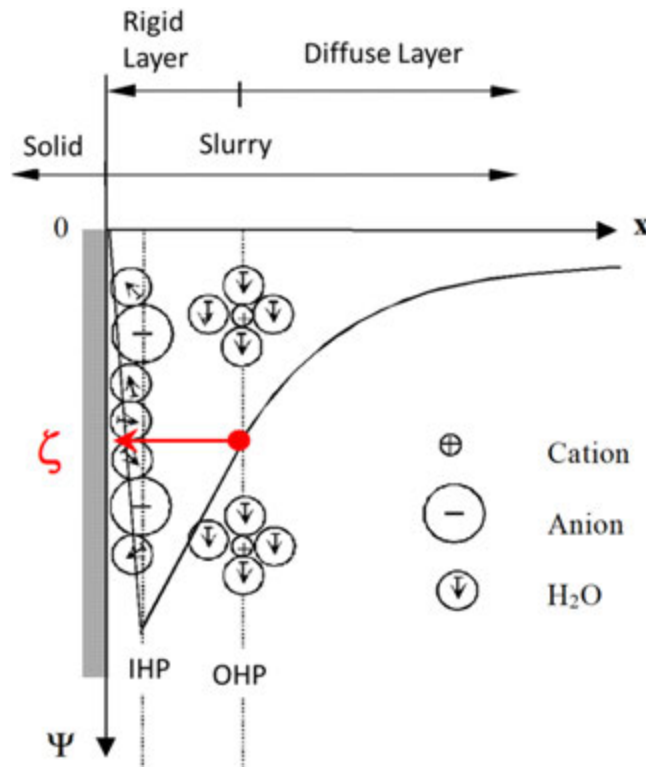


Fig. 3 Model of the double layer and variation of the associated potential in the solution. Reproduced from Bockris, J.O., Devanathan, M., Müller, K., 1963. On the structure of charged interfaces. *Proc. R. Soc. Lond. A* 274 (1356), 55–79.

grinding action. However, this stage is either preparatory to the use of the slurry before attrition grinding, or after grinding to maintain good dispersion and avoid sedimentation of the powder.

Stabilization

Stabilization of a suspension means that well-divided, wetted solid particles distributed within the environment will no longer flocculate, i.e., spontaneously assemble to form clusters which could be either agglomerates or flocs (a set of agglomerates gathered into a macrostructure). Then, there is no more change over time, neither in the total number nor in the size distribution of the particles.

This step of limiting the phenomenon of flocculation or coagulation of the particles is the most important in the realization of suspensions. When dispersing very fine powders, an extremely extensive liquid-solid interface is created and a system with a high excess of free energy is formed, which is therefore thermodynamically unstable. This system tends, a priori, to evolve towards a more stable state so that flocculation must inevitably occur within any suspension.

Two physical factors are known to destabilize the suspensions:

- (1) Sedimentation. Under the effect of gravity, particles cannot remain in suspension. However, the higher the viscosity of the dispersing medium, the lower the sedimentation forces will be.
- (2) Brownian movement. Van Smoluchowski developed a theory of flocculation according to which an unstabilized suspension flocculates as a result of collisions between primary particles agitated by Brownian motion.

Physical Factors Improving Stabilization

To avoid flocculation, contact and collisions between individual particles must be limited. This can be achieved by changing the surface electrical properties of solid grains to promote electrostatic repulsion and/or by changing the minimum approach distance between the particles by adsorption of polymers on their surface, so that steric repulsion occurs.

Stabilization by Electrostatic Repulsion

This principle is based on the notions of surface charges and electrical double layer, the essential points of which are shortly reviewed below.

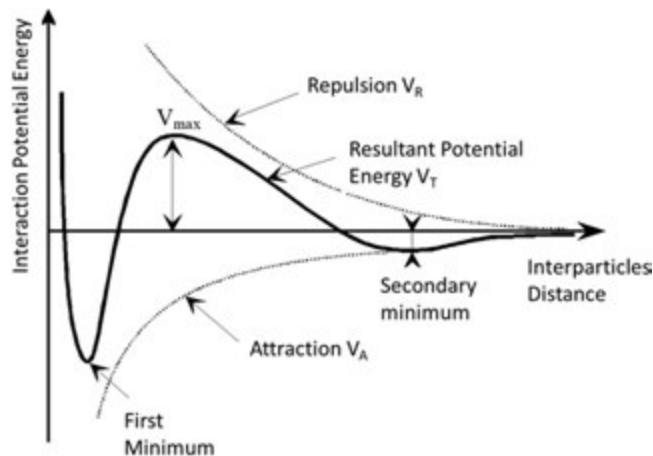


Fig. 4 Variations in the potential energies of attraction V_A and electrostatic repulsion V_R as a function of the separation distance between two spherical particles.

Electrical Characteristics of Powders in Aqueous Suspension

Most solid surfaces are electrically charged. On the crystal surface, not all bonds are saturated, which causes the chemisorption phenomenon. This phenomenon consists of the surface capture of foreign chemical entities (atoms or molecules) by ionic forces. The surface charge of particles dispersed in water or an electrolyte solution can become much higher than in air. This development of surface charges results either from the partial dissolution of the solid, or from the ionization of surface groups (OH^- in particular), or from the substitution of ions in the crystal lattice of the solid. These charges are compensated by charges of opposite signs (principle of electroneutrality) coming from ions in the solution (counter ions). This creates a double electrical layer, as shown in Fig. 3.

- (1) The first layer, known as the rigid (Stern) layer, is formed by contact adsorption, then by adsorbed ions with their solvation molecules. The whole is close to the solid and moves with it, hence the name rigid layer;
- (2) The second layer, known as the diffuse layer, is formed by the rest of the charges that neutralize the surface charges and are distributed within the solution.

The potential associated with this load distribution varies as also shown in Fig. 3. Its value at the OHP ("Outer Helmholtz Plane", passing through the center of the solvated ions) is assimilated to the zeta potential (ζ).

Stabilization Principle by Electrostatic Repulsion

The principle of stabilization by electrostatic repulsion has been established within the framework of the D.L.V.O. theory (named after its authors Deryagin, Landau, Verwey and Overbeek). According to this theory, the layer of adsorbed ions carries the charges and if the adsorption is uniform, all particles are charged identically. Stabilization results from the Coulombic repulsion that occurs between these particles, the value of which is directly dependent on the zeta potential. This repulsion potential is associated with the charge distribution and decreases exponentially with the distance between the particles.

The particles are also subject to the forces of attraction of London and Van Der Waals, depending in first approximation on their diameter, the nature of the material and the dispersion medium. An attraction potential V_A is associated with these forces and is inversely proportional to the distance between the particles.

As shown in Fig. 4, stabilization can only take place if the repulsion forces are greater than the attraction forces between two neighboring particles. The maximum of the resulting potential energy V_{MAX} is the energy barrier that prevents the particles from getting closer. The V_{MIN} potential represents the energy for which coagulation occurs. Flocculation would rather be the consequence of interactions that occur at approach distances and energy corresponding to a secondary minimum (Fig. 5).

Parameters That can Change the Electrostatic Repulsion Stabilization

According to the DLVO theory, under isothermal conditions and in the absence of mechanical agitation, stabilization by electrostatic repulsion depends on particle radius and their surface potential (ψ_0). Therefore, for a given suspension, the conditions of stability can be modified by changing ψ_0 . However, its value depends directly on phenomena at the origin of the surface charges like the pH of the medium, the concentration of adsorbed ions or the exchange capacity.

The diagrams in Fig. 6 show how the zeta potential and the surface charge σ_0 varies as a function of the concentration of the potential-determining ions in the medium. In particular, it can be seen that ζ and σ_0 can cancel each other out at the isoelectric

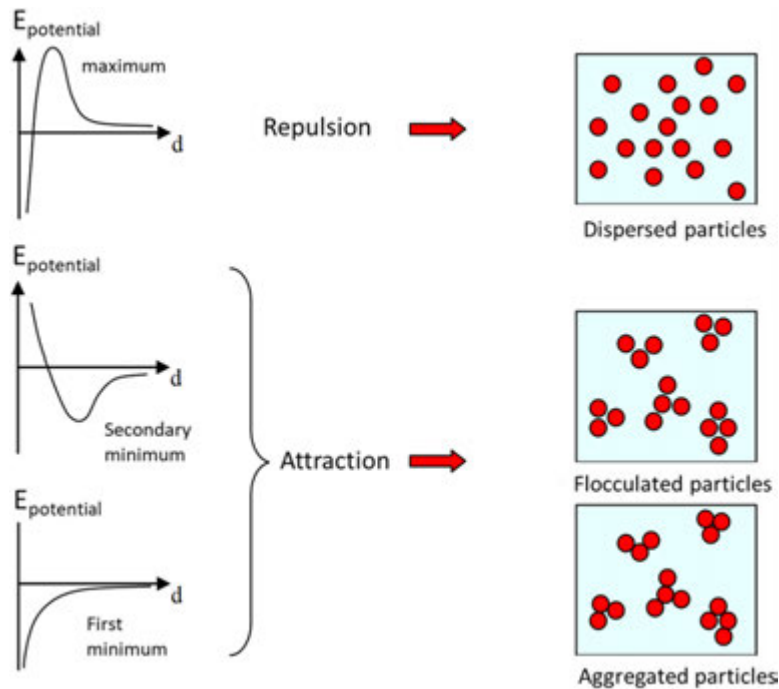
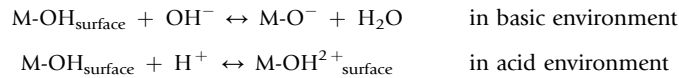


Fig. 5 Dispersion state as a function of the potential energy profile.

point (IEP) or zero charge point (ZCP), in which case V_R cancels out occurs. Conversely, the higher ζ potential, the greater the repulsive forces V_R and the more stable the suspension.

In the case of oxides in aqueous suspension, after the surface reaction which corresponds to a very strong chemisorption of the water, there are amphoteric hydroxide groups, of the M-OH type, which will be able to dissociate like weak acids or bases:



The concentrations of H^+ and OH^- ions determine the surface charge. Therefore, the pH of the suspension medium influences the stability of the suspension.

Stabilization by Steric Repulsion

Electrostatic repulsion forces alone are often insufficient to stabilize the dispersions. A main reason for this is the compression of the double layer due to too high ionic concentration. This may be due to the presence of impurities but also to the partial dissolution of ceramic powders at pH values that are in principle necessary for stabilization. These two factors become more predominant in concentrated dispersions where the solid to liquid volume ratio is high and where a low degree of dissolution can greatly increase the ionic concentration. Consequently, it is necessary to resort to other repulsion mechanisms such as those involved in the addition of soluble polymers.

Indeed, it has been observed experimentally that addition of such a polymer to a colloidal suspension can improve its stability or, on the contrary, cause its flocculation. The interpretation of these behaviors is given by the theory of stabilization by steric repulsion. The steric hindrance of the grain, surrounded by its adsorbed layer, limits the approach between particles and, therefore, at distances between particles for which Van der Waals forces predominate. This theory considers the interactions that occur when the adsorbed polymer layers on the surface of two particles come into contact (**Fig. 7**).

Another context leading to the use of polymers is that of non-aqueous dispersions, used in the case of powders that react with water, but difficult to stabilize electrostatically because of the complex charging process that prevails in these media.

Shear-Thickening Grinding Slurries

It is important that grinding slurry is characterized by a slightly shear-thickening behavior with good dispersion and low viscosity. Otherwise, a large part of the energy expended in the mill is used to deform the highly viscous fluid and to destroy the agglomerates, to the detriment of the grinding action itself.

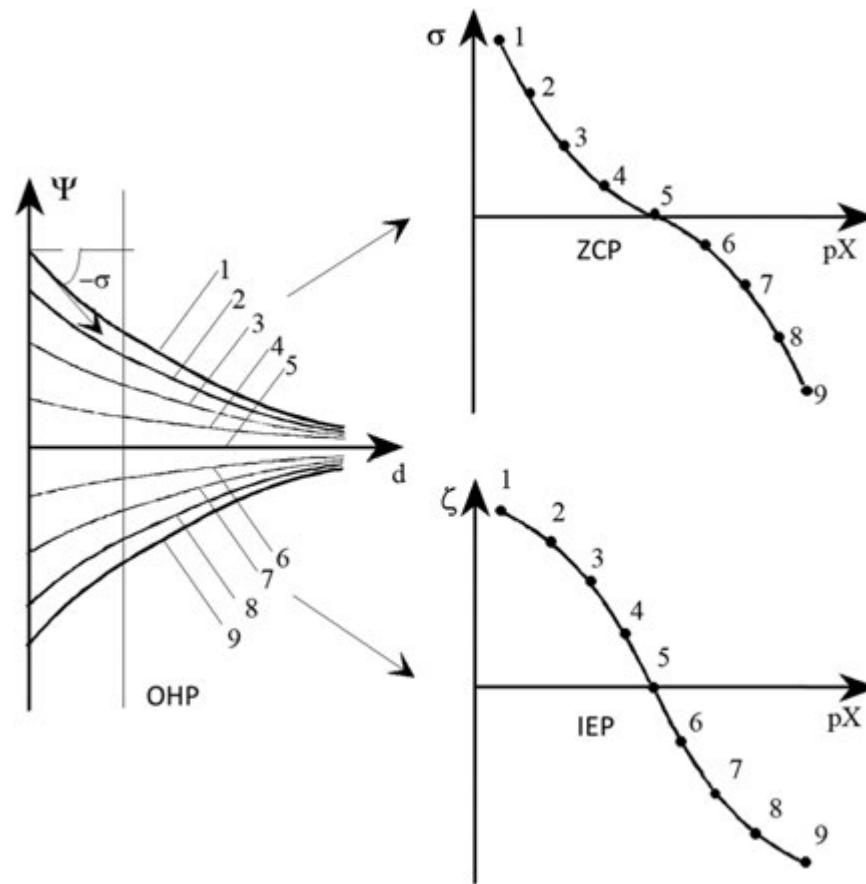


Fig. 6 Illustration of the relationships between zeta potential, surface charges and potential variation in the double layer, in the presence of the only ions determining the potential. the charge 0 is given by the slope at the origin of $\psi(d)$, the ζ zeta potential is given by the charge values at the O.H.P.

Parameters Influencing the State of Dispersion

Certain parameters will have a direct effect on electrostatic repulsion, such as pH, steric repulsion or addition of dispersants. However, other important parameters as temperature, solid content and particle size and shape must also be taken into account.

pH

Theoretical reminders help to understand how, by tuning the pH value of the suspension medium, which directly influences the concentration of the medium in ions determining the potential; one can modulate the repulsion forces between neighboring particles. This property is known to traditional ceramists who control the flocculation or deflocculation of clay slurries by playing on the pH value generally by basic additions. In this case of traditional ceramics, the rheology is complicated, which is a consequence of the anisotropic shape of the particles as well as the inhomogeneous distribution of the fillers. At pH values below about 8, kaolinite platelets carry negative charges on the developed surfaces and positive charges on the tips and edges. This leads to a microstructure like a house of cards which, in the case of high volume fractions, leads to a continuous network and the existence of a flow threshold. At higher pH values, all surfaces become negative and a minimum of the viscosity value is observed (Fig. 8). As the particle size decreases, both the flow threshold and the minimum viscosity increase due to the higher number of contacts per unit volume, although the force per pair of interactions decreases.

Other examples of the evolution of the viscosity of suspensions as a function of pH and consequently of the zeta potential will be studied in experimental applications described below, with their associated rheological behavior.

To adjust the pH of the slurries all types of acids or bases can be used. In the traditional ceramic industry are used: sodium silicate, bicarbonate, metaphosphate, triphosphate, soda, potash, etc. They are called inorganic dispersants; in addition to adjusting the pH, they increase the ionic strength of the medium by adding sodium or potassium cations. In the preparation of technical ceramics, acids or bases that can bring undesirable ions are excluded. This limits the range of products that can be used. Diluted ammonia solutions can be used to adjust basic pH values and for acid pH values hydrochloric or citric acids.

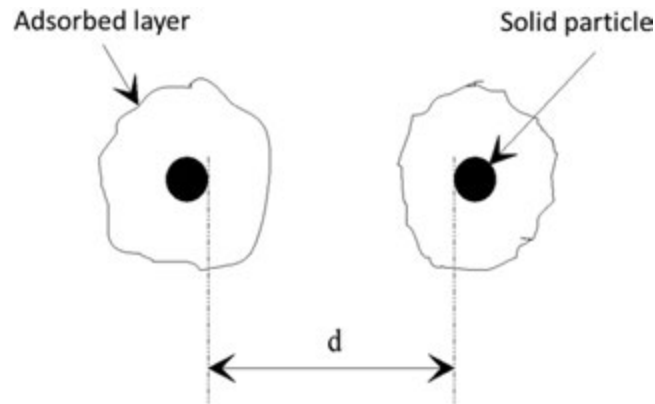


Fig. 7 Diagram illustrating the steric prevention of contact between two solid particles thanks to the layer of polymer adsorbed on the periphery of the particles.

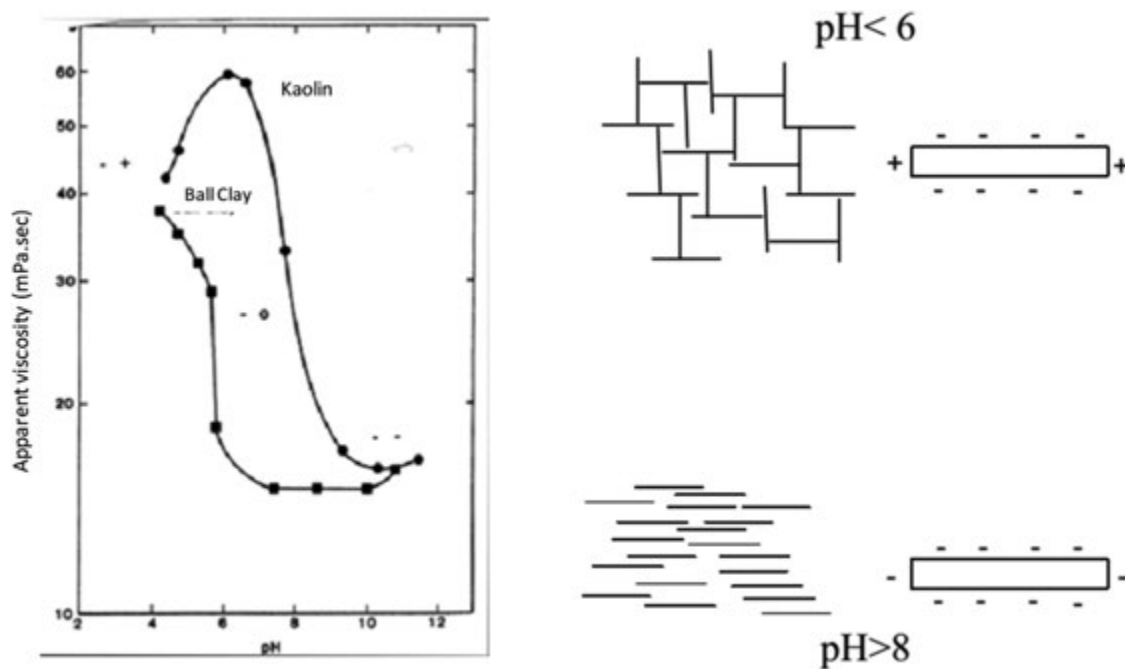


Fig. 8 Viscosity variation of kaolin and ball clay suspensions as a function of pH and schematic representation of the microstructure of the suspension.

Solid Content

It is also understandable that the slurry behavior also depends on its dry matter concentration (the solid content, often expressed as a mass or volume % of dry powder in the slurry): the final electrical equilibrium of the suspension and the pH of the slurry depend, among others, on the total surface area of the powder grains likely to react with the dispersing medium. In general, as any other parameter is constant, increasing the solid load will change the rheological behavior: for example suspensions with low concentrations of oxide in water will maintain Newtonian behavior and this behavior will become shearthinning by increase of the solid load with increase in viscosity values as shown in [Fig. 9\(a\)](#).

Temperature

Temperature is a parameter to be considered, especially in high energy mills where the slurries temperature can exceed 60°C. Generally speaking, the increase in temperature favors the Brownian movement and reduces the viscosity of the slurries and the flow threshold, as shown in [Fig. 9\(b\)](#).

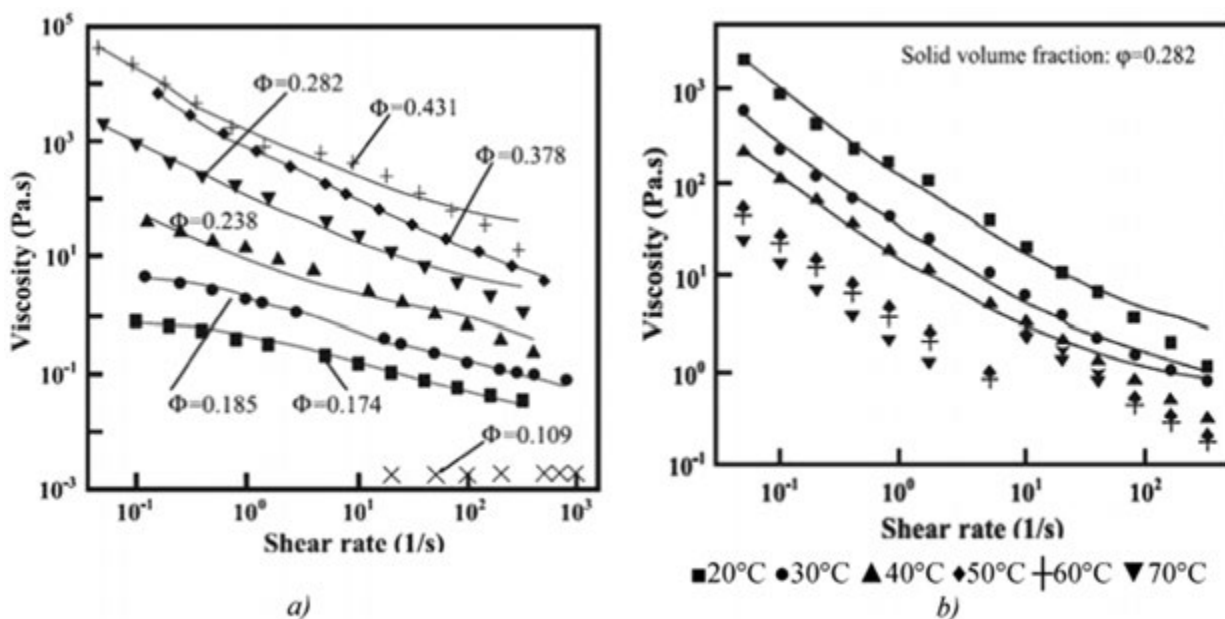


Fig. 9 Effect of (a) the solid load (Φ being the volume charge) and (b) the temperature on the rheological behavior of aqueous TiO_2 slurries according to Yang *et al.* Reproduced from Yang, H.-G., Li, C.-Z., Gu, H.-C., Fang, T.-N., 2001. Rheological behavior of titanium dioxide suspensions. *Journal of Colloid and Interface Science* 236, 96–103.

Dispersants

Although the term dispersant is also used for pH-adjusting inorganic compounds, we will only refer here to organic dispersants, which are also called deflocculants or surfactants. They provide steric stabilization and also have a pH-adjusting role.

The types of polymers used are very varied. They include polyelectrolytes, used in the case of aqueous or polar media; non-ionic polymers, mainly used for low-polar media; copolymers (random or block) which have one (or more) adsorbant entities and one (or more) entities which are not adsorbed and tend towards solution.

The Fig. 10 shows the main water-soluble polymeric dispersants used in the ceramic industry. There are also a large number of dispersants sold by suppliers under trade names and it is often difficult to know their precise formulation.

A typical example of an ionic surfactant with a hydrophilic head and a hydrophobic tail is sodium dodecyl sulfonate (DSS) shown Fig. 11. The chemical nature of the powder (hydrophilic or hydrophobic) and the dispersive liquid can greatly influence its wettability and the dispersion of the powder.

Random copolymers have non-ordered side chains like a bottle brush and block copolymers have ordered side chains like a toothbrush. Stabilization by these polymers obviously requires their adsorption as an essential first step. This is due to the respective affinities of the solvent and the polymer for the surface of the ceramic powder or, in other words, the adsorption energy required to develop sufficient adhesion of the polymer to the surface. This can have implications for the shaping process as the polymer can then be subjected to high shear rates. Desorption of the polymer would reduce the degree of overlap with the result that the particles would be brought closer together or bridged by the polymers still present. In both cases, strong attractive forces develop and can strongly modify the rheological behavior. It should therefore be noted that in order to achieve good repulsion, the surface must first of all be well covered by the polymer and then this covering must remain constant during the approach of the particles (which is tantamount to expressing that the time scale of desorption is much greater than that of adsorption).

The polymer must also have a certain affinity for the solvent. This is necessary so that it can spread sufficiently towards the solution to develop good steric repellency. Indeed, it is at the moment when the covering of the adsorption layers begins that the repulsion is felt. The more these layers are extended, the more the approach and therefore the effect of the Van der Waals forces will be limited. When the layers overlap, there is interpenetration of the polymers and the contact between the solvent and the polymer chains is reduced (due to polymer-polymer contact). As a result of the adsorbed layer approach, each polymer can no longer adopt as many configurations as before. The density and configuration of the adsorbed polymers play therefore a critical role in dispersion stabilization.

Adsorption conformation plays a key role in steric stabilization. For example, the different modes of adsorption used to describe the adsorption at different pH values of polyacrylic acid (PAA) on an alumina surface are schematically depicted in Fig. 12. (Pederson and Bergström, 1999).

At low pH values, PAA is not dissociated and is only adsorbed with few points of contact on the surface. The volume it occupies in such a way is close to that which it occupies when in solution. In this case we speak of a random ball configuration (Fig. 12(a)). At higher pH but still below the isoelectric point of alumina (e.g., pH 6), the PAA is completely dissociated into a negatively charged polyelectrolyte which will be adsorbed onto the positively charged alumina in a horizontal configuration. This is known

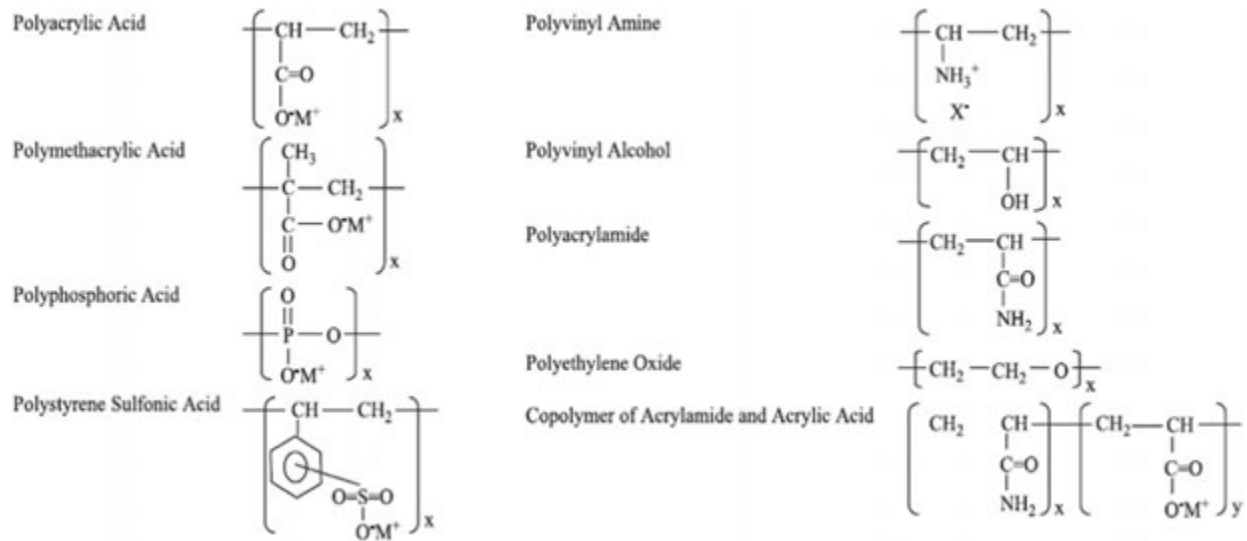


Fig. 10 Main water-soluble polymeric dispersants.

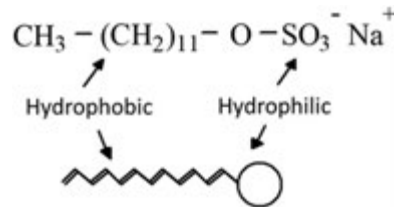


Fig. 11 An ionic surfactant: sodium dodecyl sulfonate (DSS) and its schematic representation.

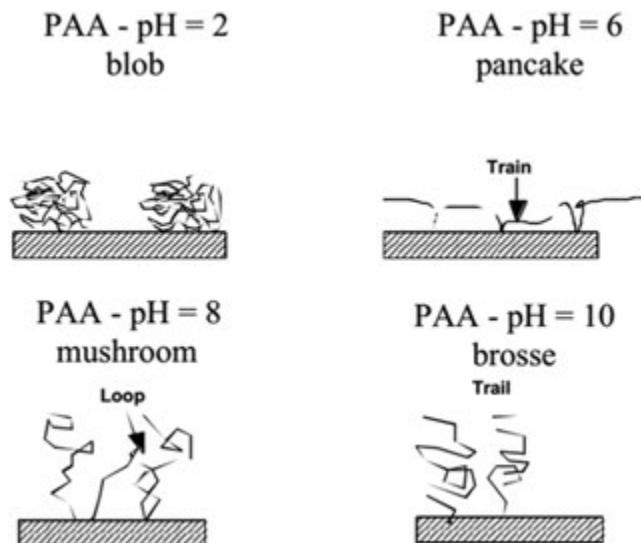


Fig. 12 Schematic representation of the adsorption of PAA on an alumina surface at different pH values showing some possible configurations: (a) random coil, (b) flattened (pancake), (c) loop (mushroom), (d) brush.

as flat or pancake adsorption (Fig. 12(b)). At even higher pH values, close to but below the isoelectric point (e.g., pH 8), the electrostatic interaction energy between the polymer and the surface decreases and the adsorption mode is described more in terms of loops and segments (Fig. 12(c)). It can also be qualified by the term *fungus* in some cases. This term suggests that the density of polymer segments is higher in the middle of the adsorbed layer than at the surface of the solid. When pH is above the isoelectric point, the surface has very few positively charged adsorption points. Most of the surface exhibits electrostatic repulsion with the

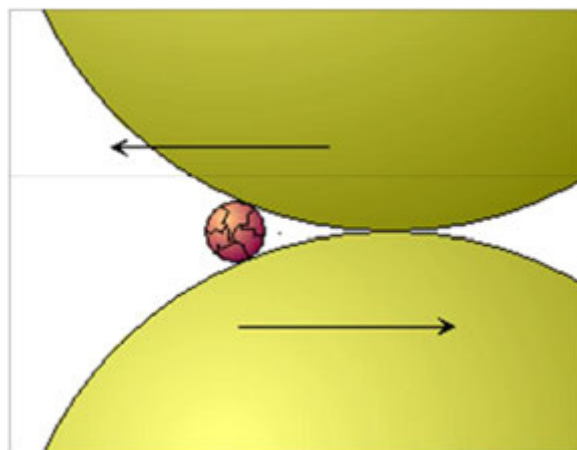


Fig. 13 Grains undergoing attrition shear between grinding balls.

polymer. As a result, the polymers will only be adsorbed at a few points and will repel each other, limiting the degree of coverage. In this case, the adsorption mode is said to be in a “brush” type configuration (**Fig. 12(d)**). It has to be noticed that between these different situations, the conformation of the polymer in solution is no longer the same, the volume of the macromolecules evolves with their dissociation rate and the thickness of the adsorption layer is therefore modified. The charge associated with the polyelectrolytes will also influence the electrostatic forces. When there are both electrostatic and steric forces, the term electrostatic repulsion is generally used.

The advantage of co-block polymers is that they can combine high adsorption while maintaining a large and better defined adsorption layer thickness than in the case of a PAA type polymer with a very large molecular weight polydispersity. Unfortunately, these polymer co-blocks are very expensive and not commercially available. For this reason, high polydispersity PAA with poorly defined and highly variable adsorption layers are still widely used and their dispersion efficiency is difficult to predict. It should be noted that an inexpensive intermediate solution is the use of polyacrylates with PEO side chains that define the thickness of the adsorption layer. These materials are already widely used in the cement industry.

The addition of organic dispersant is necessary when simple electrostatic repulsion is insufficient, or even impossible in the case of powder mixtures that have opposite evolutions of their zeta potential according to the pH. It will then allow the viscosity values of the slurries and the flow thresholds to be lowered and the rheological behavior to be completely changed from shear-thinning to -thickening when the slurry is completely deflocculated. This is for example the case of mixtures of TiO_2 and MgO in water which will be detailed below.

Grinding

When grinding slurries, if it is efficient, there will be an increase in the surface area developed by the powder. The new surface created will react with the dispersing medium. This will result in a modification of the pH of the slurry and/or a change of the surface concentration of adsorbed dispersants. In addition, there will be a decrease in the diameter of the powder grains, resulting in evolution of the Van der Waals forces. Thus, very large changes in slurry rheological behavior are to be expected during grinding. Therefore, even if efforts have been made to obtain low viscosity and a slightly rheo-thickening rheological behavior of well deflocculated slurry for the grinding process, then it is highly likely that this behavior will change with re-flocculation of the slurry. This can then be damaging to the grinder, which may even block. Such an example will be described in a case study at the end of this chapter. A preliminary study is therefore often necessary before implementing powder treatment in a mill. Indeed, the modes of action of the various grinding devices are quite different as described below.

The Different Shredders

Grinding reduces particles down to a few tens of microns or even less. Fine grinding produces submicron particles, typically with a diameter between 1 and 0.1 μm . Fine grinding is generally associated with a greater input of energy through vibration, shear (attrition mills) or high speeds (impact mills). Such high energies allow finer products to be obtained and submicronic particles can be obtained as long as the grinding bodies are judiciously chosen to limit contamination.

Attrition Mill

In the attrition mill, the incoming material has generally a diameter of less than 50 μm . The high turbulence due to agitation results in stresses being applied to the large particles in compression and shear, as well as high collision frequencies which lead to

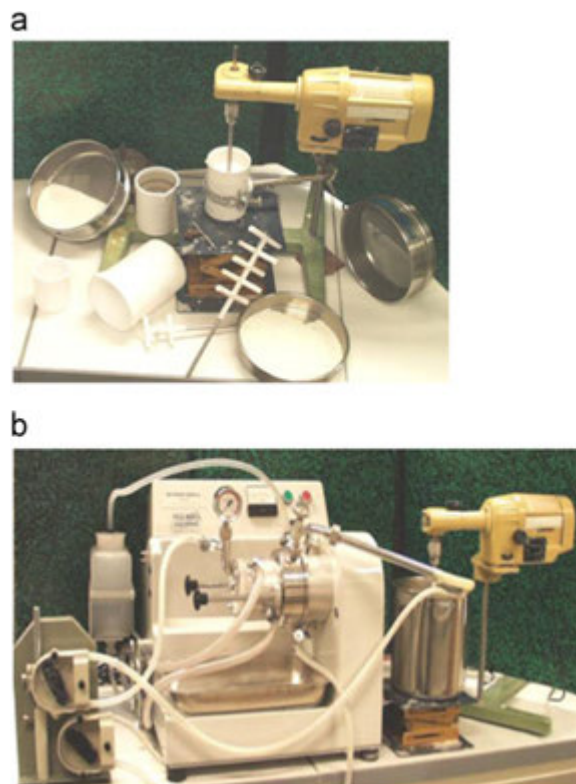


Fig. 14 (a) Vertical laboratory grinder, (b) horizontal grinder Dyno-mill ©.

rapid grinding kinetics. High stress is induced when the particles friction between the balls. This results in the predominant phenomenon of shear attrition. Attrition arises in addition to compressive stresses resulting from direct collisions. The diagram of [Fig. 13](#) clearly shows that there must be a match between the diameter of balls and the diameter of grains to be ground: if the ratio between the two diameters is too large, the limit angle determined by the value of the friction coefficient is exceeded and the grain is pushed and no longer ground between adjacent balls. This is why attrition is only used for powders that are already micron-sized.

Typical attrition mill or grinders are presented in [Fig. 14](#). Balls are agitated by blades or arms. The viscosities of the slurries, as well as the dispersion state of the particles are critical factors in such mills. These types of mills can be used in continuous mode ([Fig. 14\(b\)](#)), by pumping the slurry through the grinding volume, with the balls being retained by a suitable screen. Slurries can be recycled if a single pass does not produce the desired grain size distribution and a classification step can be added to remove the finest particles that no longer change size but occupy unnecessary volume in the grinding chamber. The solids content of a suspension is normally between 30% and 70% by mass, depending on the viscosity of the liquid phase and the size of the incoming product. The grinding balls used in attrition mills are very hard (mostly yttria-doped zirconia) and well calibrated. Ball diameters range from 2 to 0.1 mm. It will be shown later that the diameter of grinding balls has a great influence on the grinding efficiency.

Planetary Mills

The planetary shredder owes its name to the planetary movement of the bowls. In this type of mill, the bowls containing the grinding balls are held on a main disc ([Figs. 15 and 16](#)). There is a double rotation movement: the rotation of the bowls on their own axis and the rotation of the main disc around its axis.

In order to achieve efficient shredding, it has been shown by computer simulation that the main disc and bowls must rotate in opposite directions. This means that the centrifugal forces act in opposite directions. As a result, the balls roll along the inner walls and grind the powder grains between the balls and the wall leading to friction effect. Under the effect of centrifugal force, the balls are then violently ejected onto the opposite wall and thus impact the powder grains ([Fig. 15\(b\)](#)).

The grinding bowls have a capacity of 12–500 mL and the balls have diameters of 5–40 mm. As the bowls are closed and sealed, some equipments allow working under controlled atmosphere. The choice of the material for bowl and balls is very important because when the balls impact onto inner wall, particles from the bowl can be ejected and therefore incorporated into the powder. This can lead to contamination and thus modify the desired composition. It is therefore essential to choose a very hard material in order to resist abrasion. Materials available are agate, corundum, silicon nitride, zirconium oxide, steels. Balls with

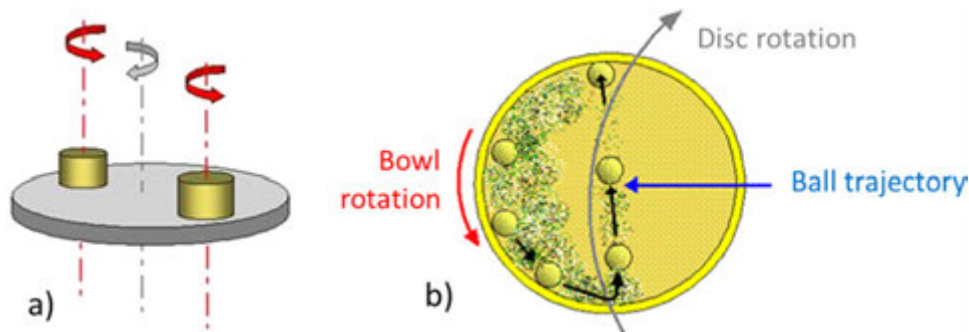


Fig. 15 (a) Principle of the planetary mill with the rotation axes of the bowls and the disc, (b) balls trajectory.

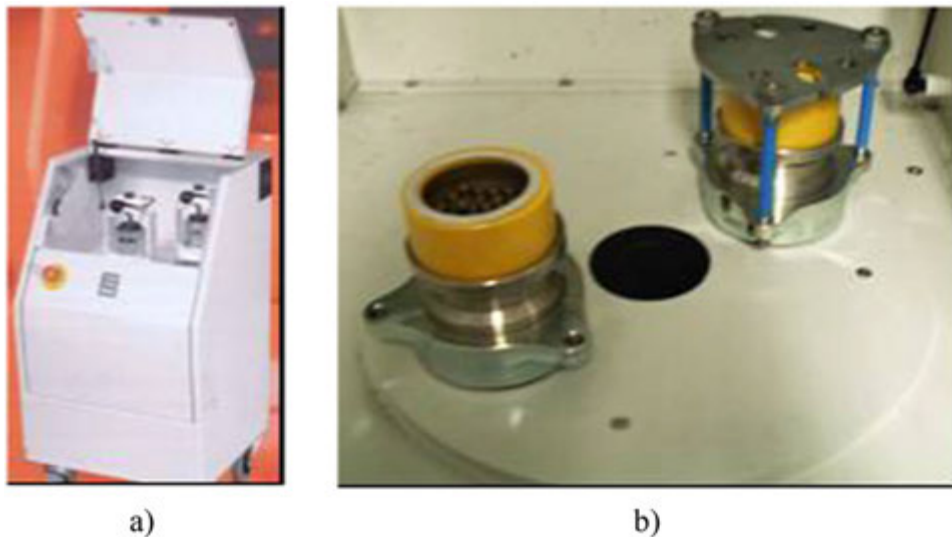


Fig. 16 (a) Pulverisette P4 Fritsch, (b) grinding bowls.

high densities are preferred because their kinetic energies are higher. The literature shows that using balls of different sizes within the same bowl is not a satisfactory solution because the trajectories of the balls are modified which prevents the homogenization of the sample.

The effectiveness of a mechanical shock depends on the density of the ball and its speed. Thus it depends on the rotation speed of the disc and bowl. As a first approximation, it is easy to estimate that the higher the speed of rotation, the higher the speed of the balls and that, consequently, the more efficient the grinding would be. This is true up to a so-called critical speed. Indeed, if the rotational speeds are too high, the centrifugal force due to the support disc is not large enough to compensate for the centrifugal force due to the rotation of the jar. This causes the balls to roll on the inner wall without ever hitting the opposite wall. This only results in friction effects, resulting in inefficient grinding. This is why it is necessary to use speeds below the critical speed but high enough to ensure efficient grinding. There is no referenced speed because it depends on the composition of the powders, the size of the balls, the nature of the balls and of the bowls. Most planetary mills have a fixed speed ratio. The speed ratio is the quotient of the bowl speed over the disc speed. Only the Fritsch planetary mill, Pulverisette 4 (Fig. 16), allows to select a ratio. Grinding can be carried out in a dry or slurry process. In both cases, the bowls should be filled to about 50% by volume. This way the balls have enough space to acquire their maximum speed. If the bowl is filled with powder and beads then the beads have a very low speed and the energy on impact with the powder is very low. On the other hand, if there are very few balls and powder in the bowl, the efficiency is very poor.

Another variable to take into account is the BPR, an acronym of Ball to Powder weight Ratio. It corresponds to the quotient of the mass of balls on the mass of powder. For example, a BPR of 10:1 means that the mass of balls in the bowl is ten times greater than the mass of powder. At high BPR values, there are a large number of balls and therefore a large number of collisions per unit of time, resulting in more efficient and faster grinding. If there is very little powder, the majority of collisions will be useless for grinding. This is why, in accordance with studies that have varied the BPR from 1:1 to 300:1, it is advisable to use a BPR of between 5:1 and 20:1.

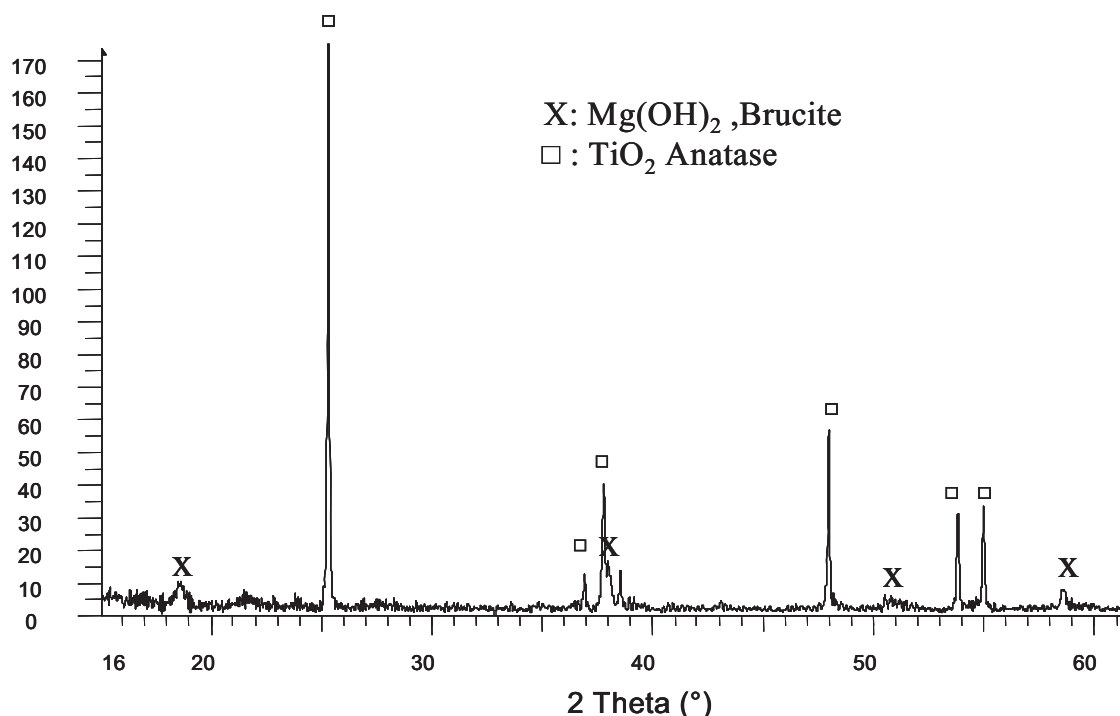


Fig. 17 Diffractogram after drying of an “MgO”/TiO₂ mixture carried out in an aqueous medium.

Examples of Application

Several papers undergoing optimization of grinding process have been published, for example grinding of TiO₂ and Al₂O₃ (Houivet and Haussonne, 2003). Two examples showing the importance of grinding and milling for electronics applications are described below. The first one will be for multilayers ceramics capacitors used for medical application and the second for use as sensor in automobile.

First Example: Synthesis of MgTiO₃ for Multilayer Capacitors Type I

The difficulty of obtaining pure MgTiO₃ ilmenite phase is frequently reported in the literature. Indeed, the synthesis of MgTiO₃ is commonly accompanied by non desirable formation of MgTi₂O₅. In industrial production, as the reproducibility of batches is crucial to obtain satisfactory type I multilayer capacitors. (Bernard *et al.*, 2008), some specific processes have been developed.

Stabilization tests by electrostatic repulsion of MgO/TiO₂ slurry

In principle, synthesis can start from pure magnesium oxide (MgO) and titania (TiO₂). As magnesium oxide has a strong tendency to form hydrate and carbonate, it should practically be calcined before handling (e.g., 2 h, 600°C). However, for economic reasons, mixing has to be carried out in aqueous medium. In these conditions MgO forms Mg(OH)₂ (brucite), while TiO₂ (anatase) retains its structural characteristics. The diffractogram (after drying) of the obtained mixture of MgO and TiO₂ after processing in aqueous medium (50% mass in solid) is shown in Fig. 17. It confirms that all the MgO is hydrated into brucite.

The zetameter analysis of this mixture is given in Fig. 18. The zeta potential values of titanium oxide as a function of pH are in accordance with a classical evolution with pH. Indeed, the potential is highly negative (< -30 mV) for basic pH values whereas it becomes positive in acidic environment. The isoelectric point is close to pH 3. The behavior of magnesium oxide is different: zeta potential of brucite remains close to 0 over the pH range 12 to 8.5 and values at pH below 8.5 cannot be determined, as Mg(OH)₂ dissolves quickly under pH 8. Therefore, it can be concluded that it is not possible to obtain a stable aqueous dispersion of a mixture of MgO and TiO₂ powders in the pH range between 8.5 and 12. Furthermore, as dissolution of magnesium hydroxide occurs at pH < 8, it is thus difficult to mix at low pH values. Moreover, low pH conditions are not favorable because the zeta potential of titanium oxide at slightly acidic pH is low. This simple zetametric study shows clearly the impossibility to obtain favorable mixing conditions for aqueous slurries starting from MgO and TiO₂ by controlling only on electrostatic repulsion.

To confirm this issue, the rheological record (Fig. 19), of MgO (Mg(OH)₂)/TiO₂ slurries in stoichiometric proportion confirms their flocculated character. In fact, in a more concentrated medium (as a slurry), magnesium oxide imposes the pH of the slurry (natural pH after mixing is 11.3). Even if the solid content is reduced (i.e., 25% mass), there is no stabilization regardless the pH values. Recording the rheogram at this low concentration and pH also shows a shearthinning behavior of the slurry, confirming the

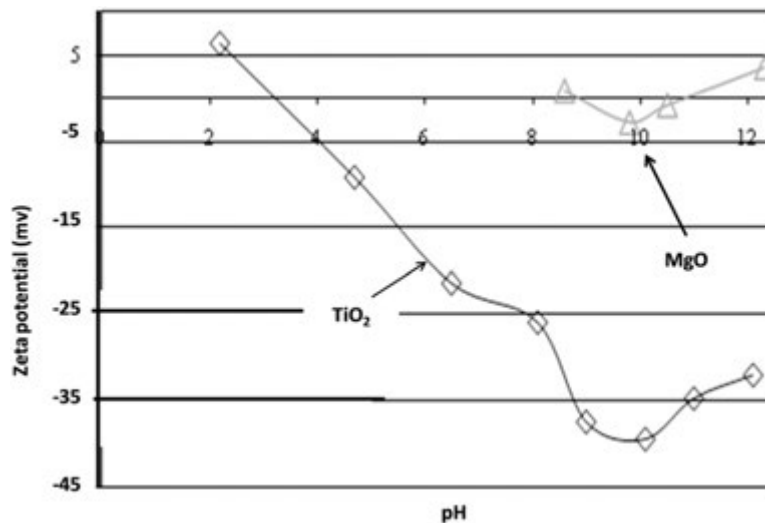


Fig. 18 Variation of the Zeta potentials of brucite and anatase as a function of pH.

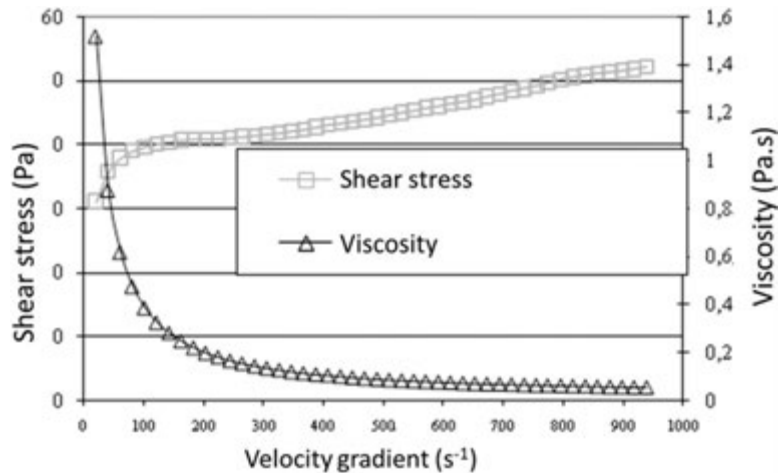


Fig. 19 Rheogram of a MgO/TiO₂ slip in an aqueous medium at 25% solid load.

flocculated character of the suspension. As a consequence, another solution has to be used: steric repulsion technique as described below.

Steric repulsion stabilization

Addition of a dispersant makes it possible to obtain deflocculated slurries by influencing the distances between particles. In this example, the dispersant chosen is Dolapix CA[®], a basic anionic polyelectrolyte.

Experimental slurries consist of a stoichiometric mixture of MgO/TiO₂. The rheograms assembled in Fig. 20 show the rheological behavior with increasing contents of Dolapix CA on 80 cm³ of slurry (25% solid mass). Addition of only 1 cm³ (i.e., 1.25% by volume) of dispersant allows to reduce the viscosity by a factor of 30 at low velocity gradients. The change from shear-thinning to shear-thickening behavior takes place, as soon as 2 cm³ of dispersant is added to the 80 cm³ of slurry. The rheo-thickening character is totally obtained for an addition of 2.5 cm³. The same shear-thickening behavior can be obtained with more concentrated slurry: 50% mass (Fig. 21). Despite a higher solid load, the volume of dispersant required to obtain 50% mass deflocculated slurries is less than that of 25% mass deflocculated slurries. This observation may seem paradoxical. The envisaged hypothesis is that there is a different grafting rate of the solid particles on the polymeric dispersant between diluted (25%) and concentrated (50%) media. Indeed, in diluted media, the distances between particles/particles and particles/dispersant are larger than in concentrated slurries. It signifies that, for 25% slurries, the particles have less probability to come into contact with the polymeric dispersant, the grafting rate of solid particles on the polymer chains is thus lower than for 50% slurries. This is equivalent to assuming that in diluted medium, the dispersing chains would remain free with a different ratio of free chains to chains grafted between 25% and 50% of suspensions. This also implies the existence of an optimum where the solid load would

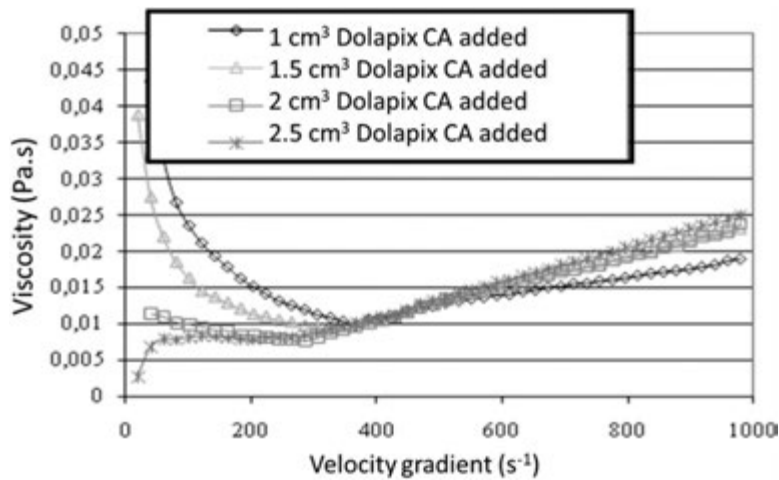


Fig. 20 Evolution of the viscosity of a MgO/TiO₂ slurry at 25% solid load as a function of the volume of dispersant added.

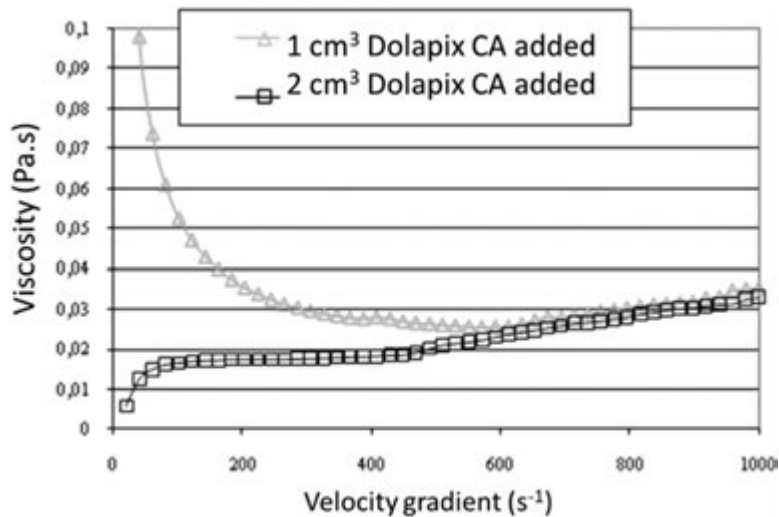


Fig. 21 Evolution of the viscosity of a 50% MgO/TiO₂ slurry in solid load as a function of the volume of dispersant added.

be maximum and the amount of dispersant to obtain shear-thickening behavior would be minimum. Tests on 66.6% solid suspensions carried out show that it is not possible to obtain deflocculated suspensions, whatever the amount of dispersant added. However, in the case of suspensions deflocculated at 50%, it should be noted that, despite the shear thickening behavior obtained, the viscosity is increased by a factor of 2 compared to the viscosity of the suspensions deflocculated at 25%. As it is possible to obtain optimum mixing/grinding conditions for the MgO/TiO₂ slurry, the influence of the mixing conditions on the formation of the ilmenite MgTiO₃ phase is studied (see below).

Influence of rheology on the synthesis of MgTiO₃

Attrition grinding tests are also carried out starting from 2 different rheological slurry behaviors: rheo-thickening and shear-thinning. The last were obtained from slurries of 50% solid load, 1 to 1 MgO/TiO₂ stoichiometry, stirring in aqueous medium. The attrition time is set at 60 min. To obtain deflocculated slurries, all the conditions defined above are followed: addition of Dolapix CA (1 and 2 cm³) to optimize dispersion. The various slurries are then spray dried to avoid any sedimentation phenomena and then calcined during the same thermal cycle including a 1000°C, 1 h dwell. After chamottage, the powders from both mixtures (flocculated and deflocculated) are analysed by X-ray diffraction. **Fig. 22(a)** shows that pure ilmenite phase is observed in the case of a mixture with perfectly controlled shear-thickening behavior. On the contrary, starting with uncontrolled viscosity (shear-thinning behavior), traces of MgTi₂O₅ phase are detected in X-ray diffraction (**Fig. 22(b)**). It shows the importance of controlling the rheology during mixing/grinding to obtain pure magnesium titanate. This can be explained because under optimized deflocculation conditions, oxide grains are more homogeneously distributed. As a consequence, diffusion distances during chamottage are lower favoring synthesis of the pure phase.

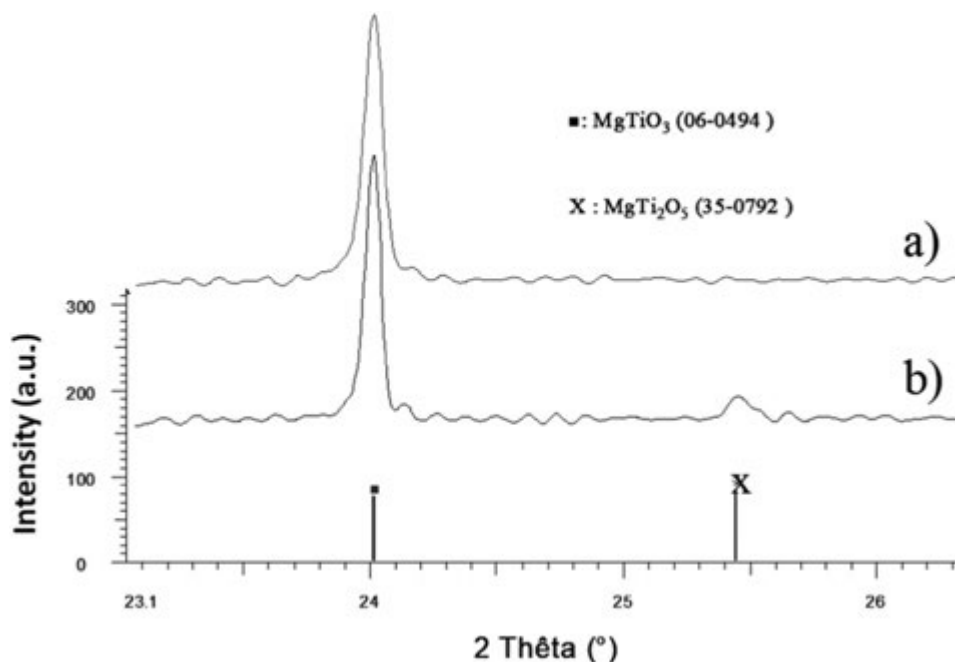


Fig. 22 Diffractogram of two calcined powders: (a) with Shear-thickening behavior during grinding. (b) Shear-fluidifying behavior during grinding.

Second Example: Negative Temperature Coefficient Ceramics – Synthesis of the NTC Ceramic $\text{YCr}_{0.5}\text{Mn}_{0.5}\text{O}_3$

The compositions belong to the Y_2O_3 - Cr_2O_3 - Mn_2O_3 system in order to produce ceramic thermistors with negative temperature coefficient (NTC) that can be used in temperature ranges from ambient to 1000°C . These compositions are often very difficult to densify because sintering temperatures are higher than 1600°C . Through the development presented below, it is intended to show how a control of mixing and grinding allows improving densification, in this example of the $\text{YCr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ phase.

Mixing conditions of the oxides

The precursors are Y_2O_3 , Cr_2O_3 and Mn_2O_3 , mixed in stoichiometric proportions to obtain $\text{YCr}_{0.5}\text{Mn}_{0.5}\text{O}_3$. **Fig. 23** represents their zeta potential as a function of pH. The 3 oxides exhibit zeta potentials larger than 30 mV (in absolute value) for pH between 10 and 12. This pH range is thus favorable for dispersion. The slurries rheological behavior is shown in **Fig. 24** (40% solid mass, water): a comparison is made between mixture at natural pH (6.6) and the same for pH increased at 10.6 by ammonia addition. On the one hand, at pH 6.6, the rheological behavior is typical of the shear-thinning type at low velocity gradients, which corresponds to a flocculated mixture. On the other hand, at basic pH, the behavior of the mixture is slightly rheofluidifying, i.e., the mixture is deflocculated, in good accordance with the zeta potential results. The perovskite $\text{YCr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ phase can be obtained almost pure after calcination above 1150°C as shown by X-ray diffractograms, **Fig. 25**. However, during the formation of the phase, there is a volume increase, shown in the dilatometric curves of **Fig. 26**. This leads to cracking of the ceramics during reactive sintering. To avoid such a phenomenon, mixing and grinding of raw materials and regrounding of $\text{YCr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ calcinated powders has to be performed.

Influence of raw material grinding times on $\text{YCr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ calcinated powders

Mixtures of the 3 raw powders are ground in a Dyno-mill[®] device, using 0.8 mm yttria zirconia balls (40% solid mass, pH = 11). During the grinding of a 500 g batch of powder mixture, slurry samples are taken after 15, 30 and 45 min. The samples are dried then calcined at 1200°C for 1 h. The calcined powders are then roughly deagglomerated with mortar.

Characterization of calcined sample powders by laser granulometry (**Fig. 27**) and by specific surface area measurement (**Fig. 28**) show that calcination leads to aggregation. Indeed, the average size of the agglomerates measured by Laser granulometry is around 5 μm , whereas the estimate of individual grains by BET would be rather around 0.5 μm for calcined powders resulting from a 45 min powder grinding. This is confirmed by SEM (**Fig. 29**). We are dealing with very porous aggregates, formed by grouping grains that have undergone a beginning of sintering as confirmed by the formation of necks between grains. Such aggregates should lead to a heterogeneous powder compact, which can lead to differential sintering and thus to the development of large pores and cracks in sintered materials. As a consequence, it is necessary to reground these calcined powders before sintering.

Grinding of calcinated $\text{YCr}_{0.5}\text{Mn}_{0.5}\text{O}_3$

A 500 g batch of A3 pre-calcined powder (45 min) is reground in the same conditions as before. Samples are taken again during grinding (B1-15, B2-30 and B3-45 min). The grain size distributions of the 3 calcined powders issued from regrounding

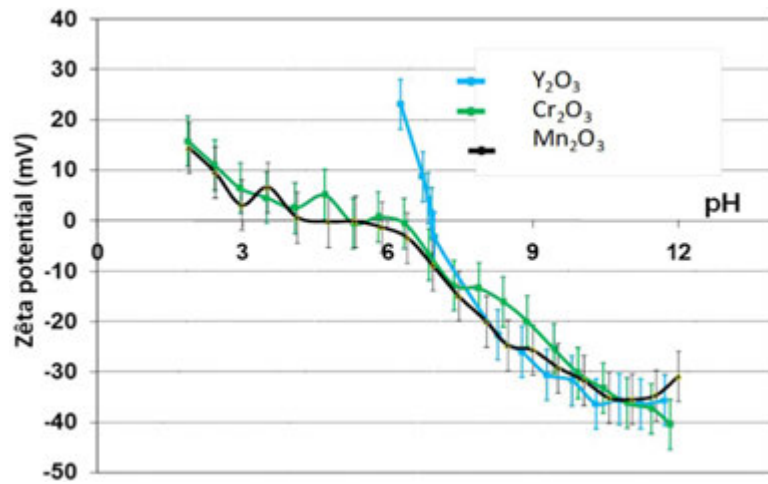


Fig. 23 Zeta potential of different starting powders as a function of pH.

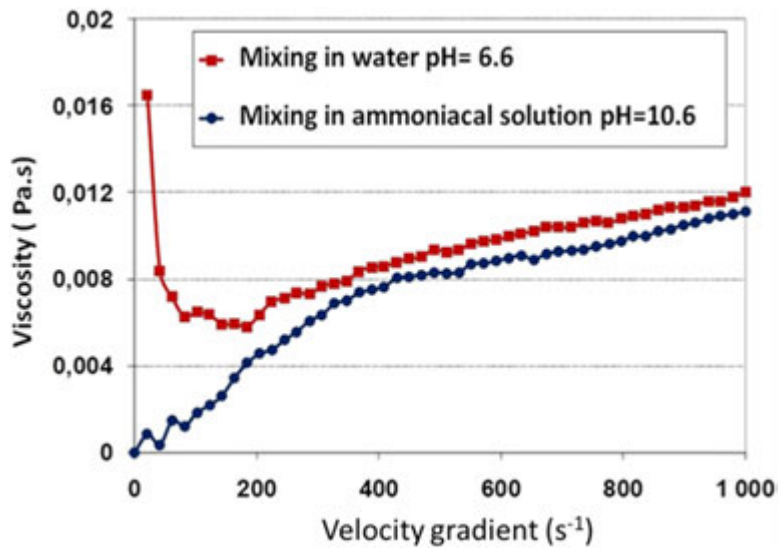


Fig. 24 Rheological behavior of oxide mixtures.

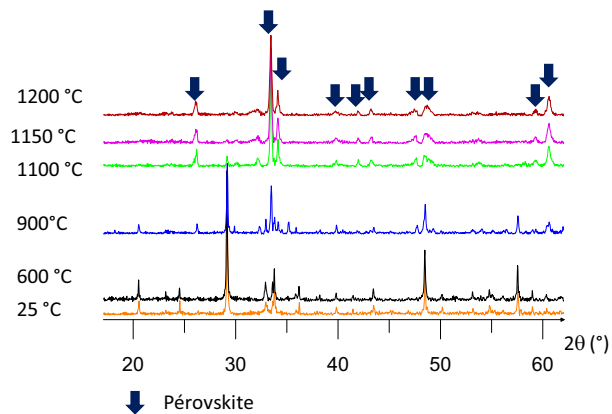


Fig. 25 Diffraction diagrams of the mixture as a function of the chamfering temperature.

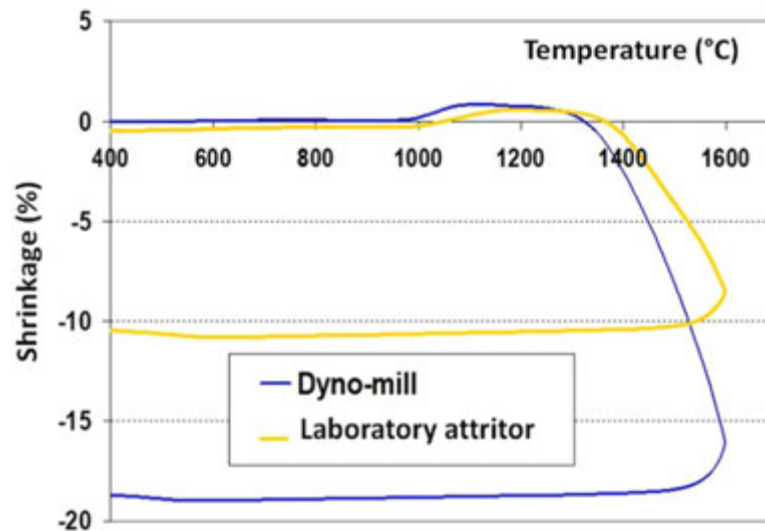


Fig. 26 Dilatometric curves of mixtures ground with Dyno-mill[®] and laboratory attritor for 30 min.

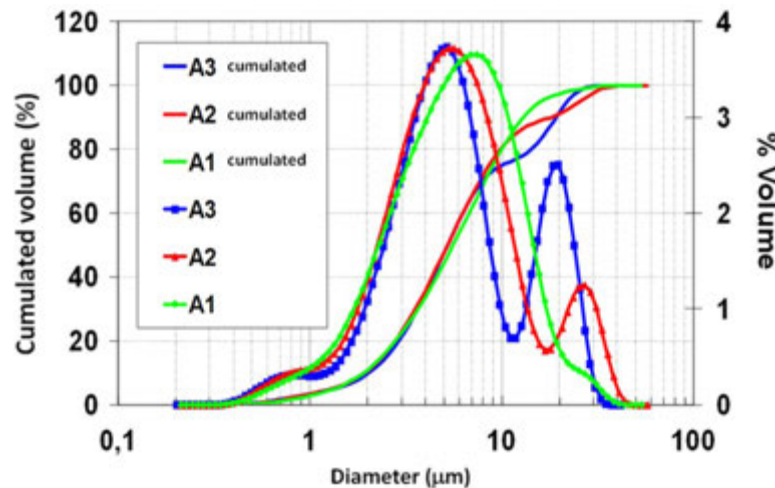


Fig. 27 Granulometric distribution of calcined powders A1, A2 and A3.

(Dyno-mill[®]) are shown in Fig. 30. Unsurprisingly, the particle size decreases with increasing regrind time. Indeed the median diameter of A3 (unground calcined powder) decreases from 4.5 μm down to between 1 and 2 μm , depending on the re-grinding time. The evolution is more evident with regard to the specific surface (Fig. 31): surface area increases from 2.1 for A3 mixture to 7.2 m^2/g for a regrinding time of 45 min. This corresponds to 0.5 and 0.1 μm BET equivalent diameter, respectively. It has to be noted that during grinding, wear of zirconia balls can occur. Indeed by weighting balls before and after twice 45 min grinding, zirconia total mass has diminished of 0.4%.

Effects of grinding on densification

Dilatometric analyses carried out under oxygen flow up to 1600°C reveal that the shrinkage start is around 1300°C for all unground calcined powders. For reground calcined powders (B series), there is a slight temperature shift at the beginning of the densification and an increase in shrinkage, which suggests that the ceramic will be denser over the grinding time, as green densities are similar (Fig. 32). It should be noted, however, that despite this slight improvement in sinterability, the shape of the curves suggests that none of these samples are fully densified during these dilatometric measurements. To increase the final density, sintering can be performed in a kiln at the same temperature (1600°C), under oxygen flow, with a dwell time of 12 h. From the densities represented in Fig. 33, it can be seen the significant effect of grinding on the densification level as the density increases up to 95%.

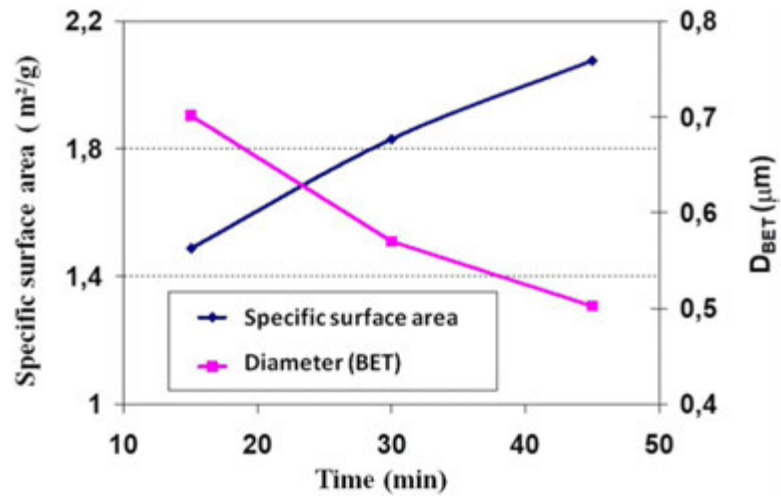


Fig. 28 BET specific surface area and equivalent diameter of calcined powders vs. time.

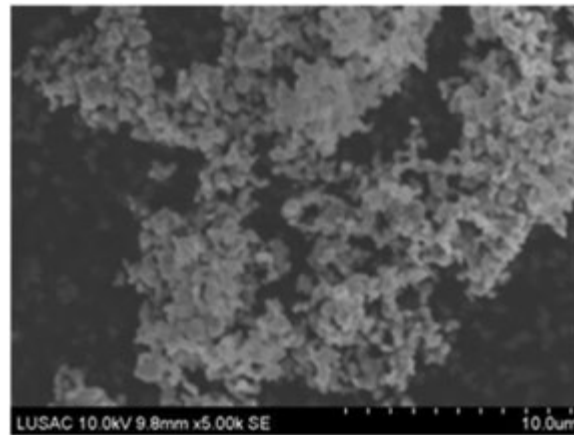


Fig. 29 SEM micrograph of A3 calcined powder.

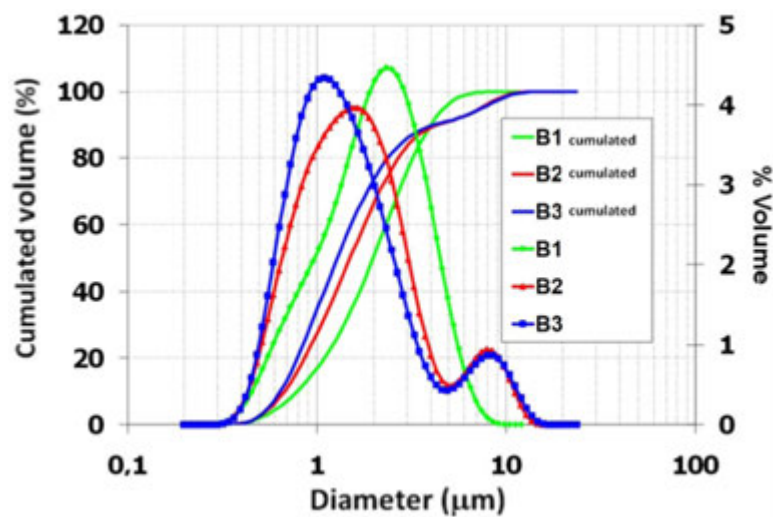


Fig. 30 Particle size distribution of Dyno-mill reground calcined powders.

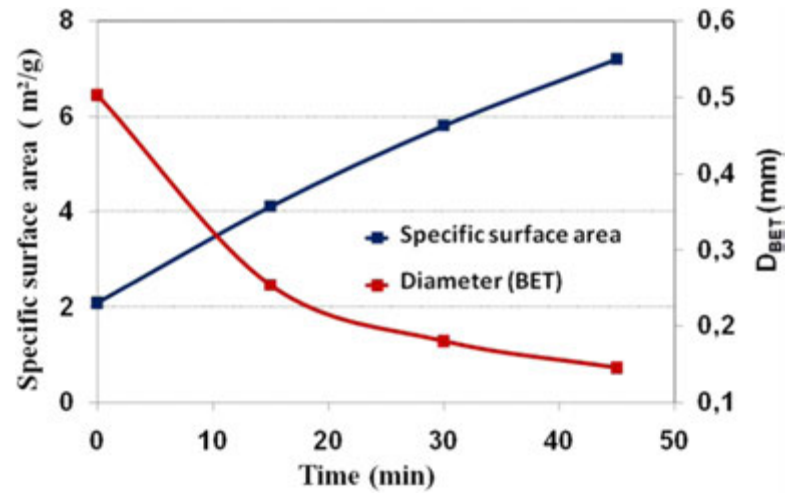


Fig. 31 BET specific surface area and calcined powders diameter as a function of regrind time.

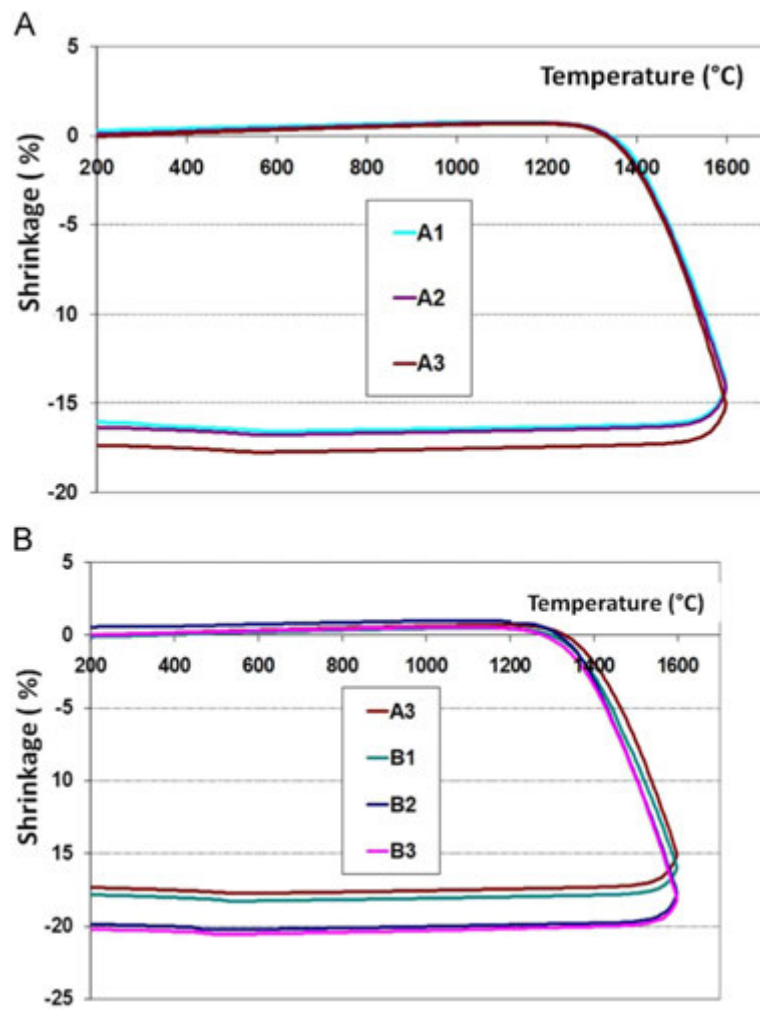


Fig. 32 Dilatometric shrinkage curves from calcined powders of series A and B.

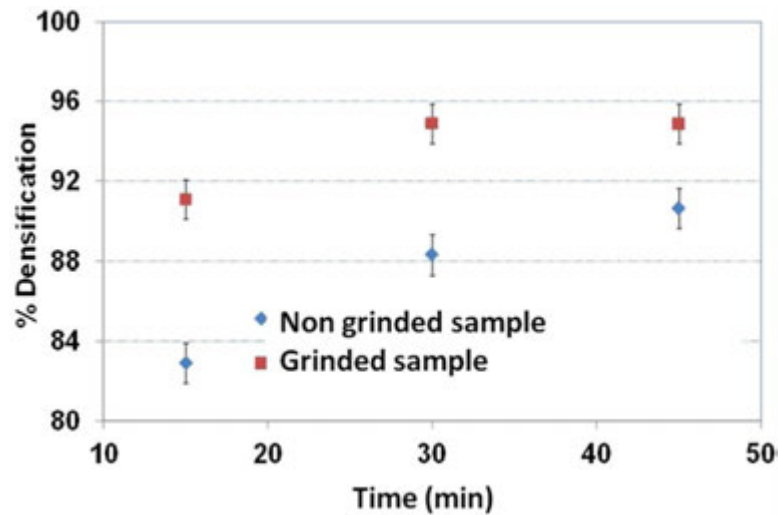


Fig. 33 Effects of (re)grinding times on the densification rate.

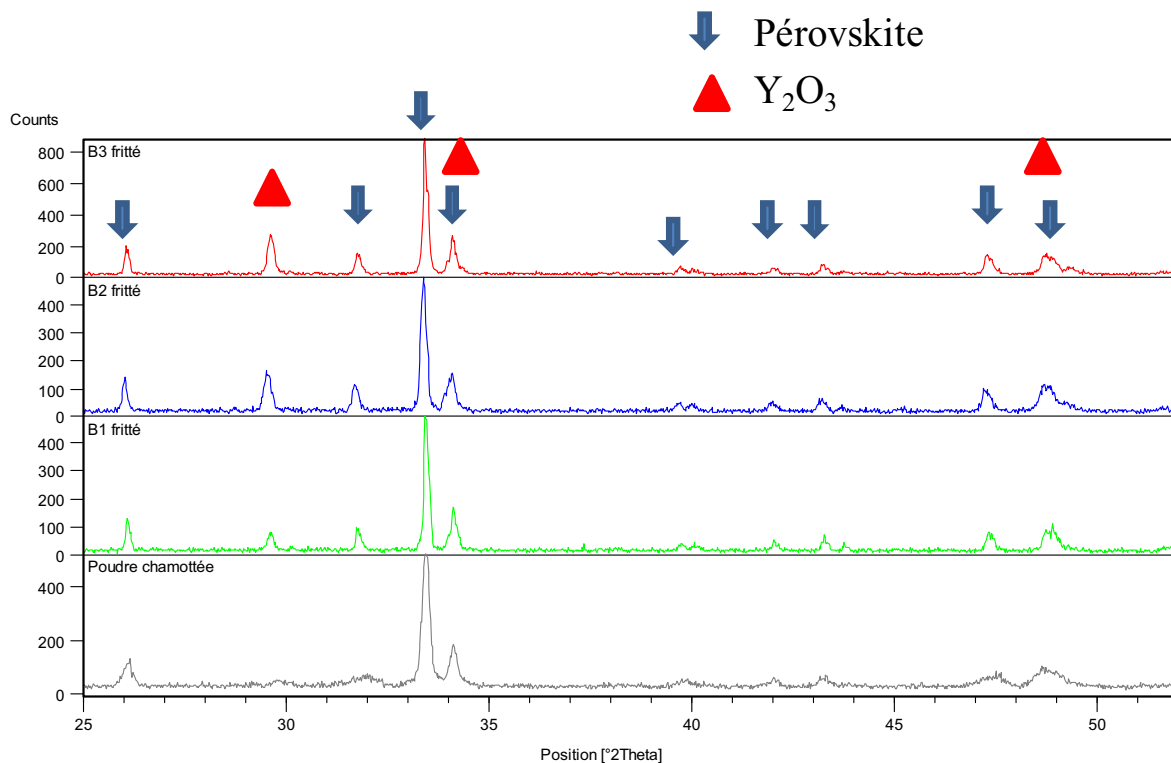


Fig. 34 Diffractograms of sintered ceramics compared to calcined powder.

Characterization of ceramics made from reground calcined powders

The diffractograms of the sintered ceramics are collected in **Fig. 34**. Two phases are present: the expected perovskite phase $Y(Cr,Mn)O_3$ which is a solid solution where Mn is substituted for Cr and which remains isomorphic to the $YCrO_3$ phase listed in JCPDF 0034-00365 and a secondary phase identified as an yttrium oxide Y_2O_3 phase. (Tachiwaki *et al.*, 2001) also observed this second phase by synthesizing $YCr_{1-x}Mg_xO_3$. In the synthesis of $Y_{0.8}Sr_{0.2}MnO_3$ and $Y_{0.9}Sr_{0.1}MnO_3$ (Agüero *et al.*, 2002) yttrium oxide is also encountered as a secondary phase. This secondary phase could be stabilized by the ZrO_2 pollution resulting from the wear of the balls. The SEM microstructures (**Fig. 35**) confirm the densification levels. EDS shows also that gray zones can be attributed to perovskites, whereas small light gray spots are richer in yttrium and would correspond to yttrium oxide, in accordance with XRD data.

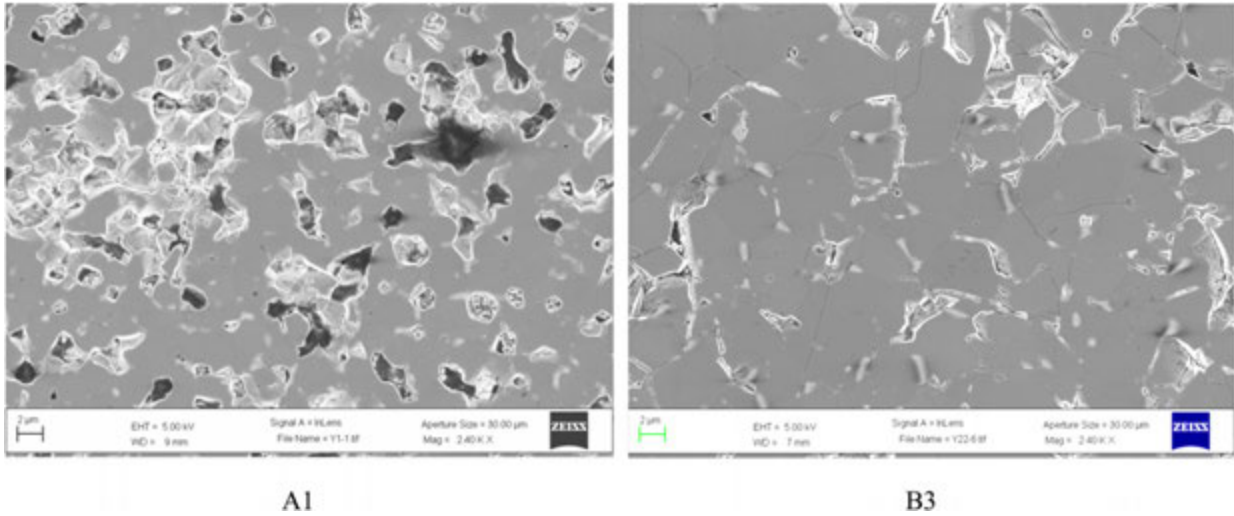


Fig. 35 SEM micrographs of ceramics made from unground (A1) and 45 min reground (B3) calcined powders.

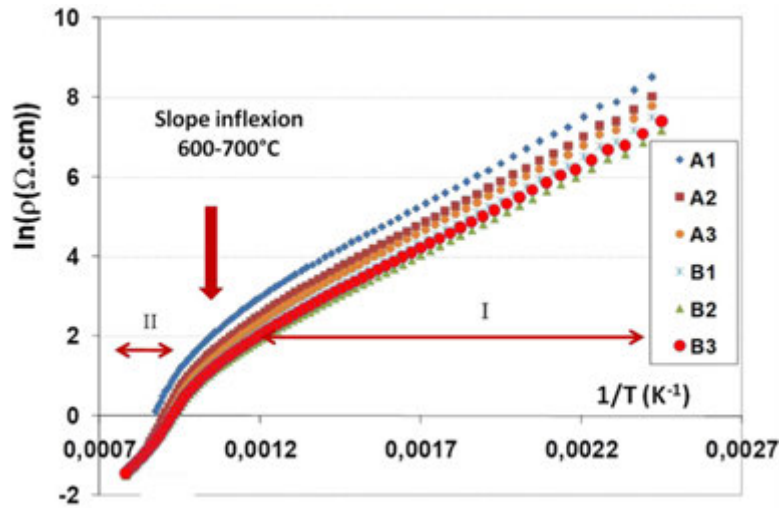


Fig. 36 Representations $\ln(\rho) = f(1/T)$ from 25 to 1000°C.

Materials for temperature sensors are mainly characterized by two electrical parameters: the resistivity (ρ) at 25°C and the energy constant (or “B” parameter) which is minus the slope of the linearization $\ln \rho = f(1/T)$. The Fig. 36 shows the variation of $\ln \rho$ as a function of $1/T$ up to 1000°C. As expected, a decrease in resistivity is observed with increasing temperature.

However, $\ln \rho$ is not linear with the inverse of temperature over the entire temperature range: an inflection in the 600–700°C zone is observed leading to identify two linear domains (noted I and II, respectively) which must represent two conduction phenomena activated in different temperature ranges. In their work on substituted YCrO_3 and LaCrO_3 , (Weber *et al.*, 1987) pointed out that the linear dependence of $\ln(\sigma T) = f(1/T)$ is characteristic of a small polaron transport mechanism between cations of the same element on the same crystallographic site, but of different valence (or hopping). In the study of electrical properties of $\text{La}_{1-x}\text{Ca}_x\text{Cr}_{1-y}\text{Ca}_y\text{O}_3$ between 400 and 1100°C, (Sakai *et al.*, 1990) found a similar dependence and claimed that this type of conduction is often a characteristic of chromium-based perovskites. With regard to the effect of grinding on resistivity, a decrease in resistivity appears as a function of grinding time with resistivity values of the same order of magnitude ($10^4 \Omega \text{ cm}$).

The energy constant of the material (B) is calculated for both temperature ranges. In range I, the constant B was evaluated between 25 and 100°C. B varies between 3600 and 3850K. It can also be seen that the energy constant decreases as the grinding time of the initial mixture increases. In range II, B was evaluated between 700 and 800°C. B values are higher reaching around 10,000K. These two decreases in resistivity and parameter B with grinding time have to be correlated on the one hand with the densification increase and with the ball contamination increase leading to the appearance of the secondary phase Y_2O_3 .

Summary

This chapter presents the main theoretical considerations concerning dispersion of mineral powders in slurries and some examples showing the strong impact of the mixing and grinding steps on the properties of ceramics for electronic: dielectric compositions for capacitors and NTC ceramics.

The importance of a perfect dispersion of the powder before grinding is highlighted in order to eliminate flocculates and agglomerates. It makes it possible to obtain sufficiently fluid slurry to undertake the grinding step with good efficiency. Rheology has proven to be an extremely effective tool for controlling slurry. Then, during the grinding process, care must also be considered to keep constant slurry dispersion conditions (by controlling viscosity and adjusting pH and/or adding dispersant) in order to maintain good grinding efficiency. By this way, reagglomeration can be avoided when shear stresses decrease, for instance at the exit of the continuous mill or when the mill is stopped or simply to avoid strong agglomeration during grinding (settling). It is then possible to obtain very homogeneous powder mixtures with fine grains (down to nanometric size) which will be more reactive and will lead to the formation of pure phase generally difficult to get by another way. These optimized powder mixtures will have a better sinterability and will develop highly controlled microstructures, particularly in the context of subsequent rapid sintering (flash, SPS or microwave sintering). The prospects of this approach considering the control of the dispersion conditions combined with grinding with high energy mills are limitless as it is applicable to all ceramic compositions. In fact, too many research works are still using recipe that is difficult to transpose to the industrial environment where powders are mixed for extremely long periods of time.

References

- Agüero, O., Leyva, A.G., König, P., *et al.*, 2002. $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ manganites: Synthesis and ESR characterisation. *Physica B* 320, 47–50.
- Bernard, J., Belnou, F., Houivet, D., Haussonne, J.-M., 2008. Synthesis of pure MgTiO_3 by optimizing mixing/grinding condition of $\text{MgO} + \text{TiO}_2$ powders. *Journal of Materials Processing Technology* 199, 150–155.
- Brongniart, A., 1844. *Traité des arts céramiques ou des poteries*. Paris: Béchét Jeune, Matthias Augustin.
- Dinger, D.R., 2002. *Rheology for Ceramists*. Dinger Ceramic Consulting Services.
- Funk, J.E., Dinger, D.R., 1994. *Predictive Process Control of Crowded Particulate Suspensions: Applied to Ceramic Manufacturing*. Kluwer Academic Publishers.
- Haussonne, M., 1954. *Technologie céramique générale*. Paris: JB Baillière et fils éditeurs.
- Haussonne, J., Carry, C., Bowen, P., Barton, J., 2005. *Céramiques et verres principe et techniques d'élaboration* (Vol. *Traité des matériaux* 16). (PPUR, Ed.).
- He, M., Wang, Y., Forssberg, E., 2004. Slurry rheology in wet ultrafine grinding of industrial minerals: A review. *Powder Technology* 147, 94–112.
- Houivet, D., Haussonne, J., 2003. Dispersion and ultra-fine grinding of oxide powders in an aqueous slurry with a controlled viscosity. *Ceramic Transactions* 150, 89–105.
- Jouenne, C., 1980. *Traité de Céramiques et Matériaux Minéraux*. Paris: Septima.
- Nachbaur, V., Tauvel, G., Verdier, T., *et al.*, 2009. Mecanosynthesis of partially inverted zinc ferrite. *Journal Alloys Compound* 473, 303–307.
- Parfitt, G., 1981. *Dispersion of Powders in Liquid with Special Reference to Pigments*. London: Applied Science Publishers.
- Pederson, H.G., Bergström, L., 1999. Forces measured between zirconia surfaces in poly (acrylic acid) solutions. *Journal American Ceramic Society* 82 (4), 1–9.
- Rumpf, H., 1962. The strength of granules and agglomerates. In: Knepper, W.A. (Ed.), *Agglomeration*. New York: John Wiley Interscience.
- Sakai, N., Kawada, T., Yokokama, H., Dokita, M., Iwata, T., 1990. Sintering and electrical conductivity of calcium-doped lanthanum chromites. *Journals of Materials Science* 25 (10), 4531–4534.
- Suryanarayana, C., 2001. Mechanical alloying and milling. *Progress in Materials Science* 46, 1–184.
- Tachiwaki, T., Kunitusa, Y., Yoshinaka, M., Hirota, K., Yamaguchi, O., 2001. Formation, densification, and electrical conductivity of air-sinterable $\text{YCr}_{1-x}\text{Mg}_x\text{O}_3$ prepared by hydrazine method. *Materials Science and Engineering B* 86, 255–259.
- Vallar, S., Houivet, D., El Fallah, J., Haussonne, J., 1999. Oxide slurry stability and powders dispersion: Optimization with zeta potential and rheological measurements. *Journal of the European Ceramic Society* 19, 1017–1021.
- Weber, W., Griffin, C., Bates, J.L., 1987. The effects of cation substitution on electrical and thermal transport of properties of YCrO_3 and LaCrO_3 . *Journal of the American Ceramic Society* 70, 265–270.

Powder Granulation and Compaction

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Ceramic components are manufactured starting from inorganic raw materials in powder form. Ceramic powders are typically granulated to improve powder handling and processability, especially when dry or semi-dry powder pressing (i.e., < 8 wt% water) is performed (Lukasiewicz and Reed 1978; Reed, 1995; Ewsuk, 2001; Oberacker 2012). Dry pressing is the preferred technology for high-volume manufacturing of relatively simple geometry powder compacts, because economical and versatile. The aim is to turn loose powders into a green compact with desired shape and maximum bulk density. In addition, minimal density gradients and close geometrical tolerances are required to green compacts. The shaping pressure (usually between 15 and 200 MPa) should be high enough to produce a homogeneous green compact with enough strength for subsequent handling/debinding/sintering, but low enough to avoid excessive wear on the press and die).

Powder Granulation

Free flowing powders are used in dry pressing to uniformly fill the die, and to form a compact with homogeneous microstructure and suitable strength. Since the particles of ceramic bodies exhibit poor flow and compaction behavior in their raw form, they must be granulated. Granulation is the process of intentionally agglomerating fine particles into larger particle clusters that exhibit improved handling and flow characteristics (Ewsuk, 2001). Spray drying typically produces subspherical granules with diameter in the 100–800 μm range and mode of 100–300 μm , starting with 0.5–10 μm median particle size powders (Lukasiewicz, 1989; Soldati *et al.*, 2018a).

Granulation

Granulated powder for pressing is generally produced by either spray granulation or spray drying (Lukasiewicz, 1989; Reed, 1995; Raghupathy and Binner, 2011; Oberacker, 2012; Vicent *et al.*, 2012). Spray granulation can be performed by different techniques (Fig. 1). Both processes tend to form equiaxial granules. Relative to spray drying, spray granulation generally produces a granule morphology having a more irregular shape, and granules of higher density. Spray drying produces spherical granules with internal cavity in case of deflocculated slurry (Walker and Reed, 1999).

Spray drying is the most common technology of granulating ceramic powders for dry pressing. It involves pumping slurry to an atomizer, where small spherical droplets are sprayed into a large chamber. Heated air flowing in the chamber dries the droplets to form granules that are collected at the base of the drier (Lukasiewicz, 1989; Bertrand *et al.*, 2005). Different layouts of spray driers can be used, according to productivity, slurry characteristics, and agglomerate size.

Spray granulation consists in spraying water on powders and promote agglomeration in rounded shapes by tumbling. Excess of water can be successively removed by partial drying (e.g., in fluid bed drier). A seed is progressively enveloped in several layers of primary particles. Techniques employed in ceramic production include: vertical axis turbine, intensive mixer, press agglomeration, and sinusoidal granulator (Fig. 1).

Another alternative to spray drying is freeze granulation, which consists in rapid freeze of slurry droplets in liquid nitrogen before being recovered and subsequently freeze-dried (Vicent *et al.*, 2012).

Characteristics of Granules

The main properties of granules are: agglomerate size and shape distribution, distribution of moisture or additives as a function of size, powder rheology, and mechanical properties (yield strength). A range of rheological properties of powders are usually determined (Santomaso *et al.*, 2003; Geldart *et al.*, 2006; Nebelung and Lung, 2009; Soldati *et al.*, 2018a) by methods resumed in Fig. 2.

The characteristics of spray-dried granules are largely influenced by the physical properties of the slurry that is sprayed into the heated chamber (Lukasiewicz, 1989; Walker *et al.*, 2000) and by processing parameters (temperature, slurry pressure, number, and type of nozzles, etc.). Properties can be controlled to get spherical granules that can pack more efficiently, and lower density granules with lower strength that can deform more readily during pressing. Flocculated and deflocculated slurries produce agglomerates, respectively, without or with an internal cavity (Walker and Reed, 1999; Bertrand *et al.*, 2005).

To ensure good packing density, free-flowing granulated powders are required to ensure packing uniformity, and reproducibility in die filling. Ideally, powders with satisfactory fluency are subspherical or equiaxial, and have a size distribution between 200 and 600 μm . However, the granule size distribution is not crucial for powder fluency, unless the orifice light is less than approximately 10 times the granule diameter.

Typically, powder flow rate is determined as the time it takes a given mass of powder to flow through a certain funnel. Powder flow also can be assessed by the angle of repose that a loose powder makes when poured onto a flat surface (static) or the average angle during powder tumbling in a rotating cylinder (dynamic). Granulated ceramic powders with good flow generally have a static angle of repose of 35° or less and a dynamic angle of repose between 40° and 45° (Geldart *et al.*, 2006; Soldati *et al.*, 2018a).

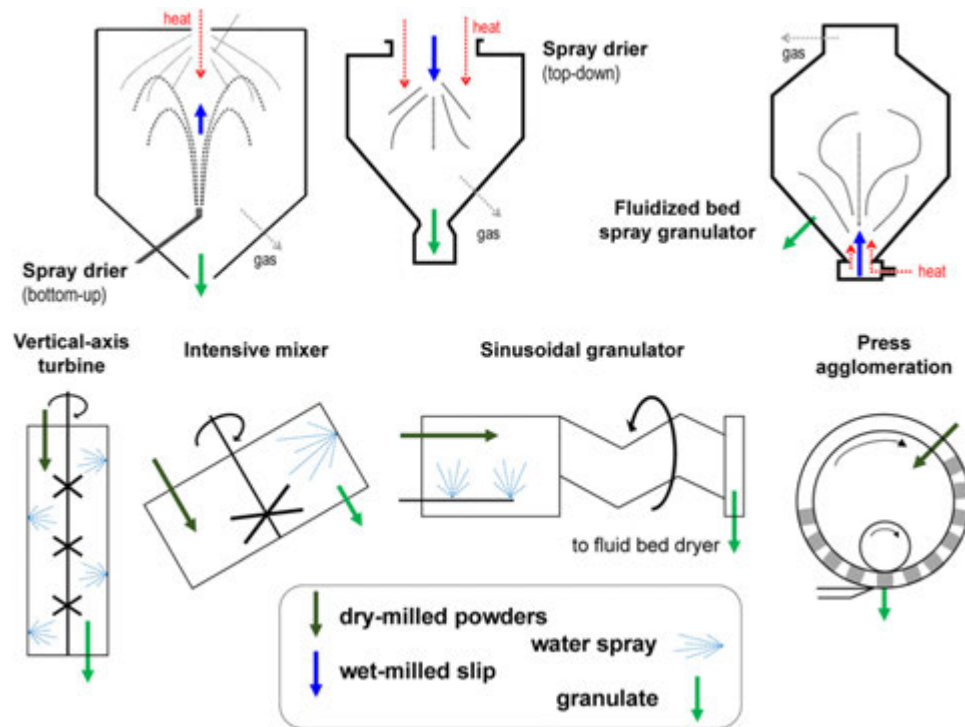


Fig. 1 Granulation techniques used to produce agglomerated ceramic powders.

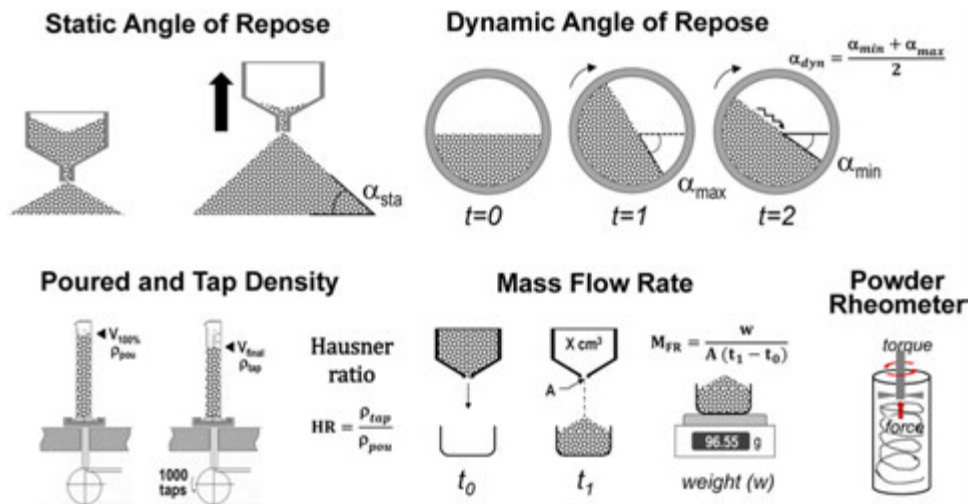


Fig. 2 Methods used to determine the rheological properties of ceramic granulates.

Poured density is a measure of the weight-to-volume ratio of a loose powder filling a given container. Tap density is the same weight-to-volume ratio after tapping with a prescribed procedure. The Hausner ratio, i.e., the ratio of the tap to the poured density, is also a measure of flow commonly used in ceramic manufacturing. Better powder flow and die fill reproducibility are achieved with a Hausner ratio below 1.2 (Santomaso *et al.*, 2003; Soldati *et al.*, 2018a).

Organic Additives

Organic additives are commonly added to a ceramic powder as processing aids. Addition can be done immediately prior to, during, or immediately following granulation. Table 1 lists some typical organic additives used in ceramic powder pressing including binders, plasticizers, and lubricants (Reed, 1995; Ewsuk, 2001).

Table 1 Organic additives commonly used in ceramic powder granulation and compaction

<i>Binders</i>	<i>Plasticizers</i>	<i>Lubricants</i>
Acrylic resins	Ethylene glycol	Aluminum stearate
Acrylic ± wax emulsions	Glycerol	Magnesium stearate
Methyl cellulose	Polyethylene glycol	Oleic acid
Polyvinyl alcohol (PVA)	Triethylene glycol	Paraffin wax
Polyethylene glycol (PEG)	Water	Stearic acid
Waxes and wax emulsions		

Note: Ewsuk, K.G., 2001. Powder granulation and compaction. In: Buschow, K.H.J., Cahn, R.W., Flemings, M.C. (Eds.), *Encyclopedia of Materials: Science and Technology*. Elsevier Science Ltd. pp. 7788–7800.

Organic binders, e.g., polyvinyl alcohol, are utilized to enhance processability and to provide strength to the pressed powder compact for subsequent handling and/or machining (Lukasiewicz, 1989; Reed, 1995). The organic binders form bridges between the particles in a granule in order to improve its strength and deformation under pressure (Ewsuk, 2001; Carneim and Messing, 2001).

Plasticizers are organic molecules that can modify the structure built by binders, systematically disrupting bridges and making them more flexible by lowering their glass transition temperature (Balasubramanian *et al.*, 2002a). Combination of plasticizers with binders allows to produce granules with improved compaction through a more deformable behavior.

Lubricants are low molecular weight organic molecules that lower interfacial frictional forces between individual particles, and between particles and die surfaces. Once added to powders, they are able to mitigate friction effects during processing, thus improving powder compaction, and to reduce the pressure required for compact ejection (Balasubramanian *et al.*, 2002b). Also, solid lubricants can be utilized, as graphite (Ravindran *et al.*, 2013).

Compaction Techniques

Granulated ceramic powders are compacted by either isostatic or uniaxial pressing or by calendaring. Mechanical, hydraulic, or direct electrically driven presses are used in ceramic manufacturing.

Typical capacity of eccentric mechanical presses is in the 0.1–8 MN range, while cam-driven mechanical presses have capacity of about 1 MN. Standard hydraulic presses exhibit a wider power range, between 0.1 and 160 MN. The direct electrically driven press may reach pressures up to 0.2 MN. Mechanical presses have production rates generally faster than those of hydraulic presses, since their maximum stroke rates are about $\sim 100 \text{ min}^{-1}$ and 10 min^{-1} , respectively (Beiss, 2010; Oberacker, 2012).

Hydraulic systems are generally best suited to producing large and/or thick compacts. Their maximum depth of powder fill is greater than in a standard mechanical press. Computer-controlled servo hydraulics allow very precise punch movements and to accurately control the pressing sequence of multiple punch tooling systems. Several closed-loop controlled axes are provided to activate the powder filling system and compaction units (rams, core rods, auxiliary platens, etc.). By this way, special parts with cross holes and undercuts, which cannot be made with conventional dies, can be produced (Oberacker, 2012).

Isostatic pressing can be used to produce small to relatively large powder compacts with good bulk density and uniformity for sintering. However, it is limited to relatively simple shapes and green machining is generally required, because of poor dimensional control, to achieve the desired size and shape of compacts. Uniaxial pressing ensures higher production rates and very large sizes, and in some cases complex parts can be formed to near-net-shape. A sort of calendaring has been recently introduced to produce large slabs (up to 10 m^2).

Isostatic Pressing

Cold isostatic pressing consists in compacting a dry or semi-dry powder in an elastomeric mold submersed in a pressurized liquid (Reed, 1995; Oberacker, 2012). Rigid tooling (e.g., a steel mandrel) is often combined with the flexible elastomeric mold to ease shaping. Typical forming pressures for ceramics are in the 20–200 MPa range. Isostatic pressing can be performed in two ways: “wet bag” and “dry bag” (Ewsuk, 2001; Oberacker, 2012). The wet bag route entails compacting a powder in a sealed elastomeric mold that is completely submersed in pressurized fluid (Fig. 3).

This route is used for low-volume production of specialty parts, for prototyping, and for research and development. The elastomeric mold is an integral part of the isostatic press in the dry bag route. Thus, the applied pressure is mostly biaxial. A major advantage of dry bag isostatic pressing is that it can be automated for high-volume production (Oberacker, 2012).

Uniaxial Pressing

Uniaxial die pressing consists in compacting powder to a prescribed size and shape within a rigid die cavity using one or more rigid plungers (Reed, 1995; Oberacker, 2012). Alternatively, dieless pressing can be performed on powders on a tape between two large

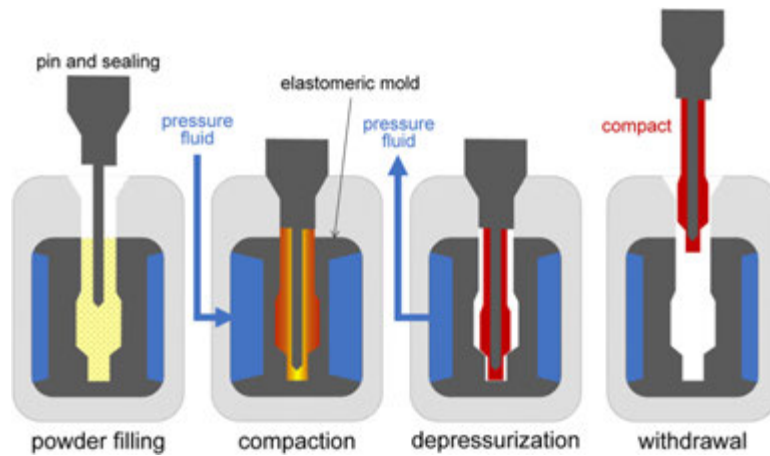


Fig. 3 Isostatic pressing: operational sequence in the wet bag route for spark plug insulators. Redrawn after Oberacker, R., 2012. Powder compaction by dry pressing. In: Riedel, R., Chen, I.-W. (Eds.), *Ceramics Science and Technology: Synthesis and Processing*, vol. 3. Wiley-VCH Verlag GmbH & Co., pp. 3–36.

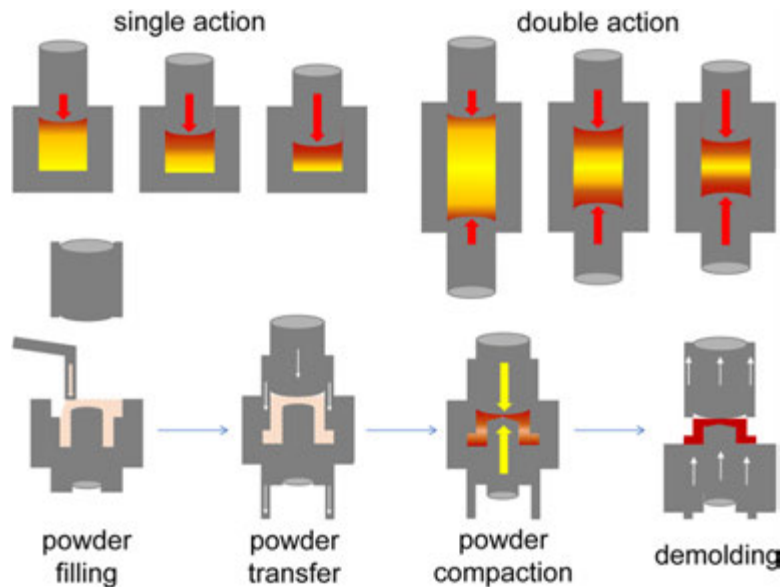


Fig. 4 Uniaxial pressing: single versus double action, and operational sequence. Redrawn after Oberacker, R., 2012. Powder compaction by dry pressing. In: Riedel, R., Chen, I.-W. (Eds.), *Ceramics Science and Technology: Synthesis and Processing*, vol. 3. Wiley-VCH Verlag GmbH & Co., pp. 3–36.

plungers. The tape is flexible and can be metallic or a polymeric composite. The dies and plungers used in uniaxial pressing are typically made of rigid materials that are hard and have good wear resistance. They can be coated with hard rubber to get a given texture. Typical production rates for die pressing, using pressures of 15–140 MPa, range from 1 to 300 parts per minute for advanced ceramic component and 7–12 m² per minute for ceramic tiles.

Die pressing can be accomplished with a single-action, dual-action, or floating die press (Fig. 4). A single-action anvil press has one moving punch, while a dual-action press has two or more moving punches. In the floating die press, most used in ceramic manufacturing, punches and die body can move independently. This allows to fabricate large pieces or more complex parts, including tapers, holes, and multiple steps. At the same time, it provides the flexibility to balance the forming pressure within different areas of the compact; thus, to minimize density gradients, in the pressed compact (Ewsuk, 2001; Oberacker, 2012).

Calendering

Calendering entails compacting a powder between two flexible tapes that pass through two rotating drums (compactors). It allows manufacturing of large slabs in a continuous way and with a high production rate. Tapes are typically metallic and provide a

smooth surface, but also structured tapes can be employed to get textured surfaces. Powder is laid on the lower tape and pressure is controlled by regulating tensor drums that impose the angle between the two tapes. Thickness is fixed by the light between compactor drums, while bulk density must be adjusted by the thickness of powder feed (soft layer). Actual size is determined after compaction by cutting the continuous sheet coming out from drums.

The Powder Pressing Process

A typical powder pressing operation has three basic steps: (1) filling the die with powder (or laying powder on the tape); (2) compacting the powder to a given pressure (or thickness in case of calendering); and (3) ejecting the powder compact from the die/drums.

Die Filling

The bulk density and packing uniformity of a granulate powder within a die (or on a tape) both influence the characteristics achieved after compaction and, eventually, the bulk density, microstructure, and properties of the final product after sintering (Reed, 1995; Glass *et al.*, 1995; Lannutti, 1997). The packing efficiency and uniformity achieved during die/tape filling are affected by the size distribution, fluency, and bulk density of granules as well as by the geometry/size of the die (Dinger and Funk, 1997). In general, narrow granule size distributions and/or small dimension of die cavities determine a lower packing density. Increasing aspect ratio (i.e., height/diameter) in small dies makes the variability in packing density to increase.

The die is usually filled by a volume-controlled feed shoe system. It consists of a bottomless box that slits over the open die and then is pulled back into a resting position. The powder, fed by a hopper, falls under gravity into the feed shoe. The tool movements can be controlled, in case of complex or thin-walled parts, to realize overfilling, suction filling, or contour filling, in order to optimize the uniformity in density distribution of the compacts. In fact, the packing density is reduced over a distance of 10–50 particle diameters from the die walls (Oberacker, 2012).

Granulates assume a hierarchical packing structure by filling the die (or laying on the tape). Porosity in this packing structure can be present at two levels (inside single granules or between granules) giving rise to four types of void (Oberacker, 2012; Soldati *et al.*, 2018b): (P1) the intragranular micro-porosity between the primary particles constituting the agglomerate; (P2) the cavity or large macro-pores inside the agglomerate; (P3) the intergranular voids between the granules; and finally larger packing flaws (Fig. 5).

Die wall effects can be minimized or eliminated if the die is sufficiently larger than the granule size. In general, smaller size granules should be used to fabricate parts of smaller dimension. For a typical, spray-dried alumina powder, the average agglomerate size should be smaller than the compact thickness and diameter, respectively, by 250-fold and 40-fold (Ewsuk, 2001).

The bulk density of a powder within the die is known as the fill density. It is usually in the range of 25%–40% of the true density of the granulated ceramic powder, considering only the inorganic constituents. Ideally, to avoid pressing defects, high fill densities are desirable to keep the compaction ratio (i.e., the pressed compact density divided by the fill density) below 2 in advanced ceramics, or below 2.5 in clay-based bodies.

Powder Compaction

During powder compaction, granule rearrangement, deformation, and consolidation of the particulate assembly are promoted by the applied pressure. This process induces an increase of particle coordination number, green bulk density, and compact strength with increasing compaction pressure (Frey and Halloran, 1984; Zheng and Reed, 1988). Overall, higher values of green density are

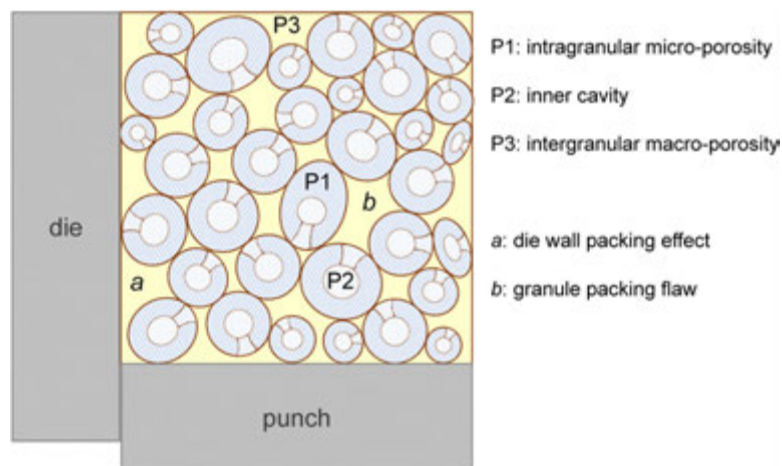


Fig. 5 Scheme of die filling with granulate: different kinds of porosity.

obtained with a higher fill density (hence a better powder fluency). This compact will sinter to a higher end point density with a lower shrinkage (Glass *et al.*, 1995; Ewsuk, 2001).

Although common in pressed powder compacts, density gradients must be minimized, because they contribute to differential sintering and shape distortion (Glass and Ewsuk, 1997; Oberacker, 2012) leading eventually to defects that limit the performance and reliability of the finished product. Density gradients occur at two scales that are important in powder compaction: (1) large-scale gradients, consequent to nonuniform die filling and/or applied load during powder compaction (Reed, 1995; Lannutti, 1997); and (2) small-scale density variations due to flaws in powder, hollow granules, and/or insufficient deformation during compaction (Shinohara *et al.*, 1999). To prevent such defects, granules should be strong enough to pack more efficiently (permitting a significant rearrangement prior to deformation/fracture) but weak enough to produce a uniform microstructure (breaking down, deforming, and knitting together during compaction) (Glass *et al.*, 1995; Oberacker, 2012). Powder compacts are comprised of discrete particles, and the stress is transmitted non uniformly through particle–particle contacts. Account must be taken of the stress network, where granule/particle bridges may support stresses higher than the applied stress, and that shield localized regions between the bridges from the applied stress (Glass and Ewsuk, 1997; Ewsuk, 2001).

Die wall friction must be controlled during pressing to minimize pressure gradients that can create defects (density gradients and/or cracks in a powder compact). Friction can be controlled through the design of the die and the pressing process or by internal or external lubricants (Balasubramanian *et al.*, 2002b). Die wall friction can be minimized with smooth surface dies and carbide tooling. Frictional effects are also minimized in simple shape, low aspect ratio parts, and by dual-action pressing in preference to single-action pressing. Deleterious die wall frictional effects also can be minimized by isostatic or biaxial pressing in preference to uniaxial die pressing (Reed, 1995; Oberacker, 2012).

Compaction Mechanisms

Several factors play an important role in determining compaction behavior: pressing conditions, granule characteristics, hierarchical packing structure, and discrete particle–die and particle–particle interactions. Pressure–density plots allow relating the compaction behavior to processing parameters and powder features (Fig. 6). Such compaction response diagrams show how the bulk density of a compact changes as a function of the applied load. Three compaction regimes are usually identified, as stages of nominally linear response when data are plotted on a log–pressure scale (Glass and Ewsuk, 1997; Carneim and Green, 2001; Oberacker, 2012):

Stage I, bulk density slightly increases from the value of poured density to a random packing density, corresponding to the first breakpoint.

Stage II, bulk density rapidly increases by progressive downsizing of intergranular macro-pores up to the second breakpoint.

Stage III, bulk density increases by a slower rate, as intergranular pores are sealed off and any further densification proceeds by closure of the larger intragranular micro-pores.

Compaction response diagrams provide general information on compaction and specific information on granule stiffness and deformability. Compaction is interpreted to occur primarily by rearrangement in mutual position of granules in the stage I, and mostly by granule deformation, cracking and knitting in the stages II and III (Reed, 1995; Carneim and Green, 2001; Carneim and Messing, 2001; Oberacker, 2012). First the large pores are eliminated (intergranular porosity P3 and inner cavity P2) during stage II, then smaller pores (compressible fraction of intragranular porosity P1) are closed during stage III. Various factors control the extent of densification due to each mechanism, such as localized pressure, and characteristics of granules and primary particles. Typically, granulated ceramic powders are compacted to a point corresponding to the beginning of stage III (Niesz, 1996).

Granule Characteristics and Compaction

Ideally, granules should deform and fracture during compaction to eliminate the intergranular porosity (present in the die fill) and subsequently knit together, resulting in a homogeneous microstructure with no remnants of the original granule structure. In

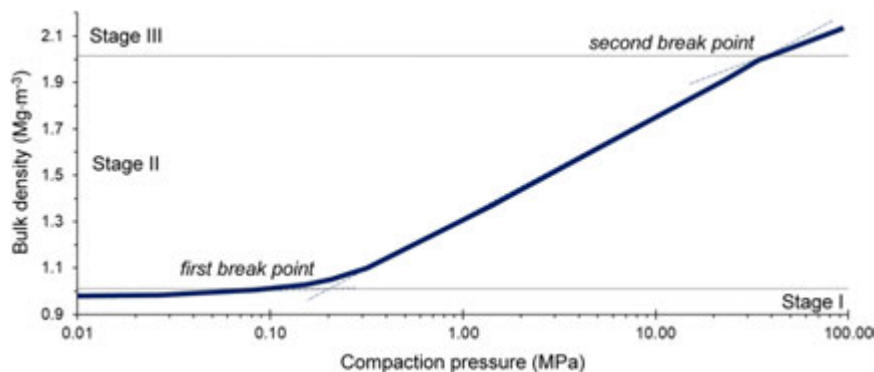


Fig. 6 Compaction response diagram showing a typical bulk density to applied pressure evolution for a spray-dried powder (porcelain stoneware). Three compressional stages are outlined (see text for details) separated by two break points.

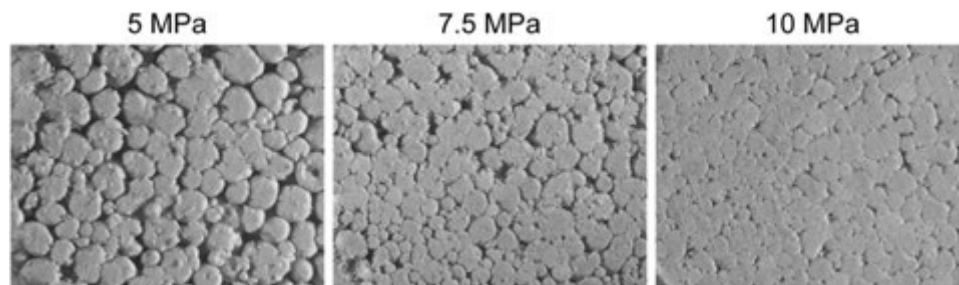


Fig. 7 Example of rearrangement, deformation, breakdown and knitting of spray-dried granules at increasing applied pressure. Powders for porcelain stoneware tile production.

particular, the granule yield strength, referred to the first break point, is related to fracture strength (Carneim and Green, 2001; Oberacker, 2012). Stiffer granules have a higher yield strength and can undergo a more extensive rearrangement at low compaction pressures to increase packing efficiency and density uniformity prior to granule deformation/fracture. However, if too stiff, the granules will not completely deform to eliminate large inter-granular porosity after compaction. Excessively hard granules can result in defects, such as a lower compact density after pressing, or large residual pores, or even a too rough surface finish. On the other hand, soft granules can produce a higher density compact by readily deforming during pressing. Nevertheless, if too soft, they will not rearrange enough in stage I to eliminate packing defects present after die filling. Compacting soft granules with strong packing heterogeneities, stemming from poor die filling, can give rise to severe density gradients after pressing, and cracking after sintering.

Granule stiffness is controlled by many factors, including the organic additives used for granulation, moisture content, and granule size (Lannutti, 1997; Shinohara *et al.*, 1999; Walker *et al.*, 2000; Uppalapati and Green, 2006). In general, weaker granules are produced with softer organic binders having a lower glass transition temperature, T_g . To make weaker granules, plasticizers can be used to lower the T_g of a binder system; moisture can act as a plasticizer as well (Shinohara *et al.*, 1999; Lannutti, 1997; Carneim and Messing, 2001).

Along with general information on compaction, bulk density to applied pressure diagrams provide specific information on granule stiffness and deformability. However, they need to be complemented with other techniques to complete a comprehensive assessment of compaction. For instance, pressed and fracture surfaces of green compacts, formed at increasing load, can be observed to characterize microstructural evolution during powder compaction (Niesz, 1996; Soldati *et al.*, 2018b). In particular, granule deformation and breakdown can be followed while large intergranular packing voids are downsized to produce a homogeneous microstructure (Fig. 7). Pressed surfaces formed at low pressures clearly exhibit the granule structure, intergranular packing voids, and some degree of granule deformation to eliminate those voids. With increasing pressure, granules knit together and the compact strength increases, as the fracture mode changes from intergranular to intra-granular. At higher pressure, compacts show fewer and fewer granule relics and microstructure becomes more homogeneous.

Ejection

In general, a pressed powder compact must be strong enough to withstand the forces exerted on it during ejection from the die. Main issues with ejection are green compact strength, die wall friction, and elastic springback. Ejection defects can be ideally avoided with a combination of a high green compact strength and a low ejection pressure. Internal lubricants and die wall lubricants are often used to lower the ejection pressure (Balasubramanian *et al.*, 2002b).

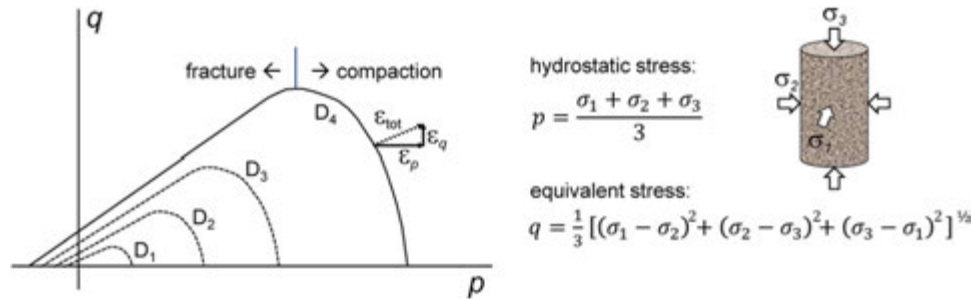
A critical factor in ejection is springback, i.e., the expansion of the compact upon ejection from the die. It is determined by the elastic energy stored in the compact during the compression. Springback can be as much as 0.5% up to 1%, with greater expansion occurring with higher pressures. In uniaxial compaction, in particular, a differential springback usually occurs, since the axial expansion is greater than the radial. Although some springback is needed to separate the compact from the die without sticking, excessive expansion can lead to catastrophic flaws within the compact (Reed, 1995; Ewsuk, 2001). In addition, a too high differential springback (i.e., perpendicular vs. parallel to the pressing direction) is also problematic, especially in case of high pressures and trapped gasses within the powder compact. Problems can be minimized by recourse to appropriate organic binders to get good green strength at low pressure, and by taking care that air can escape from the compact during pressing. Defects due to differential springback can be avoided by ejecting the compact under “punch hold-down”, which maintains axial pressure on the compact during ejection (Ewsuk, 2001).

Compaction Defects

Many of the defects observed in powder compacts are defects that manifest upon ejection. They originate from inadequate values of powder properties or processing conditions (Ewsuk, 2001; Balasubramanian *et al.*, 2002a,b) as summarized in Table 2.

Table 2 Typical defects in ceramic powder pressing: nature and causes

Defect	Description	Poor green strength	High springback	High die-wall friction	High specific pressure	Poor punch-die tolerance	High compaction ratio	High stroke rate
End-capping	Cone-shaped separation at the pressing punch face and into the compact	X	X	X	X			
Ring-capping	Ring separation at the outer edge of the punch face and out of the compact		X			X		
Lamination	Periodic circumferential cracks perpendicular to the pressing direction	X	X	X	X			
Vertical cracks	Elongated cracks parallel to the pressing direction	X	X				X	X

**Fig. 8** Yield surfaces for increasing density (D) on the stress plane (p - q) and expression of stresses.

Compaction Modeling

Numerical modeling provides powerful and promising tools to better understand and control, once experimentally validated, powder packing and compaction, so improving the earlier analytical micromechanical models (Brewin *et al.*, 2007; Sinka, 2007). These tools are distinguished as either: *phenomenological models*, aimed to simulate the pressing of real parts by finite element methods (FEM), which are based on continuum soil mechanics, or *micromechanical models*, which calculate the interactions between powder particles to derive the bulk powder properties; two approaches can be followed (Harthong *et al.*, 2009): discrete element method (DEM) and meshed DEM (MDEM). However, a combination of these different methods is needed for an effective modeling. Ideally, MDEM should be used to derive force–displacement laws for DEM, whilst DEM simulations should be exploited to get suitable constitutive equations, by which FEM calculations should simulate the compaction of a real compact (Oberacker, 2012).

In the phenomenological models, a constitutive model can be combined with numerical modeling by FEM to get realistic predictions of the density gradients in a powder compact after pressing. The most often-used model in FE simulations is the Drucker–Prager Cap model (Sinka and Cocks, 2007; Pizette *et al.*, 2010) by which the material response is expressed in terms of stress and strain invariants (e.g., hydrostatic pressure, p , and equivalent stress, q) that amount to a yield surface on the p - q plane (Fig. 8). This surface depends, along with the stress invariants, mainly on the bulk density of compacts, as shown by its expansion with densification. The compact deforms elastically at stress levels within the yield surface but, when the stress reaches the yield surface, plastic deformation takes place. The strain vector (i.e., the incremental deformation) is in the direction normal to the surface: densification ensues from a positive component in the p -direction, while a negative component will turn into a shear failure.

The main applications of the phenomenological models are in the tool design for complicated multilevel parts. The required constitutive laws can be derived from hydrostatic and triaxial compression tests (Shridar and Fleck, 2000; Wikman *et al.*, 2006; Sinka and Cocks, 2007). Additionally, these same tests have been used to assess other bulk properties (e.g., pressure-dependent bulk and shear modulus and Poisson's ratio) necessary to model ceramic powder compaction. Moreover, the die wall friction coefficient can be realistically estimated, given that good powder data be available for input into the model. Eventually FEM compaction modeling may be employed, in combination with readily measurable powder characteristics, to address the design and development of more performing powders.

The micromechanical approach can be successfully applied to reproduce either particle rearrangement (DEM models) or powder compaction up to high densities (MDEM) with some limitations. DEM calculations are based on a local model of the contact behavior between two particles that assumes no interaction in the individual contact zones. Although both tangential

forces and contact friction mechanisms are taken into consideration, their application is limited to stage I and stage II of powder compaction. MDEM is based on FEM calculations of meshed discrete particles arranged as 2-D or 3-D random packings. Computing time restrictions limit simulation to assemblies of approximately 100 particles.

In particular, the stage I of compaction can be modelled by DEM for various stress states and agglomerate strength and size. In addition, the effect of particle size and polydispersity, agglomerate density, and attractive interparticle forces on die filling can be considered. Simulations provide packing configurations, and microstructure development as a function of fundamental material parameters and boundary conditions (Skrinjar and Larsson, 2004). DEM simulations suggest that only some granules support external pressure during early compaction, hence the force is transmitted non homogeneously during packing. About the stage II, DEM was applied to both aggregated powders with primary particles bonded by solid bridges and agglomerated powders with weakly bonded primary particles. Results support the role of granule cracking in the compaction mechanism by contact deformation (Martin and Bouvard, 2006; Balakrishnan *et al.*, 2010).

References

- Balakrishnan, A., Pizette, P., Martin, C.L., Joshi, S.V., Saha, B.P., 2010. Effect of particle size in aggregated and agglomerated ceramic powders. *Acta Materialia* 58, 802–812.
- Balasubramanian, S., Shanefield, D.J., Niesz, D.E., 2002a. Effect of externally applied plasticizer on compaction behavior of spray-dried powders. *Journal of the American Ceramic Society* 85 (4), 749–754.
- Balasubramanian, S., Shanefield, D.J., Niesz, D.E., 2002b. Effect of internal lubricants on defects in compacts made from spray-dried powders. *Journal of the American Ceramic Society* 85 (1), 134–138.
- Beiss, P., 2010. Trends and innovations in powder compaction presses and die sets. In: *International Powder Metallurgy Directory*, fourteenth ed. Inovar Communications Ltd., p. 29.
- Bertrand, G., Roy, P., Filiatre, C., Coddet, C., 2005. Spray-dried ceramic powders: A quantitative correlation between slurry characteristics and shapes of the granules. *Chemical Engineering Science* 60, 95–102.
- Brewin, P.R., Coube, O., Doremus, P., Tweed, J.H., 2007. *Modelling of Powder Die Compaction*. London: Springer.
- Carneim, T.J., Green, D.J., 2001. Mechanical properties of dry-pressed alumina green bodies. *Journal of the American Ceramic Society* 84 (7), 1405–1410.
- Carneim, R.D., Messing, G.L., 2001. Response of granular powders to uniaxial loading and unloading. *Powder Technology* 115 (2), 131–138.
- Dinger, D.R., Funk, J.E., 1997. Particle-packing phenomena and their application in materials processing. *MRS Bulletin* 22 (12), 19–23.
- Ewsuk, K.G., 2001. Powder granulation and compaction. In: Buschow, K.H.J., Cahn, R.W., Flemings, M.C., *et al.* (Eds.), *Encyclopedia of Materials: Science and Technology*. Elsevier Science Ltd, pp. 7788–7800.
- Frey, R.G., Halloran, J.W., 1984. Compaction behavior of spray-dried alumina. *Journal of the American Ceramic Society* 67 (3), 199–203.
- Geldart, D., Abdullah, E.C., Hassanpour, A., Nwoke, L.C., Wouters, I., 2006. Characterization of powder flowability using measurement of angle of repose. *China Particology* 4 (3–4), 104–107.
- Glass, S.J., Ewsuk, K.G., Readey, M.J., 1995. Ceramic granule strength variability and compaction behavior. SAND-95–1889C, CONF-951033-17. Albuquerque, NM, USA: Sandia National Labs.
- Glass, S.J., Ewsuk, K.G., 1997. Compaction science and technology. *MRS Bulletin* 22 (12), 24–28.
- Harthong, B., J  r  , J.-F., Doremus, P., Imbault, D., Donz  , F.-V., 2009. Modeling of high-density compaction of granular materials by the discrete element method. *International Journal of Solids and Structures* 46, 3357–3364.
- Lannutti, J.J., 1997. Characterization and control of compact microstructure. *MRS Bulletin* 22 (12), 38–44.
- Lukasiewicz, S.J., 1989. Spray-drying ceramic powders. *Journal of the American Ceramic Society* 72 (4), 617–624.
- Lukasiewicz, S.J., Reed, J.S., 1978. Character and compaction response of spray dried agglomerates. *American Ceramic Society Bulletin* 57, 798–891.
- Martin, C.L., Bouvard, D., 2006. Discrete element simulation of the compaction of aggregated powders. *Journal of the American Ceramic Society* 89, 3379–3387.
- Nebelung, M., Lung, B., 2009. Flowability of ceramic bulk materials. Part 1: Methods. *Ceramic Forum International* 86, E35–E40.
- Niesz, D.E., 1996. A review of ceramic powder compaction. *KONA Powder and Particle* 14, 43–51.
- Oberacker, R., 2012. Powder compaction by dry pressing. In: Riedel, R., Chen, I.-W. (Eds.), *Ceramics Science and Technology: Synthesis and Processing*, vol. 3. Wiley-VCH Verlag GmbH & Co., pp. 3–36.
- Pizette, P., Martin, C.L., Delette, G., Sornay, P., Sans, F., 2010. Compaction of aggregated ceramic powders: From contact laws to fracture and yield surfaces. *Powder Technology* 198, 240–250.
- Raghupathy, B.P., Binner, J.G., 2011. Spray granulation of nanometric zirconia particles. *Journal of the American Ceramic Society* 94 (1), 42–48.
- Ravindran, P., Manisekar, K., Narayanasamy, R., Narayanasamy, P., 2013. Tribological behaviour of powder metallurgy-processed aluminium hybrid composites with the addition of graphite solid lubricant. *Ceramics International* 39 (2), 1169–1182.
- Reed, J.S., 1995. *Introduction to the Principles of Ceramic Processing*. New York: Wiley, pp. 378–445.
- Santomaso, A., Lazzaro, P., Canu, P., 2003. Powder flowability and density ratios: The impact of granules packing. *Chemical Engineering Science* 58 (13), 2857–2874.
- Shinohara, N., Okumiyu, M., Hotta, T., *et al.*, 1999. Seasonal variation of microstructure and sintered strength of dry-pressed alumina. *Journal of the American Ceramic Society* 82, 3441–3446.
- Shridar, I., Fleck, N.A., 2000. Yield behaviour of cold compacted composite powders. *Acta Materialia* 48, 3341–3352.
- Sinka, I.C., 2007. Modelling powder compaction. *Kona Powder and Particle* 25, 4–22.
- Sinka, I.C., Cocks, A.C.F., 2007. Constitutive modelling of powder compaction – I. Theoretical concepts – II. Evaluation of material data. *Mechanics of Materials* 39 (392–403), 404–416.
- Skrinjar, O., Larsson, P.-L., 2004. Cold compaction of composite powders with size ratio. *Acta Materialia* 52, 1871–1884.
- Soldati, R., Zanelli, C., Guarini, G., *et al.*, 2018a. Characteristics and rheological behaviour of spray-dried powders for porcelain stoneware slabs. *Journal of the European Ceramic Society* 38 (11), 4118–4126.
- Soldati, R., Zanelli, C., Guarini, G., *et al.*, 2018b. Pore evolution and compaction behaviour of spray-dried bodies for porcelain stoneware slabs. *Journal of the European Ceramic Society* 38 (11), 4127–4136.
- Uppalapati, M., Green, D.J., 2006. Effect of relative humidity on the viscoelastic and mechanical properties of spray-dried powder compacts. *Journal of the American Ceramic Society* 89 (4), 1212–1217.
- Vicent, M., S  nchez, E., Molina, T., Nieto, M.I., Moreno, R., 2012. Comparison of freeze drying and spray drying to obtain porous nanostructured granules from nanosized suspensions. *Journal of the European Ceramic Society* 32 (5), 1019–1028.
- Walker, J., Reed, J.S., 1999. Influence of slurry parameters on the characteristics of spray dried granules. *Journal of the American Ceramic Society* 82, 1711–1719.

- Walker Jr., W.J., Reed, J.S., Verma, S.K., 2000. Selection of slurry parameters for engineered granule characteristics. In: Puri, V.M., Adair, J.H., Knobloch, C.L. (Eds.), 1999 Fine Powder Processing Conference. Pennsylvania State University, pp. 264–271.
- Wikman, B., Bergman, G., Oldenburg, M., Haggblad, H.-A., 2006. Estimation of constitutive parameters for powder pressing by inverse modelling. *Structural and Multidisciplinary Optimization* 31, 400–409.
- Zheng, J., Reed, J.S., 1988. Particle and granule parameters affecting compaction efficiency in dry pressing. *Journal of the American Ceramic Society* 71, C456–C458.

Colloid Casting Processes: Slip Casting, Centrifugal Casting, and Gel Casting

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Introduction

The reliability of ceramic materials can be improved using colloidal synthesis and processing techniques (Lange, 1989; Moreno *et al.*, 1998). Colloidal casting processes are used to produce high performance ceramics with a complex shape from a specially formulated slurry that is typically composed of a broad range of raw materials including oxides, carbides, nitrides etc. (Schilling, 2001). Processing of ceramics into useful shapes needs to start with ceramic powders (Askeland and Phule, 2003) and requires intimate control of solution chemistry and particle dispersion in suspensions for manufacturing of bulk forms (Bell *et al.*, 2015).

The colloidal shape forming methods can be classified as slip casting (Schilling and Aksay, 1991; Schilling, 2001), tape casting (Blugan *et al.*, 2007), dip coating (Scriven, 1988), gel casting (Young *et al.*, 1991), centrifugal casting (Huisman *et al.*, 1995b), freeze casting (Deville, 2008), injection molding (Fanelli *et al.*, 1989), direct coagulation casting (Graule *et al.*, 1994; Si *et al.*, 1999), and colloidal iso-pressing (Yu and Lange, 2001). A fabrication of a ceramic complex shape with colloidal processing typically involves (1) powder synthesis, (2) suspension preparation, (3) consolidation into the desired shape to form (known as a green body), (4) removal of solvents, and (5) densification using firing or sintering under a controlled heat treatment and atmosphere (Lange, 1989; Lewis, 2000). This process requires a colloiddally stable environment, where each component is properly dispersed in order to avoid unintentional heterogeneities (or defects) during the fabrication process (Lewis, 2000; Bell *et al.*, 2015). Subsequently, the material can be exposed to numerous additional operations such as grinding, polishing, or machining to get the final shape for a specific application.

In other conventional techniques of ceramics shaping such as dry pressing, starting powders must be carefully conditioned by wet mixing and consecutively need to be dried, which can lead to undesirable agglomeration. However, in colloidal techniques, green bodies are obtained directly from suspension, which in turn lead to high uniformity of the final products and considered as one of the major advantages of the colloidal casting systems.

Slip Casting

Slip casting the one of the oldest and most common industrial green forming techniques among colloidal casting processes that is typically used for fabrication of widely used ceramics such as porcelain, tableware, sanitary ware, structural tubing, automotive, and biomedical components (Schilling, 2001; Bengisu, 2013).

Slip casting is a batch process and its basic steps are represented in Fig. 1. Initially, an aqueous slurry of fine ceramic powders is poured into a permeable mold with micro-pores (Fig. 1(a)). Subsequently, partial drying of the slurry is achieved, i.e., liquid (typically water) begins to move out from the slip through the porous mold walls, under the effect of a capillary action (Fig. 1(b)). This leads to formation of a thick layer or body of densely packed particles along the mold walls. After desired thickness of the body is reached, the remaining slip is drained from the mold (drain casting, Fig. 1(c)). Production of shell and hollow components are typically achieved by partial drying of the slip and subsequent draining of the remaining liquid (Bengisu, 2013). In production of bulk and solid pieces, slip is continuously added/poured until solid cast forms and called as solid casting (Schilling, 2001). Separation of the solid body from the mold typically can be achieved easily as a result of shrinkage upon drying (Fig. 1(d)).

The slip casting process relies on numerous control parameters including casting rate, rheology of the slurry during filling and draining, density and yield strength of the cast, shrinkage and release properties of the cast when removing from the mold. The colloidal and rheological properties of aqueous powder slurries are important factors that need to be carefully examined. Ideally, casting slurries should be pseudoplastic with a viscosity that is sufficiently low (usually $< 2 \text{ Pa s}$ at a shear rate of $1\text{--}10 \text{ s}^{-1}$) for ease of handling during pumping and mold filling. High solid loadings are also advantageous for enhanced filtration during slip casting. Furthermore, the density and yield point of the slurry needs to be high enough to avoid differential settling of the particles in the slurry. Thus, to address these requirements polydisperse particle size systems and organic polymers (dispersants, plasticizers, binders, viscosity modifiers) are suggested to be utilized (Lange, 1989).

Water is the most typical liquid in slurry preparation, however, some of the powders such as MgO , CaO , Si_3N_4 , and AlN , can react with water. In such cases, alcohols, trichloroethylene, and methyl ethyl ketone can be used instead of water (Reed, 1995; Bengisu, 2013) as a solvent.

Another critical point is the packing density of the cast, which needs to be uniform to mitigate non-uniform shrinkages as such shrinking can in turn lead to crack formation during drying, debinding and sintering steps (Schilling, 2001). Additionally, the diffusion of organic polymers to the capillaries of the molds can cause severe problems and affect the reproducibility of the casting process and can damage the mold.

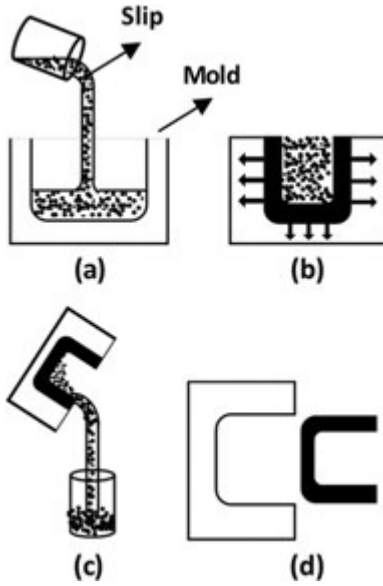
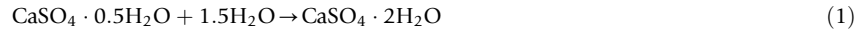


Fig. 1 Basic steps of slip casting process (a) filling of the mold with slip, (b) removal of liquid (due to capillary action) and formation of a cast layer along the mold walls, (c) draining of the excess slip from the mold; (d) green body removal after partial drying. Reproduced according to Askeland, D.R., Phule, P.P., 2003. *The Science and Engineering of Materials*, fourth ed. Springer, p. 639.

Mold is a critical component of a slip casting process, which is in charge of capillary withdrawal of the liquid through its pores (Hampton *et al.*, 1988; Francis and Roberts, 2016). The most common mold material is gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), produced by the reaction of plaster of Paris and water according to Eq. (1).



As a permeable mold, gypsum molds possess 40%–50% porosity and are highly advantageous due to its low costs, high availability, small pore size, good reproducible water adsorption properties, smooth surface, and wide variety of shapes. The pores of gypsum crystals are interconnected with capillaries (typical diameter range of 100 nm to 5 μm), and filled with water during cast process. The pore size and porosity depends on water/plaster ratio. The higher water/plaster ratio results in higher porosity and larger pores, which in turns results in higher water adsorption capacity, however strength of the molds decay in parallel. Furthermore, gypsum molds typically have low thermal shock resistance and desiccation of the gypsum is observed when heated above 40°C during drying (Reed, 1995). The crystal structure and setting time of the gypsum molds depend on temperature, mixing time and electrolytes in the water, and should ideally be taken under control for reproducibility of molds and slip casting process (Schilling, 2001; Reed, 1995).

Even if gypsum/plaster molds are suitable for machining and considered as a cost-effective option in slip casting, they possess a limited service life (80–100 maximum casts) and exhibit long drying time for removal of the water due to their low wear resistance and limited temperature stability. Therefore, mass production of commonly used ceramic parts can preferably done by using durable polymer molds (Kryuchkov and Neklyudova, 2015). The polymeric materials with an open pore structure can show high water permeability, mechanical, and fatigue performance with less deformation and long service life (depending on the type of the material utilized). Polymethyl methacrylate (PMMA)-based porous materials are the most widely used polymer molds that can shorten casting period due to mitigation of the drying step. In polymeric molds the dewatering can be achieved through air-purging system (Inoue *et al.*, 1988; Ergün *et al.*, 2004).

The major factors affecting the growth rate of a cast are reported to rely on (1) the permeability to water of the cast layer, (2) the specific gravity of the slip, and (3) the suction pressure of the mold (Adcock and McDowall, 1957).

Numerous theoretical and experimental studies have been performed to estimate the mechanics and behavior of slip casting process (Kocatopce, 1946; Adcock and McDowall, 1957; Haerle and Haber, 1995; Banno *et al.*, 1999). The casting layer thickness, L , can be estimated with the cast layer growth rate according to casting kinetic models (Adcock and McDowall, 1957; Schilling and Aksay, 1991; Bengisu, 2013), as defined in Eq. (2):

$$L = \left\{ (2P_m g E^3 t) / [5S^2 \eta (\gamma - 1)(1 - E)^2] \right\}^{1/2} \quad (2)$$

$$P_m = S_m \sigma \cos \gamma \quad (3)$$

where E is the porosity of the casting layer, t is time, S is the surface area of suspended particles, η is the viscosity of the slip, g is the gravitational acceleration, and γ is the volume of the slip containing a volume equals to $1 - E$ of solids. P_m is the pressure drop across the mold (estimated according Eq. (3) by the Laplace equation), S_m is the specific surface area of the mold, σ is the surface tension of the liquid, and γ is the contact angle ($\cos \gamma = 1$ for plaster of Paris in contact with water). The casting rate is constant with time

(L vs $t^{1/2}$) when the mold suction and resistance reach to constancy and indicate presence of a uniformly dense cast layer if a linear plot is obtained (Reed, 1995; Schilling, 2001). Deviations in the linear plot are indicative of presence of large agglomerates as a result of gravity sedimentation during slip casting or changes in rheological properties of the slip with time (Schilling, 2001).

To manufacture desirable and reproducible complex ceramic shapes with slip casting, numerous parameters such as particles size of the starting powders, viscosity, mold type, casting time and temperature, pH, and additive organic polymer properties need to be carefully controlled. Slip casting has a wide range of application areas from traditional ceramic parts like kitchenware or porcelain products to gas turbine rotor or aluminum titanate exhaust port liners for engines (Kennard, 1986; Bell *et al.*, 2015). However, this technique is a batch and relatively slow process and suitable for limited production elements (Bengisu, 2013).

Non-traditional casting processes such as pressure casting, vacuum casting and centrifugal casting on the other hand offer increased filtration rate, filling rates and uniformity that in turn results in faster production rates.

Pressure Casting

Pressure casting is an automated production process where an external pressure is applied to increase the filtration rate for large-scale production of complex and thicker parts in a shorter production cycle compared to conventional slip casting. Unlike slip casting, where filtration occurs by capillary action (~ 0.1 MPa) (Reed, 1995), pressure casting is achieved by application of an external pressure that typically varies from medium (0.3–0.4 MPa) to high (up to 4 MPa) levels depending on manufactured material size and mold type (Buschow *et al.*, 2001).

Pressure casting process is working in a similar principle with pressure filtration process, where liquid is removed through pressing the slip into a porous mold serving as a filter (Bengisu, 2013). A schematic diagram of pressure casting is shown in Fig. 2. Pressure casting technique can decrease the production time up to an order of magnitude that in turn results in a significant decay in the fabrication costs. In the study of Gainer and Carter, it was reported that application of a slip pressure up to 1.5 MPa led to increase of the cast thickness by factor of 2–3 and the casting time of a ~ 1 cm thick wall decreased from 1 to 2 h to less than 20 min (Gainer and Carter, 1964). Furthermore, drying of plaster molds is one of the most time consuming and labor-intensive steps while occupying large floor spaces in conventional casting systems. In pressure casting these problems can also be avoided (Buschow *et al.*, 2001).

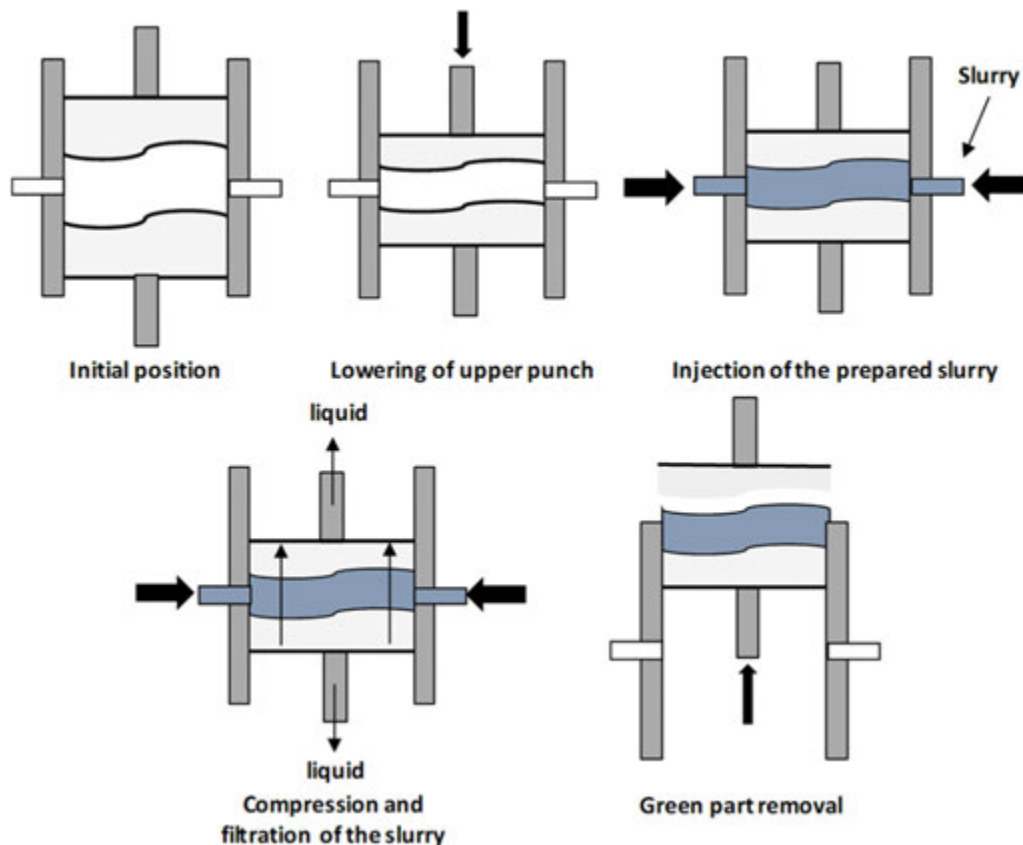


Fig. 2 Schematic diagram of pressure casting process. Reproduced according to Bengisu, M., 2013. Engineering ceramics. Springer Science & Business Media, p. 123.

Conventional molds (gypsum molds) prone to fracture at high pressures, therefore high strength polymeric molds are needed in pressure casting. This leads to relatively higher capital costs when compared to conventional molds, however, enhanced production levels enables pressure casting still an economically favorable option (Schilling, 2001). Polymeric molds are more resistant to possible chemical reactions between mold and metal ions metal ions in the slip and possess a longer lifetime (can withstand to $\sim 10,000$ cycles) than that of plaster molds (~ 100 cycles) (Lyckfeldt *et al.*, 1994; Bengisu, 2013). Another drawback of the plaster molds is the presence of Ca^{2+} in the cast detected after interaction of the cast surface with the mold which in turn causes a contamination in the green bodies (Moreno *et al.*, 1998). Polymeric molds are not prone to surface wear and providing proper fit of the slip to the mold with an increased consistency in the edges and sharp corners, and decreased surface roughness of the greenware when compared to conventional molds. In pressure casting, the process relies on the degree of the pressure (external pressure gradient) used rather than extraction of water with capillary suction from the molds (Fennelly and Reed, 1972). This bypasses the need of additional mold drying step and accelerates the production rate. More importantly, with its automated production operation, fluctuations in the quality of manufactured parts are reduced and uniform greenware with less moisture can be produced with pressure casting.

Vacuum Casting

In vacuum casting, the capillary suction of a mold is increased by applying external suction under vacuum conditions in order to create pressure gradient for faster casting rate. Vacuum casting was previously widely used in production of standard samples and porous refractory insulation materials (Reed, 1995). The permeable preform, connected to a vacuum line, is submerged and kept in a slurry, until desired thickness is reached.

After utilization of silicon rubber as a mold material, vacuum casting has started to be considered as a versatile and rapid indirect soft tooling technology for production of small series of functional plastic parts i.e., high quality prototypes or end-use products, with a high degree of dimensional accuracy. (Tang *et al.*, 2007; Abu Bakar *et al.*, 2009; Strube *et al.*, 2014; Wortmann *et al.*, 2018). It is an indirect technique since a master pattern is required prior to mold tooling (Tang *et al.*, 2007).

Fig. 3 represents an example of the vacuum casting process that is used in manufacturing of micro-gears and its micro-molds (Tang *et al.*, 2007). Initially, a master pattern of the desired product is produced typically using stereolithography or laser sintering (Wortmann *et al.*, 2018), with a high-quality surface finish. In parallel, a silicone mold is produced by casting silicone around the master copy under vacuum conditions to mitigate the presence of air bubbles. After hardening of the silicone mold, the mold is cut

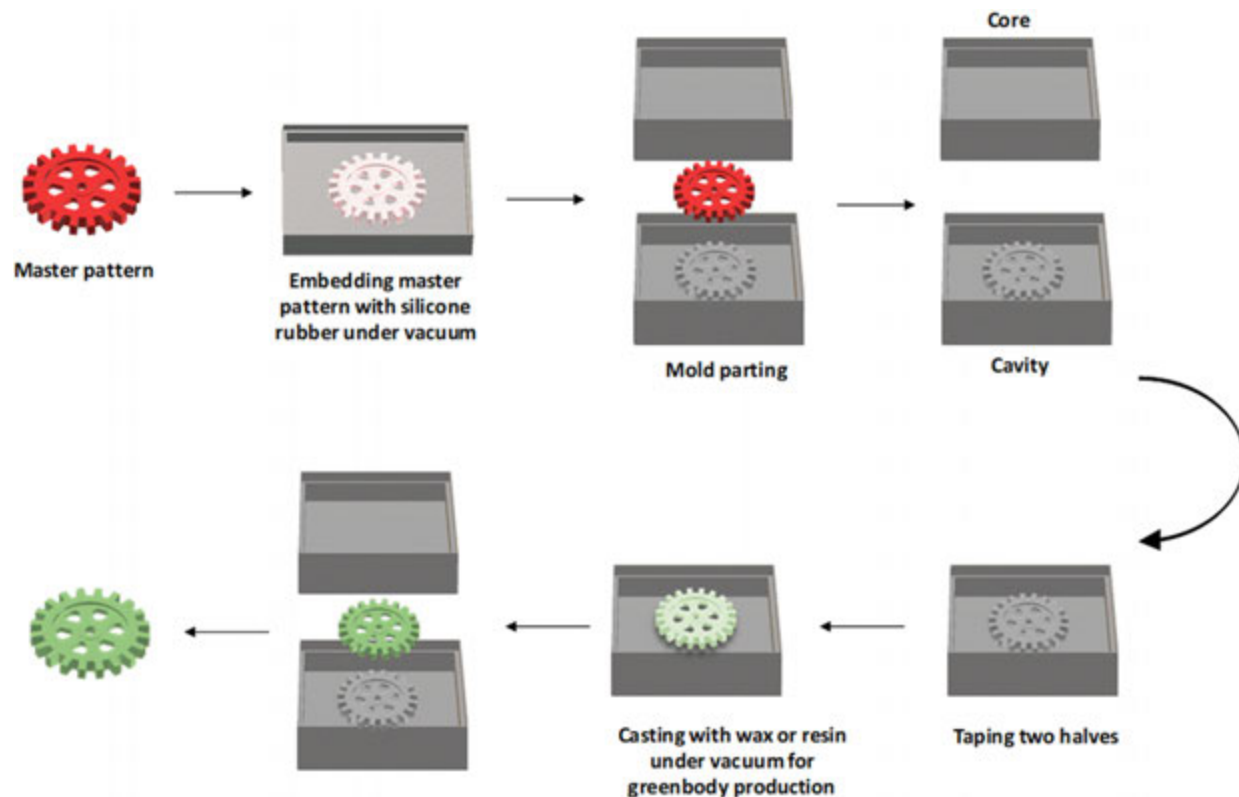


Fig. 3 Manufacturing steps involved in vacuum casting. Reproduced according to Tang, Y., Tan, W.K., Fuh, J.Y.H., *et al.*, 2007. Micro-mold fabrication for a micro-gear via vacuum casting. *Journal of Materials Processing Technology* 192–193, 334–339.

according to pre-defined parting planes. Subsequently, master pattern is removed to obtain the micro-mold by leaving a cavity to be used in production of copies. Besides silicone rubber, numerous types of plastic materials including polyurethane, rubber, nylon, and polycarbonate can be used in vacuum casting systems (Abu Bakar *et al.*, 2009).

Vacuum casting can be used in casting of resins, plastic, and metals due to high chemical resistance characteristics of silicone rubber molds (Tang *et al.*, 2007). Furthermore, this technique is widely applied in medical area (Ng *et al.*, 2009), part miniaturization for production of polymer biomicrosystems (Denoual *et al.*, 2005) and manufacturing of ceramics (He *et al.*, 2002). Further studies have been performed in micro-electro mechanical (MEMS) fabrication for production of optical switching, chips, micro-fluidic channels (Denoual *et al.*, 2006; Wang *et al.*, 2013). Even if vacuum casting has a significant potential in manufacturing of plastic functional parts, there are still some challenges existing on mass production.

Centrifugal Casting

Centrifugal casting is originally known from cement industry from 1978, as being the most common method used to manufacture tubes and pipes in cement industry (Glasser and Zhang, 2001; Kaufmann, 2004). Centrifugal casting involves solid-liquid separation by spinning a mold in lab-scale centrifuge in order to accelerate the sedimentation of colloidal suspension for the compaction of powders. The molds used in centrifugal casting do not need to be porous and can be fabricated from different metals and plastic materials (Buschow *et al.*, 2001; Schilling, 2001).

In this technique, the mold is located at the bottom of centrifugal bucket that can produce the centrifugal action in the direction of the mold. Centrifugal force can accelerate the casting speed and significantly shorten the casting time. Different from slip casting, the liquid in the slurry is removed from the top of the cake in this technique. Centrifugal casting technique allows manufacturing of thicker parts in a faster manner compared to other casting methods.

Centrifugal casting is one of the least common industrial casting technique in ceramics due to the following drawbacks: (1) differential settling during the consolidation stage and (2) significant gradients in compaction stress observed within the cake at different radial distances from the center of the centrifuge (Buschow *et al.*, 2001; Bengisu, 2013). These factors result in gradients also in packing density and formation of subsequent shrinkage cracks during drying and debinding. The compressibility problems can be addressed by avoiding flocculated slips (Schilling *et al.*, 1998; Buschow *et al.*, 2001). To avoid segregation problems, consolidation is suggested to be in the flocculated or in the coagulated state or utilize highly concentrated dispersed suspensions (Huisman *et al.*, 1995a,b; Schilling *et al.*, 1998; Buschow *et al.*, 2001).

Centrifugal casting is also a common method for obtaining functionally graded materials (FGM) and manufacturing of layered micro-composites through the sequential casting of different slip formulations (Marshall *et al.*, 1991; Bengisu, 2013). The layer thickness can be arranged via controlling the centrifuging speed and the solid concentration in the slurry (Marshall *et al.*, 1991). Mainly composite materials such as SiC reinforced Al-based FGMs or metallic materials having high differences of density and low solubility on different phases can also be produced with centrifugal casting (Chirita *et al.*, 2008).

Alternatively, the slip is located in a hollow cylindrical plaster mold and rotated around its axis to manufacture tubular or axisymmetrical bodies (Bengisu, 2013). For instance, rings, tubes, pipes, and large motor housings are typically produced using centrifugal casting (Campbell, 2015).

Gel Casting

Gel casting is one of the ceramic forming processes that was developed to overcome challenges like long binder burnout times, size and geometry limitations, or non-uniform density issues of conventional complex shape forming techniques. Gel casting was first developed in Oak Ridge National Laboratory (ORNL), USA in 1980s by bringing together traditional slip casting process and polymer chemistry.

Gel casting process is completely based on organic materials. Here, initially a suspension of the fine ceramic powders mixed with organic monomers composed of organic dispersants and binders is prepared. The prepared slurry is subsequently poured into a nonporous mold and kept for in situ polymerization or gel formation to obtain a green body with the shape of the mold cavity. After gelation, the material is removed from the mold for drying, binder burnout, and finally sintering. The basic manufacturing steps of gel casting process is summarized in Fig. 4.

It is important to distinguish gel casting and sol-gel process. Sol-gel process is previously developed by Yoldas (1992) in which solid is produced as a part of the process in the form of an inorganic gel with a low solid loading. On the other hand, gel casting is comprised of commercial powders in a dispersion (with a high solid loading) containing organic monomers that are used for polymerizing the dispersion into an organic gel in order to hold the powders together in the desired shape (cavity of the mold) (Omatete *et al.*, 1997).

In gel casting, ceramic powders are dispersed in an aqueous monomer solution that is composed of a solvent, chain former monomers, crosslinking agents, free-radical initiators, and a catalyst plus surfactant. Reactive organic monomers, used for polymerization, are one of the key components of this process. Similar to other polymerization systems, gel-casting ingredients are reactive chemicals and can cause health and environmental problems with their release or exposure to workers (Janney *et al.*, 1998). Therefore, monomer selection in gel casting requires special attention.

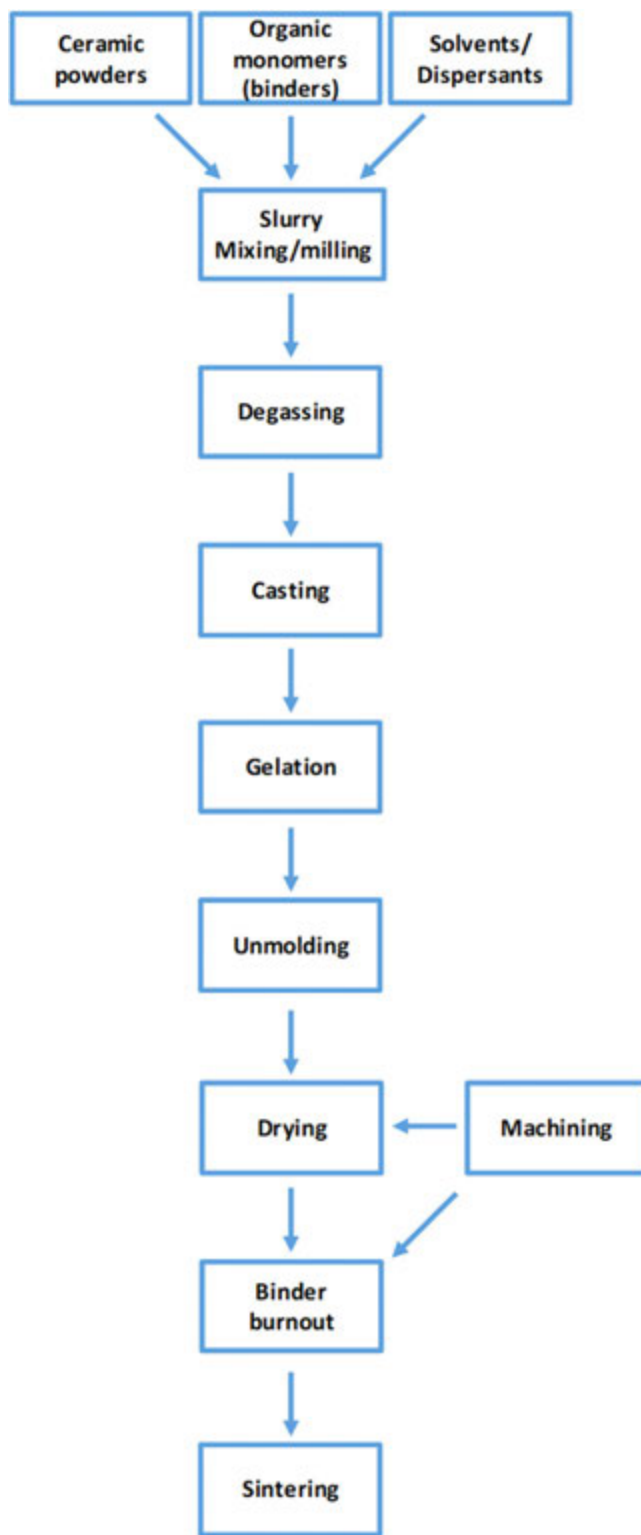


Fig. 4 Manufacturing steps involved in gel casting. Reproduced according to Omatete, O.O., Janney, M.A., Nunn, S.D., 1997. Gelcasting: From laboratory development toward industrial production. *Journal of the European Ceramic Society* 17 (2–3), 407–413.

Both aqueous and non-aqueous solutions can be used in gel-casting, however, aqueous systems i.e., water as a medium/solvent, are highly preferred due to environmental concerns. In aqueous gel casting acrylic acid and acrylamide (AM) were initially widely used as a monomer together with N,N'-methylenebisacrylamide (MBAM) as a crosslinker. Even if AM system enabled advanced ceramics products, AM monomer is neurotoxic. Therefore, many attempts were done to replace AM with a less toxic and safer

monomer. In this regard, low toxic methacrylamide was started to be utilized in later stages of this process. In the study of Janney *et al.* it was reported that MAM-MBAM monomer systems produces green bodies with a sufficient strength for further machining (Yang *et al.*, 2011). Hydroxymethylacrylamide (HMAM), N-vinyl pyrrolidone (NVP), and methoxy poly (ethylene glycol) mono-methacrylate (MPEGMA) (Bengisu, 2013) are some of the monomers that are widely used in gel casting systems. As crosslinking polymers MBAM, 2-hydroxyethyl methacrylate (HEMA), poly(ethylene glycol) dimethacrylate (PEGDMA), temperature activated crosslinking polymers such as agarose and carrageenans and crosslinking of polymers with metal-ion complexation route are highly preferable (Yang *et al.*, 2011; Bengisu, 2013). Additionally, ammonium persulfate (APS) together with tetramethylethylenediamine (TEMED) are typically used to catalyze the polymerization and crosslinking reactions.

In gel casting, narrowly dispersed submicron ceramic powders are preferred in the suspensions to enable uniform grain growth during sintering and obtain high homogeneity in the end material. Therefore, it is crucial to have high solid loadings, up to 50 vol% solids in a slurry, which is known to minimize the shrinkage and deformations during drying and sintering. Such high solid loadings also require further consideration in rheology of the slurries i.e. utilization of dispersants, to avoid problems during pouring of the fluid to the mold. Consequently, the prepared slurry is first poured into the complex shaped molds, then polymerized and crosslinked in situ to form polymer-water gel, which gets the form of the mold. There is a wide variety of mold materials for gel casting. Molds for gel casting can be made of metals, glass, wax and plastics, and only limited with the ability by the design of the mold shape.

In the next step, the gelled parts need to be dried under controlled conditions. Drying is the bottleneck of gel casting since it is the slowest and most critical step. The inner stress in the green material is mostly caused during transformation from suspension to green body or during drying stage. To avoid formation of cracks, drying of the gels needs to be conducted initially under relatively high humidity conditions (>90%) which is prolonging the drying step. Upon shrinkage in the body stops, the drying temperature is increased while decreasing the relative humidity. The burnout of the binders also needs to be done with slow heating rates to avoid problems that might be caused by carbonaceous residuals in the final material. The burnout temperature is slurry specific and depends on the ceramic powders and monomers used.

Gel casting is a well-established colloidal processing technique for manufacturing of high performance ceramics in a short time with high yields, a high green strength (allowing machining operations after drying), a high reproducibility, and low-cost machining. It has been widely applied in the industry for production of highly porous ceramic materials and near net complex shaped ceramics including rutile capacitor, thin-wall tube, turbine rotors, refractory nozzle, and microbeads (Yang *et al.*, 2011).

References

- Abu Bakar, N.S., Kadir, M.A., Alkahari, M.R., 2009. Review on vacuum casting technology. In: Proceedings of the International Conference on Recent and Emerging Advanced Technologies in Engineering (iCREATE2009).
- Adcock, D.S., McDowall, I.C., 1957. The mechanism of filter pressing and slip casting. *Journal of the American Ceramic Society* 40 (10), 355–360.
- Askeland, D.R., Phule, P.P., 2003. *The Science and Engineering of Materials*, fourth ed. Springer. p. 639.
- Banno, T., Sano, S., Oda, K., 1999. Application of a two-dimensional computer simulation to cake growth in slip casting with complicated-shape gypsum molds. *Journal of the American Ceramic Society* 82 (12), 3401–3406.
- Bell, N.S., Monson, T.C., Di Antonio, C.B., Wu, Y., 2015. Practical colloidal processing of multication ceramics. *Journal of Ceramic Science and Technology* 7. (Sandia National Lab. (SNL-NM), Albuquerque, NM (United States), 7 (SAND-2015-4670J)).
- Bengisu, M., 2013. *Engineering Ceramics*. Springer Science & Business Media. p. 123.
- Blugan, G., Morawa, K., Koebel, S., *et al.*, 2007. Development of a tape casting process for making thin layers of Si_3N_4 and $\text{Si}_3\text{N}_4 + \text{TiN}$. *Journal of the European Ceramic Society* 27 (16), 4789–4795.
- Buschow, K.H.J., Cahn, R., Flemings, M., *et al.*, 2001. *Encyclopedia of Materials: Science and Technology*. 1. Elsevier. p. 11.
- Campbell, J., 2015. Chapter 16 – Casting. In: Campbell, J.B.T. (Ed.), *Campbell's Complete Casting Handbook: Metal Casting Processes, Techniques and Design*, second ed. Boston: Butterworth-Heinemann, pp. 821–882. doi:10.1016/B978-0-444-63509-9.00016-9.
- Chirita, G., Soares, D., Silva, F.S., 2008. Advantages of the centrifugal casting technique for the production of structural components with Al–Si alloys. *Materials & Design* 29 (1), 20–27.
- Denoual, M., Mace, Y., Le Pioufle, B., *et al.*, 2006. Vacuum casting to manufacture a plastic biochip for highly parallel cell transfection. *Measurement Science and Technology* 17 (12), 3134.
- Denoual, M., Mognol, P., Le Pioufle, B., 2005. Vacuum casting, a new answer for manufacturing biomicrosystems. *Proceedings of the Institution of Mechanical Engineers, Part B: Journal of Engineering Manufacture* 219 (9), 697–701.
- Deville, S., 2008. Freeze-casting of porous ceramics: A review of current achievements and issues. *Advanced Engineering Materials* 10 (3), 155–169.
- Ergün, Y., Dirier, C., Tanoğlu, M., 2004. Polymethyl methacrylate based open-cell porous plastics for high-pressure ceramic casting. *Materials Science and Engineering: A* 385 (1–2), 279–285.
- Fanelli, A.J., Silvers, R.D., Frei, W.S., Burlew, J.V., Marsh, G.B., 1989. New aqueous injection molding process for ceramic powders. *Journal of the American Ceramic Society* 72 (10), 1833–1836.
- Fennelly, T.J., Reed, J.S., 1972. Compression permeability of Al_2O_3 cakes formed by pressure slip casting. *Journal of the American Ceramic Society* 55 (8), 381–383.
- Francis, L.F., Roberts, C.C., 2016. Dispersion and solution processes. *Materials Processing*. 415–512.
- Gainer, T., Carter, J., 1964. Casting sanitary ceramics under pressure. *Glass and Ceramics* 21 (10), 615. doi:10.1007/BF00675921.
- Glasser, F.P., Zhang, L., 2001. High-performance cement matrices based on calcium sulfoaluminate–belite compositions. *Cement and Concrete Research* 31 (12), 1881–1886.
- Graule, T.J., Baader, F.H., Gauckler, L.J., 1994. Direct coagulation casting (DCC)-principles of a new green shaping technique. In: Yan, D.S., Fu, X.F., Shi, S.X., (Eds.) *Proceedings of the 5th International Symposium on Ceramic Materials and Components for Engines*, pp. 626–631. Shanghai.
- Haerle, A.G., Haber, R.A., 1995. Ultrasonic real-time monitoring of cake structure during slip casting. *Journal of the American Ceramic Society* 78 (3), 819–823.
- Hampton, J.H.D., Savage, S.B., Drew, R.A.L., 1988. Experimental analysis and modeling of slip casting. *Journal of the American Ceramic Society* 71 (12), 1040–1045.
- He, T., Lu, Z., Huang, Y., *et al.*, 2002. Characterization of YSZ electrolyte membrane tubes prepared by a vacuum casting method. *Journal of alloys and compounds* 337 (1–2), 231–236.

- Huisman, W., Graule, T., Gauckler, L.J., 1995a. Alumina of high reliability by centrifugal casting. *Journal of the European Ceramic Society* 15 (9), 811–821.
- Huisman, W., Graule, T., Gauckler, L.J., 1995b. Conditions to Obtain Reliable High Strength Alumina via Centrifugal Casting. Westerville, OH: American Ceramic Society.
- Inoue, S., Kiriya, S., Imada, K., 1988. Manufacturing Process of Porous Resin Mold Containing Continuous Holes and Casting Mold. Google Patents.
- Janney, M.A., Omatete, O.O., Walls, C.A., *et al.*, 1998. Development of low-toxicity gelcasting systems. *Journal of the American Ceramic Society* 81 (3), 581–591.
- Kaufmann, J., 2004. Development of special mortars for an application in centrifugal casting process. In: *Proceedings of the International Symposium on Ultra High Performance Concrete*, pp. 757–768.
- Kennard, F.L., 1986. Ceramic component fabrication. In: *Proceedings of the 13th Automotive Materials Conference: Ceramic Engineering and Science Proceedings*, pp. 1095–1111. Wiley Online Library.
- Kocatopce, S.S., 1946. Fundamental study of clay: VII, Effect of particle size on properties of casting slips. *Journal of the American Ceramic Society* 29 (4), 99–107.
- Kryuchkov, Y.N., Neklyudova, T.L., 2015. Structure of gypsum and polymer molds for slip casting. *Glass and Ceramics* 71 (9–10), 324–326.
- Lange, F.F., 1989. Powder processing science and technology for increased reliability. *Journal of the American Ceramic Society* 72 (1), 3–15.
- Lewis, J.A., 2000. Colloidal processing of ceramics. *Journal of the American Ceramic Society* 83 (10), 2341–2359.
- Lyckfeldt, O., Liden, E., Persson, M., Carlsson, R., Apell, P., 1994. Progress in the fabrication of Si_3N_4 turbine rotors by pressure slip casting. *Journal of the European Ceramic Society* 14 (5), 383–395.
- Marshall, D.B., Ratto, J.J., Lange, F.F., 1991. Enhanced fracture toughness in layered microcomposites of Ce-ZrO_2 and Al_2O_3 . *Journal of the American Ceramic Society* 74 (12), 2979–2987.
- Moreno, R., Salomoni, A., Castanho, S.M., 1998. Colloidal filtration of silicon nitride aqueous slips. Part I: Optimization of the slip parameters. *Journal of the European Ceramic Society* 18 (4), 405–416.
- Ng, W.C., Seet, H.L., Lee, K.S., *et al.*, 2009. Micro-spike EEG electrode and the vacuum-casting technology for mass production. *Journal of Materials Processing Technology* 209 (9), 4434–4438.
- Omatete, O.O., Janney, M.A., Nunn, S.D., 1997. Gelcasting: From laboratory development toward industrial production. *Journal of the European Ceramic Society* 17 (2–3), 407–413.
- Reed, J.S., 1995. *Principles of Ceramics Processing*. New York: Wiley.
- Schilling, C.H., Aksay, I., 1991. Slip casting. In: *Engineered Materials Handbook 4*. ASM International, pp. 153–160.
- Schilling, C.H., 2001. Colloid casting. In: Buschow, K.H.J., Cahn, R.W., Flemings, M.C., *et al.* (Eds.), *Encyclopedia of Materials: Science and Technology*, second ed. Oxford: Elsevier, pp. 1314–1319. doi:10.1016/B0-08-043152-6/00248-5.
- Schilling, C.H., Garcia, V.J., Smith, R.M., Roberts, R.A., 1998. Ultrasonic and mechanical behavior of green and partially sintered alumina: Effects of slurry consolidation chemistry. *Journal of the American Ceramic Society* 81 (10), 2629–2639.
- Scriven, L.E., 1988. Physics and applications of dip coating and spin coating. *MRS Online Proceedings Library Archive* 121.
- Si, W., Graule, T.J., Baader, F.H., Gauckler, L.J., 1999. Direct coagulation casting of silicon carbide components. *Journal of the American Ceramic Society* 82 (5), 1129–1136.
- Strube, O.I., Brikmann, J., Hüsgen, B., 2014. Enhancement of the long life cycle of silicone molds for vacuum casting processes. *Polymer-Plastics Technology and Engineering* 53 (13), 1327–1332.
- Tang, Y., Tan, W.K., Fuh, J.Y.H., *et al.*, 2007. Micro-mould fabrication for a micro-gear via vacuum casting. *Journal of Materials Processing Technology* 192–193, 334–339.
- Wang, L.-F., Liu, J.-Q., Yan, X.-X., Yang, B., Yang, C.-S., 2013. A MEMS-based pyramid micro-needle electrode for long-term EEG measurement. *Microsystem Technologies* 19 (2), 269–276.
- Wortmann, M., Frese, N., Heide, A., *et al.*, 2018. Examination of interpenetrating polymer networks of polyurea in silicone molds arising during vacuum casting processes. *Polymer-Plastics Technology and Engineering* 57 (15), 1524–1529.
- Yang, J., Yu, J., Huang, Y., 2011. Recent developments in gelcasting of ceramics. *Journal of the European Ceramic Society* 31 (14), 2569–2591.
- Yoldas, B.E., 1992. Thermochemically induced photoluminescence in sol-gel-derived oxide networks. *Journal of Non-Crystalline Solids* 147–148, 614–620.
- Young, A.C., Omatete, O.O., Janney, M.A., Menchhofer, P.A., 1991. Gelcasting of alumina. *Journal of the American Ceramic Society* 74 (3), 612–618.
- Yu, B.C., Lange, F.F., 2001. Colloidal isopressing: A new shape-forming method. *Advanced Materials* 13 (4), 276–280.

Processing of Ceramics by Direct Coagulation Casting

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Introduction

Processing of most advanced ceramics from powders requires high degree of control to obtain desired microstructural characteristics and producing less-defective components from powders at lower costs. Selection of the appropriate processing technique depends on the raw materials, the shape and the number of pieces to produce.

Wet processing routes allow a better control of powder particles interactions in suspension, a greater homogeneity of particle packing and the achievement of final microstructures with less defects. Consolidation of colloidal suspensions into dense and homogeneous green bodies is a main characteristic of colloidal processing. As compared to dry processing techniques, colloidal processing has played a major role in the development of ceramic components with enhanced properties, capabilities and reliability, due to an improved control of the structure of compacts (Lewis, 2000). Besides some drawbacks, such as the low production rates, colloidal processing presents advantages over other techniques. The possibility to avoid aggregates and a better dispersion of the powder in a low viscosity medium enables to attain a better control of the microstructure and reproducibility of processed bodies with complex shapes and at low cost.

Processes such as slip casting, pressure casting, centrifugal casting, direct coagulation casting, tape casting, gel casting, injection molding and electrophoretic deposition are examples of colloidal processing methods. Among the several processes, three main routes for improving the ceramic processing of solid green bodies by using powder suspensions can be considered: (1) consolidation of the suspending medium – Gel Casting; (2) centrifugation – Centrifugation Casting and (3) flocculation/coagulation of the particles – Direct Coagulation Casting (DCC).

As one of the colloidal forming methods for near-net shape ceramics, direct coagulation casting (DCC) is characterized as a no or low organic binder involved (an advantage over gel casting process), high mechanical strength and high reliability of the ceramics.

Our main purpose is to analyze the process of Direct Coagulation Casting (DCC), reviewing the basic concepts supporting it and the developments introduced to improve the properties of the processed bodies by this technique.

Fundamentals of Direct Coagulation Casting

Electrical Double Layer

Powder particles in aqueous suspension develop an electric charge on their surface by the adsorption of charged species, either potential determining ions H_3O^+ and OH^- or other charged ions (specifically adsorbed). The positively or negatively charged particle surface will be balanced by the ions of the suspending medium and the total charge in the system is zero. Due to ionic attraction and repulsion an electrical double layer (EDL) is formed nearby each particle surface, that it will be surrounded by counter-ions (ions of the medium with charge of opposite signal of the surface) and co-ions (with charge of the same signal as the surface). High counter-ion density is localized on the surface and diffuse (co- and counter-ion) layer extends into the solution.

When pH of the medium is changed the amount of adsorbed species on particle surfaces varies and there is a value where the amount of both positive and negative types is equal, the isoelectric point of the powder (IEP). Therefore, the presence of the surface charges determines the electric interaction potential between the particles and the neighborhood ions of the medium.

Stern model for the EDL considers that the variation of the electric potential has two regimes: (1) first, near the particles surface, in the so-called Stern layer, there is a linear decrease of the potential, from a maximum value at the particle surface down to the Stern potential and; (2) after that, it shows an exponential decay with the increase of the distance to the surface, that is in the diffuse layer. If ψ_δ is the electric potential in the Stern layer and δ the thickness of the Stern layer, the double layer thickness becomes

$$\kappa^{-1} = \left[\frac{4\pi e^2 \sum n_i z_i^2}{\epsilon \epsilon_0 K_B T} \right]^{-1/2} \quad (1)$$

with $I = \frac{1}{2} [\sum n_i z_i^2]$ the ionic strength of the medium. In this equation, n_i is the ion concentration, z_i the valence of counter-ions; ϵ the electric permittivity, ϵ_0 the vacuum electric permittivity, e the electron charge, K_B the Boltzmann constant and T the temperature.

In the diffuse layer the potential decays exponentially and can be explained according to the Debye-Hückel equation:

$$\psi(x) = \psi_\delta \exp^{-\kappa(x-\delta)} \quad (2)$$

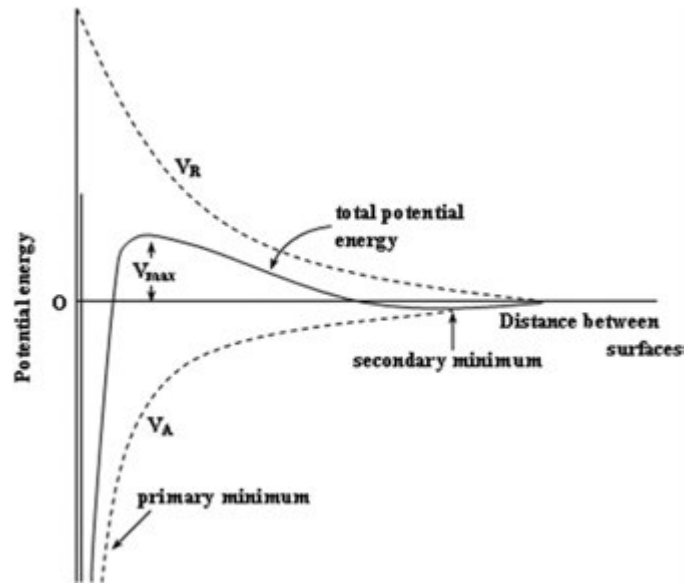


Fig. 1 Total curve of interaction potential between particles in a suspension vs. distance, according to DLVO theory. Reproduced from Balzer, B., Gauckler, L.J. 2003. Chapter 5.5 – Novel colloidal forming technique: Direct coagulation casting. In: Somya, S., Aldinger, F., Claussen, N., *et al.* (Eds.), Handbook of Advanced Ceramics: Materials, Applications, Processing, and Properties. Volume 1: Materials Science. Academic Press; Elsevier Inc., pp. 435–458.

It is seen that it depends mainly on the Stern potential and on both the Stern and the double layer thickness, which is controlled by the characteristics of the suspending medium i.e., through its ionic strength (Gauckler *et al.*, 1999). EDL thickness decreases with the increase in the ionic strength, either due to an increase of the concentration of the electrolyte or due to an increase on the valence of the present ions. The diffuse layer can move and can be considered a slipping or shear plane that separates the mobile fluid from the fluid that remains attached to the surface. The electric potential at this plane is the so-called electrokinetic potential or zeta potential (ζ). It measures the electrostatic potential at, or very near to the beginning of the diffuse layer and can be considered not be much different of the Stern potential.

Stability of Suspensions – DLVO Theory

Interaction between charged surfaces in suspension can be explained by the DLVO theory considering that the total potential of interaction between the surfaces of the particles is the sum of an attractive (V_A) potential, mainly due to van der Waals attraction forces, and a repulsive potential (V_R), dependent on several factors, such as temperature, double layer thickness (κ^{-1}) and Stern potential (ψ_δ)

$$V_T = V_A + V_R \quad (3)$$

The van de Waals attraction potential, V_A is given by

$$V_A = \frac{Aa}{12H} \quad (4)$$

where A is the Hamaker constant, a the particle radius and H the distance between particles.

The EDL repulsive potential, V_R , is

$$V_R = \frac{Be K_B^2 T^2 a_l^2}{z^2} \exp(-\kappa H) \quad (5)$$

where B is a constant and

$$\gamma = \frac{\exp\left(\frac{ze\psi_\delta}{2K_B T}\right) - 1}{\exp\left(\frac{ze\psi_\delta}{2K_B T}\right) + 1} \quad (6)$$

The total energy curve of interaction is depicted in Fig. 1.

DLVO theory allows defining the stability/instability conditions of a suspension: a stable suspension must have a high Stern potential and a thick double layer. Those conditions of stability are also related with the IEP value: the suspension will be stabilized for a pH value far away from the IEP and coagulated nearby to it.

Colloidal suspensions can be prepared in the dispersed, weakly flocculated or strongly flocculated states. In the dispersed state, the repulsive barrier (V_{max}) (Fig. 1) between the particles is higher than $K_B T$, the particles repel each other. In a weakly flocculated

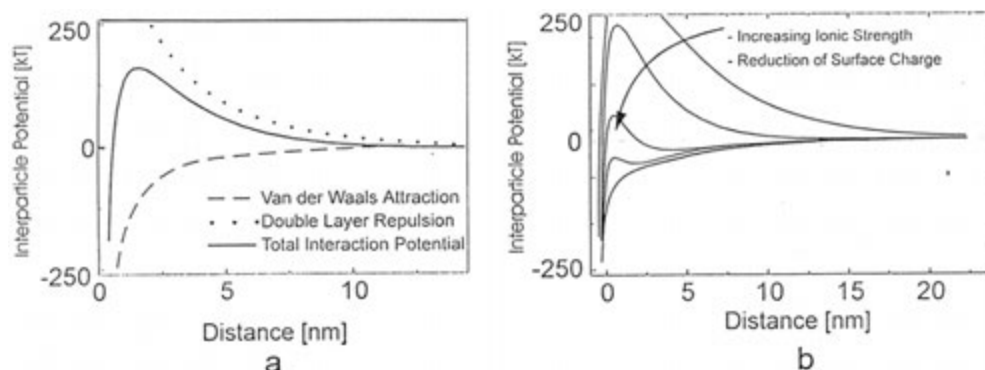


Fig. 2 Interparticle energy interaction – Influence of the conditions of the medium. Reproduced from Balzer, B., Gauckler, L.J. 2003. Chapter 5.5 – Novel colloidal forming technique: Direct coagulation casting. In: Somiya, S., Aldinger, F., Claussen, N., *et al.* (Eds.), Handbook of Advanced Ceramics: Materials, Applications, Processing, and Properties. Volume 1: Materials Science. Academic Press; Elsevier Inc., pp. 435–458.

state, particles can aggregate in a low secondary minimum forming flocs in suspension at low volume fractions, or a particle network at higher volume fractions. In this case, there is an equilibrium separation distance between aggregated easy destroyed by stirring. On the contrary, when particles are aggregated into a deep primary minimum (V_A) the suspension will be strongly flocculated and for high solids loading slurries the particles will form a touching particle network. For more diluted suspensions individual clusters will be formed (Lewis, 2000). This explains the fact that, for a low solids loaded suspension, the coagulation process leads to non bridging particle aggregates and for high solids loading (higher than 50 vol% solids) coagulation leads to the formation of a continuous network without any macroscopic shrinkage.

As predicted by DLVO theory, in a stabilized suspension the repulsive interparticle forces are dominant. If they are eliminated, either by changing the pH of the medium towards the IEP or by an increasing of its ionic strength (Fig. 2(a) and (b)), the repulsive energy barrier ($K_B T$) decreases and the attractive forces between the particles will cause the high solids loading suspension to coagulate, forming a stable particle network that behaves like a viscoelastic solid (Balzer and Gauckler, 2003).

This is the main idea behind Direct Coagulation Casting (DCC), a ceramic green body forming process via colloidal suspensions, first developed and patented by Gauckler *et al.* (1999) to be analyzed in the following paragraphs.

Contrary to the slip casting process where the body is consolidated by removal of the liquid by the capillary forces through a porous mold, in DCC the green body is obtained by the coagulation process of the slurry casted in a non-porous mold. Accordingly, the green density closely corresponds to the solid loading of the starting slurry. Therefore, it is advantageous to use a solid loading as high as possible in order to control the final geometry, and to achieve higher dimensional tolerances by minimizing the possible distortion during drying and sintering shrinkage. On the other hand, the shaping of complex parts requires the slurry to fill easily molds of possible complex geometry, which means that the viscosity of the slurry has to be kept below some acceptable level in order to be poured and fill all the parts of the mold.

Direct Coagulation Casting (DCC)

Fundamentals of the method

As already referred, direct coagulation casting (DCC) process is based on the concept of the balance of repulsive and attractive forces between surface of charged particles.

A well stabilized aqueous ceramic suspension is cast into a non-porous mold and in-situ coagulation is carried out by shifting the repulsive force between the particles in the suspension to the attractive regime. This can be achieved via the control of the reaction rate of an organic reagent (the so-called substrate), already present in suspension. Decomposition products of the substrate can either shift the pH of the suspension towards the IEP or increase the ionic strength of the medium (compressing the EDL) both contributing to the destabilization of the suspension (Fig. 3). The internal reaction of the decomposition of the organic reagent may be either enzymatic catalyzed at room temperature (for example urea decomposition by urease) or thermally activated self-decomposing.

According to the range of stabilization of the suspension of the ceramic powder and to the value of its IEP, different organic reagents can be used to produce the coagulation of the suspension.

Examples are:

- A pH shift from acid to alkaline range can be obtained by: (1) enzymatic decomposition of urea catalyzed by urease (pH change from 4 to 9) or of amides by amidase; or (2) by thermally activated self-decomposition of urea, formamide, etc.
- For slurries stabilized in the alkaline range and with a lower IEP, a pH shift from alkaline to acid range obtained by: (1) enzymatic decomposition of glucose by glucose oxidase; or by (2) a thermally activated self decomposition of esters and lactones

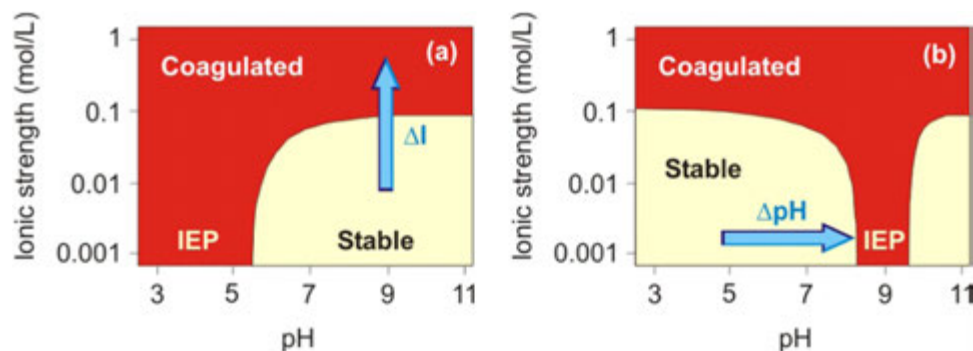
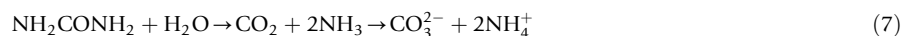


Fig. 3 Coagulation of alumina suspensions by ionic strength increase (a); and by pH shift (b). Reproduced from Gauckler, L.J., Graule, T., Baader, F., 1999. Ceramic forming using enzyme catalyzed reactions. *Mater. Chem. Phys.* 61, 78–102.

- For example, the enzymatic hydrolysis of urea $\text{-CO(NH}_2\text{)}_2\text{-}$ catalyzed by urease in aqueous medium, leads to the formation of ammonia and carbon dioxide, and their reaction in water produces NH_4^+ and HCO_3^- and a small amount of CO_3^{2-} , with the buffer pH of the main products around 9. Those reactions will contribute to the destabilization of the aqueous suspensions by two effects: by a pH shift, until the value of the pH buffer and to an increase of the ionic strength due to the formation of ions (Balzer and Gauckler, 2003; Yu *et al.*, 2011).
- For example, alumina suspensions stabilized in the acid range, can be coagulated by the increase of the pH towards its IEP (around 9), due to the ammonia produced by the hydrolysis of urea. For powders with an IEP higher than 9, the suspension will be coagulated by an increase of the ionic strength.
- Urea can also be decomposed at $T > 75^\circ\text{C}$ allowing for a pH shift from acid to neutral and then, at the end, to alkaline, as ammonia is formed.



The strength of the wet shaped green bodies depends on the coagulation method used: it was found that flocculated bodies resulting from the coagulation of the slurry by pH shift has higher strength than those coagulated by ionic strength increase (Balzer and Gauckler, 2003). The result was justified by the short range hydration forces acting between the particles when the coagulation was done by increasing the salt concentration.

Although DCC has been successfully applied in the processing of oxide (alumina, zirconia) and non-oxide (silicon carbide, silicon nitride) (Gauckler *et al.*, 1999) there are some drawbacks of DCC that need to be eliminated (or minimized) (Xu *et al.*, 2016).

For example, coagulation of the suspensions by enzymatic hydrolysis of urea is an expensive process due to the high costs of the enzyme urease. Also, when the coagulation is due to an increase of ionic strength by monovalent ions a long coagulation time is needed. To avoid the use of the hydrolysis reaction catalyzed by enzymes the coagulation of the suspensions by thermally activated decomposition of organic reagents has been suggested (Santacruz and Binner, 2008). A new method based on the use of carboxylic acid derivatives, viz., lactones, as coagulants to obtain alumina bodies swiftly, without the addition of catalyzers in DCC process was proposed (Binner *et al.*, 2006b). In the next section the utilization of the thermal decomposition of carboxylic lactones will be analyzed.

Coagulation of suspensions by thermal decomposition of lactones

Hydrolysis of specific carboxylic-acid lactones allowed coagulation of concentrated ceramic slurries to the point that demolding of casted piece can be practiced without appreciable distortion (Binner and McDermott, 2006a). The increase of concentration of the weak C-acid decreases pH of the slurry to the point that it loses stability and moves towards the isoelectric point of the particles in suspension. Coagulation occurs when the balance of attraction of van der Waals forces between suspended particles and electrostatic repulsion of the molecules of dispersants adsorbed to their surface comes to the local minimum of potential energy between particles. There are specific advantages in using C-acid lactones as proton release source for direct coagulation casting (Binner and McDermott, 2006a; Studart *et al.*, 2002; Yin *et al.*, 2006). Coagulants are metal free organics. Water, ionic radicals in solution and active sites of solid surfaces act as nucleophiles to operate the additive hydrolysis reaction progressively turning the ring lactones into the corresponding conjugated acid. The time scales of reactions of hydrolysis of specific lactones and dissociation of the conjugated acids are of the order of minute or hours permitting addition of the C-acid lactones to stable slurries, degassing, casting into molds before the occurrence of coagulation. Detail descriptions of the ring-type molecular structure of C-acid lactones of 4-, 5-, 6- up to 9-membered rings can be found in the works of Binner and co-workers (Binner and McDermott, 2006a; Yin *et al.*, 2006). Stability of C-acid lactones to nucleophilic attack leading to hydrolysis may change by orders of magnitude depending of polar species in solution, ring coordination number, ring strain of cis and trans configuration and polar effect of added side radicals (Binner and McDermott, 2006a; Yin *et al.*, 2006).

The sequence reactions in DCC using C-acid lactones, as in the case of DCC of concentrated Al_2O_3 slurries with the 4-membered ring β -Butyrolactone (β -BAL), develops in three steps, the chemical reactions of hydrolysis of the β -BAL and

dissociation of the β -hydroxybutyric acid and the physical process of gelation of suspension (Yin *et al.*, 2006). In the temperature range 1–55°C the addition reaction of β -BAL hydrolysis in deionized water and in the Al_2O_3 slurry stabilized with ammonium polyacrylate exhibits first order kinetics with activation energy $Q_h = 59 \pm 5 \text{ kJ mol}^{-1}$, the corresponding time constant τ decreasing from $\tau = 270 \text{ min}$ at 25°C to less than half an hour, $\tau = 29 \text{ min}$ at 55 °C. The activation energy of the identical reaction in de-ionized water is higher, $Q_h = 87 \pm 5 \text{ kJ mol}^{-1}$, the reaction rate at 25°C being one order of magnitude slower than in the Al_2O_3 slurry. As hydrolysis proceeds by attack of a single nucleophile H_2O molecule, first-order is also displayed by the reaction mechanism of hydrolysis of most lactones (Yin *et al.*, 2006).

Henderson-Hasselbalch equation determines the proportion of weak carboxylic acid that dissociates and sets the value of pH of the solution, or slurry. Values of the dissociation constant of β -hydroxybutyric acid pK_a in de-ionized water at 25°C are in the range 4.68–4.82. For values of pH between 9.5 (stable Al_2O_3 slurries) and 6.5 (IEP of Al_2O_3), β -hydroxybutyric acid would be dissociated in pure water to more than five parts in one hundred (Yin *et al.*, 2006). Adsorption of β -hydroxybutyric acid on the surfaces of the slurry particles, complexation and forming of salts with surfactants hinders the dissociation of acid and decreases the effective values of pK_a in concentrated slurries. As in the Al_2O_3 slurries the hydrolysis of β -BAL yielding the β -hydroxybutyric acid is faster by approximately three orders of magnitude than the observed increase of H^+ ion concentration with time (Yin *et al.*, 2006). Phenomenological models that describe in quantitative ways the increasing of H^+ ion concentration, which determines the time for coagulation of concentrated slurries, necessarily differ from the observed kinetics of hydrolysis if the butyric acid lactones. The parabolic relationship for the change of pH with time, $\Delta\text{pH} = A(T,C)t^{1/2}$, was reported for dissociation of β -hydroxybutyric acid in concentrated Al_2O_3 slurries, the proportionality factor $A(T,C)$ increasing with temperature T (activation energy $Q_d \approx 89 \text{ kJ mol}^{-1}$) and initial concentration C of β -BAL (Binner and McDermott, 2006a; Yin *et al.*, 2006). In more general way good fitting to experimental results was found by applying the following power law of the $[\text{H}^+]$ ion concentration,

$$[\text{H}^+]^n = \left(K_0 e^{-\frac{Q_d}{RT}} \right) C^m t + [\text{H}^+]_0^n \quad (8)$$

with K_0 a constant, t time, n and m exponents of the power laws of time and of dependence lactone initial concentration, respectively, and Q_d the activation energy of the effective acid dissociation reaction. Integer order with $n = 1$, $m = 1$ was found from fitting Eq. (8) to the decrease in pH of 57.7 vol% castable Al_2O_3 slurry with $C = 1.6 \text{ wt\%}$ of glucuronic acid lactone (GrAL) as coagulant. Replacing the coagulant of same slurry for 0.5 wt% and 0.8 wt% of gluconic acid lactone (GAL) yields a fractional order with $n = 1.4$ and $m = 3.25$ (Studart *et al.*, 2002). Fitting of Eq. (8) to decrease of pH of concentrated Al_2O_3 slurries with D-gulonic- γ -lactone (D-GAL) at concentration of $2.5 \times 10^{-5} \text{ mol g}^{-1}$ yields $n = 2.2$ and $m = 1.4$ and $Q_d = 64 \text{ kJ mol}^{-1}$. This value is close to $Q_d = 68 \text{ kJ mol}^{-1}$ determined for the same system at 81 wt% solids (Binner and McDermott, 2006a). In analysis of the effect of C at 25°C in the same system exponents n and m present a dependence on C , decreasing from $n \approx m = 3.1$ at $0.52 \times 10^{-5} \text{ mol g}^{-1}$ to $n \approx m = 1.6$ at $5.3 \times 10^{-5} \text{ mol g}^{-1}$. From fitting of Eq. (8) to the same data one determines the following logarithmic decrease of pH with the concentration of D-GAL, at the fixed time $t = 5 \text{ h}$: $\text{pH} = -1.1 \ln(C) + 8.32$, with $C (10^{-5} \text{ mol g}^{-1})$. Eq. (8) is not adequate to describe the decrease of pH with time in concentrated Al_2O_3 slurries as a function of concentration of β -BAL at 25°C. An analogous logarithmic decrease of pH for this system was found, yielding for $t = 10 \text{ h}$, $\text{pH} = -1.28 \ln(C) + 8.78$, with $C (10^{-5} \text{ mol g}^{-1})$ (Yin *et al.*, 2006). Values of activation energy Q_d of coagulation rate constants for lactones span in a wide range of values from $Q_d = 61 \text{ kJ mol}^{-1}$ for D-glucono- γ -lactone to the $Q_d = 95 \text{ kJ mol}^{-1}$ and $Q_d = 96 \text{ kJ mol}^{-1}$ of γ -butyrolactone and ϵ -caprolactone, respectively (Binner and McDermott, 2006a). The effect of heating on acceleration of the processes and achieving short coagulation times by pH shifts closely follows the values of the activation energy (Binner *et al.*, 2006b; Yin *et al.*, 2006).

A summary of major effects and secondary factors that regulate reactions (I) of hydrolysis of CA-lactones, (II) of dissociation of carboxylic acids and (III) gelation of particle suspension is given in Table 1. Temperature, initial pH of the stable slurries,

Table 1 Dominant and secondary effects on the carboxylic acid lactone hydrolysis (I), carboxylic acid dissociation and slurry coagulation (III) reactions. (IEP – isoelectric point of solid surface, Ψ_δ – Stern potential $\sim$ zeta potential)

Reaction	I – lactone hydrolysis	II – acid dissociation	III – gelation
pH of suspension	High rates at high values of pH	pH limited	Converging to IEP
Lactone initial concentration	Rate of reaction (1st order kinetics)	Non-integer order, slow dissociation of weak acids from interaction with solid	Drying fracture for high contents. Ionic strength coagulation/rheofluidifying
Temperature of slurries	Thermally activation, $Q_h \approx 65\text{--}130 \text{ kJ mol}^{-1}$	Thermally activation, $Q_d \approx 60\text{--}100 \text{ kJ mol}^{-1}$	Thermal activation, $Q \approx \Psi_\delta$
Dispersant	–	OH^- neutralization	Desorption, IEP changes
Particle surface chemistry	Nucleophilic sites	Complexes	van der Waals binding strength
Impurities	Nucleophilic activity	Buffering	Heteroflocculation

Note: Balzer, B., Gauckler, L.J. 2003. Chapter 5.5 – Novel colloidal forming technique: Direct coagulation casting. In: Sorniya, S., Aldinger, F., Claussen, N., *et al.* (Eds.), Handbook of Advanced Ceramics: Materials, Applications, Processing, and Properties. Volume 1: Materials Science. Academic Press; Elsevier Inc., pp. 435–458. Binner, J.G.P., McDermott, A.M., 2006a. In-situ acidification of electrosterically dispersed alumina suspensions: Effect of coagulant structure. J. Mater. Sci. 41, 1893–1903. Gauckler, L.J., Graule, T., Baader, F., 1999. Ceramic forming using enzyme catalyzed reactions. Mater. Chem. Phys. 61, 78–102. Yin, Y., Binner, J.G.P., Hey, M.J., Mitchell, J.R., 2006. Hydrolysis of carboxylic lactones in alumina slurries. J. Eur. Ceram. Soc. 26, 1171–1177.

concentration of CA-lactone, volume fraction of solids and composition and concentration of dispersants are major variables that control coagulation (Balzer and Gauckler, 2003; Binner and McDermott, 2006a; Gauckler *et al.*, 1999; Yin *et al.*, 2006). Reaction (III) gelation is mostly physical. Safe demolding of the piece requires a minimum threshold of yield strength of 6–10 kPa that makes the piece self-supported (Balzer and Gauckler, 2003; Binner *et al.*, 2006c). Mold removal becomes feasible when viscosity comes to 16 Pa s for shear rates in the range of 100 s^{-1} . This threshold corresponds to a pH shift from $\text{pH} \approx 9.5$ to approximately $\text{pH} = 7.5$ in gelation of concentrated Al_2O_3 slurries with solid fraction of 52–55 vol% (Binner *et al.*, 2006b; Yin *et al.*, 2006). The crossing point of dynamic storage (G') and loss (G'') moduli in small amplitude oscillatory rheometry allows a more precise definition of gelling time. It broadly corresponds to values of storage modulus $G' > 6 \text{ kPa}$ (Binner *et al.*, 2006b). DCC imposes conflicting requirements on solid volume fraction of the slurries. While one needs high solid loading to arrive to such high compressive strength in the gelled body, pouring and degassing of concentrated slurries require acceptably low viscosities of the slurry before coagulation. The low yield strength increases the probability of cracking during drying and slowed the acceptance of the DCC process by industry (Binner *et al.*, 2006c; Chen *et al.*, 2017; Gauckler *et al.*, 1999).

Convective heating to the isothermal temperature with protection of slurries from water evaporation and drying allows controlled gelling for values of gelling time above 1 h (Binner *et al.*, 2006c). The method was applied to prepare near-net shape pieces of Al_2O_3 ceramics in non-porous molds by DCC using D-gulonic- γ -lactone the slurries being heated to temperatures up to 80°C . Gelation of these slurries above 40°C is fast. Gelling time falls below the half hour and the volume inside may not reach isothermal conditions because of low thermal conductivity of slurries (Binner *et al.*, 2006c). Direct coagulation casting of white porcelain slips with 55 vol% solids is attainable with D-glucuronic-6,3-lactone (DGL) in concentrations of 2–3 wt% by heating the slips to 70°C and holding for approximately 15 min. The clay suspensions are stable at $\text{pH} \approx 7.5$. Fast hydrolysis of the DGL lactone at 70°C displaced the pH values of the porcelain slip towards $\text{pH} = 4.5$ (Mota, 2011).

Volume heating of the castable slurries with microwave energy allowed fast and homogenous heating in slip casting of sanitary ware (Das *et al.*, 2009). $\text{Al}_2\text{O}_3/\text{SiC}_n$ micro/nanocomposites of Al_2O_3 reinforced with nanoinclusions of SiC display high hardness and mechanical strength (Dong *et al.*, 2009). Large difference of isoelectric points of Al_2O_3 (IEP ≈ 9) and SiC (IEP < 3) would lead to heteroflocculation of concentrated slips during colloidal processing of $\text{Al}_2\text{O}_3/\text{SiC}_n$ composites. Addition of diammonium citrate to the slurry displaces the isoelectric point of modified Al_2O_3 surfaces to low pH values (IEP ≈ 3.5) and allow preparation of stabilized $\text{Al}_2\text{O}_3\text{-SiC}_n$ suspensions at $\text{pH} = 9$ with 5 wt% SiC_n and solid loading of 55 vol% to which D-glucurono-6,3-lactone (DGL) ($2.5 \times 10^{-5} \text{ mol g}^{-1}$) was added. Microwave heating of the concentrated slurry casted in plastic molds to 60°C and holding for 30 min accelerated hydrolysis of DGL lactone. The pH shifted from 9 to 6 and resulted in direct coagulation (Vieira, 2009). Time-dependent in situ hydrolysis/dissociation of DGL thermally activated by microwave energy promoted the coagulation of $\text{Al}_2\text{O}_3\text{-SiC}_n$ suspensions of high-volume fractions. Processed bodies presented high relative green density. Hydrolysis of DGL followed by the dissociation of the acid promotes coagulation in suspensions with solid volume fraction close to the critical packing.

Coagulation by high valence counter-ions (DCC-HVCI)

DCC by pH shift to IEP is a reliable process to produce ceramic bodies, but the wet strength might be not high enough for their handling. Shifting the interparticle forces from the repulsive to the attractive regime by increasing the monovalent ionic concentration through, for example the decomposition of urea catalyzed by urease, requires very high concentration of monovalent salt (2 mol L^{-1}) and the coagulation time became too long (Xu *et al.*, 2012a,b).

To overcome such limitations a modification of the DCC method, inducing the slurry coagulation by increasing the concentration of high-valence counter-ions was developed. The main idea behind the process is that the destabilizing power of an electrolyte is determined by the minimum concentration required to coagulate rapidly a suspension – the so-called critical coagulation concentration (CCC). DLVO theory is used to derive the expression that relates CCC with the counter-ion valence, z :

$$\text{CCC} = \frac{\text{constant}}{z^6} \quad (9)$$

Eq. (9) is the Schulze-Hardy rule, indicating that the minimum counter-ions concentration that will make the transition from a stabilized to coagulated slurry is inversely proportional to the sixth power of valence z . For $z = 1, 2$ and 3 the ratio of the CCCs are 1, 0.016 and 0.0014, respectively. As a consequence much lower concentrations of divalent and trivalent electrolytes needed to coagulate the suspension, comparing with larger concentration of monovalent electrolytes.

Results reported by the authors showed the potential application of high valence counter ions in colloidal forming (Xu *et al.*, 2012a). Based on this concept, a modification of DCC was proposed with a combination of the DLVO theory and the Schulze-Hardy rule, the so-called direct coagulation casting via controlled release of high valence counter ions (DCC-HVCI) (Chen *et al.*, 2017).

Although the process refers to the use of high valence counter-ions, all the reported work by the several authors had only employ divalent ions, mainly calcium Ca^{2+} and magnesium Mg^{2+} to increase the ionic strength of the medium, resulting in the compressing of the EDL of the surface particles and coagulation of the suspension. The method was applied to process alumina, zirconia (YSZ), silica and alumina-silica composites with calcium iodate, calcium citrate and calcium phosphate as the most common reagents to the release of Ca^{2+} ion. Concerning the release of Mg^{2+} magnesium citrate and magnesium oxide had been used. Besides the coagulation due to the increase of ionic strength, in some of the studies a thermally activated hydrolysis decomposition of an ester (Glycerol diacetate) was the other coagulation mechanism also to be present. Most of the studies found out that both coagulation mechanisms allow to obtain dense, homogeneous and high strength bodies in a short time (Xu *et al.*, 2015).

Alumina fiber-reinforced silica matrix composites with improved mechanical properties were prepared by this method (Xiao *et al.*, 2017) using the Ca^{2+} released by calcium iodate and the hydrolysis decomposition of glycerol diacetate (GDA) thermally activated at 70°C. Electrostatically stabilized suspension of silica with alumina fiber was coagulated by the release of Ca^{2+} ions from calcium iodate and also by pH shift due to the hydrolysis of GDA. This decomposition reaction occurs at high temperatures (70°C) forming acetic acid and glycerol. The acetic acid shifts the pH toward the IEP, promoting the coagulation of the suspension. Besides, with the increase in temperature the solubility of calcium iodate increases, releasing Ca^{2+} ions. Both mechanisms accelerate the coagulation of the suspension at high temperature (70°C). Processed bodies with homogeneous microstructure and good mechanical properties suggest that this colloidal method is promising to obtain ceramic-matrix composites with complex shapes, with uniform composition and high mechanical strength.

Calcium phosphate is another reagent that has been used for the release of Ca^{2+} ions to coagulate alumina suspensions stabilized in the acidic region with HCl (Xu *et al.*, 2012a). Calcium compounds formed in the alumina suspension release Ca^{2+} ions that will compress the EDL of the alumina particles and the suspension coagulates. Besides, the hydrolysis of hydrogenophosphate ionic species (HPO_4^{2-} and H_2PO_4^-) generates OH^- , which contributes to the pH shift to the IEP. The increase of the temperature of the suspensions will contribute to a rapid coagulation of the suspensions, due to faster release of Ca^{2+} ions.

The coagulation of alumina suspensions by the controlled release of Ca^{2+} from calcium citrate complex assisted by pH shift in the presence of glycerol diacetate has also been reported (Xu *et al.*, 2016). Alumina was added to a calcium citrate complex suspension obtained by mixing tri-ammonium citrate and calcium chloride. Afterwards the addition of glycerol diacetate (GDA) induced the coagulation of alumina in the chelated suspension, at different temperatures (40–70°C).

The release of Mg^{2+} ions from magnesium citrate and the pH shift in the presence of GDA has been also applied to the coagulation of stabilized Ytria-stabilized zirconia (YSZ) suspensions (Xu *et al.*, 2015). GDA hydrolysis reaction allows the decomposition of magnesium citrate, with the production of Mg^{2+} . Besides it will shift the pH of the YSZ suspensions and both those mechanisms will allow to process complex-shaped bodies.

Magnesium oxide (MgO) has been used by several authors as a coagulant agent. Alumina suspensions stabilized with ammonium poly (acrylate) (APA) were coagulated by MgO. Time-delayed in situ generated Mg^{2+} reacts with the dispersant, forming Mg-poly(acrylate), and shifting the adsorption equilibrium of the dispersant on the particles surface, with the consequent coagulation of the concentrated alumina suspension (Prabhakaran *et al.*, 2008, 2010). Fast coagulation with the increase in temperature by heating to 70°C may be due to an increase of the rate of reaction of MgO with the molecules of the dispersant, due to an increase in solubility of MgO and concentrating Mg^{2+} ions. These results were recently corroborated by other authors (Nair *et al.*, 2019) who performed similar studies.

The strength of wet-coagulated samples prepared by DCC-HVCI was found to be higher than that prepared by increasing monovalent electrolytes (urea). The coagulation mechanism of DCC-HVCI is the compression of electrical double layer by the high valence counter ions that lead to the close contact of suspended particles. During the process the aggregation of particles results in the shrinkage of the suspension and loss of water. The shrinkage rate decreases with increase in coagulation temperature which is similar to the effect observed in compressive strength. Large shrinkage rates mean strong aggregation of particles and water is squeezed out of the sample which leads to high green density and contributes to high compressive strength. Also, cracks are easy generated at high temperature and are detrimental to the mechanical properties of the green body. The increase of strength of dry samples with calcium iodate concentration may be due to the slow decomposition of excessive calcium iodate during drying processing.

Advantages and Limitations of DCC

In CICECO laboratory, high density ($\approx 60\%–80\%$) (MgAl_2O_4) green bodies were prepared by colloidal casting methods (slip casting (SC), DCC and Centrifugal Casting (CC)). (Curveira, 2008). Electrostatically stabilized aqueous suspensions with solids content varying between 50 and 65 vol% were prepared to produce samples by the three different casting techniques. Enzymatic decomposition of urea catalyzed by urease at room temperature was used in the direct coagulation casting via pH modification. Compressive strength measurements were performed on cylindrical samples of wet coagulated bodies with different enzyme concentration and coagulation time. Results of relative density after sintering showed that higher particle packing is promoted by DCC (relative density around 88%) and by centrifugal casting (around 97%), when comparing with slip casting (75%). Although nearly full densified samples were achieved by CC, differential settling is observed, creating density gradients along the bodies.

DCC was also applied in our laboratory in the study of the consolidation process of a porcelain slurry stable at pH ≈ 7.5 , promoted by the thermal activated self decomposition of D-glucorono-6,3-lactone (DGL) (Mota, 2011). The coagulation rate of processed bodies depends on slurry solid loading, temperature and DGL concentration. The results revealed that the thermal decomposition of DGL decreases the pH of the medium. A kinetic model based on a first order hydrolysis and dissociation reactions can describe the pH changes inside slurry due to the DGL thermal decomposition.

Conclusions

Basic concepts behind the DCC processing, and the developments introduced to improve the properties of the processed bodies are reviewed.

Direct Coagulation Casting (DCC) is an advanced ceramic powder compact forming process that has demonstrated the capability for fabricating complex near-net shapes. It is potentially advantageous to process dense, homogeneous bodies at low costs. In this paper the basic concepts behind this technique have been discussed, as well as the developments introduced. The coagulation of high concentrated stabilized slurries by the decomposition products of thermally activated hydrolysis of carboxylic acids have been analyzed in detail, with the interpretation of the factors influencing the hydrolysis reaction rate and weak acid dissociation.

Based on the combination of DLVO theory and Schulze-Hardy rule the coagulation of high solids stabilized slurries by divalent ions controlled release in the slurry, was also investigated.

DCC has been applied to a variety of ceramic materials (advanced as well to conventional clay-based). Comparing to slip casting the application of DCC to the processing of the same type of material has proved to produce bodies of better properties.

Although all of the potential advantages of this colloidal technique, as far as to the present knowledge of the authors, commercial applications have been initiated only for smaller productions of small pieces. For industrial applications there are still some drawbacks ought to be removed.

References

- Balzer, B., Gauckler, L.J., 2003. Chapter 5.5 – Novel colloidal forming technique: Direct coagulation casting. In: Sorniya, S., Aldinger, F., Claussen, N., *et al.* (Eds.), *Handbook of Advanced Ceramics: Materials, Applications, Processing, and Properties*. Volume 1: Materials Science. Academic Press; Elsevier Inc., pp. 435–458.
- Binner, J.G.P., McDermott, A.M., 2006a. In-situ acidification of electrosterically dispersed alumina suspensions: Effect of coagulant structure. *J. Mater. Sci.* 41, 1893–1903.
- Binner, J.G.P., Santacruz, I., McDermott, A.M., 2006b. Rheological characterisation of electrosterically dispersed alumina suspensions during *in situ* coagulation. *J. Am. Ceram. Soc.* 89 (3), 863–868.
- Binner, J.G.P., McDermott, A.M., Yin, Y., Sambrook, R.M., Vaidyanathan, B., 2006c. In situ coagulation moulding: A new route for high quality, net-shape ceramics. *Ceram. Int.* 32, 29–35.
- Chen, A.-N., Wu, J.-M., Liu, M.-Y., *et al.*, 2017. Rapid in-situ solidification of SiO_2 suspension by direct coagulation casting via controlled release of high valence counter ions from calcium iodate and pH shift. *Ceram. Int.* 43, 1930–1936.
- Curveira, P., 2008. Colloidal Processing of Aluminium Magnesium Spinel MgAl_2O_4 . MSc Thesis, University of Aveiro, (in Portuguese).
- Das, S., Mukhopadhyay, A.K., Datta, S., Basu, D., 2009. Prospects of microwave processing: An overview. *Bull. Mater. Sci.* 32 (1), 1–13.
- Dong, Y.L., Xu, F.M., Shi, X.L., *et al.*, 2009. Fabrication and mechanical properties of nano-/micro-sized $\text{Al}_2\text{O}_3/\text{SiC}$ composites. *J. Mater. Sci. Eng. A* 504, 49–54.
- Gauckler, L.J., Graule, T., Baader, F., 1999. Ceramic forming using enzyme catalyzed reactions. *Mater. Chem. Phys.* 61, 78–102.
- Lewis, J.A., 2000. Colloidal processing of ceramics. *J. Am. Ceram. Soc.* 83 (10), 2341–2359.
- Mota, L., 2011. Direct Coagulation Casting in the Processing of Porcelain Bodies. MSc Thesis, University of Aveiro, (in Portuguese).
- Nair, S.-L., Krishnan, R., Vijaya, S., Wilson, P., Prabhakaran, K., 2019. MgO calcination for easy direct coagulation casting of aqueous alumina slurries. *Ceram. Int.* 45, 5717–5723.
- Prabhakaran, K., Joseph, K., Sooraj, R., Durgaprasad, C., 2010. Magnesia induced coagulation of aqueous PZT powder suspensions for direct coagulation casting. *Ceram. Int.* 36, 2095–2101.
- Prabhakaran, K., Raghunath, S., Melkeri, A., Gokhale, N.M., Sharma, S.C., 2008. Novel coagulation method for direct coagulation casting of aqueous alumina slurries prepared using a poly(acrylate) dispersant. *J. Am. Ceram. Soc.* 91 (2), 615–619.
- Santacruz, I., Binner, J., 2008. Rheological characterization and coagulation casting of Al_2O_3 -nano zirconia suspensions. *J. Am. Ceram. Soc.* 91 (1), 33–40.
- Studart, A.R., Pandolfelli, V.C., Tervoort, E., Gauckler, L.J., 2002. In situ coagulation of high-alumina zero-cement refractory castables. *J. Am. Ceram. Soc.* 85 (8), 1947–1953.
- Vieira, P., 2009. Colloidal Processing of Al_2O_3 -SiC Nanocomposites – Direct Coagulation Casting. MSc Thesis, (in Portuguese).
- Xiao, H., Wu, J., Chen, A., *et al.*, 2017. Alumina fiber-reinforced silica matrix composites with improved mechanical properties prepared by a novel DCC-HVCI method. *Ceram. Int.* 43, 16436–16442.
- Xu, J., Gan, K., Yang, M., *et al.*, 2015. Direct coagulation casting of yttria stabilized zirconia using magnesium citrate and glycerol diacetate. *Ceram. Int.* 41, 5772–5778.
- Xu, J., Yang, M., Gan, K., *et al.*, 2016. Reliable high strength alumina fabricated by DCC-HVCI using submicron calcium citrate complex. *Ceram. Int.* 42, 8030–8037.
- Xu, J., Wen, N., Qi, F., Li, H., Yang, J., 2012a. Direct coagulation casting of positively charged alumina suspension by controlled release of high valence counter ions from calcium phosphate. *J. Am. Ceram. Soc.* 95, 2155–2160.
- Xu, J., Qu, Y., Xi, X., Yang, J., 2012b. Properties of alumina coagulated bodies prepared by direct coagulation casting via high valence counter ions (DCC-HVCI). *J. Am. Ceram. Soc.* 95 (11), 3415–3420.
- Yin, Y., Binner, J.G.P., Hey, M.J., Mitchell, J.R., 2006. Hydrolysis of carboxylic lactones in alumina slurries. *J. Eur. Ceram. Soc.* 26, 1171–1177.
- Yu, J., Yang, J., Huang, Y., 2011. The transformation mechanism from suspension to green body and the development of colloidal forming. *Ceram. Int.* 37, 1435–1451.

Extrusion

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Extrusion

Extrusion is a process where a material undergoes plastic deformation by the application of a force causing that material to flow through an orifice or die. The material adopts the cross-sectional profile of the die and if the material has suitable properties, that shape is retained in the final extrudate. The force required for this process is normally achieved by either a moving piston or rotating auger in a barrel. In the latter case the process is continuous and discrete parts are created by cutting the extrudate into pieces of a predefined length.

Extrusion of ceramic materials can be traced back to 1643 with the manufacture clay bodies and with commercialization being first reported for brick manufacture at the turn of the 19th century, [Reh \(2007\)](#). In terms of manufacturing volume and mass, clay based building products still account for the vast majority of items made by this shaping method today. Almost any ceramic material can be extruded if the process gives the required shape. Thus, ceramics extrusion is in principle a simple process, at least in concept. There are three key aspects to the process: a machine is required to generate the pressure (the extruder, piston or screw), a die is required to shape the material and a formulation is needed to render the ceramic powder or precursor plastically deformable.

The Extrusion Process and Material Examples

Pressure Generation

Piston extrusion

Piston or ram extrusion, where force is directly transferred to the paste or plastic body by movement of a piston within a barrel, is the simplest of approaches to generate the required pressure for extrusion ([Fig. 1](#)). Ram extruders are batch machines however, with appropriate feed systems; they can be refilled to give a cyclic but automated extrusion process. The piston or ram may be driven mechanically by lead screws or by hydraulics. Degassing the paste feed can be an issue in these machines, but a vacuum can be applied or air forced from the system by holding the paste under pressure in the barrel prior to extrusion. Ram extruders are able to generate pressure independently of the material properties giving them a key advantage over auger systems for some materials. As a result of this feature and their simple geometric movement, they are useful for precise work and material characterization.

Auger/screw extrusion

In screw extruders, the plastic body is transported by a screw configuration and the interaction between the material, the screw, and the barrel wall, cause the material to be conveyed and to develop pressure ([Burbidge and Bridgwater, 1995](#); [Botten et al., 2003](#)).

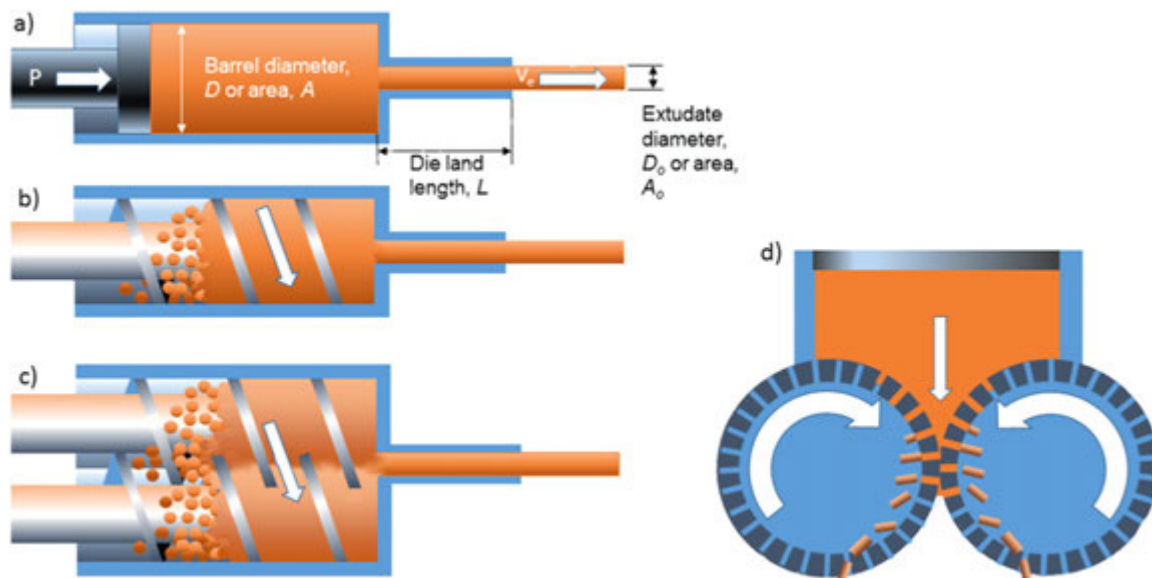


Fig. 1 A schematic of the extrusion methods, (a) ram extrusion, (b) single screw extrusion (c) twin screw extrusion (here co-rotating and intermeshing) and (d) roll extrusion. P is Pressure.

Thus, the amount of pressure generated is a combination of the material formulation, the geometry of the extruder and the pressure drop developed by the die. This means that not all materials can be extruded from certain designs of screw extruder however, when they work the major advantage of screw extruders is that they produce continuous extrudate.

There are two common forms of screw extruder, machines with single or twin augers. Single screw extruders are the most common and frequently found in the extrusion of clay bodies. They are often two-stage machines where the first auger compacts the material and passes it through a perforated plate into a vacuum chamber where the paste strands are degassed. A second screw/auger then re-compresses the paste and generates the pressure required to extrude the material through the chosen die. Mixing in single screws is limited, because the flow is plug-like within the screw channel between the flights. Twin screw extruders come in many forms and the screws may be co- or counter-rotating and non-intermeshing or intermeshing. Intermeshing co-rotating twin screws are capable of generating pressure where other systems would fail to do so. This is due to them being able to develop positive pressure if the screws are configured appropriately. They can, by the appropriate selection of the screw and kneading elements, be used to mix the formulation into a paste before extruding it. This combined mixing and extrusion is perhaps most commonly practiced in catalyst manufacture.

In other extrusion systems, for example, in the field of catalyst manufacture, it is possible to generate pressure by roll extrusion where the paste is squeezed into the nip of two counter-rotating perforated rolls ([Fig. 1](#)). This allows the manufacture of short extrudate sections at extremely high throughput rates.

The Die

The main function of the die is to create the required cross-sectional shape and generate a pressure drop. The entrance can be shaped to ease flow and reduce or eliminate dead-zone formation. [Patel et al. \(2007\)](#) shows that a well profiled entry can reduce defects and phase migration (see later sections). Anything more complicated than a simple solid rod will require the die to have cores in place (sometimes called mandrels) and they will need to be supported by bridges (sometimes called spiders). This is true for the simplest tube to the most complex honeycomb designs.

Paste Formulation

Manufacturing cycle

When considering manufacture by extrusion it is important not to think only of the extrusion process itself but also of the full process cycle, which includes: solid particle preparation and conveying, dry mixing, wet mixing, pugging (kneading), degassing, die extrusion, extrudate (exiting material) handling, cutting; drying and firing/calcining. For brevity in this review, we consider only aspects which specifically influence the extrusion process. The reader is referred to other works such as [Onoda and Hench \(1978\)](#), [Funk and Dinger \(1994a\)](#) and [Rahaman \(2017a\)](#) for a broader description.

Requirements

Before delving into how to design and make a paste it is worth stating what properties are important in extrusion. For processing, a ceramic paste should be:

- *Shear thinning*: This property is almost always encountered in pastes if an appropriate particle packing and solids loading are used. During processing material undergoes a transition from highly “viscous” to less ‘viscous’ meaning that pressure does not rise monotonically with increasing extrusion speed. After extrusion the paste should recover its initial high “viscosity” (*viscosity used here to define consistency, not a measured value*) almost instantaneously. Further the paste may exhibit an apparent yield which, again if recovered rapidly, is an advantage for shape retention. Should the material exhibit slow recovery of the original properties (thixotropy), this can lead to problems with handling after extrusion.
- *Slip at the wall*: [Benbow and Bridgwater \(1993\)](#) indicate that because a fluid maldistribution develops at the interface between the paste and the extruder wall, that slip occurs. Wall slip can be exploited to ease extrusion and reduce wear, for example by:
 - Introducing fluids at the wall
 - Inducing fluid migration to the walls

However, it can also be detrimental, as it can prevent the forward conveying of the paste in a single screw extruder or in extreme cases cause the extrusion process to fail as the pressure drop in the system increases through fluid drainage.

- *Stable under a range of shear conditions*: In a good formulation the pressure should not change with time as the extrusion process continues (i.e., reasonably large processing window). The components of the paste should remain uniformly mixed without phase separation (no gross liquid maldistribution).
- *Stable after extrusion*: In essence the paste should have a sufficiently high yield stress or apparent viscosity to not slump under its own weight, [Benbow and Bridgwater \(1993\)](#).

These aspects are of course desirable but in formulating a paste the properties of the final product must be considered and so frequently a compromise is required between what is necessary for optimal extrusion and product performance.

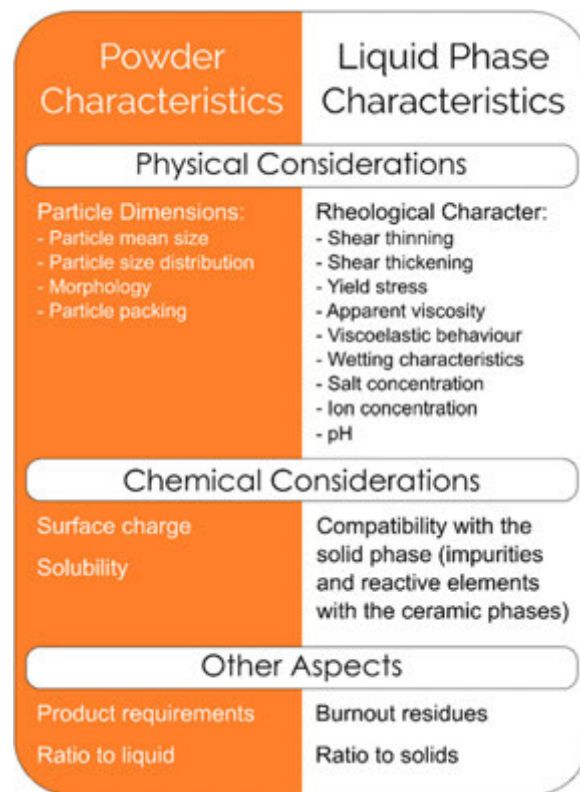


Fig. 2 Some important factors which influence the behavior of pastes.

Basic formulation

Paste formulations comprise two main components: the ceramic precursor powder and binding liquid. The simplest of all systems would be a clay water suspension where the interaction between the clay particles and the water are sufficient to impart the required plasticity. However, for most materials, they require some further additions to render the mix plastic. Some factors which influence the characteristics of a paste are summarized in [Fig. 2](#).

Particle packing

If the liquid phase is fixed in composition then for any given powder volume addition it is particle packing that imparts the greatest rheological change to the paste. Many studies on particle packing refer to the packing density, which describes the ratio of the volume of solids (particles) to the total volume of the arrangement (particles with voids between them). In random packing, the packing fraction is typically 0.635–0.640 for mono-sized spheres but it is probable that in real systems with interactions between the particles this value falls to 0.57–0.61 and is termed loose random packing, [Rahaman \(2017c\)](#). In this arrangement the particles would be in direct contact and as a consequence the frictional forces would be high if the mass was sheared with a liquid volume sufficient to fill just the voids. [Blackburn and Wilson \(2008\)](#) indicate that in conventional extruded products an excess of 2–5 vol% of the binding liquid is typically added to allow flow. This will decrease the solids loading of the extrudate slightly.

The remarks on solid-liquid ratio hold true even when the particle packing density is increased. In practice packing density can be increased by using wider particle size distributions and typically bi- or tri-modal particle size distributions are used to illustrate this behavior. As smaller particles fill the voids between the larger ones, less binding liquid will be required to fill the interparticle voids and to have the same free fluid to allow flow. Increasing the packing density of the solid phase has several advantages:

- The body will have higher green density on drying. With less binder to remove defects can be reduced to give denser bodies.
- Phase migration (paste stability in flow) will be reduced as the free path for the separation mechanism is reduced.
- The same rheological character can be achieved by reducing the liquid content. Alternatively for the same liquid phase content the flow at the same velocity will require commensurately less force.

A number of equations have been derived to predict the relationship between the relative viscosity and the incorporated solids loading as described by [Rutgers \(1962\)](#). Nevertheless, the majority of them are derived for hard spheres; any colloidal, electrostatic or steric interactions are not included and thus a divergence from the experimental plots has been observed, especially for high solids loading as described by [Mew and Wagner \(2012a\)](#). Some of the popular relationships for hard spheres that the reader may encounter are the Krieger-Dougherty and Chong equations, the former described in [Blackburn and Wilson \(2008\)](#). These equations

do not offer an explanation for shear thinning behavior of pastes as they only consider viscosity; the changes in voidage brought about by flow of non-spherical powders as they align are not incorporated either.

Particle packing is clearly influenced by particle shape. A perfect spherical morphology is assumed in most of the calculations and the real packing density with irregular particle shapes is lower than the spherical prediction (see sphericity or relative roundness and particle roughness in [Rahaman \(2017c\)](#) and [Shinohara \(1997\)](#)). A more dense packing could be realized by mixing different morphologies of significantly different size, [Rahaman \(2017c\)](#), [Blackburn and Wilson \(2008\)](#), [Shinohara \(1997\)](#), [Brouwers \(2006\)](#), [German \(1989\)](#) and [Blackburn and Böhm \(1994\)](#). One of the simplest ways to mitigate high viscosity during processing is to use powders with wide particle size distribution and obtain a homogenous distribution of particles throughout the specimen (which might be detrimental to sintering). This is discussed further in the following section.

Designing paste formulations

The final formulation of the paste will require accurate control of the liquid content as small variations can significantly affect the flow characteristics. For pastes formulated directly to the final composition, the proportion of binder must be determined. An estimate of the required liquid volume can be established by the so called Water Adsorption Test (WAT). A small amount of powder (2–4 g) can be mixed manually with predefined amounts of demineralized water numerous times. Formation of a paste-like mass is assessed by visual and physical inspection. With this approximate water content a larger mass can be prepared generally reducing the number of trials to reach the required consistency. Preparation of pastes with different liquid contents allows a plot of a reciprocal of pressure for a given ram speed against a ratio of the binding liquid to the powder to be constructed. Through extrapolation to the solids loading axis – indicating an infinite pressure – the minimal required liquid content can be identified, this approach is described by [Blackburn and Wilson \(2008\)](#), [Clemens et al. \(2007\)](#) and [Blackburn and Böhm \(1994\)](#). It is commented on by [Benbow et al. \(1987\)](#) and [Blackburn and Böhm \(1993\)](#) that this extrapolation shows an approximate linear relationship in this setting but the reasons behind this behavior are not yet fully explained.

Particle size distribution – Adjustment by modeling

The particle size distribution can be adjusted to lower the paste viscosity. There are some competing aspects to consider in any discussion of mixing particles of different size. There will be reducing returns as more distributions are combined in terms of increasing packing density and thus reducing viscosity for a given liquid content, each particle in the system would need to be placed in an ideally shaped void to achieve substantial improvement, [Shinohara \(1997\)](#) and [Rahaman \(2017c\)](#). Furthermore, although the density of the resultant green body will increase this may not be an advantage to the final sintered product as it may promote, for example, abnormal grain growth and/or not give the required microstructure. Of course these statements are very general and each product will have its own issues. [German \(1989\)](#) and [Brouwers \(2006\)](#) state that bi- or tri-modal size distributions should contain particles that differ in size by at least 7 times between each neighboring modality to give optimum results. The ratio between two different sized powders is termed R . This minimum size difference value comes from the requirement for the particles to sit discreetly in the structure such that the smaller fraction does not affect the packing of the larger one. This concept was first described in the works of Furnas (citation of Furnas' works available in [Brouwers \(2006\)](#)). Equations to calculate bimodal packing density and the remaining porosity with this assumption yield:

$$f_2 = f_1 + (1 - f_1)f_1 \quad (1)$$

$$\Phi_2 = 1 - f_2 = (1 - f_1)^2 = \Phi_1^2 \quad (2)$$

where f_1 and f_2 are the packing densities of the mono-sized and bimodal mixture, respectively, and Φ_1 , Φ_2 are the interstitial pore fractions for the respective packing densities. An example of this calculation is provided by [Rahaman \(2017c\)](#). Here it is worth pointing out the apparent increase in the packing density as the ratio of the size of large particles to small particles tends to infinity. The aforementioned assumption of non-disturbance holds with the minimum ratio values of 7–10. There are modifications which provide solutions when the particles interact, where the smaller particles influence the effective volume, and therefore the packing density, of the larger particles. For this reason [Karlsson and Spring \(1970\)](#) modified their initial approach and accounted for the change in the volume for bimodal mixtures, when even a miniscule inclusion of the finer particles causes an expansion. [Blackburn and Böhm \(1993,1994\)](#) demonstrate good agreement in pastes containing alumina and alumina with glass fibers when applying these principles.

In most real situations changing the particle packing comes from mixing continuous size distributions, as discrete monodispersed fractions are rarely encountered. This is reflected in the models created to calculate idealized distributions. One of the most popular approaches to calculating ideal particle size distributions stems from the Andreassen equation, [Andreassen and Andersen \(1930\)](#), [Rahaman \(2017c\)](#) and [Sutcu and Akkurt \(2007\)](#), modified by [Funk and Dinger \(1994a\)](#):

$$F_M(D) = \frac{D^n - D_S^n}{D_L^n - D_S^n} \quad (3)$$

where $F_M(D)$ is the cumulative mass fraction of particles finer than a size D (also called cumulative volume percentage finer – CVPF), D_L is the largest particle size in the distribution, n is an empirical constant (fitted numerically) and D_S is the minimum particle size in the distribution. The n exponent that is fitted to the equation has no physical explanation and derivations such as one presented by [Zheng et al. \(1990\)](#) have attempted to mitigate the issue. This approach led to defining n as:

$$n = -\log \Phi / \log R \quad (4)$$

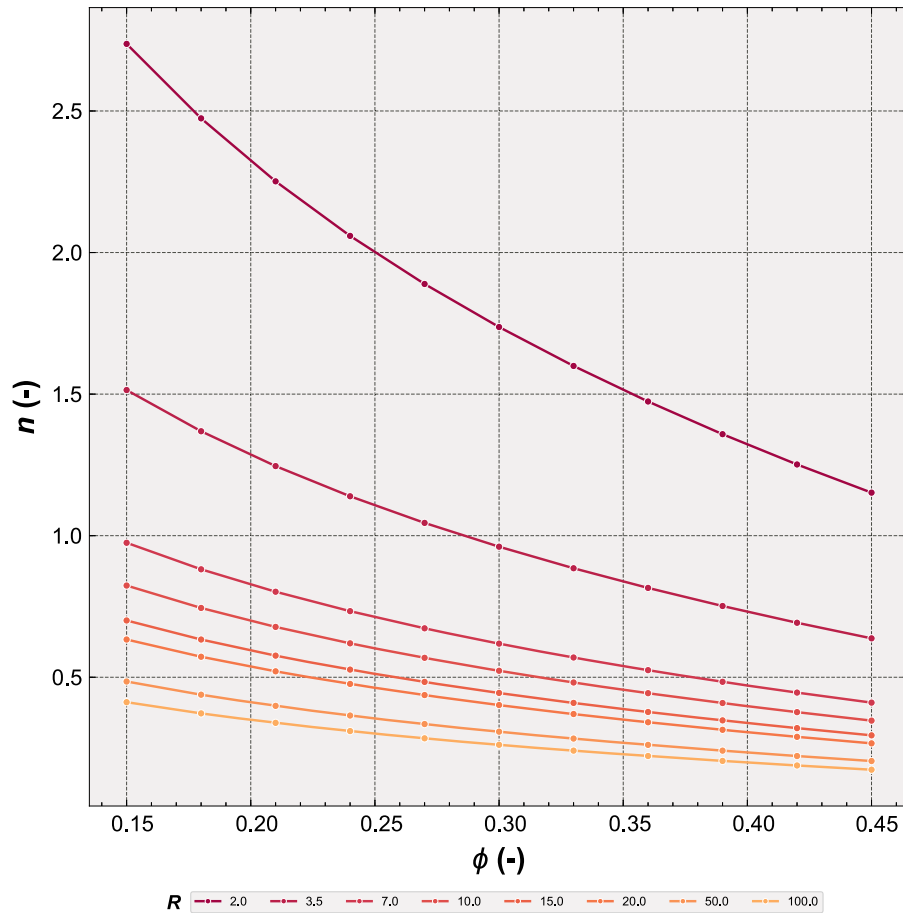


Fig. 3 The exponent n calculated for different values of interstitial pore fraction ϕ and size ratios R . The lower the pore fraction (the higher the packing density), the greater the differences between each size ratio (n value).

where Φ is the interstitial pore fraction and R the size ratio for the packing of the system. The original work by Andreasen predicted values of n between 0.3 and 0.5 whereas 0.37 was predicted by the Dinger-Funk particle size distribution, [Zheng et al. \(1990\)](#). n has lower values with the increasing size of particles due to larger pore fraction present between them. What directly follows is that the calculations of CVPF (Eq. (3)) indicate larger amounts of finer particles are needed for optimal packing. As shown by [Yu et al. \(1997\)](#) the evaluation of the exponent value from the Dinger and Funk equation can differ for non-idealized situations. In their study the lowest porosity was shown to be for $n > 1$. The discrepancy when compared with the previous works is ascribed to the agglomerates forming in the mix; models like the one presented by [Yu et al. \(1996, 1997\)](#) consider more realistic descriptions of empirical examples. The aforementioned minimum size ratio of 7–10 between particles can be easily justified by drawing a graph for each given size ratio R : the calculated values of n plotted against the assumed voids volume or packing density. Starting from $R = 7$ the differences between higher size ratios with regard to the value of the exponent n at the same values of void ratios start to disappear, as shown by [Fig. 3](#). In practice, the model described by [Funk and Dinger \(1994a\)](#), yields the optimum particle size distribution for a given particle size range and packing density.

In conclusion the packing density might seem to constitute a good basis for high quality components predictions and to a large extent it does. Unfortunately the second important factor is the uniformity of the particle spatial distribution – changes in the fractional density across the specimen. [Burk and Apte \(1987\)](#) show that with wide distributions, there is a higher degree of inhomogeneity in terms of density that scales proportionally with the width of the particle size distribution. [German \(1989\)](#) states that most of the models do not account for this aspect. This phenomenon may pose a significant issue during sintering when the densification can cause significant differential strains in the component. The solution requires good and efficient mixing.

Mixing

Mixing plays an important role in paste formulation. While extrusion can create its own defect forms (Section “Extrusion Defects”), if the feed itself is not properly homogenized, then mixing defects will arise which can significantly influence the final properties of the ceramic. There are essentially two main routes to preparing extrudable highly loaded suspensions: the first is preparation from a suspension with lower solids loading by either removal of the fluid phase to the required paste liquid concentration, phase

change or induced rheological change and the second is preparation by forcing the ingredients to mix at the required concentration.

Any ceramic system of interest can be dispersed using colloidal chemistry techniques in combination with a mixing system (often ball milling or some form of a stirred tank) to generate a low viscosity, agglomerate free suspension. With clay based systems such as porcelains for insulators, the suspension or slip can then be dewatered by filtration. The filter cake which is produced can be sufficiently plastic to allow extrusion if the liquid phase content is controlled. The method has also found favor in high purity ceramic extrusion where ultra-clean sols are conditioned, gelled and dewatered to give an extrudable paste. When pushed to the limits of practical processing high strengths are attained. For example zirconia-toughened alumina extrudates with strengths in excess of 1.2 GPa have been reported by *Kaya and Butler (2003)*. This technology is also used to make high surface area γ -alumina catalyst supports, *Winstone (2011)*. Even in these systems mechanical mixing is required and here the body of literature developed in colloid and chemical engineering science can be useful in designing an efficient and defect limiting production line. There have been a number of papers which have essentially used elements of the direct coagulation casting process (*Graule et al., 1996; Baader et al., 1996; Gauckler et al., 1999*) to develop paste materials. In these a highly concentrated but dispersed suspension is formed and the paste is developed by either changing the pH or the electrolyte concentration. By way of example *Davies and Binner (2000)* produced alumina slurries at around 50 vol% with ammonium polyacrylate and then coagulated the system using ammonium chloride. *Pagnoux et al. (2006)* used a commercial anionic polyelectrolyte with sulfonate and carboxylate functionalities to stabilize an alumina powder and then a cationic polymer (chitosan) to complex with the ionic stabilizer to coagulate the system in situ, followed by extrusion.

For many applications the system may separate on filtration leading to performance issues. Thus it is common to mix the formulation ingredients directly to the final formulation. The order in which the various components are added as mixing continues is perhaps a matter of preference and/or practice. For example should the powder be added to the liquid or the liquid to the powder? It is possible to make the binder system and add that liquid to the insoluble particles or add the particles to the binder system. Generally, in the authors' experience the former is more successful at dispersing agglomerates as the initial material is rather stiff. One should think of it like making a roux in the preparation of a white sauce, there is a good reason why this has been practiced by chefs; it stops the paste being lumpy. Alternatively all the dry ingredients, including some of the solid binder phases which are subsequently solubilized, can be pre-mixed and then the solvent added. When taking these approaches the mixer needs to be rather robust, Z-blade and planetary mixers are used as well as calendar rolls. Generally, they all have high levels of material deformation but the rate at which that deformation is applied, be it elongation or shear, is relatively slow, such that shear rate might be described as moderate. The greater the degree of shear or elongational strain applied the better in most cases, though some materials can be sensitive to this aspect (catalysts for example). It can be shown that elongation is better than shear at mixing pastes and the reasons for this are demonstrated mathematically by *Cogswell (1981)*. A comparative table of mixers for plastic forming (kneaders) is presented by *Takahashi (2006)*, where classifying factors such as particle size, viscosity, power and kneading capabilities are used.

There are two main aspects to mixing that should be considered: (1) how well does the system disperse the ingredients (breakdown the agglomerates and generate homogenous system on a micro-scale) and (2) how well does the system ensure uniformity throughout the mixed body, known as distributive mixing. Ram extrusion and single screw extrusion are not good distributive mixers due to them running predominantly in laminar and plug flow. Dispersive mixing will of course occur as the material is forced from the barrel through the much smaller die, *Böhm and Blackburn (1994a,b)* and *Wildman and Blackburn (1998)*. Co-rotating intermeshing twin screw extruders can be used as very effective paste mixers because they can have kneading and hold up elements incorporated in the screw design. Twin screw extrusion where the mixing is undertaken penecontemporaneously to extrusion is not commonly practiced in general ceramics but has found application in catalyst support manufacture. The mixing performance of these systems has been evaluated by a number of workers and it has been shown that highly efficient mixing is possible if the flight geometry and hold up are optimized, see for example, *Edirisinghe and Evans (1986)*, *Diemer et al. (2011)*, *Wei et al. (2014)*, *McGuire et al. (2007)* and *Onoda and Hench (1978)*.

Paste additives

As mentioned in Section "Basic formulation" the plasticity of pastes prepared with powders other than clays can pose significant problems. A major issue is liquid phase migration which if extreme can lead to equipment damage due to a rapid and sudden increase in pressure. To prevent such issues and improve the overall paste-like, plastic behavior, a number of additive types are commonly incorporated and these include binders, surfactants, plasticizers and lubricants (*Hölzgen and Quirmbach, 2007; Onoda and Hench, 1978*). The function of these is described in the following paragraphs:

- *Binders (thickeners)* are added to improve the coherence of the paste usually by increasing its yield stress. They influence the rheology of the binding liquid by raising its viscosity, preferably transforming it into a shear thinning fluid, *Onoda (1978)*. Generally, a shear thinning liquid aids flow at higher extrusion rates and helps retain shape in the final extrudate. However, *Collomb et al. (2004)* show that care must be taken when imparting such behavior as liquid phase migration may increase to a significant level when the shear thinning exponent is too low. The fluid consistency, κ_s (see *Eq. (6)*), also plays a role and can decrease the process speed value at which phase migration occurs, acting to counter the shear thinning advantage or possible disadvantage.

The choice of the binder is related to the type of imparted stabilization at the particle level (electrostatic, steric or electrosteric) and compatibility with a given paste system, when both the molecular and final product properties are considered. A simple guide

for binder selection is to consider the following aspects: solubility of the binder, its burnout behavior, compatibility with other additives (e.g., dispersants) and its rheological behavior (the shear rate, temperature and – in undesirable cases – time dependence). To simplify the selection even further, it is possible to classify the binders according to their viscosity by arbitrarily assigning viscosity levels for grading, based on the concentration equivalent required of each grade to substitute the other. With categorized binders it is possible to calculate the binder content with Eq. (5):

$$b = \left(\frac{100 - f}{f} \right) \left(\frac{\rho_L}{\rho_B} \right) \frac{\gamma \log \mu}{100(V_B/V_S)} \quad (5)$$

where b is the parameter describing the viscosity grade of a binder, f is the packing density of the powder, ρ_L the density of the liquid, ρ_B the density of the dry binder, γ – liquid saturation of the voids (ratio of the liquid used and voids volume), μ – the dynamic binder viscosity (~ 100 Pa s for extrusion, Onoda (1978)), V_B and V_S are binder and solid volumes, respectively. The fundamentals and examples of this methodology are given by Onoda (1978) and a modern description of organic binders is given by Rahaman (2017b).

Examples of common binders include: methyl cellulose (and many other cellulose derivatives such as hydroxypropyl methylcellulose), bentonite (clay), polyethylene glycol, boehmite peptised with nitric acid, ammonium polyacrylate, polyvinyl alcohol, glycerin and guar gum (Blackburn and Wilson, 2008; Onoda, 1978; Rahaman, 2017b). There are many others gums and resins that exhibit similar behavior. Many binders could be used for the same core powder as evidenced in the review by Blackburn and Wilson (2008) but their compatibility in the final component (in a commercial setting) may be quite different from the processing compatibility.

- *Surfactants* are compounds that affect interfacial interactions between particles and liquids. The resultant wetting by the liquid is increased and may cause changes in the total amount of liquid required to impart plasticity. Surfactants tend to be compounds with hydrophobic and hydrophilic ends (Hölzgen and Quirnbach, 2007).
- *Plasticizers* are materials that have the ability to decrease the yield stress by preventing the binder from creating bonds; the result is increased flexibility (a softer binder). Examples include glycerin, polyethylene glycol, polypropylene glycol and propylene glycol (Onoda, 1978).
- *Lubricants* are classified according to the type of lubrication they provide: this may be internal between the particles or external, with regard to interaction with the containing surfaces. Lubricants decrease the overall pressure by aiding materials sliding. Examples include fatty acids and polyethers (Hölzgen and Quirnbach, 2007).

It should be noted here that there is an emerging field of particulate suspensions with relatively low solids loading of 15–45 vol%, where the formulations are enhanced by secondary immiscible liquid additions with either better or worse wetting capabilities than the main liquid. A number of workers have investigated the possible implications of this including Koos and Willenbacher (2011), Schneider *et al.* (2017) and Danov *et al.* (2018). In the most recent study by Weiß *et al.* (2019) this technique was tested by extruding such formulations with a twin screw extruder. Although the apparent yield stress increase achieved with these compositions may provide enough plasticity for the extrusion process, it is somewhat doubtful that it would be sufficient for the post-extrusion handling (see the yield stress description in the next section).

Characterization of Paste Formulations

General Characterization

Physically extrudable pastes lie in narrow region of the possible liquid solid ratios that can be formulated. They are concentrated suspensions in which the solids loading in combination with the interactions between the particles and the fluid lead to the material exhibiting an apparent yield stress yet exhibit the ability to flow without excessive damage to the equipment being used. The consequence of this is that these materials require some thought in terms of how to quantify their behavior. The materials exhibit some aspects of solid behavior and some of fluid. Conventionally the tests for the material's suitability for extrusion have focused on simple physical tests and on the determination of plasticity. There are a number of tests for plasticity such as indentation, primarily used to determine yield (Benbow and Bridgwater, 1993), torsion (Chandler *et al.*, 2002; Vandeneede *et al.*, 1997) and unconfined compression (Norton, 1970). They generally apply a load either statically or sinusoidally and measure the deformation of the body. The values quoted tend to be specific to the test. A common index is workability which is measured during the axial compression of a billet, defining the maximum stress before failure or fracture occurs, as described by Norton (1970). The complexity of measuring the flow has been highlighted by Chandler *et al.* (2002) in discussing the constitutive laws and the common tests employed to measure paste materials. In order to determine the true constitutive behavior, techniques such as confined triaxial testing, can be applied and these have been shown to be useful in developing computer simulations. Most of these methods could be considered to measure small deformation increments and extending them to large scale deformation can be undertaken through computer simulation (Patel *et al.*, 2017). They can yield interesting data on the structural development during the extrusion process but are generally computationally intensive (Patel *et al.*, 2007).

As a consequence of some of the limitations encountered in using the methods outlined above it is logical to evaluate the material in the extrusion environment. Capillary rheometry (ram extrusion) clearly represents the process of extrusion closely but it does have its limitations as the boundary conditions are not necessarily known, Gleißle and Graczyk (2007), ASTM International (2017). In these experiments, pressure is recorded as a function of flow rate for a given die of circular cross-section. Several such

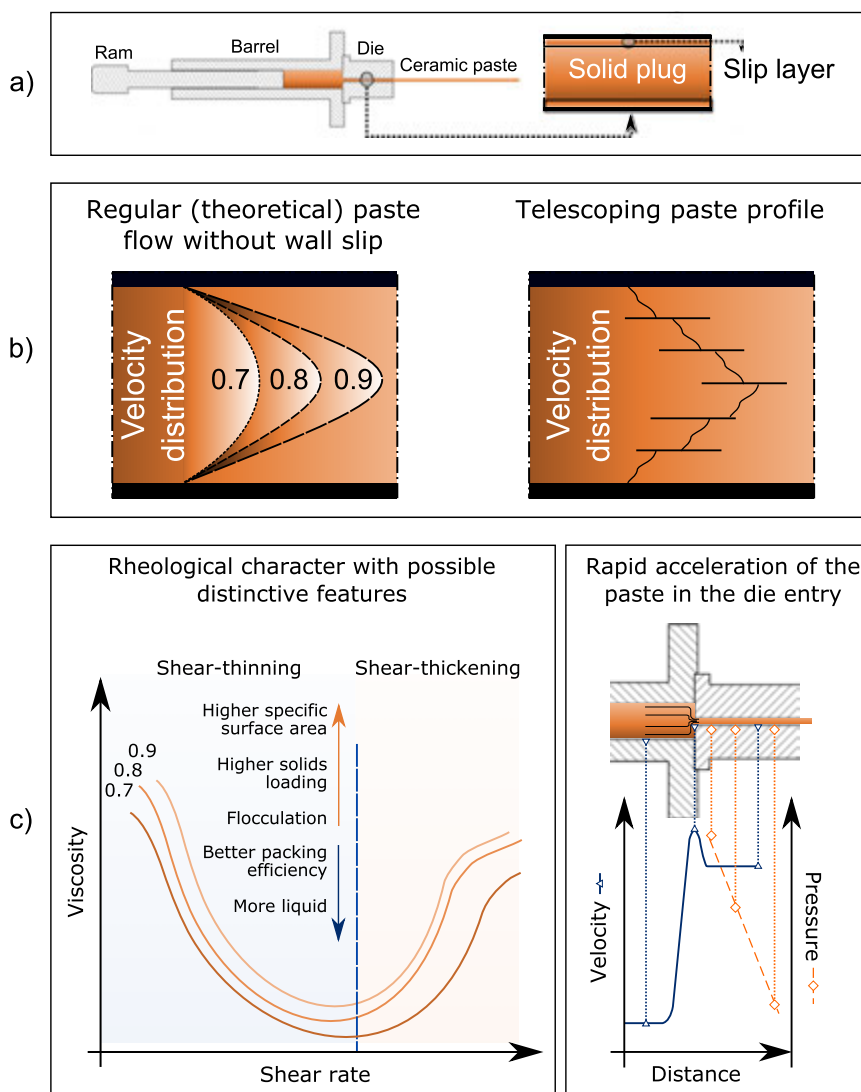


Fig. 4 Flow behavior of pastes: (a) schematic of plug flow in a ram extruder, (b) paste flow profiles without wall slip and the telescoping profile which may develop in the flow of non-uniform bodies, (c) the flow behavior based on solids concentration and the expected pressure and velocity profile in the barrel and die regions of a ram extruder. 0.7, 0.8 and 0.9 are the shear thinning indexes for the shear thinning region only; possible shear thickening region after critical shear rate. Figure developed from the texts of Barnes, H.A., Hutton, J.F., Walters, K., 1989. *An Introduction to Rheology*. Oxford: Elsevier. Barnes, E.C., Wilson, D.I., Johns, M.L., 2006. Velocity profiling inside a ram extruder using magnetic resonance (MR) techniques. *Chemical Engineering Science* 61 (5), 1357–1367. Benbow, J.J., Jazayeri, S.H., Bridgwater, J., 1991. The flow of pastes through dies of complicated geometry. *Powder Technology* 65 (1–3), 393–401. Chhabra, R.P., Richardson, J.F., 1999. Flow in pipes and in conduits of non-circular cross-sections. In: Chhabra, R.P., Richardson, J.F. (Eds.), *Non-Newtonian Flow in the Process Industries: Fundamentals and Engineering Applications*. Oxford: Butterworth-Heinemann, pp. 73–161. Funk, J.E., Dinger, D.R., 1994b. Viscosity and rheology. In: Funk, J.E., Dinger, D.R. (Eds.), *Predictive Process Control of Crowded Particulate Suspensions: Applied to Ceramic Manufacturing*. Norwell: Kluwer Academic Publishers, pp. 235–252. Funk, J. E., Dinger, D.R., 1994c. Practical rheology. In: Funk, J.E., Dinger, D.R. (Eds.), *Predictive Process Control of Crowded Particulate Suspensions: Applied to Ceramic Manufacturing*. Norwell: Kluwer Academic Publishers, pp. 327–371. Funk, J.E., Dinger, D.R., 1994d. Extrusion and extruders. In: Funk, J. E., Dinger, D.R. (Eds.), *Predictive Process Control of Crowded Particulate Suspensions: Applied to Ceramic Manufacturing*. Norwell: Kluwer Academic Publishers, pp. 517–546.

tests with barrels and dies of different diameters (and lengths for the latter) give a succinct description of the behavior of the bulk material. The underlying assumptions of the technique are:

- The paste is incompressible,
- The paste is homogeneous and unchanging with time,
- Laminar and steady flow is developed,
- That at the wall there is either no slip (conventional liquid assumption) or pure slip (conventional plastic assumption).

All of these assumptions are subjects of debate as practical tests have shown high variability and interpretation can be challenging. The following discussion considers some issues that arise when examining capillary data and Fig. 4 gives a pictorial aid to the concepts being described.

Yield stress

Zheng *et al.* (1992) states that depending on the definition, yield stress can be identified as the stress at which flow starts. In capillary flow this can be identified by extrapolation of the flow data to zero flow rate or shear stress depending on the adopted approach. It is important to note that usually the assumption of uniformity fails and the measured yield stress values are different in different tests even when the tests are scaled with constant part dimensions ratios (barrel to capillary diameter ratio and capillary length to its diameter ratio), Khan *et al.* (2001) and Bryan *et al.* (2017). The existence of a yield stress is not argued for or against here but due to the wide acceptance of its applicability in the engineering field of extrusion, with materials being characterized more commonly on a macro-, rather than a micro-scale, it is included. It is interesting to note that when the data is fitted by using curve fitting routines it is common to find no yield stress but an extremely strong power law relationship. The reader is referred to works that discuss this property at length: Zheng *et al.* (1992), Barnes and Walters (1985), Coussot (2014) and Barnes and Nguyen (2001). For engineering purposes, the value of the yield stress for ceramic pastes should be equal to a certain minimum required to retain shape after extrusion. Some authors like Toutou *et al.* (2005) and Khelifi *et al.* (2013) cite 0.02 MPa, others like Blackburn and Böhm (1994) indicate 0.2 MPa. These differences stem from the requirements of the applications being considered. Here it is recommended taking both the geometric complexity and overall size of the final component into account. Shapes like solid rods can be close to the lower boundary, whereas hollow tubes and catalysts with flow channels will need to be close or higher than the latter value. The maximum is dictated by the lack of lubrication at the die wall – this is easily distinguished by strong discoloration present on the extrudate after extrusion. According to Blackburn and Böhm (1994) this occurs when the paste yield is above 2 MPa.

Liquid phase migration

Liquid Phase Migration or Liquid Phase Maldistribution (LPM) is the separation of the binding liquid from particles under an applied pressure and the flow experienced in extrusion. The assembly of particles may be thought of as a filter bed (moving slowly) through which the liquid may pass if the conditions are favorable. The phenomenon may lead to process failure through overpressure as the paste becomes depleted in liquid via drainage. This process is generally considered undesirable in the extrusion of ceramic pastes (Benbow and Bridgwater, 1993; Blackburn and Wilson, 2008; O'Neill *et al.*, 2016; Bardsley and Bridgwater, 2012; Chen *et al.*, 2000; Chen *et al.*, 1997) and other materials (Bayfield *et al.*, 1998; Wilson and Rough, 2012). On the other hand some liquid flow to the walls can help by providing lubrication. Looking at the literature on filtration, it becomes apparent that phase migration can be minimized by increasing the viscosity of the fluid and/or by reducing the effective porosity. Reducing the porosity increases tortuosity of the channels through which the fluid can flow. By these actions and operating the system close to the minimum fluid volume to avoid bed compaction the liquid tends not to separate from the solid (Benbow and Bridgwater, 1993; Collomb *et al.*, 2004; Draper *et al.*, 1999).

Wall slip

Wall slip is a phenomenon of wall depletion, where due to the higher particle concentration near the flow axis there is a gradient of both solid and liquid contents in the capillary cross-section, particularly as the wall of the extruder is approached. This is caused by different shear stress at the wall and in the center of the capillary, the particles will naturally flow away from a region of high stress at the wall to the region of lower stress in the center. Furthermore as the particles can only approach the wall by point contact there will be a lower volume of solids within half a particle diameter of the wall. Mooney (1931) developed an analysis to quantify the contribution of slip to the overall flow, which is described by Mewis and Wagner (2012a,b). A slip layer therefore exists between the solid boundary and the material inside the die. This layer has a macroscopic non-zero velocity (apparent slip velocity), therefore violating the no-slip condition present in fluid mechanics, for example in Hagen-Poiseuille equation (Fox and McDonald, 1994a,b). There have been attempts at calculating the thickness of the slip layer and its velocity (Khan *et al.*, 2001; Cloitre and Bonnecaze, 2017). Improvements by Jastrzebski (1967), in the form of capillary diameter dependence have been criticized by Martin and Wilson (2005) and Tikhonov regularization has been proposed as a more valid method for wall slip assessment. Even with these refined approaches there are experimental results that show capillary diameter dependence, see Mewis and Wagner (2012b) and citations therein. To eliminate wall slip, roughened surfaces of the die in a capillary rheometer can be utilized. The roughness should be at least equal to the smallest particle size. Where there is a significant difference between the smooth and the rough results, slip can be assumed responsible (Cloitre and Bonnecaze, 2017; Coussot, 2005). Another way of mitigating this effect for ceramic pastes is to impose higher stress upon the paste (higher volumetric flow rate) so that the wall slip is insignificant compared to the bulk flow (Coussot, 2005). Although this phenomenon is detrimental to the quality of measurements it can be exploited to aid the extrusion process by improving sliding of the material on surfaces (a somewhat self-induced lubrication, (Wilson and Rough, 2006)).

Binding liquid and paste characteristics

There is an intimate link between the nature of the liquid and the resulting paste properties and this relationship can be evaluated by capillary rheometry. Calculating the ratio of pressure for the paste to the pressure for the binding liquid and plotting it for different ram speeds can reveal if there is an ongoing interaction between them, Benbow *et al.* (1998).

Air bubble inclusion

This breaks the assumption of paste uniformity and incompressibility. These can be identified on pressure-extension velocity plots when there is a sudden local pressure drop at a constant ram speed, [Amarasinghe and Wilson \(1998\)](#).

Mixedness

Capillary data will be influenced by the mixedness of the paste being analyzed. Not only from the noise within the data, but also it is common to see unexplained non-standard behavior as the paste changes while being extruded.

The calculations and the methodology pertaining to the capillary rheometry is available in several texts: [Benbow and Bridgwater \(1993\)](#), [Cogswell \(1981\)](#), [Draper et al. \(1999\)](#), [Morrison \(2001\)](#), [Williams \(1999\)](#), [Chhabra and Richardson \(1999\)](#), [Gleißle and Graczyk \(2007\)](#), [ASTM International \(2017\)](#) and [Mewis and Wagner \(2012b\)](#). Typical plots for ram extrusion (capillary rheometry) with explanations are presented by [Gleißle and Graczyk \(2007\)](#).

Paste Behavior in Mathematical Expressions

The behavior of paste-like materials can be quantified mathematically using various equations. The first thing to consider is what is going on at the wall of the extruder. If the paste is treated as a uniform continuous fluid then the initial assumption would normally be that there is no flow (no-slip) at the wall as in classical rheological analysis. The favored equation then becomes that of Herschel-Bulkley:

$$\tau = \tau_0 + \kappa_s \dot{\gamma}^n \quad (6)$$

where τ is the shear stress, τ_0 is the yield stress, κ_s is the shear consistency, $\dot{\gamma}$ is the effective shear strain rate, and n is the flow index. If no yield is present [Eq. \(6\)](#) simplifies to the power law relationship. To obtain these parameters as accurately as possible from capillary rheometry, an experiment is run to measure the variance of pressure with extrudate velocity for a number of dies of different length but of the same diameter. The pressure data and shear rate can be calculated readily from that data set but the shear stress must be corrected. Undertaking a Bagley correction accounts for any die entry effects and departures from Newtonian behavior are accounted for through the application of a Weissenberg-Rabinowitsch correction ([Morrison, 2001](#)).

There is however, a body of evidence from flow visualization techniques that suggests that paste-like, particulate materials exhibit plug flow (pure slip at the wall). This assumption leads to a different approach in which the body is treated as a plastic (yield stress approach). Benbow and others ([Benbow et al., 1987](#); [Ovenston and Benbow, 1968](#); [Benbow et al., 1989, 1991](#)) developed an equation for extrusion of paste-like particulate materials. In its early development it contained 4 paste parameters (σ_0 , α , τ_0 and β) taking the form:

$$P = (\sigma_0 + \alpha V) \ln\left(\frac{A_0}{A}\right) + (\tau_0 + \beta V) \frac{ML}{A} \quad (7)$$

where P is pressure, σ_0 is the bulk yield stress, α is the bulk velocity factor, V is the mean extrudate velocity, A_0 is the cross-sectional area of the barrel, A is the cross-sectional area of the die, τ_0 is the die wall shear stress and β is the die wall velocity factor, M is the perimeter length of the die, L is the die land length. Later exponents were added to account for the curvature observed in some pressure velocity data. Giving:

$$P = (\sigma_0 + \alpha_1 V^m) \ln\left(\frac{A_0}{A}\right) + (\tau_0 + \beta_1 V^n) \frac{ML}{A} \quad (8)$$

where m and n are the velocity exponents for the die entry and die land respectively, noting that α_1 and β_1 have different units to α and β . This work was summarized in a book, [Benbow and Bridgwater \(1993\)](#). These equations are fitted to the same data set used in conventional capillary flow analysis. [Eq. \(8\)](#) has been widely applied, examples are: in predicting pressure drop in honeycomb dies ([Blackburn and Böhm, 1997](#)), in forecasting the pressure development in single and twin screw extruders ([Burbidge and Bridgwater, 1995](#); [Botten et al., 2003](#); [McGuire et al., 2006](#)). The parameters were said to be independent of the geometry but there is frequently a significant discrepancy between the prediction and the measured pressure in more complex geometries. [Stitt et al. \(2015\)](#) gives a number of reasons for this, in [Eq. \(8\)](#) the number of input variables are less than the number of fitted parameters and thus the solution is ill-conditioned leading to fitting errors. This is exasperated by using the derived parameters to predict behavior in geometries far removed from those used to derive them. However, the equations developers commented on this issue ([Benbow et al., 1991](#)) and confirmed by [Benbow \(2018\)](#). Thus care must be taken in the use of these equations. With the provisos mentioned the equation remains a useful tool in the evaluation of these complex materials.

There have been attempts to modify the Benbow-Bridgwater model to account for some of these points. [Zheng et al. \(1992\)](#) used computer simulation to develop a modified Benbow-Bridgwater model in which die size is accounted for:

$$P = 2 \ln\left(\frac{D_0}{D}\right) \left(\sigma_0 + a'_b \left(\frac{V}{D}\right)^n \right) + \frac{ML}{A} (\tau_0 + \beta_1 V^m) \quad (9)$$

where D_0 is the barrel diameter, D is the die diameter and a'_b is a modified die entry velocity factor. [Basterfield et al. \(2005\)](#) focus on the die entry term only suggesting Herschel-Bulkley be used for the die land calculation such that the pressure drop for the die entry section becomes:

$$P = 2\sigma_0 \ln \frac{D_0}{D} + A\kappa_u \left(\frac{2V}{D} \right)^n \left(1 - \left(\frac{D}{D_0} \right)^{3n} \right) \quad (10)$$

where

$$A = \frac{2}{3n} (\sin\theta_{\max}(1 + \cos\theta_{\max}))^n \quad (11)$$

and κ_u is flow consistency. This equation requires the selection of the cone angle θ formed by the paste at the entry to the die. The advantage of Eq. (10) is that it has physically meaningful parameters compared to Benbow-Bridgwater.

The assumption of paste uniformity has received significant attention from researchers. The critique of the Benbow-Bridgwater approach extends to the fundamentals from which it was derived, with claims of very poor accuracy even in the field of metal extrusion (Chandler *et al.*, 2002). Others point out the non-uniformity of the paste flow within the barrels/dies. The idealized rheological paste profile, be it more or less shear thinning, may display telescoping segments, i.e., there may be parts of the paste that do not follow the generally described smooth profile from fluid mechanics texts. The liquid between the segments provides lubrication, whereas the segments themselves are in semi-plug flow (Funk and Dinger, 1994b,c). Telescoping layers could be induced by low and high shear rates close to the critical values, i.e., when the paste is sheared slightly above its yield stress or above the dilatant stress (in the shear thickening regime), respectively. Such telescoping segments also contribute to defect formation (see Section “Extrusion Defects”). The authors remark here that this effect may pertain to especially large components like electrical porcelain bodies as observations of smaller extrudates do not present the described features of telescoping.

Of course it must be considered how computer simulations might be used for the analysis of flow during extrusion. The models described so far represent a continuum approach. The Benbow-Bridgwater fits this category but is not represented in most Computational Fluid Dynamics, (CFD) programs. In CFD it is most common to fit a flow model such as Carreau (or derivatives) and adjust the boundary conditions to account for the chosen slip criterion, along with the variation in properties with temperature, noting that not all commercial packages will be able to do this directly. An example of this is given by Cademartori *et al.* (2018) who used the approach to good effect on ceramic injection molding compounds. Of course this is not ideal as the conditions and models do not capture the complexity of the paste system and can lead to some concerns over the results as phase separation and pore pressure are not taken into account. Flow properties are not always captured perfectly when compared to experimental evidence.

The concerns with CFD have led to approaches which consider the behavior by looking at the microscopic structure more closely. This was probably first attempted by Yuan *et al.* (2001). In that work the particles were modeled separately by a Discrete Element Method (DEM) and the fluid then modelled within the pore structure resulting from the DEM step by CFD approaches. This was computationally intensive for the time and not pursued for a number of years after that initial paper. The concept of using DEM has been taken further by Ness *et al.* (2017) who looked at the extrusion of non-Brownian spheres in a Newtonian fluid counteracting the hydrodynamic interactions between the individual particles. They showed good correlation between pressure drop across the extruder and the extrusion flow rate linking the empirical fitting parameters to the practical properties. Surface friction and wall roughness interactions were demonstrated. Dead zones were observed to develop as would be expected from experimental observation and the flow profile appeared well captured. While all looked promising there were variances in behavior on a local scale which were not captured. Some inhomogeneous results for the first normal stress difference calculated inside the die near the entry seemed to indicate a practical way of identifying a possible breakdown of extrudate if the die was to be shortened.

Patel *et al.* (2017, 2018) have taken a different approach to computationally modeling paste flow. Treating pastes as a clay, applying the Cam-Clay model and incorporating a simplified Tresca wall friction condition it was possible to closely monitor the liquid phase behavior in the extruder. It proved useful in seeing how phase migration is controlled by the geometry of the die for example. Other earlier models, such as Khelifi *et al.* (2013) may differ in the predictions of permeability, for the fluid mal-distribution could be calculated with other models than Kozeny-Carman solution (in this case the Taylor model).

As computing power improves, these approaches in combination with method refinement and process understanding point the way to future development. On a practical level the adoption of these more complex computational methods over the continuum approaches looks to be some way off.

Solid Free Form Fabrication

One area of forming that has experienced enormous growth in the last two decades is freeform fabrication. The methods in this category of processing are many and are summarized by Travitzky *et al.* (2014) but almost all take a Computer-Aided Design (CAD) object and section it into layers such that the object can then be built by laying down those layers sequentially in the material of choice. Many of the routes to manufacture do not use extrusion as the method of deposition but there is a small group of techniques that do. Collectively these have been called Extrusion Freeform Fabrication (EFF) but as each variant developed they were given different names to distinguish them. These terms are well reviewed in Travitzky *et al.* (2014) and here their simplified notation will be used. Other reviews on this area include Tay *et al.* (2003) and Yang and Miyanaji (2017). The processes can be more or less subdivided into three approaches which Travitzky *et al.* (2014) name as: Fused Deposition of Ceramics (FDC) in which the feedstock is melted and extruded, these compounds have much in common with injection molding, Robocast (RC) in

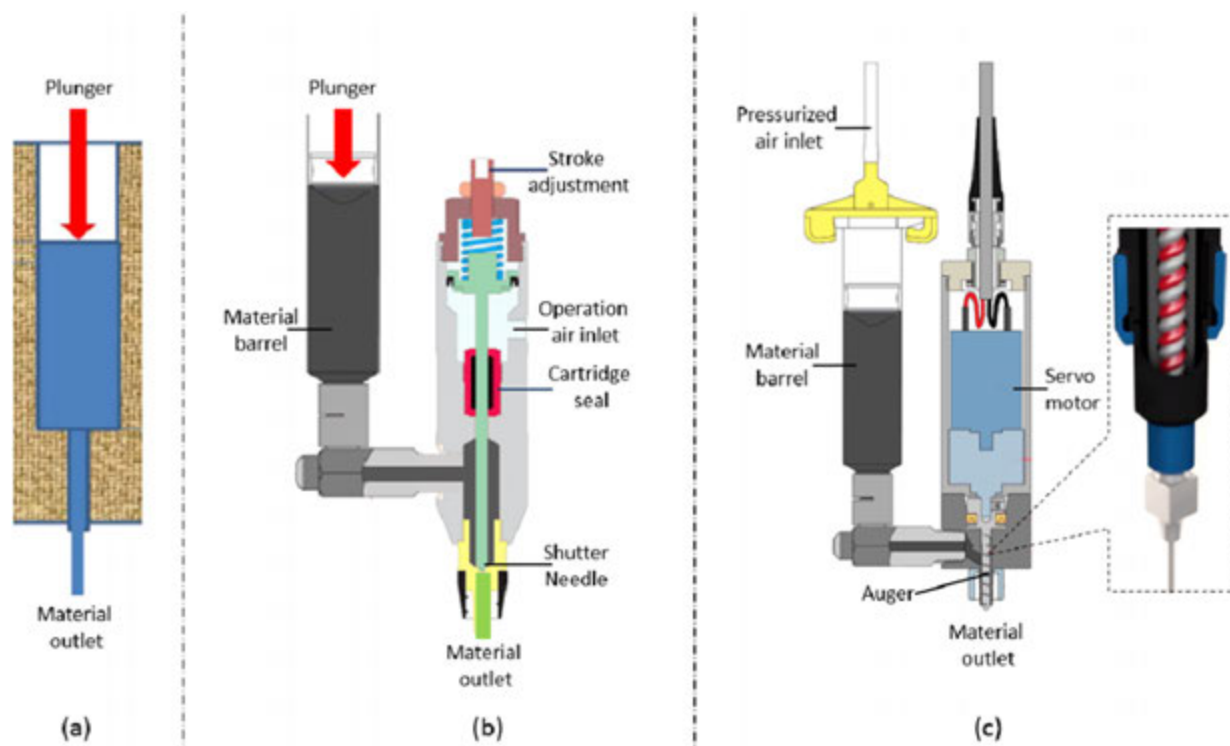


Fig. 5 Metering methods for extrusion freeform fabrication, (a) conventional extrusion, (b) needle valve control, (c) auger metering. From Li, W., Ghazanfari, A., Leu, M.C., Landers, R.G., 2017. Extrusion on demand methods for high solids loading ceramic pastes in free form extrusion fabrication. *Virtual and Physical Prototyping* 12 (3), 193–205.

which a suspension or colloidal gel is deposited at ambient temperature and Freeze-Form Extrusion Fabrication (FEF) in which a suspension or colloidal gel is deposited and frozen onto a cooled substrate. It can be said that this technology has its origins in coil pottery making where the object is made by laying down plastic clay strands to build a three dimensional object. Sharma (1967) states that coil building has been practiced since Neolithic times. The innovation in EFF is in carrying out the process in a far more controlled and reproducible way by the use of computing power and carefully controlled formulations.

While shape retention is required in EFF, it is also important that the individual extruding strand adheres to the assembly to bond the filaments together to make the 3D object. The solidification, be that by thermoplastic solidification, drying, gelling or freezing needs to be controlled appropriately for the build process to be successful. By necessity the materials need to have relatively low viscosity at the point of extrusion compared to conventional extrusion, Travitzky *et al.* (2014) states that viscosities should lie between 10 and 100 Pa s but does not give the associated shear rates.

The extrusion process in these systems will start and stop frequently within a layer as the travel path will be designed to develop the fill without overlap thus it is often referred to as extrusion on demand. As such the flow must start and end when required and be of uniform thickness throughout the process. This can be controlled using two approaches. The first is described by Zhao *et al.* (2010) and involves programming the extrusion through adaptive control. The second concerns improved metering. To give greater delivery control, mechanical devices have been introduced between the extruder barrel and the nozzle. Two methods are shown in Fig. 5.

Wang and Shaw (2005) show the importance of colloidal control on the form of the laid down extrudate in extrusion freeform fabrication. The filament morphology is influenced by pH, particle size, extrusion rate and nozzle height and speed. In this area of extrusion there is again a discussion over which is the best flow equation to use. The models that have been applied are largely the same as those discussed in Section “Paste Behavior in Mathematical Expressions”. Wang and Shaw (2005) use for example a power law model and for looking at nozzle geometry Benbow-Bridgwater (in this case for multi-hole geometries). Lui *et al.* (2015) also consider Benbow-Bridgwater and Herschel-Bulkley however, they go on to develop a viscoelastic-plastic model described by a spring and dashpot (Voigt/Kelvin element) in series with a yield-dashpot segment. On the other hand, Li *et al.* (2013a,b) developed a modified Herschel-Bulkley model to help in the aspect of flow and shape retention in the presence of compressibility from air entrapment and compare their findings to experimental data with some success. It would be fair to say that Benbow-Bridgwater in these relatively fluid systems should be used with some caution because of the basic assumption made: to be valid the material needs to be highly plastic and flow as a plug and as Powell *et al.* (2013) have shown this is only truly representative of flow at the highest possible solids loadings before extrusion ceases.

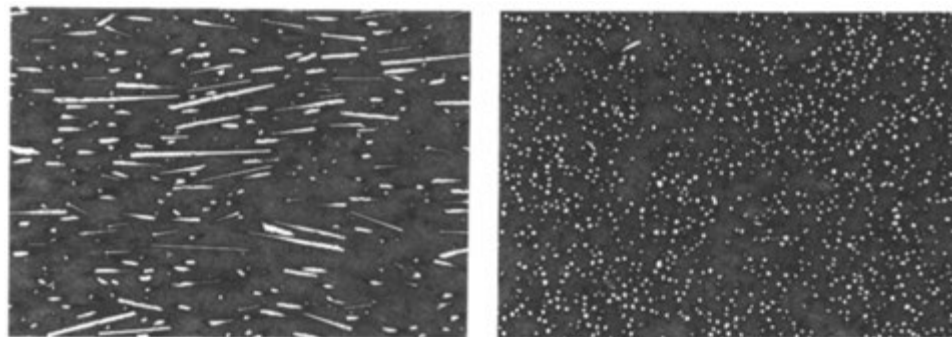


Fig. 6 Alignment of short silicon carbide fibers (30 vol%) in an alumina particulate paste. Left image flow left to right, right image a section perpendicular to flow, fiber diameter approximately 15 μm (adapted from Blackburn, S., Böhm, H., 1995. Silicon carbide fiber-reinforced alumina extrusion. *Journal of Materials Research* 10 (10), 2481–2487).

Extrusion Defects

Ceramics formed by extrusion will be prone to the same defects as those made by any other forming route but of course the process of extrusion can give rise to its own specific defects. These defects arise due to the material flow and include lamination, edge tearing, preferred particle orientation and internal defects (cracking or gas entrapment) (Onoda and Hench, 1978; Händle, 2007).

Particle Re-Orientation

Earlier it was suggested that pastes exhibit plug flow, Section “General Characterization”, but of course where there is a constriction in the flow there will be shear and elongation. Such flows cause non spherical particles in the formulation to rotate and take up a preferred orientation. This orientation leads to differential behaviors in post processing in the axial direction of extrusion compared to the orthogonal directions. Shrinkage and the final properties after firing will be different. This could be advantageous for example in the extrusion of hexaferrites for magnetic property development (Yuan *et al.*, 2002). The image (Fig. 6) shows a short fiber composite extrusion parallel and perpendicular to flow, the alignment of the fibers is clear to see (Blackburn and Böhm, 1995). However, it commonly occurs in clay and alumina bodies because these powders exhibit plate-like form and can lead to other defects such as internal cracking and lamination as a result.

Lamination

Laminar flow is always present in extrusion and this can itself lead to issues where the laminar flow generates a propensity to crack along the flow direction which may result from maldistribution of the phases or flow streams being forced together with little mixing after an obstruction such as a spider arm. In this circumstance the structure may be weakened if the two streams do not knit back together well. Mantle *et al.* (2004) consider the phenomenon with Magnetic Resonance Imaging (MRI) and showed the importance of an extended die land and constriction after the obstruction and that higher extrusion rates could aid in better closure. Blackburn *et al.* (1998) reported a method to evaluate the lamination. Funk and Dinger (1994a) developed a different form of spider legs (Z-shape – corrugated instead of straight) to eliminate the elliptically shaped discontinuities arising from radial body compression. In screw extruders lamination resulting from the paste leaving the end of the screw flight may manifest itself by cracks of a spiral form in the extrudate (Onoda and Hench, 1978).

Edge Tearing

Edge tearing tends to occur more often in dies producing shapes with sharp corners in their cross-section. It is a phenomenon where the material cracks because of internal stress developing through differential flows close to the surface. As a result the surface of the extrudate peels back as flow continues due to the tensile weakness of the paste. The stress is relieved by this process and normal flow resumes for a brief period. This leads to the characteristic repetitive defect form shown in Fig. 7. Domanti and Bridgwater (2000) looked at the origins of this fracture form and showed that it was generally found to initiate at the die exit though occasionally it was seen to propagate back into the die land. They concluded that the defect could not be linked to the rheological properties measured by capillary flow and that tensile strength of the paste is important. In the extrusion of honeycomb monoliths the outer cells may be lost to this type of defect. The onset of this defect type has been detected by pressure signal processing by Russell *et al.* (2003) using fractal analysis to look for patterns in the data. The results from modeling such as those presented by Ness *et al.* (2017) could also be of use when considering the onset of probable material discontinuity due to internal stress differences within the paste in the die land.



Fig. 7 Example of surface tearing in a cylindrical rod nominally 3 mm in diameter, formulated from alumina clay and glycerol for the purpose of illustration by the authors.

Phase Migration

Where phase migration is present but not catastrophic it can lead to defects in the extrudate (see Section “General Characterization” for a discussion of phase migration). Liquid tends to migrate to the die-paste interface and this in combination with a concentration of finer particles close to the wall contributes to defects associated with differential drying and lamination.

Co-Extrusion

Some complex structures have been produced by co-extruding more than one formulation at once. Two methods have been proposed, in the first the pastes are laid up on a larger scale than the final extrudate. The body is then simply extruded and because of the laminar flow the cross-section is reduced while maintaining the cross sectional pattern (Van Hoy *et al.*, 1998). It can be an effective method but because of the time consuming hand preparation it has not been used to any great extent outside Micro-Tubular Fuel Cells (MTFCs). In the second the pastes to be combined are held in different extruders feeding a common complex die through a manifold. Using the methodologies outlined in this review it is possible to generate pastes of different composition with similar rheological behavior which can thus be forced through the multi-channel system in a predictable way. This method has been demonstrated by Powell and Blackburn (2009, 2010) for the extrusion of MTFCs. However, even if the flows are matched defects may form through differential post processing behavior (drying and sintering). Others extend the approach of co-processing for fuel cell systems by using phase inversion technologies, (Droushiotis *et al.*, 2009; Othman *et al.*, 2012).

Concluding Remarks & Other Literature

The reader is referred to other works that summarize well the field of extrusion and highly loaded suspensions, such as Coussot (2005), Wilson and Rough (2006), Blackburn and Wilson (2008), Wilson and Rough (2012) and Kalyon and Aktas (2014).

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References

- Amarasinghe, A.D.U.S., Wilson, D.I., 1998. Interpretation of paste extrusion data. *Chemical Engineering Research and Design* 76 (1), 3–8.
- Andreasen, A.H.M., Andersen, J., 1930. Ueber die beziehung zwischen kornabstufung und zwischenraum in produkten aus losen körnern (mit einigen experimenten). *Kolloid-Zeitschrift* 50 (3), 217–228.
- ASTM International, 2017. D5099 – 08(2017): Standard Test Methods for Rubber – Measurement of Processing Properties Using Capillary Rheometry. West Conshohocken: ASTM International.
- Baader, F.H., Graule, T.J., Gauckler, L.J., 1996. Direct coagulation casting – A new green shaping technique part II. Application to alumina. *Industrial Ceramics* 16, 36–40.
- Bardesley, M.A., Bridgwater, J., 2012. Evaluation of liquid phase migration in pastes and gels. *Industrial & Engineering Chemistry Research* 51 (4), 1774–1781.
- Barnes, H.A., Walters, K., 1985. The yield stress myth? *Rheologica Acta* 24 (4), 323–326.
- Barnes, H.A., Nguyen, Q.D., 2001. Rotating vane rheometry – A review. *Journal of Non-Newtonian Fluid Mechanics* 98 (1), 1–14.
- Basterfield, R.A., Lawrence, C.J., Adams, M.J., 2005. On the interpretation of orifice extrusion data for viscoplastic materials. *Chemical Engineering Science* 60 (10), 2599–2607.
- Bayfield, M., Hagggett, J.A., Williamson, M.J., Wilson, D.I., Zargar, A., 1998. Liquid phase migration in the extrusion of icing sugar pastes. *Food and Bioproducts Processing* 76 (1), 39–46.
- Benbow, J.J., Bridgwater, J., 1993. *Paste Flow and Extrusion*. Oxford University Press.
- Benbow, J.J., Oxley, E.W., Bridgwater, J., 1987. The extrusion mechanics of pastes: The influence of paste formulation on extrusion parameters. *Chemical Engineering Science* 42 (9), 2151–2162.

- Benbow, J.J., Jazayeri, S.H., Bridgwater, J., 1991. The flow of pastes through dies of complicated geometry. *Powder Technology* 65 (1–3), 393–401.
- Benbow, J.J., Blackburn, S., Mills, H., 1998. The effects of liquid-phase rheology on the extrusion behaviour of paste. *Journal of Materials Science* 33 (24), 5827–5833.
- Benbow, J.J., Lawson, T.A., Oxley, E.W., Bridgwater, J., 1989. Prediction of paste extrusion pressures. *American Ceramic Society Bulletin* 68 (10), 1821–1824.
- Benbow, J.J., 2018. Personal Communication.
- Blackburn, S., Böhm, H., 1993. The influence of powder packing on paste extrusion behaviour. *Chemical Engineering Research and Design* 71 (Part A), 250–256.
- Blackburn, S., Böhm, H., 1994. The influence of powder packing on the rheology of fibre-loaded pastes. *Journal of Materials Science* 29 (16), 4157–4166.
- Blackburn, S., Böhm, H., 1995. Silicon carbide fiber-reinforced alumina extrusion. *Journal of Materials Research* 10 (10), 2481–2487.
- Blackburn, S., Böhm, H., 1997. A method of calculating pressure drop in honeycomb dies. *Journal of the European Ceramic Society* 17 (2–3), 183–189.
- Blackburn, S., Wilson, D.I., 2008. Shaping ceramics by plastic processing. *Journal of the European Ceramic Society* 28 (7), 1341–1351.
- Blackburn, S., Mills, H., El-Bakbaki, N., 1998. Extrusion of pastes containing plate like particles. *British Ceramics Transactions* 97 (5), 205–213.
- Böhm, H., Blackburn, S., 1994a. Effect of mixing procedure on fine alumina paste extrusion. *British Ceramic Transactions* 93 (5), 169–177.
- Böhm, H., Blackburn, S., 1994b. Agglomerate breakdown in fine alumina powder by multiple extrusion. *Journal of Materials Science* 29 (22), 5779–5786.
- Botten, A.J., Burbidge, A.S., Blackburn, S., 2003. A model to predict the pressure development in single screw extrusion. *Journal of Materials Processing Technology* 135 (2–3), 284–290.
- Brouwers, H.J.H., 2006. Particle-size distribution and packing fraction of geometric random packings. *Physical Review E* 74 (3), 031309 (1–14).
- Bryan, M.P., Rough, S.L., Wilson, D.I., 2017. Flow visualisation and modelling of solid soap extrusion. *Chemical Engineering Science* 173, 110–120.
- Burbidge, A.S., Bridgwater, J., 1995. The single screw extrusion of pastes. *Chemical Engineering Science* 50 (16), 2531–2543.
- Burk, R., Apte, P., 1987. Packing scheme for real size distributions. *American Ceramic Society Bulletin* 66 (9), 1389–1392.
- Cademartori, S., Humphreys, N., Gebelin, J.C., Brooks, J., 2018. Implementing CFD modelling to address defect formation in core injection moulding. In: Nastac, L., Pericleous, K., Sabau, A., Zhang, L., Thomas, B.G. (Eds.), *CFD Modelling and Simulation in Materials Processing* 2018. Springer.
- Chandler, H.W., George, S.D., Liddle, J., 2002. Deformation and flow of stiff pastes: Review of rheology of some soft solids. *British Ceramic Transactions* 101 (2), 47–58.
- Chen, Y., Burbidge, A., Bridgwater, J., 1997. Effect of carbohydrate on the rheological parameters of paste extrusion. *Journal of the American Ceramic Society* 80 (7), 1841–1850.
- Chen, Z., Ikeda, K., Murakami, T., Takeda, T., 2000. Drainage phenomenon of pastes during extrusion. *Journal of Materials Science* 35 (10), 2517–2523.
- Chhabra, R.P., Richardson, J.F., 1999. Flow in pipes and in conduits of non-circular cross-sections. In: Chhabra, R.P., Richardson, J.F. (Eds.), *Non-Newtonian Flow in the Process Industries: Fundamentals and Engineering Applications*. Oxford: Butterworth-Heinemann, pp. 73–161.
- Clemens, F.J., Wallquist, V., Buchser, W., Wegmann, M., Graule, T., 2007. Silicon carbide fiber-shaped microtools by extrusion and sintering SiC with and without carbon powder sintering additive. *Ceramics International* 33 (3), 491–496.
- Cloitre, M., Bonnecaze, R.T., 2017. A review on wall slip in high solid dispersions. *Rheologica Acta* 56 (3), 283–305.
- Cogswell, F.N., 1981. *Polymer Melt Rheology: A Guide for Industrial Practice*. Cambridge: Woodhead Publishing.
- Collomb, J., Chaari, F., Chaouche, M., 2004. Squeeze flow of concentrated suspensions of spheres in Newtonian and shear-thinning fluids. *Journal of Rheology* 48 (2), 405–416.
- Coussot, P., 2005. *Rheometry of Pastes, Suspensions, and Granular Materials: Applications in Industry and Environment*. Hoboken, NJ: John Wiley & Sons, Inc.
- Coussot, P., 2014. Yield stress fluid flows: A review of experimental data. *Journal of Non-Newtonian Fluid Mechanics* 211, 31–49.
- Danov, K.D., Georgiev, M.T., Kralchevsky, P.A., *et al.*, 2018. Hardening of particle/oil/water suspensions due to capillary bridges: Experimental yield stress and theoretical interpretation. *Advances in Colloid and Interface Science* 251, 80–96.
- Davies, J., Binner, J.G.P., 2000. Coagulation of electrostatically dispersed concentrated alumina suspensions for paste production. *Journal of the European Ceramic Society* 20 (10), 1555–1567.
- Diemer, J., Chilles, C., Colbert, J., *et al.*, 2011. Flow visualisation in co-rotating twin screw extruders: Positron emission particle tracking and numerical particle trajectories. *International Polymer Processing* 26 (5), 540–550.
- Domanti, A.T.J., Bridgwater, J., 2000. Surface fracture in axisymmetric paste extrusion: An experimental study. *Chemical Engineering Research and Design* 78 (1), 68–78.
- Draper, O., Blackburn, S., Dolman, G., Smalley, K., Griffiths, A., 1999. A comparison of paste rheology and extrudate strength with respect to binder formulation and forming technique. *Journal of Materials Processing Technology* 92–93, 141–146.
- Droushiotis, N.D., Doraswami, U., Othman, M., Li, K., Kelsall, G., 2009. Co-extrusion/phase inversion/co-sintering for fabrication of hollow fiber solid oxide fuel cells. *ECS Transactions* 25 (2), 665–672.
- Edirisinghe, M.J., Evans, J.R.G., 1986. Compounding ceramic powders prior to injection moulding. *Proceedings of the British Ceramic Society* 38, 67–80.
- Fox, R.W., McDonald, A.T., 1994a. Fundamental concepts. In: Fox, R.W., McDonald, A.T. (Eds.), *Introduction to Fluid Mechanics*, fourth ed. Chichester: John Wiley & Sons, pp. 17–51.
- Fox, R.W., McDonald, A.T., 1994b. Flow in pipes and ducts. In: Fox, R.W., McDonald, A.T. (Eds.), *Introduction to Fluid Mechanics*, fourth ed. Chichester: John Wiley & Sons, pp. 310–408.
- Funk, J.E., Dinger, D.R., 1994a. Predictive Process Control of Crowded Particulate Suspensions: Applied to Ceramic Manufacturing. Norwell: Kluwer Academic Publishers.
- Funk, J.E., Dinger, D.R., 1994b. Viscosity and rheology. In: Funk, J.E., Dinger, D.R. (Eds.), *Predictive Process Control of Crowded Particulate Suspensions: Applied to Ceramic Manufacturing*. Norwell: Kluwer Academic Publishers, pp. 235–252.
- Funk, J.E., Dinger, D.R., 1994c. Practical rheology. In: Funk, J.E., Dinger, D.R. (Eds.), *Predictive Process Control of Crowded Particulate Suspensions: Applied to Ceramic Manufacturing*. Norwell: Kluwer Academic Publishers, pp. 327–371.
- Gauckler, L.J., Graule, T., Baader, F., 1999. Ceramic forming using enzyme catalyzed reactions. *Materials Chemistry and Physics* 61 (1), 78–102.
- German, R.M., 1989. *Particle Packing Characteristics*. NJ: Metal Powder Industries Federation.
- Gleißle, W., Graczyk, J., 2007. Rheology and extrudability of ceramic compounds. In: Händle, F. (Ed.), *Extrusion in ceramics*. Leipzig: Springer, pp. 175–188.
- Graule, T.J., Gauckler, L.J., Baader, F.H., 1996. Direct coagulation casting – A new green shaping technique part I. Processing principles. *Industrial Ceramics* 16, 31–35.
- Händle, F. (Ed.), 2007. *Extrusion in Ceramics. Engineering Materials and Processes*. Leipzig: Springer.
- Hölzgen, M., Quimbach, P., 2007. Additives for extrusion. In: Händle, F. (Ed.), *Extrusion in Ceramics*. Leipzig: Springer, pp. 233–244.
- Jastrzebski, Z.D., 1967. Entrance effects and wall effects in an extrusion rheometer during flow of concentrated suspensions. *Industrial & Engineering Chemistry Fundamentals* 6 (3), 445–454.
- Kalyon, D.M., Aktas, S., 2014. Factors affecting the rheology and processability of highly filled suspensions. *Annual Review of Chemical and Biomolecular Engineering* 5, 229–254.
- Karlsson, K., Spring, L., 1970. Packing of irregular particles. *Journal of Materials Science* 5 (4), 340–344.
- Kaya, C., Butler, E.G., 2003. Zirconia-toughened alumina ceramics of helical spring shape with improved properties from extruded sol-derived pastes. *Scripta Materialia* 48 (4), 359–364.
- Khan, A.U., Briscoe, B.J., Luckham, P.F., 2001. Evaluation of slip in capillary extrusion of ceramic pastes. *Journal of the European Ceramic Society* 21 (4), 483–491.
- Khelifi, H., Perrot, A., Lecompte, T., Rangeard, D., Ausias, G., 2013. Prediction of extrusion load and liquid phase filtration during ram extrusion of high solid volume fraction pastes. *Powder Technology* 249, 258–268.
- Koos, E., Willenbacher, N., 2011. Capillary forces in suspension rheology. *Science* 331 (6019), 897–900.

- Li, M., Tang, L., Landers, R.G., Leu, M.C., 2013a. Extrusion process modeling for aqueous-based ceramic pastes – Part 1: Constitutive model. *Journal of Manufacturing Science and Engineering* 135. (051008-1–051008-7).
- Li, M., Tang, L., Landers, R.G., Leu, M.C., 2013b. Extrusion process modeling for aqueous-based ceramic pastes – Part 2: Experimental verification. *Journal of Manufacturing Science and Engineering* 135. (051009-1–051009-7).
- Lui, H., Li, Y., Li, D., 2015. Research on rheological properties and extrusion behavior of aqueous alumina paste in paste-extrusion based SFF processes. *The International Journal of Advanced Manufacturing Technology* 83 (9–12), 2039–2047.
- Mantle, M.D., Bardsley, M.H., Gladden, L.F., Bridgwater, J., 2004. Laminations in ceramic forming – Mechanisms revealed by MRI. *Acta Materialia* 52 (4), 899–909.
- Martin, P.J., Wilson, D.I., 2005. A critical assessment of the Jastrzebski interface condition for the capillary flow of pastes, foams and polymers. *Chemical Engineering Science* 60 (2), 493–502.
- McGuire, P.A., Blackburn, S., Holt, E.M., 2006. Twin screw extrusion modelling. *Advances in Science and Technology* 45, 436–441.
- McGuire, P.A., Blackburn, S., Holt, E.M., 2007. An X-ray micro-computed tomography study of agglomerate breakdown during the extrusion of ceramic pastes. *Chemical Engineering Science* 62 (22), 6451–6456.
- Mewis, J., Wagner, N.J., 2012a. Hydrodynamic effects: Non-colloidal particles. In: Mewis, J., Wagner, N.J. (Eds.), *Colloidal Suspension Rheology*. New York: Cambridge University Press, pp. 36–79.
- Mewis, J., Wagner, N.J., 2012b. Rheometry of suspensions. In: Mewis, J., Wagner, N.J. (Eds.), *Colloidal Suspension Rheology*. New York: Cambridge University Press, pp. 291–324.
- Mooney, M., 1931. Explicit formulas for slip and fluidity. *Journal of Rheology* 2 (2), 210–222.
- Morrison, F.A., 2001. *Understanding Rheology*. Oxford: Oxford University Press.
- Ness, C., Ooi, J.Y., Sun, J., *et al.*, 2017. Linking particle properties to dense suspension extrusion flow characteristics using discrete element simulations. *American Institute of Chemical Engineers* 63 (7), 3069–3082.
- Norton, F.H., 1970. *Fine Ceramics, Technology and Applications*. New York: McGraw-Hill.
- O'Neill, R., McCarthy, H.O., Cunningham, E., *et al.*, 2016. Extent and mechanism of phase separation during the extrusion of calcium phosphate pastes. *Journal of Materials Science: Materials in Medicine* 27 (29), 1–13.
- Onoda, G.Y., 1978. The rheology of organic binder solutions. In: Onoda, G.Y., Hench, L.L. (Eds.), *Ceramic Processing Before Firing*. Chichester: John Wiley & Sons, pp. 235–251.
- Onoda, G.Y., Hench, L.L., 1978. *Ceramic Processing Before Firing*. Chichester: John Wiley & Sons.
- Othman, M.H.D., Li, K., Ismail, A.F., 2012. High performance micro-tubular solid oxide fuel cell fabricated using a novel co-extrusion/co-sintering technique. *Procedia Engineering* 44, 989–991.
- Ovenston, A., Benbow, J.J., 1968. Effects of die geometry on the extrusion of clay-like material. *Transactions of the British Ceramic Society* 67 (11), 543–567.
- Pagnoux, C., Mougenot, M., Perez, P.G., Chartier, T., Baumard, J.F., 2006. Coagulation of mixed organic systems and alumina particles for paste production. *Journal of The European Ceramic Society* 26 (15), 3091–3098.
- Patel, M.J., Blackburn, S., Wilson, D.I., 2007. Modelling paste flows subject to liquid phase migration. *International Journal for Numerical Methods in Engineering* 72 (10), 1157–1180.
- Patel, M.J., Blackburn, S., Wilson, D.I., 2017. Modelling of paste ram extrusion subject to liquid phase migration and wall friction. *Chemical Engineering Science* 172, 487–502.
- Patel, M.J., Blackburn, S., Wilson, D.I., 2018. Modelling of pastes as viscous soils – Lubricated squeeze flow. *Powder Technology* 323, 250–268.
- Powell, J., Blackburn, S., 2009. The unification of paste rheologies for the co-extrusion of solid oxide fuel cells. *Journal of the European Ceramic Society* 29 (5), 893–897.
- Powell, J., Blackburn, S., 2010. Co-extrusion of multilayered ceramic micro-tubes for use as solid oxide fuel cells. *Journal of the European Ceramic Society* 30 (14), 2859–2870.
- Powell, J., Assabumrungrat, S., Blackburn, S., 2013. Design of ceramic paste formulations for co-extrusion. *Powder Technology* 245, 21–27.
- Rahaman, M.N., 2017a. *Ceramic Processing*, second ed. Boca Raton: CRC Press; Taylor and Francis Group.
- Rahaman, M.N., 2017b. Processing additives. In: Rahaman, M.N. (Ed.), *Ceramic Processing*, second ed. Boca Raton: CRC Press; Taylor and Francis Group, pp. 193–212.
- Rahaman, M.N., 2017c. Granulation, mixing, and packing of particles. In: Rahaman, M.N. (Ed.), *Ceramic Processing*, second ed. Boca Raton: CRC Press, Taylor and Francis Group, pp. 213–240.
- Reh, H., 2007. Current classification of ceramic materials. In: Händle, F. (Ed.), *Extrusion in Ceramics*. Leipzig: Springer, pp. 39–62.
- Russell, B.D., Lasenby, J., Blackburn, S., Wilson, D.I., 2003. Characterising paste extrusion behaviour by signal processing of pressure sensor data. *Powder Technology* 132 (2–3), 233–248.
- Rutgers, I.R., 1962. Relative viscosity and concentration. *Rheologica Acta* 2 (4), 305–348.
- Schneider, M., Maurath, J., Fischer, S.B., *et al.*, 2017. Suppressing crack formation in particulate systems by utilizing capillary forces. *American Chemical Society Applied Materials & Interfaces* 9 (12), 11095–11105.
- Sharma, T.C., 1967. A note on neolithic pottery of Assam. *Man* 2 (1), 126–128.
- Shinohara, K., 1997. Fundamental and rheological properties of powders. In: Fayed, M.E., Otten, L. (Eds.), *Handbook of Powder Science & Technology*, second ed. London: Chapman & Hall, pp. 96–145.
- Stitt, H., Marigo, M., Wilkinson, S., 2015. How good is your model. *Johnson Matthey Technology Review* 59 (2), 74–89.
- Sutcu, M., Akkurt, S., 2007. ANN model for prediction of powder packing. *Journal of European Ceramic Society* 27 (2–3), 641–644.
- Takahashi, M., 2006. Kneading and plastic forming. In: Masuda, H., Higashitani, K., Yoshida, H. (Eds.), *Powder Technology Handbook*, third ed. Boca Raton: CRC Press, Taylor & Francis Group, pp. 615–619.
- Tay, B.Y., Evans, J.R.G., Edirisinghe, M.J., 2003. Solid freeform fabrication of ceramics. *International Materials Reviews* 48 (6), 341–370.
- Toutou, Z., Roussel, N., Lanos, C., 2005. The squeezing test: A tool to identify firm cement-based material's rheological behaviour and evaluate their extrusion ability. *Cement and Concrete Research* 35 (10), 1891–1899.
- Travitzky, N., Bonet, A., Dermeik, B., *et al.*, 2014. Additive manufacturing of ceramic-based materials. *Advanced Engineering Materials* 16 (6), 729–754.
- Van Hoy, C., Barda, A., Griffith, M., Halloran, J.W., 1998. Microfabrication of ceramics by co-extrusion. *Journal of the American Ceramic Society* 81 (1), 152–158.
- Vandeneede, V., Moortgat, G., Cambier, F., 1997. Characterisation of alumina pastes for plastic moulding. *Journal of the European Ceramic Society* 17 (2–3), 225–231.
- Wang, J.W., Shaw, L.L., 2005. Rheological and extrusion behavior of dental porcelain slurries for rapid prototyping applications. *Materials Science and Engineering: A* 397 (1–2), 314–321.
- Wei, J., Liang, X.L., Chen, D.B., Yang, Y.L., Zhou, D.M., 2014. Evaluation of the mixing performance for one novel twin screw kneader with particle tracking. *Polymer Engineering and Science* 54 (10), 2407–2419.
- Weiß, M., Maurath, J., Willenbacher, N., Koos, E., 2019. Shrinkage and dimensional accuracy of porous ceramics derived from capillary suspensions. *Journal of the European Ceramic Society* 39 (5), 1887–1892.
- Wildman, R.D., Blackburn, S., 1998. Breakdown of agglomerates in ideal pastes during extrusion. *Journal of Material Science* 33 (21), 5119–5124.
- Williams, P.R., 1999. Rheometry for non-Newtonian fluids. In: Chhabra, R.P., Richardson, J.F. (Eds.), *Non-Newtonian Flow in the Process Industries: Fundamentals and Engineering Applications*. Boston: Butterworth-Heinemann, pp. 37–72.
- Wilson, D.I., Rough, S.L., 2006. Exploiting the curious characteristics of dense solid-liquid pastes. *Chemical Engineering Science* 61 (13), 4147–4154.

- Wilson, D.I., Rough, S.L., 2012. Paste engineering: Multi-phase materials and multi-phase flows. *The Canadian Journal of Chemical Engineering* 90 (2), 277–289.
- Winstone, G., 2011. Production of Catalyst Supports by Twin Screw Extrusion of Pastes. EngD Thesis. University of Birmingham.
- Yang, L., Miyajiri, H., 2017. Ceramic additive manufacturing: A review of current status and challenges. In: Bourell, D.L., Crawford, R.H., Seepersad, C.C., Beaman, J.J., Fish, S. (Eds.), *Proceedings of the 28th Annual International Solid Freeform Fabrication Symposium*. Austin, TX: University of Texas, pp. 652–679.
- Yu, A.B., Zou, R.P., Standish, N., 1996. Modifying the linear packing model for predicting the porosity of nonspherical particle mixtures. *Industrial & Engineering Chemistry Research* 35 (10), 3730–3741.
- Yu, A.B., Bridgwater, J., Burbidge, A., 1997. On the modelling of the packing of fine particles. *Powder Technology* 92 (3), 185–194.
- Yuan, W.X., Burbidge, A.S., Blackburn, S., *et al.*, 2001. A micro-scale model of paste flow in the ram extrusion process. In *Proceedings of 6th World Congress of Chemical Engineering*. Melbourne: IChemE.
- Yuan, Z.C., Blackburn, S., Williams, A.J., Harris, I.R., 2002. Extrusion of strontium hexaferrite magnets with radial alignment using hydrothermally synthesized powder. *IEEE Transactions on Magnetics* 38 (5), 2925–2927.
- Zhao, X., Landers, R.G., Leu, M.C., 2010. Adaptive extrusion force control of freeze-form extrusion fabrication processes. *Journal of Manufacturing Science and Engineering* 132 (6), (064504-1–064504-9).
- Zheng, J., Johnson, P.F., Reed, J.S., 1990. Improved equation of the continuous particle size distribution for dense packing. *Journal of the American Ceramic Society* 73 (5), 1392–1398.
- Zheng, J., Carlson, W.B., Reed, J.S., 1992. Flow mechanics on extrusion through a square-entry die. *Journal of the American Ceramic Society* 75 (11), 3011–3016.

Ceramic Injection Molding

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Historical Background

In July 1938, a method for making a refractory body was patented by the US patent office. The inventor was Karl Schwartzwalder (Schwartzwalder, 1938). Independently from this, in November 1940, Klinger *et al.*, 1940, obtained a German patent claiming a method of producing spark plugs by injecting a ceramic compound with the addition of organic binders into a mold by application of pressure. During the first thirty years, however, ceramic injection molding was of minor interest to the wider ceramics industry (Mutsuddy, 1989). The progression into financial viability was based on research and development efforts undertaken during the 1970s and 1980s (German, 2007). Injection molding provided a cost-effective fabrication method suitable for the mass production of the parts of a heat engine whose complex shape caused fabrication problems (Mutsuddy, 1987). For the decade between 2000 and 2009, PIM had generally experienced growth, mostly in the 8%–14% range (German, 2013). Nowadays, CIM is identified as one of the lead technologies in the field of technical ceramics.

CIM Processing Chain

In contrast to the raw materials used for traditional ceramics, which contain clay minerals and therefore showing a pseudoplastic behavior, the powders for advanced ceramic products are synthetic high purity materials with no “plastic shaping” ability. For this reason, the powders must be combined with organic additives to give them the desired plasticity (Moritz *et al.*, 2009). After shaping of components by injection molding into a so-called “green part”, the binder system has to be removed completely for sintering and for attaining the final desired properties of a ceramic component. A schematic processing chain is given in Fig. 1.

The CIM processing chain is explained in more detail below.

Initial Powder

The selection of the ceramic powder is based on the requirements for the material properties of the planned component, its intended use and location and the stresses to which the component may be exposed. There are no limits to the chemical composition of the ceramic powders. These can be, i.e., oxides, non-oxides, silicates, silicides, nitrides and carbides (Witzleben *et al.*, 2008c). Ideally wet milled or chemically precipitated powders with a uniform particle shape are preferred, but for economic reasons cannot always be used due to their high price. As far as possible, raw powders should be free from chemical additives that reduce their surface wetting properties (Schlieper, 2015).

Particle size distribution, specific surface and the chemical composition are the main characteristics of ceramic powders. Powders with a particle size distribution greater than 40 μm are very rarely utilized (Witzleben *et al.*, 2008c). CIM generally uses powders with particle sizes in the range between 200 and 2000 nm and a specific surface between 3 and 20 m^2 per gram. For the control of the shrinkage, however, these characteristics must be specified within much closer limits (Schlieper, 2015).

The main requirements that are placed on powder for ceramic injection molding are:

- Good injection – flow properties without the excessive use of binder
- High sinterability (firing at the lowest possible temperature)
- Constant shrinkage

The proportion of a ceramic powder that can be incorporated into a continuous binder matrix in order to obtain a tight dimensional tolerance after sintering depends on the packaging properties (Witzleben *et al.*, 2002).

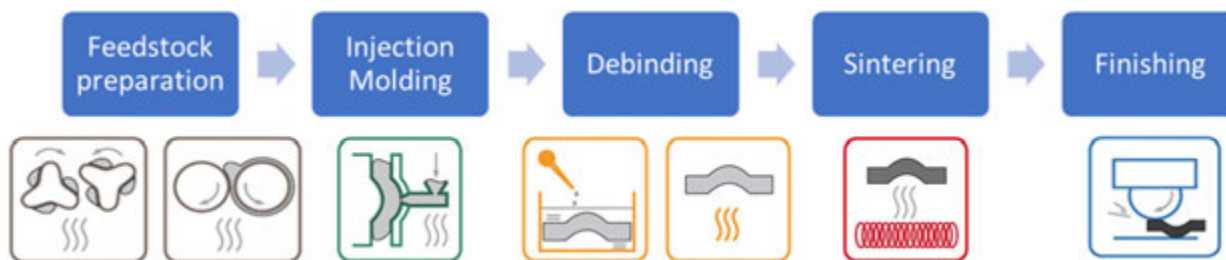


Fig. 1 Schematic CIM processing chain.

Necessity of Feedstock and Feedstock Preparation

Key target of feedstock preparation is homogeneity. In this context, it describes two types of homogeneity, related to the composition, i.e., the powder content in the binder and related to the dispersion of powder particles in the binder and the degree of division of agglomerates (Wang *et al.*, 2016). Avoiding the formation of agglomerates is essential for 2 reasons:

- Ceramic agglomerates act as minute porous sponges that trap binder (Trunec *et al.*, 2002) which is then lost for ensuring the rheological properties
- Agglomerates function as defect points in the final sintered components with the result of reduction the ceramic properties of the end part (Hohlbaum, 2019).

The standard of compounding technology involves powder blending and shear roll extrusion (Witzleben *et al.*, 2008a) of the powder-binder mix with subsequent pelletizing (Witzleben *et al.*, 2008b).

Shear roll extrusion is a process that guarantees intimate compounding with a maximum shear rate which is important to avoid agglomerates of the ultrafine ceramic powders, to coat each ceramic particle and obtain a homogeneous product with excellent consistency on a high-quality level. Archiving highest and even green density in the injected part is the precondition for a dense end-contour part finally after debinding and sintering (Hajek, 2015).

Fig. 2 shows the set of two parallel shear rolls. Between the rolls there is a small gap of usually less than 1 mm width. The feedstock, which is fed into the gap at one end of the shear rolls, sticks on one roll and the other roll is clean.

Although the shear roll extruder has a higher energy input in comparison to a twin-screw extruder or a sigma-blade kneader, usually not all agglomerates can be divided (Walcher *et al.*, 1999).

In order to produce high solid loaded submicron and nanoparticle containing feedstocks is suggested to pre-mill, to disperse, and to deagglomerate ceramic powders (Moritz *et al.*, 2010).

Binder Systems and Debinding Concepts

When the powder blend has been determined, the next step is the selection of the most suitable binder for the designated application. The processing of a ceramic feedstock requires polymer components which are able to withstand the severe forces, needed to break up agglomerates. Only a few polymers can be used for this purpose – keeping in mind that they have to have the property of being willingly injection molded with a high load of ceramic powder. The minimal requirements for binder systems include low viscosity to ensure complete filling of mold cavities, relatively high mechanical stability to ensure safe removing from a mold, good shape retention and low shrinkage during debinding and sintering (Hajek, 2015).

Binders are made up of several components (Chartier *et al.*, 2001):

- A basic low molecular polymer for an easier extraction during debinding and as plasticizers (Bleyan *et al.*, 2015) between the long polymer chains of the backbone polymer to lower the feedstocks dynamic viscosity and provide a suitable rheological property to ensure a complete cavity filling during injection of the feedstock into the mold (Moritz *et al.*, 2009),
- A backbone binder for the strength of the component (Hausnerova *et al.*, 2017; Wroblewska, 2001) and
- Often, but not always additives like lubricants or dispersing agents (Chartier *et al.*, 2001).

The aim is to have fewer components than possible in order to reduce the tendency of demixing through the injection molding process due to high injection molding pressures.

Polymers commonly chosen for CIM are polypropylene, low density polyethylene, ethylene vinyl acetate (Edirisingh *et al.*, 1987), polystyrene, polymethyl methacrylate, polyvinyl butyral, polyacetal (Hens *et al.*, 1995) or polyamide (Mannschatz *et al.*, 2014).



Fig. 2 Shear roll used for feedstock homogenization. Courtesy INMATEC Technologies.

Depending on the binder composition different debinding procedures are available. Polyacetal based binders can be debound via a catalytic procedure (in nitric acid containing atmosphere) (Hens *et al.*, 1995) or acetone. In case of the catalytic procedure, an outstanding performance in terms of extremely short debinding times is here to emphasize.

Pure thermal debinding as an alternative is widely used (Burger, 2009; Schlieper, 2016; Trunec *et al.*, 2002). Due to decomposed products need to leave the bulk by diffusion, the heating process has to be carried out very slowly to prevent the creation of internal pressures which cases in cracks and voids in parts (Moritz *et al.*, 2009).

The most common debinding procedure is the combination of a pre-debinding with a solvent (water, acetone, isopropanol, heptane) and a subsequent thermal debinding process (Trunec *et al.*, 2002; Mannschatz *et al.*, 2014). The purpose of solvent debinding is to remove a soluble binder additive to create open porosity. Open porosity allows during the thermal debinding step decomposed organics to diffuse easily to the surface (Hajek, 2015; Schlieper, 2016). By this way, the debinding time and the risk of cracks and voids can be reduced (Mannschatz *et al.*, 2014). Debinding time depends on used solvent, wall thickness and particle size distribution.

The choice of the binder system depends on targeted properties of the part, the amounts to be produced, company and regional regulations and market needs.

Less common feedstock systems are based on carrageenan (Millán *et al.*, 1997), cellulose derivatives (Huzzard *et al.*, 2003) or ceramic precursors including silanes, carbosilanes, siloxanes and silicanes (Wroblewska, 2001).

A further alternative technique for debinding, extraction of organic binders by supercritical fluids has been investigated (Chartier *et al.*, 2001; Chartier *et al.*, 1995).

Injection Molding Process

High pressure CIM is in principle borrowed from the plastic injection molding industry. It can be automated easily and is, unlike other ceramic shaping techniques, suited to high volume production (Moritz *et al.*, 2009). The equipment used for injection molding CIM parts is the same as the equipment that is used in the plastic injection molding industry, with small modifications to reduce wear, like a hardened screw and barrel, and assure homogeneity (modification of screw design and equipment of screw with backflow barrier) during plasticization (Verpoort *et al.*, 1996). For injection the granulated feedstock is fed into the barrel of the machine and heated to produce a semi-fluid mass (see Fig. 3). In a screw machine, a major portion of heat comes from the frictional forces between screw material and cylinder. The semi-fluidized feedstock is then forced into the mold cavity through a gated runner system of the tool. In screw machines the backflow barrier allows the auger to act as a piston, pushing the molding medium into the tool cavity.

At a certain degree of mold filling (approx. 95%–97%), the so-called switching point, the injection pressure switches to hold pressure for avoiding a volume reduction of the injection molded piece due to cooling until the gate of the runner freezes and the part becomes solid. After a specific cooling time (typically 10–300 s) which depends on the volume of the injection molded part and the solidification behavior of the semi-fluid mass the tool opens, and by pushing the ejector system of the machine forward the part is ejected and removed by a handling system in an automated process or simply by hand. The sprue is removed and the CIM part can be put into sintering trays for the subsequent thermal treatment (debinding and sintering). During the cooling step of the part in the closed tool, the screw is pushed back and starts feedstock retraction and metering again for the next shot.

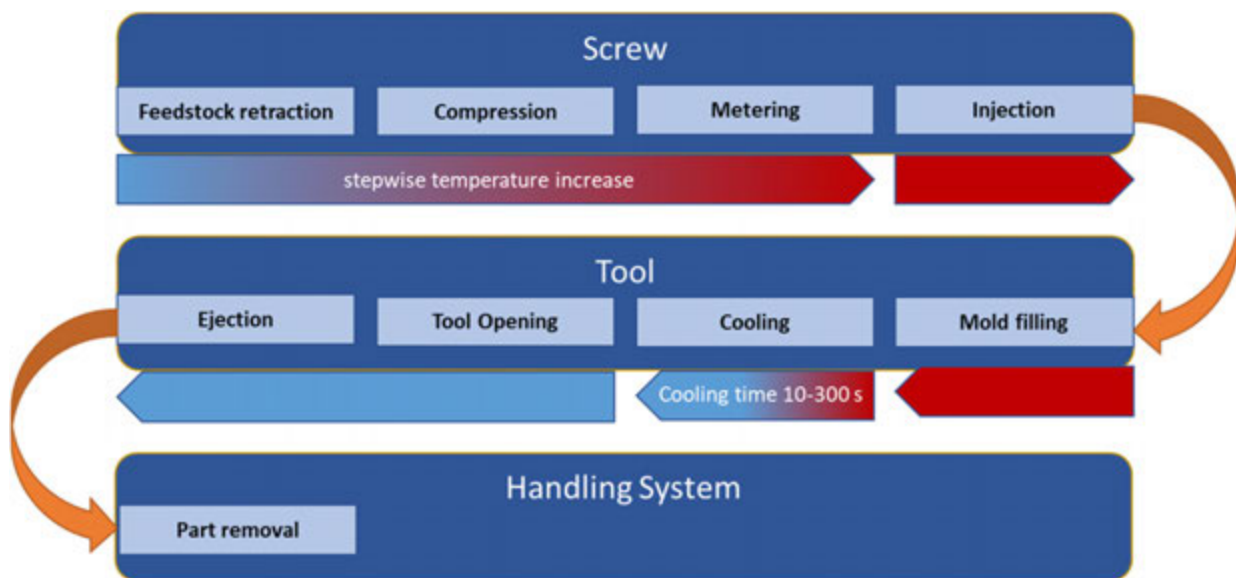


Fig. 3 Schematic view of the injection molding process within the injection molding machine.

For higher productivity in Ceramic Injection Molding increasingly multiple tool cavities are used. When it comes to incorporating multiple cavities in a CIM tool, it is essential that the route of the runner to each cavity is of equal length (Kim *et al.*, 2014). The sprue runner must therefore be branched accordingly. For material saving which would be needed for filling the runner system, hot runner systems can be used. Moreover, hot runners allow to manufacture parts with fewer internal stresses, because green parts that at first appear to be of good quality can possess internal stresses, which may in turn lead to cracks during later processing steps such as debinding (Michaeli *et al.*, 1996).

The temperature control of the injection molding process, especially tool temperature control, plays a dominant role for reliable production and high quality of the injection molded parts. Mainly, CIM processes rely on an isothermal mold temperature to produce parts. Typically, polymer and wax-based molding compounds are heated in the molding machine to temperatures of 130–200°C and are injected using barrel pressures between 50 and 150 MPa. Since the tool temperature is considerably lower than the melting point of the feed material, high injection speeds are required. Without these higher speeds, adequate filling of the cavities cannot be achieved without the premature freezing of the feed material. Accordingly, the mold temperature must be brought to the melting point of a controlled manner during injection. Ultimately, as CIM parts become larger and ever more complex, but also for production of micro parts or thin-walled parts so-called variotherm temperature control guarantees the highest possible part quality of the final product. By switching between defined temperatures, the user can directly influence the surface molding and the solidification behavior of the feedstock (Hohlbaum, 2019).

For tool design, the geometry of a component and the production volume are crucial aspects. They affect the position of the component in the tool and the number of cavities, the design of the runner system, the type and the position of the sprue, the operating mode and the removal of the injection molded parts (manually or automated) such as the ejection system (mold parting surface, core pullers) (Merz *et al.*, 2003). Further, it has to be taken into consideration that ceramic parts typically shrink during sintering by approx. 14%–22% linearly according to the packing density of the green parts. This property is considered as an oversize factor for tool construction.

Defects which result from the injection molding process are irreversible and impair the quality of the finished ceramic components. A comprehensive overview of injection molding errors, their sources and helpful counteractions has been compiled in (Maetzig *et al.*, 2002).

The key value in CIM for component quality and reproducibility is a constant viscosity of the feedstock. The most common way and widely applied in industry to analyze the melt progression in a tool cavity is by producing a short shot study (Karatas *et al.*, 2008; Zhang *et al.*, 1997; Moritz *et al.*, 2010). By interrupting the injection phase at different volumes a sequence of filling stages is created. The obvious advantage is its universal applicability to all tools using normal production conditions. Furthermore, it requires only modest time and cost. However, the produced samples show only the state at one moment and do not reflect the flow pattern in the final part. According to Walcher (2010), an alternative method for feedstock validation on a real injection molding machine by measuring the flow behavior is introduced. In this case the maximum injection pressure at the switching point to the holding pressure in an injection molding machine working under thermal equilibrium conditions is estimated exactly. The used testing tool produces parts while the tool cavity is filled to less than 100% with different injection speeds. The machine control registers the pressure at switch over point. From the pressure values, statements concerning the feedstock quality can be derived which can be applied directly to the machine process parameters (see Fig. 4).

Quality control of ceramic components in the green, debound and sintered state is commonly carried out by weighing and by visual inspection. Combining both simple methods allows for the detection of surface cracks, impurities, pores, voids, distortions, incomplete parts or sink marks. Measuring the density of the ceramic component after sintering is another indispensable method

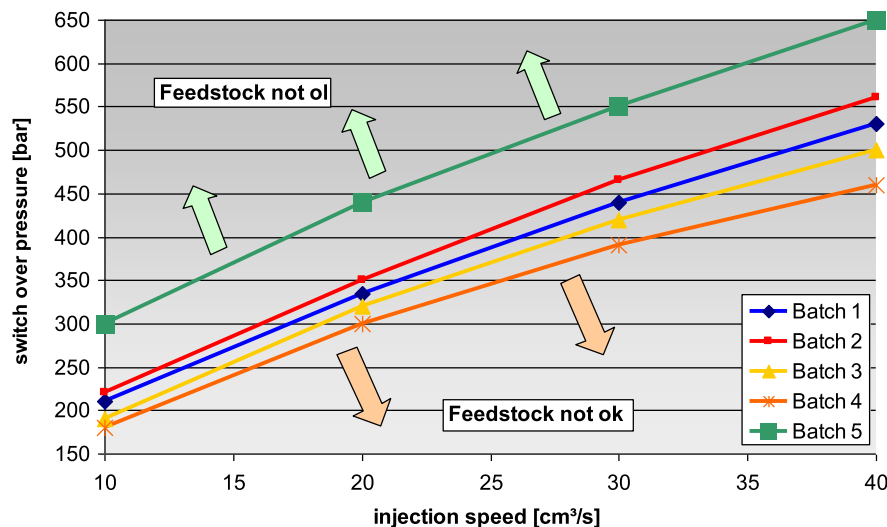


Fig. 4 Curves which are created with the ARBURG Feedstock test. Source: ARBURG GmbH + Co KG.

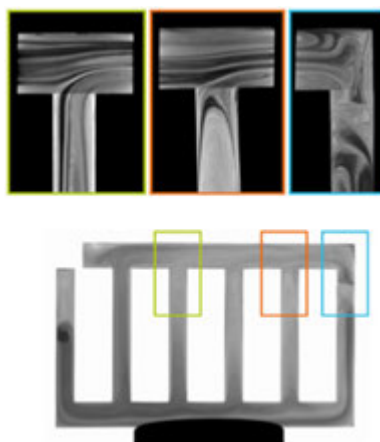


Fig. 5 Radiographic image of an injection molded testing part. The flow lines of the feedstock are visualized by means of a so-called tracer feedstock. Reproduced from Moritz, T., 2020. Ceramic injection molding: Developments in production technology, materials and applications. Powder Injection Molding International 14 (4), 3–29.

for characterizing the performance of the injection molded part, because most of the defects introduced in the green body during injection molding either increase or even become obvious after sintering (Moritz *et al.*, 2009).

More precise methods for detecting deviations from the desired geometry or distortion of components are 3D coordinate measuring or 3D scanning. For detecting defects inside components already in the green state computed tomography or simply X-ray radiography are the methods of choice. Entrapped air, voids, cracks, pores, inclusions, impurities, as well as weld lines, powder-binder separations and density inhomogeneities can be detected. A further visualization method uses a tracer material (Mannschatz *et al.*, 2011) which can be detected by X-ray computed tomography. A marker material feedstock that differs in X-ray attenuation but has the same flow behavior is added to the base feedstock during the molding process. Due to inhomogeneous mixing, the flow pattern become visible in CT scans (see Fig. 5).

Process Variants

Low-Pressure Injection Molding (LP-CIM)

According to the type of organic additive and thus the viscosity of the resulting powder-binder-mixtures, the feedstocks are suited to one of two plastic shaping methods. These methods are “low pressure” (LP-CIM) and “high pressure” injection molding. Applied injection pressures between 0.2 and 5 MPa are counted as a low-pressure area of the injection molding process. The advantages of LP-CIM in comparison to high-pressure CIM are:

- Less wear on the machine parts in contact with the powder
- Lower tooling costs
- Easier control of the flow behavior of the batch in LP-CIM

However, several disadvantages limit the use of this processing technology. In particular, defects which may remain in the molded parts after sintering, the difficult debinding step by so-called wicking, i.e., the melting wax component of the binder is soaked by a fine-grained powder bed, and the low degree of automation achievable with this process variant.

Micro Ceramic Injection Molding (MicroCIM)

Besides the distinction between high-pressure and low-pressure ceramic injection molding, a number of variations have been derived from the CIM process. One method – named after the size of the injection molded parts – is Micro Ceramic Injection Molding (MicroCIM) which can produce parts with complex shapes on a large scale and which is particularly used to make ceramic micro-holes. MicroCIM allows the manufacturing of precision products characterized by minimal wall thicknesses of 20 μm , aspect ratios up to 20 or structural details in the range of 50 μm or in certain cases less than 20 μm , with a surface roughness of about $R_z < 0.05 \mu\text{m}$ (Piotter *et al.*, 2001; Sutter, 2009; Petzoldt, 2008). The initial powder requirements for MicroCIM are more stringent than that for conventional CIM. The powder must be homogeneous; and the grain size of the sintered part should be at least about one order of magnitude smaller than the minimum internal dimensions of the micro-component in order to obtain a reasonably isotropic behavior (Bauer *et al.*, 2004). With respect to the surface quality of the replicated structures, the best results have been achieved by using ceramic powders with a mean particle diameter of 0.5 μm or even smaller. To obtain a viscosity of the plastic melt which is low enough to fill even the smallest structural details down to the sub micrometer range, a variotherm temperature conductor is used for

heating the molding tool near the melting point of the feedstock prior to its injection into the tool (Piotter *et al.*, 2009). To improve the precision and the accuracy of surface micro structures such as the homogeneity of injection molded parts, the shaping process can also be carried out as injection compression molding. This means, after injecting the feedstock in the mold cavity, the tool is compressed by a stroke of 0.2–0.3 mm providing an additional embossing step.

As a typical widely used microstructure, micro-holes act as transfer and exchange media in the form of micro-channels or nozzles that can be used as fuel injection nozzles, spinnerets, jet turbine blade cooling holes, printer jets, micro-structures of an array hole in a micro-pump, and micro-hole structures in fiber optic connectors and biomedical filters (Wang *et al.*, 1864; Sen *et al.*, 2005; Hanemann *et al.*, 2009; Su *et al.*, 2014). A further benefit can be obtained when two materials are combined in a micro device and so different functions can be realized. This can be enabled by the so-called two-component micro powder injection molding (2C-MicroPIM) (Islam *et al.*, 2012).

Future Process Variants

With regard to the extension of the potential of CIM, the necessity of new solutions in ceramic due to new component concepts, the pressure of reduction of the development for ceramic components or ceramic systems, a number of variations are in the focus research and development.

Hybridization of Materials

Multi-component Ceramic Injection Molding (multi-C-CIM), In-mold Labeling (IML) and In-mold Embossing (IME).

For more than one decade, material hybrids enveloping two different material classes have increasingly emerged. Combinations of polymers and ceramics are reported by Becker (2010) where the ceramic component has a key position for a certain application, as well as metal-ceramic material combinations (Gal *et al.*, 2019; Yeo *et al.*, 1998a,b). The major advantage of 2C-PIM is the direct combination of two materials with different properties in a single production step, therefore eliminating the need for a subsequent joining process (Petzoldt, 2010). However, combining different materials and processes requires the adjustment of the material properties and a tuning of co-processing and process technology. The co-processing of two materials from the green state to the sintered state involves a number of challenges and demands to be met. Choosing a suitable material couple is one key issue for a successful co-sintering process because chemical and physical properties cannot easily be changed by process adjustments. According to Hohlbaum (2019), the following materials properties need attention:

- Coefficient of thermal expansion (CTE): Differences in CTE lead to stresses in the interfaces during thermal treatment especially during cooling if thermal contraction deviates too much.
- Chemical compatibility: During co-sintering chemical reactions in the interface between the different materials may cause the formation of instable or brittle phases which may limit the long-term stability of the interface.
- Sintering conditions: Both materials should sinter within the same temperature range and atmosphere without melting or decomposition of one partner but still reach desired densities.

In addition, the process technologies each have their individual requirements, which include:

- The properties of slurries, pastes and feedstocks depend on the solid loading, which influences greatly the viscosity. The viscosity in turn effects flow as well as mold filling behavior and therefore defect formation.
- Chemically incompatible binders can lead to delamination between the components. Both involved binder systems have to fit co-debinding conditions.
- When the second component is added, the first component has to withstand mechanical and thermal stresses without deformation or delamination.
- The final shrinkage of the involved materials must be in the same order to keep the stress gradients at a low level. A mismatch of constrained deformation leads to warpage or even defect formation. This can be adjusted by the solid loading which effects the particle packing density in the green body. However, using too high or low solid loadings may cause insufficient flow behavior, warpage during debinding or high residual porosity. Therefore, solid loading has to be treated with care for both partners. It is advantageous to invest high efforts into modifying the raw powders (e.g., by bimodal powder mixtures or alloyed powders) for tailoring the pairing.
- Sintering should start at a similar temperature in order to prevent cracking of the fragile debound body caused by stress gradient.

In two-component powder injection molding (2C-PIM), two feedstocks are used which are adjusted in shrinkage behavior in order to form a two-component part with integrated functions. Several examples of 2C-CIM of different ceramic materials, stainless steel and ceramics, or glasses are shown in Edirisingh *et al.* (1987); Kim *et al.* (2014); Hohlbaum (2019); Karatas *et al.* (2008) and Zhang *et al.* (1997). Up today, up to four different components are combined in this way in the field of powder injection molding.

In-mold Labeling is well-known from plastics industry for instance for the production of yogurt pots with colored labels. As a variant of CIM, a ceramic or metallic green tape made by tape casting or extrusion is inserted into the mold cavity of the injection

molding tool. Afterwards, the CIM feedstock is injected and a material bonding between tape and feedstock is established. Thus, IML allows to integrate a joining step into the shaping process. In the case of use of a micro structured tool insert, the green tape is pushed into these microstructures by the injection pressure of the feedstock. Thus, a micro structured surface of the tape can be attained. This method is called In-mold Embossing. The micro structuring effect can be increased by an additional embossing stroke of 0.2–0.3 mm of the injection molding machine after injection of the feedstock.

After combining tape and feedstock, the completed green part must be co-debindered and co-sintered as known from two-component CIM parts. For that purpose, the binder composition of the tape should be adjusted to the feedstock binder system for a sufficient adhesion between both components and for avoiding detaching of the tape from the injection molded part during co-debinder. Furthermore, the sintering behavior of the tape must be precisely adjusted to those of the feedstock. IML or IME allow for providing injection molded parts with a very thin (approx. 50 μm to 1 mm) layer of a materials with different properties, like different color, electrical or magnetic properties, hardness, or wear resistance. Examples for IML components are described in [Edirisingh et al. \(1987\)](#) and [Moritz et al. \(2017\)](#).

Micro in-mold labeling (MicroIML)

Micro powder in-mold labeling (MicroIML) is a variant of macroscopic in-mold labeling. It is capable of applying a functional material on the surface of a MicroPIM part of complex geometry. For this approach, a thin ceramic or metallic green tape, made by tape casting, is inserted into the cavity of the injection molding tool. Next, the ceramic or metallic feedstock is injected and combined with the green tape by using the applied injection pressure of the feedstock and by a certain inner tool surface microstructure ([Mannschatz et al., 2014](#); [Piotter et al., 2015](#)). After debinding and sintering, the functional material is firmly connected with the substrate material ([Schlieper, 2013](#)).

Hybridization of Forming Processes

It is very difficult to determine the break-even point between CIM and Additive Manufacturing (AM), because there are two main drivers that play a crucial role. For CIM, it is the complexity of the part, which in turn determines the costs of the tool. For AM, it is the size of the part. This determines how many parts can be built in parallel and how long it takes to finish one run. From the viewpoint of the composition of the initial materials, the two feedstock-based AM methods, Fused Filament Fabrication (FFF) and Multi Material Jetting (MMJ), are having much in common with CIM. Both methods can be regarded as close relatives of CIM ([Moritz et al., 2018](#)). Advantageously, both processes can be easily implemented in existing PIM production settings, using the same feedstock preparation machines and expanding the potential range of products through, for example, individualization or personalization. All powders which can be processed by CIM can also be used for FFF or MMJ. Furthermore, the same debinding equipment used in the CIM industry can also be used for the AM components. In the near future, a closer connection between AM and CIM can be expected. For example, parts could be injection molded by CIM, followed by an individualization process by AM. A piece of ceramic jewelry, for example, could be created with unique details. This flexibility could be taken to the point where the end customer chooses or designs individual features which are then applied to a piece of jewelry. This combination of ceramic shaping technologies could also lead to customized medical products covering a very wide range of applications, from dental parts to surgical tools and other medical devices ([Hajek, 2018](#)).

The major advantage of ceramic parts combined by 2 or more materials with different properties is the elimination of a subsequent joining process ([Petzoldt, 2010](#)) and the reduction of the properties of the multifunctional parts by this joining. Property combinations such as conductive/insulating, magnetic/nonmagnetic, thermal conductive/thermal insulating or ductile/hard have been achieved ([Ziesche et al., 2017](#)).

Variothermal Temperature Control

There is a growing interest in the production of larger parts with higher aspect ratios. The main focus of this development is to achieve a faultless surface finish and narrow part tolerances. The key to success in the case of parts with long flow paths and thin wall thickness is to perfectly coordinate the interaction between the mold, the hot runner system and the dynamic mold temperature control system through the use of variothermal temperature control ([Moritz, 2020](#)).

Examples of Materials and Applications

Table 1 shows examples of typical materials and applications made by ceramic injection molding.

Summary

The ceramic shaping process, ceramic injection molding (CIM), is borrowed from the plastics process. The shaping process is particularly suitable for complex, near-net-shape or net-shape components in large numbers. A feedstock, which is processed by means of a shear roll extruder, is used as the basis for the shaping process. The shear roll extruder simultaneously enables the

Table 1 Examples of typical Materials and Applications made by Ceramic Injection Molding.

Alumina



Figure 6 Prick needle made of alumina. Courtesy Kläger Spritzguss GmbH.



Figure 7 Internal screw thread made of alumina. Courtesy Kläger Spritzguss GmbH.



Figure 8 Coffee mill grinder disc made of alumina. Courtesy Kläger Spritzguss GmbH.

Figure 9 Watch components made of translucent alumina. *Source:* Fraunhofer IKTS, INMATEC Technologies GmbH.

Figure 10 Alumina CIM component sintered in hydrogen, equipped with conductive paths, series resistor, and LED, 3-dimensionally structured by Direct Laser Structuring. Courtesy Hahn Schickard and IFKB, University of Stuttgart.

Casting cores ([German, 2019](#))

Zirconia

Figure 11 MicroCIM parts made of zirconia. *Source:* KIT-IAM.Figure 12 Luxury watch made of zirconia. *Source:* Chanel.

Oxygen sensors for steel melt

Si₃N₄-SiC-MoSi₂
composites

Figure 13 Ceramic glow plug made of electrically insulating and conductive silicon nitride by Multi-component injection molding. Courtesy BorgWarner.

Barium titanates

Positive thermal coefficient (PTC) elements for battery powered devices and heating elements for glue guns ([Schlieper, 2015](#))

incorporation of a binder for plasticizing the molding compound and the division of the powder agglomerates. Only in the case of a high degree of dispersion of the agglomerates is it possible to achieve uniform behavior of the feedstock along all value-added steps, injection molding, debinding and sintering. The chapter also shows in which direction the molding process ceramic injection molding is being further developed, in the direction of the hybridization of different materials or the hybridization of different molding processes on the basis of the same feedstock. This means that the process will become more and more widespread in the future.

References

- Bauer, W., *et al.*, 2004. Pulverspritzgießen von keramischen Mikroteilen. *Keramische Zeitschrift* 5, 292–297.
- Becker, U., 2010. Mit Synergien substituieren. Available at: <https://www.plastverarbeiter.de/33540/mit-synergien-substituieren/28.02.2020>.
- Bleyan, D., *et al.*, 2015. Specific interactions of low molecular weight analogues of carnauba wax and polyethylene glycol binders of ceramic injection moulding feedstocks. *Ceramics International* 41, 3975–3982.
- Burger, W., 2009. Gegen Biegen und Brechen. *Kunststoffe* 10, 83–86.
- Chartier, T., *et al.*, 1995. Supercritical debinding. *Ceramics Transactions* 51, 327–331.
- Chartier, T., *et al.*, 2001. Injection moulding of hollow silicon nitride using fusible alloy cores. *Ceramics International* 27, 821–827.
- Edirisingh, M.J., *et al.*, 1987. Rheology of ceramic injection moulding formulations. *British Ceramic Transactions Journal* 86, 18–22.
- Gal, C.W., *et al.*, 2019. Investigation of stainless steel 316L/zirconia joint part fabricated by powder injection moulding. *International Journal of Applied Ceramic Technology* 16, 315–323. doi:10.1111/ijac.13027.
- German, R.M., 2007. Global research and development in powder injection molding. *Powder Injection Moulding International* 1 (2), 33–36.
- German, R.M., 2013. Powder injection moulding: Statistical trends and forward forecasts for the industry. *Powder Injection Moulding International* 7 (1), 35–43.
- German, R.M., 2019. The evolution of powder injection moulding: Past perspectives and future growth. *Powder Injection Moulding International* 13 (1), 57–68.
- Hajek, K., 2015. Answers to demand – Fitting binder concepts for growing CIM requirements. *Ceramic Application* 3 (2), 2–4.
- Hajek, K., 2018. Ceramic Injection Moulding: Binder innovations and Additive Manufacturing open up new opportunities. *Powder Injection Moulding International* 12 (1), 67–72.
- Hanemann, T., *et al.*, 2009. Process chain development for the realization of zirconia microparts using composite reaction moulding. *Ceramics International* 35, 269–275.
- Hausnerova, B., *et al.*, 2017. Effect of backbone binders on rheological performance of ceramic injection moulding feedstocks. *Polymer Engineering and Science* 57, 739–745.
- Hens, K.F., *et al.*, 1995. Injection moulding of various metals and ceramics using an acetalbinder™ PMITEC. In: *Advances in Powder Metallurgy & Particulate Materials* vol. B2, pp. 627–636.
- Hohlbaum, S., 2019. Regloplas variothermal temperature controls and hot runners: expanding the capabilities of PIM technology. *Powder Injection Moulding International* 13 (1), 79–84.
- Huzzard, R.J., *et al.*, 2003. A water-based system for ceramic injection moulding. *Journal of the European Ceramic Society* 23, 2053–2060.
- Islam, A., *et al.*, 2012. Two-component micro injection moulding for hearing aid applications. *The International Journal of Advanced Manufacturing Technology* 62, 605–615.
- Karatas, C., *et al.*, 2008. Investigation of mouldability for feedstocks used powder injection moulding. *Materials & Design* 29, 1713–1724.
- Kim, J., *et al.*, 2014. Imbalance filling of multi-cavity tooling during powder injection molding. *Powder Technology* 257, 124–131.
- Klinger, E., *et al.*, 1940. German Pat. 699080.
- Maetzig, M. *et al.*, 2002. Strategies for injection moulding metals and ceramics. In: *Proceedings of the 2002 World congress on Powder Metallurgy & Particulate Materials*, pp. 10–33–10–41. Orlando, FL.
- Mannschätz, A., *et al.*, 2011. 3D visualization of flow patterns in injection moulded ceramic green parts. *Powder Injection Moulding International* 5 (2), 60–65.
- Mannschätz, A., *et al.*, 2014. Manufacturing of two-colored co-sintered zirconia components by in mould-labelling and 2C-injection moulding. *cfi/Ber. DKG91* 8, E1–E5.
- Merz, L., *et al.*, 2003. In form gebracht – spritzgegossene Keramikbauteile mit maßgeschneidertem Eigenschaftsprofil. *Pulvermetallurgie in Wissenschaft und Praxis* 21, 277–289.
- Michaeli, W., *et al.*, 1996. Hot runner molds aid powder injection molding. *Modern Plastics International* 5, 75.
- Millán, A., *et al.*, 1997. Aqueous gel-forming of silicon nitride using carrageenans. *Journal of the American Ceramic Society* 17, 211–216.
- Moritz, T., *et al.*, 2009. Ceramic injection moulding: A review of developments in production technology, materials and applications. *Powder Injection Moulding International* 3 (3), 23–34.
- Moritz, T., *et al.*, 2010. Verification of the simulation results for mould filling processes in ceramic injection moulding. *Ceramic Forum International* 87.
- Moritz, T., *et al.*, 2017. Material- and process hybridization for multifunctional ceramic and glass components. *Ceramic Applications* 5 (2), 66–71.
- Moritz, T., *et al.*, 2018. Ceramic injection moulding and thermoplastic additive manufacturing side by side: Opportunities and challenges. *Powder Injection Moulding International* 12 (4), 1–8.
- Moritz, T., 2020. Ceramic Injection Moulding: developments in production technology, materials and applications. *Powder Injection Moulding International* 14 (4), 3–29.
- Mutsuddy, B.C., 1987. Mechanical properties of injection molded ceramics. *Powder Metallurgy International* 19 (2), 43–45.
- Mutsuddy, B.C., 1989. Equipment selection for injection molding. *Ceramic Bulletin* 68 (10), 1796–1802.
- Petzoldt, F., 2008. Micro powder injection moulding – Challenges and opportunities. *Powder Injection Moulding International* 2 (1), 37–42.
- Petzoldt, F., 2010. Multifunctional parts by two-component powder injection moulding (2C-PIM). *Powder Injection Moulding International* 4 (1), 21–27.
- Piotter, V., *et al.*, 2009. Micro powder injection molding – Latest developments, PM2TEC. In: *Advances in Powder Metallurgy & Particulate Materials* 4, pp. 200–205.
- Piotter, V., *et al.*, 2015. Micro powder injection moulding: Processes, materials and applications. *Powder Injection Moulding International* 9 (3), 63–70.
- Piotter, V. *et al.*, 2001. Fabrication of micro-components by micromachining and injection moulding. In: *Proceedings of 2nd International Euspen Conference*. Turin.
- Schlieper, G., 2013. PIM at Euro PM2013: Innovations in materials and processing highlighted in Gothenburg. *Powder Injection Moulding International* 7 (4), 47–56.
- Schlieper, G., 2015. INMATEC technologies GmbH: A feedstock supplier at the forefront of CIM technology. *Powder Injection Moulding International* 9 (3), 43–50.
- Schlieper, G., 2016. Philips lighting: The evolution of PIM HID lighting components and the potential for transparent alumina injection moulding feedstocks. *Ceramic International* 42, 17045–17052.
- Schwarzwalder, K., 1938. US Pat. 2,122,960.
- Sen, M., *et al.*, 2005. A review of electrochemical macro- to micro-hole drilling processes. *The International Journal of Machine Tools and Manufacture* 45, 137–152.
- Su, B., *et al.*, 2014. Centrifuge-assisted micromoulding of ceramic microparts. *Ceram. Int.* 40, 13735–13739.
- Sutter, M., 2009. Mikrospritzgießen bringt Keramik in Hochform. *Mikroproduktion* 1, 48–51.
- Trunec, M., *et al.*, 2002. Thermal removal of multicomponent binder from ceramic injection mouldings. *Journal of the European Ceramic Society* 22 (13), 2231–2241.
- Verpoort, P.J., *et al.*, 1996. Overview of powder injection moulding. *Advanced Performance Materials* 3 (2), 121–151.
- Walcher, H., *et al.*, 1999. Aufbereiten von keramischen Spritzgießmassen. *Werkstoffe in der Fertigung*.

- Walcher, H., 2010. Pulverspritzgießen erfordert präventive QS. *Kunststoffberater* 55 (1–2), 27–29.
- Wang, C., *et al.*, 1864. Fabrication of micro-parts with high-aspect ratio micro-hole array by micro-powder injection moulding. *Materials* 2018, 11. doi:10.3390/ma11101864.
- Wang, J., *et al.*, 2016. Ceramic injection moulding. In: *Reference Module in Materials Science and Materials Engineering*, pp. 1–22.
- Witzleben, M.V., *et al.*, 2002. Keramikpulver-Spritzgießen in der Praxis. *KU Kunststoffe* 92 (6), 52–57.
- Witzleben, M.V., *et al.*, 2008a. Maßgeschneiderte Feedstocks für den keramischen Spritzgießprozess. *Keramische Zeitschrift* 5, 344–346.
- Witzleben, M.V., *et al.*, 2008b. Tailor-made feedstocks for ceramic injection moulding. *International Ceramic Review* 57 (6), 406–408.
- Witzleben, M.V., *et al.*, 2008. Maßgeschneiderte Feedstocks für den keramischen Spritzguss. In: Kriegesmann, J., Hrsg., *Technische keramische Werkstoffe*, vol. 106. Ergänzungslieferung, S. 3.3.3.7, pp. 1–22.
- Wroblewska, G.H., 2001. Structural ceramics with complex shape – Forming methods. *Ceramic Engineering and Science Proceedings* 22 (3), 43–50.
- Yeo, J.G., *et al.*, 1998a. Zirconia-stainless steel functionally graded material by tape casting. *Journal of the European Ceramic Society* 18, 1281–1285.
- Yeo, J.G., *et al.*, 1998b. Design and microstructure of ZrO₂/SUS316 functionally graded materials by tape casting. *Materials Letters* 37, 304–311.
- Zhang, T., *et al.*, 1997. The orientation of binders and particles during ceramic injection moulding. *Journal of the European Ceramic Society* 14, 212–222.
- Ziesche, S., *et al.*, 2017. Mehrlagenkeramik und Keramikspritzguss – eine technologische Kombination zur Herstellung dreidimensionaler funktioneller Keramikkomponenten. *Keramische Zeitschrift* 01–02, 029–033.

Tape Casting and Lamination

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Tape Casting and Lamination

Tape casting of ceramics was first patented by Howatt in 1952 (Howatt, 1952) for the production of thin capacitor sheets. Tape casting is still one of the primary techniques for ceramic capacitor manufacture today. Tape casting is also known as the “doctor blading” or “knife coating” process since a doctor blade or doctor knife is typically the primary tool involved in the forming process. Other coating techniques such as gravure, micro-gravure, slot die and tension coating are also widely used. The goal of tape casting is the creation of a thin, essentially two-dimensional, sheet from a liquid suspension of particles (ceramic, metal or other). Equipment manufacturers and capacitor manufacturers report tape thicknesses as low as two microns, with fired films as low as one micron. Tapes in excess of three-millimeter thickness can also tape cast, but are generally easier to produce by other methods. The bulk of commercial tape production is between 0.025 mm and 1.27 mm dry thickness with most between 50 and 250 μm .

Single layers of sintered tape, typically 0.1–1.0 mm thick, are used in applications including electronic substrates, porous membranes, monolithic capacitors, wear resistant plates, and electrolyte supported fuel cells. Three dimensional composite products such as multilayer ceramic capacitors (MLCC), packages (MLCP) from both high temperature and low temperature ceramics, ceramic multichip modules, functionally graded materials, and ceramic fuel cells (SOFC and MCFC) are produced by laminating multiple tape layers.

The tape casting process is similar to the slip casting process in that it is a fabrication technique using a fluid suspension of ceramic or metal particles as the forming medium. There are significant differences, however, between the two processes. Modern tape casting often utilizes a high-volatility nonaqueous solvent since the drying process is evaporative rather than absorptive into a plaster mold. There is a balance each manufacturer must consider; the lower cost and environmentally friendly solvent water versus the lower energy needs, increased evaporative speed and increased solubility of other organics offered by nonaqueous organic solvents. Much effort and expense has been undertaken in recent years/decades toward increasing the capability and utility of water-based tape casting. Depending on the unit of measure (tons, companies or acreage) it is arguable whether water based or organic solvent-based tape casting is more prevalent. It is noteworthy that the Howatt patent reported the use of plaster batts as the tape casting surface and that water was the primary liquid vehicle. In the mid-1950s, Park, of the American Lava Corporation, patented the use of a non-absorptive carrier in place of the porous casting surface (Park, 1961). Non-absorptive carriers including polymers, metals and glass are used for the vast majority of modern tape casting, whether aqueous or non-aqueous.

The Doctor Blade Process

The horizontal bed tape casting process, illustrated in Fig. 1, consists of a stationary, adjustable height doctor blade, a moving carrier surface, and a drying chamber. The ‘heart’ of the tape casting process appears to be mechanically simple; however, the design of blades, casting machines, and the slip formulations that make the process work remain subjects of extensive research and development.

Materials Selection

Since the material to be cast is predetermined on the basis of required material properties downstream, organic additives are selected depending upon the powder(s) chosen, often according to the firing atmosphere needed for those powders. The most important selection is that of a binder/plasticizer combination that will yield a strong, flexible tape without damaging final properties after sintering. The binder and plasticizer must facilitate formation of the desired part but burn off cleanly during the pre-sintering operation. Most binder systems chosen are long-chain film forming thermoplastic polymers. Many organic systems meet clean burn-off criteria when the sintering is done in an oxidizing atmosphere at relatively high temperatures, i.e., above 650°C. Many modern ceramic and metallic systems, however, include nitrides, carbides, low melting glasses and reactive braze materials which require the use of organic systems that can be removed in the absence of oxygen and in some cases at temperatures

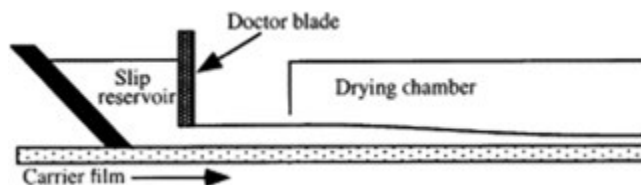


Fig. 1 Schematic of the doctor blade tape casting process.

Table 1 Selected organic systems for tape casting

<i>Nonaqueous solvent systems</i>			
<i>Solvent(s)</i>	<i>Binder</i>	<i>Plasticizer(s)</i>	<i>Deflocculant</i>
MEK/toluene	Poly(propylene carbonate)	Butyl benzyl phthalate	Z-3 Menhaden fish oil
MEK/ethanol	Poly(vinyl butyral)	Dibutyl phthalate/polyalkylene glycol	Synthetic waxy ester
MEK/ethanol/cyclohexanone	Poly(ethyl methacrylate)	Dibutyl phthalate	Z-3 Menhaden fish oil
<i>Aqueous solvent systems</i>			
<i>Binder</i>	<i>Plasticizer(s)</i>	<i>Cross-linker</i>	<i>Deflocculant</i>
Hydroxypropyl methyl cellulose	Poly(ethylene glycol)/glycerol	–	Ammonium polyacrylate
Acrylic emulsion	–	Poly(oxyalkylene-diamine)	Ammonium polyacrylate

as low as 300°C and in a few seconds rather than in minutes or hours. Acrylic and polycarbonate binders that evaporate or “unzip” upon heating are often used in tape casting systems requiring inert or reducing sintering atmospheres. Commonly used binders for oxidizing firing include poly(vinyl butyral), poly(ethyl methacrylate), poly(methyl methacrylate) and various other acrylic and vinyl copolymers. Other necessary considerations during binder/plasticizer selection include the thickness of the tape to be cast, the surface upon which the cast is to be made, and the solvents desired. Some binders have a greater affinity for and thus adhere more readily to the casting surface chosen. High volatility solvents such as acetone or methyl ethyl ketone (if not water) are often used for casting thin tapes (below 0.25 mm) while less volatile solvents are typically used for thicker tapes to avoid skin formation during drying. The type of solvent(s) used limits the binder/plasticizer systems that can be used (or vice versa) since the binder must fully dissolve in the solvent(s). The ongoing interest in many laboratories and production facilities involves aqueous binder systems to address health and safety concerns. Aqueous tape casting tends to employ non-soluble emulsion binders rather than water-soluble polymers. Extensive lists of solvents and organic additives are available in published literature. [Table 1](#) includes some systems found in literature and industry. As a final consideration in polymer and solvent selection, it has been extensively reported (though published infrequently) that a dissolved polymer in organic solvents tends to retain more tensile drying stress than a water-based emulsion in similar circumstances. This retained stress can have significant impact on downstream processes relying on flatness and positional tolerances.

Tape casting binders typically require plasticizers to improve room temperature flexibility by lowering the T_g of the thermoplastic polymer. It is often beneficial to use dual plasticizers (especially for thicker tapes), one to soften the polymer and a second to lubricate the tape matrix. The primary plasticizer is a low volatility solvent for the binder polymer. The second, non-soluble plasticizer can also act as a carrier release agent. Common plasticizers include various phthalates and glycols. All of the organics should be compatible with each other, if not fully miscible or soluble with the others to prevent segregation during drying.

The selection of a deflocculant/dispersant is also important since the dispersant prevents re-agglomeration of discrete particles after they are broken apart during milling. Proper use of a dispersant/deflocculant permits higher solids in the slurry thus accelerating gel formation and drying in the tape cast product and a more uniform dry tape. A shorter drying time helps to prevent binder segregation and potential density or chemical gradients in the tape as well as lowering manufacturing cost. Organic solvents tend to have low dielectric constants compared with water and thus tend to rely upon the steric hindrance dispersing mechanism to achieve a stable suspension. Aqueous suspensions can make good use of both electrostatic and steric separation forces (see [Lane and Nikles, 2001](#)).

Batching and Slip Preparation

The preparation of slurries for the tape casting process is similar to standard ceramic processing techniques, i.e., ball milling in a dense container with a charge of grinding media. Bead milling, attrition milling, ultrasonic techniques, and basket mills may also be used, among others. A powder dispersion step typically precedes binder and plasticizer addition to optimize both tape density and homogeneity. The purpose of a dispersion-milling step is to break up agglomerates and aggregates and to prevent re-agglomeration prior to binder addition. The solvent(s), dispersant and powder are processed in a jar mill filled approximately to one third with grinding media. The remainder of the charge fills to about one half to three quarters of the mill, which is rotated for 12+ hours. The slurry usually becomes quite fluid during this step due to the activity of the dispersant on particle surfaces.

Binder(s) and plasticizer(s) are dissolved or mixed into the slurry after dispersion milling. The slurry usually becomes more viscous with binder incorporation since relatively high molecular weight binders are used. There are cases, however, where the addition of a binder makes the slip less viscous since the binder can act as a secondary dispersant and replace the dispersant on particle surfaces during mixing. This type of dispersant/binder interaction must be accounted for in the development of a slip formulation and preparation process. Any addition of an aqueous emulsion binder decreases the slurry viscosity due to the water content of the emulsion binder. Non-aqueous dissolution of binder is typically complete within 12–48 h, their aqueous counterparts in less than an hour of low energy mixing. Tape casting slips tend to have a pseudoplastic rheology after all of the components are incorporated.

Slip Conditioning and Characterization

After thorough mixing of all components, the slip is conditioned in preparation for the tape casting process. The first procedure performed after discharging the slip from the ball mill is a de-airing process to remove entrained air introduced during milling, mixing and pouring. Slow rolling without milling media tends to coalesce small bubbles and break large bubbles but is a long procedure that can take up to 150 h to complete at rotational speeds less than 10 rpm. Centrifugation of the slurry concentrates entrained air on one side of the slip body leading to coalescence and rupture, but also tends to concentrate particulates on the opposite side leading to inhomogeneity. The most common technique used for nonaqueous slips is vacuum deairing with continuous agitation or stirring. Vacuum de-airing is done in a vacuum chamber or desiccator under a vacuum of 635–700 torr. The use of higher vacuum pressures can be detrimental to the slip since rapid boiling of the slurry will cause excessive solvent loss and the formation of a solvent depleted layer or skin on the slip surface. Since many water-based emulsion binders are damaged by being under vacuum, this deairing step is done prior to binder mixing if these binders are used. Deairing time is determined by experimentation and depends upon the slip volume and viscosity as well as other factors. Deairing times range from less than eight minutes to a few hours. A good rule of thumb is to use about 4–8 min for a volume of ~ 4 L of 1500cP slurry. A paddle or blade mixer is used to shear the slip during deairing to lower slip viscosity and to help break bubbles on the slip surface.

The deaired slip can be used directly in the tape casting process. Manufacturing processes, however, tend to include a filtration process prior to coating. Filtration is essential when processing tapes below 100 μm . Filtration involves the pumping or pressure feeding of slip through a sieve or series of sieves to remove agglomerates or aggregates not broken down during milling and debris introduced during milling or handling, including pieces of media or mill lining. Filtration also aids removal of air bubbles not removed through deairing. Sieve mesh openings are determined by the critical size of the defect-causing objects being removed, and the final thickness of the tape being cast. The use of submicron filters in 5 μm MLCC tapes is common, while 100 μm filtration is often adequate for thicker tapes or substrates. After filtration, the casting slip is typically pseudoplastic with a viscosity between ~ 500 and 6000 mPa s (cP).

Tape Casting

The heart of the horizontal bed tape casting process is the doctor blade assembly. This assembly consists of an adjustable metering blade with a reservoir to hold the slip. Many variations of doctor blade tape casting exist, all falling into one of two categories, moving blade or stationary blade casting. Most moving blade/stationary carrier machines are used in laboratories or very small-scale production facilities whereas the more prevalent stationary blade/moving carrier systems are used in larger manufacturing processes. The stationary blade configuration permits roll-to-roll continuous production using automated carrier payout and take-up systems. Roll-to-roll processing can then be used in later forming processes if desired. The doctor blade, whether moving or static, is set at a specific height above the casting surface using micrometers or precision shim stock. For casting very thin tapes, or large quantities of a single tape thickness, a precision machined, fixed height doctor blade may be used.

Blade height, or 'blade gap' is one of four primary factors that determine the wet film thickness. The other factors governing this thickness, and thus requiring control, are viscosity, casting speed and reservoir fill depth. The machine operator controls as many of these parameters as possible and then adjusts the blade gap as the last measure of thickness control. The viscosity, being temperature dependent, can be controlled by controlling slip temperature during casting, though it is more common not to do so and to adjust blade gap to account for lot to lot changes in viscosity. Control of reservoir height behind the doctor blade is often automated using a sensor to detect slip level in concert with a feed valve to modulate replenishment slip flow into the reservoir. Since the ratio of doctor blade height to dry tape thickness can vary from unity to 2.5, trial and error is often the only means to achieve the final desired thickness. The wet thickness of a tape can be monitored using laser or optical reflection, gamma backscatter equipment or other non-contact methods. If thickness monitoring is done just downstream from the doctor blade, a feedback loop to the slip level sensor can adjust reservoir depth and thus control wet film thickness very accurately. The expense of doing this, however, makes it a rare feature in industrial tape casting.

Typical doctor blade assemblies consist of one or more rigid blades mounted on a (typically aluminum or plastic) frame. The frame assembly also defines the reservoir that holds the slip. Many different shapes of reservoir and the metering edge of the blade have been reported ranging from a standard box shape with flat bottom blade to a rounded bar to a 'comma' shape with fitted reservoir walls. Angular and parabolic blade bottoms find use mainly in laboratory operations. From a practical standpoint, the use of a flat-bottomed blade has been preferred since it maintains dimensional integrity for a longer time compared to other blade shapes. The thickness of the blade along the casting direction at the casting interface (blade bottom) has also been varied from a knife edge to over three inches depending, apparently, on individual preferences. Some major considerations influencing blade design include: weight, lifetime, ability to mediate reservoir height fluctuations and cost of refinishing. Some tape casters use a double doctor blade – two metering blades in series – in applications where very close tolerances must be maintained. In theory, the first metering blade defines a very precise, if very low, reservoir that aids in the uniformity achievable by the second blade. The net gain achieved by using a double blade versus a thicker single blade remains in debate.

As mentioned earlier, coating or 'slip laydown' techniques other than doctor blading include gravure, micro or reverse gravure, slot die coating as well as "waterfall" coating. While doctor blade and waterfall coating are nearly always performed on horizontally or near-horizontally oriented machines, gravure or slot die coating can be done on a significant incline, vertically or even upside down, depositing the slip on the underside of the carrier film.

Regardless of design or orientation, the coating mechanism meters the slip onto a moving carrier film that transports the deposited slip into a controlled atmosphere drying chamber. The carrier film itself is chosen based on several factors including non-reactivity with the slurry, surface quality, surface finish, cost, stiffness, tensile properties under drying conditions, and ease of dry tape release. Common carrier materials include plain, corona treated, fluorinated or silicone coated Mylar®, plain or silicone coated polypropylene, Teflon®, carbon steel, stainless or valve steel, or polymer- or wax-coated paper. The carrier film is required to withstand downstream drying conditions such as elevated temperatures without degrading the desired properties or characteristics of the cast tape. Very thin thermoplastic carriers, for example, can exhibit excessive tensile yield under elevated drying temperatures and thus degrade tape quality. Products such as thin-film electronic substrates that have specific surface finish requirements may be cast on very smooth carriers since the tape surface dried against the carrier film then displays a lower as-fired surface roughness than the air-dried surface.

Casting speed is typically determined by the length of the drying chamber (or vice versa), the thickness of the tape being cast, and the volatility of the solvent system used. Typical speeds for casting can range from 15 cm min^{-1} to over 5 m min^{-1} . Extremely thin tapes dry more rapidly and thus can be cast at speeds in excess of 10 m min^{-1} , or even upwards of a meter per second.

After a thin, uniform slurry layer is deposited onto the carrier film, the tape is dried to remove the solvent(s). Since the slip is supported on an impermeable carrier, evaporation occurs from only one side of the tape, potentially leading to gradients in solids loading, porosity, and organic constituents. These gradients can significantly affect densification later in the process. Various heating profiles, slurry solids loading and/or organic compositions, air flow rates, location of heating sources (above vs. underneath), and the use of azeotropic solvent mixtures have been explored to avoid compositional gradients during drying of tapes. While gradients can be minimized by combinations of the above approaches, the one-side-drying inherent in the tape casting process makes the formation of gradients through the tape thickness inherent as well.

The use of flowing air speeds the drying process by maintaining low solvent vapor concentrations in the local atmosphere. Local safety regulations may also mandate a maximum vapor concentration allowed. Air used for drying is often filtered to remove dust particles and may be preheated to maximize tape drying rate. Airflow is typically directed countercurrent to the casting direction to form both a solvent vapor gradient and a temperature gradient within the drying chamber. If heated air is used, a hot air inlet at the end of the drying chamber results in a maximum temperature at the end of the drying process to remove remnant solvents while allowing a lower temperature at the beginning of the drying process to minimize skinning or 'case hardening'. Drying can also be accelerated by the use of underbed heating and/or overhead radiant heating to heat the wet cast. Underbed heating is very common, while air heating and overhead heating are rarer.

Shaping

The green tape, after drying, is a strong, flexible sheet of thermoplastic polymer filled with ceramic, metallic or other powder. Due to the evaporative drying process, green tapes also typically include 5%–25% porosity or more. Green densities of 50%–65% of theoretical are routinely achieved for both ceramic and metal powders. This green density can be further increased by reducing the porosity of the green tape through pressing or calendaring. Calendaring, though uncommon, reduces the tape porosity by compaction between two counter-rotating rollers. It can also be used as a partial solution to the compositional gradients mentioned earlier, though the perceived benefit seldom outweighs the cost. Pressing, similar to lamination described below, also reduces porosity and corresponding density gradients.

Long lengths of cast tape are typically cut or 'blanked' into manageable sizes by either cutting the tape, or stamping with a tool and die. The resulting 'blanks', 'sheets', or 'cards' may be sized to include alignment or registration holes around the perimeter and are often sized to manufacture multiple small parts from a single sheet. The blanking process also avoids use of the cast tape edges which are tapered in thickness and thus unusable. Single layer substrate applications blank desired green substrate sizes and sinter at this point.

Tapes used in three-dimensional interconnected circuitry, such as MLCP's, are punched with through-holes at this stage. These holes, or vias, are typically made using punch and die but can also be made with water-jet, laser or microdrill. The vias are then filled with conductive ink. Circuit patterns are also added to each tape layer by screen printing conductive ink(s) onto the unfired blanks. Alignment through each of these stages is paramount and is accomplished by either mechanical (registration holes) or optical (registration marks) means. Some high-performance applications require positioning with better than $5 \mu\text{m}$ accuracy. Stacking and alignment of the metallized layers forms the three-dimensional structure (Fig. 2). Tape layers are often tacked together at this point to preserve alignment through further processing.

Lamination

A low temperature lamination process fuses multiple tape layers into a single, composite structure. This structure typically either includes multiple material types, or includes internal screen-printed conductive features. Laminates containing over 200 individual layers are not uncommon for MLCCs. Lamination methods vary depending on both the tape properties and final part requirements. The four most common approaches are uniaxial, isostatic single plate (wet bag), Isostatic double plate (wet bag) and tape

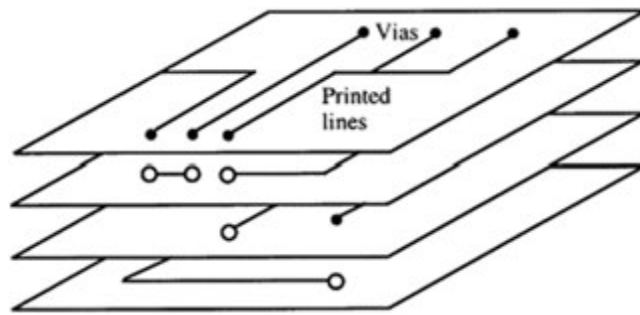


Fig. 2 After via punching and metallization, tape layers are stacked to form a three-dimensional, interconnected circuit within the ceramic material.

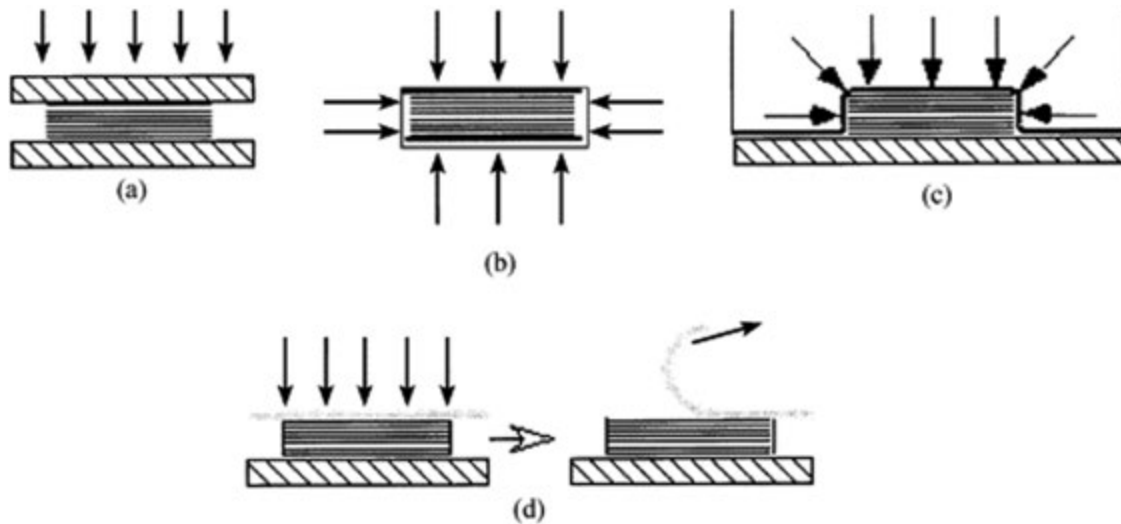


Fig. 3 Individual tape layers are formed into a single part by: (a) uniaxial lamination, (b) double plate isostatic lamination, (c) single plate isostatic lamination, and may be pre-laminated by (d) a tape transfer process.

transfer (**Fig. 3**). Lamination pressures range from 3 MPa to over 50 MPa while temperatures are generally kept below 100°C, often between 60°C and 90°C. In an ideal case, individual tape layers are no longer discernable in the laminate.

Uniaxial lamination, the simplest lamination method, fuses single tape layers together by the application of pressure and heat through two opposing heated platens. The edges of a tape stack can be constrained by die walls or left unconstrained during lamination. Isostatic lamination applies uniform temperature and pressure to all surfaces of the tape stack by means of a wet bag isostatic press with a heated fluid bath. Isostatic lamination is more widely used than uniaxial lamination in manufacturing environments due to uniform application of pressure and the resulting increase in laminate uniformity. Tape layers are protected from the fluid bath within a protective, vacuum sealed envelope or 'vacuum bag'. Vacuum sealing of the bags also avoids air pockets between tape layers and ensures full contact of one layer to the next. The use of a fluid bath in isostatic lamination also allows the lamination of multiple, separately sealed stacks in a single pressing. It is typical in isostatic lamination to use a rigid backing plate (often anodized aluminum) to maintain flatness of the stack after being laminated in the fluid bath. While the face against the backing plate is flat and smooth, the pressed face of the stack typically shows topography in accordance with any internal features in the stack such as screen-printed circuitry. Using two rigid plates, top and bottom of the stack, in the isostatic lamination process is often known as "double plate lamination" and is a hybrid of uniaxial and isostatic lamination. This method still uses the vacuum bag, avoiding trapped air bubbles between layers, but trades the uniformity of pressure offered in order to achieve a laminated stack having flat top and bottom faces with minimal topography. The tape transfer process, sometimes used as a pre-lamination 'stack and tack' process, applies layers to the stack one by one, typically pressing at a lower temperature and pressure than final lamination. This stack and tack process facilitates automation of the stacking process while maintaining alignment of the layers and internal features.

Laminates are considerably more rigid than individual tape layers due to the increased thickness and reduction of internal porosity. This increased stiffness allows for a multitude of possible cutting operations to separate an array of smaller parts. Dicing of multicomponent laminates, or simply edge trimming of single component laminates, is accomplished by gang saw, laser cutting, or hot knife cutting. Hot knife cutting, guillotine separation using a heated bed and heated knife, is far and away the most

common method for singulation of green multicomponent arrays due to the desirable balance of speed, cleanliness, and cost. Gang saw is rarely used due to speed, cost, and potential contamination considerations. Laser cutting is most often used for shapes with non-straight edges. Green laminates can also be scored or perforated with rows of vias to create weakened areas between components. The creation of these weakened areas in a multicomponent array allow the array to be sintered as a single part and snapped apart easily after the sintering process.

References

- Howatt, G.N., 1952. Method of Producing High-Dielectric High-Insulation Ceramic Plates. U.S. Patent 2582993.
- Lane, A.M., Nikles, D.E., 2001. Magnetic recording media: Particulate dispersions. In: Buschow, K.H.J., Flemings, M.C., Kramer, E.J., *et al.* (Eds.), *Encyclopedia of Materials: Science and Technology*, second ed. Elsevier, pp. 4897–4902.
- Park, J.L. Jr., 1961. Manufacture of Ceramics. U.S. Patent 2966719.

Further Reading

- Mistler, R.E., 1992. Tape casting. In: Schneider Jr., S.J. (Ed.), *Engineered Materials Handbook Volume 4: Ceramics and Glasses*, vol. 4. Materials Park, OH: ASM International, pp. 161–165.
- Mistler, R.E., Twiname, E.R., 2000. *Tape Casting: Theory and Practice*. Westerville, OH: American Ceramic Society.
- Shanefield, D.J., 1995. *Organic Additives and Ceramic Processing*. Boston, MA: Kluwer Academic.

Freeze Casting

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Introduction

Porous ceramics are widely used for SOFC (Chen *et al.*, 2012), thermal barrier (Scheffler and Colombo, 2005), filtration (Gauckler *et al.*, 1985), ceramic metal composites (Hautcoeur *et al.*, 2016), and so on applications. They are usually fabricated through foaming techniques (direct or indirect) and replica from natural as wood or organic as PMMA beads or sponge matters (Studart *et al.*, 2006). A thermal treatment is done for removing the template which leads to the formation of the porosity inside the material.

Freeze casting is a more recent technique which has been developed for a couple of decades, even if its first utilization is older (Smith-Johannsen, 1994). Freeze casting is a technic to process porous material, but also used to obtain dense specimen (Araki and Halloran, 2004). Freeze casting consists of freezing a suspension of particles down to the solvent solidification and removing it by solid solvent sublimation. The green part so obtained is sintered, without debinding owing to the small quantities of organic additives.

Depending on the device, isotropic or anisotropic porous specimen can be processed. The control of this porous structure is a difficult challenge. Indeed, a series of parameters, such as powder content, freezing rate and so on, have a direct impact on the structure characteristics (pore size, porosity, ...). Most of the studies carried out on freeze casting are concerned by the processing of anisotropic porous ceramics. This chapter will also be focused on this aspect.

How Does it Work?

During solidification of a liquid, the creation of a stable crystal starts with the formation of a nucleus from which the crystal can grow. Nuclei are stable germs (clusters of molecules) that act as interfaces for the condensation of additional molecules. If the nuclei are formed by an accumulation of molecules of the cooled liquid, the nucleation is named homogeneous or spontaneous. In all other cases (nuclei formed by particles, onto surfaces, ...), nucleation is called heterogeneous. Homogeneous nucleation of ice occurs at temperatures of about -40°C (Tremeac, 2005).

For freeze casting process, nucleation is mainly heterogeneous (Deville *et al.*, 2010), indeed the size of ice crystals depends on the ceramic particle size, as it has been observed for a constant particle number. The smaller the particles are, the greater the number of nucleation sites, which promote nucleation over growth. Nevertheless, the roughness and nature of the cooling medium do not influence nucleation (Donchev, 2005). However, it has been observed that the macroscopic organization of the pores can be modified by the texturing the cooling support surface or by the presence of a preformed layer of ice (Munch *et al.*, 2009).

During solidification, limit between solvent crystals created and the remaining liquid forms a solidification front. As described by Mullins and Sekerka's theory (Mullins, 1964), in the early state this front is flat and then could be destabilized. During the freezing of a ceramic suspension, two cases occur, depending on the stability of the solidification front. In the absence of destabilization (flat solidification front), the ceramic particles are pushed forward of the front, as illustrated at Fig. 1. This leads to the separation between the solvent and the particles and the formation of a powder compact. This phenomenon can be used to obtain, after freeze drying and sintering, dense part.

If destabilization of the front occurs, the particles can, under given conditions, be ejected laterally which leads to the creation of a lamellar structure, which after freeze drying and sintering, makes it possible to obtain anisotropic porous materials. In this particular case, the phenomenon of interaction between the solidification front and one or more particles have been widely studied for the past 30 years (Korber *et al.*, 1985; Shanti *et al.*, 2006; Deville *et al.*, 2009a). In the case of a particle close to the solidification front, three interactions are possible, as shown Fig. 2:

- Capture of the particle by the front of solidification: called " engulfment", which can occur even if the solidification front is stable (Fig. 2 particle 1).
- Ejection of the particle between the crystals of the solidification front (Fig. 2 particle 2).
- Ejection followed by a capture of the particle by secondary dendrites (Fig. 2 particle 3).

Only the ejection of the particle is wanted to produce anisotropic porous part, the engulfment of the particle is to be avoided. Indeed, this phenomenon causes an accumulation of particles in the solid solvent which could obstruct the porosity after lyophilization and sintering of the porous material. If we consider the interaction between a particle and the solidification front, its engulfment or ejection depends on the couple of forces involved during the freezing: the attraction (F_a) and repulsion (F_r) forces, define by Eqs. (1) and (2) (Korber *et al.*, 1985), respectively.

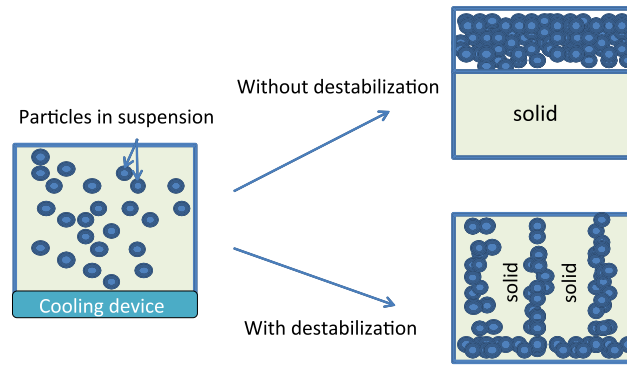


Fig. 1 Diagram of oriented freezing: obtaining the lamellar structure.

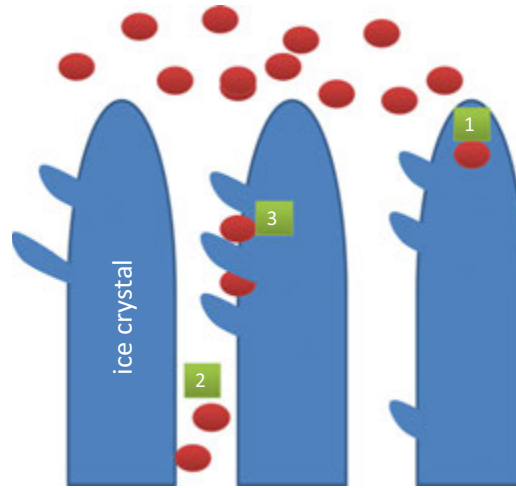


Fig. 2 Diagram of Interaction between particles/solidification front.

$$F_a = \frac{6\pi\eta vr^2}{d} \quad (1)$$

$$F_r = 2\pi r \Delta\sigma_0 \left(\frac{a_0}{d}\right)^n \quad (2)$$

with η the slurry viscosity, n an exponent value between 1 and 5, a_0 the average intermolecular distance and $\Delta\sigma_0$ interfacial free energy.

If the liquid film becomes too thin, there is contact between the particle and the solidification front, which will lead to the engulfment of the particle. This occurs when the attractive force becomes larger than the repulsion force or when the velocity of the solidification front exceeds a critical velocity V_c defined by Eq. (3):

$$v_c = \frac{\Delta\sigma_0 d}{3\eta A} \left(\frac{a_0}{d}\right)^n \quad (3)$$

with A , a characteristic quantity depending on the shape and size of the particle. Even if the front is stable, a velocity of the freezing front higher than the critical velocity will lead in the same way to an engulfment of the particle.

Considering the importance of the freezing front velocity, the temperatures involved during the process need to be well controlled. For that reason, several types of equipment have been developed.

How is it Possible to Process Porous Ceramic by Freeze Casting?

Isotropic porous materials are obtained by putting the slurry within a mold in a freezing device without any control of the solidification. For example, the freezing step can be performed directly inside a freezer. Moreover, if the slurry is put on a one side metallic plate (thermal conductor part) and polymeric mold (thermal insulator part) is used and placed in a freezer anisotropic structure could be obtained.

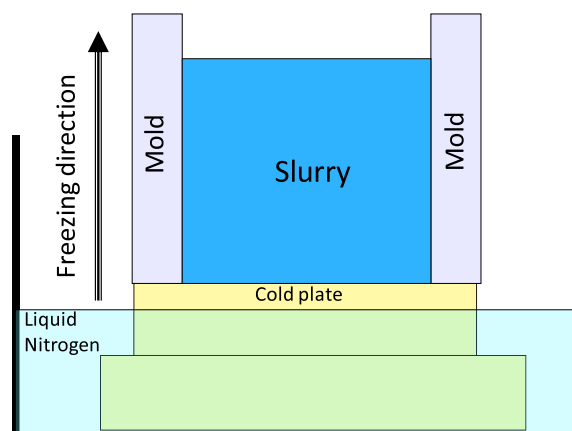


Fig. 3 Diagram of the classic freeze casting device.

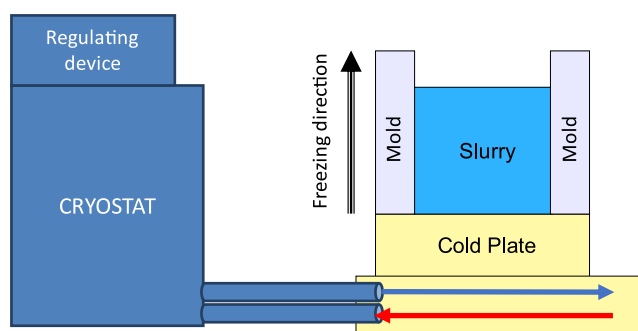


Fig. 4 Diagram of one side freeze casting device.

Several devices have been developed for controlling the solidification, or not, in order to obtain the porous anisotropic ceramic, all of them coming from the same original device. Indeed, devices are always divided in 3 parts: a mold for casting the slurry, a metallic plate where is settled the mold, the frozen media which might control the freezing step. In this way, basic device is simply a polymer mold place onto a metal plate which is frozen by liquid nitrogen (Fukasawa *et al.*, 2001), as described by Fig. 3.

In order to have a better control of the solidification of the slurry, a one side cooling device is used. The only modified part, in comparison with the basic device, is the freezing media system. Indeed, instead of using liquid nitrogen which leads to a fast and uncontrolled freezing, a cryostat, or heating element can be placed on the metallic plate. The first one can be employed for reaching a cooling freezing rate between 0.5° and $10^{\circ}\text{C min}^{-1}$. The second one, heating systems, can be used to reach faster freezing rate as $20^{\circ}\text{C min}^{-1}$ (Zhao *et al.*, 2011) as illustrated by Fig. 4.

Another way to ensure a good control both of the temperature and the structure is to regulate not only one side but two sides. A two-side cooling device leads to obtaining a control of the thermal gradient (Deville *et al.*, 2007) which is kept constant during all the freezing step. The device is composed of two metal fingers which are immersed in alcohol frozen by liquid nitrogen. The thermal regulation is ensuring by two heating elements for each metal finger. This system has been used to determine the effect of the freezing parameters on the pore size evolution.

An alternative two-side cooling device has been developed (Waschkies *et al.*, 2009). Instead of controlling the thermal gradient during the freezing step, the temperatures are regulated at both side in order to control the freezing front velocity. Several thermal sensors are placed in the mold to follow temperature along the specimen. By this way, it is possible to regulate not only the temperature but also the freezing front displacement. The interest of this technology is the ability to change the freezing speed or keep it constant in order to control the structure. Indeed, it has been shown that the structure is dependent of the freezing front velocity and by controlling it, you control the pore size evolution.

“Hybrid” technologies or special device have been setup for special applications. Basically, those techniques were set up for obtaining special shape of the sample or of the macroporosity. The simple way to control the macrostructure orientation is to swap the material for the freezing and isolated parts. Indeed, using metallic mold can induce a freezing of the slurry by the side instead of by the bottom (Moon *et al.*, 2002).

Further research has been conducted on the use of the dipole moment of the water molecule or the magnetic properties of the powder used to carry out the freezing step under electric (Tang *et al.*, 2010; Zhang *et al.*, 2009) or magnetic field (Porter *et al.*, 2012).

In the case of aqueous suspensions, imposing an electric field in the freezing direction makes it possible to control the thickness of the walls (Tang *et al.*, 2010). In addition, a radial field (perpendicular to the freezing direction) causes a change in the direction of ice crystals growth. The same type of effect is observed during the freezing of the suspension containing iron oxide particles under a magnetic field (Porter *et al.*, 2012). Another example of hybrid technology is the processing of porous film for membrane applications made by a freeze tape casting technology. This consists of freezing a tape after its processing by tape casting (Rachadel *et al.*, 2017).

How to Control the Porous Structure?

In addition to the freezing rate, which is controlled by the device, other parameters influence the structure of the final material. The structure is divided into 4 main characteristics: the porosity level, the pore size, the wall thickness and the structure morphology. In order to control these characteristics, the researcher has several strings to its bow: the amount of dry matter, the solvent, additive, freezing parameters and so on.

Freeze casting can be achieved by employing many solvents which have the particularity to solidify at different temperatures and specific porous structures are obtained. The three main solvents used are: tert-butyl alcohol (Sofie, 2007) with a melting temperature (T_m) of 25°C; camphene ($T_m = 51^\circ\text{C}$) (Lee *et al.*, 2008), or water ($T_m = 0^\circ\text{C}$) (Lasalle, 2011).

In the case of tert-butyl alcohol, the microstructure will be of centro-symmetric with prismatic pore (Sofie, 2007; Choi *et al.*, 2012). Freezing a suspension of a powder content of 10% in volume lead to obtaining a pore size around 140 μm (Choi *et al.*, 2012). It has been shown that in the case of tert-butyl alcohol, there is a pore size gradient along the freezing axis (Hu *et al.*, 2010) (freezing direction imposed by the thermal gradient).

The second solvent, camphene, is used for its high melting temperature (Araki and Halloran, 2004) which allows to sublime it at room temperature. As for the previous solvent, the pore size is high and varies from 140 to 280 μm as a function of the freezing time, from 1 to 7 days (Yook *et al.*, 2009). The porous structure is cellular because of the dendritic solidification of the solvent.

Water is still the most used solvent (Deville, 2007). As described in the literature (Ananth and Gill, 1989), ice crystals grow in the shape of an ellipse, which explains the morphology of the pores. However, the use of additives (Sofie and Dogan, 2001) may result in a change in morphology. These additives, commonly used as binder (Deville, 2007) or cryoprotectant (Zhang *et al.*, 2010), change the lamellar morphology previously described into more cellular morphology, similar to that obtained for camphene suspensions. For example, it has been shown that the addition of 10% of glycerol strongly modifies the morphology of the structure without variation of the porosity level (Zhang *et al.*, 2010).

Since water is the most used solvent, the following paragraphs will detail the studies with water carried out on the parameters influencing the main characteristics of the porous structure.

The stability of the solidification front is at the origin of the defect presence in the structure. After sintering and cutting a sample, heterogeneity of the morphology of the structure can be observed as shown by Fig. 5. Close to the freezing source, a dense area is observed. Beyond this zone, a cellular type transition zone is observed before obtaining the conventional lamellar morphology when using water as solvent. The formation of this dense zone was initially explained by the formation of a stable solidification front that push particles, as Mullins' theory (Mullins, 1964) predicts. However, in-situ observations of the structure formation were performed to determine the real cause for the formation of the dense zone.

The solidification front rate was measured during the first freezing moments of an alumina suspension by tomography (Deville *et al.*, 2009b). The ratio between the freezing time and the size of the frozen zone was used to estimate that the initial speed of the front is about of 750 $\mu\text{m s}^{-1}$. At this velocity, even if the front is stable, it will engulf all particles, which will lead after sintering to the dense zone, which is in fact porous with isotropic morphology. As the solidified layer grows, the velocity of the solidification front decreases very rapidly. This leads to the formation of a transition zone between the dense and lamellar zones, characterized by a porous structure with isotropic cellular morphology, which corresponds to the second zone.

The formation of the zone with cellular morphology was also observed by X-ray tomography (Deville *et al.*, 2009a,b; Lasalle *et al.*, 2012a,b). The authors explain that, during the first moments of freezing, not all ice crystals are oriented in the same direction. They identify two types of crystals: the first ones that will favor the lamellar morphology because their growth is oriented in the same direction as the thermal gradient (Type Z). The second type of crystals is oriented according to the other directions (Type R). The transition from cell morphology to lamellar can be described in several stages:

- Formation of both types of ice crystals in the same proportion.
- Decrease in the number of R-type crystals (growth stopped) at the expense of Z types, which leads to the start of lamellar morphology.
- Suppression of second type crystals.
- The structure remains lamellar until the end of freezing, beginning of steady state.

Another type of defects was observed by X-ray tomography during freezing. This is the formation of ice crystals perpendicular to the thermal gradient (Deville *et al.*, 2009a) during the stationary regime (lamellar growth). After lyophilization, these crystals generate cracks in the walls that would lead to a decrease in mechanical strength (Lasalle *et al.*, 2012a,b). The presence of excess

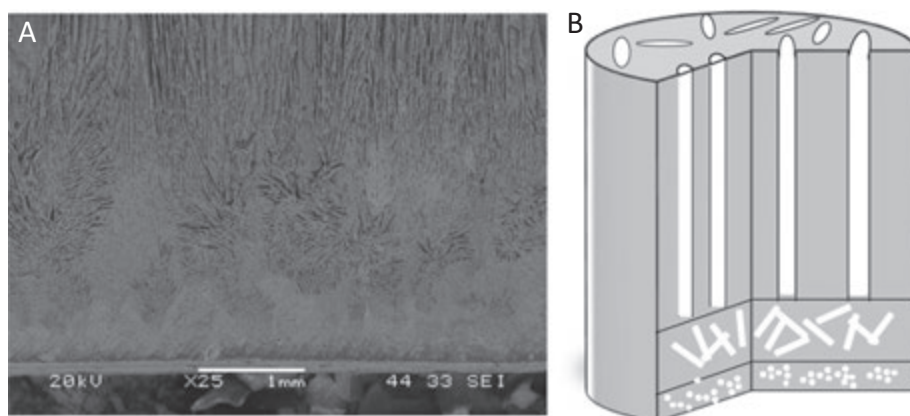


Fig. 5 (a) SEM micrograph of the bottom part of an alumina specimen, (b) diagram of the structure.

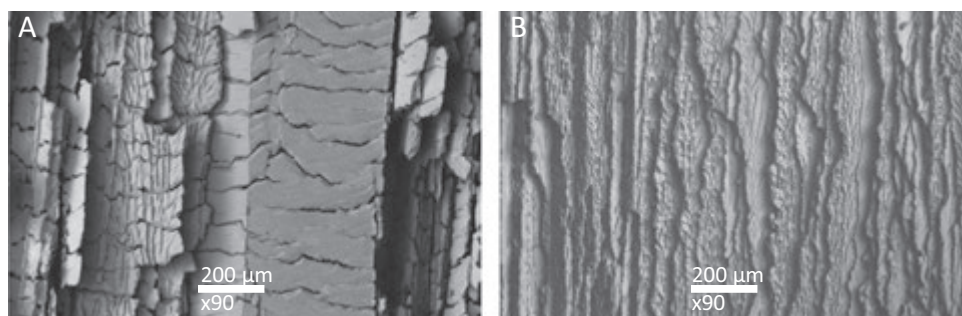


Fig. 6 SEM micrographs of alumina specimens (a) with cracks (without binder) and (b) without crack (with binder).

Table 1 Impact of processing conditions on the pore size

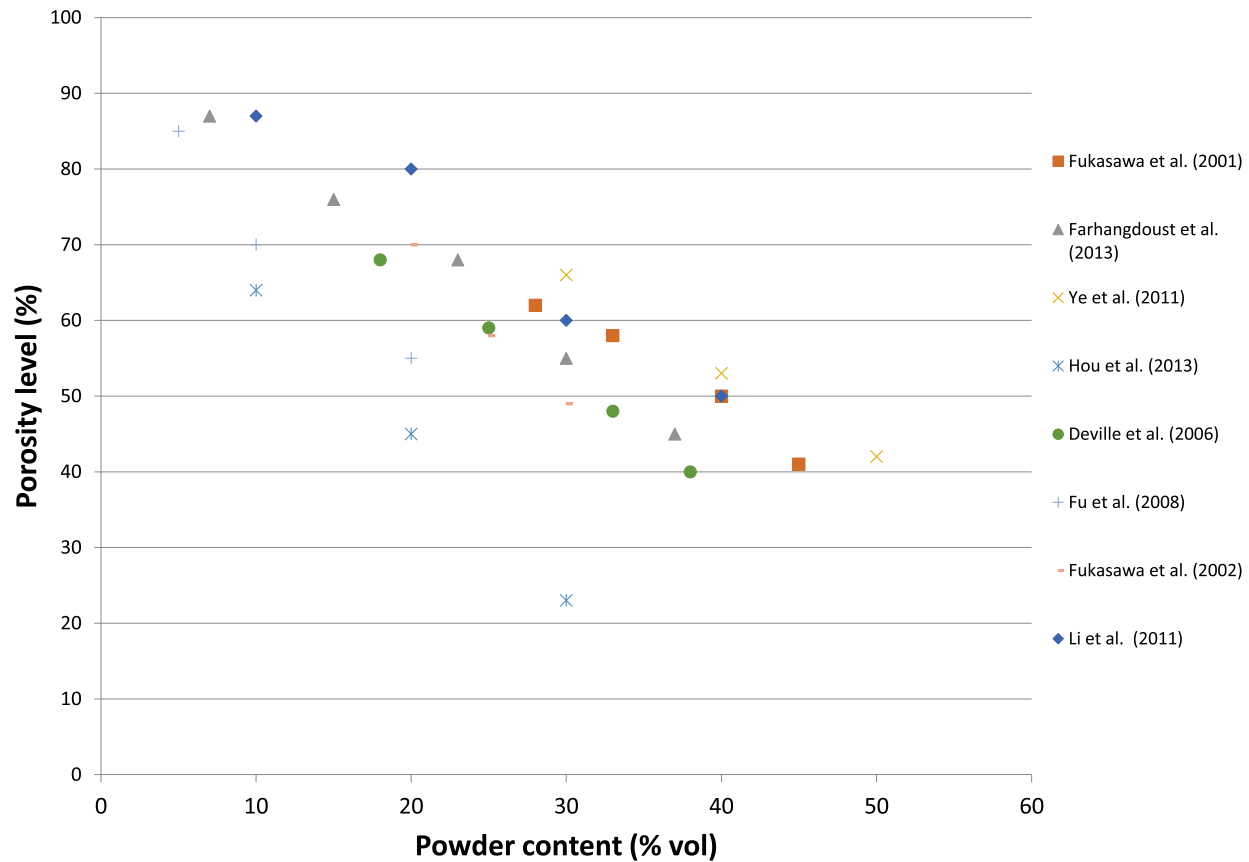
Parameter	Variation of the parameter	Impact on the pore size
Freezing rate	1–20K min ⁻¹ Zhao <i>et al.</i> (2011) 1–9K min ⁻¹ Deville <i>et al.</i> (2006)	700–80 μm 40–15 μm
Freezing temperature	77–233K Pekor <i>et al.</i> (2008) 193–233K Fukasawa <i>et al.</i> (2001)	10–50 μm 20–40 μm
Powder content	20% to 40% vol Pekor <i>et al.</i> (2008) 5% to 20% vol Fu <i>et al.</i> (2008)	60–30 μm to 233K et 20 to 10 at 77K 50–15 μm at 253K
Specimen height	From 0–25 mm Waschkies <i>et al.</i> (2009) From 0–10 mm Pekor <i>et al.</i> (2008)	From 50–250 μm at 263K From 17–50 μm at 233K From 16–34 μm at 77K
Solvent Fu <i>et al.</i> (2008)	water water/glycerol (80/20) water/dioxane (40/60)	25 μm 10 μm 100 μm)
Binder	PEG ^a Pekor <i>et al.</i> (2008) 0%–6% PVA ^b Zuo <i>et al.</i> (2010) 0%–12%	68–35 μm 90–2 μm

^apolyethylene glycol.

^bpolyvinyl alcohol.

Table 2 Impact of processing condition on the wall thickness

Parameter	Variation of the parameter	Impact on the wall thickness
Freezing rate	1–10K min ⁻¹ Hunger et al. (2013)	5.8–2.8 μm at 1K min ⁻¹ and 0.55–0.32 μm at 10K min ⁻¹
Powder content	5% to 20% vol Fu et al. (2008)	8–25 μm at 253K
	20% to 40% vol Pekor et al. (2008)	31–28 μm at 233 K and 6–9 at 77K
	11% to 30% vol Liu et al. (2010)	4–17 μm at 77K
Particle size	0.4–10 μm Hunger et al. (2013)	5.8–0.55 μm at 1K min ⁻¹
Binder	PEG Pekor et al. (2008) de 0%–6%	25–30 μm at 233K and 8–10 at 77K

**Fig. 7** Relation between porosity level and powder content.

dispersant or binder seems necessary to avoid this problem. They propose that under, given conditions, the solidification is metastable which lead to the porous lamellar structure. If the conditions switch into the unstable zone, then cracks are formed perpendicular to the solidification front direction. Moreover, during freezing, the ice crystals preferentially grow in the direction of the thermal gradient. At low speed of movement of the solidification front, a supercooling zone is present in front of the latter. In this zone, it is possible to observe a nucleation of ice crystals. The growth orientation of these crystals can then be in other directions than that imposed by the thermal gradient (because of the supercooling zone). Ice bridges are thus formed between the main crystals which will become, after freeze drying, cracks in the ceramic wall as shown at [Fig. 6](#).

Many parameters can influence the pore size ([Pekor et al., 2008](#)): the freezing rate ([Munch et al., 2009](#)), the dry matter content ([Farhangdoust et al., 2013](#)), the particle size ([Waschkies et al., 2011](#)), the sample size ([Pekor et al., 2008](#)), the amount of additive and its nature ([Lasalle et al., 2012a,b](#)).

Table 1 summarizes the impact of these parameters on the pore size. The value of the pore size corresponds to the small diameter of the ellipsoidal pore as schematized by [Fig. 5\(b\)](#). Note that for the data presented in this table, the other parameters than the one studied can be very different, which explain the differences between the obtained values.

In addition to the pore size, one of the important features is the thickness of the walls (Deville, 2007). Factors modifying wall thickness (Hunger *et al.*, 2013) are freezing rate, particle size, dry matter content and binder content (Pekor *et al.*, 2008). Table 2 summarizes the impact of these parameters on the wall thickness.

The porosity level of an anisotropic porous specimen is mainly dependent on the powder content as shown in Fig. 7. Indeed, the porosity is generated by ice removing during the freeze drying. It explains why the freezing parameters (freezing temperature and rate) have very few impact, on the porosity level.

What About the Mechanical Properties?

Considering the anisotropic macrostructure, freeze casted specimens present a great interest for mechanical applications. A significant effect of the orientation of the structure on the compressive or flexural strength was observed (Munch *et al.*, 2009). A compressive strength parallelly to the freezing direction 15 times higher than in the perpendicular direction was obtained. Analytical models were often used for predicting the relation between the structure and the mechanical properties. Exponential model adapted from isotropic porous models (Gibson and Ashby, 1999) have been used in compression (Zhao *et al.*, 2011) and in flexion (Xia *et al.*, 2012). However, these analytical models were developed only as a function of the porosity level, without any adjustment for the pore size, shape and orientation.

In the literature, the characterization of the compressive strength is the most measured mechanical property. Biomaterials such as hydroxyapatite are often used as study materials. Thus, a comparison between isotropic and anisotropic porous hydroxyapatite has been performed (Deville *et al.*, 2006). This study shows that isotropic materials have a compressive strength of less than 40 MPa for porosity levels between 40% and 80%. In comparison, porous specimens prepared by freeze casting tested in compression along freezing direction have compressive strengths of between 60 and 120 MPa, with a porosity level higher than 50%. However, for this study, only the porosity level is considered. Indeed, the pore size, the porosity of the ceramic walls, the morphology of the structure should also be taken into account. In this case, it is found that the reduction in pore size (Farhangdoust *et al.*, 2013) or porosity level (Liu *et al.*, 2010; Farhangdoust *et al.*, 2013) seems to favor a better compressive strength.

Other materials have been studied (Yoon *et al.*, 2008; Zhang *et al.*, 2013) such as alumina or zirconia. A complete study on zirconium boride (ZrB_2) has also been achieved (Landi *et al.*, 2013) for which the compressive strength was deep impacted by the modification of pore size, porosity level and wall thickness. The conclusions are generally the same whatever the powder nature.

A last parameter was studied, the amount of binder introduced into the suspension. Thus, in the case of zirconia, it has been shown that without a binder, the samples have a low compressive strength of the order of 20 MPa for a porosity of 35% (Zuo *et al.*, 2008). The addition of a binder (PVA) leads to a compressive strength of 60 MPa, despite an increase in the porosity level (50%). This result is attributed to a decrease in pore size from 100 μm to 2 μm due to the binder content increase from 0% to 6%.

References

- Ananth, R., Gill, W.N., 1989. Dendritic growth of an elliptical paraboloid with forced convection in the melt. *Journal of Fluid Mechanics* 208, 575–593.
- Araki, K., Halloran, J.W., 2004. New freeze-casting technique for ceramics with sublimable vehicles. *Journal of the American Ceramic Society* 87 (10), 1859–1863.
- Chen, Y., Bunch, J., Li, T., Mao, Z., Chen, F., 2012. Novel functionally graded acicular electrode for solid oxide cells fabricated by the freeze-tape-casting process. *Journal of Power Sources* 213, 93–99.
- Choi, H.J., Yang, T.Y., Yoon, S.Y., Kim, B.K., Park, H.C., 2012. Porous alumina/zirconia layered composites with unidirectional pore channels processed using a tertiary-butyl alcohol-based freeze casting. *Materials Chemistry and Physics* 133, 16–20.
- Deville, S., Maire, E., Lasalle, A., *et al.*, 2009a. Metastable and unstable cellular solidification of colloidal suspensions. *Nature Materials* 8, 966–974.
- Deville, S., Maire, E., Lasalle, A., *et al.*, 2009b. In situ x-ray radiography and tomography observations of the solidification of aqueous alumina particle suspensions – Part I: Initial instants. *Journal of the American Ceramic Society* 92 (11), 2489–2496.
- Deville, S., Maire, E., Lasalle, A., *et al.*, 2010. Influence of particle size on ice nucleation and growth during the ice template process. *Journal of the American Ceramic Society* 93 (9), 2507–2510.
- Deville, S., Saiz, E., Tomsia, A.P., 2006. Freeze casting of hydroxyapatite scaffolds for bone tissue engineering. *Biomaterials* 27, 5480–5489.
- Deville, S., Saiz, E., Tomsia, A.P., 2007. Ice-templated porous alumina structures. *Acta Materialia* 55, 1965–1974.
- Deville, S., 2007. Freeze casting of porous ceramics: A review of current achievements and issues. *Advanced Engineering Materials* 10 (3), 155–169.
- Donchev, D., 2005. Controlling porosity and pore size distribution in green ceramic bodies via freeze-casting. PhD Thesis, Martin-Luther-Universität Halle-Wittenberg.
- Farhangdoust, S., Zamanian, A., Yasaei, M., Khorami, M., 2013. The effect of processing parameters and solid concentration on the mechanical and microstructural properties of freeze-casted macroporous hydroxyapatite scaffolds. *Materials Science and Engineering C* 33, 453–460.
- Fu, Q., Rahaman, M.N., Dogan, F., Bal, B.S., 2008. Freeze casting of porous hydroxyapatite scaffolds. I. Processing and general microstructure. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 86, 125–135.
- Fukasawa, T., Deng, Z.-Y., Ando, M., 2001. Pore structure of porous ceramics synthesized from water-based slurry by freeze-dry process. *Journal of Materials Science* 36, 2523–2527.
- Gauckler, L.J., Waerber, M.M., Conti, C., Jacob-Duliere, M., 1985. Ceramic foam for molten metal filtration. *Journals of Metals* 37 (9), 47–50.
- Gibson, L.J., Ashby, M.F., 1999. *Cellular Solids: Structure and properties*. Cambridge Solid State Science Series. Cambridge University Press.
- Hautcoeur, D., Lorgouiloux, Y., Leriche, A., *et al.*, 2016. Thermal conductivity of ceramic/metal composites from preforms produced by freeze casting. *Ceramics International* 42, 14077–14085.
- Hu, L., Wang, C.-A., Huang, Y.H., *et al.*, 2010. Control of pore channel size during freeze casting of porous YSZ ceramics with unidirectionally aligned channels using different freezing temperatures. *Journal of the European Ceramic Society* 30 (16), 3389–3396.

- Hunger, P.M., Donius, A.E., Wegst, U.G.K., 2013. Structure-property-processing correlations in freeze-cast composite scaffolds. *Acta Biomaterialia* 9, 6338–6348.
- Korber, C., Rau, G., Cosman, M.D., Cravalho, E.G., 1985. Interaction of particles and a moving ice-liquid interface. *Journal of Crystal Growth* 72, 649–662.
- Landi, E., Sciti, D., Melandri, C., Medri, V., 2013. Ice templating of ZrB₂ porous architectures. *Journal of the European Ceramic Society* 33, 1599–1607.
- Lasalle, A., 2011. Les céramiques venues du froid... Formulation, congélation et structuration par ice-templating. PhD Thesis, Institut National des Sciences Appliquées de Lyon.
- Lasalle, A., Guizard, C., Leloup, J., *et al.*, 2012a. Ice templating of alumina suspensions: Effect of supercooling and crystal growth during the initial freezing regime. *Journal of the American Ceramic Society* 95 (2), 799–804.
- Lasalle, A., Guizard, C., Maire, E., Adrien, J., Deville, S., 2012b. Particle redistribution and structural defect development during ice templating. *Acta Materialia* 60, 4594–4603.
- Lee, S.-H., Jun, S.-H., Kim, H.-E., 2008. Piezoelectric properties of PZT-based ceramic with highly aligned pores. *Journal of the American Ceramic Society* 91 (6), 1912–1915.
- Liu, G., Zhang, D., Meggs, C., Button, T.W., 2010. Porous Al₂O₃-ZrO₂ composites fabricated by an ice template method. *Scripta Materialia* 62, 466–468.
- Moon, J.-W., Hwang, H.J., Awano, M., Maeda, K., Kanzaki, S., 2002. Preparation of dense thin film electrolyte on novel porous structure with parallel pore channel. *Journal of the Ceramic Society of Japan* 110 (5), 479–484.
- Mullins, W.W., 1964. Stability of a planar interface during solidification of a dilute binary alloy. *Journal of Applied Physics* 35 (2), 444–451.
- Munch, E., Saiz, E., Tomsia, A.P., 2009. Architectural control of freeze-cast ceramics through additives and templating. *Journal of the American Ceramic Society* 92 (7), 1534–1539.
- Pekor, C.M., Kisa, P., Nettlehip, I., 2008. Effect of polyethylene glycol on the microstructure of freeze-cast alumina. *Journal of the American Ceramic Society* 91 (10), 3185–3190.
- Porter, M.M., Yeh, M., Strawson, J., *et al.*, 2012. Magnetic freeze casting inspired by nature. *Materials Science and Engineering A* 556, 741–750.
- Rachadel, P.L., Souza, D.F., Nunes, E.H.M., *et al.*, 2017. A novel route for manufacturing asymmetric BSCF-based perovskite structures by a combined tape and freeze casting method. *Journal of the European Ceramic Society* 37 (16), 5249–5257.
- Scheffler, M., Colombo, P., 2005. *Cellular ceramics: Structure, Manufacturing, Properties and Application*. Wiley-VCH.
- Shanti, N.O., Araki, K., Halloran, J.W., 2006. Particle redistribution during dendritic solidification of particle suspensions. *Journal of the American Ceramic Society* 89 (8), 2444–2447.
- Smith-Johannsen, R., 1994. US. Pat. 117788A.
- Sofie, S.W., Dogan, F., 2001. Freeze casting of aqueous alumina slurries with glycerol. *Journal of the American Ceramic Society* 84 (7), 1459–1464.
- Sofie, S.W., 2007. Fabrication of functionally graded and aligned porosity in thin ceramic substrates with the novel freeze-tape-casting process. *Journal of the American Ceramic Society* 90 (7), 2024–2031.
- Studart, R., Gonzenbach, U.T., Tervoort, E., Gauckler, L.J., 2006. Processing routes to macroporous ceramics – A review. *Journal of The American Ceramic Society* 89 (6), 1771–1789.
- Tang, Y.F., Zhao, K., Wei, J.Q., Qin, Y.S., 2010. Fabrication of aligned lamellar porous alumina using directional solidification of aqueous slurries with an applied electrostatic field. *Journal of the European Ceramic Society* 30, 1963–1965.
- Tremeac, B., 2005. Étude expérimentale et numérique des phénomènes thermomécaniques lors de la congélation de produits alimentaires. Application à des structures multicouches. PhD Thesis, Génie des procédés. Université de Nantes
- Waschkies, T., Oberacker, R., Hoffmann, M.J., 2009. Control of lamellae spacing during freeze casting of ceramics using double-side cooling as a novel processing route. *Journal of the American Ceramic Society* 92 (S1), 79–84.
- Waschkies, T., Oberacker, R., Hoffmann, M.J., 2011. Investigation of structure formation during freeze-casting from very slow to very fast solidification velocities. *Acta Materialia* 59, 5135–5145.
- Xia, Y., Zeng, Y.-P., Jiang, D., 2012. Microstructure and mechanical properties of porous Si₃N₄ ceramics prepared by freeze-casting. *Materials and Design* 33, 98–103.
- Yook, S.-W., Kim, H.-E., Koh, Y.-H., 2009. Fabrication of porous titanium scaffolds with high compressive strength using camphene-based freeze casting. *Materials Letters* 63, 1502–1504.
- Yoon, B.-H., Choi, W.-Y., Kim, H.-E., Kim, J.-H., Koh, Y.-H., 2008. Aligned porous alumina ceramics with high compressive strengths for bone tissue engineering. *Scripta Materialia* 58, 537–540.
- Zhang, Y., Hu, L., Han, J., 2009. Preparation of a dense/porous bilayered ceramic by applying an electric field during freeze casting. *Journal of the American Ceramic Society* 92 (6), 1874–1876.
- Zhang, Y., Hu, L., Han, J., Jiang, Z., 2010. Freeze casting of aqueous alumina slurries with glycerol for porous ceramics. *Ceramics International* 36, 617–621.
- Zhang, Y., Zhou, K., Bao, Y., Zhang, D., 2013. Effects of rheological properties on ice-templated porous hydroxyapatite ceramics. *Materials Science and Engineering C* 33, 340–346.
- Zhao, K., Tang, Y.-F., Qin, Y.-S., Wei, J.-Q., 2011. Porous hydroxyapatite ceramics by ice templating: freezing characteristics and mechanical properties. *Ceramics International* 37 (2), 635–639.
- Zuo, K.H., Zeng, Y.-P., Jiang, D., 2008. Properties of microstructure-controllable porous yttria-stabilized zirconia ceramics fabricated by freeze casting. *International Journal of Applied Ceramic Technology* 5 (2), 198–203.
- Zuo, K.H., Zeng, Y.-P., Jiang, D., 2010. Effect of polyvinyl alcohol additive on the pore structure and morphology of the freeze-cast hydroxyapatite ceramics. *Materials Science and Engineering C* 30, 283–287.

Further Reading

- Fukasawa, T., Deng, Z.-Y., Ando, M., 2002. Synthesis of porous silicon nitride with unidirectionally aligned channels using freeze-drying process. *Journal of the American Ceramic Society* 85 (9), 2151–2155.
- Hou, Z., Ye, F., Liu, L., Liu, Q., Zhang, H., 2013. Effects of solid content on the phase assemblages, mechanical and dielectric properties of porous α -SiAlON ceramics fabricated by freeze casting. *Ceramics International* 39, 1075–1079.
- Li, Z., Zhang, Y., Zhang, D., Zhang, X., Zhou, K., 2011. Porous hydroxyapatite ceramics fabricated by an ice-templating method. *Scripta Materialia* 64 (5), 426–429.
- Ye, F., Zhang, J., Liu, L., Zhan, H., 2011. Effect of solid content on pore structure and mechanical properties of porous silicon nitride ceramics produced by freeze casting. *Materials Science and Engineering A* 528, 1421–1424.

Additive Manufacturing

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Introduction

Solid freeform fabrication (SFF), Rapid Prototyping or 3D printing, describe a class of technologies, i.e., additive manufacturing technologies, in which a part is directly generated from a virtual model by adding material to form the part. Additive manufacturing is defined by [ISO/ASTM 52900 \(2015\)](#) (Additive manufacturing – General principles – Terminology) as the “process of joining materials to make parts from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing and formative manufacturing methodologies” ([ISO/ASTM 52900, 2015](#)). According to the philosophy of AM, the choice of a 3D computer graphic, 3D model, and material system is sufficient to build a part. Consequently, it is possible to generate parts with arbitrary geometries without the need of adapting the typical manufacturing process itself. AM of ceramics has the potential to open new markets for ceramic products, as it is not strictly bound by the paradigms of ceramic processing, such as high processing cost for small lot productions, low flexibility, complex machining and limited molding shaping technologies.

Preferably, parts ready to use, i.e., possessing the final physical properties of the desired object, are generated using AM technologies, but also the manufacture of semi-finished parts, requiring additional processing, has turned out to be technically and economically feasible. The material (feedstock) is typically fed into the process as a powder/granulate, filament, paste or suspension, that is, the material is in a state optimized for the layer deposition process. In the manufacturing process itself, the material is used to build up the desired object and it is simultaneously transferred into a state possessing its final physical properties, or at least a mechanical strength sufficient to transfer the built object to further processing steps. According to the needs of the particular material used, the desired geometry or the purpose of the object being built, an entire set of AM technologies has been developed. Polymeric, metallic, ceramic materials and composites can be all processed by these technologies. The initial motivation for the development of rapid prototyping technologies, that is, technologies for the manufacturing of individual products without any requirement for dedicated tooling, was to reduce the time to market of new products by shortening the time span between design, testing and implementation. While in the 80s and 90s the basic technologies for AM were envisioned and flexibility in design was first priority for their development, nowadays the physical properties of the parts generated are a major concern. Accordingly, the terminology for this class of technologies shifted gradually from Rapid Prototyping (RP) from the 80s to Additive Manufacturing (AM) nowadays. The term “manufacturing” implies that a product is generated. Not only a product must meet tight quality constraints, but it also must be traded and applied to the advantage of the manufacturer or user. In this respect, additively manufactured parts are in competition with conventionally manufactured products, which unsurprisingly have a huge advantage in terms of price and reliability due to a long period of optimization. The return on investment for AM products is often a critical point, as capital expenditure and running costs, such as personnel and raw materials (feedstocks) are generally high and little experience exists concerning the performance and reliability of AM parts in service. This explains why the development and optimization of AM technologies is still a very vital field of research and it is difficult to provide a comprehensive picture of the state of the art, considering that innovations and equipment improvements are continuous. On the other hand, the technical challenges of AM of ceramics are more general and will likely remain the same for some time.

In order to develop a more general understanding of the technical challenges associated with AM of ceramics, it makes sense to divide the following introduction into two main categories, defined by the macroscopic physical properties and architecture of the ceramics parts generated via AM, that is: (1) porous components and (2) fully dense monolithic components. Accordingly, we will distinguish between three classes of AM technologies:

(1) technologies not capable of producing dense structures (which means, only a microstructure with residual porosity can be generated), (2) technologies capable of producing fully dense monolithic ceramic bodies with restriction in dimension, i.e., dense filaments or small structures including solid ceramic parts not larger than a few mm in diameter, and (3) technologies capable of producing fully dense monolithic ceramic bodies without restriction in dimension.

It is well known that the many AM technologies successfully applied to the manufacture of ceramics have been used to fabricate porous structures, e.g., scaffolds for biological applications, filters, lightweight structures etc. In these cases, the success of the respective technology is based on the fact that a certain amount of random and residual porosity in the solid ceramic part of the scaffold is tolerated or even desired, as it provides further functionality to the component.

The fact that, so far, a major part of the research on AM of ceramics has focused on porous structures, is due mainly to two reasons:

- (1) AM enables the production of complex shaped porous architectures with a precise control of the dimension, shape and amount of pores, which is not achievable by any other technology currently used for the fabrication of macro-porous bodies. In these cases, AM is not in competition with traditional manufacturing, but it opens up completely new fields of research and applications. Indeed, an increasing number of publications nowadays deals with the design and manufacturing of cellular and lattice structures possessing specific advantages in terms of strength-to-density ratio, stiffness, permeability or other significant properties.
- (2) Many of the AM technologies currently existing are intrinsically particularly suited for the generation of fine filigree structures. The specific reason for this statement will be discussed later, when describing the individual technologies, because it is different from case to case. However, a general observation that can be made here is that technologies that are suitable for fine porous structures have often shortcomings when scaling up to large bulk parts, and, vice-versa, technologies more suitable for the fabrication of dense parts may have difficulties in producing highly porous and fine geometries.

There are very few AM technologies on the market capable of generating fully dense monolithic ceramic bodies. AM of monolithic ceramics, enabling the components to fully retain their superior physical-chemical properties, is still a challenge and remains the most important task that needs to be solved in order to promote AM of ceramics to more than a niche technology.

In the following, the current status and performance of additive manufacturing of ceramics will be discussed. An overview of technologies for the fabrication of porous and monolithic components will be given, and particular applications will be highlighted.

Overview of Technologies

By comparing the main characteristics of the AM techniques with respect to both the properties of generated parts and processing-related aspects, this paragraph gives an overview and a comparison of the AM technologies currently available for ceramic materials, see also Fig. 1.

Table 1 summarizes some of the general characteristics of the most used AM technologies described in literature for the manufacturing of ceramic components. Indications about the quality and size of the produced parts (ability of making dense and/or monolithic parts, precision, surface quality) and cost of the production (cost of the feedstock preparation and cost of the process) are included.

Before commenting on the individual technologies, it is appropriate to qualify further the content of the columns in **Table 1**.

- (1) *Dense struts*: this term indicates technologies that can provide a dense material (that is, without any residual porosity), at least for some of the possible geometries and features that they can produce (specifically, only features possessing a small length scale or volume) and some ceramic material systems. Importantly, it is relevant to notice that there is a correlation between the use of a liquid-based feedstock and the possibility of achieving a dense microstructure in the struts (or small printed features), as opposite to solid-based and, in particular, powder-based technologies.
- (2) *Monolithic*: this term indicates technologies that are able to generate parts without residual micro-porosity, at least for some ceramic material systems, regardless of their volume and feature size, that is, e.g., wall thickness. A part with these characteristics is what we define as a “ceramic monolithic part”. Naturally, the possibility to sinter to full density is related, as for ceramic processing in general, to the composition of the feedstock (i.e., presence of sintering aids, composition of the ceramic, particle size, etc.) and on the sintering schedule and technique employed. Here, however, we consider as given that the ceramic powder could be sintered to full density (for instance if it was shaped into a tablet by cold pressing) and are interested in discussing whether it is the AM process itself that prevents this full sintering to happen in the final produced part.
- (3) *Part dimension*: this is the maximum part size that can be produced. Based on the fact that the dimension of the process area (printing envelope) can be potentially scaled-up for most technologies, it is difficult to provide precise data and trends. However, at the current state-of-the-art, it is often the case that, for dimensions outside a certain range, it becomes more convenient, for economic and technical reasons, to switch from one technology to another. These dimensional ranges are indicated as sizes from XS to XL, corresponding to 100 μm or to 1 m, respectively, as explained in the table caption.
- (4) We should also note that it is not only the dimension of the printing envelope for each AM technology that imposes a limit to the maximum part size (area or volume), but also the mechanical properties of the parts during the printing process. For instance, structures constituted by thin filaments and not supported by a liquid or powder bed can deform by their own weight during fabrication, when they're still not consolidated by sintering.
- (5) Precision and surface quality are related to the dimension and cost of the part (printing speed) to be produced. On the other hand, the surface of a part can become smoother due to the minimization of its free surface energy, if sufficient material transport can occur during fabrication or sintering, or artifacts such as steps deriving from deposited layers can be smoothed out by the presence of a liquid phase during sintering. Here, only the best state-of-the-art results achieved so far are listed. As the dimension of the part increases, the precision in many technologies can be reduced (e.g., by increasing the diameter of

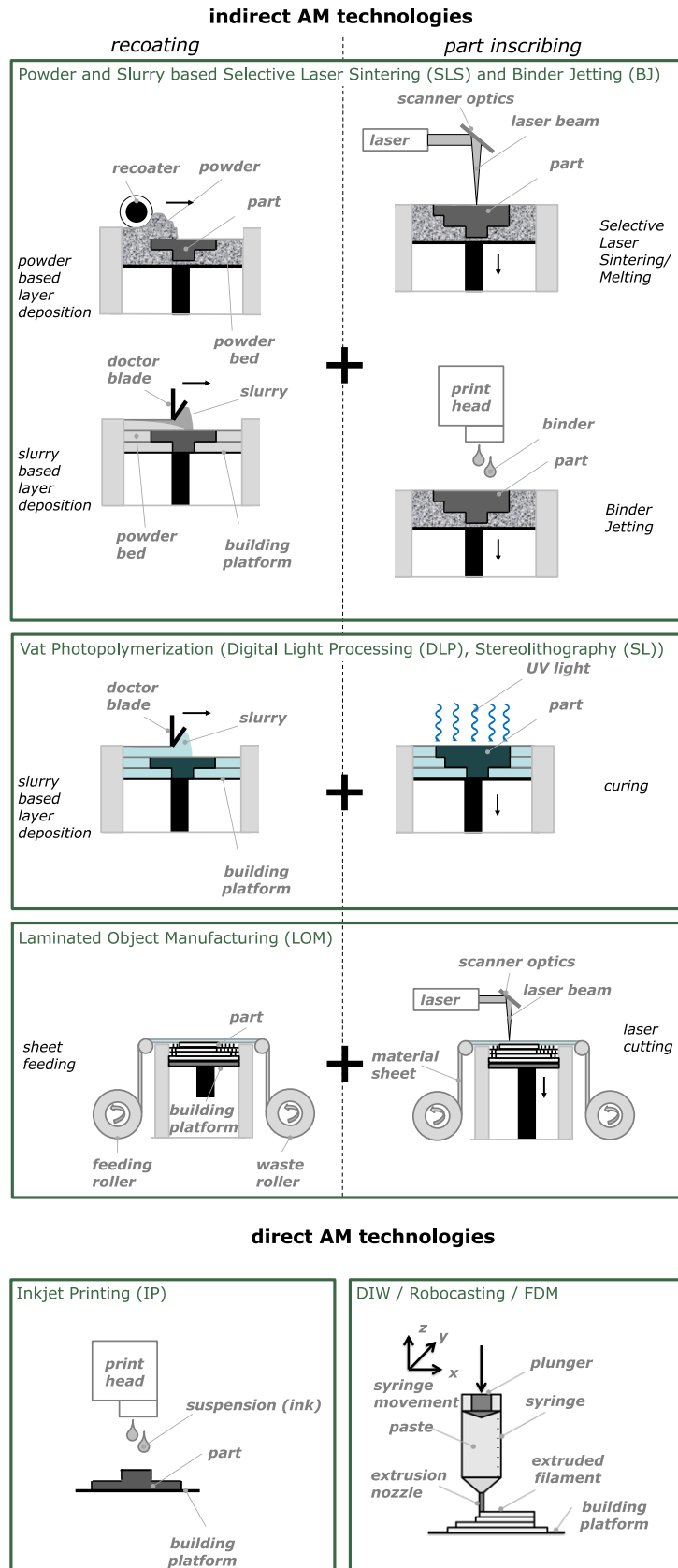


Fig. 1 Schematic of AM technologies.

Table 1 Main Characteristics of additive manufacturing technologies used for ceramics

<i>Process category according to ISO/ASTM 52900</i>	<i>Technology^a</i>	<i>Feedstock (liquid or solid)</i>	<i>Dense struts (dense ceramic, but limited volume)</i>	<i>Monolithic</i>	<i>Part dimension^b (size that can be produced economically)</i>	<i>Surface (quality of parts, not of single struts)</i>	<i>Resolution</i>	<i>Cost of feedstock preparation</i>	<i>Cost of process</i>	<i>Direct vs. Indirect</i>
Binder Jetting	BJ	Solid (Powder)	No	No	M-XL	Medium	100 μm	Low	Medium	Indirect
Powder bed fusion	P-SLS	Solid (Powder)	No	No	M-L	Medium	100 μm	Low	High	Indirect
	P-SLM	Solid (Powder)	No	No	M-L	Medium	100 μm	Low	High	Indirect
Vat photopolymerization	SL/DLP	Liquid (Particle suspension)	Yes	No	XS-L	High	< 1 μm	Medium-High	Medium	Indirect
<i>Slurry-based variations of Binder Jetting and Powder bed fusion</i>	S-BJ	Liquid (Particle suspension)	Yes	Yes	M-XL	High	100 μm	Low	Medium	Indirect
	S-SLS	Liquid (Particle suspension)	Yes	Yes	M-L	High	100 μm	Low	High	Indirect
Sheet lamination	LOM	Solid (Sheet)	Yes	Yes	M-L	Medium	100 μm	Medium	Medium	Indirect
Material Jetting	IP	Liquid (Particle suspension)	Yes	Yes	S-M	Medium	10 μm	High	Medium	Direct
	Thermoplastic 3DP	Liquid (Particle suspension)	Yes	Yes	S-L	Medium	100 μm	Medium	Medium	Direct
Material extrusion	DIW/Robocasting	Liquid (Particle suspension/paste)	Yes	No	S-XL	Low	10 μm	Low-Medium	Low	Direct
	FDM	Solid (Filament)	Yes	No	S-M	Low	100 μm	Medium	Low	Direct

^athe definition of the acronyms for each technology are given later in the text.^bXS = 100 μm ; S = 1 mm; M = 10 mm; L = 0.1 m; XL = 1 m.

extrusion nozzles or the thickness of deposited powder layers) in order to obtain an economical building rate. It is noteworthy that surface quality is important not only for aesthetical reasons, but also because it can influence the mechanical properties of the printed ceramic components. It is furthermore noteworthy that filament-based technologies can provide very smooth surfaces on a micro-scale level but, by fusing multiple filaments a textured surface is generated, which can significantly deviate from the surface contour of the 3D model.

- (6) The cost parameter is divided into two factors: cost related to the feedstock and cost related to the process. Cost for feedstock does not include the cost for ceramic raw materials, as this would be similar for a conventional fabrication process. Low feedstock costs imply that the material can be bought commercially and is usable with none or minimal further processing, irrespective of the cost of the specific ceramic raw material selected; this is typically the case for powders to be used in powder-based and slurry-based technologies. Medium and high cost indicates that the material requires extensive secondary processing involving expensive additives, and often has to be designed specifically for the application. An example is the ink designed for extrusion through very fine nozzles or a photocurable suspension with a high ceramic particle loading. Finally, the process cost considers depreciation of capital expenditure and operating expenses for the particular AM equipment, and costs related to necessary processing and post-processing of the final product. Machines which employ lasers, for example, are usually quite expensive and not very productive compared to equipment based on binder jetting. On the other hand, the extrusion of pastes through fine tips is typically based on a rather cheap setup, and the production rate can be adapted by changing the diameter of the tip, which makes this a low-cost process.

It is also helpful to divide the existing AM technologies into two categories: direct and indirect. Direct 3D printing means that the material is directly deposited only at the positions giving the desired shape of the final object. Indirect 3D printing means that, first a layer of material is deposited, subsequently the cross section (slice) of the part is inscribed in the layer and, after printing all layers to complete the process, the excess material surrounding the part is removed to release the final object. Inscribing can be done in several ways, each one with its own characteristics. It should be noted that, differently from metal additive manufacturing, in the case of ceramics the term “direct printing” does not indicate the production of a ready-to-use part, since no AM technologies currently exist capable of directly providing a 3D shaped, sintered body without requiring a post-forming firing step.

Already from this distinction, some general considerations concerning the potentials and drawbacks of the two approaches can be outlined:

- (1) The excess material in indirect technologies forms a support for the successive layers, enabling the generation of parts with large overhangs. Direct techniques, on the other hand, require support structures for overhangs above a certain dimension, which may be often impractical or time consuming, and furthermore need to be removed in order to obtain the precise desired shape of the final object.
- (2) Indirect technologies require the removal of the excess material in the form of powder, liquid or solid pieces of a sheet, which can be difficult or impossible for certain geometries. For example, if the excess material is a powder, it may be complicated to remove it completely from small open pores and cells. In any case, it is not possible to print any form of closed porosity, because the material inside the pores that has not been inscribed cannot be removed. The direct deposition of material, instead, does not have such geometrical limitations.
- (3) Indirect technologies have the potential to be faster, because the material is deposited in one complete layer and the layer information, that is the cross section of the part to be built, can be printed on the entire area, selectively inscribing the desired profile. Moreover, the simultaneous fabrication of multiple individual parts can be achieved. In direct technologies, instead, the material is usually deposited only in specific positions and in a sequence.
- (4) Direct technologies offer straightforward possibilities to use multi-material systems (ceramic/ceramic with functional grading, ceramic/plastic, ceramic/metal interfaces). Indirect technologies can also do this, but with much more limitations, e.g., the addition of metallic materials acting as conductor in multilayer ceramic systems is possible, but their concentration is limited (Espera *et al.*, 2019).

State-of-the-Art, Technology by Technology

By describing the main technologies developed so far, this section reviews the current state-of-the-art of AM of ceramics. Specifically, the paragraph includes a description of the ability of a particular technology to: (1) fabricate lattice structures with a designed macro-porosity and considerations about the residual micro-porosity in the parts, which might be resulting from the various fabrication technologies; (2) the possibility of producing monolithic ceramics, according to our previous definition.

Indirect AM Technologies

Powder-based 3D printing

Powder-based 3D printing includes Binder Jetting and Powder Bed Fusion. In powder-based AM technologies, a solid structure is realized by the successive deposition of layers of a flowable powder. A layer of powdered material is first spread and subsequently the corresponding layer information is selectively inscribed by e.g., local compaction or gluing; these steps are iteratively replicated



Fig. 2 (a) 3D printer for concrete, (b) powder-based 3D-printed “Nautilus” artwork model (the part is 0.8 m tall) still half embedded in the powder bed. Image courtesy of Antonino Italiano, Desamanera SRL, Italy.

until the object is completed. The layer information is defined by the corresponding cross-section of a sliced virtual 3D model of the object to be built. At the end, the part is completely embedded in a powder-bed, from which it can be easily extracted and cleaned. The technology used to inscribe the layer information depends on the specific process considered: two of the most well-known and world-wide spread processes are: “Three-dimensional printing” (3DP) and “Selective laser sintering” (SLS) (Bourell *et al.*, 1992). The milestone patent “Three-dimensional printing techniques” by Sachs *et al.* was filed in 1989 (Sachs *et al.*, 1993), while Deckard’s patent “Method and apparatus for producing parts by selective sintering” dates back to three years earlier (Deckard, 1989). Within powder-based AM technologies, powders are bound or fused to more or less dense parts, often ready to use (in particular in the case of artificial stone components, where no sintering process is required). The former method uses a printing head to selectively spread out droplets of a liquid binder (Binder Jetting), while the latter employs the energy of a focused laser beam to selectively sinter/melt a powder.

Binder jetting

In the binder jetting (BJ) process, an inkjet printing head ejects a binding liquid onto a powder bed, thus defining the cross-section of the object in that layer. Some BJ setups stabilize the powder layer by misting with water droplets to avoid disturbance of the powder by the ballistic impact of the binder droplets (Butscher *et al.*, 2013). Multiple nozzles can also be used, allowing covering a wide printing area. Printing machines with print heads consisting of hundreds up to thousands of parallel working jets are standard. Printing envelopes as large as $6 \times 6 \times 6 \text{ m}^3$ are used to fabricate ceramic objects for architectural applications based on the cold consolidation of inorganic powders (such as marble) using a hydraulic or non-hydraulic binder. In Fig. 2, an example of a large artwork piece using such an equipment is shown.

(1) Porous components

The vast majority of the research on powder-based 3D printed porous parts has been devoted to the shaping of biomedical scaffolds for tissue engineering, namely hard tissue, which are bone substitutes. Two major classes of material-binder systems have been used for this purpose: (1) the ceramic powder is bound by an organic glue, which is dissolved in a water- or solvent-based liquid and sprayed on the printing bed; alternatively, a polymer can be mixed with the ceramic powder and then used to glue the powder when in contact with a jetted solvent for the polymer. The green part has to be successively sintered at high temperatures in order to obtain the final ceramic object. (2) a reactive liquid-powder system is employed, which involves a setting reaction at low temperature. There are several examples of systems based on calcium phosphates using phosphoric acids as a binder.

An excellent review of the important scaffold parameters for this specific application, as well as of the most important processing aspects can be found in the literature (Butscher *et al.*, 2011). Typically, tissue engineering scaffolds should have pores in the range 50–1000 μm and a porosity $> 60\%$, because these characteristics are considered a requisite for successful bone ingrowth and full vascularization of the implants. Residual micro-porosity ($< \sim 10 \mu\text{m}$) in the printed part (i.e., not the designed macro-porosity) was also recognized to be important for increasing the surface area, which leads to higher protein absorption and ion exchange. It should be noted that small pores ($< \sim 500 \mu\text{m}$) cannot be printed because of resolution limits and, more importantly, because of the difficulty in removing the excess, unbound powder.

Calcium phosphate scaffolds made by BJ tend to have exactly this bimodal porosity: a designed porosity produced by BJ, in the range of $\sim 0.5\text{--}2 \text{ mm}$, and micro-porosity in the struts due to incomplete densification after binder/powder reaction and/or after sintering. In particular, sintering of the 3D-printed material to high density is hindered by the large particle size (indicatively 20–100 μm) of the powder used for printing, which is necessary in order to have a suitable level of flowability (appropriate Hausner ratio) during the deposition of the layers. Even though the flowability can be improved by granulation of a fine ($< 10 \mu\text{m}$) powder, during the heat treatment a good level of densification can be achieved within the single

granules, but only sintering necks are formed between the individual granules.

Parts made by BJ generally have a high level of residual porosity and this limits their mechanical properties. Chumnanklang *et al.* (2007) made Hydroxyapatite (HA) samples by BJ which had 20–40 vol% micro-porosity and a 3-points-bending strength < 1.5 MPa. Klammer *et al.* (2009) developed a BJ process for Brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) which had a micro-porosity of 38.8 vol% and a compressive strength of 23.4 MPa, and similarly for Monetite (CaHPO_4), obtaining 43.8 vol% of micro-porosity and 15.3 MPa compressive strength. Castilho *et al.* (2015) measured the compressive strength of calcium phosphate cylinders, which reached a maximum of 23.8 MPa for a micro-porosity of 43.1 vol%.

Besides applications for tissue engineering, BJ of silicate ceramics for different applications, including art and architecture, and foundry sands are rapidly growing markets (Huson and Hoskins, 2014).

With the aim of producing parts with improved mechanical properties, fibers can be embedded in the powder bed; their size, however, cannot exceed the layer height, and their amount is limited by the flowability requirements of the powder bed. Singh *et al.* (2015) added up to 75%vol of SiC fibers ($\sim 70 \mu\text{m}$ length) to a SiC powder bed in order to fabricate demonstrators for turbine engine component applications. Fibers were well distributed, showed no preferred orientation on the horizontal plane and angles as much as 45° in the vertical plane.

(2) Monolithic components

BJ is very well suited to generate porous ceramic structures. Still, a major issue, hampering a completely autonomous production of parts and even restricting the freedom of design by means of these technologies, is the low density and stability of the parts during the building process, which is a direct result of the low powder packing in the powder-bed. The powder bed surrounding the part has an essential role, since it should support the structure during building, until it's ready for removal. Furthermore, powders with appreciable flowability for the deposition of thin layers are in a particle size range $> 20 \mu\text{m}$, which generally does not provide sufficient sintering activity to form dense ceramics. One straightforward approach to increase the density of the powder bed and to use more fine powders is the deposition of ceramic slurries instead of dry powders. This strategy will be introduced in a following section. Another approach is the gas flow assisted powder deposition (Zocca *et al.*, 2014). While the first approach results in powder beds with powder packing densities $> 55\%$ TD, and thus sufficient for a full densification in subsequent sintering steps, the latter has just shown its potential for the deposition of fine powders ($< 20 \mu\text{m}$ particle size) with appreciable packing densities. The low powder packing density has two major causes: the particle shape, which is generally far from spherical, and the tendency to form agglomerates. Also, particle charging due to the low electrical conductivity of ceramic materials might contribute to low packing densities.

Even though, as discussed above, the microstructure of parts obtained by BJ usually contains a high amount of residual porosity, some authors achieved high density values after the heat treatment process. Three different approaches have been mainly investigated with this aim.

The first approach consists in modifying the composition of the ceramic material in order to enhance the sintering, by addition of dopants or of a viscous liquid-forming phase. Fielding *et al.* (2012), for example, obtained 95% density when adding ZnO and SiO_2 to tricalcium phosphate (TCP), while Suwanprateeb *et al.* (2009) took advantage of liquid phase sintering producing a 97.5% dense HA + HA/woollastonite glass-ceramic composite.

The second approach is the infiltration of a porous preform produced by BJ. Melcher *et al.* (2006) used BJ to print alumina preforms which had a porosity of 36% after sintering and infiltrated them with Cu/Cu₂O. The resulting $\text{Al}_2\text{O}_3/\text{Cu}/\text{CuO}$ material had a flexural strength of 236 MPa and fracture toughness of $5.5 \text{ MPa m}^{1/2}$ thanks to the crack bridging mechanism of the metallic phase. A similar process was followed to infiltrate alumina preforms with glass (Zhang *et al.*, 2009).

Another interesting material system achievable with this approach is the formation of RBSiC ceramics (reaction-bonded silicon carbide). In a first example, Fu *et al.* (2013) printed by BJ a mixture of Si, SiC and dextrin. Successive infiltration with a liquid silicone resin and pyrolysis at 1000°C in nitrogen yielded carbon from the dextrin and an amorphous SiOC residue from the silicone resin. Infiltration of liquid silicon at 1500°C in vacuum finally lead to the RBSiC material, also designated as SiSiC. Moon *et al.* (2001), instead, printed by BJ a carbon preform which had 48% open porosity, by using a binder based on furfuryl resin. Following infiltration of Si at 1450°C in nitrogen led to the desired RBSiC composite. It is interesting to notice that in this latter example part of the carbon was derived from the polymeric binder, and this allowed the generation of functionally graded parts by varying the dosage of carbon-yielding binder and thus controlling the amount of SiC formed. Fig. 3 shows a voluminous SiSiC part, which has been obtained by BJ of SiC powders followed by Si infiltration during sintering.

The first two approaches may be however difficult to apply to pure technical ceramics, such as alumina or silicon nitride. A third approach has been developed which consists of cold isostatic pressing (CIP) or warm isostatic pressing (WIP) the green body printed by BJ, before sintering. Yoo *et al.* (1993) obtained almost dense parts (99.2% relative density) by applying WIP to alumina parts (with MgO dopant) which had a flexural strength of 324 MPa after sintering. This method has been applied also to other ceramic systems, such as Ti_3SiC_2 , yielding almost dense microstructures, but it poses geometrical limitations when applied to complex geometries, such as parts with internal cavities (Sun *et al.*, 2003).

Concluding, BJ is very attractive because it has almost no limitation regarding the parts geometry (except for closed porosity) and dimension; however, it is potentially able to produce ceramic monolithic parts only for specific material systems, typically involving post-printing infiltration with metals or semimetals.

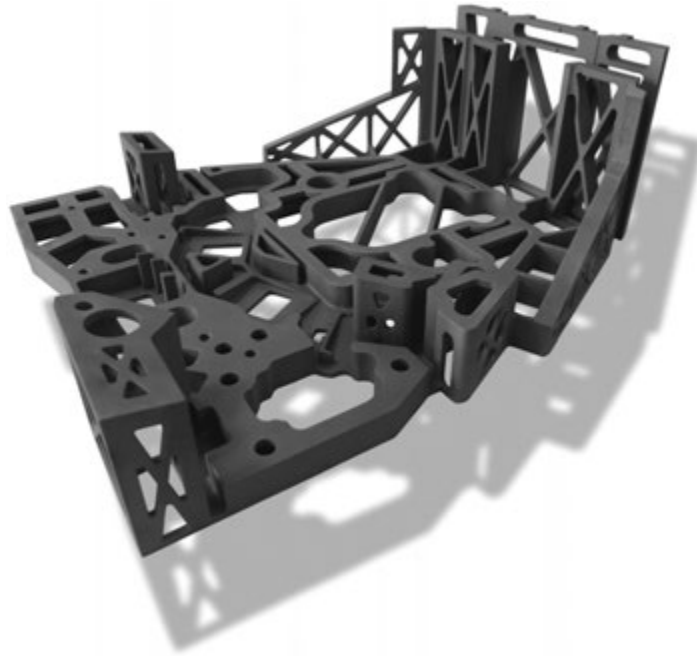


Fig. 3 Complex structure made from RBSiC by the BJ process with dimensions: $880 \times 750 \times 300$ mm, volume 9.000 cm^3 . Image courtesy of Schunk Ingenieurkeramik GmbH, Germany.

Powder bed fusion

The powder bed fusion process comprises both Selective Laser Sintering (SLS) and Selective Laser Melting (SLM). It works similarly to BJ, with the difference that the cross sections of the part to be built are inscribed by means of a laser beam. The local densification of the powders can be obtained by directly sintering the ceramic powder, or by mixing the powder with a binder phase (inorganic or, more often, polymeric) which is then melted by the laser light. Direct laser sintering of ceramics is complicated by the poor resistance of this class of materials to thermal shock. Furthermore, the short interaction time between laser and powder limits material diffusion, leading to poor sintering (Kruth *et al.*, 2007; Regenfuß *et al.*, 2007). Binders within the powder which can be thermally activated, on the other hand, have been successfully used to shape porous ceramic parts, for applications and with results similar to those produced by BJ (Juste *et al.*, 2014).

(1) Porous components

Kolan *et al.* (2011) produced bioglass scaffolds with 50% porosity and pores in the range $300\text{--}800 \mu\text{m}$ by using an acrylic binder, followed by sintering at $675\text{--}695^\circ\text{C}$. Liu *et al.* (2012) deposited layers of a slurry made of hydroxyapatite powder and silica sol, exploiting the gelling of silica as binding mechanism, followed by sintering at 1200°C . The produced scaffolds had pores in the range $750\text{--}1050 \mu\text{m}$ and a porosity of 25%–32%.

(2) Monolithic components

Similarly to BJ, there are some rare examples in which dense monolithic ceramics have been obtained by SLS by infiltration with metals or semimetals after printing a porous ceramic preform. One of the early results concerns the generation of Si/SiC parts. Within the SLS process, SiC particles are glued together as a result of the formation of SiO_2 in oxidizing atmospheres, that is, ambient air. The highly porous parts have been used as preforms for the silicon infiltration (Löschau *et al.*, 2000).

More recent work concentrates on selective laser melting, where the formation of a liquid phase ensures rapid densification (Wilkes *et al.*, 2013). The use of dense alumina and zirconia spherical particles ($30 \mu\text{m}$) as feedstock results in a high packing density of the particles in the powder bed. Preheating of the powder bed to a temperature of at least 1600°C reduces the thermal shock within the part to be built. Alumina-Zirconia eutectic mixtures reduce the melting temperature of the powder bed to about 1860°C . With this approach, dense ceramic parts with remarkable mechanical properties could be generated via SLM. Nonetheless, crack formation within the ceramic bodies could not be avoided completely, and an uncontrolled infiltration of the preheated powder bed by the liquid phase formed within the laser spot results in an ill-defined outer contour of the parts generated.

Exploitation of viscous flow drives the fabrication of soda lime silica glass components via SLM (Datsiou *et al.*, 2019). Complex multilayer structures with good resolution were fabricated after optimization of laser processing parameters; however, the built parts showed no transparency but an opaque appearance which can be jointly attributed to residual porosity (above 11%) and to the presence of partially fused powder particles on the outer surface of the parts, which is typical for powder bed processes.

Even though there is currently no strategy in sight which would allow for the formation of dense monolithic ceramic parts via SLM, with precise contour and properties similar to conventional manufactured ceramic parts, the laser based technologies

SLS and SLM are the only processes which could potentially deliver ready to use ceramic parts from ceramic materials that require sintering.

Vat photopolymerization

This category includes Stereolithography, Digital Light Processing and Two-Photon Polymerization.

The vat polymerization technique is based on the photopolymerization of a liquid organic resin filled with ceramic particles, in a layer-by-layer fashion similarly to the other indirect AM technologies. Typical compositions for the slurry include a monomer solution, a photo-initiator and additives for the dispersion of the ceramic powder, with a concentration of 40–60 vol%. The formulation of stable suspensions requires a careful use of appropriate additives, and matching of the refractive index of powders and liquid medium is necessary for achieving high resolutions (Zhou *et al.*, 2010; Chartier *et al.*, 2008).

Stereolithography (SL) uses a laser beam to selectively and sequentially irradiate the liquid forming each layer, while Digital Light Processing (DLP) projects the entire layer image on the liquid by means of Micro-Mirror-Arrays (MMA). Differences among the techniques include equipment, cost, speed of manufacturing, resolution and surface quality (notably, DLP generates the so-called “stair stepping effect”, leading to unsmooth features on inclined lines). MMA’s or galvanometer mirror scanners are commonly used to project the light. The MMA technology enables a faster processing while scanners can provide higher lateral resolution; hence sometimes both technologies are combined.

Contrary to powder-based AM, in vat polymerization the material surrounding the part is liquid and therefore it is unable to provide any support; for this reason, depending on the specific geometry of the part, support structures are often built together with the part, requiring subsequent removal. Due to the high green densities and the use of fine ceramic particles, vat polymerization permits the production of almost dense ceramic parts after sintering.

Different technical solutions exist on the market for the vat polymerization process, depending on the position of the light source with respect to the vat, and the way in which the new slurry layer to be photopolymerized is provided. In the bottom-up approach, the light source is positioned below the vat containing the photopolymerizable slurry, while in the top-down approach the opposite occurs. “Top” and “bottom”, in this context, refers to the position of the building platform relative to the part and the light source: bottom-up, the building platform moves up at each layer while the part is built hanging on the platform with the light source below, top-down, the building platform moves down at each layer while the part is built standing on the platform with the light source above. Fig. 1 shows the top-down approach. Because of the way in which the new layer of unpolymerized slurry forms on the already polymerized part, the top-down approach shows some restrictions in terms of the printing of components possessing large cross sections parallel to the vat surface, while the bottom-up method has some limitations in terms of the length/width ratio of the component being fabricated (Santoliquido *et al.*, 2019). Continuous or semi-continuous printing is possible with the top-down approach, with building speeds up to a few mm/min.

Some equipment adopts an approach in which the part built is not fully immersed in the liquid feedstock, but mounted upside down (bottom-up process) on the building platform and dipped in a thin slurry layer deposited on a glass plate (Homa and Schwentenwein, 2014). The striking advantage of this strategy is the small amount of slurry required for building the part, and that different approaches can be developed for spreading each new layer of suspension (such as the use of a doctor blade), enabling the use of highly concentrated slurries with high viscosity.

Densities of parts manufactured by vat photopolymerization after debinding are typically around 50%–55% TD. The powder compact after debinding is sometimes denoted as “brown” compact. Due to the fact that very fine powders can be processed by this technique, it is possible to achieve densities exceeding 99% TD after sintering.

The binding phase is not always completely removed; if the debinding step is performed under inert atmosphere, pyrolyzed carbon remains within the structure, forming a ceramic matrix composite with electrical conductivity and enhanced microporosity suitable for photochemical applications (Mei *et al.*, 2019).

Two-photon polymerization (2PP) is a novel nano-stereolithography technique allowing cross-linking of a polymer with a resolution down to 200 nm. As this technology generally writes the structures directly in the volume of the resin with an optical setup of extremely short focal length comparable to optical microscopes, scattering of the light on the ceramic particles is an issue which has to be solved. One approach is the use of a photocurable preceramic polymer instead of ceramic powders (Brigo *et al.*, 2018). Another approach suggests using ceramic powders with a particle size about 10 times smaller than the wavelength of the light employed for photocuring. Particles of this size are no longer able to scatter the light and two-photon polymerization could be used to generate ceramic powder compacts with extremely small feature sizes. However, all parts need to be fabricated attached to a solid substrate, whose removal can be complicated.

(1) Porous components

The utilization of the vat photopolymerization technology was investigated for the generation of porous ceramics for various applications, taking advantage of the high precision that this technology provides and the possibility of obtaining dense struts. In all cases, the struts density ranged between 95% and 98% TD. Furthermore, complex lattice structures can be rather easily manufactured.

(2) Monolithic components

Generally, it is possible to produce dense monolithic ceramic parts via vat photopolymerization, because powder compacts with powder packing densities higher than 55% can be generated. The only restriction is imposed by the debinding step, which is required to remove the binding additives from the green compacts before sintering. The thermally activated

debinding steadily transforms the binder into gaseous species and is one of the most critical steps in the vat photopolymerization process due to the possible formation of defects in the brown compact. Since thermal debinding takes place in the volume of the part and dissociation and combustion products must leave the bulk by diffusion, the heating process has to be carried out very slowly keeping the pressure inside the part below a critical threshold avoiding the formation of cracks and voids. On the other hand, there already exists a vast expertise on the thermal-, catalytic- and solvent-based debinding of ceramic green compacts, from injection molding of ceramics. Injection molding also uses pastes with high organic content, as binders, plasticizers, dispersants and lubricants, to produce parts with high complexity. Thus, regarding the production of dense monolithic parts, a clear restriction of the vat photopolymerization process is, similarly to injection molding, the maximum volume or wall thickness of the ceramic green body at which debinding can be achieved in a reasonable time. At wall thicknesses of about 1 cm, debinding already requires a thermal treatment over a time period of several days.

The high packing densities achievable with vat photopolymerization processes make them appealing for the fabrication of glass components. Full density, however, is just one of the requirements in order to produce transparent parts; in fact, the starting powder also needs to be very fine (about 10 times smaller than the wavelength). Transparent fused silica glass components were produced by DLP from a colloidal suspension of fused silica particles with a mean diameter of 40 nm (Kotz *et al.*, 2017). By doping the ink with metal salts, colored glass components were also demonstrated.

Similar results were obtained by Cooperstein *et al.* (2018) using a different approach, i.e., the development of a silica glass component via a sol-gel route. The ink contains no particles and is based on a hybrid ceramic precursor, 3-acryloxypropyl trimethoxysilane (APTMS), that can crosslink both via photopolymerization and via sol – gel process. The ink is first printed via DLP and then aged and converted from a gel to a xerogel and then to a transparent silica glass component.

Slurry-based BJ (S-BJ) and slurry-based SLS (S-SLS)

S-BJ and S-SLS are technologies which are a logic extension of powder-based technologies. Instead of spreading a dry powder into thin layers, a ceramic slurry or slip is used, in order to increase the powder packing density in the powder bed. Each layer is inscribed either by using a multi-jet printhead (S-BJ) or by using a laser beam (S-SLS).

In S-BJ and S-SLS, a liquid suspension of ceramic particles is spread as a thin layer comparable to tape casting, while within this layer a cast is formed comparable to slip casting. In the slip casting process, the slip is brought into contact with a porous body, the casting mold. When a liquid is wetting a porous body, capillary forces draw the liquid phase of the suspension into the porous mold. The particles start to form a powder compact, the cast, at the molds surface. The cast formation kinetics obeys a square-root-of-time law, by depositing individual particles from the suspension to the surface of the mold. In case of the Layerwise Slurry Deposition (LSD) process, the mold is formed by the previously deposited and dried layers (Mühler *et al.*, 2015). Slip casting results in the formation of powder compacts with densities potentially exceeding 60% TD. Furthermore, due to the free settling of the powder particles from the suspension, no obvious interface is formed between individual layers.

In the powder-based BJ and SLS processes, the part built is easily released from the powder bed, but this is not the case for the slurry-based process. After deposition of all layers required for building up the desired geometry, the laser sintered or printed body is embedded in the powder bed which now is a block of densely packed particles (Mühler *et al.*, 2015). For the release of the part, the powder compact must be dissolved by a solvent. In case water-based slurries are used for the layer deposition, water can act as a solvent for the powder bed.

For the manufacture of a powder compact with properties comparable to those produced by classical powder processing, S-BJ has a high potential (Zocca *et al.*, 2019). By the use of small amounts of organic or inorganic binders provided by a printing head, the particles in the densely packed powder bed are locally glued together, and compacts generated by this technology don't require any additional treatment prior to sintering. The laser treatment in S-SLS, however, will affect the microstructure of the powder compact typically in a direction which is not favorable for the production of advanced ceramic.

(1) Porous components

Like powder-based 3D printing, including Binder Jetting and Powder Bed Fusion, the ability of generating porous structures by slurry based 3D printing primarily depends on the volumetric resolution of the technology. As very fine particles with high sintering activity can be processed, which potentially sinter to dense ceramics, structures with designed porosity and dense struts can be obtained. Also, it is possible to use coarse powders for obtaining a random micro-porosity by incomplete sintering, similarly to binder jetting using dry powders.

(2) Monolithic components

S-BJ is particularly well suited for the generation of monolithic ceramic parts (Fig. 4). Fine particles enable a high sintering activity of the powder compacts printed and low binder contents facilitates a rapid debinding without generation of defects. The laser based S-SLS process, however, is not taking advantage of these features, as the inhomogeneous heat treatment by the local laser irradiation is resulting in defect structures, such as cracks and bubbles, which cannot be removed in a subsequent sintering step.

Laminated object manufacturing (LOM)

Originally known as Layered Laminated Manufacturing (LLM), later on commercialized under the trade names Laminated Object Manufacturing (LOM) by Helysis or CerLAM and MetLAM by Javelin 3D, this AM process builds 3D parts by the lamination of

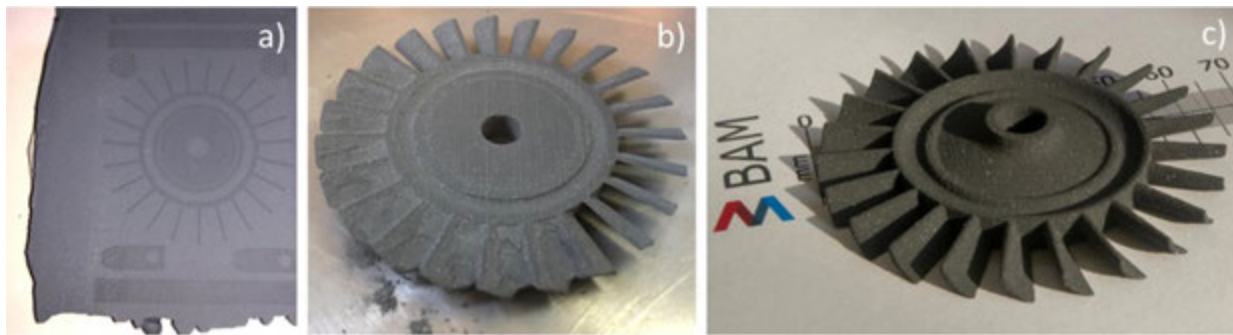


Fig. 4 Release of a turbine made of SiC by employing the Layerwise Slurry Deposition (LSD) technology in combination with binder jetting. (a) powder bed, formed by 120 layers with a thickness of 100 μm , containing the turbine; (b) turbine partially released from the powder bed; (c) turbine green body.

paper, tapes or similar shapes at low-medium temperature and pressure (Gomes *et al.*, 2008). LOM has been considered as an alternative for the lamination of green ceramic tapes into 3D dense or semi-dense parts.

The main advantage of this technique is the possibility of producing laminates directly from green tapes, which in turn are produced by established technologies, such as extrusion or tape casting. Compared to some conventional manufacturing processes such as injection molding, extrusion, or roll pressing, LOM parts exhibit moderate values of flexural strength at relatively high porosities. Values of mechanical strength for silicon nitride parts obtained by LOM of $\sim 475 \pm 34$ MPa have been reported (Liu *et al.*, 2015), which is comparable to silicon nitride ceramics prepared by pressureless sintering (Penas *et al.*, 2001) and higher than for components fabricated by gel casting (54.5 ± 2.3 MPa) (Wang *et al.*, 2013).

The main drawbacks of this technology, as in most lamination processes, are related with the quality of the interfaces between tapes and the presence of defects. Common issues being reported are delamination, interfacial porosities and differential shrinkage (Gomes *et al.*, 2008, 2011).

(1) Porous components

The LOM process uses tapes or papers as feedstock, which needs to be shredded in small pieces layer by layer by means of a knife or laser. These pieces do not provide flowability like ceramic powders. Hence, the removal of the excessive material embedding the part is one major concern. LOM is basically not the right choice to build up filigree structures or structures with complex designed porosity. On the other hand, random porosity can be obtained by incomplete sintering of coarse-grained powders or by the burn out of sacrificial organic fillers added to the tapes.

(2) Monolithic components

In principle with LOM dense monolithic parts can be generated, since the ceramic tapes can be very well optimized regarding sintering properties. One concern is, however, the interfaces between laminated tapes which are prone to defects. Nonetheless, ceramics revealing properties comparable to conventionally manufactured ones can be obtained.

Direct AM Technologies

Material jetting

Material jetting, or inkjet printing (IP) is a technology which uses a ceramic suspension to build up structures by the successive deposition of individual drops provided by a printing head. The ceramic suspension, or ink, consists of ceramic particles (typically > 20 vol%) dispersed in a liquid carrier containing different additives to stabilize the suspension, adjusts its viscosity and surface tension, and to control the spreading and drying of the deposited droplets (Özkol *et al.*, 2010; Teng and Edirisinghe, 1998). As liquid carrier, water or organic liquids can be used, depending on the specific requirements of the printing head. In order to ensure that ceramic particles can be fed as a suspension through the individual deposition nozzles of the printing head, their size (d_{50}) is typically kept in the sub-micrometer range at a narrow particle size distribution (Derby, 2011). Different to powder based 3D printing, IP builds up structures directly from the material provided by the ink. IP technology is capable to generate complex structures with a high powder packing density, as it uses ceramic suspensions. Together with a good sintering activity of the generated green parts, ensured by the use of submicron powders, IP can provide parts from oxide and non-oxide ceramics with appreciable mechanical properties. Furthermore, due to the small volume (picoliter) of the individual droplets provided by the printing head, the generation of structures with well controllable material gradients is possible in multi material IP setups (Wätjen *et al.*, 2014). The printing of complex shaped structures with overhangs and undercuts can be realized by printing support structures with an ink providing a sacrificial material (e.g., carbon black), which is conveniently removed during firing in oxidizing conditions. Currently, IP of ceramic materials is industrially developed for the fabrication of 2D components (e.g., printed electronics) (Tomov *et al.*, 2010) as well as 3D parts.

A relatively new technology, similar to IP, is the direct deposition of wax droplets filled with ceramics (Thermoplastic 3D Printing). This technology generally uses different print heads than those of most IP technologies, but it shares many features

with IP especially the capability to generate multi material components (Scheithauer *et al.*, 2014). The building rates are, however, significantly higher than IP because of the larger droplets formed by the wax deposition process. Dewaxing of the printed powder compacts, on the other hand, requires an additional thermal treatment before sintering to dense ceramic bodies.

Material extrusion

This category comprises different technologies, in which a viscous liquid is passed through a nozzle and is deposited layer-by-layer following a continuous path. The technologies *Direct ink writing* and *Fused Deposition Modelling* are described in the following.

Direct ink writing

Direct ink writing (DIW), also known as Robocasting, is based on the extrusion (using a syringe or a proper screw extruder) of a ceramic paste (ink) of suitable rheology in the form of a filament. The control of the rheological properties of the filament is essential to prevent deformation of the part after extrusion and sagging of the filaments, especially when the geometry includes spanning features as in most porous components. The fluid should show an initial yield stress and have a viscosity which decreases with increasing the shear rate (Herschel-Bulkley fluid). The technique was originally patented and developed by Cesarano and Calvert (2000) at the Sandia National Laboratories in the USA under the name of "Robocasting". In Robocasting, a ceramic suspension with a high solid loading undergoes a transformation from a pseudoplastic to a dilatant behavior when extruded in air, triggered by minimal drying of the slurry. Drying in air, however, limits the minimum diameter of the printing nozzle to about 500 μm , otherwise clogging is experienced. In order to overcome these issues, inks have been developed which have a reversible gel transformation and are deposited in a non-wetting (often oil) bath. Briefly, they behave like a viscous gel when loaded in the printing head, but as they are extruded the shear stress breaks the gel structure and the viscosity decreases of several orders of magnitude. After extrusion, the fluid undergoes a quick gelation increasing again the viscosity to a level before shearing which prevents deformation of the filament. This behavior can be achieved by controlled flocculation of a ceramic suspension (e.g., by a change in pH, ionic strength of the solvent, addition of polyelectrolytes) to form a gel (Lewis *et al.*, 2006), or by using gelling additives, for example by using an inverse thermo-reversible gel (Saiz *et al.*, 2011). More recently, Eqtesadi *et al.* (2014) showed that the use of polyelectrolytes and the control of the pH may be a difficult approach for bioglass inks, because of the glass dissolution and leaching of ions in water. In this case, carboxymethyl cellulose was successfully used as an additive to disperse the glass powder and to obtain a suitable rheological behavior. Another possibility is the formulation of a ceramic ink containing a polymeric binder and plasticizer (e.g., PVB and PEG), which can be added up to 23 wt% (relative to the ceramic phase). For fine lattice structures, defects generated by debinding were not reported. These variations of Robocasting have been mostly denominated "direct ink writing" (DIW) technologies.

Typical nozzle sizes are in the range 100–1000 μm and, after drying, the material has a high green density (up to 60%), which allows to achieve an almost complete densification upon sintering. The combination of fine and dense filaments makes the technology particularly attractive for the production of components suitable for several applications, based on structural and functional ceramics.

In all material extrusion processes, the ink flow through the nozzle is associated with shear stresses reaching their maximum at the tip; when directional fillers, such as platelets or fibers, are embedded in the inks, the stress field will align them in the flow direction. Exploiting this phenomenon, Feilden *et al.* (2017) fabricated composites with alumina nanoplatelets aligned along the printing direction and demonstrated that such architecture can be used to direct crack propagation (twisting and tilting) at the microscopic level.

Alignment of short fibers inside a ceramic matrix also shows great potential for anisotropic, localized reinforcement designed and informed by the CAD file. Carbon fibers (100 μm length) were embedded in a preceramic polymer ink yielding SiOC matrix after pyrolysis under inert atmosphere (Franchin *et al.*, 2017a). The composite material also comprised SiC powder in order to hinder its shrinkage. The flexural behavior of single filaments was studied in a later work, showing fiber alignment and pull-out mechanisms at the fracture surface; the filaments could deflect consistently before breaking, and showed improved toughness and graceful failure (Franchin *et al.*, 2018).

(1) Porous components

The direct deposition of ceramic inks is arguably the most used AM technology for the generation of porous structures. Stuecker *et al.* (2003) reported the production of mullite porous meshes with 100–1000 μm pore sizes and 225–1000 μm filament diameter, obtaining a relative green strut density of 55% and a sintered strut density of 96%. Smay *et al.* (2002) produced lead zirconate titanate (PZT) periodic lattices with a diameter of 200–400 μm , consisting of linear or radial arrays. The rod spacing varied from 300 to 1200 μm , thus determining spanning features. The same material system has been used later to produce PZT arrays for ultrasonic sensing applications in the 2–30 MHz frequency range (Smay, 2004). These arrays were densified and infiltrated with an epoxy resin to fabricate PZT–polymer composites with 2–2 connectivity. Smay *et al.* (2007) also demonstrated the DIW of ternary mixtures of BaTiO₃, BaZrO₃, SrTiO₃ by using a nozzle mixer. Furthermore, they produced Ni–BaTiO₃ metal-ceramic multilayer structures by using an array of single nozzles, demonstrating that by this technique it is possible to fabricate graded and multi-material porous structures. The use of geopolymer inks enabled the fabrication of porous inorganic structures suitable for filtration and other applications (Franchin *et al.*, 2017b).

For this fabrication method too, a major part of the research has focused on the shaping of bioceramics into porous scaffolds. Genet *et al.* (2013) modeled the compressive strength of HA porous scaffolds based on a Weibull approach. They

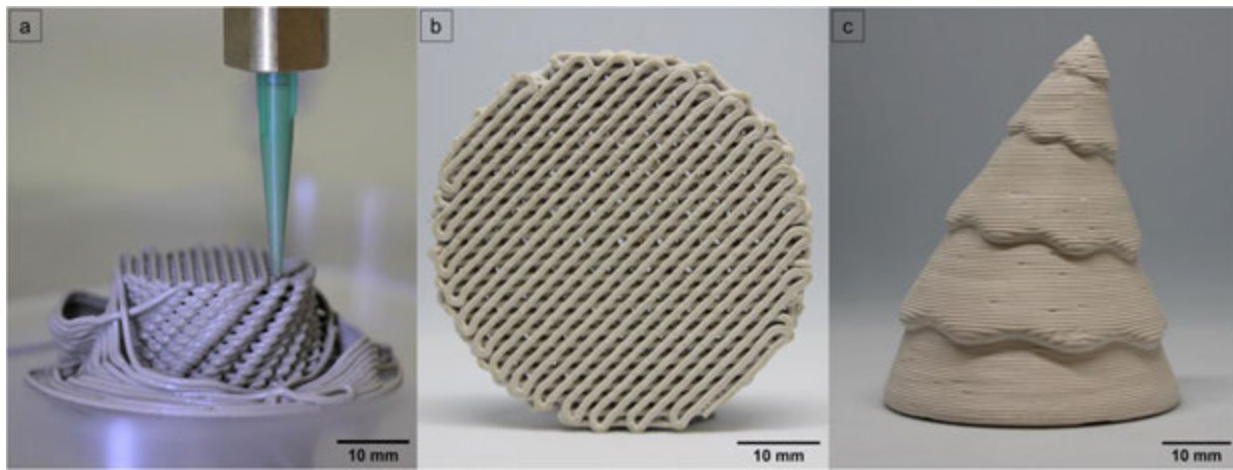


Fig. 5 Direct ink writing with geopolymer-based inks (example composition reported in Franchin *et al.*): (a) fabrication of a twisted lattice structure with a 0.8 mm nozzle tip; (b) porous lattice structure with 45° alignment (for filtration purposes); (c) solid object (the stacking of different layers is clearly visible on the surface). Geopolymeric components consolidate at room temperature and do not require a following sintering step.

could fit well experimental data, showing a decrease in compressive strength upon increasing rod spacing (i.e., porosity), keeping a constant rod diameter. Interestingly, even when the rod spacing (400–985 μm) and diameter (200–610 μm) were varied in order to keep the porosity constant (45 vol%), there was almost a four folds decrease in strength as the rod diameter increased. Franco *et al.* (2010) formulated an ink containing a thermo-reversible gel which had low viscosity at low extrusion temperature and underwent a quick gelation following deposition in a warm (60°C) oil bath. They produced HA, TCP and biphasic calcium phosphate (BCP) scaffolds and found that the micro-porosity in the struts varied in a wide range of 5%–40% as the content of thermo-reversible gel was increased, and the bending strength decreased accordingly from ~ 25 MPa to ~ 2 MPa.

Miranda *et al.* (2007, 2008) produced HA scaffolds which had 39% total porosity and 15% strut micro-porosity and studied their fracture modes under uniaxial compression. These scaffolds had a compressive strength of ~ 50 MPa, and in a similar work it was shown that this value was doubled after two weeks immersion in simulated body fluid (SBF). Fu *et al.* (2011) produced particularly strong bioglass scaffolds with completely dense rods of 100 μm diameter and a total porosity of 60%. These scaffolds had unidirectional pores and, as expected, anisotropic mechanical properties, reaching 136 MPa in the channel direction and 55 MPa in the perpendicular direction. The dependence of the compressive strength on the porosity in the 60%–80% range was also in good agreement with the Gibson-Ashby model for cellular ceramics.

It is worth noting, however, that by DIW it is also possible to obtain scaffolds with porous struts by adding a porogen to the ceramic paste (Dellinger *et al.*, 2007). They added PMMA microspheres to the ink and produced scaffolds with three levels of porosity: macropores (100–600 μm) were designed by controlling the arrangement and spacing between rods of HA; micropores (1–30 μm) were produced within the rods by including PMMA microspheres; submicron pores (less than 1 μm) were the result of incomplete sintering. Hierarchical porous ceramics with tunable pore sizes across three different length scales were also produced using inks in the form of particle-stabilized emulsions and foams, that were sufficiently stable to resist coalescence during printing (Minas *et al.*, 2016).

A further degree of versatility for this 3D printing technique can be achieved when using extrusion nozzles which enable the fabrication of cross-sections different from the standard circular one, such as square, hexagonal and other complex micron-sized geometries, or even hollow filaments (Schlordt *et al.*, 2013).

Scaffolds produced by DIW generally possess better mechanical properties compared to scaffolds produced by powder-based technologies. It seems reasonable to correlate this observation with the micro-porosity in the scaffold struts: even though this value depends also on the specific material system used, there is a clear influence of the process, which can be found when examining the properties of parts shaped without designed porosity. Parts produced by BJ generally have a high level of residual micro-porosity, while parts produced by liquid-based processes can be almost completely dense after sintering.

(2) Monolithic components

Monolithic components can certainly be fabricated with this AM technology; however, one has to be aware that the surface of printed components will show a distinct roughness formed by the individual filaments and, given the rheology of the ink, the cross-section can contain voids between adjacent circular filaments. A non-isotropic mechanical behavior can also be expected, due to the preferred orientation of the filaments within the printed structure, and therefore the parts do not typically perform as the homogeneous ceramic monoliths produced by traditional ceramic technologies.

As an example, which illustrates the capabilities of DIW to generate lattice structures and dense ceramic parts, in Fig. 5 images of a zirconia lattice structure during printing (Fig. 5(a)) and after printing (Fig. 5(b)) and a dense part before sintering (Fig. 5(c)) are shown. Note that, the dense part shows a distinct corrugation of the surface resulting from the deposition of individual filaments.

Similar to DLP, with DIW it is possible to produce transparent glass components from suspensions of nano-sized silica particles (Nguyen *et al.*, 2017). Rheology of the inks can be tailored for spanning features or for seamless interfaces in monolithic parts. Nguyen *et al.* also demonstrated the fabrication of multi-composition glass parts using a second dispensing unit filled with a gold nanoparticle-doped silica ink.

A sol-gel approach is also applicable to DIW and seems to be a promising route for transparent multi-component glass parts. The sol-gel chemistry can be tuned for both rheology control and for preparing a wide range of glass-forming metal oxide feedstocks. Destino *et al.* (2018) demonstrated this approach by fabricating SiO₂ and SiO₂-TiO₂ glass monoliths of optical quality from Si- and Ti-alkoxide derived inks.

Fused deposition modeling

In parallel with the extrusion of ceramic pastes, and in analogy with the most popular process used for the production of polymeric components, another approach has been developed: the fused deposition modeling of ceramics (FDM). This technique is based on the use of a flexible filament comprised of a significant amount of polymer (usually, a wax) and a ceramic powder, which is melted during the extrusion because the printing head is heated and solidifies by cooling immediately after in order to prevent deformation of the filament. Ideally, in analogy with FDM of conventional polymers, a continuous filament should be produced and fed to the printing head, but it is very difficult to prepare a filament with a high loading of ceramic particles that is not brittle and can be collected in spools to be continuously supplied to the printing head. After printing, the polymeric binder is burnt out and the ceramic phase is sintered. Grida and Evans (2003) extruded a mixture of 55 vol% zirconia in wax through nozzles with diameter between 76 and 510 µm. The minimum diameter of the nozzle is similar in FDM and in DIW (0.1 mm). The same authors observed that fine log-pile structures could be produced with a 100 µm diameter filament but not with a 76 µm filament. The reason was that the latter filament solidified too quickly in ambient air. Park *et al.* instead extruded 40 wt% HA mixed with PCL at 100°C through nozzles with diameter 400–600 µm (Park *et al.*, 2011). They also measured the influence of the deposition pattern on the compressive modulus and they studied the attachment and proliferation of osteoblast-like cells.

Gorjan *et al.* (2017, 2019) investigated the processing of piezocomposites and mullite structures by FDM. At Rutgers University (New Jersey, USA), an FDM apparatus has been developed which is able to deposit up to four different materials in the same layers, employing four deposition units (Jafari *et al.*, 2000). Jafari *et al.*, in the same work also produced a multilayer piezoelectric component transducer composed of soft and hard PZT, and they suggested the fabrication of components based even more complex composite materials, for example through the simultaneous deposition of ceramic, metal, electrode and fugitive phases.

The printing envelope for current FDM printers can be rather large, and robot-based systems can enable free-form fabrication, due to the fast cooling of the molten filament on exiting the nozzle.

Similarly to DIW, FDM is well suited for the manufacture of scaffolds. The presence of a large amount of organic binder makes however processing of monolithic components cumbersome, and the exothermic decomposition reaction can lead to the generation of microdefects decreasing the strength of the part.

We should also mention that it is possible to couple filament-based AM technologies with computer numerical control (CNC) machining that, at the same time, shapes the object and produces a good surface finish. In any case, the surface texture is not always problematic, but since it is a specific characteristic of these extrusion-based technologies, it has to be taken into account when designing a component. Concluding, extrusion-based AM technologies are particularly suitable for producing arrays of separate struts but are not yet able to produce proper monolithic ceramics, at least according to a most general definition.

Such limitation does not exist when the filament or feedstock does not involve any organic binder: this is the case with glass, which can be molten and deposited similarly to thermoplastic polymers, only at higher temperature (~1000°C, depending on glass composition). In 2015, Israeli company Micron3DP demonstrated extrusion of soda lime and borosilicate glass fibers thanks to their proprietary high temperature heated head. They were able to produce components of few centimeters, but were limited to simple shapes and low resolutions and were experiencing issues in terms of thermal shock of the printed components. In the same year, researchers at Massachusetts Institute of Technology (MIT) revealed the first prototype of a glass printer composed of high temperature modular elements able to process glass from the melting stage to the final, annealed product (Klein *et al.*, 2015). The printer operates at a different scale, with a 10 mm diameter nozzle and a build volume of 250 × 250 × 300 mm³. For this reason, the feedstock is not a fiber; it is either glass nuggets or (for higher production volumes) molten glass collected from a furnace and directly poured into the crucible. The addition of an annealing chamber, in which glass is deposited and slowly cooled down after printing, allows releasing tension and avoids thermal shock.

Both Micron3DP and MIT developed their systems over the following years. The first one developed an improved printer implementing an annealing chamber as well as continuous filament feeding (Bracha and Gal-Or, 2018a, b, c) and used it to fabricate microfluidic systems (Gal-Or *et al.*, 2019). The group at MIT improved and scaled up their platform towards and industrial scale glass printer and used it for the fabrication of architectural scale (3 m tall) structures (Inamura *et al.*, 2018); their spin-off, Lios, is currently taking on the system development and using it to create new design installations and products, starting with lighting.

Negative AM Technologies

While most current research focuses on the use of AM technologies that can directly produce ceramic components, negative replica methods are sometimes attractive because they can overcome at least some of the limitations in the physical, functional and geometrical characteristics of components produced. In this approach, a sacrificial polymeric mold is fabricated by AM and then, generally, impregnated with a ceramic slurry. After polymer removal (by decomposition, burn-out or dissolution) and sintering, a ceramic component is obtained. The fabrication of molds by AM adds a step to the processing route, but it allows for the use of AM technologies typical of polymeric materials, some of which are at a greater stage of development compared to AM of ceramics, implying an easier process and often better resolution and surface quality. We should also note that negative replica methods have been long used for the casting of metals, by producing using AM either a ceramic mold or a wax pattern for the investment casting process (Chhabra and Singh, 2011).

Almost every AM technology can be used to fabricate the mold. Detsch *et al.* (2008) used a printer which deposited a wax dropwise and impregnated the wax mold with a HA slurry. They also replicated a similar geometry by Robocasting, obtaining scaffolds with 44% porosity in the case of negative AM and 37% for the sample produced by Robocasting. In both cases, the pore size and strut diameter were 300 μm and 500 μm respectively, and the strut relative density reached 96% after sintering, indicating the two approaches are fully interchangeable. A similar fabrication route was followed to produce epoxy molds by SL to generate $\text{TiO}_2/\text{SiO}_2$ diamond structures for application as photonic crystals (Yin *et al.*, 2004). SL has also been used to produce resin molds for HA scaffolds with 50% geometrical porosity; in this case, a gel-casting technique was employed to improve the strength of the ceramic green body (Woesz *et al.*, 2005). Bose *et al.* (2003) produced molds by fused deposition modeling (FDM) of a commercial thermoplastic polymer, which were subsequently impregnated with TCP or Al_2O_3 slurries in order to produce porous scaffolds and investigated the influence of the pore size (300–500 μm) and porosity (25%–45%) on in-vitro cell tests (Bose *et al.*, 2003). Guo *et al.* (2004) instead produced polystyrene molds by SLS, which were then used as molds for PZT ceramic components obtained by gel casting; the selection of the polymer and of the decomposition thermal treatment is essential to avoid deformation of the parts, which was instead observed when using molds produced by FDM of ABS polymer. Ortona *et al.* (2012) applied a technology (“Polyjet”) which dropwise deposits a photo-curable resin to produce a polymeric template possessing a complex, regular three-dimensional cellular structure. In this case, the polymeric template was coated with a SiC slurry and after pyrolysis it was reactively infiltrated with molten Si to generate RBSiC cellular structures with hollow struts. Finally, Franchin and Colombo (2015) used FDM to fabricate polymeric scaffolds which were infiltrated by a geopolymer slurry, resulting in parts with different pore geometries.

Feasibility of AM processing of Monolithic Ceramics

As already mentioned, AM of dense monolithic ceramics is still a major challenge. The problem can be reduced down to a few issues:

- (1) The superior physicochemical properties of advanced ceramics critically depend on their microstructure, which is intrinsically linked to the particle packing of the powder compact and the sintering schedule applied, as well as to their composition (e.g., presence of sintering aids). Obtaining a green compact with the desired microstructure is far from trivial when using AM as an advanced shaping technology. From an economical perspective, this statement should be understood as a well meant advice: the integration of AM technologies into existing industrial ceramic production is a prerequisite for making AM of ceramics reliable, high quality and economically viable.
- (2) Advanced ceramics are generally produced from very fine powders showing a poor flowability. A good flowability is, however, required for the deposition of layers in powder-based AM, such as BJ or SLS. Spreading fine, submicron powders into thin layers is very difficult to impossible. Furthermore, fine ceramic powders are prone to agglomeration and electrostatic charging and, thus, do not pack well. Packing densities of dry ceramic powders in a particle size range from 20 to 100 μm are generally below 50% of the theoretical density (typically between 25% and 45%) (Zocca *et al.*, 2014). The density also depends on the particular layer spreading technology used, i.e., blade, roller etc. The use of ceramic suspensions or pastes, on the other hand, enables deposition of very thin layers, down to 10 μm thickness in case of stereolithography, and the use of finer particulates. After removal of the liquid phase or of the plasticizer, appreciably high densities can be achieved. However, according to the state of the art, the majority of ceramic suspensions or pastes used as feedstock for AM are based on a significant amount of organic binders (40–60 vol%). The removal of organics remaining as a residue in the produced green powder compact is time consuming and restricts the maximum volume or wall thickness of the generated features. Nonetheless, organic plasticizers are favored because their rate of evaporation can be very well adapted to the specific needs of the particular additive manufacturing process. In this context, one of the most successful technologies is stereolithography (SL), using ceramic slurries containing photosensitive resins for the layerwise buildup of ceramic compacts.
- (3) Concerning ready-to-use parts, the first question must be: can the sintering step be directly integrated into an AM process? This would imply that sintering is achieved simultaneously to adding the material. Sintering is a very delicate process step, as it ultimately defines the microstructure of the material, its final physical-chemical properties and has also a strong influence on the parts geometry and dimensional constraints. Therefore, a technology allowing sintering during additive buildup of a ceramic part with physical properties comparable to a conventionally processed part is hard to envision. Based on the selective laser sintering technology, ceramic powders have been sintered layer by layer by the local application of laser energy.

Different to conventional sintering, which works with heating rates of some K at most up to some 10K per minute and dwell times at maximum temperature in the range of hours, the so-called laser sintering requires significantly higher heating rates and provides shorter dwell times. Accordingly, densification of the powder to a non-porous material is hardly achieved. From all the experimental work done in this direction, it can be concluded that short annealing times associated with a local laser irradiation can result in the bonding of particles by the in situ formation of a liquid phase. In this context, two different laser annealing strategies can be applied, on the basis of existing laser systems. The first strategy maximizes the time the material is annealed at a certain position, and laser systems providing continuous laser radiation are used. In the second strategy, lasers providing short pulses, typically of the order of some nano-seconds, are used to apply extremely high radiation intensities. The first approach aims to initiate, similarly to classical sintering, diffusion driven material transport and the formation of a liquid phase for consolidation of powder particles (Kruth *et al.*, 2007). The second approach aims to produce a liquid phase for a short time interval and, by the formation of an ablation plume, an additional force parallel to the surface normal resulting in a compression and fusion of powder particles (Regenfuss *et al.*, 2007).

The formation of a liquid phase is the only way to achieve a rapid densification, which is fast enough to meet the requirements of selective laser sintering technologies. In case an appreciable densification is achieved, cracks are often formed due to the high thermal gradients introduced into the material by the local laser treatment (Juste *et al.*, 2014; Wilkes *et al.*, 2013). To the best of our knowledge, no dense and crack free ceramic parts comprising multiple layers of deposited material could be produced by selective laser sintering or melting up to now. It is noteworthy to observe also that post sintering of laser-sintered and not fully densified ceramic bodies not always leads to a significant additional densification. The local formation of a liquid phase during laser sintering results in extended structural defects in the sintered body, such as larger pores and cracks, which cannot be removed during sintering even though the initial powders used provide a high sintering activity. Furthermore, one must bear in mind, that sintering does not only result in the densification of a powder compact, but also determines the phase composition of the material. In this context, liquid phase formation might provide a route for the rapid densification of a powder compact, but not necessarily results in the desired phase composition and, thus, does not lead to the desired properties of the part generated. Alternatively, sintering could be a final treatment embedded in an AM process. This scenario, however, is basically a direct replication of the powder process chain for the manufacturing of ceramics, in which shaping of a powder compact precedes sintering and, as already mentioned, it must be ensured that the sintering activity of the powders used is not reduced in the AM process prior to the final sintering.

Future Developments

Similarly to what occurred for AM of metals, it can be expected that powder based technologies, in which a powder bed is built up layer by layer, will become the most economically relevant class of additive technologies for ceramics, as their specific merits are: low cost of raw materials, easy scale up to very large parts and parallel processing of multiple parts, high flexibility in design, and direct manufacture of ceramic green bodies with low content of organic additives. However, a very important issue that nowadays remains to be satisfactorily solved is the low powder packing density and stability of the powder bed, when dry powders are used as feedstock, which implies the need of support structures. Instead of dry powders, ceramic slurries can be used for the layer by layer buildup of powder beds with high powder packing densities. Moreover, slurries facilitate the use of powders in a wide range - typically between 100 nm to 100 μm - and classical ceramic processing know-how can be applied for preparing slurries. This concept is already realized in vat polymerization, which at present is the only technology available on the market for AM of advanced ceramics and which will likely dominate marketplaces requiring high precision, small components with complex geometries. Based on these considerations, the following strategies and outlook for the production of high quality ceramic parts via AM can be formulated:

- (1) AM of high quality ceramic parts is inevitably linked to the sintering of powder compacts with appropriate particle size distribution and homogeneous particle packing density;
- (2) Cost-effective AM of high quality dense monolithic ceramic parts must follow the powder processing route of classical ceramic manufacturing;
- (3) The more classical powder processing know-how can be implemented into AM of ceramics, the higher the quality of parts and more cost-effective the manufacturing process will be;
- (4) AM technologies capable of providing powder compacts with appropriate particle size distribution and homogeneous, high particle packing density and with maximum freedom in design will be economically the most successful. Until this goal is reached, the successful implementation of AM technologies for ceramics at an industrial scale will be limited to a few specific material systems and component geometries;
- (5) AM technologies capable of producing complex ceramic parts with very fine (from micro- down to the nano- size scale) filigree but dense lattice structures (struts) will hold an outstanding position within all AM technologies, as ceramic materials are thermodynamically more stable than metals and polymers. In this context, Polymer-Derived-Ceramics (PDCs) can be considered as an enabling technology;
- (6) AM of ready-to-use ceramic parts will remain a challenge, and solutions will likely significantly deviate from the powder processing route of classical ceramic manufacturing.

For the sake of completeness, it should be noted that the preceramic polymer approach to obtain Polymer-Derived-Ceramics (PDCs) offers a viable alternative to the powder processing route, not only in terms of classical fabrication technologies, but also in the context of additive manufacturing. The striking advantage of Polymer-Derived-Ceramics arises from their relatively simple processing starting from polymeric precursors, which enables the components to be fabricated using technologies suited for polymers (Colombo *et al.*, 2017). However, there are several technological challenges associated with the pyrolysis of the polymeric structure into a ceramic. The most critical, in this context, is the release of gaseous species during the pyrolysis of the preceramic polymer, with its associated shrinkage, which prevents the direct production of bulk components. Strategies exist to reduce these issues, such as adding inert or reactive fillers, but the production of fully dense parts remains a challenge. Moreover, most preceramic polymers would lead only to silicon-based ceramics, with boron-based systems being a notable exception (Colombo *et al.*, 2010). Nonetheless, for filigree, porous and small structures, PDCs are an attractive alternative to conventional ceramics, and the presence of carbon nano-sized clusters in their microstructure can afford useful functional properties to the printed parts.

Finally, we should mention that different efforts are currently underway to combine AM technologies with different characteristics in terms of resolution or geometrical capabilities. Hybridization is a term used in the field to indicate the combination/integration (either in parallel or in series) of different technologies to generate components with features typically not obtainable when using a single approach (Bernardino *et al.*, 2020), or to provide additional manufacturing benefits (Gao *et al.*, 2015). Examples include coupling 2PP and DLP, to generate parts with details ranging from the sub-micron to the mm scale, or BJ and DIW, to obtain multi-material components or parts with narrow communicating channels, or DIW and SL, to enable photocuring of the ink and therefore eliminate the stringent requirements on rheology of that extrusion technique, or DIW and SLS, to directly sinter the upon ink exiting from the nozzle.

References

- Bernardino, R.M., Valentino, S., Franchin, G., Günster, J., 2020. Manufacturing of ceramic components with internal channels by a novel additive/subtractive hybridization process. *Open Ceramics* 2, 100010.
- Bose, S., Darsell, J., Kintner, M., Hosick, H., Bandyopadhyay, A., 2003. Pore size and pore volume effects on alumina and TCP ceramic scaffolds. *Mater. Sci. Eng. C* 23, 479–486.
- Bourell, D.L., Marcus, H.L., Barlow, J.W., Beaman, J.J., 1992. Selective laser sintering of metals and ceramics. *Int. J. Powder Metall.* 28, 369–381.
- Bracha, A., Gal-Or, E., 2018a. 3D Printing System for Printing High Melting Temperature Materials. WO/2018/163006.
- Bracha, A., Gal-Or, E., 2018b. Continuous Filament Feeding for Additive Manufacturing. WO/2018/163007.
- Bracha, A., Gal-Or, E., 2018c. 3D Printing Nozzle Calibration inside a Heated Chamber. WO/2018/163008.
- Brigo, L., Schmidt, J.E.M., Gandin, A., *et al.*, 2018. 3D nanofabrication of SiOC ceramic structures. *Adv. Sci.* 1800937.
- Butscher, A., Bohner, M., Doeblin, N., *et al.*, 2013. Moisture based three-dimensional printing of calcium phosphate structures for scaffold engineering. *Acta Biomater.* 9, 5369–5378.
- Butscher, A., Bohner, M., Hofmann, S., Gauckler, L., Müller, R., 2011. Structural and material approaches to bone tissue engineering in powder-based three-dimensional printing. *Acta Biomater.* 7, 907–920.
- Castilho, M., Gouveia, B., Pires, I., Rodrigues, J., Pereira, M., 2015. The role of shell/core saturation level on the accuracy and mechanical characteristics of porous calcium phosphate models produced by 3Dprinting. *Rapid Prototyp. J.* 21, 43–56.
- Cesarano, J., Calvert, P.D., 2000. US Patent 6027326 A.
- Chartier, T., Duterte, C., Delhote, N., *et al.*, 2008. Fabrication of millimeter wave components Via ceramic stereo- and microstereolithography processes. *J. Am. Ceram. Soc.* 91, 2469–2474.
- Chhabra, M., Singh, R., 2011. Rapid casting solutions: A review. *Rapid Prototyp. J.* 17, 328–350.
- Chumnanklang, R., Panyathanaporn, T., Sitthiseriratip, K., Suwanprateeb, J., 2007. 3D printing of hydroxyapatite: Effect of binder concentration in pre-coated particle on part strength. *Mater. Sci. Eng. C* 27, 914–921.
- Colombo, P., Mera, G., Riedel, R., Soraru, G.D., 2010. Polymer-derived ceramics: 40 years of research and innovation in advanced ceramics. *J. Am. Ceram. Soc.* 93, 1805–1837.
- Colombo, P., Schmidt, J., Franchin, G., Zocca, A., Günster, J., 2017. Additive manufacturing of ceramics using preceramic polymers. *Am. Ceram. Soc. Bull.* 96, 18–23.
- Cooperstein, I., Shukrun, E., Press, O., Kamysny, A., Shlomo, M., 2018. Additive manufacturing of transparent silica glass from solutions. *Appl. Mater. Interfaces* 10, 18879–18885.
- Datsiou, K.C., Saleh, E., Spirret, F., *et al.*, 2019. Additive manufacturing of glass with laser powder bed fusion. *J. Am. Ceram. Soc.* 102, 4410–4414.
- Deckard, C.R., 1989. US Patent 4,863,538.
- Dellinger, J.G., Cesarano, J., Jamison, R.D., 2007. Robotic deposition of model hydroxyapatite scaffolds with multiple architectures and multiscale porosity for bone tissue engineering. *J. Biomed. Mater. Res. A* 82A, 383–394.
- Derby, B., 2011. Inkjet printing ceramics: From drops to solid. *J. Eur. Ceram. Soc.* 31, 2543–2550.
- Destino, J., Dudukovic, N.A., Johnson, M.A., *et al.*, 2018. 3D printed optical quality silica and silica–titania glasses from sol–gel feedstocks. *Adv. Mater. Technol.* 1700323.
- Detsch, R., Uhl, F., Deisinger, U., Ziegler, G., 2008. 3D-Cultivation of bone marrow stromal cells on hydroxyapatite scaffolds fabricated by dispense-plotting and negative mould technique. *J. Mater. Sci. Mater. Med.* 19, 1491–1496.
- Eqtasadi, S., Motealleh, A., Miranda, P., *et al.*, 2014. Robocasting of 45S5 bioactive glass scaffolds for bone tissue engineering. *J. Eur. Ceram. Soc.* 34, 107–118.
- Espera Jr, A.H., Dizon, J.R.C., Chen, Q., Advincula, R.C., 2019. 3D-printing and advanced manufacturing for electronics. *Prog. Add. Manuf.* 4, 245–267.
- Feilden, E., Ferraro, C., Zhang, Q., *et al.*, 2017. 3D printing bioinspired ceramic composites. *Sci. Rep.* 7.13759.
- Fielding, G.A., Bandyopadhyay, A., Bose, S., 2012. Effects of silica and zinc oxide doping on mechanical and biological properties of 3D printed tricalcium phosphate tissue engineering scaffolds. *Dent. Mater.* 28, 113–122.
- Franchin, G., Colombo, P., 2015. Porous geopolymer components through inverse replica of 3D printed sacrificial templates. *J. Ceram. Sci. Technol.* 6, 105–112.
- Franchin, G., Maden, H.S., Wahl, L., *et al.*, 2018. Optimization and characterization of preceramic inks for direct ink writing of ceramic matrix composite structures. *Materials* 11, 515.
- Franchin, G., Wahl, L., Colombo, P., 2017a. Direct ink writing of ceramic matrix composite structures. *J. Am. Ceram. Soc.* 100, 4397–4401.
- Franchin, G., Scanferla, P., Zeffiro, L., *et al.*, 2017b. Direct ink writing of geopolymeric inks. *J. Eur. Ceram. Soc.* 37, 2481–2489.

- Franco, J., Hunger, P., Launey, M.E., Tomsia, A.P., Saiz, E., 2010. Direct-write assembly of calcium phosphate scaffolds using a water-based hydrogel. *Acta Biomater.* 6, 218–228.
- Fu, Q., Saiz, E., Tomsia, A.P., 2011. Bioinspired strong and highly porous glass scaffolds. *Adv. Funct. Mater.* 21, 1058–1063.
- Fu, Z., Schlier, L., Travitzky, N., Greil, P., 2013. Three-dimensional printing of SiSiC lattice truss structures. *Mater. Sci. Eng. A* 560, 851–856.
- Gal-Or, E., Gershoni, Y., Scotti, G., *et al.*, 2019. Chemical analysis using 3D printed glass microfluidics. *Anal. Methods* 11, 1802–1810.
- Gao, W., Zhang, Y., Ramanujan, D., *et al.*, 2015. The status, challenges, and future of additive manufacturing in engineering. *Comput. -Aided Des.* 69, 65–89.
- Genet, M., Houmard, M., Eslava, S., Saiz, E., Tomsia, A.P., 2013. A two-scale Weibull approach to the failure of porous ceramic structures made by robocasting: Possibilities and limits. *J. Eur. Ceram. Soc.* 33, 679–688.
- Gomes, C.M., Oliveira, A.P.N., Hotza, D., Travitzky, N., Greil, P., 2008. LZSA glass-ceramic laminates: Fabrication and mechanical properties. *J. Mater. Process. Technol.* 206, 194–201.
- Gomes, C., Travitzky, N., Greil, P., *et al.*, 2011. Laminated object manufacturing of LZSA glass-ceramics. *Rapid Prototyp. J.* 17, 424–428.
- Gorjan, L., Lusiola, T., Scharf, D., Clemens, F., 2017. Kinetics and equilibrium of eco-debinding of PZT ceramics shaped by thermoplastic extrusion. *J. Eur. Ceram. Soc.* 37, 5273–5280.
- Gorjan, L., Tonello, R., Sebastian, T., Colombo, P., Clemens, F., 2019. Fused deposition modeling of mullite structures from a preceramic polymer and γ -alumina. *J. Eur. Ceram. Soc.* 39, 2463–2471.
- Grida, I., Evans, J.R., 2003. Extrusion freeforming of ceramics through fine nozzles. *J. Eur. Ceram. Soc.* 23, 629–635.
- Guo, D., Li, L., Cai, K., Gui, Z., Nan, C., 2004. Rapid prototyping of piezoelectric ceramics via selective laser sintering and gelcasting. *J. Am. Ceram. Soc.* 87, 17–22.
- Homa, J., Schwentenwein, M., 2014. A Novel Additive Manufacturing Technology for High-Performance Ceramics. In: Ohji, T., Singh, M., Mathur, S. (Eds.), *Advanced Processing and Manufacturing Technologies for Nanostructured and Multifunctional Materials*. Ceramic Engineering and Science Proceedings 35. Hoboken: John Wiley & Sons, Inc, pp. 33–40.
- Huson, D., Hoskins, S., 2014. 3D printed ceramics for tableware, artists/designers and specialist applications. *Key Eng. Mater.* 608, 351–357.
- Inamura, C., Stern, M., Lizardo, D., Houk, P., Oxman, N., 2018. Additive manufacturing of transparent glass structures. *3D Print. Addit. Manuf.* 5, 269–283.
- ISO/ASTM 52900, 2015. Additive manufacturing – General Principles – Terminology, International Organization for Standardization, Geneva, Switzerland (or, prEN ISO/ASTM 52900:2018, draft status).
- Jafari, M.A., Han, W., Mohammadi, F., *et al.*, 2000. A novel system for fused deposition of advanced multiple ceramics. *Rapid Prototyp. J.* 6, 161–175.
- Juste, E., Petit, F., Lardot, V., Cambier, F., 2014. Shaping of ceramic parts by selective laser melting of powder bed. *J. Mater. Res.* 29, 2086–2094.
- Klammert, U., Reuther, T., Jahn, C., *et al.*, 2009. Cytocompatibility of brushite and monetite cell culture scaffolds made by three-dimensional powder printing. *Acta Biomater.* 5, 727–734.
- Klein, J., Stern, M., Franchin, G., *et al.*, 2015. Additive manufacturing of optically transparent glass. *3D Print. Addit. Manuf.* 2, 92–105.
- Kolan, K.C.R., Leu, M.C., Hilmas, G.E., Brown, R.F., Velez, M., 2011. Fabrication of 13-93 bioactive glass scaffolds for bone tissue engineering using indirect selective laser sintering. *Biofabrication* 3.025004.
- Kotz, F., Arnold, K., Bauer, W., *et al.*, 2017. Three-dimensional printing of transparent fused silica glass. *Nature* 544, 337–339.
- Kruth, J.-P., Levy, G., Klocke, F., Childs, T.H.C., 2007. Consolidation phenomena in laser and powder-bed based layered manufacturing. *CIRP Ann. -Manuf. Technol.* 56, 730–759.
- Lewis, J.A., Smay, J.E., Stuecker, J., Cesarano, J., 2006. Direct ink writing of three-dimensional ceramic structures. *J. Am. Ceram. Soc.* 89, 3599–3609.
- Liu, F.-H., Shen, Y.-K., Lee, J.-L., 2012. Selective laser sintering of a hydroxyapatite-silica scaffold on cultured MG63 osteoblasts in vitro. *Int. J. Precis. Eng. Manuf.* 13, 439–444.
- Liu, S., Ye, F., Liu, L., Liu, Q., 2015. Feasibility of preparing of silicon nitride ceramics components by aqueous tape casting in combination with laminated object manufacturing. *Mater. Des.* 66 (Part A), 331–335.
- Löschau, W., Lenk, R., Scharek, S., *et al.*, 2000. Prototyping of complex-shaped parts and tools of Si/SiC-ceramics by selective laser sintering. *Ind. Ceram.* 20, 95–96.
- Mei, H., Huang, W., Liu, H., Pan, L., Cheng, L., 2019. 3D printed carbon-ceramic structures for enhancing photocatalytic properties. *Ceram. Int.* 45, 15223–15229.
- Melcher, R., Martins, S., Travitzky, N., Greil, P., 2006. Fabrication of Al_2O_3 -based composites by indirect 3D-printing. *Mater. Lett.* 60, 572–575.
- Minas, C., Carnelli, D., Tervoort, E., Studart, A., 2016. 3D printing of emulsions and foams into hierarchical porous ceramics. *Adv. Mater.* 28, 9993–9999.
- Miranda, P., Pajares, A., Saiz, E., Tomsia, A.P., Guiberteau, F., 2007. Fracture modes under uniaxial compression in hydroxyapatite scaffolds fabricated by robocasting. *J. Biomed. Mater. Res. A* 83A, 646–655.
- Miranda, P., Pajares, A., Saiz, E., Tomsia, A.P., Guiberteau, F., 2008. Mechanical properties of calcium phosphate scaffolds fabricated by robocasting. *J. Biomed. Mater. Res. A* 85A, 218–227.
- Moon, J., Caballero, A.C., Hozer, L., Chiang, Y.M., Cima, M.J., 2001. Fabrication of functionally graded reaction infiltrated SiC–Si composite by three-dimensional printing (3DPTM) process. *Mater. Sci. Eng. A* 298, 110–119.
- Mühler, T., Gomes, C.M., Heinrich, J., Günster, J., 2015. Slurry-based additive manufacturing of ceramics. *Int. J. Appl. Ceram. Technol.* 12, 18–25.
- Nguyen, T.D., Meyers, C., Yee, T.D., *et al.*, 2017. 3D-printed transparent glass. *Adv. Mater.* 1701181.
- Ortona, A., D'Angelo, C., Gianella, S., Gaia, D., 2012. Cellular ceramics produced by rapid prototyping and replication. *Mater. Lett.* 80, 95–98.
- Özkol, E., Ebert, J., Telle, R., 2010. An experimental analysis of the influence of the ink properties on the drop formation for direct thermal inkjet printing of high solid content aqueous 3Y-TZP suspensions. *J. Eur. Ceram. Soc.* 30, 1669–1678.
- Park, S.A., Lee, S.H., Kim, W.D., 2011. Fabrication of porous polycaprolactone/hydroxyapatite (PCL/HA) blend scaffolds using a 3D plotting system for bone tissue engineering. *Bioprocess Biosyst. Eng.* 34, 505–513.
- Penas, O., Zenati, R., Dubois, J., Fantozzi, G., 2001. Processing, microstructure, mechanical properties of Si_3N_4 obtained by slip casting and pressureless sintering. *Ceram. Int.* 27, 591–596.
- Regenfuss, P., Streek, A., Hartwig, L., *et al.*, 2007. Principles of laser micro sintering. *Rapid Prototyp. J.* 13, 204–212.
- Sachs, E.M., Haggerty, J.S., Cima, M.J., Williams, P.A., 1993. US Patent 5,204,055.
- Saiz, E., Fu, Q., Tomsia, A.P., 2011. Direct ink writing of highly porous and strong glass scaffolds for load-bearing bone defects repair and regeneration. *Acta Biomater.* 7, 3547–3554.
- Santoliquido, O., Colombo, P., Ortona, A., 2019. Additive manufacturing of ceramic components by digital light processing: A comparison between the “bottom-up” and the “top-down” approaches. *J. Eur. Ceram. Soc.* 39, 2140–2148.
- Scheithauer, U., Bergner, A., Schwarzer, E., Richter, H.-J., Moritz, T., 2014. Studies on thermoplastic 3D printing of steel–zirconia composites. *J. Mater. Res.* 29, 1931–1940.
- Schlördt, T., Schwanke, S., Keppner, F., *et al.*, 2013. Robocasting of alumina hollow filament lattice structures. *J. Eur. Ceram. Soc.* 33, 3243–3248.
- Singh, M., Halbig, M.C., Grady, J.E., 2015. Additive manufacturing of light weight ceramic matrix composites for gas turbine engine applications. In: Ohji, T., Singh, M., Halbig, M. (Eds.), *Advanced Processing and Manufacturing Technologies for Nanostructured and Multifunctional Materials II: A Collection of Papers Presented at the 39th International Conference on Advanced Ceramics and Composites 2015*. Hoboken, NJ: John Wiley & Sons, Inc.
- Smay, J.E., Cesarano III, J., Tuttle, B.A., Lewis, J.A., 2002. Piezoelectric properties of 3-X periodic Pb (ZrTi_{1-x}) O_3 -polymer composites. *J. Appl. Phys.* 92, 6119–6127.
- Smay, J.E., Cesarano III, J., Tuttle, B.A., Lewis, J.A., 2004. Directed colloidal assembly of linear and annular lead zirconate titanate arrays. *J. Am. Ceram. Soc.* 82, 293–295.
- Smay, J.E., Nadkarni, S.S., Xu, J., 2007. Direct writing of dielectric ceramics and base metal electrodes. *Int. J. Appl. Ceram. Technol.* 4, 47–52.

- Stuecker, J.N., Cesarano III, J., Hirschfeld, D.A., 2003. Control of the viscous behavior of highly concentrated mullite suspensions for robocasting. *J. Mater. Process. Technol.* 142, 318–325.
- Sun, W., Dcosta, D.J., Lin, F., El-Raghy, T., 2003. Freeform fabrication of Ti_3SiC_2 powder-based structures: Part I – Integrated fabrication process. *J. Mater. Process. Technol.* 127, 343–351.
- Suwanprateeb, J., Sanngam, R., Suvannapruk, W., Panyathanmaporn, T., 2009. Mechanical and in vitro performance of apatite–wollastonite glass ceramic reinforced hydroxyapatite composite fabricated by 3D-printing. *J. Mater. Sci. Mater. Med.* 20, 1281–1289.
- Teng, W.D., Edirisinghe, M.J., 1998. Development of ceramic inks for direct continuous jet printing. *J. Am. Ceram. Soc.* 81, 1033–1036.
- Tomov, R.I., Krauz, M., Jewulski, J., *et al.*, 2010. Direct ceramic inkjet printing of yttria-stabilized zirconia electrolyte layers for anode-supported solid oxide fuel cells. *J. Pow. Sour.* 195, 7160–7167.
- Wang, S., Jia, D., Yang, Z., *et al.*, 2013. Effect of BN content on microstructures, mechanical and dielectric properties of porous $\text{BN}/\text{Si}_3\text{N}_4$ composite ceramics prepared by gel casting. *Ceram. Int.* 39, 4231–4237.
- Wätjen, A.M., Ginter, P., Kramer, M., Telle, R., 2014. Novel prospects and possibilities in additive manufacturing of ceramics by means of direct inkjet printing. *Adv. Mech. Eng.* e141346.
- Wilkes, J., Hagedorn, Y.-C., Meiners, W., Wissenbach, K., 2013. Additive manufacturing of $\text{ZrO}_2\text{-Al}_2\text{O}_3$ ceramic components by selective laser melting. *Rapid Prototyp. J.* 19, 51–57.
- Woesz, A., Rumpel, M., Stampfl, J., *et al.*, 2005. Towards bone replacement materials from calcium phosphates via rapid prototyping and ceramic gelcasting. *Mater. Sci. Eng. C* 25, 181–186.
- Yin, H., Kirihaara, S., Miyamoto, Y., 2004. Fabrication of ceramic photonic crystals with diamond structure for microwave applications. *J. Am. Ceram. Soc.* 87, 598–601.
- Yoo, J., Cima, M.J., Khanuja, S., Sachs, E.M., 1993. Structural ceramic components by 3D printing. In: *Proceedings of the Solid Freeform Fabrication Symposium. DTIC Document*. pp. 40–50.
- Zhang, W., Melcher, R., Travitzky, N., Bordia, R.K., Greil, P., 2009. Three-dimensional printing of complex-shaped alumina/glass composites. *Adv. Eng. Mater.* 11, 1039–1043.
- Zhou, W., Li, D., Wang, H., 2010. A novel aqueous ceramic suspension for ceramic stereolithography. *Rapid Prototyp. J.* 16, 29–35.
- Zocca, A., Gomes, C.M., Mühlner, T., Günster, J., 2014. Powder-bed stabilization for powder-based additive manufacturing. *Adv. Mech. Eng.* 6, 491581. doi:10.1155/2014/491581.
- Zocca, A., Lima, P., Diener, S., Katsikis, N., Günster, J., 2019. Additive manufacturing of SiSiC by layerwise slurry deposition and binder jetting (LSD-print). *J. Eur. Ceram. Soc.* 39, 3527–3533.

Relevant Websites

- <https://www.3dceram.com>
3DCERAM ceramic 3D printing.
- <https://www.admateceurope.com>
Admatec.
- <https://www.ceradrop.com>
Ceradrop.
- <https://www.euroceram.org>
Euroceram.
- <https://www.lithoz.com>
Lithoz: 3D-Druck für Keramik.
- <http://www.3ders.org/articles/20150622-micron-3dp-announces-breakthrough-in-3d-printing-glass-materials.html>
Micron 3DP announces breakthrough in 3D printing glass materials.
- <https://www.robocasting.com/>
Robocasting Enterprises.
- <https://www.xjet3d.com>
Xjet.

Green Machining of Ceramics

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Introduction

Although technical ceramics exhibit superior properties (chemical stability, inertness, high wear resistance, strength, refractoriness...) they are very challenging materials for machining by conventional methods such as milling, grinding or turning due to their brittle nature and high hardness. As a consequence machining of ceramics is very expensive and according to [Marinescu et al. \(2007\)](#), it may represent up to 80% of the overall manufacturing expenses. Dense machining is very often a barrier hindering further industrial application.

To overcome these limitations, ceramic parts may also be effectively machined before the final sintering stage either in the “pre-sintered” state or even in the green “non-sintered” compact state. In the pre-sintered stage, conventional machining methods can be applied (milling, drilling, turning) and high material removal rate ($10,000 \text{ mm}^3 \text{ min}^{-1}$) can be obtained (see “Relevant Websites section”). However shrinkage and warping of the ceramic part occurring during the sintering prevents achieving tight tolerances and smooth surface finish. Despite those limitations, this approach is intensively used in the industry as it allows a significant reduction of the machining costs in comparison with parts milled in the dense state.

Machining in the green state is not yet widely studied and documented in the literature. Although it is much more challenging than machining in the pre-sintered stage it also presents several advantages:

- As there is no pre-sintering required, machining in the green state is highly beneficial both from an economical point of view and for environmental issues.
- In the compact state, the blank (i.e., the block to be machined) can be recycled more easily than a pre-sintered body.
- As the green body is basically a collection of grains bound together by an organic phase, its hardness and strength are lower than a pre-sintered ceramic and much less efforts are required to machine it. Potentially, the material removal rate in the green state can be higher than in any other states with less tool wear.
- Finally, non-contact machining operations like laser milling can also be easily used to shape green bodies. This is highly suitable and efficient to create fine features without breakage issues.

Currently, green machining is not yet widely applied in the industry as there is a huge lack of documentation and protocol guidelines. Experimental settings and conditions still remain empirical and/or proprietary information. The main driving force for machining ceramics in the green state is short production runs for which injection molding (CIM) expenses exceeds the cost of green machining. Tooling costs in CIM are so high that it cannot be competitive for producing small batches of parts (most notably when the parts exhibit complicated features like holes, threads...). For those specific cases, green machining is in competition with additive manufacturing (especially SLA – stereolithography). However, in its current state of development, SLA is only compatible to a limited number of ceramics (e.g., silicon carbide is not yet accessible to SLA) and the reliability is not yet at an acceptable level (cracks and other defects tend to be formed during the debinding stage of SLA parts).

Mechanical Machining – The Green Ceramic Cutting Process

In machining, material is removed from a workpiece thanks to the relative motion between this workpiece and a cutting edge. In metals, the cutting process generates a significant heat that causes plastic deformation, chips and curl of the material. In a green ceramic however, the behavior is completely different. The material is removed by a fracturing/crushing process instead than plastic deformation. Small debris taking the form of fine chips of dust are formed but no curl occurs. As there is no need to plastically deform the material, the relative speed between the machining tool and the workpiece can be reduced which also helps increasing the tool lifetime.

In green machining, the crushing effect is not significantly affected by small feeds and depth of cut. Light feed should even be avoided to prevent significant tool wear to occur and inefficient machining conditions. Contrarily to expectation, increasing feed not only increases the material removal rate but also expands the tool life. In terms of settings, the rule is to set the cutting depth to one-third of the tool diameter. [Larson \(1991\)](#) showed that as increasing amount of material is removed with each pass, a lower milling speed should be used to prevent overheating and to allow more time for the removal of the debris.

Formed residues are small agglomeration of grains with size ranging from a few micrometers to several dozens of micrometers (depending from the grain size). To ensure operator safety a dust collection system must be used. Screening of the dust using filters to catch different particle size (down to the nm range) is suitable such that air, free from machining dust, can be rejected.

As any green body contains some organic phases (most notably a binder) one of the main issues in green machining is excessive grains agglomeration in between the cutting edges of the tool. Sometimes grains and debris are not removed fast enough and tend to accumulate on the tool. Cutting becomes less efficient and the level of pressure on the workpiece increases which may

result in cracks or even breakage of the part. To prevent this happening, compressed air blown directly on the tool head helps removing the ceramic particles while maintaining constant fresh cutting edges.

Unlike metals, fixture of green bodies in machining machine can be very tricky. As the material remains very brittle and easily crushable some specific fixtures and chucks have to be used. It has been demonstrated that vacuum works nicely for normal clamping while for lateral clamping a mechanical stop is preferable. Whenever mechanical fixture devices are preferred or necessary, they should be cushioned with a soft material (tape, hard foam...) to prevent breaking during tightening. Too soft materials should be avoided as they will result in deleterious vibrations. Some authors have reported the benefit in using emery cloth wrapped around the ceramic body to prevent slippage.

Mechanical Machining – Green Ceramic Characteristics

Using green machining very complex shapes can be produced more easily than using ceramics in the dense state or pre-sintered ones. However, green bodies of technical ceramics are usually very brittle. Increasing the mechanical strength is therefore a prerequisite for machining. Consequently, the binder system is of primary importance Sheppard (1999). Most common binders are organic compounds like polyethylene glycol (PEG), polyvinyl alcohol (PVA), acrylics or methyl cellulose or even some preceramic polymers. They typically amount to a few weight percent. The typical strength of green bodies does not exceed a few MPa which is still very low. For a green body to be machined a gain of strength of just 1 MPa may be considered as a modest one but it can make all the difference. Usually, green bodies have to be stored in controlled room with a stable temperature and humidity level. Certain aqueous binders are very prone to moisture absorption from air which may affect the dimensions of the green body as well as its mechanical resistance.

Usually, green bodies for machining are obtained through pressing (uniaxial and/or isostatic). There is unavoidably some variation in green density both locally and from part to part. These variations may affect the quality of the machined parts and introduce as well some variability in shrinkage (or warping) during sintering. Isostatic pressing helps reducing significantly the gradient densities within the green body which allows parts to retain their shape during sintering. For most purposes however, the parts obtained after sintering are considered as “near net shape” as the dimensional accuracy is around 20 μm at best (green machining is similar to bisque or pre-sintered machining to that respect). Of course, green machining is not restricted to pressed samples only and it can be used as well in combination with other shaping technologies. Some recent works have considered gel casting instead of pressing for shaping the blank.

Bukvic *et al.* (2012) has shown that there is a direct relation between the machined surface quality and the mechanical strength after sintering (with variations up to 10% of the nominal values). While it may seem as a major drawback, it is always possible to find machining parameters giving smooth surface roughness even in the green state.

Mechanical Machining – Parameters

Different machining procedures exist. Grinding, drilling, turning or milling (to name the principal ones) have all been successfully applied to green bodies. Green machining also took advantage of computer numerically controlled (CNC) machine tools which has further increased the interest of the approach.

For endmilling, drilling or profiling it is usually recommended to use square endmills with a small radius. Carbide tools should be preferred over diamond ones as they can more easily break upon entry especially at high feed rates. If settings are not fine, diamond coatings can also suffer from excessive heating and oxidize. HSS tools durability is usually not satisfactory. For roughing a 2-flute endmills is usually a good option as it reduces the risk of tool breakage from matter packing. For low feed rates and finishing operations a four flutes can be used with more security. The Tables 1 and 2 hereafter show recommended parameters for machining (those are just starting values which have to be fine-tuned depending on the green body characteristics and machine setup).

In terms of tools, not all grades of carbides are satisfactory and very tough grades of carbides should be preferred. K-type grade of cemented carbide seem to offer the best performance both in terms of machining quality and tool durability. They are also more cost effective than diamond tools. Besides being more expensive, diamond cutters can also be much trickier to use (mostly

Table 1 Parameters for drilling green ceramic

<i>Drill diameter (mm)</i>	<i>Peck size (mm)</i>	<i>Feed rate (mm rev⁻¹)</i>
1.0 – 5.0	.25 – 1.25	.025 – .075
5.0 – 6.0	1.25 – 1.5	.025 – .1
6.0 – 8.0	1.5 – 2.0	.025 – .13
8.0 – 10.0	2.0 – 2.5	.025 – .15
10.0 – 12.0	2.5 – 3.0	.025 – .2

Source: Yigit, R., Celik, E., 2014. General tool conditions for green machining. Journal of Science and Technology 2 (1).

Table 2 Parameters for milling green ceramic

	Cutting speed (mm min^{-1})	Feed rate (mm tooth^{-1})
General settings	500–1000	.05–.015

Source: Yigit, R., Celik, E., 2014. General tool conditions for green machining. *Journal of Science and Technology* 2 (1).

because of oxidation issues). However, some authors have reported better machined surfaces and a significant increase in tool life. CBN (cubic boron nitride) cutters exhibit similar performances to diamond ones. Based on the existing knowledge, it seems that specific tools for green machining should be considered: coatings capable of withstanding higher temperatures and providing some lubricating effect should help increasing the reliability and effectiveness of green machining.

Other Approaches for Machining: Laser Milling

To shape a green body conventional mechanical machining is not mandatory in all cases. Other alternatives exist that might be more efficient options to produce certain parts. Since green bodies are brittle, fine features or details still remain challenging to reproduce. As a non-contact technology, laser machining is a clever approach to produce parts having a very high level of details and/or for difficult to machine parts – Samant and Dahotre (2009). The non-contact operation ensures that almost no stress is exerted on the workpiece during machining. Furthermore, thanks to the very small spot sizes of focused laser (typically between 20 μm and 80 μm – e.g., much finer than any existing mechanical endmills) details down to a few dozens of micrometers (or less) can be obtained without part breakage, something that is obviously not possible using mechanical milling.

Laser machining is mostly for cutting or milling. Cutting of green ceramic tapes is commonly used in the electronic industry. Laser used for that purpose can operate in continuous or pulsed mode. As the ceramic is unfired, low average powers are required. Continuous lasers tend to produce a significant heat affected zone – HAZ in the green tape which may affect the cutting quality (ceramic particles may sinter or even melt in the HAZ). For cutting as well as milling, pulsed laser sources are therefore preferred. Matter is then removed not through melting but through ablation which requires high peak power ($> 10 \text{ kW}$) and short pulse duration (from μs down to fs). Nowak *et al.* (2008) explained that in a green body the laser energy is primarily absorbed by the ceramic grains. The surrounding binder (as well as any other organic phase) is then rapidly heated up and vaporizes. Upon vaporization the green body is locally disrupted and the ceramic grains are ejected. A crater is formed. As the laser is continuously moved on the surface of the green body (with speeds up to 3 m s^{-1}), a groove is generated with a depth as high as 0.1 mm in one single pass. Cutting is obtained by repeating the same pattern layer after layer until the laser goes through the whole thickness. Milling is obtained by changing the pattern for each removed layer in order to reproduce a desired geometry.

Laser milling in the green state is not yet widely used. But thanks to a continuous decrease of the prices of laser sources the approach is gaining more and more attention. Usually sources operating in the near IR at a wavelength of 1.06 μm are considered (e.g., Nd:YAG, Nd:YVO₄, fiber lasers). CO₂ lasers are less used for machining because of the poorer resolution they offer (as a consequence of their wavelength, e.g., 10.6 μm) and their trend to enhance the HAZ. However using near-IR lasers is not free from issues. Some ceramics are poorly absorbing in the near-IR region. Alumina or zirconia, for instance have an absorptivity not exceeding 0.2 at 1.06 μm . Although it is still possible to machine those ceramics in the green state, higher powers are required to compensate the poor absorptivity. The process becomes less efficient and the machining quality is often degraded as the HAZ extends further. To improve absorptivity of the green body, a small amount of a specific additive highly absorbing at the laser wavelength can be mixed with the ceramic grains. At 1.06 μm , black carbon or graphite (under different forms: grains, colloids, fibers) are usually selected as their intrinsic absorptivity is very high (> 0.9). Obviously adding of few percent of graphite or black carbon in the green body is not only valuable to enhance the absorptivity (Juste *et al.*, 2014), it also helps reducing the undesirable thermal effects occurring during ablation. In absence of carbon when laser ablation occurs, ceramic grains are ejected from the green body but locally it heats up and local sintering may occur. Whenever carbon is dispersed in the ceramic green body it creates strong diffusion barriers which somehow inhibit sintering. The laser machining becomes almost non-thermal (or cold) even with ns pulsed lasers.

Trends: Hybridization

The combination of conventional mechanical machining with laser machining is a recent trend in manufacturing. The idea is to synergistically combine in one single setup the two approaches and take advantage of both. Usually two discrete sequential processes are employed to achieve the final part specifications. Some recent developments have shown that mechanical milling and laser milling combines very well together. A very promising approach is the combination of mechanical milling for roughing and laser milling to bring fine features to the part and/or to finish it. For metals (but same arguments hold for ceramics as well) hybridization appears relevant in many different ways. Firstly, as one single holistic



Fig. 1 Examples of laser milled Zirconia parts in the green state (the images show the parts after sintering without post-treatment). Courtesy OPTEC – Available at: <https://optec-laser-systems.com/>.

machine is used instead of two, the investment need is dramatically reduced. Furthermore, there is no more any part re-positioning or referencing issues as it is when using different machines. A second advantage is a significant reduction of the machining time and a decrease of breakage risks. Again mechanical milling can rough the parts easily at locations where there is no risk of rupture while the laser can mill the finest features for which there are significant risks of failure. Some ceramics parts have been shown recently which were obtained using this combination of milling approaches (OPTEC – see “Relevant Websites section”). It is obvious that hybridization can capture and combine the strengths of both approaches in a very efficient way (Fig. 1).

Green machining is also promising when it is combined with additive manufacturing (AM). Material extrusion AM (like robocasting or fused deposition modeling of ceramics) is still suffering from the poor resolution of the printed parts. Whenever combined with mechanical machining better geometric dimensioning and tolerances can be achieved as well as improved surface finish and mechanical properties. Such an approach has been pushed forward by Weiss *et al.* (1997). The authors report a hybrid system called shape deposition manufacturing which effectively combines additives and subtractive manufacturing. The principle was demonstrated on polymers but ceramics (hydroxyapatite) as well. Thanks to the hybridization the error in fabricated parts can be reduced well below 1% while it is incredibly higher (> 20%) for parts obtained using deposition only.

Appendix A Supplementary Material

Supplementary data associated with this chapter can be found in the online version at [doi:10.1016/B978-0-12-803581-8.11731-X](https://doi.org/10.1016/B978-0-12-803581-8.11731-X).

References

- Bukvic, G., Fiocchi, A.A., Sanchez, L.E.A., *et al.*, 2012. Effect of green machining on distortion and surface finishing in advanced ceramic. Proceedings of NAMRI/SME 40, 175–183.
- Juste, E., Petit, F., Lardot, V., Cambier, F., 2014. Shaping of ceramic parts by selective laser melting of powder bed. Journal of Materials Research 29, 2086–2094.
- Larson, D., 1991. Green machining. In Engineered Materials Handbook 4. Ceramics and Glasses. Materials Park, OH: ASM International, pp. 181–185.
- Marinescu, I.D., Hitchner, M., Uhlman, E., Inasaki, I., 2007. Handbook of Machining With Grinding Wheels. USA: CRC Press.
- Nowak, K.M., Baker, H.J., Hall, D.R., 2008. A model for “cold” laser ablation of green state ceramic materials. Applied Physics A 91 (2), 341–348.
- Samant, N., Dahotre, N.B., 2009. Laser machining of structural ceramics – A review. Journal of the European Ceramic Society 29 (6), 969–993.
- Sheppard, L.M., 1999. Green machining. Ceramic Industry 149 (6), 65–69.
- Weiss, L.E., Merz, R., Prinz, F.B., *et al.*, 1997. Shape deposition manufacturing of heterogeneous structures. Journal of Manufacturing Systems 16 (4), 239–248.

Relevant Websites

- http://www.substech.com/dokuwiki/doku.php?id=machining_of_ceramics
Machining of ceramics [SubsTech].
- <https://optec-laser-systems.com/>
Optec Laser Systems.

Screen Printing

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Short History

Screen printing is a method for depositing a patterned layer onto various substrates by pressing a suspension, called the screen-printing paste, through a mesh onto the substrate. The earliest forms of screen printing began in China at the end of the first millennium, and consisted of weaving human hair across a wooden frame as a mesh, with leaves being attached to the hair as a stencil. Later, the process was adapted, by replacing the hair with a piece of silk mounted between two pieces of strong, waterproof paper with some openings cut into them. The paint flowed through the silk, leaving a motive on the substrate (made of ceramic or silk), identical to the openings cut in the paper. This technique, silk-screen printing, arrived in Europe in the late 18th century, but only saw widespread use in the 20th century thanks to the greater availability of silk from Asia. The first screen-printing machine was patented in 1907, and photo-imaged stencils, developed in 1910, led to greatly improved printing quality and control. Initially, silk-screen printing was used to decorate luxury wallpapers and later to print multicolor posters and textiles (Sheng, 1999). In the late 1930s screen printing was, for the first time, applied in the electronics industry as a method for manufacturing capacitor electrodes and later for the processing of hybrid circuit resistor-capacitor networks. Later, the electronics industry rapidly expanded screen printing as a method for packing electronic components in response to the need for the efficient, affordable, large-scale production of thick films. By the 1960s screen printing had become the dominant technology for fabricating printed-circuit boards, which are the basis for almost all consumer electronics (Cote, 1974).

Today, screen printing is integral to the fine arts and the textile industry for decorating fabrics as well as dominating the electronics industry as a mature technology for producing conductive patterns for electronic components, such as touch panels and solar cells, and for various thick-film electronic components, such as sensors and fuel cells.

Screen-Printing Process

Screen printing can be used to reproduce uniform layers or patterns on a substrate. In the conventional screen-printing process the paste is placed on the mesh of the screen mask and the flat substrate is placed under the screen mask. The substrate is held in the holder by a vacuum hold-down system during the printing. A small gap of 0.5–1 mm is kept between the mesh and the substrate. To deposit the pattern onto the substrate, the squeegee, which consists of a polyurethane rubber in a metal support, presses the paste through the open areas of the otherwise filled mesh with a certain speed and force onto the substrate, either manually or automatically. The typical speed ranges from a few to 300 mm s⁻¹ while force ranges from 10 to 200 N. After the deposition, the screen mask is removed, leaving the paste on the substrate. The general principle of the screen-printing process is shown in Fig. 1.

The thickness per screen-printed layer is from a few micrometers to ~ 30 μm. To achieve a thicker deposit, multiple printing steps are performed, including screen printing and curing of the first layer, followed by an overprint of the paste on the cured first layer and drying and curing of the second layer. This process is repeated until the target thickness is reached. At present, 35-micrometer-wide screen-printed lines are used in commercial printed electronics products, while 20–30-micrometer-wide lines are obtained under laboratory conditions for conventional screen-printing technology (Dorey, 2012; Tepner *et al.*, 2019).

The quality of the printed pattern is affected by a combination of many parameters, including the printing parameters, the properties of the screen-printing paste, the properties of the mesh and the screen mask, and the properties of the substrate, all of which need to be optimized and properly adjusted for each individual application.

Screen Mask

The screen mask defines the pattern of the layer and affects the amount of ink deposited onto the substrate. The screen mask consists of a rigid metal frame onto which a mesh, coated with a photosensitive emulsion, is stretched. The common wire-to-frame angles are 22.5, 30 and 45°. The frame has to be flat and structurally stable to provide a stable mesh support that does not affect the dimensional accuracy. The common frame materials are die-cast or extruded aluminum.

The mesh is a weaved cloth of silk, synthetic fibers or metal threads with well-defined windows that reproduce the pattern to be printed. The pattern to be printed is made by coating the mesh with a photosensitive emulsion, usually a polyvinyl acetate or polyvinyl alcohol, sensitized with a dichromate solution. Then the pattern to be printed is masked with a photo-mask and the mesh is exposed to the ultraviolet (UV) light. The photosensitive emulsion that was not exposed to the UV light is washed out with water and becomes the area for printing. (Haskard and Pitt, 1997). A schematic presentation of a cross-section of a mesh is illustrated in Fig. 2.

The material of the mesh is selected based on the properties of the paste and the target application. The material must be chemically inert with mesh openings that are as equal as possible, suitable mechanical properties and sufficient life time. The most

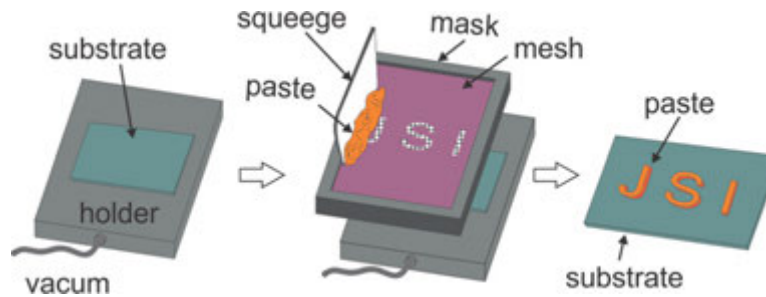


Fig. 1 Schematic presentation of the screen-printing process.

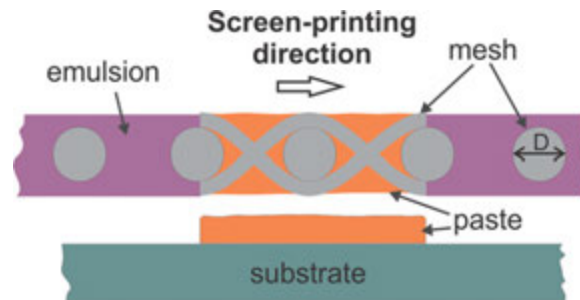


Fig. 2 Scheme of the cross-section of a mesh. D is the diameter of the mesh element.

frequently used materials for the mesh are polyamide (nylon), polyester and stainless steel. The polyamide and polyester are available as monofilaments with diameters from $\sim 30 \mu\text{m}$ to a few hundred μm . Both materials are resilient, strong and elastic, with a high extensibility of 4%–6%. The polyamide and polyester meshes easily deform, which results in a distorted shape and a relatively thin printed pattern. The higher elasticity of polyamide compared to polyester makes it possible to print on uneven substrates, but the tendency to absorb water limits the printing accuracy and consequently polyamide meshes are used less frequently than polyester. A polyester-based mesh is sufficiently flexible for printing on substrates with normal irregularities. It is characterized by a higher tension, better dimensional accuracy and longer life time compared to polyamide. Polyester-based meshes are used for applications where the high resolution of the patterns is not of paramount importance, but production costs need to be limited.

A mesh based on stainless steel is characterized by thin and uniform wires with a diameter from $15 \mu\text{m}$, a consistent mesh thickness with evenly tensioned waves having a very low extension of 0.5% and a high tensile strength, which makes it possible to print patterns with high definition and good printing accuracy. The flattened standard stainless mesh, i.e., the calendared stainless-steel mesh, is thinner, smoother and more uniform than standard mesh and allows the printing of layers with excellent definition. The poor flexibility of the stainless steel means that it is possible to print solely onto flat surfaces, and thus the stainless-steel meshes are used for realizing very-high-resolution patterns on flat and relatively small surfaces (White, 1994). Stainless steel meshes are largely used in electronics.

The factors influencing the characteristics of the printed layers include many parameters, such as the number of mesh elements, i.e., wires or fibers, per inch (mesh count, M), the type and diameter of the mesh element, the tension, the wire-to-frame orientation, the type and thickness of the photosensitive material, the exposure time, the dimensional accuracy of the photomask etc.

For a given mesh count $M [\text{in}^{-1}]$ the smaller diameter of the mesh element is reflected in larger mesh openings, which results in a larger volume of the printed paste. Thus, the mesh count is one of the factors controlling the thickness of the deposit. The percentage of open area (OA) is defined as $[1 - (M \times D)]^2$, where M is the mesh count and $D [\text{in}]$ is the diameter of the mesh element. Knowing the OA, the mesh thickness (MT), and the thickness of the emulsion (ET) we can estimate the wet thickness of the printed pattern $WT = (MT \times OA) + ET$. For most applications the ET is $\sim 13 \mu\text{m}$.

Another important parameter is the size of the mesh openings, which must be at least 3–5 times larger than the size of the particles or agglomerates in the screen-printing paste.

Properties of the Screen-Printing Paste

A stable and homogeneous paste is of great importance to the screen printing of uniform patterns in a reproducible manner. Furthermore, the paste needs to be formulated in such a way that it possesses good printability and provides uniformity and a good aspect ratio of the printed pattern.

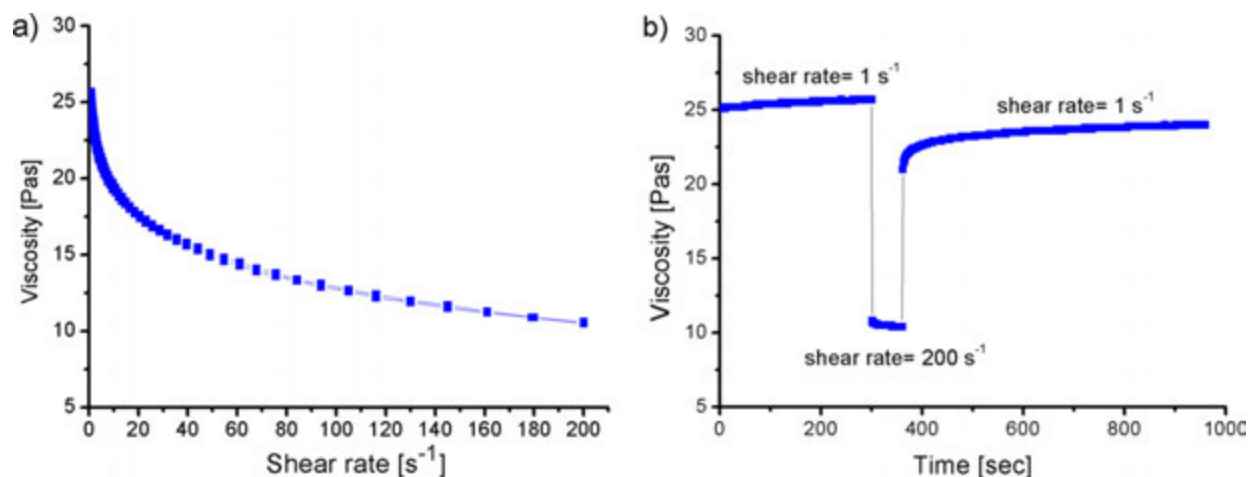


Fig. 3 (a) Viscosity of the ceramic paste (60 wt% of $K_{0.5}Na_{0.5}NbO_3$ and 40 wt% organic phase) as a function of shear rate. (b) Viscosity of the ceramic paste as a function of time and shear rate.

The paste consists of an active material distributed in a certain solvent. In the case that the active material is a powder, the particles sediment over time, if gravity overcomes the Brownian motion. In addition, the particles spontaneously agglomerate as a result of the van der Waals attractive forces. The sedimentation and agglomeration reduce the quality of the printing pattern and need to be avoided. To prevent agglomeration and sedimentation of the particles it is necessary to introduce repulsive forces between the particles, either by charging the particles or by preventing their close approach with steric hindrance.

In electrostatic stabilization, the interactions between the particles and the solvent yield a charge on the surface of the particles as a result of the ionization of the surface groups, ion adsorption, dissolution of the ions or the isomorph substitution of ions. Electrical repulsion is an important type of stabilization for particles dispersed in water-based systems or in liquids with a moderate polarity, like alcohols. In these systems the stability of the particles is controlled by the particle size, ion type, its concentration and the value of the zeta-potential. The zeta-potential of a particle with an absolute value over 25 mV results in a stable suspension.

In steric stabilization the particles are covered by a layer of uncharged polymers, either through the adsorption or through chemical grafting. The polymer layer physically prevents the close approach of the particles. To keep the particles well dispersed in a solvent the polymer must be strongly adsorbed on the particles, must completely cover the surface of the particle, while the concentration of the non-adsorbed polymer must be low. Steric stabilization is appropriate for stabilizing the particles in low-polarity solvents.

Electrosteric stabilization is a combination of the electrostatic and steric stabilization mechanisms. It utilizes a polyelectrolyte with a long-chain polymer and a functional group. The functional group can dissociate in the solvent, thereby creating charged moieties that contribute to the electrostatic effect, while the polymer chains contribute to the steric hindrance. Examples of polyelectrolytes are polyacrylic acid with a carboxylic group that dissociates at high pHs and polyethylene amine with an amino group that dissociates at low pHs.

The printability of the paste is directly related to its rheological properties, in particular to the shear-rate-dependent viscosity and thixotropy. During the printing process the paste is mechanically forced through the mesh. The resistance of the paste to flow is determined by means of viscosity, defined as the ratio of the shear stress (τ) to the shear rate (dy/dt). A high viscosity means a high resistance to flow and vice versa. The viscosity of the paste can be independent of the shear rate (Newtonian behavior), shear-thinning where the viscosity decreases with the shear rate or shear-thickening where the viscosity increases with the shear rate. The composition of the screen-printed paste should be designed to be shear-thinning (**Fig. 3(a)**). The paste is put on the mesh before printing and while it rests, the viscosity of the paste should be high. During printing under the pressure of the squeegee, the viscosity of the paste should decrease to be able to flow through the mesh. However, once the pattern is formed on the substrate, the viscosity of the paste must increase within a short time period to maintain the high-definition shape of the pattern (**Fig. 3(b)**). The printing step takes into the consideration the change in viscosity with the shear rate, while the last step includes the change in viscosity with time, evaluated as the thixotropy. Thixotropy covers the reduction of the structural strength of the paste by a shear process and the structural regeneration of the paste in a subsequent period of rest (*Mezger, 2006*). The shear rate during printing is typically between 100 and 1000 s^{-1} , and pastes with a viscosity up to 150 Pas at 100 s^{-1} are generally suitable for screen printing (*Reed, 1995*).

Chemical Composition of the Screen-Printing Paste

The composition of the paste for screen printing is complex and consists of an active material, solvent and various additives, such as a dispersant and a binder. The solvent serves as a dispersion medium for the active material and a medium to dissolve all the

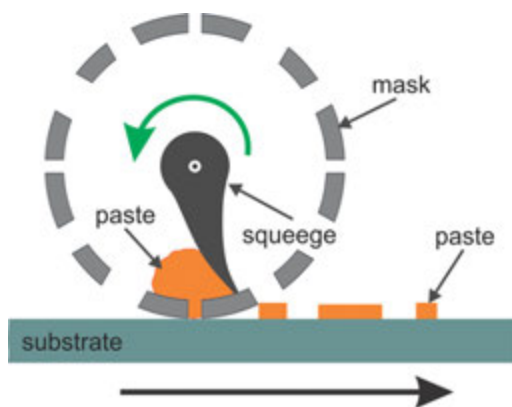


Fig. 4 Rotary screen printing.

other components. Traditionally, organic-solvent-based pastes have been used for screen printing. Terpineol (2-(4-methylcyclohex-3-en-1-yl)propan-2-ol) and texanol (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate) with boiling points of 219 and 254°C, respectively, are commonly used solvents. As the major phase the solvent dictates the properties of the paste, in particular the drying and wetting behaviors. If the drying rate is too fast, defects can form in the printed pattern, while a slow drying rate results in a wet pattern for a long time and consequently difficult handling of the sample, possible phase separation and losing the accurate dimensions of the printed pattern. Wetting is an important parameter that controls the dispersion of the active materials in the solvent and also the behavior of the paste on the substrate. The contact angle θ measures the wetting tendency of a liquid on a solid and is related to the surface energies of solid-vapor γ_{SV} , solid-liquid γ_{SL} and liquid-vapor γ_{LV} : $\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$.

A small contact angle indicates that the liquid spreads on the solid surface, which results in poor definition of the pattern, while large contact angles with well-defined drops of liquid indicate a poor wettability of the solid. The wettability of the solid can be improved by surfactants, whose short-chain molecules consist of hydrophobic (oil-soluble) and hydrophilic (water-soluble) parts. Such molecules have a tendency to adsorb very strongly at the solid-liquid or vapor-liquid interfaces, causing the removal of the hydrophobic part from the aqueous media, while the hydrophilic part remains in the water. They form new surfaces with a lower energy, which improves the wettability (Hunter, 2009). The approach to enhance the wettability of the paste on the substrate is also to clean the substrate with solvent or to treat the substrate with plasma.

Dispersants are added to screen-printed pastes to increase the repulsive forces between the particles and thus to improve the long-term stability of the paste. Dispersants are long-chain molecules that adsorb onto the particles and stabilize the particles using a steric or electrosteric mechanism. The dispersants, such as polyethylene glycol, pentastearic acid oligomer, and alcohol polyoxyethylene phosphoric acid ester, with a content of a few wt%, are frequently used in screen-printing pastes. The dispersant also decreases the viscosity of the paste, which makes it possible to process the paste with a large number of particles, i.e., a higher solids load. The maximum acceptable solids load in the paste is determined by the particle size and the particle size distribution, as well as by the amount of solvent and additives. Typical solids loading ranges from 40 to 60 wt%. The patterns fabricated with a low solids loading have a tendency to crack and delaminate due to the large shrinkage of the pattern during the drying and debinding processes, while high-solids-loading pastes result in a thicker layer with a high surface roughness.

Binders are additives used in screen-printing pastes to improve the particle network in the as-printed pattern and thus provide the strength for handling. The binders consist of polymer molecules that adsorb onto the particles and bridge the particles. They prevent the formation of defects and enable adhesion of the paste to the substrate after drying. The binders can be roughly classified based on the composition of the inorganic and organic binders or based on the structure of the particle and molecular types. In screen-printing pastes the organic, molecular-type binders are the most frequently used, e.g., ethylene cellulose, polyvinyl butyral, polyvinyl acetate, and polymethyl methacrylate. The amount of binder in the paste, commonly added in the amount of 1 wt%, has an impact on the rheological properties of the paste. Too high an amount of the binder can affect the printability and reduces the quality of the printed pattern.

Water-based systems for screen printing have been investigated less intensively, regardless of increasing environmental and health concerns. For example, the screen printing of Ag nanoparticles was realized by dispersing 77 wt% of the particles in a mixture of water and polyethylene using polyacrylic acid as a dispersant (Hyun *et al.*, 2015).

In addition to organic-solvent- and water-based systems, polymerizable pastes can be used for screen printing. The composition of such a paste is complex and contains monomers, polymers, initiator, active material such as particles and additives to enhance certain properties, for example, shelf life, adhesion, and wettability. Most formulations contain a complex mixture of numerous monomers and oligomers to obtain suitable rheological properties of the paste for the printing process. The monomers and oligomers are predominantly acrylates that undergo radical polymerization initiated by reactive species from the initiator. The common initiators generate radicals under thermal or ultraviolet (UV) curing. Thermal curing needs temperatures up to 200°C and curing times up to a few tens of minutes, while UV curing requires exposure of the paste to UV light, commonly in the range of 200–400 nm for less than 1 min (Licari and Swanson, 2011). The advantages of UV curing are the almost instant drying of the

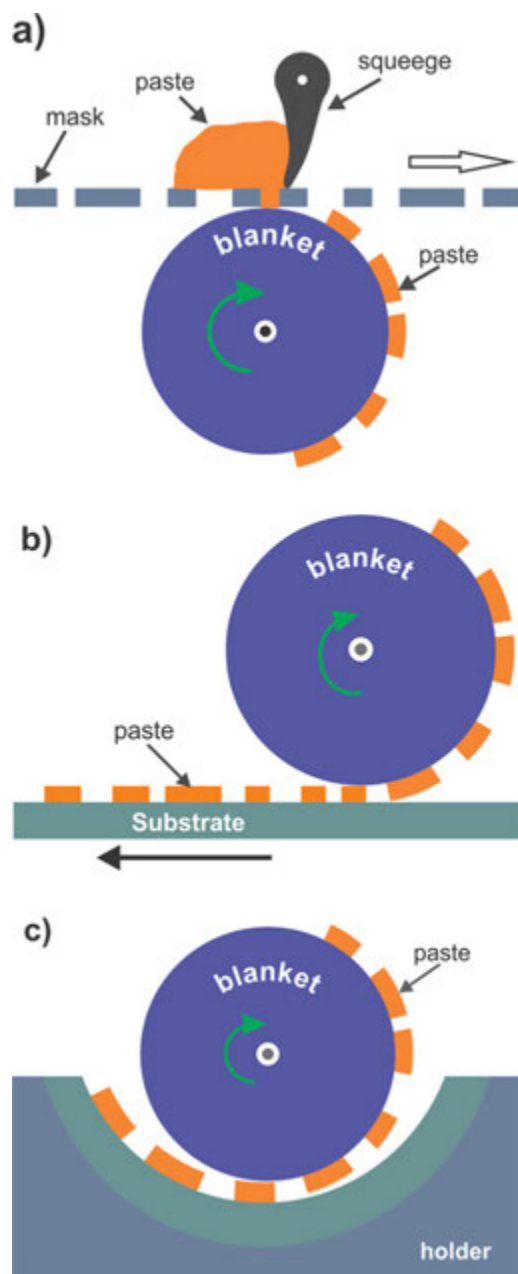


Fig. 5 Schematic presentation of screen-off-set printing. (a) Screen-printing of the paste onto a blanket. Transformation of the paste to the flat (b) and curved surface (c).

paste, solvent-free pastes, adhesion of the paste to various substrates, low costs and a fast production process (Edison, 2010; Hutchinson, 2010).

The typical method for the preparation of the paste includes the weighting of the constituents and their homogenization in a three-roll mill. This mill is composed of three rollers rotating in opposite directions at different speeds relative to each other that squeeze the material through the adjustable gaps and thus mixes, disperses or homogenizes the paste.

Alternative to Traditional Screen Printing

Rotary screen printing uses the same principle as conventional screen printing, but in this case cylindrical-shaped masks are utilized as illustrated in Fig. 4. A paste is located inside the cylinder together with a squeegee at a fixed position. As the screen rotates with the same speed as the substrate the paste is continuously pressed through the mesh by the squeegee forming a pattern onto the substrate.

Rotary screen printing is widely used in the textile industry and recently in electronics for the metallization owing to the fact that it is a continuous process that allows for a high printing speed up to 1700 mm s^{-1} , and thus, reduced costs. However the cylindrical masks are quite costly and difficult to clean (Lorenz *et al.*, 2017).

Screen-offset (SOS) printing and screen-offset curved-surface (SOS-CS) printing are based on screen printing the paste onto a cylindrical silicon blanket (Fig. 5(a)) and the subsequent transformation of the paste onto the substrate. In SOS printing the substrate is flat, while in SOS-CS printing the substrate is curved (Fig. 5(b) and (c)).

In the first step the paste is put on the flat mask, which moves as a consequence of the rotation of the blanket. The squeegee is at a fixed position and forces the paste through the mesh openings onto the blanket. The pattern printed onto the silicon blanket retains its original shape due to the ability of the blanket to absorb the solvent from the paste. In the next step the pattern is transformed from the blanket to the flat or curved substrate.

This technique enables the printing of patterns with thicknesses of $5\text{--}7 \text{ }\mu\text{m}$ and a minimum line width of $\sim 15 \text{ }\mu\text{m}$. The pattern is characterized by a rectangular and well-defined shape. Multiple printings (2 passes) results in thicker patterns of $12\text{--}15 \text{ }\mu\text{m}$ and a similar rectangular shape. This technique is highly applicable in the electronics industry in response to the growing demands for printing low-width, high-thickness patterns on curved surfaces (Nomura *et al.*, 2018).

References

- Cote, R.E., 1974. Facilities, equipment, and manufacturing operations for circuit deposition and testing. In: Harper, C.A. (Ed.), *Handbook of Thick Film Hybrid Microelectronics: A Practical Sourcebook for Designers, Fabricators, and Users*. New York: McGraw-Hill. (pp. 3-1-3-47).
- Dorey, R., 2012. *Ceramic Thick Films for MEMS and Microdevices*. Amsterdam-Boston-Heidelberg/New York Oxford/Paris/San Diego-San Francisco/Singapore/Sydney/Tokyo: Elsevier.
- Edison, S.E., 2010. Formulating UV curable inkjet inks. In: Magdashi, S. (Ed.), *The Chemistry of Inkjet Inks*. New Jersey/London/Singapore/Beijing/Shanghai-Hong Kong/Taipei/Chennai: World Scientific, pp. 161-176.
- Haskard, M., Pitt, K., 1997. *Thick-Film Technology and Applications*. Port Erin: Electrochemical Publications.
- Hunter, R.J., 2009. *Foundation of Colloid Science*, second ed. Oxford-New York: Oxford University Press.
- Hutchinson, I., 2010. Raw materials for UV curable inks. In: Magdashi, S. (Ed.), *The Chemistry of Inkjet Inks*. New Jersey/London/Singapore/Beijing-Shanghai-Hong Kong/Taipei/Chennai: World Scientific, pp. 177-201.
- Hyun, W.J., Lim, S., Ahn, B.Y., *et al.*, 2015. Screen printing of highly loaded silver inks on plastic substrates using silicon stencils. *ACS Applied Materials & Interfaces* 7, 12619-12624.
- Licari, J.J., Swanson, D.W., 2011. *Adhesives Technology for Electronic Applications: Materials, Processing, Reliability*, second ed. Amsterdam/Boston/Heidelberg/London/New York/Oxford/Paris/San Diego-San Francisco/Singapore/Sydney/Tokyo: Elsevier.
- Lorenz, A., Münzer, A., Lehner, M., *et al.*, 2017. High-throughput front and rear side metallization of silicon solar cells using rotary screen printing. *Energy Procedia* 124, 680-690.
- Mezger, T.G., 2006. *The Rheology Handbook*. Hannover: Coating Compendia.
- Nomura, K., Horii, Y., Ushijima, H., Ikeda, H., Nagase, K., 2018. Advanced screen-offset printing for fabricating thick electrodes on the concave surface of cylindrically curved glass. *Microelectronic Engineering* 197, 23-27.
- Reed, J.S., 1995. *Principles of ceramic processing*, second ed. New York/Chichester/Brisbane/Toronto/Singapore: John Wiley & Sons.
- Sheng, A., 1999. Why ancient silk is still gold: Issues in Chinese textile history. *Ars Orientalis* XXIX, 147-168.
- Tepner, S., Wengenmeyr, N., Ney, L., *et al.*, 2019. Improving wall slip behavior of silver pastes on screen emulsions for fine line screen printing. *Solar Energy Materials and Solar Cells* 200, 109969.
- White, N.M., 1994. Thick film technology. In: Prudenziati, M. (Ed.), *Thick Film Sensors*. Amsterdam/Lousanne/New York/Oxford/Shannon/Tokyo: Elsevier, pp. 3-33.

Sintering of Ceramics: An Overview

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Introduction

Ceramics are inorganic, non-metallic materials, produced from minerals or synthetic powders which are formed into a shape and consolidated by a high temperature process to densify and strengthen the material and reduce the porosity. Traditional ceramics including pottery and industrial products such as whitewares, heavy clay-ware, and building materials are formed mainly from natural aluminosilicates and the presence of other minerals including micas and feldspars and some impurities leads to molten viscous phases at the firing temperature. In contrast, advanced ceramics are pure oxides or non-oxides (nitrides, carbides, borides, etc.) or composites of these and include materials that have been developed with designed microstructures for (1) structural applications, making use of their mechanical, tribological or high temperature properties for cutting and drilling tools, bearings, seals, dies, engine components, and coatings on other materials to improve corrosion resistance or thermal stability, and (2) functional applications, such as electronic, dielectric and magnetic components, biomedical implants or devices, filters, membranes, and catalyst supports.

Most ceramic materials are processed from powders which are shaped and then densified during a heat treatment, where the temperature is sufficiently high, in the range $0.5\text{--}0.8 T_m$ (where T_m is the melting point) to allow diffusion of material. To favor the densification, uniaxial or isostatic external pressure can be applied during thermal treatment (Hot Pressing or Hot Isostatic Pressing as opposed to Pressureless Sintering). In addition, an electric current can be used simultaneously with uniaxial pressure (Spark Plasma Sintering) or without pressure (flash sintering) or microwave heating can be applied in order to improve the process. A more recent technique called “Cold Sintering” which uses a transient transport phase, most often liquid, and an applied uniaxial force, to assist in powder compact densification is also briefly described.

Thermal Treatment of Ceramics – Sintering

General Outline

Owing to the generally high melting points of the raw materials involved, the fabrication of ceramic materials commonly includes a heat treatment in which a powder, already formed into a required shape, is converted into a dense solid. The matter transport to reduce the porosity occurs by diffusion of atoms in the vapor phase, in the liquid phase or in the solid state, or by viscous flow of a glassy phase. Most mechanisms are activated thermally because the action of temperature is necessary to overcome the potential barrier between the initial state of higher energy (porous powder compact) and the final state of lower energy (consolidated dense material).

The term sintering is used to refer to all the phenomena occurring during heating, leading to the densification of a powder compact. There are three main types of process for this consolidation to take place and these are dependent on the composition being fired and, in particular, on the extent to which a liquid phase is formed during heat treatment:

- (1) “Solid State Sintering” in the absence of any liquid phase,
- (2) “Liquid Phase Sintering” in the presence of a small volume percent of liquid phase,
- (3) “Viscous Flow Sintering” when the liquid phase volume is high and similar to the porosity of the powder compact.

In all cases, the driving force for densification lies in the reduction of the surface energy resulting from the reduction in the interfacial area between gas and liquid/solid phases. Fig. 1 shows a schematic view of the three types of sintering mechanisms.

In this chapter only the Solid State Sintering and Liquid Phase Sintering mechanisms will be presented as the Viscous Sintering concerning mostly the clay based ceramics or glasses is largely described by Scherer (2019).

The green density of the shaped powder compact is usually around 55–60 vol%. This means that full densification of the ceramic will be accompanied by a large amount of shrinkage (decrease of dimensions) of approximately 35 to 40 vol% and 18–20 linear %. There is also a change in shape of the powder particles with time usually resulting in an increase in average grain size. As shown in Fig. 2, the densification rate of a powder compact heated at fixed temperature decreases with time.

The shrinkage of the ceramic compact can be followed at different stages of the process using dilatometry as shown in Fig. 3. At the beginning of heating, the sample expands due to increase in the amplitude of thermal vibration of atomic bonds. At higher temperatures, densification commences with reduction of porosity. When the thermal treatment is maintained after complete

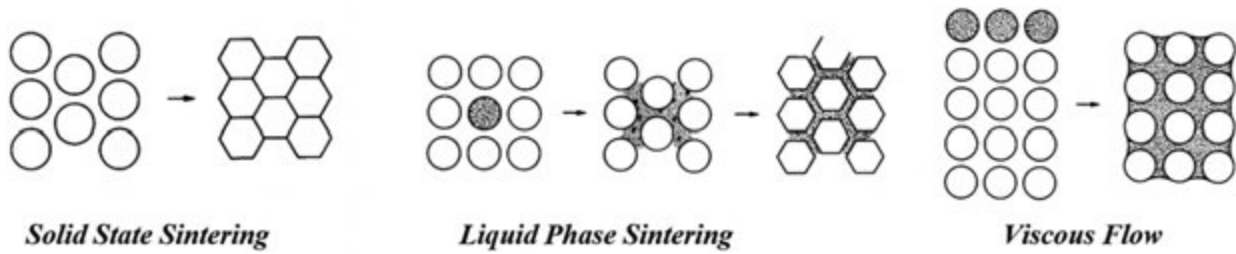


Fig. 1 Sintering mechanisms.

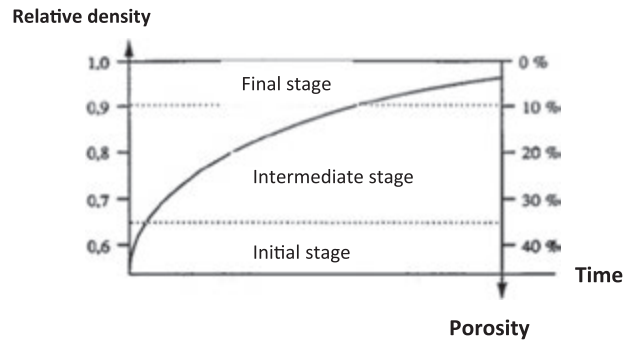


Fig. 2 Schematic curve of densification of a powder compact with time.

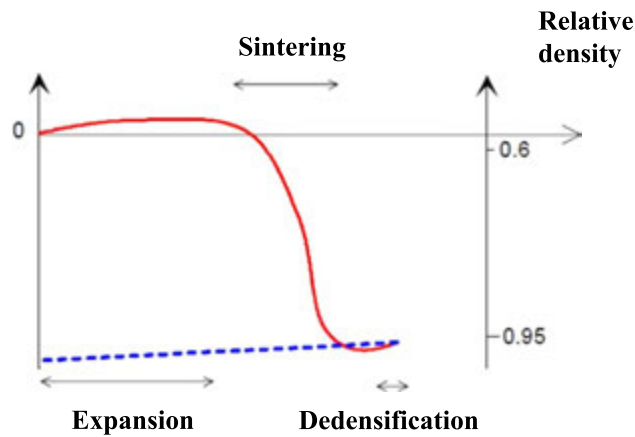


Fig. 3 Classical dilatometric curve.

densification, in some instances, expansion (or dedensification) can occur provoking the appearance of residual porosity and is often associated with initial grain growth.

As shown in **Figs. 2** and **4**, sintering can be presented in three stages:

- (1) Initial stage, during which necks are growing at contact points between particles,
- (2) Intermediate stage (65%–90% density), during which pores become cylindrically shaped with interconnections, so-called “open porosity”,
- (3) Final stage (90%–100% density), during which pores become more spherical and isolated: “closed porosity”.

The total interfacial energy of a powder compact is expressed as γA , where γ is the specific surface or interfacial energy and A is the total surface or interfacial area within a powder compact. The reduction in this total energy can be expressed by (Kang, 2005):

$$\Delta(\gamma A) = \Delta\gamma A + \gamma \Delta A \quad (1)$$

The change in interfacial energy, $\Delta\gamma$, is due to densification and the change in interfacial area, ΔA , occurs because of grain coarsening. $\Delta\gamma$ is related to replacement of solid/vapor interfaces (particle surfaces) by solid/solid interfaces (grain boundaries).

Then, the reduction of total interfacial energy occurs through densification and grain growth (coarsening) as shown schematically in **Fig. 5** (Kang, 2005).

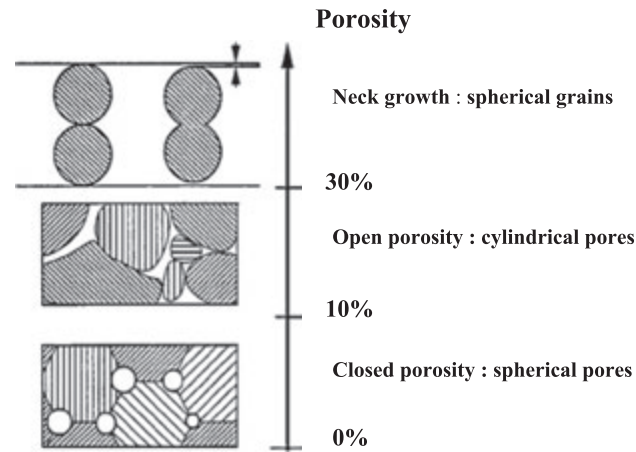


Fig. 4 Grain shape modification during sintering.

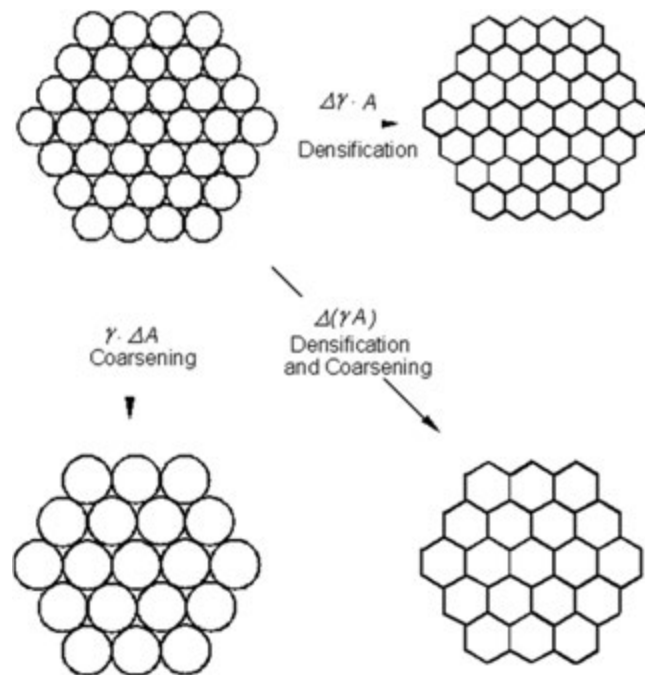


Fig. 5 Basic phenomena (densification and grain coarsening) occurring under the driving force for sintering, $\Delta(\gamma A)$. Reproduced from Kang, S.-J.L., 2005. Sintering, Densification, Grain Growth and Microstructure. Oxford: Elsevier Butterworth-Heinemann, by kind permission.

It has been shown that the grain growth becomes predominant during the final stage as illustrated in **Figs. 6** and **7** for sintered titania (Rahaman, 1995) and alumina (Madhav Reddy *et al.*, 2010) powders.

Solid State Sintering

Description of matter transport mechanism

In solid state sintering, the densification relies wholly on diffusion of atoms (1) at the surface, (2) through the volume, or (3) at grain boundaries with no formation of liquid.

In the absence of liquid phase, the reactions within and between solids require the mobility of atoms and ions. The mechanism of diffusion in solids is the movement of atoms or ions either into vacant lattice sites (vacancies) or between positions that are not normally occupied (interstitial sites).

The driving force for sintering can be described from a macroscopical view as the decrease of free energy by replacement of solid–gas interfaces by solid–solid interfaces and from a microscopical view as the free energy (pressure P) difference across a

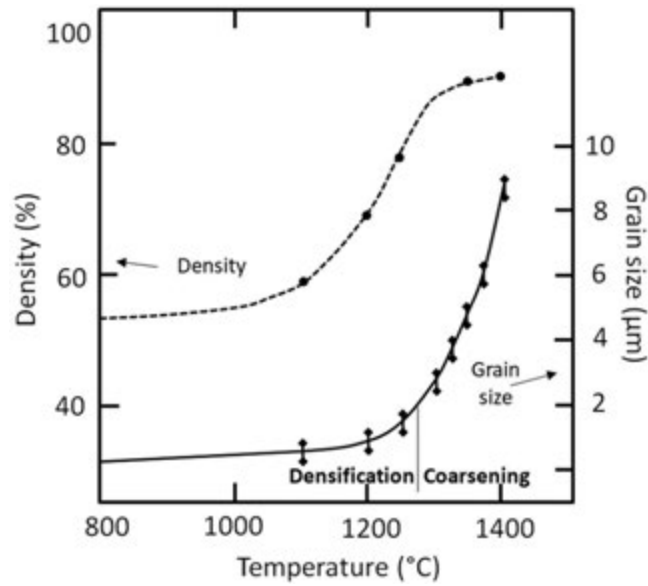
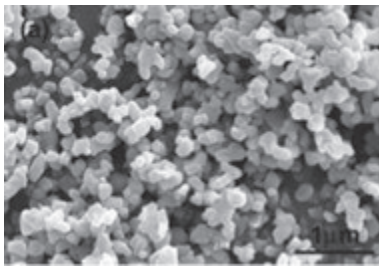
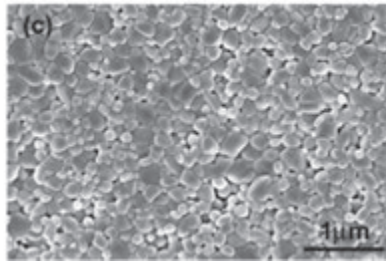


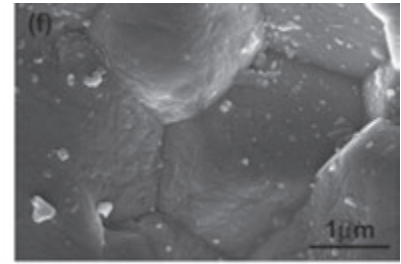
Fig. 6 Density and grain size for powder compact TiO_2 versus sintering temperature. Reproduced from Rahaman, M.N., 1995. *Ceramic Processing and Sintering*, vol. 1995, Marcel Dekker Inc.



$\alpha\text{-Al}_2\text{O}_3 - 0,5 \mu\text{m}$



SPS 1175 °C – 94 %



SPS 1250 °C – 99,9 % - 3 μm

Fig. 7 Microscopic view of alumina powder and resulting microstructure at different densification rates. Reproduced from Madhav Reddy, K., Kumar, N., Basu, B., 2010. Inhibition of grain growth during final stage of multistage spark plasma sintering of oxide ceramics. *Scripta Materialia* 63, 585–588.

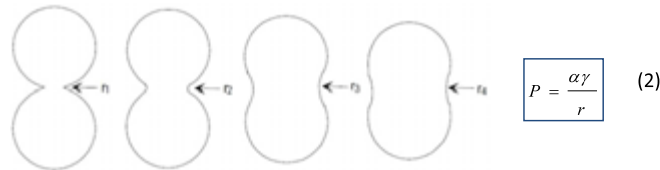


Fig. 8 Shrinkage and shape change of two joined grains.

curved grain boundary. The difference in free energy between the neck area and the surface of the particle provides a driving force which causes the transfer of material by the fastest means available.

The diffusion of atoms occurs in the reverse direction to vacancies which move from areas of higher concentration to ones of lower concentration that is from concave surfaces to convex surfaces. As presented in **Fig. 8**, the necks between spherical particles are the sink of matter with a diffusion rate as high as the grain curvature ($1/r$) is high (the case of small particles). The driving force P (a few MPa) decreases as sintering progresses, which explains the decrease of densification rate:

$$P = \frac{\alpha\gamma}{r} \quad (2)$$

The matter flux “ J ” induced by the pressure difference “ P ” can be expressed by the following **Eq. (3)** where D is diffusion coefficient, x the transport distance and T the temperature:

$$J = -\frac{D}{kT} \frac{dP}{dx} \quad (3)$$

The value of the diffusion coefficient depends on the transport mechanisms that may operate during solid state sintering of a polycrystalline ceramic and these are shown schematically in Fig. 9 and are classified in Table 1.

The first three mechanisms with the surface as the source of matter lead to neck growth but no shrinkage and include:

- (1) *Vapor transport* D_g : which allows material to be transported from one source surface to another sink surface by evaporation of atoms and condensation at another site, through the pore network. This can also take place because of vapor pressure difference Δp .
- (2) *Lattice diffusion* D_l : which allows material to be transported from a particle surface to the neck area by diffusion through the bulk lattice with no increase in densification of the material.
- (3) *Surface diffusion* D_s : which involves the diffusion of atoms along surfaces where the source is a particle surface and the sink is a neck. It only occurs to a depth of approximately one to two atomic distances (0.3–0.5 nm) (Rahaman, 2003). This type of diffusion is initiated at lower temperatures due to its lower activation energy and is usually the dominant mass-transport mechanism during the early stages of neck growth, as the compact is heated up to the sintering temperature. It becomes less dominant as neck formation between particles increases.

The final three mechanisms with grain boundaries or the bulk material as the source of matter do lead to shrinkage and include:

- (4) *Plastic flow* η : which is only active where there is a very high initial dislocation density and therefore is not usually operative in ceramics.
- (5) *Bulk lattice diffusion* D_l : also called volume diffusion which allows atoms from the grain boundary to be transported from the grain boundary through the lattice to a neck or pore surface and so the boundary acts as a site for vacancy annihilation.
- (6) *Grain boundary diffusion* D_b : which allows atoms from the grain boundary to be transported along the grain boundary to a neck region or pore surface, driven by the high level of disorientation of the atoms along the grain boundary. Even though grain boundaries are quite narrow they are very active transport paths.

Overall, there is a competition between densification and grain growth and to obtain dense and fine grained ceramics, it is necessary to favor the material transport mechanisms leading to shrinkage and to limit the surface diffusion mechanisms.

The activation energies for surface, grain boundary, and lattice diffusivity increase in that order (Barsoum, 2002) as shown in Fig. 10 and so the type of matter transport mechanism in operation is highly dependent on the sintering temperature. Thus, surface diffusion is favored at lower temperature whereas bulk lattice diffusion is favored at higher temperatures:

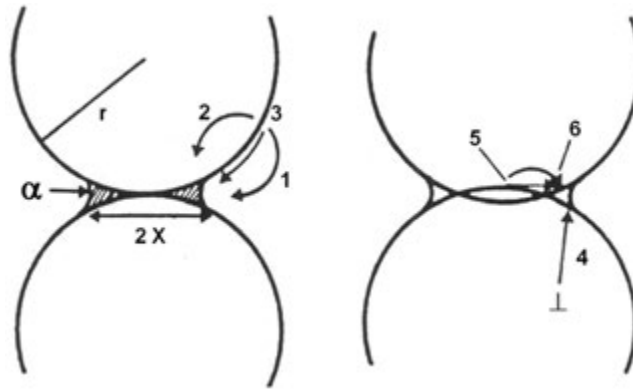


Fig. 9 Transport mechanisms operating during solid state sintering.

Table 1 Different atom diffusion paths in solid state sintering

Mechanism number	Transport path	Source of matter	Sink of matter
1	Vapor	Surface	Neck
2	Lattice diffusion	Surface	Neck
3	Surface diffusion	Surface	Neck
4	Lattice diffusion	Dislocations	Neck
5	Lattice diffusion	Grain boundary	Neck
6	Boundary diffusion	Grain boundary	Neck

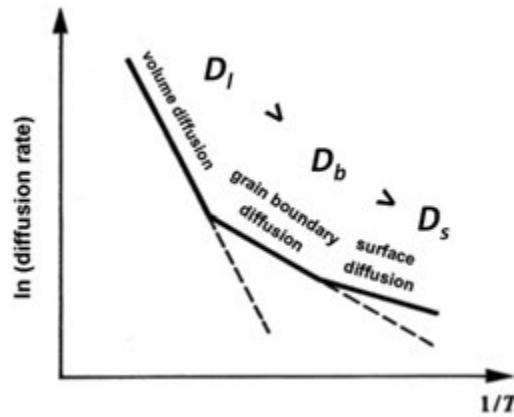


Fig. 10 Temperature dependence of atom diffusion activation energies.

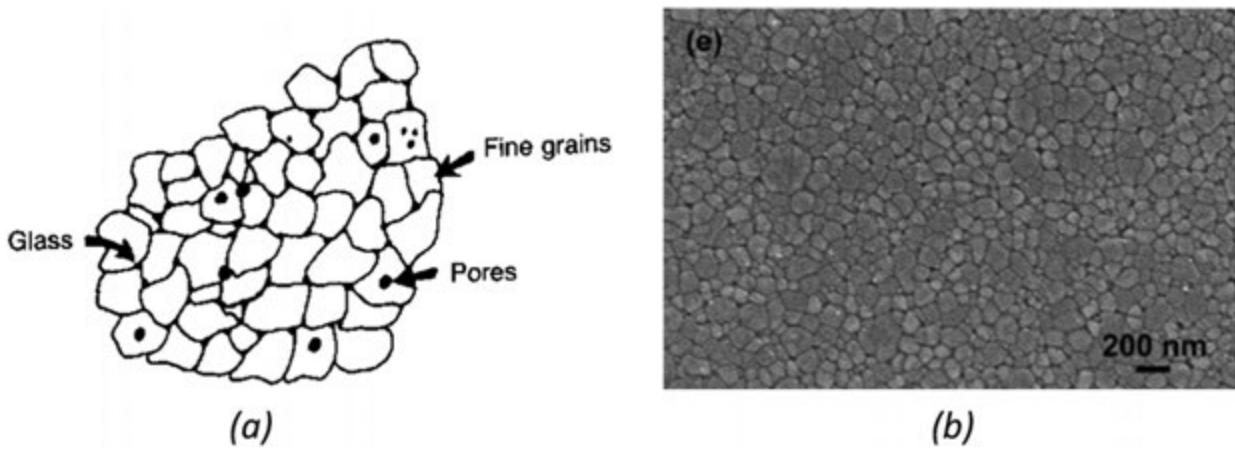


Fig. 11 Typical solid state sintered microstructures (a) schematic, (b) SEM ZrO_2 . (a) Reproduced from Lee, W.E., Rainforth, W.M., 1994. Property Control by Processing. Chapman & Hall.

$$J = -\frac{D}{kT} \frac{dP}{dx} \quad D_i = D_{0i} e^{-\frac{Q_i}{RT}} \quad (4)$$

The diffusion coefficient is also affected by impurity solutes. In general the presence of solutes which enhance either boundary or volume diffusion coefficients increases the rate of solid-state sintering. For oxides in which the slowest diffusing species is oxygen, the addition of cations with lower valence state or the use of reducing atmosphere will enhance sintering (e.g., Li_2O in NiO). If the slowest diffusing species is a cation (as for ZrO_2 , Y_2O_3 , UO_2 , etc.), the addition of a higher charged valence state cation will increase the number of host cation vacancies and will thus enhance sintering (e.g., TiO_2 into Y_2O_3).

Fig. 11 presents a typical schematic figure of the microstructure of an oxide and a SEM micrograph of a pure oxide (zirconia) after thermal etching. Typically the microstructure of a sintered oxide ceramic consists of equiaxed grains with residual porosity and little or no glassy phase at grain boundaries.

Grain growth mechanisms (GG)

The driving force for grain growth is the difference in energy between a fine-grained material and one with a larger grain size resulting from the decrease in grain-boundary area and total boundary energy. As the average grain size increases, it is obvious that some grains must shrink and disappear. Due to the free energy difference across a curved grain boundary, the atoms move from a concave to a convex interface and the grain boundary moves toward its center of curvature until the grain disappears (**Figs. 12** and **13**).

The grain growth velocity, v_B , can be estimated from atom flow, J , through a grain boundary:

$$v_B = J\Omega \quad (5)$$

$$J = \frac{D_b}{kT} \frac{\Delta P}{dx} = \frac{-D_b}{kT} \frac{\alpha\gamma}{r} \frac{1}{\delta_b} \quad (6)$$

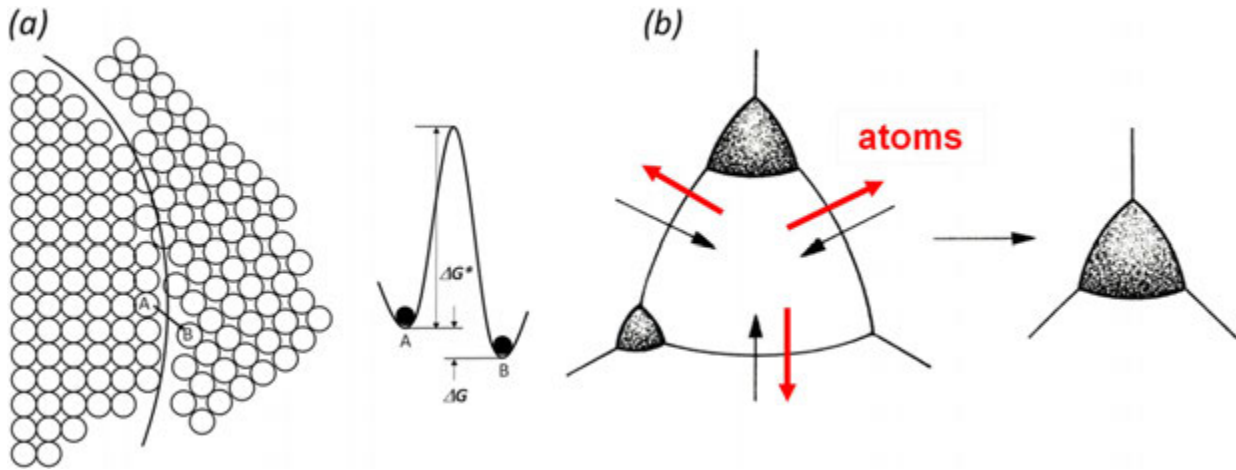


Fig. 12 Disappearance of the grain by atom jumps and pore coalescence. Reproduced from Kingery, W.D., Bowen, H.K., Uhlmann, D.R., 1960. Introduction to Ceramics. John Wiley and Sons.

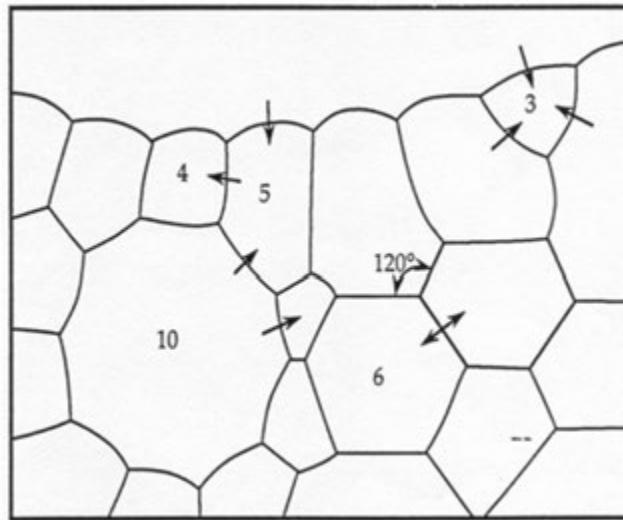


Fig. 13 Grain growth mechanism: arrows indicate the directions in which the boundaries migrate. Small grains (less than 6 sides) will decrease and finally disappear and the large grains (more than 6 sides) will increase. Reproduced from Lee, W.E., Rainforth, W.M., 1994. Property Control by Processing. Chapman & Hall.

$$\frac{d(GG)}{dt} \sim d^{-2} \quad (7)$$

where Ω is atomic volume and δ_b the grain boundary thickness.

Simultaneously, with normal grain growth, exaggerated grain growth (EGG) can occur as illustrated in Figs. 14 and 15. This phenomenon can be avoided by addition of dopants which segregate at grain boundaries (e.g., ~300 ppm MgO in alumina).

Simultaneously with grain growth, pore shape distortion can occur from a spherical shape by the moving boundary and pore agglomeration. The stability of a pore depends on both the dihedral angle and the number of surrounding grains which gives N_c , the critical number of grains surrounding a pore as shown in Figs. 16 and 17. When the number of surrounding grains is higher than N_c for a given dihedral angle, the pore size increases and it decreases when the number of surrounding grains is lower as illustrated Fig. 18 (Kingery *et al.*, 1960).

The pore stability conditions change with pore size as shown in Fig. 19 (Ewsuk and Messing, 1989). The larger is the pore, the greater will be the dihedral angle to eliminate the pore. When grain growth occurs, many pores become isolated from the grain boundaries and the diffusion distance between pores and a grain boundary becomes large, and the rate of sintering decreases. The most satisfactory way of obtaining densification is to prevent or to slow boundary migration by various methods like segregation of dopant at grain boundary or addition of inclusions provoking a pinning of grain boundary.

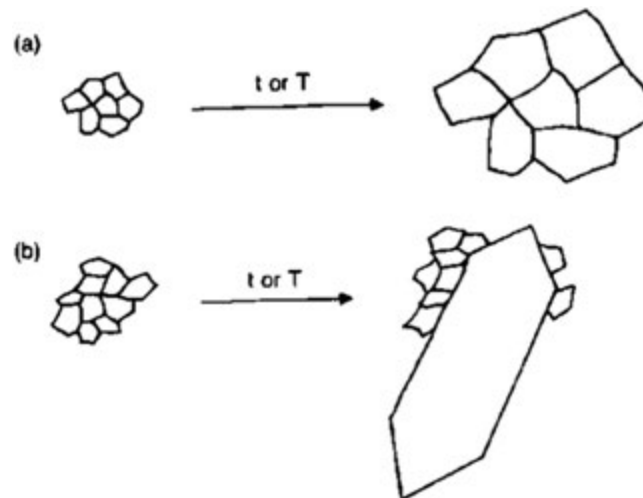


Fig. 14 Grain growth phenomena: (a) Normal grain growth, (b) Exaggerated grain growth.

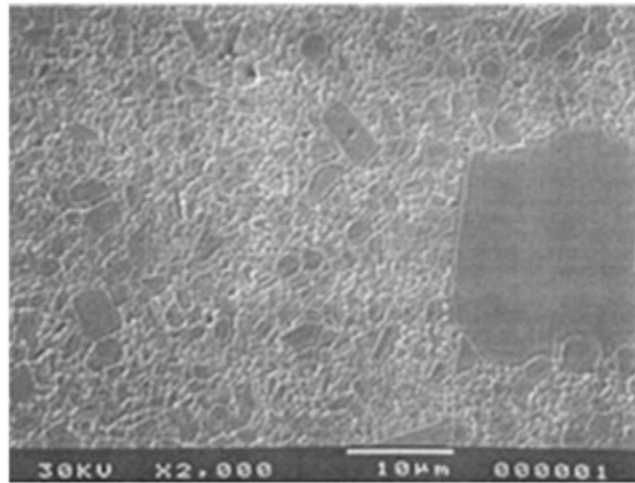


Fig. 15 Microstructure of alumina with EGG.

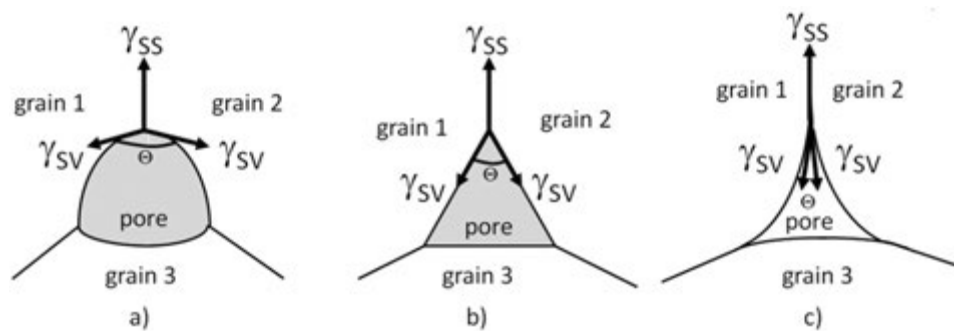


Fig. 16 Conditions for pore stability versus dihedral angle (a) $\theta > \Psi$, pore shrinkage, (b) $\theta = \Psi$, pore stability, (c) $\theta < \Psi$, pore growth.

Liquid Phase Sintering

Description of matter transport mechanisms

Contrary to sintering by viscous flow, the liquid volume formed by the partial melting of one or more components has to be limited to a small volume percent in order to keep the compact shape and to limit the amount of glassy/amorphous phase in the

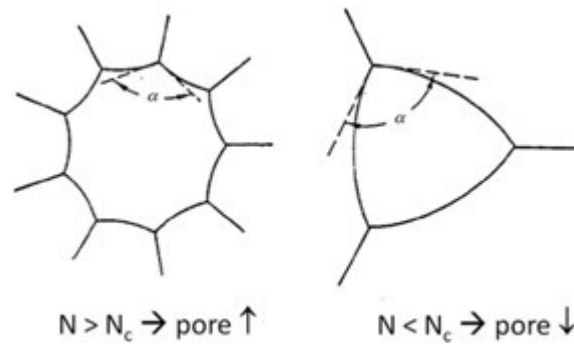


Fig. 17 Conditions for pore stability versus surrounding grain number.

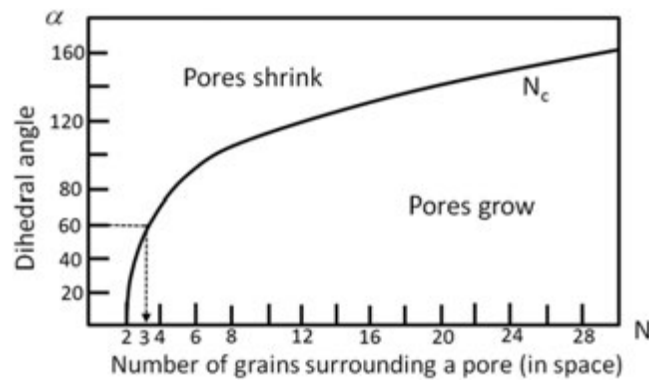


Fig. 18 Conditions for pore stability. Reproduced from Kingery, W.D., Bowen, H.K., Uhlmann, D.R., 1960. Introduction to Ceramics. John Wiley and Sons.

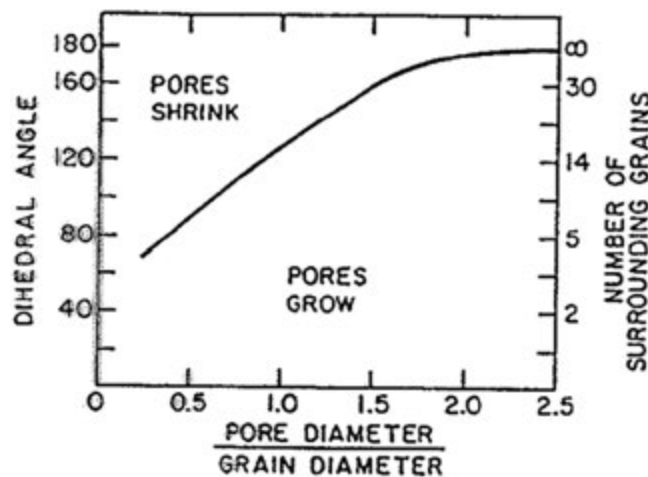


Fig. 19 Pore stability versus pore size. Reproduced from Ewsuk, K.G., Messing, G.L., 1989. A theoretical and experimental analysis of final-stage densification of alumina during hot isostatic pressing. In: Schaefer, R.J., Linzer, M. (Eds.), Proceedings of the 2nd International Conference on HIP: Theory and Applications, pp. 23–33. ASM International.

final product. It is represented in **Fig. 20** as a low thickness liquid layer around each particle. The matter transport occurs by atom diffusion through the superficial liquid phase (D_{liq}):

$$J = - \frac{D_{liq}}{kT} \frac{dP}{dx} \quad (8)$$

Therefore, the parameters which control densification include grain size and shape, pore size and shape, liquid volume and viscosity, solubility of the solid, wetting of the solid by the liquid, phase distribution and phase-boundary energies.

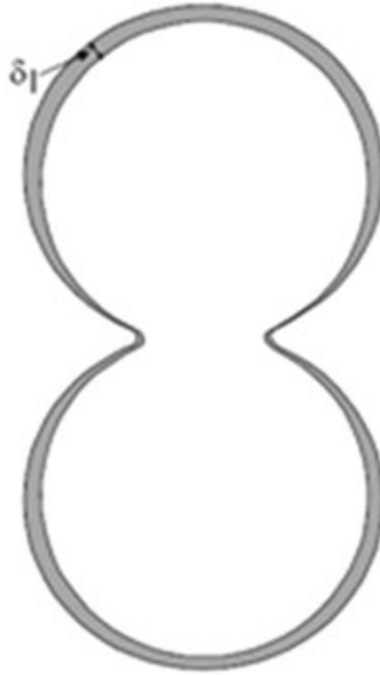


Fig. 20 Superficial liquid phase on two spherical particles.

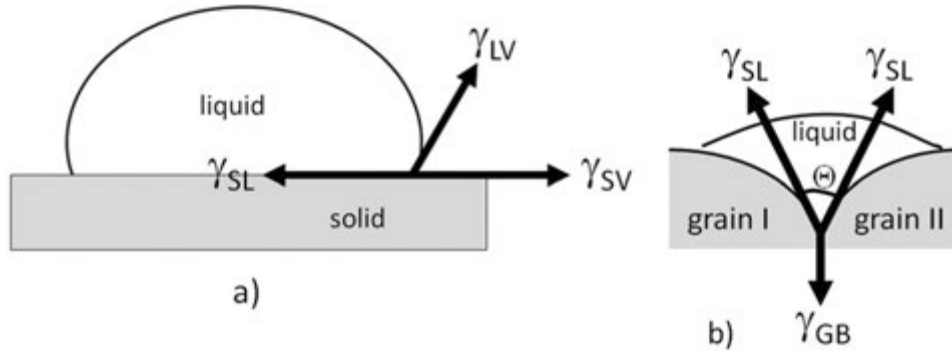


Fig. 21 (a) liquid drop on solid substrate showing contact angle, θ ; (b) liquid penetration along grain boundary depends on dihedral angle, Φ . Reproduced from Smith, C.S., 1948. Grains, phases and interfaces – An interpretation of microstructure. Transactions of the American Institute of Mining Engineers 175, 15–51.

Consider a drop of liquid resting on the surface of a solid phase (Smith, 1948), as in Fig. 21(a), the system will reach equilibrium such that:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (9)$$

where γ is the surface energy of the respective interfaces (SV – solid/vapor; SL – solid/liquid; LV – liquid/vapor).

If $\theta < 90^\circ$, then the liquid wets the solid.

If $\theta = 0^\circ$, the liquid will spread along the solid surface but complete wetting cannot occur if $\gamma_{LV} > \gamma_{SV}$.

If the liquid is surrounded by the solid as in a pore, the conditions are slightly different because spreading generates only new liquid–solid interface but no new liquid–vapor interface. A wetting liquid will always tend to rise up a capillary or be drawn into a pore, even if it would not spread on a free surface. Where the liquid phase is in contact with a solid grain boundary as in Fig. 21(b), penetration of the liquid between the grains will be dependent on the surface energies involved:

$$\text{At equilibrium: } \gamma_{GB} = 2\gamma_{SL} \cos(\phi/2) \quad (10)$$

where ϕ is the dihedral angle. In the case of complete wetting, the liquid phase can penetrate along the grain boundaries and separate the grains.

To be efficient, the liquid phase should wet the grains and penetrate along the grain boundary. For this to occur, the dihedral angle must be less than 60° as shown in Fig. 22.

It was shown that increasing the dihedral angle and the degree of solid–solid contact between grains tends to increase the resistance to shrinkage and densification (Jackson *et al.*, 1963). This occurs mainly during the initial rapid formation of the liquid phase when any grain-to-grain contact inhibits the ability of the particles to rearrange within the liquid phase.

The driving force for densification is derived from this capillary pressure of the liquid phase located between the fine solid particles. Each interparticle space becomes a capillary in which capillary pressure is developed. For submicron particle sizes, capillaries with diameters in the range of $0.1\text{--}1\text{ }\mu\text{m}$ develop pressures in the range of $1.25\text{--}12.5\text{ MPa}$.

The presence of liquid and the capillary pressure result in densification via three distinct stages:

- (1) Particle rearrangement stage.
- (2) Solution-diffusion-precipitation stage.
- (3) Coalescence stage.

During the first stage, the liquid which is first formed is drawn by capillary forces to the points of contact between grains at a rate which is determined by the surface tension and viscosity of the liquid. Particle rearrangement thus occurs by viscous flow. The proportion of complete densification that can be achieved through a rearrangement process with spherical particles depends on the volume fraction of liquid present (Fig. 23).

The shrinkage may also depend on particle shape and size distribution, the solubility of the solid in the liquid and interfacial energies.

The second stage involves atom transport in the liquid by solution, diffusion and reprecipitation and proceeds in three steps: (1) atom migration to the grain surface followed by interfacial reaction leading to dissolution of solid in the liquid phase; (2) matter transport by diffusion through the liquid to points away from the contact areas; and finally (3) the re-precipitation of solid material either at grain boundaries or on existing seed crystals (e.g., in silicon nitride, where initially α -silicon nitride is dissolved and β -silicon nitride precipitates on existing β seeds).

For very small crystals, the interfacial tensions between the crystals and their saturated solution are greater than that for large crystals. According to the Gibbs–Thompson equation, the solubility of small grains is larger than large grains:

$$\log \frac{S_r}{S} = \frac{2M\gamma}{N_0 k T \rho r} \quad (11)$$

where S_r and S are solubilities of particles with radius r or infinite radius, M is molar mass, γ is surface energy, k is Boltzmann's constant, T is absolute temperature, ρ is particle density, and r is grain curvature radius.

The third stage of sintering involves a reduction in the densification rate which may be caused by a number of different processes including (1) grain growth which prevents further transport of liquid phase, (2) trapping of gases in closed pores with the resulting pressure acting against the capillary pressure normally causing shrinkage, etc.

Successful systems require sufficient liquid volume, a good wettability of the powder particles by the liquid and partial solubility of the solid in the liquid.

Fig. 24 shows typical examples of microstructures: (1) mullite-zirconia composites synthesized by reaction sintering from zirconium silicate and alumina and (2) silicon nitride with $\text{MgO}/\text{Y}_2\text{O}_3$ as sintering additives. The chemically etched

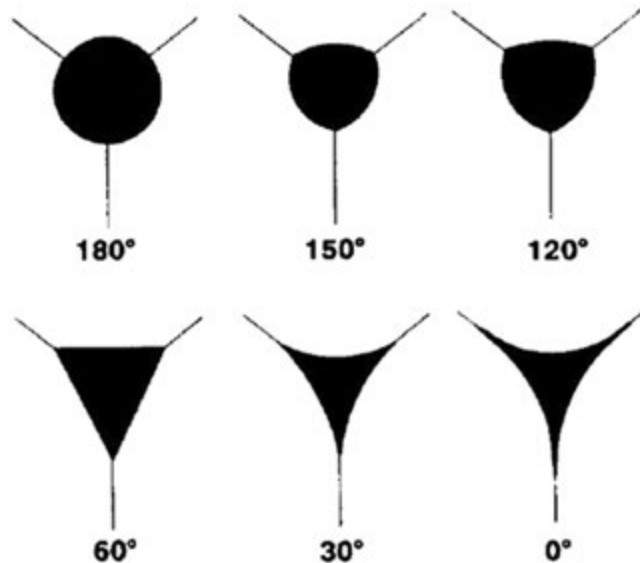


Fig. 22 Penetration of the liquid between the grains as a function of the contact angle.

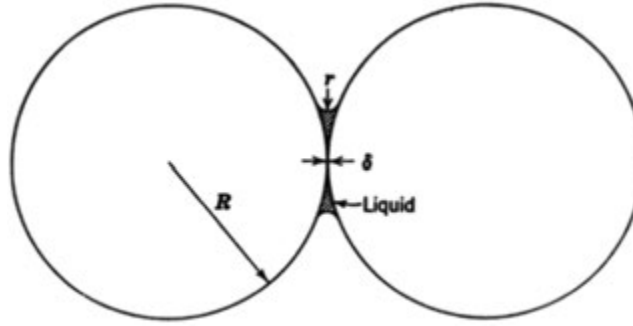


Fig. 23 Draw of liquid by capillary forces to the points of contact between grains. Reproduced from Kingery, W.D., Bowen, H.K., Uhlmann, D.R., 1960. Introduction to Ceramics. John Wiley and Sons.

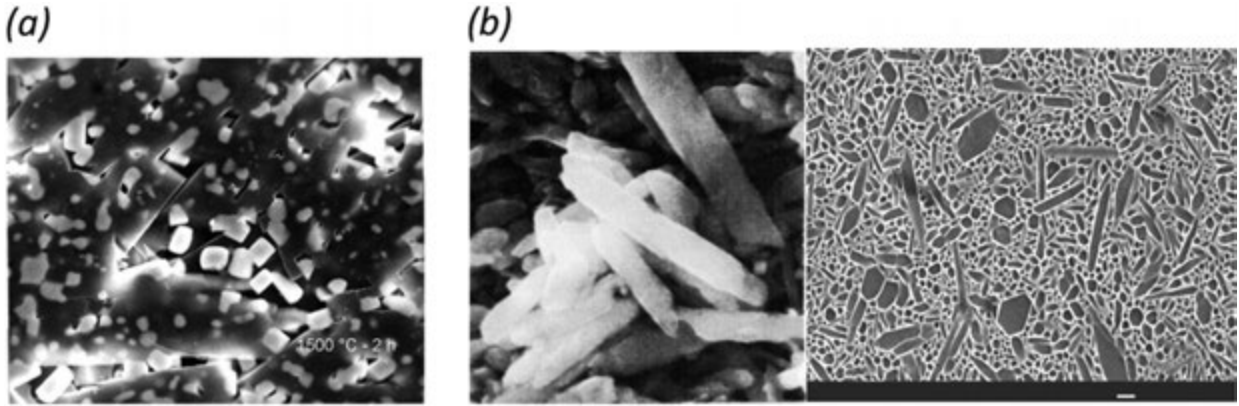


Fig. 24 Some typical microstructures of liquid phase sintered ceramics: (a) reaction-sintered mullite-zirconia and (b) sintered silicon nitride (left: grain morphology, right: 2D section showing elongated grains surrounded by secondary glass phase. Reproduced from (a) Leriche, A., 1986. Influence of the Process Parameters on the Microstructure of Mullite-Zirconia Composites (in French), Ph.D. Belgium: University of Mons. (b) Hampshire, S., Pomeroy, M.J., 2012. Grain boundary glasses in silicon nitride: A review of chemistry, properties and crystallisation. Journal of the European Ceramic Society 32, 1925–1932.

microstructures show needle-like elongated grains of mullite or silicon nitride. The glassy phase formed by cooling from the liquid phase is located at grain boundaries.

Grain growth mechanisms

For Liquid Phase Sintering, the grain growth can be controlled either by the dissolution step or by the diffusion step.

In the case of the rate control by diffusion, the grain growth follows the relationship:

$$d^3 - d_0^3 = k_1 t \quad (12)$$

where d_0 is initial grain size and k_1 is a constant depending on D_L , Ω , C , γ_{SL} , k , T .

A similar dependence exists for a model described for the creep of materials containing an intergranular liquid phase (Raj and Chyung 1980):

$$\frac{d\varepsilon}{dt} = \frac{3.7 \sigma \Omega C \alpha}{(1-x) \eta d^3} \quad (13)$$

where ε is the strain, σ is the applied stress, η is viscosity of the liquid, C is molar content of solute in the liquid phase and x is the amount of liquid. This relationship has the advantage of showing the influence of liquid viscosity on diffusion rate.

If the grain growth is controlled by the interfacial reaction (as occurs in the case of a low viscosity liquid), the phenomenon can be described by the relationships in Eq. (14) giving square of grain size, d^2 , dependence and the liquid phase viscosity does not affect the grain growth rate:

$$d^2 - d_0^2 = k_2 t \quad k_2 = \frac{256 C \Omega \gamma_{SL} k_R}{81 k T} \quad (14)$$

where k_2 is a constant depending on Ω , C , γ_{SL} , k_R (the atom transfer rate between crystal and liquid), k , T .

The comparison with the creep rate model for dissolution reaction gives a different dependence with grain size:

$$\frac{d\varepsilon}{dt} = \frac{\sigma \Omega K'}{2(1-x)k T d} \quad (15)$$

where x is the surface volume fraction occupied by the liquid at the grain boundary.

Densification Kinetics

The rate of growth of the neck during the initial stage was analyzed for various mechanisms of transport of material into the neck from the particle surface (Kuczynski, 1949) and the effects of particle size were included after by Herring (1951). For all mechanisms, a general relationship follows:

$$(x/r)^n = K_1 t / r^m \quad (16)$$

where r is particle radius, x is the radius of the interparticle contact area, t is time and n , m and K_1 are constants. Plots of $\log(x/r)$ versus $\log t$ or $\log r$ should result in linear plots with slopes of n or m .

During the second intermediate stage, depending on the mechanism of material transport, shrinkage may occur according to:

$$\Delta L / L_0 = K_2 t^y \quad (17)$$

where ΔL is change in length, L_0 is original length, t is time, and y and K_2 are constants. A plot of $\Delta L / L_0$ versus $\log t$ should be linear with slope y .

The mechanism of material transport is then deduced from the slope as follows (Table 2).

Particle size, packing, degree of agglomeration, presence of impurities, sintering atmosphere, etc., can affect the mechanism of sintering, the extent of pore/grain boundary interactions (Brook, 1969) and whether densification or coarsening occurs.

Fig. 25 shows schematic curves of relative density versus time and the effects of temperature, pressure, and particle size (Kang, 2005).

Increase in temperature favors atomic diffusion through the Arrhenius relationship, external pressure will increase the sintering driving force (γ/r) and decrease in grain size decreases the diffusion distance. For an identical particle size, a temperature increase favors successively D_s , D_b , and D_l . So, low temperature sintering favoring D_s (neck growth without shrinkage) will be chosen to process porous materials, whereas achievement of high densities will require high temperature sintering to favor D_l (shrinkage).

Pressure and/or Plasma Assisted Sintering

Densification of ceramics can be achieved more effectively using pressure-assisted forming techniques which combine external pressure with temperature in order to enhance the final density. These include hot pressing, hot isostatic pressing, sinter forging, hot extrusion and gas pressure sintering. More recently, electrical field assisted sintering techniques have been developed.

Table 2 Deduction of mechanism of material transport from linear plots of Eqs. (16) and (17)

	n	m	y
Surface diffusion D_s	7	4	No shrinkage
Evaporation/Condensation D_g	3	2	No shrinkage
Volume (bulk) diffusion D_l	5	3	0.4/0.5
Grain boundary diffusion D_b	5	3	0.3/0.33
Viscous/Plastic flow η	2	1	1

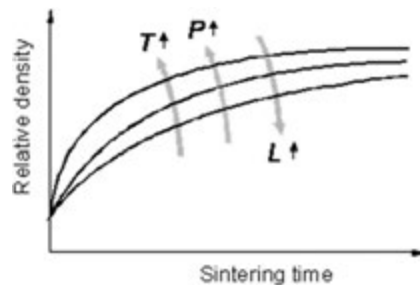


Fig. 25 Effect of sintering parameters (T – Temperature, P – Pressure, L – particle size) on densification. Reproduced from Kang, S.-J.L., 2005. Sintering, Densification, Grain Growth and Microstructure. Oxford: Elsevier Butterworth-Heinemann, by kind permission.

Uniaxial and isostatic hot pressings

The driving force leading to densification can be increased by external pressure application. The pressure can be uniaxially applied through punches on powdered sample inserted in a die (Hot Pressing) or isostatically applied through gas surrounding hermetically encapsulated powder compact (Hot Isostatic Pressing). In these cases, the driving force P due to the free energy difference across a curved grain boundary which has a few MPa range value is implemented by the external applied force which can reach 50 MPa (Hot Pressing) and 500 MPa (Hot Isostatic Pressing), respectively.

The application of an external pressure (σ_a) allows the acceleration of densification but also modifies the pore stability conditions as shown in Fig. 26 (Ewsuk and Messing, 1989) which allows to eliminate pores which by pressureless sintering would be stable or would have grown:

$$DF = \frac{2\gamma}{\kappa} + \sigma_a \quad \kappa = r \frac{\sin\left(90 - \frac{\psi}{2}\right)}{\sin\left(\frac{\theta}{2} - \frac{\psi}{2}\right)} \quad (18)$$

These two techniques allow theoretical density to be reached at lower temperatures than by pressureless sintering with limited grain growth.

Spark plasma sintering (SPS)

Spark plasma sintering (SPS) (Nygren and Shen, 2003), also known as field assisted sintering technique (FAST), uses an electrical current (DC, pulsed DC, or AC) which is passed through a conducting pressure die (graphite) and, if the material has reasonable electrical conductivity, through the ceramic itself. The die therefore acts as a heat source, so the sample is heated both internally and externally. Contrary to HIP, the SPS technique allows very rapid heating and cooling rates, very short holding times (a few minutes) and results in densification at much lower sintering temperatures, usually a few hundred degrees lower than for conventional sintering with restricted grain growth occurring only at the last sintering stage.

Flash sintering (FLASH)

This method is also referred to as the "Two-Electrode Experiment" (Raj *et al.*, 2011) and the process consists in heating the ceramic piece in a conventional furnace but applying an electrical current (DC or AC). The green sample is hung in the middle of the kiln by two platinum electrodes allowing the passage of current. At low fields (less than 40 V cm^{-1}), the sintering rate increase is

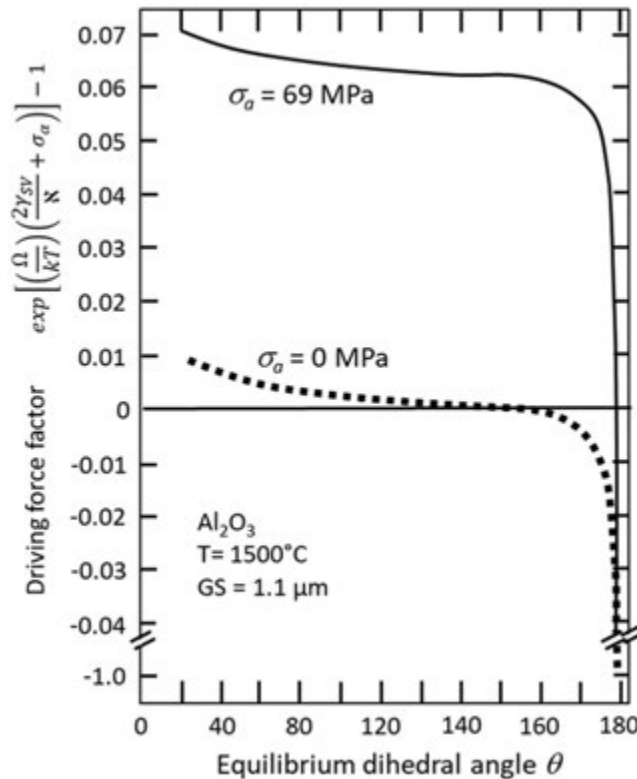


Fig. 26 Densification driving force factor versus dihedral angle for pressureless sintering and hot isostatic pressing. Reproduced from Ewsuk, K.G., Messing, G.L., 1989. A theoretical and experimental analysis of final-stage densification of alumina during hot isostatic pressing. In: Schaefer, R.J., Linzer, M. (Eds.), Proceedings of the 2nd International Conference on HIP: Theory and Applications, pp. 23–33. ASM International.

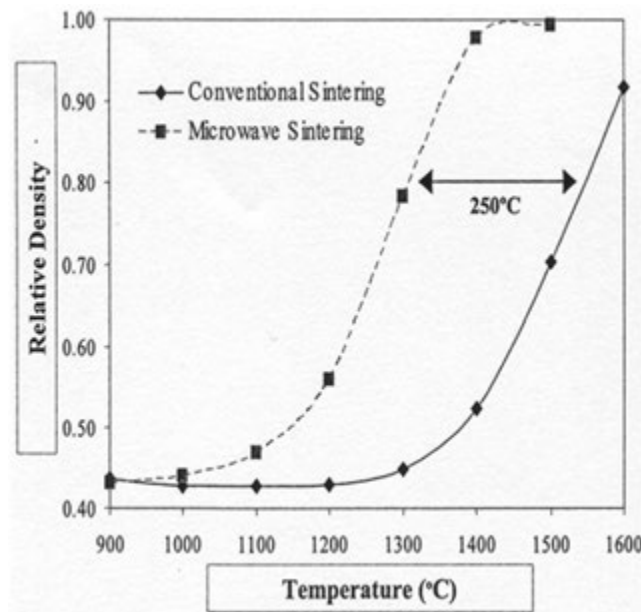


Fig. 27 Decrease of sintering temperature for microwave sintering for alumina. Reproduced from Brosnan, K.H., Messing, G.L., Agrawal, D.K., 2003. Microwave sintering of alumina at 2,45 GHz. *Journal of the American Ceramic Society* 86 (8), 1307–1312.

attributed to a reduction of the grain growth under an applied field; at higher fields, the specimens sinter almost instantaneously, as if in a flash, above a critical temperature (Cologna *et al.*, 2010).

Alternative Sintering Techniques

Microwave sintering

Microwave sintering allows reduction both in sintering temperature and time as there is direct coupling of the microwaves with electric dipoles within the ceramic (Binner and Vaidhyanathan, 2008). Full densification of alumina powders doped with Y_2O_3 and MgO within a few minutes and 250 degrees below the conventional sintering temperature, whereas the sintering trajectory showing grain size vs relative density was similar with both heating techniques (Fig. 27) (Brosnan *et al.*, 2003). These results were confirmed with a lower onset temperature of densification and smaller activation energy (Croquesel *et al.*, 2016).

The reasons for these specific microwave effects on sintering are still under debate with several hypothesis such as the possibility of a thermal effect related to local overheating at particle contacts under electric field, which could act on grain boundary diffusion or grain growth or the existence of a ponderomotive force induced by the electromagnetic field and acting on diffusion mechanisms (Croquesel *et al.*, 2016).

Cold sintering

This densification process requires the use of a few vol% fraction of a transport phase like water to facilitate the mass transfer between powder particles in combination with uniaxial force between 100 and 400 MPa. The mechanism is considered to be a multistep process similar to liquid phase sintering combining capillary forces and dissolution-solute supersaturation-precipitation phenomena (Guo *et al.*, 2019). Relative density levels between 70% and 99% can be reached with short holding time (a few tenth minutes) at modest temperatures 120–300°C depending on ceramic. First assays carried out on ZnO cold sintered with acetic acid as liquid transient phase between 70 and 305°C under 350 MPa have revealed a highly lower activation energy of grain growth compared to conventional sintering (Funahashi *et al.*, 2017).

Summary

Fabrication of ceramics includes a heat treatment of a powder compact to form a dense solid. This process of sintering involves matter transport to reduce porosity by diffusion of atoms in the vapor phase, in the liquid phase or in the solid state. Most mechanisms are activated thermally in order to overcome the potential barrier between the initial state of higher energy (porous powder compact) and the final state of lower energy (consolidated dense material). The chapter has outlined the processes involved in *Solid State Sintering* in the absence of any liquid phase and *"Liquid Phase Sintering"* in the presence of a small volume

percent of liquid phase. In all cases, the driving force for densification lies in the reduction of the surface energy resulting from the reduction in the interfacial area between gas and liquid/solid phases.

Fully dense ceramic materials with limited grain growth can be obtained by applying new technologies adding supplementary effects (application of external pressure and/or electric current) to fine grain size and well-dispersed powders. Moreover, these new techniques allow decrease of temperature and the duration of sintering and so are particularly promising for potential energy savings. Even if the grain growth phenomenon seems to be enhanced for the cold sintering, the huge sintering temperature decrease is promising for the development of faster and lower-energy processes and for new products not suffering high temperature treatment as ceramic-polymer composites.

References

- Barsoum, M.W., 2002. *Fundamentals of Ceramics*. Oxford: Taylor and Francis.
- Binner, J., Vaidyanathan, B., 2008. Processing of bulk nanostructured ceramics. *Journal of the European Ceramic Society* 28 (7), 1329–1339.
- Brook, R.J., 1969. Pore-grain boundary interactions and grain growth. *Journal of the American Ceramic Society* 52, 56–57.
- Brosnan, K.H., Messing, G.L., Agrawal, D.K., 2003. Microwave sintering of alumina at 2.45 GHz. *Journal of the American Ceramic Society* 86 (8), 1307–1312.
- Cologna, M., Rashkova, B., Raj, R., 2010. Flash sintering of nanograin zirconia in < 5 s at 850°C. *Journal of the American Ceramic Society* 93 (11), 3556–3559.
- Croquesel, J., Bouvard, D., Chaix, J.M., *et al.*, 2016. Direct microwave sintering of pure alumina in a single mode cavity: Grain size and phase transformation effects. *Acta Materialia* 116, 53–62.
- Evsuk, K.G., Messing, G.L., 1989. A theoretical and experimental analysis of final-stage densification of alumina during hot isostatic pressing. In: Schaefer, R.J., Linzer, M. (Eds.), *Proceedings of the 2nd International Conference on HIP: Theory and Applications*. ASM International, pp. 23–33.
- Funahashi, S., Guo, J., Guo, H., *et al.*, 2017. Demonstration of the cold sintering process study for the densification and grain growth of ZnO ceramics. *Journal of the American Ceramic Society* 100 (2), 546–553.
- Guo, J., Floyd, R., Lowum, S., *et al.*, 2019. Cold sintering: Progress, challenges, and future opportunities. *Annual Review of Materials Research* 2019 (49), 275–295.
- Herring, C., 1951. Surface tension as a motivation for sintering. In: Kington, W.E. (Ed.), *The Physics of Powder Metallurgy*. New York: McGraw-Hill, pp. 143–179.
- Jackson, B., Ford, W.F., White, J., 1963. The influence of Cr₂O₃ and Fe₂O₃ on the wetting of periclase grains by liquid silicate. *Transactions & Journal of the British Ceramic Society* 62, 577–601.
- Kang, S.-J.L., 2005. *Sintering, Densification, Grain Growth and Microstructure*. Oxford: Elsevier Butterworth-Heinemann.
- Kingery, W.D., Bowen, H.K., Uhlmann, D.R., 1960. *Introduction to Ceramics*. John Wiley and Sons.
- Kuczynski, G.C., 1949. Self-diffusion in sintering of metallic particles. *Journal of Metals* 1, 169–178.
- Madhav Reddy, K., Kumar, N., Basu, B., 2010. Inhibition of grain growth during final stage of multistage spark plasma sintering of oxide ceramics. *Scripta Materialia* 63, 585–588.
- Nygren, M., Shen, Z., 2003. On the preparation of bio-, nano- and structural ceramics and composites by spark plasma sintering. *Solid State Sciences* 5, 125–131.
- Rahaman, M.N., 1995. *Ceramic Processing and Sintering*. 1995. Marcel Dekker Inc.
- Rahaman, M.N., 2003. *Ceramic Processing and Sintering*, second ed. Boca Raton, FL: CRC Press – Taylor and Francis.
- Raj, R., Chyung, C.K., 1980. Solution-precipitation creep in glass ceramics. *Acta Metallurgica* 29, 159–166.
- Raj, R., Cologna, M., Francis, J.S.C., 2011. Influence of externally imposed and internally generated electrical fields on grain growth, diffusional creep, sintering and related phenomena in ceramics. *Journal of the American Ceramic Society* 94 (7), 1941–1965.
- Scherer, G.W., 2019. Viscous sintering. *Reference Module Materials Science and Materials Engineering* 1173. doi:10.1016/B978-0-12-803581-8.11732-1.
- Smith, C.S., 1948. Grains, phases and interfaces – An interpretation of microstructure. *Transactions of the American Institute of Mining Engineers* 175, 15–51.

Solid-State Sintering

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Solid-state sintering is the bonding and densification of particles by the application of heat below the melting point of a material. During sintering, the free surface area of the compact decreases, and this is normally accompanied by an increase in the density, but it is possible for the compact to decrease its surface area and increase its cohesion without a perceptible increase in density. There will be changes in other properties of the compact, such as increased strength, an increase in electrical and thermal conductivity. For most applications, an increase in density is the desired result of sintering. As with any physical process, there must be a lowering of the total internal energy of the system to drive the process. In sintering this reduction in energy is the reduction in the total surface energy of the powder particles due to the replacement of surfaces by grain boundaries and due to coarsening. Overall, the reduction in internal energy is the difference in total surface energy of the powder compact and the remaining surface energy plus the total grain boundary energy of the sintered body.

Although sintering is the oldest method of forming materials from powders, an understanding of the processes occurring during heating of a powder compact is rather recent. Frenkel (1945), who was the first to propose a model for sintering, assumed that sintering occurred by the deformation of crystalline particles under the influence of surface tension, as would occur for amorphous materials such as glass. However, the predictions of this model did not agree with experimental results using crystalline particles. Kuczynski (1949) demonstrated that sintering occurs by diffusive processes. He proposed several models to describe the early stages of sintering for different transport mechanisms and diffusion paths. Coble (1961) developed models for the later stages of sintering for the case of lattice diffusion or grain boundary diffusion. Although later developments (see reviews by Exner, 1979; German, 1996; Handwerker *et al.*, 1989, 1990; Rahaman, 2008; Kang, 2005; Castro and van Benthem, 2013; Bordia *et al.*, 2017) have refined these basic ideas, the early models serve well to describe sintering processes. As sintering is a result of diffusive processes, two factors have the major influence on the rate of sintering: temperature (which controls the diffusion rate) and powder particle size (which controls the length scale for diffusion).

Sintering Stages

Sintering is conceptually divided into three stages: initial, intermediate, and final, expressing transitions in the connectivity of the particles within an ideal compact of single sized spheres. Within each stage, the pore shape change is well defined and the shrinkage of pores occurs with the pores maintaining a nearly constant shape. The initial stage refers to the growth of contacts or “necks” between the individual powder particles in the compact (Fig. 1). The radius of the necks grown in the initial stage ranges from zero to ~ 0.2 of the radius of the particles at which point the necks begin to overlap. In the intermediate stage, the pores are approximated as continuous channels coincident with the three-particle junctions (Fig. 2). The final stage begins when the pore channels break up into isolated pores located at the four-grain junctions (Fig. 3). This usually occurs when the density of the sample has increased to $\sim 92\%$ of the theoretical density of the material.

Driving Force for Sintering

During sintering the surface area of the powder compact is reduced. There are two processes that can cause this – coarsening and densification – shown schematically in Fig. 4. For an initial array of n spheres of size R the surface area is $n \cdot 0.4\pi R^2$. For coarsening of the spheres to a size $2R$, the number of spheres must decrease (to conserve mass) by a factor of eight and the surface area will be reduced by a factor of two. Thus, coarsening of the structure results in a reduction of the total surface energy. Notice that in this schematic there is no growth of the contacts between the particles and no decrease in the porosity of the sample. In contrast, if the spherical particles change their shape, the centers of the particles can move together and the volume of the sample will decrease. The surface area is completely converted to grain boundaries with an area of $n \cdot 2.15R^2$ (for a cubic array). The energy of a grain boundary is less than the energy of the two free surfaces that are eliminated (typically by about one order of magnitude), and thus the total energy is reduced. A reduction in total energy is a requirement for any process to occur.

The driving force for coarsening and densification arises from the pressure gradients at curved surfaces, and is conceptually described as, $\Delta P = \frac{2\gamma}{R}$, where γ is the surface energy and R is the radius of curvature.

Although both coarsening and densification result in a reduction in the surface area of the compact, coarsening does not induce densification but lowers the remaining driving force for densification and, as such, is usually an undesired process. Coarsening occurs if surface diffusion is dominating, while densification needs significant rates of grain boundary or volume diffusion. To determine which process dominates, it is necessary to determine the kinetics of these different diffusion mechanisms.

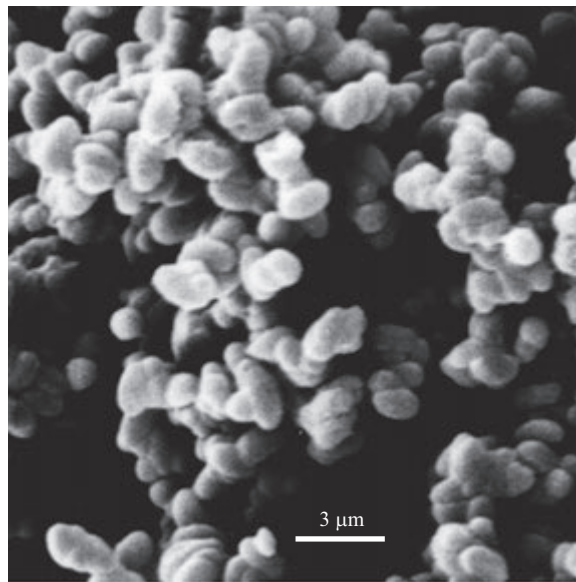


Fig. 1 Particles in the initial stage of sintering. Small “necks” can be seen connecting the particles.

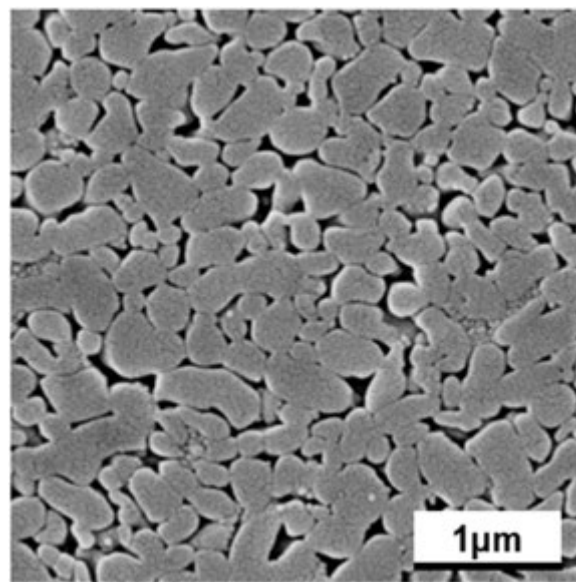


Fig. 2 Structure showing the intermediate stage of sintering. Necks between particles have grown, resulting in a structure that contains continuous pore channels through the compact.

Initial Stage

The simplest model for initial stage sintering is the two-sphere model (Fig. 5), that contains all important features necessary for understanding sintering (Exner, 1979). The basic premise of the model is that matter is transported from regions of high chemical potential to regions of low chemical potential. In this model, the regions of high chemical potential are at the contact region (grain boundary) and along the convex surface of the sphere. The concave neck region is at a lower chemical potential relative to these areas. Matter can be transported to the neck region through the gas phase (by evaporation from the convex surface and condensation on the concave surface), by surface diffusion (from convex surface to concave surface), lattice diffusion (from either the convex surface or the grain boundary), or grain boundary diffusion. If the source of matter is the grain boundary, the two particle centers approach resulting in densification. If the source of matter is the convex particle surfaces, the two particles change shape without center approach (coarsening). Thus, in the initial stage of sintering, evaporation and condensation and surface diffusion result in coarsening, grain boundary diffusion results in densification and lattice diffusion can result in either, depending on the source of the matter transported.

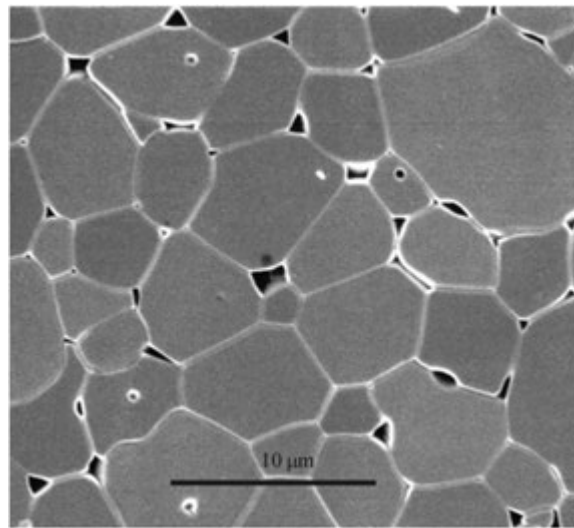


Fig. 3 Polished surface of compact showing the final stage of sintering. Pores are isolated and generally located on the grain boundaries. Pore shape differences depending on location can be seen.

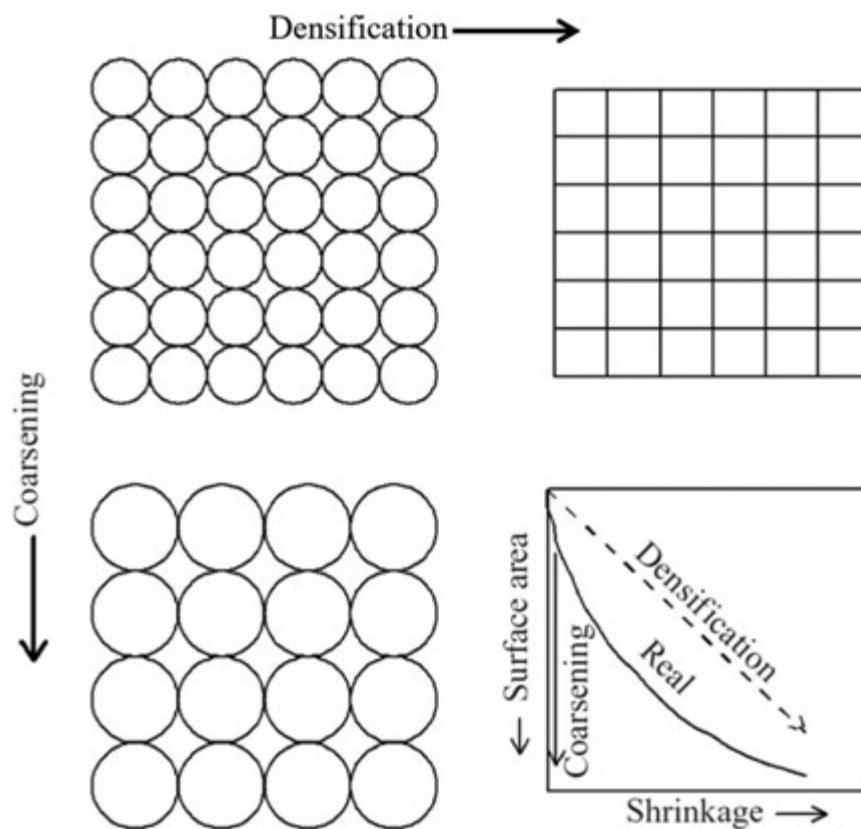


Fig. 4 Schematic of the competitive processes that occur during sintering. Densification results in surface area reduction, pore removal, and shrinkage of the compact. Coarsening results only in surface area reduction.

The driving force for transport during sintering is the difference in chemical concentration between the source of matter (particle surface or grain boundary) and the sink for matter (neck region). The concentrations are different due to the chemical potential differences that result from the curvature differences (Johnson, 1978). Along the particle surface the curvature changes from positive at the particle surface to negative at the neck region. Regions of positive curvature correspond to compressive stresses and will have a higher vapor pressure than a flat surface. Conversely, regions of negative curvature will have a tensile stress and a

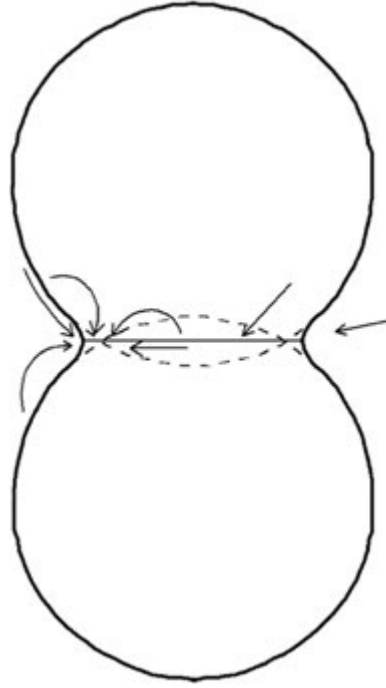


Fig. 5 Two-particle model for initial-stage sintering. Transport of matter is from the particle surface or grain boundary to the neck region resulting in neck growth and densification.

lower vapor pressure than a flat surface. The vapor pressure difference tends to transport matter through the vapor phase into the neck region. The stress difference leads to transport by diffusion to the neck region. Both mechanisms will be active and the total neck growth will be the sum of the two processes. The tensile stress at the neck region is balanced by a compressive stress on the grain boundary. This compressive stress raises the concentration of atoms in the grain boundary region and the tensile stress lowers the concentration of atoms in the neck region. This concentration gradient leads to transport of matter from the grain boundary region to the neck region by grain boundary and lattice transport. In this case, there is densification of the compact.

Many different models have been proposed to describe the initial stage of sintering. In general, each model first assumes a geometry, determines the resulting chemical potential difference that is driving transport, calculates the mass flux based on the geometry and the concentration differences, and then relates the flux to the neck growth rate or the densification rate. If it is assumed that all the transport processes are independent and additive, the rate of neck growth in the initial state can be expressed as:

$$\frac{\partial x}{\partial t} = \frac{C_1 \gamma D_l R}{x^2} + \frac{C_2 \gamma D_b R^2}{x^5} + \frac{C_3 \gamma D_s R^2}{x^5} + \frac{C_4 \gamma p_0 R}{x}$$

where x is the radius of the neck, γ is the surface energy, R is the particle radius, C_i is a constant which takes into account the specific diffusion path and the geometry of the model, p_0 is the vapor pressure, and D_i is the diffusion coefficient for lattice (l), grain boundary (b), or surface (s) diffusion (Johnson, 1978).

Intermediate Stage

As neck growth proceeds there will be a transition in the pore structure to a system of tubular pores lying along the particle junctions; this is the intermediate stage. In this stage, the pore channels shrink in diameter until the geometry becomes unstable to fluctuations of the surface (Rayleigh instability). While the pore channels can shrink by surface diffusion, the path length for transport becomes very large and, thus, shrinkage is controlled by lattice or grain boundary diffusion (Rahaman, 2008). The geometry of the intermediate stage can be envisioned as a truncated octahedron (truncated octahedron) simple model of tubular pores intersected by 3 grain boundaries, Fig. 6(a). With transport from the grain boundary to the pores, Fig. 6(b), the densification rate for lattice diffusion control is

$$\frac{1}{\rho} \left(\frac{dp}{dt} \right) = \frac{10 D_l \gamma_{sv} \Omega}{\rho G^3 k T}$$

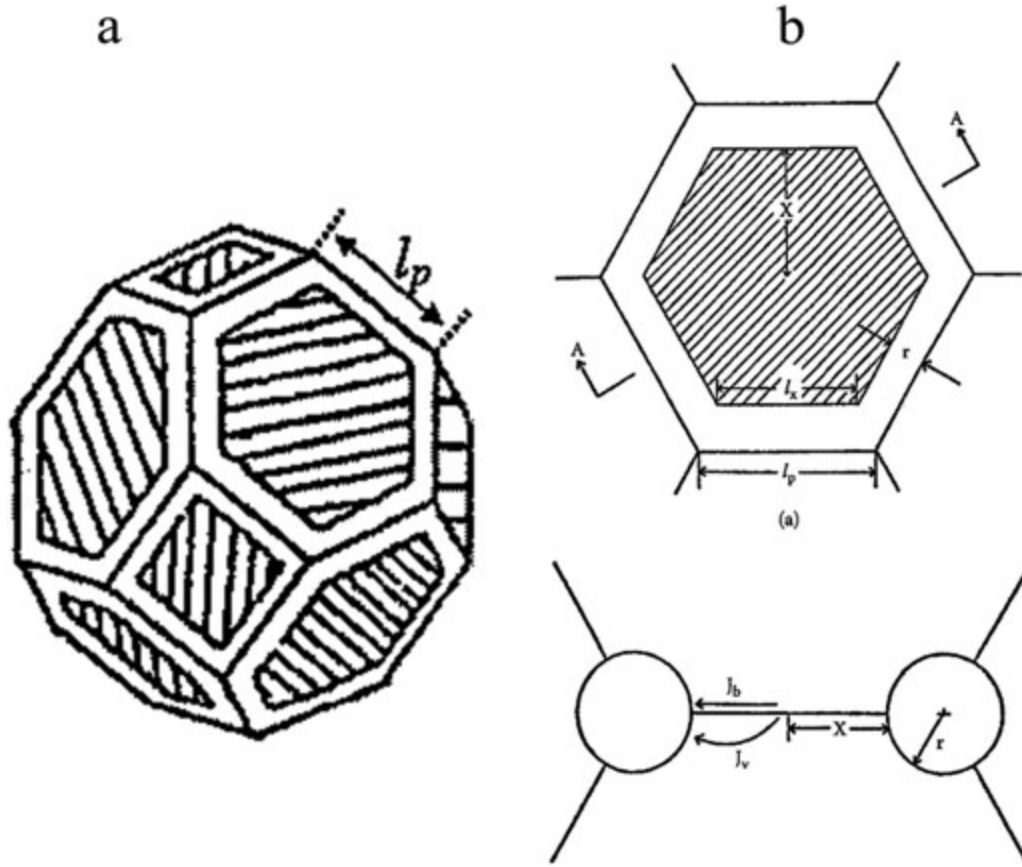


Fig. 6 Intermediate stage sintering model with pore channels being formed along the triple junctions.

When boundary diffusion is the rate controlling mechanism, the densification rate is

$$\frac{1}{\rho} \left(\frac{d\rho}{dt} \right) = \frac{4}{3} \left[\frac{D_{gb} \delta_{gb} \gamma_{sv} \Omega}{\rho (1 - \rho)^{1/3} G^4 kT} \right]$$

Modifications to this model have been developed to account for a realistic pore-boundary intersection that includes the dihedral angle. The size dependence, G^3 or G^4 , is not changed but additional terms are included to account for the more complicated geometry of the pore surface.

Final Stage

When the tubular pores have shrunk to the point where they are unstable, they will break up into isolated pores located at the grain junctions. This is the final stage of sintering and is the critical stage for most applications. It is during this stage that the properties of the compact reach the desired values. In the final stage, several factors must be considered in order to understand the process by which pores are eliminated. The driving force for shrinkage of the pores is the difference in concentration between the atoms on the curved surfaces of the pores and the grain boundaries. As the pores are isolated, surface diffusion can only change the shape of the pores. Shrinkage of the pores is controlled by grain boundary and lattice diffusion. For nearly spherical pores the flux of matter, J , to the pore is approximately:

$$J = K_i D_i \Delta c \left(\frac{r \mathfrak{R}}{\mathfrak{R} - r} \right)$$

where K is a geometric constant, D_i is either the lattice or grain boundary diffusion coefficient, Δc is the concentration difference, r is the radius of the pore, and $\mathfrak{R}$ is the effective source radius of matter being transported to the pore, roughly half the average distance to the neighboring pores.

Dihedral Angle Effect

In the discussion of the initial and intermediate stages it was assumed that the dihedral angle of the grain boundary with the pore surface is 180° , implying that the energy of the grain boundary is very much lower than the energy of the surface. As shown in Fig. 3, many pores have dihedral angles of less than 180° . For a pore on a grain boundary, the dihedral angle, ψ , is defined by the ratio of the grain boundary energy, γ_b , to the surface energy, γ_s , such that

$$\frac{\gamma_b}{\gamma_s} = 2 \cos\left(\frac{\psi}{2}\right)$$

Fig. 7 shows the shapes of pores for different values of the dihedral angle. The curvature of the pore surface increases as the dihedral angle increases, so the driving force for pore shrinkage also increases as the dihedral angle increases. When a pore is located on the junction of three or more grains, the curvature of the pore surface is determined by both the dihedral angle and the number of grains the pore contacts. For a three-sided pore and if $\psi = 60^\circ$ the pore will have straight sides and there will not be a driving force for shrinkage. Hence, this angle is a critical dihedral angle, ψ_{crit} for pore shrinkage. For a four-sided pore, $\psi_{crit} = 70.5^\circ$. The critical dihedral angle as a function of the number of surrounding grains is shown in Fig. 8 (Kingerly and Francois, 1967). Thus, when the dihedral angle is too low, pores will be stable in the structure and there will be a limiting density even though removal of the pores would lower the energy of the system. Ultimately, as grain growth occurs the number of grains intersecting the pore will decrease so that pores will become unstable and shrink. However, as the grain size increases, the diffusion distances increase and the shrinkage rate slows down, making pore removal a relatively slow process.

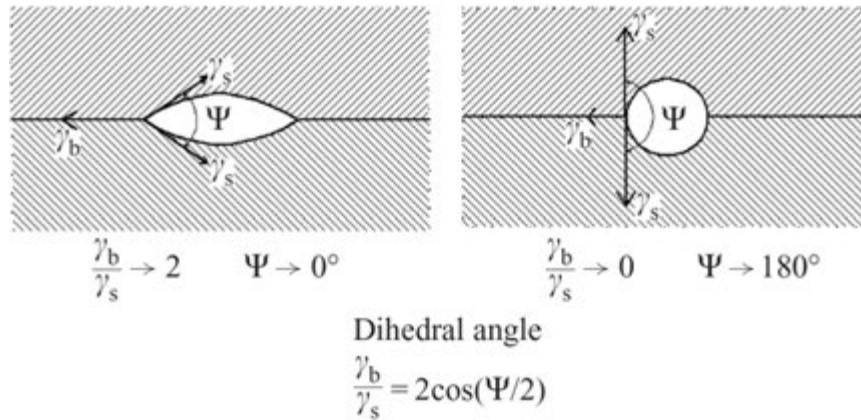


Fig. 7 Dihedral angle shows the effect of surface energy to grain boundary energy ratio on the shape of pores. Low dihedral angles result in elongated pores and high dihedral angles result in spherical pores.

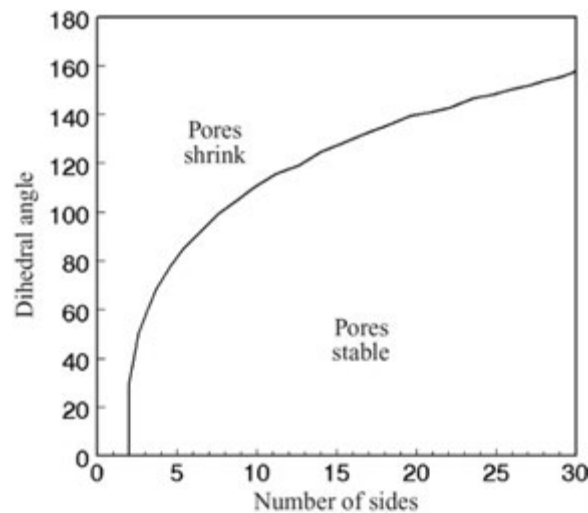


Fig. 8 The stability of pores in the final stage of sintering as a function of the number of grains that the pore contacts. Pores with high numbers of sides will tend to be stable and remain in the structure.

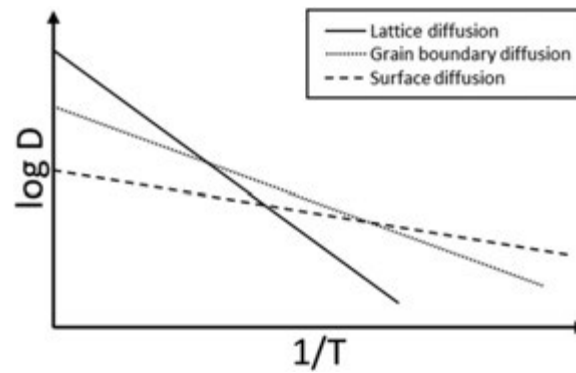


Fig. 9 Typical temperature dependence of lattice, grain boundary and surface diffusion coefficients with temperature.

Pore Entrapment

The rate of pore shrinkage given above assumes that the pore is located on a grain boundary. During grain growth, pores can become entrapped inside a grain. In this case, lattice diffusion is the dominant transport mechanism for pore shrinkage and the diffusion distance is the pore–boundary separation distance. Practically, such pores cannot be eliminated during sintering. Pores can become trapped inside a grain if grain growth occurs during final stage sintering. In the intermediate stage of sintering, large pore channels inhibit grain growth due to the strong drag effect of pores on grain boundary motion. As the densification continues and the final stage of sintering is reached, the pores shrink and their drag effect on grain boundary motion decreases until eventually grain boundaries detach from the pores and grain growth occurs and pores become entrapped in the grains.

For isolated pores (final stage of sintering) on grain boundaries that contain a gas phase that is insoluble in the lattice, shrinkage will be limited by the rate at which the gas can diffuse to the surface of the sample. This can also lead to a limiting density, but changing the atmosphere during sintering can minimize the effect.

Effects of the Heating Rate

The mass transfer mechanisms during sintering have different temperature dependences due to different thermal activation (Fig. 9). Usually, surface diffusion dominates the sintering process at low temperatures, grain boundary diffusion at intermediate temperatures and volume diffusion at high temperatures. For some materials, some of these processes play no significant role, and some might have additional mass transfer processes as e.g., evaporation and condensation at very high temperatures. As surface diffusion does not result in densification but in coarsening and lowers the driving force for densification, fast heating rates are beneficial for densification as less time is available for surface diffusion coarsening. This rationale resulted in the emergence of the fast firing technique: powder compacts are inserted in a furnace that is pre-heated to the sintering temperature to achieve the fastest possible heating rates. Other techniques that utilize fast heating rates to improve densification are SPS and flash sintering (see below) and laser flash sintering.

Effects of Mechanical Pressure

If a mechanical pressure P_a is applied to the system by external means, this pressure adds to the driving force for sintering. However, as the powder compact is not fully dense, the pressure acts on the particle contact area resulting in a higher pressure in the sintering neck area. The effective pressure ΔP_{eff} is higher by a stress intensification factor ϕ :

$$\Delta P_e = \phi P_a$$

The stress intensification factor accounts for the size of the sintering neck relative to the particle size. Usually, it is assumed that ϕ is inversely proportional to the relative density ρ . The modified driving force for sintering is the sum of the two pressures,

$$\Delta P = \frac{2\gamma}{R} + \phi P_a$$

Using this modified driving force for sintering, the shrinkage rate can be obtained for the different diffusion mechanisms and sintering stages as shown in Table 1. Note that for $P_a = 0$ the equations reduce to the pressureless densification rates.

In general, applying a mechanical pressure is useful for materials where high densities are not achieved with pressure-less sintering as e.g., classically the case for refractory or transparent materials. There are different ways of applying mechanical pressure to a powder compact. Uniaxial pressures are applied in hot pressing and spark plasma sintering (SPS).

Table 1 Densification rate $\frac{1}{\rho} \frac{d\rho}{dt}$ for pressure assisted sintering with different mass transport mechanisms. D is the respective diffusion coefficient (l: lattice, gb: grain boundary), Ω the molecular volume, G the grain size, k the Boltzmann constant, γ_{sv} the surface energy, r the pore radius

Mechanism	Intermediate stage	Final stage
Lattice diffusion	$\frac{1}{\rho} \frac{d\rho}{dt} = \frac{40}{3} \left(\frac{D_l \Omega}{G^2 kT} \right) \left(P_a \phi + \frac{\gamma_{sv}}{r} \right)$	$\frac{1}{\rho} \frac{d\rho}{dt} = \frac{40}{3} \left(\frac{D_l \Omega}{G^2 kT} \right) \left(P_a \phi + \frac{2\gamma_{sv}}{r} \right)$
Grain boundary diffusion	$\frac{1}{\rho} \frac{d\rho}{dt} = \frac{95}{2} \left(\frac{D_{gb} \Omega}{G^3 kT} \right) \left(P_a \phi + \frac{\gamma_{sv}}{r} \right)$	$\frac{1}{\rho} \frac{d\rho}{dt} = \frac{15}{2} \left(\frac{D_{gb} \Omega}{G^3 kT} \right) \left(P_a \phi + \frac{2\gamma_{sv}}{r} \right)$
Dislocation motion ^a	$\frac{1}{\rho} \frac{d\rho}{dt} = A \left(\frac{D_{\mu b}}{kT} \right) \left(\frac{P_a \phi}{\mu} \right)^n$	$\frac{1}{\rho} \frac{d\rho}{dt} = B \left(\frac{D_{\mu b}}{kT} \right) \left(\frac{P_a \phi}{\mu} \right)^n$

^aA and B are numerical constants; n is an exponent that depends on the mechanism of dislocation motion.

In hot pressing, a punch-die combination (typically graphite) is used in a vacuum furnace and with a load frame. Heating rates are limited by the furnace (typically <50 K/min). Maximum pressures and temperatures are limited by the heater and die materials and are in the order of 2200°C and 100 MPa.

Spark plasma sintering (SPS) is similar to hot pressing in that a uniaxial pressure is applied to a graphite-based punch-die combination. However, the punch-die combination is heated directly by an electrical current resulting from a voltage between the two rams of the press. While maximum pressures and temperatures are comparable to hot pressing, much higher heating rates (more than 200K/min) can be used, resulting in less time for coarsening during heating as discussed above. SPS sintering is used for refractory materials, but also for applications where a fine-grained microstructure is needed.

Hot isostatic pressing (HIP) uses gas pressure in an autoclave. Mostly, nitrogen or argon is used along with graphite heaters. Typical maximum temperatures and pressures are 2200°C and 400 MPa. Note that this method only densifies the closed porosity as, for open porosity, the pressure does not load the particle contact area. This requires a pre-sintering to about 94% relative density by conventional sintering.

Applying a mechanical pressure to closed porosity can result in a build-up of high gas pressure in the remaining porosity as it shrinks. This pressure can result in pore swelling and de-sintering if high temperatures are subsequently applied without pressure e.g., during pressureless cooling after sintering or during a high-temperature application.

Effects of Electric Fields and Currents

The impact of electric fields and currents on sintering have been observed to greatly affect the densification rate as observed recently in flash sintering. For flash sintering, the powder compact is contacted by electrodes and a voltage is applied during the heating ramp. If the conductivity of the powder compact increases with increasing temperature, an increasing current flow occurs resulting in a direct heating of the sample, until a thermal runaway event occurs. The electric current during flash sintering results in Joule heating of the powder compact and this can result in very high heating rates, many hundred K/min that are beneficial for densification. While SPS sintering does not involve a thermal run-away of the sample, electric currents might flow through the powder compact if its conductivity is higher than the surrounding graphite die.

The impact of the electric field itself is controversial and still being investigated. While the electric field is not relevant to the curvature driving force for sintering, it can result in electromigration of charged defects and result in a microstructure gradient and a variation of properties along the electric field. Electric fields can result in the nucleation of additional defects (e.g., point defects and dislocations) that may increase transport. Electrolytic decomposition at the electrodes is another effect that can occur due to electric field assisted sintering.

Effects of Constraints

Mechanical constraints inhibit the shrinkage of a powder compact during sintering and can result in anisotropic densification and cracking. Such constraints occur when a powder layer is sintered on a dense substrate or if a composite with different densification rates are co-sintered. In general, the constraint results in a lower densification rate:

$$\left(\frac{\dot{\rho}}{\rho} \right)_{\text{constraint}} = \frac{1+v}{1-v} \times \frac{1}{3} \times \left(\frac{\dot{\rho}}{\rho} \right)_{\text{free}}$$

with the shrinkage rate $(\dot{\rho}/\rho)$, the relative density ρ and the viscous Poisson's ratio v . Constraints on sintering frequently result in residual porosity, delamination and sintering distortion due to mechanical stresses developed at the constraint.

Summary

This chapter is a summary of the basic ideas of solid-state sintering. Many of the features of sintering are well understood. It is clear from the modeling and experiments that particle size is a dominant factor in controlling sintering rates. Other important

parameters are the transport mechanisms that dominate sintering in a given case, heating rates and mechanical pressures. Along with an emerging understanding of these parameters, different sintering techniques are being developed, as e.g., SPS sintering which utilizes fast heating rates and a mechanical load to obtain fast densification.

References

- Bordia, R.K., Kang, S.-J.L., Olevsky, E.A., 2017. Current understanding and future research directions at the onset of the next century of sintering science and technology. *Journal of the American Ceramic Society* 100, 2314–2352.
- Castro, R., van Benthem, K. (Eds.), 2013. *Sintering: Mechanisms of Conventional Nanodensification and Field Assisted Processes*. Springer.
- Coble, R.L., 1961. Sintering crystalline solids. *Journal of Applied Physics* 32, 789–792.
- Exner, H.E., 1979. Principles of single phase sintering. In: *Reviews on Powder Metallurgy and Physical Ceramics*, 1. Israel: Freund Publishing House, pp. 1–4.
- Frenkel, J., 1945. Viscous flow of crystalline bodies under the action of surface tension. *The Journal of Physics* 9, 385.
- German, R.M., 1996. *Sintering Theory and Practice*. New York: Wiley.
- Handwerker, C.A., Blendell, J.E., Coble, R.L., 1989. Sintering of ceramics. In: Uskokovic, D.P., Palmour III, H., Spriggs, R.M. (Eds.), *Science of Sintering*. New York: Plenum Press, pp. 3–37.
- Handwerker, C.A., Blendell, J.E., Kaysser, W.A., 1990. Ceramic transactions. In: *Sintering of Advanced Ceramics*, 7. Westerville, OH: American Ceramic Society.
- Johnson, D.L., 1978. Fundamentals of the sintering of ceramics. In: Palmour, H., Davis, R.F., Hare, T.M. (Eds.), *Processing of Crystalline Ceramics*. New York: Plenum Press.
- Kang, S.-J.L., 2005. *Sintering*. Boston: Elsevier.
- Kingery, W.D., Francoise, B., 1967. Sintering of crystalline oxides. In: Kuczynski, G.C., Hooton, N.A., Gibson, C.F. (Eds.), *Sintering and Related Phenomena*. New York: Gordon and Breach, p. 471.
- Kuczynski, G.C., 1949. Self-diffusion in sintering of metal particles. *Trans. AIME* 185, 169–178.
- Rahaman, M.N., 2008. *Sintering of Ceramics*. New York: CRC Press.

Liquid Phase Sintering: Fundamentals

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When a powder mixture compact of at least two different components is heated up above the eutectic temperature of the components or the melting temperature of a component with a low melting point, a liquid phase forms and sintering proceeds in the presence of the liquid phase. This sintering process is called liquid phase sintering (LPS) as long as the liquid phase is retained during the whole period of sintering time. (If the liquid phase disappears during sintering, the process is called transient liquid phase sintering. We will not consider this case in this chapter).

The liquid phase sintering technique has been used for several thousand years for fabricating traditional ceramics as an art in pottery, bricks and porcelains. This technique is now widely utilized as an essential technique for fabricating modern ceramic materials and components, such as Al_2O_3 -, ZnO -, TiO_2 -, BaTiO_3 -, $\text{Pb}(\text{Zr,Ti})\text{O}_3$ -, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -, $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ -, $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ -, SiC -, Si_3N_4 -, and SiAlON -based ceramics for structural, functional and electronic applications.

Scientific studies on sintering, including LPS, started in the late 1940s and early 1950s (Kang, 2005). Several models (Cannon and Lenel, 1953; Kwon and Yoon, 1981; Kang *et al.*, 1991; Svoboda *et al.*, 1996) and theories (Kingery, 1959; Kwon, 1996; Mortensen, 1997; Lee and Kang, 1998) have been developed. The developed models are basically for different stages, where a dominant mechanism was postulated for each stage. For example, a classical model (Cannon and Lenel, 1953) suggested three stages of densification: (1) particle rearrangement due to liquid flow at the early stage, (2) contact flattening between particles by dissolution and precipitation of a solid phase through the liquid, and (3) solid-state sintering between particles. Later, filling pores with liquid was another mechanism of densification (Kwon and Yoon, 1981; Kang *et al.*, 1991). The pore filling stage has sometimes been presumed to be the last stage of LPS.

The available models and theories of LPS concern different roles of the liquid in the compact: (1) the provision of a diffusion path of atoms dissolved from particles and (2) capillary action of the liquid that leads its flow. The former plays a passive role for densification as well as grain growth and the latter an active role for densification. If these two roles of liquid are absent, the sintering behavior and kinetics must be similar to those in solid-state sintering. In this chapter, we will describe these two different roles of liquid in relation to densification and grain growth.

General Phenomena of Liquid Phase Sintering

For LPS to proceed, the solid must be soluble in the liquid and the wetting angle must be low. If the solubility is negligible, the transport of atoms through the liquid and its contribution to densification and grain growth must also be negligible. If the wetting angle is large, densification will not proceed and swelling of the compact or sweating of liquid at the compact surface can occur.

Fig. 1 is an example of microstructural evolution during LPS (Park *et al.*, 1989). (Although the system is metallic, the figure clearly shows the typical evolution of microstructure during LPS.) Considerable densification as well as remarkable grain growth took place during the LPS. At the LPS temperature of this W-Ni-Fe sample, such a considerable sintering is impossible for a W powder compact (with a melting point of 3422°C) without a liquid phase in the sample. When a liquid phase forms in a powder compact, atom transport through the liquid and mass flow of the liquid itself can take place. The former can induce densification and grain growth, while the latter only densification.

For densification during LPS, a few models and theories have been developed for different stages. They include particle rearrangement with the appearance of a liquid, contact flattening in the presence of a liquid film at the areas of particle contact, and liquid filling of pores. For grain growth, basically two models are available, a diffusion control model and a mixed (either diffusion or interface reaction) control model. We will describe and discuss the mechanisms of densification and then the mechanisms of grain growth and related microstructural evolution.

Densification During Liquid Phase Sintering

Densification during LPS is a process for developing a dense and equilibrium microstructure for a given volume fraction of liquid and given sizes of particles. In a fully dense sample with the minimum total interfacial energy, the liquid is in a hydrostatic pressure and no excess pressure is present between particles. There are a few processes that can contribute to densification and obtaining an equilibrium microstructure. They include (1) a change in powder packing (particle rearrangement) due to liquid flow at the moment of liquid formation, (2) atom transport from the contact area to the off-contact area, and (3) liquid filling of pores.

Particle Rearrangement

When a liquid phase forms, liquid redistribution takes place because of uneven capillary forces around particles. For a system with a low wetting angle, liquid penetration between solid particles occurs as the sizes of the capillaries at the contact and neck regions

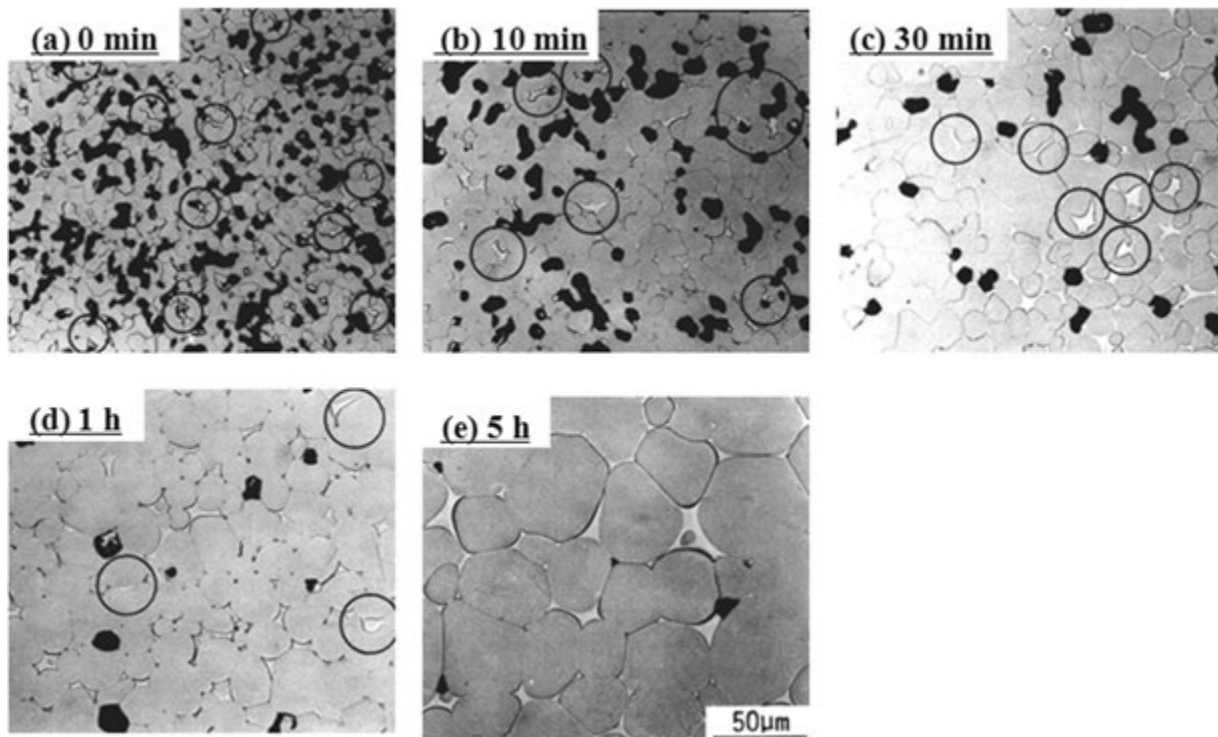


Fig. 1 Microstructural change during liquid phase sintering of 98W(5 μ m)–1Ni–1Fe (wt%) at 1460°C for various periods of time. Circles indicate liquid pockets formed by pore filling. Reproduced from Park, J.K., Kang, S.-J.L., Eun, K.Y., Yoon, D.Y., 1989. The microstructural change during liquid phase sintering. *Metall. Trans. A* 20, 837–845.

are, in general, smaller than that of the bulk liquid formed between particles. This process is similar to the flow of water in a glass tube with two different diameters from the region with a large diameter to that with a small diameter. During liquid flow (penetration) between particles, the particles can move along with the flow (particle rearrangement). The particle rearrangement is possible only for systems with no solid bonding between particles at the moment of liquid formation and those with the dihedral angle of zero degrees. If grain boundaries form during heating to the liquid phase sintering temperature and the dihedral angle is non-zero, such as the case in [Fig. 1\(a\)](#), particle rearrangement is impossible even right after the liquid formation.

Assuming that each particle is surrounded by liquid, it was suggested that particle rearrangement during LPS could be modeled as a viscous flow ([Kingery, 1959](#); [Kwon, 1996](#)) and could considerably enhance densification. A mass flow of a solid-liquid mixture, however, seems to be possible only in systems with a dihedral angle of zero degrees and pores much larger than particles, as in a previous experiment ([Kang et al., 1984](#)). If the pore size is comparable with the particle size and the liquid volume fraction is not sufficient for filling all the pores, only a local rearrangement of particles would be possible. [Fig. 2](#) ([Lee et al., 1999](#)) shows simulated microstructural evolution after liquid formation in a two-dimensional compact of spherical particles with a coating of a low melting component. The microstructures show that overall densification occurred, forming fairly dense regions, and at the same time, the size of relatively large original pores increased due to local rearrangement and densification. Although this simulation study as well as previous studies ([Kingery, 1959](#); [Kwon, 1996](#)) suggest the possibility of considerable contribution of particle rearrangement to densification, its contribution, however, may be inconsiderable in real systems. The literature has not, so far, reported a considerable enhancement of densification for an expected time period of liquid flow.

Contact Flattening Versus Pore Filling

Contact flattening

After the formation and redistribution of a liquid, the microstructure of a powder compact generally consists of fairly dense agglomerated (clustered) regions of particles and liquid, and pores distributed between the agglomerated regions, as shown in [Fig. 1\(a\)](#). In such a sample with agglomerated regions, fast transport of atoms can occur through the liquid phase via dissolution and precipitation of solid among grains.

At the early stage of LPS, a compressive force can be exerted between particles in contact with one another due to the capillary pressure and surface tension of the liquid. Material can be transported from the contact area to an off-contact area (this process is called contact flattening), which can contribute to grain shape accommodation, and to densification and shrinkage. This is the basic idea of the classical contact flattening theory of LPS ([Kingery, 1959](#)). Under the assumption that the microstructure was

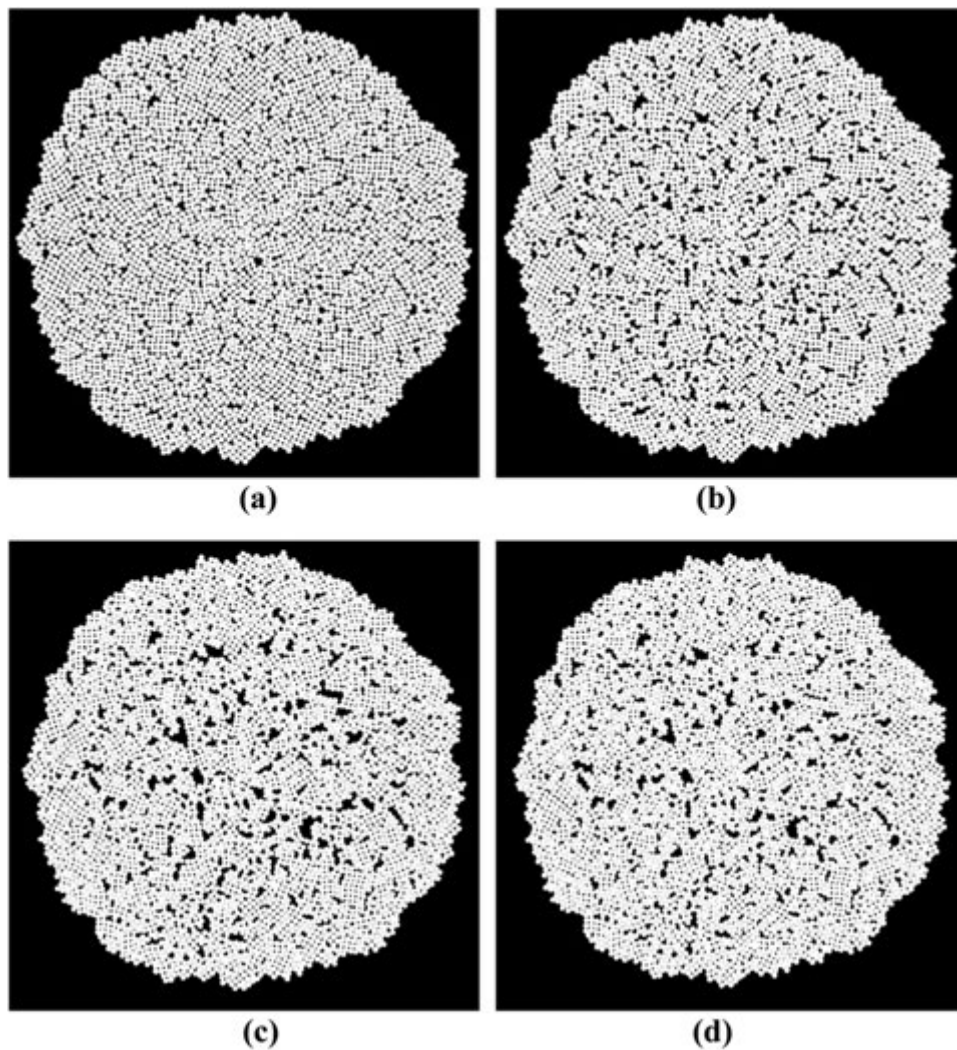


Fig. 2 Simulated microstructural evolution of a two-dimensional particle array with holding time for liquid viscosity of $1 \text{ mPa} \cdot \text{s}$: (a) 0.08 , (b) 0.2 , (c) 0.6 , and (d) $3 \mu\text{s}$. Reproduced from Lee, S.-M., Chaix, J.-M., Martin, C.L., Allibert, C.H., Kang, S.-J.L., 1999. Computer simulation of particle rearrangement in the presence of liquid. *Metals Mater.* 5, 197–203.

simplified as mono-sized particles with a dihedral angle of zero degrees and uniformly distributed pores at the neck of the particles, the theory claims a continuous and considerable contribution of contact flattening to densification until the complete elimination of pores. The theory, however, much overestimates the material removal from the contact area because the driving force for the material transport quickly decreases with grain shape accommodation.

When the grains attain their equilibrium shape with the minimum total interfacial energy for a given liquid volume fraction around the grains, the driving force for contact flattening disappears in an agglomerate. Thus, there is no shrinkage of pores that are located around the agglomerate. If we ignore the shape of grains at the surface, the microstructure of a dense agglomerate with grains of an equilibrium shape must be the same as that of a dense bulk material with the same liquid volume fraction. The only difference is the size of the sample and the size of pores. The pore size is infinite for a bulk sample, while the pore size is finite for an agglomerate.

For an agglomerated region of particles (grains) and liquid, grain shape accommodation can occur not only by the removal of solid from the contact area but also by growth of grains. A model calculation (Lee and Kang, 2001) showed that the contribution of grain growth to grain shape accommodation is more significant than that of contact flattening. Therefore, the driving force for contact flattening can quickly decrease and disappear. As a result, the contribution of contact flattening to densification is much less than that predicted by the contact flattening theory.

For the hypothesized microstructure of the contact flattening theory, where grain growth does not take place, the contribution of contact flattening can be significant for systems with a zero dihedral angle until liquid filling of pores takes place (Kang, 2005). In real systems, however, it is not possible that no grain growth would occur in an LPS sample. In addition, for systems with a non-zero dihedral angle, where the material transport from the contact area occurs in a solid state, the con-

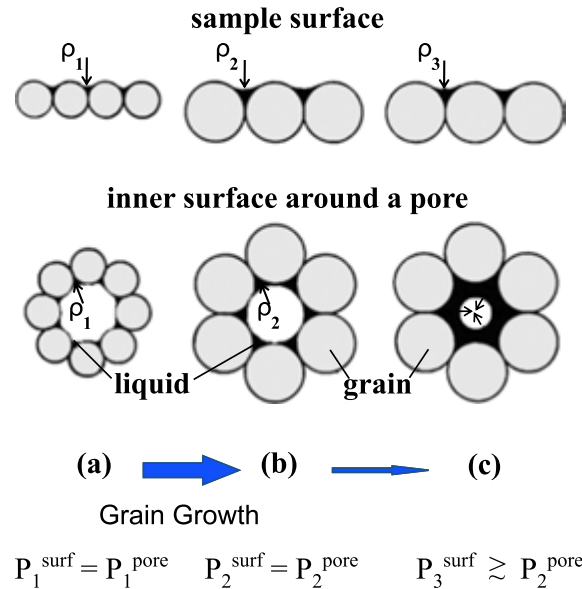


Fig. 3 Schematic changes in the liquid meniscus radius at the sample surface and at a pore surface during grain growth. (a) before liquid filling of the pore (stable state of the pore), (b) critical moment for pore filling (complete wetting of the pore surface) and (c) liquid flow into the pore (pore filling) immediately after the critical moment. P : pressure in the liquid; ρ : the radius of liquid meniscus ($\rho_1 < \rho_2$, $\rho_2 \lesssim \rho_3$). Reproduced from Kang, S.-J.L., Greil, P., Mitomo, M., Moon, J.-H., 1989. Elimination of large pores during gas-pressure sintering of β' -Sialon. *J. Am. Ceram. Soc.* 72, 1166–1169.

tribution of contact flattening must be almost nil. It appears that densification by contact flattening is insignificant in real systems, in particular those with a non-zero dihedral angle.

Pore filling

It was observed in the early 1980s that pores with a much bigger size than grains were eliminated by liquid flowing into them (liquid filling of pores) (Kwon and Yoon, 1981). Several subsequent experiments supported the pore filling to be the major mechanism of densification during LPS, irrespective of the shape and size of pores (Kang *et al.*, 1984; Park *et al.*, 1989). The pore filling model and theory were developed in the 1990s (Kang *et al.*, 1991; Lee and Kang, 1998).

Pore filling is a result of a liquid flow in a sample, as in the case of liquid penetration among particles. When the driving force for contact flattening disappears with grain shape accommodation, the pores around a dense solid-liquid agglomerate become stable. As long as a pore is stable, no matter the size, the microstructure of the dense region with an equilibrium microstructure will evolve in a self-similar manner. Whenever the pressure in a liquid becomes uneven, liquid flows from a region with a high pressure to a region with a low pressure. Such a situation can arise during growth of grains.

Fig. 3 (Kang *et al.*, 1989) schematically depicts the growth of grains and a related change in liquid meniscus radius at the sample surface and at a pore surface. If the gas pressure in the pores is the same as that outside the sample, the radius of the liquid meniscus is the same everywhere, including the sample surface and the pore surface because of the hydrostatic pressure in the liquid. As grains grow, the radius of the liquid meniscus increases in proportion because the microstructure in a dense body evolves self-similarly. When the radius of the liquid meniscus becomes the same as the radius of a pore (in the case of a wetting angle of zero degrees), the pore surface is completely wetted by the liquid (**Fig. 3(b)**). With further growth of grains (**Fig. 3(c)**), the radius of the liquid meniscus at the sample surface and other unwetted pore surfaces increases further. However, at the surface of the just wetted pore, the meniscus radius is limited to the pore radius. A pressure imbalance arises in the liquid and liquid flows into the wetted pores from all the densified region (pore filling). The critical radius of the liquid meniscus for liquid filling of pores is proportional to the pore size, which is, in turn, proportional to the grain size. Therefore, liquid filling occurs in temporal sequence: small pores earlier and large pores later. Experimental observations, including that in **Fig. 1**, show that small pores disappear earlier and large pores remain intact for a longer time, which supports the prediction of the pore filling model (Kang *et al.*, 1991).

Based on the understanding of the pore filling process, the pore filling theory was developed, which predicts the effects of various processing parameters, including pore size and distribution, liquid volume fraction, wetting and dihedral angle, and entrapped insoluble gases (Lee and Kang, 1998). As the densification by pore filling is induced by grain growth (grain growth-induced densification), its kinetics is dependent on the grain growth kinetics. If grain growth kinetics follows a cubic law, the densification kinetics with respect to scale also follows a cubic law. It is also possible to describe the microstructural evolution on a relative density versus grain size plane, for example, as shown in **Fig. 4** (Lee and Kang, 2005). It appears that pore filling, which is a result of grain growth, is the dominant mechanism of densification during LPS.

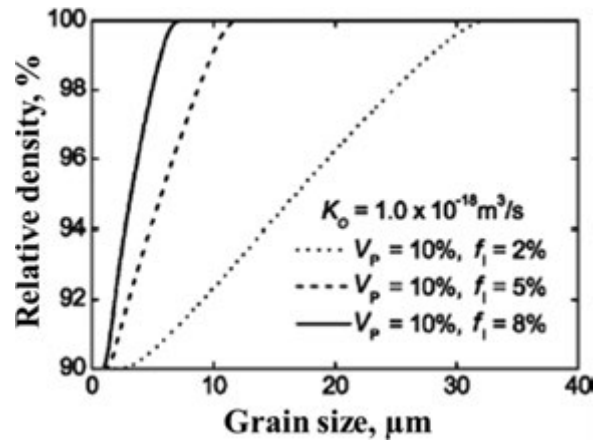


Fig. 4 Calculated microstructural evolution diagram during liquid phase sintering showing the effect of the liquid volume fraction according to the pore filling theory. K_0 : grain growth constant; V_p : pore volume; f_l : liquid volume fraction. Reproduced from Lee, S.-M., Kang, S.-J.L., 2005. Microstructure development during liquid-phase sintering. *Z. Metallkd.* 96, 141–147.

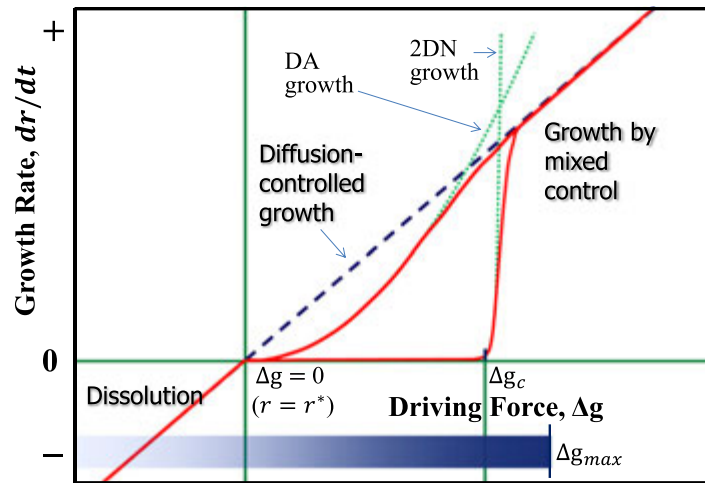


Fig. 5 Schematic showing the growth rate of a single crystal in a liquid as a function of the driving force for different growth modes. A schematic range of the driving force in a powder compact is also shown to explain the mixed control model of grain growth. 2DN: two-dimensional nucleation; DA: defect-assisted; $\Delta g_{\max}$: the maximum driving force for the largest grain in the sample. Reproduced from Kang, S.-J.L., Jung, Y.-I., Jung, S.-H., Fisher, J.G., 2013. Interface structure-dependent grain growth behavior in polycrystals. In: Molodov, D.A. (Ed.), *Microstructural Design of Advanced Engineering Materials*. Weinheim:Wiley-VCH Verlag GmbH & Co.

Grain Growth During Liquid Phase Sintering

Grain growth (coarsening) in a matrix, either a liquid or a solid, is called Ostwald ripening. Ostwald ripening is the result of growth and shrinkage of individual single crystal grains in a matrix. Therefore, crystal growth and dissolution theories (Hirth and Pound, 1963; Peteves and Abbaschian, 1991) can be useful for understanding grain growth behavior during LPS.

Growth of a single crystal is the result of serial processes of diffusion of atoms through the matrix towards the crystal and attachment (interface reactions) of the transported atoms at the surface of the growing single crystal. According to the crystal growth theories, in the growth of a spherical crystal, which has an enormous number of surface defects, there is no energy increase with atom attachment, and the interface reaction kinetics is much faster than the diffusion of atoms through the liquid. Therefore, the growth rate is linearly proportional to the driving force for crystal growth (diffusion), as schematically shown in Fig. 5 (Kang *et al.*, 2013) as a dashed straight line.

On the other hand, for a faceted polyhedral crystal with atomically ordered surfaces, the attachment of a transported atom (interface reaction) increases the surface energy because it has an energy barrier for atom attachment. If the growth of a faceted single crystal is governed by the formation of a two-dimensional nucleus (2DN) and its growth on a flat surface, the interface reaction rate is expressed as an exponential function of the driving force for crystal growth, as schematically shown in Fig. 5 (Kang *et al.*, 2013) as a

dotted curve. If there are surface defects, for example screw dislocations on the surface, the kinetics is enhanced and expressed to be proportional to the square of the driving force. Therefore, for the growth of a faceted crystal, there is a range where interface kinetics is slower than diffusion kinetics and another range where interface kinetics is faster than diffusion kinetics. (Note that the dissolution rate is always linearly proportional to the driving force for dissolution because each corner of a faceted crystal acts as a dissolution source without an energy barrier and multilayer dissolution can occur (Jung *et al.*, 2009)). As the slower process governs the overall kinetics in serial processes, the interface reaction is the governing process for a small driving force while the diffusion is the governing process for a large driving force, as schematically shown in Fig. 5 as thick solid lines. A critical driving force is present for the transition from the interface reaction control to the diffusion control. The critical driving force is affected by the faceting tendency of the crystal; it increases with an increasing faceting tendency.

In a sample being sintered, where numerous grains are present, each grain has its own driving force for growth or dissolution relative to the grain that neither grows nor shrinks at the moment of observation. Therefore, there is a range of driving force in a sample as schematically shown in Fig. 5. The maximum driving force for growth is for the largest grain in the sample.

For a sample with spherical grains, the growth rate of grains is linearly proportional to the driving force. For such a system, the well-known Lifshitz-Slyozov-Wagner (LSW) theory (Lifshitz and Slyozov, 1961; Wagner, 1961) and related theories (German and Olevsky, 1998) predict normal grain growth with an invariable distribution of grain sizes relative to the average grain size. A cubic law, where the cube of the average grain size is proportional to the annealing time, is valid for a system with spherical grains. Many experimental observations confirm normal grain growth in systems with spherical grains.

In a sample with faceted grains, the growth rate of grains whose driving forces are smaller than a critical value is insignificant, in particular for the growth by 2DN. On the other hand, the growth rate of grains whose driving forces are larger than the critical value is considerable and linearly proportional to the driving force for growth. The growth of a grain is controlled either by interface reaction or diffusion (mixed control). The grain growth behavior in a faceted system is then governed by the relative value between the maximum driving force for the largest grain in the sample, $\Delta g_{\max}$, and the critical driving force for diffusion control, Δg_c . Based on this understanding, Kang and his coworkers (Jung *et al.*, 2009; Kang *et al.*, 2009) deduced the mixed mechanism principle of microstructural evolution. The principle predicts various types of time dependent grain growth behavior in terms of the relative value between $\Delta g_{\max}$ and Δg_c :

- (1) $\Delta g_c = 0$: Normal grain growth (NGG)
- (2) $0 < \Delta g_c \ll \Delta g_{\max}$: Pseudo-normal grain growth (PNGG)
- (3) $0 < \Delta g_c \lesssim \Delta g_{\max}$: Abnormal grain growth (AGG)
- (4) $\Delta g_{\max} \ll \Delta g_c$: Stagnant grain growth (SGG)

From the principle, they also deduced some strategies for suppressing AGG (Fisher and Kang, 2018). The validity and the generality of the mixed mechanism principle seem to be well supported by a large number of experiments for metals as well as ceramics (Kang *et al.*, 2013).

As densification by pore filling is induced by grain growth, even AGG can be beneficial for densification. A beneficial effect of AGG for densification was observed in a few cemented carbide systems. It seems that densification in a faceted system occurs mostly via pore filling with grain growth.

Concluding Remarks

Densification during liquid phase sintering is a process for developing an equilibrium microstructure with the minimum total interfacial energy for a given grain size and a given liquid volume fraction. During this process grain growth also takes place. In LPS, the role of liquid is critical for both densification and grain growth. A liquid phase provides a diffusion medium of atoms dissolved from grains and also flows by itself during sintering. The former contributes mostly to grain growth (Ostwald ripening) but marginally to densification (contact flattening). The flow of liquid right after the formation of a liquid phase can rearrange particles, of which the contribution to densification seems to be insignificant. Most densification can be achieved by liquid filling of pores, which is induced by grain growth. The pore filling theory predicts the effects of various processing parameters on densification by pore filling.

Various types of microstructures appear during LPS. The conventional Ostwald ripening theory (the LSW theory), which predicts only normal grain growth, is valid for systems with spherical grains. For systems with (even partially) faceted grains, grain growth behavior varies with sintering time. Based on the crystal growth theories, the mixed control theory of grain growth and the mixed mechanism principle of microstructural evolution were developed. Many experimental observations for metals as well as ceramics supported the validity and the generality of the microstructural evolution principle.

References

- Cannon, H.S., Lenel, F.V., 1953. Some observations on the mechanism of liquid phase sintering. In: Benesovsky, F. (Ed.), *Pulvermetallurgie (Proceedings First Plansee Seminar)*. Reutte: Metallwerk Plansee, pp. 106–121.
- Fisher, J.G., Kang, S.-J.L., 2018. Strategies and practices for suppressing abnormal grain growth during liquid phase sintering. *J. Am. Ceram. Soc.* 102, 717–735.
- German, R.M., Olevsky, E.A., 1998. Modeling grain growth dependence on the liquid content in liquid-phase-sintered materials. *Metall. Mater. Trans. A* 29, 3057–3067.

- Hirth, J.P., Pound, G.M., 1963. Condensation and Evaporation, Nucleation and Growth Kinetics. Oxford: Pergamon Press.
- Jung, Y.I., Yoon, D.Y., Kang, S.-J.L., 2009. Coarsening of polyhedral grains in a liquid matrix. *J. Mater. Res.* 24, 2949–2959.
- Kang, S.-J.L., 2005. Sintering: Densification, Grain Growth, and Microstructure. Oxford: Elsevier Butterworth-Heinemann.
- Kang, S.-J.L., Kim, K.-H., Yoon, D.N., 1991. Densification and shrinkage during liquid phase sintering. *J. Am. Ceram. Soc.* 74, 425–427.
- Kang, S.-J.L., Lee, M.G., An, S.M., 2009. Microstructural evolution during sintering with control of the interface structure. *J. Am. Ceram. Soc.* 92, 1464–1471.
- Kang, S.-J.L., Kaysser, W.A., Petzow, G., Yoon, D.N., 1984. Elimination of pores during liquid phase sintering of Mo-Ni. *Powder Metall.* 27, 97–100.
- Kang, S.-J.L., Greil, P., Mitomo, M., Moon, J.-H., 1989. Elimination of large pores during gas-pressure sintering of β' -Sialon. *J. Am. Ceram. Soc.* 72, 1166–1169.
- Kang, S.-J.L., Jung, Y.-I., Jung, S.-H., Fisher, J.G., 2013. Interface structure-dependent grain growth behavior in polycrystals. In: Molodov, D.A. (Ed.), *Microstructural Design of Advanced Engineering Materials*. Weinheim: Wiley-VCH Verlag GmbH & Co.
- Kingery, W.D., 1959. Densification during sintering in the presence of a liquid phase. I. Theory. *J. Appl. Phys.* 30, 301–306.
- Kwon, O.-H., 1996. Liquid-phase sintering. In: Brook, R.J. (Ed.), *Processing of Ceramics. Part II. Materials Science and Technology 17B*. New York: VCH.
- Kwon, O.J., Yoon, D.N., 1981. Closure of isolated pores in liquid phase sintering of W-Ni. *J. Powder Metall. Powder Technol.* 17, 127–133.
- Lee, S.-M., Kang, S.-J.L., 1998. Theoretical analysis of liquid phase sintering: Pore filling theory. *Acta Mater.* 46, 3191–3202.
- Lee, S.-M., Kang, S.-J.L., 2001. Evaluation of densification mechanisms of liquid-phase sintering. *Z. Metallkd.* 92, 669–674.
- Lee, S.-M., Kang, S.-J.L., 2005. Microstructure development during liquid-phase sintering. *Z. Metallkd.* 96, 141–147.
- Lee, S.-M., Chaix, J.-M., Martin, C.L., Allibert, C.H., Kang, S.-J.L., 1999. Computer simulation of particle rearrangement in the presence of liquid. *Metals Mater.* 5, 197–203.
- Lifshitz, I.M., Slyozov, V.V., 1961. The kinetics of precipitation from supersaturated solid solutions. *J. Phys. Chem. Solids* 19, 35–50.
- Mortensen, A., 1997. Kinetics of densification by solution-reprecipitation. *Acta Mater.* 45, 749–758.
- Park, J.K., Kang, S.-J.L., Eun, K.Y., Yoon, D.Y., 1989. The microstructural change during liquid phase sintering. *Metall. Trans. A* 20, 837–845.
- Peteves, S.D., Abbaschian, R., 1991. Growth kinetics of solid-liquid Ga interfaces: Part II. Theoretical. *Metall. Trans. A* 22, 1271–1286.
- Svoboda, J., Riedel, H., Gaebel, R., 1996. A model for liquid phase sintering. *Acta Mater.* 44, 3215–3226.
- Wagner, C., 1961. Theorie der altering von Niederschlaegen durch Umloesen (Ostwald-reifung). *Z. Elektrochemie* 65, 581–591.

Viscous Sintering

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Viscous Sintering

Viscous sintering is a process by which a noncrystalline material reduces its surface area, and thereby reduces its free energy. The process is illustrated in Fig. 1, which shows spherical particles of glass coalescing, just as raindrops on a window merge to reduce their surface area. In contrast to crystalline materials, where sintering involves diffusion of vacancies in the crystal lattice, noncrystalline materials sinter by viscous flow. The rate of viscous sintering is found to be insensitive to the details of the microstructure of the material, so the rate of densification can be estimated given only the viscosity and surface tension of the material and its average pore size. In practice, materials are often constrained during sintering; for example, the densification rate of a film is reduced by its attachment to a substrate that does not shrink as the film does. The sintering rate can be calculated in such cases, if the mechanical properties of the porous material are known. An important type of constraint is crystallinity, because crystalline inclusions sinter more slowly than glass, so they retard the overall shrink-age.

Sintering Models

The theoretical basis for viscous sintering was established by Frenkel (1945), who argued that the energy needed to drive viscous flow is provided by reducing the surface area of the body (thereby releasing the surface energy); therefore, the rate of sintering can be found by equating those two energies. To calculate the energy that is dissipated by viscous flow as a certain amount of surface area is eliminated, it is necessary to choose a particular microstructural model. Frenkel analyzed the coalescence of spheres, as in Fig. 1. That is a surprisingly difficult problem to solve exactly, because the region of contact between particles has a complicated shape, so Frenkel had to make severe simplifying assumptions about the pattern of viscous flow. The distance, L , between the centers of a pair of sintering spheres was found to decrease linearly with time, t , according to

$$\frac{L[0] - L[t]}{L[0]} = \frac{3 \gamma r}{8 \eta a} \quad (1)$$

where γ is the surface tension, η is the viscosity, and a is the initial radius of the spheres.

This linear shrinkage rate has been experimentally verified. A detailed numerical simulation of the flow within sintering spheres was performed by Jagota and Dawson (1990). They showed that Frenkel's assumptions are poor, but his result is rather close to the exact solution, evidently as a result of offsetting errors.

The next major step in the analysis of viscous sintering was by Mackenzie and Shuttleworth (1949), who calculated the rate of shrinkage of a spherical shell. This is an excellent model for the final stages of sintering, when the pores become isolated, and it is relatively easy mathematically, because the spherical shape of the shell is preserved as the shell contracts. They found that the volume fraction of solids (also called the *relative density*), ρ , varies with time as

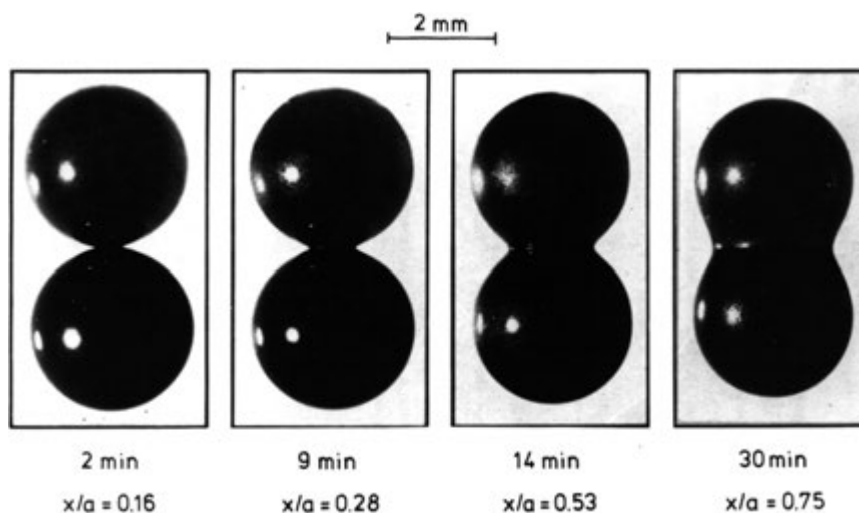


Fig. 1 Coalescence of spherical particles of glass. Reproduced from Exner, H.E., 1979. Principles of single phase sintering. In: Reviews on Powder Metallurgy and Physical Ceramics – 1/1–4, pp. 1–251. Freund Publishing House.

$$\frac{\gamma n^{1/3} t}{\eta} = f[\rho[t]] - f[\rho[0]] \quad (2)$$

where

$$f[\rho] = -\frac{2}{3} \left(\frac{3}{4\pi} \right)^{1/3} \left(\sqrt{3} \tan^{-1} \left[\frac{2(1/\rho - 1)^{1/3} - 1}{\sqrt{3}} \right] + \frac{3}{2} \log \left[(1 - \rho)^{1/3} + \rho^{1/3} \right] \right) \quad (3)$$

The dimensionless time axis is $\gamma n^{1/3} t / \eta$, where n is the number of pores per unit volume of solid; in this case, n is 1 divided by the volume of solid in the shell (which is independent of time). The shape of the densification curve is indicated in **Fig. 2**.

To compare this result with Frenkel's, consider a simple cubic packing of spheres where each unit cell contains one particle (1/8 of each of the 8 particles at the corners of the cell) and has one pore in the center. For that structure, there is one pore per particle, so $n = 1/(4 \pi a^3/3)$, and since $L(t)/L(0) = \rho(0)^{1/3}/\rho(t)^{1/3}$, **Eq. (1)** can be written as

$$\frac{\gamma n^{1/3} t}{\eta} = \frac{8}{3} \left(\frac{3}{4\pi} \right)^{1/3} \left(1 - \left(\frac{\rho[0]}{\rho[t]} \right)^{1/3} \right) \quad (4)$$

In view of the geometrical assumptions made by Frenkel, **Eq. (4)** should only apply to the first 5%–10% of linear shrinkage, while the particles are nearly spherical. For the simple cubic packing, $\rho(0) = 0.52$, so the range of applicability would include densities up to ~ 0.65 . As indicated by the dashed curve in **Fig. 2**, **Eq. (4)** agrees well with the MS model, **Eq. (2)**, for $0.52 \leq \rho \leq 0.7$, so these models predict almost identical sintering kinetics, even though they are based on completely different geometries.

Frenkel's model is expected to apply only at the beginning of sintering, whereas the MS model only applies near the end of sintering, after the pores have become isolated bubbles. For bodies with low initial densities, such as gels or vapor-deposited optical waveguide preforms, there is a large increase in ρ that is not realistically described by either model. For such materials, **Scherer (1977, 1991)** introduced a model where the solid phase is represented by cylindrical rods joined at nodes to create a network. The rate of densification for a network of any shape (e.g., cubic, octahedral, tetrahedral) is found to obey the following equation:

$$\frac{1}{\rho} \frac{d\rho}{dt} = \frac{\gamma S \rho_s}{2 \eta} \quad (5)$$

where S is the specific surface area and ρ_s is the density of the solid phase. The predicted sintering rate for a cubic array of cylinders is indicated by the dotted curve in **Fig. 2**, and it is seen to agree well with the other models. Thus, the theoretical analyses predict similar sintering kinetics for widely different geometries. Experimental studies (see review in **Brinker and Scherer, 1990**) verify that the sintering rate of non-crystalline particles follows the curves predicted by the MS or network models.

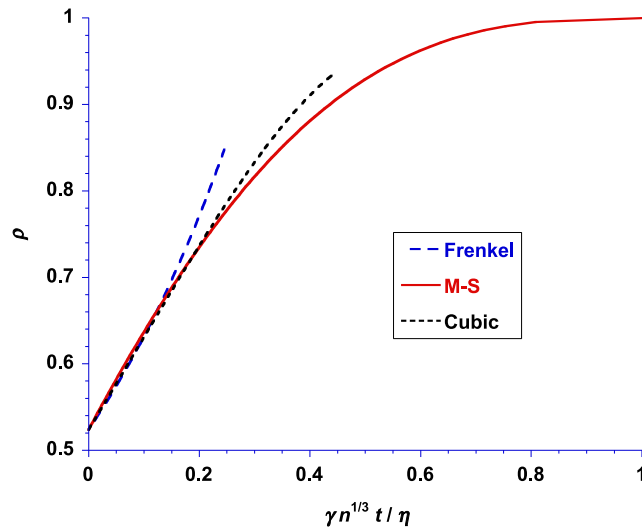


Fig. 2 Relative density ρ versus time for spheres (Frenkel), spherical shell (M-S), and cubic network (Cubic), calculated assuming an initial density of $\rho(0) = \pi/6 (=0.52)$ as for a simple cubic packing of spheres. Frenkel's model is only expected to apply to the early stage of sintering (in this case, up to $\rho \leq 0.65$). The curve for the cubic network terminates at $\rho \approx 0.94$, where the pores become isolated; beyond that point, the MS model applies.

Factors Affecting Sintering Rate

If the initial density of the body lies between $0.2 < \rho < 0.8$, which covers the range of practical interest, then Fig. 2 shows that the time needed to complete sintering, t_s , is approximately $\gamma n^{1/3} t_s/\eta \approx 1$, or

$$t_s \approx \frac{\eta}{\gamma n^{1/3}} \approx \frac{1.6 \eta a}{\gamma} \quad (6)$$

where the second equality applies for the simple cubic packing of spheres. Eq. (6) indicates that smaller particles sinter faster; Eq. (5) leads to the same conclusion, since S is inversely proportional to particle size ($S = 2/(a \rho_s)$ for cylinders and $S = 3/(a \rho_s)$ for spheres). For crystalline materials, t_s is much more sensitive to particle size, varying as a^3 or a^4 . The sintering rate increases (or, t_s decreases) as the surface tension increases, because the surface energy is the driving force for the process. The dependence of γ on temperature and composition is weak for liquids; its value is on the order of 0.1 J/m^2 for organics and $0.25\text{--}0.4 \text{ J/m}^2$ for oxide liquids. In contrast, the viscosity is extremely sensitive to both temperature and composition, so the sintering rate can be drastically reduced by raising the temperature (for glass-forming silicate liquids, t_s drops an order of magnitude for an increase of $\sim 100^\circ\text{C}$). The viscosity of oxides is strongly reduced by hydroxyl (OH) groups, so the sintering rate is greatly accelerated by moisture in the air; for silica, the sintering rate is an order of magnitude faster in air than in a dry gas, such as helium (Brinker and Scherer, 1990). The solid phase of a gel contains large amounts of OH that is gradually lost during sintering, resulting in continuously increasing viscosity and decreasing densification rate; consequently, it is advantageous to use a constant heating rate when sintering a gel, so that the effect on η of rising temperature offsets the loss of OH (Brinker and Scherer, 1990).

Sintering Under Constraint

In practice, sintering often occurs under some sort of constraint. Unless the sintering is done under vacuum, gases will be trapped in the isolated pores and will resist densification; that problem was analyzed by Mackenzie and Shuttleworth (1949). Another sort of internal constraint arises when the body contains a distribution of pore sizes or particle sizes; then, as indicated by Eq. (5), the sintering rate varies from place to place within the body. Regions that tend to contract more rapidly (i.e., locations where S is large) are subjected to restraint (tensile stress) by the surrounding regions that contract more slowly. A similar situation results when there is a gradient in composition that creates a spatial variation in viscosity. This was found to be a significant issue in the sintering of preforms for optical waveguides (Scherer, 1979), where a composition gradient is deliberately created to produce total internal reflection within the fiber; that gradient also causes a strong spatial variation in sintering rate, affecting the course of densification. In a composite, there may be filler particles or fibers that impede the contraction of the porous glassy matrix in which they are embedded. In addition to these internal constraints, there may be external constraints, as when a sintering film is attached to a rigid substrate, or when a mechanical load is applied during sintering (a process called *hot pressing*).

Constitutive Equation

To analyze constrained sintering, it is necessary to generalize Frenkel's energy balance, by adding a term for the mechanical work done by the stresses. The result is a constitutive equation for a sintering material with the following form (Scherer, 1979):

$$\dot{\epsilon}_x = \dot{\epsilon}_f + \frac{1}{F} (\sigma_x - N(\sigma_y + \sigma_z)) \quad (7)$$

where $\dot{\epsilon}_x$ is the strain rate in the x direction and σ_x , σ_y , σ_z are the applied stresses in the x , y , and z directions. The free strain rate,

$\dot{\epsilon}_f$, is the linear contraction rate of the sintering body in the absence of applied stresses; since the linear contraction rate is $1/3$ of the volumetric contraction rate,

$$\dot{\epsilon}_f = \frac{1}{3} \frac{dV}{V dt} = - \frac{1}{3} \frac{d\rho}{\rho dt} \quad (8)$$

The negative sign reflects the fact that the body contracts as its density increases. Using Eq. (5), the free strain rate can be written as

$$\dot{\epsilon}_f = - \frac{\gamma S \rho_s}{6 \eta} \quad (9)$$

The quantity $F(\rho)$ in Eq. (7) is the uniaxial viscosity for the porous viscous material, which is a measure of the additional strain rate resulting from the applied stress. For example, if the material is subjected to a uniaxial stress σ_x , that stress causes the strain rate in the x direction to change by σ_x/F , so that the total strain rate in that direction is

$$\dot{\epsilon}_x = \dot{\epsilon}_f + \frac{\sigma_x}{F} \quad (10)$$

If the stress is compressive ($\sigma_x < 0$), then the contraction rate increases (becomes more negative), whereas tensile stress opposes the free strain rate and retards the contraction. For a nonporous liquid, $F(1) = 3\eta$, but for a porous body $F(\rho) < 3\eta$. The quantity

$N(\rho)$ in Eq. (7) is Poisson's ratio for the porous body; for a nonporous liquid, $N(1) = 1/2$, but for a porous body $N(\rho) < 1/2$. A variety of functional forms that have been proposed for F and N are reviewed by Bordia and Scherer (1988) and Olevsky (1998). Most of those models predict that F increases roughly as ρ^2 ; however, the actual dependence depends strongly on the microstructure. For example, if particles are packed into a random dense arrangement, with $\rho \approx 0.63$, the viscosity F may be very small, because the particles initially make point contacts with one another. As sintering causes the contact area to increase (as illustrated in Fig. 1), the resistance to deformation increases and F rises rapidly. This effect is captured in the simulations by Jagota and Dawson (1988), who found that F was approximately proportional to the square root of the contact area between sintering spheres during the initial stage of sintering.

Practical Applications

Given an expression, such as Eq. (9), for the free strain rate and theoretical or experimental expressions for $F(\rho)$ and $N(\rho)$, it is possible to use Eq. (7) to analyze sintering in the presence of internal constraints (such as non-densifying inclusions, or gradients in density, viscosity, or pore size) or external constraints (such as applied loads or attachment of a sintering layer to a substrate). Thorough reviews of the literature on constitutive equations and numerical analyses of problems in constrained sintering are given by Olevsky (1998) and Bordia *et al.* (2017). Analytical solutions can be obtained for the rate of densification in some cases of practical importance (Scherer, 1992). For a film on a rigid substrate, the rate is

$$\frac{1}{\rho} \frac{d\rho}{dt} = - \left(\frac{1+N}{1-N} \right) \dot{\epsilon}_f \quad (11)$$

Comparison with Eq. (8) reveals that the film sinters more slowly than a free body, as long as $(1+N)/(1-N) < 3$, which is the case whenever $\rho < 1$. By inhibiting its contraction, the substrate imposes tensile stress within the sintering layer. Bordia and Jagota (1993) showed that cracking of the film can occur when the layer thickness exceeds a critical value.

For a porous body containing a small volume fraction v of rigid (i.e., non-sintering) inclusions, the viscous sintering rate is

$$\frac{1}{\rho} \frac{d\rho}{dt} = (3(1-v)\dot{\epsilon}_f) / \left(1 + \frac{2(1-2N)}{1+N} v \right) \quad (12)$$

Eq. (12) is valid only if the inclusions do not interact, which means that v must be less than ~ 0.1 . At higher volume fractions, the inclusions are likely to form a percolating network, so the densification rate is much more strongly retarded than is predicted by Eq. (12). If a noncrystalline material begins to crystallize while it is sintering, the crystals constitute rigid inclusions. If the fraction crystallized is small, then the effect can be described by Eq. (12), but if the crystallites form a continuous network, then sintering is drastically slowed (Brinker and Scherer, 1990).

In hot pressing, the applied load is usually so large that the effect of surface tension on viscous flow is negligible. The MS model then reduces to

$$\frac{\ln[1-\rho[t]]}{\ln[1-\rho[0]]} = \frac{3 p t}{4 \eta} \quad (13)$$

where p is the applied pressure. Eq. (13) indicates that an infinite amount of time is required to reach full density, $\rho = 1$, whereas full density is reached in a finite time when no pressure is applied. The discrepancy results from the fact that the capillary pressure in a pore with radius r is equal to $2\gamma/r$, so it becomes infinite as the pore collapses; therefore, the capillary pressure cannot be neglected with respect to the applied pressure at the end of sintering. That is, Eq. (13) only applies while the pores are large enough to justify the assumption that $p \gg 2\gamma/r$. Nevertheless, applied pressure can drastically reduce the time required to sinter a body, particularly if the pores are initially large.

Future Directions

Compared to crystalline materials, the sintering behavior of noncrystalline materials is quite simple: the rate is relatively insensitive to the details of the microstructure, so the time needed to reach full density can be estimated with reasonable accuracy given only the viscosity and the mean pore size. To predict in detail the evolution of the density and pore size distribution with time, it is necessary to know the initial state of the sample (distribution of pore size, density, and viscosity); however, such calculations are possible with the existing theory. The most challenging problem remaining in the field of viscous sintering is to develop appropriate constitutive equations for the analysis of constrained sintering. The difficulty is that the functions F and N are sensitive to the microstructure (particle shape, contact area, connectivity of voids, and so on). Moreover, the properties may be anisotropic as a result of processing of the unfired body (such as pressing of powder compacts), or may be isotropic at the start of sintering, then become anisotropic as a result of the constraint (e.g., during uniaxial pressing). Considerable progress is being made in this area through careful experimental work and detailed numerical simulations. Much of this work is described in the review by Bordia *et al.* (2017).

References

- Bordia, R.K., Jagota, A., 1993. Crack growth and damage in constrained sintering films. *J. Am. Ceram. Soc.* 76 (10), 2475–2485.
- Bordia, R.K., Kang, S.J.L., Olevsky, E.A., 2017. Current understanding and future research directions at the onset of the next century of sintering science and technology. *J. Am. Ceram. Soc.* 100, 2314–2352.
- (a) Bordia, R.K., Scherer, G.W., 1988. On constrained sintering – I. Constitutive model for a sintering body. *Acta Metall.* 36 (9), 2393–2397, (b) Bordia, R.K., Scherer, G.W., 1988. On constrained sintering – II. Comparison of constitutive models. *Acta Metall.* 36 (9), 2399–2409, (c) Bordia, R.K., Scherer, G.W., 1988. On constrained sintering – III. Rigid inclusions. *Acta Metall.* 36 (9), 2411–2416.
- Brinker, C.J., Scherer, G.W., 1990. *Sol-Gel Science*. Boston, MA: Academic Press, (Chapter 11).
- Frenkel, J., 1945. Viscous flow of crystalline bodies under the action of surface tension. *J. Phys.* 9 (5), 385–391.
- Jagota, A., Dawson, P.R., 1988. Micromechanical modeling of powder compacts – I. Unit problems for sintering and traction induced deformation. *Acta Metall.* 36 (9), 2551–2561.
- Jagota, A., Dawson, P.R., 1990. Simulation of the viscous sintering of two particles. *J. Am. Ceram. Soc.* 73 (1), 173–177.
- Mackenzie, J.K., Shuttleworth, R., 1949. Phenomenological theory of sintering. *Proc. Phys. Soc. Lond.* 62 (12-B), 833–852.
- Olevsky, E.A., 1998. Theory of sintering: From discrete to continuum. *Mater. Sci. Eng.* R23, 41–100.
- Scherer, G.W., 1977. Sintering of low-density glasses: I, theory. *J. Am. Ceram. Soc.* 60 (5–6), 236–246.
- Scherer, G.W., 1979. Sintering inhomogeneous glasses: Application to optical waveguides. *J. Non-Cryst. Solids* 34, 239–256.
- Scherer, G.W., 1991. Cell models for viscous sintering. *J. Am. Ceram. Soc.* 74 (7), 1523–1531.
- Scherer, G.W., 1992. Constitutive models for viscous sintering. In: Mehrabadi, M.M. (Ed.), *Mechanics of Granular Materials and Powder Systems*. New York: ASME, pp. 1–18.

Hot Pressing and Hot Isostatic Pressing

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In addition to Gas Pressure Sintering, Field-Assisted Sintering Technology/Spark Plasma Sintering (FAST/SPS) and High-Pressure, High Temperature (HP/HT) methods (production of polycrystalline diamond) Hot Pressing (HP) and Hot Isostatic Pressing (HIP) are pressure-assisted sintering methods. They allow.

- (1) To densify materials that are difficult to sinter,
- (2) To significantly reduce the sintering temperatures, which makes it possible to produce particularly fine-grained or thermally unstable materials,
- (3) To produce materials with increased reliability and strength, since the additional external pressure increases the driving force of the compaction and thus the number of defects (pores, microcracks, etc.) can be decreased.

Both methods are fundamentally different. In hot pressing, a powder or a compacted preform is densified by simultaneous application of a uniaxial pressure and temperature (Fig. 1). On the other hand, in hot isostatic pressing, pre-sintered, gas-tight components or components encapsulated into gas-tight metallic or glass containers are exposed to an isostatic gas pressure and temperature, which allows the compaction of complex-shaped components (Fig. 2). While in the hard metal industry, for example, the term HIP is used for sintering with gas pressures of 50–100 atm (5–10 MPa), in the ceramic industry the term gas pressure sintering is attributed for processes with these pressures. HIP of ceramic materials usually requires 1000–2000 atm (100–200 MPa).

Hot Pressing

Technology

Hot presses typically consist of two counter-moving punches and a die, which enclose the pre-compacted powder, integrated in a furnace (induction or resistance). This allows pressure and temperature to be applied simultaneously. Often the systems allow the atmosphere to be controlled by appropriate furnace design. Also, the hot pressing systems are very similar to FAST/SPS-systems with the main differences that in the hot press the heat is generated outside the sample whereas in FAST/SPS a direct current is passing through the material, punches and dies. Therefore, the heating rates applied are usually much lower than for the FAST/SPS processes (Guillon *et al.*, 2014).

Graphite is typically used as punch and die material which can be used up to 2500°C. It possesses the following advantages: low cost, easy machinability, superior thermal shock and creep resistance up to high temperatures and acceptable bending and compressive strength values. The low coefficient of thermal expansion compared to those of most other suitable tool materials enables the ejection of the sample, as the die does not shrink onto the material. Due to the average strength values of the graphite,

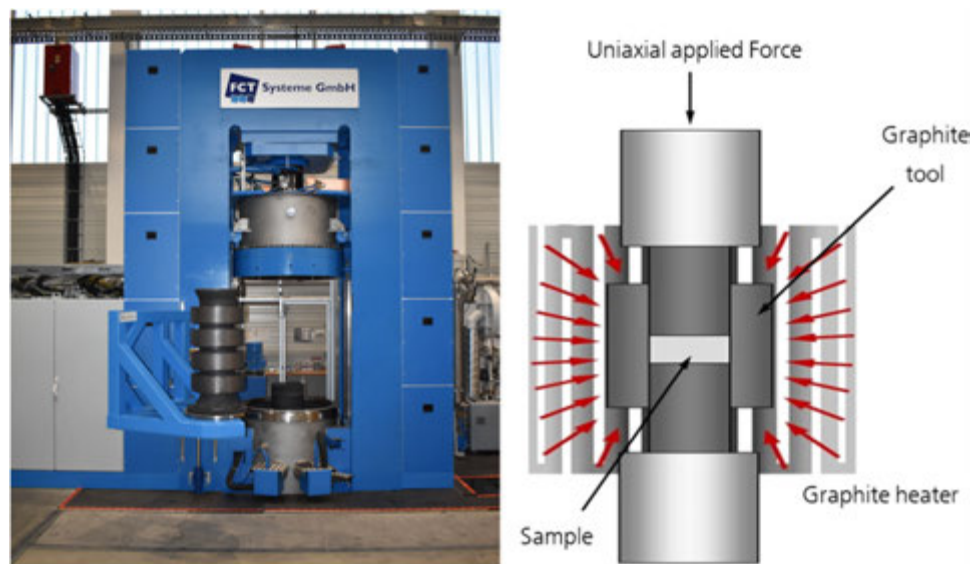


Fig. 1 Figure of a typical hot press allowing to densify several samples at once and schematic view of the internal part of the hot press. Reproduced from "FCT Systeme GmbH, 2020". Available at: <http://www.fct-systeme.de/Vakuumheisspressen>.

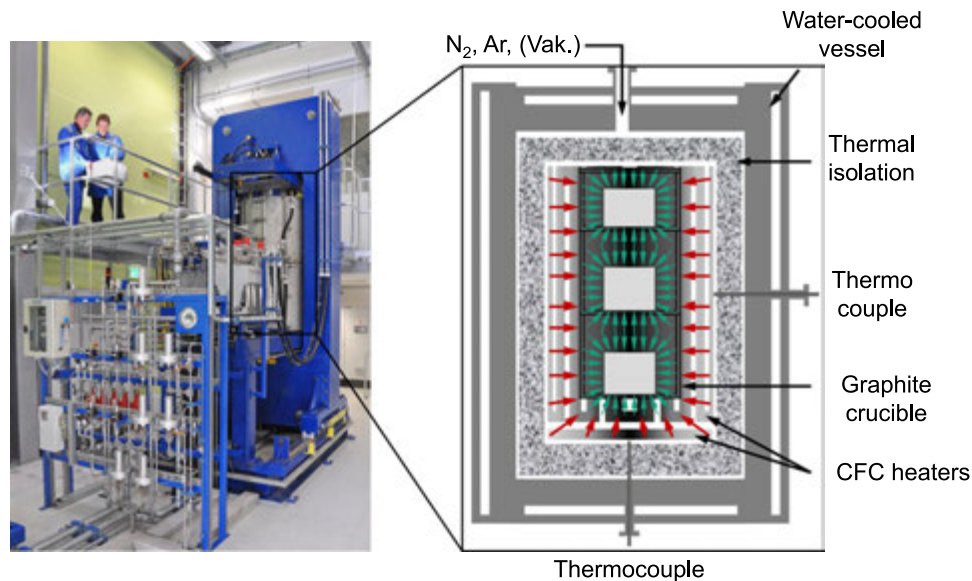


Fig. 2 Hot isostatic press operating in the IKTS Dresden with maximum usable volume of 300 mm diameter and 400 mm height and schematic view of the furnace.

the typical applied pressures are limited in the range 10–30 MPa for larger sized tools. The use of Carbon Fiber Composites (CFC) dies or CFC covers sleeves on graphite dies increasing safety and maximum applicable pressure.

The high reactivity of graphite with ceramic systems is sometimes critical. To limit this problem, hexagonal Boron Nitride (hBN) coatings established on tool parts are of particular interest. For special applications (e.g., lower temperatures or higher pressures, sensitivity of the material to graphite) other materials or at least “inliners” such as W, Mo-alloys BN, Al_2O_3 , SiC, TiB_2 , TiC, hard metals, WC and other could be applied.

Since the powder is situated in a dense press mold, it is relatively well shielded from the atmosphere. This means that the atmosphere inside the press mold can significantly differ from the furnace atmosphere. Therefore, it is possible to sinter Si_3N_4 -ceramics without inert gas in an inductive hot press without oxidation of the material. Such relatively simply constructed hot presses without a controlled adjustable atmosphere have not become established for non-oxide materials, as their operation showed no good enough reproducibility.

The main disadvantages of hot pressing are its limitation to relatively simple geometries, typically plates and cylinders, the difficultness to full automation and comparatively high operation costs. There are attempts described in literature to quasi-isostatically sinter parts, encapsulated into a non-sintering powder as pressure transmitting medium, but this is so far of academic interest only (German, 1996).

In addition, the use of the process is limited by the relatively low productivity, since usually only single components are produced. Special techniques such as tandem systems, rapid cooling, simultaneous pressing of several components (Fig. 1), approaches to (partially) automatize the process etc. are applied to increase productivity. An example of such a system which can produce up to 40,000 panel-shaped parts per year is shown in Fig. 3.

Therefore, hot pressing is limited to materials that cannot be compacted in another technology in an effective way (e.g., BN based ceramics, SiC-whisker-reinforced Al_2O_3 ceramics, B_4C materials, scintillator materials, etc.), or where small quantities and/or the highest demands on density and purity with relatively simple geometries are required, e.g., sputter targets. However, complicated multi-layer plate heaters with electrically conductive and insulating areas can be produced by hot pressing too (“Bach Resistor Ceramics GmbH, 2020”).

Today, hot pressing systems up to 700 mm diameter and 2500 °C are available on the market (“FCT Systeme GmbH, 2020”; “FCT Anlagenbau GmbH, 2020”).

In addition to industrial applications hot presses are used in academic field to test the potential of new materials, since sophisticated processing and shaping to avoid defects is not necessary and testing samples can be fast and easily produced by this technology. Hot pressing is a primary forming technology. Within the last three decades, FAST/SPS systems have been increasingly used for these purposes, which offer quick heating and therefore, a much faster production of samples (Guillon *et al.*, 2014; Nygren and Shen, 2012).

Densification Mechanisms During Hot Pressing

The application of a uniaxial pressure represents a significant additional driving force, which enforces the sintering in various ways:



Fig. 3 Continuous–Hot pressing system with preheating channel, double pressing station and cooling channel (rapid cooling). Reproduced from “FCT Systeme GmH, 2020”. Available at: <http://www.fct-systeme.de/Vakuumheisspressen>.

- (1) The permanently acting force increases strongly the particle rearrangement in the initial phase of sintering. This is especially true when, due to the formation of a liquid phase or due to impurities on the surface, lubricating films are formed which allow grains to slide easily against each other. Especially in systems with anisotropic grains (e.g., Si_3N_4 -ceramics) this leads to the formation of textures due to the alignment of the grains.
- (2) Grain boundary sliding and diffusion creep are enhanced. In many solid phase sintered materials, this mechanism becomes the dominant one in the intermediate and final stage of sintering.
- (3) Especially in the final stage of sintering, mass transport is favored by increasing gradients of chemical potential or dislocations.

The rearrangement intensified by the external pressure (initial stage of sintering) is rather difficult to describe analytically and it strongly depends on the pre-compaction, the grain shape, size, and the formation of viscous phases.

The compaction in the main phases of the densification (Phase II and III) can be described with different equations depending on the mechanism (Rahaman, 2008; Kang, 2008):

Provided that the applied pressure P_a is much higher as the sintering stress (this is usually the case), for solid phase and viscous sintering the densification rate can be described by

$$\frac{d(\rho)}{\rho dt} = \left(\frac{HD}{G^m kT} \right) (P_a \phi)^n \quad (1)$$

where ρ is the relative density, H is a constant, k the Boltzmann constant, T the temperature, D is the diffusion coefficient of the relevant diffusion mechanism (grain boundary; lattice diffusion) G is the grain size P_a is the applied pressure and ϕ is a stress intensification factor that reflects the stress amplification at pores,

The exponent m and n depend on the densification mechanism. m can be between 0 for viscous flow and 3 for grain boundary diffusion. The values of n could be $n = 1$ (grain boundary or lattice diffusion), $n = 1 \dots 2$ for grain boundary sliding, particle rearrangement and $n > 3$ for viscous flow.

Different functions are proposed for the dependence of ϕ on the density (German, 1996). A common one is

$$\phi = e^{aV_p} \quad (2)$$

where a is a constant and V_p is the porosity. It approaches 1 when the porosity is 0 and can exceed 10–50 for compacts with 60% theoretical density. This means, that the influence of the applied pressure is higher for less dense materials and corresponds to the applied pressure for dense materials.

Using Eq. (1), the value of the exponent n and thus the densification mechanism can be determined by evaluating the dependence of the densification rate on the applied pressure at constant density. In most solid-phase sintered ceramic materials, this value is approximately 1, which suggests a diffusion mechanism as the speed-determining mechanism. However, often the results are inconclusive and additional investigation or modeling of the compaction with separately determined constants is necessary to unambiguously determine the mechanism. Especially for the model system of high-purity Al_2O_3 ceramics, the dependence of the densification mechanisms on the grain size and the densification temperature are determined in detail (Rahaman, 2008; Kang, 2008).

In the case of liquid- phase sintering the following equation can be applied (German, 1996):

$$\frac{d(\rho)}{dt} = \frac{3\phi P_a V_p}{4\eta} \quad (3)$$

Where ρ is the relative density and V_p is the porosity ($V_p = 1 - \rho$), P_a is the applied pressure, and ϕ is a stress intensification factor that reflects the stress amplification at pores.

The viscosity is the apparent viscosity depending on the viscosity of the liquid and the volume fraction of the solid:

$$\eta = \frac{\eta_0 \exp(-aV_p)}{(1-c\phi^*)^2} \quad (4)$$

where a and c are empirical constants that are typically between 1 and 2, and ϕ^* the relative volume fraction of solid. The inherent viscosity of the liquid phase (η_0) depends on the temperature and composition.

Rahaman (2008) describes an alternative approach:

$$\frac{d(\rho)}{pdt} = \frac{AD_l\delta_l\Omega}{G^3kT} P_a\phi \quad (5)$$

where A is a constant depending on geometry, δ_l is the thickness of the liquid layer around the grains, D_l is the diffusion coefficient in the liquid and Ω is the atomic volume of the rate controlling species. Since the diffusion coefficients are indirectly proportional to viscosity, the Eqs. (3) and (5) result in a similar dependence on viscosity. The thickness of the films of the liquid phase δ_l (equation) is a measure of the volume fraction of the liquid phase. Therefore, if other parameters are constant, the densification rate should be proportional to the volume of the liquid phase. However, it must be taken into consideration that grain growth is also dependent on the amount of liquid phase, so, the dependencies are often only qualitative in accordance with the prediction. The maximal useful amount of liquid phase is limited to <10–20 vol% due to the fact, that excess of liquid phase will be quizzed out in the final densification step. This strongly depends on the applied load, the wetting behavior and the viscosity of the liquid.

The modeling of processes often based on parameters obtained from experimental compaction curves and some fitting parameters. A detailed description of the modeling of hot pressing and very similar FAST/SPS processes are summarized in (Guillon *et al.*, 2014; Bordia *et al.*, 2017; Olevsky *et al.*, 2012; Guyot *et al.*, 2014).

Models predict that with shear stresses the densification could be additionally improved. Therefore, different setups for sinter forging or hot extrusion were explored, showing the possibilities of these methods especially for fine grained materials. However, up to now they have not found its industrial application.

The recently developed cold sintering process is a special kind of a reactive hot pressing. The powder is mixed with small amount of water and additional substances to control the dissolution reaction under hydrothermal conditions. The densification of ceramic components takes place at relatively low temperatures $\leq 400^\circ\text{C}$ at 100–300 MPa pressure under hydrothermal conditions. The solvent enhanced recrystallization under pressure is the mechanism of this kind of densification. The slow escape of water and additional substances has to be controlled by a special die design. Detailed information about this new hot topic could be found elsewhere (Grasso *et al.*, 2020; Vakifahmetoglu and Karacasulu, 2020).

Hot Isostatic Pressing (HIP)

Hot isostatic pressing (HIP) is a sintering process used for the consolidation of both metallic and ceramic components receiving parts with the highest reliability and lowest scattering of properties. The principle of HIP technology is that a shaped body, gas-tight (in rare cases a powder in a gas-tight mold) which is simultaneously exposed to high gas pressure and high temperatures up to 2000°C . In order to generate an isostatic pressure on the component, the component itself must be gas-tight or gas-tight encapsulated (see below). The commonly used pressure range is 70–400 MPa, which is higher than the 10–30 MPa used for typical hot pressing or gas pressure sintering (up to 20 MPa). As a result of the high isostatic pressure, non-porous components with greatly reduced scattering of mechanical properties in particular can be produced. Therefore, the process is used especially for products requiring highest reliability, e.g., ceramic hip implants, ball bearings or demanding ceramic wear parts. However it is also used to remove inner defects like shrink holes of metallic alloys, like Ti-alloys (aircraft components, medical devices), Al-alloys, Ni-base super alloys (jet engine turbine blades...), 17–4PH stainless steel and others ("Kobelco Kobe Steel Group 2020"; Bocanegra-Bernal, 2004; Atkinson and Davies, 2000; European Powder Metallurgy Association, 2018).

In addition, sintering temperatures can often be lowered compared to a pressureless sintering process, which reduces grain growth, in some cases eliminates or at least reduces the need for sintering additives and growth inhibitors. In addition to the production of such highly stressed ceramic components, HIP-technology is also used for transparent and optically active ceramics, such as MgAl_2O_4 , cubic- ZrO_2 or rare earth compounds with a cubic structure (e.g., garnet). In these materials, the porosity can be reduced to values below 0.001% by isostatic pressure. This is necessary because the pores act as scattering centers. The effect of the HIP process on the transparency of MgAl_2O_4 ceramics is shown in Fig. 4.

Additionally, the importance of the HIP-technology is currently increasing in connection with the additive manufacturing of metallic components, since components made of titanium and other superalloys, which are produced in this way, are hot isostatically post-compacted to reduce porosity and to achieve the corresponding properties and reliability. In most cases, it is worth to print parts at higher speed with low accuracy and Post-HIP those parts to fully density them.

In addition to sintering of components, HIP can be used for diffusion bonding (diffusing bonding of nuclear fuel elements was a starting point of the development in the 1960th in the US) as well as for cladding and reactive HIP processes or syntheses (Bocanegra-Bernal, 2004).

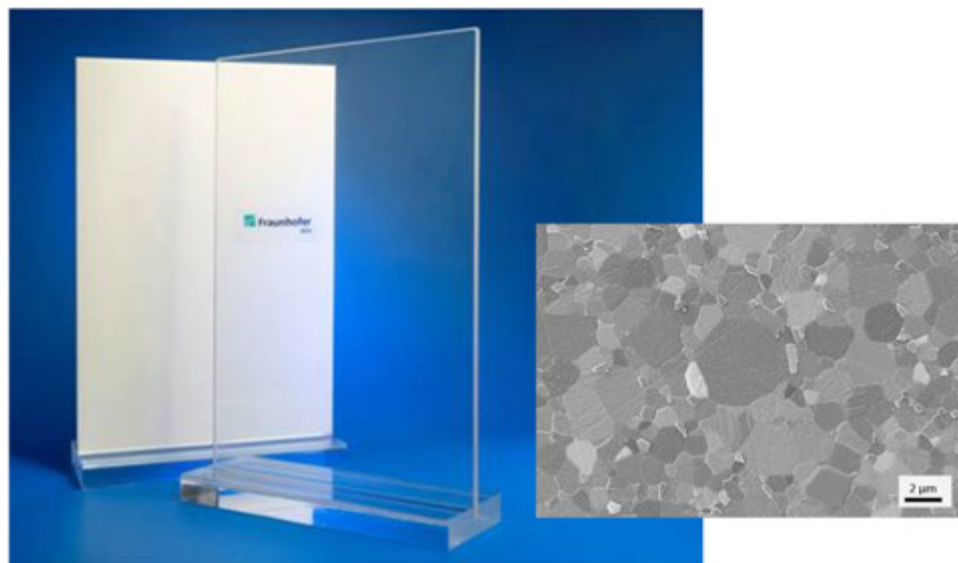


Fig. 4 Photo of a spinel plate before and after HIP process (a). Figure (b) shows the micrograph after HIP showing the elimination of the porosity.

Unfortunately, HIP processes cannot completely eliminate all defects (see Mechanisms), therefore the process does not replace sophisticated processing especially in ceramic technology.

A HIP- system and its schematic operation is shown in [Fig. 2](#).

Two types of pressure vessel are used today, on the one hand a pre-stressed and wire-wound with high tensile cold-rolled spring steel ribbon (Quintus Technologies, Sweden), or on the other hand, forged vessels, massive, monolithic pieces of forged steel (EPSI Belgium, Cremer HIP Innovations GmbH, Germany). The York frame is typically made of steel or wire-wound ensuring a calculated fatigue life of more than 20,000 cycles. Two main types of heaters are in operation, metallic heaters (steel or molybdenum) for medium temperature applications up to 1350°C or graphite and/or Carbon Fiber composite (CFC) heater installation for temperatures of up to 2200°C reported in literature. Argon as pressure transmitting media is commonly used, but also nitrogen and in few cases air or hydrogen.

They are available for a wide range of dimensions (diameters from some centimetres up to more than a meter) and temperatures ([EPSI Hot Isostatic Presses, 2020](#)). Due to the high gas pressure, special safety systems and special thermal insulation are necessary, as the gases have a high density (Ar has a density $> 1 \text{ g/cm}^3$ at room temperature and 100 MPa) and low viscosity. In addition, appropriate monitoring and control systems and peripheral safety equipment ensure safe operation. The majority of used in the ceramic production HIP systems work with nitrogen or argon and use graphite or CFC-heaters up to 2000°C. There are only a few systems that can operate under oxidizing conditions $> 1000\text{--}1200^\circ\text{C}$. These typically have Pt/Rh heaters. For metals that are compressed at lower temperatures and where carburization must be avoided, metallic heaters, Nichrome, Kanthal or even Mo- or W-heater for higher temperatures are used.

The use of carbon or Carbon Fiber Composite (CFC) heaters for Post-HIP consolidation of oxide ceramic materials (Al_2O_3 ; ZrO_2 ; ATZ, spinel...) can lead to oxygen vacancies in the ceramic, which can cause a gray coloring. In order to minimize these effects, the samples are shielded by crucible materials or even powder beds. If necessary, discoloration can often be achieved by subsequent oxidizing annealing.

The additional driving force by the external pressure requires that the porous ceramic preform is separated from the gas by a gas-tight casing. This can be done in various ways. Three main routes are used:

- (1) Sinter-HIP process.
- (2) Encapsulation method.
- (3) Glass bath method.

These processes are shown schematically in [Fig. 5](#).

The route mainly used in ceramics production today is the Post-HIP or Sinter-HIP-process [Fig. 5\(a\)](#): Ceramic or powder metallurgical produced metallic green bodies have essentially open porosity, i.e., the pores have a connection to the surface. The gas pressure in these pores corresponds to the gas pressure in the environment. Therefore, no pressure gradient can occur with increasing gas pressure during HIP. Open porosity is typically the dominant one up to sinter densities of 90%–95% theoretical density. At higher densities, the sintered bodies have closed porosity, which have no connection to the surface of the component ([Fig. 6](#)). Only in this stage of sintering a pressure difference arises between the body and the surrounding gas when the gas pressure is increased, which facilitates the sintering. This means that the component has to be pre-sintered to a density of $> 90\%\text{--}95\%$ of

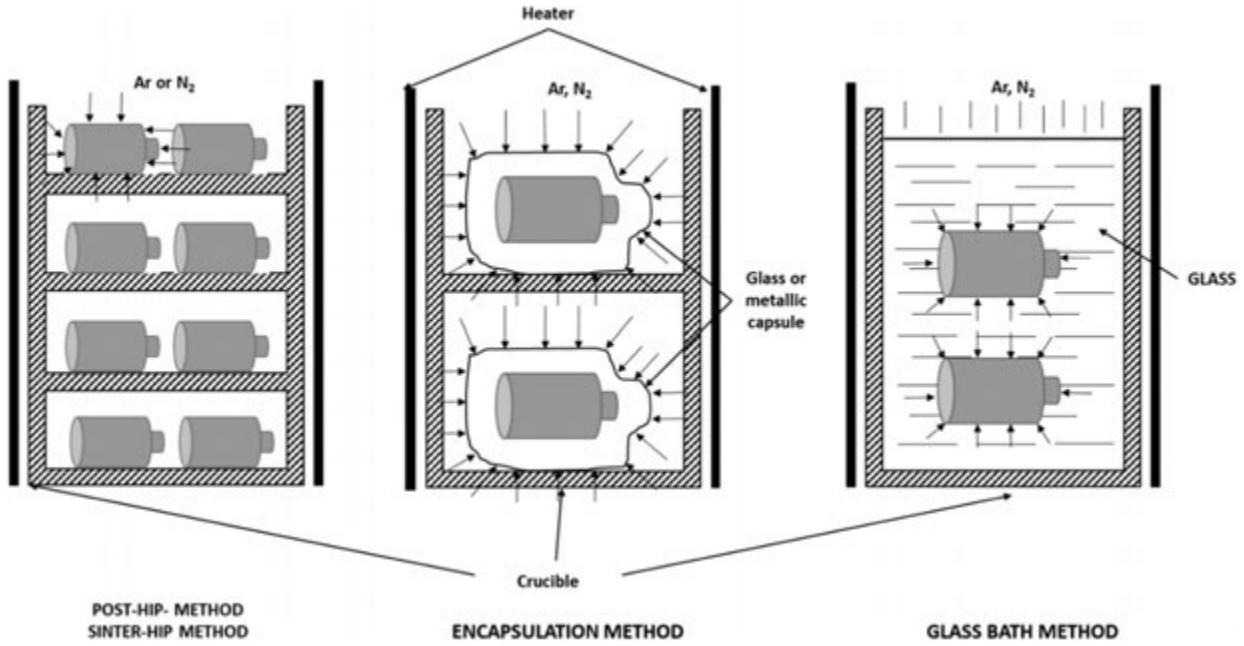


Fig. 5 Schematic view of the different HIP-technologies.

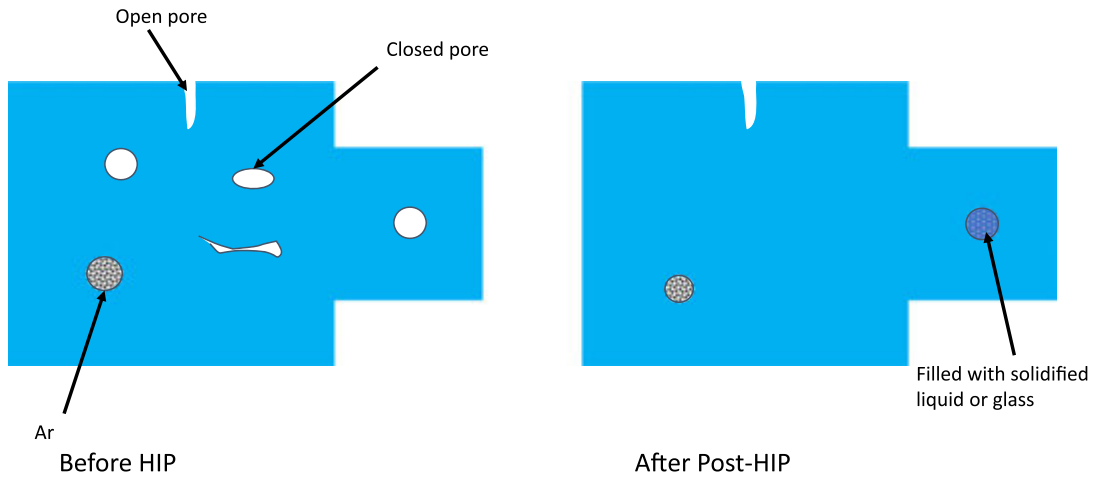


Fig. 6 Schematic view of the cross section of the component before and after Post-HIP. Open pores and cracks with a connection to the surface could not be healed out. Empty closed pores or filled with a gas, which diffuse along grain boundaries or solve in the matrix, could disappear completely. Pores filled with Argon (Ar) or another non-diffusing gas could shrink, but will not completely disappear. Large pores could be filled in liquid phase sintered materials during post HIP with the liquid component. It will then solidify during cooling (see also Fig. 7).

theoretical density at a low gas pressure (1 atm) or in vacuum and only then the high gas pressure has to be applied to accelerate the final densification. The pre-sintering can be done in the HIP or in an external unit. The latter increases the flexibility of the usable atmospheres. For this reason, separate pre-sintering and post-HIP-ing are usually used, especially for oxide ceramic components.

The influence of the gas pressure on the densification rate during post-compaction can be described as follows for grain boundary, volume diffusion - diffusional flow (German, 1996; Atkinson and Davies, 2000):

$$\frac{d(\rho)}{dt} = (1 - \rho)B \left(g \frac{\gamma_{sv}}{r} + P_{ae} - P_p \right) \quad (6)$$

where γ is the surface energy, r is the pore radius and g is a term determined by the geometry, P_{ae} is the effective external gas pressure and P_p is the gas pressure in the pores. For densification by plastic flow or creep, the densification rate is a power function of pressure (Kang, 2008; European Powder Metallurgy Association, 2018). A corresponding detailed discussion of the mechanisms

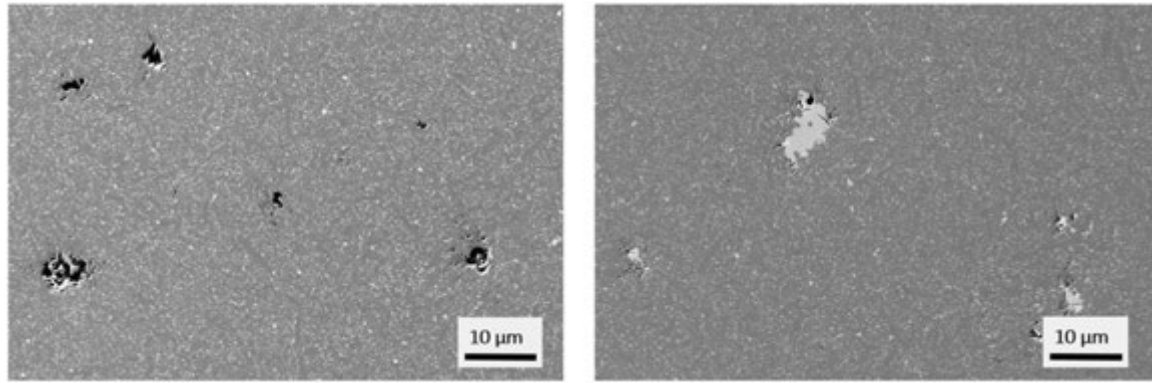


Fig. 7 Microstructure of Si_3N_4 material in the sintered state showing some defects from the processing and in the hipped state. In the HIP-ed state the pores are filled with the Y_2O_3 rich glassy phase.

can be found in (Kang, 2008; Bocanegra-Bernal, 2004; Atkinson and Davies, 2000), whereby for solid-phase sintering ceramics under typical conditions the diffusion processes are the dominant ones.

From equation (Fig. 6) it can be deduced that if non-diffusing gas is trapped in the pores the pores cannot be removed completely. An equilibrium pore size is reached when the expression in brackets becomes 0. Based on this the equilibrium pore size can be calculated:

$$\frac{P_{in}}{P_a} = \left(1 + \frac{2\gamma}{P_a r_{eq}} \right) \left(\frac{r_{eq}}{r_{in}} \right)^3 \quad (7)$$

where r_{in} and P_{in} are the initial radius of the pores and pressure at the moment of pore closure respectively, r_{eq} and P_a are the equilibrium radius and the external gas pressure during the sinter-HIP stage (Herrmann *et al.*, 1992; Kang *et al.*, 1989).

Therefore, pre-sintering should be carried out at the lowest possible gas pressure, or the gas used should exhibit as fast diffusion along the grain boundaries or in the liquid phase. The conditions for the gas to be used in the pressure stage is, that it has only a low solubility in the solid, otherwise the pores can be stabilized by the inward diffusion of the gas. This could result also in swelling in post HIP heat treatments (Kwon and Messing, 1989).

For liquid phase sintering systems, large pores can also be healed by filling with liquid phase. Due to the external pressure, it is possible that not only small pores are filled with the liquid phase due to capillary forces, but also large ones. Fig. 6 shows this for a Si_3N_4 ceramic. However, these larger glass pockets are similarly critical for Si_3N_4 bearing balls (ISO, 2017). This is one example showing the limitations of the HIP sintering. It cannot heal all defects during shaping. Therefore, high quality materials do not only require pressure assisted methods, but also sophisticated processing. The healing of pores in the final stage is mostly done by diffusion processes, therefore larger pores need longer sintering times for complete healing, which can significantly affect the microstructure. Which defects could be healed out is shown schematically in Fig. 6.

For metallic components not only Post-HIP processes are carried out. A combination of Post-HIP and subsequent annealing, solution treatment or aging can be performed as part of one HIP cycle. For that HIP devices can be equipped with a fan or channel blower and nozzles to increase the convection of compressed gas which allows fast cooling (up to 200K/min for small parts).

If pre-sintering up to densities > 90%–95% theoretical density is not possible, then gas tightness must be achieved with the aid of a capsule (Fig. 5(b)). The basic requirements for the capsule are ("Kobelco Kobe Steel Group 2020"; Bocanegra-Bernal, 2004; Atkinson and Davies, 2000):

- (1) Gas tightness at room and high temperatures but plastic deformability under the temperature and pressure conditions used to transfer the external pressure.
- (2) Compatibility with the encapsulated component to avoid reactions that can lead to leakage of the capsule or to diffusion zones in the material. Sometime it can be avoided by using intermediate coatings.
- (3) Low cost of capsule material and encapsulation and
- (4) Easy removability.

In the case of metals, the components or directly the starting powder are filled in the capsule (steel, super alloys Ta, Mo, W) and usually welded in vacuum. It should be noted that the edges of the capsules are deformed differently during the HIP process and therefore the pressure is not applied completely isostatic, which can lead to deviations in the shape of the component ("Kobelco Kobe Steel Group, 2020"; Bocanegra-Bernal, 2004; Atkinson and Davies, 2000; European Powder Metallurgy Association, 2018).

Additive manufacturing also enables the printing of complex-shaped parts combined with the printing of a gas-tight can. It thus opens up new possibilities for an effective capsule HIP process (Riehm *et al.*, 2019). In the future, it may also open up new possibilities for capsule technology for glass capsules, which are used in ceramic production. Until now, attempts have been made to create such capsules by immersion or spraying, but this has not been widely established.

Glass ampoules are often used for ceramics. In this process the workpiece is typically embedded in boron nitride powder by cold isostatic pressing before it is encapsulated in a quartz glass tube under vacuum. In this case the boron nitride powder acts as a pressure transmitter and avoids stress and reaction zones. This technology is the only one that has enabled the densification of Si_3N_4 materials without additional sintering additives (1800–1900°C; 1–2 GPa Ar pressure). Only the low amount of SiO_2 on the surface of the powder was sufficient for the densification.

To simplify the process of encapsulation, the glass bath method was invented (Fig. 5(c)), e.g., for Si_3N_4 ball bearing balls, this modified capsule technology is used. The balls are embedded in a fritted glass powder in a crucible and then the mixture is heated in a vacuum until the glass melts and the balls are embedded in the melt. The viscous glass is then used as a transmitter of the pressure. After the HIP-process it will be mechanically removed. High quality balls even with low sintering additives can be produced by this method.

All capsule methods have the disadvantage that they involve additional process steps of encapsulation and decapsulation, so that capsule-free Sinter-HIP methods are increasingly preferred.

Besides these mainly used methods of compression by means of HIP there is a whole range of process variants, such as high pressure reaction sintering methods, liquid-HIP methods (the latter uses liquid salts as pressure medium), which are tailored to special requirements (German, 1996; Atkinson and Davies, 2000).

Irrespective of the HIP process selected, materials with extremely high density can be produced which have both special optical properties (transparent ceramics), improved wear behavior increased strength and reliability (e.g., Al_2O_3 -hip implants, Ti alloys for aircraft components, Ni base alloys for power plant components). In addition, the absence of defects reduces the fatigue behavior of metallic alloys (e.g., Ti alloys) and ceramics. For example, it could be shown that the healing of small defects by a post HIP treatment in Y-stabilized ZrO_2 (TZP-ceramics) suppresses low temperature aging.

In addition to these improvements in the properties of conventional materials, it enables the production of materials or microstructures that could not be manufactured without the high pressure.

References

- Atkinson, H.V., Davies, S., 2000. Fundamental aspects of hot isostatic pressing: An overview. *Metallurgical and Materials Transactions A* 31, 2981–3000.
- Bach Resistor Ceramics GmbH, 2020. Available at: <https://www.bachrc.de/start/?Language=en>.
- Bocanegra-Bernal, M.H., 2004. Review hot isostatic pressing (HIP) technology and its applications to metals and ceramics. *Journal of Materials Science* 39, 6399–6420.
- Bordia, R.K., Kang, S.-J.L., Olevsky, E.A., 2017. Current understanding and future research directions at the onset of the next century of sintering science and technology. *Journal of the American Ceramic Society* 100, 2314–2352.
- EPSI Hot Isostatic Presses, 2020. Available at: <https://epsi-highpressure.com/products/hot-isostatic-presses/>.
- European Powder Metallurgy Association, 2018. Introduction to Hot Isostatic Pressing Technology: A Guide for Designers and Engineers, second ed. EPMA.
- FCT Anlagenbau GmbH, 2020. Available at: <https://www.fct-anlagenbau.de/de/sinterofen-und-anlagen/vakuum-heisspressen>.
- FCT Systeme GmbH, 2020. Available at: <http://www.fct-systeme.de/Vakuumheisspressen>.
- German, R.M., 1996. *Sintering Theory and Practice*. New York: John Wiley & Sons Inc.
- Grasso, S., Biesuz, M., Zoli, L., et al., 2020. A review of cold sintering processes. *Advances in Applied Ceramics* 119, 115–143. doi:10.1080/17436753.2019.1706825.
- Guillon, O., Gonzalez-Julian, J., Dargatz, B., et al., 2014. Field-assisted sintering technology/ spark plasma sintering: Mechanisms, Materials and technology developments. *Advanced Engineering Materials* 16, 830–849. doi:10.1002/adem.201300409.
- Guyot, P., Antou, G., Pradeilles, N., et al., 2014. Hot pressing and spark plasma sintering of alumina: discussion about an analytical modelling used for sintering mechanism determination. *Scripta Materialia* 84–85, 35–38. doi:10.1016/j.scriptamat.2014.04.013.
- Herrmann, M., Putzky, G., Siegel, S., Hermel, W., 1992. Einfluß von Zersetzungsreaktionen auf die Sinterung. *Ceramic Forum International* 69, 375–382.
- ISO, 2017. *Fine Ceramics (Advanced Ceramics, Advanced Technical Ceramics) – Silicon Nitride Materials for Rolling Bearing Balls and Rollers*. ISO 26602:2017-10. ISO.
- Kang, S.-J. L., Mitomo, M., Greil, P., Moon, J.H., 1989. Elimination of large pores during gas-pressure sintering of β -SiAlON. *Journal of the American Ceramic Society* 72, 1166–1169. doi:10.1111/j.1151-2916.1989.tb09702.x.
- Kang, S.J.L., 2008. *Sintering*. Amsterdam: Elsevier.
- Kobelco Kobe Steel Group, 2020. Available at: <https://www.kobelco.co.jp/english/products/ip/technology/hip.html>.
- Kwon, O.H., Messing, G.L., 1989. Gas diffusion during containerless hot isostatic pressing of liquid-phase sintered ceramics. *Journal of the American Ceramic Society* 72, 1011–1015.
- Nygren, M., Shen, Z., 2012. Hot pressing and Spark plasma sintering. In: Riedel, R., Chen, I.-W. (Eds.), *Ceramic Science and Technology* 3. Weinheim: Wiley-VCH, pp. 189–213.
- Olevsky, E.A., Garcia-Cardona, C., Bradbury, W.L., 2012. Fundamental aspects of spark plasma sintering: II. Finite element analysis of scalability. *Journal of the American Ceramic Society* 95, 2414–2422.
- Rahaman, M.N., 2008. *Sintering of Ceramics*. Boca Raton, London: Taylor & Francis.
- Riehm, S., Kaletsch, A., Broeckmann, C., et al., 2019. Tailor-made net-shape composite components by combining additive manufacturing and hot isostatic pressing. In: Dayal, P., Triani, G. (Eds.), *Hot Isostatic Pressing HIP'17*, vol. 10. Materials Research Forum LLC, pp. 203–209. (Materials Research Proceedings).
- Vakifahmetoglu, C., Karacasulu, L., 2020. Cold sintering of ceramics and glasses: A review. *Current Opinion in Solid State and Materials Science* 24, 100807. doi:10.1016/j.cossms.2020.100807.

Reaction Sintering

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Introduction

The Concept

The term sintering is used to describe the phenomena that occur when solid products are made from inorganic powder compacts. It is an important step in the fabrication of ceramics, metals, and cermets. During the sintering process, a powder compact is heated to a suitable temperature at which the mass transport mechanisms are operative. As a result of the initial misfit of the particles, the porous compact shrinks as much as the void volume is eliminated.

The sintering driving force is the decrease in the total free energy of the body leading to a minimal energy state. When the constituents of the particles in the porous compacts are solid state compatible and the thermal treatment temperatures are lower than those necessary to form liquid phases, the decrease in the total free energy of the body occurs due to the reduction of the overall interfacial free energy (solid-solid and solid-vapor). This process is referred as *solid state sintering*.

Reaction sintering (reactive sintering) is an alternative sintering process in which chemical reaction between the constituents of the green compact and its densification occur during the same thermal treatment.

Shrinkage of the compact is one main point in reaction sintering, therefore, it is different from processes in which only slight dimensional changes occur during densification and involve relatively low temperatures such as reaction bonding of non-oxides (e.g., Si_3N_4 , RBSN; B_4C , RBBC; SiC bonded with Si_3N_4) or oxides (Al_2O_3 , RBAO) or the directed metal oxidation (DMO) processes used for processing ceramic matrix composites (CMCs) with a continuous interconnected three-dimensional network of ceramic phase (Travitzky *et al.*, 2018; Nesmelov and Perevislov, 2015). These processes have high potential for near to net shape fabrication of parts. Even though they are sometimes included in the term reaction sintering, they will not be discussed in this chapter.

Since the energy changes for chemical reactions are much larger than those for surface area changes it would be very desirable if the free energy of the reaction could be used to drive the densification process (Rahaman, 2008). However, there is no evidence that the energy of the reaction can act directly as a driving force for densification. Major advantage of reaction sintering is the elimination of additional thermal and milling treatments needed to fabricate powders with the characteristics required in the final material. Therefore, it appears as an attractive industrial process for cost-saving (Brook, 1991).

Technological Interest

Reaction sintering has long been successfully used in the case of the so called *traditional ceramics*. Building ceramics – bricks, roof and floor tiles-, crockery, and sanitary products are fabricated from mixtures of minerals, being phyllosilicates, feldspar, carbonates, and quartz the most frequently used.

Different mixtures that include non-calcined raw materials and depend on the desired microstructure and properties are also used to process shaped refractories. For instance, fireclays, andalusite, or sillimanite minerals are used for alumina-silica and high alumina bricks, which experience reaction sintering during the thermal treatment. In general, the refractory industry does not use un-calcined carbonates as raw materials even though a careful control of composition, grain size distribution, and firing temperature allows achieving magnesia-calcium zirconate refractories with optimized microstructures (Obregón *et al.*, 2011).

Reaction sintering is also a fundamental process in monolithic refractories. Performance of these materials in which reactions occur during use is closely linked to the microstructural development at high temperatures. In this sense, the strict control of the development of high temperature calcium aluminate phases in those containing cements, or mullite in the no cement alumina castables and the shrinkage of the material is a main technological requirement.

For more information about traditional ceramics and refractories, readers are directed to comprehensive books and/or handbooks such as Boch and Niepce (2007), Heimann (2010), and Schacht (2004).

Highly-performing ceramic materials with specific mechanical, electrical, thermal, and/or biochemical properties are usually referred as *technical ceramics* (or *advanced ceramics*). Most developments on technical ceramics have been taken place since the last quarter of the last century. There are many books and handbooks dedicated to technical ceramics. Also they are usually addressed in generalist books of ceramics (e.g., Boch and Niepce, 2007; Heimann, 2010).

In the production of technical ceramics, it is usual to have synthetic powders as raw materials because, in general, their use helps achieving final products with superior final properties. As it will be discussed in which follows, reaction sintering of compacts made of synthetic powders has been developed for the fabrication of electronic as well as structural ceramics. Also, reaction sintering of milled powders of natural raw materials with controlled amount and nature of impurities has been demonstrated as an adequate method for the fabrication of technical ceramics. Moreover, the necessity of solid waste control has opened a new opportunity for reaction sintering.

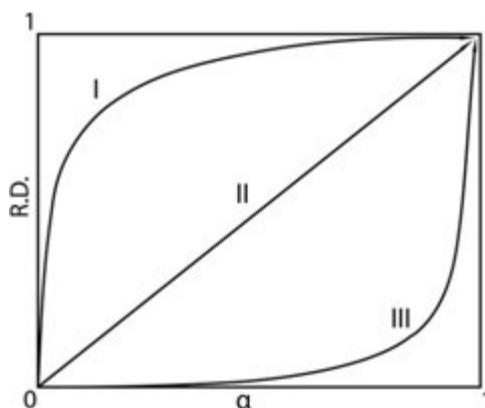


Fig. 1 Relative density (R.D.) vs. fraction of advance of reaction (α) for the different paths that reaction sintering can follow: I: First densification of the compact followed by reaction. II: Simultaneous densification and reaction. III: First reaction between the constituents of the compact followed by densification.

It has to be highlighted that the use of natural raw materials and reaction sintering allows obtaining materials based on compounds such as mullite, of high interest for traditional as well as technical ceramics, which are scarcely found in nature and their synthesis via solid state reactions require repeated milling processes and high temperatures.

Processes and Factors

As described above, there are two main points regarding this alternative sintering process: (1) two or more incompatible reactants are homogeneously mixed and subsequently heated to a suitable temperature where sintering and reaction take place; and (2) the possible appearance during heating of a liquid phase that enhances sintering and/or reaction at lower temperature. This liquid might disappear after the thermal treatment – transitory liquid – or remain in the material as glassy phase. In this later case, its distribution through the microstructure is determinant of the properties of the material. Many variants of liquid phase sintering are applied to a wide range of engineering materials, a complete updated review can be found in reference (German *et al.*, 2008). In reacting powder systems, reaction and densification can both occur, and it is useful to be able to control the rate at which each of those phenomena proceeds when fabricating the desired microstructures.

The potential trajectories that a reactive compact can follow at high temperature are plotted schematically in Fig. 1. Systems following path I are those in which densification occurs prior to reaction and in those following path III reaction occurs before densification starts. Path II combines reaction and densification during the thermal treatment. Apart from the composition of the starting mixture, the path followed by a reactive green compact depends on processing parameters such as particle size, temperature, heating rate, and applied pressure (Rahaman, 2008). When the objective is to prepare fully dense (i.e., zero porosity) fine grain materials, it would be preferable to complete porosity removal prior to the reaction (Path I). If reaction precedes porosity removal, the heat treatment necessary to eliminate the pores also would allow grain growth, making it difficult to retain the grains at the desired size. For the reaction to take place in dense materials without microstructure degradation, the difference between the molar volumes of the reactants and the product has to be small.

In principle, single as well as multiphase materials can be processed by reaction sintering. However, this process presents practical shortcomings that preclude its general use, in particular, for the fabrication of single-phase ceramics. Incomplete reaction might lead to compositional heterogeneities and the microstructural changes associated to the reaction would lead to reduced densification rates and difficult the microstructural control. Reaction sintering is better applied to the fabrication of composites, i.e., materials that require heterogeneity as a microstructural characteristic.

Reaction Sintering in the Presence of Transitory Liquids

A goal of great interest in advanced polycrystalline materials technology is the preparation of theoretically dense sintered compacts with specific microstructure. In this sense, reaction sintering was proposed as an inexpensive way to obtain advanced composite ceramic materials with controlled microstructures following quite conventional processing routes by using the concept of transitory liquid phase.

In such a case, during the reaction sintering process a liquid phase appears at a fixed temperature below the temperature of treatment. This liquid phase will enhance the rate of the reaction sintering because the driving force will be the one corresponding to a reaction sintering in the presence of a permanent liquid phase. Along the process the liquid composition will change up to its disappearance. In this way, it is possible to avoid a decrease in the mechanical properties of the final compact, produced by the presence of a liquid phase.

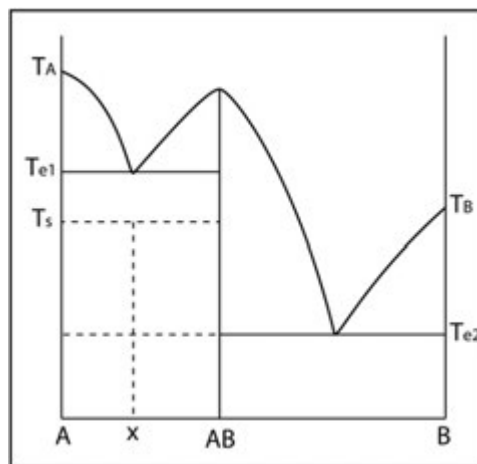


Fig. 2 Phase equilibrium diagram of a binary system, A-B, with two eutectic points at temperatures T_{e1} and T_{e2} and an intermediate compound, AB.

Reaction sintering by transient liquid phase can be easily understood taking into account a binary system, A-B, such as the one plotted in **Fig. 2**, in which a binary compound AB, compatible with A and B, is formed and which has two eutectic points at temperatures T_{e1} and T_{e2} . It is possible to prepare a sintered material of composition x starting from a homogeneous mixture of either A and AB or A and B. In the first case, to avoid the presence of a permanent liquid phase in the final compact, the starting powders must be heated at a temperature below T_{e1} . Reaction and densification will take place in solid state, thus, rates will be relatively slow even for those temperatures close to the eutectic point T_{e1} . When a mixture of A and B is used as starting powder, a local reaction takes place in the grain boundary between A and B during the first stages of the process giving AB as a product. Then, when the treatment temperature is higher than T_{e2} , the liquid phase corresponding to the invariant point of the system AB-B will appear at the grain boundaries AB-B. As the process proceeds, the binary compound and the transitory liquid form. This liquid increases the mass transport rate leading to an increase in the reaction and in the densification rates. At the end, the amounts of AB and A obtained in the presence of a transient liquid are the same as those in the case of a homogeneous mixture of A and AB. The advantages of the former method against the latter one are (1) the temperature necessary for the reaction sintering to take place is lower and (2) the kinetics of the process are higher due to the presence of the transitory liquid phase.

It is also possible to have the advantages of a transient liquid by using starting powders that will form a solid solution at equilibrium but will pass through a liquid stage before equilibrium is reached. Some other processes that can also lead to materials with good properties are liquid phase sintering followed by the crystallization of the liquid at the grain boundaries or working with systems in which the liquid remains isolated by the crystalline grains in the final material.

Reaction Sintered Technical Ceramics

In the field of advanced (or technical) ceramics reaction sintering was first proposed for structural ceramics and nowadays it has been proposed for a broader range of applications, especially for electronic ceramics (Loiu, 2015). Reaction sintering to fabricate single-phase or composite ceramics requires different technological approaches. In this section, the specificity of each approach is described. For composites, mullite-zirconia materials are discussed because reaction sintering in this system is one of the most studied and nowadays it can be considered as a model system to analyze the potential of this processing method.

Single-Phase

Reaction sintering to reach single-phase materials occurs via path III because reaction is relatively fast as compared to densification, thus, reaction is nearly finished before densification starts. Reaction sintering to form single-phase materials has been fully analyzed by Rahaman (2003, 2008). In this case, any change originated by the reaction in the microstructure of the compact plays a critical role. In those systems in which the molar volume of the mixture of reactants is similar to that of the product, reaction implies little volume changes and densification of the reacted compact occurs in the same way as that of a single phase compact. This is the case of zinc ferrite materials for which reaction sintering is an adequate production method. When the microstructure of the mixture compact is disrupted significantly by the reaction, reaction sintering cannot be applied for production. This is the case of the reaction of ZnO and Al_2O_3 to form ZnAl_2O_4 that implies large volume expansion (25–30 vol%) and the reaction product forms predominantly on a percolative network of the original Al_2O_3 particles that impede further densification.

The use of reaction sintering aids has been proposed in order to perform the reaction and densification simultaneously (Path II). The case of magnesium-aluminate spinel materials is a good example of such practice. “Spinelisation” reaction from its

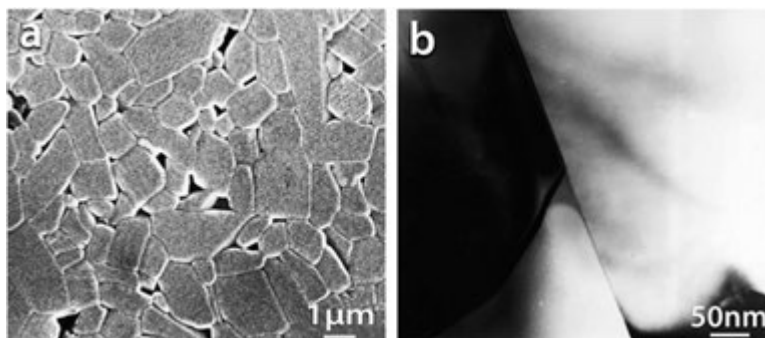


Fig. 3 Characteristic microstructure of advanced mullite materials. (a) Scanning electron microscopy micrograph of a polished and thermally etched surface. (b) Transmission electron microscopy micrograph of an ion thinned specimen. From Baudín, C., 1997. Fracture mechanisms in a stoichiometric $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ mullite. *Journal of Materials Science* 32, 2077–2086.

oxide precursors starts at 1000°C and continues beyond 1400°C and is accompanied by volume expansion, which hinders the densification of a reaction sintered spinel body in single step. In order to obtain full density and complete reaction, complex processing routes involving high temperature pressures (hot pressing or hot isostatic pressing) and two steps thermal treatments would be required. Therefore, enormous efforts have been concentrated to achieve the reaction sintering of spinel materials in a single treatment due to their technological interest. It has been proposed to use additives that would aid sintering by forming solid solutions (Sinhamahapatra *et al.*, 2018, 2019), or permanent or transitory liquids (Huang *et al.*, 1997). When the liquids are permanent their presence as intergranular phases might cause some degradation of the mechanical properties of the product, especially at high temperature.

Mullite-Zirconia Based Composites

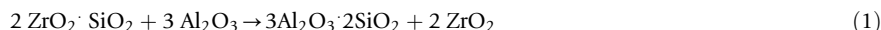
Mullite ($\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ to $2\text{Al}_2\text{O}_3\cdot \text{SiO}_2$) is a desirable phase to be present in ceramics because its low thermal expansion and thermal conductivity, creep resistance and high temperature stability (Schneider *et al.*, 2008). A reference book on mullite and mullite materials is Schneider and Komarneni (2005).

Main deficiency of mullite materials is their low toughness (e.g., Osendi and Baudín, 1996) which limits their use in responsibility applications. Improvement of the mechanical performance of mullite-based materials has been a goal of great technological interest during years. One classical means of enhancing the toughness of mullite is the dispersion of metastable tetragonal zirconia (ZrO_2) particles in the matrix that transform during fracture hindering crack propagation. Transformation toughening in mullite composites is also analyzed in the above mentioned book (Schneider and Komarneni, 2005).

Mullite is scarce in nature, only small amounts are found in the island of Mull, in Scotland, and its solid state synthesis requires high temperatures ($>1500^\circ\text{C}$) and repeated milling. Moreover, sintering of mullite-based materials requires relatively high thermal treatment temperatures ($\geq 1570^\circ\text{C}$). During the last quarter of the last century, reaction sintering was proposed and successfully applied for obtaining fully dense mullite-zirconia based composites.

The characteristic microstructure of advanced single phase mullite materials is shown in Fig. 3. It is formed by equidimensional mullite grains with small amounts of residual glass at triple points that comes from liquid formed during the heat treatment. The angles between this glass and the mullite grains (Fig. 3(b)) reveal that high temperature liquid wet mullite leading to an intergranular film of residual glass.

Reaction sintering of mullite-zirconia composites is done using zircon ($\text{ZrO}_2\cdot \text{SiO}_2$) and alumina (Al_2O_3) as starting materials. Initially, fabrication of mullite-zirconia composites using the stoichiometric proportions of the starting compounds given by Eq. (1) was proposed:



Different accounts of the reaction and densification sequence have been reported for this system. Powders with smaller sizes and higher level of impurities would densify first. In addition, the specific thermal treatment schedule can modify the kinetics of the process, as shown in classical works on this subject. For instance, Claussen and Jurgen (1980) used a two step thermal treatment in which densification of the compact occurred at 1450°C and a dispersion of fine zirconia particles in the mullite matrix was formed at temperatures above 1500°C (Path I Fig. 1). Di Rupo *et al.* found that reaction and densification were concurrent mechanisms (Path II, Fig. 1) in both, conventional sintering at temperatures between 1400 and 1600°C (Di Rupo *et al.*, 1979) and hot pressing at 1450°C (Gilbart *et al.*, 1979) and 1550°C (Di Rupo *et al.*, 1979).

Path III (Fig. 1) is not useful in this system because zirconia grain growth would take place during densification and the control of zirconia grain size is fundamental for the retention of zirconia in the metastable tetragonal phase needed for toughening to take place in the material.

The microstructure of the materials processed by two step sintering process was characterized by a close packing of fine faceted zirconia and fine mullite grains. When a single step thermal treatment in absence of pressure is used (Miranzo, 1985;

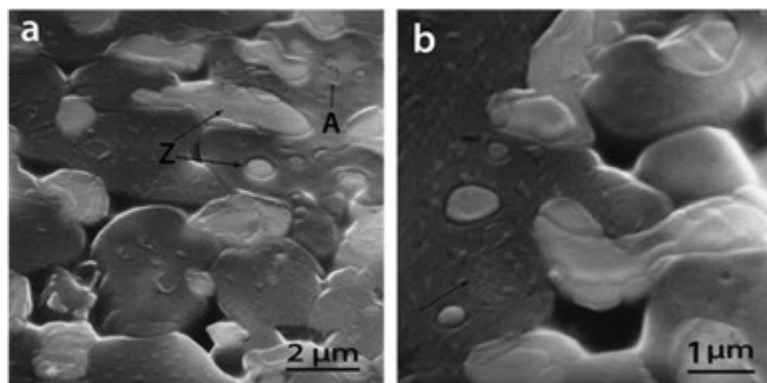


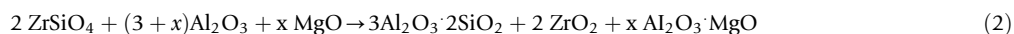
Fig. 4 Characteristic microstructure of reaction sintered mullite-zirconia composites sintered using a single thermal step (RSMZ). The major phase (gray) is the mullite matrix. Scanning electron microscopy micrograph of a polished and thermally etched surface. (a) Two kinds of zirconia particles (Z, white) and small alumina particles (A gray) embedded in mullite are observed. (b) Two kinds of zirconia particles, small alumina particles and partially reacted zircon grain (gray, arrow) are observed. Reproduced thanks to the kind permission of Miranzo, P., 1985. *Comportamiento mecánico de los materiales cerámicos tenaces multifásicos obtenidos por sinterización reactiva*. Universidad Autónoma de Madrid Spain (PhD Thesis).

Torrecillas *et al.*, 1993), the morphology of zirconia particles in the materials is different, as shown in Fig. 4. The microstructure of these materials is characterized by a close packing of equidimensional mullite grains and relatively large irregular shaped zirconia particles at the grain boundaries and some small rounded zirconia grains embedded in the mullite grains. Some non reacted zircon (Fig. 4(b)) and/or residual glassy phases are found in compacts because part of the mullite forms entrapping alumina grains (Fig. 4(a)).

In order to enhance reaction and densification in this system, the group of Instituto de Cerámica y Vidrio (CSIC, Spain) proposed the addition of small amounts of different oxides (e.g., CaO (Pena *et al.*, 1985), MgO (Miranzo *et al.*, 1985), and TiO₂ (Melo *et al.*, 1985)) to the mixtures as sintering aids. These aids allow nearly full reaction and densification of the materials at relatively low temperatures (1425–1450, 1450–1500, and 1450–1550°C, for CaO, MgO, and TiO₂, respectively) due to the formation of transitory liquids at temperatures lower than those of final treatment (<1400, ≤1425, and 1400°C, for CaO, MgO, and TiO₂, respectively). Small excess of alumina was added to the materials with CaO and MgO in order to form anortite (CaO·Al₂O₃·2SiO₂) or spinel (MgO·Al₂O₃) in the final materials.

Main problem of anortite is that it leads to degradation of the mechanical performance of the materials. The main advantage of TiO₂ is that it can enter in solid solution in mullite and ZrO₂.

In the case of MgO, Eq. (1) would be modified as:



In the presence of liquids, mullite grows as crosslinked tabular grains that form a tridimensional skeleton with zirconia particles embedded. In general, some residual glass is observed in regions of the microstructures isolated by the mullite skeleton. In materials with MgO, these regions are larger and more frequent when no alumina excess is added to form spinel (Orange *et al.*, 1985). Modifications of the initial compositions described by Eqs. (1) and (2) by adding significant amounts of extra alumina in the presence (Baudín *et al.*, 1986, 1987) or not (Torrecillas *et al.*, 1993) of MgO as sintering additive have been proposed as alternative means of reaching full reaction. The developed mullite-zirconia-alumina composites present much higher creep resistance due to the sharp reduction in the amount of harmful residual phases.

As described above (Fig. 4), most zirconia particles in reaction sintered mullite-zirconia materials without additives are relatively large (≥2 μm). These large grains transform into the stable monoclinic phase during cooling from the sintering temperature and, consequently, only small fractions of tetragonal zirconia are available for toughening of these materials (e.g., tetragonal zirconia fraction ≈0.2 Miranzo, 1985).

The microstructure originated by liquid phase sintering in mullite-zirconia-alumina materials fabricated with small additions of MgO (Fig. 5) is mostly formed by large mullite tabular grains with small (≤1 μm) intragranular zirconia round particles. There are also small areas with larger zirconia particles, alumina grains, some spinel particles, and residual glass, surrounded by the mullite matrix. The fraction of retained tetragonal zirconia in these materials is much higher (tetragonal zirconia fraction ≈0.6).

The reaction sintered mullite-zirconia and mullite-zirconia materials present a wide range of mechanical behaviors, determined by the specific microstructures. As an example, Fig. 6 plots results of thermal shock tests in water at room temperature for the three materials which microstructures are shown in Figs. 3–5. The composite material with equidimensional microstructure, small fraction of tetragonal zirconia and residual glass at grain boundaries presents just a slight improvement of the thermal shock behavior with respect to the single-phase mullite. On the contrary, the mullite-zirconia-alumina composite has higher strength, before and after thermal shock degradation and higher critical temperature interval.

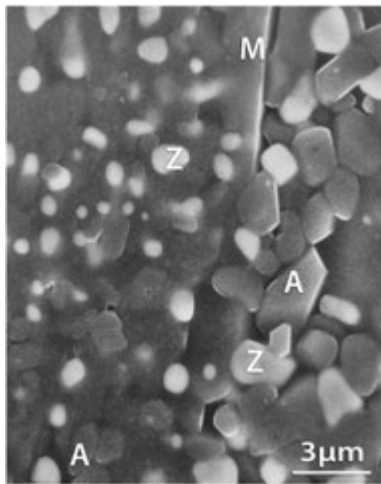


Fig. 5 Characteristic microstructure of reaction sintered mullite-zirconia-alumina composites sintered using a single thermal step with MgO (MgO-RSMZA). Mullite (M) tabular grain with small alumina (A) and zirconia (Z) particles embedded (left) and larger alumina and zirconia particles at the boundaries (right) are observed. Scanning electron microscopy micrograph of a polished and chemically etched surface. (Baudín *et al.*, 1986, 1987).

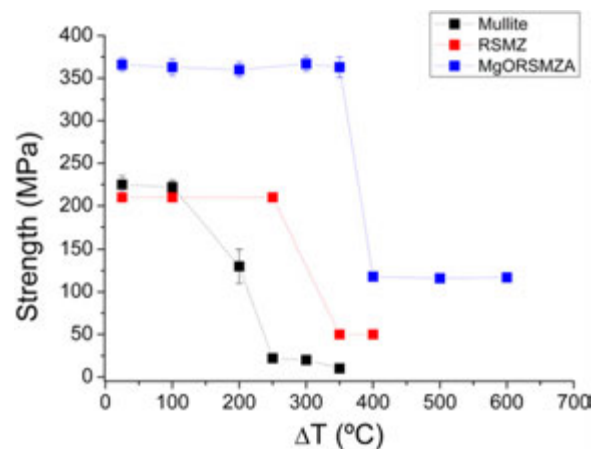


Fig. 6 Results of thermal shock tests in water at 25°C for the materials of Fig. 3 (Mullite), Fig. 4 (RSMZ) and Fig. 5 (MgO-RSMZA). For Mullite and MgO-RSMZA, testing was done using bars of $3 \times 4 \times 50$ mm machined from the sintered blocks. Prior to testing, the bars were chamfered and the surfaces were rectified and polished (diamond 6 μm). Strength was measured in four points bending with 40–20 mm as outer and inner spans using 0.5 mm/min as loading rate. Data for the mullite-zirconia material come from the work by Torrecillas, R., Moya, J.S., De Aza, S., Gros, H., Fantozzi, G., 1993.

Zirconia transformation, together with the interaction of the crack with the specific microstructure – crack deflection and crack bowing, are responsible for this improvement.

Reaction Sintering Nowadays

Reaction sintering allows producing ceramic microstructures with unique properties. For instance, reaction sintering of alumina (Al_2O_3) and titania (TiO_2) to reach alumina-aluminum titanate ($\text{Al}_2\text{O}_3\text{-TiO}_2$) composites promotes the formation of aluminum titanate nanometric grains at the alumina grain boundaries. This microstructure is responsible for microcracking as the main toughening mechanism leading to a significant increment of fracture energy (Bueno *et al.*, 2008).

There is recent increased interest in reaction sintering due to the needs of alternative raw materials and of recycling waste from different industries. In these two fields reaction sintering has great opportunities due to its adequacy to modify the characteristics of the starting materials due to reactions. In this sense, reaction sintering of compacts constituted of mixtures of natural or recycled raw materials can be used to fabricate low cost ceramics with technological applications.

For instance, the reaction sintering of kaolin/phosphate mixtures has been proposed as feasible method to obtain hydroxyapatite and anortite based materials to be used in the electronics industry, for industrial heat exchangers and for biomedical applications (Chouia *et al.*, 2015).

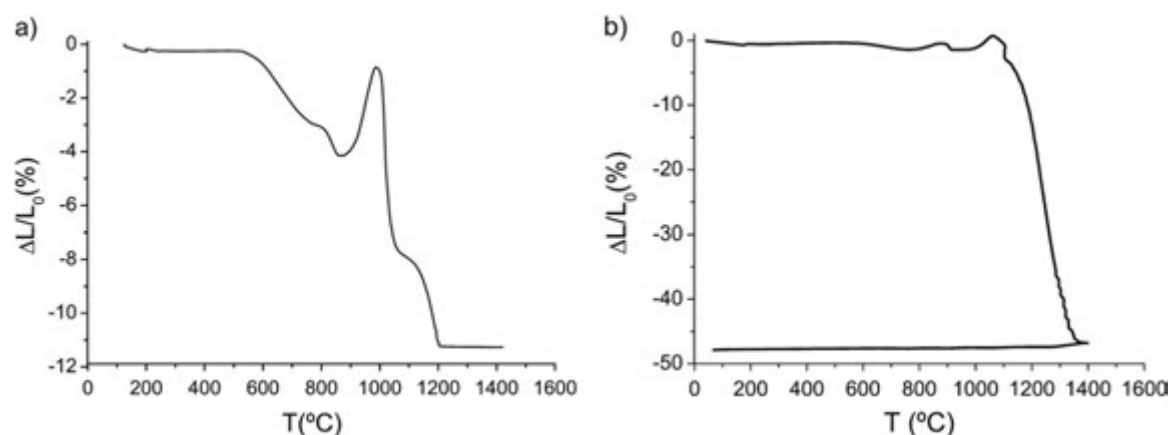


Fig. 7 Linear shrinkage, $\Delta L/L_0$, vs. temperature for compacts of dolomite-zirconia used to process calcium-zirconate-magnesia composites. (a) Constant heating rate: Initial shrinkage is large and unstable. Low final shrinkage. (b) Constant shrinkage rate: Initial shrinkage is small. High final shrinkage. Reproduced from Booth, F., Garrido, L., Aglietti, E., *et al.*, 2016. CaZrO_3 -MgO structural ceramics obtained by reaction sintering of dolomite-zirconia mixtures. *Journal of the European Ceramic Society* 36, 2611–2626.

The most investigated waste sources are those suitable to be constituents of mixtures to obtain reaction sintered mullite-based materials. Some examples are: Fly ash, a by-product of the thermal power plants that contains relatively large amounts of SiO_2 and Al_2O_3 (Dey *et al.*, 2018); rice husk ash, a highly reactive source of SiO_2 (Serra *et al.*, 2016); and sillimanite and zircon sand, which is the industrial by-product generated during the extraction of rare earth compounds from beach sand (Kumar *et al.*, 2015).

A number of heating techniques different from the conventional furnaces and thermal treatment schedules are available to process high density materials with controlled grain size and they have also been applied to reaction sintering. Examples of these techniques and references where updated reviews on their use in ceramics can be found are spark plasma sintering (Franceschin *et al.*, 2017), microwave sintering (Karayannis, 2016), and hot pressing (Travitzky *et al.*, 2018).

The traditional approach to sintering is to optimize the time at the treatment temperature without paying attention to the characteristics of the heating rates employed in reaching the soak temperature. However, the effects of the non-isothermal portion of the heat treatment could determine the properties of the final product. The rate-controlled sintering, that has as independent variable the densification rate, has been proposed as alternative sintering method especially for systems in which reactions occur, such those involved in reaction sintering. In general, rate-controlled sintering firing profiles traverse slowly the permeable intermediate stages of shrinkage (density between 75% and 90% of theoretical), allowing the outgassing of the compact at relatively low temperatures, minimizing pore coarsening and grain growth. This alternative approach is especially adequate when using natural raw materials as carbonates. As an example, rate-controlled sintering has been used to fabricate fine grain and dense calcium zirconate-magnesia composites from mixtures of dolomite ($\text{CaMg}(\text{CO}_3)_2$) and zirconia (Booth *et al.*, 2016). As observed in Fig. 7(a), when the conventional constant heating rate is used, shrinkage variations at low temperatures are relatively large and non monotonous and total shrinkage is extremely low. When constant shrinkage rate is used as control variable (Fig. 7(b)), shrinkage at low temperatures ($<1200^\circ\text{C}$), where dolomite decomposition and the expansive formation of calcium zirconate occur, is low and total shrinkage at high temperature is very high.

To summarize, reaction sintering appears as a processing technique that allows reaching the main requirement of ceramics which is the microstructural control. A strict design of the composition and powder characteristics in the green compact together with the thermal treatment schedule is needed to obtain sintered materials with adequate microstructures. As it is now generally accepted in ceramic science and technology, for successful reaction sintering it is necessary to integrate raw materials selection, green processing and thermal treatment schedule in a single processing methodology.

References

- Baudin, C., Cambier, F., Delaey, L., 1986. Fractographic study of the alumina and zirconia particles embedded in mullite prepared by reaction sintering. *Journal of Materials Science* 21, 4024–4028.
- Baudin, C., Cambier, F., Delaey, L., 1987. Fractographic and acoustic emission studies of mullite-alumina zirconia composites prepared by reaction sintering. *Journal of Materials Science* 22, 4398–4402.
- Boch, P., Niepce, J.-C. (Eds.), 2007. *Ceramic Materials: Processes, Properties and Applications*. USA: ISTE Ltd.
- Booth, F., Garrido, L., Aglietti, E., *et al.*, 2016. CaZrO_3 -MgO structural ceramics obtained by reaction sintering of dolomite-zirconia mixtures. *Journal of the European Ceramic Society* 36, 2611–2626.
- Brook, R.J., 1991. Reaction sintering. In: Brook, R.J., Cahn, R.W., Bever, M.B. (Eds.), *Concise Encyclopedia of Advanced Ceramic Materials*. Oxford: Pergamon Press.
- Bueno, S., Berger, M.H., Moreno, R., Baudin, C., 2008. Fracture behaviour of microcrack-free alumina-aluminium titanate ceramics with second phase nanoparticles at alumina grain boundaries. *Journal of the European Ceramic Society* 28, 1961–1971.
- Chouia, F., Belhouichet, H., Sahnounec, F., Bouzrara, F., 2015. Reaction sintering of kaolin-natural phosphate mixtures. *Ceramics International* 41, 8064–8069.

- Claussen, N., Jurgen, J., 1980. Mechanical properties of sintered, in situ-reacted mullite-zirconia composites. *Journal of the American Ceramic Society* 63, 228–229.
- Dey, S., Ray, D., Mondal, A., Parya, T.K., 2018. Effect of yttria on sintering and microstructural behavior of reaction sintered mullite based on bauxite, fly ash and precipitated silica. *Ceramics International* 44, 10087–10093.
- Di Rupo, E., Anseau, M.R., Brook, R.J., 1979. Reaction sintering: Correlation between densification and reaction. *Journal of Materials Science* 14, 2924–2928.
- Franceschin, G., Flores-Martínez, N., Vázquez-Victorio, G., Ammar, S., Valenzuela, R., 2017. Sintering and Reactive Sintering by Spark Plasma Sintering (SPS). *IntechOpen*. doi:10.5772/intechopen.68871.
- German, R.M., Suri, P., Park, S.J., 2008. Review: Liquid phase sintering. *Journal of Materials Science* 44, 1–39.
- Gilbart, E., Carruthers, T.G., Brook, R.J., Di Rupo, E., 1979. Reaction hot-pressing of zircon-alumina mixtures. *Journal of Materials Science* 14, 705–711.
- Heimann, R.B., 2010. *Classic and Advanced Ceramics: From Fundamentals to Applications*. Weinheim: WILEY-VCH Verlag GmbH & Co.
- Huang, J.-L., Sun, S.-Y., Ko, Y.-C., 1997. Investigation of high-alumina spinel: Effect of LiF and CaCO₃ addition. *Journal of the American Ceramic Society* 80, 3237–3241.
- Karayannis, V.G., 2016. Microwave sintering of ceramic materials. *IOP Conference Series: Materials Science and Engineering* 161, 1–6. (012068).
- Kumar, P., Nath, M., Ghosh, A., Tripathi, H.S., 2015. Enhancement of thermal shock resistance of reaction sintered mullite-zirconia composites in the presence of lanthanum oxide. *Materials Characterization* 101, 34–39.
- Loiu, Y.-C., 2015. Reaction-sintering process for preparing electronic ceramics. *Recent Patents on Materials Science* 8, 225–238.
- Melo, M.F., Moya, J.S., Pena, P., De Aza, S., 1985. Multicomponent toughened ceramic materials obtained by reaction sintering. Part 3 System ZrO₂-Al₂O₃-SiO₂-TiO₂. *Journal of Materials Science* 20, 2702–2718.
- Miranzo, P., 1985. *Comportamiento mecánico de los materiales cerámicos tenaces multifásicos obtenidos por sinterización reactiva*. Spain: Universidad Autónoma de Madrid, (PhD Thesis).
- Miranzo, P., Pena, P., Moya, J.S., De Aza, S., 1985. Multicomponent toughened ceramic materials obtained by reaction sintering. Part 2 System ZrO₂-Al₂O₃-SiO₂-MgO. *Journal of Materials Science* 20, 2711–2710.
- Nesmelov, D.D., Perevislov, S.N., 2015. Reaction sintered materials based on boron carbide and silicon carbide (review). *Glass and Ceramics* 71, 313–319.
- Obregón, Á., Rodríguez-Galicia, J.L., López-Cuevas, J., Pena, P., Baudín, C., 2011. MgO-CaZrO₃-based refractories for cement kilns. *Journal of the European Ceramic Society* 31, 61–74.
- Orange, G., Fantozzi, G., Cambier, F., *et al.*, 1985. High temperature mechanical properties of reaction-sintered mullite/zirconia and mullite/alumina/zirconia composites. *Journal of Materials Science* 20, 2533–2540.
- Osendi, M.I., Baudín, C., 1996. Mechanical properties of mullite materials. *Journal of the European Ceramic Society* 16, 217–224.
- Pena, P., Miranzo, P., Moya, J.S., De Aza, S., 1985. Multicomponent toughened ceramic materials obtained by reaction sintering. Part 1 System ZrO₂-Al₂O₃-SiO₂-CaO. *Journal of Materials Science* 20, 2011–2022.
- Rahaman, M.N., 2003. *Ceramic Processing and Sintering*. CRC Press, Taylor & Francis Group.
- Rahaman, N.M., 2008. *Sintering of Ceramics*. CRC Press, Taylor & Francis Group.
- Schacht, C.A. (Ed.), 2004. *Refractories Handbook*. New York: Marcel Dekker, Inc.
- Schneider, H., Komarneni, S. (Eds.), 2005. *Mullite*. Weinheim: WILEY-VCH Verlag GmbH & Co.
- Schneider, H., Schreuer, J., Hildmann, B., 2008. Structure and properties of mullite – A review. *Journal of the European Ceramic Society* 28, 329–344.
- Serra, M.F., Conconi, M.S., Gauna, M.R., *et al.*, 2016. Mullite (3Al₂O₃·2SiO₂) ceramics obtained by reaction sintering of rice husk ash and alumina, phase evolution, sintering and microstructure. *Journal of Asian Ceramic Societies* 4, 61–67.
- Sinhamahapatra, S., Dana, K., Mukhopadhyay, S., Tripathi, H.S., 2019. Role of different rare earth oxides on the reaction sintering of magnesium aluminate spinel. *Ceramics International* 45, 11413–11420.
- Sinhamahapatra, S., Dana, K., Tripathi, H.S., 2018. Enhancement of reaction-sintering of alumina-excess magnesium aluminate spinel in presence of titania. *Ceramics International* 44, 10773–10780.
- Torrecillas, R., Moya, J.S., De Aza, S., Gros, H., Fantozzi, G., 1993. Microstructure and mechanical-properties of mullite-zirconia reaction-sintered composites. *Acta Metallurgica et Materialia* 41, 1647–1652.
- Travitzky, N., Fu, Z., Knyazeva, A., *et al.*, 2018. Reactive synthesis of ceramic-metal composites. *Advanced Engineering Materials* 20, 1–5. (1800324).

Flash Sintering and Other Rapid Sintering Techniques

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Innovative and novel sintering techniques are response to demand for sintering techniques that can effectively and predictably control the microstructure of powder pressed materials. It has been shown that the densification of powders by rapid heating and under external electromagnetic fields provides a finer control over the microstructure.

The idea to heat ceramics very rapidly is old, but it was for a long time believed that it is impossible due to the low thermal conductivity and thermo-shock resistance of these materials. Formation of a hard shell which then geometrically constrains the shrinkage and densification of the interior was reported during rapid rate sintering of nanocrystalline ZrO_2 –3 mol% Y_2O_3 powder (Chen and Mayo, 1996). Development of novel sintering techniques, such as Spark Plasma Sintering, demonstrated that under certain conditions ceramic materials can be sintered very fast (within minutes) without any gradient or crack formation (Shen *et al.*, 2002). Recently, interesting results have been achieved even faster (below 1 min) by so-called ultra-fast sintering, applying the electric current assisted/activated process (Zapata-Solvas *et al.*, 2015). Further research is conducting on the Electro-Discharge-Sintering (EDS) to achieve sintering below 1 s (Fais, 2018). Current heating techniques, which allow rapid (flash) sintering, are demonstrated in Fig. 1.

The current techniques demonstrated in Fig. 1 can be divided by an application of mechanical pressure (Fig. 1(a, b) versus Fig. 1(c, d, e, f)) or electric current (Fig. 1(a, b, c) versus Fig. 1(d, e, f)). An application of the mechanical pressure brings a possibility to sinter materials at lower temperatures and to obtain better microstructure. On the other hand, pressure-assisted techniques are more expensive and have volume/shape limitations. The second main difference between rapid sintering methods is an application of electric current or electromagnetic field (radiation). The electric current can directly pass through a material and sinter the ceramic material by Joule heating (also known as Ohmic heating). Joule heating is not the only reason for the rapid (flash) sintering; however, it's the most important reason for the Flash Sintering technique and Spark Plasma Sintering (SPS) of the electrically conductive materials (also for Capacitor discharge sintering). The electromagnetic field is used for the rapid heating during Induction sintering or Microwave sintering. Coherent monochromatic electromagnetic radiation (laser) is used to quickly heat up relatively small volume of the ceramic material at extremely high temperatures (thousands of degrees Celsius).

The common rapid sintering techniques suitable for the densification of advanced ceramic materials are:

- (1) Spark Plasma Sintering (SPS)/Field-assisted Sintering Technique (FAST),
- (2) Flash Sintering,
- (3) Capacitor discharge sintering (Electro-Discharge-Sintering or Electric Pulse Consolidation)
- (4) Selective Laser Sintering (SLS),
- (5) Induction sintering,
- (6) Microwave sintering.

Each method has several specifics and all of them require special equipment. A common feature is very rapid heating via the energy dissipation inside the sample or by the absorption from the outside source.

We can generally see two ways to divide these techniques:

- (1) Pressure-assisted and pressure-less techniques.
- (2) Electric current internal heating and heating by external electromagnetic field or laser.

Electric Current as a Source of Internal Heating

Electrical current can at certain conditions heat up ceramic materials similarly to heating a metal wire inside a conventional heater. Ceramic materials are typically electrical isolators at room temperature and only a few exceptions are borides or carbides. However, even very good electrical isolator such as aluminum oxide (alumina) can be sintered by Flash Sintering after doping and heating to high temperature with consequent application of high voltage (Cologna *et al.*, 2011). The second possibility how to make ceramic materials electrically conductive is to incorporate a conductive phase inside the isolating matrix. An example is the doping of the alumina matrix by carbon nanotubes and other additives before the flash sintering procedure (Muccillo *et al.*, 2019). The following description of methods using electric current as source of internal heating is based on the sintering of pure ceramic material, if it's not stated otherwise.

Flash Sintering

In flash sintering, a powder preform is slowly heated up, and then DC electrical field is applied directly to the specimen by a pair of electrodes. The specimen is densified in a few seconds during so-called "flash event" at significantly lower furnace temperature than that used during conventional sintering. This phenomenon occurs in several oxide systems, including yttria stabilized

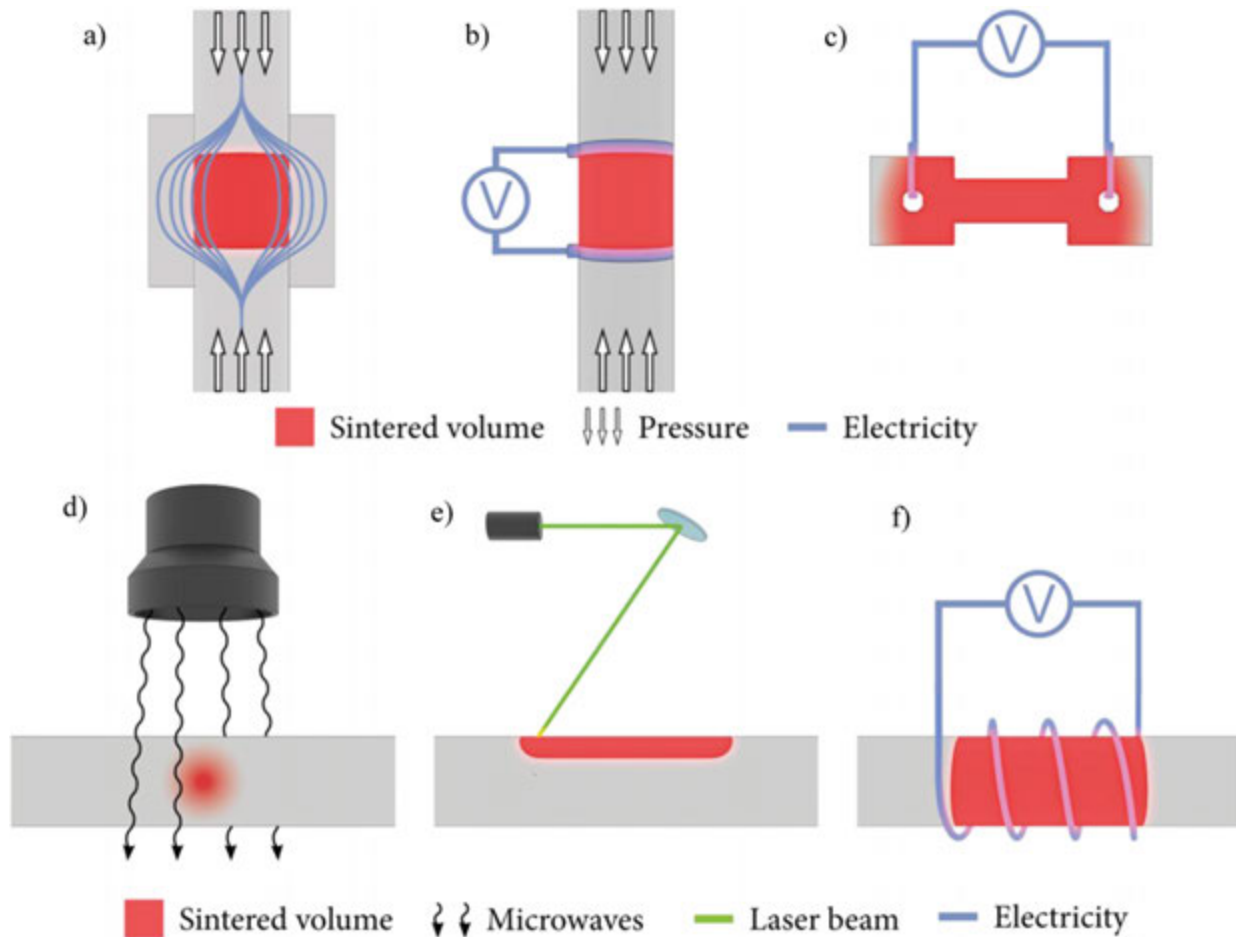


Fig. 1 Simplified schema of the heat generation during rapid sintering of ceramic materials. (a) Spark Plasma Sintering, (b) Pressure-assisted flash sintering, (c) Flash Sintering, (d) Microwave sintering, (e) Selective laser sintering, (f) Induction sintering.

zirconia, magnesia doped alumina, strontium titanate, cobalt manganese oxide, titania and magnesium aluminum spinel, etc (Yu *et al.*, 2016). A characteristic feature of this process is that the sudden onset of sintering is accompanied by an equally abrupt increase in the conductivity of the specimen. The temperature of specimen is increasing as more electrical current can pass through the specimen, which eventually results in a thermal runaway and the specimen is densified in a few seconds. Immediately the power supply must be switched to current control due to limited current density provided by a power source. In the current control mode, the power expended in the specimen decline with the resistance of the specimen continues to fall. The total sintering time is just from a few seconds to several minutes and the temperature required for sintering in a just a few seconds can be extrapolated from the conventional time and temperature through the activation energy for the diffusion. One example of the flash event is shown in Fig. 2. The temperature of the specimen is not equal the furnace temperature, but its several hundred °C higher. The specimen temperature is a function of power dissipation calculated from thermal expansion as a function of power input (Baraki *et al.*, 2012) or by numerical simulation (Grasso *et al.*, 2011). The final specimen density is largely determined by the pre-set maximum current density, see Fig. 2, and that determine the specimen temperature at the steady state.

The flash event is characterized by three phenomenological effects:

- (1) The sample is quickly heated by an internal Joule effect.
- (2) The material shows a transition from insulator to conductor-like.
- (3) The sample starts to emit light – flash effect is observed (Biesuz and Sglavo, 2019).

Technical specification of the flash sintering apparatus

Possible experimental setups for the Flash Sintering are demonstrated in Fig. 3, the technique is relatively new and often are experimental setups modified. The critical part of the apparatus is the power source of direct electric current (DC) or alternating electric current (AC). This power source is modular and has to allow voltage and electric power setup. Voltage is usually from hundreds to thousands of Volts, depending on the electrical resistivity of sintered specimen. Beside possible high voltage, it's

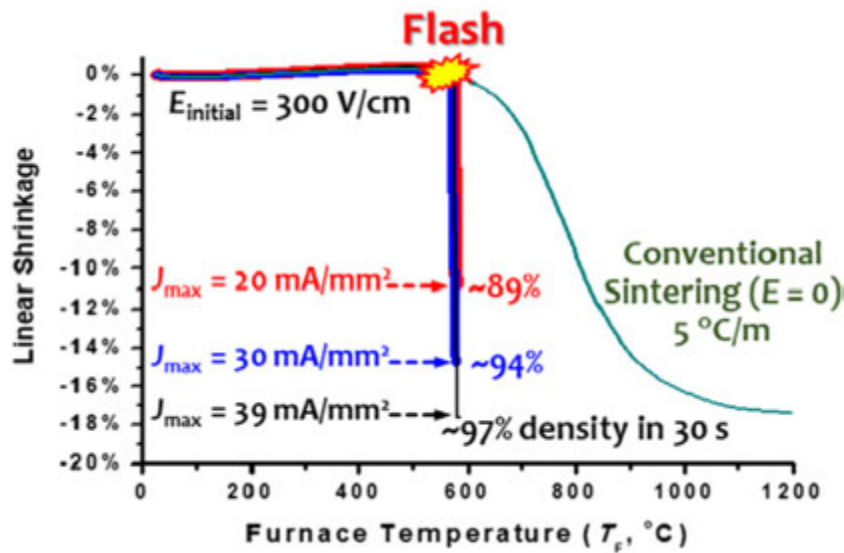


Fig. 2 Examples of the measured linear shrinkage vs. furnace temperature curves for flash and conventional sintering of ZnO in air with a constant furnace ramp rate of $5^{\circ}\text{C min}^{-1}$. With an initial applied electric field of 300 V cm^{-1} , flashes started slightly below 600°C . The densifications occurred mostly within 30 s. The sintered densities depend on the pre-set maximum current (density) limits replotted after revision. Reproduced from Luo, J., 2018. The scientific questions and technological opportunities of flash sintering: From a case study of ZnO to other ceramics. *Scripta Materialia* 146, 260–266. Zhang, Y.Y., Nie, J.Y., Chan, J.M., Luo, J., 2017. Probing the densification mechanisms during flash sintering of ZnO. *Acta Materialia* 125, 465–475.

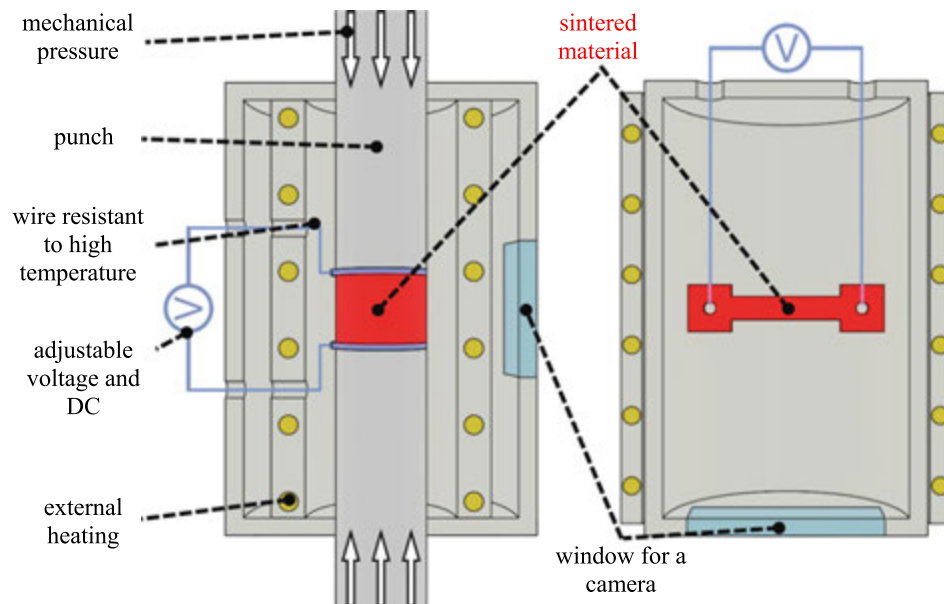


Fig. 3 Schematic figure of flash sintering apparatus with pressure-assisted or pressure-less technique. Note that anode and cathode are usually present, but flash sintering with AC is also possible.

necessary to regulate the electrical current during the flash event. Technically sensitive part is the connection between a specimen and the power source because the contact resistance can easily destroy part of the sample or connecting wires before the flash event. Application of mechanical pressure (Fig. 3 left) can help to decrease the contact resistance; however it brings also the shape limitation. On the other hand, pressure-less setup (Fig. 3 right) require careful green body preparation to avoid inhomogeneous electric current distribution. The flash event is observed by a camera and real temperature inside the sintered specimen is only estimated. Although the whole processing time is not very fast due to the slow external heating by conventional heating elements, the temperature is generally lower than during the flash event and it is a necessary step to make ceramic specimen conductive.

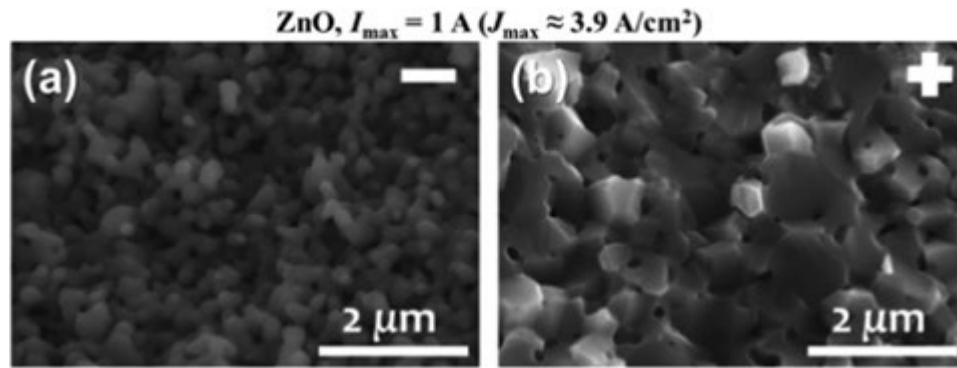


Fig. 4 SEM micrographs of (a) the cathode (–) side and (b) the anode (+) side of a fractured surface of a pure ZnO specimen flash-sintered with a low current density. The starting particle size was slightly smaller than 0.5 μm and limited grain growth occurred at the cathode side, while the grain size doubled at the anode side. Reproduced from Zhang, Y., Jung, J.-I., Luo, J., 2015. Thermal runaway, flash sintering and asymmetrical microstructural development of ZnO and ZnO–Bi₂O₃ under direct currents. *Acta Materialia* 94, 87–100.

Mechanism of flash sintering

The proposed mechanisms for flash sintering try to explain both mass and charge transport. Since 2010 four mechanisms were proposed:

- (1) Joule heating of the specimen by the current flow at grain boundaries that enhances grain boundary diffusion and electrical conductivity; (Cologna *et al.*, 2010).
- (2) The formation of an avalanche Frenkel pairs driven by the applied field and enhancement of mass transport by the defect population (Naik *et al.*, 2014).
- (3) Selective Joule heating and a non-linear interaction between intrinsic fields (space charges) and the applied field that produces “a catastrophic change in self-diffusion at grain boundaries” (Cologna *et al.*, 2010).
- (4) Formation of particularly reduced structures and defect catastrophe that includes unusual generation of electrons, holes and point defects, resulting in sintering, electronic conductivity, electroluminescence, and phase transformations (Jha *et al.*, 2016). If the material is partially reduced its electrical properties would change (Bonola *et al.*, 1991) leading to an increase electronic contribution to conduction or it could change the activation energy for cations (Qin *et al.*, 2016) diffusion leading to non-conventional grain growth (Kim *et al.*, 2011; Qin *et al.*, 2016) and densification phenomena.

The mechanisms driving the rapid densification will be further clarified by modeling work, advanced in situ analysis techniques and by established theories applied to electric current assisted/activated sintering techniques (Yu *et al.*, 2016).

Generally, it is possible to define flash sintering as a current assisted sintering technology characterized by rapid densification (matter of few seconds-minutes) and by the simultaneous observation of the flash event, including a thermal runaway of internally generated Joule heating, electrical conductivity abrupt drop and strong bright light emission. The flash event is reproduced when specific onset electric power dissipation is reached in the ceramic body, typically, in the range 10–50 mW mm^{-3} . Often inhomogeneous sintering is observed on cathode and anode, see Fig. 4. This cathode-side abnormal grain growth can be explained from the electric-potential-induced accumulation of electrons and an associated oxidation reaction to form excess cation vacancies at ZnO grain boundaries that promote interfacial diffusion (Tuller, 1999). Other explanations are potential-induced abnormal grain growth (Kim *et al.*, 2011) or the idea of grain boundary complexion transitions (Cantwell *et al.*, 2014).

- Advantages: No shape limitation, various atmospheres, pressure/pressure-less alternative, unique microstructures, energy efficient, low investment.
- Disadvantages: Technically difficult electrode connections, low control over the process, often inhomogeneous sintering, depends on green body quality.

Spark Plasma Sintering (SPS) or Field Assisted Sintering (FAST)

The Spark Plasma Sintering (SPS) technique, also known as plasma activated sintering or field-assisted sintering technique (FAST), requires mechanical pressure, specific sintering die, and the application of a high pulsing DC current. The word “plasma” is often misleading, because this sintering technique is not derived from a plasma generating machine and even the presence of plasma inside the sintered powders is questionable.

The SPS is especially useful for densifying hard to sinter ceramics including carbides, nitrides, borides and their composites. Furthermore, it is also promising with regard to achieving dense materials with nano and submicrometric structure in nano-powder based materials.

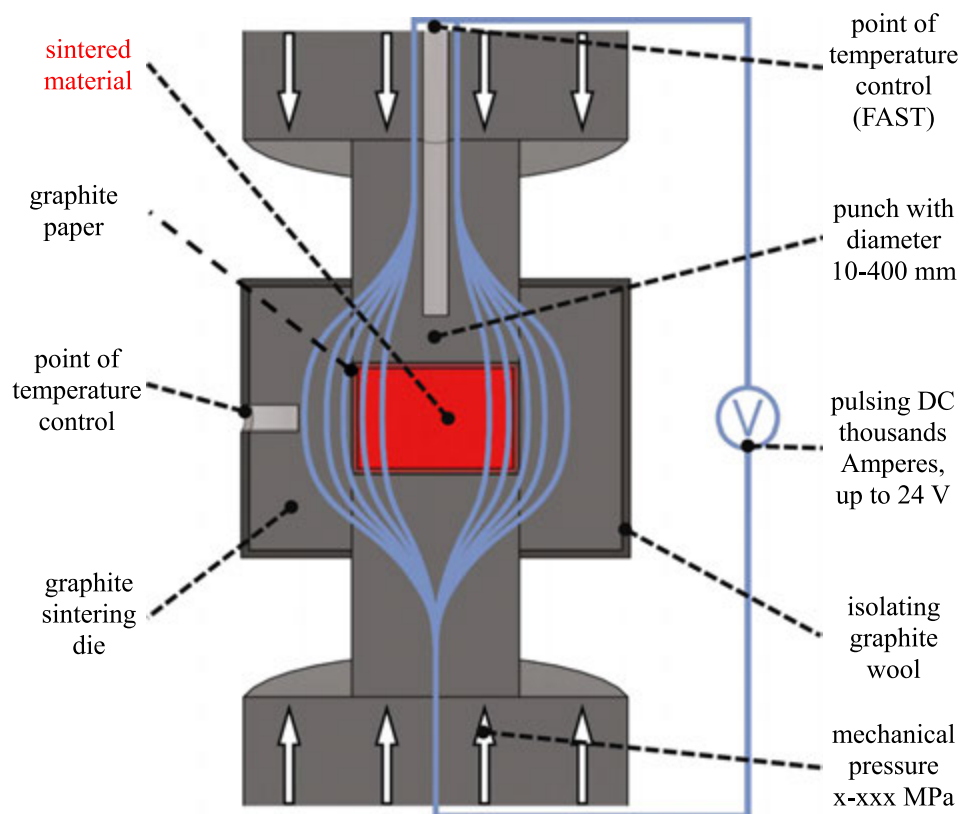


Fig. 5 Simplified schema of the spark plasma sintering apparatus with focus on the sintering die.

Technical aspects

The technique provides direct contact of heating elements (sintering die) with the samples, very rapid heating/cooling rates (several hundreds of $^{\circ}\text{C min}^{-1}$), and uniaxial mechanical pressure. A part of the SPS/FAST apparatus is shown in [Fig. 5](#).

Technical differences between SPS, FAST and other apparatus are significant, but all have a source of pulses of direct current (DC) described by ON:OFF ratio. Producers of SPS apparatus can have even different electrical source of DC pulses with various possibilities ON:OFF pulse setting and various “sharpness” of the electric pulses. The SPS (Fuji, Japan) have the very reliable long-life source, but with less sharp pulses and with limited range of possible pulse frequencies compare to the FAST (FCT, Germany) apparatus. Some producers can have very sharp pulses (Thermal technology, USA), however, the impact of the pulse setting is still debated. All SPS sources have relatively low voltage (up to 12 or 24 V depends on a producer) and very high electric current (limited to 1000–50000 A depends on a model), this limits the use of SPS apparatus for internal heating of low electrically conductive samples. On the other hand, heating of the graphite sintering die can be very fast up to $1000^{\circ}\text{C min}^{-1}$ due to possible high current density.

Every SPS apparatus uses graphite sintering dies with good electrical conductivity and mechanical strength. The shape design is different and FAST apparatus has one extra control point for the temperature measurement, however this hole influences the heat distribution inside the punch. Graphite needed for SPS tools has to provide excellent electrical and mechanical properties and some companies produce special “SPS-ready” graphite. Mechanical properties of graphite limit an applied mechanical pressure to approximately 100 MPa for the standard setting, however special die settings including “small die in big die” allows mechanical pressure up to 1000 MPa ([Anselmi-Tamburini et al., 2006](#)). However, this is limited to small diameters of the sample and relatively low temperatures. High-temperature stability of the graphite allows achieving temperature above 2200°C inside the SPS die, but atmosphere inside the sintering chamber is limited to inert gases. The most common atmosphere is “running vacuum”, that means constantly running vacuum pump during the sintering process (usually 5–10 Pa). Due to the tightly closed graphite sintering die (using graphite paper as sealing medium, see [Fig. 5](#)), it is possible to sinter also materials decomposing in vacuum such as silicon nitride, etc. ([Shen et al., 2002](#)). Disadvantage of the graphite dies is presence of carbon and reductive environment inside the powder during the sintering process. Carbon is spread also by gas phase and therefore it is very difficult to avoid the contamination just by isolating the sintered powder. Several approaches can be used such as.

- (1) Lower the sintering temperature (higher contamination with increasing temperature).
- (2) Carefully remove residual oxygen from inert gas between the sintered powder, particle size also plays a role ([Bertrand et al., 2014](#)).
- (3) Use sintering additives reacting with residual carbon and forming removable gas ([Meir et al., 2009](#)).
- (4) Use a platinum foil instead of a graphite foil to make a carbon free environment ([Biswas et al., 2016](#)).

Spark Plasma Sintering was originally referred as sintering at lower temperatures compared with conventional techniques. Nowadays, numerical modeling (primarily finite elements) supported by experimental results demonstrated that real internal temperature is higher than measured (Vanmeensel *et al.*, 2005). Models predicting the real temperature of sintering dies are already available (Li and Shen, 2015; Vanmeensel *et al.*, 2005) and show variation between electrically conductive and not conductive samples. The electrically conductive samples are internally heated by Joule heating and temperature inside the sintered samples is much higher than measured outside. On the other hand electrically not conductive samples have the hottest part close to the sintering die, but measured temperature is from outside of the sintering die. The temperature gradient inside the sample can be limited by design of the sintering die (tailored current flow) or by adding isolating graphite wool (see Fig. 1). However, homogeneous and crack-free microstructures are obtained after spark plasma sintering (Orrù *et al.*, 2009) even when the thermal gradient is extremely high. A number of explanations of how a thermal gradient can be balanced have been proposed. Firstly, plasma is generated inside the sintering sample. Secondly, internal heating is present when the electric current passes through the sample. Thirdly, high mechanical pressure significantly enhances the heat transfer from the outside to the inside of the sample. All three explanations are controversial (Hulbert *et al.*, 2008; Orrù *et al.*, 2009; Salamon and Shen, 2008). Pressure-less SPS indicates that the mechanical pressure or DC current passing through samples are not crucial parameters for rapid heating in the whole volume (Salamon *et al.*, 2012). Furthermore, an advantage of this technique is the possibility of flexible geometries of a thermal radiation source by the machining of sintering dies (Li and Shen, 2015). In addition, application of very low mechanical pressure brings significant advantages for sintering of porous materials from hollow particles/spheres when internal porosity is preserved after preparation of machinable compacts (Dudina *et al.*, 2019).

- (1) Advantages – Unique densification possibilities, reductive environment or inert atmosphere, mechanical pressure, fast and low energy process,
- (2) Disadvantages – Shape and size limitations, presence of carbon, unique and expensive equipment.

Capacitor Discharge Sintering (CDS)

Capacitor discharge sintering (Fais, 2010) is an electric current assisted sintering (ECAS) technique. The technique is based on storage of electromagnetic energy in a high voltage capacitor bank, and discharge on one step into the sintering apparatus at low voltage (below 30 V) and high current through step-down transformers (sinters) on a pre-compacted powder compact. The sintering die and Electrodes are technically similar to those employed in field-assisted sintering techniques (SPS, FAST) and single electromagnetic pulse sintering technologies.

Nowadays, only samples containing metals were compacted and ceramics trials on electrically conductive ceramics (such as TiB₂) have been made but sintering them has not been completely successful. Electrically insulating ceramics such as oxides do not seem to be sinterable since the dies are made of insulating materials to force the current flow through the powders and no preheating is applied. Experiments showed that combining insulating dies and electrically conductive ceramic powders, although the electric potential increases to 50 V on the compacted powders, barely any current will flow and the material will not sinter. (Fais, 2018).

- (1) Advantages: Whole process is very fast, energy efficient, mechanical pressure, no impact of atmosphere,
- (2) Disadvantages: Shape limitation, unique equipment, difficult to control, limited to ceramic-metal composites.

Heating by External Electromagnetic Field

Selective Laser Sintering (SLS)

Selective laser sintering or melting is the mostly used as a rapid prototyping method where a solid object is built by joining powder particles together via a focused laser beam. In the SLS process, a thin layer of powder is spread across a platform by a blade or a roller mechanism. A modulated laser writes the computer-aided design (CAD) data selectively on the powder bed so that only the particles in an area with the cross-section of the object are fused by laser energy. However, for direct sintering of most ceramic powders the power of the laser beam is not sufficient, because ceramic materials require very high energy densities, approximately an order of magnitude higher than those required for metals (Hayden, 2006). Furthermore, ceramic/laser beam interaction often causes melting, evaporation and ablation rather than sintering. Then the laser beam is used for precise machining of ceramic parts rather than for sintering (Perrie *et al.*, 2005). Nevertheless, the recent development of the laser beam control brings unique opportunities for achieving hierarchically structured heterogeneities and non-equilibrium phase assemblages in bulk ceramics (Qian and Shen, 2013). The residual thermal stresses must be controlled and the dimensional tolerances must achieve micron levels to use the laser for microstructure tailoring. A possible strategy besides sintering is the melting of crystalline ceramic materials and its recrystallization during the cooling process. Usually, complex structural hierarchies are formed due to wide energy dissipation (Wang *et al.*, 2015) and many challenges have to be overcome to use the SLS as a rapid prototyping method (Sing *et al.*, 2017):

- (1) Powder layer deposition – distribution of particle size has to be tailored to increase flowability and decrease powder agglomeration.
- (2) Laser interaction with powder – suitable wavelength and power are necessary for each composition of powder.

- (3) Melting and consolidation mechanism – melted ceramics have certain viscosity and bubbles can easily appear.
- (4) Thermal and residual stresses analysis – sintered parts easily contain cracks therefore thermal and residual stresses have to be managed.
 - Advantages – Controlled wavelength and energy, localization of exposed area, possibility to implement laser into various environments (conventional furnace, SEM etc.), energy efficient.
 - Disadvantages – Limited number of wavelengths, high price for one unit, limited area of exposure at the same time, difficult to control (often melting), thermal stresses, no mechanical pressure.

Induction Sintering

Induction sintering is done by a non-contact heating process. It uses a high frequency electric field to heat up electrically conductive materials. Since it is a non-contact method, the heating process does not contaminate the material being heated. It is also very efficient since the heat is actually generated inside the sample, and the process is often used for metallurgical heat treatment (quenching, hardening, brazing), surface coating or melting (Davies, 1990). Advanced ceramics, which are usually non-electrically conductive, can be sintered by induction heating of a sintering die or susceptor, and in this case the internal heating of a sample is negligible (Kim *et al.*, 2007). Induction sintering is one of the rapid sintering alternatives for ceramic materials with dopants, however more often the induction heating is used for rapid heating of graphite sintering die. The induction heating allows very high heating rates similarly with Spark Plasma Sintering method and rapid densification was also observed (Kim and Khalil, 2006).

- (1) Advantages: Possibility to penetrate deep inside the ceramic green body, energy efficient,
- (2) Disadvantages: Necessity of using dopants (susceptor), limited options for exposure areas and intensity of the field, high price of the unit.

Microwave Sintering

Microwave energy is a form of electromagnetic energy with a frequency range of 300 MHz to 300 GHz. Microwave heating is a process in which the materials couple with microwaves, absorb the electromagnetic energy volumetrically, and transform it into heat. Microwave heating contrary to conventional heating generates heat within the material first and then heats the entire volume of the furnace (Yadoji *et al.*, 2003). The various heating regimes lead to the development of global and localized thermal instabilities and the role of the temperature dependence of the materials dielectric properties (in the microwave range) in the formation of instabilities was also demonstrated (Kulumbaev *et al.*, 2007). The optimization of microwave distribution requires extensive process modeling. The both the fundamentals and numerical calculation methods demand extensive computation resources for the simulation of large multimode microwave cavity applicators (Rybakov *et al.*, 2013). Nowadays microwave heating is often applied in hybrid mode when microwave power source is combined with conventional heating elements. Besides advantages, microwave sintering is not widely used due to the complexity of microwave heating and its implications for large objects.

Recently, microwave heating was applied for flash sintering of ceramics, where microwave heating with high absorbed power per unit volume of material ($10\text{--}500\text{ W cm}^{-3}$) is presented (Bykov *et al.*, 2016). During microwave heating from the core of the sample the particles melt and form the liquid phase inside. In effect, a densification front propagates from core of the sample to its periphery, producing a fully dense ceramic material in a very short time. Microwave flash sintering is a novel process and the authors suggest that the mechanism of ultra-rapid densification are similar or even identical with DC or low-frequency AC flash sintering (Bykov *et al.*, 2016).

- (1) Advantages: No shape limitation, various atmosphere, fast densification, low energy consumption, low investments.
- (2) Disadvantages: Sensitive due to local instabilities, problems with large samples.

Summary and Perspectives

Rapid sintering techniques are due to the recent fast development in a group of novel sintering techniques. These methods should predictably and effectively (low energy consumption and short time) control ceramic microstructure during the sintering process. However, nowadays it's still very challenging to control microstructure during such fast sintering. Microwave, Induction and Spark Plasma Sintering already have several specific applications, where the energy saving and unique microstructures are the main benefits. Capacitor discharge sintering is originally designed for specific applications and the amount of research carried out is relatively small because a unique device is needed.

Selective Laser Sintering, often design as a rapid prototyping method, is changing quickly with improvements in the laser technology, but several challenges have to be overcome to achieve expected industrial applications (Sing *et al.*, 2017). Multi-disciplinary approach and long-term research should be applied to study selective laser sintering (or melting) for industrial rapid prototyping of ceramic materials, but a wide range of applications and gained benefits are a strong motivation.

Flash sintering by an electric current is very new in the field of ceramic materials and research has boomed since 2010 (Cologna *et al.*, 2010). A reason is the relatively simple and low cost apparatus with a large variation of experimental settings. Therefore, hundreds of valuable articles have been published and nowadays basic theoretical knowledge is available. Due to unique possibilities, future applications are expected to follow in the next decade.

References

- Anselmi-Tamburini, U., Garay, J.E., Munir, Z.A., 2006. Fast low-temperature consolidation of bulk nanometric ceramic materials. *Scripta Materialia* 54, 823–828.
- Baraki, R., Schwarz, S., Guillon, O., 2012. Effect of electrical field/current on sintering of fully stabilized zirconia. *Journal of the American Ceramic Society* 95, 75–78.
- Bertrand, A., Carreard, J., Delaizir, G., *et al.*, 2014. A comprehensive study of the carbon contamination in tellurite glasses and glass-ceramics sintered by spark plasma sintering (SPS). *Journal of the American Ceramic Society* 97, 163–172.
- Biesuz, M., Sglavo, V.M., 2019. Flash sintering of ceramics. *Journal of the European Ceramic Society* 39, 115–143.
- Biswas, P., Chakravarty, D., Suresh, M.B., Johnson, R., Mohan, M.K., 2016. Fabrication of graphite contamination free polycrystalline transparent MgAl_2O_4 spinel by spark plasma sintering using platinum foil. *Ceramics International* 42, 17920–17923.
- Bonola, C., Camagni, P., Chiodelli, P., Samoggia, G., 1991. Study of defects introduced by electroreduction in YSZ. *Radiation Effects and Defects in Solids* 119, 457–462.
- Bykov, Y., Egorov, S., Ereemeev, A., *et al.*, 2016. On the mechanism of microwave flash sintering of ceramics. *Materials* 9, 684.
- Cantwell, P.R., Tang, M., Dillon, S.J., *et al.*, 2014. Grain boundary complexions. *Acta Materialia* 62, 1–48.
- Chen, D.-J., Mayo, M.J., 1996. Rapid rate sintering of nanocrystalline $\text{ZrO}_2 - 3 \text{ mol\% Y}_2\text{O}_3$. *Journal of the American Ceramic Society* 79, 906–912.
- Cologna, M., Rashkova, B., Raj, R., 2010. Flash sintering of nanograin zirconia in <5 s at 850°C. *Journal of the American Ceramic Society* 93, 3556–3559.
- Cologna, M., Francis, J.S.C., Raj, R., 2011. Field assisted and flash sintering of alumina and its relationship to conductivity and MgO-doping. *Journal of the European Ceramic Society* 31, 2827–2837.
- Davies, E.J., 1990. *Conduction and Induction Heating*. London: Peter Peregrinus Ltd.
- Dudina, D.V., Bokhonov, B.B., Olevsky, E.A., 2019. Fabrication of porous materials by spark plasma sintering: A review. *Materials* 12.
- Fais, A., 2010. Processing characteristics and parameters in capacitor discharge sintering. *Journal of Materials Processing Technology* 210, 2223–2230.
- Fais, A., 2018. A faster FAST: Electro-sinter-forging. *Metal Powder Report* 73, 80–86.
- Grasso, S., Sakka, Y., Rendtorff, N., *et al.*, 2011. Modeling of the temperature distribution of flash sintered zirconia. *Journal of the Ceramic Society of Japan* 119, 144–146.
- Hayden, C., 2006. Excimer laser micromachined three-dimensional microstructures – Techniques and applications. In: Leondes, C.T. (Ed.), *MEMS/NEMS Handbook: Techniques and Applications*. Springer, pp. 880–904.
- Hulbert, D.M., Anders, A., Dudina, D.V., *et al.*, 2008. The absence of plasma in “spark plasma sintering”. *Journal of Applied Physics* 104, 033305.
- Jha, S.K., Terauds, K., Lebrun, J.M., Raj, R., 2016. Beyond flash sintering in 3 mol% yttria stabilized zirconia. *Journal of the Ceramic Society of Japan* 124, 283–288.
- Kim, H.-C., Shon, I.-J., Jeong, I.-K., Ko, I.-Y., Munir, Z.A., 2007. Sintering of ultra-fine tetragonal yttria-stabilized zirconia ceramics. *Journal of Materials Science* 42, 9409–9414.
- Kim, S.W., Khalil, K.A.R., 2006. High-frequency induction heat sintering of mechanically alloyed alumina-yttria-stabilized zirconia nano-bioceramics. *Journal of the American Ceramic Society* 89, 1280–1285.
- Kim, S.W., Kim, S.G., Jung, J.I., Kang, S.J.L., Chen, I.W., 2011. Enhanced grain boundary mobility in yttria-stabilized cubic zirconia under an electric current. *Journal of the American Ceramic Society* 94, 4231–4238.
- Kulumbaev, E.B., Semenov, V.E., Rybakov, K.I., 2007. Stability of microwave heating of ceramic materials in a cylindrical cavity. *Journal of Physics D: Applied Physics* 40, 6809–6817.
- Li, D., Shen, Z., 2015. Sintering by intense thermal radiation (SITR): A study of temperature distribution by simulation and experiments. *Journal of the European Ceramic Society* 35, 3303–3309.
- Meir, S., Kalabukhov, S., Froumin, N., Dariel, M.P., Frage, N., 2009. Synthesis and densification of transparent magnesium aluminate spinel by SPS processing. *Journal of the American Ceramic Society* 92, 358–364.
- Muccillo, R., Ferlauto, A.S., Muccillo, E.N.S., 2019. Flash sintering samaria-doped ceria-carbon nanotube composites. *Ceramics* 2, 64–73.
- Naik, K.S., Sglavo, V.M., Raj, R., 2014. Flash sintering as a nucleation phenomenon and a model thereof. *Journal of the European Ceramic Society* 34, 4063–4067.
- Orrù, R., Licheri, R., Locci, A.M., Cincotti, A., Cao, G., 2009. Consolidation/synthesis of materials by electric current activated/assisted sintering. *Materials Science & Engineering: R-Reports* 63, 127–287.
- Perrie, W., Rushton, A., Gill, M., Fox, P., Oneill, W., 2005. Femtosecond laser micro-structuring of alumina ceramic. *Applied Surface Science* 248, 213–217.
- Qian, B., Shen, Z., 2013. Laser sintering of ceramics. *Journal of Asian Ceramic Societies* 1, 315–321.
- Qin, W., Majidi, H., Yun, J., van Benthem, K., 2016. Electrode effects on microstructure formation during FLASH sintering of yttrium-stabilized zirconia. *Journal of the American Ceramic Society* 99, 2253–2259.
- Rybakov, K.I., Olevsky, E.A., Krikun, E.V., Green, D.J., 2013. Microwave sintering: Fundamentals and modeling. *Journal of the American Ceramic Society* 96, 1003–1020.
- Salamon, D., Shen, Z., 2008. Pressure-less spark plasma sintering of alumina. *Materials Science and Engineering: A* 475, 105–107.
- Salamon, D., Maca, K., Shen, Z., 2012. Rapid sintering of crack-free zirconia ceramics by pressure-less spark plasma sintering. *Scripta Materialia* 66, 899–902.
- Shen, Z.J., Zhao, Z., Peng, H., Nygren, M., 2002. Formation of tough interlocking microstructures in silicon nitride ceramics by dynamic ripening. *Nature* 417, 266–269.
- Sing, S.L., Yeong, W.Y., Wiria, F.E., *et al.*, 2017. Direct selective laser sintering and melting of ceramics: A review. *Rapid Prototyping Journal* 23, 611–623.
- Tuller, H.L., 1999. ZnO grain boundaries: Electrical activity and diffusion. *Journal of Electroceramics* 4, 33–40.
- Vanmeensel, K., Laptev, A., Hennicke, J., Vleugels, J., Vanderbiest, O., 2005. Modelling of the temperature distribution during field assisted sintering. *Acta Materialia* 53, 4379–4388.
- Wang, D.-Z., Ma, J., He, G., *et al.*, 2015. Complex structural hierarchies observed in $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ eutectic ceramics prepared by laser melting. *Journal of Asian Ceramic Societies* 3, 13–17.
- Yadoji, P., Peelamedu, R., Agrawal, D., Roy, R., 2003. Microwave sintering of Ni-Zn ferrites: Comparison with conventional sintering. *Materials Science and Engineering: B* 98, 269–278.
- Yu, M., Grasso, S., McKinnon, R., Saunders, T., Reece, M.J., 2016. Review of flash sintering: Materials, mechanisms and modelling. *Advances in Applied Ceramics*. 1–37.
- Zapata-Solvas, E., Gomez-Garcia, D., Dominguez-Rodriguez, A., Todd, R.I., 2015. Ultra-fast and energy-efficient sintering of ceramics by electric current concentration. *Scientific Reports* 5.8513

Spark Plasma Sintering

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Introduction

The term Spark Plasma Sintering (SPS) is generally used to identify a sintering technique involving the contemporaneous use of uniaxial pressure and high-intensity, low-voltage, pulsed current. In general terms, SPS can be considered a modification of hot pressing, where the furnace is replaced by the mold containing the sample, that is heated by a current flowing directly through it and eventually through the sample. However, since there is no general agreement on the details of the technique, an unequivocal definition of the SPS and its associated procedures cannot be defined (Grasso *et al.*, 2009; Orrù *et al.*, 2009). The name SPS itself has been often disputed as, despite several attempts, the presence of plasma and electric discharges during the process it has never been proved unequivocally.

SPS has been receiving growing attention in the last two decades due to its remarkable effectiveness, allowing to obtain fast sintering and densification, particularly in the case of materials considered hard to sinter, such as extremely refractory materials, metastable phases or nanomaterials. For some of these materials, SPS has already become the sintering technique of choice.

SPS belongs to a quite extensive group of techniques involving the use of electric current for the sintering of materials. Some of these techniques have been introduced, and found widespread application, since the beginning of the last century, particularly for metallic materials. More details on this historical evolution can be found in recent reviews (Olevsky and Dudina, 2018; Guillon *et al.*, 2014; Munir *et al.*, 2011; Orrù *et al.*, 2009). The most distinctive characteristics of SPS, represented by the use of pulsed DC, appeared originally in a patent by Inoue in the mid '60 of the last century (Inoue, 1966), while the term SPS was introduced later on, by the Japanese producers of the first commercial machines. In the beginning, the technique found application mostly in Japan and in a few other far-east countries. The diffusion in western countries, mainly in research institutions, started in the mid '90 of the last century and spread rapidly in the industrial environment.

Machines similar to SPS, but using electric currents presenting a time pattern different from pulsed DC have also been proposed over the years. In particular, the use of plain DC or AC has been suggested. Although there is no generally recognized nomenclature, such techniques are usually referred to as 'Field Assisted Sintering' (acronym FAST) (Orrù *et al.*, 2009). However, a thorough investigation on the role played by the current pattern in determining the characteristics of the sintering process has never been presented. Available indications are suggesting that the current pattern might play a significant role only in a few specific cases, while the main characteristics remain quite similar. For this reason, the coupled acronym SPS/FAST is often used in recent literature to indicate all pressure-assisted, current-assisted, rapid sintering techniques.

General Characteristics

When compared to other more conventional sintering techniques, such as pressureless sintering, hot-pressing, and hot isostatic pressing, SPS is characterized by some distinctive features, represented by the combination of faster heating rates, shorter sintering cycles, lower sintering temperatures, and reduced grain growth. SPS systems can typically operate using heating rate in the range of hundreds of degrees per minute, but values above $1000^{\circ}\text{C min}^{-1}$ can in principle be achieved. These values are between one and three orders of magnitude higher than in conventional sintering and allow for a drastic reduction in the length of the sintering cycles. Besides faster heating rates, the technique also allows shorter sintering times. The two effects combined allow the reduction of typical sintering cycles to a few minutes, which compares with the few hours generally used in conventional sintering. This increase in sintering efficiency allows also reducing the sintering temperatures, sometimes hundreds of degrees, particularly in the case of very refractory materials. This decrease in the sintering temperature produces a general reduction in grain growth, producing materials characterized by smaller grain size and better mechanical properties.

Experimental Setup

Machine Layout

As mentioned before, the general layout of SPS systems presents several similarities with that of a hot-pressing. A simplified schematic is reproduced in Fig. 1. The sample is placed in a mold, or die. No preliminary forming of the material to be sintered is required, as it is generally introduced in the mold in powder form. The mold is warmed up through the passage of a high intensity/low voltage electric current directly through it. A uniaxial pressure is applied by an hydraulic system. These pistons also act as electrodes, supplying the high-intensity current that must flow through the die and the sample. The hydraulic pistons are water-cooled in order to protect them from the heat deriving from the die. The pressure is controlled by a PID feedback system in order to keep it constant during the sintering process. In fact, the sample and the die experience a considerable change in volume during

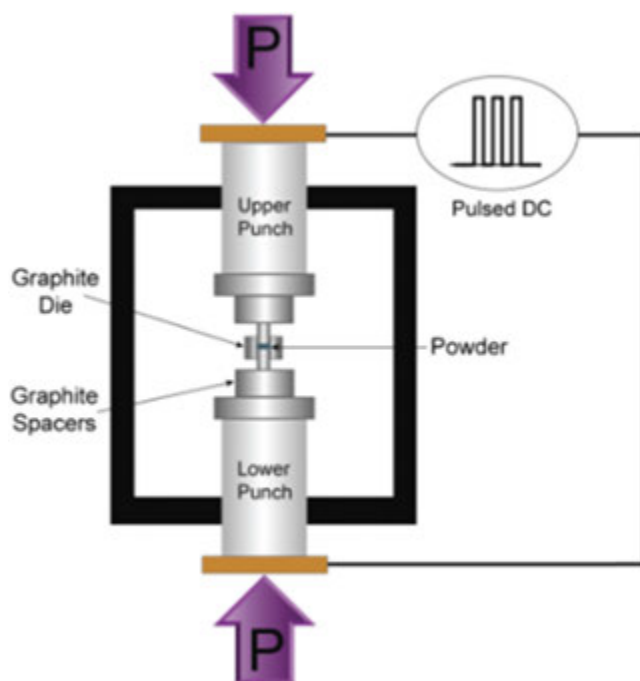


Fig. 1 Schematic of a typical SPS system. Reproduced from Munir, Z.A., Quach, D.V., Ohyanagi, M., 2011. Electric current activation of sintering: A review of the pulsed electric current sintering process: Electric current activation of sintering. *J. Am. Ceram. Soc.* 94, 1–19.

the process, that, if not properly compensated, can result in significant changes in the applied pressure. An example of the overall variations in the linear dimension of the die/sample assembly during a typical SPS sintering cycle is presented in Fig. 2. The actual sample volume contraction due to the densification cannot be directly obtained from these curves unless a calibration based on the thermal expansion characteristics of the tool and of the fully densified samples is performed first.

The most distinctive feature of SPS systems is represented by the use of pulsed electric current. As mentioned in the introduction, this current can present different characteristics. Typically low-voltage (<10 V) and high-intensity currents (between 1 and 50 kA) are used. Different time patterns can be used. In early SPS systems, the current was always pulsed DC, presenting pulses of constant duration (about 3 ms) that could be assembled in predefined sequences (Fig. 3). More recent machines offer more flexibility, allowing to define the duration of the pulses, the delay time between them, the total number of pulses in the sequence, and the number of pulses on and off. In some cases, plain DC or AC can also be used.

The temperature control is generally realized using a thermocouple or a pyrometer, depending on the maximum required temperature. The thermocouple is usually positioned in a small hole drilled halfway through the lateral wall of the die body. A larger hole (few mm in diameter), acting as a black-body cavity, is used in the case of pyrometer reading. Alternative positioning for the pyrometer and the thermocouples have been suggested. The most common involves positioning on the central axis of one of the punches of the die. This axial positioning is more accurate but it is less used because more complicated to setup.

Experimental Procedure

A typical SPS process involves the following sequence of operations. The starting material, generally in the form of fine powders, is placed in the die. The characteristics of this die must be selected on the basis of considerations that will be discussed in the following sections. The die is then positioned between the two hydraulic pistons and the uniaxial pressure is applied. Different kinds of pressure cycles can be used. In most cases, the pressure is applied at the beginning of the process and is maintained constant throughout the sintering cycles. A common alternative is to apply only a minimum pressure at the beginning and the full pressure only when the sample reaches the target sintering temperature. The system is evacuated to a low vacuum (generally few Pa). The main purpose of the vacuum is just to protect the graphite tools from oxidation and to reduce the thermal conduction. An atmosphere of inert gas can be used when overheating is not an issue. The use of an inert atmosphere might also help to reduce the evaporation of volatile samples. Air, on the other hand, requires an oxidation-resistant tool material, such as SiC. The sintering cycle is then started. The temperature profile generally involves a linear ramp to the target temperature with a heating rate between 50 and $200^{\circ}\text{C min}^{-1}$. More complex temperature cycles can be used in the case of reacting or outgassing materials. At the end of the sintering process the heating is turned off and the pressure released. In most cases, the sample is let to cool naturally. This involves a very rapid initial cooling, in the range of several hundreds of degrees per minute. The sample can be removed after 20–60 min, depending on the type of machine and the size of the sample.

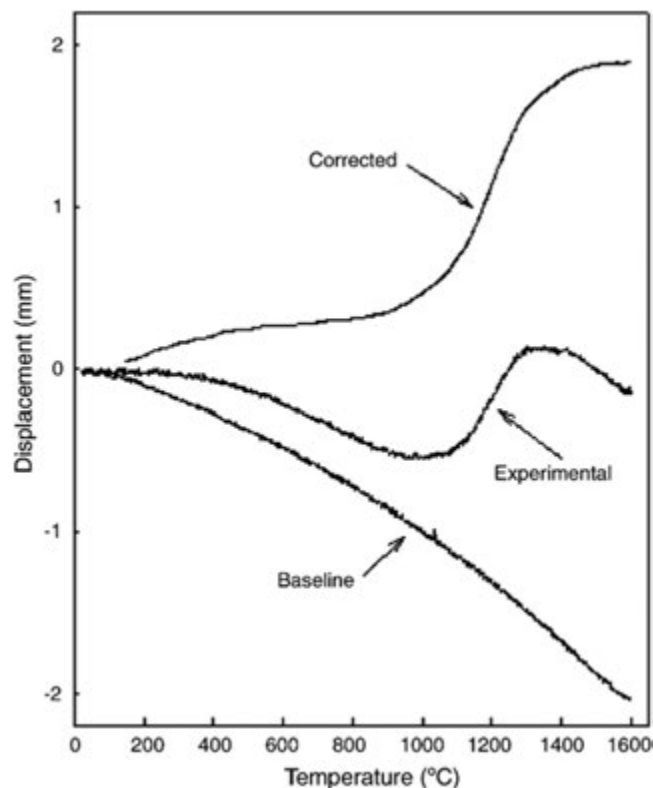


Fig. 2 Example of the variation in the linear dimension of the SPS tool during a typical densification experiment. The experimental curve indicates the overall modification. The baseline indicates the changes due only to the thermal expansion of the die and the fully dense sample. The corrected line is obtained subtracting the two previous curves and indicates the actual change in the dimension of the sample due to the densification process. Reproduced from Anselmi-Tamburini, U., Garay, J.E., Munir, Z.A., 2005. Fundamental investigations on the spark plasma sintering/synthesis process. *Mater. Sci. Eng. A* 407, 24–30.

Temperature, Current and Stress Distribution

A crucial aspect of SPS technology is represented by the possible presence of inhomogeneities in the final product deriving from an uneven distribution in temperature, current density, and mechanical stress during the densification process. This point was largely underestimated in the early applications of the technique, but has been clarified in subsequent investigations, thanks mostly to numerical modeling (Muñoz and Anselmi-Tamburini, 2013; Olevsky and Froyen, 2006; Olevsky *et al.*, 2012; Pavia *et al.*, 2013).

The most critical aspect is represented by the presence of temperature inhomogeneities. These inhomogeneities represent the downside of otherwise positive characteristics of SPS, represented by its fast response time and low thermal inertia. The absence of a furnace makes the control of the temperature distribution much more challenging. In SPS systems the heating of the sample derives only from the current flowing through the die and the sample itself. The current distribution, however, could be quite complex, depending primarily on the die geometry and the electrical properties of the sample. The portion of the punches sticking out of the die, for instance, usually represents the part of the tool with the smaller cross-section and the higher current density; as a result, these parts tend to heat up faster and to remain hotter throughout the process. Within the die body, the current densities can vary considerably, depending on the sample conductivity. In the case of samples presenting an elevated electrical conductivity most of the current flows through the sample itself, with only a minimal amount of current flowing in the graphite walls of the die (see Fig. 4). However, since the joule heating is dependent also on the resistivity of the material, regions with low resistivity give a little contribution in terms of heat generation (Fig. 5). On the other hand, in the case of non-conducting samples, a much more complex current distribution is expected, with the higher current densities being observed within the die walls and on the edges of the sample.

Heat losses contribute also in determining the temperature distribution. Since SPS experiments are generally performed in a vacuum, at low temperatures the only significant heat loss is due to the conduction along the die punches towards the cooler hydraulic cylinders. At higher temperatures, above 700–800°C, radiation losses tend to dominate. To further complicate the picture, it must be considered that the electrical properties of the die and of the sample change with temperature and the extent of the densification process. It is not unusual for metallic samples, for instance, to present very low electrical conductivity at the beginning of the densification process, when still in powder form, and become very conductive when the densification is completed. All these factors contribute to producing complex and difficult to predict temperature distributions. Experimental investigations on these aspects have been quite limited, but extensive numerical modeling has been used to clarify the influence of

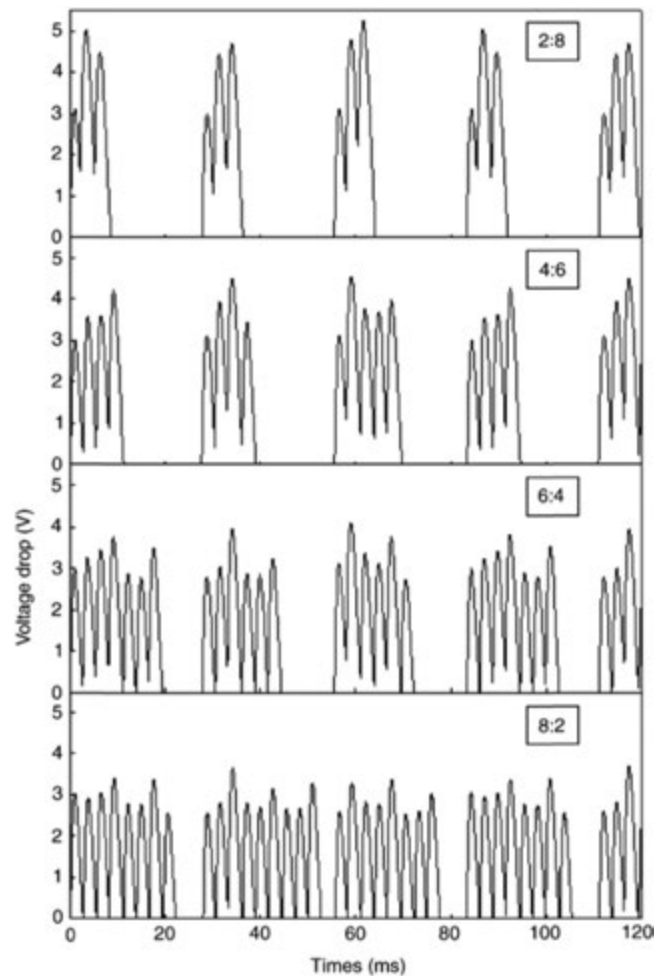


Fig. 3 Example of a typical current pattern used in SPS machines of the first generation. The pulses width is constant (3 ms), while the number of pulses on and off in the sequence can be modified (see boxes). Reproduced from Chen, W., Anselmi-Tamburini, U., Garay, J.E., Groza, J.R., Munir, Z.A., 2005. Fundamental investigations on the spark plasma sintering/synthesis process. *Mater. Sci. Eng. A394*, 132–138.

the various parameters on the temperature uniformity within the samples (Muñoz and Anselmi-Tamburini, 2013; Olevsky and Froyen, 2006; Olevsky *et al.*, 2012; Pavia *et al.*, 2013). These studies evidenced, for instance, as the temperature distribution is strongly dependent on the size of the sample. Samples with small diameter, up to 1–2 cm, always present quite limited temperature inhomogeneities. In these samples the radial temperature distribution is generally characterized by a maximum in the center of the sample, which can be more or less evident depending on the electrical properties of the sample. Obtaining a uniform temperature distribution becomes challenging in the case of larger samples, presenting a diameter of 5 cm or higher. For very large samples temperature differences in the range of tens of even hundreds of degrees between the center and the edges of the samples have been reported. Some actions can be taken to mitigate such inhomogeneities. First and foremost, an appropriate design of the die must be optimized through numerical modeling. In some cases, a reduction in the heat losses can be helpful, particularly if very high temperatures are involved. It is a quite common practice, for instance, to wrap the dies with carbon or alumina felt in order to reduce heat losses by radiation. Although this might help in the case of radial temperature distribution presenting a maximum in the center, it might be detrimental when, as in the case of non-conducting samples, the temperature maximum tends to be located on the sample edges.

Besides temperature, stress might also present non-uniform distribution within the sample. This point has been less investigated also because it is very difficult, if not impossible, to monitor the stress distribution within the die and the sample during the process. The available information derives only from numerical modeling. A relevant point evidenced by these studies is the role of the difference in thermal expansion between the sample and the die. Materials with thermal expansion larger than graphite, such as metals, experience a significant increase in the stress in the proximity of the sample edges. The role of these stress distribution on the microstructure of the densified materials has never been thoroughly investigated, although, in principle, might be relevant. On the other hand, differences in thermal expansion might induce large stress in the peripheral region of the sample during the cooling, which is generally fast and uncontrolled in typical SPS processes, producing fracture in brittle materials.

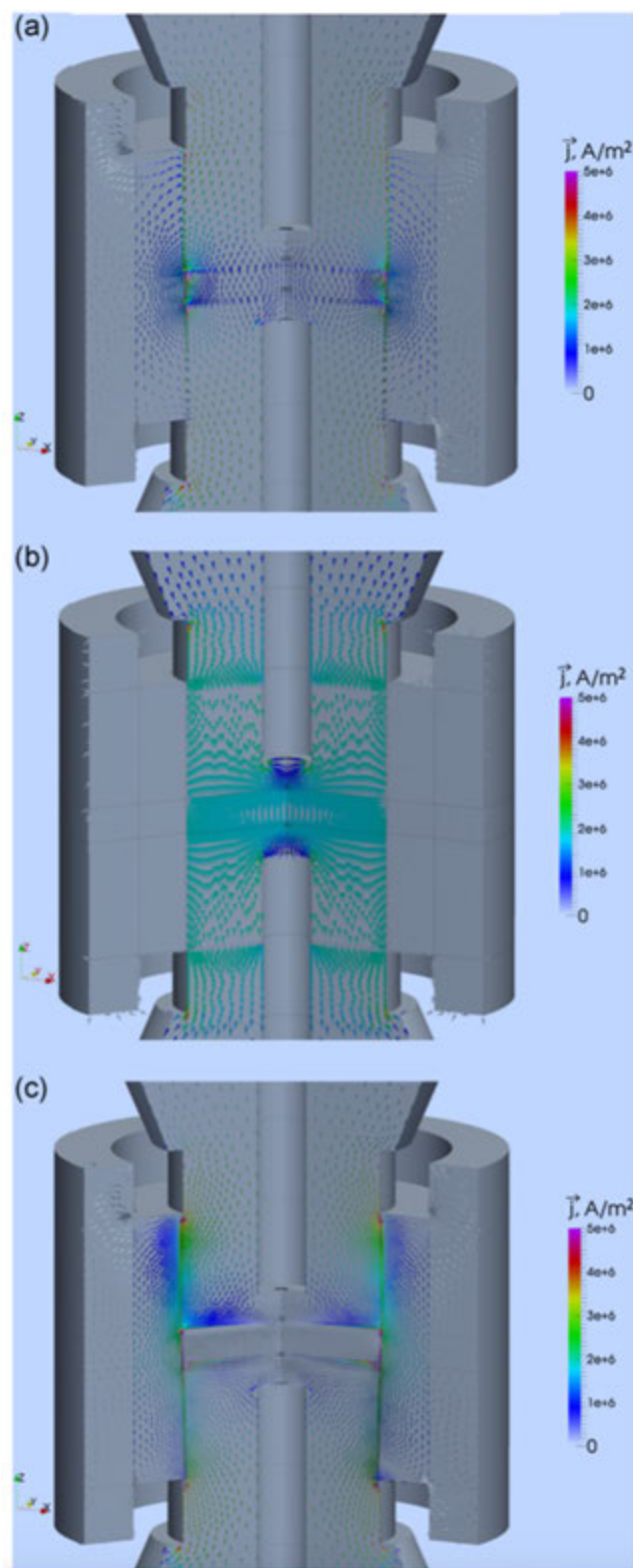


Fig. 4 Distribution of the current flow in the case of (a) conductive powder and die, (b) conductive powder, insulating die, (c) non-conductive powder, conductive die (note the vertical hole in the punch to enable temperature measurement by an axial pyrometer). Reproduced from Guillon, O., Gonzalez-Julian, J., Dargatz, B., *et al.*, 2014. Field-assisted sintering technology/spark plasma sintering: Mechanisms, materials, and technology developments: FAST/SPS: Mechanisms, materials, and technology developments. *Adv. Eng. Mater.* 16, 830–849.

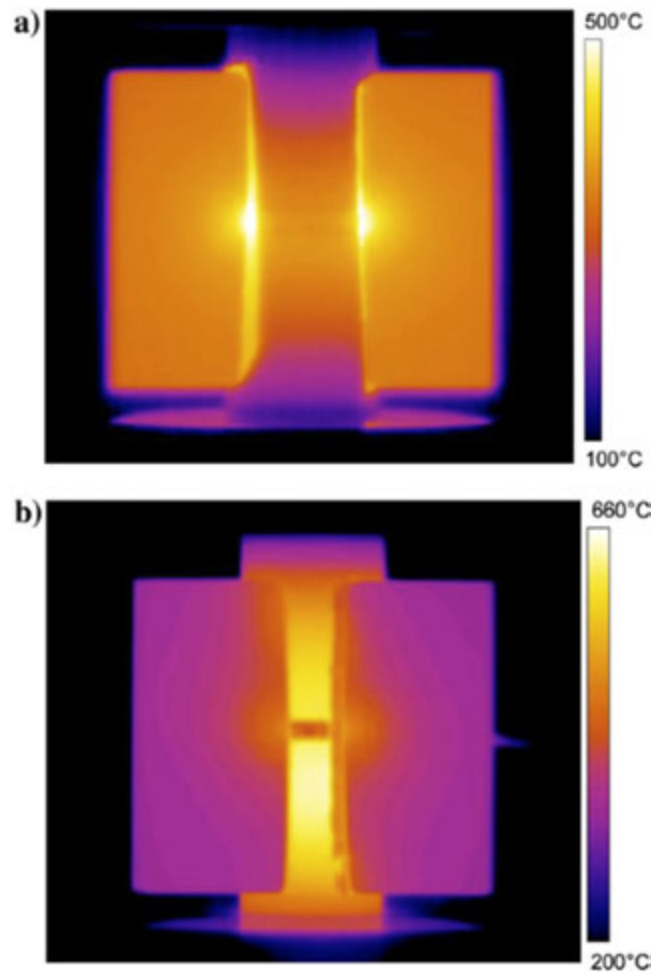


Fig. 5 Infrared thermal images of open die containing: (a) Alumina sample. (b) Copper sample. Reproduced from Manière, C., Pavia, A., Durand, L., *et al.*, 2016. Finite-element modeling of the electro-thermal contacts in the spark plasma sintering process. *J. Eur. Ceram. Soc.* 36, 741–748.

Tooling

The choice of the material used as a die represents a critical point of SPS technology. In order to be effective, the die must present the appropriate combination of thermo-mechanical-electrical properties within the temperature range used for the densification process. Regarding the mechanical stresses, it must be considered that while the punches experience only compressive stress, the body of the die experience a complex, mostly tensile stress. The die must also present low reactivity towards the sample and suitable electrical properties. This last requirement implies an electrical conductivity that is high enough to allow high-intensity current to flow, but low enough to produce a significant Joule heating. Although ideal for most applications, graphite presents several limitations. Even the best graphites, characterized by high density, low porosity, and small grain size, present a quite limited compressive strength (< 150 MPa). This limitation reduces the maximum uniaxial pressure that can be applied to the sample. Another obvious limitation of graphite is related to the possible reaction/contamination of the sample. Several transition metals can, in fact, form very stable carbides. Besides altering the chemical composition of the surface of the sample, this might result in the formation of a strong bond, that in some cases can make even impossible to remove the sample from the die without breaking it. In these cases some sort of a superficial lining is necessary. Graphite contamination can also derive from the release of graphite powders during the sample loading or from high-temperature fast diffusivity of graphite in some materials. Finally, it must be considered that graphite dies can be used only in vacuum or in an inert atmosphere. This environment, on the other hand, can be damaging towards some kind of samples, as they result exposed to a very strong reducing environment during the sintering process. Low-stability oxides represent a typical case, as they can be partially or totally reduced during SPS processing. Unfortunately, alternatives to graphite are quite limited. When high temperatures are involved, the only materials presenting mechanical and chemical properties better than graphite are silicon carbide and tungsten carbide. Silicon carbide also represents the only alternative when oxidizing atmosphere must be used. SiC and WC dies, however, are very expensive, particularly when large samples are involved. Furthermore, being a semiconductor, the electrical resistance of SiC decreases significantly with temperature, complicating the temperature control. Metallic dies, such as high-strength, low-conductivity steel, can be used only for low-temperature

applications, where plastic deformation and creep are not a concern. The same considerations hold for cemented carbides (hard metals) presenting much higher compressive strength, but only at temperatures below 700°C. A combination of ceramic dies with conducting punches is sometimes used, although this requires the sample to be conductive.

Microscopic Mechanisms

The remarkable ability of SPS to produce fast densification generated, from the beginning, an intense debate about the underlying microscopic mechanisms. Several excellent reviews are available in the literature discussing this topic in detail (Anselmi-Tamburini *et al.*, 2013; Cao *et al.*, 2019; Olevsky and Dudina, 2018; Garay, 2010; Grasso *et al.*, 2009; Guillon *et al.*, 2014; Munir *et al.*, 2011, 2006). It must be noted, however, that the number of proposed microscopic mechanisms is quite large and single out the importance of each one of them proved to be very difficult. The number of available experimental and modeling approaches that can be used to test their relevance is, in fact, limited. In general, it can be concluded that there is probably not a single process that is responsible for all the SPS characteristics, but a number of them, that vary depending on the thermal, electrical and chemical characteristics of the material to be sintered. It also often forgotten that the growth of interest towards SPS coincided with the increased availability of materials in the form of nanopowders. Due to the fast heating rates, SPS can take better advantage than conventional sintering of the intrinsic faster sinterability of the nanopowders. However, the understanding of the basic mechanisms is still largely a work in progress, which is crucial for bringing this technique on a solid basis and it is expected to continue receiving large attention in future investigations.

Arc and Plasma Discharges

In early works it was suggested that the unique SPS characteristics derived entirely from the type of pulsed current used during the process (Tokita, 1999). Short pulses of high-intensity current were, in fact, believed to generate local conditions enhancing the atomic mobility through the formation of plasma, or electric discharges, in the small volumes between the grains. Although it was believed that these phenomena were active mostly in the early stages of the process, their beneficial effects were supposed to influence also the late stages of the sintering process. This interpretation enjoyed a large fortune and is still often presented today when discussing the SPS characteristics. Later investigations, however, questioned this interpretation evidencing some major inconsistencies it implies (Hulbert *et al.*, 2008a). Most types of vacuum discharges, such as arc, spark and glow discharges, require high voltages, that are not compatible with the SPS experimental conditions, generally characterized by voltages below 10 V. Only arc discharges can in principle be sustained under low voltages, but they require high electrical conductivity, while SPS is very effective even in the case of insulating ceramic materials. More importantly, the presence of plasma or electrical discharges was never substantiated by any sound experimental evidence, with few exceptions limited to some specific situation (Bonifacio *et al.*, 2013; Saunders *et al.*, 2015; Zhang *et al.*, 2014). So, it became more and more difficult to justify the characteristics of the SPS considering only a single mechanism.

Applied Electric Fields

The possible influence of the applied electric fields plays a central role in the discussion on the mechanisms responsible for the SPS characteristics. This interest is suggested by the consideration that SPS processes involve the use of very high current intensities, up to several kA. In reality, it must be considered that the intensity of the electric field and the currents experienced by the sample are usually quite modest. As evidenced by Fig. 1, the graphite die and the sample can be seen as two electric loads in parallel to each other. Since the electrical resistance of the die is quite low, the voltage drop across the die and the sample is always limited to a few mV, regardless of the voltage generated by the power supplier (usually below 10 V) and of the sample resistivity. For the same reason, the current flow is usually mostly confined within the die components, except in the case of very conducting samples, such as metals in the late stages of densification. These considerations drive to the conclusion that the influence of the electric fields and currents on the densification mechanisms involved in SPS processes, has probably been often overstated.

However, applied electric fields can indeed modify considerably the atomic mobility in solid materials. The most direct evidence is observed in ionic materials, where applied electric fields can induce the movement of the constitutive ions (electromigration), or produce polarization when the electric charges are not free to move. Both phenomena have been largely investigated in solid state science and have the potential to produce profound modifications in the sintering mechanisms. Despite that, the possibility to enhance or decrease the rate of sintering and densification of ionic materials through the application of an electric field is still largely unexplored. However, it must be considered that the influence of electrotransport can be quite complex and depends strongly on the characteristics of the material under consideration. Not in all cases, in fact, the ionic flux produced by the applied electric field can produce the kind of material transport required in sintering. Complete decomposition and reconstruction of crystallographic sites are required, not just the movement of one component. However, in ionic materials intense fluxes of single charged elements might induce mobility of other elements through correlation effects. A typical example is represented by the correlation between electrons and ions movements in mixed conductors. In the case of dielectric materials, polarization might play a significant role, particularly when very small grains are considered. In the point of contact between small particles the polarization effect might produce an amplification of the applied electric field that might extend to several orders of magnitude, producing extreme localized conditions that might enhance atomic mobility.

Another phenomenon associated with applied electric fields often mentioned in SPS literature is electromigration. This term generally relates to the transport of material in metals when elevated electronic current densities ($> 1000 \text{ A/cm}^2$) are present. Electromigration has been extensively investigated for its implication in microelectronics but has never been well characterized in materials presenting complex microstructures, such as powder compacts in the early stages of sintering. Its association with SPS is suggested by the intense electric currents involved with this technique although, as mentioned earlier, the local current densities experienced by SPS samples are usually orders of magnitude below the threshold required for the electromigration phenomena to become evident. Direct experimental evidence on the role played by electromigration in SPS sintering, is limited to model systems where all the current is forced to flow through the sample (Frei *et al.*, 2007).

Other physical effects that are often associated with the presence of applied electric fields in SPS are elastoplasticity, ponderomotive forces, electromagnetic ‘pinch’ effect, and Peltier effect. The relevance of these effects on the actual sinter process has still largely to be determined.

Applied Pressure

SPS belongs to the group of the pressure-assisted sintering techniques, as hot-pressing and hot-isostatic pressing. Similar arguments relative to the influence of the pressure on densification apply to all these techniques. The pressure is generally expected to enhance densification through plastic deformation and grain boundary sliding. These processes reduce the pore volume and the dependence of the densification from bulk diffusion. As a result, also grain growth is generally reduced applying pressure. As noted before, in SPS the maximum applied pressure is limited by the compressive strength of the tooling. Graphite dies do not allow pressures above 100–150 MPa. High-pressure modification of the conventional technique has been presented and be described later on.

Heating Rates

Another typical feature often associated with SPS superior sintering capability is represented by the possibility to use very high heating rates. As mentioned before, in the SPS practice it is quite common to use heating rates in the range of hundreds of degrees per minute. These values are between one and three orders of magnitude higher than in hot-pressing, hot-isostatic pressing, or even in conventional pressureless sintering. Such a relevant increase in the heating rate has a profound influence on the sintering process. Although in general the heating rate does not modify the densification mechanisms, it can influence the relative importance of competing processes presenting different activation energy. During sintering, in fact, several mass transport processes are active at the same time. We can mention, in order of increasing values of activation energy, surface diffusion, grain boundary diffusion, power-law creep, and bulk diffusion. Surface diffusion is a non-densifying process, as it cannot contribute to the growth of the intergranular necks. It contributes significantly, on the other hand, on grain growth. As a result, long exposure of the green compact at temperatures where surface diffusion is dominating ($0.25\text{--}0.4 T_m$) might result in a microstructure characterized by poorly sintered large grains and large pores, reducing the effectiveness of the following high-temperature densification process, as the driving force for bulk diffusion is reduced. In this respect, high heating rates, allowing to reduce or skip the lower temperature processes entirely, increase the effectiveness of the densifying processes. This argument is particularly relevant when the starting powder is nanometric. Nanopowders, in fact, present an intrinsic higher sinterability, that might be lost in the presence of long, low-temperature annealing.

It has also been suggested that a higher heating rate might enhance densification through thermomigration or thermotransport effect, driven by the presence of macroscopic and microscopic temperature gradients generated when high heating rates are involved. The details of these phenomena are quite complex and strongly dependent on the thermo-electrical characteristics of the materials. We already discussed the macroscopic temperature gradients before. For conducting materials, the possibility of microscopic temperature gradients at the point of contact between the grains has often been suggested in the literature. A quantitative analysis of such a phenomenon, however, shows that it might become relevant only in the case of very large grains of materials presenting low thermal conductivity. When nano or submicrometric powders are involved, the build-up of temperature gradients within each grain is impossible, as the thermal conduction is too fast, even in the presence of large currents flowing between the grains.

Examples of Application

In the last three decades, SPS enjoyed a growing success as a method for the densification of functional and structural materials. There are countless examples of applications including almost any class of material. A comprehensive list of these applications can be found in the available reviews and in the extensive original literature (Grasso *et al.*, 2009; Guillon *et al.*, 2014; Orrù *et al.*, 2009). Most of these applications involve materials that can also be obtained using more conventional sintering techniques, but that benefit from the reduction in sintering times, in sintering temperatures, and grain growth offered by SPS. Materials that are traditionally considered harder to sinter received more attention. Among them, there are surely refractory metals, such as W, Ta, and Re, that present outstanding mechanical and thermal properties, but are difficult to densify completely due to their high melting point. The use of SPS allows, in this case, to reduce the maximum required temperature and sintering time, with a consequent reduction in contamination, from oxygen and graphite, and a reduction in the grain size. Similar results have been

obtained in the case of intermetallic phases for advanced high-temperature structural applications. Typical examples are represented by the intermetallic phases present in the Nb/Al and Ti/Al systems. In this case, reactive sintering has often been applied using SPS. In this approach, mixtures of the basic metals have been treated, performing synthesis and densification in the same process. SPS is generally quite effective in enhancing solid-state reactions kinetics, as the applied uniaxial pressure helps maintaining the ideal contact between the reacting phases. Smaller grain size has been obtained using this approach, with beneficial effects on the mechanical properties. Another typical area of application is represented by ultra-high-temperature ceramics, such as borides, carbides, and nitrides of Zr, Ti, and Hf. These materials, with their extreme thermal characteristics, have always represented a challenge for material processing. The interest towards them, on the other hand, has been growing significantly in the last two decades. Long sintering cycles using HP or HIP have always been the only viable approach for their densification. However, this approach produced significant grain growth and contamination, reducing the possibility of obtaining full densification. The use of SPS allowed reducing the processing time drastically, with an overall beneficial effect on the material properties and a significant reduction in the production costs. Another field where SPS attracted large interest is represented by transparent ceramics for optical applications. The possibility of obtaining transparent polycrystalline ceramics, characterized by lower costs and better mechanical properties than single crystals, has driven this interest. Many applications can be found in the literature, with particular emphasis on yttrium-aluminum-garnet (YAG), spinels, zirconia, and alumina. However, contamination from graphite and formation of crystallographic defects, mostly oxygen vacancies, deriving from the strongly reducing conditions typical of SPS, have been found to reduce the in-line transmission in most cases.

Besides these more conventional applications, SPS opened the possibility to realize materials that are problematic or even impossible to obtain using conventional sintering approaches. In the following sections we present a brief review of these applications.

Nanostructured Bulk Materials

The nanostructure has a profound influence on the physical and chemical properties of materials. For this reason, the possibility of obtaining bulk materials preserving the unique properties deriving from the nanostructure is considered particularly attractive. Bulk materials presenting a grain size between 10 and 50 nm present, in fact, superior mechanical properties and, in some cases, unique functional characteristics. The nanometric grain size can also alter the phase equilibria in polymorphic materials, allowing to stabilize materials in unusual crystallographic forms. Sintering and grain growth, however, share the same mechanisms and obtaining full densification without the loss of the nanostructure is a challenging feat. Conventional sintering approaches have largely failed in this respect. The introduction of SPS offered a valuable alternative, that proved to be particularly effective. Because of this, SPS has become the technique of choice for the production of bulk nanostructured materials. Fig. 6 shows how the use of short sintering times (5 min) and high uniaxial pressure allow reducing drastically the grain growth in the case of SPS sintering of nano-YSZ.

Functionally Graded Materials

FGM represents a class of materials characterized by a gradient in composition or microstructure along one direction. Although these materials have been introduced well before the SPS technology became available, the use of SPS opened new possibilities for their development, particularly regarding the materials presenting a gradient of microstructure. In early acceptance, FGMs were

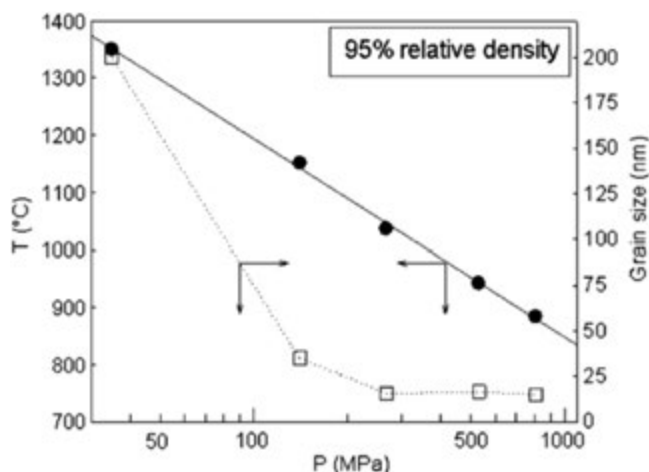


Fig. 6 Relationship between the sintering temperature, applied pressure and final grain size in the case of nanometric fully-stabilized zirconia (8% Y₂O₃). Reproduced from Anselmi-Tamburini, U., Garay, J.E., Munir, Z.A., 2006. Fast low-temperature consolidation of bulk nanometric ceramic materials. *Scr. Mater.* 54, 823–828.

characterized only by the presence of compositional gradients. Typical examples were represented by materials presenting a gradual transition from metallic to ceramics (see Fig. 7). Even in the case of these conventional FGM, the SPS approach offers some advantages, as the shorter sintering times allow reducing the possibility of interdiffusion and chemical reaction between the individual components during the process. Obtaining FGM presenting a gradient in porosity or in grain size is much more difficult using conventional sintering methods. The realization of these materials, in fact, requires the presence of steep temperature gradients. The localized heat generation mechanism, typical of SPS, is in principle well suited for obtaining these conditions. It has been shown that significant temperature gradients can be obtained quite simply just modifying the assembly of the die or changing its shape, as shown in Fig. 8. A simple offset of the die body, leaving only one of the punches outside can produce strong axial temperature gradients, in the range of hundreds of degrees per cm. More complex temperature gradients can be obtained modifying the shape of the die. An example of an innovative material that can be obtained using this approach is shown in Fig. 9. Here a sample of B_4C presents an axial gradient of porosity that was then backfilled with molten aluminum under vacuum. This allowed realizing a material that is extremely hard and wear-resistant on one end and presenting a high toughness on the other. Radial instead that an axial gradient of porosity and composition can also be obtained. The proper control of the temperature gradients requires careful design of the die, which must be guided by appropriate numerical modeling.

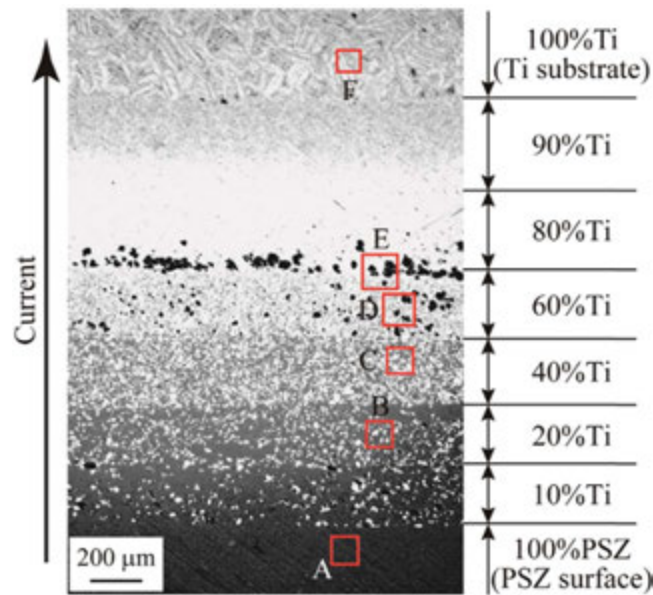


Fig. 7 The microstructure of an eight-layer FGM produced by SPS. Reproduced from Fujii, T., Tohgo, K., Isono, H., Shimamura, Y., 2017. Fabrication of a PSZ-Ti functionally graded material by spark plasma sintering and its fracture toughness. *Mater. Sci. Eng. A* 682, 656–663.

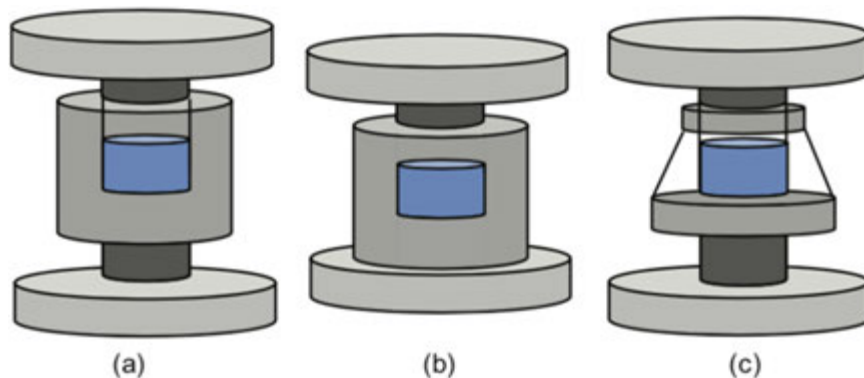


Fig. 8 Tool configurations generating different temperature distributions: (a) symmetric configuration, (b) asymmetric location of the die body, and (c) asymmetric graphite die. Reproduced from Guillon, O., Gonzalez-Julian, J., Dargatz, B., *et al.*, 2014. Field-assisted sintering technology/spark plasma sintering: Mechanisms, materials, and technology developments: FAST/SPS: Mechanisms, materials, and technology developments. *Adv. Eng. Mater.* 16, 830–849.

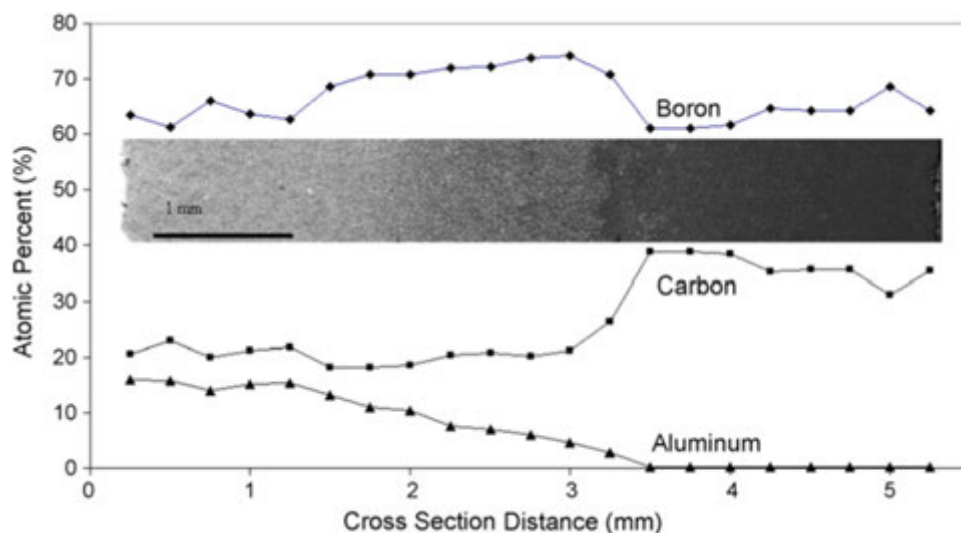


Fig. 9 The microstructure of a B_4C -Al FGM along with an EDS profile of the constituent elements relative to the cross-section distance. The darker region is B_4C rich, while the lighter areas contain Al. Al infiltration occurred from left to right. Reproduced from Hulbert, D.M., Jiang, D., Anselmi-Tamburini, U., Unuvar, C., Mukherjee, A.K., 2008b. Experiments and modeling of spark plasma sintered, functionally graded boron carbide/aluminum composites. *Mater. Sci. Eng. Struct. Mater. Prop. Microstruct. Process* A488, 333–338.

Non-Equilibrium Materials

The short sintering times involved in the SPS technology offer the unique possibility to realize the densification of materials that are out of equilibrium. This is generally impossible to obtain with conventional sintering, as the long high-temperature treatments involved with these techniques drive necessarily the materials towards their most stable state. Over the last few years, a large number of densifications of non-equilibrium materials using SPS have been reported. A typical example, already mentioned before, is represented by nanometric materials. The intrinsic instability of most nanophases towards high-temperature treatment makes them impossible to densify using conventional sintering methods. Other non-equilibrium materials are represented by amorphous phases or glasses. A very interesting example of application in this area is represented by the densification of metallic glasses (**Fig. 10**). These materials are generally obtained by rapid solidification, an approach that limits strongly the possibility to produce objects with complex shapes and in bulk form. The possibility to densify powders deriving from gas atomization or by mechanical alloying opens new and interesting possibilities of application. Numerous examples have been reported (Choi *et al.*, 2007; Chu *et al.*, 2012). Another interesting application is represented by the possibility to produce bulk materials presenting an unstable or metastable crystallographic structure. Several examples have been reported, particularly in the case of metastable crystallographic forms stabilized by the nanostructure, as for undoped cubic/tetragonal zirconia and titania in anatase crystallographic form (Maglia *et al.*, 2010; Masahashi, 2007). The densification of supersaturated solid solutions represents another field of particular interest. The densification of Al alloys with a content of other metals above their saturation limit has been reported (Zhang *et al.*, 2013). Particularly interesting is the possibility to maintain local compositional gradients, in the micro or nanometric range, as it opens the possibility to realize materials with unique functional or transport properties not accessible to homogeneous materials. A typical example is represented by the densification of core-shell powders (Airimioaei *et al.*, 2017), avoiding the homogenization by interdiffusion. Recently the possibility to obtain doping localized at the grain boundary, taking advantage of the low-temperature surface diffusion has also been demonstrated. Other examples of technologically relevant metastable material are represented by the formation of non-equilibrium composites containing diamond or cubic boron nitride (Herrmann *et al.*, 2012).

Innovative Aspects and Future Evolutions

SPS technology has grown in the last two decades to become one of the most relevant innovations in sintering. However, the area of field-assisted sintering is still evolving, and in the last few years some new trends emerged, that might challenge the more 'conventional' applications. Some of these evolutions try to answer unresolved limitations of the technique; others are just attempting to expand its application limits. In the following sections, some of the most interesting new evolutions will be briefly described.

High and Ultra-High Pressures

As already noted before, the maximum uniaxial pressure achievable with a standard SPS tooling, made out of high-density graphite, falls in the range between 100 and 150 MPa. In the last few years, however, attempts to extend such limit has been

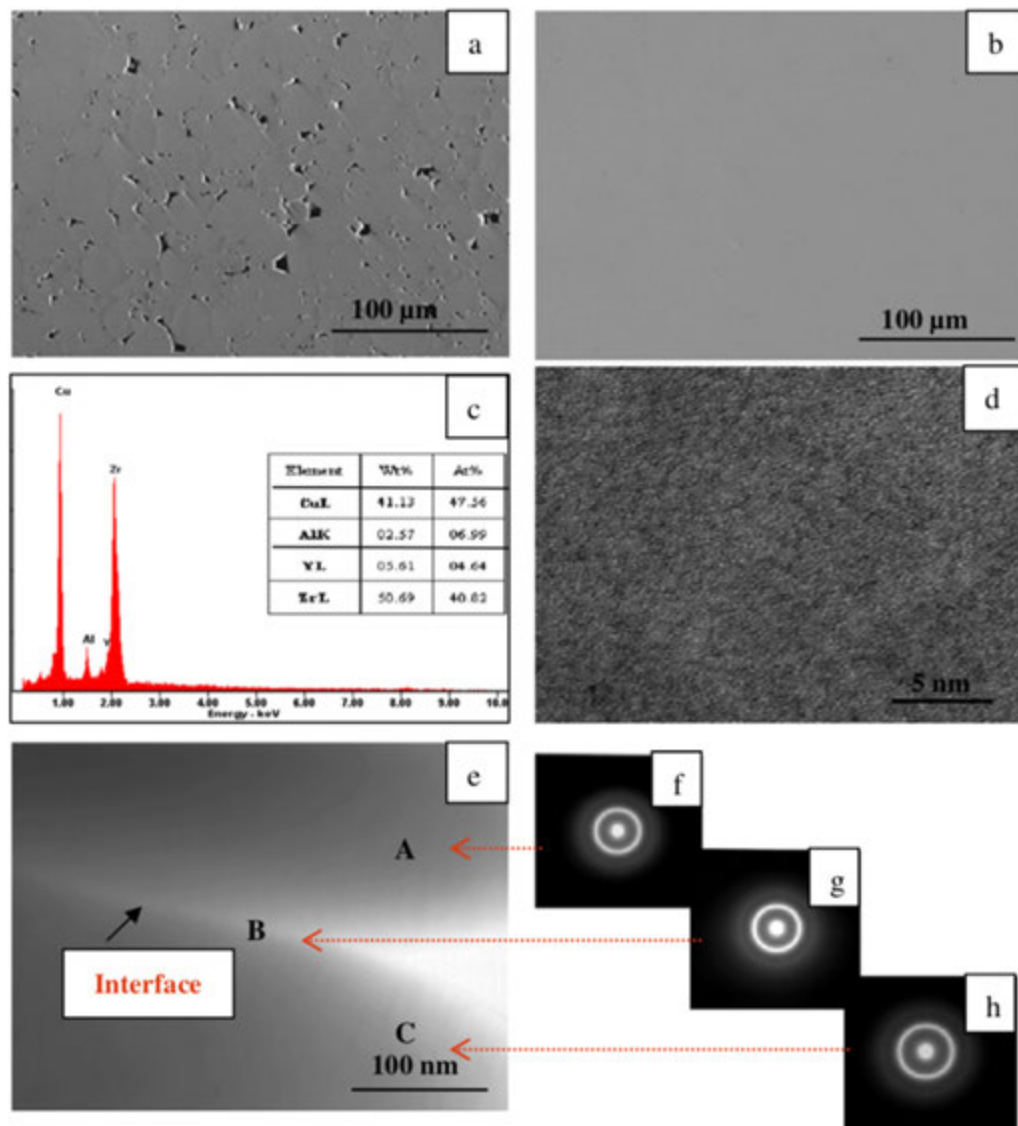


Fig. 10 SEM images of the specimens of $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ metallic glass sintered at 593K (a) and 653K (b); EDS spectra taken from the specimen sintered at 653K (c); high-resolution TEM micrograph taken from the specimen sintered at 653K (d); Bright-field TEM image of the specimen sintered at 653K (e) and the corresponding SAD patterns (f)–(h) taken from the indicated by “A”, “B” and “C” in (e), respectively. Reproduced from Chu, Z.H., Kato, H., Xie, G.Q., *et al.*, 2012. Consolidation and mechanical properties of $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ metallic glass by spark plasma sintering. *J. Non-Cryst. Solids* 358, 1263–1267.

reported several times. The possibility to use much higher pressure can be particularly beneficial for applications involving the densification of nanocrystalline materials. As reported in Fig. 6, the temperature required to obtain a certain level of densification decrease drastically with the increase of the uniaxial pressure. As a result, high-pressure densification is particularly beneficial when the grain growth must be controlled, as in the case of the densification of nanopowders. High or ultra-high pressure may also induce phase transformation in some solid materials.

To achieve uniaxial pressures in the range of the hundreds of MPa or even of few GPa, the typical SPS tooling must be properly modified. An example of a high-pressure setup is reported in Fig. 11 (Anselmi-Tamburini *et al.*, 2006). The external part of the die is very similar to a standard SPS tool and is made out of high-density graphite. This part is where most of the current flows and the heating takes place. The internal part of the die is where the sample is placed and the high pressure is realized. This part must be made with materials with the appropriate compressive strength, such as silicon carbide, tungsten carbide, or cemented carbide. This setup allows achieving 3–4 GPa on samples that are few mm in diameter. Although this pressure is still at least an order of magnitude below the limit achievable with diamond anvil systems, it is enough to observe some pressure-induced phase transformations. The highest temperature achievable is limited to 700–800°C when cemented carbides are used, but can be much higher in the case of silicon carbide or tungsten carbide tools.

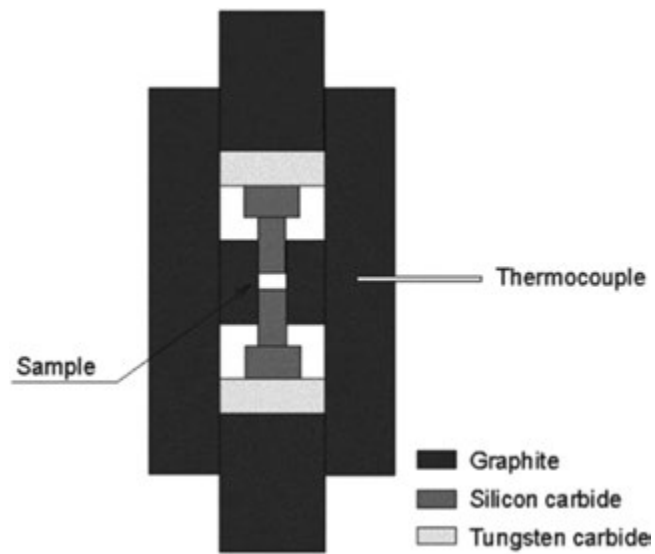


Fig. 11 Two stages SPS die for high-pressure applications. Reproduced from Anselmi-Tamburini, U., Garay, J.E., Munir, Z.A., 2006. Fast low-temperature consolidation of bulk nanometric ceramic materials. *Scr. Mater.* 54, 823–828.

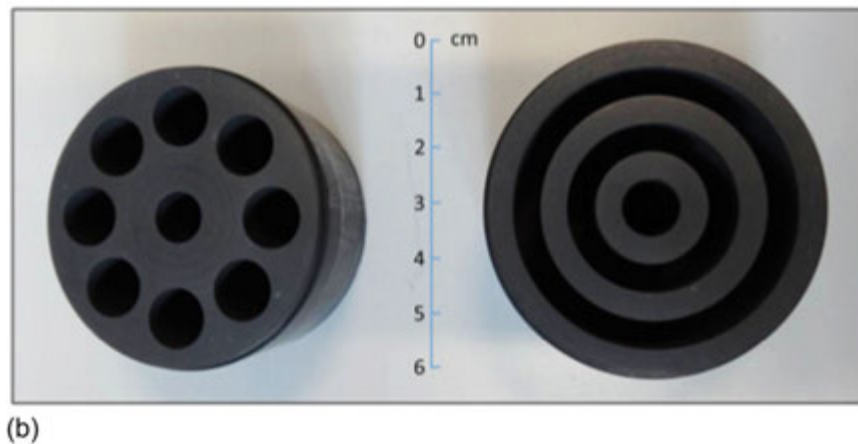
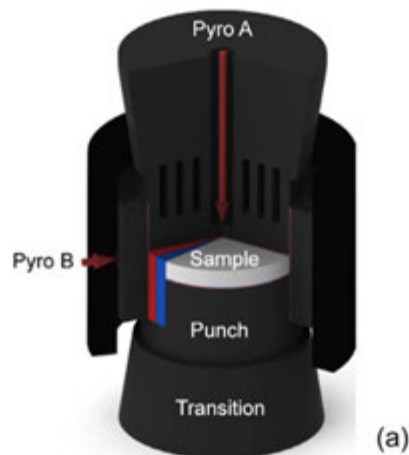


Fig. 12 Die design presenting a reduction of the cross-section allowing a reduction in the electric power required to reach the target temperature and improved temperature uniformity. (a) View of the sample/die assembly; (b) details of the punches presenting holes (left) and rings (right). Reproduced from (a) Giuntini, D., Raethel, J., Herrmann, M., Michaelis, A., Olevsky, E.A., 2015. Advancement of tooling for spark plasma sintering. *J. Am. Ceram. Soc.* 98, 3529–3537. (b) Giuntini, D., Raethel, J., Herrmann, M., *et al.*, 2016. Spark plasma sintering novel tooling design: Temperature uniformization during consolidation of silicon nitride powder. *J. Ceram. Soc. Jpn.* 124, 403–414.

Tooling Optimization

Despite a large number of successful applications, SPS is often considered a technique with limited applicability to large scale industrial processes. This conviction derives in part from few misconceptions developed in early applications, but is also based on some real issues that are limiting its scaling up. In this respect SPS presents two main limitations: there is a limit to the maximum size of the samples that can be produced and it allows to obtain only one sample at a time. Despite their relevance, little effort has been paid in trying to mitigate these two limitations. Both limitations are ultimately related to the tooling design. The maximum sample dimension is mostly controlled by two factors: (1) the maximum current that can be delivered by the power supplier used in SPS machines, and (2) the difficulty of maintaining a uniform temperature distribution in very large samples. Regarding the first point, it must be noted that current intensities above 40–50 kA are impractical for economic and logistic reasons. This threshold limits the maximum achievable sample dimension to disks of 30–40 cm in diameter, as the graphite tools used in SPS require very high current to produce enough joule heating to warm up large samples. In this respect, hot pressing and HIP can produce even larger samples with lower investment and operating costs. However, the geometry of large dies is never usually optimized, as it is generally obtained by a simple scaling up of dies used for the smaller samples. Recently it has been shown that a proper design of the tools can save considerable electric power through an optimization of the current fluxes (Giuntini *et al.*, 2016, 2015). A careful design of the tools, achieved through numerical modeling, also allows optimizing the temperature distribution in the case of large samples. An example of this approach is shown in Fig. 12, where the electrical cross-section of the punches has been properly reduced in order to obtain a substantial reduction in the electric power required to reach high temperatures and uniform temperature distribution within the sample.

Analogous considerations can be applied to the other limitation of SPS, represented by the possibility to produce only one sample for each sintering cycle. Also in this case, the limitation is mostly related to a lack of evolution in the tooling design. In fact, it is possible, at least in principle, to produce several samples with a single sintering cycle using an appropriate tool. In Fig. 13 few examples of possible setups are reported, presenting parallel, serial, or parallel-serial alignment of tool cavities. This approach, however, has received very limited attention in the SPS practice. Such complex tools, in fact, are difficult to make and to control, particularly in terms of temperature uniformity, as the current fluxes are in this case even more complex and difficult to predict without an accurate numerical modeling (Fig. 14).

Finally, it is worth mentioning the possibility of realizing objects characterized by complex shapes. Traditionally, SPS samples present a disk-like or cylindrical shape. Recently, however, it has been presented the possibility of realizing more complex shapes through near-*net*-shape approaches involving the use of the so-called “deformable interfaces” or “controllable interfaces” method (Manière *et al.*, 2019). In this approach, a layer of deformable material, usually a graphite foil, is shaped to define a complex geometry. The foil is then placed within a traditional SPS tool, and the two volumes separated by the foil are filled with similar or different powders. At the end of the SPS densification, the two regions can be easily separated, producing one or two complex shape elements.

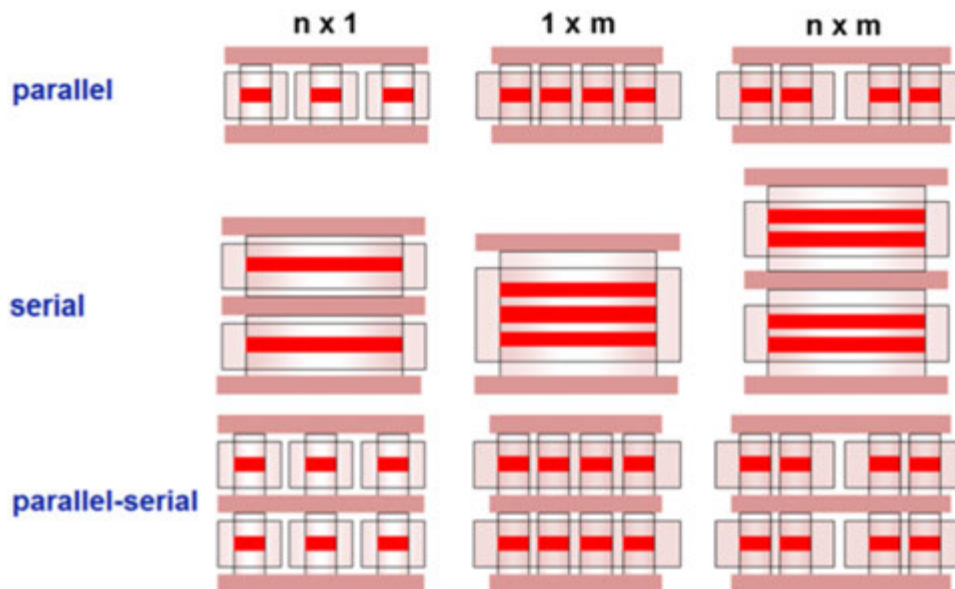


Fig. 13 Tools configuration for the production of multiple parts in a single sintering cycle. Reproduced from Guillon, O., Gonzalez-Julian, J., Dargatz, B., *et al.*, 2014. Field-assisted sintering technology/spark plasma sintering: Mechanisms, materials, and technology developments: FAST/SPS: Mechanisms, materials, and technology developments. *Adv. Eng. Mater.* 16, 830–849.

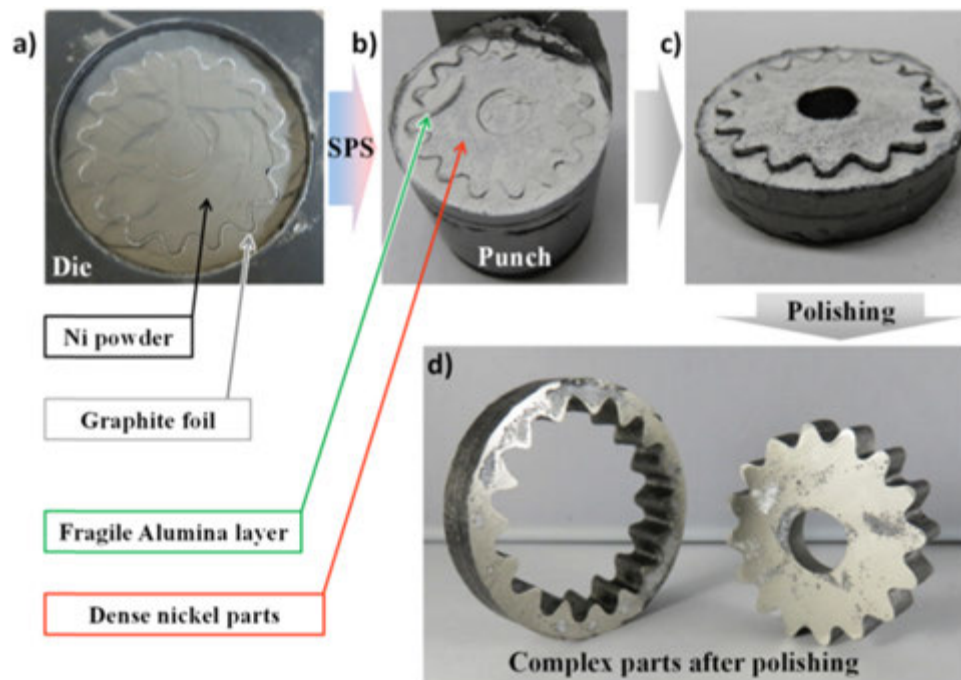


Fig. 14 Main steps of the spark plasma sintering (SPS) process involving the ‘controllable interface’ approach. (a) loading; (b) assembly after SPS sintering; (c) releasing; and (d) final components after polishing. Reproduced from Manière, C., Torresani, E., Olevsky, E., 2019. Simultaneous spark plasma sintering of multiple complex shapes. *Materials* 12, 557.

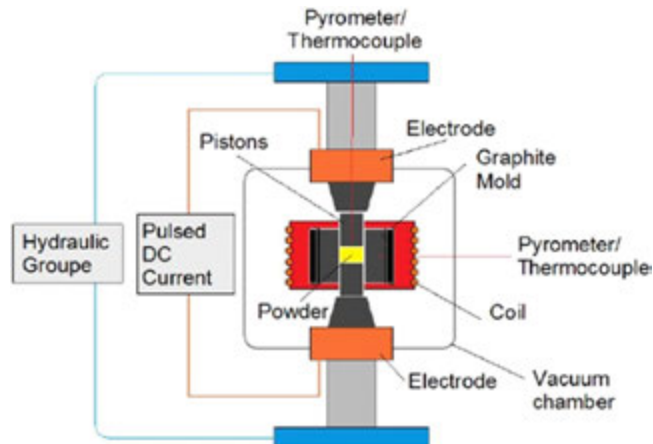


Fig. 15 Schematic of a hybrid SPS system including an induction heater. Reproduced from Yushin, D.I., Smirnov, A.V., Pinargote, N.W.S., Peretyagin, P.Y., Millan, R.T.S., 2015. Modeling process of spark plasma sintering of powder materials by finite element method. *Mater. Sci. Forum* 834, 41–50.

Hybrid Heating

As mentioned before, one of the main challenges in SPS technology is represented by the possibility to control the temperature distribution during the sintering process; a problem that is particularly relevant in the case of very large samples. We have seen as a way to mitigate this problem lays in the optimization of the tool design through numerical modeling. Such an approach, however, is time-consuming and must be repeated every time a change in the sample size or geometry is required. A more general-purpose approach involves the use of a secondary heating source, allowing a more uniform temperature distribution. The use of a secondary heating element also allows mitigating the other factor affecting the scaling up of SPS, represented by the maximum power allowed by SPS power supplier. Machines allowing to use two heating methods at the same time are usually identified by

the term ‘hybrid SPS’ and have become commercially available in the last few years. Two different methods of secondary heating are generally used: conventional resistance furnace and induction heating. The first approach is less expensive, but it goes somehow in conflict with the most typical characteristic of SPS, represented by the possibility to use fast heating rates. In this respect induction heating is more congruent and received more attention. An example of the typical setup used in a hybrid SPS with induction heating is shown in Fig. 15. Despite their advantages, the use of a hybrid SPS is still very limited, in part due to the high cost of the apparatus, but appear very promising when scaling up towards very large sample dimensions is crucial for the application.

References

- Airimioaei, M., Buscaglia, M.T., Tredici, I., *et al.*, 2017. SrTiO₃–BaTiO₃ nanocomposites with temperature independent permittivity and linear tunability fabricated using field-assisted sintering from chemically synthesized powders. *J. Mater. Chem. C* 5, 9028–9036.
- Anselmi-Tamburini, U., Spinolo, G., Maglia, F., *et al.*, 2013. Field assisted sintering mechanisms. In *Sintering Mechanisms of Conventional Nanodensification and Field Assisted Processes*. Engineering Materials. Springer. pp. 159–191.
- Anselmi-Tamburini, U., Garay, J.E., Munir, Z.A., 2006. Fast low-temperature consolidation of bulk nanometric ceramic materials. *Scr. Mater.* 54, 823–828.
- Bonifacio, C.S., Holland, T.B., van Benthem, K., 2013. Evidence of surface cleaning during electric field assisted sintering. *Scr. Mater.* 69, 769–772.
- Cao, G., Estournes, C., Garay, J., Orrù, R., 2019. *Spark Plasma Sintering: Current Status, New Developments and Challenges*. Elsevier.
- Choi, P.P., Kim, J.S., Nguyen, O.T.H., *et al.*, 2007. Al-La-Ni-Fe bulk metallic glasses produced by mechanical alloying and spark-plasma sintering. *Mater. Sci. Eng. A* 449–451, 1119–1122.
- Chu, Z.H., Kato, H., Xie, G.Q., *et al.*, 2012. Consolidation and mechanical properties of Cu₄₆Zr₄₂Al₇Y₅ metallic glass by spark plasma sintering. *J. Non-Cryst. Solids* 358, 1263–1267.
- Olevsky, E.A., Dudina, D.V., 2018. *Field-Assisted Sintering: Science and Applications*. New York, NY: Springer Science + Business Media.
- Frei, J.M., Anselmi-Tamburini, U., Munir, Z.A., 2007. Current effects on neck growth in the sintering of copper spheres to copper plates by the pulsed electric current method. *J. Appl. Phys.* 101, 114914/1–114914/8.
- Garay, J.E., 2010. Current-activated, pressure-assisted densification of materials. *Annu. Rev. Mater. Res.* 40, 445–468.
- Giuntini, D., Raethel, J., Herrmann, M., *et al.*, 2016. Spark plasma sintering novel tooling design: Temperature uniformization during consolidation of silicon nitride powder. *J. Ceram. Soc. Jpn.* 124, 403–414.
- Giuntini, D., Raethel, J., Herrmann, M., Michaelis, A., Olevsky, E.A., 2015. Advancement of tooling for spark plasma sintering. *J. Am. Ceram. Soc.* 98, 3529–3537.
- Grasso, S., Sakka, Y., Maizza, G., 2009. Electric current activated/assisted sintering (ECAS): A review of patents 1906–2008. *Sci. Technol. Adv. Mater.* 10, 053001.
- Guillon, O., Gonzalez-Julian, J., Dargatz, B., *et al.*, 2014. Field-assisted sintering technology/spark plasma sintering: Mechanisms, materials, and technology developments: FAST/SPS: Mechanisms, materials, and technology developments. *Adv. Eng. Mater.* 16, 830–849.
- Herrmann, M., Matthey, B., Höhn, S., *et al.*, 2012. Diamond-ceramics composites – New materials for a wide range of challenging applications. *J. Eur. Ceram. Soc.* 32, 1915–1923.
- Hulbert, D.M., Anders, A., Dudina, D.V., *et al.*, 2008a. The absence of plasma in “spark plasma sintering”. *J. Appl. Phys.* 104, 033305/1–033305/7.
- Inoue, K., 1966. Apparatus for Electrically Sintering Discrete Bodies, 3250892.
- Maglia, F., Dapiaggi, M., Tredici, I., Maroni, B., Anselmi-Tamburini, U., 2010. Synthesis of fully dense nanostabilized undoped tetragonal zirconia. *J. Am. Ceram. Soc.* 93, 2092–2097.
- Manière, C., Torresani, E., Olevsky, E., 2019. Simultaneous spark plasma sintering of multiple complex shapes. *Materials* 12, 557.
- Masahashi, N., 2007. Fabrication of bulk anatase TiO₂ by the spark plasma sintering method. *Mater. Sci. Eng. A* 452–453, 721–726.
- Munir, Z.A., Anselmi-Tamburini, U., Ohyanagi, M., 2006. The effect of electric field and pressure on the synthesis and consolidation of materials: A review of the spark plasma sintering method. *J. Mater. Sci.* 41, 763–777.
- Munir, Z.A., Quach, D.V., Ohyanagi, M., 2011. Electric current activation of sintering: A review of the pulsed electric current sintering process: Electric current activation of sintering. *J. Am. Ceram. Soc.* 94, 1–19.
- Muñoz, S., Anselmi-Tamburini, U., 2013. Parametric investigation of temperature distribution in field activated sintering apparatus. *Int. J. Adv. Manuf. Technol.* 65, 127–140.
- Olevsky, E., Froyen, L., 2006. Constitutive modeling of spark-plasma sintering of conductive materials. *Scr. Mater.* 55, 1175–1178.
- Olevsky, E.A., Garcia-Cardona, C., Bradbury, W.L., *et al.*, 2012. Fundamental aspects of spark plasma sintering: II. Finite element analysis of scalability. *J. Am. Ceram. Soc.* 95, 2414–2422.
- Orrù, R., Licheri, R., Locci, A.M., Cincotti, A., Cao, G., 2009. Consolidation/synthesis of materials by electric current activated/assisted sintering. *Mater. Sci. Eng. R Rep.* 63, 127–287.
- Pavia, A., Durand, L., Ajuston, F., *et al.*, 2013. Electro-thermal measurements and finite element method simulations of a spark plasma sintering device. *J. Mater. Process. Technol.* 213, 1327–1336.
- Saunders, T., Grasso, S., Reece, M.J., 2015. Plasma formation during electric discharge (50 V) through conductive powder compacts. *J. Eur. Ceram. Soc.* 35, 871–877.
- Tokita, M., 1999. Development of large-size ceramic/metal bulk FGM fabricated by spark plasma sintering. *Mater. Sci. Forum* 308–311, 83–88.
- Zhang, Z.-H., Liu, Z.-F., Lu, J.-F., *et al.*, 2014. The sintering mechanism in spark plasma sintering – Proof of the occurrence of spark discharge. *Scr. Mater.* 81, 56–59.
- Zhang, F., Reich, M., Kessler, O., Burkel, E., 2013. The potential of rapid cooling spark plasma sintering for metallic materials. *Mater. Today* 16, 192–197.

Further Reading

- Anselmi-Tamburini, U., Garay, J.E., Munir, Z.A., 2005. Fundamental investigations on the spark plasma sintering/synthesis process. *Mater. Sci. Eng. A* 407, 24–30.
- Anselmi-Tamburini, U., Groza, J.R., 2017. Critical assessment: Electrical field/current application – A revolution in materials processing/sintering? *Mater. Sci. Technol.* 33, 1855–1862.
- Cao, G., Estournes, C., Garay, J., Orrù, R., 2019. *Spark Plasma Sintering: Current Status, New Developments and Challenges*. Elsevier.
- Chen, W., Anselmi-Tamburini, U., Garay, J.E., Groza, J.R., Munir, Z.A., 2005. Fundamental investigations on the spark plasma sintering/synthesis process. *Mater. Sci. Eng. A* 394, 132–138.

- Fujii, T., Tohgo, K., Isono, H., Shimamura, Y., 2017. Fabrication of a PSZ-Ti functionally graded material by spark plasma sintering and its fracture toughness. *Mater. Sci. Eng. A* 682, 656–663.
- Garay, J.E., 2010. Current-activated, pressure-assisted densification of materials. *Annu. Rev. Mater. Res.* 40, 445–468.
- Hulbert, D.M., Jiang, D., Anselmi-Tamburini, U., Unuvar, C., Mukherjee, A.K., 2008b. Experiments and modeling of spark plasma sintered, functionally graded boron carbide-aluminum composites. *Mater. Sci. Eng. Struct. Mater. Prop. Microstruct. Process* A488, 333–338.
- Manière, C., Pavia, A., Durand, L., *et al.*, 2016. Finite-element modeling of the electro-thermal contacts in the spark plasma sintering process. *J. Eur. Ceram. Soc.* 36, 741–748.
- Munir, Z.A., Quach, D.V., Ohyanagi, M., 2011. Electric current activation of sintering: A review of the pulsed electric current sintering process: Electric current activation of sintering. *J. Am. Ceram. Soc.* 94, 1–19.
- Olevsky, E.D., Dudina, D.V., 2018. *Field-Assisted Sintering: Science and Applications*. New York, NY: Springer Science + Business Media.
- Orrù, R., Licheri, R., Locci, A.M., Cincotti, A., Cao, G., 2009. Consolidation/synthesis of materials by electric current activated/assisted sintering. *Mater. Sci. Eng. R: Rep.* 63, 127–287.
- Yushin, D.I., Smirnov, A.V., Pinargote, N.W.S., Peretyagin, P.Y., Millan, R.T.S., 2015. Modeling process of spark plasma sintering of powder materials by finite element method. *Mater. Sci. Forum* 834, 41–50.

Cold Sintering and Hydrothermal Sintering

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Introduction

Sintering is an essential step in the processing of ceramic, metallic materials and composites, under which particles are bonded to form a coherent solid structure with the help of heat and/or pressure. The oldest known man-made sintered ceramic specimen date from ~26.000 years before present (B.P.) in the upper Paleolithic period and were found in Dolni Věstonice, currently in Czech Republic. [Vandiver et al. \(1989\)](#) estimated that the oldest ceramics specimen were fabricated from local soils (loess) at a temperature range of 500–800°C and that the mechanism of sintering was impurity-initiated, most likely liquid phase sintering. The other specimen found helped to confirm that this processing method was further used in many parts of the world to fabricate different types of objects, such as fired clay water vessels in ancient Egypt ~10.000 years B.P., the first sintered metals specimen such as gold, bronze, copper, silver in the Middle East ~3.000 years B.P., the first porcelains in China ~1.600 years B.P. and gold-platinum alloy jewelry in Colombia and Ecuador 300 years B.P. ([German, 2013, 2014](#)).

Important milestones in sintering were achieved in the 20th century thanks to the rapidly growing electricity industry. We can take as examples the use of “electric spark sintering” patented by [Voelker \(1900\)](#) in 1900 to sinter refractory metals like tungsten, the highlight of sintering atmospheres by [Coolidge \(1913\)](#) during the investigations and development of sintered rods *via* direct current sintering and then drawing these down to form. These advances in the sintering of refractory metals led to the development of WC-Co composites dies, allowing significant technical advances on liquid phase sintering, and carbides for machinery obtained by hot pressing, invented by [Bridgman \(1933\)](#).

From ~1940, a surge in the production of sintering products in the automotive, electronics and medical sectors was observed, following World War II ([German, 2014; Danninger et al., 2017](#)). The first theoretical concepts on solid state sintering were proposed by [Frenkel \(1945\)](#) and [Kuczynski \(1949\)](#) the one for liquid phase sintering by [Lenel \(1948\)](#) and [Kingery \(1959\)](#). Coble later introduced the different stages of sintering as well as different mass transport mechanisms ([Coble, 1961a,b](#)). New multi-parametric methodologies to optimize physical properties, master microstructural evolution and costs of sintered materials, were rationalized by Ashby thanks to sintering maps ([Ashby, 1974; Ashby and Jones, 1996](#)). From the late 60's to date, new sintering techniques emerged. We can list microwave sintering, ([Voss, 1973](#)) selective laser sintering ([Deckard, 1989](#)) and those belonging in the category of Field Assisted Sintering Technology (FAST) taking advantage of fast firing to enhance densification (Flash Sintering, ([Cologna et al., 2010](#)) Spark Plasma Sintering (SPS), ([Inoue, 1966a,b,c](#)), etc...). Very recently, intensive efforts were focused on low-temperature sintering (<400°C) through the development of energy efficient and environmentally friendly processes. From a general point of view, major new opportunities were thus opened including the integration of inorganic materials with different structures, the processing of nanostructured ceramics, the co-sintering of ceramics, polymers or metals. The search for reducing the sintering temperature has also led to the emergence of new materials and composites in the field of multiferroics materials (Cool-SPS) ([Hérisson de Beauvoir et al., 2018](#)) and for microwave devices (Ultra Low Temperature Co-fired Ceramic (ULTCC)). Besides, the cold sintering process (CSP) and the hydrothermal sintering (HS- also called hydrothermal hot pressing), both based on the use of solvent and uniaxial pressure, have shown an impressive potential for the fabrication and the design of high performance ceramics at low temperature.

This chapter focuses on these two different low sintering temperature processes. Besides the cost- and energy-efficiency and low environmental impact, both these techniques are enabling the fabrication of ceramics and ceramics-based composites with advanced properties at low temperatures, while overcoming some technological barriers associated with high temperature processing methods, such as the sintering of metastable and low decomposition temperature materials as well as the co-sintering of multimaterials of a new kind. The main difference between these two techniques is that hydrothermal sintering operates in closed conditions whereas CSP operates in open conditions. Fundamental aspects of the two processes as well as illustrations of their potentialities in terms of materials are discussed and described. Then, through a comparative study based on ZnO, the complementarity of the two processes is emphasized. The current challenges and future outlook will end this chapter.

Design of Experimental Set Up

In both cold sintering and hydrothermal sintering, a liquid which acts as a solvent is introduced into powder and mixed *via* conventional powder processing techniques (*e.g.*, mortar and pestle, cryomilling, ball milling, *etc.*) or by a vapor transport process prior to sintering ([Fig. 1](#)). In the existing literature, it was shown that for both these processes, the liquid selection depends critically upon the materials to densify. The interaction between the liquid and the powder throughout all the steps of sintering is

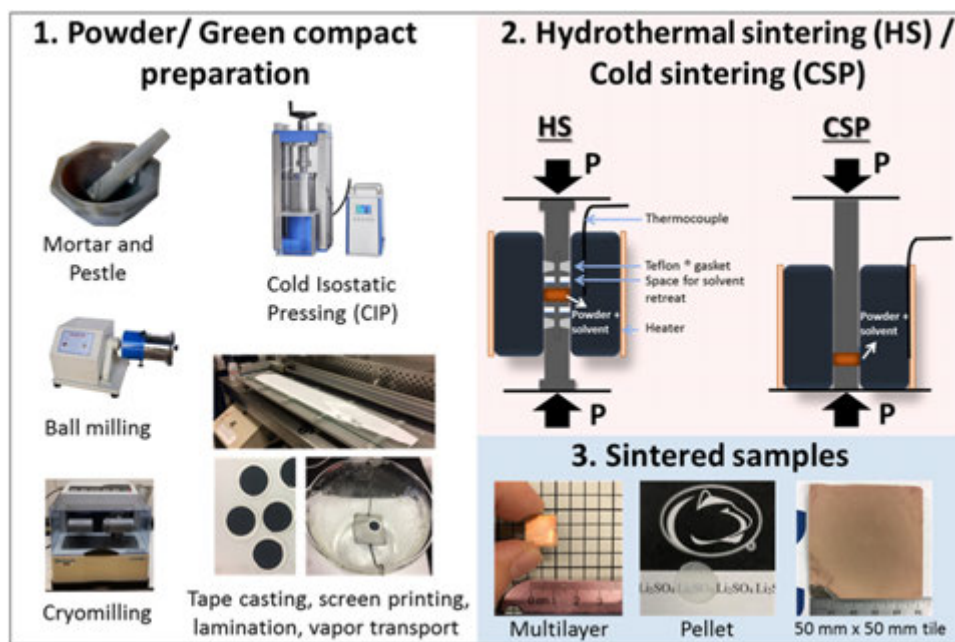


Fig. 1 Description of different processing steps in HS and CSP. (Images 1: CIP: <https://www.chuanghelab.com/cip-press/100-ton-electric-cold-isostatic-pressing-machine.html>; Ball milling: <https://www.indiamart.com/proddetail/laboratory-ball-mill-16084562491.html>; image 2 Reprint with permission from Ndayishimiye, A., Sengul, M.Y., Bang, S.H., *et al.*, 2019. Comparing hydrothermal sintering and cold sintering process: Mechanisms, microstructure, kinetics and chemistry. *Journal of the European Ceramic Society*, 1–13. doi:10.1016/j.jeurceramsoc.2019.11.049. Copyright 2019 Elsevier; image 3 Reprint with permission from Hérisson de Beauvoir, T., Dursun, S., Gao, L., *et al.*, 2019. New Opportunities in Metallization Integration in Cofired Electroceramic Multilayers by the Cold Sintering Process. *ACS Applied Electronic Materials* 1, 1198–1207. doi:10.1021/acsaelm.9b00184. Copyright 2019 American Chemical Society).

central to obtain high relative densities. In both CSP and HS, the mixture powder/liquid is externally and mechanically compressed either in a die (CSP) or in an autoclave (HS) over short periods of time. Each process requires a specific set up.

Hydrothermal Sintering

In the early 70's, Roy *et al.* (1972), Roy and Gouda (1973) prepared, at Penn State University, cement pastes with excellent mechanical properties and almost no porosity by hot pressing cementitious powders and water. In the mid-70's, further studies were made by Hirano and Sōmiya (1976) and Toraya *et al.* (1982) on reactive hydrothermal sintering to obtain densified oxides, starting from metal powders at temperatures higher than 900°C. In combining both these approaches, Yamasaki *et al.* (1986) from Kochi University developed an apparatus for “hydrothermal hot pressing”, based in uniaxial pressure of a mixture of powder and solvent in a system sealed with PTFE (Teflon™) gaskets. This technique was further developed and renamed “hydrothermal sintering” (or “solvothetmal sintering” when water is replaced by a non-aqueous solvent) by the group of Goglio at the University of Bordeaux (Ndayishimiye *et al.*, 2018a,b,c). The hydrothermal sintering operates in a closed system, which requires a specific design of the pistons to recover the solvent expelled during the densification in tanks designed for this purpose. Moreover, they have succeeded to reach higher experimental performances (higher temperatures and pressures) while keeping gaskets out of the hot zone and maintain the system hermetically sealed to control the hydrothermal equilibrium conditions under the sintering (Fig. 2) (Goglio *et al.*, 2018, 2019).

Cold Sintering

The cold sintering process operates in an open system, with non-equilibrium conditions (Guo *et al.*, 2019). The die used in the cold sintering process (center of Fig. 3) allows the evaporation of the solvent during the process. As shown in Fig. 3, many different materials systems and configurations such as ceramics (Funahashi *et al.*, 2016), metals, ceramic/ceramic composites (Guo *et al.*, 2018a,b,c), layered ceramic/metal composites (Guo *et al.*, 2017), layered ceramic/ceramic composites (Funahashi *et al.*, 2017), ceramic/polymer composites (Guo *et al.*, 2018a,b,c), layered ceramic/polymer composites (Funahashi *et al.*, 2017), and low temperature metallization (Hérisson de Beauvoir *et al.*, 2019) were demonstrated as a proof of concept under CSP.

Overview of Experimental Conditions

The experimental conditions implemented are given in Table 1.

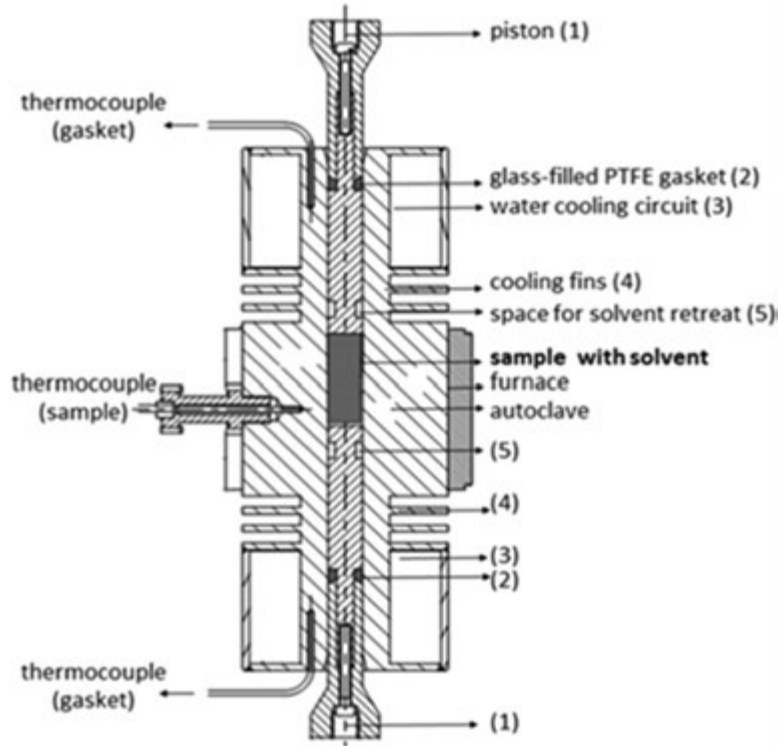


Fig. 2 Hydrothermal sintering apparatus designed Goglio *et al.* The design of pistons and specific cooling systems favor improved performances. Reproduced from Goglio, G., Largeau, A., Ndayishimiye, A., *et al.*, 2018. Procédé et dispositif de densification des matériaux ou deconsolidation d'un assemblage de matériaux par frittage hydrothermal ousolvothermal. Patent WO 2018/215559. France.

Sintering Mechanisms

HS and CSP are both geologically-inspired processes as their operating conditions are based upon the use of a transient liquid, temperature and pressure (Table 1), which are close to what is observed in the earth's upper crust, about 10 km under our feet (Fig. 4). In this region of the earth, we can find several minerals such as limestone, quartz or gypsum, which densify under geochemical conditions over very long times. One of the major mechanisms that drives this densification is the pressure solution creep (or dissolution-precipitation creep), which is a three-step process: dissolution → mass transport → precipitation, occurring through chemical potential gradients induced by the presence a solvent and pressure. In both CSP and HS, most of the densification is driven by mechanical-chemical effects (pressure solution creep) in synergy with chemical effects.

Mechanical-Chemical Effects

The mechanical-chemical effects in CSP and HS are based on a pressure solution mechanism. This deformation mechanism takes place following chemical potential gradients from highly constrained areas ($\mu_{s,1}$) with enhanced dissolution and high chemical potential to low constrained areas at particle surfaces with a lower chemical potential ($\mu_{s,2}$), through the liquid film separating particles. The driving force of pressure solution ($\Delta\mu_{tot}$) is therefore defined as Eq. (1): (Gratier *et al.*, 2013)

$$\Delta\mu_{tot} = \mu_{s,1} - \mu_{s,2} \quad (1)$$

This process is divided into three main steps (Fig. 5(a)): dissolution at the contact points between particles, mass transport through the liquid film and precipitation at pore surfaces, whose driving forces are $\Delta\mu_D$ Eq. (2), $\Delta\mu_T$ Eq. (3), $\Delta\mu_P$ Eq. (4), respectively.

$$\Delta\mu_D = \mu_{s,1} - \mu_{l,1} \quad (2)$$

$$\Delta\mu_T = \mu_{l,1} - \mu_{l,2} \quad (3)$$

$$\Delta\mu_P = \mu_{l,2} - \mu_{s,2} \quad (4)$$

$\mu_{l,1}$ and $\mu_{l,2}$ represent the chemical potential of the solute-rich and the solute-poor liquid phase, respectively.

The pressure solution is a stress-driven mass transfer process that is conceptually similar to Coble and Nabarro-Herring creep laws which are driven by grain boundary and intragranular diffusion, respectively (Urai *et al.*, 1986; Gratier *et al.*, 2013). The main

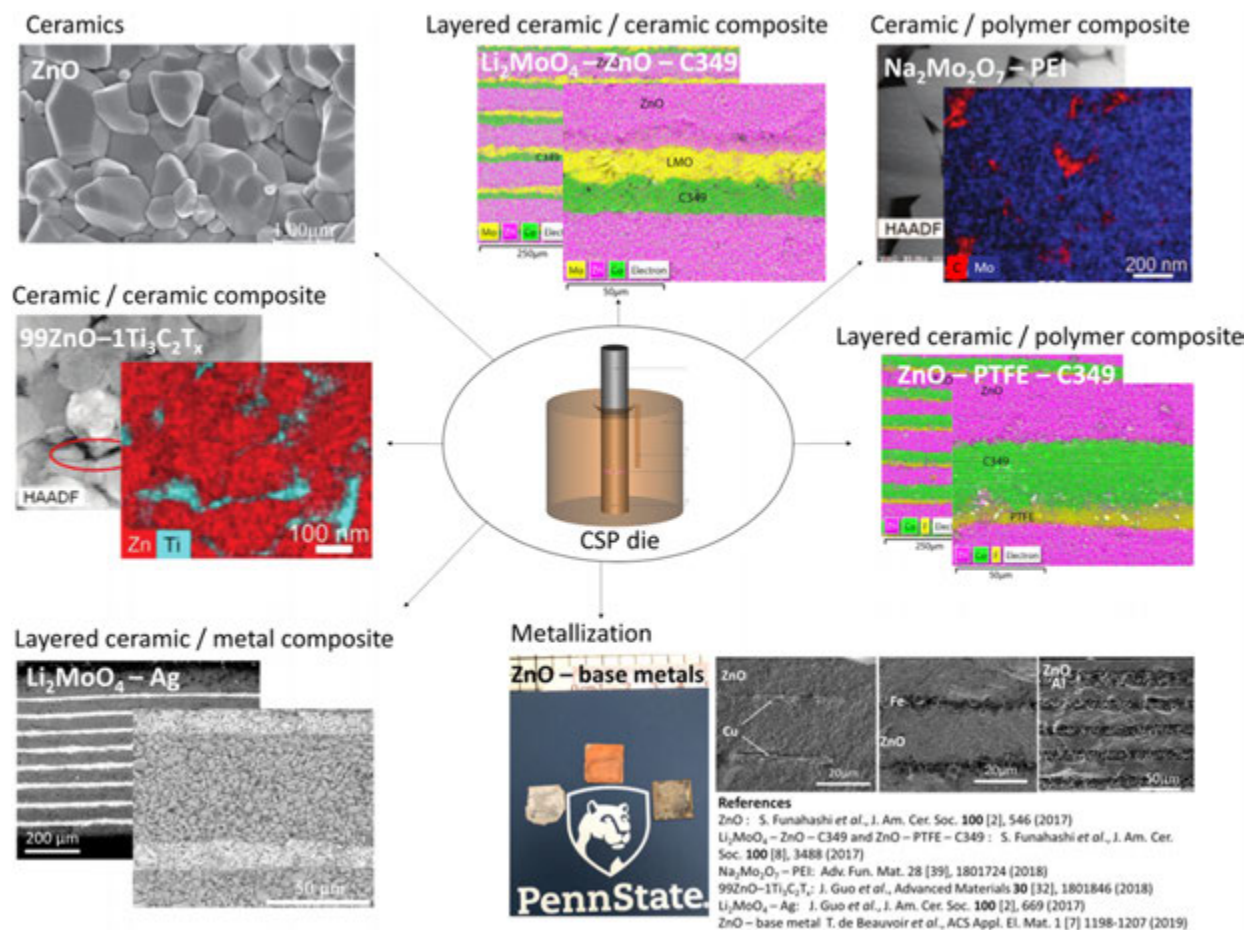


Fig. 3 Different materials systems and configurations tested by CSP (Reprint with permission from references indicated in the lower right corner. Copyright 2019 American Ceramic Society (ZnO; $\text{Li}_2\text{MoO}_4 - \text{ZnO}$; $\text{Li}_2\text{MoO}_4 - \text{Ag}$), Wiley ($\text{Na}_2\text{Mo}_2\text{O}_7 - \text{PEI}$; $99\text{ZnO}-1\text{Ti}_3\text{C}_2\text{Tx}$), American Chemical Society (ZnO -base metal)).

Table 1 Experimental conditions implemented in CSP and HS

	CSP	HS
Sintering conditions	T: 25–350°C P: 0–700 MPa (uniaxial)	T: From boiling point of the solvent up to 500°C P: 0–350 MPa (uniaxial)
	Specific solvents: Molten hydroxides or salts, chelating agents and deep eutectic solvents	
	Time: Several minutes to few hours	
	Solvent: Aqueous and non-aqueous solvent (hydrothermal sintering becomes solvothermal sintering) solutions	
	The use of a co-solvent or a mineralizer is possible	
	Shrinkage monitoring <i>via in situ</i> dilatometry	

difference is that, due to the lower activation energy of diffusion in liquids than in solids or at grain boundaries, pressure solution (or solution-precipitation) creep occurs at lower temperature than these two other mechanisms (Fig. 5(b)).

Chemical Effects

The dynamic interaction of the liquid solvent and the surface of inorganic materials during HS or CSP is quite complex and very challenging to predict experimentally. The reactive force field (ReaxFF) molecular dynamics technique is suitable for theo-

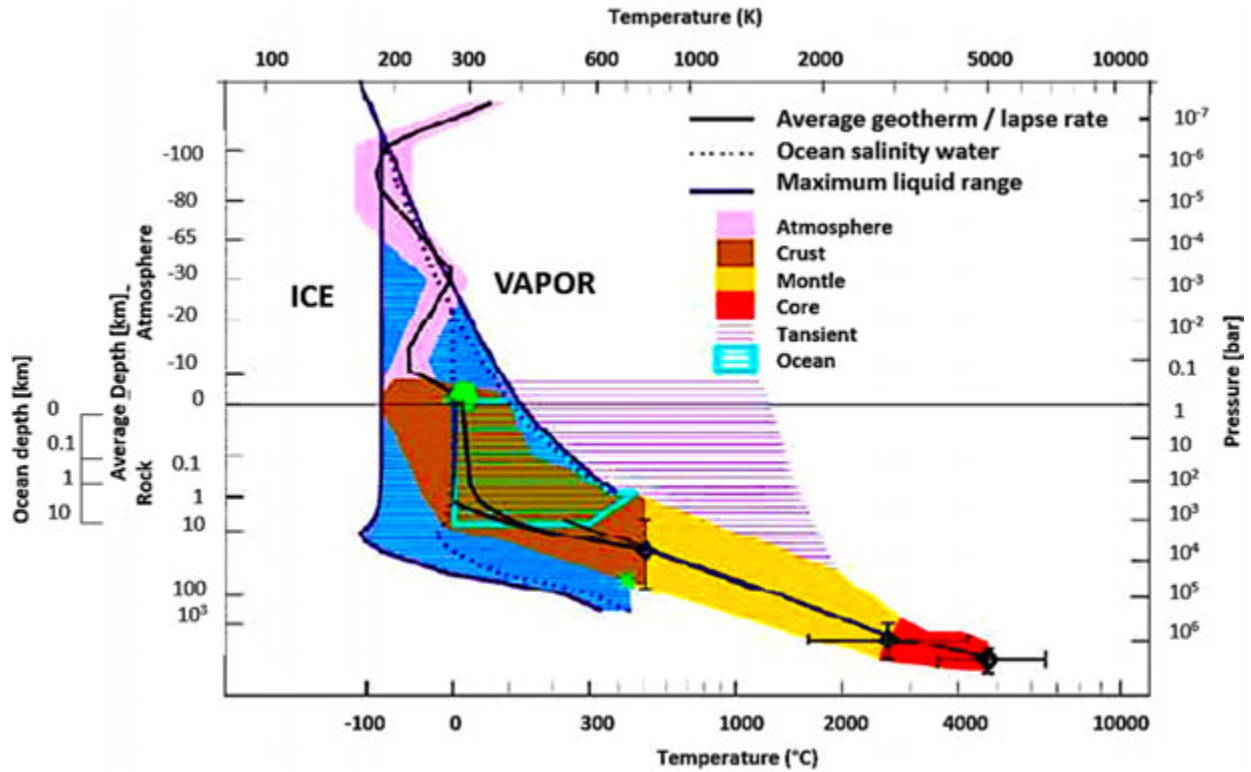


Fig. 4 Superposition of terrestrial environments on the P-T diagram of water. The Earth's core, mantle, crust and atmosphere are shaded medium gray and are centered on the average geotherm (subsurface) and lapse rate (atmosphere). The ocean and crust geotherms are plotted separately and meet at $P = 2000$ bar, $T = 200^\circ\text{C}$, corresponding to a depth of ~ 10 km. (ARXIV <https://arxiv.org/abs/1005.2440>).

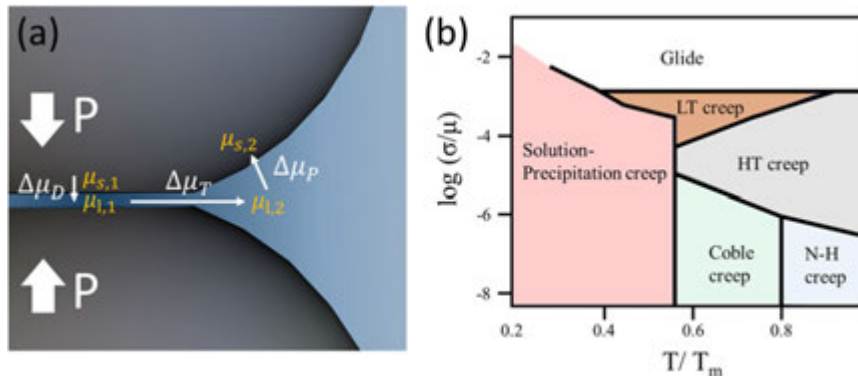


Fig. 5 (a) Three steps of the pressure solution creep: $\Delta\mu_D$, $\Delta\mu_T$ and $\Delta\mu_P$ are driving forces for dissolution, mass transport and precipitation, respectively. (b) Deformation mechanism map for halite modified to include solution-precipitation. The map was constructed for a grain size of 1 mm and intergranular fluid pressure of 10 MPa. LT, low-temperature; HT, high-temperature; N-H, Nabarro-Herring. Reprint with permission from Urai, J.L., Spiers, C.J., Zwart, H.J., *et al.*, 1986. Weakening of rock salt. *Nature* 324, 554–557. Ndayishimiye, A., Sengul, M.Y., Bang, S.H., *et al.*, 2020. Comparing hydrothermal sintering and cold sintering process: Mechanisms, microstructure, kinetics and chemistry. *Journal of the European Ceramic Society*, 40 (4), 1312–1324. doi:10.1016/j.jeurceramsoc.2019.11.049. Copyright 2019 Elsevier.

retical investigation of the chemical interactions between solvents and inorganic surfaces in cold sintering conditions (Sengul *et al.*, 2018a,b, 2019). Indeed, these interactions generally involve dynamic chelating reactions, dehydration and cluster formation whose understanding is critical to thoroughly investigate the *in situ* chemical effects in cold sintering. As an example, Fig. 6 shows the entire dynamic of the precipitation of Zn^{2+} ion from zinc acetate species on ZnO surfaces during the CSP of ZnO with an acetic acid solution. Fig. 6(a) shows acetate and water molecules prior to the decomposition reactions. Fig. 6(b) shows the deprotonation of methyl hydrogen by surface oxygen. Then, the water molecule dissociated into bridging hydroxyl and terminal hydroxyl (Fig. 6(c)), which is followed by a nucleophilic attack to methyl carbon, resulting in $\text{C}_2\text{H}_3\text{O}_3$ radical formation (Fig. 6(d)). Fig. 6(e) shows the dissociation of the $\text{C}_2\text{H}_3\text{O}_3$ radical, followed by its decomposition to carbon dioxide and formaldehyde (Fig. 6(f)).

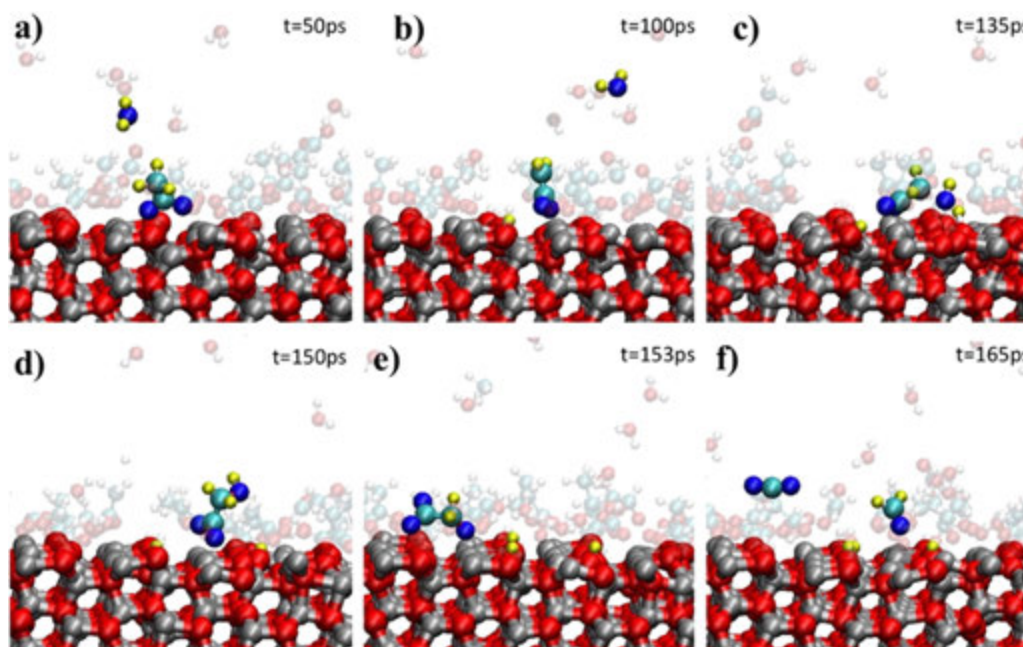


Fig. 6 Snapshots from ReaxFF MD simulations showing the acetic acid decomposition to formaldehyde and carbon dioxide at different time frames: (a) 50 ps, (b) 100 ps, (c) 135 ps, (d) 150 ps, (e) 153 ps and (f) 165 ps. Oxygen, hydrogen, carbon, and zinc atoms are visualized as red, white, cyan, and silver spheres. Oxygen and hydrogen atoms that participate into decomposition reaction are visualized as blue and yellow, respectively. All visuals are prepared by using VMD software. Reprint with the permission from Sengul, M.Y., Randall, C.A., van Duin, A.C.T., 2018b. ReaxFF molecular dynamics study on the influence of temperature on adsorption, desorption, and decomposition at the acetic acid/water/ZnO (10 $\bar{1}$ 0) interface enabling cold sintering. ACS Applied Materials & Interfaces 10, 37717–37724. doi:10.1021/acsami.8b13630. Copyright 2019 American Chemical Society.

It is important to note that ReaxFF molecular dynamics technique can be used to simulate chemical effects in hydrothermal sintering as well (Ndayishimiye *et al.*, 2019).

The influence of chemical effects in HS and CSP can also be investigated by *post mortem* classic structural or microstructural analysis techniques on as-obtained densified materials such as X-ray diffraction (XRD), thermogravimetric analysis (TGA), X-ray photoelectron spectrometry (XPS), scanning electron microscopy (SEM) or transmission electron microscopy (TEM) coupled with energy dispersive X-ray spectroscopy (EDS), Fourier transform Infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) or time-of-flight–secondary ion mass spectrometry (TOF-SIMS). The use of several of these complementary characterization techniques is often necessary to understand complex chemical phenomena.

In the case of hydrothermal sintering of amorphous silica, the nature of chemical effects and their evolution depending on the initial amount of water in the sample have been studied using FTIR and solid state NMR (^1H MAS NMR and ^1H) ^{29}Si CP-MAS NMR) (Ndayishimiye *et al.*, 2018a,b,c). Goglio *et al.* have shown that, during sintering, native silanol groups (both internal and at the surfaces) polycondensate to induce the *in situ* chemisorbed water release, form siloxane Si-O-Si bridges in particular between touching particles and then initiate the creation of sintering necks (Fig. 7). The initial surface functionalization favors these chemical effects which favor the densification synergistically with the mechanical-chemical ones. In this way, it has been shown that physisorbed water may act as solvent released *in situ* and may be sufficient to activate the dissolution-precipitation mechanisms.

Different Pathways Towards Densification Under Solvent-Assisted Sintering Processes

Different pathways towards densification can be considered with cold sintering (and hydrothermal sintering) as shown in Fig. 8, which illustrates the basic steps and feasible strategies for various material systems based upon their dissolution nature. Guo *et al.* (2019) indicated that these steps depend on the materials, solvents and processing parameters considered. The “material” parameters determined by chemical and structural characteristics are the chemical composition, crystal structure, particle size and particle size distribution and surface functionalization. As previously stated, it is obvious that solvent selection is critical in HS (or solvothermal process in the case of non-aqueous solvent) and CSP. Both aqueous and non-aqueous solvents can be used, enabling chemical reactions with the powder under the carefully chosen processing conditions (heating and cooling ramps, temperature, pressure, pressure profile, time). They must exhibit a good affinity with the powder (wetting ability and solubility) and must ensure efficient mass transport in HS and CSP systems.

Three different routes are possible upon the dissolution nature in HS and CSP systems:

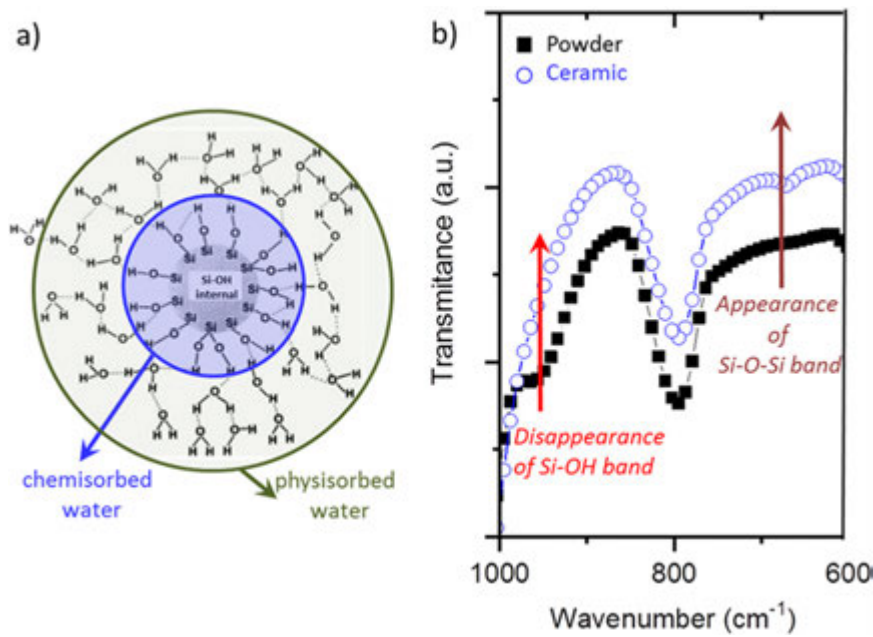


Fig. 7 (a) Schematic representation of a silica nanoparticle. (b) Infrared spectra of hydrated powder (5 wt% H₂O) and ceramic obtained after hydrothermal sintering at 300°C, 190 MPa (90 min) without addition of water. Reprint with the permission from Ndayishimiye, A., Largeau, A., Mornet, S., *et al.*, 2018. Hydrothermal sintering for densification of silica. Evidence for the role of water. *Journal of the European Ceramic Society* 38 (4), 1860–1870. doi:10.1016/j.jeurceramsoc.2017.10.011. Copyright 2019 Elsevier.

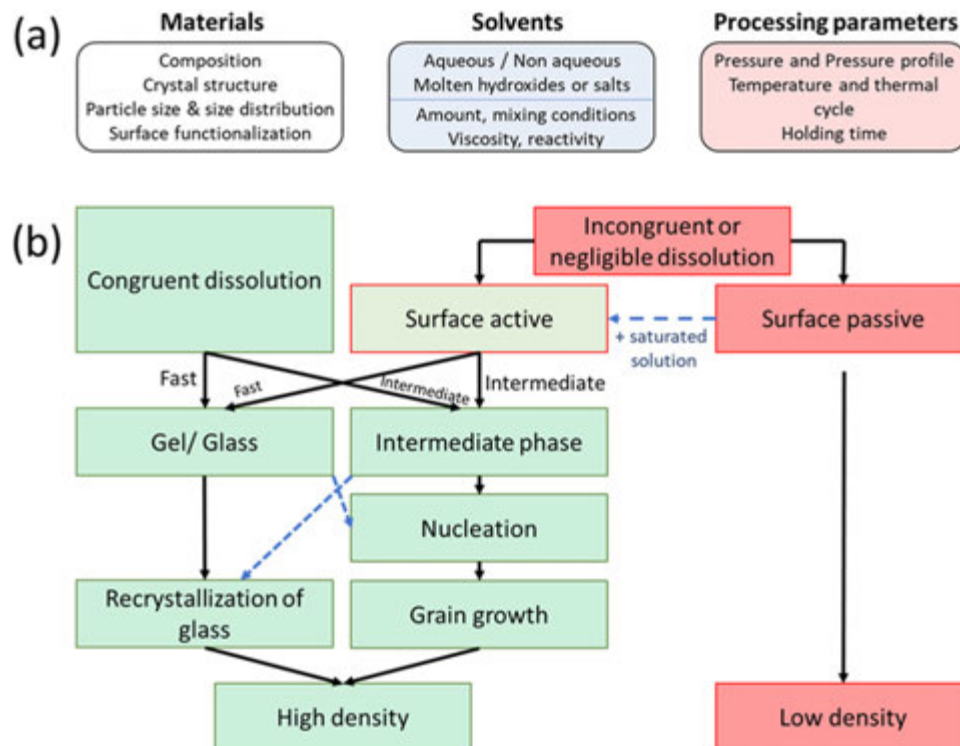


Fig. 8 Flowchart showing (a) the key parameters to consider for sintering and (b) different pathways that cold sintering can take for different materials under different conditions to densify. In panel b, the solid lines are typical pathways; the dashed lines denote pathways that are less common but that have been observed.

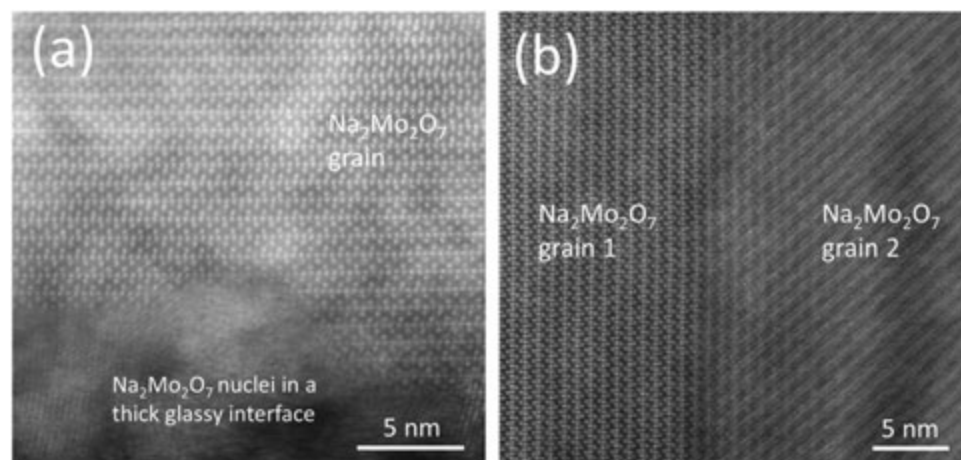


Fig. 9 HAADF-STEM images of $\text{Na}_2\text{Mo}_2\text{O}_7$ ceramics cold sintered at 120°C : (a) Interface of crystalline grains and thick glassy interphases, (b) Highly developed clean interfaces between adjacent grains.

- In the case of congruent dissolution, HS or CSP are straightforward as the material dissolves into the solvent with a homogeneous chemical stoichiometry, then the supersaturated solution precipitates to contribute to crystal growth. [Guo *et al.* \(2019\)](#) have also shown that solute gelation and the precipitation of an amorphous phase at grain boundaries can be observed in CSP if the evaporation is rapid. **Fig. 9** shows an example of an amorphous grain boundary observed after CSP of $\text{Na}_2\text{Mo}_2\text{O}_7$ ceramics. However, sharp grain boundaries are observed in the vast majority of the material.
- In the case of incongruent dissolution, ions with higher dissolution kinetics are leached. As a consequence, particle surfaces become passive, which separate the solvent and the crystalline phase, potentially hindering the densification. One of the strategies used to overcome incongruent dissolution is the use of a solvent saturated containing ions with the same nature of the leached ones. But there are systems like $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}\text{P}_3\text{O}_{12}$ (LAGP), for which densification still occurs under cold sintering even when the incongruent dissolution of Li^+ and PO_4 does occur ([Berbano *et al.*, 2017](#)). As such, there must be additional interactions between surface structures and solvent species, allowing chemical effects with potentially many events to occur during cold sintering. The amorphous or secondary phases present at grain boundaries following this incongruent dissolution under cold sintering can be deleterious to properties, such as limiting ionic or electronic conduction ([Guo *et al.*, 2018a,b,c, 2019](#)) and, in the case of high-permittivity dielectrics, additional contribution of low permittivity interfacial regions ([Guo *et al.*, 2016a,b,c](#)).

The Role of Solvents

Illustration in the case of hydrothermal and solvothermal sintering of amorphous SiO_2

Goglio *et al.* designed a study to understand the role of physisorbed/chemisorbed/added water in hydrothermal sintering of amorphous silica. Naturally hydrated (5 wt% H_2O), partially dehydrated (3.4 wt% H_2O) and almost-fully dehydrated SiO_2 nanopowders (1.1 wt% H_2O) were used as starting materials. In the first two powders, water is present in the form of chemisorbed and physisorbed water while in the last case only physisorbed water is observed. From these nanopowders, pellets were obtained after hydrothermal sintering without the addition of solvent at 300°C , 190 MPa and 90 min. Another ceramic was obtained in the same temperature, pressure and time conditions starting with the naturally hydrated powder mixed with added water (42 wt% of added H_2O). The microstructures of these ceramics are presented in **Fig. 10**.

The microstructure significantly evolves with the hydration rate of the starting powder. Starting from the poorest hydrated powder (**Fig. 10(a)**), a compact with a homogeneous microstructure consisting in an array of closed-packed silica nanoparticles is obtained. In this sample, no densification is observed. When the initial water amount in the starting powder increases, a remarkable close packing of particles, partially embedded into an amorphous silicic phase is observed (**Fig. 10(b)**). This starting water amount, even quite low, favors the cohesion of the assembly as it is sufficient to initiate dissolution-precipitation promoted by the presence of physisorbed water which acts as the solvent, mainly in the most constrained areas in the material. When the powder is the most naturally hydrated, a highly dense microstructure with residual pores is observed all over the sample, alongside with some few areas with vermicular-type microstructure; which confirms that the sintering has been efficiently promoted by the presence of chemisorbed water (enhancement of chemical effects) and physisorbed water (mass transport is favored during mechanical-chemical process) (**Fig. 10(c)**). When water is added in a large amount, a significant increase in densification and a drastic microstructural change are observed (**Fig. 10(d)**). Indeed, the absence of reminiscence of both the initial morphology and organization of nanoparticles attests to an effective densification of the powder. In the case of spherical SiO_2 , an excess of water indeed disturbs the natural self-organization of nanoparticles and the observed removal of the excess water generates some local

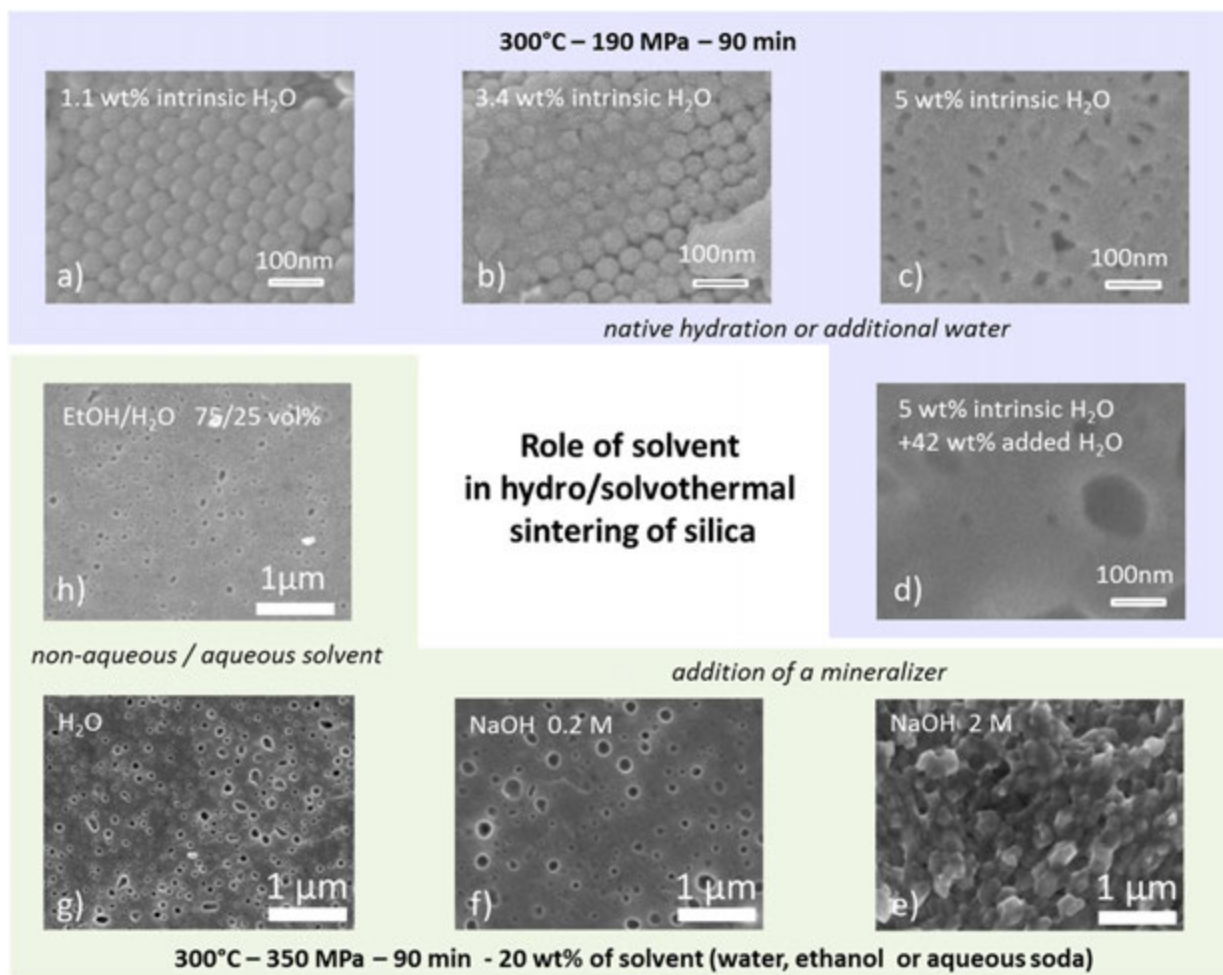


Fig. 10 Role of solvent in the case of hydro/solvothermal sintering of silica (HRSEM images). Reprint with the permission from (a–d) Ndayishimiye, A., Largeteau, A., Mornet, S., *et al.*, 2018. Hydrothermal sintering for densification of silica. Evidence for the role of water. *Journal of the European Ceramic Society* 38 (4), 1860–1870. doi:10.1016/j.jeurceramsoc.2017.10.011. (e–g) Ndayishimiye, A., Largeteau, A., Prakasam, M., *et al.* 2018c. Low temperature hydrothermal sintering process for the quasi -complete densification of nanometric α -quartz. *Scripta Materialia*, 145, pp. 118–121. doi:10.1016/j.scriptamat.2017.10.023. (h) Goglio, G., Ndayishimiye, A., Largeteau, A., *et al.*, 2019. View point on hydrothermal sintering: Main features, today's recent advances and tomorrow's promises. *Scripta Materialia* 158, 146–152. doi:10.1016/j.scriptamat.2018.08.038. Copyright 2019 Elsevier.

turbulences that induce major stacking faults. It appears then necessary to define the best experimental conditions to find a compromise between the progress of densification and the water release.

One solution may consist in the promotion of dissolution for a given solvent amount. In this way, mineralizers can be added. In the case of silica, it is well known that the silica dissolution is enhanced by a pH increase. As a consequence, relative density increases up to 86% when 0.2 M NaOH (20 wt% of solvent in the system) is added under 300°C and 350 MPa (Fig. 10(f)). In such a case, all the mesopores (10 vol%) that were observed when solvent was pure water (Fig. 10(g)) totally disappear, due their filling by precipitation after a promoted dissolution step. Moreover, if the NaOH concentration is ten times higher under the same pressure and temperature conditions, a 98% dense ceramic consisting in pure-quartz is obtained (Fig. 10(e)) with a remarkable epitaxial growth at the grain boundaries. In this case, the use of a mineralizer in aqueous solution allows to control the crystallographic nature of the precipitated phase (Ndayishimiye *et al.*, 2018c).

Another solution to regulate the dissolution and precipitation steps is to use a co-solvent or a non aqueous solvent (solvothermal process). For example, the less polar nature of ethanol relative to water makes the silica dissolution lower, thus favoring the precipitation near the zone of dissolution and leading to a slower propagation of the densification and to a slower release of the water. Moreover, ethanol is more compressible than water which favors its transport into the matrix (Goglio *et al.*, 2019). Consequently, the use of ethanol as a co-solvent favors a fine control of the microstructure through a change from macroporous matrix in the case of pure water to mesoporous one with a pore size all the lower as the proportion of ethanol is high. When the sintering is performed at 300°C under 350 MPa during 90 min with 20 wt% of solvent, the relative density reaches 88% with mesoporosity in

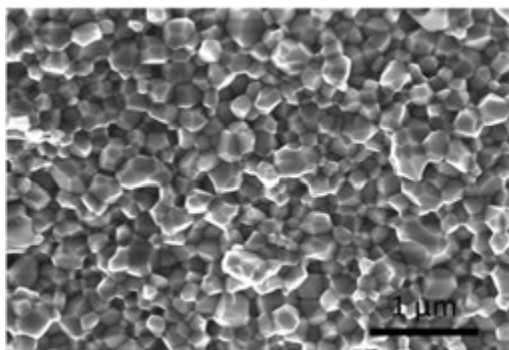


Fig. 11 SEM image of BaTiO₃ sintered in a single step by CSP at 300°C using a NaOH-KOH eutectic flux as solvent. Reprint with the permission from Tsuji, K., Ndayishimiye, A., Lowum, S., *et al.*, 2020. Single step densification of high permittivity BaTiO₃ ceramics at 300°C. Journal of the European Ceramic Society 40 (4). doi:10.1016/j.jeurceramsoc.2019.12.022. Copyright 2019 Elsevier.

Table 2 Inorganic materials densified by CSP

<i>Inorganic materials densified by CSP</i>	
Binary	MoO ₃ , WO ₃ , V ₂ O ₃ , V ₂ O ₅ , ZnO, Bi ₂ O ₃ , CsBr, MgO, PbTe, Bi ₂ Te ₃ , NaCl, ZnTe, AgI, CuCl, ZrF ₄ , ZrO ₂ , Al ₂ O ₃
Ternary	Li ₂ CO ₃ , CsSO ₄ , CaCO ₃ , Li ₂ MoO ₄ , Na ₂ MoO ₇ , K ₂ MoO ₇ , ZnMoO ₄ , Gd ₂ (MoO ₄) ₃ , Li ₂ WO ₄ , Na ₂ WO ₄ , LiVO ₃ , BiVO ₄ , AgVO ₃ , Na ₂ ZrO ₃ , BaTiO ₃ , NaNO ₂ , Mg ₂ P ₂ O ₇ , BaMoO ₄ , Cs ₂ WO ₄ , Na _x Co ₂ O ₄ , Ca ₃ Co ₄ O ₉ , KPO ₃
Quaternary	LiFePO ₄ , LiCoPO ₄ , KH ₂ PO ₄ , Ca ₅ (PO ₄) ₃ (OH), (LiBi) _{0.5} MoO ₄
quinary	Li _{1.5} Al _{0.5} Ge _{1.5} (PO ₄) ₃ , Li _{0.5x} Bi _{1-0.5x} Mo _x V _{1-x} O ₄

the case of a mix made of 75 vol% ethanol – 25 vol% water (**Fig. 10(h)**), while it equals to 84% with dominant macroporosity in the case of pure water (**Fig. 10(g)**).

As a conclusion it is obvious that the nature (aqueous/non aqueous, with/without mineralizer) and the amount of solvent in the case of hydrothermal sintering are a key point to achieve the densification while finely control the microstructure.

Illustration in the case of CSP

Besides, the emergence of cold sintering allowed to demonstrate the possibility to use other types of aqueous organic acid solutions (acetic acid, citric acid, ...), ketone, ester solvents or mixtures with boiling points below 200°C. Very recently, other very reactive solvents such as molten hydroxides or molten salts were used to densify high performance BaTiO₃ (Tsuji *et al.*, 2020) (**Fig. 11**), CeO₂, (Na_{0.5}K_{0.5})NbO₃, SrTiO₃, Na₃Zr₂Si₂PO₁₂ and many other polycrystalline ceramics in a single step at temperatures of 400°C or lower.

Sintering of Ceramics and Composites

Cold Sintering

More than 50 material systems, including quaternary and quinary compounds were successfully densified by the cold sintering process (**Table 2**). Among the inorganic materials that have been densified using cold sintering are microwave dielectrics with (Väätäjä *et al.*, 2017; Faouri *et al.*, 2019) or without magnetic phases (Guo *et al.*, 2017; Induja and Sebastian, 2018; Faouri *et al.*, 2019), ferroelectrics (Guo *et al.*, 2016a,b), piezoelectrics (Wang *et al.*, 2018), Li-ion cathodes (Seo *et al.*, 2017) and Li-/Na-ion electrolytes (Borbano *et al.*, 2017; Gustavo *et al.*, 2019; Lee *et al.*, 2019), semiconductors (Guo *et al.*, 2017; Gonzalez-Julian *et al.*, 2018), ceramic adhesives (Chen *et al.*, 2017) and refractories (Guo, *et al.*, 2017).

It is of interest to develop composite materials that possess better properties than the individual components. One of the major breakthroughs in cold sintering is that the technique enabled the fabrication of ceramic-polymer composites with a high volume fraction of ceramics (up to 99.9%), that were initially impossible to obtain, due to temperature gaps between elevated temperatures conventionally necessary to sinter ceramics and decomposition temperatures of polymers (Guo *et al.*, 2016c, 2018c). The other types of ceramic-based composites are with 2D materials, carbon nanofillers and metals, with amounts generally about 5 vol% or less. These new materials exhibit modified/enhanced electrical, mechanical and/or thermal properties, and are most importantly sintered at low temperatures.

The fabrication of new and usual dense composites composed of ceramics, polymers and metals is now possible. This construction, called “polycermet”, is still yet to be explored as it opens the door for new possibilities in Materials Science.

Hydrothermal Sintering

The hydrothermal sintering (or hydrothermal hot pressing) was used previously by Japanese groups for the densification of several oxides (either porous or compact) such as SiO_2 , TiO_2 , hydroxyapatite, CaCO_3 , $\text{Ca}_3\text{Co}_4\text{O}_9$, zeolites, ZrO_2 , $\text{Na}_x\text{Co}_2\text{O}_4$, $\text{Sn}_{1.24}\text{Ti}_{1.94}\text{O}_{3.66}(\text{OH})_{1.50}\text{F}_{1.42}$, (Yamasaki *et al.*, 1990; Yanagisawa *et al.*, 1990; Yamasaki *et al.*, 1992; Katsuyama *et al.*, 2007; Xie *et al.*, 2009) with relative densities ranging between 30% and 80%, and up to 99% in some cases (Nishizawa *et al.*, 1984; Katsuyama *et al.*, 2006; Li and Hashida, 2007). Other studies highlighted that hydrothermal sintering might be suitable for the treatment of industrial or nuclear wastes. (Yanagisawa *et al.*, 1989).

Recently, Goglio *et al.* have shown that in addition to an accurate control of the thermodynamic parameters (related to temperature and pressure), the surface functionalization and crystallinity of the starting powder, as well as the nature of the solvent are powerful chemical levers to easily achieve relative densities ranging from 98% to 100%. They can be applied to oxides with the possibility of matching the crystalline nature of the phase in the final ceramic (Ndayishimiye *et al.*, 2018c, 2019).

One of the challenges is to perform the sintering of complex assemblies with materials that exhibit differences in their chemical and physical characteristics. The bonding of hydroxyapatite on titanium metals or magnesium alloys with no specific surface treatment of the metals/ alloys, developed by Onoki *et al.* (2005, 2009, 2011), was the first type of also multimaterials developed by hydrothermal sintering. More recently, Goglio *et al.* developed a manufacturing strategy based, on the one hand, on grain boundary engineering to design 0–3 type $\text{La}_{0.66}\text{Sr}_{0.34}\text{MnO}_3/\text{SiO}_2$ nanocomposites hydrothermally sintered starting from core@shell nanoparticles, discriminating inert from reactive interfaces during the densification (Ndayishimiye *et al.*, 2018a; Kaman *et al.*, 2019). The enhanced reactivity at the liquid/solid interfaces in hydrothermal (or solvothermal) conditions should appear as an interesting lever to design specific multimaterial assemblies.

Comparison Between Cold Sintering and Hydrothermal Sintering: Case Study on ZnO

To investigate the similarities and differences between HS and CSP, ZnO has been chosen as a case study: a ZnO powder has been sintered with aqueous 2 M acetic acid solution at 155°C and 320 MPa with different holding times, the experimental protocol implemented in both processes being the same (Ndayishimiye *et al.*, 2019). All as-obtained ceramics consist in highly densified wurtzite zinc oxide.

At first glance, both processes show close values of relative density (systematically $\geq 97\%$) and analogous evolutionary trends. The relative density first decreases with time probably due to a pore growth induced by pore migration along with boundary migration and then increases, which may indicate a near-similar mechanical-chemical contributions, governed by the pressure solution creep.

However some slight differences between both processes exist underlining the influence of the open/closed system specificity (Fig. 12). First, the stabilization of zinc acetate bridges is highlighted in HS samples by SEM and XRD characterizations. ReaxFF molecular dynamics simulations have been conducted for the theoretical investigation of the chemical interactions between solvents and inorganic surfaces. Indeed, these interactions generally involve dynamic chelating reactions, dehydration and cluster formation whose understanding is critical to thoroughly investigate the chemical effects during sintering. In the case of CSP the solvent is considered in a gaseous state while it is kept liquid in the case of HS. The dissociation of water and acetic acid at the surface of particles leads to the formation of an hydroxide layer, tightly bounded to a solvent layer. The simulations show that CSP and HS mainly differ due to a distinctive chemical activity in the system: (1) in the case of CSP, the evaporation of the solvent induces the removal of the solvent layer, making the surface accessible to Zn^{2+} for precipitation, the process being highly governed by surface kinetics; (2) in the case of HS, the closed conditions make the tightly bounded solvent layer hydrothermally active as expected for such specific conditions which favors the formation of connected metal-organic complexes (zinc atom connected by acetate molecules); these chains then evolve towards clusters and are further converted into zinc-acetate crystals in longer timescale, which is consistent with a process governed by thermodynamics. Another difference between CSP and HS relies upon the grain size evolution over time (Ndayishimiye *et al.*, 2019). In both cases the grain sizes increases with holding time but if it is in a first stage higher in HS, it becomes higher in CSP for longer holding times. This can be explained by the fact that the dissolution is promoted in hydrothermal conditions favoring initial higher grain sizes in HS; however at longer times, the solvent remains in higher amount in HS than in CSP (evaporation) which makes more difficult to reach supersaturation and precipitation in HS; on the same time, evaporation considerable favors the supersaturation, hence the grain size increases significantly in the case of CSP. The different grain size evolution observed between both processes may also originate from the presence of oxygen vacancies, grain boundary thickness, grain surface roughness and the presence of residual acetates at grain boundaries.

The nature either closed (HS) or open (CSP) of the system influences the balance between thermodynamics and kinetics, hence the predominance of the elementary steps involved in the sintering pathway. In this way, solubility, dissolution/mass transport/precipitation kinetics, surface reactivity, pore shrinkage, water release, achievable densification, for example, will be dependent on the chosen process.

By their specificities, Cold Sintering and Hydrothermal Sintering represent complimentary low temperature sintering methods that cover an extremely wide range of experimental conditions from thermodynamic to strongly off-equilibrium conditions (Table 3). As a result, investigations conducted using these two processes undoubtedly enable deeper understanding of sintering mechanisms and versatile densification capabilities in terms of chemical compositions and nature of the target (multi)materials.

By taking advantage of this complementarity and flexibility, unique opportunities are opening for the design of microstructures combining ceramics, metals and/or polymers. Areas of applications that could not previously be exploited due to sintering conditions constraints are now accessible *via* simple to implement, inexpensive and energy-efficient processes.

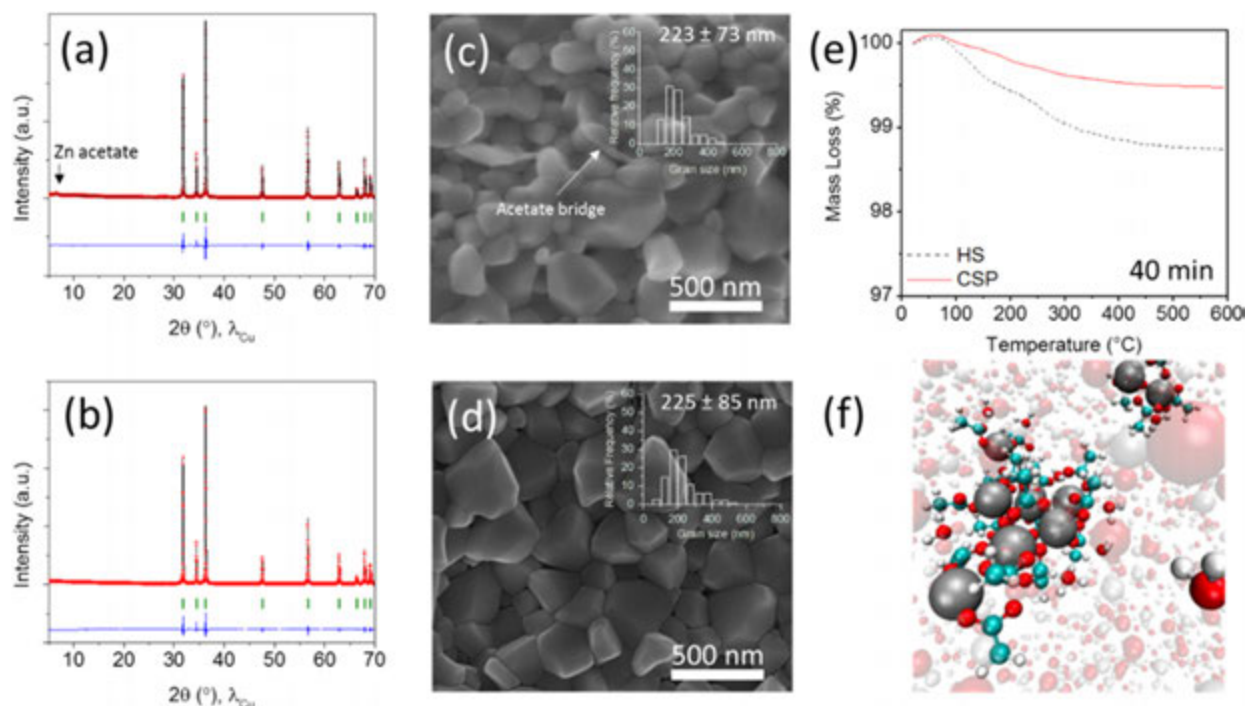


Fig. 12 XRD patterns of ZnO obtained by (a) HS, (b) CSP; SEM images of ZnO obtained by (c) HS, (d) CSP; TGA analysis of ZnO obtained by HS and CSP at $155 \pm 5^\circ\text{C}$, 320 MPa for 40 min. Visualization of zinc-acetate cluster and metal-organic complex obtained by ReaxFF MD simulations. Key: Zn^{2+} ion (gray), Oxygen atom (red), Hydrogen atom (white), Carbon atom (cyan). Reprint with the permission from Ndayishimiye, A., Sengul, M.Y., Bang, S.H., *et al.*, 2019. Comparing hydrothermal sintering and cold sintering process : Mechanisms, microstructure, kinetics and chemistry. Journal of the European Ceramic Society 1–13. doi:10.1016/j.jeurceramsoc.2019.11.049. Copyright 2019 Elsevier. Copyright 2019 Elsevier.

Table 3 Common features and main differences concerning mechanisms and materials in CSP and HS

		CSP	HS
Differences	Experimental set up	Open system	Closed system
	Water/solvent removal during densification	State of the matter: Gas	State of the matter: Sub- (Liquid or liquid + gas) or super-critical fluid
	Dominant contribution	Mechanism: Evaporation	Mechanism: Flow in specific tanks
	Sintering mechanism	Kinetics	Thermodynamics
Similarities	Sintering mechanism	Solvent-assisted sintering enabled by dissolution-precipitation process with possible synergistic chemical effects	
	Materials	Ceramics, ceramic-based composites, metals	

Current Challenges and Future Outlook

From a general point of view, the introduction of such solvent assisted sintering processes opens many major new opportunities in terms of material processing while ensuring cost saving, energy efficient and sustainable manufacturing process with a lower CO_2 emission, as illustrated in Section “Socio-Economic and Environmental Impact”. In addition, the sintering of thermodynamically unstable materials and the co-sintering of organic/inorganic composites has become possible thanks to the use of cheap and green solvents associated with a strong reduction of sintering temperature. However, to fully exploit the aforementioned potentialities offered by the Cold Sintering and the Hydrothermal Sintering, some key milestones, which are outlines below, still need to be completed.

Socio-Economic and Environmental Impact

Ibn-Mohammed *et al.* (2019) made a techno-economic analysis of several sintering techniques, such as hot pressing, conventional sintering, spark plasma sintering, flash sintering, microwave sintering, liquid phase sintering and cold sintering. In the study, the Sterling Pounds per ton of CO_2 saved ($\text{£}/\text{t}_{\text{CO}_2\text{-eq}}$) was used to evaluate the cost- and energy- efficiency in the manufacturing of three functional oxides: ZnO, PZT and BaTiO_3 . This figure of merit links the initial capital investment with

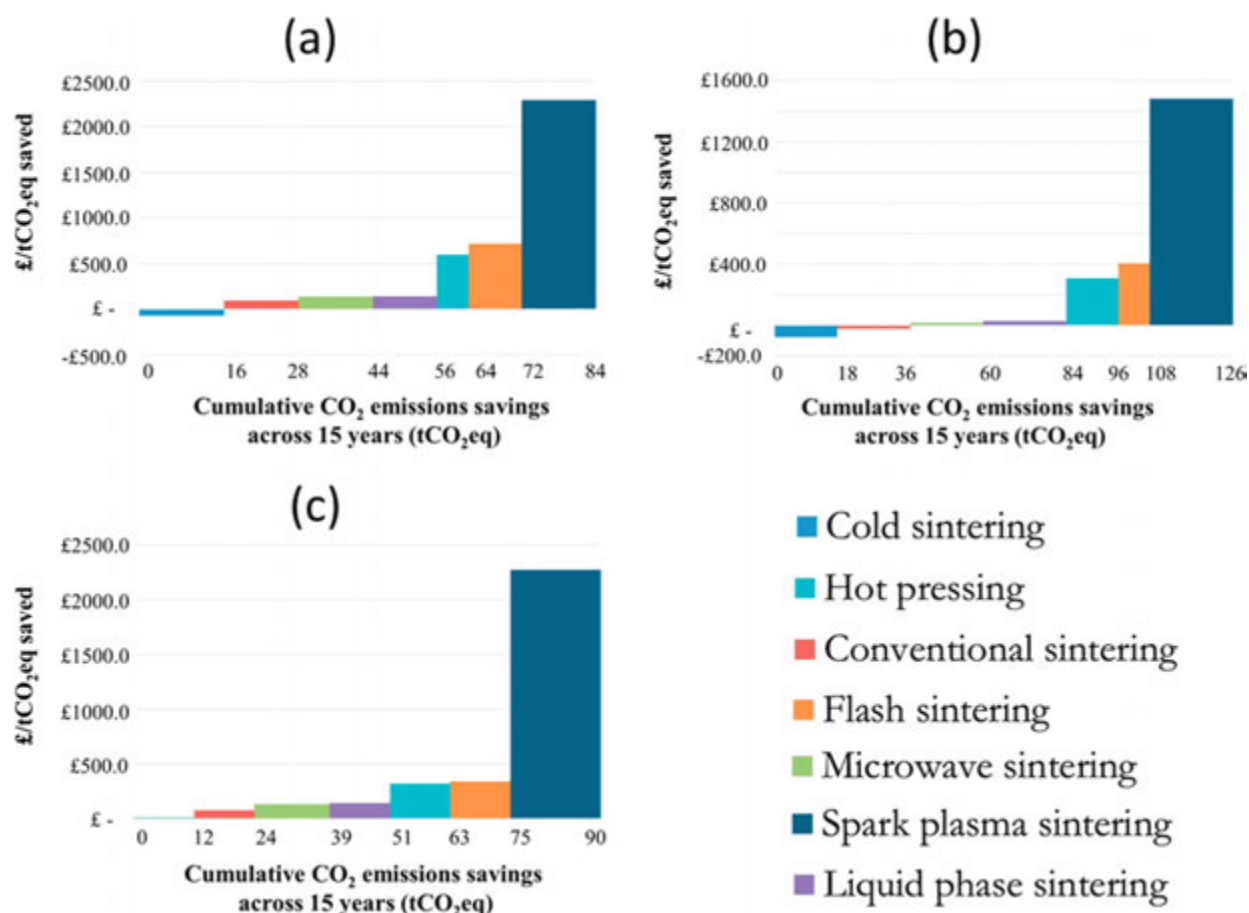


Fig. 13 Ranking of cost-effectiveness of sintering techniques for (a) ZnO, (b) PZT and (c) BaTiO₃ ceramics. Reprint from Ibn-mohammed, T., Randall, C.A., Mustapha, K.B., *et al.*, 2019. Decarbonizing ceramic manufacturing: A techno-economic analysis of energy efficient sintering technologies in the functional materials sector. *Journal of the European Ceramic Society* 39 (16), 5213–5235. doi:10.1016/j.jeurceramsoc.2019.08.011. Copyright 2019 academic journals/Creative Commons Attribution License 4.0.

energy savings, within a framework derived from ranking principles such as marginal abatement cost curves and Pareto optimization.

It was estimated that for the three functional oxides, CSP was the most economically attractive sintering option, indicating lower capital cost and best return on investment as well as considerable energy and emission savings (Fig. 13).

The authors of the study reminded that even though the viability of CSP was established as a competitive and sustainable alternative to other sintering techniques, its transition from laboratory to industry will require hugely different facilities and instrumentation as well as relevant property/performance validation to fully validate its potential.

Modeling for a Better Understanding of the Involved Mechanisms

One of the main challenges in CSP and HS is to provide a detailed fundamental understanding of the mechanisms required not only to be able to extend these processes to a wider range of materials but also to control more accurately the microstructure, in particular in terms of grain size. One of the leads towards a better fundamental understanding of the mechanical-chemical effects in CSP and HS is to evaluate and adapt the already-rich geochemistry/geophysics work on the pressure solution creep to “experimental” and laboratory-scale systems. In terms of chemical effects, several ReaxFF molecular dynamics simulations have been experimentally validated. The investigated systems helped to raise the awareness on the high importance of a deep understanding of the solvent-particle interface chemistry in confined spaces, as well as the complexity of the cascade of chemical reactions taking place in these areas during sintering processes. Several unpublished observations let us assume that a better knowledge of chemical species/complexes obtained during the dissolution step may be key to perfect some of the theoretical models, as well as understand the implications they have on the mass transport step as well as on the kinetics of precipitation, which may lead to a certain extend on grain growth. It is clear that all this information may help to shape a comprehensive roadmap for solvent selection in HS and CSP, the development of new types of functional ceramic-polymer, ceramic-metal or polycermet composites; multiscale modeling approaches are also essential to reach in-depth insights on sintering mechanisms and

control the microstructures. The different mass transport pathways and reactions, which are all interrelated, must be clearly specified in order to identify the limiting mechanisms and then densification kinetics. The confrontation between experiments and modeling at different scales is essential here. These aspects are currently addressed as part of the “Hydlic” project (2018) funded by the French National Research Agency (ANR-18-CE08-0006).

Aging of As-Sintered Ceramics

The two processes aim to produce ceramics dedicated to a very wide range of applications. Whether considering applications in the field of electronics or biomedical, the issue of reliability, durability and recyclability of ceramics will be essential. Lifetime and aging of ceramics performed at low temperature must be tested to prove the competitiveness of the processes. In the case of HS, it has been discussed to the presence of residual water confined into pores may induce a further surface modification as a rehydration, hence contributing to the aging of the material. In addition, one microstructural feature that is inherently affected by the sintering process is the grain boundaries. Defect chemistry at the grain boundaries will prevail the quality of ceramics and to a large extent the structural and functional properties. Their in-depth characterization is thus mandatory.

In a very fast-moving industry, introducing new materials and/or processes asks for a new assessment of life cycle whose different steps must be considered to ensure the reliability and safety of future products.

Increase of the TRL (Technological Readiness Level): From Laboratory to Factory

The early focus on driving the TRL has been in the form of strategic demonstrations of different materials and showing property performances in the form of monolithic and complex multilayer functional devices. So; currently the work is at a TRL 1–3 to 4 stages, with companies confirming the early data. It is obvious that the transition from laboratory to factory is also a major challenge, and identify the appropriate applications to drive the transition is under discussion. Technological specifications mainly related to the pressure will have to be considered, as the ceramic industry preferably uses relatively low pressures. Although it is noteworthy that in the powder metallurgy industry the warm pressing forming stage uses equipment that operates above 500 MPa. It was recently observed that the homogeneity of densification will be an essential parameter to control, especially for larger sintered components. The control of a pressure applied homogeneously as well as the kinetically-controlled solvent elimination during sintering can be major factors that can guarantee success under CSP. Even at the laboratory level samples above areal dimensions of $7 \times 7 \text{ cm}^2$ have been reported. In the same way, the design of both production equipment and experimental procedure will have to be adapted to the sintering of components with complex shapes, as it has been demonstrated in the case of the SPS (Manière *et al.*, 2017). Additive manufacturing of dies and punches offer interesting opportunities in this regard. Furthermore, the development of continuous processes on a certain number of products is an exciting perspective for both these low temperature sintering techniques.

References

- Ashby, M.F., 1974. A first report on sintering diagrams. *Acta Metallurgica* 22 (3), 275–289. doi:10.1016/0001-6160(74)90167-9.
- Ashby, M.F., Jones, D.R.H., 1996. The yield strength, tensile strength, hardness and ductility. *Engineering Materials* 1, 77–92.
- Berbano, S.S., Guo, J., Guo, H., *et al.*, 2017. Cold sintering process of $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ solid electrolyte. *Journal of the American Ceramic Society* 100, 2123–2135. doi:10.1111/jace.14727.
- Bridgman, P.W., 1933. The physics of high pressure. *Nature* 131 (3304), 259. doi:10.1038/131259a0.
- Chen, W.-T., Gurdal, E.A., Tuncdemir, S., *et al.*, 2017. Considering the possibility of bonding utilizing cold sintering for ceramic adhesives. *Journal of the American Ceramic Society* 100, 5421–5432. doi:10.1111/jace.15098.
- Coble, R.L., 1961a. Sintering crystalline solids. I. Intermediate and final state diffusion models. *Journal of Applied Physics* 32 (5), 787–792. doi:10.1063/1.1736107.
- Coble, R.L., 1961b. Sintering crystalline solids. II. Experimental test of diffusion models in powder compacts. *Journal of Applied Physics* 32 (5), 793–799. doi:10.1063/1.1736108.
- Cologna, M., Rashkova, B., Raj, R., 2010. Flash sintering of nanograin zirconia in $< 5 \text{ s}$ at 850°C . *Journal of the American Ceramic Society* 93 (11), 3556–3559. doi:10.1111/j.1551-2916.2010.04089.x.
- Coolidge, W.D., 1913. Production of refractory conductors. Google Patents. Available at: <https://www.google.com/patents/US1077674>.
- Danninger, H., de Oro Calderon, R., Gierl-Mayer, C., 2017. Powder metallurgy and sintered materials. In *Encyclopedia of Industrial Chemistry*. Wiley-VCH.
- Deckard, C.R., 1989. Methods and apparatus for producing parts by selective laser sintering. United States: Google Patents. Available at: <https://www.google.com/patents/US4863538>.
- Fauri, S.S., Mostaed, A., Dean, J.S., *et al.*, 2019. High quality factor cold sintered $\text{Li}_2\text{MoO}_4\text{-BaFe}_{12}\text{O}_{19}$ composites for microwave applications. *Acta Materialia* 166, 202–207. doi:10.1016/j.actamat.2018.12.057.
- Frenkel, J., 1945. Viscous flow of crystalline bodies under the action of surface tension. *Journal of Physics USSR* 9, 385–391.
- Funahashi, S., Guo, J., Guo, H., *et al.*, 2016. Demonstration of the cold sintering process study for the densification and grain growth of ZnO ceramics. *Journal of the American Ceramic Society* 6, 1–6. doi:10.1111/jace.14617.
- Funahashi, S., Guo, H., Guo, J., *et al.*, 2017. Cold sintering and co-firing of a multilayer device with thermoelectric materials. *Journal of the American Ceramic Society* 100 (8), 3488–3496. doi:10.1111/jace.14852.
- German, R.M., 2013. History of sintering: Empirical phase. *Powder Metallurgy* 56 (2), 117–123. doi:10.1179/1743290112Y.0000000025.
- German, R.M., 2014. Chapter 2 – History of sintering. In: German, R.M. (Ed.), *Sintering: From Empirical Observations to Scientific Principles*. Boston: Butterworth-Heinemann, pp. 13–40. Available at doi:10.1016/B978-0-12-401682-8.00002-1.
- Goglio, G., Largeteau, A., Ndayishimiye, A., *et al.*, 2018. Procédé et dispositif de densification des matériaux ou de consolidation d'un assemblage de matériaux par frittage hydrothermal ou solvothérmal. Patent WO 2018/215559. France.
- Goglio, G., Ndayishimiye, A., Largeteau, A., *et al.*, 2019. View point on hydrothermal sintering: Main features, today's recent advances and tomorrow's promises. *Scripta Materialia* 158, 146–152. doi:10.1016/j.scriptamat.2018.08.038.

- Gonzalez-Julian, J., Neuhaus, K., Bernemann, M., *et al.*, 2018. Unveiling the mechanisms of cold sintering of ZnO at 250°C by varying applied stress and characterizing grain boundaries by Kelvin Probe Force Microscopy. *Acta Materialia* 144, 116–128. doi:10.1016/j.actamat.2017.10.055.
- Gratier, J.-P., Dysthe, D.K., Renard, F., 2013. The role of pressure solution creep in the ductility of the Earth's upper crust. *Advances in Geophysics* 54, 47–179.
- Guo, H., Bayer, T.J.M., Guo, J., *et al.*, 2017. Cold sintering process for 8 mol%Y₂O₃-stabilized ZrO₂ ceramics. *Journal of the European Ceramic Society* 37 (5), 2303–2308. doi:10.1016/j.jeurceramsoc.2017.01.011.
- Guo, H., Baker, A., Guo, J., Randall, C.A., *et al.*, 2016a. Cold sintering process: A novel technique for low-temperature ceramic processing of ferroelectrics. *Journal of the American Ceramic Society* 99 (11), 3489–3507. doi:10.1111/jace.14554.
- Guo, H., Baker, A., Guo, J., Randall, C.A., 2016b. Protocol for ultralow-temperature ceramic sintering: An integration of nanotechnology and the cold sintering process. *ACS Nano* 10 (11), 10606–10614. doi:10.1021/acsnano.6b03800.
- Guo, J., Berbano, S.S., Guo, H., *et al.*, 2016c. Cold sintering process of composites: Bridging the processing temperature gap of ceramic and polymer materials. *Advanced Functional Materials* 26 (39), 7115–7121. doi:10.1002/adfm.201602489.
- Guo, J., Guo, H., Heidary, D.S.B., *et al.*, 2017. Semiconducting properties of cold sintered V₂O₅ ceramics and Co-sintered V2O5-PEDOT: PSS composites. *Journal of the European Ceramic Society* 37 (4), 1529–1534. doi:10.1016/j.jeurceramsoc.2016.11.021.
- Guo, J., Baker, A.L., Guo, H., *et al.*, 2017. Cold sintering process: A new era for ceramic packaging and microwave device development. *Journal of the American Ceramic Society* 100, 669–677. doi:10.1111/jace.14603.
- Guo, J., Legum, B., Anasori, B., *et al.*, 2018a. Cold sintered ceramic nanocomposites of 2D MXene and zinc oxide. *Advanced Materials* 30 (32), 1–6. doi:10.1002/adma.201801846.
- Guo, J., Pfeifferberger, N., Beese, A., *et al.*, 2018b. Cold sintering Na₂Mo₂O₇ ceramic with Poly(ether imide) (PEI) polymer to realize high-performance composites and integrated multilayer circuits. *ACS Applied Nano Materials*. American Chemical Society 1 (8), 3837–3844. doi:10.1021/acsanm.8b00609.
- Guo, J., Zhao, X., Hérisson de Beauvoir, T., *et al.*, 2018c. Recent progress in applications of the coldsintering process for ceramic – Polymer composites. *Advanced Functional Materials* 28 (39), 1–15. 1801724. doi:10.1002/adfm.201801724.
- Guo, J., Floyd, R., Lowum, S., *et al.*, 2019. Cold sintering: Progress, challenges, and future opportunities. *Annual Review of Materials Research* 49, 275–295.
- Gustavo, J., Bram, M., Laptev, A.M., *et al.*, 2019. Ceramic society sintering of a sodium-based NASICON electrolyte: A comparative study between cold, field assisted and conventional sintering methods. *Journal of the European Ceramic Society* 39 (8), 2697–2702. doi:10.1016/j.jeurceramsoc.2019.03.023.
- Hérisson de Beauvoir, T., Sangregorio, A., Cornu, I., *et al.*, 2018. Cool-SPS: An opportunity for low temperature sintering of thermodynamically fragile materials. *Journal of Materials Chemistry C* 6, 2229–2233. doi:10.1039/c7tc05640k.
- Hérisson de Beauvoir, T., Dursun, S., Gao, L., *et al.*, 2019. New opportunities in metallization integration in cofired electroceramic multilayers by the cold sintering process. *ACS Applied Electronic Materials* 1, 1198–1207. doi:10.1021/acsaem.9b00184.
- Hirano, S.-I., Sōmiya, S., 1976. Hydrothermal reaction sintering of pure Cr₂O₃. *Journal of the American Ceramic Society* 59 (11–12), 534. doi:10.1111/j.1151-2916.1976.tb09432.x.
- Ibn-mohammed, T., Randall, C.A., Mustapha, K.B., *et al.*, 2019. Decarbonising ceramic manufacturing: A techno-economic analysis of energy efficient sintering technologies in the functional materials sector. *Journal of the European Ceramic Society* 39 (16), 5213–5235. doi:10.1016/j.jeurceramsoc.2019.08.011.
- Induja, I.J., Sebastian, M.T., 2018. Microwave dielectric properties of cold sintered Al₂O₃ – NaCl composite. *Materials Letters* 211, 55–57. doi:10.1016/j.matlet.2017.09.083.
- Inoue, K., 1966a. Apparatus for electrically sintering discrete bodies. Google Patents. Available at: <https://www.google.com/patents/US3250892>.
- Inoue, K., 1966b. Electric-discharge sintering. Google Patents. Available at: <https://www.google.com/patents/US3241956>.
- Inoue, K., 1966c. Electric discharge sintering. United States.
- Kaman, O., Jirak, Z., Hejtmánek, J., *et al.*, 2019. Tunneling magnetoresistance of hydrothermally sintered La_{1-x}Sr_xMnO₃-silica nanocomposites.pdf. *Journal of Magnetism and Magnetic Materials* 479, 135–143.
- Katsuyama, S., Kishida, A., Ito, M., 2006. Synthesis of Na_xCo₂O₄ by the hydrothermal hot-pressing and its thermoelectric properties. *Journal of Alloys and Compounds* 414 (1–2), 215–220. doi:10.1016/j.jallcom.2005.05.050.
- Katsuyama, S., Takiguchi, Y., Ito, M., 2007. Synthesis of Ca₃Co₄O₉ ceramics by citric acid complex and hydrothermal hot-pressing processes and investigation of its thermoelectric properties. *Materials Transactions* 48 (8), 2073–2078. doi:10.2320/matertrans.E-MRA2007805.
- Kingery, W.D., 1959. Densification during sintering in the presence of a liquid phase. I. Theory. *Journal of Applied Physics* 30 (3), 301–306. doi:10.1063/1.1735155.
- Kuczynski, G.C., 1949. Self-diffusion in sintering of metallic particles. *Journal of Metals* 1 (2), 160–178. doi:10.1007/978-94-009-0741-6_33.
- Lee, W., Lyon, C.K., Seo, J., *et al.*, 2019. Ceramic – Salt composite electrolytes from cold sintering. *Advanced Functional Materials* 1807872, 1–8. doi:10.1002/adfm.201807872.
- Lenel, F.V., 1948. Sintering in the presence of a liquid phase. *Transactions of the Metallurgical Society of AIME* 15 (4), 1–19.
- Li, J., Hashida, T., 2007. Preparation of hydroxyapatite ceramics by hydrothermal hot-pressing method at 300°C. *Journal of Materials Science* 42 (13), 5013–5019. doi:10.1007/s10853-006-0613-7.
- Manière, C., Nigito, E., Durand, L., *et al.*, 2017. Spark plasma sintering and complex shapes: The deformed interfaces approach. *Powder Technology* 320, 340–345. doi:10.1016/j.powtec.2017.07.048.
- Ndayishimiye, A., Buffière, S., Dourges, M.A., *et al.*, 2018a. Design of 0–3 type nanocomposites using hydrothermal sintering. *Scripta Materialia* 148, 15–19. doi:10.1016/j.scriptamat.2018.01.013.
- Ndayishimiye, A., Largeteau, A., Mornet, S., *et al.*, 2018b. Hydrothermal sintering for densification of silica. Evidence for the role of water. *Journal of the European Ceramic Society* 38 (4), 1860–1870. doi:10.1016/j.jeurceramsoc.2017.10.011.
- Ndayishimiye, A., Largeteau, A., Prakasam, M., *et al.*, 2018c. Low temperature hydrothermal sintering process for the quasi -complete densification of nanometric α -quartz. *Scripta Materialia* 145, 118–121. doi:10.1016/j.scriptamat.2017.10.023.
- Ndayishimiye, A., Sengul, M.Y., Bang, S.H., *et al.*, 2020. Comparing hydrothermal sintering and cold sintering process: Mechanisms, microstructure, kinetics and chemistry. *Journal of the European Ceramic Society* 40 (4), 1312–1324. doi:10.1016/j.jeurceramsoc.2019.11.049.
- Nishizawa, H., Tebika, H., Yamasaki, N., 1984. Fabrication of stabilized zirconia compressed body under hydrothermal conditions and its sintering. *Journal of the Ceramic Society of Japan* 92 (7), 420.
- Onoki, T., Hosoi, K., Hashida, T., 2005. New technique for bonding hydroxyapatite ceramics and titanium by hydrothermal hot-pressing method. *Scripta Materialia* 52, 767–770. doi:10.1016/j.msec.2010.09.002.
- Onoki, T., Wang, X., Zhu, S., *et al.*, 2009. Effects of growing integrated layer [GIL] formation on bonding behavior between hydroxyapatite ceramics and Ti-based bulk metallic glasses via hydrothermal hot-pressing. *Materials Science and Engineering B: Solid-State Materials for Advanced Technology* 161 (1–3), 27–30. doi:10.1016/j.mseb.2008.11.011.
- Onoki, T., Yamamoto, S., Onodera, H., *et al.*, 2011. New technique for bonding hydroxyapatite ceramics and magnesium alloy by hydrothermal hot-pressing method. *Materials Science and Engineering C* 31 (2), 499–502. doi:10.1016/j.msec.2010.09.002.
- Roy, D.M., Gouda, G., 1973. High strength generation in cement pastes. *Cement and Concrete Research* 3 (6), 807–820.
- Roy, D.M., Gouda, G.R., Bobrowsky, A., 1972. Very high strength cement pastes prepared by hot pressing and other high pressure techniques. *Cement and Concrete Research* 2, 349–366.
- Sengul, M.Y., Guo, J., Randall, C.A., *et al.*, 2019. Water-mediated surface diffusion mechanism enabling the Cold Sintering Process: A combined computational and experimental study. *Angewandte Chemie – International Edition* 58 (36), 12420–12424. doi:10.1002/anie.201904738.

- Sengul, M.Y., Randall, C.A., van Duin, A.C.T., 2018a. ReaxFF molecular dynamics simulation of intermolecular structure formation in acetic acid-water mixtures at elevated temperatures and pressures. *Journal of Chemical Physics* 148 (1–6), 164506. doi:10.1063/1.5025932.
- Sengul, M.Y., Randall, C.A., van Duin, A.C.T., 2018b. ReaxFF molecular dynamics study on the influence of temperature on adsorption, desorption, and decomposition at the acetic acid/water/ZnO (10 $\bar{1}0$) interface enabling cold sintering. *ACS Applied Materials & Interfaces* 10, 37717–37724. doi:10.1021/acsami.8b13630.
- Seo, J.-H., Guo, J., Guo, H., *et al.*, 2017. Cold sintering of a Li-ion cathode: LiFePO₄-composite with high volumetric capacity. *Ceramics International* 43 (17), 15370–15374. doi:10.1016/j.ceramint.2017.08.077.
- Toraya, H., Yoshimura, M., Sōmiya, S., 1982. Hydrothermal reaction – Sintering of monoclinic HfO₂. *Journal of the American Ceramic Society* 65 (9), c159–c160. doi:10.1111/j.1151-2916.1982.tb10527.x.
- Tsuji, K., Ndayishimiye, A., Lowum, S., *et al.*, 2020. Single step densification of high permittivity BaTiO₃ ceramics at 300°C. *Journal of the European Ceramic Society* 40 (4). doi:10.1016/j.jeurceramsoc.2019.12.022.
- Urai, J.L., Spiers, C.J., Zwart, H.J., *et al.*, 1986. Weakening of rock salt. *Nature* 324, 554–557.
- Väättäjä, M., Kähäri, H., Juuti, J., *et al.*, 2017. Li₂MoO₄-based composite ceramics fabricated from temperature- and atmosphere-sensitive MnZn ferrite at room temperature. *Journal of the American Ceramic Society* 100, 3626–3635. doi:10.1111/jace.14914.
- Vandiver, P.B., Soffer, O., Klima, B., *et al.*, 1989. The origins of ceramic technology at Dolní Věstonice, Czechoslovakia. *Science* 246, 1002–1008.
- Voelker, W.L., 1900. Improvements in the Manufacture of Filaments for Incandescing Electric Lamps, and in Means Applicable for Use in Such Manufacturer. Patent GB 6149, Great Britain.
- Voss, W.A.G., 1973. Microwave power in industry. In: Voss, W.A.G., Tinga, W.R. (Eds.), *Microwave Circuits*. International Microwave Power Institute. Available at: <https://books.google.fr/books?id=K08dMgAACAAJ>.
- Wang, D., Guo, H., Morandi, C.S., *et al.*, 2018. Cold sintering and electrical characterization of lead zirconate titanate piezoelectric ceramics. *Applied Physics Letters* 6. 016101. doi:10.1063/1.5004420.
- Xie, Y., Yin, S., Yamane, H., *et al.*, 2009. Low temperature sintering and color of a new compound Sn_{1.24}Ti_{1.94}O_{3.66}(OH)_{1.50}F_{1.42}. *Solid State Sciences* 11 (9), 1703–1708. doi:10.1016/j.solidstatesciences.2009.05.025.
- Yamasaki, N., Yanagisawa, K., Nishioka, M., *et al.*, 1986. A hydrothermal hot-pressing method: Apparatus and application. *Journal of Materials Science Letters* 5, 355–356. doi:10.1007/BF01748104.
- Yamasaki, N., Kai, T., Nishioka, M., *et al.*, 1990. Porous hydroxyapatite ceramics prepared by hydrothermal hot pressing. *Journal of Materials Science Letters* 9, 1150.
- Yamasaki, N., Weiping, T., Jiajun, K., 1992. Low-temperature sintering of calcium carbonate by a hydrothermal hot-pressing technique. *Journal of Materials Science Letters* 11, 934–936.
- Yanagisawa, K., Nishioka, M., Yamasaki, N., 1989. Immobilization of Radioactive Wastes by Hydrothermal Hot Pressing, in *Hydrothermal Reactions for Materials Science and Engineering*. Springer. pp. 425–429.
- Yanagisawa, K., Nishioka, M., Ioku, K., *et al.*, 1990. Neck formation of spherical silica particles by hydrothermal hot pressing. *Journal of Materials Science Letters* 9 (1), 7–8. doi:10.1007/BF00724415.

Microwave Sintering of Ceramics

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Introduction

Microwave sintering refers to techniques that use microwaves for heating and sintering powder beds or compacts, in particular ceramic powders. It has given rise to an increasing number of scientific papers since 1995, with a specific development in China in the last 15 years (Fig. 1).

All these techniques use the interaction (*coupling*) between the electromagnetic field and materials for producing heat. The coupling material can be the powder compact to be sintered or specific coupling parts (*susceptors*) which capture the microwave energy then heat the compact by classical heat transfer (conduction, convection, radiation). This heat production inside the oven, limited to the processed parts and susceptors, differs from the classic heating by the hot walls, which requires heating large volumes, so that microwave heating is expected to enable higher heating rates and reduced energy consumption. Beyond these economical positive aspects, the high heating rates open the possibility to get improved materials with finer microstructure, and the interaction of microwave with the ceramic powder is expected to enhance sintering phenomena, opening ways for processing materials at lower temperatures. The bulk internal heating should also help getting a better temperature homogeneity. These potential advantages have been extensively listed and partly discussed in various review papers (Katz, 1992; Oghbaei and Mirzaee, 2010; Bhattacharya and Basak, 2016).

However, sintering ceramics requires high temperature (over 1200°C), and ceramists willing to use microwaves meet a major problem: the ability of ceramics to couple with microwaves is low at room temperature and may drastically increase at high temperature. It is uneasy to heat ceramics at low temperature, while they exhibit a tendency to show thermal runaway and hot spots at high temperature. Controlling temperature and heating homogeneity is also far from being easy, as the parts to be sintered, as well as thermal insulators, can strongly modify the field distribution inside the oven and its evolution with temperature during the process. The interpretation of experimental data therefore requires very careful and hard observations, so that a number of results from literature should be handled with care... and criticism!

For these reasons, microwave sintering is a very attractive technique for processing ceramics, but requires understanding the major aspects of electromagnetic fields and interactions inside microwave ovens dedicated to sintering ceramics, from both physical and technological points of view. The purpose of the present chapter is to provide the reader with knowledge and information for a fruitful use of microwaves in sintering ceramics.

Microwaves and Dielectric Heating

The information presented in this section and the following one is simplified and limited to aspects that appear necessary for understanding what is involved in microwave sintering of ceramics. The reader wishing to have more complete details should read basic physics books or books dedicated to microwave engineering (Owyang, 1989; Pozar, 2012).

Propagation of Electromagnetic Fields

Microwaves are electromagnetic waves with frequencies f in the range [300 MHz, 300 GHz], *i.e.*, between the FM radio and the infrared radiations. In an infinite medium, two orthogonal electric E and magnetic B fields constitute electromagnetic waves (Fig. 2) which propagate in direction z defined by the wave vector k according to:

$$\left. \begin{aligned} E &= E_0 \sin(2\pi ft - kz) \\ B &= B_0 \sin(2\pi ft - kz) \end{aligned} \right\} \quad (1)$$

In vacuum or air, the wave moves at the speed of light c , so that $k = \frac{2\pi f}{c}$. The corresponding wavelength $\lambda = \frac{c}{f}$ is in the range [1 mm, 1 m].

Microwaves are mainly used for telecommunication applications, and only a few wavelengths are available for heating in domestic and industrial application, the most common ones being 2.45 GHz ($\lambda = 12.25$ cm) 915 MHz ($\lambda = 32.79$ cm) but higher frequencies around 30 ($\lambda = 1$ cm) or 60 GHz ($\lambda = 0.5$ cm) are also used (Katz, 1992).

Electromagnetic fields obey the Maxwell's equations. In the case of sinusoidal fields, E and B fields can be written using complex numbers $X = X_0 \exp(j\omega t)g(x)$, where $j = \sqrt{-1}$, $\omega = \frac{f}{2\pi}$ the angular frequency and $g(x)$ the space distribution, so that Maxwell's equations in an homogeneous medium write:

$$\left. \begin{aligned} \nabla \cdot E &= 0 & \nabla \cdot H &= 0 \\ \nabla \times E &= -j\mu_0\mu_r\omega H & \nabla \times H &= -j\omega\varepsilon_0\varepsilon_{er}E \end{aligned} \right\} \quad (2)$$

in which ε_0 and μ_0 are the dielectric permittivity and magnetic permeability of vacuum ($\varepsilon_0\mu_0 = c^2$). In the case of ceramic materials,

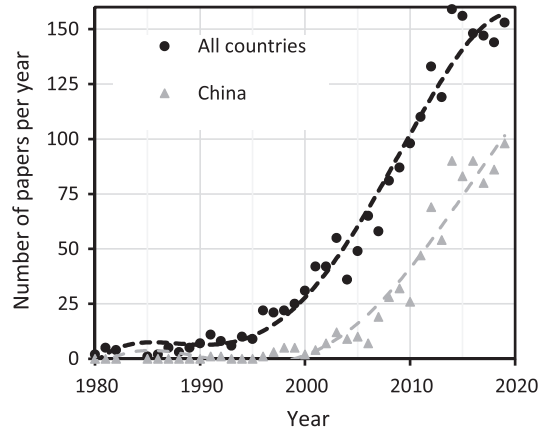


Fig. 1 Number of paper published with a title containing 'microwave' and 'sintering'. Source: Web of Science.

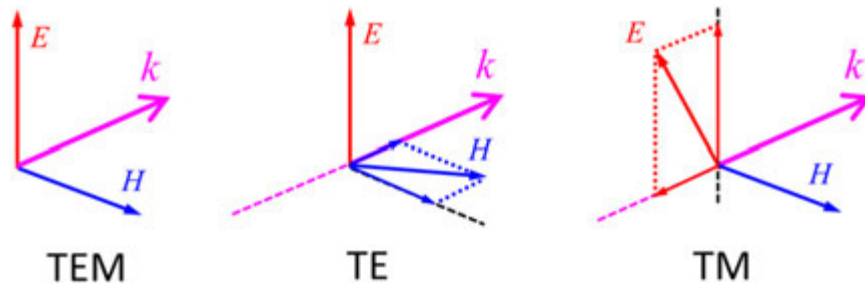


Fig. 2 Propagation wave vector k , electric (E) and magnetic (B) fields of electromagnetic waves in an infinite medium (plane wave, transverse electromagnetic TEM) and in a waveguide with transverse electric (TE) and transverse magnetic (TM) modes.

the relative magnetic permeability μ_r is almost equal to unity, so that the major characteristic of the material-microwave interaction is the effective relative permittivity ϵ_{er} , a complex value which accounts for dielectric interactions and electrical conductivity

$$\epsilon_{er} = \epsilon' - j\left(\epsilon'' + \frac{\sigma}{\omega}\right) = \epsilon' - j\epsilon_e'' \quad (3)$$

The real part of the permittivity ϵ' is always ≥ 1 ; the imaginary part ϵ'' accounts for the dipolar response. Both of them depend on the frequency, while $\frac{\sigma}{\omega}$ accounts for the contribution of the electrical conductivity σ . The effective imaginary part $\epsilon_e'' = \epsilon'' + \frac{\sigma}{\omega}$ is the practical parameter that governs the absorption of electromagnetic energy by dielectric heating in ceramics (see below section "Microwave Heating of Ceramics").

A major consequence of Eqs. (2) and (3) is that both E and H fields must be zero in perfect metals with infinite electrical conductivity ($\sigma = \infty$).

Dielectric Heating

Dielectric heating is the result of physical interaction between the electric field E and the material. It is the main microwave heating phenomenon in ceramic materials, so that the description will be limited here to the electric field effect. The effect of the magnetic field component can be significant in metals (El Khaled *et al.*, 2018), in particular Fe, Ni and Co and ferromagnetic materials (Mishra and Sharma, 2016), for which significant heating results from interactions with the magnetic field B . When a field of amplitude E ($E = \sqrt{2}E_{RMS}$) and frequency f is present in the material, the power dissipated per unit volume of the material is:

$$P = 2\pi f \epsilon_0 \frac{\epsilon_e'' E^2}{2} = 2\pi f \epsilon_0 \frac{\epsilon' \tan \delta_e E^2}{2} \quad (4)$$

The ratio $\tan \delta_e = \frac{\epsilon_e''}{\epsilon'}$ is the *loss tangent*. It is often used for characterizing the ability of a material to be heated by microwave energy dissipation and available in literature. Some techniques for measuring the dielectric properties of materials are calibrated for measuring $\tan \delta_e$ values. A material can be characterized either by the pair $(\epsilon', \epsilon_e'')$ or by the pair $(\epsilon', \tan \delta_e)$. Some authors call ϵ' the *dielectric constant* and ϵ_e'' the *loss factor*.

The physical origin of this energy dissipation is twofold: on one hand, the dielectric polarization effects associated to dipoles and charge carriers interaction with the oscillating field (ϵ'' in Eq. (3)), on the other hand the electric conduction ($\frac{\sigma}{\omega}$ in Eq. (3)).

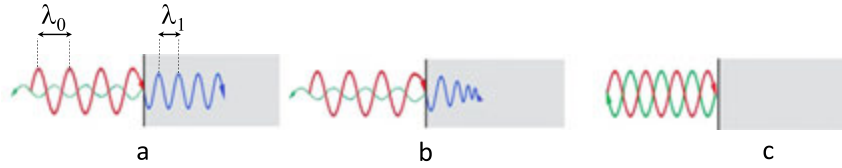


Fig. 3 Reflection and transmission of a plane wave at the surface of a material: (a) transparent material; (b) absorbing material; (c) reflecting (opaque) material.

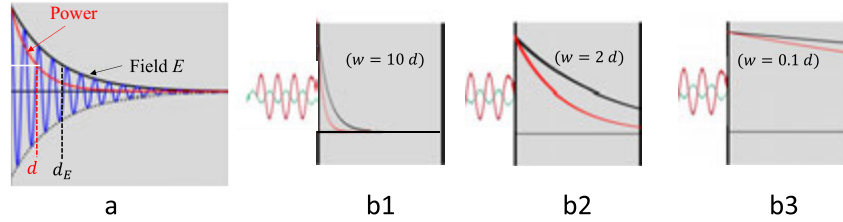


Fig. 4 Penetration depth in an absorbing material: (a) definitions in an infinite medium; (b) typical situations for different finite widths $w = 10 d$ (b1), $w = 2 d$ (b2) and $w = 0.1 d$ (b3).

These interactions have been detailed in reference books and review papers (Mishra and Sharma, 2016; Sun *et al.*, 2016). It is to be noticed that ε'' intrinsically depends on the wave frequency f , while $\frac{\sigma}{\omega}$ of course varies as $\frac{1}{f}$, so that, in practice, the dissipated power is not proportional to frequency f as Eq. (4) suggests.

Penetration Depth

Eq. (4) requires that the electric field is present inside the material. An important issue is therefore the penetration of the field into the material. When a wave in vacuum or air meets the interface with a material, part of it is reflected (Fig. 3). This reflection depends on the incidence angle and on the complex dielectric permittivity ε_e (Fresnel equations). In the case of normal incidence, the transmitted electric field relative intensity is typically:

$$\frac{E_t}{E_{ti}} = \frac{2}{1 + \sqrt{\varepsilon_e'}} \text{ when } \varepsilon_e'' \ll \varepsilon_e' \quad \frac{E_t}{E_i} = \frac{2}{\sqrt{2\varepsilon_e''}} \text{ when } \varepsilon_e'' \gg \varepsilon_e'. \quad (5)$$

Materials are often classified in 3 categories (Fig. 3):

- (1) transparent materials, in which the transmitted wave is not absorbed. This situation is observed when $\varepsilon_e'' = 0$. A significant part of the field is nevertheless reflected at the surface.
- (2) absorbing materials, in which the transmitted field is damped, due to heat dissipation, when ε_e'' is nonzero. Such materials can therefore be microwave heated.
- (3) Opaque materials, in which the electric field does not enter. "Fully reflective" would be a more convenient term. This is in particular the case in highly conductive metals, in which the imaginary part of the permittivity can be written $\varepsilon_e'' = \frac{\sigma}{\omega}$ with $\sigma \rightarrow \infty$, and the transmitted field is almost 0.

In absorbing materials, the energy absorption (Eq. (4)) leads to an exponential decrease of the field intensity as the wave goes on (Fig. 4(a)): $E = E(0)e^{-x/d_E}$. The characteristic length d_E is the penetration depth of the field, while $d = \frac{d_E}{2}$ is the penetration depth of the wave energy ($W \propto E^2 = E^2(0)e^{-2x/d_E}$). At these distances, the field (resp. energy) is decreased by a factor of $e = 2.718$ (Fig. 4(a)). These characteristic lengths depend on the dielectric properties as:

$$d = \frac{d_E}{2} = \frac{1}{2} \frac{c}{2\pi f} \frac{\sqrt{2}}{\sqrt{\varepsilon_e'^2 + \varepsilon_e''^2 - \varepsilon_e'}} = \frac{\lambda}{2\pi\sqrt{2}} \frac{1}{\sqrt{\varepsilon_e'^2 + \varepsilon_e''^2 - \varepsilon_e'}} \quad (6)$$

As expected from Eq. (4), the penetration depth in infinite when $\varepsilon_e'' = 0$, as no energy dissipation occurs, and decreases when ε_e'' increases. It is zero in perfect conductors ($\sigma = \infty$, $\varepsilon_e'' = \infty$). Calculated typical values for metals are a few micrometers around $f = 1$ GHz, Eq. (6).

Penetration depths enable to analyze the behavior of materials by considering a part with a finite width w (Fig. 4(b)). If d is small with respect to the material with (Fig. 4(b1)), field and energy will be absorbed in a thin layer: in such cases, the power dissipation is mainly located close to the surface. If d is large with respect to the material size (Fig. 4(b3)), heating is homogeneously distributed in the bulk, but only a limited amount of the wave energy is absorbed, which means that the heating may be

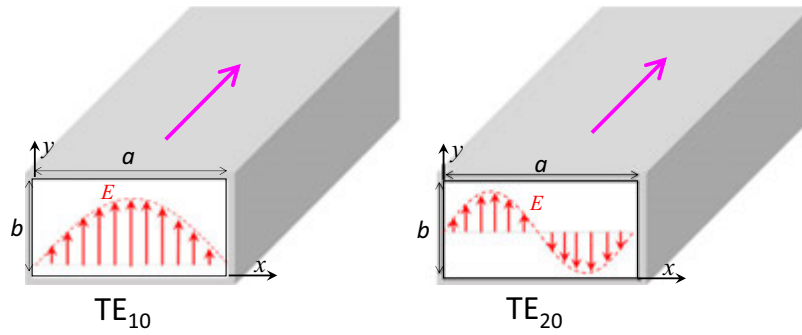


Fig. 5 Electric field distribution in the cross section of a waveguide in TE_{10} and TE_{20} modes.

poorly efficient. In the intermediate case, the absorption is optimal and distributed in the bulk, but might be poorly homogeneous in the bulk. Indeed, Fig. 4 is a simplified view, as a fraction of the emerging wave is also reflected back inside the materials when it reaches the second side, so that the situation when the penetration depth is not very small with respect to the sample size is more complex.

Waveguides and Applicators

A microwave furnace is generally constituted by a microwave generator, a waveguide, and the cavity in which the parts to be heated are placed, also called *applicator*.

Waveguide

In microwave processing of materials, the waveguide is generally a rectangular channel with metal walls, with cross section $a \times b$, with $b < a$ (Fig. 2). Due to reflections on the metallic walls, i.e., to boundary conditions which require the tangent components of E and B to be zero at the walls (assumed to be perfect conductors with infinite electrical conductivity), the electric and magnetic fields cannot be simultaneously orthogonal to the propagation direction z (Transverse Electric magnetic, TE) (Fig. 2(b)). Two main propagation ways are of practical interest, the so-called *Transverse Electric* (TE) and *Transverse Magnetic* (TM) modes (Fig. 2) in which either E or B is orthogonal to the propagation direction, the direction of second field being oscillating in the orthogonal plane (Chakravorty, 2014; Pozar, 2012). The TE mode presented here is generally more adapted to ceramics and dielectric heating, but results for TM mode are quite similar (Owyang, 1989). In the TE propagation mode, the solution of Maxwell's equations evidences that only a discrete series of propagation eigenmodes TE_{mn} exist, each of them defined by two integer numbers m and n . The E field amplitude in a cross section depends on the position (x, y) :

$$\left. \begin{aligned} E_x &= B_0 \frac{\lambda_c^2 f}{2\mu_0 b} \cos \frac{m\pi x}{a} \sin \frac{n\pi y}{b} \\ E_y &= B_0 \frac{\lambda_c^2 f}{2\mu_0 a} \sin \frac{m\pi x}{a} \cos \frac{n\pi y}{b} \\ E_z &= 0 \end{aligned} \right\} \quad (7)$$

While the amplitude of the z component of the magnetic field is

$$B_z = B_0 \cos \frac{m\pi x}{a} \cos \frac{n\pi y}{b} \quad (8)$$

Those relations show that m is the number of half-periods of the fields along the x -axis, n the number along the y one (see example on Fig. 5). The critical value λ_c is to the maximum value of the wavelength λ above which the waves cannot propagate in the waveguide, associated to a minimum frequency $f_c = \frac{c}{\lambda_c}$.

$$\lambda_c = \frac{2}{\sqrt{\left(\frac{m}{a}\right)^2 + \left(\frac{n}{b}\right)^2}} \quad (9)$$

In this case, the effective wavelength is not the free wavelength λ of plane waves, but the *guided wavelength* λ_g associated to the considered mode:

$$\lambda_g = \frac{\lambda}{\sqrt{1 - \left(\frac{\lambda}{\lambda_c}\right)^2}} \quad (10)$$

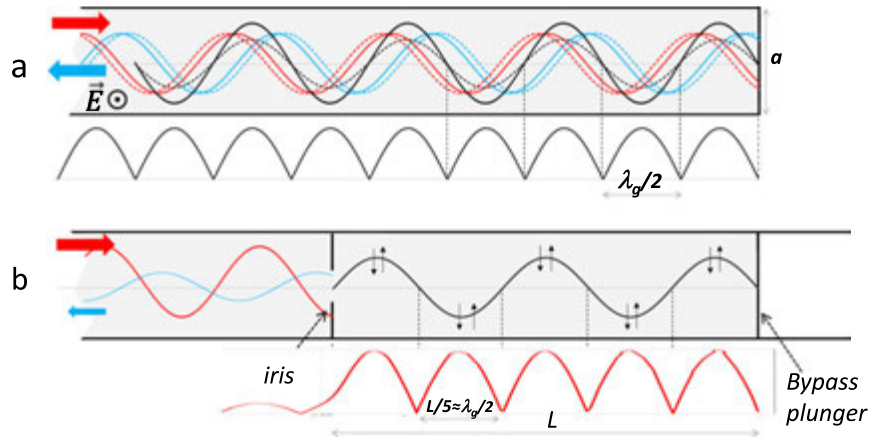


Fig. 6 Schematic view of a waveguide and single mode cavity in the case of propagation mode TE_{10} . (a) waveguide ended by a metal wall, forward wave (red), backward wave reflected by the wall (blue), and resulting standing wave (black) at arbitrary times t (dashed) and $t + dt$ (solid) with $dt \ll 1/f$; (b) single mode cavity, with a partially open wall (iris) which partially reflects the backward wave, and a mobile wall (plunger) which enables adjusting the cavity length L . The amplitude of the standing wave along the guide or cavity is shown below the guide.

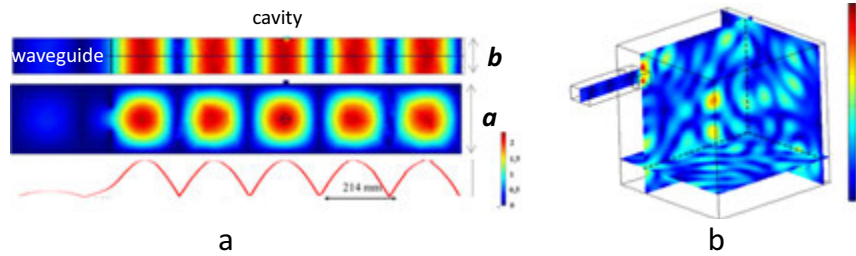


Fig. 7 Computed electric field intensity in empty cavities: (a) a single mode cavity with TE_{105} mode in a WR340 standard waveguide (orthogonal cross sections along the propagation axis); (b) example of cubic multimode cavity (3 arbitrary orthogonal sections).

The lowest frequency and largest wavelength are when $m = 1$ and $n = 0$, $\lambda_c = 2a$ (Eq. (9)). In TE_{m0} modes (Eq. (7)), the electric field is parallel to the y -axis (Fig. 5). The so-called fundamental mode, TE_{10} has a single maximum along x in the center part of the waveguide cross section and provides the widest high field area.

Waveguides have to be adapted to the microwave frequency. Standards for waveguides, mapping the microwave range of wavelengths, have been defined for many years (Harvey, 1955). Several families of standards coexist (Brady, 1965). In the WR (Waveguides Rectangular) standard, the number refers to the size $a = 2b$ in 0.254 mm (0.01 in.) units. The WR340 ($a = 2b = 8.636$ mm) and WR975 ($a = 2b = 24.765$ mm) waveguides are commonly used for 2.45 GHz and for 915 MHz, respectively.

Tunable Single Mode Cavity

A single mode cavity is based on a waveguide bounded by a metallic wall at its end (*plunger*, *bypass*, *short*) and by a partially open wall (*iris*) on the generator side.

When a waveguide is ended by a metallic wall (Fig. 6(a)), the forward wave is reflected on the wall and gives rise to a backward wave, which is so that sum of fields is zero on the metallic wall. The superposition of the forward and backward waves results in a standing wave with the wavelength λ_g , and in a distribution of nodes and antinodes at distance $\frac{\lambda_g}{2}$ from each other.

A single mode cavity is obtained by adding an *iris*, i.e., a partly open wall, or an equivalent device, which roughly acts as a semi-transparent mirror (Fig. 6(b)), in a way that enables the cavity length to be adjusted (in many cases using a mobile bypass plunger to end the cavity). The multiple reflections between the iris and the plunger lead to a set of stationary waves inside the cavity. The amplitude of this standing wave reaches maximum values when the resonance condition is satisfied, i.e., when the length L of the cavity is tuned to $\frac{p\lambda_g}{2}$, where p is an integer number. The resonance mode is then denoted TE_{mnp} (TE_{105} on Figs. 6(b) and 7). When the length L departs from $\frac{p\lambda_g}{2}$, the distance between nodes departs from $\frac{\lambda_g}{2}$, and the amplitude of the electric field decreases. In such cavities, the parts to be heated are generally positioned at places where the electric field is maximal (antinodes).

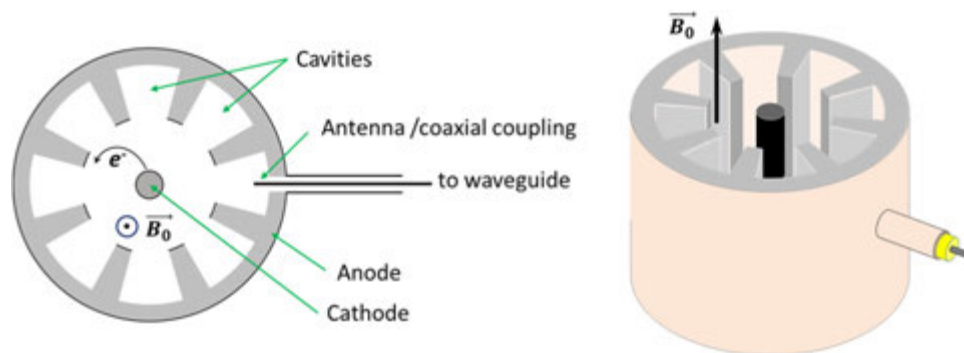


Fig. 8 Schematic 2D and 3D cross sections a magnetron. The trajectories of electrons emitted by the heated cathode are curved by the magnetic field B_0 of a permanent magnet; their interaction with the cavities induces an oscillatory resonant electromagnetic phenomenon. The oscillatory electromagnetic field is collected by a side antenna and transmitted via a coaxial line.

Homogeneous heating can therefore be expected only for parts with a size significantly smaller than $\frac{\lambda_g}{2}$, typically 2–4 cm at $f = 2.45$ GHz or 5–10 cm at $f = 915$ MHz in a TE_{10p} , for WR340 and WR975 standards, respectively. In a real heating experiment, part of the power is dissipated in the cavity, so that, in the waveguide, the forward wave has a larger amplitude than the backwards one, resulting in the superposition of a progressive wave and a standing one.

Multimode Cavity

Multimode cavities are cylinders or parallelepipeds with much larger dimensions than the wavelength (Fig. 7). As the waves are no longer guided, multiple reflections on the cavity walls lead to a complex set of standing waves, which result from the combination of many different propagation modes. The typical length scale between nodes is of the order of $\frac{\lambda}{2}$, but with a very irregular and almost unpredictable distribution of intensities, including significant variations of the average amplitude inside the cavity (Fig. 7(b)). Two main techniques are used to counterbalance the field inhomogeneity: (1) rotating stirring blades, which generate varying wave reflections and periodically change the field space distribution; (2) rotating plates as sample supports. In both cases, the time averaged field seen by the part is more homogeneous, but actual heating homogeneity is far from being guaranteed. Using high frequencies (e.g., 30 GHz, $\lambda/2 = 5$ mm) leads to a large number of nodes/antinodes inside parts: this can be viewed as a way for ensuring better heating homogeneity (Bykov *et al.*, 2004).

These cavities have fixed dimensions, so that there is no possibility for tuning any resonance, but they can contain large parts or many parts at the same time: they are therefore considered more suitable for industry applications in most cases.

Microwave Generators

Magnetrons are the most common microwave power sources, which have enabled the development of microwave use since the years 1980 (Atuonwu and Tassou, 2018; Brittain, 1985; Thostenson and Chou, 1999). A magnetron is a vacuum tube device involving a central anode and a surrounding cathode holed by a series of open cavities, placed in a permanent magnet. The electromagnetic wave is produced by the motion of electrons in the inter electrode vacuum, the holes playing the role of resonant cavities (Fig. 8). The frequency of the emitted wave is defined by the dimensions and distribution of these cavities. Magnetrons are considered to have a high power conversion efficiency (70%–90%). They are the most commonly used devices at 915 MHz and 2.45 GHz. These cheap, robust and reliable devices produce polarized waves, with delivered powers from 500 W to several kW. The limitations are the polychromatic character of the emitted wave (a few MHz bandwidth at 2.45 GHz), the impossibility to control the phase of the wave, and the frequency shift when the delivered power is varied, which may be detrimental to the resonance adaptation in single mode cavities.

Gyrotrons (Bykov *et al.*, 2004) and travelling wave tubes (Thostenson and Chou, 1999) are also based on field emission by electrons, but in a quite different way. In gyrotrons, an electron gun produces an electron beam, and then a high magnetic field (superconducting magnet) induces helicoidal trajectories and radial field emission at cyclotron resonance. These devices are very large and much more complex than magnetrons, but produce a coherent monochromatic radiation at controlled frequency between typically 20 and 200 GHz. High powers ranging from some kW to 1 MW are possible. Gyrotrons applications include nuclear fusion research experiments and industry for heating applications.

Solid state microwave generators based on electronic transistors have emerged in the last past years as cost-effective alternatives to magnetrons for domestic and industrial applications (Atuonwu and Tassou, 2018). Such systems appear versatile and promising for heating applications. They enable a tunable microwave frequency with a very narrow bandwidth, independently of the power control.

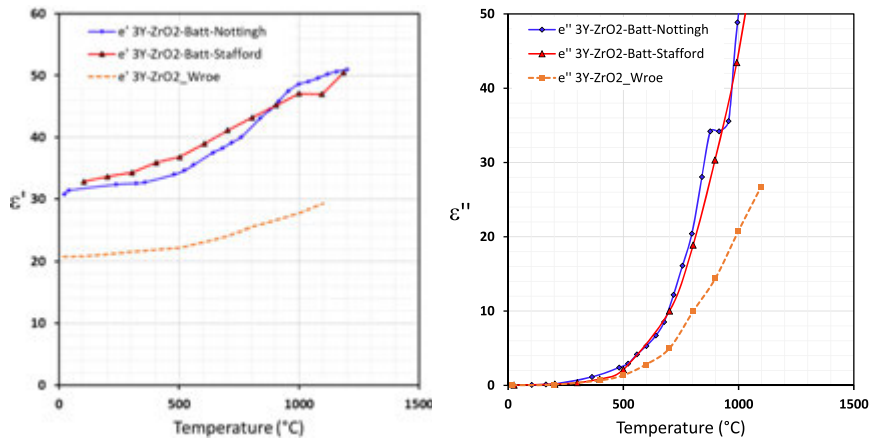


Fig. 9 Measured dielectric properties of 3Y-ZrO₂. Data denoted “Batt-xx”, were obtained on the same dense material in two different labs, data denoted “Wroe” were obtained on a material from a different source. Adapted from Batt, J., Binner, J., Cross, T.E., *et al.*, 1995. A parallel measurement program in high Temperature dielectric property measurements: An update. In: *Microwaves: Theory and Application in Materials Processing III*, Ceramics Transactions. American Ceramic Society. pp. 243–250. Wroe, R., Rowley, A.T., 1996. Evidence for a non-thermal microwave effect in the sintering of partially stabilized zirconia. *J. Mater. Sci.* 31, 2019–2026.

Temperature Control in MW Heating

In conventional heating, the furnace temperature is transferred to the sample by classic heat transfer mechanisms (conduction, convection, radiation). Input energy is transformed into heat by the furnace, so that the temperature control is performed by adjusting the input power to balance the power required to heat the samples and walls and heat losses of the furnace and parts to be heated, which monotonously depend on temperature.

In a microwave furnace, the cavity is not heated: only the sample and its local surroundings (susceptor, thermal insulators: see next sections) are heated by the microwaves. We will call this the *load* of the cavity. The load itself must be considered as an active part of the heating system. Fig. 6 shows in the case of a resonant single mode empty cavity that part of the waves is reflected through the iris. This reflected part exists as well in loaded single or multimode cavities, and depend of the geometric and dielectric characteristics of the load. In a resonant cavity, the load changes the resonance conditions with respect to an empty cavity. Let us consider a cavity in which the length is adjusted to resonance with the load. The field will therefore be maximal and the dissipated power ($P \propto \epsilon'' E^2$) high, with a probably low reflected power. If the increase of temperature changes the dielectric properties of the load, which is generally the case, two very different consequences can be observed. If E is not too much changed, the increase of ϵ'' will increase P , causing a further increase of ϵ'' , and so on, leading to possible thermal runaway (see below section “Direct Heating, Inverted Gradient, Thermal Runaway”). The opposite result can be observed with even smaller dielectric property changes: the change in dielectric properties of the load tends to make the cavity out of resonance, so that the electric field drops down. In this case, the field and the absorbed power decrease while the reflected power increases, so that a higher input power is required, with the cost of a drop in power efficiency. This simple example shows that the temperature control by only adjusting the input power may have dramatic consequences on the efficiency. In practice, whatever the type of cavity, it can even lead to quite inefficient heating. The characteristics of the cavity must therefore be adjusted together with the input power, through the cavity length in the case on single mode cavities or by devices placed along the waveguide between the generator. This is also-called impedance matching and tuning, as the microwave furnace can be seen as an electric circuit or transmission line (Owyang, 1989; Pozar, 2012). The high temperatures required for sintering ceramics makes this phenomenon an important issue.

The present chapter does not aim at giving details on the technical aspects of temperature control, but the reader can find in literature some examples of possible strategies (Croquesel *et al.*, 2015; Marinel *et al.*, 2018). Anyway, it is important to understand and keep in mind that technical difficulties exist and explain that, in a number of papers dealing with microwave sintering, the temperature cycle is not accurately controlled.

Microwave Heating of Ceramics

Dielectric Properties of Ceramics

In ceramics, the real part ϵ' of the permittivity slowly increases with temperature (Figs. 9(a) and 10(a)). On the contrary, the imaginary part ϵ'' may in some cases exhibit a strong increase, which tends to be exponential-like, while other materials have a limited evolution.

The strong increase is often associated to the thermal activation of conduction phenomena, which make the term $\frac{\sigma}{\omega}$ in Eq. (3) increase drastically. It is for instance the case in zirconia (Figs. 9(b) and 10(b)), known as a ionic conductor at high temperature:

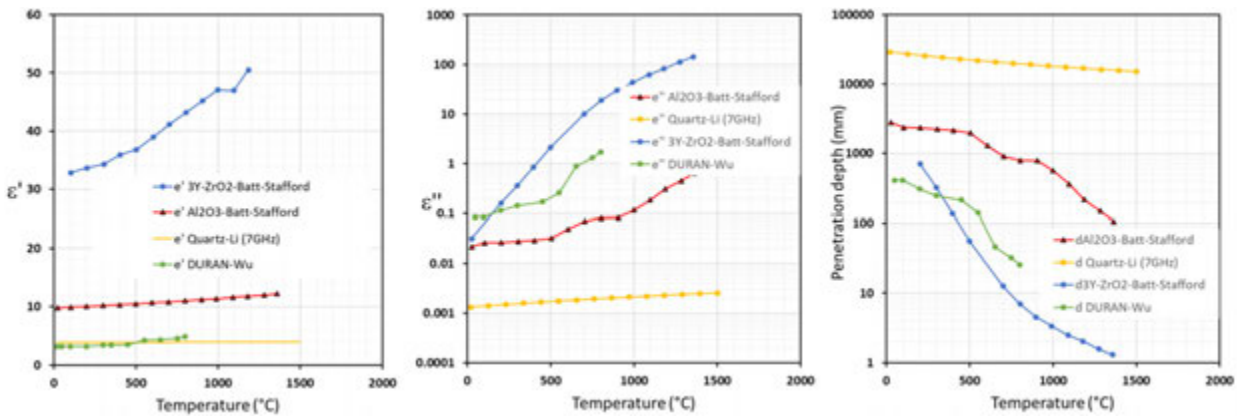


Fig. 10 Examples of dielectric properties and penetration depth of different ceramics and glasses at 2.45 MHz: quartz, Duran ceramic-glass, alumina and 3Y zirconia: (a) Permittivity real part ϵ' ; (b) Permittivity imaginary part ϵ'' ; (c) Penetration depth d . Adapted from Li, E., Nie, Z., Guo, G., Zhang, Q., 2009. Broadband measurements of dielectric properties of low-loss materials at high temperatures using circular cavity method. *Prog. Electromagn. Res.* 92, 103–120. Wu, L., Zhang, Y., Wang, F., *et al.*, 2019. An On-Line System for High Temperature Dielectric Property Measurement of Microwave-Assisted Sintering Materials. *Materials* 12, 665. doi:10.3390/ma12040665. Batt, J., Binner, J., Cross, T.E., *et al.*, 1995. A parallel measurement program in high temperature dielectric property measurements: An update. In: *Microwaves: Theory and Application in Materials Processing III*, Ceramics Transactions. American Ceramic Society. pp. 243–250.

several authors (Greenacre, 1996; Wroe and Rowley, 1996) found that conductivity was predominant at high temperature and proposed relationships including an activation energy Q : $\epsilon''_e = \frac{\sigma}{\omega} = A \exp(-Q/RT)$. In spite of a relatively low coupling at room temperature, microwaves can heat these good coupling materials, but the strong evolution of ϵ''_e with temperature makes the temperature control difficult (see below). Materials such as some ceramic glasses (Fig. 10) or silicon carbide (SiC) have an intermediate value of ϵ''_e which moderately evolves with temperature.

Materials such as pure alumina show a significant increase in ϵ''_e (Fig. 10), but the value of ϵ''_e remains small below 500 or 1000°C: these low coupling (*low-loss*) materials are therefore quite uneasy to heat from room temperature. Quartz is a remarkable example of quasi-transparent material, with a low (<5) and almost constant real part ϵ' , and a very small value of the imaginary part ϵ''_e , which remains far below 10^{-2} at 1500°C (Fig. 10). This makes quartz a good material for sample supports and thermal insulator parts, although its mechanical properties quickly drop down above 1000°C.

It is necessary to point out that these dielectric properties are very sensitive to the structure and composition of the material, including contamination and doping, porosity in the case of powder and sintered materials, and to microstructure. The large difference between the two authors' values in 3Y-zirconia on Fig. 9 is probably due to the use of different materials. The smaller but significant difference between the two "Batt" curves, obtained on dense parts from the same provider come from the measurements made in two different labs, in the background of a comparison program (Batt *et al.*, 1995). Techniques for measuring complex dielectric permittivity are based on the microwave response of a cavity when a sample is placed inside it (or at a boundary) and on the analysis of this response using a model (Li *et al.*, 2009; Murthy, 1994; Volkovskaya *et al.*, 2018; Wu *et al.*, 2019). These measurements are sensitive to the sample density, size, shape and surface state, and even more difficult in the case of high temperature measurements. In this context, data from literature must be considered as mainly indicative.

Direct Heating, Inverted Gradient, Thermal Runaway

Direct heating is when the parts to be heated (and for instance sintered) are placed in the cavity and heated by the field. In this situation, as the cavity walls are cold and the heat produced in the bulk of the part, an inverted gradient is expected with respect to classical furnaces. Unlike in classical furnaces, where gradients are transient and occur during heating, the inverted gradient can be stable even during an isothermal stage, as heat is continuously produced in the bulk and removed at the surface. Indirect proofs of such situations can be observed on Fig. 11: the coarse microstructure in the center of the microwave sintered alumina evidences a large overheating, while the microstructure close to the surface is similar to the one of the homogeneous part sintered using the same thermal cycle in a conventional furnace.

Because of the permittivity evolution, penetration depths decrease when temperature increases (Fig. 10). The expected bulk heating is often effective when the width of sintered parts is below 1 or 2 cm, which is the case of most ceramic parts, as penetration depths generally remain above 1 cm (Fig. 10) in most ceramics. However, in the case of ceramics such as zirconia, with a strong loss factor increase and the need for reaching high temperatures during sintering, the penetration depth can become millimetric, leading heat production to be localized close to the surface.

A more dramatic issue associated to the strong variation of the dielectric permittivity imaginary part in high coupling (high loss) materials is the thermal runaway: an increase of temperature generates an increase in ϵ''_e , which in turn (Eq. (4)) generates a

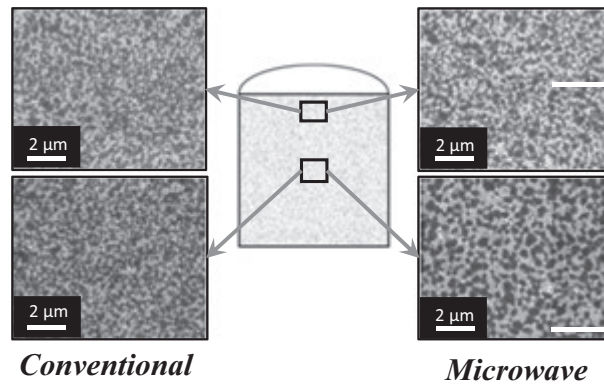


Fig. 11 Compared microstructures of Al_2O_3 –40vol% ZrO_2 mixed powders samples sintered at 1500°C by conventional and microwave heating observed on axial cross sections, at the center and close to the top surface. Temperature is measured by thermocouple close to the sample the conventional furnace, and by calibrated IR camera in the (single mode) microwave cavity. Adapted from Guyon, A., 2013. *Frittage Ultra-rapide Naturel: Chauffage par micro-ondes et par induction* (PhD). Université de Grenoble, Grenoble.

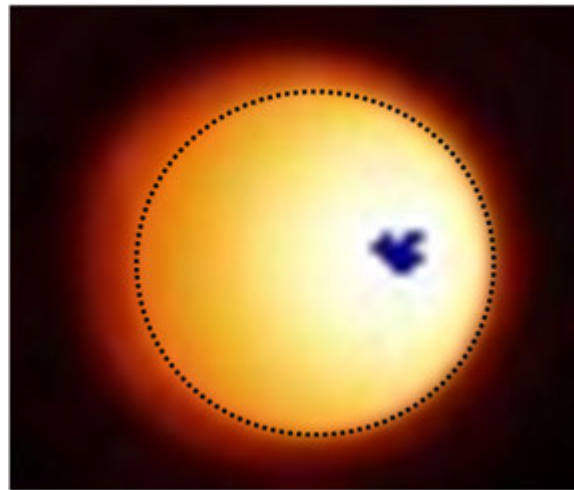


Fig. 12 Hot spot observed by IR camera during direct heating of a 3Y-TZP 8 mm cylinder. The temperature difference between the blue points and the average surface of the sample is about 400°C. The dotted black line marks the limit of the top surface of the sample. Picture by T. Garnault, Univ. Grenoble Alpes.

temperature increase... When it occurs at the whole part scale, this thermal instability induces an increase in the heating rate, leading to a hardly uncontrollable temperature increase.

A less controllable effect is the appearance of *hot spots*, when the non-uniform electric field or some composition/density variations in the material induce a local over-temperature, amplified by the runaway. Such hot spots during a sintering process can induce local over densification or melting, as well as thermomechanical gradient leading to fractures. In most cases, anyway, the user will try to avoid or limit the effects of thermal runaway, in particular temperature gradients. Thermal runaway and hot spots are tempered by heat diffusion phenomena: they are therefore limited by low heating rates/power but in turn limit the high heating rates that can be practically reached with safe samples.

Indirect and Hybrid Heating With Susceptors

A common solution to both heating low loss materials and improving thermal homogeneity of highly temperature sensitive medium- or high-loss ones is to introduce intermediate parts, called *susceptors*, in the cavity. These parts made of medium- or high coupling materials with low temperature sensitivity catch the electromagnetic field power then transmit heat to the material of interest by classic heat transfer mechanisms (conduction, convection and mainly radiation at high temperature) and limit the field seen by the material. A classic material is silicon carbide (SiC), in the form of dense parts or powders (Fig. 12).

The nature, geometry and position of susceptors determines the heating efficiency, but also the electromagnetic field around and inside the parts (Fig. 13). A fully closed susceptor acts as a field barrier, leading to *indirect heating* of the material. An open

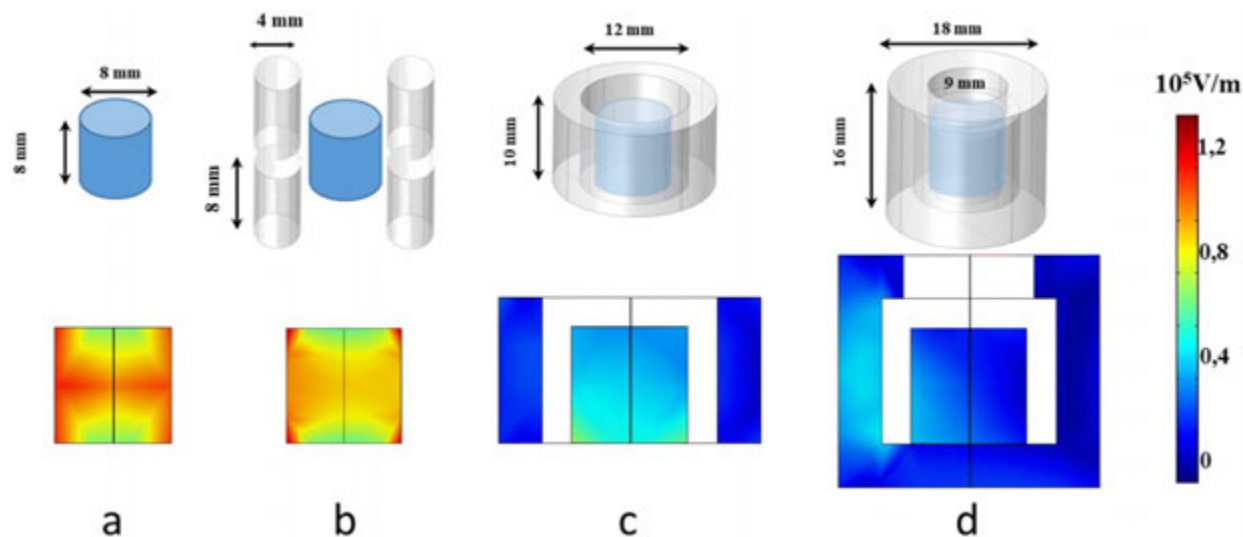


Fig. 13 Simulation of the electric field of a low coupling material ($\epsilon' = 5$, $\epsilon'' = 0.05$) in direct heating and two cases of hybrid heating: 4 rods (picket fence) and tube susceptors (typically SiC $\epsilon' = 40$, $\epsilon'' = 3$). The sample is centered on an antinode of electric field of a single mode TE_{10n} 2.45 GHz cavity.

susceptor allows the material to be partly heated by the field. In this *hybrid heating*, the materials benefit from some aspects of bulk heating (inverted gradient) and from potential specific effects of the field-materials interactions (*e.g.*, sintering enhancement). Using a closed configuration to have a lower field is a way for limiting hot spots and improving homogeneity in high temperature sensitive materials such as zirconia. An open configuration will promote an assisted heating at low temperature and maximize the direct part of heating in a low-loss material such as alumina. Various strategies have been developed for optimizing susceptor configurations with respect to the properties of materials to be processed (Bhattacharya and Basak, 2016).

Thermal Insulators and Casketing

The high temperature of samples and susceptors while the cavity walls are kept close to room temperature requires the use of thermal insulators, and refractory supports. These materials must be as transparent as possible to microwaves at room and at high temperature. The large amount of air in highly porous granular or fibrous thermal insulators is a favorable factor, but materials with intrinsic low absorption of microwave (large penetration depth) are necessary. Typical convenient materials are aluminosilicate fibers, cordierite, quartz, yttria, boron nitride BN, silicon nitride Si₃N₄ (Bhattacharya and Basak, 2016; Evans *et al.*, 1999). The upper limit temperature, the thermal efficiency and the absorption widely differs from one material to another. Efficient thermal insulation is obtained by placing the sample and susceptors inside closed caskets (Fig. 14), which can be constituted by several layers of insulating materials (Bhattacharya and Basak, 2016; Holcombe and Dykes, 1990).

Although the absorption of these materials is low, their volume can be much larger than the sample, so that, in the case of direct heating of low-loss materials, the insulator package can absorb a major part of microwave radiation and act as a susceptor. This effect could be enough for initiating the heating of materials such as alumina, which exhibits a very low coupling at room temperature and a significant increase of its loss factor when temperature is increased.

Microwave Sintering of Ceramics

A Successful Way for Sintering Almost All Ceramics

A great variety of ceramics have been successfully sintered using microwaves over the past 30 years: structural ceramics (Al₂O₃, ZnO, SiC, MgAl₂O₄, Y-PSZ, Y-TZP/Al₂O₃, TiO₂), bioceramics (hydroxyapatite), functional ceramics (ZnO, BaTiO₃), composites (MgO-Y₂O₃, ZrB₂-B₄C, WC-Co), magnetic ceramics (Ni-Zn ferrites), translucent or transparent ceramics (AlN, MgO, ALON)... Details can be found in various review papers (Das *et al.*, 2009; Karayannis, 2016; Katz, 1992; Oghbaei and Mirzaee, 2010). Experiments involve a high diversity of frequencies (from 915 MHz to 50 GHz and above), of cavities (single mode, multimode, rectangular or cylindrical), using direct, hybrid or indirect heating.

Beyond the very effective possibility to save time and energy by heating directly a volume (sample and susceptors if any) smaller than the entire oven in conventional heating, several specific advantages were studied or observed, which are discussed in the following sections.

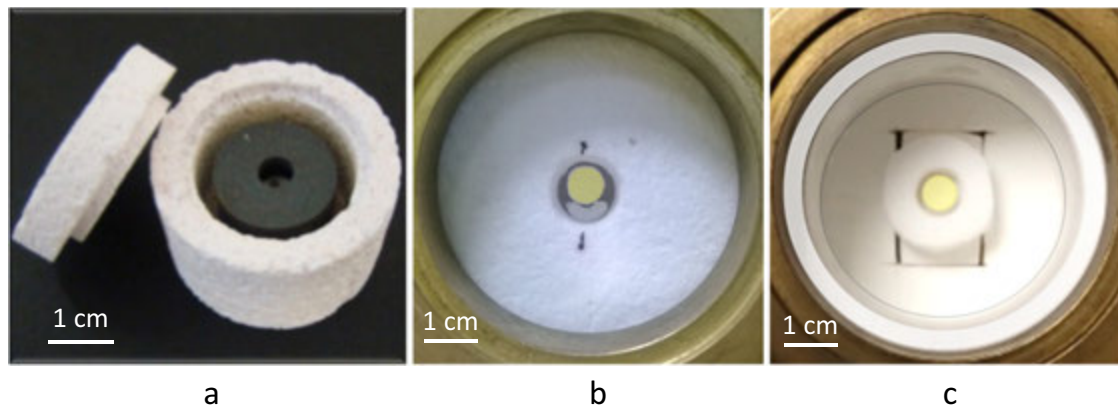


Fig. 14 Examples of sintering caskets used in a 2.45 GHz single mode cavity with 8 mm cylinders powder compacts: (a) porous material insulating box and (black) SiC cylinder susceptor (configuration of Fig. 13(d)); (b) fibrous insulator cylinder for direct heating; (c) insulating casket constituted by an inner and an outer cylinders separated by air for optimizing field absorption (the casket cap has been removed). The sample is marked in yellow in (b) and (c) and is inside the SiC box in (a).

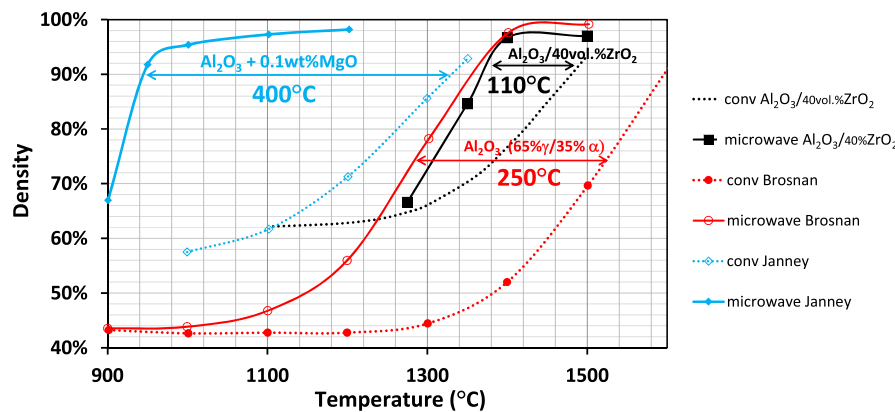


Fig. 15 Example of results showing densification by microwave sintering (full lines) at much lower temperatures than in conventional furnaces (dotted lines) for different powders: Al_2O_3 -0.1 wt%MgO, Al_2O_3 65% γ /35% α , Al_2O_3 -40 vol.% ZrO_2 . Adapted from Janney, M.A., Kimrey, H.D., 1991. Diffusion-controlled processes in microwave-fired oxide ceramics. In: Microwave Processing of Materials II. Materials Research Society. pp. 215–227. Brosnan, K.H., Messing, G.L., Agrawal, D.K., 2003. Microwave sintering of alumina at 2.45 GHz. J. Am. Ceram. Soc 86, 1307–1312. Guyon, A., 2013. Frittage Ultra-rapide Naturel: Chauffage par micro-ondes et par induction (PhD). Université de Grenoble, Grenoble.

Densification Enhancement and Lowered Sintering Temperature

Many papers, in particular in early works on microwave sintering, have shown surprising results, with high densification obtained at temperatures far below the temperature required in conventional furnaces (Fig. 15), with shorter dwell times. The temperature shifts between densification curves reach 100–400°C. This must however be considered carefully. A first point is that some papers compared results obtained with different and maybe uncontrolled heating rates, significantly higher in microwave heating than in conventional heating. The use of high heating rates to minimize non-densifying sintering mechanisms such as surface diffusion and promote densifying mechanisms such as GB or bulk diffusion, which generally show higher activation energies, is a classic strategy for improving densification (and minimizing grain size). This phenomenon could explain, at least partly, some observations when microwave heating is fast. A second explanation, which applies even in case of identical heating rates, is the misvaluation of temperature in microwave experiments.

Sample temperature evaluation during microwave heating is a fundamental issue. Placing thermocouples inside samples can induce strong effects due to perturbations or concentration of the electric field as well as measurement bias due to heat conduction by the metallic thermocouple or microwave heating of the thermocouple itself (Pert *et al.*, 2004). Recent works (Santos *et al.*, 2019) showed in the case of porcelain that temperature was underestimated 50°C when thermocouples were used, with respect to calibrated pyrometers and PTCRs (process temperature control rings), as thermocouples measure temperature apart from the sample. The authors estimated that the sintering temperature reduction by microwaves for porcelain sintering was therefore not

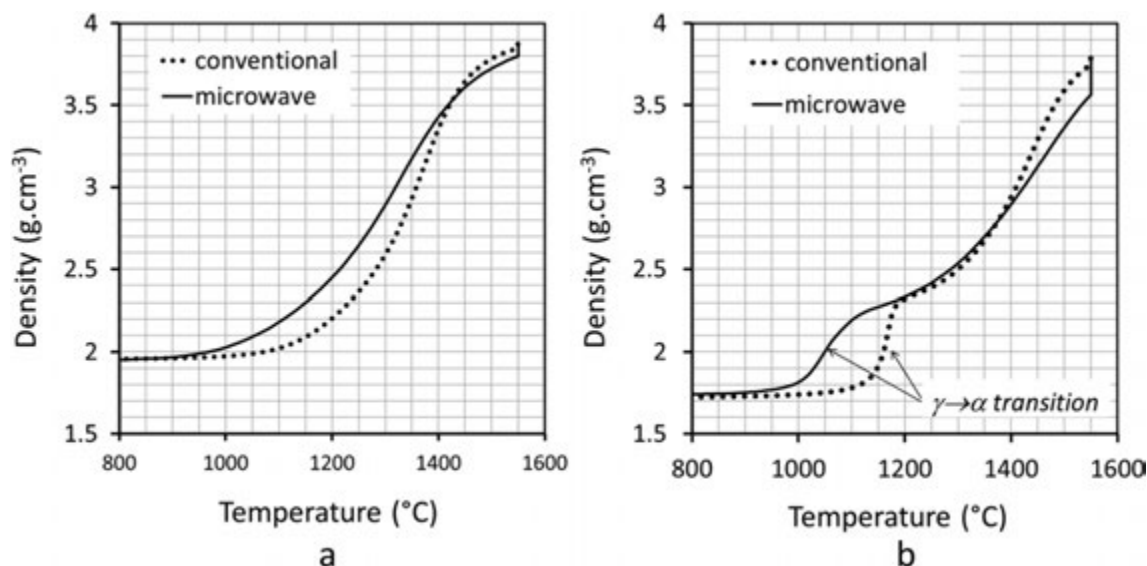


Fig. 16 Compared densification (dilatometric) curves of alumina compacts using conventional and (direct) microwave heating (single mode) at 25°C/min. (a) γ -alumina; (b) α -alumina, with evidence of the $\gamma \rightarrow \alpha$ phase transition. After Croquesel, J., 2015. Etude des spécificités du frittage par micro-ondes de poudres d'alumine alpha et gamma (PhD). Grenoble-Alpes, Grenoble. Croquesel, J., Bouvard, D., Chaix, J.-M., Carry, C.P., Saunier, S., 2015. Development of an instrumented and automated single mode cavity for ceramic microwave sintering: Application to an alpha pure alumina powder. *Mater. Des.* 88, 98–105. doi:10.1016/j.matdes.2015.08.122.

verified. Radiation based devices (optical pyrometers, IR cameras) are therefore preferred. They read temperature directly on the sample surface. As the sample emissivity (or emissivity ratio in two-color pyrometers) is sensitive to the material composition, density and surface roughness, calibration is a key point for valuable measurements. Around 1200°C, using an emissivity of 1 or 0.9 when the actual sample emissivity is 0.75 typically leads to temperature underestimations of 75 and 50°C, respectively; these underestimations increase with temperature. In early papers, these aspects were either ignored or not clearly mentioned, but as time goes on, works on microwave sintering give increasing attention to correct temperature calibration.

Another source of temperature underestimation is the above-mentioned inverted temperature gradient in microwave heating: the surface temperature evaluated by pyrometers can be much lower than the bulk temperature. The results for Al_2O_3 -40 wt% ZrO_2 on Figs. 11 and 15 are from the same experiments: the grain size difference observed on Fig. 11 between the center and the top of the sample, where temperature was measured, clearly agrees between the 110°C shift observed on Fig. 15.

The addition of these effects makes that a number of conclusions about the large decrease of the sintering temperature associated to microwave heating should be revisited. This does not mean that this microwave effect is not real, but it is probably less systematic and of lower magnitude than announced in many cases.

An important point to consider is whether this lower temperature densification is effective until full density. In some systems (Fig. 16(a)), the densification of compacts starts at lower temperature, but slows down when the sample density is above 90%, so that full density is not reached at lower temperature than in conventional sintering.

A variant of the observation of lowered densification temperature in microwave sintering is that the activation energy evaluated from densification curves is lower than in conventional heating. Apparent activation energy Q is a useful tool for comparing densification curves, a practical concept that enables to handle a simple form of the relationship between the densification rate and temperature. It is based on the assumption that the effects of temperature T and density ρ can be separated: typically $d\rho/dt = f(\rho)\exp(-Q/RT)$. This is characteristic of thermally activated mechanisms, and Q is frequently associated to a thermally activated dominant (rate limiting) mechanism for interpreting the results. In this background, the apparent decrease of the apparent activation energy of densification during microwaves heating is a practical way for characterizing the effect of microwaves. Interpretations in terms of mechanisms would be hazardous. Biased temperature measurements of course induce biased calculations of activation energy.

Finer Microstructures

The possibility to obtain smaller grain size by microwave sintering is often pointed out as an expectation related to either the high heating rate or specific field-material interactions (microwave effects). Independently of the heating technique, high heating rates and ultrafast firing are considered as ways to get fine microstructures and interesting properties (Ji *et al.*, 2017). Recent works (Bykov *et al.*, 2016) suggest that an efficient control of the microwave input power could take advantage of the thermal runaway phenomenon, which is similar to the so-called *flash sintering* by Joule heating, driven by the thermal runaway due to thermally activated conductivity (Dancer, 2016).

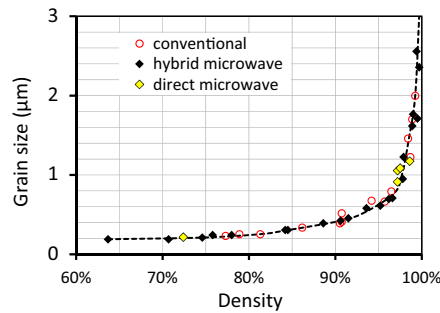


Fig. 17 Sintering trajectories in a pure alumina powder, using conventional and microwave heating modes. Data from Croquesel, J., Bouvard, D., Chaix, J.-M., Carry, C.P., Saunier, S., 2015. Development of an instrumented and automated single mode cavity for ceramic microwave sintering: Application to an alpha pure alumina powder. *Mater. Des.* 88, 98–105. doi:10.1016/j.matdes.2015.08.122. Zuo, F., Saunier, S., Marinel, S., *et al.*, 2015. Investigation of the mechanism(s) controlling microwave sintering of α -alumina: influence of the powder parameters on the grain growth, thermodynamics and densification kinetics. *J. Eur. Ceram. Soc.* 35, 959–970. doi:10.1016/j.jeurceramsoc.2014.10.025.

Regarding microwave effects on microstructure, very different results were obtained. Some papers indicate smaller grain sizes using microwaves; other papers observe higher grain sizes, consistent with higher bulk temperatures. Enhanced coarsening would be compatible with specific microwave effects as such effects can also enhance grain growth. Some results indicate smaller grain size in microwave sintering. It is however important to keep in mind that comparing two microstructures with almost the same density is often irrelevant, as the experimental correlations between density and grain size clearly show a drastic increase when density is above 98%. Fig. 17 shows an example in which a large number of experiments in a wide range of final densities have shown that the size *vs.* density curve strongly varies above 98% density and is the same for conventional and microwave sintering. Obtaining high density, even using microwaves, requires final stages at high temperatures. During this final stage, density evolves much slowly than in earlier stages, and grain growth can take place, and is even enhanced if the first densification step was short and kept a high driving force for grain growth.

Non-thermal Effects

The words *non-thermal effects* refer to effects of microwaves that cannot be attributed to the heat dissipation of the electromagnetic energy, through the thermal activation of diffusion in sintering mechanisms. Non-thermal effects consequently result from specific direct interactions, and their consequences are changes in the evolution (densification, grain growth...) with respect to observations at the same temperature when no electromagnetic field is present. The densification enhancement at low temperature presented in the previous section is an example. Another example is the effect on phase transitions (Fig. 16(b)) (Croquesel *et al.*, 2016; Rybakov *et al.*, 2008).

The *ponderomotive force* in microwave assisted materials processing was introduced to account for microwave effects on plasticity and sintering (Rybakov *et al.*, 2012; Rybakov and Semenov, 1994). It is based on the observation that the motion of charged vacancies is influenced by the instantaneous electric field E . An additional driving force must therefore be considered and added to the concentration gradient ∇C in the vacancy diffusion flux J :

$$J = D \left(-\nabla C + C \frac{q}{kT} E \right) \quad (11)$$

As E symmetrically oscillates as $\sin(2\pi ft)$, its time average over a time period is expected to be 0 and to have no average effect. However, in regions close to interfaces with high field and charge concentration gradients, the promoters of this theory calculated that the time average $\langle C \frac{q}{kT} E \rangle$ is nonzero. This induces vacancy fluxes at interfaces and surfaces, which modify the mass balance. Theoretical calculations and computer modelling were used to analyze the resulting effect on surfaces and around the grain-grain-pore triple lines. They led to the conclusions that the effect depends on the orientation of the field with respect to the surface or grain boundary, and can induce mass flow which contribute to densification. It was calculated that the associated driving force is proportional to E^2 and may in some cases be significant when compared to classic driving forces (Booske *et al.*, 1998; Rybakov *et al.*, 2013). As these effects require triple lines, they are expected to be more effective in the first steps of sintering than in the final stage. This is in agreement with some observations, as for instance the early densification under microwave which seems to be slowed down when high densities are reached, as observed in the case of α -alumina (Fig. 16(a)). Unfortunately, no macroscopic formulation that could be included in sintering models is available for introducing ponderomotive force effects in usable densification models.

Other theoretical works have shown that, due to so-called *micro-focusing effects*, the electric field can be strongly amplified at particle contacts due to local sharp shapes (Birnbom *et al.*, 1998; Li *et al.*, 2015) and that the local field is favorably polarized to enhance the ponderomotive effects. Microfocusing however rapidly decreases when particle necks evolve, and should merely occur in the early stages of sintering.

In spite of a significant number of papers indicating the effectiveness of these non-thermal effects, it is indeed difficult to evaluate, and even more to predict the amplitude of these effects and their importance for practical applications in ceramics processing.

Towards Applications in Ceramics Production

Although efficient, the microwave sintering technique still has a limited number of known applications in industry. Recent review papers (Bhattacharya and Basak, 2016; Oghbaei and Mirzaei, 2010) clearly listed the advantages of microwave sintering when compared to conventional heating techniques of ceramic industry: lower energy consumption, higher heating rates and time reductions, and in some cases improved properties associated to high heating rates or some non-thermal effects of microwaves. These advantages were only expected 30 years ago, as pointed out by Katz (1992), but significant technical and scientific progress has occurred since these early works. Evaluations on some practical cases showed very significant shorter sintering times and cycle times: for instance, when conventional sintering of a Y-TZP part requires 60 min sintering time, 6 h processing time, and more than 4 kWh, microwave sintering enabled to obtain the same final properties with 20 min, 1.5 h, and 0.4 kWh, respectively (Zhao *et al.*, 2000). Microwave furnaces of various types (muffle furnaces, batch or pusher kilns, gas and vacuum furnaces), sizes (from 50 cm to several meters), enabling processing temperature up to 1600°C and more, have been developed by different providers all over the world and can be seen on their websites. Some of them, said *hybrid kilns*, associate microwave with another heating technique (gas, electric power) which ensures reaching temperature at which materials efficiently couple with microwaves. However, the microwave technique is not much implemented in the ceramic industry and remains limited to the laboratory scale or specific applications. There is indeed few information available from ceramic manufacturers, but communication of some microwave furnace providers cites effective industrial applications with significant gains in processing time and energy consumption (Shulman *et al.*, 2008). Microwave sintering ovens are available for dentistry, which take advantage of the very simple use by dental technicians, fast processing and low energy consumption, and maybe of the small batches inherent to this production.

Limitations may come from the difficulty to ensure heating homogeneity. One of the consequences is the limited size of parts: 16 cm pieces are still considered as large and require careful attention and efforts for being obtained by microwave sintering (Chen *et al.*, 2016; Thuault *et al.*, 2014). The required investment can however become valuable in the future, as far as knowledge progresses, either for specific applications or for massive energy savings. Computer simulation and modelling as effective tools for understanding and design, should significantly contribute to make applications of microwave sintering effective in future in ceramic materials production.

References

- Atuonwu, J.C., Tassou, S.A., 2018. Quality assurance in microwave food processing and the enabling potentials of solid-state power generators: A review. *J. Food Eng.* 234, 1–15. doi:10.1016/j.jfoodeng.2018.04.009.
- Batt, J., Binner, J., Cross, T.E., *et al.*, 1995. A parallel measurement program in high temperature dielectric property measurements: An update. In *Microwaves: Theory and Application in Materials Processing III*, Ceramics Transactions. American Ceramic Society. pp. 243–250.
- Bhattacharya, M., Basak, T., 2016. A review on the susceptor assisted microwave processing of materials. *Energy* 97, 306–338. doi:10.1016/j.energy.2015.11.034.
- Birnboim, A., Calame, J.P., Carmel, Y., 1998. Microfocusing and polarization effects in spherical neck ceramic microstructures during microwave processing. *J. Appl. Phys.* 85, 478–482. doi:10.1063/1.369411.
- Booske, J.H., Cooper, R.F., Freeman, S.A., Rybakov, K.I., Semenov, V.E., 1998. Microwave ponderomotive forces in solid-state ionic plasmas. *Phys. Plasmas* 5, 1664–1670. doi:10.1063/1.872835.
- Brady, M.M., 1965. Rectangular waveguide flange nomenclature (Correspondence). *IEEE Trans. Microw. Theory Tech.* 13, 469–471. doi:10.1109/TMTT.1965.1126031.
- Brittain, J.E., 1985. The magnetron and the beginnings of the microwave age. *Phys. Today* 38, 60–67. doi:10.1063/1.880982.
- Bykov, Y., Egorov, S., Ereemeev, A., *et al.*, 2016. On the mechanism of microwave flash sintering of ceramics. *Materials* 9, 684. doi:10.3390/ma9080684.
- Bykov, Y., Ereemeev, A., Glyavin, M., *et al.*, 2004. 24–84-GHz gyrotron systems for technological microwave applications. *IEEE Trans. Plasma Sci.* 32, 67–72. doi:10.1109/TPS.2004.823904.
- Chakravorty, P., 2014. Analysis of rectangular waveguides – An intuitive approach. *IETE J. Educ.* 55, 76–80. doi:10.1080/09747338.2014.1002819.
- Chen, Y., Fan, B., Shao, G., Zhang, R., 2016. Preparation of large size ZTA ceramics with eccentric circle shape by microwave sintering. *J. Adv. Ceram.* 5, 291–297. doi:10.1007/s40145-016-0202-4.
- Croquesel, J., Bouvard, D., Chaix, J.-M., Carry, C.P., Saunier, S., 2015. Development of an instrumented and automated single mode cavity for ceramic microwave sintering: application to an alpha pure alumina powder. *Mater. Des.* 88, 98–105. doi:10.1016/j.matdes.2015.08.122.
- Croquesel, J., Bouvard, D., Chaix, J.-M., *et al.*, 2016. Direct microwave sintering of pure alumina in a single mode cavity: grain size and phase transformation effects. *Acta Mater.* 116, 53–62. doi:10.1016/j.actamat.2016.06.027.
- Dancer, C.E.J., 2016. Flash sintering of ceramic materials. *Mater. Res. Express* 3, 102001. doi:10.1088/2053-1591/3/10/102001.
- Das, S., Mukhopadhyay, A.K., Datta, S., Basu, D., 2009. Prospects of microwave processing: An overview. *Bull. Mater. Sci.* 32, 1–13. doi:10.1007/s12034-009-0001-4.
- El Khaled, D., Novas, N., Gazquez, J.A., Manzano-Agugliaro, F., 2018. Microwave dielectric heating: Applications on metals processing. *Renew. Sustain. Energy Rev.* 82, 2880–2892. doi:10.1016/j.rser.2017.10.043.
- Evans, N.G., Hart, N.A., Hamlyn, M.G., 1999. Dielectric property measurements in design of industrial scale hybrid kiln. *Br. Ceram. Trans.* 98, 93–99. doi:10.1179/096797899680309.
- Greenacre, N.R., 1996. Measurement of the High Temperature Properties of Ceramics at Microwave Frequencies. University of Nottingham.
- Harvey, A.F., 1955. Standard waveguides and couplings for microwave equipment. *Proc. IEE – Part B Radio Electron. Eng.* 102, 493–499. doi:10.1049/pi-b-1.1955.0095.
- Holcombe, C.E., Dykes, N.L., 1990. Importance of “casketing” for microwave sintering of materials. *J. Mater. Sci. Lett.* 9, 425–428. doi:10.1007/BF00721019.

- Ji, W., Parker, B., Falco, S., *et al.*, 2017. Ultra-fast firing: Effect of heating rate on sintering of 3YSZ, with and without an electric field. *J. Eur. Ceram. Soc.* 37, 2547–2551. doi:10.1016/j.jeurceramsoc.2017.01.033.
- Karayannis, V.G., 2016. Microwave sintering of ceramic materials. *IOP Conf. Ser. Mater. Sci. Eng.* 161, 012068. doi:10.1088/1757-899X/161/1/012068.
- Katz, J.D., 1992. Microwave sintering of ceramics. *Annu. Rev. Mater. Sci.* 22, 153–170. doi:10.1146/annurev.ms.22.080192.001101.
- Li, E., Nie, Z., Guo, G., Zhang, Q., 2009. Broadband measurements of dielectric properties of low-loss materials at high temperatures using circular cavity method. *Prog. Electromagn. Res.* 92, 103–120.
- Li, Y., Xu, F., Hu, X., *et al.*, 2015. Micro-focusing effect of electromagnetic fields and its influence on sintering during the microwave processing of ceramic particles of SiC. *Ceram. Int.* 41, 14554–14560. doi:10.1016/j.ceramint.2015.07.172.
- Marinel, S., Renaut, N., Savary, E., *et al.*, 2018. Tuning, impedance matching, and temperature regulation during high-temperature microwave sintering of ceramics. *Adv. Mater. Sci. Eng.* 2018, 1–8. doi:10.1155/2018/4158969.
- Mishra, R.R., Sharma, A.K., 2016. Microwave–material interaction phenomena: Heating mechanisms, challenges and opportunities in material processing. *Compos. Part A* 81, 78–97. doi:10.1016/j.compositesa.2015.10.035.
- Murthy, V.R.K., 1994. Methods of measurement of dielectric constant and loss in the microwave frequency region. In: Murthy, V.R.K., Sundaram, S., Viswanathan, B. (Eds.), *Microwave Materials*. Berlin, Heidelberg: Springer Berlin Heidelberg, pp. 100–111. doi:10.1007/978-3-662-08740-4_4.
- Oghbaei, M., Mirzaei, O., 2010. Microwave versus conventional sintering: A review of fundamentals, advantages and applications. *J. Alloys Compd* 494, 175–189.
- Owyang, G.H., 1989. *Foundations for microwave circuits*. New York, NY: Springer New York, [10.1007/978-1-4613-8893-7].
- Pert, E., Carmel, Y., Birnboim, A., *et al.*, 2004. Temperature measurements during microwave processing: The significance of thermocouple effects. *J. Am. Ceram. Soc.* 84, 1981–1986. doi:10.1111/j.1151-2916.2001.tb00946.x.
- Pozar, D.M., 2012. *Microwave Engineering*, fourth ed. Hoboken, NJ: Wiley.
- Rybakov, K.I., Ereemeev, A.G., Egorov, S.V., *et al.*, 2008. Effect of microwave heating on phase transformations in nanostructured alumina. *J. Phys. Appl. Phys.* 41, 102008. doi:10.1088/0022-3727/41/10/102008.
- Rybakov, K.I., Olevisky, E.A., Krikun, E.V., 2013. Microwave sintering: Fundamentals and modeling. *J. Am. Ceram. Soc.* 96, 1003–1020. doi:10.1111/jace.12278.
- Rybakov, K.I., Olevisky, E.A., Semenov, V.E., 2012. The microwave ponderomotive effect on ceramic sintering. *Scr. Mater.* 66, 1049–1052. doi:10.1016/j.scriptamat.2012.02.043.
- Rybakov, K.I., Semenov, V.E., 1994. Possibility of plastic deformation of an ionic crystal due to the nonthermal influence of a high-frequency electric field. *Phys. Rev. B Condens. Matter* 49, 64–68.
- Santos, T., Henriet, L., Costa, V.A.F., Costa, L.C., 2019. Microwave versus conventional porcelain firing: Temperature measurement. *J. Manuf. Process.* 41, 92–100. doi:10.1016/j.jmapro.2019.03.038.
- Shulman, H.S., Fall, M.L., Strickland, P., 2008. Ceramic processing using microwave assist technology. *Am. Ceram. Soc. Bull.* 87, 34–36.
- Sun, J., Wang, W., Yue, Q., 2016. Review on microwave-matter interaction fundamentals and efficient microwave-associated heating strategies. *Materials* 9, 231. doi:10.3390/ma9040231.
- Thostenson, E.T., Chou, T.-W., 1999. Microwave processing: Fundamentals and applications. *Compos. Part A* 30, 1055–1071.
- Thuault, A., Savary, E., Bazin, J., Marinel, S., 2014. Microwave sintering of large size pieces with complex shape. *J. Mater. Process. Technol.* 214, 470–476. doi:10.1016/j.jmatprotec.2013.09.030.
- Volkovskaya, I.I., Ereemeev, A.G., Bykov, Y.V., 2018. High-temperature measurements of the microwave absorption coefficient in ceramic and composite materials. *Radiophys. Quantum Electron.* 61, 286–295. doi:10.1007/s11141-018-9890-7.
- Wroe, R., Rowley, A.T., 1996. Evidence for a non-thermal microwave effect in the sintering of partially stabilized zirconia. *J. Mater. Sci.* 31, 2019–2026.
- Wu, L., Zhang, Y., Wang, F., *et al.*, 2019. An on-line system for high temperature dielectric property measurement of microwave-assisted sintering materials. *Materials* 12, 665. doi:10.3390/ma12040665.
- Zhao, C., Vleugels, J., Groffils, C., Luyt, P.J., Van der Biest, O., 2000. Hybrid sintering with a tubular susceptor in a cylindrical single-mode microwave furnace. *Acta Mater.* 48, 3795–3801. doi:10.1016/S1359-6454(00)00160-9.

Porous Ceramics Processing

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Partial Sintering

A ceramic material is typically produced by sintering a powder compact. Both the degree of porosity and pore sizes in a porous monolith can be controlled by varying the initial particle size, green density, sintering additives and sintering condition during the heat treatment, so as to obtain varying degrees of densification. The initial and middle stages of sintering are very important in terms of creating the porous network, and different porosities and pore sizes can result from partial sintering techniques. Sintering always includes both densification and grain growth, with rounding of the angular, convex surfaces of particles occurring during the initial stage. Subsequent to this, adjacent particles in contact with one another bond together due to surface diffusion or evaporation–condensation processes. The material transfer from the particle surfaces to so-called neck regions through either surface diffusion or vapor transport does not decrease the distance between particle centers. That is, neither shrinkage nor densification takes place, while the neck areas between grains are enlarged during heating. This mass transfer can be greatly enhanced by applying a sintering temperature higher than that used during the initial sintering stage. The addition of carefully selected sintering aids can also promote neck growth along with grain boundary migration, followed by grain coarsening and densification in the middle and/or final stage of sintering. Through these sintering stages, the morphological changes of the grains can greatly affect various functional properties of porous ceramics, because the properties are directly correlated with pore size and porosity. Sintering a powder compact at an elevated temperature can increase the pore size because the pores are surrounded by large grains due to grain growth, while porosity is decreased due to densification, and vice versa. Thus, the particle size of the raw powder is also an important factor determining the pore size and porosity of the final product. Generally, the particle size of the raw powder should be two to five times larger than the desired pore size. However, even if the raw powder particle size and sintering conditions are properly tuned, it is frequently not possible to fully predict the resulting pore size and porosity of the sintered compact, due to the agglomeration of fine particles. For this reason, the raw particles are often subjected to ball milling (to break up such agglomerations) and high pressure forming, both of which are critical to obtaining the desired pore size and porosity in the final product. This partial sintering technique is the approach most commonly used to prepare many porous materials currently on the market, because it can easily be combined with the other techniques discussed in the following sections.

Fibrous Ceramics

Fig. 1 presents a typical image showing a fibrous ceramic microstructure. These ceramics are typically produced by blowing molten glass, natural rock or silicates in conjunction with a high-speed airflow and centrifugal force. Recently, very fine ceramic fibers with diameters of less than 10 μm have been developed, primarily made of mixtures of silica and alumina. The thermal stability of these materials decreases with increasing the silica ratio. Fibers with high silica content are usually produced by the melt blowing process

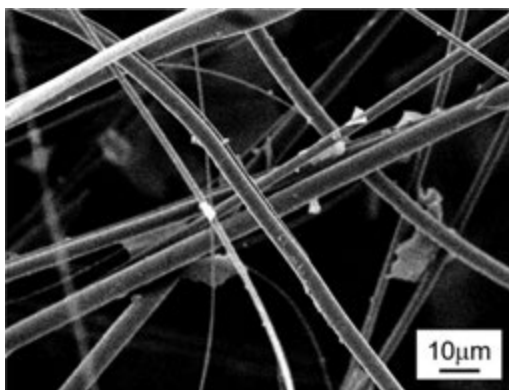


Fig. 1 The microstructure of fibrous ceramics used as thermal insulation in industrial furnaces and plants.

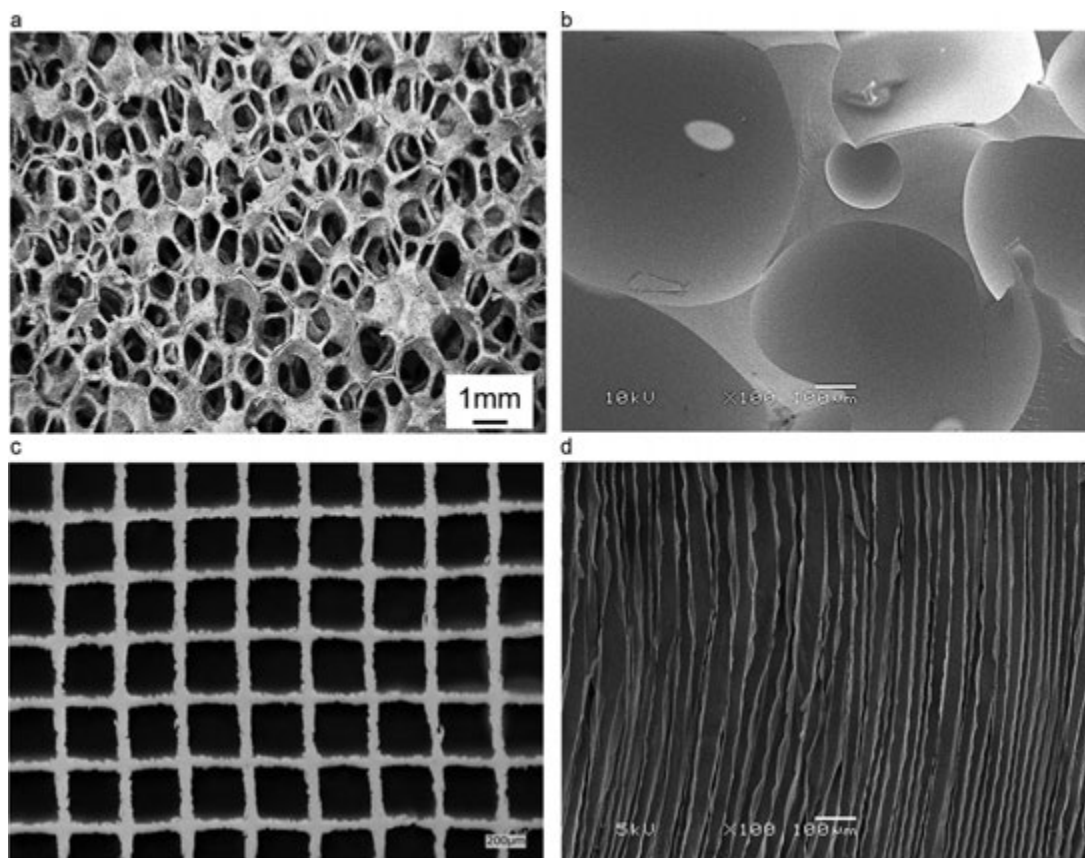


Fig. 2 The microstructure of various cellular ceramics prepared by (a) replica templating, (b) direct foaming, (c) extrusion and (d) gelation freezing.

described above, while ceramic fibers with lower silica contents can be manufactured by spinning a viscous sol solution prepared through the hydrolysis and condensation of an aluminum alkoxide. The latter process manufactures fibers having a higher alpha-alumina content that can be used at temperatures up to 1700°C. In these materials, the pores are formed from spaces between the fibers, and the properties are affected by their composition (silica/alumina ratio), fiber diameter, fiber length and volume fraction, as well as the degree of contact between adjacent fibers and the packing degree (density). Fiber boards, felts and blankets can all be produced by combining these ceramics with thermally cured organic or inorganic binders, followed by unidirectional pressing and laminating. These products have been widely utilized as thermal insulators in industrial furnaces, chemical plants and energy storage systems operating at elevated temperatures, because they can have very high porosity (above 90%) and narrow fiber diameters, and so have thermal conductivities typically less than 0.1 W/mK. As ceramic fibers do not include any volatile organic compounds, they have also been extensively utilized as building materials for sound absorption as well as thermal insulation. These materials can be readily processed and formed into various shapes at relatively low temperatures, as a result of their high degree of flexibility.

Cellular Ceramics

Fig. 2 presents typical microstructure of various cellular ceramics prepared by (a) replica templating, (b) direct foaming, (c) extrusion and (d) freeze casting (Ohji and Fukushima, 2012). Ceramic foams are typically manufactured by dip-coating a polymeric foam, acting as a replica template, into a ceramic powder dispersed as a slurry, a sol-gel precursor solution or a molten/liquid preceramic polymer, followed by burn-off or pyrolysis of the polymeric substrate and sintering. Typical microstructure is shown in **Fig. 2(a)**. This method is still the most widely used by industry for the manufacturing of ceramic foams for applications as molten metal filters or burners. A polymeric sponge, typically made of polyurethane, can be employed as the template material, but bio-derived porous materials such as wood or paper can also be used to create a cellular structure. However, because the expansion and gas evolution of the polymer during the burn-off step can damage the ceramic coating, it is challenging to create a defect-free ceramic coating on the template. This, plus the presence of voids inside the struts after elimination of the template tends to limit the mechanical strength of the ceramic foam, such that compression strength values are typically less than 1 MPa, albeit still suitable for some applications. The cell size of the foam generally ranges from several tens of micrometers to the millimeter

scale, and is primarily determined by the cell size of the original polymer template. Improvement of the strength can be achieved by multiple infiltration and sintering procedures.

A great variety of alternative processing approaches have been proposed for the fabrication of ceramic foams having improved mechanical properties. Direct foaming is based on the introduction of a gas into a liquid (either a slurry or sol solution) or softened polymer (a molten preceramic polymer with a thermoplastic binder) and the typical microstructure of the products is shown in [Fig. 2\(b\)](#). The gas can be introduced by various routes, such as mechanical frothing (mixing to generate bubbles), phase separation (segregation of a dissolved gas), in situ gas generation by a chemical reaction, thermal decomposition of a blowing agent, or the evaporation of a solvent. Various methods have been proposed to stabilize bubbles during this process so as to create fine, possessing the desired interconnectivity in the final porous bodies. These include the use of surfactants, the evaporation of emulsified alkane droplets and the use of surface-modified particles to prevent Ostwald ripening and coalescence among gas bubbles contained in the suspension (which otherwise lead to an inhomogeneous pore size distribution or the collapse of the liquid foam). The final microstructure frequently exhibits an anisotropic size gradient, associated with the floating direction of bubbles generated in the slurry, molten preceramic polymer or sol solution. [Shimamura et al. \(2016\)](#) developed a dry foaming method to mitigate this phenomenon. In this process, a powder compact containing a thermoset resin is foamed at a temperature that softens the polymer but is lower than the curing temperature. The morphology can be relatively homogeneous, because the particles are not strongly affected by buoyancy forces.

[Fig. 2\(c\)](#) shows the microstructure of a ceramic honeycomb. These materials have a substantial market position in catalytic converters, heat exchangers, combustors and filters and are manufactured by extrusion, conventional binder burn-off and sintering processes. In the case of extrusion, the die can be designed to produce a wide variety of cell geometries, such as square, triangular and hexagonal. The extrusion process requires the use of moldable natural clay or fine ceramics as raw materials, together with water and/or a binder having a degree of plasticity. This is required to ensure adequate rheological behavior of the mixture as well as structural rigidity and stability without excessive die wear. The size ratio between the die and container in which the raw mixture is held is also important.

Another novel processing method that enables the fabrication of unidirectional pore channels is the freeze casting of slurry or a gel body containing raw ceramic particles or ceramic precursors. The porous structure is templated by solidifying a solvent (typically water, although tert-butyl alcohol and camphene can also be used), leading to unique morphologies, such as lamellar, ellipsoidal or dendritic structures grown along the solidification direction. The freezing process generates porosity in the slurry or gel body, due to sublimation under vacuum of the solvent crystals, and is followed by sintering. This method produces materials with very good mechanical properties (such as compressive strength) along the freezing direction, because the struts are surrounded by cells aligned parallel to this direction within the entire sample. Pioneering work in this field was performed by [Fukasawa et al. \(2001\)](#), while [Fukushima et al. \(2010\)](#) proposed a gelation freezing process. Applying this method under carefully controlled freezing conditions, unidirectional cellular structures with very high porosity (up to 98 vol%) based on micrometer sized cells can be prepared, as shown in [Fig. 2\(d\)](#). The resulting cellular components possess substantially improved fluid permeability close to the ideal value calculated based on the capillary model, and very high mechanical strength due to micrometer-sized unidirectional structures without any defects. These cellular materials could be used as catalyst supports and for filtration, thermal insulation and biomedical applications, as well as lightweight structural components.

In addition to the various methods described above, the degree of porosity can be increased through the elimination of sacrificial fugitive additives acting as pore forming agents and mixed with raw ceramic particles or preceramic polymers. These are burned off or evaporated either before or during sintering of the particles or during pyrolysis of the polymer. This technique allows for the precise control of the degree of porosity and the pore size distribution and tends to give a wider range of cell sizes, typically from several tens of nanometers to the submillimeter range ([Colombo and Bernardo, 2003](#)). This method can be applied by itself or combined with other fabrication routes, such as partial sintering, templating, extrusion or blowing. Polymer beads, organic fibers, carbon, natural organic matter and liquids (water, gels and emulsions) have all been used as sacrificial pore forming agents, while poly(methylmethacrylate) (PMMA) beads have been most frequently employed as sacrificial additives, because that can be thermally decomposed and certainly removed.

Additive Manufacturing

Additive manufacturing (AM) is a promising new technique with the potential to change conventional industrial manufacturing processes. This process has been used to manufacture ceramics having non-stochastic porous structures for the applications as scaffolds for biological applications, filters and lightweight materials ([Zocca et al., 2015](#)). AM also allows for the fabrication of porous architectures having complex shapes together with precisely-controlled pore dimensions, shapes and volume fractions, which cannot be achieved by any other technology currently used for the production of macro-porous bodies. However, the technologies that are suitable for the fabrication of fine porous structures have shortcomings when scaled up to generate large bulk parts and vice versa. Thus, methods that are well-suited to the fabrication of dense materials may have difficulties in producing highly porous, fine geometries. The AM researches on porous products have been so far substantially devoted to the shaping of biomedical scaffolds for tissue engineering, although the possibility of generating catalyst supports with a well reproducible geometric surface and optimized flow properties is gaining attention.

AM methods can be classified, according to ISO/ASTM 52900:2015, “Additive manufacturing – General principles – Terminology”. Sintered porous ceramic bodies are usually not prepared by AM, because that requires high temperature heating above 1200°C. Thus, AM has been generally utilized to prepare green bodies, followed by sintering. Among AM methods, binder jetting has been widely used to create porous green body. Binder jetting is especially applicable to the formation of porous ceramic structures. In this process, a solid structure is produced by the sequential deposition of layers of a flowable powder. Each layer of the powdered substrate material is spread out, after which the desired morphology is selectively inscribed using an ink-jet printing head that selectively deposits a liquid binder. This process is repeated until the object is complete, thus producing a final product that is completely contained in a powder bed from which it can be easily extracted and cleaned. Residual porosity (up to 50 vol%) is always present in the sintered body, due to the requirement of using coarse powders to enable particle flowing when generating each layer. An alternative process, powder bed fusion, a laser beam induces local densification of the powder either by direct sintering of the ceramic or by melting a binder phase mixed in with the ceramic powder. In order to obtain porous products, the binders within the powder must be thermally cured. One challenge associated with this process is that the direct laser sintering of ceramics is complicated by the poor resistance of ceramic materials to thermal shock. The direct deposition of ceramic slurries, i.e., material extrusion, is also an AM technology often used to fabricate porous structures. In such process, a viscous ceramic paste or preceramic polymer is extruded through a nozzle or orifice to produce a filament. The rheological properties of this paste or preceramic polymer are critical to preventing deformation or sagging, especially when the geometry includes spanning features, as in most porous components.

References

- Colombo, P., Bernardo, E., 2003. Macro- and micro-cellular porous ceramics from preceramic polymers. *Composites Science and Technology* 63 (16), 2353–2359.
- Fukasawa, T., Ando, M., Ohji, T., Kanzaki, S., 2001. Synthesis of porous ceramics with complex pore structure by freeze-dry processing. *Journal of the American Ceramic Society* 84 (1), 230–232.
- Fukushima, M., Nakata, M., Zhou, Y., Ohji, T., Yoshizawa, Y.-I., 2010. Fabrication and properties of ultra highly porous silicon carbide by the gelation–freezing method. *Journal of the European Ceramic Society* 30 (14), 2889–2896.
- Ohji, T., Fukushima, M., 2012. Macro-porous ceramics: Processing and properties. *International Materials Reviews* 57 (2), 115–131.
- Shimamura, A., Fukushima, M., Hotta, M., Ohji, T., Kondo, N., 2016. New approach for macro porous RB-SiC derived from SiC/Novolac-type phenolic composite. *Journal of the American Ceramic Society* 99 (2), 440–444.
- Zocca, A., Colombo, P., Gomes, C.M., Gunster, J., 2015. Additive manufacturing of ceramics: Issues, potentialities, and opportunities. *Journal of the American Ceramic Society* 98 (7), 1983–2001.

Porous Ceramics Including Fibrous Insulation, Structure and Properties of

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Introduction

For structural applications of brittle ceramic materials, the presence of porosity is generally considered problematic because the pores act as defects and crack initiation sites and degrade the mechanical reliability. However, there are many engineering applications, where the presence of pores can be advantageous, ranging from refractories, filters, membranes, absorbents, catalysts and catalyst supports to lightweight structural components and thermal insulators. While ceramic materials can exhibit useful intrinsic properties such as thermal and chemical stability, and excellent mechanical properties, the presence of porosity provides decreased density, additional surface area, thermal or electrical insulation, energy absorption, and fluid permeability. Porous materials can be described according to the average pore size, the pore size distribution, the volume fraction of pores (total porosity), and the degree of interconnectivity among the pores (ratio between open and closed pores). These morphological features affect all the properties of porous ceramics, such as density, mechanical strength, adsorption, permeability to fluids, and thermal/electrical insulations. Comprehensive reviews on macroporous ceramics, processing and properties have been written by Colombo (2006), Studart *et al.* (2006), and Ohji (2012).

This chapter focuses mainly on cellular ceramics, including fibrous insulation, and their structure and properties.

Structure and Properties of Highly Porous Ceramics

Fibrous Ceramics

Ceramic thermal fibrous insulators have been extensively utilized in the form of blankets, felts, or monoliths in high temperature furnaces and industrial plants, because their very high porosity and narrow fiber diameter reduce heat transfer. The performance and shape of the fibrous insulators can be freely changed depending on their flexibility. Fibers are usually produced by blowing of molten silicates or by the sol–gel route, via hydrolysis and condensation of alkoxides. Figure 1 shows a typical example of a fibrous insulator. Fibrous insulators generally possess very low thermal conductivities of around $0.1\text{--}0.2\text{ W mK}^{-1}$ or less. In the fibrous insulators, the solid conduction and radiation contributes to the effective thermal conductivity can be controlled by adjusting their microstructural characteristics, such as the fiber diameter, volume fraction of fibers, and packing density. The solid conduction in fibrous insulators can be affected by the conduction through the solid phase (fiber), and conduction from the solid phase to air (and vice versa). Thus, smaller fiber diameters with narrow transfer paths can decrease the thermal conduction. The solid conduction contributes to the total conductivity according to the volume fraction of the solid phase. The radiation transfer also contributes to the effective conductivity of an insulator, particularly at elevated temperature. Most of oxide ceramics are relatively transparent to wavelengths in the near infrared region, although the thermal radiation for oxide fibrous insulators can be intensively scattered by the effect of microstructural features such as the air–solid interfaces, the shape of the pores, and the fiber diameter in the insulators. Verschoor (1952) reported that, in the temperature range of $500\text{--}1200\text{ }^{\circ}\text{C}$, silica fibrous insulators with a fiber diameter of $1\text{--}3\text{ }\mu\text{m}$ exhibited lower thermal conductivity than those with a fiber diameter of $10\text{--}15\text{ }\mu\text{m}$, because of the effect of radiative scattering on the thermal conductivity at elevated temperature. However, at room temperature, there is a limited effect of radiative thermal transfer on the total conductivity. Although the thermal conductivity of silica fibrous insulators with porosity of 95–99 vol% was reported to be around 0.04 W mK^{-1} at room temperature, the radiation contribution is negligible.

Cellular Ceramics

A wide range of processing methods has been proposed for the production of cellular ceramics. Figure 2 shows various morphologies of cellular ceramics as examples. Each fabrication method results in a different morphology of the cellular architecture and different properties depending on the cell size, distribution, shape, and interconnection, the cell wall thickness, the volume fraction of pores as well as the composition used.

Figure 2(a) shows the morphology of partially sintered porous alumina. Particles of powder compact are bonded at the appropriate sintering temperature that should be lower than the sintering temperature used to prepare fully dense materials. The formation of thick and strong inter-particle necks can be achieved by employing adequate processing factors such as starting

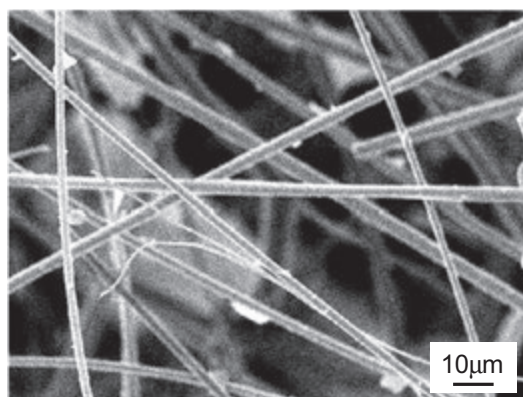


Figure 1 Structure of fibrous ceramics used as thermal insulation in industrial furnaces and plants.

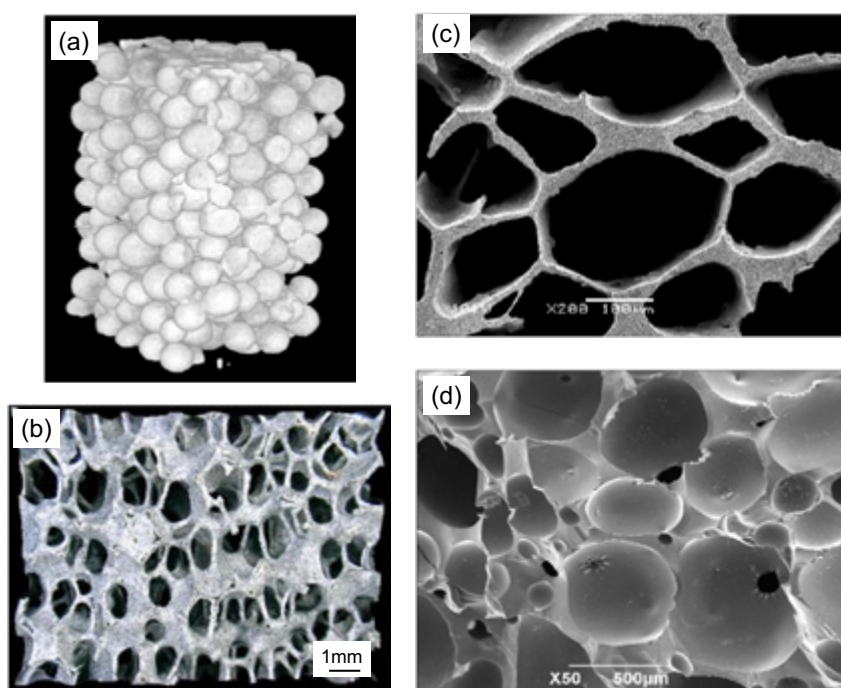


Figure 2 Structure of cellular ceramics prepared through (a) partial sintering, (b) replica templating, (c) gelation freezing (Reproduced with permission of Elsevier. All rights reserved.), and (d) direct foaming (Reproduced with permission of Elsevier. All rights reserved.).

particle size and size distribution, green density, and sintering conditions (the type and amount of sintering additives, temperature, time, atmosphere, pressure, etc.). Thus, a precise control of the initial or middle stage of sintering, occurring typically through surface diffusion, is required to manipulate the thickness of the inter-particle necks, because that affects the mechanical strength of the final products.

Ceramic foams, shown in **Figure 2(b)**, are typically manufactured by dip-coating a polymeric foam into a ceramic powder dispersed slurry or sol-gel derived precursor solution or a molten/liquid preceramic polymer, followed by burnout of the polymeric substrate and sintering (pyrolysis). This method is still the one mostly adopted by industry for the manufacturing of ceramic foams used as molten metal filters or burners. Concerning the replica template, a polymeric sponge, typically made of polyurethane, can be used, but bio-derived porous materials such as wood or paper can be also used to create a cellular structure. However, due to fact that struts can crack during the burn off the host substrates, the difficulty to create a homogeneous and defect-free ceramic particles coating on the template, and the presence of a void in the struts after the elimination of the template, the mechanical strength of these porous ceramics is quite limited (typically, the compression strength is not higher than 1 MPa). Thus, a great variety of approaches has been proposed to produce ceramic foams possessing improved mechanical properties using alternative processing methods. Cell size of the foams generally ranges from several tens of micrometers to millimeters.

Porosity can be created through the elimination of sacrificial fugitive additives as pore forming agents, mixed with ceramic raw particles or preceramic polymer, by burning out or evaporating the fugitive phase before or during sintering the particles or pyrolyzing the polymer, providing precise control on the average pore size distribution, with a wider range of cell size, typically ranging from several tens of nanometers to submillimeters, and amount of porosity. This method can be applied by itself or combining that with other fabrication routes. As sacrificial pore forming agents, polymer beads, organic fibers, carbon, natural organic matter, and liquids (water, gels, and emulsions) have been used. Polymethylmethacrylate (PMMA) beads have been frequently employed as sacrificial fugitives.

Another novel processing method, that enables the fabrication of unidirectional pore channels, is the freeze casting of a slurry or a gel body containing ceramic raw particles or ceramic precursors. The porous structure is templated by solidifying a solvent, typically water but tert-butyl alcohol and camphene can also be used, leading to unique morphologies such as lamellar or ellipsoidal or dendritic structures grown along the solidification direction. In this freezing process, porosity is created, after the freezing of the slurry or gel body, by sublimation by vacuum drying of the solvent crystals and subsequent sintering. This method allows to obtain very good mechanical properties (compressive strength) along the freezing direction, because the struts are surrounded by cells aligned parallel to freezing direction within the whole sample. A pioneering work in this field was carried out by Fukasawa *et al.* (2001). Fukushima *et al.* (2014) proposed the gelation freezing process. By applying this method under carefully controlled freezing conditions, uniformly arranged honeycomb-like structures with very high porosity (up to 98 vol%), comprised of micrometer-sized cells, can be prepared, as shown in Figure 2(c). The cellular components obtained possess substantially improved fluid permeability, comparable to the ideal permeability computed by the capillary model, and very high mechanical strength due to micrometer-sized honeycomb structures without any defects. Deville *et al.* (2007), and Devilles (2008) systematically discussed the solid/liquid interface kinetics which control the morphology of ice-derived structures. These cellular materials with micrometer-sized cell size could be used for catalyst support, filtration, thermal insulation applications, biomedical applications as well as lightweight components.

Direct foaming consists of the introduction of gas into a liquid (slurry or sol solution) or softened polymer (molten preceramic polymer and thermoplastic binder), as shown in Figure 2(d). Gas can be introduced by various routes, such as mechanical frothing (mixing to generate bubbles), phase separation (segregation of a dissolved gas), in situ gas generation by a chemical reaction, thermal decomposition of a blowing agent, or the evaporation of a solvent. Various methods to stabilize the bubbles have been proposed to create fine and controlled pores in the final porous bodies, including use of surfactants, evaporation of emulsified alkane droplets, and use of surface-modified particles to prevent Ostwald ripening and coalescence among gas bubbles contained in the suspension, which would lead to an inhomogeneous pore size distribution or the collapse of the liquid foam.

The novel processing routes discussed above lead to cellular ceramics possessing improved mechanical properties. Several models have been proposed, particularly by Ashby *et al.* (1983) and Gibson (2005), to predict the mechanical response of cellular ceramics as a function of relative density (or the amount of porosity), according to different microstructural models for porous components with open cells, closed cells, or honeycomb-like structure.

References

- Ashby, M.F., Medalist, R.F.M., 1983. *Metall. Trans. A* 14, 1755–1769.
- Colombo, P., 2006. *Phil. Trans. R. Soc. A* 364, 109–124.
- Deville, S., 2008. *Adv. Eng. Mater.* 10, 155–169.
- Deville, S., Saiz, E., Tomsia, A.P., 2007. *Acta. Mater.* 55, 1965–1974.
- Fukasawa, T., Ando, M., Ohji, T., Kanzaki, S., 2001. *J. Am. Ceram. Soc.* 84, 230–232.
- Fukushima, M., Yoshizawa, Y., Ohji, T., 2014. *Adv. Eng. Mater.* 16, 607–620.
- Gibson, L.J., 2005. *J. Biomech.* 38, 377–399.
- Ohji, T., Fukushima, M., 2012. *Int. Mater. Rev.* 57(2), 115–131.
- Stuart, A.R., Gonzenbach, U.T., Tervoort, E., Gauckler, L.J., 2006. *J. Am. Ceram. Soc.* 89, 1771–1789.
- Verschoor, J.D., Greebler, P., Manville, N.J., 1952. *Trans. Am. Soc. Mech. Eng.* 74, 961–968.

Control of the Microstructure in Ceramics

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Introduction

The microstructure of ceramics can be defined as the arrangement of grains (individual crystals) and pores of different size and shape and occasionally of a crystalline or vitreous intergranular phase. This microstructure is generated at the end of the densification process from a powder compact following heat treatment. No microstructure is perfect and homogeneous and it is strongly dependent on powder characteristics and sintering mechanism. The matter transport to reduce the porosity of a powder compact occurs at high temperature by:

- (1) diffusion of atoms through the crystal lattice (D_l), along the surface (D_s) or the grain boundaries (D_b) in the absence of liquid phase,
- (2) dissolution-diffusion-precipitation mechanisms in the presence of a liquid phase, or
- (3) by viscous flow in the case of a large amount of liquid phase.

In all cases, there is a competition between the densification⁷⁷ phenomenon and grain growth which strongly impacts the final grain size. As most of the ceramic properties, particularly sensitive properties such as mechanical resistance or electric conductivity depend on microstructure, it is therefore crucial to control all the steps leading to the microstructural development.

Microstructure can be controlled by optimization of each of the fabrication process steps:

- (1) careful choice of raw materials particularly taking into account the chemical purity and particle size and shape,
- (2) selection of the appropriate shaping technology with optimized parameters, and
- (3) optimization of the temperature–time schedule and furnace atmosphere during sintering (air, O₂–Ar, Ar, N₂, water,...).

As examples, Fig. 1 illustrates the appearance of microstructural defects:

- (1) porosity induced by the presence of an uncrushed alumina granule remaining after pressing step due to non-optimized slurry for the spray-drying operation,
- (2) exaggerated grain growth due to non-optimized sintering conditions.

In addition, the thermal treatment can be modified, for example using:

- (1) pressure assisted methods such as Hot Pressing, HIP, Post-sintering HIP treatments, where the driving force includes an extra parameter related to external pressure ($2\gamma/r + P_{\text{ext}}$),
- (2) methods such as Spark Plasma Sintering and Flash Sintering where the application of an electrical field induces increases in densification rates, and
- (3) microwaves, a process which involves more homogeneous heat source distribution.

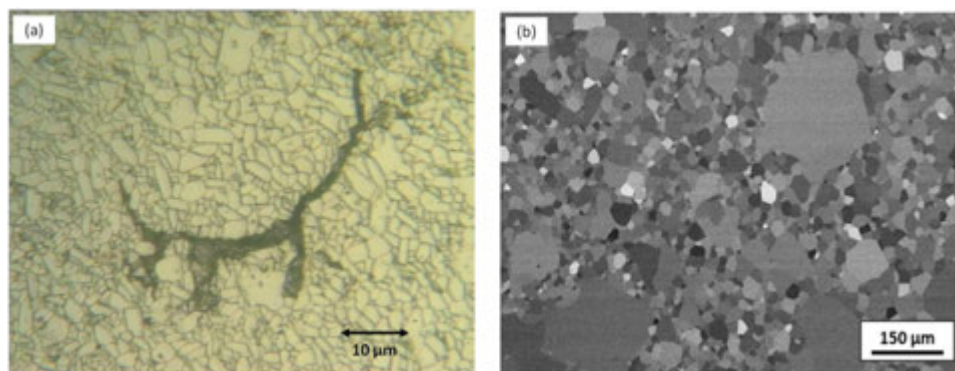


Fig. 1 Examples of microstructural defects. (a) porosity induced by the presence of an un-crushed alumina granule remaining after pressing step, (b) exaggerated grain growth in spinel due to non-optimized sintering conditions. (a) Courtesy: Cambier, F., 2011. European Ceramic Society Stuijts Award presentation. Stockholm (private communication). (b) Adapted from Gajdowski, C., 2018. Elaboration de spinelle MgAl₂O₄ transparent par frittage naturel et post-HIP pour des applications en protections balistiques. France: Université Polytechnique Hauts-de-France/ Université de Valenciennes et du Hainaut Cambrésis, (PhD Thesis).

The purpose of this chapter is to describe the various strategies allowing a better control of the microstructure for ceramic materials in order to counteract the presence of defects.

Microstructural Development During Ceramic Processing

The fabrication of ceramic materials commonly starts from a compacted powder, which is converted into a dense solid by heat treatment.

Most green bodies fabricated by various shaping techniques possess relative densities between 50% and 60% which means that at least 40 vol% of porosity has to be eliminated during sintering and densification of the part is accompanied by a large shrinkage (decrease of dimensions) of about 35–40 vol% (i.e., 18–20 linear%).

The densification driving force ($2\gamma/r$) activated by temperature can be (1) macroscopically viewed as the decrease of free energy as solid-vapor interfaces are replaced by solid-solid interfaces and (2) microscopically viewed as the free energy (pressure) difference across a curved grain boundary. In the absence of liquid phase, the matter transfer occurs by atom diffusion through different paths: lattice, grain surface, grain-boundary or vaporization and condensation on grain surfaces. Only diffusion through the lattice and grain-boundaries leads to shrinkage of the powder compact although the surface phenomena induce changes in particle shape and grain growth without shrinkage.

The densification occurs within 3 stages with accompanying changes in pore content and geometry as shown in Fig. 2:

- (1) initial stage, during which necks are growing at contact points between particles,
- (2) intermediate stage (65%–90% density), during which pores become cylindrically shaped with interconnections, so-called “open porosity”,
- (3) final stage (90%–100% density), during which pores become more spherical and isolated: “closed porosity”.

During this last stage, grain growth becomes predominant compared with densification because of the driving force decrease. The larger grains grow at the expense of the smaller ones. This phenomenon has been well observed by combined HT-ESEM/dilatometry by Clavier *et al.* (2013) for ThO₂ powders (Fig. 3).

As shown in Fig. 3, the grain growth rate becomes predominant versus densification rate during the last stage of sintering and the microstructure shows a polycrystalline ceramic with a dispersion of isolated pores located at the grain boundaries. The pore mobility is as slow as its size is large.

Two hypotheses are invoked to explain the phenomena:

- (1) the pore stays immobile and the grain boundary overcomes it so that the pore becomes isolated. In this case, further pore elimination becomes very difficult.
- (2) the pore can move with the grain boundary as illustrated in Fig. 4. The pore surface located towards the center of curvature of the grain boundary possesses a larger radius of curvature than that of the other face which causes atom flow from the back surface to the front one. This atom flow can occur by lattice, surface or vapor diffusion and the pore moves towards the center of curvature of the boundary.

When the pore is mobile, the boundary migration rate is controlled either by its intrinsic mobility or by the pore mobility. If the boundary moves faster than the pores, a separation between the pore and boundary occurs. As illustrated in Fig. 5, which shows the relationship between grain size and pore size when the atom flow is managed by surface diffusion, this separation phenomenon occurs in the region above the domain where the grain growth is controlled by the pore mobility (slope +1) and below the domain where the grain growth is controlled by the boundary mobility (slope +3). The intersection of the 2 straight lines corresponds to the critical grain size above which a pore/ boundary separation can occur (Fig. 5).

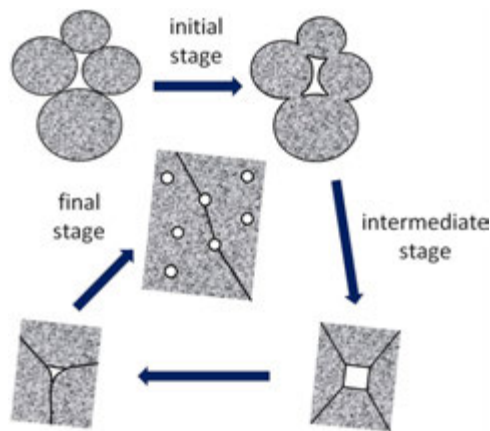


Fig. 2 Schematic illustration of grain compaction and pore shape changes during sintering.

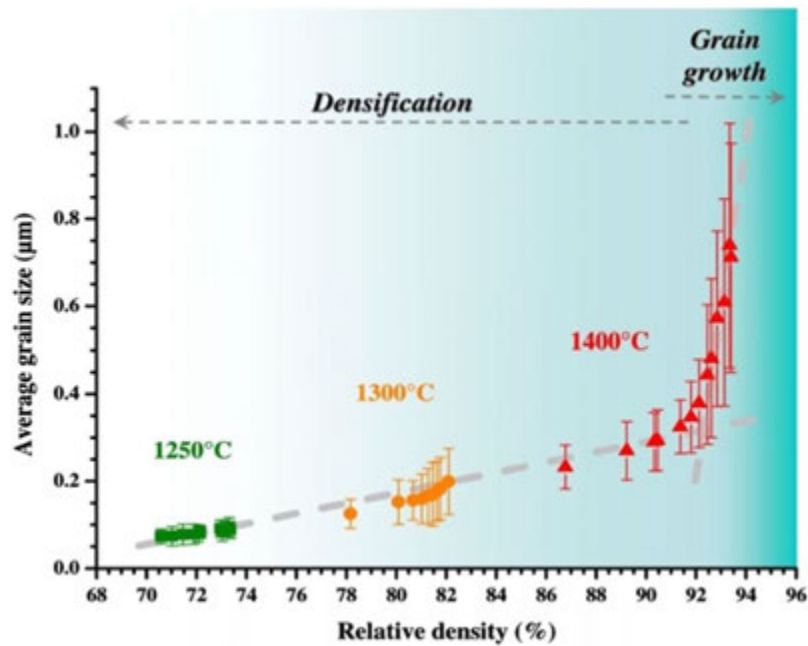


Fig. 3 Sintering trajectory of ThO_2 obtained from combined HT-ESEM/dilatometer. Adapted from Clavier, N., Podor, R., Deliere, L., Ravau, J., Dacheux, N., 2013. Combining in situ HT-ESEM observations and dilatometry: An original and fast way to the sintering map of ThO_2 . *Materials Chemistry and Physics* 137 (3), 742–749.

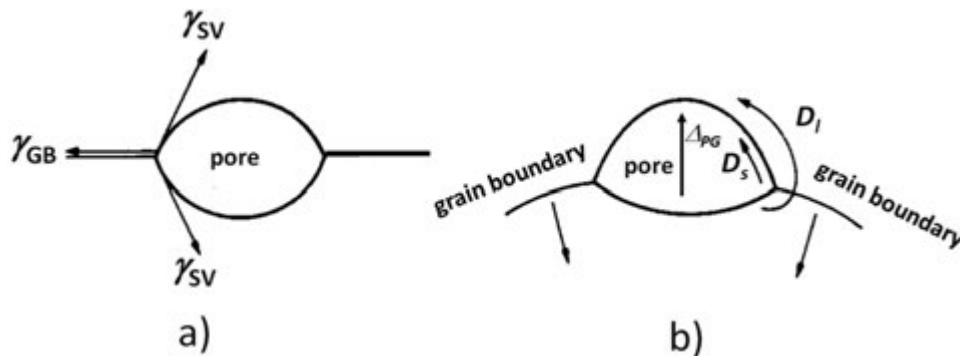


Fig. 4 Morphology of (a) an isolated pore located at grain boundary and (b) a pore at grain boundary migrating to its center of curvature. Adapted from Rahaman, M.N., 1995. *Ceramic Processing and Sintering*. Marcel Dekker Inc.

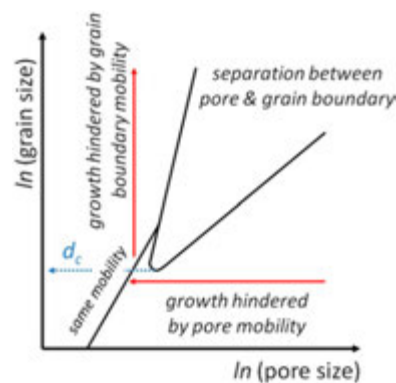


Fig. 5 Diagram showing the various possible interactions between pores and grain boundaries in the case of surface diffusion and definition of a critical grain size above which a pore/boundary separation can occur. Adapted from Rahaman, M.N., 1995. *Ceramic Processing and Sintering*. Marcel Dekker Inc.

The same types of map can be constructed for the other pore mobility mechanisms like volume diffusion or vapor diffusion and present the same configuration. These maps are beneficial in determining the optimal trajectory to avoid the pore-boundary separation. Therefore, it is necessary to decrease the pore size before grain growth starts. For that, several strategies can be adopted that are described in the following paragraphs.

In presence of liquid phase, the capillary pressure results in densification via a dissolution-diffusion-precipitation mechanism. In such a case, grain growth can be controlled either by the dissolution step or by the diffusion step. If the grain growth kinetics are controlled by the dissolution step, it will depend on various parameters such as atom volume, temperature, solid/liquid surface energy, molar content of solute in the liquid phase and atom transfer rate between crystal and liquid. If the kinetics are controlled by the diffusion step, it will depend on atom diffusion coefficient in the liquid.

As this grain growth phenomenon can be deleterious to some ceramic properties, it is necessary to develop different ways of achieving high densification rates by limiting grain growth during sintering.

Strategies to Control Microstructural Development

Choice of Powder Characteristics

It should be noted that the most important parameter influencing densification and grain growth is the powder characteristics and in particular its mean size and grain size distribution. Thus, narrow grain size distribution is preferable for obtaining a high density. A theoretical approach carried out by M.I.T. (Barringer and Bowen, 1982) showed the existence of a limiting density value as a function of the grain diameter distribution expressed as the ratio: D_{max}/D_{aver} . This ratio would be ≤ 2 to avoid the pore separation from grain boundary as illustrated in Fig. 6.

This was experimentally confirmed by the work of Barringer and Bowen (1982) for a submicron TiO_2 powder which was fully sintered at 300K below the temperature normally required for a powder with the usual grain size distribution.

The influence of different crystallographic phases in a powder on sintering and subsequent mechanical properties is well illustrated by the microstructural development of silicon nitride ceramics. The strong covalent bonds impede pressureless sintering due to low self-diffusivity; consequently oxide dopants have to be added which allows formation of an oxynitride liquid phase leading to densification at 1750°C, below the silicon nitride decomposition temperature. The mechanism of dissolution of the predominant α phase in the liquid phase followed by diffusion and precipitation of the β phase onto β - Si_3N_4 seeds already present in the initial powder as the minor constituent is illustrated in Fig. 7. The resulting microstructure, which consists of elongated and

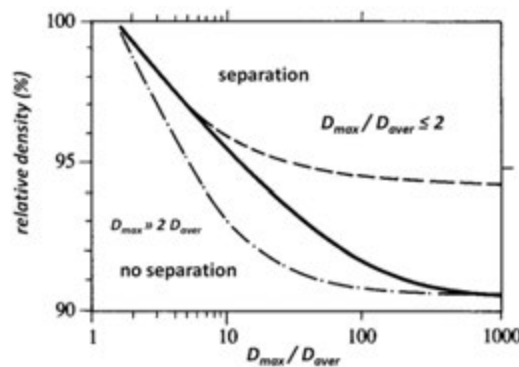


Fig. 6 Maximal density values for a powder versus maximal grain diameter size to mean grain diameter ratio. Adapted from Rahaman, M.N., 1995. Ceramic Processing and Sintering. Marcel Dekker Inc.

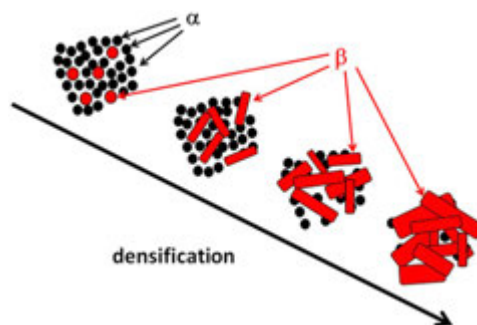


Fig. 7 Morphological change of silicon nitride grains by solution-diffusion-precipitation during liquid phase sintering.

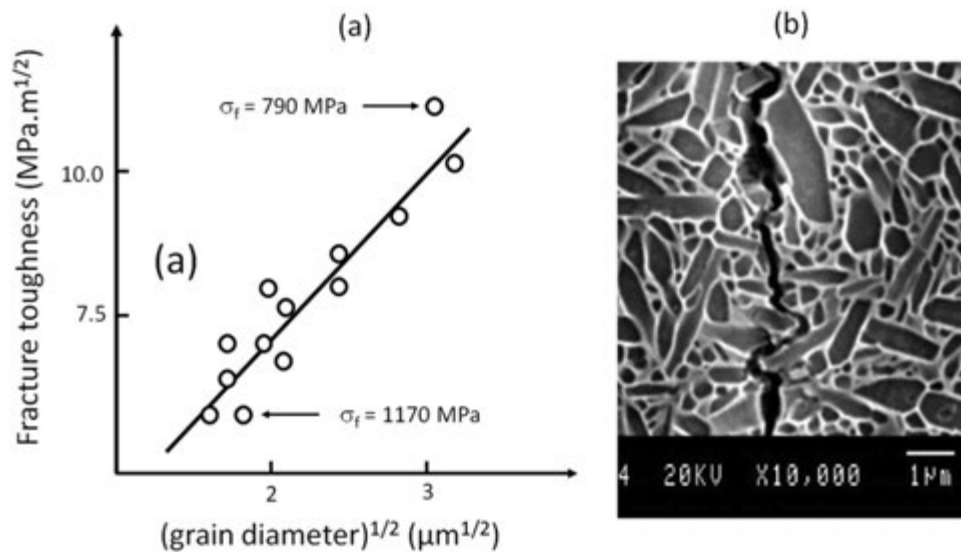


Fig. 8 (a) Increase of toughness versus silicon nitride grain diameter, (b) intergranular crack path through a silicon nitride. Adapted from: (a) Kawashima, T., Okamoto, H., Yamamoto, H., Kitamura, A., 1991. Grain size dependence of the fracture toughness of silicon nitride ceramics. *Journal of the Ceramic Society of Japan* 99, 1–4. (b) Hampshire, S., Pomeroy, M.J., 2012a. Grain boundary glasses in silicon nitride: A review of chemistry, properties and crystallization. *Journal of the European Ceramic Society* 32, 1925–1932. Hampshire, S., Pomeroy, M.J., 2012b. SiAlON bulk glasses and their role in silicon nitride grain boundaries: composition-structure-property relationships. *Journal of the Korean Ceramic Society* 49, 301–307.

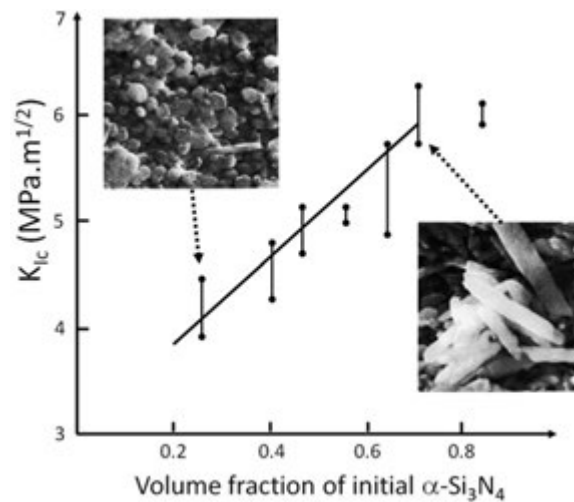


Fig. 9 Influence of the initial α -Si₃N₄ content in silicon nitride powder on the toughness of the sintered β -Si₃N₄ ceramic. Adapted from Lange, F.F., 1979. Fracture toughness of Si₃N₄ as a function of the initial α -phase content. *Journal of the American Ceramic Society - Discussions and Notes* 62 (7–8), 428–430. The microstructures are from Cambier, F., Leriche, A., Gilbert, E., Brook, R.J., Riley, F.L., 1990. Silicon nitride: Relations between powder characteristics and sinterability. In: Freer, R. (Ed.), *The Physics and Chemistry of Carbides, Nitrides and Borides*. NATO-ARW Series. Kluwer Academic Publishers, pp. 13–28.

crosslinked β -Si₃N₄ grains with an amorphous oxynitride intergranular phase, is favorable for high ceramic toughness (up to ~ 11 MPa $\sqrt{m}$), mainly by crack bridging and crack deviation mechanisms (Fig. 8). The development of this favorable microstructure depends on the α -to- β conversion rate which is a function of the content of β phase seeds in the initial powder as reported in Fig. 9

Choice of Optimal Sintering Parameters: Temperature, Time, Heating Rate

In Section “Microstructural Development during Ceramic Processing”, it was explained that temperature favors the densification rate but also that the concurrent grain growth phenomenon becomes predominant during the final stage of densification. A close control of the temperature cycle is therefore needed to obtain the optimum microstructure. Several sintering methods are based on heating rate control.

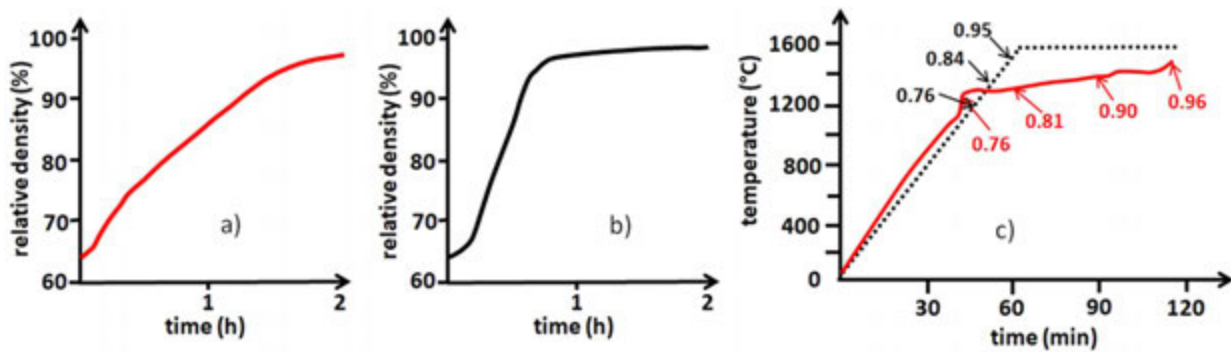


Fig. 10 Density-time curve (a) during controlled rate sintering as suggested by Palmour III, H., (b) during conventional sintering. (c) Temperature-time dependence with relative densities. Adapted from Haussonne, J.M., Carry, C., Bowen, P., Barton, J., 2005. *Céramiques et verres. Principes et techniques d'élaboration; Traité des Matériaux*. (16), [Presses polytechniques et universitaires romandes]. Palmour III, H., Huckabee, M.L., Hare, T.M., 1977. Rate controlled sintering, principles and practice in sintering. New developments. In: Ristic, N.N. (Ed.) *Proceedings of the 4th Round Table Conference on Sintering*, pp. 46–66. Dubrovnik.

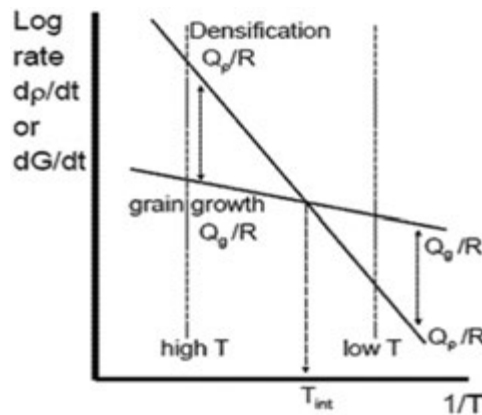


Fig. 11 Densification rate or grain growth rate as a function of temperature. Adapted from Harmer, M.P., Brook, R.J., 1981. Fast firing – Microstructural benefits. *Transactions & Journal of the British Ceramic Society* 80, 147–149.

Controlled rate sintering

This technique was proposed by Palmour III and Johnson (1967). It allows optimization of grain size and pore elimination by maintaining the densification rate constant at relative densities greater than 0.75 to favor grain boundary diffusion, D_b , rather than surface diffusion, D_s which is deleterious to shrinkage (Fig. 10).

Fast sintering

The objectives of the following methods are to heat a powder compact at much higher heating rates than in conventional sintering in order to reduce the dwell time during the low temperature range which favors densification with minimal grain growth.

The first method, called “Fast Firing”, was proposed by Harmer and Brook (1981) as a sintering method in order to enhance densification and suppress grain growth and consists of the introduction of green samples rapidly into the hot zone of a furnace so that the samples attain higher temperatures very quickly where the activation energy for densification, Q_p , is higher than Q_g , the activation energy for grain growth as shown in Fig. 11. Fast firing thus allows a powder compact to reach temperatures above an intermediate temperature, T_{int} , very quickly thus minimizing grain coarsening during heating.

Unfortunately, this technique has to be restricted to small-sized samples because of the large thermal gradients generated by fast heating and cooling. For instance, small disks of barium titanate capacitors can be sintered by this method.

Fig. 12 illustrates the finer microstructure obtained for fast fired (FF) yttria doped zirconia ceramics (YSZ) compared to conventional sintering (CS). CS samples presented larger grain sizes by a factor of ~ 2 to ~ 4 in comparison with the initial 3YSZ (3 mol.% Y_2O_3) and 8YSZ (8 mol.% Y_2O_3) powders. Conversely, the FF method significantly suppressed grain growth with a growth factor of ~ 1 . (Gómez et al., 2016).

The second method is to use microwave assisted firing techniques that allows direct coupling of the microwaves with electric dipoles within the ceramic which results in high heating rates and therefore avoids the lower temperature region where the rate of grain growth is higher than the rate of densification (Binner and Vaidhyanathan, 2008). Full density can be achieved within a few

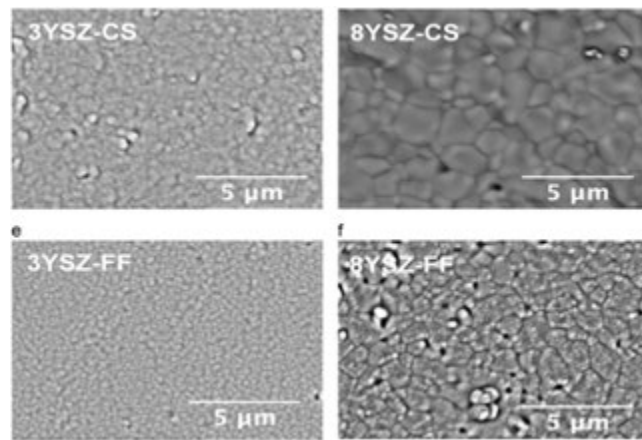


Fig. 12 Scanning electron micrographs of yttria doped zirconia ceramics (YSZ) sintered by conventional sintering (CS) and by fast firing (FF). Adapted from Gómez, S.Y., DaSilva, A.L., Gouvêa, D., Castro, R.H.R., Hotza, D., 2016. Nanocrystalline yttria-doped zirconia sintered by fast firing. *Materials Letters* 166, 196–200.

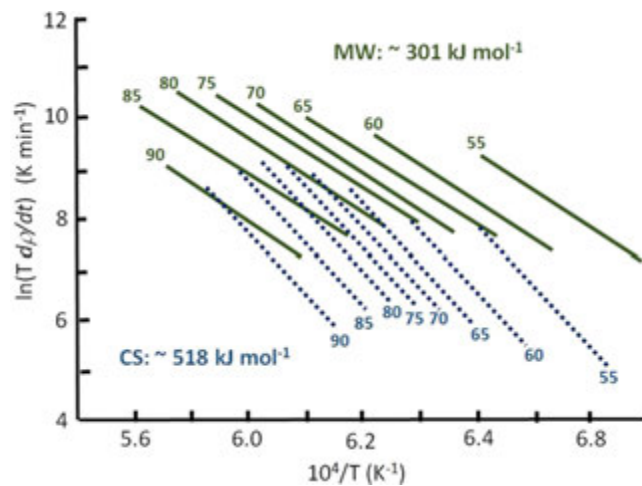


Fig. 13 Arrhenius-type plots of densification rate in 55 to 90% relative density range, measured during conventional (CS) sintering and direct microwave (MW) sintering of alumina powder compacts at various heating rates (from 1.6 to 158°C/min). Adapted from Croquesel, J., Bouvard, D., Chaix, J.M., *et al.*, 2016. Direct microwave sintering of pure alumina in a single mode cavity: Grain size and phase transformation effects. *Acta Materialia* 116, 53–62.

minutes. Croquesel *et al.* (2016) have shown that the use of microwaves to sinter alumina powder compacts results also in a significant decrease of the densification activation energy from $518 \pm 18 \text{ kJ mol}^{-1}$ for conventional heating to $301 \pm 14 \text{ kJ mol}^{-1}$ which proves the existence of a “microwave effect” (Fig. 13).

Two-step sintering (TSS)

This technique exploits the difference in kinetics between grain boundary diffusion leading to elimination of porosity and grain boundary migration responsible for grain growth (Chen and Wang, 2000). There are different ways to apply the two step sintering method. The first one was developed by Chu *et al.* (1991) and consisted of a first stage at a relatively low temperature, over a long period of time, to perform pre-coarsening of grains to achieve a uniform grain size distribution; this is followed by a second stage at higher temperature to finalize the densification (Fig. 14). The technique was applied by Lin *et al.* (1997) for microstructural refinement of alumina with a pre-coarsening step at 800°C for 50 h followed by a second dwell at 1450°C. In normal direct sintering, smaller particles densify faster resulting in uneven pore size distribution which leads to non-uniform grain size distribution in the later stages. In TSS, pore channels become smoother after pre-coarsening and the longer time at lower temperature allows smaller grain sizes with narrower grain size distribution which can be explained by minimization of differential densification and resulting delay of the pore channel closure to achieve higher density. The TSS technique was also applied to silicon nitride ceramics without using β -Si₃N₄ seeds. The first step allows the α -to- β phase transformation without densification whilst the second step promotes densification and grain growth (Kim *et al.*, 2002).

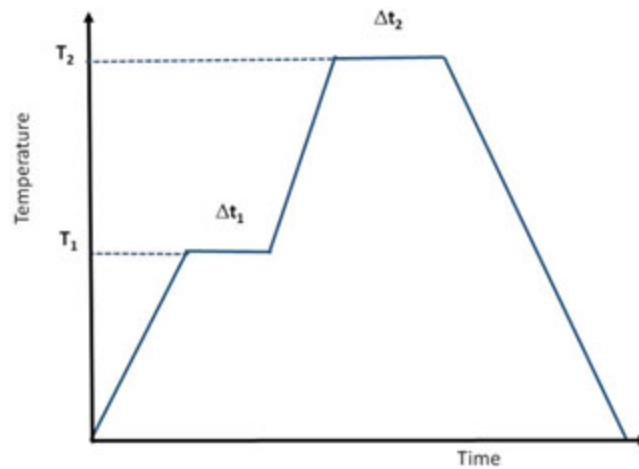


Fig. 14 Schematic of a typical two-step sintering schedule. As used by Chu, M.-Y., De Jonghe, L., Lin, M.F.K., Lin, F.J.T., 1991. Precoarsening to improve microstructure and sintering of powder compacts. *Journal of the American Ceramic Society* 74 (11), 2902–2911. Chen, L.W., Wang, X.H., 2000. Sintering dense nanocrystalline oxide without final stage grain growth. *Nature* 404, 168–171.

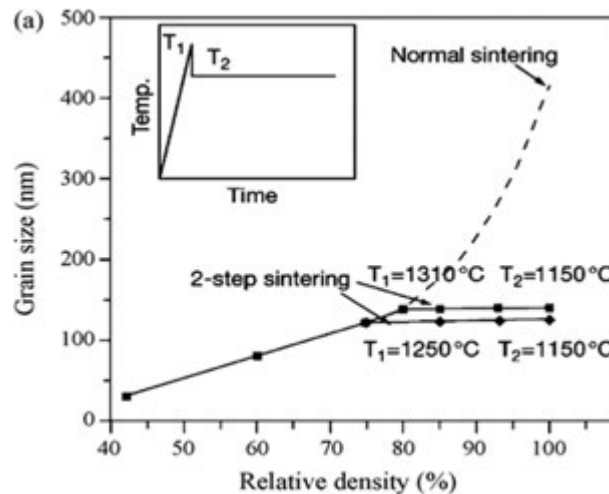


Fig. 15 Grain size versus density of Y_2O_3 as a result of TSS. After Lóh, N.J., Simão, L., Jiusti, J., De Noni Jr., A., Montedo, O.R.K., 2017. Effect of temperature and holding time on the densification of alumina obtained by two-step sintering. *Ceramics International* 43, 8269–8275.

Chen and Wang (2000) changed radically the concept of TSS by inverting the temperature dwells. In their work, the ceramic body (Y_2O_3) was rapidly subjected to a high temperature for a short time and was subsequently cooled and kept at a lower temperature until densification was complete (Fig. 15). Fig. 15 shows the results of applying this inverted temperature TSS approach to a study of densification of Y_2O_3 . It is clear that almost no grain growth occurs during the second stage of the process compared with normal sintering (Lóh *et al.*, 2016).

The microstructure of an alumina powder obtained using the TSS method is compared with one conventionally sintered (C) in Fig. 16. This illustrates very well the achievement of full density without grain growth in the case of TSS (Lóh *et al.*, 2017).

Pressure and/or Electric Field Assisted Sintering

The idea is to increase the driving force for densification ($2\gamma/r$) which arises from free energy differences across a curved grain boundary. This may be estimated at around 1–2 MPa and by adding external pressure ($2\gamma/r + P_{\text{ext}}$), densification is enhanced by modifying the pore stability conditions allowing the elimination of smaller sized pores. Several methods such as hot pressing, hot isostatic pressing and spark plasma sintering obey this principle.

Hot pressing (HP)

Hot pressing involves the application of a uniaxial pressure through a simple shaped die. The use of such an applied pressure (10–30 MPa) at the sintering temperature increases the densification rate and the ability to reach near-theoretical density in a

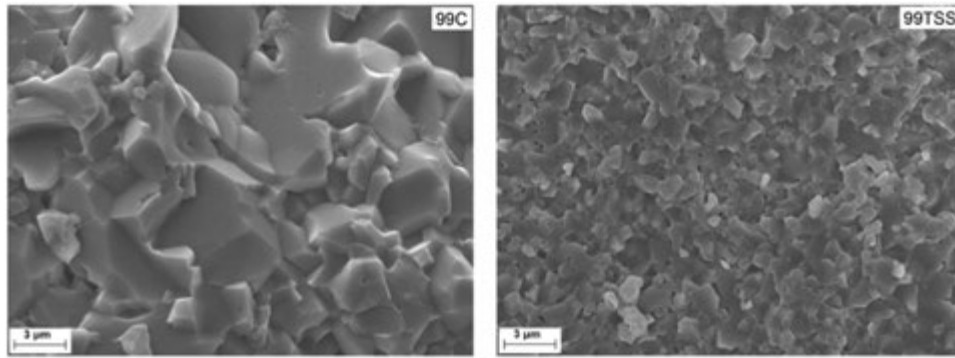


Fig. 16 SEM observations of microstructures of pure (> 99.7%) alumina powders densified up to 99% relative density by conventional sintering (C) at 1600°C for 10 h holding time, and by two-step sintering (TSS) $T_1 = 1450^\circ\text{C}$, $t_1 = 5$ min, $T_2 = 1500^\circ\text{C}$, $t_2 = 4$ h. Adapted from Lóh, N.J., Simão, L., Jiuisti, J., De Noni Jr., A., Montedo, O.R.K., 2017. Effect of temperature and holding time on the densification of alumina obtained by two-step sintering. *Ceramics International* 43, 8269–8275.

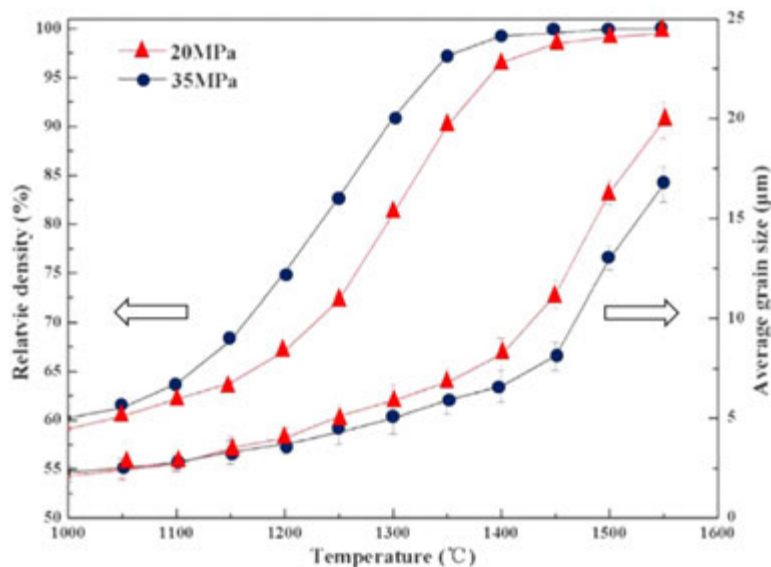


Fig. 17 Changes in relative density and grain size of hot pressed MgO ceramics with sintering temperature under 20 and 35 MPa. Adapted from Kingery, W.D., Woulbroun, J.M., Charvat, F.R., 1963. Effects of applied pressure on densification during sintering in the presence of a liquid phase. *Journal of the American Ceramic Society* 46, 391–395.

reasonable time. It is generally considered that several simultaneous mechanisms contribute to densification during hot-pressing. As well as diffusion, enhanced by the applied pressure, grain-boundary sliding and plastic flow have some effect. A significant grain size reduction is obtained by this method, as illustrated in Fig. 17 which shows the changes in relative density and grain size of MgO ceramics with temperature when hot pressed under different pressures. With a liquid phase present, the applied pressure is thought to be merely additive to the capillary pressure (Kingery *et al.*, 1963).

Hot isostatic pressing (HIP)

Hot isostatic pressing (HIP) combines high temperature (up to 2200°C) and a gas pressure (200–500 MPa), which is uniformly applied to the powder compact in all directions, usually through an impermeable membrane to encapsulate the ceramic component. Almost full density with no open porosity can also be achieved by HIP directly without encapsulation. This technique allows theoretical density to be reached with limited grain growth where this may not be possible by conventional pressureless sintering.

As an example, post sintering treatment by HIP (referred to as post-HIP) is currently used to fully eliminate residual porosity during fabrication of transparent ceramic parts. Fig. 18 shows the transparency obtained when the porosity is completely eliminated by post-HIP treatment.

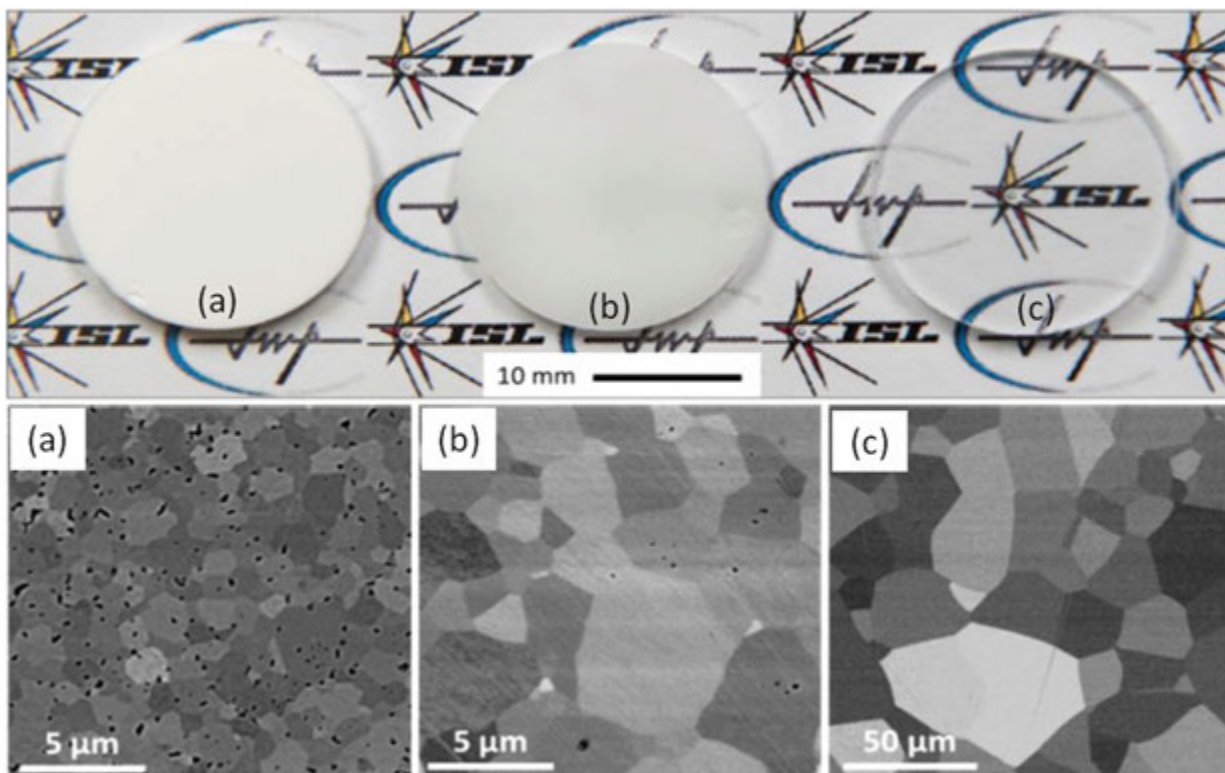


Fig. 18 First row: Visual aspect of disks, and Second row: SEM micrographs of MgAl_2O_4 spinel after (a) pressureless sintering, at 1500°C for 2 h, (b) after post-HIP at 1500°C for 10 h, and (c) after post-HIP at 1800°C for 1 h. Adapted from Gajdowski, C., Böhmeler, J., Lorgouilloux, Y., *et al.*, 2017. Influence of post-HIP temperature on microstructural and optical properties of pure MgAl_2O_4 spinel: From opaque to transparent ceramics. *Journal of the European Ceramic Society* 37, 5347–5351.

Spark plasma sintering (SPS)

More recently, electrical field assisted sintering techniques have been developed. Spark plasma sintering (SPS—**Fig. 19(a)**), also known as pulse electric current sintering or field assisted sintering technique (FAST), uses an electrically conducting pressure die (graphite) containing the green powder compact which is then subject to applied pressure and a pulsed electric current (Nygren and Shen, 2003). The die provides heat externally to the powder compact, but, if the ceramic has sufficient electrical conductivity, heat is also generated internally which leads to rapid heating rates in the range $100\text{--}1000^\circ\text{C min}^{-1}$. This enhances material diffusion and allows full density to be achieved with limited grain growth at comparatively low sintering temperatures, typically a few hundred degrees lower than in normal hot pressing (HP) after very short holding times (a few minutes).

Fig. 19(b) shows the relative densities obtained for submicron pure ($>99.7\%$) alumina powder sintered at different heating rates using SPS (FAST), Resistive Hot-pressing (HP) and Inductive Hot-pressing (HPind) techniques. As can be noted, densities are between 85% and 98%, after 6 min dwell time at 1600°C , under 16 MPa. Such densities were achieved by SPS depending on heating rate whereas densities of only 70% were achieved by HP under similar conditions.

The positive effect of current application on densification could be due to a number of factors:

- (1) the enhancement of surface phenomena like surface diffusion which favors neck formation explaining low temperature “advantage”,
- (2) the electromigration observed in conductive materials, or
- (3) the generation of charges at the particle surfaces due to impurities in the powder.

Fig. 20 compares grain size as a function of relative density for the same submicron pure ($>99.7\%$) alumina powder as in **Fig. 19** sintered using SPS, HP (resistive) and HPind (Inductive). Grain growth only becomes predominant once relative density reaches around 98% and smaller grain size is obtained by SPS during this last stage of densification compared with HP.

Flash sintering (FLASH)

Flash sintering involves heating a ceramic powder compact in a conventional sintering furnace and simultaneously applying a dc or ac electric field. The green sample, often in a “dog-bone” shape, is attached to two platinum electrodes allowing the passage of current. At high fields, the specimens sinter to high densities almost instantaneously above a critical temperature, hence the term Flash Sintering as used by Raj R. (Raj *et al.*, 2011; Yoshida *et al.*, 2014; Jesus *et al.*, 2016; Mishra *et al.*, 2020). In some of the first

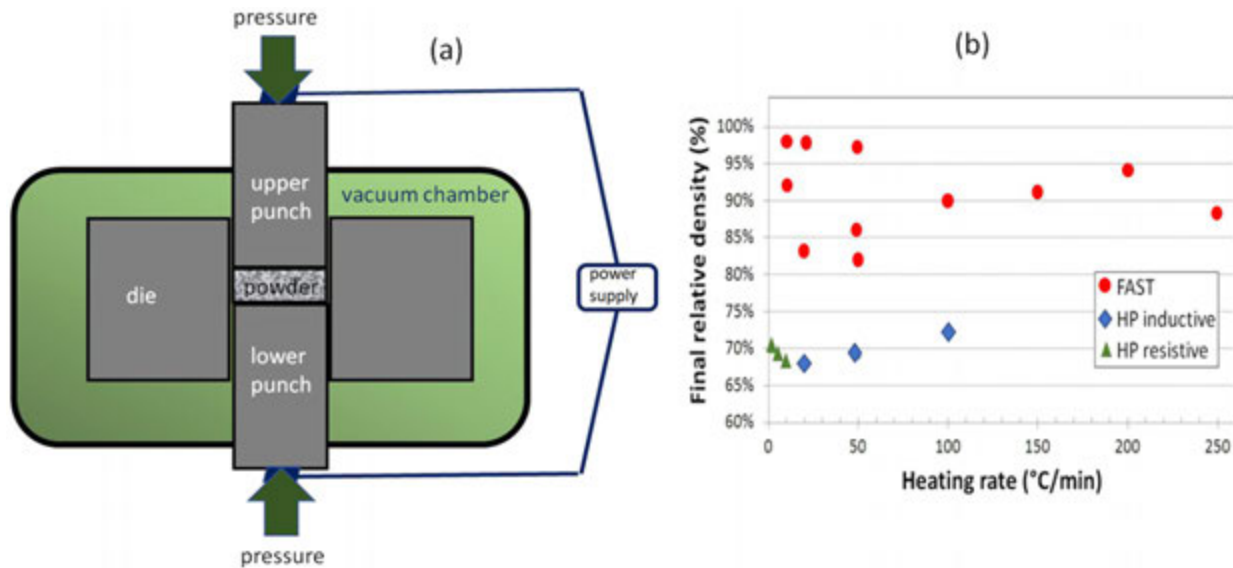


Fig. 19 (a) schematic of a SPS equipment (b) Comparison of final relative densities obtained for alumina ceramics sintered at different heating rates using SPS (FAST), Resistive Hot-pressing (HP) and Inductive Hot-pressing (HPind) techniques. Adapted from Demuynck, M., 2011. Spark plasma sintering (SPS). Evaluation critique d'une methode de frittage rapide et de son applicabilité aux céramiques techniques et composites. Belgium: Université Catholique de Louvain, [PhD Thesis]. Demuynck, M., Erauw, J.P., Van der Biest, O., Delannay, F., Cambier, F., 2012. Densification of alumina by SPS and HP: A comparative study. Journal of the European Ceramic Society 32 (9), 1957–1964.

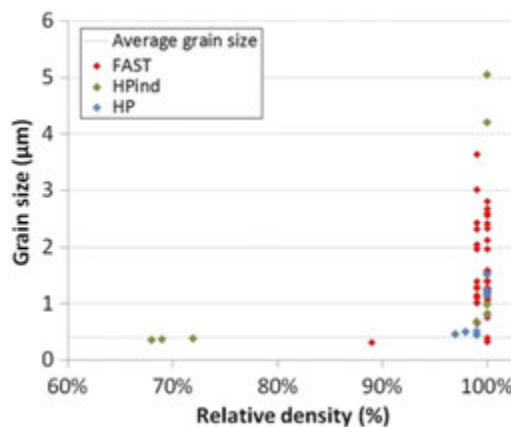


Fig. 20 Grain size versus density for alumina ceramics sintered using SPS (FAST), Resistive Hot-pressing (HP) and Inductive Hot-pressing (HPind) techniques. Adapted from Demuynck, M., Erauw, J.P., Van der Biest, O., Delannay, F., Cambier, F., 2012. Densification of alumina by SPS and HP: A comparative study. Journal of the European Ceramic Society 32 (9), 1957–1964.

experiments (Cologna *et al.*, 2010) yttria-stabilized zirconia was sintered in a few seconds at $\sim 850^\circ\text{C}$ to full density, starting from a green density of 50%, by the application of a dc electric field. Normally, a temperature of 1450°C is required over several hours to complete the densification. This can be explained by local Joule heating at grain boundaries, which promotes grain-boundary diffusion (a kinetic effect), and at the same time hinders grain growth (a thermodynamic effect). Several oxides have been sintered using this technique such as cobalt-manganese spinel, MgO-doped alumina, and cubic and tetragonal zirconia but the fundamental mechanism of the very rapid mass transport involved remains obscure.

Fig. 21 compares the linear shrinkage for conventional and several electric fields assisted sintering experiments conducted on BaTiO_3 specimens, from 0 to 150 V cm^{-1} (M'Peko *et al.*, 2014). Without an electric field (0 V), the samples densify slowly as the temperature rises. The application of an electric field results in nearly instantaneous densification. The threshold temperature for the onset of flash sintering moves lower as the electric field increases.

Similar experiments were conducted on zirconia samples. Fig. 22 shows the comparison of conventionally and flash sintered zirconia samples with $1 \mu\text{m}$ initial particle size, it can be seen that grains of less than 100 nm are more heavily populated in the flash-sintered specimen.

There is growing evidence that oxides of complex chemistries, for example $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, can be formed in one step by reactive flash sintering of their constituent oxides (Jesus *et al.*, 2016).

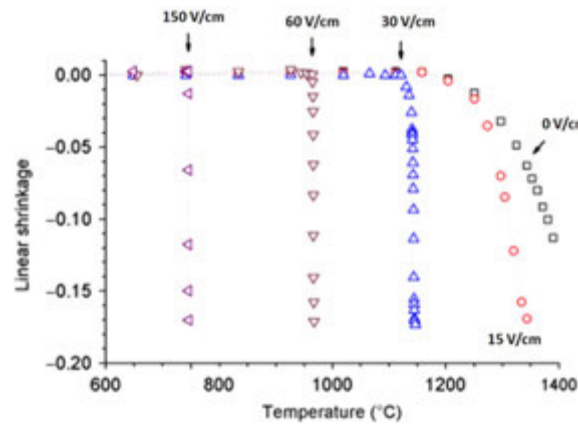


Fig. 21 Linear shrinkage versus temperature for conventional (0 V) and flash sintering (up to 150 Vcm^{-1}) of barium titanate. Adapted from M'Peko, J.C., Francis, J.S.C., Raj, R., 2014. Field assisted sintering of undoped BaTiO₃: microstructure evolution and dielectric permittivity. *Journal of the European Ceramic Society* 34, 3655–3660.

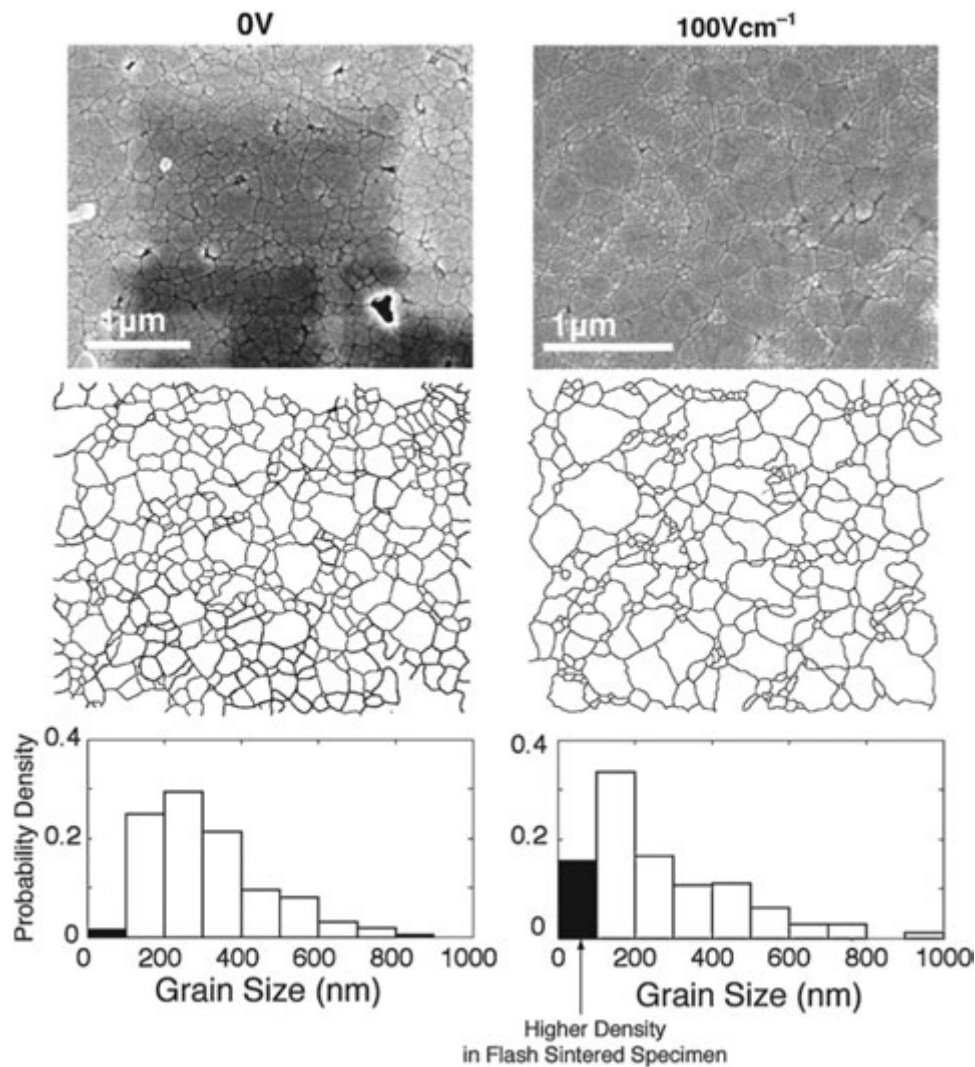


Fig. 22 Scanning electron micrographs and grain size distributions in conventionally (0 V) and flash (100 Vcm^{-1}) sintered yttria stabilized tetragonal zirconia powders (initially $1 \mu\text{m}$ particle size). Adapted from Francis, J.S.C., Cologna, M., Raj, R., 2012. Particle size effects in flash sintering. *Journal of the European Ceramic Society* 32, 3129–3136.

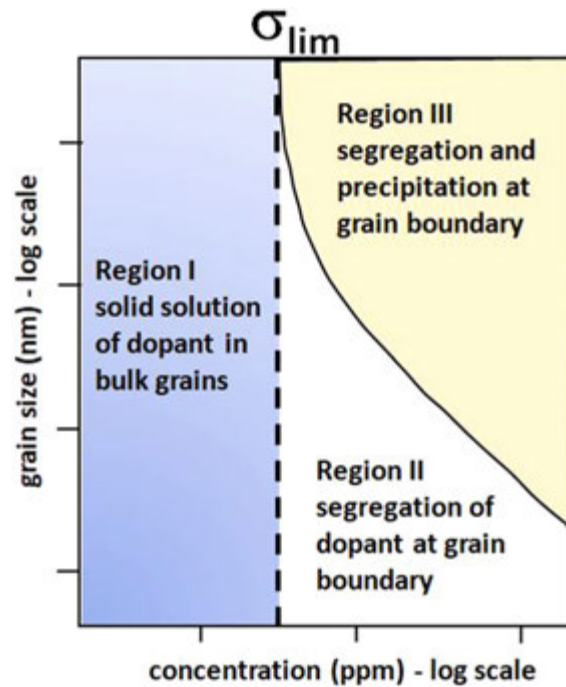


Fig. 23 Grain boundary segregation-precipitation for doped polycrystal as a function of grain size and dopant concentration.

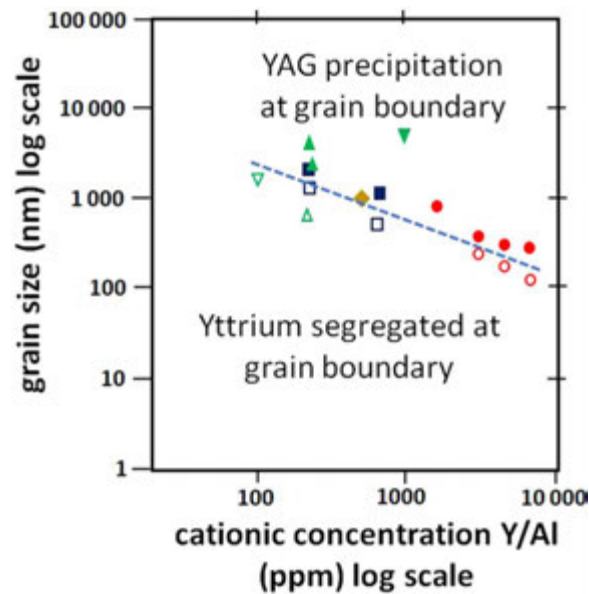


Fig. 24 Grain size versus Y^{3+} concentration in alumina showing regions of segregation or precipitation of YAG at grain boundaries. Adapted from Haussonne, J.M., Carry, C., Bowen, P., Barton, J., 2005. *Céramiques et verres. Principes et techniques d'élaboration; Traité des Matériaux*. (16), [Presses polytechniques et universitaires romandes].

Composition Modification

Addition of dopant elements to modify grain boundary energy

Dopants are very often introduced to modify grain boundary energy. The dopant may be partially soluble in the major component (Region I in Fig. 23) but eventually the solubility limit is reached, above which segregation occurs at grain boundaries (Region II in Fig. 23). Grain boundary mobility is slowed down by segregated dopant ions. The maximum concentration of segregated dopant at grain boundaries increases with surface to volume ratio of the grains, i.e., it is higher for nanosized grains. Above a given

concentration, a new (dopant-rich) phase precipitates and this occurs at lower dopant concentrations as grain size increases (Region III in Fig. 23).

Fig. 24 shows grain boundary segregation or precipitation of YAG for Y^{3+} -doped alumina as a function of grain size and dopant concentration. As Y^{3+} concentration increases, the precipitation of YAG suppresses grain growth.

Fig. 25 compares grain growth rates for pure and MgO-doped alumina and shows clearly the effect of the dopant in restricting grain growth.

Fig. 26 presents an example of the combined effects of using SPS and yttria doping for a zirconia ceramic which results in a nanosized microstructure.

Addition of extra small particles at grain boundaries

If insoluble particles are dispersed in a ceramic matrix, grain growth will be retarded or even halted. These particles will exert blocking forces which will oppose grain boundary mobility, resulting in so-called “pinning” of grain boundaries as shown in Fig. 27. The blocking force is equal to the grain boundary migration force for a given grain size d (Zener equation according to Manohar *et al.*, 1998):

$$d_{\max} = 8r_i/3f_i \quad (1)$$

where r_i is the inclusion particle radius and f_i is the volume fraction of inclusions.

Eq. (1) demonstrates that the limiting grain size, $d_{\max}$ decreases as the volume fraction of second-phase particles is increased and their size is reduced.

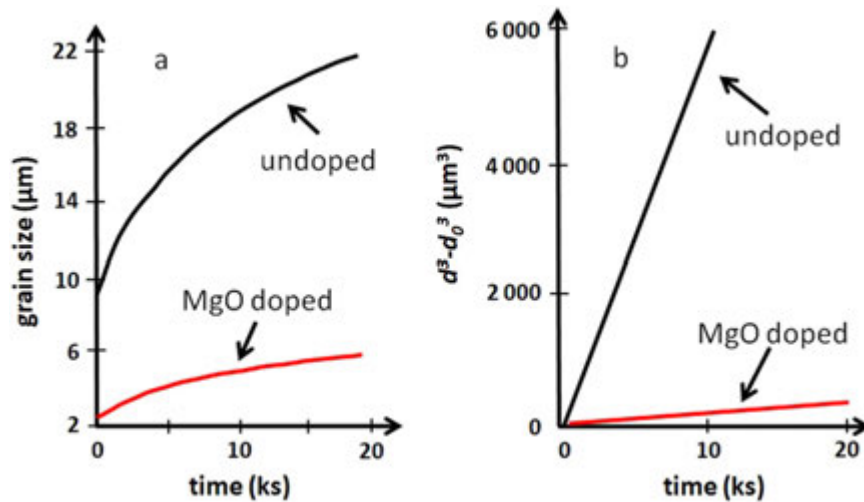


Fig. 25 Comparison of grain growth rates for pure alumina and MgO-doped alumina. Adapted from Lee, W.E., Rainforth, W.M., 1994. Property Control by Processing. Chapman and Hall.

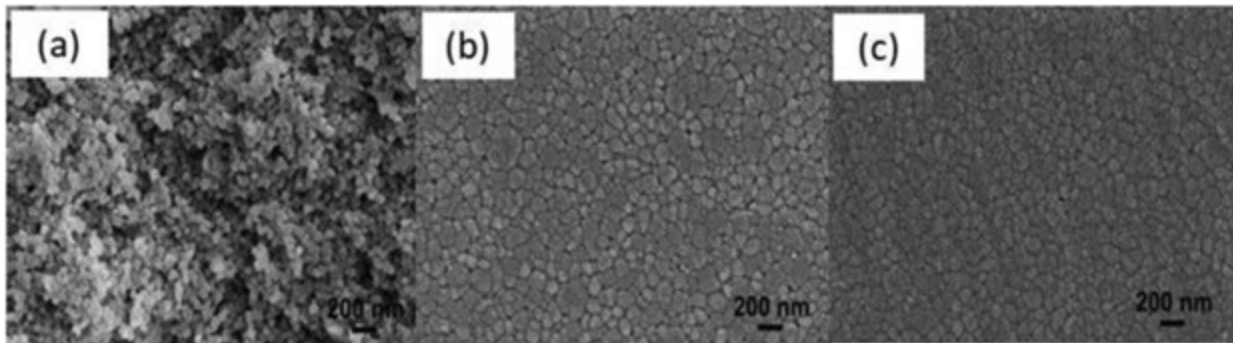


Fig. 26 SEM micrographs showing grain growth during Spark Plasma Sintering of zirconia powder (60 nm – 3 mol% Y_2O_3): (a) initial powder, (b) SPS 1225°C – 98.5% density, (c) SPS 1250°C – 99.9% density. Adapted from Reddy, K.M., Kumar, N., Basu, B., 2010. Inhibition of grain growth during the final stage of multi-stage spark plasma sintering of oxide ceramics. Scripta Materialia 63, 585–588.

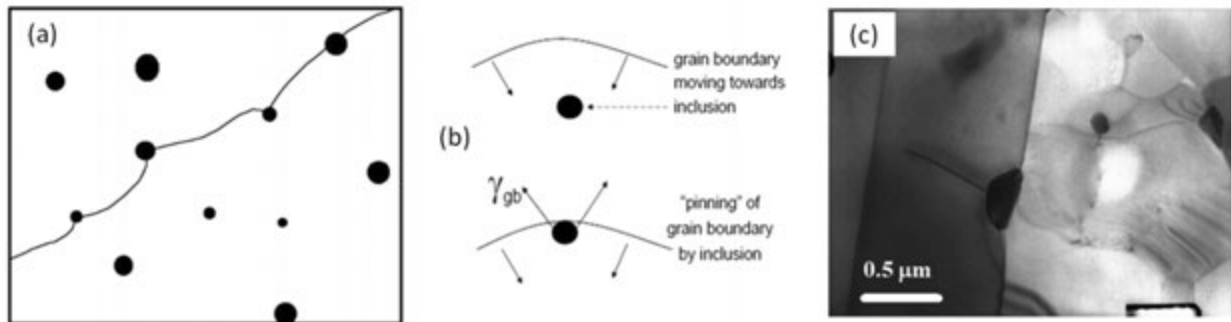


Fig. 27 (a) and (b) Schematic illustrations of the effects of inclusions on grain boundary mobility and (c) TEM image showing the pinning effect of SiC particles in an alumina matrix. Adapted from Petit, F., 2002. Synthèse et propriétés de composites à matrice céramique renforcée par du métal. Université de Valenciennes. [PhD Thesis].

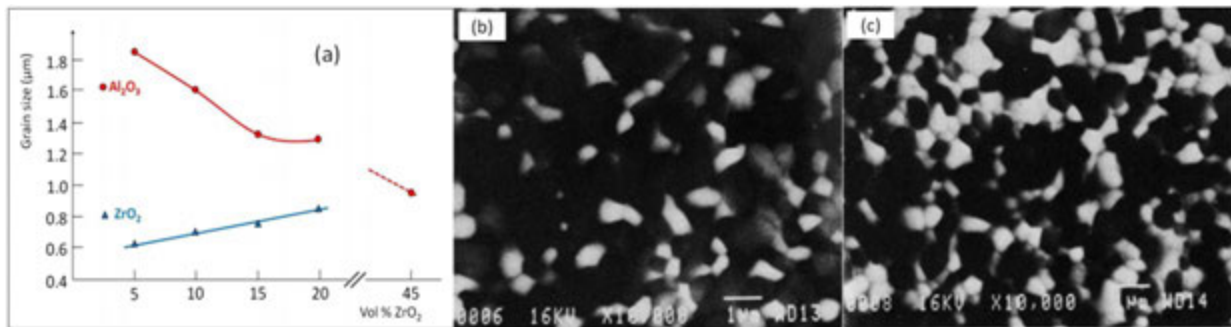


Fig. 28 Zirconia toughened alumina composites densified by pressureless sintering (a) decrease of matrix grain size versus zirconia content; SEM micrographs of composites containing (b) 15 and (c) 45 vol% zirconia. Adapted from Leriche, A., Moortgat, G., Cambier, F., *et al.*, 1988. Preparation and microstructure of zirconia-toughened alumina ceramics. Advances in Ceramics 254. [Science and Technology of Zirconia III, pub American Ceramic Society, Inc].

Fig. 28 shows the influence of insoluble particle content (zirconia) on matrix grain growth (alumina grains) for zirconia toughened alumina composites.

Bodisova *et al.* (2015) studied the effect of addition of zirconia as insoluble particles to alumina using the two step sintering (TSS) method. A first step was carried out at 1475°C followed by a second step at 1300°C which resulted in very limited grain growth compared with the composite conventionally sintered (CS) in one step at 1485–1500°C as shown in **Fig. 29**.

Fig. 30 shows the influence of insoluble particle content (nanosized silicon carbide) on alumina matrix grain growth in alumina-silicon carbide nanocomposites. The addition of only 1 vol% of nanometric silicon carbide into an alumina matrix allows the reduction of the matrix grain size and induces a change in fracture mode from intergranular to transgranular.

If the thermal expansion coefficient of the dispersed particles is lower than that of the matrix coefficient, dislocations can move under traction and form a substructure inside the matrix grains as shown in **Fig. 31** for alumina matrices containing nanoparticles of Mo or SiC. This usually results in a refinement of the matrix grain size with a consequent increase in flexural strength and this is shown for SiC reinforced tetragonal zirconia (TZP) in **Fig. 32**.

If the particle inclusions are slightly soluble in the matrix then Ostwald ripening may occur leading to a decrease in the number of small particles and growth of larger ones. According to Laplace's law, the atoms of a particle close to the inclusion-matrix interface are submitted to compressive forces which increase as the size of the inclusion decreases. The chemical potential of these atoms thus increases which enhances their solubility resulting in a flow of atoms from small particles to larger ones through a dissolution – diffusion – precipitation mechanism. This phenomenon was well illustrated in the case of zirconia-mullite composites obtained by reaction sintering from zircon and alumina in the presence of a small amount of MgO which favors formation of a small amount of liquid phase. The microstructural modifications of the composites as sintering temperatures increase (1500, 1550, and 1600°C) and dwelling times increase (0.5, 2, and 10 h) are clearly governed by Ostwald ripening as shown in **Fig. 33** (Leriche, 1986).

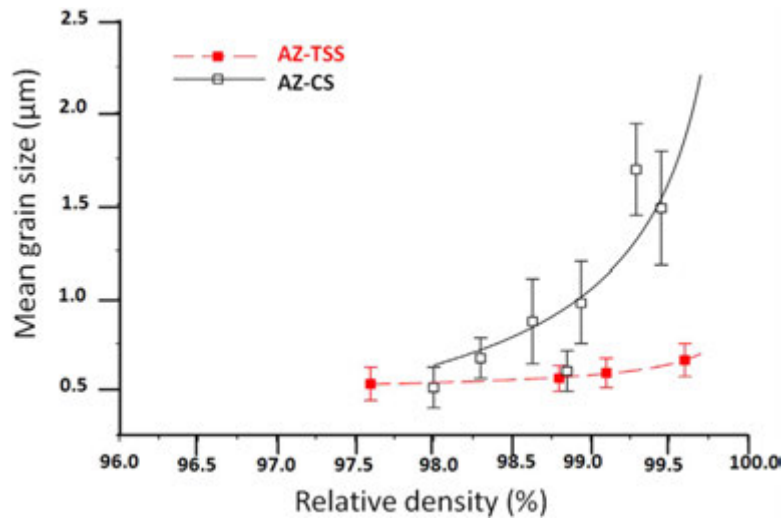


Fig. 29 Refinement of alumina matrix grain size by combining ZrO_2 addition and 2 step sintering (TSS) compared with same composite conventionally sintered (CS). Adapted from Bodisova, K., Galusek, D., Švančárek, P., Pouchlý, S., Maca, K., 2015. Grain growth suppression in alumina via doping and two-step sintering. *Ceramics International* 41, 11975–11983.

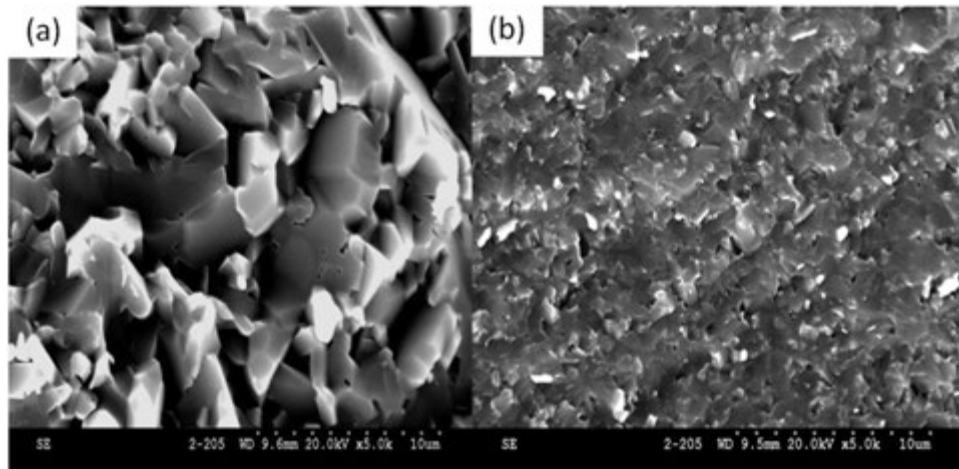


Fig. 30 SEM micrographs of fracture surfaces of abrasive grains (a) Pure alumina, (b) Alumina + 1 vol% SiC after sintering at 1500°C for 30 min. Adapted from Möltgen, P., Wilhelm, F., Leriche, A., Kermel-Kim, C., Gottschamel, G., 2001. $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites abrasive grains. Method for producing them and their use. Patent, WO 01/21547 A1. Kermel, C., 2003. Fabrication et caractérisation de micro et nanocomposites alumine-carbure de silicium pour des applications abrasives. Polytechnic University Hauts-de-France [PhD Thesis].

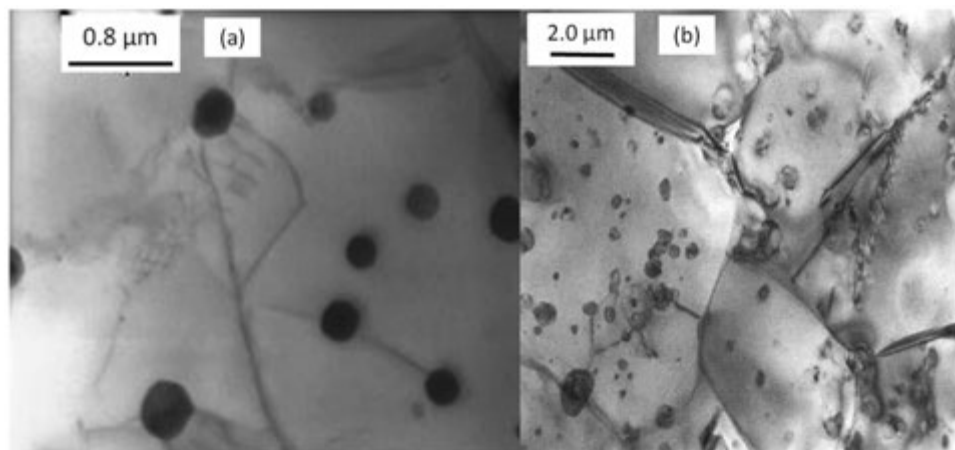


Fig. 31 Substructure forming by dislocation movement in (a) alumina + nanometric Mo particles, (b) alumina + nanometric SiC particles. Adapted from (a) Petit, F., 2002. Synthèse et propriétés de composites à matrice céramique renforcée par du métal. Université de Valenciennes. [PhD Thesis]. (b) Kermel, C., 2003. Fabrication et caractérisation de micro et nanocomposites alumine-carbure de silicium pour des applications abrasives. Université de Valenciennes. [PhD Thesis].

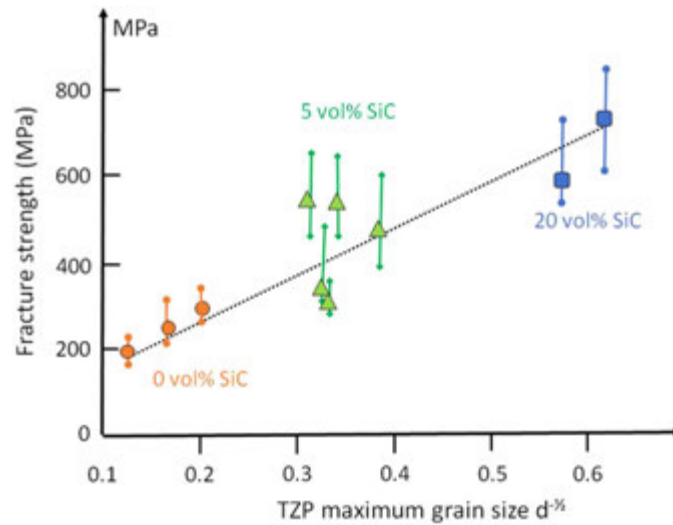


Fig. 32 Flexural strength increase of SiC particle reinforced TZP with decrease in matrix grain size. Adapted from Bamba, N., Choa, Y., Sekino, T., Niihara, K., 1998. Microstructure and mechanical properties of yttria stabilized zirconia-silicon carbide nanocomposites. *Journal of the European Ceramic Society* 18, 693–699.

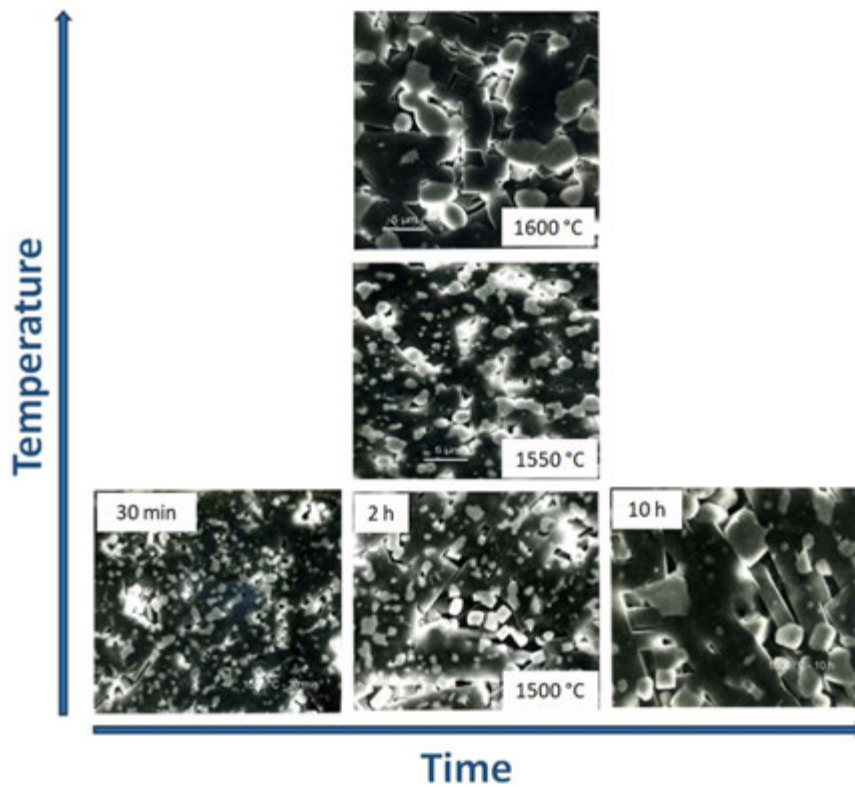


Fig. 33 Grain growth of zirconia particles in a mullite matrix by Ostwald ripening through the grain boundary liquid phase. Adapted from Leriche, A., 1986. Influence des paramètres d'élaboration de composite mullite-zircone sur leur microstructure. Université de Mons, Belgium. [PhD Thesis].

Summary

Ceramics are consolidated by heating powder compacts which results in their densification and elimination of porosity. The type of sintering mechanism directly influences the microstructural development of the ceramic. In all cases, simultaneously with densification, grain growth occurs. Therefore, it is crucial to know the impact of all process parameters on grain growth and densification mechanisms in order to control the final ceramic microstructure and the resulting properties.

The methods to control the microstructure of ceramics depend on the final product. Ceramic materials with 97%–98% densification level and normal grain growth can be processed by pressureless sintering. This involves appropriate thermal treatment conditions (temperature, duration) which favor lattice or grain boundary atomic diffusion enhancing densification and which limit surface diffusion responsible for grain growth. For systems which are susceptible to exaggerated grain growth, it is necessary to use special thermal regimes or schedules such as “fast firing”, “controlled rate sintering” or “microwave sintering” or to add very small amounts of other chemical species (grain growth inhibitors, submicron particles) in order to limit the grain growth by decreasing the grain boundary mobility. For liquid phase sintered ceramics, the microstructure can be controlled by adapting the intergranular phase viscosity and the seed content.

Several examples were presented showing the possibility of using different methods favoring grain growth reduction and achieving fully dense ceramic materials with nanosized microstructures.

References

- Barringer, A., Bowen, H., 1982. Formation, packing and sintering of monodisperse TiO_2 powders. *Journal of the American Ceramic Society* 65, 199–201.
- Binner, J., Vaidyanathan, B., 2008. Processing of bulk nanostructured ceramics. *Journal of the European Ceramic Society* 28 (7), 1329–1339.
- Bodisova, K., Galusek, D., Švančárek, P., Pouchlý, S., Maca, K., 2015. Grain growth suppression in alumina via doping and two-step sintering. *Ceramics International* 41, 11975–11983.
- Chen, L.W., Wang, X.H., 2000. Sintering dense nanocrystalline oxide without final stage grain growth. *Nature* 404, 168–171.
- Chu, M.-Y., De Jonghe, L., Lin, M.F.K., Lin, F.J.T., 1991. Precoarsening to improve microstructure and sintering of powder compacts. *Journal of the American Ceramic Society* 74 (11), 2902–2911.
- Clavier, N., Podor, R., Deliere, L., Ravoux, J., Dacheux, N., 2013. Combining in situ HT-ESEM observations and dilatometry: An original and fast way to the sintering map of ThO_2 . *Materials Chemistry and Physics* 137 (3), 742–749.
- Cologna, M., Rashkova, B., Raj, R., 2010. Flash sintering of nanograin zirconia in <5 s at 850°C. *Journal of the American Ceramic Society* 93 (11), 3556–3559.
- Croquesel, J., Bouvard, D., Chaix, J.M., *et al.*, 2016. Direct microwave sintering of pure alumina in a single mode cavity: Grain size and phase transformation effects. *Acta Materialia* 116, 53–62.
- Gómez, S.Y., DaSilva, A.L., Gouvêa, D., Castro, R.H.R., Hotza, D., 2016. Nanocrystalline yttria-doped zirconia sintered by fast firing. *Materials Letters* 166, 196–200.
- Harmer, M.P., Brook, R.J., 1981. Fast firing – Microstructural benefits. *Transactions & Journal of the British Ceramic Society* 80, 147–149.
- Jesus, L.M., Silva, R.S., Raj, R., M'Peko, J.-C., 2016. Electric field-assisted flash sintering of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$: Microstructure characteristics and dielectric properties. *Journal of Alloys and Compounds* 682, 753–758.
- Kim, H.-D., Han, B.-D., Park, D.-S., Lee, B.-T., Becher, P.F., 2002. Novel two-step sintering process to obtain a bimodal microstructure in silicon nitride. *Journal of the American Ceramic Society* 85 (1), 245–252.
- Kingery, W.D., Woulbroun, J.M., Charvat, F.R., 1963. Effects of applied pressure on densification during sintering in the presence of a liquid phase. *Journal of the American Ceramic Society* 46, 391–395.
- Leriche, A., 1986. Influence des paramètres d'élaboration de composite mullite-zircone sur leur microstructure. Université de Mons, Belgium. [PhD Thesis].
- Lin, F.J.T., De Jonghe, L.C., Rahaman, R.M., 1997. Microstructure refinement of sintered alumina by a two-step sintering technique. *Journal of the American Ceramic Society* 80 (9), 2269–2277.
- Löh, N.J., Simão, L., Jiusti, J., De Noni Jr., A., Montedo, O.R.K., 2017. Effect of temperature and holding time on the densification of alumina obtained by two-step sintering. *Ceramics International* 43, 8269–8275.
- Löh, N.J., Simão, L., Faller, C.A., De Noni Jr., A., Montedo, O.R.K., 2016. A review of two-step sintering for ceramics. *Ceramics International* 42, 12556–12572.
- M'Peko, J.C., Francis, J.S.C., Raj, R., 2014. Field assisted sintering of undoped BaTiO_3 : Microstructure evolution and dielectric permittivity. *Journal of the European Ceramic Society* 34, 3655–3660.
- Manohar, P.A., Ferry, M., Chandra, T., 1998. Five decades of the Zener equation. *ISIJ International* 38 (9), 913–924.
- Mishra, T.P., Ingraci Neto, R.R., Raj, R., Guillon, O., Bram, M., 2020. Current-rate flash sintering of gadolinium doped ceria: Microstructure and defect generation. *Acta Materialia* 189, 145–153.
- Nygren, M., Shen, Z., 2003. On the preparation of bio-, nano- and structural ceramics and composites by spark plasma sintering. *Solid State Sciences* 5, 125–131.
- Palmour III, H., Johnson, D.R., 1967. *Sintering and Related Phenomena*. New York: Gordon & Breach Publishers, p. 779.
- Palmour III, H., Huckabee, M.L., Hare, T.M., 1977. Rate controlled sintering, principles and practice in sintering. New developments. In: Ristic, N.N. (Ed.) *Proceedings of the 4th Round Table Conference on Sintering*, pp. 46–66. Dubrovnik.
- Raj, R., Cologna, M., Francis, J.S.C., 2011. Influence of externally imposed and internally generated electrical fields on grain growth, diffusional creep, sintering and related phenomena in ceramics. *Journal of the American Ceramic Society* 94 (7), 1941–1965.
- Yoshida, H., Sakka, Y., Yamamoto, T., Lebrun, J.-M., Raj, R., 2014. Densification behaviour and microstructural development in undoped yttria prepared by flash sintering. *Journal of the European Ceramic Society* 34, 991–1000.

Templated Grain Growth of Textured Ceramics

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Introduction

Crystallographic texture has been shown to bestow unique properties on ceramics by taking advantage of intrinsic property anisotropy. Texture refers to either the preferred orientation of grains of a specific morphology (i.e., shape) or preferred crystallographic orientation. Morphological and crystal texture are often observed in the same material because the processing and grain growth processes leading to grain shape anisotropy in a microstructure are related to crystal anisotropy. In most textured systems strong preferred orientation is observed in only one crystallographic direction and is referred to as fiber texture. Biaxially-oriented materials with crystallographic orientation in two different axes are described as sheet-textured and have similar property anisotropy as a single crystal of the same composition. Sheet texture is typically observed in thin film ceramics in which a single crystal substrate directs oriented growth of the thin film. Sheet direction has only been achieved in thick film polycrystalline ceramics by the Rolling Assisted Biaxially Textured Substrates process (RABiTS) which uses a biaxially oriented metallic substrate to control oriented growth of the thick film (Goyal *et al.*, 2004). Low quality fiber texture in bulk ceramics with <20% texture is commonly observed when starting with particles with an aspect ratio of >2 and application of a shaping process in which unidirectional forces induce physical alignment of the anisometric particles. For example, dry pressing, hot pressing and spark plasma sintering often yield ceramics with weak texture as a result of the unidirectional action and associated particle reorientation of anisometric particles during the unidirectional pressing strain. Texture can also be slightly enhanced by grain rotation during hot pressing, or hot forging, of a dense ceramic but, unlike metals, the degree of texture is limited by very low plasticity in ceramics. In either case, the use of hot forming techniques, and the associated high cost, limits the use of such approaches to fabricate high quality textured ceramics in which the texture fraction is >90%.

Many powder and sol-gel processing techniques produce texture in ceramics. These processing methods are categorized in Fig. 1 by the driving force for particle alignment as either mechanical or electromagnetic (Messing *et al.*, 2017). It is noted that uniformly applied heating alone cannot create texture but does enhance pre-existing texture via preferential growth of aligned grains. However, thermal gradients, as used in directional solidification, can create texture during forming. Two general techniques have been developed in the past few decades to achieve ceramics with a high texture fraction (e.g., >95% texture fraction), including templated grain growth (TGG) (Seabaugh *et al.*, 1997) and reactive templated grain growth (RTGG) (Takeuchi *et al.*, 1999; Hong and Messing, 1999; Tani, 2006), and strong (7–14 T) magnetic field alignment (MA) of particles (Sakka and Suzuki, 2005; Suzuki *et al.*, 2006). Some of these processes can be used in tandem to achieve texture as indicated by the overlapping areas of diagram in Fig. 1 (Poterala *et al.*, 2013).

There is increasing interest in textured ceramics due to the development of the templated grain growth (TGG) process which enables access to high quality crystallographic texture. Templated grain growth (TGG) (Seabaugh *et al.*, 1997) is a process that takes advantage of the preferred growth of large grains in a dense microstructure by Ostwald ripening (i.e., large grains grow at the

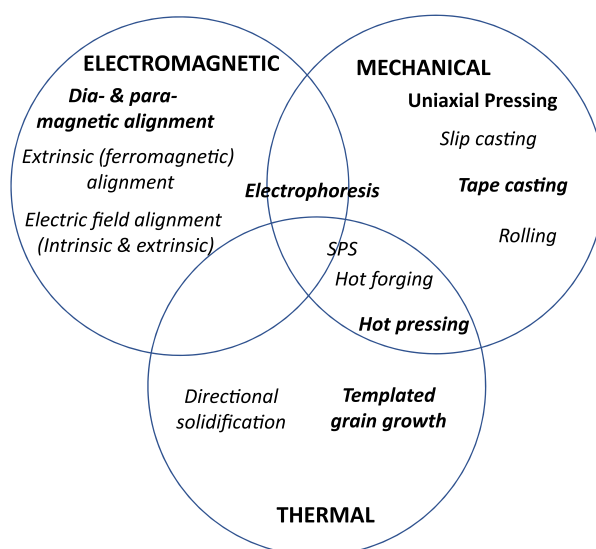


Fig. 1 Electromagnetic, mechanical and thermal processing methods utilized to produce grain alignment in ceramic materials. Most commonly used processing methods are shown in bold. Adapted from Messing, G.L., Poterala, S., Chang, Y., *et al.*, 2017. Texture-engineered ceramics – Property enhancements through crystallographic tailoring. J. Mater. Res. 32, 3219–3241.

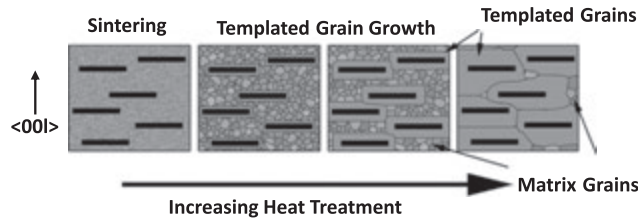


Fig. 2 A schematic of texture development by templated grain.

expense of smaller grains). In the TGG process, a minority of relatively larger, anisometric single crystal particles is mixed into a slurry of equiaxed, submicrometer particles. The template particles are oriented in the matrix powder by a shear-forming process like tape casting to align the template particles with a preferred crystallographic orientation (Fig. 2). Tape casting and extrusion are the most used processes for TGG but any process that imposes directional shear on the anisometrically-shaped particles results in alignment. Bulk ceramics are fabricated by stacking tape cast layers and laminating the stack. Heating the bulk composite of template particles dispersed in a fine particle matrix results in densification of the matrix powder around the template particles and then subsequent growth of the template particles by Ostwald ripening once the matrix reaches >95% density.

TGG has many advantages for fabricating oriented materials relative to single crystal growth processes. First, the technology is founded on the well-established industrial scale tape casting technology and is much less expensive than single crystal growth processes. Ceramics of much greater size and superior compositional uniformity are possible than with single crystal growth processes since the compositional uniformity of the powder processed ceramic is retained during sintering and templated grain growth. In contrast, single crystals grown from the melt undergo long range chemical segregation during crystal growth and thus only small portions of the single crystal are usable when exacting chemical composition is important for properties. Finally, textured ceramics are mechanically more robust than single crystals.

The templated grain growth (TGG) process is the focus of this chapter since it has been shown, since its invention in 1997, to yield high quality textured ceramics and because of the commercial interest in fabricating textured piezoelectric ceramics by TGG. The powder, template, process, sintering and grain growth conditions critical for fabrication of high-quality textured bulk ceramics with single crystal-like properties are presented. Progress over the last 20 years of textured ceramic properties of all types, and especially for textured piezoelectric ceramics, was recently reviewed (Messing *et al.*, 2017).

Templated Grain Growth

Several criteria need to be satisfied to obtain a textured material by TGG (Suvaci and Messing, 2000). Growth of the template particles depends on (1) the thermal stability and crystallographic properties of the template particles relative to the matrix material, and (2) maintaining favorable thermodynamic and kinetic conditions for template growth. The amount of growth, and thus the degree of texture, depends on the number, size and size distribution of the template particles relative to the matrix powder.

Template particles must satisfy several physical and crystallographic conditions to achieve high quality texture by TGG. First, templates must be anisometric, single crystals or nominally single crystal with a large aspect ratio (e.g., >10) to allow for alignment of a particle in a defined crystal axis direction during forming. Since most available template particles are tabular in shape, tape casting is the most common technique used for producing textured ceramics by TGG. Acicular particles can be well-aligned during tape casting by using a gated doctor blade (Messing *et al.*, 2004). Extrusion is also used for TGG when acicular template particles, such as silicon nitride and mullite, are available. Alignment of tabular particles by extrusion depends on the aspect ratio of the extrusion die; circular dies lead to coaxial orientation.

Walton *et al.* (2019) showed that the magnitude of torque on the template particle during tape casting significantly affects the quality of anisometric particle orientation. Orientation of anisotropic particles during tape casting is related to the velocity profile in the slurry and the resistance to motion of the viscous slurry as the slurry passes under the doctor blade (Fig. 3). The velocity profile under the doctor blade can be modeled as a combination of pressure-driven flow and drag driven flow (Fig. 3(b)), and is primarily dominated by drag driven flow under typical tape casting conditions (e.g., 2–50 mm s^{−1} casting velocity, 0.25–2 mm gap height, 2–30 mm reservoir height).

The shear rate at any point in the velocity profile is calculated by taking the slope of the velocity profile. If the rheological behavior of the slurry is known, the gradient in the shear stress under the doctor blade can be determined. Furthermore, the shear stress (τ) acting on the surface of the template particle at any position under the doctor blade can be calculated for a known shear rate ($\dot{\gamma}$) and the experimentally determined dynamic viscosity (η_D) using Eq. (1).

$$\eta = \dot{\gamma} \eta_D \quad (1)$$

The gradient in shear stress across the major axis of the template particle (i.e., diameter or length) generates a torque that rotates and aligns the template particle parallel to the velocity profile. Eq. (2) is a 1D torque approximation, where M is the torque, δ_y is the projection height of the particle, and $\tau_{(y + \delta_y)}$ and τ_y are the shear stress values on either end of the particle.

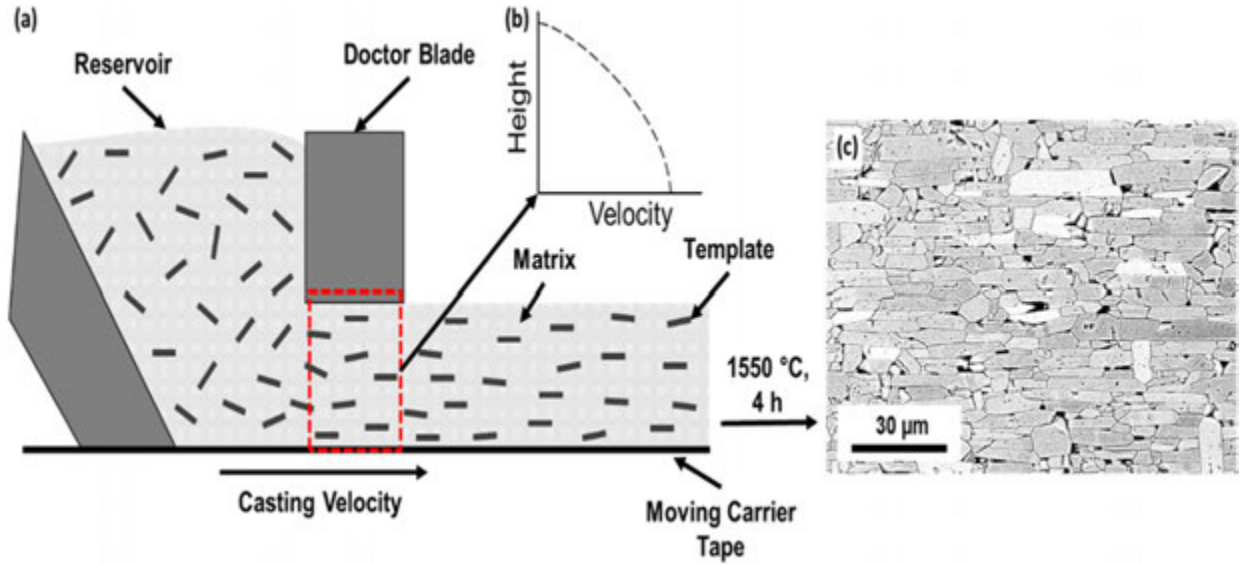


Fig. 3 Schematic of a (a) tape casting setup illustrating the (b) velocity profile under the doctor blade and (c) the resulting microstructure of a laminated and TGG textured alumina. Adapted from Walton, R.L., Vaudin, M.D., Hofer, A.K., *et al.*, 2019. Tailoring particle alignment and grain orientation during tape casting and templated grain growth. *J. Am. Ceram. Soc.* 102, 2405–2414.

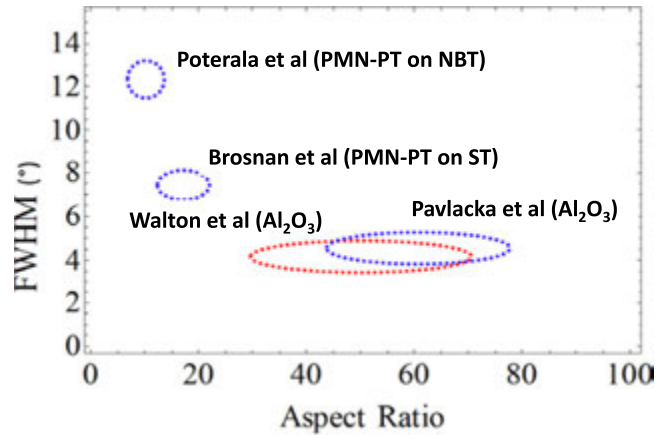


Fig. 4 A comparison of full width at half maximum (FWHM) for tape cast TGG ceramics as a function of template aspect ratio. Adapted from Walton, R.L., Vaudin, M.D., Hofer, A.K., *et al.*, 2019. Tailoring particle alignment and grain orientation during tape casting and templated grain growth. *J. Am. Ceram. Soc.* 102, 2405–2414.

$$M = (\tau_{(y + \delta_y)} - \tau_y) \delta_y \quad (2)$$

When the face of a platelet particle is oriented perpendicular to the casting direction, the projection height (δ_y) is at a maximum at the platelet or fiber major dimension. As the platelet angle relative to the casting direction approaches 0° , the projection height approaches the thickness of the platelet (approximately zero as platelet thickness $\ll$ platelet diameter). When perfectly aligned, the diameter of the platelet or fiber length is parallel to the direction of the applied shear. The dynamic viscosity (resistance to shear flow) of the slurry creates resistance to the template particle changing orientation, and thus the magnitude of the viscous resistance depends on the dynamic viscosity, rotational velocity of the platelet, and the surface area of the template. Particle alignment under any set of tape casting conditions therefore depends on how the magnitude of torque balances with the viscous resistance of the slurry. If the torque generated during casting is sufficient to overcome the viscous resistance and rotate the particle while it is under the doctor blade, then the template particles will become well aligned. After casting the templates will remain well aligned, since the aligned particles must overcome the rest viscosity (i.e., zero shear rate) of the slurry to rotate further. Thus, changes in casting speed, rheology and casting height, and particle aspect ratio can dramatically affect particle alignment by virtue of the torque acting on the particle during shear.

As indicated by Eq. (2), the higher the aspect ratio of the template particle, the easier it is to align individual template particles. Fig. 4 shows how the quality of texture depends on the aspect ratio of the tabular particle aligned by tape casting. In this case the quality of orientation is quantified using an x-ray rocking curve to measure the orientation distribution of the grains in the final sintered ceramic. The full width at half maximum (FWHM) of the distribution function is a measure of orientation quality with a small value of FWHM indicating a high degree of platelet orientation. Although shape anisotropy is a necessary characteristic for template orientation during shear forming, particle shape is not necessary if crystallographic alignment is accomplished using a high field magnet (i.e., 7–14 T) (Sakka and Suzuki, 2005). Poterala and Messing combined TGG and a 3 T magnet to align templates during slip casting to texture PMN-PT (Poterala *et al.*, 2013).

The template particle must be nominally single crystal and satisfy conditions for epitaxial growth during the TGG process. For example, tabular, single crystal alumina template particles with (0001) basal surfaces are used to template [0001]-textured alumina by TGG. This is a classic case of homoepitaxy in which there is no lattice parameter misfit between template and matrix, and thus homoepitaxial growth of the template particle readily occurs. Tabular (001)_c BaTiO₃ (BT) particles are used as heteroepitaxial templates for producing [001] textured lead-based piezoelectrics like 0.675Pb(Mg_{1/3}Nb_{2/3})O₃–0.325PbTiO₃ (PMN-PT) and Pb(In_{1/2}Nb_{1/2})O₃–Pb(Mg_{1/3}Nb_{2/3})O₃–PbTiO₃ (PIN-PMN-PT) since it is possible to synthesize high aspect ratio tabular BT particles by a molten salt process. Also, the lattice parameter mismatch with the matrix is <2%. For heteroepitaxial growth the template particles must have a similar crystal structure and <15% lattice parameter matching. When templates do not have the same composition as the matrix material they can either dissolve in the matrix after TGG, as happens in the case of SrTiO₃-templated PMN-PT (Kwon *et al.*, 2005), or, as in the case of textured lead-based and non-lead based perovskites, the BT templates remain at the core of the templated grains.

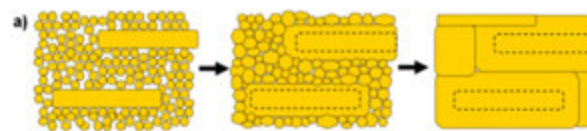
When the matrix is a chemical precursor (e.g., sol gel) or mixture of powders to the final ceramic phase, the template particles can act as nucleation sites (see Calcination and Phase Transformations) and seed the solid state reaction or phase transformation of the matrix. This process is referred to as Reactive TGG (RTGG) because of the dual role of the templates (Takeuchi *et al.*, 1999; Hong and Messing, 1999; Yilmaz *et al.*, 2003). It is important to note that the material seeded by the template has the same crystallographic orientation as the template and thus the effective volume of oriented material after phase formation and prior to densification can be significantly greater than with TGG. The RTGG process is useful when the template is unstable at high temperature. By acting as a seed for the phase transformation the oriented material formed on the surfaces acts as the effective template once the ceramic is densified. Tani reported a unique means to form the template particle by an *in situ* topochemical process. (Fig. 5).

The degree of texture is directly related to the amount of growth on the template grains. The grain size of the textured ceramic of a fully textured can be calculated by assuming the rectangular templates are distributed on a rectangular lattice such that the surface to surface distance of the templates is the same in all directions.

The final grain size is the same as the spacing of templates (x_t), which depends on the number frequency of the templates per unit volume (f_t) according to Eq. (3).

$$x_t = \left(\frac{6}{\pi f_t} \right)^{1/3} \quad (3)$$

Templated Grain Growth



Reactive Templated Grain Growth

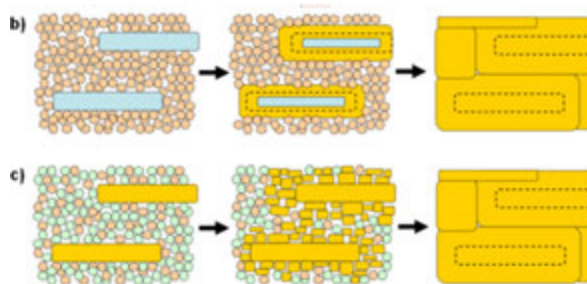


Fig. 5 Schematic of the TGG and reactive TGG process. The *in situ* topochemical conversion texturing process (b) The oriented seeding of a phase transformation texturing process. Adapted from (c) Messing, G.L., Poterala, S., Chang, Y., *et al.*, 2017. Texture-engineered ceramics – Property enhancements through crystallographic tailoring. J. Mater. Res. 32, 3219–3241.

where

$$f_t = \frac{N_t}{V_{tot}} = \frac{6m_t}{\pi\rho_o V_{tot}} \sum_{i=1}^n \frac{wf_i}{d_i^3} \quad (4)$$

and N_t is the number of templates, V_{tot} is the total volume of the powder, m_t is the weight of the templates added, ρ_o is the theoretical density of the template material, and d_i is the template size for a given weight fraction, wf_i .

Fig. 6 shows how grain size depends on the template size and the number of templates per unit volume (f_t). If 5 vol% of $10 \mu\text{m} \times 10 \mu\text{m} \times 1 \mu\text{m}$ templates are added, then $< 10 \mu\text{m}$ growth is needed on each templated side to achieve 100% texture and the grain size of the textured ceramic is nominally $20 \mu\text{m}$. For smaller templates even less growth is required since the number fraction of particles scales with template size⁻³. However, template size cannot be decreased too much without reducing shear alignment and the thermodynamics of growth. On the other hand, very small concentrations of large template particles require a significant amount of growth to obtain 100% texture. Finally, increasing the template loading to $> 10 \text{ vol}\%$ leads to a degradation of the quality of the orientation as evidenced by broadening of the orientation distribution function (i.e., increase in FWHM).

After orienting the template particles in the matrix, the formed part must be densified before the templated grains can grow. When equiaxed powders are sintered, pores on the grain boundaries retard grain growth until about 92% density, at which point matrix grains undergo normal grain growth. Likewise, there is not significant template growth until $> 95\%$ density in most systems (Suvaci and Messing, 2000). Fig. 7 shows the progress of [001] texture evolution in CuO-doped PIN-PMN-PT templated on tabular BaTiO₃ template particles as a function of sintered density (Chang *et al.*, 2017). Only when the ceramics are $> 96\%$ density is there substantial oriented templated grain growth on the BT templates and 95% texture is achieved. Note that the grains have a cuboidal shape as a result of the isotropic growth of the pseudocubic PIN-PMN-PT formed. This example illustrates that anisotropic, or so-called exaggerated, grain growth is not necessary for TGG.

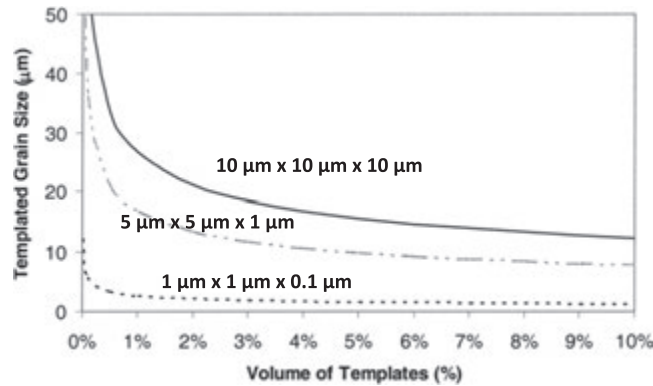


Fig. 6 Calculated templated grain size as a function of template size and concentration for a 100% textured material.

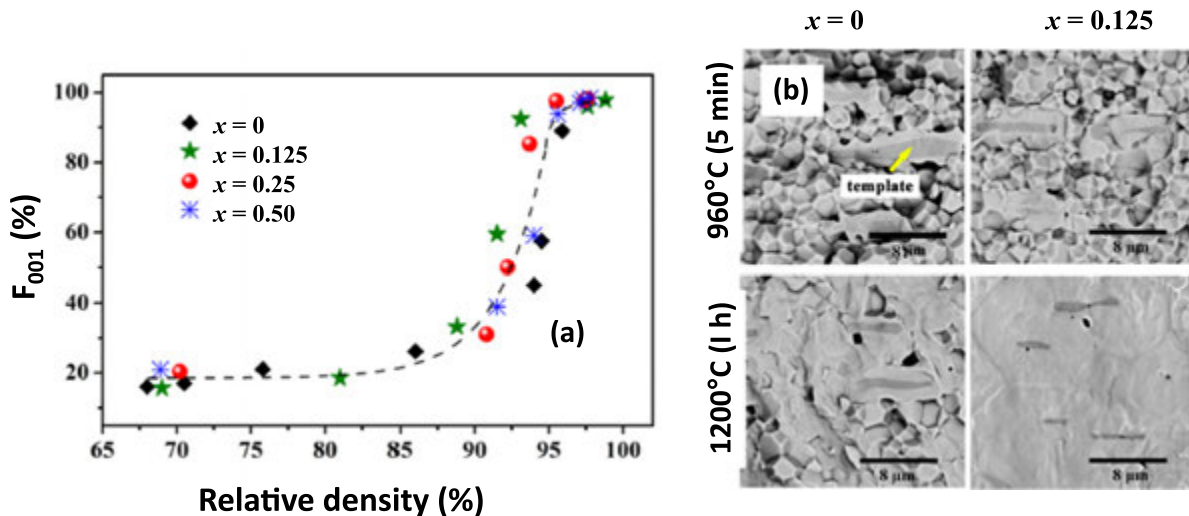


Fig. 7 Texture fraction (F_{001}) of [001] textured 0.28PIN-0.40PMN-0.32PT ceramics (a) as a function of relative density for different CuO contents (x) and (b) cross-sectional SEM micrographs of templated 0.28PIN-0.40PMN-0.32PT ceramics with no dopant and 0.125% CuO dopant. Adapted from Chang, Y., Watson, B., Walton, *et al.*, 2017. Enhanced texture evolution and piezoelectric properties in CuO-doped $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ grain-oriented ceramics. *App. Phys. Lett.* 111, 232901–232905.

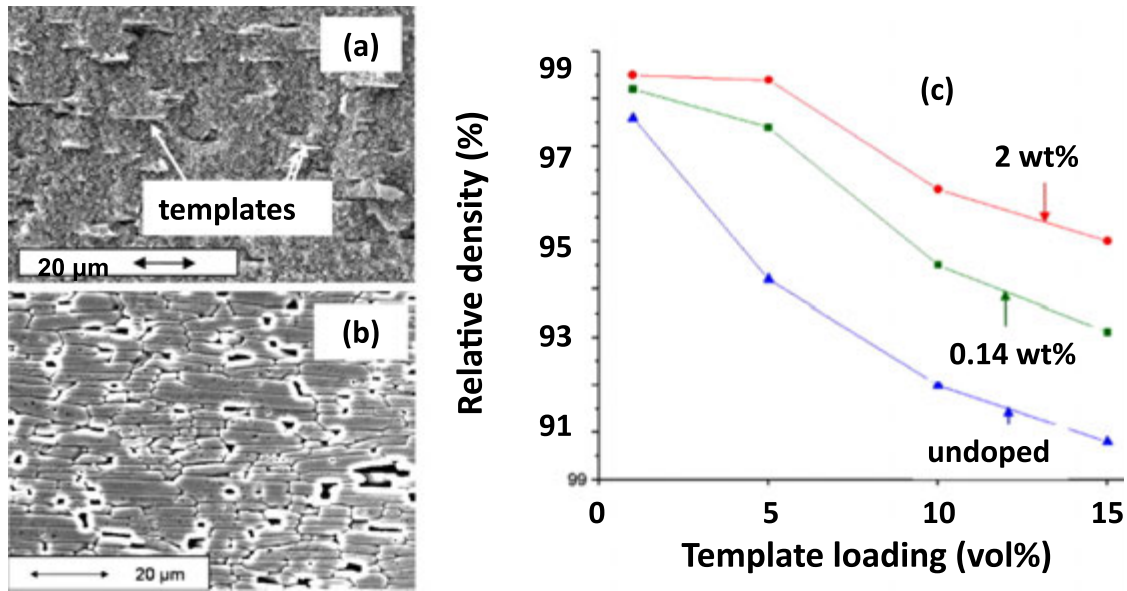


Fig. 8 Micrographs of cross-sections of (a) a templated alumina green body and (b) TGG alumina doped with 2% CaO/SiO₂ dopant after heating at 1550°C for 90 min (c) Sintered density of textured alumina vs. template loading for samples with no dopant, 0.14% dopant, and 2% dopant after heating at 1550°C for 90 min. Adapted from Pavlacka, R.L., Messing, G.L., 2010. Processing and mechanical response of highly textured Al₂O₃. *J. Eur. Ceram Soc.* 30, 2917–2925.

Fig. 8(a) shows a cross-sectional view of alumina with 5 vol% tabular alumina particles aligned in the matrix and the textured alumina formed when a 2% wt% dopant is added and sintered at 1550°C for 90 min (**Fig. 8(b)**). **Fig. 8(c)** demonstrates the effect of adding template concentrations of 1–15 vol% and 0–2 vol% liquid phase-forming dopants on densification. As the template concentration increases, the sintered density decreases to 94% for 5 vol% templates and 91% when 15 vol% templates are added. With no dopant, alumina densifies by a solid-state mechanism and thus the large alumina template particles impose constraining stresses in the sintering system and also decrease densification by forming a percolating network of template particles in the x-y plane of the ceramic. To alleviate the stresses from the large template particles, a dopant that forms a liquid during sintering is added. **Fig. 8(b)** shows the liquid formed during sintering reduces the constraining stresses, and as a result 95% dense textured alumina can be attained with 15 vol% template particles. To avoid the adverse effects of template particles on densification, a liquid phase is used in almost all cases of TGG. Besides assisting densification, the liquid phase also increases the kinetics of template growth. It is important to note that dopant chemistry should be designed to avoid having a negative impact on the properties of the textured ceramic.

The calcium silicate dopant was specifically chosen for textured alumina to facilitate anisotropic growth on the templated grains. Rapid growth was perpendicular to the basal plane and stops once the growing grains ‘impinge’ and finer grains no longer exist and thus the thermodynamic driving force for growth in that direction is nearly zero. A slower growth process perpendicular to the fast growth direction continues until the matrix is completely consumed or the matrix grains coarsen to the point where the thermodynamic driving force is eliminated. TGG in the absence of a liquid is also possible but issues of constrained densification and slower solid-state diffusion processes, as noted above, limit the viability of solid-state diffusion driven TGG.

Most TGG systems use a liquid phase to reduce constraining stresses on sintering due to the large particles, and to increase the kinetics of template growth. The driving force for template growth in the presence of a liquid is provided by the solubility difference between the matrix grains and the template material in the surrounding liquid (S_m and S_t , respectively). Supersaturation arises from the curvature of the matrix grains relative to the growing template surface and thus underscores the importance of a matrix with a fine grain size after the sintering stage of TGG (Seabaugh *et al.*, 2000). The relative degree of supersaturation can be described by the Gibbs-Thomson equation. Thus, for a matrix of average grain size r and a growing template surface of radius R_t

$$\Delta S = \frac{2S_o M}{\rho RT} \left(\frac{\sigma_m}{r} - \frac{\sigma_t}{R_t} \right) \quad (5)$$

where σ_m and σ_t are the surface energies of the matrix grains (average) and the growing surface of the template grains, respectively, S_o is the intrinsic solubility of alumina in the liquid phase during growth and M is the molar volume of alumina. For tabular particles the smaller dimension surface is most important for initial growth by TGG since that is the highest energy surface for the template particle.

In anisotropic crystal systems the growth of highly packed atomic planes is relatively faster because such surfaces have a higher surface energy. This growth anisotropy means that the dimension (e.g., thickness or diameter of whiskers) of the growing surface must be greater than the matrix grain size to maintain a thermodynamic advantage for growth. As shown for the growth of single

crystals by solid-state conversion, matrix grain growth can reduce the thermodynamic driving force enough that template growth stops (Rehrig *et al.*, 2000). Thus, a greater size difference between the matrix grains and the templates result in a higher driving force for template growth. It has been shown that the minimum size ratio to sustain template growth is ~ 1.5 , which is consistent with critical size criteria for exaggerated grain growth attributed to Hillert (Hillert, 1965). Since the matrix grains also begin to grow during TGG once the matrix achieves $>92\%$, then heating conditions may need to be tailored to limit excessive matrix grain growth so as to preserve the size advantage of the template relative to the matrix grains. The kinetics of template growth is well explained by either interface reaction-control or diffusion-controlled models. As shown for alumina and PMN-PT, initial growth is diffusion-controlled but growth mechanism changes to interface reaction control once the grains become faceted.

Summary

Templated grain growth is an excellent, relatively low-cost process for producing high quality textured materials with $>95\%$ texture fraction and a full width at half maximum in a rocking curve of $<10^\circ$. Fiber and biaxial textured ceramics require template particles of uniform size and shape, and more control over their distribution during forming. While this chapter describes the application of TGG to ceramics it is apparent that the process can be applied to a variety of inorganic material systems, and may even have some possibilities for organic systems.

References

- Chang, Y., Watson, B., Walton, *et al.*, 2017. Enhanced texture evolution and piezoelectric properties in CuO-doped $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ grain-oriented ceramics. *App. Phys. Lett.* 111, 232901–232905.
- Goyal, A., Paranthaman, M., Schoop, U., 2004. The RABiTS approach: Using rolling-assisted biaxially textured substrates for high-performance YBCO superconductors. *MRS Bull.* 29, 552–561.
- Hillert, M., 1965. On the theory of normal and abnormal grain growth. *Acta Metall.* 13, 227–238.
- Hong, S.H., Messing, G.L., 1999. Development of textured mullite by templated grain growth. *J. Am. Ceram. Soc.* 82, 867–872.
- Kwon, S.T., Sabolsky, E.M., Messing, G.L., Trolrier-McKinstry, S., 2005. High strain $\langle 001 \rangle$ textured $0.675\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.325\text{PbTiO}_3$ ceramics: templated grain growth and piezoelectric properties. *J. Am. Ceram. Soc.* 88, 312–317.
- Messing, G.L., Poterala, S., Chang, Y., *et al.*, 2017. Texture-engineered ceramics – Property enhancements through crystallographic tailoring. *J. Mater. Res.* 32, 3219–3241.
- Messing, G.L., Trolrier-McKinstry, S.T., Sabolsky, E.M., *et al.*, 2004. Templated grain growth of textured piezoelectric ceramics. *Crit. Rev. Solid State Mater. Sci.* 29, 45–96.
- Pavlacka, R.L., Messing, G.L., 2010. Processing and mechanical response of highly textured Al_2O_3 . *J. Eur. Ceram Soc.* 30, 2917–2925.
- Poterla, S.F., Meyer, R.J., Messing, G.L., 2013. Low-field dynamic magnetic alignment and templated grain growth of diamagnetic PMN-PT ceramics. *J. Mater. Res.* 28, 2960–2969.
- Rehrig, P.W., Messing, G.L., Trolrier-McKinstry, S., 2000. Templated grain growth of barium titanate single crystals. *J. Am. Ceram. Soc.* 83, 2654–2660.
- Sakka, Y., Suzuki, T.S., 2005. Textured development of feeble magnetic ceramics by colloidal processing under high magnetic field. *J. Ceram. Soc. Jpn.* 113, 26–36.
- Seabaugh, M.M., Kerscht, I.H., Messing, G.L., 1997. Texture development by templated grain growth in liquid phase sintered α -alumina. *J. Am. Ceram. Soc.* 80, 1181–1188.
- Seabaugh, M.M., Suvaci, E., Messing, G.L., 2000. Modeling anisotropic single crystal growth kinetics in liquid phase sintered α - Al_2O_3 . *J. Interface Sci.* 8, 257–267.
- Suvaci, E., Messing, G.L., 2000. Critical factors in the templated grain growth of textured reaction-bonded alumina. *J. Am. Ceram. Soc.* 83, 2041–2048.
- Suzuki, T.S., Uchikoshi, T., Sakka, Y., 2006. Control of texture in alumina by colloidal processing in a strong magnetic field. *Sci. Technol. Adv. Mater.* 7, 356–364.
- Takeuchi, T., Tani, T., Saito, Y., 1999. Piezoelectric properties of bismuth layer structured ferroelectric ceramics with a preferred orientation processed by the reactive templated grain growth method. *Jpn. J. Appl. Phys.* 38, 5553–5556.
- Tani, T., 2006. Texture engineering of electronic ceramics by the reactive-templated grain growth method. *J. Ceram. Soc. Jpn.* 114, 363–370.
- Walton, R.L., Vaudin, M.D., Hofer, A.K., *et al.*, 2019. Tailoring particle alignment and grain orientation during tape casting and templated grain growth. *J. Am. Ceram. Soc.* 102, 2405–2414.
- Yilmaz, H., Messing, G.L., Trolrier-McKinstry, S., 2003. (Reactive) templated grain growth of textured sodium bismuth titanate ($\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{-BaTiO}_3$) ceramics – I. Processing. *J. Electroceram.* 11, 207–215.

Functionally Graded Ceramics

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Introduction

Functionally graded materials (FGMs) are multifunctional materials, which contain a gradual spatial variation in composition and/or microstructure for the specific purpose of controlling variations in structural or functional properties. An important aspect is that the spatial distribution of microstructure and/or composition is tailored and quantitatively controlled in order to achieve an improvement in properties of the final component with respect to a homogeneous material (Mortensen and Suresh, 1995; Neubrand and Rödel, 1997; Gasik, 1995).

The concept of FGMs derives from the consideration that the service conditions and required materials performance vary with the location in a large number of components. Consider for example a turbine blade, which must withstand high non-stationary heat fluxes and centrifugal acceleration. An ideal structure for this application would consist of a tough metal core and a corrosion and heat resistant ceramic at the hot surface of the blade. If the ceramic is directly bonded to the metal, spalling may occur during thermal cycling because of the high thermal stresses at the interface. A graded material with a smooth transition from the ceramic surface to the metal core can reduce the thermo-mechanical stress concentration at the interface, and thus has better performance. There are many other applications where the requirement for properties cannot be attained by a single material (Neubrand and Rödel, 1997). In all these cases, graded materials offer the possibility to combine two materials properties, avoiding most of the disadvantages of a bi-material. Fundamental and applied research in the past has clearly shown that the introduction of compositional step and profile gradients in FGMs can be a benefit on many accounts (Suresh and Mortensen, 1997; Munz *et al.*, 1998; Bao and Cai, 1997).

FGMs are commonly found in nature with examples such as the varying spongy trabecular structures of bone (Wegst *et al.*, 2014) or local tissue variation in seashells and plants e.g., Norway spruce (Eder *et al.*, 2009) and bamboo (Habibi *et al.*, 2015).

There are also examples of early synthetic materials taking advantage of property gradients such as case-hardened steels in which a hard surface is combined with a tough interior. In fact, this idea has been exploited for hundreds of years in the iron or steel production (Gasik, 1995). Although it is not difficult to find some examples in the history of our civilization using the idea of graded materials, as a systematic engineering approach it is far from being the norm. Instead, current engineering practice generally involves the design of a part using one of a large number of generally mass-produced uniform materials. When a structure requires vastly different materials, different uniform materials are joined along sharp boundaries using a variety of joining or coating methods. The task of the materials engineer is defined as seeking to improve materials, while the task of the structural part designer is using the handbooks of available materials. With the innovative FGM concept, component design and fabrication are based not on a list of existing materials but on a choice of available basic material ingredients and material processes, combined with three-dimensional mechanical analysis of graded structures. These two engineering disciplines are combined to synergistically design both the component and its processing. Here lies a second definition of the functionally graded materials concept, as an approach in engineering rather than a physical entity (Mortensen and Suresh, 1995). When additive manufacturing processes are used to fabricate a part, the manufacturing must start from a full 3D design of the part from which the software is generated to steer the machine that usually will build up the part layer by layer. In the most advanced forms of these new technologies, the file will also need information on the local material combination that has to be generated by the machine at a particular location.

Niino *et al.* (1987) first proposed the concept of manufacturing a thermally graded metal-to-ceramic phase for a thermal barrier application. An FGM was seen as an “inhomogeneous composite”, in which the material’s mechanical, physical, and chemical properties change continuously, and which have no discontinuities within the material. FGMs have been intensively investigated since then.

Meanwhile it has become common practice to use the term FGM not only for composites, as defined above, but also for all materials with a macroscopic property gradient. Thus, materials containing only one phase such as graded glasses or graded single crystals are also FGMs. In such materials the spatial property variation is caused by a gradient in chemical composition. The vast majority of FGMs are composite materials with a macroscopic micro-structural gradient i.e., with more than one phase present. For example, the composite may contain a spatially varying volume fraction of one of the phases (Fig. 1(a)). On the other hand, a composition gradient is not inherent to all FGMs. Microstructural gradients may also be obtained in composites by changing the shape (Fig. 1(b)), orientation (Fig. 1(c)), or size (Fig. 1(d)) of the dispersed phase.

There are a number of possibilities to classify graded materials (Cherradi *et al.*, 1994; Neubrand and Rödel, 1997):

- (1) According to the relative extension of the gradient, i.e., to what extent the gradient is distributed across a component. In a bulk FGM the property variation extends over a large part of the component, whereas in a graded coating or joint it is restricted to a volume near the surface of the material or to a restricted interfacial region.
- (2) According to the material classes which the graded component combines, e.g., metal/ceramic, polymer/ceramic, metal/metal, ceramic/ceramic, etc. In this text we will focus on FGM in which one of the materials/phases is a ceramic compound.

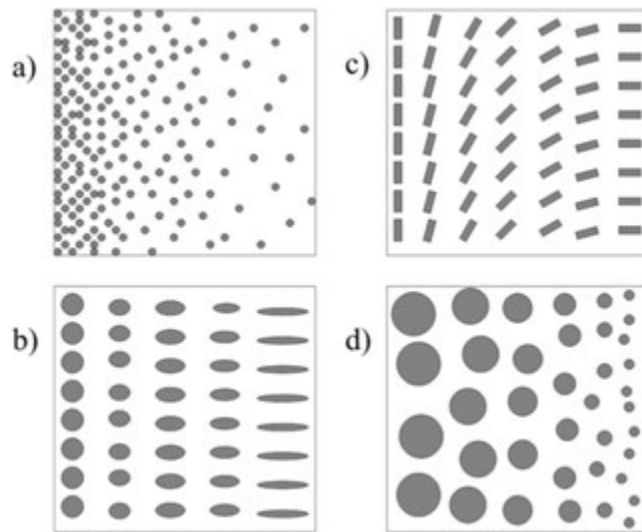


Fig. 1 Different types of functionally graded composites. Gradient of: (a) fraction, (b) shape, (c) orientation, and (d) size of material. Reproduced from Neubrand, A., 2001. Functionally graded materials. In: Jürgen Buschow, K.H., Cahn, R.W., Flemings, M.C., *et al.* (Eds.), *Encyclopedia of Materials: Science and Technology*. Amsterdam: Elsevier, pp. 3407–3413, (ISBN: 0-08-043152-6).

Properly designed property gradients in materials lead to a performance that cannot be achieved with a homogeneous material or by the joining of two different materials. The gradient can thus be regarded as an additional material design parameter which may be adapted and optimized to meet the requirements of a particular application. This leads to the unusual situation that the performance of the material is strongly influenced by geometric factors such as the shape of the material, and the extension and profile of the property gradient. Thus, a gradient material cannot be fully characterized by materials constants only, and already comprises certain aspects of the design of a component. Hence material selection and component design are closely intertwined and one cannot be divorced from the other. The gradient composition in FGMs results not only in a spatial variation in properties but will also generate residual stresses, which will affect the mechanical properties. One of the potential advantages of FG components is the positive influence of compressive residual surface stresses on the strength and wear resistance. A correct design of the gradient for an optimal distribution of the residual stresses is therefore important, as discussed later.

The present summary builds on and updates reviews that both authors have been involved in during the early years of FGM research (Neubrand, 2001; Anné *et al.*, 2006). Due to the context of this chapter the focus will be on FGM systems involving ceramics and glasses, i.e., functionally graded ceramics and glasses. Examples involving other materials may occasionally be referred to in order to inspire further research on ceramic containing FGMs. It is worth mentioning also that because of the large differences in stiffness between ceramics on one side and metals and polymers on the other side, functionally graded transitions between these classes of materials have been widely investigated.

As research on FGM has matured, FGMs are becoming of greater interest for numerous applications, including aerospace engineering, nuclear power generation, sensors, biomedical implants, optoelectronic devices, and energy absorption systems. Some FGM applications involving ceramics will be discussed at the end of this chapter.

Theoretical Research

The steepness of the gradient in an FGM can be described by the use of a transition function $f(x,y,z)$. In many practical cases the compositional variation will be restricted to one coordinate, say z , and different gradients can then be described by a so-called transition function of the type:

$$f(z) = (z/d)^p \quad (1)$$

where f denotes the composition or volume fraction of one of the phases, d is the thickness of the graded region, and p is the so-called gradation exponent.

Most of the theoretical research on FGMs has been devoted to their macroscopic mechanical and thermal behavior and there has been considerable progress in understanding the effects of gradients on the stress distribution within such materials (reviewed by Suresh and Mortensen, 1998). A gradation of the elastic modulus and/or of the thermal expansion coefficient changes the stress distribution in a component when it is mechanically or thermally loaded. A simple but illustrative example is a three-layered beam of infinite length in the x -direction, and unit width in the z -direction. In the y -direction it consists of two homogeneous layers of thickness h_1 and h_2 and a graded interlayer of thickness g (Fig. 2). For this simple geometry the stresses inside the beam can be conveniently calculated using classical continuum mechanics. It is assumed that plane stress conditions prevail in the center of the

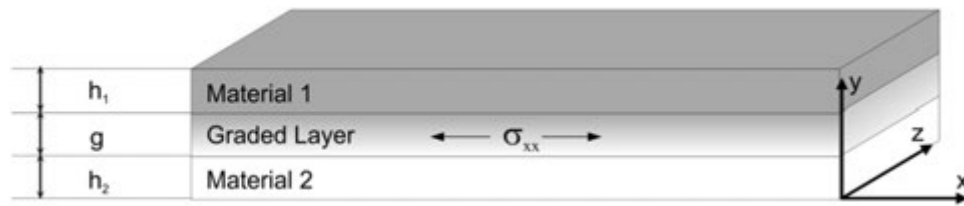


Fig. 2 Geometry of FGM bar used for stress calculations. Reproduced from Neubrand, A., 2001. Functionally graded materials. In: Jürgen Buschow, K.H., Cahn, R.W., Flemings, M.C., *et al.* (Eds.), *Encyclopedia of Materials: Science and Technology*. Amsterdam: Elsevier, pp. 3407–3413, (ISBN: 0-08-043152-6).

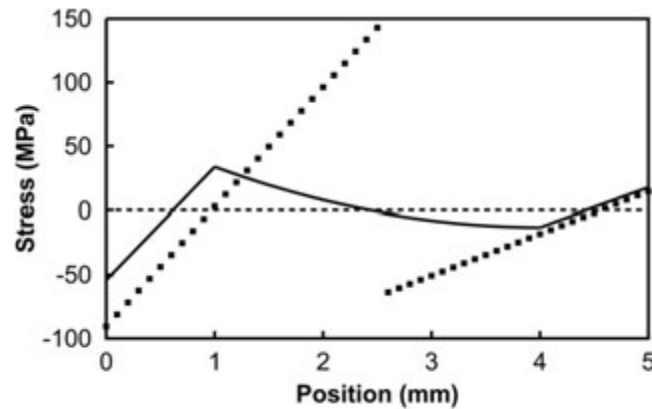


Fig. 3 Stresses σ_{xx} along the y -axis of a thin Cu/Al₂O₃ bar after a temperature change of 100K from the stress-free temperature: ■ ■ ■ ■ ■: direct joint; —: with graded layer of 3 mm thickness in the center;: linear gradation across the entire thickness of the bar. Reproduced from Neubrand, A., 2001. Functionally graded materials. In: Jürgen Buschow, K.H., Cahn, R.W., Flemings, M.C., *et al.* (Eds.), *Encyclopedia of Materials: Science and Technology*. Amsterdam: Elsevier, pp. 3407–3413, (ISBN: 0-08-043152-6).

beam. If the beam is subjected to a uniform temperature change from a stress-free temperature, a strain gradient in the thickness direction y will evolve due to the difference in thermal expansion of the two materials and the beam will bend. The only nonzero stress in the center of the beam is $\sigma_{xx}(y)$. The stress distribution $\sigma_{xx}(y)$ for a Cu/Al₂O₃ beam of 5 mm thickness after a uniform temperature change of 100K is shown in Fig. 3. In the case of a simple bimaterial ($g = 0$, $h_1 = h_2 = 2.5$ mm) a large stress jump with high compressive stresses in the Al₂O₃ and high tensile stresses in the copper is predicted near the interface. If a layer that possesses a linear variation of thermal expansion coefficient and elastic modulus from copper to Al₂O₃ is introduced in the central part of the beam ($h_1 = h_2 = 1$ mm, $g = 3$ mm, exponent p of the transition function = 1), the stresses $\sigma_{xx}(y)$ will be substantially reduced and the abrupt change in sign of the stress disappears. Instead, a gradual transition from tensile to compressive stress is observed and the stress becomes zero in the center of the beam. If desired, the exact location y , where $\sigma_{xx}(y)$ vanishes can be shifted to a different position by choosing an appropriate transition function. If the linear gradation of the thermal expansion coefficient extends over the whole plate thickness ($h_1 = h_2 = 0$, $g = 5$ mm), the thermal stresses will even vanish completely, although differences in thermal strains across the bar will always be present and the bar will bend after a uniform temperature change of 100K. On the other hand, if the graded layer is thin compared to the homogeneous layers ($g < h_1 + h_2$) the force balance inside the whole beam will not be affected and the stress reduction in the nongraded part will be negligible.

It should be pointed out that a stress reduction in bimaterials is not a general feature of FGMs. For arbitrary geometry and loading situation, the gradient will not always lead to a decrease in stress. However, a properly chosen gradient in the elastic properties can aid in redistributing stresses in a favorable manner. This can be an important feature in situations where the size or shape of a component is restricted.

So far, only stresses in the interior of an FGM have been considered. There is another important effect of the gradient on the stresses at the free edge of the beam, in particular at the locations where the interface intersects the free boundaries. Assuming elastic material behavior, the stresses become singular (infinite) at these locations. A similar stress singularity for the stress σ_y and the shear stress τ_{xy} is predicted at an elliptical pore located at the interface of dissimilar materials (Yang *et al.*, 1997). The stress concentrations at the free edges or pores are sites where the nucleation of critical cracks (leading to delamination) is likely to occur. If a graded zone with continuously varying mechanical properties is introduced, the stresses at the free edge of the interface become finite (Yang, 1998). It was also demonstrated that the introduction of a gradient leads to finite values of σ_y and zero shear stresses τ_{xy} at a pore located at an interface. It is therefore expected that delamination cracking in bimaterial joints or coatings can

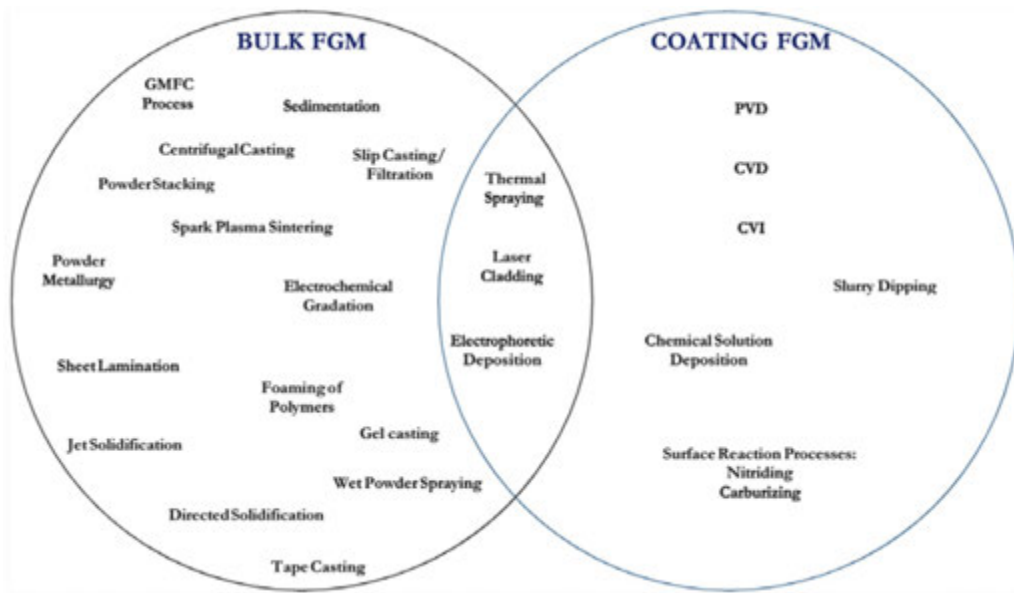


Fig. 4 Overview of conventional manufacturing methods (CM) for FGM materials. GMFC: gradient materials by foam compaction (Kieback *et al.*, 2003); PVD: Physical vapor deposition; CVD: Chemical vapor deposition; CVI: Chemical vapor infiltration. Reproduced from Naebe, M., Shirvanimoghaddam, K., 2016. Functionally graded materials: A review of fabrication and properties, *Appl. Mater. Today*, 5, 223–245. Published by Elsevier.

be substantially reduced or suppressed by the introduction of a property gradient. This rather universal feature of FGM's is particularly relevant for graded ceramics where stress concentrations or singularities cannot be relaxed by plastic flow.

In the above, only the effect of a gradient in elastic and thermal properties on the stress distribution in a crack-free material was discussed. However, a gradient will not only affect crack initiation, but also the mechanical energy release rate of an existing crack. Fracture mechanics calculations show that an edge crack propagating along the interface of a homogeneous coating possesses a higher mechanical energy release rate compared to a crack in a graded coating (Erdogan, 1995). Furthermore, a suitable local variation of fracture toughness and subcritical crack growth behavior can improve the fatigue life of a component considerably. An example is a titanium alloy with gradual transition from a fully aged, brittle, high-strength surface to a ductile, low-strength interior, which leads to a considerably improved high-cycle fatigue strength (Berg and Wagner, 1999).

Processing Techniques for FGM

A large part of the research work on FGMs has been dedicated to processing and a large number of production methods have been developed (reviewed by Suresh and Mortensen, 1998; Neubrand and Rödel, 1997; Kieback *et al.*, 2003). Initially, most of the processes for FGM production were based on a variation of conventional manufacturing methods (CM) which are already well established. Later on, around 2010, additive manufacturing (AM) methods have been explored and have given the research field of FGM a new boost. AM will be discussed in detail below. Fig. 4 (Naebe and Shirvanimoghaddam, 2016) shows an overview of the CM methods. Which of these production methods is most suitable depends mainly on the material combination, type of transition function required, and geometry of the desired component.

When selecting the processing method, the property difference of the two constituent phases of the FGM is of primary importance. In a compositional FGM for example, the difference in heat resistance between the two phases is a key factor. If the two phases have a significantly different melting point, like in ceramic/metal FGMs, the composition gradient can be formed by producing a porosity gradient preform of the refractory phase subsequently infiltrated by the molten metallic phase to get a dense final product. If the two phases have a similar melting point, infiltration cannot be used because the skeleton cannot keep its strength during infiltration. The dimension and geometry of the FGM has to be considered as well. For instance, it is feasible to produce FGMs in many material systems with thermal spraying technologies. Their low efficiency however makes them useless for the production of three-dimensional bulk FGMs.

Conventional manufacturing methods (CM) can be broadly classified into two fields: bulk processing methods such as sedimentation, powder stacking, and centrifugal casting, and coating methods (Fig. 4). Table 1 presents a summary of various fabrication techniques for FGMs. Some studies describe bulk processes. Other processes are only suitable for the coating of surfaces for instance by slurry dipping, chemical solution deposition, and chemical vapor deposition. Some methods sit in between these two categories, such as thermal spraying, laser cladding, and electrophoretic deposition. However, even with one of the most widely accepted and applied CM methods, that is, the thermally sprayed coatings, limitations are obvious because they can only

Table 1 An overview of conventional manufacturing methods for FGM processing

Classifications	Techniques	Characteristics	Materials	Applications	References
Gas phase processes	Vapor deposition (CVD/CVI/CVS)	Energy intensive, low efficiency	SiC/C, TiC/SiC, ZnO TiO ₂ /Ti-O-Si etc.	Optoelectronics and electronics	Sasaki and Hirai (1994); Seifried <i>et al.</i> (2001), Wang <i>et al.</i> (2014)
	Thermal spraying	Optimal technological conditions affected by various parameters	ZrO ₂ /NiCrAlY, Polyimide/WC-Co, CeO ₂ -Y ₂ O ₃ -ZrO ₂ , etc.	Aerospace, military and commercial	Heimann (1996), Khor and Gu (2000), Ivosevic <i>et al.</i> (2005), Pakseresht <i>et al.</i> (2014), (2015)
	Surface reaction process	Depended on diffusing reactive gases, surface contact reactions	Titanium alloys, WC-Co/Ni, etc.	Surface treatment for metals	Guo <i>et al.</i> (2011), Liang <i>et al.</i> (2003), Zhecheva <i>et al.</i> (2005)
	Sedimentation casting	Gravity/centrifugal forces	Metals	Special needs like forging, poor plasticity	Fishman (1988), Fu <i>et al.</i> (2008), Arsha <i>et al.</i> (2015), Mahmoodian <i>et al.</i> (2014)
Liquid phase processes	Combustion	Productive, energy saving,	TiC-Fe-Al ₂ O ₃ , TiC-Ni, TiC-Cu	Nanomaterials, ceramic and catalyst industries	Matson and Munir (1992), Zhang <i>et al.</i> (2000), Shon and Munir (2005)
	Tape casting	Raw materials control drying and sintering processes	Ceramic powder	Multilayer ceramic substrates	Hotza and Greil (1995), Yeo <i>et al.</i> (1998)
	Gel casting	Time-saving, environmental-friendly, low-cost	Mixed dispersant, monomer, dimer, initiator and catalyst	Ceramic components	Tallon and Franks (2011)
	Electrophoretic deposition	Simple processes and equipment, little restriction in shape, no binder burnout	ZrO ₂ /Al ₂ O ₃ and WC/Co, HA-TiO ₂ , Ti-6Al-4 V, etc.	Emitter for electrons, ceramic appliances	Farnoush <i>et al.</i> (2015), Put <i>et al.</i> (2003b), Besra and Liu (2007)
Solid phase processes	Spark plasma sintering, laser direct deposition	Short processing time fine microstructure	ZrB ₂ -SiC/ZrO ₂ , ZrO ₂ and B ₄ C, etc.	Wear resistant materials, fabrication of glass-lens molds	Hong <i>et al.</i> (2008), Wilson and Shin (2012)
	Powder metallurgy	Good control of microstructure and composition	Mullite/Mo, hydroxyapatite (HA)-Ti, etc.	Auto industry and equipment manufacturing industry	Ma and Tan (2001), Takeuchi Jin <i>et al.</i> (2005)

Note: After Li, Y., Feng, Z., Hao, L., *et al.*, 2020. A review on functionally graded materials and structures via additive manufacturing: From multi-scale design to versatile functional properties. *Adv. Mater. Technol.* 5, 1900981.

construct simple FGM objects with uncomplicated gradient structures. Methods that are capable of accommodating a gradation step include powder processing, thermal spraying, melt processing, and coating processes. These will now be reviewed in turn.

Powder Processing

Shaping and consolidation processes for FGMs

For the fabrication of bulk FGMs, powder processing is most economic and suitable for mass production. The processes used for powdered ceramics are in principle the same as those used for powdered metals i.e., powder metallurgy (PM) processes. However, some ceramics, in particular non-oxides can be produced from the so-called pre-ceramic polymers. In order to produce a FGM by conventional powder processing, a green body with the desired gradient in phase volume fraction is first fabricated. After shaping and consolidation, this green body has to be densified by sintering.

The gradation methods can be divided into two groups: dry and wet processes (Fig. 5, Neubrand and Rödel, 1997). Dry processes are fast, but in general only allow to generate step-graded profiles. In wet processing, a drying step is required for the removal of the liquid but continuous mixing is facilitated and smoother continuous gradients may be produced. Furthermore, transport processes occurring in suspensions, e.g., sedimentation and electrophoresis, may be used to produce gradients at low cost. The main challenge associated with powder processing is frequently the densification of the graded powder compact. Sintering rates differ with position and uneven shrinkage may lead to warping and cracking, unless sophisticated sintering techniques are employed.

A widely used technique for ceramic/ceramic gradient materials is sequential slip casting where slips of different compositions are cast one after and over another (Requenna *et al.*, 1993). By using a premixing system, the casting composition can be tailored continuously (Chu *et al.*, 1993).

In a process called wet spraying (Schindler *et al.*, 1998), suspensions of two powders are created, and mixtures of variable composition are sprayed on a heated substrate in a computer-controlled process. After forming, the green body is removed from the substrate, for bulk FGMs, or bonded with the substrate, for FGM foils. Centrifugal casting (Fukui *et al.*, 1994; Watanabe *et al.*, 1998) is another FGM consolidation method using suspension mixing to realize the gradient. When suspensions of two powders of different density or different grain size are mixed and injected into a cylindrical cavity, which is rotating at high speed, the centrifugal forces cause a compositional or porosity gradient in the growing powder compact in the radial direction. Before stopping the rotation, wax is injected into the system to bind the powders in order to increase the green strength for body

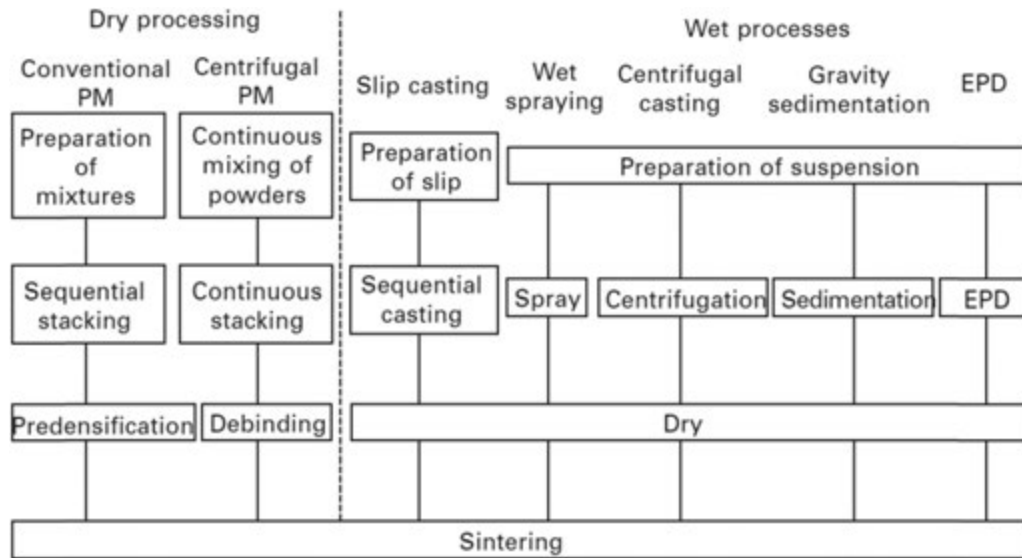


Fig. 5 Conventional manufacturing (CM) via powder processing, also called powder metallurgy (PM) for bulk FGM (after Neubrand and Rödel, 1997). Reproduced from Anné, G., Vleugels, J., Van der Biest, O., 2006. Functionally graded ceramics. In: Low, I.M. (Ed.), *Ceramic-Matrix Composites: Microstructure, Properties and Applications*. Cambridge: Woodhead Publishing Limited. pp. 575–596.

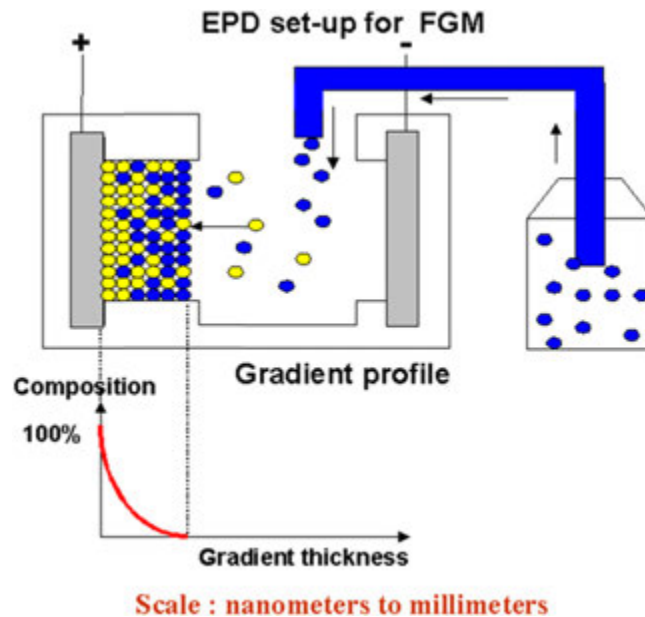


Fig. 6 Electrophoretic deposition (EPD) process for FGM materials. Reproduced from Anné, G., Vleugels, J., Van der Biest, O., 2006. Functionally graded ceramics. In: Low, I.M. (Ed.), *Ceramic-Matrix Composites: Microstructure, Properties and Applications*. Cambridge: Woodhead Publishing Limited. pp. 575–596.

handling. The porous FGMs with a gradient distribution in porosity can be used as a pre-form for filters, or for ceramic membranes. A process similar to centrifugal casting is gravitational sedimentation (Bernhardt *et al.*, 1999). Centrifugal casting can only be used for cylindrically shaped parts, whereas gravitational sedimentation is suitable for flat FGMs.

Among the different colloidal processing techniques, electrophoretic deposition (EPD) is a very promising method (Put *et al.*, 2003a,b, 2002; Vleugels *et al.*, 2003; Anné *et al.*, 2004) because it is a fairly rapid, low-cost process for the fabrication of ceramic coatings, monoliths, composites, laminates and functionally graded materials varying in thickness from a few nanometers to centimeters (Van Der Biest and Vandeperre, 1999). Electrophoretic deposition is a two-step process (Fig. 6). In a first step, particles having acquired an electric charge in the liquid in which they are suspended are forced to move towards one of the electrodes by applying an electric field to the suspension (electrophoresis). In a second step (deposition), the particles collect at one of the

electrodes and form a coherent deposit on it. The deposit takes the shape imposed by this electrode. After drying and removal from the electrode, a shaped green ceramic body is obtained. Firing this green body then results in a ceramic component. Gradient materials can be obtained since the composition of the next powder layer that deposits is determined by the composition of the suspension at that moment (Fig. 6). Judiciously adapting the powder concentration in the suspension allows to generate a well-controlled gradient profile in a continuous shaping step. The process is not material specific, since a wide variety of materials including metal powders, ceramics, glasses, and polymers have already been deposited (Van Der Biest and Vandeperre, 1999). In general, the only shape limitation is the feasibility to remove the deposit from the electrode after deposition.

Continuously graded materials in the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ (Vleugels *et al.*, 2003c), ZrO_2/WC (Put *et al.*, 2002), and WC/Co (Put *et al.*, 2001) system have been explored by means of EPD. A prerequisite for successful production of FGM materials by means of EPD is

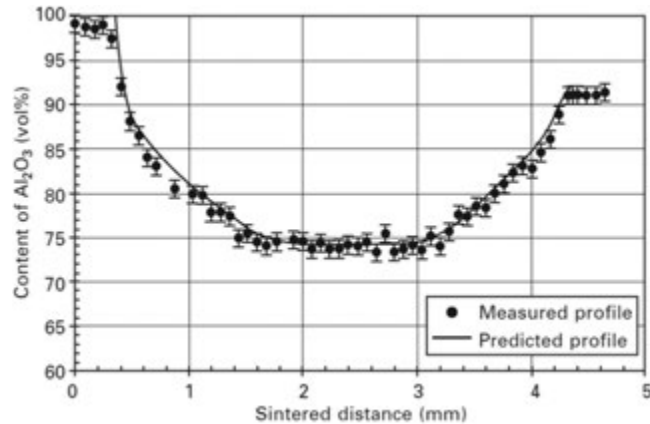


Fig. 7 Measured and FGM profile predicted from a model by Put *et al.*, 2003c, for $\text{Al}_2\text{O}_3/\text{ZrO}_2$ FGM disk, prepared by electrophoretic deposition (EPD). Reproduced from Anné, G., Vleugels, J., Van der Biest, O., 2006. Functionally graded ceramics. In: Low, I.M. (Ed.), *Ceramic-Matrix Composites: Microstructure, Properties and Applications*. Cambridge: Woodhead Publishing Limited. pp. 575–596.

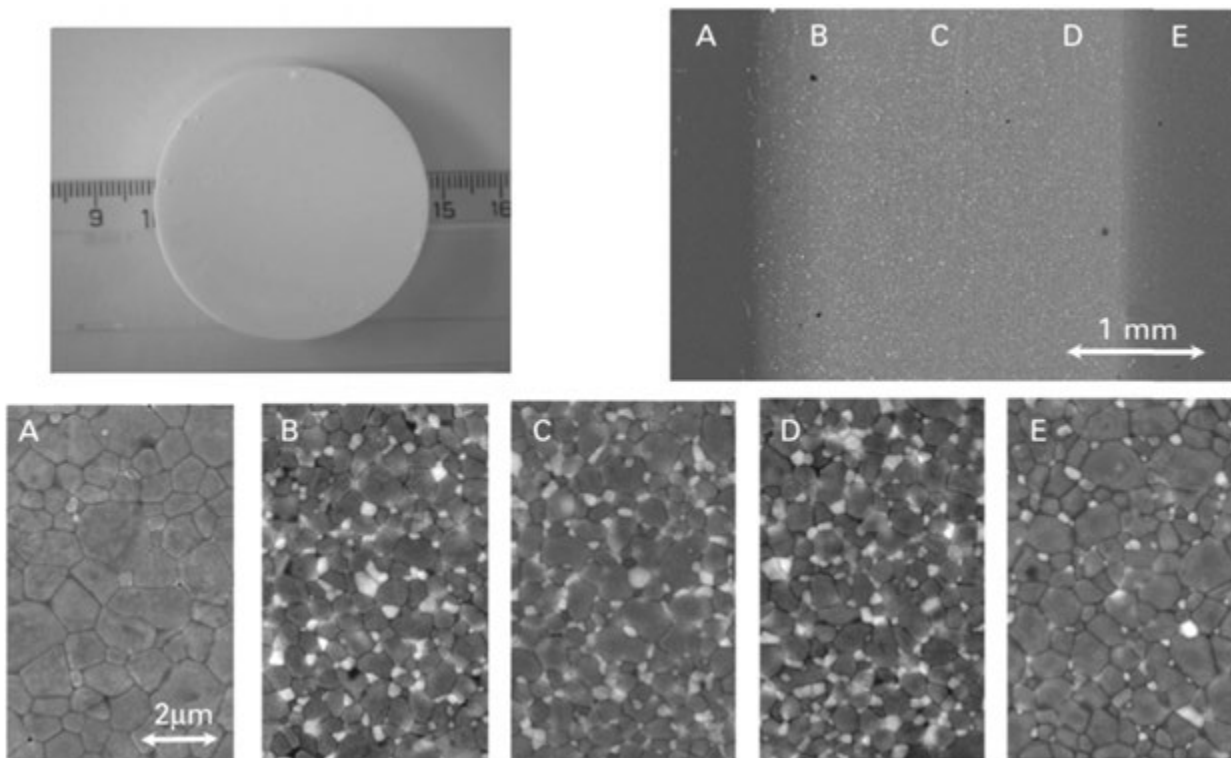


Fig. 8 General overview and some detailed micrographs of specific locations in an $\text{Al}_2\text{O}_3/\text{ZrO}_2$ FGM disk. Al_2O_3 gray contrast; ZrO_2 bright contrast. Reproduced from Anné, G., Vleugels, J., Van der Biest, O., 2006. Functionally graded ceramics. In: Low, I.M. (Ed.), *Ceramic-Matrix Composites: Microstructure, Properties and Applications*. Cambridge: Woodhead Publishing Limited. pp. 575–596.

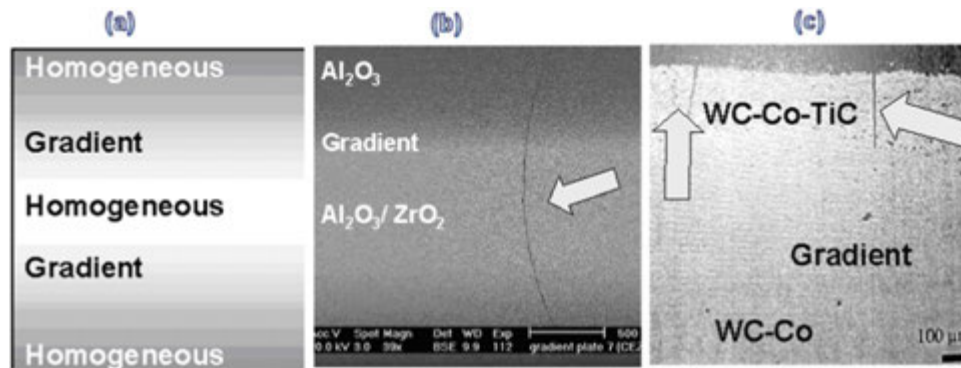


Fig. 9 FGM schematic (a) and typical cracks marked by broad white arrows, observed in $\text{Al}_2\text{O}_3/\text{TZP}$ (b) and WC-Co-TiC (c) FGM. Reproduced from Anné, G., Vleugels, J., Van der Biest, O., 2006. Functionally graded ceramics. In: Low, I.M. (Ed.), *Ceramic-Matrix Composites: Microstructure, Properties and Applications*. Cambridge: Woodhead Publishing Limited. pp. 575–596.

a full control of the kinetics of the process. Kinetic models have therefore been developed for processing an FGM in a multi-component system by means of EPD (Put *et al.*, 2003a). As an example, the composition profile (Fig. 7) and the microstructure (Fig. 8) of an $\text{Al}_2\text{O}_3/\text{ZrO}_2$ FG disk (Vleugels *et al.*, 2003) with a homogeneous composite core (75 vol% Al_2O_3), a pure Al_2O_3 surface layer on one side and a homogeneous composite (90 vol% Al_2O_3) on the other side, and intermediate symmetrically profiled graded layers is presented. As will be explained below, a convex alumina gradient profile is suggested to result in the highest compressive stress in the alumina outer layers and the lowest tensile stresses in the core of the disk. The ZrO_2 (white) and Al_2O_3 (gray) phases can be clearly differentiated in the microstructure. The ZrO_2 phase is well dispersed in the Al_2O_3 matrix in the gradient parts and in the core of the FGM.

Densification of FGM powder compacts

Almost all ceramic/ceramic bulk FGMs are densified by conventional pressureless sintering (Wu *et al.*, 1996; Marple and Boulanger, 1994; Cichocki and Trumble, 1998) or hot pressing (Kawai and Wacamatsu, 1995; Vanmeensel *et al.*, 2004), depending on the sintering properties of the two components. In metal/ceramic FGMs with a continuous metal phase and a discontinuous ceramic phase, the sintering rates are controlled by the densification of the metal phase and such FGMs can be densified by conventional sintering methods (Neubrand and Rödel, 1997). In most FGMs where a high ceramic phase content is envisaged however, some special approaches have to be considered for full densification. The major problem when sintering FGMs are the sintering rates which may differ by orders of magnitude depending on composition leading to cracking or warping of the compacts. Numerous efforts to counterbalance unequal sintering activity have been undertaken (Miyamoto *et al.*, 1999), including adaptation of particle size of the powder components in such a way that the sintering rate becomes similar over a wide range of temperature, and addition of a sintering aid to the more refractory component to increase its sintering rate. Local sintering rates can also be equalized by sintering in a temperature gradient which can be produced by laser surface heating or plasma-activated sintering in a stepped or tapered die (Tokita, 2003). Hot pressing is also an efficient means to prevent deformation. It should be born in mind that when sintering succeeds and a near full density FGM material is obtained at the sintering temperature, thermal stresses may originate during cooling due to differences in thermal expansion coefficients between the phases. The inability of the phases to accommodate these stresses by plastic deformation may lead to permanent residual stresses in the microstructure, which when they exceed the local strength of the material, will lead to cracks. Hence, due to excessive thermal residual stresses, cracks and other defects may often be observed in the final FGM component unless properly manufactured.

Fig. 9 shows typical cracks observed in symmetrically graded $\text{Al}_2\text{O}_3/\text{ZrO}_2$ (b) and WC-Co-TiC (c) disks, shaped by electrophoretic deposition and densified by pressureless sintering. Transverse cracks were observed in the ZrO_2 -rich core of the sintered symmetric TZP/ Al_2O_3 disks. The crack propagation however stopped in the outer pure Al_2O_3 layer indicating that the in-plane tensile stress is located in the center of the disks, which should be lowered. Transverse cracks were also observed perpendicularly to the surface at both outer TiC-containing sides in symmetrical WC-Co/TiC FGM disks (see Fig. 9(c)). In this case, the outer surface is facing higher tensile stresses during sintering.

Hillman *et al.* (1996) observed similar defects in symmetrical laminates with $\text{Al}_2\text{O}_3/\text{ZrO}_2$ layers at the surface and a ZrO_2 central layer. Cai *et al.* (1997a,b) discussed the embryonic stage of a sinter crack as observed in Fig. 9(b), and found regions of low density and cavitation defects in $\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{Al}_2\text{O}_3$ laminates. These defects are most susceptible to residual tensile stresses during cooling in the core, due to the higher coefficient of thermal expansion (CTE) of zirconia. These regions of lower density (pores) must have formed as a result of the tensile stress that develops during the differential shrinkage during densification between the Al_2O_3 and the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ layers. The pores then act as pre-existing flaws for the generation of thermal expansion mismatch cracks during cooling via linkage of the pores and cavitation defects.

Elimination of the transverse cracks can be accomplished by decreasing the overall shrinkage of the composites. This is done by either decreasing the compositional difference between the different layers (Cai *et al.*, 1997a,b), or by adjusting the green density of

the different layers (Novak *et al.*, 2005). Another possibility is to decrease the cooling and heating rate during sintering (Cai *et al.*, 1997b). The mismatch stresses during the heating cycle are decreased by the viscous nature of the FGM material at the sintering temperature. The sintering mismatch stress is proportional to the mismatch sintering rate. Reduced cracking under a slow cooling rate is probably due to the relaxation of residual stresses during the initial period of cooling.

A more advanced technique called Spark Plasma Sintering (SPS) or Pulsed Electric Current Sintering (PECS) (Tokita, 1999) is also used for FGM fabrication. It is a pressure-assisted sintering method in which a high current is pulsed through a die/punch/sample set-up, which can be compared with that of conventional hot pressing. The sintering mechanism and mechanical properties of the sintered compacts show characteristics different from conventional pressure-assisted sintering processes and parts. This technique offers significant advantages for various kinds of new materials and consistently produces a dense compact in a shorter sintering time and with finer grain size than conventional methods. Spark plasma sintering of FGMs can take advantage of a temperature gradient in the system, which allows a homogeneous densification of FGMs by matching the temperature gradient to the shrinkage rate gradient of the compact. With a spark plasma system, large size ceramic/metal bulk FGMs ($d = 100$ mm) can be homogeneously densified in a short time with heating up and holding times totaling less than one hour. Amongst the reported spark plasma sintered systems are WC-based materials (WC/Co, WC/Co/steel, WC/Mo), ZrO₂-based composites (ZrO₂/Steel, ZrO₂/TiAl, ZrO₂/Ni), Al₂O₃/TiAl, etc. (Tokita, 1999). A systematic introduction on the technology of spark plasma sintering can be found in a review by Tokita (1999) and a paper of Hennicke (Hennicke and Kessel, 2004), where the process, mechanical properties, size and shape effects, and production machine systems are reported.

Microwave sintering uses microwave irradiation to heat the ceramic or ceramic-based composite compact (Gerdes and Willert-Porada, 1994; Willert-Porada *et al.*, 1995; Zhao *et al.*, 2000). The mechanism of microwave heating is based on the dielectric loss of the ceramic phases involved, resulting in a volumetric heating technique in which the heat is generated by the compact itself. Microwave Sintering is another promising technique for ceramic/metal FGMs to cope with the inequality of the shrinkage rate.

Coating

Thermal spraying

Thermal spraying has been frequently used to produce FGM coatings. Thermal spraying of FGM's, offers the possibility to combine highly refractory phases with low-melting metals and allows for direct setting of the gradation profile. The powders for each component can be delivered through multiple feeders using a single torch or using separate torches.

Materials produced by thermal spraying have a porosity between 5% and 20%. It is thus particularly attractive for applications where this porosity can be tolerated or is even advantageous such as in graded NiCrAlY/YSZ thermal barrier coatings. There are a number of variants of thermal spraying. Usually, the feedstock consists of dry powder, if necessary agglomerated to improve flowability, that is fed into a plasma torch. Recently the use of liquid feedstock has been investigated where liquid means a suspension of powder but also a solution of a ceramic compound (Joshi *et al.*, 2020). This allows the build-up of coatings with a very variable microstructure including also FGM as shown in Fig. 10 (Björklund *et al.*, 2018).

Thinner graded coatings have been produced by vapor deposition processes such as conventional physical vapor deposition (PVD), electron beam physical vapor deposition (EBPVD), magnetron sputtering, chemical vapor deposition (CVD), and galvanic plating. In all of these processes the composition gradient is produced by a controlled release of the components from a source such as an anode, ingot, liquid, or gas reservoir (see Table 1 for references).

Melt Processing

Bulk FGMs containing a low-melting metal can be favorably produced by melt processing. Particles of the more refractory phase are added to the melt and the gradient is produced by sedimentation or centrifuging during solidification. The more refractory phase can also be provided as a graded preform which is infiltrated with the melt. Processes used to prepare graded preforms include sequential slip casting of dispersions with a variable content of short fibers, weaving long-fiber preforms with a variable content of spacer particles, electrochemical generation of porosity gradients in homogeneous preforms, and in-homogeneous compression of polymer foams. Table 1 gives references.

Additive Manufacturing

Additive manufacturing (AM), often also called 3D printing, is a range of processes whereby parts are built by adding material usually layer by layer directly from a computer-generated 3D model. It can be considered as a near net shape manufacturing process, which can directly manufacture complicated 3D objects without requiring molds, tooling or the need for joining or assembling.

A useful general introduction to AM across all material classes can be found in Gibson *et al.* (2021). Fig. 11 gives an overview of the different steps involved in AM starting with the computer aided design of the part. It is important to realize that computer modeling of the part is an essential activity, in fact the initial activity in AM. Generally, the workflow of AM involves several steps, starting with the modeling (geometrical modeling, materials modeling and microstructural design), slicing, simulation, manufacturing, followed by characterization, and performance analysis. Modeling is an essential part for successful AM and even more so for AM of FGM.

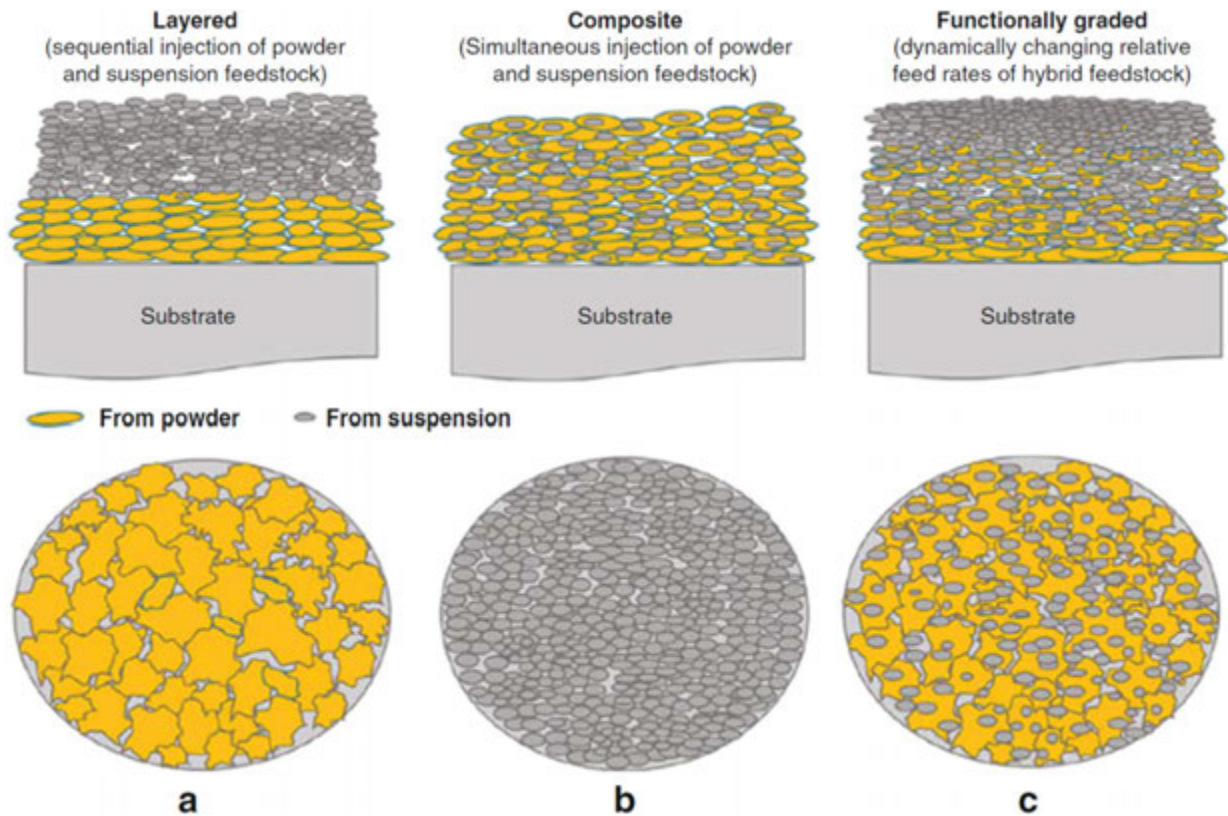


Fig. 10 Schematic illustration of (top) different coating architectures achievable using hybrid powder-liquid plasma spraying including also a FGM coating and (bottom) surface morphologies depicting (a) “coarse” powder derived splats, (b) “fine” splats originating from suspension/solution precursor, and (c) the mixed coarse-fine splats formed in case of a composite coating. Reproduced from Björklund, S., Goel, S., Joshi, S., 2018. Function-dependent coating architectures by hybrid powder-suspension plasma spraying: Injector design, processing and concept validation. *Mater. Des.* 142, 56–65.

Many AM techniques can be adapted to produce FGM components with complex geometry. Since we focus here on FGM with at least one ceramic phase and ceramics are commonly fabricated from powders we will focus here on AM methods which involve the use of powders. The present state of the art for AM manufacturing of homogeneous ceramics can be found in [Lakhdar et al. \(2021\)](#).

Ceramic AM processes can be categorized according to whether they are “single-step” or “multi-step” processes. Multi-step AM processes result in the formation of a green body that requires subsequent debinding and sintering thermal treatments in order to obtain the final part. Most AM technologies, as they have been implemented up until now, belong to this category. On the other hand, there are currently only two AM processes that have been demonstrated to be capable of directly shaping and sintering advanced ceramics in a single-step: [Fig. 12](#) provides a list of ceramic AM processes whereby the distinction between single-step and multi-step processes is made. Another type of ceramic AM is so-called negative ceramic AM. In this process a mold for suspension casting the component is made by AM, not the 3D component itself. The different processing steps in this classification are shown in [Fig. 13](#).

Many AM processes are well suited to accommodate changes in material composition since they are building up the part layer by layer. Another feature of many processes is that they can build up lattice structures. These are single material open, low density but also stiff structures. In addition, it is possible to build graded structures where the density is varied in a programmed way ([Maskery et al., 2016](#)). These are often called Functionally Graded Structures (FGS). In fact, they are a way to vary the density or porosity in a material ([Fig. 14](#)). For another example, see [Choy et al. \(2017\)](#). Some AM processes also allow varying the material composition by a mixing process as a single layer is build up. The combination of density grading and composition grading is also possible.

Direct energy deposition (DED)

DED (also known as Laser Engineered Net Shaping) is a process whereby focused thermal energy is used to fuse materials by melting. As shown in [Fig. 12](#) it is a single-step AM process so that the final geometry of the part and its final properties are defined during the AM process.

During fabrication, ceramic or metal powder particles are fed from a nozzle into the focal point of a laser beam, where the powder is fully melted and solidifies onto the substrate. [Fig. 15](#) shows how a combination of ceramic and/or metal powder and wire can also be used to manufacture composite structures. Feed rates can be adjusted during fabrication to generate composition

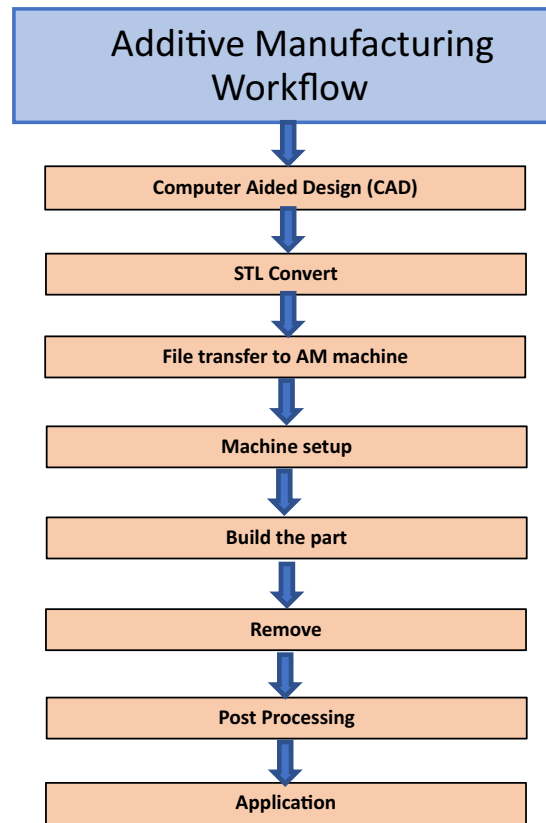


Fig. 11 Generic workflow for additive manufacturing from CAD to the finished part. STL is a file format that can be generated by most CAD programs and is also accepted by most AM machines. Detailed information on the different steps can be found in [Gibson *et al.* \(2021\)](#).

gradients ([Wang *et al.*, 2007](#)). Furthermore, by using several nozzles, DED also enables depositing multiple materials at a time, allowing for the direct fabrication of ceramic-ceramic ([Niu *et al.*, 2015](#)) and metal-ceramic ([Wang *et al.*, 2007](#)) composites. Besides, material composition can also be adjusted by varying the powder feed-rate, thus enabling a fine level of control over both material grading and composition grading.

However, DED has some significant limitations. In the case of ceramics, high thermal gradients and extremely fast cooling rates invariably result in the development of thermal stresses, which usually induce delamination and cracking. Therefore, the energy density of the laser beam – which is a function of laser power, beam spot size, scan spacing and scan speed – must be perfectly controlled and optimized ([Niu *et al.*, 2016](#)). This process parameter optimization is largely material dependent and must be carried out every time the composition or size and morphology of the ceramic powder/wire feedstock is modified. Other disadvantages are the limited geometrical complexity achievable, limited resolution, poor control over the shape of manufactured parts, and its low dimensional and geometrical accuracy, resulting in the need for post-machining to achieve net-shape. The DED process involves complex melting/solidification behavior, and a better understanding of the relationship between starting material composition, process parameters, microstructure, and final properties is required.

Powder bed fusion (PBF)

Similar to DED technology, PBF also uses lasers to build metal or polymer prototypes, and covers various methods including direct metal laser sintering, electron beam melting (EBM), selective laser sintering (SLS) and selective laser melting (SLM).

Direct powder bed fusion (PBF)

The term PBF encompasses AM processes where particles in a powder bed are selectively fused together under the application of a concentrated heat source ([ISO/ASTM, 2015](#)). Three well-known AM technologies fall into the general PBF category: laser melting (LM), laser sintering (LS) and electron beam melting (EBM). Whilst the first two can be used to produce ceramics, the latter is generally not applicable as most ceramic materials are not sufficiently electrically conductive. Several variants of the original laser sintering and laser melting processes, which were initially created to process polymers and metals respectively, have been investigated to adapt them to the specific requirements of ceramics. Local densification of the powder bed can be obtained either by direct laser sintering (dLS) of the ceramic powder itself or by indirect laser sintering (iLS) of a sacrificial organic or inorganic binder phase that acts as a temporary matrix for the ceramic powder until it is removed or converted to a ceramic phase by heat treatment.

Direct Additive Manufacturing of Advanced Ceramics								
Single-step processes		Multi-step processes						
Bedless	Bed	Bed			Bedless			
Directed Energy Deposition	Powder Bed	Fusion	Binder Jetting	Sheet Lamination	Material Extrusion		Material Jetting	Vat Photopolymerisation
LENS	Powder-dLS	Powder-iLS	Powder-BJ	LOM	Wax-based	Water-based	Solvent-DIP	SL
	Slurry-dLS	Slurry-iLS	Slurry-BJ	CAM-LEM	FDC	RC / DIW	Wax-DIP	DLP / LCM
					MJS	FEF		SPPW
					T3DP	CODE		2PP
					PHASE*	3DGP		

LENS: Laser Engineered Net Shaping
dLS/iLS: direct/indirect Laser Sintering
BJ: Binder Jetting
LOM: Laminated Object Manufacturing
CAM-LEM: Computer-Aided Manufacturing of Laminated Engineering Materials
SL: Stereolithography
DLP: Digital Light Projection
LCM: Lithography-based Ceramic Manufacturing
SPPW: Self-Propagating Photopolymer Waveguide
2PP: Two-Photon Photopolymerisation

FDC: Fused Deposition of Ceramics
MJS: Multiphase Jet Solidification
T3DP: Thermoplastic 3D Printing
PHASE: PHotopolymerisation-ASsisted Extrusion - *suggested acronym
RC: Robocasting
DIW: Direct Ink Writing
FEF: Freeze-Form Extrusion Fabrication
CODE: Ceramic On-Demand Extrusion
3DGP: 3D Gel Printing
DIP: Direct Inkjet Printing

Fig. 12 Additive manufacturing (AM) technologies applied to ceramic materials in literature. Reproduced from Lakhdar, Y., Tuck, C., Binner, J., Terry, A., Goodridge, R., 2021. Additive manufacturing of advanced ceramic materials. *Prog. Mater. Sci.* 116, 100736, published by Elsevier.

Direct laser sintering (dLS)

In the PBF AM approach, called direct laser sintering (dLS), a laser selectively scans a powder bed, layer-by-layer, to fuse or sinter material. It can be applied to obtain sintered ceramic parts in a single step directly out of the AM process. The ceramic material itself is brought to a high enough temperature so that it sinters/melts. Alternatively, the laser beam can induce a chemical reaction from a non-ceramic feedstock resulting in the formation of a ceramic material in the brown or sintered state. Ideally, there is no need for post-thermal treatment nor additional densification steps after dLS. However, the inherent properties of technical ceramics, a very high melting point, low thermal shock resistance and plasticity, make dLS of ceramics significantly more challenging than with metals. Indeed, the very short laser-powder interaction time, combined with extreme temperature gradients, tend to result in poor ceramic sintering with high residual porosity and high thermal residual stress causing crack formation (Juste *et al.*, 2014; Kruth *et al.*, 2007). Nevertheless, the dLS process has been investigated for a number of technical ceramics (Lakhdar *et al.*, 2021).

Perhaps the most successful attempt to use dLS has been with reaction bonded silicon carbide (RBSiC) parts produced by dLS from a 67:33 wt/wt SiC/Si powder mixture by Meyers *et al.* (2015). The laser was used to selectively melt the Si in argon atmosphere, resulting in a porous SiSiC preform that was subsequently impregnated with a graphite suspension and infiltrated with molten Si at 1450°C. Highly dense RBSiC parts (95% TD) could be obtained after infiltration. It is debatable whether this should be considered a single-step AM process since the post-AM infiltration was an essential step of the manufacturing process to increase the density of SiSiC parts. However, the AM process still resulted in a fully ceramic part before infiltration was carried out, albeit a very porous one; in principle this process is single-step though it is multi-step in practice due to current limitations that may be overcome in the future.

Since mixtures of powders can be used in this dLS method, it should be possible in principle to induce also a gradient in composition in a direction normal to the plane of the layers, but this has not been reported.

Indirect powder bed fusion

Powder-based indirect laser sintering (p-iLS)

For completeness sake we should mention that a number of methods have been investigated which are called powder based indirect (selective) laser sintering (P-iLS; iLS; SLS; iSLS or P-SLS). In these techniques a coarse ceramic powder, typically 45–90 µm, is mixed with a low melting point polymeric or inorganic binder phase, and local sintering of the powder mix is performed through melting of the binder by the laser beam. The molten and resolidified binder provides a solid matrix for the ceramic powder and keeps the green body together. When polymeric binders are used, the part needs to be “debinded” by heating in a furnace up to a temperature where the organic is removed by decomposition, evaporation or oxidization, followed by furnace sintering at a higher temperature to obtain the final pure ceramic body. P-iLS with organic binders has been used to process a wide range of technical ceramics, including Al₂O₃, SiO₂, ZrO₂, SiC, ZrB₂, as well as apatite-mullite and apatite-wollastonite glass-ceramics. (see Lakhdar *et al.*, 2021). Inorganic binders on the other hand cannot be removed by heat treatment but need to be able

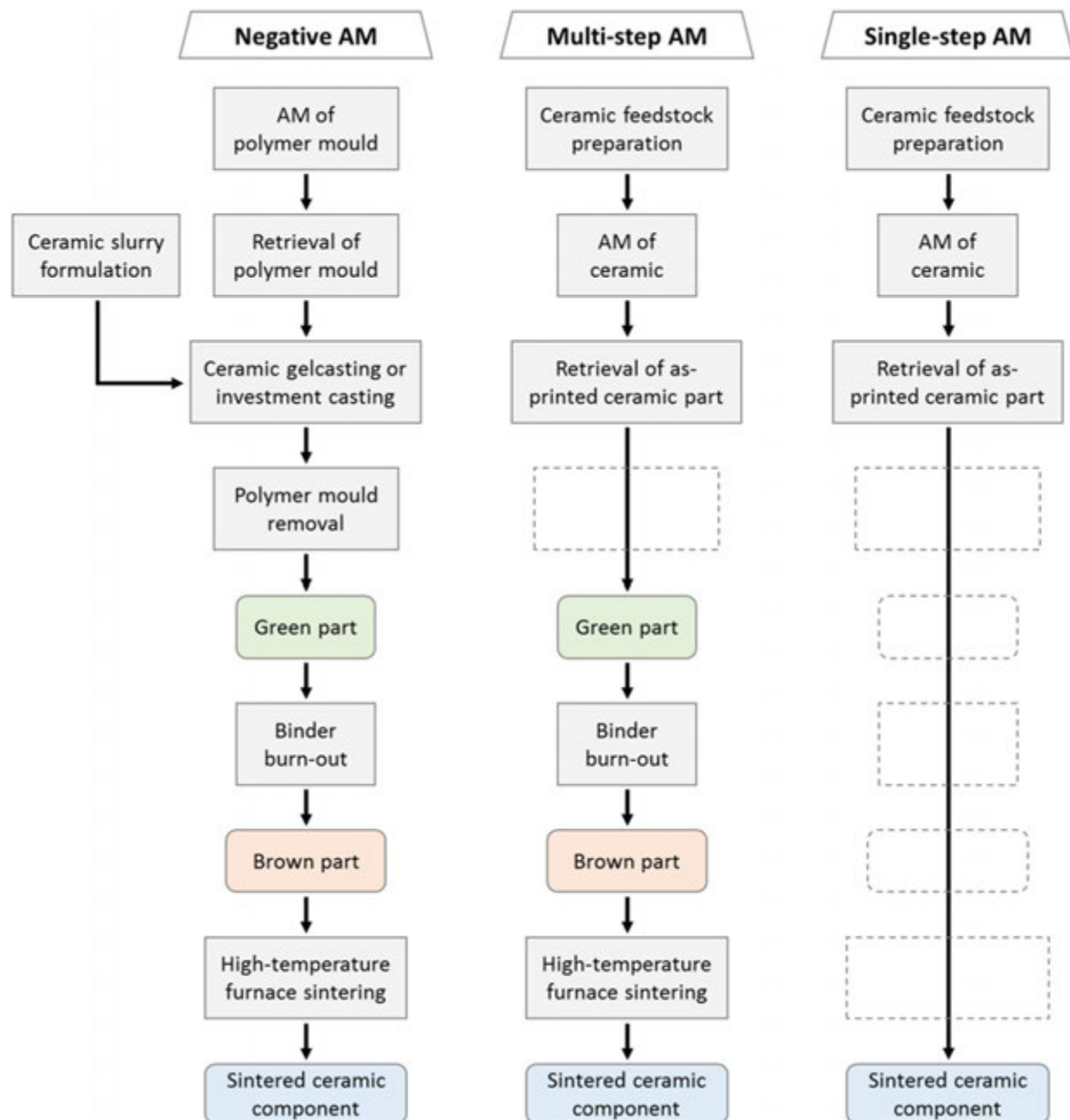


Fig. 13 Flowchart showing the number of steps of negative ceramic AM, multi-step direct AM and single-step direct AM; from AM feedstock to sintered ceramic part. Reproduced from Lakhdar, Y., Tuck, C., Binner, J., Terry, A., Goodridge, R., 2021. Additive manufacturing of advanced ceramic materials. *Prog. Mater. Sci.* 116, 100736., published by Elsevier.

to be converted to for instance a crystalline salt or a ceramic compound. Additional ceramic processing operations can be added to the workflow to enhance density, for instance by infiltration with a suspension of small particles, cold isostatic pressing prior to sintering or hot isostatic pressing (HIP).

Two pre-processing powder preparation methods were developed by Shahzad and Deckers to produce polymer-coated ceramic powders more adapted to the indirect LS process: dispersion polymerization (Deckers *et al.*, 2013) and temperature-induced phase separation (TIPS) (Deckers *et al.*, 2012a; Shahzad *et al.*, 2012, 2013, 2014). However, the benefits of these methods were limited as the formation of inter-agglomerate pores and cracks still occurred, and sintered densities between 36% and 66% only were achieved without post-processing. The same research team also investigated the influence of several post-LS densification strategies on the final density of complex-shaped alumina parts: laser remelting; cold, warm or quasi-isostatic pressing (CIP, WIP and QIP, respectively); and pressure, pressureless or vacuum infiltration of the green or brown body with alumina suspensions (Deckers *et al.*, 2012a,b).

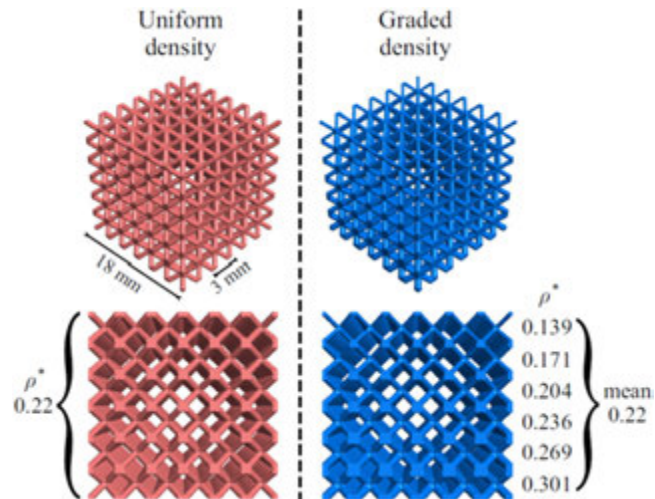


Fig. 14 CAD representations of uniform (left) and a functionally graded density (right) lattice structure (FGS). Reproduced from Maskery, I., Aboulkhair, N.T., Aremu, A.O., *et al.*, 2016. A mechanical property evaluation of graded density Al-Si10-Mg lattice structures manufactured by selective laser melting. *Mater. Sci. Eng. A* 670, 264–274. published by Elsevier.

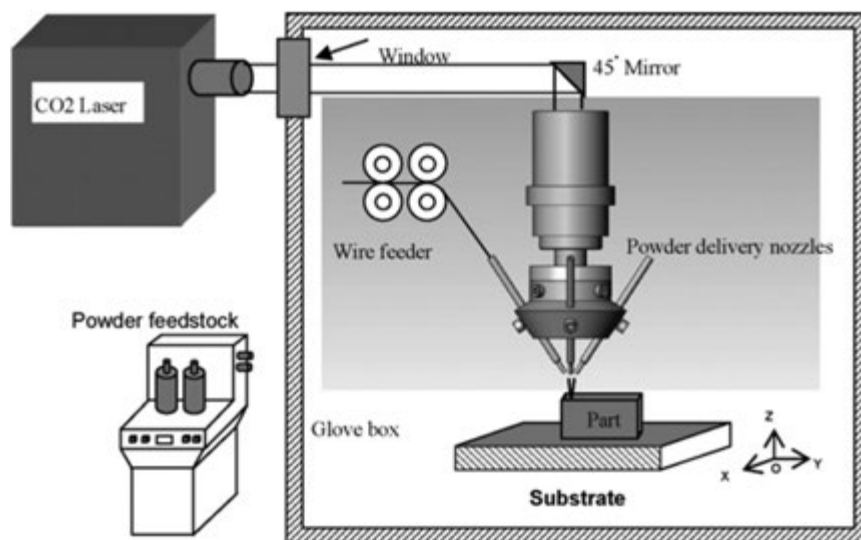


Fig. 15 Schematic of direct laser fabrication with simultaneous powder and wire feed. Reproduced from Wang, F., Mei, J., Jiang, H., Wu, X., 2007. Laser fabrication of $\text{Ti}_6\text{Al}_4\text{V}/\text{TiC}$ composites using simultaneous powder and wire feed. *Mater. Sci. Eng. A* 445–446, 461–466. Published by Elsevier.

Other powder bed based techniques

Binder jetting

Powder bed-based binder jetting is the oldest AM technique invented at MIT in the 1980s (Sachs *et al.*, 1993). 3D structures are generated by placing droplets of binder in computer selected spots in a powder bed of coarse ceramic powder. Locally powder particles are bound together whereas elsewhere they stay loose. When the binder printing is terminated the loose powder is removed and the remaining shaped green body can be further processed by debinding and sintering steps.

One intrinsic limitation of PB processes, including also powder bed fusion and powder bed sintering, comes from the use of dry powders to deposit layers of ceramic material. Only coarse ceramic particles can be used to form layers in dry PBF processes, because fine submicron ceramic powders are subjected to agglomeration by Van der Waals inter-particle forces during layering, which leads to poor powder flow and preventing the formation of uniform powder layers. The use of coarse powders leads to a low density of the final sintered parts. Additional processing steps in the workflow such as isostatic pressing can remedy the situation somewhat but can generally only partially solve the problem of the poor packing density of

the ceramic feedstock that is used for layer formation. Increasing the packing density of the powder bed remains the most critical issue to address in order to prevent the formation of inter-particle and inter agglomerate pores and enable the direct production of fully-dense parts.

One approach that researchers have started to investigate is the incorporation of small amounts of nanoparticles into the binder liquid in order to fill the interparticle voids in the powder bed with finer powders, whereas another approach lies in the use of colloidal slurries instead of coarse dry powders.

Slurry based binder jetting

In Slurry-based binder jetting (s-BJ) the powder bed is formed by depositing layers of ceramic slurries instead of dry powders. Submicron powders can be used which improve the powder bed packing density and therefore also increase green and sintered densities. (Sachs *et al.*, 1993; Grau, 1998; Moon *et al.*, 2000; Kernan *et al.*, 2007). Ceramic green layers can be deposited by different techniques (inkjet printing, slip casting, doctor blading) (Grau, 1998).

As already mentioned, since mixtures of powders can be used, either with dry powders or with slurries it should be possible in principle to induce also a gradient in composition normal to the plane of the layers, but this has not been reported.

Sheet lamination

Sheet lamination processes such as laminated object manufacturing (LOM) and its variants, fabricate desired objects by joining different layers and foils. For each layer, the outline of the part is first cut with a computer-controlled knife or CO₂ laser. Layers are sequentially stacked, cut and bonded. Ceramic green tapes may be produced by tape casting (Cui *et al.*, 2003), extrusion (Weisensel *et al.*, 2004; Zhang *et al.*, 1999), or preceramic paper (polymer) (Windsheimer *et al.*, 2007), to form the desired geometry. A heated roller is then applied on the surface to thermally activate the binder and promote bonding between adjacent layers. LOM works at low temperature and rolling pressure, which helps minimize issues with warping and delamination. The resulting green body needs to be debinded and sintered.

Only few examples in the literature related to FGMs using sheet lamination are found (Zhang *et al.*, 2001; Zeng *et al.*, 2000).

Materials extrusion

Ceramic material extrusion

In this AM process, a ceramic-loaded paste, or polymer filament, or a preceramic polymer filament, is extruded through a nozzle and deposited onto a platform layer-by-layer to form a 3D green body. There are many variants of this process and accordingly also a many different names and acronyms. An overview of these can be found in Lakhdar *et al.* (2021). Important advantages of these ceramic extrusion processes are their relative ease of operation as well as the low manufacturing costs since a high-energy beam is not involved.

The success of these material extrusion processes relies on the precise control of the rheological properties of the extruded paste or filament. Feedstocks must have a high solid loading of well-dispersed ceramic particles to minimize shrinkage and prevent the formation of porosity and cracks during debinding and sintering heat treatments. They must also have a pseudoplastic (shear-thinning) behavior to ensure that the very high starting viscosity decreases by several orders of magnitude when subjected to a small increase in shear rate inside the nozzle during deposition (Baer *et al.*, 1997). These viscoelastic materials are formulated to have a significant yield stress (Fu *et al.*, 2011). Yield stress increases with ceramic loading as well as with the addition of a viscosifying binder. Pastes suitable for extrusion typically have yield stress values ranging between 100 and 1000 Pa (Leu *et al.*, 2011; Rueschhoff *et al.*, 2016; Schlördt *et al.*, 2013; Costakis *et al.*, 2016). There are two main types of ceramic material extrusion processes: (1) wax-based extrusion processes, and (2) water-based extrusion processes.

In wax-based ceramic material extrusion processes, ceramic powders are suspended in a polymeric dispersion medium, and the resulting polymer/ceramic composite paste or filament is extruded through a small orifice onto a platform. Upon deposition the molten feedstock needs to solidify to give strength to the green body as it is built. For polymer-based filament the paste will solidify as the temperature drops below the polymer glass-transition temperature.

These extrusion techniques are well suited to create FGM materials. Scheithauer *et al.* (2015) developed a process called Thermoplastic 3D printing (T3DP), that combines the additive fabrication of metal, ceramic and metal-ceramic composites, and used it to fabricate FGM structure with alternating dense (> 99% TD) and porous (~5% porosity) regions by co-depositing a 36 vol% zirconia suspension and a zirconia suspension containing 5 vol% polysaccharide powder as a pore-forming agent, respectively (Scheithauer *et al.*, 2017).

R&D on wax-based extrusion processes has been reduced in recent years in favor of water-based ceramic extrusion processes. These aqueous pastes are typically characterized by a high ceramic powder loading and a low organic content. Several variants of the ceramic extrusion process are based on this approach. These water-based extrusion techniques have a number of advantages compared to wax-based extrusion: (1) high green densities, (2) simplified debinding schedule, (3) low sintering shrinkage, (4) environmentally-friendly, (5) low cost of feedstock and hardware (Baer *et al.*, 1997).

A well-known example of such a technique is the robocasting process developed by Cesarano *et al.* (1998) at Sandia National Laboratories, USA. In robocasting, which is also often called direct ink writing (DIW), a highly loaded viscous ceramic paste is extruded through a nozzle at ambient temperature and solidifies onto the substrate upon drying in air (Baer *et al.*, 1997). Suspension solidification and shape retention after deposition is due to evaporation of the solvent and the pseudoplastic to dilatant transition that it induces. Other aqueous paste formulations have been developed such as reversible colloidal gels that can coagulate by

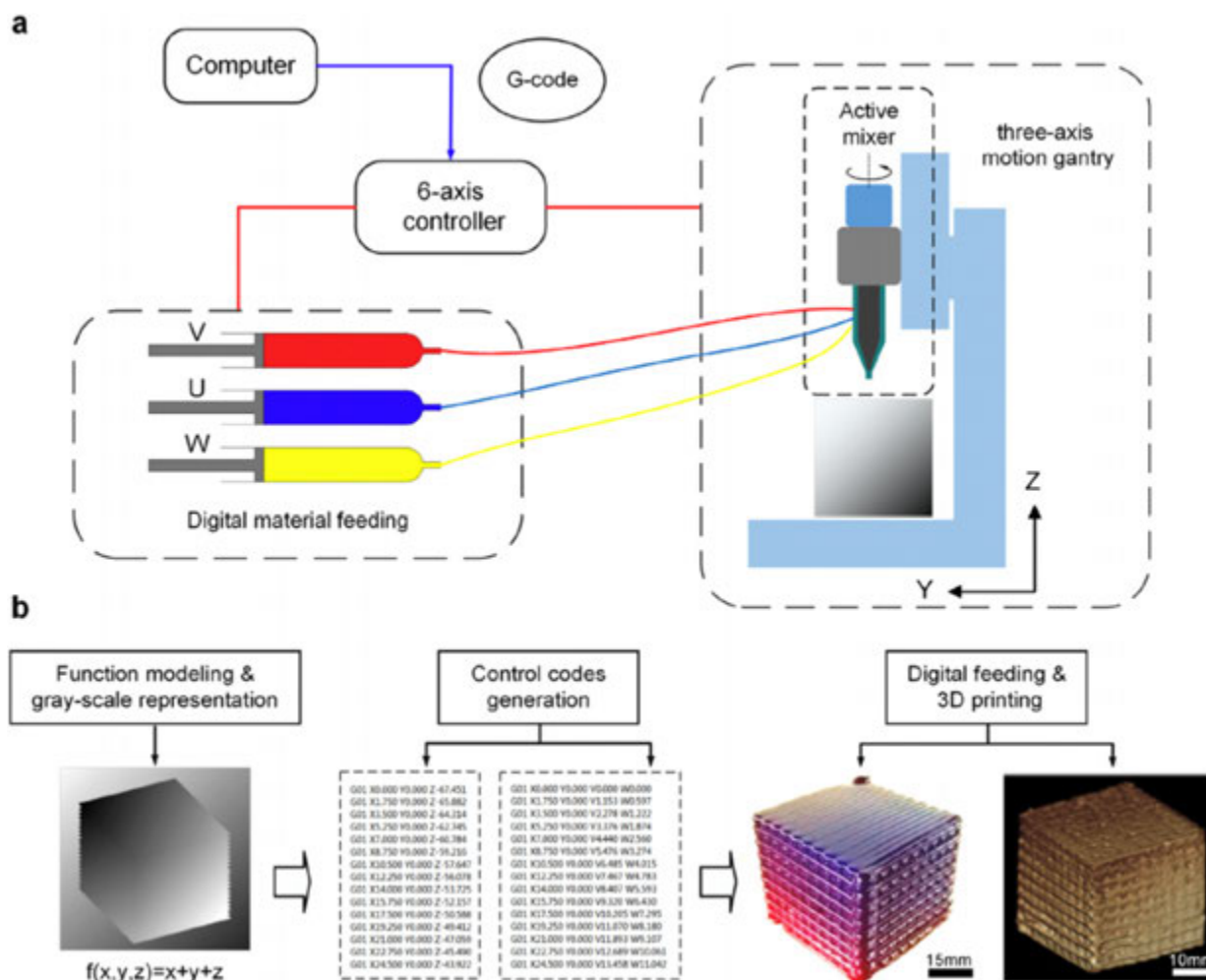


Fig. 16 Gradient 3D printing system. (a) Schematics of the gradient 3D printing mechanical setup and printing control system. (b) Process of gradient 3D printing. Reproduced from Ren, L., Song, Z., Liu, H., *et al.*, 2018. 3D printing of materials with spatially non-linearly varying properties. *Mater. Des.* 156, 470. Published by Elsevier.

controlled flocculation with additions of salts or polyelectrolytes, which set immediately after deposition without drying (Tuttle Bruce *et al.*, 2001; Smay *et al.*, 2002; Nadkarni and Smay, 2006; Feilden *et al.*, 2016). These colloidal inks display improved shape retention properties for the fabrication of free spanning geometries such as lattices (Fig. 14) without support structures.

In freeze-form extrusion fabrication (FEF) an aqueous ceramic suspension or colloidal gel is extruded through a nozzle and frozen onto the cold substrate as it is deposited. A triple-extruder FEF system was developed to fabricate parts with functionally graded material (FGM) structure. Test bars with discrete material grading were produced by varying $\text{Al}_2\text{O}_3/\text{ZrO}_2$ ratios from 100% Al_2O_3 to 50% Al_2O_3 –50% ZrO_2 (Leu *et al.*, 2011, 2012). FGM parts from aqueous-based colloidal suspensions of ZrC and W consisting of a graded composition from 100% ZrC to 50%W–50%ZrC were also produced (Li *et al.*, 2012).

Another variant of water based ceramic extrusion is called ceramic on-demand extrusion (CODE). An aqueous ceramic paste (50–60 vol%) is extruded using an Auger valve onto a substrate located in a tank designed to hold a fluid. After each layer is deposited, a mineral oil is pumped into the tank at a controlled-flow rate to a level just below the top surface of the layer. Infrared heating is then applied to partially dry the layer, with the oil precluding undesirable non-uniform water evaporation from the sides, thus preventing warpage and crack formation. With CODE, FGM specimens could be produced with a compositional gradient extending from pure Al_2O_3 to $\text{Al}_2\text{O}_3/\text{ZrO}_2$ with varying composition (Li *et al.*, 2018b). A 1% average error in material composition was observed compared to the original design of compositions, and it was found that greater material composition gradients led to larger delamination and curling.

The material extrusion method usually uses a single- or multiple extruders, each extruding a paste of materials layer-by-layer. A multi-nozzle device allows for the production of arbitrary components by controlling the flow ratio of different pastes. Fabrication of FGMs with linearly varying properties has been realized with a wide range of material extrusion techniques. Continued development of equipment and technologies has made it possible to produce a material with nonlinear gradients. Ren *et al.* (2018) developed a 3D printer equipped with a three- axis motion gantry, an active mixing device and a digital material feeding

device (**Fig. 16(a)**). During the printing process, mathematical functions were used to depict the graded distribution of material properties. Then, through gray-scale representation and controlling code generation, nano-sized Al_2O_3 particles were digitally fed into the printer to fabricate 1D, 2D, and 3D graded objects as shown in **Fig. 16(b)**.

Direct inkjet printing (DIP)

Material jetting is defined as an AM process in which droplets of build material are selectively deposited to directly shape 3D parts onto a substrate (*ISO/ASTM, 2015*). Material jetting is usually called direct inkjet printing (DIP). In DIP, the jetted ink is either (1) a well-dispersed suspension of submicron ceramic particles in water or an organic solvent, or (2) a wax-based ink containing submicron ceramic particles.

A continuous flow (CIJ) and a drop on demand (DoD) approach is possible (*Vaezi et al., 2013a*). In continuous inkjet printing (CIJ), an uninterrupted flow of individual droplets of electrically charged ink is generated. Unwanted droplets are caught before hitting the substrate using deflecting electrodes. These unprinted droplets are captured and can be reused.

DoD on the other hand is a non-continuous approach where individual droplets are generated by the pressure pulses induced by for instance the excitation of a piezoelectric actuator at controlled frequencies. Hence ink droplets are deposited only when and where required. Whilst the building rate of DoD is slower than that of CIJ, its wider range of jettable materials, lower risk for ink contamination, higher resolution, and better accuracy make it more suited to the fabrication of 3D objects (*Vaezi et al., 2013b*). DoD inkjet printing performance is highly dependent on the physical properties of the ink, particularly its viscosity and surface tension (*Jo et al., 2009*). Beside ink properties, printing parameters such as jetting frequency, travel speed, acoustic wave speed, and nozzle-substrate distance also have a strong influence on the jetability (*Reis and Derby, 2000; Reis et al., 1999*). Because jetting nozzles typically have a diameter between 10 and 60 μm , only fine submicrometric or nanopowders must be used in order to avoid nozzle clogging and improve suspension stability. It is vital that the ceramic solid loading be high enough so that a high green density can be obtained as well as to avoid issues with excessive shrinkage and cracking, whilst ensuring viscosity remains low enough for the ink to be printable. Therefore, powder loading is usually formulated in the range 20–30 vol% (*Seerden et al., 1999*).

Advantages and limitations of DIP

DIP is characterized by a high resolution thanks to the deposition of droplets with a volume of a few picolitres. Fully dense components with an excellent surface finish can be obtained. Solvent-DIP enables the fabrication of green parts containing very low amounts of organics, providing improved sintering behavior and a lower linear shrinkage upon firing. Aqueous-DIP in particular is desirable for a more environmentally friendly and less hazardous alternative to organic solvent-based DIP.

The suitability of DIP for manufacturing dense fully ceramic parts from both oxide and non-oxide ceramic materials has already been demonstrated. DIP can be used to shape any ceramic material as long as a stable suspension of submicron powders with the required physical properties for jetting can be formulated. The use of submicron or nanoparticles results in a higher particle packing in the green body and a higher sintering activity, which are both highly beneficial to the final density of printed products. By the use of multiple printheads DIP has the unique advantage over all other AM technologies in the ability to deposit droplets of multiple materials simultaneously. This enables the fabrication of FGMs and in fact microstructure tailoring on a voxel-level. *Mott and Evans (1999)* fabricated a one-dimensional $\text{ZrO}_2/\text{Al}_2\text{O}_3$ FGM but experienced issues with differential sintering and cracking. *Gingter et al. (2015)* manufactured 3Y-TZP/ Al_2O_3 FGMs cylinders with a diameter of 10 mm; cylinders made of 800 individual layers with a 2 μm thickness were printed on a substrate at 80°C. A high sintered density was obtained (97.5% TD). Simultaneous jetting is also useful for the deposition of droplets of support material, and it has already been used to print sacrificial support structures based on carbon black to enable the fabrication of complex shapes and overhangs such as dental bridge frameworks (*Özkol et al., 2012*).

Vat photopolymerization

Vat photopolymerization is a lithography-based AM process in which a liquid photopolymer in a vat is selectively cured by light-activated polymerization" (*ISO/ASTM, 2015*). To manufacture ceramic parts using lithography-based processes, fine ceramic powders are dispersed into the liquid photopolymer to form a UV-curable slurry (*Chartier et al., 2002; Snelling, 2013; Hinczewski et al., 1998*). Alternatively, the process can be based on the photopolymerization of UV-curable liquid preceramic polymers (*Zhou et al., 2010*).

The reactive colloidal system consists of monomer, photo initiator, submicron ceramic particles, dispersant, and additional additives such as diluent and solvent. Upon curing by UV light, the photopolymer acts as a matrix for the ceramic particles and provides shape, cohesion, and strength to the green part. The green body is subjected to a binder burnout heat treatment to ensure complete removal of the polymer matrix and then sintering to yield the final ceramic part. Several technological variants of the vat photopolymerization process exist for the layerwise freeform fabrication of ceramic components: stereolithography (SL), Digital Light Processing (DLP).

In SL, selective solidification of the liquid photocurable resin suspension is induced by a UV laser that is steered using a scanning galvanometer mirror positioning system to scan selectively the resin surface at the locations specified by the STL file.

DLP, which has also been called Direct Photo Shaping Large Area Maskless Photopolymerization (LAMP) or Mask-Image-Projection-based Stereolithography (MIP-SL) has at its core the digital micromirror device (DMD) technology. A DMD chip is a digitally controlled micro-opto-electro-mechanical system (MOEMS) invented at Texas Instruments in 1987 made of a 2D array composed of several hundred thousand individually switchable micromirrors producing a dynamic image that is projected onto

the photopolymer surface. The main advantage of DLP over laser-based SL is its much greater manufacturing speed, because the entire surface of the polymer is cured at once, whilst SL provides a point-based photopolymerization method. Different types of homogeneous ceramics have been fabricated using both techniques with good properties (Lakhdar *et al.*, 2021), although there are limitations in the choice of ceramic. Depending on the details of the implementation of the technique it should be possible to fabricate FGM ceramics with a gradient normal to the layer direction, i.e., normal to the surface of the bath, but this potential has not yet been explored.

Applications

The abrupt change in mechanical behavior (stiffness) at the interfaces between dissimilar materials in monolithic form can easily lead to weak interfaces and mechanical failure. Compared with monolithic composites, FGMs can be much more robust because their gradient interfaces can help minimize thermo-mechanical stress concentrations, hence preventing delaminations and improving the lifetime of load bearing structures.

The advantages of gradient materials are not restricted though to structural applications. Gradients can display functional properties that cannot be achieved by a homogeneous material or directly joined material. Indeed, one of the earliest uses of property gradients in functional materials were graded refractive index lenses and graded refractive index glass fibers for data transmission which allow outstanding transfer rates even for long transmission paths (Uchida *et al.*, 1970). Additionally, the absence of sharp interfaces in FGMs offers the chance to eliminate undesired effects of interfaces such as reflections of electromagnetic or acoustic waves or pile-up of dislocations in hetero-epitaxy. Such tailor-made properties make FGM's attractive for many acoustic, optic, electronic, magnetic, piezoelectric, thermoelectric, and photovoltaic applications.

The practical use of FGMs in industry is still very limited. There are, however, a few examples of early applications of materials that are FGMs by definition. Already in the 1960s glass/metal joints with a gradient in thermal expansion coefficient were used to reduce thermal stresses at the interface of the two materials and thus prevent failure of the glass/metal joint. Glasses with graded refractive index were developed in the early 1970s and were probably the first materials in which a very specific and precise gradation profile was essential for application. A circular plate with a gradient in refractive index can act as a miniature focusing lens with no spherical aberration. Glass rods with a radial index gradient drawn to a fiber can be used in wide-band optical fiber cables. Another well-established application of FGMs is in polymer skin foams with a dense surface layer and an increasing porosity towards the interior. These foams can provide high impact strength at low weight in applications such as instrument panels.

All the materials mentioned above are graded glasses or polymers, which are comparatively easy to manufacture. Gradient composite materials consisting of components with strongly different properties, i.e., graded ceramic/metal or ceramic/ceramic composites, have been manufactured only since the 1990s and tests of graded components from such materials in a real environment are still a rarity. Therefore, they are not widely used in commercial products. Nevertheless, they are expected to provide useful solutions for challenging engineering problems (Miyamoto *et al.*, 1999). The rapid development of additive manufacturing techniques has increased the prospects of applying the FGM concept in practice. In particular for polymer based and metallic materials systems industrial applications may be on the horizon. For ceramics and in particular when the ceramic phase has to be the majority phase, the technical difficulties are higher as should have become clear from the discussion above.

Nevertheless, FGMs for ceramics are worthy of continued research. They promise and they will enable solutions where the material operating conditions are severe. For example, wear-resistant linings for handling large heavy abrasive ore particles, very high-speed cutting tools, rocket and space plane heat shields, heat exchanger tubes, thermoelectric generators, heat-engine components, plasma facings for fusion reactors, and electrically insulating metal/ceramic joints, generally, ceramic-metal FGMs for minimizing the thermo-mechanical mismatch in metal-ceramic bonding. As shown in Fig. 3 a stress discontinuity is generated in case of a bi-material combination, which may result in poor adhesion or even delamination, whereas a significantly lower stress concentration can be established for a graded interface, thereby improving the materials adhesion and reducing the probability of delamination.

Mechanical Properties and Applications

In recent years, polymer/ceramic/metal-based FGMs made by AM have been widely studied to overcome the shortcomings (such as crack initiation and propagation) of each of the individual components. By monitoring and simulating the forces acting on a topology optimized quadcopter's arm, Li *et al.* (2018a) designed a lightweight, functionally graded, cellular structured quadcopter's arm without compromising its performance compared to a traditionally designed structure. Both simulation and experimental data showed that the optimized FGSs could significantly improve the structural stiffness of a quadcopter's arm. FGSs may improve and optimize mechanical behavior of a component by reducing mass without sacrificing load-bearing capabilities.

Graded gyroid cellular structures (GCS), a kind of functionally graded cellular structure with the gradient parallel to the loading direction, exhibited layer by-layer deformation and failure behavior. Mathematical models were developed to predict and customize the mechanical properties of GCS by optimizing the relative density of each layer (Yang *et al.*, 2019).

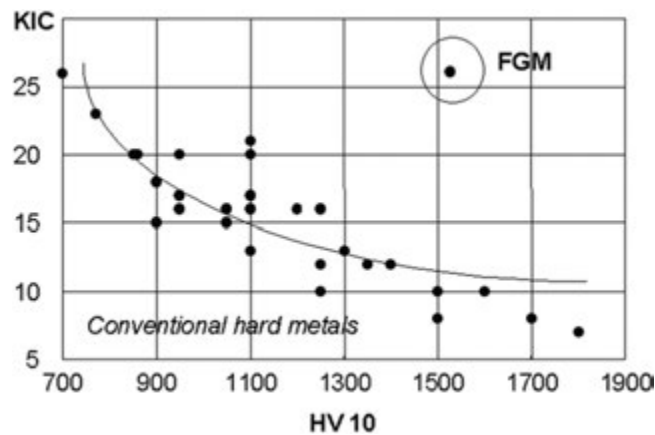


Fig. 17 Hardness-toughness relationship for WC-Co hardmetals. Reproduced from Anné, G., Vleugels, J., Van der Biest, O., 2006. Functionally graded ceramics. In: Low, I.M. (Ed.), *Ceramic-Matrix Composites: Microstructure, Properties and Applications*. Cambridge: Woodhead Publishing Limited. pp. 575–596.

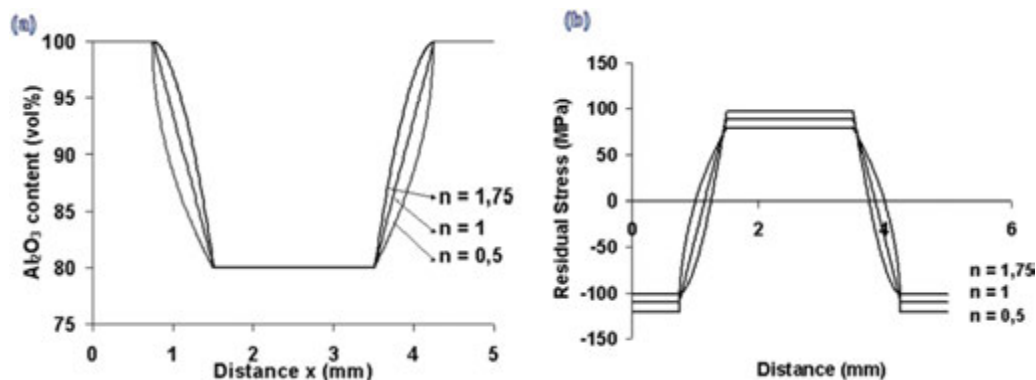


Fig. 18 Composition and corresponding residual stresses for a FGM disk with a convex ($n = 0.5$), linear ($n = 1$) and concave ($n = 1.75$) composition profile. Reproduced from Anné, G., Vleugels, J., Van der Biest, O., 2006. Functionally graded ceramics. In: Low, I.M. (Ed.), *Ceramic-Matrix Composites: Microstructure, Properties and Applications*. Cambridge: Woodhead Publishing Limited. pp. 575–596.

Wear protection

The wear resistance of tools can be substantially increased by a hard surface layer in a compressive stress state (Lin *et al.*, 1998). However, if a coating is under compressive stress the risk of delamination is considerable for many material combinations. A WC/Co FGM with a gradual variation in cobalt binder content from the surface to the interior will develop a compressive stress state at the surface. However as explained by Fig. 3 spallation of the top layer is unlikely to occur. Sandvik AB and Sumitomo Electric Industries already use this concept in tools for special applications such as drill bits. The improved resistance to delamination of an FGM coating was also exploited in an FGM cutting tool where a diamond surface layer was applied to a SiC substrate. Such a tool has a very high cutting precision due to its high stiffness compared to a tool based on a metallic alloy substrate (Li *et al.*, 1994).

A 3D gel-printed TiC-high manganese steel cermet showed gradient distributions in density, hardness, transverse failure strength, abrasion wear resistance and impact toughness due to its graded structure (Zhang *et al.*, 2018).

Using graded WC/Co hardmetals, it is possible to improve wear resistance and toughness at the same time (Fig. 17). This can be achieved by a gradation in the binder content from the center to the surface of the tool. The improved mechanical properties of the FGM cemented carbide are due to compressive stresses near the surface, which enable a reduction of the Co-phase content from 6 to 3 wt% without any loss in apparent fracture toughness.

Two existing industrial technologies have been reported to produce graded WC-Co hardmetals, i.e., liquid phase sintering of homogeneous WC-Co in a controlled atmosphere or pressure assisted sintering of graded WC-Co compacts. The first method is mainly used for nitride-containing WC-Co or WC-Ni cermets (Chen *et al.*, 2000a; Narasimhan *et al.*, 1995). The graded Co distribution is formed during liquid phase sintering through the establishment of a nitrogen partial pressure gradient (Zackrisson *et al.*, 2000; Chen *et al.*, 2000b) or by a high temperature carburization treatment of a WC-Co composite with sub-stoichiometric

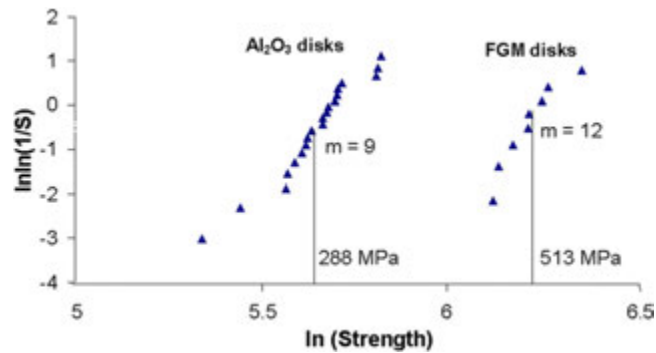


Fig. 19 Weibull plot of the biaxial strength (ISO 6474) of homogeneous Al_2O_3 and $\text{Al}_2\text{O}_3/\text{ZrO}_2$ FGM disks with 80 vol% Al_2O_3 in the core, pure Al_2O_3 on the outside and intermediated convex graded profile. The FGM disks were made by electrophoretic deposition and pressureless sintering. Reproduced from Anné, G., Vleugels, J., Van der Biest, O., 2006. Functionally graded ceramics. In: Low, I.M. (Ed.), *Ceramic-Matrix Composites: Microstructure, Properties and Applications*. Cambridge: Woodhead Publishing Limited. pp. 575–596.

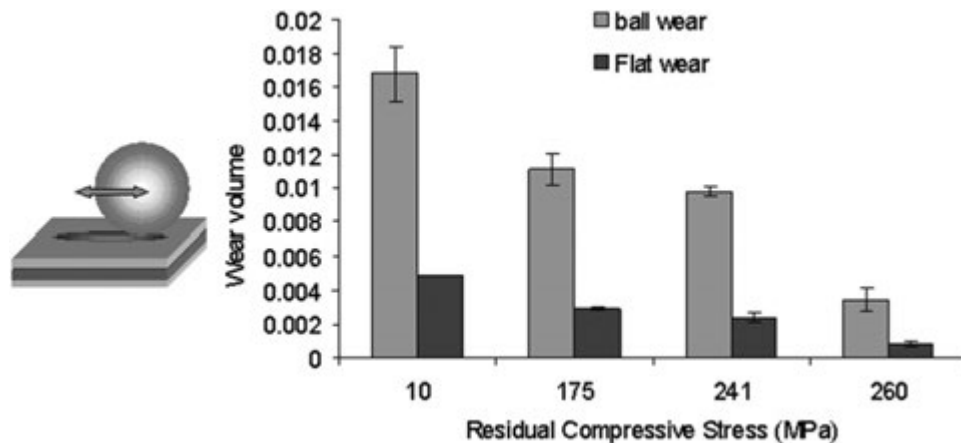


Fig. 20 Wear volume of step-graded $\text{Al}_2\text{O}_3/\text{ZrO}_2$ FGM disks with 80 vol% Al_2O_3 in the core and pure Al_2O_3 on the outside (data from Novak *et al.*, 2007). Reproduced from Anné, G., Vleugels, J., Van der Biest, O., 2006. Functionally graded ceramics. In: Low, I.M. (Ed.), *Ceramic-Matrix Composites: Microstructure, Properties and Applications*. Cambridge: Woodhead Publishing Limited. pp. 575–596; Woodhead publishing is now owned by Elsevier.

carbon content (Fischer *et al.*, 1988). Pressure assisted sintering techniques such as hot pressing, hot isostatic pressing and SPS can also be used to consolidate graded WC-Co compacts by solid state sintering (Tokita, 2003). Microwave sintering methods of graded WC/Co cemented carbides have also been reported (Willert-Porada *et al.*, 1995).

Other graded cermet systems reported include $\text{Cr}_3\text{C}_2/\text{Ni}$ (Seefeld *et al.*, 1999), TiC/Ti (Cline, 1995), and TiC/Ni (Sabatello *et al.*, 2000). The design concept of the graded cermets is similar to that of WC/Co cemented carbide FGMs.

As mentioned above residual stresses have a large influence on the properties of a structural body. They can be detrimental, but they can also be taken advantage of. For instance, a correct design of the composition gradient can generate compressive stresses at those locations, which are loaded in tension during application. The stresses can be calculated using finite element methods for the more complex geometries. For simple geometries such as in Fig. 2, analytical methods can be used.

Fig. 18 shows the results for an $\text{Al}_2\text{O}_3/\text{ZrO}_2$ FGM disk with homogeneous pure Al_2O_3 surface layers, a homogeneous $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite core and intermediate graded layers with a convex, linear and concave profile. The composition profiles and corresponding residual stresses for the FGM disks sintered at 1550°C are shown. These calculations reveal that the FGM disks with a convex ($n = 0.5$) alumina gradient profile result in the highest compressive stress in the alumina outer layers and the lowest tensile stresses in their core. Compressive surface stresses in the outer alumina layer have a beneficial effect on the strength (Fig. 19) and the wear resistance (Fig. 20). Additionally, an increased toughness can be observed in this kind of graded ceramic composite (Tilbrook, 2005).

Thermal Protection Systems

One of the earliest applications of the FGM concept was the thermal protection of space re-entry vehicles. A SiC/C FGM nose cone for a space plane was developed at the Japanese National Aerospace Laboratory. A nose cone with a SiC protection layer on a C/C



Fig. 21 (Left) Overview of $\text{Al}_2\text{O}_3/\text{TZP}$ FGM ball-heads for hip prostheses, made by electrophoretic deposition; (Right) residual stress analysis of FGM ball heads; the outer surface is pure alumina; the core is about 20 vol% zirconia. The color is a measure of the residual stress. Red corresponds to the highest tensile stress; blue corresponds to the highest compressive stresses. Reproduced from Anné, G., Vleugels, J., Van der Biest, O., 2006. Functionally graded ceramics. In: Low, I.M. (Ed.), *Ceramic-Matrix Composites: Microstructure, Properties and Applications*. Cambridge: Woodhead Publishing Limited. pp. 575–596; Woodhead publishing is now owned by Elsevier.

composite exposed to a supersonic gas flow at 1900°C deteriorated after the first thermal cycle. In contrast, a nose cone with an additional graded SiC/C interlayer did not show any change after 10 cycles (Sohda *et al.*, 1993).

Turbine blades of gas turbines must withstand high stresses at elevated temperatures and are thus made from superalloys. The efficiency of the turbine increases with increasing gas inlet temperature and thus the superalloy is coated with a bond coat of NiCrAlY and a heat-insulating layer of ZrO_2 in state-of-the-art gas turbines. The major mechanism limiting the lifetime of such a thermal barrier coating (TBC) is the growth of an oxide layer of alumina at the interface of the bond coat and the ZrO_2 which causes stresses and, ultimately, spallation of the TBC. A gradation of the zirconia coating and the bond coat improved considerably the resistance of the coating to spallation in thermal cycling experiments (Kawasaki and Watanabe, 1999). However, it is expected that the oxidation resistance and thus the long-term stability of such a graded system will be insufficient due to the dispersed metal particles in the graded layer. It has therefore been proposed to introduce an additional graded alumina layer between the bond coat and the zirconia. It is not clear yet whether such a design will provide a substantial long-term improvement compared to conventional TBCs.

FGMs were investigated to improve the durability of heat exchangers. With the development of hypersonic vehicles, more complex geometries have been applied to the design of integrated thermal protection (ITP) structures. Inspired by the structure of the spruce stem, Kaijie *et al.* (2019) used SLM to fabricate a series of ITP structures consisting of hollow tubular sections with graded diameters. They achieved a bottom surface temperature 21°C lower than that of non-graded structures. Additive manufacturing of a functionally graded material from Ti-6Al-4V to Invar was reported by Bobbio *et al.* (2017). The properties of a wire arc additively manufactured titanium aluminide FGM for high temperature service were described by Wang *et al.* (2018).

Medical Implants

ZrO_2 -based FGMs have been of high interest (Marple and Boulanger, 1994; Anné *et al.*, 2004; Zhao *et al.*, 2000; Put *et al.*, 2002) because of the high toughness and excellent strength of tetragonal ZrO_2 polycrystalline ceramics (TZP). ZrO_2 -based FGMs are mainly developed for energy conversion systems (turbine blades) and for cutting tools, where a high hardness has to be combined with high toughness or where thermal stresses have to be released (Sanchez-Herencia *et al.*, 2000).

Both Al_2O_3 and ZrO_2 are biocompatible materials. Pure high strength Al_2O_3 is in fact used for total hip prostheses comprising both the femur head and the hip bearing. The motion of ceramic against another ceramic surface generates a very low amount of wear. Today, a majority of the joint prostheses consist of metallic components, articulating against polymer counterparts, of which more than 10% need revision after only 10 years. This is expensive and reduces the quality of life of the patients. Also, the clinical effects of metallic ion releasing implants and polymer wear debris are a matter of concern. This demonstrates the need for more wear resistant and biocompatible materials such as ceramics. $\text{Al}_2\text{O}_3/\text{ZrO}_2$ FGMs were studied intensively for biomedical applications, specifically for implants like hip prostheses (Anné *et al.*, 2004). The FGM idea was applied to increase the performance of total hip replacement prostheses through design and development of alumina/zirconia functionally graded materials using electrophoretic deposition as a near-net shaping technique (Fig. 21). Therefore alumina-zirconia graded femoral ball-heads were developed. The potential of this system follows from the properties of alumina (low wear, high hardness) and zirconia (high strength, high toughness). By combining alumina and zirconia, a functional gradient in hardness (high at the alumina surface) and toughness (high in the zirconia rich core) can be established. Due to the difference in thermal expansion coefficient of Al_2O_3 and ZrO_2 , residual stresses are developed during cooling from the sintering temperature, with a compressive stress at the surface and tensile stress in the core of the material (Fig. 21). These strongly influence the mechanical properties like strength and toughness.

It is generally acknowledged that a porous surface of a bioactive material such as hydroxyapatite is ideal for rapid bone ingrowth and good mechanical bonding in prosthetic devices. However, for the sake of mechanical stability it is often necessary to use metals as load-carrying materials in implants. As a result, titanium coated with hydroxyapatite is used as an implant material. The adhesion of hydroxyapatite on titanium is only moderate and failure of the interface may occur after implantation. However, it has been demonstrated that the bonding of certain glasses to titanium is quite strong. Therefore, a coating of glass on a Ti-6Al-4V substrate possessing an increasing volume fraction of hydroxyapatite and pores close to its outer surface is an excellent material for cementless artificial joints and dental implants. Such a graded composite showed a good apposition *in vivo*, and the pull-out strength of dog femur implants was three times higher than that of a sandblasted titanium implant (Maruno *et al.*, 1999). The pull-out strength increased with time due to bone growth into the interior of the coating layer, and after 76 months of plantation no separation of the glass layer from the titanium was observed. A graded composite of this type therefore has a considerable potential as cementless artificial joint or endosseous dental implant.

Future Outlook

Already a lot of scientific work has been established in processing graded bulk ceramics and in modeling and optimization of the properties of these materials. Despite these technological successes, the number of commercial successes is still limited because the production costs are in most cases still too high compared to homogeneous materials. However, new production processes such as additive manufacturing (AM) are emerging on the market. They are expected to allow the production of FGM bulk ceramics and ceramic-metal FGM in an economical way.

Many new target applications have appeared or new ones are emerging, including (see also Li *et al.* (2020)):

- (1) Thermo mechanical applications.
- (2) Energy conversion.
- (3) Applications in optics and electronics.
- (4) Electric and magnetic applications.
- (5) Graded cemented carbide coatings on steel substrates.
- (6) Biomedical applications.

Additional Information

Since 1990, an international congress on Functional Graded Materials is organized by the International Advisory Committee of FGM (IACFGM) every 2 years. The proceedings of these congresses, although sometimes not easily available, give a lot of information about research on FGM materials. The symposia on FGM's were held in Sendai (1990), San Francisco (1992), Lausanne (1994), Tsukuba (1996), Dresden (1998), Estes Park (U.S., 2000), Beijing (2002), Leuven (2004), Hawaii (2006), Sendai (2008), Guimaraes (2010), Sao Paulo, Brazil (2014), Bayreuth (2016), Kitakyushu, Japan (2018). The 16th International Symposium on Functionally Graded Materials will take place in Hartford Connecticut, US, August 7–10, 2022.

References

- Anné, G., Vleugels, J., Van der Biest, O., 2006. Functionally graded ceramics. In: Low, I.M. (Ed.), *Ceramic-Matrix Composites: Microstructure, Properties and Applications*. Cambridge: Woodhead Publishing Limited, pp. 575–596.
- Anné, G., Vanmeensel, K., Vleugels, J., 2004. Electrophoretic deposition as a near net shaping technique for functionally graded biomaterials. *Mater. Sci. Forum* 492–493, 213–218.
- Arsha, A.G., Jayakumar, E., Rajan, T.P.D., Antony, V., Pai, B.C., 2015. Design and fabrication of functionally graded in-situ aluminum composites for automotive pistons. *Mater. Des.* 88, 1201–1209.
- Baer, T., Cesarano III, J., Calvert, P., 1997. Recent developments in freeform fabrication of dense ceramics from slurry deposition. In: *Proceedings of Solid Freeform Fabrication Symposium*, vol. 1997, pp. 25–32.
- Bao, G., Cai, H., 1997. Delamination cracking in functionally graded coating/metal substrate system. *Acta Mater.* 45 (3), 1055–1066.
- Berg, A., Wagner, L., 1999. Near-surface gradient microstructures in metastable beta-titanium alloys for improved fatigue performance. In: Kaysner, W.A. (Ed.), *Proceedings of the 5th International Symposium Functionally Graded Materials '98*, Materials Science Forum, Vols. 308–311. Switzerland: Trans Tech Publications, pp. 307–312.
- Bernhardt, R., Meyer-Olbersleben, F., Kieback, B., 1999. The influence of hydrodynamic effects on the adjustment of gradient patterns through gravity sedimentation of polydisperse particle systems in newtonian and viscoelastic fluid. *Mater. Sci. Forum* 308–311, 31–35.
- Besra, L., Liu, M., 2007. A review on fundamentals and applications of EPD. *Prog. Mater. Sci.* 52, 1–61.
- Björklund, S., Goel, S., Joshi, S., 2018. Function-dependent coating architectures by hybrid powder-suspension plasma spraying: Injector design, processing and concept validation. *Mater. Des.* 142, 56–65.
- Bobbio, L.D., Otis, R.A., Borgonia, J.P., *et al.*, 2017. Additive manufacturing of a functionally graded material from Ti-6Al-4V to invar: Experimental characterization and thermodynamic calculations. *Acta Mater.* 127, 133.
- Cai, P.Z., Green, D.J., Messing, G.L., 1997a. Constrained densification of alumina/zirconia hybrid laminates. 1. Experimental observations of processing defects. *J. Am. Ceram. Soc.* 80 (8), 1929–1939.
- Cai, P.Z., Green, D.J., Messing, G.L., 1997b. Constrained densification of alumina/zirconia hybrid laminates. 2. Viscoelastic stress computation. *J. Am. Ceram. Soc.* 80 (8), 1940–1948.
- Cesarano, J., King, B.H., Denham, H.B., Cesarano III, J., Denham, H.B., 1998. Recent developments in robocasting of ceramics and multimaterial deposition. In: *Proceedings of Solid Freeform Fabrication Symposium*, pp. 697–703.

- Chartier, T., Chaput, C., Doreau, F., Loiseau, M., 2002. Stereolithography of structural complex ceramic parts. *J. Mater. Sci.* 37 (15), 3141–3147.
- Chen, L.M., Lengauer, W., Ettmayer, P., *et al.*, 2000a. Fundamentals of liquid phase sintering for modern cermets and functionally graded cemented carbonitrides (FGCC). *Int. J. Refract. Met. Hard Mater.* 18 (6), 307–322.
- Chen, L.M., Lengauer, W., Dreyer, K., 2000b. Advances in modern nitrogen-containing hard-metals and cermets. *Int. J. Refract. Met. Hard Mater.* 18 (2–3), 153–161.
- Cherradi, N., Kawasaki, A., Gasik, M., 1994. Worldwide trends in functional gradient materials research and development. *Compos. Eng.* 4 (8), 883–894.
- Choy, S.Y., Chen-Nan, S., Kah, F.L., Jun, W., 2017. Compressive properties of functionally graded lattice structures manufactured by selective laser melting. *Mater. Des.* 131, 112–120.
- Chu, J., Ishibashi, H., Hayashi, K., Takebe, H., Morinaga, K., 1993. Slip casting of continuous functionally gradient material. *J. Ceram. Soc. Jpn.* 101, 818–820.
- Cichocki Jr., F.R., Trumble, K.P., 1998. Tailored porosity gradients via colloidal infiltration of compression-molded sponges. *J. Am. Ceram. Soc.* 81 (6), 1661–1664.
- Cline, C.F., 1995. Preparation of gradient TiC cermet cutting tools. In: Iltschner, B., Cherradi, N. (Eds.), *Pmc. 3rd International Symposium on Structural and Functional Gradient Materials*. Lausanne: Presses Polytechniques et Universitaires Romandes. 595.
- Costakis, W.J., Rueschhoff, L.M., Diaz-Cano, A.I., Youngblood, J.P., Trice, R.W., 2016. Additive manufacturing of boron carbide via continuous filament direct ink writing of aqueous ceramic suspensions. *J. Eur. Ceram. Soc.* 36 (14), 3249–3256.
- Cui, X., Ouyang, S., Yu, Z., Wang, C., Huang, Y., 2003. A study on green tapes for LOM with water-based tape casting processing. *Mater. Lett.* 57 (7), 1300–1304.
- Deckers, J., Kruth, J.-P., Shahzad, K., Vleugels, J., 2012a. Density improvement of alumina parts produced through selective laser sintering of alumina-polyamide composite powder. *CIRP Ann. Manuf. Technol.* 61 (1), 211–214.
- Deckers, J., Shahzad, K., Vleugels, J., Kruth, J.P., 2012b. Isostatic pressing assisted indirect selective laser sintering of alumina components. *Rapid Prototyp. J.* 18 (5), 409–419.
- Deckers, J., Kruth, J.-P., Cardon, L., Shahzad, K., Vleugels, J., 2013. Densification and geometrical assessments of alumina parts produced through indirect selective lasersintering of alumina-polystyrene composite powder. *Stroj Vestnik-J Mech Eng* 59 (11), 646–661.
- Eder, M., Jungnickl, K., Burgert, I., 2009. A close-up view of wood structure and properties across a growth ring of Norway spruce (*Picea abies* [L.] Karst). *Trees* 23, 79–84.
- Erdogan, F., 1995. Fracture mechanics of functionally graded materials. *Compos. Eng.* 5 (7), 753–770.
- ISO/ASTM, 2015. Standard 52900: (2015) (E), "Standard Terminology for Additive Manufacturing – General Principles – Terminology". West Conshohocken, PA: ASTM International.
- Farnoush, H., Mohandesi, J.A., Çimenoglu, H., 2015. Micro-scratch and corrosion behavior of functionally graded HA-TiO₂ nanostructured composite coatings fabricated by electrophoretic deposition. *J. Mech. Behav. Biomed. Mater.* 46, 31–40.
- Feilden, E., Blanca, E.G.T., Giuliani, F., Saiz, E., Vandeperre, L., 2016. Robocasting of structural ceramic parts with hydrogel inks. *J. Eur. Ceram. Soc.* 36 (10), 2525–2533.
- Fischer, U.K.R., Hartzell, E.T., Akerman J.G.H., 1988. Cemented Carbide Body used Preferably for Rock Drilling and Mineral Cutting, US Patent No. 4,743,515.
- Fishman, S.G., 1988. Advances in cast metal composites. *JOM* 40 (11), 8–9.
- Fu, P.X., Kang, X.H., Ma, Y.C., *et al.*, 2008. Centrifugal casting of TiAl exhaust valves. *Intermetallics* 16, 130–138.
- Fu, Q., Saiz, E., Tomsia, A.P., 2011. Direct ink writing of highly porous and strong glass scaffolds for load-bearing bone defects repair and regeneration. *Acta Biomater.* 7 (10), 3547–3554.
- Fukui, Y., Takashima, K., Ponton, C.B., 1994. Measurement of Young's modulus and internal friction of an in-situ Al-Al₃Ni functionally gradient material. *J. Mater. Sci.* 29, 2281–2286.
- Gasik, M., 1995. Principles of functional graded materials and their processing by powder metallurgy, *Acta Polytech. Scand. Chem. Technol.* 226, 72–90. (Helsinki).
- Gerdes, T., Willert-Porada, M., 1994. Microwave sintering of metal-ceramic and ceramic-ceramic composites. *Mater. Res. Soc. Symp. Proc.* 347, 531.
- Gibson, I., Rosen, D., Stucker, B., Khorasani, M., 2021. *Additive Manufacturing Technologies*, third ed. Springer.
- Gingter, P., Wätjen, A.M., Kramer, M., Telle, R., 2015. Functionally graded ceramic structures by direct thermal inkjet printing. *J. Ceram. Sci. Technol.* 6 (2), 119–124.
- Grau, J.E., 1998. *Fabrication of Engineered Ceramic Components by the Slurry-Based Three-Dimensional Printing Process*. Massachusetts Institute of Technology.
- Guo, J., Fang, Z., Fan, P., Wang, X., 2011. Kinetics of the formation of metal binder gradient in WC-Co by carbon diffusion induced liquid migration. *Acta. Mater.* 59, 4719–4731.
- Habibi, M.K., Samaei, A.T., Gheshlaghi, B., Lu, J., Lu, Y., 2015. Asymmetric flexural behavior from bamboo's functionally graded hierarchical structure: Underlying mechanisms. *Acta Biomater.* 16, 178–186.
- Heimann, R.B., 1996. Principles of plasma spraying. In: Heimann, R.B. (Ed.), *Plasma-Spray Coating 1996*. Weinheim: John Wiley & Sons, pp. 17–25.
- Hennicke, J., Kessel, H.U., 2004. Field assisted sintering technology (FAST) for the consolidation of innovative materials. *Ceram. Forum Int.* 81 (11), E14–E16.
- Hillman, C., Suo, Z.G., Lange, F.F., 1996. Cracking of laminates subjected to biaxial tensile stresses. *J. Am. Ceram. Soc.* 79 (8), 2127–2133.
- Hinczewski, C., Corbel, S., Chartier, T., 1998. Ceramic suspensions suitable for stereolithography. *J. Eur. Ceram. Soc.* 18 (6), 583–590.
- Hong, C.Q., Zhang, X.H., Li, W.J., Han, J.C., Meng, S.H., 2008. A novel functionally graded material in the ZrB₂-SiC and ZrO₂ system by spark plasma sintering. *Mater. Sci. Eng. A* 498, 437–441.
- Hotza, D., Greil, P., 1995. Review: Aqueous tape casting of ceramic powders. *Mater. Sci. Eng. A* 202, 206–217.
- Ivosevic, M., Knight, R., Kalidindi, S.R., Palmese, G.R., Sutter, J.K., 2005. Adhesive/cohesive properties of thermally sprayed functionally graded coatings for polymer matrix composites. *J. Therm. Spray Technol.* 14, 45–51.
- Jo, B.W., Lee, A., Ahn, K.H., Lee, S.J., 2009. Evaluation of jet performance in drop-on-demand (DOD) inkjet printing. *Korean J. Chem. Eng.* 26 (2), 339–348.
- Joshi, S., Markocsan, N., Nylén, P., Sivakumar, G., 2020. New-generation ceramic coatings for high-temperature applications by liquid feedstock plasma spraying. In: Mahajan, Y.R., Johnson, R. (Eds.), *Handbook of Advanced Ceramics and Composites*. Switzerland AG: Springer Nature.
- Juste, E., Petit, F., Lardot, V., Cambier, F., 2014. Shaping of ceramic parts by selective laser melting of powder bed. *J. Mater. Res.* 29 (17), 2086–2094.
- Kaijje, L., Kaiming, H., Dongdong, G., 2019. Metallic integrated thermal protection structures inspired by the Norway spruce stem: Design, numerical simulation and selective laser melting fabrication. *Opt. Laser Technol.* 115, 9–19.
- Kawai, C., Wacamatsu, S., 1995. Synthesis of a functionally gradient material based on C/C composites using an electro-deposition method. *J. Mater. Sci. Lett.* 14, 467–469.
- Kawasaki, A., Watanabe, R., 1999. Cyclic thermal fracture behavior and spallation life of PSZ/NiCrAlY functionally graded thermal barrier coatings. In: Kaysser, W.A. (Ed.), *Proceedings of the 5th International Symposium Functionally Graded Materials '98*, Materials Science Forum, Vols. 308–311. Switzerland: Trans Tech Publications, pp. 402–409.
- Kernan, B.D., Sachs, E.M., Oliveira, M.A., Cima, M.J., 2007. Three-dimensional printing of tungsten carbide-10 wt% cobalt using a cobalt oxide precursor. *Int. J. Refract. Met. Hard Mater.* 25 (1), 82–94.
- Khor, K.A., Gu, Y.W., 2000. Effects of residual stress on the performance of plasma sprayed functionally graded ZrO₂: NiCoCrAlY coatings. *Mater. Sci. Eng. A* 277, 64–76.
- Kieback, B., Neubrand, A., Riedel, H., 2003. Processing techniques for functionally graded. *Mater. Sci. Eng. A* 362, 81–105.
- Kruth, J.-P., Levy, G., Klocke, F., Childs, T.H.C., 2007. Consolidation phenomena in laser and powder-bed based layered manufacturing. *CIRP Ann. Manuf. Technol.* 56 (2), 730–759.
- Lakhdar, Y., Tuck, C., Binner, J., Terry, A., Goodridge, R., 2021. Additive manufacturing of advanced ceramic materials. *Prog. Mater. Sci.* 116, 100736.
- Leu, M.C., Tang, L., Deuser, B., *et al.*, 2011. Freeze-form extrusion fabrication of composite structures In: *Proceedings of the Solid Freeform Fabrication Symposium*. pp. 111–124.
- Leu, M.C., Deuser, B.K., Tang, L., *et al.*, 2012. Freeze-form extrusion fabrication of functionally graded materials. *CIRP Ann.* 61, 223–226.
- Li, A., Thornton, A.S., Deuser, B., *et al.*, 2012. Freeze-form extrusion fabrication of functionally graded material composites using zirconium carbide and tungsten. In: *Proceedings of the Solid Freeform Fabrication Symposium*. pp. 467–479.

- Li, D., Liao, W., Dai, N., *et al.*, 2018a. Optimal design and modeling of gyroid-based functionally graded cellular structures for additive manufacturing. *Comput. Aided Des.* 104, 87–99.
- Li, W., Martin, A.J., Kroehler, B., *et al.*, 2018b. Fabricating functionally graded materials by ceramic on-demand extrusion with dynamic mixing. In: *Proceedings of the 29th Annual International Solid Freeform Fabrication Symposium*. pp. 1087–1099.
- Li, J.-F., Watanabe, R., Nishio, N., Kawasaki, A., 1994. Design and fabrication of diamond tools with ceramic shank using the concept of functionally gradient materials. In: *Proceedings of the Powder Metallurgy World Congress (PM'94)*. Paris. pp. 553–556.
- Li, Y., Feng, Z., Hao, L., *et al.*, 2020. A review on functionally graded materials and structures via additive manufacturing: From multi-scale design to versatile functional properties. *Adv. Mater. Technol.* 5, 1900981.
- Liang, C., Ma, W., Feng, Z., Li, C., 2003. Activated carbon supported bimetallic CoMo carbides, synthesized by carbothermal hydrogen reduction. *Carbon* 41, 1833–1839.
- Lin, J.S., Miyamoto, Y., Tanihata, K., Yamamoto, M., Tanaka, R., 1998. Toughening effects of WC/Co particles and compressive surface stress on $(\text{Al}_2\text{O}_3\text{WC/Co})/\text{TiC/Ni}$ graded materials. *J. Mater. Sci.* 33, 869–876.
- Ma, G.E., Tan, B., 2001. Processing and characterization of metal–ceramics functionally gradient materials. *J. Mater. Process. Technol.* 113, 446–449.
- Mahmoodian, R., Hassan, M., Hamdi, M., Yahya, R., Rahbari, R., 2014. A novel fabrication method for $\text{TiC-Al}_2\text{O}_3\text{-Fe}$ functional material under centrifugal acceleration. *Compos. Part B: Eng.* 59, 279.
- Marple, B.R., Boulanger, J., 1994. Graded casting and materials with continuous gradients. *J. Am. Ceram. Soc.* 77 (10), 2747–2750.
- Maruno, S., Iwata, H., Ban, S., Itoh, H., 1999. Bone bonding studies and implant application of HA-G-Ti functionally graded composites. In: Kaysser, W.A. (Ed.), *Proceedings of the 5th International Symposium on Functionally Graded Materials '98*, Materials Science Forum, vols. 308–311. Switzerland: Trans Tech Publications, pp. 344–349.
- Maskery, I., Aboulkhair, N.T., Aremu, A.O., *et al.*, 2016. A mechanical property evaluation of graded density Al-Si10-Mg lattice structures manufactured by selective laser melting. *Mater. Sci. Eng. A* 670, 264–274.
- Matson, D.M., Munir, Z.A., 1992. Combustion synthesis of intermetallic compounds using titanium, nickel and copper wires. *Mater. Sci. Eng. A* 153, 700–705.
- Meyers, S., Kruth, J.-P., Vleugels, J., 2015. Direct selective laser sintering of reaction bonded silicon carbide. In: *Proceedings of the Solid Freeform Fabrication Symposium*. pp. 1750–1758.
- Miyamoto, Y., Kaysser, W.A., Rabin, B.H., Kawasaki, A., Ford, R.G. (Eds.), 1999. *Functionally Graded Materials: Design, Processing and Applications*. Boston/Dordrecht/London: Kluwer Academic Publishers, p. 320.
- Moon, J., Grau, J.E., Cima, M.J., Sachs, E.M., 2000. Slurry chemistry control to produce easily redispersible ceramic powder compacts. *J. Am. Ceram. Soc.* 83 (10), 2401–2403.
- Mortensen, A., Suresh, S., 1995. Functionally graded metals and metal–ceramic composites: Part 1 processing. *Int. Mater. Rev.* 40 (6), 239–265.
- Mott, M., Evans, J.R., 1999. Zirconia/alumina functionally graded material made by ceramic ink jet printing. *Mater. Sci. Eng. A271* (1–2), 344–352.
- Munz, D., Schaller, W., Yang, Y., 1998. Where is the benefit of a graded materials?. Presented at FGM'98 Workshop: 'Computer Aided Design of Functionally Graded Materials', Dresden, Germany.
- Nadkarni, S.S., Smay, J.E., Concentrated barium titanate colloidal gels prepared by bridging flocculation for use in solid freeform fabrication. *J. Am. Ceram. Soc.* 89 (1), 96–103.
- Naebe, M., Shirvanimoghaddam, K., 2016. Functionally graded materials: A review of fabrication and properties. *Appl. Mater. Today* 5, 223–245.
- Narasimhan, K., Boppana, S.P., Bhat, D.G., 1995. Development of a graded TiCN coating for cemented carbide cutting tools – A design approach. *Wear* 188 (1–2), 123129.
- Neubrand, A., 2001. Functionally graded materials. In: Jürgen Buschow, K.H., Cahn, R.W., Flemings, M.C., *et al.* (Eds.), *Encyclopedia of Materials: Science and Technology*. Amsterdam: Elsevier, pp. 3407–3417.
- Neubrand, A., Rödel, J., 1997. Gradient materials: An overview of a novel concept. *Z. Metallkd.* 88 (5), 358–371.
- Niino, M., Hirai, T., Watanabe, R., 1987. Functionally graded materials-Aiming for ultra-heat resistant materials for spacecraft. *J. Jpn. Soc. Compos. Mater.* 13, 257. (in Japanese).
- Niu, F., Wu, D., Ma, G., *et al.*, 2015. Nanosized microstructure of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (Y_2O_3) eutectics fabricated by laser engineered net shaping. *Scr. Mater.* 95 (1), 39–41.
- Niu, F., Wu, D., Ma, G., *et al.*, 2016. Rapid fabrication of eutectic ceramic structures by laser engineered net shaping. *Proc. CIRP*. 91–95.
- Novak, S., Kalin, M., Lukas, P., *et al.*, 2007. The effect of residual stresses in functionally graded alumina–ZTA composites on their wear and friction behavior. *J. Eur. Ceram. Soc.* 27, 151–156.
- Özkol, E., Zhang, W., Telle, R., Ebert, J., 2012. Potentials of the direct inkjet printing method for manufacturing 3Y-TZP based dental restorations. *J. Eur. Ceram. Soc.* 32 (10), 2193–2201.
- Pakseresht, A.H., Javadi, A.H., Nejati, M., *et al.*, 2014. Statistical analysis and multi-objective optimization of process parameters in plasma spraying of partially stabilized zirconia. *Int. J. Adv. Manuf. Technol.* 75, 739.
- Pakseresht, A.H., Ghasali, E., Nejati, M., *et al.*, 2015. Development empirical-intelligent relationship between plasma spray parameters and coating performance of Yttria-Stabilized Zirconia. *Int. J. Adv. Manuf. Technol.* 76, 1031–1045.
- Put, S., Vleugels, J., Anné, G., Van der Biest, O., 2003a. Processing of hardmetal coatings on steel substrates. *Scr. Mater.* 48 (9), 1361–1366.
- Put, S., Vleugels, J., Anné, G., Van der Biest, O., 2003b. Functionally graded ceramic and ceramic-metal composites shaped by electrophoretic deposition. *Colloids Surf. A* 222, 223–232.
- Put, S., Vleugels, J., Van der Biest, O., 2003c. Gradient profile prediction in functionally graded materials processed by electrophoretic deposition. *Acta Mater.* 51 (20), 6303–6317.
- Put, S., Vleugels, J., Van der Biest, O., 2001. Functionally graded WC-Co materials produced by electrophoretic deposition. *Scr. Mater.* 45 (10), 1139–1145.
- Put, S., Anné, G., Vleugels, J., Van der Biest, O., 2002. Functionally graded $\text{ZrO}_2\text{-WC}$ composites processed by electrophoretic deposition. *Key Eng. Mater.* 206–213, 189–192.
- Reis, N., Derby, B., 2000. Ink jet deposition of ceramic suspensions: modeling and experiments of droplet formation. *Mater. Res. Soc. Symp. Proc.* 625, 117–122.
- Reis, N., Seerden, K.A.M., Derby, B., Halloran, J., Evans, J.R.G., 1999. Direct inkjet deposition of ceramic green bodies: II – Jet behavior and deposit formation. *Mater. Res. Soc. Symp. Proc.* 542.
- Ren, L., Song, Z., Liu, H., *et al.*, 2018. 3D printing of materials with spatially non-linearly varying properties. *Mater. Des.* 156, 470.
- Requenna, J., Moya, J.S., Pena, P., 1993. $\text{Al}_2\text{TiO}_3\text{-Al}_2\text{O}_3$ Functionally gradient materials obtained by sequential slip casting. In: Holt, J., B, Koisumi, M., Hirai, T., Munir, Z.A., (Eds.), *Functionally Gradient Materials*, Westerville, OH: American Ceramic Society, pp. 203–210.
- Rueschhoff, L., Costakis, W., Michie, M., Youngblood, J., Trice, R., 2016. Additive manufacturing of dense ceramic parts via direct ink writing of aqueous alumina suspensions. *Int. J. Appl. Ceram. Technol.* 13 (5), 821–830.
- Sabatello, S., Frage, N., Dariel, M.P., 2000. Graded TiC-based cermets. *Mater. Sci. Eng. A288*, 12–18.
- Sachs, E.M., Haggerty, J.S., Cima, M.J., Williams, P.A., 1993. *Three-Dimensional Printing Techniques*. US5204055.
- Sanchez-Herencia, A.J., Moreno, R., Jurado, J., 2000. Electrical transport properties in zirconia/alumina functionally graded materials. *J. Eur. Ceram. Soc.* 20, 1611–1620.
- Sasaki, M., Hirai, T., 1994. Thermal fatigue resistance of CVD SiC/C functionally gradient material. *J. Eur. Ceram. Soc.* 14, 257–260.
- Scheithauer, U., Slawik, T., Schwarzer, E., *et al.*, 2015. Additive manufacturing of metal-ceramic-composites by thermoplastic 3D-printing (3DTP). *J. Ceram. Sci. Technol.* 6 (2), 125–132.
- Scheithauer, U., Weingarten, S., John, R., *et al.*, 2017. Ceramic-based 4D-components: Additive manufacturing (AM) of ceramic-based functionally graded materials (FGM) by thermoplastic 3D-printing (T3DP). *Materials* 10 (1368).
- Schindler, J., Meyer-Olbersleben, F., Kirbach, B., 1998. Fabrication of FGM-Foils for Joining application by wet powder spraying. Presented at *Proceedings of the 5th International Symposium on FGM*. Dresden.
- Schlödt, T., Schwanke, S., Keppner, F., *et al.*, 2013. Robocasting of alumina hollow filament lattice structures. *J. Eur. Ceram. Soc.* 33 (15–16), 3243–3248.

- Seefeld, T., Theiler, C., Schubert, E., Sepold, G., 1999. Laser generation of graded metal-carbide components. *Mater. Sci. Forum* 308–311, 459–464.
- Seerden, K.A.M., Reis, N., Derby, B., *et al.*, 1999. Direct ink-jet deposition of ceramic green bodies: I – Formulation of build materials. *Mater. Res. Soc. Symp. Proc.* 542, 141–146.
- Seifried, S., Winterer, M., Hahn, H., 2001. Nanocrystalline gradient films through chemical vapor synthesis. *Materials* 44, 2165–2168.
- Shahzad, K., Deckers, J., Boury, S., *et al.*, 2012. Preparation and indirect selective laser sintering of alumina/PA microspheres. *Ceram. Int.* 38 (2), 1241–1247.
- Shahzad, K., Deckers, J., Kruth, J.P., Vleugels, J., 2013. Additive manufacturing of alumina parts by indirect selective laser sintering and post processing. *J. Mater. Process. Technol.* 213 (9), 1484–1494.
- Shahzad, K., Deckers, J., Zhang, Z., Kruth, J.-P., Vleugels, J., 2014. Additive manufacturing of zirconia parts by indirect selective laser sintering. *J. Eur. Ceram. Soc.* 34 (1), 81–89.
- Shon, I.J., Munir, Z.A., 2005. Synthesis of TiC, TiC-Cu composites, and TiC-Cu functionally graded materials by electrothermal combustion. *J. Am. Ceram. Soc.* 81.3243.
- Smay, J.E., Cesarano, J., Lewis, J.A., 2002. Colloidal inks for directed assembly of 3-D periodic structures. *Langmuir* 18 (14), 5429–5437.
- Snelling, D., 2013. The effects of 3D printed molds on metal castings. In: *Proceedings of the 24th International SFF Symposium – An Additive Manufacturing Conference SFF827–45*.
- Sohda, Y., Kude, Y., Uemura, S., *et al.*, 1993. Carbon/carbon composites graded with SiC/C functionally gradient compositions. In: Holt, J.B., Koizumi, M., Hirai, T., Munir, Z.A. (Eds.), *Proceedings of the 2nd International Symposium Functionally Graded Materials '92*. Westerville, OH: American Ceramic Society, pp. 125–132.
- Suresh, S., Mortensen, A., 1997. Functionally graded metals and metal-ceramic composites: Part 2 Thermomechanical behavior. *Int. Mater. Rev.* 42 (3), 85–116.
- Suresh, S., Mortensen, A., 1998. *Fundamentals of Functionally Graded Materials: Processing and Thermomechanical Behavior of Graded Metals and Metal-Ceramic Composites*. London: IOM Communications.
- Takeuchi Jin, M., Honda, S., Nishikawa, T., Awaji, H., 2005. Properties of multilayered mullite/Mo functionally graded materials fabricated by powder metallurgy processing. *Mater. Chem. Phys.* 89, 238–243.
- Tallon, C., Franks, G.V., 2011. Recent trends in shape forming from colloidal processing – A review. *J. Ceram. Soc. Jpn.* 119, 147–160.
- Tilbrook, M., Moon, R., Hoffman, M., 2005. Crack Propagation in Graded Composites. *Compos. Sci. Technol.* 65, 201–220.
- Tokita, M., 1999. Development of large-size ceramic/metal bulk FGM fabricated by spark plasma sintering. *Mater. Sci. Forum* 308–311, 83–88.
- Tokita, M., 2003. Large-size WC/Co functionally graded materials fabricated by spark plasma sintering (SPS) method. *Mater. Sci. Forum* 39, 423–425.
- Tuttle Bruce, A., Smay James, E., Cesarano, J., *et al.*, 2001. Robocast Pb(Zr_{0.95}Ti_{0.05})O₃ ceramic monoliths and composites. *J. Am. Ceram. Soc.* 74, 872–874.
- Uchida, T., Furukawa, M., Kitano, I., Koizumi, K., Matsamura, H., 1970. Optical characteristics of a light-focusing fiberoptic and its applications. *IEEE J. Quantum Electron.* 6 (10), 606–612.
- Vaezi, M., Seitz, H., Yang, S., 2013b. A review on 3D micro-additive manufacturing technologies. *Int. J. Adv. Manuf. Technol.* 67 (5–8), 1721–1754.
- Vaezi, M., Chianrabutra, S., Mellor, B., Yang, S., 2013a. Multiple material additive manufacturing – Part 1: A review. *Virtual Phys. Prototyp.* 8 (1), 19–50.
- Van Der Biest, O., Vandeperre, L., 1999. Electrophoretic deposition of materials. *Ann. Rev. Mater. Sci.* 29, 327–352.
- Vanmeensel, K., Anné, G., Jiang, D., Vleugels, J., Van der Biest, O., 2004. Homogeneous and functionally graded Si₃N₄-TiCN composites shaped by electrophoretic deposition. *Silic. Industriels* 69 (7–8), 233–239. (Special Issue).
- Vleugels, J., Anné, G., Put, S., Van der Biest, O., 2003. Thick plate-shaped Al₂O₃/ZrO₂ composites with a continuous gradient processed by electrophoretic deposition. *Mater. Sci. Forum* 423–425, 171–176.
- Wang, F., Mei, J., Jiang, H., Wu, X., 2007. Laser fabrication of Ti₆Al₄V/TiC composites using simultaneous powder and wire feed. *Mater. Sci. Eng. A* 445–446, 461–466.
- Wang, J., Pan, Z., Ma, Y., *et al.*, 2018. Characterization of wire arc additively manufactured titanium aluminide functionally graded material: Microstructure, mechanical properties and oxidation behavior. *Mater. Sci. Eng. A* 734, 110–119.
- Wang, X., Chu, X., Zhao, H., *et al.*, 2014. Controllable growth of functional gradient ZnO material using chemical vapor deposition. *Integr. Ferroelectr.* 151.
- Watanabe, Y., Yamanaka, N., Fukui, Y., 1998. Control of composition gradient in a metal-ceramic functionally graded material manufactured by the centrifugal method. *Compos. Part A* 29A, 595–601.
- Wegst, U.G.K., Bai, H., Saiz, E., Tomsia, A.P., Ritchie, R.O., 2014. Bioinspired structural materials. *Nat. Mater.* 14, 23–36.
- Weisensel, L., Travitzky, N., Sieber, H., Greil, P., 2004. Laminated object manufacturing (LOM) of SiSiC composites. *Adv. Eng. Mater.* 6 (11), 899–903.
- Willert-Porada, M., Gerdes, T., Borchert, R., 1995. Application of microwave processing to preparation of ceramic and metal-ceramic FGM. In: IIschner Cherradi, N. (Eds.), *Proceedings of the 3rd International Symposium on Structural and Functional Gradient Materials 1521*. Lausanne: Presses Polytechniques et Universitaires Romandes.
- Wilson, J.M., Shin, Y.C., 2012. Microstructure and wear properties of laser-deposited functionally graded Inconel 690 reinforced with TiC. *Surf. Coat. Technol.* 207, 517–522.
- Windsheimer, H., Travitzky, N., Hofenauer, A., Greil, P., 2007. Laminated object manufacturing of preceramic-paper-derived Si-SiC composites. *Adv. Mater.* 19 (24), 4515–4519.
- Wu, C.C.M., Kahn, M., Moy, W., 1996. Piezoelectric ceramics with functional gradients: A new application in material design. *J. Am. Ceram. Soc.* 79 (3), 809–813.
- Yang, L., Mertens, R., Ferrucci, M., *et al.*, 2019. Continuous graded gyroid cellular structures fabricated by selective laser melting: Design, manufacturing and mechanical properties. *Mater. Des.* 162, 394.
- Yang, Y., 1998. Stress analysis in a joint with a functionally graded material under a thermal loading by using the Mellin transform method. *Int. J. Solids Struct.* 35 (12), 1261–1287.
- Yang, Y., Munz, D., Schaller, W., 1997. Effect of the stress jump at the interface of a joint on the failure behavior. *J. Fract.* 87, L113–L118.
- Yeo, J.G., Jung, Y.G., Choi, S.C., 1998. Design and microstructure of ZrO₂/SUS316 functionally graded materials by tape casting. *Mater. Lett.* 37, 304–311.
- Zackrisson, J., Rolander, U., Jansson, B., Andren, H.O., 2000. Microstructure and performance of a cermet material heat-treated in nitrogen. *Acta Mater.* 48 (17), 4281–4291.
- Zeng, Y.P., Jiang, D.L., Watanabe, T., 2000. Fabrication and properties of tape-cast laminated and functionally gradient alumina–titanium carbide materials. *J. Am. Ceram. Soc.* 83, 2999–3003.
- Zhang, X., Guo, L., Yang, F., *et al.*, 2018. 3D gel printing of graded TiC-high manganese steel cermet. *J. Mater. Sci.* 54, 2122.
- Zhang, X.H., Han, J.C., Du, S.Y., Wood, J.V., 2000. Microstructure and mechanical properties of TiC-Ni functionally graded materials by simultaneous combustion synthesis and compaction. *J. Mater. Sci.* 35, 1925–1930.
- Zhang, Y., Han, J., Zhang, X., *et al.*, 2001. Rapid prototyping and combustion synthesis of TiC/Ni functionally gradient materials. *Mater. Sci. Eng. A* 299 (2001), 218–224.
- Zhang, Y., He, X., Han, J., Du, S., 1999. Ceramic green tape extrusion for laminated object manufacturing. *Mater. Lett.* 40 (6), 275–279.
- Zhao, C., Vleugels, J., Vandeperre, L., Van Der Biest, O., 2000. Cylindrical Al₂O₃/TZP functionally graded materials by EPD. *Br. Ceram. Trans.* 99 (6), 284–287.
- Zhecheva, A., Sha, W., Malinov, S., Long, A., 2005. Enhancing the microstructure and properties of titanium alloys through nitriding and other surface engineering methods. *Surf. Coat. Technol.* 200, 2192–2207.
- Zhou, W., Li, D., Wang, H., 2010. A novel aqueous ceramic suspension for ceramic stereolithography. *Rapid Prototyp. J.* 16 (1), 29–35.

Transparent Ceramics: Materials, Processing, Properties and Applications

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Introduction

Transparent ceramics exhibit a great-variety of desirable and/or unique properties and property combinations that are often unachievable with other materials, enabling applications ranging from transparent armor and electronics to laser hosts. Metals and alloys are opaque, leaving polymers, glasses, glass-ceramics and ceramics as transparent materials. Polymers, glasses and glass-ceramics can have excellent visible transparency, low density, high toughness (polymers) and low cost, but they generally have poor infrared transparency and thermal resistance and are relatively soft (Tropf *et al.*, 2000). Whereas, ceramics transmit further into the ultraviolet and infrared than any other materials while exhibiting a wide-range of refractive indices (Harris, 1999). They can also exhibit much higher hardness, strength and stiffness; the potential for far higher toughness than glasses; and higher thermal, thermal-shock, thermal conductivity and chemical resistance, as well as much broader ranges for some of these properties. Moreover, transparent ceramics can exhibit properties such as luminescence, lasing, electronic properties varying from insulating to electronic or ionic conduction, ferroelectricity, and electro- and magneto-optic behavior. Furthermore, interesting combinations exist, such as visible and infrared transparency combined with high strength and hardness and thermal shock resistance (Goldstein and Krell, 2016). As such, for some applications, only transparent ceramics can suffice.

This chapter focusses on crystalline materials that are transparent in the visible and/or infrared and have ‘ceramic’ (non-metallic/polymeric) properties. Although they are important infrared materials, low-bandgap semiconductors like silicon, germanium and gallium arsenide are not described. ‘Ceramic’ also refers to polycrystalline material, which is the focus of this chapter. However, single crystals representing important applications are also discussed. Although transparent single crystals were produced as early as the 1800s, transparent polycrystalline varieties were not realized until the 1950s and 60’s, and even then, only as small samples with poor transmission. While they are a relatively recent addition, transparent ceramics are rapidly expanding and are now used in a broad-range of applications (Goldstein and Krell, 2016; Evans, 2020). Moreover, despite often being used in only small quantities, they frequently enable the applications they are used in. This chapter provides an introduction to transparent ceramics and describes common materials and their processing, properties and applications.

Transmission Physics

Due to non-zero bandgaps, ceramics are transparent to at least some wavelengths of the electromagnetic spectrum. Of interest are the ultraviolet (UV, 10–380 nm), visible (Vis, 380–780 nm), infrared (IR, 0.78–1000 μm) and sometimes the microwave (MW, 1–100 mm). Within these ranges, absorption by atmospheric gases gives rise to windows in the visible, and in the near (NIR, 0.78–1 μm), shortwave (SWIR, 1.4–3 μm), midwave (MWIR, 3–5 μm) and longwave (LWIR, 8–14 μm) infrared (Harris, 1999; Goldstein and Krell, 2016).

Light interacts with ceramics primarily by interaction of its electric field with valence electrons. Shorter wavelengths, with higher energy than the bandgap ($E = hc/\lambda$, where h is Planck’s constant, c the speed of light in vacuum and λ wavelength), are absorbed by exciting electrons to the conduction band. In turn, excited electrons can lose energy by interacting with phonon (vibrational) modes and generating thermal energy and/or by relaxing to their ground state and re-emitting (luminescence), typically at lower frequency. Whereas, longer wavelengths are absorbed and transformed to thermal energy by phonon interactions. Both the short- and long-wave absorption edges are gradual, characterized by the Urbach and multi-phonon absorption tails, respectively (Savage, 1991). Wavelengths between the intrinsic absorption edges constitute the transmission window, where the alternating electric field polarizes atoms and accelerates electrons, which subsequently omnidirectionally re-radiate at the same frequency (Huygens’ principle). Interference between re-radiated intensities results in propagation through the material. Moreover, when a wavefront, or a planar array of intensities containing image information is incident upon the smooth planar interface of a transparent window, interference between re-radiated intensities results in only reflected (specular) and refracted (transmitted) intensities, the latter transmitting the image information through the window (Tropf *et al.*, 2000; Saleh and Teich, 1991) (Fig. 1).

Reflected and transmitted intensities (reflectance, transmittance) at interfaces depend on the media on either side, incidence angle, wavelength and electric field orientation (polarization). The speed of light is reduced due to interaction with matter, as quantified by the refractive index; $n = c/v$, where v is the phase velocity in the medium. In turn, the refractive index depends on a medium’s atoms and their structure, crystallographic orientation and state. The greater the interaction, the higher the index and the intrinsic reflection (reflectivity), which in turn limits maximum theoretical transmittance. In vacuum and approximately in air, the reflectivity of the surface of a medium with refractive index n is given by $R_1 = (n - 1/n + 1)^2$ and $R_2 = 2R_1/(1 + R_1)$ for a window with two interfaces (Fresnel’s equations). A full description of attenuation (α) due to high intrinsic absorption near absorption edges is given by the complex refractive index; $N = n - ik$, where $k = \alpha\lambda/4\pi$. However, since k is usually small within the transmission window, n is a good approximation (Harris, 1999; Saleh and Teich, 1991).

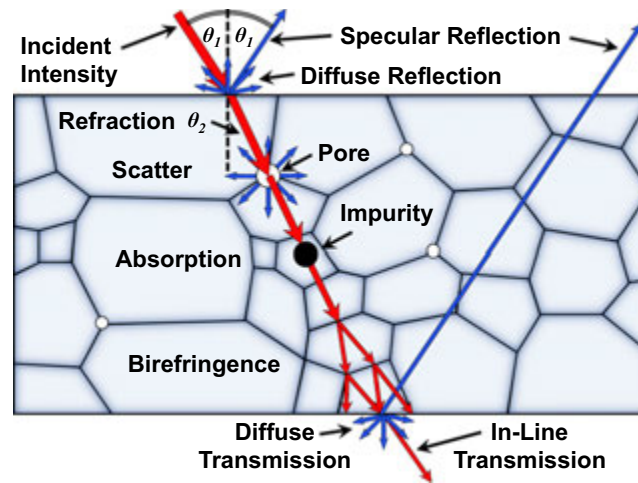


Fig. 1 Light transmission through a polycrystalline ceramic window. Transmitted intensity is decreased by specular and diffuse reflection at both interfaces, internal scatter (including birefringence) and absorption. Non-specular backscatter includes diffuse reflection and contributions from internal scatter, while forward scatter is comprised of internal scatter contributions, birefringence and diffuse refraction.

Reflection can significantly decrease the transmittance of windows and optical components for high-index materials, but it can be reduced with antireflective coatings. Since reflectance increases as the difference between the refractive indices bounding interfaces increases, coating with lower-index materials lowers reflectance at air/coating interfaces. The coating refractive index for maximum transmittance is the geometric mean of the refractive indices bounding interfaces; $n_{\text{coating}} = \sqrt{n_{\text{air}} \cdot n_{\text{substrate}}}$, which also corresponds to equal reflection intensities from each interface (Harris, 1999). Although coatings add an additional reflection at coating/substrate interfaces, the net reflection is still lower than without a coating. For example, a window with $n = 2$ suffers an 11% reflection at the air/window interface. By adding a coating with $n = 1.4$, the air/coating and coating/window losses are 3% each (6% total). Moreover, if the coating thickness is $\frac{1}{4}$ of a wavelength of interest, the air/surface and coating/bulk reflections destructively interfere since they are 180° out-of-phase, reducing reflection to zero near that wavelength (even for higher-index coatings). Conversely, high-index coatings can be used to increase reflection or to reject unwanted wavelengths (such as for heat-mirrors), for UV protection and to protect sensitive electronics and detectors. Reflection can also be modified by using multi-layer coatings, grading the refractive index or using moth-eye coatings. Interference of multiply-reflected and transmitted intensities can also affect transmission in thin components (Etalon effect) (Harris, 1999).

The refractive index varies with wavelength (dispersion) and is described by empirical Sellmeier relations within the transmission window. The magnitude of the variation is quantified by the Abbe number, with higher values representing lower dispersion, which is in turn typically associated with lower refractive indices (Krell *et al.*, 2009a). Refractive index also varies with stress and strain (stress-optical, elasto-optic coefficients), stoichiometry, temperature (thermo-optic coefficient, dn/dT) and electric field intensity (Pockels and Kerr effects) (Harris, 1999). Non-cubic materials have different refractive indices along different directions, scattering different polarizations at every grain (birefringence) and rendering thick sections translucent. Thus, cubic (isotropic) materials are preferred. However, birefringence scattering can be greatly reduced by reducing grain size to less than $\sim 1/20$ th of transmitted wavelengths (Harris, 1999). Although this increases the number of grain intersections, birefringence scattering is decreased such that transmittance is still improved (Apetz and van Bruggen, 2003). Intrinsic birefringence in cubic single crystals due to refractive index difference along cube diagonals becomes important in the UV, but it is negligible for polycrystalline material and longer wavelengths (Krell *et al.*, 2009b).

While the reflection angle to the surface normal always equals the incidence angle (θ_i), the refraction angle (θ_r) deviates according to Snell's law; $\sin\theta_i/\sin\theta_r = v_i/v_r = n_r/n_i$, where i refers to incident and r refracted (Saleh and Teich, 1991). Reflection occurs at all interfaces bounded by different refractive indices, with non-planar or rough interfaces causing diffuse reflection and refraction (scatter). Internal scatter is caused by variations in stoichiometry and strain, secondary phases, phase transitions, cracks, pores and birefringence. It is thickness-dependent; $I_T = I_0 e^{-\alpha_{sc} t}$, where I_0 is incident and I_T transmitted intensity, α_{sc} (cm^{-1}) the scattering coefficient and t thickness (Saleh and Teich, 1991). Pores are typically the main source of scatter in transparent ceramics and scatter is maximized for pore sizes near those of transmitted wavelengths (Apetz and van Bruggen, 2003). Models, depending on scatterer sizes (Rayleigh $\ll \lambda$ and Mie $\approx \lambda$), indicate that for 5 mm-thick isotropic ceramic windows, 0.1 vol% of ~ 500 nm pores decreases in-line transmittance at $\lambda = 600$ nm to $\sim 1\%$ (55% transmittance for 0.01 vol%) (Fig. 2) (Apetz and van Bruggen, 2003). For 1–5 mm thick windows in the visible, tolerable pore-sizes are < 60 nm and concentrations < 200 ppmv and preferably < 100 ppmv ($< 1/100$ th of 1%), and likely < 5 ppmv for more demanding applications like laser media (Goldstein and Krell, 2016).

Transmittance is also attenuated by extrinsic absorption, which is caused by impurities (carbon, OH⁻), secondary phases and ions with lower bandgaps or electronic transitions (transition metals, rare earths), luminescent species, absorbing or luminescent point defects (color centers) and by free-carriers in semiconductors (Tropf *et al.*, 2000; Harris, 1999; Goldstein and Krell, 2016). Like scatter, absorption is thickness-dependent (Beer-Lambert law); $I_T = I_0 e^{-\alpha_{abs} t}$, where t is thickness and α_{abs} (cm^{-1}) the absorption coefficient. For a window with reflection losses included; $I_T \approx (1 - R_2)^2 e^{-\alpha_{abs} t}$, and if scatter is also present it can be

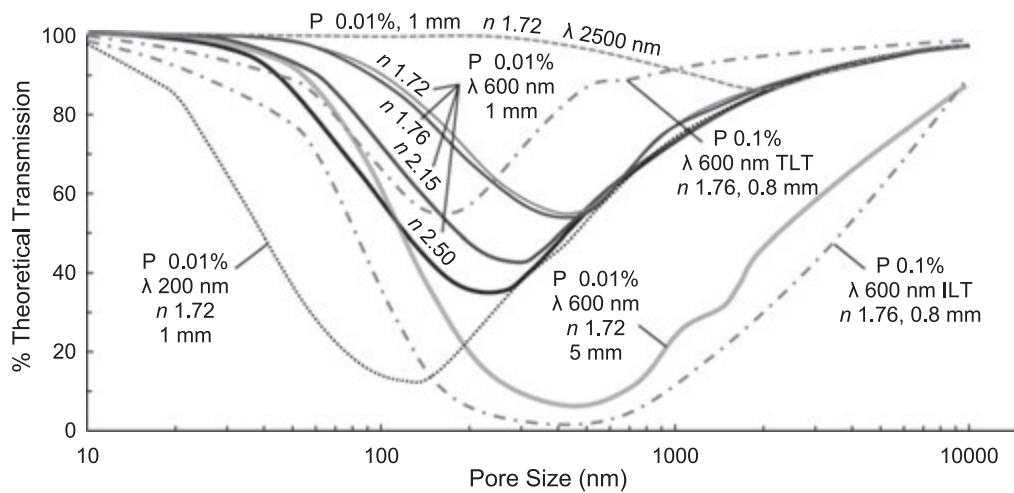


Fig. 2 Percent theoretical transmission as a function of porosity (P 0.01% and 0.1% [dash-dot lines]), thickness (1 mm and 5 mm [gray solid line]), wavelength (200 [dotted line], 600 and 2500 nm [dashed line]), refractive index (1.72 [spinel], 1.76 [Al₂O₃], 2.15 [c-ZrO₂], 2.50 [PLZT]) [solid lines] and total (TLT) and in-line (ILT) [dash-dot lines] transmittance calculated using a Mie model. Reproduced from Apetz, R., van Bruggen, M.P.B., 2003. Transparent alumina: A light-scattering model. *J. Am. Ceram. Soc.* 3, 480–486. Krell, A., Klimke, J., Hutzler, T., 2009b. Transparent compact ceramics: Inherent physical issues. *Opt. Mater.* 31, 1114–1150. Krell, A., Hutzler, T., Klimke, J., Potthoff, A., 2010. Nano-processing for larger fine-grained windows of transparent spinel. In: Swab, J.J. (Ed.), *Advances in Ceramic Armor VI*. ACerS. Goldstein, A., Krell, A., 2016. Ceramics at 50: Progress made and further prospects. *J. Am. Ceram. Soc.* 99 (10), 3173–3197.

combined with absorption in an attenuation coefficient; $I_T \approx (1 - R_2)^2 e^{-\alpha_{att} L}$, where $\alpha_{att} = \alpha_{abs} + \alpha_{sc}$ (Harris, 1999; Fox, 2001; Van Damme *et al.*, 1991; Li *et al.*, 2005). In which case it is a measure of in-line transmission since total transmittance also includes diffuse scatter. Alternatively, these variables are related by; $I_0 = I_T + I_R + I_A + I_S$, where R is reflectance, A absorbance, and S scatter. In terms of attenuation, optical elements and high-power optics typically require $\alpha_{att} < 1-0.1$ (Tropf *et al.*, 1995). Radiant emission can also obscure transmittance or saturate detectors in IR applications. It is quantified by emittance, the fraction of radiant power emitted compared to a blackbody, which is proportional to the fourth power of temperature and whose intensity and peak wavelength vary with temperature (Harris, 1999).

Transmittance, reflectance and absorbance can be determined by spectrophotometry and resolution quantified by methods like the modulation transfer function (Harris, 1999). Due to their effect on attenuation, the thickness and the measurement method should be taken into account for comparisons. The total transmitted intensity (TLT) through a window includes forward scatter and so the in-line transmittance (ILT), within a narrow cone of 3°–5°, or the real in-line transmission (RIT) within a cone of <0.5° are better representations of transmission (Krell *et al.*, 2009a). ‘Transparent’ sometimes refers to high transmittance that is nearly thickness-independent, while ‘translucent’ refers to lower values. Transparency can also be defined in terms of the absorption coefficient, for example $\alpha < 1 \text{ cm}^{-1}$ (Tropf *et al.*, 2000; Goldstein and Krell, 2016; Krell *et al.*, 2009a). Microwave transmittance is important for radomes and some IR applications and is quantified like visible transmittance, with the absorption coefficient replaced by $(2\pi/\lambda)\tan \delta$ (where $\tan \delta$ is the loss tangent) and the refractive index with the dielectric constant $\epsilon = n^2$, with higher transmittance for low dielectric constants and loss tangents (Harris, 1999).

Transparent ceramics can also exhibit special optical properties, such as total internal reflection, fluorescence (non-coherent re-emission), multi-photon absorption and re-emission at shorter wavelengths (upconversion), phosphorescence (delayed re-emission), stimulated emission with a population inversion in a resonant cavity (lasing), refractive index variation with applied voltage (electrooptic effect) or field (magneto-optic effect), and color change with applied voltage (electrochromic), temperature (thermochromic) or illumination (photochromic). Moreover, some these properties can be combined by fabricating composites or laminates (i.e., smart windows) (Goldstein and Krell, 2016; Kong *et al.*, 2015). Some of these effects are caused by nonlinear responses in frequency, polarization, phase or path, especially in the presence of high fields (i.e., lasers) and are quantified by various nonlinear optical coefficients (Tropf *et al.*, 2000). Common electro/magneto-optic effects include the linear change in refractive index with applied electric field (Pockels effect), usually described by the largest electrooptic tensor element (i.e., r_{33} or r_c [$10^{-10} \text{ m} \cdot \text{V}^{-1}$]); the nonlinear Kerr effect quantifying the change with the square of the field, expressed by the Kerr coefficient K [$\text{m} \cdot \text{V}^{-2}$] for a DC field, and the R coefficient [$10^{-16} \text{ m}^2 \text{ V}^{-2}$] and second-order nonlinear refractive index n_2 [$10^{-16} \text{ m}^2 \text{ W}^{-1}$] for an AC (optical) field; and the Verdet constant ($\text{V} [\text{rad} \cdot \text{T}^{-1} \text{ m}^{-1}]$) describing the strength of plane-polarization rotation by a magnetic field (Faraday effect) (Tropf *et al.*, 1995).

Physical Properties

Transparent ceramics exhibit a host of other sought-after mechanical, chemical, thermal, electronic and magnetic properties, which are discussed in more detail in sections on individual materials. Properties are generally assessed as for opaque ceramics, with

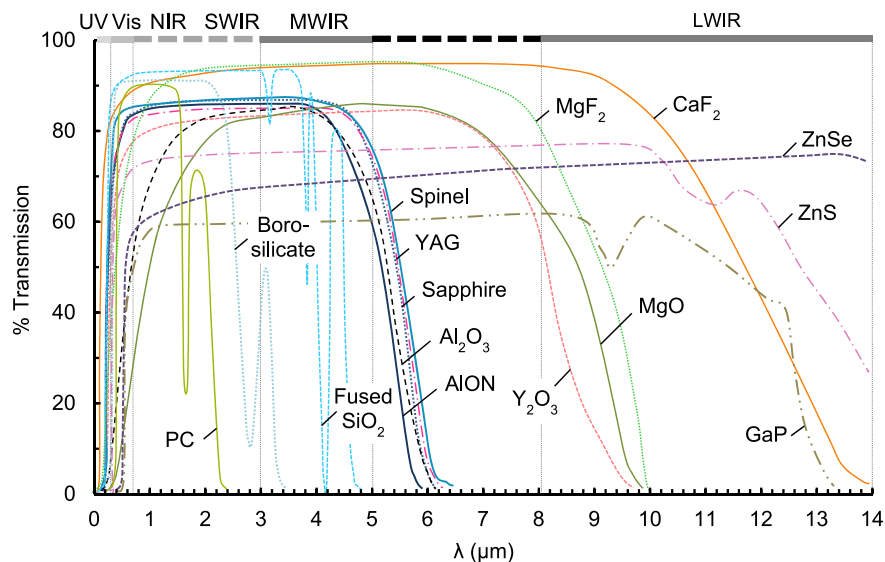


Fig. 3 Transmission spectra for common transparent ceramics and reference materials; thicknesses variable from coatings to 0.5–5 mm; PC polycarbonate. Reproduced from Harris, D.C., 1999. *Materials for Infrared Windows and Domes: Properties and Performance*. SPIE Optical Engineering Press. Weber, M., 2003. *Handbook of Optical Materials*. CRC Press. Wei, G.C., 2005. Transparent ceramic lamp envelope materials. *J. Phys. D: Appl. Phys.* 38, 3057–3065. Jiang, N., Xie, R.-J., Liu, Q., Li, J., 2007. Fabrication of sub-micrometer MgO transparent ceramics by spark plasma sintering. *J. Eur. Ceram. Soc.* 37, 4947–4953. Krell, A., Hutzler, T., Klimke, J., 2009a. Transmission physics and consequences for materials selection, manufacturing, and applications. *J. Eur. Ceram. Soc.* 201–207. Benitez, T., Gómez, S.Y., de Oliveira, A.P.N., Travitzky, N., Hotza, D., 2017. Transparent ceramic and glass-ceramic materials for armor applications. *Ceram. Int.* 43 (16), 13013–13046. Surmet Corp., 2020. MgAl₂O₄ and AION Products. Available at: www.surmet.com, accessed 2020. Goldstein, A., Krell, A., Burshtein, Z., 2020. *Transparent Ceramics: Materials, Engineering, and Applications*. John Wiley & Sons.

some methods preferred depending on the application (i.e., ring-on-ring equibiaxial flexure for window strength). Typical transmission spectra and windows for common transparent ceramics are shown in **Figs. 3** and **4**, with common non-ceramic optical materials and single crystals included for comparison. These should be used for relative comparison only as optical properties vary significantly depending on material quality and sample thickness.

General physical properties for common materials are given in **Tables 1, 2** and other materials or properties can be found in referenced texts (Tropf *et al.*, 1995; Harris, 1999; Tropf *et al.*, 2000; Weber, 2003; Kong *et al.*, 2015; Goldstein *et al.*, 2020). Common glasses and polymers are included for comparison, and less common materials with exceptional properties are included to show the full range of properties attainable. As for optical properties, caution should be exercised when making comparisons. Wherever possible data is for polycrystalline and preferably transparent material, and when known it is indicated if for coatings or single crystals. However, some mechanical and thermal properties and many optical properties (i.e., n , dn/dT) are invariably for single crystals. Physical properties vary significantly depending on testing conditions, specimen geometry and thickness, surface finish, stoichiometry, impurity content, point defects, and flaws and flaw-size distribution. This is especially true for polycrystalline material, where local variations in these properties and also grain orientation, grain size and grain-size distribution can occur. Properties like hardness, strength and toughness often increase with decreasing grain-size (Hall-Petch relation) and are significantly affected by surface finish (Harris, 1999). The figures of merit (R' for mild and R for severe) are important for aerothermal window and laser applications and provide a semiquantitative comparison of thermal shock resistance, where the larger the figure, the greater the heat flux withstood without failure (Harris, 1999).

Some general property trends emerge depending on bonding and constituent atoms. Strong covalent bonds (SiO₂) or ionic character (LiF) are typically associated with higher-energy bandgaps (thus shorter-wavelength UV absorption edges) and lower refractive indices (thus higher transmittance), but lower IR absorption edges, especially for materials with lighter constituent atoms. Strongly-bonded materials also usually have high moduli, hardness, strength and room-temperature thermal conductivity, but lower thermal expansion. Higher structural symmetry can also increase hardness and reduce the number of unique lattice vibrations, reducing IR absorption and extending the absorption edge, as in diamond (Saleh and Teich, 1991; Tropf *et al.*, 1995; Bass, 1995; Harris, 1999; Tropf *et al.*, 2000; Weber, 2003). Materials with heavier elements and weaker bonds (ZnS, KBr) typically have lower thermo-mechanical properties, but since vibrational energy increases with bond strength and decreases with increasing atomic mass, they have longer-wavelength IR absorption edges (Harris, 1999). Carbides can feature excellent thermo-mechanical properties, but lack oxidation resistance, and apart from diamond typically have low visible transparency. Oxides, nitrides and oxynitrides generally exhibit good visible and MWIR transparency and good to excellent thermo-mechanical properties and oxidation resistance. alkaline/alkaline fluorides and chlorides (CaF₂, KCl) have low UV absorption edges, refractive indices and dispersion, rendering high transmission from the UV (MgF₂) to the LWIR (BaF₂), but they tend to have lower thermo-mechanical

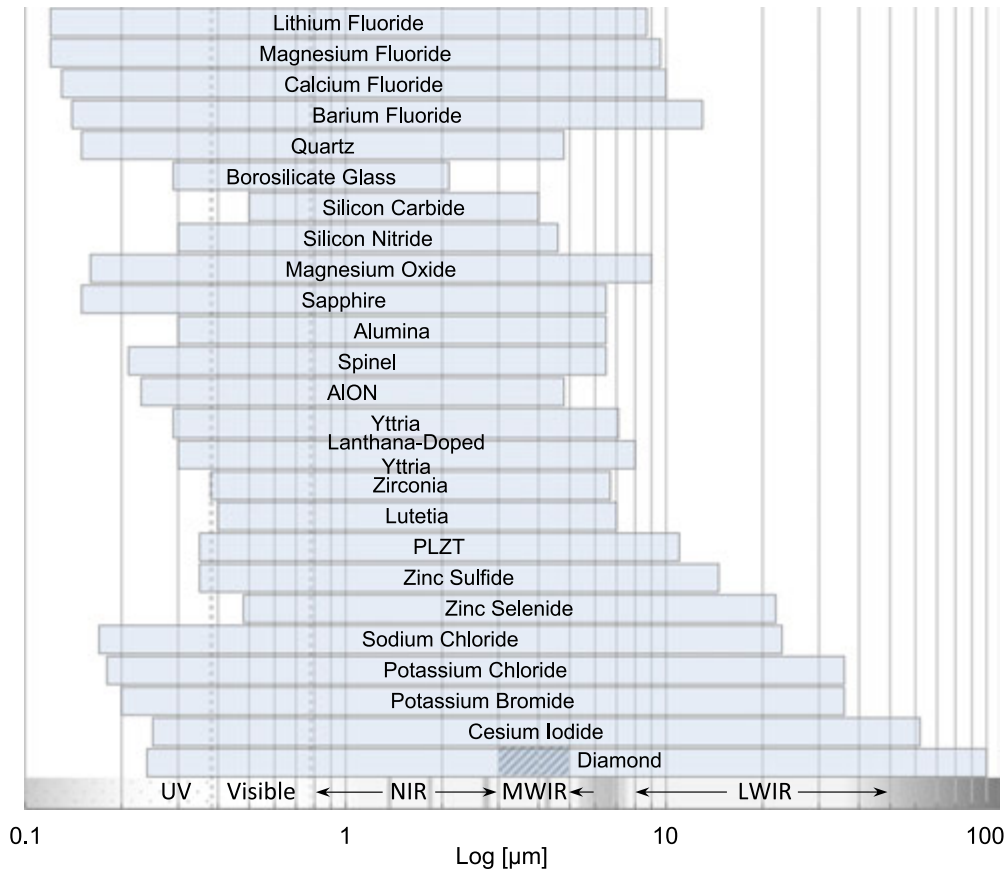


Fig. 4 Transmission windows for select transparent ceramics and reference materials based on >10% transmittance near absorption edges. Adapted from Harris, D.C., 1999. *Materials for Infrared Windows and Domes: Properties and Performance*. SPIE Optical Engineering Press. Values from Weber, M., 2003. *Handbook of Optical Materials*. CRC Press. Harris, D.C., 1999. *Materials for Infrared Windows and Domes: Properties and Performance*. SPIE Optical Engineering Press.

mechanical properties than oxides and can be hygroscopic (LiF) or even water-soluble (NaCl). Phosphides, sulfides, selenides, tellurides, bromides and iodides generally have lower thermo-mechanical properties and limited visible transmittance, but can have high transmittance up to the far-IR (CsI), competing with semiconductors (Si, Ge, GaAs). An important metric is cost, with some materials, like diamond and Y_2O_3 being more expensive than materials with comparable properties. A general ranking of select transparent ceramics is shown in [Table 3](#).

Processing

Processing depends on whether single crystal, bulk polycrystalline or coating material is sought ([Table 4](#)), the anion type (which can affect sintering atmosphere); properties like bonding, phase transitions, diffusion, volatility and melting point (which influence the sintering regime and the need for additives and/or pressure); and the component geometry and production scale. To ensure transparency, the goal is obtaining fully-dense, homogeneous (in phase, stoichiometry and residual stress) bodies with minimal porosity, secondary phases, impurities and absorption centers. This is a difficult prospect considering the extreme sensitivity of transparent ceramics to impurities and processing parameters. Even when transparency is attained, processing must be taken a step further than for opaque ceramics as virtually every type of defect is observable through the thickness. Although this presents a challenge, transparency enables easily finding defects to uncover their nature.

Single crystals are produced by melt-growth methods like the Czochralski process, where an oriented seed crystal is slowly pulled from a melt to produce a boule. However, extensive machining is required to obtain desired shapes. Newer methods like edge-defined film-fed growth can competitively produce sheets, windows and cylinders. Since they lack grain boundaries, single crystals are less prone to pores and secondary phases and typically have higher refractive index homogeneity ([Tropf et al., 2000](#); [Stevenson et al., 2011](#)). However, they can still have compositional and refractive index gradients and stoichiometry control can be difficult for complex systems. Moreover, processing is often slower and more expensive, geometry is limited, fewer toughening

Table 1 Optical properties of select transparent ceramics

Compound	Formula	Structure ^a	Refractive index ^b		dn/dT ^b		Transmittance			Bandgap eV	Cut-Off (μm) ^c	
			n	λ (nm)	10^{-6}K^{-1}	λ (nm)	R_2^d	Calc.	Achieved ^e		UV	IR
Polycarbonate	(C ₁₆ H ₁₄ O ₃) _n	p	1.59	633	−1	—	9%	91%	~91%	3–4	0.40	1.6
Quartz (s.c.)	α -SiO ₂	h	1.56/1.55	633	−5/−6	365	9%	91%	~91%	8.2	0.15	4.8
Fused Silica	SiO ₂	a	1.46	589	10	600	7%	93%	~92%	8–9	0.16	4.7
Borosilicate	SiO ₂	a	1.52	589	3	436	8%	92%	~92%	4	0.29	2.1
Diamond (CVD)	C	c	2.42	633	10	546	29%	71%	70%	5.47	0.24	2.7 (>100) ^f
Silicon Carbide	β -SiC	h(α),c(β)	2.64	600	37	IR	34%	66%	<40% CVD	2.6	0.50	4
Boron Nitride	c-BN	c	2.12	633	—	—	23%	77%	~77% ALD	6–7.5	0.20	6
Silicon Nitride	Si ₃ N ₄	tr(α),h(β),c,a	2.03	600	25	—	21%	79%	<40%	5	0.30	4.6
Aluminum Nitride	α -AlN	h	2.02	600	30	IR	24%	76%	75%	6.2	0.20	13.6
SiAlON	α Si _{12-x-y} Al _{x+y} O _y N _{16-y} , β (M)Si _{6-x} Al _x O _x N _{8-x}	tr(α),h(β)	2.15	—	—	—	24%	76%	66%	5	—	—
Boron Phosphide (CVD)	BP	c,a	2.8	633	—	—	37%	63%	60% IR	2	0.50	6 (>50) ^f
Gallium Phosphide (CVD)	GaP	c	3.35	633	160	633	45%	55%	—	2.2–2.8	0.54	10.5
Beryllium Oxide	BeO	h	1.73/1.72	633	8/13	458	13%	<87%	—	10.6	0.13	4.5
Magnesium Oxide	MgO	c	1.74	633	20	365	13%	87%	55%	7.8	0.16	9
Sapphire (s.c.)	Al ₂ O ₃	h	1.77/1.76	633	13	458	14%	86%	~86%	10	0.15	6.5
Aluminum Oxide (p.c.)	Al ₂ O ₃	h	1.77/1.76	600	13	458	14%	<86%	71%, 82% IR	10	0.30	6.5
Aluminum Oxynitride	Al ₂₃ O ₂₇ N ₅ (AlON)	c	1.79	633	15	633	15%	85%	>80%	6.5	0.23	4.8
Magnesium Aluminate	MgAl ₁₂ O ₄ (Spinel)	c	1.72	688	9	589	13%	87%	84%	7.7	0.21	6.5
Scandium Oxide	Sc ₂ O ₃	c	1.96	633	—	—	19%	81%	80%	6.0	0.25	7
Lutetium Oxide	Lu ₂ O ₃	c	1.93	589	—	—	18%	82%	80%	5.4	0.40	7
Yttrium Oxide	Y ₂ O ₃	c	1.92	633	3	633	18%	82%	82%	5.6	0.29	7.1
Lanthana-Doped Ytria	La:Y ₂ O ₃	c	1.97	546	32	IR	19%	81%	77%, 80% IR	—	0.30	8
Ytria Stabilized Zirconia	ZrO ₂ :Y ₂ O ₃ (12 YSZ)	c	2.12	633	10	458	23%	77%	65%	4.1	0.38	6.7
Yttrium Aluminum Garnet	Y ₃ Al ₅ O ₁₂ (YAG)	c	1.83	633	10	633	16%	84%	84%	5.5–6.5	0.21	6.2
Indium-Tin Oxide	In ₂ O ₃ :SnO ₂ (ITO)	c	1.78	633	—	—	15%	85%	~85%	3.5–4.3	0.35	3
PLZT (65:35)	(Pb,La)(Zr,Ti)O ₃	c,t	2.45	630	—	—	30%	70%	57%	3–4	0.35	11
Zinc Sulfide	ZnS	c	2.36	600	64	633	28%	72%	75% IR	3.7	0.35	14.6
Zinc Selenide	ZnSe	c	2.61	600	106	633	33%	67%	65% IR	2.71	0.48	22
Lithium Fluoride (s.c.)	LiF	c	1.39	633	−22	458	5%	95%	~95%	13.6	0.12	8.7
Magnesium Fluoride	MgF ₂	t	1.38	593	1	458	5%	<95%	92% IR	10.8	0.12	9.6
Calcium Fluoride	CaF ₂	c	1.43	600	−13	458	6%	94%	90%	10.0	0.13	10
Sodium Chloride (s.c.)	NaCl	c	1.53	633	−34	458	8%	92%	~92%	9.0	0.17	23
Potassium Bromide	KBr	c	1.56	633	−39	458	9%	91%	—	7.6	0.20	36
Cesium Iodide	CsI	c	1.78	633	−99	633	15%	85%	82% IR	6.2	0.25	62

^aCrystal structure; a (amorphous), c (cubic), h (hexagonal), p (polymer), t (tetragonal), tr (trigonal).^bRefractive index and thermo-optic coefficient values mainly from single crystal data at T_{amb}.^cMaximum transmission window reported based on 10% absorption at edges at T_{amb} and with variable thickness.^dR₂ calculated window reflectance from *n* (expected lower if birefringent).^eHighest reported transmittance in literature (thickness variable from coating to mm's, typically 0.5–2 mm).^fDiamond and boron phosphide have low transmission far into the IR.

Note: Values mainly from Tropf, W.J., Thomas, M.E., Harris, T.J., 1995. Chapter 33. Properties of crystals and glasses, part IV. In: Bass, M. (Ed.), Handbook of Optics, Devices, Measurements, & Properties, second ed. McGraw-Hill, Inc. Harris, D.C., 1999. Materials for Infrared Windows and Domes: Properties and Performance. SPIE Optical Engineering Press. Tropf, W.J., Harris, T.J., Thomas, M.E., 2000. Electro-Optics Handbook, second ed. McGraw-Hill. Weber, M., 2003. Handbook of Optical Materials. CRC Press. Goldstein, A., Krell, A., 2016. Ceramics at 50: Progress made and further prospects. J. Am. Ceram. Soc. 99 (10), 3173–3197. Goldstein, A., Krell, A., Burshtein, Z., 2020. Transparent Ceramics: Materials, Engineering, and Applications. John Wiley & Sons and references for individual materials in text.

Table 2 Thermo-mechanical properties of select transparent ceramics

Compound	Formula	Density $g \cdot cm^{-3}$	Hardness HV, HK		Flexure strength MPa	Toughness $MPa \cdot m^{-1/2}$	Young's Modulus GPa	Thermal expansion $10^{-6} K^{-1}$	Characteristic temperatures $^{\circ}C$		Thermal conductivity $W \cdot m^{-1} K^{-1}$	Thermal shock	
			$kg \cdot mm^{-2}$	GPa								R' $10^3 W \cdot m^{-1}$	R $10^3 K$
Polycarbonate	$(C_{16}H_{14}O_3)_n$	~1.2	~20	0.2	~90	4–7	13–21	60–80	150	tg	0.2	–	–
Quartz (s.c.)	α -SiO ₂	2.65	820	8	50–70	0.9	95	7/12	572, 1713	p,m	6–10	–	2.4
Fused Silica	SiO ₂	2.20	600	4.5–6	50–60	0.8	70	0.5	1100, 1650	tg,ts	1.4	3.4	2.4
Borosilicate	SiO ₂	2.51	520	5	50	0.7	80	3–7	563, 766	tg,ts	–	–	–
Diamond (CVD)	C	3.52	9000	57–88	200–800	2–8	1050–1150	0.8	1497, ~700	p,o	2000	410	0.2
Silicon Carbide	β -SiC	3.21	2540	25–29	600	4	465	2.2–2.8	2830	d	490	82	0.39
Boron Nitride	c -BN	3.48	4600	45	600	5.3	830	3.5	> 827, 2967	p,m	~760	–	–
Silicon Nitride	Si ₃ N ₄	3.24	2200	19–22	600–880	5	165	1.4	> 2030	m	33	24	0.74
Aluminum Nitride	α -AlN	3.26	1225	12	225	3	295	4–5	2200–3000	m	320	37	0.12
SiAlON	α Si _{12–x–y} Al _{x+y} O _y N _{16–y} , β (M) Si _{6–x} Al _x O _x N _{8–x}	~3.3	~2000	18–21	–	6.1	–	–	–	–	–	–	–
Boron Phosphide (CVD)	BP	2.97	3600	35–47	–	1–2	270	3.6–4.6	1400	d	400	–	–
Gallium Phosphide (CVD)	GaP	4.13	2200	22	120	0.9	100	5.3	1467	m	100–110	15	0.14
Beryllium Oxide	BeO	3.01	1250	12	275	–	395	5.6–7.5	2100, 2452	p,m	350	–	–
Magnesium Oxide	MgO	3.58	690	6–7	250	2	195–250	10.5	2800	m	59	3.7	0.06
Sapphire (s.c.)	Al ₂ O ₃	3.99	2200	14–22	300–1000	2–3.5	345–400	4.4	2072	m	24–36	4.3	0.12
Aluminum Oxide (p.c.)	Al ₂ O ₃	3.99	2000	19–21	500–800	3–3.5	400	6	2072	m	–	–	–
Aluminum Oxynitride	Al ₂₃ O ₂₇ N ₅ (AION)	3.69	1800	15–18	300	2.4	315–330	5.8	2050	m	12.6	1.5	0.12
Magnesium Aluminate	MgAl ₂ O ₄ (Spinel)	3.58	1600	12–16	220	1.9	190–290	5.6	2135	m	15	1.9	0.13
Scandium Oxide	Sc ₂ O ₃	3.84	–	–	–	2	221	6.7	–	–	17	–	–
Lutetium Oxide	Lu ₂ O ₃	9.43	–	–	–	2	178	12.5	–	–	13	–	–
Yttrium Oxide	Y ₂ O ₃	5.03	720	7	150–200	0.7	165	6.6	2377	m	13.5	1.3	0.1
Lanthana-Doped Ytria	La:Y ₂ O ₃	~5.1	760	7–8	165	0.7	165	6.6	–	–	5.3	0.5	0.1
Ytria Stabilized Zirconia	ZrO ₂ :Y ₂ O ₃ (12 YSZ)	5.94	1377	13.5	300	2.8	230	7.3	2837	m	2	–	–
Yttrium Aluminum Garnet	Y ₃ Al ₅ O ₁₂ (YAG)	4.56	~1500	13–17	200	2.2	280	4.2	1957	m	13.4	1.3	0.12
Indium-Tin Oxide	In ₂ O ₃ :SnO ₂ (ITO)	~6.8	600	6	–	2–3	–	–	–	–	10	–	–
PLZT (65:35)	(Pb,La)(Zr,Ti)O ₃	7.92	5	0.05	80–120	1	105	4.2	1450	m	–	–	–
Zinc Sulfide	ZnS	4.09	250	2.5	100–220	0.8	75	6–7	1020, 1827	p,m	17–19	2.6	0.14
Zinc Selenide	ZnSe	5.27	105	1.0	50	0.5	70	7	1517	m	16–18	1.1	0.03

(Continued)

Table 2 Continued

Compound	Formula	Density $g \cdot cm^{-3}$	Hardness HV, HK		Flexure strength MPa	Toughness $MPa \cdot m^{-1/2}$	Young's Modulus GPa	Thermal expansion $10^{-6} K^{-1}$	Characteristic temperatures $^{\circ}C$		Thermal conductivity $W \cdot m^{-1} K^{-1}$	Thermal shock	
			$kg \cdot mm^{-2}$	GPa								R' $10^3 W \cdot m^{-1}$	R $10^3 K$
Lithium Fluoride (s.c.)	LiF	2.64	110	1.1	–	–	–	34.4	842	m	11.3	–	–
Magnesium Fluoride	MgF ₂	3.18	580	5.7	150–160	1	140	10.4	1263	m	14.7	0.9	0.06
Calcium Fluoride	CaF ₂	3.18	160	1.6	55	0.5	75	18.9	1151, 1357	p,m	9.7	0.3	0.03
Sodium Chloride (s.c.)	NaCl	2.16	17	0.2	10	–	40	40	801	m	6.5	0.03	0.005
Potassium Bromide	KBr	2.75	6–7	0.1	3	–	25	38.5	734	m	4.8	–	–
Cesium Iodide	CsI	4.51	1–2 Mohs	–	6 s.c.	–	20	48	625	m	1.1	–	–

Note: Density (SiAlON, La:Y₂O₃, ITO, PLZT variable), hardness (Vickers or Knoop).

Thermal expansion (most values 300K, avg. values for s.c.), characteristic temps. (m, melting; p, phase change; d, decomposition; o, oxidation; tg, glass transition; ts, softening).

Figures of merit R (mild) = $\sigma(1 - \nu)/kE$ and R (severe) = $\sigma(1 - \nu)/\alpha E$, where σ is strength, ν Poisson's ratio, k thermal diffusivity and E modulus.

s.c. (single crystal), p.c. (polycrystalline), CVD (chemical vapor deposition or other coating).

Typically highest referenced values (many approximate), mostly from Harris, D.C., 1999. Materials for Infrared Windows and Domes: Properties and Performance. SPIE Optical Engineering Press. Tropf, W.J., Thomas, M.E., Harris, T.J., 1995. Chapter 33.

Properties of crystals and glasses, part IV. In: Bass, M. (Ed.), Handbook of Optics, Devices, Measurements, & Properties, second ed. McGraw-Hill, Inc. Tropf, W.J., Harris, T.J., Thomas, M.E., 2000. Electro-Optics Handbook, second ed. McGraw-Hill.

Weber, M., 2003. Handbook of Optical Materials. CRC Press. Goldstein, A., Krell, A., 2016. Ceramics at 50: Progress made and further prospects. J. Am. Ceram. Soc. 99 (10), 3173–3197. Goldstein, A., Krell, A., Burshtein, Z., 2020. Transparent Ceramics:

Materials, Engineering, and Applications. John Wiley & Sons and individual-material references.

mechanisms are available and thermo-mechanical properties are typically lower (Harris, 1999; Stevenson *et al.*, 2011). Furthermore, single crystals lack the doping flexibility and property tailoring ability of polycrystalline ceramics by microstructure modification (Tropf *et al.*, 1995; Stevenson *et al.*, 2011). Whereas, polycrystalline ceramics can be formed into complex near-net shapes at lower cost and properties can be tailored or improved by modifying grain size, composition and phase transitions, and by introducing dopants. Moreover, they typically have higher hardness, strength, fracture toughness, and thermal shock resistance, while retaining good optical properties (Stevenson *et al.*, 2011). Single crystals are typically used in applications requiring small components and/or homogeneous, directional or specialty optical properties, while polycrystals are often used when larger sizes, coatings, or better mechanical properties are required (Tropf *et al.*, 1995).

Although materials like diamond and ZnS are more easily produced by deposition, most bulk polycrystalline transparent ceramics are made by sintering powders. Research studies often cold-press and sinter dry powders, but fine powders cause dusting issues, and high frictional forces cause density gradients and require high pressing loads, limiting green-body size due to press-size limitations. Thus, bulk commercial polycrystalline transparent ceramics are usually made by traditional ceramic processing. This can consist of aqueous or solvent-based milling with ceramic media to deagglomerate powders, filtering, adding organic binders and lubricants to produce easy-to-press granules by spray- or freeze-drying, sieving, uniaxial and/or cold-isostatic pressing to form green bodies, debinding to remove organics, sintering to closed porosity, pressure-assisted sintering to remove remnant pores and annealing to restore stoichiometry. For materials like Y_2O_3 all of these steps may be used, while for others like Al_2O_3 and ALON only some are used (Harris, 1999; Savage, 1991; Mroz *et al.*, 2005).

The availability of high-purity nanometer-sized powders was one of the keys to enabling transparent ceramics. Powders are synthesized as for opaque ceramics, but they typically require higher purity, more precise stoichiometry, higher surface area and finer and/or better-defined crystallite and particle sizes and size-distributions. Such powders typically consist of high-purity (< 100–1000 ppm impurities) soft agglomerates with narrow particle-size distributions that are composed of near-spherical high surface-area nanometer-sized crystallites. Precursors often contain species not contributing to the final structure that can be completely removed after reaction (hydroxides, nitrates, carbonates, chlorides, fluorides, alkoxides, etc.). Common synthesis methods include solid-state (decomposition, chemical reaction, mechano-chemical), wet-chemical (precipitation, liquid-evaporation [spray drying, spray pyrolysis, freeze drying], gel [sol-gel, pechini, citrate, glycine-nitrate]), and gas-phase processes, with many of these requiring a calcination step (Kong *et al.*, 2015). Although the high sintering activity of nanometer-sized (< 100 nm) crystallites is desired, these tend to agglomerate during milling. Often an optimum size consisting of slightly larger crystallites or particle agglomerates is desired (Krell *et al.*, 2009a, 2003). Care must also be taken with process air and water and the purity of organic additives. More attention has also recently been given to the importance of green bodies, and increasing homogeneity can be much more effective in avoiding visible defects than attempting fixes during later steps (Krell and Klimke, 2006). In that respect, colloidal processes such as slip-, gel- and tape-casting and pressure-filtration are well-suited to achieve higher homogeneity (Jung *et al.*, 2018).

Scattering by pores is typically the main attenuating phase in polycrystalline material, and so reducing porosity often becomes the crux of fabrication. Although nanometer-sized crystallites can provide the sintering activity required to reach near-theoretical density, materials with high melting-points, covalent bonding, low diffusion and/or volatility often require additional driving forces. Sintering additives have been used since the outset and assist densification by forming liquid phases and/or increasing diffusion. Small quantities are used to avoid secondary-phase formation and/or fugitive compounds that evaporate prior to closed porosity are chosen. Although pressureless sintering is preferred to lower cost, pressure is often required to increase sintering kinetics and/or close residual pores by methods like hot-pressing (HP), hot isostatic pressing (HIP), hot-forging, gas-pressure sintering and ultra-high-pressure sintering (Oparina *et al.*, 2019). For example, MgF_2 can be made by HP, Y_2O_3 by sinter-HIP and MgAl_2O_4 by HP-HIP (Harris, 1999). Recently-introduced processes like spark-plasma sintering (SPS) and field-assisted sintering (FAST) can yield transparent specimens in minutes, but geometry is limited and they are rarely applicable to commercial production. One promising method is full-crystallization from glass precursors and other methods are continually being introduced (Goldstein and Krell, 2016; Allix *et al.*, 2012; Xiao *et al.*, 2019). Although processing to closed porosity is a difficult endeavor, the last steps in fabrication (machining, grinding and polishing) can often be the most expensive for hard materials (Harris, 1999; Patel *et al.*, 2000).

Since the advent of high-purity powders, impurity-based absorption can be virtually eliminated with careful processing. One exception is carbon-contamination from graphitic furnaces during sintering. CO_2/CO atmospheres produced at high temperatures can result in migration of carbon along boundaries and cause broad-based absorption. This can be reduced by using non-graphitic elements (i.e., MoSi_2), shielding with refractory foils or sprays, sintering in powder beds and post-annealing in air. For materials like Al_2O_3 and ZrO_2 , reducing conditions generate vacancies that act as absorbing color centers (Goldstein and Krell, 2016), which can be removed by annealing in air. Another source of absorption in the IR is -OH stretching due to adsorbed water vapor, which can be reduced by annealing in dry argon (Harris, 1999). However, annealing treatments should be used with care as they are often associated with pore growth.

Many transparent ceramics are applied as coatings (thin-films, < 100 μm thick) and to a lesser extent, claddings (thick free-standing films, > 100 μm). They are used to modify optical behavior (antireflection, anti-glare, heat-mirror, wavelength-selectivity, electromagnetic interference protection) and/or to improve mechanical or chemical behavior (strength, toughness; scratch, wear and erosion resistance; and anti-static and hydrophobic properties), or they can serve as the active layer (transparent conducting oxides) (Harris, 1999; Xie and Hintzen, 2013a; Rubat du Merac *et al.*, 2018; Dobrowolski, 1995; Lee and Kuo, 2013). Advantages include imparting required functional properties while minimizing the amount of material used and the ability to use materials that are difficult to fabricate in bulk form (i.e., diamond). Although, this is sometimes at the expense of mechanical properties.

Table 3 General ranking of select transparent ceramics

<i>Property</i>	<i>Rank</i>
<i>Optical</i>	
High Bandgap	LiF, MgF ₂ , BeO, CaF ₂ , BaF ₂ , sapphire, Al ₂ O ₃ , NaCl, (SiO ₂), MgO
Low <i>n</i> (0.6 μm)	MgF ₂ , CaF ₂ , (SiO ₂), BaF ₂ , KBr, MgAl ₂ O ₄ , BeO, MgO, Al ₂ O ₃ , AlON
High <i>n</i> (0.6 μm)	GaP, BP, SiC, ZnSe, PLZT, diamond, ZnS, ZrO ₂ , BN, AlN, Si ₃ N ₄
Low <i>dn/dT</i> (Vis.)	MgF ₂ , (SiO ₂), Y ₂ O ₃ , spinel, diamond, YSZ, YAG, CaF ₂ , Al ₂ O ₃ , BeO
Low <i>dn/dT</i> (4 μm)	MgF ₂ , AlON, sapphire, (SiO ₂), LiF, diamond
High Abbe Number	MgF ₂ , LiF, CaF ₂ , BeO, NaF, sapphire, (SiO ₂), YAG, spinel, AlON
Theo. Transmittance	LiF, MgF ₂ , CaF ₂ , (SiO ₂), NaCl, (PC), spinel, sapphire, AlON, YAG
Low UV Cut-Off	LiF, MgF ₂ , CaF ₂ , BeO, SrF ₂ , (SiO ₂), sapphire, MgO, spinel, YAG
High IR Cut-Off	diamond, (Si), CsI, CsBr, TlBr, KI, KBr, KCl, NaCl, (Ge), ZnSe
Low MWIR Cut-Off	MgF ₂ , Y ₂ O ₃ , MgO, spinel, sapphire, AlON
Low Emittance (700K)	Y ₂ O ₃ , spinel, sapphire, AlON
<i>Mechanical</i>	
Low Density	NaCl, (SiO ₂), LiF, KBr, MgF ₂ , CaF ₂ , SiC, Si ₃ N ₄ , AlN, diamond, MgO, spinel
High Strength	diamond, <i>t</i> -ZrO ₂ , sapphire, Si ₃ N ₄ , Al ₂ O ₃ , SiC, AlON, spinel, Y ₂ O ₃ , ZnS, MgF ₂
High Stiffness	diamond, <i>c</i> -BN, SiC, sapphire, Al ₂ O ₃ , BeO, AlON, AlN, spinel, YAG, BP
High Hardness	diamond, <i>c</i> -BN, SiC, Si ₃ N ₄ , Al ₂ O ₃ , sapphire, AlON, MgAl ₂ O ₄ , ZrO ₂ , Y ₂ O ₃ , MgO
High Toughness	<i>t</i> -ZrO ₂ , diamond, SiAlON, BN, Si ₃ N ₄ , SiC, <i>c</i> -YSZ, sapphire, Al ₂ O ₃ , spinel, AlON
<i>Thermal</i>	
Low Thermal Expansion	(SiO ₂), diamond, Si ₃ N ₄ , SiC, BP, sapphire, AlN, GaP, spinel, (GaAs), AlON
High Thermal Resistance	ThO ₂ , AlN, SiC, ZrO ₂ , MgO, BeO, Y ₂ O ₃ , Si ₃ N ₄ , spinel, Al ₂ O ₃ , AlON
High Thermal Conductivity	diamond, BN, SiC, BP, BeO, AlN, GaP, MgO, GaAs, sapphire, Si ₃ N ₄
Low Thermal Conductivity	BrTiI ₂ , CsBr, CsI, (SiO ₂), ZrO ₂ , KBr, La:Y ₂ O ₃ , NaCl, KCl, CaF ₂ , LiF
High Thermal Shock	diamond, SiC; GaP, sapphire, GaAs; (SiO ₂), MgO, ZnS, ZnSe, AlON

Note: Diamond (s.c., p.c. or CVD), SiO₂ (glass, fused-SiO₂ or quartz), PC polycarbonate.

Approximate ranking of select materials for relative comparison only, mainly from Tropf, W.J., Thomas, M.E., Harris, T.J., 1995. Chapter 33. Properties of crystals and glasses, part IV. In: Bass, M. (Ed.), Handbook of Optics, Devices, Measurements, & Properties, second ed. McGraw-Hill, Inc. Harris, D.C., 1999. Materials for Infrared Windows and Domes: Properties and Performance. SPIE Optical Engineering Press. Tropf, W.J., Harris, T.J., Thomas, M.E., 2000. Electro-Optics Handbook, second ed. McGraw-Hill. Weber, M., 2003. Handbook of Optical Materials. CRC Press. Goldstein, A., Krell, A., 2016. Ceramics at 50: Progress made and further prospects. J. Am. Ceram. Soc. 99 (10), 3173–3197. Goldstein, A., Krell, A., Burshtein, Z., 2020. Transparent Ceramics: Materials, Engineering, and Applications. John Wiley & Sons and individual material-related references in text.

Table 4 Typical fabrication form of select transparent ceramics

<i>Form</i>	<i>Material</i>
Single Crystal	sapphire, YAG, LiF, MgF ₂ , CaF ₂ , BaF ₂ , NaCl, KCl, KBr, SrI ₂ , CsI
Polycrystalline	MgF ₂ , ZnS, ZnSe, CaF ₂ , MgO, spinel, AlON, Y ₂ O ₃ , La-Y ₂ O ₃ , YSZ
Coating	diamond, GeC, SiC, Si ₃ N ₄ , AlN, BN, BP, GaP, ITO, ZnO, TiO ₂

Note: Harris, D.C., 1998. Durable 3–5 μm transmitting infrared window materials. Infrared Phys. Technol. 39, 185–201. Harris, D.C., 1999. Materials for Infrared Windows and Domes: Properties and Performance. SPIE Optical Engineering Press.

Coatings are commonly applied by evaporation processes (CVD and PVD), sputtering, solution-deposition methods (dip- and spin-coating) and lamination for thicker coatings. They are often associated with tensile or compressive residual stress and sometimes require an interlayer for bonding or to accommodate thermal-expansion mis-match during operation (Harris, 1999). They can consist of single or multiple layers, be continuously-graded or be made as moth-eye surfaces (Dobrowolski, 1995). Fig. 5 shows microstructures for select bulk transparent ceramics and coatings.

Applications

Transparent ceramics are used in a wide-range of applications determined by the required functional properties and property combinations (Gagliardi, 2017). Major uses include scratch-resistant windows, transparent armor, durable UV and IR windows and domes, lamp envelopes, optical elements, laser hosts, scintillators and functional thin-films (Goldstein and Krell, 2016; Kong *et al.*, 2015; Goldstein *et al.*, 2020; Xiao *et al.*, 2019). Translucent lamp envelopes for high-intensity sodium-vapor lamps were the first commercial application (Burke, 1996). These must withstand corrosive sodium vapor at high temperature and pressure, requiring sufficient

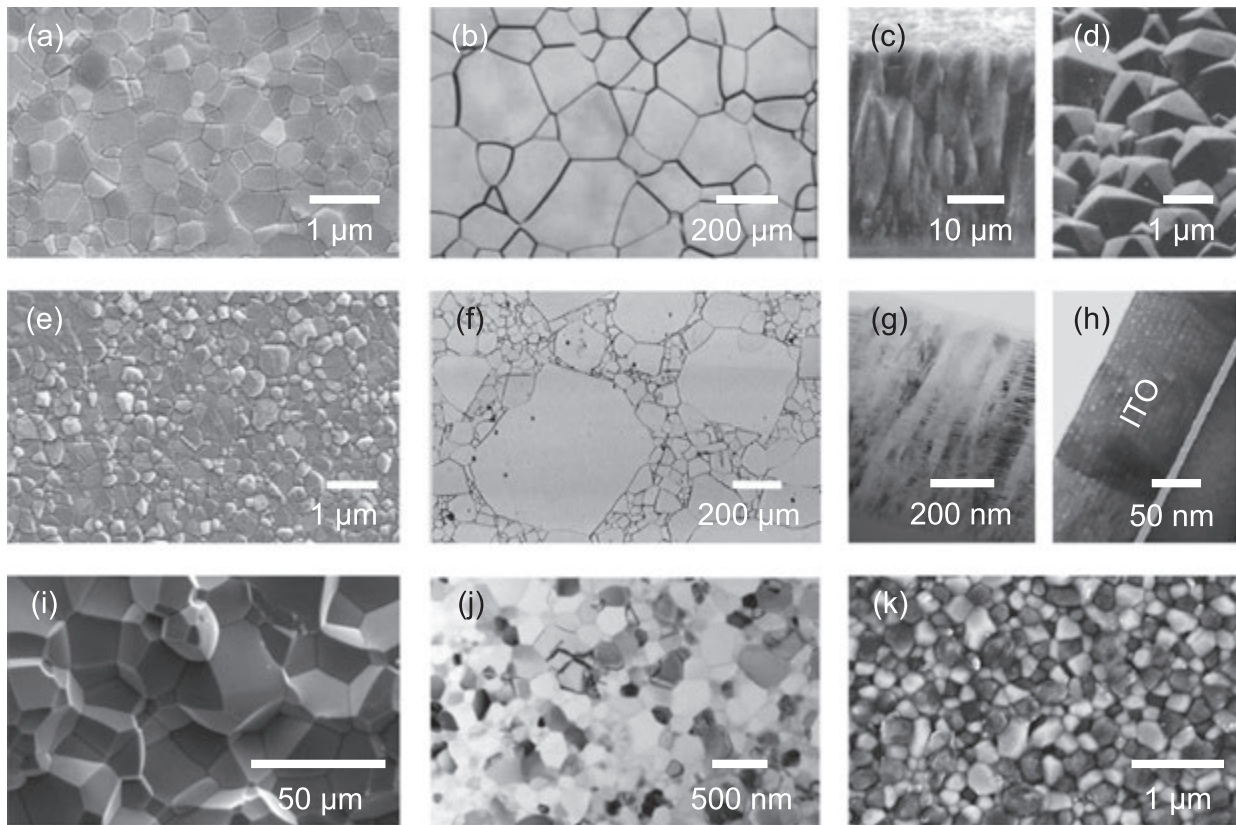


Fig. 5 Microstructure of select transparent ceramics; (a) sinter-HIP Al_2O_3 , (b) sinter-HIP AlON , CVD diamond coating (c) cross-section and (d) surface, (e) SPS spinel, (f) HP-HIP spinel with LiF additive, (g) CVD columnar SiC coating on glass, (h) solution-deposited spin-coat textured ITO coating on silicon with native SiO_2 , (i) sinter-HIP gelcast $\text{Nd}^{3+}:\text{YAG}$ fracture surface, (j) high-pressure synthesis $\alpha\text{-Si}_3\text{N}_4$, (k) sinter-HIP $\text{MgO-Y}_2\text{O}_3$ nanocomposite (commercial ceramics often have larger grain sizes; 10–100's μm 's). Reproduced from (a) Krell, A., Blank, P., Ma, H., Hutzler, T., Nebelung, M., 2003. Processing of high-density submicrometer Al_2O_3 for new applications. *J. Am. Ceram. Soc.* 86 (4), 546–553. (b) Warner, C.T., Hartnett, T.M., Fisher, D., Sunne, W., 2005. Characterization of ALON™ optical ceramic. In: *Proceedings of SPIE Defense and Security Symposium, Window and Dome Technologies and Materials IX*, vol. 5786, Orlando, FL. (c) and (d) Harris, D.C., 1999. *Materials for Infrared Windows and Domes: Properties and Performance*. SPIE Optical Engineering Press. (e) Morita, K., Kim, B.-N., Yoshida, H., Hiraga, K., 2009. Spark-plasma-sintering condition optimization for producing transparent MgAl_2O_4 spinel polycrystal. *J. Am. Ceram. Soc.* 92 (6), 1208–1216. (f) Gilde, G., Patel, P., Sands, J., *et al.*, 2006. Evaluation of hot isostatic pressing parameters on the optical and ballistic properties of spinel for transparent armor. *J. Am. Ceram. Soc.* 88 (10), 2747–2751. (g) Finger, F., Astakhov, O., Bronger, T., *et al.*, 2009. Microcrystalline silicon carbide alloys prepared with HWCVD as highly transparent and conductive window layers for thin film solar cells. *Thin Solid Films* 517, 3502–3512. (h) Mottern, M.L., Tyholdt, F., Ulyashin, A., *et al.*, 2007. Textured indium tin oxide thin films by chemical solution deposition and rapid thermal processing. *Thin Sol. Films*, 3918–3926. (i) Xiao, Z., Yu, S., Li, Y., *et al.*, 2019. Materials development and potential applications of transparent ceramics: A review. *Mater. Sci. Eng. R* 139, 1–8. (j) Nishiyama, N., Ishikawa, R., Ohfuji, H., *et al.*, 2017. Transparent polycrystalline cubic silicon nitride. *Sci. Rep.* 7 (44755), 1–8. (k) Harris, D.C., 1999. *Materials for Infrared Windows and Domes: Properties and Performance*. SPIE Optical Engineering Press.

strength and chemical, thermal and thermal-shock resistance, although typically only translucency is required. Transparent ceramics are also an integral part of lighting as transparent phosphors and potentially luminescent windows in LED's (Xie *et al.*, 2013b).

Windows for scanners, machinery, outdoor lighting and consumer goods are an emerging application with significant growth potential. These require high visible transparency, moderate strength and toughness, high hardness and scratch and impact resistance. Although ceramics have significantly higher hardness and scratch-resistance than strengthened glasses, glass-ceramics and polymers, they face stiff competition due to higher cost. Transparent armor is also a growing segment that additionally requires low areal density, ballistic resistance, multi-hit capability and sometimes multi-spectral (UV-IR) transmittance (Harris, 1999). Although they can be used on their own, armor ceramics are typically part of a laminate consisting of a hard ceramic strike-face that erodes and breaks-up projectiles, and one or more layers of glass and polymer that absorb energy, increase stiffness and prevent spalling, interspersed with thermal-expansion mis-match interlayers (Patel *et al.*, 2000). Moreover, while ceramics can reduce areal density by up to 65% compared to competing materials, higher cost makes them more attractive for areal (helicopters, aircraft) applications where low weight is a greater priority (Crouch *et al.*, 2017). Aerothermal IR windows and domes additionally require low thermal expansion and emissivity, high thermal diffusivity and erosion and thermal-shock resistance, a combination few materials can match (Harris, 1999). Sight-glasses for thermal and chemical processes are a niche application also requiring chemical and thermal resistance.

Table 5 Typical wavelength-range and application of common transparent ceramics

Range/Sector	Common ceramics [Potential in brackets]
UV materials	CaF ₂ , sapphire, KBr, [BeO, LiF, MgF ₂ , MgO, spinel]
Vis/armor materials	sapphire, spinel, AlON, [YSZ, YAG, diamond]
MWIR materials	Y ₂ O ₃ , AlON, spinel, MgF ₂ , ZnS, ZnSe, Al ₂ O ₃ , sapphire, KBr, BP
LWIR materials	MgF ₂ , CaF ₂ , ZnS, ZnSe, GaP, diamond, [MgO]
Laser hosts	YAG, Y ₂ O ₃ , ZnSe, ZnS, [Sc ₂ O ₃ , La ₂ O ₃ , LuAG, LiF, CaF ₂ , SrF ₂]
Scintillators	(Y,Gd,Eu) ₂ O ₃ , Gd ₃ Ga ₅ O ₁₂ , YAG, LuAG, SrI ₂ , [many potential]
Lighting	Al ₂ O ₃ , GaN, GaP, YAG, [sapphire, MgAl ₂ O ₄ , Y ₂ O ₃ -La ₂ O ₃ , AlON]

Note: Harris, D.C., 1998. Durable 3–5 μm transmitting infrared window materials. *Infrared Phys. Technol.* 39, 185–201. Harris, D.C., 1999. Materials for Infrared Windows and Domes: Properties and Performance. SPIE Optical Engineering Press. Burnett, J.H., Kaplan, S.G., Shirley, E.L., *et al.*, 2005. High-index materials for 193 nm immersion lithography. In: *Proceedings of the 2nd International Symposium on Immersion Lithography*. Bruges, Belgium. Sanghera, J., Kim, W., Villalobos, G., *et al.*, 2012. Ceramic laser materials. *Materials* 5, 258–278. Xie, R.-J., Hintzen, H.T., 2013a. Optical properties of (oxy)nitride materials: A review. *J. Am. Ceram. Soc.* 96 (3), 665–687. Xie, R.-J., Mitomo, M., Hirotsaki, N., 2013b. Ceramic lighting. In: Riedel, R., Chen, J.-W. (Eds.), *Ceramics Science and Technology: Applications*, first ed., vol. 4. Wiley.

Laser hosts are another early application and ceramics are now the leading solid-state laser material (Hatch *et al.*, 1964; Goldstein and Krell, 2016). Hosts are the material to which rare-earth or transition-metal dopants are added to result in stimulated emission and gain when optically-pumped within an optical resonator made by (partially) mirroring ends. In addition to properties required for IR windows and domes, laser hosts require lower absorption/defect concentrations, low dn/dT and the ability to uniformly incorporate active dopants. Moreover, they must withstand high thermal energy gradients and radiation damage (Goldstein and Krell, 2016; Kong *et al.*, 2015; Sanghera *et al.*, 2012). Scintillators have similar requirements regarding dopants and must be transparent while allowing radiation of emitted photons. Moreover, they require high absorption (X-ray or gamma-ray stopping power) and re-emission (light yield) cross-sections that are proportional to detected radiation, short decay times, tolerance to radiation damage and good mechanical properties (Cherepy *et al.*, 2007; Greskovich and Duclos, 1997).

UV–vis–IR optical elements were also early applications that still employ a wide variety of single-crystal and polycrystalline materials (Goldstein *et al.*, 2020; Stevenson *et al.*, 2011). Special optical properties like low or high refractive index, low dispersion, UV or IR transmittance, luminescence and nonlinear optical behavior are necessary for many optical elements (lenses, prisms, beamsplitters, mirrors, nonlinear and wave-mixing crystals, acoustooptical and polarization devices and interference filters). Moreover, electro- and magneto-optical properties are needed to enable technologies like touchscreens, sensors, photovoltaics and smart windows. Hard, scratch-resistant coatings, with antireflective, heat-mirror, solar-selective or other functional properties are another important application (Goldstein *et al.*, 2020; Xie and Hintzen, 2013a). Transparent ceramics have also been used in luxury goods such as watches and as artificial gemstones. Cost is a driving factor for many applications, with competition from single crystals, glasses, glass-ceramics and polymers.

With the advent of new materials and advanced processing, new applications are continually emerging. For example, the lowest UV absorption edge of known optical materials combined with low intrinsic birefringence could enable UV lithography windows and optics for the next-generation of microprocessors (Burnett *et al.*, 2005). Common materials used in select applications are summarized in Table 5. Applications are described in more detail in the sections on individual materials and in referenced articles.

Materials

There are hundreds of transparent ceramic compounds and new ones are continually being added, so only more common materials are described in detail. Moreover, the emphasis is on materials that are well-developed, commercially-available and/or have commercial/military relevance. Although, some newly-developed and less common materials with exceptional properties are described to show the full-range of attainable properties. Many materials that are not described because they occupy small niche applications can nevertheless be essential in enabling those applications, and more exhaustive treatments are found in optical materials references (Tropf *et al.*, 1995; Harris, 1999; Tropf *et al.*, 2000; Weber, 2003; Sanghera *et al.*, 2012; Xie and Hintzen, 2013a; Kong *et al.*, 2015; Xiao *et al.*, 2019). Figs. 6 and 7 give an overview of the range and appearance of common transparent ceramics. Oxides constitute the vast majority by market share, mainly Al₂O₃, yttrium aluminum garnet (YAG) and MgAl₂O₄, and these are described in greater detail. Materials are loosely-grouped by anion group (carbides, nitrides, phosphides, oxides, oxynitrides, other chalcogenides, fluorides, other halogens) and their order in the periodic table, structure (perovskite, pyrochlore), application (conducting oxides, ferroelectrics) and form (nanocomposites, coatings) in order to combine materials with similar properties and/or applications.

Carbides

Carbides can feature transparency combined with extreme physical properties. Strong covalent bonds confer the highest strength, stiffness, hardness and thermal conductivity of known optical materials (Harris, 1999). However, covalent bonding, polymorphism

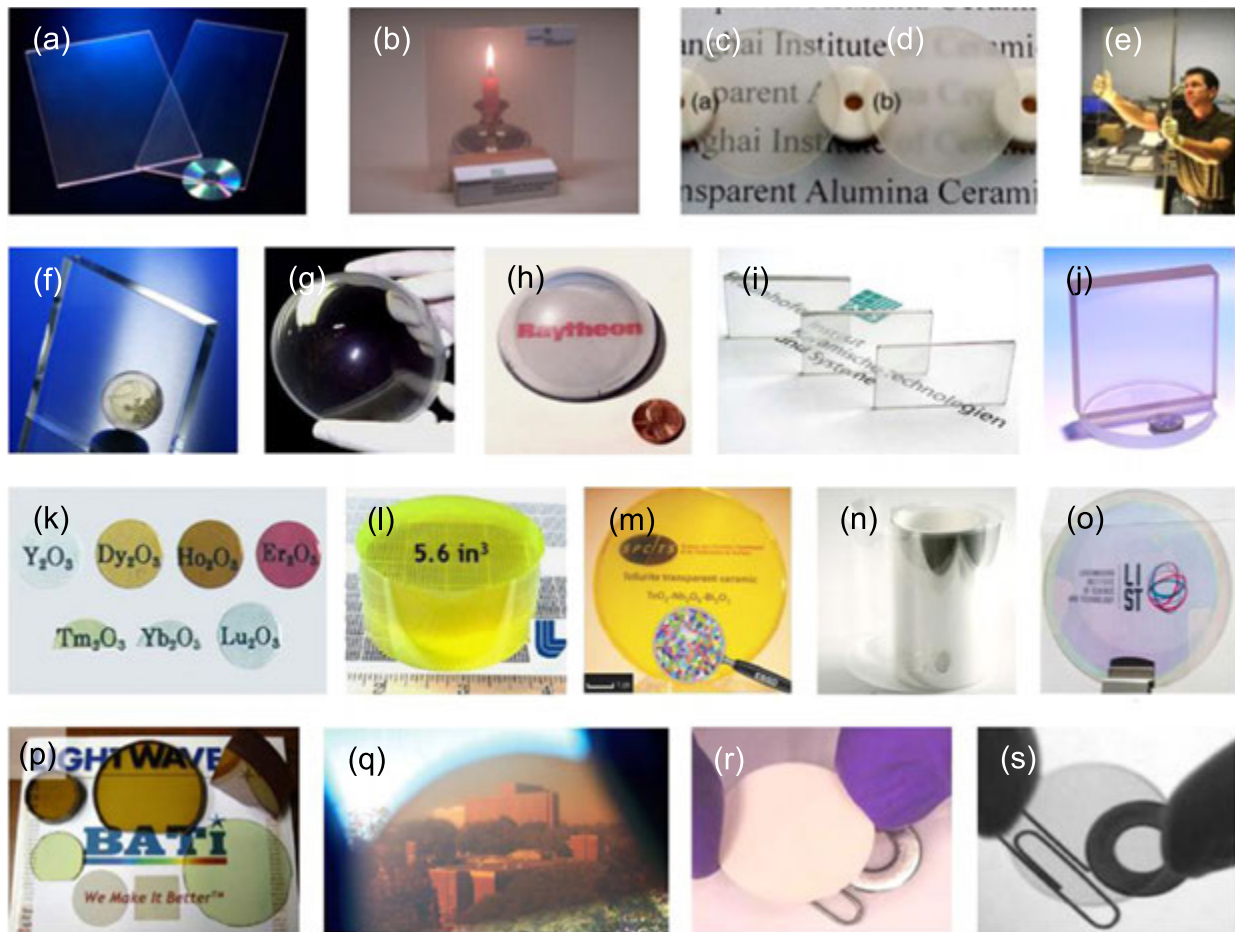


Fig. 6 Select transparent oxide-based ceramics: (a) sapphire windows, (b) polycrystalline Al_2O_3 , (c) magnetically-oriented and (d) unoriented Al_2O_3 , (e) AlON window, (f) MgAl_2O_4 window, (g) MgAl_2O_4 dome, (h) Y_2O_3 dome, (i) ZrO_2 windows, (j) $\text{Nd}^{3+}:\text{YAG}$ laser slab, (k) RE oxide samples, (l) $(\text{Gd},\text{Y})_3(\text{Gd},\text{Al})_5\text{O}_{12}$ scintillator, (m) $\text{TeO}_2\text{-Nb}_2\text{O}_5\text{-Bi}_2\text{O}_3$, (n) ITO on PET, (o) PZT on glass, (p) various electrooptic ceramics, (q) $\text{MgAl}_2\text{O}_4\text{-Si}_3\text{N}_4$ nanocomposite and $\text{MgO}:\text{Y}_2\text{O}_3$ nanocomposite under (r) visible and (s) IR light. Reproduced from (a) Saint-Gobain S.A., 2020. Synthetic Sapphire Products. Available at: www.saint-gobain.com, accessed 2020. (b) Krell, A., Klimke, J., Hutzler, T., 2009. Advanced spinel and sub- μm Al_2O_3 for transparent armour applications. J. Eur. Ceram. Soc. 29, 275–281. (c) and (d) Mao, X., Wang, S., Shimai, S., Guo, J., 2008. Transparent polycrystalline alumina ceramics with oriented optical axes. J. Am. Ceram. Soc. 91 (10), 3431–3433. (e) and (g) Surmet Corp., 2020. MgAl_2O_4 and AlON Products. Available at: www.surmet.com, accessed 2020. (f) CeramTec GmbH, 2020. Perlucor Products. Available at: www.ceramtec.com, accessed 2020. (h) Raytheon Technologies Corp., 2020. Yttria Products. Available at: www.rtx.com, accessed 2020. (i) Fraunhofer Institute for Ceramic Technologies and Systems, 2020. Transparent Zirconia Ceramics. Available at: www.ikts.fraunhofer.de, accessed 2020. (j) Sanghera, J., Kim, W., Villalobos, G., *et al.*, 2012. Ceramic laser materials. Materials 5, 258–278. (k) Konoshima Chemical Co. Ltd., 2020. Rare-Earth Oxide Ceramic Products. Available at: www.konoshima.co.jp, accessed 2020. (l) Cherepy, N.J., Seeley, Z.M., Payne, S.A., *et al.*, 2014. High energy resolution with transparent ceramic garnet scintillators. In: Proceedings of SPIE, Hard X-Ray, Gamma-Ray, and Neutron Detector Physics XVI, vol. 9213. (m) Bertrand, A., Carraud, J., Chenu, S., *et al.*, 2016. Scalable and formable tellurite-based transparent ceramics for near infrared applications. Adv. Opt. Mater., 1–9, (201600230). (n) Optical Filters USA, 2020. EMI-ITO Film Products. Available at: www.opticalfiltersusa.com, accessed 2020. (o) Sette, D., Girod, S., Leturcq, R., Glinsek, S., Defay, E., 2017. Transparent ferroelectric capacitors on glass. Micromachines 8 (313), 1–6. (p) Boston Advanced Technologies Inc., 2020. Electrooptic Products. Available at: www.bostonati.com, accessed 2020. (q) Gledhill, A.D., Li, D., Mroz, T., Goldman, L.M., Padture, N.P., 2012. Strengthening of transparent spinel/ Si_3N_4 nanocomposites. Acta Mater. 60, 1570–1575. (s) Harris, D.C., Cambrea, L.R., Johnson, L.F., *et al.*, 2013. Properties of an infrared-transparent $\text{MgO}:\text{Y}_2\text{O}_3$ nanocomposite. J. Am. Ceram. Soc. 96 (12), 3828–3835.

and high melting temperatures pose significant processing challenges. As such, carbides are mainly used as thin-coatings, with diamond and SiC being common. However, many other carbides (GeC [germanium-carbon], TaC, etc.) are used in niche applications and some like BC are still being developed (Monaghan *et al.*, 1992; Hu *et al.*, 2006; Mondal *et al.*, 2015).

Diamond

Diamond is in a class by itself with its extraordinary physical properties. It has an exceptionally-wide transmission window (250 nm to $>100\ \mu\text{m}$), low dn/dT ($\sim 10 \times 10^{-6}\text{K}^{-1}$ at 600 nm) and a low dielectric constant (ϵ 5.7) (Tropf *et al.*, 1995; Harris, 1999). Diamond features the highest hardness ($9000\ \text{kg}\cdot\text{mm}^{-2}$) and stiffness (1143 GPa) of known materials, excellent fracture toughness

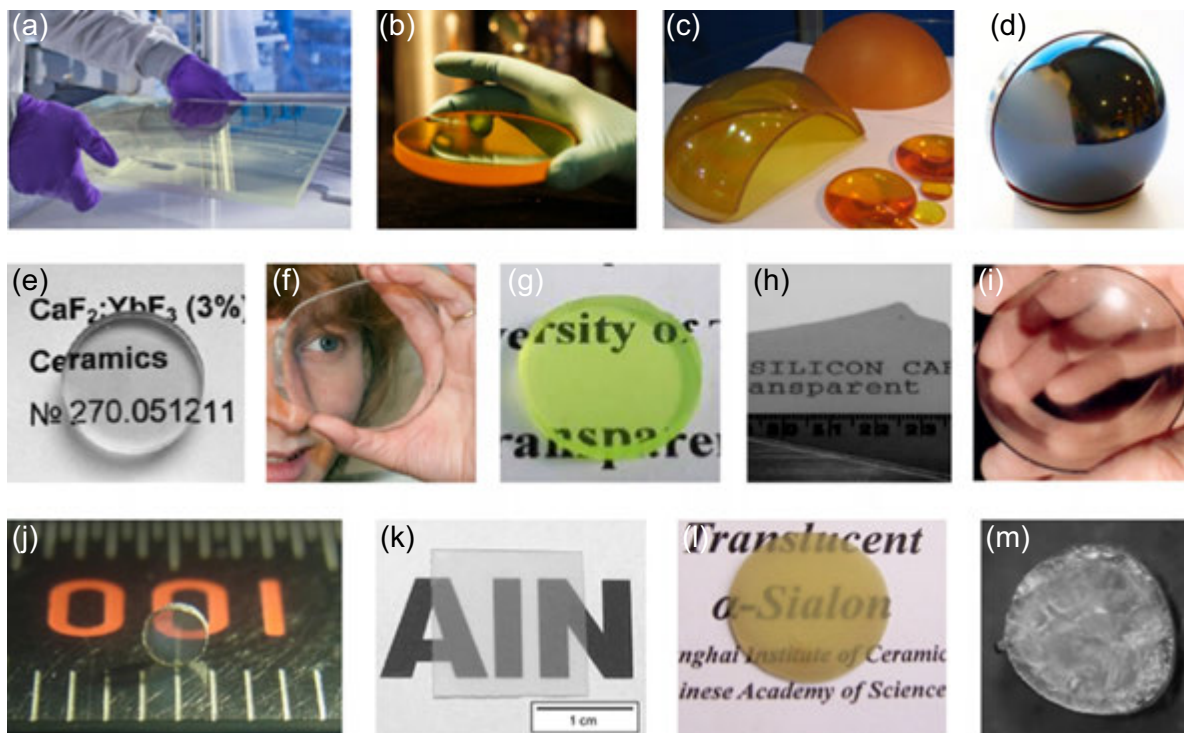


Fig. 7 Select transparent non-oxide ceramics: (a) ZnS slab, (b) ZnS disc, (c) ZnSe domes, (d) BP-coated IRST detector, (e) YbF₃:CaF₂, (f) CaF₂, (g) SrF₂, (h) SiC, (i) diamond dome, (j) *c*-Si₃N₄, (k) AlN, (l) α -SiAlON, (m) *c*-BN. Reproduced from (a) Zygo Corp., 2020. Optical Materials Products. Available at: www.zygo.com, accessed 2020. (b) Optical Products Factory LLC, 2020. ZnS Products. Available at: www.optics.spb.ru, accessed 2020. (c) Crystaltechno Ltd., 2020. Zinc Selenide Products. Available at: www.crystaltechno.com, accessed 2020. (d) Excelita Technologies Corp., 2020. IRST Sensor Products. Available at: www.excelitas.com, accessed 2020. (e) and (f) Akchurin, M.S., Basiev, T.T., Demidenko, A.A., *et al.*, 2013. CaF₂:Yb laser ceramics. *Opt. Mater.* 35, 444–450. (g) Yi, G., Mei, B., Li, W., *et al.*, 2019. Synthesis and luminescence characterization of Pr³⁺, Gd³⁺ Co-doped SrF₂ transparent ceramics. *J. Am. Ceram. Soc.* 103 (1), 279–286. (h) Goela, J.S., 1998. CVD growth and characterization of β -SiC for IR windows, Morton Advanced Materials. (i) Harris, D.C., 2002. Review of Navy Program to Develop Optical Quality Diamond Windows and Domes, Naval Air Systems Command Report. (j) Nishiyama, N., Ishikawa, R., Ohfuji, H., *et al.*, 2017. Transparent polycrystalline cubic silicon nitride. *Sci. Rep.* 7 (44755), 1–8. (k) Honma, T., Kuroki, Y., Okamoto, T., *et al.*, 2008. Transmittance and cathodoluminescence of AlN ceramics sintered with Ca₃Al₂O₆ as sintering additive. *Ceram. Int.* 34, 943–946. (l) Liu, Q., Wei, H., Zhong, H., Zhang, K., Gui, L., 2012. Transmittance improvement of Dy- α -SiAlON in infrared range by post hot-isostatic pressing. *J. Eur. Ceram. Soc.* 32, 1377–1381. (m) Tian, Y., Xu, B., Yu, D., *et al.*, 2013. Ultrahard nanotwinned cubic boron nitride. *Nature* 493 (11728), 385–388.

($K_{IC} \sim 5.3 \text{ MPa}^{-1/2}$), extreme scratch and erosion resistance, high strength (200–1000 MPa), low thermal expansion ($0.8 \times 10^{-6} \text{ K}^{-1}$), the highest room temperature thermal conductivity of any known material ($2000 \text{ W} \cdot \text{m}^{-1} \text{ K}^{-1}$ at 25°C) and outstanding thermal shock resistance ($R' 410 \text{ kW} \cdot \text{m}^{-1}$) (values for CVD diamond) (Tropf *et al.*, 1995; Harris, 1999, 2002). However, it can't be used in the MWIR due to absorption from 3 to $5 \mu\text{m}$, its high refractive index ($n 2.4$) limits theoretical transmittance ($< 70\%$), it oxidizes above 700°C if uncoated and graphitizes above 1500°C , and grinding and polishing costs are high due the high hardness (Goela, 1998; Harris, 1999). Diamond's exceptional properties make it a candidate for strong, tough, multi-spectral (Vis–UV–IR–MW) windows; scratch-, wear- and chemical-resistant windows or components; the ultimate laser window (the preferred material for CO₂ lasers) and laser host, and heat-sink substrates for electronics. Although industrial diamond is made as small single crystals by high-pressure high-temperature growth, transparent polycrystalline material is made by plasma-CVD substrate growth in H₂ atmosphere (Harris, 1999, 2002). Processing is made difficult by the high temperature/pressure required and contamination (i.e., nitrogen and boron) (Savage, 1991). CVD diamond is currently thickness-limited, contains internal flaws and exhibits light-scattering at grain boundaries. Although thin windows several centimeters across and domes up to 1 mm thick have been produced, larger and thicker optical quality diamond is still being developed and it remains one of the most expensive optical materials (Harris, 1999, 2002).

Silicon carbide

Silicon carbide (SiC) has hundreds of polytypes, the most common being hexagonal α -SiC forming above ~ 1700 – 2000°C and β -SiC forming below (Kimoto and Cooper, 2014). β -SiC is of great interest due to its diamond-like properties. It has a cubic zincblende structure, high refractive index ($n 2.6$ at 633 nm), low density ($3.21 \text{ g} \cdot \text{cm}^{-3}$), moderately high strength (300–828 MPa); high fracture toughness ($K_{IC} 2$ – $6 \text{ MPa} \cdot \text{m}^{1/2}$), hardness (up to 25 GPa) and stiffness (310–500 GPa); high-temperature resistance (sublimes > 1800 – 2000°C), unlike diamond high oxidation resistance, low thermal expansion ($4 \times 10^{-6} \text{ K}^{-1}$), outstanding thermal conductivity (up to $490 \text{ W} \cdot \text{m}^{-1} \text{ K}^{-1}$ at 300 K) and thermal shock resistance ($R 12 \times 10^3 \text{ K}$) and chemical inertness. It's a

semiconductor with high electric field breakdown strength ($2.1 \text{ MV} \cdot \text{cm}^{-1}$), maximum current density and electron mobility ($800\text{--}1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), and electroluminescence properties (Goela, 1998; Gerhardt, 2011; Kimoto and Cooper, 2014). However, it is only transparent from $\sim 0.5\text{--}5.0 \text{ }\mu\text{m}$, has low impact resistance, high emittance between $4\text{--}5 \text{ }\mu\text{m}$ and transparent material is still being developed (Gerhardt, 2011; Bayya *et al.*, 2013; Naftaly *et al.*, 2016). First made by carbothermic reduction of SiO_2 in an Acheson furnace, transparent single crystals are made using the Lely method and polycrystalline material has been made by CVD, HP, reaction-bonding and SPS (Goela, 1998; Bayya *et al.*, 2013; Kimoto and Cooper, 2014). Applications include the first commercial LED, UV-detectors, diamond gemstone simulants, lightweight mirrors; hard, scratch-resistant anti-reflective coatings (especially for silicon photovoltaics); and potentially transparent armor, aerothermal windows and heat-sink laser windows (Harris, 1999; Bayya *et al.*, 2013; Kimoto and Cooper, 2014).

Nitrides

Nitrides share similarities with oxides and can feature exceptional hardness and fracture toughness, high strength and wear resistance, chemical and thermal stability, outstanding thermal conductivity, and interesting semiconducting, optoelectronic and luminescent properties. However, covalent bonding and high melting points complicate processing, and development and achieved transmittances have lagged that of oxides. Densification typically requires additives and liquid-phase sintering in N_2 atmosphere. Silicon nitride is a common antireflection coating material, while SiAlONs and aluminum nitride are being developed for their unique functional properties. Moderate refractive indices combined with excellent mechanical properties enable use as thin-film antireflection (Si_3N_4), surface passivation (Si_3N_4 , AlN, TiN, ZrN), heat-mirror (TiN, ZrN) and absorbing solar-selective coatings. Moreover, photoluminescent properties (GaN, AlN, BN, SiAlONs) are sought for phosphors and LED's, with many other potential applications (transparent armor, windows, transparent conductors, optoelectronic devices) likely to arise (Xie and Hintzen, 2013a).

Silicon nitride

Silicon nitride (Si_3N_4) occurs as trigonal α - Si_3N_4 , higher-temperature hexagonal β - Si_3N_4 and a high-pressure cubic spinel γ - Si_3N_4 (or c - Si_3N_4) polymorph. The α and β polymorphs exhibit exceptional hardness (up to 22 GPa) and fracture toughness (K_{IC} up to $7.2 \text{ MPa} \cdot \text{m}^{1/2}$) combined with moderate density ($3.24 \text{ g} \cdot \text{cm}^{-3}$) and a wide bandgap (5.3 eV) with potential transparency from the visible to the SWIR, but they have relatively high refractive indices (n 2.1 at 600 nm) and are translucent due to birefringence (Harris, 1999; Xie and Hintzen, 2013a; Yang *et al.*, 2013; Li *et al.*, 2015). Nevertheless, translucent β - Si_3N_4 has been made by methods like HP and SPS, typically with sintering additives (Xiao *et al.*, 2019). Si_3N_4 is also made by CVD, typically as amorphous hydrated (SiN_xH) material for transparent antireflective coatings for solar cells (Xie and Hintzen, 2013a). c - Si_3N_4 has higher density ($4.08 \text{ g} \cdot \text{cm}^{-3}$), but exceptional stiffness (583 GPa) and hardness (HV 34.9 GPa), high fracture toughness (K_{IC} $3.5 \text{ MPa} \cdot \text{m}^{-1/2}$) and high thermal resistance in air (up to 1400°C). However, only small samples with visible transmittance of 18%–38% have been made by high-pressure (13 GPa) synthesis (Nishiyama *et al.*, 2017). If successfully developed, c - Si_3N_4 would make an excellent candidate for aerothermal windows operating in harsh environments in the $0.5\text{--}4 \text{ }\mu\text{m}$ range (Xiao *et al.*, 2019).

SiAlON

SiAlONs are isostructural Si_3N_4 solid-solutions with the hexagonal β - Si_3N_4 structure stabilized by replacing Si and N with Al and O, and the trigonal α structure stabilized by replacing Si with Li, Mg, Ca, Sc, Y and most rare earths (Jack, 1976; Cao and Metselaar, 1990; Mandal, 1999), with the wide-variety of dopants allowing property tailoring. In spite of birefringence, SiAlONs feature promising properties including high strength (up to 1000 MPa) even at temperature, high hardness (up to 21 GPa), exceptional fracture toughness (K_{IC} up to $8 \text{ MPa} \cdot \text{m}^{1/2}$), low friction coefficient and high wear resistance, high-temperature and thermal-shock resistance, low thermal expansion, outstanding corrosion resistance and good oxidation resistance $<1000^\circ\text{C}$ (Cao and Metselaar, 1990; Mandal, 1999; Jones *et al.*, 2003; Xiong *et al.*, 2008). Although visible transmittance is low ($\sim 70\%$ Lu-doped), IR transmittance is usually higher, and up- (Er^{3+} , Tm^{3+}) and down-conversion (Eu^{3+}) luminescence has been demonstrated (Xie and Hintzen, 2013a; Joshi *et al.*, 2015; Xiao *et al.*, 2019). α -SiAlON typically has equiaxed grains and higher hardness, while β -SiAlON features elongated grains and better toughness (Cao and Metselaar, 1990; Mandal, 1999). Translucent/transparent material has been made by gas-pressure sintering, HP, HIP and SPS in N_2 atmosphere, sometimes by transient liquid-phase sintering (Mitomo *et al.*, 1982; Cao and Metselaar, 1990; Jones *et al.*, 2003, 2004; Xie and Hintzen, 2013a). Transparent SiAlONs are emerging materials that have potential as luminescent up/down converting materials, phosphors and hard antireflecting films (Liu *et al.*, 2013; Joshi *et al.*, 2015; Kshetri *et al.*, 2016; Xiao *et al.*, 2019).

AlN

Aluminum nitride (AlN) has high temperature stability (T_{M} $2200\text{--}3000^\circ\text{C}$ [inert atm.], T_{D} $\sim 1800^\circ\text{C}$), good oxidation resistance due to oxide-layer formation, outstanding thermal conductivity ($320 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$) for an insulator (ρ $10^{11}\text{--}10^{13} \text{ }\Omega \cdot \text{cm}$), a high breakdown field strength, and it exhibits piezoelectricity and luminescence (Harris, 1999; Inoue *et al.*, 2009; Xie and Hintzen, 2013a; Ioffe Database, 2020). In addition to its use as heat-sink substrates, it is of interest for applications in optics, lighting, electronics and renewable energy (Harris, 1999; Xie and Hintzen, 2013a). Although it has a high refractive index (2.02 at 600 nm) and hexagonal structure, the wide bandgap (6.2 eV) should enable visible transparency (Xie and Hintzen, 2013a; Ioffe Database,

2020). However, only poor transmittance has been achieved, with translucent (up to 77% at 800 nm) material made by sintering, HP and SPS with calcium-based sintering additives (Honma *et al.*, 2008; Xiong *et al.*, 2008; Xie and Hintzen, 2013a).

c-BN

Cubic boron nitride (c-BN) has a cubic structure and extraordinary properties, including low density ($2.51 \text{ g} \cdot \text{cm}^{-3}$); exceptional hardness ($\text{HV} > 45 \text{ GPa}$), fracture toughness ($K_{\text{IC}} > 12 \text{ MPa} \cdot \text{m}^{1/2}$) and thermal conductivity ($760 \text{ W} \cdot \text{m}^{-1}\text{K}^{-1}$); high temperature resistance ($T_{\text{M}} > 2950^\circ\text{C}$ [inert atm.]) and potential for transparency from the visible to the MWIR (Weber, 2003; Tian *et al.*, 2013; Hushur *et al.*, 2016). However, only tiny transparent samples have so far been made by high-pressure high-temperature synthesis. It is nevertheless a promising material should fabrication issues be solved.

Phosphides

Phosphides can feature wide transmission windows combined with outstanding thermo-mechanical properties. Boron phosphide (BP) has a cubic zincblende structure and IR transparency to at least $25 \mu\text{m}$, high modulus (830 MPa), exceptional hardness (up to 59 GPa [CVD]) and erosion resistance, chemical inertness and outstanding thermal conductivity ($460 \text{ W} \cdot \text{m}^{-1}\text{K}^{-1}$ at 300K [single crystal]) (Gibson *et al.*, 1994; Harris, 1999; Kang *et al.*, 2017). However, it has limited visible transmittance, the high refractive index (n 2.8 at 633 nm) limits transmittance ($< 60\%$ in the IR) and it exhibits absorption above $12 \mu\text{m}$ (Gibson *et al.*, 1994; Harris, 1999). Fabrication is complicated by the different reactivities of boron and phosphorous and although made as single-crystals and polycrystalline films, it is commonly deposited as amorphous hydrogen-containing CVD films to protect LWIR materials (Harris, 1999). Gallium phosphide (GaP) has similar properties with some transmission in the visible and up to $9 \mu\text{m}$ in the IR with higher transmittance than BP (70% IR) (Gibson *et al.*, 1994). It has good erosion and thermal shock resistance (R' 11.5) and high thermal conductivity ($97 \text{ W} \cdot \text{m}^{-1}\text{K}^{-1}$), but also much higher density ($4.13 \text{ g} \cdot \text{cm}^{-3}$) and only moderate hardness and fracture toughness (Savage, 1991; Monachan *et al.*, 1992; Gibson *et al.*, 1994; Harris, 1999). It is also deposited as protective IR films, while single crystals are used in LED's. Other phosphides, such as AlGaP, have been reported, but applications are currently limited to antireflective and/or erosion-resistant coatings (Harris, 1999).

Oxides

Oxides are the most widely-used and technologically-mature transparent ceramics. Oxygen bonding confers high strength and hardness, chemical stability, oxidation and thermal resistance, often relatively low refractive indices (n 1.56 for $\alpha\text{-SiO}_2$ at 633 nm), excellent transmission from the UV/Vis to the NIR/MWIR and relative ease of synthesis and fabrication in spite of high melting temperatures (Tropf *et al.*, 1995). However, the relatively light oxygen anion and strong bonds limit transmission in the LWIR (Harris, 1999). Oxides are typically classified as binary (BeO , MgO , ZrO_2), sesquioxides (Al_2O_3 , Y_2O_3 , Sc_2O_3 , Lu_2O_3) and multi-cation/anion species (spinel, garnets, pyrochlores, perovskites, silicates, apatites, etc.), which are grouped separately along with materials with unique properties (conducting oxides, ferroelectrics).

Binary oxides

Beryllia

Beryllia (BeO) has a low refractive index (n 1.72 at 600 nm), a very wide bandgap (10.7 eV) conferring an exceptional transmission window ($120 \text{ nm} - 9 \mu\text{m}$, MW), high resistivity ($\rho > 10^{15} \Omega \cdot \text{cm}$), low density ($3.01 \text{ g} \cdot \text{cm}^{-3}$), good mechanical properties ($E \sim 350 \text{ GPa}$, σ 180–250 MPa); thermal ($T_{\text{M}} \sim 2500^\circ\text{C}$), chemical and radiation resistance; outstanding thermal conductivity ($250\text{--}330 \text{ W} \cdot \text{m}^{-1}\text{K}^{-1}$) for an insulator, and piezoelectric and pyroelectric behavior (Budnikov and Belyaev, 1960; Harris, 1999; Kiido *et al.*, 2003; Ivanovskii *et al.*, 2009; Akishin *et al.*, 2009). However, it is toxic and the stable hexagonal $\alpha\text{-BeO}$ polymorph is birefringent and reacts with water above 830°C (Akishin *et al.*, 2009). Transparent polycrystalline BeO has been made by HP and deposition methods, but finds limited application due to toxicity. Actual/potential applications include lightweight UV-IR windows, electronic substrate heat-sinks, ballistic missile domes, microwave furnace windows, UV-emitters, UV-MWIR laser components, transparent mirror coatings, dosimetry scintillators, lamp envelopes and hollow dielectric waveguides (Kiido *et al.*, 2003; Goldstein and Krell, 2016).

Magnesia

Magnesia (MgO) has a cubic structure, relatively low refractive index (n 1.74 at 600 nm), the potential for high transmittance from 0.2 to $9 \mu\text{m}$ (87% theoretical at 600 nm), low density ($3.58 \text{ g} \cdot \text{cm}^{-3}$), good mechanical properties, and high thermal resistance ($T_{\text{M}} 2850^\circ\text{C}$) and thermal conductivity ($47\text{--}53 \text{ W} \cdot \text{m}^{-1}\text{K}^{-1}$ at 54°C) (Weber, 2003; Itatani *et al.*, 2006; Hutzler and Krell, 2013). Transparent MgO has been fabricated by pressureless sintering in air and vacuum with and without additives (LiF being common), HP, sinter-HIP and SPS (Chen *et al.*, 2008). However, processing is complicated by the high melting point and MgO volatility, and until recently only small samples with moderate transparency have been achieved despite a significant development history (Hutzler and Krell, 2013; Kong *et al.*, 2015). When larger and/or more transparent material become available, MgO will likely be considered for applications requiring high temperatures and/or thermal diffusivity.

Zirconia

Zirconia (ZrO_2) has exceptional toughness, high thermal resistance (T_M 2715°C), low thermal conductivity, high oxygen diffusivity, a high dielectric constant and a higher refractive index (n 2.17) than achievable with common glasses (Kong *et al.*, 2015). These attributes make it a candidate for tough transparent windows, miniaturized lenses and artificial gemstones. However, it has high density (5.89 g·cm⁻³) and without anti-reflective coatings the high refractive index decreases transmittance (Rubat du Merac *et al.*, 2018). Zirconia undergoes a cubic→tetragonal→monoclinic phase transition upon cooling (Hannink *et al.*, 2000; Simeone *et al.*, 2003). Substitution of aliovalent cations on Zr^{4+} sites stabilizes the desirable cubic phase by generating oxygen vacancies (Barsoum, 2003). The most typical is Y^{3+} (yttria-stabilized zirconia, YSZ), but Mg^{2+} , Ca^{2+} and $\text{Ce}^{3/4+}$ are also used. Greater than 8 wt% yttria fully-stabilizes the cubic phase (*c*-YSZ), 3%–7% results in cubic and tetragonal (partially-stabilized zirconia, PSZ) and <3% is tetragonal (*t*-YSZ) (Scott, 1975; Standard and Sorrell, 1998; Hannink *et al.*, 2000). Zirconia is the only commercial ceramic exploiting transformation toughening, where volume expansion from the metastable *t*→*m* transition counteracts crack-opening. Thus, a trade-off exists with *t*-YSZ having higher strength (>900 MPa vs <600 MPa) and toughness (8 MPa^{-1/2} vs 2.8 MPa^{-1/2}) than *c*-YSZ, but lower transmittance due to birefringence (Krell *et al.*, 2009b; Kong *et al.*, 2015). However, transparency can be improved by reducing grain-size or magnetically-aligning crystallites during green-body formation (Goldstein and Krell, 2016). Transparent *c*-YSZ has been made by pressureless sintering, HP, sinter-HIP, SPS, and multi-step sintering among others, with TiO_2 commonly used to enhance densification and impart transparency (Wang *et al.*, 2013). Transparent *t*-YSZ has been fabricated by pressureless-sinter-HIP and SPS (Kong *et al.*, 2015). Dissociated uncharged oxygen vacancies caused by processing in reducing atmospheres can render zirconia dark black, requiring post-annealing in oxygen to restore transparency (Janek and Korte, 1999). Despite promising properties, transparent zirconia has so far found limited application, for example as high-index lenses (with 68% transmittance at 0.6 μm) and artificial gemstones (Goldstein and Krell, 2016).

Sesquioxides

Alumina

Alumina (Al_2O_3) was the first synthetic transparent ceramic material and laser host as single-crystal ruby ($\text{Cr}:\text{Al}_2\text{O}_3$), the most technologically-mature and widely-used as single-crystal sapphire and the first commercial polycrystalline transparent ceramic (Lucalox®) (Patel *et al.*, 2000; Goldstein and Krell, 2016; Gagliardi, 2017; Evans, 2020). The development of sapphire spurred advances in crystal-growth, while that of polycrystalline alumina for use as high-pressure sodium-vapor lamp envelopes in the late 1950s increased the understanding of how sintering aids restrict grain-growth to avoid pore occlusion (Burke, 1996). Alumina has several polymorphs, including disordered cubic $\gamma\text{-Al}_2\text{O}_3$ and thermodynamically-stable hexagonal $\alpha\text{-Al}_2\text{O}_3$. It features high transmittance (86% at 600 nm) from the UV to the MWIR (~0.35–6 μm; polycrystalline), high strength even at temperature (up to ~1000 MPa; single crystal), exceptional hardness (>20 GPa; polycrystalline); high wear, erosion and scratch resistance; relatively high fracture toughness; excellent chemical, thermal (T_M 2072°C), thermal-shock and radiation resistance; and high resistivity (Harris, 1999; Savage, 1991; Krell *et al.*, 2004; Dobrovinskaya *et al.*, 2009; Kong *et al.*, 2015). $\alpha\text{-Al}_2\text{O}_3$ is birefringent, causing optical distortion for curved-geometry sapphire and rendering polycrystalline components thicker than a few hundred microns translucent or opaque. Sapphire windows aligned perpendicular to the *c*-axis have equivalent in-plane refractive indices, imparting near-isotropic behavior. Whereas for polycrystals, birefringence can be offset by reducing grain-size below that of transmitted wavelengths or by magnetically-aligning crystallites along the *c*-axis during green-body formation (Liu *et al.*, 2015). Decreasing grain size also increases hardness (up to 22 GPa) and strength (up to 600–800 MPa) (Goldstein and Krell, 2016; Kong *et al.*, 2015). However, even with fine grains, transparency is still far below that of sapphire and other cubic transparent materials (~<60% at 600 nm). Although, IR transmittance can be much higher if wavelengths are much larger than grain size.

Sapphire was first made using the Verneuil method, and later by methods like Czochralski, Kyropoulos, heat-exchanger, gradient-solidification, and horizontal directed-solidification, which are relatively slow, expensive and require machining components from boules (Maiman, 1960; Goldstein and Krell, 2016; Kurlow, 2016). Windows (up to 30 × 200 cm) and cylinders are now made by methods like edge-defined film-fed growth, non-capillary shaping, element-of-shape growth and variable-shaping technique (Goldstein and Krell, 2016; Saint-Gobain, 2020). Sapphire's lower manufacturing costs through industries of scale and near-net shape pit it against polycrystalline ceramics. Excellent optical properties, high strength and photochemical resistance make it an attractive laser host, with laser quality Cr^{3+} and Ti^{3+} -doped sapphire commercially-available (Savage, 1991; Dobrovinskaya *et al.*, 2009). Sapphire is used as scratch-resistant windows (watch faces, scanners), Vis-IR windows and domes, transparent armor, optical elements, laser hosts, scintillators, electronic substrates, artificial gemstones, wear-resistant bearings and components, fiber reinforcement, pressure sensors, insulators, chemical ware and medical implants (Dobrovinskaya *et al.*, 2009; Kurlow, 2016). However, it is difficult to machine and is susceptible to chipping and its hardness increases polishing costs (Bernard-Granger *et al.*, 2011). Although raw materials are relatively inexpensive, single crystals are expensive to manufacture and have limited toughening mechanisms (Harris, 1999; Bernard-Granger *et al.*, 2011). Polycrystalline alumina was initially made by high-temperature sintering in H_2 with MgO sintering additive. It has since been made using various green-body forming methods (cold-pressing, CIP, float-packing, injection molding; gel-, tape- and slip-casting, etc.) combined with methods such as two-step sintering, sinter forging, sinter-HIP, SPS, and microwave sintering, with recent emphasis on grain-size reduction using additives (Kwon *et al.*, 1995; Kong *et al.*, 2015). Applications include envelopes for high-pressure metal halide lamps, scratch-resistant windows and thin-coatings, and IR windows and domes (Harris, 1999; Goldstein and Krell, 2016).

Yttria

Yttria (Y_2O_3) has excellent transmission from the visible to the MWIR (0.2–8.0 μm , >80% up to 7 μm , even at elevated temperature), low emittance, good mechanical properties, excellent corrosion and heat resistance (T_M 2430°C), good thermal conductivity (13.6 $\text{W} \cdot \text{m}^{-1}\text{K}^{-1}$ at 300K) and lower thermal expansion ($6\text{--}7 \times 10^{-6}\text{K}^{-1}$) than YAG ($7.8 \times 10^{-6}\text{K}^{-1}$) (Hogan *et al.*, 2004; Kong *et al.*, 2015). These qualities make it a candidate for laser hosts and scintillators and IR aerothermal domes and windows. The first ceramic scintillator was made from the related compound $\text{Eu}^{3+}:\text{Y}_{1.34}\text{Gd}_{0.60}\text{Eu}_{0.06}\text{O}_3$ and the second ceramic laser was made from $\text{Nd}^{3+}:\text{ThO}_2(10\%)\text{-Y}_2\text{O}_3$ (Greskovich and Duclos, 1997; Sanghera *et al.*, 2012). The high effective atomic number and density (5.01 $\text{g} \cdot \text{cm}^{-3}$) are attractive for scintillators, but along with yttria's relatively low thermal-shock resistance and higher cost, they are a disadvantage for aerospace applications. Yttria's high melting point requires exceptionally high sintering temperatures and transparency was first achieved ~50 years ago by sintering >2000°C using up to 10 wt% ThO_2 . Transparent yttria has since been made by sintering without additives, two-step sintering, HP, sinter-HIP, SPS, and microwave sintering (Hogan *et al.*, 2004; Jin *et al.*, 2010; Kong *et al.*, 2015). Other additives (La_2O_3 , HfO_2 , ZrO_2 , BeO , LiF , and Al_2O_3) have been used to aid sintering or to improve properties (Jung *et al.*, 2018). La_2O_3 addition exploits polymorphism that restricts grain-growth at higher temperature and the mix of cubic and hexagonal phases after sintering are converted to cubic by annealing. La_2O_3 -doping increases visible transmittance and room-temperature strength, but decreases thermal conductivity and high-temperature resistance (Goldstein and Krell, 2016). Grain-size reduction using colloidal processing and SPS or microwave sintering offer further promise to increase mechanical properties. Yttria has been used or considered for IR windows and domes for missiles, laser hosts (Eu-doped), scintillators and NIR-upconverters (rare-earth co-doped) (Kong *et al.*, 2015).

Other sesquioxides

Scandia (Sc_2O_3) and lutetia (Lu_2O_3) have recently garnered considerable interest due to favorable properties. Scandia has a cubic crystal structure with high transmittance, refractive index (n 2.0 at 300 nm) and bandgap (5.7 eV); low UV cut-off (215 nm), good mechanical properties, high melting point (T_M 2430°C), good thermal conductivity (17 $\text{W} \cdot \text{m}^{-1}\text{K}^{-1}$) and chemical resistance. These properties are attractive for damage-resistant high-reflection material in LED's, high-power UV laser components, IR windows and domes and heat-resistant optical windows (Kong *et al.*, 2015). Like other sesquioxides, scandia can accommodate high doping levels of active rare-earth ions, making it attractive for laser hosts (Tm^{3+} doped). However, Sc_2O_3 , Lu_2O_3 and Y_2O_3 have relatively high non-linear refractive indices, which can cause beam distortion at high radiation intensities (Sanghera *et al.*, 2012). Highly-transparent material is commonly made by vacuum sintering with post-HIP, although it is not yet commercially-available (Kong *et al.*, 2015). Lutetia (Lu_2O_3) features a wide bandgap, good mechanical properties, low thermal expansion, high thermal conductivity and chemical stability. Its high density (9.42 $\text{g} \cdot \text{cm}^{-3}$) and atomic mass confer stopping power for ionizing radiation in scintillators, while the ability to accommodate large concentrations of Yb^{3+} ions make it an attractive laser host. Transparent Lu_2O_3 ceramics have been made by vacuum sintering, HIP and SPS. Although Eu, Nd, and Yb-doped Lu_2O_3 show promise for scintillators and have been manufactured for lasers, they are relatively expensive (Kong *et al.*, 2015; Furuse and Yasuhara, 2017; Xiao *et al.*, 2019). Sesquioxides also have promising magneto-optical properties for isolators and Faraday rotators in high-power lasers. Terbium oxide (Tb_2O_3) and holmium oxide (Ho_2O_3) have Verdet constants of 128 and 45 $\text{rad} \cdot \text{T}^{-1}\text{m}^{-1}$ at 1064 nm, respectively, comparable or higher than for terbium aluminum garnet (TAG, 47 $\text{rad} \cdot \text{T}^{-1}\text{m}^{-1}$) and terbium gallium garnet (TGG, 35 $\text{rad} \cdot \text{T}^{-1}\text{m}^{-1}$, the most common magneto-optic material for high-power lasers) (Furuse and Yasuhara, 2017; Snetkov *et al.*, 2016). Moreover, dysprosium oxide (Dy_2O_3) has a Verdet constant of 300 $\text{rad} \cdot \text{T}^{-1}\text{m}^{-1}$ at 633 nm, more than twice that of TGG at that wavelength (Furuse and Yasuhara, 2017). Scintillators based on Gd_2O_3 have also been successfully fabricated (Zeeman *et al.*, 1995).

Complex oxides

Spinel (MgAl_2O_4)

Magnesium aluminate (MgAl_2O_4 , spinel) is the only intermediate compound of the $\text{MgO-Al}_2\text{O}_3$ system and the archetype for the cubic spinel structure. It has excellent transmission from the UV to the MWIR (up to 87% at ~600 nm, also MW transparency), relatively-low refractive index (n 1.71 at 532 nm) and density (3.58 $\text{g} \cdot \text{cm}^{-3}$), slightly lower strength (~200 MPa) and hardness (16 HV) than Al_2O_3 , high-temperature resistance (T_M 2105°C) and good thermal conductivity (Rubat du Merac *et al.*, 2013; Goldstein and Krell, 2016). The slightly higher IR absorption edge than ALON and sapphire, combined with ease of manufacture and lower polishing cost makes spinel competitive for hard, scratch- and impact-resistant Vis-IR windows (Harris, 1999). Moreover, the low UV absorption edge offers potential for UV windows and optics, while the low Abbe number is interesting for lenses (Burnett *et al.*, 2005; Rubat du Merac *et al.*, 2013). Although a line compound at equilibrium, the spinel phase spans 38–90 mol% Al_2O_3 at higher temperature, and 50 to ~80 mol% can be cooled without constituent precipitation. Stoichiometry affects most properties of spinel, and although it is difficult to control partly due to MgO vaporization during sintering, it offers the potential to tailor properties (Rubat du Merac *et al.*, 2013). Transparent material was first produced over 50 years ago by pressureless sintering pressed compacts in H_2 with Li_2O and SiO_2 additives (Gatti, 1969). Since then, green bodies have been formed by cold pressing, CIP and slip-, gel- and tape-casting, and densified by HP-HIP with LiF , pressureless sinter-HIP without additives, SPS, microwave sintering and others, sometimes combined with reactive sintering (Rubat du Merac *et al.*, 2013). Windows up to 48 × 48 cm, or larger by diffusion edge-bonding smaller panes, have been made (Destefani, 2013). Although

many sintering additives have been used, the trend is avoiding them and emphasis has been on grain-size reduction. Spinel has been used as transparent armor for military vehicles, multi-spectral (Vis-IR) windows and domes; scratch-resistant windows for outdoor, consumer goods, and scanners; temperature and chemical-resistant windows and Q-switches, and it is being considered for UV and laser applications (Rubat du Merac *et al.*, 2013). Other transparent spinels like ZnAl_2O_4 have also recently been investigated or developed (Goldstein *et al.*, 2012).

Garnets (YAG)

Yttrium aluminum garnet (YAG, $\text{Y}_3\text{Al}_5\text{O}_{12}$) has excellent optical properties (transmission from 0.2 to 6 μm with up to 84% transmittance), good mechanical properties, reasonable thermal conductivity ($10.8 \text{ W} \cdot \text{m}^{-1}\text{K}^{-1}$), high thermal resistance ($T_M \sim 1950^\circ\text{C}$) and a cubic crystal structure that easily accommodates rare-earths dopants, enabling use as a laser host (Sanghera *et al.*, 2012). In addition, it is cheaper and/or optical quality material is easier to make than comparable materials, making it the most widely-used solid-state laser medium (Goldstein and Krell, 2016; Lupei, 2016). The most common dopants are Nd^{3+} (first demonstrated in 1964) and Er^{3+} for lasers, and Ce^{3+} for phosphors and scintillators, but a variety of other dopants (Yb^{3+} , Ho^{3+} , Cr^{2-4+} , Tm^{3+}) are used (Kong *et al.*, 2015; Lupei, 2016; Xiao *et al.*, 2019). It typically emits at 1064 nm, but can be frequency doubled (tripled, etc.) to emit in the visible. However, it has higher thermal expansion and lower thermal conductivity than sesquioxides (Sanghera *et al.*, 2012). Although typically made as single crystals, YAG is increasingly made polycrystalline. The intermediate compounds $\text{Y}_4\text{Al}_2\text{O}_9$ (monoclinic YAM) and YAlO_3 (perovskite YAP) in the Y_2O_3 - Al_2O_3 phase system at higher yttria contents require stoichiometry control during processing (Kong *et al.*, 2015). The reasonably-low vapor pressure up to 1850°C enables vacuum sintering of polycrystalline YAG at high temperature, but it has also been made by HP, SPS, and solid-state reaction and sintering, sometimes with added HIP, and additives like SiO_2 , MgO and CaO have been used to promote densification (Sanghera *et al.*, 2012; Kong *et al.*, 2015; Goldstein and Krell, 2016). Rods $> 20 \text{ cm}$ long and slabs $> 10 \times 10 \times 2 \text{ cm}$ have been fabricated and laser power outputs of over 100 kW achieved (Sanghera *et al.*, 2012). YAG has been used as laser hosts, phosphors and scintillators; in Q-switches and LED's, and as gemstones, but it also has potential as windows (Goldstein and Krell, 2016; Gemological Institute of America, 1995).

Other transparent garnets, such as $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG), $(\text{Y,Gd})(\text{Ga,Sc})_3\text{Al}_5\text{O}_{12}$, $\text{Dy}_3\text{Al}_5\text{O}_{12}$ (DyAG), $\text{Tb}_3\text{Al}_5\text{O}_{12}$ (TbAG) and $\text{Tm}_3\text{Al}_5\text{O}_{12}$ (TmAG) have also been reported. These generally feature good thermo-mechanical properties with some being used or showing promise as laser hosts, scintillators, transparent luminescent ceramics for LED's and for magneto-optic applications (Sanghera *et al.*, 2012; Xie *et al.*, 2013b; Kong *et al.*, 2015; Li *et al.*, 2019). TbAG in particular has a high Verdet constant ($137 \text{ rad} \cdot \text{T}^{-1}\text{m}^{-1}$), which is useful for optical Faraday isolators in lasers to prevent back-reflected light from returning to the cavity (Li *et al.*, 2019).

Pyrochlores

Pyrochlore oxide ceramics with the general formula $\text{A}_2\text{B}_2\text{O}_{6/7}$, where cations are typically rare-earth or transition-metals, have a cubic structure and can exhibit good Vis-NIR transmittance, luminescence, excellent thermal resistance; insulating, ionic or metallic conduction; and piezo- and ferro-electric behavior (similar to perovskites) (Subramanian *et al.*, 1983). Several transparent pyrochlore ceramics with general type $(\text{La,Lu,Y,Gd,Nd})_2(\text{Zr,Hf})_2\text{O}_7$ (i.e., $\text{La}_2\text{Hf}_2\text{O}_7$) and $(\text{Y,Lu})_2\text{Ti}_2\text{O}_7$ (i.e., $\text{Y}_2\text{Ti}_2\text{O}_7$) have been reported, some featuring high transmittance (Wang *et al.*, 2018; Xiao *et al.*, 2019). Although they have potential for use as high-index lenses, lasers, transparent armor and scintillators, they are still being developed (Wang *et al.*, 2018).

Ferroelectrics

Perovskites (PLZT, PMN, PZN)

The cubic ABX_3 perovskite structure, where A and B are metal cations and X is typically oxygen, is adopted by a wide-range of compounds. In addition to transparency, perovskites can exhibit interesting properties such as electronic and ionic conduction, superconductivity, lasing, scintillating, ferroelectricity and magnetoresistance (Vasylechko *et al.*, 2009). Among these, ferroelectric behavior, which occurs below the Curie temperature (T_C) where a transition to paraelectric occurs, and which also consequently implies pyro- and piezo-electric behavior, can give rise to useful electrooptic effects (Haertling, 1999; Goldstein *et al.*, 2020).

Common ferroelectric ceramics include lead-lanthanum zirconate-titanate (PLZT, $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$), lead-magnesium niobate - lead titanate (PMN-PT, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_3\text{-PbTiO}_3$) and lead-zirconium niobate - lead titanate (PZN-PT, $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$), with many other elemental partial-substitutions possible. These combine pseudo-cubic perovskite (or distorted, pyrochlore or tetrahedral structures depending on doping, poling and temperature) with relaxor-ferroelectric, photorefractive and photochromic behavior, enabling unique applications (Haertling, 1999). Although visible transparency is low ($< 70\%$) due to high refractive indices, electrooptic coefficients are high (Xiao *et al.*, 2019). The most widely-used and mature is PLZT, with lanthanum substitution exceptionally beneficial for transparency (Goldstein *et al.*, 2020). Depending on composition, $T_C \sim 75\text{--}250^\circ\text{C}$ and electrooptic coefficients ($r_c 1.2\text{--}5.2 \times 10^{-10} \text{ m} \cdot \text{V}^{-1}$, $R 3.8\text{--}9.1 \times 10^{-16} \text{ m}^2\text{V}^{-2}$) are five times or more those of LiNbO_3 (a common ferroelectric with $r_c 0.17 \times 10^{-10} \text{ m} \cdot \text{V}^{-1}$) (Haertling, 1999; Uchino, 2000; Goldstein and Krell, 2016; Xiao *et al.*, 2019). However, PLZT exhibits high induction fields, polarization-dependent scattering and relatively large hysteresis (Kamzina *et al.*, 2010). PMT requires solid-solution with PT to increase T_C above ambient and has electrooptic coefficients ($r_c 24 \times 10^{-10} \text{ m} \cdot \text{V}^{-1}$, $R 66 \times 10^{-16} \text{ m}^2\text{V}^{-2}$) over 100 times greater than LiNbO_3 and a strong photorefractive effect (Haertling, 1999; Goldstein and Krell, 2016; Xiao *et al.*, 2019).

Goldstein *et al.*, 2020). PZN also features excellent ferroelectric properties and requires solid-solution with PMN or PT (Xiao *et al.*, 2019). Many other compositions have been fabricated, but lead toxicity and volatility during processing have motivated the development of lead-free transparent ferroelectrics. For example, $(\text{Sr},\text{Ba}_{1-x})\text{Nb}_2\text{O}_6$ (SBN), $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ (KTN), KH_2PO_4 (KDP), $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ (KSN), $(\text{K},\text{Na})\text{NbO}_3$ (KNN), $(\text{K},\text{Na})\text{Nb}_{1-x}\text{Bi}_x\text{O}_3$ and BaZrO_3 - BaTiO_3 (BZT), with some of these featuring additional functional properties such as luminescence and photochromism (Dupuy *et al.*, 2016; Cao *et al.*, 2019; Xiao *et al.*, 2019; Goldstein *et al.*, 2020). Transparent ferroelectrics have been made using solid-state reaction, pressure-sintering, HP, SPS, and microwave sintering and are often made as thin-films using deposition methods (Xiao *et al.*, 2019). Applications include optical modulators and shutters, flash goggles, color filters, polarization controllers, segmented displays, image storage, energy storage, viewing systems, and night-vision systems (Levinson, 1987; Haertling, 1999; Kong *et al.*, 2015; Goldstein and Krell, 2016; Chai *et al.*, 2017). Non-ferroelectric perovskites can also have desirable properties, with $\text{Ba}(\text{Zr},\text{Mg},\text{Ta})\text{O}_3$ with $n = 2.08$ – 2.2 and Abbe number 40 commercialized as a high-index lens for electronics, and other compositions like SrHfO_3 investigated for laser media and thin-film epitaxy substrates (Krell *et al.*, 2009b; Goldstein and Krell, 2016).

Conducting oxides (ITO)

Transparent conducting oxides (TCOs) have the unique combination of transparency and electronic conductivity and are key enablers of technologies like pressure-sensitive displays. TCOs are dominated by combinations of indium (In_2O_3), zinc (ZnO) and tin oxide (SnO_2), and to a lesser extent gallium (Ga_2O_3) and cadmium oxide (CdO), with indium-tin oxide (ITO) prevalent (Pasquarelli *et al.*, 2011). TCOs generally have relatively high melting points but also high density, low hardness and high refractive indices. However, they transmit in the visible and can feature luminescence, high electron mobilities and semiconductor and piezoelectric behavior (Weber, 2003). TCOs are produced polycrystalline or amorphous and are often doped (i.e., Cl, F, Sb, Ti, Mo) (Pasquarelli *et al.*, 2011). Visible transparency can be up to 90% (thin coatings) with transmission windows spanning from 0.35 to 3.5 μm and resistivities from 1 to $8 \times 10^{-4} \Omega \cdot \text{cm}$ for ITO (Bright, 2013). Moreover, they can absorb UV and reflect IR wavelengths, making them useful heat reflectors with UV protection. TCO's are applied as thin-films and have been made by spray-pyrolysis, sputtering, CVD, PVD, PLD, ALD and chemical solution deposition (Pasquarelli *et al.*, 2011). Applications include flat-panel/LCD displays, TV monitors; touch-sensitive displays, electrochromic windows and LED's (as transparent electrodes); photovoltaics (as transparent current collectors), conductive antireflection coatings, transparent heating conductors for aircraft windshields, transparent thin-film transistors (TFT's) for flexible electronics, electromagnetic interference shielding, laser diodes and antistatic films (Pasquarelli *et al.*, 2011; Lewis and Paine, 2000). The individual oxides used in TCOs also have interesting properties and are used in niche applications. For example, ZnO features good transparency, low thermal expansion, high thermal resistance (T_D 1974°C), high electron mobility ($2000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ at 80K), and luminescent, semiconducting and piezoelectric behavior, finding (potential) use in UV laser diodes, heat-protection and transparent conducting coatings (Borysiewicz, 2019).

Complex-anion (silicates, apatites) and other oxides

Transparent complex-anion ceramics have been reported but they are not yet used commercially. Mullite is a solid-solution with general formula $\text{Al}_6\text{Si}_2\text{O}_{13}$ and orthorhombic structure. It is a widely-used opaque engineering material due to low density ($\sim 3.2 \text{ g} \cdot \text{cm}^{-3}$) and reasonable strength (200 MPa), fracture toughness ($K_{IC} \sim 2.5$) and hardness (10 GPa), combined with superior high-temperature stability ($T_M \sim 1830^\circ\text{C}$), high thermal-shock resistance, and low thermal expansion ($\sim 4.5 \times 10^{-6} \text{ K}^{-1}$), thermal conductivity ($\sim 7 \text{ W} \cdot \text{m}^{-1} \text{ K}^{-1}$) and dielectric constant. It has been prepared by HP, HP-HIP, pressureless sinter-HIP, microwave sintering, vacuum sintering and SPS. Although visible transmittance is low, up to 88% transmittance has been achieved in the IR (Ren *et al.*, 2015; Xiao *et al.*, 2019). Translucent/transparent rare-earth doped Lu_2SiO_3 and oxy- and fluoro-apatite ($\text{Sr}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2$, $\text{Sr}(\text{PO}_4)_3\text{F}$ and $\text{Ca}_5(\text{PO}_4)_3\text{F}$) ceramics with promising laser and scintillator properties and transparent hydroxyapatites for biomedical applications have also been reported (Uematsu *et al.*, 1989; Shen *et al.*, 2012; Chen *et al.*, 2013; Kim *et al.*, 2017; Furuse *et al.*, 2019). Transparent strontium aluminosilicate ($\text{Sr}_{1+x/2}\text{Al}_2+x\text{Si}_{2-x}\text{O}_8$) ceramics with high transmission (90%, 1.5 mm thick), tellurite ceramics (TeO_2 - Nb_2O_5 - Bi_2O_3) and ion-conducting transparent ceramics ($\text{Ln}_{1+x}\text{Sr}_{1-x}\text{Ga}_3\text{O}_7$) have been fabricated by full crystallization from glass (Saghir, 2014; Boyer *et al.*, 2018), as have other simpler structures (BaAl_4O_7 , $\text{Sr}_3\text{Al}_2\text{O}_6$), with potential applications ranging from lenses to laser hosts (Bertrand *et al.*, 2016). Many other transparent oxides are being investigated, developed or used in niche applications. Examples range from high-hardness coesite SiO_2 , to optoelectronic TiO_2 , conductive vanadium oxides, and refractories like HfO_2 , CeO_2 and ThO_2 (T_M 3350°C) to name a few (Anderson, 1972; Chain, 1991; Weber, 2003; Xie and Hintzen, 2013a; Mazzolini *et al.*, 2015; Kulik *et al.*, 2018).

Oxynitrides

Oxygen and nitrogen share similar chemical and electronic characteristics that enable their substitution in oxides and nitrides, forming the large oxynitride group. These feature substantial structural diversity and unique properties that can be tailored by varying the O/N ratio. ALON is the only bulk material used commercially, while other compositions (MgAlON , LiAlON , TiO_xN_y) are being investigated, developed or used as coatings (Xiao *et al.*, 2019). Oxynitrides have similar potential applications as oxides and nitrides, such as transparent armor, scratch-resistant windows, optical elements, and thin-film antireflection, heat-mirror and solar absorber coatings (Xie and Hintzen, 2013a).

AlON

It was discovered in the 1970s that substituting ~ 5 wt% nitrogen for oxygen in Al_2O_3 stabilizes the cubic γ - Al_2O_3 phase, enabling the possibility of highly-transparent thick-sections with similar mechanical properties as Al_2O_3 (McCauley and Corbin, 1980; McCauley *et al.*, 2009). The material was trademarked as ALONTM with composition $\sim 9\text{Al}_2\text{O}_3\text{-}5\text{AlN}$ ($\text{Al}_{23}\text{O}_{27}\text{N}_5$). The Al_2O_3 -AlN phase diagram is complex, with the cubic solid-solution phase existing within a range centered at 35.7 mol% AlN (McCauley *et al.*, 2009). ALON has similar physical properties as Al_2O_3 , with high transmission from the UV to the MWIR but with a slightly lower IR cut-off (Harris, 1999). Commercial ALON has relatively large grain size (150–200 μm) and hardness HV ~ 15 –16 GPa. Although hardness is lower than Al_2O_3 , it is higher than competing materials and there is ample opportunity for further improvement through grain-size refinement. ALON fabrication is complicated by high-temperature vapor phases and requires precise temperature and atmosphere control. It was first produced by reaction sintering cold-pressed Al_2O_3 and AlN reactants in N_2 at high temperature (Savage, 1991). It has since been made using green-body formation methods like slip-casting and injection molding, and densified by pressureless sintering, transient liquid-phase sintering, HP, HIP, microwave sintering, and SPS in N_2 atmosphere, often starting with ALON powders, which are themselves difficult to synthesize (Savage, 1991; Patel *et al.*, 2000; McCauley *et al.*, 2009; Kong *et al.*, 2015; Kumar and Johnson, 2016). Sizes up to 45×90 cm or larger by edge-bonding have been made (Surmet Co., 2020). Although it has excellent properties and the technology is well-developed, ALON is more expensive than competing ceramics like spinel (Patel *et al.*, 2000). Applications are similar to sapphire and spinel, including missile domes, military lenses and windows, transparent armor, laser and scanner windows, high-energy discharge and sodium-vapor lamp envelopes and semiconductor applications (Silva and Boccacini, 2008; McCauley *et al.*, 2009). Other oxynitrides find use as hard, scratch-resistant and/or antireflective coatings (Xie and Hintzen, 2013a).

Chalcogenides

Non-oxide chalcogenides (sulfides, selenides, and tellurides) are characterized by high melting points, chemical stability, moderate thermo-mechanical properties and IR transmittance. Zinc sulfide and selenide are common IR materials, while others are used in niche applications, such as CdS thin-coatings for photovoltaics and single-crystal PbF_2 for IR detectors (Harris, 1999).

Sulfides/Selenides (ZnS, ZnSe)

Zinc sulfide (ZnS) and selenide (ZnSe) are wide-bandgap semiconductors with a long history as the most important IR optical materials. Both are cubic, but ZnS transforms to a hexagonal phase $> 1020^\circ\text{C}$ (McCloy, 2007). ZnS has a high refractive index (n 2.36 at 600 nm), a wide transmission window (0.4–12.5 μm), sometimes high visible and usually excellent IR transmittance, especially in the LWIR (8–10 μm). It has relatively poor mechanical properties and high density ($4.09 \text{ g} \cdot \text{cm}^{-3}$), but moderate thermal-shock resistance and increasing strength with temperature. ZnS oxidizes $> 800^\circ\text{C}$ and sublimates $> 1200^\circ\text{C}$, while ZnSe sublimates $> 400^\circ\text{C}$ (Goldstein *et al.*, 2020). ZnSe has better optical quality, with excellent MWIR (3–5 μm) and LWIR transmittance, but lower mechanical properties and poor thermal-shock resistance. Attempts have been made to improve this by alloying with diamond, GaP or other materials, and by laminating with ZnS. Although ZnSe is an excellent material for laser windows, it is not durable enough for external use. Both materials are relatively soft, have low erosion resistance and usually require coatings for demanding applications (Harris, 1999). ZnS and ZnSe are primarily made by chemical vapor deposition (CVD) and HIP, and previously by HP. CVD ZnS typically has an amber color and is composed of cubic and hexagonal phases and can contain absorbing hydride impurities. Post-HIP restores stoichiometry, removes hydrogen, and converts hexagonal grains to cubic, albeit at the expense of grain growth (Harris, 1999). ZnS and/or ZnSe are used or proposed as IR windows and domes, phosphors and anti-reflective thin-films, and in CO_2 laser optics, LED's, blue LED lasers, IR laser gain media and scintillators (Harris, 1999; McCloy, 2007).

Fluorides

The highly-ionic character of alkaline/alkaline-metal fluorides confers exceptionally-low refractive indices (1.33 at 633 nm for NaF) and dispersion along with wide transmission windows (including the MW), enabling transmittances surpassing SiO_2 over a broad range (Harris, 1999; Weber, 2003; Stevenson *et al.*, 2011). LiF and MgF_2 have the lowest UV absorption edges of known materials (~ 0.11 – 0.12 nm) (Tropf *et al.*, 1995). However, many fluorides are water-soluble (NaF) or hygroscopic (LiF, MgF_2) and uncoated LiF degrades in humidity (Elliot, 1995; Xiao *et al.*, 2019). Fluorides with heavier cations (CaF_2 , SrF_2 , BaF_2 , and PbF_2) transmit further in the IR while maintaining UV-vis transparency, enabling use in the MWIR and LWIR (Stevenson *et al.*, 2011). Fluorides also have desirable laser properties, including low or negative thermo-optic coefficients (dn/dT), which can partially compensate thermal lensing effects, high absorption/emission cross sections, and lower thermal expansion and non-radiative decay rates and weaker crystal fields than some oxides (Stevenson *et al.*, 2011). Although, thermal expansions are higher and thermal conductivities lower than garnets and sesquioxides (Sanghera *et al.*, 2012). The main laser-gain materials are CaF_2 , LiYF_4 , LiSrAlF_6 and LiCaAlF_6 , while CaF_2 , BaF_2 and CeF_3 have been investigated as scintillators for ionizing radiation (Stevenson *et al.*, 2011). Fluorides are also used as UV-Vis-IR optical components, coatings and windows and domes. Although fluorides are commonly used as single-crystals, MgF_2 and CaF_2 (more commonly), and SrF_2 are also made polycrystalline (Harris, 1998). Other transparent polycrystalline fluorides, including high-entropy compositions have also been reported (Chen and Wu, 2019). Although they can have low density and high melting points,

fluorides are relatively soft, often lack thermal-shock resistance, have high thermal expansions and are susceptible to solarization (Harris, 1999; Elliot, 1995; Sanghera *et al.*, 2012; Xiao *et al.*, 2019).

Magnesium fluoride

Magnesium fluoride (MgF_2) has a low refractive index (n 1.37), low dn/dT ($1.2/0.6 \times 10^{-6} \text{K}^{-1}$ at 633 nm), an exceptionally-low UV absorption edge ($\sim 0.12 \text{ nm}$), a wide transmission window (up to $7\text{--}9 \mu\text{m}$), low density ($3.15 \text{ g}\cdot\text{cm}^{-3}$) and moderate thermomechanical properties (Harris, 1999; Weber, 2003). However, the tetragonal structure is slightly birefringent and the strength and thermal-shock resistance are relatively low (Harris, 1999; Xiao *et al.*, 2019). It is nevertheless rugged enough to be used in missile domes and has resistance to laser damage (Harris, 1999; Kong *et al.*, 2015). Transparent material is typically HP but achieved transparency remains low (Xiao *et al.*, 2019). Applications include UV and UV-laser components, antireflection coatings and IR windows and domes (Elliot, 1995; Kong *et al.*, 2015; Goldstein and Krell, 2016).

Calcium fluoride

Calcium fluoride (CaF_2) has a cubic fluorite structure, a low refractive index (n 1.43) rendering high transmittance ($> 90\%$ in the IR) and a wide transmission window ($0.13\text{--}10\text{--}12 \mu\text{m}$), enabling use from the UV to the MWIR/LWIR. $\text{U}^{3+}:\text{CaF}_2$ was the second laser material and HP $\text{Dy}^{2+}:\text{CaF}_2$ was the first ceramic laser material (Sorokin and Stevenson, 1960; Hatch *et al.*, 1964; Stevenson *et al.*, 2011). Although it has low density ($3.18 \text{ g}\cdot\text{cm}^{-3}$) and good thermal conductivity ($9.7 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$), it is relatively fragile, with weaker thermomechanical properties and higher thermal expansion than MgF_2 and it colors under UV irradiation (Elliot, 1995; Stevenson *et al.*, 2011). Transparent material has been made by HP, sinter-HIP and SPS with various dopants (Yb^{3+} , Er^{3+} , Ho^{3+}) for laser applications (Xiao *et al.*, 2019). CaF_2 is used in UV and IR lasers, with $\text{Yb}:\text{CaF}_2$ of interest for high-power lasers; windows and lenses for thermal imaging, spectroscopy and telescopes; scintillators, thermoluminescent dosimeters and previously as high-performance single-crystals in optical devices due to its low dispersion (Elliot, 1995; Stevenson *et al.*, 2011; Goldstein and Krell, 2016).

Chlorides, Bromides and Iodides

Halogens such as chlorides, bromides and iodides generally have poor thermomechanical properties and are often water-soluble, but they can feature low refractive indices and dispersion (chlorides) and wide transmission windows with excellent transmittance up to the far IR (bromides and iodides). They are generally used as single-crystal IR materials (NaCl , KCl , KBr , KI , CsI , AgBr , AgI , etc.), but some materials, like KCl and SrI_2 (a widely-used commercial scintillator material) have also been made polycrystalline, for example by hot forging (KCl) (Harris, 1999; Cherepy *et al.*, 2011).

Nanocomposites

Nanocomposites aim to take advantage of synergetic effects of constituents to potentially yield improved properties. However, depending on the refractive index difference, the grain size must be less than $20\text{--}30$ times smaller than transmitted wavelengths to maintain reasonable transmittance (Harris *et al.*, 2013). Fortunately, this can be assisted by grain-growth inhibition due to constituent immiscibility. Several transparent composites have been reported, including $\text{ZrO}_2\text{--ThO}_2$, $\text{MgO--Y}_2\text{O}_3$, $\text{ZrO}_2\text{--MgO--Y}_2\text{O}_3$, $\text{MgAl}_2\text{O}_4\text{--Si}_3\text{N}_4$ and $\text{MgAl}_2\text{O}_4\text{--YAG}$ (Gledhill *et al.*, 2012; Wang *et al.*, 2012; Kong *et al.*, 2015). $\text{MgO--Y}_2\text{O}_3$ was developed as an IR-transmitting ceramic and generally has physical properties intermediate between the constituents, but it exhibits twice the strength and thermal shock resistance (Harris *et al.*, 2013).

Coating Materials

Thin- and thick-films, and to a lesser extent, claddings, represent one of the most important applications for transparent ceramics in terms of diversity, comprising the entire gamut of materials. Coating materials are too numerous to iterate here, but examples include diamond, SiC , GeC , AlN , TiN , Si_3N_4 , MgO , ITO , ZnO , SnO_2 , TiO_2 , ZrO_2 , HfO_2 , ThO_2 , HfO_2 , CeO_2 , Al_2O_3 , Y_2O_3 , Sc_2O_3 , Cr_2O_3 , Ta_2O_5 , Nb_2O_5 , TiON , ZnS , As_2S_3 , ZnSe , GaP , BP , LiF , MgF_2 , AlF_3 , PbF_2 , LaF_3 , HfF_4 , YF_4 , ZrF_4 , ThF_4 , and CeF_3 (Dobrowolski, 1995; Xie and Hintzen, 2013a; Lee and Kuo, 2013). Coatings are used in applications ranging from flat-panel displays, LED's, sunglasses, automotive and aircraft windows, Vis-IR windows and domes, laser windows and UV-protective and heat-mirror windows.

Summary

Considering their remarkable and varied properties, if the last half-century is any guide, transparent ceramics will likely not only experience strong growth in their current niches, but also find use in many new applications. Hundreds of new materials are in the pipeline or yet to be discovered, and these will undoubtedly add to the great variety of current materials. Advances in processing are enabling ever more complex structures and difficult to sinter materials to be produced. As technology improves and costs are

reduced, transparent ceramics are finding application where only polymers and glasses were used. Moreover, polycrystalline materials will surely continue to expand into applications where previously only single crystals were used. Furthermore, polycrystalline ceramics will continue to be optimized with fewer flaws and ever smaller grain sizes, resulting in improved physical properties. Manufacturing technology is also rapidly advancing to produce ever larger sizes and geometries while reducing cost. Finally, thin-films and thicker coatings, whether single or multi-layer, are especially promising to enable new applications in fields as varied as mobility, energy and health care.

References

- Akishin, G.P., Turnaev, S.K., Vaispapis, V.Y., *et al.*, 2009. Thermal conductivity of beryllium oxide ceramic (Russian). *Novye Ogneup.* 12, 43–47.
- Allix, M., Alahrache, S., Fayon, F., *et al.*, 2012. Highly transparent BaAl_2O_7 polycrystalline ceramic obtained by full crystallization from glass. *Adv. Mater.* 24, 5570–5575.
- Anderson, R.C., 1972. Transparent Zirconia, Hafnia, and Thoria Rare-Earth Ceramics, US Patent 3,640,887.
- Apetz, R., van Bruggen, M.P.B., 2003. Transparent alumina: A light-scattering model. *J. Am. Ceram. Soc.* 3, 480–486.
- Barsoum, M.W., 2003. *Fundamentals of Ceramics*. NY: Taylor and Francis, pp. 356–380.
- Bass, M.J., 1995. *Handbook of Optics, Fundamentals, Techniques, & Design*, vol. I. McGraw-Hill.
- Bayya, S., Villalobos, G.R., Hunt, M.P., *et al.*, 2013. Development of transparent polycrystalline beta-silicon carbide. *Proc. SPIE* 88370S, 1–7.
- Bernard-Granger, G., Guizard, C., Monchalán, N., 2011. Sintering of an ultrapure α -alumina powder: II. mechanical, thermo-mechanical, optical properties and missile dome design. *Int. J. Appl. Ceram. Technol.* 8 (2), 366–382.
- Bertrand, A., Carreud, J., Chenu, S., *et al.*, 2016. Scalable and formable tellurite-based transparent ceramics for near infrared applications. *Adv. Opt. Mater.* 1–9. (201600230).
- Borysiewicz, M.A., 2019. ZnO as a functional material, a review. *Crystals* 9 (505).
- Boyer, M., Yang, X., Carrión, A.J.F., *et al.*, 2018. First transparent oxide ion conducting ceramics synthesized by full crystallization from glass. *J. Mat. Chem. A* 6 (13), 5276–5289.
- Bright, C., 2013. Transparent conductive thin films. In: Piegari, A., Flory, F. (Eds.), *Optical Thin Films and Coatings*. Woodhead Publishing.
- Budnikov, P.P., Belyaev, R.A., 1960. Beryllium oxide and its properties (Russian). *Zhur. Priklad. Khim* 33.
- Burke, J.E., 1996. Lucalox alumina: The ceramic that revolutionized outdoor lighting. *MRS Bull.* 61–68.
- Burnett, J.H., Kaplan, S.G., Shirley, E.L., *et al.*, 2005. High-index materials for 193 nm immersion lithography. In: *Proceedings of the 2nd International Symposium on Immersion Lithography*. Bruges, Belgium.
- Cao, G.Z., Metselaar, R., 1990. α -sialon ceramics: A review. *Chem. Mater.* 3 (2), 242–252.
- Cao, S., Gao, F., Xu, J., *et al.*, 2019. Photochromic effect of transparent lead-free ferroelectric $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ ceramics. *J. Eur. Ceram. Soc.* 39, 5260–5266.
- Chai, Q., Yang, D., Zhao, X., Chao, X., Yang, Z., 2017. Lead-free $(\text{K},\text{Na})\text{NbO}_3$ -based ceramics with high optical transparency and large energy storage ability. *J. Am. Ceram. Soc.* 101 (6).
- Chain, E.E., 1991. Optical properties of vanadium dioxide and vanadium pentoxide thin films. *Appl. Opt.* 30 (19), 2782–2787.
- Chen, D., Jordan, E.H., Gell, M., 2008. Pressureless sintering of translucent MgO ceramics. *Scr. Mater.* 59, 757–759.
- Chen, S., Wu, Y., Yang, Y., 2013. Spark plasma sintering of hexagonal structure Yb^{3+} -doped $\text{Sr}_5(\text{PO}_4)_3\text{F}$ transparent ceramics. *J. Am. Ceram. Soc.* 96 (6), 1694–1697.
- Chen, X., Wu, Y., 2019. High-entropy transparent fluoride laser ceramics. *J. Am. Ceram. Soc.* 1–7.
- Cherepy, N.J., Kuntz, J.D., Tillotson, T.M., *et al.*, 2007. Cerium-doped single crystal and transparent ceramic lutetium aluminum garnet scintillators. *Nucl. Inst. Meth. Phys. Res. A* 579, 38–41.
- Cherepy, N.J., Payne, S.A., Sturm, B.W., *et al.*, 2011. Performance of Europium-Doped Strontium Iodide, Transparent Ceramics and Bismuth-Loaded Polymer Scintillators, LLNL-PROC-497351. Lawrence Livermore National Laboratory.
- Crouch, I.G., Franks, G.V., Tallon, C., Thomas, S., Naebe, M., 2017. Glasses and ceramics. In *The Science of Armor Materials*. Elsevier.
- Destefani, J., 2013. Companies race to scale up spinel for armor, optical applications. In *Ceramic Tech Today*. The American Ceramic Society. Available at: www.ceramics.org
- Dobrovinskaya, E.R., Lytvynov, L.A., Pishchik, V., 2009. *Sapphire: Material, Manufacturing, Applications*. New York: Springer.
- Dobrowolski, J.A., 1995. Optical properties of films and coatings. In: Bass, M. (Ed.), *Handbook of Optics: Fundamentals, Techniques, and Design*, Vol. I. McGraw-Hill Inc.
- Dupuy, A.D., Kadera, K., Garay, J.E., 2016. Unprecedented electro-optic performance in lead-free transparent ceramics. *Adv. Mater.* 1–8. (201600947).
- Elliott, D.J., 1995. *Ultraviolet Laser Technology and Applications*. San Diego, CA: Academic Press Inc.
- Evans, J., 2020. *The History of Synthetic Ruby*. vol. 16. *Lustre Gemmology*.
- Fox, M., 2001. *Optical Properties of Solids*. Oxford University Press.
- Furuse, H., Yasuhara, R., 2017. Magneto-optical characteristics of holmium oxide (Ho_2O_3) ceramics. *Opt. Mater. Express* 7 (3).
- Furuse, H., Horiuchi, N., Kim, B.-N., 2019. Transparent non-cubic laser ceramics with fine microstructure. *Sci. Rep.* 9, 10300.
- Gagliardi, M., 2017. Transparent ceramics. *Am. Ceram. Soc. Bull.* 96 (6), 12. (ACerS).
- Gatti, A., 1969. Development of a Process for Producing Transparent Spinel Bodies, Final Report: Contract N00019-69-C-0133. General Electric Co.
- Gemmological Institute of America, 1995. *GIA Gem Reference Guide*.
- Gerhardt, R., 2011. Properties and Applications of Silicon Carbide. *Intech*. pp. 361–388.
- Gibson, D.R., Waddell, E.M., Wilson, S.A.D., Lewis, K.L., 1994. Ultra-durable phosphide-based antireflective coatings for sand and rain erosion protection. *Opt. Eng.* 33 (3).
- Gledhill, A.D., Li, D., Mroz, T., Goldman, L.M., Padture, N.P., 2012. Strengthening of transparent spinel/ Si_3N_4 nanocomposites. *Acta Mater.* 60, 1570–1575.
- Goela, J.S., 1998. CVD growth and characterization of β -SiC for IR windows. *Morton Advanced Materials*.
- Goldstein, A., Krell, A., 2016. Ceramics at 50: Progress made and further prospects. *J. Am. Ceram. Soc.* 99 (10), 3173–3197.
- Goldstein, A., Krell, A., Burshtein, Z., 2020. *Transparent Ceramics: Materials, Engineering, and Applications*. John Wiley & Sons.
- Goldstein, A., Yeshurun, Y., Vulfson, M., Kravits, H., 2012. Fabrication of transparent ZnAl_2O_4 – A new optical bulk ceramic. *J. Am. Ceram. Soc.* 95, 879–882.
- Greskovich, C., Duclos, S., 1997. Ceramic scintillators. *Annu. Rev. Mater. Sci.* 27, 69–88.
- Haertling, G.H., 1999. Ferroelectric ceramics: History and technology. *J. Am. Ceram. Soc.* 82, 797–818.
- Hannink, R.H.J., Kelly, P.M., Muddle, B.C., 2000. Transformation toughening in zirconia-containing ceramics. *J. Am. Ceram. Soc.* 83, 641–687.
- Harris, D.C., 1998. Durable 3–5 μm transmitting infrared window materials. *Infrared Phys. Technol.* 39, 185–201.
- Harris, D.C., 1999. *Materials for Infrared Windows and Domes: Properties and Performance*. SPIE Optical Engineering Press.
- Harris, D.C., Cambrea, L.R., Johnson, L.F., *et al.*, 2013. Properties of an infrared-transparent $\text{MgO}:\text{Y}_2\text{O}_3$ nanocomposite. *J. Am. Ceram. Soc.* 96 (12), 3828–3835.
- Harris, D.C., 2002. Review of Navy Program to Develop Optical Quality Diamond Windows and Domes, Naval Air Systems Command Report.
- Hatch, S.E., Parsons, W.F., Weagley, R.J., 1964. Hot-pressed polycrystalline $\text{CaF}_2:\text{Dy}^{2+}$ laser. *Appl. Phys. Lett.* 5 (8), 153–154.

- Hogan, P., Stefanik, T., Wilingham, C., Gentilman, R., 2004. Transparent yttria for IR windows and domes – Past and present. In: Proceedings of the 10th DoD Electromagnetic Windows Symposium, Norfolk, VA.
- Honma, T., Kuroki, Y., Okamoto, T., *et al.*, 2008. Transmittance and cathodoluminescence of AlN ceramics sintered with $\text{Ca}_3\text{Al}_2\text{O}_6$ as sintering additive. *Ceram. Int.* 34, 943–946.
- Hu, C.Q., Zheng, W.T., Li, J.J., *et al.*, 2006. $\text{Ge}_{1-x}\text{C}_x$ double-layer antireflection and protection coatings. *Appl. Surf. Sci.* 252, 8135–8138.
- Hushur, A., Manghnani, M.H., Werheit, H., 2016. High-pressure phase transition makes $\text{B}_{4.3}\text{C}$ boron carbide a wide-gap semiconductor. *J. Phys. Condens. Matter.* 28 (4), 045403.
- Hutzler, T., Krell, A., 2013. MgO – Transparent Ceramics with High Thermal Conductivity. Available at: www.ikts.fraunhofer.de, accessed 2020.
- Inoue, K., Hirosaki, N., Xie, R.-J., Takeda, T., 2009. Highly efficient and thermally stable blue-emitting $\text{AlN}:\text{Eu}^{2+}$ phosphor for ultraviolet white light-emitting diodes. *J. Phys. Chem. C* 113, 9392–9397.
- Ioffe Database, 2020. AlN – Aluminium Nitride. Sankt-Petersburg: A. F. Ioffe Institute, Russian Federation.
- Itatani, K., Tsujimoto, T., Kishimoto, A., 2006. Thermal and optical properties of transparent magnesium oxide ceramics fabricated by post hot-isostatic pressing. *J. Eur. Ceram. Soc.* 26, 639–645.
- Ivanovskii, A.L., Shein, I.R., Makurin, Y.N., Kiiko, V.S., Gorbunova, M.A., 2009. Electronic structure and properties of beryllium oxide. *Inorg. Mater.* 45 (3), 223–234.
- Jack, K.H., 1976. Review: Sialons and related nitrogen ceramics. *J. Mater. Sci.* 2, 1135–1158.
- Janek, J., Korte, C., 1999. Electrochemical blackening of yttria-stabilized zirconia – Morphological instability of the moving reaction front. *Solid State Ion.* 116, 181–195.
- Jin, L., Zhou, G., Shimai, S., Zhang, J., Wang, S., 2010. ZrO_2 -doped Y_2O_3 transparent ceramics via slip casting and vacuum sintering. *J. Eur. Ceram. Soc.* 30, 2139–2143.
- Jones, M.I., Hyuga, H., Hirao, K., 2003. Optical and mechanical properties of α/β composite sialons. *J. Am. Ceram. Soc.* 86 (3), 520–522.
- Jones, M.I., Hyuga, H., Hirao, K., Yamauchi, Y., 2004. Highly transparent Lu- α -SIALON. *J. Am. Ceram. Soc.* 97 (4), 714–716.
- Joshi, B., Kshetri, Y.K., Adhikari, R., Lee, S.W., 2015. IR to visible upconversion luminescence of transparent (Mg,Er)- α -sialon ceramics. *Ceram. Int.* 41, 6455–6462.
- Jung, W.K., Ma, H.J., Kim, H.-N., Kim, D.K., 2018. Transparent ceramics for visible/IR windows: Processing, materials and characterization. *Korean J. Mater. Res.* 28 (10).
- Kamzina, L.S., Wei, R., Li, G., Zeng, J., Ding, A., 2010. Electro-optical properties of PMN-xPT compounds: Single crystals and transparent ferroelectric ceramics. *Phys. Sol. State* 52 (10), 2142–2146.
- Kang, J.S., Wu, H., Hu, Y., 2017. Thermal properties and phonon spectral characterization of synthetic boron phosphide for high thermal conductivity applications. *Nano Lett.* 17, 7507–7514.
- Kiido, V.S., Dimitriev, I.A., Makurin, Y.N., Sofronov, A.A., Ivanovskii, A.L., 2003. Synthesis and application of transparent beryllium ceramics. *Glass Phys. Chem.* 30 (1), 109–111.
- Kim, B.-N., Horiuchi, N., Dash, A., *et al.*, 2017. Spark plasma sintering of highly transparent hydroxyapatite ceramics. *J. Jpn. Soc. Powder Metall.* 64 (10), 547–551.
- Kimoto, T., Cooper, J.A., 2014. Fundamentals of Silicon Carbide Technology: Growth, Characterization, Devices, and Applications. John Wiley & Sons. pp. 11–33.
- Kong, L.B., Huang, Y., Que, W., *et al.*, 2015. Transparent ceramics. In: Bergmann, C.P. (Ed.), Topics in Mining, Metallurgy and Materials Engineering. Springer.
- Krell, A., Klimke, J., 2006. Effects of the homogeneity of particle coordination on solid-state sintering of transparent alumina. *J. Am. Ceram. Soc.* 89, 1985–1992.
- Krell, A., Blank, P., Ma, H., *et al.*, 2004. Transparent sintered corundum with high hardness and strength. *J. Am. Ceram. Soc.* 86, 12–18.
- Krell, A., Hutzler, T., Klimke, J., 2009a. Transmission physics and consequences for materials selection, manufacturing, and applications. *J. Eur. Ceram. Soc.* 201–207.
- Krell, A., Klimke, J., Hutzler, T., 2009c. Transparent compact ceramics: Inherent physical issues. *Opt. Mater.* 31, 1114–1150.
- Krell, A., Blank, P., Ma, H., Hutzler, T., Nebelung, M., 2003. Processing of high-density submicrometer Al_2O_3 for new applications. *J. Am. Ceram. Soc.* 86 (4), 546–553.
- Kshetri, Y.K., Joshi, B., Lee, S.W., 2016. Intense visible upconversion emission in transparent (Ho^{3+} , Er^{3+})- α -sialon ceramics under 980 nm laser excitation. *J. Eur. Ceram. Soc.* 36.
- Kulik, E., Nishiyama, N., Higo, Y., Gaida, N.A., Katsura, T., 2018. Hardness of polycrystalline SiO_2 coesite. *J. Am. Ceram. Soc. Rapid Commun.* 102, 2251–2256.
- Kumar, R.S., Johnson, R., 2016. Aqueous slip casting of transparent aluminum oxynitride. *J. Am. Ceram. Soc.* 99 (10), 3320–3325.
- Kurlow, V., 2016. Sapphire: Properties, growth, and applications. In Reference Module in Materials Science and Materials Engineering. Elsevier. pp. 1–11.
- Kwon, O.-H., Nordahl, C.S., Messing, G.L., 1995. Submicrometer transparent alumina by sinter forging seeded γ - Al_2O_3 powders. *J. Am. Ceram. Soc.* 78 (2), 491–494.
- Lee, C.-C., Kuo, C.-C., 2013. Optical coatings for displays and lighting. In: Piegari, A., Flory, F. (Eds.), Optical Thin Films and Coatings. Woodhead Publishing.
- Levinson, L.M. (Ed.), 1987. Electronic Ceramics: Properties, Devices and Applications. Marcel Dekker.
- Lewis, B.G., Paine, D.C., 2000. Applications and processing of transparent conducting oxides. *MRS Bulletin* 25, 22–27.
- Li, J.-G., Ikegami, T., Mori, T., 2005. Fabrication of transparent, sintered Sc_2O_3 ceramics. *J. Am. Ceram. Soc.* 88 (4), 817–821.
- Li, P., Wang, H., Gui, L., *et al.*, 2015. A transparent and tough β - Si_3N_4 ceramic with a whiskery microstructure. *Key Eng. Mater.* 655, 1–5.
- Li, X., Liu, Q., Jiang, N., *et al.*, 2019. Fabrication and characterizations of highly transparent $\text{Tb}_3\text{Ga}_5\text{O}_{12}$ magneto-optical ceramics. *Opt. Mater.* 88, 238–243.
- Liu, G., Zhou, Z., Fei, F., *et al.*, 2013. Hard antireflective films of SiAlON for zinc sulfide in 3–5 μm regions. *Infrared Phys. Technol.* 60, 118–120.
- Liu, P., Yi, H., Zhou, G., Zhang, J., Wang, S., 2015. HIP and pressureless sintering of transparent alumina shaped by magnetic field assisted slip casting. *Opt. Mater. Expr.* 5 (2), 441–446.
- Lupei, A., 2016. YAG at its 50th anniversary: Still to learn. *J. Lumin.* 169 (Part B), 426–439.
- Maiman, T.H., 1960. Stimulated optical radiation in ruby. *Nature* 187, 493–494.
- Mandal, H., 1999. New developments in α - SiAlON ceramics. *J. Eur. Ceram. Soc.* 19, 2349–2357.
- Mao, X., Wang, S., Shimai, S., Guo, J., 2008. Transparent polycrystalline alumina ceramics with oriented optical axes. *J. Am. Ceram. Soc.* 91 (10), 3431–3433.
- Mazzolini, P., Gondoni, P., Russo, V., *et al.*, 2015. Tuning of electrical and optical properties of highly conducting and transparent Ta-doped TiO_2 polycrystalline films. *J. Phys. Chem. C* 119 (13), 6988–6997.
- McCauley, J.W., Corbin, N.D., 1980. Transparent, Polycrystalline Cubic Aluminum Oxide, AMMRC MS 80-7. Watertown, MA: Army Materials and Mechanics Research Center.
- McCauley, J.W., Patel, P., Chen, M., *et al.*, 2009. AlON: A brief history of its emergence and evolution. *J. Eur. Ceram. Soc.* 29, 223–236.
- McCloy, J., 2007. International development of chemical vapor deposited zinc sulfide. In: Tutison, R.W. (Ed.), Proceedings of SPIE, vol. 6545, Window and Dome Technologies and Materials X.
- Mitomo, M., Moriyoshi, Y., Sakai, T., Ohasaka, T., Kobayashi, M., 1982. Translucent β - SiAlON ceramics. *J. Mater. Sci. Lett.* 1, 25–26.
- Monaghan, B.C., Morrison, A.D., Waddell, E.M., *et al.*, 1992. Boron Phosphide IR Coatings. 10261. SPIE.
- Mondal, S., Bykova, E., Day, S., *et al.*, 2015. Disorder and defects are not intrinsic to boron carbide. *Sci. Rep.* 6, 19330.
- Mroz, T.M., Hartnett, T.M., Wahl, J.M., *et al.*, 2005. Recent advances in spinel optical ceramic, defense and security. In: Proceedings of the Window and Dome Technologies and Materials IX, vol. 5786, Orlando, FL: Proc. of SPIE.
- Naftaly, M., Molly, J.F., Magnusson, B., Andreev, Y.M., Lanski, G.V., 2016. Silicon carbide – A high-transparency nonlinear material for THz applications. *Opt. Expr.* 24 (3), 1–8.
- Nishiyama, N., Ishikawa, R., Ohfuji, H., *et al.*, 2017. Transparent polycrystalline cubic silicon nitride. *Sci. Rep.* 7 (44755), 1–8.
- Oparina, I.B., Kolmakov, A.G., Sevost'yanov, M.A., Lysenkov, A.S., 2019. Production of optically transparent shock-resisting ceramics by the methods of powder metallurgy (review). *Inorg. Mater. Appl. Res.* 10 (4), 825–835.
- Optical Products Factory LLC, 2020. ZnS Products. Available at: www.optics.spb.ru, accessed 2020.
- Pasquarelli, R.M., Ginley, D.S., O'Hayre, R., 2011. Solution processing of transparent conductors: From flask to film. *Chem. Soc. Rev.* 240, 5406–5441.
- Patel, P.J., Gilde, G.A., Dehmer, P.G., McCauley, J.W., 2000. Transparent ceramics for armor and EM window applications. In: Marker III, A.J., Arthurs, E.G. (Eds.), Proceedings of the SPIE Inorganic Optical Materials II, vol. 4102, pp. 1–14.

- Ren, L., Fu, Z., Wang, Y., *et al.*, 2015. Fabrication of transparent mullite ceramic by spark plasma sintering from powders synthesized via sol-gel process combined with pulse current. *Heat. Mater. Des.* 83, 753–759.
- Rubat du Merac, M., Bram, M., Malzbender, J., *et al.*, 2018. Increasing fracture toughness and transmittance of transparent ceramics using functional low-thermal expansion coatings. *Sci. Rep.* 8, 15644.
- Rubat du Merac, M., Kleebe, H.-J., Müller, M.M., Reimanis, I.E., 2013. Fifty years of research and development coming to fruition; unravelling the complex interactions during processing of transparent magnesium aluminate (MgAl_2O_4) spinel. *J. Am. Ceram. Soc.* 96 (11), 3341–3365.
- Saghir, K.A., 2014. Transparent Ceramics by Full Crystallization From Glass: Application to Strontium Aluminosilicates (PhD Thesis). Université d'Orléans.
- Saint-Gobain S.A., 2020. Synthetic Sapphire Products. Available at: www.saint-gobain.com, accessed 2020.
- Saleh, B.E.A., Teich, M.C., 1991. *Fundamentals of Photonics*. John Wiley & Sons Inc.
- Sanghera, J., Kim, W., Villalobos, G., *et al.*, 2012. Ceramic laser materials. *Materials* 5, 258–278.
- Savage, J.A., 1991. Preparation and properties of hard crystalline materials for optical applications – A review. *J. Cryst. Growth* 113, 698–715.
- Scott, H.G., 1975. Phase relationships in the zirconia-yttria system. *J. Mat. Sci.* 10, 1527–1535.
- Shen, Y., Chen, R., Gurzadyan, G.G., *et al.*, 2012. Fabrication and spectroscopic characterization of Ce^{3+} doped $\text{Sr}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2$ translucent ceramics. *Opt. Mater.* 34, 1155–1160.
- Silva, D.D., Boccaccini, A.R., 2008. Industrial developments in the field of optically transparent inorganic materials: A survey of recent patents. *Recent Patents Mater. Sci.* 1, 56–73.
- Simeone, D., Baldinozzi, G., Gosset, D., *et al.*, 2003. Monoclinic to tetragonal semireconstructive phase transition of zirconia. *Phys. Rev. B* 67, 1–8.
- Snetkov, I.L., Permin, D.A., Balabanov, S.S., Palashov, O.V., 2016. Wavelength dependence of verdet constant of $\text{Tb}^{3+}:\text{Y}_2\text{O}_3$ ceramics. *Appl. Phys. Lett.* 108 (161905), 1–3.
- Sorokin, P.P., Stevenson, M.J., 1960. Stimulated infrared emission from trivalent uranium. *Phys. Rev. Lett.* 5 (12), 557–559.
- Standard, O.C., Sorrell, C.C., 1998. Densification of zirconia – Conventional methods. *Key Eng. Mater.* 153–154, 251–300.
- Stevenson, A.J., Serier-Brault, H., Gredin, P., Mortier, M., 2011. Fluoride materials for optical applications: Single crystals, ceramics, glasses, and glass-ceramics. *J. Fluor. Chem.* 132, 1165–1173.
- Subramanian, M.A., Aravamudan, G., Subba Rao, G.V., 1983. Oxide pyrochlores – A review. *Prog. Solid State Chem.* 15, 55–143.
- Surmet Corp., 2020. MgAl_2O_4 and AION Products. Available at: www.surmet.com, accessed 2020.
- Tian, Y., Xu, B., Yu, D., *et al.*, 2013. Ultrahard nanotwinned cubic boron nitride. *Nature* 493 (11728), 385–388.
- Tropf, W.J., Thomas, M.E., Harris, T.J., 1995. Chapter 33. Properties of crystals and glasses, part IV. In: Bass, M. (Ed.), *Handbook of Optics, Devices, Measurements, & Properties*, second ed. McGraw-Hill, Inc.
- Tropf, W.J., Harris, T.J., Thomas, M.E., 2000. *Electro-Optics Handbook*, second ed. McGraw-Hill.
- Uchino, K., 2000. *Ferroelectric Devices*. Marcel Dekker.
- Uematsu, K., Takagi, M., Honda, T., Uchida, N., Saito, K., 1989. Transparent hydroxyapatite prepared by hot isostatic pressing of filter cake. *J. Am. Ceram. Soc.* 72 (8), 1476–1478.
- Van Damme, N.S., Sutherland, A.E., Jones, L., Bridger, K., Winzer, S.R., 1991. Fabrication of optically transparent and electrooptic strontium barium niobate ceramics. *J. Am. Ceram. Soc.* 74 (8), 1785–1792.
- Vasylechko, L., Senyshyn, A., Bismayer, U., 2009. Perovskite-type aluminates and gallates. In: Gschneider Jr., K.A., Bünzli, J.-C.G., Pecharsky, V.K. (Eds.), *Handbook on the Physics and Chemistry of Rare Earths* 39. Elsevier.
- Wang, J., Zhang, L., Chen, D., Jordan, E.H., Gell, M., 2012. $\text{Y}_2\text{O}_3\text{-MgO-ZrO}_2$ infrared transparent ceramic nanocomposites. *J. Am. Ceram. Soc.* 95 (3), 1033–1037.
- Wang, S.F., Zhang, J., Luo, D.W., *et al.*, 2013. Transparent ceramics: Processing, materials and applications. *Prog. Solid State Chem.* 41, 20–54.
- Wang, Z., Zhou, G., Jiang, D., Wang, S., 2018. Recent development of $\text{A}_2\text{B}_2\text{O}_7$ system transparent ceramics. *J. Adv. Ceram.* 7 (4), 289–306.
- Weber, M., 2003. *Handbook of Optical Materials*. CRC Press.
- Xiao, Z., Yu, S., Li, Y., *et al.*, 2019. Materials development and potential applications of transparent ceramics: A review. *Mater. Sci. Eng. R* 139.
- Xie, R.-J., Hintzen, H.T., 2013a. Optical properties of (oxy)nitride materials: A review. *J. Am. Ceram. Soc.* 96 (3), 665–687.
- Xie, R.-J., Mitomo, M., Hirosaki, N., 2013b. Ceramic lighting. In: Riedel, R., Chen, J.-W. (Eds.), *Ceramics Science and Technology: Applications*, first ed., vol. 4. Wiley.
- Xiong, Y., Fu, Z.Y., Wang, H., *et al.*, 2008. Microstructure and properties of translucent Mg-SiAlON ceramics prepared by spark-plasma sintering. *Mater. Sci. Eng. A* 488, 475–481.
- Yang, W., Hojo, J., Enomoto, N., Tanaka, Y., Inada, M., 2013. Influence of sintering aid on the translucency of spark-plasma-sintered silicon nitride ceramics. *J. Am. Ceram. Soc.* 96 (8), 2256–2261.
- Zeeman, H.D., DiBianca, F.A., Lovhoiden, G., 1995. High-resolution X-ray imaging with a $\text{Gd}_2\text{O}_3(\text{Eu})$ transparent ceramic scintillator. In: *Proceedings of SPIE, Physics of Medical Imaging*, vol. 2432.

Geopolymers and Geopolymer-Derived Composites

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Introduction

Geopolymers are polysilicate-aluminate, inorganic polymers or chemically bonded ceramics made under highly alkaline (NaOH, KOH, CsOH) or highly acidic (H_3PO_4) conditions. (Davidovits, 1982, 1988, 1991, 2020; Barbosa *et al.*, 2000; Barbosa and MacKenzie, 2003; Duxson *et al.*, 2005; Kriven *et al.*, 2003; Kriven, 2010, 2018; Kriven *et al.*, 2007a,b). The alkali-based geopolymers have been reasonably well studied over the past twenty years, while the acid-derived polymers are the subject of more recent study. The alkali-based composition is centered around the stoichiometric composition $\text{M}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 11\text{H}_2\text{O}$ where M is a Group I alkaline element in the Periodic Table. The number of water molecules varies depending on the desired viscosity and the particle size and specific surface area of the starting aluminosilicate powder. Acid-based geopolymers are centered around the composition $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{P}_2\text{O}_5$ and do not contain free charge-balancing cations. These are sometimes referred to as di silico-alumino-phosphates, silico-alumino-phosphates or “SAPs” and their atomic structure consists of covalently bonded SiO_4 , AlO_4^- and PO_4 tetrahedra.

Geopolymers can be thought of as a refractory “glue” which binds various filler phases or reinforcements together to form structural composites that can be scaled up to large sizes without the need for firing. Since the geopolymer reaction takes place during high shear and under ambient conditions in aqueous solution or as a paste containing filler phases, the reinforcements can be traditional particulates, chopped fibers, unidirectional or woven fibers of ceramics as well as of polymers, metals or biological reinforcements. The fabrication of geopolymer composites can be readily scaled up or additively manufactured into large bodies due to their ambient setting conditions.

The properties of alkali activated geopolymer (GP) from metakaolin have been compared with those of Ordinary Portland Cement (OPC) by Davidovits (2020) and Kriven (2018). The synthesis of GP releases only 25% of the carbon dioxide that the synthesis of OPC which releases ~ 0.95 tons of CO_2 per ton of cement manufactured. However, the intrinsic compressive strength of geopolymer composites (GPC) is almost double that of OPC (100–120 MPa) as compared to ~ 60 MPa for OPC composites. The flexural strength of GPCs are at least 2–5 times stronger than that of OPC composites, while the density of geopolymers is of the order of 1.5 g/cc which is half that of OPC. A significant advantage of GPC is that their setting time to achieve full strength is 1–3 days as compared to 28 days for OPC.

Since geopolymers consist of nanoparticulate and nano-porous bodies under ambient temperatures, the self-assembled nanoparticles result in nano diffusion path lengths, which open the way to the synthesis of ultra-high temperature ceramics, via lower energy pathways than are currently being used. While geopolymer composites are made under ambient conditions, alkali activated, metakaolin-based geopolymers are able to withstand high temperatures up to $\sim 1000^\circ\text{C}$, whereupon they crystallize and convert into a polycrystalline ceramic. Depending on the charge-balancing cation composition the resulting crystallized ceramic exhibits a range of tailorable thermal expansion coefficients, opening up the possibilities for their application as thermal barrier coatings on metals or on other ceramics to which they may adhere. As a refractory glue of tailorable thermal expansions, alkali-based geopolymers can act as adhesives and join ceramic and metals with minimal stresses upon heating.

The loss in mechanical properties resulting from dehydration and microcracking at ~ 250 – 400°C , as well as crystallization at $\sim 1000^\circ\text{C}$, can be counterbalanced by “self-healing” of the composite with the inclusion of a glass frit which melts and flows into the matrix, restoring some of the mechanical properties up to the melting temperature of the glass. This leads to the introduction of amorphous self-healed geopolymer (ASH-G) or amorphous self-healed ceramics (ASH-C). Thus, geopolymers are a new generation of inorganic polymers that are made under ambient temperatures, like a polymer or cement, but can have the eventual high temperature properties of a ceramic.

Metakaolin-Based, Alkali-Activated Geopolymers

The alkali-based geopolymers have a solid solution range which can be approximated by the formula $\text{M}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 11\text{H}_2\text{O}$ where M is a group I element, such as Na, K, Cs. Traditionally this composition has been chosen, because for K or Cs, high temperature heat treatment to $\sim 1000^\circ\text{C}$ would lead to crystallization into a single phase, stoichiometric compound, rather than into a mixture of ceramic plus glass, which occurs when the formulation deviates from this stoichiometry, according to their corresponding phase diagrams. In the case of $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 11\text{H}_2\text{O}$ leucite starts to crystallize at 950°C and melts at 1693°C (Bell *et al.*, 2008b, 2009b). The composition $\text{Cs}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ crystallizes at 1050°C into pollucite which melts at 1940°C (Bell *et al.*, 2008a, 2009a). In the case of sodium, the geopolymer crystallizes into glass plus nepheline ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) which melts at 700°C (after forming at 1000°C). The $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ analog does not form under ambient pressures but it requires a geological pressure of 1.7 GPa and 1250°C to form jadeite, the toughest mineral known. The amount of water is variable, depending on the particle size and specific surface area of the aluminosilicate starting material, as well as the desired viscosity and workability of the paste. It is released during heating at ~ 250 – 400°C .

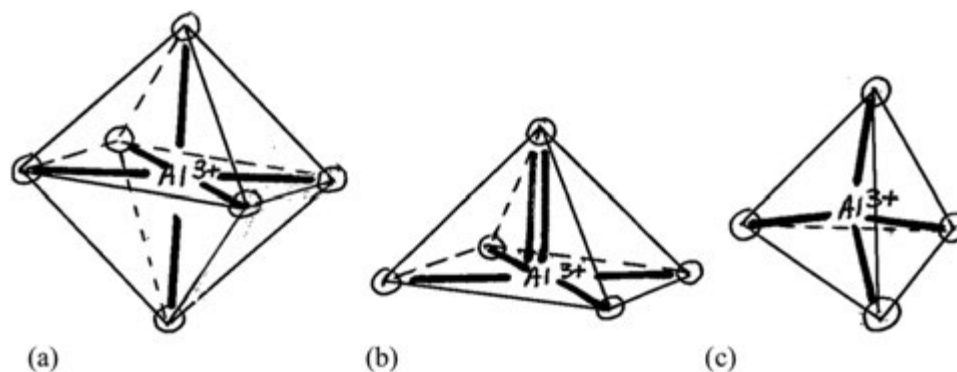


Fig. 1 Dissolution of the aluminosilicate source (e.g., metakaolin, $\text{Al}_2\text{O}_3 \bullet 2\text{SiO}_2 \bullet 2\text{H}_2\text{O}$) is due to dehydration of crystalline kaolinite (a) where the Al^{3+} is in 6-fold octahedral coordination, to decompose into amorphous metakaolin (b) where a highly strained 5-fold coordinated Al^{3+} polyhedron forms a double bond with oxygen. Upon dissolution in waterglass, a regular AlO_4^- tetrahedron (c) springs into existence and is ready to polymerize in 3D with silicate tetrahedra.

Alkali-based geopolymers are refractory, inorganic polymers formed from both aluminum and silicon sources containing AlO_4^- and SiO_4 tetrahedral units and set under highly alkaline conditions (e.g., NaOH, KOH, CsOH) at ambient temperatures (Davidovits, 1982, 1988, 1991, 2020; Barbosa *et al.*, 2000; Barbosa and MacKenzie, 2003; Kriven *et al.*, 2003, 2005, 2007a,b; Kriven, 2010; 2018; Duxson *et al.*, 2005, 2007; Sa Ribeiro *et al.*, 2017). In materials science, geopolymers are made from kaolinite clay of composition $\text{Al}_2\text{O}_3 \bullet 2\text{SiO}_2 \bullet 2\text{H}_2\text{O}$ which is heated at $\sim 750^\circ\text{C}$ for 2 h and converted to amorphous metakaolin ($\text{Al}_2\text{O}_3 \bullet 2\text{SiO}_2$). Geopolymers can also be formed from other aluminosilicate clays such as bentonite, laterite or halloysite, the latter being basically nanotubular kaolinite (Barbosa *et al.*, 2000; Barbosa and MacKenzie, 2003). When mixed under high shear with the waterglass solution (e.g., of composition $\text{M}_2\text{O} \bullet 2\text{SiO}_2 \bullet 11\text{H}_2\text{O}$), it undergoes dissolution, polycondensation and precipitation reactions under ambient conditions to form a geopolymer solid, where all the silicate and aluminate tetrahedra are corner-shared.

Geopolymers are a rigid, hydrated, alumino-silicate solid or gel containing group I, charge-balancing cations. The reason that these ceramic-like, aluminosilicates form under ambient temperatures is attributed to the highly strained state of the pentavalent AlO_5 molecule in the amorphous metakaolin, as illustrated in Fig. 1 (Kriven (2018)). The $\text{Al}=\text{O}$ double bond is susceptible to attack by the highly concentrated alkali solution which constitutes the rate determining step. Upon dissolution of the aluminosilicate source, tetrahedra of AlO_4^- and SiO_2 form in solution and polymerize to form the 3D bonded aluminosilicate, where the AlO_4^- is charge balanced by nearby Group I cations of Na^+ , K^+ , or Cs^+ surrounded by waters of solvation.

The currently accepted molecular structure of geopolymers is represented in Fig. 2, taken from Barbosa *et al.* (2000), Barbosa and MacKenzie (2003). In magic angle spinning, nuclear magnetic resonance (MAS NMR) it is seen that the silicate and aluminate (AlO_4^-) tetrahedra share all four of their corners with each other, forming $\text{Si}-\text{O}-\text{Si}$ or $\text{Si}-\text{O}-\text{Al}$ bonds, corresponding to the Q^4 notation used in NMR (MacKenzie and Smith, 2002). They form in an amorphous, cross-linked, impervious, acid-resistant, 3-D structure and their microstructure, as seen by high resolution TEM in Fig. 3, is nanoparticulate ($\sim 20\text{--}40\text{ nm}$) and nanoporous ($\sim 6.8\text{ nm}$ diameter) (Kriven, 2018). The intrinsic mechanical properties of metakaolin-based, alkali activated geopolymers have been measured and summarized (Cho, 2015; Kriven, 2018) and theoretically predicted (Akono *et al.*, 2019).

The intrinsic mechanical properties of geopolymers derived from BASF Metamax® metakaolin were systematically studied by several workers, as reviewed by Kriven (2018) and analyzed in terms of Weibull statistics (Weibull, 1951). The intrinsic mechanical properties of single-phase, potassium-based geopolymers (KGP) made from BASF metakaolin are summarized in Table 1. Some of these properties have also been predicted by Akono *et al.* (2019).

Metakaolin-Based, Acid-Activated Geopolymers

Metakaolin can be reacted with concentrated phosphoric acid (H_3PO_4) and converted into an alumino disilicate phosphate geopolymer. Chemically, the inorganic polymer consists of tetrahedra of silica, alumina and phosphate (PO_4), without the need for charge balancing cations. A confirmed composition is $\text{Al}_2\text{O}_3 \bullet 2\text{SiO}_2 \bullet \text{PO}_4$ in a 1:2:1 molar or 1:1:1 atomic cation ratio, and is also called a "SAP". These inorganic polymers having been gaining interest in the past few years, (Perera *et al.*, 2008; Wagh, 2004; Prabakar *et al.*, 1991; Liu *et al.*, 2010; Cui *et al.*, 2011; Colorado *et al.*, 2011; Gualtieri *et al.*, 2015; He *et al.*, 2016; Douiri *et al.*, 2016; Tchakouté *et al.*, 2017; Wang *et al.*, 2017, 2019; Celerier *et al.*, 2018; Katsiki *et al.*, 2019; Mathivet *et al.*, 2019; Zribi *et al.*, 2019; Davidovits, 2020).

The aluminosilicate phosphate polymers are thought to have superior thermal stability, ionic conductivity, as well as higher compressive and flexural strengths compared to alkali activated, metakaolin-based geopolymers. Enhanced dielectric properties have been reported for this class of inorganic polymers (He *et al.*, 2016; Douiri *et al.*, 2016; Cui *et al.*, 2011). The aluminosilicate phosphates can be prepared from metakaolin, but have also been prepared from a sol-gel derived aluminosilicate. In this method, tetraethylorthosilicate (TEOS) is mixed with aluminum nitrate nonahydrate in ethanol, followed by drying at 100°C for

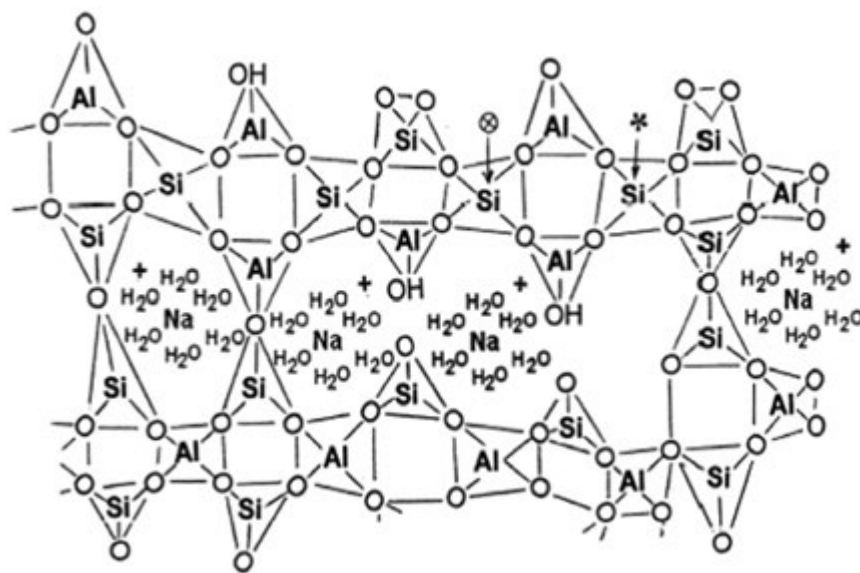


Fig. 2 Molecular structure of Na-based geopolymer where all tetrahedra share 4 corners (Q^4). From Barbosa, V.F.F., KacKenzie, K.J.D., Thaumaturgo, C., 2000. Synthesis and characterization of materials based on inorganic polymers of alumina and silica: Sodium polysialate polymers. *Int. J. Inorg. Mater.* 2 (4), 309–317. Barbosa, V.F.F., MacKenzie, K.J.D., 2003. Synthesis and thermal behavior of potassium sialate geopolymers. *Mater. Lett.* 57, 1477–1482.

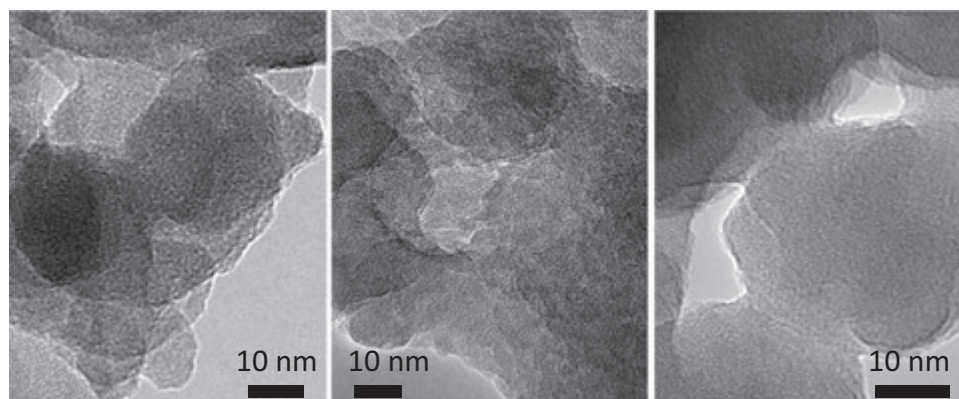


Fig. 3 High resolution transmission electron microscopy (HRTEM) micrographs of (a) NaGP, (b) KGP and (c) CsGP. From Kriven, W.M., 2018. Chapter 5.9 – Geopolymer-based composites. In: Beaumont, P.W.R., Zweben, C.H. (Eds.), *Comprehensive Composite Materials II*, vol. 5. Oxford: Academic Press, pp. 269–280.

24 h, and then calcining at 800°C for 2 h. Ball milled particles of this aluminosilicate of composition $Al_2O_3 \cdot 2SiO_2$ are reacted with 10 molar phosphoric acid (H_3PO_4) at RT and after ~ 1 day an aluminosilicate network is formed. When this sol gel derived polymer is heated slowly from 40 to 200°C however, phase separation occurs to form SiO_2 and aluminum phosphate ($AlPO_4$) (Morris *et al.*, 1977). The nature and stability of these product phases is not well understood at present.

Ground particles of SAPs that have been cured at room temperature for 6 months tended to be amorphous and featureless in the TEM (Fig. 4). This is unlike the TEM microstructure of alkali activated, metakaolin-based geopolymers seen in Fig. 3. When a SAP was cured at 50°C for 24 h followed by heat treatment at 140°C for a further 24 h, its microstructure as seen by SEM was nanoporous (Fig. 5) and contained submicron precipitates, presumably of submicron aluminum phosphate ($AlPO_4$) and phase separated silica (SiO_2) (Fig. 6). Further, more detailed studies are in progress.

Metakaolin-Based Geopolymers Versus Alkali Activated Cements From Slag and Fly Ash Waste Materials

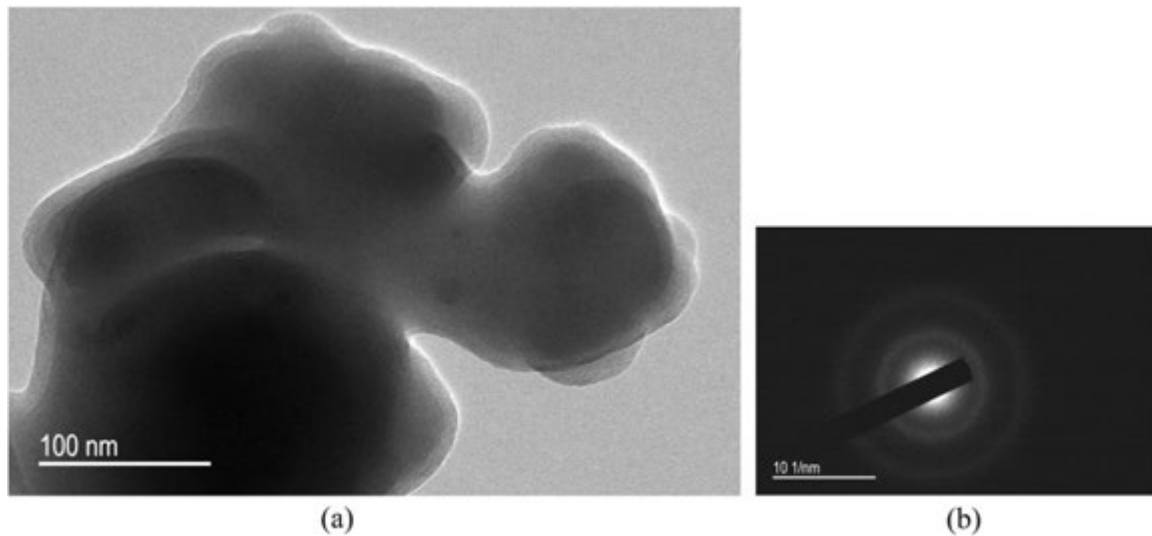
The term “geopolymer” has different meanings to different scientific communities. In the civil engineering community, the term “geopolymers” refers to the product resulting from high shear mixing of class F fly ash and ground granulated blast furnace slag

Table 1 Intrinsic mechanical properties of pure potassium-based geopolymer

Mechanical property (MPa)	Weibull parameters				
	Scale value (σ_0 , MPa)	# of samples	Shape (m)	Standard deviation (MPa)	95% CI (MPa)
Uniaxial compressive strength ^a	107.0	12	9.0	13.4	100.3–114.3
4-pt SENB flexure strength ^b	8.3	23	3.2	2.6	7.3–9.5
Biaxial tensile strength ^c	14.4	16	5.5	2.8	13.1–15.8
Fracture strength ^c	8.9	–	–	–	–
Fracture toughness ^d (MPa m ^{1/2})	0.14	–	–	–	–
Vickers Hardness	331 ± 24	–	–	–	–
Young's modulus ^e (GPa)	8.07	–	–	–	–
Shear modulus ^e (GPa)	3.36	–	–	–	–
Poisson's ratio ^e	0.20	–	–	–	–
Young's modulus ^f (GPa)	8.28	–	–	–	–
Shear modulus ^f (GPa)	3.61	–	–	–	–
Poisson's ratio ^f	0.15	–	–	–	–
Acoustic longitudinal wave (m/s) ^e	2497	–	–	–	–
Acoustic shear wave (ms) ^e	1603	–	–	–	–

^aMeasured according to ASTM C1424–10.^bMeasured in 4-point bending according to ASTM C78/C78M–10.^cMeasured by ring on ring method according to ASTM 1499–09 [1499–09 2009].^dMeasured in 4-point SENB according to ASTM5045.^eMeasured by the impulse excitation method, using Buzz-o-Sonic, BuzzMac, WI, according to ASTM 1876–07.^fMeasured by resonant ultrasound spectroscopy.

Note: Cho, S.-H., 2015. Geopolymer Composites and their Applications in Stress Wave Mitigation. Ph.D. Dissertation. Urbana, IL: University of Illinois at Urbana-Champaign. Department of Mechanical Science and Engineering. Kriven, W.M., 2018. Chapter 5.9 – Geopolymer-based composites. In: Beaumont, P.W.R., Zweben, C.H. (Eds.), Comprehensive Composite Materials II, vol. 5. Oxford: Academic Press, pp. 269–280.

**Fig. 4** TEM micrograph of aluminosilicate phosphate (SAP) made from a sol gel aluminosilicate precursor ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) cured at room temperature for 6 months (a), showing featureless, amorphous microstructure as seen by its amorphous diffraction pattern in the corresponding SAD pattern (b).

waste products. They are prepared under high shear mixing in the same way as are metakaolin-based, alkali-activated geopolymers. The solid is also amorphous or crystalline but it is based on the calcium silicate hydrate (CSH), calcium aluminosilicate hydrate i.e., C(A)SH, potassium aluminosilicate hydrate (KASH), and sodium aluminosilicate hydrate (i.e., NASH) (i.e., charge balanced with Na^+ or K^+ ions) binder phases, all of which are the binder phases in cements. They are made up of Q^2 and some Q^3 tetrahedral units and contain only minor amounts of Q^4 bonded tetrahedral units, if any. In the cements structure, the silicate or aluminate tetrahedra form layers sharing only two or sometimes three corners, and are separated by layers of $\text{Ca}(\text{OH})_2$ or CaO . CSH is the main binder phase in Portland cement (Sankar et al., 2017, 2019a,b). One main difference between the cements versus metakaolin-based geopolymers is that the metakaolin-based geopolymers are chemically stable up to $\sim 1000^\circ\text{C}$, after which they

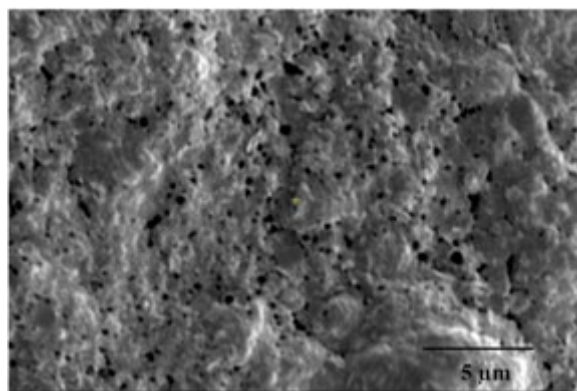


Fig. 5 SEM micrograph of alumino disilicate phosphate (SAP) (cured at 50°C/24 h followed by heat treatment at 140°C/24 h). Nanoporosity is evident.

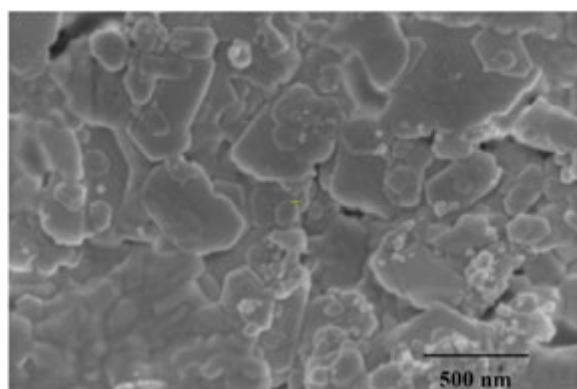


Fig. 6 SEM micrograph of submicron precipitates of alumino disilicate phosphate (SAP) that had been cured at 50°C/24 h followed by heat treatment at 140°C/24 h. Submicron precipitates assumed to be aluminum phosphate (AlPO_4) in a silicate matrix were observed.

crystallize into a polycrystalline ceramic. When composites are formed with metakaolin-based geopolymers, some mechanical strength can be still be retained. Cements, on the other hand, contain significantly more water and so steadily decompose with increasing temperature, losing most of their mechanical strength by 700°C.

The difference between the molecular structures of alkali activated cements versus geopolymers is illustrated in [Fig. 7](#). Calcium silicate hydrates in cement contain significantly more water than do geopolymers. Thus metakaolin-based geopolymers are made like a cement, except under higher shear than in cements, but can behave like a ceramic. Cements will always remain as mainly low temperature capable materials ([Fig. 8](#)). While cements can be 3D printed, geopolymers exhibit thixotropic rheology and so can also be 4D printed, with time as the 4th parameter.

Geopolymer Composites

Numerous metakaolin-based, alkali-activated geopolymer composites have been made and reported as summarized by [Davidovits \(2020\)](#) and [Kriven \(2018\)](#). In general, their flexural strengths tend to be lower than those of conventional ceramics fired at high temperatures, but geopolymers usually exhibit higher toughness or graceful failure. Examples of flexural strengths of metakaolin-based, alkali activated, geopolymer composites are summarized in [Tables 2](#) and [3](#). Uniaxial carbon fiber reinforced geopolymer exhibited a dramatic increase in flexure strengths.

Porous Geopolymers

Geopolymers can be made porous by several means ([Bell and Kriven, 2004](#); [Kriven et al., 2004, 2007a,b](#); [Bell and Kriven, 2008](#); [Landi et al., 2013](#); [Glad and Kriven, 2014, 2015](#); [Medpelli et al., 2014](#); [Seo et al., 2013](#); [Sharma et al., 2015](#); [Ge et al., 2015](#); [Rincón Romero et al., 2018](#); [Tang et al., 2015](#); [Zhao et al., 2020](#); [Prud'homme et al., 2010, 2015](#); [Kamseu et al., 2012](#); [Akono et al., 2019](#)). Discrete pores of 45 μm in diameter can be made by addition of hydrogen peroxide ([Bell and Kriven, 2004](#); [Kriven et al., 2004, 2007a,b](#)). Another ecologically friendly way to make porous geopolymer is through the addition of vegetable canola oil to

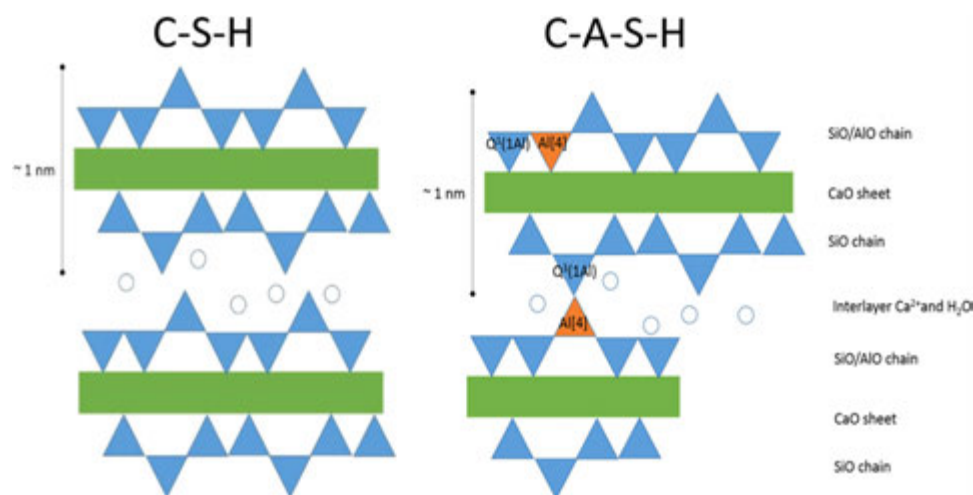


Fig. 7 Molecular structure of C-S-H and CASH cements. Tetrahedra share only 2 or 3 corners (Q2, Q3). From Sankar, K., Kriven, W.M., 2017. Geopolymer reinforced with E-Glass Leno Weaves. *J. Am. Ceram. Soc.* 100 (6), 2492–2501. Available at: Geopolymer reinforced with E-glass Leno weave. Sankar, K., Sutrisno, A., Kriven, W.M., 2019a. Slag-fly ash and slag-metakaolin binders: Part II – Properties of precursors and NMR study of poorly ordered phases. *J. Am. Ceram. Soc.* 102, 3204–3227. Sankar, K., Stynoski, P., Kriven, W.M., 2019b. Sodium silicate activated slag – Fly ash binders: Part III – Composition of soft gel and calorimetry. *J. Am. Ceram. Soc.* 102, 3175–3190.

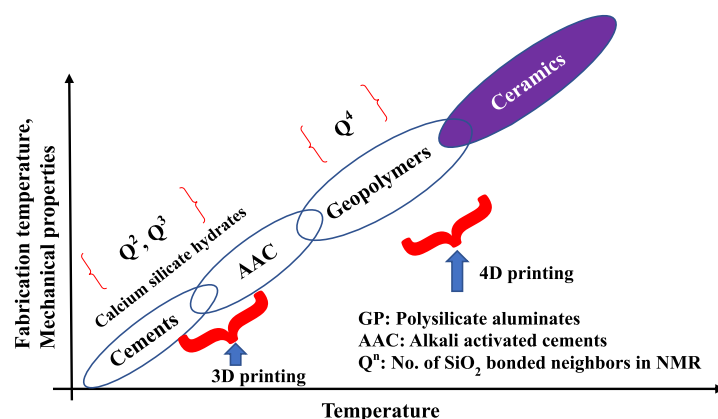


Fig. 8 Schematic diagram of the relationship between metakaolin-based geopolymers and waste material, class F fly ash and slag-based, alkali-activated cements.

geopolymer paste during synthesis causing phase separation to form an oil - aqueous phase emulsion (Medpelli *et al.*, 2014; Seo *et al.*, 2013; Sharma *et al.*, 2015). After the geopolymer has set, the oil is removed by boiling in water, leaving an interconnected porous network.

Geopolymer aerogels have been made containing 70 vol% porosity of just less than 1 mm pore size which have been developed through the Pickering emulsion effect (Glad and Kriven, 2014, 2015). Alkylalkoxysilanes were used to form a hydrophobic film on pore interiors during synthesis and drying, allowing for drainage without pore collapse. Pore volume and pore size could be tuned by manipulating initial water content, quantity of hydrophobic phase, drying humidity, and emulsion stability. Geopolymer reactivity was notably increased via premixing the geopolymer reagents in a dilute slurry prior to creating the emulsion. The geopolymers created were monolithic solids, which could be optionally calcined in inert atmosphere to form a porous ceramic glass with a crystalline β -SiC minor phase.

Conversely, mesoporosity (defined as pores of 2–50 nm diameter) in metakaolin Na-based GP can be reduced by an order of magnitude through the addition of acrylate-functional silane coupling agents (Glad and Kriven, 2014). Geopolymer densification and porosity reduction were achieved through the use of hydrogel chemistry. While traditional hydrogels are difficult to integrate into the GP matrix during the curing process, alkoxysilanes functionalized with methacrylate groups mixed into the GP slurry and formed micrometer-sized membranes and rolled tubes. It was found that a critical concentration of approximately 0.06 mol methacryloxypropyltrimethoxysilane/mol GP was necessary for extensive property modification.

The methacrylate/ mol GP was required for substantial surface area reduction, increased linear shrinkage and increased water retention characteristics, and that smaller amounts of the additive may even reverse the trends. It is suspected that the critical

Table 2 Summary of flexure strengths of geopolymer composites (GPCs) with various inorganic reinforcements

Reinforcement	wt% Additions	Flexure strength (MPa)
Chamotte (25 μm)	50	15.33
Dolomite (45 μm)	20	15.92
Mica phlogopite platelets (50–100 μm)	20	11.4
Granite powder ($\leq 90 \mu\text{m}$)	55	10.3
Dicalcium phosphate ($2\text{CaO} \cdot \text{P}_2\text{O}_5$)	15	10.4
Hydroxyapatite bone ash	15	10.0
Bangladeshi Mymensingh clay containing 40 wt.% quartz reinforced with dicalcium phosphate ($2\text{CaO} \cdot \text{P}_2\text{O}_5$) and glass frit	7.5	14.3
Alumina platelet grinding media (50 μm)	70	20 (RT) to 40 (at 1200°C)
Alumina chopped Saffil [®] fibers ($\phi = 3 \mu\text{m}$)	20	20
Carbon chopped fibers (60 $\mu\text{m} \times 7 \mu\text{m} \phi$)	20	22.2
Carbon chopped fibers (100 $\mu\text{m} \times 7 \mu\text{m} \phi$)	20	29.9
Basalt chopped fibers (1/4")	10	19.5
Basalt chopped fibers (1/2")	10	27
Graphene nanoplatelets	3	12
Basalt felt	10	22.2
Fiberglass felt	10	5.6
Basalt 4" chopped strand mat	20	31
Basalt fiber weave	30	41
E-glass Leno weave	25	25.6
Carbon unidirectional fiber	20	269
Nextel 610 alumina (8 satin weave)	50	45.8
Nextel 720 (mullite + 15 vol% alumina)	50	46
Xtegra [®] auxetic fibers from Advanced Fiber Technologies, Inc.	50	12.9 i.e., 25% strain to failure

Note. From Kriven, W.M., 2018. Chapter 5.9 – Geopolymer-based composites. In: Beaumont, P.W.R., Zweben, C.H. (Eds.), *Comprehensive Composite Materials II*, vol. 5. Oxford: Academic Press, pp. 269–280. Available at: <https://doi.org/10.1016/B978-0-12-803581-8.09995-1>. Musil, S.S., Kriven, W.M., 2013. In situ mechanical properties of chamotte particulate reinforced, potassium geopolymer. *J. Am. Ceram. Soc.* 97 (3), 907–915. Available at <https://doi.org/10.1111/jace.12736>. Cho, S.-H., 2015. Geopolymer Composites and their Applications in Stress Wave Mitigation. Ph.D. Dissertation. Urbana, IL: University of Illinois at Urbana-Champaign. Department of Mechanical Science and Engineering. Keane, P.F., Kriven, W.M., 2019. Microstructure and flexure strengths of dolomite particulate-reinforced geopolymer composites. In: Wang, J., Kriven, W. M., Fey, T., *et al.*, (Eds.), *Proceedings of the 42 International Conference on Advanced Ceramics and Composites. Cer. Eng. and Sci. Proceedings*. vol 39, issue 3, 173–181. Keane, P.F., Foltz, J.S., Chadha, V., Marsh, C.P., Kriven, W.M., 2021. Amorphous self-healed, chopped basalt fiber-reinforced, geopolymer composites. *J. Am. Ceram. Soc.* 2021b. Available at: <https://doi.org/10.1111/jace.17648>. (In press). Bhuiya, A.W., Hu, M., Sankar, K., *et al.*, 2021. Bone ash reinforced geopolymer composites. *J. Am. Ceram. Soc.* Available at: <https://doi.org/10.1111/jace.17621>. (In press). Chadha, V., Kriven, W.M., 2021. Amorphous self-glazed, chopped basalt fiber reinforced, geopolymer-based composites. *Int. J. Appl. Ceram. Technol.* (In press). Akono, A.T., Koric, S., Kriven, W.M., 2019. Influence of pore structure on the strength behavior of particle- and fiber-reinforced, metakaolin-based geopolymer composites. *Cem. Concr. Compos.* 104, 103361. Available at: <https://doi.org/10.1016/j.cemconcomp.2019.103361>. Kutyla, G.P., Kriven, W.M., 2020. Mechanical properties and characterization of alumina platelet reinforced geopolymer composites. *J. Am. Ceram. Soc.* 103, 5178–5185. Available at: <https://doi.org/10.1111/jace.17169>. Sankar, K., Stynoski, P., Al-Chaar, G.K., Kriven, W.M., 2017. Sodium silicate activated slag – Fly ash binders: Part I – Processing, microstructure and mechanical properties. *J. Am. Ceram. Soc.* 101 (6), 2228–2244. Available at: <https://doi.org/10.1111/jace.15391>. Musil, S.S., 2014. Novel Inorganic Composites Using Porous, Alkali-activated Aluminosilicate Binders. University of Illinois at Urbana-Champaign. Department of Mechanical Science and Engineering Urbana, IL. Trindade, A.C., de Andrade, Silva, F., Kriven, W.M., 2021. Mechanical behavior of K-geopolymers reinforced with silane-coated basalt fibers. *J. Am. Ceram. Soc.* 104 (1), 437–447. Available at: <https://doi.org/10.1111/jace.17446>. Samuel, D.M., Sutrisno, A., Kriven, W.M., 2021. Relative importance of Al(V) and reinforcement to the flexural strength of geopolymer composites. *J. Am. Ceram. Soc.* Available at: <https://doi.org/10.1111/jace.17656>. (In press)

composition observed may occur at the concentration where the GP network is fully saturated with organic additive, so that only additional additive causes the observed porosity reduction. With 0.10 mol methacrylate/mol GP, the natural GP mesoporosity was reduced by approximately an order of magnitude, and the Weibull modulus was increased by almost 50% even for reinforced GP composites. Above this concentration, membranes and tubes of organic material could be observed, suggesting that only this surplus additive contributed to mesoporosity reduction. The source of this mesoporosity reduction was shown to be segregation of free water via hydrogel-like interaction caused by the formation of sodium acrylate groups.

Amorphous Self-Healed Geopolymer Composites

Bone ash reinforced geopolymer composites (Bhuiya *et al.*, 2021)

Potassium-based, geopolymer composites have been made with metakaolin and Mymensingh clay from Bangladesh, which was heated and decomposed at 750°C for 2 h to form ~60% metakaolin and ~40% quartz plus impurities. A synthetic analog of the natural calcined clay was made by adding ~40% quartz particulates to metakaolin. By analogy with bone china, bone ash or calcined hydroxyapatite ($5\text{CaO} \cdot 3\text{P}_2\text{O}_5$ or “HA”) particles, having a Ca:P ratio of 3.3 to 1, were added to make the two types of

Table 3 Summary of flexure strengths of metakaolin-based geopolymer composites with organic or biological reinforcements

Reinforcement	wt% Additions	Flexural strength (MPa)
Polypropylene chopped fibers (1/2")	2.5	14.5
Polypropylene chopped fibers (1")	2.5	15
Polypropylene chopped fibers (2")	2.5	18.3
Cork particles	60	2.5 (0.75% strain to failure)
<i>Abaca</i> (banana leaf fibers or "Manila hemp")	8	52
<i>Corn husk</i> fibers	13	7.6 (7% strain)
Rice husk stems in <i>rice husk silica-based</i> GP	7	12.4
<i>Jute</i> weave	30	20.5
Colombian <i>fique/sisal</i> (unidirectional)	50	11.4
Amazonian <i>malva</i> (unidirectional)	5.5	31.55
Amazonian <i>curaua</i> (unidirectional)	8.3	18.86
Amazonian <i>Guadua angustifolia</i> chopped bamboo dispersed in Amazonian clay-based geopolymer	5	7.5
Bangladeshi <i>coconut coir</i>	10	7.50
Bangladeshi <i>palm tree coir</i>	10	7.61
Hemp felt	3.8	17.4
Flax felt	3.8	17.3

Note: From Kriven, W.M., 2018. Chapter 5.9 – Geopolymer-based composites. In: Beaumont, P.W.R., Zweben, C.H. (Eds.), *Comprehensive Composite Materials II*, vol. 5. Oxford: Academic Press. pp. 269–280. Sankar, K., Kriven, W.M., 2017. Geopolymer reinforced with E-glass Leno weaves. *J. Am. Ceram. Soc.* 100 (6), 2492–2501. Available at: <https://doi.org/10.1111/jace.14783>.

natural and synthetic geopolymer-based composites. For less refractory additions, dicalcium phosphate ($2\text{CaO} \cdot \text{P}_2\text{O}_5$ or "DCP") particles, having a Ca:P ratio of 2:1, were also added to another set of the two types of geopolymers composites.

The composites made were as follows, corresponding to Fig. 9:

- (1) Potassium geopolymer with metakaolin (MetaMax, BASF Corp) - KGP (MT).
- (2) Potassium geopolymer with metakaolin from Mymensingh clay - KGP (MW).
- (3) Potassium geopolymer from metakaolin clay and containing 40% quartz -KGP (MW-SYN).
- (4) Potassium geopolymer reinforced with hydroxyapatite - HA.
- (5) Potassium geopolymer reinforced with dicalcium phosphate - DCP.

Their compressive and 3-point flexural strengths were measured at ambient temperatures for all of the geopolymer composites. The HA or DCP reinforced geopolymer composites were also heat-treated to $1150^\circ\text{C}/1\text{ h}$ and converted to their mineralogical analogs. Their mechanical properties of compressive and 3-point flexural strengths were again measured. Flexural strengths of $22.42 \pm 11.0\text{ MPa}$ and $31.97 \pm 8.3\text{ MPa}$ were measured in $1 \times 1 \times 10\text{ cm}^3$ heat-treated geopolymer bars reinforced with 10 wt% of DCP and in geopolymer reinforced with 10 wt% DCP + 40 wt% quartz additions, respectively. The room temperature compressive strength of K-based metakaolin-derived geopolymer was 49.3 MPa. Significant improvements to ambient temperature properties were observed due to the self-healing effect of the flowing amorphous DCP, whose presence was verified by SEM (Fig. 10).

SEM micrographs of pure geopolymer at room temperature revealed fully reacted microstructures, while those in geopolymer composites showed reinforced particles in the consolidated geopolymer matrix. The higher flexural strength in thermally treated samples containing 15 wt.% DCP was attributed to the development of phosphate glass, which sealed dehydration and crystallization cracks, as well as development of crystalline phases of leucite, quartz, monetite and tuite in the geopolymer matrix.

The geopolymer samples after thermal treatment exhibited water absorption within 0.03%–0.5%, compared with those at room temperature except in KGP(MT)-15DCP (9.32%). The higher water absorption in KGP containing 15 wt.% DCP was attributed to higher grain size and higher refractoriness in the DCP. Potassium based, metakaolin derived GP containing 15 wt% DCP could be further studied for possible biomedical applications as a bone-like implant material subject due to forming an apatite layer on the porous geopolymer composite surface.

Amorphous self-healed, basalt fiber-reinforced, geopolymer composites (Keane et al., 2021)

The melting and bonding of a molten glass phase dispersed into a surrounding potassium activated, metakaolin-based geopolymer (KGP) matrix, produced a self-healing effect on a dehydrated and cracked geopolymer matrix (Keane et al., 2021). The addition of more reinforcements produced a self-glazing effect on the composite, thereby sealing the surface cracks. At temperatures up to 900°C , the geopolymer composite containing chopped basalt fiber (from Technobasalt[®], Kiev, Ukraine) remained amorphous and a low melting glass frit ($T_m = \sim 800^\circ\text{C}$) flowed into dehydration cracks in the geopolymer matrix. This type of composite could be described as "amorphous self-healed geopolymer (ASH-G)". The room temperature flexure strength of samples heat treated up to 900°C significantly increased after adding glass frit, owing to the "self-healing" effect. At 950°C , the K-based geopolymer started to form crystalline leucite ceramic of composition $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ or KAlSi_2O_6 which is stable up to its melting temperature of 1693°C .

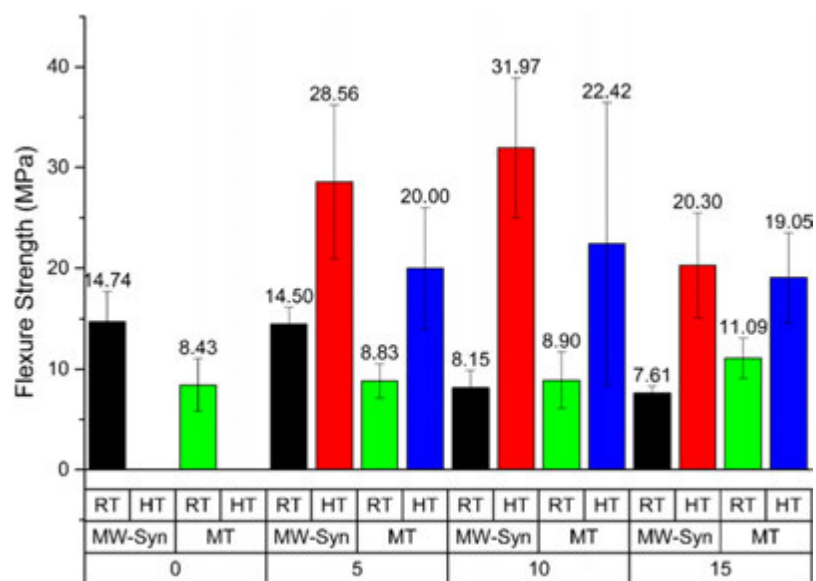


Fig. 9 Comparison of 3-point flexural strength of composites heat treated at 1150°C/1h. Synthetic metakaolin containing 40 wt% quartz particulates (MW-Syn) were stronger than metakaolin-based (MT) composites containing DCP. Their high temperature properties are superior to RT properties due to amorphous self-healing glass formation (ASH) from the DCP phosphate glass. The optimum DCP content was 10 wt% which gave flexure strengths of ~32 MPa after heat treatment.

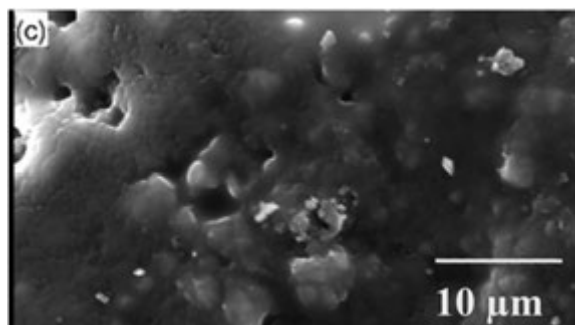


Fig. 10 SEM micrograph of K-based, metakaolin derived geopolymer containing 15 wt.% of dicalcium phosphate after being heated and cooled at 5°C/min to 1125°C with a 1.5-h hold time.

By 1000°C, the geopolymer converted to a ceramic, but the basalt fibers remained intact, and the melted glass frit flowed into cracks formed due to crystallization and liquid phase sintering and sealed the cracks. Thus, this type of composite could be described as an “amorphous self-healed ceramic (ASH-C)”. 1150°C was determined to be the optimum heat treatment temperature since at 1200°C the basalt fibers melted and the strength of the reinforcement would have been lost in the composite. In samples heat treated at 900°C a maximum room temperature flexure strength of 4.5 MPa was achieved. Furthermore, in samples heat treated at 1150°C a maximum room temperature flexure strength of 6 MPa was measured. A Weibull statistical analysis was performed showing how the amorphous self-healing effect of the glass frit significantly improved the room temperature flexure strength of the heat-treated geopolymer and ceramic composites. Thus, geopolymer composites have been developed that can be scaled up and fabricated by high shear, similar to for cements, but can have the properties of ceramics after in situ exposure to high temperatures up to 1200°C (Figs. 11 and 12).

Tailorable Thermal Expansion Ceramics Derived From Metakaolin-Based, Alkali Activated Geopolymers

The thermal expansion and phase transition behavior in the leucite-pollucite compositional series synthesized by geopolymer crystallization have been shown to differ due to structural changes in the aluminosilicate framework (Stevenson and Kriven, 2021). Crystallographic intra- and inter-tetrahedral distortion mechanisms have been proposed to explain the changes in thermal expansion and phase transitions. Tetrahedral rotation and bond swinging in tetragonal phases led to a rapid expansion and

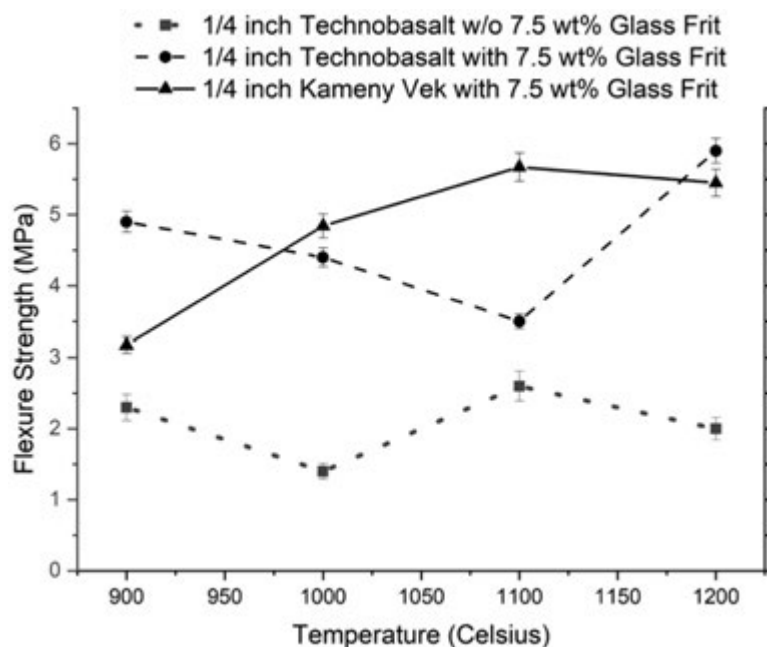


Fig. 11 Room temperature three-point flexural strength of “1/4” chopped Technobasalt fiber-reinforced KGP, with and without 7.5 wt.% glass frit, after heat treatment at 7.5°C/min ramp rate and 2 h hold time. This illustrates the role of amorphous self-healing (below 1000°C ASH-G) and (above 1000°C ASH-C) in improving the flexural strengths of composites.

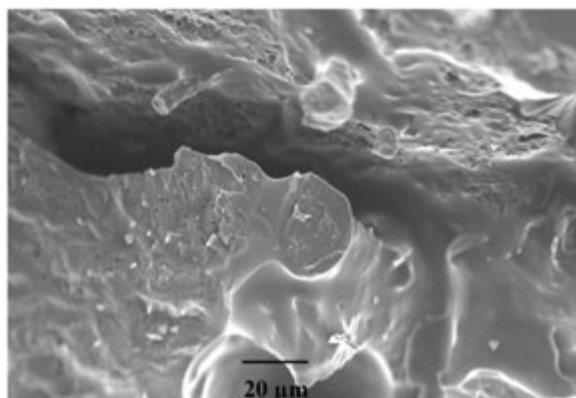


Fig. 12 Potassium-based geopolymer composite containing glassy phase (KGP ASH-C) heated treated at 1200°C/2 h showing melted glassy phase clearly visible in the bottom right hand corner of this SEM micrograph. From Keane, P.F., Foltz, J.S., Chadha, V., Marsh, C.P., Kriven, W.M., 2021. Amorphous self-healed, chopped basalt fiber-reinforced, geopolymer composites. *J. Am. Ceram. Soc.* 2021b Available at: <https://doi.org/10.1111/jace.17648>. (In press).

distortion of the unit cell that accelerated with temperature, culminating in a phase transition to cubic symmetry. Elongation of coordination bonds in cubic leucite and mixed-cation systems caused moderate expansion of the cell that decelerated with temperature. Cubic pollucite exhibited a constant, low thermal expansion across the temperature range probed. For application as environmental barrier coatings (EBCs), suppressing the phase transition in leucite is important to avoid the associated discontinuous volume change. The phase transition temperature was suppressed below room temperature in materials containing greater than 40 mol% cesium. Samples with greater than 80 mol% cesium exhibited very good thermal expansion matches to the SiCf/SiC ceramic matrix composite (CMC) system with higher melting points than current alternatives (Fig. 13).

The range of thermal expansion values attainable in the $K_xCs_{1-x}[AlSi_2O_6]$ system offers reduced CTE mismatch with SiCf/SiC compared to rare earth-based systems. For the successful application of these materials as EBCs, however, further investigation into their reactivity with contaminants in the combustion environment, namely calcium magnesium aluminosilicates, and resilience to thermal cycling is critical.

Low Energy Fabrication Routes to Ceramic Powders

Several potential applications as well as fabrication routes to ceramic powders and polycrystalline ceramics via the geopolymerization route have been identified by Bağcı *et al.* (2014, 2016, 2019). By carbothermal reduction, silicon carbide can be cost effectively synthesized from metakaolin-based geopolymer precursor containing carbon additions as a reducing agent. Crystallization of silicon carbide from geopolymers represents a novel approach to forming highly reactive, ceramic powders. Using the nanoporous, nanoparticulate geopolymer, and a higher amount of nanosized carbon gave rise to improved reaction between constituents. While the commercial Acheson process needs heating at 2500°C for ~2 days, the process described in the work of Bağcı *et al.*, 2019 produced a 97% conversion to SiC starting from K-based geopolymer and excess carbon, producing phase pure silicon carbide, at 1600°C in 2 h. This systematic research compared Na, K, and Cs geopolymers as precursors to silicon carbide synthesis. Heating above 1400°C was sufficient to synthesize silicon carbide and its yield increased with increasing temperature in

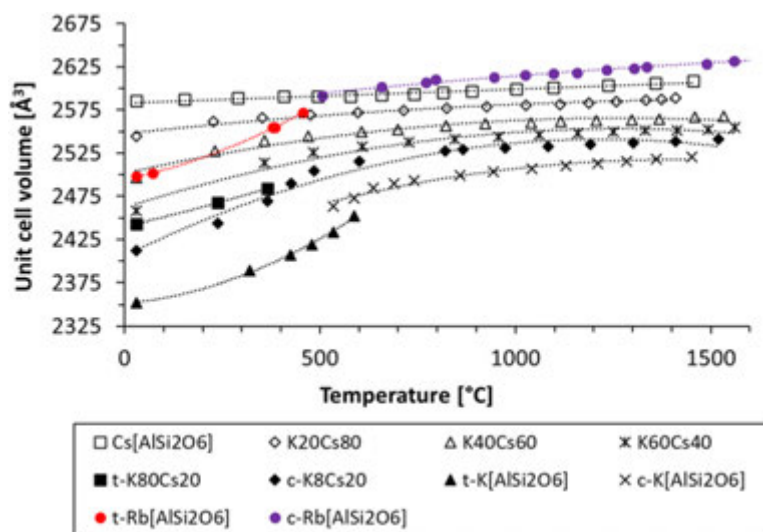


Fig. 13 Measured unit cell volumes for the $K_xCs_{1-x}[AlSi_2O_6]$ series. From Steveson, A.J., 2020. Geopolymer-Derived Ceramics and Composites. (Ph.D. Dissertation). Urbana, IL: University of Illinois at Urbana-Champaign. Department of Material Science and Engineering. Available at: <http://hdl.handle.net/2142/108009>. Steveson, A.J., Kriven, W.M., 2021. Tailorable thermal expansion in leucite-pollucite materials derived from geopolymers for thermal barrier coatings. J. Am. Ceram. Soc. Available at: <https://doi.org/10.1111/jace.17630>. (In press).

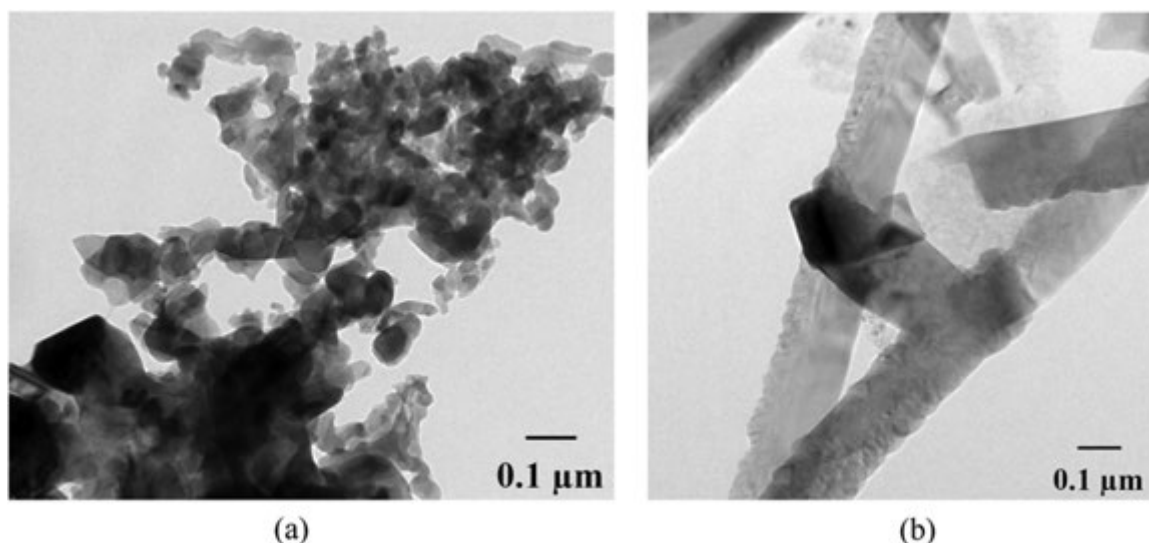


Fig. 14 TEM of Si_3N_4 nanoparticles made from metakaolin-based, potassium geopolymer mixed with 18 moles of excess carbon and heat treated at 1600°C/2 h under flowing argon. (a) equiaxed particulates (b) needles of SiAlON made from $Na_2O \cdot Al_2O_3 \cdot 4SiO_2$ plus 9 moles of excess carbon heated at 1400°C/2 h under flowing argon.

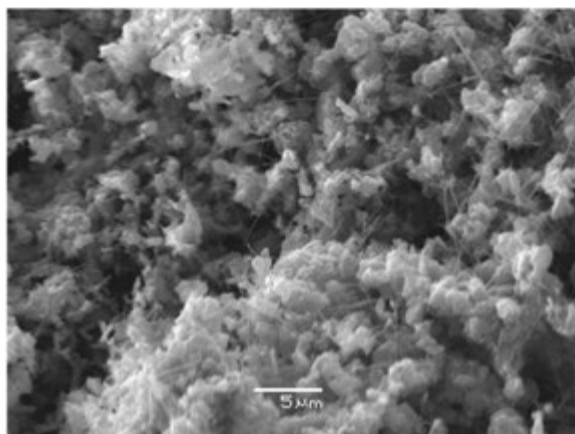


Fig. 15 SiAlON completely converted from $K_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 11H_2O$ geopolymer mixed with 9 mol% ground carbon and heated at $1500^\circ C/2$ h under flowing N_2 . From Bagci, C., Kutyla, G.P., Kriven, W.M., 2014. In situ carbothermal reduction/nitridation of geopolymer composites containing carbon nanoparticles. *Ceram. Eng. Sci. Proc.* 38 (10), 15–28.

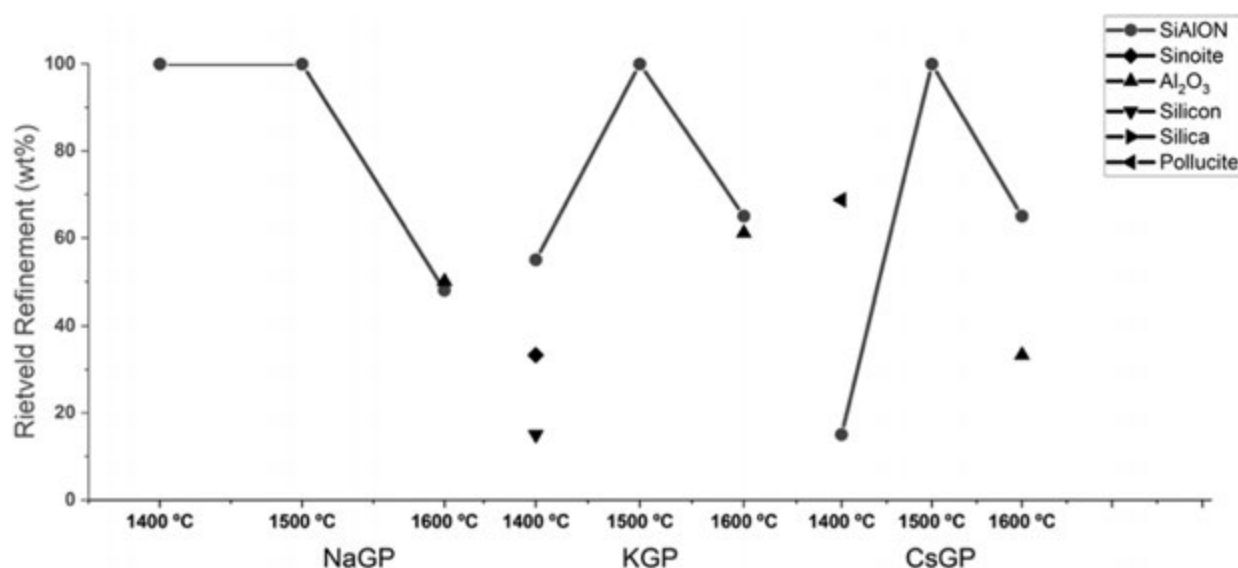


Fig. 16 Phase analysis and microstructural transformation of products converted from nanoparticulate GP + 9C by carbothermal reduction under flowing N_2 . Rietveld refinement results of reaction products from GP + 9C after being fired in flowing nitrogen in a tube furnace.

the case of sodium based geopolymer (NaGP) and potassium-based geopolymer (KGP). Additionally, NaGP had an advantage over the KGP and cesium-based geopolymer (CsGP) in terms of high yield and phase pure, silicon carbide at $1400^\circ C$ as well as its low cost. CsGP failed to convert to silicon carbide but produced predominantly alumina instead (Figs. 14–16).

Compositionally variable, nitride crystalline phases were also successfully synthesized from metakaolin-based geopolymer precursors containing nano-carbon, via carbothermal reduction and nitridation. This geopolymer processing route is a cost-effective method whereby the nano porous nature of GPs served to improve the reaction with nano-carbon particles during carbothermal reduction. A high yield of over 95% of silicon nitride (Si_3N_4) containing two polymorphs (mainly alpha) was synthesized from sodium ($Na_2O \cdot Al_2O_3 \cdot 4.5SiO_2 \cdot 12H_2O$) and potassium ($K_2O \cdot Al_2O_3 \cdot 4.5SiO_2 \cdot 12H_2O$) precursors to mainly beta (Si_3N_4) on heating at $> 1400^\circ C$ under flowing nitrogen. Furthermore, a high yield of SiAlON (over 90%) was synthesized in the case of cesium ($Cs_2O \cdot Al_2O_3 \cdot 4.5SiO_2 \cdot 12H_2O$) precursor using only 9 mol% of excess C and the same synthesis route.

Conclusion

The field of geopolymers is a new, low energy way to make inorganic polymer materials that are intermediate between cements and ceramics. They are made under higher shear, as compared to a cement, but can have higher temperature capabilities than

cements when they set. Both alkali-activated as well as acid-activated aluminosilicates form ceramic-like bodies. Alkali activated geopolymers having nominal compositions centered around $M_2O \bullet Al_2O_3 \bullet 4SiO_2$ while the phosphoric acid activated geopolymers have compositions centered at $Al_2O_3 \bullet 2SiO_2 \bullet P_2O_5$.

The amorphous aluminosilicate results from calcination of crystalline, kaolinite-type clays (e.g., kaolinite, halloysite) of composition $(Al_2O_3 \bullet 2SiO_2 \bullet 2H_2O)$ at $750^\circ C/2$ h. The chemical reactions occur by dissolution of the amorphous aluminosilicate source, polycondensation in a highly concentrated aqueous solution, and precipitation to form a solid body. A key requirement for alkali reacted geopolymers is to have the Al atoms in five-fold coordination with oxygen atoms, forming a double bond with one oxygen atom, which causes the molecule to be in a highly strained state. These AlO_5 molecules are thus susceptible to attack by the water glass solution and hence dissolution. AlO_4^- and SiO_2 tetrahedra form in solution, upon which then polymerize and precipitate under mildly exothermic conditions up to $100^\circ C$. Since lower amounts of water than in cements are necessary and the water is "recycled" after the precipitation of the nanoparticles, the resulting inorganic polymer is stronger and more rigid than a gel and hence more like a ceramic.

The intrinsic microstructure of alkali activated geopolymers is nano porous (40 vol%, 6.8 nm diameter) and nanoparticulate (20–40 nm), having densities of ~ 1.5 g/cc. The nano regions of water dispersed in the crosslinked, polysialate molecular structure are removed on heating to 250 – $400^\circ C$, forming microcracks. However, when filler phases or reinforcements are added during polymerization, the geopolymer cross-links around them to form strong, flaw-tolerant ceramic bodies which are stable up to the crystallization temperature at $\sim 950^\circ C$ to $1050^\circ C$, for Na, K, and Cs-based geopolymers, respectively. Na-based geopolymers form nepheline ($Na_2O \bullet Al_2O_3 \bullet 2SiO_2$) plus SiO_2 glass, since the formation of jadeite ($Na_2O \bullet Al_2O_3 \bullet 4SiO_2$) requires geological pressures of 1.7 GPa and $1250^\circ C$. K and Cs-based geopolymers form leucite ($K_2O \bullet Al_2O_3 \bullet 4SiO_2$) and pollucite ($Cs_2O \bullet Al_2O_3 \bullet 4SiO_2$) under ambient pressures, however. Geopolymers based on mixtures of K- and Cs-based waterglass solutions open the way to tailorable thermal expansion geopolymers and geopolymer-derived thermal barrier or environmental barrier (TBC, EBC) coatings.

A wide variety of geopolymer composites have been made and their mechanical properties (mostly flexural strengths) have been measured. Due to the low setting temperature under ambient conditions, ceramic, metal, polymer and biological reinforcements can be incorporated. The reinforcements can be particulate, elongated or faceted-shaped particles of various sizes, chopped fibers, directional fibers, weaves or 3D meshes. The composites can be scaled up, for construction and road work purposes, as well as applied as coatings, since there is no need for firing. They can be pre-fabricated and readily shaped in plastic molds to which geopolymers generally do not adhere. Geopolymers can also readily be 3D or 4D printed due to their thixotropic rheology as a composite material.

In the case of refractory reinforcements such as ceramic particulates or chopped fibers, the microcracking results from dehydration and crystallization can be self-healed by the presence of glassy phase upon heat treatment above the melting temperature of the glass. Amorphous self-healed geopolymer (ASH-G) and amorphous self-healed ceramic (ASH-C) enable the geopolymer to retain significant strength and impermeability upon exposure to high temperatures. This self-healing pre-treatment leads the way to versatile, intermediate temperature ceramics, up to $1200^\circ C$ at present. The nanoparticulate particle sizes can be exploited as nano-diffusion distances to fabricate ultra-high temperature ceramic powders such as SiC, Si_3N_4 , and SiAlONs by carbothermal reduction and carbothermal nitridation of geopolymer-carbon mixtures at significantly reduced temperatures (1400 – $1600^\circ C$) and costs compared to current technologies. Thus geopolymers can provide a versatile new class of inorganic polymers that can lead to low energy syntheses of ceramics.

References

- Akono, A.T., Koric, S., Kriven, W.M., 2019. Influence of pore structure on the strength behavior of particle- and fiber-reinforced, metakaolin-based geopolymer composites. *Cem. Concr. Compos.* 104, 103361. <https://doi.org/10.1016/j.cemconcomp.2019.103361>.
- Bagci, C., Kutyla, G.P., Kriven, W.M., 2014. In situ carbothermal reduction/nitridation of geopolymer composites containing carbon nanoparticles. *Ceram. Eng. Sci. Proc.* 38 (10), 15–28.
- Bagci, C., Yang, Q., Kriven, W.M., 2019. Formation of α/β - Si_3N_4 nanoparticles by carbothermal reduction and nitridation of geopolymers. *J. Am. Ceram. Soc.* 102 (11), 6542–6551. <https://doi.org/10.1111/jace.16529>.
- Bagci, C., Kutyla, G.P., Seymour, K.C., Kriven, W.M., 2016. Synthesis and characterization of silicon carbide powders converted from metakaolin-based geopolymers. *J. Am. Ceram. Soc.* 99 (7), 2521–2530. <https://doi.org/10.1111/jace.14254>.
- Barbosa, V.F.F., MacKenzie, K.J.D., 2003. Synthesis and thermal behaviour of potassium sialate geopolymers. *Mater. Lett.* 57, 1477–1482.
- Barbosa, V.F.F., MacKenzie, K.J.D., Thaumaturgo, C., 2000. Synthesis and characterization of materials based on inorganic polymers of alumina and silica: sodium polysialate polymers. *Int. J. Inorg. Mater.* 2 (4), 309–317.
- Bell, J.L., Kriven, W.M., 2008. Preparation of ceramic foams from metakaolin-based geopolymer gels. In: Lin, H.-T., Koumoto, K., Kriven, W.M., *et al.* (Eds.) *Developments in Strategic Materials: Ceramic Engineering and Science Proceedings*. The American Ceramic Society, Volume 29, Issue 10, pp. 97–112.
- Bell, J.L., Sarin, P., Provis, J.L., *et al.*, 2008a. Atomic structure of a cesium aluminosilicate geopolymer: A pair distribution function study. *Chem. Mater.* 20 (14), 4768–4776. <https://doi.org/10.1021/cm703369s>.
- Bell, J.L., Sarin, P., Driemeyer, P.E., *et al.*, 2008b. X-Ray pair distribution function analysis of a metakaolin-based, $KAlSi_2O_6 \bullet 5.5H_2O$ inorganic polymer (geopolymer). *J. Mater. Chem.* 18 (48), 5974–5981. <https://doi.org/10.1039/b808157c>.
- Bell, J.L., Driemeyer, P.E., Kriven, W.M., 2009a. Formation of ceramics from metakaolin-based geopolymers: Part I. Cs-based geopolymer. *J. Am. Ceram. Soc.* 92 (1), 1–8. <https://doi.org/10.1111/j.1551-2916.2008.02790.x>.
- Bell, J.L., Driemeyer, P.E., Kriven, W.M., 2009b. Formation of ceramics from metakaolin-based geopolymers: Part II. K-based geopolymer. *J. Am. Ceram. Soc.* 92 (3), 607–615. <https://doi.org/10.1111/j.1551-2916.2008.02922.x>.
- Bell, J.L., Kriven, W.M., 2004. Nanoporosity in geopolymeric cements. *Microsc. Microanal.* 10, 590–591. (Proceedings of 62nd Annual Meeting of the Microscopy Society of America).

- Bhuiya, A.W., Hu, M., Sankar, K., *et al.*, 2021. Bone ash reinforced geopolymer composites. *J. Am. Ceram. Soc.* Available at: <https://doi.org/10.1111/jace.17621>. (In press).
- Celerier, H., Jouin, J., Mathivet, V., Tessier-Doyen, N., Rossignol, S., 2018. Composition and properties of phosphoric acid-based geopolymers. *J. Noncryst. Solids* 493, 94–98. <https://doi.org/10.1016/j.jnoncrysol.2018.04.044>.
- Cho, S.-H., 2015. Geopolymer Composites and their Applications in Stress Wave Mitigation. Ph.D. Dissertation. University of Illinois at Urbana-Champaign. Department of Mechanical Science and Engineering, Urbana, IL. <http://hdl.handle.net/2142/88053>.
- Colorado, H.A., Hahn, H.T., Hiel, C., 2011. Pultruded glass fiber- and pultruded carbon fiber-reinforced chemically bonded phosphate ceramics. *J. Compos. Mater.* 45 (23), 2391–2399.
- Cui, X.-M., Liu, L.-P., He, Y., Chen, J.-U., Zhou, J., 2011. A novel aluminosilicate geopolymer material with low dielectric loss. *Mater. Chem. Phys.* 130, 1–4.
- Davidovits, J., 1988. Geopolymer chemistry and properties. In: Davidovits, J., Orlinski, J. (Eds.), *Proceedings of Geopolymer'88 First European Conference on Soft Mineralogy*, vol. 1. Compiegne: Geopolymer Institute and Technical University, pp. 25–48.
- Davidovits, J., 1991. Geopolymers – Inorganic polymeric new materials. *J. Therm. Anal.* 37, 1633–1656.
- Davidovits, J., 2020. Geopolymer: Chemistry and Applications, fifth ed. Saint-Quentin: Institut Geopolymere, www.geopolymer.org.
- Davidovits, J., 1982. U.S. Patent 4,349,386 Mineral Polymers and Methods of Making Them.
- Douiri, H., Louati, S., Baklout, S., Arous, M., Fakfakh, Z., 2016. Enhanced dielectric performance of metakaolin–H₃PO₄ geopolymers. *Mater. Lett.* 164, 299–302. <https://doi.org/10.1016/j.matlet.2015.10.172>.
- Duxson, P., Provis, J.L., Lukey, G.C., *et al.*, 2005. Understanding the relationship between geopolymer composition, microstructure and mechanical properties. *Coll. Surf. A Physicochem. Eng. Asp.* 269 (1–3), 47–58. <https://doi.org/10.1016/j.colsurfa.2008.11.019>.
- Duxson, P., Mallicoat, S.W., Lukey, G.C., Kriven, W.M., van Deventer, J.S.J., 2007. Effect of alkali and Si/Al ratio on the development of mechanical properties of metakaolin-based geopolymers. *Coll. Surf. A Physicochem. Eng. Asp.* 292, 8–20. <https://doi.org/10.1016/j.colsurfa.2006.05.044>.
- Ge, Y., Cui, X., Kong, Y., *et al.*, 2015. Porous geopolymeric spheres for removal of Cu(II) from aqueous solution: Synthesis and evaluation. *J. Hazard. Mater.* 283, 244–251. <https://doi.org/10.1016/j.jhazmat.2014.09.038>.
- Glad, B.E., Kriven, W.M., 2014. Geopolymer with hydrogel characteristics via silane coupling agent additives. *J. Am. Ceram. Soc.* 97 (1), 295–304. <https://doi.org/10.1111/jace.12643>.
- Glad, B.E., Kriven, W.M., 2015. Highly porous geopolymers through templating and surface interactions. *J. Am. Ceram. Soc.* 98 (7), 2052–2059. <https://doi.org/10.1111/jace.13584>.
- Gualtieri, M.L., Romagnoli, M., Gualtieri, A.F., 2015. Preparation of phosphoric acid-based geopolymer foams using limestone as pore forming agent – Thermal properties by *in situ* XRPD and rietveld refinements. *J. Eur. Ceram. Soc.* 35, 3167–3178.
- He, Y., Liu, L.-P., He, L., Cui, X.-M., 2016. Characterization of chemosynthetic H₃PO₄–Al₂O₃–2SiO₂ geopolymers. *Ceram. Int.* 42 (2016), 10908–10912. <https://doi.org/10.1016/j.ceramint.2016.03.224>.
- Kamseu, E., Nait-Ali, B., Bignozzi, M.C., *et al.*, 2012. Bulk composition and microstructure dependence of effective thermal conductivity of porous inorganic polymer cements. *J. Eur. Ceram. Soc.* 32 (8), 1593–1603. <https://doi.org/10.1016/j.jeurceramsoc.2011.12.030>.
- Katsiki, A., Hertel, Tine Tysmans, T., Pontikes, Y., Rahier, H., 2019. Metakaolinite phosphate cementitious matrix: Inorganic polymer obtained by acidic activation. *Materials* 12), 442–457. <https://doi.org/10.3390/ma12030442>.
- Kearney, P.F., Foltz, J.S., Chadha, V., Marsh, C.P., 2021. Amorphous self-healed, chopped basalt fiber-reinforced, geopolymer composites. *J. Am. Ceram. Soc.* <https://doi.org/10.1111/jace.17648> (In press).
- Kriven, W.M., 2010. Inorganic polysialates or “geopolymers”. *Bull. Am. Ceram. Soc.* 89 (4), 31–34.
- Kriven, W.M., 2018. Chapter – 5.9 Geopolymer-based composites. In: Beaumont, P.W.R., Zweben, C.H. (Eds.), *Comprehensive Composite Materials II* 5, Academic Press, Oxford, pp. 269–280. <https://doi.org/10.1016/B978-0-12-803581-8.09995-1>.
- Kriven, W.M., Bell, J.L., Gordon, M., 2003. Microstructure and microchemistry of fully-reacted geopolymers and geopolymer matrix composites. *Ceram. Trans.* 153, 227–250.
- Kriven, W.M., Gordon, M., Bell, J.L., 2004. Geopolymers: Nanoparticulate, nanoporous ceramics made under ambient conditions. *Microsc. Microanal.* 10, 404–405. (Proceedings 62nd Annual Meeting of Microscopy Society of America).
- Kriven, W.M., Bell, J.L., Gordon, M., 2007a. Microstructure and nanoporosity of as-set geopolymers. *Ceram. Eng. Sci. Proc.* 27 (2), 491–503.
- Kriven, W.M., Bell, J.L., Gordon, M., Wen, G., 2005. Geopolymers: More than just cements. In: Davidovits, J. (Ed.), *Geopolymer, Green Chemistry and Sustainable Development Solutions: Proceedings of the World Congress Geopolymer 2005*. St. Quentin: Geopolymer Institute publisher, pp. 179–183.
- Kriven, W.M., Bell, J.L., Mallicoat, S.W., Gordon, M., 2007b. Intrinsic microstructure and properties of metakaolin-based geopolymers. In *Proceedings of International Workshop on Geopolymer Binders – Interdependence of Composition, Structure and Properties*. Weimar: Geopolymer Institute, St. Quentin, France, pp. 71–86.
- Landi, E., Medri, V., Papa, E., *et al.*, 2013. Alkali-bonded ceramics with hierarchical tailored porosity. *Appl. Clay Sci.* 73, 56–64. <https://doi.org/10.1016/j.clay.2012.09.027>.
- Liu, L.-P., Cui, X.-M., Qui, S.-H., Yu, J.-L., Zhang, L., 2010. Preparation of phosphoric acid-based porous geopolymers. *Appl. Clay Sci.* 50, 600–603. <https://doi.org/10.1016/j.clay.2010.10.004>.
- Mac Kenzie, K.J.D., Smith, M.E., 2002. Multinuclear solid-state nuclear magnetic resonance of inorganic materials. In: Cahn, R.W. (Ed.), *Pergamon Materials Series*. Oxford: Elsevier.
- Mathivet, W., Jouin, J., Gharzouni, A., *et al.*, 2019. Acid-based geopolymers: Understanding of the structural evolutions during consolidation and after thermal treatments. *J. Non Cryst. Solids* 512, 90–97. <https://doi.org/10.1016/j.jnoncrysol.2019.02.025>.
- Medpelli, D., Seo, J.-M., Seo, D.-K., 2014. Geopolymer with hierarchically meso-/macroporous structures from reactive emulsion templating. *J. Am. Ceram. Soc.* 97 (1), 70–73. <https://doi.org/10.1111/jace.12724>.
- Morris, J.H., Perkins, P.G., Rose, A.E.A., Smith, W.E., 1977. The chemistry and binding properties of aluminium phosphates. *Chem. Soc. Rev.* 6, 173–194. <https://doi.org/10.1039/CS9770600173>.
- Perera, D.S., Hanna, J.V., Davis, J., *et al.*, 2008. Relative strengths of phosphoric acid-reacted and alkali-reacted metakaolin materials. *J. Mater. Sci.* 43, 6562–6566. <https://doi.org/10.1007/s10853-008-2913-6>.
- Prabakar, S., Rao, K.J., Rao, C.N.R., 1991. A MAS NMR investigation of aluminosilicate, silicophosphate, and aluminosilicophosphate gels and the evolution of crystalline structures on heating the gels. *J. Mater. Res.* 6 (3), 592–601.
- Prud'homme, Joussein, E., Rossignol, S., 2015. Use of silicon carbide sludge to form porous alkali-activated materials for insulating application. *Eur. Phys. J. Spec. Top.* 224 (9), 1725–1735. <https://doi.org/10.1140/epjst/e2015-02494-7>.
- Prud'homme, E., Michaud, P., Joussein, E., *et al.*, 2010. Silica fume as porogen agent in geo-materials at low temperature. *J. Eur. Ceram. Soc.* 30 (7), 1641–1648. <https://doi.org/10.1016/j.jeurceramsoc.2010.01.014>.
- Rincón Romero, A., Elsayed, H., Bernardo, E., 2018. Highly porous mullite ceramics from engineered alkali activated suspensions. *J. Am. Ceram. Soc.* 101 (3), 1036–1041. <https://doi.org/10.1111/jace.15327>.
- Sa Ribeiro, R.A., Sa Ribeiro, M., Kriven, W.M., 2017. A review of particle and fiber-reinforced metakaolin-based geopolymer composites. *J. Ceram. Sci. Technol.* 8 (3), 307–321.
- Sankar, K., Sutrisno, A., Kriven, W.M., 2019a. Slag-fly ash and slag-metakaolin binders: Part II – Properties of precursors and NMR study of poorly ordered phases. *J. Am. Ceram. Soc.* 102, 3204–3227. <https://doi.org/10.1111/jace.16224>.
- Sankar, K., Stynoski, P., Kriven, W.M., 2019b. Sodium silicate activated slag - fly ash binders: Part III – Composition of soft gel and calorimetry. *J. Am. Ceram. Soc.* 102, 3175–3190. <https://doi.org/10.1111/jace.16219>.

- Sankar, K., Stynoski, P., Al-Chaar, G.K., Kriven, W.M., 2017. Sodium silicate activated slag – fly ash binders: Part I – Processing, microstructure and mechanical properties. *J. Am. Ceram. Soc.* 101 (6), 2228–2244. <https://doi.org/10.1111/jace.15391>.
- Seo, D.-K., Seo J. M., Medpellii, D., 2013. Porous Geopolymer Materials. US Patent Serial Number 15322, March 14th (2013).
- Sharma, S., Medpellii, D., Chen, S., Seo, D.-K., 2015. Calcium-modified hierarchically porous aluminosilicate geopolymer as a highly efficient regenerable catalyst for biodiesel production. *R. Soc. Chem. Adv.* 5 (80), 65454–65461. <https://doi.org/10.1039/C5RA01823D>.
- Stevenson, A.J., Kriven, W.M., 2021. Tailorable thermal expansion in leucite-pollucite materials derived from geopolymers for thermal barrier coatings. *J. Am. Ceram. Soc.* <https://doi.org/10.1111/jace.17630> (In press).
- Tang, Q., Ge, K., Wang, K.T., He, Y., Cui, X., 2015. Preparation and characterization of porous metakaolin-based inorganic polymer spheres as an adsorbent. *Mater. Des.* 88, 1244–1249. <https://doi.org/10.1016/j.matdes.2015.09.126>.
- Tchakouté, H.K., Ruscher, C., Kamseu, E., Andreola, F., Leonelli, C., 2017. Influence of the molar concentration of phosphoric acid solution on the properties of metakaolin-phosphate-based geopolymer cements. *Appl. Clay Sci.* 147, 184–194. <https://doi.org/10.1016/j.clay.2017.07.036>.
- Wagh, A., 2004. *Chemically Bonded Phosphate Ceramics*, first ed. New York: Elsevier.
- Wang, Y.-S., Alrefaei, Y., Dai, J.-G., 2019. Silico-aluminophosphate and alkali-aluminosilicate geopolymers: A comparative review. *Front. Mater.* 6, 106. <https://doi.org/10.3389/fmats.2019.00106>.
- Wang, Y.-S., Dai, J.G., Ding, Z., Xu, W.T., 2017. Phosphate-based geopolymer: Formation mechanism and thermal stability. *Mater. Lett.* 190, 209–212. <https://doi.org/10.1016/j.matlet.2017.01.022>.
- Weibull, W., 1951. A statistical distribution function of wide applicability. *J. Appl. Mech.* 18 (3), 293–297.
- Zhao, S., Qin, S., Jia, Z., *et al.*, 2020. From bulk to porous structures: Tailoring monoclinic $\text{SrAl}_2\text{Si}_2\text{O}_8$ ceramic by geopolymer precursor technique. *J. Am. Ceram. Soc.* 103(9) 4957–4968. <https://doi.org/10.1111/jace.17166>.
- Zribi, M., Samet, B., Baklouti, S., 2019. Effect of curing temperature on the synthesis, structure and mechanical properties of phosphate-based geopolymers. *J. Non Cryst. Solids* 511, 62–67. <https://doi.org/10.1016/j.jnoncrsol.2019.01.032>.

Overview: Characterization and Modelling of Ceramics and Glasses

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This section is devoted to modeling and characterization. Thus, it contains chapters which describe how ceramics and glass structures can be designed and understood from fundamental first principle calculations, how stable phases are and how phase diagrams can be predicted from fundamental thermodynamics. The remainder of the chapters in Section 2 describe analytical techniques commonly used for glass and ceramic materials to determine information relating to fine structure (i.e., coordination number, bond angles, bond lengths), crystal structure and microstructure.

The first three chapters cover modeling of ceramic and glass structures. The chapter by Ching outlines an exciting area of ceramics research related to ceramic genomics. He relates the use of total bond order density to not only predict formulae and structures of new ceramic materials, but also to predict mechanical properties such as moduli, Poisson's ratio and yield strength for example. Guerin *et al.* explore the modeling of ceramics in more detail and explain the use of density functional theory to extend molecular dynamics. They then exemplify this by the clarification of crystal structures and using modeling to assess ceramic elastic strain tensors, time and temperature dependent phenomena and piezoelectric charge tensors and voltage constants. The chapter by Edén relates the use of molecular dynamics simulations to develop models of glass structures in melt quenched oxide glass systems and how pair distribution and bond angle data can be obtained from such exercises. In addition, the effects of modifier ratio and type on glass structures can be readily predicted and are in excellent agreement with MAS-NMR analyses. The final chapter in the section on prediction is the Computation of Phase diagrams. This chapter gives an excellent background to the fundamental thermodynamics associated with the calculation of phase diagrams and examines the CALPHAD methodology in some detail. The chapter then goes on to look at calculated binary and ternary phase diagram examples.

Murtagh and Venopaul initially review what they call “static characterization techniques” for ceramic powders e.g. chemical composition, phase assemblage, particle size distribution, specific surface area, bulk density etc. They then go on to indicate that whilst these parameters may be of great use in terms of characterizing a small batch, when it comes to fully understanding inter-relationships between powder parameters and the microstructure of a processed ceramic then additional factors must be considered. These additional factors are related to consistency of mixed powder flow and how various factors, such as humidity, affect it. In addition, powder permeability and powder compressibility can be affected by so-called dynamic powder characteristics. Thus, this original approach to powder characterization has greatly assisted the understanding of particle behavior in powder mixtures during processing into fired components.

Four chapters follow which are related to fine structure (bond lengths, coordination number) and crystal structure analysis. McMillan's chapter on vibrational spectroscopy covers the analysis of chalcogenide, silicate, alumino-silicate, phosphate, borate and fluoride glasses. Of particular interest is the ability of the IR/Raman techniques described to provide fine structure detail of glasses. Thus, for example, McMillan shows how peak positions change with the number of bridging oxygens in silicate glasses as well as how the characteristic spectra for borate glasses change as compositional changes allow boron to change its coordination from III to IV. The chapter by Gao on Magic Angle Spinning (MAS) – NMR, gives a very good introduction to the background behind the technique. Following this introduction, Gao then goes on to give examples of the use of MAS -NMR in ceramics and glass research, paying particular attention to ^{29}Si , ^{31}P , ^{19}F , and ^{27}Al analyses. Such analyses allow fine structure analysis of ceramics and glasses (e.g. determination of coordination number). Thus for example, the relative amounts of aluminum acting as a glass modifier (Al (V), Al (VI)) compared to that acting as a glass former (Al(IV)) can be readily obtained using MAS-NMR techniques. Additionally, MAS-NMR is the only technique which can readily confirm the presence of fluorine in hydroxyapatite and that it substitutes in OH^- positions in the lattice. In his chapter on X-ray diffraction, Misture outlines the use of X-rays for Pair Distribution Function (PDF) determination. This aspect of X-ray analysis is of great use in determining nearest neighbor atoms in ceramics, as well as glasses. Associated structural modeling assists in the interpretation of the PDF data. The chapters by Misture and Gonon deal in detail with X-ray diffraction (XRD) and its typical applications in ceramic science. Thus, both chapters, but particularly that by Misture, detail the interaction of X-rays with crystals, the fundamentals of structure, phase identification, quantitative phase analysis, unit cell indexing, refining lattice parameters, Rietveld refinement, preferred orientation, residual stress and crystallite size. Gonon's chapter provides excellent case studies of the use of XRD which reinforce and extend the fundamental information in the technique descriptions.

Fetzer *et al.* explain the basics behind transmission electron microscopy (TEM) and how the technique, which has 10^{-10} m resolution, can be used to examine 20–100 nm thick samples. Such thin samples are made using specimen preparation techniques such as dimpling/argon ion thinning, tripod polishing (tapered section) or focused ion beam milling. The chapter gives a concise account of electron beam generation and control, how the electron beam interacts with specimens facilitating electron contrast and thus imaging. Electron diffraction and dark field imaging are explained as well as imaging contrasts arising from thickness effects, bends in specimens or defects (e.g. dislocations). Electron diffraction is explained extremely well in the chapter of Fetzer *et al.* and enables the early researcher to understand how TEM can be used to determine crystallographic properties of various phases. The final section in the chapter deals with high resolution imaging and introduces the concept of being able to identify atom types in atom columns in engineering and electronic ceramics. Cookman *et al.* extend this knowledge base in their chapter on high

resolution analytical electron microscopy of ceramics and glasses. This chapter looks at the use of aberration corrected scanning transmission electron microscopy (STEM) and how chemical contrast can be generated and mapped by annular dark field STEM as well as the relatively new differential phase contrast imaging method. In addition to chemical/phase contrast the chapter also addresses how energy dispersive X-ray analysis (EDX) and electron energy loss spectroscopy (EELS) can be used to identify the location of specific elements with very high spatial resolution, facilitating atomic resolution images of atom positions on specific atomic planes. Another exciting possibility arising from EELS analysis is its use in fine structure analysis. Cookman *et al.* report the use of EELS in understanding differences in bonding between phase separated regions in an alumino-silicate glass. Stewart and Kolb's chapter on 3D electron crystallography is an overview of this exciting new approach to crystallographic analysis. Having established the background to the technique, the authors then go on to show how it can be used to investigate the crystallography of nanocrystalline materials including glass ceramics.

Whilst the chapter by Pomeroy on preparation of specimens for microstructural examination may seem very practically oriented, it is very interesting to note that very, very few journal papers explain the steps taken to produce a polished and etched specimen for microstructural analysis. This can be exceedingly frustrating for a new researcher who may be working in relative isolation and cannot benefit from the experience of a group. The chapter thus gives the background to choosing and using the various consumables (sectioning saws, mounting media, grinding and polishing platens and abrasives) involved in preparing a sample for microstructural analysis. It also reviews the various etching methods and the ceramics they are typically used for. Pomeroy's chapter on scanning electron microscopy of ceramics and glasses gives an introduction to the current scope afforded by SEM technology to investigate the microstructure of ceramics. Having described the basic anatomy of a SEM and beam specimen interactions, this chapter goes on to look at how image contrast is generated and how that results in image generation. Of particular interest is compositional imaging which allows an understanding of the development of phase assemblage in glass ceramics for example. This chapter also examines the analysis of X-rays emitted from specimen surfaces during SEM examination. Mecholski Jr. describes the fractography of brittle materials and how it contributes to understanding brittle failure and the failure of materials with reasonable toughness due to R-curve behavior. The chapter also explains how fractography can determine not just the origin of failure but also whether the failure results from a processing defect or overload.

The chapter by Pomeroy on thermal analysis of ceramics and glasses deals with thermogravimetry, differential thermal analysis/differential scanning calorimetry and dilatometry. Each technique is briefly described and then examples related to the understanding of ceramic and glass science are given. Thus, precursor decomposition, binder loss and oxidation of ceramics are dealt with under thermogravimetric analysis; differential thermal analysis/differential scanning calorimetry methods deal with the determination of glass properties (e.g. glass transition temperature, inference of effect of temperature on glass viscosity, glass nucleation and crystallization temperatures) and temperatures and energies associated with phase transformations; the part of the chapter dealing with dilatometry covers sintering rate analysis, measurements of coefficients of thermal expansion as well as glass transition and dilatometric softening temperatures and temperatures at which ceramics undergo phase transformation. Sukenaga and Shibata look in detail at the measurement of the viscosity, density, and surface tension of molten oxides using a variety of techniques. They discuss the use of the rotating cylinder and levitation methods for viscosity measurement and then go on to look at the measurement of the density of molten oxides using Archimedian, sessile drop and levitation methods and how surface tension can be measured using a ring technique, the maximum bubble pressure technique or a levitation method. Extremely useful information can be extracted from the data obtained which can contribute to advanced glass processing and the understanding of composition – structure – property relationships in such systems.

Ceramic Genomics: Total Bond Order Density

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Introduction

The word geno or genome originating from biology has been pervasive in materials science discipline within last two decades. This started at the initiation of materials genome project at the federal level that follows the same approach of the Human Genome Project in the biomedical community decades ago, which resulted in the now mature discipline of bioinformatics (Service, 2015). Since ceramic materials have many outstanding properties, functionalities and applications, it is not surprising the ceramic geno becomes a popular topic at conferences and in scientific arena. This is consistent with the general concept that the gene is the essence that controls what are evolving from it to its offspring or derivatives. Thus seeking the gene inevitably becomes the Holy Grail in pursuing the fundamental origin of material properties.

In all materials, there are always different metrics for its characterization on different aspects of its properties. For example, experimentally measured quantities such as mass density, melting point, refractive index, hardness, fracture toughness, ductility etc. They can related to the genes based on their atomic compositions, arrangements, interactions, and their thermodynamic states etc. Non-measurable quantities are generally inferred from experiment, theory, experience, intuition or perceptions. These include the position in the Periodic Table, atomic number, atomic radius, electronic configuration, temperature, pressure, lattice parameter, diffraction pattern, and much more. Many of these quantities can be obtained from simple or elaborate measurements. They can also be obtained from empirical and ab initio calculations. The development of the density functional theory (DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) and the rapid increase in computational power have accelerated the computational trend. It is now possible to obtain accurate results on properties of materials and even predict experimental observations. In the last few years, I have been advocating the use of total bond order density (TBOD) as a single quantum mechanically derived metric that can be used to assess many of the materials properties. Total bond order (TOB) is the sum of all pairs of bond order values. When normalized by the volume of the system under consideration, we obtain the TBOD that represent the internal cohesion of the material and is related to materials geno in some way. It could play a crucial role in materials informatics if large database of TBOD for different classes of materials are available to facilitate predictions.

In recent years, information collection, classification, analysis, interpretation, utilization and dispersion have emerged as an interdisciplinary research platform involving computer science, information science, and various disciplines in science and arts such as physics, chemistry, biology, medicine, materials engineering, earth science, design technology, education, social science, legal community etc. In particular, materials informatics has developed into a flourishing field of study (Vapnik, 2013; Ching, 2016; Rajan, 2005). It aims to find more efficient ways of solving scientific problems related to all kinds on materials using large databases. This ultimately connects to fashionable subject of machine learning (ML) and artificial intelligence (AI) (Raccuglia *et al.*, 2016; Cubuk *et al.*, 2015; Ramprasad *et al.*, 2017; Sun *et al.*, 2017b). In this regard, the input will be some key parameters called descriptors and when feed into carefully designed equations and sophisticated algorithms, it can predicate unknown materials with desired structure, composition and properties. There are many different ways of collecting large data and building powerful databases for applications such as demonstrated by (Tancrét *et al.*, 2017; Islam *et al.*, 2018; Lookman *et al.*, 2017; Xue *et al.*, 2016). More recently, large amounts of data may be obtained through calculations using different computational methods and packages based on different theories. TBOD mentioned above could be one of such descriptors that could play a dominating role.

In this chapter I start with a short description of the methods and approach used in calculating the TBOD. The focus is on the application of TBOD to different materials beyond just ceramics and glasses based on the data obtained from computation. The database constructed can be used in ML strategy to facilitate new materials discovery, In particular, we point out the use of TBOD in complex metallic alloys and glasses, which have very different types of bonding than in ceramic materials. We also show the very promising progress in applying it to complex biological materials and their interfaces with inorganics where the weak but ubiquitous hydrogen bonding (HB) are prevailing. Most of the work described here have been published within the last few years but many of them are from projects currently in progress.

Methods and Approach

Crystal Structure and Supercell Models

In any experimental work in materials science, the most important starting point is the availability of material samples. In fact, without the real material samples, there would be no materials science. It is the same in computational research, we need theoretical samples. In case of crystalline materials, they can be directly obtained from many experimental measurements deposited in well documented database such as: Cambridge Crystallographic Data Center (CCDC) (see "Relevant Websites sections"), protein data bank (PDB) (see "Relevant Websites sections") The Materials project (see "Relevant Websites sections"). They can be further refined or optimized if necessary using different methods and level of accuracy. In case of hypothetical

materials, newly proposed structures or disordered materials such as glasses, we need to construct plausible models based on which simulations can be carried out. This is tantamount to theoretical sample preparation, the starting point similar to experimental research. For glasses or complex materials, we need to use supercells with at least ~ 1000 atoms and fully relax the structure which could be computationally very expensive. Depending on the nature of the problem, the complexity of the system and the properties to be computed, smaller supercells may be used without compromising the key conclusions. Most of the supercells maintain the periodic boundary condition to mimic the infinite solid or liquid materials. Small supercells may introduce inaccuracy due to the size effect. In case of complex bimolecular systems, one can simply put the molecules inside a large cell and solvate it with appropriate number of water molecules if necessary for large-scale simulations.

An important point that must be emphasized is that the supercell models must be fully relaxed based on energy minimizations. The quality of electronic structure calculation depends on the atomic positions in the model based on which the TBOD is evaluated. There are many DFT-based computational packages for structural relaxation and they need not to be the same one used in the electronic structure calculations since they have different focuses. One is for the preparation of the theoretical sample, the other is for the calculation of electronic structure and bonding. We use the Vienna Ab initio simulation package (VASP) (see “Relevant Websites sections”) for structure relaxation. VASP is one of the most popular packages using pseudopotential and plane wave expansion. It is highly accurate, efficient and with many different choices for the exchange correlation potentials. The accurate atomic structure and the volume of the cell control the accuracy of the TBOD. Other similar packages such as Quantum Espresso (see “Relevant Websites sections”), ABINIT (see “Relevant Websites sections”), Amsterdam Density Functional (ADF) (see “Relevant Websites sections”) and Gaussian-09 (see “Relevant Websites sections”) and many others are also popular and can be used for structural relaxation. We will illustrate this strategy with applications to different materials in later sections.

Electronic Structure and Interatomic Bonding

The evaluation of TBOD for a crystal or a supercell model starts with the calculation of electronic structure using *ab initio* DFT-based methods. While many different types of DFT calculations on systems large and small are available, we will focus of a method we developed in house for such calculations, the orthogonalized linear combination of atomic orbitals (OLCAO) method (Ching and Rulis, 2012). The VASP-relaxed structures are used as input. The OLCAO method uses atomic orbitals for the basis expansion and is highly efficient as well as economic, especially for large complex systems. In most OLCAO calculations, a more localized minimal basis (MB) set is used for the calculation of effective charges Q_α^* and the bond order (BO) values $\rho_{\alpha\beta}$ between a pair of atoms (α, β) using Mulliken population analysis scheme (Mulliken, 1955a,b).

$$Q_\alpha^* = \sum_i \sum_{m,occ} \sum_{j,\beta} C_{ix}^m C_{j\beta}^m S_{ix,j\beta} \quad (1)$$

$$\rho_{\alpha\beta} = \sum_{m,occ} \sum_{j,\beta} C_{ix}^m C_{j\beta}^m S_{ix,j\beta} \quad (2)$$

In Eqs. (1) and (2), $S_{ix,j\beta}$ are the overlap integrals between the i th orbital in the α th atom and j th orbital in the β th atom. $C_{j\beta}^m$ are the eigenvector coefficients of the m th band for the j th orbital in the β th atom. We usually calculate the partial charge ΔQ or the charge transfer for each atom which is the deviation from neutral charge (Q^0) and the effective charge (Q^*) of the same atom i.e., $\Delta Q = Q^0 - Q^*$. Accurate partial charge is extremely important in interpreting many of material properties and their functionality especially in biomolecular systems. As an example, the MB set used in the study of the pyrophosphate crystal ($K_2Mg(H_2P_2O_7)_2 \cdot 2H_2O$) (see Section 3.1 below) have the following atomic configurations: P: $1s^2 2s^2 2p^6 3s^2 3p^3$; Mg: $1s^2 2s^2 2p^6 3s^2$; K: $1s^2 2s^2 2p^6 3s^2 3p^6 3d 4s^1$; O: $1s^2 2s^2 2p^4$ and H: $1s^1$. A full basis (FB) set that has one more shell of atomic orbitals in the basis than the MB is used for the calculation of self-consistent potential, total density of states (TDOS), and partial density of states (PDOS), band structure and optical properties. The BO $\rho_{\alpha\beta}$ in Eq. (2) provides a quantitative measure for the strength of the bond between atom α and β . The summation of all BOs normalized by the cell volume gives us the TBOD which is a single metric to assess the internal cohesion in the crystal. TBOD can be resolved into partial components or the partial BO density (PBOD) from different types of atomic pairs, or different groups of atoms in the structural units in the crystal or the supercell. This decomposition of TBOD to PBOD is very useful for proper interpretation of the results on the interatomic interactions as will be illustrated in many examples later in Section 3.

There are many other methods and theories for the bond order or effective charge calculations (Manz, 2017). Some of these methods can be very accurate and elaborate but are generally limited to smaller crystals or molecules. Therefore, there is always a tradeoff between efficiency and accuracy in material-related data generation using computational approach. It should be emphasized that the calculations of PC and BO is basis dependent. In many instances, even the definition of BO and PC can be different in different DFT methods, or computational packages. It is quite meaningless to compare BO or TBOD obtained using different methods or using different bases. Our experience of using the OLCAO method based on Mulliken scheme of BO evaluation is very satisfactory and consistent. It is most natural to use atomic wave functions in the basis expansion and extremely efficient for application to large complex systems.

Physical Properties Calculation

For the TBOD to be claimed as a material geno, it must be correlated with the physical properties calculated or measured. These include interatomic bonding, spectroscopic and vibrational properties, elastic and mechanical properties, and much more. Most importantly, it should be applicable to all materials systems, ordered or disordered, perfect or defective. Since TBOD and its partial components the PBOD measure the internal cohesion of the material and their constituent components, correlation with the mechanical properties would be the most obvious. Other properties such as the spectroscopic properties are less important since they are usually related to excitation of the electron, from the valence band or from deep core levels such as in electron energy loss spectroscopy (ELNES) and x-ray absorption near edge spectroscopy (XANES). Mechanical properties are usually reflected in their elastic constants, modulus values, and Poisson's ratio and other parameters derived for them. We will illustrate such correlations in many examples later.

For mechanical properties calculation, we do not use the OLCAO method but use the fully relaxed structure from VASP or other computational packages. This is the vivid example that in computational materials research, using the combination of different methods in order to take their respective advantages is most effective. For elastic properties calculation, we use the stress (σ_j) vs strain (ϵ_i) response analysis scheme (Nielsen and Martin, 1983; Yao *et al.*, 2007). In this scheme, we apply a small strain ϵ (usually $\pm 0.5\%$) to the fully relaxed structure to obtain the elastic coefficients C_{ij} and compliance tensor S_{ij} ($i, j = 1, 2, 3, 4, 5, 6$) in solving the set of linear equations. From the calculated C_{ij} , other mechanical properties such as bulk modulus (K), shear modulus (G), Poisson's ratio (η), Young's modulus (E) are obtained using Voight-Reuss-Hill (VRH) polycrystals approximation (Reuss, 1929; Hill, 1952). Additional related mechanical properties such as elastic anisotropy, hardness, yielding strength etc. can be separately calculated if desired.

Application of TBOD to Ceramic Materials

Oxides, Nitrides, Carbides and Phosphates

Most ceramics are oxides, nitrides, carbides, borides or phosphides. They are all covalently bonded and may have ionic characters. The bond order values in these crystals are clear and well defined. Here we cite some of the examples for the application of TBOD to these most fundamental ceramics. Fig. 1 shows the crystal structure of three basic silicon nitrides, α -Si₃N₄, β -Si₃N₄ and γ -Si₃N₄ together with an oxynitride crystal Si₂N₂O. γ -Si₃N₄ is also called the cubic Si₃N₄ in the spinel structure. The electronic structure of these crystals have been investigated by us long time ago (Ren and Ching, 1981; Xu and Ching, 1995; Ching *et al.*, 2000, 2002; Zerr *et al.*, 2006; Ching, 2000) but their BO and TBOD have been calculated only recently and listed in Table 1. As can be seen that Si₂N₂O have less TBOD due to the presence of weaker Si-O bonds compare with Si-N bonds, and γ -Si₃N₄ has the largest TBOD because of additional bonding from the strong Si-N bonds at the octahedral site of Si. It is also interesting to see that α -Si₃N₄ has larger TBOD than β -Si₃N₄ mainly because it has shorter Si-N bond length (BL) hence larger BO values.

Figs. 2 and 3 show the structures of the two most basic silicon oxides (stishovite and α -quartz), three forms of TiO₂ (rutile, anatase and brookite) as well as two most well-known ternary oxides, spinel Mg₂SiO₄ and perovskite SrTiO₃, and lastly four of the many polymorphs of SiC (3C, 2H, 4H, 6H). Their electronic structure and properties have been investigated by us long time ago (Li and Ching, 1985; Ching, 1986; Xu and Ching, 1995; Mo and Ching, 2001, 1995; Ching *et al.*, 2006b). However, the TBOD for these crystals were not calculated since TBOD is a relative new concept introduced in recent years. Nevertheless, they can be calculated very easily and could be part of the valuable parameters in the database for interpretation of more complex structures. In Table 2, we list the TBOD and PBOD for these 11 crystalline of oxides and carbides. The silicon carbides have the same composition but different structures. As can be seen from their TBOD and PBOD values in Table 2, they reveal some of the common and well-known facts. The most noticeable is that the high-density stishovite SiO₂ has its TBOD 2.64 times larger than alpha quartz, since it may be the hardest material known second only to diamond. In TiO₂, The most common phase rutile has the highest TBOD. The perovskite SrTiO₃ has a higher TBOD than the spinel Mg₂SiO₄ and the four polymorphs of SiC have very similar TBOD indicating the stacking layers in the hexagonal structure do not make much difference in terms of crystal strength. These results illustrate the power and utility of TBOD as a ceramic geno for ceramic crystals with different structures, symmetries and compositions.

Next we focus on a relatively complex crystal pyrophosphate K₂Mg(H₂P₂O₇)₂ · 2H₂O with five different atomic species studied recently (Adhikari *et al.*, 2017). Fig. 4 shows the crystals structure of this pyrophosphate crystal which is far more complicated than other not so simple phosphate crystals such as aluminum phosphate (AlPO₄), potassium titanyl phosphate (KTP, KTiOPO₄), calcium pyrophosphate dihydrate ((Ca₂P₂O₇) · 2H₂O), hydroxyapatite (HAP, Ca₁₀(PO₄) · 6(OH)₂) and many others. Our result shows the complex interplay of different bonding between specific local structures and compositions that can result in large differences in reactivity and interaction which are rare in other classes of inorganic crystals. We divide this pyrophosphate crystal into three structural units: H₂P₂O₇ is the most important and dominating unit. The other two are the cationic groups of metals and the water molecules. The strong P-O bond in P₂O₅ contribute most to TBOD but O-H, N-H bonds including hydrogen bond (HB) also play an important part. All these complex bonding affects their physical properties. More importantly, this work showed that the experimentally reported structure was not sufficiently accurate resulting in unrealistically short O-H bonds that were rectified with full-scale optimization of the crystal structure. As expected, the TBOD of the relaxed crystal is slightly higher than that of the measured structure (Adhikari *et al.*, 2017).

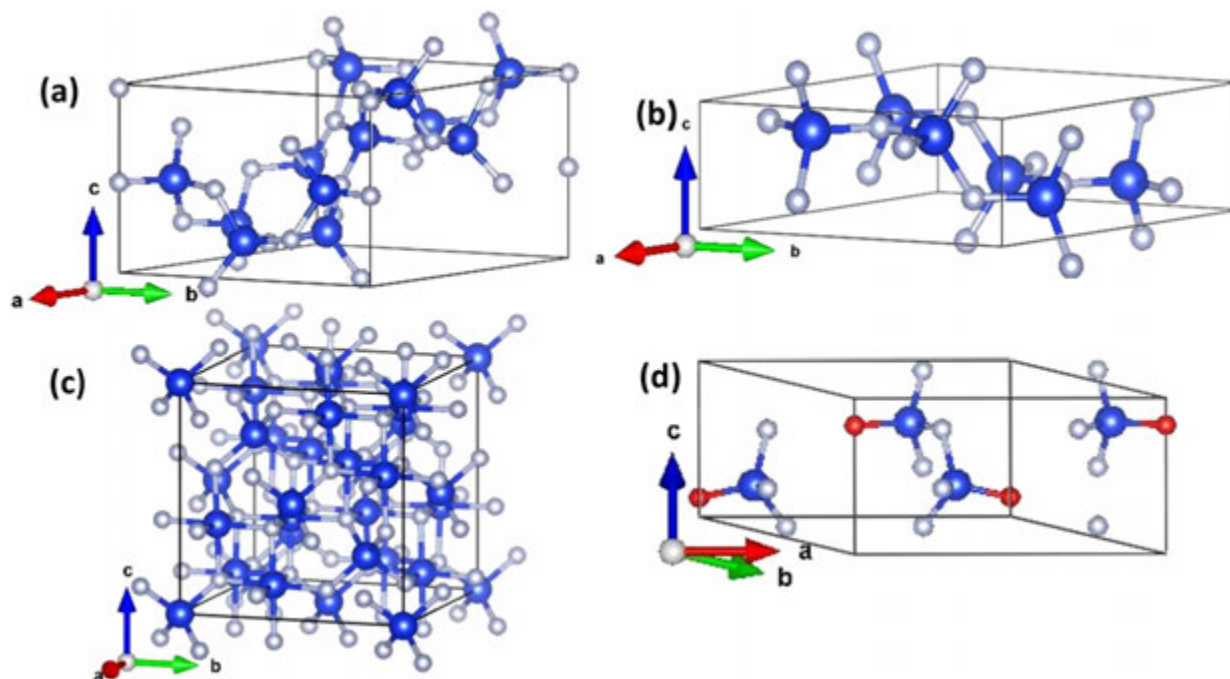


Fig. 1 Ball & stick figures for three Si_3N_4 crystals (a) $\alpha\text{-Si}_3\text{N}_4$, (b) $\beta\text{-Si}_3\text{N}_4$, (c) $\gamma\text{-Si}_3\text{N}_4$ and (d) $\text{Si}_2\text{N}_2\text{O}$ crystal.

Table 1 TBOD, PBOD for the three Si_3N_4 crystals and $\text{Si}_2\text{N}_2\text{O}$ crystal

Crystal	Bond	TBO (electron)	TBOD (electron/Å ³)	PBO (electron)	PBOD (electron/Å ³)
$\alpha\text{-Si}_3\text{N}_4$	Si-N	16.7532	0.0560		
$\beta\text{-Si}_3\text{N}_4$		7.5032	0.0512		
$\gamma\text{-Si}_3\text{N}_4$		33.71840	0.07143		
$\text{Si}_2\text{N}_2\text{O}$	Si-N	5.2596	0.0432	4.1316	0.0339
	Si-O			1.1280	0.0092

The above limited examples on the calculation of TBOD in oxides, nitrides, carbides and phosphates can be extended to many other ceramic phases or explore new phases where the TBOD can be an extremely useful parameter, the ceramic geno. A specific example on the allocation to a model of complex intergranular glassy film in $\beta\text{-Si}_3\text{N}_4$ will be discussion in Section 3.6.

Max Phases

In this section, we present the genomic approach to the stability, elastic and electronic properties of a very important class of layered ternary compounds called MAX ($\text{M}_{n+1}\text{AX}_n$) phases (Barsoum, 2013). Within the last ten years, we have made systematic calculations on a large number of MAX phases and their properties (Mo *et al.*, 2012; Ching, 2016; Ching *et al.*, 2013; Li and Ching, 2014; Mo *et al.*, 2014; Dhakal *et al.*, 2015; Wang *et al.*, 2013). Here M stands for a transition metal, A is a group III, IV, V, or VI element with Al the most common and X is either C or N with $n = 1-5$. Fig. 5 shows the sketch for the MAX crystals with $n = 1, 2, 3, 4$. A large database of 665 viable crystals with $\text{M} = \text{Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo}$; $\text{A} = \text{Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As, S}$ and, $\text{X} = \text{C or N}$ was constructed and various correlations among and between them were fully explored (Aryal *et al.*, 2014). It is shown that the key parameter is TBOD and its partial components PBOD. They could explain many correlations with mechanical properties and the role played respectively by M, A, X. Detailed analysis of various correlation plots shows that there is a clear correspondence between bulk modulus K and TBOD, especially with the M-A even though the M-X PBOD makes the largest contribution to the TBOD. The correlation becomes less clear for Shear modulus G and other mechanical parameters. These correlations also show a marked difference between the carbides and nitrides, and that Sc as a metal is an exception in many of these trends.

This large database is also used to test the efficacy of data mining algorithms and statistical machine learning approach for materials genome. It is shown that by using 50% of the electronic structure data, we can predict the mechanical parameters of the other 50% data quite accurately with a correlation coefficient of over 80%. The TBOD is the key descriptor that controls the predictability (Ching, 2016). We further identified several thermodynamically stable new MAX phases that have never been synthesized in the laboratory or theoretically investigated. All the experimentally verified MAX phases passed the screening using

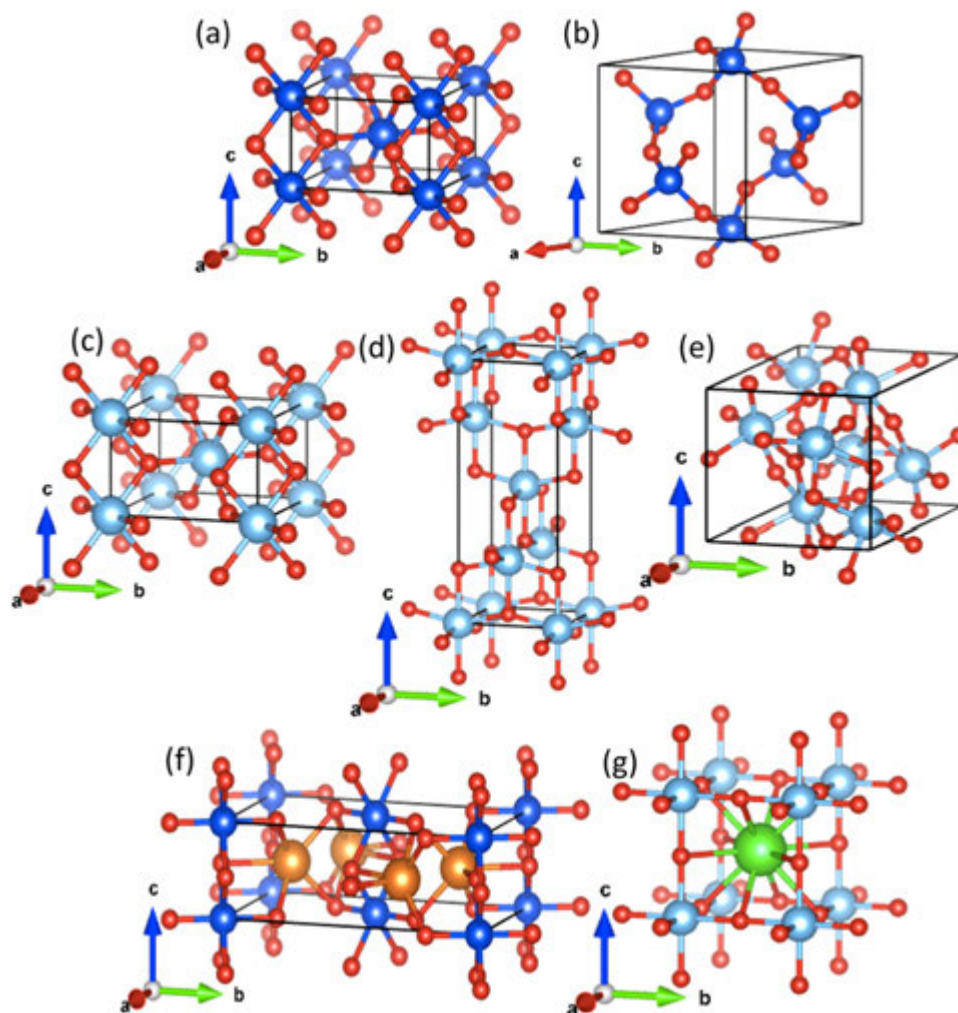


Fig. 2 Ball & stick figures for six oxides: (a) stishovite SiO_2 , (b) α -quartz, (c) rutile, (d) anatase, (e) brookite (f) Mg_2SiO_4 , (g) SrTiO_3 .

the TBOD as a key parameter. **Table 3** shows the TBOD for the 68 MAX phases in the database that were confirmed to exist. The same data are plotted in **Fig. 6**. Their TBOD generally lie between 0.022 and 0.049 ($\text{e}/\text{\AA}^3$), consistent with their properties, in that they behave like metals and ceramics. Most of these are 211 phases and there are far more MAX oxides than nitrides. It is also interesting to note that Sc_2InC has the smallest TBOD among these 68 phases. It has been pointed out in [Aryal et al. \(2014\)](#) that MAX phases with $M = \text{Sc}$ have been outliers in many of their properties.

C-S-H Cement Crystals

Cement and concretes are important construction and building materials worldwide. They have very complex composition and disordered structures with several known crystalline phases as ingredients ([Richardson, 2008](#)). Calcium silicate hydrate (C-S-H) is the main binding phase of Portland cement, which is the most prominent and main construction material in the world. Following the earlier calculations on some of these complex C-S-H phases such as Jennite and Tobermorite ([Dharmawardhana et al., 2013](#)), we studied the electronic structure and bonding of a large subset of C-S-H minerals with known crystal structures ([Dharmawardhana et al., 2014](#)). Our results revealed the contributions from a wide range of bonding including the hydrogen bonding to the internal cohesion of the cement crystals. It shows that TBOD is the ideal overall metric for assessing these complex C-S-H crystals and should replace the conventional practice of using C/S ratio (Ca to Si ratio) for cement materials. A rarely known orthorhombic C-S-H phase Suolunite ($\text{Ca}_2\text{Si}_2\text{O}_5(\text{OH})_2 \cdot \text{H}_2\text{O}$) is found to have the highest TBOD. **Table 4** lists the 20 crystalline C-S-H crystals used in this study and **Fig. 7** shows the crystal structure of Suolunite ([Ma et al., 1999](#)). In **Fig. 8**, we plot TBOD of these crystals vs the C/S ratio. It shows that using C/S ratio in characterizing C-S-H crystals is only approximate and need to be replaced by the more accurate quantum mechanical metric TBOD. Further detailed investigation also revealed that different types of HBs that can exist in the complex C-S-H crystals based on the TBOD and PBOD in relation to their properties ([Dharmawardhana et al., 2016](#)). Very recently, electronic structure and bonding were studied for the two very complex and highly hydrated

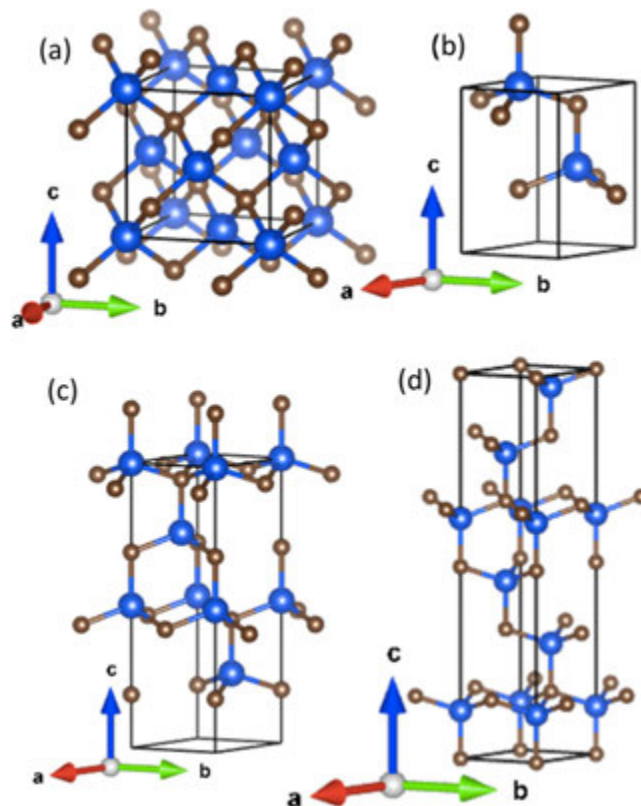


Fig. 3 Ball & stick figures for 4 Si carbides.

cement crystals Ettringite and Thaumasite (San *et al.*, 2018). They are rare mineral crystals with high water content. Table 5 compares their mechanical properties and TBOD with suolunite and confirms that the latter has a higher TBOD with less water content. Such detailed information on TBOD and PBOD in conjunction to various properties enable us to design new emerging cement materials and will be discussed later in the section on bio-inspired cements.

Transition Metal Carbides

In this section, we move to the application of TBOD for a specific metallic crystal between transition metal elements and C to illustrate the power and utility of TBOD. The presence of precipitate phases $M_{23}C_6$ ($M = Cr, Fe, Mo$ and W) play a significant role in the mechanical strength and creep resistance of Ni-based superalloys (Donachie and Donachie, 2002). The crystal structure of these complex carbides comprises of 116 atoms in a cubic cell of FCC lattice. We reported the investigation of the electronic structure, interatomic bonding and mechanical properties of four binary phases of $M_{23}C_6$, and $M_{23}N_6$, and six ternary phases of $(M1, M2)_{23}C_6$ (Adhikari *et al.*, 2019a). Fig. 9 shows the crystal structure of $Cr_{23}C_6$ in two different angles. Based on the results of comprehensive calculations and the evaluation of TBOD and PBOD on these binary and ternary crystals, we conclude that Fe tends to make the intermetallic structure less stable whereas W makes the crystal more compressible. The root of these observations can be traced to the size of the metal ions as well as the complex interatomic bonding of C atom with the d electrons in these metals. Fig. 10 shows the TBOD and PBOD contributions in the 10 binary and ternary $M_{23}C_6$ crystals. Interestingly, we can correlate the calculated mechanical properties in these metallic carbides with TBOD and analyze various competing factors for their interaction. Fig. 11 shows the plot of the Pugh modulus ratio G/K (Shear modulus over bulk modulus) which is used to characterize the ductility or brittleness for a material vs the TBOD, showing a very close correlation. We unequivocally confirm $Cr_{23}C_6$ to be the most stable precipitate phase with superior overall physical properties. Here, we showed the merit of using TBOD as the key parameter in assessing the metallic materials as well. Replacing C with N in these crystals does not result in any discernable difference in their properties and the TBOD of $M_{23}N_6$ is only lightly less than $M_{23}C_6$. Such investigation in using TBOD shed much light on the stabilization strategy of the presence of carbides precipitates in Ni-based superalloys.

Chalcogenide Crystals

Chalcogenide crystals and glasses are important class of compounds with relatively high refractive index. They have many unique applications in a number of industrial sectors including infrared (IR) sensors and IR optics in communications, imaging, remote

Table 2 Structures, TBOD and PBOD of some oxides and carbides

<i>Crystal</i>	<i>No. of atoms</i>	<i>Space group</i>	<i>a, b, c (Å)</i>	<i>α, β, γ (degree)</i>	<i>Vol. (Å³)</i>	<i>Bond</i>	<i>TBO (electron)</i>	<i>TBOD (e/Å³)</i>	<i>PBO (electron)</i>	<i>PBOD (e/Å³)</i>
SiO ₂ (Stishovite)	6	<i>P4₂/mnm</i> (No 136)	4.1790, 4.1790, 2.6649	90°, 90°, 90°	46.5399	Si-O	2.3992	0.0497	—	—
α -SiO ₂	9	<i>P3₂21</i> (No 154)	4.9123, 4.9123, 5.4038	90°, 90°, 120°	112.9326		2.2562	0.0188	—	—
TiO ₂ (Rutile)	6	<i>P4₂/mnm</i> (No 136)	4.1790, 4.1790, 2.6649	90°, 90°, 90°	46.5399	Ti-O	2.6220	0.0406	—	—
TiO ₂ (Anatase)	12	<i>I4₁/amd</i> (No 141)	3.7850, 3.7850, 9.5140	90°, 90°, 90°	136.2997		5.1712	0.0365	—	—
TiO ₂ (Brookite)	24	<i>Pbca</i> (No 61)	9.1840, 5.4470, 5.1450	90°, 90°, 90°	257.3799		5.0336	0.0189	—	—
Mg ₂ SiO ₄	14	<i>Pb-am</i> (No 55)	4.9800, 8.8500, 2.7500	90°, 90°, 90°	121.2007	Mg-O	3.0490	0.0240	1.6442	0.0129
						Si-O			1.4048	0.0110
SrTiO ₃	5	<i>Pm-3m</i> (No 221)	3.9052, 3.9052, 3.9052	90°, 90°, 90°	59.5602	Sr-O	1.8885	0.0306	0.3081	0.0050
						Sr-Ti			0.0213	0.0003
						Ti-O			1.5591	0.0253
SiC-2H	4	<i>P6₃mc</i> (No 186)	3.0760, 3.0760, 5.0480	90°, 90°, 120°	41.3640	Si-C	2.9074	0.0692		
SiC-4H	8	<i>P6₃mc</i> (No 186)	3.0760, 3.0805, 10.0848	90°, 90°, 120°	82.8787		5.9092	0.0704		
SiC-6H	12	<i>P6₃mc</i> (No 186)	3.0950, 3.0950, 15.1700	90°, 90°, 120°	125.8454		8.8608	0.0703		
SiC-3C	8	<i>F-43m</i> (No 216)	4.3480, 4.3480, 4.3480	90°, 90°, 90°	82.1993		5.8384	0.0695		

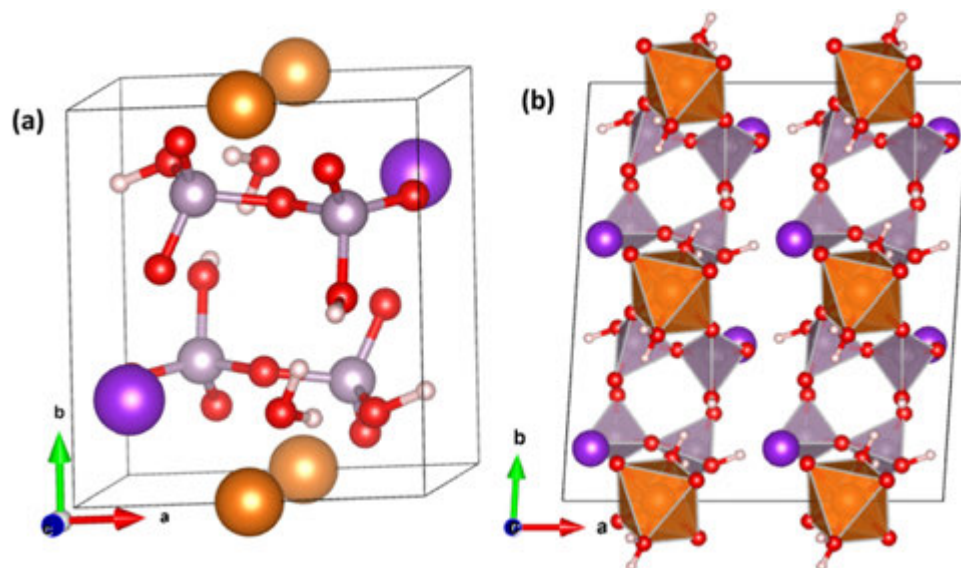


Fig. 4 (a) Ball and stick diagram for pyrophosphate crystal $K_2Mg(H_2P_2O_7)_2 \cdot 2H_2O$; (b) polyhedral diagram for $2 \times 2 \times 2$ supercell. MgO_6 octahedra, PO_4 tetrahedra are shown in a two different color. Dark purple sphere for K, small red sphere for O and small white sphere for H.

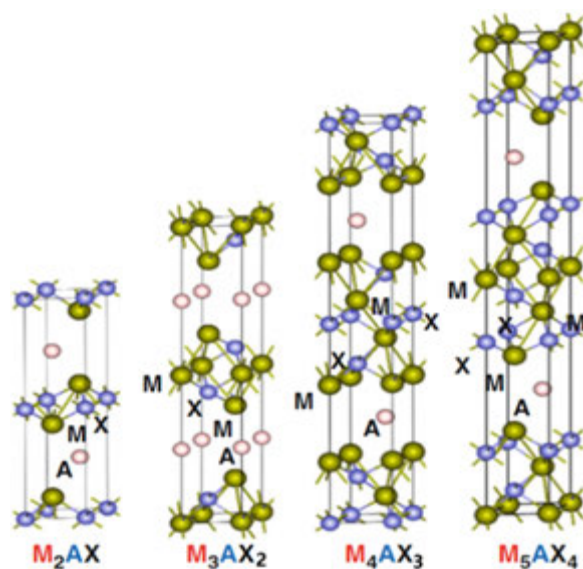


Fig. 5 Structure of four $M_{n+1}AX_n$ phases M_2AX , M_3AX_2 , M_4AX_3 , M_5AX_4 (i.e., $n = 1, 2, 3, 4$).

sensing and laser power delivery (Liu *et al.*, 2016; Zhang *et al.*, 2015; Dai *et al.*, 2015; Mirov *et al.*, 2015). They are used in optical fibers, solar cells and optoelectronics as well as in bio-medical applications. First-principles calculations of the electronic structure, optical and mechanical properties of 25 chalcogenide crystals: Ag_2S , Ag_2Se , Ag_2Te , As_2S_3 , As_2Se_3 , As_2Te_3 , As_4Se_4 , Cu_2S , Cu_2Se , Cu_2Te , Cu_4GeS_4 , Cu_2SnS_3 , Cu_2SnSe_3 , GeS_2 , $GeSe_2$, Ge_4Se_9 , Sb_2S_3 , Sb_2Se_3 , Sb_2Te_3 , SnS , $SnSe$, $CdSe$, $CdTe$, $ZnSe$ and $ZnTe$ have been carried out recently (Hasan *et al.*, unpublished) using the methodology outlined in Section 2. Extensive DFT calculations of the electronic structure, interatomic bonding, optical and mechanical properties of a large number of chalcogenide crystals within one method in relation to TBOD enable us to reveal several new findings and hidden correlations on their properties. This could facilitate the exploration and development of new chalcogenide glasses for potential new applications. Table 6 lists the names and structures of these 25 crystals together with some of the calculated properties including the TBOD. In Fig. 12 we plot the distribution of all the BO vs BL pairs in the 25 crystals. No trend or special features can be identified since the composition, structure and bonding in these crystals can be significantly different. However, the TBOD for each of the 25 crystals provides a new perspective. Fig. 13 shows the TBOD of these crystals divided into 8 groups are generally controlled by the first atomic element in the formula (Ag, Cu, As, Ge, Sb, Sn, Cd and Zn) and less on the chalcogen elements (S, Se, Te). It shows that groups lead by Cu or

Table 3 TBOD for the 68 confirmed MAX phases

211											
1	Sc ₂ InC	0.0223	13	Cr ₂ GaC	0.0428	25	Hf ₂ TiC	0.0261	37	Nb ₂ GeC	0.0306
2	Ti ₂ AlC	0.0383	14	Cr ₂ GaN	0.0373	26	Hf ₂ AlC	0.0297	38	Hf ₂ SnC	0.0271
3	Ti ₂ AlN	0.0371	15	Zr ₂ AlC	0.0278	27	Ta ₂ AlC	0.0428	39	Hf ₂ SnN	0.025
4	Ti ₂ GaC	0.038	16	Zr ₂ InC	0.0258	28	Ta ₂ GaC	0.0421	40	Hf ₂ PbC	0.0248
5	Ti ₂ GaN	0.0364	17	Zr ₂ InN	0.0246	29	Ti ₂ GeC	0.0371	41	V ₂ PC	0.0432
6	Ti ₂ InC	0.0342	18	Zr ₂ TiC	0.0248	30	Ti ₂ SnC	0.0333	42	V ₂ AsC	0.0386
7	Ti ₂ InN	0.0322	19	Zr ₂ TiN	0.0233	31	Ti ₂ PbC	0.0298	43	Nb ₂ PC	0.0318
8	Ti ₂ TiC	0.0324	20	Nb ₂ AlC	0.0326	32	V ₂ GeC	0.0386	44	Nb ₂ AsC	0.0295
9	V ₂ AlC	0.0424	21	Nb ₂ GaC	0.0317	33	Cr ₂ GeC	0.0394	45	Ti ₂ SC	0.0386
10	V ₂ GaC	0.041	22	Nb ₂ InC	0.0291	34	Zr ₂ SnC	0.0258	46	Zr ₂ SC	0.0275
11	V ₂ GaN	0.0369	23	Mo ₂ GaC	0.0399	35	Zr ₂ PbC	0.0237	47	Nb ₂ SC	0.028
12	Cr ₂ AlC	0.0451	24	Hf ₂ InC	0.0274	36	Nb ₂ SnC	0.0279	48	Hf ₂ SC	0.0293
312			412								
49	Ti ₃ AlC ₂	0.0423	61	Ti ₄ AlN ₃	0.0418						
50	Ti ₃ GaC ₂	0.0422	62	Ti ₄ GaC ₃	0.0445						
51	Ti ₃ InC ₂	0.0391	63	V ₄ AlC ₃	0.0488						
52	V ₃ AlC ₂	0.0464	64	Nb ₄ AlC ₃	0.0355						
53	Zr ₃ AlC ₂	0.03	65	Ta ₄ AlC ₃	0.0481						
54	Hf ₃ AlC ₂	0.032	66	Ta ₄ GaC ₃	0.0478						
55	Ta ₃ AlC ₂	0.0466	67	Ti ₄ SiC ₃	0.0456						
56	Ti ₃ SiC ₂	0.0435	68	Ti ₄ GeC ₃	0.0441						
57	Ti ₃ GeC ₂	0.0416									
58	Ti ₃ SnC ₂	0.0385									
59	Zr ₃ SnC ₂	0.0285									
60	Hf ₃ SnC ₂	0.0301									

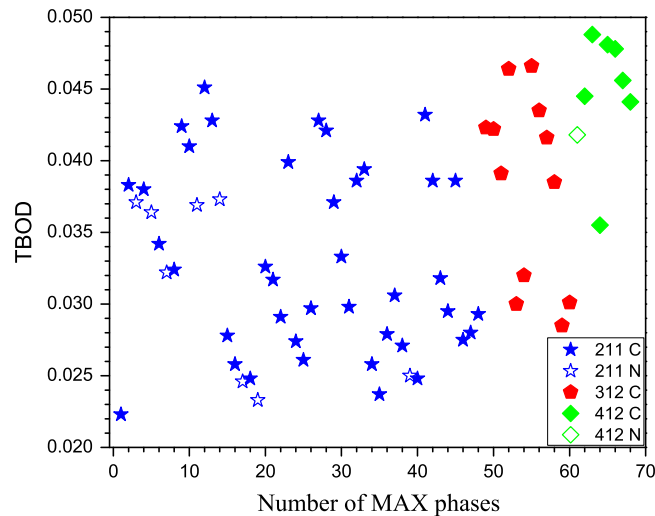


Fig. 6 TBOD of 68 confirmed MAX Phases listed in Table 3. Solid symbols are carbides and open symbols are nitrides.

Table 4 List of 20 CS and CSH crystals divided into four groups

	Mineral name	Sym/space group	Chemical formula	Ca/Si	ρ (g/cc)	TBOD($e/\text{\AA}^3$)
(a)	Clinker/Hydroxide					
a.1	Belite	O:P121/n1	$2(\text{CaO})\text{SiO}_2$	2	3.316	0.0226
a.2	Alite	M:P-1	$3(\text{CaO})\text{SiO}_2$	3	3.084	0.0197
a.3	Portlandite	M:P-3m1	$\text{Ca}(\text{OH})_2$	N/A	2.668	0.0177
(b)	Nesosubsilicates					
b.1	Afwillite	M:P1	$\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$	1.5	2.59	0.0243
b.2	α -C2SH	O:P21/b21/c21/a	$\text{Ca}_2(\text{HSiO}_4)(\text{OH})$	2	2.693	0.0216
b.3	Dellaite	Tc:P-1	$\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{SiO}_4)(\text{OH})_2$	2	2.929	0.0210
b.4	Ca Chondrodite	M:P1121/b	$\text{Ca}_5[\text{SiO}_4]_2(\text{OH})_2$	2.5	2.828	0.0194
(c)	Sorosilicates					
c.1	Rosenhahnite	Tc:P-1	$\text{Ca}_3\text{Si}_3\text{O}_8(\text{OH})_2$	1	2.874	0.0241
c.2	Suolunite	O:Fd2d	$\text{Ca}_2[\text{Si}_2\text{O}_5(\text{OH})_2]\text{H}_2\text{O}$	1	2.649	0.0255
c.3	Kilchoanite	O:I2cm	$\text{Ca}_6(\text{SiO}_4)(\text{Si}_3\text{O}_{10})$	1.5	2.937	0.0209
c.4	Killalaite	M:P121/m1	$\text{Ca}_{6.4}(\text{H}_{0.6}\text{Si}_2\text{O}_7)_2(\text{OH})_2$	1.6	2.838	0.0217
c.5	Jaffeite	Tg:P3	$\text{Ca}_6[\text{Si}_2\text{O}_7](\text{OH})_6$	3	2.595	0.0192
(d)	Inosilicates					
d.1	Nekoite	Tc:P1	$\text{Ca}_3\text{Si}_6\text{O}_{15} \cdot 7\text{H}_2\text{O}$	0.5	2.204	0.0240
d.2	T11Å	M:B11m	$\text{Ca}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$	0.67	2.396	0.0248
d.3	T14Å	M:B11b	$\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$	0.83	2.187	0.0226
d.4	T9Å	Tc:C1	$\text{Ca}_5\text{Si}_6\text{O}_{17} \cdot 5\text{H}_2\text{O}$	0.83	2.579	0.0247
d.5	Wollastonite	Tc:P-1	$\text{Ca}_3\text{Si}_3\text{O}_9$	1	2.899	0.0224
d.6	Xonotlite	Tc:A-1	$\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$	1	2.655	0.0214
d.7	Foshagite	Tc:P-1	$\text{Ca}_4(\text{Si}_3\text{O}_9)(\text{OH})_2$	1.33	2.713	0.0211
d.8	Jennite	Tc:P-1	$\text{Ca}_9\text{Si}_6\text{O}_{18}(\text{OH})_6 \cdot 8\text{H}_2\text{O}$	1.5	2.310	0.0223

Ag have high TBOD where as those lead by As, Sb, Sn and Cd have low TBOD. Such deep insight can only be revealed by calculating the TBOD, or the geno for each chalcogenide crystal. It is anticipated that additional calculations on other chalcogenide crystals will make a reasonable size database to be even more useful.

IGF Models

Ceramic materials are usually polycrystalline and contain many types of defects. One of the defective structures that is ubiquitous in Si_3N_4 and SiC is a thin layer of glassy matter, approximately 1–3 nm thick situated between different crystalline grains in the sintered samples (Clarke, 1987; Tanaka *et al.*, 1994; Subramaniam *et al.*, 2006; Kleebe, 1992). These so-called intergranular glassy films (IGFs) are the key factor in controlling the mechanical properties of Si_3N_4 . The glassy film contains a varying mixture of Si, O, and N with an almost constant thickness depending on sintering adds. The films can intersect at triple junctions of the

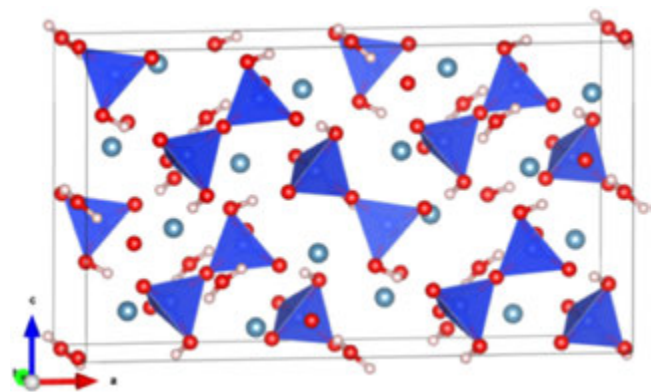


Fig. 7 Ball-stick figure of Suolunite crystal.

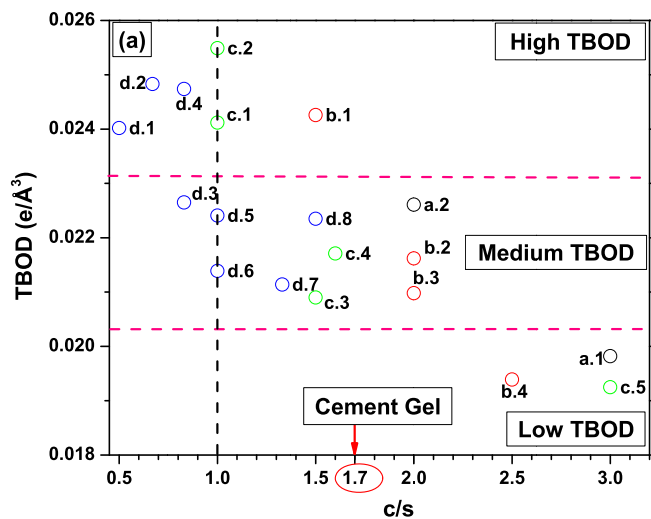


Fig. 8 Total bond order density vs C/S ratio in 19 crystals. (Portlandite (a.3) is excluded since it has no Si atoms.) Each data point is described in Table 4.

Table 5 Comparison of structures and properties Suolunite, thaumasite and Ettringite

Properties	Suolunite	Thaumasite	Ettringite (1 × 1 × 2 supercell)
Water molecules	1	12	104
Crystal System	Orthorhombic	Hexagonal	Trigonal
TBOD (e/Å ³)	0.025	0.024	0.022
K (GPa)	75.3	40.45	32.55
G (GPa)	50.1	19.53	16.54
E (GPa)	123.0	50.46	42.44
η (Poisson's ratio)	0.23	0.29	0.28
Unit cell volume	1355.92 Å ³	1115.11 Å ³	4739.61 Å ³
Mass density	1.583 g cm ⁻³	1.264 g cm ⁻³	1.061 g cm ⁻³
No of atoms	128	122	500

polycrystalline grains. Based on a previously constructed IGF model for bulk β -silicon nitride (Yoshiya *et al.*, 2002) a large periodic model of 3864 atoms (1152 Si, 1536 N in the crystalline part and 432 Si, 240 N, and 504 O in the glassy region) containing two grains of opposite orientations and two IGFs was fully relaxed using the *ab initio* density-functional theory (Ching *et al.*, 2018). Fig. 14 shows the sketch of the structure of this IGF model in 2-dimension showing the regions for bulk β -Si₃N₄ grain, the IGF region and their interfacial transition regions. This is a much larger and realistic IGF model than previous studied IGF models by us

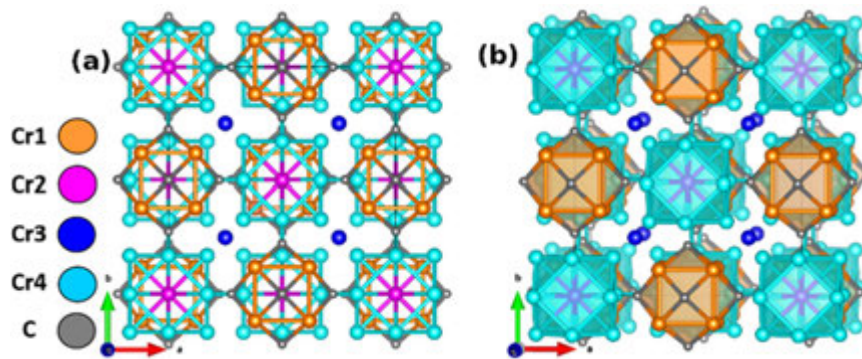


Fig. 9 (a) Crystal structure of cubic $\text{Cr}_{92}\text{C}_{24}$ viewed in 2 directions and sketches: (a) ball and stick and (b) polyhedral form.

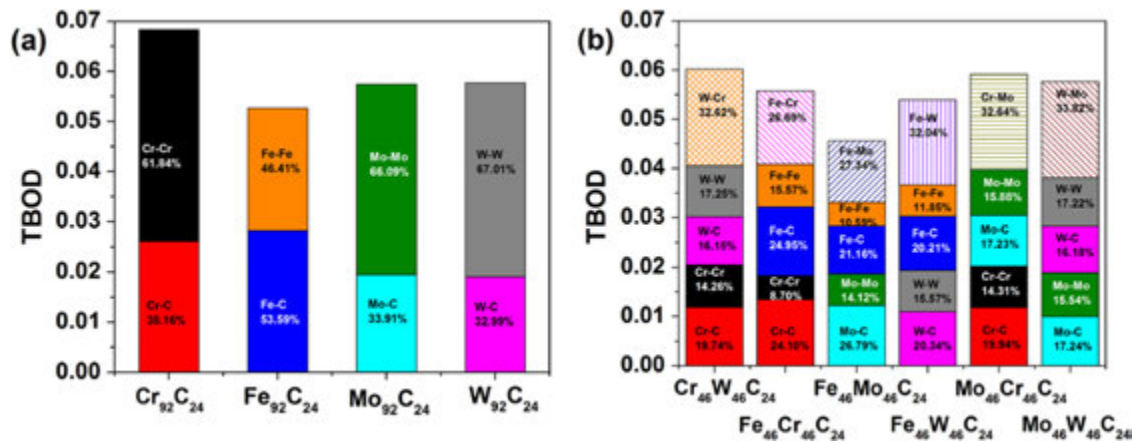


Fig. 10 TBOD for (a) binary and (b) ternary transition metal carbides. The bar graphs with different colors show the percent contribution from different pairs PBODs.

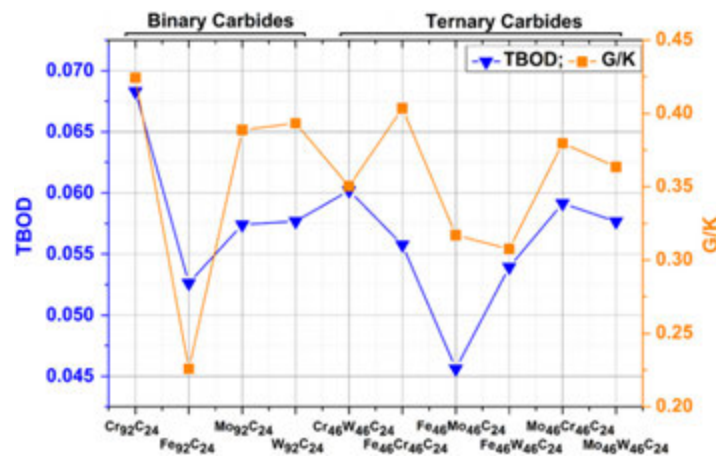


Fig. 11 Total bond order density and G/K ratio for the binary and ternary carbides with each crystal labeled in the x-axis.

with identical interfaces within the models and contain only one IGF in order to maintain the periodicity of the model (Ching *et al.*, 2010; Rulis *et al.*, 2005; Chen *et al.*, 2005; Ching *et al.*, 2006a; Misra *et al.*, 2007; Ching *et al.*, 2009).

The electronic structure, density of states, interatomic bonding, partial charge distribution for this large IGF model are obtained and analyzed focusing on the interfacial regions between bulk $\beta\text{-Si}_3\text{N}_4$ and the Si-O-N glass layer with different orientations (Ching *et al.*, 2018). All the interatomic bond pairs and BO values are calculated and fully analyzed. Fig. 15 shows the distribution of BO vs BL in this IGF model where the location of these bonds in the model are designated with different symbols and colors.

Table 6 Calculated TBOD and properties band gap E_g , (D, direct; ID, indirect), effective charge Q^* (atom), refractive index n and Plasmon frequency ω_p) in 25 chalcogenide crystals

<i>Crystal</i>	E_g (eV)	<i>Average Q^* (in e^-)</i>	<i>TBOD ($e^-/\text{\AA}^3$)</i>	n, ω_p (eV)
Ag ₂ S	0.823(ID)	10.858(Ag), 6.283(S)	0.01394	2.960, 19.99
Ag ₂ Se	0.298(ID)	10.875(Ag), 6.248(Se)	0.01455	4.580, 18.49
Ag ₂ Te	0.000	11.005(Ag), 5.990(Te)	0.01412	4.700, 16.49
As ₂ S ₃	1.906(ID)	4.506(As), 6.329(S)	0.0059	2.290, 18.19
As ₂ Se ₃	1.523(ID)	4.664(As), 6.223(Se)	0.0058	3.090, 18.29
As ₄ Se ₄	1.494(ID)	4.809(As), 6.190(Se)	0.00717	2.770, 17.69
As ₂ Te ₃	0.627(ID)	4.951(As), 6.032(Te)	0.00508	6.010, 17.49
Cu ₂ S	0.299(D)	10.908(Cu), 6.182(S)	0.02566	3.670, 20.99
Cu ₂ Se	0.530(D)	10.984(Cu), 6.030(Se)	0.02225	4.120, 19.99
Cu ₂ Te	0.000	11.158(Cu), 5.683(Te)	0.02858	5.470, 16.99
Cu ₄ GeS ₄	0.201(D)	10.930(Cu), 3.384(Ge), 6.223(S)	0.02234	3.430, 20.19
Cu ₂ SnS ₃	0.016	11.027(Cu), 3.070(Sn), 6.291(S)	0.01996	3.930, 19.49
Cu ₂ SnSe ₃	0.015	11.047(Cu), 3.274(Sn), 6.210(Se)	0.01703	4.410, 18.99
GeS ₂	2.484(D)	3.337(Ge), 6.331(S)	0.01178	2.280, 17.99
GeSe ₂	1.800(D)	3.534(Ge), 6.232(Se)	0.00989	2.450, 17.49
Ge ₄ Se ₉	1.375(D)	3.554(Ge), 6.198(Se)	0.00932	2.480, 17.99
Sb ₂ S ₃	1.050(D)	4.242(Sb), 6.505(S)	0.00604	3.780, 18.29
Sb ₂ Se ₃	0.550(ID)	4.362(Sb), 6.425(Se)	0.00535	4.310, 17.99
Sb ₂ Te ₃	0.236(ID)	4.637(Sb), 6.241(Te)	0.00471	7.070, 17.39
SnS	0.112(D)	3.481(Sn), 6.518(S)	0.00534	5.010, 16.29
SnSe	0.092(D)	3.525(Sn), 6.474(Se)	0.00509	5.650, 14.99
CdSe	1.64(D)	0.584(Cd), 7.415(Se)	0.00473	2.29, 17.89
CdTe	1.97(D)	0.626(Cd), 7.374(Te)	0.00399	2.35, 16.1
ZnSe	1.57(D)	11.705(Zn), 6.294(Se)	0.02016	2.7, 17.4
ZnTe	1.92(D)	11.95(Zn), 6.05(Te)	0.01786	2.8, 16.5

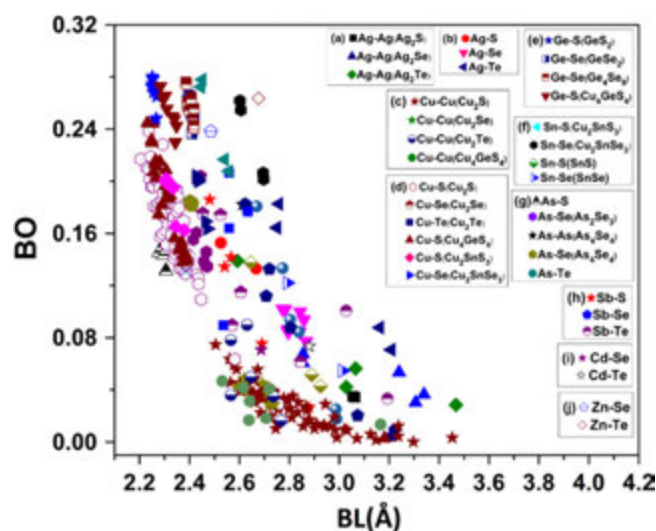


Fig. 12 BL vs BO in 25 chalcogenide crystals listed in [Table 6](#).

This illustrates the versatility of using the BO concept to relate to their physical structure and properties. We have further calculated its mechanical properties of the model (Adhikari *et al.*, 2019b) in order to link the subtle connections to TBOD and PBOD to its mechanical properties, and to demonstrate the use of TBOD in applying to systems beyond the simpler crystalline phases. The TBOD of the IGF is $0.0512 \text{ e}^-/(\text{\AA})^3$ and can be compared with the TBOD of crystalline $\alpha\text{-Si}_3\text{N}_4$, $\beta\text{-Si}_3\text{N}_4$, $\text{c-Si}_3\text{N}_4$ and $\text{Si}_2\text{N}_2\text{O}$ listed in Table 1 in Section 3.1 above. The TBOD for $\beta\text{-Si}_3\text{N}_4$ and $\text{Si}_2\text{N}_2\text{O}$ are $0.0512 \text{ e}^-/(\text{\AA})^3$ and $0.0432 \text{ e}^-/(\text{\AA})^3$ respectively. This seems to suggest that the IGF model has retained its crystalline TBOD. Apparently, the weaker PBOD within the glassy region is compensated by the increase in the PBOD at the interfacial region. This appears to be a natural explanation as to why the presence of IGF in structural ceramics such as silicon nitrides and Si carbides are ubiquitous.

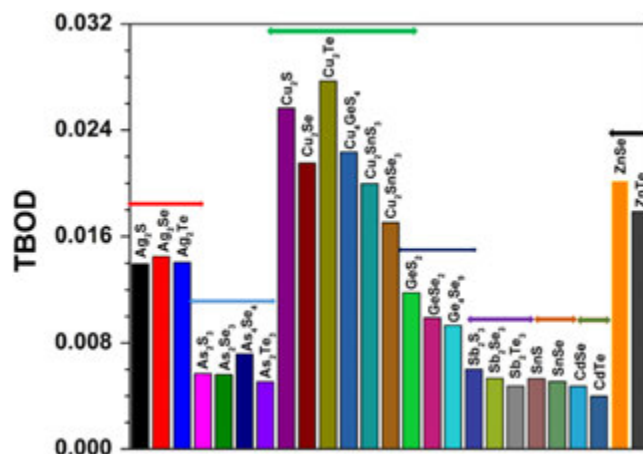


Fig. 13 Distribution of total bond order density for 25 chalcogenide crystals in eight groups.

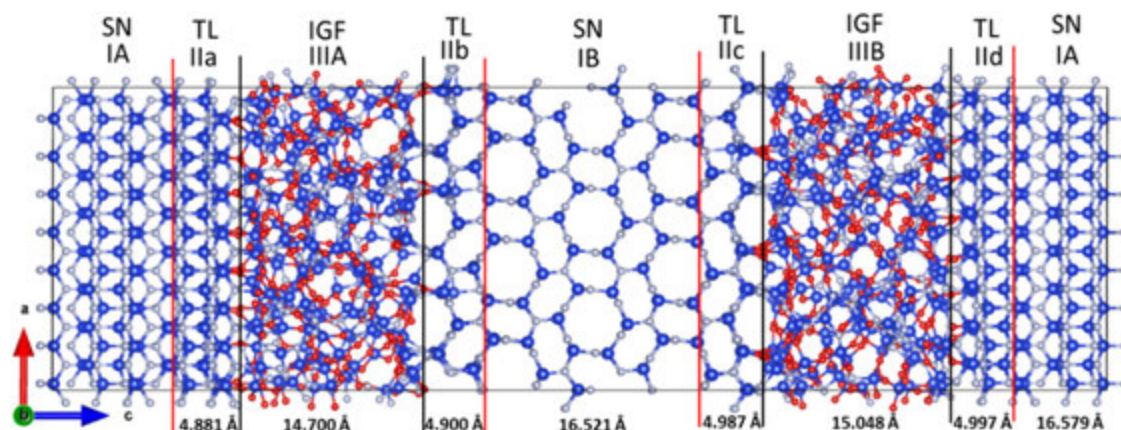


Fig. 14 Ball and stick sketch of the relaxed IGF model with the division into different regions and their width in Å centered at bulk crystal region IB. Si: blue, N: gray and O: red.

Application of TBOD Different Glasses

Insulating Glasses

Over the years, we have done a lot of research related to amorphous SiO_2 (a- SiO_2). In recent years, we rely on the concept of TBOD for interpretations on various doped and hydrated silicate glasses with more complex structures. It all started with a periodic model with 54 SiO_2 molecules (Ching, 1981). The beauty of this model is it has small bond angle (BA) and bond length (BL) distortions, a near ideal distribution of ring structure and no over- or under-coordinated Si or O atoms. Such model is very difficult to construct because of the strong directional Si-O bonds across the periodic boundary. This model was later expanded to a $2 \times 2 \times 2$ supercell with 1296 atoms with other additional refinements, making it an ideal model for many studies on a- SiO_2 and related glasses (Li *et al.*, 2014; Baral *et al.*, 2017; Baral and Ching, 2017; Baral *et al.*, 2019; Huang and Ching, 1996).

With the development of the novel concept of TBOD within last years, application of TBOD to silicate and other glasses is obvious. Simultaneously, the adoption of *ab initio* molecular dynamics (AIMD) makes the reliance on the original 162-atom a- SiO_2 model less important and the size of more complex models can be made more flexible since AIMD simulation with more than 1000 atoms is still impractical. In the following, we provide examples of specific application of TBOD to several insulating glasses.

An obvious extension from the well-studied near-perfect continuous random network (CRN) a- SiO_2 model with 1296 atoms is the systematic replacement of Si by Ge to amorphous $\text{Si}_{1-x}\text{Ge}_x\text{O}_2$ models with x ranging from 0 to 1 (Baral *et al.*, 2016). The x -dependence of the variations of the properties are analyzed and critically compared with available experimental data. The mass density, volume, TBOD, bulk mechanical properties and refractive index are found to vary linearly as a function of x . For $x = 0.5$, we constructed six different kinds of particle immersion models to test the effect of inclusion of spherical particles of different sizes

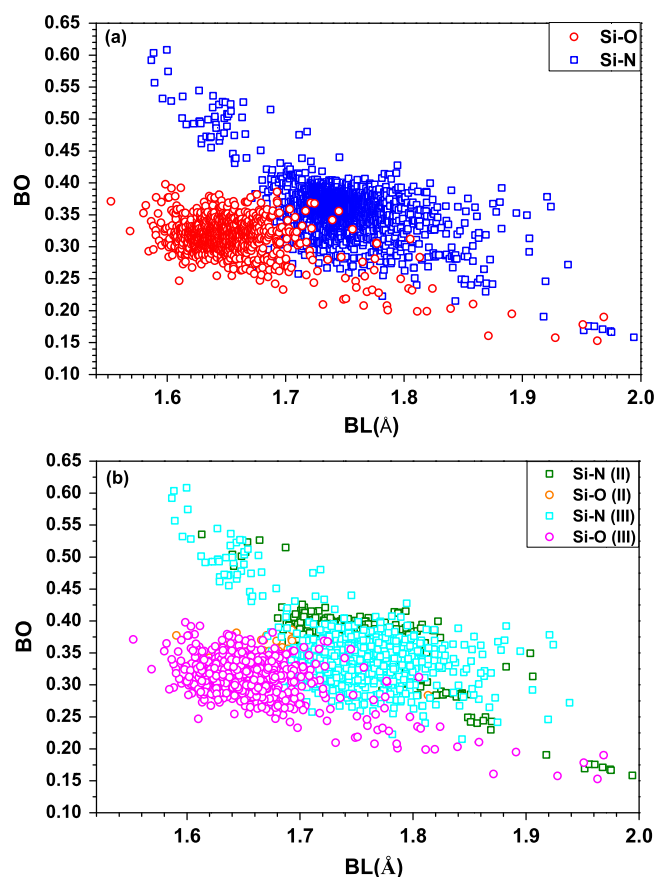


Fig. 15 (a) BO vs BL distributions for all atomic pairs in the relaxed IGF model. (b) Same plot as (a) but with bond pairs from the bulk region removed showing on those in the IGF (region III) and in the transition layer (region II).

of one glass in the medium of the other glass. This is illustrated in **Fig. 16**. The results show that particle size does affect the properties of particle immersion. These calculations provide a deep insight on the properties of mixture and nanocomposites of a-SiO₂ and a-GeO₂ and the role of the TBOD in affecting their properties originating from the slight difference in Si-O and Ge-O bonding.

AIMD has been applied to construct seven sodium silicate glass models with Na₂O concentration ranging from 0 to 50 mol % (Baral and Ching, 2017). All models are based on the 162 atom near-perfect CRN model for a-SiO₂ introduced earlier which facilitates the model construction. AIMD is necessary since the introduction of Na ions disrupts the network structure and their interactions. The structure of the simulated (Na₂O)_x(SiO₂)_{1-x} glasses are critically analyzed and validated by experimental data. The TBOD is used to characterize the internal cohesion of sodium silicate glass, which decreases with the increasing Na content as shown in **Fig. 17**. The calculated mass density and refractive index increase with *x* while the band gap decreases with *x* which are in good agreement with experimental data. The calculated mechanical properties of these models indicate that alkali-silicate glass tends to be unstable for *x* greater than 0.4 due to total destruction of the SiO₂ network consistent with the TBOD data.

The AIMD simulation on Na₂O-doped glasses was extended to models of Li- and K-doped single and mixed alkali silicate glasses with two different molar concentrations of alkali oxides. The structural environments and spatial distributions of alkali ions in the 10 simulated models with 20% and 30% of Li, Na, K and Li-Na, Na-K in equal proportions were studied for subtle variations among these models. Results on the electronic structures, interatomic bonding, mechanical and optical properties are compared with other simulations and are in good agreement with the experimental data. TBOD is used to characterize the internal cohesion in these alkali-doped models and to explain the mixed alkali effect (MAE) in their bulk mechanical properties, but is less obvious in other physical properties studied (Baral et al., 2017). It is also shown that Li-doping deviates from expected trend due to the much stronger Li-O bonds than those of Na-O and K-O bonds. The approach we used in alkali-doped silicate glasses is in contrast with other existing studies that are based purely on geometric characterizations. The study on alkali-doped Silicate models was further extended to include the effect of water (Baral et al., 2019). Silica-water interaction plays an essential role for the mechanical strength and chemical durability of alkali-doped silicate glasses. It was confirmed that water in the solvated bulk models can either dissociate or remain as H₂O molecule depending on the local distribution and specific alkali elements. We also confirmed that the mechanical strength of bulk alkali silicate glasses is enhanced by hydration with some evidence that mixing of

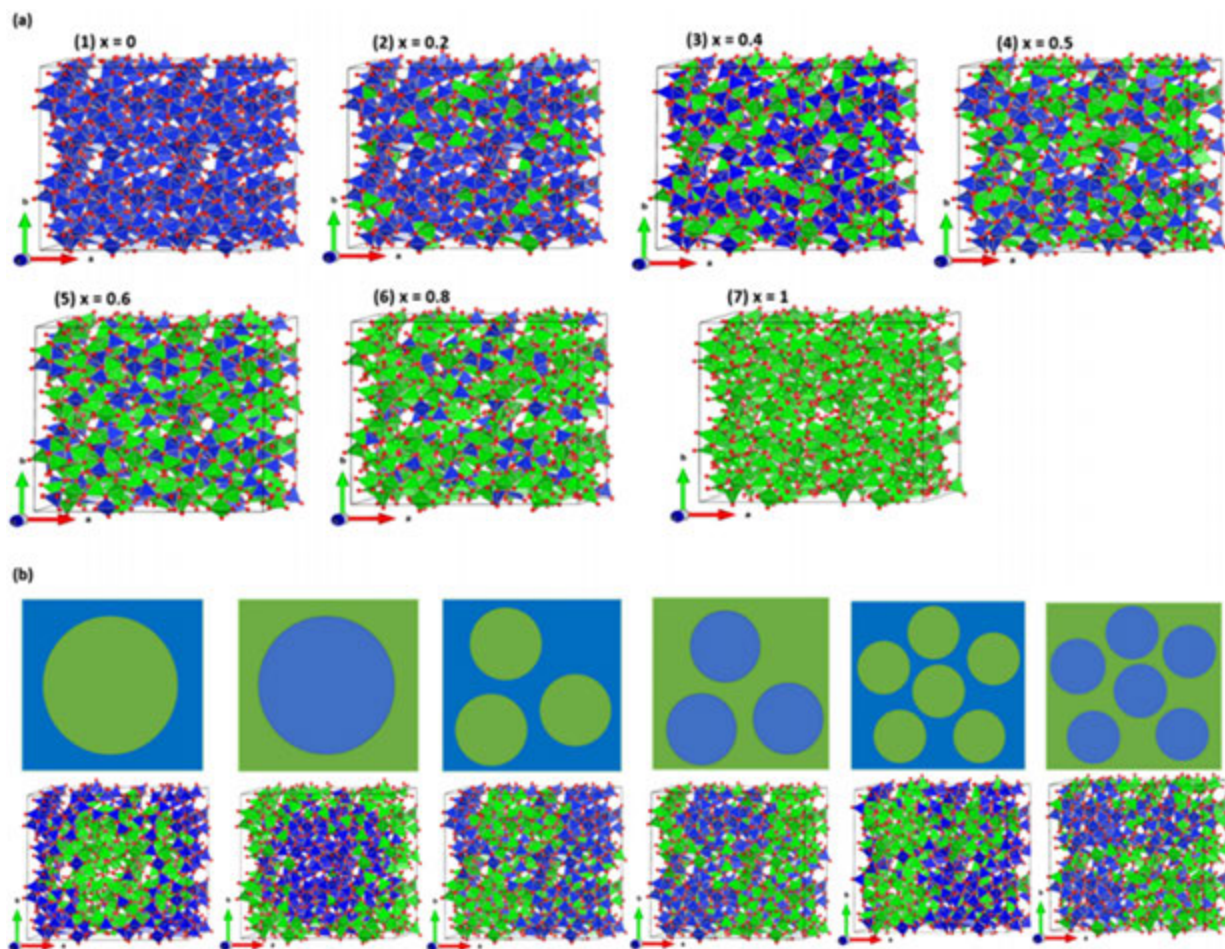


Fig. 16 (a) Polyhedral structures of Part I for $(a\text{-SiO}_2)_{1-x}(a\text{-GeO}_2)_x$ glass, $0 \leq x \leq 1$. (b) Two dimensional and three dimensional illustration of 6 models of Part II for spherical particle inclusion of one glass into the medium of other glass.

alkali ions tends to degrade the strength of the hydrated glasses. Again, TBOD is used here as a key parameter to unravel the atomistic origin of the internal cohesion and strength of glasses in different environments.

The above studies are further extended to even more complex glasses by adding Al_2O_3 to the Na-doped silicate glasses (Baral *et al.*, unpublished), or the sodium aluminosilicate (NAS) glasses. In this case, AIMD simulation with larger models of about 700 atoms are necessary. Four such NAS glass models $(\text{SiO}_2)_{0.6}(\text{Al}_2\text{O}_3)_{0.4-x}(\text{Na}_2\text{O})_x$ for $x = 0, 0.135, 0.20$ and 0.24 corresponding to ratio Na/Al ratio of 0.0, 0.5, 1.0 and 1.5 are constructed. The electronic structure, bonding, partial charge, mechanical and optical properties of these models are calculated and analyzed in detail. These results enable us to understand the role played by Al and Na in silicate glass network and the changes in glass properties when glass composition varies. We also find that the silica network can largely recover after removing the Al_2O_3 component but with weakened internal cohesion and strength compared to pure silicate glass as characterized by TBOD.

The above examples simply demonstrate the effectiveness of using TBOD as the geno for insulating glasses, a step beyond in applying just to ceramic crystals. In the following, we further demonstrate the application of TBOD to another very different type of glasses, the metallic glasses.

Metallic Glasses

$\text{Zr}_x\text{Cu}_{1-x}$ and $\text{Zr}_x\text{Cu}_y\text{Al}_z$

Metallic glasses (MG) are another class of non-crystalline materials but completely different from the insulating glasses discussed above. This is because metallic bonding is multi-atomic in nature, completely different from the covalent or ionic bonding where the definition of BL is well-accepted as the distance between the two atoms that form the bond. In MG, the geometric parameter of BL has no meaning since all atoms within certain distance of separation can contribute to metallic bonding. As such, any theory or scheme based on the geometric parameter of BL is ill-defined. This is a highly contentious issue in MG community that is still hotly debated. However, the concept of TBOD, being a quantum mechanical metric, still applies without any compromise as long as all the BO values of the contributing atoms nearby are counted. This point has already been strongly argued for in reference (Ching 2019) with examples. Here we reiterate them and

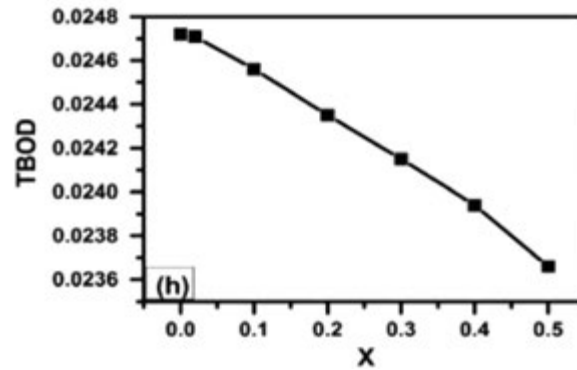


Fig. 17 TBOD vs x in $(\text{Na}_2\text{O})_x(\text{SiO}_2)_{1-x}$ glasses.

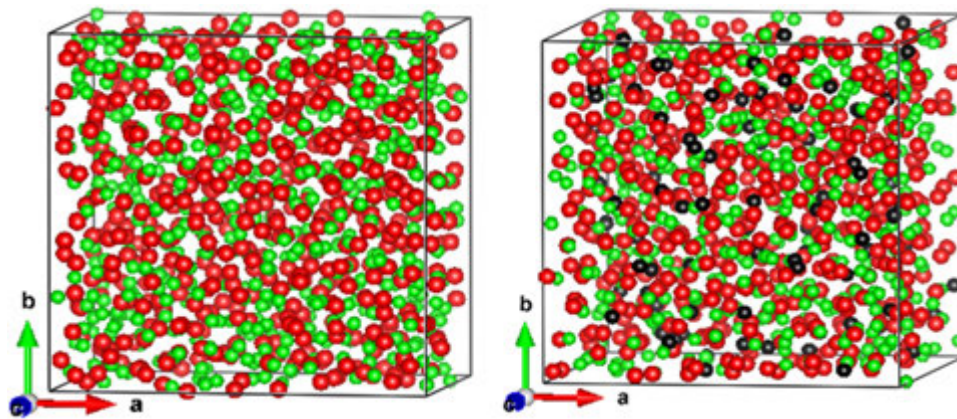


Fig. 18 Illustrative sketch of models for $\text{Zr}_{50}\text{Cu}_{50}$ (left) and $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ (right). Red, Zr; Green, Cu; Black, Al.

with some additional evidences. The two MG systems discussed here are (1) binary $\text{Zr}_x\text{Cu}_{1-x}$ glass ($x = 0.32 - 0.54$) and (2) ternary $\text{Zr}_x\text{Cu}_y\text{Al}_z$ glass. All models have 1024 atoms and fully relaxed using VASP without any volume constraint. The initial starting model is generated from quenching with classical MD. The electronic structure and interatomic bonding of these MG models are fully calculated (Ching, 2019). Fig. 18 shows the ball and stick sketch for $\text{Zr}_{50}\text{Cu}_{50}$ and $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$. For both MG models, additional simulations were carried out for the MG under compression by reducing the volume of the cell 5% and 10% respectively. In Table 7, we list the TBOD for of $\text{Zr}_{50}\text{Cu}_{50}$ and $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ (p0 for the equilibrium model and p1, p2 their compressed models). It can be seen that the TBOD is increased when under compression.

In Fig. 19 we show the BO vs BL plots for the two MG models $\text{Zr}_{50}\text{Cu}_{50}$ and $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$. Here we must emphasize that the “BL” refers to distance of separation between 2 metallic atoms whereas the BO is calculated by summing the contributions to the metallic bonding from all other metallic ions within the distance of 4.5 Å of these two atoms. These plots clearly shows that for a fixed “BL” there are many possible BO values, and for a fixed BO value, there could be a range of “BL” or the distances of many atomic pairs having this BO value. This fact unequivocally refute any assertion of using geometric BL in MG in describing their structure and structural units.

Fig. 12 shows the dependence of TBOD on x for the binary $\text{Zr}_x\text{Cu}_{1-x}$ glass. The TBOD steadily decrease as x increases but not in a perfect linear dependence indicating that TBOD can reflect more hidden details in the variation. This has been discussed in Ching (2019) in comparison of some experimental observations (Li et al., 2008) based on preliminary data.

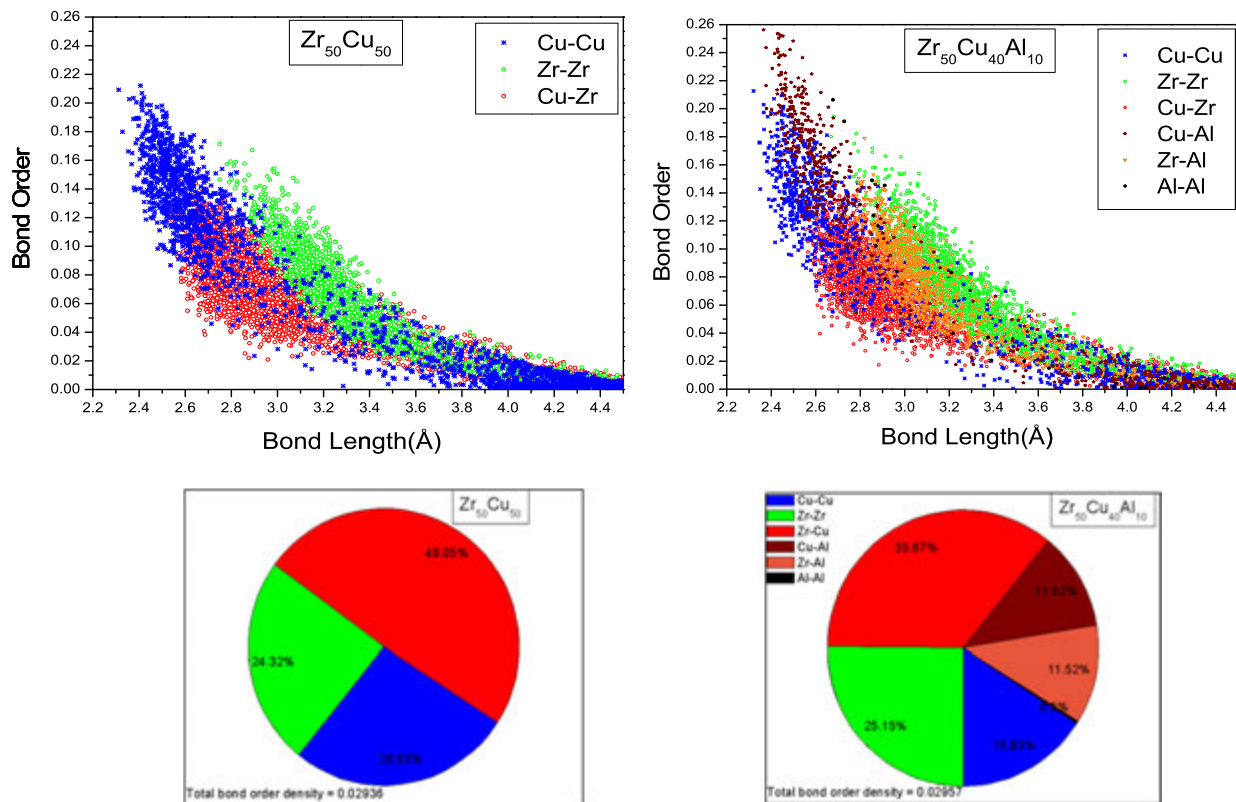
Atomic scale investigation beyond using classical parameters for structural characterization in MG is still in the early stage of development. There are tremendous opportunities in research on MB with 2-D structures or with crystallite inclusions as precipitates. All such expansion in the scope of research will expand the range of applications not envisioned, but certainly require will high-level analysis and modeling using the new concept of TBOD and PBOD (Fig. 20).

Vitreloy ($\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$)

Vitreloy is a special class of MG also coined as bulk metallic glasses (BMG). It was first reported in 1993 (Peker and Johnson, 1993) due to the desirable ability to form in bulk instead of thin ribbon using fast cooling (Jun et al., 1960). We reported the structure and electronic bonding for a particular BMG vitreloy ($\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$) (Hunca et al., 2016). For such multi-component BMG,

Table 7 TBOD and PBOD of $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{50}\text{Zr}_{50}\text{Al}_{10}$ metallic glasses at pressures P0, P1 and P2

Pair		PBOD and TBOD ($e/\text{\AA}^3$)		
		P0	P1	P2
$\text{Cu}_{50}\text{Zr}_{50}$	Cu-Cu	0.00778	0.00813	0.00848
	Zr-Cu	0.01437	0.01467	0.01495
	Zr-Zr	0.00729	0.00750	0.00771
	Total	0.02945	0.03030	0.03114
$\text{Cu}_{50}\text{Zr}_{50}\text{Al}_{10}$	Cu-Cu	0.00471	0.00491	0.00512
	Zr-Cu	0.01069	0.01091	0.01113
	Zr-Zr	0.00740	0.00763	0.00785
	Al-Al	0.00011	0.00011	0.00012
	Cu-Al	0.00340	0.00354	0.00370
	Zr-Al	0.00341	0.00351	0.00360
	Total	0.02971	0.03062	0.03152

**Fig. 19** BO vs BL in $\text{Zr}_{50}\text{Cu}_{50}$ (top left) and $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ (top right). Percentage of the TBOD components in $\text{Zr}_{50}\text{Cu}_{50}$ (lower left) and $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ (lower right).

classical MD is not useful since reliable potential is nonexistent and accurate AIMD simulations is the only way. The size of the model was limited to 512 atoms. **Fig. 21** shows the sketch of this vitreoloy model and **Fig. 22** display the total and partial pair distribution function for this vitreoloy, which is in good agreement with experiment (Gerold *et al.*, 1999). Detailed calculation of the electronic structure and bonding at the DFT level was obtained for the first time (Hunca *et al.*, 2016).

Fig. 23 shows the calculated total and atom-resolved PDOS for this model. **Fig. 24** is a Pei chart showing the contributions to the TBOD from all pairs of atoms in vitreoloy. It is not surprising to see that Zr-Zr and Zr-Cu have the highest percentage of contribution to TBOD since they have the top two atomic composition. But the Zr-Ti pair has 12.64% contribution compare to only 8.38% from Zr-Cu pair even though Ti has far less atomic percentage of only 3.8% compared to 12.5% for Cu. This can only be attributed to the strong Zr-Ti bond compared to Zr-Cu bond. We again use this example to advocate the use of TBOD and PBOD to characterize the interatomic bonding in multi-component glasses such as vitreoloy.

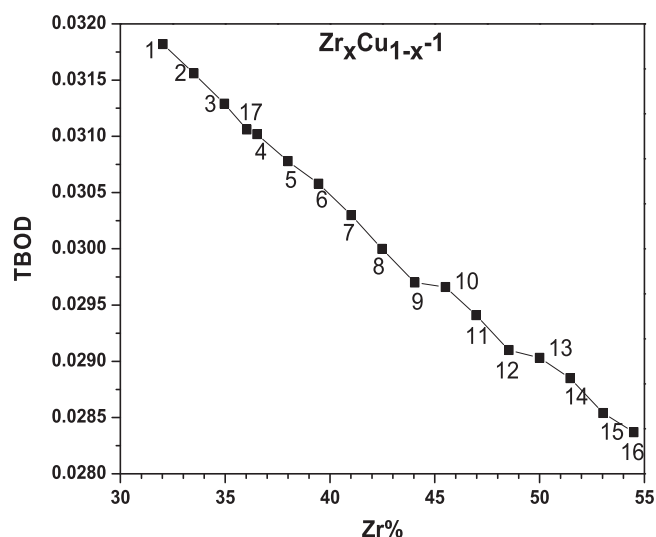


Fig. 20 Dependence of TBOD on x in binary Zr_xCu_{1-x} glasses.

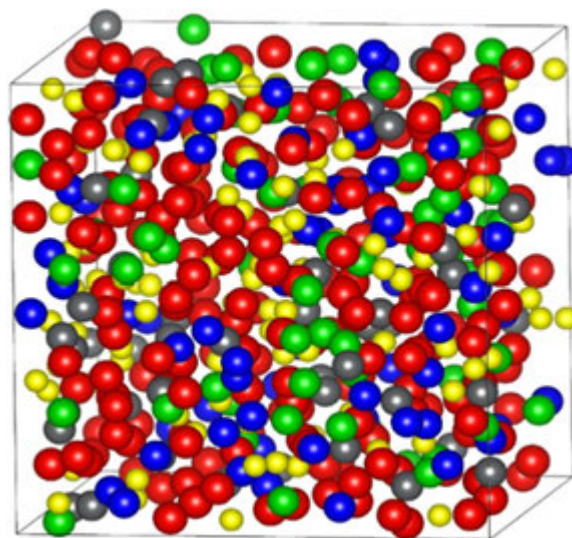


Fig. 21 A configuration from AIMD simulation for vitreoloy. Red, Zr; blue, Ti; green, Cu; yellow, Ni; gray, Be.

We believe that the TBOD is correlated with the glass forming ability (GFA) in conventional MG and in BMG. The reason is quite simple, for complex glasses, metallic or insulating, the use of pure geometric parameters for their characterization is not tenable or reliable. It has to rely on quantum mechanical treatment to accurately account for both the structure arrangement and the interatomic interaction.

Metal-Organic Frameworks Glasses

Zeolitic imidazolate frameworks (ZIFs), a subset of metal-organic frameworks (MOFs) have recently attracted immense attention (Furukawa *et al.*, 2013). Many crystalline ZIFs (c-ZIFs) have zeolite structure with large-porosity that are ideal for molecular encapsulation (Banerjee *et al.*, 2008; Tran *et al.*, 2011). More recently, non-crystalline or amorphous ZIFs (a-ZIFs) with similar short-range order are of great interest because it represents another class of organic-based glass. We have constructed a unique a-ZiF model with 918 atoms that maintains the network topology analogous to silica. The same 162-atom a-SiO₂ model (Ching, 1981) discussed in the beginning of Section 4 is used as the seed model. In the network, the corner-sharing SiO₄ tetrahedra are replaced by MN₄ tetrahedra (M = a metal, Zn in this case) linked by organic linker imidazolate (IM) (C₃N₂H₃)⁻ anions (Adhikari *et al.*, 2016). The fully relaxed structure of this a-ZiF is illustrated in Fig. 25. This unique a-ZiF model maintains all the structural integrity required for the metal organic glass and has since be employed in many recent studies (Adhikari *et al.*, 2016, 2018; Wang *et al.*, 2019).

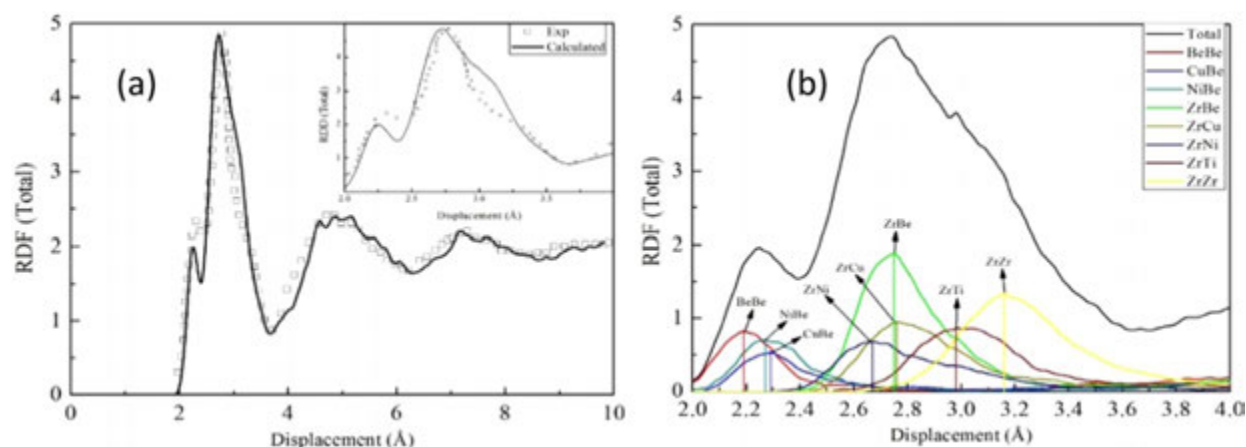


Fig. 22 (a) Total and (b) partial pair distribution function for $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$. The solid line is from the calculation and the dashed line is from experiment.

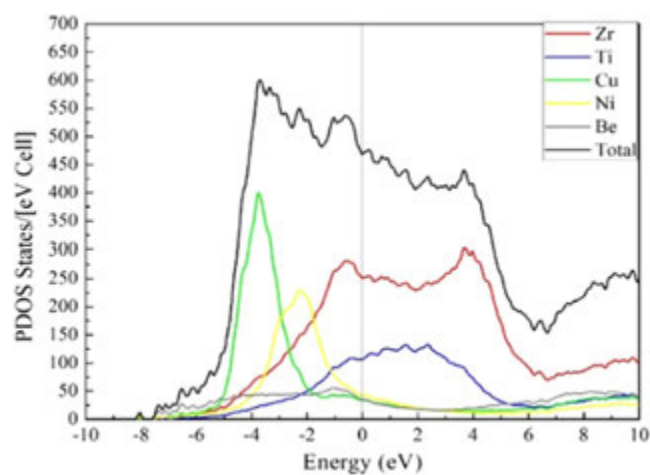


Fig. 23 Calculated DOS and PDOS of Zr, Ti, Cu, Ni and Be for vitreloy model.

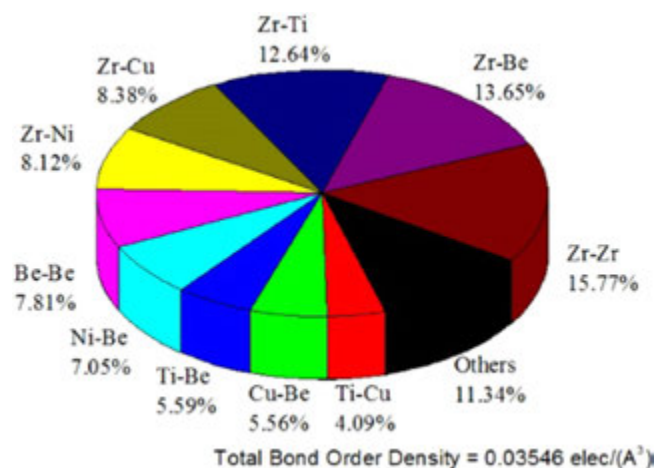


Fig. 24 Percentage contribution from PBOD to the TBOD in the vitreloy model.

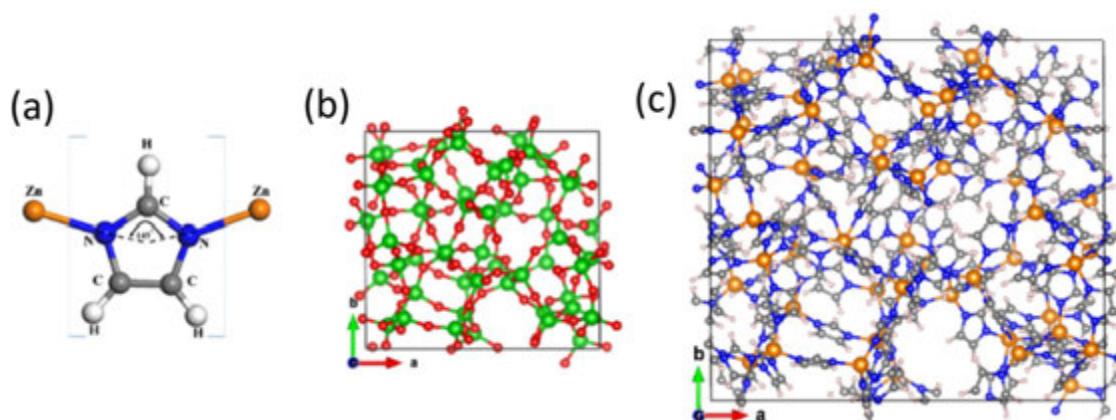


Fig. 25 (a) Zn-Im-Zn unit of ZIFs, (b) 162 atom a-SiO₂ model, (c) a-ZIF model. Orange, blue, gray and white balls represent Zn, N, C and H, respectively.

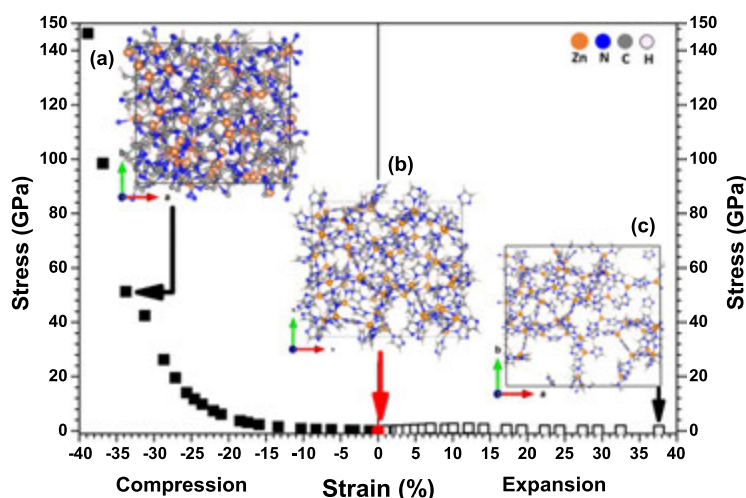


Fig. 26 Illustration for compression and extension. Stress vs strain in percentage. Compression is shown on the left and expansion on the right side. The inset shows the ball and stick diagrams of a complex organic/inorganic glassy alloy at different stages of compression/expansion: (a) compressed with a strain of 33.75% into a metallized a-ZIF; (b) the equilibrium a-ZIF model and; (c) expanded a-ZIF model at a tensile strain of 37.6% with large porosity and super-soft framework.

A computational study on the deformation behavior of this unique a-ZIF model by simulating step-wise compression and expansion with strains between -0.389 and $+0.376$ is recently accomplished by us (Adhikari *et al.*, 2018). This is illustrated in Fig. 26 starting from the model p0 at equilibrium to model p21 at high compression and model t19 at the end of extension. An insulator-to-metal transition is observed at pressure of 51 GPa in step p19 leading to a multicomponent light weight amorphous metallic alloy of low weight density of only $3.68 \text{ g}/(\text{cm})^3$. An amorphous-to-amorphous phase transition is observed due to the sudden formation of N-N bond pairs at this compression. This is illustrated in Fig. 27 where the BO vs BL distribution for all the bond pairs for model p19 is plotted. The N-N bonds with BL ranging from $1.27 \text{ \AA}$ to $1.50 \text{ \AA}$ and large BO values (indicated by star symbol) was not observed in the similar plot for the preceding model p18. Also apparent are the formation of three H-H bonds in forming the H₂ molecules. Systematic expansion of a-ZIF retains the framework softness until it fractures at high strain. This large scale simulation again demonstrated the pivotal role played by TBOD in understanding the metalization process and also the in overview of the change in TBOD and PBOD during the deformation process. In Fig. 28, we plot the TBOD and the PBOD at each strain during the deformation. It can be seen that the sudden appearance of the PBOD from N-N pairs at model p19 immediately after the model p18.

Extension to Transition Metal Random Alloys

Why do we extend this chapter to include random transition metal (TM) alloys which are neither ceramics nor glasses? They are complex metallic systems where theory and modeling techniques are still in early stage of development. TBOD as a geno for materials can substantially contribute to the advancement of this sector of materials science.

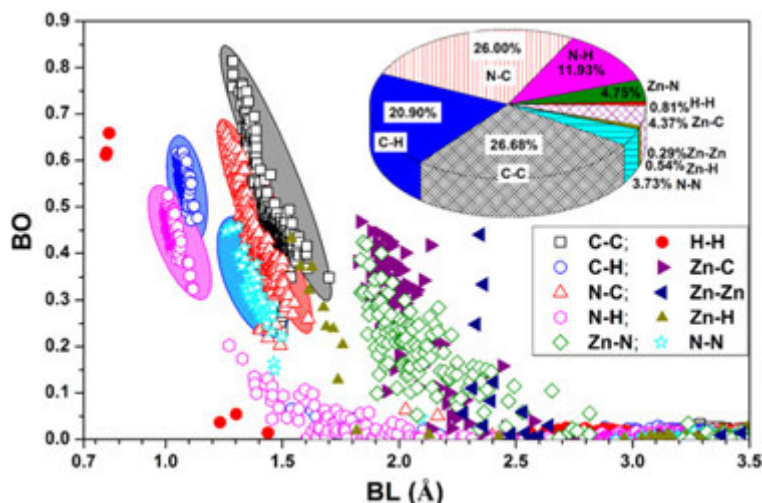


Fig. 27 Interatomic bonding for p19. Bond order (e) vs bond length (Å) for the metallic phase at strain 33.75%. Inset: % contribution to the TBOD from different bonds.

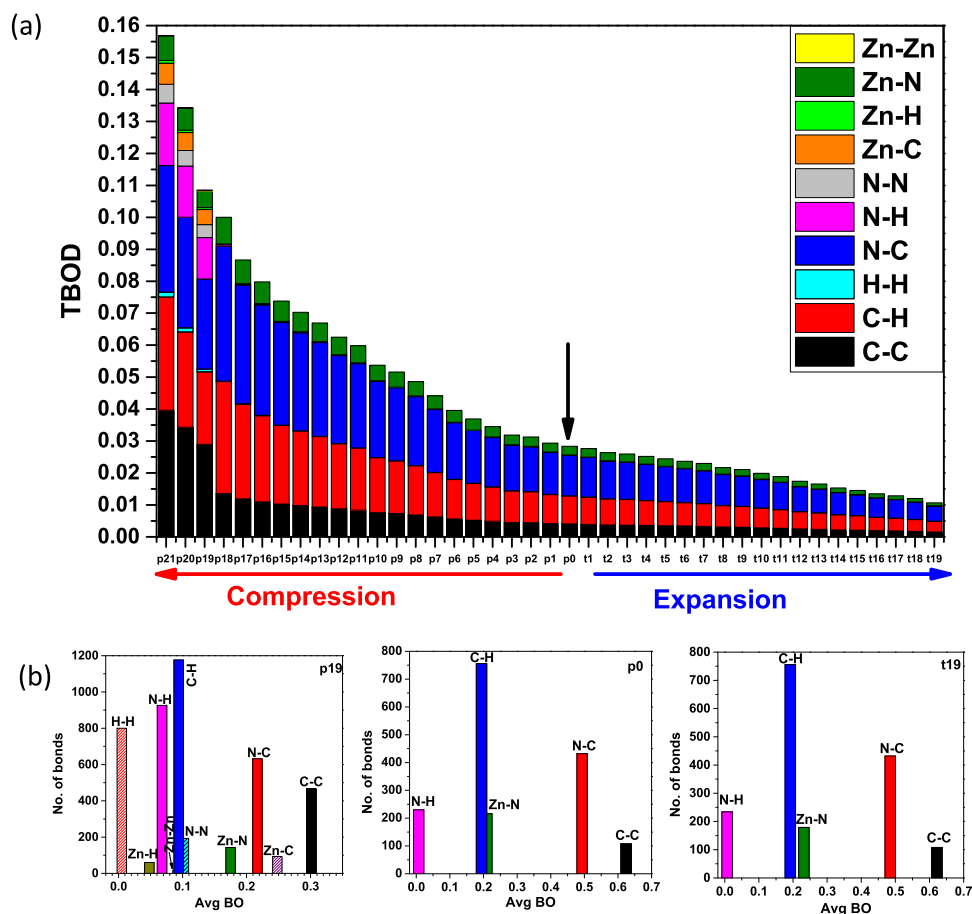


Fig. 28 Change in bonding throughout the deformation: (a) Total bond order density (TBOD) vs strain % for compression and expansion. The color segments show the contributions (PBOD from different bond pairs). (b) Number of bonds vs average bond order for p19, p0 and t19.

High Entropy Alloys

High entropy alloys (HEA) are a relatively new class special multicomponent metallic alloys in FCC, BCC or HCP lattices or in mixed phases with many promising applications (Gao *et al.*, 2016). It originated more than 20 years ago (Yeh *et al.*, 2004). These unique alloys, in sharp contrast to traditional alloys based on one or two principal elements, have four or more atomic components resulting in unusually high entropy of mixing. These solid solution alloys in equal or near-equal molar composition are also named as multi-principle element alloys (MPEAs) (Cantor *et al.*, 2004). HEA have attracted an ever-increasing interest from academia and industries in recent years and is now an emergent new area of alloy research mainly because of their potential promising applications and new science for its fundamental understanding (Ye *et al.*, 2016; Miracle and Senkov, 2017; Pollock and Van der Ven, 2019).

Since the fundamental theory for the formation of HEA is still lacking and numerous different modeling techniques and computational tools are being rapidly developed (Ding *et al.*, 2018; Guo *et al.*, 2011; Sun *et al.*, 2017a; Jiang *et al.*, 2004). We feel that TBOD can play a critical role for this class of alloys. Although HEA and vitreloy discuss above are both disordered alloys, HEAs are more suitable for systematic application to materials informatics based on data from DFT calculations because the structural part of the alloy sampling is simpler to model than in BMGs. To this end, we have recently constructed nine realistic random solid solution models in BCC lattice and calculated their electronic structure and mechanical properties for possible correlations with TBOD and PBOD. The motivation is to design the light weight, high strength, ductile, bio-compatible, corrosion resistant, cost effective HEA for bio medical applications such as in bone, tissue and joint replacements or implements (Koval *et al.*, 2019; Nguyen *et al.*, 2018; Yuan *et al.*, 2019; Todai *et al.*, 2017). These need atomic scale understanding. The 9 alloys are: TiNbTaV, TiNbTaZr, TiNbTaZrMo, HfNbTaV, NbTaTiVZr, TiZrHfNbTa, TiHfNbTa, TiZrHfTa, TiZrHfNb. Six of them have 4 components and the other three have 5 components. Some preliminary results have been obtained (Ching *et al.*, unpublished results). Table 8 lists the structure of the fully relaxed model and the calculated TBOD and PBOD. It should be pointed out that although the models with 250 atoms each all have BCC backbone, they are severally distorted. Table 9 shows the calculated mechanical properties in the form of elastic coefficient and mechanical parameters including the Poisson's ratio. Fig. 29 shows the bar plot of the TBOD and the PBOD for the nine HEAs. TiNbTaV has the highest and TiZrHfNb has the lowest TBOD. Detailed inspection of these data suggests that TBOD does not correlate with the number of atomic components but has more to do with the atomic size. Light atoms such as Ti or V favor the TBOD since the smaller size implied a smaller volume for the model and increase the TBOD. It also shows that PBOD can have a large variations indicating the strength of bonding between different types of atoms matters. For example Nb-Nb PBOD have relatively small contributions to the TBOD whereas Nb-Ta PBOD are relatively strong. So the data from these 12 HEAs again illustrates the merit of using TBOD to characterize the strength for a complex material. Additional modeling and data analysis are currently in progress.

Table 8 TBOD and PBOD in 9 BCC high entropy alloys (HEAs)

BCC	HEAs	Volume ($\text{\AA}^3$)	TBOD ($e/\text{\AA}^3$)
1	TiNbTaV	4161.047	0.04799
2	TiNbTaZr	4739.407	0.03902
3	TiNbTaZrMo	4537.862	0.04236
4	HfNbTaV	4481.912	0.04077
5	TiNbTaZrV	4474.812	0.04177
6	TiNbTaZrHf	4905.735	0.03617
7	TiHfNbTa	4699.020	0.03980
8	TiZrHfTa	5026.873	0.03651
9	TiZrHfNb	5012.223	0.03193

Table 9 Elastic constants and mechanical parameters in 9 BCC high entropy alloys in unit of GPa

BCC	HEAs	C_{11}	C_{12}	C_{14}	K	G	E	η	G/K
1	TiNbTaV	217.33	132.09	29.09	160.43	33.79	94.73	0.402	0.211
2	TiNbTaZr	167.56	111.81	34.61	130.39	31.72	88.02	0.388	0.243
3	TiNbTaZrMo	207.45	119.69	33.20	148.89	37.05	102.65	0.385	0.249
4	HfNbTaV	203.29	126.71	35.27	152.23	36.40	101.14	0.389	0.239
5	NbTaTiVZr	174.02	113.93	29.99	133.94	29.98	83.70	0.396	0.224
6	TiZrHfNbTa	154.08	108.90	37.38	123.84	30.52	84.61	0.386	0.246
7	TiHfNbTa	178.70	118.79	42.12	138.73	36.73	101.25	0.378	0.265
8	TiZrHfTa	141.22	101.91	39.71	114.63	29.92	82.57	0.380	0.261
9	TiZrHfNb	139.60	98.72	37.11	112.15	29.17	80.53	0.380	0.260

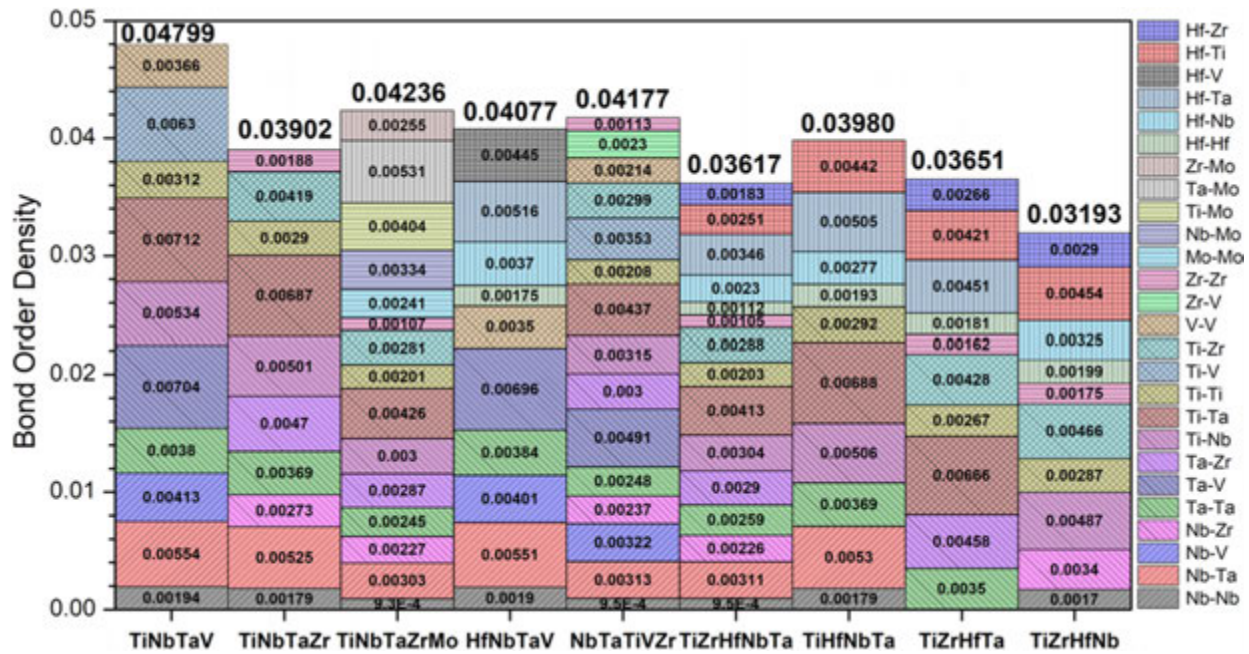


Fig. 29 Total bond order density plotted in the form of vertical bars and their PBOD in the nine high entropy alloys in BCC lattice: from left to right: TiNbTaV, TiNbTaZr, TiNbTaZrMo, HfNbTaV, NbTaTiVZr, TiZrHfNbTa, TiHfNbTa, TiZrHfTa, TiZrHfNb.

Table 10 Elastic constants and mechanical parameters for Haynes282 and Inconel740 models in GPa

	C_{11}	C_{12}	C_{44}	K	G	E	η	G/K
Haynes	244.608	174.889	106.356	194.552	68.043	182.816	0.343	0.350
Inconel	262.821	182.849	116.951	206.248	76.064	203.211	0.336	0.369

Ni-Based Superalloys

Ni-based superalloy is another class of multi-component alloys developed more than several decades ago mainly for high temperature applications (Donachie and Donachie, 2002; He *et al.*, 1994; Hong *et al.*, 2001; Fayman, 1987; Ruiz *et al.*, 1992). They all have extremely complex structures and a variety of important applications especially in power plants that need corrosion-resistant alloys at elevated temperature (Nagode *et al.*, 2011; Klueh, 2005; Fujita, 1992). It has a lot of similarities and differences with HEA or BMG. HEAs have almost equally compositions to boost the entropy whereas Ni superalloys have a lot more compositions large and small and many of them are form precipitates structural defects. Since it is Ni-based with Ni (gamma phase) as the major component, the base structure is FCC but can also be multi-phased. It contains a lot of defects, especially the precipitate phases such as γ' (Ni_3Al), γ'' (Ni_3Nb) and Cr_{23}C_6 etc. at grain boundaries, and surface of voids. It can contain elements of more than a dozen of atomic components ranging from less than 1% to over 50% with the major components from transition metals in addition to Ni. All these factors control their mechanical behavior, durability and corrosion resistance. Almost all commercially produced Ni-based superalloy are fabricated by trial and error approach and atomic-scale understanding of these complex superalloy is non-existent. This offers another opportunity to test the efficacy of using TBOD and PBOD as gene for complex materials design based on large-scale computation with tremendous economic benefit to alloy industry.

We have some preliminary results on the investigation of Ni-based superalloys. We choice commercially available alloys Inconel740 and Haynes282 as examples, each of them contain 11 different atomic components. This is shown in the Table 10. The structure of these two alloys is represented by the random solid solution model (RSSM) similar to HEA except the large difference in the atomic percentage of the constituent elements. Hence a large supercell must be used. Due to computational limitations, we choice to use an 864-atoms model in FCC lattice as shown in the ball and stick model in Fig. 30(a) and (b).

These models are fully relaxed using VASP and their electronic structure and bonding are obtained using OLCAO method. The results are summarized in Table 11 showing that Haynes282 has a slightly larger TBOD than Inconel740. On the other hand; Inconel740 has slightly larger total BO and modulus values in general. A larger Pugh's ratio (G/K) for Inconel implies it to be slightly more ductile. (Ching *et al.*, unpublished results). It will be more desirable to confirm these results when another set of random solid solution model to ascertain the degree of statistical fluctuations due to the random distribution of the atoms. On the

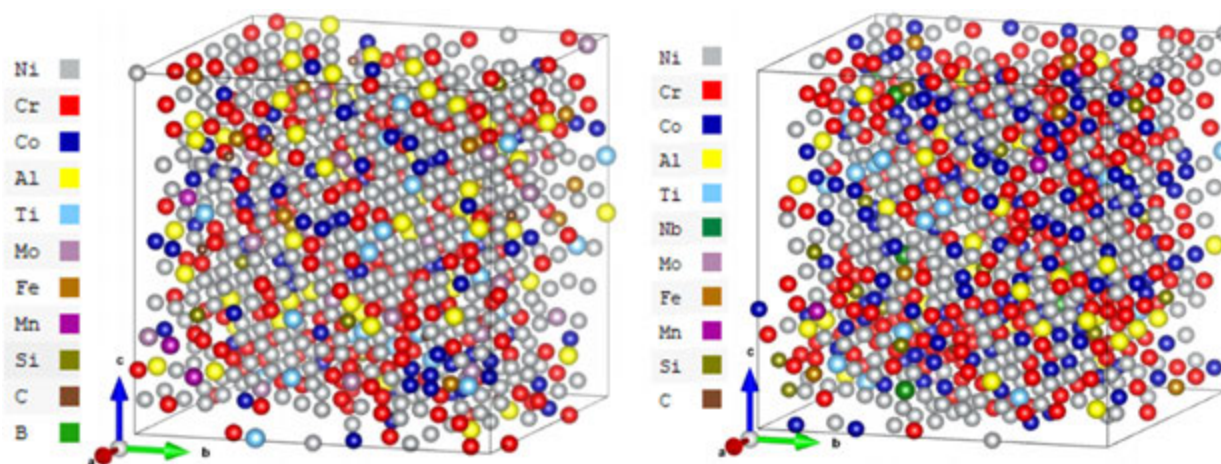


Fig. 30 Sketch of Ni-based superalloy models Haynes282 (left) and Inconel740 (right) models.

Table 11 Total bond order and TBOD (in unit of electron/ $\text{\AA}^3$) for Haynes282 and Inconel740 models

	Ni	Cr	Co	Al	Ti	Nb	Mo	Fe	Mn	Si	C	B	TBO	TBOD
Haynes	51.37	23.42	9.11	6.53	2.9	0	2.92	1.35	0.31	0.61	1.33	0.15	421.0233	0.04274
# Atoms	444	202	79	56	25	0	25	12	3	5	12	1		
Inconel	43.13	28.46	17.72	3.81	2.41	0.71	0.17	0.69	0.31	1.95	0.64	0	412.9632	0.04263
# Atoms	373	246	153	33	21	6	1	6	3	17	5	0		

other hand, it also demonstrate that these two commercially developed Ni-superalloys have similar desirable properties other than the differences in atomic constituents and their compositions.

From these very preliminary results for the complex Ni-based superalloys, it seems that our strategy and design for TM based metallic alloys is on the right track. The challenges are large but are not insurmountable.

Extension to Biomolecular Systems and Their Interfaces

We add this section to this chapter since the term geno originated from biology. Over the years, we used the same methods described in Section 2 to study the electronic structure and bonding in biomolecular systems including water. The first successful calculation for large biomolecules in 2003 on cyanocobalamin (vitamin B12) (Ouyang *et al.*, 2003). The ability to calculate hydrogen bonding accurately made a lot of difference (Ouyang *et al.*, 2003; Liang *et al.*, 2009, 2011; Poudel *et al.*, 2014; Adhikari *et al.*, 2014; Poudel *et al.*, 2015; Eifler *et al.*, 2016; Poudel *et al.*, 2016; Gong *et al.*, 2017; Poudel *et al.*, 2017a,c). Unlike the crystalline system or other materials represented by supercell with a definitive volume, in biomolecular systems, volume is not a useful or relevant parameter. Nevertheless, we can still use the concept to total bond order (TBO) or partial bond order (PBO) in analyzing the much more complex bonding situation involving biomolecules as will be presented in three selected examples below.

Complex Biomolecules

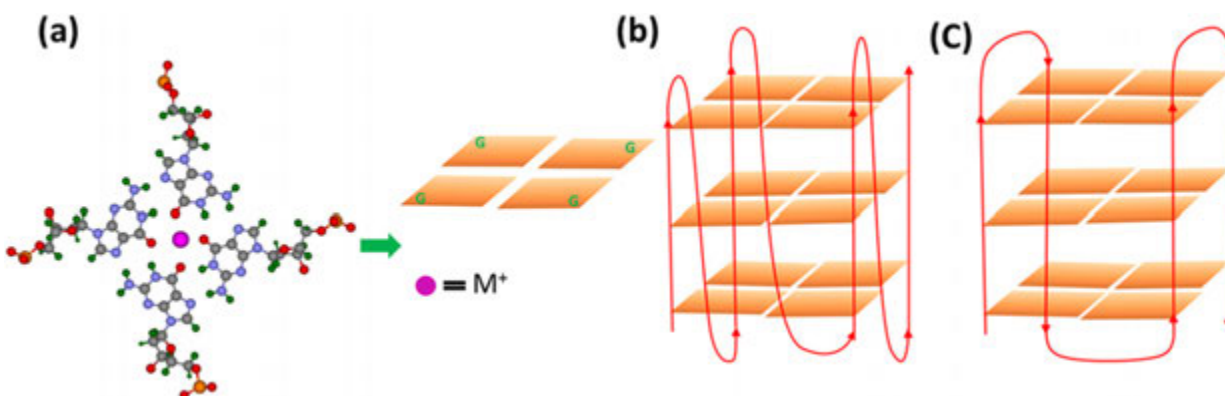
For complex biomolecular systems, we chose the calculation of G-quadruple DNA as an example (Poudel *et al.*, 2016) since this work encompasses the complexity of the system with solvent effect, metal ions, topology and hydrogen bonding in human telomeric G-quadruplex DNA through electronic structure calculation using DFT. 12 well-designed 3-dimensional G-quadruplex (G4-DNA) models (A1-A6, B1-B6) in different environments are constructed and their TBOs, total energies and HOMO-LUMO gaps are calculated. (Tables 12 and 13). Fig. 31 illustrate the basics of the 12 models. In the parallel structure (A models), the polarities for all strands are in the same direction, whereas in the anti-parallel type (B models), each strand has opposite orientation with respect to adjacent strands. Our study shows that the parallel strand structures are more stable in dry environment. The parallel G4-DNA (A models) has larger TBO and lower total energy than the anti-parallel one (B models) for all solvated and non-solvated models. The only exception is for the case of inner Na^+ ions with water molecules (A4 vs B4). Therefore, the parallel structures of G4-DNA are more stable than the anti-parallel structures for non-solvated and K^+ solvated ones (A4), whereas the anti-parallel structure is more stable when solvated with Na^+ (B4).

Table 12 The 12 G4-DNA models. Left column originates from the parallel 1KF1 structure, right column originates from the anti-parallel 143D structure. The environment of each pair in the row is the same

Name	Parallel G4-DNA	Name	Anti-Parallel DNA
A1	1KF1 + 21Na(b)	B1	143D + 21Na(b)
A2	1KF1 + 21Na(b) + 68H ₂ O	B2	143D + 21Na(b) + 68H ₂ O
A3	1KF1 + 18Na(b) + 3Na(c)	B3	143D + 18Na(b) + 3Na(c)
A4	1KF1 + 18Na(b) + 3Na(b) + 68H ₂ O	B4	143D + 18Na(b) + 3Na(c) + 68H ₂ O
A5	1KF1 + 18Na(b) + 3K(c)	B5	143D + 18Na(b) + 3K(c)
A6	1KF1 + 18Na(b) + 3K(c) + 68H ₂ O	B6	143D + 18Na(b) + 3K(c) + 68H ₂ O

Table 13 Calculated total energy, total bond order values and HOMO-LUMO gap of G4-DNA models

Models	Total energy (eV)	TBO (e)	HOMO-LUMO gap (eV)	Models	Total energy (eV)	TBO (e)	HOMO- LUMO gap (eV)
A1	− 4786.021	312.478	3.11	B1	− 4785.828	312.679	2.67
A2	− 5794.530	353.073	2.46	B2	− 5794.034	353.559	2.14
A3	− 4794.104	313.515	1.38	B3	− 4792.813	313.359	0.98
A4	− 5800.260	354.017	1.93	B4	− 5800.510	354.597	1.74
A5	− 4793.337	312.360	1.12	B5	− 4792.247	312.419	1.04
A6	− 5797.100	352.831	1.99	B6	− 5796.565	352.995	1.69

**Fig. 31** Structure and topology of two G-quadruplex (G4) DNA conformations. Arrows represent the direction of DNA strands from 5' to 3' end. (a) G-tetrad with alkali ion (M^+), (b) parallel type uni-molecular G4, and (c) anti-parallel basket type uni-molecular G4.

The presence of metal ions within the tetrad of the guanine channel always enhances the stability of the G4-DNA models. The parallel strand structures have larger HOMO-LUMO gaps than antiparallel structures. Partial charge calculations show that sugar and alkali ions are positively charged whereas nucleobases, PO_4 groups and water molecules are all negatively charged. Partial charges on each functional group with different sign and magnitude contribute differently to the electrostatic interactions involving G4-DNA and favor the parallel structure. Comparative study between specific pairs of different G4-DNA models shows that the Hoogsteen $O\cdots H$ and $N\cdots H$ hydrogen bonds in the guanine tetrad are significantly influenced by the presence of metal ions and water molecules, collectively affecting the structure and stability of G4-DNA. **Fig. 32** shows the Hoogsteen HB for model A4 and A6. This example is one of the most complex and challenging biomolecular systems we studied so far. Some of the details can be found in the published paper (Poudel *et al.*, 2016).

Interfaces of Biomolecules and Inorganic Crystals

This topic focuses on the interfaces between biological peptides and inorganic crystals which has attracted a lot of attention recently (Nel *et al.*, 2009; Patwardhan *et al.*, 2012; Alava *et al.*, 2013). TBOD again plays a key role as a parameter for explanation of the mechanism involved for interfacial interaction. Many materials formed in Nature always take such advantage (Munch *et al.*, 2008). Here we show a specific example of the solvated interface between a peptide with an 8 amino acid sequence (HIS-THR-GLN-ASN-MET-ARG-MET-TYR-GLU-PRO-TRP-PHE) (Sarıkaya *et al.*, 2004; Evans *et al.*, 2008) and

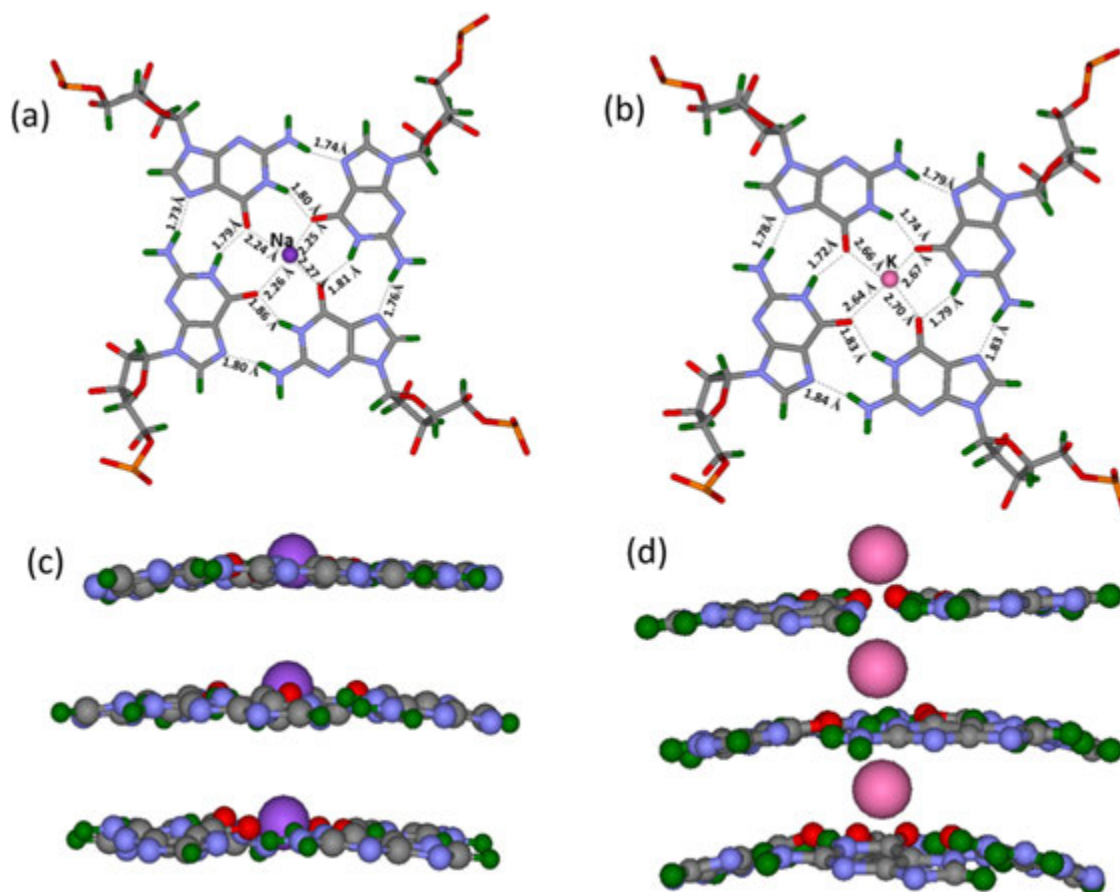


Fig. 32 (a) Hoogsteen hydrogen bonds (N...H, O...H) in the 2-D planar view (BLs) for Model A4 showing Na ion at the center. (b) Model A6 with K ion at the center. (c) and (d) are the side view of the (a) and (b) for model A4 and A6, respectively. The color designation for atoms are: H(green), N(blue), C(gray), O(red), P(orange), K(pink), and Na(purple).

aragonite or Nacre, a very strong crystalline calcium carbonate CaCO_3 (Brown *et al.*, 2014). Large scale computational modeling on this interface model (see Fig. 33) constructed by using AIMD and DFT calculations were carried out (Poudel *et al.*, 2017a,b,c). The calculated TBOD in this interface model show the dynamic interplay of different competing bonds in the interactions. Four amino acids HIS1, ARG6, MET7 and TRP11 in the peptide sequence have strong interfacial Ca-O bonding and O...H hydrogen bonding between aragonite and peptide. The TBOD for this interface model is $0.029 \text{ e}/(\text{\AA})^3$. Fig. 34 shows the distributions of the BO vs BL plots for bonds between three structural units: aragonite, peptide and water. It shows that the TBO between water and peptide units are much more than the sum of the TBO between other two structure units. The calculated Young's modulus is 33.37 GPa is in line with measured value for Nacre (Jackson *et al.*, 1988). This approach for interfacial study on the binding mechanism between aragonite and binding peptide in the presence of water provided a broad perspective in probing complex interactions at the biomimetic interfaces. Systematic evaluation of TBOD on models of different interfaces involving different biomolecules and inorganic crystals can rank the efficacy of peptide-surface interactions and in providing a programmable design for bio-inspired material interfaces based on computational means.

Bio-Inspired Cements

This last example we give for biomaterials is somewhat similar to the one above but with different motivations. Cement and concretes are important construction materials throughout human history. Hardened cement paste possesses extremely complex composition and structure at different length and time scale. There is an urgent need to explore novel and untraditional cementitious materials in response to increased infrastructure demand worldwide. Exploring bio-inspired cement obviously makes sense (Qian *et al.*, 2018; Phua and Røyne, 2018; Krizkova *et al.*, 2014; Ariyanti *et al.*, 2012). We have constructed a composite model between an inorganic crystal and a peptide and with water added (Ching *et al.*, 2019). It is an explicitly solvated mixture of a mineral calcium silicate hydrate (C-S-H) crystal suolunite ($\text{Ca}_2\text{Si}_2\text{O}_5(\text{OH})_2 \cdot \text{H}_2\text{O}$) (described in Section 3.3) and a specific silicon binding peptide with amino acid sequence PRO-PRO-PRO-TRP-LEU-PRO-TYR-MET-PRO-PRO-TRP-SER. The final model

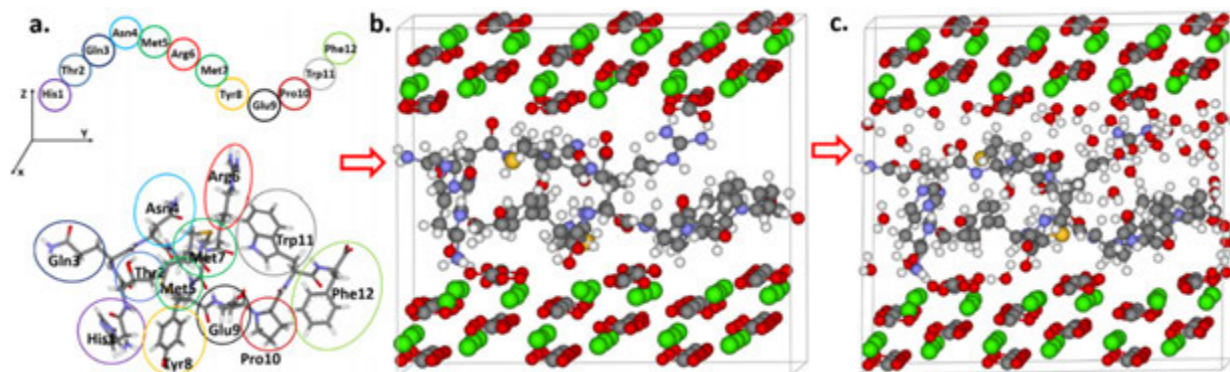


Fig. 33 The structure of (a) CaCO_3 binding peptide, (b) supercell of APA interface model, and (c) supercell of APWA model. O (red), C (gray), N (blue), H (white) and Ca (green), S (yellow).

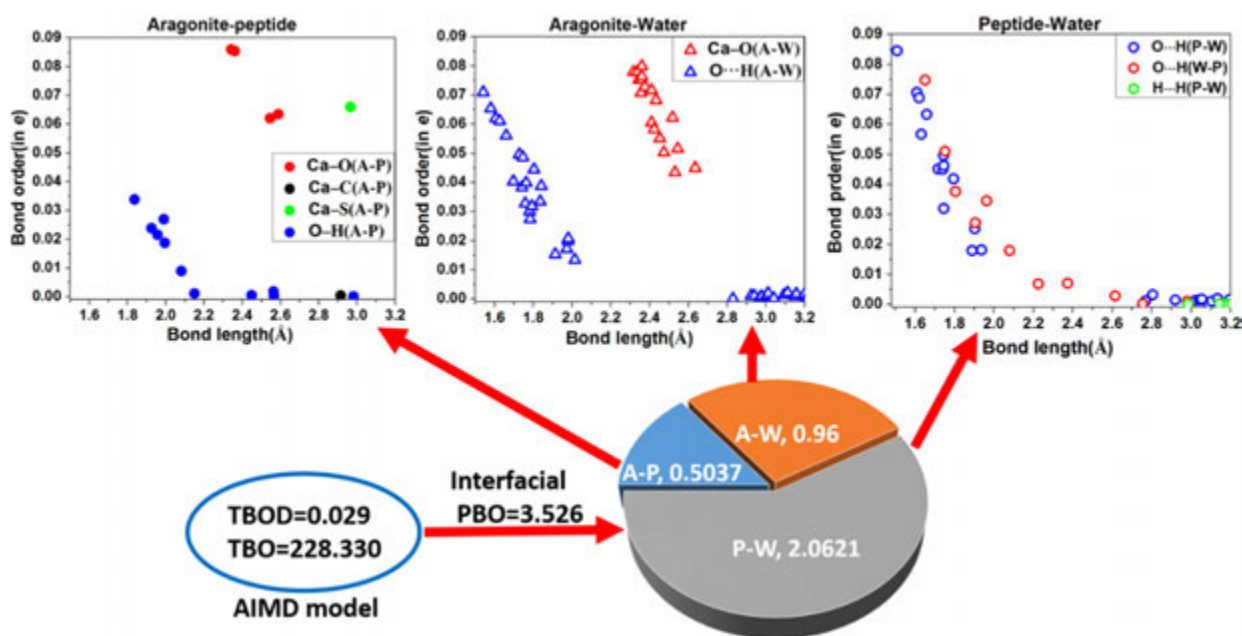


Fig. 34 Bond order vs bond length distributions for the AIMD model for bonding between pairs of structural units from left to right: aragonite-peptide (A-P), aragonite-water (A-W), and peptide-water (P-W). Each data point for a particular pair of atoms is designated with a specific symbol and color. The pie-chart represents the partial bond order in each structural unit.

structure is determined by using ab initio molecular dynamics (AIMD). The step-wise model building procedure is shown in Fig. 35. We explore the interface structure, interatomic bonding, mechanical properties and solvent effect of this bio-inspired cement. At each step in the modeling process, TBOD is used as a parameter for characterization. The importance of using AIMD in the construction of this composite model for bio-inspired cements is supported by the data shown in Table 14 for three models (AIMD0, AIMD1 and AIMD2, the final model). The solvated model has a slightly larger TBOD than the dried one. Therefore TBOD can be used in assessing the internal cohesion of bio-inspired cements and it could lead to a systematic search and design for different types of bio-inspired cements with other inorganic minerals and organic peptides.

Conclusions and Outlook

In this chapter we present many examples of using TBOD as the geno of materials. Although it started with the early calculations on ceramic crystals and glasses, it is not restricted to these classes of materials, but can be effectively extended to many complex materials.

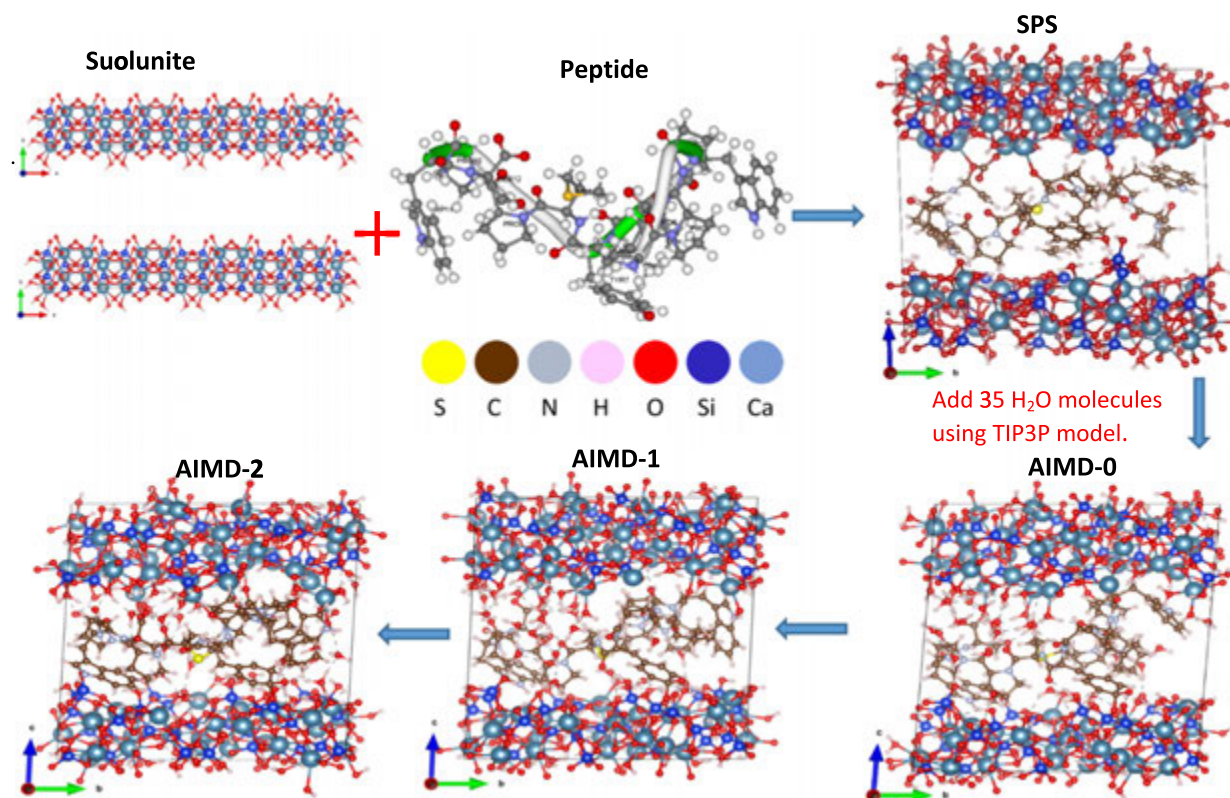


Fig. 35 Illustration of the steps in model construction for the final SPW (AIMD-2) model.

Table 14 Comparison of the properties of 3 models in the AIMD process

	AIMD-0	AIMD-1	AIMD-2
Volume ($\text{\AA}^3$)	10816.643	10269.766	9983.951
Total energy (eV)	−5069.0485	−5074.9997	−5082.0988
Band gap (eV)	0.89	1.91	1.87
TBO (electron)	247.449	248.07020	248.4164
TBOD (electron $\text{\AA}^{-3}$)	0.02288	0.02416	0.02488

In particular, applications to the metallic materials and biomolecular systems are extremely promising. Systematic analysis of TBOD and the PBOD in relation to correlation with structures and properties provide simpler explanations on some fundamental issues of very complex systems, similar to what genomics play in biology and medicine. In a related trend, large databases on different classes of materials can be constructed purely based on computational means. TBOD and PBOD can be used as effective and important descriptors in various data mining protocols and machining learning tools far more economic than data from laboratory measurements. **Fig. 36** shows an example of applying to the MAX phases compounds. Using the data base of 664 MAX phases, half of the data is used as the training set to predict the properties of the other half. A deeper level of iterative loops using TBOD and PBOD as descriptors in artificial neural network can now predict the Poisson's ratio with over 93% of correlation coefficient ([Sakidja, private communication](#)), better than previous attempts described in the section on MAX phases. This clearly provides a strong argument to include TBOD and PBOD in machine learning algorithm for controlled improvement for specific properties ([Ball, 2019](#)). These applications are still in the early stage and I expect rapid development in the near future.

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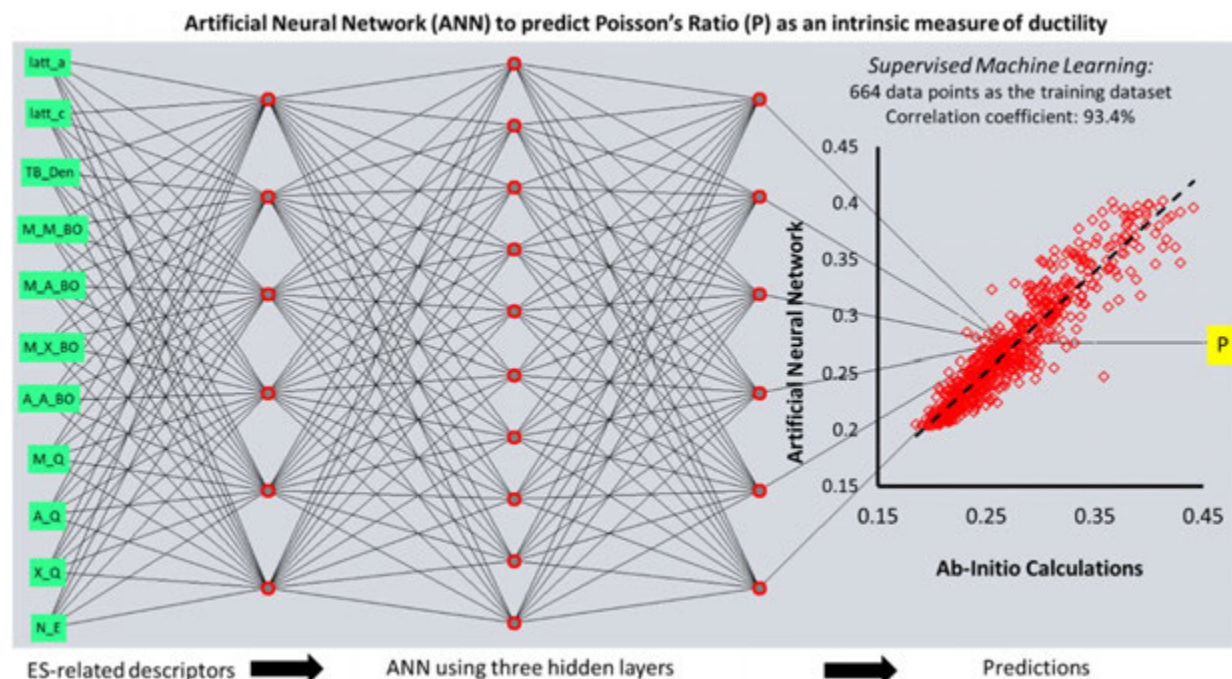


Fig. 36 Schematic illustration of machine learning exercise for predicting the Poisson ratios in MAX phases using TBOD and PBOD as important descriptors in the input data.

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References

- Adhikari, P., Khaoulaf, R., Ez-Zahraoui, H., Ching, W.-Y., 2017. Complex interplay of interatomic bonding in a multi-component pyrophosphate crystal: $K_2Mg(H_2P_2O_7)_2 \cdot 2H_2O$. *Royal Society Open Science* 4, 170982.
- Adhikari, P., Li, N., Rulis, P., Ching, W.-Y., 2018. Deformation behavior of an amorphous zeolitic imidazolate framework – From a supersoft material to a complex organometallic alloy. *Physical Chemistry Chemical Physics* 20, 29001–29011.
- Adhikari, P., San, S., Zhou, C., Sakidja, R., Ching, W.Y., 2019a. Electronic structure and mechanical properties of crystalline precipitate phases $M_{23}C_6$ (M= Cr, W, Mo, Fe) in Ni-based superalloys. *Materials Research Express*, 6 (11), 116323.
- Adhikari, P., Shafei, L., San, S., Rulis, P., Ching, W.Y., 2019b. Origin of the existence of inter-granular glassy films in β - Si_3N_4 . *Journal of the American Ceramic Society*.
- Adhikari, P., Wen, A.M., French, R.H., *et al.*, 2014. Electronic structure, dielectric response, and surface charge distribution of RGD (1FUV) peptide. *Scientific Reports* 4, 5605.
- Adhikari, P., Xiong, M., Li, N., *et al.*, 2016. Structure and electronic properties of a continuous random network model of an amorphous zeolitic imidazolate framework (a-ZIF). *The Journal of Physical Chemistry C* 120, 15362–15368.
- Alava, T., Mann, J.A., Théodore, C.C., *et al.*, 2013. Control of the graphene-protein interface is required to preserve adsorbed protein function. *Analytical Chemistry* 85, 2754–2759.
- Ariyanti, D., Handayani, N., Hadiyanto, 2012. Feasibility of using microalgae for biocement production through biocementation. *Journal of Bioprocessing & Biotechniques* 2, 2.
- Aryal, S., Sakidja, R., Barsoum, M.W., Ching, W.Y., 2014. A genomic approach to the stability, elastic, and electronic properties of the MAX phases. *Physica Status Solidi (b)* 251, 1480–1497.
- Ball, P., 2019. Using artificial intelligence to accelerate materials development. *MRS Bulletin* 44, 335–344.
- Banerjee, R., Phan, A., Wang, B., *et al.*, 2008. High-throughput synthesis of zeolitic imidazolate frameworks and application to CO_2 capture. *Science* 319, 939–943.
- Baral, K., Adhikari, P., Ching, W.Y., 2016. Ab initio modeling of the electronic structures and physical properties of $a-Si_{1-x}Ge_xO_2$ Glass ($x = 0$ to 1). *Journal of the American Ceramic Society* 99, 3677–3684.
- Baral, K., Ching, W.-Y., 2017. Electronic structures and physical properties of Na_2O doped silicate glass. *Journal of Applied Physics* 121, 245103.
- Baral, K., Li, A., Ching, W.-Y., 2017. Ab initio modeling of structure and properties of single and mixed alkali silicate glasses. *The Journal of Physical Chemistry A* 121, 7697–7708.
- Baral, K., Li, A., Ching, W.Y., 2019. Understanding the atomistic origin of hydration effects in single and mixed bulk alkali-silicate glasses. *Journal of the American Ceramic Society* 102, 207–221.
- Barsoum, M.W., 2013. MAX Phases: Properties of Machinable Ternary Carbides and Nitrides. John Wiley & Sons.

- Brown, A.H., Rodger, P.M., Evans, J.S., Walsh, T.R., 2014. Equilibrium conformational ensemble of the intrinsically disordered peptide n16N: Linking subdomain structures and function in nacre. *Biomacromolecules* 15, 4467–4479.
- Cantor, B., Chang, I., Knight, P., Vincent, A., 2004. Microstructural development in equiatomic multicomponent alloys. *Materials Science and Engineering: A* 375, 213–218.
- Chen, J., Ouyang, L., Rulis, P., Misra, A., Ching, W.-Y., 2005. Complex nonlinear deformation of nanometer intergranular glassy films in β -Si₃N₄. *Physical Review Letters* 95, 256103.
- Ching, W.-Y., 2016. Materials informatics using ab initio data: Application to MAX phases. In: *Information Science for Materials Discovery and Design*. Springer.
- Ching, W.-Y., 2019. First principles calculations, book chapter. In: Musgraves, J.D., Hue, J., Calvez, L. (Eds.), *Handbook of Glass* by Springer. Springer.
- Ching, W.-Y., Rulis, P., 2012. Electronic Structure Methods for Complex Materials: The Orthogonalized Linear Combination of Atomic Orbitals. Oxford University Press.
- Ching, W.-Y., Rulis, P., Ouyang, L., Aryal, S., Misra, A., 2010. Theoretical study of the elasticity, mechanical behavior, electronic structure, interatomic bonding, and dielectric function of an intergranular glassy film model in prismatic β -Si₃N₄. *Physical Review B* 81, 214120.
- Ching, W.-Y., Rulis, P., Ouyang, L., Misra, A., 2009. Ab initio tensile experiment on a model of an intergranular glassy film in β -Si₃N₄ with prismatic surfaces. *Applied Physics Letters* 94, 051907.
- Ching, W., 1981. Microscopic calculation of localized electron states in an intrinsic glass. *Physical Review Letters* 46, 607.
- Ching, W., Chen, J., Rulis, P., Ouyang, L., Misra, A., 2006a. Ab initio modeling of clean and Y-doped grain boundaries in alumina and intergranular glassy films (IGF) in β -Si₃N₄. *Journal of Materials Science* 41, 5061–5067.
- Ching, W.-Y., San, S., Brechtel, J., *et al.*, unpublished.
- Ching, W.-Y., San, S., Zhou, C., Sakidja, R., unpublished.
- Ching, W.-Y., Poudel, L., San, S., Baral, K., 2019. Interfacial interaction between suolunite crystal and silica binding peptide for novel bio-inspired cement. *ACS combinatorial science*. 21 (12), 794–804. doi:10.1021/acscmbsci.9b00131.
- Ching, W., Ouyang, L., Gale, J.D., 2000. Full ab initio geometry optimization of all known crystalline phases of Si₃N₄. *Physical Review B* 61, 8696.
- Ching, W., Xu, Y.-N., Rulis, P., Ouyang, L., 2006b. The electronic structure and spectroscopic properties of 3C, 2H, 4H, 6H, 15R and 21R polymorphs of SiC. *Materials Science and Engineering: A* 422, 147–156.
- Ching, W.-Y., 1986. Electronic structures of crystalline and amorphous silicon dioxide and related materials. In: Walrafen, G.E., Revesz, A.G. (Eds.), *Structure and Bonding in Noncrystalline Solids*. Boston, MA: Springer.
- Ching, W.-Y., 2000. First Principles Calculation of the Electronic Structure of Crystalline and Amorphous Forms of SiO₂. John Wiley & Sons Inc.
- Ching, W.-Y., Mo, S.D., Chen, Y., 2002. Calculation of XANES/ELNES spectra of all edges in Si₃N₄ and Si₂N₂O. *Journal of the American Ceramic Society* 85, 11–15.
- Ching, W.-Y., Mo, Y., Aryal, S., Rulis, P., 2013. Intrinsic mechanical properties of 20 MAX-phase compounds. *Journal of the American Ceramic Society* 96, 2292–2297.
- Ching, W.-Y., Yoshiya, M., Adhikari, P., *et al.*, 2018. First-principles study in an inter-granular glassy film model of silicon nitride. *Journal of the American Ceramic Society* 101, 2673–2688.
- Clarke, D.R., 1987. On the equilibrium thickness of intergranular glass phases in ceramic materials. *Journal of the American Ceramic Society* 70, 15–22.
- Cubuk, E.D., Schoenholz, S.S., Rieser, J.M., *et al.*, 2015. Identifying structural flow defects in disordered solids using machine-learning methods. *Physical Review Letters* 114, 108001.
- Dai, X., Liu, X., Liu, L., Zhu, B., Fang, Z., 2015. A novel image-guided FT-IR sensor using chalcogenide glass optical fibers for the detection of combustion gases. *Sensors and Actuators B: Chemical* 220, 414–419.
- Dhakal, C., Aryal, S., Sakidja, R., Ching, W.-Y., 2015. Approximate lattice thermal conductivity of MAX phases at high temperature. *Journal of the European Ceramic Society* 35, 3203–3212.
- Dharmawardhana, C., Bakare, M., Misra, A., Ching, W.-Y., 2016. Nature of interatomic bonding in controlling the mechanical properties of calcium silicate hydrates. *Journal of the American Ceramic Society* 99, 2120–2130.
- Dharmawardhana, C., Misra, A., Ching, W.-Y., 2014. Quantum mechanical metric for internal cohesion in cement crystals. *Scientific Reports* 4, 7332.
- Dharmawardhana, C.C., Misra, A., Aryal, S., Rulis, P., Ching, W., 2013. Role of interatomic bonding in the mechanical anisotropy and interlayer cohesion of CSH crystals. *Cement and Concrete Research* 52, 123–130.
- Ding, J., Yu, Q., Asta, M., Ritchie, R.O., 2018. Tunable stacking fault energies by tailoring local chemical order in CrCoNi medium-entropy alloys. *Proceedings of the National Academy of Sciences* 115, 8919–8924.
- Donachie, M.J., Donachie, S.J., 2002. *Superalloys: A Technical Guide*. ASM International.
- Eifler, J., Podgornik, R., Steinmetz, N.F., *et al.*, 2016. Charge distribution and hydrogen bonding of a collagen α 2-chain in vacuum, hydrated, neutral, and charged structural models. *International Journal of Quantum Chemistry* 116, 681–691.
- Evans, J.S., Samudrala, R., Walsh, T.R., Oren, E.E., Tamerler, C., 2008. Molecular design of inorganic-binding polypeptides. *MRS Bulletin* 33, 514–518.
- Fayman, Y.C., 1987. Microstructural characterization and elemental partitioning in a direct-aged superalloy (DA 718). *Materials Science and Engineering* 92, 159–171.
- Fujita, T., 1992. Heat-resistant ferritic steels for advanced power plants. *Advanced Materials and Processes* 141, 42–48.
- Furukawa, H., Cordova, K.E., O'keefe, M., Yaghi, O.M., 2013. The chemistry and applications of metal-organic frameworks. *Science* 341, 1230444.
- Gao, M.C., Yeh, J.-W., Liaw, P.K., Zhang, Y., 2016. *High-Entropy Alloys*. Cham: Springer International Publishing.
- Gerold, U., Wiedenmann, A., Bellissent, R., Macht, M.-P., Wollenberger, H., 1999. Local atomic correlations of bulk amorphous ZrTiCuNiBe alloys. *Nanostructured Materials* 12, 605–608.
- Gong, Y., Adhikari, P., Liu, Q., *et al.*, 2017. Designing the interface of carbon nanotube/biomaterials for high-performance ultra-broadband photodetection. *ACS Applied Materials & Interfaces* 9, 11016–11024.
- Guo, S., Ng, C., Lu, J., Liu, C., 2011. Effect of valence electron concentration on stability of fcc or bcc phase in high entropy alloys. *Journal of Applied Physics* 109, 103505.
- Hasan, S., Adhikari P., Baral, K., Ching, W.-Y., unpublished.
- He, J., Fukuyama, S., Yokogawa, K., 1994. γ'' precipitate in inconel 718. *Journal of Materials Science and Technology* 10, 293–303.
- Hill, R., 1952. The elastic behaviour of a crystalline aggregate. *Proceedings of the Physical Society. Section A* 65, 349.
- Hohenberg, P., Kohn, W., 1964. Inhomogeneous electron gas. *Physical Review* 136, B864.
- Hong, S., Chen, W., Wang, T., 2001. A diffraction study of the γ'' phase in INCONEL 718 superalloy. *Metallurgical and Materials Transactions A* 32, 1887–1901.
- Huang, M.-Z., Ching, W., 1996. Electron states in a nearly ideal random-network model of amorphous SiO₂ glass. *Physical Review B* 54, 5299.
- Hunca, B., Dharmawardhana, C., Sakidja, R., Ching, W.-Y., 2016. Ab initio calculations of thermomechanical properties and electronic structure of vitreloy Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni₁₀Be_{22.5}. *Physical Review B* 94, 144207.
- Islam, N., Huang, W., Zhuang, H.L., 2018. Machine learning for phase selection in multi-principal element alloys. *Computational Materials Science* 150, 230–235.
- Jackson, A., Vincent, J.F., Turner, R., 1988. The mechanical design of nacre. *Proceedings of the Royal Society of London. Series B. Biological Sciences* 234, 415–440.
- Jiang, C., Wolverton, C., Sofo, J., Chen, L.-Q., Liu, Z.-K., 2004. First-principles study of binary bcc alloys using special quasirandom structures. *Physical Review B* 69, 214202.
- Jun, W.K., Willens, R., Duwez, P., 1960. Non-crystalline structure in solidified gold-silicon alloys. *Nature* 187, 869.
- Kleebe, H.-J., 1992. Influence of secondary phase chemistry on grain-boundary film thickness in silicon-nitride. *Zeitschrift für Metallkunde* 83, 610–617.
- Klueh, R., 2005. Elevated temperature ferritic and martensitic steels and their application to future nuclear reactors. *International Materials Reviews* 50, 287–310.
- Kohn, W., Sham, L.J., 1965. Self-consistent equations including exchange and correlation effects. *Physical Review* 140, A1133.

- Koval, N.E., Juaristi, J.I., Muñio, R.D., Alducin, M., 2019. Elastic properties of the TiZrNbTaMo multi-principal element alloy studied from first principles. *Intermetallics* 106, 130–140.
- Krizkova, M.C., Kuckova, S.H., Santrucek, J., Hynek, R., 2014. Peptide mass mapping as an effective tool for historical mortar analysis. *Construction and Building Materials* 50, 219–225.
- Li, N., Ching, W.-Y., 2014. Structural, electronic and optical properties of a large random network model of amorphous SiO₂ glass. *Journal of Non-Crystalline Solids* 383, 28–32.
- Li, N., Sakidja, R., Aryal, S., Ching, W.-Y., 2014. Densification of a continuous random network model of amorphous SiO₂ glass. *Physical Chemistry Chemical Physics* 16, 1500–1514.
- Li, Y., Ching, W., 1985. Band structures of all polycrystalline forms of silicon dioxide. *Physical Review B* 31, 2172.
- Li, Y., Guo, Q., Kalb, J., Thompson, C., 2008. Matching glass-forming ability with the density of the amorphous phase. *Science* 322, 1816–1819.
- Liang, L., Rulis, P., Kahr, B., Ching, W., 2009. Theoretical study of the large linear dichroism of herapathite. *Physical Review B* 80, 235132.
- Liang, L., Rulis, P., Ouyang, L., Ching, W., 2011. Ab initio investigation of hydrogen bonding and network structure in a supercooled model of water. *Physical Review B* 83, 024201.
- Liu, L., Cheng, T., Nagasaka, K., *et al.*, 2016. Coherent mid-infrared supercontinuum generation in all-solid chalcogenide microstructured fibers with all-normal dispersion. *Optics Letters* 41, 392–395.
- Lookman, T., Balachandran, P.V., Xue, D., Hogden, J., Theiler, J., 2017. Statistical inference and adaptive design for materials discovery. *Current Opinion in Solid State and Materials Science* 21, 121–128.
- Ma, Z., Shi, N., Mou, G., Liao, L., 1999. Crystal structure refinement of suolunite and its significance to the cement techniques. *Chinese Science Bulletin* 44, 2125–2130.
- Manz, T.A., 2017. Introducing DDEC6 atomic population analysis: Part 3. Comprehensive method to compute bond orders. *RSC Advances* 7, 45552–45581.
- Miracle, D.B., Senkov, O.N., 2017. A critical review of high entropy alloys and related concepts. *Acta Materialia* 122, 448–511.
- Mirov, S.B., Fedorov, V.V., Martyshev, D., *et al.*, 2015. Progress in mid-IR lasers based on Cr and Fe-doped II–VI chalcogenides. *IEEE Journal of Selected Topics in Quantum Electronics* 21, 292–310.
- Misra, A., Ouyang, L., Chen, J., Ching, W., 2007. Ab initio calculations of strain fields and failure patterns in silicon nitride intergranular glassy films. *Philosophical Magazine* 87, 3839–3852.
- Mo, S.-D., Ching, W., 1995. Electronic and optical properties of three phases of titanium dioxide: Rutile, anatase, and brookite. *Physical Review B* 51, 13023.
- Mo, S.-D., Ching, W., 2001. X-ray absorption near-edge structure in alpha-quartz and stishovite: Ab initio calculation with core-hole interaction. *Applied Physics Letters* 78, 3809–3811.
- Mo, Y., Aryal, S., Rulis, P., Ching, W.-Y., 2014. Crystal structure and elastic properties of hypothesized MAX phase-like compound (Cr₂Hf)₂Al₃C₃. *Journal of the American Ceramic Society* 97, 2646–2653.
- Mo, Y., Rulis, P., Ching, W., 2012. Electronic structure and optical conductivities of 20 MAX-phase compounds. *Physical Review B* 86, 165122.
- Mulliken, R., 1955a. Electronic population analysis on LCAO–MO molecular wave functions. II. Overlap populations, bond orders, and covalent bond energies. *The Journal of Chemical Physics* 23, 1841–1846.
- Mulliken, R.S., 1955b. Electronic population analysis on LCAO–MO molecular wave functions. I. *The Journal of Chemical Physics* 23, 1833–1840.
- Munch, E., Launey, M.E., Alsem, D.H., *et al.*, 2008. Tough, bio-inspired hybrid materials. *Science* 322, 1516–1520.
- Nagode, A., Kosec, L., Ule, B., Kosec, G., 2011. Review of creep resistant alloys for power plant applications. *Metallurgija* 50, 45–48.
- Nel, A.E., Mädlar, L., Velegol, D., *et al.*, 2009. Understanding biophysicochemical interactions at the nano–bio interface. *Nature Materials* 8, 543.
- Nguyen, V., Qian, M., Shi, Z., *et al.*, 2018. A novel quaternary equiatomic Ti–Zr–Nb–Ta medium entropy alloy (MEA). *Intermetallics* 101, 39–43.
- Nielsen, O., Martin, R.M., 1983. First-principles calculation of stress. *Physical Review Letters* 50, 697.
- Ouyang, L., Randaccio, L., Rulis, P., *et al.*, 2003. Electronic structure and bonding in vitamin B12, cyanocobalamin. *Journal of Molecular Structure: THEOCHEM* 622, 221–227.
- Patwardhan, S.V., Emami, F.S., Berry, R.J., *et al.*, 2012. Chemistry of aqueous silica nanoparticle surfaces and the mechanism of selective peptide adsorption. *Journal of the American Chemical Society* 134, 6244–6256.
- Peker, A., Johnson, W.L., 1993. A highly processable metallic glass: Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}. *Applied Physics Letters* 63, 2342–2344.
- Phua, Y.J., Roynne, A., 2018. Bio-cementation through controlled dissolution and recrystallization of calcium carbonate. *Construction and Building Materials* 167, 657–668.
- Pollock, T.M., van der Ven, A., 2019. The evolving landscape for alloy design. *MRS Bulletin* 44, 238–246.
- Poudel, L., Podgornik, R., Ching, W.-Y., 2017a. The hydration effect and selectivity of alkali metal ions on poly (ethylene glycol) models in cyclic and linear topology. *The Journal of Physical Chemistry A* 121, 4721–4731.
- Poudel, L., Rulis, P., Liang, L., Ching, W.-Y., 2014. Electronic structure, stacking energy, partial charge, and hydrogen bonding in four periodic B-DNA models. *Physical Review E* 90, 022705.
- Poudel, L., Steinmetz, N.F., French, R.H., *et al.*, 2016. Implication of the solvent effect, metal ions and topology in the electronic structure and hydrogen bonding of human telomeric G-quadruplex DNA. *Physical Chemistry Chemical Physics* 18, 21573–21585.
- Poudel, L., Tamerler, C., Misra, A., Ching, W.-Y., 2017b. Atomic-scale quantification of interfacial binding between peptides and inorganic crystals: The case of calcium carbonate binding peptide on aragonite. *The Journal of Physical Chemistry C* 121, 28354–28363.
- Poudel, L., Twarock, R., Steinmetz, N.F., Podgornik, R., Ching, W.-Y., 2017c. Impact of hydrogen bonding in the binding site between capsid protein and MS2 bacteriophage ssRNA. *The Journal of Physical Chemistry B* 121, 6321–6330.
- Poudel, L., Wen, A.M., French, R.H., *et al.*, 2015. Electronic structure and partial charge distribution of doxorubicin in different molecular environments. *ChemPhysChem* 16, 1451–1460.
- Qian, C., Yu, X., Wang, X., 2018. A study on the cementation interface of bio-cement. *Materials Characterization* 136, 122–127.
- Raccuglia, P., Elbert, K.C., Adler, P.D., *et al.*, 2016. Machine-learning-assisted materials discovery using failed experiments. *Nature* 533, 73.
- Rajan, K., 2005. Materials informatics. *Materials Today* 8, 38–45.
- Ramprasad, R., Batra, R., Pilania, G., Mannodi-Kanakithodi, A., Kim, C., 2017. Machine learning in materials informatics: Recent applications and prospects. *npj Computational Materials* 3, 54.
- Ren, S.-Y., Ching, W., 1981. Electronic structures of β - and α -silicon nitride. *Physical Review B* 23, 5454.
- Reuss, A., 1929. Berechnung der fließgrenze von mischkristallen auf grund der plastizitätsbedingung für einkristalle. *Journal of Applied Mathematics and Mechanics/Zeitschrift für Angewandte Mathematik und Mechanik* 9, 49–58.
- Richardson, I., 2008. The calcium silicate hydrates. *Cement and Concrete Research* 38, 137–158.
- Ruiz, C., Obabueki, A., Gillespie, K., 1992. Evaluation of the microstructure and mechanical properties of delta processed alloy 718. *Superalloys 1992*, 33–42.
- Rulis, P., Chen, J., Ouyang, L., *et al.*, 2005. Electronic structure and bonding of intergranular glassy films in polycrystalline Si₃N₄: Ab initio studies and classical molecular dynamics simulations. *Physical Review B* 71, 235317.
- Sakidja, R., Private communication.
- San, S., Li, N., Tao, Y., Zhang, W., Ching, W.-Y., 2018. Understanding the atomic and electronic origin of mechanical property in thaumasite and ettringite mineral crystals. *Journal of the American Ceramic Society* 101, 5177–5187.
- Sarikaya, M., Tamerler, C., Schwartz, D.T., Baneyx, F., 2004. Materials assembly and formation using engineered polypeptides. *Annual Review of Materials Research* 34, 373–408.

- Service, R., 2015. Biochemistry. Origin-of-life puzzle cracked. *Science* 347, 1298.
- Subramaniam, A., Koch, C.T., Cannon, R.M., Rühle, M., 2006. Intergranular glassy films: An overview. *Materials Science and Engineering: A* 422, 3–18.
- Sun, X., Zhang, H., Lu, S., *et al.*, 2017a. Phase selection rule for Al-doped CrMnFeCoNi high-entropy alloys from first-principles. *Acta Materialia* 140, 366–374.
- Sun, Y., Bai, H., Li, M., Wang, W., 2017b. Machine learning approach for prediction and understanding of glass-forming ability. *The Journal of Physical Chemistry Letters* 8, 3434–3439.
- Tanaka, I., Kleebe, H.J., Cinibulk, M.K., *et al.*, 1994. Calcium concentration dependence of the intergranular film thickness in silicon nitride. *Journal of the American Ceramic Society* 77, 911–914.
- Tancret, F., Toda-Caraballo, I., Menou, E., Díaz-Del-Castillo, P.E.J.R., 2017. Designing high entropy alloys employing thermodynamics and Gaussian process statistical analysis. *Materials & Design* 115, 486–497.
- Today, M., Nagase, T., Hori, T., *et al.*, 2017. Novel TiNbTaZrMo high-entropy alloys for metallic biomaterials. *Scripta Materialia* 129, 65–68.
- Tran, U.P., Le, K.K., Phan, N.T., 2011. Expanding applications of metal-organic frameworks: Zeolite imidazolate framework ZIF-8 as an efficient heterogeneous catalyst for the Knoevenagel reaction. *ACS Catalysis* 1, 120–127.
- Vapnik, V., 2013. *The Nature of Statistical Learning Theory*. Springer Science & Business Media.
- Wang, H., Li, N., Hu, Z., *et al.*, 2019. Structural, electronic, and dielectric properties of a large random network model of amorphous zeolitic imidazolate frameworks and its analogues. *Journal of the American Ceramic Society* 102 (8), 4602–4611.
- Wang, L., Rulis, P., Ching, W., 2013. Calculation of core-level excitation in some MAX-phase compounds. *Journal of Applied Physics* 114, 023708.
- Xu, Y.-N., Ching, W., 1995. Electronic structure and optical properties of α and β phases of silicon nitride, silicon oxynitride, and with comparison to silicon dioxide. *Physical Review B* 51, 17379.
- Xue, D., Balachandran, P.V., Hogden, J., *et al.*, 2016. Accelerated search for materials with targeted properties by adaptive design. *Nature Communications* 7, 11241.
- Yao, H., Ouyang, L., Ching, W.Y., 2007. Ab initio calculation of elastic constants of ceramic crystals. *Journal of the American Ceramic Society* 90, 3194–3204.
- Ye, Y., Wang, Q., Lu, J., Liu, C., Yang, Y., 2016. High-entropy alloy: Challenges and prospects. *Materials Today* 19, 349–362.
- Yeh, J.W., Chen, S.K., Lin, S.J., *et al.*, 2004. Nanostructured high-entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes. *Advanced Engineering Materials* 6, 299–303.
- Yoshiya, M., Tatsumi, K., Tanaka, I., Adachi, H., 2002. Theoretical study on the chemistry of intergranular glassy film in $\text{Si}_3\text{N}_4\text{-SiO}_2$ ceramics. *Journal of the American Ceramic Society* 85, 109–112.
- Yuan, Y., Wu, Y., Yang, Z., *et al.*, 2019. Formation, structure and properties of biocompatible TiZrHfNbTa high-entropy alloys. *Materials Research Letters* 7, 225–231.
- Zerr, A., Riedel, R., Sekine, T., *et al.*, 2006. Recent advances in new hard high-pressure nitrides. *Advanced Materials* 18, 2933–2948.
- Zhang, B., Guo, W., Yu, Y., *et al.*, 2015. Low loss, high NA chalcogenide glass fibers for broadband mid-infrared supercontinuum generation. *Journal of the American Ceramic Society* 98, 1389–1392.

Further Reading

- Adhikari, P., Li, N., Rulis, P., Ching, W.-Y., 2018. Deformation behavior of an amorphous zeolitic imidazolate framework – From a supersoft material to a complex organometallic alloy. *Physical Chemistry Chemical Physics* 20, 29001–29011.
- Adhikari, P., Xiong, M., Li, N., *et al.*, 2016. Structure and electronic properties of a continuous random network model of an amorphous zeolitic imidazolate framework (a-ZIF). *The Journal of Physical Chemistry C* 120, 15362–15368.
- Aryal, S., Sakidja, R., Barsoum, M.W., Ching, W.Y., 2014. A genomic approach to the stability, elastic, and electronic properties of the MAX phases. *Physica Status Solidi (b)* 251, 1480–1497.
- Baral, K., Adhikari, P., Ching, W.Y., 2016. Ab initio modeling of the electronic structures and physical properties of a-Si_{1-x}Ge_xO₂ Glass (x = 0–1). *Journal of the American Ceramic Society* 99, 3677–3684.
- Barsoum, M.W., 2013. *MAX Phases: Properties of Machinable Ternary Carbides and Nitrides*. John Wiley & Sons.
- Ching, W.-Y., Rulis, P., 2012. *Electronic Structure Methods for Complex Materials: The Orthogonalized Linear Combination of Atomic Orbitals*. Oxford University Press.
- Ching, W., 1981. Microscopic calculation of localized electron states in an intrinsic glass. *Physical Review Letters* 46, 607.
- Ching, W., Xu, Y.-N., Rulis, P., Ouyang, L., 2006b. The electronic structure and spectroscopic properties of 3C, 2H, 4H, 6H, 15R and 21R polymorphs of SiC. *Materials Science and Engineering: A* 422, 147–156.
- Ching, W.Y., Yoshiya, M., Adhikari, P., *et al.*, 2018. First-principles study in an inter-granular glassy film model of silicon nitride. *Journal of the American Ceramic Society* 101, 2673–2688.
- Dharmawardhana, C., Misra, A., Ching, W.-Y., 2014. Quantum mechanical metric for internal cohesion in cement crystals. *Scientific Reports* 4, 7332.
- Gao, M.C., Yeh, J.-W., Liaw, P.K., Zhang, Y., 2016. *High-Entropy Alloys*. Cham: Springer International Publishing.
- Hunca, B., Dharmawardhana, C., Sakidja, R., Ching, W.-Y., 2016. Ab initio calculations of thermomechanical properties and electronic structure of vitreloy $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$. *Physical Review B* 94, 144207.
- Li, N., Sakidja, R., Aryal, S., Ching, W.-Y., 2014. Densification of a continuous random network model of amorphous SiO₂ glass. *Physical Chemistry Chemical Physics* 16, 1500–1514.
- Liang, L., Rulis, P., Ouyang, L., Ching, W., 2011. Ab initio investigation of hydrogen bonding and network structure in a supercooled model of water. *Physical Review B* 83, 024201.
- Poudel, L., Steinmetz, N.F., French, R.H., *et al.*, 2016. Implication of the solvent effect, metal ions and topology in the electronic structure and hydrogen bonding of human telomeric G-quadruplex DNA. *Physical Chemistry Chemical Physics* 18, 21573–21585.

Relevant Websites

www.abinitio.com
 Ab Initio.
<https://www.ccdc.cam.ac.uk>
 CCDC.
 www.gaussian.com
 Gaussian.
<https://www.materialsproject.org>
 Materials Project.

www.quantum-espresso.org

Quantum-espresso.

www.scm.com

SCM.

www.vasp.at

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<https://www.wwpdb.org>

wwPDB: Worldwide Protein Data Bank.

Predictive Modeling of Ceramic Materials

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Introduction

The vital relationship between theory and experiment in materials science is both well-established and constantly evolving. Our ability to model, rationalize, and predict the properties of materials spans a variety of time scales and length scales; from the quantum realm up to long-term macroscopic behaviors. In this chapter we track the history of ceramics modeling, moving from analytical models and finite element analysis, up to modern *ab initio* methods such as Density Functional Theory (DFT) and classical Molecular Dynamics (MD) that are now computationally feasible for large and complex crystal structures due to advances in high performance computing (HPC) and software development. The chapter will start by exploring how models of fundamental ceramic properties have been developed, and then we will delve into recent developments in the predictive modeling of piezoelectric ceramics, which are widely used as sensors, actuators, and ultrasonic transducers (Jaffe, 2012).

As ceramics continue to expand their range of applications, from aerospace to advanced electronics, sophisticated theoretical and phenomenological models are needed to predict the behavior of these complex materials under realistic working conditions, and to guide rational design of advanced structures (Padture, 2016). Taking for example the testing of composite materials in the aerospace industry – requiring real engine conditions and characterization across diverse length and time scales – predictive models promise to drastically reduce the cost and effort of both the discovery and development of new materials, which could potentially provide greener, more cost-effective solutions.

Modeling Ceramics at the Macroscale

The oldest traditional use of ceramics is the porous inorganic materials used as bricks and roof tiles, the production of which remains a significant contributor to the construction industry. The infrastructural ceramics sector employs about 338,000 people in the EU and accounts for €27.8 billion in production value (CEPS, Economisti Associati and Ecorys, 2017). The widespread application of these materials is mostly due to the cheap raw materials and the standardized manufacturing processes, which follow procedures that were developed thousands of years ago. In this process clays are mixed with water to the desired plasticity, then shaped, dried and baked at $\sim 1000^{\circ}\text{C}$. Bricks and roof tiles have all the prototypical characteristics of ceramics, with high strength, durability, longevity, low reactivity, and high electrical and chemical resistance.

Despite its long history, there is still an ongoing need for modeling in the infrastructural ceramics sector, particularly when studying ceramics in historic buildings. To characterise such porous ceramics, researchers often measure a property known as sorptivity, which is associated with the principal ceramic properties listed above. Experimentally this test cannot always be performed, such as in cultural heritage sites, or even in a high-throughput automated industrial process. This has necessitated the development of analytical formulae that can accurately predict the sorptivity coefficient. For example, Pia and colleagues developed an Intermingled Fractal Units (IFU) model that reproduces pore size distributions, simulates the water absorption process, and estimates the sorptivity coefficient (Pia *et al.*, 2016b). The results of the model have been benchmarked against multiple experimental datasets and theoretical predictions (Pia *et al.*, 2016a; Pia and Sanna, 2013, 2014), illustrating the power of predictive models for designing future materials and predicting their lifespans.

Sadowski and Samborski (2003) took a different approach and developed a mesomechanical model to study porous polycrystalline ceramics under tension and compression. The model assumes the porosity of the material is distributed homogeneously inside the grains and along the grain boundaries. In their paper, two different crack initiation mechanisms are proposed and analysed for tension and compression. The proposed description of two different mechanisms of crack nucleation and propagation results in formulation of constitutive relations in order to specify differences in the material behavior under strain.

It is also important to highlight the role of predictive modeling as regards the processing of ceramics. Olevsky *et al.* (2005) present a model that describes anisotropic shrinkage during sintering in a powder compact of aligned, elongated particles by deriving the anisotropic sintering stress and the anisotropic generalized viscosity as a function of material and geometric parameters. The powder compact consists of elongated particles, which are perfectly aligned and simply packed with elliptical pores between the particles. Their model considers mass transport by grain boundary diffusion and surface diffusion. Shrinkage rates are calculated for a variety of geometries and are compared to kinetic Monte Carlo simulations.

The high strength of ceramics makes them useful in the development of reduced-weight steel armors for high-speed military vehicles. Forquin *et al.* (2003) describe a bilayered geometry, with the ceramic front end dampening any projectile and spreading out the energy of impact. They modeled silicon carbide ceramics to determine the root causes of damage and failure and developed an anisotropic damage model to rationalize the experimentally observed failure scenarios. Numerical simulations substantiate the hypothesis of failure caused by the tensile stresses induced by roughness defects, and match observations from experiments. Wang and Li (2015) similarly examined the failure and fracture mechanisms of ceramics under dynamic loading, specifically alumina ceramics in composite armor. In

this study, a pressure bar technique combined with high speed photography was used to directly observe the dynamic macro-cracking and fragmentation process in alumina and to characterise the stress and strain histories. An experimentally validated 3D finite element model of the full-scale test was developed to predict the stress distribution and damage evolution in alumina. It was found that the damage evolution is determined by the multiaxial stress state, the substantial localized tensile stress concentration, and the stress direction. The cracking process leads to longitudinal axial splitting failure on the surface and internal diagonal damage bands. The dynamic failure process in alumina is dominated by both the intergranular and transgranular fracture mechanisms.

Numerical simulation methods such as finite element (FE) modeling have been extensively used to predict the stress distribution in ceramics subjected to dynamic loads, and investigate the damage evolution that it is usually difficult to observe experimentally due to the instantaneous nature at high rates. For accurate numerical simulation, various constitutive models have been developed to quantify the mechanical response of ceramics under different loading rates, such as mixed-mode cohesive laws and the Johnson–Holmquist material model with damage (JH-2). The JH-2 model has been widely accepted to simulate the mechanical behavior of damaged brittle materials subjected to high pressures, large strain, and high strain rates. However, a major limitation of the methods presented in this section is that they all require prior knowledge of the physical properties of the material. Hence, while they are invaluable for testing how to incorporate known materials in new applications and in a variety of environments, they cannot predict material properties, or screen for new ceramic materials. For this, we rely on molecular modeling, as outlined in detail in the following section.

Modeling Ceramics at the Nanoscale

Atomic-scale investigations continue to highlight how a nanoscale understanding of physical phenomena is necessary to enhance macroscopic material properties (Guerin *et al.*, 2019b). In this section the basic concepts and principles of the quantum mechanical modeling technique density functional theory (DFT) are introduced. The section outlines the physics of DFT and describes how DFT is used to predict the physical properties of ceramics. At its core, DFT is an electronic structure calculation that allows highly accurate prediction of a plethora of properties from an optimized theoretical structure at 0 Kelvin, including but not limited to: atomic charges, density of states, band gaps, binding energies, dielectric and elastic properties, lattice vibrations and phonons. Thermal effects and weak dispersion effects are now also being routinely incorporated into DFT models, which increases their relevance for ceramics modeling. DFT can complement classical molecular dynamics (MD) simulations, which essentially treat interacting atoms as Newtonian spheres connected by springs and so can treat millions of atoms for microsecond timescales beyond the reach of DFT calculations.

What is Density Functional Theory?

For single electron systems (2D potential well, hydrogenic atom) it is possible to obtain an exact solution to the Schrodinger equation (Pertsch, 1990). However, for any system more complicated than this it is impossible to precisely solve the Schrödinger equation and obtain a mathematical description of the system, i.e., the wave function, which is squared to generate the electron density. Density functional theory (DFT) provides an approximate solution to the many-body Schrodinger equation, which gives the ground state properties of the system.

The term DFT comes from the fact that the functional used in DFT calculations is the electron density, which is itself a function of space and time (mathematically, a functional takes a function and gives a resulting scalar value). The Hohenberg–Kohn (Hohenberg and Kohn, 1964) theorem tells us that the total ground state energy of a many-electron system is a functional of the density (shown for glycine in Fig. 1). The total energy of the system is written in terms of several individual energy contributions, each of which is a functional of the charge density: ion–electron potential energy; ion–ion potential energy; electron–electron energy; kinetic energy; exchange–correlation energy.

The most computationally challenging energy contributions are the kinetic energy and the exchange–correlation energy. The kinetic energy is calculated using the Kohn–Sham orbitals that map the system of interacting electrons on to a system of non-interacting electrons moving in an effective potential. The exchange–correlation energy accounts for the exchange interaction due to repulsion between electrons with parallel spins, and the correlation interaction, which is the correlated motion between electrons of anti-parallel spins due to their mutual Coulombic repulsion. Exchange–correlation effects in ceramics are often treated via the Perdew, Burke, and Ernzerhof (PBE) (Perdew *et al.*, 1992) implementation of the generalized gradient approximation (GGA) (Perdew *et al.*, 1996). GGA builds on what is known as the local density approximation (LDA), by considering both the local electron density and its gradient, as the electron density can vary rapidly over a small region of space.

Predicting Material Properties

The general methodologies outlined in the following sections are detailed as for the DFT software VASP (Vienna ab initio simulation package) (Hafner, 2007), which uses plane wave basis sets (Kresse and Furthmüller, 1996), and the projector augmented-wave (PAW) method (Kresse and Joubert, 1999) to solve the electronic structure of periodic crystalline materials. However, there are multiple

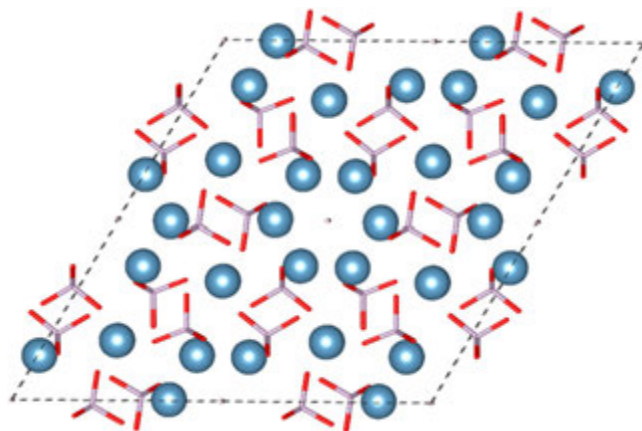


Fig. 1 The unit cell of the biomineral hydroxyapatite (HA), discussed in the following sections as a novel polycrystalline ceramic material, showing the positions of the calcium and phosphite ions (calcium in turquoise, phosphorous in lilac, oxygen in red). DFT allows us to predict the material properties, and rationalize the behavior of crystalline ceramics, starting with the unit cell (visualized using VESTA. (Momma and Izumi, 2011)).

flavors of DFT available in widely used software packages such as Quantum Espresso (Giannozzi *et al.*, 2009), cp2k (Hutter *et al.*, 2014), Gaussian (Frisch *et al.*, 2009), and ABINIT (Gonze *et al.*, 2009) which span from molecules to crystals to interfaces. Modern developments in DFT include hybrid functionals, advanced dispersion and thermal corrections; interested readers are directed to the following works: Chai and Head-Gordon (2008), Marsman *et al.* (2008), Grimme *et al.* (2010), Marom *et al.* (2013), and Reilly and Tkatchenko (2014).

Geometry Optimization

The first step in DFT ceramics modeling is to take the experimental structure of interest and allow its unit cell parameters to relax in order to obtain ideal ground state geometry. This structure could be a crystal unit cell for polycrystalline ceramics, a bulk ceramic interacting with a molecular coating, or another bulk material. Structures can be generated from experimental data, for example solved X-ray structures hosted at the Cambridge Crystallographic Data Centre (CCDC).

Structures are generally optimized using the conjugate gradient algorithm. For a periodic system, integrals in real space over the infinitely extended system are replaced by integrals over the finite first Brillouin zone in reciprocal space, in accordance with Bloch's theorem. These integrals are solved at a finite number of points in the Brillouin zone, called the k -point mesh, or grid. For the highest accuracy, a dense k -point grid should be used for geometry optimizations; and a high plane wave energy cut-off (all plane waves with a kinetic energy less than this are included in the basis set). Γ -centered k -point grids are generally recommended for non-centrosymmetric unit cells. Values should be selected after energy convergence tests with respect to N (where N = number of subdivisions of the reciprocal lattice vector), and plane wave cut off energy. Minimum converged values should be chosen to balance calculation accuracy with computational expense.

Case Study: Calculation of Elastic Constants

One of the most useful properties of ceramics is their mechanical strength, with high hardness and elastic moduli. For piezoelectric and ferroelectric ceramics, discussed in the next section, the elastic stiffness constants c_{kij} are required to calculate the piezoelectric strain constants d_{ik} (Ikeda, 1996). The elastic compliance can easily be derived from the stiffness and measured using impedance spectroscopy, as can the Young's modulus.

The elastic constants are calculated in the form of the stiffness tensor, C , presented as a 6×6 matrix (Eq. (1)). VASP outputs this tensor in Voigt notation in kB, so some post-processing is required to produce C in matrix notation in GPa.

$$C = \begin{pmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ c_{21} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ c_{31} & c_{32} & c_{33} & c_{34} & c_{35} & c_{36} \\ c_{41} & c_{42} & c_{43} & c_{44} & c_{45} & c_{46} \\ c_{51} & c_{52} & c_{53} & c_{54} & c_{55} & c_{56} \\ c_{61} & c_{62} & c_{63} & c_{64} & c_{65} & c_{66} \end{pmatrix} \quad (1)$$

The number of non-zero elements in the elastic matrix will vary according to the symmetry of the system being studied. For more information on these constants, their matrix representations and their units, readers are directed to Nye (1985). Two

methods are described below to calculate the elastic constants of ceramics; one for relatively small systems, and one for systems with a unit cell greater than approximately 250 atoms.

Finite differences

A finite difference method is the most efficient way to calculate the elastic stiffness tensor, with every atom in the unit cell displaced along each Cartesian axis by ± 0.01 Å. Generally a low density Γ -centered k -point grid can be used – multiple reports (Guerin *et al.*, 2019a, 2018b) show the negligible dependence of predicted elastic constants on the number of k -points used, once $N > 1$. If computationally feasible via HPC, a high plane wave energy cut-off ≥ 1000 eV allows the stress tensor to fully converge if there are oxygen and nitrogen atoms in the system (Tulip and Clark, 2004). Elastic moduli can be derived from the stiffness matrix components. For crystalline materials of known dimensions the approximations of Nye (1985) can be used, otherwise Voigt–Reuss approximations (Voigt, 1928; Reuss, 1929) are recommended.

Strain controlled calculations

The computational expense of a finite difference calculation scales very rapidly with increasing number of atoms in the unit cell. This is because more atoms mean more degrees of freedom, i.e., more atomic displacements need to be carried out. For larger ceramic unit cells (approx. 250 atoms at time of writing) it is computationally prudent to use single point energy calculations, following the more traditional method of applying individual volume conserving strains to the system and measuring the corresponding stress tensor (Guerin *et al.*, 2018a). As conjugate gradient relaxations can be restarted from checkpoint files, these calculations are not limited by HPC restrictions on individual runs and individual elastic constants of larger systems can be calculated.

Along with elastic properties, Petrov *et al.* (2017) used experimentally validated DFT calculations to study ion mobility in layered perovskite-like compounds. They combined DFT with impedance spectroscopy and classical molecular dynamics simulations to understand, rationalize and quantify the phenomenon across time and length scales. Using DFT, the group calculated the charges of atoms in the crystal structure and fed this into MD simulations of sodium mobility in the temperature range of 523–923K. Based on these calculations, the dependence of the diffusion coefficients of sodium atoms on temperature was studied. The mobility of sodium ions in NaLaTiO₄ is demonstrated to be higher in certain compounds due to an increase in ionic character of the chemical bonds. This study demonstrates well how to use and combine DFT and MD to study time dependent and temperature dependent phenomena. This method can also be seen in the work of Kroll (2005), who investigated the structures, energies, and elastic properties of some polymer-derived nitride ceramics. These model structures ranged in size from 104 to 448 atoms and were generated by an empirical network algorithm prior to DFT and MD calculations due to the paucity of available crystal structures, even as non-oxide ceramics were gaining attention due of their covalent bonding providing mechanical reliability and high-temperature stability. Synthesized from polymers, all nitride ceramics remain amorphous at least up to 1000°C. Even at higher temperatures much of the material is featureless and amorphous, with some materials retaining a predominantly amorphous structure at 2000°C.

An interesting use of DFT calculations in biocompatible ceramics modeling can be found in the work of Haverty *et al.* (2005). Hydroxyapatite (HA) is a leading biocompatible material extensively used for bone implants as a porous ceramic graft and as a bioactive coating (Shikinami and Okuno, 2001, 1999). Electrical characteristics of HA can be employed in implantable devices for real-time in vivo pressure sensor applications such as in knee or hip prosthetics (Tofail *et al.*, 2015). In this work, DFT calculations combined with Rietveld analysis (a technique used to extract crystal characteristics from Powder XRD measurements) was used to challenge the proposed crystal structure of HA. By studying the structure and energetics of HA, the previously proposed P6₃/m and P6₃ hexagonal structural models were found to be energetically unfavorable when compared to both the previously proposed P2₁/b symmetry and a newly proposed monoclinic P2₁ structural model. A detailed analysis of the symmetry restrictions and inconsistencies between the reported physical properties, such as diffraction and birefringence, with hexagonal symmetry questioned the validity of the previous models. Rietveld analysis carried out on a synthetic sample, reported to be predominantly hexagonal at room temperature, showed that the diffraction pattern of this material can be interpreted as a mixed monoclinic phase, 23% monoclinic P2₁/b and 77% monoclinic P2₁. This interpretation reconciled many anomalies in reported experimental observations.

DFT for Piezoelectric Ceramics

Piezoelectric ceramics generate a surface charge that is proportional to an applied force, and conversely strain in the presence of an electric field. The most widely used piezoelectric ceramic is Lead Zirconium Titanate (PZT) (Chen *et al.*, 2010, Lobl *et al.*, 1999), followed by its lead-free alternative Barium Titanate (Berlincourt and Jaffe, 1958, Gao *et al.*, 2011). In the past decade, research has intensified to find high-performance lead-free piezoceramics (Shrout and Zhang, 2007), due to stricter environmental regulations, and also due to the growing field of implantable piezoceramics for medical device applications. Molecular modeling is an invaluable tool to screen for piezoceramic compositions that could challenge PZT as regards high piezoelectric constants, low permittivity, high Curie temperature, and high electromechanical efficiency. However, there is also a wide variety of applications for piezoceramics with more modest piezoelectric constants (Damjanovic, 1998), particularly organic piezoceramics (Wu *et al.*, 2016, You *et al.*, 2017). For example, hydroxyapatite, as mentioned in the previous section, is a biocompatible piezoceramic when poled under a high electric field (Gandhi *et al.*, 2014, Tofail *et al.*, 2009). The selective adsorption of proteins on polarized domains indicate the potential for real-time biosensing applications of HA (Korostynska *et al.*, 2013).

Calculation of piezoelectric charge tensor

Piezoelectric charge constants, e_{ij} , can be calculated using density functional perturbation theory (DFPT) (Wu *et al.*, 2005). Similar considerations for k -point grids and plane wave cut off values should be made as for elastic constant calculations. The magnitudes of piezoelectric constants calculated with a single k -point are generally not physically realistic, nor consistent with crystal symmetries. Using the piezoelectric charge coefficients, e_{ij} , which are calculated directly by VASP, and the elastic stiffness constants, c_{kj} , we can calculate the more useful piezoelectric strain coefficient, d_{ik} , using the relationship

$$d_{ik} = e_{ij} / c_{kj} \quad (2)$$

Currently, VASP only supports calculation of the ionic contribution to the elastic stiffness constants using DFPT, and so cannot be used to derive the full elastic stiffness tensor in the same calculation. Typical deviations between finite difference calculations and DFPT range from 0% to 15% (Guerin *et al.*, 2017) with the maximum deviation providing an estimate of the theoretical error in the predictions.

Derivation of voltage constants

DFPT calculations can also predict the static dielectric tensor of the ceramic being studied (Gonze and Lee, 1997). Using the dielectric tensor, we can extract the final piezoelectric constant: the voltage constant, g_{ik} . This is an important figure of merit (FoM) for energy harvesting applications, and in motion and pressure sensing. To obtain these g_{ik} values we can divide the corresponding piezoelectric strain constant, d_{ik} , by the relevant dielectric constant ϵ_{ii} , as shown in Eq. (3). These constants are measured in V m/N.

$$g_{ik} = d_{ik} / \epsilon_{ii} \epsilon_0 \quad (3)$$

Future of Ceramics Modeling

The range of applications for ceramic materials continues to expand and diversify. As it does, modeling needs to develop alongside it – in particular, accurate high-throughput screening of structures and properties is required, to provide atomic-scale insight into macroscopic phenomena. We are already beginning to see the emergence of machine learning in ceramics modeling (de Jong *et al.*, 2015), which will become even more exciting and influential as machine learning and artificial intelligence become more prominent in both research and industry. As exemplified by the work reviewed in this work, ceramic composites and bio-compatible ceramics are very active areas of research, and simulation-guided experiments will be crucial to increase the variety of available compositions and structures and so accelerate applications for these materials. An ongoing challenge for all computational models, particularly DFT, is to accurately simulate the properties of ceramic materials in presence of dopants (Alay-e-Abbas *et al.*, 2019; Mathew *et al.*, 2018), additives (Barauskas *et al.*, 2018; Chen *et al.*, 2018) and fillers (Agrawal and Satapathy, 2015; Song *et al.*, 2019), the use of which is common practice and hugely impacts the final application. Continuous improvements and expansion of computational modeling methods such as polarizable force fields and combined DFT/MD models, coupled with advances in HPC and data processing, should soon provide researchers with truly predictive computational tools to steer and speed discovery and development of ceramic materials for an ever expanding range of technology applications.

References

- Agrawal, A., Satapathy, A., 2015. Mathematical model for evaluating effective thermal conductivity of polymer composites with hybrid fillers. *International Journal of Thermal Sciences* 89, 203–209.
- Alay-e-Abbas, S.M., Yousaf, M.W., Abbas, G., Amin, N., Laref, A., 2019. Theoretical investigation of thermodynamic and optoelectronic properties of Ce^{4+} doped SrZrO_3 ceramics: A DFT study. *Ceramics International* 45 (15), 18281–18290.
- Barauskas, R., Sankauskaite, A., Abraitienė, A., 2018. Investigation of the thermal properties of spacer fabrics with bio-ceramic additives using the finite element model and experiment. *Textile Research Journal* 88, 293–311.
- Berlincourt, D., Jaffe, H., 1958. Elastic and piezoelectric coefficients of single-crystal barium titanate. *Physical Review* 111, 143.
- CEPS, Economisti Associati and Ecorys, 2017. Cumulative Cost Assessment of the EU Ceramics Industry – Key Findings & Executive Summary. Available at: <https://ec.europa.eu/docsroom/documents/25021/attachments/1/translations/en/renditions/native>.
- Chai, J.-D., Head-Gordon, M., 2008. Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Physical Chemistry Chemical Physics* 10, 6615–6620.
- Chen, X., Wu, Y., Lu, Z., *et al.*, 2018. Assessment of conversion efficiency of Cr^{4+} ions by aliovalent cation additives in Cr: YAG ceramic for edge cladding. *Journal of the American Ceramic Society* 101, 5098–5109.
- Chen, X., Xu, S., Yao, N., Shi, Y., 2010. 1.6 V nanogenerator for mechanical energy harvesting using PZT nanofibers. *Nano Letters* 10, 2133–2137.
- Damjanovic, D., 1998. Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics. *Reports on Progress in Physics* 61, 1267.
- de Jong, M., Chen, W., Geerlings, H., Asta, M., Persson, K.A., 2015. A database to enable discovery and design of piezoelectric materials. *Scientific Data* 2, 150053.
- Forquin, P., Denoual, C., Cotténot, C., Hild, F., 2003. Experiments and modelling of the compressive behaviour of two SiC ceramics. *Mechanics of Materials* 35, 987–1002.
- Frisch, M.J., Hratchian, H.P., Niels, A.B., 2009. Gaussian 09: Programmer's Reference, Gaussian.
- Gandhi, A.A., Wojtas, M., Lang, S., Kholkin, A.L., Tofail, S.A., 2014. Piezoelectricity in poled hydroxyapatite ceramics. *Journal of the American Ceramic Society* 97, 2867–2872.
- Gao, J., Xu, Z., Li, F., *et al.*, 2011. The hydrostatic pressure dependence of the piezoelectric properties for the barium titanate and lead titanate crystals: Thermodynamic analysis. *Journal of Applied Physics* 109, 114111.
- Giannozzi, P., Baroni, S., Bonini, N., *et al.*, 2009. QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter* 21, 395502.

- Gonze, X., Amadon, B., Anglade, P.-M., *et al.*, 2009. ABINIT: First-principles approach to material and nanosystem properties. *Computer Physics Communications* 180, 2582–2615.
- Gonze, X., Lee, C., 1997. Dynamical matrices, born effective charges, dielectric permittivity tensors, and interatomic force constants from density-functional perturbation theory. *Physical Review B* 55, 10355.
- Grimme, S., Antony, J., Ehrlich, S., Krieg, H., 2010. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *The Journal of Chemical Physics* 132, 154104.
- Guerin, S., O'donnell, J., Haq, E.U., *et al.*, 2019a. Racemic amino acid piezoelectric transducer. In: *Physical Review Letters*, 122, p. 047701.
- Guerin, S., Stapleton, A., Chovan, D., *et al.*, 2017. Control of piezoelectricity in amino acids by supramolecular packing. In: *Nature Materials*, 17, p. 180.
- Guerin, S., Syed, T.A., Thompson, D., 2018a. Deconstructing collagen piezoelectricity using alanine-hydroxyproline-glycine building blocks. *Nanoscale* 10, 9653–9663.
- Guerin, S., Tofail, S.A., Thompson, D., 2018b. Longitudinal piezoelectricity in orthorhombic amino acid crystal films. *Crystal Growth & Design* 18, 4844–4848.
- Guerin, S., Tofail, S.A., Thompson, D., 2019b. Organic piezoelectric materials: Milestones and potential. *NPG Asia Materials* 11, 10.
- Hafner, J., 2007. Materials simulations using VASP – A quantum perspective to materials science. *Computer Physics Communications* 177, 6–13.
- Haverty, D., Tofail, S.A., Stanton, K.T., Mcmonagle, J.B., 2005. Structure and stability of hydroxyapatite: Density functional calculation and Rietveld analysis. *Physical Review B* 71, 094103.
- Hohenberg, P., Kohn, W., 1964. Inhomogeneous electron gas. *Physical Review* 136, B864.
- Hutter, J., Iannuzzi, M., Schiffmann, F., Vandevondele, J., 2014. cp2k: Atomistic simulations of condensed matter systems. *Wiley Interdisciplinary Reviews: Computational Molecular Science* 4, 15–25.
- Ikeda, T., 1996. *Fundamentals of Piezoelectricity*. Oxford University Press.
- Jaffe, B., 2012. *Piezoelectric Ceramics*. Elsevier.
- Korostynska, O., Gandhi, A.A., Mason, A., Al-Shamma'a, A., Tofail, S.A., 2013. Biomedical sensing with hydroxyapatite ceramics in GHz frequency range. *Key Engineering Materials*. 26–29. (Trans Tech Publ).
- Kresse, G., Furthmüller, J., 1996. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B* 54, 11169.
- Kresse, G., Joubert, D., 1999. From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review B* 59, 1758.
- Kroll, P., 2005. Modelling polymer-derived ceramics. *Journal of the European Ceramic Society* 25, 163–174.
- Lobl, H., Klee, M., Wunnicke, O., *et al.*, 1999. Piezo-electric AlN and PZT films for micro-electronic applications. In: *Proceedings of the 1999 IEEE Ultrasonics Symposium*, pp. 1031–1036. IEEE.
- Marom, N., Distasio Jr., R.A., Atalla, V., *et al.*, 2013. Many-body dispersion interactions in molecular crystal polymorphism. *Angewandte Chemie International Edition* 52, 6629–6632.
- Marsman, M., Paier, J., Stroppa, A., Kresse, G., 2008. Hybrid functionals applied to extended systems. *Journal of Physics: Condensed Matter* 20, 064201.
- Mathew, S., Ganguly, P., Rhatigan, S., *et al.*, 2018. Cu-doped TiO₂: Visible light assisted photocatalytic antimicrobial activity. *Applied Sciences* 8, 2067.
- Momma, K., Izumi, F., 2011. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography* 44, 1272–1276.
- Nye, J.F., 1985. *Physical Properties of Crystals: Their Representation by Tensors and Matrices*. Oxford University Press.
- Olevsky, E., Kushnarev, B., Maximenko, A., Tikare, V., Braginsky, M., 2005. Modelling of anisotropic sintering in crystalline ceramics. *Philosophical Magazine* 85, 2123–2146.
- Padture, N.P., 2016. Advanced structural ceramics in aerospace propulsion. *Nature Materials* 15, 804.
- Perdew, J.P., Burke, K., Ernzerhof, M., 1996. Generalized gradient approximation made simple. *Physical Review Letters* 77, 3865.
- Perdew, J.P., Chevary, J., Vosko, S., *et al.*, 1992. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Physical Review B* 46, 6671.
- Pertsch, D., 1990. Exact solution of the Schrodinger equation for a potential well with a barrier and other potentials. *Journal of Physics A: Mathematical and General* 23, 4145.
- Petrov, A.A., Melnikova, N.A., Petrov, A.V., *et al.*, 2017. Experimental investigation and modelling of the Na⁺ mobility in NaLnTiO₄ (Ln = La, Nd) ceramics. *Ceramics International* 43, 10861–10865.
- Pia, G., Casnedi, L., Ricciu, R., *et al.*, 2016a. Thermal properties of porous stones in cultural heritage: Experimental findings and predictions using an intermingled fractal units model. *Energy and Buildings* 118, 232–239.
- Pia, G., Sanna, U., 2013. A geometrical fractal model for the porosity and thermal conductivity of insulating concrete. *Construction and Building Materials* 44, 551–556.
- Pia, G., Sanna, U., 2014. An intermingled fractal units model to evaluate pore size distribution influence on thermal conductivity values in porous materials. *Applied Thermal Engineering* 65, 330–336.
- Pia, G., Siligardi, C., Casnedi, L., Sanna, U., 2016b. Pore size distribution and porosity influence on Sorptivity of ceramic tiles: From experimental data to fractal modelling. *Ceramics International* 42, 9583–9590.
- Reilly, A.M., Tkatchenko, A., 2014. Role of dispersion interactions in the polymorphism and entropic stabilization of the aspirin crystal. *Physical Review Letters* 113, 055701.
- Reuss, A., 1929. Calculation of the flow limits of mixed crystals on the basis of the plasticity of monocrystals. *Zeitschrift für Angewandte Mathematik und Mechanik* 9, 49–58.
- Sadowski, T., Samborski, S., 2003. Prediction of the mechanical behaviour of porous ceramics using mesomechanical modelling. *Computational Materials Science* 28, 512–517.
- Shikinami, Y., Okuno, M., 1999. Bioresorbable devices made of forged composites of hydroxyapatite (HA) particles and poly-L-lactide (PLLA): Part I. Basic characteristics. *Biomaterials* 20, 859–877.
- Shikinami, Y., Okuno, M., 2001. Bioresorbable devices made of forged composites of hydroxyapatite (HA) particles and poly L-lactide (PLLA). Part II: Practical properties of miniscrews and miniplates. *Biomaterials* 22, 3197–3211.
- Shrout, T.R., Zhang, S.J., 2007. Lead-free piezoelectric ceramics: Alternatives for PZT? *Journal of Electroceramics* 19, 113–126.
- Song, H., Kim, B.G., Kim, Y.S., *et al.*, 2019. Synergistic effects of various ceramic fillers on thermally conductive polyimide composite films and their model predictions. *Polymers* 11, 484.
- Tofail, S.A.M., Gandhi, A.A., Gregor, M., Bauer, J., 2015. Electrical properties of hydroxyapatite. *Pure and Applied Chemistry* 87, 221–229.
- Tofail, S., Haverty, D., Cox, F., *et al.*, 2009. Direct and ultrasonic measurements of macroscopic piezoelectricity in sintered hydroxyapatite. *Journal of Applied Physics* 105, 064103.
- Tulip, P., Clark, S., 2004. Dielectric and vibrational properties of amino acids. *The Journal of Chemical Physics* 121, 5201–5210.
- Voigt, W., 1928. *Lehrbuch der Kristallphysik* (BG Teubner, Leipzig und Berlin), 980 S. Google Scholar.
- Wang, Z., Li, P., 2015. Dynamic failure and fracture mechanism in alumina ceramics: Experimental observations and finite element modelling. *Ceramics International* 41, 12763–12772.
- Wu, X., Vanderbilt, D., Hamann, D., 2005. Systematic treatment of displacements, strains, and electric fields in density-functional perturbation theory. *Physical Review B* 72, 035105.
- Wu, B., Wu, H., Wu, J., *et al.*, 2016. Giant piezoelectricity and high Curie temperature in nanostructured alkali niobate lead-free piezoceramics through phase coexistence. *Journal of the American Chemical Society* 138, 15459–15464.
- You, Y.-M., Liao, W.-Q., Zhao, D., *et al.*, 2017. An organic-inorganic perovskite ferroelectric with large piezoelectric response. *Science* 357, 306.

Molecular Dynamics Simulations of Glass Structure

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Introduction

The utilization of atomistic molecular dynamics (MD) simulations to model glass structures has increased markedly over the past two decades, where it nowadays has emerged as a valuable complement to experimental techniques, such as X-ray/neutron diffraction, and infrared (IR), Raman, X-ray absorption (XAS), and nuclear magnetic resonance (NMR) spectroscopies. Furthermore, an MD-generated glass model comprises a wealth of structural information, much of which is currently not experimentally attainable even for simple binary glasses. This introduction to, and overview of, applications of atomistic MD simulations to probe glass structure focusses on *oxide-based* glasses, which are targeted by an overwhelming majority of all literature reports on non-metallic glasses. Moreover, this review solely covers structural aspects of glasses, while another important branch concerns the modeling of physical, mechanical, and chemical properties for unveiling composition–structure–property correlations to assist a rational design for tuning the glass properties.

This paper is organized as follows: We start by accounting for the basic structural features of oxide-based glasses (Section “Introduction to Oxide-Based Glass Structures”), while Section “Salient Features of Atomistic MD Simulations” provides a gentle introduction to atomistic MD simulations, where we outline the principles of *ab initio* as well as classical MD simulations. Section “Melt-Quench Simulations” describes the modeling of the melt-quench process, which is the prevailing procedure to prepare oxide-based glasses, and which is also emulated by the computer simulations. Section “Force Fields” describes how interatomic interactions are modeled using force fields in classical MD simulations, where we review various common force field parameterizations, including those that account for ion polarizations effects. Next, Section “Evaluation of Short-Range Structural Parameters” illustrates how short-range (local) structural features may be assessed from the glass models, whereas Section “Modeling of Various Glass Systems” concludes by reviewing several key structural problems addressed in recent MD simulation reports of various glass systems, encompassing modified silicate, phosphosilicate, and aluminosilicate glasses, as well as borate and borosilicate glasses.

Introduction to Oxide-Based Glass Structures

Glass Building Blocks

Oxide-based glasses are built from *network formers* (F), the most common being B, Si, Al, and P, which are interlinked by *bridging* oxygen (BO) atoms via covalent $-O-$ linkages to form polymeric networks (Greaves and Sen, 2007; Edén, 2012). The network-building blocks are FO_p polyhedra, where tetrahedra ($p=4$) prevails, such as for Si (SiO_4), and notably P (PO_4), as illustrated by the network fragment of an MD-generated $Na_2O-CaO-B_2O_3-SiO_2-P_2O_5$ glass model in Fig. 1. While AlO_4 groups normally also dominate the networks of aluminate and aluminosilicate glasses, higher-coordination AlO_5 and AlO_6 polyhedra are frequently encountered across certain glass composition domains (see Section “Aluminosilicates”), particularly in aluminophosphate glasses where the strong propensity of P to remain in tetrahedral coordination leads to the formation of AlO_5 and AlO_6 moieties. Similarly, besides BO_4 tetrahedra, the small B atom commonly forms planar BO_3 units in B-bearing glasses [Fig. 1(a)], whereas the structure of vitreous B_2O_3 consists entirely of BO_3 moieties, most of which are condensed further into “boroxol” rings (B_2O_6) (Greaves and Sen, 2007; Edén, 2012). The coordination number Z_E of a species E will onwards be specified by appending the element symbol by a superscript: $E^{[p]}$.

Electropositive cations of alkali (M^+) and alkaline earth (M^{2+}) metals are termed *glass-network modifiers* because they depolymerize the networks by converting BO atoms into *non-bridging* oxygen (NBO; O^-) ions (Edén, 2012); see Fig. 1. This alters the physical and chemical properties of the glass and its corresponding melt, with implication for materials design as well as for geological processes, such as the flow properties (e.g., viscosity) of magma. The positive modifier ions balance primarily the negatively charged NBO ions, at which they locate through predominantly electrostatic $M^{z+} \cdots O^-$ interactions. Nonetheless, $M-BO$ contacts also occur, such that a non-negligible number of BO atoms contribute to the MO_p polyhedra. The glass-network modifier ions (M^{z+}) are normally larger than their F^{z+} counterparts and therefore feature higher coordination numbers, as in crystalline phases. For example, the similar-sized Na^+ and Ca^{2+} ions are typically surrounded by 5–7 O species [see Fig. 1(b)], whereas larger cations adopt six- to nine-fold coordination and the small Mg^{2+} ion may even participate in the glass network as MgO_4 groups (Edén, 2012).

Owing to the prevalence of tetrahedral coordination of Si and P, their coordination numbers will not be indicated explicitly. Rather, the symbols Q^n_i and Q^n_p will be employed for an SiO_4 and PO_4 tetrahedron with n BO atoms (and consequently $4 - n$ NBO ions), respectively (Engelhardt and Michel, 1987); see Fig. 2. Likewise, $Al^{[4]}$ species are denoted Q^n_{Al} , although generally Q^4_{Al} groups prevails in Al-bearing glasses (see Section “Aluminosilicates”). Here “Q” stands for “quaternary” to stress the fourfold coordination of Si, P, and Al. The Q^n notation is frequently encountered in the literature on silicate (and phosphate) glasses, where the fractional

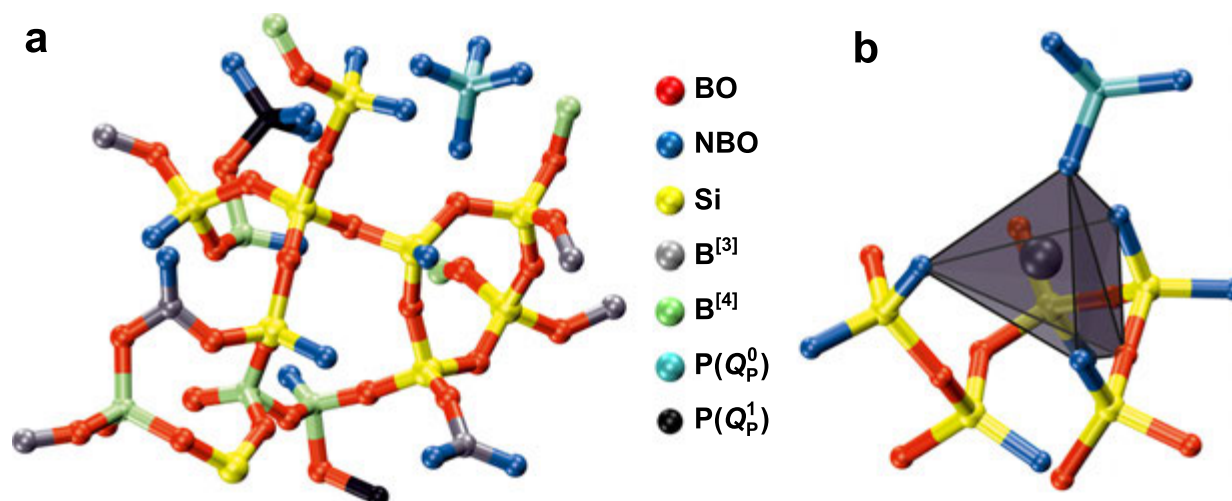


Fig. 1 (a) MD-generated network fragment from a borophosphosilicate glass of composition $24\text{Na}_2\text{O}-23\text{CaO}-15\text{B}_2\text{O}_3-34\text{SiO}_2-4\text{P}_2\text{O}_5$ (the coefficients here and in other figures specify mol%). Note that only the BO/NBO and the network-forming (Si, B, P) atoms are displayed. (b) Structural motif around a NaO_5 polyhedron, indicating its coordination to four NBO and one BO species and their respective bonds to Si and P. The structure fragment in (a) is reproduced with permission from The American Chemical Society from [Yu, Y., Stevansson, B., Edén, M., 2017. Medium-range structural organization of phosphorus-bearing borosilicate glasses revealed by advanced solid-state NMR experiments and MD simulations: Consequences of B/Si substitutions. *J. Phys. Chem. B* 121, 9737–9752].

populations $\{x_{\text{Si}}^0, x_{\text{Si}}^1, x_{\text{Si}}^2, x_{\text{Si}}^3, x_{\text{Si}}^4\}$ of $\{Q_{\text{Si}}^0, Q_{\text{Si}}^1, Q_{\text{Si}}^2, Q_{\text{Si}}^3, Q_{\text{Si}}^4\}$ silicate groups directly relates to the NBO content of the glass and the polymerization degree of the silicate network and thereby to its average topology. A measure of the average glass network topology is given by the silicate *network connectivity* (Engelhardt and Michel, 1987; Edén, 2011), corresponding to the *average* number of BO atoms per SiO_4 group ($\bar{N}_{\text{BO}}^{\text{Si}}$) and given by:

$$\bar{N}_{\text{BO}}^{\text{Si}} \equiv \bar{n} = \sum_{n=0}^4 n x_{\text{Si}}^n, \quad (1)$$

with the fractional populations obeying the normalization $\sum_n x_{\text{Si}}^n = 1$.

The description of phosphate glasses is analogous, where a weighted average involving the set of fractional populations $\{x_{\text{P}}^n\}$ of $\{Q_{\text{P}}^n\}$ groups is linked to the average number of BO atoms per PO_4 group ($\bar{N}_{\text{BO}}^{\text{P}}$). The only essential difference to the silicate case is the restriction $n \leq 3$ of the Q_{P}^n groups due to the $\text{P}=\text{O}$ bond of each PO_4 moiety.

Structural Order

Notwithstanding that glasses are amorphous phases and thereby lack “long-range” order in the sense that no periodicity exists beyond ≈ 0.5 nm from a given spatial coordinate—the presence of well-defined FO_p polyhedra that form the glass network along with its associated MO_p moieties—implies that an oxide-based glass possesses *short-range* order, just as its crystalline phase of similar stoichiometry (Zachariasen, 1932; Engelhardt and Michel, 1987). However, in contrast with the latter, a “geometrical” disorder is introduced in the glass structure due to distributions of $\text{F}-\text{O}-\text{F}'$ bond angles and $\text{F}-\text{O}$ distances, which in turn dictates the precise positions of the network modifiers. Moreover, in glass networks involving either more than one network-former species ($\text{F}, \text{F}', \text{F}'', \dots$), or multiple coordination numbers (e.g., $\text{Al}^{[4]}, \text{Al}^{[5]}, \text{Al}^{[6]}$), a “chemical” disorder results from distributions of $\text{F}-\text{O}-\text{F}'$ bonding patterns, although they are partially constrained by preferences for certain $\text{F}-\text{O}-\text{F}'$ bonding scenarios, such as the favoring of $\text{Al}-\text{O}-\text{P}$ linkages but the avoidance of $\text{Al}^{[4]}-\text{O}-\text{Al}^{[4]}$ bridges; the latter feature is known as the “Loewenstein Al avoidance” rule (Loewenstein, 1954) and stems from the negative charge of the $[\text{AlO}_4]^-$ tetrahedron (although Loewenstein himself emphasized spatial/geometrical constraints rather than charge arguments). Hence, the disordered and thereby less dense glass structure readily admits exceptions to bonding “rules” that may be much stricter in analogous crystalline phases, such as the Loewenstein rule in aluminosilicates (e.g., zeolites) (Engelhardt and Michel, 1987).

The presence of constraints on $\text{F}-\text{O}-\text{F}'$ bonding preferences is one reason why oxide-based glasses often possess *medium-range order* over a few hundred picometers (0.3–0.5 nm). Unfortunately, the experimental probing of this particular range is challenging: The limitations of diffraction/scattering methods are obvious because they require long-range structural order, while the most widely exploited spectroscopic techniques, i.e., IR and Raman spectroscopy, are limited by poor spectral resolution and may in general only inform about short-range ($\lesssim 0.3$ nm) features. Although routine solid-state NMR experimentation suffers from similar problems, advanced NMR techniques may reveal some features of the glass structure across the 0.3–1.0 nm scale (Edén, 2012), such as preferential $\text{F}-\text{O}-\text{F}'$ bonding patterns or the nature of the spatial distribution of a few network modifier species (e.g., Na and Li). Yet, application of such experimentation is non-standard and comparatively sparse. Here atomistic MD

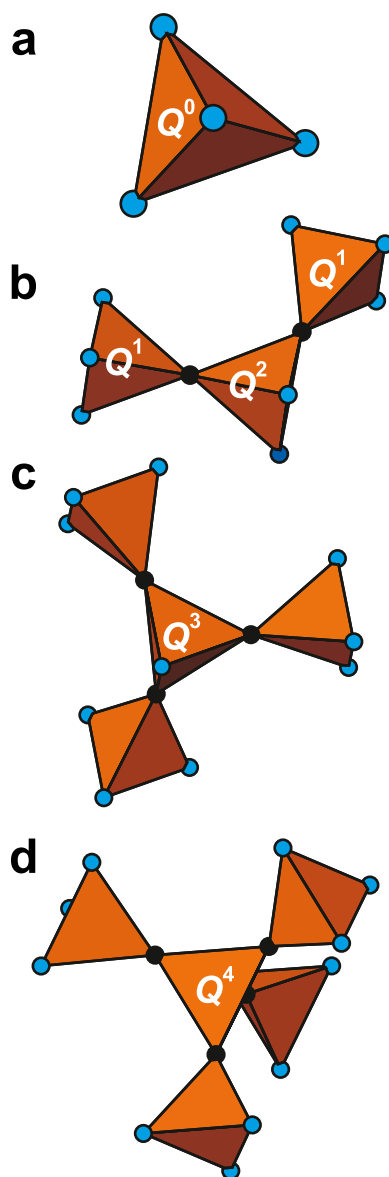


Fig. 2 Illustration of the Q^n nomenclature for tetrahedrally coordinated network formers, here assuming SiO_4 groups. Only oxygen atoms are indicated, with bridging and non-bridging species depicted in black and blue color, respectively. (a) An isolated Q^0_{Si} (orthosilicate) tetrahedron. (b) A Q^2_{Si} unit linked to two Q^1_{Si} terminal tetrahedra. (c, d) A central (c) Q^3_{Si} and (d) Q^4_{Si} tetrahedron connected to Q^1_{Si} groups.

simulations offer great opportunities for gaining complementary structural insight to that accessible from experiments. MD simulations may provide short-range structural parameters that are in principle attainable experimentally but that in practice remain unreported, as well as insight into some medium-range glass structural features that are exceedingly difficult to obtain by other means.

Salient Features of Atomistic MD Simulations

Classical and *Ab Initio* Calculations

Notwithstanding that the $F\text{--O}$ bonds (e.g., Si--O and B--O) have a significant covalent character and oxide-based glasses form polymeric networks, glass structures are almost without exceptions modeled *atomistically*, meaning that the dynamic control is at the atomic level rather than considering larger molecular units, such as the SiO_4 or AlO_6 moieties. An obvious advantage with this approach is its lack of bias concerning the chemical bonds. Moreover, to what extent a minor species is present (such as AlO_6 groups in aluminosilicate glasses), is *a priori* unknown and is merely the task of the simulation to predict. Atomistic MD simulations involve a repositioning of atoms until an “equilibrium structure” is reached, within the practical limitations of

actually reaching such an equilibrium state, where we also note that glasses are thermodynamically metastable phases. Strictly, “equilibrium” is here taken to mean that the atom ensemble has reached a sufficiently low potential energy (concerning all atom pairs as well as any larger atom aggregates) such that no significant changes are observed in the structure as time proceeds.

As implied by its name, “modeling” by atomistic MD simulations yields an energy-minimized structure that represents a *model* of the real physical structure. The accuracy of this model depends on the assumptions underlying its production, i.e., how precisely the forces acting on each atom reflect the “real” ones. Broadly, there are two options for reaching the MD-derived model:

- (1) To perform *ab initio* MD (AIMD), i.e., “first principle” calculations, which is tantamount to solving the Schrödinger equation for the atom ensemble and thereby defining the position of each nucleus and its surrounding electrons. While representing the most accurate modeling, such computations become extremely time and computer-memory consuming albeit some approximations are made, such as those of Car–Parrinello MD (CPMD) simulations, where the electron dynamics is handled by density functional theory (DFT) at each time step (Car and Parrinello, 1985). Current AIMD simulations are restricted to handling a few hundred atoms over a period of ≈ 100 ps. These limitations of AIMD calculations lead to obstacles such as obtaining a sufficiently long time scale for reaching the energy minimum, and uncertainties in the populations of minor species in the structure (see Section “Atom Ensembles”).
- (2) To ignore the electron dynamics and assume that classical mechanics provides a sufficiently accurate representation of the equation of motion of each atom. The latter is dictated by *force fields*, which are also referred to as *interatomic potentials*. Below we will use these two synonymous terms interchangeably. The potentials represent functionals that provide the interatomic energy, as discussed in more detail in Section “Force Fields.” By omitting the electrons from the dynamic picture, the *classical* MD simulations rely on the Newtonian equations of motion (Allen and Tildesley, 1987). Yet, this permits handling atom ensembles comprising 10^3 – 10^5 atoms, as well as using timescales of hundreds of ps and beyond. However, the results depend critically on the accuracy of the force field functional and its precise parameters.

Atom Ensembles

Regardless of whether AIMD or classical mechanics are employed, the physical constraints of the atomistic MD simulations may be selected to involve *NPT*, *NVT*, or *NVE* ensembles, where each letter specifies a parameter that is fixed at any given time-point during the simulation. Here, *N* corresponds to the number of atoms, whereas *T*, *P*, *V*, and *E* represent the temperature, pressure, volume, and (net) energy of the atom ensemble, respectively. Consequently, an *NVT* (*NPT*) ensemble requires that the volume (pressure) is kept constant at each time-point of the simulation stage, whereas the pressure (volume) is allowed to vary freely. *NPT* calculations are normally preferred over their *NVT* counterparts. Hence, a force field that reproduces the experimental glass density under *NPT* conditions must be considered as the most favorable one relative to other options. Yet, such scenarios are rare, thereby in practice rendering *NVT* simulations that employ the experimental glass density preferable for obtaining an accurate glass model of a given chemical composition.

Atomistic MD simulations employ a (cubic) box with periodic boundary conditions, meaning that once an atom traverses one boundary face of the box (e.g., at the top) during the course of the simulation, it will reappear at the opposite face (at the bottom). While such periodic boundary conditions artificially expand the “box size” and efficiently avoids undesirable “surface” effects, false periodicities (i.e., “ordering” effects) may be introduced for (too) small boxes. The choice of the side length of the cubic box (which is usually a few nanometers) is dictated mainly by the total number of atoms, which in turn must be selected by considering the glass composition to be sufficiently large to provide adequate statistics about the least abundant species in the final glass model. For *NVT* simulations, the box size is selected by the constraint that the mass density of the atom ensemble must match the experimental counterpart at all times throughout the simulation. Fig. 3 depicts a glass model generated in a box.

Atomistic MD simulations are bound to give “discretization” effects of the structural-parameter statistics, such as of the various populations of $F^{[p]}$ and $M^{[p]}$ species, as well as the F – O – F' bonding constellations in the glass model. While the loss in accuracy due to limited statistics may, for instance, be significant for the comparably rare $Al^{[6]}$ species in alkali/alkaline-earth based aluminosilicate glasses with low Al contents (Section “Aluminosilicates”), they are usually insignificant for the most abundant species, such as the BO and NBO populations. Consequently, classical simulations of (say) binary Na_2O – SiO_2 glasses with comparable Na_2O and SiO_2 contents only require 2000–3000 atoms to give precise assessments of the distributions of the $\{Q_{Si}^n\}$ and $\{Na^{[p]}\}$ species, as well as many other structural parameters, such as the Si–O–Si bond-angle distributions (Section “Evaluation of Short-Range Structural Parameters”). Yet, typically 5000–10,000 atoms are required for multi-component glasses, or if precise information is required about a species present in minute amounts in the modeled structure. Hence, the choice of the total number of atoms must be made as a compromise between the largest possible atom ensemble for improving the statistics on the evaluated structural parameters, while keeping the system sufficiently small to avoid excessively time-consuming computations (where obviously also the precise choice of force-field becomes important, for which similar compromises between accuracy and computational speed must be made; see Section “Force Fields”).

Melt-Quench Simulations

The Procedure

Glass structures are modeled by emulating the traditional experimental melt-quench process for glass production, where a melt is gradually cooled until the system “freezes” and transforms into a glass. The simulation starts from an ensemble of atoms placed

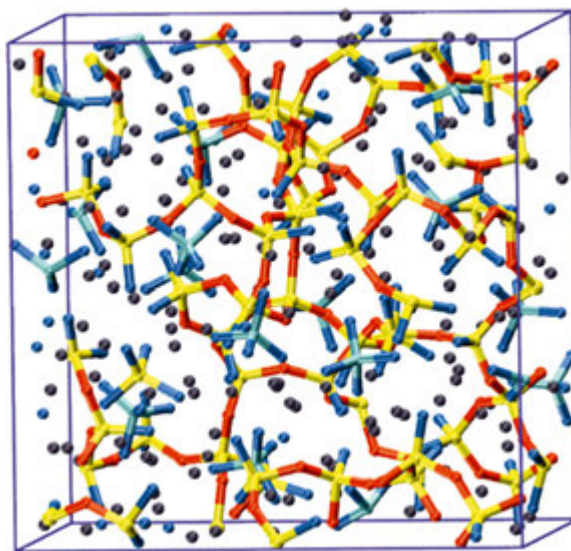


Fig. 3 Illustration of a small ensemble of ≈ 500 atoms from a $\text{Na}_2\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5$ glass model generated by a melt-quench procedure.

randomly (but subject to a minimum distance to any neighbor) in a box with periodic boundary conditions. The system is then equilibrated for ~ 100 ps at high temperature (typically, $3000\text{--}6000^\circ\text{C}$) to ensure freely moving atoms in a liquid state (melt) and for removing any “memory effects” of the atom ensemble.

As for all other parts of the (classical) MD simulation, the atom dynamics during the initial equilibration stage is dictated by the force field and involves integrating the equations of motion (Newton’s second law) (Allen and Tildesley, 1987). This leads to an updated spatial coordinate of each atom at each new time-point, where the time progression of the atom ensemble—which is often referred to as the trajectory—depends on the previous set of atom coordinates and the interatomic forces at the previous time-point; see Allen and Tildesley (1987) for details about the practical integration of the Newtonian dynamics. Depending on the precise choice of force field, the MD simulation trajectory is typically sampled in small time steps, where ≈ 0.2 fs and ≈ 1 fs are typical for force fields involving shell and rigid-ion models, respectively (see Section “Force Fields”). In contrast, a ≈ 0.1 fs step is required for AIMD computations that consider the dynamics of the nuclei as well as electrons.

Once the equilibration of the atom ensemble representing a high-temperature “melt” is completed, the system is gradually cooled to a “low” temperature ($\sim 20^\circ\text{C}$) by a cooling rate (q_c ; in units of K s^{-1}). The melt cooling may be implemented either as an essentially “continuous” (yet, step-wise by q_c) temperature reduction, or by invoking “equilibration stages” during the procedure. The temperature is in practice controlled by a “thermostat” procedure, the most common being those of Berendsen, and Nosé-Hoover (Allen and Tildesley, 1987). Further improved thermostats were devised by gently adding stochastic forces to ensure that the kinetic energy distribution is sampled efficiently and for improving ergodicity (Bussi *et al.*, 2007; Samoletov *et al.*, 2007).

Once the final temperature is reached, the MD calculation ends with a final equilibration stage that spans tens and hundreds of ps for AIMD and classical MD simulations, respectively. In classical and AIMD simulations, the last 100–200 ps and 10–20 ps of the equilibration interval, respectively, is employed for deriving the average structural parameters of the glass model; this period is in MD-jargon language referred to as the “production run.” To improve statistics and enabling the assessment of uncertainties of the modeled structural parameters, the entire melt-quench process should be repeated in a few independent simulations (at least three), each starting from randomly distributed atoms at high temperature.

There are several open-source MD simulation codes for implementing melt-quench simulations, including options for efficiently distributing the calculations among multiple computer processors (“parallelization”): For classical MD simulations, the most commonly utilized simulation platforms are DLPOLY (Smith and Forester, 1996; Todorov *et al.*, 2006) and LAMMPS (Plimpton, 1995), whereas the QUANTUM ESPRESSO (Giannozzi *et al.*, 2009) package is popular for AIMD computations.

The Cooling Rate

Cooling rates in current literature that involve classical MD simulations are typically $5\text{--}10\text{ K ps}^{-1}$, whereas modeling work reported 2–3 decades ago merely utilized $20\text{--}100\text{ K ps}^{-1}$. Although this nearly tenfold reduction in q_c is by no means insignificant for suppressing some “exotic” structural species that otherwise arise as simulation artifacts (e.g., $\text{Si}^{[5]}$ and $\text{Al}^{[3]}$ species in silicate and aluminosilicate glass models), the $\approx 10^{10}$ orders-of-magnitude faster melt-quenching employed in atomistic MD simulations relative to the $100\text{--}1000\text{ K s}^{-1}$ cooling rates attainable routinely for real melts, constitutes a main limitation of atomistic MD simulations. Hence, the fictive temperature (T_f) of the glass model is markedly higher than that of the physical glass. The extremely rapid melt-cooling in MD simulations is also a source of skepticism by many researchers in the glass area. These problems are particularly acute for *ab initio* calculations, where for instance simulations involving the popular CPMD approach

nowadays involve similar cooling rates ($\geq 20 \text{ K ps}^{-1}$) as those employed by classical simulations 20–30 years ago. When also considering the significantly lower statistics of the structural parameters offered by the AIMD calculations (Section “Atom Ensembles”), their accuracy and precision might be overrated by the modeling research community.

Yet, the $\sim 10^{10}$ orders of magnitude more rapid cooling employed to prepare glass models by MD simulations relative to real glasses may not be as problematic as it appears: Firstly, the atom ensembles of laboratory-prepared glasses are $\approx 10^{17}$ – 10^{20} times larger than their modeled counterparts, which lowers the demand on the cooling rate for the latter to equilibrate (Corrales and Du, 2005). Secondly, force fields utilized in classical MD simulations are often developed (“fitted”) to reproduce experimentally derived structural parameters, which leads to a “self-compensation” effect because the force fields are constructed to mimic the structural features of the slowly quenched glass structure under conditions of much more rapid cooling.

Force Fields

The predictive power of classical MD simulations is crucially dependent on the precise choice of force fields to model the local interionic/interatomic interactions, which ultimately also control the medium-range organization of the ions/atoms. We start by discussing some general aspects of the force fields, which initially will assume that the atoms in the system are represented by electrostatic interactions among essentially hard spheres; such interatomic potentials are referred to as “rigid ion” force fields. More realistic interatomic potentials that mimic the presence of ion polarization effects (primarily the O species) are discussed in Section “Force Fields Accounting for Polarization Effects.”

Long-Range Coulombic Interactions

Evaluations of the interaction energy $U_{\alpha-\beta}^{jk}(r_{\alpha-\beta}^{jk})$ in a pair of atom/ion-species α and β with indices j and k that are separated at a distance $r_{\alpha-\beta}^{jk}$ need to account for both “long-range” Coulombic ($\approx 1 \text{ nm}$ and beyond) and more local “short-range” (yet, evaluated out to 0.5 – 1 nm) interactions involving both attractive and repulsive forces. In oxide-based glasses, the latter are normally dominated by O–O, M–O, and F–O pair-wise interactions. In contrast, the net Coulombic interaction energy is (formally) obtained by summing over all pairs of α and β species according to (Allen and Tildesley, 1987):

$$U(\text{Coulomb}) = \frac{1}{2} \sum_{\alpha, \beta} \sum_{j, k} \frac{q_{\alpha}^j q_{\beta}^k}{4\pi\epsilon_0 r_{\alpha-\beta}^{jk}}, \quad (2)$$

where the summation includes all interionic distances within a radius r_{max} , which is often referred to as the “cut-off” distance. To obtain a converged Coulomb energy, Eq. (2) is in practice calculated by a smoothed particle mesh Ewald summation (Essmann *et al.*, 1995).

The choice of charges q_{α}^j and q_{β}^k of the ions (“atoms”) is of pivotal importance for the performance of the force field. There are two options: The first assumes “formal” charges of each cation/anion species $\alpha = \{M^{z+}, F^{z+}, O^{2-}\}$, i.e., a charge equal to the (signed) oxidation number, yielding $q_{\alpha}^j = z_{\alpha}e$ in Eq. (2), where e is the elementary charge. However, it is well known that complete electron transfers are very rare in practice, notably so for the polymeric networks of oxide-based glasses. Consequently, *partial charges* are more commonly assumed, which may be expressed $q_{\alpha}^j = k_{\alpha} z_{\alpha} e$, where $k_{\alpha} < 1$. Examples of popular force fields constructed around partial charges are those of “BKS” (van Beest *et al.*, 1990) and “Teter” (Cormack *et al.*, 2002). Note that the charges q_{α}^j may also enter the functionals describing the more localized interaction terms discussed below, although such cases are relatively rare.

Short-Range Interactions

We next consider the short(er)-range interaction component of the force-field, which is required to avoid a “system collapse” due to the typically predominant attractive Coulombic forces. Hence, these interatomic potentials always include a repulsive term that dominates at short distances $r_{\alpha-\beta}^{jk}$, the most common parameterization being that of Born and Mayer (1932):

$$U(\text{Born–Mayer}) \equiv U_{\alpha-\beta}^{jk}(r_{\alpha-\beta}^{jk}) = A_{\alpha-\beta} \exp\left\{-r_{\alpha-\beta}^{jk}/\rho_{\alpha-\beta}\right\}, \quad (3)$$

where $A_{\alpha-\beta}$ and $\rho_{\alpha-\beta}$ are parameters. Note that the summation over all pairs in the structure [as indicated in Eq. (2)] is omitted in Eq. (3) and those that follow below. The by far most popular force-field functional utilized in MD simulations of oxide-based glasses is that of Buckingham (1938):

$$U(\text{Buckingham}) \equiv U_{\alpha-\beta}^{jk}(r_{\alpha-\beta}^{jk}) = A_{\alpha-\beta} \exp\left\{-r_{\alpha-\beta}^{jk}/\rho_{\alpha-\beta}\right\} - C_{\alpha-\beta} \cdot \left(r_{\alpha-\beta}^{jk}\right)^{-6}, \quad (4)$$

which besides the Born–Mayer form [Eq. (3)] also includes an r^{-6} -dependent attractive interatomic potential term [hence its negative sign in Eq. (4)], analogously to that of the well-known Lennard–Jones potential that accounts for interactions between two (induced) dipoles (Allen and Tildesley, 1987). However, as inclusion of the attractive term in Eq. (4) may lead to insufficient repulsive forces among the particles at very short interatomic distances, and thereby a system collapse during the course of the calculations, it is customary to additionally include another (empirically deduced) repulsive term of the form $D_{\alpha-\beta} \cdot \{r_{\alpha-\beta}^{jk}\}^{-n}$ with

$6 < n \leq 12$ in the Buckingham potential (where n may be a non-integer number). Although the Born–Meyer/Buckingham functionals are most frequently adopted in atomistic modeling of oxide-based glasses by MD simulations, other functional forms of the interatomic energy are encountered, such as that of Morse (Morse, 1929):

$$U(\text{Morse}) \equiv U_{\alpha-\beta}^{jk} \left(r_{\alpha-\beta}^{jk} \right) = D_{\alpha-\beta} \left(\left[1 - \exp \left\{ -a_{\alpha-\beta} \left(r_{\alpha-\beta}^{jk} - r_{\alpha-\beta}^0 \right) \right\} \right]^2 - 1 \right), \quad (5)$$

where $\{D_{\alpha-\beta}, a_{\alpha-\beta}, r_{\alpha-\beta}^0\}$ are parameters. In analogy with the relationship between the Born–Meyer (Eq. (3)) and Buckingham [Eq. (4)] pair potentials, the repulsive Morse functional may also be combined with additional attractive or repulsive terms (Pedone et al., 2006).

Force Fields Accounting for Polarization Effects

Although a multitude of options exist for mimicking polarization effects of the ions/atoms, those employed in atomistic MD simulations of oxide glasses may largely be grouped into two classes: *shell models* (Dick and Overhauser, 1958; Sanders et al., 1984) and *polarized ion models* (PIM) (Wilson et al., 1996; Madden and Wilson, 1996).

The most common shell-model force fields employed in simulations of silicate-based glasses build on that introduced by Sanders and co-workers for amorphous SiO_2 (Sanders et al., 1984). Here, all M^{z+}/F^{z+} cations bear full formal charges, but each O^{2-} ion is represented by a core (O_C^i) and a shell (O_S^j) portion with masses m_C^i and m_S^j , respectively, and corresponding charges $z_C = +0.8482e$ and $z_S = -2.8482e$ that obeys $z_C^i + z_S^j = -2$. Here, the “electron-cloud”-emulating “shell” has a minute mass, thereby requiring a very short time-step (0.2 fs) for integrating the equations of motion. This renders shell-model simulations much more time-consuming than their rigid-ion counterparts, yet comparable (or even faster) than those involving PIM force fields. The core-shell units are connected by a harmonic potential of the form

$$U(\text{core-shell}) \equiv U_{C-S}^{ij} \{ r_{C-S}(\text{O}_C^i - \text{O}_S^j) \} = \frac{1}{2} k_{C-S} [r_{C-S}(\text{O}_C^i - \text{O}_S^j)]^2, \quad (6)$$

where k_{C-S} is the force constant. Eq. (6) is in practice added to the Buckingham potential [Eq. (4)] or another interatomic functional, where all cation-shell interactions are considered in the summation, i.e., all $F^i-\text{O}_S^k$ and $M^j-\text{O}_S^k$ pairs, as well as $\text{O}_S^i-\text{O}_S^k$ from distinct O atom pairs.

The PIM force field and variations thereof, such as the aspherical ion model (AIM) (Jahn and Madden, 2007), also assume formal charges of all ions, but implement polarization effects of each atom/ion by solving a set of equations so as to minimize its polarization energy at each time step of the simulation (Wilson et al., 1996; Jahn and Madden, 2007). PIM/AIM force fields have proven useful for improving the accuracy of the modeling of (for instance) vitreous B_2O_3 and borosilicate glasses (Maranas et al., 2001; Zeidler et al., 2014; Pacaud et al., 2017).

Three-Body Interatomic Potentials

All interatomic potentials considered thus far only described *atom-pair* interactions. A force field that faithfully accounts for the glass structure without relying on explicit control of atoms within larger aggregates—i.e., multi-body interactions—presents decisive advantages in that any “longer-range” order is not artificially introduced. Consequently, and in sharp contrast to the common simulation strategies of molecular systems—such as organic molecules where three- and four-body interactions are normally always accounted for (Vanommeslaeghe et al., 2014)—atomistic MD simulations of glasses should ideally avoid explicit consideration of many-body interactions. Indeed, their necessity reflects imperfect performance of the pair-potentials. However, for network-forming species such as SiO_4 and PO_4 , it is not uncommon that the force fields (regardless of whether they are of rigid-ion or shell-model types) also implement three-body terms to control the O–Si–O and O–P–O *intratetrahedral* angles to remain close to the ideal value 109.47° . Such precautions avoid unrealistic deviations from the tetrahedral geometry, but should be avoided for groups such as AlO_4 and BO_4 , because tight constraints around a tetrahedral geometry precludes transitions between coordination numbers, such as $\text{B}^{[4]} \rightarrow \text{B}^{[3]}$ and $\text{Al}^{[4]} \rightarrow \text{Al}^{[5]}$, which are commonly encountered in borate/borosilicate (Section “*Borates and Borosilicates*”) and aluminosilicate (see Section “*Aluminosilicates*”) glasses, respectively, that incorporate high-field modifiers. Here, determining the corresponding relative BO_3/BO_4 and $\text{AlO}_4/\text{AlO}_5/\text{AlO}_6$ populations is key to characterizing the glass structure and properties.

Evaluation of Short-Range Structural Parameters

Short-range structural parameters, such as bond lengths and intrapolyhedral angles, are readily extracted from an MD-derived glass model. The (average) interatomic distance of an atom pair E – F may be evaluated by using the *radial distribution function* (RDF). It essentially projects the 3D structure onto a one-dimensional distance-dependent function that provides the probability of finding an atom of species F at a distance (radius) r from E . As it involves atom-pairs, the RDF is often referred to as the *pair distribution function* (PDF). Fig. 4 shows the PDF for the Si–O pair in a borophosphosilicate glass. It shows a strong peak at 164 pm, which corresponds to the *most probable* Si–O distance in the glass model. The *average* Si–O distance is obtained by integrating the product $r_{\text{Si-O}} \cdot \text{PDF}(r_{\text{Si-O}})$ over all distances $r_{\text{Si-O}}$. For increasing $r_{\text{Si-O}}$, the values of the PDF first diminish, but then approach the asymptotic value of unity;

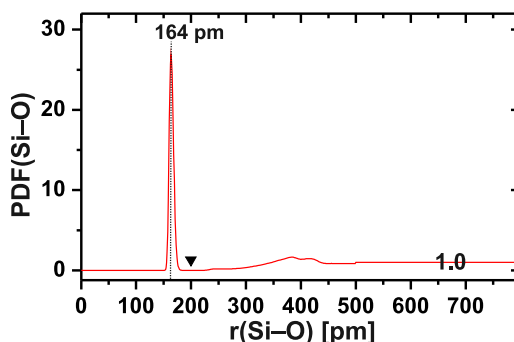


Fig. 4 MD-derived pair-distribution function (PDF) for the Si-O pair in a silicate-based glass of stoichiometry $24\text{Na}_2\text{O}-23\text{CaO}-15\text{B}_2\text{O}_3-34\text{SiO}_2-4\text{P}_2\text{O}_5$ (Yu *et al.*, 2017). The first maximum reveals the closest Si-O distance, while integrating the PDF out to its first minimum (marked by the triangle) provides the average coordination number $\bar{Z}_{\text{Si}}$, i.e., the number of O atoms in the first coordination sphere of Si. Note that the asymptotic PDF value of 1.0 is observed for large $r_{\text{Si-O}}$ distances.

this common property of all pair distribution functions reflects that the probability of finding another O at long distances $r_{\text{Si-O}}$ is unity. Moreover, integrating $\text{PDF}(r_{E-F})$ out to its first minimum yields the average coordination number of E with respect to F. In the case of Si-O, this implies $\bar{Z}_{\text{Si}} = 4$, as expected for SiO_4 tetrahedra. A triangle marks the distance ($r_{\text{Si-O}} \approx 200$ pm) at the PDF minimum in Fig. 4, i.e., the “cut-off” distance used in the integration.

We next consider the PDFs displayed for the various cation-oxygen atom pairs in the left panel of Fig. 5, all of which were observed from a borophosphosilicate glass of composition $24\text{Na}_2\text{O}-23\text{CaO}-15\text{B}_2\text{O}_3-34\text{SiO}_2-4\text{P}_2\text{O}_5$ (see Fig. 1), except for the $\text{PDF}(r_{\text{Al-O}})$ results that were obtained from a La aluminosilicate glass. Besides the net PDF of Si-O, $\text{PDF}(r_{\text{Si-O}})$, Fig. 5(a) also includes the $\text{PDF}(r_{\text{Si-BO}})$ and $\text{PDF}(r_{\text{Si-NBO}})$ components: The latter reveals a slightly shorter (most probable) distance of $r_{\text{Si-NBO}} = 161$ pm than that of the Si-BO pair ($r_{\text{Si-BO}} = 165$ pm). This is expected, because the Si-NBO bond length is shorter than its Si-BO counterpart, while the net Si-O bond length $r_{\text{Si-O}} = 164$ pm is the weighted average of the two $r_{\text{Si-NBO}}$ and $r_{\text{Si-BO}}$ distances, where the PDFs of Fig. 5(a) reveal a domination of Si-BO pairs. The PDFs for P-O, Al-O, and Na-O are shown in Fig. 5(c), (e), and (g), respectively. Note the bond-distance order $r_{\text{P-O}} < r_{\text{Si-O}} < r_{\text{Al-O}} < r_{\text{Na-O}}$, as well as the concurrent broadening of the PDFs. These trends mirror that of a decreasing cation field strength (CFS), where the CFS of M^{z+} is given by z/r^2 , and r is the ion radius. Consequently, a small ion of high charge controls the O atoms in its first coordination shell more tightly than a larger ion of lower charge.

The right panel of Fig. 5 plots the bond-angle distributions (BADs) of selected polyhedra in the borophosphosilicate glass. As expected, the intratetrahedral O-Si-O angles of the SiO_4 tetrahedra are 109.5° [Fig. 5(b)], while the average O-B^[3]-O angle of the planar BO_3 groups is close to 120° [Fig. 5(d)]. Moreover, Figs. 5(f) and (h) show the Si-O-Si and Al-O-Al intertetrahedral BADs (the latter obtained from a La aluminosilicate glass model). Note the small peak at 94° observed for the Al-O-Al BAD, which stems from a minor degree of edge-shared polyhedra that primarily involve AlO_5 and AlO_6 moieties (Okhotnikov *et al.*, 2013).

Modeling of Various Glass Systems

Silicates

The network organization of silicate glasses involving one or several glass-network modifiers has been studied extensively both experimentally and by modeling. The central tasks involve determining (1) the set of coexisting Q_{Si}^n species and their corresponding fractional populations $\{x_{\text{Si}}^n\}$, as well as (2) how the various Q_{Si}^n tetrahedra are (preferentially) interlinked. The $\{Q_{\text{Si}}^n\}$ speciation (“silicate speciation”) may readily be determined for binary $M_2\text{O-SiO}_2$ glasses by Raman or ^{29}Si MAS NMR spectroscopy (Greaves and Sen, 2007; Edén, 2012). We comment that although the $\{Q_{\text{Si}}^n\}$ speciation is often (incorrectly) referred to as a medium-range structural feature, it merely represents statistics on the short-range structure, as it conveys the relative numbers of Si-BO and Si-NBO bonds at the SiO_4 tetrahedra, which are the smallest building units of the glass network (see Section “Glass Building Blocks”). Likewise, while the intratetrahedral O-Si-O bond angles of the SiO_4 groups reflect the short-range structure (Section “Evaluation of Short-Range Structural Parameters”), the intertetrahedral Si-O-Si counterpart [see Fig. 5(f)] is a medium-range structural parameter, as are the $Q_{\text{Si}}^n-Q_{\text{Si}}^m$ interconnectivities [problem (2)]. As such, the latter is much more difficult to probe experimentally than the $\{Q_{\text{Si}}^n\}$ speciation. Here, double-quantum (2Q) ^{29}Si MAS NMR is a most promising option, although it has hitherto only been applied to a few binary $M_2\text{O-SiO}_2$ glasses with $M = \{\text{Na}, \text{K}\}$ (Olivier *et al.*, 2001; Malfait *et al.*, 2007). However, atomistic MD simulations may readily address both problems (1) and (2), each of which is discussed below.

The distribution of BO and NBO species among the SiO_4 tetrahedra in the silicate glass, i.e., the set of $\{x_{\text{Si}}^n\}$ populations, is generally intermediate of two limiting scenarios: (i) A binary BO/NBO distribution (Edén *et al.*, 2011), which implies the coexistence of (at most) two distinct tetrahedral units, Q_{Si}^n and Q_{Si}^{n+1} (whose fractional populations obey $x_{\text{Si}}^n + x_{\text{Si}}^{n+1} = 1$), except for

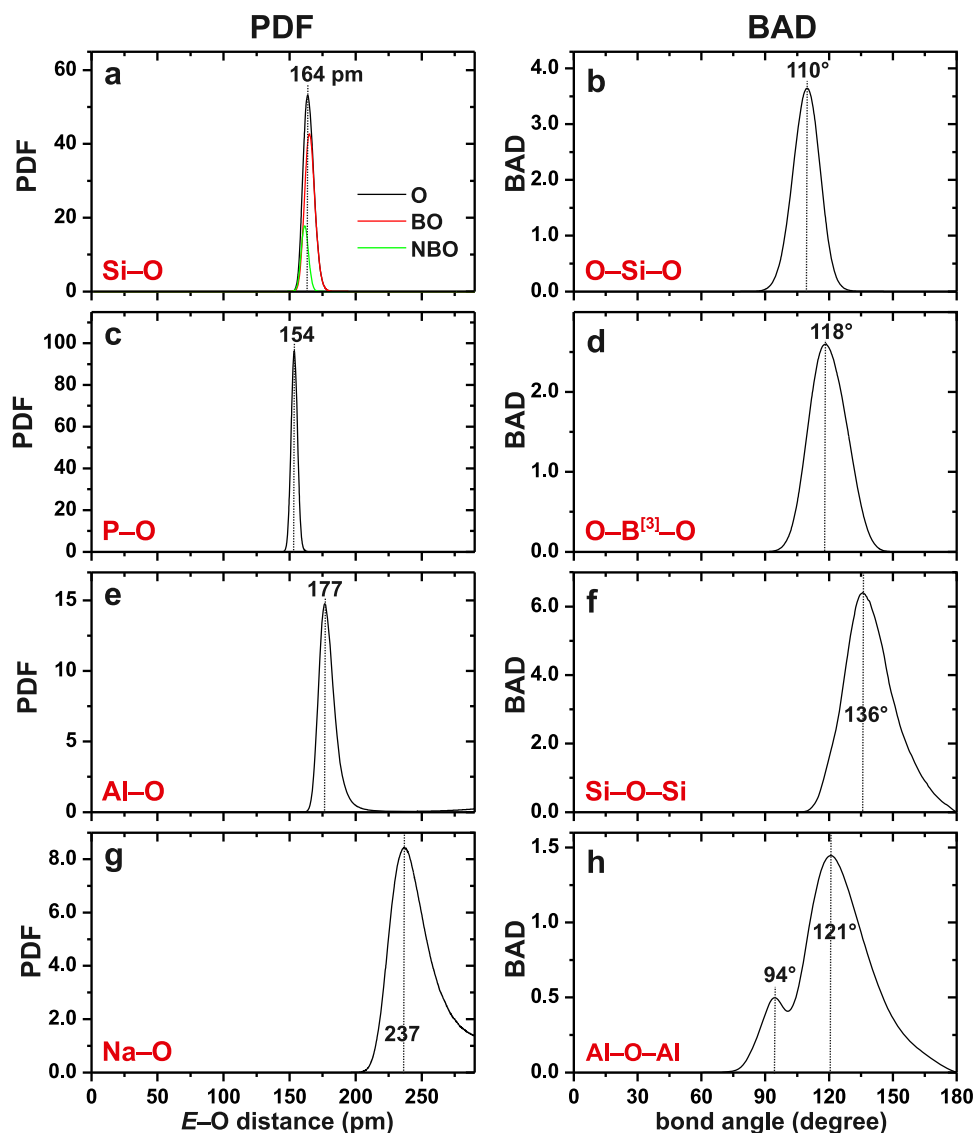


Fig. 5 Left panel: PDFs for the pairs (a) Si-O, (c) P-O, (e) Al-O, and (g) Na-O. Besides the net Si-O PDF, the plot in (a) also provides the results for its Si-BO and Si-NBO components. Right panel: Bond-angle distribution (BAD) functions for (b) O-Si-O, (d) O-B^[3]-O, (f) Si-O-Si, and (h) Al-O-Al. Note that the angles in (b) and (d) concern the *intratetrahedral* and *intratriangular* bond angles of SiO₄ and BO₃ moieties, respectively, whereas (f, h) inform about *intertetrahedral* angles. The respective average E-O bond-lengths (in pm), as well as O-E-O and E-O-E bond angles (in degrees) are specified in each diagram. All results were generated by classical MD simulations of a borophosphosilicate glass of stoichiometry 24Na₂O-23CaO-15B₂O₃-34SiO₂-4P₂O₅, except for those in (e, h) that were obtained from an aluminosilicate glass of composition 17La₂O₃-28Al₂O₃-55SiO₂. Parts (a-d, f, g) are reproduced from [Stevensson, B., Yu, Y., Edén, M., 2018. Structure-composition trends in multicomponent borosilicate-based glasses deduced from molecular dynamics simulations with improved B-O and P-O force fields. *Phys. Chem. Chem. Phys.* 20, 8192-8209], with permission from PCCP Owner Societies. Parts (e, h) are reproduced from [Okhotnikov, K., Stevensson, B., Edén, M., 2013. New interatomic potential parameters for molecular dynamics simulations of rare-earth (RE = La, Y, Lu, Sc) aluminosilicate glass structures: Exploration of RE³⁺ field-strength effects. *Phys. Chem. Chem. Phys.* 17, 15041-15055] with permission from PCCP Owner Societies.

glass stoichiometries associated with $\bar{N}_{\text{BO}}^{\text{Si}} = 0, 1, 2, 3$ and 4, for which the network is assumed to comprise one sole Q_{Si}^n type with $n = \bar{N}_{\text{BO}}^{\text{Si}}$; (ii) A *random* distribution, where the NBO ions are shared statistically among the tetrahedra, such that each Q_{Si}^n population (x_{Si}^n) is obtained from a binomial distribution (Lacy, 1965; Edén *et al.*, 2011). While experiments reveal that most Na₂O-SiO₂ glasses conform well to the binary model (Edén, 2012), the BO/NBO distribution in $\text{MO}_{z/2}$ -SiO₂ glasses deviate progressively from a binary n -distribution for increasing modifier content, as well as for an increase in either the field strength of the M^{z+} cation or the melt-cooling rate (and thereby T_f). Such elements of “randomness” may be accounted for by “disproportionation equilibria”, such as $2Q_{\text{Si}}^n \rightleftharpoons Q_{\text{Si}}^{n-1} + Q_{\text{Si}}^{n+1}$ with $n = 1, 2, 3$ (Stebbins, 1988; Maekawa *et al.*, 1991). Consequently,

silicate glasses incorporating alkaline earth (M^{2+}) cations manifest a significant “randomization” in their $\{Q_{Si}^n\}$ distributions due to the moderately high CFS of the network modifiers.

Atomistic MD simulations of silicate-based glasses reveal in general at least three co-existing Q_{Si}^n species (Pedone *et al.*, 2010; Mathew *et al.*, 2014), where deviations from the binary $\{Q_{Si}^n, Q_{Si}^{n+1}\}$ scenario are evident even for binary Na_2O-SiO_2 glasses (Du and Cormack, 2004). Hence, MD simulations tend to overestimate the “randomness” of the $\{Q_{Si}^n\}$ speciation relative to experiments. This partially stems from the higher fictive temperatures associated with the glass models, stemming from the high cooling rates employed in the glass model production (see Section “The Cooling Rate”). However, the accuracy of the modeled $\{Q_{Si}^n\}$ speciation relative to its experimental counterpart also depends on the choice of force field, where shell-model calculations generally provide $\{x_{Si}^n\}$ sets closer to experiments (e.g., see Tilocca, 2008; Fortino *et al.*, 2019).

The degree of discrepancies between $\{Q_{Si}^n\}$ speciations obtained by ^{29}Si MAS NMR and atomistic shell-model MD simulations may be gauged from Fig. 6, which displays results from $Na_2O-CaO-SiO_2-P_2O_5$ glasses with increasingly polymerized networks, i.e., increasing $\bar{N}_{BO}^{Si}$. (Notably, the glass design implied that the low P_2O_5 contents had little bearings on the $\{Q_{Si}^n\}$ distribution; see Mathew *et al.*, 2014). Also shown are the predictions from the “binary” and “random” BO/NBO bonding scenarios. The presence of large amounts of Ca^{2+} cations of relatively high field strength ($1.5 \lesssim n_{Na}/n_{Ca} \lesssim 1.8$) implies significant deviations from a simple binary $\{Q_{Si}^n\}$ speciation, where the ^{29}Si NMR-derived results reveal predominantly three coexisting $\{Q_{Si}^{n-1}, Q_{Si}^n, Q_{Si}^{n+1}\}$ groups in each glass, whereas the glass models are intermediate between the two limiting binary/random n -distributions, meaning that they manifest noticeably wider $\{Q_{Si}^n\}$ ensembles than that of a binary distribution (as well as their NMR-derived counterparts), yet the co-existence of fewer Q_{Si}^n species than the prediction from a statistical BO/NBO partitioning among the SiO_4 groups.

We next consider the intermixing of the various Q_{Si}^n groups in binary silicate glasses. According to Zachariasen’s *random network model* (RNM) (Zachariasen, 1932), both the Q_{Si}^n species and the network-modifier ions are randomly distributed across the structure. Such a glass lacks medium-range order because there is no preference for any particular $Q_{Si}^n-Q_{Si}^m$ connectivity. Over the past few decades, however, many experiments and MD simulations suggest that silicate glasses merely comprise SiO_4 -rich domains involving predominantly $Q_{Si}^4-Q_{Si}^4$ motifs that are interleaved with modifier-rich “channels” at their boundaries; the latter are built predominantly by lower- n Q_{Si}^n groups ($n \leq 3$); see Greaves (1985), Olivier *et al.* (2001), and Du and Cormack (2004) and references therein. Such a structural scenario, termed the *modified random network model* (MRNM), was introduced by Greaves and colleagues (Greaves *et al.*, 1981; Greaves, 1985), building on earlier ideas by Bockris *et al.* (1955). Notably, it is not restricted to binary silicate glasses, but is also advocated from experiments and MD simulations of aluminosilicate glasses (Le Losq *et al.*, 2017; Ganisetti *et al.*, 2019).

The MRNM implies structural domains rich in NBO ions and network modifiers, that co-exist with Q_{Si}^4 -dominated portions. Hence, probing the spatial distribution of the network modifiers provides an independent assessment of the structural inhomogeneities inherent to the MRNM. Although early ^{23}Na NMR experiments on Na_2O-SiO_2 glasses did not reveal any pronounced Na clustering (Gee and Eckert, 1995), subsequent MD simulations suggested slight Na aggregation tendencies (Du and Cormack, 2004). Moreover, both NMR experiments and MD simulations on silicate glasses incorporating cations with relatively high CFS (e.g., Li^+) accord in their inferences of a non-negligible network-modifier clustering (Voigt *et al.*, 2005).

Phosphates and Phosphosilicates

As their silicate analogs, $M_{(2)}O-P_2O_5$ glasses form polymeric networks of interconnected phosphate tetrahedra with variable number of BO/NBO species at the Q_P^n moieties. However, modeling of the structures of phosphate glasses (without any network co-formers) by MD simulations has received comparatively little attention. Nonetheless, studies of the $\{Q_P^n\}$ speciations in binary $Li_2O-P_2O_5$ (Liang *et al.*, 2000), $ZnO-P_2O_5$ (Tischendorf *et al.*, 2003), and $FeO-P_2O_5$ (Al-Hasni and Mountjoy, 2011) glasses are reported, as well as the distribution of coordination numbers of the respective Li^+ , Zn^{2+} , and Fe^{2+}/Fe^{3+} cations. Out of the relatively sparse modeling studies of phosphate glasses, most were published during the last decade and targeted modifier-rich $Na_2O-CaO-P_2O_5$ glasses (reviewed below), stemming from their potential use as *bioactive glasses* for biomedical implants (Christie *et al.*, 2017).

The structural role of P has been explored extensively in various glass systems that involve multiple glass network formers by atomistic modeling, notably so bioactive glasses from the $Na_2O-CaO-SiO_2-P_2O_5$ system. Such glasses degrade in body fluids and have the capacity to integrate with bone/tooth tissues. Consequently, they are exploited for bone grafting and tissue engineering applications (Hench, 1991). The first bioactive glass composition—and hitherto also the clinically most utilized—has the stoichiometry $24.6Na_2O-26.7CaO-46.1SiO_2-2.6P_2O_5$ and is termed “45S5 Bioglass®” (Hench, 1991). Both *in vivo* and *in vitro* bioactivity assessments suggest that the bioactivity (“bone-bonding capacity”) enhances concurrently with the P_2O_5 content of the glass (up to ≈ 6 mol%, beyond which glass-in-glass separation occurs), which is hypothesized to largely stem from the structural role of P, whose speciation is dominated by readily released orthophosphate (Q_P^0) groups for the most bioactive glass compositions. Bioactive $Na_2O-CaO-SiO_2-P_2O_5$ glasses feature silicate networks of low polymerization degree ($2.1 \leq \bar{N}_{BO}^{Si} \leq 2.6$) so as to be readily degradable in body fluids (Edén, 2011). For increasing silicate network connectivity, i.e., lower NBO content of the glass (but independently on the amount of P), the fractional population of Q_P^0 groups (x_P^0) is decreased, whereupon Q_P^1 species forms, as evidenced both by MD simulations and NMR experiments (Mathew *et al.*, 2014).

Modeling by atomistic MD simulations have sought to improve the insight into the composition–structure–dissolution trends. The initial modeling work on bioactive glasses have contributed significantly to the present understanding of the structure of bioactive glasses, such as predicting that the more polymerized Q_P^1 species are linked to a silicate tetrahedron *via* a Si–O–P linkage (Tilocca and de Leeuw, 2006; Tilocca and Cormack, 2007; Tilocca *et al.*, 2007), as opposed to P–O–P, as was (is still) often

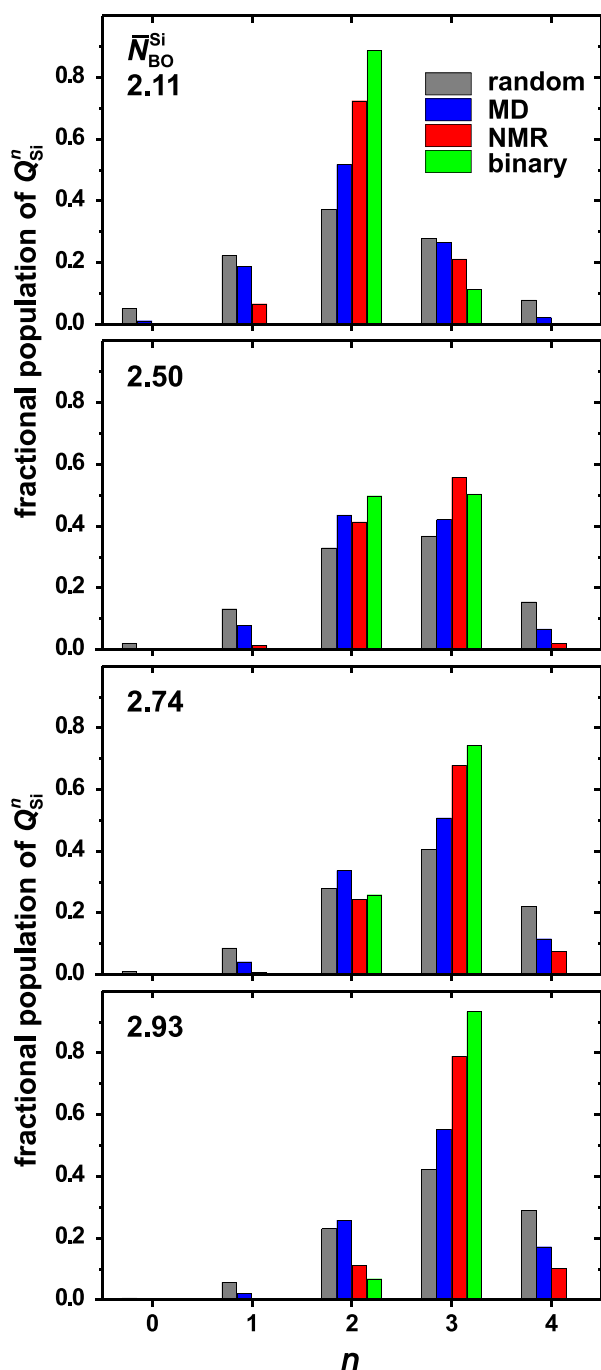


Fig. 6 Q^n_{Si} fractional populations $\{x^n_{Si}\}$ from different Na_2O – CaO – SiO_2 – P_2O_5 phosphosilicate glasses determined either by ^{29}Si NMR or shell-model MD simulations, and plotted against the number of BO atoms (n) at each SiO_4 group. Results are shown for increasing average silicate network connectivity N_{BO}^{Si} ; note that the glasses also comprise ≤ 6 mol% P_2O_5 , but nearly all P is present as orthophosphate groups that do not contribute to the network. The experimental and modeled data are compared with the predictions from binary and random NBO/BO distribution calculated from the expressions of Edén *et al.* (2011). Reproduced with permission from The American Chemical Society from [Mathew, R., Stevansson, B., Tilocca, A., Edén, M., 2014. Toward a rational design of bioactive glasses with optimal structural features: Composition-structure correlations unveiled by solid-state NMR and MD simulations. *J. Phys. Chem. B* 118, 833–844].

speculated in the literature. Yet, the low P contents (a few at%) in bioactive glasses present some hurdles: The $\{Q^n_P\}$ speciations from AIMD simulations are highly imprecise due to the insufficient statistics available from the few P atoms in the atom ensembles (see Section “Salient Features of Atomistic MD Simulations”), while current force fields in classical MD simulations cannot accurately reproduce the markedly stronger propensity for P–NBO contacts relative to Si–NBO at practically accessible melt-quench rates $q_C \leq 1 \text{ K ps}^{-1}$. Consequently, the Q^1_P (and Q^2_P) populations become overestimated at the expense of the

orthophosphate counterpart. Yet, the latter is shown experimentally to dominate the phosphate speciations in all Na_2O – CaO – SiO_2 – P_2O_5 glass compositions that exhibit sufficiently large $\text{Na}^+/\text{Ca}^{2+}$ contents for balancing all negative charges of the Q_p^0 tetrahedra (Pedone *et al.*, 2010; Mathew *et al.*, 2014). The limitations of *quantitative* predictions of $\{\text{Q}_\text{p}^n\}$ speciations by classical MD simulations are most acute for relatively polymerized glass networks ($\overline{N}_{\text{BO}}^{\text{Si}} \gtrsim 2.3$) (Stevensson *et al.*, 2018).

Most CPMD or classical MD simulation efforts to model the phosphate speciations in bioactive glasses targeted the 45S5 glass composition (Tilocca and de Leeuw, 2006; Tilocca *et al.*, 2007; Tilocca and Cormack, 2007; Pedone *et al.*, 2010; Xiang and Du, 2011; Tilocca, 2013; Mathew *et al.*, 2014). For a standard cooling rate of 10 K ps^{-1} , MD simulations employing shell-model P–O force fields typically yield orthophosphate fractions in a range from 0.73 (Pedone *et al.*, 2010) to 0.93 (Stevensson *et al.*, 2018), whereas analogous calculations based on rigid-ion force fields produce significantly lower values of $x_\text{p}^0 \approx 0.5$ (Tilocca, 2008; Xiang and Du, 2011). These numbers may be contrasted with the experimental result $x_\text{p}^0 = 0.96$ obtained by ^{31}P MAS NMR (Mathew *et al.*, 2014). Notwithstanding that the extremely rapid quench rates of the simulations partially account for the underestimated orthophosphate fractions—and thereby overestimated degree of Si–O–P bonding (Tilocca, 2013)—the *primary* deficiency originates from current force field parameterizations used in classical MD simulations, as discussed—and also partially remedied—by Stevensson *et al.* (2018). There should be significant room for future force-field improvements.

The medium-range structural organization of bioactive glasses potentially also influences their degradation properties in aqueous media. Hence, atomistic MD simulations have been employed to assess features such as the network organization in terms of chain lengths and ring sizes of silicate groups (Tilocca, 2013), also encompassing modeling of the glass surface at which the reactions occur that ultimately leads to glass degradation (Tilocca and Cormack, 2010; Berardo *et al.*, 2013). Moreover, the spatial distribution of the orthophosphate anions across the glass structure is likely to affect their leaching into the surrounding body fluids. While early MD simulations indicated a non-negligible clustering of the orthophosphate anions even in fragmented glasses such as 45S5 (Tilocca and Cormack, 2007; Tilocca *et al.*, 2007), more recent simulations suggest a near—random distribution of the Q_p^0 moieties around the silicate network, in full consistency with direct experimental constraints from $2\text{Q } ^{31}\text{P}$ NMR experiments (Stevensson *et al.*, 2014).

Although still very sparse, combined use of MD simulations and non-routine solid-state NMR experimentation on bioactive phosphosilicate glasses—as well as B-bearing analogs (see Fig. 1)—is a most promising route to advance the insight into their composition-structure-bioactivity relationships (Pedone *et al.*, 2010; Stevensson *et al.*, 2014; Mathew *et al.*, 2015; Yu *et al.*, 2017, 2019).

MD simulations of (Si-free) bioactive phosphate glasses have thus far almost exclusively focussed on $(55-x)\text{Na}_2\text{O}$ – $x\text{CaO}$ – $45\text{P}_2\text{O}_5$ compositions with variable Na and Ca contents (i.e., x specifies mol%), for which both AIMD and shell-model MD simulations are reported (Tang *et al.*, 2010; Di Tommaso *et al.*, 2013; Ainsworth *et al.*, 2012; Christie *et al.*, 2013). These glasses are associated with an average phosphate network connectivity of $\overline{N}_{\text{BO}}^{\text{P}} = 1.8$, meaning that the networks are built primarily from Q_p^2 (major) and Q_p^1 (minor) groups. Yet, notwithstanding that $\overline{N}_{\text{BO}}^{\text{P}}$ is fixed, experiments demonstrate that the glass solubility in water diminishes concurrently for increasing Ca content. This feature was shown to stem from the enhanced cross-linking of *distinct* network fragments by the higher CFS Ca^{2+} species: The higher Ca–NBO affinity implies a higher coordination of NBO species from phosphate groups located at different network segments as compared with Na^+ , which merely coordinates BO atoms from neighboring PO_4 tetrahedra of the *same* network fragment (Christie *et al.*, 2013, 2017).

Aluminosilicates

Besides modified (phospho)silicate glasses, amorphous aluminosilicates have probably attracted most attention in the MD simulation community. The focus on the modeling activities also matches well that of the experimental counterparts, where the Na_2O – Al_2O_3 – SiO_2 and (particularly) the CaO – Al_2O_3 – SiO_2 glass systems are particularly well studied (Himmel *et al.*, 1991; Cormier *et al.*, 2003; Pedone *et al.*, 2012; Jakse *et al.*, 2012; Xiang *et al.*, 2013; Bouhadja *et al.*, 2014; Atila *et al.*, 2019). Here, the structural role of Al and its intermixing with Si in the aluminosilicate glass networks represent key structural features that have been addressed experimentally, as well as by AIMD and classical MD simulations.

We start by briefly outlining the current understanding of aluminosilicate glass structures, such as that conveyed by the structural fragment in Fig. 7(a). From information gathered over the past 20 years, this structural picture is known not to hold strictly, but it nevertheless captures the most fundamental aspects. Moreover, it is also largely supported by atomistic MD simulations. Yet, the latter have assisted the experiments in clarifying some important deviations from the relatively simple set of rules governing the structure of aluminosilicate glasses [Fig. 7(a)]: Provided that a M^{z+} -bearing aluminosilicate glass with stoichiometry $n_{\text{M}}\text{MO}_{z/2}$ – $n_{\text{Al}}\text{AlO}_{3/2}$ – $n_{\text{Si}}\text{SiO}_2$ obeys the following criteria, (A) $n_{\text{Al}}/n_{\text{M}} \leq z$ and (B) $n_{\text{Al}}/n_{\text{Si}} \leq 1$, the glass network consists predominantly of corner-shared Q_{Si}^n and Q_{Al}^4 tetrahedra interconnected *via* Si–O–Si and Si–O–Al^[4] bonds, while all NBO species are located solely at the SiO_4 groups and Al^[4]–O–Al^[4] linkages are absent. All these features are direct consequences of the excess negative charge of each Q_{Al}^4 group (i.e., $[\text{AlO}_4]^-$), which lead to the “Loewenstein Al avoidance” (see Section “Structural Order”), as well as to the reluctance of Q_{Al}^4 groups to accommodate additional negative charges, meaning that Al^[4]–NBO bonds are absent (Engelhardt and Michel, 1987; Edén, 2015). If any of the criteria (A) and (B) is violated, the glass network responds by minimizing the number of Al^[4]–O–Al^[4] linkages by the formation of higher coordination Al^[5] (AlO_5) and Al^[6] (AlO_6) species. This occurs either whenever $n_{\text{Al}}/n_{\text{Si}} > 1$, or when incomplete charge-compensation is available from the glass-network modifiers ($n_{\text{Al}}/n_{\text{M}} > z$).

Yet, even aluminosilicate glasses that indeed obey both criteria (A) and (B) deviate from the (oversimplified) structural picture outlined above. The extent of such deviations depends on the CFS of the M^{z+} cations (Edén, 2015). For increasing M^{z+} field

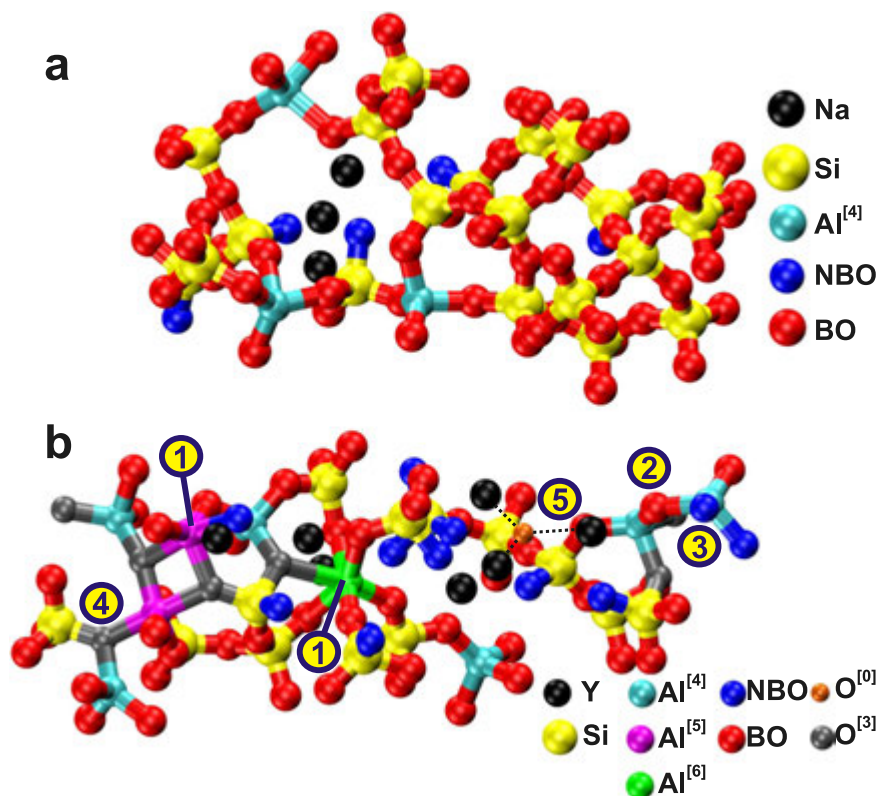


Fig. 7 (a) MD-generated structural fragment representative of a Si-rich and highly polymerized Na₂O–Al₂O₃–SiO₂ glass, forming a network of corner-shared Q_{Si}^n and Q_{Al}^4 tetrahedra. This model conforms well to the conventional structural picture of aluminosilicate glasses (Section “Aluminosilicates”). (b) A structural fragment from a Y₂O₃–Al₂O₃–SiO₂ glass model (Iftekhar *et al.*, 2012). The high CFS of Y³⁺ induces the following “unconventional” structural features, not observed in the Na-based counterpart in (a): (1) Significant amounts of AlO₅ and AlO₆ polyhedra that frequently connect to other polyhedra by edge-sharing; (2) direct Al^[4]–O–Al^[4] linkages that violates the Loewenstein’s Al avoidance; (3) AlO₄ groups with NBO ions (Al^[4]–NBO bonds). Moreover, besides the BO/NBO species, (4) oxygen triclusters (O^[3]) and (5) free O^{2–} ions (O^[0]) are present.

strength, the glass structure tends to “randomize”, which is reflected in (i) a high disorder of the intermixing of the SiO₄/AlO₄ network groups; (ii) progressively increasing AlO₅ and AlO₆ populations; and (iii) a stabilization of Al^[4]–NBO bonds, which alters the NBO-partitioning among the SiO₄ and AlO₄ tetrahedra (Edén, 2015). For instance, tectosilicate glasses feature $n_{\text{Al}} = n_{\text{Si}} = zn_M$ and are thereby expected to manifest fully polymerized 3D aluminosilicate networks with strictly alternating Q_{Si}^4 and Q_{Al}^4 groups. Yet, ²⁷Al and ¹⁷O MAS NMR experiments reveal a few percent of NBO species in such CaO–Al₂O₃–SiO₂ glasses, as well as minor AlO₅ populations ($\lesssim 7\%$ out of the entire $\{\text{Al}^{[p]}\}$ speciation), whereas their Na₂O–Al₂O₃–SiO₂ analogs of similar compositions adhere much closer to the conventional aluminosilicate glass picture outlined above (Stebbins and Xu, 1997; Edén, 2015).

Ca- and Na-based aluminosilicate glass models generated either by classical shell model MD simulations (followed by energy minimization by DFT) (Pedone *et al.*, 2012), or by rigid-ion force fields (Xiang *et al.*, 2013), overall reproduce the experimental findings outlined above. The glass models also confirm that the violation of the Loewenstein Al avoidance is larger for glasses that incorporate solely the higher-CFS Ca²⁺ cation than those involving solely Na⁺ or a mixture of Na⁺ and Ca²⁺. Nonetheless, even the largest fraction of Al^[4]–O–Al^[4] linkages observed out of the BO speciation remained modest ($\leq 6\%$) (Pedone *et al.*, 2012). Similar results were observed from MD simulations of SrO–Al₂O₃–SiO₂ glasses (Charpentier *et al.*, 2018). In contrast and contrary to expectations, markedly higher abundances of Al^[4]–O–Al^[4] bridges are reported from recent MD simulations using rigid-ion force fields for CaO–Al₂O₃–SiO₂ glasses (Atila *et al.*, 2019), a mixed Ca/Mg aluminosilicate glass (Ganisetti *et al.*, 2019), and even in glasses simultaneously incorporating the low-CFS Na⁺ and K⁺ cations (Le Losq *et al.*, 2017). However, all those studies only had, at best, qualitative experimental support for the significant violations of the Loewenstein rule revealed by the glass models.

Moreover, previous suggestions/predictions (Mysen *et al.*, 1980; Lee and Sung, 2008) about distinct structural roles of Na⁺ and Ca²⁺ species in mixed-cation Na₂O–CaO–Al₂O₃–SiO₂ glasses were confirmed by MD simulations: While the monovalent Na⁺ cations mainly serve as charge-compensators of the $[\text{AlO}_4]^-$ tetrahedra, the Ca²⁺ counterparts preferentially act as modifiers (thereby charge-balancing Si–NBO motifs of the Q_{Si}^n groups) (Gambuzzi *et al.*, 2014).

Notwithstanding that both experiments and MD simulations reveal negligible deviations from the conventional aluminosilicate structural picture for Na-based glasses [see Fig. 7(a)], and very modest discrepancies for those involving Ca²⁺ cations with moderately high field-strength, significantly altered glass networks are observed for glasses incorporating Mg²⁺ or trivalent rare-earth (RE³⁺) cations: this is illustrated by Fig. 7(b) that displays an MD-generated glass model of an Y-based glass of composition Y_{0.56}Al_{0.40}SiO_{3.44}

(which notably obeys both criteria of (A) and (B) above). For $\text{RE}_2\text{O}_3\text{--Al}_2\text{O}_3\text{--SiO}_2$ glasses along the series of increasing RE^{3+} CFS— $\text{La}^{3+} < \text{Y}^{3+} < \text{Lu}^{3+} < \text{Sc}^{3+}$ —both NMR experiments and classical MD simulations reveal the following trends (Iftekhar *et al.*, 2012; Jaworski *et al.*, 2012; Okhotnikov *et al.*, 2013; Jaworski *et al.*, 2015, 2016): (1) The fractional populations of $\text{AlO}_5/\text{AlO}_6$ polyhedra is dramatically increased, where AlO_5 polyhedra account for $\approx 8\%$ and $\approx 30\%$ in La and Sc based glasses, respectively; (2) the $\text{SiO}_4/\text{AlO}_4$ intermixing manifests a significant disorder in all RE-based glasses, where $\text{Al}^{[4]}\text{--O--Al}^{[4]}$ are abundant network motifs, while (3) the relative preference for Si–NBO contacts weakens such that $\text{Al}^{[4]}\text{--NBO}$ bonds form progressively for increasing CFS.

There is no experimental evidence for any significant formation of $\text{Al}^{[4]}\text{--NBO}$ bonds in Na-based aluminosilicate glasses, whereas such bonds are only encountered in $\text{CaO--Al}_2\text{O}_3\text{--SiO}_2$ glasses that are simultaneously (very) rich in both Al and Ca (Allwardt *et al.*, 2003; Cormier *et al.*, 2005); note that a high NBO content naturally boosts the $\text{Al}^{[4]}\text{--O--Al}^{[4]}$ bridges and promotes $\text{Al}^{[4]}\text{--NBO}$ bonds due to the limited number of Si–BO contacts of the depolymerized $\{Q_{\text{Si}}^n\}$ groups (Edén, 2015; Ganisetti *et al.*, 2019). Hence, it is evident that $\text{Al}^{[4]}\text{--NBO}$ motifs are energetically unstable in $\text{Na}^+/\text{Ca}^{2+}$ -based aluminosilicate glasses, as opposed to the scenario of the highly charged RE^{3+} cations in $\text{RE}_2\text{O}_3\text{--Al}_2\text{O}_3\text{--SiO}_2$ glass networks of similar composition. The presence of $\text{Al}^{[4]}\text{--NBO}$ bonds in Si-rich and highly polymerized $\text{RE}_2\text{O}_3\text{--Al}_2\text{O}_3\text{--SiO}_2$ glasses is one example where classical MD simulations predicted a structural feature (Iftekhar *et al.*, 2012) that was only later unambiguously established experimentally (Jaworski *et al.*, 2015). Yet, the modeled $\text{Al}^{[4]}\text{--NBO}$ populations are ≈ 3 times larger (20%–40% of all NBO species) than those determined experimentally by ^{17}O NMR (7%–12%). Similar overestimations likely also apply to the very recent MD-derived predictions of the degree of Al–NBO bonding in modifier-rich $\text{CaO--Al}_2\text{O}_3\text{--SiO}_2$ (Atila *et al.*, 2019) and $\text{CaO--MgO--Al}_2\text{O}_3\text{--SiO}_2$ glasses (Ganisetti *et al.*, 2019), for which direct experimental quantifications are not available.

Borates and Borosilicates

In contrast with the SiO_2 and P_2O_5 glass formers, adding low or moderately large amounts of glass network modifier cations to B_2O_3 do not induce NBO formation, but merely leads to an increased coordination number of B. For each M^+ cation included, one planar BO_3 group converts into a $[\text{BO}_4]^-$ tetrahedron (Dell *et al.*, 1983; Wright, 2010). For $\text{M}_{(2)}\text{O--B}_2\text{O}_3\text{--}(\text{SiO}_2)$ glasses, such $\text{BO}_3 \rightarrow [\text{BO}_4]^-$ conversions prevail for increasing amount of $\text{M}_{(2)}\text{O}$, up to a content at which the fractional $\text{B}^{[4]}$ population ($x_{\text{B}}^{[4]}$) is maximized—whose precise value depends on the CFS of the modifier. For Na borate/borosilicate glasses with modest Na_2O contents and compositions parameterized as $\text{RNa}_2\text{O--B}_2\text{O}_3$ and $\text{RNa}_2\text{O--B}_2\text{O}_3\text{--KSiO}_2$, Bray and co-workers showed that $x_{\text{B}}^{[4]}(\text{max}) = R = 1/2 + K/16$ (Dell *et al.*,

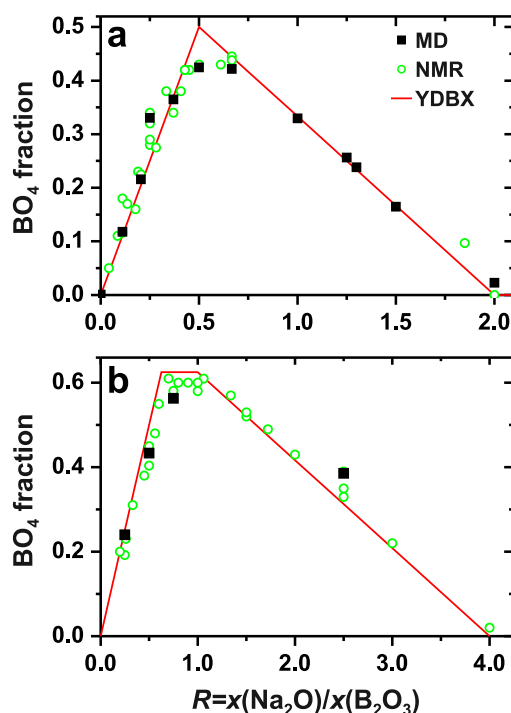


Fig. 8 Fractional populations of BO_4 groups out of the $\{\text{BO}_3, \text{BO}_4\}$ speciation, as obtained either by MD simulations (squares) or NMR experiments (circles) and plotted against the ratio of molar fractions $R = x(\text{Na}_2\text{O})/x(\text{B}_2\text{O}_3)$ for (a) $\text{RNa}_2\text{O--B}_2\text{O}_3$, and (b) $\text{RNa}_2\text{O--B}_2\text{O}_3\text{--KSiO}_2$ glasses with $K = 2$. The red lines are predictions from the Yun–Dell–Bray–Xiao (YDBX) model of Dell *et al.* (1983). Data uncertainties are within/around the symbol sizes. The experimental data were selected from various literature sources, specified in the caption to Fig. 1 of [Stevansson, B., Yu, Y., Edén, M., 2018. Structure-composition trends in multicomponent borosilicate-based glasses deduced from molecular dynamics simulations with improved B–O and P–O force fields. *Phys. Chem. Chem. Phys.* 20, 8192–8209], from which the figure was modified with permission from the PCCP Owner Societies.

1983). When the Na_2O content is increased further, NBO ions are created, which are either located at the SiO_4 tetrahedra or at the BO_3 groups forming from the $[\text{BO}_4]^-$ moieties (Dell *et al.*, 1983; Wright, 2010). The alterations of $x_{\text{B}}^{[4]}$ for increasing molar-fraction ratio $R = x(\text{Na}_2\text{O})/x(\text{B}_2\text{O}_3)$ are illustrated in Fig. 8, which contrasts results from ^{11}B NMR experiments, atomistic MD simulations, and the predictions of Dell *et al.* (1983).

The $\text{BO}_3 \leftrightarrow \text{BO}_4$ conversions occurring for increasing glass-network modifier content lead to non-linear changes in the physical properties of borate/borosilicate glasses (such as the glass transition temperature and density), known in the early literature as the “boron anomaly” (Wright, 2010). Given that the glass properties are strongly related to the relative BO_3/BO_4 populations, predicting their values is of pivotal importance for the rationalization of composition–structure–property relationships in B-bearing glasses. However, the $\text{BO}_3 \rightleftharpoons \text{BO}_4$ equilibrium in the melt is temperature dependent and shifts to the right during melt-cooling, thereby elevating the BO_4 content in the glass structure relative to the melt (Sen *et al.*, 1998). This feature, coupled with the extremely rapid cooling rates of atomistic MD simulations (Section “The Cooling Rate”) and the strong glass-composition dependence of the borate speciation, present major challenges for classical MD simulations to accurately model the $\{\text{BO}_3, \text{BO}_4\}$ populations in B-bearing glasses. Successful attempts to mitigate these obstacles have been made by invoking glass-composition dependent B–O force fields (Kieu *et al.*, 2011; Inoue *et al.*, 2012; Wang *et al.*, 2018; Deng and Du, 2019), however, at the price of glass system/composition-dependent force fields with limited transferability among distinct glass systems.

Another challenge for atomistic MD simulations of borate/borosilicate glasses concerns the reproduction of “superstructural units” in the structure. Whereas the presence of such larger molecular/ionic aggregates of connected borate groups in B-bearing multicomponent glasses often lacks unambiguous experimental evidence—thereby also rendering predictions from MD simulations extremely valuable—hitherto existing force-fields exhibit significant limitations to reproduce superstructural units. One example is the fraction of boroxol rings (B_3O_6) in vitreous B_2O_3 , whose presence and amount ($\approx 70\%$) is well-established experimentally (Wright, 2010). Yet, current rigid-ion force fields used in classical MD simulations will at best predict a few percent of B as present in B_3O_6 rings. Here AIMD simulations provide much better predictions (Alderman *et al.*, 2015). Force fields that account for polarization effects of the B–O bonds offer significant improvements for enhancing the modeled boroxol fraction in B_2O_3 glass/melt (Maranas *et al.*, 2001; Zeidler *et al.*, 2014; Alderman *et al.*, 2015), as well as for reproducing the fractional populations of BO_3/BO_4 groups in borate/borosilicate glasses, as demonstrated both by shell model (Stevenson *et al.*, 2018) and PIM (Pacaud *et al.*, 2017) force fields. Yet, further developments of B–O force fields are required to improve the predicting power of atomistic MD simulations: they should combine high accuracy in their predictions of structural features with transferability among glass compositions, not only within a given system, but also among distinct glass systems.

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References

- Ainsworth, R.I., Di Tommaso, D., Christie, J.K., de Leeuw, N.H., 2012. Polarizable force field development and molecular dynamics study of phosphate-based glasses. *J. Chem. Phys.* 137, 234502.
- Alderman, O.L.G., Ferlat, G., Baroni, A., *et al.*, 2015. Liquid B_2O_3 up to 1700 K: X-ray diffraction and boroxol ring formation. *J. Phys.: Condens. Matter* 27, 455104.
- Al-Hasni, B., Mountjoy, G., 2011. Structural investigation of iron phosphate glasses using molecular dynamics simulation. *J. Non-Cryst. Solids* 357, 2775–2779.
- Allen, M.P., Tildesley, D.J., 1987. *Computer Simulation of Liquids*. Oxford: Clarendon Press.
- Allwardt, J.R., Lee, S.K., Stebbins, J.F., 2003. Bonding preferences of non-bridging O atoms: Evidence from ^{17}O MAS and 3QMAS NMR on calcium aluminosilicate and low-silica Ca-aluminosilicate glasses. *Am. Mineral.* 88, 949–954.
- Atila, A., Ghardi, E.M., Hasnaoui, A., Ouaskit, S., 2019. Alumina effect on the structure and properties of calcium aluminosilicate in the percalcic region: A molecular dynamics investigation. *J. Non-Cryst. Solids* 525, 119470.
- Berardo, E., Pedone, A., Ugliengo, P., Corno, M., 2013. DFT modeling of 45S5 and 77S soda-lime phospho-silicate glass surfaces: Clues on different bioactivity mechanism. *Langmuir* 29, 5749–5759.
- Bockris, J.O'M., MacKenzie, J.D., Kitchener, J.A., 1955. Viscous flow in silica and binary liquid silicates. *Trans. Faraday Soc.* 51, 1734–1748.
- Born, M., Mayer, J.E., 1932. Zur gittertheorie der ionenkristalle. *Z. Physik* 75, 1–18.
- Bouhadja, M., Jakse, N., Pasturel, A., 2014. Striking role of non-bridging oxygen on glass transition temperature of calcium aluminosilicate glass-formers. *J. Chem. Phys.* 140, 234507.
- Buckingham, R.A., 1938. The classical equation of state of gaseous helium, neon and argon. *Proc. R. Soc. A* 168, 264–283.
- Bussi, G., Donadio, D., Parrinello, M., 2007. Canonical sampling through velocity rescaling. *J. Chem. Phys.* 126, 014101.
- Car, R., Parrinello, M., 1985. Unified approach for molecular dynamics and density-functional theory. *Phys. Rev. Lett.* 55, 2471–2474.
- Charpentier, T., Okhotnikov, K., Novikov, A.N., *et al.*, 2018. Structure of strontium aluminosilicate glasses from molecular dynamics simulation, neutron diffraction, and nuclear magnetic resonance studies. *J. Phys. Chem. B* 122, 9567–9583.
- Christie, J.K., Ainsworth, R.I., Di Tommaso, D., de Leeuw, N.H., 2013. Nanoscale chains control the solubility of phosphate glasses for biomedical applications. *J. Phys. Chem. B* 117, 10652–10657.
- Christie, J.K., Ainsworth, R.I., Hernandez, S.E.R., de Leeuw, N.H., 2017. Structures and properties of phosphate-based bioactive glasses from computer simulation: A review. *J. Mater. Chem. B* 5, 5297–5306.
- Cormack, A.N., Du, J., Zeitter, T.R., 2002. Alkali ion migration mechanisms in silicate glasses probed by molecular dynamics simulations. *Phys. Chem. Chem. Phys.* 4, 3193–3197.

- Cormier, L., Neuville, D.R., Calas, G., 2005. Relationship between structure and glass transition temperature in low-silica calcium aluminosilicate glasses: The origin of the anomaly at low silica content. *J. Am. Ceram. Soc.* 88, 2292–2299.
- Cormier, L., Ghaleb, D., Neuville, D.R., Delaye, J.-M., Calas, G., 2003. Chemical dependence of network topology of calcium aluminosilicate glasses: A computer simulation study. *J. Non-Cryst. Solids* 332, 255–270.
- Corrales, L.R., Du, J., 2005. Thermal kinetics of glass simulations. *Phys. Chem. Glasses* 46, 420–424.
- Dell, W.J., Bray, P.J., Xiao, S.Z., 1983. ^{11}B NMR studies and structural modeling of $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glasses of high soda content. *J. Non-Cryst. Solids* 58, 1–16.
- Deng, L., Du, J., 2019. Development of boron oxide potentials for computer simulations of multicomponent oxide glasses. *J. Am. Ceram. Soc.* 102, 2482–2505.
- Di Tommaso, D., Ainsworth, R.I., Tang, E., de Leeuw, N.H., 2013. Modelling the structural evolution of ternary phosphate glasses from melts to solid amorphous materials. *J. Mater. Chem. B* 1, 5054–5066.
- Dick Jr., B.G., Overhauser, A.W., 1958. Theory of the dielectric constants of alkali halide crystals. *Phys. Rev.* 112, 90–103.
- Du, J., Cormack, A.N., 2004. The medium range structure of sodium silicate glasses: A molecular dynamics simulation. *J. Non-Cryst. Solids* 349, 66–79.
- Edén, M., 2011. The split network analysis for exploring composition-structure correlations in multi-component glasses: I. Rationalizing bioactivity-composition trends of bioglasses. *J. Non-Cryst. Solids* 357, 1595–1602.
- Edén, M., 2012. NMR studies of oxide-based glasses. *Annu. Rep. Prog. Chem. Sect. C: Phys. Chem.* 108, 177–221.
- Edén, M., 2015. ^{27}Al NMR studies of aluminosilicate glasses. *Annu. Rep. NMR Spectrosc.* 86, 237–331.
- Edén, M., Sundberg, P., Stålhandke, C., 2011. The split network analysis for exploring composition-structure correlations in multi-component glasses: II. Multinuclear NMR studies of aluminoborosilicates and glass-wool fibers. *J. Non-Cryst. Solids* 357, 1587–1594.
- Engelhardt, G., Michel, D., 1987. *High-Resolution Solid-State NMR Spectroscopy of Silicates and Zeolites*. Chichester: Wiley.
- Essmann, U., Perera, L., Berkowitz, M.L., *et al.*, 1995. A smooth particle mesh Ewald method. *J. Chem. Phys.* 103, 8577–8593.
- Fortino, M., Berselli, A., Stone-Weiss, N., *et al.*, 2019. Assessment of interatomic parameters for the reproduction of borosilicate glass structures via DFT-GIPAW calculations. *J. Am. Ceram. Soc.* 102, 7225–7243.
- Gambuzzi, E., Pedone, A., Menziani, M.C., *et al.*, 2014. Probing silicon and aluminium chemical environments in silicate and aluminosilicate glasses by solid state NMR spectroscopy and accurate first-principles calculations. *Geochim. Cosmochim. Acta* 125, 170–185.
- Ganisetti, S., Gaddam, A., Kumar, R., *et al.*, 2019. Elucidating the formation of Al–NBO bonds, Al–O–Al linkages and clusters in alkaline-earth aluminosilicate glasses based on molecular dynamics simulations. *Phys. Chem. Chem. Phys.* 21, 23966–23977.
- Gee, B., Eckert, H., 1995. ^{23}Na nuclear magnetic resonance spin echo decay spectroscopy of sodium silicate glasses and crystalline model compounds. *Solid State Nucl. Magn. Reson.* 5, 113–122.
- Giannozzi, P., Baroni, S., Bonini, N., *et al.*, 2009. QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials. *J. Phys.: Condens. Matter* 21, 395502.
- Greaves, G.N., 1985. EXAFS and the structure of glass. *J. Non-Cryst. Solids* 71, 203–217.
- Greaves, G.N., Sen, S., 2007. Inorganic glasses, glass-forming liquids and amorphizing solids. *Adv. Phys.* 56, 1–166.
- Greaves, G.N., Fontaine, A., Lagarde, P., Raoux, D., Gurman, S.J., 1981. Local structure of silicate glasses. *Nature* 293, 611–616.
- Hench, L.L., 1991. Bioceramics: From concept to clinic. *J. Am. Ceram. Soc.* 74, 1487–1510.
- Himmel, B., Weigelt, J., Gerber, T., Nofz, M., 1991. Structure of calcium aluminosilicate glasses: Wide-angle X-ray scattering and computer simulation. *J. Non-Cryst. Solids* 136, 27–36.
- Iftekhar, S., Pahari, B., Okhotnikov, K., *et al.*, 2012. Properties and structures of $\text{RE}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ ($\text{RE}=\text{Y}, \text{Lu}$) glasses probed by molecular dynamics simulations and solid-state NMR: The roles of aluminum and rare-earth ions for dictating the microhardness. *J. Phys. Chem. C* 116, 18394–18406.
- Inoue, H., Masuno, A., Watanabe, Y., 2012. Modeling of the structure of sodium borosilicate glasses using pair potentials. *J. Phys. Chem. B* 116, 12325–12331.
- Jahn, S., Madden, P.A., 2007. Modeling Earth materials from crustal to lower mantle conditions: A transferable set of interaction potentials for the CMAS system. *Phys. Earth Planet. Inter.* 162, 129–139.
- Jakse, N., Bouhadja, M., Kozaily, J., *et al.*, 2012. Interplay between non-bridging oxygen, triclusters, and fivefold Al coordination in low silica content calcium aluminosilicate melts. *Appl. Phys. Lett.* 101, 201903.
- Jaworski, A., Stevansson, B., Edén, M., 2015. Direct ^{17}O NMR experimental evidence for Al–NBO bonds in Si-rich and highly polymerized aluminosilicate glasses. *Phys. Chem. Chem. Phys.* 17, 18269–18272.
- Jaworski, A., Stevansson, B., Edén, M., 2016. The bearings from rare-earth ($\text{RE}=\text{La}, \text{Lu}, \text{Sc}, \text{Y}$) cations on the oxygen environments in aluminosilicate glasses: A study by solid-state ^{17}O NMR, molecular dynamics simulations, and DFT calculations. *J. Phys. Chem. C* 120, 13181–13198.
- Jaworski, A., Stevansson, B., Pahari, B., Okhotnikov, K., Edén, M., 2012. Local structures and Al/Si ordering in lanthanum aluminosilicate glasses explored by advanced ^{27}Al NMR experiments and molecular dynamics simulations. *Phys. Chem. Chem. Phys.* 14, 15866–15878.
- Kieu, L.-H., Delaye, J.-M., Cormier, L., Stolz, C., 2011. Development of empirical potentials for sodium borosilicate glass systems. *J. Non-Cryst. Solids* 357, 3313–3321.
- Lacy, E.D., 1965. A statistical model of polymerization/depolymerization relationships in silicate melts and glasses. *Phys. Chem. Glasses* 6, 171–180.
- Le Losq, C., Neuville, D.R., Chen, W., *et al.*, 2017. Percolation channels: A universal idea to describe the atomic structure and dynamics of glasses and melts. *Sci. Rep.* 7, 16490.
- Lee, S.K., Sung, S., 2008. The effect of network-modifying cations on the structure and disorder in peralkaline Ca–Na aluminosilicate glasses: ^{29}Si MAS NMR study. *Chem. Geol.* 256, 326–333.
- Liang, J.-J., Cygan, R.T., Alam, T.M., 2000. Molecular dynamics simulation of the structure and properties of lithium phosphate glasses. *J. Non-Cryst. Solids* 263–264, 167–179.
- Loewenstein, W., 1954. The distribution of aluminium in the tetrahedra of silicates and aluminates. *Am. Mineral.* 39, 92–96.
- Madden, P.A., Wilson, M., 1996. “Covalent” effects in “ionic” systems. *Chem. Soc. Rev.* 25, 339–350.
- Maekawa, H., Maekawa, T., Kawamura, K., Yokokawa, T., 1991. The structural groups of alkali silicate glasses determined by ^{29}Si MAS NMR. *J. Non-Cryst. Solids* 127, 53–64.
- Malfait, W.J., Halter, W.E., Morizet, Y., Meier, B.H., Verel, R., 2007. Structural control on bulk and melt properties: Single and double quantum ^{29}Si NMR spectroscopy on alkali-silicate glasses. *Geochim. Cosmochim. Acta* 71, 6002–6018.
- Maranas, J.K., Chen, Y., Stillinger, D.K., Stillinger, F.H., 2001. Polarization interactions and boroxol ring formation in boron oxide: A molecular dynamics study. *J. Chem. Phys.* 115, 6578–6589.
- Mathew, R., Stevansson, B., Edén, M., 2015. Na/Ca intermixing around silicate and phosphate groups in bioactive phosphosilicate glasses revealed by heteronuclear solid-state NMR and molecular dynamics simulations. *J. Phys. Chem. B* 119, 5701–5715.
- Mathew, R., Stevansson, B., Tilocca, A., Edén, M., 2014. Toward a rational design of bioactive glasses with optimal structural features: Composition-structure correlations unveiled by solid-state NMR and MD simulations. *J. Phys. Chem. B* 118, 833–844.
- Morse, P.M., 1929. Diatomic molecules according to the wave mechanics. II. Vibrational levels. *Phys. Rev.* 34, 57–64.
- Mysen, B.O., Virgo, D., Scarfe, C.M., 1980. Relations between the anionic structure and viscosity of silicate melts – A Raman spectroscopic study. *Am. Mineral.* 65, 690–710.
- Okhotnikov, K., Stevansson, B., Edén, M., 2013. New interatomic potential parameters for molecular dynamics simulations of rare-earth ($\text{RE}=\text{La}, \text{Y}, \text{Lu}, \text{Sc}$) aluminosilicate glass structures: Exploration of RE^{3+} field-strength effects. *Phys. Chem. Chem. Phys.* 17, 15041–15055.
- Olivier, L., Yuan, X., Cormack, A.N., Jäger, C., 2001. Combined ^{29}Si double quantum NMR and MD simulation studies of network connectivities of binary $\text{Na}_2\text{O}-\text{SiO}_2$ glasses: New prospects and problems. *J. Non-Cryst. Solids* 293–295, 53–66.

- Pacaud, F., Delaye, J.-M., Charpentier, T., Cormier, L., Salanne, M., 2017. Structural study of $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glasses from molecular dynamics simulations using a polarizable force field. *J. Chem. Phys.* 147, 161711.
- Pedone, A., Gambuzzi, E., Menziani, M.C., 2012. Unambiguous description of the oxygen environment in multicomponent aluminosilicate glasses from ^{17}O solid state NMR computational spectroscopy. *J. Phys. Chem. C* 116, 14599–14609.
- Pedone, A., Charpentier, T., Malavasi, G., Menziani, M.M., 2010. New insights into the atomic structure of 45S5 bioglass by means of solid-state NMR spectroscopy and accurate first-principles simulations. *Chem. Mater.* 22, 5644–5652.
- Pedone, A., Malavasi, G., Menziani, M.C., Cormack, A.N., Segre, U., 2006. A new self-consistent empirical interatomic potential model for oxides, silicates, and silica-based glasses. *J. Phys. Chem. B* 110, 11780–11795.
- Plimpton S., 1995. Fast parallel algorithms for short-range molecular dynamics, *J. Comp. Phys.* 117, 1–19.
- Samoletov, A.A., Dettmann, C.P., Chaplain, M.A.J., 2007. Thermostats for “slow” configurational modes. *J. Stat. Phys.* 128, 1321–1336.
- Sanders, M.J., Leslie, M., Catlow, C.R.A., 1984. Interatomic potentials for SiO_2 . *J. Chem. Soc., Chem. Commun.* 1271–1273.
- Sen, S., Xu, Z., Stebbins, J.F., 1998. Temperature dependent structural changes in borate, borosilicate and borosilicate liquids: High-resolution ^{11}B , ^{29}Si and ^{27}Al NMR studies. *J. Non-Cryst. Solids* 226, 29–40.
- Smith, W., Forester, T.R., 1996. DL_POLY_2.0: A general-purpose parallel molecular dynamics simulation package. *J. Mol. Graphics* 14, 136–141.
- Stebbins, J.F., 1988. Effects of temperature and composition on silicate glass structure and dynamics: Si-29 NMR results. *J. Non-Cryst. Solids* 106, 359–369.
- Stebbins, J.F., Xu, Z., 1997. NMR evidence for excess non-bridging oxygen in an aluminosilicate glass. *Nature* 390, 60–62.
- Stevensson, B., Mathew, R., Edén, M., 2014. Assessing the phosphate distribution in bioactive phosphosilicate glasses by ^{31}P solid-state NMR and MD simulations. *J. Phys. Chem. B* 118, 8863–8876.
- Stevensson, B., Yu, Y., Edén, M., 2018. Structure-composition trends in multicomponent borosilicate-based glasses deduced from molecular dynamics simulations with improved B–O and P–O force fields. *Phys. Chem. Chem. Phys.* 20, 8192–8209.
- Tang, E., Di Tommaso, D., de Leeuw, N.H., 2010. An *ab initio* molecular dynamics study of bioactive phosphate glasses. *Adv. Eng. Mater.* 12, B331–B338.
- Tilocca, A., 2008. Short- and medium-range structure of multicomponent bioactive glasses and melts: An assessment of the performances of shell-model and rigid-ion potentials. *J. Chem. Phys.* 129, 084504.
- Tilocca, A., 2013. Cooling rate and size effects on the medium-range structure of multicomponent oxide glasses simulated by molecular dynamics. *J. Chem. Phys.* 139, 114501.
- Tilocca, A., de Leeuw, N.H., 2006. *Ab initio* molecular dynamics study of 45S5 bioactive silicate glass. *J. Phys. Chem. B* 110, 25810–25816.
- Tilocca, A., Cormack, A.N., 2007. Structural effects of phosphorus inclusion in bioactive silicate glasses. *J. Phys. Chem. B* 111, 14256–14264.
- Tilocca, A., Cormack, A.N., 2010. Surface signatures of bioactivity: MD simulations of 45S5 and 65S silicate glasses. *Langmuir* 26, 545–551.
- Tilocca, A., Cormack, A.N., de Leeuw, N.H., 2007. The structure of bioactive silicate glasses: New insights from molecular dynamics simulations. *Chem. Mater.* 19, 95–103.
- Tischendorf, B.C., Alam, T.M., Cygan, R.T., Otaigbe, J.U., 2003. The structure and properties of binary zinc phosphate glasses studied by molecular dynamics simulations. *J. Non-Cryst. Solids* 316, 261–272.
- Todorov, I.T., Smith, W., Trachenko, K., Dove, M.T., 2006. DL_POLY_3: New dimensions in molecular dynamics simulations via massive parallelism. *J. Mater. Chem.* 16, 1911–1918.
- van Beest, B.W.H., Kramer, H.J., van Santen, R.A., 1990. Force fields for silicas and aluminophosphates based on *ab initio* calculations. *Phys. Rev. Lett.* 64, 1955–1958.
- Vanommeslaeghe, K., Guvench, O., MacKerell Jr., A.D., 2014. Molecular mechanics. *Curr. Pharm. Des.* 20, 3281–3292.
- Voigt, U., Lammert, H., Eckert, H., Heuer, A., 2005. Cation clustering in lithium silicate glasses: Quantitative description by solid-state NMR and molecular dynamics simulations. *Phys. Rev. B* 72, 064207.
- Wang, M., Krishnan, N.M.A., Wang, B., *et al.*, 2018. A new transferable interatomic potential for molecular dynamics simulations of borosilicate glasses. *J. Non-Cryst. Solids* 498, 294–304.
- Wilson, M., Madden, P.A., Costa-Cabral, B.J., 1996. Quadrupole polarization in simulations of ionic systems: Application to AgCl. *J. Phys. Chem.* 100, 1227–1237.
- Wright, A.C., 2010. Borate structures: Crystalline and vitreous. *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. Part B* 51, 1–39.
- Xiang, Y., Du, J., 2011. Effect of strontium substitution on the structure of 45S5 bioglasses. *Chem. Mater.* 23, 2703–2717.
- Xiang, Y., Du, J., Smedskjaer, M.M., Mauro, J.C., 2013. Structure and properties of sodium aluminosilicate glasses from molecular dynamics simulations. *J. Chem. Phys.* 139, 044507.
- Yu, Y., Stevensson, B., Edén, M., 2017. Medium-range structural organization of phosphorus-bearing borosilicate glasses revealed by advanced solid-state NMR experiments and MD simulations: Consequences of B/Si substitutions. *J. Phys. Chem. B* 121, 9737–9752.
- Yu, Y., Stevensson, B., Edén, M., 2019. Structural role of sodium in borosilicate, phosphosilicate, and borophosphosilicate glasses unveiled by solid-state NMR and MD simulations. *J. Phys. Chem. C* 123, 25816–25832.
- Zachariasen, W.H., 1932. The atomic arrangement in glass. *J. Am. Chem. Soc.* 54, 3841–3851.
- Zeidler, A., Wezka, K., Whittaker, D.A.J., *et al.*, 2014. Density-driven structural transformations in B_2O_3 glass. *Phys. Rev. B* 90, 024206.

Computation of Phase Diagrams for Ceramics

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Introduction

Phase diagrams are used in materials science and engineering to understand the interrelationship between composition, microstructure and processing. They are graphical representations of the equilibrium state of a system as a function of constituent component concentrations (x); temperature (T) and pressure (P).

Classical methodology for determining phase diagrams is based on experimental results obtained from different dynamic and static techniques such as Differential Thermal Analysis (DTA); X-Ray Diffraction (XRD); Scanning Electron Microscopy (SEM), or Raman Spectroscopy (RAMAN) among others. However, this method is a time-consuming and costly job that becomes even tougher as the number of components increases or complex conditions (several variables, T , P , E (electric-magnetic fields)...) are considered. Thereby, while the equilibrium state of a two-component system can be represented as a binary x - T (composition-temperature at constant P) or x - P (composition-pressure at constant T); for three-components systems an additional dimension is necessary, so that they are usually represented by a series of isothermal (stable phases at each composition at constant temperature) or isoplethal sections (stable phases at a constant composition ratio of the components as a function of temperature) or liquidus surface projections as on composition plane.

On the other hand, considering that a phase diagram is the graphical representation of the thermodynamic properties of a system it can be regarded that, at least in principle, such diagrams can be calculated from thermochemical relationships and therefore find their basis of development in the thermodynamics. In practice, this is not easy due to the complexity of the process and because many of the necessary fundamental thermodynamic data for ceramics, in most cases, are not known. However, with the development of computers, it has been possible to address the treatment of multicomponent and multiphase systems using a thermodynamic approach, in which the composition of coexisting phases can be evaluated (Rao, 1970; Ansara, 1979).

The CALPHAD (CALculation of PHase Diagram) methodology has been widely developed during the past 50 years and great progress has been achieved; model descriptions have been improved and advances of the computational technology (Saunders and Miodownik, 1998; Lukas *et al.*, 2007) have allowed a better thermodynamic assessment of the systems. This method is based on the calculation of phase diagrams from mathematical descriptions of the thermodynamic properties of the phases of the system. This calculation allows reliable phase diagrams of high order systems to be obtained from constituent's subsystems that can guide experimentation and reduce the effort required to determine equilibrium. On the other hand, the difficulty of graphically representing multicomponent systems is overcome since calculations can be customized for the interest zone.

Through the years, the expression "calculation of phase diagrams" is being replaced by "computational thermodynamics" and CALPHAD is nowadays named Computer Coupling of Phase Diagrams and Thermochemistry because the phase diagram is only a portion of the information that can be obtained from these calculations. Furthermore, the recent studies of coupling phase diagrams and thermodynamic calculations with kinetic, diffusion process or microstructural models (phase field models) are enabling the thermodynamic calculations to approach more realistic work conditions of the materials and predict their chemical, physical and mechanical properties.

Nowadays, thermodynamic calculation is not an isolated field in material simulations; it is included in multi-scale modeling to accomplish optimizations of new materials and their associated processes (Wang *et al.*, 2015). These integrated projects are more advanced for metal than for ceramic systems (Yang *et al.*, 2019; Du *et al.*, 2019); but it is undoubtedly a challenge that ceramic material simulation is facing today.

Brief History of Calphad for Ceramics

Initially, the use of computational calculation methods to assemble phase diagrams and thermochemical data were applied to metallic systems (Kaufman and Nesor, 1974; Kaufman, 1977, 1979a) where the knowledge of the necessary thermodynamic data was broader than in the ceramic field. Kaufman and Bernstein (1970) gave an outline of the general features of the calculation of phase diagrams and they also gave listings of computer programs for the calculation of binary and ternary phase diagrams, thus laying the foundation for the CALPHAD method. Later, in 1973, Kaufman organized the first meeting of the international CALPHAD group. However, it was not until 1977 in the workshop on "Applications of Phase Diagrams in Metallurgy and Ceramics" held at the National Bureau of Standards in Gaithersburg (Maryland) (Carter and Bennett, 1977) when many gaps in ceramic thermodynamic data were detected and the need to develop computational methods to bridge these gaps for ceramics was noted.

Although in the 1960s there were several simple and specific applications of the use of thermodynamic data for the outline of binary phase diagrams such as: MgO-FeO (Phillips *et al.*, 1961); Al_2O_3 - Cr_2O_3 (Knapp, 1953); Al_2O_3 - ZrO_2 (Pena and De Aza, 1979);

indicating the possibilities of such procedures, it was not until the late 1970s that considerable efforts were applied toward developing an extensive database for ceramics systems. Kaufman and Nesor (1978) and Kaufman (1979b) developed a database for calculation of quasi-binary and quasi-ternary phase diagrams of ceramic systems. At the beginning, the database was restricted to a few oxides: Cr_2O_3 , MgO , FeO , Fe_2O_3 , Fe_3O_4 , Al_2O_3 , CaO , and SiO_2 , traditionally used in important industrial processes (slags, clinker, etc.). The usefulness of this approximation was illustrated by computing isothermal sections for ternary systems composed of these oxides. The above mentioned database was expanded to cover combinations of the oxides with silicon nitride, Si_3N_4 , and aluminum nitride, AlN , thus permitting computation of SiAlON or Si-Al-Zr/N-O ceramic systems (Kaufman, 1979c; Weiss *et al.*, 1981) and the development of materials with practical interest in aluminum, oil and gas industries, due to their excellent chemical stability and corrosion and wear resistance properties.

The biggest breakthrough in calculation of phase diagrams for ceramic systems took place during the nineties. The advance on the calculation methods and the development of new thermodynamic models more suitable to describe liquid and solid solution phases of oxides allowed reliable thermodynamic assessment of Al_2O_3 and/or SiO_2 containing systems among others. The first thermodynamic assessments of the systems $\text{CaO-Al}_2\text{O}_3$ and CaO-SiO_2 were made by Hallstedt (1990) and Hillert *et al.* (1990) using the CALPHAD technique and the new program PARROT for optimization of parameters. In these assessments, the liquid phase was described by a two-sublattice model for ionic solutions. Also, a thermodynamic assessment of the Si-O system (Hallstedt, 1992) was made using a two-sublattice model for ionic liquids and a regular solution model to describe the solid solution of oxygen in silicon. Afterwards, ternary systems such as $\text{CaO-MgO-Al}_2\text{O}_3$ were also assessed by Hallstedt (1995). Simultaneously, Jin and Du (1994) assessed phase diagrams and thermodynamic properties of zirconia-based systems which were of technological importance. The $\text{ZrO}_2\text{-YO}_{1.5}$ (Du *et al.*, 1991a) and $\text{ZrO}_2\text{-MgO}$ (Du and Jin, 1991b) systems were reevaluated with critically assessed Gibbs free energy functions. Furthermore, new ternary phase diagram data on the $\text{ZrO}_2\text{-YO}_{1.5}\text{-MgO}$ (Du *et al.*, 1991c) and $\text{ZrO}_2\text{-YO}_{1.5}\text{-CaO}$ (Du and Jin, 1992a) systems were published. The same authors carried out the thermodynamic evaluation of the $\text{ZrO}_2\text{-CaO-MgO}$ (Du *et al.*, 1992b) system combining the previous descriptions of the binary subsystems by means of Bonnier and Caboz's extrapolation (Bonnier and Caboz, 1960). Calculation of nitrogen or carbon containing systems such as: Si-Al-O-N (Hillert and Jonsson, 1992; Dumitrescu and Sundman, 1995); Si-C-N (Seifert *et al.*, 2001) and Al-C-N-Si-O (Pavlyuchkov *et al.*, 2012) was also addressed in this time-frame. These systems are useful for developing refractories and components in latest generation of engines or gas turbines, where mechanical engineering devices and components are designed to work at high temperatures.

From the late 1990s up to the present, calculation of new phase diagrams for ceramics with more oxide and non-oxide components have been addressed, covering a range of materials from classic refractory, slags or clinker materials to advanced ceramics. Important applications can be found in diverse fields such as $\text{ZrO}_2\text{-TiO}_2$ or BaO-TiO_2 quasibinary systems (Gong *et al.*, 2001; Xiaogang and Zhanpeng, 2000) for electroceramics, $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$ (Utlak and Besmann, 2019) for development of nuclear waste, $\text{ZrO}_2\text{-HfO}_2$ (Wang *et al.*, 2006) system for thermal barrier coatings or solid oxide fuel cells, Si-C-Al-Y-O (Pan *et al.*, 2010) to improve SiC -based engineering ceramics or $\text{SrO-Al}_2\text{O}_3\text{-SiO}_2$ system for environmental barrier coating and prediction of SiC recession caused by SiO_2 volatility under combustion environments (Zhang *et al.*, 2014). Some of the most recent assessments are related to P_2O_5 -based systems with important applications as phosphate bioceramics and/or in steelmaking industries among others, such as the $\text{CaO-P}_2\text{O}_5$ (Serena *et al.*, 2011) and $\text{CaO-P}_2\text{O}_5\text{-SiO}_2\text{-ZnO}$ (Jantzen *et al.*, 2019) systems.

From the beginning, thermodynamic calculation has been a very dynamic investigation field, new models and calculations methods have been developed, different systems have been constantly calculated or reassessed based on recent experimental data or new thermodynamic descriptions, and simulations of complex physicochemical processes have been addressed through the years.

The development of advanced thermodynamic software accessible to the general user and generalist and multicomponent databases confirm that CALPHAD is in fact a powerful tool increasingly used in recent years to explain multiple behaviors of ceramic materials in processes of technological interest.

Calphad Methodology

The aim of the CALPHAD method is to obtain a description of the phase diagram and thermodynamic properties to reliably predict the set of stable phases even in regions without experimental information. For this, the Gibbs energy of each phase must be calculated and then, equilibrium conditions can be established based on the minimization of the free energy of the system.

The most used state function for thermodynamic modeling is the Gibbs energy (G) which is a function of T , P and the components (N_i):

$$G = G(T, P, N_i, \dots) \quad (1)$$

When a process takes place, Gibbs free energy change (ΔG) is given by:

$$\Delta G = \Delta U + P\Delta V - T\Delta S \quad (2)$$

where U is the internal energy and S is the entropy and V is the volume. For a process at constant pressure ΔG is written as:

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

where H is the enthalpy.

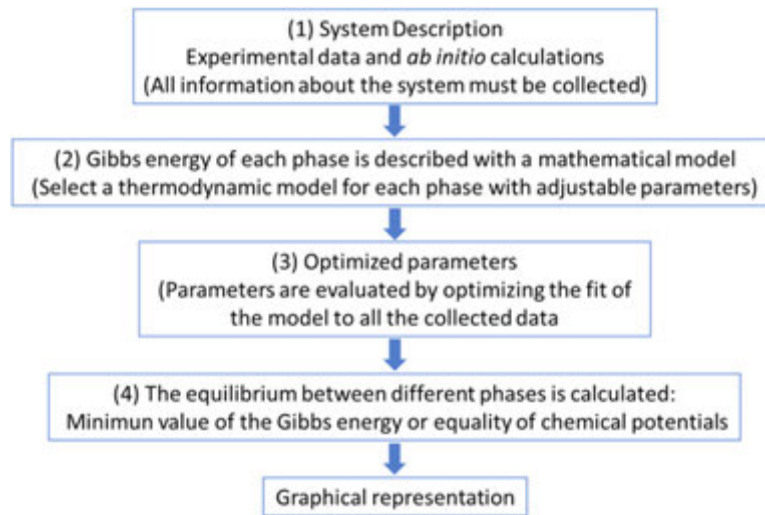


Fig. 1 Flow chart of the sequential steps in thermodynamic calculation for multicomponent systems.

Correlation between thermodynamics and phase equilibria in a multicomponent system is established on the basis of minimum Gibbs energy criteria for the system:

$$G = \sum_{\varphi} n^{\varphi} \cdot G_m^{\varphi} = \text{minimum} \quad (4)$$

where G_m^{φ} and n^{φ} are the molar Gibbs energy and the number of moles of phase φ respectively.

Considering this, in equilibrium conditions at T , P and N_i , the Gibbs energy has a minimum. dG can be expressed as:

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P, N_i} dT + \left(\frac{\partial G}{\partial P} \right)_{T, N_i} dP + \left(\frac{\partial G}{\partial N_i} \right)_{T, P} dN_i \quad (5)$$

From the derivation of the Gibbs energy the following relationships are established:

$$S = - \left(\frac{\partial G}{\partial T} \right)_{P, N_i} ; \quad V = \left(\frac{\partial G}{\partial P} \right)_{T, N_i} ; \quad \mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{T, P} \quad (6)$$

where μ_i is the chemical potential of component i .

A schematic CALPHAD route for calculating phase diagrams is shown in **Fig. 1**. First, the existing information is collected including both experimental results and data from *ab initio* or *first-principle* calculations. Second, Gibbs energy of each phase, attending to its chemical-physical properties, is described with a mathematical model containing adjustable parameters. Third, these parameters are evaluated by optimizing the fit of the model for all the collected information related to the system such as phase stability relationships and thermochemical and thermophysical studies of the phases. Finally, the results of equilibrium calculation can be represented in a graphical form.

Once databases have been developed, consistent and reliable phase diagrams can be calculated on the basis of thermodynamic equilibrium relationships.

Experimental Data and *ab initio* Calculation

Calculation of phase diagram by the CALPHAD approach needs a basic amount of experimental data to develop robust, consistent and reliable thermodynamic databases. The experimental measurements can be classified as "Structural data", "Phase-diagram data" and "Thermodynamic data".

Structural data are crystalline structure of the phases, ordering in solid and liquid phases. The most used techniques for determining the crystalline structure in ceramic systems are: X-ray Diffraction (XRD); Infrared Spectroscopy (IR) and Nuclear Magnetic Resonance (NMR).

Phase diagram data are obtained from isothermal and dynamic methods.

The aim of isothermal methods is to characterize the phases appearing in the material in equilibrium conditions so that samples are subjected to long time thermal treatments to ensure equilibrium has been reached. This is especially complex in ceramics because of high temperatures and remilling processes are sometimes needed to reach homogeneity and equilibrium conditions. The quench technique accompanied by characterization is still the best and most accurate way to determine a phase equilibria diagram. Phase stabilities and compatibility relationships can be established from microscopy techniques such as

optical and scanning electron microscopy with EPMA (Electron Probe Microanalysis). Mineralogical characterization is also essential in ceramics in terms of X-ray diffraction techniques.

Phase boundaries can be determined from non-isothermal techniques observing the evolution of a specific quantity as a function of temperature cycles for a determined composition. The preferred method for dynamic equilibria analyses is in-situ high-temperature XRD. Other techniques to establish energy or temperature variations in the sample are DTA, Differential Scanning Calorimetry (DSC); Electromotive Force Measurement (EFM) techniques in non-isothermal conditions and changes in magnetic susceptibility or resistivity while cooling or heating the sample.

All this information, such as equilibrium phases, phase quantity, phase composition, phase boundaries and temperature and composition of invariant points can be used to determine phase equilibrium diagrams.

Thermodynamic data for H , S and C_p can be obtained from calorimetric methods; activity ($a_i = p_i/p_0$) values from gas/phase equilibria measurements through static and dynamic conditions; chemical potential μ_i can be obtained from EFM using the Nernst equation.

In order to describe the contribution of pressure to the Gibbs energy, the measurement of bulk modulus, thermal expansion or elastic constants as a function of pressure and temperature are needed.

Another set of data comes from so-called *ab initio* or *first-principle* calculations, devoted to directly solve the Schrödinger equation and obtain the wave functions of quantum mechanics for the desired system (Liu, 2009). This approach provides a consistent description of both thermodynamic and thermophysical properties of a compound in gaseous, liquid or solid state using several parameters having physical meanings.

To carry out *ab initio* calculations it is necessary to know the atomic species and crystal structure of the compound, then, quantities related to the electronic structure and total energy of a given structure can be obtained. In short, Gibbs energy of a solid phase can be calculated expressing it as the summation:

$$G(T, P) = E^{\text{tot}} + F^{\text{trans}} + F^{\text{rot}} + F^{\text{vib}} + F^{\text{conf}} + PV \quad (7)$$

Being E^{tot} total electronic energy, F^{trans} and F^{rot} translational and rotational free energy, respectively, F^{vib} vibrational free energy, F^{conf} conformational free energy and PV the expansion term, for a specific compound and crystalline structure. Each term can be calculated in the frame of different approximations. Afterwards, enthalpy, entropy and heat capacity functions can be obtained applying classical thermodynamic relationships.

Several *ab initio* molecular dynamics software packages have been developed for calculating and simulating properties of a wide range of materials or liquid phases.

Thermodynamic Modeling

The CALPHAD method employs a variety of models to describe the temperature, pressure and concentration dependencies of the Gibbs functions of the phases. Specifically, the aim is to obtain an expression for G including parameters to be optimized in terms of experimental data. The selection of the model should be based on its physical and chemical properties, for example, crystallography, type of bonding, order in solid solutions or liquid phases, or magnetic aspects. Nevertheless, the last objective is to develop generalist and consistent databases so the simplicity of the model should also be considered.

The more general expression for the Gibbs energy of a phase (G^ϕ) can be described as:

$$G^\phi = G_T^\phi(T, x) + G_P^\phi(P, T, x) + G_M^\phi(T_C, \beta_0, T, x) \quad (8)$$

where $G_T^\phi(T, x)$ is the contribution to the Gibbs energy of T and x (composition) and $G_P^\phi(P, T, x)$ is the contribution of P while $G_M^\phi(T_C, \beta_0, T, x)$ is the magnetic contribution of the Curie (T_C) or Néel temperature (T_N) and the average magnetic moment per atom (β_0).

Temperature dependence of Gibbs free energy

Omitting magnetic contributions, thermodynamic functions of the different stable phases of elements and stoichiometric compounds only depends on temperature and pressure.

Attending to the recommendation of the Scientific Group Thermodata Europe (SGTE), at constant pressure, Gibbs energy can be expressed as a sum of terms:

$$G_i - H_i^{\text{SER}}(298.15\text{K}) = a + bT + cT \ln T + dT^2 + eT^{-1} + fT^3 + \dots \quad (9)$$

where $H_i^{\text{SER}}(298.15\text{K})$ is the molar enthalpy of the element i at 298.15 K in its standard state and a , b , c , ... are adjustable parameters.

Gibbs energy can be obtained from $C_p(T)$ functions, $\Delta H_{298.15}$ and $\Delta S_{298.15}$ (standard enthalpy and entropy of formation respectively) by the equations:

$$\Delta H_T = \Delta H_{298.15} + \int_{298.15}^T C_p \, dT; \Delta S_T = \Delta S_{298.15} + \int_{298.15}^T \frac{C_p}{T} \, dT \quad (10)$$

$$\Delta G_T = \Delta H_{298.15} + \int_{298.15}^T C_p \, dT - T \left(\Delta S_{298.15} + \int_{298.15}^T \frac{C_p}{T} \, dT \right) \quad (11)$$

Values for C_p , $\Delta H_{298.15}$ and $\Delta S_{298.15}$ of stoichiometric compounds are collected in thermodynamic databases (See Section on "Calculation Software Packages").

Pressure dependence of Gibbs free energy

Pressure affects the properties and phase stability of gaseous and condensed phases, especially at high pressure and temperature, but this dependence is often omitted in the thermodynamic modeling of condensed phases. In ceramic phases, molar volume (V_m) changes can be very important in some phase transitions and it is fundamental to know this to obtain the volume fraction of a phase.

The effect of P on Gibbs energy is given by the well known relationship:

$$G_P^\phi(P, T) = \int V_m dP \quad (12)$$

so that, a state equation $V(T, P)$ of a phase must be established in terms of the proper thermodynamic model.

In a first approximation, the ideal gas equation of state can be applied to a gaseous phase:

$$PV = nRT \quad (13)$$

so that Gibbs energy is established by:

$$G^{gas}(p_f) = {}^oG_{gas} + nRT \ln\left(\frac{p_f}{p_o}\right) \quad (14)$$

However, defining a state equation for condensed phases is a complex question. Although several relationships have been proposed based on different theoretical assumptions, their ability to extrapolate the behavior of solids at high pressure is sometimes questionable and none of them is valid for the entire range of T and P . This situation became even more complex when modeling solution phases, so that the application of CALPHAD at high pressures is unresolved.

The relationship between the volume (V) of a body and the pressure (P) to which it is subjected is given by the equation:

$$K = -V \left(\frac{\partial P}{\partial V} \right)_T \quad (15)$$

where K is the bulk modulus.

The classical approach proposed by Murnaghan is that the bulk modulus is a linear function of pressure (Murnaghan, 1944). This model is useful in limited pressure ranges but it is used nowadays as a first approach. An example of application of different state functions to oxides (forsterite Mg_2SiO_4) has been developed by Jacobs and Oonk (2001). A new pressure-dependent model was proposed by Lu *et al.* (2005) which includes composition dependent parameters in the modeling of solution phases.

Attending to the recommendation of the SGTE, pressure dependent contribution $G_P^\phi(P, T)$ for condensed phases is expressed in the form of the Murnaghan equation:

$$G_P^\phi(P, T) = \frac{A \exp(a_0 T + a_1 T^2/2 + a_2 T^3/3 + a_3 T^{-1})}{(K_0 + K_1 T + K_2 T^2)(n-1)} \left[(1 + nP(K_0 + K_1 T + K_2 T^2))^{1-1/n} - 1 \right] \quad (16)$$

where A , a_0 , a_1 , a_2 and a_3 , K_0 , K_1 and K_2 , and n are constants for a particular element and phase. Taking into account the well know relationships:

$$V_m = \left(\frac{\partial G}{\partial P} \right)_T; \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T; \quad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (17)$$

where α is the expansivity and κ is the compressibility, it can be seen from the above Eq. (16) that the parameter A is equivalent to the molar volume of the material at 0 K and 0 Pa. Furthermore, the parameters a_0 , a_1 , a_2 and a_3 represent the thermal expansibility of the material as a function of temperature for a pressure of 0 Pa. In an equivalent way, the parameters K_0 , K_1 , and K_2 represent the variation of the compressibility with temperature at zero pressure.

Compositional dependence of Gibbs free energy of multicomponent solution phases

Dependence of the Gibbs energy with composition is the core of the CALPHAD method. Rarely do the calculations involve purely stoichiometric compounds and solution phases.

Gibbs energy of stoichiometric compounds can be calculated from the stoichiometric contribution of the components at the corresponding reference state (oG_i) and the Gibbs energy of formation ($\Delta^f G^\phi$), thus for a binary stoichiometric phase (A_aB_b):

$$G^\phi = x_A {}^oG_A + x_B {}^oG_B + \Delta^f G^\phi \quad (18)$$

where x_A and x_B are mole fractions of components A and B given by the compound stoichiometry.

For solution phases, compositional dependence of the Gibbs energy can be expressed as the general equation:

$$G^\phi = {}^{ref}G_{mix}^\phi + {}^{ideal}G_{mix}^\phi + {}^{xs}G_{mix}^\phi \quad (19)$$

where the contribution of the pure components is ${}^{ref}G_{mix}^\phi$ while ${}^{ideal}G_{mix}^\phi$ is the ideal mixing contribution and finally ${}^{xs}G_{mix}^\phi$ is the contribution due to the non-ideal interactions between the components (excess Gibbs energy).

The contribution of the pure components (i) of a phase, to the Gibbs energy of a solution is given by:

$${}^{ref}G_{mix}^\phi = \sum_i x_i {}^oG_i^\phi \quad (20)$$

being x_i the constituents of the phase.

It is important to note that the term ${}^{\circ}G_i^{\phi}$ is the Gibbs energy of the component i in the solution phase even though it may not be as stable as the considered phase. The relative Gibbs energy for various phases of the metastable states of pure components of the system, referred to as "lattice stabilities" can be defined as a reference state. Then, ${}^{\circ}G_I^{\phi}$ means the Gibbs energy of formation of the constituent array I in ϕ from the reference state of the elements (i, j) included in the constituents and is a function of T and P :

$${}^{\circ}G_I^{\phi} - \sum_k b_{ij} H_j^{REF} = f(T, P) \quad (21)$$

Gibbs energy of a multicomponent phase can be attributed to two main factors: the bonding between the constituents and their configuration. The configurational part always enhances the mixing of unlike atoms. The bond energy between two unlike atoms may be either more negative than the bond energy between two equal atoms (creating a tendency for compound formation or ordering) or more positive (creating a tendency for there to be a miscibility gap).

Thermodynamic models for ceramic systems

The first models used to describe solution phases were based on the random mixture of components. Afterward, models considering the existence of some kind of order in the structure of the solutions were developed. This was especially relevant in the modeling of both liquid and solid solution phases in oxide and non-oxide ceramic systems. In fact, the behavior of SiO_2 , Al_2O_3 or B_2O_3 melts prompted the development of new liquid models to address the non-continuous behavior observed in the thermodynamic properties of these phases. Several models were developed to include the short ordering observed in liquids, as cellular models, modified quasichemical models, sublattice models, and associated solution models. Sublattice models are nowadays the most used in ceramic solid solutions modeling.

There are many models to simulate solution phases (Saunders and Miodownik, 1998; Lukas *et al.*, 2007) and to illustrate this some of the more commonly used in ceramic systems are described below.

Random substitutional models

These were the first proposed models for describing binary solutions and have been used in several ceramic systems. Random models can be applied to describe solid solutions where the constituents have the same probability of occupying any site in the crystalline unit cell and liquid phases.

In this case, ideal mixing contribution to Gibbs energy is given by:

$${}^{ideal}G_{mix}^{\phi} = -T^{ideal}S_{mix}^{\phi} = RT \sum_{i=1}^n x_i \cdot \ln(x_i) \quad (22)$$

so that, from Eq. (19), the molar Gibbs energy of a solution with n components, can be calculated:

$$G_m^{\phi} = \sum_{i=1}^n x_i \cdot {}^{\circ}G_i^{\phi} + RT \sum_{i=1}^n x_i \cdot \ln(x_i) + {}^{xs}G_{mix}^{\phi} \quad (23)$$

Deviation from the ideal behavior is considered in the excess Gibbs energy and several specific cases can be distinguished:

- (1) An ideal solution is characterized by the random distribution of non-interacting constituent so that ${}^{xs}G_{mix}^{\phi} = 0$. The mixing Gibbs energy is thus dependent only on the configurational entropy:

$$G_m^{\phi} = \sum_{i=1}^n x_i \cdot {}^{\circ}G_i^{\phi} + RT \sum_{i=1}^n x_i \cdot \ln(x_i) \quad (24)$$

The ideal model is applied to describe diluted solutions and ideal solutions.

- (2) For solution phases with significant interaction between constituents, ${}^{xs}G_{mix}^{\phi}$ can be described in terms of a Redlich–Kister power series (Redlich and Kister, 1948) of interaction parameters ${}^vL_{ij}$:

$${}^{xs}G_{mix}^{\phi} = \sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i x_j L_{ij}; \quad L_{ij} = \sum_{v=0}^k (x_i - x_j)^v \cdot {}^vL_{ij} \quad (25)$$

Being ${}^vL_{ij}$ temperature dependent: ${}^vL_{ij} = {}^v a_{ij} + {}^v b_{ij} T$

For $v = 0$, the equation gives just a single interaction parameter for the phase in the binary i - j system so the interaction is constant with composition (*regular solution model*). For $v \geq 1$ this leads to the *subregular solution model* where interaction energies are considered to change linearly with compositions.

A typical example of application of random substitutional models to ceramics is the MgO–CaO system. The structural studies on the MgO–CaO solid phases clearly show that Mg^{2+} and Ca^{2+} can replace each other in the corresponding lattice. Both MgO and CaO adopt a cubic structure so that solid solutions can be described as a unique structure: Halite, representing both MgO-rich (Halite-MgO) and CaO-rich (Halite-CaO) solid solution phases (Fig. 2). Likewise, no order is observed in the liquid phase so that this model can be also applied to this phase.

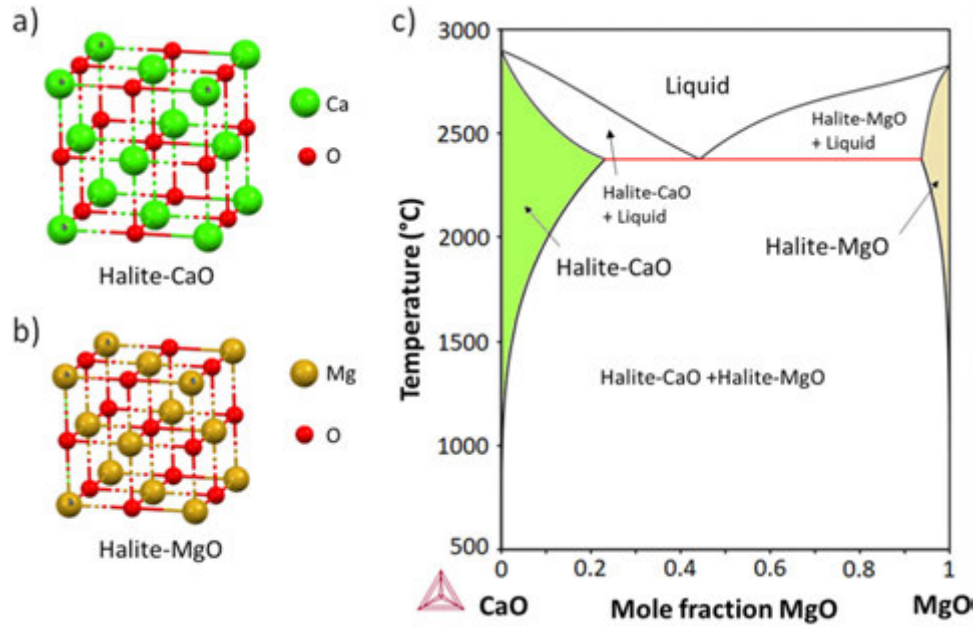


Fig. 2 Crystal structure of Halite phase (*Fd3m*) (a) Halite-CaO and (b) Halite-MgO, (c) Calculated phase equilibrium diagram of the CaO-MgO system.

Associate species solution models

These models were developed to describe solution phases when the equilibria cannot be represented with only species of the same stoichiometry as the end-members (Pelton and Kang, 2007). Typically, associate species solution models are applied when a sharp minimum is observed in the thermodynamic properties (as enthalpy of formation of the phase) at a defined composition. This behavior can be related to the presence of short-range order in the solution phase around singular compositions. When applied to liquid phases, the short-range order is comprised in the model defining intermediate “chemical species” or associates formed inside the liquid from reaction between the components of the system. This reduces the configurational entropy so that their corresponding thermodynamic data represent the negative, non-ideal mixing of the end-member components in the system. The thermodynamic properties of the liquid depend predominantly on the Gibbs energy of formation of these complexes; nevertheless, the interaction between chemical species was further considered in the modified associate solution model.

Considering the formation of a single associate with a formula A_iB_j in a binary system A-B, that liquid can contain n_A and n_B moles of A and B in equilibrium with $m_{A_iB_j}$ moles of the single associate A_iB_j . Then, ${}^{xs}G^\phi$

$${}^{xs}G^\phi = G_{asso}^\phi + G_{regular\ mix}^\phi \quad (26)$$

where G_{asso}^ϕ is the Gibbs energy of formation of an associate, defined as:

$$G_{asso}^\phi = m_{A_iB_j} {}^\circ G_{A_iB_j}^\phi \quad (27)$$

Being ${}^\circ G_{A_iB_j}^\phi$ the energy of formation of one mole of the associate and $G_{regular\ mix}^\phi$ considers the Gibbs energy due to the interactions between the components A and B themselves and with the associate A_iB_j such that

$$G_{regular\ mix}^\phi = G_{A,B}^\phi \frac{n_A n_B}{n} + G_{A,A_iB_j}^\phi \frac{n_A A_i B_j}{n} + G_{B,A_iB_j}^\phi \frac{n_B A_i B_j}{n} \quad (28)$$

$$S_{conf\ mix}^\phi = -R(n_A \ln(x_A) + n_B \ln(x_B) + n_{A_iB_j} \ln(x_{A_iB_j})) \quad (29)$$

${}^\circ G_{A_iB_j}^\phi$ and the interaction parameters can be used to fit experimental data.

This model has been used to describe the thermodynamic properties of liquid phases in several oxide ceramic systems (Besmann and Spear, 2002). As an example, to describe the liquid phase in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ binary oxide system, it is necessary to consider an ideal liquid solution phase from end-member liquid components Na_2O (liquid) and Al_2O_3 (liquid); and intermediate associate species NaAlO_2 (liquid) and $\text{Na}_2\text{Al}_4\text{O}_7$ (liquid). The NaAlO_2 associate specie appears in the system as a crystalline phase, while the $\text{Na}_2\text{Al}_4\text{O}_7$ specie has no crystalline corresponding phase but it is necessary to accurately reproduce the phase relations in the compositional region near $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3 = 1:2$.

Modified quasichemical model

This model was developed to consider short range order (SRO) in oxide liquids but it can be also applied to solid solutions as a special case, when the number of lattice sites and coordination numbers are constant.

The modified quasichemical model (Pelton and Wu, 1999) considers that liquid has a strong tendency to order around specific compositions, associated with specific physical phenomena.

Atoms or molecules of the N components of the solutions are distributed over the sites of a quasi-lattice. In the pair approximation, we consider the pair-exchange reactions:

$$(m - m) + (n - n) = 2(m - n); \quad \Delta g_{mn} \quad (30)$$

where m and n are $1, 2, \dots, N$; and $(m - m)$, $(n - n)$ and $(m - n)$ represent first-nearest-neighbor pairs. The non-configurational Gibbs energy change for the formation of two moles of $(m - n)$ pairs is Δg_{mn} .

$$G = \sum n_m g_m^o - T\Delta S^{\text{config}} + \sum_{m>n} n_{mn} (\Delta g_{mn}/2) \quad (31)$$

where g_m^o is the molar Gibbs energy of pure component m , and ΔS^{config} is an approximate expression for the configurational entropy of mixing, given by randomly mixing the $(m - n)$ pairs:

$$\Delta S^{\text{config}} = -R \sum n_m \ln(X_m) - R \left(\sum n_m \ln(X_m/Y_m^2) + \sum_{m>n} n_{mn} \ln(X_m/2Y_m Y_n) \right) \quad (32)$$

where X_m is the pair fraction and Y_m coordination-equivalent fraction.

$$\Delta g_m = \Delta g_m^o + \sum_{i>1} {}^i L_{mn} (Y_m - Y_n)^i \quad (33)$$

Δg_m^o and ${}^i L_{mn}$ are empirical binary parameters to be optimized from experimental data.

This model has been used in thermodynamic assessment of several ceramic systems such as MgO–Al₂O₃, CaO–MgO–Al₂O₃, and MgO–Al₂O₃–SiO₂ (Jung *et al.*, 2004) and it is included in different powerful databases for multicomponent systems.

Sublattice models

The most complex and general model applied nowadays to solid solutions is the sublattice model (Sundman and Ågren, 1981). In crystalline solids the atoms may occupy different types of sublattices with different coordination numbers, bond lengths, etc. A solid phase can be seen as a mixture of interlocking sublattices on which various components can mix randomly. In nature the model does not define any crystal structure within its general mathematical formulation, although it is possible to define internal parameter relationships, which reflect structure with respect to different crystal types.

One simple case of a sublattice model would be two-sublattices with several constituents in each sublattice. A shorthand notation of this would be:

$$(A, B, \dots)_a (U, V, W, \dots)_c \quad (34)$$

where the subscripts a and b give the ratio of sites on the two sublattices. The constituents $A, B, \dots, U, V$ can represent atoms, ions, anti-site atoms, vacancies, etc.

Considering the general Eq. (19); the Gibbs energy for the two sublattice model is:

$$G_m^\phi = \sum_i \sum_j \gamma_i' \gamma_j'' \text{Ref } G_{ij}^\phi + RT \left(a \sum_i \gamma_i' \ln(\gamma_i') + b \sum_j \gamma_j'' \ln(\gamma_j'') \right) + {}^{xs} G_m^\phi \quad (35)$$

where γ_i' and γ_j'' are the constituent fractions on sublattices 1 and 2, respectively. The term $\text{Ref } G_{ij}^\phi$ is the Gibbs energy of the phase ϕ when only one pure component exists on each sublattice and then a reference energy surface is defined.

For two components in each sublattice $(A, B)_m (C, D)_n$, considering a random mixture of the species in a sublattice, ${}^{xs} G_m^\phi$ can be written as:

$${}^{xs} G_m^\phi = \gamma_A' \gamma_B' \gamma_C'' \gamma_D'' L_{AB:C} + \gamma_A' \gamma_B' \gamma_D'' \gamma_C'' L_{AB:D} + \gamma_A' \gamma_C' \gamma_D'' \gamma_B'' L_{A:CD} + \gamma_B' \gamma_C' \gamma_D'' \gamma_A'' L_{B:CD} + \gamma_A' \gamma_B' \gamma_C'' \gamma_D'' L_{AB:CD} \quad (36)$$

In this expression, there are two interaction parameters for each sublattice depending on the constituent on the other sublattice. The binary interaction parameters can be expanded as a Redlich-Kister polynomial.

This model has been widely applied to describe solid solution phases in oxide and non-oxide ceramic systems. An illustrative example is spinel structures such as MgAl₂O₄-spinel (Ma and Liu, 2019) which is usually assigned to the cubic space group $Fd\bar{3}m$. It is formed as an approximately cubic, close-packed array of oxygen atoms, between which are tetrahedral T-sites and octahedral O-sites (Fig. 3). Some thermodynamic assessments describe a spinel solution within the framework of the two-sublattices compound energy formalism (Jung *et al.*, 2004) modeling it as:

$$(Mg^{2+}, Al^{3+})^T (Mg^{2+}, Al^{3+}, Va)_2 O_4 \quad (37)$$

with $m = 1$ and $n = 2$ sites on the tetrahedral and octahedral sublattices, respectively. Non-stoichiometry can occur through the introduction of vacancies, Va , on octahedral sites.

Ionic two-sublattice models for ionic liquids

This model is an extension of the sublattice model that has been widely used to describe the thermodynamic properties of liquid phases in ceramic systems (Sundman, 1991).

This model addresses short range order (SRO) in liquids considering that the structure can be described as two sublattices, with anionic, cationic, and neutral species. This does not mean the existence of fixed sites in space but a complete separation of cations in one sublattice, and anions, vacancies and neutral species in the other. The sublattice formula for the model can then be written as:

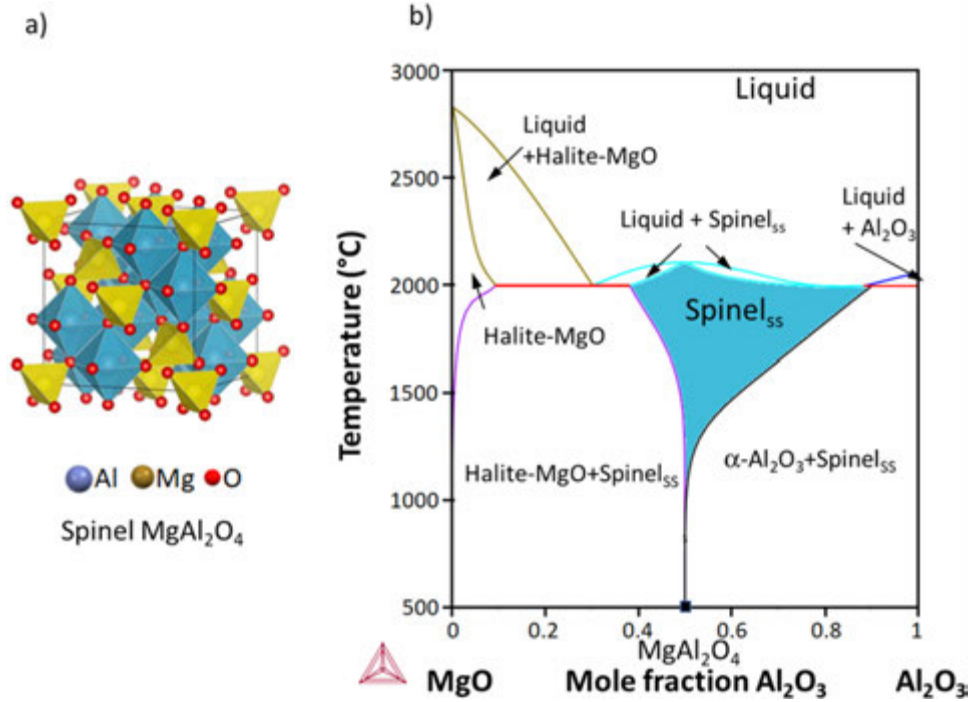


Fig. 3 (a) Crystal structure of MgAl₂O₄-spinel phase. (b) Calculated phase equilibrium diagram of the MgO-Al₂O₃ system.

$$(C_i^{+v_i})_P (A_j^{-v_j}, Va, B_k^0)_Q \quad (38)$$

where C represents cations, A anions, Va hypothetical vacancies and B neutral species. The charge of an ion is denoted as v_i and the indices i , j and k are used to denote specific constituents. To simplify, the notation superscripts v_i , v_j and 0 will be omitted in the following. The number of sites on the sublattices is varied so that electroneutrality is maintained and values of P and Q are calculated from the equation:

$$P = \sum_j v_j \cdot \gamma_{A_j} + Q \gamma_{Va}; \quad Q = \sum_i v_i \cdot \gamma_{C_i} \quad (39)$$

where P and Q are stoichiometric numbers that vary with the composition to maintain electroneutrality.

Taking into account the above, the total Gibbs energy of the liquid phase is given by:

$$\begin{aligned} G_M^{\text{Liquid}} - H^{\text{SER}} = & \sum_i \sum_j \gamma_{C_i} \gamma_{A_i}^{\text{Ref}} G_{C_i A_i}^{\text{Liquid}} + Q \gamma_{Va} \sum_k \gamma_{C_i}^o G_{C_i}^{\text{Liquid}} + Q \sum_k \gamma_{B_i}^o G_{B_i}^{\text{Liquid}} \\ & + RT \left[P \sum_i \gamma_{C_i} \log_e \gamma_{C_i} + Q \left(\sum_j \gamma_{A_j} \log_e \gamma_{A_j} + \gamma_{Va} \log_e \gamma_{Va} + \sum_k \gamma_{B_k} \log_e \gamma_{B_k} \right) \right] + {}^{\text{xs}}G_m^{\text{Liquid}} \end{aligned} \quad (40)$$

By considering the general expression (25) ${}^{\text{xs}}G_m$ can be written as:

$$\begin{aligned} {}^{\text{xs}}G_m = & \sum_{i_1} \sum_{i_2} \sum_j \gamma_{i_1} \gamma_{i_2} \gamma_j \cdot L_{i_1 i_2 j} + \sum_{i_1} \sum_{i_2} \gamma_{i_1} \gamma_{i_2} \gamma_{Va} \cdot L_{i_1 i_2 Va} + \sum_{i_1} \sum_{j_1} \sum_{j_2} \gamma_{i_1} \gamma_{j_1} \gamma_{j_2} \cdot L_{i_1 j_1 j_2} + \sum_i \sum_j \gamma_i \gamma_j \gamma_{Va} \cdot L_{ij Va} \\ & + \sum_i \sum_j \sum_k \gamma_i \gamma_j \gamma_k \cdot L_{ijk} + \sum_i \sum_k \gamma_i \gamma_j \gamma_{Va} \cdot L_{i Va k} + \sum_{k_1} \sum_{k_2} \gamma_{k_1} \gamma_{k_2} \cdot L_{k_1 k_2} \end{aligned} \quad (41)$$

where ${}^oG_{C_i A_i}^{\text{Liquid}}$ is the Gibbs energy of formation for $(v_i + v_2)$ moles of atoms of liquid $C_i : A_i$ and ${}^oG_{C_i}^{\text{Liquid}}$ and ${}^oG_{B_i}^{\text{Liquid}}$ are the Gibbs energy of formation per mol of atoms of liquid C_i and B_i . In this expression, there are interaction parameters between species in each sublattice depending on the constituent in the other sublattice, which can be expanded as a Redlich-Kister polynomial.

This model has been widely used in oxide and non-oxide ceramic systems from the beginning. One of the most significant applications is the description of melts in glass forming systems such as silicates. Silicate glasses are the typical representatives of the covalently bonded glasses and their structure is well described by the continuous random network model (Osipov and Osipova, 2013) as a continuous network of SiO₄ tetrahedra randomly interconnected via the oxygen apexes. One example is the thermodynamic assessment of the CaO-SiO₂ system provided by Mao *et al.* (2006) in which the liquid was described with the formula:

$$(Ca^{2+})_P (O^{2-}, SiO_4^{4-}, SiO_2^0)_Q \quad (42)$$

where the SiO_2^0 species represents the tetrahedral network of pure liquid silica, and the mixture of the SiO_4^{4-} and SiO_2^0 species represent the variable polymerization degree in compositions between Ca_2SiO_4 and SiO_2 . In the case of $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ the expression is:

$$(\text{Al}^{3+}, \text{Ca}^{2+})_P (\text{AlO}_2^-, \text{O}^{2-}, \text{SiO}_4^{4-}, \text{SiO}_2^0)_Q \quad (43)$$

Optimization of Parameters

Thermodynamic optimization can be considered as the fitting of certain parameters of Gibbs energy functions in order to obtain the most realistic representation of experimental studies of phase diagrams and available thermodynamic properties of the system. These parameters are determined by optimizing the fit of the model to all the experimental and theoretical information collected about the system (See Section on “Experimental Data and *ab initio* Calculation”). To ensure a reliable calculation that allows the extrapolation to high order systems, all experimental information must be critically analyzed to identify the less reliable data and discard possible erroneous data.

There are “optimizer” codes, which are used for the thermodynamic assessment of phase equilibria. The essential aim of these codes is to reduce the statistical error between calculated phase equilibria, thermodynamic properties and the equivalent measured quantities. The accuracy can be mathematically defined through some optimization software. The Lukas program and PARROT program are the main codes currently used for minimization. The aim in both cases is reduction of the error between calculated and experimental variables.

The Lukas program uses a Gaussian least-squares method (Lukas *et al.*, 1977). Equations of error are given for each type of measurement: (1) Calorimetric measurements, which are usually enthalpies, (2) EMF and vapor pressure which provide partial G and c) phase diagram information.

In the PARROT program (Jansson, 1984) the criterion for best fit is based on the maximum likelihood principle, where the best estimate of the model parameters should maximize the likelihood function for the different experimental observations. The best fit between various calculated results and all the input of experimental data is found where the sum of the squares of the weighted residuals is at its minimum.

Extrapolation of the Gibbs Energy to Higher Order Systems

Extrapolation to multicomponent systems is one of the main objectives of the CALPHAD methodology. Several “geometric” models have been proposed to estimate thermodynamic properties of a ternary solution from optimized data of its binary subsystems. The most common are the Muggianu *et al.* (1975), Kohler (1960) and Toop (1965) models. Attending to the geometrical representation (Fig. 4; it can be seen that the Muggianu and Kohler equations are considered “symmetric” as they treat the components in the same way. On the contrary, the Toop model is “asymmetric” since one component is singled out.

In short, the contribution of binary excess Gibbs energies ($^{xs}G_{ij}^{q-bin}$) to the total molar ternary excess Gibbs energy ($^{xs}G_m^{q-ter}$) is given by:

$$^{xs}G_m^{q-ter} = \sum_{i,j} w_{ij} \cdot ^{xs}G_{ij}^{q-bin} \quad (44)$$

where the binary weighting factor, w_{ij} , depends on the geometric model selected.

In symmetric models the weighting factor is equivalent for the three binary systems, while in the asymmetric model the contribution of each binary system can be different.

Considering that a subregular substitutional solution model (Eqs. 19–21) has been used to describe the binary phases, $^{xs}G_m^{q-ter}$ applying the Muggianu model is given by the equation:

$$^{xs}G_m^{q-ter} = x_A x_B [{}^0L_{AB} + {}^1L_{AB}(x_A - x_B)] + x_B x_C [{}^0L_{BC} + {}^1L_{BC}(x_B - x_C)] + x_A x_C [{}^0L_{AC} + {}^1L_{AC}(x_A - x_C)] \quad (45)$$

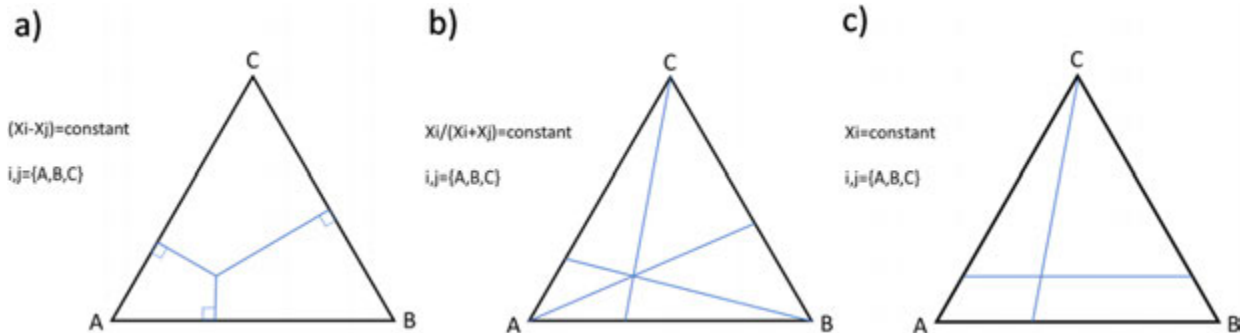


Fig. 4 Geometrical representation of classical extrapolation methods. (a) Muggianu, (b) Kohler and (c) Toop models.

If the Kohler model is applied to the extrapolation then:

$$^{xs}G_m^{\varphi-ter} = x_A x_B \left[{}^0L_{AB} + {}^1L_{AB} \left(\frac{x_A - x_B}{x_A + x_B} \right) \right] + x_B x_C \left[{}^0L_{BC} + {}^1L_{BC} \left(\frac{x_B - x_C}{x_B + x_C} \right) \right] + x_A x_C \left[{}^0L_{AC} + {}^1L_{AC} \left(\frac{x_A - x_C}{x_A + x_C} \right) \right] \quad (46)$$

When the Toop model is used, Gibbs energy of the ternary solution is essentially different because the contribution of one binary system B – C is different:

$$^{xs}G_m^{\varphi-ter} = x_A x_B \left[{}^0L_{AB} + {}^1L_{AB} (x_A - x_B - x_C) \right] + x_A x_C \left[{}^0L_{AC} + {}^1L_{AC} (x_A - x_C - x_B) \right] + x_B x_C \left[{}^0L_{BC} + {}^1L_{BC} \left(x_B - x_C + \frac{x_B - x_C}{x_B + x_C} x_A \right) \right] \quad (47)$$

A proper selection of “geometric” models is very important for ceramic systems because oxide components can be dissimilar and the deviations from ideality can be very important. For systems with strong interactions, different extrapolation techniques can give quite different results. On the other hand, although the direct extrapolation provides the correct feature of higher order systems, a more accurate modeling of the diagrams could include ternary interaction parameters (L_{ABC}).

Calculation of Equilibrium and Phase Diagram

Once G^φ of the phases of the system are known, minimum energy criteria can be applied to calculate the equilibrium conditions (Eq. 4).

In equilibrium conditions, at constant P and T, the partial Gibbs energies of all phases are identical to the equilibrium chemical potentials, μ_i (Eq. 6):

$$G_i^\varphi(T, P, x_i^\varphi) = \mu_i^\varphi; (i = 1, \dots, c, \varphi = 1, \dots, p) \quad (48)$$

so that, Eq. (48) results in n non-linear equations that can be used in numerical calculation:

$$\begin{aligned} \mu_1^1 &= \mu_1^2 = \dots \mu_1^\varphi \\ \mu_2^1 &= \mu_2^2 = \dots \mu_2^\varphi \\ &\dots\dots\dots \\ \mu_n^1 &= \mu_n^2 = \dots \mu_n^\varphi \end{aligned} \quad (49)$$

The minimum of G can be evaluated numerically by iterative techniques like the Newton–Raphson method (Deiters, 1985). In this approach, one needs an initial constitution for each phase in order to find the minimum of the Gibbs energy surface for the given conditions.

The classical method for obtaining the minimum of the Gibbs energy is the use of Lagrange multipliers μ_i and λ^φ related to the $N_{el} + N^\varphi$ physical constraints (mass balance equation for each of the N_{el} elements, sum of the molar fractions equal to unity in each of the N^φ phases). The Lagrange function, L , is written as:

$$L = \sum_{\varphi=1}^{N^\varphi} n^\varphi G_m^\varphi + \sum_{\varphi=1}^{N^\varphi} \mu_i \left(n_i - \sum_{\varphi=1}^{N^\varphi} n^\varphi x_i^\varphi \right) + \sum_{\varphi=1}^{N^\varphi} \lambda^\varphi \left(1 - \sum_{i=1}^{N_{el}} x_i^\varphi \right) \quad (50)$$

where the molar Gibbs energy of the phase φ is G_m^φ , n^φ is the number of moles of the phase φ and x_i^φ is the molar fraction of the i^{th} element in the phase φ . Then, a non-linear system of $N^\varphi(N_{el} + 1)$ Lagrange-type equations (Eqs. (51) and (52)) must be solved, usually using a Newton-Raphson algorithm, in addition to the $N_{el} + N^\varphi$ initial constraints (53) and (54):

$$\frac{\partial L}{\partial n^\varphi} = G_m^\varphi - \sum_{i=1}^{N_{el}} \mu_i x_i^\varphi = 0 \quad (51)$$

$$\frac{\partial L}{\partial x_i^\varphi} = n^\varphi \left(\frac{\partial G_m^\varphi}{\partial x_i^\varphi} - \mu_i \right) - \lambda^\varphi = 0 \quad (52)$$

$$1 - \sum_{i=1}^{N_{el}} x_i^\varphi = 0 \quad (53)$$

$$n_i - \sum_{\varphi=1}^{N^\varphi} n^\varphi x_i^\varphi = 0 \quad (54)$$

The final results give the values of the initially unknown quantities: the amount n^φ of the various phases, their compositions given by the x_i^φ and the Lagrange multipliers λ^φ and μ_i , these μ_i being considered as the chemical potentials of the i^{th} elements. In summary, all information regarding the thermodynamic equilibrium has been calculated.

Calculation Software Packages

Finding the *real* thermodynamic equilibrium conditions in a system from Gibbs energy minimization is a core issue in calculation software. Nowadays, a variety of database and powerful thermodynamic software packages enable phase diagram calculations of

multicomponent systems. A few of the more well-known commercial ones are: ChemSage (Eriksson and Hack, 1990); Thermo-Calc (Sundman *et al.*, 1985); FacTSage (Bale *et al.*, 2009); MTDATA (Davies *et al.*, 2002); PANDAT (Cao *et al.*, 2009); HSC (See Relevant Websites section) or CaTCalc (Shobu, 2009). There are also general noncommercial sources for thermodynamic calculations like, for example, the classic Lukas program (Lukas *et al.*, 1977; Solgasmix Eriksson, 1975) or more recently, the Open Calphad (Sundman *et al.*, 2015) initiative devoted to develop free software and databases for thermodynamic calculations for different applications.

Some of the first generation software packages such as for example ChemSage, Lukas programs or Thermo-Calc already have the availability of optimizing modules for the calculation of the Gibbs energy functions, which enables users to develop their own database. In spite of the enormous advances made in phase diagram calculations, serious shortcomings of the first generation software became obvious (Chen *et al.*, 2001) due to the fact that the algorithms used in calculating equilibrium conditions were based on local function minimization routines. Chen *et al.* (2001) used a second-generation software package, PANDAT, based on global optimization algorithms to calculate the stable phase diagrams for a given set of thermodynamic parameters. From early 2000, Global Minimization Technique has been implemented in the most generalist software packages.

Subsequently, capacities of the calculation programs have improved at all levels: user interfaces, development of databases, calculation algorithms and special task. The development of increasingly user-friendly computer interfaces makes phase-diagram information more accessible for the occasional user. The user needs only to supply a bulk composition and temperature limits for the calculation, and the programs generate the remaining conditions that are needed for the calculation.

More recently, the challenge of integrating the simulation of kinetic processes with equilibrium calculations has been addressed. Simulation of precipitation, diffusion or phase field simulation of microstructure in metallic systems can actually be performed with, for example, MatCalc, PANDAT, Thermo-calc (DICTRA) or FacTSage software.

The reliability of the results of thermodynamic modeling depends on the quality of the underlying thermodynamic database. Currently, several databases for metals, non-metals, oxides, salts, nitrates, aqueous solutions, etc., have been developed making it impossible to list all of them here so that only a short note about generalist thermodynamic databases widely used in thermodynamic calculations in ceramic systems is presented next. Through the years, there have been a significant interest in defining and collecting thermodynamic data to develop simple and generalist databases such as, for example, those of Dinsdale (1991), Barin and Knacke (1973) or Glusko *et al.* (1982); a short review is given by Jacobson (2001). Since the middle of the 20th century, several international organizations have dedicated efforts to generate comprehensive and self-consistent databases. Some significant examples are SGTE (Scientific Group Thermodata Europe); NIST (United States National Institute of Standards and Technology); NEA (Nuclear Energy Agency); and NPL (National Physical Laboratory, UK) which develop work collecting and normalizing databases for applications in different fields.

The SGTE Pure Substances Database has been widely adopted within the international community as a rigorous basis for the critical assessment of thermodynamic data. In addition to pure substances, thermodynamic data of solution phases have been also considered in the database in terms of non-ideal substitutional and sublattice models.

The JANAF Tables (Joint-Army-Navy-Air-Force) project was established in 1959 to collect thermochemical data for rocket propellant performance calculations by industry and agencies of the Defense Department of USA. Nowadays, the NIST-JANAF thermodynamic table is a computerized database maintained by the United States National Institute of Standards and Technology.

There are some databases comprising thermodynamic properties of multicomponent oxide and non-oxide solution phases which are of great interest in ceramic materials. General databases are focused on specific applications such as those containing Al_2O_3 , CaO , MgO , SiO_2 , $\text{FeO}/\text{Fe}_2\text{O}_3$ and SO_4^{2-} with applications to cements or slags, ZrO_2 or Si-Al-N-O solution phases among others. These databases are a very dynamic field of research and are continuously being revised and updated. Some of the most extensive for oxide solution phases are the FToxid database (Decterov, 2018), (FactSage) for slags, glasses, ceramics or refractories and TCOX, SLAG4 and ION databases (Thermo-Calc) for oxides, slags or cement.

Examples

As examples of application of CALPHAD methodology to ceramic systems, thermodynamic assessments of the binary $\text{CaO-P}_2\text{O}_5$ and ternary $\text{ZrO}_2\text{-CaO-MgO}$ systems are presented.

Thermodynamic Assessment of the Binary $\text{CaO-P}_2\text{O}_5$ System

This system with solid and liquid phases is very interesting because of its application to different biomaterials. Phosphorus is also important in slags and it has been included in other databases in low concentrations.

Serena *et al.* (2011) used the CALPHAD methodology to carry out the thermodynamic assessment of the $\text{CaO-P}_2\text{O}_5$ systems using the Thermo-Calc Software. The system $\text{CaO-P}_2\text{O}_5$ presents several intermediate compounds with different polymorphic forms: P_2O_5 , $\text{CaP}_4\text{O}_{11}$ (CP2); $\text{Ca}_2\text{P}_6\text{O}_{17}$ (C2P3); $\text{Ca}(\text{PO}_3)_2$ (CP); $\text{Ca}_2\text{P}_2\text{O}_7$ (C2P); $\text{Ca}_3(\text{PO}_4)_2$ (C3P); $\text{Ca}_4(\text{PO}_4)_2\text{O}$ (C4P); and CaO . No solid solutions have been reported in the system. The standard Gibbs free energy of P_2O_5 , CaO , CP, $\gamma/\beta/\alpha\text{-C2P}$ and $\beta/\alpha/\alpha'\text{-C3P}$ were taken from the SSUB4 database (SGTE Substance databases). Taking into account bibliographic information, a set of thermodynamic functions were optimized for the $\text{CaP}_4\text{O}_{11}$, $\text{Ca}_2\text{P}_6\text{O}_{17}$, and $\text{Ca}_4(\text{PO}_4)_2\text{O}$ compounds. Very scarce thermodynamic data have been published about thermodynamic properties of CP2 and C2P3 compounds. From structural studies of

phosphate phases it was established that CP2 and C2P3 compounds are constituted by Q^3 and Q^2 tetrahedra so that in this assessment, their Gibbs energies were calculated as binary stoichiometric phases (Eq. 18) from mixtures of P_2O_5 and $Ca(PO_3)_2$ phases:

$$^{\circ}G_{CaP_4O_{11}}^{Solid} - H^{SER} = ^{\circ}G_{Ca(PO_3)_2}^{Solid} + ^{\circ}G_{P_2O_5}^{Solid} + A_{CP2} + B_{CP2}T \quad (55)$$

$$^{\circ}G_{Ca_2P_6O_{17}}^{Solid} - H^{SER} = 2 \cdot ^{\circ}G_{Ca(PO_3)_2}^{Solid} + ^{\circ}G_{P_2O_5}^{Solid} + A_{C2P3} + B_{C2P3}T \quad (56)$$

Standard Gibbs energy of C4P was fitted to various experimental data collected from literature using the general expression from (Eq. 9):

$$^{\circ}G_{Ca_4(PO_4)_2}^{Solid} - H^{SER} = A + BT + CT \ln(T) + DT^2 \quad (57)$$

However, the key to model this glass-forming system is the selection of a suitable thermodynamic model to describe the liquid phase. The authors selected the ionic two-sublattice model (Sundman, 1991) to describe the liquid phase of the CaO- P_2O_5 system. In this model, the liquid phase is described by ionic-two lattices, one of the cations and the other of anions and neutral species following that described in the Section on "Thermodynamic models for ceramic systems". In this way, Serena et al. (2011) described the constitution of the liquid phase based on the structure of phosphate melts and glasses collected in the literature. Structures of typical phosphate melts and glasses have been previously established and they are constituted by a network of $[PO_4]$ tetrahedral (Stocha et al., 2016). These tetrahedra are classified using the Q^n terminology where n represent the number of bridging oxygen per tetrahedron. The phosphate tetrahedral sites that can exist in phosphate glasses are: Q^3 related to P_2O_5 species, Q^2 related to PO_3^{3-} species, Q^1 related to $P_2O_7^{4-}$ species, and finally Q^0 without bridging oxygens corresponding to the PO_4^{3-} species (Fig. 5). The addition of a modifying oxide to P_2O_5 results in the creation of nonbridging oxygens, at the expense of bridging oxygens, so that the speciation of the P_2O_5 occurs and PO_3^- ; monophosphate (PO_4^{3-}) and diphosphate ($P_2O_7^{4-}$) species appear in the glass structure.

Considering the previous, the liquid phase of the system, was defined by the formula $(Ca^{2+})_P:(O^{2-}, PO_3^-, PO_{7/2}^{2-}, PO_4^{3-}, PO_{5/2}^-)_{Q^i}$ where P and Q change with composition to maintain electroneutrality as described by the equations:

$$P = \sum_i \gamma_i (-\gamma_i) = 2\gamma_{O^{2-}} + \gamma_{PO_3^-} + 2\gamma_{PO_{7/2}^{2-}} + 3\gamma_{PO_4^{3-}} + 0\gamma_{PO_{5/2}^-} \quad (58)$$

$$Q = \sum_j \gamma_j (\gamma_j) = 2\gamma_{Ca^{2+}} = 2 \cdot 1 = 2$$

where γ_i and γ_j are the site fraction, i.e., the fraction of the species i and j in a particular sublattice, and γ_i the corresponding electrical charge.

Considering the general expression for the Gibbs energy of the ionic two-sublattice model, (Eqs. 38–41; the Gibbs energy of the liquid phase in the system CaO- P_2O_5 , is given by the equation:

$$G_m^{Liquid} = \gamma_{Ca^{2+}} \gamma_{O^{2-}} ^{\circ}G_{Ca^{2+}:O^{2-}}^{Liquid} + \gamma_{Ca^{2+}} \gamma_{PO_3^-} ^{\circ}G_{Ca^{2+}:PO_3^-}^{Liquid} + \gamma_{Ca^{2+}} \gamma_{PO_{7/2}^{2-}} ^{\circ}G_{Ca^{2+}:PO_{7/2}^{2-}}^{Liquid} + \gamma_{Ca^{2+}} \gamma_{PO_4^{3-}} ^{\circ}G_{Ca^{2+}:PO_4^{3-}}^{Liquid} + 2\gamma_{PO_{5/2}^-} ^{\circ}G_{PO_{5/2}^-}^{Liquid} \\ + P \cdot RT \left(\gamma_{O^{2-}} \ln(\gamma_{O^{2-}}) + \gamma_{PO_3^-} \ln(\gamma_{PO_3^-}) + \gamma_{PO_{7/2}^{2-}} \ln(\gamma_{PO_{7/2}^{2-}}) + \gamma_{PO_4^{3-}} \ln(\gamma_{PO_4^{3-}}) + \gamma_{PO_{5/2}^-} \ln(\gamma_{PO_{5/2}^-}) \right) \\ + Q \cdot RT (\gamma_{Ca^{2+}} \ln(\gamma_{Ca^{2+}})) + {}^{xs}G^{Liquid} \quad (59)$$

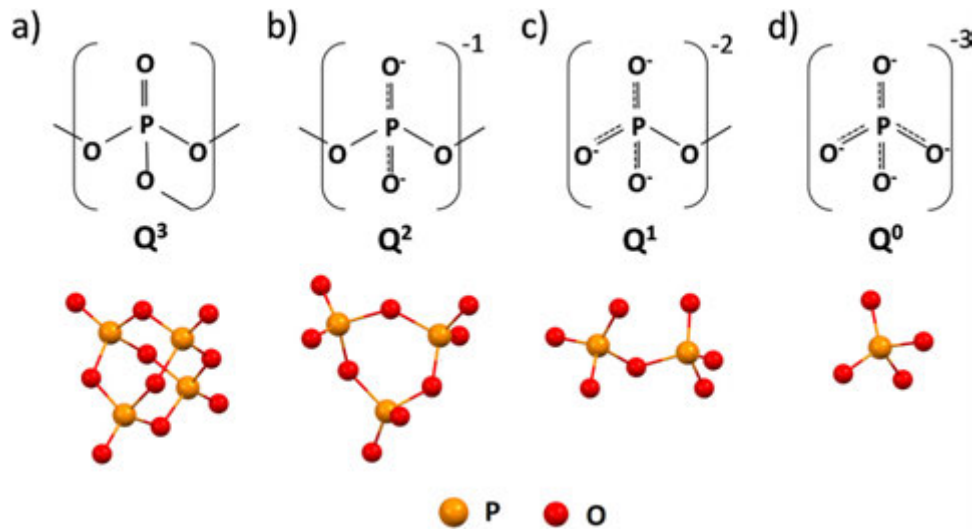


Fig. 5 Schematic representation of PO_4 tetrahedral units in phosphate glass structure, described using the Q^n designation. (a) Q^3 three Bridging oxygens, (b) Q^2 two Bridging oxygens, (c) Q^1 one Bridging oxygen and (d) Q^0 no Bridging oxygens.

where ${}^{\circ}G_{Ca^{2+},O^{2-}}^{Liquid}$ is equal to the standard Gibbs energy of two moles of pure liquid CaO, and ${}^{\circ}G_{PO_5/2}^{Liquid}$ the corresponding value for $\frac{1}{2}$ mol of pure liquid P_2O_5 . On the other hand, ${}^{\circ}G_{Ca^{2+},PO_3^-}^{Liquid}$, ${}^{\circ}G_{Ca^{2+},PO_2^-}^{Liquid}$ and ${}^{\circ}G_{Ca^{2+},PO_4^{3-}}^{Liquid}$ can be related to standard Gibbs energy of pure solid with stoichiometry $Ca(PO_3)_2$, $Ca_2P_2O_7$, and $Ca_3(PO_4)_2$, respectively.

The excess Gibbs energy depends upon the interactions between species within the same sublattice, in this case, the anionic sublattice, which is given by the equation:

$${}^{xs}G^{Liquid} = \sum_{i \neq k} \gamma_i \gamma_k \left[(\gamma_i - \gamma_k)^n \cdot {}^nL_{Ca^{2+};i,k}^{Liquid} \right] \quad (60)$$

where i and k are the species in the anionic sublattice and ${}^nL_{Ca^{2+};i,k}^{Liquid}$ is the interaction parameter between the species i and k in the presence of the ion Ca^{2+} .

Afterwards, the optimization of the introduced parameters was made using the module PARROT (parameters optimization module) in Thermo-Calc Software. As a result of the optimization, one set of model parameters for the Gibbs energies of the compounds CaP_4O_{11} , $Ca_2P_6O_{17}$, and $Ca_4(PO_4)_2O$ and the liquid phase were assessed.

Phase equilibrium diagram of the system CaO - P_2O_5 resulting from the assessment, compared to experimental data is presented in Fig. 6. The calculation predicts that CP2, CP, C2P, and C3P compounds melt congruently while the C2P3 and C4P compounds melt incongruently. C4P evidences a peritectic relationship with CaO, and an eutectic point with α' -C3P.

An acceptable agreement between the thermodynamic calculation and the experimental invariant points can be observed in the P_2O_5 -rich region of the system. The liquidus surface as well as the invariant points in the region between 0.3 up to 0.75 mol fraction of CaO were very well reproduced by these calculations.

Besides, site distributions calculated for the liquid could be compared with the experimental tetrahedral distributions of Q^n in calcium-phosphate glasses. To illustrate this, species distribution in the metastable liquid phase at 300°C and liquid phase at 1500°C were also calculated (Fig. 7). The distribution of species in the melt at different temperatures are in line with the proportions of Q^i tetrahedra observed in the corresponding glasses collected from the literature. At 300°C , the distribution of species calculated matched the ideal relations. However, at higher temperatures, the proportion of species deviated from the ideal behavior and the mixture of species increased in all the compositions. The ability of liquids to accommodate different structural configurations as a function of temperature distinguished them from solids, and the increased disorder with temperature in the distribution of species has been experimentally observed in melts and glasses, so that the proposed model is very realistic.

Thermodynamic Assessment of the ZrO_2 -CaO-MgO Ternary System

Zirconia can be found in three crystalline forms: monoclinic, tetragonal and cubic, depending on temperature and presence of doping elements. This offers the possibility of designing high-performance materials with advanced properties by controlling the phase relations and microstructure of the material. Ceramic materials based on cubic- ZrO_2 present high refractoriness, chemical

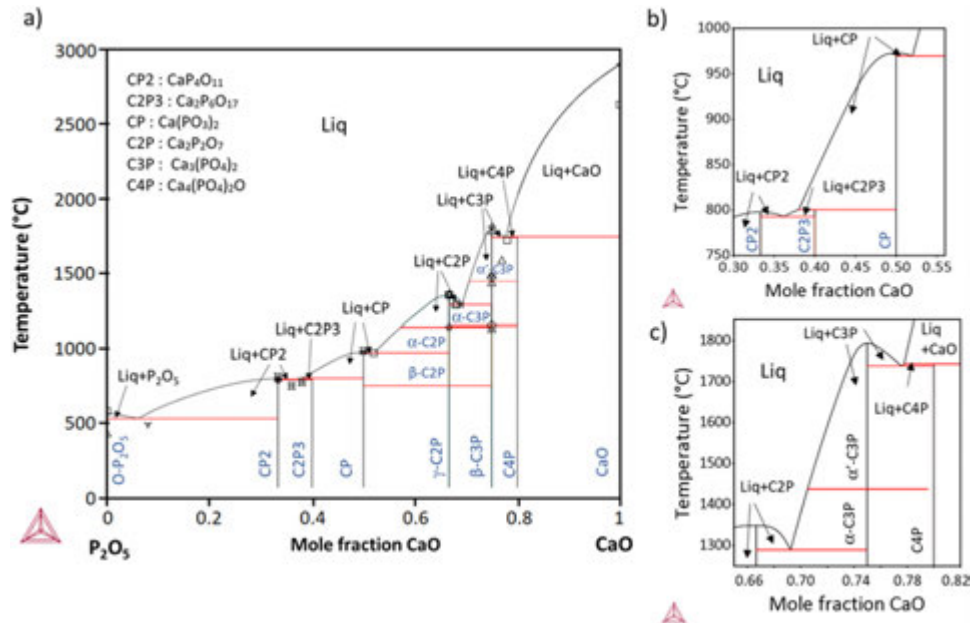


Fig. 6 Calculated phase equilibrium diagram of the P_2O_5 -CaO system, after [Serena et al. \(2011\)](#). (a) Overall view, (b) 0.3–0.55 mol fraction CaO and (c) 0.66–0.82 mol fraction CaO. Experimental data provided by various authors are represented in the figure.

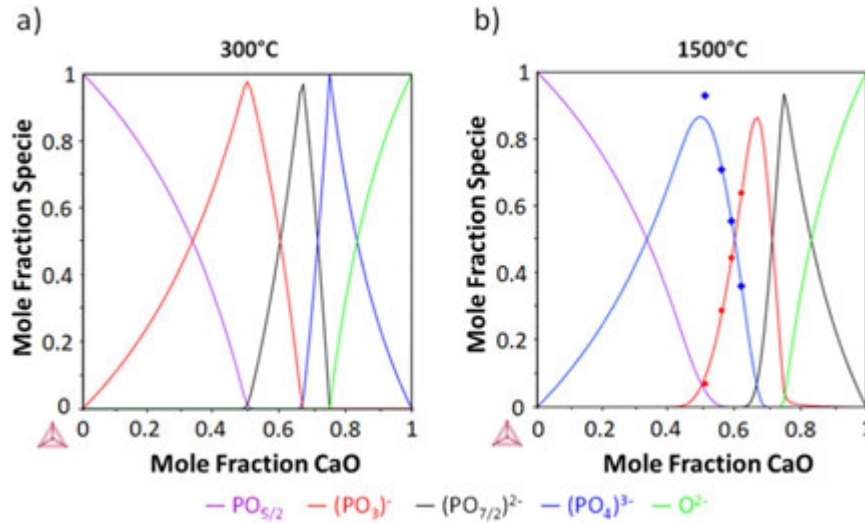


Fig. 7 Calculated species distribution in the liquid phase of the system P_2O_5 -CaO, after *Serena et al. (2011)*. (a) Metastable liquid at 300°C and (b) Stable liquid at 1500°C. Experimental data provided by various authors.

inertness and corrosion resistance at high temperatures and those with tetragonal- ZrO_2 show excellent mechanical properties. Some outstanding applications of these materials are: (1) c - ZrO_2 as oxygen sensors, thermocouple protection tubes, furnace muffles, liners, crucibles, high temperature heating element supports, (2) ceramics based on ZrO_2 -CaO system are used as high-temperature electrolytes in fuel cells, piezoelectric oscillator transducers, heat-resistant linings in furnaces, and protective coatings on alloys, and more recently, (3) MgO-stabilized zirconia as a biomaterial with biomechanical compatibility for zirconia-based osteoimplants.

Because of their high interest, several thermodynamic assessments of ZrO_2 -based systems have been published and some of them have been included in commercial databases. As an example, thermodynamic assessment for the system ZrO_2 -CaO-MgO from its binary sub-systems developed by *Serena et al. (2005)* is summarized below.

In this assessment, the binary systems MgO-CaO, ZrO_2 -CaO and ZrO_2 -MgO were evaluated and then extrapolated to the ternary system using the symmetric model proposed by *Muggianu et al. (1975)*. These calculations were carried out using Thermo-Calc Software.

The stable solid forms of the end-components of the system are: CaO (cubic), MgO (cubic) and ZrO_2 which presents three polymorphic forms depending on temperature: monoclinic (m- ZrO_2) $T < 1170^\circ C$; tetragonal (t- ZrO_2) ($1170^\circ C < T < 2370^\circ C$) and cubic (c- ZrO_2) ($T > 2370^\circ C$).

Beside liquid phase, different solution phases were considered: CaO and MgO adopt solid solution with MgO and CaO respectively and both have fcc cubic structure so that they were modeled as one unique phase named Halite, and t- ZrO_2 and c- ZrO_2 polymorphs with solid solutions of both CaO and MgO (Tss and Css). No ordering effects were reported in the liquid nor in the solid solution phases so that a random substitutional model was selected. Therefore, Gibbs energy of the binary solution phases ϕ were calculated using a subregular solution model (see *Eqs. 19–21*):

$$G_m^{\phi-bin} = \sum_i x_i \cdot {}^0G_i^{\phi} + RT \sum_i x_i \cdot \ln(x_i) + {}^{xs}G_{ij}^{\phi-bin} \quad (61)$$

$${}^{xs}G_{ij}^{\phi-bin} = x_i x_j ({}^0L_{ij} + (x_i - x_j) {}^1L_{ij})$$

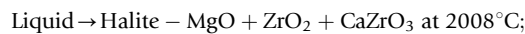
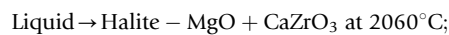
$i, j = MgO, CaO, ZrO_2; \phi = Liquid, Halite, Tss, Css$ (62)

In this assessment, m- ZrO_2 was considered as pure phase and two stable stoichiometric compounds $CaZrO_3$ and $Ca_6Zr_{19}O_{44}$ (named F2 phase) were considered in the binary system ZrO_2 -CaO. ${}^0G_i^{\phi}(T)$ of these phases was expressed according to *Eq. (6)*.

Lattice stabilities for the stable forms were taken from SSUB4 database while data for metastable forms and binary intermediate compounds were those reported by *Yin and Argent (1993)*. Binary interaction parameters ${}^0L_{ij}$ and ${}^1L_{ij}$ were optimized for each binary phase.

Once the agreement with the experimental data of the binary systems was verified, Gibbs energy of ternary solution phases was extrapolated from binaries. A ternary parameter for the Css phase was necessary to properly fit the liquidus and solid solution experimental data.

The liquidus surface, calculated for the ternary system (*Fig. 8*); presents three eutectic invariant points:



and

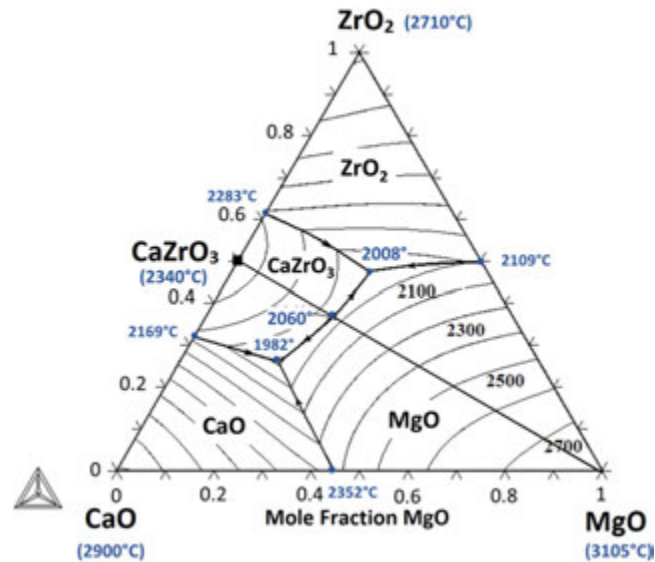


Fig. 8 Calculated liquid surface of the ZrO_2 - MgO - CaO system, modified to include quantitative information about the invariant points of the system. After [Serena et al. \(2005\)](#).

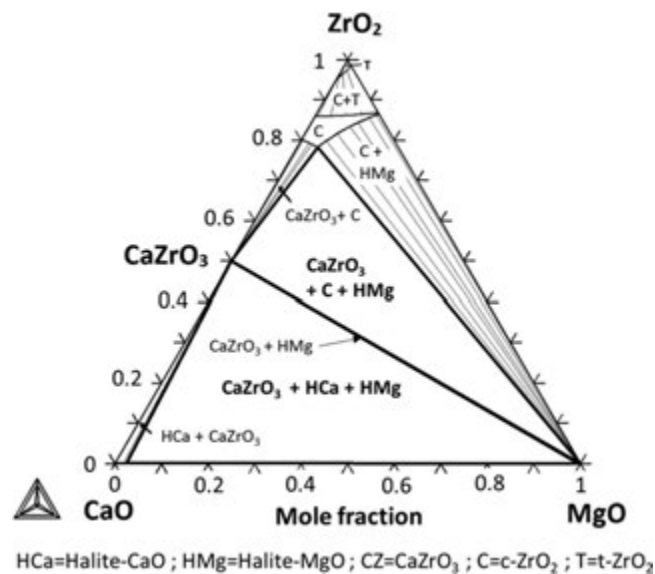


Fig. 9 Calculated isothermal section at 1400°C of the system ZrO_2 - MgO - CaO . After [Serena et al. \(2005\)](#).

Liquid $\rightarrow$ Halite - MgO + Halite - CaO + CaZrO_3 at 1982°C .

Only experimental data for the first eutectic point were reported in the literature by [de Aza et al. \(1974\)](#).

The calculated isothermal section at 1400°C is shown in [Fig. 9](#). Phase compatibility of CaZrO_3 and MgO -rich Halite phase is evidenced. Due to the significant solid solutions of MgO and CaO in the ZrO_2 structures, wide stability fields of C_{ss} and $\text{C}_{ss} + \text{T}_{ss}$ can be observed. Once the thermodynamic assessment is performed, any isothermal section of the system could be calculated which provides a basic tool to design ZrO_2 -based ceramics.

Finally, the calculated isoplethal section $\text{MgO} \cdot \text{CaO} \cdot \text{ZrO}_2$ (dolomite-zirconia) is presented in [Fig. 10](#) which shows phase compatibilities through the line $\text{MgO}/\text{CaO} = 1$ to ZrO_2 . Knowledge of this section is basic to designing ceramic materials from a natural raw material such as Dolomite ($\text{MgCa}(\text{CO}_3)_2$) with a molar ratio of $\text{MgO}/\text{CaO} = 1$. The primary crystallization fields of ZrO_2 , CaZrO_3 , MgO and CaO appear in the section. The three eutectic invariant points of the system as well as eutectoid invariant

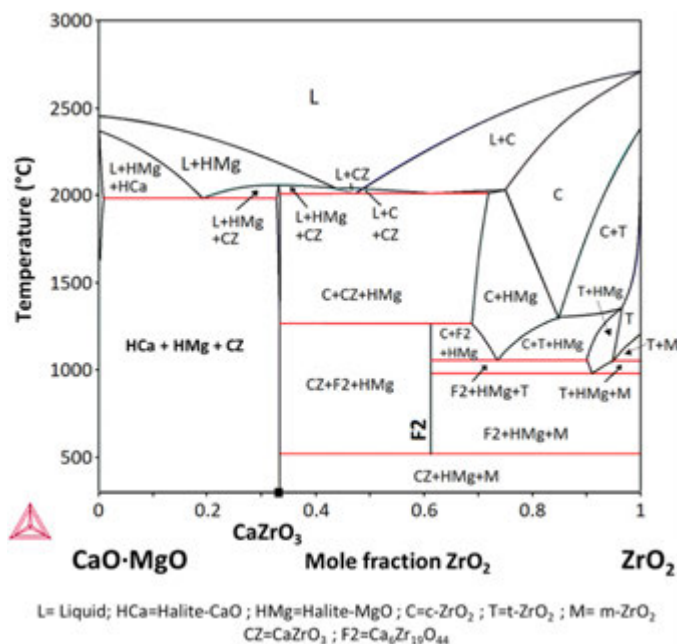


Fig. 10 Calculated isoplethal section $\text{CaO} \cdot \text{MgO}-\text{ZrO}_2$ of the system $\text{ZrO}_2\text{-MgO-CaO}$. After *Serena et al. (2005)*.

point associated with the ZrO_2 polymorphic transformations are projected in/on the isoplethal section. The stability field of the F2 phase is included in the section too.

Phase compatibilities of CaZrO_3 as a function of temperature are very important to design the composition and thermal treatment of MgO-CaZrO_3 based materials for refractories applications while studies in the ZrO_2 -rich region provide evidence for the compatibility, solid solution limits and transformation temperatures of the different polymorphs of ZrO_2 phases which are fundamental to design of zirconia based materials.

References

- Ansara, I., 1979. Comparison of methods for thermodynamic calculation of phase diagrams. *International Metals Reviews* 1, 20–53.
- Bale, C.W., Bélisle, E., Chartrand, P., *et al.*, 2009. FactSage thermochemical software and databases- recent developments. *Calphad* 33, 295–311.
- Barin, I., Knacke, O., 1973. *Thermochemical properties of inorganic substances*. 921S. Berlin: Springer Verlag, p. 303.
- Besmann, T.M., Spear, K.E., 2002. Thermochemical modelling of oxide glasses. *Journal of the American Ceramic Society* 85 (12), 2887–2894.
- Bonnier, E., Caboz, R., 1960. Sur L'estimation de L'enthalpie Libre de Melange de Certains Alliages Metalliques Liquides Ternaires. *Comptes rendus de l'Académie des Sciences* 250, 527.
- Cao, W., Chen, S.L., Zhang, F., *et al.*, 2009. PANDAT software with PanEngine, PanOptimizer and PanPrecipitation for multi-component phase diagram calculation and materials property simulation. *Calphad* 33, 328–342.
- Carter, C.G., Bennett, L.H. (Eds.), 1977. *Proceeding of Workshop on Applications of Phase Diagrams in Metallurgy and Ceramics*. Gaithersburg, Maryland: National Bureau of Standards.
- Chen, S.L., Daniel, S., Zhang, F., *et al.*, 2001. On the calculation of multicomponent stable phase diagrams. *Journal of Phase Equilibria* 22, 373–374.
- Davies, R.H., Dinsdale, A.T., Gisby, *et al.*, 2002. MTDATA – Thermodynamic and Phase Equilibrium Software from the National Physical Laboratory. *Calphad* 26, 229–271.
- de Aza, S., Richmond, C., White, J., 1974. Compatibility relationships of periclase in the system $\text{CaO-MgO-ZrO}_2\text{-SiO}_2$. *Transactions and Journal of the British Ceramic Society* 73, 109–116.
- Decterov, S.A., 2018. Thermodynamic database for multicomponent oxide systems. *Chimica Technologia Acta* 5 (1), 16–48.
- Deiters, U.K., 1985. A modification of newton-raphson algorithm for phase equilibria calculations using numerical differentiation of the Gibbs energy. *Fluid Phase Equilibria* 19, 287–293.
- Dinsdale, A.T., 1991. SGTE data for pure elements. *Calphad* 15 (4), 317–425.
- Du, J., Jindal, V., Sanders, A.P., Ravi Chandran, K.S., 2019. CALPHAD-guided alloy design and processing for improved strength and toughness in titanium boride (TiB) ceramic alloy containing a ductile phase. *Acta Materialia* 171 (1), 18–30.
- Du, Y., Jin, Z.P., Huang, P.Y., 1991a. Thermodynamic assessment of the $\text{ZrO}_2\text{-YO}_{1.5}$ system. *Journal of the American Ceramic Society* 74 (7), 1569–1577.
- Du, Y., Jin, Z.P., 1991b. Optimization and calculation of the $\text{ZrO}_2\text{-MgO}$ system. *CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry* 15 (1), 59–68.
- Du, Y., Jin, Z.P., Huang, P.Y., 1991c. Thermodynamic calculation of the $\text{ZrO}_2\text{-YO}_{1.5}\text{-MgO}$ system. *Journal of the American Ceramic Society* 74 (9), 2107–2112.
- Du, Y., Jin, Z.P., 1992a. Thermodynamic calculation of the $\text{ZrO}_2\text{-YO}_{1.5}\text{-CaO}$ phase diagrams. *CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry* 16 (4), 405–412.
- Du, Y., Jin, Z.P., Huang, P.Y., 1992b. Calculation of the $\text{ZrO}_2\text{-CaO-MgO}$ phase diagram. *CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry* 16 (3), 221–230.
- Dumitrescu, L., Sundman, B., 1995. Thermodynamic Reassessment of the Si-Al-O-N System. *Journal of the European Ceramic Society* 15, 239–247.
- Eriksson, G., 1975. Thermodynamic studies of high-temperature equilibria. 12. SOLGASMIX, A computer-program for calculation of equilibrium compositions in multiphase systems. *Chemica Scripta* 8, 100–103.

- Eriksson, G., Hack, K., 1990. A computer program for the calculation of complex chemical equilibria. *Metallurgical Transactions B* 21, 1013–1023.
- Glushko, V.P., Gurvich, L.V., Weitz, I.V., Medvedev, V.A., *et al.*, 1982. *Thermodynamic Properties of Pure Substances*, I–IV. Moscow: Nauka Publishers, [in Russian].
- Gong, W.P., Chen, T.F., Jin, Z.P., Gongcheng, K., 2001. Thermodynamic calculation of the $\text{ZrO}_2\text{-TiO}_2$ phase diagram and the microwave dielectric property. *Mining and Metallurgical Engineering* 21 (3), 93–95.
- Hallstedt, B., 1990. Assessment of the $\text{CaO-Al}_2\text{O}_3$ System. *Journal of the American Ceramic Society* 73 (1), 15–23.
- Hallstedt, B., 1992. Thermodynamic assessment of the silicon-oxygen system. *Calphad* 16 (1), 53–61.
- Hallstedt, B., 1995. Thermodynamic assessment of the $\text{CaO-MgO-Al}_2\text{O}_3$ system. *Journal of the American Ceramic Society* 78 (1), 193–198.
- Hillert, M., Jonsson, S., 1992. Thermodynamic calculation of the Si-Al-O-N system. *Zeitschrift für Metallkunde* 83 (10), 720–728 <https://www.hsc-chemistry.com/>
- Hillert, M., Sundman, B., Wang, X., 1990. An assessment of the CaO-SiO_2 system. *Metallurgical Transactions B* 21, 303–312.
- Jacobs, M.H.G., Oonk, H.A.J., 2001. The Gibbs energy formulation of the α , β and γ forms of using Grover, Getting and Kennedy's empirical relation between volume and bulk modulus. *Physics and Chemistry of Minerals* 28, 572–585.
- Jacobson, N.S., 2001. Use of tabulated thermochemical data for pure compounds. *Journal of Chemical Education* 78 (6), 814.
- Jansson, B., 1984. *Evaluation of Parameters in Thermochemical Models Using Different Types of Experimental Data Simultaneously*. Stockholm: Report of Royal Institute of Technology, (Trita-Mac-0234).
- Jantzen, T., Yazhenskikh, E., Hack, K., Müller, M., 2019. Thermodynamic assessment of the $\text{CaO-P}_2\text{O}_5\text{-SiO}_2\text{-ZnO}$ system with special emphasis on the addition of ZnO to the $\text{Ca}_2\text{SiO}_4\text{-Ca}_3\text{P}_2\text{O}_8$ phase. *Calphad* 67, 101668.
- Jin, Z.P., Du, Y., 1994. A reassessment of the $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-MgO}$ system. *Ceramics International* 20 (1), 17–25.
- Jung, I.H., Decterov, S.A., Pelton, A.D., 2004. Critical Thermodynamic Evaluation and Optimization of the $\text{MgO-Al}_2\text{O}_3$, $\text{CaO-MgO-Al}_2\text{O}_3$, and $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ Systems. *Journal of Phase Equilibria and Diffusion* 25 (4), 329–345.
- Kaufman, L., 1979a. Coupled phase diagrams and thermochemical data for transition metal binary systems-VI. *Calphad* 3 (1), 45–76.
- Kaufman, L., 1979b. Calculation of quasibinary and quasiternary oxide systems II. *Calphad* 3 (1), 27–44.
- Kaufman, L., 1979c. Calculation of quasibinary and quasiternary oxynitride systems III. *Calphad* 3 (4), 275–291.
- Kaufman, L., Bernstein, H., 1970. *Computer calculation of phase diagrams with special reference to refractory metals*. New York: Academic Press.
- Kaufman, L., Nesor, H., 1974. Calculation of superalloy phase diagrams: Part I. *Metallurgical Transaction* 5, 1617–1621.
- Kaufman, L., Nesor, H., 1978. Calculation of quasibinary and quasiternary oxide systems I. *Calphad* 2 (1), 35–53.
- Kaufman, L., 1977. In: *Proceedings of the Fourth Calphad Meeting, Workshop on Computer Based Coupling of Thermochemical and Phase Diagram Data*. Gaithersburg, Maryland: National Bureau of Standard 1(1), 7–89.
- Knapp, W.J., 1953. Use of free energy data in the construction of phase diagrams. *Journal of the American Ceramic Society* 36 (2), 43–47.
- Kohler, F., 1960. Estimation of the thermodynamic data for a ternary system from the corresponding binary systems. *Monatshefte für Chemie* 91 (4), 738–740.
- Liu, Z.K., 2009. First-principles calculations and CALPHAD modeling of thermodynamics. *Journal of Phase Equilibria and Diffusion* 30 (5), 517–534.
- Lu, X.G., Selleby, M., Sundman, B., 2005. Implementation of a new model for pressure dependence of condensed phases in Thermo-Calc. *Calphad* 29, 49–55.
- Lukas, H.L., Henig, E.T., Zimmermann, B., 1977. Optimization of phase diagrams by a least squares method using simultaneously different types of data. *Calphad* 1 (3), 225–236.
- Lukas, H.L., Friess, S.G., Sundman, B., 2007. *Computational Thermodynamics: The Calphad Method*. The Edinburgh Building, Cambridge CB2 8RU, UK: Cambridge University Press, (ISBN 978-0-521-86811-2 hardback).
- Ma, Y., Liu, X., 2019. Kinetics and thermodynamics of Mg-Al disorder in MgAl_2O_4 -spinel: A review. *Molecules* 24 (9), 1704.
- Mao, H., Hillert, M., Selleby, M., Sundman, B., 2006. Thermodynamic assessment of the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system. *Journal of the American Ceramic Society* 89 (1), 298–308.
- Muggianu, Y.M., Gambino, M., Bross, J.P., 1975. Enthalpies of formation of liquid alloys bismuth-gallium-tin at 723 deg.K. choice of an analytical representation of integral and partial excess functions of mixing. *Journal de Chimie Physique* 72 (1), 83–88.
- Murnaghan, F.D., 1944. The compressibility of media under extreme pressures. *Proceedings of the National Academy of Sciences United States of America* 30 (9), 244–247.
- Osipov, A.A., Osipova, L.M., 2013. New approach to the modelling of a local structure of silicate glasses and melts. *Journal of Physics: Conference Series* 410 (1), 012019. Budapest, Hungary.
- Pan, Z., Fabrichnaya, O., Seifert, H.J., *et al.*, 2010. Thermodynamic evaluation of the Si-C-Al-Y-O system for LPS-SiC application. *Journal of Phase Equilibria and Diffusion* 31 (3), 238–249.
- Pavlyuchkov, D., Fabrichnaya, O., Herrmann, M., Seifert, H.J., 2012. Thermodynamic Assessments of the $\text{Al}_2\text{O}_3\text{-Al}_4\text{C}_3\text{-AlN}$ and $\text{Al}_4\text{C}_3\text{-AlN-SiC}$ Systems. *Journal of Phase Equilibria and Diffusion* 33 (5), 357–368.
- Pelton, A.D., Wu, P., 1999. Thermodynamic modelling in glass-forming melts. *Journal of Non-Crystalline Solids* 253, 178–191.
- Pelton, A.D., Kang, Y.B., 2007. Modeling short-range ordering in solutions. *International Journal of Materials Research* 98, 910–917.
- Pena, P., De Aza, S., 1979. Cálculo termodinámico de los Diagramas de Fases. *Boletín de la Sociedad Española de Cerámica y Vidrio* 19 (5), 333–339.
- Phillips, B., Somya, S., Muan, A., 1961. Melting relations of magnesium oxide iron oxide mixtures in air. *Journal of the American Ceramic Society* 44, 167–169.
- Rao, Y.K., 1970. Thermodynamics of phase diagrams. In: Alper, A.M. (Ed.), *Phase Diagrams: Materials Science and Technology*. New York: Academic Press, pp. 1–43.
- Redlich, O., Kister, A., 1948. Algebraic representation of thermodynamic properties and the classification of solutions. *Industrial and Engineering Chemistry* 40, 345–348.
- Saunders, N., Miodownik, A.P., 1998. *CALPHAD (Calculation of Phase Diagrams): A Comprehensive Guide*. Pergamon Materials Series. Pergamon: British Library Cataloguing Publication Data.
- Seifert, H.J., Peng, J., Lukas, H.L., Aldinger, F., 2001. Phase equilibria and thermal analysis of Si-C-N ceramics. *Journal of Alloys and Compounds* 320 (2), 251–261.
- Serena, S., Sainz, M.A., de Aza, S., Caballero, A., 2005. Thermodynamic assessment of the system $\text{ZrO}_2\text{-CaO-MgO}$ using new experimental results: calculation of the isoplethal section MgO-CaO-ZrO_2 . *Journal of the European Ceramic Society* 25 (5), 681–693.
- Serena, S., Carbajal, L., Sainz, M.A., Caballero, A., 2011. Thermodynamic assessment of the system $\text{CaO-P}_2\text{O}_5$: Application of the ionic two-sublattice model to glass-forming melts. *Journal of the American Ceramic Society* 94 (9), 3094–3103.
- Shobu, K., 2009. CaTCalc: New thermodynamic equilibrium calculation software. *Calphad* 33, 279–287.
- Stocha, P., Stocha, A., Ciecinska, M., *et al.*, 2016. Structure of phosphate and iron-phosphate glasses by DFT calculations and FTIR/Raman spectroscopy. *Journal of Non-Crystalline Solids* 450, 48–60.
- Sundman, B., 1991. Modification of the two-sublattice model for liquids. *Calphad* 15 (2), 109–119.
- Sundman, B., Ågren, J., 1981. A regular solution model for phases with several components and sublattices, suitable for computer applications. *Journal of Physics and Chemistry of Solids* 42, 297–301.
- Sundman, B., Jansson, B., Andersson, J.O., 1985. The Thermo-Calc databank system. *Calphad* 9, 153–190.
- Sundman, B., Kattner, U.R., Palumbo, M., Fries, S.G., 2015. OpenCalphad – A free thermodynamic software. *Integrating Materials and Manufacturing Innovation* 4, 1–15.
- Toop, G.W., 1965. Predicting ternary activities using binary data. *Transactions of the American Institute of Mining* 233 (5), 850–855.
- Utlak, S.A., Besmann, T.M., 2019. Thermodynamic assessment of the $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$ pseudo-binary and ternary systems. *Journal of Chemical Thermodynamics* 130, 251–268.
- Wang, C., Zinkevich, M., Aldinger, F., 2006. The zirconia – hafnia system: DTA measurements and thermodynamic calculations. *Journal of the American Ceramic Society* 89 (12), 3751–3758.

- Wang, H., Zhang, X., Lai, C., Kuang, W., Liu, F., 2015. Thermodynamic principles for phase-field modeling of alloy solidification. *Current Opinion in Chemical Engineering* 7, 6–15.
- Weiss, J., Gauckler, L.J., Lukas, H.L., Petzow, G., Tien, T.Y., 1981. Determination of phase equilibria in the system Si-Al-Zr/N-O by experiment and thermodynamic calculation. *Journal of Materials Science* 16 (11), 2997–3005.
- Xiaogang, L., Zhanpeng, J., 2000. Thermodynamic assessment of the BaO-TiO₂ quasibinary system. *Calphad* 24 (3), 319–338.
- Yang, Q., Kirshtein, A., Ji, Y., *et al.*, 2019. A thermodynamically consistent phase-field model for viscous sintering. *Journal of the American Ceramic Society* 102, 674–685.
- Yin, Y., Argent, B.B., 1993. The phase diagrams and thermodynamics of the ZrO₂-CaO-MgO and MgO-CaO systems. *Journal of Phase Equilibria* 14 (5), 588–600.
- Zhang, F., Zhang, C.L., Chen, S.-L., Cao, W.-S., Zhu, J., 2014. A combined thermodynamic/kinetic modeling approach to predict SiC recession due to SiO₂ scale volatility under combustion environments. *Journal of Phase Equilibria and Diffusion* 35 (6), 724–734.

Relevant Websites

- <https://calphad.org/>
CALPHAD.
Computer Coupling of Phase Diagrams and Thermochemistry.
- <http://www.openalphad.com/>
Open Calphad.

Characterization of Ceramic Powders

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Introduction

Historically, methods that represent particle-level (static) characterizations have been deemed necessary to qualify component raw materials and batch in the processing of various oxides, carbides, nitrides and other materials used in ceramic and glass batching (Reed, 1995; Schubert and Petzow, 1990; Balasubramanian *et al.*, 2012). While these represent well-established protocols, these measures are necessary but often insufficient to adequately describe specific particle-level attributes that influence the bulk processing of a given component or batch (Tomas, 2001a).

Inattention to flow regimes (e.g., transformative attributes such as frictional slow flow (quasi-static) elastic-inertial (intermediate), and inertial-collisions (fluidization) as well as compressibility, permeability, internal angles of friction, etc.) favors a predisposition towards classic static characterization techniques obscuring valuable information necessary to understanding de-mixing of complex inorganic granular and powder bed systems (Mort *et al.*, 2015; Tomas, 2001b). Conventional approaches in materials processing establish three commonplace topics: as formed structure, properties and performance. It is our intent to show that an understated and insufficiently addressed portion of processing of materials is the quasi-static, intermediate and fluidized flow regimes during bulk processing of batch (multicomponent) systems.

Current Static Measures

Materials science and technology is based on control of the triaxial space of structure, properties and processing. To achieve the desired properties and structure of a final product, various comminuted raw materials are blended with the interest of meeting a target chemical composition to be processed to meet the final product's specifications.

To assess the suitability of comminuted materials to meet the target attributes of organic and inorganic processing, classic static raw material characterization protocols have required one or more of the following seven types of measurement:

- (1) Chemical composition.
- (2) Mineral and crystallite makeup.
- (3) Particle shape and size distribution.
- (4) Pore shape and size distribution.
- (5) Specific surface area.
- (6) Bulk and/or skeletal density.
- (7) Microscopy and imaging methods.

Common chemical analysis techniques available for static measure of powders are typically spectroscopic methods. These include inductively coupled plasma (ICP) flame emission/mass spectrometry, X-ray fluorescence (either via standalone methods or in tandem with electron microscopy such as electron dispersive spectroscopy or EDS and wavelength dispersive spectroscopy or WDS). Additional spectroscopic methods available include dissolution and digestion of powder species for spectrophotometry or ion chromatography for chemical speciation. Additional solution methods include Fourier transformed infrared spectroscopy (FTIR). The aforementioned techniques should be noted as being bulk characterization methods for powder elemental analysis. When expanded to predominantly surface characterization techniques, additional methods such as Raman spectroscopy, secondary ion mass spectrometry (SIMS), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and Rutherford backscattering spectroscopy (RBS) should also be noted for surface chemistry measurement (King, 2002).

Mineral and crystallite makeup for powders is most commonly characterized via X-ray diffraction and associated quantitative analysis techniques such as Rietveld refinement. Alternate mineralogical analysis is performed via birefringence of polarized light in optical microscopy (King, 2002; Bloss, 1961).

Historically particle sizing has been conducted through the use of sieves of varying apertures to construct a distribution of the mass of material retained on a screen of known mesh aperture size. Due to these origins in screening, particle size conventions originated with the so-called cumulative percent coarser than distribution or CPCT (which, when reversed, creates the so-called cumulative percent finer than distribution or CPFT). The use of sieves is commonplace in modern sizing based on low equipment cost, sampling considerations, measurement size range and resolution of the desired distribution. It should be noted that sieves are not commonly used for characterizing particles below 45 μm or 325 mesh. Based on tendencies to emphasize utility of histograms for representation of data, the differential between sieve retention populations can be used to generate the so-called incremental of differential size distributions. When evaluated over infinitesimal differentials in particle diameter, the convenience of incremental distributions is the ability to fit to mathematical functions for describing particle size distribution (Allen, 2003).

Alternate classical sizing principles such as gravitational (or centrifugal) sedimentation have been incorporated into techniques such as X-ray sedigraphs, which measure the attenuation of a turbid suspension over time to quantify particle size distribution. In

the modern era, the Coulter principle is used to characterize particle size through obscuration of an electrical sensing zone. Particle counting is typically performed via obscuration of photodiode detectors or via microscopy methods. Among the most prevalent methods used today are static and dynamic light scattering, which utilize Mie scatter/Fraunhofer diffraction and photon correlation spectroscopy respectively to quantify particle size distribution. All of the aforementioned techniques can be represented via cumulative and/or incremental distributions (Allen, 2003).

Alternate techniques utilized today include the Sauter mean diameter, which manipulates the particle skeletal density and the powder specific surface area to calculate the equivalent spherical diameter. Through manipulation of pycnometric and surface area data, this method is typically used to characterize primary particles in highly agglomerated systems where techniques such as static light scattering may misleadingly characterize the agglomerate size as the particle size. Alternate methods used primarily for characterization of agglomerated nanosized particles can include differential mobility analysis, which uses the electrical mobility of particles to determine their size (Eggersdorfer *et al.*, 2012).

One additional technique to consider is the so-called undertone method whereby colorimetry is used as a proxy for particle size measurement. In titanium dioxide for example, the addition of carbon black changes the proportions of red and blue light absorbed by the powder and thereby causes varying colors based on particle size, where coarser particles upon addition of carbon black would scatter more red light wavelengths and finer particles would scatter more blue light wavelengths (Völz *et al.*, 2000).

Pore shape and size distribution of powders can be achieved through various techniques. Mercury porosimetry utilizes the controlled wetting and intrusion of mercury into particles to measure the volumetric size distribution of voids. Physisorption methods such as *t*-plots or capillary condensation utilize the controlled adsorption of nitrogen, argon, or carbon dioxide to measure the pore size distribution. Additional methods that have been employed or explored include cryo- and/or T2 shift NMR and thermoporometry via measurement of melting/freezing point shifts in differential scanning calorimetry. Alternate techniques for porosity measurement include X-ray tomography and image analysis (Allen, 1997; Diamond, 1971; Sing *et al.*, 1985; Alnaimi *et al.*, 1994; Wulff, 2004).

Powder specific surface area is often measured via gas physisorption methods whereby a quantity of powder material is cooled to cryogenic temperatures and the volume of gas adsorbing onto the powder surface below saturation vapor pressures is measured. Additional techniques that have been historically employed to measure specific surface area include the addition of dyes such as methylene blue and measuring the quantity of dye required to fully coat the powder surface. This has been particularly of use in the clay industry (Allen, 1997; Brunauer *et al.*, 1938; Sing *et al.*, 1985; Kipling and Wilson, 1960).

Classical methods for bulk or skeletal density measurement are pycnometric in nature (i.e., requiring the measurement of the powder volume in a vessel previously characterized for its empty volume, thereby rendering the difference in fill volume after addition of the powder species as a measure of bulk and/or skeletal density). The filling medium to facilitate this difference measurement varied depending on the target analyte (powder bulk density or skeletal density) (Allen, 2003).

Skeletal or “true” density of a powder has been measured by a Gay-Lussac pycnometer where a liquid of well-characterized density was added to a pre-measured mass of powder in a vessel of calibrated volume. The evolution of the Gay-Lussac pycnometer is modern-day helium pycnometry whereupon helium gas is used in place of an infiltrant and the dosing and measurement procedure is typically automated and computerized. Similarly, mercury porosimetry can be manipulated to perform pycnometric measurements according to the same principle of measuring the differential between an empty and vessel volume and the intruded volume of a powder species. An alternate non-pycnometric method for measurement of skeletal density would be the aforementioned Rietveld refinement via X-ray diffraction to determine atom positioning and calculation of the “true” density based on the identified unit cell (Allen, 2003).

Bulk density measurements are similarly performed using pycnometric principles. The most prevalent technique is gravitational pycnometry or “tap density” whereupon a quantity of powder is filled to a measured height in a graduated cylinder and the cylinder is tapped by a controlled number of repetitions. The number of taps and the graduated cylinder volume is established for various materials and varies according to written ASTM methods (Allen, 2003; Völz *et al.*, 2000).

For measurement of interparticle void volume and the envelope volume of particles with high pore volume and/or highly fractal surface texture, horizontal pycnometry uses the infiltration of incompressible solid media to occupy the interstitial volume of a powder bed in a pre-calibrated chamber volume. Upon knowing the volume of media added in comparison with the vessel free available volume, the envelope volume and/or density of the particles can be measured (Allen, 2003).

The use of microscopy and imaging for characterizing particles can be to infer qualitative characteristics of powders and particles or to directly measure particle attributes such as size distribution and/or shape. Historical characterization via imaging techniques, whether by optical or electron microscopy have been restricted to capturing two-dimensional characteristics of particles, with three-dimensional information obtained via techniques such as stereoscopic imaging. Recent advances have expanded visualization to the use of three dimensional methods such as scanning laser confocal microscopy or tomographic methods via focused ion beam, X-ray or electrical capacitance. For quantitative metrics, imaging is often utilized to calibrate measurement data from alternate techniques where the assumptions of equiaxed shape are believed to skew measurement data and interpretation based on the limitations of physical principles involved in measurement. A common example cited is the measurement of highly anisotropic particles where light scattering data interpretation becomes ambiguous with respect to the axis of orientation. Methods to circumvent this limitation via imaging involve the use of common size measurements based on an arbitrary axis of rotation. Examples of these include the Feret diameter and the Equivalent Spherical Diameter (or equivalent circular diameter) which measures the three-dimensional volume (or two-dimensional area, depending on the method of imaging) and then identifies the diameter of a sphere required to have an equivalent volume (or circle required to have an equivalent two-dimensional area). These various metrics and others utilizing similar computational and numerical principles are accessed through common third-party image analysis software packages when not directly acquired through instrument analysis packages. Examples of commercially available third party packages for image analysis

can include Adobe Photoshop®, ImageJ, MatLab® and Python-based platforms via SciPy image processing kits such as Anaconda® (Maire *et al.*, 2011; Zhu *et al.*, 2003; Tang *et al.*, 2008; Cierpka and Kähler, 2012).

It should be noted that for characterization of size distribution via imaging, the pathway to quantification includes identifying individual particles and is therefore reflective of a number-based size distribution. By contrast, sieving, light scattering and sedigraph methods are reflective of particle volumetric distributions and/or mass. The distinction is crucial and necessary due to common practices of correlating imaging data to alternate techniques of sizing including the aforementioned light scattering and sieve data (Pieri *et al.*, 2006).

Quantification of shape is most commonly thought of as measurement of particle aspect ratio, defined typically as the major (or longer) axis of the particle divided by the minor (or shorter) axis; the reciprocal of this value are also used to confine the values between 0 and 1. Alternate shape characterization metrics include particle perimeter, area, orientation, rectangularity, roundness and texture. As with size measurement, these various shape metrics can be accessed by image analysis techniques. Common instrumentation operating on principles of micro-fluid imaging passes suspensions of particles through a measurement flow cell where the imaging and quantification of these particle properties is done on-line in real-time via optical techniques (Mikli *et al.*, 2001; Cierpka and Kähler, 2012).

Granular and Powder Batch flowability

Granular (size distribution $>100\ \mu\text{m}$) and powder (size distribution $<100\ \mu\text{m}$) bed flowability are not described via classical descriptors as for fluids & gases due to inadequate understanding of the bulk state of granular and powder materials from the particle level (Zhua *et al.*, 2007; Bell, 2005). Restricting granular and powder bed characterization to the seven aforementioned techniques ignores complexities and interactive effects of multi-component batches in transport.

First principle models exist for effects such as particle-level (static) flowability and friction, adsorption kinetics, hygroscopicity, etc. (Zhua *et al.*, 2007; Kamrin, 2008). Academic and industrial scientists are not ignorant of the quasi-static, intermediate and fluidized regimes impact on transformative transport properties. However, these are essentially handled in “brute force” techniques such as spray drying to wholly transform powder flow properties where economically viable. Quantification of flowability of the bulk solid mass has historically been limited to the widely-criticized angle of repose measurement, which itself is not one of the aforementioned “stock” protocols. Literature on spray drying in the bulk processing of inorganics has been more strongly focused on optimizing the parameters to facilitate this “brute force” technique than to correlate its improvements to spray drying process parameters (Lukasiewicz, 1989).

This is not to suggest that spray drying is exclusively motivated by concerns of powder flow (and in the absence of knowledge and/or tests a “brute force” mass spray drying is employed); many other advantages and motives exist for spray drying beyond achieving high flowability but this is an example of the awareness of concerns regarding flow without a rigorous method to measure it.

The lack of full understanding of bulk powder flow from the particle level as a continuum, forces empirical modeling of bulk systems with the inability to sufficiently define continuum and successfully bridge powder to particle-level mechanics and modeling (Tomas, 2004).

The following are examples of complementary tests at the granular and powder scale obtained through the authors’ experimentation measuring bulk behavior (albeit empirically). It is the authors contention that these complementary tests provide more insight into the processing of complex single or multicomponent (batch) systems than spurious correlations drawn from the exclusive use of static measures.

(1) Example of powder flow consideration in an industrial holding bin

An example is shown in Fig. 1 of a multi-component powder batch system, its constituent particle size distributions, their mathematical reconstitution per nominal formulation and a measurement of particle size of the actual mixed batch.

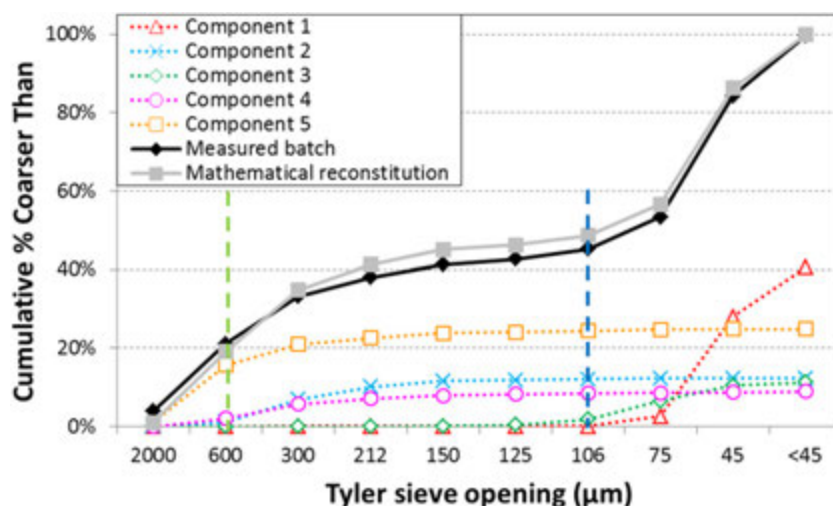


Fig. 1 Composite particle size distribution including batch subcomponents and mathematical reconstitution per batch formula.

Fig. 1 and **Table 1** show how the individual components of a batch can be mathematically proportioned to create a composite master batch to meet a target stoichiometry in the bulk. However, merely addressing the stoichiometry from a bulk perspective denies potential consequences of inhomogeneous transport (quasi-static flow, i.e., slow frictional flow) during a process event such as discharging a mixed batch from a silo. As shown in **Fig. 2**, an experiment was conducted where a holding bin (comprised of an axi-symmetrical cylinder and a conical outlet section) was dispensed from 85% fill in the cylindrical section to a level above entry into the cone (represented by “X”, with the level prior to entry into the cone re-scaled to 100%) was utilized to facilitate mass flow of the batch; a second experiment was conducted where the refilling and dispensing of the bin to a height below this level was intended to facilitate funnel flow, as shown on the right hand side of **Fig. 2**.

Attempting to dispense the holding bin in a mass flow regime results in a relatively unchanged particle size distribution as measured by the weight percent retained on screens for fine material ($< 106 \mu\text{m}$) and coarse material ($> 600 \mu\text{m}$). However, note that when bin refill practices allow dispensing material to levels below the fill height of the cone (i.e., less than 100% of the fill level of the cone), transient effects of particle size distribution variation due to bin fill are evident, as measured by the increased variation of the aforementioned sieve weight percent retained on a coarse screen and the fine fraction collected in the pan. These values of coarse and fine are represented in **Table 1** by the weight percent retained on the $600 \mu\text{m}$ opening (30 mesh) and the cumulative fraction finer than $106 \mu\text{m}$ (represented by the cumulative sum of the “Pan”, 325 mesh and 200 mesh retentions shown in **Table 1**).

The aforementioned data shows how in the bulk we can meet target properties of particle size distribution of a batch and meet target composition of reconstituted batch with measurements in a very bulk scale. However, the time series data for sieve analysis above shows how inattention to transport effects, such as dispensing a holding bin into conditions that foster funnel flow leads to segregation by particle size, thereby causing localized variation of particle size distribution. By definition, segregation in a single component system is by particle size only; for multicomponent systems where discrete batch component particle sizes are present and where local uniformity of components is necessary, inattention to transport properties creates unwanted variation in mix- edness (by phase) at whatever the critical length scale of the process is. As seen in **Fig. 1**, while particle size distribution is not a

Table 1 Composite particle size distribution including batch subcomponents (C1-C5) and mathematical reconstitution per batch formula by weight percent

Sieve opening (μm)	Tyler mesh	C1 (%)	C2 (%)	C3 (%)	C4 (%)	C5 (%)	Mathematical reconstitution (%)	Measured batch (%)
2000	10	0.00	0.01	0.00	0.00	1.03	1.04	3.93
600	30	0.00	1.15	0.00	2.10	15.7	19.1	21.1
300	50	0.03	6.87	0.00	5.78	21.0	34.8	33.2
212	70	0.05	10.1	0.01	7.13	22.6	41.3	38.0
150	100	0.06	11.6	0.09	7.99	23.8	45.1	41.3
125	120	0.08	11.9	0.40	8.25	24.1	46.3	42.7
106	140	0.12	12.1	1.85	8.46	24.5	48.6	45.3
75	200	2.63	12.3	6.57	8.63	24.8	56.6	53.4
45	325	28.0	12.4	10.5	8.78	25.0	86.3	84.3
< 45	Pan	40.6	12.4	11.3	8.97	25.0	99.9	99.7

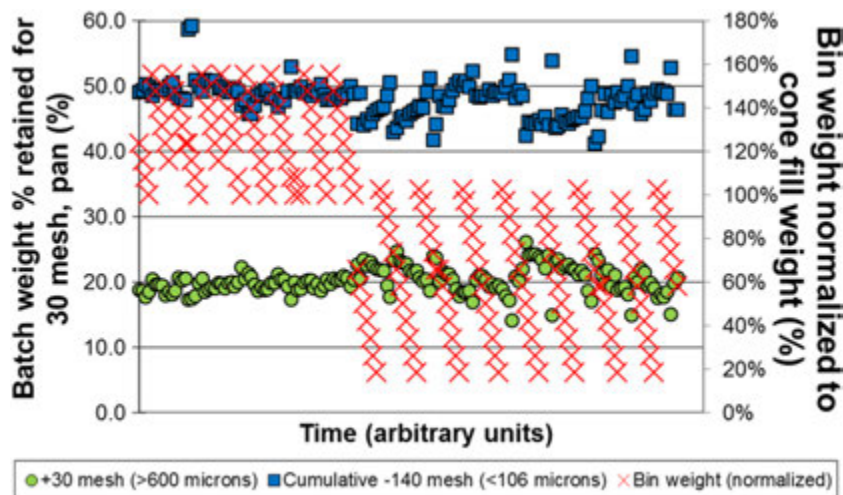


Fig. 2 Batch weight percent for fine and coarse components relative to discharge refill level; 100% bin weight normalized refers to a fill level above entry into the cone.

material property in the classic sense, strong variations of particle size distribution within a batch such as the one shown make it effectively a pseudo-material property confined to this system. Temporal variation in particle size can therefore be seen as a potential temporal variation in material chemical composition due the invariant transport properties.

(1) Batch flowability and aeration at a research-scale

The particle size distributions shown in Fig. 3 were obtained via a common static light scattering method of particle size measurement and show little or no differentiation between a set of four powder batches.

Fig. 4 shows laboratory research-scale ribbon extrusions of these powder batches.

Clearly, particle size distribution alone is insufficient to describe the suitability of the powder batch to form a cohesive contiguous ribbon, as shown by the inferior quality of the extrudate shown in the pictures of 3 and especially 4. Additional characterization of the powder batches was performed by a Freeman Technologies' FT4 powder spindle rheometer (intermediate flow: inertial-elastic) coupled with vessel aeration to monitor the energy of fluidization (fluidized flow: inertial-collisions). Fig. 5(a) and (b) is a plot of the aeration specific flow energy as a function of the aeration flow rate. Fig. 5(a) shows the full range of the data collected while Fig. 5(b) isolates the regime from 0 to 20 mm s⁻¹.

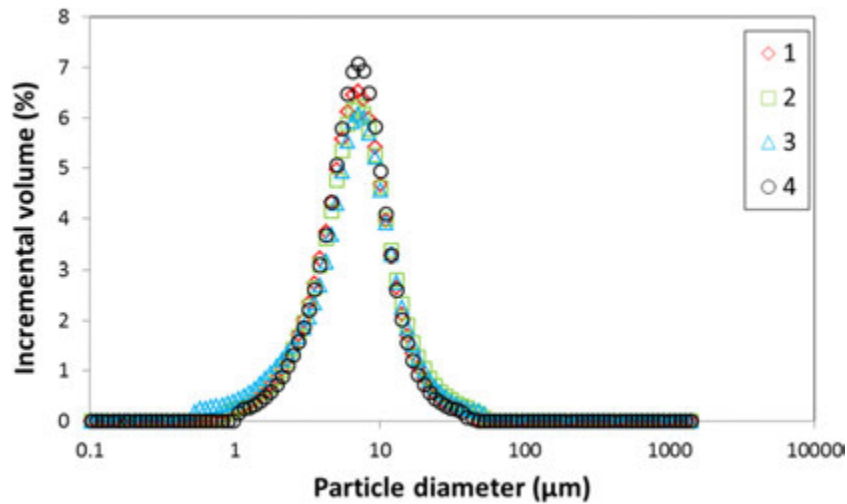


Fig. 3 Particle size distributions for four powder batches.

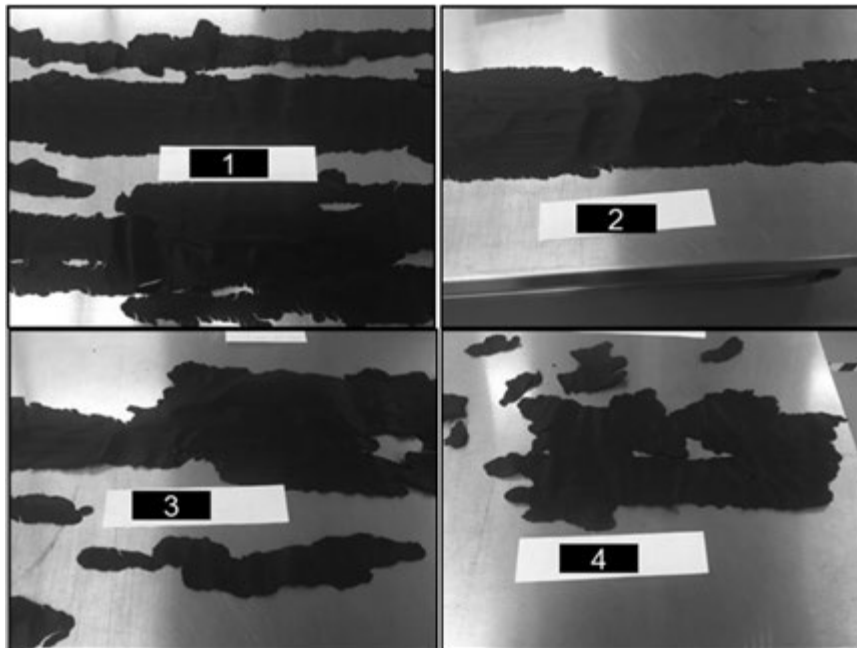


Fig. 4 Ribbon extrusions of the four batches (labeled “1”, “2”, “3” & “4”), whose particle size distributions were shown previously in Fig. 3.

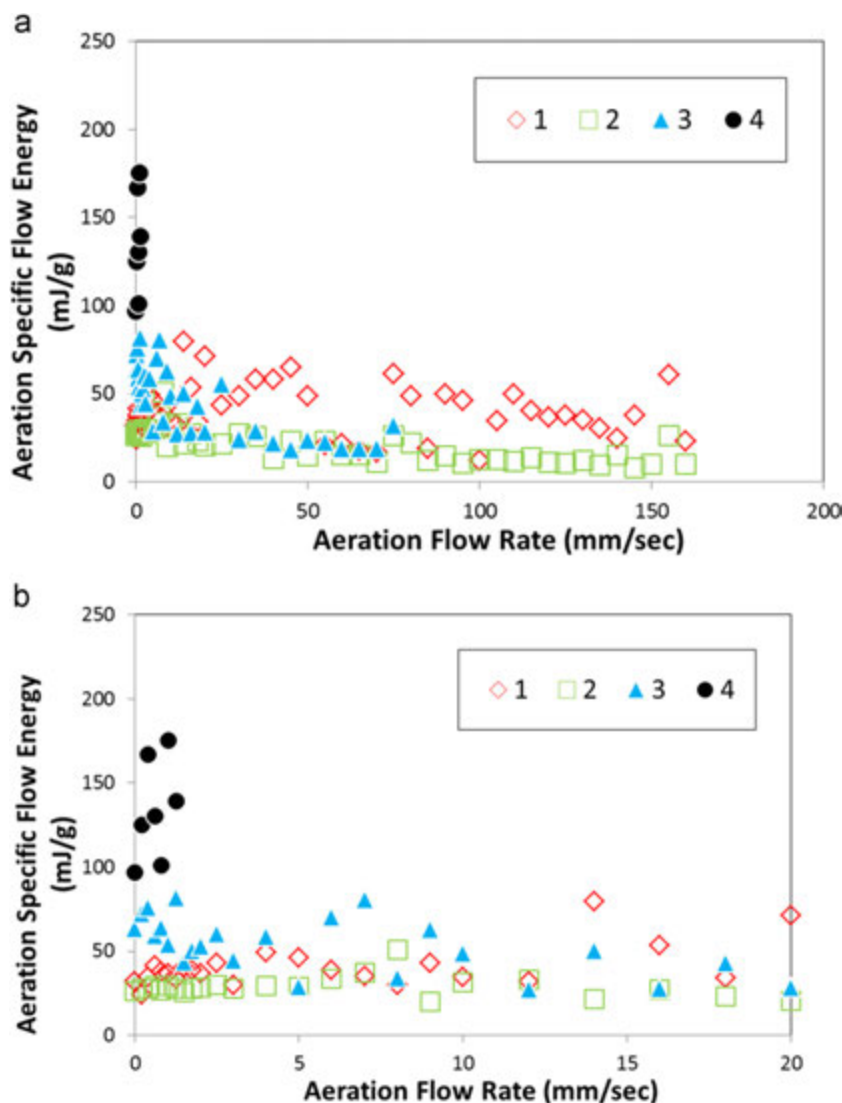


Fig. 5 (a) Aeration specific flow energy as a function of the aeration flow rate as measured via a Freeman Technologies FT4 powder spindle rheometer. (b) Aeration specific flow energy as a function of the aeration flow rate as measured via a Freeman Technologies FT4 powder spindle rheometer.

Sample 1 shows a continuous steady-state specific energy over the available range of aeration flow rates. Sample 2 similarly shows this continuous profile at a lower steady state specific flow energy, which correlates with the superior quality of extrudate compared with Sample 1, as seen in the pictures above. Sample 3 showed a truncated specific energy steady state due to overloading encountered at 75 mm s^{-1} due to the presence of stubborn agglomerates. Sample 4 exhibited stronger agglomerates and a greater steady-state specific flow energy than Sample 3, causing its specific flow energy measurements to be truncated at a lower aeration flow rate.

Sample 4 was a highly fibrillated “ball”. The greater ease of dispersion and lower effective energy for a given aeration flow rate correlates with the better quality of the extrudate produced (hence the better quality of the ribbon produced in “2”).

(2) Dynamic vapor sorption of phosphate materials and impact of humidity on flowability

Two phosphate raw materials’ (with different cations) particle size distributions are shown in [Fig. 6](#):

Both of the presented phosphate materials show similar particle size distribution ranges falling within the broad classification of granulates. Their susceptibility to moisture sorption can be compared via dynamic vapor sorption (DVS) measurements, as in [Fig. 7\(a\)](#) and [\(b\)](#) while [Fig. 7\(c\)](#) is a plot of relative mass changes at 70% and 90% relative humidity compared with the 0% humidity starting mass. [Fig. 7\(a\)](#) indicates that the relative mass change at 90% relative humidity for phosphate material 1 of 0.3%. By contrast, [Fig. 7\(b\)](#) shows that phosphate material 2 exhibits a relative mass change of 84% of the initial mass, despite the relative similarity in particle size distribution to phosphate material 1. These differences are graphically shown in [Fig. 7\(c\)](#), particularly to highlight the further divergence of the two materials’ behavior between 0% and 90% relative humidity (including the rapid increase observed for phosphate material 2 between 70% and 90% relative humidity).

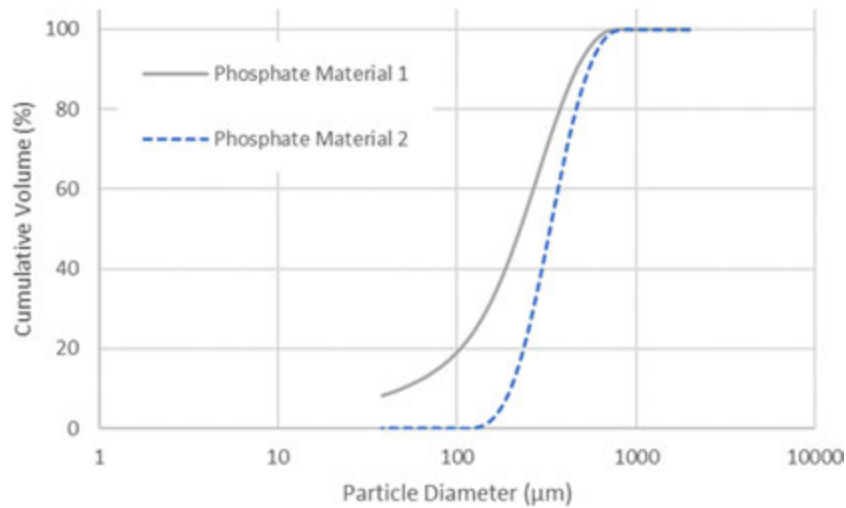


Fig. 6 Cumulative particle size distributions of two phosphate raw materials by static light scattering.

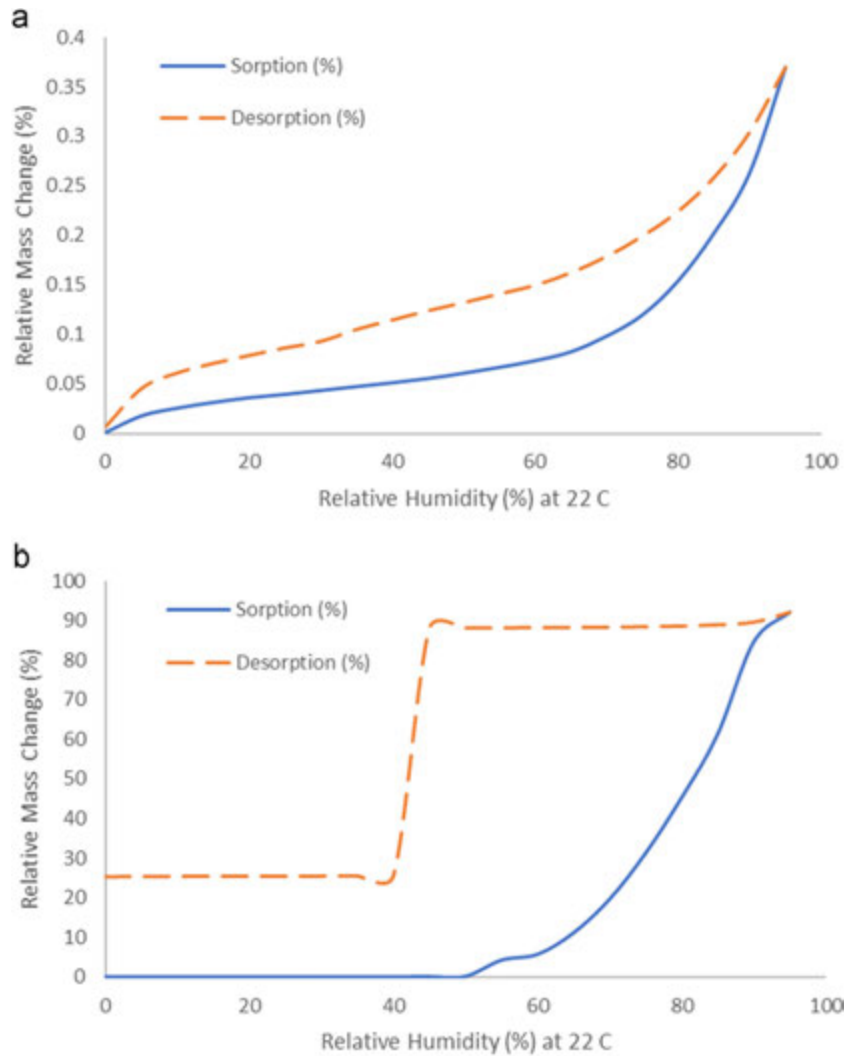


Fig. 7 (a) Moisture sorption/desorption isotherms at 22°C as a function of relative humidity for Phosphate material 1 (note the relative y-axis scaling) as measured by Dynamic Vapor Sorption. (b) Moisture sorption/desorption isotherms at 22°C as a function of relative humidity for Phosphate material 2 (note the relative y-axis scaling) as measured by Dynamic Vapor Sorption. (c) Mass percent change at select relative humidity values (22°C) for the two phosphate raw materials as measured by Dynamic Vapor Sorption (inset is rescaled to show relative comparisons for Phosphate material 1).

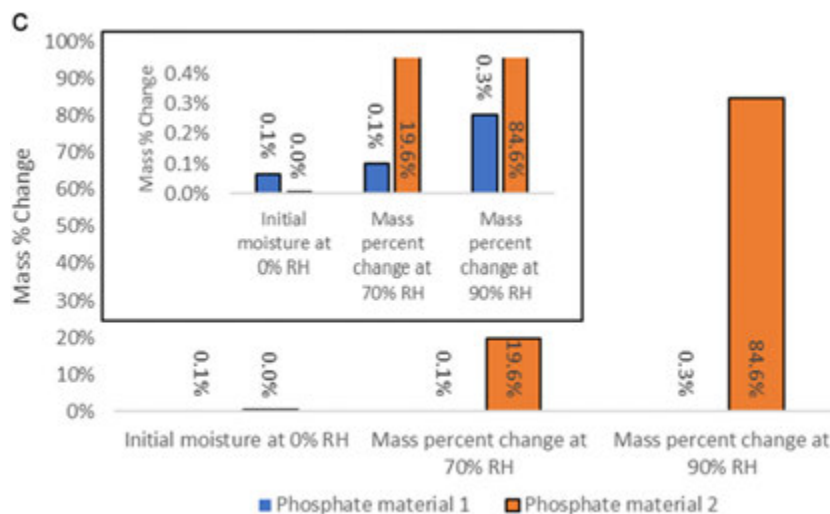


Fig. 7 Continue.

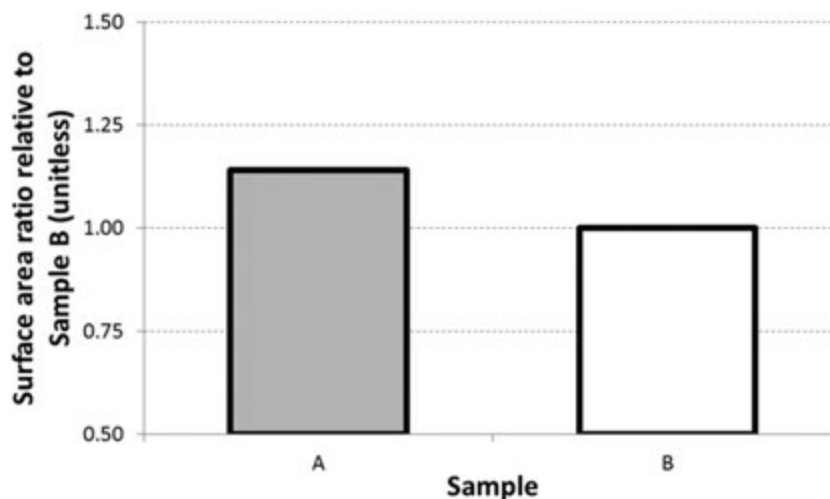


Fig. 8 Relative differences in specific surface area between samples A & B as measured by Brunauer-Emmett-Teller (BET) gas physisorption methods.

The DVS data for phosphate material 2 shows both an irreversible phase change on the desorption step compared with material 1 and two orders of magnitude shift in mass change on exposure to ambient moisture, indicating a spontaneous irreversible reaction at ambient environmental conditions. This irreversible mass change indicates the presence of deliquescence despite similarities in particle size distribution and batching by target mole percent phosphate. The consequence of this effect is an excess of moisture that forces compositional adjustments due to changes in batch stoichiometry by the use of this alternate phosphate source. Moreover, the deliquescence observed for phosphate material 2 indicates further requirements for storage in industrial manufacturing, specifically the requirement for storage below 70% relative humidity as indicated in Fig. 7(c).

Powder Batch Permeability & Compressibility

Figs. 8 and 9 show powder specific surface area (relative) and particle size (hydro-dispersed static light diffraction) for two candidate raw materials, identified as A & B. Fig. 10 is a plot of the bulk density and compressibility of the two materials. Compressibility data was obtained using a Freeman FT4 powder rheometer. Bulk density vs. applied normal stress was captured simultaneously, also via the FT4 rheometer. Fig. 10 that despite common observations of compaction in response to the normal stress, re-scaling indicates that Material B shows a 40% compressibility relative to the 20% compressibility of Material A.

Fig. 11 is a Weibull plot of the data shown in Fig. 10 (bulk density vs. the applied normal stress). The Weibull scaling parameter, or alpha, is the characteristic stress or the stress value required to reach 63.2% of the final bulk density increase. The

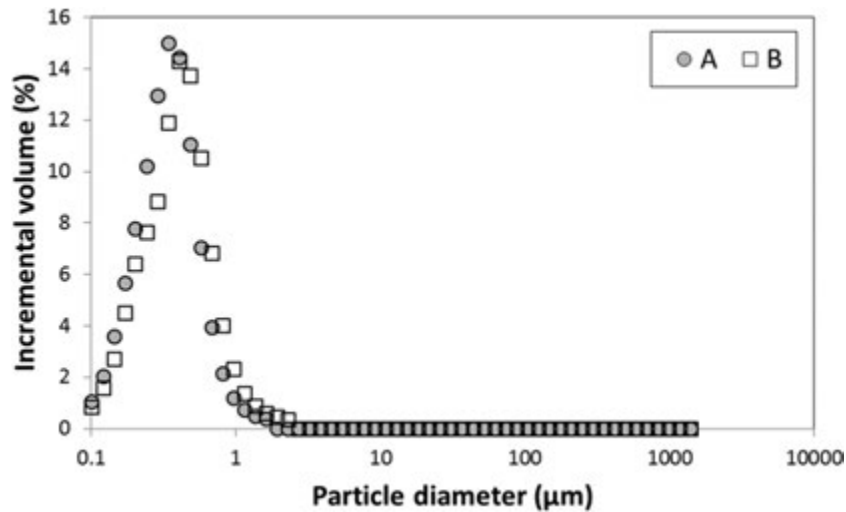


Fig. 9 Particle size distribution for samples A & B as measured via a common static light scattering technique.

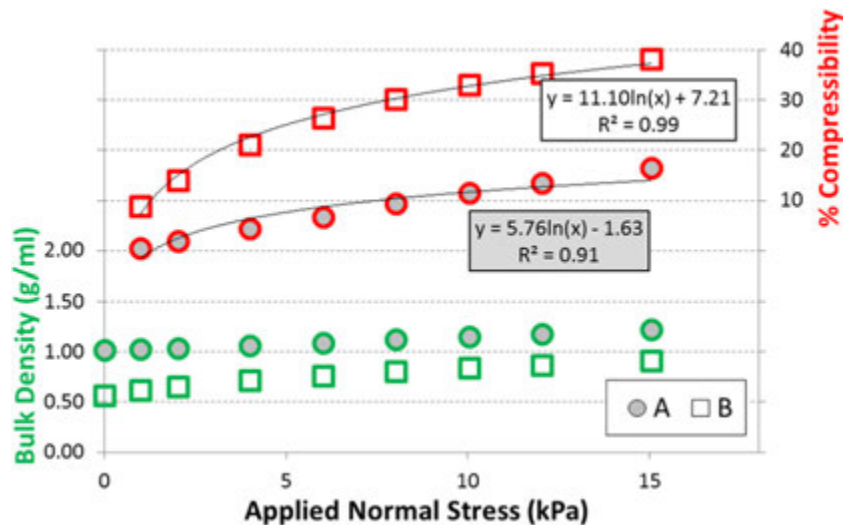


Fig. 10 Bulk density (g mL⁻¹) and percent compressibility as a function of applied normal stress (kPa) for samples A & B.

Weibull modulus, (β), is the slope of the Weibull plot and represents the narrowness of the compaction rate distribution, i.e., the greater β value the narrower compaction rate distribution. **Fig. 11** indicates that both materials compressibility data fit a Weibull distribution with a correlation coefficient above 0.990 and that Material B shows lower α and β fit parameters than Material A.

The differences observed in particle size (**Fig. 8**) and surface area (**Fig. 9**) are minor when compared to the large differences observed in the compressibility, which impacts the bulk density during a forming process or in the final product attributes. Moreover, in spite of the higher compressibility of material A, note that material B exhibits a greater rate of densification than material A as evidenced by the larger β value in the Weibull plot of **Fig. 11**.

Another example is shown in **Fig. 12** for the evaluation of two lots of the aforementioned raw material "B" via aerodynamic/dry dispersion in static light scattering along with a corresponding generic measurement of the material via hydrodynamic dispersion via the same static light scattering system. The conventional 10th, 50th and 90th percentile diameters are given in **Table 2**.

The "good" and "bad" lots were observed to exhibit differences in manufacturing with respect to bin discharge, assisted with pneumatic conveyance. The so-called "bad" lot was observed to exhibit the common rat holing defect (last in, first out), whereby the effective storage capacity of the bin for refill and discharge was constricted.

Aerodynamic dispersion for static light scattering was used to provide an in-process particle size profile of the two powder lots. Note again that particle size is insufficient to differentiate between the two powder lots.

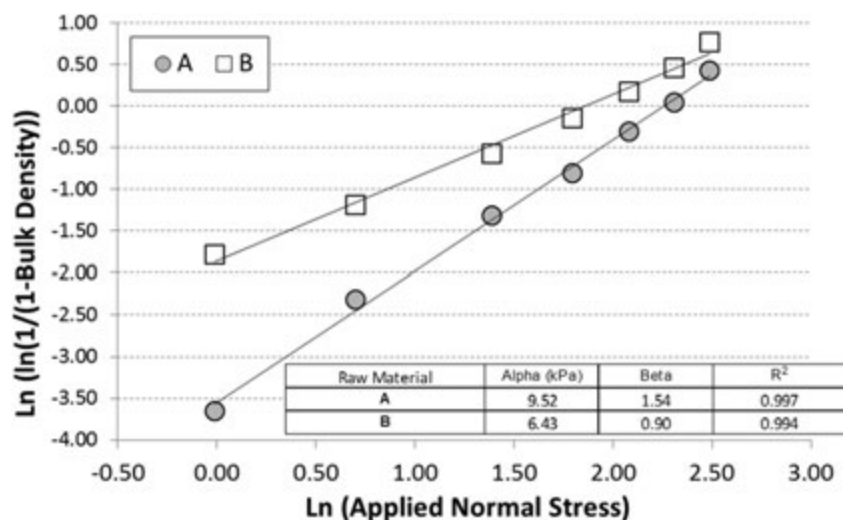


Fig. 11 Weibull plot of bulk density (g mL^{-1}) as a function of applied normal stress (kPa).

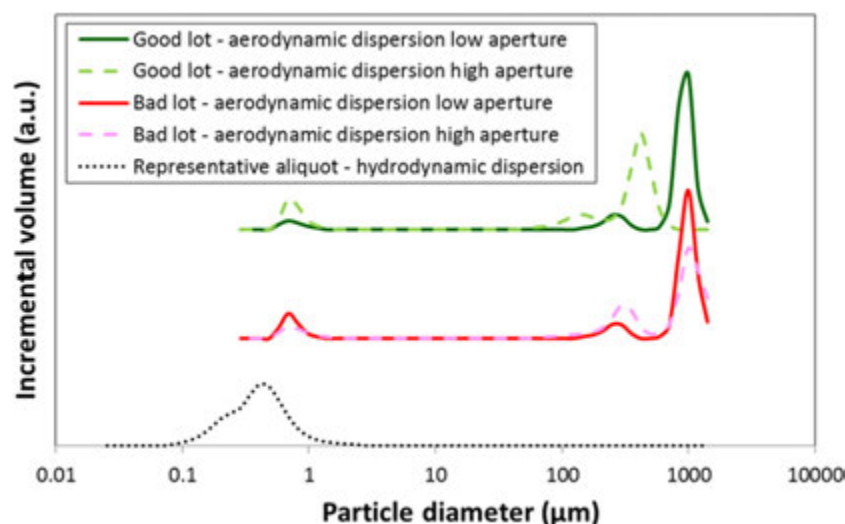


Fig. 12 Comparing so-called “good” and “bad” lots via aerodynamic dispersion at low and high aperture settings to vary aerodynamic dispersion power in comparison with conventional hydrodynamic dispersion and suspension media-based results for static light scattering particle size distribution measurement (a.u. refers to “arbitrary units”).

Table 2 Tabulation of 10th, 50th & 90th particle diameter percentiles for so-called “good” and “bad” lots at low and high aperture settings in comparison with conventional hydrodynamic dispersion and suspension media-based results for static light scattering particle size distribution

Measurement	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
Good lot - aerodynamic dispersion low aperture	0.734	850.3	1077.0
Good lot - aerodynamic dispersion high aperture	0.694	325.2	465.8
Bad lot - aerodynamic dispersion low aperture	223.0	828.4	1013.0
Bad lot - aerodynamic dispersion high aperture	99.76	793.3	1174.0
Representative aliquot - hydrodynamic dispersion	0.172	0.367	0.687

To address the issue of flowability during discharge, a Jenike & Johansen fluidized segregator was utilized to circulate material and determine the quantity collected at stages positioned at various heights in the aeration column (bottom, middle, top, funnel and filter paper atop the funnel). A photograph of the configuration is provided in [Fig. 13](#).

Segregation results are shown in [Fig. 14](#).

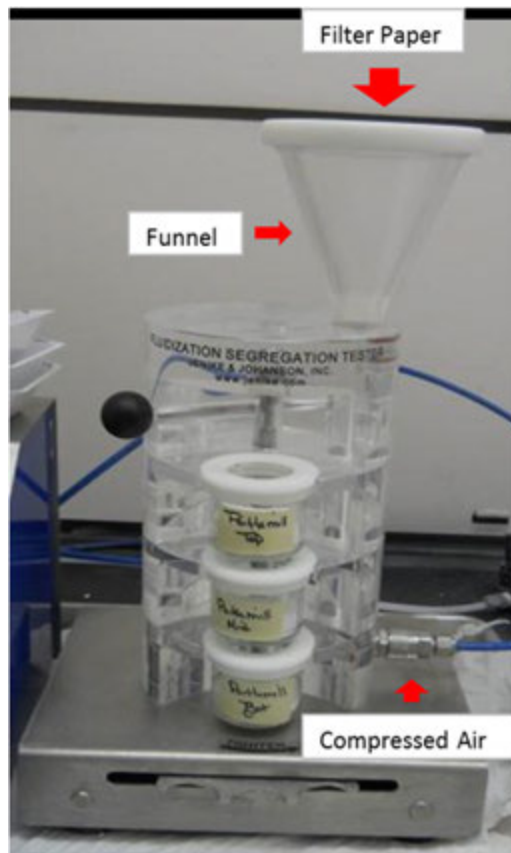


Fig. 13 Photograph of Jenike fluidized segregation apparatus.



Fig. 14 Weight percent retained on Funnel, Top, Middle and Bottom portions of Jenike Fluidized Segregator for Good and Bad lots.

As seen in the bar graph above a high percentage of the so-called "bad" lot is retained in the funnel portion. Photographs are shown in Fig. 15. The photographs of increased retention of material in the funnel portion for the so-called "bad" lot correlates with the reduced degree of particle size shift at higher aperture settings in aerodynamic dispersion and observations of increased cohesion in the so-called "bad" lot.

Fig. 16 shows the results of aeration permeability measurements on the previously presented "good" and "bad" lots as a function of applied normal stress, as measured by the air pressure drop across the powder bed. A less permeable powder bed (i.e., a

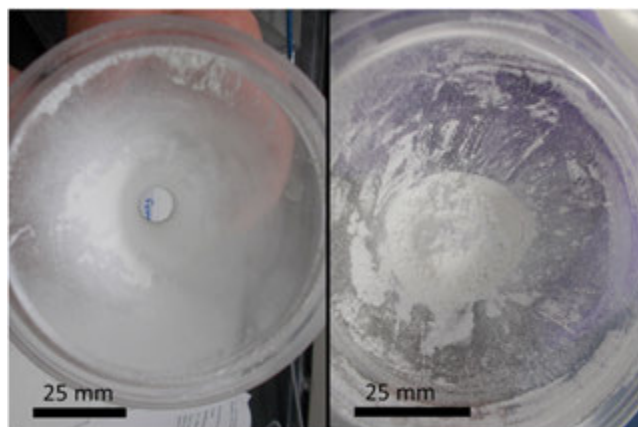


Fig. 15 At rest photographs of the funnel portion of the fluidized segregation results upon completion of the test for the “good” lot (left) and the “bad” lot (right).

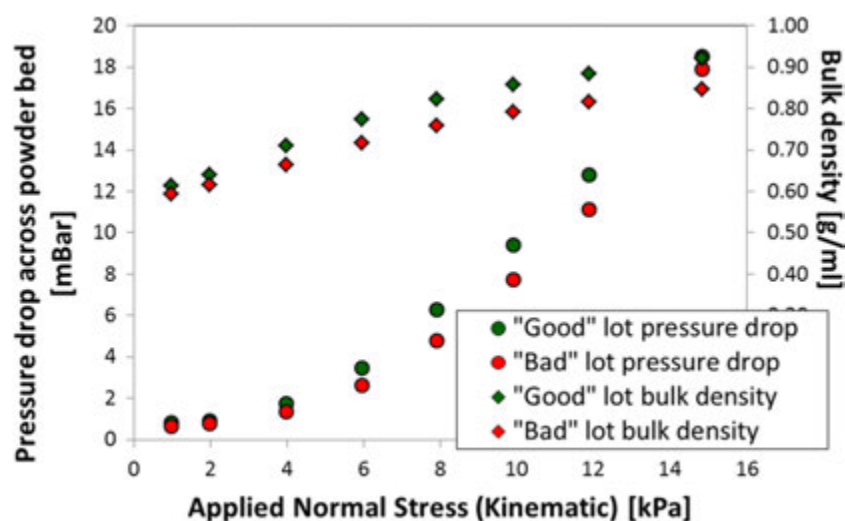


Fig. 16 Pressure drop across powder bed and bulk density as a function of applied normal stress for the “good” and “bad” lots.

powder bed with a higher pressure drop) is more susceptible to unstable powder flow due to the inability to effectively displace powder volume with air. Despite the apparent divergence of the bulk density between the two lots under increasing normal stress, the ultimate convergence of the permeability of good and bad lots indicates that the pressure drop is inadequately explained by the densification of the powder bed. This shows that the “bad” lot (despite not being as dense relative to the “good” lot) is more vulnerable to challenges of powder flow from a storage bin due to the prohibitively high pressure drop at higher normal stresses.

Summary

The set of dynamic characterization techniques are presented above with the intent of conveying adjacencies to the aforementioned classical suite (the stock seven techniques described in the introduction) of characterizations performed on granular and powder raw materials. These are intended primarily to convey a nuanced understanding of granular or powder systems and not to convey a supposed “missing link”; indeed a concession of this work is that characterization of particulate materials for materials processing is highly dependent on the application and instances where the methods discussed above in detail may not be applicable. Conversely the stock seven techniques described earlier may similarly be parsed to glean useful information from the dynamic characterization techniques relevant to a given application.

Numerous other dynamic characterization techniques are available to obtain better understanding of an inorganic/organic batch system. Two examples not discussed above but highly relevant to powder systems include powder vibratory assisted auto agglomeration (Barletta and Poletto, 2012; Ku *et al.*, 2015), and powder vapor sorption characterization by non-aqueous sources (Arlabosse *et al.*, 2003).

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References

- Allen, T., 1997. Particle Size Measurement: Volume 2: Surface Area and Pore Size Determination. Springer.
- Allen, T., 2003. Powder Sampling and Particle Size Determination. Elsevier.
- Alnaimi, S.M., Strange, J.H., Smith, E.G., 1994. The characterization of porous solids by NMR. Magnetic Resonance Imaging 12 (2), 257–259.
- Arlabosse, P., Rodier, E., Ferrasse, J.H., Chavez, S., Lecomte, D., 2003. Comparison between static and dynamic methods for sorption isotherm measurements. Drying Technology 21 (3), 479–497.
- Balasubramanian, S., Sadangi, R.K., Kear, B.H., Shukla, V., Elliott, G., 2012. Effect of powder characteristics in phase transformation in plasma sprayed alumina 13 wt% titania coatings. In: Bansal, N.P., Singh, J.P. (Eds.), Innovative Processing and Synthesis of Ceramics, Glasses, and Composites VI. New York: John Wiley & Sons, pp. 125–135.
- Barletta, D., Poletto, M., 2012. Aggregation phenomena in fluidization of cohesive powders assisted by mechanical vibrations. Powder Technology 225, 93–100.
- Bell, T.A., 2005. Challenges in the scale-up of particulate process – An industrial perspective. Powder Technology 150, 60–71.
- Bloss, F.D., 1961. An introduction to the methods of optical crystallography (No. 548 BLO).
- Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. Journal of the American Chemical Society 60 (2), 309–319.
- Cierpka, C., Kähler, C.J., 2012. Particle imaging techniques for volumetric three-component (3D3C) velocity measurements in microfluidics. Journal of visualization 15 (1), 1–31.
- Diamond, S., 1971. A critical comparison of mercury porosimetry and capillary condensation pore size distributions of portland cement pastes. Cement and Concrete Research 1 (5), 531–545.
- Eggersdorfer, M.L., Gröhn, A.J., Sorensen, C.M., McMurry, P.H., Pratsinis, S.E., 2012. Mass-mobility characterization of flame-made ZrO₂ aerosols: Primary particle diameter and extent of aggregation. Journal of Colloid and Interface Science 387 (1), 12–23.
- Kamrin, K.N., 2008. Stochastic and deterministic models for dense granular flow. PhD Thesis, Massachusetts Institute of Technology. Cambridge MA.
- King, A.G., 2002. Ceramic Technology and Processing. Now York: Noyes publications.
- Kipling, J.J., Wilson, R.B., 1960. Adsorption of methylene blue in the determination of surface areas. Journal of Applied Chemistry 10 (3), 109–113.
- Ku, N., Hare, C., Ghadiri, M., *et al.*, 2015. Auto-granulation of fine cohesive powder by mechanical vibration. Procedia Engineering 102, 72–80.
- Lukasiewicz, S.J., 1989. Spray-drying ceramic powders. Journal of the American Ceramic Society 72 (4), 617–624.
- Maire, E., Gulda, M.P., Nakamura, N., *et al.*, 2011. Three dimensional confocal microscopy study of boundaries between colloidal crystals. In: Optical Measurements, Modeling, and Metrology, 5. New York, NY: Springer, pp. 69–74.
- Mikli, V., Kaerdi, H., Kulu, P., Besterci, M., 2001. Characterization of powder particle morphology/Pulbriosakeste morfoloogia kirjeldamine. Proceedings of the Estonian Academy of Sciences: Engineering 7 (1), 22–34.
- Mort, P., Michaels, J.N., Behringer, R.P., *et al.*, 2015. Dense granular flow – A collaborative study. Powder Technology 284, 571–584.
- Pieri, L., Bittelli, M., Pisa, P.R., 2006. Laser diffraction, transmission electron microscopy and image analysis to evaluate a bimodal Gaussian model for particle size distribution in soils. Geoderma 135, 118–132.
- Reed, J.S., 1995. Chapter 5: Characteristics and specifications of ceramic materials. In Principles of Ceramic Processing, second ed. New York: John Wiley & Sons, pp. 69–75.
- Schubert, H., Petzow, G., 1990. Chapter 3: preparation and characterization of ceramic powders. In: Smiya, S. (Ed.), Advanced Ceramics III, first ed. Netherlands: Springer, pp. 45–56.
- Sing, K.S.W., Everett, D.H., Haul, R.A.W., *et al.*, 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. Pure and Applied Chemistry 57 (4), 603–619.
- Tang, X., De Rooij, M.R., Van Duynhoven, J., Van Breugel, K., 2008. Dynamic volume change measurements of cereal materials by environmental scanning electron microscopy and videomicroscopy. Journal of Microscopy 230 (1), 100–107.
- Tomas, J., 2001a. Assessment of mechanical properties of cohesive particulate solids. Part 1: Particle contact constitutive model. Particulate Science and Technology 19 (2), 95–110.
- Tomas, J., 2001b. Assessment of mechanical properties of cohesive particulate solids. Part 2: Powder flow criteria. Particulate Science and Technology 19 (2), 111–129.
- Tomas, J., 2004. Fundamentals of cohesive powder consolidation and flow. Granular Matter 6, 75–86.
- Völz, H.G., Kischkewitz, J., Woditsch, P., *et al.*, 2000. Inorganic pigments. In: Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH.
- Wulff, M., 2004. Pore size determination by thermoporometry using acetonitrile. Thermochimica Acta 419 (1–2), 291–294.
- Zhu, K., Rao, S.M., Wang, C.H., Sundaresan, S., 2003. Electrical capacitance tomography measurements on vertical and inclined pneumatic conveying of granular solids. Chemical Engineering Science 58 (18), 4225–4245.
- Zhua, H., Mehrabadi, M.M., Massoudib, M., 2007. The frictional flow of a dense granular material based on the dilatant double shearing model. Computers and Mathematics with Applications 53, 244–259.

Amorphous Materials: Vibrational Spectroscopy

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Amorphous materials do not possess long-range order, so that understanding their structures at different length scales requires application of various diffraction and spectroscopic techniques, combined with computer modeling (Wong and Angell, 1976; Brawer, 1985; Rao, 2002; Mysen and Richet, 2005; Wang, 2013). Vibrational spectroscopy provides a detailed probe of molecular structure and bonding in amorphous solids and liquids as well as molecules and crystals (Nakamoto, 2009). Infrared (IR) spectroscopy and Raman scattering are the most convenient laboratory techniques for studying vibrational excitations in these systems (McMillan and Wolf, 1995). Inelastic neutron and X-ray scattering give additional information on the dynamics of disordered systems (Galeener *et al.*, 1983; Duffy, 2005; Greaves *et al.*, 2005; Haworth *et al.*, 2010). Molecular dynamics simulations and *ab initio* calculations give further insights into the nature of vibrations in glasses and liquids, as well as on relaxation processes (Brawer, 1985; Clark *et al.*, 1997).

IR and Raman Spectroscopy

In IR spectroscopy, a change in electric dipole moment ($\Delta\mu(t)$) associated with a vibrational mode of the sample interacts with the oscillating electric field ($E(t)$) of the incident IR beam, giving rise to an absorption signal. IR studies of amorphous materials are readily carried out using powder transmission, in which ground aliquots of sample are pressed into discs along with IR-transparent support material (nujol®, KBr), or by carrying out transmission experiments directly on thin films. Quantitative information on optical constants, including real and imaginary parts of the refractive index (n , k), dielectric constant (ϵ' and ϵ''), and the absorption coefficient $\alpha(\nu)$, is best obtained from IR reflectivity studies (Efimov, 1995).

Raman scattering spectroscopy is an inelastic light-scattering technique, in which the electric field (E_o) of the incident light oscillates at much higher frequency (ν^*) than the vibrational modes (ν_i). The incident light causes instantaneous displacements of the electron density relative to the nuclei, creating an induced dipole, $\vec{\mu}_{\text{ind}} = \alpha \vec{E}$: α is the molecular polarizability. For small vibrational displacements q_i ,

$$\mu_{\text{ind}}(t) = E_o \left(\alpha_o \cos 2\pi \nu^* t + \frac{1}{2} \left(\frac{d\alpha}{dq_i} \right)_o q_i \cos 2\pi (\nu^* \pm \nu_i) t \right)$$

The time-dependent terms result in re-emission of light not only at the Rayleigh-scattered incident frequency (ν^*), but also at Raman-shifted frequencies ($\nu^* - \nu_i$) and ($\nu^* + \nu_i$). Raman spectroscopy is carried out by passing a laser beam through the sample, and recording the vibrational spectrum of frequency shifts (usually $\nu^* - \nu_i$) expressed in wavenumber (cm^{-1}) units.

In addition to the features due to vibrational excitations, Raman spectra of glasses typically show a broad temperature-dependent low-frequency maximum that results from the combined T - and ν -dependence of the Raman scattering. At low frequency, amorphous materials show a near-continuum of vibrational states. The temperature dependence of the Raman scattered intensity gives rise to a multiplying factor which increases exponentially at small wavenumber. The two effects combine to give an apparent maximum in the Raman spectrum, which disappears if the sample is cooled well below room temperature, or if the spectra are 'reduced' by multiplying the observed intensities by the Bose factor $\nu/[n(\nu, T) + 1]$ ($n = 1/\exp(h\nu/kT) - 1$) (Daisenberger *et al.*, 2011). A distinct 'boson peak' feature is also found in inelastic scattering spectra of amorphous polymers and inorganic systems at low wavenumber values. This feature and its temperature dependence is indicative of the mesoscopic disordered structure of the glass (Shintani and Tanaka, 2008; Champagnon *et al.*, 2009). Excitations associated with the boson peak may play a role in defining the properties of the system at the glass transition (Angell, 1995; Greaves *et al.*, 2005). In resonance Raman spectroscopy, the incident laser excitation frequency corresponds nearly with electronic absorption transitions of the sample. The intensity of particular Raman-active modes is greatly enhanced, and the technique provides a powerful probe of local structure and vibrational-electronic coupling in the sample. Resonance Raman spectroscopy is used in studies of semiconducting glasses, for example, GeSe_2 or As_2S_3 (Wang, 2013).

Amorphous Tetrahedral Semiconductors

Vibrational excitations in amorphous semiconductors such as a-Si and a-Ge are studied primarily by Raman scattering spectroscopy (Tauc, 1975; Brodsky, 1983; Lucovsky and Pollard, 1984; Daisenberger *et al.*, 2011). The structures mainly consist of covalently bonded tetrahedral units, linked into a continuous random network (CRN). The Raman spectra have principal maxima at 460 cm^{-1} (a-Si) and 240 cm^{-1} (a-Ge), and resemble broadened vibrational density of states ($g(\nu)$) functions of the crystalline

semiconductors. This observation is due to loss of translational symmetry in the disordered semiconductors. The same process results in loss of inversion symmetry, and the vibrations of the amorphous solids are IR-active. Raman spectroscopy is highly sensitive for studying the onset of crystallization in a-Si or Ge, and for studies of disordering (due to, e.g., irradiation damage) of the crystals. Vibrational spectroscopy is useful for characterizing SiH_x and GeH_x sites in hydrogenated amorphous alloys (Lucovsky and Pollard, 1984; Vergnat *et al.*, 1993).

Disordered carbon-based materials have structures based upon sp²-bonded sheets as in crystalline graphite, which has its principal Raman mode at 1575 cm⁻¹. With increasing disorder, this band broadens and moves to ~1600 cm⁻¹, and a broad band at ~1355 cm⁻¹ grows in intensity. The result is interpreted as a gradual loss of crystalline selection rules and more of the crystalline phonon branches appear in the Raman spectrum as the average 'unit cell' becomes larger (Lespade *et al.*, 1982). Interpretation of the Raman spectra must take account of resonant effects appearing as a function of the incident laser wavelength (Ferrari and Robertson, 2001). The 1355 cm⁻¹ feature lies close to the Raman peak of tetrahedrally-coordinate diamond, and part of its intensity can be assigned to sp³-bonded regions in the structure using appropriate excitation (Ferrari and Robertson, 2001). Differences in band width, shape, and relative intensities of ~1600 and ~1355 cm⁻¹ features distinguish a-C samples with differing degree and type of disorder. Amorphous carbon nitride materials can be studied in a similar way (Ferrari *et al.*, 2003).

In amorphous III-V semiconductors, features in Raman and IR spectra are interpreted as broadened 'crystalline' *g*(*v*) functions within a CRN model, as for a-Si and -Ge. The a-(III-V) spectra show additional broadening due to separation of transverse and longitudinal modes in the polar semiconductor. The spectra also give information on local structure. In a-InP, a band near 440 cm⁻¹ is assigned to P-P linkages, revealing the presence of 'wrong bonds' in the amorphous semiconductor. a-Si_xGe_{1-x} alloys show features near 500, 250, and 370 cm⁻¹, assigned to Si-Si, Ge-Ge, and Si-Ge bonds (Lucovsky and Pollard, 1984). The relative intensities vary systematically with Si:Ge ratio. This example of 'two-mode' behavior demonstrates how the CRN 'density of states' model for a-Si and a-Ge is extended to a more local, 'molecular,' interpretation, in intermediate compounds. Raman spectra of a-Si_xC_{1-x} samples show bands at 525 and 1430 cm⁻¹, assigned to Si-Si and C-C bonds in the sample. In this case, the C-C bonding is planar sp², unlike the tetrahedral sp³ bonding of the a-Si network.

Chalcogenide Glasses

The second large family of amorphous semiconductors is that of amorphous chalcogenides (X=S, Se, Te), and their binary (GeS_x, AsS_x), ternary, and more complex (Ge-As-X, etc.) compounds. These have applications as IR transmitting optical materials due to the low vibrational frequencies associated with the heavy atoms and relatively weak interatomic bonding present (Lucas, 1999; Wang, 2013). Liquid S just above its melting point shows a rich Raman spectrum with peaks at 474, 218, 151, and 77 cm⁻¹ (Brodsky, 1983). The spectrum resembles that of the orthorhombic crystal, with 'isolated' S₈ ring units held together by van der Waals forces. The Raman spectrum of the liquid is thus given a 'molecular' interpretation, contrasting with the CRN interpretation of a-Si and a-Ge. As temperature is increased, the S₈ chains begin to open into S_n polymeric chain units, and the viscosity increases. The Raman spectrum of a-Se is dominated by a band at 235 cm⁻¹, with a prominent shoulder at 255 cm⁻¹. These features correspond to the Se-Se stretching peaks of the trigonal (helical Se_∞ chains) and monoclinic (Se₈ rings) crystalline forms. The IR spectrum shows pairs of bands in the 220–260 cm⁻¹ and 90–150 cm⁻¹ ranges, assigned to Se-Se stretching and bending modes within chain and ring units. The glass consists of Se_n chain units with some proportion of Se₈ rings. In the case of a-Te, the Raman spectrum is dominated by a broad band at ~160 cm⁻¹, with a weaker feature appearing at ~85 cm⁻¹. Although the spectrum is usually given a 'density of states' interpretation like a-Si, it does not correspond to a broadened *g*(*v*) function for known crystalline forms of Te.

Crystalline As₂S₃ and As₂Se₃ have planar structures containing pyramidal AsX₃ (X=S,Se) units linked by bridging X atoms. The Raman spectrum of a-As₂S₃ has a strong, polarized band at 360 cm⁻¹ due to As-S stretching, whereas the IR spectrum is dominated by a band at 310 cm⁻¹. The complementarity between IR and Raman spectra indicate that the pyramidal AsX₃ molecular units have high symmetry. The units vibrate 'independently' because the AsXAs angle is narrow (90°–100°). The polarized Raman band is assigned to symmetric (*v*₁) AsS₃ breathing, and the IR band to asymmetric (*v*₃) stretching. Weaker features at 130–150 cm⁻¹ range are due to bending vibrations.

A CRN 'density of states' interpretation could equally well be applied to a-As₂S₃ and a-As₂Se₃, in that the glass spectra resemble broadened *g*(*v*) functions derived from the crystalline materials. This observation illustrates convergence between the two 'extreme' models for interpreting spectra of amorphous materials. When phonon branches show little dispersion, as in c-As₂S₃, they correspond to 'localized' vibrational excitations, and they give rise to sharp peaks and rich structure in the vibrational spectra of the amorphous material that are readily interpreted in terms of 'molecular' structures. When crystal dispersion is large, as is the case in c-Si and c-Ge, a range of frequency-dependent coherence lengths occurs in the corresponding amorphous material, and detailed information on local 'molecular' structure is difficult to extract from the vibrational spectra.

In binary As-S glasses, Raman and resonance Raman studies reveal the presence of As-As (peak at 231 cm⁻¹) and S-S (490 cm⁻¹) linkages, including S₈ ring units at high sulfur content. The glasses contain As₄S₄ molecular units, identified by their spectroscopic signature peaks at 220 and 190 cm⁻¹. These units undergo light-initiated polymerization upon prolonged exposure to the laser beam.

Amorphous GeX₂ (X=S, Se, Te) systems consist essentially of tetrahedral GeX₄ units linked by two-coordinated X atoms, as in the crystalline materials. a-GeSe₂ shows a strong, polarized Raman mode at 342 cm⁻¹, assigned to symmetric stretching (*v*₁) of GeS₄

groups in the structure. The corresponding ν_3 mode (asymmetric stretching) is found in the IR spectrum at 367 cm^{-1} . In $\text{Ge}_x\text{S}_{1-x}$ glasses with $x > 0.67$, the characteristic Raman mode of S_8 rings (470 cm^{-1}) is observed in the spectra, confirmed by IR data. At high Ge concentrations, broadening of the Ge–S stretching band and increased intensity in the 300 cm^{-1} region reveals the formation of Ge–Ge linkages in partly substituted $\text{Ge}(\text{Ge,S})_4$ tetrahedral units.

Silicate and Aluminosilicate Glasses

This large class of amorphous materials is significant for geology as well as glass science (Wong and Angell, 1976; McMillan and Wolf, 1995). $\alpha\text{-SiO}_2$ consists of a 3-D network of corner-shared SiO_4 tetrahedra. The vibrational spectrum measured by neutron scattering resembles $g(\nu)$ of crystalline SiO_2 polymorphs, and is dominated by broad bands at ~ 1100 , 800 , and 350 cm^{-1} (Galeener *et al.*, 1983; Figure 1). The Raman and IR spectra contain similar bands, assigned to Si–O stretching and OSiO, SiOSi bending vibrations within the tetrahedral network. Much discussion has been concerned with the cooperative nature (i.e., correlation length) of these excitations. Hyper-Raman experiments indicate that the highest frequency modes are highly localized, but vibrational coherence exists for the lowest frequency excitations, from neutron studies. The Raman spectrum contains sharp peaks at 606 and 492 cm^{-1} that are not predicted by structural models based on known polymorphs. These features are due to 3- and 4-membered siloxane rings present as ‘defect’ species within the glass. Their formation enthalpies are $\sim 42\text{ kJmol}^{-1}$ and $\sim 15\text{ kJmol}^{-1}$, and the Raman intensities are a useful indicator of the state of thermal equilibration of the glass. Ring formation has a negative ΔV , so that the 3-ring peak intensity increases both with density, and also in glasses prepared from gels or from the vapor phase. The Raman spectrum is dominated by a polarized 430 cm^{-1} band due to symmetric SiOSi bending in intertetrahedral linkages. The frequency is dependent upon intertetrahedral (SiOSi) angle, and it shows anomalous behavior with temperature due to anharmonicity below the glass transition and structural relaxation at high temperature.

Adding alkali or alkaline earth metal oxide components (M_xO_y) to SiO_2 causes depolymerization of the framework and ‘non-bridging oxygens’ (NBO) appear with increased O:Si ratio. Silicon is a strong Lux-Flood acid, so that all O atoms are usually bound to at least one Si. Exceptions include Pb–O–Pb linkages occurring in lead silicate glasses and liquids and Al–O–Al linkages in aluminosilicates (characteristic Raman peaks at ~ 200 and $\sim 570\text{ cm}^{-1}$). Changing polymerization of the silicate framework results in the successive appearance of silicate units with 1, 2, 3, and 4 NBO, labeled Q^n ($4 - n$ is the number of NBO present). Characteristic Raman peaks at ~ 1100 , 1000 , 900 , and 850 cm^{-1} are assigned to symmetric Si–O stretching vibrations of Q^3 , Q^2 , Q^1 , and Q^0 species. Coexistence of Q^n species at a given composition in equilibria like $2\text{Q}^3 = \text{Q}^4 + \text{Q}^2$ is studied by Raman and NMR spectroscopy. The reactions are endothermic, with $\Delta H^\circ \sim 15\text{--}30\text{ kJmol}^{-1}$. In IR reflectance, the strong SiO_2 glass band at $\sim 1150\text{ cm}^{-1}$ decreases rapidly in reflectivity with added ‘modifier’ oxide component, accompanied by the growth in intensity of a band near 1075 cm^{-1} . This band shifts to lower frequency as SiO_2 is decreased, and it is joined by a second component at $1000\text{--}900\text{ cm}^{-1}$. These features correspond to asymmetric Si–O stretching in structures dominated by Q^3 and Q^2 . Features at $800\text{--}900\text{ cm}^{-1}$ in spectra of glass compositions with lower silica contents are due to asymmetric stretching of Q^1 and Q^0 species.

The vibrational bands of aluminosilicate glasses are broader than for silicates because of a greater distribution in structural environments, and the perturbing effect of Al on silicate vibrations. ‘Charge-balanced’ $\text{SiO}_2\text{--MAl}_2\text{O}_4$ ($\text{M} = 2\text{M}^+$ or M^{2+}) glasses have structures based on a polymerized network of SiO_4 and AlO_4 . Mg-containing glasses have very broad spectra, and contain five- and six-coordinated Al. The spectra between 850 and 1250 cm^{-1} contain unresolved bands due to (Si,Al)–O stretching vibrations of the tetrahedral framework: components are assigned to ‘ $\text{Q}^4(n\text{ Al})$ ’ species, in which SiO_4 tetrahedra share up to four linkages with Al atoms. At high SiO_2 content, Raman spectra indicate that clustering of Al-rich domains occurs, consistent with positive deviations from ideality found in heats of mixing in M^{2+} -bearing systems. IR and Raman bands at $400\text{--}600\text{ cm}^{-1}$ region are assigned to TOT or OTO ($\text{T} = \text{Si, Al}$) bending.

Pure aluminates are highly ‘fragile’ (non-Arrhenian) liquids that are marginal glass formers (Angell, 1995). $\text{CaO}(\text{Ga,Al})_2\text{O}_3$ bulk glasses and fibers are useful IR-transmitting materials. The three-dimensional network of corner-linked AlO_4 tetrahedra in CaAl_2O_4 is analogous to SiO_2 , ‘stuffed’ with Ca^{2+} ions. The Raman spectrum contains a strong polarized band at 580 cm^{-1} due to AlOAl bending. The band is sharper than its counterpart in SiO_2 because the range in intertetrahedral angles is smaller (average AlOAl angle $\sim 135^\circ$). For $\text{CaO}:\text{Al}_2\text{O}_3 > 1$, Raman and IR spectra indicate depolymerization of the tetrahedral network analogous to binary silicates. In glasses with $\text{CaO}:\text{Al}_2\text{O}_3 < 1$, AlO_5 and AlO_6 species appear, and extreme broadening of vibrational spectra occurs. Similar broadening is found in Raman and IR spectra of $\text{SiO}_2\text{--Al}_2\text{O}_3$ glasses. Here, the Raman signature of SiO_2 -rich regions is superimposed on a background due to the featureless vibrational ‘density of states’ of an alumina-rich matrix, consistent with the observation of unmixing in the system.

Carbonate and Nitrate Glasses

Carbonate glasses are mainly studied because of their importance for understanding geochemically important carbonatite magmas (Genge *et al.*, 1995) whereas nitrate compositions are well known ‘marginal’ glass formers (Angell, 1995). IR and Raman spectroscopy show that the glasses are based upon the CO_3^{2-} anion, and that different types of carbonate environment exist within the glass. Similar IR and Raman studies show that nitrate glasses (e.g., $\text{KNO}_3\text{--Ca}(\text{NO}_3)_2$) contain NO_3^{2-} anions. The

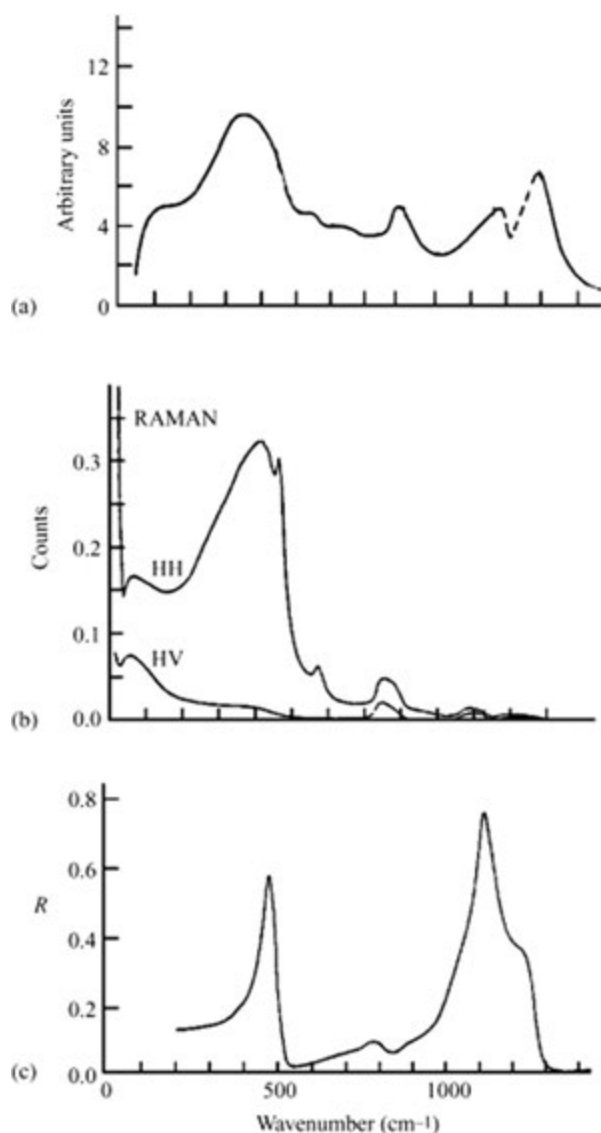


Figure 1 Comparison of the inelastic neutron scattering (a), polarized (HH and HV) Raman (b), and IR reflectance (c), spectra of SiO₂ glass. The sharp 'defect' peaks at 500 and 600 cm⁻¹ are clearly visible in the HH Raman spectrum. The strongly IR-active modes above 1000 cm⁻¹ are assigned to tetrahedral Si–O stretching vibrations: the highly polarized Raman band at 430 cm⁻¹ is assigned to symmetric SiOSi linkage bending vibrations. Adapted from Galeener, F.L., Leadbetter, A.J., Stringfellow, M.W., 1983. Comparison of the neutron, Raman, infrared vibrational spectra of vitreous SiO₂, GeO₂, BeF₂. *Physical Review B* 27, 1052–1078.

Raman-active symmetric stretching (ν_1) vibration is particularly characteristic of the trigonal planar units. IR and Raman spectroscopy can detect small concentrations (>50 ppm) of these species dissolved in glass.

Borate and Phosphate Glasses

Glasses based upon B₂O₃ form a large class of technologically important materials (Konijnendijk, 1975; Wong and Angell, 1976). The Raman spectrum of α -B₂O₃ is dominated by a narrow, polarized band at 808 cm⁻¹ due to symmetric breathing of B₃O₃ 'boroxol' rings within the glass structure based upon linked trigonal BO₃ units. The IR spectrum shows a strong band at ~1250 cm⁻¹, due to B–O stretching, and a weaker band at ~700 cm⁻¹ due to OBO/BOB bending. As metal-oxide 'modifier' component is added to B₂O₃, the boroxol ring peak in the Raman spectrum is replaced by a feature at ~770 cm⁻¹ and broad B–O stretching vibrations at 1400–1500 cm⁻¹ become prominent. These changes indicate the appearance of tetrahedral BO₄ groups in the glass. The structures of alkali and alkaline earth borosilicate and boroaluminate glasses have been investigated using Raman and IR spectroscopy. In borosilicates close to a 'charge balanced' join (SiO₂-M⁺BO₂), the glass structures are analogous with

aluminosilicates, with tetrahedral B^{3+} replacing Si^{4+} in the network. For ternary glasses with high B_2O_3 contents, the boroxol ring peak becomes prominent in the spectra indicating the presence of BO_3 units.

Phosphate glasses have applications in biomedicine, in high-power lasers, and in semiconductor packaging. Hygroscopic $\alpha-P_2O_5$ has a network structure based on tetrahedral PO_4 , in which three oxygens are bridging (POP linkages) and the fourth is terminal ($P=O$). The Raman spectrum is dominated by a polarized narrow band at 1390 cm^{-1} due to $P=O$ stretching, and strong IR and Raman bands in the $650\text{--}800\text{ cm}^{-1}$ region characteristic of POP linkages. Bulk glasses and fibers are easily formed from melts around the metaphosphate ($-PO_3^{2-}$) to pyrophosphate ($P_2O_7^{4-}$) compositions. Metaphosphates are based upon chains of PO_4 tetrahedra, with two bridging oxygens and two NBO per tetrahedron (i.e., $=PO_2$ units). The IR and Raman spectra show peaks at $1100\text{--}1200\text{ cm}^{-1}$ and $\sim 700\text{ cm}^{-1}$ due to $P-O$ stretching and POP bending, respectively. The width and frequency of each peak is sensitive to the number and type of counter ion present. Low-frequency (far-IR) peaks are due to characteristic cation modes decoupled from the phosphate glass framework (Exarhos, 1983). Vibrational spectroscopy is useful in studies of phase separation and fluorine incorporation in silicophosphate glasses for laser applications. Characteristic $P-F$ and $Si-F$ stretching vibrations are observed in the $750\text{--}900\text{ cm}^{-1}$ region of the spectra.

Fluoride Glasses

$\alpha\text{-BeF}_2$ has a tetrahedral network structure based upon tetrahedral BeF_4 units linked by bridging F^- ions (Galeener *et al.*, 1983; Brawer, 1985). Fluorides based upon fluorozirconate (ZrF_4) and fluorohafnate (HfF_4) components give rise to a wide range of binary ($ZrF_4\text{--}BaF_2$), ternary ($ZrF_4\text{--}BaF_2\text{--}NaF$: ZBN), and complex ($ZrF_4\text{--}BaF_2\text{--}LaF_3\text{--}NaF$: ZBLAN) glass-forming compositions with applications as IR-transmitting fibers (Lucas, 1999). The liquids are highly fragile (Angell, 1995), and vibrational spectroscopy is used to study changes in glass and liquid structure with temperature and composition (Simmons *et al.*, 1991; Aasland *et al.*, 1996). Fluorozirconate glasses and liquids have structures containing Zr polyhedra in 6-, 7-, and 8-fold coordination, linked by bridging F^- ions. The 'doubly-bridged' $Zr(F,F)\text{--}Zr$ unit formed by edge sharing between adjacent ZrF_n polyhedra is also important. Systematic variations in glass properties with composition are explained by changes in the Zr coordination and the relative numbers of bridging and non-bridging fluorines.

The main Raman peak at $570\text{--}590\text{ cm}^{-1}$ is assigned to symmetric stretching (ν_s) of terminal $Zr\text{--}F$ bonds within ZrF_n polyhedra. The IR band at $490\text{--}520\text{ cm}^{-1}$ is due to asymmetric (ν_{as}) $Zr\text{--}F$ stretching, involving bridging and non-bridging fluorines. The Raman bands at $330\text{--}490\text{ cm}^{-1}$ are assigned to $Zr\text{--}F$ stretching within $Zr\text{--}F\text{--}Zr$ linkages. The lowest frequency bands ($180\text{--}200\text{ cm}^{-1}$ in the Raman spectrum, and $250\text{--}285\text{ cm}^{-1}$ in the IR spectrum) are assigned to ZrF_n bending vibrations, as well as counter-cation vibrations.

The stretching frequencies (ν_s and ν_{as}) in fluorozirconate glasses occur at lower frequency than in corresponding melts, indicating that the average Zr coordination number is greater in the glass. This is achieved by increased formation of $Zr\text{--}F\text{--}Zr$ linkages on vitrification. The rapid structural change with temperature is used to rationalize the extreme fragility in these systems. Both ν_s and ν_{as} frequencies also decrease with increasing F/Zr ratio for glasses and melts. This observation indicates increased average $Zr\text{--}F$ distance, as shorter, stronger terminal $Zr\text{--}F$ bonds are replaced by longer $Zr\text{--}F\text{--}Zr$ bridges associated with increased Zr coordination and degree of polymerization (Aasland *et al.*, 1996).

References

- Aasland, S., Einarsrud, M.A., Grande, T., McMillan, P.F., 1996. Spectroscopic investigations of fluorozirconate glasses in the ternary systems $ZrF_4\text{--}BaF_2\text{--}AF$ ($A=Na, Li$). *Journal of Physical Chemistry* 100, 5457–5463.
- Angell, C.A., 1995. Formation of glasses from liquids and biopolymers. *Science* 267, 1924–1935.
- Brawer, S.A., 1985. *Relaxation in Viscous Liquids and Glasses*. Columbus: American Ceramic Society.
- Brodsky, M.H., 1983. Raman scattering in amorphous semiconductors. In: Cardona, M. (Ed.), *Light Scattering in Solids I*. Berlin: Springer-Verlag, pp. 205–251.
- Champagnon, B., Wondraczek, L., Deschamps, T., 2009. Boson peak, structural inhomogeneity, light scattering and transparency of silicate glasses. *Journal of Non-Crystalline Solids* 355, 712–714.
- Clark, S.J., Crain, J., Ackland, G.J., 1997. Comparison of bonding in amorphous silicon and carbon. *Physical Review B* 55, 14059–14062.
- Daisenberger, D., Deschamps, T., Champagnon, B., *et al.*, 2011. Polyamorphic amorphous silicon at high pressure: Raman and spatially resolved X-ray scattering studies. *Journal of Physical Chemistry B* 115, 14246–14255.
- Duffy, T.S., 2005. Synchrotron facilities and the study of the Earth's deep interior. *Reports on Progress in Physics* 68, 1811–1859.
- Efimov, A.M., 1995. *Optical Constants of Inorganic Glasses*. Boca Raton: CRC Press.
- Exarhos, G.J., 1983. Vibrational studies of glass structure and localized interactions. In: Walrafen, G.E., Revesz, A.G. (Eds.), *Structure and Bonding in Noncrystalline Solids*. New York: Plenum Press, pp. 203–217.
- Ferrari, A.C., Robertson, J., 2001. Resonant Raman spectroscopy of disordered, amorphous, and diamondlike carbon. *Physical Review B* 64, 075414.
- Ferrari, A.C., Rodil, S.E., Robertson, J., 2003. Interpretation of infrared and Raman spectra of amorphous carbon nitrides. *Physical Review B* 67, 155306.
- Galeener, F.L., Leadbetter, A.J., Stringfellow, M.W., 1983. Comparison of the neutron, Raman, infrared vibrational spectra of vitreous SiO_2 , GeO_2 , BeF_2 . *Physical Review B* 27, 1052–1078.
- Genge, M.J., Jone, A.P., Price, G.D., 1995. An infrared and Raman study of carbonate glasses: Implications for the structure of carbonatite magmas. *American Mineralogist* 59, 927–937.
- Greaves, G.N., Meneau, F., Majerus, O., Jones, D.G., Taylor, J., 2005. Identifying vibrations that destabilize crystals and characterize the glassy state. *Science* 308, 1299–1302.
- Haworth, R., Mountjoy, G., Corno, M., Uglierio, P., Newport, R.J., 2010. Probing vibrational modes in silica glass using inelastic neutron scattering with mass contrast. *Physical Review B* 81, 060301.

- Konijnendijk W.L., 1975 The structure of borosilicate glasses. Philips Research Reports Supplements, No. 1. Centrex Publishing Co: Eindhoven, The Netherlands.
- Lespade, P., Al-Jishi, R., Dresselhaus, M.S., 1982. Model of Raman scattering from incompletely graphitized carbons. *Carbon* 20, 427–431.
- Lucas, J., 1999. Infrared glasses. *Current Opinion in Solid State and Materials Science* 4, 181–187.
- Lucovsky, G., Pollard, W.B., 1984. Vibrational properties of amorphous alloys. In: Joannopoulos, J.D. (Ed.), *The physics of hydrogenated amorphous silicon II: Electronic and vibrational properties*. Topics in Applied Physics, vol. 56. Berlin-Heidelberg: Springer-Verlag, pp. 301–355.
- McMillan, P.F., Wolf, G.H., 1995. Vibrational spectroscopy of silicate liquids. In: Stebbins, J.F., McMillan, P.F., Dingwell, D.B. (Eds.), *Structure, Dynamics and Properties of Silicate Melts*. Washington DC: Mineralogical Society of America, pp. 247–315.
- Mysen, B., Richet, P., 2005. *Silicate Glasses and Melts: Properties and Structure*. Amsterdam: Elsevier B.V.
- Nakamoto, H., 2009. *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A and Part B*, sixth ed. New York: Wiley.
- Rao, K.J., 2002. *Structural Chemistry of Glasses*. Oxford: Elsevier.
- Shintani, H., Tanaka, H., 2008. Universal link between the boson peak and transverse phonons in glass. *Nature Materials* 7, 870–877.
- Simmons, J.H., Simmons, C.J., Wright, A.C., 1991. Fluoride glass structure. In: Aggarwal, I.D., Lu, G. (Eds.), *Fluoride Glass Fiber Optics*. Boston: Academic Press, pp. 37–84.
- Tauc, J., 1975. Infrared and Raman spectroscopy of amorphous semiconductors. In: Bendow, B., Mitra, S.S. (Eds.), *Optical Properties of Highly Transparent Solids*. New York: Plenum Press, pp. 525–540.
- Vergnat, M., Houssaini, S., Marchal, G., Mangin, P.H., Vettier, C., 1993. Hydrogen diffusion and densification in amorphous silicon. *Physical Review B* 47, 7584–7587.
- Wang, R. (Ed.), 2013. *Amorphous Chalcogenides: Advances and Applications*. Boca Raton: CRC Press.
- Wong, J., Angell, C.A., 1976. *Glass Structure by Spectroscopy*. New York: Marcel Dekker, (also available from University Microfilms, 1991).

MAS NMR Analysis of Ceramics and Glasses

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The Origin of NMR Spectroscopy

The first successful observation of a NMR signal was in 1945. There were two groups of physicists working independently: Bloch, Packard and Hansen (Stanford University) observed a signal from the protons of water, and Purcell, Torrey and Pound (Harvard University) detected a signal from the protons in paraffin wax. In 1952 Bloch and Purcell were awarded the Nobel Prize for physics for this outstanding discovery (Iggo, 2000).

Nuclear spin arises from unpaired proton and neutron spins in the nucleus. It depends on the number of protons and neutrons of it. Only nuclei with non-zero spins ($I \neq 0$) can absorb and emit electromagnetic radiation and induce observed "resonance". There are some rules for the determination of nuclear spin (I), which are listed in Table 1. If the mass number of the element is odd, it has half spin. If the mass number is even, the nuclear spin depends on the numbers of protons and neutrons. Both numbers being even result in spin-zero, while spin is an integer when the number of protons and neutrons is odd (Iggo, 2000). One of the distinguishing features of NMR is that its signals are isotope-specific. For example, ^{12}C is spin-zero and does not have a NMR signal, but ^{13}C is spin half and can be studied by NMR. Due to the isotope-specificity, the natural abundance of each isotope plays an important role in the NMR experiment. Using ^{12}C and ^{13}C as an example again, the zero-spin ^{12}C isotope has a natural abundance of nearly 99%, and which means the NMR visible ^{13}C is only 1.1% abundant. This results in only 1% carbon atoms contributing to the NMR signal. Therefore, ^{13}C NMR experiments need a much longer signal acquisition time due to this. Nuclear spin values ranging from $I = 0$ to $I = 8$ in 1/2-unit increments can be found across the entire periodic table. These are listed in Support materials Table 1 (Paralla, 1998).

The number of protons is equal to the atomic number of the isotope, and the number of neutrons is calculated by atomic mass minus atomic number. Fig. 1 is an example of how to determine the number of proton and neutrons of ^{23}Na (Paralla, 1998).

When a nucleus is placed in a magnetic field, the spinning generates a magnetic moment μ . The moment is proportional to the spin I ; the proportionality constant is named the gyromagnetic ratio γ . Every isotope has its different gyromagnetic ratio, which also gives it a unique magnetic moment. That is why each isotope has a characteristic NMR resonance frequency. High gyromagnetic ratios correspond to high NMR sensitivity. The origin of NMR spectroscopy comes from the nuclear spin interaction with a magnetic field. When putting a nucleus in an external magnetic field, the nuclear magnetic moment will have different orientations. However, only certain orientations with respect to the applied field direction are allowed due to the nuclear spin I being quantized. Each orientation corresponds to a quantum number m_I which can take integer or half-integer values depending on the number of unpaired protons and neutrons, and there are $2m_I + 1$ orientations allowed, which correspond to $2m_I + 1$ discrete energy levels. This is called Zeeman splitting. The energy of each level depends on the applied magnetic field, nuclear magnetic gyromagnetic ratio γ and the orientation of the nuclear magnetic moment to the applied field m_I . Due to both γ and m_I being intrinsic features of each isotope, the energy change of the transition between the different energy levels can be used to identify each element. The transition between the nuclear spin energy levels can be excited by irradiating the nuclear magnetic moment at the Larmor frequency (see Eq. (4) below). However, according to the selection rules, not all the transitions are allowed, only $\Delta m_I = \pm 1$ can happen, for example, spin $I = 1/2$ has two energy levels ($2m_I + 1 = 2 \times \frac{1}{2} + 1 = 2$): $m = +1/2$ and $m = -1/2$. It is convention to name energy level $+1/2$ as spin up (α) and $-1/2$ as spin down (β), $\Delta m = -1/2 - (+1/2) = -1$, therefore, the transition from α to β is allowed. The energy of the allowed transition is given in Eq. (1) (Iggo, 2000).

$$\Delta E = E_\beta - E_\alpha = -m_\beta \left(\frac{h}{2\pi} \right) \gamma B_0 - \left(-m_\alpha \left(\frac{h}{2\pi} \right) \gamma B_0 \right) = \left(\frac{h}{2\pi} \right) \gamma B_0 \quad (1)$$

Where h is Planck's constant ($6.62607 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$), B_0 is the magnetic field strength (T), and γ is the gyromagnetic ratio ($\text{rad. s}^{-1} \cdot \text{T}^{-1}$). This energy gap corresponds to the frequency of the photon as shown in Eq. (2) (Iggo, 2000)

$$E = h\nu \quad (2)$$

So the transition is at the frequency (Hz)

$$\nu = \frac{\Delta E}{h} = \frac{\gamma B_0}{2\pi} \quad (3)$$

The definition of Larmor frequency is

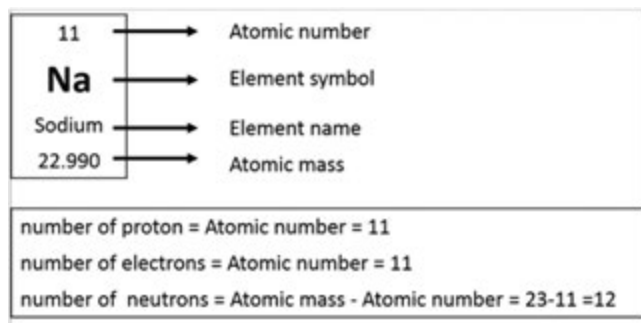
$$\nu_0 = -\frac{\gamma B_0}{2\pi} \quad (4)$$

In conclusion then, for a single spin, there is one allowed transition which results in resonance at minus the Larmor frequency in the spectrum (Keeler, 2010).

The basic NMR experiment is conducted as follows. When a sample is placed in a spectrometer field, it takes time to build up bulk magnetization along the z-axis, which is the equilibrium magnetization stage; typically this delay is the order of a few

Table 1 Rules for determination of nuclear spin (I)

Mass number	Number of Protons	Number of neutrons	Spin (I)	Example
Odd	Even	Odd	Half-Integer (1/2, 3/2...)	^{13}C
	Odd	Even	Half-Integer (1/2, 3/2...)	^{23}Na
Even	Even	Even	0	^{12}C , ^4He , ^{16}O and ^{32}S
	Odd	Odd	Integer(1,2 ...)	^2H

**Fig. 1** Number of protons and neutrons of ^{23}Na .

seconds. In the second stage, a very short burst of high power RF, lasting no more than 20 μs is applied, this excites a transient signal, known as free induction decay (FID), which is then recorded for a time called the acquisition time, which usually lasts between 50 ms and a few seconds. Finally, the time-domain signal that NMR spectroscopy measures is transformed to a frequency-domain signal, which we are more familiar with, by Fourier transformation. The FID signal can be considered as arising from a vector of length M_0 rotating at frequency Ω ; the x and y components of the vector give M_x and M_y , which shown in Eq. (5) (Keeler, 2010).

$$M_x(t) = M_0 \cos \Omega t \text{ and } M_y(t) = M_0 \sin \Omega t \quad (5)$$

As a consequence of the way the Fourier transform works, it regards $M_x(t)$ and $M_y(t)$ as the real and imaginary parts of a complex signal $S(t)$ (Eq. 6). We are not concerned too much with the mathematical details here (Keeler, 2010)

$$S(t) = S_x(t) + iS_y(t) = M_0 \cos \Omega t + iM_0 \sin \Omega t = M_0 \exp(i\Omega t) \quad (6)$$

In an NMR experiment, the signal also decays over time due to the transverse magnetization. This decay can be represented by an exponential decay with a time constant T_2 , and Eq. (7) gives the frequency domain signal, which produces the spectrum (Keeler, 2010).

$$S(t) = M_0 \exp(i\Omega t) \exp\left(\frac{-t}{T_2}\right) \quad (7)$$

If the size of FID increases, the signal height of the resonance increases in direct proportion, which means by integrating the lines in the spectrum, the relative number of protons contributing to the lines can be determined.

In Eq. (4), the resonance frequency, ν , is related to the applied magnetic field, B_0 . In the early days of NMR, resonance was detected by varying the applied field B_0 . In order to avoid the confusion of different NMR results being produced by different magnetic fields, in 1972, IUPAC recommended the convention of resonance frequency for sample X ($\nu_{X, \text{sample}}$) being reported as its chemical shift ($\delta_{X, \text{sample}}$) (Eq. 8) (Keeler, 2010). For convenience, the chemical shift is reported in ppm (parts per million), and the simple conversion from measured frequencies to chemical shift in ppm is shown in Eq. (9) (Keeler, 2010)

$$\delta_{X, \text{sample}} = \left(\frac{\nu_{X, \text{sample}} - \nu_{X, \text{reference}}}{\nu_{X, \text{reference}}} \right) \times 10^6 \quad (8)$$

$$\delta_{X, \text{sample}} / \text{ppm} = \frac{(\nu_{X, \text{sample}} - \nu_{X, \text{reference}}) / \text{Hz}}{\nu_{X, \text{reference}} / \text{MHz}} \quad (9)$$

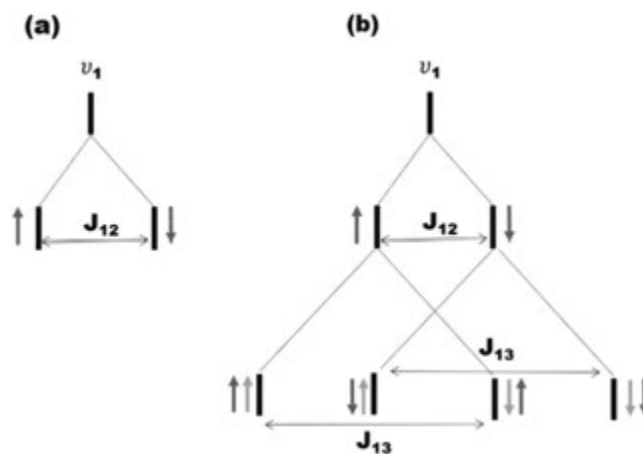


Fig. 2 Illustration of tree diagram for (a) J coupling of two spins (b) J coupling of three spins.

Fundamental Effects in NMR

The energy levels involved in NMR spectroscopy arise from the interaction of the nuclear spin with the magnetic field. However, the real magnetic field which the nucleus experiences is not the same as the applied field. There are three additional fields could be involved in the NMR spectroscopy, which provide more structure information.

(1) Chemical shielding

Chemical shielding arises from the electrons near the nucleus. When the charged electrons move in the molecular orbitals, in the applied magnetic field, they produce an induced field surrounding the nucleus. If the induced field opposes the spectrometer field, the nucleus will experience a smaller magnetic field; so the electrons are said to shield the nucleus. When the induced field has the same direction as the applied field, it reinforces the spectrometer field, and the nucleus is said to be deshielded. The additional field due to electron motion depends on the bonding elements and the type of bonding. So chemically different groups of nuclei will experience different shielding effects and generate different resonance frequencies. This is chemical shielding. The magnitude of chemical shielding depends on the strengths of the applied field. Since not every laboratory uses the same magnets, even the same chemical shielding might give a different resonance frequency. So to avoid confusion, the chemical shift is reported as the shift of the resonance line position from that of a reference compound, i.e., as a chemical shift.

(2) J coupling

Coupling arises because the nuclear magnetic moments of other nuclei surrounding the nucleus under analysis produce extra magnetic fields. It only depends on the interaction of coupled nuclei, so the magnitude of J-coupling does not vary with the applied field, and the unit of the J-coupling constant is Hertz. J-coupling is through chemical bonds, and it diminishes with an increasing number of bonds between two coupling nuclei. Usually with J-coupling, more than four bonds are too weak to be detected. The information related to J-coupling can be used to map the bonding framework of the molecular structure. The presence of J-coupling gives rise to multiplets in the spectrum. The form of these multiplets can be predicted by tree diagrams, which are shown in **Fig. 2** (Keeler, 2010). At the top, there is one spin and its resonance is ν_1 , in **Fig. 2(a)**, there is a doublet, which is the spin one splits symmetrically into two, one shifted by $\frac{1}{2}J_{12}$ to the left and another one shifted to the right by $\frac{1}{2}J_{12}$. These split lines correspond to the second spin being in the up and down spin states. In **Fig. 2(b)** a third spin is introduced, each line from the second spin is split symmetrically into two and shift by $\frac{1}{2}J_{13}$. The results are four-line multiplets.

However, sometimes a 1D spectrum could be obscured by overlapping multiplets, the more straightforward coupling map can be obtained by 2D spectra. The most popular 2D J-coupling experiments involve COSY (correlation spectroscopy) which is for homonuclear interaction, and for heteronuclear there are HMBBC (heteronuclear multiple-bond correlation) and HMQC (heteronuclear multiple-quantum correlation). TOCSY (total correlation spectroscopy) can be used to detect an unbroken J-coupling chain (Ashbrook and Duer, 1995).

(3) Relaxation

By giving radiofrequency pulses, the magnetic moment will move from the longitudinal plane (z axis) to the transverse plane (xy axis). When the RF pulses are switched off, the magnetic moments will return to their original position. This process is called relaxation. There are two types of relaxation: T_1 and T_2 . T_1 relaxation, also known as longitudinal relaxation or spin-lattice relaxation, which is when the z-magnetization, is returned to its equilibrium value and transfers its RF energy to its surrounding environment non-radioactively. It is the process by which the system re-establishes the Boltzmann equilibrium. T_1 relaxation is thus related to z-magnetization. When T_1 relaxation occurs, the longitudinal magnetization increases. T_2 relaxation is related to the xy-plane. When the magnetic moment is excited, the magnetic moments in xy plane are in phase. Once the RF is switched off, the in-phase spin experiences the field change and becomes out of phase. This is so-called dephasing. There are two modes by which T_2 relaxations arise. A non-secular part is contributed by the fluctuation in the local magnetic fields when the magnetic

Table 2 Relaxation properties

<i>Spin number</i>	<i>Magnetic properties</i>	<i>Relaxation properties</i>	<i>Isotopes</i>
1/2	Large magnetogyric ratio	Short T_1	^{133}Cd ^{199}Hg
1/2	Small magnetogyric ratio	Long T_1	^{57}Fe ^{103}Rh
> 1/2	Large magnetogyric ratio	Short T_2	^{51}V ^{53}Cr
> 1/2	Small magnetogyric ratio	Very short T_2	^{55}Mn ^{59}Co

moment reorients to the equilibrium position. A secular part is a relatively small change in the amount of the local field arising due to z-magnetization change. T_2 relaxation is also known as spin-spin relaxation. The spin exchange could be faster than the Boltzmann equilibrium so $T_2 \leq T_1$. The relaxation occurs when the nuclear spin within a magnetic field is near the Larmor frequency. This field could arise from other nuclei spins (dipole-dipole relaxation), unpaired electron spins and nuclear quadrupolar interaction (quadrupolar relaxation). Isotopes with spin = 1/2 exhibit sharp resonance while those with spins ≥ 1 show very broad lines due to the short T_2 . [Table 2](#) lists the relaxation properties of some isotopes.

The relaxation is an important effect in NMR and can give useful structural information. Because the relaxation is through space, it can be used to study the neighboring nuclei and to determine molecular conformation. The popular experiments to study relaxation are NOESY (Nuclear overhauled effect spectroscopy) and ROESY (Rotation frame nuclear-overhauled effect spectroscopy) ([Ashbrook and Duer, 1995](#)).

The Spectrometer

Available spectrometers are complex instruments. The basic components include a magnet, a probe, a transmitter, a receiver, a digitizer, and a computer to control everything and a pulse programmer to produce timed pulses and delays. A simplified diagram of an NMR spectrometer is shown in [Fig. 3](#) ([Rankin et al., 2014](#)).

The magnet in the modern NMR spectrometer is a superconducting magnet which generates an intense, homogeneous and stable magnetic field B_0 . The magnet is wrapped by a coil of wire, and when current passes through the coil, a magnetic field is generated. As the coil is superconducting, the resistance of the coil is zero. Thus, an electric current passing through the superconducting coil can persist forever and generate a stable magnetic field without consuming any powder. The coil has to be immersed in a bath of liquid helium in order to maintain the superconducting state. This liquid helium bath also needs to be surrounded by a bath of liquid nitrogen as a “heat shield”. In [Fig. 3](#), the vertical tube passing through the magnet is called the bore tube, which is a room temperature region in which to put a finely powdered sample in the magnetic field ([Keeler, 2010](#)).

The probe is inserted into the bore of the magnet and consists of a small coil to excite and detect the NMR signal and various other electronic components designed to heat or cool the sample. The typical arrangement of the RF transmitter includes a synthesizer which produces the RF output. This low level RF passes the gate and an attenuator to a high-power amplifier. Switching on or off of the RF is controlled by the gate, and the input of the amplifier is controlled by the attenuator. The amplifier boosts the controlled input RF and creates hard pulses. Therefore the RF transmitter is capable of delivering short high-power pulses, and longer low-power pulses for selective excitation.

The receiver is used to capture and amplify the NMR signals. The signal from the probe is very small; thus, the very sensitive receiver is usually placed as close to the probe as possible and, more importantly, it needs to be designed to minimize any noise. The voltage signal from the receiver is converted to a binary number and stored in the computer by an analog to digital converter (ADC) which represents the FID as data points. The pulse programmer is used to produce precisely timed pulses and delays. Usually, the acquisition of data is also executed by a pulse programmer ([Keeler, 2010](#)).

The Basics of MRI

MRI (magnetic resonance imaging) is an imaging technique used primarily in medical settings to produce high-quality images of the inside of the human body. MRI examination is widely used for brain, spinal cord, musculoskeletal, abdominal/pelvic, cardiovascular, mammographic and pregnancy examinations. MRI is based on the principles of NMR. When the human body is placed in a strong magnetic field, the collective effect of vast numbers of hydrogen nuclei produces a net tissue magnetization. Each

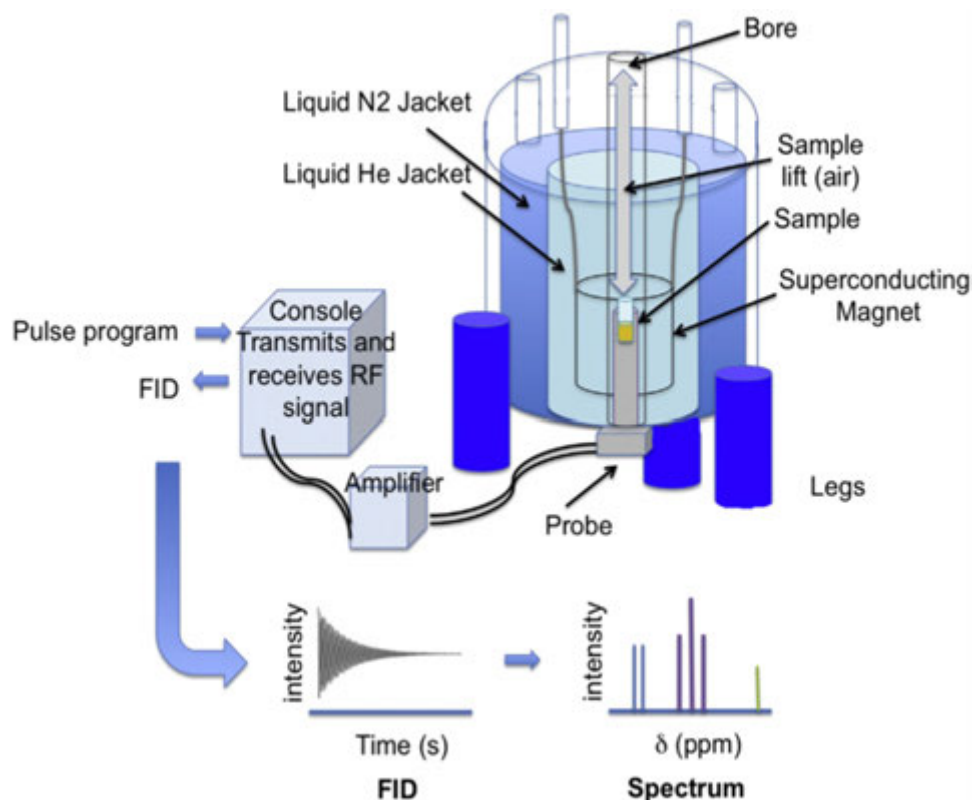


Fig. 3 Illustration of the NMR spectrometer. Reproduced with permission from Rankin, N.J., *et al.*, 2014. The emergence of proton nuclear magnetic resonance metabolomics in the cardiovascular arena as viewed from a clinical perspective. *Atherosclerosis* 237 (1), 287–300. Available at: <https://doi.org/10.1016/j.atherosclerosis.2014.09.024>. Copyright (2014), Elsevier, Ireland Ltd.

MRI image consists of a T_1 component and a T_2 component. In a T_1 weighted sequence, the contrast of the image is determined by the difference in T_1 relaxation time between fat and water. Fat is white in the resulting image as it has a high signal intensity, while water is black in the image. T_1 weighted imaging is preferred in musculoskeletal system checks because the fat-containing bone marrow gives high signal intensity and any bone marrow edema or bone marrow infiltration can be captured easily. In a T_2 weighted sequence, the fluid-containing part is highlighted; thus, it is suitable to detect pathology. Whether to use T_1 or T_2 weighted images, is decided as a general rule by the fluid-filled structure. The fluid has a high signal intensity on T_2 weighted image and is a more reliable marker than fat (Hendrick, 2008).

Solid State MAS NMR

One significant disadvantage of static solid state NMR compared to solution NMR, is the resultant broad and symmetric resonance, which is caused by the fixed molecular orientations arising in the solid state. The interaction between the nuclear spin and applied field depends on the angle between them. In solution NMR, this angular dependence is averaged out by the fast molecular tumbling in solution samples. There are two interactions in solid-state NMR which have line broadening effects. These are:

(1) Shielding Anisotropy

If the distribution of electrons around the nucleus is not isotropic, it gives rise to anisotropic shielding of the nucleus, which generates a non-symmetric NMR lineshape.

(2) Dipolar interaction

In the solid sample, the dipolar interaction through space can be very large. This increases the line width of NMR resonances.

However, both interactions depend on the geometric factor, $3\cos^2\theta = 1$, i.e., for $\theta = 54.74^\circ$. This is the so-called magic angle. When the sample spins at 54.74° to the magnetic field, the effects of shielding anisotropy and dipolar interaction on the line broadening are much diminished (Iggo, 2000). As a result, MAS NMR is a powerful tool for inorganic materials structure characterization. The commonly used pulse program is CP (cross-polarization). It is used to transfer spin polarization from the protons with abundant spins to less sensitive nuclei. This high power decoupling aims to eliminate dipolar coupling between proton spins and the nucleus under observation.

MAS NMR Studies of Ceramics and Glasses

MAS NMR has been successfully used to investigate the structure of various glasses, glass-ceramics and ceramics. It is a powerful tool to probe the chemical bonding and local chemical structure. In a comparison to another commonly used structure characterization technique, XRD (X-Ray Diffraction), NMR can be used to study both amorphous and crystalline materials, whereas XRD is only able to give information about the lattice structure of crystalline materials. NMR analysis is also able to focus on the local structure or nearest neighbor bonding, which makes it extremely useful when similar atomic weight cations or anions are substituted into a structure. This is sometimes difficult to prove by XRD pattern analysis, but can be easily detected by the chemical shift of the bonding nucleus in NMR. ^{29}Si , ^{31}P , ^{19}F , ^{27}Al MAS NMR spectroscopy are commonly used to study ceramics and glasses and examples of the application of MAS NMR to the study of these materials are now discussed.

(1) Silica-29 NMR

^{29}Si is a $\frac{1}{2}$ spin nucleus with a natural abundance of 4.9%, which is higher than ^{13}C (1.1%). It can be characterized as a magnetically diluted isotope of medium sensitivity (Uhlir and Marsman, 2008). It gives rise to narrow resonance lines, and the full-width at half maximum height (FWHM) is typically < 1 ppm. Because of its important role as a structural framework constituent and its high sensitivity to structural effects, ^{29}Si is one of the most favorable isotopes for structure studies of ceramics and glass-ceramics. However, a broad background signal at ~ 110 ppm and a long relaxation time are common problems of the ^{29}Si experiment. Applying population transfer pulse programs such as DEPT or INEPT can avoid or improve these problems (Uhlir and Marsman, 2008). In crystalline silicates, Si atoms are surrounded by different numbers of bridging oxygens (BO). With decreasing numbers of BO atoms, the silicon nucleus is deshielded and its isotropic chemical shift shifts to a more negative position in NMR spectra. The number of BO atoms can be identified by ^{29}Si NMR and denoted by Q^n (n : numbers of bridging oxygen atoms bonded to Si). The total range of ^{29}Si chemical shifts in silicates is from -60 to -120 ppm. For monosilicates (Q^0), the chemical shift range is -60 to -70 ppm; the chain end group (Q^1) is from -70 to -80 ppm; middle groups in chains (Q^2) is between -80 to -90 ppm; the chain branching sites (Q^3) is around -90 to -100 ppm and the three-dimensional cross-linked framework (Q^4) is around -100 to -110 ppm. ^{29}Si chemical shifts are sensitive to the Si-O bond length, bridging angles and second and third neighbor environments, and so the different chemical shifts can be observed between the chemically equivalent but crystallographically inequivalent Si atoms (Uhlir and Marsman, 2008). Each resonance represents structurally inequivalent Si sites, and quantitative information for the different sites can be determined from normalized peak intensities. Moreover, the local environment of the SiO_4 tetrahedron in the framework can be interpreted by chemical shift change, for example, increasing the degree of SiO_4 polymerization introduces high-field shifts of chemical shift and low-field shifts can be observed when Al is substituted for Si in the second coordination sphere (Lippmaa *et al.*, 1980; Uhlir and Marsman, 2008).

For some binary silicate glasses $M_{(1 \text{ or } 2)}\text{O-SiO}_2$, ($M = M^+$ or M^{2+}) the typical ^{29}Si NMR resonance for Q^4 is around -110 ppm, with FWHM between 7–13 ppm. Introducing each additional NBO results in Q^n to Q^{n-1} conversions, which can be observed by the downfield shifting by between 9 and 12 ppm in the ^{29}Si NMR spectrum (Edén, 2012). Typical ranges of the ^{29}Si chemical shifts for the various $\text{Si}(\text{O})_{4-n}(\text{OSi})_n$ and $\text{Si}(\text{OSi})_{4-m}(\text{OAl})_m$ (m = numbers of bridging oxygen atoms associated with Al) units in glass has been well established (Uhlir and Marsman, 2008). The quantity information of each Q^n species can be acquired by spectral deconvolution, and Gaussian peak shapes are normally applied. In binary silicate glass networks, the relative Q^n populations and BO and NBO species among its tetrahedral structures can be derived from ^{29}Si NMR experiment. Linear relationships between $1/R$ (R = radius of cation) and the ^{29}Si FWHM of each Q^n structure are reported (Murdoch and Stebbins, 1985; Maekawa *et al.*, 1991; Malfait *et al.*, 2007). Intensive studies have been carried out on the BO/NBO effect (Eckert *et al.*, 1989; Szu *et al.*, 1992; Cong *et al.*, 1993; MacKenzie *et al.*, 1994; Sen and Stebbins, 1995; Bhasin *et al.*, 1998; Schneider *et al.*, 2000, 2003; Shrikhande *et al.*, 2001; Takaishi *et al.*, 2005; Malfait *et al.*, 2007). There are two models: (1) a binary distribution model, where two tetrahedral units, Q^n and Q^{n+1} coexist in the network, where the fractional populations $X_n + X_{n+1} = 1$, (2) a random distribution, implying the statistical sharing of the NBO ions among the tetrahedra, for which the mathematical expressions are described by Edén *et al.* (2011). Some research providing high-quality NMR spectra confirms that BO/NBO distribution is close to a binary distribution but with some elements of a random distribution (Dupree *et al.*, 1986; Stebbins, 1987; Grimmer *et al.*, 1988). Because of this randomness in the glass structure, the number of Q^n species is increased. This broadens the distribution of Si-O bond lengths and Si-O-Si bond angles for each species, which causes the loss of NMR spectral resolution (Dupree *et al.*, 1986; Schneider *et al.*, 2000, 2003). Spectral resolution degradation also occurs when the alkaline-earth content is increased, or additional network formers (B or Al) are introduced (Schneider *et al.*, 2000; Schneider *et al.*, 2003). Certain binary silicate glass systems, such as Rb and Cs silicate glasses, have limited ^{29}Si NMR resolution for distinct Si sites. However, the signal can be enhanced by increasing the alkali content up to 50 mol% (Malfait *et al.*, 2007; Dupree *et al.*, 1986).

(2) Phosphorus-31 NMR Spectra

With a moderately large magnetic moment, ^{31}P provides a favorable sensitivity for NMR experiments. It can be used to analyze short-range structures around the nucleus, because of the correlations between anisotropic chemical shift and structural features. From previous studies (Roufosse *et al.*, 1984; Aue *et al.*, 1984; Miquel *et al.*, 1990a,b; Wu *et al.*, 1994; Grossmann *et al.*, 2000; Oliveira *et al.*, 2000; Hartmann *et al.*, 2001; Kolodziejski and Klinowski, 2002; Jaeger *et al.*, 2005; Tseng *et al.*, 2006; Tsai *et al.*, 2008; Marti-Muñoz *et al.*, 2019), it is well known that the values of the ^{31}P chemical shift

anisotropy varies with different Q^n -group structural units in solid phosphates, either crystalline or amorphous. The isotropic chemical shift also correlates with the field strength of the cations around the phosphate anions. Thus, the isotropic chemical shift parameters can be used to investigate the relationship between cations and the PO_4 -tetrahedra (Griffin *et al.*, 1990; Miquel *et al.*, 1990a,b).

There are substantial studies related to ceramic structures being investigated by ^{31}P NMR. Different ^{31}P pulse sequences including proton-decoupled Bloch decay, cross-polarization (CP), and dipolar suppression techniques are employed to study hydroxyapatite and carbonate-hydroxyapatite (Aue *et al.*, 1984). The different pulse sequences alter the contribution of specific types of PO_4 tetrahedra (Roufosse *et al.*, 1984). In ^{31}P CP MAS NMR experiments, the spinning frequency is set to 4.2 kHz. The ^{31}P resonance at 2.9 ppm assigned to PO_4^{3-} groups and two weaker shoulder peaks at 5.4 and 0.8 ppm which were respectively assigned to unprotonated PO_x and protonated PO_x (Aue *et al.*, 1984; Griffin *et al.*, 1990; Miquel *et al.*, 1990a,b; Wu *et al.*, 1994). CP experiments show that it is possible to detect the presence of phosphoproteins in bone at the very earliest stages of bone mineralization. CP experiments also can be used to monitor the formation of an initially amorphous calcium phosphate layer and its subsequent crystallization into hydroxycarbonate apatite, and such a method provides a valuable criterion for the design of osseointegration biomaterials (Wu *et al.*, 1998; Cassella *et al.*, 2000).

Advanced double-resonance NMR experiments combined with X-ray powder diffraction can be used to identify the chemical composition of crystallization intermediates, and to study crystallization mechanisms in glasses (Chan *et al.*, 2001). The Rotational Echo Double Resonance (REDOR) experiment allows quantitative determination of the dipolar coupling. For example, in ^{13}C - $\{^{31}P\}$ REDOR experiment, it makes a quantitative determination of the ^{13}C - ^{31}P distance possible. This is very useful for study of bone tissue since ^{13}C nuclei are very largely found in the organic matrix while ^{31}P spins are very largely confined to the inorganic component. Thus any ^{13}C - ^{31}P distances in the bone structure are relevant to the organic-inorganic interface (Jaeger *et al.*, 2005).

Structural features of silica-phosphate glasses and glass-ceramics have been studied by ^{31}P MAS NMR (Yang *et al.*, 1986; Oliveira *et al.*, 2000; Yan *et al.*, 2001; Chan *et al.*, 2001; Stamboulis *et al.*, 2004; Kharlamova *et al.*, 2008; Tsai *et al.*, 2008; Dietrich *et al.*, 2009; Mason *et al.*, 2009; Brauer *et al.*, 2010; Mneimne *et al.*, 2011; Bradtmüller, 2019). These researchers have found that the introduction of phosphorus in to alkaline-earth silicate glasses increases the degree of polymerization of the silicate network (Yang *et al.*, 1986).

(3) Fluorine-19 NMR Spectra

^{19}F NMR is widely used in many fields because the F nucleus has experimental advantages. It has spin one-half, and fluorine chemical shifts are highly sensitive to the local environment, which is due to an F ion normally surrounded by eight electrons. This full occupation of 2s-2p orbitals yields more information about the fluorine's neighborhood than hydrogen which only has a single electron. This facilitates the study of the structure and dynamics in fluorine compounds.

^{19}F NMR has been extensively used to study fluoride substituted apatite ($Ca_{10}(PO_4)_6(OH/F)_2$) (FHA) (White *et al.*, 1988; Kreinbrink *et al.*, 1990; Cho and Yesinowski, 1996; Rafferty *et al.*, 2004; Mason *et al.*, 2009). It occurs naturally in tooth enamel. In the inorganic apatite component, F ions replace OH^- ions to a level as high as 50 mol% (Mason *et al.*, 2009). In bone, approximately 1 wt% F can be found in the inorganic component. The natural FHA provides low solubility and good acid resistance to the enamel surface. In bone, it helps prevent reductions in bone density. Due to these biological benefits, FHA can be utilized as an implant material for bone and dental restoration. The fluoridation level of FHA is crucial in biomedical applications. This is because the different fluorine contents have major effects on the crystallization, solubility and thermal stability of the bulk apatitic material. The ^{19}F MAS NMR is the most and only reliable technique to detect fluoride substitution in apatite. This is because FHA has a similar crystal lattice to hydroxyapatite. They both belong to the hexagonal crystal system with space group $P6_3/m$. The only difference is that along the c axis, F atoms substitute for OH groups. The ionic radii of the OH^- and F^- are very close, which are 1.68 and 1.32 Å, respectively (Braun and Jana, 1995a). Thus, apart from a contraction of the c -axis in the lattice structure, there are no significant crystallographic dimensional changes. This structural similarity causes a major challenge in determining the fluoridation levels of FHA using Powder X-ray Diffraction (PXRD) solely. Besides, detection of the light elements such as F, O and H is known to be problematic for PXRD. Crystallographic studies of F substituted hydroxyapatite have been carried out previously, it found the (002) peak of FHA is shifted toward the lower angle and (300) peak is shifted toward the higher angle, also (211) and (112) peaks show merging and overlapping to each other (Braun *et al.*, 1995b; Jana and Braun, 1996). That XRD pattern analysis merely proved that the F^- ion incorporation in the c -channel in the apatite structure and the F/OH solid solution formation. Fourier transform infrared spectroscopy (FTIR) has found that F^- substituted OH^- results in the OH^- vibrational mode at 631 cm^{-1} shifting to higher wavenumbers at 747 cm^{-1} depending on the number of OH^- groups in the positions between each F^- position (Freund *et al.*, 1977; Barinov *et al.*, 2004). Other techniques such as Energy Dispersive X-ray Spectroscopy (EDS) and Atom Probe Tomography (APT) can be used to quantify the amount of F in the samples but they fail to distinguish the different chemical environments of F (Mitric *et al.*, 2004; Rodriguez-Lorenzo, *et al.*, 2003; Bachhav *et al.*, 2013). So ^{19}F MAS NMR is one of the few techniques available that can unambiguously qualify and quantify analyses of fluoridated apatite, whether the solid is crystalline or amorphous. In Gao's paper (Gao *et al.*, 2016), a series of FHA with various fluoridation levels from 0% to 200% were studied by PXRD, FTIR, ^{31}P and ^{19}F MAS NMR. A non-linear relation between ^{19}F NMR chemical shift and fluorine substitution level has been found. With increasing F contents, the ^{19}F CS shifts from -104 to -106 ppm. ^{19}F MAS

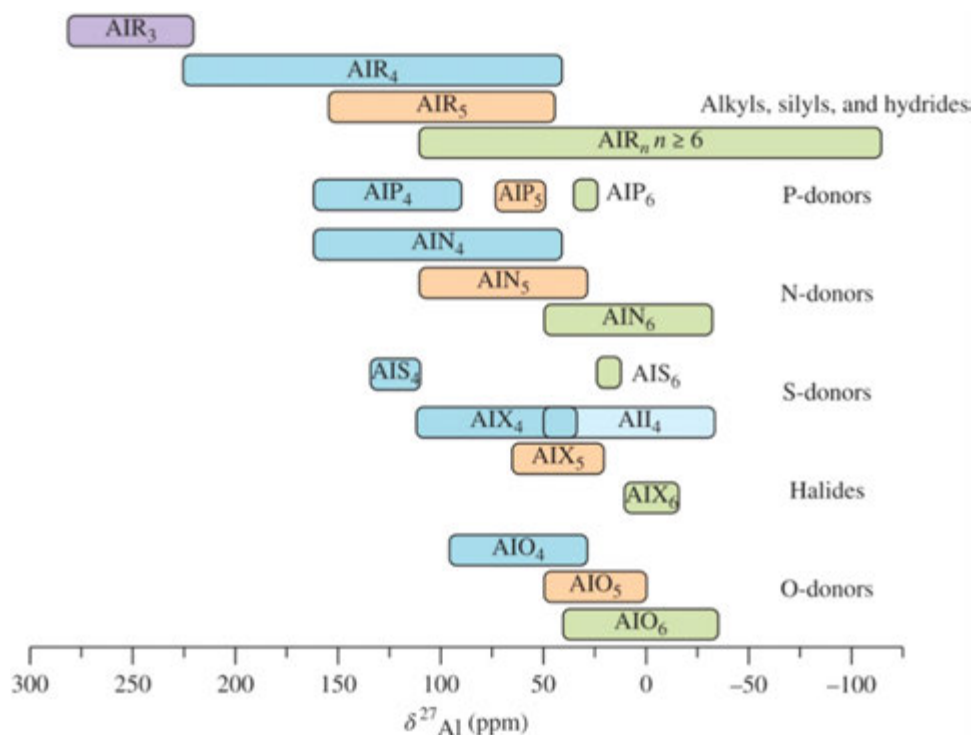


Fig. 4 ^{27}Al chemical shift range (green represents the coordination number six or higher, orange coordination number five, blue four and purple three). Reproduced with permission from Martineau, C., *et al.*, 2016. The use of ^{27}Al NMR to study aluminum compounds: A survey of the last 25 years. In: Patai's Chemistry of Functional Groups. John Wiley & Sons, Ltd. Copyright (2009–2016), John Wiley & Sons, Ltd.

NMR also can be used to distinguish the level of crystallinity for the environment F^- in of FA. When F⁻ is in a low degree of crystallinity environment, the ^{19}F CS occurs at -103 ppm, while if it is in the high crystallinity environment, the ^{19}F MAS NMR resonance arises at -102 ppm.

Braun and Jana's (1995a) work also found a correlation between ^{19}F chemical shift and the F content in the apatite. In Mason's work (Mason *et al.*, 2009), a second ^{19}F resonance was observed and this corresponded to a second F environment in the apatite structure at a concentration similar to that of B-type carbonate. In 2013, Yi *et al.* (2013) proved that this additional ^{19}F signal corresponds to isolated fluoride ions in the apatite structure, which is close to the substituted carbonate group.

(4) Aluminum-27 NMR Spectra

^{27}Al has 100% natural abundance with a nuclear spin 5/2, making it a quadrupole nucleus. Quadrupolar nuclei ($I > 1/2$) is classified into those with integer spins (1, 3 etc.) and half-integer spins (3/2, 5/2 etc.). For example, deuterium (^2H) and nitrogen (^{14}N) have nuclear spin 1, and ^{10}B has nuclear spin 3; spin 3/2 are ^{17}O and ^{23}Na , 5/2 are ^{25}Mg and ^{27}Al , 7/2 are ^{59}Co and ^{43}Ca , and 9/2 are ^{87}Sr and ^{93}Nb . 75% of NMR active nuclei are quadrupolar (Duer, 2002), and they are dominant in several molecular systems ranging from porous materials, ceramics and glasses, to superconductors and biological systems such as nucleic acids and proteins (Engelhardt, 1989).

Quadrupolar nuclei not only possess a magnetic dipole moment, they also have an electric quadrupole moment. This electric quadrupole moment interacts with the electric field gradient. The size of the electric field gradient is determined by the molecular and electronic structure around the nucleus, or more precisely, it depends on the orientation of the molecule with respect to the applied magnetic field, which is anisotropic. The interaction can be rather large, resulting in powder patterns of megahertz in width for non-cubic symmetric solid samples. Typically, the quadrupolar interactions vary from a few kHz to a few MHz leading up to 2000–3000 MHz in the case of ^{127}I (Martineau *et al.*, 2016). Apart from the line broadening arising from the interaction between the quadrupole moment and the electric field gradient, the complexity in spin dynamics due to the presence of more than two energy levels has also impeded the routine study of quadrupolar nuclei (Tsai *et al.*, 2008). The established spin-1/2 techniques, such as magic-angle-spinning (MAS) and cross polarization (CP), do not always provide isotropic high resolution spectra in quadrupolar systems (Martineau *et al.*, 2016).

^{27}Al is a useful tool for structural characterization of numerous crystalline or amorphous Al-containing ceramics and glasses. ^{27}Al chemical shifts cover a range of resonances from -100 to 300 ppm relative to the chosen reference, $\text{Al}(\text{H}_2\text{O})_6^{3+}$, at 0 ppm (Martineau *et al.*, 2016). The coordination number of aluminum can be revealed by the chemical shift (see Fig. 4). In general, aluminum atoms with lower coordination numbers are at the downfield part of the spectrum. For example Al(III) is in the

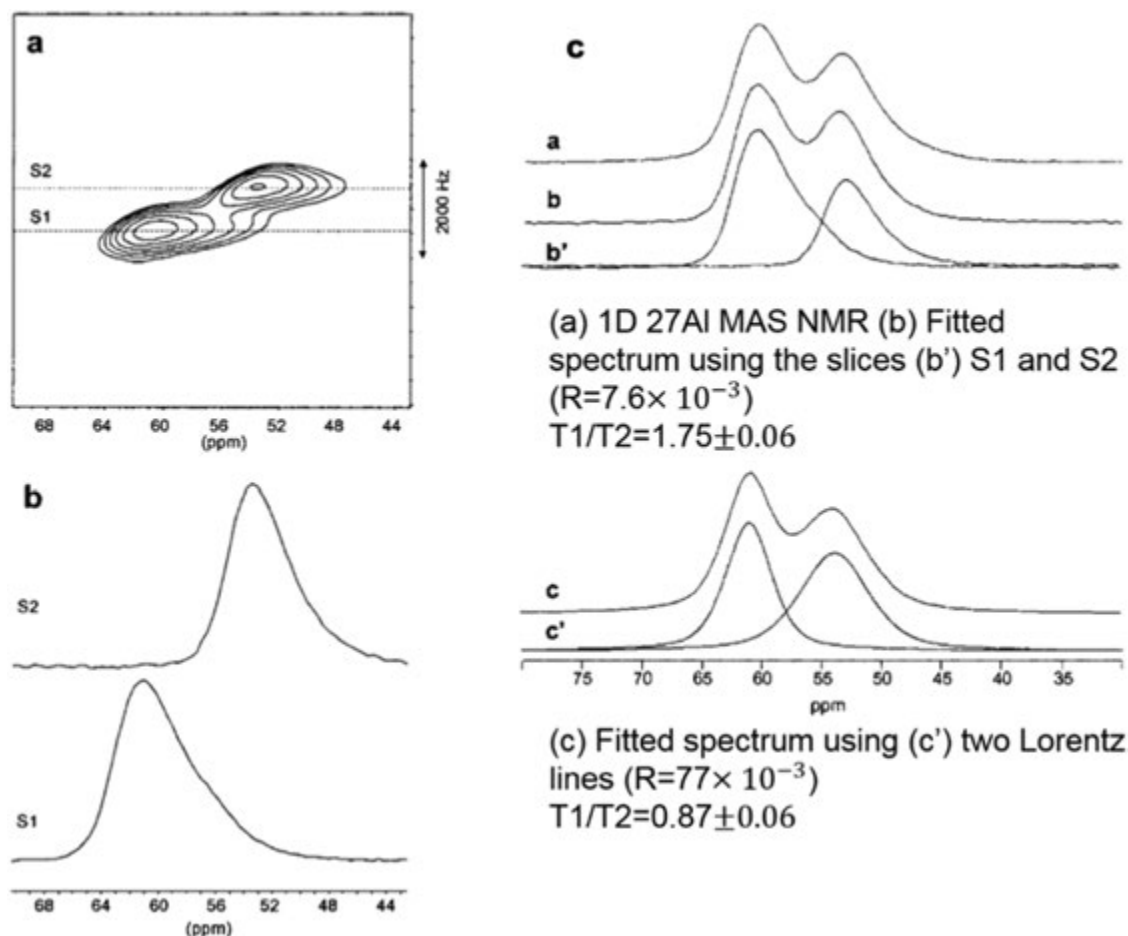


Fig. 5 (a) 2D ^{27}Al 3Q MAS NMR spectrum of a mazzite zeolite sample (b) 1D projection of the slices S1 and S2 (c) 1D ^{27}Al MAS NMR of mazzite zeolite sample and the fitting comparison of using Lorentz lines and 3Q MAS NMR spectrum. Reproduced with permission from Pike, K.J., *et al.*, 2000. Multiple-quantum MAS NMR of quadrupolar nuclei. Do five-, seven- and nine-quantum experiments yield higher resolution than the three-quantum experiment. *Solid State Nuclear Magnetic Resonance* 16, 203–215. Copyright (1999), American Chemical Society. Wouters, B.H., *et al.*, 1999. Determination of the $\text{Al}^{\text{T1}}/\text{Al}^{\text{T2}}$ ratio in MAZ zeolites using line shapes of MQ MAS NMR. *Journal of Physical Chemistry B*, 103 (38), 8093–8096.

range between 300 to 250 ppm. With increasing coordination number, the ^{27}Al chemical shift shifts to the up-field which is lower and negative values of δ as shown in detail in Fig. 4. (Martineau *et al.*, 2016).

As ^{27}Al is a quadrupolar nucleus, the NMR pulse program for $1/2$ spins is not necessarily straightforward. Several techniques have been developed to deal with quadrupolar nuclei with a broad central transition such as DAS (dynamic angle spinning), MQMAS (multiple-quantum magic-angle spinning) and STMAS (Satellite transitions magic-angle spinning). More structural information can be obtained from MQMAS NMR spectra, such as the relative distance between the Al nucleus and other nuclei (^{27}Al , ^{29}Si and ^1H) (Edén, 2012).

The high-resolution NMR experiment MQMAS, introduced by Frydman in 1995 (Baltisberger *et al.*, 1996), has greatly extended the use of NMR for half-integer quadrupolar spins. MQMAS is a 2D solid state MAS NMR experiment, which separates quadrupolar from chemical-shift interactions by observing them differently, along with two different directions in the frequency domain. Under MAS conditions, the vertical dimension F1 is the isotropic indirect spectral dimension and the direct horizontal dimension F2 corresponds to the central transition. The projection of the resonance onto the F1 is free from anisotropic line broadening, therefore, the F1 dimension is well resolved. For quadrupolar nuclei with nuclear spin $I > 3/2$, 3QMAS ($-3/2 \rightarrow -3/2$ transition), this is the most used approach. Higher order 5QMAS can offer better signal separation, but at the price of a significant loss of efficiency (Amoureux and Fernandez, 1998; Fernandez and Amoureux, 1995; Wouters *et al.*, 1999).

Zeolites are a unique class of porous solid aluminosilicates. Structural studies of zeolites attracts much attention due to their stability and catalytic activity with high selectivity, which makes them an ideal catalyst materials. ^{27}Al MAS NMR can offer aluminum coordination information. However, it fails to resolve sites with similar environments. ^{27}Al MQMAS provides good resolution for the various ^{27}Al sites and becomes a useful tool for structural characterization of zeolites. Fig. 5 was published by Wouters *et al.* (1999); Pike (2000). They studied a mazzite zeolite with ^{27}Al 3QMAS spectra. There are two crystallographically distinct tetrahedral sites, T1

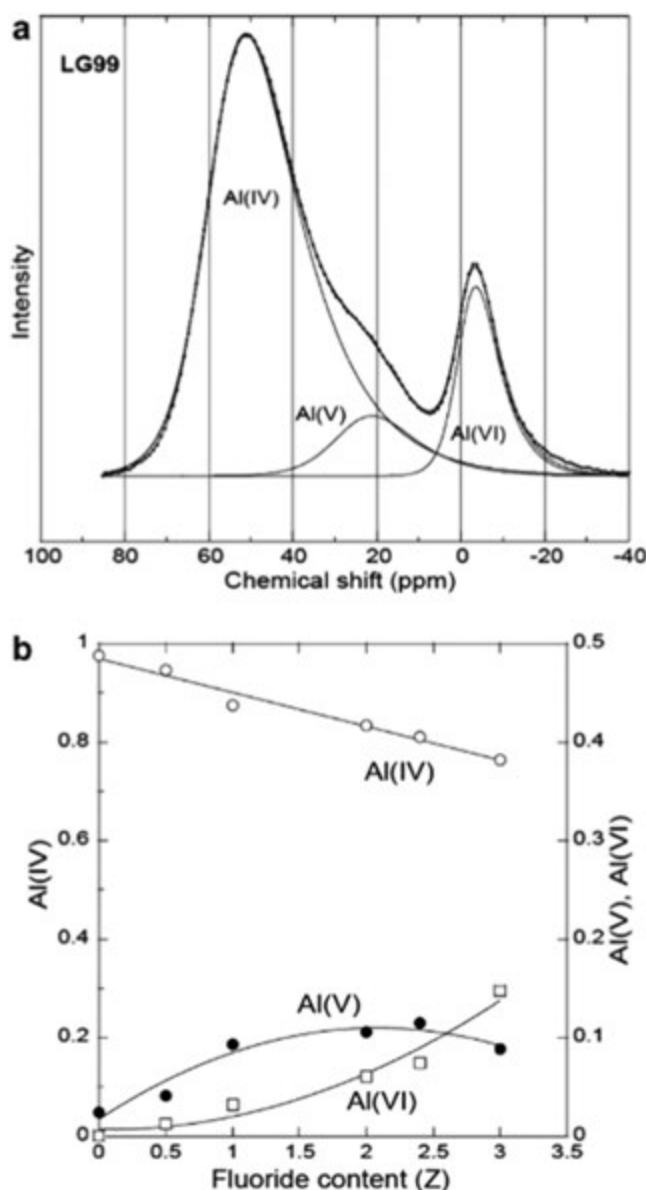


Fig. 6 (a) ^{27}Al MAS NMR spectrum and deconvolution of Al (IV), Al (V) and Al(VI) for a $4.5\text{SiO}_2\text{-}3\text{Al}_2\text{O}_3\text{-}1.5\text{P}_2\text{O}_5\text{-(}5\text{-z)}\text{CaO-zCaF}_2$ glass and (b) relationship between the fraction of each Al coordination number and fluoride content of the glass. Reproduced with permission from Matsuya, S., *et al.*, 2007. Structural characterization of ionomer glasses by multinuclear solid state MAS NMR spectroscopy. *Journal of Non-Crystalline Solids* 353 (3), 237–243. Copyright (2006), Elsevier B.V.

and T2, into which Al can be incorporated. The $\text{Al}_{\text{T1}}/\text{Al}_{\text{T2}}$ ratio can be determined by Lorentzian line fitting the 1D ^{27}Al MAS NMR. However, two tetrahedral Al lines showed substantial narrowing with increasing magnetic field from 9.4 to 14.1 T (Engelhardt, 1989). This indicated that quadrupolar interactions have an impact on the NMR line shapes. So instead of using Lorentzian-Gaussian line shapes, slices S1 and S2 from MQMAS were used to deconvolute the 1D MAS spectrum (Fig. 5(C)), which not only resulted in the different Al distribution ($\text{T1}/\text{T2}$) also much better fit ($R = 7.6 \times 10^{-3}$).

A bioactive glass based on $\text{Na}_2\text{O-CaO-SiO}_2\text{-P}_2\text{O}_5$ system was developed by Hench in 1971 (Hench and Paschall, 1973). It showed excellent biocompatibility and bone bonding ability. By modifying the glass compositions, the ion release rate, degradation rate and bonding affinity of bioactive glass can be adjusted to facilitate bone tissue engineering (Kirkpatrick and Brow, 1995; Chan *et al.*, 2001; Brauer *et al.*, 2009; Mathew *et al.*, 2011; Pedone *et al.*, 2012). Combining ^{27}Al , ^{19}F , ^{29}Si and ^{31}P MAS NMR is a comprehensive way to characterise the structure of bioactive glasses (Baltisberger *et al.*, 1996; Karpukhina *et al.*, 2007). Matsuya *et al.* (2007) studied $4.5\text{SiO}_2\text{-}3\text{Al}_2\text{O}_3\text{-}1.5\text{P}_2\text{O}_5\text{-(}5\text{-z)}\text{CaO-zCaF}_2$ ($z = 0\text{--}3$) glasses using ^{27}Al , ^{31}P , ^{19}F , and ^{29}Si . Three resonances were de-convoluted from ^{27}Al MAS NMR spectra, including an asymmetric broad peak at 50 ppm, a shoulder peak at 30 ppm and a small peak at -5 ppm (Fig. 6(a)). These corresponded to Al(IV), Al(V) and Al(VI), respectively. Furthermore, on the basis of this

structural analysis, a correlation between Al coordination numbers and F content was discovered (see Fig. 6(b)). It was found that the proportion of Al(IV) decreased linearly with increasing F content. Al(V) increased with fluoride content up to $z = 1$ then became almost constant between $z = 1$ –3. The proportion of Al(VI) increased with increasing fluoride content $z \geq 1$ (Matsuya *et al.*, 2007). This data showed that as fluorine substituted for oxygen in the glass then more aluminum was present in the glass as a modifier {Al(V), Al(VI)}.

Outlook

Thanks to the advancement of hardware and methodology in MAS NMR, significant progress has been achieved on the understanding of the structure of ceramics and glasses. Apart from the ^{29}Si , ^{31}P , ^{19}F , and ^{27}Al MAS NMR, ^{13}C , ^{43}Ca , ^{25}Mg and ^{17}O analyses have also proved to be feasible techniques for structure characterization. However, ^{43}Ca , ^{25}Mg and ^{17}O have low-gamma half integer quadrupole nuclei, and so sensitivity is an issue for the application of MAS NMR to them. Further development of the signal enhancement techniques is required, such as dynamic nuclear polarization (DNP) (Griffin *et al.*, 2010).

Appendix A Supplementary material

Supplementary data associated with this chapter can be found in the online version at doi:10.1016/B978-0-12-818542-1.00058-8.

References

- Amoureux, J., Fernandez, C., 1998. Triple, quintuple and higher order multiple quantum MAS NMR of quadrupolar nuclei. *Solid State Nuclear Magnetic Resonance* 10, 211–223.
- Ashbrook, S.E., Duer, M.J., 1995. Structural information from quadrupolar nuclei in solid state NMR. *Concepts In Magnetic Resonance* 28, 155–179.
- Aue, W.P., *et al.*, 1984. Solid-state phosphorus-31 nuclear magnetic resonance studies of synthetic solid phases of calcium phosphate: potential models of bone mineral. *Biochemistry* 23 (25), 6110–6114.
- Bachhav, M.N., *et al.*, 2013. Quantitative compositional analysis of fluorhydroxyapatite by atom probe. *Microscopy and Microanalysis* 19 (Suppl 2), 2012–2013.
- Baltisberger, J.H., *et al.*, 1996. Nuclear magnetic resonance spectroscopic study of aluminosilicate and aluminate crystals and glasses. *Journal of American Chemistry society* 118 (15), 7209–7214.
- Barinov, S.M., *et al.*, 2004. Solid solution formation at the sintering of hydroxyapatite-fluorapatite ceramics. *Science and Technology of Advanced Materials* 5, 537–541.
- Bhasin, G., *et al.*, 1998. Short range order in sodium borosilicate glasses obtained via deconvolution of ^{29}Si MAS NMR spectra. *Physics and Chemistry of Glasses* 39 (5), 269–274.
- Bradt Müller, H., *et al.*, 2019. Structural characterization of boron-containing glassy and semi-crystalline Biosilicate® by multinuclear NMR. *Journal of Non-Crystalline Solids* 505, 390–399.
- Brauer, D.S., *et al.*, 2009. Structure of fluoride-containing bioactive glasses. *Journal of Materials Chemistry* 19 (31), 5629–5636.
- Brauer, D.S., *et al.*, 2010. Fluoride-containing bioactive glasses: Effect of glass design and structure on degradation, pH and apatite formation in simulated body fluid. *Acta Biomaterialia* 6 (8), 3275–3282.
- Braun, M., Jana, C., 1995a. ^{19}F NMR spectroscopy of fluoridated apatites. *Chemical Physics Letters* 245 (1), 19–22.
- Braun, M., Hartmann, P., Jana, C., 1995b. ^{19}F and ^{31}P NMR spectroscopy of calcium apatites. *Journal of Materials Science: Materials in Medicine* 6 (3), 150–154.
- Cassella, J.P., Barrie, P.J., Garrington, N., Ali, S.Y., 2000. A Fourier transform infrared spectroscopic and solid-state NMR study of bone mineral in osteogenesis imperfecta. *Journal of Bone and Mineral Metabolism* 18, 291–296.
- Chan, J.C.C., *et al.*, 2001. Apatite crystallization in an aluminosilicate glass matrix: Mechanistic studies by X-ray powder diffraction, thermal analysis, and multinuclear solid-state NMR spectroscopy. *Chemistry of Materials* 13 (11), 4198–4206.
- Cho, G., Yesinowski, J.P., 1996. ^1H and ^{19}F multiple-quantum NMR dynamics in quasi-one-dimensional spin clusters in apatites. *Journal of Physical Chemistry* 100 (39), 15716–15725.
- Cong, X.D., Kirkpatrick, R.J., Diamond, S., 1993. ^{29}Si MAS NMR spectroscopic investigation of alkali silica reaction product gels. *Cement and Concrete Research* 23 (4), 811–823.
- Dietrich, B.E., *et al.*, 2009. In vitro chemical reactivity of doped bioactive glasses: An original approach by solid-state NMR spectroscopy. *Advanced Engineering Materials* 8, 98–105.
- Duer, M.J., 2002. *Solid-State NMR Spectroscopy Principles and Applications*. Blackwell Science Ltd.
- Dupree, R., Holland, D., Williams, D.S., 1986. The structure of binary alkali silicate glasses. *Journal of Non-Crystalline Solids* 81, 185–200.
- Eckert, H., *et al.*, 1989. Structural transformation of thiosilicate glasses: ^{29}Si MAS NMR evidence for edge-sharing in the system $\text{Li}_2\text{S-SiS}_2$. *Journal of Non-Crystalline Solids* 113 (2–3), 287–293.
- Edén, M., 2012. NMR studies of oxide-based glasses. *Annual Reports on the Progress of Chemistry – Section C* 108, 177–221.
- Edén, M., Sundberg, P., Stalhandske, C., 2011. The split network analysis for exploring composition-structure correlations in multi-component glasses: ii. multinuclear NMR studies of aluminoborosilicates and glass-wool fibers. *Journal of Non-Crystalline Solids* 357 (6), 1587–1594.
- Engelhardt, G., 1989. Multinuclear solid-state NMR in silicate and zeolite Chemistry. *Trends in Analytical Chemistry* 8 (9), 343–347.
- Fernandez, C., Amoureux, J.P., 1995. 2D multiquantum MAS NMR spectroscopy of ^{27}Al in aluminophosphate molecular sieves. *Chemical Physics Letters* 242, 449–454.
- Freund, F., *et al.*, 1977. Distribution of fluorine in hydroxyapatite studied by infrared spectroscopy. *Dalton Transactions* 1136, 1136–1140.
- Gao, Y., Karpukhina, N., Law, R.V., 2016. Phase segregation in hydroxyfluorapatite solid solution at high temperatures studied by combined XRD/solid state NMR. *RSC Advances* 6 (105), 103782–103790.
- Griffin, R.G., *et al.*, 1990. Solid State Carbon-13 and Proton NMR Studies of carbonate containing calcium phosphates and enamel. *Journal of Solid State Chemistry*. 71–81.
- Griffin, R.G., *et al.*, 2010. Solid-state dynamic nuclear polarization at 263 GHz: Spectrometer design and experimental results. *Physical Chemistry Chemical Physics* 12, 5850–5860.
- Grimmer, A., *et al.*, 1988. ^{29}Si -MAS NMR investigation on silica glass prepared by the drying control chemical additives method. *Journal of Non-Crystalline Solids* 99, 371–378.

- Grossmann, G., *et al.*, 2000. Solid-state NMR of bisphosphonates adsorbed on hydroxy apatite. *Magnetic Resonance in Chemistry* 38 (1), 11–16.
- Hartmann, P., *et al.*, 2001. Solid state NMR, X-ray diffraction, and infrared characterization of local structure in heat-treated oxyhydroxyapatite microcrystals: An analog of the thermal decomposition of hydroxyapatite during plasma-spray procedure. *Journal of Solid State Chemistry* 160 (2), 460–468.
- Hench, L.L., Paschall, H.A., 1973. Direct chemical bond of bioactive glass-ceramic materials to bone and muscle. *Journal of Biomedical Materials Research* 7 (3), 25–42.
- Hendrick, R.E., 2008. *Breast MRI: Fundamentals and Technical Aspects*. Springer.
- Iggo, J.A., 2000. *NMR Spectroscopy in Inorganic Chemistry*. Oxford Chemistry Primers.
- Jaeger, C., *et al.*, 2005. Investigation of the nature of the protein-mineral interface in bone by solid-state NMR. *Chemistry of Materials* 17 (12), 3059–3061.
- Jana, C., Braun, M., 1996. ^{19}F NMR spectroscopy of glass ceramics containing fluorapatites. *Biomaterials* 17 (21), 2065–2069.
- Karpukhina, N.G., *et al.*, 2007. Preferential binding of fluorine to aluminum in high peccalkaline aluminosilicate glasses. *Journal of Physical Chemistry B* 111 (35), 10413–10420.
- Keeler, J., 2010. *Understanding NMR Spectroscopy*, second ed. John Wiley & Sons.
- Kharlamova, T., *et al.*, 2008. Low-temperature synthesis and characterization of apatite-type lanthanum silicates. *Solid State Ionics* 179 (21–26), 1018–1023.
- Kirkpatrick, R.J., Brow, R.K., 1995. Nuclear magnetic resonance investigation of the structures of phosphate and phosphate-containing glasses: a review. *Solid State Nuclear Magnetic Resonance* 5 (1), 9–21.
- Kolodziejki, W., Klinowski, J., 2002. Kinetics of cross-polarization in solid-state NMR: A guide for chemists. *Chemical Reviews* 102 (3), 613–628.
- Kreinbrink, A.T., *et al.*, 1990. Fast-magic-angle-spinning ^{19}F NMR of inorganic fluorides and fluoridated apatitic surfaces. *Journal of Magnetic Resonance* (1969) 88 (2), 267–276.
- Lippmaa, E., *et al.*, 1980. Structural studies of silicates by solid-state. *Journal of American Chemistry society of America* 102 (15), 4889–4893.
- MacKenzie, J.W., *et al.*, 1994. ^{29}Si MAS NMR study of the short range order in alkali borosilicate glasses. *Journal of Non-Crystalline Solids* 177 (C), 269–276.
- Maekawa, H., *et al.*, 1991. The structural groups of alkali silicate glasses determined from ^{29}Si MAS NMR. *Journal of Non-Crystalline Solids* 127 (1), 53–64.
- Malfait, W.J., *et al.*, 2007. Structural control on bulk melt properties: Single and double quantum ^{29}Si NMR spectroscopy on alkali-silicate glasses. *Geochimica et Cosmochimica Acta* 71 (24), 6002–6018.
- Marti-Muñoz, J., *et al.*, 2019. Feasible and pure P_2O_5 -CaO nanoglasses: An in-depth NMR study of synthesis for the modulation of the bioactive ion release. *Acta Biomaterialia* 94, 574–584.
- Martineau, C., *et al.*, 2016. The use of ^{27}Al NMR to study aluminum compounds: A survey of the last 25 years. In *Patai's Chemistry of Functional Groups*. John Wiley & Sons, Ltd.
- Mason, H.E., *et al.*, 2009. Solid-state NMR and IR spectroscopic investigation of the role of structural water and F in carbonate-rich fluorapatite. *American Mineralogist* 94 (4), 507–516.
- Mathew, R., *et al.*, 2011. Solid-state ^{31}P and ^1H NMR investigations of amorphous and crystalline calcium phosphates grown biomimetically from a mesoporous bioactive glass. *Journal of Physical Chemistry C* 115 (42), 20572–20582.
- Matsuya, S., *et al.*, 2007. Structural characterization of ionomer glasses by multinuclear solid state MAS NMR spectroscopy. *Journal of Non-Crystalline Solids* 353 (3), 237–243.
- Miquel, J.L., Facchini, L., Legrand, A.P., *et al.*, 1990a. Characterisation and conversion study into natural living bone of calcium phosphate bioceramics by solid state NMR spectroscopy. *Clinical Materials* 5 (2–4), 115–125.
- Miquel, J.L., Facchini, L., Legrand, A.P., Rey, C., Lemaître, J., 1990b. Solid state NMR to study calcium phosphate ceramics. *Colloids and Surfaces* 45 (C), 427–433.
- Mitric, M., *et al.*, 2004. Mechanochemical synthesis of nanostructured fluorapatite/fluorhydroxyapatite and carbonated fluorapatite/fluorhydroxyapatite. *Journal of Solid State Chemistry* 177, 2565–2574.
- Mneimne, M., *et al.*, 2011. High phosphate content significantly increases apatite formation of fluoride-containing bioactive glasses. *Acta Biomaterialia* 7 (4), 1827–1834.
- Murdoch, I.B., Stebbins, J.F., 1985. Carmichael, I.S.E., High-resolution ^{29}Si NMR study of silicate and aluminosilicate glasses: the effect of network-modifying cations. *American Mineralogist* 70, 332–343.
- Oliveira, J.M., *et al.*, 2000. Influence of the CaO/MgO ratio on the structure of phase-separated glasses: A solid state ^{29}Si and ^{31}P MAS NMR study. *Journal of Non-Crystalline Solids* 265, 221–229.
- Paralla, T., 1998. eNMR NMR periodic table. BRUKER Biospin. Available at: <http://triton.iqfr.csic.es/guide/eNMR/chem/NMRnuclei.html>.
- Pedone, A., *et al.*, 2012. The structure of fluoride-containing bioactive glasses: New insights from first-principles calculations and solid state NMR spectroscopy. *Journal of Materials Chemistry* 22 (25), 12599–12608.
- Pike, K.J., *et al.*, 2000. Multiple-quantum MAS NMR of quadrupolar nuclei. Do five-, seven- and nine-quantum experiments yield higher resolution than the three-quantum experiment. *Solid State Nuclear Magnetic Resonance* 16, 203–215.
- Rafferty, A., *et al.*, 2004. Influence of fluorine content in apatite-mullite glass-ceramics. *Journal of the American Ceramic Society* 83 (11), 2833–2838.
- Rankin, N.J., *et al.*, 2014. The emergence of proton nuclear magnetic resonance metabolomics in the cardiovascular arena as viewed from a clinical perspective. *Atherosclerosis* 237 (1), 287–300. doi:10.1016/j.atherosclerosis.2014.09.024.
- Rodriguez-Lorenzo, L.M., Hart, J.N., Gross, K.A., 2003. Influence of fluorine in the synthesis of apatites. Synthesis of solid solutions of hydroxy-fluorapatite. *Biomaterials* 24, 3777–3785.
- Roufosse, A.H., *et al.*, 1984. Investigation of the mineral phases of bone by solid-state phosphorus-31 magic angle sample spinning nuclear magnetic resonance. *Biochemistry* 23 (25), 6115–6120.
- Schneider, J., *et al.*, 2000. ^{29}Si MAS NMR studies of Qn structural units in metasilicate glasses and their nucleating ability. *Journal of Non-Crystalline Solids* 273 (1–3), 8–18.
- Schneider, J., *et al.*, 2003. Qn distribution in stoichiometric silicate glasses: Thermodynamic calculations and ^{29}Si high resolution NMR measurements. *Journal of Non-Crystalline Solids* 325 (1–3), 164–178.
- Sen, S., Stebbins, J.F., 1995. Structural role of Nd^{3+} and Al^{3+} cations in SiO_2 glass: A ^{29}Si MAS NMR spin-lattice relaxation, ^{27}Al NMR and EPR study. *Journal of Non-Crystalline Solids* 188 (1–2), 54–62.
- Shrikhande, V.K., *et al.*, 2001. ^{29}Si MAS NMR and microhardness studies of some lead silicate glasses with and without modifiers. *Journal of Non-Crystalline Solids* 283 (1–3), 18–26.
- Stamboulis, A., *et al.*, 2004. MAS NMR study of the crystallisation process of apatite-mullite glass ceramics. *Physics and Chemistry of Glasses* 45 (2), 127–133.
- Stebbins, J.F., 1987. Identification of multiple structural species in silicate glasses by ^{29}Si NMR. *Nature* 330 (6147), 465–467. doi:10.1038/330465a0.
- Szu, S.P., Klein, L.C., Greenblatt, M., 1992. Effect of precursors on the structure of phosphosilicate gels: ^{29}Si and ^{31}P MAS NMR study. *Journal of Non-Crystalline Solids* 143 (C), 21–30.
- Takaishi, T., *et al.*, 2005. Structural study on PbO-SiO_2 glasses by X-ray and neutron diffraction and ^{29}Si MAS NMR measurements. *Journal of the American Ceramic Society* 88 (6), 1591–1596.
- Tsai, T.W.T., *et al.*, 2008. Solid-state NMR study of bioactive binary borosilicate glasses. *Journal of Physics and Chemistry of Solids* 69 (11), 2628–2633.
- Tseng, Y.H., Mou, C.Y., Chan, J.C.C.C., 2006. Solid-state NMR study of the transformation of octacalcium phosphate to hydroxyapatite: a mechanistic model for central dark line formation. *Journal of the American Chemical Society* 128 (21), 6909–6918.
- Uhlir, F., Marsman, H.C., 2008. ^{29}Si NMR – Some practical aspects. In: Arkles, B., Larson, G.L. (Eds.), *Silicon Compounds: Silanes and Silicones – A Survey of Properties and Chemistry*. second ed. pp. 208–222. Gelest Inc.
- White, D.J., *et al.*, 1988. ^{19}F MAS NMR and solution chemical characterization of the reactions of fluoride with hydroxyapatite and powdered enamel. *Acta Odontologica Scandinavica* 46 (6), 375–389.

- Wouters, B.H., *et al.*, 1999. Determination of the $\text{Al}^{\text{T1}}/\text{Al}^{\text{T2}}$ Ratio in MAZ Zeolites Using Line Shapes of MQ MAS NMR. *Journal of Physical Chemistry B* 103 (38), 8093–8096.
- Wu, Y., *et al.*, 1994. A unique protonated phosphate group in bone mineral not present in synthetic calcium phosphates. Identification by phosphorus-31 solid state NMR spectroscopy. *Journal of Molecular Biology*. 423–435.
- Wu, Y., *et al.*, 1998. Evaluation of bone mineral density using three-dimensional solid state phosphorus-31 NMR projection imaging. *Calcified Tissue International* 10, 512–518.
- Yan, H., *et al.*, 2001. In vitro hydroxycarbonate apatite mineralization of CaO-SiO_2 sol-gel glasses with a three-dimensionally ordered macroporous structure. *Chemistry of Materials* 13 (4), 1374–1382.
- Yang, W.-H., Kirkpatrick, R.J., Turner, G., 1986. ^{31}P and ^{29}Si magic-angle sample-spinning NMR investigation of the structural environment of phosphorus in alkaline-earth silicate glasses. *Journal of the American Ceramic Society* 69 (10), C-222–C-223.
- Yi, H., 2013. A carbonate-fluoride defect model for carbonate-rich fluorapatite. *American Mineralogist* 98 (5–6), 1066–1069.

X-Ray Powder Diffraction

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Introduction

X-Ray diffraction has acted as the cornerstone of twentieth-century science. Its development has catalyzed advances in solid-state science and much of our understanding of chemical bonding. X-Ray powder diffraction (XRPD) plays a critical role in materials research and development because many materials and minerals are not readily available in single-crystal form. Some 10,000–20,000 powder diffractometers are in use worldwide, and more than 1 million reference patterns are available in the International Center for Diffraction Data Powder Diffraction File (PDF) electronic database. Although the technique is termed “powder diffraction”, any polycrystalline specimen may be studied using the technique, including monolithic solids, thin films, and powders (Cullity, 1978; Jenkins and Snyder, 1996; Klug and Alexander, 1974). Among the applications of powder diffraction are:

- (1) Qualitative identification of the phases present in a specimen using the powder pattern as a “fingerprint” of the phase which may be compared to known powder patterns stored in a database.
- (2) Quantitative analysis of the concentrations of each phase present in a multiphase specimen can be carried out.
- (3) The unit cell metrics, i.e., the size and shape of the unit cell, of any crystalline material can be determined, and then refined to very high accuracy. Because the lattice parameters of a material change with chemical composition, XRPD finds widespread use in solid solution analysis, phase diagram work, and for measuring the true density of materials.
- (4) Full orientation distribution functions that describe the crystallite orientation in polycrystalline materials can be determined.
- (5) Residual and applied stress can be determined by measuring the strain present in the crystallites composing a monolithic body.
- (6) Microstructural features of a polycrystalline material including the crystallite size, microstrain within crystallites, and defect densities may be determined.
- (7) In situ techniques under controlled gaseous atmosphere, temperature, pressure, field, and mechanical loading provide a means of determining phase diagrams and reaction kinetics, and provide a means of tracking changes in materials during synthesis and processing.
- (8) Full structure solution from powders (*ab-initio* structure solution).
- (9) Analysis of local versus long-range structure, using the Pair Distribution Function (PDF) method.

The applications listed above are strictly for polycrystalline materials. It is important to note, however, that powder diffractometers may be equipped to study thin films using X-Ray reflectivity and high-resolution diffraction.

Origins of X-Ray Powder Patterns

X-Rays are relatively short wavelength, high-energy electromagnetic radiation. Diffraction experiments require X-Ray wavelengths of the order of the interatomic spacing to produce interference, and hence typical wavelength ranges are 0.07–0.2 nm. The most common radiation used in the laboratory is Cu K_α radiation with $\lambda = 0.15406$ nm.

A typical X-Ray powder diffraction pattern is shown in Fig. 1 and consists of diffraction peaks, or “lines”, as a function of the diffraction angle, 2θ . Diffraction occurs when waves scattering from an object constructively and destructively interfere with each other (Hahn, 1983; Gilmore *et al.*, 2019). The diffraction peaks in Fig. 1 are a result of constructive interference of waves scattered from the atoms or ions composing a crystal. M. von Laue in 1912 first determined that X-Rays diffract from the periodic arrangement of atoms in a crystal, exactly analogous to the diffraction of visible light from a grating. Based on the work of von Laue, both Bragg and Bragg (1913) showed that diffraction from a crystal is described by the equation now known as Bragg’s law:

$$\lambda = 2d_{hkl} \sin\theta \quad (1)$$

This equation allows one to measure the perpendicular distance (d_{hkl}) between imaginary planes which form parallel families and which intersect the repeating unit cell filled with atoms in a way described by the Miller indices (hkl). X-Rays of wavelength λ may be thought of as reflecting from these imaginary planes at the measurable angle θ , where θ is one-half of the diffraction angle as shown in Fig. 1. A powder pattern therefore contains a set of diffraction peaks at 2θ positions that correspond to the interplanar spacings in the crystal. Although d_{hkl} may be calculated using geometry for any set of (hkl) planes in any unit cell, the interplanar spacings are most easily calculated in reciprocal space. Ewald (1913, 1921) developed what is by far the most useful method for describing diffraction phenomena using reciprocal space.

Ewald showed that a reciprocal lattice can be constructed by using the reciprocals of all of the distances in a real unit cell. The reciprocal lattice has the same symmetry as the real crystal lattice, but the points in the reciprocal lattice are equally spaced and hence simple to manipulate. In an orthogonal lattice (cubic, tetragonal, orthorhombic), all distances are the reciprocals of the real space distances. $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ are the reciprocal lattice parameters, while the interaxial angles are α^* , β^* , and γ^* , where the

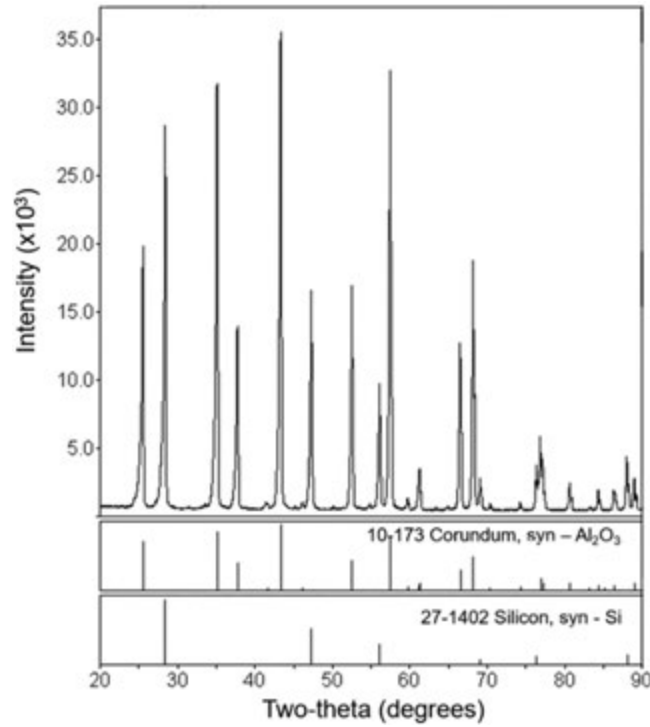


Fig. 1 A powder diffraction pattern for a mixture of two phases, with the standard patterns from the PDF database shown below the data.

reciprocal of an angle is defined as the complement or 180° minus the angle. Likewise, the reciprocal of $\mathbf{d}_{hkl}$ is $\mathbf{d}_{hkl}^*$. In the non-orthogonal systems, one must account for the interaxial angles when calculating the reciprocal lattice parameters.

The convenience of using reciprocal space is demonstrated when calculating the $\mathbf{d}_{hkl}^*$ values. Since the length of $\mathbf{d}_{hkl}^*$ is simply related to the real space d -spacing, one simply uses the $\mathbf{d}_{hkl}^{*2}$ equation:

$$\mathbf{d}_{hkl}^{*2} = h^2 \mathbf{a}^{*2} + k^2 \mathbf{b}^{*2} + l^2 \mathbf{c}^{*2} + 2hka^* \mathbf{b}^* \cos \gamma^* + 2hla^* \mathbf{c}^* \cos \beta^* + 2klb^* \mathbf{c}^* \cos \alpha^* \quad (2)$$

This expression relates the square of the inverse of $\mathbf{d}_{hkl}$ to the size and shape of the reciprocal unit cell for any plane in any crystal system. For many applications then, Eq. (2) reduces to a particularly simple form. For example, Eq. (2) becomes:

$$\mathbf{d}_{hkl}^{*2} = (h^2 + k^2 + l^2) \mathbf{a}^{*2} \text{ for a cubic crystal.}$$

The intensity of each diffraction peak in a pattern is governed by the structure of the crystal and the physical configuration of the diffractometer. First we must consider how much intensity a single electron will coherently scatter (the more massive nucleus is a very inefficient scatterer and may be ignored). Next we need to consider the interference effects which will occur due to the electrons being distributed in space around atoms and the fact that atoms are not stationary in a lattice but vibrate in an anisotropic manner. Then the interference effects of atoms scattering from different regions of the unit cell must be allowed for, and finally the optical configuration of the diffractometer and absorption effects must be considered.

The intensity of peak i of phase α in a powder pattern measured using Bragg–Brentano geometry (see Fig. 2) is described by the following equation:

$$I_{ix} = \frac{I_0 \lambda^3 e^4}{32 \pi m_e^2 c^4} \frac{M_i}{2 V_\alpha^2 \mu} |F_{ix}|^2 \frac{[(1 + \cos^2 2\theta_i \cos^2 2\theta_m)]}{[(\sin^2 \theta_i \cos \theta_i)]} \quad (3)$$

where:

$$F_{hkl} = \sum_{j=1}^N \left[(f_{j0} + \Delta f_j' + \Delta f_j'') \exp(-B_j) \times \sin^2(\theta/\lambda)^2 \right] \exp 2\pi i (hx_j + ky_j + lz_j) \quad (4)$$

N = No. of atoms in cell.

The first term in Eq. (3) describes classical scattering from an electron as described by J. J. Thomson in 1899 (Nobel Prize for Physics, 1906), while the last term in parentheses is a correction for the polarization of the X-Ray beam on diffraction. The term M_i accounts for the multiplicity of (hkl) planes with identical d -spacings that diffract at the same angle; for example, there are six $(h00)$ peaks in a cubic crystal. The structure factor, F_{hkl} , is the most important quantity in crystallography and contains the atomic scattering factor, f_j , and the atom positions in the unit cell, x_j , y_j , and z_j . The exponential term in F_{hkl} (Eq. (4)) accounts for the phases of the scattered waves, while the atomic scattering factor accounts for the amplitudes scattered from each atom. f_j

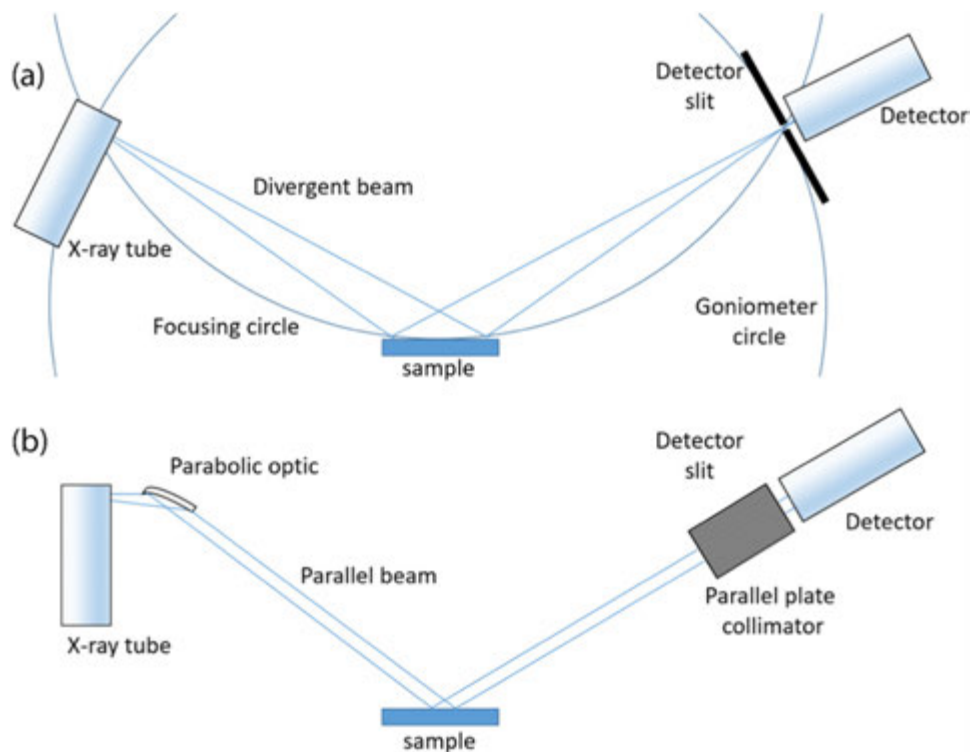


Fig. 2 Schematics of two x-ray powder diffractometers: (a) Bragg-Brentano parafofocusing geometry; (b) parallel beam geometry using a parabolic multilayer optic.

completely describes scattering from an atom by including the number of electrons and their spatial distribution around the atom, including thermal vibrations (B_j). It is important to note that f_j explicitly includes the atomic number of each element in a crystal, demonstrating that X-Rays scatter more strongly from heavy elements than from light ones.

It is a triumph of our understanding of physics that computations of diffraction intensities, using Eq. (3), produce the observed values. This triumph has been heavily exploited in determining the crystal structure of materials. This ability, first used by the Braggs in 1913, has established the basis of modern solid-state science.

The most common application of our ability to compute a powder pattern, in the materials laboratory, is to compare it with any features of the experimental pattern (like preferred orientation of the crystallites, solid solution effects, etc.) to determine any crystal structure or microstructural modifications which may have taken place.

Instrumentation for X-Ray Powder Diffraction

Traditional Parafofocusing Instruments

Beginning in 1945 and continuing through the 1950s, William Parrish developed the powder diffractometer for recording powder patterns electronically (Parrish, 1949). The diffractometer is shown schematically in Fig. 2. The parafofocusing geometry is called Bragg-Brentano but should more appropriately be called Parrish geometry (Bish and Post, 1990). The parafofocusing principle in the diffractometer comes from keeping the X-Ray source (i.e., the X-Ray tube target), the specimen, and the receiving slit on a common circle, called the focusing circle. To meet the condition of Bragg's law we must move the sample through an angle of θ while the detector is scanned through an angle of 2θ . This θ - 2θ motion implies that the radius of the focusing circle is continually changing throughout a diffraction pattern scan.

The need to make the beam monochromatic follows directly from Bragg's law. If more than one wavelength is present in the beam, each set of planes will yield a diffraction peak for each wavelength. This would hopelessly complicate the diffraction pattern. The most common method to produce "monochromatic" radiation is to employ a diffracted-beam monochromator. Most Bragg-Brentano instruments include a quasi single-crystal graphite monochromator which allows only the $K_{\alpha 1}$ and $K_{\alpha 2}$ radiation to reach the detector, as shown in Fig. 2. The elimination of all spectral wavelengths from the X-Ray tube except the $K_{\alpha 1}$ and $K_{\alpha 2}$ greatly improves the quality of the powder pattern. Placing the monochromator in the diffracted beam not only removes spectral impurities from the X-Ray tube but also any fluoresced X-Rays from the specimen.

Although Bragg-Brentano geometry is by far the most common configuration for powder diffraction, the parafofocusing nature of the measurement makes it prone to significant systematic errors. By far the most serious of these is due to a displacement of the

sample from the focusing circle. This, of course, can never be avoided because even if the sample surface is perfectly tangent to the focusing circle, the X-Rays penetrate into the sample to an average depth dependent on the absorption coefficient of the sample. Thus, there is always a “sample displacement” (or “sample transparency”) error present. One can remove these errors to obtain high-accuracy measurements of peak positions by using certified line position standards available from NIST.

Parallel-Beam Diffractometers

Revolutionary new X-Ray optics have been developed that have proved to be effective for laboratory measurements. Multilayer optics, polycapillary optics, and high-performance channel-cut crystals have been used independently or together to build high-intensity and/or high-resolution parallel-beam diffractometers.

A parallel-beam measurement minimizes or completely eliminates systematic errors arising from sample displacement and transparency. In addition, a parallel beam is required for asymmetric diffraction experiments, including thin-film diffraction. A parallel-beam diffractometer, therefore, lends itself to powder and thin-film measurements with little or no systematic errors. The only potential disadvantage of a parallel-beam diffractometer is termed “particle statistics”. Compared to a divergent beam Bragg–Brentano instrument, a parallel-beam instrument will reduce the number of crystalline grains in a powder specimen that are exactly oriented to produce a diffraction peak. One must therefore take special care to ensure that powder specimens are finely ground or polycrystalline samples are rotated or oscillated to increase the number of grains bathed in the X-Ray beam.

Both graded multilayer and polycapillary optics may be used to convert a divergent beam into a parallel beam, or to focus an X-Ray beam. Multilayer optics consist of thin-film stacks of alternating high atomic number materials with low atomic number materials. The alternating thin films therefore act as a crystal, the diffraction angle of which is determined by the thickness of the films and is typically below 3° . Herbert Göbel first showed that by grading the film thickness of each layer along the length of a multilayer optical element and bending it to a parabola or ellipse, either parallel or focusing beams may be produced. This optic is now called a Göbel mirror.

Polycapillary X-Ray optics use hollow capillaries as waveguides for X-Rays, where multiple total external reflection of X-Rays from the smooth inner walls of capillary channels can be used to redirect an X-Ray beam. The curvature of the capillary determines the final direction of the X-Ray beam, and bundles of capillaries may be used to produce parallel or focusing beams.

One optical assembly includes a parabolically curved graded multilayer coupled to channel-cut silicon or germanium crystal monochromators. The multilayer produces a beam with divergence of the order of 100 s of arc, which is then diffracted by the latest generation of two- or four-bounce channel-cut crystals. The result is a high-intensity, highly monochromatic beam that allows extremely high-resolution measurements in the laboratory. In fact, diffraction peak widths as narrow as 0.035° 2θ have been measured, which is commonplace when using a synchrotron source but unheard of for a laboratory instrument.

A schematic of a parallel-beam diffractometer is also shown in Fig. 2 for comparison with the Bragg–Brentano geometry.

Modern X-Ray Detectors

The nature of X-Ray detectors and the electronics used with them is an important part of understanding the approaches to, and limitations of, X-Ray applications. Many modern X-Ray diffractometers employ “point” detectors that collect data through a very fine receiving slit, but one- and two-dimensional detectors are becoming common in powder diffraction, as shown schematically in Fig. 3.

The standard point detectors work using a scintillation crystal to convert X-Ray photons to blue light, which is then converted to an electrical signal using a photoelectric material. Solid-state detectors are another variety of point detector, and convert the incident X-Ray photon directly to an electrical signal by creating electron–hole pairs in a doped semiconductor crystal.

Solid-state and scintillation detectors are both point detectors because there is no means of determining where the photon collides with the detector. In contrast, one- and two-dimensional position-sensitive detectors sense where the X-Ray photons strike the detector and can therefore be used to collect some angular range of data in parallel. Collecting diffraction data in parallel significantly decreases the measurement time, often down to seconds and even microseconds.

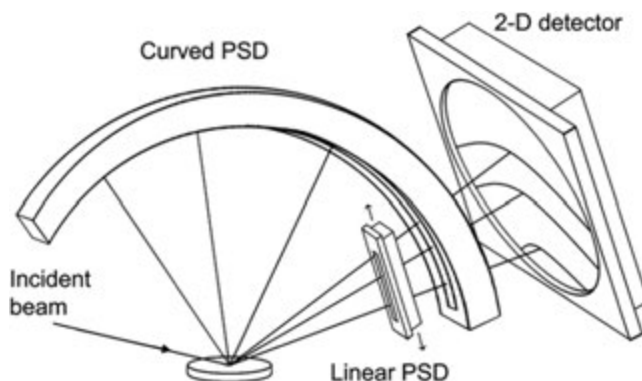


Fig. 3 Schematic of detector configurations.

The common one-dimensional position-sensitive detectors (PSDs) cover angular ranges of some 5° – 120° 2θ and work using gas ionization to absorb the photon and a timing signal to detect the arrival of the electrical pulses at a position analyzer.

Two-dimensional detectors include gas proportional designs, charge-coupled devices, or image plates to collect a large area of the cone of diffracted intensity from a powder specimen. Most recently, amorphous Si and CMOS technologies have become commonplace, which have 2-D pixel sizes near $100\ \mu\text{m}$ with excellent dynamic range. 2-D detectors can be used to collect the entire Debye cone of diffracted radiation if the detector is centered on the beam, or some part of the diffracted cone of radiation, with the option of re-positioning the detector during measurement. As of the year 2020, it has become common to employ such solid state 2-D technologies in both 1-D and 2-D detection schemes. For laboratory diffractometers, 2-D detectors are generally as large as 10 cm diameter for gas-filled counters or 5 cm for solid state devices. Data collection times using two-dimensional detectors are often of the order of seconds or less per image.

Applications of Powder Diffraction

Phase Identification by X-Ray Diffraction

The set of diffracted d and I values for any material is as characteristic as a fingerprint is for a human. We must now face the same problem the crime solvers have had to face – an observed set of fingerprints is useless unless you have an extensive collection of reference patterns for comparison. Our problem is even more complex in that unknown materials are commonly composed of more than one phase. When this occurs, the observed pattern contains all the diffraction peaks of each phase present.

Scientists have answered the need for a powder diffraction pattern database by creating an organization called the International Center for Diffraction Data (ICDD), which publishes the Powder Diffraction File (PDF) in annual installments. The powder patterns published in the PDF include experimentally determined patterns from the literature and calculated patterns from crystal structure databases. They are reviewed by editors and published in book and computer formats (e.g., CD-ROM). There are about 160,000 patterns in the file.

An example of phase identification is shown in Fig. 1, which is a pattern for a two-phase mixture. The phases are identified using the PDF entries shown in Fig. 1. A number of manual and computer searching methods have been developed over the years to accomplish phase identification. These methods place an emphasis on the accuracy of the intensities (Hanawalt method) or the d_{hkl} values (Fink method) or on the elements present (alphabetical search). Modern highly automated computer search routines use a combination of chemical information, intensity, and peak position, generally coded into heuristic algorithms, to quickly search the database for possible matches. A modern computer search requires only a few seconds, and will often correctly identify at least two phases in any unknown on the first attempt.

Quantitative Phase Analysis

Quantitative phase analysis by X-Ray powder diffraction dates back to 1925 when Navias at GE quantitatively determined the amount of mullite in fired ceramics, and to 1936 when Clark and Reynolds reported an internal-standard method for mine dust analysis. Alexander and Klug (1948) presented the theoretical background for quantitative analysis based on diffracted intensities. Since then there have been numerous methods developed, based on their basic equations. Methods applicable to a wide range of phases and samples include the method of standard additions (also called the spiking method) the absorption diffraction method, the internal-standard method, and the Rietveld method (described below).

Quantitative analysis using any method is a difficult undertaking. It requires careful calibration of the instrument using carefully prepared standards and will require multiple measurements unless the Rietveld method is used. After the technique and standards have been established, routine analyses may be completed in as little as a few minutes to an hour per sample, depending on the precision desired.

The intensity of a diffraction line i from a phase α in a specimen containing a mixture of phases can be rewritten from Eq. (3) as:

$$I_{iz} = K_{iz} X_{\alpha} / [\rho_{\alpha} (\mu/\rho)_m] \quad (5)$$

where K_{iz} = a set of constants describing the diffracted intensity, including the Thomson equation, polarization, etc., X_{α} = weight fraction of phase α , ρ_{α} = density of phase α , and $(\mu/\rho)_m$ = the mass absorption coefficient of the mixture. $(\mu/\rho)_m$ is calculated using tabulated values of (μ/ρ) for each element as a weighted average.

The fundamental problem in quantitative analysis lies in the $(\mu/\rho)_m$ term in Eq. (5). To solve for the weight fraction of phase α , we must be able to compute $(\mu/\rho)_m$ and this requires knowledge of the weight fractions of each phase. Special techniques are therefore required to eliminate the unknown $(\mu/\rho)_m$ and quantify the phase concentrations.

Application of one of the techniques listed above centers on removing the unknown $(\mu/\rho)_m$ term from the analysis. Consider for example the internal standard quantification method, which is the most general of any of the methods for quantitative phase analysis and is based on elimination of the absorption factor $(\mu/\rho)_m$, by dividing Eq. (5) by itself, giving:

$$I_{iz}/I_{js} = k(X_{\alpha}/X_s) \quad (6)$$

which is linear in the weight fraction of phase α . The subscripts i and j refer to different hkl reflections. k is the slope of the internal standard calibration curve: a plot of I_{iz}/I_{js} versus X_{α}/X_s .

The addition of a known amount, X_s , of an internal standard to a mixture of phases, which may include amorphous material, permits quantitative analysis of each of the components of the mixture by first establishing the values of k for each phase, i.e., the slope of the internal standard plot of $(I_{i\alpha}/I_{js})X_s$ versus X_{α} , from standards of known concentration. Use of a pre-established calibration curve, defining the slope k , permits the weight fraction of any phase α in the original mixture to be computed.

Unit Cell Indexing

Determining the size and shape of the unit cell from a powder pattern of a pure phase is simply a 3-dimensional problem linking the set of observed d-spacings to the unit cell metrics (axial dimensions and interaxial angles, also called the lattice parameters). Indexing a diffraction pattern used to be a formidable problem. Indexing is the procedure used in assigning hkl values to the set of planes which give rise to each diffraction line, or, in other words, determining the lattice parameters that define the unit cell. The problem becomes more difficult as one goes to lower symmetry because the number of unknowns one must determine increases. Nonetheless, computer methods can often be used to determine the lattice parameters of an unknown crystal if, and only if, the patterns are measured very accurately and corrected for systematic errors.

The problem of indexing can then be stated as having to solve the d_{hkl}^* equation for up to six unknown lattice parameters. Solving the d_{hkl}^* equation using experimental data will result in some amount of error, and it is convenient to have a means of quantifying the “goodness of fit” of the experimental data to the unit cell determined by solving the d_{hkl}^* equation. A figure of merit (FOM) is used to determine the goodness of fit. The most common FOM was developed by Smith and Snyder (1979) and is defined as:

$$F_N = \frac{N}{|\Delta 2\theta| N_{\text{poss}}} \quad (7)$$

where N is the number of observed lines used in the calculation, N_{poss} is the number of possible diffraction peaks allowed by the space group out to the 2θ of line N , and $|\Delta 2\theta|$ is the average error between the observed and calculated 2θ values of the first N lines in the pattern. This figure of merit is useful both in evaluating the quality of powder patterns and in establishing the correctness of an indexing. The advantage for indexing is that its value is independent of the crystal system, so a common scale can be applied to all crystal systems. With only one unknown lattice parameter the problem of indexing a cubic powder pattern is always solvable. Lower symmetry crystals are significantly more difficult to index, and three fundamental approaches have been useful. Since the problem gets progressively more difficult numerically as we decrease symmetry, all three approaches employ computers. The three approaches are (1) intelligent algorithms, (2) searches of solution space and (3) searches of index, or (hkl), space.

The intelligent procedures try to determine the lattice parameters by applying known relationships from both geometry and crystallography and even previous experience with indexing problems. Two quite successful methods of this type have been developed by Visser (1969) and Werner (1976).

Search methods do a systematic search of solution space (i.e., look at all possible solutions within some boundaries). There are two types of searching index procedures: those that work in parameter space and those that examine index or hkl space. Some of the search methods make assumptions about the regions of solution space that should be examined while others are exhaustive.

We should pause here to discuss the concept of a solution space. This space for an exhaustive parameter search is envisioned as having up to six dimensions in a plane (corresponding to functions relating to a , b , c , α , β , and γ) and the F_N figure of merit plotted perpendicular to this plane. For cubic problems this means a two-dimensional problem: vary all possible values of a along the x axis with F_N plotted vertically. One needs to use caution, however, because there are a great number of incorrect cells that will almost describe the crystal within reasonable error limits. Each of these “solutions” will correspond to a maximum of F_N in solution space. Our assumption is that the highest maximum in F_N corresponds to the correct unit cell.

An exhaustive indexing procedure working in parameter space examines all possible values of a , b , c , α , β , and γ within some reasonable limits defined by the user. The lattice parameters are divided into small increments and each possible set is used in an attempt to index the unknown pattern. Louër and Louër (1972) established an extremely successful program based on this approach.

Exhaustive procedures using index or hkl space examine all possible combinations of h , k , and l which can be used to index each of the lines in the unknown pattern. Here our solution space is four dimensional for all symmetries: axes in integer units of h , k , and l in a plane with F_N perpendicular to that plane. A very powerful algorithm based on hkl space searching was developed by Taupin (1973).

Before the days of powerful, fast PCs, exhaustive search procedures were only practical in relatively high symmetry systems and in a few exceptional cases. For example, the classic case of a manual orthorhombic indexing was performed by Jacob and Warren (1937) in the determination of the crystal structure of α -uranium. As the symmetry decreases to triclinic, the amount of computation required became impractical. Today, however, monoclinic and triclinic problems are routinely solved on researchers’ desktop workstations.

Refining Accurate Lattice Parameters

Once a powder pattern is indexed we may routinely write from one to six d_{hkl}^* equations with all terms known except the one to six lattice parameters. These equations may be solved simultaneously to give values for the lattice parameters, but these will not be the most precise values (Pecharsky and Zavalij, 2009).

The precise and accurate measurement of lattice parameters, or unit cell dimensions, have been used for various purposes such as: determining thermal expansion coefficients, finding the true density of a material, providing a direct measure of interatomic distances, and studying interstitial and substitutional solid solutions.

In order to obtain accurate lattice parameters, the minimization and elimination of a number of errors is necessary. All sources of error in 2θ affect the accuracy of the lattice parameters, and may be classified into two categories: (1) random errors and (2) systematic errors. Random errors are those made in locating and recording the center of the diffraction peak. These errors vary randomly with the angle 2θ .

Systematic errors are those whose magnitude depends upon the position of the line, that is, upon the angle 2θ . Systematic errors are best eliminated by using an internal standard, which is a material certified by NIST to have well-known diffraction peak locations. With systematic error handled in this manner, the common approach for obtaining the most precise parameters from observed data is to use the method of least squares. Least squares minimizes the differences between the observed d_{hkl} values and d_{hkl} values calculated from the d_{hkl}^2 equation by varying the lattice parameters. This very powerful method will simultaneously produce estimates of the standard deviations of the lattice parameters.

Preferred Orientation

Preferred orientation of crystallites in polycrystalline materials is a vital subject to many materials industries. A number of industrial materials are based on directional physical properties of the crystallites. For example, barium hexaferrite ceramic magnets, used commonly as seals on refrigerator doors, are polycrystalline materials in which only the $(00l)$ crystallite directions have a magnetic moment. Thus, the fabrication and quality control procedures must involve manipulating and measuring the degree of preferred orientation in the ceramic. Extruded wires show a characteristic preferred orientation as do most rolled metals, pressed powders, and thin-film materials. The most common way of evaluating the type and extent of preferred orientation is to measure the pole figure for a particular crystallographic direction. The pole figure is simply the intensity of a particular Bragg diffraction peak plotted as a function of the three-dimensional orientation of the specimen. It is determined on a pole figure diffractometer which is essentially the same as a single-crystal diffractometer, able to rotate the specimen through all orientations while monitoring the diffraction intensity of a specific hkl reflection. The results are displayed as a pole figure which is a two-dimensional stereographic projection.

By collecting several pole figures, a complete orientation distribution function (ODF) can be calculated, which describes the orientation of the crystallites in the coordinates of the specimen geometry. The full ODF is often critical for understanding the variation in properties as a function of direction in monolithic polycrystalline parts.

Crystallite Size

When a well-crystallized powder sample with an average crystallite size of $\approx 10 \mu\text{m}$ diffracts, the diffraction peaks are sharp, symmetrical, and well defined. However, if the specimen contains crystallites that are smaller than $\approx 500 \text{ nm}$, possess large internal microstrains, or have a large density of stacking faults or other defects, the diffraction peaks will be broadened and/or asymmetric.

The simple case of crystallite size peak broadening can be understood by considering the interference of X-Rays scattered from different positions in the crystallite (Snyder *et al.*, 2000). A large crystallite, i.e., larger than a few micrometers, contains some 50,000 successive (hkl) planes and produces a narrow diffraction peak. The diffraction peak is narrow because at angles slightly above and below the Bragg angle, complete destructive interference occurs. A photon scattered from the top (hkl) plane will be exactly out of phase with a photon scattered from an (hkl) plane deep within the crystallite; for example 40,000 planes from the surface, at angles very close to the Bragg angle. However, if the crystallite is smaller than the 40,000 planes used in our example, complete destructive interference will not occur and some diffracted intensity will be observed at angles slightly different from the Bragg angle. Naturally, as the crystallite gets smaller, the destructive interference near the Bragg angle decreases and the diffraction peak becomes wider.

The crystallite size broadening (β_τ) of a peak can usually be related to the crystallite size (τ) via the Scherrer equation:

$$\tau = k\lambda / \beta_\tau \cos\theta \quad (8)$$

The additional broadening in diffraction peaks beyond the inherent peak widths due to instrumental effects can be used to measure crystallite sizes as low as 1.0 nm. However, a second cause of broadening, due to microstress within the crystallites, can complicate the picture.

Whatever the cause of microstress in a crystallite, the effect will cause a distribution of d -values about the normal, unstrained, d_{hkl} value.

The broadening in a peak due to microstress (ϵ) has been shown to be related to the peak width as:

$$\beta_\epsilon = 4\epsilon \tan\theta \quad (9)$$

The fact that microstress-induced diffraction peak broadening follows the tangent of θ while crystallite size broadening follows $1/\cos\theta$ allows us to separate these effects. The most common procedure for accomplishing this was developed by Warren and Averbach (1950). In this method, the Fourier transformation of the diffraction peaks of a broadened sample and a standard

material exhibiting no sample broadening are computed. A deconvolution procedure is then carried out in Fourier space to determine the peak broadening that results from crystallite size and/or microstrain.

A significant amount of research is underway to determine appropriately the microstructural features of a powder or polycrystalline body from powder diffraction data. Most of these approaches involve rather detailed computations of the peak widths as a function of diffraction angle. The angular dependence of the peak width is then used to quantify the crystallite size, microstress, stacking faults, and other atomic-scale defects present in a specimen.

Residual Stress

Stresses in a monolithic body at the macroscale are called a macrostress and the distances within the unit cell will become smaller or larger, depending upon the direction and sense (compressive or tensile) of the residual stress. This will be observed as a shift in the location of the diffraction peaks. Essentially, the individual crystallites in a polycrystalline body act as strain gauges, where the diffraction peak location indicates the strain value at the location of the crystallite that is diffracting. Since most stresses in materials are a result of heat treatment, machining, etc., X-Ray measurements of macrostress are normally referred to as residual stress measurements (Noyan and Cohen, 1987).

Careful measurement of the locations of diffraction peaks with the sample in several orientations (with respect to the beam) directly provides the strain present in the specimen as a function of direction. By using a goniometer that allows the specimen to be rotated in three directions, one can determine a full triaxial strain distribution. Given the diffraction elastic constants, the full second-rank stress tensor may be determined.

Like lattice parameter refinements, residual stress measurements are prone to peak location errors and special care must be taken to ensure instrument alignment. When using a Bragg–Brentano diffractometer, stress measurements are best done using high-angle peaks to minimize systematic errors. Typically, a stress-free powder specimen is measured to confirm the instrument performance.

Parallel beam measurements offer the advantage of reduced systematic peak location errors and allow thin-film and stress depth profiling measurements. Surface and near-surface stresses are important in most technological applications because surfaces and films often define the performance of materials.

Profile Fitting and Rietveld Analysis

The most exciting of the profile fitting developments has been the continuing development of a whole pattern X-Ray refinement method to obtain crystal structure information, begun by Rietveld (1969), who applied it to neutron diffraction data.

Rietveld refinement is conducted by fitting a calculated diffraction pattern to the observed data by adjusting each of the variables that describe the diffraction pattern (Young, 1993; Pecharsky and Zavalij, 2009; Dinnebier and Billinge, 2008). Rietveld computations are relatively intensive, and require minimizing the sum of the weighted, squared differences between observed and calculated intensities at every step in a digital powder pattern. The Rietveld method requires knowledge of the approximate crystal structure of all phases present in the specimen.

The input data to a refinement include the space group, atomic positions, site occupancies, and lattice parameters. This method goes beyond the simple computation of intensities from Eq. (3) by distributing the calculated intensity over the kind of profile found using a particular instrument. Appropriately describing the shape of each peak in an X-Ray pattern remains a challenge, but several successful analytical profile shapes have been developed. Of interest are the Voigt, the pseudo-Voigt, and the split Pearson VII profile functions. The Voigt function is an analytical convolution of a Gaussian and a Lorentzian. It therefore ranges from pure Lorentzian to Gaussian type, depending on the ratio of both half-widths. The pseudo-Voigt conveniently allows the refinement of a mixing parameter determining the fraction of Lorentzian and Gaussian components needed to fit an observed profile. The Pearson VII function also allows for the variation in shape from Lorentzian to Gaussian and can rather easily be split to describe asymmetric X-Ray diffraction peaks.

Another approach for distributing intensity in a profile is called fundamental parameters convolution. Instead of using a mathematical function to approximate the shape of each diffraction peak, the fundamental parameters approach “builds” each diffraction peak by convolution of the X-Ray emission profile with the instrumental and sample contributions to the profile shape. Hence, an accurate peak profile is obtained that explicitly includes all aspects of the experiment and sample; the X-Ray source size, receiving slit width, beam divergence, crystallite size, etc. The development of the fundamental parameters method is now quite mature and it is integrated into various programs for XRD analysis including Rietveld refinement.

In a typical Rietveld refinement, individual scale factors (related to the concentration of each phase) and profile, background, and lattice parameters are varied. In favorable cases, the atomic positions and site occupancies can also be successfully varied to obtain the most correct models of the structures of the phases. Preferred orientation, polarization, and systematic errors may also be modeled.

Fig. 4 includes the results of a completed Rietveld refinement. The observed and calculated patterns are shown, along with the difference pattern and the peak position markers. The refinement in Fig. 4 includes all variables except the atomic positions and thermal parameters, i.e., the background, profile shapes, preferred orientation, sample displacement, and scale factors.

Thus the Rietveld method is used to describe all of the features of the specimen, from the crystal structure to full orientation distribution functions in the case of monolithic polycrystalline specimens. It is the most accurate method available for quantitative analysis and provides estimated uncertainties for each of the refined values.

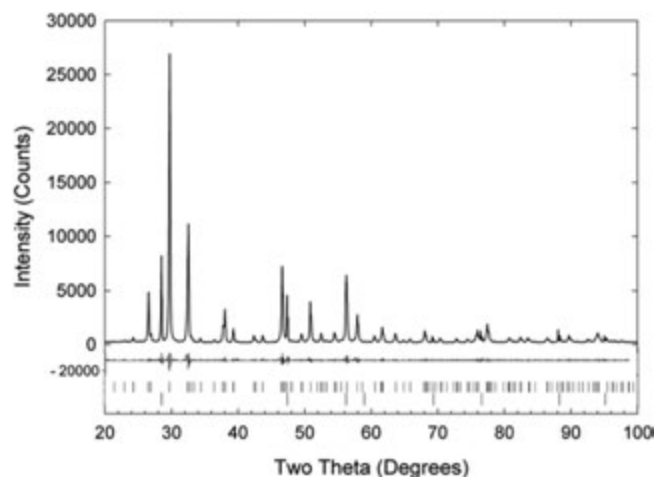


Fig. 4 Rietveld refinement of a two phase mixture of powders.

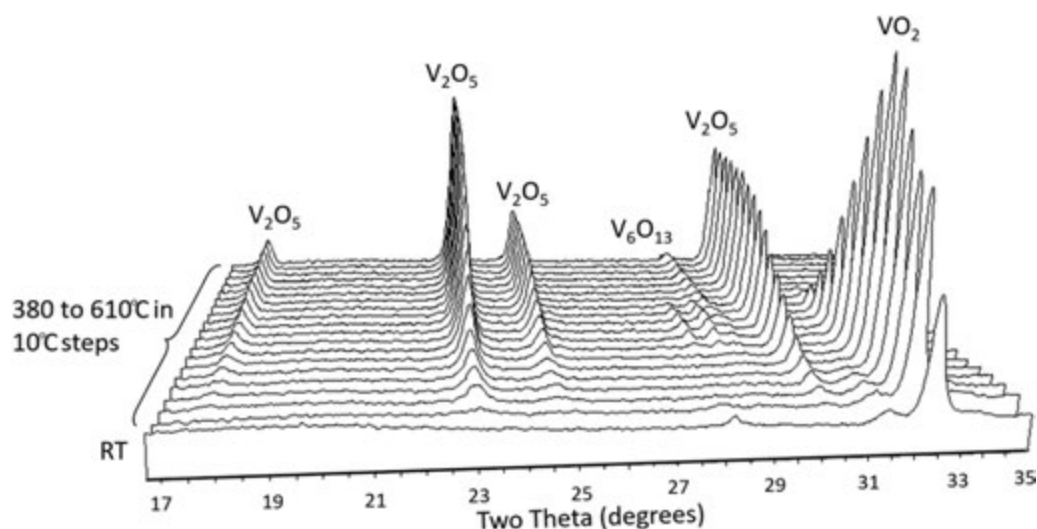


Fig. 5 High temperature atmosphere controlled XRD study of vanadium oxide polycrystalline thin films. Reoxidation of VO_2 under reduced oxygen partial pressure is shown.

In Situ Analysis

In situ powder diffraction methods can be used to characterize complex systems under controlled conditions of temperature, atmosphere, pressure, applied electric or magnetic field, mechanical loading, or time. Powder diffraction lends itself well to both basic science and materials processing problems. Crystal structures, phase equilibria, anisotropic thermal expansion tensors, volume change in response to gaseous atmospheres, and reaction kinetics are examples of fundamental studies which are enormously simplified using in situ diffraction. In situ diffraction is quite often the only means to determine structures and phase equilibria in systems that cannot be quenched reliably to ambient conditions; for example, in high-pressure geological studies or peritectic melting systems that crystallize on quenching.

Typical materials science problems can often be investigated using laboratory in situ instruments fitted with furnaces, helium displexes for cooling, and controlled-atmosphere chambers. Generally, in situ measurements involve multiple measurements as a function of an external variable, and position-sensitive 1-D or 2-D detectors that reduce the data collection time are convenient. Reaction kinetics can also be investigated using one- and two-dimensional detectors.

Most high-pressure studies incorporate diamond anvil cells to apply pressures up to several hundred kilobars, often at high temperature, and are typically conducted using synchrotron sources.

An elegant example of an in situ measurement is shown in [Fig. 5](#) where we track the evolution of phases in a polycrystalline thin film as a function of oxygen partial pressure and temperature. [Fig. 5](#) shows the reoxidation of VO_2 through V_6O_{13} to V_2O_5 at sub-ambient oxygen partial pressure. Attempting to get the desired phase assemblage in the thin film using trial and error annealing under controlled oxygen partial pressure would take an extensive effort, but in-situ study requires only a few hours or days instead of weeks.

Structure Solution

Ab initio structure solution from powder diffraction data has become more popular as a result of our abilities to extract intensities from powder patterns (Stout and Jensen, 1989). The integrated intensities from a powder pattern are treated as single-crystal intensities and the traditional single-crystal structure solving and refinement procedures can be employed.

The one-dimensional nature of a powder pattern, however, complicates the extraction of intensities because of overlapping reflections. Several pattern decomposition methods have been developed, including individual profile fitting, the Pawley method, and the LeBail method. The former two methods involve fitting peak profiles with positions that are not constrained by the lattice parameters, while the LeBail method relies on the lattice parameters to constrain the peak positions.

After extracting the intensities for each reflection in a powder pattern, traditional methods such as the Patterson method or direct methods can be used to phase the crystal, and Rietveld refinement is then employed to refine the structure. Structure solution from powders has been quite successful for many inorganic materials with small unit cells, and is an emerging technique for larger organic structures.

More recent advances include the use of simulated annealing methods to solve crystal structures from powder diffraction data and also the use of charge flipping algorithms. For both methods, the unit cell is first indexed, and the structure solution formalisms applied next. Simulated annealing involves, in a simple sense, introducing the correct number of atoms into the unit cell and directing the algorithm to randomly place the atoms in the unit cell until a best fit to the data is found. Of course such an approach is not necessarily successful, so constraints and restraints can be introduced, such as bond length limits, and rigid or semi-rigid bodies can be used instead of atoms or ions. Rigid bodies might be a molecule (in the case of molecular solids) or a coordination polyhedron, for example an SiO_4 tetrahedron in a silicate. The latter are often structural configurations that are commonly found in related solids and the use of rigid bodies is often key to successful structure solution from powder data.

The reader is referred to the literature to study charge flipping and its application in powder diffraction, but it is a method that has been used with great success in both single crystal and powder diffraction despite its theoretical complexity.

Pair Distribution Functions

The PDF method is a recent development in the world of powder diffraction, and is related to the radial distribution function used decades ago to understand amorphous structures. While the XRD experiment describes the overall bulk long-range structure of solids via the diffraction peak locations and intensities, total scattering experiments capture all the scattered intensity which includes diffuse scattering between the diffraction peaks. As described by Egami and Billinge (2012), the total scattering pattern is converted to the reduced structure function which is then Fourier transformed to give the reduced pair distribution function, typically denoted $G(r)$ (see Fig. 6). The PDF is therefore a sum of the set of interatomic distances, r , in real space (because of the preceding Fourier transform) and as such the PDF is of great utility in the study of amorphous and nanocrystalline materials. In fact, even “bulk” crystalline solids with complex chemical makeup may have nanoscale order or disorder that is not described by the diffraction data but is easily captured using PDF analysis.

PDF analysis is best done under experimental conditions that capture a wide range of momentum transfer, or in other words, using short wavelengths and/or wide angular ranges. Large data ranges are needed because the peak widths in the $G(r)$ function sharpen as the data range increases because of the Fourier transform operation. In a laboratory setting, it is common to use Mo or Ag radiation, with wavelengths near 0.71 and 0.56 Å, respectively, instead of the more commonly employed Cu, Fe, or Co sources. While it is feasible to measure PDFs in a laboratory diffractometer, the measurements are time intensive; they may take 5–20 h or

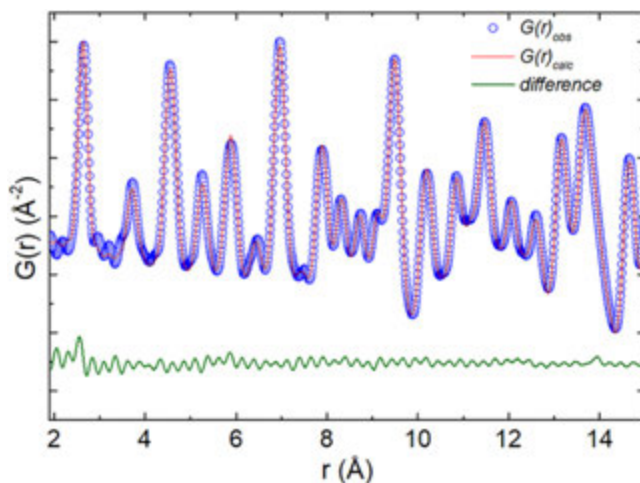


Fig. 6 X-ray pair distribution function for a Au-Cu disordered alloy showing measured, modeled and difference patterns.

even longer. Naturally, the use of synchrotron radiation improves data collection times; purpose-built PDF beamlines today can collect full high-quality PDFs using large area detectors and wavelengths as short as 0.15 Å in <5 min for bulk samples.

Fitting models to measured PDF data is handled as it is in Rietveld analysis, using a model of a unit cell, at least in its simplest form. Naturally, describing amorphous solids or nanoscale disordered materials is not feasible using a traditional unit cell, so modeling approaches employ the use of supercells or even “big-box” models with tens of thousands of atoms. While the topic of modeling complex structures is beyond the scope of this chapter it is worth noting that new approaches are under development for describing more and more complex solids using diffraction and PDF data integrated with advanced computing and statistical methods.

Acknowledgments

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References

- Alexander, L., Klug, H.P., 1948. Basic aspects of X-Ray absorption in quantitative diffraction analysis of powder mixtures. *Analytical Chemistry* 20, 886–889.
- Bish, D.L., Post, J.E. (Eds.), 1990. *Modern Powder Diffraction, Reviews in Mineralogy* 20. Washington, DC: Mineralogical Society of America.
- Bragg, W.H., Bragg, W.L., 1913. The reflection of X-Rays by crystals. *Proceedings of the Royal Society A* 88, 428–438.
- Cullity, B.D., 1978. *Elements of X-Ray Diffraction*, fourth ed. Reading, MA: Addison Wesley.
- Dinnebier, R.E., Billinge, S.J.L. (Eds.), 2008. *Powder Diffraction: Theory and Practice*, Royal Society of Chemistry.
- Egami, T., Billinge, S.J.L., 2012. *Underneath the Bragg Peaks: Structural Analysis of Complex Materials*. Amsterdam: Elsevier.
- Ewald, P.P., 1913. Zur theorie interferenzen der Röntgen-strahlen in kristallen. *Physikalische Zeitschrift XIV*, 465–472.
- Ewald, P.P., 1921. VII. Das “reziproke Gitter” in der Strukturtheorie. *Zeitschrift für Kristallographie – Crystalline Materials* 56, 129–156.
- Gilmore, C.J., Kaduk, J.A., Schenk, H. (Eds.), 2019. *International Tables for Crystallography, Volume H: Powder diffraction*, Wiley.
- Hahn, T. (Ed.), 1983. *International Tables for Crystallography, Vol. A: Space-Group Symmetry*. Dordrecht: Reidel. (For the International Union of Crystallography).
- Jacob, C.W., Warren, B.E., 1937. The crystalline structure of uranium. *Journal of the American Chemical Society* 59, 2588–2591.
- Jenkins, R., Snyder, R.L., 1996. *An Introduction to X-Ray Powder Diffractometry*. New York: Wiley.
- Klug, H.P., Alexander, L.E., 1974. *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, second ed. New York: Wiley.
- Louër, D., Louër, M., 1972. Méthode d’Essais et Erreurs pour l’Indexation Automatique des Diagrammes de Poudre. *Journal of Applied Crystallography* 5, 271–275.
- Noyan, I.C., Cohen, J., 1987. *Residual Stress: Measurement by Diffraction and Interpretation*. New York: Springer.
- Parrish, W., 1949. X-Ray powder diffraction analysis film and Geiger counter techniques. *Science* 110, 368–371.
- Pecharsky, V., Zavalij, P., 2009. *Fundamentals of Powder Diffraction and Structural Characterization of Materials*, second ed. New York: Springer.
- Rietveld, H.M., 1969. A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography* 2, 65–71.
- Smith, G.S., Snyder, R.L., 1979. FN: A criterion for rating of powder diffraction patterns and evaluating the reliability of powder pattern indexing. *Journal of Applied Crystallography* 12, 60–65.
- Snyder, R.L., Fiala, J., Bunge, H.-J., 2000. *Defect and Microstructure Analysis by Diffraction*. Oxford: OUP.
- Stout, G.H., Jensen, L.H., 1989. *X-Ray Structure Determination: A Practical Guide*, second ed. New York: Wiley.
- Taupin, D., 1973. A powder-diagram automatic-indexing routine. *Journal of Applied Crystallography* 6, 380–385.
- Visser, J.W., 1969. Some calculations for powder patterns. *Journal of Applied Crystallography* 2, 142–143.
- Warren, B.E., Averbach, B.L., 1950. The effect of cold-work distortion on x-ray patterns. *Journal of Applied Physics* 21, 595–598.
- Werner, P.-E., 1976. On the determination of unit-cell dimensions from inaccurate powder diffraction data. *Journal of Applied Crystallography* 9, 216–219.
- Young, R.A., 1993. *The Rietveld Method*. International Union of Crystallography. Oxford: OUP.

Case Studies in the X-ray Diffraction of Ceramics

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Introduction

The principle of crystalline phase analysis by X-ray diffraction (XRD) was established by William Lawrence Bragg in the 1920s following Max von Laue's discovery. Since then, XRD has emerged as a powerful tool widely used in research and industry. More specifically, the identification and quantification of the crystalline phases by XRD, at different steps of the process, is a key task of the process control in the ceramic industry. For instance, for traditional silicate ceramics, the characterization the mineral composition of natural raw materials, such as clays, feldspars, talcs, etc, is of major importance as it strongly influences the reactions during sintering, and consequently, the microstructure and properties of the final product (Bonnet and Gaillard, 2007). The crystalline composition also directly affects the mechanical and functional properties of the ceramics. One typical example is given by tetragonal zirconia (TZP) based ceramics in which hydrothermal aging induce a transformation to the monoclinic form that severely degrades strength and toughness (Chevalier *et al.*, 2006; Arata *et al.*, 2014).

However, while XRD is usually well known for qualitative and quantitative analyses of crystalline phases in materials, far more information can be obtained from a careful analysis of the diffraction patterns or by using specific XRD settings. Hence, the characterization of solid solutions (Kima *et al.*, 2013), crystallite size and shape (Popa and Balzar, 2008), preferred crystal orientations (Pentecost and Wright, 1963), internal elastic strains/stresses at different levels (Serbena and Zanotto, 2012), effects of temperature (Diasa *et al.*, 2005), close surface analysis (Angerera and Strobl, 2014; Strasberg *et al.*, 2014) are all possible. The objective of this paper is to show some examples of these advanced applications of XRD in the field of ceramic materials. First, the basics of XRD analysis required to understand these examples will be summarized. Next, two case studies will be developed: (1) the investigation of the anisotropic thermal expansion behavior of cordierite honeycomb substrates, (2) the development of piezoelectric glass ceramics.

Basics of XRD Analysis

Diffraction Conditions and Diffracted Intensity

The XRD technique is based on the interferences between the waves elastically diffused by the periodically ordered atoms of a crystal lattice. X-ray diffraction conditions can be expressed by the Laue condition (Fig. 1). The interferences between the waves elastically diffused by the atomic patterns of the lattice points are constructive if the difference between the diffused wave vector $\vec{k}$ and the incident wave vector $\vec{k}_i$ corresponds to a reciprocal vector $\vec{s}_{(hkl)}$ (1):

$$\vec{k} - \vec{k}_i = \vec{s}_{(hkl)} \quad (1)$$

As $\vec{s}_{(hkl)}$ is normal to planes (hkl) and its length is $1/d_{(hkl)}$, diffraction condition can also be expressed by the Bragg's law (2):

$$\lambda = 2d_{(hkl)} \sin \theta \quad (2)$$

The interplanar distance between (hkl) planes is linked to the unit cell parameters $(a, b, c, \alpha, \beta, \gamma)$ by the relation (3):

$$d_{(hkl)} = \sqrt{\frac{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}{\frac{h^2}{a^2} \sin^2 \alpha + \frac{k^2}{b^2} \sin^2 \beta + \frac{l^2}{c^2} \sin^2 \gamma - \frac{2hk}{bc} (\cos \alpha - \cos \beta \cos \gamma) - \frac{2lh}{ca} (\cos \beta - \cos \gamma \cos \alpha) - \frac{2hk}{ab} (\cos \gamma - \cos \alpha \cos \beta)}} \quad (3)$$

Diffraction conditions are expressed with respect to the lattice points of the crystal lattice. Actually, it is every atom within the crystal unit cell that scatters the X-rays. Consequently, the diffracted intensities are modulated according to the nature and the relative positions of the atoms. It follows that the intensity $I_{(hkl)}$ of the observed diffraction peak when given planes (hkl) meet the diffraction conditions is proportional to the square of the structure factor $F_{(hkl)}$ (4):

$$F_{(hkl)} = \sum_e f_e^x \exp[2\pi j(x_e + \gamma_e + z_e)] \quad (4)$$

- $x_e; y_e; z_e$ are the coordinates of the atoms in the unit cell.
- f_e^x are the scattering factors of these atoms.

The X-ray Diffractometer

Although different kinds of devices can be used for operating X-ray diffraction analyses, the most common equipment is the diffractometer Fig. 2(a). This equipment uses an X-ray tube as radiation source. The most common anticathode is Cu ($k\alpha_1 = 154.056$ pm, $k\alpha_2 = 154.152$ pm) but other sources (e.g., Co, Fe) of shorter or longer wavelengths can be use in specific

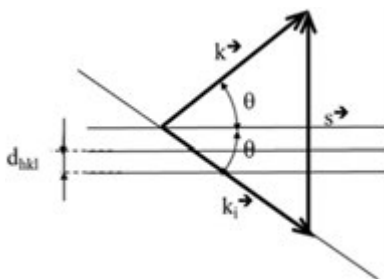


Fig. 1 Schematization of Laue and Bragg diffraction conditions.

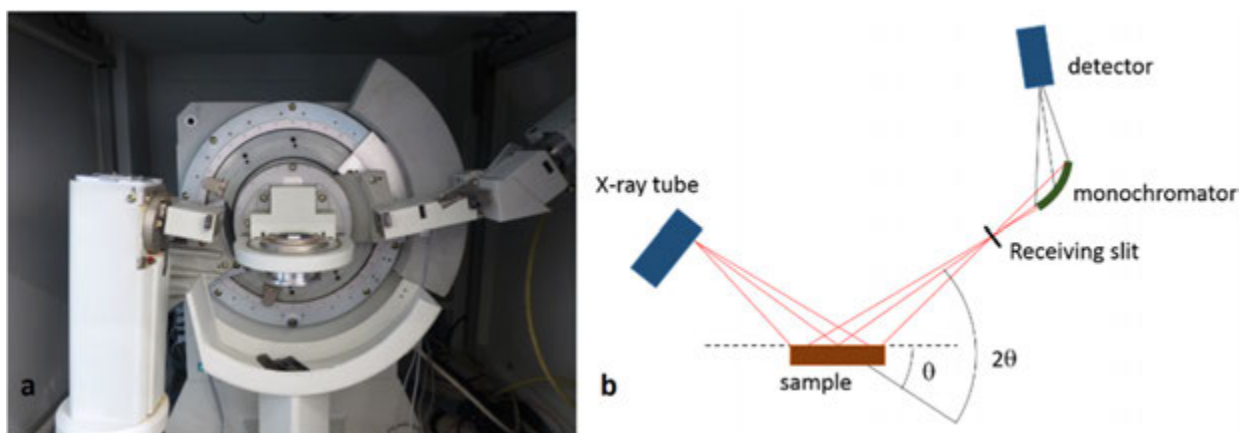


Fig. 2 Conventional X-ray diffractometer (a) and schematic diagram of the Bragg-Brentano configuration (b).

cases. A scintillator counter is commonly used as X-ray detector. Radiation filtering is operated by means of a thin filter or of a curved monochromator in order to remove the background and undesired spectral lines of the X-ray source but also the fluorescence emissions of the specimen. Divergence angles of incident and diffracted beams are controlled by slits.

A goniometer allows control of the deviation angle 2θ and the incident angle γ with respect to the analyzed surface of the specimen **Fig. 2(b)**. In a conventional configuration (Bragg-Brentano), the incident angle is equal to θ , so that the normal $\vec{n}$ to the surface of the specimen corresponds to the normal $\vec{s}_{(hkl)}$ to the diffracted planes. Consequently, only the planes (hkl) that are parallel to specimen surface can meet the diffraction conditions. When analyzing solid specimens, a possible preferential orientation of the crystals will affect the relative intensities of the diffraction peaks observed on the diffraction pattern and possibly will make some peaks disappear. To avoid this, XRD is usually performed on fine powder milled specimens (powder diffraction method) which normally leads to a random orientation of the crystals. However, one must be vigilant when analyzing a powder exhibiting a particular shape of grains such as wires or platelets (for example raw materials such as kaolin or talc). Indeed, the grains may easily be oriented when preparing specimens for analysis.

Some goniometers use an Euler cradle **Fig. 3(a)** that allows the control of the orientation of the normal to the diffracting planes $\vec{s}_{(hkl)}$ with respect to the normal to specimen surface $\vec{n}$ through the χ and φ angles **Fig. 3(b)**. The application fields of the Euler cradle are the characterization of crystals textures (preferred orientation) and characterization of internal stresses.

Diffraction Peak Shifts and Broadening

According to Bragg's law, for a given crystal structure the diffraction peaks appear at well-defined angles $\theta_{(hkl)}$. Experimentally, a distribution of the intensity $I_{(hkl)}$ is observed around the diffraction angle. In addition, shifts of peaks with respect to expected $\theta_{(hkl)}$ angles are sometime observed.

From the differential of the Bragg law, shifts $d\theta_{(hkl)}$ result of changes in $d_{(hkl)}$ spacing (5)

$$\frac{d(d_{(hkl)})}{d_{(hkl)}} \sim -\cot\theta_{(hkl)} \cdot d\theta_{(hkl)} \quad (5)$$

Note that well defined $d\theta_{(hkl)}$ require homogeneous changes $d(d_{(hkl)})$ over all the diffracting volume.

Among the origins of the changes in $d_{(hkl)}$, we mainly find solid solutions, elastic strains due to internal stresses and lattice thermal expansion in the case of high temperature XRD analyses (HT-XRD).

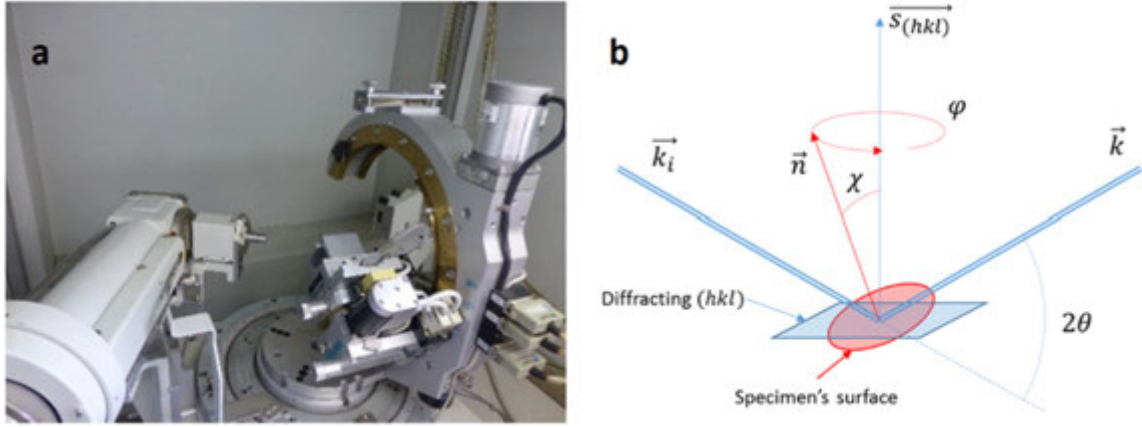


Fig. 3 X-ray diffractometer with Euler cradle (a) and schematic diagram of the control of the orientation of the diffracting planes with respect to the specimen surface.

The broadness of diffraction peaks is usually characterized through β , the FWHM (Full Width at Half Maximum), and is a function of θ . One part is linked to the configuration of the equipment (β_{inst}), and the other part characterizes the analyzed specimen (β_{sp}) (6):

$$\beta^n = \beta_{inst}^n + \beta_{sp}^n \quad (6)$$

With n between 1 and 2 according to the shape of the peaks (Lorentzian, Gaussian, Pseudo-Voigt,...).

Equipment contribution β_{inst} can be calibrated by determining the Caglioti function (7) from a reference sample (usually LaB_6):

$$\beta_{inst}^2 = W + V \tan \theta + U \tan^2 \theta \quad (7)$$

Considering the differential of the Bragg's law, one possible reason for a peak broadening is a non-homogeneous change $d(d_{(hkl)})$ over all the diffracting volume that leads to a range of $d\theta_{(hkl)}$. The main origins of this are: i). microstrains associated with lattice defects and ii). non-homogeneous solid solutions. The second reason for peak broadening is the limited size T of the crystallites.

The contribution β_{cs} of the crystallite size T for a given (hkl) diffraction peak is obtained by the Scherrer relation (8):

$$\beta_{cs} = \frac{K\lambda}{T \cos \theta_{(hkl)}} \quad (8)$$

K is a constant with a value between 0.8 and 1.2 depending on the peak shape. The value of T corresponds to the size of the crystallites in the normal direction to (hkl) plane. If the crystallite shape is anisotropic, the contribution β_{cs} varies from one (hkl) diffraction peaks to another.

The contribution $\beta_{\mu s}$ of the microstrains is given by the relation (9):

$$\beta_{\mu s} = 4\epsilon_{\mu} \tan \theta_{(hkl)} \quad (9)$$

One way to evaluate the average crystallite size and the microstrains is to use the Williamson-Hall relation (10) which assumes that β_{sp} is the arithmetic sum of the two contributions. Consequently, $\beta_{sp} \cos \theta_{(hkl)}$ becomes a function of $\sin \theta_{(hkl)}$:

$$\beta_{sp} \cos \theta_{(hkl)} = \frac{K\lambda}{T} + 4\epsilon_{\mu} \sin \theta_{(hkl)} \quad (10)$$

The intersection with the Y-axis gives the crystallite size T and the slope gives the microstrains ϵ_{μ} **Fig. 4**.

Penetration Depth of X-rays

The information collected during an XRD analysis comes from a limited depth below the specimen surface. Absorption of X-rays follows the Beer-Lambert law (11):

$$I_{\lambda}(x) = I_{\lambda}^0 \exp(-\mu \cdot x) \quad (11)$$

With μ the linear absorption coefficient of the material.

In the case of a Bragg-Brentano configuration, the intensity $I_{\lambda}(z)$ of the radiation emerging out of the sample after diffraction at a depth z is given by the relation (12):

$$I_{\lambda}(z) = I_{\lambda}^0 \exp\left(-\mu \cdot \frac{2z}{\sin \theta}\right) \quad (12)$$

With I_{λ}^0 the intensity of the incident radiation.

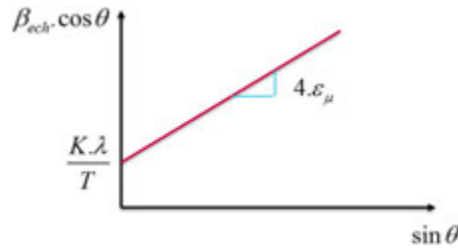


Fig. 4 Determination of crystallite size T and microstrains ϵ_{μ} from the Williamson-Hall relation.

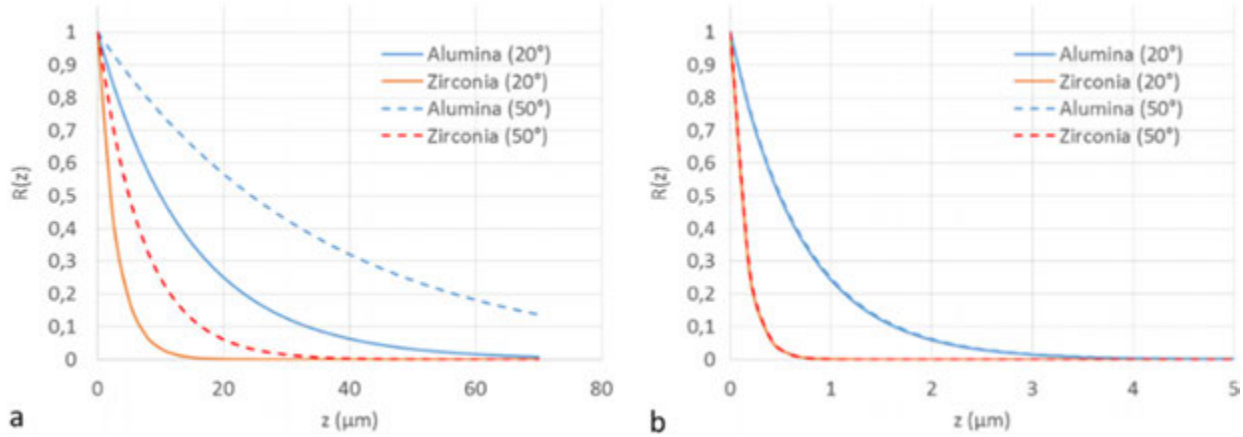


Fig. 5 Contribution of the emerging radiation to diffracted signal in the Bragg-Brentano configuration (a) and in the grazing incidence configuration with $\gamma = 0.5^\circ$ (b).

The contribution $R(z)$ of emerging radiation for depth $> z$ to diffracted signal is given by (13):

$$R(z) = \frac{\int_0^z \exp\left(-\mu \cdot \frac{2z}{\sin\theta}\right)}{\int_0^\infty \exp\left(-\mu \cdot \frac{2z}{\sin\theta}\right)} = \exp\left(-\mu \cdot \frac{2z}{\sin\theta}\right) \quad (13)$$

$R(z)$ strongly depends on the absorption coefficient as it is shown in **Fig. 5(a)** for alumina and zirconia. We also notice on these figures the strong influence of the 2θ angle.

When the analysis requires a low depth penetration of the X-rays, the grazing incidence configuration is used and γ is set to low values ($< 2^\circ$). The intensity $I_\lambda(z)$ of the radiation emerging out of the sample after diffraction at a depth z is given by the relation (14):

$$I_\lambda(z) = I_\lambda^0 \exp\left(-\mu \cdot \left(\frac{z}{\sin\gamma} + \frac{z}{\sin 2\theta - \gamma}\right)\right) \quad (14)$$

Contribution $R(z)$ of emerging radiation for depth $> z$ to diffracted signal is given by (15):

$$R(z) = \frac{\int_0^z \exp\left(-\mu \cdot \left(\frac{z}{\sin\gamma} + \frac{z}{\sin 2\theta - \gamma}\right)\right)}{\int_0^\infty \exp\left(-\mu \cdot \left(\frac{z}{\sin\gamma} + \frac{z}{\sin 2\theta - \gamma}\right)\right)} = \exp\left(-\mu \cdot \left(\frac{z}{\sin\gamma} + \frac{z}{\sin 2\theta - \gamma}\right)\right) \quad (15)$$

$R(z)$ rapidly decreases with depth even for low absorption coefficients as it is shown in **Fig. 5(b)** for alumina and zirconia. Moreover, the analyzed depth is negligibly dependent on the 2θ angle.

The Rietveld Method

The Rietveld method is based on the comparison of a calculated diffraction pattern with an experimental pattern in order to refine the structural and microstructural parameters of the model used for calculation. The intensities observed on the pattern depend on:

- The crystalline phases: crystal structure, microstructure, quantity, cell volume, texture, stress, defects etc;
- The instrument settings: beam intensity, Lorentz-Polarization, background, resolution, aberrations, radiation etc;
- The sample: position, shape and dimensions, orientation.

Refinement aims to minimize the residual function using a non-linear least squares algorithm (16):

$$WSS = \sum_{i=1}^N \frac{(I_i^{exp} - I_i^{calc})^2}{I_i^{exp}} \quad (16)$$

Where I_i^{exp} is the intensity observed on the experimental pattern for the angle $2\theta_i$. The calculated intensity I_i^{calc} for the angle $2\theta_i$ is given by Eq. (17):

$$I_i^{calc} = bkg_i + S \sum_{j=1}^n \frac{f_j}{V_j^2} \sum_{k=1}^p L_{kj} |F_{kj}|^2 T_{kj} (2\theta_i - 2\theta_{kj}) P_{kj} A_j \quad (17)$$

With:

- j , index of the n phases
- k , index of the p diffracting (hkl) planes
- bkg_i , the background
- S , the scale factor
- f_j , the weight fraction of phase j
- V_j , the molar volume of phase j
- L_{kj} , the Lorentz polarization factor
- F_{kj} , the structure factor for diffraction peak k of phase j
- $T_{kj}(2\theta_i - 2\theta_{kj})$, the peak profile function for diffraction peak k of phase j
- $2\theta_{kj}$, the diffraction angle for peak k of phase j
- P_{kj} , the preferential orientation factor for diffraction peak k of phase j
- A_j , the absorption correction factor for phase j

The main information obtained for a given j phase after refinement is:

- The weight fraction f_j ;
- The unit cell parameters from the exact $2\theta_{kj}$ diffraction angles;
- The crystallites size and microstrains from the peak profile $T_{kj}(2\theta_i - 2\theta_{kj})$;
- The preferential orientation from the P_{kj} factor;
- The atom positions and occupation factor from the structure factor F_{kj} ;

Note that for the quantitative evaluation of the phase weight fractions, the microabsorption effects can severely affect the accuracy of the measurements when the phases that are present in the sample exhibit strong differences in absorption coefficients and grain sizes (Pederson *et al.*, 2003). Most of the Rietveld analysis software include correction of microabsorption effects through a coefficient A_j based on different models.

For further readings on X-ray diffraction and experimental methods: Hammond (2009); Suryanarayana and Norton (1998); Will (2006).

Case Study #1: Investigation of the Anisotropic Thermal Expansion Behavior of Cordierite Honeycomb Substrates

This case study will show how XRD has been used to investigate the anisotropic microstructure of cordierite ($MgO \cdot Al_2O_3 \cdot 5SiO_2$) substrates used as catalyst support for automobile exhaust gas (Callebaut *et al.*, 2007). These substrates present a honeycomb structure composed of channels shaped by extrusion of a green paste Fig. 6.

Ceramic honeycomb structures are widely used as a catalyst support for exhaust gas purification by the three-way catalysis in automobiles and industries, but also as filters or heat exchangers. Among the materials used for producing honeycomb structures, cordierite is a low-cost ceramic that exhibits a high resistance to thermal shock due to its low thermal expansion coefficient.

Cordierite is usually produced by reactive sintering of raw materials as talc, natural and/or calcined kaolin, and alumina. The first part of this work shows the characterization by XRD analyses of the successive phase transformations and reactions that occur with the increasing temperature during the sintering. The second part focuses on investigation of the preferential orientation of the grains of raw materials in the extruded green body, and its consequences on the cordierite crystallites in the fired ceramic. Finally, the third part shows the characterization of the thermal expansion of the cordierite unit cell by High Temperature XRD.



Fig. 6 Green cordierite honeycomb substrate.

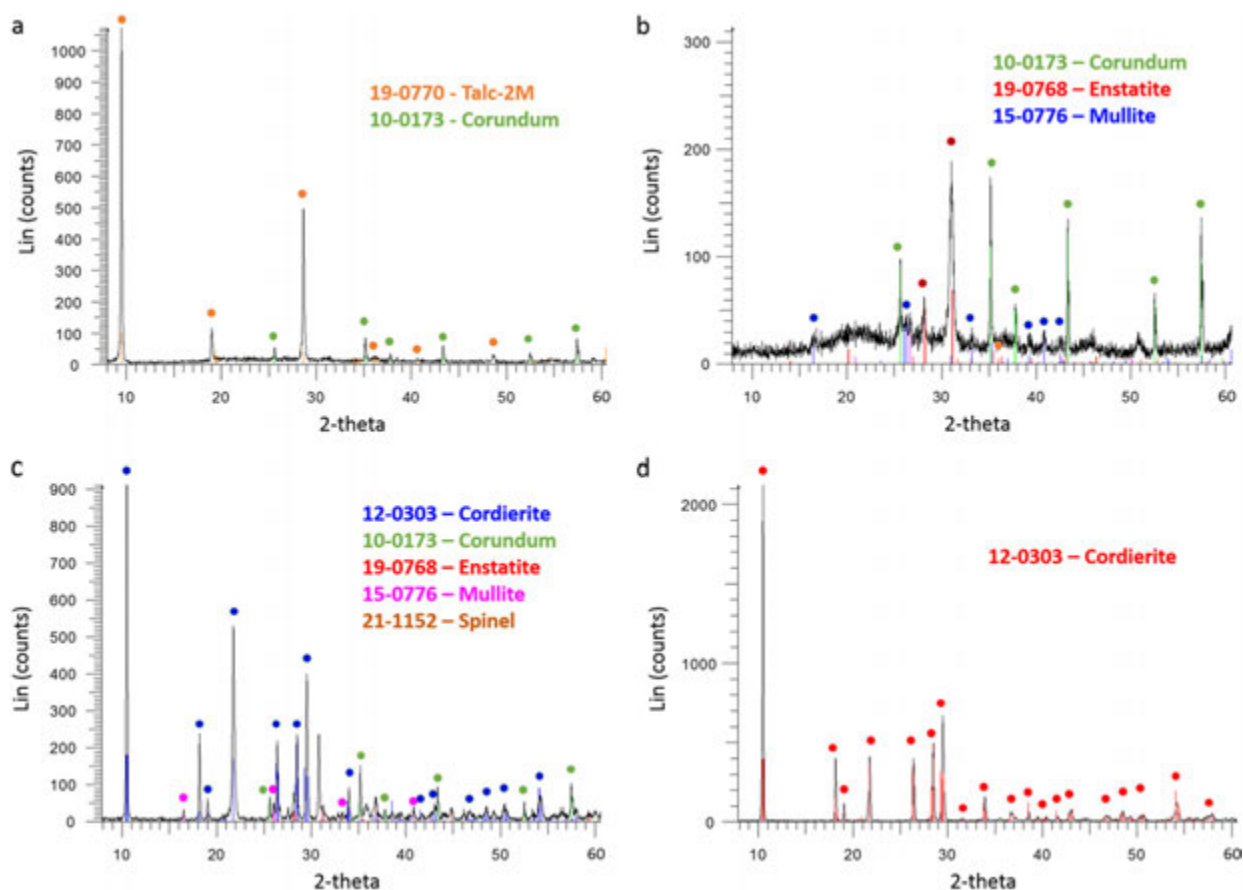


Fig. 7 XRD patterns collected on the samples heat treated at 800°C (a), 1050°C (b), 1200°C (c) and 1400°C (d).

Characterization of the Phase Transformations During Reactive Sintering

Samples of the raw materials blend (i.e., talc, natural and calcined kaolin, and alumina) were pressed into pellets and heat treated at 800°C, 1050°C, 1200°C, and 1400°C. X-ray diffraction patterns were collected thanks to a $\theta - \theta$ diffractometer Siemens D5000 (Bragg-Brentano configuration) with CuK_α radiation and graphite monochromator.

The diffraction peaks observed on the XRD pattern of the sample heat treated at 800°C **Fig. 7(a)** correspond to those of the initial talc (JCPDS # 19-0770) and α -alumina (JCPDS # 13-0173). Peaks of kaolinite (JCPDS # 14-0164) are not present due to its transformation into metakaolinite which does not show long range order. This transformation, which leads to the loss of the hydroxyl groups, usually occurs around 500°C:

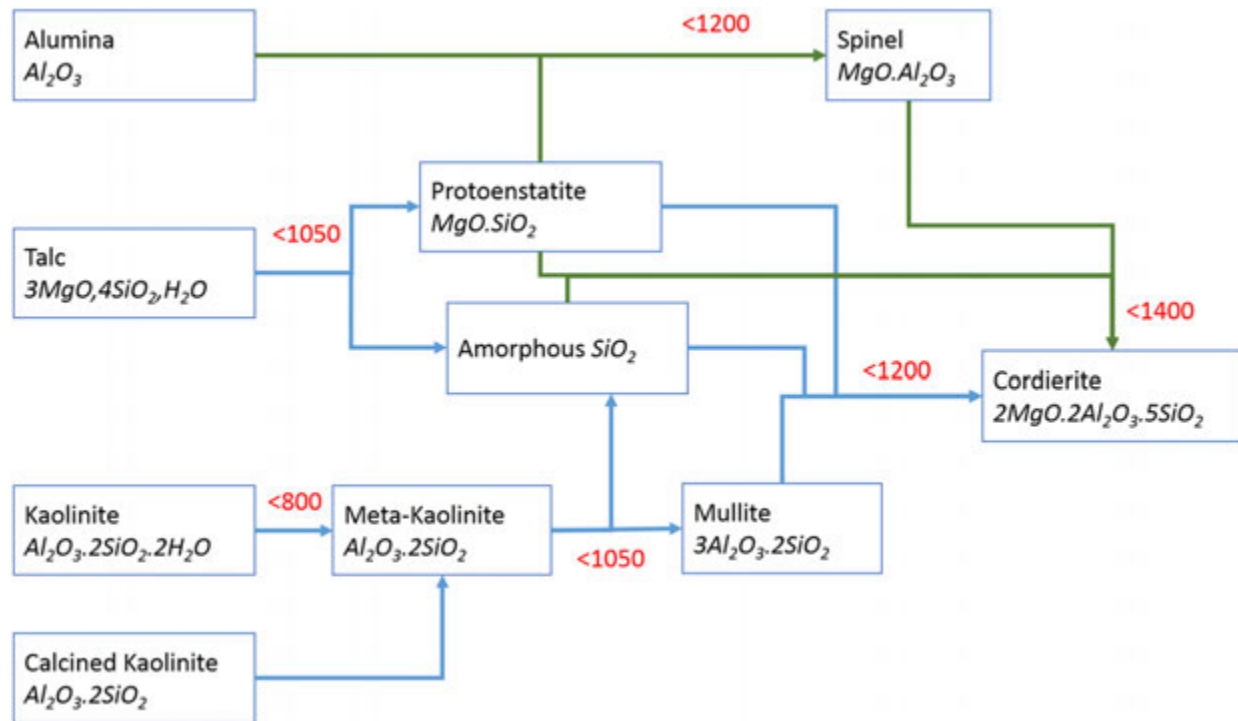
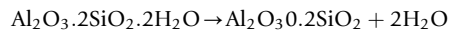


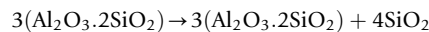
Fig. 8 Mechanism of formation of cordierite.



The XRD pattern of the sample heat treated at 1050°C does not exhibit the diffraction peaks of the talc anymore Fig. 7(b). Alumina is still present and new peaks are observed. These peaks correspond the protoenstatite $\text{MgO} \cdot \text{SiO}_2$ (JCPDS # 19-0768) resulting from the transformation of the talc according to the reaction:



One can also observe peaks of weak intensities belonging to mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (JCPDS # 15-0776) formed from the metakaolinite:



The heat treatment at 1200°C leads to the formation of cordierite Fig. 7(c). However, diffraction peaks of alumina, enstatite, and mullite are still present. In addition spinel $\text{MgO} \cdot \text{Al}_2\text{O}_3$ (JCPDS # 21-1150) is evidenced. The cordierite present in the sample at this temperature is the result of the reaction between protoenstatite, mullite, and silica coming from talc and metakaolinite as it is shown in blue in Fig. 8.

Finally, the sample heat treated at 1400°C contains only cordierite as crystalline phase Fig. 7(d). The completion of the transformation is obtained by the reaction between protoenstatite, spinel, and silica coming from talc and metakaolinite as it is shown in green in Fig. 8.

Characterization of Textures in the Green and Fired Bodies

During the synthesis, numerous parameters may influence the apparent expansion coefficient of the final ceramic (Evans *et al.*, 1980). Among these parameters, the size and shape of the raw material particles combined with the shaping process may lead to an orientation of the cordierite crystallites (Lachman *et al.*, 1981; Saha *et al.*, 2001).

The investigated honeycombs are produced by extrusion of the green paste. Green and fired structures were cut and polished to obtain samples corresponding to the sidewall of the honeycomb cells Fig. 9.

XRD analyses were performed on the green and fired honeycomb cells and on the same samples ground into powders. It can be seen on the XRD patterns that the relative intensities of talc and kaolinite peaks do not match with that of the JCPDS files, for both powder and honeycomb cell Fig. 10. Indexing the diffraction peaks with their corresponding Miller indices highlights that for both phases, (00 l) planes exhibit higher intensities, which suggests that (00 l) planes are preferentially oriented parallel to the analyzed surface. Note that this effect is stronger for the honeycomb cell than for the powder.

With the objective of characterizing this orientation, a $\theta - 2\theta$ diffractometer Siemens D5000 with Euler cradle Fig. 3, CuK_α radiation and Fe filter was used to collect pole figures relative to (002) planes of kaolinite and (006) planes of talc. These planes were selected for their high intensities and also for their low convolution with others peaks. The pole figures Fig. 11(a)

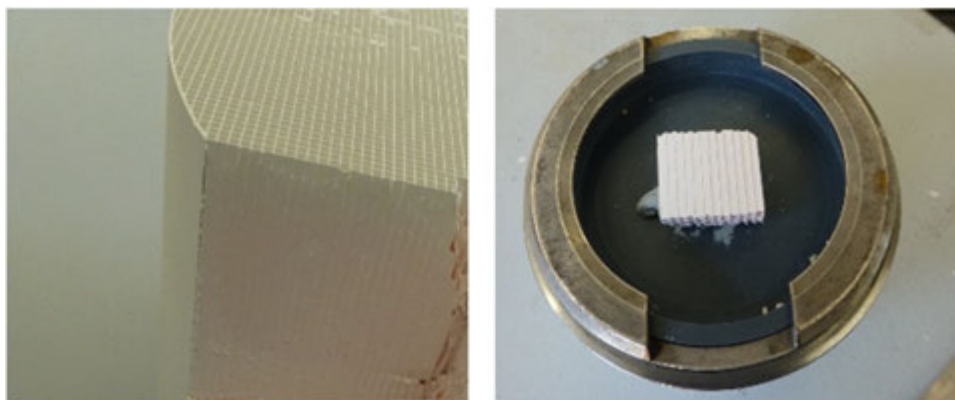


Fig. 9 Sample preparation for XRD analysis.

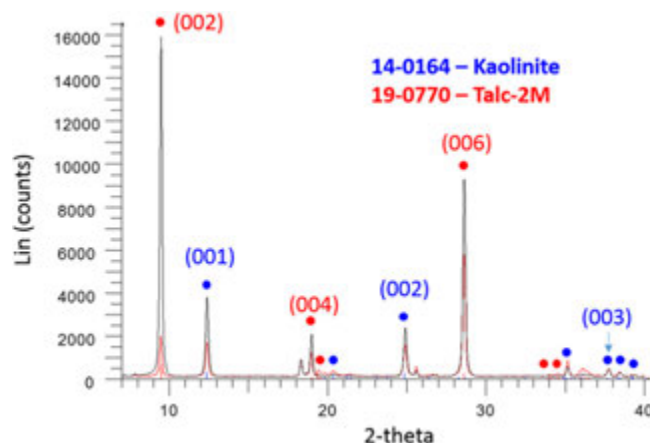


Fig. 10 XRD pattern collected on the green powder (red pattern) and green honeycomb cell (black pattern).

represent, on a stereographic projection, the value of mrd (multiple of random distributions) according to the orientation of the normal to specimen surface $\vec{n}$ with respect to the normal to diffracting planes $\vec{s}_{(hkl)}$ through φ and χ angles **Fig. 3**. In a non-textured sample, $\text{mrd} \approx 1$ for all angles. In the present case the (002) pole figure of kaolinite shows a maximum $\text{mrd} \approx 6$ for $\chi = 0$ and $\varphi = 0$ **Fig. 11(b)**. For the (006) pole figure of talc, the mrd reaches 10 also for $\chi = 0$ and $\varphi = 0$ **Fig. 11(c)**. These results allow it to be concluded that these planes are preferentially oriented parallel to the analyzed surface (the honeycomb cell's sidewalls) and consequently that crystallographic c-axes of kaolinite and talc crystals are preferentially oriented perpendicularly to the direction of extrusion **Fig. 12(a)**. The shape of the platelets of kaolinite crystals and talc combined with the shear stresses generated by the extrusion process can explain this result.

When comparing the XRD patterns of the fired powder and the fired honeycomb cell, it can be seen that the relative intensities of cordierite peaks match with those of the JCPDS file (# 13-0294) for the powder but not for the Honeycomb **Fig. 13**. In order to clearly identify which planes are over or under represented, Rietveld refinement has been performed from data of synthetic cordierite structure (Gibbs, 1966). As expected, the calculated pattern is in good agreement with the experiment in the case of the powder sample **Fig. 14(a)**. On the contrary, strong differences between calculated and experimental relative intensities are observed for the honeycomb cell **Fig. 14(b)**. For this latter, the diffraction peaks corresponding to (hk0) planes are stronger than they should be. This is the case for example for (310) and (020) planes at respectively 17.965° and 18.116° **Fig. 14(c)**.

These analyses pointed out that cordierite crystals grow in a way that the c-axis is perpendicular to the c-axes of talc and kaolinite **Fig. 12(b)**. It must be highlighted that as there is not preferential orientation of the a and b axes of kaolinite and talc, there is no reason for a preferential orientation of the c-axis of cordierite in the sidewall plane.

Characterization of the Thermal Expansion Behavior

HT-XRD patterns were collected on the fired powder using a Bruker D8 Advance instrument (Cu anticathode) with a high temperature chamber. In order to avoid peak shifts due to specimen surface displacement during heating, parallel beam geometry

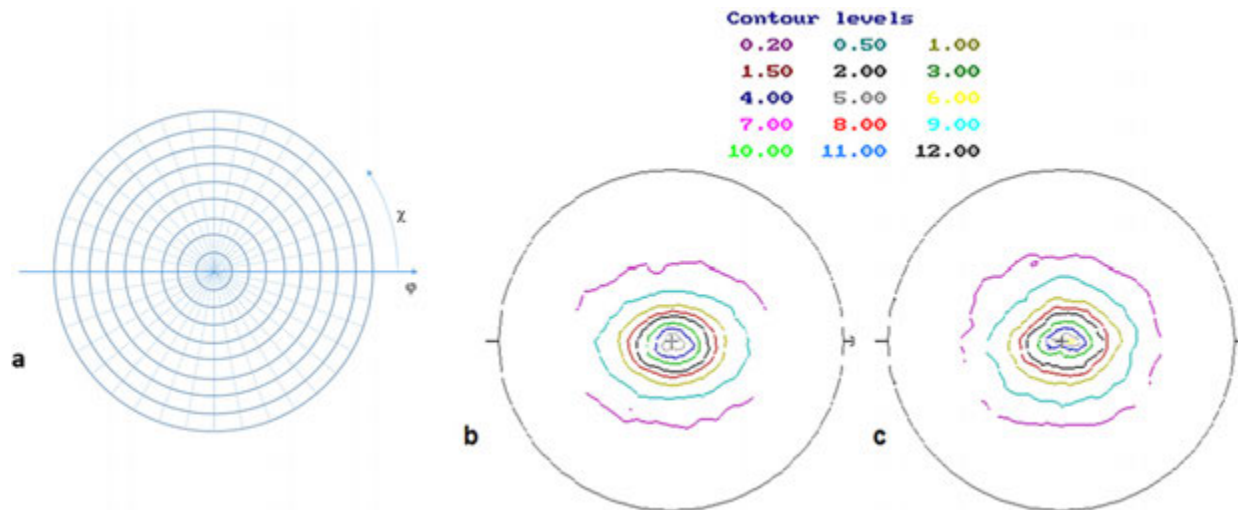


Fig. 11 Stereographic projection of directions given by angle ϕ and χ (a) and pole figures of (006) talc planes (b) and (002) kaolinite planes (c).

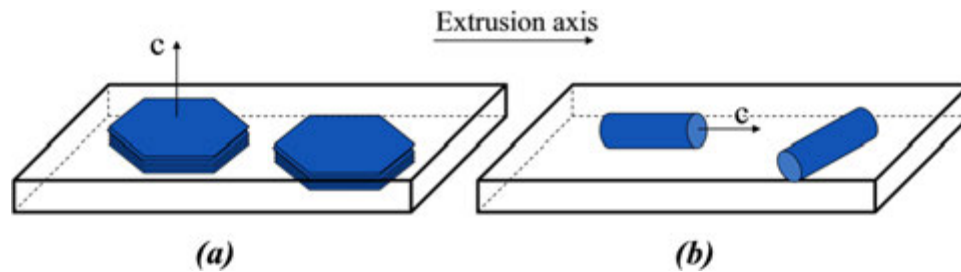


Fig. 12 Preferential orientation of the c-lattice axes of talc and kaolinite grains (a) and of cordierite grains (b).

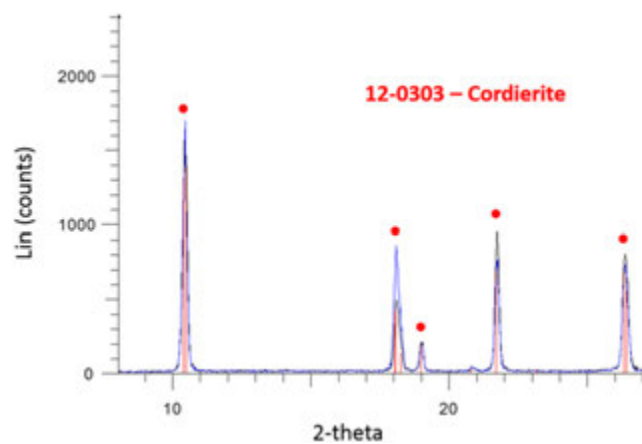


Fig. 13 XRD patterns collected on the fired powder (black pattern) and fired honeycomb cell (blue pattern).

was realized by a primary Göbel mirror and post-specimen Soller slits. Patterns were collected at RT, 200, 400, 600, 800, and 1000°C on heating (red patterns on Fig. 15 near here) and 900, 700, 500, 300, and 100°C on cooling (blue patterns on Fig. 15 near here).

For most of the diffraction peaks, HT-XRD patterns show shifts to lower angles with increasing temperatures due to lattice thermal expansion (increase in d-spacing). However, these shifts are function of the (*hkl*) planes, and the (002) peak near 19° shifts on the contrary to higher angles. These shifts indicate a strong anisotropic behavior.

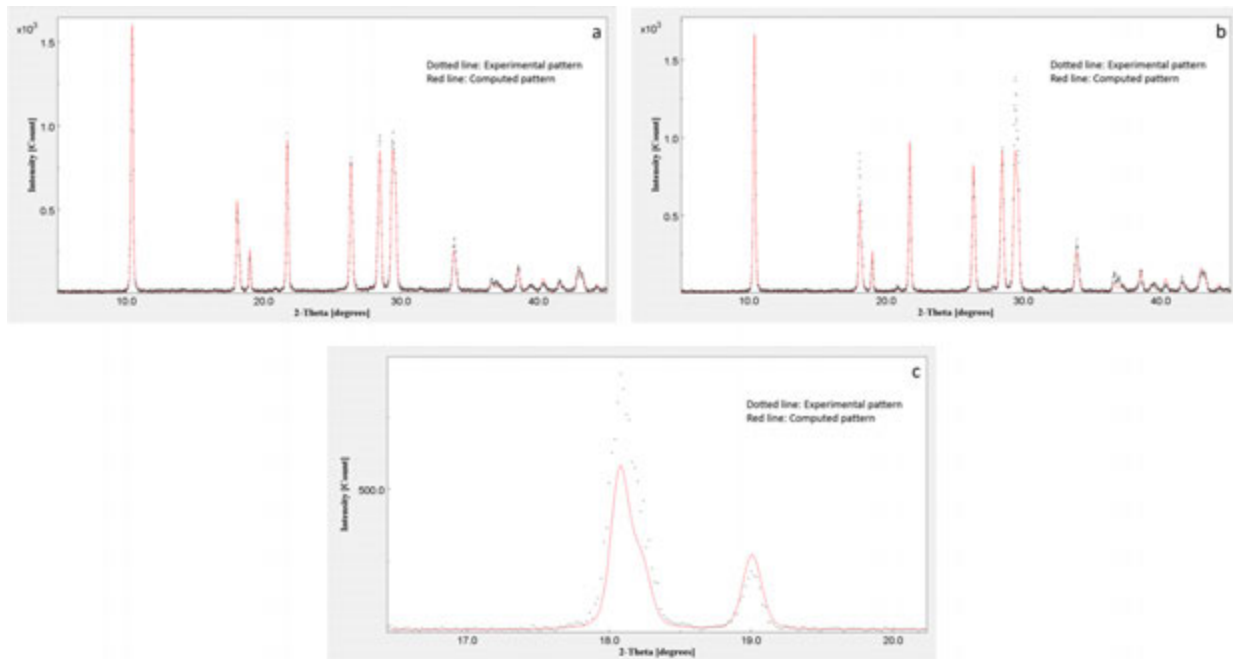


Fig. 14 Rietveld refinements of XRD patterns collected on the fired powder (a) and fired honeycomb cell (b)–(c).

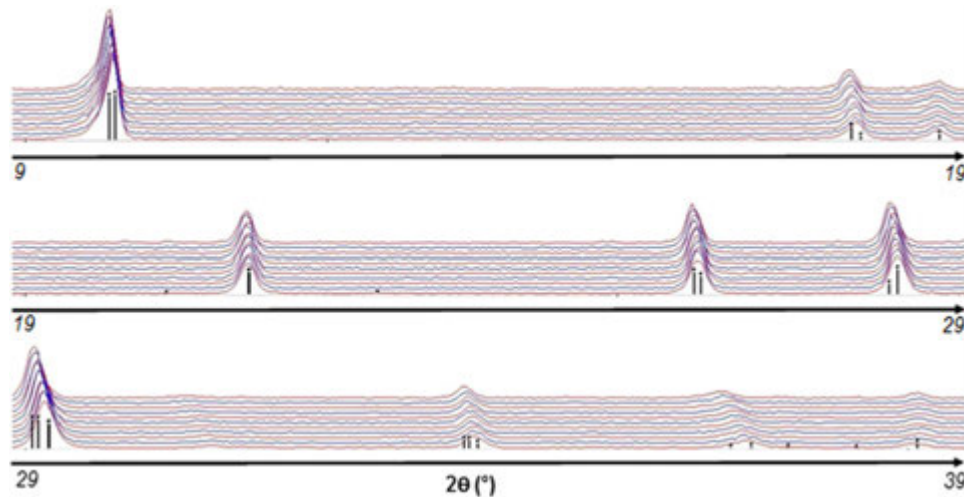


Fig. 15 HT-XRD patterns collected on the fired powder (a) and fired honeycomb cell (b).

From the Rietveld refinement of the lattice parameters, the relative variations of these parameters (with reference to room temperature) have been calculated and plotted versus the temperature [Fig. 16](#). Significant differences are observed between the a , b and c lattice axes. The c parameter exhibits almost no change with temperature, unlike a and b . The thermal expansion coefficients (between RT and 1000°C) have been calculated from these graphs: α_c is slightly negative ($-0.7 \times 10^{-6} \text{K}^{-1}$) whereas α_a and α_b are respectively equal to $4.2 \times 10^{-6} \text{K}^{-1}$ and $4.9 \times 10^{-6} \text{K}^{-1}$.

This anisotropic behavior, associated with the preferential orientation of the cordierite crystals, explains the significant differences between the apparent thermal expansion coefficient α measured parallel to extrusion axis ($0.45\text{--}0.55 \times 10^{-6} \text{K}^{-1}$) and the coefficient measured on a non-textured sample of cordierite ($\sim 3 \times 10^{-6} \text{K}^{-1}$).

In addition, the strong anisotropic thermal expansion behavior of cordierite crystals highlights the importance to control the texture of the final microstructure as differences in shrinkage on cooling after sintering may be source of stresses and directly cause cracks in the final parts.

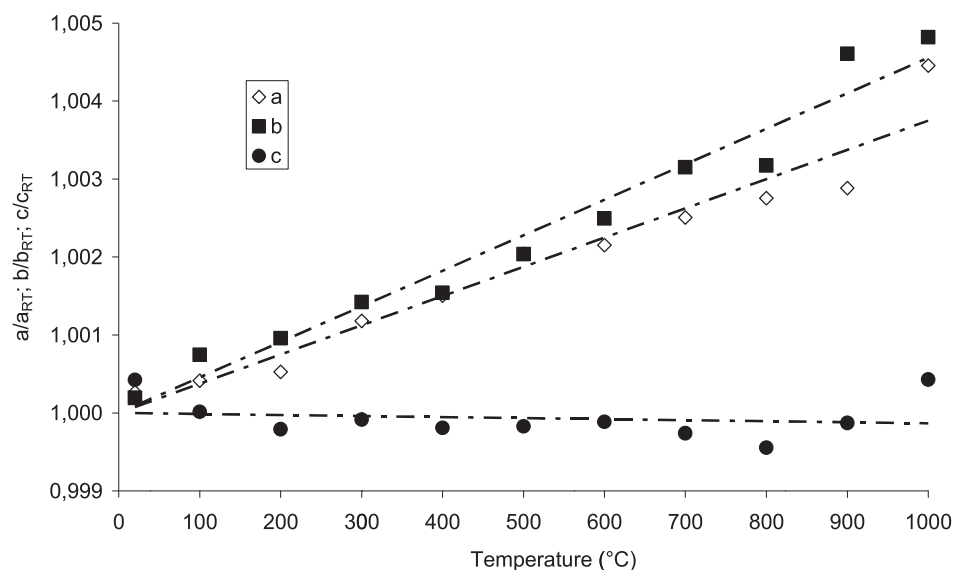


Fig. 16 Relative variations of lattice parameters with temperature.

Case Study #2: Development of Piezoelectric Glass Ceramics

A glass-ceramic is a polycrystalline material obtained by controlled crystallization of a parent glass (Aitken and Beall, 1994). It results in a multiphase material composed of one or several crystalline phases embedded in a residual glass matrix. Properties of the resulting material are mainly given by those of the crystalline phases.

The present case study will highlight the role of X-ray diffraction in the development of piezoelectric glass-ceramics for high temperature applications.

Strontium fresnoite $\text{Sr}_2\text{TiSi}_2\text{O}_8$ is a pyroelectric but non-ferroelectric phase (Schneider *et al.*, 1998). It shows a quadratic symmetry that belongs to the space group $P4bm$, and its lattice parameters are $a = 832.18$ pm and $c = 502.92$ pm. The dipole moment of the unit cell is oriented along the $[001]$ direction.

Its non-ferroelectric behavior is the result of the single domain configuration of the crystals. Consequently, in the case of polycrystalline material, a preferential orientation of the crystallites polar c -direction needs to be induced during the elaboration process to obtain a macroscopically piezoelectric material. This is possible using the glass-ceramics process (Halliyal *et al.*, 1985).

Investigation of the Crystallization of a Glass-Ceramic

The glass-ceramic here presented is obtained by melting, casting and post-crystallizing Fig. 15 a parent glass of composition $2\text{SrO } 1\text{TiO}_2 \text{ } 3.3\text{SiO}_2 \text{ } 0.2\text{K}_2\text{O } 0.1\text{Al}_2\text{O}_3$ (Renoirt *et al.*, 2019) (Fig. 17).

Crystallization treatments performed for various dwell times at temperatures ranging from 850°C to 950°C evidence a surface crystallization mechanism with a crystallization front propagating from the surfaces to the center over time Fig. 18.

After the crystallization treatment, qualitative analyses of the crystalline phases were carried out by XRD with a Siemens D5000 θ - 2θ diffractometer using a CoK_α radiation source. The XRD pattern collected on a powder milled sample after complete crystallization shows fresnoite as the only crystalline phase and a good agreement of the relative intensities with the JCPDS file # 39-0228 Fig. 19(a). Contrarily to the powder specimen, the XRD patterns collected on the glass-ceramic surface exhibit very strong intensities for (001) planes Fig. 19(b), evidencing thereby a preferential orientation of these planes parallel to analyzed surfaces.

Investigation of the Preferential Orientation

In order to follow possible changes in the preferential orientation over depth, XRD analyses were performed at each step of a step-by-step grinding Fig. 20.

Considering a linear absorption coefficient of $0.0316 \mu\text{m}^{-1}$ for the glass-ceramic and a Co K_α radiation, the thickness of the layer of material contributing to the XRD pattern is less than $50 \mu\text{m}$ as it can be seen from the curves R versus z Fig. 21. On that base, the thickness removed at each grinding step between two analyses was set to $100 \mu\text{m}$.

The obtained XRD analyses highlight that the (002) peak intensity decreases in favor of (201) peaks Fig. 22. Pole figures of (002) and (201) planes were also collected after each grinding step. They show a progressive tilt of the (002) planes over the first $300 \mu\text{m}$ Fig. 23. After $300 \mu\text{m}$, (201) planes are parallel to the surfaces and no more changes are observed deeper in the samples.

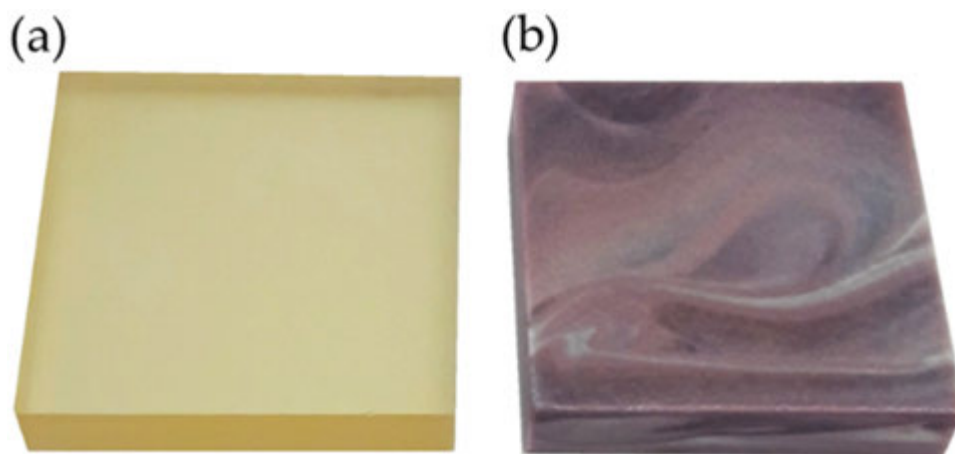


Fig. 17 Parent glass (a) and glass-ceramic after crystallization treatment (b). Adapted from Renoirt, M.-S., Maury, N., Dupla, F., Gonon, M., 2019. Structure and properties of piezoelectric strontium fresnoite glass-ceramics belonging to the Sr-Ti-Si-Al-K-O system. *Ceramics 2*, 86–97.

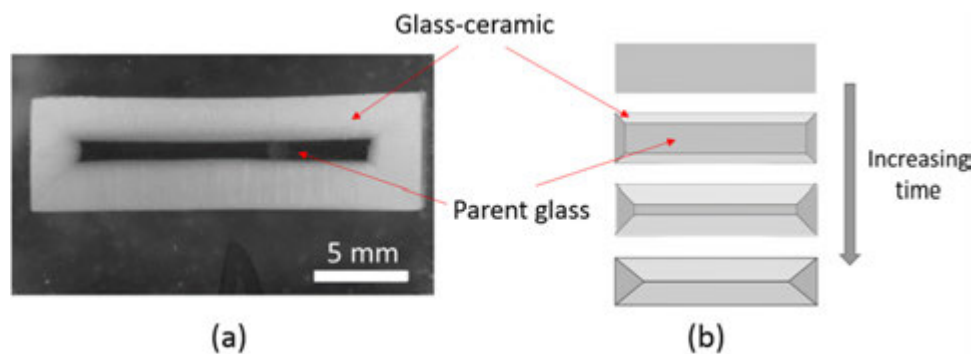


Fig. 18 (a) Image of a polished cross section of specimen A10 after crystallization treatment for 2 h at 950°C; (b) schematization of the motion of the crystallization front over time. Adapted from Renoirt, M.-S., Maury, N., Dupla, F., Gonon, M., 2019. Structure and properties of piezoelectric strontium fresnoite glass-ceramics belonging to the Sr-Ti-Si-Al-K-O system. *Ceramics 2*, 86–97.

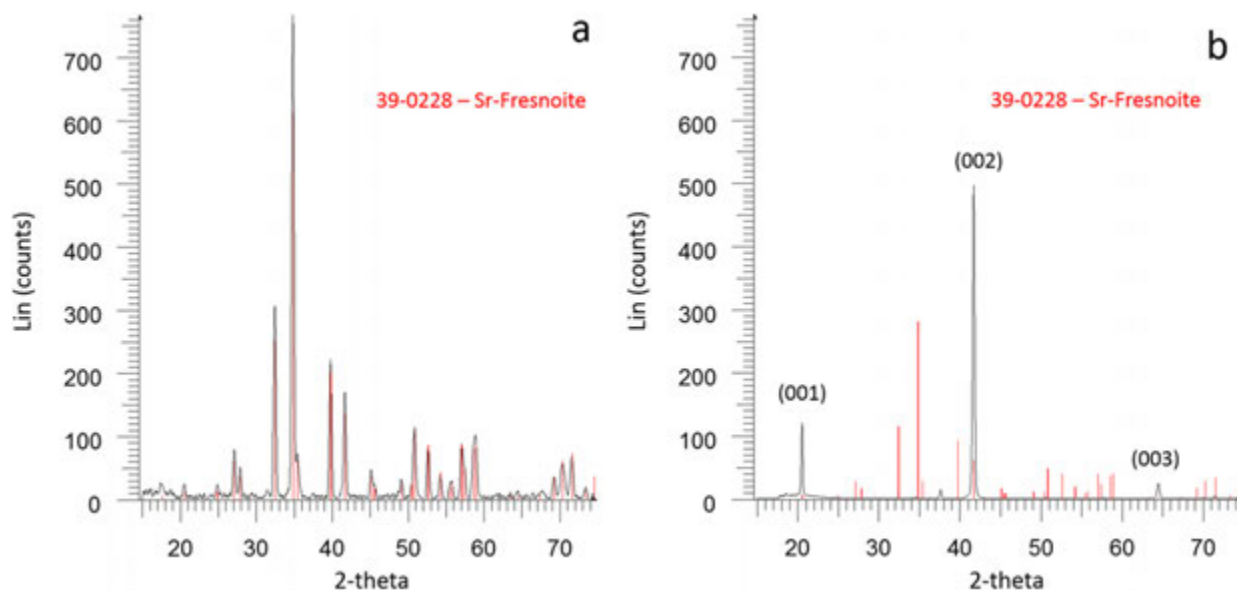


Fig. 19 Examples of XRD patterns collected on glass-ceramic crystallized at 900°C for 20 h. Powder milled sample (a), glass-ceramic surface (b).

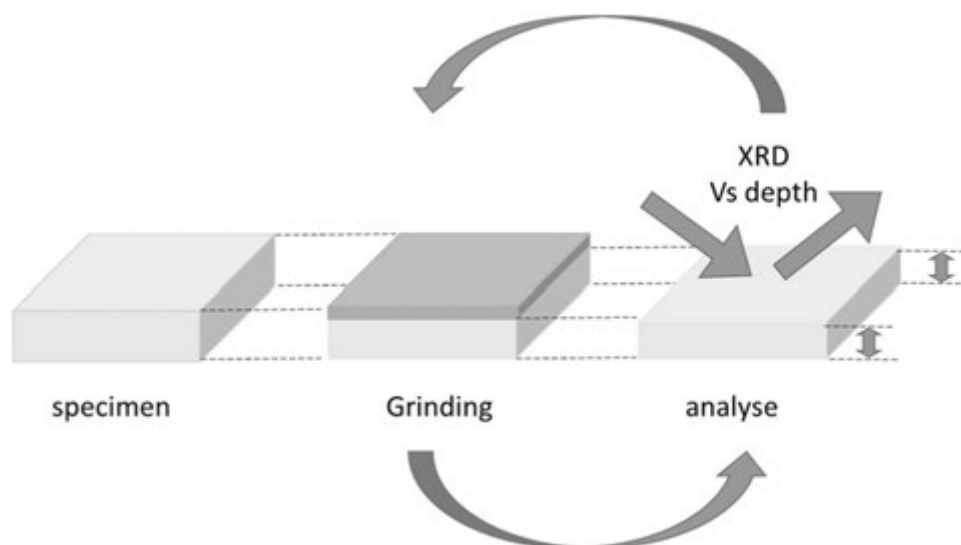


Fig. 20 XRD characterization of the specimens. Adapted from Renoirt, M.-S., Maury, N., Dupla, F., Gonon, M., 2019. Structure and properties of piezoelectric strontium fresnoite glass-ceramics belonging to the Sr-Ti-Si-Al-K-O system. *Ceramics 2*, 86–97.

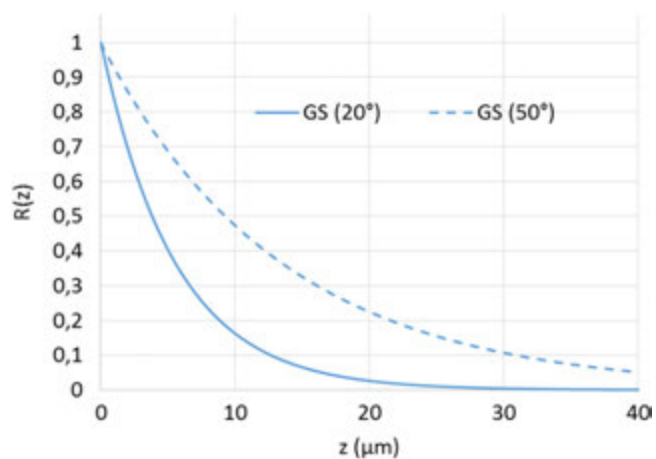


Fig. 21 Contribution of the emerging radiation to diffracted signal of Fresnoite in the glass-ceramic (Bragg-Brentano configuration).

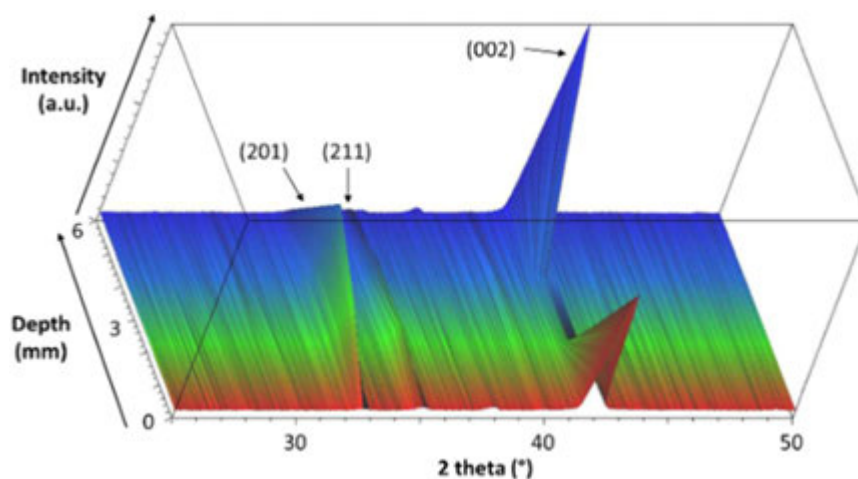


Fig. 22 Evolution of X-ray patterns vs depth. Adapted from Renoirt, M.-S., Maury, N., Dupla, F., Gonon, M., 2019. Structure and properties of piezoelectric strontium fresnoite glass-ceramics belonging to the Sr-Ti-Si-Al-K-O system. *Ceramics 2*, 86–97.

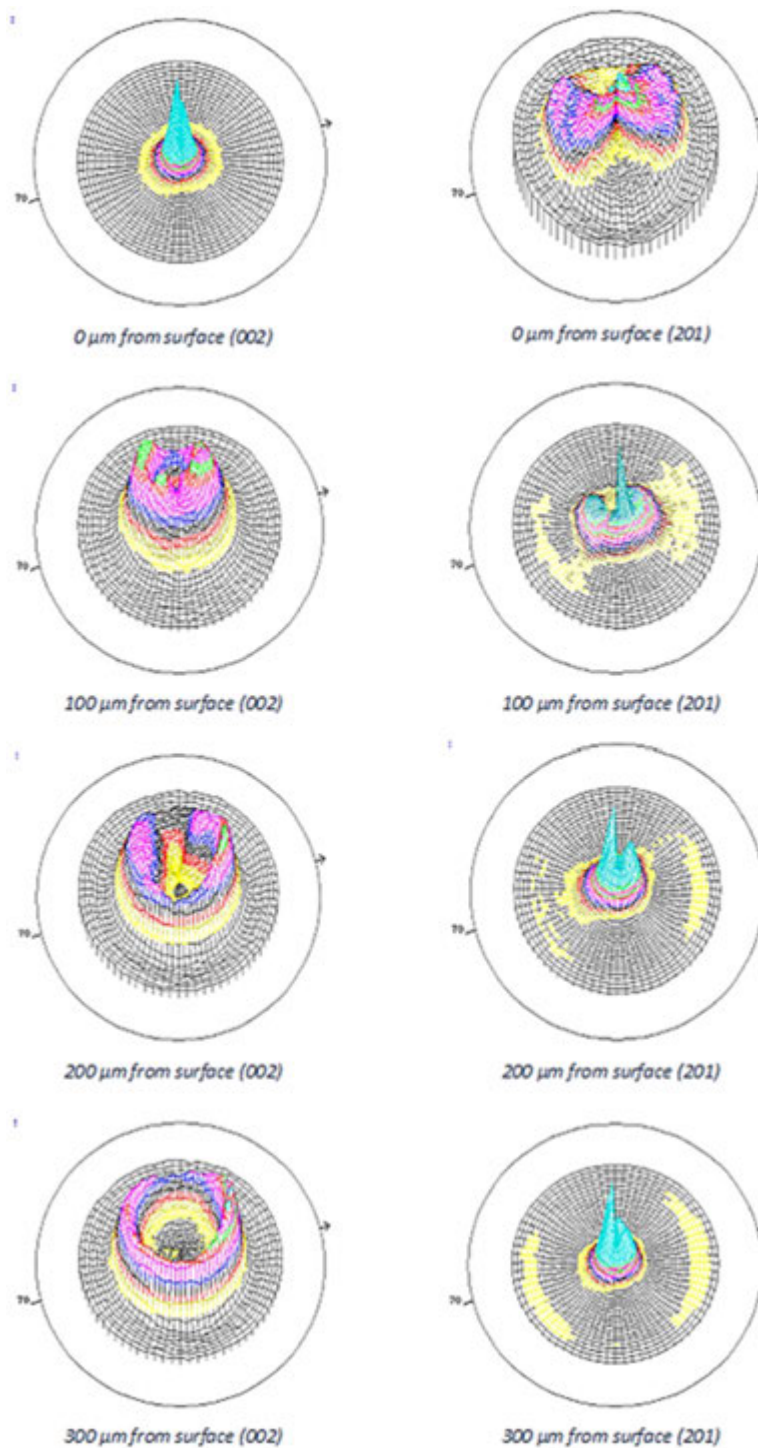


Fig. 23 Pole figures of (002) and (201) lattice planes over depth. Adapted from Renoirt, M.-S., Maury, N., Dupla, F., Gonon, M., 2019. Structure and properties of piezoelectric strontium fresnoite glass-ceramics belonging to the Sr-Ti-Si-Al-K-O system. *Ceramics* 2, 86–97.

Investigation of Internal Stresses due to Thermal Expansion Mismatch

The glass-ceramic can be seen as a composite material composed of fresnoite crystals embedded in the residual glass. During the cooling step at the end of the crystallization treatment, the difference in thermal expansion coefficient between the two phases generates homogeneous internal stresses. To evidence this phenomenon, the thermal expansion of the Sr-fresnoite crystals has been characterized by HT-XRD.

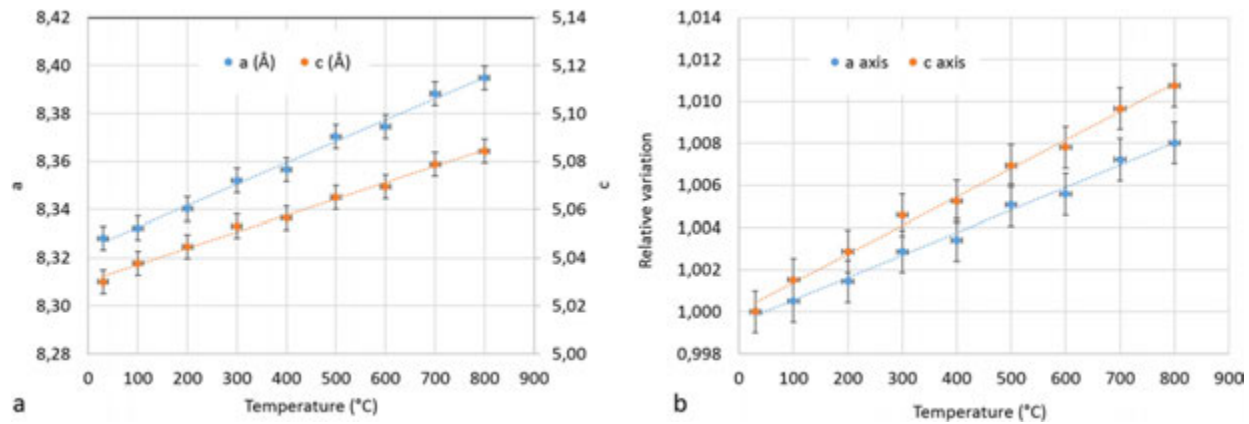


Fig. 24 Variations of Sr-Fresnoite lattice parameters *a* and *b* with temperature (a). Relative variations (b).

Table 1 Thermal expansion coefficients $\alpha_{(20-600^{\circ}\text{C})}$ of the *a* and *c* axis of fresnoite crystal measured from HT-XRD

Axis	Fresnoite Powder	Glass-ceramic Powder	Glass-ceramic Solid
<i>a</i>	10.3×10^{-6}	10.9×10^{-6}	8.3×10^{-6}
<i>c</i>	13.7×10^{-6}	14.1×10^{-6}	9.7×10^{-6}

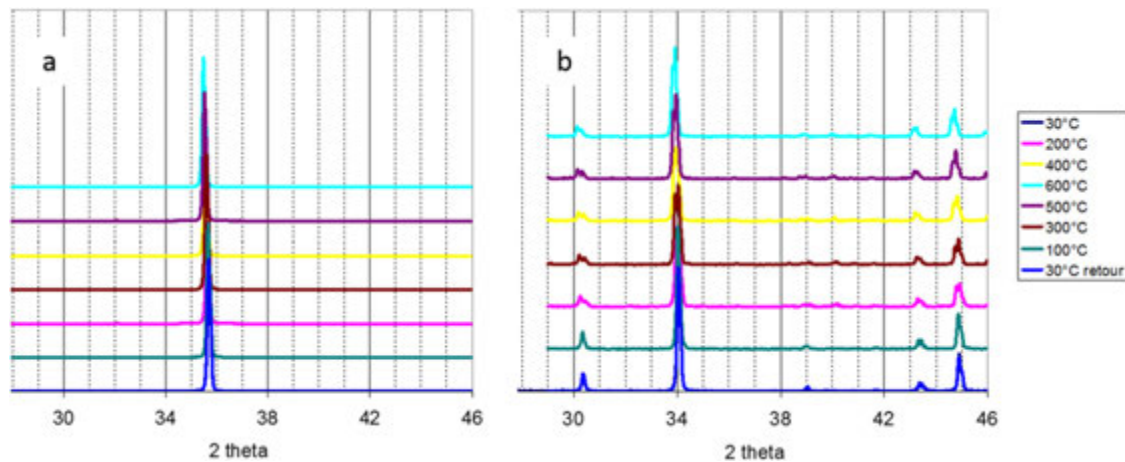


Fig. 25 HT-XRD patterns of the glass-ceramic. (a) Surface. (b) Cross section.

Table 2 Fresnoite room temperature unit cell parameters *a* and *c* for the glass-ceramic powder and glass-ceramic solid

	JCPDS 39-0228	Powder		Solid	
<i>a</i> (pm)	832.18	832.16	± 0.10	832.65	± 0.24
<i>c</i> (pm)	502.92	502.91	± 0.07	503.50	± 0.51

Characterization of thermal expansion of the Sr-fresnoite crystals

In order to characterize the thermal expansion of the Sr-fresnoite crystals, a stoichiometric fresnoite parent glass has been melted and crystallized. After milling it into a fine powder, HT-XRD has been performed using a Brucker D8 Advance instrument (Cu anticathode) with a high temperature chamber. Patterns were collected at 30°C; 200°C; 400°C; 600°C; 800°C on heating and 700°C; 500°C; 300°C; 100°C; 30°C on cooling. Variations of lattice parameters *a* and *c* with temperature have been evaluated by

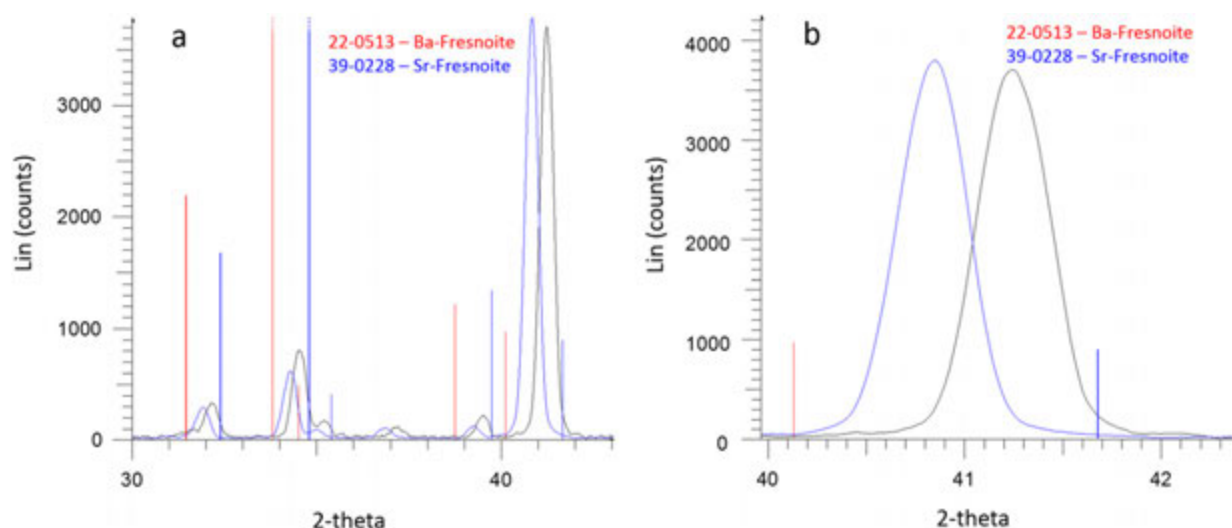


Fig. 26 XRD patterns of the glass-ceramic with 25 wt% (black) and 50 wt% (blue) Ba substitutions (a). Zoom on (002) diffraction peaks (b).

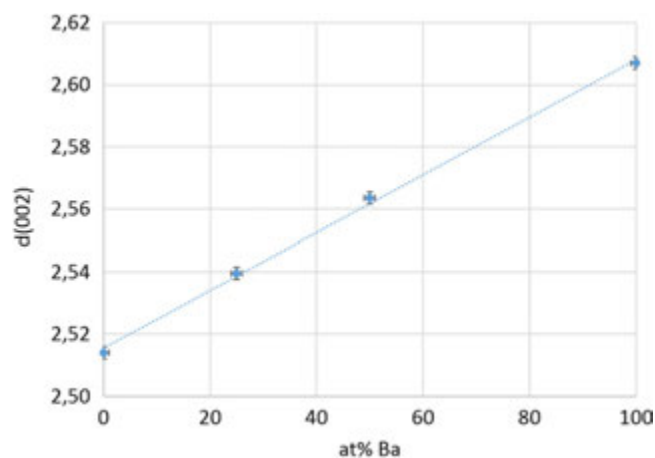


Fig. 27 Evolution of the d-spacing of the (002) planes with the amount of barium.

Rietveld refinement of the patterns [Fig. 24\(a\)](#). The average thermal expansion coefficients α_a and α_c have been calculated [Table 1](#) from the slopes of the curves given the relative variations $\Delta a/a_0$ and $\Delta c/c_0$ as a function of T [Fig. 24\(b\)](#).

Characterization of thermal expansion of the Sr-fresnoite crystals in the glass-ceramic

In a second step, high temperature XRD analyses have been performed on the surface of the glass-ceramic in order to measure the thermal expansion coefficient of the fresnoite crystals constrained in the residual glass matrix. As the fresnoite crystals are strongly preferentially oriented in the glass-ceramic, XRD patterns collected on the surface only exhibit (00 l) planes [Fig. 25\(a\)](#) and only the lattice parameter c can be refined from these patterns. In order to refine the a parameter, HT-HRD patterns were also collected on a cross section of the glass-ceramic [Fig. 25\(b\)](#) on which mainly the (hk0) planes are observed. The maximum temperature was limited at 600°C so as not to exceed the glass transition temperature of the residual glass. Patterns were collected at 30°C; 200°C; 400°C; 600°C on heating and 500°C; 300°C; 100°C; 30°C on cooling.

As for the fresnoite powder, the thermal expansion coefficients α_a and α_c have been calculated from the slopes of the curves given the relative variations $\Delta a/a_0$ and $\Delta c/c_0$ as a function of T. The coefficients obtained are significantly lower than for the fresnoite powder [Table 1](#). The same analyses have been realized on a powder milled glass-ceramic. In this late case, the expansion coefficients are close to that of the fresnoite powder. These results highlight that the fresnoite crystals embedded in the residual glass are not free to expand or shrink normally during a thermal cycle. As the fresnoite expansion coefficients α_a and α_c measured on the solid specimen of glass-ceramic are lower, it can be concluded that the crystals experience tensile stresses during the cooling stage that follows the crystallization treatment.

To verify the validity of this conclusion, the accurate measurement of the fresnoite room temperature unit cell parameters a and c has been realized by Rietveld analysis on 5 samples of glass-ceramic powder and 5 samples of glass-ceramic solids. The parameters calculated for the powder are in agreement with those given by the JCDCS file, whereas those calculated for the solid are slightly higher **Table 2**. This confirms the tensile stresses supported by the fresnoite crystals.

Investigation of the Influence of Barium Substitutions

The effect of substituting strontium with barium on the crystallization of the fresnoite crystals in the glass-ceramic has been investigated. Two new glass-ceramics based on parent glass compositions $1.5\text{SrO } 0.5\text{BaO } 1\text{TiO}_2 \text{ } 3.3\text{SiO}_2 \text{ } 0.2\text{K}_2\text{O } 0.1\text{Al}_2\text{O}_3$ and $1\text{SrO } 1\text{BaO } 1\text{TiO}_2 \text{ } 3.3\text{SiO}_2 \text{ } 0.2\text{K}_2\text{O } 0.1\text{Al}_2\text{O}_3$ have been prepared in the same conditions than for the one without substitution. **Fig. 26** shows the XRD patterns obtained on these two glass-ceramics and the diffraction peaks position for Ba-fresnoite (JCPDS # file 22-0513) and Sr-fresnoite (JCPDS file # 39-0228). These diffraction patterns highlight that the crystalline phases obtained corresponds to fresnoite with a strong (00 l) preferential orientation and that the peak positions are between those of Ba-fresnoite and Sr-fresnoite. These shifts are explained by the largest radius of the barium cations by comparison to the strontium cations. The barium substitution leads to an enlargement of the fresnoite unit cell, and consequently, an increase in the planes d-spacing. Checking of the actual substitution rates is possible by applying Vegard's law. This law considers that the lattice parameters of a solid solution of two constituents are approximately a weighted mean of the two constituents' lattice parameters at the same temperature. In the present case, the application of the Vegard's law to the d-spacing of the (002) planes confirms the expected substitution rates **Fig. 27**.

Conclusion

The objective of this paper was to highlight the potential of use of XRD in the field of the ceramic materials. Two works, for which XRD was the key analysis tool, have been developed. If some of the characterizations performed have require specific equipment that are usually only encountered in research laboratories, one must keep in mind that numerous information can however be extracted from conventional X-ray patterns collected from a basic equipment commonly used in industry for process control. Now for many years, the Rietveld method has been increasingly recognized as essential for the in-depth analysis of the X-ray patterns. A large number of Rietveld software are available, and they integrate more and more features. Finally, technical progresses have also been realized on the hardware. Modern diffractometers provide diffraction patterns showing weak instrumental broadening while keeping short acquisition time.

References

- Aitken, B.G., Beall, G.H., 1994. Glass-ceramics. In: Cahn, R.W., Haasen, P., Kramer, E.J. (Eds.), *Material Science and Technology: A Comprehensive Treatment*, first ed. New York: VCH Weinheim, pp. 265–294.
- Angerera, P., Strobl, S., 2014. Equi-penetration grazing incidence X-ray diffraction method: Stress depth profiling of ground silicon nitride. *Acta Materialia* 77, 370–378.
- Arata, A., Campos, T.M.B., Machado, J.P.B., *et al.*, 2014. Quantitative phase analysis from X-ray diffraction in Y-TZP dental ceramics: A critical evaluation. *Journal of Dentistry* 42, 1487–1497.
- Bonnet, J.-P., Gaillard, J.-M., 2007. Silicate ceramics. In: Boch, P., Niepce, J.-C. (Eds.), *Ceramic Materials: Processes, Properties and Applications*. London: ISTE, pp. 95–122.
- Callebaut, S., Gonon, M., Veys, J.-N., 2007. X-ray diffraction investigation of the anisotropic microstructure of cordierite honeycombs used for catalytic filters. In: Heinrich, J.G. (Ed.), *Proceeding of 10th international Conference of ECerS. Baden-Baden: Göller*, pp. 1089–1092.
- Chevalier, J., Gremillard, L., Deville, S., 2006. Low-temperature degradation of zirconia and implications for biomedical implants. *Annual Review of Materials Research* 37, 1–32.
- Diasa, A.G., Skaklec, J.M.S., Gibson, I.R., Lopesa, M.A., Santosa, J.D., 2005. In situ thermal and structural characterization of bioactive calcium phosphate glass ceramics containing TiO_2 and MgO oxides: high temperature – XRD studies. *Journal of Non-Crystalline Solids* 351, 810–817.
- Evans, D.L., Fischer, G.R., Geiger, J.E., Martin, F.W., 1980. Thermal expansion and chemical modification of cordierite. *Journal of the American Ceramic Society* 63, 629–634.
- Gibbs, G., 1966. The polymorphism of cordierite I: The crystal structure of low cordierite. *American Mineralogist* 51, 1068–1087.
- Halliyal, A., Bhalla, A.S., Cross, L.E., Newnham, R.E., 1985. Dielectric, piezoelectric and pyroelectric properties of $\text{Sr}_2\text{TiSi}_2\text{O}_8$ polar glass-ceramic: A new polar material. *Journal of Materials Science* 20, 3745–3749.
- Kima, S.W., Choia, H.I., Leeb, M.H., *et al.*, 2013. Electrical properties and phase of BaTiO_3 - SrTiO_3 solid solution. *Ceramics International* 39, 487–S490.
- Lachman, I.M., Bagley, R.D., Lewis, R.M., 1981. Thermal expansion of extruded cordierite ceramics. *American Ceramic Society Bulletin* 60, 202–205.
- Pederson, B.M., Gonzalez, R.M., Winburn, R.S., 2003. Minimization of microabsorption effects in complex mixtures. *Advances in X-ray Analysis* 46, 68–73.
- Pentecost, J.L., Wright, C.H., 1963. Preferred orientation in ceramic materials due to forming techniques. *Advances in X-ray Analysis* 7, 174–181.
- Popa, N.C., Balzar, D., 2008. Size-broadening anisotropy in whole powder pattern fitting. Application to zinc oxide and interpretation of the apparent crystallites in terms of physical models. *Journal of Applied Crystallography* 41, 615–627.
- Renoirt, M.-S., Maury, N., Dupla, F., Gonon, M., 2019. Structure and properties of piezoelectric strontium fresnoite glass-ceramics belonging to the Sr–Ti–Si–Al–K–O system. *Ceramics* 2, 86–97.
- Saha, B.P., Johnson, R., Ganesh, I., *et al.*, 2001. Thermal anisotropy in sintered cordierite monoliths. *Materials Chemistry and Physics* 67, 140–145.
- Serbena, F.C., Zanolto, E.D., 2012. Internal residual stresses in glass-ceramics: A review. *Journal of Non-Crystalline Solids* 358, 975–984.
- Schneider, M., Richter, W., Keding, R., Rüssel, C., 1998. XPS investigations on coordination and valency of Ti in fresnoite glasses and glass ceramics. *Journal of Non-Crystalline Solids* 226, 273–280.
- Strasberg, M., Barrett, A.A., Anusavice, K.J., Mecholsky Jr., J.J., Nino, J.C., 2014. Influence of roughness on the efficacy of grazing incidence X-ray diffraction to characterize grinding-induced phase changes in yttria-tetragonal zirconia polycrystals (Y-TZP). *Journal of Materials Science* 49, 1630–1638.

Further Readings

- Hammond, C., 2009. The Basics of Crystallography and Diffraction, third ed. New York: Oxford University Press.
- Suryanarayana, C., Grant Norton, M., 1998. X-ray Diffraction: A Practical Approach, first ed. New York: Springer.
- Will, G., 2006. Powder Diffraction: The Rietveld Method and the Two Stage Method to Determine and Refine Crystal Structures From Powder Diffraction Data, first ed. Berlin: Springer.

Introduction to Transmission Electron Microscopy; The Basics

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Preface

This chapter on transmission electron microscopy (TEM) is dedicated to serve the unfamiliar reader as a brief introduction to this exciting and versatile characterization technique, which literally allows the scientist to “take a look” into the complex nature of materials. Since imaging is conducted via electrons that are transmitted through a very thin slice of the material of the order of 1/10,000th of a human hair, details in the interior of the sample can be studied with very high magnifications of up to 25,000,000x. Therefore, we invite you to this hopefully easy-accessible introduction to TEM and its various applications for the investigation of materials on the micro- and nanoscopic scale. Note that in addition to this chapter, two other contributions shed light on the exciting TEM techniques of high-resolution scanning TEM (HR-STEM) and automated diffraction tomography (ADT).

Introduction and Brief History

Transmission electron microscopy (TEM) is a diverse characterization method for solid samples of various materials with a high local resolution capacity. A high-energy electron beam is transmitted through a very thin specimen. This allows the detection of structural features and details in the respective material not only on the surface, but also within the specimen volume. In order to examine structures with a small spatial dimension, the wavelength of the radiation source has to be smaller than the structure itself. With the short wavelength of accelerated electrons, it is possible to achieve a resolving power of 1.0 Ångström (10^{-10} m) or even lower in current state-of-the-art TEM instruments. In combination with the possibility of conducting chemical analysis with similarly high lateral resolution, TEM has become an important characterization tool for many scientific research areas. The possibility of resolving structures down to the atomic level is not only a great achievement for material sciences and nanotechnological applications, but also for other research fields such as for example geoscience, mineralogy and life sciences.

In general, the three main parameters crucial for obtaining a good microscopic image are contrast, magnification and resolution. In microscopy, the resolution limit is defined by the minimum distance two structural features need to maintain, in order to be perceived as two individual objects. The resolution limit is directly coupled to the wavelength λ of the light source. In 1873 Ernst Karl Abbe described this relationship for optical light microscopy:

$$d_{\min} = \frac{\lambda}{n * \sin(\alpha)} = \frac{\lambda}{NA} \quad (1)$$

NA describes the numerical aperture, which is defined as $n * \sin(\alpha)$. Here, n is the refractive index of the immersion medium between objective and object and α stands for the half aperture or objective opening angle. This correlation between wavelength and resolution is also valid for electron microscopy, including scanning electron microscopy (SEM) and TEM. As the resolving power of a light microscope is restricted by the wavelength of the visible spectrum (380–750 nm), the search for other radiation sources became of interest. With the discovery of the electron, Sir Joseph John Thomson laid the foundation for subsequent research in this area in 1897. In the early 1920s, Louis de Broglie introduced the concept of the wave-particle duality and postulated the wave nature of electrons. In consequence, the idea of using electrons as the light source in a microscope gained more and more attention. Since electrons are charged particles, they can be manipulated with electromagnetic fields. This allowed for the development of electromagnetic lenses, which fulfill the same function as optical lenses in a light microscope. In the early 1930s, Max Knoll and Ernst Ruska developed and built the first TEM at the University of Berlin. It took some effort until their TEM reached a resolving power significantly better than any light microscope. The TEM they built in 1933 had three lenses, a magnification of 12,000x and a resolving power of 50 nm. A “few years later” in 1986 Ernst Ruska gained the Nobel Prize in Physics for his achievements; sadly, Max Knoll had already died. The first commercial TEM was built by Siemens in 1939. While the basic components of the TEM have not changed, successive improvement in lens quality, as well as stabilization of high voltage currents was achieved. Also, a better theoretical understanding of electron optics led to the development of special correctors to minimize the effect of lens aberrations (see the section on “Resolution and Lens Aberrations” below). Overall, significant improvements in design and performance are realized in modern TEM instruments.

With an electron wavelength in the range of 0.0037–0.00087 nm, approximately six orders of magnitude smaller than for visible light, the currently routinely available resolution of a TEM lies in the Ångström range. Here, the relativistic electron wavelength depends on the acceleration voltage, which is generated in the electron gun:

$$\lambda = \frac{h}{\left[2m_0eE \left(1 + \frac{eE}{2m_0c^2}\right)\right]^{1/2}} \quad (2)$$

The potential difference (acceleration voltage) is described by E , while h is the Planck's constant, m_0 and e are the electron rest mass and electron charge, respectively, and m_0c^2 is the rest energy. For a non-relativistic consideration, the wavelength can be estimated with following formula: $\lambda = 1.22/(E)^{1/2}$. Even though the scattering and diffraction half angle α is smaller for electrons than for visible light, the significantly shorter wavelength of the electrons compensates for this disadvantage by far (see Eq. (1)), which results in the small d_{min} values achieved with modern electron microscopes.

During the electron beam irradiation and the resulting electron-specimen interaction, a variety of signals is generated. Besides the main signal arising from elastically scattered electrons, Auger electrons, secondary and backscattered electrons, X-rays or inelastically scattered electrons are also created. TEM machines are therefore often equipped with additional detectors for e.g., energy-dispersive X-ray spectroscopy (EDS) or electron energy-loss spectroscopy (EELS), which allow a detailed chemical analysis combined with the high spatial resolution of the microscope. However, these analytical techniques are not covered in this chapter on the basics of TEM; for more information, we refer to the corresponding literature, as for example: Goldstein *et al.*, 1986; Echlin *et al.*, 1986; Flegler *et al.*, 1993; Reed, 2005; Goldstein *et al.*, 2017; Brydson, 2001; Egerton, 2011, 2016.

Sample preparation

With respect to TEM sample preparation, many different techniques and preparation routes exist, which are adapted to the vast variety of investigated materials, their specific properties as well as to the requirements of the individual studies and research questions. Although the procedures significantly differ from each other, one goal is always identical: to prepare a sample that is electron transparent. In order to allow electrons to be transmitted through the sample, the required thickness is commonly of the order of 20 nm to 100 nm. Furthermore, there are certain techniques, such as high-resolution TEM (HRTEM) or EELS, which require especially thin TEM foils.

In this chapter, the main focus is laid upon the preparation of solid non-metallic materials, for example ceramics or glasses, where standard methods such as mechanical grinding and polishing with subsequent ion thinning can be deployed. While these well-established procedures are preferable for hard non-metallic inorganics, other materials benefit from different preparation techniques. Metals are often electrochemically etched (Petzow, 1999); thus no mechanical stress is applied in this method, preventing undesired artefacts from shear forces in the rather soft metals. Very soft materials, like biological samples, are even more sensitive and require other techniques such as ultramicrotomy. Here, upon fixation of the sample in a resin, thin slices are cut from the sample with a sharp steel or diamond knife, which are already thin enough to facilitate electron transparency.

Besides material specific requirements on the preparation method, two main approaches can be distinguished in general: the preparation of (1) powder versus (2) solid or bulk samples. For powder samples, e.g., ceramic powders or nanoparticles of sufficiently small grain size, the preparation via drop coating is comparably simple and fast. The powder is mixed with an appropriate solvent, such as ethanol or acetone, and dispersed in an ultrasonic bath. Subsequently, one droplet of the suspension is placed onto a special TEM grid with a carrier film.

For solid ceramic samples, the preparation is significantly more laborious. First, a sufficiently small piece needs to be cut from the sample material. Ideally, the sample consists of a 3 mm disc, which is compatible with the standardized geometry of TEM grids and sample holders. Subsequently, one side of the sample is ground and polished to form an even surface, ideally without any scratches which would typically result in inhomogeneous ion-milling. A variety of tools exists ranging from simple handheld disc grinders to sophisticated polishing machines. SiC, Al₂O₃, B₄C, SiO₂ or diamond are typically used as abrasive materials. The last polishing steps are usually conducted with lapping paper or abrasive pastes of very small grain sizes less than 1 μ m, in order to obtain high quality surfaces. After completion, the second side of the sample is ground plane-parallel and polished as well, down to a remaining sample thickness of approximately 10–20 μ m. The thin section needs to be mounted onto a TEM grid for support. Grids of different geometries (holes, slots, square or hexagonal meshes) and materials (Cu, Mo, Ni, Au, etc.) are available in order to meet the demands of the individual sample and anticipated TEM investigation.

Besides the described plane-parallel polishing, the so-called dimple grinder is another well-established method for TEM sample preparation. After regular polishing of the first side of the sample disc, an indentation is ground into the middle of the second side. This is done via a fast-turning dimpling wheel with abrasive paste, placed on the likewise rotating sample piece. The process is stopped when the sample center reaches the desired minimum thickness of 10–20 μ m. The outer rim is usually left with a sufficient thickness ($\sim$ 100 μ m) to ensure a self-supporting sample. Dimple grinding is therefore a well-suited method when grids and mounting glue need to be avoided, as is the case for in-situ heating experiments.

Subsequent to polishing or dimple grinding, Ar⁺-ion milling is used to achieve electron transparency by creating one or several small holes in the sample ($\sim$ 10–100 μ m in diameter). At the edge of the hole the sample is typically thin enough to enable the transmission of electrons. In the ion mill, the sample is exposed to a stream of Ar⁺-ions, which are accelerated towards the sample by applying voltages of 0.5 kV to 8 kV (see Fig. 1). The Ar⁺-ions successively remove sample material from the surface, eventually leading to a perforation of the sample. Besides the acceleration voltage, the incident angle of the Ar⁺-ion beam is an important parameter. The larger the angle, the more effectively material is abraded. However, at an angle of approximately 18° and higher, incorporation of Ar⁺-ions becomes the predominant effect. Furthermore, the thickness of the amorphized layer on the sample surface strongly increases. Therefore, an optimum milling angle exists, which is typically in the range of 6°–14°. During thinning, the sample is usually rotated to assure homogenous erosion. Optional cooling with liquid N₂ can be used to avoid heat damage and reduce amorphization. Ion milling with low incident angles and low acceleration voltages can also be applied to remove the

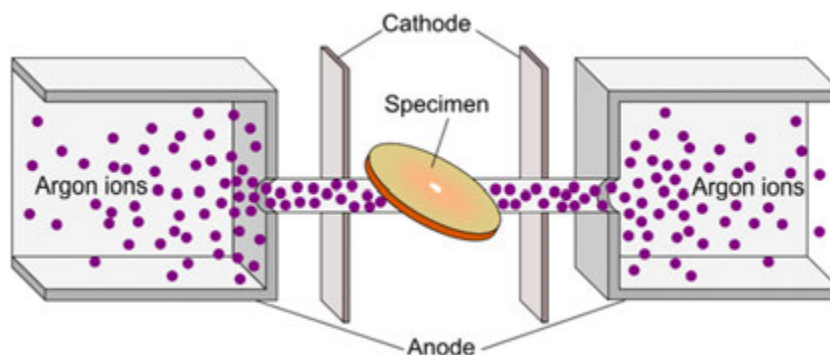


Fig. 1 Schematic illustrating the Ar^+ -ion thinning process. The sample is rotated while Ar^+ -ions bombard the top and the bottom side of the sample. Small volume fractions of the sample are continuously removed until a small hole is generated in the center, being electron transparent at its rim.

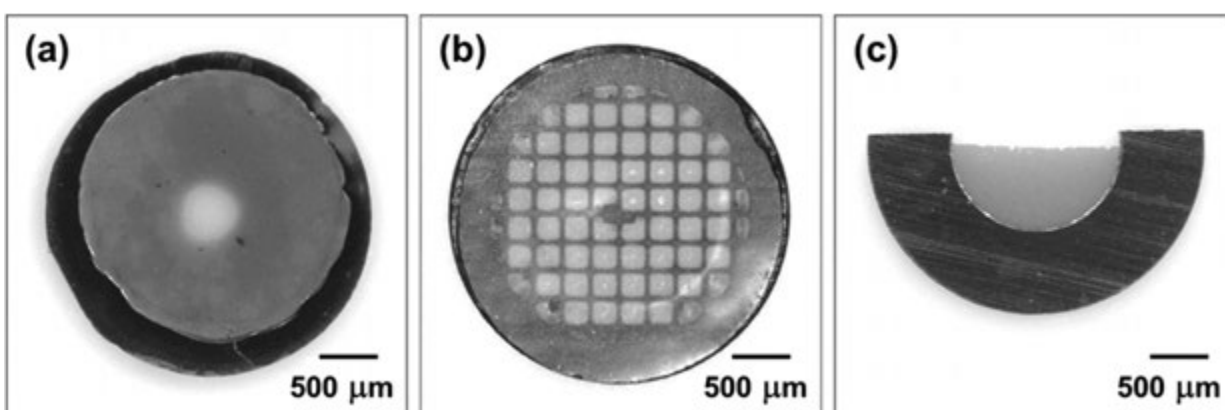


Fig. 2 Optical micrographs of thinned TEM samples; (a) an Ar^+ -ion milled dimpled sample, (b) an ion milled plane-parallel thin section with numerous perforations and (c) a wedge-shaped sample prepared via tripod polishing.

residual amorphous layer from the surface. Since non-conductive TEM samples suffer from charging under the electron beam, a carbon coating is applied subsequent to the ion-milling procedure.

If more complex sample geometries need to be investigated with TEM, like multilayer systems or surface coatings, a more target-oriented sample preparation is required. Cross-section techniques exist, where the sample is sliced perpendicular to the desired interface and then glued on the grid in a sandwich-like manner. For the preparation of wedge-shaped samples, *tripod polishing* machines are valuable devices. In this case, after the first side of the sample is polished, the second side is ground down under a low angle of $< 1^\circ$, resulting in a thin electron transparent wedge. If the wedge is very thin, refraction fringes parallel to the edge can be observed under a light microscope which help to control the grinding process. As an advantage of the wedge-shaped sample, Ar^+ -ion thinning can be omitted or reduced to a minimum. **Fig. 2** reveals a comparison of three TEM samples prepared via different routes.

If a specific region within the sample, such as an intrinsic precipitation or a local defect has to be studied in detail, the *focused ion beam* (FIB) technique allows the extraction of TEM foils from the sample with a high spatial resolution. The FIB acts as a normal SEM and utilizes Ga^+ -ions to precisely cut a thin lamella out of the sample, which already has the desired thickness below 100 nm. The lamella is typically in the order of $5\ \mu\text{m} \times 5\ \mu\text{m}$ and needs to be mounted onto a special TEM grid for support and handled via a specific lift-out technique.

A variety of different TEM *sample holders* exist, such as double-tilt holders for tilting the specimen to desired directions and zone axes, heating and cooling holders for in-situ temperature experiments, electrical stages for in-situ E-field experiments or nanoindenters to locally strain the sample. It should also be mentioned that certain sample holders, e.g., for advanced heating in combination with E-field in-situ experiments, essentially depend on FIB preparation.

Components of a TEM Instrument

The setup of a TEM comprises three main parts. The gun as electron source is located at the top, followed by the column, which includes the condenser, objective, intermediate and projector lens systems. At the bottom, the viewing screen is located with a

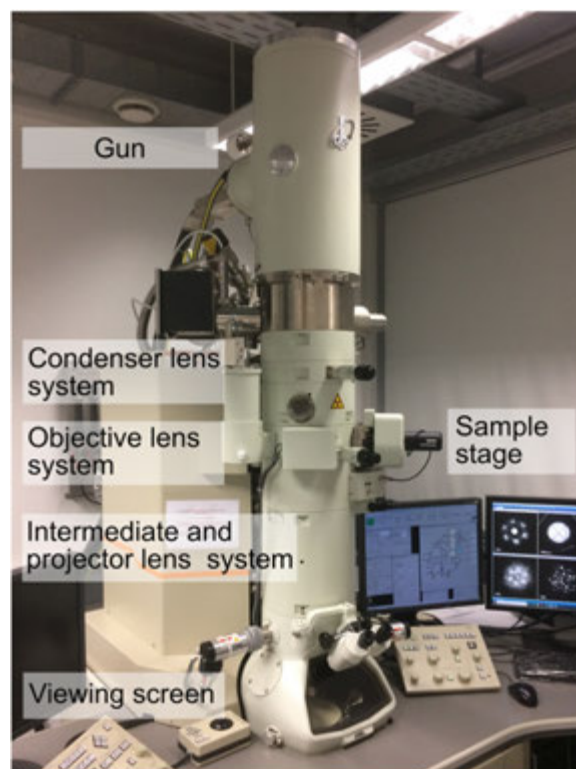


Fig. 3 Image of a TEM instrument depicting the main components, which are the gun, condenser, objective, intermediate and projective lens system, the sample stage and the viewing screen.

camera chamber or a charge-coupled device (CCD) camera below (Fig. 3). In many ways, the general setup of a TEM instrument is similar to a normal light microscope (LM) viewed upside down. However, while the LM uses visible light, an electron beam is utilized in the TEM. Therefore, the entire column is always kept under high vacuum of $\sim 10^{-5}$ Pa to avoid scattering of the electrons upon collision with gas molecules. This high vacuum in turn requires the sample to be inserted into the TEM via an airlock.

In contrast to a LM, where glass lenses are used, electromagnetic lenses are applied in the TEM to control the electron beam. The magnification can be tuned by changing the current of the respective lenses. Due to the similarities regarding the beam path through the instrument, both types of microscopes have a multi-step image formation in common, which includes the generation of intermediate images and diffraction patterns. An important and unique feature of the TEM is the ability to choose between the two with the intermediate lens system and, hence, to switch between image and diffraction mode (real versus reciprocal space). Considering the upper part of a TEM with the electron gun and the condenser lens system, this setup strongly resembles that of a SEM. However, in the TEM, there is an additional objective lens and further intermediate and projector lens systems below it. While the magnification is changed by simply defining smaller or larger scan areas in the SEM, the projector lens system of the TEM allows adjustment to the desired magnification.

The gun generates and accelerates the electron beam with voltages typically between 100 kV and 300 kV. Thereby, the electrons are released by either thermionic or field emission. In case of thermionic emission, the electrons are emitted via resistance heating of the cathode material, which is commonly a tungsten filament or a LaB₆ single crystal. The emitted electrons pass a Wehnelt cylinder, where they experience a negative voltage (Wehnelt bias) and are converged in a gun cross-over to pass through a hole in the anode plate. The Wehnelt bias controls the electron current and coherence of the electrons to achieve optimal brightness. Best conditions are usually obtained when the cathode emission is in a slightly undersaturated state. A field emission gun (FEG) releases electrons by the application of a high electric field to a cathode with a fine needle-shaped tungsten tip. Their higher emission current density and brightness as well as the lower energy spread renders FEGs superior to guns with thermionic emission. Hence, the majority of modern TEMs relies on this type of beam generation. FEGs can be further distinguished as Schottky type FEGs, with the cathode being coated with ZrO₂ and heated to around 1800 K, and “cold” FEGs, where emission happens at room temperature. The cold FEG has an even higher brightness and a better energy resolution as compared to the Schottky emitter. However, the total current of a cold emission FEG is typically limited to only a few nA, which is adverse for applications where a high current is of advantage. Furthermore, cold field emission requires sequential flashing to clean the emitter surface from contamination due to residual hydrocarbon molecules in the microscope column. Otherwise, this contamination would strongly impede the emission of electrons.

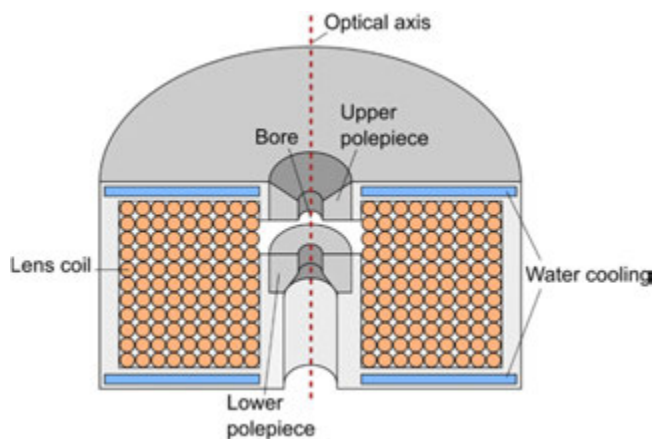


Fig. 4 Schematic depicting the cross-section of an electromagnetic lens built up of a rotational symmetric copper coil, in which the polepieces, made of a soft-magnetic material, are placed. The electron beam passes through the hole in the polepieces, where an electromagnetic field is generated when a current is applied to the copper coil.

The electromagnetic lenses that control the electron beam are built up of rotationally symmetric copper coils, in which the *polepieces* are placed. They are made of a soft magnetic material like iron. The electron beam passes through a hole in the polepiece, where an electromagnetic field is generated as soon as a current is applied to the copper coil (Fig. 4).

The electromagnetic field is axially symmetric and by changing its strength, the refractive power of the lens can be adjusted. When the electrons enter the electromagnetic field, they are affected by the *Lorentz force* $\vec{F} = -e * (\vec{v} \times \vec{B})$, where $\vec{F}$ runs perpendicular to the velocity vector $\vec{v}$ and the magnetic field vector $\vec{B}$. Due to radial field components normal to the optic axis and longitudinal components parallel to the axis, the electrons are forced on a spiral way around the center axis through the lens by the Lorentz force. This also means that the generated image is rotated with respect to the specimen. The degree of rotation changes with magnification; however, in modern instruments this image rotation is compensated for.

The Lens Systems

The first lens system that the electrons pass on their way down from the gun is the *condenser lens system*. Mostly, TEMs comprise two condenser lenses called C1 and C2, where C1 is used to control the spot size (probe) of the focused electron beam. A weakly excited C1 lens results in a large probe (assigned to a small spot size number), while a strongly excited lens causes a small probe. C2 allows either focusing the beam on the specimen for local chemical analysis and convergent beam electron diffraction (CBED) studies, or opening the beam to form parallel beam conditions for conventional and high-resolution imaging or selected area electron diffraction (SAED). The condenser aperture limits the number of electrons reaching the specimen, allowing for adjustment of the beam intensity to which the sample is exposed. It also controls the convergence semi-angle α . For high-resolution imaging especially, a smaller condenser aperture (smaller α) can be used to remove high angle electrons from the beam, which reduces the adverse influence of lens aberrations.

Further down the column, the condenser lens system is followed by the *objective lens*, which is often termed the “heart” of the microscope. Here, the images and diffraction patterns are formed from electrons passing through the sample. The objective lens is often split into two polepieces with the upper one called the condenser-objective lens (C3). The image quality of the TEM is strongly influenced by the electron optics inside the objective lens. The sample sits right inside the lens between the upper and the lower polepiece. In this way it is ensured that the sample is surrounded by a homogenous electromagnetic field, which strongly benefits the image quality. Furthermore, placing the specimen inside the objective lens is crucial for achieving a high magnification. The *magnification* M in a microscope, no matter if it is constructed with electromagnetic or glass lenses, is defined as $M = v/u$, where v is the image distance (from the center of the lens to the image plane) and u is the object distance (from the specimen to the center of the lens). It follows that a high magnification is best achieved by making u very small instead of v larger, which would also imply a longer and more instable column. By placing the specimen within the objective lens, the distance u is reduced to a minimum and high magnifications can easily be achieved. The downside of this setup is the restriction of the sample holder dimensions to fit into the small gap between the upper and lower polepiece. In addition, the objective aperture is mounted between the specimen and the lower objective lens polepiece. Electrons passing the sample are scattered under varying angles. Depending on its diameter, the aperture restricts the angular spread of electrons entering the lower lens, since beams scattered above a certain angle β (collection semi-angle) are stopped by the aperture; hence, only electrons scattered by an angle $\leq \beta$ contribute to the image forming process.

Below the objective lens, an *intermediate lens* system is installed, which allows the operation of the TEM in two different modes: (1) imaging and (2) diffraction mode. It either selects the back focal plane of the objective lens, where the first diffraction pattern is generated, or the image plane of the objective lens, where the first intermediate image is formed, projecting the selected plane on

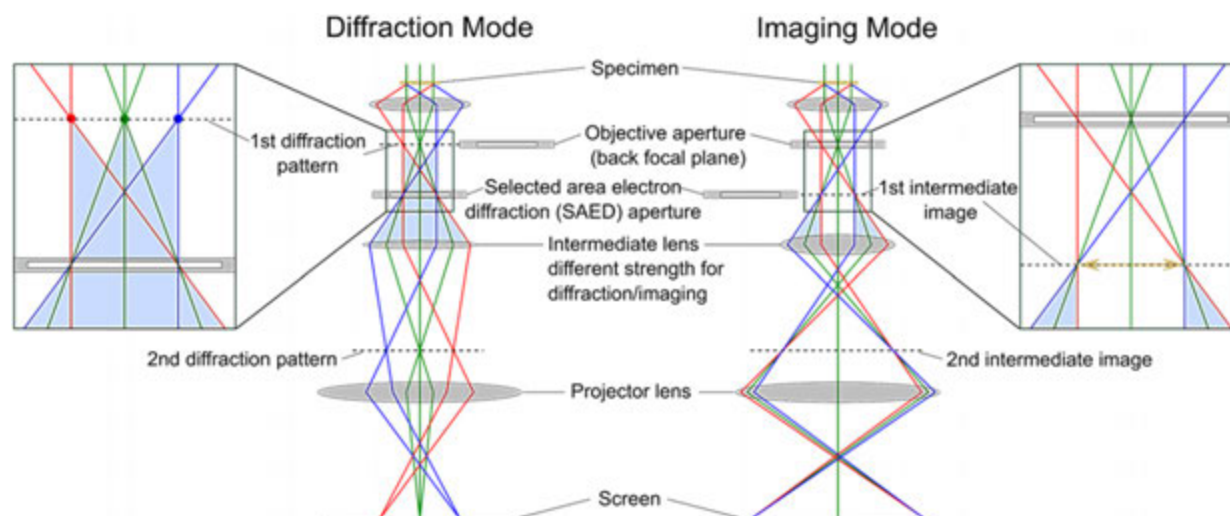


Fig. 5 Schematic illustrating the two possible modes: diffraction (left) and imaging mode (right). The selection is done by changing the lens current (diffraction strength) of the intermediate lens focusing on either the plane where the first diffraction pattern or where the first intermediate image is formed.

the viewing screen. Thus, it is possible to gain complementary information from real space (image mode) and reciprocal space (diffraction mode), which is a unique feature of the TEM. The schematic drawing in Fig. 5 displays the ray path for both modes.

The area which contributes to the diffraction pattern can be limited by the selected area electron diffraction (SAED) aperture. This aperture is inserted between the objective and intermediate lens system in the height of the 1st intermediate image plane, creating a smaller virtual aperture above the specimen plane. Only electrons passing the SAED aperture contribute to the diffraction pattern monitored.

The *projector lens system* in the lower part of the TEM column is a multi-lens system. It controls the final magnification of the image, which is displayed on the viewing screen. Furthermore, deflection coils are installed along the TEM column, enabling control of the beam tilt and shift, which becomes important for the general alignment of the instrument and for dark-field imaging techniques (see also the section on “Image Contrast in TEM” below).

If suitably equipped, a TEM can also be operated in *scanning TEM (STEM)* mode. Here, certain scan coils are required that allow the incident beam to scan over a small sample region instead of being stationary. The beam is focused to a fine spot and scans the sample while it is always kept parallel to the optical axis. Below the sample, a detector collects the information from the transmitted beam. Commonly, bright-field (BF) and annular dark-field (ADF) detectors are employed, which are differentiated by their acceptance angle. Low acceptance angles mandatorily including the primary beam are characteristic for BF detectors, while ADF or HAADF (high angle ADF) detectors collect only electrons scattered at higher angles. A detailed introduction to STEM can be found in a separate chapter of this Encyclopedia.

Resolution and Lens Aberrations

The resolution of an optical system is defined as the minimum distance between two objects, which can be imaged separately, for example neighboring atoms in a crystal lattice. As shown in the introductory part, the theoretical resolution, assuming ideal lenses and stability, only depends on the wavelength of the light source λ , the refractive index n of the medium, which is 1 for vacuum in the microscope column, and the convergence semi-angle α of the magnifying lens. By convention, α is often denoted as the collection semi-angle β in the context of electron microscopy. Therefore, it is possible to improve the resolution of the instrument by using either shorter wavelengths or increasing β . However, in reality, i.e., for non-ideal electromagnetic lenses, the resolution of the microscope is mainly limited by *lens aberrations*.

Due to mechanical imperfections, lenses and their corresponding electromagnetic fields are never perfectly rotational symmetric. If two perpendicular wave planes, the sagittal and meridional wave pass a lens, they exhibit different focal lengths Δf_A , depending on the deviation from the ideal symmetry. This effect is termed *astigmatism*, causing differences in the otherwise equal defocus settings of the transmitted beams from one single object of the image. Therefore, a point image is transformed into a small ellipse with the length r_A at the focus crossover according to:

$$r_A = \Delta f_A \beta \quad (3)$$

A correction of the astigmatism is possible by the application of stigmators, which are small octupoles that introduce a compensating field to eliminate the respective lens inhomogeneities.

Apart from astigmatism, there are two other main lens aberrations, which are the spherical and the chromatic aberration. Since the magnetic field inside a rotational symmetric lens is not perfectly homogeneous, distal rays of electrons passing the outer rim of the lens experience a stronger magnetic field than those traveling close to the optical axis. In consequence, outer rays are more strongly deflected than inner rays. As a result, a point is imaged in the Gaussian image plane as a small disc with radius r_s , depending on the *spherical aberration* coefficient C_s and the collection semi-angle β of the electromagnetic lens, according to the relationship:

$$r_s = C_s \beta^3 \quad (4)$$

The electron beam in the TEM is generated by a thermionic or a field emission source with a beam energy E_0 , including a narrow intrinsic energy spread. Due to instabilities in the high-tension (HT) supply, inelastic electron-electron and beam-specimen interactions, the ideal energy distribution E_0 is further broadened by a small amount ΔE . Electrons with different energies are refracted differently by the magnetic field of the lens, which leads to the so-called *chromatic aberration* (different colors have different wavelengths and hence different energies). In this case, a point source is imaged as a small disc with radius r_c , depending on the chromatic aberration coefficient C_c , the energy spread $\frac{\Delta E}{E_0}$ and the angle β :

$$r_c = C_c \frac{\Delta E}{E_0} \beta \quad (5)$$

If the spherical and the chromatic aberration are compared with respect to their importance for practical TEM work, the spherical aberration is significantly more relevant in most cases due to its β^3 dependence. However, since real and with that non-ideal samples are investigated, electrons will always experience some energy loss when transmitted through the material. Nevertheless, for thin samples < 100 nm and a HT range of 100–300 kV, the chromatic aberration can in principle be neglected.

Whenever a ray path in an optical or electron optical system is limited by the edge of a lens or by an aperture, the outer rim of the limiting object produces the *diffraction error*, projecting a local point source as a so-called Airy disc in the image (Rayleigh criterion). The smallest distance between two such incoherent point sources, which can still be recognized by the human eye, is defined as the overlap of the intensity minimum of the first with the intensity maximum of the second disc, resulting in the resolution r_{th} of the corresponding electromagnetic lens, which is also termed the *theoretical resolution*:

$$r_{th} = 0.61 \frac{\lambda}{\beta} \quad (6)$$

As shown, the effect of all aberrations depend on β , the collection semi-angle. However, it is not possible to infinitely reduce their effect by using arbitrarily small angles of β , since the diffraction error, with its inverse $\frac{1}{\beta}$ dependency, has the opposite effect. While the lens astigmatism can be corrected and the chromatic aberration is usually neglected in a first approximation, an optimal value for β being the best compromise between the spherical lens aberration r_s and the diffraction error r_{th} , can be calculated by:

$$\beta_{opt} = 0.77 \frac{\lambda^{1/4}}{C_s^{1/4}} \quad (7)$$

$$\text{Inserting } \beta_{opt} \text{ into equation } r(\beta) = (r_s^2 + r_{th}^2)^{1/2} \rightarrow r(\beta) = \sqrt{\left(0.61 \frac{\lambda}{\beta}\right)^2 + (C_s \beta^3)^2}, \quad (8)$$

which can be used to calculate the minimal resolvable distance or best possible resolution achievable in the TEM:

$$r_{min} = 0.91 (C_s \lambda^3)^{1/4} \quad (9)$$

The *resolution limit* r_{min} of a standard transmission electron microscope lies typically around 0.25–0.3 nm; see also Goodhew *et al.*, 2000; De Graef, 2003; Williams and Carter, 2009; Thomas and Gemming, 2013 and Kumar, 2014 as reference. Since the resolution depends on the electron wavelength and hence on the acceleration voltage, TEM instruments with very high acceleration voltages were developed in the late 1980s, in order to achieve an even higher resolution, such as the atomic resolution microscope (ARM) at the Max-Planck-Institute in Stuttgart. With an operating voltage of 1250 kV, this instrument was able to resolve 0.1 nm.

It is interesting to note that shortly after the development of the first commercial TEMs, the search for *aberration correctors* already started in the late 1940s (Scherzer, 1947). Otto Scherzer, who was a faculty member of the physics department at the TH Darmstadt at that time, developed first concepts for C_s correction, which was later further pursued by Harald Rose. In the 1990s, Harald Rose, together with Max Haider and Knut Urban, built the first C_s -corrected TEM instrument (Rose, 1990; Haider *et al.*, 1998; Erni, 2015). In such a C_s -corrected TEM, multipole non-rotational symmetric lenses are combined to generate a negative C_s value, canceling out the existing positive C_s value of the condenser or the objective lens system. More recent developments address the design of correctors for the chromatic aberration. Nowadays, state-of-the-art TEM machines are equipped with combined C_s/C_c correctors, reaching a resolution down to 0.05 nm.

Image Contrast in TEM

Elastic Scattering

In the TEM, image contrast is primarily generated by electron diffraction and scattering events, which occur when the incident electron beam interacts with the specimen. Contrast formation by absorption of electrons plays only a subordinate role. Elastic scattering describes the interaction of an electron with the electric field, *Coulomb interaction*, without altering the momentum of the interacting electron (McLaren, 1991; Williams and Carter, 2009; Pennycook and Nellist, 2011). Coherent scattering occurs under a scattering angle θ smaller than 10° , while an interaction with the positively charged atomic nucleus results in larger scattering angles and incoherent elastic scattering of the electrons; *Rutherford scattering*. The probability that a certain scattering event occurs, is described by the respective scattering cross-section σ . The unit for the cross-section is "Barn". In nuclear physics, 1 b (Barn) = $10^{-28} \text{ m}^2 = 10^{-4} \text{ pm}^2$ is commonly used, while in atomic physics the dimension of 1 Mb = $10^{-4} \text{ nm}^2 = 100 \text{ pm}^2$ is preferred. The cross-section expresses the likelihood that the incident electron initiates a scattering event. The *differential cross-section* $\frac{d\sigma(\theta)}{d\Omega}$ describes the angular distribution of electron scattering at a single atom. The electron is scattered through θ into the solid angle Ω . The differential cross-section can be expressed by:

$$\frac{d\sigma(\theta)}{d\Omega} = \left(\frac{1}{4\pi\epsilon_0} * \frac{Ze^2}{4E_0} \right)^2 * \frac{1}{\sin^4 \frac{\theta}{2}} \quad (10)$$

where Z is the atomic number, ϵ_0 the dielectric constant, e the elementary charge and E_0 the primary electron energy. The scattering intensity of electrons is related to the *atomic form factor* $f_{el}(\theta)$ (or atomic scattering factor), which is a measure of the amplitude of an electron wave scattered by a single atom. Both the atomic form factor and the differential cross-section describe the dependence of the scattering intensity from the scattering angle θ and are related to each other by:

$$\frac{d\sigma(\theta)}{d\Omega} = |f_{el}(\theta)|^2 \quad (11)$$

The atomic form or scattering factor $f_{el}(\theta)$ and the probability σ for elastic scattering to occur decreases with increasing scattering angle θ . Since $f_{el}(\theta)$ depends on the atomic number Z , it implies that the atomic form factor increases with higher atomic number, as illustrated in Fig. 6.

The atomic form factor for electrons can be expressed as:

$$f_{el}(\theta) = \frac{m_0 e^2}{2h^2} \left(\frac{\lambda}{\sin\theta} \right)^2 * (Z - f_X(\theta)) \quad (12)$$

with h as the Planck's constant, m_0 the electron mass, λ the corresponding wavelength and f_X the atomic form factor for X-rays. The first term describes Rutherford scattering from the nucleus of the atom, while the second term correlates to scattering events from the electron cloud. For X-rays, the respective atomic form factor can be expressed as:

$$f_X(\theta) = \frac{-e^2}{mc^2} \int \rho(r) e^{(-2\pi i K \cdot r)} dr \quad (13)$$

where ρ is the electron charge density, K the scattering vector in reciprocal space, with K being $|K| = \frac{2\sin\theta}{\lambda}$ and r the distance between electron and atom core. Note that electrons interact 10^6 – 10^7 times more strongly with the sample as compared to X-rays,

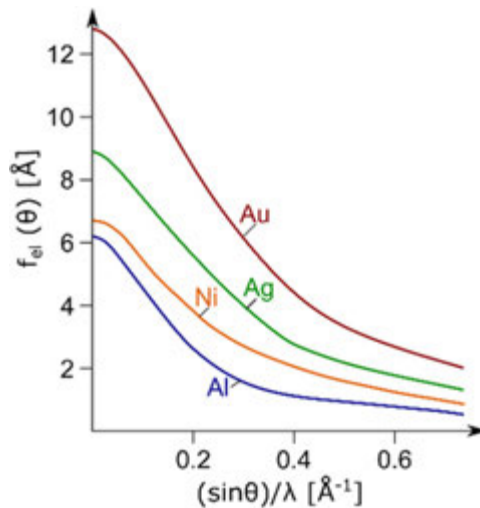


Fig. 6 Atomic scattering factors of different metals as a function of $(\sin\theta)/\lambda$. Redrawn after Hirsch et al., 1965 and McLaren, 1991.

since X-rays only interact with the electron cloud. The stronger interaction of the electron has the advantage that diffracted electron beams have a rather high intensity; however, dynamical effects such as multiple scattering have to be taken into account (see also the sections on "Volume Scattering" and "Bend Contours and Thickness Fringes").

Another parameter that describes the average distance between elastic collisions in a sample is the *mean free path* for elastic scattering Λ_{el} :

$$\Lambda_{el} = \frac{A}{N_A \rho \sigma} \quad (14)$$

where A is the atomic weight, N_A the Avogadro constant, ρ the electron charge density and σ the cross-section. Hence, the lighter the element in the specimen, the larger is the mean free path and less scattering events will occur, thereby lowering the contrast of the TEM image. Note that samples composed of heavy elements have a low mean free path and therefore need to be considerably thinner (sample preparation), as compared to light-weight materials such as for example boron suboxide, B_2O_3 or boron carbide, B_4C .

Volume Scattering

In the section on "Elastic Scattering" above it was shown how scattering occurs at a single atom within the unit cell, taking the atomic scattering factor $f_{el}(\theta)$ into account. When scattering from the entire unit cell of a crystal is of interest, the contribution from all atoms within the unit cell needs to be included and summed. Their relative position to the origin of the unit cell is expressed by the lattice vector r . The resulting phase difference attributed to each atom is described as $2\pi(K * r)$. The intensity of a diffracted beam from a unit cell is then related to the summation over the entire cell, giving the *structure factor* $F(\theta)$:

$$F(\theta) = \sum_j f_j(\theta) e^{-2\pi i(K * r_j)} \quad \text{or} \quad F_g = \sum_j f_j(\theta) e^{-2\pi i(g * r_j)} \quad (15)$$

The scattering vector K can be replaced by the reciprocal lattice vector g , if only the value of $F(\theta)$ at a specific reciprocal lattice point is of interest. The term $g * r$ then equals $(h * x_j + k * y_j + l * z_j)$. For $g * r = N$ with N being an integer, constructive interference results and diffracted intensity is visible. From the structure factor it can be deduced that the *scattering potential* $P(r)$ of the crystal, resulting from the interaction of electron beam and specimen, can be expressed as:

$$P(r) = \frac{h^2}{2\pi m_0 e V_c} \sum_n F_g e^{-2\pi i(g * r_n)} \quad (16)$$

where h is the Planck's constant, m_0 the rest mass, V_c the volume of the unit cell and r_n is the distance between the origin of the crystal and the n^{th} unit cell. The *extinction distance* ξ_g plays an important role on the image contrast formation, as it is closely related to the structure factor via the expression:

$$\xi_g = \frac{\pi V_c \cos \theta}{\lambda F_g} \quad (17)$$

Note that ξ_g represents the characteristic length of a reciprocal lattice vector g . It is related to the lattice parameter via V_c , the atomic number through F_g and the respective energy applied via the wavelength λ . The amplitude ϕ_g of a diffracted beam from a certain specimen volume arises from the summation of the scattering contribution over each unit cell. It is given by the following equation, where F_g is the scattering amplitude of the n^{th} unit cell and r_n defines its origin:

$$\phi_g = \sum_n F_g e^{-2\pi i(K * r_n)} \quad (18)$$

When the *excitation error* s is taken into account, the equation can be rewritten, since $g * r_n$ is always an integer and therefore $e^{-2\pi i(g * r_n)}$ equals 1. With $e^{-2\pi i(g+s) * r_n} = e^{-2\pi i(g * r_n)} * e^{-2\pi i(s * r_n)}$, it follows that:

$$\phi_g = \sum_n F_g e^{-2\pi i(g+s) * r_n} = \sum_n F_g e^{-2\pi i(s * r_n)} \quad (19)$$

The lattice vector r_n can be expressed as $r_n = (xa + yb + zc)$ and the excitation error as $s = (ua^* + vb^* + wc^*)$. It can be assumed that the transmitted volume of the specimen holds a large number of unit cells. The equation for the amplitude ϕ_g of the illuminated volume of the specimen can then be rearranged as a triple integral, including the unit cell volume V_c and $n_x * n_y * n_z$ with $A = n_x * a$:

$$\phi_g = \frac{F_g}{V_c} \int_0^A \int_0^B \int_0^C e^{-2\pi i(ux + vy + wz)} dx dy dz \quad (20)$$

Solving the integrals gives following expression:

$$|\phi_g| = \frac{F_g}{V_c} * \frac{(\sin \pi A u)}{(\pi u)} * \frac{(\sin \pi B v)}{(\pi v)} * \frac{(\sin \pi C w)}{(\pi w)} \quad (21)$$

with u , v and w being the components of the excitation error s along x , y and z . Since TEM samples are typically very thin foils with a thickness of approximately 20–100 nm, while the other two in-plane directions can be considered as infinite from the viewpoint of a traveling electron, the parts describing the x - and y -direction can be set to 1 and hence can be omitted. The intensity of the

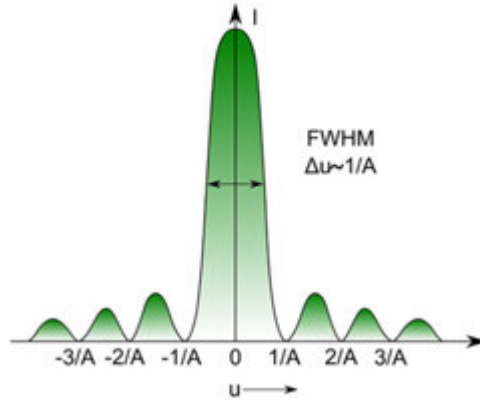


Fig. 7 Schematic showing the intensity distribution along u for $v = w = 0$. The full width half maximum (FWHM) $\Delta u \sim 1/A$ is indicated (with $A = n_x \cdot a$). Redrawn after Hirsch *et al.*, 1965.

diffracted beam is related to a $\sin^2$ -function, as illustrated in Fig. 7. The intensity equals the square of the absolute amplitude of the diffracted beam $I = |\phi_g|^2$.

For thin TEM samples, the intensity of a diffracted beam is then described by a sinusoidal function, controlled by the thickness t and the excitation error s , where both variables are perpendicular to g and the surface of the crystal (recall $\frac{\pi V_c \cos \theta}{\lambda F_g} = \xi_g$ being the extinction distance):

$$I_g(s, t) = \left(\frac{\lambda F_g t}{V_c \cos \theta} \right)^2 * \frac{\sin^2 \pi t s}{(\pi s)^2} \quad (22)$$

The scattering and diffraction events described above are considered under the *kinematic theory of diffraction*, where the intensity of the diffracted beam is described under the assumption that only a single scattering event occurs when the electron passes through the TEM sample. This may hold true for very thin TEM foils and in this case, the intensity of the diffracted beam is proportional to the square of the absolute value of the structure factor: $I_g \propto |F_g|^2$. Although most contrast variations in TEM can qualitatively be described by the kinematic theory, in reality however, the kinematic assumption is often insufficient. It does not take the interaction of the diffracted wave with the crystal lattice into account, whereas multiple scattering events are considered in the *dynamical theory of diffraction*. In this case, the intensity distribution of the diffracted waves around reciprocal lattice peaks is described by *dispersion surfaces*, taking extinction and interference effects into consideration, as well as the shape and width of the diffraction peaks. For example, why kinematically forbidden reflections are sometimes observed in diffraction patterns of thicker sample regions can be explained with the dynamical theory. Under these conditions, dynamical effects have to be accounted for and Eq. (22) can be reformulated, leading to the Howie-Whelan equations ("Pendellösung"), as given in Eqs. (23) and (24) in the section on "Bend Contours and Thickness Fringes" below, including the effective excitation error $s_{\text{eff}} = \sqrt{s^2 + \frac{1}{\xi_g^2}}$ instead of s .

Amplitude Contrast

Since the electron wave of the incident beam can change both its amplitude and its phase while it is transmitted through the specimen, two basic image-formation mechanisms can be distinguished: *amplitude contrast* and *phase contrast*.

Amplitude contrast dominates the image formation process for low to intermediate magnifications up to approximately 150,000x, while phase contrast is responsible for the contrast formation at higher magnifications and in HRTEM imaging in particular. Amplitude contrast can be further divided into two principle types: *mass-thickness contrast* and *diffraction contrast* with the latter being most important when analyzing crystalline samples. Mass-thickness contrast is the main mechanism generating image contrast, when the specimen is amorphous. The scattering intensity depends on the atomic number Z (compare Eq. (10)), but also on the thickness of the sample, since when the sample thickness exceeds the mean free path (Eq. (14)), more scattering events will occur.

In order to generate an image from mass-thickness contrast, it is crucial to use the objective aperture, which sits in the back focal plane of the objective lens. While weakly scattered electrons travel close to the optical axis of the lens, more strongly scattered electrons exhibit a larger scattering angle θ . By choosing a certain aperture size, electrons with a larger scattering angle are blocked by the aperture and are, therefore, excluded from the image forming process, which in turn increases the observed contrast.

If the sample is a single- or polycrystalline material, *diffraction* becomes the crucial contrast forming mechanism. When a crystal is orientated in a way that the angle between the lattice planes and the incident electron beam fulfills Bragg's Law, $2d \sin \theta = n\lambda$, constructive interference occurs. If the respective diffraction angle is larger than the semi-angle of collection, a diffracted beam cannot pass the objective aperture and is blocked out. Then, crystals or crystalline areas that fulfill the Bragg condition appear dark, because their diffracted beams are excluded from the image formation process. Therefore, in addition to the objective aperture size, the diffraction contrast always depends on the orientation of the sample. If the sample is tilted, lattice planes which were in Bragg

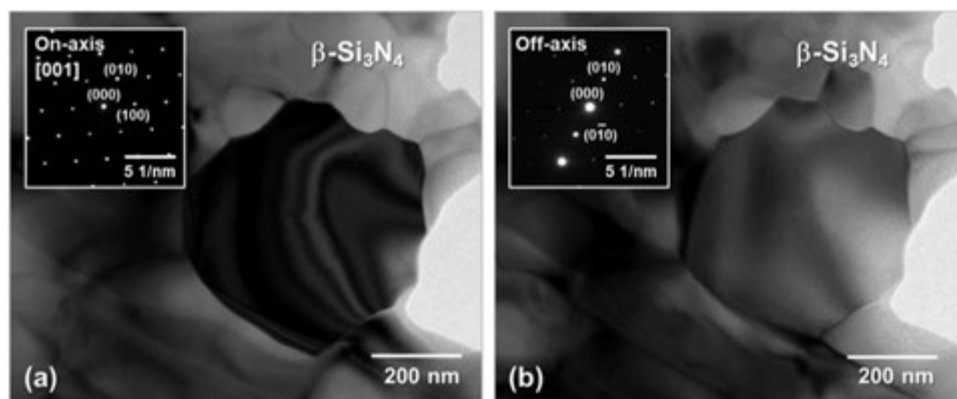


Fig. 8 TEM bright-field images showing one crystallite in a β - Si_3N_4 ceramic observed in two different orientations; (a) oriented along the [001] zone axis, while in (b) the crystallite is tilted about 3° out of the zone axis (compare also the corresponding diffraction patterns as insets in the upper left corners). The resulting contrast is rather different in both BF-images (orientation contrast). While in (a) the central grain appears dark (Bragg condition), in (b) it shows a similar contrast as the surrounding Si_3N_4 crystallites.

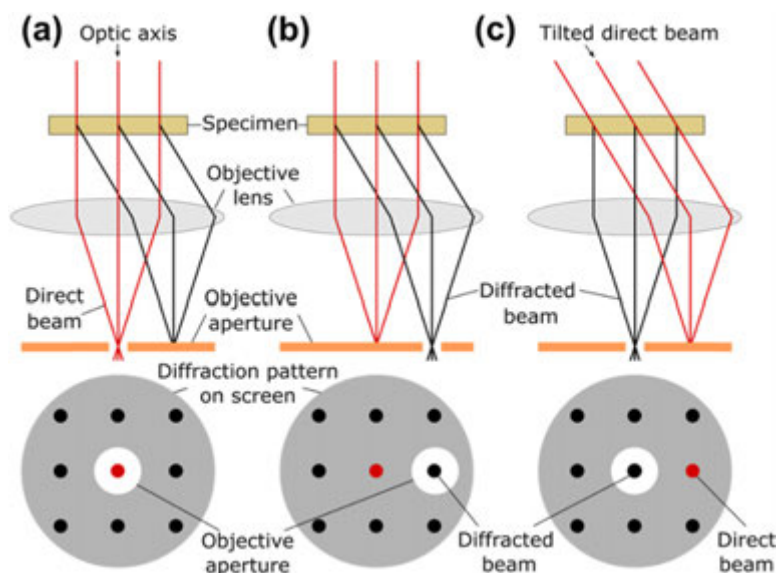


Fig. 9 Imaging techniques employing amplitude contrast by selecting the direct (incident) or one diffracted beam; (a) bright-field (BF) imaging using the direct beam, (b) dark-field (DF) imaging using one off-axis diffracted beam and (c) on-axis dark-field imaging, where the incident beam is tilted to shift the diffracted beam onto the optic axis to minimize the effect of lens aberrations.

condition are rotated out of it, changing the observed image contrast, as illustrated in [Fig. 8](#), where a β - Si_3N_4 grain reveals a different contrast, depending on its respective on-axis versus off-axis orientation. This also serves as a helpful tool, easily allowing a distinction between diffraction and mass-thickness contrast, since the latter does not change significantly when the sample is tilted.

By positioning the objective aperture, located in the back-focal plane of the objective lens, one can choose whether a diffracted or a non-diffracted (the direct or primary) beam is included in the image formation process. In *bright-field (BF) imaging* ([Fig. 9\(a\)](#)), the aperture selects the direct beam and may also select further diffracted beams, depending on the chosen aperture size. A smaller aperture excludes more diffracted beams and hence increases the image contrast.

In contrast to BF, *dark-field (DF) imaging* typically selects only one diffracted beam which is allowed to pass the objective aperture, while the incident beam is blocked out. In this case, only the specifically chosen diffracted beam forms the image. This imaging mode can be further distinguished in *off-axis* and *on-axis DF*. In off-axis DF, the direct beam is kept on the optical axis and the objective aperture is simply moved to the desired diffracted beam ([Fig. 9\(b\)](#)). However, choosing a diffracted beam traveling away from the optical axis, which implies a larger collection semi-angle β , enhances the contribution of the spherical lens aberration $r_s = C_s \beta^3$. Deploying on-axis DF by tilting the desired diffracted beam onto the optical axis avoids this disadvantage ([Fig. 9\(c\)](#)). In [Fig. 10](#), an example for bright- and dark-field imaging is given. Here, thin lamellae of braunite, $\text{Mn}_7\text{SiO}_{12}$, are embedded in a bixbyite $(\text{Mn,Fe})_2\text{O}_3$ single crystal, running along the (100) planes of the host crystal. The corresponding SAED

patterns are shown as insets and the diffraction spots utilized for BF- and DF-imaging mode are indicated (circle in inset). Note that this bixbyite crystal also contains secondary inclusions of nanosized jacobite crystallites, $(\text{Mn,Fe})_3\text{O}_4$.

Bend Contours and Thickness Fringes

Some of the most common contrast variations observed in TEM imaging are due to the usually uneven surface and inhomogeneous thickness of the TEM foil, which results in the so-called *bend contours* and *thickness fringes*. Furthermore, contrast can be generated by imperfections in the sample (crystal defects) such as stacking faults, dislocations, or local precipitations.

Diffraction contrast strongly depends on the orientation of the crystal lattice planes with respect to the incident electron beam. Deviations from this orientation immediately cause a variation in diffraction contrast. If a TEM foil is bent, the crystal structure is deformed and hence the orientation of the lattice planes is changed in consequence. Therefore, only some areas of the bent foil can be exactly aligned in Bragg condition simultaneously, while other areas necessarily are out of Bragg condition. When the diffracted beams are then blocked by a small objective aperture, the corresponding in-Bragg areas are seen as dark lines (**Fig. 11**), while the others remain bright. Because the TEM foil is typically bent in two directions (dome-like structure), the contours appear as areas of contrast, which are bent and curved as well.

Thickness variations of the TEM sample produce the so-called *thickness fringes*. These alternating bright and dark lines are typically observed at the edge of the sample, where it thins out into a wedge shape. Note that ion milling can cause thickness variations of the TEM foil, leading to the appearance of thickness fringes. They also occur, when phase and grain boundaries are inclined with respect to the incident electron beam, which can be explained with the help of the *Howie-Whelan equations* (Hirsch *et al.*, 1965). The change in amplitude of the direct beam ϕ_0 and one strong diffracted beam ϕ_g (two-beam case) passing through a thin slice with thickness d_z of the specimen, can be expressed by two differential equations, which are coupled with each other:

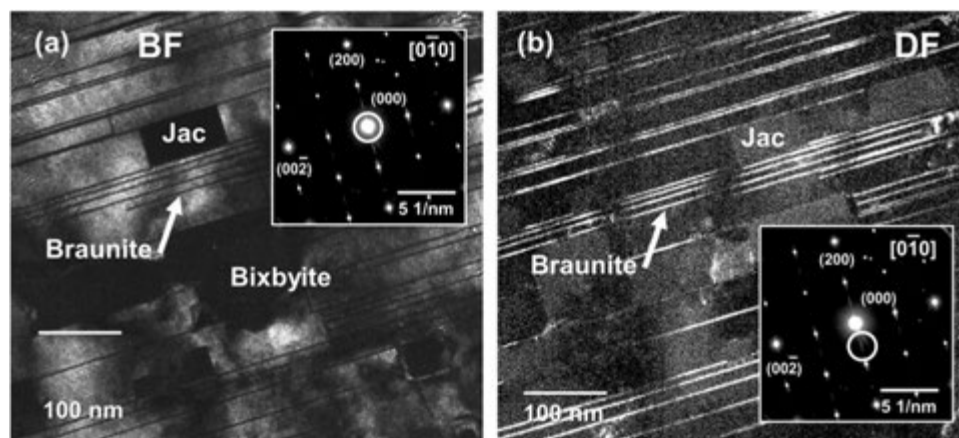


Fig. 10 TEM bright-field and dark-field images of one bixbyite $(\text{Mn,Fe})_2\text{O}_3$ single crystal with braunite $\text{Mn}_7\text{SiO}_{12}$ lamellae. (a) BF of the bixbyite host crystal, (b) DF of braunite lamellae running along the (100) planes of bixbyite. The insets show the corresponding SAED patterns with the respective diffraction spots used for the BF and DF mode. Note that the bixbyite crystal also contains additional inclusions of jacobite $(\text{Mn,Fe})_3\text{O}_4$ labeled as Jac.

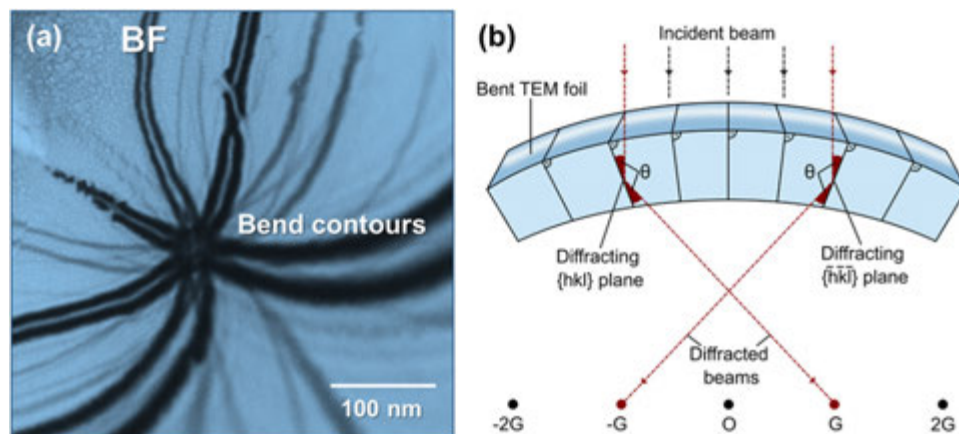


Fig. 11 (a) TEM bright-field image revealing dark contrast lines, so-called bend contours, originating from the buckled nature of the thin TEM sample (aluminum foil). (b) Schematic showing the scattering event from a bent crystal; (b) redrawn after Williams and Carter, 2009.

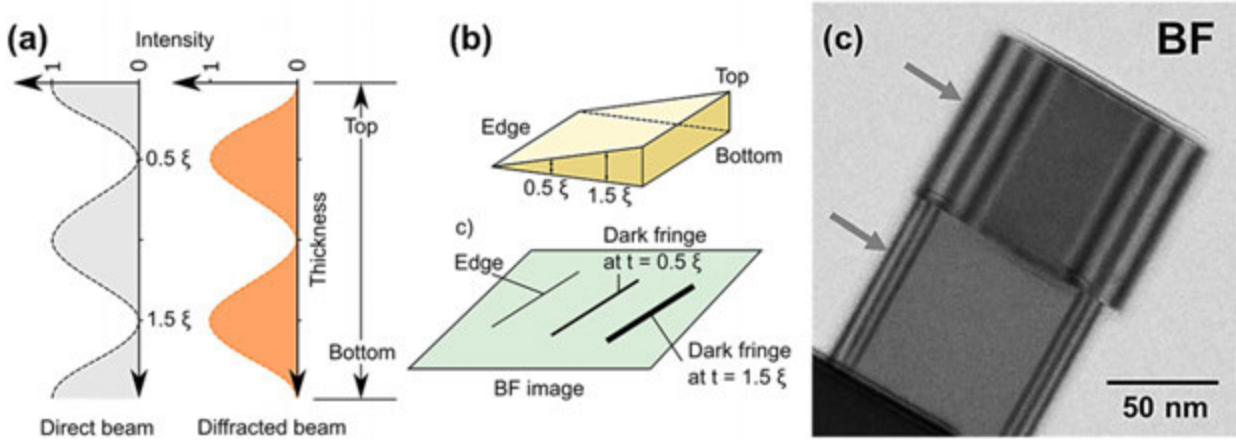


Fig. 12 Schematic of thickness fringes; (a) for two-beam condition ($s = 0$), the intensities of the direct and diffracted beam oscillate in a complementary way (s is fixed and t varies), (b) for a wedge specimen, the fringe separation is determined by the wedge angle and the extinction distance ξ_g , (c) Bright-field TEM image showing thickness fringes marked by arrows in small MgO crystallites; (a) and (b) redrawn after Williams and Carter, 2009.

$$\frac{d\phi_g}{dz} = \frac{\pi i}{\xi_g} \phi_0 e^{-2\pi i s z} + \frac{\pi i}{\xi_0} \phi_g \quad \text{and} \quad \frac{d\phi_0}{dz} = \frac{\pi i}{\xi_0} \phi_0 + \frac{\pi i}{\xi_g} \phi_g e^{2\pi i s z} \quad (23)$$

where z is the height of the TEM sample in beam direction, s is the excitation error and ξ_g the extinction distance. The two equations show that the intensity of the direct and the diffracted beam is coupled and oscillates with changing z -height, which corresponds to the local specimen thickness t . Maxima of the direct beam intensity correlate with minima of the diffracted beam and vice versa, as illustrated in Fig. 12.

The equation describing the intensity of the Bragg diffracted beam I_g is given by:

$$I_g = |\phi_g|^2 = \left(\frac{\pi t}{\xi_g}\right)^2 * \frac{\sin^2(\pi t s_{eff})}{(\pi t s_{eff})^2} \quad \text{with} \quad s_{eff} = \sqrt{s^2 + \frac{1}{\xi_g^2}} \quad (24)$$

where ξ_g is the extinction distance with $\xi_g = \frac{\pi V_{cos\theta}}{\lambda F_g}$ (see Eq. (17) in the above section on "Volume Scattering"), s_{eff} is the effective excitation error and t the thickness of the TEM foil. When the observed crystal in the TEM sample is well aligned, with $s = 0 \rightarrow s_{eff} = \frac{1}{\xi_g}$, the intensity of the diffracted beam (and complimentary to the direct beam) depends on changes in the thickness t , being the origin of the thickness fringes. However, if the sample has a constant thickness but is tilted or the TEM foil is strongly bent, the excitation error s or the effective excitation error s_{eff} strongly influence the observed image intensity.

Contrast of Crystal Defects

While the idealized crystal structure is an unlimited as well as an exact recurrence of the atomic arrangement in the underlying unit cell, real crystal structures contain a variety of defects. The most obvious one, due to the impossibility of infinite structures, is a grain-boundary or the sample surface, which naturally creates contrast by the implied and obviously inevitable change in crystal potential. In general, crystal defects are point-like, linear, planar or three-dimensional modifications of the ideal structure within a single crystal. While local point defects, such as Schottky or Frenkel defects, are usually not visible in the TEM, except when they are locally agglomerated, line defects like screw and edge dislocations or planar defects such as stacking faults and anti-phase domain boundaries are easily observed. *Dislocations* can be described as local positions of atoms being displaced by a vector R from their ideal position in the crystal lattice. This displacement results in an additional phase shift given by $\Phi = 2\pi gR$, with the reciprocal lattice vector g and the displacement vector R . If Φ is not equal to zero, this additional phase shift can be observed as contrast in bright- or dark-field TEM. However, if $g \cdot R$ is zero, the dislocation itself is not visible. Hence it must be noted that, not seeing a dislocation does not mean it is not there! This is the so-called *invisibility criterion*, as illustrated in Fig. 13.

While this criterion is sufficient for pure screw dislocations, invisibility of mixed or pure edge dislocations additionally requires $g \cdot R \times u = 0$, with u being a lattice vector describing the direction of the dislocation line. By utilizing these criteria, it is possible to determine the specific displacement vector of the dislocation, the so-called *Burgers vector* giving $g \cdot b \times u = 0$. Furthermore, when the direction of the dislocation line u is known, the dislocation type can be determined as well. For edge dislocations, u and b are perpendicular to each other, while they are parallel for screw dislocations. In the case of pure edge or screw dislocations, the dislocation line is straight and u can be determined from trace analysis of the dislocation line by comparing at least two images with corresponding diffraction patterns in different orientations. However, it should be noted that mixed dislocations, which have both edge and screw components and bent dislocation lines, implying a variation of u , more frequently occur than pure edge or screw dislocations.

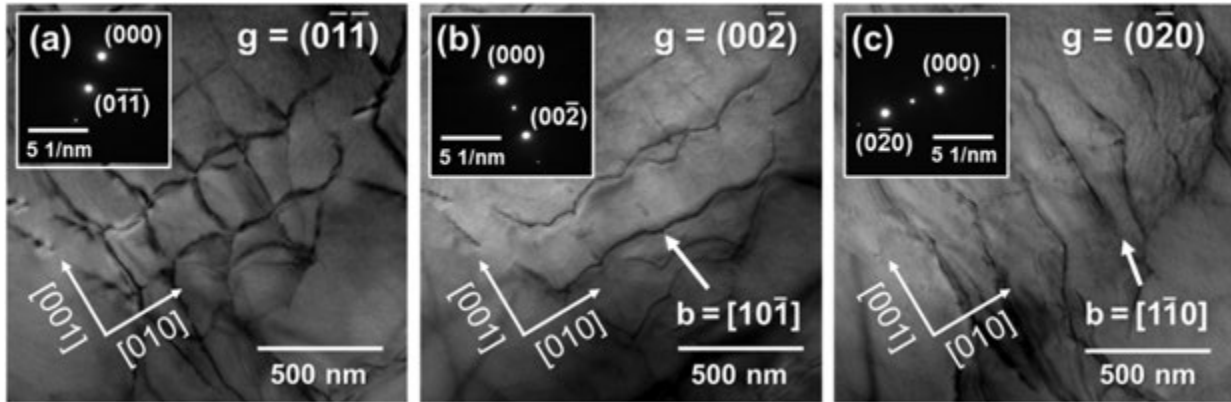


Fig. 13 Illustration of the invisibility criterion: (a) $g = (0\bar{1}\bar{1})$ two-beam bright-field image of $(\bar{1}\bar{1}0)[\bar{1}\bar{1}0]$ and $(101)[10\bar{1}]$ edge dislocations in a pseudo-cubic KNbO_3 single crystal. The invisibility criterion is not fulfilled in (a) and both types of dislocations create contrast. The insets display the corresponding diffraction patterns with the respective g vectors indicated. (b) Using $g = (00\bar{2})$, the edge dislocations with $u = [001]$ are invisible due to $(00\bar{2}) \cdot [\bar{1}\bar{1}0] = 0$ and $(00\bar{2}) \cdot [\bar{1}\bar{1}0] \times [001] = 0$. (c) Using $g = (0\bar{2}0)$, the edge dislocations with $u = [010]$ are invisible due to $(0\bar{2}0) \cdot [10\bar{1}] = 0$ and $(0\bar{2}0) \cdot [10\bar{1}] \times [010] = 0$.

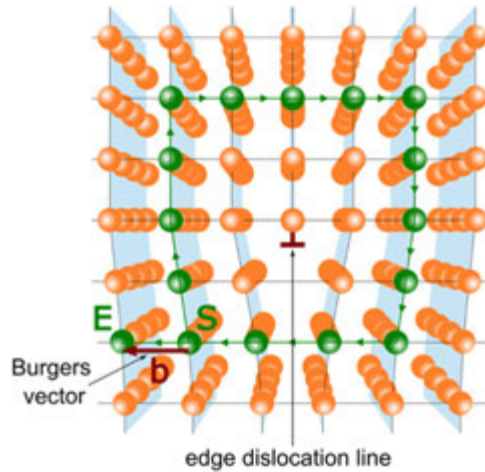


Fig. 14 Illustration of the Burgers circuit: start (S) and endpoint (E) of the Burgers circuit are shown around an edge dislocation line. Start and endpoint do not coincide and the displacement vector pointing from S to E equals the Burgers vector.

Since high-resolution TEM imaging allows a detailed investigation of local crystal structures, it can also be used to determine the Burgers vector of edge dislocations by the so-called *Burgers circuit*. This method requires a HR-(S)TEM image showing the endpoint of a dislocation line, i.e., the dislocation line needs to be parallel to the direction of view. Upon clock-wise “drawing” a rectangle around the dislocation, with the start point on an arbitrary lattice site and the edge length being a defined number of discrete steps from lattice site to lattice site, start and endpoint will not coincide. The vector pointing from the start to the endpoint is the Burgers vector (see Fig. 14). In contrast to edge dislocations, both points will coincide for screw dislocations and the Burgers vector appears to be invisible (the same as if no dislocation is present at all), which is due to b being parallel to the dislocation line and the viewing direction.

Imaging of dislocations is best done by using the so-called *weak beam dark field* (WBDF) technique. In this special setup, the sample is oriented in such a way that only those lattice planes of a certain reciprocal lattice vector g , with a high excitation error, which are bent due to a nearby dislocation contribute to the image contrast, i.e., appear bright. This so-called $3g$ condition allows the display of the dislocation lines to be sharp and well-defined, as compared to the more diffuse and broad lines observed in conventional bright- or dark-field imaging.

Another origin for defect-related contrast in TEM images is the presence of volume defects such as small precipitates, which distort the crystal lattice in their vicinity and cause the occurrence of sometimes large *strain-field contrast*. For small local strain fields, the corresponding contrast is easy to recognize, since it often resembles the shape of small coffee beans and therefore is termed *coffee-bean contrast*. Fig. 15 shows such a coffee-bean contrast originating from local strain fields in the Lorandite, TlAsS_2 , host crystal, running along specific (001) lattice planes.

Electron Diffraction

Switching from image mode to *diffraction mode* in the TEM can simply be done by “pressing a button”, which appropriately changes the intermediate lens current. In consequence, the focus point of the intermediate lens is moved from the intermediate image plane of the objective lens to its back focal plane and hence the diffraction pattern instead of the image is projected onto the viewing screen (compare also Fig. 5; Hirsch, 1999). By inserting the SAED aperture, the sample area contributing to the diffraction pattern can be limited and a well-defined sample region can be investigated in reciprocal space. This aperture, which is positioned in the 1st intermediate image plane, is demagnified back to the specimen plane by a factor of approximately 50x. Therefore, it is possible to select small and very specific sample areas of down to 200–300 nm in size, such as individual grains or even intergranular phases at grain boundaries and triple junctions. Furthermore, in diffraction mode, it is easy to distinguish between *crystalline* and *amorphous* materials. Due to the missing long-range order in amorphous materials, the diffraction pattern only displays characteristically diffuse rings, representing the varying short- and medium-range order in the amorphous material (Fig. 16(a)). Such ring patterns can be employed to extract the *radial-distribution function* (RDF) of the amorphous material, which describes the probability to find atom pairs as a function of pair separation, providing structural information of the amorphous phase. In contrast, in crystalline materials the electron beam is diffracted by the periodic nature of the crystal lattice according to Bragg’s Law. If a *polycrystalline* material is studied, which features a multitude of randomly orientated crystallites in the illuminated volume, a ring pattern is formed, where each ring around the central beam correlates to a certain lattice plane distance d_{hkl} , as shown in Fig. 16(b).

If only one single crystal is examined, discrete diffraction spots will be imaged in reciprocal space, where every diffraction spot correlates to a specific lattice spacing distance (Fig. 16(c)) and the corresponding integrated diffraction intensity (Vincent

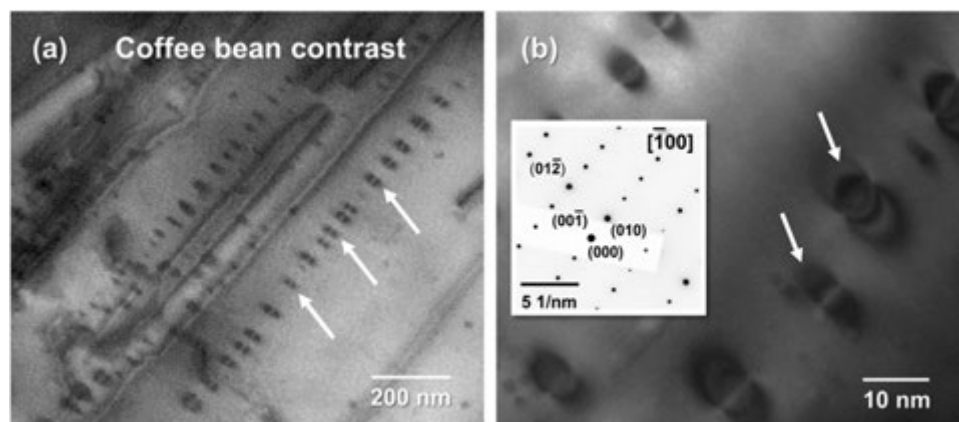


Fig. 15 TEM bright-field images of coffee-bean contrast in a Lorandite TIAsS_2 single crystal, originating from local strain fields along specific (001) lattice planes; (b) higher magnification with the corresponding SAED pattern as inset.

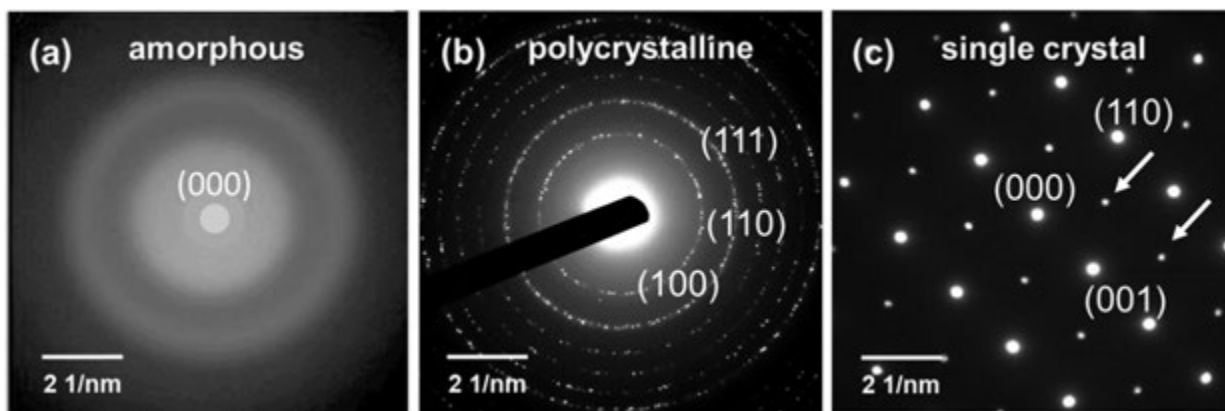


Fig. 16 Selected area diffraction (SAED) patterns of (a) an amorphous polymer-derived ceramic featuring the characteristic halo ring pattern; (b) a polycrystalline, simple cubic powder sample of TiCl with consecutive, continuous rings. Note that the distance from the center (incident beam) to these rings allows the determination of the d -spacing of the crystal lattice. In (c), an individual grain within a polycrystalline $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3 - x\text{BaTiO}_3$ ($x=0.03$) ceramic (lead-free ferroelectric) is shown, featuring a pattern of sharp diffraction spots typical for single crystalline materials. The $1/2\{000\}$ superlattice reflections of this crystal structure are indicated by arrows.

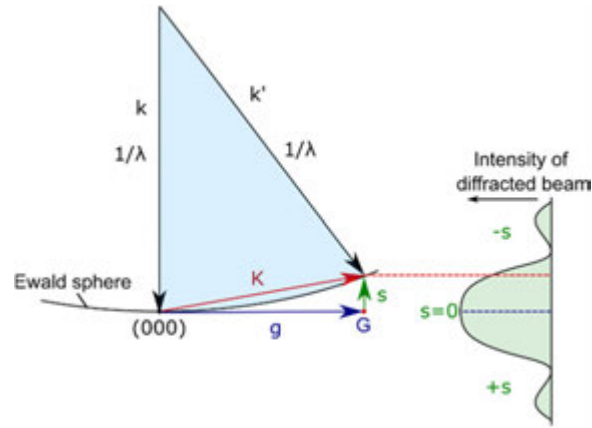


Fig. 17 Schematic diagram showing the scattering geometry for a thin TEM-foil normal to the incident electron beam. The graph on the right reveals the intensity variation of the diffracted beam depending on the deviation from the exact Bragg condition, given by the excitation error s .

and Midgley, 1994). The spacing between the lattice planes d_{hkl} equals the inverse length of the reciprocal lattice vector g_{hkl} given by:

$$d_{hkl} = \frac{1}{|g_{hkl}|} \quad (25)$$

For a detailed interpretation of diffraction patterns, the *Ewald sphere construction* is the usual method applied. The diameter of the sphere is defined by the wave vector k with its length being equal to the reciprocal wavelength of the accelerated electrons: $|k| = \frac{1}{\lambda}$. The wave vector $k' = k + g$, starting from the center of the Ewald sphere, points to a reciprocal lattice point (Fig. 17). If this reciprocal lattice point lies on the circumference of the sphere, the Laue criteria and the Bragg equation are fulfilled and diffracted intensity, i.e., a diffraction spot will be visible. Due to its relation to the wavelength, the radius of the Ewald sphere in TEM is very large as for example compared to X-ray diffraction. Therefore, the sphere can be approximated as an almost flat plane intersecting a multitude of reciprocal lattice points in the Zero Order Laue Zone (ZOLZ) at once (see also Fig. 20). In consequence, not only one individual, but a number of diffraction spots are simultaneously visible, generating a pattern related to the specific symmetry of the illuminated single crystal in its respective orientation.

Theoretically, the diffraction spots are solely mathematical points in reciprocal space. However, due to the very small thickness of the TEM foil, it can be mathematically proven that these points are elongated parallel to the optical axis (z-direction) with a rotational elliptic shape, so-called *relrods* (reciprocal lattice rods). If a relrod is cut by the Ewald sphere, a corresponding diffracted beam exists with its intensity being determined by the deviation from the exact Bragg condition, which is measured by the vector of the excitation error s . For $s \neq 0$, the diffraction vector g does not lie directly on the Ewald sphere and the deviation from the exact position on the sphere is described by the actual scattering vector $K = g + s$. If g lies outside the Ewald sphere, s is negative and if g lies within the Ewald sphere, s is positive. When the crystal is tilted, the reciprocal space sweeps through the Ewald sphere with the excitation error s changing from $+s$ to $-s$ and vice versa.

In order to evaluate s , another characteristic of the diffraction mode in TEM can be deployed: the *Kikuchi lines*. When the incident beam interacts with the sample, besides elastic scattering, also *inelastic scattering* occurs. These inelastically scattered electrons (incoherent beams) can subsequently be diffracted by a set of lattice planes (hkl), which coincidentally is in Bragg condition. In consequence, two diffraction cones are formed, the so-called *Kossel cones*, which correspond to $+g$ and $-g$ and thus to (hkl) and $(\bar{h}\bar{k}\bar{l})$. They also intercept with the Ewald sphere forming a pair of Kikuchi lines (Fig. 18(a)). The line closest to the incident beam is called *deficiency line*, since it has an intensity even lower than the surrounding background of diffuse scattering, while the one further away is termed *excess line* due to its comparably high intensity. Simplified, this phenomenon can be understood by the fact that inelastic scattering occurs predominantly in the forward direction and the excess line ($+g$) contains, in contrast to the deficiency line ($-g$), Bragg-diffracted electrons from such rather forward-biased incoherent beams. When $s = 0$, the deficiency Kikuchi lines run directly through the primary beam and the excess line through the corresponding diffraction spot. When $s \neq 0$, the lines deviate from this position (Fig. 18(b)); for $s > 0$, the line pair moves further away from the direct beam in the direction of the diffracted spot, while it moves in the opposite direction for $s < 0$.

Furthermore, under certain conditions, two excess or two deficiency lines from Kikuchi line pairs corresponding to lattice planes (hkl) and $(\bar{h}\bar{k}\bar{l})$ can together form an excess or deficiency Kikuchi band, respectively. Note that the term Kikuchi band is also often imprecisely used to describe Kikuchi line pairs and the area between them. Since the positions of Kikuchi lines and bands with regard to the direct beam reflect the deviation from the respective g vectors and, hence, the actual orientation of the reciprocal lattice, they can be utilized to easily orientate crystalline samples into crystallographic zone axis conditions. In the case of a perfect zone axis condition, which is usually desirable for SAED patterns, the Kikuchi bands that correspond to the diffraction spots in the pattern, cross each other at the center of the direct beam. Hence, in order to orientate the sample, it just needs to be tilted in such a way that the merging point of the respective Kikuchi band is positioned in coincidence with the direct beam. Note that in perfect

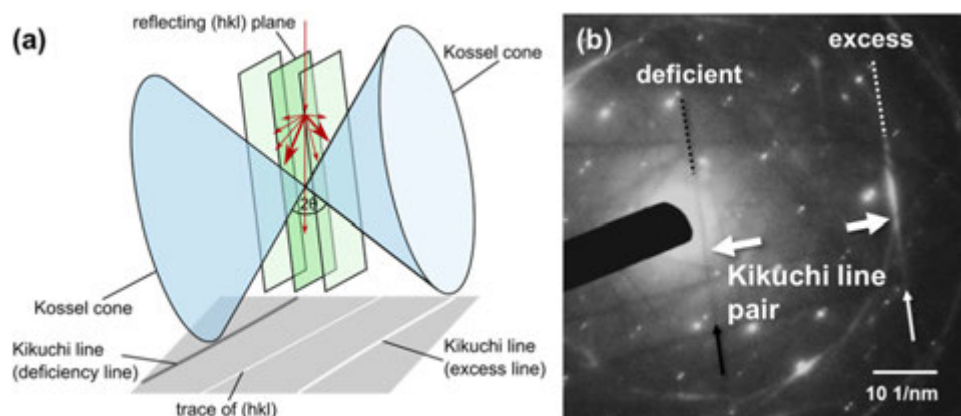


Fig. 18 (a) Schematic illustrating the origin of Kikuchi lines (Kossel cones) and (b) diffraction pattern of a bixbyite single crystal (Mn,Fe)₂O₃ from a thicker sample area (inelastic scattering), showing the presence of a Kikuchi line pair for $s > 0$. Note that these line pairs can be used to easily orientate the crystal in a zone axis or a $s_{hkl} = 0$ condition.

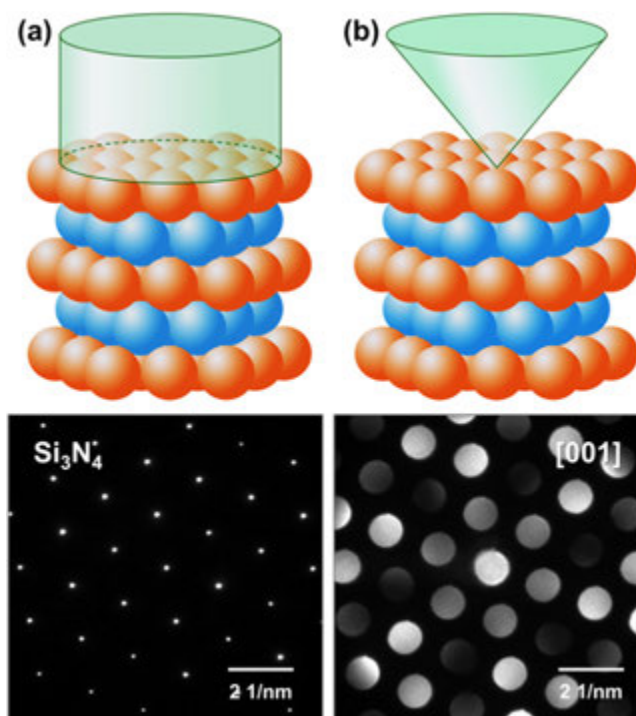


Fig. 19 Comparison of (a) a SAED diffraction pattern with parallel illumination of the sample and (b) a CBED pattern (focused beam) from a [001] zone axis of a β -Si₃N₄ crystal taken at 200 kV. Note that both diffraction images show a sixfold symmetry (Friedel's law $I_{hkl} = I_{\bar{h}\bar{k}\bar{l}}$). The schematic drawings illustrate the corresponding convergence of the electron beam.

zone axis condition, for none of the diffracted beams $s_{hkl} = 0$ is valid; it rather resembles a compromise leveling out all excitation errors to obtain a point-symmetric diffraction pattern with evenly distributed intensities. Furthermore, it should be noted that, in addition to inelastic scattering, Kikuchi lines can also be induced by illuminating the sample with an intense convergent beam, rendering this method of orientating the sample readily available in almost every case.

While SAED patterns, as shown in Fig. 19(a), are generated using a parallel electron beam, so-called *convergent beam electron diffraction* (CBED) patterns are formed when a focused, i.e., convergent beam is used; see for example: Edington (1975), Spence and Zuo (1992), Loretto (1994), Fultz and Howe (2007), Reimer and Kohl (2008). Utilizing the spot-like illumination of such a focused beam (Fig. 19(b)), it is possible to select sample areas even smaller than feasible with the smallest SAED aperture. Therefore, the terms μ -diffraction or nano-diffraction are also commonly used for this technique. Due to the convergent beam setting in CBED, diffraction disks instead of diffraction spots are formed. For a convergent angle α smaller than the diffraction

angle θ , separated non-overlapping disks are observed. The corresponding diffraction pattern is called a *Kossel-Möllenstedt diagram*. For higher convergence angles, the individual diffraction disks overlap, forming a *Kossel diagram*. The disks can exhibit characteristic details, e.g., diffraction lines that carry additional information about the specific crystal symmetry, which is beyond those data obtainable from normal SAED patterns under parallel illumination.

Another difference between CBED and SAED is the excitation of different g_{hkl} diffraction vectors in CBED, which are not necessarily perpendicular to the optical axis due to the high convergent angle α . Therefore, not only diffraction spots from the *Zero Order Laue Zone* (ZOLZ) are visible in CBED (where the Ewald sphere intersects the crystal lattice at the 000-position), but also diffraction information from *Higher Order Laue Zones* (HOLZ) can be displayed (1st, 2nd, etc. lattice planes above the 000-plane), giving information about the third dimension of the crystal parallel to the z-direction, as depicted in Fig. 20. Note that with the projected distance D_s , the distance of the reciprocal lattice plane that lies perpendicular to the incident beam direction can be calculated with:

$$D_s = \sqrt{2n \frac{g_{hkl}}{\lambda}} \rightarrow g_{hkl} = \frac{D_s^2 \lambda}{2n} \quad (26)$$

where g_{hkl} is the distance to be calculated, n is the order of the Laue zone and λ is the electron wavelength.

Under certain circumstances, CBED allows for the determination of the point and space group symmetry. For example, with the help of CBED, it is possible to distinguish between trigonal α -Al₂O₃ with space group $R\bar{3}c$ and hexagonal α -SiC with space group $P6_3mc$. In a conventional SAED pattern, a 6-fold symmetry is displayed in both cases, because regular SAED diffraction patterns are strictly centrosymmetric according to Friedel's law (intensity $I_{hkl} = I_{\bar{h}\bar{k}\bar{l}}$; Laue symmetry), while in CBED mode, the 3-fold symmetry of alumina becomes visible by the faint HOLZ lines within the central diffraction disc.

A versatile but rather complicated CBED method, which is especially suitable for the investigation of dislocations and other defects, is *large angle convergent beam electron diffraction* (LACBED). In simple words, this technique utilizes a combination of

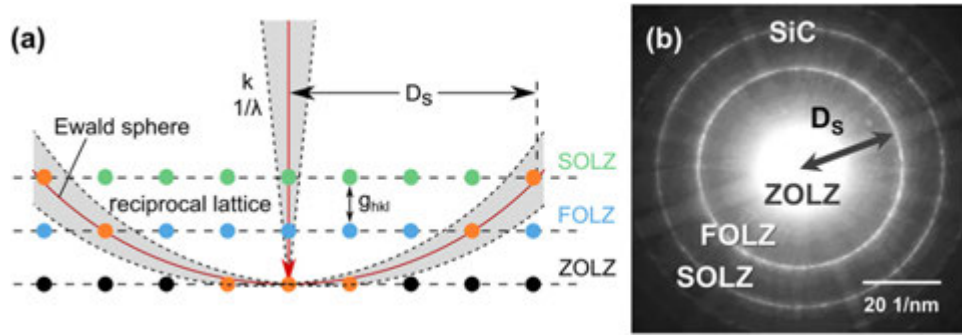


Fig. 20 (a) Schematic of the Ewald sphere construction for a convergent incident electron beam showing the origin of Higher Order Laue Zones (HOLZ). The intersection of the Ewald sphere with the Zero, First and Second Order Laue Zones are shown. Note that the projected distance D_s allows determination of the spacing of the reciprocal lattice planes g_{hkl} along the electron beam direction (Eq. 26). (b) CBED pattern of a SiC crystal revealing the Zero (ZOLZ), First (FOLZ) and Second Order Laue Zone (SOLZ).

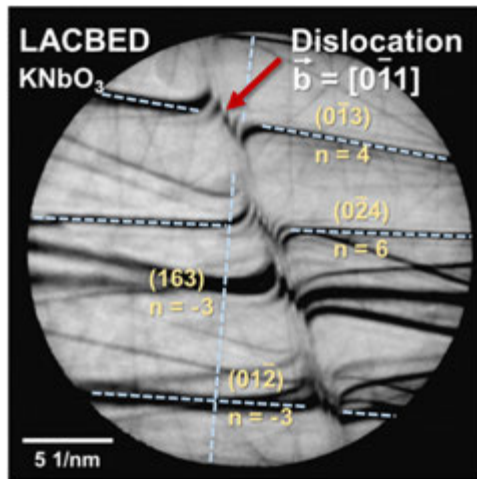


Fig. 21 LACBED image of a $[0\bar{1}1][\bar{1}11]$ edge dislocation in a pseudo-cubic KNbO₃ single crystal. The identification of the diffraction lines g_{hkl} (light blue) intersecting the dislocation (marked in red) allows the calculation and determination of the Burgers vector b , based on the number of interfringes n at the intersection point.

imaging and diffraction effects, which is induced by employing a large beam convergence angle of 1° to 5° , a highly defocused beam or offset z-height, and the selection of only the direct beam by the SAED aperture. The resulting LACBED image contains diffraction lines (deficiency lines only) as well as a BF image of the illuminated area. By carefully tilting the specimen, the diffraction lines are moved with respect to the image in such a way that they intersect the dislocation of interest (Fig. 21).

At the intersection point, a diffraction line corresponding to a certain g_{hkl} is twisted and interrupted n times depending on the Burgers vector b according to:

$$g_{hkl} * b_{uvw} = h * u + k * v + l * w = n \quad (27)$$

with $n \in \mathbb{N}$. While the absolute value of n simply equals the number of interfringes, the sign of n depends, according to the so-called *Cherns-Preston rules*, on the twist character, the direction of the dislocation line u , and the direction of the deviation parameter s (excitation error) for the respective g_{hkl} line. If at least three identified and appropriately different diffraction lines are investigated and their corresponding n is determined, an equation system can be set up which allows the calculation of the three unknown variables u, v, w and hence the determination of b . If performed thoroughly, this method is very distinct and works well not only for edge, screw and mixed dislocations, but also for stacking faults and anti-phase domain boundaries (APBs). However, since the number of visible diffraction lines can be very high, it typically requires the simulation of LACBED images beforehand, in order to unambiguously identify the chosen g_{hkl} lines. A detailed introduction to this powerful technique and its applications can be found in Morniroli (2018).

High-Resolution Imaging

For *high-resolution imaging* in TEM (HRTEM), which is usually conducted at magnifications higher than 150,000x, the observable image contrast is correlated to a phase shift of the incident electron wave. Therefore, the contrast in this imaging mode is termed *phase contrast* (Buseck *et al.*, 1988; Williams and Carter, 2009; Spence, 2013), as opposed to the *amplitude contrast* discussed earlier. The essential part of the total phase shift is generated as the direct beam passes through the sample volume. However, as the electron beam travels through the microscope, an additional phase shift is introduced by the spherical aberration r_s and the focus setting of the objective lens (defocus Δf), generating contrast in the HRTEM image. Interference of the differing phase vectors of the exiting electron waves from the direct and the various diffracted beams then results in altered amplitudes, which makes the phase contrast visible and creates the observed image (cameras as well as the human eye can only detect amplitude contrast). Since

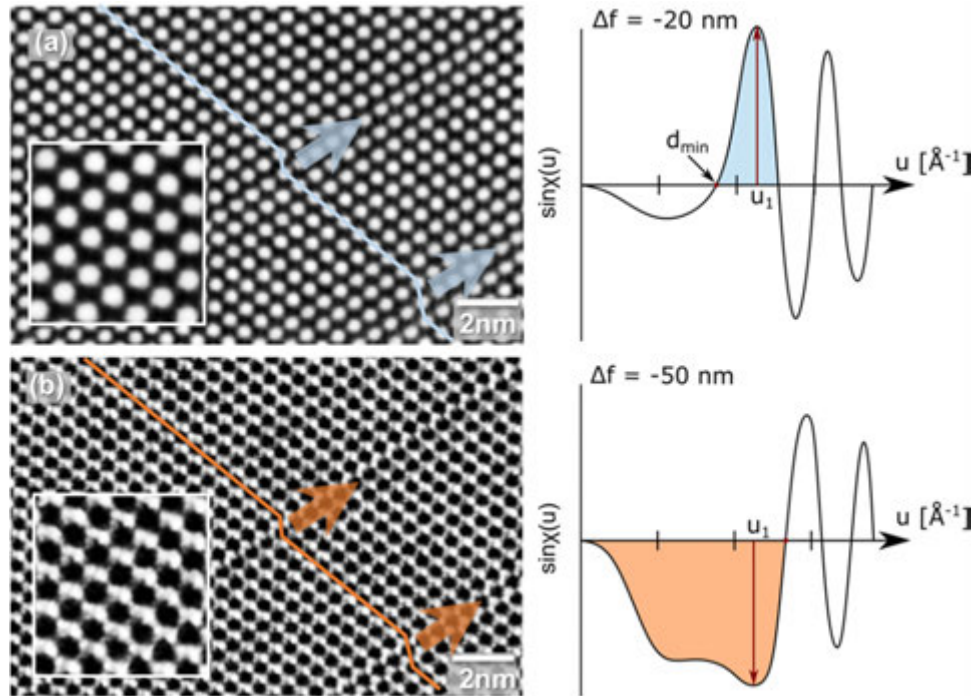


Fig. 22 The plot $\sin\chi(u)$ versus u and the corresponding HRTEM micrographs of the identical area of a boron suboxide B_6O single crystal imaged at different defocus values: (a) at a defocus value of $\Delta f = -20$ nm and (b) at Scherzer defocus $\Delta f = -50$ nm ($E_0 = 200$ kV, $C_s = 2.3$ mm). The colored areas in both plots of $\sin\chi(u)$ versus u indicate the resulting negative contrast shown in (a) versus a positive contrast in (b) for the spatial frequency u_1 . Note that, by convention, negative contrast describes the case when the atoms appear bright on dark background (going back to the times, when film negatives were used to record the images). The arrows in the HRTEM images indicate stacking faults in the B_6O structure, proving that identical areas are imaged in (a) and (b). The insets show a higher magnification.

the image contrast is strongly linked to the focus setting and the thickness of the specimen, HRTEM images, in general, cannot be intuitively interpreted (compare also Fig. 22).

The spatial information from a single point of the specimen is projected onto the screen or a CCD camera as an extended region, the Airy disc, mainly due to the existing lens imperfections. Each point in the specimen can be described by a specimen function $f(r) = f(x, y)$. The intensity in the image that corresponds to a point (x, y) within the specimen is described by the image function $g(r) = g(x, y)$, given by:

$$g(r) = \int f(r')h(r-r')dr' = f(r) \otimes h(r) \quad (28)$$

where $h(r) = h(x, y)$ is the *point spread function* (or *smearing function*), used as a measure for the contribution of a specimen point (x, y) to the image, being convoluted with $f(r)$. Assuming uniform coherent illumination, the specimen function can generally be described with respect to the amplitude $A(x, y)$ and the phase $\phi_t(x, y)$ of the electron wave:

$$f(x, y) = A(x, y)e^{(-i\phi_t(x, y))} \quad (29)$$

Since the contrast in HRTEM is created by a phase shift and not by a change in amplitude, as is the case for the amplitude contrast in for example bright-field imaging, the amplitude term $A(x, y)$ can be set to 1. The phase shift that is generated while the electron beam passes the specimen, depends on the specimen potential $V(x, y, z)$ the electron sees. For very thin samples of thickness t , the projected potential $V_t(x, y)$ is used and the specimen transfer function can then be rearranged as:

$$f(x, y) = e^{[-i\sigma V_t(x, y) - \mu(x, y)]} \quad (30)$$

Here, the specimen is described as an independent phase object, termed the *phase object approximation* (POA). The variable σ is called the *interaction constant* and depends on the electron wavelength and acceleration voltage E , which can be expressed as $\sigma = \pi/\lambda E$. The function $\mu(x, y)$ considers the absorption, which occurs when the electron beam passes through the specimen volume. For very thin specimens with $V_t \ll 1$, the absorption contribution can be neglected and $f(x, y)$ can be simplified to the following expression termed the *weak phase object approximation* (WPOA):

$$f(x, y) = 1 - i\sigma V_t(x, y) \quad (31)$$

Using the WPOA model and applying this term to Eq. 28, the wave function as observed in the HRTEM image can be expressed by:

$$\Psi(x, y) = [-i\sigma V_t(x, y)] \otimes h(x, y) \quad (32)$$

The intensity distribution in the recorded HRTEM image is given by $I = \Psi\Psi^* = |\Psi|^2$. When multiplying this out, substituting $h(x, y)$ by $\cos(x, y) + i\sin(x, y)$ and neglecting the σ^2 terms, since σ is rather small, the equation can be rearranged and reduced to:

$$I = 1 + 2\sigma V_t(x, y) \otimes \sin(x, y) \quad (33)$$

The *contrast transfer function* $H(u)$ is a Fourier transform of $h(r)$, with u being the spatial frequency. Hence, for a certain direction, $H(u)$ is described by the product of the aperture function $A(u)$, the envelope function $E(u)$, which accounts for the damping property of the objective lens system, and the aberration function $B(u)$:

$$H(u) = A(u)E(u)B(u) \quad (34)$$

Taking Eq. 32 into consideration, the *objective lens transfer function* $T(u)$ can be derived. Here, only the imaginary part of $B(u) = e^{i\chi(u)}$ is considered, since it contributes to the intensity of the image. When the aberration function $B(u)$ is further set to $B(u) = 2\sin\chi(u)$, it follows for the transfer function $T(u)$:

$$T(u) = A(u)E(u)2\sin\chi(u) \quad (35)$$

The term $\chi(u)$, also called the *phase distortion function*, describes the shift of the electron phase vector in the specimen, depending on the defocus of the objective lens Δf , the spherical aberration coefficient C_s , the electron wavelength λ , and the spatial frequency u :

$$\chi(u) = \pi\Delta f\lambda u^2 + \frac{1}{2}\pi C_s\lambda^3 u^4 \quad (36)$$

Fig. 22 illustrates how the objective lens transfer function and the information in the high-resolution TEM image correlate with each other.

Here, $\sin\chi(u)$ is plotted versus u , the spatial frequency. The area between $u = 0$ and the value for u , where $\sin\chi(u)$ intersects the zero line for the first time, u_{int} , is termed the zero-order *passband*. The first intersection point defines the *resolution limit* of the lens system, being $d_{min} = 1/u_{int}$.

From Eq. 36 it can be seen that $\sin\chi(u)$ is predominantly coupled to the defocus Δf , because the spherical aberration coefficient C_s is a constant (for a given TEM instrument), and the electron wavelength λ can at first approximation also be assumed constant. To some degree, defocusing the objective lens allows for a partial compensation of the effect of the spherical aberration. This was first discovered by Otto Scherzer in 1949 and the defocus value for the optimum resolution, the so-called *Scherzer defocus*, is named after him (Scherzer, 1949). The corresponding resolution limit can then be described as:

$$\Delta f_{Scherzer} = -1.2(C_s\lambda)^{\frac{1}{3}} \text{ giving } d_{min} = 0.66(C_s\lambda^3)^{\frac{1}{4}} \quad (37)$$

In order to be able to apply the weak phase object approximation and to interpret the HRTEM image recorded, the TEM specimen thickness has to be reduced to an absolute minimum, since the WPOA directly correlates to the specimen volume, which is required

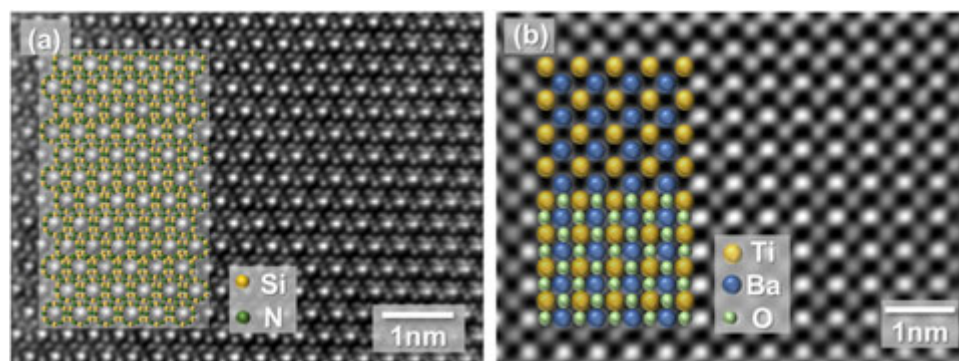


Fig. 23 HRTEM micrographs of (a) β - Si_3N_4 and (b) BaTiO_3 with real atomic positions shown as inset. The simulation revealed that depending on the defocus employed, positive phase contrast occurs in both cases; however, in (a) the bright contrast in the image is related to intrinsic channels in the structure, while in (b) the contrast coincides with the real atomic positions of Ba and Ti. Note that in (b) the oxygen cannot be seen due to its low scattering intensity.

to be very small. Then the contrast in the image, consisting of bright and dark structures, is directly linked to the objective lens transfer function. If $T(u)$ is negative within the zero-order passband, positive image contrast arises. This means that atoms appear black on a bright background, whereas they appear as bright spots on a dark background when $T(u)$ is positive, which creates a negative contrast. If $T(u) = 0$ is valid, no contrast arises for the corresponding value or range of u , even if there are atoms positioned at exactly this spatial frequency. From the value of u , which corresponds to minima and maxima of the lens transfer function due to the oscillating nature of $T(u)$, the atomic distance between bright (or dark) spots in the image can be derived. In the HRTEM images shown in Fig. 22, negative respective positive contrast contributes to the final image (here shown for the spatial frequency u_1).

In order to interpret the observed contrast correctly, especially when questions regarding the location of specific atomic positions are addressed, it is often necessary (as well as helpful) to conduct image simulations of the investigated sample. Fig. 23 shows two examples, where the actual atom positions are indicated and correlated with the bright intensities in the HRTEM images.

To enable a direct comparison between the obtained HRTEM and the simulated image, it is necessary to know the specific experimental parameters such as the defocus value, sample thickness and the spherical aberration of the objective lens (Cowley and Moodie, 1957). In order to model the interaction of electrons and atoms within the specimen, a commonly applied simulation method is the *multi-slice approach* (Stadelmann, 1987; Kirkland, 1998; Koch, 2002). Here, the specimen is virtually cut into thin slices perpendicular to the electron beam and the interaction of the propagating electron wave with each slice, resulting in a phase shift according to the WPOA model, is calculated. Other simulation methods include (1) the Bloch wave approach, (2) the reciprocal or real space approach or (3) the FFT formalism. By using such simulation techniques and knowing the exact atomic positions of the investigated crystal structure, the corresponding image intensities can be calculated and the result can directly be compared to the experimentally observed contrast in the HRTEM micrograph. As shown in Fig. 23(a), the bright spots that give a hexagonal array do not correlate with any atomic position in the β - Si_3N_4 crystal structure, but rather represent channels in the crystal, running parallel to $[001]_{\text{Si}_3\text{N}_4}$ and along the optical axis of the microscope. In contrast, the bright contrast in the HRTEM image of BaTiO_3 in Fig. 23(b) coincides with the actual positions of the Ba and Ti atoms/ions.

Concluding Remarks

We hope that we have succeeded to arouse your interest and at the same time convinced you of the power and versatility of transmission electron microscopy for detailed characterizations of ceramics, glasses and other solid-state materials. Perhaps in the future you will become a fervent advocate and user of this technique and if so, discover that TEM is indeed far more versatile than we were able to illustrate in this short introduction.

References

- Brydson, R., 2001. *Electron Energy-Loss Spectroscopy*. New York: Garland Science.
- Buseck, P.R., Cowley, J.M., Eyring, L., 1988. *High-Resolution Transmission Electron Microscopy*. New York: Oxford University Press.
- Cowley, J.M., Moodie, A.F., 1957. The scattering of electrons by atoms and crystals. I. A new theoretical approach. *Acta Crystallographica* 10 (10), 609–619.
- De Graef, M., 2003. *Introduction to Conventional Transmission Electron Microscopy*. Cambridge: Cambridge University Press.
- Echlin, P., Fiori, C.E., Goldstein, J.I., Joy, D.C., Newbury, D.E., 1986. *Advanced Scanning Electron Microscopy and X-Ray Microanalysis*. New York: Plenum Press.
- Edington, J.W., 1975. *Electron Diffraction in the Electron Microscope*. London: Macmillan.
- Egerton, R.F., 2011. *Electron Energy-Loss Spectroscopy in the Electron Microscope*, third ed. New York: Springer.
- Egerton, R.F., 2016. *Physical Principles of Electron Microscopy: An Introduction to TEM, SEM and AEM*, second ed. Cham: Springer.
- Erni, R., 2015. *Aberration-Corrected Imaging in Transmission Electron Microscopy: An Introduction*, second ed. London: Imperial College Press.

- Flegler, S.L., Heckman Jr., J.W., Klomparens, K.L., 1993. Scanning and Transmission Electron Microscopy: An Introduction. Oxford: Oxford University Press.
- Fultz, B., Howe, J., 2007. Transmission Electron Microscopy and Diffractometry of Materials, fourth ed. Berlin: Springer.
- Goldstein, J.I., Joy, D.C., Romig Jr., A.D., 1986. Principles of Analytical Electron Microscopy. New York: Springer.
- Goldstein, J.I., Newbury, D.E., Michael, J.R., *et al.*, 2017. Scanning Electron Microscopy and X-ray Microanalysis, fourth ed. New York: Springer.
- Goodhew, P.J., Humphreys, J., Beanland, R., 2000. Electron Microscopy and Analysis, third ed. Boca Raton: Taylor & Francis.
- Haider, M., Uhlemann, S., Schwan, E., *et al.*, 1998. Electron microscopy image enhanced. *Nature* 392 (6678), 768–769.
- Hirsch, R.B., Howie, A., Nicholson, R.B., Pashley, D.W., Whelan, M.J., 1965. Electron Microscopy of Thin Crystals. London: Butterworths.
- Hirsch, P.B., 1999. Topics in Electron Diffraction and Microscopy of Materials. Bristol: Institute of Physics Publishing.
- Kirkland, E.J., 1998. Advanced Computing in Electron Microscopy. New York: Springer.
- Koch, C.T., 2002. Determination of Core Structure Periodicity And Point Defect Density Along Dislocations. Arizona State University. [PhD thesis].
- Kumar, C.S.S.R., 2014. Transmission Electron Microscopy Characterization of Nanomaterials. Berlin Heidelberg: Springer Verlag.
- Loretto, M.H., 1994. Electron Beam Analysis of Materials, second ed. London: Chapman & Hall.
- McLaren, A.C., 1991. Transmission Electron Microscopy of Minerals and Rocks. New York: Cambridge University Press.
- Mornioli, J.-P., 2018. Large-Angle Convergent-Beam Electron Diffraction Applications to Crystal Defects. Taylor & Francis Ltd.
- Pennycook, S.J., Nellist, P.D., 2011. Scanning Transmission Electron Microscopy: Imaging and Analysis. New York: Springer Science & Business Media.
- Petzow, G., 1999. Metallographic Etching: Techniques for Metallography, Ceramography, Plastography, second ed. Metals Park, Ohio: American Society for Metals.
- Reed, S.J.B., 2005. Electron Microscopy Analysis and Scanning Electron Microscopy in Geology, second ed. New York: Cambridge University Press.
- Reimer, L., Kohl, H., 2008. Transmission Electron Microscopy: Physics Of Image Formation and Microanalysis, fifth ed. New York: Springer.
- Rose, H., 1990. Outline of a spherically corrected semiaplanatic medium-voltage transmission electron microscope. *Optik* 85, 19–24.
- Scherzer, O., 1947. Sphärische und chromatische Korrektur von Elektronen-Linsen. *Optik* 2, 114–132.
- Scherzer, O., 1949. The theoretical resolution limit of the electron microscope. *Journal of Applied Physics* 20 (1), 20–29.
- Spence, J.C.H., Zuo, J.M., 1992. Electron Microdiffraction. New York: Springer.
- Spence, J.C.H., 2013. High-Resolution Electron Microscopy, fourth ed. New York: Oxford University Press.
- Stadelmann, P.A., 1987. EMS – A software package for electron diffraction analysis and HRTEM image simulation in material science. *Ultramicroscopy* 21 (2), 131–145.
- Thomas, J., Gemming, T., 2013. Analytische Transmissionselektronenmikroskopie: eine Einführung für den Praktiker. Wien: Springer.
- Vincent, R., Midgley, P.A., 1994. Double conical beam-rocking system for measurement of integrated electron diffraction intensities. *Ultramicroscopy* 53 (3), 271–282.
- Williams, D.B., Carter, C.B., 2009. Transmission Electron Microscopy, second ed. Boston: Springer.

High Resolution Analytical Electron Microscopy of Ceramics and Glasses

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Analytical Transmission Electron Microscopy

Analytical Electron Microscopy (AEM) describes the collation of techniques with which spatially resolved spectroscopic information of a sample can be acquired and quantified. In addition to revealing the structure of materials, information about their elemental composition, bonding state and bandstructure can be obtained on a highly spatially resolved level, via spectroscopic methods carried out in the Transmission Electron Microscope (TEM), e.g., Energy Dispersive X-ray spectroscopy (EDX) and Electron Energy Loss Spectroscopy (EELS).

These analytical assessments can be carried out quantitatively alongside TEM and High-Resolution Transmission Electron Microscopy (HRTEM) imaging. Beyond this, AEM can be carried out on an unprecedented temporospatially resolved scale, providing spectroscopic information down to the atomic scale, when carried out in combination with Scanning Transmission Electron Microscopy (STEM), especially in Angular Dark Field (ADF) and High Angle Annular Dark Field (HAADF) imaging mode. HAADF, alone, reveals elemental information about the material, due to the impact of the material's atomic number on the elastic scattering intensity and direction of the traversing electron beam. This then reveals the materials properties in terms of chemical composition. Fig. 1(a) shows a sketch of the principal interactions of the electron beam with the TEM specimen, with emissions utilized for EDX, EELS and HAADF detection indicated by red, blue and green arrows, respectively.

After its transmission through the sample and having passed through the annular (HAADF and ADF) detectors, the undeviated (not elastically scattered) e-beam, a great part of which has lost energy due to inelastic scattering events, enters a magnetic 90° prism (Fig. 1(b)), which is part of the electron energy loss spectrometer. The magnetic field of the prism bends the electron beam to a larger or smaller extent, according to the larger or smaller energy losses inflicted by the sample. Monitoring the intensity of the outcoming beam at varying beam directions along the axis across a detector, provides a display of these intensities as a function of energy loss, i.e., resulting in the acquisition of an energy loss spectrum (right most feature in Fig. 1(b)).

In this chapter, the fundamental aspects and recent applications of STEM and HAADF, especially on the highly spatially resolved level, as well as of EDX and EELS will be addressed.

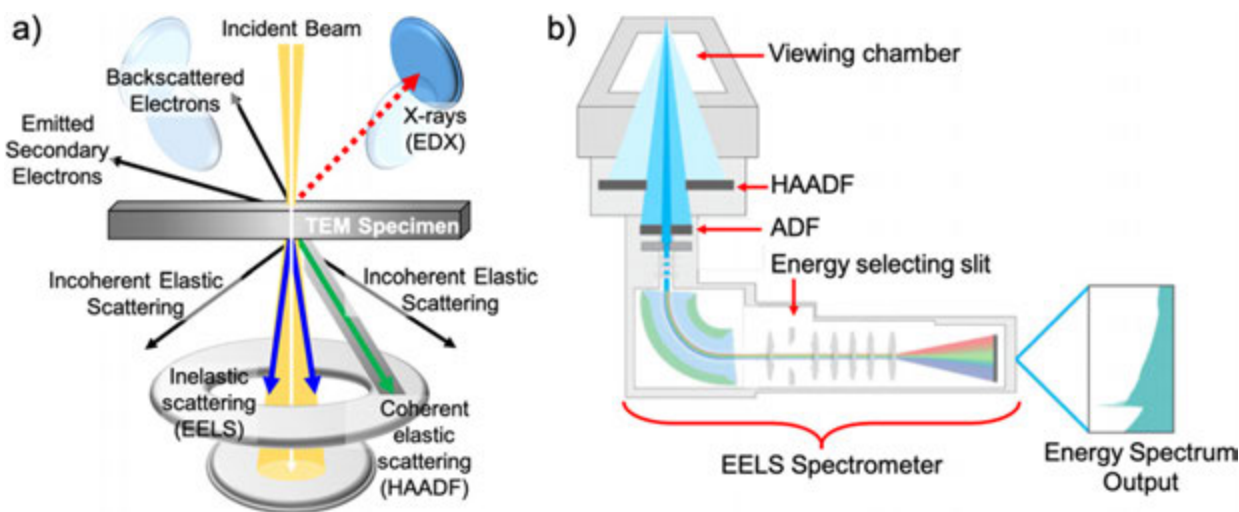


Fig. 1 (a) This schematic details some of the scattering events that happen when an electron beam interacts with a TEM specimen. The scattering events that contribute to AEM (and focused on in this chapter) are X-rays (red) which are captured by a (usually) side-entry EDX detector (four quadrant detectors are available in newer instrument setups and shown here gray-ed out), coherent elastic scattering (green) at high angles and captured by a high angle annular detector used for HAADF-STEM imaging, and inelastic scattering (blue) which follows the trajectory of the undeviated beam, passing through the annular HAADF detector to (b) an EELS spectrometer. Schematics amended from reference. Bluescientific, 2020. Gatan Advanced STEM Detectors. Available at: <https://www.blue-scientific.com/nordic-products/gatan/advanced-stem-detectors/> (accessed 23.11.2020). Gatan, 2020b. What is EELS – EELS.info. Available at: <https://eels.info/about/overview> (accessed 4.12.2020).

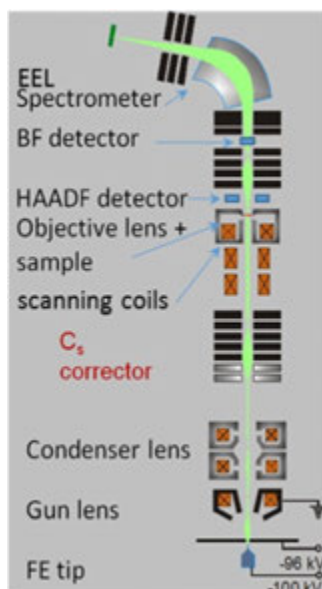


Fig. 2 An illustration showing the instrumental design of the dedicated STEM. Unlike the conventional TEM with STEM capabilities, the electron source of a dedicated STEM is positioned at the bottom. Reproduced from Bangert, U., Gass, M., Zan, R., Pan, C.T., 2011. Scanning transmission electron microscopy and spectroscopy of suspended graphene. In: Mikhailov, S. (Ed.), *Physics and Applications of Graphene – Experiments*. Rijeka: IntechOpen pp. 377–408.

Principles of Scanning Transmission Electron Microscopy (STEM)

STEM can be carried out in TEM instruments with scanning probe capacities, or in an instrument, which is designed for TEM measurements to be carried out solely in scanning mode (known as a dedicated STEM), a sketch of which is shown in Fig. 2. Due to their specific layout STEM instruments can only be operated in scanning mode (for imaging and analytical measurements). This design provides high operational stability, because the instrument does not need to be switched between imaging and scanning mode, which often requires re-alignment of imaging and spectroscopy parameters. In STEM mode a narrow beam (of diameter < 1 nm) is scanned across a sample in a rastering fashion. Modern aberration corrected, dedicated STEM instruments produce a beam diameter of down to $1 \text{ \AA}$ owing to a probe corrector, which reduces the high order aberrations (Brydson, 2011). The objective lens recombines the transmitted, primary electrons from every point scanned by the probe to a fixed region in the back focal plane, where an electron detector captures them. STEM imaging can typically be carried out using various modes depending on the collection angle of the transmitted beam and the available detectors. In the High Angle Annular Dark Field (HAADF) mode the HAADF imaging detector is used (see Figs. 1(a) and 2) (Bangert *et al.*, 2011). STEM can also be carried out in Bright Field (BF) mode, where the intensity of the undeviated beam (Fig. 1(a)) is monitored at each scan point. Imaging in scanning mode results in a 2D array of pixel intensities, which, when displayed altogether, constitute an image contrast map. The BF-STEM mode can be correlated with the conventional parallel beam TEM mode. BF-STEM contrast provides a direct comparison with, and opposite to, the Z-contrast in HAADF-STEM imaging, the latter revealing the atomic number of the material.

In HAADF-STEM imaging mode electrons that have been elastically scattered into high angles (sketch in Fig. 1(a)) are detected with annular detectors (a.k.a., doughnut detectors), therefore excluding the undeviated beam, and also the electrons inelastically scattered into small angles whose function will be explained later with respect to EELS. HAADF imaging in scanning mode can be carried out at *atomic resolution*, revealing the chemical nature of individual atoms, because of the relationship between the scattering intensity (I) and the atomic number (Z), as $I \propto Z^2$, (more accurately $I \propto Z^{1.7}$) (Williams and Carter, 1996; Egerton, 2011). The contrast in atomic resolution BF and HAADF-STEM images is in reverse, i.e., in BF, positions of atoms appear dark since the electron beam is scattered outside the collecting aperture, whereas in HAADF-STEM the atomic positions appear bright, since the electrons reaching the high angle angular detector are scattered into higher angles by the atoms, thus here the dark areas indicate absence of electron scattering.

Fig. 3(a) and (b) show atomic resolution BF-STEM and HAADF-STEM micrographs, respectively, of lanthanum calcium cobalt oxide (LCCO) perovskite with the electron beam entering the crystal along the $[110]$ direction. The images display $[110]$ projections of the crystal (see the unit cell in Fig. 3(c)), showing an example of the reverse contrast that distinguishes BF from HAADF-STEM images. Fig. 3(d) is an enlargement of the area in the red frame indicated in Fig. 3(b), where the atomic columns projected along the $[110]$ direction of the electron beam appear as bright dots. The model of the unit cell with its zone axes and different color elements is shown in Fig. 3(c). The unit cells viewed along the $[110]$ direction (the direction of the incoming electron beam) is overlaid on the atomic columns revealed in the image in Fig. 3(d). According to the contrast, which scales with the Z -number of the elements as $Z^{1.7}$, the columns containing La and Ca, additionally interlinked with O, when projected along the $[110]$ direction

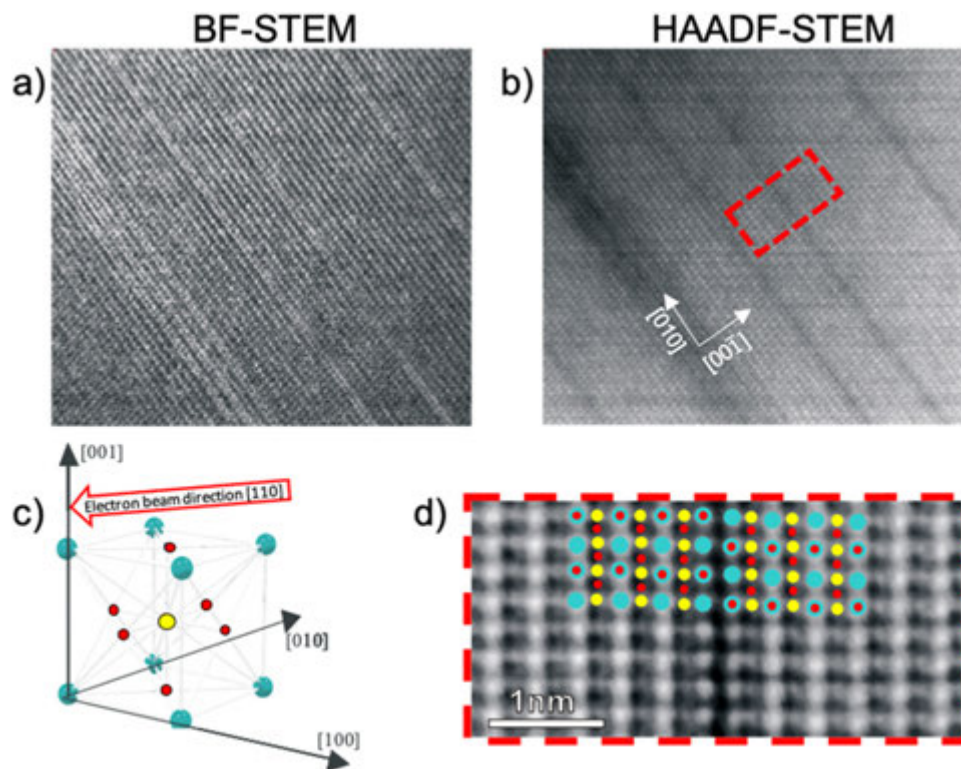


Fig. 3 A direct comparison of (a) BF-STEM and (b) HAADF-STEM imaging of the perovskite material lanthanum calcium cobalt oxide (LCCO). (c) the unit cell of the material is shown (Co – yellow, Ca/La – blue, O – red) with the electron beam entering along the [110] direction. (d) A higher magnified image of the area indicated by the red box in (b) with the unit cell model overlaid in the [110] plane. Amended from reference Bangert, U., Falke, U., Weidenkaff, A., 2006. Nature of domains in lanthanum calcium cobaltite perovskite revealed by atomic resolution Z-contrast and electron energy loss spectroscopy. *Materials Science and Engineering: B* 133, 30–36.

(red dots on blue in Fig. 3(d)), are the brightest, followed by the less bright contrast of the Co columns (yellow dots), and the columns containing only O are dark (red dots). The bright and dark boundary in Fig. 3(a) and (b), respectively, can be seen at the higher resolution in the HAADF-STEM micrograph in Fig. 3(d), to be a boundary between different crystal domains.

In HRTEM, apart from the regular contrast variations on the Ångström scale representing atomic columns, contrast variations on the larger scale, which impact on, and change the HRTEM contrast, can also be seen (Fig. 4). These contrast changes arise from thickness variations as well as from diffraction effects, in places, where the TEM sample is slightly bent, leading to deviations from the exact zone axis orientation. This contrasts with (and compliments) HAADF-STEM, where intensities are due to the elemental nature of the atoms in the material.

In Fig. 4, a selection of HRTEM micrographs is displayed (the HRTEM technique is explained in the previous chapter), showing the nanostructure of grain boundaries and intergrowth in layered, machinable and electrically conductive Ti_2AlC and Ti_3AlC_2 ceramics (Wang and Zhou, 2010). HRTEM allows clear identification of the misorientation of the [001] plane in Fig. 4(a). At a higher magnification the intergrowth between Ti_3AlC_2 and Ti_2AlC can be identified by simply referring to the unit cell configuration and noting, in this case, that the Ti layers are separated by three Al layers in Ti_3AlC_2 and by two Al layers in Ti_2AlC . Another example of ceramic intergrowth of TiC can also be identified between two domains of Ti_2AlC in Fig. 4(c).

Electro-magnetic lenses used in electron microscopes are inherently imperfect compared to glass lenses in optical microscopes, leading to, e.g., spherical and chromatic aberrations. In order to achieve atomic resolution, as shown in the images presented in this section, these aberrations need to be corrected. Explained in simplistic terms, this can be achieved by adding lenses with “inverse” imperfections after, e.g., the objective lens, acting as an image corrector, or after the condenser lens, acting as probe corrector. The electron beam has furthermore, an energy spread, which has consequences, especially for analytical and spectroscopic investigations, and can be corrected by addition of a monochromator (after the electron gun). Modern TEMs have image and probe correctors as well as a monochromator. Using aberration corrected and monochromated TEM, information of the atomic structure can be obtained down to the sub-atomic, i.e., Ångström scale, revealing, shifts in atomic positions, which can lead to atomic dipole constellations, e.g., in ferro-electric materials, which are sought after for applications in next generation IT components, e.g., capacitors, mobile nano-switches and nano-sensors (Chen et al., 2017; Zhao et al., 2019; Guan et al., 2020).

To achieve reliable atomic resolution HAADF-STEM images, the benefit of minimizing and eliminating high order aberrations can be seen. Although atomic resolution TEM and STEM observations reveal *qualitative* information about the atomic structure of

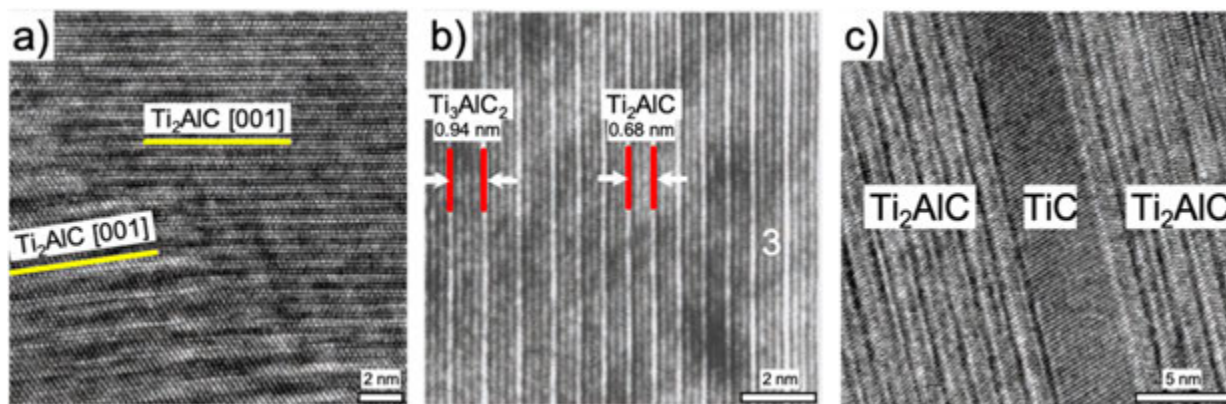


Fig. 4 HRTEM images of (a) a grain boundary in Ti_2AlC revealing misorientation of the [001] plane, (b) intergrowth of Ti_2AlC and Ti_3AlC_2 , confirming, by the distance between the intergrowth boundaries, the existence of two Al layers in Ti_2AlC and 3 Al layers in Ti_3AlC_2 and (c) intergrowth of TiC sandwiched between Ti_2AlC . Amended from Wang, X.H., Zhou, Y.C., 2010. Layered machinable and electrically conductive Ti_2AlC and Ti_3AlC_2 ceramics: A review. *Journal of Materials Science & Technology* 26, 385–416.

materials, in order to confirm this *quantitatively* and to ensure appropriate interpretation of HRTEM and HRSTEM images, as well as to prove the agreement with theoretical models and predictions, image simulations are required.

Fig. 5 demonstrates how simulations of HAADF-STEM images can supplement and/or verify observations made in experimental images. Open source simulation software such as Dr. Probe can be used as a method to verify the observations in experimental images of known materials (Barthel, 2018). **Fig. 5(a)** displays a micrograph of a monolayer of MoS_2 , doped with Se ions via an experimental technique known as ion-implantation. Ion implantation is an indispensable method, employed since several decades, to dope semiconductor materials for device manufacture for IT, and is applied here to controllably dope monolayer materials to tailor them for nano-opto-electronic applications, in this case to achieve single photon emitters.

The enlarged overlaid image of the area in the red frame shows different types of imperfections in the MoS_2 lattice. These are indicated by the colored arrows, i.e., red – a Se atom in a chalcogen position, blue – an unidentified foreign atom in a Mo position, green – an unidentified foreign adatom and yellow – a sulfur divacancy. The molecular model of MoS_2 is overlaid, with S atoms (two S atoms overlaid) in yellow, Mo atoms in blue and Se-implants in red. The Z^2 dependency of the contrast of elements with the corresponding atomic numbers is distinctive when scrutinizing the materials in HAADF-STEM. The above example is a good indication of how clear the distinction can be made by the human eye; however, simulation techniques are used to confirm this. In **Fig. 5(b)**, each of the atomic constellations in the color-framed boxes agrees quantitatively with the respective (same colored

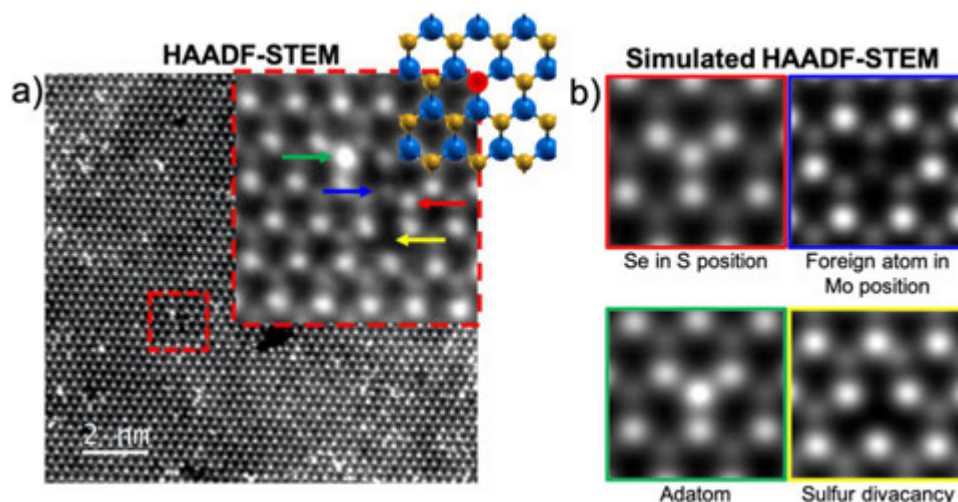


Fig. 5 (a) a HAADF-STEM micrograph of MoS_2 after undergoing ion implantation with Se. The area in the red box is shown at higher magnification in the inset with the molecular model overlaid. The red, blue, green and yellow arrows correspond to imperfections in the MoS_2 lattice. (b) The imperfections are displayed individually as simulated HAADF-STEM micrographs (enabled by Dr. Probe simulation software), with the red, blue, green and yellow boxes corresponding to the same color arrows in (a). The images are original work from the authors' research group, presented at the Nanotech2019 conference. Enabled by Barthel, J., 2018. Dr. Probe: A software for high-resolution STEM image simulation. *Ultramicroscopy* 193, 1–11.

arrow) arrangements in the HAADF-STEM inset in Fig. 5(a) and provides proof of the information extracted from the experimental HAADF-STEM image, regarding atomic structure and elemental constellations.

Experimental atomic resolution images can be refined to reduce the signal-to-noise ratio by using the Fast Fourier Transform (FFT) technique (De Jong *et al.*, 1989). In the FFT map, the image, which contains regular structures in direct image space, is transformed into a diffraction pattern in reciprocal space. In the FFT map, “masks” are then overlaid on the diffraction spots, eliminating other intensities in the FFT, i.e., arising from noise or other irrelevant diffraction spots, to identify specific lattice projections. When inversely transforming the “masked” FFT, a sharpened, contrast enhanced image is acquired.

Fig. 6 shows an example of how FFT masking can filter a noisy HAADF-STEM micrograph to provide a clearer representation of what atom configurations are expected in Cr_2AlC ceramics when imaging along the $\langle 1\bar{2}10 \rangle$ direction (Fig. 6(b)), resulting in atomic column projections as displayed in the model unit cell in Fig. 6(a). It can be seen that two Cr layers are intercalated and mirrored by Al atomic sheets. The atomic positions of the Cr and Al atomic columns are clearly identified in comparison to the unit cell. An intensity profile is extracted (the plot is shown in the inset in Fig. 6(b)) to show the distinction between the Cr and Al atoms in the lattice via their HAADF intensities, further confirming the stacking sequence of Cr and Al.

In this example the microscope software suite Digital Micrograph (more recent versions are called Gatan Microscopy Suite, a.k.a., GMS3) is used to filter out the noise by using the FFT generated from the image in Fig. 6(b). The filtered image in Fig. 6(c) is presented in a colored schematic related to the image intensities (with brightest intensities in yellow and darkest intensities in blue, according to the temperature scale) to enable a clearer identification of the atomic columns. Fig. 6(c) (like the intensity profile plot in Fig. 6(b)) shows the intensity fluctuations with two strongly intense atomic rows and one of weak intensity, further indicating the layer stacking sequence of Cr and Al, and moreover, the atomic number difference between the *M* and *A* elements in the MAX phases. The atomic number distinction between Al and Cr is relatively large, which allows HAADF-STEM to be an efficient method of identifying the atomic positions and hence stacking patterns of layered ternary ceramics. Grain boundary cores, and thus grain boundary structures have crucial influence on the fracture properties of ceramics. Fig. 7 reveals the atomic-bond breaking path within a dopant-segregated Al_2O_3 grain boundary core, via HAADF-STEM atomic-scale observations of the crack tip interface (Fig. 7(a)), introduced by in situ nanoindentation experiments inside a TEM. The HAADF-STEM image shows an example of the unfractured (blue box), crack tip (yellow box) and fractured (red box) areas in the same image. The unfractured area clearly shows distinction between the atomic columns whereas the crack tip and fractured areas display increased noise and decreased intensity distinction between the atomic columns. The observations show that the atomic fracture path occurs to produce less coordination-deficient oxygen polyhedra of dopant cations, which is also supported by using simulations, i.e., first-principles calculations (Kondo *et al.*, 2019). The fracture paths are overlaid on the material unit cell and indicated by the dashed lines in Fig. 7(b). The findings indicate that the atomic coordination geometry at the grain boundary core affect the fracture process. This is directly compared with the HAADF-STEM image in Fig. 7(c) where the zig-zag fracture geometry (Fig. 7(c) – top, from the schematics in Fig. 7(b) – bottom) and the straight Zr-Zr fracture (Fig. 7(c) – bottom, from the schematics in Fig. 7(b) – top) is overlaid confirming that both have taken place. The observations indicate that the local coordination geometry at the grain boundary core has a strong influence on the selection of the preferential atomic fracture path.

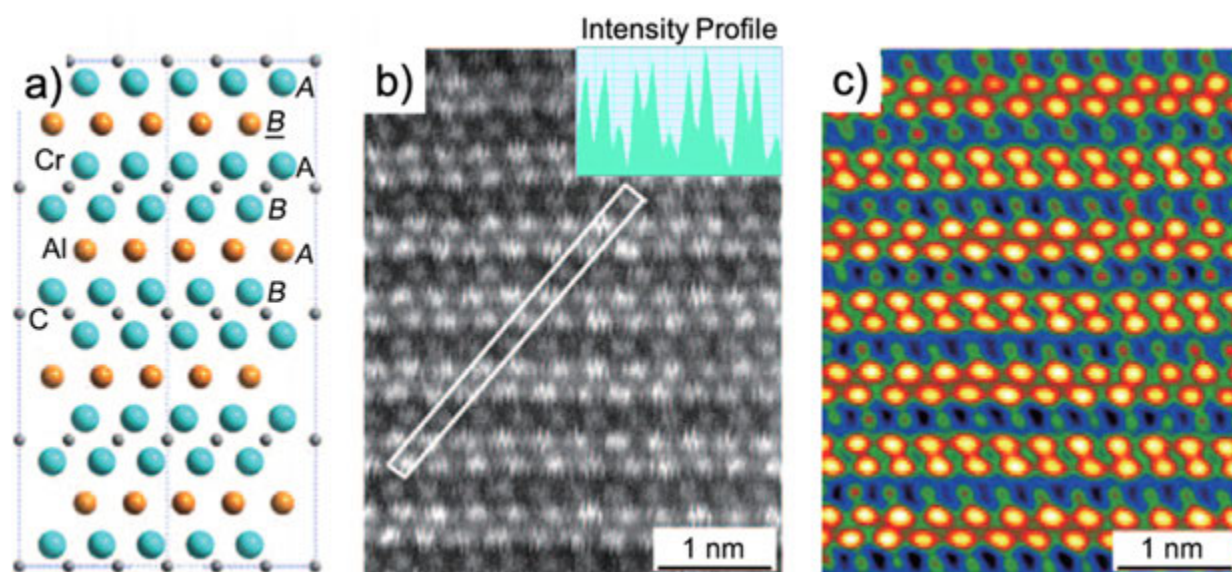


Fig. 6 (a) Unit cell configuration in the $[1\bar{2}10]$ projection, of Cr_2AlC (Cr – blue, Al – orange, C – gray), (b) HAADF-STEM micrograph of Cr_2AlC imaged along $\langle 11\bar{2}0 \rangle$ with an intensity profile taken along the white rectangle and displayed in the inset, (c) FFT filtered image of (b) with intensity dependent temperature-scale colored overlay to more clearly reveal the atomic columns. Amended from References Lin, Z., Zhuo, M., Zhou, Y., Li, M., Wang, J., 2006. Atomic scale characterization of layered ternary Cr_2AlC ceramic. *Journal of Applied Physics* 99, 076109. Lin, Z., Li, M., Zhou, Y., 2007. TEM investigations on layered ternary ceramics. *Journal of Materials Science and Technology* 23, 145–163.

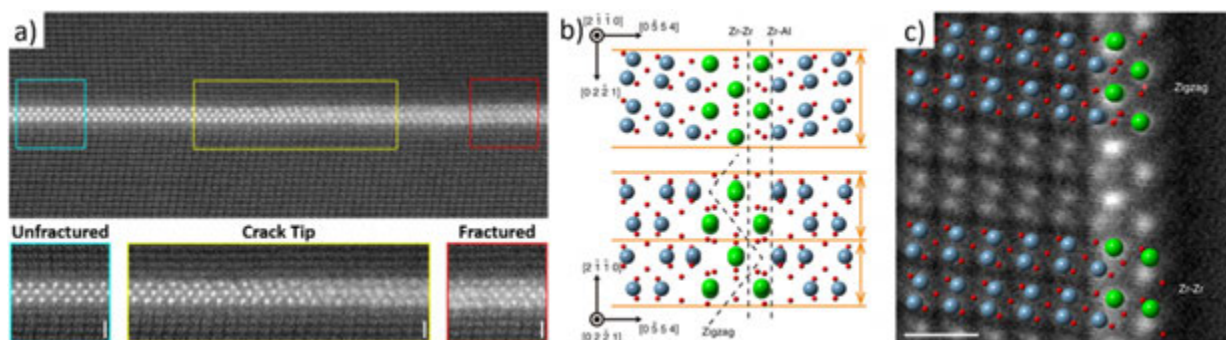


Fig. 7 After in situ nanoindentation, a Zr doped Al_2O_3 grain boundary was imaged using HAADF-STEM to observe the atomic-scale fracture path; (a) HAADF-STEM micrograph with three highlighted areas identifying the unfractured, crack tip and fractured areas, (b) fracture path models calculated based on cleavage energies showing the three potential fracture paths, Zigzag, Zr-Zr and Zr-Al, (c) a HAADF-STEM image of the fracture surface with the structural models superimposed, identifying that the Zigzag and Zr-Zr fracture paths took place. The scale bars are 0.5 nm. Figures are amended from the reference Kondo, S., Ishihara, A., Tochigi, E., Shibata, N., Ikuhara, Y., 2019. Direct observation of atomic-scale fracture path within ceramic grain boundary core. *Nature Communications* 10, 2112.

Since HAADF Z-contrast depends roughly on the square of the atomic number of the element imaged, it is very well suited to reveal heavy elements and compare these and their positions to elements of different intensities in a compound. However, it is impossible to reveal light elements, e.g., O, N, C using STEM (inclusive of BF and HAADF) alone, due to their weak contrast and susceptibility to irreversible damage from the electron beam amongst other difficulties associated with the high current used for STEM imaging techniques. Therefore, additional imaging techniques can be employed to allow undestructive imaging of light elements, such as the STEM imaging technique, integrated Differential Phase Contrast (iDPC).

Integrated Differential Phase Contrast (iDPC)

Differential Phase Contrast (DPC) imaging is a revolutionary STEM imaging method to visualize an electromagnetic field in a specimen by measuring the deflection of an electron beam due to the field at each beam-scan point. STEM images are collected on pixelated quadrant ring detectors. DPC images are then formed by subtracting intensities on the detector segments diametrically opposed with respect to the optical axis. This converts beam deflection, which relates closely to the gradient of the phase change through the specimen, into image contrast. This relationship arises from the fact that the deflection is caused by the sample's electric field, which is proportional to the potential and the phase differential, i.e., $E \propto \Delta V \propto \Delta\Phi$. So, the subtraction of the signal from opposite quadrants represents the gradient of the potential and phase differential: $(\Delta V_1 - \Delta V_2) \propto (\Delta\Phi_1 - \Delta\Phi_2)$. DPC imaging has been utilized for observations of micrometer to nanometer scale magnetic domains. In recent years, this imaging method has been applied to the analysis of electric fields, and the electric field at the atomic scale has been observed using a transmission electron microscope equipped with a Cs corrector. An iDPC-STEM image, then represents the *scalar* electrostatic potential field of

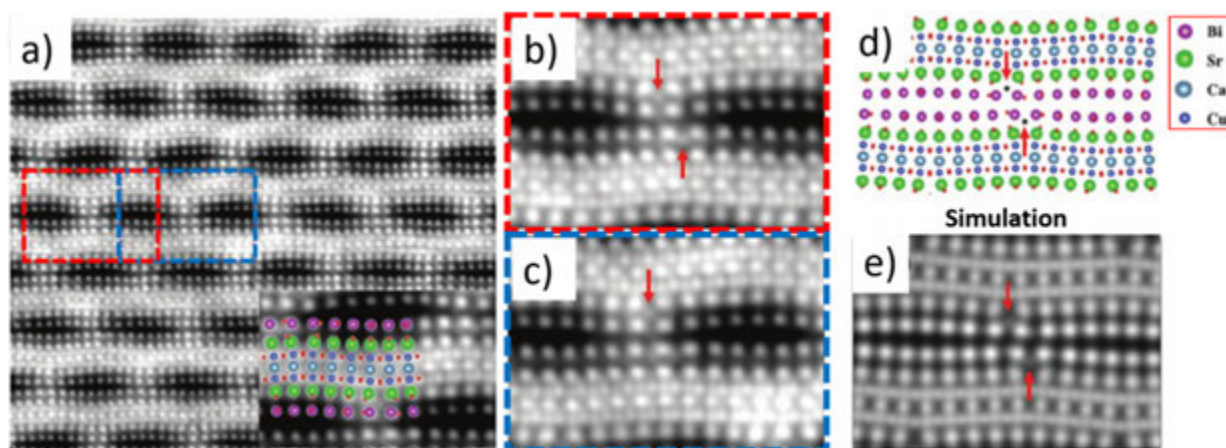


Fig. 8 (a) iDPC-STEM micrograph of a bismuth based cuprate material; the inset shows an enlarged area of (a) with the atomic model superimposed showing the oxygen positions (red dots) in the CuO_2 planes, (b) and (c) correspond to the red and blue boxes (respectively) from (a) identifying the position of the oxygen dopants. (d) The atomic model of the cuprate is shown with the oxygen dopants (black) and (e) the HAADF-STEM simulation including the positions of oxygen dopants, thus verifying the observations on the experimental iDPC-STEM. Amended from reference Song, D., Zhang, X., Lian, C., et al., 2019. Visualization of dopant oxygen atoms in a $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ superconductor. *Advanced Functional Materials* 29, 1903843.

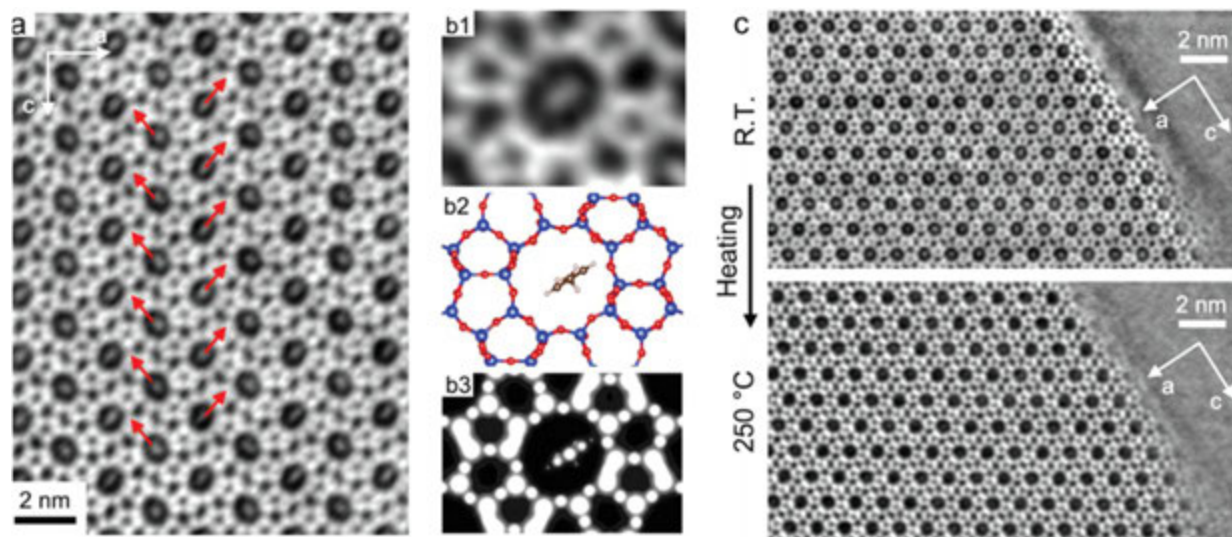


Fig. 9 iDPC-STEM imaging of a zeolite, ZSM-5. (a) After adsorption of paraxylene, the small hydrocarbons can be seen in the pores of the zeolite structure. (b1) shows an enlarged area of a pore from (a), (b2) shows the calculated structural model of ZSM-5 considering the paraxylene introduction, (b3) shows the corresponding electrostatic potential. (c) To show the desorption and study the adaption of the structure, the sample underwent heating up to 250°C, after which the paraxylene has desorbed from the zeolite material. Reproduced from Shen, B., Chen, X., Cai, D., *et al.*, 2020. Atomic spatial and temporal imaging of local structures and light elements inside zeolite frameworks. *Advanced Materials* 32, 1906103.

the sample, obtained by the 2D integration of the vector image acquired by DPC-STEM, (consisting of two components: DPCx and DPCy), representing the *vector* electric field of the sample.

Therefore by using the iDPC, direct imaging of the phase of the “transmission function” of the material is possible for non-magnetic samples, even resulting in direct interpretation of the electrostatic potential from the images (Yücelen *et al.*, 2018; Lazić *et al.*, 2016). A notable capability of this relatively complex iDPC-STEM technique is the ability to measure piezoelectric polarization fields (Lohr *et al.*, 2012) and to allow atomic resolution imaging of light and heavy elements together with high signal-to-noise ratios at low beam currents, i.e., at $<40 \text{ e}^- \cdot \text{\AA}^{-2}$, which is 2–3 orders of magnitude lower than typical electron doses used in STEM. The relationship between the intensity and the atomic number is (almost) directly proportional, in contrast to the $I \propto Z^{1.7}$ relationship in HAADF-STEM (Shen *et al.*, 2020; Yücelen *et al.*, 2018). For materials such as layered cuprates, where identification of the excess oxygen atoms is crucial in revealing the facilitation of hole doping, iDPC-STEM can accurately determine their positions within the planes for better characterization of these promising superconductive materials.

Fig. 8 directly visualizes the incommensurate atomic structure and (excess) dopant oxygen atom locations in a $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ cuprate (Fig. 8(a)) (Song *et al.*, 2019). The unit cell model of the material is overlaid (inset in Fig. 8(a)) which accurately locates the oxygen positions, which would be impossible to identify with conventional (BF) and HAADF STEM. Specific areas from Fig. 8(a) are shown in Fig. 8(b) and (c) to indicate the positions of the dopant oxygen atoms (indicated by red arrows). Simulated iDPC-STEM was conducted to ascertain the effects of oxygen dopants on the local atomic configuration and the electronic structure (Fig. 8(e)). Local strain analysis explains the favorable positions for dopant oxygen between the BiO and SrO planes, consistent with the experimental iDPC-STEM images. The dopant oxygen atoms (causing hole doping of the CuO_2 planes) are accommodated by shifting the surrounding atoms, especially the oxygen atoms, thus aggravating the local distortions.

For complex lattice structures in porous zeolites, iDPC-STEM can provide significant information to aid their applications in catalysis and energy storage. One such zeolite, ZSM-5, consists of a largely hydrocarbon aromatic framework forming channels that “will influence the sorption and diffusion of small molecules” (Shen *et al.*, 2020). Fig. 9 shows atomic resolution iDPC-STEM images of the local structures of the zeolite framework in the [010] projection upon adsorption of paraxylenes (PXs), which are similar in size to the hydrocarbon pools. iDPC-STEM reveals the low Z element containing paraxylenes in the ZSM framework, verified by the calculated structural model (Fig. 9(b2)) and electrostatic potential (Fig. 9(b3)). In an in situ experiment the PXs were desorbed from the ZSM-5 framework by heating the material from room temperature to 250°C, and the same area (before and after heating) was imaged. This is the first time that small aromatics and their behaviors were observed in (S)TEMs, after substantially reducing the electron beam current, which led to nearly non-destructive imaging of the ZSM-5 framework and the adsorbed PXs. iDPC-STEM helped reveal the local structures of ZSM-5 due to the high-contrast imaging of light O elements during in situ heating experiments, by which the temporal changes of channel geometry could be monitored. These results help the understanding of the surface terminations and interfaces of nanosized ZSM-5 catalysts and the investigation of the host-guest interactions in the frameworks, which are of great significance for the study of the physical and chemical properties of reactants and products during diverse catalytic reactions.

A variety of STEM imaging techniques and supplementary simulation methods have been summarized to exemplify their potential in revealing atomic resolution structural information on ceramic and glass materials. In the absence of elemental

analysis, simulation techniques can be conducted to compound the imaging observations. Whilst HAADF-STEM requires high beam current, iDPC-STEM can be used to image lighter elements alongside higher elements using low dose conditions and hence retain the structural integrity of a beam-sensitive sample. Alongside and beyond obtaining structural composition via STEM imaging, direct quantitative analysis can be carried out via EDX and EELS in the TEM, providing information on elemental arrangement in the samples on the atomic level.

Principles of Energy Dispersive X-Ray (EDX) spectroscopy

In EDX spectroscopy, signals from X-rays indicated as red dotted arrow in Fig. 1(a), are collected. Fig. 10(a) shows a schematic of the EDX set up in the TEM with respect to the specimen. Apart from the characteristic fluorescence peaks of the elements in the sample, Coherent Bremsstrahlung (CB) peaks (or breaking radiation as directly translated from German) are part of the EDX spectrum in Fig. 10(b). These CB peaks are generated as a result of Coulomb interactions between electrons and regularly spaced nuclei in thin crystalline specimen.

Conventional EDX detector setups allow for side-entry detectors close to the TEM specimen. To increase the signal reaching the detector a common solution is to tilt the sample towards the EDX detector. In more novel instruments, four-quadrant detectors are available (see Fig. 1(a)) and integrated in the objective lens system to improve the signal to noise ratio.

For quantification of EDX measurements, commercial software packages are available, which enable extraction and quantification of the intensities of X-ray peaks, arising from the relaxation of electrons into lower energy orbitals (after excitation into higher orbitals), i.e., the K, L, M, N and O shells of the chemical elements in the sample, and assigning the respective elements by comparison with established standard spectra (e.g., from Cu or Si). With this software, spectra are automatically saved and corrected with respect to effects impacting on these (e.g., geometry factors, and detector dead times), and are quantified by using the K-factors of the respective elements ($K = \text{number of atoms of the element/measured X-ray counts}$), which need to be known. Alternatively, registered relative K-factors, e.g., K_{Asi} (established by relating the K-factor of element A (i.e., K_A) to that of a standard element, e.g., Si (i.e., K_{Si})) can be used. For a sample with two elements, the concentrations of these elements can be found by applying the equation, $C_A/C_B = (K_{\text{Asi}}/K_{\text{Bsi}}) I_A/I_B$, where $C_A + C_B = 1$. Here C_A and C_B are the relative concentrations of elements A and B and I_A and I_B , their EDX intensities (i.e., the measured EDX counts). This process can also be employed in quantification of samples containing a number of unknown elements.

In order to obtain elemental maps of desired sample areas, EDX must be carried out in STEM imaging mode, where at each scan (pixel) position, an EDX spectrum is taken. Fig. 11 shows results of elemental mapping of a metal on graphene with near atomic sensitivity and resolution (images of Fig. 11 were obtained by the group of the author).

Fig. 11(a) is an atomic resolution HAADF-STEM image of graphene, with the brighter white dots (higher Z) representing Ti atoms at the edge of a hole (black area) in the graphene sheet. The light gray patches are C and O contamination with additional aggregates of Ti atoms. This is supported by the EDX map in Fig. 11(b), showing a uniform distribution of the C atoms in the graphene monolayer sheet as thinly spread light blue dots. Enhancement in the density of C atoms (light blue contrast) can be seen in the typical carbon contamination patches (Fig. 11(a) and (b) – top left), which appear brighter in the HAADF-STEM image, as they enhance the thickness and thus the number of C atoms in the layer, which also contain O atom clusters (dark blue) and Ti atoms (red). A couple of red dots (Ti atoms) can also be seen near the edge of the hole in Fig. 11(b), which correspond to the white dots in Fig. 11(a). Although Fig. 11(a) and (b) are

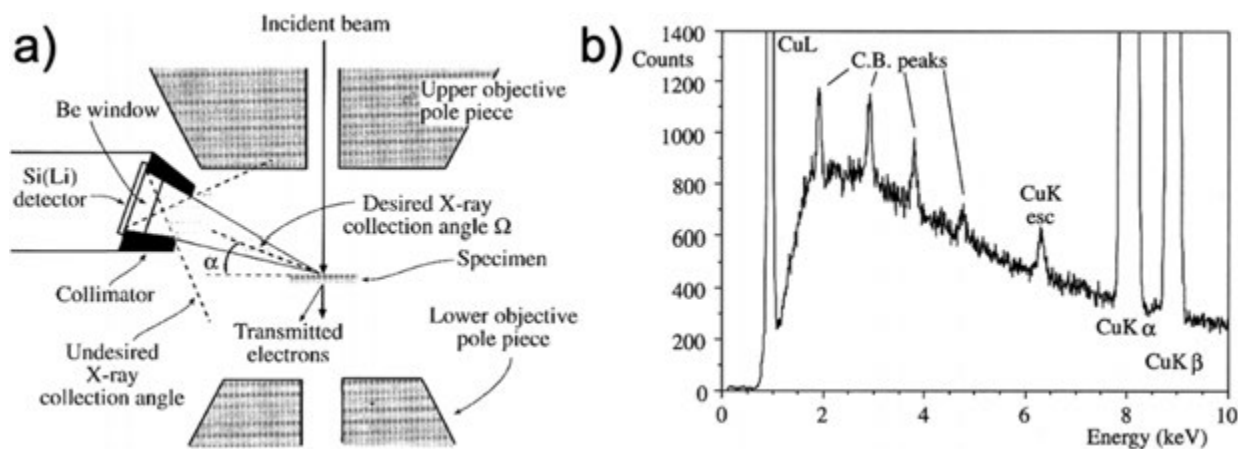


Fig. 10 (a) Schematic of the interface between the EDX detector and the Analytical Electron Microscopy (AEM) stage, showing how the detector can ‘see’ undesired X-rays other than from the specimen. The desired collection angle Ω , and the “take-off” angle α , i.e., the angle between the central beam direction towards the detector and its projection onto the specimen surface, are also shown. (b) Features an X-ray spectrum of copper (Cu), showing the characteristic fluorescence peaks (CuL , $\text{CuK}\alpha$, $\text{CuK}\beta$) of elements present in the sample, as well as Coherent Bremsstrahlung (CB) peaks. Reproduced from Williams, D.B., Carter, C.B., 1996. Transmission Electron Microscopy. Boston, MA: Springer US.

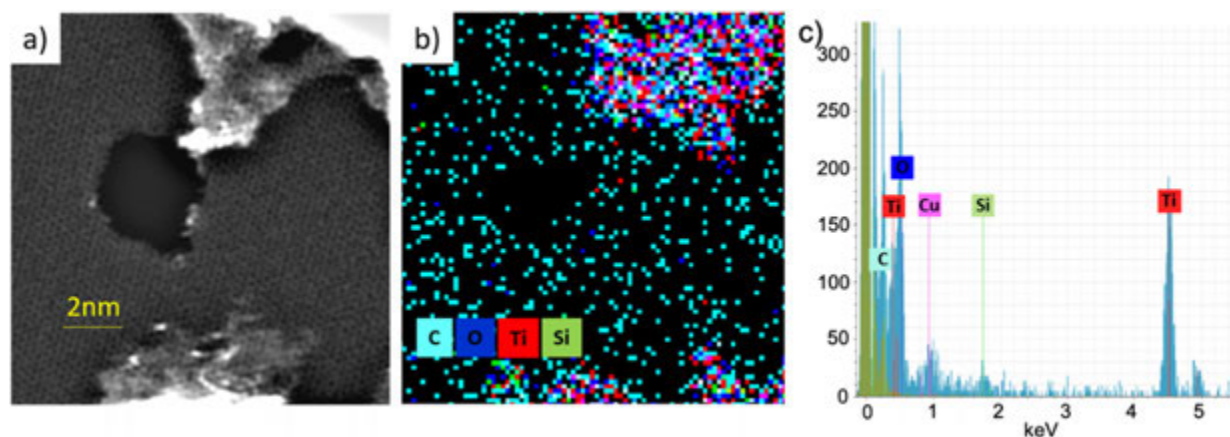


Fig. 11 (a) High resolution HAADF-STEM image of graphene, with Ti atom deposition (white dots and clumps). The black area is a hole in the graphene sheet and the light gray patches are contamination. (b) EDX map of the image in (a), showing the different elements in corresponding colors. (c) EDX spectrum taken over the entire area in (a) detailing the detection of C, O, Ti, Cu and Si in the sample. Images are original work from the research group of the author and also in reference. Reproduced from Withers, P.J., 2012. 3-D materials characterization over a range of time and length scales. *Advanced Materials & Processes* 170, 28–32.

of the same area, the reason why there appear to be slight changes in the topography is that the measurements were taken in a time sequence of several seconds and the sample might have drifted in that time. Furthermore, electron beam interaction might have caused slight changes, on the sub nm-scale, in the contamination distribution at the hole's edge, accounting for the minute differences in the topography in Fig. 11(a) and (b). Fig. 11(c) is an EDX spectrum taken over the entire area in 11a, giving proof of the elements seen in the EDX map in Fig. 11(b). EDX spectra as in Fig. 11(c), which do not require high resolution mapping but are needed to confirm the existence or presence of certain elements, can be conducted in conventional TEM mode as a simple and quick method of verifying elemental composition.

Another example of how EDX mapping can reveal detailed elemental information about a sample is shown in Fig. 12, where particle precipitation in metal doped CeO_2 is studied. In situ thermal treatment and ion irradiation techniques are used to emulate the irradiation of fuels, in order to predict the fuel performance of the material and potentially improve fuel design and operations (Jiang *et al.*, 2019). It was previously found that metallic particles formed in oxide fuels, e.g., UO_2 , during neutron irradiation,

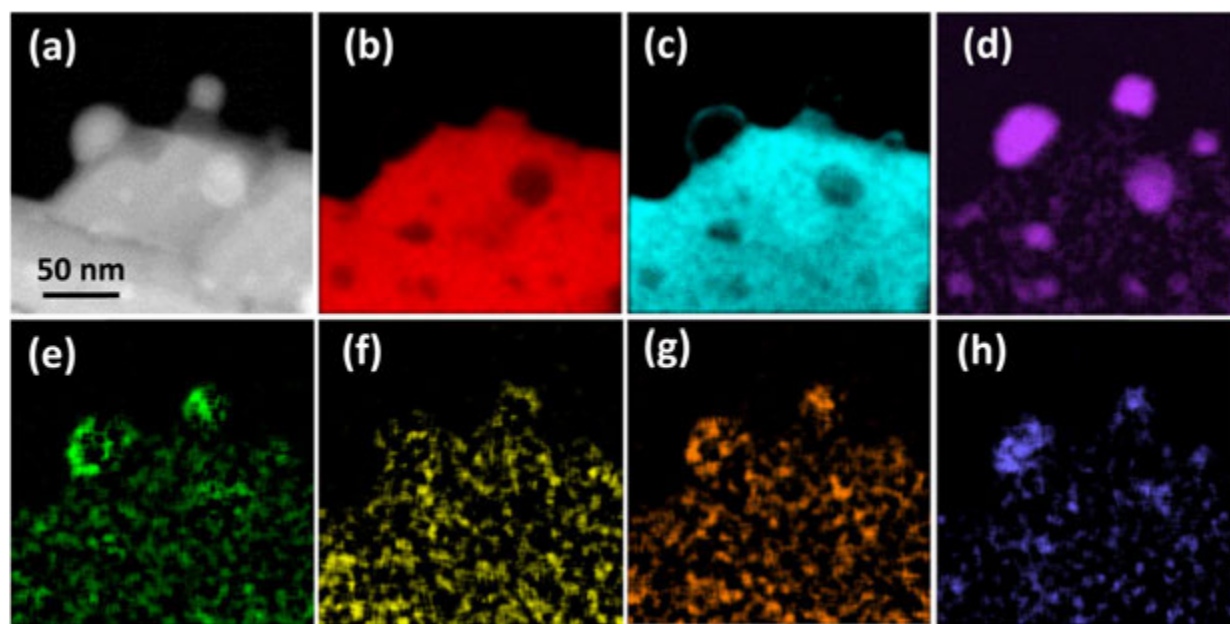


Fig. 12 (a) HAADF-STEM micrograph and STEM – EDS maps of (b) cerium, (c) oxygen, (d) molybdenum, (e) ruthenium, (f) rhodium, (g) palladium and (h) rhenium near the surface (irradiated) of a metal-doped CeO_2 film on Yttria Stabilized Zirconia (YSZ) irradiated with 90 keV He^+ ions to a fluence of $4 \times 10^{17} \text{ He}^+ \text{ cm}^{-2}$, after annealing at 1373K. Figure adapted from reference Jiang, W., Conroy, M.A., Kruska, K., *et al.*, 2019. In situ study of particle precipitation in metal-doped CeO_2 during thermal treatment and ion irradiation for emulation of irradiating fuels. *Journal of Physical Chemistry C* 123, 2591–2601.

which has an adverse impact on fuel performance. In this study, precipitation of Mo-dominant β -phase particles in polycrystalline CeO_2 (a surrogate for UO_2) films doped with Mo, Pd, Rh, Ru, and Re (surrogates for Tc) is reported. *In situ* heating experiments were conducted in HAADF-STEM imaging mode which indicated that particle precipitation starts at $\sim 1073\text{K}$ with limited particle growth to $\sim 10\text{ nm}$. While particle concentration increases with increasing temperature, particle size remains largely unchanged up to 1273K . There is a dramatic change in the microstructure following vacuum annealing at 1373K (Fig. 12), likely due to phase transition of reduced CeO_2 . Also at 1373K particles grow up to 75 nm or larger with distinctive facets. The particles are predominantly composed of Mo (Fig. 12(d)) with a body-centered cubic structure (β phase). An oxide layer was observed after storage at ambient conditions (Fig. 12(c)).

The maps extracted from EDX measurements in Fig. 12 show that simultaneous detection of low and high Z-elements is possible, and the comparison of the signal intensities in the EDX maps in Fig. 12(b) and (c) with those in Fig. 12(c) – (f) directly confirms that the bulk of the sample consists of CeO_2 and that Ru, Rh, Pd and Re form a dense distribution of very small particles, whilst Mo particles are significantly larger and less densely distributed.

EDX spectroscopy, can be carried out down to atomic resolution with the aid of specialized software and averaging methods. The resolution of elemental maps in STEM is jointly dependent on stepping the sharply focused electron probe in a precise raster, on collecting a significant number of characteristic X-rays over time, and on avoiding damage to the sample. Fig. 13 shows aberration-corrected STEM-EDX mapping performed at 80 kV on ordered precipitates of three phases (S, β'' and Q') in aluminum (Al-Mg-(Si)-(Cu)) alloys (Wenner *et al.*, 2017). Probe and sample instability problems are handled by acquiring a series of annular dark-field (ADF) images and simultaneous EDX spectrum maps, which are aligned and non-rigidly registered after acquisition (by using software, e.g., the Smart Align (Jones *et al.*, 2015)). The summed EDX spectrum maps yield elemental maps of Al, Mg, Si, and

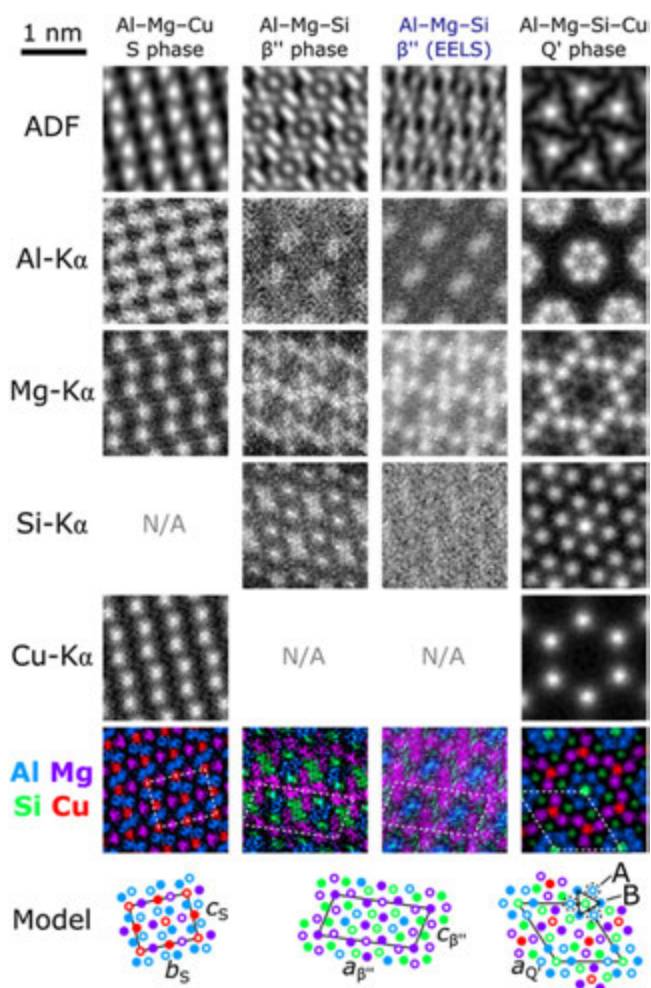


Fig. 13 Symmetry-averaged ADF and EDX images for three precipitates (S, β'' and Q' phases) in Al-Mg-(Si)-(Cu) alloys. EELS images from β'' are shown for comparison in column 3. All images are spatially averaged, and S and β'' are 2-fold rotation averaged, while Q' is 6-fold averaged. A common scale bar of 1 nm is given in the upper left corner. Color codes in the last two rows: blue = Al, purple = Mg, green = Si, red = Cu. In the atomic models, filled and empty circles, representing atoms at the 0 and the $1/2$ position (respectively) along the z-axis direction, are separated by $a_{\text{Al}}/2 = 202\text{ pm}$ in the paper normal direction. Reproduced from Wenner, S., Jones, L., Marioara, C.D., Holmestad, R., 2017. Atomic-resolution chemical mapping of ordered precipitates in Al alloys using energy-dispersive X-ray spectroscopy. *Micron* 96, 103–111.

Cu, with sufficient resolution and signal-to-noise ratio to determine the elemental species of each atomic column in a periodic structure (Fig. 13 rows 2 – 5), and in some cases the species of single atomic columns. Column 3 presents images acquired from EELS mapping of a β'' phase particle for comparison, showing equivalent analogies.

To obtain atomically resolved images and elemental maps, if necessary, small corrections of stage position, focus and probe astigmatism, must be made between acquisition of the individual frames, i.e., after every ADF-STEM image and EDX map acquisition. Small mis-registrations between frames, and non-linear scan distortions within frames, are then corrected in post-processing, and probe offsets from the ADF images are used to correct the corresponding EDX spectrum maps before summing these together. If the crystal structures have translational or rotational symmetry, then images and spectral maps can also be averaged by summing up images that are translationally shifted or rotated. Symmetry averaging procedures have also been applied to the measurements, from which the atomic-resolution EDX maps of nanometer-sized precipitate structures in the aluminum alloys in Fig. 13 were created. Although the example in Fig. 13 is from an alloy, it was chosen as a very good example of this atomic scale analytical imaging capability. This is also possible for ceramic materials. The images in column 3 relate to EELS analysis rather than EDX analysis. Further examples of EELS analysis are given in the following section in Fig. 18(b).

Principles of Electron Energy Loss Spectroscopy (EELS) and Energy Filtered Transmission Electron Microscopy (EFTEM)

EELS is an absorption spectroscopy technique, in which the signals indicated by the blue arrows in Fig. 1(a), are collected. The inelastically scattered, transmitted electron beam, having lost energy, proceeds through a magnetic prism, which bends the beam, and its trajectory is dependent on its energy (see schematics in Fig. 14 for details of the EELS acquisition procedure). An aperture, which can be shifted, then selects a specific energy range of the transmitted beam which enters the detector. An energy filtered TEM (EFTEM) image, i.e., taken with electrons with a specific energy loss, can then be obtained. An alternative collection method allows the beam in its entirety to be detected on a CCD camera, where each pixel detects a different energy of the beam, because, due to its different energies, it impinges at specific pixels on the camera. Spectra can then be constructed by extracting the beam intensity along a line of pixels of the detector. This can also be done in scanning mode, i.e., in each position on a raster, when the beam is scanned across a sample region in STEM imaging mode (STEM-EELS).

The energy loss region in the spectra to be acquired depends on the magnetic field strength applied to the prism (causing different deflection angles of the incoming electron beam). EELS spectra consist of a “zero-loss” peak, i.e., the undeviated beam

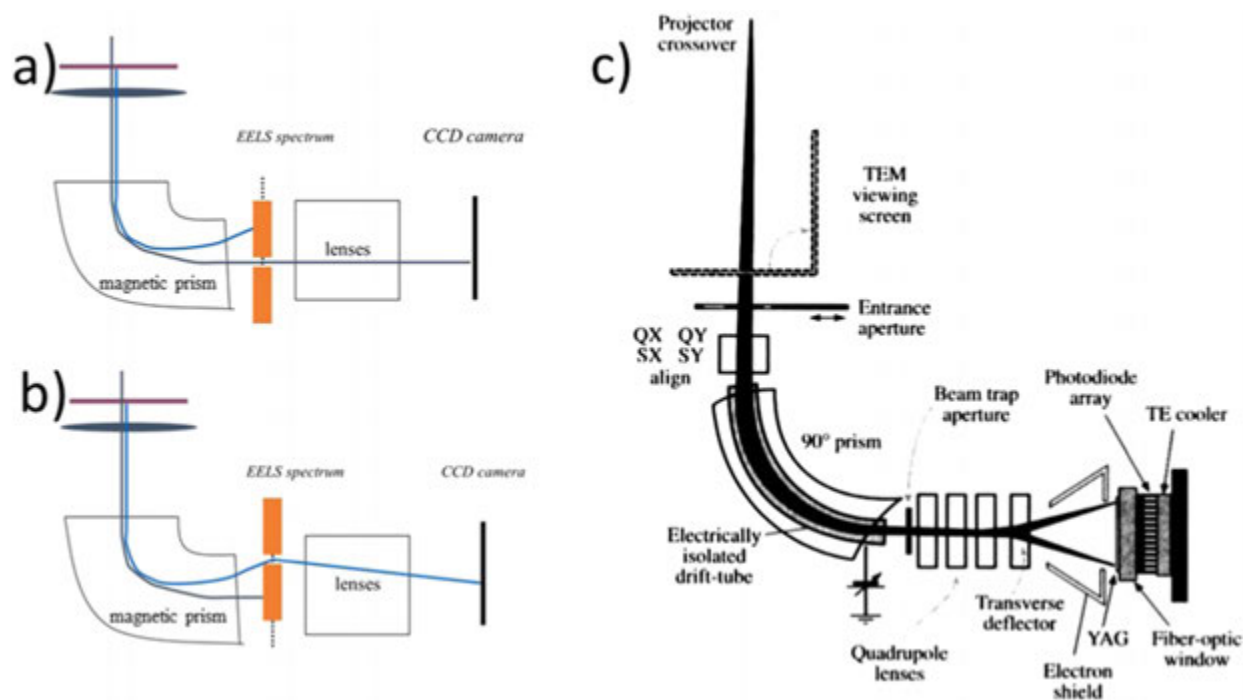


Fig. 14 (a) & (b) Sketches of the electron beam path through the EELS spectrometer; after having penetrated through the sample the beam passes through a magnetic prism. Depending on its energy, it is bent over many angles. In (a) the gray beam with zero-loss energy and in (b) the blue beam having lost energy, is selected by an aperture (orange) to pass through to the CCD camera. (c) Detailed schematics of the energy loss detection procedure. After passing through the prism and lenses, the beams is collected on an Yttrium Aluminum Garnet (YAG) scintillator/detector coupled with a thermoelectrically cooled (TE) semiconductor diode array. Q = quadrupole, S = sextupole. Reproduced from Williams, D.B., Carter, C.B., 1996. Transmission Electron Microscopy. Boston, MA: Springer US.

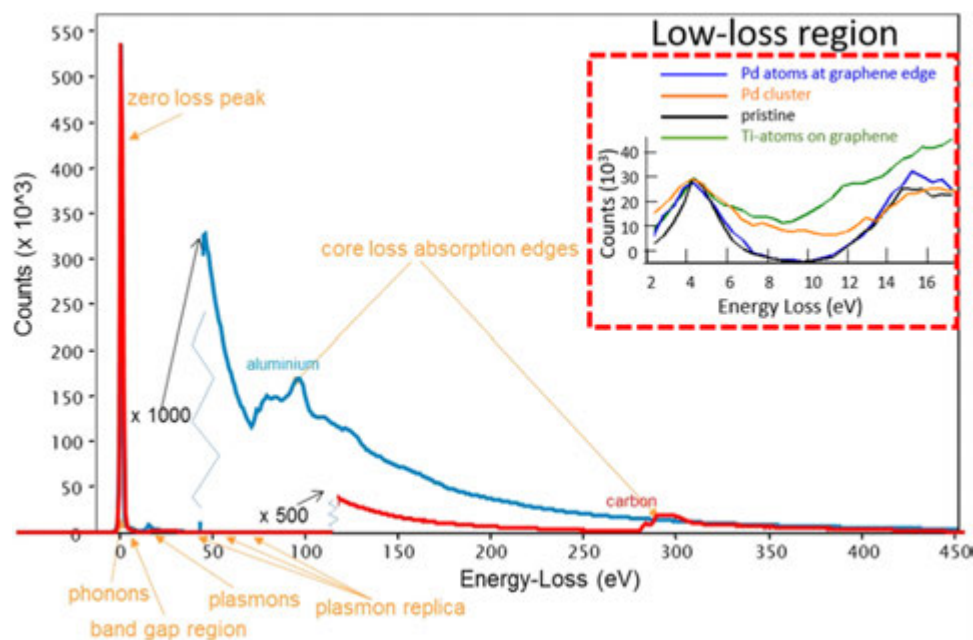


Fig. 15 EELS spectrum of aluminum (blue) and carbon (red), showing the zero-loss regions (with plasmon peaks), and the core-loss regions with Al and C K-shell absorption edges; due to the strong decrease in intensity of the core-loss edges the intensity of the graph in this energy region has been enlarged by 1000x for the Al, and by 500x for the C spectrum. The inset in the red dashed frame shows an enlarged part of EELS spectra in the low-loss region (band gap and plasmon) regime from which information on the materials bandstructure can be obtained. The spectra are of pristine and metal deposited graphene, revealing changes/enhancement of the intensity in the π -plasmon region around 3 eV (potentially leading to UV emission) in the metal deposited samples. The spectra in this figure were obtained by the group of the author; the low loss EEL spectra of graphene are adapted from Bangert, U., Pierce, W., Boothroyd, C., Pan, C.T., Gwilliam, R., 2016. Collective electronic excitations in the ultra violet regime in 2-D and 1-D carbon nanostructures achieved by the addition of foreign atoms. *Scientific Reports* 6, 1–10.

(Fig. 1(a)), a “low-loss” region due to electrons having lost energy by exciting phonons, interband (e.g., valence to conduction band) transitions or plasmons, and a “core-loss” region, due to electrons, having lost energy by exciting transitions in the K, L, M shell, etc., in the sample (Williams and Carter, 1996; Egerton, 2011). Fig. 15 shows EELS spectra of aluminum and carbon, with the mentioned transitions ascribed to the energy loss peaks. EELS can reveal the elemental nature of individual atoms (see Fig. 18). In TEM instruments equipped with a monochromator, enabling high energy resolution, EELS spectra acquired in the low-loss regime can provide information on electronic bandstructure properties (bandgaps, excitons, plasmons) complementing optical and electronic measurements. (Egerton, 2011).

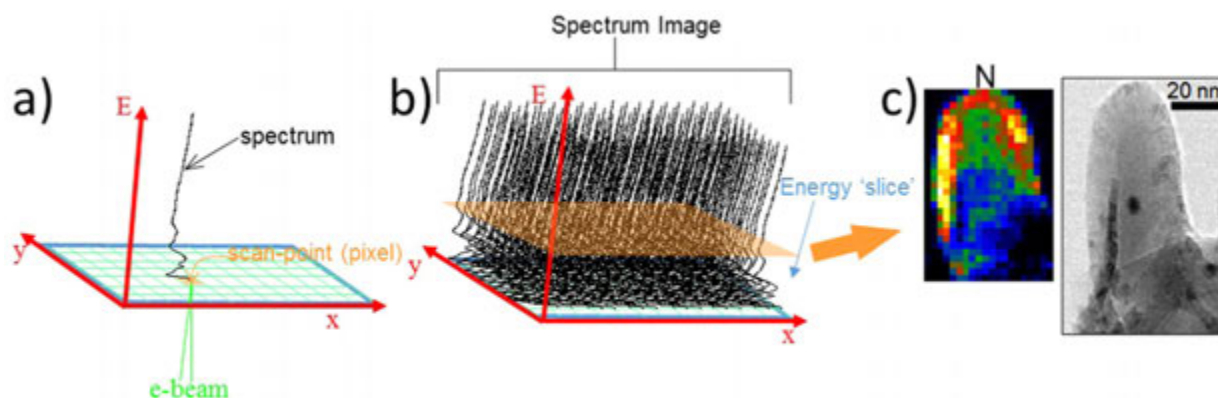


Fig. 16 (a) EELS spectrum imaging carried out by the electron beam being scanned in a pre-defined raster, and in each pixel (x,y) an EELS spectrum is acquired, whose intensity is displayed along the energy (E) axis. (b) Spectrum image displayed as a 4D data array, including x, y, E and intensity. An energy ‘slice’, i.e. x,y positions at a constant energy is indicated in orange. (c) Intensity in the energy “slice” at 401 eV (nitrogen K-edge) in each x,y pixel position displayed on the “temperature scale”, to show the distribution of nitrogen in the tip of a nitrogen and boron doped carbon nanotube (spectra of the latter are not shown here). The nitrogen is incorporated at the surface of the tube, forming a shell. The image on the right is a BF STEM image of the nanotube. Sketches and images are original work obtained by the group of the author; the images in (c) are also published in reference Blank, V.D., Seepujak, A., Polyakov, E.V., *et al.*, 2009. Growth and characterisation of BNC nanostructures. *Carbon* 47, 3167–3174.

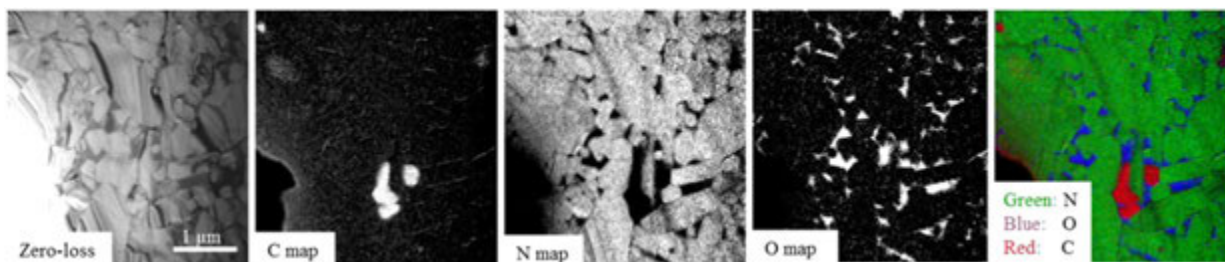


Fig. 17 Energy filtered transmission electron microscopy (EFTEM) images of a metal nitride; the electron beam energies, with which the Carbon, Nitrogen and Oxygen maps were taken are the ones of the core loss energies of the respective elements. The left-most image is taken with the original electron beam energy, i.e., is a TEM image. The right-most image is the overlay of the three differently colored elemental maps (Carbon, Nitrogen and Oxygen) and the zero-loss map. Original work from the author's research group.

The energy resolution in EELS is usually defined by the half width full maximum (HWHM) of the zero loss peak (ZLP), however, its tail, whose drop to the zero level extends over several eV (in uncorrected TEMs), also has a major impact. Energy losses in this energy regime, arising from interband transition as well as from photonic and phononic excitations, have very low intensities compared to, and are superimposed on, the ZLP tail. The ZLP intensity therefore needs to be subtracted from the energy loss spectrum, and in order to do this the shape of the ZLP tail needs to be precisely known, so that it can be fitted by a function. Due to the high intensity of the ZLP tail compared to the loss events in this (few eV) energy region, the extraction of transitions in the low loss regime revealing the material's bandstructure is very restricted, and often not possible. The use of a monochromator helps to reduce the FWHM of the ZLP from several 100 to 10 s of meV, resulting in the same resolution (10 s of meV) of the spectrum features (see example [Fig. 21](#)). This also results in the drop of its tail over only several 10 s of meV. Hence low loss events in this energy regime (phonons) can directly be monitored with high spatial (near atomic) resolution.

EELS acquisition can be carried out in various ways. In STEM spectrum imaging mode, an EELS spectrum is taken at every scan position of the beam on the sample, across the sample region selected (EEL Spectrum Imaging). This leads to a 4D data stack (x, y, E and intensity; see [Fig. 16\(a\)](#) and [\(b\)](#)), from which spectra in individual positions/pixels (along the energy axis direction), can be extracted with a position accuracy down to the atomic level. The 4D data stack can also be sliced at certain energies across the entire acquisition area, leading to a map of a specific energy loss of this area (see [Fig. 16\(c\)](#)) ([Blank et al., 2009](#)).

One of the most commonly used resources for electron microscopists engaging in EELS measurements is the EELS atlas (See Relevant Website section) which provides standard elemental EELS spectra of common materials ([Gatan, 2020a](#)). The "atlas" provides expected edge energies for elemental materials and predicted energy shifts. It is available in book format where each spectrum is displayed, in a quick guide that is commonly found in most EELS microscopy units and more recently as an app available on Android and Apple devices.

EELS can also be carried out in energy filtered TEM (EFTEM) mode. In this case the EELS aperture is positioned in a place to only collect electrons of a certain energy to form an image. If the aperture, which selects the direction (and thus energy) of the electron beam after having gone through the magnetic prism (see [Fig. 14](#)) is shifted in subsequent image acquisitions, a 4D stack can be acquired of images with different energies like in the Spectrum Imaging (SI) mode (see [Fig. 16](#)). To obtain individual EELS spectra, intensities along the energy axis in the 4D stack must be extracted at a certain position.

[Fig. 17](#) shows EFTEM images of a metal nitride sample acquired with the zero-loss energy signal (left), and energies of the core-loss energies for C, N, and O K-edge excitations (middle three images). The right-most image is an overlay of the elemental maps, and the TEM image. Nitrogen deficient pockets in the grain boundaries of the material can be identified, arising from carbon and oxygen enriched regions in these boundaries. Very thin films of carbon can be seen at all grain boundaries in the carbon map, whereas oxygen is present at higher levels and is also present in triple point regions.

Applications of High Spatially and Energy Resolved EELS

[Fig. 18](#) shows the power of EEL Spectrum Imaging with regards to spatial resolution. Shown in [Fig. 18\(a\)](#) and [\(b\)](#) (left most images) are atomic resolution images of an epitaxial double perovskite $\text{La}_2\text{CoMnO}_6$ (LCMO) thin film acquired via atomic resolution ADF-STEM and HAADF-STEM, respectively. The images following to the right of the ADF image in [Fig. 18\(a\)](#) are maps of intensities of specific energy losses of the electron beam, due to core electron excitations in Co, Mn and La atoms. These maps are extracted from EEL spectrum images and reveal elemental nature and composition on the atomic level. The color maps, constructed by overlaying the Co, Mn and La maps, demonstrate an ordered Co/Mn cation arrangement. For comparison, maps of the intensities of X-rays excited in, and emitted from, Co, Mn and La atoms due to the electron beam, are shown in [Fig. 18\(b\)](#) (to the right of the HAADF image). As with EELS mapping, EDX mapping can also be carried with atomic resolution, and results from both analytical techniques show very good agreement.

EELS studies have proven to have far-reaching implications for the safe use of nuclear materials by revealing the behavior of oxygen in uranium oxide ([Spurgeon et al., 2019](#)). The key finding is that excess oxygen from the environment can be incorporated at far greater levels than previously thought, while still preserving the nominal cubic crystal structure of the widely used nuclear fuel, UO_2 . This insight, enabled by atomic resolution EELS and theoretical calculations, allows the development of better, more reliable models for nuclear waste

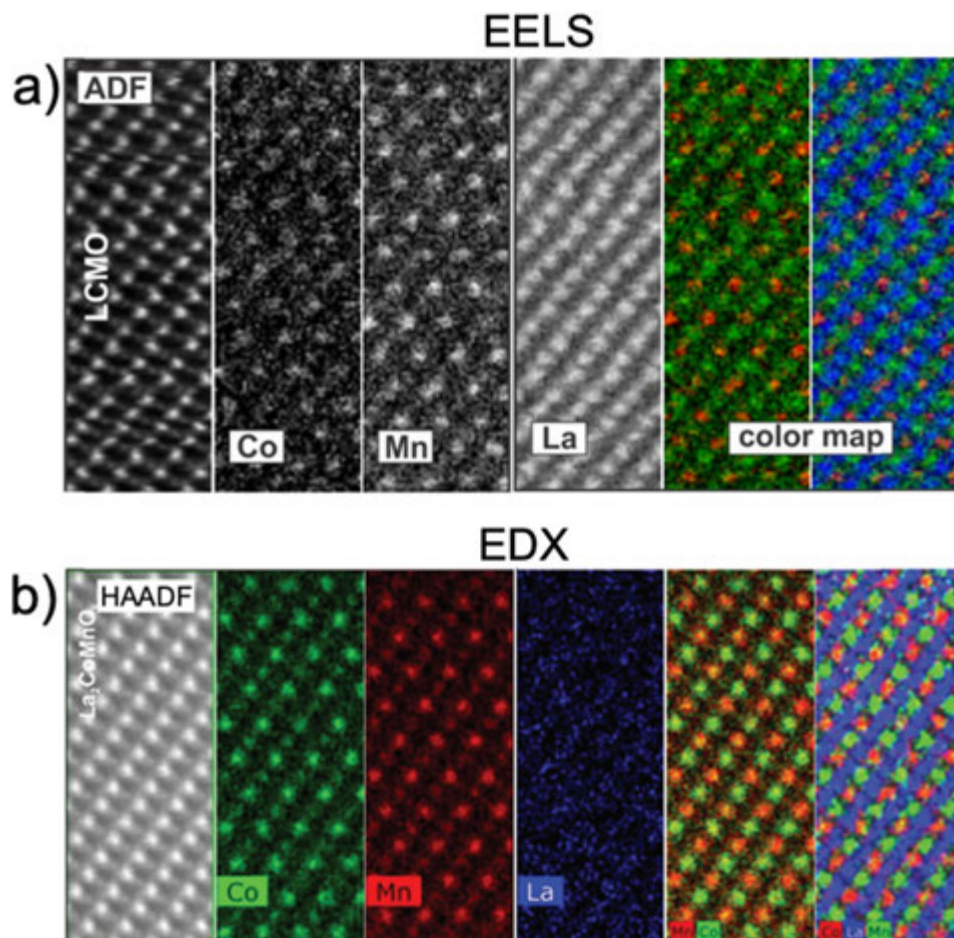


Fig. 18 (a) Atomic resolution ADF image and the corresponding EEL Spectrum Imaging maps of a $\text{La}_2\text{CoMnO}_6$ (LCMO) thin film; the chemical elemental maps are shown in grayscale. The color maps with Co (green), Mn (red) and La (blue) demonstrate the Co/Mn cation arrangement. (b) Atomic resolution HAADF image shown in grayscale and the corresponding EDX elemental maps shown in the colors assigned to the elements as in (a). The overlaid colourmaps again demonstrate the Co/Mn cation arrangement. Figs. (a) and (b) demonstrate a good agreement between the data acquired from atomic resolution EELS and EDX. Adapted from reference Egoavil, R., Hühn, S., Jungbauer, M., *et al.*, 2015. Phase problem in the B-site ordering of $\text{La}_2\text{CoMnO}_6$: Impact on structure and magnetism. *Nanoscale* 7, 9835–9843.

storage and disposal. As for safe usage, the storage and disposal of actinide oxides in the nuclear fuel cycle and understanding of the O-related defects is important; their oxidation state influences fuel lifetimes, stability, and the contamination of groundwater. Aberration corrected HAADF-STEM and EELS can resolve changes in the local oxygen defect environment in UO_{2+x} surfaces. Atomically resolved STEM-EELS mapping in Fig. 19 reveals uranium oxidation states resulting from oxygen defects, i.e., local O-interstitials, through changes in the fine structure of the oxygen core-loss EELS edge in the spectra in Fig. 19(c) and (e), giving information on the mechanisms for uranium oxidation on the atomic level. (Experimental results were supported by first-principles calculations (Spurgeon *et al.*, 2019)).

Fig. 19(a) shows a composition map of the U-M_{4,5} edge collected at the un-oxidized [111] surface, illustrating compositional uniformity and crystallinity of the sample up to its top monolayer. Fig. 19(b) and (c) show the O-K edge spectra extracted from a map of the [111] surface region, progressing from the topmost layer of the crystal to its bulk. The colors in Fig. 19(b) (and also Fig. 19(d)) indicate the O-K edge intensity, and the spectra in Fig. 19(c) and (e) are from the entire area of the respective boxes, and not just from individual atomic positions, so as to provide a sum of spectra of a number of atoms, leading to higher intensity and, therefore, better statistics. The O-K edge displays two sharp peaks at 533 and 538.75 eV, followed by a shoulder at 543.25 eV and two broader features at 553 and 566 eV. There is little variation upon moving from the surface (Fig. 19(b) - spectrum 1) to the bulk (Fig. 19(b) - spectrum 7). In comparison, O-K edge measurements of the oxidized [001] surface, shown in Fig. 19(d) and (e), exhibit markedly different behavior. The overall bulk spectrum 7 is quite similar to that of the [111] sample, with a minor change in the ratio of the two sharp peaks at lower energy loss, whereas, moving closer to the sample surface, there is a redistribution of spectral features that coincides with the presence of the surface contrast band (Fig. 19(f) and (g) - spectra 1–4). These features are highlighted in the difference spectra in Fig. 19(f) and (g), where the emergence of a distinct shoulder at 530.5 eV (feature 1), changes the ratio of the two dominant peaks (features 2 and 4), and an increase in the minimum at 535.5 eV (feature 3) can be seen, as well as the emergence of a broad peak at 548 eV (feature 5). Collectively these results suggest the possibility of distinct local structures giving rise to these spectral features in the oxidized [001]

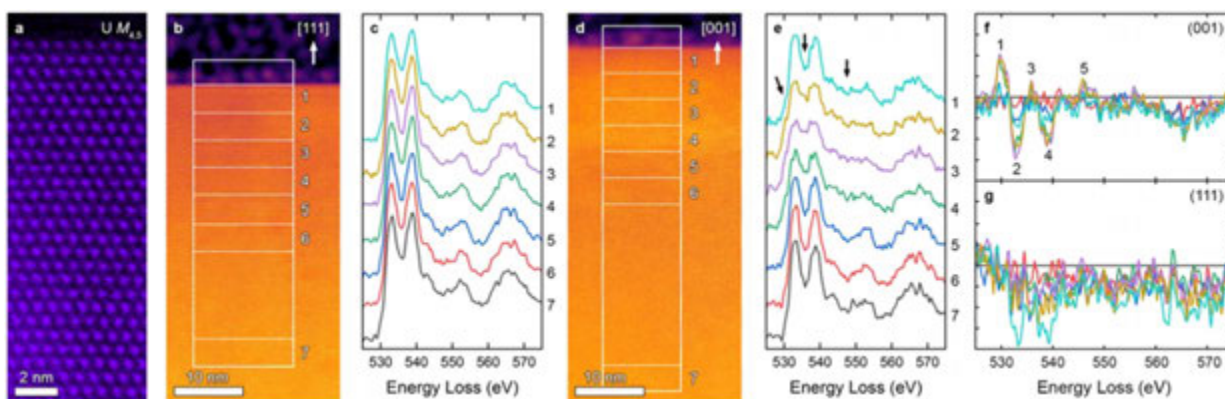


Fig. 19 Spectroscopy of UO_2 sample surfaces. (a) STEM-EELS composition map of the U-M4,5 edge measured at the un-oxidized [111] sample surface. (b) and (c) HAADF-STEM image of the [111] surface and corresponding O-K edge spectra extracted from the numbered windows, respectively. (d) and (e) HAADF-STEM image of the oxidized [001] surface and corresponding O-K edge spectra extracted from the numbered windows, respectively. (f and g) Difference plots showing changes in spectral features relative to the bulk, marked 1–5 for the [001]- and [111]-oriented sample surfaces, respectively. Reproduced from Spurgeon, S.R., Sassi, M., Ophus, C., *et al.*, 2019. Nanoscale oxygen defect gradients in UO_{2+x} surfaces. *Proceedings of the National Academy of Sciences of the United States of America* 116, 17181–17186.

surface, arising from a large amount of excess oxygen distributed across a gradient near the sample surface due to O-interstitials (although there is no evidence for a large-scale phase transition from the fluorite structure).

The EELS investigations of the samples in **Figs. 19** and **20** demonstrate the capability of core loss EELS, when spectra are taken with high energy resolution, to provide bandstructure information via the resolved core loss edge fine structure, with spatial resolutions down to the atomic level.

Fig. 20 shows again the proficiency of assessing oxygen defects (in this example, vacancies) in bismuth oxide through EELS measurements supported by Density Functional Theory (DFT) simulations. EELS measurements of $\alpha\text{-Bi}_2\text{O}_3$ are performed on three samples obtained through different synthesis methods (nanocrystals, pellet and nanowire pellet; see images in **Fig. 20(a – c)**). Experimental acquisition of low-loss and core-loss EELS spectra (shown in **Fig. 20(d)** are core-loss spectra) combined with detailed

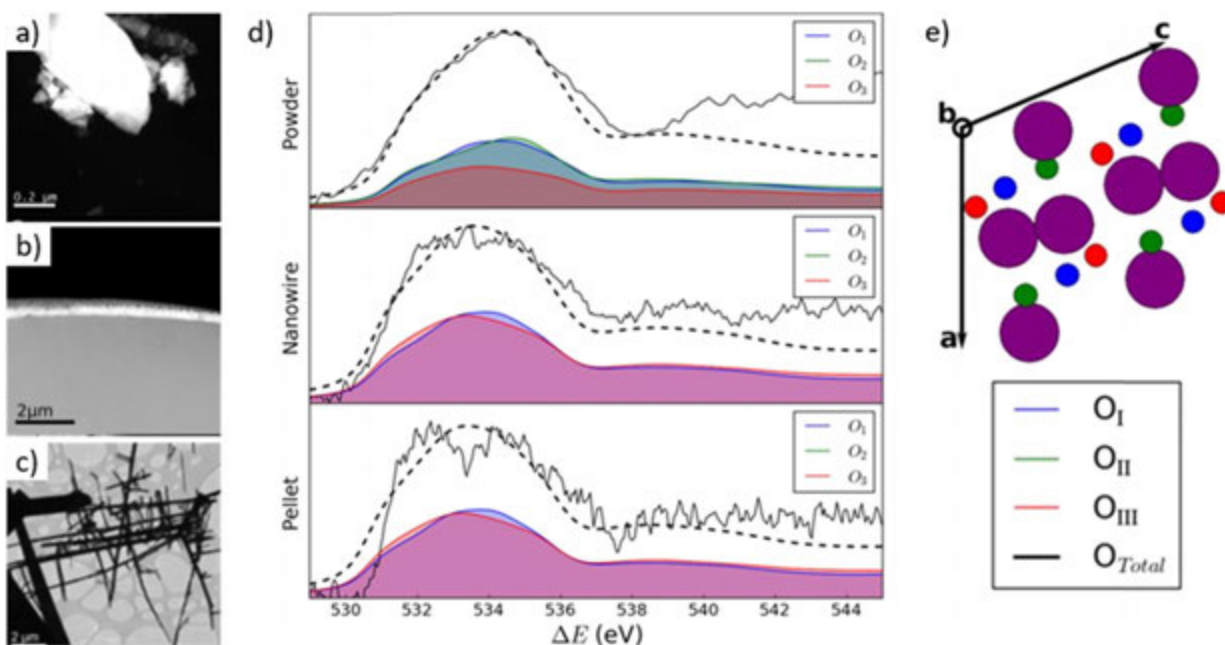


Fig. 20 Low magnification images and fitted EELS core loss experimental spectra of three different Bi_2O_3 samples. STEM-HAADF images of (a) a group of nanocrystals, (b) a FIB-prepared Bi_2O_3 pellet and (c) an α -phase nanowire, (d) core-loss EELS spectra of the O-edge (the top, middle and bottom spectrum are of the samples in (a), (b) and (c) respectively) with the weighted contributions of each non-equivalent oxygen atom and an energy shift (blue, green and red curves). (e) The $\alpha\text{-Bi}_2\text{O}_3$ unit cell seen along the [010] zone axis with the positions of the non-equivalent oxygens in blue, red, and green (the Bi atoms are shown in purple). Figure adapted from reference Torruella, P., Coll, C., Martín, G., *et al.*, 2017. Assessing oxygen vacancies in bismuth oxide through EELS measurements and DFT simulations. *Journal of Physical Chemistry C* 121, 24809–24815.

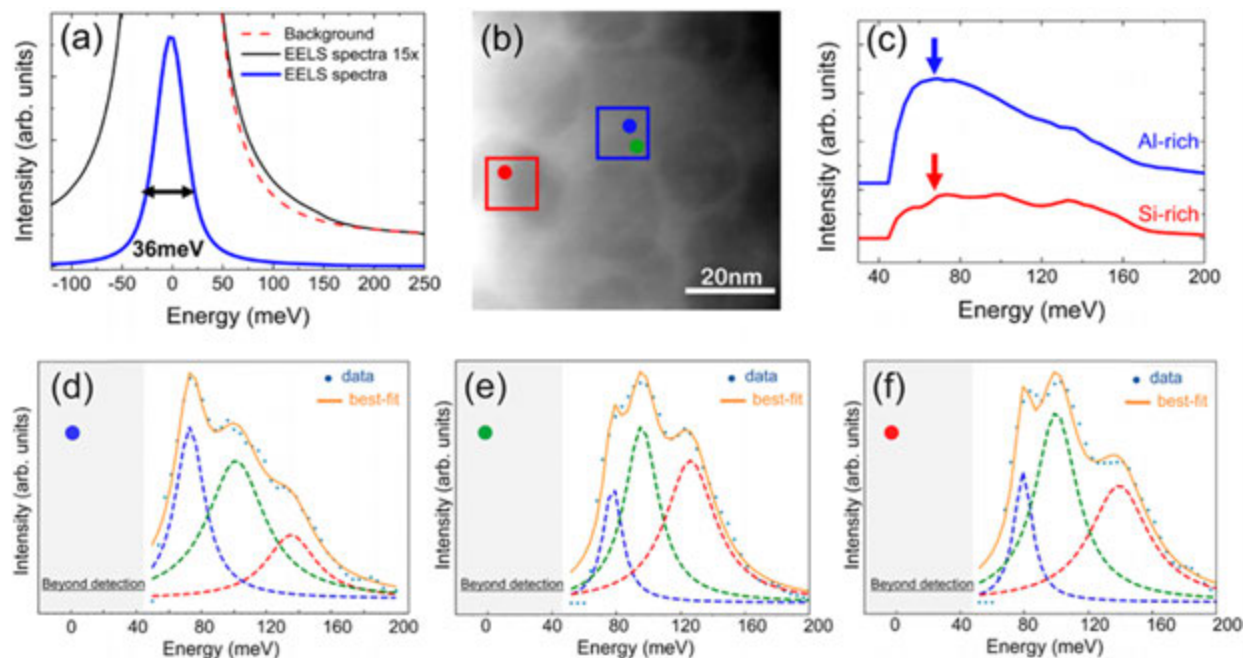


Fig. 21 Vibrational signals in Al- and Si-rich regions. (a) ZLP recorded in a glass specimen shows 36 meV energy resolution. (b) HAADF-STEM image of a phase separated region. Blue and red boxes represent the place, where vibrational spectra of the Al- and Si-rich regions, shown in c), were recorded. (c) Comparison of integrated vibrational signals in the Al- and Si-rich regions. (d - f) Single pixel signals recorded from different regions. Colored points refer to the positions of recorded pixels. Each spectrum was fitted with three Lorentzian functions. Reproduced from Liao, K., Haruta, M., Masuno, A., *et al.*, 2020. Real-space mapping of oxygen coordination in phase-separated aluminosilicate glass: Implication for glass stability. *ACS Applied Nano Materials* 3, 5053–5060.

structural characterization and DFT simulations, enables to detect and evaluate the presence of oxygen vacancies in the samples. The DFT simulations establish the relationship between oxygen vacancy concentration and the O-K edge onset, the latter occurring steeper and at slightly higher energies in the pellets and nanowires and missing out the shoulder at the O-K edge rise in the powder. Hence, EELS spectral analysis confirms an increase in oxygen vacancies in the nanowires and the pellet sample, occupying preferably the O_{II} crystallographic site.

As described above at the beginning of this paragraph, to extract bandstructure information from absorption peaks directly in the low loss regime, high energy resolution has to be achieved by employing monochromators, reducing the FWHM of the ZLP (which determines the energy resolution), to monitor absorption events in energy regimes below 1 eV. In the following examples, bandstructure information is extracted from EELS studies in the ultra-low loss regime (Figs. 21 and 22), i.e., revealing oxygen coordination in a phase-separated aluminosilicate glass via real-space mapping of the phonon properties. These properties are different and specific for different O co-ordinations.

In monochromated instruments, EELS can be carried out with ultra-high energy resolution (down to tens of meV), revealing bandstructure information on the phononic and vibrational energy level. Fig. 21 presents STEM-EELS of real-space mapping of oxygen coordination in phase-separated aluminosilicate glass, which has implications on glass stability (Liao *et al.*, 2020). This can be revealed through an understanding of the local chemistry and structure of the glass networks particularly regarding the local structures around oxygen atoms, which are the most abundant species in oxide glasses and have impact on various macroscopic properties such as viscosity, photo-absorption, hardness, and elastic modulus. The triply bonded O in the Si – O – Al configuration is more energetically favored than Si – O – Si and Al – O – Al bonds. To establish whether and where these bonds exist in the glass, nanoscale investigations are required. With the newly developed vibrational EELS technique enabled by a monochromator (termed monochromated EELS), differently coordinated oxygens in an aluminosilicate glass ($50Al_2O_3 - 50SiO_2$) can be probed at the nanometer-scale. Rather than extracting information from the fine structure of core-loss EELS, measurements are carried out directly in the vibrational (0–200 meV low-loss) energy regime. In Fig. 21(d – e), the blue peak is associated with stretching modes of AlO_5 , the green one with stretching modes of AlO_4 , and the red peak with stretching modes of the SiO_4 group.

Identical ultra high-resolution STEM-EELS mapping, i.e. in the phononic loss regime, was carried out on the same sample to achieve the results presented in Fig. 22, here concentrating on quantifying the energy difference and the distribution of the stretching modes of SiO_4 in regions of different compositions.

An energy difference of 7 meV in the peak position of SiO_4 due to (tetrahedral) stretching, i.e. a change of the local structure, was observed between the Al-rich phase and Si-rich phase indexed by white and black dashed circles in Fig. 22(b). The origin of the peak shift in the SiO_4 stretching mode is associated with a change of the Si – O bond length, although one cannot determine whether the shift originated from the Si – O bond or Al – O bond due to the overlapping of two correlations. In the amorphous

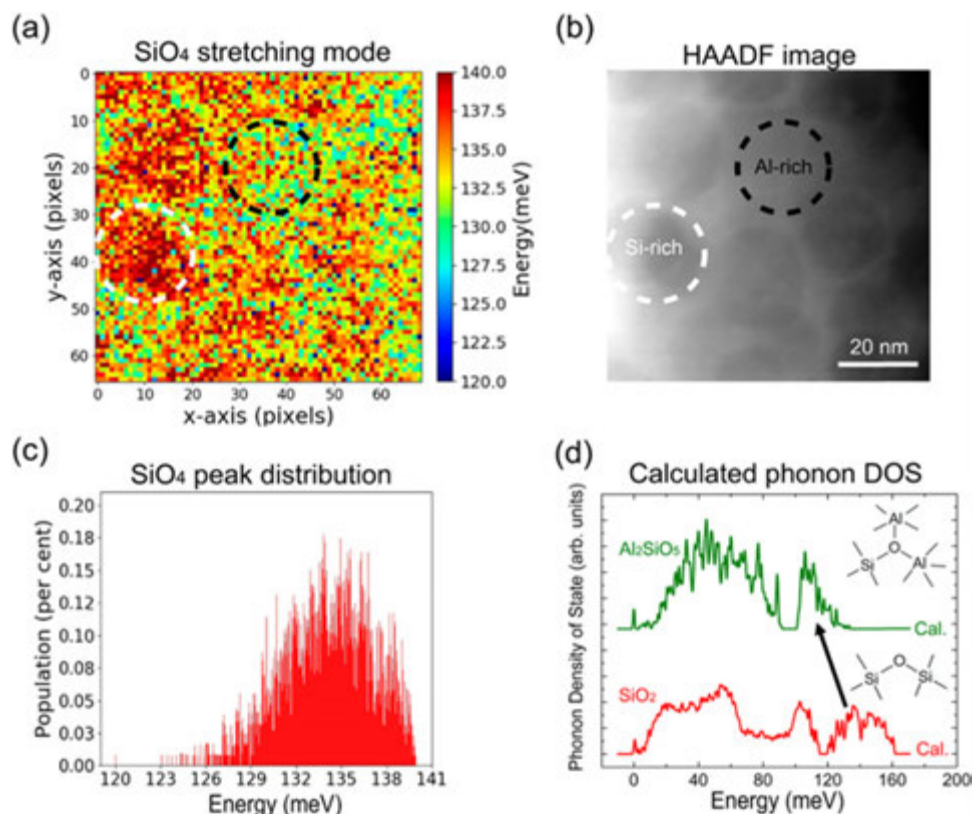


Fig. 22 Vibrational mode mapping of SiO₄ asymmetric stretching modes. (a) Mapping of the SiO₄ peak position obtained from profile fitting. The size of each pixel is 1.4 nm × 1.4 nm. A peak shift of around 10 meV is observed in the black and white circled regions. (b) HAADF-STEM image of the mapped areas. Black and white circled regions correspond to the Al- and Si-rich regions. (c) Distribution of the fitted peak positions. (d) calculated phonon DOS of the Al₂SiO₅ structure, where O atoms are mainly ¹³O. The band for the SiO₄ stretching mode is located at lower energy than that of amorphous SiO₂ (indicated by the black arrow), which is the origin of the peak shifts observed in (a). Reproduced from Liao, K., Haruta, M., Masuno, A., *et al.*, 2020. Real-space mapping of oxygen coordination in phase-separated aluminosilicate glass: Implication for glass stability. *ACS Applied Nano Materials* 3, 5053–5060.

SiO₂, all O atoms are ¹²O, as known from random network theory, whereas O atoms are favored to form a triply coordinated kyanite structure, bonded with two Al and one Si. The simulated result, based on density functional theory (DFT) calculations, is shown in Fig. 22(d). The band corresponding to the SiO₄ stretching mode undergoes a negative energy shift in the Al₂SiO₅ structure in combination with an increase in the Si–O bond length. ¹³O connected with two Al and one Si possesses a higher residual charge than ¹²O at the Si–O–Si bond, possibly leading to the formation of a weaker covalent bond between Si and ¹³O. Weak bonds possess longer bond length and result in the lower stretching frequency (leading to the downwards shift). The distribution of ¹³O can serve as a map of local glass stability, as the ¹³O fraction in the melt is regarded as a proxy of losing glass-forming ability. So, the local coordination change between ¹²O and ¹³O is resolved by the peak shift of the Si–O stretching mode. The observations confirm that the ¹³O is mainly present in the high Al content environment. This finding elucidates a long-standing mystery in glass science and gives insight into the correlation between the atomic short-range orders and nanostructures, which, on the meV energy and highly spatially resolved level, can only be achieved via monochromated STEM low-loss EELS.

Conclusion and Outlook

Analytical TEM of ceramics and glasses has proven essential in gaining an understanding of their properties on a highly spatially and energy resolved level, i.e., by revealing positions and elemental nature of atoms, as well as their bonding states, which is crucial information for targeted tailoring of these materials regarding their important universal applications. The literature reviewed in this chapter reveals highlights of information provided by employing these TEM methods. In particular, STEM-EELS has been used for real-space mapping of the oxidation state and coordination of oxygen atoms, which, being the most abundant elements in oxide glasses, have impact on various macroscopic properties such as viscosity, photo-absorption, hardness, stability and elastic modulus. High resolution HAADF STEM also revealed fracturing mechanisms in ceramics. Moreover, ion irradiation and in situ heating TEM experiments (e.g., of CeO₂, as surrogate for UO₂, to emulate irradiation of fuels, in order to predict the fuel performance) have shown particle precipitation, which has an adverse effect on oxide fuel performance.

Advancements in TEM, having led to ultra-high spatial and spectroscopic resolution, will result in increasing future use of this characterization technique to provide insight into the correlation between materials' macroscopic properties/functionalities and individual atom arrangements and dynamics giving rise to these. Having predominantly been used for investigations of inorganic materials in the past, TEM is now also progressively employed for investigations of amorphous and crystalline organic materials. This achievement is due to developments of low voltage TEM and ultra-sensitive detection equipment, reducing electron beam damage effects in beam-sensitive materials. A further ground-breaking development is in-situ TEM, by which observations of the structural behavior, down to the atomic level, can be made in gaseous and liquid conditions, as well as under heating, cooling, biasing and straining. This is especially beneficial for observing and understanding the effects of external and environmental conditions on materials' behavior regarding impacts on their functionalities. In-situ techniques have promising applications, and have already been employed, for investigations (on the nano-scale) of, e.g., the structural behavior of ceramics and glasses, under certain mechanical and chemical straining conditions, i.e., when used as materials for reinforcement and wear resistance in the construction sector, or for nuclear fuel storage.

References

- Bangert, U., Gass, M., Zan, R., Pan, C.T., 2011. Scanning transmission electron microscopy and spectroscopy of suspended graphene. In: Mikhailov, S. (Ed.), *Physics and Applications of Graphene – Experiments*. Rijeka: IntechOpen, pp. 377–408.
- Barthel, J., 2018. Dr. Probe: A software for high-resolution STEM image simulation. *Ultramicroscopy* 193, 1–11.
- Blank, V.D., Seepujak, A., Polyakov, E.V., *et al.*, 2009. Growth and characterisation of BNC nanostructures. *Carbon* 47, 3167–3174.
- Brydson, R., 2011. *Aberration-Corrected Analytical Transmission Electron Microscopy*. Chichester: John Wiley & Sons Ltd.
- Chen, Z., Hong, L., Wang, F., *et al.*, 2017. Facilitation of ferroelectric switching via mechanical manipulation of hierarchical nanoscale domain structures. *Physical Review Letters* 118.017601.
- De Jong, A.F., Coene, W., Van Dyck, D., 1989. Image processing of HRTEM images with non-periodic features. *Ultramicroscopy* 27, 53–65.
- Egerton, R.F., 2011. *Electron Energy-Loss Spectroscopy in the Electron Microscope*, third ed. New York: Springer.
- Gatan, 2020a. EELS Atlas – EELS.info. Available at: <https://eels.info/atlas> (accessed 24.11.2020).
- Guan, Z., Hu, H., Shen, X., *et al.*, 2020. Recent progress in two-dimensional ferroelectric materials. *Advanced Electronic Materials* 6, 1900818.
- Jiang, W., Conroy, M.A., Kruska, K., *et al.*, 2019. In situ study of particle precipitation in metal-doped CeO₂ during thermal treatment and ion irradiation for emulation of irradiating fuels. *Journal of Physical Chemistry C* 123, 2591–2601.
- Jones, L., Yang, H., Pennycook, T.J., *et al.*, 2015. Smart align – A new tool for robust non-rigid registration of scanning microscope data. *Advanced Structural and Chemical Imaging* 1, 8.
- Kondo, S., Ishihara, A., Tochigi, E., Shibata, N., Ikuhara, Y., 2019. Direct observation of atomic-scale fracture path within ceramic grain boundary core. *Nature Communications* 10, 2112.
- Lazić, I., Bosch, E.G., Lazar, S., 2016. Phase contrast STEM for thin samples: integrated differential phase contrast. *Ultramicroscopy* 160, 265–280.
- Liao, K., Haruta, M., Masuno, A., *et al.*, 2020. Real-space mapping of oxygen coordination in phase-separated aluminosilicate glass: Implication for glass stability. *ACS Applied Nano Materials* 3, 5053–5060.
- Lohr, M., Schregle, R., Jetter, M., *et al.*, 2012. Differential phase contrast 2.0– Opening new “fields” for an established technique. *Ultramicroscopy* 117, 7–14.
- Shen, B., Chen, X., Cai, D., *et al.*, 2020. Atomic spatial and temporal imaging of local structures and light elements inside zeolite frameworks. *Advanced Materials* 32, 1906103.
- Song, D., Zhang, X., Lian, C., *et al.*, 2019. Visualization of dopant oxygen atoms in a Bi₂Sr₂CaCu₂O_{8+δ} superconductor. *Advanced Functional Materials* 29, 1903843.
- Spurgeon, S.R., Sassi, M., Ophus, C., *et al.*, 2019. Nanoscale oxygen defect gradients in UO_{2+x} surfaces. *Proceedings of the National Academy of Sciences of the United States of America* 116, 17181–17186.
- Wang, X.H., Zhou, Y.C., 2010. Layered machinable and electrically conductive Ti₂AlC and Ti₃AlC₂ ceramics: A review. *Journal of Materials Science & Technology* 26, 385–416.
- Wenner, S., Jones, L., Marioara, C.D., Holmestad, R., 2017. Atomic-resolution chemical mapping of ordered precipitates in Al alloys using energy-dispersive X-ray spectroscopy. *Micron* 96, 103–111.
- Williams, D.B., Carter, C.B., 1996. *Transmission Electron Microscopy*. Boston, MA: Springer US.
- Yücelen, E., Lazić, I., Bosch, E.G.T., 2018. Phase contrast scanning transmission electron microscopy imaging of light and heavy atoms at the limit of contrast and resolution. *Scientific Reports* 8.2676.
- Zhao, P., Wang, H., Wu, L., *et al.*, 2019. High-performance relaxor ferroelectric materials for energy storage applications. *Advanced Energy Materials* 9, 1803048.

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Introduction to Three Dimensional Electron Crystallography

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Preface

The development of new materials in Physics, Materials Science and Chemistry in most cases requires knowledge of the crystal structure enabling the calculation of materials properties to gain a deeper understanding of how they function. Since most of the functional materials developed today are micro- or nano-crystalline, a transmission electron microscope (TEM) is the optimal tool for structural characterization. Using a TEM, it is possible to switch between imaging in direct space and diffraction in reciprocal space thus allowing large variety of experimental methods to be available. In comparison to imaging, electron diffraction experiments are less sensitive to lens aberrations and require lower electron fluxes on the sample to achieve atomic resolution data. When comparing Electron Diffraction (ED) to X-ray diffraction (XRD) methods, currently the most common approach for crystal structure solution, it is not necessary to invest time, money or resources, to grow crystals sufficiently large in size for single-crystal X-rays, or to collect a volume of microcrystals sufficient for X-ray powder diffraction, similarly for X-ray free-electron experiments, as described by [Fetzer et al. \(2021\)](#), a single parallel (ED) or convergent electron diffraction pattern (CBED) provides important information. But for ab-initio crystal structure solution, which refers to solving a new crystal structure only from electron diffraction data using no additional information, the information must be more complete and 3-dimensional electron diffraction (3D-ED) experiments are necessary.

Introduction and Brief History

Three-dimensional electron diffraction (3D-ED), while seen as a very recent breakthrough, has undergone a long development to reach the point of being more widely adopted by the electron microscopy community. Initial experiments by [Henderson and Unwin \(1975\)](#) on Bacteriorhodopsin used a combination of image and diffraction data and obtained the 3D diffraction volume at 7 Å resolution. A few years later [Hovmöller et al. \(1984\)](#), published work on niobium oxide structures, using imaging and diffraction data from low index zone axes to determine the metal positions. Apart from this being an extremely challenging and time-consuming work, a major problem needs to be described. Zone axes are where the most dynamical scattering occurs, making its use for crystal structure solution very challenging or impossible since one of its core assumptions is that the data is elastically scattered and only once, often referred to as kinematic scattering. The advent of the double conical beam-rocking system ([Vincent and Midgley, 1994](#)), otherwise known as electron beam precession, where the electron beam is rocked in a cone above the sample (scanned by beam deflectors), and then rocked in a cone in the opposite direction below the specimen (descanned by image deflectors) producing precessed electron diffraction patterns (PED) in the back focal plane of the objective lens (see [Fig. 1](#)). This tilting of the beam away from the optic axis in an angle α reduces the dynamical scattering content of the electron diffraction data. Precession around a cone allows for summing up hundreds of diffraction patterns, all differently oriented, resulting in a less dynamically modified diffraction pattern. Thus, precession data is often referred to as pseudo-kinematic diffraction. Moving the electron beam away from the zone axis during data collection causes the Ewald sphere to precess and thus integrate the reciprocal space over a wedge with the angle α as sketched in [Fig. 2](#).

In comparison to convergent beam electron diffraction (CBED), where all incident angles inside the illumination cone are available, the precessed parallel electron beam provides one incident angle resembling a hollow cone. PED can be used with a parallel illumination selecting the region of interest (ROI) see ([Fig. 1a](#)) with an selected area electron diffraction aperture (SAED) as well as by addressing it with a nano beam. The probe for nano beam electron diffraction (NBED), often referred to as nano electron diffraction (NED) or nano beam diffraction (NBD), is set up by using a small C2 aperture (CA). Thus, a significant portion of the beam is blanked and the electron flux rate is reduced. In comparison to SAED, which covers a ROI of down to 200 nm, NBED allows adaption of the probe size down to a few nanometers and is dependent upon the microscope lens system and electron source. As an example, for a lanthanum hexaboride (LaB₆) cathode to achieve a quasi-parallel beam using a TEM with a two condensor lens system and a condensor mini lens a beam diameter of ~ 14.6 nm, can be achieved with a flux ~ 250 e/Å²s, and a convergence angle ~ 0.5 mrad. With a three condensor lens system the extra control of the beam enables a smaller diameter of ~ 11.3 nm, with an increased electron flux of ~ 650 e/Å²s, and an improved convergence angle ~ 0.3 mrad, for an beam which is even closer to parallel. For a fully converged probe, the beam diameter of ~ 8.5 nm, with a flux rate ~ 800 e/Å²s and convergence angle ~ 3.6 mrad will be reached ([Plana-Ruiz, 2021](#)). ED intensities, improved by electron beam precession, can in principle be used for crystal structure solution combining several oriented zones ([Remennik et al., 2012](#); [Goujon et al., 2008](#); [Dorset, 1996](#); [Dorset et al., 2005](#)). Nevertheless, in order to derive even the positions of light atoms like H, Li, O, C, N the reciprocal space coverage needs to be as complete as possible reaching for the highest possible resolution.

The next stage in the evolution of 3D-ED methods starting in 2007 was Automated Diffraction Tomography (ADT) ([Kolb et al., 2007, 2008](#); [Mugnaioli et al., 2009](#)) which aimed to mimic the single-crystal X-ray diffraction experiment within the electron microscope by tilting the crystal over an angular range and measuring an electron diffraction pattern at a defined tilt step to get a complete coverage

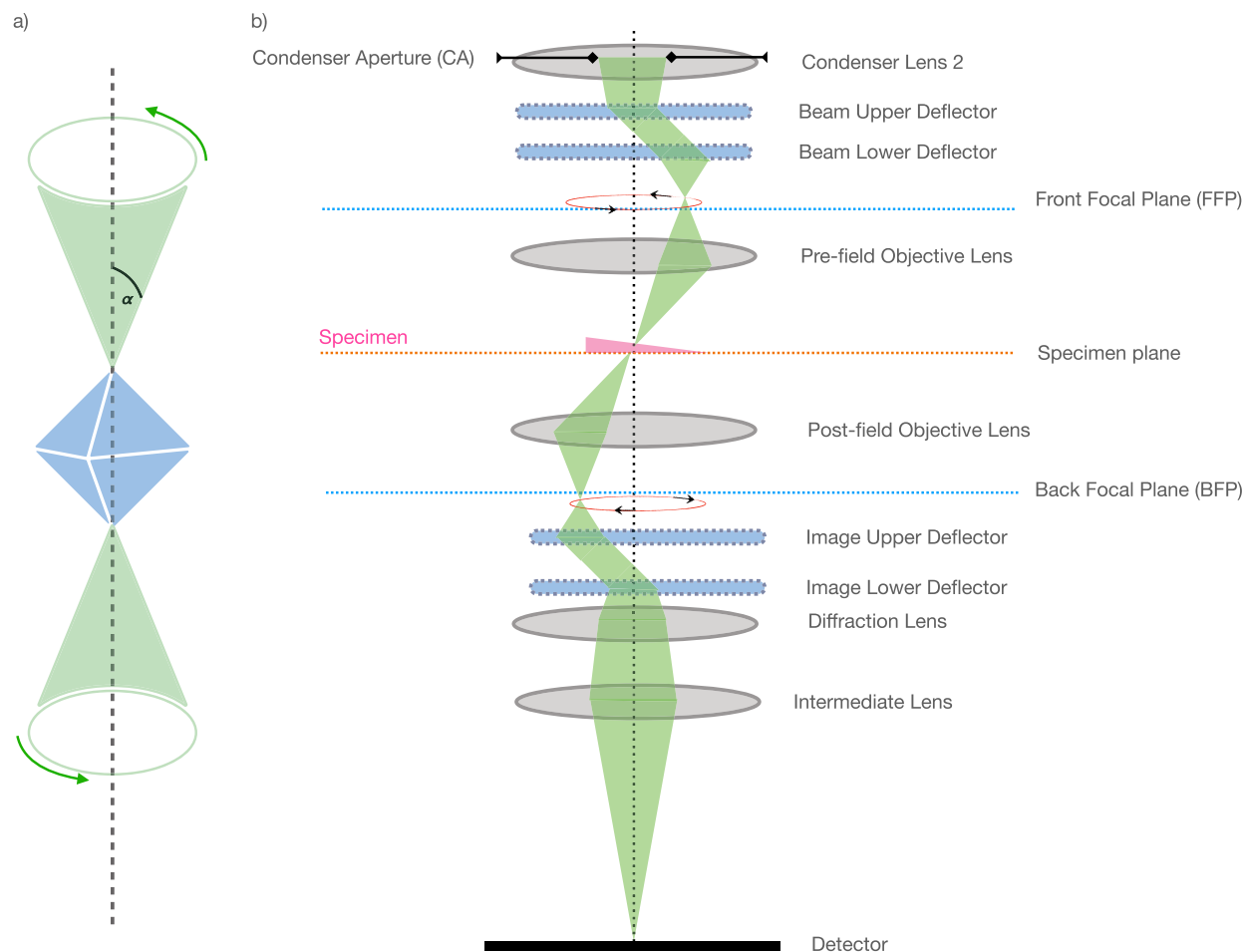


Fig. 1 (a) Electron beam precession, the beam is tilted off axis in a hollow cone at angle α . (b) The electron beam precesses anti-clockwise above the sample and, clockwise below the sample to bring it back onto the optic axis.

of the reciprocal space. The diffraction experiment does not require orientation of the specimen onto a zone axis. Instead, it is possible to use the crystal as found in a random orientation. The general idea, to tilt an arbitrarily oriented crystal in the TEM under an electron beam with low convergency and record diffraction data while keeping track of the crystal's movement by means of imaging, is nowadays realized by various methods which, differ in terms of illumination mode defining the probe size or diffraction area and convergency, the applied tilt sequence and the imaging protocol for crystal tracking (Gemmi *et al.*, 2019).

The PED-ADT data collection transpires in a series of electron diffraction patterns, each step an integrated intensities pattern is recorded by oscillating the beam using precession (Mugnaioli, 2009), and the goniometer moves the crystal in defined steps (0.2° – 1°). A typical collection range for a single crystal 121° or $\pm 60^\circ$ around the zero-point of the goniometer (Fig. 2a). The range obtainable by a given crystal will depend upon the given geometric restrictions of the microscope, and the surrounding of the crystal, as described in Section “Sample Preparation and Crystal Selection”.

A few years later the method of Rotation Electron Diffraction (RED) (Zhang *et al.*, 2010) using the SAED mode was developed, where rather than applying precession the beam was stepped in very fine increments of 0.01° – 0.1° making fine slices through the reflections in order to find the reflection maximum (see Fig. 2b).

With the innovation in detectors technologies and the arrival of direct electron detectors like the Medipix 2 (Georgieva *et al.*, 2011; Llopart *et al.*, 2002), it was possible to collect diffraction data exactly analogously to single-crystal x-ray diffraction, where oscillating the crystal integrated the measured intensities, rather than moving the electron beam. As shown in Table 1, the full integration of the reciprocal space is achieved by applying either electron beam precession (PEDADT) causing a circular integration of a conical wedge, or electron beam tilt (RED) respectively continuous crystal tilt delivering a trapezoidal integration of a wedge in the direction perpendicular to the tilt axis (see Fig. 2). The high frame rates of direct detectors make it possible to continuously record electron diffraction data during the rotation of the crystal, this principle was first demonstrated by Abrahams group based on CMOS technology (Nederlof *et al.*, 2013), and the first structure was from the Gonen group (Shi *et al.*, 2013), not using a direct detector but using a TVIPS camera based on CMOS technology with high sensitivity and frame rate. Detectors used for electron diffraction experiments should have a large dynamic range and ($> 12\text{bit}$) and the detector size ($> 28\text{mm}$) minimal dead-time between frames (see Fig. 3).

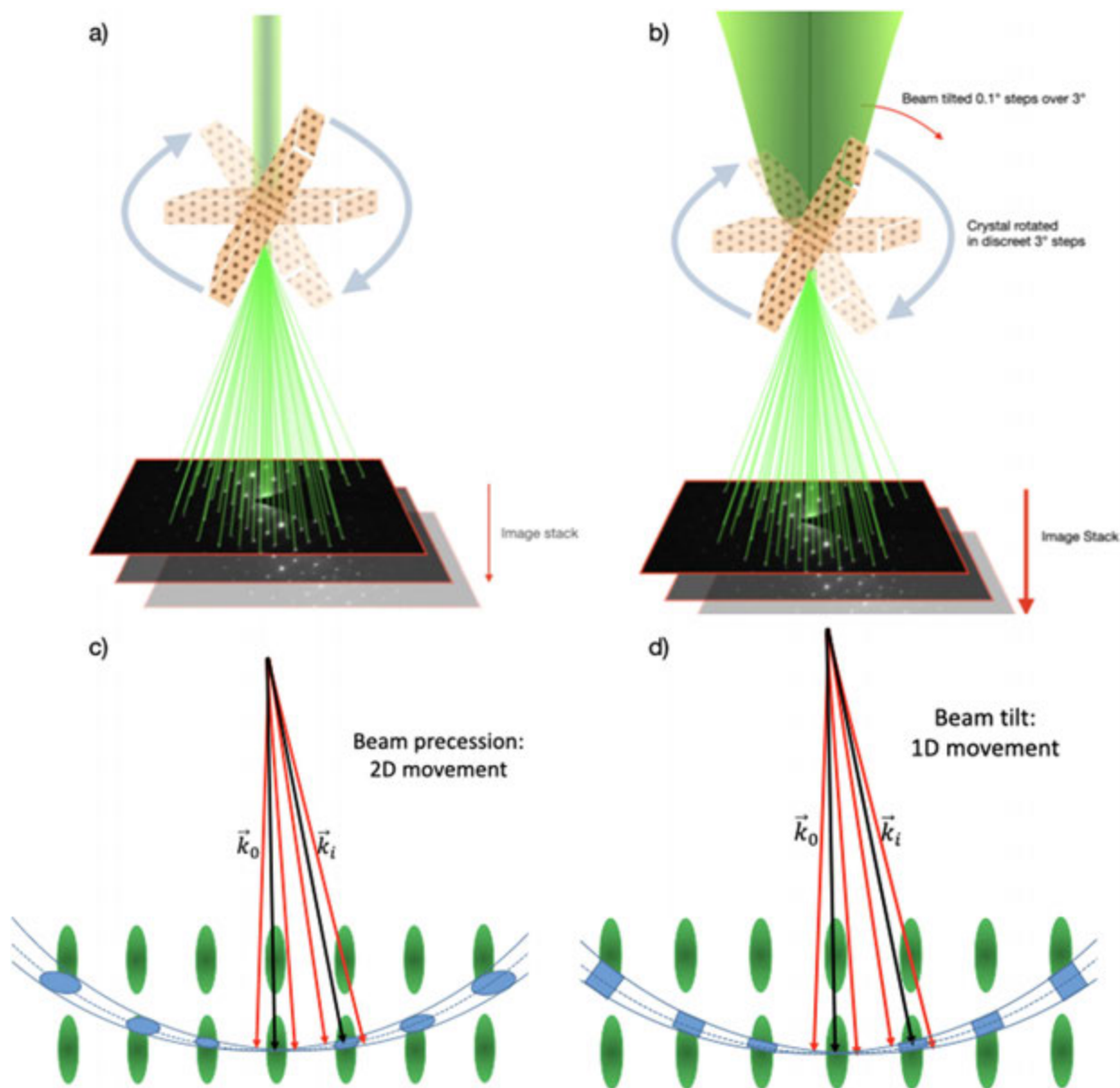


Fig. 2 ADT using NED (probe size 200–20 nm, tilt step ($^{\circ}$ –0.2 $^{\circ}$)) and RED using SAED (probe size >200 nm) experimental geometry for data acquisition. Below the difference in reciprocal space integration is sketched. (a) PED (left side), (b) Beam tilt (right side). (c) and (d) Blue areas: integrated reciprocal volume sections per tilt.

In the following, automated diffraction tomography (ADT) or (PED-ADT) will be used exemplarily to inform the reader about how 3D-ED experiments are performed in transmission electron microscopes and used to solve, *ab initio*, the average crystal structure of a material from a sub-micron sized crystal.

Sample Preparation and Crystal Selection

The correct preparation of the sample and the selection of a crystal is one of the most crucial tasks to gain reliable and useful diffraction data in order to perform single crystal structure determination. As necessary for all TEM experiments the sample needs to be electron transparent. While for HR-TEM and EELS ultrathin samples are needed, the requirements for the application of 3D-ED are less demanding. Usually, a powder produced by sample grinding in an agate mortar is dispersed in a liquid, which will not alter the sample, using ultra sound and applied onto the grid by drop casting or spraying it with an ultra sound impulse onto a grid (Mugnaioli *et al.*, 2009). For ultra hard materials a tungsten carbide pestle can be used. If the quantity of the sample is very limited or it tends to adhere to the glass surface of the vial it is possible to crush the sample carefully between two blades and to apply it dry to a grid, by dipping the

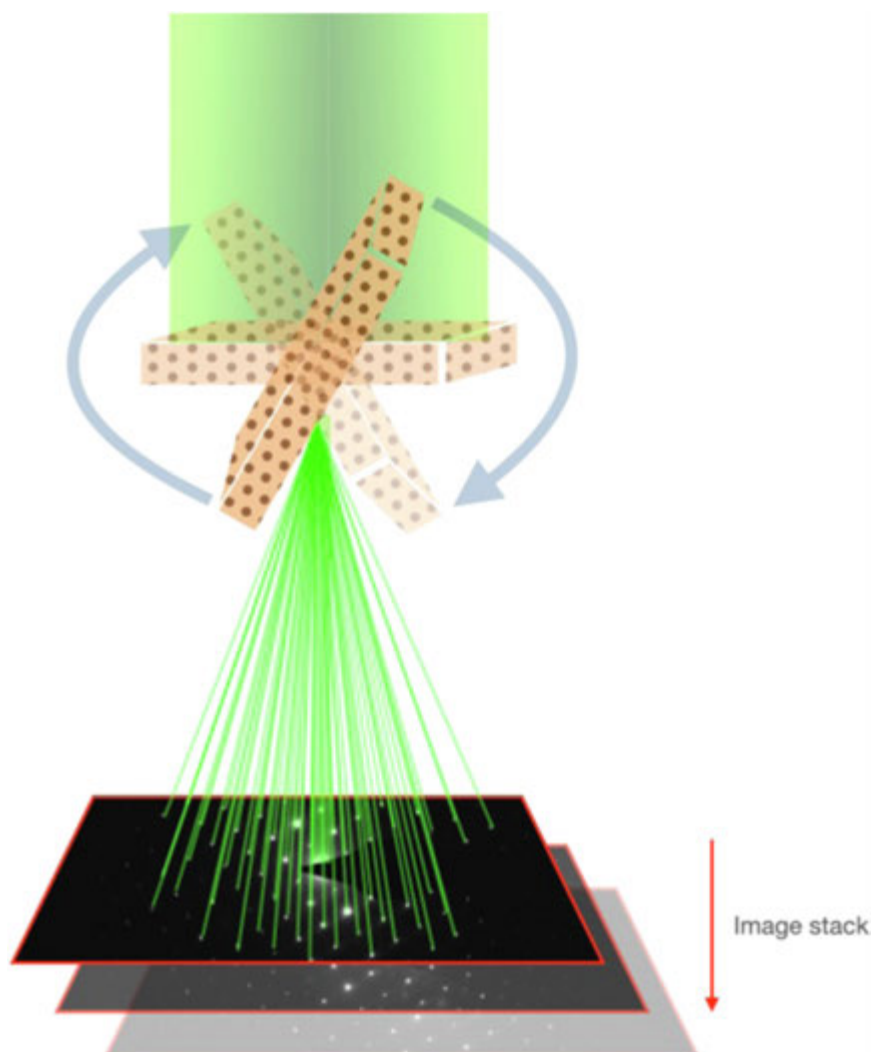


Fig. 3 Rotating crystal: The crystal is continuously rotating in the electron beam, with a fast detector reading out the frames at a specified time interval.

Table 1 Comparison of three dimensional electron diffraction techniques imaging and data acquisition modes

Method	Imaging mode	Probe size	Crystal movement	Data acquisition	References
Automated diffraction tomography (ADT)	μ Probe-STEM	200–20 nm	Static crystal with 1° – 0.2° rotation steps	1° – 0.2° steps wait for data readout	(Kolb <i>et al.</i> , 2007, 2008)
Rotation electron diffraction (RED)	Selected area electron diffraction (SAED)	> 200 nm	Static crystal with 3° rotation steps	0.1° – 0.01° steps wait for data readout	(Zhang <i>et al.</i> , 2010)
Precession-assisted automated diffraction tomography (PED-ADT)	μ Probe-STEM	200–20 nm	Static crystal with 1° – 0.2° rotation steps	Integrated data 1° – 0.2° steps wait for data readout	(Mugnaioli <i>et al.</i> , 2009)
Integrated electron diffraction tomography (IEDT)	Selected area electron diffraction (SAED)	> 200 nm	Continuous rotation	step size determined by frame acquisition, 0.3 – 1°	(Nederlof <i>et al.</i> , 2013; Shi <i>et al.</i> , 2013; Gemmi <i>et al.</i> , 2015; Yonekura <i>et al.</i> , 2019)
Fast & automated diffraction tomography (FAST-ADT)	STEM nanobeam diffraction	200–20 nm	Static crystal with 1° – 0.2° rotation steps	Step-wise wait for data readout	(Plana-Ruiz <i>et al.</i> , 2020)

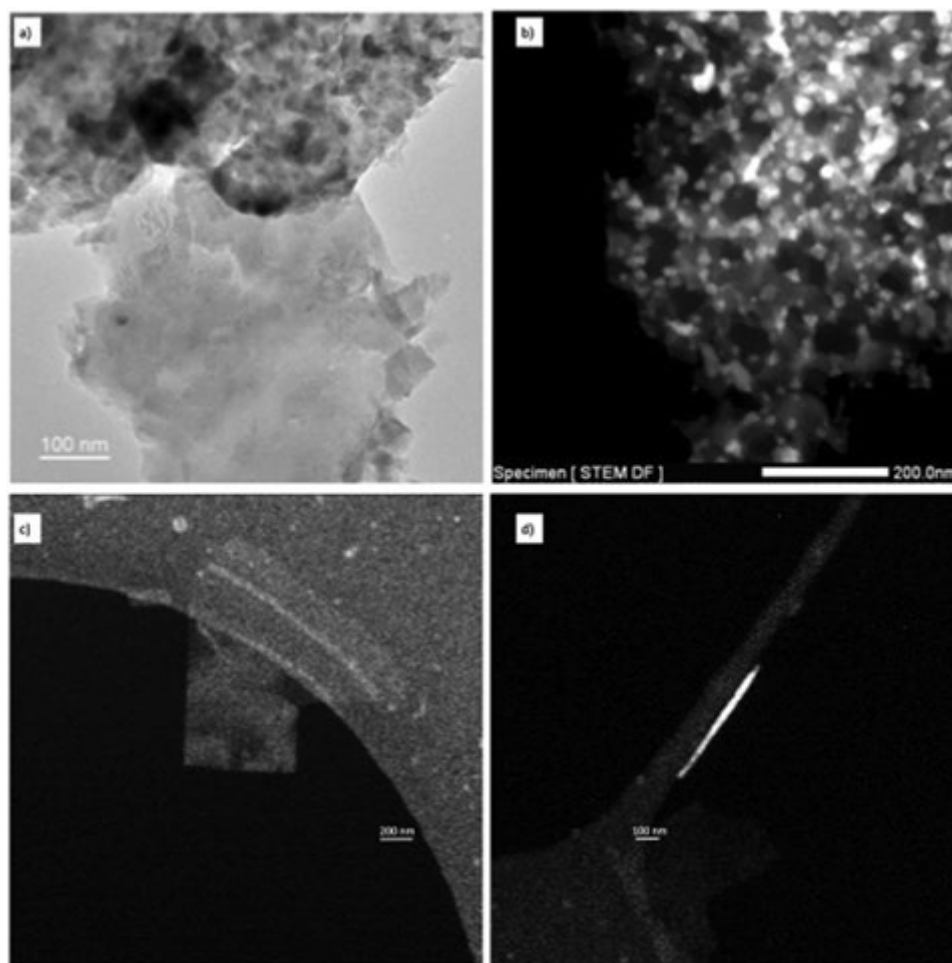


Fig. 4 TEM image of glass ceramic sample prepared as powder on continuous carbon support (a); STEM-DF image of glass ceramic sample prepared by ion milling (b) STEM-HAADF image of zeolite RUB-05 powder prepared on holey carbon support. Crystal positioned planar on the grid (c) and in the upright position (d).

TEM grid into the material and knocking the excess gently off the grid by tapping the tweezers holding the grid. A second, more tedious way is the preparation of thin films by ion-milling ([Fig. 4\(a\)](#) and [\(b\)](#)), described in detail by [Fetzer et al. \(2021\)](#).

Electron diffraction experiments are not as sensitive as HR-TEM to additional background originating from the carbon film. Thus, usually a continuous carbon support is used, which at the same time allows better heat and charge conduction and prevents the particles from falling through the holes in the grid. One exception is in the case of preferred orientation, where a holey carbon film is used to allow the crystals to be attached in an upright position at the rim of the holes, as shown in [Fig. 4\(c\)](#) and [\(d\)](#).

In order to acquire high quality 3D-ED data, a single crystalline grain should be selected. If the crystal is separated from other particles the probe size can be chosen freely and the tilt range is only limited by the sample holder and the microscope geometry [Fig. 4\(c\)](#). If it is attached to other crystals or embedded in a thin foil, as shown in [Fig. 4\(a\)](#) and [\(b\)](#), the tilt range is limited by the angles where the grain starts to overlap with other grains. Rotating the grid inside or outside the TEM can help to optimize the position of the crystal towards the tilt axis and change the achievable tilt range significantly.

In the special case of nano crystalline glass ceramics, thinned samples are recommended. The grains in powder samples, see [Fig. 4\(a\)](#), are usually thicker for eg., not overlapping with other grains only at the very rim, some tend to break at preferred grain boundaries and are surrounded by a thin edge of amorphous SiO_2 glass causing problems with imaging and tracking the grain over the whole tilt range. Powder samples have the advantage that the sample is not likely to be altered. In thinned samples, the grains are much more visible and less overlapped. In a corresponding powder sample can not be detected anymore. But one has to be careful to not introduce artifacts as many glass ceramics containing alkalis are beam sensitive. Another problem in multiphase systems is that one phase might be removed preferentially as it is the case for the silica glass matrix in the sample in [Fig. 4](#). In this sample Quartz crystals found in a corresponding powder sample cannot be detected in the thin foil anymore.

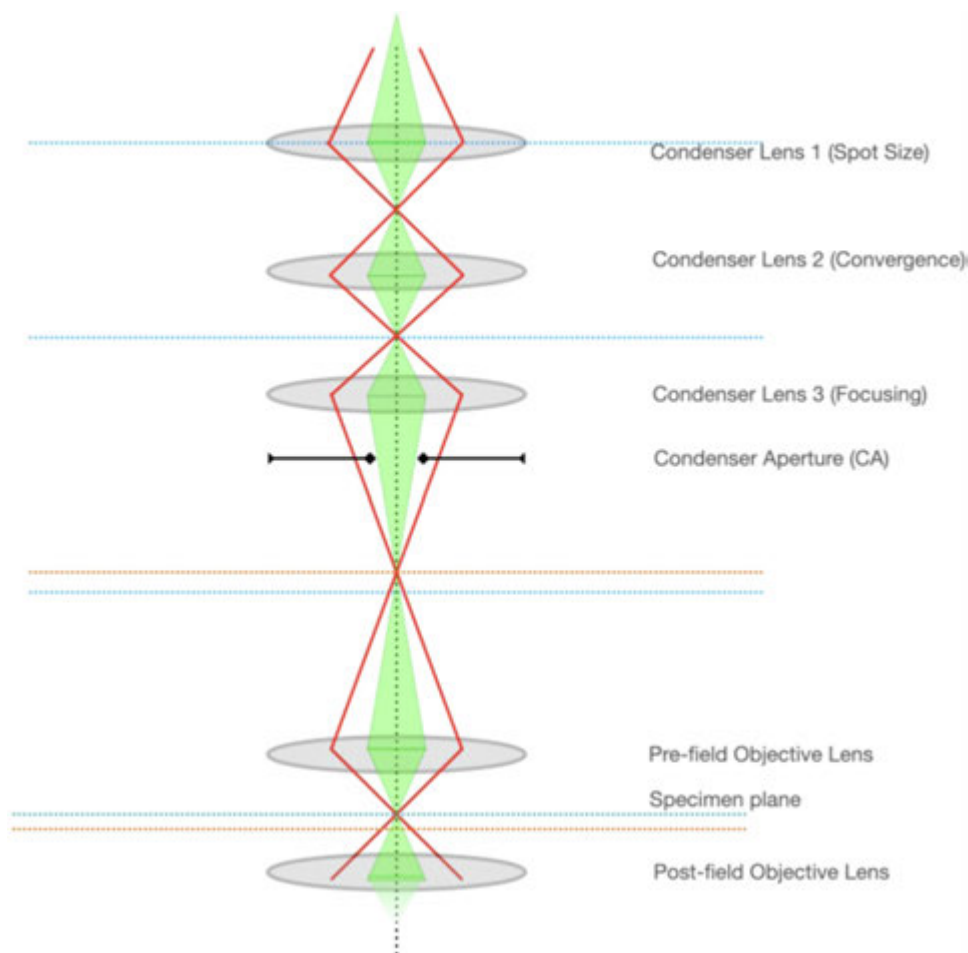


Fig. 5 ADT beam alignment in STEM mode with a small 10 μm C2 aperture to limit the beam size and provides higher coherency.

Illumination Mode and Imaging

In general, 3D-ED experiments apply imaging for crystal searching and tracking combined with electron diffraction for data acquisition.

The ADT experimental geometry uses a small narrow parallel beam (NED) to collect the diffraction data providing practical advantages over SAED. The illuminated area during data collection is limited to just that of the crystal which minimizes the background and improves the signal to noise ratio for the diffraction spots, which is of particular importance for low Z materials having significant amounts of inelastic scattering and therefore a high background in the measured intensities (Plana-Ruiz, 2021). It also reduces the probability of accidental collection of data from a neighboring crystal in another orientation. In addition, crystals in the surrounding area are not being damaged and for beam sensitive material a fresh part of the crystal can be selected by moving the beam over the crystal during a tilt sequence Fig. 5.

In comparison to TEM imaging, STEM does not need the lower objective lens and the image is formed from a sequentially recorded signal (Cookman and Bangert, 2021). Therefore, the electron beam can be positioned exactly on the ROI without errors caused by the aberrations of the objective lens. Another advantage of the STEM geometry is that it is easy to switch from imaging, where the beam is convergent for crystal searching and tracking, by changing a minimal number of lenses in order to defocus the beam to make it parallel for the collection of discrete reflections, referred to as the Bragg diffraction patterns. Thus, the ADT method utilizes μSTEM -HAADF imaging, where the mini lens is excited, combined with NED, where only the focus of the upper pole piece and the diffraction lens current need to be adapted to switch the modes. Agglomerated samples like glass ceramics are difficult to track, because of strong Bragg contrast changes during the tilt. Here, a HAADF detector is helpful as well and a smaller camera length should be selected for imaging. Using the NED illumination mode, where electron dose rate is reduced strongly, it is difficult to image the crystal in TEM mode. This is especially true for very thin crystals. For example the thin platelets of the zeolite sample, as shown in Fig. 4, were not visible in TEM using the NBED setting, but could be detected by the μSTEM -HAADF technique.

The ADT technique can more effectively track an individual crystal. Even if the crystal of interest is part of an agglomeration or within a matrix of material it will still be possible to collect and analyse the 3D electron diffraction from the crystal successfully.

One example is a solid polyphase material like glass ceramics, as shown in Fig. 4(b). The NED probe size should be adapted according to the projected size of the grain perpendicular the tilt axis at highest tilt angle as shown in Eq. (1).

$$\text{Grain dimension}_{x^\circ} = \text{Grain dimension}_{0^\circ} * \cos(x_{\max}^\circ) \quad (1)$$

TEM Set-up and Data Collection: Automated Diffraction Tomography (ADT)

Electron Diffraction (ED) patterns are collected by ADT while the crystal is tilted sequentially in fixed-tilt steps in the range of 1–0.2° depending on the goal of the experiment (Remennik *et al.*, 2012; Plana-Ruiz *et al.*, 2020). Whereas a standard crystal structure analysis is usually successful with 1° steps, a quantitative analysis of crystal defects, like stacking faults, demands a better scan of the reciprocal space by steps of 0.2° or lower.

Once a crystal of interest has been identified; the next step is to align the crystal to the eucentric height, ensuring it will be within the field of view during the tilt series. TEM stages are not precise enough to keep the crystal at the eucentric point, thus, the crystal will move away from its position under the beam throughout the tomographic series and crystal tracking is needed. If a crystal is large enough and separated on the grid, the goniometer sample shift, often used for SAED acquisition like for RED, can be applied to move the crystal back, but this is hardly applicable for agglomerated nanocrystals. In the ADT method the crystal can be tracked by recording an image after each tilt step and positioning the beam through a beam shift manually or according to a shift value derived from an auto-correlation of two images. In the FAST-ADT method a crystal tracking file can as well be initially set-up by acquiring images for example in 5° steps and calculating beam shift values by image correlation. By applying these values in a second tilt operation it is possible to keep diffraction conditions throughout the whole tilt series without intermediate acquisition mode changes. This approach allows the recording of ADT data sets of several crystals situated next to each other automatically in one go as well as continuous rotation of the crystal (Plana-Ruiz *et al.*, 2020). The ADT data acquisition protocol defines how often the acquisition mode is switched between imaging and diffraction. It can range from switching after every tilt step to switching one time between recording a crystal tracking file and data acquisition.

In summary, applying ADT, PED-ADT or FAST-ADT a general sequence for using μ STEM-HAADF together with NED includes (Mugnaioli *et al.*, 2009):

- Set-up a convergent beam with upper objective lens focussed on the sample for imaging recorded by HAADF.
- Set-up a parallel or quasi-parallel beam and define beam diameter for diffraction experiment recorded on CCD, CMOS, Direct Detector.
- Select an appropriate crystal and align it to eucentric height.
- Define the accessible tilt range, where the crystal will not be eclipsed by other features on the grid.
- Select a crystal tracking method, as described below.
- Start the ADT data acquisition protocol.

When precession is applied to integrate the data, after a careful alignment, as described in Plana-Ruiz *et al.* (2018) precession will be on during both the electron diffraction data collection and crystal imaging.

As demonstrated in Fig. 6 the precessing of the electron beam integrates the reciprocal volume. As the beam precesses around the hollow cone it rocks the Ewald sphere back and forth integrating a slice of reciprocal space, the width of the integration is determined by the size of the α angle, the semi-angle of the precessing beam, typically between 1° and 2°. The precession angle, α , is set to an angle such that it overlaps the integration of reciprocal space between the crystal rotation steps, meaning all reflections within the accessible reciprocal volume will be integrated. (see also Fig. 1).

The crystal is repeatedly tilted by the predetermined step size until the crystal reaches a geometric restriction of the experimental setup, which impedes any further data acquisition. This can be caused by a range of circumstances, from overlapping crystals during the tilt series, to a grid bar starting to shadow the crystal, or the goniometer reaches a physical limit. Alternatively, the crystal may show significant signs of radiation damage, typically observed by the Bragg spots at the higher resolutions being no longer observed, or being significantly weaker as the data collection progresses (Kolb *et al.*, 2010).

Data Processing and Analysis

In order to process and analyse the acquired data from a randomly orientated crystal, it is necessary to reconstruct the diffraction space volume, which will enable us to find the crystal orientation, unit cell parameters as well as define possible space groups before extracting the reflection intensities (Kolb *et al.*, 2019; Gorelik *et al.*, 2012).

The first significant difference between x-ray and electron data processing is the initial data processing step, aligning all of the diffraction patterns to a common center point, the main beam. Even an offset of a few pixels causes a blurring in the reconstructed volume. During data acquisition, switching between direct and reciprocal space induces hysteresis in the TEM magnets, leading to a small shift in SAED diffraction patterns. ADT, using NBED, shifts the beam to correct for the crystal shift during a tilt series (see section “Illumination Mode and Imaging”). If the pivot points are not accurately aligned, the beam shift will cause a remaining beam tilt and thus a significant diffraction shift. If a beam stopper was used during data acquisition, the center of the diffraction

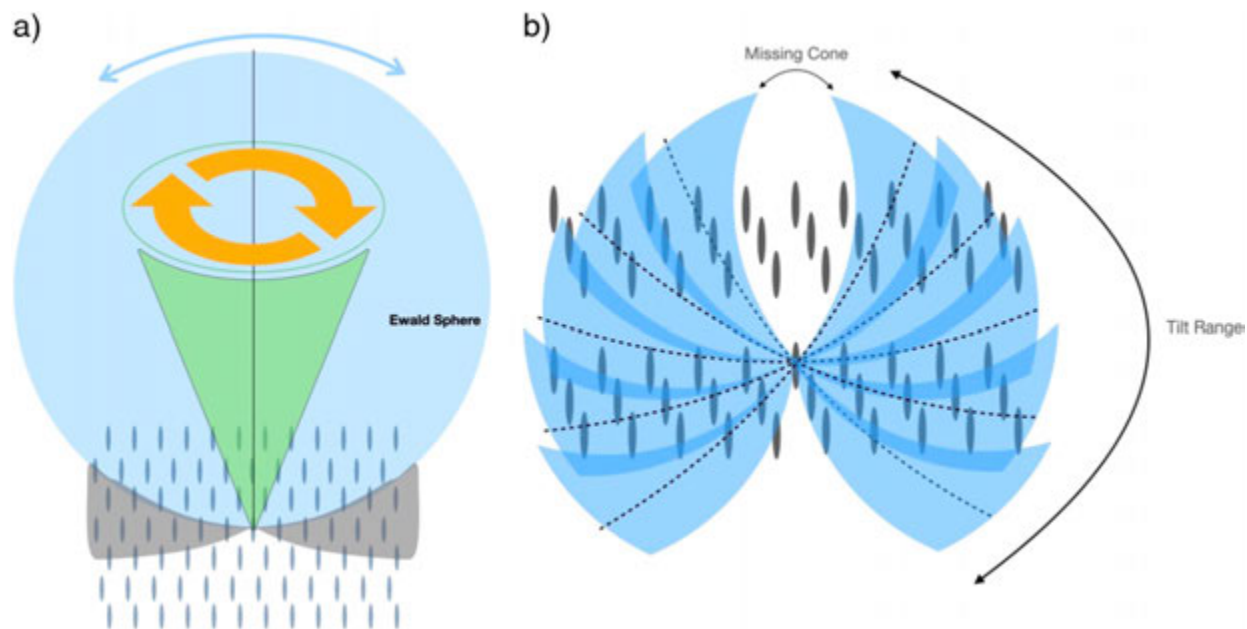


Fig. 6 Precession reflection integration (a) the integration caused by the electron beam precession for one cut of reciprocal space, (b) A series of precession integrations taken over successive crystal tilt angles, note the overlap of integration to maximize the integration of the reciprocal volume.

patterns can be found by assigning half of the distance between Friedel pairs as the center. Usually, NBED mode allows one to work without a beam stopper and the maximum intensity within the central diffraction disk can be automatically located by assuming the highest value in the image, ignoring any hotspots, i.e., ensuring the central disk is larger than a few pixels. There are occasions when this is not the case due to large intensity variations caused by dynamical scattering or for very strong scatterers; these occasions can be checked for by manual inspection of the data. Next is to locate the spot positions on the stack of the centered diffraction patterns. The simplest way to search for the reflections is to assume any cluster with a user-defined number of members, being pixels above a user-defined threshold, as a Bragg reflection. Ideally, these clusters of pixels above the threshold should be round, or at least oval, but this is not an assumed condition of assigning the reflection spot.

The identified reflection positions are necessary for tilt axis determination, a critical step in obtaining a high-quality reconstruction of the reciprocal volume thus for cell parameter determination. In a TEM, the position of the tilt axis is mechanically defined by the goniometer axis, but the position in a diffraction pattern depends on the camera length. Inaccuracies in the diffraction lens current and the alignment for NBED with quasi-parallel illumination, when the diffraction lens excitation is used to adapt the focus of the diffraction pattern, change the camera length to an effective camera length and cause scaling and rotation of the diffraction patterns.

To search for the tilt axis a 3D reciprocal space using the determined 2D reflection positions is set up for all tilt axis values $0\text{--}180^\circ$. The difference vectors, which resemble an auto-correlation of the reciprocal space setting up a spherical surface (similar to a Wulff net), are projected into a stereographic projection as shown in Fig. 7. Each projection is analysed for its sharpness (variance) reaching a maximum for the correct tilt axis position according to a maximum of difference vector correlation (Fig. 8). An identified tilt axis angle from a coarse 1° search can be refined using a finer step size, e.g., 0.1° , $\pm 2^\circ$ around the preliminary tilt angle search, to obtain a more precise tilt axis angle (Fig. 8).

As an additional aspect, the curvature of the Ewald sphere needs to be taken into account. The gradient of the Ewald sphere curvature is small for electrons due to the large radius of the sphere. (Recall that the radius of the Ewald sphere is $1/\lambda$ with λ being between 0.019 and $0.025\text{ \AA}$ for most electron diffraction experiments). Taking account of this curvature is especially critical for the high-resolution reflections, ensuring that the spots will be inside the integration box and adequately integrated. These corrected spot positions will enable a more precise calculation of the unit cell parameters.

The unit cell determination is based on the reconstructed 3D diffraction space using 2D reflection positions, and again the difference vector space of all reflection positions is calculated. The difference vectors, which should form a lattice in difference vector space, will vary from a perfect lattice, typically by a few pixels. These inaccuracies manifest as bundles of vectors, which look like a sheaf of wheat at harvest time, rather than the vectors perfectly aligned on top of each other at a single length and orientation. Cluster analysis, in this case DBSCAN (Schlitt *et al.*, 2012), is applied to overcome the noise problem and only accept difference vectors within a pixel or two in length and a small amount of variation in angle, along with a minimum number of points in order to be considered a cluster. The centroid of this cluster is the lattice point. In applying this clustering method, we omit points from reflections from overlapping crystals, hot spots or detector defects, which have not already been taken into account.

From the clustered difference vectors, we take the three shortest non-collinear vectors to be the basis of lattice vectors. Each cluster should be an integer multiple of the shortest basis vectors. The difference vector space is not sensitive to serial or planar extinctions, but adjustments are required in the case of integral extinctions found for centered cells. The cluster routines strongly

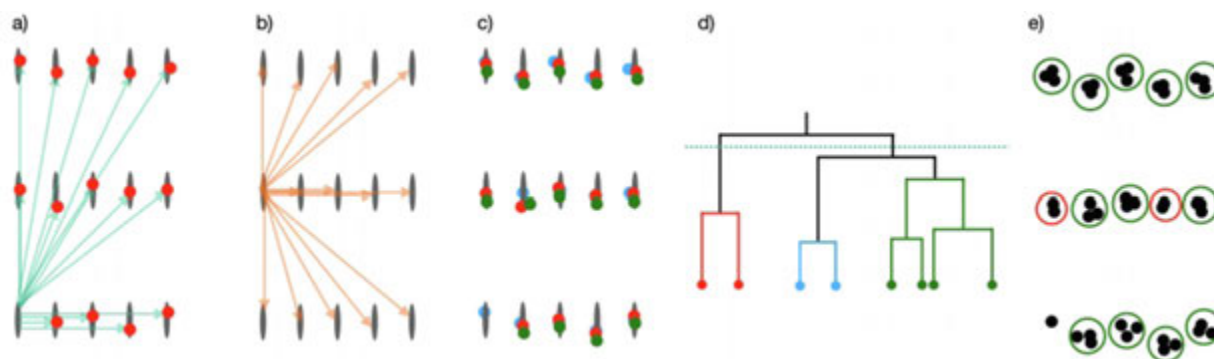


Fig. 7 Difference vector space, and the clustering of vectors to achieve the unit cell parameters. (a) the difference vectors from one reflection to all others. (b) difference vectors from another reflection to all other reflections. (c) each reflection then accumulates a number of points the vector points to, these should form a lattice mirroring the crystal lattice. (d) all the difference vectors are then clustered by length to find the unit cell parameters, these are determined by the clustering parameters of neighborhood and number of points within the neighborhood. A dendrogram shows the graphical representation of the cutoff (e) the cluster points which satisfy the cluster analysis.

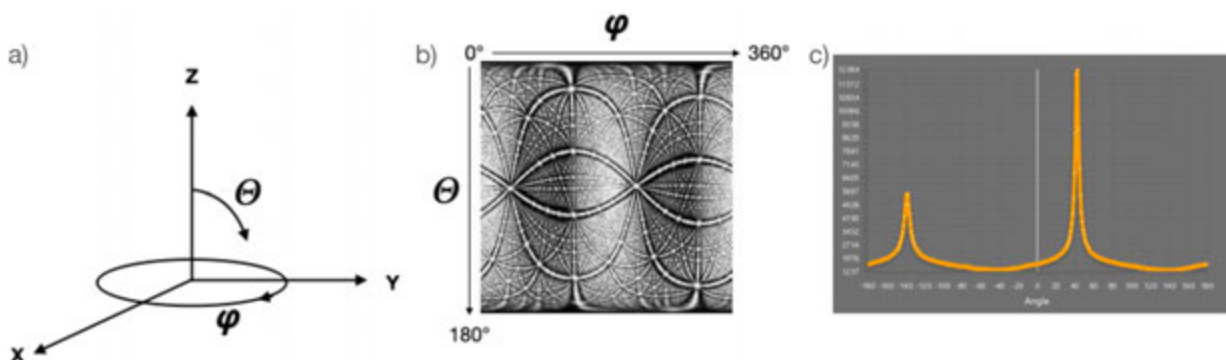


Fig. 8 Scheme of stereographic projection, stereographic projection for example SnN_2O_2 (see section “Examples”) using optimal tilt axis 42.4° and variance analysis of the tilt axis search.

depend on the parameters of the 2D peak search and fail if data is too sparse demanding a definition of the cell based on visual examination of the reciprocal space (Schlitt *et al.*, 2012). Errors in cell parameters range around 1%–2% for cell axes and 1° for angles. This can be improved by taking inaccuracies in tilt angles, tilt axis position and effective camera length into account.

With the unit cell determined and the curvature of the Ewald sphere taken into account, the positions of the Bragg peak intensities can be found in every 2D diffraction pattern and integrated, after individual background subtraction, over a user-defined area. This area should be selected to cause no overlap with neighboring integration areas, large enough to cover even strong reflections adequately and small enough not to overestimate background contribution. Since reflections have a rod-like shape in reciprocal space due to the excitation error they will be cut several times, thus, appearing in several consecutive diffraction patterns. A plot of these intensities, as provided in Fig. 9, is called a rocking curve, showing one maximum for data acquired without beam precession and two maxima if precession is applied. Lit for double peak: Palatinus *et al.* (2019). For electron diffraction data there are two main approaches to measuring the Bragg spot intensity, by analysis of the rocking curve one, fully integrate the peak shape and sum the total intensity, or take the value of the highest detected intensity within the Bragg peak assuming this to be the best approximation.

For crystal structure solution based on electron diffraction data, there are a few statistics to check before proceeding with solving the structure by for example direct methods. A first measure of the data quality is the internal R-value, which reflects the similarity of symmetrically equivalent reflections for this Laue class. Data sets with $R_{\text{int}} > 25\%$ are usually due to experimental errors or very strong dynamical effects or might indicate the choice of a wrong space group, or additional crystallographic features like twinning or diffuse scattering or simply the choice of a wrong space group. A second indicator is the isotropic Debye-Waller factor B_{iso} , which should be positive and around $2 \text{ \AA}^2$. From our experience, a negative B_{iso} is another indicator of dynamical effects or a wrong space group. Due to limitations of the tilt angle defining the size of the missing wedge (see Fig. 6 right for schematic drawing and Fig. 10, bottom right for experimental data) the number of non-accessible reflections in the reciprocal space can be large. This lack of diffraction data, which is especially problematic for space groups with low symmetry, causes uncertainties in the derived scattering density maps, thus, leading to poorly defined

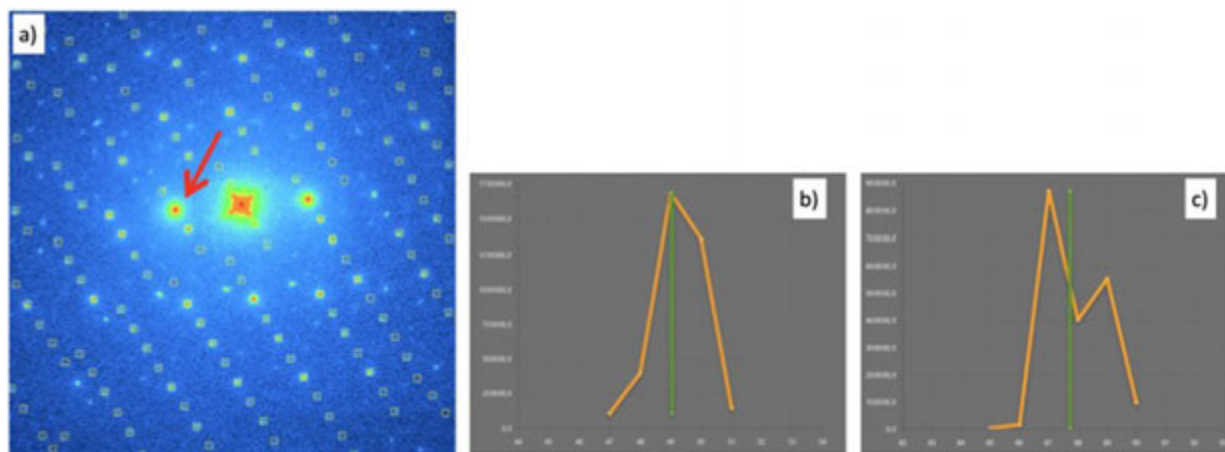


Fig. 9 Diffraction pattern selected from a tilt series using ADT method (a). Rocking curve of reflection 2–3–1 as indicated by red arrow in a. The green line indicates the reflection position calculated from cell parameters (b) and for comparison Rocking curve of reflection 1–30 taken from a PED-ADT acquisition (c).

atomic positions. A crystal structure can be solved usually with a completeness of the reciprocal space of approx. 40%–60% (see sample LaPO_4 in see section eg., Fig. 14), but for a reliable refinement of atomic positions and displacement factors a high completeness ($> 80\%$) is desirable. The resolution should extend beyond $1.2 \text{ \AA}$, for many structures it will extend even out to $0.6 \text{ \AA}$ depended on the scattering power and the long-range order. However, the data used for structure solution is usually limited to $1 \text{ \AA}$ because higher-resolution reflections are usually the first to be affected by radiation damage and thus are the most prone to errors which may interfere with the assumed statistical distributions of direct methods.

To determine a set of possible space groups, the same procedure as in x-ray single-crystal approach, rules using systematic absences are applied as demonstrated. While screw axis extinctions are only visible in main zones, extinctions based on centering or glide planes, as marked in Fig. 10 with red circles, are directly visible in the 3D volume. For example, in all three views of the reconstructed volume from a PED-ADT data set (sample SnN_2O_2 ; see section “Examples”) glide planes are visible. The view down the *a* axis (top left) reveals a *c* glide plane perpendicular *b* (extinction rule $0kl: l = 2n$), the view down the *c* axis (top right) shows a *b* glide plane perpendicular *a* (extinction rule $h k 0: k = 2n$) and the view along the diagonal vector $(1-10)^*$ (middle left) exhibits a *n*-glide plane perpendicular *c*. The *n*-glide plane is directly visible in a cut of the $[001]$ zone from the reciprocal volume (middle right) showing the chess pattern like intensity distribution (extinction rule $h k 0: h + k = 2n$) as well as the area of missing reflections due to the missing wedge problem. In combination, this leads to the centrosymmetric space group Pbcn (#60). One small note of caution, systematic absences rules sometimes may be violated due to dynamical scattering. If this is the case look at the surrounding rows of reflections and compare the magnitude of the scattering to the reflections which violate the systematic absences. If they differ significantly in size and shape from the allowed diffraction spots, then it will be permissible to try this space group and argue that the symmetry breaking reflections are dynamical scattering anomalies. In Fig. 10 (bottom left) the view of the reciprocal volume from an ADT data set down the *a* axis is provided. The violations of the extinction rule $0kl: l = 2n$ of the *c* glide plane clearly visible here are lost due to the application of electron beam precession in the comparable view in Fig. 10 (top left).

There are several direct methods programs for solving crystal structures, available from the x-ray crystallography community the most popular two are SIR (Burla *et al.*, 2015) and SHELX (Sheldrick, 2008). To deploy these programs for structure solution with electron diffraction data ensure electron scattering factors (Susi *et al.*, 2019) are being used rather than x-ray scattering factors. Input the data parameters obtained from the processing of the electron diffraction patterns, a list of *hkl*s and intensities, the unit cell parameters and a space group.

When analysing the results of the direct methods software, the crystallographic R-factor for a single crystal x-ray experiment is typically only a few percent. Whereas for electron diffraction data, the dynamical scattering causes this number to increase to 20%–25%, values more akin to the structure solution of macromolecular crystallography (Reimer, 1984). Occasionally, even with high R-factors a structure can be considered as solved if there is an apparent reason for the data to be sub-optimal such as diffuse scattering from defects, or guest molecules and ions within porous materials (Jiang *et al.*, 2011).

Once a structure has been identified by direct methods, it is critical to perform structure validation, typically in the form of refinement. While kinematic refinement can work for electron crystallography data sets, we again face the issue of dynamical diffraction (Palatinus *et al.*, 2015). For data sets with low amounts of dynamical diffraction present, kinematic refinement, of the type.

Examples

Keeping the focus on oxides and especially glass ceramics this section introduces some examples of crystal structure analysis from powder and solid material. In a first step, the analysis of a high pressure modification of $\text{Sn}_2\text{N}_2\text{O}$ is used to explain the general

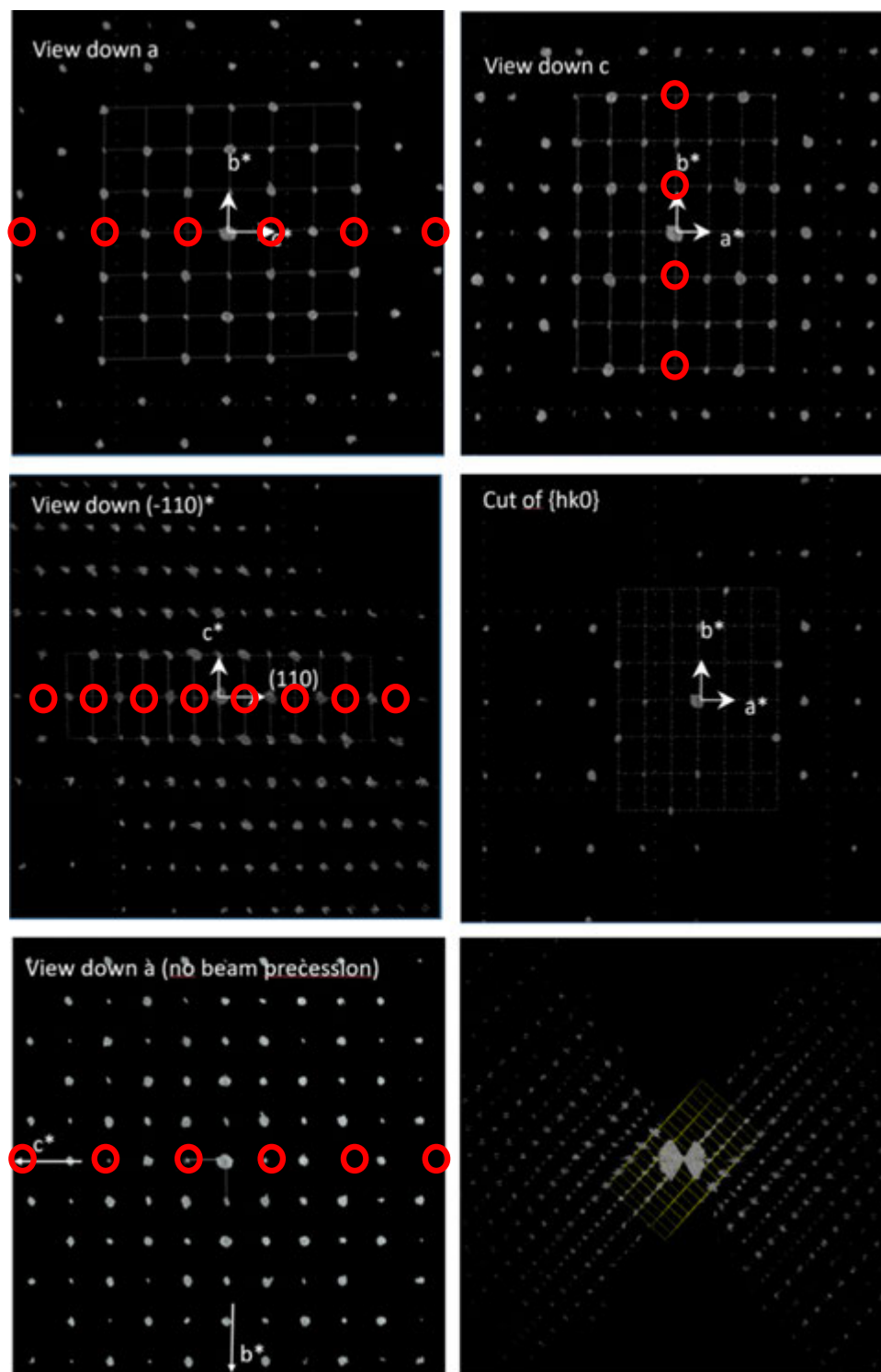


Fig. 10 Three-dimensional reconstruction of the reciprocal space based on PED-ADT data for sample $\text{Sn}_2\text{N}_2\text{O}$ (see section “Examples”). The diffraction volume with indicated extinct reflection rows (red circle) viewed along the a -axis (top left); the c -axis (top right); down $(-110)^*$ axis (middle left) leading to space group Pbcn . A cut of zone $[001]$ including the n -glide plane perpendicular the c -axis (middle right); a reconstructed reciprocal volume viewed down a axis from ADT data, (bottom left) for comparison with PED-ADT data (top left) view down tilt axis with a clear view of the missing wedge of 60° (bottom right).

procedure of an ADT experiment. As a second example the more challenging case of a polyphase nanocrystalline glass ceramic containing a previously unknown LaPO_4 polymorph measured with ADT will be discussed.

High Pressure Modification of $\text{Sn}_2\text{N}_2\text{O}$ (Bhat *et al.*, 2020)

The sample was synthesized in an HT-HP experiment at 20 GPa and 1200–1500°C in a large volume press from oxygen containing precursors (Li *et al.*, 2016). The resulting pellet (Fig. 11(a)) was crushed to powder. Synchrotron x-ray powder diffraction experiments (s-XRPD) revealed nicely resolved reflections of which the majority did not fit to any known crystal structure and a small quantity could be identified as remaining spinel Sn_3N_4 Fig. 11 (b). A structure solution based on XRPD data was not possible. The powdered material was dispersed in ethanol and sprayed on a carbon-coated copper grid using a modified ultra-sound sonifier (Kolb *et al.*, 2008). As shown in Fig. 11(c) a single crystal of approx. 200 nm size was selected, taking care that it sits vertically above or below the tilt axis at a sufficient distance to avoid interference from other crystals.

The accessible tilt range was identified to be $\pm 60^\circ$, defined by the limit of the tomography tilt holder used in a FEI Tecnai F30 equipped with a Super-Twin lens, and the probe size was set to 200 nm. μSTEM -HAADF images for crystal tracking were taken every 5° preliminary to diffraction data acquisition. A tracking file was stored including crystal shifts calculated by cross-correlation, which were used during subsequent ADT data acquisition with and without PED. After reconstruction of the three dimensional reciprocal space using eADT software (Kolb *et al.*, 2019) the cell parameters were derived ($a = 7.89 \text{ \AA}$, $b = 5.49 \text{ \AA}$, $c = 5.58 \text{ \AA}$, $\alpha = 89.9^\circ$, $\beta = 90.0^\circ$, $\gamma = 90.2^\circ$). The inspection of the reconstructed reciprocal space viewed in a , b and $(-110)^*$ direction reveals extinctions rules $hk0$: $k = 2n$, $h0l$: $l = 2n$, and $0kl$: $k + l = 2n$ indicating a c -glide plane perpendicular b^* and a n -glide plane perpendicular c^* . Using the derived space group Pbcn the cell parameters could be refined by Pawley-Fit on synchrotron X-ray powder diffraction data ($a = 7.8257(8) \text{ \AA}$, $b = 5.5315(5) \text{ \AA}$, $c = 5.5438(4) \text{ \AA}$) Fig. 10.

Extraction of intensity data from ADT as well as PED-ADT data was carried out with the software packages eADT and PETS for kinematical and dynamical refinement, respectively. Due to the high space group symmetry the completeness of the reciprocal space was close to 100%. The structure could be solved with both ADT and PED-ADT data based on 4529 respectively 4151 measured intensities with a limit of $0.8 \text{ \AA}$ resolution using SIR2014. Crystal structure refinement was performed using SHELX with a limit of $0.5 \text{ \AA}$ resolution covering the full width of the CCD detector. For structure refinement the quality of diffraction data is considered more important, thus, for kinematical refinement, PED-ADT data was used. In total 5176 single-crystal reflections were observed with a resolution of $0.5 \text{ \AA}$ resulting in 1046 unique reflections. After averaging, equivalent reflections in space group Pbcn . The final residual is $R_1 = 0.26$. Dynamical refinement in JANA 2006 reduced the residual further to $R_1 = 0.09$. Table 2 provides a comparison of atomic distances derived from DFT calculations in the SnN_4O_2 octahedron to the kinematic and dynamic refinement results.

High Pressure Modification of LaPO_4

A glass ceramic developed at the Fraunhofer Institute for Silicate Research ISC in Würzburg (Germany), from the SiO_2 , MgO , Al_2O_3 (MAS) system with nucleating agents Ti- and Zr-oxides as well as a series of oxide additives including La_2O_3 and P_2O_5 has been prepared by a 2-step heat treatment. Investigations by XRPD revealed several known compounds, but major reflections could not be assigned to any known phase.

As mentioned in section “Sample Preparation and Crystal Selection” the material was prepared for TEM measurement as a powder as well as a thin foil prepared by Argon thinning with a Gatan Duo Mill. The STEM-HAADF image of the thin foil in Fig. 12 exhibits crystal sizes in the range of 200 nm and below. The corresponding EDX-mapping reveals the distribution of the multiple phases present in the glass ceramic.

The grains containing Zr-Ti-O (Zr:Ti=2:1) mostly have an isometric shape and are predominantly between 20 and 40 nm in size. The La-P-O (La:P=1:1) grains have an elongated shape with lengths of up to 200 nm and a width of approx. 40nm.

For ADT experiments a probe size of 20 nm was selected, accepting that this gave a slight disk shape to the diffraction spots. The tilt range was set to $\pm 25^\circ$, which would shorten the size of the crystal along the tilt axis to 36.3 nm due to projection (see Eq. (1)).

Crystal structure analysis was successfully carried out on a series of different phases, but here the La-P-O phase will be discussed exemplarily. Cell parameters could be derived as: $a = 5.26 \text{ \AA}$, $b = 8.14 \text{ \AA}$, $c = 6.65 \text{ \AA}$, $\alpha = 90.2^\circ$, $\beta = 90.5^\circ$, $\gamma = 90.4^\circ$. For the

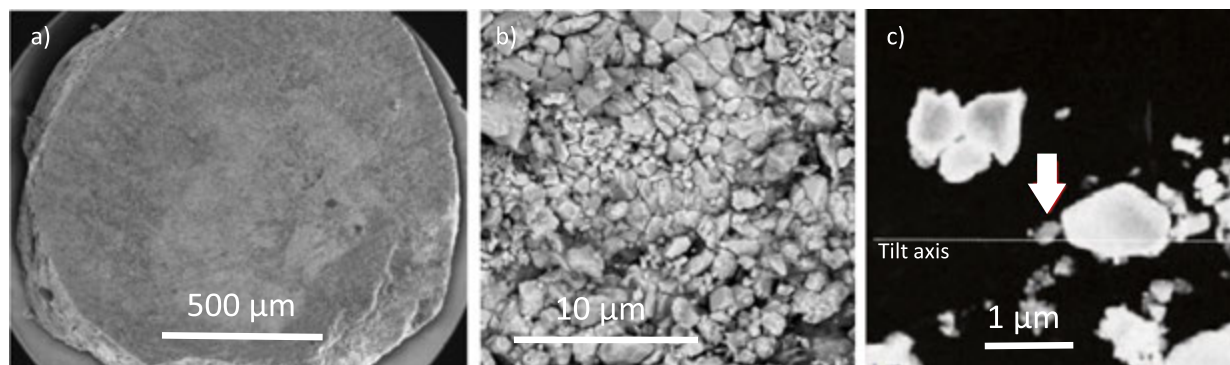
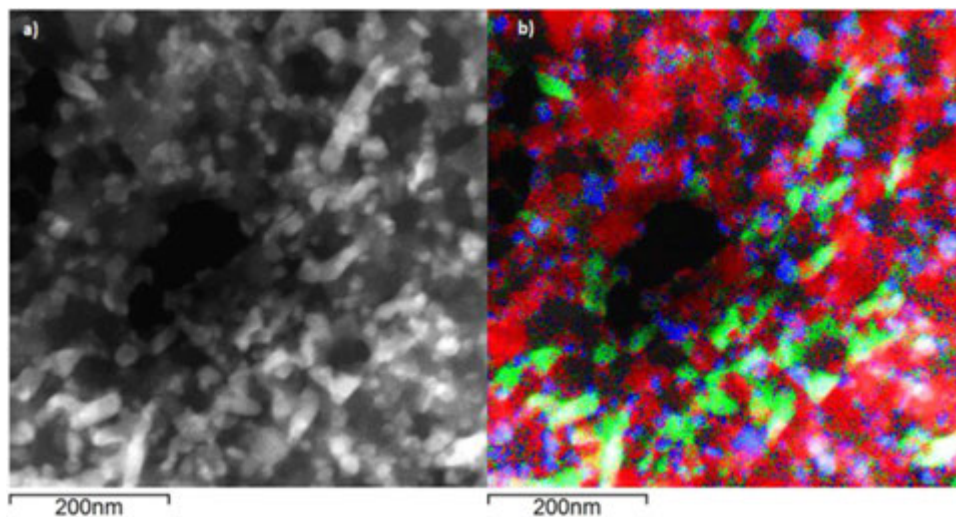
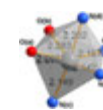


Fig. 11 SEM micrographs of HP-HT sample showing (a) an overview of the sample pellet after HP-HT treatment; (b) a zoom view showing crystals of varied dimensions; (c) a μSTEM -HAADF image showing the distribution of crystals on the TEM grid. The arrow indicates the crystal selected for ADT measurements and the dotted line the position of the tilt axis.

Table 2 Atomic distances of $\text{Sn}_2\text{N}_2\text{O}$ from different measurement and refinement strategies in comparison to DFT calculations. Labels of atoms as indicated in the Figure. Bond distances d (Å) with estimated standard deviations and their differences Δd (Å) from DFT and experiment

Bond	DFT	ADT (kinematic ref.)		ADT/PED (dynamic ref.)	
	d (Å)	d (Å)	Δd (Å) (DFT-exp)	d (Å)	Δd (Å) (DFT-exp)
Sn – O(a)	2.169	2.089(8)	0.080	2.110(3)	0.059
Sn – O(b)	2.343	2.323(11)	0.020	2.286(4)	0.057
Sn – N(a)	2.202	2.233(10)	– 0.031	2.190(5)	0.012
Sn – N(b)	2.174	2.107(8)	0.067	2.130(4)	0.044
Sn – N(c)	2.136	2.141(9)	– 0.005	2.124(4)	0.012
Sn – N(d)	2.223	2.183(9)	0.040	2.233(4)	0.010

**Fig. 12** (a) STEM-HAADF image of crystallized MAS glass ceramic (b) EDX-Mapping color code: AlMg(red), TiZr(blue), LaP(green), Si (not colored).

metrics of the determined cell, expected error ranges of 1%–2% for distances and 1° for angles would be indicative of an orthorhombic space group. A cut of the reconstructed reciprocal space, as shown in **Fig. 13(a)**, reveals a n -glide plane ($h0l$: $h + l = 2n$) and the a diffraction pattern selected from a second data set reveals the existence of a screw axis along b ($0k0$: $k = 2n$) **Fig. 13 (b)**. These extinction rules lead to the monoclinic space group $P2_1/n$. A Pawley refinement against XRPD data provided the cell parameters $a = 5.3251$ Å, $b = 8.2549$ Å, $c = 6.7799$ Å, $\beta = 89.94^\circ$.

Intensities extracted from ADT data sets delivered only a completeness of 40%–49% due to the limited tilt range often found for thin foil experiments. As a work around, non-processed ADT data sets from different crystals were merged and used for crystal structure solution. In **Table 3** the results for two merged ADT data sets (Cr_2 and Cr_6) and one PED-ADT data set (Cr_3) are provided. Revealing a distorted baryte structure instead of the expected monazite structure type stable at ambient conditions. While the space groups of both structures are the same, the cell parameter change is mainly described by the reduction of the monoclinic angle to around 90° due to a shearing motion along the a -axis being the most compressible axis in the monazite structure. The influence of the completeness of intensity information clearly visible by the anisotropic broadening of Coulomb map residual (in yellow) is clearly visible along the missing cone direction and the resulting structural distortion is clearly visible. The LaPO_4 crystal structure is provided in **Fig. 14** together with the scattering density map.

Diffuse Scattering

In addition to the analysis of an average crystal structure 3D-ED providing a three dimensional reciprocal space allows diffuse scattering to be used to investigate defects. Stacking faults, which are 2D defects in direct space for example, will cause 1D diffuse scattering, so called streaks, in the direction perpendicular to the stacked planes. The special benefit of ADT comes into play particularly when the stacking direction does not lie perpendicular to the electron beam but parallel causing diffuse streaks along the incident beam direction. For Zeolite beta, where polytypes of Zeolite beta A and B are closely intergrown, the streaks are found perpendicular to the electron beam but for Zeolite RUB05, the streaks were not directly visible. The average structure of both materials could be solved directly from the discrete reflections, the Bragg intensities. For quantitative analysis of the diffuse scattering single zones were cut directly from the reconstructed reciprocal volume, as shown in **Fig. 15(a)** and **(b)** reveals for zeolite beta two diffraction rows which exhibit streaks whereas the third line

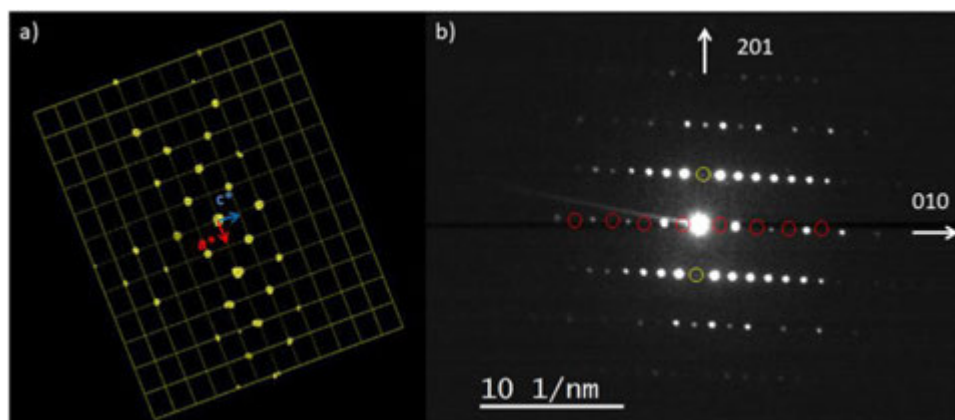


Fig. 13 (a) Three-dimensional reconstruction of the reciprocal space based on ADT data. Cut of $h0l$ including the n -glide plane perpendicular the b -axis with extinction rule $h0l:h + l = 2n$; (b) selected single diffraction pattern including b -axis with $0k0:k = 2n$.

Table 3 Structure solution based on kinematic approach using eADT with SIR14 on merged ADT data Cr2 and Cr6 and on PED-ADT data Cr3

	Cr2 and Cr6 (merged data)	Cr3
Completeness %	61.6 (45/49)	40.7
B_{iso}	1.76	2.59
R_{int}	25.6	13.6
$R(obs)$	26.1	26.9
$wR^2(obs)$	27.6	26.8
Reflections/Parameter	325/25	229/25
GOF(S)	1.73	1.65
Resolution (Å)	0.82	0.82

Note: Kolb, U., Krysiak, Y., Plana-Ruiz, S., 2019. Automated electron diffraction tomography – Development and applications. *Acta Crystallographica Section B* 75 (4), 463–474. Burla, M.C., *et al.*, 2015. Crystal structure determination and refinement via SIR2014. *Journal of Applied Crystallography* 48 (1), 306–309.

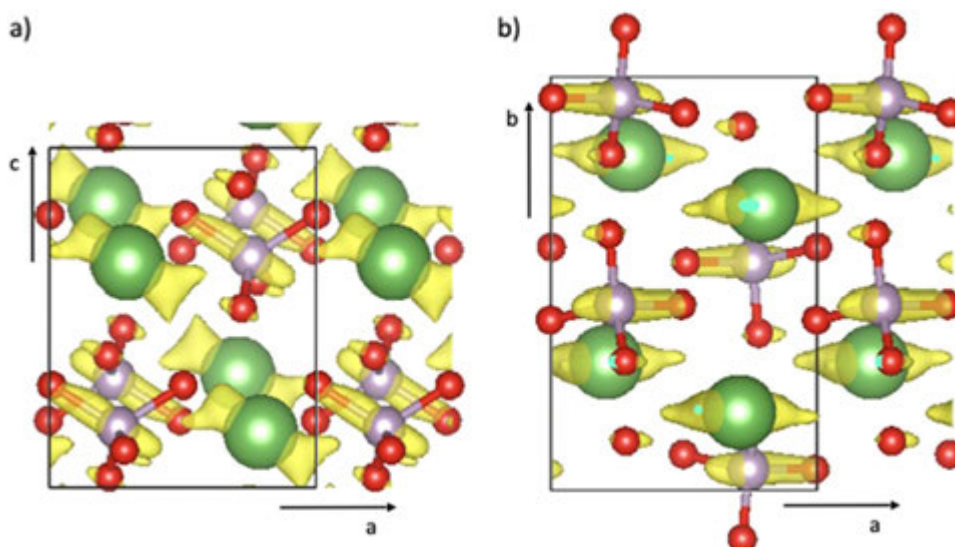


Fig. 14 $LaPO_4$ in the distorted baryte structure derived from a ADT data set with 40% completeness view down b -axis (a) and view down c -axis (b); yellow Coulomb map residuals are plotted using a $2\sigma(\Delta V)$ threshold (σ is the standard deviation of map values) calculated with JANA and visualized in Vesta.

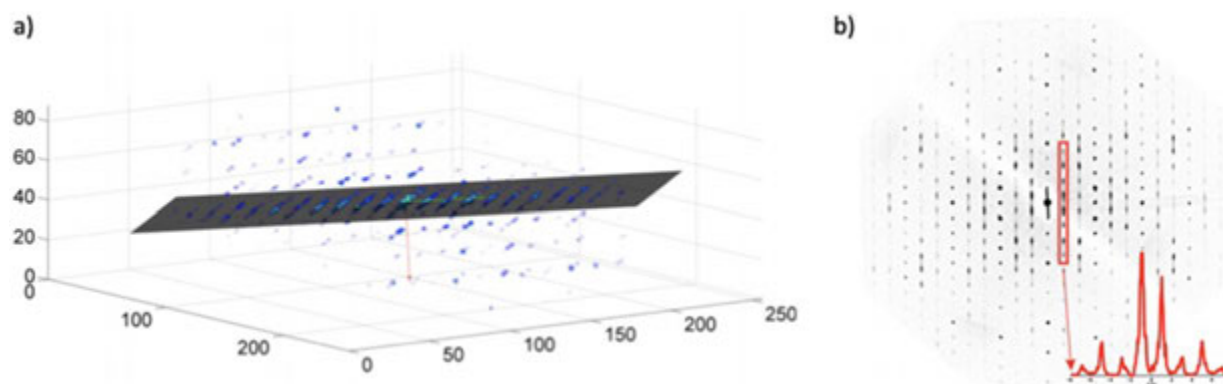


Fig. 15 Reconstructed reciprocal diffraction volume of Zeolite beta with diffuse streaks and indicated zone cut (a); [0 1 0] zone extracted by diffuse extractor (right) and intensity profile of diffraction line 10l (inset in red) (b).

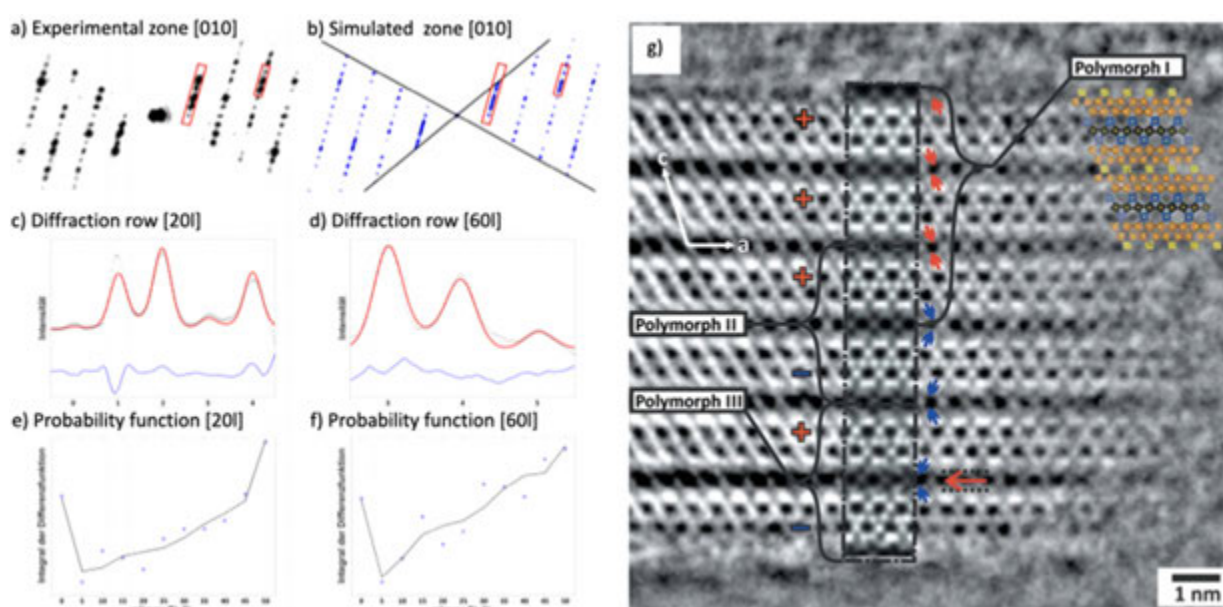


Fig. 16 Analysis of diffuse streaks for Zeolite RUB05 from zone [0 1 0]: experimental (a) and simulated (b) electron diffraction pattern; intensity profiles along reflection lines 20l (c) and 60l (d) as indicated in zone cuts by red rectangles: (experimental (grey line), simulated for stacking probability $p_x = 0.05$ (red line), difference (blue line); Diagram of the integrated difference function between simulated and experimental line profile as a function of the stacking probability of layer b for the line profile 20l (e) and 60l (f); HR-TEM reconstructed phase image zone [010] overlaid with polymorph I model and indicating the visible stacking sequence (g).

only contains discrete reflections indicating a coherent shift of $1/3$ of the cell. According to this a model was set up and diffraction patterns were simulated using DISCUS (Proffen and Neder, 1997). A refinement of the model underlying the simulated diffraction patterns versus the experimental data provided the probability of statistical intergrowth between Zeolite beta A and B.

Contrarily, the diffuse scattering of Zeolite RUB05, which is a layered structure and exhibits platelike crystals as shown in Fig. 4(c) and (d), was found along the electron beam direction. After the zones are cut the same principle like for Zeolite beta could be followed (Krysiak *et al.*, 2018). The simulated zone [010] is shown beside the experimental zone in Fig. 16(a) and (b). The missing wedge of the three dimensional reciprocal volume is clearly visible. The intensity distribution of the set of reflections 20l and 60l containing the majority of diffuse scattering are cut exemplarily. The extracted intensity distribution (gray line) is showing in Fig. 16(c) and (d), respectively. In this example, model building was not straightforward and additional information was necessary. The reconstructed phase image derived from HR-TEM images at different foci in Fig. 16(g) reveals the intergrowth of the solved RUB05 structure with a second polymorph by flipping polymorph I 180° around the a axis with an additional shift of $\Delta x = -0.29$. A detailed description can be found in Krysiak *et al.* (2020). Together with the experimental intensity distribution the simulated one (red line) and the difference between the two (blue line) are plotted in Fig. 16(c) and (d). Both refinements result in a stacking probability, p_x , of 0.05 provided in Fig. 16(e) and (f).

Concluding remarks

3D-ED as a promising and upcoming method uses three dimensional electron diffraction data for crystal structure analysis of unknown non-crystalline materials. The general approach of collecting non-oriented diffraction patterns through a crystal tilt, comparable to a scan of the reciprocal space, and the integration of reflections in the reciprocal space by electron beam precession or fine beam tilt reduces dynamical effects strongly, allowing the application of ab-initio structure solution methods based on kinematical diffraction theory. In particular, the methods PED-ADT and FAST-ADT, where μ STEM-HAADF imaging is applied for crystal tracking and for e.g., NBED for data acquisition, allow analyses of nanocrystals down to some tens of nanometers in agglomerated multiphase samples as found in nano-crystalline glass ceramics. Data sets with high completeness deliver atomic positions with an accuracy comparable to DFT calculations and reveals accurate information about special crystallographic features like twinning, disorder, superstructures or modulations. Combining 3D-ED with other methods available in the TEM, like EDX-Mapping or HR-TEM imaging can allow the complete crystallographic characterization of nanocrystalline glass ceramics even containing unknown phases.

References

- Bhat, S., *et al.*, 2020. A novel high-pressure tin oxynitride $\text{Sn}_2\text{N}_2\text{O}$. *Chemistry – A European Journal* 26 (10), 2187–2194.
- Burla, M.C., *et al.*, 2015. Crystal structure determination and refinement via SIR2014. *Journal of Applied Crystallography* 48 (1), 306–309.
- Cookman, J., Bangert, U., 2021. High Resolution Analytical Electron Microscopy of Ceramics and Glasses. In: Pomeroy, M.J. (Ed.), *Encyclopedia of Materials: Technical Glasses and Ceramics*. Netherlands: Elsevier.
- Dorset, D.L., 1996. Electron crystallography. *Acta Crystallographica Section B: Structural Science* 52, 753.
- Dorset, D.L., Roth, W.J., Gilmore, C.J., 2005. Electron crystallography of zeolites – The MWW family as a test of direct 3D structure determination. *Acta Crystallographica Section A, Foundations of Crystallography* 61, 516.
- Fetzer, A.-K., Trapp, M., Lauterbach, S., Kleebe, H.-J., 2021. Introduction to Transmission Electron Microscopy; The Basics. In: Pomeroy, M.J. (Ed.), *Encyclopedia of Materials: Technical Glasses and Ceramics*. Netherlands: Elsevier.
- Gemmi, M., *et al.*, 2015. Fast electron diffraction tomography. *Journal of Applied Crystallography* 48, 718.
- Gemmi, M., *et al.*, 2019. 3D electron diffraction: The nanocrystallography revolution. *ACS Central Science* 5 (8), 1315–1329.
- Georgieva, D., *et al.*, 2011. Evaluation of Medipix2 detector for recording electron diffraction data in low dose conditions. *Journal of Instrumentation* 6. (C01033).
- Gorelik, T.E., S., S., Kolb, U., 2012. Uniting electron crystallography and powder diffraction. In: Kolb, U., *et al.* (Eds.), *NATO Science for Peace and Security Series B: Physics and Biophysics*. Netherlands: Springer.
- Goujon, C., *et al.*, 2008. High pressure synthesis of BiCrO_3 , a candidate for multiferroism. *Journal of Physics: Conference Series* 121 (2), 022009.
- Henderson, R., Unwin, N.T., 1975. Three-dimensional model of purple membrane obtained by electron microscopy. *Nature* 257, 28.
- Hovmöller, S., *et al.*, 1984. Accurate atomic positions from electron microscopy. *Nature* 311 (5983), 238–241.
- Jiang, J., *et al.*, 2011. Synthesis and structure determination of the hierarchical meso-microporous zeolite ITQ-43. *Science* 333 (6046), 1131–1134.
- Kolb, U., *et al.*, 2007. Towards automated diffraction tomography: Part I – Data acquisition. *Ultramicroscopy* 107 (6), 507–513.
- Kolb, U., *et al.*, 2010. Structural characterization of organics using manual and automated electron diffraction. *Polymer Review* 50, 385.
- Kolb, U., Gorelik, T., Otten, M.T., 2008. Towards automated diffraction tomography. Part II – Cell parameter determination. *Ultramicroscopy* 108, 763.
- Kolb, U., Krysiak, Y., Plana-Ruiz, S., 2019. Automated electron diffraction tomography – Development and applications. *Acta Crystallographica Section B* 75 (4), 463–474.
- Krysiak, Y., *et al.*, 2018. Ab initio structure determination and quantitative disorder analysis on nanoparticles by electron diffraction tomography. *Acta Crystallographica Section A* 74 (2), 93–101.
- Krysiak, Y., *et al.*, 2020. New zeolite-like RUB-5 and its related hydrous layer silicate RUB-6 structurally characterized by electron microscopy. *IUCrJ* 7 (3), 522–534.
- Li, X., *et al.*, 2016. Evaluation of nanocrystalline Sn_3N_4 derived from ammonolysis of $\text{Sn}(\text{NEt}_2)_4$ as a negative electrode material for Li-ion and Na-ion batteries. *Journal of Materials Chemistry A* 4 (14), 5081–5087.
- Llopart, X., *et al.*, 2002. Medipix2: A 64-k pixel readout chip with 55 μm square elements working in single photon counting mode. *IEEE Transactions on Nuclear Science* 49, 2279.
- Mugnaoli, E., Gorelik, T., Kolb, U., 2009. “Ab initio” structure solution from electron diffraction data obtained by a combination of automated diffraction tomography and precession technique. *Ultramicroscopy* 109 (6), 758–765.
- Nederlof, I., *et al.*, 2013. A Medipix quantum area detector allows rotation electron diffraction data collection from submicrometre three-dimensional protein crystals. *Acta Crystallographica Section D: Biological Crystallography* 69, 1223.
- Palatinus, L., Brázda, P., Jelínek, M., *et al.*, 2019. Specifics of the data processing of precession electron diffraction tomography data and their implementation in the program PETS2.0. *Acta Crystallogr B Struct Sci Cryst Eng Mater* 75, 512–522.
- Palatinus, L., Petricek, V., Corrae, C.A., 2015. Structure refinement using precession electron diffraction tomography and dynamical diffraction: theory and implementation. *Acta Crystallographica Section A* 71 (2), 235–244.
- Plana-Ruiz, S., *et al.*, 2018. Quasi-parallel precession diffraction: Alignment method for scanning transmission electron microscopes. *Ultramicroscopy* 193, 39–51.
- Plana-Ruiz, S., *et al.*, 2020. Fast-ADT: A fast and automated electron diffraction tomography setup for structure determination and refinement. *Ultramicroscopy* 211, 112951.
- Plana-Ruiz, S., 2021. Institut für Angewandte Geowissenschaften. Darmstadt: Technische Universität Darmstadt.
- Proffen, T., Neder, R.B., 1997. DISCUS: A program for diffuse scattering and defect-structure simulation. *Journal of Applied Crystallography* 30 (2), 171–175.
- Reimer, L., 1984. Kinematical and dynamical theory of electron diffraction. In: Reimer, L. (Ed.), *Transmission Electron Microscopy: Physics of Image Formation and Microanalysis*. Berlin; Heidelberg: Springer Berlin Heidelberg, pp. 259–313.
- Remennik, S., *et al.*, 2012. Crystal structure of a new quaternary Mg–Zn–Ca–Li phase. *Intermetallics* 22, 62–67.
- Schlitt, S., *et al.*, 2012. Application of clustering techniques to electron-diffraction data: Determination of unit-cell parameters. *Acta Crystallographica Section A* 68 (5), 536–546.
- Sheldrick, G.M., 2008. A short history of SHELX. *Acta Crystallogr., Sect. A: Found. Crystallogr.* 64, 112.
- Shi, D., *et al.*, 2013. Three-dimensional electron crystallography of protein microcrystals. *eLife* 2. e01345.
- Susi, T., *et al.*, 2019. Efficient first principles simulation of electron scattering factors for transmission electron microscopy. *Ultramicroscopy* 197, 16–22.
- Vincent, R., Midgley, P.A., 1994. Double conical beam-rocking system for measurement of integrated electron diffraction intensities. *Ultramicroscopy* 53, 271.
- Yonekura, K., Ishikawa, T., Maki-Yonekura, S., 2019. A new cryo-EM system for electron 3D crystallography by eEFD. *Journal of Structural Biology* 206 (2), 243–253.
- Zhang, D., *et al.*, 2010. Collecting 3D electron diffraction data by the rotation method. *Zeitschrift für Kristallographie* 225, 94.

Preparation of Ceramic, Glass-Ceramic and Glasses for Microstructural Examination

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Introduction

“Samples were mounted, ground and polished” is a quote which frequently, and albeit frustratingly, appears in articles which report characterization of ceramics by optical or scanning electron microscopy. Because of the lack of further detail, researchers, particularly new researchers, face the challenge of how to obtain “true microstructures” which can be correlated with material processing conditions (Chinn, 2002) and with material properties: e.g., mechanical, optical, thermal, electrical and other bulk properties (Chinn, 2002; Geels *et al.*, 2007).

It is hoped that this chapter will allow the reader to become familiar with the various stages of obtaining a true microstructure, so that with equipment and consumables vendors, they can make informed choices as to the best approaches to sectioning, mounting, planar grinding, fine grinding, polishing and etching. Prior to discussing the various processes, it is worthwhile looking at what a “True microstructure” is and how it relates to the microstructure of the volume it is supposed to represent.

Geels *et al.* (2007) and Buehler (2018a) both emphasize that a true microstructure is that which is being sought when preparing samples for microscopic investigation. The major requirement for this true microstructure is that it contains no artifacts. Arguably, an artifact free microstructure cannot be obtained, as various defects will inevitably arise. Such artifacts have been typified in ceramics by Geels *et al.* (2007) and Buehler (2018a) as follows: scratches, pull-outs, contamination, smearing, relief and edge rounding. Any of these defects, or combinations thereof, compromise the clarity of a microstructure where distinct features with dimensions in the range 0.010–100 μm should be readily resolved using a scanning electron microscope.

A near artifact free, and therefore a close to true microstructure, can be obtained with due care during grinding and polishing. However, it must be realized that the end result of careful grinding, polishing and etching is a 2D structure which is frequently used as the “signature microstructure”. This signature is frequently correlated with certain processing conditions and the various resulting properties as described above. However, the real signature microstructure is a 3D entity, and in some cases the 3D microstructure might be very poorly represented by its 2D counterpart. This is particularly the case when grains are elongated and randomly oriented. Fig. 1(a) shows, what can be taken, as a 3D representation of a specimen of silicon nitride comprising grains, which are long randomly oriented thin hexagonal rods. A typical 2D SEM micrograph of a ground, polished and plasma etched silicon nitride ceramic sample can be seen in Fig. 1(b). Clearly, the question is “What is the relationship between 2D and 3D microstructures?”. For the long randomly oriented hexagonal rods, Geels *et al.* (2007) explain that the estimation of rod size from the 2D structure leads to smaller values than expected for the 3D microstructure. Indeed, they relate that a statistical extrapolation of the 2D surface microstructure results in 80% of the grains within a given volume being shorter than expected, and thus almost equi-axed. Stereological calculations lead to more accurate descriptions of the 3D microstructure, and thus high aspect ratio silicon nitride grains with lengths generally greater than those forecast by extrapolation of the 2D view. For more equi-axed structures, the 2D and 3D microstructures are virtually the same, statistically. Thus, it is quite apparent that the “true 2D microstructure” is wholly useful for comparison sake but not necessarily reflective of the “true 3D microstructure”.

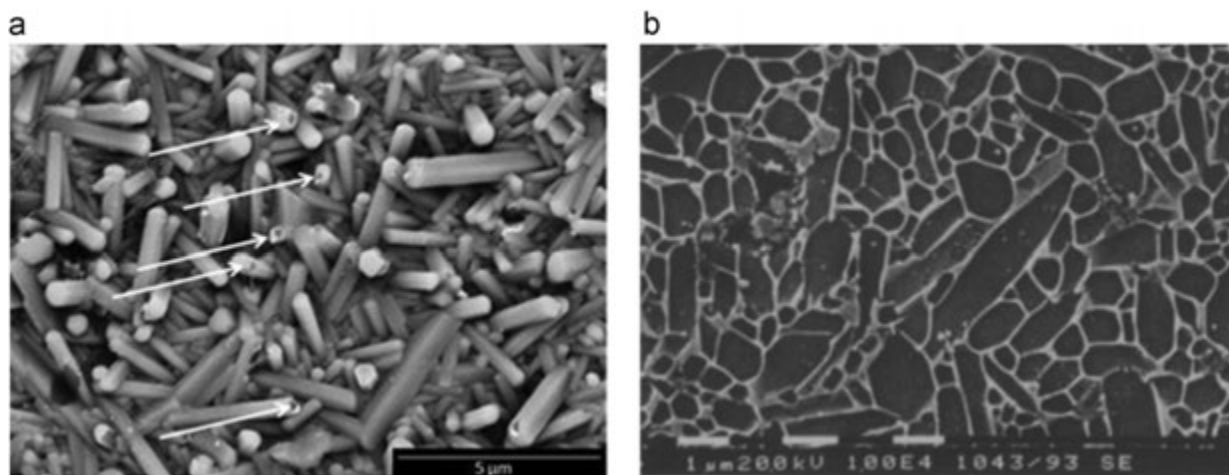


Fig. 1 (a) Micrograph of deep etched silicon nitride ceramic. (b) Ground polished and plasma etched cross-section of silicon nitride. After (a) Bock, R.M., McEntire, B.J., Sonny Bal, B., *et al.*, 2015. Surface modulation of silicon nitride ceramics for orthopaedic applications. *Acta Biomaterialia* 26, 318–330. (b) Erauw, J.P., Gilissen, R., Sleurs, J., 1994. Gas pressure sintering of silicon nitride: The influence of additive type and sintering parameters on the microstructural development. *Transactions of the Materials Research Society of Japan* 14A, 879–882.

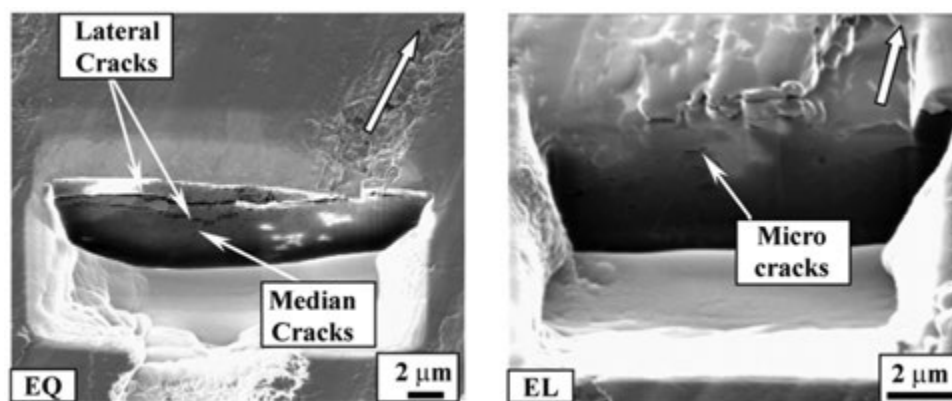


Fig. 2 Focused Ion Beam micrographs of subsurface cross-sections (normal to the ground surface) of a fine grained equi-axed α -sialon (EQ) and the same α -sialon composition processed to give long elongated grains (EL). The arrows represent the grinding direction. Note the sub-surface crack damage arising from grinding. After Xie, Z.-H., Moon, R.J., Hoffman, M., Munroe, P., Cheng, Y.-B., 2003. Role of microstructure in the grinding and polishing of α -sialon ceramics. *Journal of the European Ceramic Society* 23, 2351–2360.

In arriving at a “true microstructure”, it is necessary to arrive at a close to optically flat surface having sequentially ground and polished a very rough surface which was heavily scratched and damaged from initial sectioning. **Fig. 2** shows how cracks develop beneath a ground surface and that the extent of sub-surface cracking can be quite significant. The depth of such damage is dependent on the severity of the grinding, and so grinding, and indeed polishing, to arrive at a “true microstructure” involves sequentially “chipping away” at the surface with ever finer abrasive particles creating ever thinner damage layers which are associated with a true microstructure.

The Material Characteristics and Properties Affecting Choice of Techniques

In setting out to obtain a representative microstructure of a sample of a ceramic, glass ceramic or glass material, it is important to have some idea of the characteristics of the sample. An immediate thought that springs to mind, is porosity. For example, a fully dense cutting tool fabricated from a sialon material will, as it were, “Hold together” during sectioning, grinding and polishing far better than a sample of say a diesel particulate filter (DPF) which comprises a honeycombe structure with thin walls in which the filtering porosity is deliberately developed. The honeycombe/porous nature of the DPF material is best infiltrated with a low viscosity resin prior to sectioning as in fact will any sample that has open porosity (e.g., RBSN, RBSiC, thermally sprayed coatings, refractory materials).

A further factor which needs to be thought about is the area of interest in the sample. For example, if the edge of a sample is the area of interest then it may well be necessary to ensure that the mounting method and polishing method affords edge retention. That is, the edge between the sample and the material it is mounted in are in exactly the same plane after preparation. Without due care, a situation can arise where the sample stands proud of the mounting material and there is a wide rounded interface between sample and mount which is (1) difficult to image and (2) unrepresentative of the surface microstructure. Methodologies for good edge retention can involve (1) using harder mounting materials to lessen material removal rate differences between the sample and mount, (2) optimizing the relative orientation of the interface in question to the grinding/polishing direction, (3) the coating of the surface in question with an adherent hard metallic material e.g., electroless nickel.

A final factor in looking at the preparation of ceramic microstructural specimens, is the effect of material properties on grinding and polishing rates. Important properties are Young’s modulus, hardness and fracture toughness, as these control material removal rates (see [Arsecularatne et al. \(2014\)](#)) as well as depths of subsurface damage. This is exemplified in **Fig. 2** where the EQ material suffers much deeper and more substantial sub-surface damage than the EL material. Observation of the properties of the EQ and EL materials given by [Xie et al. \(2003\)](#) show the latter to have twice the toughness of the former. The hardness of the EQ material exceeds that of the EL material. Thus, tough materials develop shallower sub-surface damage.

Sectioning

Selection of Volume to be Sampled

Sectioning of a sample of ceramic or glass is carried out to obtain a specimen which is can be fully polished and, if necessary, etched ([Geels et al., 2007](#)). In making a specimen from a component or research sample of ceramic, glass ceramic or glass, certain criteria should be taken into account. For example, fired ceramic components or samples have thin surface layers which have a very different character to the interior bulk due to the surface having more opportunity to interact with the surrounding environment

(Mörtel, 1991). This is also the case for glasses and glass-ceramics where mold – surface interactions give rise to potentially different chemistries and structures extending quite a distance (1–2 mm) into the bulk material. Consideration must be given to the possibility that a sample may have preferred orientation. For example, extruded AlTi_2O_5 can demonstrate preferred orientation effects (Chen *et al.*, 2020) as can glass ceramics which surface nucleate and crystallize from the free external surface inwards (Renoirt *et al.*, 2019). Accordingly, it is very necessary to think about the relationship between the orientation of the sample and the orientation of the section. For samples where a surface coating or contaminant may be present, the sample should be taken such that any sectioning occurs with the coating/contaminant meeting the sectioning blade first (see Elssner *et al.*, 1999, Chapter 2, pages 5 and 6). In addition, orienting the surface to be cut at 45° to the blade surface will keep the coating in compression leading to a better result (Johnson *et al.*, 2015). If coatings/surface layers are particularly friable, e.g., porous coatings on metallic substrates for biomedical applications, it may well be worth impregnating the coating with a resin to maintain its integrity during sectioning. Pre-impregnation of porous materials may also be advisable for two reasons: (1) the integrity of the material is preserved during sectioning, grinding and polishing and (2) the pre-impregnated sample will not hold lubricant/coolant containing cutting debris etc. in the porous structures which may well contaminate finer polishing activities. For coatings, surface layers and surface contaminants, the use of tapered sections may assist resolution of detail. Tapering is more usually done at the mounting stage and so will be discussed there.

Preferred Sectioning Speeds and Loads

Sectioning involves the use of thin, some as thin as 150 μm , circular blades with diamond impregnated metal or resin matrix rims (see Fig. 3) operating with a lubricant/coolant. Motion is transferred by a shaft rotating in the arbor attached to the blade via flanges, friction fitted to the blade surface (Fig. 3). Blade speeds, the concentration of diamond grit in the rim, the size of the diamond grit, the nature of the rim (metal or resin) and load applied or cutting feedrate must all be balanced correctly to achieve optimum cutting rates. The selection of the settings of these parameters depends very much on the nature of the ceramic and this is generally categorized in terms of relative brittleness/toughness and hardness. For brittle relatively soft materials, resin bonded fine diamond grit wheels running at low speeds and under low loads/feedrate are preferred. For very tough and hard ceramics e.g., silicon nitride, metal bonded coarse diamond grit wheels running at high speeds under high loads are preferred (Zipperian *et al.*, 1992; Täffner *et al.*, 2004; Zipperian, 2011).

Zipperian *et al.* (1992) and Zipperian (2011) indicate that typical blade speeds range from 50 to 1000 rpm for low speed machines and up to 5000 rpm for higher speed sectioning saws. Slow speed saws are best employed for more brittle materials e.g., friable ceramics, electronic ceramics, CaF_2 , MgF_2 , glasses with cutting speeds of 500–700 rpm. For hard brittle ceramics e.g. AlN , Al_2O_3 the same authors suggest speeds of in excess of 1500 rpm up to 2500 rpm. Zipperian *et al.* (1992) and Zipperian (2011), suggest that for hard and tough ceramics such as B_4C , silicon nitride, silicon carbide, etc. wheel speeds in excess of 3500 rpm are required for sectioning. There is no doubt, given the evidence provided by Elssner *et al.* (1999), that slower speeds will result in less surface damage. These authors sectioned silicon carbide, silicon nitride and alumina using saw speeds of 200 and 3400 rpm. The comparative levels of surface damage are quite striking, with the slow speed saw yielding a much better starting surface to grind and polish and much less grain pull out. While this is typically true, Zipperian *et al.* (1992) show the significant time penalties incurred by slow speed blades with low loads compared to high speed blades with high loads. For example a 12.7 mm bar sample of B_4C could not be cut with the slow speed low load conditions employed. A similarly sized sample of silicon carbide took 19 h to cut under the same conditions while an alumina sample took 26 min. For the same samples, each was sectioned in 30 s using the high speed, high load conditions. Accordingly, it may be beneficial to use high load, high speed sectioning for hard and particularly hard and tough ceramics. It is quite often beneficial to begin a cut at low load/low speed so that the correct kerf (cut width) can be established.

Sectioning Blade: Diamond Concentration, Diamond Grit Size and Holding Matrix

The concentration and size of the grit in the sectioning blade rim are varied, as necessary, to suit tough very hard engineering ceramics, hard ceramics and sintered carbides and soft friable brittle ceramics (Buehler, 2018a). As a rule of thumb, the harder the material to be cut, the lower the concentration of diamond required in the cutting surface (Zipperian *et al.*, 1992; Geels *et al.*, 2007).

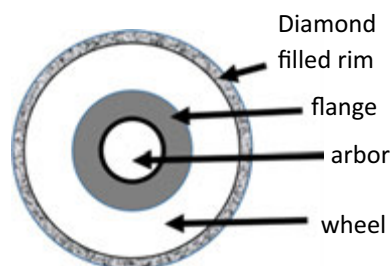


Fig. 3 Schematic of diamond cutting wheel for sectioning.

Täffner *et al.* (2004) explain that the lower the diamond concentration, the higher the stress applied to the diamond surface in contact with the ceramic surface being cut. Greater contact stresses on each operating abrasive particle lead to greater cutting rates. Clearly, higher loads also increase these contact stresses and thus induce greater cutting rates. The same of course can be said of material feedrates, since the higher the feedrate the higher the force applied to the material.

Johnson *et al.* (2015) give a table of materials and respective recommended diamond wafering blades. The table indicates that diamond loadings in the rim of the cutting wheels range from 20LC for hard tough ceramics, through 15LC and 10LC, to the lowest loading of 5LC which is for brittle, friable materials. Other manufacturers will have a similar grading of diamond grit concentrations. Grit sizes are likely to diminish in a similar way with finer grit sizes being used to section brittle, friable materials and coarser grits being used for hard/tough ceramics. Zipperian (2011) indicates that coarse diamond grits for sectioning are about 120 grit (120 μm) and fine diamond grit is typically 600 grit (26 μm).

The selection of the matrix in which the diamond particles are held is important. This is best demonstrated by the reportage of Mörtel (1991) who sectioned quartz with brass bonded and resin bonded diamond grit wheels. Whilst the resin bonded diamond cut the quartz successfully, the brass bonded diamond left a lubricating smear of brass in the cut. The resin bond allowed blunted diamond particles to be pulled out of the resin leaving a continually sharp collection of diamond particles in contact with the work piece. Elssner *et al.* (1999) indicate that the harder the material then the softer the holding matrix, indicating that hard and tough non-oxide ceramics can be sectioned using resin bonded diamond whilst oxide ceramics are frequently sectioned using metal bonded wheels. Friable, brittle ceramics are typically best sectioned with resin bonded diamond (Täffner *et al.* 2004). Clearly, a drawback of using resin bonded diamond wheels is their greater tendency to wear. The wealth of knowledge developed by companies selling cut off blades is now significant and so from a basic knowledge of what material needs to be sectioned and its properties and the background information given here, the correct selection of cut off blade can be made by the user in conjunction with a preferred supplier.

Prior to first use or after periods of use indicated by a falloff in cutting performance, it is important to dress the abrasive sectioning wheel. This bares diamond particles from the metal or resin bond and allows them to become fully effective when put into use for sectioning. Dressing sticks are clamped into position and the sectioning blade made to make a cut into it. The dressing stick is typically a porous resin material containing alumina abrasive particles. Zipperian (2011) shows clear evidence of the effect of wheel dressing on sectioning times of the same thicknesses of silicon nitride. Cutting times for one and two sections are very similar, however, for the third cut though the time taken is six times that for the previous two cuts. Following dressing, after the third section has been made, cutting times revert to those seen for the first and second cuts. Thus, it is very useful to monitor how long each section takes and to dress the diamond impregnated wheel as appropriate.

Sample Support

As already indicated, sectioning blades are extremely thin (some as thin as 150 μm), and thus fragile. In the writer's experience, blades are most likely to fail from poor anchoring or alignment of the specimen during sectioning. In general, blade failure arises by local spallation of the abrasive diamond loaded rim. Any movement whatsoever during cutting of the sample will cause the wheel, particularly its rim, to be pinched within the cut and thus induce failure. As well as blade failure, correct specimen support can prevent the fracture of a very thin section of sample at the end of the cut, leading to non-planarity prior to grinding. This is best avoided by the use of a double chuck arrangement where both sides of the cut are supported (Chinn, 2002). For porous and friable ceramic samples, sectioning is best performed using rubber pads between the jaws of the chuck and the sample and this is also a solution to preventing the development of vibration within the sample during sectioning (Zipperian, 2011). Chinn (2002) shows a selection of simple specimen holders for tube or bar, mounted samples and for making thin sections. Examination of current fixing devices shows that they are much the same with subtle variation e.g., tear drop geometries for holding mounted samples (to accommodate difference in size), irregular specimen chucks etc. For currently available chucks and specimen vices, it is best to consult materialography manufacturers (e.g., Buehler, Struers, Kemet, Presi, PACE Technologies) websites.

The orientation of the sample to the cutting wheel can alter the efficiency of cutting. The best orientation appears to be when the thinnest part of the sample is presented perpendicularly to the wheel (Fig. 4(a)). Johnson *et al.* (2015) indicate that this is the preferred arrangement for optimal cutting, drawing attention to a "door-wedging" effect (Fig. 4(b)) or lower efficiency cutting if the sample is angled in the opposite orientation (Fig. 4(c)). Note however, as indicated in Section "Selection of Volume to be

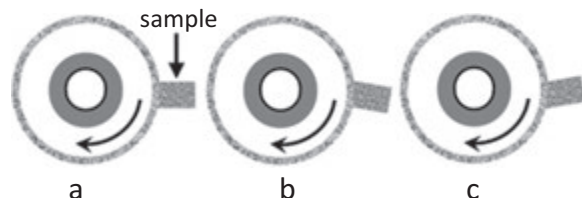


Fig. 4 Schematic diagram of preferred orientations of presentation of sample to cutting wheel: (a) optimum, (b) "door wedge" opposing blade motion more strongly, (c) lower efficiency orientation but preferred in the case of coatings surface contaminants with coating surface first contacting the blade.

Sampled", that coatings/surface layers should be oriented such that the coating is presented to the blade first, albeit at a greater angle than in Fig. 4(c).

Coolants/Lubricants

The purpose of a lubricant used during sectioning is to remove cutting debris, including degraded bond and diamond, from the cut, keep the sample, blade and cutting rim cool and provide lubrication for the blade to glide through the cut (Geels *et al.*, 2007). Coolants/lubricants can be either water- or oil-based and can be best selected in consultation with consumables suppliers. In choosing between water- or oil-based coolants, the nature of the sample should be considered. Clearly, a material, coating or surface contaminant that is water soluble or whose integrity affected by water should be sectioned using oil-based lubricants. Elssner *et al.* (1999) refers to β -alumina, CaO, MgO, magnesite as being materials affected by the use of water-based coolants. The writer has used such coolants as petroleum spirit and white spirit during the low speed sectioning of corrosion products and deposits (particularly $(K,Na)_2SO_4$ and Ca-Zn-P-S-O deposits) on both metallic and ceramic (sialon) substrates. Better oil based lubricants are on the market which will act equally as well. Correct environmental disposal protocols must be taken in disposing of coolants and these may affect the choice of lubricant/coolant.

Cleaning

Mörtel (1991), Elssner *et al.* (1999), Chinn (2002) and Geels *et al.* (2007) all very clearly state that cleaning samples after sectioning and other steps during the sectioning, grinding and polishing procedure is, arguably, as important as carrying out the steps themselves. This is because there is a significant likelihood of specimens becoming damaged by abrasives and cutting/polishing debris left as contaminants on them after each step in the preparation of a polished specimen. Such damage would of course require reworking of the specimen, with attendant time and indeed material losses. Geels *et al.* (2007) give a comprehensive analysis of methods for specimen cleaning. They also mention the importance of carrying out other measures (e.g., hand washing, equipment cleaning, minimizing dust) in order to reduce the potential of specimen damage due to contaminants.

Generally the agreed best way of specimen cleaning is to use ultrasonic agitation of a suitable detergent solution or, if the specimen contains water soluble components, a non-aqueous solvent. The ultrasonic agitation creates bubbles in the liquid that impinge on and implode on surfaces in the cleaning fluid. This process is referred to as cavitation. These impingements and implosions set up shock waves on the surfaces to be cleaned with the result that a specimen sample is gently cleaned both chemically (solution of grease etc.) and physically (scouring effect of bubbles).

Non-aqueous solvents must be selected and treated with care because of health and safety concerns. Risk is minimized if they be used under a fume hood and the correct fire-retardant is available should any untoward situation arise. Aqueous cleaning agents are usually based on highly alkaline solutions which are designed to remove oil and grease. In removing oil and grease from a cut specimen, diamond and cutting debris is removed also. 30–120 s is a suitable time for the cleaning of most specimens after sectioning and indeed grinding and polishing. For brittle, friable specimens, shorter times should be used to avoid their decrepitation by the cavitation effects referred to above. It may well be better to impregnate such sample types with a resin to "anchor" the structure and prevent the possibility of its damage during ultrasonic cleaning.

After cleaning, specimens should be rinsed with distilled or de-ionized water and dried, unless they contain water soluble phases when a solvent such as ethanol might be used for rinsing. Drying is best carried out with a fan type heater, even a hair drier! Additional information on specimen cleaning and equipment (polishing wheels etc.) is given in following sections.

Mounting

Introduction and Initial Considerations

Mounting a specimen is carried out to make the specimen more readily held, either by hand or machine, during grinding and polishing (Buehler, 2018a). Specimen sizes should be no more than 50% of the diameter of the mount and mounts should be at least 20 mm high. The writer has seen many examples of thin (10 mm high) mounts which either cannot be sufficiently well gripped by the heads of a semi-automatic grinding and polishing machine, or indeed by hand. Clearly, it is important that a specimen is not damaged during mounting (Buehler, 2018a). As well as realizing that the selection of the mounting method and material contributes greatly to quality of the finished polished microstructure. Accordingly, a holistic approach must be taken when selecting a mounting procedure. Initial considerations prior to mounting are based upon the specimen size and characteristics. These considerations go to help answer the following questions: which mounting method should be used (simple clamping, hot compression or cold casting), does the specimen need support during mounting and how that might be effected, will examination of the specimen edge be important, does the specimen need any pre-treatment before mounting e.g., pre-impregnation, will the available resins/polymers have the right characteristics as a mount for the specimen, will the hardness of the mounting material need to be augmented by the addition of hard particles, is a conductive mount needed to aid electron microscopy, if etching is required will the mount be resistant to the etchant(s) or will it need removal, etc.? Indications of the answers to these questions are given in the following sections.

Pre-Treatments Including Pre-Impregnation

It is important to have a clean dry specimen to which the mounting medium adheres very well. If this is not the case, then grinding/polishing media and fluids can become entrapped in gaps between the specimen and the mount and lead to contamination of finer polishing steps and smearing of the polished surface by fluids being drawn over the surface by surface tension effects. Cleaning methods are addressed in the previous section. Mörtel (1991) suggests drying samples for at least 1 h at 110°C to ensure that any moisture on the sample surface is removed resulting in a good mount – specimen bond. Such good mount-specimen bonding also helps good edge retention (Geels *et al.*, 2007).

For more porous materials e.g. with porosities greater than 15%, it may be useful to pre-impregnate them with a low viscosity resin (e.g., an epoxy) prior to mounting them (Chinn, 2002). This is done by holding the specimen in a vacuum chamber, evacuating the chamber to low pressure, typically 10–25 kPa and then allowing the resin to flow into a mold in which the specimen sits. Once a sufficient depth of resin covers the sample, the vacuum can be released and the vacuum chamber allowed to come up to atmospheric pressure which then “pushes” the resin into the pores of the porous ceramic (Chinn, 2002). For specimens with 5%–15% porosity, vacuum impregnation can be similarly effected. However, as this porosity level is associated both with open as well as closed pores, it may be necessary to repeat the impregnation process after planar grinding to seal the newly exposed porosity in the face being prepared for examination (Elssner *et al.*, 1999). Resins with added dyes can be obtained or made up so that prior porosity can be seen under the optical microscope if the dye fluoresces (see Brindley and Leonhardt, 1990; Elssner *et al.*, 1999; Buehler, 2018a). Simple pre-impregnation systems can be put together from a vacuum dessicator with a central port for the admission of the resin and a side port for the application of the vacuum which can be developed by a water jet pump as well as by a roughing vacuum pump. The major materialographic suppliers (Buehler, Struers, Kemet, PACE Technologies and others) can supply suitable equipment for the vacuum impregnation of several samples in the same vacuum chamber.

Better edge retention can be afforded by the application of a layer of hard nickel deposited on the specimen by electroless deposition. Of course this is not suitable if surface layers contain water soluble components as the solution in which the specimen is plated is an aqueous solution. This applied coating will support the edge during grinding and polishing. Geels *et al.* (2007) detail the composition of an electroless nickel solution and indicates a plating rate of $15 \mu\text{m h}^{-1}$ if a temperature of between 90 and 100°C is employed. Geels *et al.* (2007) state further on in their article on mounting that, because of the availability of resins and polishing procedures including semi-automatic ones, electroless nickel plating is not often necessary.

Taper Sectioning

In order to thicken a coating or surface contaminant layer for detailed microstructural examination, taper sectioning can be employed. Fig. 5 shows how a coating of thickness T is amplified to an effective thickness ET by gradually decreasing the angle α . For an $\alpha = 10^\circ$ the magnification factor is 5.8. This then makes examination of coatings or surface layers easier, although this might not be the case for electron microscopy where the beam may penetrate through the thinner parts of the coating and be backscattered from the substrate. Care should also be taken if microhardness measurements are to be taken as the thickness of the coating will vary across its effective thickness (width as it is being looked at). The simplest way to create a taper section is to glue a piece of wire at one end of a coated sample. For example, a 3 mm diameter wire glued one end of a 20 mm square specimen will give an α angle of about 8° and a magnification factor of 6.5. An excellent description of the application of the taper sectioning technique to a detailed transcolumnar analysis of EBPVD thermal barrier coatings, is given by Kelly *et al.* (2008).

Mounting Methods

Mounting in clamps

Mörtel (1991), Geels *et al.* (2007) and Buehler (2018) all refer to clamping of samples in metal fixtures as a suitable way to support and grip a specimen for subsequent grinding and polishing. Mörtel (1991) shows typical schematics of fixtures which can be used to hold wire, rod or plate samples between metal plates which can apply a suitable gripping force via screws which pull

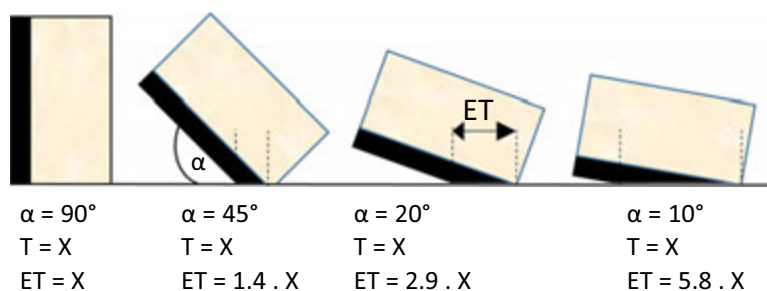


Fig. 5 Schematic of taper sectioning, showing how a surface layer of thickness (T) = X can be extended to an effective thickness, ET by angling the surface layer toward the horizontal at different angles α .

metal plates together. He also shows how a ceramic rod can be gripped by holding it within a metallic tube with a screw applying a holding force. In general, clamping is used for larger samples and manual grinding and polishing. Advantages of clamping are: (1) it is simple to effect, given suitable machining facilities to cut, drill and tap steel plates or tubes, (2) it can be used for large specimens, (3) It can give excellent edge retention as the edge is supported by the steel clamp which is much harder than the polymers used for hot or cold mounting. Disadvantages of clamping are: (1) Clamping can cause cracking or crushing of samples or surface coatings, (2) As clamping involves potential gaps between specimen and clamp and in other areas, contamination of grinding laps and polishing can occur without sufficient cleaning between steps, (3) Polishing cloths can be damaged by sharp clamp edges and so it is advisable to bevel the clamp edges.

Hot mounting

Hot mounting, or compression mounting, involves the embedding of a specimen in a thermoplastic or thermosetting polymer under the influence of pressure and heat. Typical pressures employed are 20–30 MPa (Geels *et al.*, 2007) and are wholly sufficient to cause cracking of specimens. The writer has seen many a glass, glass ceramic or ceramic specimen ruined by the presence of a “mounting crack” at or near an area of interest which cannot be photographed for publication! Temperatures up to 200°C are employed during compression mounting (Zipperian, 2011). Available polymers for hot mounting are: acrylic, phenolic, epoxy or diallyl phthalate in powder form. The acrylic material is a thermosetting resin whilst the others are thermosets. It is the thermosetting resins which are preferred for glass and ceramic materials due to their higher hardness and wear resistance. This is particularly the case for the diallyl phthalates and epoxy resins when filled with silica fibers or glass particles (see hardness and wear data provided by Elssner *et al.*, 1999). Elssner *et al.* also indicate that the adhesion of epoxies or diallyl phthalate mounting media to the specimen is excellent giving two advantages: (1) improved edge retention and (2) negligible interface gaps reducing contamination transport to finer grinding and polishing steps. The filled resins also improve edge retention due to the increased hardness of the composite mounting medium compared to the resin alone. In addition to fillers imparting hardness, conductive fillers such as fine copper or carbon particles can be added to the mounting medium. These aid clarity of scanning electron microscope images by helping to reduce charging. Detailed characteristics of the various resins are given by Elssner *et al.* (1999), Chinn (2002), Geels *et al.* (2007) and Zipperian (2011).

Chinn (2002) and Geels *et al.* (2007) give instruction as to how the hot mounting method is carried out, and this corresponds reasonably closely to operating instructions given by equipment and mounting material manufacturers. Other useful tips are as follows: (1) While thermosetting resins must be heated and cooled under pressure, thermoplastics can be cooled without being under pressure (Buehler, 2018a). (2) Specimens should be centered within the mounting area and then a small amount of mounting powder poured around it. This anchors the specimen in the center of the mount when the requisite remaining powder is poured into the die and pressure and heat applied. (3) Economies can be made in the use of more expensive mounting resins by using a small amount around the specimen, perhaps 5–8 mm thick which is backed by a cheaper resin layer (Chinn, 2002; Geels *et al.*, 2007). Chinn also suggests using a top 2–3 mm layer of a transparent mounting material through which an identity label can be read.

Mörtel (1991) and Chinn (2002) give examples of mounting defects which are serious enough to render a mount and the sample it contains unusable for subsequent grinding and polishing. Such defects can be listed as follows: Radial splitting, Edge shrinkage, Burst bottom, Burst top, Incomplete fusion and Circumferential splitting. These authors give reasons for the creation of the defects and methods by which they can be eradicated. It is always worth discussing any such problems with powder and equipment suppliers as well as consulting the useful information of Mörtel (1991) and Chinn (2002).

Cold mounting

Cold mounting using castable resins is perhaps the best method for mounting ceramic and glass materials for examination. This is because the resulting mounts are relatively hard, adhere well to the specimen and can be sufficiently fluid to penetrate surface and linked porosity and, perhaps, most importantly, in many instances, avoids the use of pressure which may cause damage to the specimen during mounting. Three types of systems exist: (1) acrylics, (2) polyesters and (3) epoxies. Generally, epoxies are preferred for ceramic and glasses as they are hard (Zipperian, 2011) and have excellent wear resistance compared to acrylics or polyesters (Elssner *et al.*, 1999). Other reasons why epoxies are preferred for mounting ceramics and glasses are: (1) they physically adhere to specimens, precluding contamination being trapped between the specimen and the mount and improving edge retention, (2) they have low shrinkage so that the mount does not “pull away” from the specimen during curing again improving edge retention, (3) low viscosity epoxy resins can infiltrate surface depressions, cracks and porosity, allowing ready observation. As with the hot mounting resins, fillers can be added to an epoxy to improve its hardness and edge retention capability (e.g., plate like ceramic particles, ceramic particles) or conductivity (e.g., graphite or copper particles). These can be added and mixed by the researcher according to supplier instructions. As pointed out by Buehler (2018a) the viscosity of the resin/filler admixture is increased. However, the viscosity of the resin is unaffected and so it can flow into surface depressions etc. just as easily as if it were filler free.

Chinn (2002), Geels *et al.* (2007) and Zipperian (2011) all give the methodology by which castable mounting is conducted. Molds for the casting can be one part flexible silicone rubber molds, rigid two part molds where the base is detachable or ring forms which are open cylinders which are placed on a glass plate and remain as part of the mount after the resin has cured. For the two part molds and ring forms, it is best to grease contacting areas to semi-seal them such that resin leakage is negligible. As the resin is poured into the mold, the flow patterns can easily displace a specimen which is not prior secured in place. Chinn (2002) suggests the use of double sided sellotape to securely locate the specimen in the center of the mold area. The writer would prefer to fill the mold very slowly to a depth of 5 mm or so and ensure that the specimen is in the correct place before filling the mold more fully. For epoxy

resins, curing times and peak curing temperatures are dependent on the type of resin and the resin to hardener ratio. These can range from 9 h with a peak temperature of 65°C to 1 h with a peak temperature of about 160°C. Curing rates can be accelerated by preheating the resin to about 50°C before carrying out the mixing and mounting, or putting the mounts to cure in an oven at 30–40°C. However, peak curing temperatures will be increased accordingly, with the result that thermal degradation of the resulting mount is likely to arise. Curing rates can be slowed by placing curing mounts in a refrigerator. Zipperian (2011) has created a troubleshooting table for problems arising during castable resin mounting. This table covers the following problems: Lack of or partial curing of resin: Soft or gummy resins (grinding produces a matted finish), Bubbling, cracking, or yellowing of resin, Curing time takes too long, and Bubbles in resin. In addition to defining these problems, Zipperian (2011) also gives the cause of the problems and how the problems might be remedied. Incidentally, bubbles in the resin can be removed by mounting under vacuum under much the same conditions as suggested for the infiltration of porous samples (see Section “Pre-Treatments Including Pre-Impregnation”).

Post mounting operations

Post mounting operations are quite simple. They comprise the following:

- (1) Beveling the edges of the mount face: The edges of the mount face which will subsequently contact the grinding and polishing wheels should be bevelled. This improves the wear of any papers or cloths used on grinding/polishing wheels and helps to prevent them ripping. Chinn (2002) describes how this might be best done in a lathe or by grinding the edges at an angle of 45° to the mount axis on a coarse abrasive paper on a belt. An abrasive paper on a wheel may also be used.
- (2) Flattening the top faces of cast mounts: Because of the meniscus formed during the casting of resins, it is useful to flatten the resulting surface protrusions after mounting. Again this can be done in a lathe or by an abrasive belt or wheel.
- (3) Identity marking: It is always important to engrave or deeply scratch an identity into the top surface or the circumference of the mount. This identity should not only have an identifier as to the specimens reference for the individual, it should also bear some indication of the owner of the specimen. Such marking can be carried out with a small hand engraver or the sharp tip of a dentist's probe.

Grinding and Polishing

Introduction

As indicated in Section “Introduction” the method by which the “true” microstructure is arrived at involves “chipping away” at a damaged surface with ever finer abrasive particles. Fig. 6 taken from Xie *et al.* (2003) shows how sub-surface cracks develop beneath a groove and contact zone created by a sliding abrasive particle contacting a sialon ceramic surface. In addition to showing how increased material toughness limits sub-surface cracking, the schematic also shows how a potential chip is formed and what volume it can assume. The depths to which the cracks form, and thus indications of depths of material damage, diminish as finer abrasives are used. Reviewing the work of Moore and King (1980), Arsecularatne *et al.* (2014) and Yin *et al.* (2018) indicates that depths of damage due to subsurface cracking and associated strain fields are dependent on the stresses applied to abrasive particles

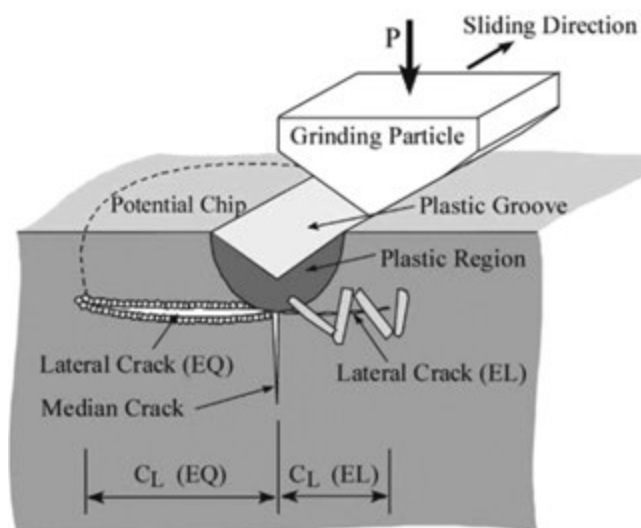


Fig. 6 Schematic of subsurface cracking during grinding and polishing of low toughness (EQ) and high toughness (EL) α -sialons. After Xie, Z.-H., Moon, R.J., Hoffman, M., Munroe, P., Cheng, Y.-B., 2003. Role of microstructure in the grinding and polishing of α -sialon ceramics. *Journal of the European Ceramic Society* 23, 2351–2360.

and their diameter. As might be expected, the lower the stresses and smaller the particles then the shallower the depth of surface damage, allowing the perfect microstructure to be approached. Of course, the amount of material removed by grinding and polishing steps is greater when stresses are high, and abrasive particle size large.

In addition to applied loads and abrasive size, the manner by which the abrasive interacts with the ceramic is also important. Zipperian (2011) explains that the abrasive may be fixed to or embedded in the polishing platen or lap, or it may be free to “roll” on the surface between the platen/lap and the ceramic surface being abraded. A third variant involves some abrasive particles being free to “roll” while others are fixed by undulations in the lap/platen surface. Materialographic suppliers each have their own variants of polishing platens/laps which correspond to the fixed, free rolling or semi-fixed variants. Fixed abrasives give more rapid stock removal but introduce more damage into the surface layers, thus requiring more material removal during subsequent stages. Zipperian *et al.* (1992) indicate that fixed abrasives are best used to grind electronic ceramic components with softer metallic interlayers because the fixation of the abrasive precludes it becoming embedded in the softer metallics such that the true microstructure cannot be revealed. Free and semi-free abrasives are best employed for edge-retention and porous samples (Zipperian *et al.*, 1992). In the writers experience, they also reduce the amount of grain pull out during coarse grinding. Extended fine grinding and polishing reduce pull outs to a minimum level (Elssner *et al.*, 1999).

The type of abrasive used for grinding and, indeed polishing, is of course important. Zipperian (2011) presents a table of typical abrasives and their hardnesses. Combining this useful information with the suggestion of Vander Voort (2009), that the hardness of the abrasive should be at least 1.5 times that of the material to be abraded, suggests that diamond is the only abrasive of choice for materials with hardnesses in excess of 15 GPa. For softer materials e.g., glasses, glass ceramics, silicon carbide may suffice.

Manual Grinding and Polishing

As indicated by Buehler (2018a), it is often the case that the forces developed between the specimen and the abrasive platen or lap are very high and cannot frequently be resisted to the required degree to facilitate efficient grinding. In addition, as material removal rates are typically slow for ceramics and glasses, the application of high force by hand for long periods of time is unlikely to be completed without breaks. This gives rise to the potential for specimens to become bevelled during extended manual preparation or the specimen to become non-level across its area. Such bevels preclude proper examination at a later stage as does a non-level surface.

Machine Grinding and Polishing

Machine grinding and polishing is much preferred for the preparation of ceramic specimens for microstructural analysis. Grinding and polishing machines allow specimens to be held in a rotating head, which pushes them against the abrasive platen/lap with a controlled force. The latest machines supplied by Buehler, PACE Technologies and Struers (see Fig. 7) have speed controls for the platen as well as the head holding the samples (see Fig. 8). Assessing the current machines offered by these suppliers shows a variety of wheel speeds and directions, head speeds and directions and ranges of force which can be applied to the rotating head, or individual specimens.

According to Zipperian (2011), the rate of material removal $\dot{G}$ is given by Preston's Law, $\dot{G} = k \cdot u \cdot f$, where k is Preston's constant u is the polishing velocity and f is the polishing pressure. Polishing velocities are complex depending on whether the directions of the

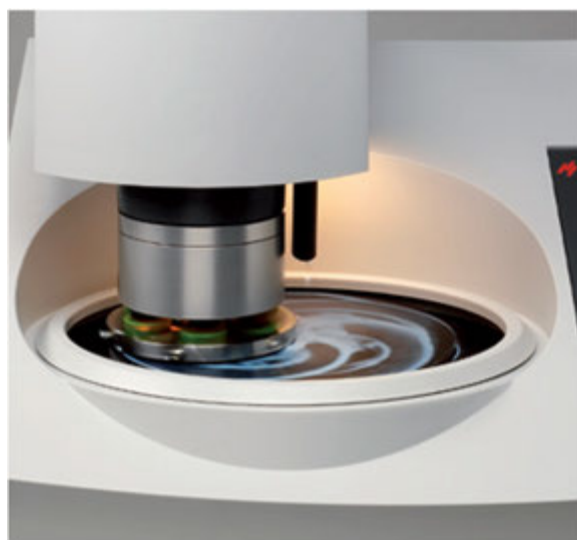


Fig. 7 Automatic polishing machine. Taken with permission from Struers, 2020a. Available at: <https://publications.struers.com/brochures/english/tegramin/> (accessed September 2020).



Fig. 8 Typical specimen holders where force is applied centrally. Taken with permission from Struers, 2020b. Available at: <https://www.struers.com/en/Products/Grinding-and-Polishing/> (accessed September 2020).

polishing platen and head holding the samples rotate in the same way (complementary-rotation) or the opposite way (contra-rotation). For the former, the relative velocity between the grinding platen and sample head is constant for all angles of rotation of the specimen holder. The actual differential velocities between the grinding platen and the sample head depends on the speed settings for them. For equal speed settings of 200 rpm, Zipperian (2011) shows a differential velocity of 1.05 m s^{-1} (2500 in min^{-1}). When the rotation is contra in direction the differential velocities vary considerably with angle of rotation of the specimen holder. With the platen rotating at 200 rpm and the sample head at -200 rpm , the differential velocities are 3.2 , 1.05 , 2.1 and 1.05 m s^{-1} for rotational angles of 0 , 90 , 180 and 270° respectively. This means that the selection of contra or complimentary rotations will have an effect on the grinding rates of specimens.

Zipperian (2011) indicates that the contra rotation mode gives rise to the highest material removal rates, particularly when the sample head rotates more slowly than the grinding platen. As already indicated, for equal but opposite rotation speeds for platen and head, the maximum relative velocity is at an angle of 0° ; i.e., when the specimen is at the outer diameter of the platen. For a similar head speed, when the platen speed is higher this relative velocity will be even greater, as of course will material removal rates. Of course, the relative velocity at when the specimen is closest to the center of the wheel is a minimum and it can be imagined that there will be a hammer like action when specimens and platen are contra rotated (Zipperian, 2011). For complementary rotation, the lower and constant relative velocities lead to less aggressive material removal rates and subsurface damage. Zipperian (2011) draws attention to the fact that specimen flatness levels and a uniform finish across the ground surfaces are also favored by complementary rotation. Perusal of grinding conditions given by Elssner *et al.* (1999), Chinn (2002) and Zipperian (2011) and those suggested by Buehler and Struers on their websites indicate that platen speeds of between 200 and 300 rpm are employed for ceramics and glasses.

The orientations with which the specimens are oriented to the abrasive travel direction is important. According to Zipperian (2011) it is best to ensure that any specimen edges with contaminants or coatings are kept in compression. This is effected by having that edge of the specimen being the first edge to be in contact with the abrasive which then goes through the remainder of the sample (see Fig. 9). Experience has shown that a slight (10°) offset from the perpendicular gives better results than when the surface is truly perpendicular to the abrasive travel direction. Specimen orientation is also important for electronic ceramics and laminar type specimens, where it is important to ensure that the abrasive strikes any metallic interlayers or lamellae in a perpendicular manner. In the writer's experience, good edge retention and integrity of surface layers and internal interlayers is best

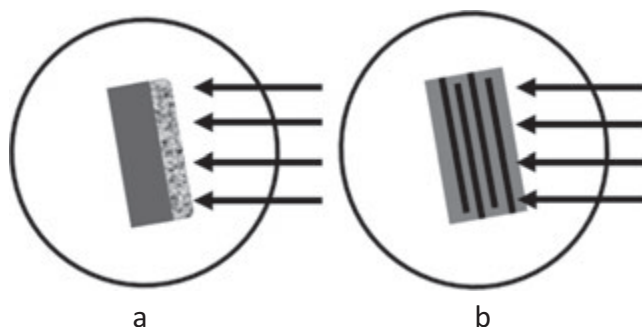


Fig. 9 Orientations of specimens toward abrasive travel direction (arrowed) (a) abrasive likely to tear surface coating (gray). (b) internal metal electrodes (black). Arrows represent abrasive travel direction.

achieved with contra rotation, such that material removal is most significant when specimens are nearly orthogonal to the outer diameter of the grinding or polishing platen. This is most probably because of the greater relative velocity when the specimen is at the 0° position on the grinding platen and this corresponds to the abrasive travel direction shown on Fig. 9.

Grinding pressure can be applied either to each sample individually or through the center of the specimen holder, putting an equal load on all specimens. The latter type of loading applies to the specimen holders shown in Fig. 8, where specimens are clamped in position and so can be oriented as required. In the case of individual loading, the specimens can freely rotate within a containment ring and so cannot be specifically oriented. Typical loadings for ceramic samples suggested by Elssner *et al.* (1999), Chinn (2002) and Zipperian (2011) are 200 N over six specimen mounts which are normally 32 mm in diameter. Zipperian (2011) points out that in fact for hard specimens, such as ceramics, in softer mounts, the real pressure applied is over the specimen area rather than the mount area. Thus, 40 kPa grinding/polishing pressures resulting from the application of 200 N to six 32 mm mounts is amplified to 410 kPa if the mounted ceramic specimens are 10 mm in diameter. Clearly, the polishing pressure on the specimen is much reduced if the mount is filled with a ceramic filler i.e., it will be very close to 40 kPa. While increased polishing pressures yield greater material removal rates, Elssner *et al.* (1999) points out that reductions in polishing pressure reduce the likelihood of pull-outs occurring, which is very important if porosity is being assessed and examined.

Abrasive Systems for Grinding

Grinding systems can be based on fixed, semi-fixed or freely rolling abrasives (Elssner *et al.*, 1999; Chinn, 2002; Täffner *et al.*, 2004; Vander Voort, 2009; Zipperian, 2011). Typical fixed abrasives are traditional SiC papers used in metallography and diamond fixed by resin or metal bonding into a platen. These platens comprise raised islands with depressed reservoirs between them to retain coolant/lubricant and to allow swarf to be taken away from the surface being ground. Fig. 10(a) shows an example of a fixed diamond grinding platen. From current consumables catalogs, typical diamond grit sizes available range from 240 to $3\ \mu\text{m}$. Semi-fixed abrasive systems comprise abrasive grits retained in lower recesses of a platen (e.g., concentric or spiral grooves or in regions between raised circular or hexagonal structures) fabricated from a composite or resin Fig. 10(b) shows an example of such a platen. Raised areas act as lapping surfaces where abrasive grains cut the specimen surface by a rolling action, thus removing material. Material removal is also effected by machining by abrasive particles which can be temporarily fixed by being entrapped at the interface between the raised part of the platen and the groove/recessed area (see Zipperian, 2011). For the semi-fixed abrasive system, diamond slurries or suspensions are applied to the platen surface. Such slurries/suspensions can also be used in conjunction with a metal mesh platen where recessed areas away from the metal hold the coolant and abrasive and the top part of the metal mesh is able to hold temporarily fixed abrasive particles in contact with the glass, glass ceramic or ceramic being ground. The most gentle mode of specimen grinding is lapping (Elssner *et al.*, 1999). In lapping, freely moving abrasive particles, typically SiC or diamond grits, roll between the specimen being ground and a cast iron wheel.

The choice of coolant/lubricant for specimen grinding depends on the nature of the specimen. If any parts of the specimen (e.g., surface layers, surface contaminants, internal phases) are water soluble or readily undergo hydrolysis, non-aqueous fluids must be used. A typical non-aqueous fluid would be alcohol based. If neither water solubility or hydrolysis are potential problems, water or water based lubricants can be used. In general, water is a recommended lubricant for fixed abrasive platens, whilst diamond suspensions used for grinding are suspended in lubricants. Again, perusal of consumables available from Struers, Buehler or PACE Technology and others shows both aqueous or non-aqueous lubricants/coolants to be available, as well as diamond suspensions which have aqueous or non-aqueous carrier fluids.

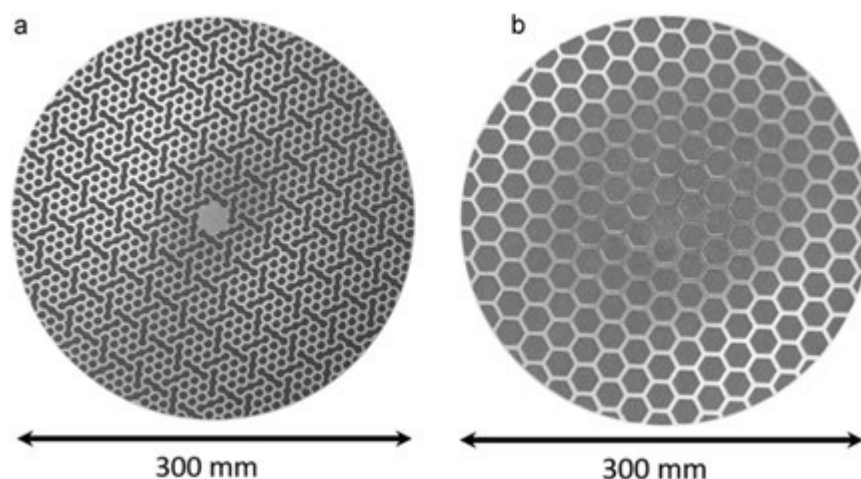


Fig. 10 (a) Fixed diamond grinding platen (gray areas are raised lighter areas are depressed) (after Struers web publication, accessed Sept. 2020 <https://www.struers.com/en/Products/Grinding-and-Polishing/>). (b) Grinding platen for use with diamond suspensions (gray areas are raised lighter areas are depressed) (after Struers web publication, accessed Sept. 2020 <https://www.struers.com/en/Products/Grinding-and-Polishing/>) with permission.

An Overview of Grinding and Polishing

Introduction

It is virtually impossible to recommend specific polishing methodologies for glasses, glass ceramics, ceramics and ceramic matrix composites, since they are often specific to an individual or a metallographic supplies vendor. Mörtel (1991), Elssner *et al.* (1999), Chinn, (2002), Xie *et al.* (2003), Täffner *et al.* (2004), Geels *et al.* (2007), Vander Voort (2009), Zipperian (2011) and Buehler (2020) all give excellent “Recipes” for arriving at a perfectly polished specimen for subsequent ceramographic examination before or after etching. The following sections attempt to provide background to planar grinding, fine grinding and polishing such that generalities in the “Recipes” are drawn out. One parameter that is not commented on is the time taken for the various stages. This is because they vary widely. For example, Xie *et al.* (2003) use a total grinding and polishing time of 1 h 40 min for the fine grinding and polishing of α -sialons whilst Zipperian (2011) recommends 15 min total fine grinding and polishing time for the engineering ceramics ZrO_2 , SiAlON and Si_3N_4 . How long each grinding and polishing stage will be determined by the person doing the ceramographic preparation.

The following sections apply to machine grinding and polishing with specimens clamped in a holder which has a central load applied. During the preparation of specimens, it is absolutely essential that the specimens and holder are thoroughly cleaned between each grinding and polishing stage. It is useful too if platens are cleaned with a mild detergent solution and rinsed after each use. This is because swarf and congealed coolant/diamond suspension can accumulate during use. Any washing up brushes should be specifically kept for a specific abrasive size to avoid the potential for cross-contamination. In addition, it is essential that specimens are not removed from the holder during cleaning because it is impossible to return the specimen to the exact position and height with micron precision. Thus, it is good to have the use of an inverted microscope to be able to look at specimen surfaces during grinding and polishing.

Planar grinding

Following sectioning and mounting, a specimen is ground before polishing. The grinding process comprises two stages: planar grinding and fine grinding. Planar grinding involves the flattening of the specimen and mount surface such that they are completely level and the specimen has a uniform level of surface roughness and material damage across its area. The grade of abrasive and the process by which planar grinding is carried out depends upon the material. Thus, for glasses, glass ceramics and softer/porous ceramics which may have been sawn using a fine diamond grit, a reasonably fine abrasive can be used which is either fixed or semi-fixed. Abrasives which can be employed are silicon carbide, cubic boron nitride or diamond. Quite frequently, silicon carbide papers used for metallographic preparation can be used. For harder and tougher ceramics and ceramic matrix composites, a coarser abrasive should be employed, because the diamond grit size used for sectioning is also coarser. For these materials, diamond is the strongly preferred abrasive. For electronic ceramic specimens containing metallic interlayers, fixed abrasives are preferred since they much reduce the potential for abrasive particles to become embedded in the metallic layers leading to loss of microstructural detail.

From the various methodologies for polishing ceramics and glasses given by (Elssner *et al.*, 1999; Chinn, 2002; Täffner *et al.*, 2004; Geels *et al.*, 2007; Vander Voort, 2009; Zipperian, 2011) the following can be said. In general, planar grinding employs abrasive sizes in the range 30–60 μm with fixed abrasives and water cooling unless the specimen type precludes this. Forces employed are generally in the range 35–40 N per sample and grinding platen rotation speeds are 200–300 rpm. Both contra and complementary rotations are suggested!

Fine grinding

Fine grinding is carried out after planar grinding, once the specimen is plane and coplanar with the mount. Glasses, glass ceramics and less dense materials can continue to be ground using silicon carbide papers. However, as Geels *et al.* (2007) point out silicon carbide abrasive particles are rapidly worn down by comminution and so lose their cutting ability in a minute or two. Incidentally, this is not the case for polycrystalline diamond, where comminution rates are much less. It is normal to go down through the grades of silicon carbide abrasive papers. Abrasive sizes are characterized using US mesh sizes or European grain sizes (see Elssner *et al.*, 1999; Zipperian, 2011). The references give the corresponding grit sizes in μm . Again, consulting the various methodologies given by Elssner *et al.* (1999), Chinn (2002), Täffner *et al.* (2004), Geels *et al.* (2007), Vander Voort (2009) and Zipperian (2011), typical abrasive sizes used are 15, 9 and 6 μm or their US or European grit/grain size equivalents. Platens can be silicon carbide papers for softer materials and this type of grinding is preferred for electronic and porous ceramics. For hard tough materials, fixed diamond abrasives are often used, particularly for the first fine grinding stage. For finer grinding, semi-fixed abrasive platens with diamond suspensions are used. These can be resin based or metal mesh or indeed hard napless polishing papers able to hold abrasive and coolant in perforations or spaces in between woven hard fibers (see Geels *et al.*, 2007 Table 13.1 for typical types of platens). Platen rotation rates suggested are in the range 150–200 rpm with both complementary or contra rotation of the specimen holder. Forces between 35 and 40 N are suggested except for glasses where loads of about half these values are suggested (see Buehler, 2018b).

Polishing

Polishing of glasses, glass ceramics and ceramics is carried out on cloths which have been specifically developed for the purpose. Chinn (2002) and Geels *et al.* (2007) list the types of cloth types available, and, although some trade names of available cloths may have changed, the descriptions of their characteristics are still valid (see for example the cloth descriptions in Buehler, 2018b). Generally, hard woven cloths are preferred as they lead to good specimen flatness and edge retention. These cloths have little pile or nap and so instead of diamond particles being presented to the specimen surface on individual strands of the cloth, fine

diamond particles are held in perforations or spaces in between hard woven fibers as for fine grinding (Section “Fine Grinding”). In certain instances, it may be beneficial to use a napped cloth because its mode of abrasion causes areas of different hardness in the specimen to be revealed as material removal rates from softer phases or grain orientations will differ. This type of polishing is referred to as relief polishing, because it generates areas of slightly different heights allowing phase or grain structures to be visible without etching or scanning electron microscopy contrast.

Polishing uses diamond grit sizes of 6, 3, 1 and 0.25 μm which are suspended in aqueous or non-aqueous suspensions and used with coolants/lubricants of the same type. The amount and viscosity of the coolant/lubricant employed can affect material removal rates. This is because too little allows the abrasive particles to penetrate most deeply into the specimen, while too much leads to a lubricant film with a thickness close to the abrasive size leading to virtually no material removal (see [Elssner et al., 1999](#)). Some authors suggest that lower platen rotation speeds are reduced for polishing while others suggest they are held at the same level as for fine grinding. Given that material removal with minimum subsurface damage is required, then it is probably preferable to keep the speed high and reduce to the applied loads.

Increased rates of material removal can be achieved by a chemo-mechanical polishing (CMP) approach. CMP involves the use of abrasive nanoparticles of for example: silica, alumina, ceria iron oxide and chromium oxide. [Zipperian et al. \(1992\)](#) shows decisive proof that CMP of silicon nitride gives greatly enhanced surface finish and a smoother finish, with R_a values being about 1/3rd of those for a mechanically polished specimen. Which abrasive to use and at what pH are of course material dependent and detailed advice can be sought from consumables suppliers (e.g., Struers, Buehler, PACE Technologies). [Wisniewski et al. \(2011\)](#) used CMP to enable them to obtain the low levels of surface damage needed for the acquisition of Electron Back Scattered Diffraction (EBSD) data of sufficient quality to facilitate crystallographic analysis of the surface crystallization of fresnoite glass ceramics. An alternative way of achieving a surface with minimal surface damage is vibratory polishing ([Buehler, 2018a](#)). In vibratory polishing, a specimen is held within a weighted holder which is free to move on the surface of a polishing cloth located on a vibrating base. The specimens oscillate up and down and move around a containment bowl ([Geels et al., 2007](#)) and this results in sufficient relative motion for gentle material removal. If necessary, CMP polishing suspensions could be used for vibratory polishing.

It is important to note that more gentle material removal rates yield more faithful 2D representations of 3D microstructures. This is particularly so for porous materials as well as materials where grain pull outs often accompany ceramographic preparation. Thus, for ceramic materials containing porosity, it is worthwhile assessing porosity levels as polishing is carried out. If the true microstructure has been revealed, the porosity levels will be seen to be similar after different times of polishing.

Etching

Introduction

In ceramography, etching is a broad term, encompassing chemical and physical methods, as well as a combination of both, used to reveal visible contrasts in microstructure. In this context, visible refers to the resolution of microstructural detail in optical or scanning electron microscopes. In general, the features revealed by etching are grain boundaries. However, surface faceting of grains can also be observed. In general, because of their chemical stability, ceramics require highly aggressive attack by chemical etchants with attendant levels of danger which should be acknowledged by the use of appropriate personal protective clothing and behavior while etching. The severity of the etching process may require specimens to be removed from their mounts. This is particularly the case for etching specimens in molten salts or etching them at high temperature (thermal etching).

[Mörtel \(1991\)](#), [Elssner et al. \(1999\)](#), [Chinn \(2002\)](#) and [Täffner et al. \(2004\)](#) all give tables of chemical etchants for a wide range of oxide and non-oxide ceramics. In addition, they give alternative or additional etching methods such as electrochemical, thermochemical, thermal, relief polishing, ion polishing, plasma etching and “etching” by tinting using heat or thin films. Clearly, the lists of etchant recipes and methodologies provided by [Mörtel \(1991\)](#), [Elssner et al. \(1999\)](#), [Chinn \(2002\)](#) and [Täffner et al. \(2004\)](#) do not need repeating. However, this section will briefly describe each etching process and where possible show a representative micrograph.

It cannot be stressed enough that etching can involve the use of dangerous chemicals and gases as well as high temperatures and that every possible measure is taken to follow safety guidelines from MSDS sheets as well as laboratory safety rules.

Before Etching

Three levels of examination should be completed before etching. These are: hardness or microhardness tests ([Chinn, 2002](#)), porosity measurements ([Chinn, 2002](#)) and chemical analysis by energy or wavelength dispersive X-ray analysis. Clearly, etching attacks the surface structure of the ceramic or glass and so accurate hardness or microhardness values will be compromised by a softer “top layer”, the depth of which will determine the deviations from true values. In some instances, particularly chemical etching, porosity levels can be increased due to preferential removal of micron size second phases which are more susceptible to solution in the etchant which leads to erroneous porosity data. The quality of chemical analysis using a scanning electron microscope fitted with X-ray analysis spectrometers can be adversely affected by etching. This is because certain phases can be removed by etching (e.g., glass in alumina by phosphoric acid etching). Thus, the overall composition of the surface layers of the alumina would be richer in aluminum than the bulk of the ceramic which contained an aluminosilicate glass phase.

Removal of Specimens From Mounts

If the etchants to be used are likely to attack the mounting material (see Zipperian, 2011) or the mount is likely to be heated to above its maximum use temperature, it may be necessary to remove the specimen from the mount before etching (Geels *et al.*, 2007). Chinn (2002) suggests sawing the mount material away from the specimen, leaving a 1 mm margin using a diamond sectioning saw. The remainder of the resin can then be removed by heating to cause the resin to combust or pyrolyse. This process should render the remnant mounting material powdery and easily removable. It is to be noted that the heating process should be conducted under a fume hood. Alternative methods of removing the residual resin after sawing are: (1) immersion of the specimen in M-Pyrol (N-Methyl-2-Pyrrolidone) or (2) immersion in N,N-Dimethyl-formamide at 150°C (Geels *et al.*, 2007). It is of course essential to follow safety guidelines when using these chemicals. Following complete removal of the specimen from the mounting material, it is always recommended that identifying saw cuts are made into back of the specimen away from the polished face. There is nothing more annoying than trying to keep unmarked specimens in a specific order on a tile or crucible only to mix them up by dropping them or some other accident!.

Etching Methods

Relief etching (polishing)

The methodology of relief polishing, which is also relief etching, is described in Section “Polishing” above. An example of a microstructure prepared using relief etching (polishing) is given in Fig. 11. As pointed out by Chinn (2002) the technique is straight forward. However, problems can arise such as edge rounding and because the very process involves generating phases or grains with different respective heights, higher magnifications in optical microscopy may be limited because of their small depth of field. It appears generally accepted that relief etching is a preferred method of “etching” metallized ceramics or electronic ceramics containing metallic electrodes.

Thermal etching

Heating a polished ceramic surface to a high enough temperature results in the formation of grooved grain boundaries and curved grain surfaces (Geels *et al.*, 2007). Calderon-Moreno and Schehl (2004) show representative micrographs of an alumina-zirconia specimen which has been thermally etched (see Fig. 12). The specimen shown in Fig. 12 was sintered at 1600°C and then thermally etched in air at 1400°C for one hour. The grooving of the grain boundaries and some curving of grain surfaces can be clearly seen in Fig. 12. The thermal etching temperature is consistent with the suggestions made by Elssner *et al.* (1999) and Chinn (2002) of temperatures 100–200°C below the sintering temperature. Typical times range from a few minutes to two or more hours. Thermal etching is an oft used etching method and Elssner *et al.* (1999), Chinn (2002) and Täffner *et al.* (2004) indicate its use for alumina, barium titanate, cemented carbides, cordierite, lanthanum strontium manganese oxide, silicon carbide, silicon nitride, spinel, titania and zirconia. For the non-oxide ceramics, care needs to be taken with respect to the gaseous environment. Nitrogen or a vacuum can be used for silicon nitride. For carbide ceramics it is necessary to use an inert gas (e.g., argon) or a vacuum.

Based on experience, it must also be said that the furnace environment must be clean and it is preferable if the specimen is housed within a pure alumina tube or chamber. This is because contaminants can be released from typical muffle or tube furnaces which can condense on to the specimen during thermal etching, leading to fields of view which are annoyingly compromised in terms of quality and clarity. Other limitations of thermal etching are (1) The potential for grain growth at the high temperatures involved and (2) the possibility of significant specimen damage if the material is allotropic. Chinn (2002) warns of potential problems etching zirconia due to phase transformations e.g., monoclinic to tetragonal which can generate transformation stresses sufficient to destroy a carefully prepared ceramographic specimen!.

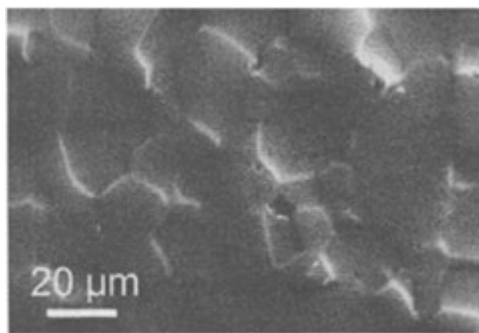


Fig. 11 Micrograph of alumina relief etched (polished) with polished with colloidal SiO₂. After Elssner, G., Hoven, H., Kiessler, G., Wellner, P., Wert, R., 1999. *Ceramics and Ceramic Composites Materialographic Preparation*. Amsterdam: Elsevier.

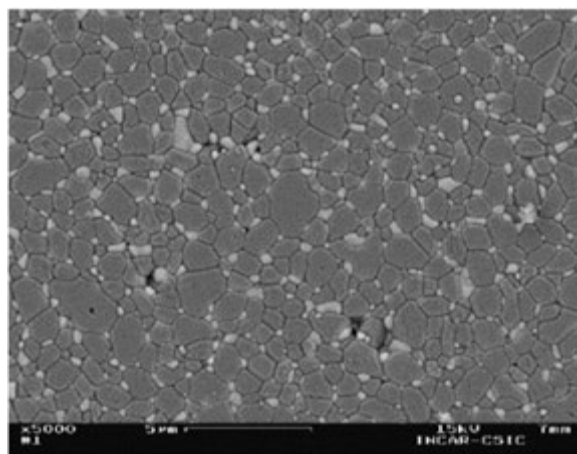


Fig. 12 SEM micrograph showing a polished cross-section an alumina 20 wt% zirconia composite thermally etched in air at 1400°C for 1 h (bar = 5 μm). After Calderon-Moreno, J.M., Schehl, M., 2004. *Journal of the European Ceramic Society* 24, 393–397.

Chemical etching

Chemical etching involves the removal of areas of lower chemical stability from the specimen surface. These areas may be a second phase, e.g., an intergranular glass, or grain boundaries whose energies are higher than the grains they surround and so are attacked preferentially. As previously mentioned, there are many chemical etchants. Many are based upon hydrofluoric acid used alone or mixed with other chemicals e.g., hydrochloric acid, nitric acid, methanol (see Chinn, 2002). Such etchants are used at room temperature. Other strong acids are used, boiling, e.g., H_3PO_4 for alumina and mullite. Molten salts are also used as chemical etchants. Cook *et al.* (1995) used molten 90 wt% KOH:10 wt% KNO_3 to etch sintered silicon carbide, siliconized silicon carbide, pressureless sintered silicon nitride and a $z = 0.5$ β -sialon. The temperature used was 480°C and the time 15 min. These authors indicated that the molten salt etch was the best method out of six tried for all but the siliconized silicon carbide. In the writer's experience, molten salt etching can be a very useful etching method for non-oxide ceramics. However, much care taken needs to be taken to get etching times correct so as not to etch the matrix grains or require much post etching cleaning. Quite often a glass like contaminant remains on the surface of the etched ceramic which compromises examination of the true microstructure and reimmersion in the molten salt is the only way to remove it. An example of a microstructure produced using chemical etching is shown in Fig. 13.

Electrolytic etching

Electrolytic etching is applicable to ceramics showing some conductivity e.g., carbides and ZrB_2 (Elssner *et al.*, 1999; Chinn, 2002). Typically, the specimen is held either in a conductive mount or a hole is drilled in the back or side of the mount to allow electrical contact to be made with the aid of a screw. Using a suitable DC power supply, the specimen is made anodic with respect to a cathodic cup in which the electrolyte is held. Examples are the etching of titanium carbide using 1% KOH solution at 5 volts for 4 min (Chinn, 2002) and the etching of B_4C in 0.1% KOH with a current density of 0.1 A cm^{-2} for 30–60 s (Rehman *et al.*, 2015). The microstructure arising from the latter etching process is shown in Fig. 14.

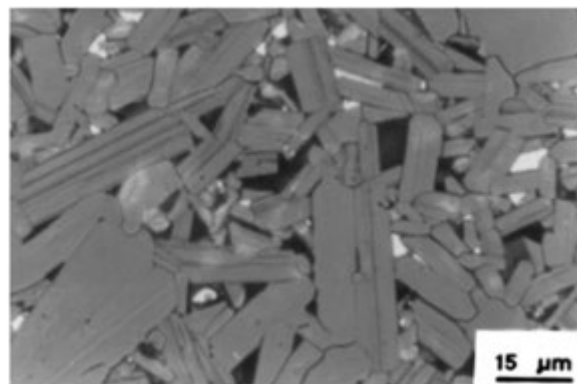


Fig. 13 Microstructure of silicon carbide densified with Y_2O_3 , Al_2O_3 and SiO_2 after etching with boiling Murakami's solution (15 g KOH + 15 g $\text{K}_3\text{Fe}(\text{CN})_6$ + 60 ml H_2O) for 5 min. After Gomez, E., Echeberria, J., Iturriza, I., Castro, F., 2004. Liquid phase sintering of SiC with additions of Y_2O_3 , Al_2O_3 and SiO_2 . *Journal of the European Ceramic Society* 24, 2895–2903.

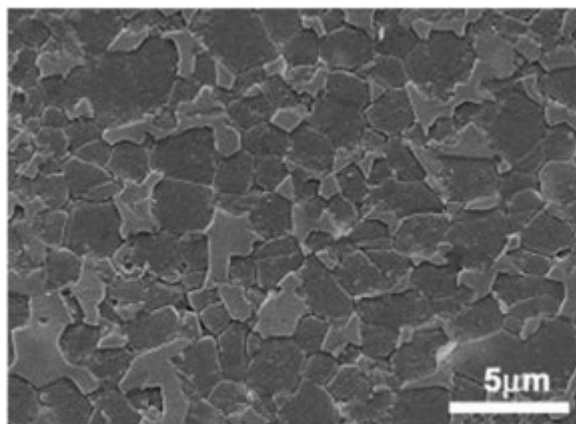


Fig. 14 SPS sintered B₄C - 4 wt% Si electrochemically etched in 1% KOH solution with a current density of 0.1 A. cm⁻² for 30–60 s. After Rehman, S.S., Ji, W., Khan, S.A., Fun, Z., Zhang, F., 2015. Microstructure and mechanical properties of B₄C densified by spark plasma sintering with Si as a sintering aid. *Ceramics International* 41, 1903–1906.

Plasma etching

The characterization of sintered silicon nitride, sialon and silicon carbide microstructures has been made significantly easier by the use of plasma etching. The micrograph shown in [Fig. 1\(b\)](#) was generated by plasma etching using a CF₄ oxygen gas mixture. The ionized CF₄ gas preferentially removes silicon atoms from the surface and thus the silicon nitride grains are preferentially removed as SiF₄. This leaves the glass phase standing slightly proud of the surface enabling excellent contrast for imaging. There are many other examples in the literature because of the clarity of image which can be obtained by scanning electron microscopy. Plasma etching systems are readily available due to their use in the electronics industry and small laboratory systems are available not only for etching but also for cleaning samples before SEM or TEM examination.

Less common etching methods

Thermochemical etching involves the use of a two stage etching process. In the first instance specimens are etched chemically and then they are subsequently thermally etched. The temperature at which the ceramic is thermally etched is much reduced compared to that used for thermal etching alone. [Chinn \(2002\)](#) indicates that alumina sintered at 1630°C could be thermochemically etched at 1150°C after chemical etching for two or three minutes. [Chinn \(2002\)](#) also recounts the etching of nickel-zinc-ferrite (Ni_{0.5}Zn_{0.5}Fe₂O₄) sintered at 1240°C could be thermochemically etched at 850°C after chemical etching. In both cases the chemical etchants were mixtures of orthophosphoric acid and nitric acid. Advantages claimed are that the lower thermal treatment temperatures reduce the likelihood of grain growth and surface modification. It should be noted that for thermal etching alone, alumina would require a temperature of 1500°C rather than the 1150°C used for the thermochemical etching.

Ion etching involves the exposure of a polished specimen surface to a beam of argon or krypton ions incident at angles of between 5° and 60° ([Mörtel, 1991](#)). The ion bombardment causes grain boundaries and grains with different orientations to undergo different rates of ion milling, resulting in relief effects being generated by the glow discharge based process. [Mörtel \(1991\)](#) reports the use of ion etching for silicon nitride and zirconia, while [Chinn \(2002\)](#) recommends the technique for alumina, sialon, silicon carbide and urania. The technique is may also be used for AlN and lead zirconium titanate (see for example see “Relevant Website section”).

Tint etching and interference film etching are specialist techniques for optical microscopy. The interested reader is directed toward excellent descriptions of the techniques by [Elssner et al. \(1999\)](#) and [Chinn \(2002\)](#). They are frequently used in conjunction with differential interference contrast optical microscopy (see [Geels et al., 2007](#)) for an explanation of this microscopic technique.

Concluding Remarks

In conclusion, it can be said that there is plenty of useful background information relating to sectioning, mounting, planar grinding, fine grinding, polishing and etching. However, as the reader will have noticed very few of the sources of information for this chapter are less than a decade old. This is not a great problem as many of the developments of equipment, accessories and consumables appear to be for reliability and patent reasons rather than radical technical change. The suppliers websites are a great source of background information. However, because a significant majority of their business is metallurgy related, much of this information is not ceramic related. That said, the suppliers and their agents will willingly help with developing a specific sectioning, mounting, planar grinding, fine grinding and polishing régime for a particular ceramic and so a researcher should not hesitate to contact them. Useful troubleshooting analyses are given in the publications of [Geels et al. \(2007\)](#) and [Zipperian \(2011\)](#). Help with etching is a little more difficult to attain except from research colleagues.

As mentioned in the very first sentence of Section “Introduction”, the phrase “samples were mounted, ground and polished” is of little use to the inexperienced researcher and so it would be highly beneficial to all in the field of ceramics and glasses research, if specimen preparation techniques were reported in the literature. In many ways this is as important to the “budding researcher” as a description of how the material was prepared!!!!.

References

- Arsecularatne, J.A., Dingeldein, J.P., Hoffman, M., 2014. An in vitro study of the wear mechanism of a leucite glass dental ceramic. *Biosurface and Biotribology* 1, 50–61.
- Brindley, W.J., Leonhardt, T.A., 1990. Metallographic techniques for evaluation of thermal barrier coatings. *Materials Characterization* 24, 93–101.
- Buehler, 2018a. Buehler® SumMet™ – A Guide to Materials Preparation and Analysis. Illinois: Buehler.
- Buehler, 2018b. Polishing Application Guide. Available at: www.buehler.com/assets/Brochures/English/Consumables (accessed September 2020).
- Calderon-Moreno, J.M., Schehl, M., 2004. Microstructure after superplastic creep of alumina–zirconia composites prepared by powder alcoxide mixtures. *Journal of the European Ceramic Society* 24, 393–397.
- Chen, C., Müllera, B.R., Prinza, C., *et al.*, 2020. The correlation between porosity characteristics and the crystallographic texture in extruded stabilized aluminium titanate for diesel particulate filter application. *Journal of the European Ceramic Society* 40, 1592–1601.
- Chinn, R.E., 2002. *Ceramography: Preparation and Analysis of Ceramic Microstructures*. Ohio: ASM International.
- Cook, S.G., Little, J.A., King, J.E., 1995. Etching and microstructure of engineering ceramics. *Materials Characterization* 34, 1–8.
- Elssner, G., Hoven, H., Kiessler, G., Wellner, P., Wert, R., 1999. *Ceramics and Ceramic Composites Materialographic Preparation*. Amsterdam: Elsevier.
- Geels, K., Fowler, D.B., Kopp, W.-U., Rückert, M., 2007. *Metallographic and Materialographic Specimen Preparation, Light Microscopy, Image Analysis and Hardness Testing*. West Conshohocken, PA: ASTM International.
- Johnson, A., Fisher, D., Vander Voort, G., 2015. Precision cutting – The Science of the Cut. In *Tech Notes*. Vol. 3 (6). Buehler, Illinois.
- Kelly, M., Singh, J., Todd, J., Copley, S., Wolfe, D., 2008. Metallographic techniques for evaluation of thermal barrier coatings produced by electron beam physical vapor deposition. *Materials Characterization* 59, 863–870.
- Moore, M.A., King, F.S., 1980. Abrasive wear of brittle solids. *Wear* 60, 123–140.
- Mörtel, H., 1991. Microstructural analysis. In: Schneider, S.J. (Ed.), *Engineered Materials Handbook Volume 4 Ceramics and Glasses*. Ohio: ASM International, pp. 570–579.
- Rehman, S.S., Ji, W., Khan, S.A., Fun, Z., Zhang, F., 2015. Microstructure and mechanical properties of B₄C densified by spark plasma sintering with Si as a sintering aid. *Ceramics International* 41, 1903–1906.
- Renoirt, M.-S., Maury, N., Dupla, F., Gonon, M., 2019. Structure and properties of piezoelectric strontium fresnoite glass-ceramics belonging to the Sr–Ti–Si–Al–K–O system. *Ceramics* 2, 86–97.
- Täffner, U., Carle, V., Schäfer, U., Hoffmann, M.J., 2004. Preparation and microstructural analysis of high-performance ceramics. In: Vander Voort, G.F. (Ed.), *ASM Handbook Volume 9: Metallography and Microstructures*. Ohio: ASM International, pp. 1057–1066.
- Vander Voort, G.F., 2009. Perfect prep. *Ceramic Industry Magazine* 159, 14–17.
- Wisniewski, W., Völksch, G., Rüssel, C., 2011. The degradation of EBSD-patterns as a tool to investigate surface crystallized glasses and to identify glassy surface layers. In: *Ultramicroscopy*, 111. pp. 1712–1719.
- Xie, Z.-H., Moon, R.J., Hoffman, M., Munroe, P., Cheng, Y.-B., 2003. Role of microstructure in the grinding and polishing of α -sialon ceramics. *Journal of the European Ceramic Society* 23, 2351–2360.
- Yin, J.-F., Bai, Q., Zhang, B., 2018. Methods for detection of subsurface damage: A review. *Chinese Journal of Mechanical Engineering* 31. (article number 41).
- Zipperian, D.C., 2011. *Metallographic Handbook*. Tucson, AZ: PACE Technologies.
- Zipperian, D.C., Chanat, S., Trujillo, A., 1992. Ceramic microstructural analysis for quality control. *American Ceramic Society Bulletin* 71, 1077–1082.

Relevant Website

<https://www.gatan.com/products/sem-specimen-preparation/pecs-ii-system>
PECS II System.

Scanning Electron Microscopy for Ceramics and Glasses

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Introduction

Scanning Electron Microscopy (SEM) was first conceptualized in 1935. However, it was not until 1965 that the first commercially available instruments were available. Since 1965 many, many improvements in the design of vacuum systems, electron columns and lenses as well as great improvements in computer controls have been effected. These improvements have all contributed to increases in resolution, such that instrument manufacturers are able to quote better than 1 nm resolution, depending on microscope operating parameters. A facility to use SEMs in low vacuum mode has greatly improved their versatility. This is especially the case for biological specimens which may relate to or be attached to biomedical ceramics and glasses. In addition, in-situ experiments can be conducted. Such experiments can be listed as: tensile testing, heating/cooling stages with very high heating/cooling rates, electrical testing, cathodoluminescence.

The first electron probe microanalysis systems, based upon wavelength analysis became readily available toward the late 1970s. Since that time, major changes have also occurred with the advent of energy dispersive X-ray analysis and more recently, soft X-ray emission analysis. In addition to X-ray analysis, it is possible to obtain chemical information from the top few nanometers of surface using Auger electron spectroscopy.

By analyzing the diffraction of electrons backscattered from the surface layers (over a depth of about 10–40 nm) with a plate analyzer, the crystallography of a specimen can be ascertained in terms of spatial distribution, crystallographic orientation and texture. Using this analytical method, grain shapes and sizes and the nature of grain boundaries can also be quantitatively assessed.

The introduction of dual SEM/FIB (Focused Ion Beam) systems has revolutionized the ability to examine a specimen using SEM, decide on a micro-feature of specific interest and then excise a cross-section of that micro-feature in its surroundings for more detailed transmission electron microscopy. Add to this capability the incorporation of an electron detector below the specimen and in-SEM STEM (scanning transmission electron microscopy) is possible! Add to this an annular dark field contrast facility and STEM with chemical contrast can be readily carried out.

In short, current SEM instruments cover a wide range of imaging capability for the analysis of a wide range of ceramics, glass-ceramics and glasses. The backgrounds to the various techniques will be outlined and examples of images and analytical data given.

Anatomy of a Scanning Electron Microscope

The schematic diagram in the work by Szyrkowska (2005), shown in Fig. 1, gives a suitable indication of the anatomy of a scanning electron microscope. As indicated by Fetzer *et al.* (2021), electrons are produced by thermionic or field emission filaments in electron microscopes. In the case of SEMs though, accelerating voltages are up to 40 kV rather than 200–300 kV as for TEMs. Again, as described by Fetzer *et al.* (2021), the beam is demagnified and focused using electromagnetic lenses and apertures and then rastered across a sample surface by the action of scan coils. The objective lens is the final lens before the sample and the sample may or may not come under the influence of the magnetic field of the lens. Goldstein *et al.* (2003) define the type of objective lens with respect to the relative position of the specimen. Thus, if the sample is outside the lens' magnetic field influence, it is referred to as a pinhole lens, if the sample is wholly within the magnetic field of the lens it is referred to as an immersion lens and if it is not within the magnetic field but under its influence, the lens is referred to as a snorkel lens. The quality of the electron beam is dependent on the electron source size and the energy spread of the electrons defined as $(\Delta E/E_0)$, where ΔE is the spread, and E_0 the accelerating voltage. The former controls spherical aberration and the energy spread chromatic aberration. The full width at half maximum beam intensity, d_p , of the electron beam is heavily dependent on its brightness (β) which is defined in Eq. (1).

$$d_p = \sqrt{\frac{4 \cdot i_p}{\beta \cdot \pi^2 \cdot \alpha^2}} \quad (1)$$

where, i_p and α are probe/beam current and convergence angle.

Table 1 gives data for brightness, source size, energy spread, expected filament life and the beam stability. Clearly, the FEG filaments have the best brightnesses and lowest energy spreads. In particular, the cold FEG filament produces a beam with the best combination of brightness, source size and energy spread. As source size controls spherical aberration and energy spread controls chromatic aberration (see Fetzer *et al.* (2021)) for an explanation of these aberrations, then the small source size and low energy spread will be minimized for the cold FEG system, giving a very bright beam with the minimum aberration problems and hence very high image resolution. The hot FEG and Schottky emitters also appear to have good characteristics. In fact the Schottky emitter is preferred for SEMs fitted with analytical X-ray systems due to the excellent beam stability ($\sim 1\% \text{ h}^{-1}$). This beam stability is important for quantitative X-ray analysis where consistency of beam is important.

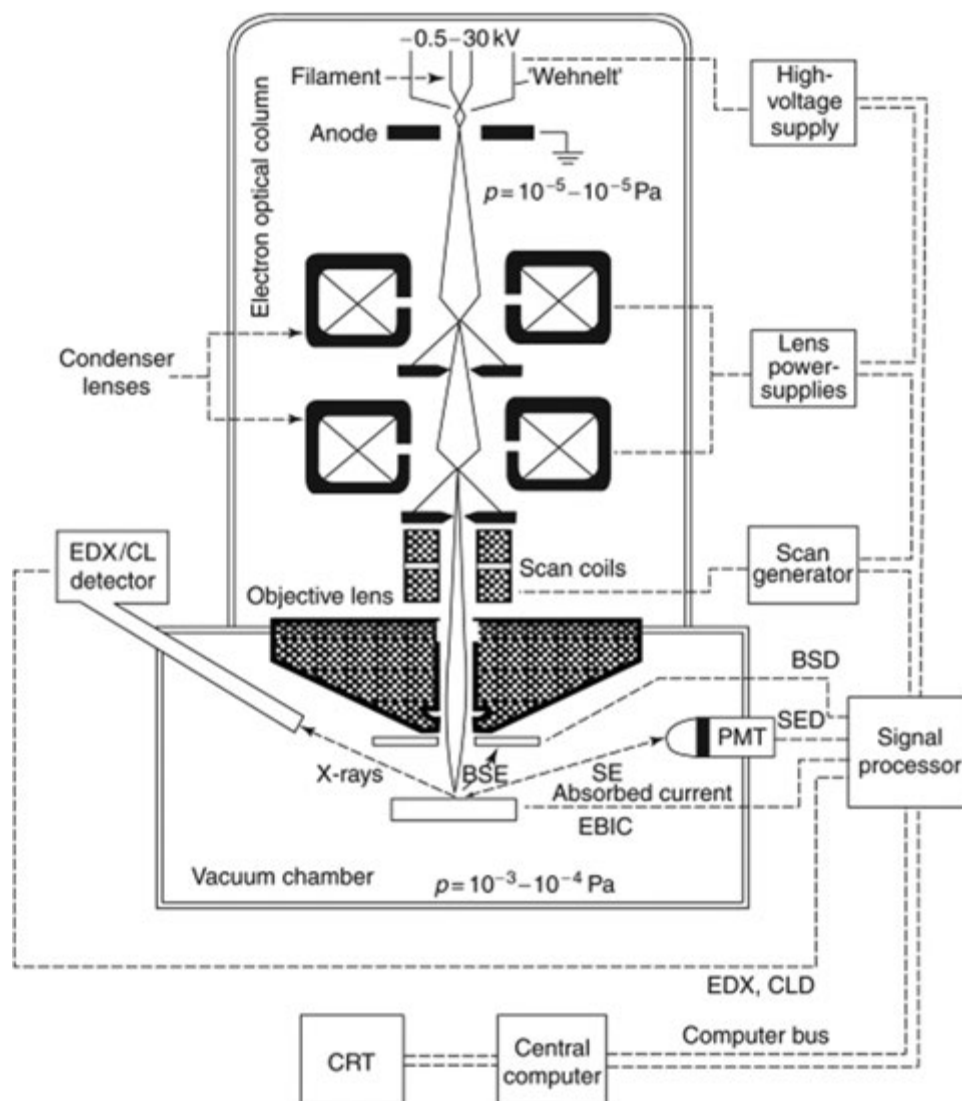


Fig. 1 Schematic of a scanning electron microscope. Reproduced from Szykowska, M.I., 2005. Microscopy techniques: Scanning electron microscopy. In: Worsfold, P., Townshend, A., Poole, C. (Eds.), *Encyclopedia of Analytical Science*. Netherlands: Elsevier, pp. 134–143.

Table 1 Typical properties of electron beams emitted by different sources

	Brightness ($\text{A cm}^{-2} \text{ sr}^{-1}$)	Source size	Energy spread ΔE (eV)	Life (h)	Stability (% per h)
W hairpin	10^5	30–100 μm	1 to 3	≤ 100	1
LaB ₆	10^6	5–50 μm	1 to 2	≤ 1000	1
Cold FEG	10^8	$< 5 \text{ nm}$	0.3	≥ 1000	5
Thermal FEG	10^8	$< 5 \text{ nm}$	1	≥ 1000	5
Schottky	10^8	$< 15\text{--}30 \text{ nm}$	0.3 to 1	≥ 1000	~ 1

Note: Data taken from Goldstein, J., Newbury, D.E., Joy, D.C., et al., 2003. *Scanning Electron Microscopy and X-Ray Microanalysis*, third ed. US: Springer.

Although the thermionic emission filaments appear to offer much lower quality electron beam generation, they are wholly adequate for a very large fraction of scanning electron microscopy requirements. In particular, their use in SEMs for X-ray analysis is wholly adequate due to the interaction volume between electron beams and specimens where X-rays are generated being independent of d_p , i_p and α , which is explained later.

As shown in Eq. (1), probe size is clearly related to probe current, i_p . Deeper analysis shows that other parameters related to aberration and wavelength (dependent on accelerating voltage), as well as i_p , control the minimum probe size. Goldstein et al. (2003)

show how probe size and probe current are related for cold FEG, Schottky and tungsten filaments for 1, 10 and 30 kV accelerating voltages. The graphical relationships show, as expected, that the smallest probe size arises for the cold FEG filament. However, depending on accelerating voltage, for high probe currents, exceeding about 200 pA, Schottky emitters develop smaller probe sizes. Tungsten thermionic filaments have probe sizes which are between 10 and 20 times that of a FEG source for 30 and 10 kV accelerating voltages.

In the analysis of electron probe size, it is of course assumed that the cross-section of the beam is circular. Under certain circumstances however, the beam cross – section may be elliptical. This is manifested by images which appear to flow in x, y or x-y directions depending on the location of the major and minor ellipse axes. This image flow is clearly visible when as the focus is manipulated between under- and over-focus as shown in JEOL (2020a). In order to obviate this imaging artifact, referred to as astigmatism, an octupole stigmator with four sets of magnetic poles is used to manipulate the beam shape from elliptical to circular and thus greatly improve image quality (Goldstein *et al.*, 2003).

Interactions of an Electron Beam with Materials

When electrons in an incident beam enter a material, they are scattered both elastically and inelastically. Elastically scattered electrons undergo changes in direction without changing their energy, whilst inelastically scattered electrons change not only direction but also their energy. These energy losses induce the generation of secondary electrons as well as X-rays. The depth to which incident electrons can penetrate a solid is dependent on their rate of energy loss per unit distance traveled in the material (dE/ds). This rate of energy loss is affected by material density (ρ), atomic number (Z), atomic weight (A), the electron energy at any point in the material (E_i) and the average energy loss per scattering event. Eq. (2) gives the expression for dE/ds .

$$\frac{dE}{ds} = -7.85 \times 10^4 \cdot \frac{Z \cdot \rho}{A \cdot E_i} \cdot \ln \left(\frac{1.166 \cdot E_i}{J} \right) \quad (2)$$

where

$$J = (9.76 \cdot Z + 58.5 \cdot Z^{-0.19}) \times 10^{-3} \quad (3)$$

Various Monte Carlo simulations of electron trajectories in materials have been presented and Fig. 2 shows those typical of C, Si, Ag and Au. It is of interest that the simulations describe a semi-circle meaning that beneath the impact point of an incident electron beam, electron scatterings result in electron trajectories fanning out, but being bounded by a hemispherical boundary. For an accelerating voltage of E_0 , Kanaya and Okayama (1972) consider that 90% of all beam interactions occur within a hemispherical volume with a radius (R_0) given according to Eq. (4). Table 2 shows typical R_0 values calculated for accelerating voltages of 20, 15 and 10 keV for selected relevant materials. Should the beam impinge at an angle i.e., when the sample is tilted at an angle θ to the incident beam this radius (R_θ) decreases according to Eq. (5). However, due to the fact that forward scattering within shallow depths occurs, the backscattered electron yield is enhanced despite the overall interaction volume being less.

$$R_0 = \left(\frac{0.0276 \cdot A}{Z^{0.89} \cdot \rho} \right) \cdot E_0^{1.67} \quad (4)$$

$$R_\theta = R_0 \cdot \cos(\theta) \quad (5)$$

Only certain of the scattered electrons reemerge from the surface, such that they can be captured by a detector. These electrons, referred to as backscattered electrons, come from depths which are between 30% and 60% of the value of R_0 for zero tilt angles. Eq. (6) gives the fractional depth, y_D , from which 95% of backscattered electrons emanate from the surface as a fraction of R_0 , for an accelerating voltage of 20 keV. This fractional depth is important, since it allows prediction of the depth from which 95% of the information, viewed as an image, comes. For lower accelerating voltages (10 keV and below), far more of the signal reaching the electron detector is from shallow depths. Thus, the values of y_D are further diminished in this instance. The lateral distance electrons can

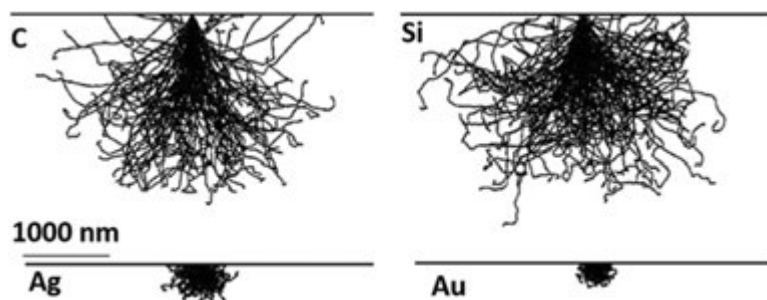


Fig. 2 Monte Carlo simulations of electron scattering within different elements: C, Si, Ag and Au. Reproduced from Szyrkowska, M.I., 2005. Microscopy techniques: Scanning electron microscopy. In: Worsfold, P., Townshend, A., Poole, C. (Eds.), *Encyclopedia of Analytical Science*. Netherlands: Elsevier, pp. 134–143.

Table 2 R_0 values calculated using Eq. (4) for different accelerating voltages for C, Al_2O_3 , Si_3N_4 , a YSiAlON glass and ZrO_2 .

	R_0 values (μm) for 0° tilt angle		
	20 keV	15 keV	10 keV
C	4.4	2.7	1.4
Al_2O_3	2.8	1.8	0.9
Si_3N_4	3.1	1.9	1.0
YSiAlON(gl.)	3.1	1.9	1.0
ZrO_2	1.6	1.0	0.5

Table 3 R_0 , R_{BS} , D_{BS} and η values calculated for an accelerating voltage of 20 keV using Eqs. (4) and (6)–(8) for C, Al_2O_3 , Si_3N_4 , a YSiAlON glass and ZrO_2

	R_0 (μm)	R_{BS} (μm)	D_{BS} (μm)	η
C	4.4	2.7	1.4	0.06
Al_2O_3	2.8	1.7	0.8	0.12
Si_3N_4	3.1	1.8	0.9	0.12
YSiAlON(gl.)	3.1	1.7	0.9	0.16
ZrO_2	1.6	0.8	0.4	0.21

travel within a sample and be ejected as backscattered electrons can be calculated as a function of Z also. Eq. (7) gives an expression for y_R , the fractional lateral distance with respect to R_0 , from which 95% of backscattered electrons emanate. Again, it is seen that y_R is dependent solely on Z .

$$\gamma_D = 0.333 - 0.00374.Z + 2.469 \times 10^{-5}.Z^2 \quad (6)$$

$$\gamma_R = 0.675 - 0.00975.Z + 6.3 \times 10^{-5}.Z^2 \quad (7)$$

$$\eta = -0.0254 + 0.016.Z - 1.86 \times 10^{-4}.Z^2 + 8.3 \times 10^{-7}.Z^3 \quad (8)$$

$$Z_{av} = \sum_0^i x_i.Z_i \quad (9)$$

From the analysis so far, it is clear that for a fixed accelerating voltage, the radius of the interaction hemisphere and also the fractional depth associated with signal generation is heavily dependent on Z , the atomic number. One might expect therefore that the intensity of backscattered electrons might also be dependent on Z . This is indeed the case and Eq. (8) shows how the backscatter coefficient, η , is related to Z . η is also defined as the ratio of the number of backscattered electrons (n_{BSE}) to incident electrons in the incident electron beam (n_B). This can of course related to the ratio of backscattered electron beam current to incident beam current (i_{BSE}/i_B). For ceramics and glasses, it is important to be able to calculate the average atomic number for the composition (Z_{av}). This is done using Eq. (9) where x_i is the atom fraction of constituent i , and Z its atomic number. Using Eqs. (4) and (6)–(8), values of R_0 , radii from which backscattered electrons emanate, R_{BS} , backscattering depths, D_{BS} , and η can be calculated. This calculated data is presented in Table 3 for C, Al_2O_3 , Si_3N_4 , a YSiAlON glass and ZrO_2 .

Fig. 3 illustrates the variation of backscattered electron coefficient, η , with Z for $Z = 6$ to $Z = 80$. It is seen that low atomic number elements have very low coefficients compared to the higher atomic number elements. Fig. 4 shows a backscattered electron image of a crystallized yttrium-SiAlON glass from original work by the writer and co-workers. The micrograph shows three distinct contrasts black, light gray and white. X-ray diffraction showed the phases silicon oxynitride ($\text{Si}_2\text{N}_2\text{O}$) residual yttrium-SiAlON glass with a modified composition and yttrium disilicate ($\text{Y}_2\text{Si}_2\text{O}_7$) to be present in the material. Given the average atomic weight for silicon oxynitride is 10, that for yttrium disilicate is 14.7 and original glass 13.2, the observed contrasts are clearly in accordance with the phases present. Incidentally, the contrast, C , between two phases is given by the ratio $(\eta_2 - \eta_1)/\eta_2$, where $\eta_2 > \eta_1$. Thus, for high average atomic number phases, contrast between them is less than for low average atomic number phases e.g., $\text{Si}_2\text{N}_2\text{O}$ and yttrium SiAlON glass.

Secondary electrons in loosely bound outer shells are released as a result of inelastic scattering effects associated with backscattering electrons. Secondary electrons are emitted over a depth of 5 mean free paths of an electron in a material. Typically, the mean free path of an electron in ceramic materials is in the region of 2.5 nm and so the depth from which a signal could be captured from a secondary electron is about 12.5 nm. Secondary electrons can be formed when the electron beam enters the specimen as well as when backscattered electrons leave the specimen. Fig. 3 shows the variation in the secondary electron yield coefficient with atomic number. For secondary electrons, the variation in yield coefficient with atomic number is negligible once an atomic number of about 15 is exceeded. As imaging is in effect a resolution of different contrasts and the electron yield controls that contrast, then only backscattered electron images can afford chemical contrast imaging over the whole range of atomic

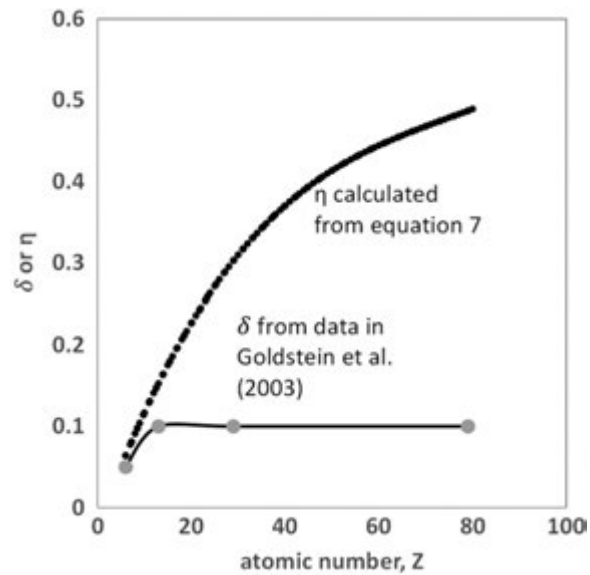


Fig. 3 Effect of atomic number on secondary electron yield coefficient (δ) and backscattered electron yield coefficient (η).

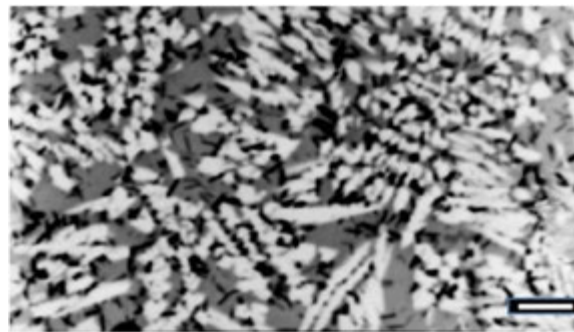


Fig. 4 Backscattered electron image of crystallized yttrium-SiAlON glass. White phase yttrium disilicate (av. At. No. = 14.7), black phase silicon oxynitride (av. At. No. = 10), gray phase residual yttrium-SiAlON glass. (White bar = 10 μm).

number. Secondary electron contrast is limited in the main to topographical contrast. **Fig. 5** shows a typical secondary electron image. The topographical detail is clearly evident in this image. The topographical contrast arises from the manner in which secondary electrons are generated since where the incident beam enters perpendicularly to the surface less secondary electrons are produced than when it enters obliquely (see [JEOL, 2020b](#)). However, the particular image in **Fig. 5** is probably generated from mixed secondary and backscattered electrons emanating from the surface.

Secondary electrons have a very low energies (50 eV or less ([JEOL, 2020b](#))) compared to backscattered electrons whose energy extends from that energy up to that associated with the accelerating voltage. Typical electron detectors in SEMs are of the Everhart-Thornley (E-T) type (see **Fig. 6**) where a biased Faraday cage guides electrons onto a scintillator disc. The light pulses thus generated are guided by a light pipe to a photomultiplier tube. When the detector is negatively biased, secondary electrons are rejected from detection, meaning that the resulting images are backscattered electron images. If positively biased, the image is constructed from secondary electrons, augmented by a few backscattered electrons. Thus, by varying the bias on the E-T detector, relatively true secondary electron images can be obtained. One useful application of changing this bias is to reduce charging effects which are manifested by a series of horizontal line distortions of SEM images. The low energies of the secondary electrons means that their paths can be readily disturbed by electrostatic effects such as charging. This is not the case for backscattered electrons whose paths are not similarly affected. Because of this, it should be possible to obviate imaging problems due to charging by filtering the electrons used to form the image to backscattered electrons.

Other types of detectors exist such as through the lens detectors also called in lens detectors and detectors specifically devoted to backscattered electrons. The former detectors are typically associated with high resolution imaging using cold FEG electron beams and because of their line of sight location are able to resolve along hole walls oriented parallel to the beam geometry. The latter detectors comprise solid state detectors responding to electron impingement on a p-type semiconductor. These solid state detectors are divided into two or four parts. This is because the signals from each sector can be added or subtracted. In simple terms, in sum

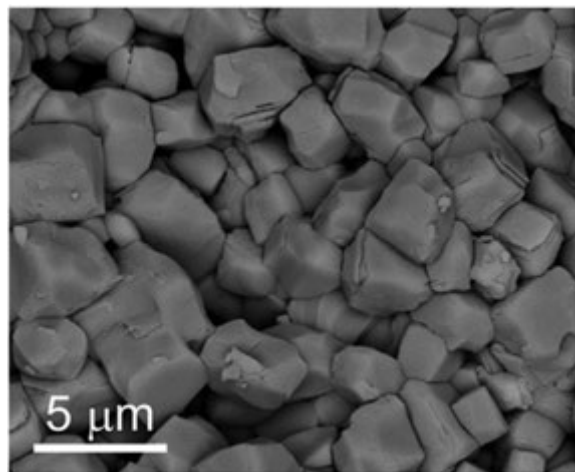


Fig. 5 Secondary electron image of BaTiO₃ polycrystalline ceramic. Reproduced from Sturm, S., Jančar, B., 2014. Microstructure characterization of advanced ceramics. In: Shen, J.Z., Kosmač, T. (Eds.), *Advanced Ceramics for Dentistry*. Netherlands: Elsevier, pp. 151–172.

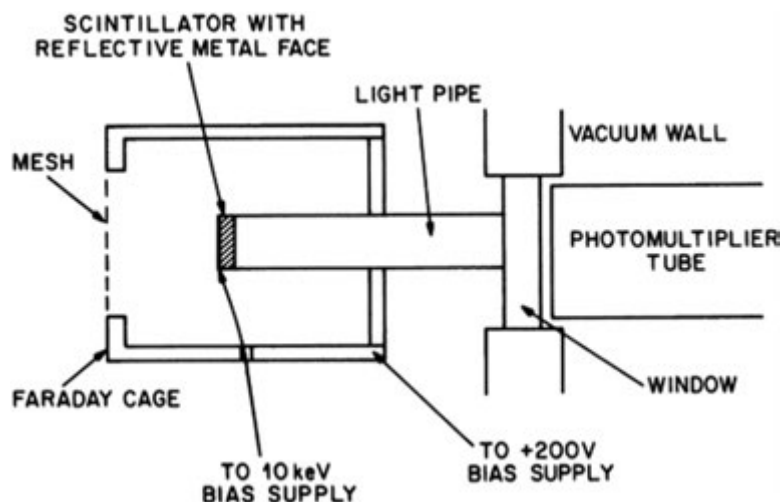


Fig. 6 Schematic of Everhart-Thornley detector. Reproduced from Joy, D.C., Howitt, D.G., 2003. Scanning electron microscopy. In: Meyers, R.A. (Ed.), *Encyclopedia of Physical Science and Technology*. Netherlands: Elsevier, pp. 457–467.

mode the signal returned relates solely to chemical differences in the specimen and images accordingly, whilst when the difference approach is employed the signal and thus image relates to surface topography. Thus the terms chemical or topographical imaging.

From the above descriptions relating to specimen beam interactions as well as electron emission and thus image formation, it should be clear, and thus appreciated when using scanning electron microscopy, that information captured may be derived from deeper in the sample than thought and the signal that arises from each point on the microscopes x-y raster can have come from a fairly large diameter area. Thus, it is always useful to think about what one is really looking at when using a SEM.

Factors Affecting Image Resolution and Apparent Quality

Probe or Beam Current

From Eq. (1), it is clear that low probe or beam currents should lead to smaller probe diameters and that smaller probe diameters should give better microscopic resolution. This is indeed true, and in addition, smaller probe currents result in less material damage which may be of importance when looking at bioceramic/bioglass tissue strictures or polymer derived ceramics and composites. Another useful factor to bear in mind for SEMs without sophisticated beam control (e.g. desktop systems) is the smaller the probe size, the less is the astigmatism effect and the easier it is to correct. Large beam currents are required for X-ray analysis, particularly if employing wavelength dispersive spectrometry (WDS). Otherwise, high beam currents give very good TV

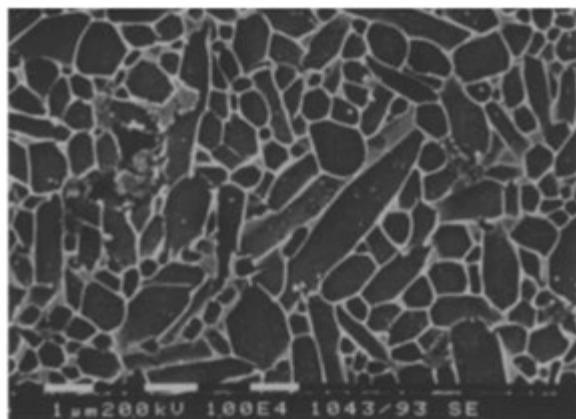


Fig. 7 Ground polished and plasma etched cross-section of silicon nitride. Reproduced from Erauw, J.P., Gilissen, R., Sleurs, J., 1994. Gas pressure sintering of silicon nitride: the influence of additive type and sintering parameters on the microstructural development. Transactions of the Materials Research Society of Japan 14A, 879–882.

scan rate images with poor resolution. The writer would very strongly suggest that image quality is developed using slow scan rates with low probe currents so as to get the best image resolution.

Accelerating Voltage

Accelerating voltage, of course, controls the interaction volume (see Eq. (4)) and thus the interaction depth and radius. Thus, it controls the depth from which image information comes from. This can sometimes cause a problem with backscattered electron images of a low atomic number phase embedded in a high atomic number phase. Thus, while Fig. 7 shows excellent clarity of image for an etched sintered silicon nitride with silicon nitride grains clearly discernible from a surrounding yttrium-SiAlON glass, it is virtually impossible to obtain such a clear image of the same material in the as polished condition because of the interaction between the glass and silicon nitride signals in the surface layers which makes boundaries between the phases diffuse. By reducing the accelerating voltage such diffuseness is reduced due to the reduced sampling depth. Such factors can also interfere with the sharpness of topographical features and so the clarity of surface structures is enhanced at low accelerating voltages. The same is true for so-called edge effects. Thus, greater clarity of edge structures is realized at low accelerating voltages (see JEOL, 2020b). Low accelerating voltages cause less damage to specimens, particularly those with organic content. Despite the marked advantages of low accelerating voltages, SEM resolution is higher with greater accelerating voltages.

Working Distance

This distance, which is that between the surface of the objective lens and the top surface of the specimen, controls resolution and depth of field (i.e., the depth over which image clarity is maintained). Lowering working distances increase microscope resolution allowing higher magnification images to be collected. But, this is at the expense of the depth of field, meaning that only a part of the image may be in sharp focus. Longer working distances reduce image resolution while increasing depth of field. Incidentally, for X-ray analysis, geometry is important and therefore the exact working distance consistent with that geometry must be employed.

Objective Aperture

A large objective aperture is associated with high probe currents, low resolution and small depth of field. A small aperture is associated with the opposite effects i.e., high resolution, greater depths of field and smaller probe currents. As for probe current settings, TV scan rate images appear good quality with a large aperture but grainy with a small aperture. In general, many SEMs either set the objective aperture automatically depending on other microscope settings, or recommend an aperture setting again depending on microscope settings.

Other Factors

Specimen tilt may be employed to greatly improve imaging of surface roughness characteristics. Such tilt angles need be fairly slight (e.g., 5° – 15°) but significant improvements can be realized as show in JEOL (2020a). Contamination of a sample during imaging is extremely annoying unless one has the capacity to move the position of the image electronically as well as physically. JEOL (2020a) notes that gases in the microscope, albeit at very low pressure can be acted on by the electron beam and decorate the specimen surface in the scan area so that it appears dark. Specimen cleanliness is clearly very important as is the cleanliness of any mounting media, including double sided adhesive tapes (even if conductive) and conductive paints and inks. These media should be thoroughly dried prior to being placed in the SEM vacuum chamber. Improving specimen and mount/holder cleanliness

should markedly decrease contamination levels. The final factor is the compromising nature of specimen charging on image quality as indicated above. Charging is best ameliorated by using thin coatings of carbon, gold or palladium applied by sputter coating. However, it can be lessened by the use of low accelerating voltages, small probe currents and small working distances (see [He et al., 2018](#)) in addition to looking at filtering the electrons used for imaging as described above. [JEOL \(2020b\)](#) gives very good initial advice on the basics of specimen preparation, including coating.

Environmental SEM

As indicated in [Fig. 1](#), the pressure inside the electron microscope column is typically of the order of 10^{-5} Pa. The mean free path of electrons in this sort of vacuum exceeds 10 km. This is drastically reduced to 1.4 cm if the pressure is increased to 133 Pa and 100 times less if the pressure is 1330 Pa. Because of this data, it is not possible to have an electron beam column at high pressures or the beam would not reach the lens assemblies. Thus, it is necessary to find a way of having the SEM column assembly under a good vacuum and the sample under a substantially higher pressure. To facilitate low pressure SEM, also called environmental SEM (ESEM) or variable pressure SEM (VPSEM), pressure limiting apertures can be located in the beam path ([Donald, 2012](#)). These apertures allow the pressure to be increased from the high vacuum region in the filament and condenser lens regions to up to 2000 Pa in the region of the specimen. Having the specimen at raised pressure allows ready imaging of samples containing moisture or volatiles as well as the specimens which are non-conductive. Non-conductive specimens can be examined because of the charge neutralizing effects of gas ionization in the high pressure regions. Clearly, the distance between the pressure limiting apertures and the specimen must be consistent with the mean free path data so that the beam does not lose its sharp focus due to appreciable broadening by the higher pressure gas environment. In addition to the very good background given by [Donald \(2012\)](#), [Podor et al. \(2012\)](#) give excellent examples of the use of ESEM for such in-situ experiments as hydration, dehydration, swelling on moisture uptake etc.

Other Possibilities

Other imaging capabilities in the SEM are magnetic imaging (see [Joy and Howitt, 2003](#); [Goldstein et al., 2003](#)), cathodoluminescence imaging (see [Joy and Howitt, 2003](#); [Goldstein et al., 2003](#); [Szyrkowska, 2005](#)) and electrical imaging of circuits ([Goldstein et al., 2003](#)). [Jiang et al. \(2017\)](#) also show how electrical analysis of materials can be conducted with in-situ instrumentation in SEMs as well as how it is possible to look at tensile, compression, bending, and electrical property measurements on nano-scale features. In addition, the use of in-situ heating stages to follow transformations e.g., crystallization of glasses further extends the capability of SEM analysis.

X-Ray Analysis

Introduction

As described by [Llovet \(2019\)](#), when an electron beam enters a material characteristic X-rays are emitted from the interaction volume as well as those leading to background X-radiation. These X-rays have characteristic wavelengths (λ) and therefore energies (E), since $E \text{ (keV)} = 1.24/\lambda \text{ (nm)}$ and can be detected either by their energy or wavelength.

Energy Dispersive X-Ray Analysis

X-rays are sorted in terms of energy by energy dispersive spectroscopy systems (EDS systems). X-rays emanating from the specimen surface impinge on the surface of a lithium drifted silicon crystal and cause ionizations within the crystal creating electron hole pairs. A high voltage across the silicon crystal causes electrons to be transported to a field effect transistor and the original X-ray impingements yield voltage step outputs which are amplified to a suitable output signal via a pulse processor. Because of this system design, it is not possible for every X-ray pulse to be recorded and the fraction of events not recorded due to pulse pileup. This gives rise to deadtime which is defined as $(1 - (\text{output rate}/\text{input rate})) \times 100\%$. This deadtime value is controlled by the time constant for the pulse processor and the beam current used in the SEM. Values in the range 10%–50% deadtimes are suggested as being suitable for analysis. However, high deadtime rates due to pulse processor settings affect the position and intensity of the carbon X-ray peak as shown in [Goldstein et al. \(2003\)](#). For high deadtimes the peak moves to lower energies and higher intensities. Experimentation by the writer shows that this artifact is only apparent if the pulse processor settings are used to increase deadtime. Increasing deadtime by increasing beam current and thus X-ray yield does not induce the artifact. This writer has always preferred to use low deadtimes (10%–20%) for qualitative and quantitative X-ray analysis by EDS.

[Fig. 8](#) shows the energies of K_{α} , L_{α} and M_{α} X-rays as a function of atomic number. It is clearly seen that over a wide range of energies, K_{α} radiation and L_{α} radiation have the same energies and so it may well be possible that two elements may emit X-rays with the same energy, although one emits K_{α} and the other L_{α} radiation. The same can be said for K_{α} , L_{α} and M_{α} albeit over a lower energy range. Because of this information, it is important to realize that characteristic X-ray energies and therefore peaks can overlap. A typical example is the overlap of Ti K_{α} and Ba L_{α} peaks as shown in [Fig. 9](#). Not only do α radiation peaks arise, β , γ and ξ peaks also arise and these can cause overlaps too. The most common overlaps are listed in [Table 4](#). These overlaps can cause problems in identifying unknowns in specimens and so it is always very useful to look at the uniformity in peak shapes i.e., they should be symmetrical. If they are not, then the

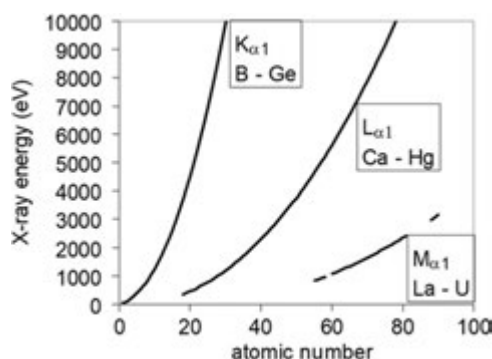


Fig. 8 Effect of atomic number on typical X-ray energies for K_α , L_α and M_α radiation.

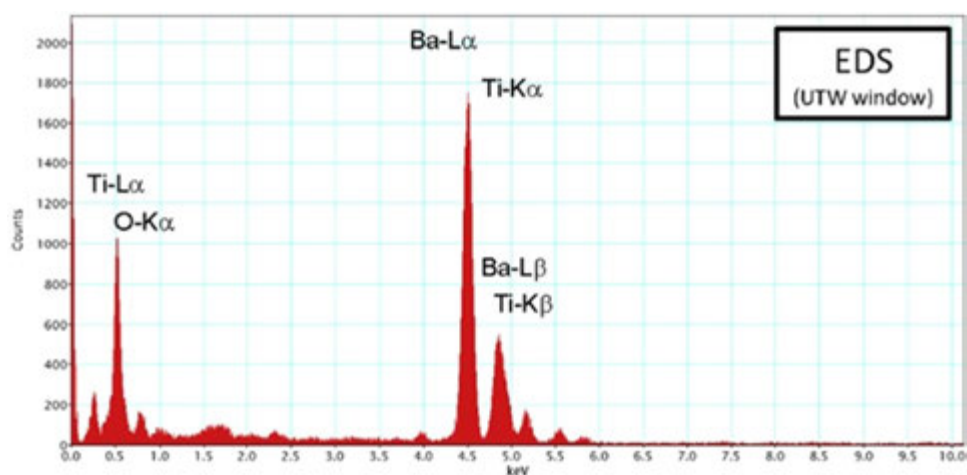


Fig. 9 EDS spectrum for BaTiO_3 showing peak overlap between Ba-L_α and Ti-K_α . Reproduced from Harada, Y., Ikuhara, Y., 2013. The latest analytical electron microscope and its application to ceramics. In: Somiya, S. (Ed.), Handbook of Advanced Ceramics, second ed. Materials, Applications, Processing, and Properties. Elsevier: Netherlands, pp. 3–21.

Table 4 Common peak overlaps in EDS analysis

Ti K_β /V K_α	V K_β /Cr K_α	Cr K_β /Mn K_α	Fe K_β /Co K_α
Co K_β /Ni K_α	S K_α , K_β /Mo L_α and Pb L_α	W M_α , M_β /Si K_α	Ta M_α , M_β /Si K_α
Ti K_α /Ba L_α	As K_α /Pb L_α	Sr L_α /Si K_α	Y L_α /P K_α

Note: After Goldstein, J., Newbury, D.E., Joy, D.C., *et al.*, 2003. Scanning Electron Microscopy and X-Ray Microanalysis, third ed. US: Springer.

major peak may well be hiding an X-ray signal from an overlap element. It is also useful to know the relative intensities of the α , β , γ peaks too. Hafner (2020) gives the following data for the relative intensities: $K_\alpha: K_\beta = 10: 1$; $L_\alpha: L_{\beta 1}: L_{\beta 2}: L_\gamma = 10: 7: 2: 1$; $M_\alpha: M_\beta = 10: 6$. Thus, for example if a K_β peak appears to have a greater intensity than 10% of a corresponding K_α peak then there is a probable overlap. In addition to overlaps, two types of counting artifacts can arise. These are sum peaks and escape peaks. The former arise when two X-rays impinge on the detector at nearly the same time and are recorded as one with twice the energy. The latter occurs when the analyzing crystal creates an X-ray itself which results in a loss of X-rays at 1.74 keV below the characteristic energy of the elements highest intensity peak. The writer has been amused on occasion when students have reported argon containing alumina in lab reports. This erroneous conclusion arises from the sum peak for Al appearing at the same energy as Ar K_α X-rays!!!.

Wavelength Dispersive X-Ray Analysis

X-rays can also be sorted by wavelength, as indicated previously. This detection is done using X-ray diffraction theory. Rather than X-rays of known wavelength being diffracted by a crystal of unknown crystal spacing to yield a diffraction angle, X-rays emitted by a specimen in a SEM are diffracted by a crystal of known interplanar spacing to generate a diffraction angle which can then be related to the element giving rise to the X-ray. A typical set up is shown in Fig. 10. Typical crystals with their associated crystal spacings are: thallium acid phthalate (TAP $2d = 25.76 \text{ \AA}$), pentaerythritol (PET $2d = 8.74 \text{ \AA}$), and lithium fluoride (LiF $2d = 4 \text{ \AA}$).

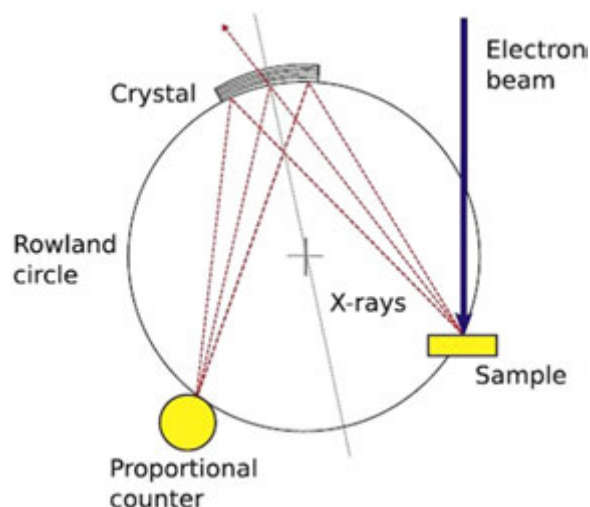


Fig. 10 Geometry of wavelength dispersive spectrometer (WDS) Reproduced from Llovet, X., 2019. Microscopy: Electron probe microanalysis. In: Worsfold, P., Townshend, A., Poole, C., Miro, M. (Eds.), *Encyclopedia of Analytical Science*, third ed. Netherlands: Elsevier, pp. 30–38.

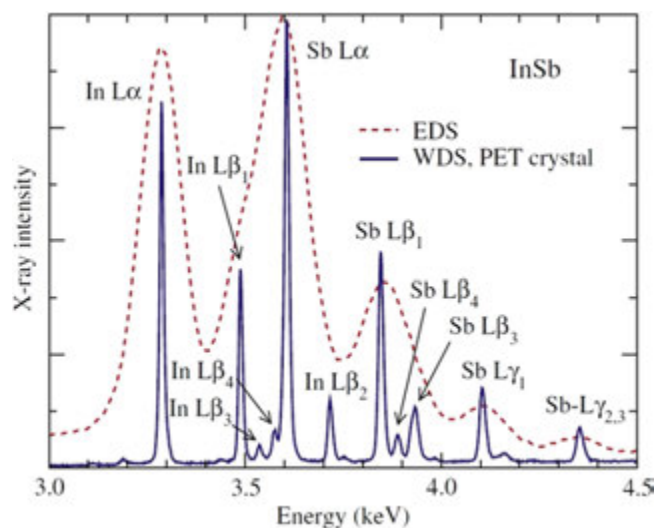


Fig. 11 Comparison of resolution of WDS and EDS X-ray analysis of InSb plotted on a common energy axis. Reproduced from Llovet, X., 2019. Microscopy: Electron probe microanalysis. In: Worsfold, P., Townshend, A., Poole, C., Miro, M. (Eds.), *Encyclopedia of Analytical Science*, third ed. Netherlands: Elsevier, pp. 30–38.

Others with larger crystal spacings are available and vary depending on manufacturer. For each crystal there is a range of elements whose X-ray wavelengths will be compatible with the analysis geometry for the specific crystal spacing.

WDS or EDS?

The advantage of EDS is that it is a very quick method of obtaining an overall chemical analysis of a material across the whole range of elements from B to U. Limits of detection for EDS systems vary depending on manufacturer, but are generally about 0.1% for the transition elements. Detection limits for WDS systems are much better with 0.01% limits being realized for low atomic number elements. In addition, WDS systems do not suffer from peak overlaps because of the much better X-ray resolution as shown by the comparison of peak widths in Fig. 11.

Uses of X-Ray Analysis

The use of X-ray analysis extends to 4 possible uses: (1) qualitative analysis, (2) X-ray maps indicating the spatial distribution of elements within a field of view (see Cookman and Bangert (2021)), (3) Line profiles i.e., intensity – distance profiles across layers

and interfaces and (4) quantitative analysis. For each of these, the operator and reporter of results must appreciate the depth and radius of the electron beam interaction zone. This can be considerable, as discussed above, and so qualitative or quantitative analysis of even a 500 nm particle in a totally dissimilar matrix will yield analyses containing matrix elements. It is of great importance that the operator and reporter of results acknowledges the type of microstructure they are analyzing in the light of the background physics.

Care needs to be exercised when making quantitative analyses as indicated by Goldstein *et al.* (2003), Llovet (2019) and Hafner (2020). This is because quantitative X-ray analysis needs to take into account the effects of atomic number (Z), X-ray absorption (A) and X-ray fluorescence (F) on the generation and escape of X-rays to and from the specimen surface. This means that apparent concentrations of each element must be corrected by a ZAF correction to get accurate data. An equally accurate approach is the use of a phi-rho-Z correction routine (see Goldstein *et al.*, 2003) used by the various EDS equipment suppliers. When carrying out quantitative analysis using EDS, it is important that the total number of counts in the spectrum exceeds at least 0.25 M counts and to ensure that a calibration standard has been analyzed in the not too distant past.

Characterization of Ceramic Microstructures

Rohrer (2014) has prepared a comprehensive review of methodologies for characterizing ceramic microstructures. This work looks in depth at electron backscattered diffraction and how it can be used to characterize grain size, grain orientation, definition of grain boundary types etc. as well as misorientation angles. It is strongly recommended that researchers read the article by Rohrer (2014) and use it as a key text to underpin their ceramic characterization approach.

A Note on Information Sources

This chapter has been written on the basis of three lectures given to Master of Science and 1st year Ph.D. students. These lectures were based on the list of material given in the reference list as well as 40 years experience using SEM systems and working with SEM engineers and demonstrators as well as excellent technicians. Because of this, this chapter makes reference to specific texts only when appropriate. Elsewhere the text is based on knowledge accumulated from the various sources mentioned.

References

- Cookman, J., Bangert, U., 2021. High resolution analytical electron microscopy of ceramics and glasses. In: Pomeroy, M.J. (Ed.), *Encyclopedia of Materials: Technical Glasses and Ceramics*. Netherlands: Elsevier. pp. 600–617.
- Donald, A.M., 2012. Environmental scanning electron microscopy. In: Matyjaszewski, K., Möller, M. (Eds.), *Polymer Science: A Comprehensive Reference*, vol. 2. Netherlands: Elsevier, pp. 539–545.
- Fetzer, A.-K., Trapp, M., Lauterbach, S., Kleebe, H.-J., 2021. Introduction to transmission electron microscopy: The basics. In: Pomeroy, M.J. (Ed.), *Encyclopedia of Materials: Technical Glasses and Ceramics*. Netherlands: Elsevier, pp. XX–XX.
- Goldstein, J., Newbury, D.E., Joy, D.C., *et al.*, 2003. *Scanning Electron Microscopy and X-ray Microanalysis*, third ed. US: Springer.
- Hafner, R., 2020. Energy Dispersive Spectroscopy on the SEM: A Primer. <https://pdf4pro.com/view/energy-dispersive-spectroscopy-on-the-sem-a-primer-bob-5b1868.html> (accessed December 2020).
- He, D., Fua, C., Xue, Z., 2018. Optimization study of direct morphology observation by cold field emission SEM without gold coating. *Micron* 109, 53–57.
- Jeol, 2020a. A Guide to Scanning Microscope Observation. <https://www.jeol.co.jp/en/applications/detail/844.html>. (accessed December 2020).
- Jeol, 2020b. Scanning Electron Microscope A To Z. <https://www.jeol.co.jp/en/applications/detail/891.html>. (accessed December 2020).
- Jiang, C., Lu, H., Zhang, H., Shen, Y., Lu, Y., 2017. Recent advances on in situ SEM mechanical and electrical characterization of low-dimensional nanomaterials. *Scanning* 2017, 1985149.
- Joy, D.C., Howitt, D.G., 2003. Scanning electron microscopy. In: Meyers, R.A. (Ed.), *Encyclopedia of Physical Science and Technology*. Netherlands: Elsevier, pp. 457–467.
- Kanaya, K., Okayama, S., 1972. Penetration and energy-loss theory of electrons in solid targets. *Journal of Physics D: Applied Physics* 5, 43–58.
- Llovet, X., 2019. Microscopy: Electron probe microanalysis. In: Worsfold, P., Townshend, A., Poole, C., Miro, M. (Eds.), *Encyclopedia of Analytical Science*, third ed. Netherlands: Elsevier, pp. 30–38.
- Podor, R., Ravoux, J., Brau, H.-P., 2012. In situ experiments in the scanning electron microscope chamber. In: Kazmiruk, V. (Ed.), *Scanning Electron Microscopy*. Rijeka: InTechOpen, pp. 31–54.
- Rohrer, G.S., 2014. Microstructural characterization of hard ceramics. In: Sarin, V.K. (Ed.), *Comprehensive Hard Materials 2*. Netherlands: Elsevier, pp. 265–284.
- Szynkowska, M.I., 2005. Microscopy techniques: Scanning electron microscopy. In: Worsfold, P., Townshend, A., Poole, C. (Eds.), *Encyclopedia of Analytical Science*. Netherlands: Elsevier, pp. 134–143.

Fractography: Brittle Materials

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Introduction

Quantitative fractography or fracture surface analysis (FSA) is the application of fracture mechanics to characteristic features on the fracture surface. FSA can identify the cause of failure, the amount of residual stress, if any, on the surface during fracture, and the existence or not of environmental slow crack growth before catastrophic failure. Thus, quantitative fractography is an essential tool used in failure analysis of components that fracture in a brittle manner. For convenience the term “brittle material” will be used to mean a material that fails in a brittle manner in the environment which results in that behavior. Fractography can be used to not only identify the source of failure, but also determine whether the failure is caused by a processing defect or by an overload on the component.

General Appearance of Fracture Surfaces

In general, brittle fracture for quasi-static loading results in one primary failure origin (Danzer *et al.*, 2008). The location of that origin is at the largest crack or flaw in the highest stressed region. The crack at the origin propagates approximately perpendicular to the principal tensile stress (alternatively, where K_{II} is zero) in an unstable manner and for a uniform stress field, radiates out in an approximately symmetric manner from the origin (Fig. 1) (Freiman and Mecholsky, 2019). Due to thermal vibrations, a distribution of bond strengths and an irregular crack front, the propagation of the crack does not occur on one plane. The crack immediately leaves the plane perpendicular to the applied stress direction at specific points along the crack front. At the start of the fracture process along the crack front, the individual bonds either act in concert and increase in amplitude, or subside, depending on entropic considerations. The number of points of departure depends on the amount of energy supplied in the fracture. If a small amount of energy is supplied, i.e., low stress fracture, then there are few points of departure initially, and the “plane” of propagation appears relatively smooth. If there is a large amount of stored strain energy before fracture, i.e., a high stress fracture, then there are many points of departure and the fracture surface appears rough near the origin (Kulawansa *et al.*, 1994). Note that these departures from the plane initially have amplitudes smaller than the wavelength of light and would appear smooth under the optical microscope.

During loading, strain energy is stored in the material. The stored strain energy is released during propagation. When the creation of surface, the release of particles, the rise in temperature and all other processes occurring during crack propagation are not great enough to satisfy the release of the stored strain energy, the main crack branches into two or more branches (Fig. 2). If there is a supply of strain energy, the process will continue until either there is no more material to fracture or the energy is dissipated and the crack arrests.

The techniques associated with fractography and the identification of features are well established (Quinn, 2016). Excellent presentations of the principles of fractography can be found in the ASTM Standard C, 1322-15 (2015) and the US Army Military handbook MIL-HDBK-790 (1992). The fractographic principles apply to all classes of materials, i.e., ceramics, metals, or polymers. As an example, Fig. 3 shows the fracture surface of a large grained ZnSe. For large grained materials, the features are often difficult to observe because of large, local crack deflections in the direction of easy propagation of grain facets or boundaries. These large deflections mask the more subtle mist and hackle markings (Beauchamp, 1996). Usually, this difficulty is compensated for because most large grained materials fail in a transgranular manner and leave classic characteristic markings on the surface, e.g., cleavage marks, “river” lines and twist hackle indicators (Fig. 3) (Frechette, 1990). The river marks (twist hackle) result from the propagating crack deflecting onto parallel planes in local, adjacent regions along the crack front (Rossmanith, 1980). These regions also result in cleavage “steps”. This chapter addresses the sources of failure in materials that fracture in a brittle manner and the quantitative analysis of the resulting fracture surfaces.

Sources of Failure

Fracture in brittle materials occurs due to the application of stress to a flaw in the material such that the combination of stress and size of flaw leads to unstable propagation of that defect. In this context, flaw, crack, and fracture origin are used interchangeably. Almost all materials have “flaws” due to fabrication, manufacturing or preparation. Use of the word “flaw” here does not imply a defect in the material, it is a naturally occurring result of fabrication and surface treatment of components. Most origins of fracture in brittle materials such as glass start from cracks, whose radii are atomically sharp and tend to be effectively 2-dimensional, i.e., their opening is of the order of angstroms or nanometers if unstressed (Mecholsky *et al.*, 1974). Even when the source is an inclusion of foreign material, the fracture generally originates from a crack at the boundary between the bulk material and the inclusion. Pores can act as a source of failure and are not as severe as a sharp crack. When pores act as a source of failure they are much larger than any sharp crack in the same stressed region.

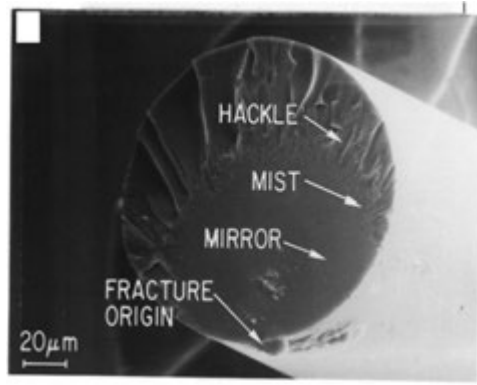


Fig. 1 Fracture surface of a silica glass fiber showing fracture origin, mirror, mist and hackle regions. The origin is a crack at the surface created by the thermal expansion difference between the fiber and the foreign “dust” particle attached to it while the fiber was still hot during fabrication.

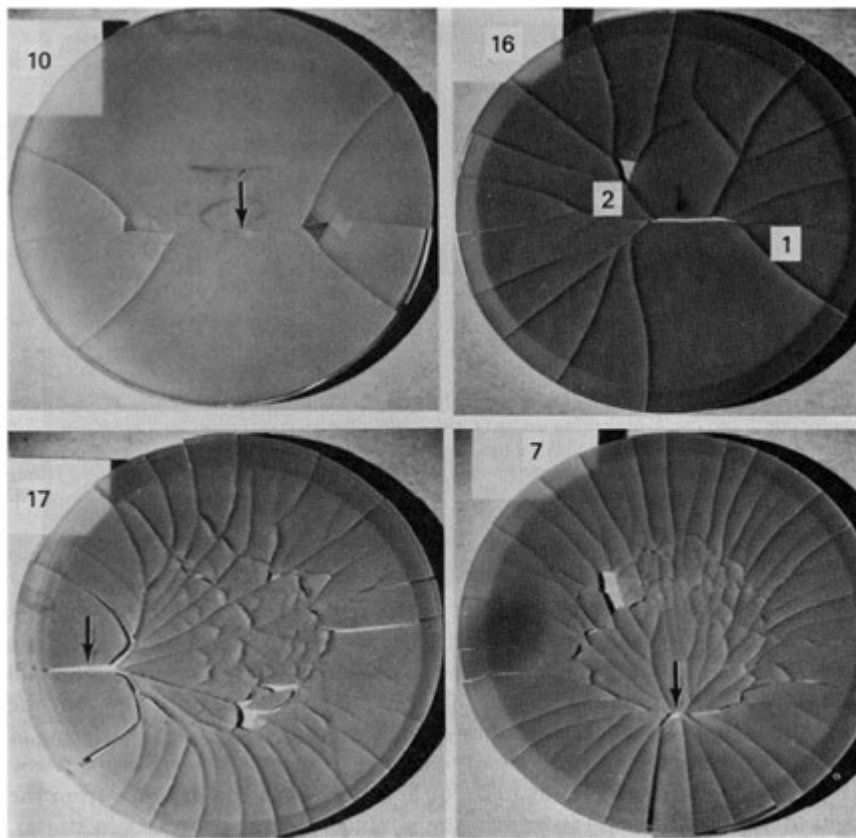


Fig. 2 Crack branching patterns in magnesium fluoride disks failed in ring-on-ring biaxial flexure. Arrows indicate origin of fracture. Failure stresses are: #10–47 MPa; #16–60.2 MPa; #17–86.9 MPa; # 7–91.5 MPa.

The shape and size of cracks are important to the fracture process, so it is necessary to understand and to investigate their sources and characterization. The types of sources can be categorized by their origination: extrinsic and intrinsic. Extrinsic origins include mechanical (handling, intentional and unintentional indentation, finishing operations, impact damage, etc.) and chemical and thermal processing and treatment (sputtering, etching, quenching, thermal shock, etc). Intrinsic origins include defects in the structure inherent in the specific fabrication or manufacturing technique such as sintering which can lead to low density regions or extrusion which can lead to non-uniform grains. Fracture origins may be characterized by their identity, location and size. Fracture origins may be volume flaws such as internal cracks, pores, agglomerates, inhomogeneous density or compositional regions, or surface origins such as cracks due to machining, surface pits or voids and impact damage due to handling ([Mecholsky and Freiman, 1979](#)). Of course, a volume-type defect can be located at the surface and a material can contain both surface and volume flaws. The location can be at the surface, in the volume, near the surface and/or at the edge of a component ([Quinn, 2016](#)).

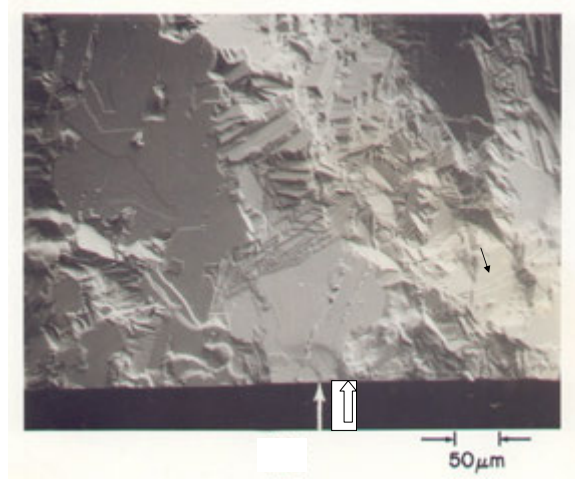


Fig. 3 Fracture surface SEM images of large grained ZnSe. The white arrows on the ZnSe surface show one end of a semi-elliptical crack from a polishing striation (thin white arrow) growing to the larger crack boundary (second, thicker arrow) before catastrophic failure. The black arrow shows an example of twist hackle (“river marks”) on a large single grain.

Quantitative Analysis

Almost all of the mechanically induced cracks can be idealized as a semi-elliptical, sharp crack of depth, a , and half-width, $2b$ (Randall, 1967; Quinn and Swab, 1996). The relationship between the stress at fracture, or strength, σ_f , and the fracture toughness, K_{IC} , is:

$$K_{IC} = Y\sigma_f(c^{1/2}) = \sqrt{(2E'\gamma_c)} \quad (1)$$

where K_{IC} is the critical stress intensity factor (fracture toughness) and Y is a geometric factor which accounts for the shape and location of the fracture-initiating crack, E' is E , the elastic (Young's) modulus for plane stress conditions, and $E' = E/(1 - \nu^2)$ for plane strain conditions where ν is Poisson's ratio, and γ_c is the critical fracture energy, i.e., all the energy involved in fracture including the creation of new surface. The quantity Y in Eq. (1) depends on the ratio a/b (Randall, 1967). However, the crack size can be approximated by an equivalent semi-circular crack size, c [$c = (a * b)^{1/2}$]. This approximation allows many irregular crack shapes to be analyzed and avoids the complications of calculating a geometric factor for each crack (Freiman and Mecholsky, 2019). For surface cracks without local residual stress and those that are small relative to the thickness of the sample, $Y \sim 1.26$ (Scherrer et al., 1999). Three-dimensional defects such as pores, pits or inclusions need special considerations (Quinn, 2016).

We observe that from the fracture origin, the crack propagates in a relatively smooth plane (the mirror region) to the boundary, r_1 , and progressively gets rougher by deviating slightly out of plane in a region that resembles mist (the mist region), between r_1 and r_2 . Finally, the crack deviates locally from the main plane of fracture (the hackle region), between r_2 and r_3 , getting very rough and finally branching into two or more cracks at r_3 . Beyond macroscopic crack branching, the process can repeat itself on each branch of the propagating crack (Quinn, 2016; Freiman et al., 1991). These regions are all related to the applied (far field) stress at fracture, σ_f :

$$\sigma_f r_j^{1/2} = \text{constant} = K_{Bj} / Y'(\theta) \quad (2)$$

where $r_j = r_1, r_2$ or r_3 corresponding to the different regions in an analogous equation to Eq. (1). K_{Bj} is the crack branching stress intensity and $Y'(\theta)$ is a crack border correction factor where θ is the angle from the surface to the interior, i.e. $\theta = 0-90^\circ$. Note that K_{Bj} is proportional to K_{IC} , i.e., $K_{Bj} = \lambda K_{IC}$ where λ is 3–5 (for $j = 1$) for most ceramic materials (Kirchner and Conway, 1988; Kirchner and Kirchner, 1979; Bradt, 2011a, 2011b). Table 1 lists values of characteristic constants for many ceramics. Fig. 4 shows the strength of silica glass versus the fracture mirror radius, r_1 , for fibers loaded in tension and bending, for disks loaded in biaxial tension and for bars loaded in three point flexure (Freiman and Mecholsky, 2019). The straight line is the graphing of Eq. (2). The fact that the relationship represented by Eq. (2) is valid for several stress states during failure provides increasing confidence that this equation is useful in analyzing in-situ field failures. Also, notice the large range of stress values and of sizes of fracture mirror radii.

Fractographic Procedures

The fracture origin can be determined by looking on the fracture surface and tracing the telltale markings back to the origin. These markings include twist hackle (river marks), fracture tails, cleavage steps, Wallner lines, and branching locations. Wallner lines are

Table 1 Fracture properties of brittle materials

Material	Grain Size (μm)	E (GPa)	γ (J/m^2)	K_{IC} ($\text{MPam}^{1/2}$)	K_2 ($\text{MPam}^{1/2}$)	D^*	a_0 (Δ)
1. ADP	S.C.	9	2	0.2	0.6		
2. MgAl_2O_4	S.C.	240	13	0.7	3.22		
3. MgO	S.C.	280	3	1.3	6.2		
4. Al_2O_3	S.C.	340	7	2.2	7.5		
5. AlSiMag 614		300	20	3.5	16.2		
6. Al_2O_3		210	13	2.3	8.0		
7. Alumina (AD99)	5	390	11	2.9		0.21	3
8. Alumina (AD999)	5	406	19	3.9		0.31	3
9. Alumina (GEND)		283	27	3.9		0.23	8
10. Alumina (Lucalox)	60-70	392	20	4.0		0.31	3
11. Alumina (UCC)		393	20	4.0		0.15	7
12. Alumina (WESGO A1500)		283	23	3.6		0.20	8
13. Alumina Silicate		89	4	0.8		0.18	5
14. B_4C	20	450	15	3.7	11.4		
15. BaTiO_2	5	120	5	1.1	6.2		
16. BaTiO_2 (LiF-MgO)		120	6	1.2	6.7		
17. CaF_2		114	0.5	0.3		0.07	1
18. CdTe		40	1	0.3		0.20	3
19. Glassy Carbon		25	8.5	0.7	2.1		
20. Graphite	8	12	85	1.4	4.1		
21. H.P. Al_2O_3 (99 +)		390	20	4.0	14.8		
22. MgAl_2O_4	< 10	240	6	1.7	9.6		
23. MgF_2	< 1	110	4	0.9	3.8	0.2	3
24. MgO		280	12	2.6	11.0		
25. Mullite		222	11	2.2	7.5		
26. PZT	5	80	4	0.8	4.5		
27. Si_3N_4 (B)	— 1	280	30	4.1	14.8		
28. Si_3N_4 (HS-130)	— 1	310	45	5.3	22.4		
29. SiC (XT)	10-100	390	19	3.9	13.2		
30. Silicate Glasses		64	3	0.7	26	0.09- 0.1	12-16
31. Spinel		240	3	1.2		0.09	3
32. SrZrO_3		280	6	1.8			
33. $3\text{BaO} - 5\text{SiO}_2$	0.5-15	80	17	2.2	0.26	20	
34. Cervit 126	< 1	92	17	1.8			
35. $\text{Li}_2\text{O} - 2\text{SiO}_2$	glass	70	7	1.0	0.09	20	
36. $\text{Li}_2\text{O} - 2\text{SiO}_2$	15	137	33	3	0.23	20	
37. Lithia Borosilicate	50	90	40.5	2.7	0.18	50	
38. Pyroceram 9606	< 1	120	25	2.5	0.17	25	
39. ZnSe	20-30	69	5.5	0.9	0.30	5	
40. ZrO_2 (Zircar)	0.4	280	70	6.3			
41. ZrO_2 (Zyttrite)	10	260	13	2.6			
42. Zinc Silicate (MS 498-5)		90	27	2.2	0.07	86	
43. Zinc Silicate (MS 500-4)		90	27	2.2	0.12	51	
44. Zinc Silicate (ZSGC No. 1)	400	90	22	2.0	0.05	98	
45. Zinc Silicate (ZSGC No. 2)	500	0	22	2.0	0.09	54	
46. Zinc Silicate (ZSGC No. 3)	1100		27		0.11		
47. 96% Al_2O_3 (flex)		320	19.5	3.2			
48. 95% Al_2O_3 (delayed)		320	19.5	3.2			
49. H.P. Al_2O_3 (flex)		380	34	5.1			
50. H.P. Al_2O_3 (delayed)		380	34	5.1			
51. H.P. Si_3N_4 NC - 132 (flex)		310	39	4.7			
52. H.P. Si_3N_4 NC - 132		310	39	4.7			
53. H.P. Si_3N_4 (flex)		310		4.7			
54. H.S. - 130		310		4.7			
55. R.B. Si_3N_4 (flex)		135	29	2.8			
56. H.P. SiC (flex)		440	18	4.1			
57. H.P. SiC (delayed)		440	18	4.1			
58. Zircon porcelain		160					
59. Steatite (clinoenstatite)		110					
60. Flint glass		69					

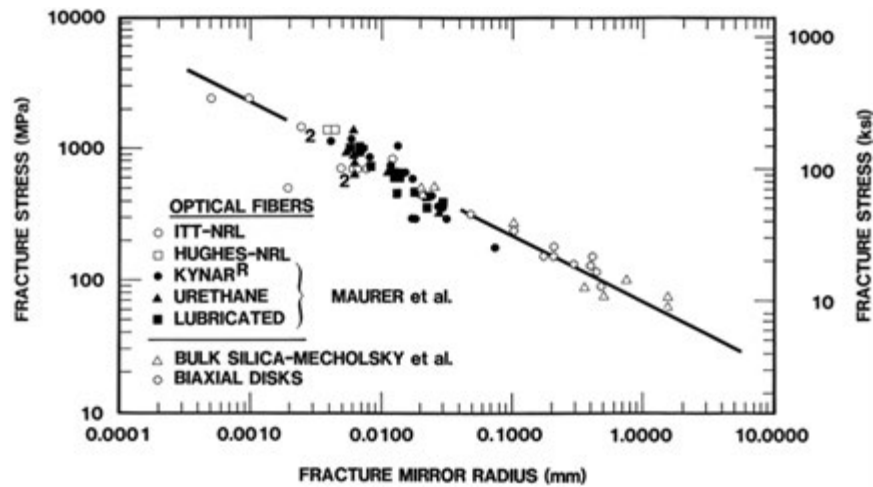


Fig. 4 Fracture Stress versus Fracture Mirror Radius, r_1 , for optical fibers and bulk silica. The solid line is a linear least squares fit with slope = -0.5 [Eq. (2)]. Solid data from Maurer, R.D., Miller, R.A., Smith, D.D., Trondsen, J.C., 1974. Optimization of Optical Waveguides Strength Studies. Final technical rept. NY: Corning Glass Works. Mecholsky, J.J., Rice, R.W., Freiman, S.W., 1974. Predictions of fracture energy and flaw size in glasses from mirror size measurements. J. Am. Ceram. Soc. 57 (10), 440–444.

the result of intersections of the crack front with a propagating elastic stress wave initiated from another source, such as the surface, an inclusion, or secondary crack. Wallner lines can be used to calculate the velocity of a crack front (Quinn, 2016).

The general fractographic procedure is outlined in ASTM Standard C1322–15 or the National Institute of Standards and Technology (NIST) WebPages [See Relevant Website Section] (Quinn, 2016). When characterizing fracture origins, photographs of the overall sample, of the fracture mirror and surrounding regions including the branching locations, if applicable, and of an enlargement of the fracture origin region should be made. Since there is a distribution of crack sizes on any component, there is a corresponding distribution of strengths. The strength and flaw size distributions have been found to follow Weibull statistics. In addition, in the cases where strength values can be obtained independently, it is useful to correlate the strength distribution probability with the flaw location, size and identity. The strength distribution, i.e., the probability of failure versus the strength, can be obtained using a Weibull analysis as outlined in ASTM standard C1239–13 (2013). A testing procedure for strength can also be obtained by following ASTM Standard C, 1161 (2018). To be complete in fractographic analysis when it is possible to obtain many strength samples, a fractographic montage should be attached to the Weibull probability graph. The fractographic montage consists of sketches or photographs of the fracture origins with arrows pointing to the location on the probability of failure-strength curve (Quinn, 1987).

Global Residual Stress

Near-surface residual stresses, σ_r , can greatly affect the performance of materials. If these global stresses are tensile ($+\sigma_r$), then the effective strength of the material is reduced. If the global near-surface stresses are compressive ($-\sigma_r$), then this often leads to superior mechanical performance. Quantitative fractography can be used to evaluate the magnitude of these global residual stresses in post-mortem analysis. Eq. (2) can be modified to include the effect of residual near-surface stresses, σ_R :

$$\sigma_c r_1^{1/2} Y(\theta) = +K_{Bj} - \sigma_R r_1^{1/2} Y_R(\theta) \quad (3)$$

where $Y_R(\theta)$ is a crack border correction factor for the residual stresses and usually assumed to be 1 and the other symbols are as described above (Conway and Mecholsky, 1989). A graph of the left side of Eq. (3) versus a selected value of r_1 , e.g., r_2 , for several samples will result in data which have either a zero slope, i.e., no residual stress, or a slope related to σ_R (Fig. 5). For individual components, the expected applied stress for samples without residual stress can be estimated from Eq. (1) after measuring the crack size or from Eq. (2) after measuring the mirror radius. Thus, the mirror-to-flaw size ratio on the surface will be the same as without residual stress. However, the shape of the mirror-mist border will be quite different. An example of this shape difference is illustrated in Fig. 6. Fractographic procedures can be combined with other techniques, such as finite element analysis (FEA) and closed form solutions of thermal mismatch, to verify the calculations of global residual stresses (Aboushelib et al., 2008).

Local Residual Stress

A typical crack may experience other components of residual stress, such as local residual stress from the creation of the crack from impact or contact events (Lawn and Marshall, 1991). Such is the case for deformation induced surface cracks produced in sharp-point contact. In these cases, $Y = 1.65$ in Eq. (1) (Marshall et al., 1980). The mirror-to-flaw size ratio for cracks with local residual stress is:

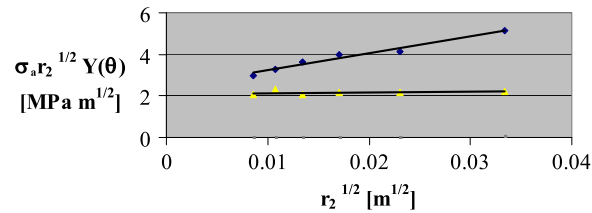


Fig. 5 Graph of Eq. (3) to determine global residual stress. The triangles represent annealed soda-lime silica glass and the diamonds represent tempered soda-lime silica glass. Tempering is a thermal-quench process which results in compressive stresses on the external surfaces of glass components. r_2 = the radius of the mist-hackle boundary. This graph indicates that there is an 82 MPa (compressive) residual stress on the tempered glass surface.

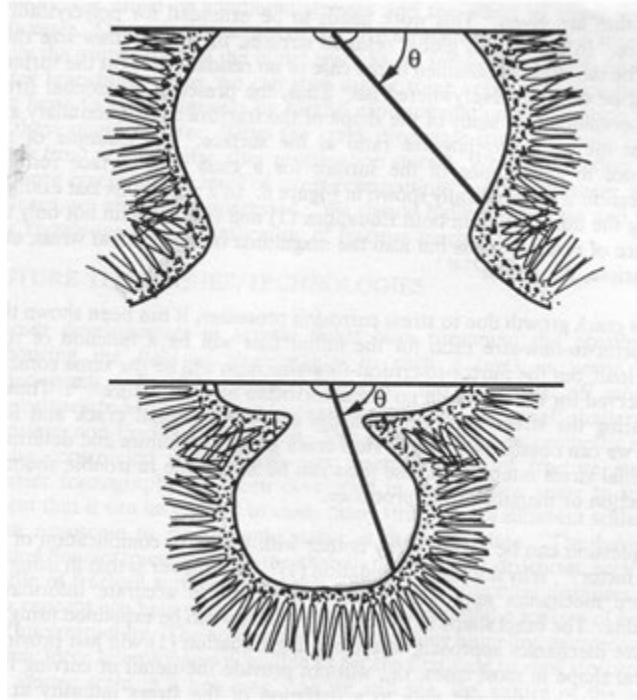


Fig. 6 Schematics of fracture mirror boundaries for materials fractured in a flexure mode. (Upper) – Fracture mechanics approach. Eq. (2) explains the inward curvature at the surface and the opening of the mirror toward the interior due to lessening of flexural stresses. (Lower) – Fracture mechanics approach. Eq. (3) can explain the shape of the mirror boundary in the presence of residual compressive stress. The critical crack size is the same in both examples.

$$r_i/c = [4 Y K_{Bj}/3 Y(\theta) K_{IC}]^2. \quad (4)$$

The value of r_i/c for cracks without local stress removes the factor $(4/3)^2$ (Marshall *et al.*, 1980).

Slow Crack Growth

In many cases environmental effects can affect the fracture of components. For example, slow crack growth can occur due to stress enhanced chemical reactions at the crack tip (Michalske and Freiman, 1983). These reactions cause the initial crack to grow slowly before catastrophic failure. At the time of failure, the mirror radius-to-critical crack size ratio is the same as for the condition of annealed, stress-free material. However, the mirror-to-initial crack size is a function of time under load. Thus, if the mirror to crack size is greater than about 20:1, then more than likely some slow crack growth had occurred before fracture (Mecholsky *et al.*, 1979). In some cases, it becomes very obvious that crack growth has occurred before rapid failure (Michalske, 1979; Mecholsky, 1981). There are markings on the surface that indicate the crack boundary before rapid fracture. In other cases, it is not obvious, but the crack size to mirror size ratio will indicate that there must have been slow crack growth due to a stress enhanced chemical process.

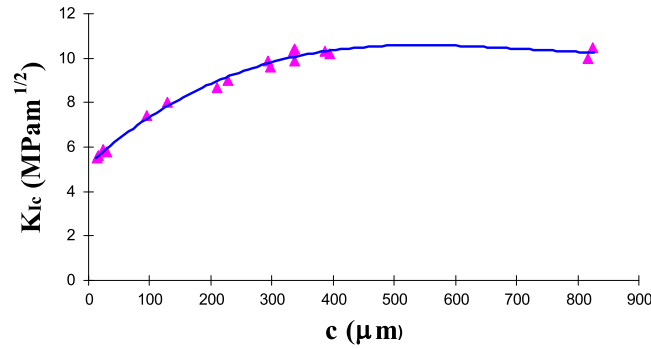


Fig. 7 The toughness of type A Si_3N_4 displays “R” curve behavior.

R-Curve Determination Using Quantitative Fractography

Materials containing microstructural features such as elongated grains, transformation phases, stress induced microcracking, fibers, or multiple grain sizes can exhibit a phenomenon known as a rising R-curve (Resistance-curve) behavior, i.e., an increased resistance to crack growth with increased crack size (Munz, 2007). Although the mechanisms around the crack tip can be different, the overall result is a toughness-crack size curve that is not constant, but increases with increasing crack size up to a limit at which point the resistance becomes constant. Typically, stable crack growth specimens are used to measure the toughness or crack growth resistance parameter as a function of crack size. Both compact tension, double cantilever beams and 3-point flexure technique using a notched beam with sharpened starter crack have been used (Moon *et al.*, 2000; Kruzic *et al.*, 2008; Steinbrech, 2005).

The determination of R-curve values can also be obtained using quantitative fractography. The strength of fractured flexure bars can be recorded and the size of the fracture initiating crack can be measured. Thus, the fracture toughness can be calculated using Eq. (1). If there is no R-curve behavior using small crack specimens such as flexure bars, then the calculated values will be the same for all crack sizes. If there is R-curve behavior, then the calculated values will increase with increased crack sizes up to a certain size. These measurements agree with the larger crack size techniques. An example of such R-curve behavior is shown for polycrystalline silicon nitride in Fig. 7. In this case, the mechanism of increased toughness with increasing crack size is grain-to-grain interlocking of the elongated grains in the microstructure, i.e., crack bridging (Mecholsky *et al.*, 2002).

Mixed Mode Fracture

Although there has been much study on the fracture of brittle materials in mixed-mode loading, to date, all studies on fractography were focused on surfaces failed from surface cracks in pure tension or pure mode I. In the past, there was little, if any, literature on the quantitative fractographic study of fracture surfaces failed in combined tension and shear (mixed-mode) loading (e.g., Freiman *et al.*, 1979). More recently, research analyzed the features of fracture surfaces failed in external mixed mode (I/II) loading. This research determined there were some distinguishing fracture surface characteristic markings due to mixed-mode loading (Gopalakrishnan and Mecholsky, 2012).

The analytical expressions for the stress intensity factors (SIF) for surface flaws under mixed-mode loading conditions has been well-established in the literature and are given by (Shetty *et al.*, 1987):

$$K_I = Y_I M_I \sigma \sqrt{c} \sin(2\theta) \quad (5)$$

$$K_{II} = Y_{II} M_{II} \sigma \sqrt{c} \sin \theta \cos \theta \quad (6)$$

where σ is the applied stress, c is the critical flaw size given by Eq. (1), Y_I and Y_{II} are the geometric constants and M_I and M_{II} are free surface correction factors. Similar equations apply for the SIFs for both as-indented and annealed samples in the case of glass ceramics as opposed to non R-curve materials, wherein the effect of residual stress needs to be accounted for in the as-indented samples. For a semi-circular surface flaw, the geometric constant, Y_I is given by (Smith *et al.*, 1967):

$$Y_I = 2\sqrt{\pi} \quad (7)$$

Kassir and Sih (1966) developed the expression for K_{II} for penny-shaped cracks with the geometric constant Y_{II} given by:

$$Y_{II} = 4\sqrt{\pi(2-\nu)} \quad (8)$$

The critical mode I SIF, K_{IC} can be determined from Eq. (9).

$$K_{IC} = Y_I M_I \sigma_c \sqrt{c} \quad (9)$$

where σ_c is the critical stress for pure mode I loading. Studies conducted by Randall (1967) and other researchers (e.g., Shetty *et al.*, 1987; Scott and Thorpe, 1981) agree that the correction factor is within 10%–12% for surface cracks. Smith and Sorensen (1974) have shown that the values of M_{II} are approximately equivalent to M_I for equivalent crack sizes and shapes. The ratio M_{II}/M_I is usually taken to be unity. Thus, once the applied stress and the flaw dimensions are measured, the SIFs can be calculated from

Eqs. (5) and (6). Once K_I and K_{II} are determined, then it is a matter of selection of the appropriate theory for combining K_I and K_{II} . We assume that when $K_C = K_{IC}$, fracture will occur for an angled crack. However, it is not well-established in the literature which method is the correct one for combining K_I and K_{II} .

The most popular theories to combine K_I and K_{II} to determine K_C are presented below.

The non-coplanar strain energy release rate (NCSERR) criterion assumes that crack growth starts at a critical value of the strain energy release rate (SERR) in a direction along which the SERR is maximum. An analysis based on the maximum SERR was first performed by Hussain *et al.* (1974). They analyzed the non-coplanar crack extension of inclined cracks based on Griffith energy balance. The condition for fracture under mixed-mode loading in this case is given by:

$$K_C = K_I [b_{11} - b_{12}(K_{II}/K_I) + b_{22}(K_{II}/K_I)^2]^{1/2} \times [(1 - (\gamma/\pi))/(1 + (\gamma/\pi))]^{\gamma/2\pi} \quad (10)$$

$$b_{11} = 4(1 + 3 \cos^2 \gamma) / [(3 + \cos^2 \gamma)^2] \quad (11)$$

$$b_{12} = 32 \sin \gamma \cos \gamma / [(3 + \cos^2 \gamma)^2] \quad (12)$$

$$b_{22} = 4(9 - 5 \cos^2 \gamma) / [(3 + \cos^2 \gamma)^2] \quad (13)$$

The combination of K_I and K_{II} results in effective mixed-mode fracture toughness and is given by K_C as shown in Eq. (10).

Erdogan and Sih (1963) hypothesized that fracture commences at the tip of the crack in a radial direction and crack growth occurs in the plane which is normal to the direction of maximum tensile stress (MTS). This hypothesis implies that crack growth starts at a critical value of the tangential stress along the direction of maximum tangential stress. The tangential stress in the neighborhood of the crack tip, in cylindrical coordinates, is given by:

$$\sigma = [1/\sqrt{(2\pi r)}] \cos(\gamma/2) [K_I \cos^2(\gamma/2) - 1.5 K_{II} \sin \gamma] \quad (14)$$

The MTS criterion can be expressed as:

$$\partial \sigma / \partial \gamma = 0 \text{ at the crack turning angle, } \gamma \quad (15)$$

The angle γ at which the tangential stress reaches a maximum value can be evaluated in terms of K_I and K_{II} which is used to derive the general expression for mixed-mode fracture, given below.

$$K_C = K_I \cos(\gamma/2) [\cos^2(\gamma/2) - 1.5 K_{II}/K_I \sin \gamma] \quad (16)$$

Eq. (16) represents the conventional MTS criterion.

The critical strain energy release rate (CSERR) criterion states that crack growth starts along the initial crack plane when the SERR reaches a critical value, leading to the relation below:

$$K_C = K_I [1 + (K_{II}/K_I)^2]^{1/2} \quad (17)$$

Sih (1974) proposed that crack growth starts at a critical value of strain energy density (SED), S_{crit} , and propagates in the direction of minimum SED (MSED). The S_{crit} value was postulated as a material constant and hence it could be used as a measure of the fracture toughness of the material under mixed-mode conditions. Based on this concept an effective fracture toughness K_C can be derived as:

$$K_C = [8(a_{11} K_I^2 + 2a_{12} K_I K_{II} + a_{22} K_{II}^2)]^{1/2} \quad (18)$$

$$a_{11} = [(3 - 4\nu - \cos \gamma)(1 + \cos \gamma)]/16 \quad (19)$$

$$a_{12} = [\sin \gamma (\cos \gamma - 1 + 2\nu)]/8 \quad (20)$$

$$a_{22} = [4(1 - \nu)(1 - \cos \gamma) + (1 + \cos \gamma)(3 \cos \gamma - 1)]/16 \quad (21)$$

where ν is the Poisson's ratio of the material.

The crack size, c , to mirror size, r , ratio can be calculated for all crack angles in mixed-mode loading for small cracks in flexure by combining Eqs. (1) and (2). We then obtain:

$$c/r = (K_c/K_{Bj})^2 (Y_2/Y_c)^2 \quad (22)$$

where K_c is determined using the appropriate mixed mode theory. K_c/K_{Bj} can be determined experimentally.

A typical fracture surface of a soda-lime-silica glass fractured in mixed-mode (I/II) loading is shown in Fig. 8 (Gopalakrishnan and Mecholsky, 2012). Compare this image to that in Fig. 1. We notice there is no mist region and we can see that the hackle markings appear as lances. Such lance like features are thought to be generated due to the influence of mode I and mode III stress intensities acting along the crack front (Pons and Karma, 2010). The schematic of the typical features on a mixed-mode fracture surface in Fig. 9 is compared to the features on mode I fracture surface in Fig. 8. The reason for the lance hackle markings can be explained by the presence of a Mode III component at the tip of the crack. Pons and Karma (2010) show that in a local mixed-mode (I-III) loading condition, a "flat parent crack segments into an array of daughter cracks that rotate toward a direction of maximum tensile stress". They refer to these daughter cracks as "lances", clearly the same as the twist hackle markings observed in Fig. 8. They further explain that their calculations imply that the creation of the twist hackle features depends on both the applied

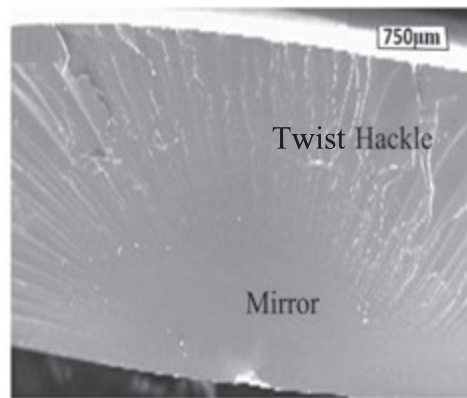


Fig. 8 Fracture surface of mixed mode fracture in a soda-lime-silica glass. Notice the absence of the mist region.

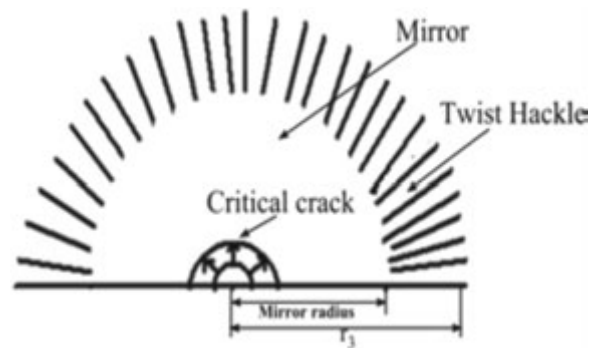


Fig. 9 Schematic of a fracture surface broken in mixed mode loading. Notice the absence of the mist region.

shear stress and the energy release rate. This would agree with the findings of [Gopalakrishnan \(2011\)](#) that the stress intensity at branching is a constant at the beginning of the microscopic twist hackle features. Other work has also shown that far field mixed mode (K_I – K_{II}) loading can result in a Mode III shear component at the tip of the crack ([Erdogan and Sih, 1963](#)). Higher order stress intensity terms at the crack tip become significant for mixed mode conditions ([Williams and Ewing, 1972](#); [Ueda et al., 1983](#)).

It has been difficult in the past to determine the appropriate mixed-mode theory to use to determine the fracture toughness for materials loaded on mixed mode loading. However, a more recent study by [Gopalakrishnan \(2011\)](#) suggests that the MSED theory appropriately describes mixed mode fracture, at least for R-curve materials. The author compared the four theories listed above for Macor® glass ceramic. The only theory that merged as one relationship was the MSED theory as shown in [Fig. 10](#).

[Mecholsky et al. \(1977\)](#) have shown that c/r is directly proportional to the fracture toughness. Thus, for an R-curve material where the fracture toughness is a function of the crack length, c/r values should increase with increasing crack length. The crack to mirror size ratio (c/r) as a function of the crack length, c for the different crack orientations in mixed-mode fracture is shown in [Fig. 11](#) for the Macor glass ceramic (MGC). The R-curve behavior of MGC ([Gopalakrishnan and Mecholsky, 2013](#)) is mimicked in the c/r versus c plot for the different crack orientations. This is contrary to the constant values of c/r obtained at a particular crack orientation for non or flat R-curve materials. The variation of c/r with crack length at a particular crack orientation for the MGC is due to the crack bridging mechanism which leads to the increasing resistance to crack growth with increasing crack extension. Although the raw data for c/r versus crack size will yield different curves for each crack orientation, if we use [Eq. \(22\)](#) to calculate c/r with the K_c values determined using [Eq. \(18\)](#), all the values for each angle at a particular crack size essentially over-lap ([Fig. 11](#)). This collapsing of the c/r graph further supports the MSED theory for use in determining the effect of mixed mode loading. In pure mode I loading, at $c > 150 \mu\text{m}$ when the fracture toughness of MGC reaches a steady value, the value of c/r is found to be approximately a constant (~ 0.15) and the value of c/r for $c > 150 \mu\text{m}$ increased to ~ 0.42 for $\theta = 45^\circ$.

Fractal Geometry

Fractal geometry ([Mandelbrot, 1982](#)) is being used in many fields of materials science, physics, chemistry and engineering because it can be applied to describe shapes and processes that are non-linear and seemingly complex. Fractal geometry is a non-Euclidean geometry which exhibits self-similarity (or self-affinity) and scale invariance. Self-similarity and scale invariance are characteristics

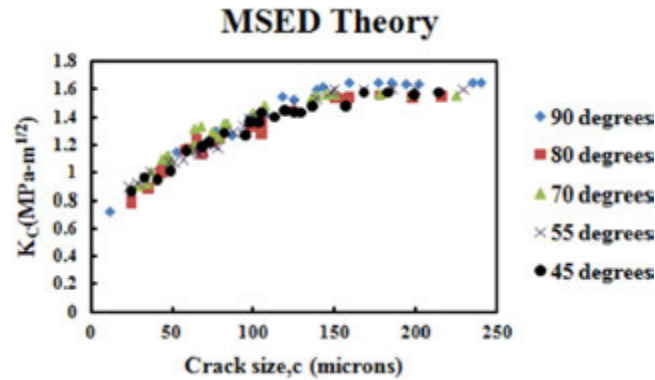


Fig. 10 Fracture toughness as a function of crack size demonstrating R-curve behavior in Mode I and Mixed Mode Loading. The only mixed mode theory that merges all the angles in mixed mode loading is the Minimum Strain Energy Density (MSSED) theory. Reproduced from Sih, G.C., 1974. Strain-energy-density factor applied to mixed mode crack problems. *Int. J. Fract.* 10, 3057–321. Gopalakrishnan, K., 2011. Mixed Mode Fracture in Brittle Materials. PhD Dissertation. University of Florida. Available at: <https://ufdc.ufl.edu/UFE0043736/00001>.

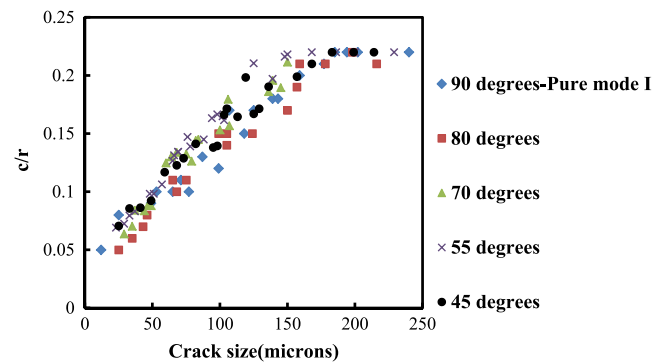


Fig. 11 Crack size to mirror size ratio as a function of the crack size. Notice that the relationship is constant regardless of Mode I or mixed mode loading.

of (scaling) fractals. A self-similar surface is one in which the length scaling is isotropic, i.e., one feature on the surface has a similar shape to another feature on the surface in any direction. A self-similar object remains invariant under the transformation $(x,y,z) \rightarrow (ax,ay,az)$ where a is a scalar constant. Typically, self-similar structures are also scale invariant, i.e., the features are not only similar in different regions, but also similar at different magnifications. A self-affine object is one which remains invariant under the transformation $(x,y,z) \rightarrow (ax,ay,az^\zeta)$ where ζ is called a roughness exponent. Fracture is one of the phenomena that has been modeled using fractal geometry (Russ, 1996).

Fundamental relationships can be derived between the fractal dimensional increment, D^* , and the fracture toughness of a material in the form of the critical stress intensity factor, K_{IC} :

$$K_{IC} = E a_0^{1/2} D^{*1/2} = Y(\theta) \sigma_f c^{1/2} \quad (23)$$

where E is the Young's modulus and a_0 is a parameter having the units of length. The relationship between K_{IC} and D^* is based on experimental observations (Fig. 12) and the relationship between K_{IC} and c is based on fracture mechanics and experimental confirmation. The measurement of D^* is an average property of the entire fracture surface and a measure of its tortuosity. The flaw size is a linear measure of the critical flaw area locally around the fracture origin. Fig. 1 shows a fracture surface depicting the origin and the surrounding tortuous topography.

It can be shown (Mecholsky and Freiman, 1991) that:

$$r_1/c = 1/D^* \quad (24)$$

The agreement of experimental data with Eq. (24) (Fig. 13) implies that there is scaling between the crack size and the point of branching. Furthermore, Eqs. (1) and (2) show that the ratio of the energy of crack initiation to that of crack branching is related to r_1/c ; there is also scaling between the energy of crack initiation and of crack branching. Thus, analyzing considering an energy scaling or a structural (geometric) scaling are equivalent. Moreover, the scaling is linear in energy or geometry. Passoja (1988) has suggested that this scaling is a general phenomenon that is observed in many materials and is related to the atomic structure.

Fractal dimensions for fracture surfaces of glasses, ceramics, glass-ceramics, single crystals, intermetallics and polymers have been measured (Mecholsky, 1996). Atomic force microscopy studies have shown that the fracture surface is not smooth at the

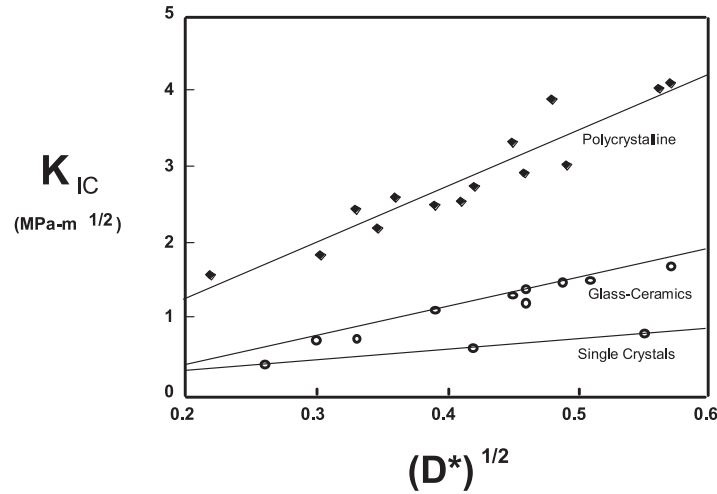


Fig. 12 Fracture toughness vs. Fractal dimensional increment, D^* . Data fall into material “families”, i.e., single crystals and large grain materials, glass ceramics, and fine grain polycrystalline materials.

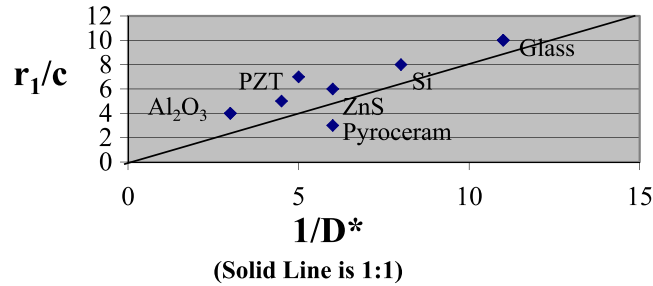


Fig. 13 Mirror-to-crack size ratio (r_1/c) as a function of the Fractal Dimensional Increment, D^* .

atomic level for many materials and has the same tortuosity at the atomic level as at the macroscopic level. Thus, the crack front is neither smooth nor continuous. A fundamental relationship between basic materials constants, fractal geometry, and fracture parameters has been shown to exist for brittle materials:

$$\gamma_c = \gamma_s + \gamma_t + \gamma_i = \gamma_o + \frac{a_o D^* E}{2} \quad (25)$$

where γ_c = critical fracture energy (toughness).

γ_s = surface energy created during fracture.

γ_t = thermal energy during fracture.

γ_i = summation of all other energy contributions during fracture.

γ_o = fracture energy for a flat surface ($\gamma_o \sim 0$).

D^* = fractal dimensional increment of the fracture surface.

E = Young's modulus.

a_o = material structure constant.

The variables D^* , E , and γ_c are independently measurable; a_o can be calculated from these three variables without introducing any adjustable parameters. Eq. (25) can be considered representative of the toughness-tortuosity relation for glass, Ocala chert, intermetallics, ceramics and glass ceramics, i.e., the toughness increases as the tortuosity. Note that a crack propagating through a perfectly homogeneous material with thermal vibrations will not result in a smooth surface. Thus, we should not expect any fracture surface that involves fracture of primary bonds to be smooth if the fracture occurs above absolute zero! Thus, the value of γ_c in Eq. (25) can be thought of as the fracture toughness, inclusive of all contributing terms.

The significance of the scaling behavior observed on fracture surfaces is that fractography (Eq. 2), fracture mechanics (Eq. 1), and fractal geometry (Eq. 23) can be used to relate properties such as fracture toughness and elastic modulus with atomic or molecular level structural units. This knowledge can help describe the creation of the surface during bond rupture and crack propagation. The values of a_o are given in Table 1 for inorganic glasses, single crystals, and glass ceramics. The values of a_o for single crystals (1–10 Å) can be thought of as the size of stretched bond lengths. The values of a_o for glasses (10–20 Å) are consistent with the size of the free volume

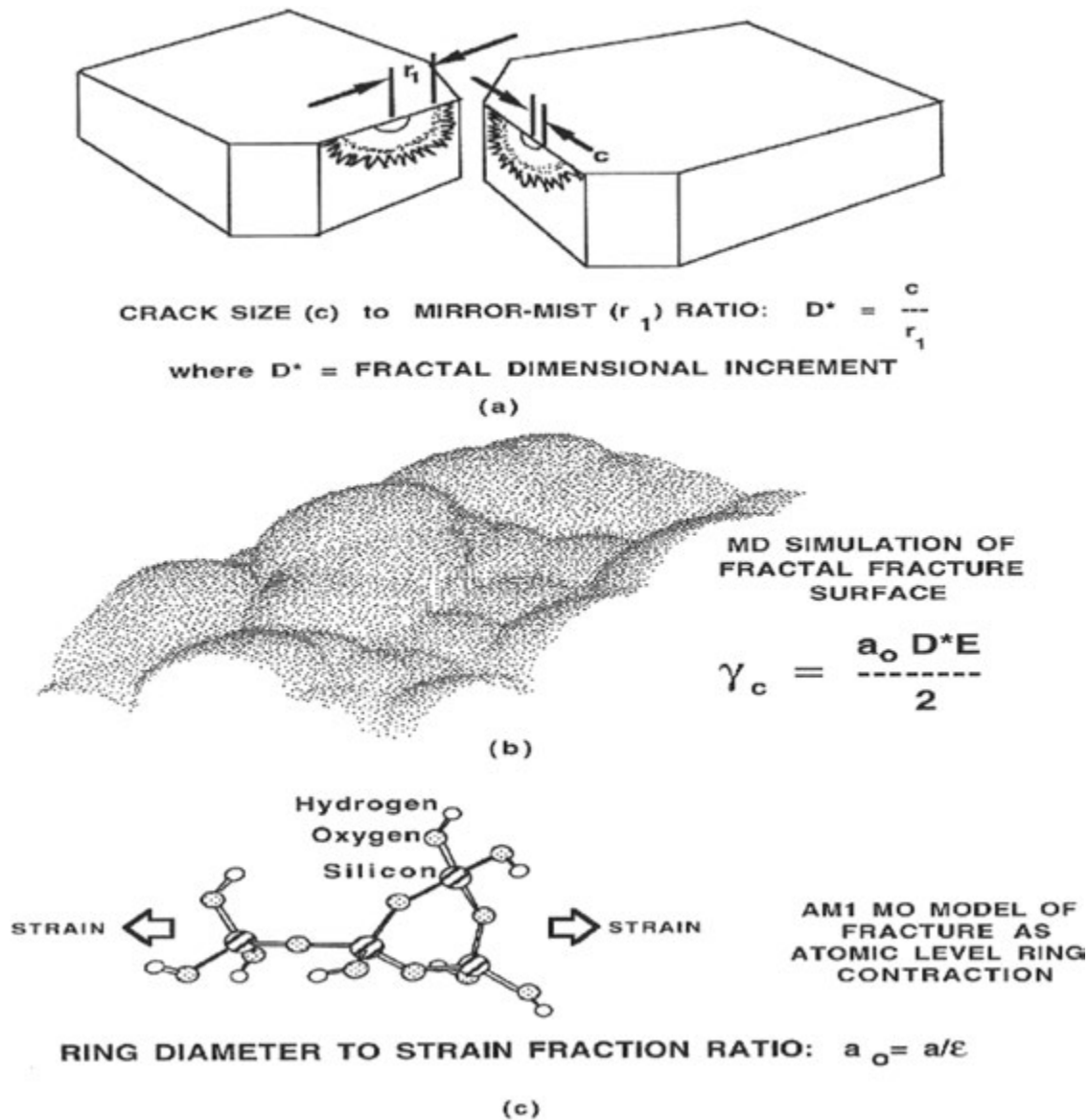


Fig. 14 Schematic of multi-scale fracture processes. (a) Macroscopic fractography; (b) Molecular level fractal behavior; (c) atomic reconfigurations. The three scale levels are related through Eqs. 9, 23, and 25.

near the crack tip. The a_0 values for glass ceramics (20–60 Å) are consistent with the size of glass-crystal clusters. Thus, we can think of a_0 as related to the sizes of the initiation region at the tip of a crack that result in the propagation of the crack by self-replication.

Brittle fracture is most likely a series of quantized, bond reconfiguration events based on minimum energy related to the production of free volume at the crack tip (West *et al.*, 1999). A series of these reconfigurations along the crack front, due to thermal vibrations and lowest energy configurations, develop into a mirror-mist-hackle pattern. a_0 is an indirect measure of the space created at a point along the crack front. These enlarged spacings, in turn, annihilate and supplement other similar spaces either to subside or to percolate into large structures, respectively. D^* is a scaling factor for both the fracture energy and the geometry of the fracture surface created. At a critical point, the crack branches macroscopically. The angle and nature of the macroscopic branching depends on energy levels, geometric atomic structure, far field stress, and lowest energy pathways.

The relationship of the fracture process at different length scales is schematically shown in Fig. 14. On the macroscopic scale, continuum (fracture) mechanics can be used to identify many macroscopic quantities to be verified using fracture mechanics, fractography and fractal analysis. The crack size-to-mirror size ratio is a constant equal to the fractal dimensional increment, D^* . The c/r_1 ratio relates the initiation of crack propagation (Fig. 1) with the resulting fractographic features quantified by Eq. (2). On the molecular scale, molecular dynamics (MD) modeling describes the creation of the fracture surface and has been shown to compare well with the experimental observations by using the atomic force microscope (AFM) and by a comparison of the fractal dimensions (Tsai *et al.*, 1995). At the atomic level we can use quantum mechanics to describe fracture as a quantized ring

contraction dictated by minimum energy and creation of free volume. The geometry of the structure formed is the basis for the structure of the ensuing crack propagation (West *et al.*, 1999).

References

- Aboushelib, M.N., Feilzer, A.J., de Jager, N., Kleverlaan, C.J., 2008. Prestresses in bilayered all-ceramic restorations. *J. Biomed. Mater. Res. Part B Appl. Biomater.* 139–145.
- ASTM Standard C 1161, 2018. Flexure Strength Measurements. Philadelphia, PA: American Society of Testing and Materials.
- ASTM Standard C1239-13, 2013. Standard Practice for Reporting Uniaxial Strength Data and Estimating Weibull Distribution Parameters for Advanced Ceramics. Philadelphia PA: American Society of Testing and Materials.
- ASTM Standard C 1322-15, 2015. Fractographic Analysis. Philadelphia, PA: American Society of Testing and Materials.
- Beauchamp, E.K., 1996. Mechanisms for Hackle formation and crack branching. In: Varner, J.R., Frechette, V.D., Quinn, G.D. (Eds.), *Fractography of Glasses and Ceramics III*. Ceramic Transactions 64. The American Ceramic Society, pp. 409–445.
- Bradt, R.C., 2011a. The fractography and crack patterns of broken glass. *J. Fail. Anal. Prev.* 11 (2), 79–96.
- Bradt, R.C., 2011b. The fractography and crack patterns of broken glass. *J. Fail. Anal. Prev.* 2011 (11), 79. doi:10.1007/s11668-011-9432-5.
- Conway Jr., J.C., Mecholsky Jr., J.J., 1989. Use of crack branching data for measuring near-surface residual stresses in tempered glass. *J. Am. Ceram. Soc.* 72 (9), 1584–1587.
- Danzer, R., Lube, T., Supanic, P., Damani, R., 2008. *Fract. Ceram. Adv. Eng. Mater.* 10 (4), 275–298.
- Erdogan, F., Sih, G.C., 1963. On the crack extension in plates under plane loading and transverse shear. *J. Basic Eng.* 85D, 519–527.
- Frechette, V.D., 1990. Failure Analysis of Brittle Materials: Advances in Ceramics. 28. The American Ceramic Society.
- Freiman, S.W., Mecholsky Jr. J.J., 2019. *Fracture of Brittle Materials*, second ed. NY New York: Wiley Pub. Co.
- Freiman, S.W., Gonzalez, A.C., Mecholsky Jr., J.J., 1979. Mixed-mode fracture in soda-lime glass. *J. Am. Ceram. Soc.* 62 (3–4), 206–208.
- MIL-HDBK-790, 1992. Fractography and Characterization of Fracture Origins in Advanced Structural Ceramics. Washington, DC: U.S. Department of Defense.
- Freiman, S.W., Mecholsky, J.J., Becher, P.F., 1991. Fractography: A quantitative measure of the fracture process. In: Frechette, V.D., Varner, J. (Eds.), *Ceramic Transactions 17, Fractography of Glasses and Ceramics II*. The American Ceramic Soc.
- Gopalakrishnan, K., 2011. Mixed Mode Fracture in Brittle Materials. PhD Dissertation. University of Florida. Available at: <https://ufdc.ufl.edu/UFE0043736/00001>.
- Gopalakrishnan, K., Mecholsky Jr., J.J., 2012. Fractography of mixed-mode fracture in soda lime silica glass. *J. Am. Ceram. Soc.* 95 (11), 3622–3627.
- Gopalakrishnan, K., Mecholsky Jr., J.J., 2013. Mixed-mode fracture in an R-curve material. *Mater. Sci.* 48, 7081–7087.
- Hussain, M., Pu, S., Underwood, J., 1974. Strain energy release rate for a crack under combined mode I and mode II. In: Irwin, G. (Ed.), *Fracture Analysis: Proceedings of the 1973 National Symposium on Fracture Mechanics, Part II*. West Conshohocken, PA: ASTM International, pp. 2–28. doi:10.1520/STP33130S.
- Kassir, M.K., Sih, G.C., 1966. Three dimensional stress distribution around an elliptical crack under arbitrary loadings. *J. Appl. Mech.* 33 (3), 601–611.
- Kirchner, H.P., Kirchner, J.W., 1979. Fracture mechanics of fracture mirrors. *J. Am. Ceram. Soc.* 62 (3–4), 198–202.
- Kirchner, H.P., Conway Jr., J.C., 1988. Fracture mechanics of crack branching in ceramics. In: Frechette, V.D., Varner, J.R. (Eds.), *Fractography of Glass and Ceramics, Advances in Ceramics 22*. Westerville, OH: The American Ceramics Society, pp. 187–213.
- Kruzic, J.J., Satet, R.L., Hoffmann, M.J., Cannon, R.M., Ritchie, R.O., 2008. The utility of R-curves for understanding fracture toughness-strength relations in bridging ceramics. *J. Am. Ceram. Soc.* 91 (6), 1986–1994.
- Kulawansa, D.M., Jensen, L.C., Langford, S.C., Dickinson, J.T., 1994. STM observations of the mirror region of silicate glass fracture surfaces. *J. Mater. Res.* 9 (2), 476–485.
- Lawn, B.R., Marshall, D.B., 1991. Indentation fractography. In: Bradt, R.C., Tressler, R.E. (Eds.), *Fractography of Glasses*. Plenum Press.
- Mandelbrot, B.B., 1982. *The Fractal Geometry of Nature*. New York: W. H. Freeman.
- Marshall, D.B., Lawn, B.R., Mecholsky Jr., J.J., 1980. Effect of residual contact stresses on mirror/flaw size relations. *J. Am. Ceram. Soc.* 63, 7–8.
- Mecholsky Jr., J.J., 1981. Intergranular slow crack growth in MgF₂. *J. Am. Ceram. Soc.* 64 (9), 563–566.
- Mecholsky, J.J., 1996. Fractography, fracture mechanics and fractal geometry: An integration. In: Varner, J.R., Frechette, V.D., Quinn, G.D. (Eds.), *Ceramic Transactions: Fractography of Glasses and Ceramics III*. Westerville: American Ceramic Society, pp. 385–393.
- Mecholsky, J.J., Freiman, S.W., 1979. Determination of fracture mechanics parameters through fractographic analysis of ceramics. In: Freiman, S.W. (Ed.), *Fracture Mechanics Applied to Brittle Materials*. ASTM STP 678. American Society for Testing and Materials, pp. 136–150.
- Mecholsky, J.J., Freiman, S.W., 1991. Relationship between fractal geometry and fractography. *J. Am. Ceram. Soc.* 74 (12), 3136–3138.
- Mecholsky, J.J., Rice, R.W., Freiman, S.W., 1974. Prediction of fracture energy and flaw size in glasses from mirror size measurements. *J. Am. Ceram. Soc.* 57 (10), 440–444.
- Mecholsky Jr. J.J., Freiman, S.W., Rice, R.W., 1977. Effect of grinding on flaw geometry and fracture of glass. *J. Am. Ceram. Soc.* 60 (3–4), 114.
- Mecholsky, J.J., Gonzalez, A.C., Freiman, S.W., 1979. Fractographic analysis of delayed failure in soda-lime glass. *J. Am. Ceram. Soc.* 62 (11–12), 577–580.
- Mecholsky Jr., J.J., Hill, T.J., Chen, Z., 2002. In: Salem, J.A., Quinn, G.D., Jenkins, M.G. (Eds.), *Fracture resistance testing of monolithic and composite brittle materials*. ASTM STP 1409. West Conshohocken PA: American Society for Testing Materials.
- Michalske, T.A., 1979. Fractography of slow fracture. In: Mecholsky, J.J., Powell, S.R. (Eds.), *Fractography of Ceramic and Metal Failures*, ASTM STP 827. Philadelphia, PA: American Society for Testing and Materials, pp. 130–150.
- Michalske, T.A., Freiman, S.W., 1983. A molecular mechanism for stress corrosion in vitreous silica. *J. Am. Ceram. Soc.* 66 (4), 284–288.
- Moon, R., Bowman, K., Trumble, K., Roedel, J., 2000. A comparison between the SEVNB and SCF measured R-curve behavior of multilayered alumina-zirconia composites. *J. Aust. Ceram. Soc.* 36 (1), 95–104.
- Munz, D., 2007. What can we learn from R-curve measurements? *J. Am. Ceram. Soc.* 90 (1), 1–15.
- Passoja, D.E., 1988. Fundamental relationships between energy and geometry in fracture. In: Frechette, V.D., Varner, J.R. (Eds.), *Fractography of Glasses and Ceramics, Advances in Ceramics 22*. Columbus OH: The American Ceramic Society.
- Pons, J.A., Karma, A., 2010. Helical crack-front instability in mixed-mode fracture. *Nature* 464, 85–89.
- Quinn, G.D., 1987. Static fatigue and creep resistance of a commercial sialon. *J. Mater. Sci.* 1822, 374–380.
- Quinn, G.D., 2016. *Fractography of Ceramics and Glasses*. NIST Special Publication 960-16e2. Gaithersburg, MD: National Institute of Standards and Technology.
- Quinn, G.D., Swab, J.J., 1996. Fractography and estimates of fracture origin size from fracture mechanics. *Ceram. Eng. Sci. Proc.* 17 (3), 51–58.
- Randall, P.N., 1967. Plane Strain Crack Toughness Testing of High Strength Metallic Materials, ASTM STP 410. Philadelphia PA: American Society of Testing and Materials, pp. 88–126.
- Rossmannith, H.P., 1980. Crack Branching in Brittle Materials: Part I. Analytical Aspects, University of Maryland Research Report. College Park, MD: University of Maryland, Photomechanics Lab.
- Russ, J.C., 1996. *Fractal Surfaces*. NY: Plenum Press.
- Scherrer, S.S., Kelly, J.R., Quinn, G.D., Xu, K., 1999. Fracture toughness (K_{IC}) of a dental porcelain determined by fractographic analysis. *Dent. Mater.* 15, 342–348.
- Scott, P.M., Thorpe, T.W., 1981. A critical review of crack tip stress intensity factors for semi elliptical cracks. *Fatigue Fract. Eng. Mater. Struct.* 4 (4), 291–309.

- Shetty, D.K., Rosenfield, A.R., Duckworth, W.H., 1987. Mixed-mode fracture in biaxial stress state: application of the diametral-compression (Brazilian disk) test. *Eng. Fract. Mech.* 26 (6), 825–840.
- Sih, G.C., 1974. Strain-energy-density factor applied to mixed mode crack problems. *Int. J. Fract.* 10, 305–321.
- Smith, F.W., Emery, A.F., Kobayashi, A.S., 1967. Stress intensity factors for semicircular cracks II. *J. Appl. Mech.* 34 (4), 953–960.
- Smith F.W., Sorensen, D.R., 1974. Mixed mode stress intensity factors for semi elliptical surface cracks. NASA Rept. No. NASA-CR-134684.
- Steinbrech, R.W., 2005. R-curve behavior of ceramics. In: Bradt, R.C., Haselman, D.P.H., Munz, D., Sakai, M., Shevchenko, V.Y. (Eds.), *Fracture Mechanics of Ceramics 9*. NY: Plenum Press, pp. 187–208.
- Tsai, Y.L., Swiler, T.P., Simmons, J.H., Mecholsky, J.J., 1995. Fractal analysis of molecular dynamics simulations of brittle fracture. In: Simmons, J.H., *et al.* (Eds.), *Computational Modeling of Materials and Processing*. Ceramic Transactions 69. Columbus, OH: American Ceramic Society.
- Ueda, Y., Ikeda, K., Yao, T., Aoki, M., 1983. Characteristics of brittle fracture under general combined modes including those under bi-axial tensile loads. *Eng. Fract. Mech.* 18, 1131–1158.
- West, J.K., Mecholsky Jr., J.J., Hench, L.L., 1999. The Quantum and Fractal Geometry of Brittle Fracture. *J. Non-Cryst. Solids* 260, 99–108.
- Williams, J.G., Ewing, P.D., 1972. Fracture under complex stress-the angled crack problem. *Int. J. Fract.* 8, 416–441.

Further Reading

ASTM E561-15a, 2015. Standard Test Method for KR Curve Determination. West Conshohocken, PA: ASTM International.

Relevant Website

<http://www.ceramics.nist.gov/webbook/fracture/fracture.html>
National Institute of Standards and Technology.

Thermal Analysis Techniques for Technical Ceramics and Glasses

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Thermogravimetric Analysis

Introduction

Thermogravimetric analysis (TGA or TG) is a technique which continuously follows weight changes with temperature as well as weight changes at constant temperature. Accordingly, it can be used for various processes which involve weight gain e.g., oxidation of boride – carbide composites (Ren *et al.*, 2019) or weight loss e.g., decomposition of cerium nitrate (Storti *et al.*, 2019). For ceramic and glass science, the technique can be used to study the following: calcination, binder burn out, decomposition, pyrolysis, weight changes during crystallization or transformation, weight changes during oxidation or decomposition of ceramics, glasses and high temperature ceramics and composites. Thus, the technique can be used to aid the understanding of the kinetics and mechanisms of various physico-chemical processes involved in materials processing or materials degradation. Experiments can be carried out in complex gas environments as well as in neutral or inert gas environments.

Fig. 1 shows a typical setup for a thermogravimetric analyzer allowing experiments to be conducted under a nitrogen-carbon dioxide gas mixture. For this system, the balance mechanism is continually purged by nitrogen. However, a reaction gas (CO_2 in this instance) can be pumped over specimens which are held in a furnace chamber. Other designs are offered by the various TGA instrument manufacturers and suppliers, but all involve a specimen located in a furnace attached to a microbalance which is remote from the furnace. Computer controlled systems allow heating rates (in the range $0.1\text{--}500\text{K min}^{-1}$) up to temperatures of 2400°C . Multistep control facilities allow several different approaches to be adopted e.g., simple constant temperature ramp rate to a defined temperature, which can then be held to facilitate isothermal experiments, or multiple ramps and holds to facilitate examination of weight change events associated with different temperatures or heating rates. Weight change resolution typically depends on sample size, thus for a 5 g sample size Linseis indicate a $0.1\text{ }\mu\text{g}$ sensitivity. For a 25 g sample a $0.5\text{ }\mu\text{g}$ accuracy is indicated by them for their TGA PT 1600 system.

Examples of Thermogravimetric Analyzes for Ceramics and Glasses

The following paragraphs give examples of the use of TGA for the analysis of different processes of interest.

Fig. 2(a) shows the percentage weight changes associated with the decomposition of cerium III acetate hydrate to cerium IV oxide. In addition to measuring the weight change, Arii *et al.* (2002) passed the gases evolved through a mass spectrometer so that the exact decomposition mechanism could be ascertained. Gas analyzes can also be conducted using FT-IR spectroscopies and gas chromatography (Dollimore, 2003). The work of Arii *et al.* (2002) shows how different environments affect the decomposition rate over the temperature range covered and how the individual stages of decomposition can be clearly identified by using Sample Controlled TGA (SCTGA – see Rouquerol (2019) for a detailed description of the technique) where the rate of weight change is held constant (see Fig. 2(b)). Thus, the work of Arii *et al.* (2002) shows how versatile TGA analysis can be. The weight changes shown in Fig. 2 are expressed as a percentage of total weight of starting cerium acetate hydrate. This is adequate for the observation of each of the changes for each of the steps of the decomposition. However, this would not be adequate to truly assess the kinetics of the processes at each step because the decomposition rates will depend on surface area. Fig. 3 shows the weight gain of uncoated and coated silicon carbide when exposed to air at 1500°C . In this work by Bundschuh *et al.* (1995), the weight gain is expressed as weight change per unit area and thus the kinetics and mechanism of the oxidation processes can be truly ascertained. Thus, the uncoated silicon carbide undergoes diffusion controlled oxidation denoted by a parabolic weight change per unit area – time relationship. Bundschuh *et al.* (1995) used the TGA experiments to help select materials for use at 1500°C in air. Ren *et al.* (2019) used TGA similarly, to test mixtures of HfB_2 and SiC powders.

While the SCTG methods used by Arii *et al.* (2002) are useful in detecting the temperatures at which samples undergo weight change, this can also be done by the use of combined thermal analysis TGA/DSC or TGA/DTA. Fig. 4 shows combined TGA/DSC data for the thermal decomposition of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ precursor used in the production of electrospun CaZrO_3 nanofibers. This work by Storti *et al.* (2019) shows that the calcium nitrate hydrate undergoes three stages of loss of physically absorbed water and water of crystallization at 51, 164 and 199°C and these events are associated with endothermic heat changes in the DSC curves. The endotherm at 557°C is said to be associated with the melting of anhydrous calcium nitrate and melting occurs prior to decomposition of the molten salt to CaO and NO_2 at 605°C . Similar analyzes can be conducted with 3D printing inks for ceramic components (Liu *et al.*, 2020). Fig. 5(a) shows the TGA/DTA curve for the decomposition of their ink. It is seen that at temperatures up to 700°C weight losses occur in stages associated with endothermic peaks. These are due to the evaporation of volatile organic constituents from the ink, although Liu *et al.* (2020) do not specifically indicate the decomposition products. They were however able to develop a temperature profile for sintering the 3D printed Li_2SiO_4 components with holds at 200 and 750°C to facilitate the total removal of the binder in the ink (see Fig. 5(b)). This then demonstrates how TGA can be used to design thermal programmes for binder or ink vehicle removal from processed green ceramics.

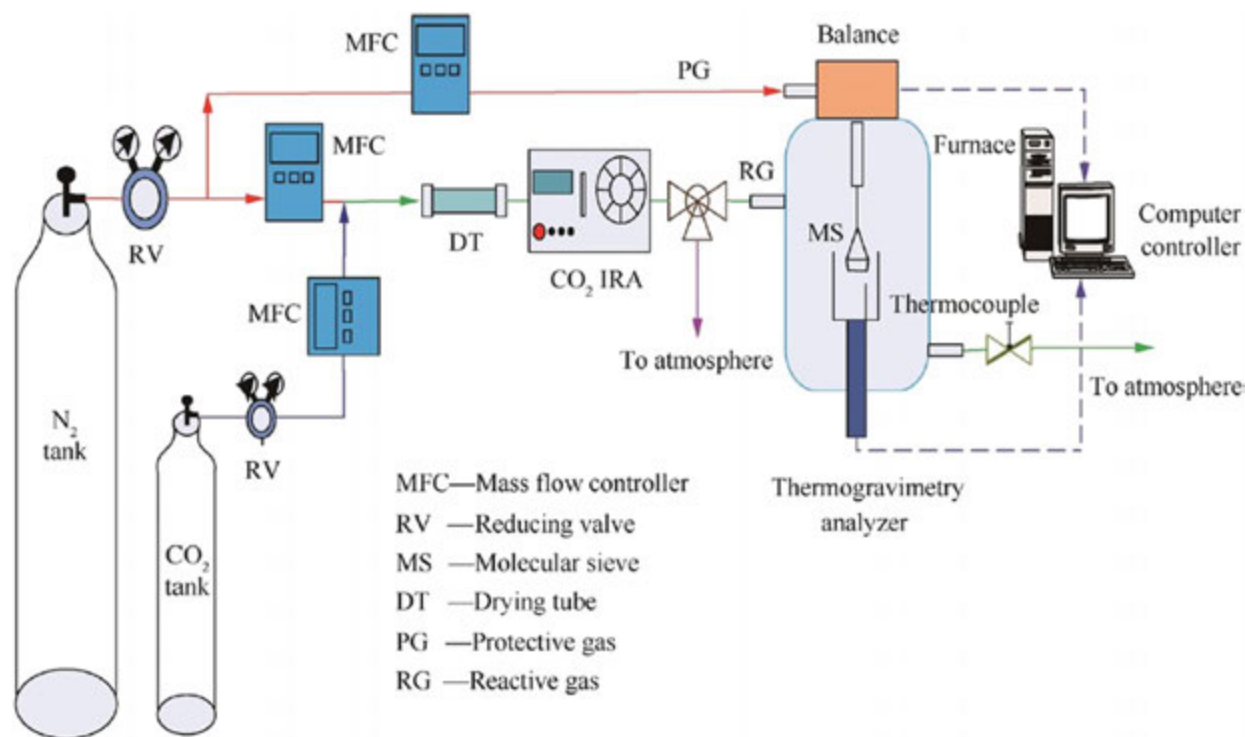


Fig. 1 Schematic of a thermogravimetric analysis system set up for experiments under nitrogen – carbon dioxide gas mixtures. Reproduced from Liu, M., Yang, D., Pang, L., Yu, Q., Huang, Y., 2015. Experimental and computational investigation of adsorption performance of TC-5A and PSA-5A for manned spacecraft. Chinese Journal of Aeronautics 28, 1583–1592.

Differential Thermal Analysis and Differential Scanning Calorimetry

Introduction

Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) are experimental techniques which enable transitions and transformations to be analyzed in terms of the temperature they occur at and the specific energy associated with them (Wunderlich, 2001; Dollimore, 2003; Schick, 2016; Kett, 2019; Zheng *et al.*, 2019). Such transitions/transformations include dehydration, transformations in crystal structure, melting, the glass transition and crystallization of glasses. Indirect information such as specific heat capacity, glass viscosity for given temperatures and glass fragility can also be inferred from DSC/DTA data (see Zheng *et al.*, 2019). Perusal of relevant supplier websites shows a vast array of standard instruments are available with heating and cooling rates in the range $0.001\text{--}50\text{K s}^{-1}$ and maximum temperatures up to 2000°C . Typically samples of the order of 50 mg weight are used.

Wunderlich (2001), Dollimore (2003), Schick (2016) and Zheng *et al.* (2019) describe DSC/DTA in detail. Both systems involve a sample and an inert reference located in a single furnace or individual furnaces. DTA is also described as heat flux DSC. For DTA, heat is supplied to both reference and sample at the same rate within a single furnace (see Law and Zhou, 2017 for a suitable schematic). Both sample and reference materials absorb a level of heat energy Q . However, due to specific heat differences, the temperature increase caused by the absorption of Q will be different between the sample and reference and this temperature difference will linearly increase or decrease with increasing temperature depending on the relative specific heats of sample and reference. If then a thermally induced event arises, the heat input into the sample will change (e.g., it will increase for an exothermic event and decrease for an endothermic event). This additional heat input will result in greater temperature differences between sample and reference, generating a peak on a ΔT versus T trace. In many instances, ΔT is replaced by ΔV the voltage difference between the two thermocouples monitoring sample and reference temperatures (See Fig. 6). DSC, also referred to as power compensated DSC, involves analysis of the differential heat input required to maintain reference and sample at the same temperature (again see Law and Zhou, 2017 for a suitable schematic). The output signals are typically, W , $W\text{ g}^{-1}$, $W\text{ mol}^{-1}$, $W\text{ s}^{-1}$ (power output) among others. Fig. 5 gives an example.

Examples of DTA/DSC Analyzes for Ceramics and Glasses

Degradation, volatilization and melting

Figs. 5(a) and 6 show DSC and DTA curves for the decomposition of an organic printing ink (Liu *et al.*, 2020) and the dehydration, desulphurization and melting of constituents typically found in gas turbine deposits which attack environmental and thermal barrier coatings (Wiesner and Bansal, 2015). In the case of the printing ink its decomposition and volatilization of decomposition

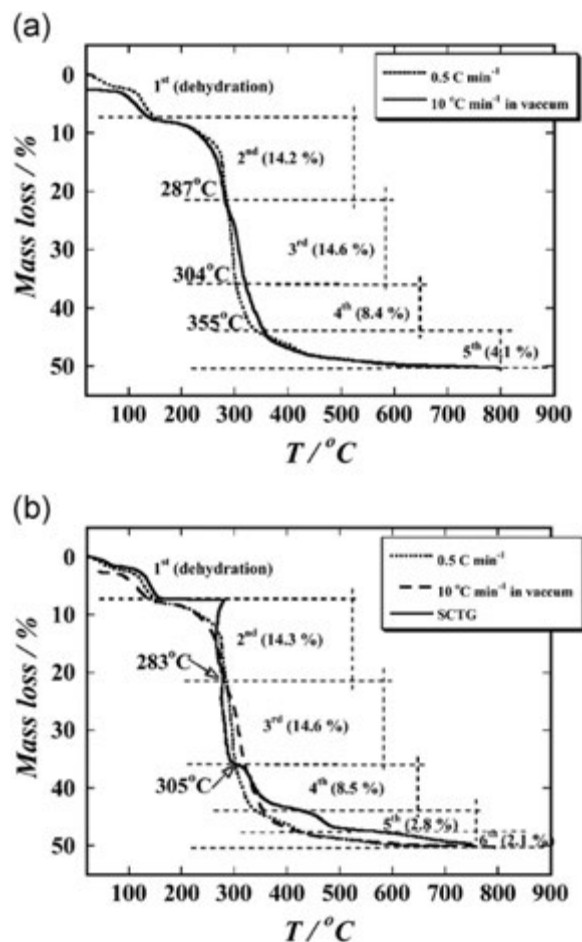


Fig. 2 (a) TGA curves for decomposition of $\text{Ce}(\text{CH}_3\text{CO}_2)_3 \cdot 1.5\text{H}_2\text{O}$ at $0.5^\circ\text{C min}^{-1}$ in helium and $10^\circ\text{C min}^{-1}$ in vacuo. (b) Comparison of mass loss curves of $\text{Ce}(\text{CH}_3\text{CO}_2)_3 \cdot 1.5\text{H}_2\text{O}$, using LHTG (linear heating controlled TG) of $0.5^\circ\text{C min}^{-1}$ in helium and $10^\circ\text{C min}^{-1}$ in vacuo with SCTG (sample controlled TG) at $0.06^\circ\text{C min}^{-1}$ in helium. Reproduced from Ariei, T., Taguchi, T., Kishi, A., Ogawa, M., Sawada, Y., 2002. Thermal decomposition of cerium (III) acetate studied with sample-controlled thermogravimetric-mass spectrometry (SCTG—MS). *Journal of the European Ceramic Society* 22, 2283–2289.

products is evidenced by three significant endotherms arising between 300 and 600 °C (Liu *et al.*, 2020). Fig. 6 presents a DTA curve for the synthetic sand with a composition (in wt%) 34 SiO₂, 30 CaSO₄ · 2H₂O, 17 (SiO₂ + KAlSi₃O₈), 14 (Ca,Mg)(CO₃)₂ and 5 NaCl. Various endothermic events occur and can be associated with various changes to the synthetic sand ingredients. Thus, Wiesner and Bansal (2015) assign the endotherms as follows: 150 °C – dehydration of the hydrated calcium sulfate, 666 and 740 °C the decomposition of the carbonate to (Ca,Mg)O, 809 °C – the melting of the sodium chloride, 1175 °C – desulphurization of the calcium sulfate to CaO, further melting of the mixture resulting from the heating to above this temperature. This DTA data enabled Wiesner and Bansal (2015) to determine how molten CMAS glass deposits could form from a mixture of typical impurities ingested into a gas turbine. Pomeroy *et al.* (2011) also used DTA to investigate reactions between cordierite and an ash typical of that arising in diesel particulate filters. In this work, Pomeroy *et al.* (2011) were able to correlate an exothermic effect due to the combustion of carbon (simulating the carbon burnout cycle in a diesel particulate filter) and subsequent endothermic effects associated the decomposition of ash components (calcium sulfate, zinc sulfate). At temperatures above 900 °C, melting endotherms could be observed. Using combined findings from DTA, dilatometry and X-ray diffraction, Pomeroy *et al.* (2011) were able to clearly identify liquefaction events and how these events could be suppressed so that they occurred at higher temperatures in the presence of either Fe or Ce, which can be added to diesel fuel in combustion catalysts as ferrocene or cerium carboxylate.

Differential thermal analysis of glasses – Glass transition temperature

Without doubt the most comprehensive article on the differential thermal analysis of glasses is that by Zheng *et al.* (2019). However, the more general aspects of the topic are addressed in this present chapter. Fig. 7 shows a typical DTA curve for a relatively simple barium silicate glass. Four events can be discerned and are related by Rodrigues *et al.* (2018). These are: (1) the glass transition temperature indicated by an endothermic event at about 980K, (2) an exothermic event at about 1140K associated with major crystallization of the glass to a metastable monoclinic form, (3) a secondary exothermic event at about 1250K

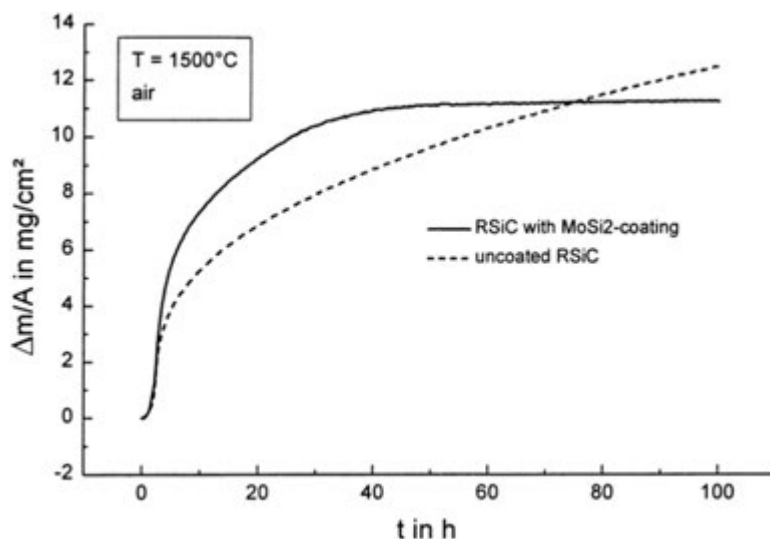


Fig. 3 Weight gain per unit area of uncoated and MoSi₂-polysiloxane coated silicon carbide. Reproduced from Bundschuh, K., Schüze, M., Müller, C., Greil, P., Heider, W., 1995. Selection of materials for use at temperatures above 1500°C in oxidizing atmospheres. *Journal of the European Ceramic Society* 8, 2389–2391.

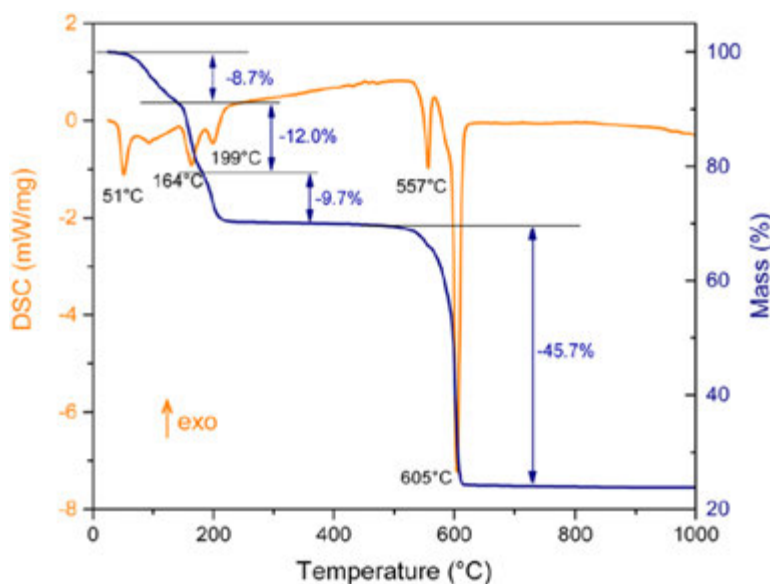


Fig. 4 DSC-TG curves of a Ca(NO₃)₂·4H₂O precursor used in the production of electrospun CaZrO₃ nanofibers. Reproduced from Storti, E., Himcinschi, C., Kortus, J., Aneziris, C.G., 2019. Synthesis and characterization of calcium zirconate nanofibers produced by electrospinning. *Journal of the European Ceramic Society* 39, 5338–5344.

associated with the transformation of the metastable monoclinic form to a stable orthorhombic form and (4) an endothermic event at about 1680K which is the system liquidus. [Rodrigues et al. \(2018\)](#) also indicate the onset of liquefaction as T_s the solidus temperature indicated by the inflexion at 1660K in [Fig. 7](#). With respect to the glass transition, it often appears as a slight deviation of

the baseline or a very small endotherm due the nature of the change in glass structure it represents. [Zheng et al. \(2019\)](#) show how more detailed analysis of T_g and temperatures related to it (T_g start, T_g end and ΔT_g – see [Fig. 7](#) in their publication), can be realised by using specific heat capacity data – T traces rather than raw DTA data. The specific heat capacity is determined using DSC data for the baseline, the reference and the sample (see [Shelby, 2005](#)). Netzsch for example have a software package to use the baseline, reference and sample data to determine C_p . [Eq. \(1\)](#) (see Hitachi website reference) gives the relevant equation where for a given temperature, C_{p_s} and C_{p_r} are the specific heat capacities of the sample and reference, H is the DSC output difference between sample and empty sample pan, h is the output difference between reference and empty sample pan and m_r and m_s are reference

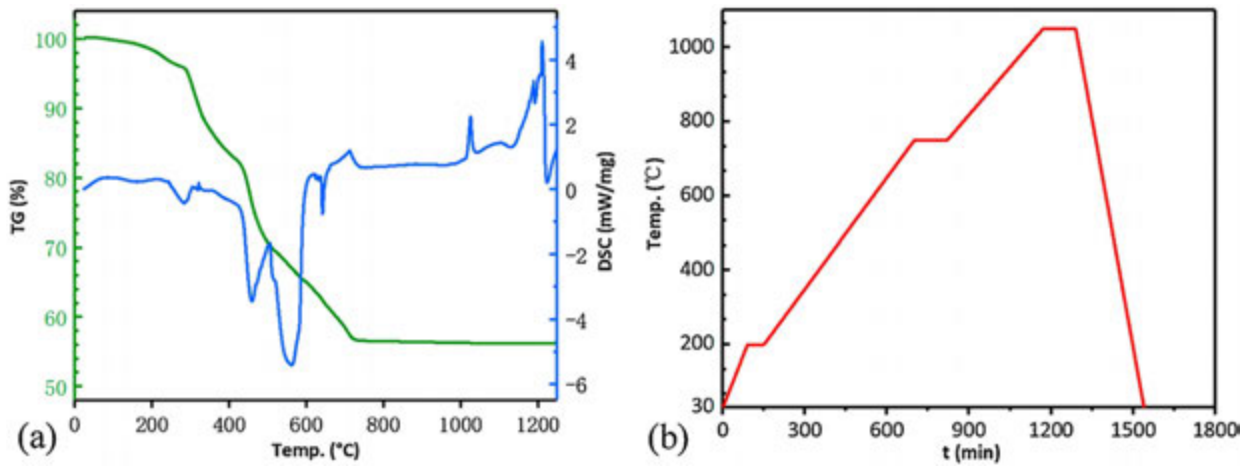


Fig. 5 Removal of organic ink components from a 3D printing ink used to produce Li_4SiO_4 cellular structures (a) TG-DSC curves, (b) de-binding and sintering scheme, based on TGA data. Reproduced from Liu, Y., Chen, Z., Li, J., *et al.*, 2020. 3D printing of ceramic cellular structures for potential nuclear fusion application. *Additive Manufacturing* 35, 101348.

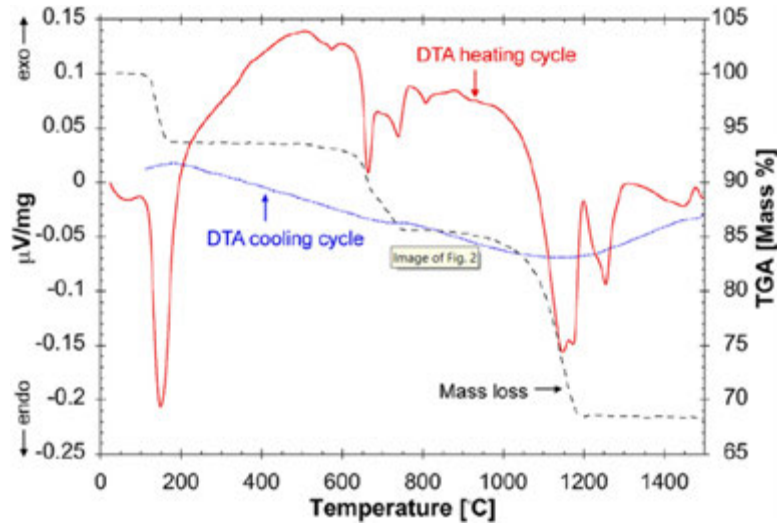


Fig. 6 DTA curve (mV mg^{-1} vs. T) for a synthetic calcium magnesium aluminosilicate typical of a CMAS glass formed as deposits on barrier layers in gas turbines. Reproduced from Wiesner, V.L., Bansal, N.P., 2015. Mechanical and thermal properties of calcium–magnesium aluminosilicate (CMAS) glass. *Journal of the European Ceramic Society* 35, 2907–2914.

and sample weights. Shelby (2005) gives a similar method and equation for establishing C_p . Analysis of the variation is C_p with T is particularly useful. Eqs. (2) and (3) (see Schick, 2016) allow enthalpy (H) and entropy (S) to be calculated, and thus with care, a complete thermodynamic analysis of glasses over a suitable temperature range should be possible.

$$C_{p_s} = (H/h) \cdot (m_r/m_s) \cdot C_{p_r} \quad (1)$$

$$H = \int_0^T C_p \cdot dT \quad (2)$$

$$S = \int_0^T \frac{C_p}{T} \cdot dT \quad (3)$$

Interpolation of other important glass properties from DTA/DSC data

Viscosity data for a given temperature can be inferred from data obtained by differential thermal analysis using the Vogel-Fulcher-Tammann equation (see for example Wiesner and Bansal, 2015; Rodrigues *et al.*, 2018). This equation, given in Eq. (4), enables the calculation of viscosity (η) for a given temperature (T), if the constants A , B and T_0 can be evaluated from known viscosities and

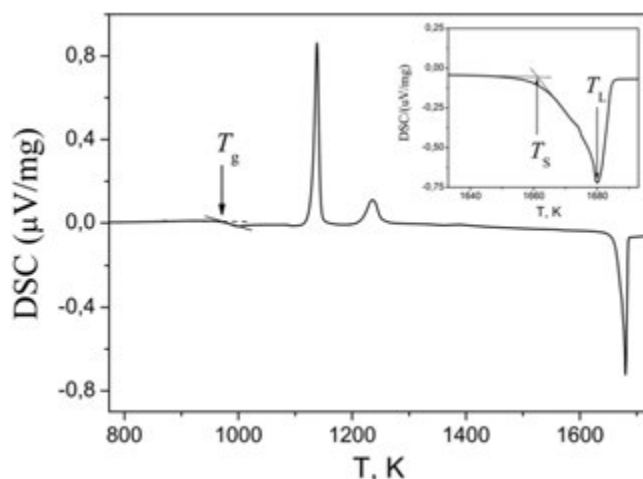


Fig. 7 DTA curve for a barium silicate glass showing glass transition temperature, T_g , exothermic peaks between 1100 and 1300K are exotherms due to crystallization the inset shows endotherm onset and peak associated with solidus and liquidus temperatures T_s and T_L . Reproduced from Rodrigues, A.M., Cassar, D.R., Fokin, V.M., Zanolto, E.D., 2018. Crystal growth and viscous flow in barium disilicate glass. *Journal of Non-Crystalline Solids* 479, 55–61.

their corresponding specific temperatures. These specific temperatures are T_g , the dilatometric softening temperature (see Section “Phase Transformations”) T_D , the melting temperature, T_m , and their associated viscosities which are $10^{12.6}$, $10^{10.3}$ and 10^5 Pa s (see Bansal and Doremus, 1986). According to Zheng *et al.* (2019) and (2020) a more accurate method of estimating viscosity for a given temperature is the MYEGA (Mauro–Yue–Ellison–Gupta–Allan) equation (see Eq. 5). In the MYEGA equation, m , defined in Eq. (6), is the fragility index of the glass and η_∞ the viscosity at the high temperature limit, given as $10^{-2.93}$ Pa s by Zheng *et al.* (2019). The MYEGA equation relates to a viscosity at T_g of 10^{12} Pa s in contrast to the value of 10^{12} Pa s of Bansal and Doremus (1986). Because T_g values are dependent on heating rates the value of viscosity at T_g changes (see Shelby, 2005). As viscosity and temperature are related, DTA/DSC data can also be to interpolate the activation energy of viscous flow E_{vf} from the Arrhenius equation given in Eq. (7), where R is the gas constant, using calculated data for viscosity at specific temperatures. Calculation of E_{vf} from raw DTA/DSC data is also possible (see Moynihan *et al.*, 1996).

$$\ln_{10}(\eta)_{(T)} = A + \frac{B}{T - T_0} \quad (4)$$

$$\ln_{10}(\eta)_{(T)} = \ln_{10}(\eta_\infty) + (12 - \ln_{10}(\eta_\infty)) \cdot \frac{T_g}{T} \cdot \exp \left[\left(\frac{m}{\ln_{10}(\eta_\infty)} - 1 \right) \cdot \left(\frac{T_g}{T} - 1 \right) \right] \quad (5)$$

$$m = \frac{\delta \log_{10}(\eta)}{\delta \left(\frac{T_g}{T} \right)} \text{ for } T = T_g \quad (6)$$

$$\eta = A \cdot \exp \left[\frac{E_{vf}}{RT} \right] \quad (7)$$

In addition to the detailed information relating to viscosity and fragility which can be interpolated from DTA/DSC data, Zheng *et al.* (2019) also indicate how fictive temperature can also be inferred from it. The reportage of Shelby (2005) and the works of Moynihan *et al.* (1996) and Yue *et al.* (2002) act as a good starting point if the reader is interested further. A further glass parameter which may also be of use is glass stability. This is really the temperature range between T_g and the onset temperature for crystallization, say T_x . However, Zheng *et al.* (2019) catalog nine different glass stability parameter definitions which are expressed in terms of T_g , T_x , T_c and T_m . They sum up the available analysis of glass stability by indicating that T_x is often very difficult to discern at typical DTA/DSC heating rates ($5\text{--}20\text{K min}^{-1}$) and accordingly the ratio T_g/T_m is a very useful, but rough, indicator of glass stability and indeed glass forming ability. A final comment on other important information which can be gleaned from DTA/DSC data is the occurrence of more than one T_g value which is indicative of phase separated glasses (see Zheng *et al.*, 2019).

Crystallization of glasses – Crystal growth

As indicated above, crystallization occurs at a temperature T_c and is an exothermic process. Thus, the barium silicate system of Rodrigues *et al.* (2018) (Fig. 7) shows an exotherm at about 1140K which is associated with glass crystallization. The area of the exotherm, say A_0 reflects the total amount of heat released due to complete crystallization of the glass or the “crystallizable fraction” at a particular T_c in the case of a glass crystallizing to more than one phase at different T_c s. If, for a constant temperature, the progress of heat release can be followed with time, t , by assessing the area under the crystallization exotherm, A , the extent of crystallization, y , can be calculated (see Zheng *et al.*, 2019). This extent of reaction can then be substituted into the Johnson, Mehl,

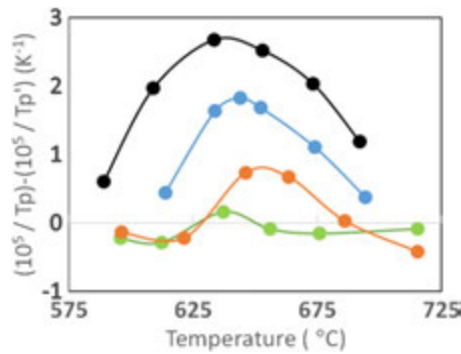


Fig. 8 Typical Optimum nucleation plots as determined by the Marotta method. The plots shown are for a Ba-K-Mg-Si-Al-O glass with various hold times using original data (green 5 min hold; orange 15 min hold; blue 60 min hold; black 300 min hold).

Avrami, Yerofeev, and Kolmogorov (JMAK) equation (see Eq. 8). If repeated DSC experiments are conducted at different temperatures, it is possible to use the Arrhenius equation (see Eq. 9) to calculate the activation energy for the crystallization process (Shelby, 2005). Zheng *et al.* (2019) give a table of values of n associated with different mechanisms of crystallization. This methodology for following the kinetics of crystallization is clearly an isothermal method.

For isochronal kinetic analysis, Shelby (2005) gives the 1956 Kissinger equation correlating heating rate, ϕ and crystallization temperature, T_p , with an activation energy for crystallization, E . This equation was modified by Matusita and Sakka (1980) due to the fact that the Kissinger equation related solely to surface crystallization events. Eq. (10) gives the modified Kissinger equation. In Eq. (10), $m = n = 1$ for surface crystallization Matusita and Sakka (1980) or $m = n = 3$ as used by Ramesh *et al.* (1998) for a glass undergoing crystallization from a fixed number of nuclei formed within the bulk of the glass. A more detailed derivation of the method and a wider range of m and n values associated with specific crystallization mechanisms is given by Matusita and Sakka (1981).

$$\ln(-\ln(1 - y)) = \ln(k) + n \cdot \ln(t) \quad (8)$$

$$\ln(k) = \ln(A) - E/RT \quad (9)$$

$$\ln\left(\frac{\alpha^n}{T_p}\right) = \ln(k) - \frac{m \cdot E}{RT_p} \quad (10)$$

Crystallization of glasses – Nucleation

As indicated above, the crystallization of glasses can occur within the bulk of a glass or at its surface, depending on whether preferred nucleation is homogeneous (bulk) or heterogeneous (surface). DSC/DTA experiments using different particle sizes enable which nucleation process predominates. Fernandes *et al.* (2019) shows a series of DSC curves for different particle size fractions of a glass. The data shows an increase in the value of the crystallization peak temperature and analysis of the glass crystallization shows that it surface nucleates and the nuclei grow inwards yielding crystals which grow from the surface into the glass. In contrast, for a bulk nucleating Y-Si-Al-O-N glass Ramesh *et al.* (1998) observed T_{p1} (first crystallization peak temperatures) of 1135, 1136 and 1136°C for glass particle sizes of <53, 53–106 and >106 μm . The differences for surface and bulk nucleation can be simply related to the fact that finer particle sizes have greater specific area and so for the same weight of glass powder, finer particle sizes will undergo greater rates of crystallization at lower temperatures. Large particles will have far less specific surface area and thus crystallization will need more thermal energy (higher temperature).

For homogeneous nucleation, it is possible to determine an optimum nucleation temperature at which the nucleation rate is a maximum. Marotta *et al.* (1985) derived a suitable equation given by Eq. (11), where I is the nucleation rate constant, n is a constant associated with nucleation mechanism, E is the activation energy for nucleation, R the gas constant, T_p° is the crystallization peak temperature for a glass and T_p the crystallization peak temperature for samples of the same glass having undergone nucleation holds at a temperature T_n . A plot of $(1/T_p) - (1/T_p^\circ)$ against T_n gives a bell shaped curve whose maximum is at the temperature of the maximum rate or, the optimum nucleation temperature (see Fig. 8). Zheng *et al.* (2019) report that plots of crystallization temperature against nucleation hold temperature, or the peak width at half maximum for the crystallization exotherm can be used to identify the optimum nucleation temperature. For the latter, as the peak width at half maximum is indicative of time for complete crystallization, for a constant crystal growth rate the smaller the width, the higher the nucleation rate. With respect to the actual value of the optimum nucleation temperature, Rafferty *et al.* (2000) note that if its value is close to T_g then the glass is highly likely to be phase separated.

$$\ln(I) = \frac{n \cdot E_c}{R} \cdot \left(\frac{1}{T_p} - \frac{1}{T_p^\circ} \right) + C \quad (11)$$

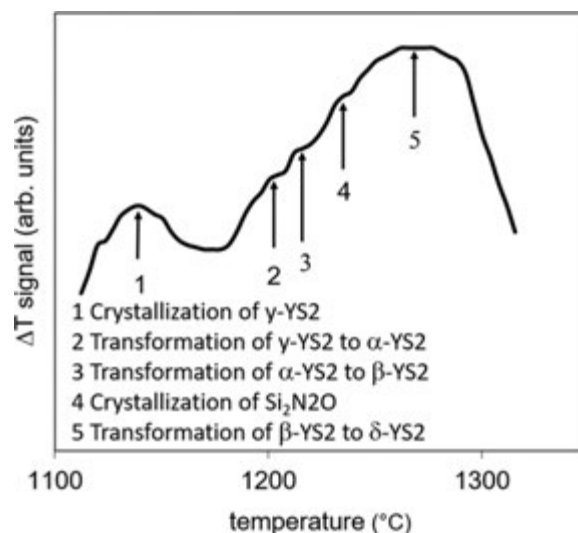


Fig. 9 Expanded DTA curve showing transformations of yttrium disilicate arising during the thermal treatment of a Y-Si-Al-O-N glass. Redrawn from Pomeroy, M.J., Hampshire, S., 2008. Controlled crystallisation of a Y-Si-Al-O-N glass typical of grain boundary glasses formed in silicon nitride-based ceramics. *Journal of the Ceramic Society of Japan* 116, 722–726.

DTA/DSC analysis of phase transformations

Many ceramic phase undergo transformations above certain temperatures. The work of [Rodrigues *et al.* \(2018\)](#) shows a DSC peak just above 1200K which is attributed to the transformation of the metastable monoclinic form of BaSi_2O_5 to a more stable orthorhombic form. No investigation of the mechanism of transformation is reported. However, it is important to indicate that as well as a solid state transformation occurring by atomic rearrangement, a solution - precipitation mechanism could also pertain. Such a transformation has been observed by [Pomeroy and Ramesh \(1993\)](#) where the β -polymorph of $\text{Y}_2\text{Si}_2\text{O}_7$ dissolves in a viscous liquid during the oxidation of β -sialons and re-precipitates as the γ -polymorph. This observation was due to X-ray analysis only. However, [Pomeroy and Hampshire \(2008\)](#) also report X-ray diffraction analysis of the devitrification of a Y-Si-Al-O-N glass to different polymorphs of $\text{Y}_2\text{Si}_2\text{O}_7$. They were able to correlate the temperatures at which the γ -form transformed to the α -form then to the β -form and then the δ -polymorph after a nucleation hold. It then became apparent that these transformations could be mapped onto an expanded DTA trace and discontinuities in the trace correlated with the formation of each polymorph and the crystallization of silicon oxynitride (see [Fig. 9](#)). Thus, [Pomeroy and Hampshire \(2008\)](#) were able to interpret the development of intergranular phases formed in silicon nitride densified with yttria and alumina.

Not only can phase transformations in glasses be followed using differential thermal analysis, but phase transformations in ceramics can also be followed. One example is the analysis of the phase transformations of $\text{La}_2\text{Mo}_2\text{O}_9$ and substituted variants from a monoclinic to cubic form on heating ([Ali *et al.*, \(2009\)](#)). This work also shows the importance of following a cooling curve as well as a heating curve. In their work, [Ali *et al.* \(2009\)](#) were able to clearly show that the reverse transformation involved the transformation to a metastable γ -form prior to that fully converting to the monoclinic form on further cooling. This shows the importance of following cooling curves, particularly since when some La was replaced by Sr, no intermediate γ -form arose.

Advanced Differential Thermal Analysis Techniques

Flash DSC and modulated DSC are modified DSC techniques, designed to yield additional and more detailed observations. Flash DSC is well described by [Schick \(2016\)](#), [Schawe and Hess \(2019\)](#) and [Zheng *et al.* \(2019\)](#). Exceedingly small samples, a few nanograms for the work of [Schawe and Hess \(2019\)](#), are heated or cooled at rates between 5K s^{-1} and $30,000\text{K s}^{-1}$ on an adiabatic heating chip. The incredible variation in heating and cooling rates facilitate more accurate assessments of glass transition temperatures as well as an ability to monitor the kinetics of this secondary transition (see [Schawe and Hess, 2019](#)). In addition to this level of detailed analysis, glass viscosity – temperature curves could be interpolated for the glass in question as could thermal relaxation times. [Zheng *et al.* \(2019\)](#) also explain how flash DSC can be used to interpolate fictive temperature and glass fragility index.

Modulated DSC involves a sinusoidal temperature modulation added to the simple linear heating rate such that the temperature cycles about a temperature step as it increases with time. According to [Dollimore \(2003\)](#) and [Kett \(2019\)](#) a sinusoidal, square or sawtooth cycle is superimposed upon a linear heating rate curve. Thus, detailed temperature cycling about each temperature is realised during heating. [Ketts \(2019\)](#) clearly indicates how the modulated approach separates out transitions related solely to heat capacity, whereas traditional DSC probes overlapping kinetic events. As clearly shown by data presented by [Ketts \(2019\)](#) the secondary transition, T_g , can clearly be identified by modulated DSC. [Zheng *et al.* \(2019\)](#) also discuss the benefits of modulated DSC for the study of glass systems.

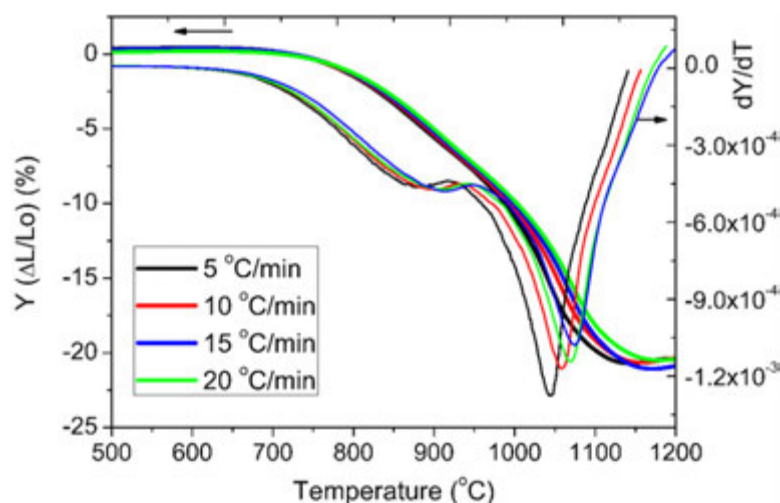


Fig. 10 Dilatometric shrinkage (Y) and shrinkage rate (dY/dT) curves for nanometric hematite at heating rates of 5, 10, 15 and $20^{\circ}\text{C min}^{-1}$. Reproduced from Togashi, M.M., Perdomo, C.P.F., Kiminami, R.H.G.A., 2020. Densification kinetics of nano-hematite using microwave assisted dilatometry. *Ceramics International* 46, 28546–28560.

Dilatometry

Introduction

Dilatometry is a relatively simple technique where a specimen is heated in a furnace and changes in length measured by an extensometer at the end of a pushrod linking the sample and the extensometer. Relating these changes in length to original length allows thermal strain to be determined over a temperature range and this enables coefficient of thermal expansion (CTE) to be determined. Typically, measurement accuracies of 0.05 nm and better are achievable and this is over a specimen of length up to 25 mm. This allows strains to be determined with accuracies of 5×10^{-9} . Current instruments (see list of supplier websites in the reference list) allow total length deflections of up to 5 mm to be followed i.e., total strains of the order of 20% for a 25 mm long specimen. Length deflections over temperature ranges from -180 to 2800°C can be conducted. More generally, the range ambient to 1600°C suffices. Sample environments can be vacuum, inert gases, nitrogen, air and oxygen. Only in graphite furnaces, used for very high temperatures, can reducing gases be employed. Typical accuracies for thermal expansion coefficients are $0.01 \times 10^{-6}\text{K}^{-1}$. The resolution of dilatometric change can be improved by using temperature modulated systems.

Dilatometers using optical sensors are now available. These dilatometers use either high resolution camera images to measure the length of a sample and reference and hence sample dimensional change (see Linseis website), or they use a shadowed light method to obtain accurate absolute length measurements of a sample (see TA Instruments website). In the case of the latter system, because it uses absolute measurement, tedious calibrations are not necessary. Depending on the system, accuracies in measurements are of the order of $0.05\text{--}1\text{ }\mu\text{m}$ and samples ranging from thin films to relatively large cylinders/trapezoids, can be measured. Experiments can be carried out in a range of environments including reducing environments.

As volume, and therefore length, changes occur when ceramic powders are sintered into dense bodies, the effect of temperature on sintering behavior can be observed as can sintering rates as a function of temperature. Sintering curves and rates can then be used to improve or optimize sintering regimes in the laboratory or in Industry. In addition to CTE data, values for glass transition temperature (T_g) and glass softening temperature (T_D) can be obtained with glasses due to the marked volume expansion which occurs at T_g and the inability of a glass to withstand a very small applied force ($\sim 1\text{ N}$) necessary to maintain contact between the sample and measuring sensor. The inability to withstand this force results in flow and a rapid contraction of the glass sample length at T_D . Another use of dilatometry is the determination of temperatures at which solid state transformations occur and the strains associated with them.

Examples of Dilatometric Analyses for Ceramics and Glasses

Analysis of sintering

Fig. 10 shows dilatometric shrinkage curves (Y or $(\Delta L/L_0)$ versus T curves) associated with the sintering of nano-sized haemetite using different heating rates in a conventional dilatometer (Togashi *et al.*, 2020). It is seen that little shrinkage occurs until about 700°C . At higher temperatures, shrinkages increase until they are complete at about 1140°C . From the $Y - T$ curves, it is difficult to identify a major effect of heating rate on shrinkage. However, Togashi *et al.* (2020) also include shrinkage rate (dY/dT versus T) curves and these allow a more informed understanding which shows that the lowest heating rate gives rise to a greater shrinkage rate at a lower temperature (just below 1050°C). Using data such as this helps selection of sintering temperatures and hold times which help to minimize grain growth and develop master sintering curves as per the work of Du (2020) for example. Pillai *et al* (2004) used sintering rate curves to identify how the use of different additives could optimize the additive type (see Fig. 11). The

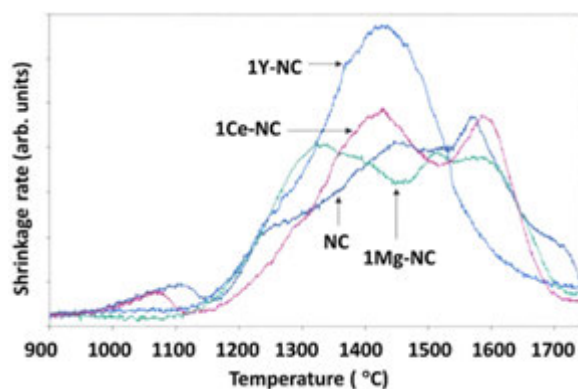


Fig. 11 Dilatometric shrinkage rate – T curves for alumina – silicon carbide nanocomposite showing the effect of different additives. Reproduced from Pillai, S.K.C., Baron, B., Pomeroy, M.J., Hampshire, S., 2004. Effect of oxide dopants on densification, microstructure and mechanical properties of alumina-silicon carbide nanocomposite ceramics prepared by pressureless sintering. *Journal of the European Ceramic Society* 24, 3317–3326.

figure shows that the best additive system to effect the densification of an alumina matrix – SiC nanoparticle nanocomposite is yttrium oxide. In addition, the sintering could be done at much lower temperatures than for the other compositions employed in the work of Pillai *et al.* (2004). A further example of the use of dilatometry to understand and optimize sintering is to use it for rate controlled sintering (RCS). Maksimov *et al.* (2018) show how pre-sintering ytterbia doped leutetia ceramics at a controlled sintering rate can limit grain growth, thus advancing transparency. Maksimov *et al.* (2018) pre-sintered samples to 97% relative density using sintering rates controlled by the dilatometer output. Following HIPping to full density, the average grain sizes of the RCS materials were much finer than those where pre-sintering had been carried out using a conventional ramp and hold sintering régime. These finer grain sizes resulted in increased optical transmittance.

Phase transformation

Tiefenbach *et al.* (2002) used dilatometry to study the effect of grain size on the tetragonal to monoclinic phase transformation which zirconia undergoes as it is heated to temperatures above 250°C. The dilatometry data these workers gathered is given in Fig. 12 and shows how the transformation temperature increases with grain size.

Barium titanate undergoes transformation from a ferroelectric perovskite phase to cubic non-polar modification at 120°C. He (2004) has shown this using dilatometry and careful experimentation showed that there was a negative CTE just above the Curie temperature as was expected. Between 0 and 50°C the observed CTE value was around $6.1 \times 10^{-6} \text{K}^{-1}$ compared to $11.3 \times 10^{-6} \text{K}^{-1}$ between 150 and 200°C. The works of Tiefenbach *et al.* (2002) and He (2004) exemplify the ability of dilatometry to identify the temperatures of phase transformations and changes in CTE values associated with them.

Measurement of coefficient of thermal expansion, glass transition temperature and dilatometric softening point of glasses

Fig. 13 shows dilatometry curves for MgO-SrO-SiO₂ glasses doped with Eu₂O₃ or Eu₂O₃-Dy₂O₃ obtained by Fernández-Rodríguez *et al.* (2021). The slopes of these curves represent the CTEs of the glasses, and these are seen to increase when the dopants are

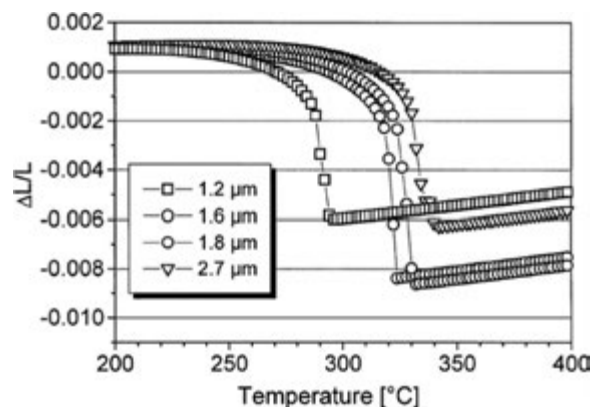


Fig. 12 Relative length change $\Delta L/L_0$ during heating of t→m transformed 9Ce-TZP. Reproduced from Tiefenbach, A., Wagner, S., Oberacker, R., Hoffmann, B., 2002. Measurement of the t→m and m→t transformations in Ce-TZP by dilatometry and impedance spectroscopy. *Journal of the European Ceramic Society* 22, 337–345.

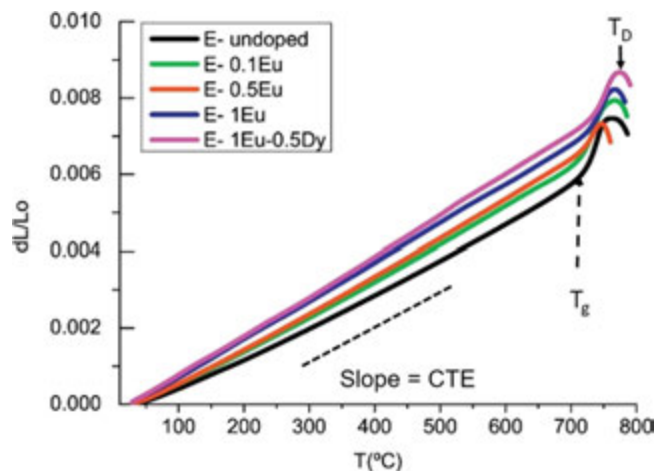


Fig. 13 Dilatometric curves for MgO-SrO-SiO₂ glasses doped with Eu₂O₃ or Eu₂O₃-Dy₂O₃, indicating data can be obtained for CTE, T_g and T_D . Reproduced from Fernández-Rodríguez, L., Levy, D., Zayat, M., *et al.*, 2021. Processing and luminescence of Eu/Dy-doped Sr₂MgSi₂O₇ glass-ceramics useful dilatometry and DTA data. *Journal of the European Ceramic Society* 41, 811–822.

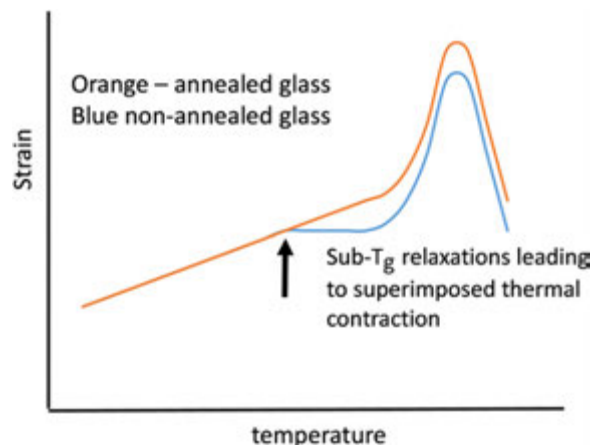


Fig. 14 Schematic dilatometry curves for annealed and non-annealed glass samples (arrow marks start of sub- T_g relaxation for the non-annealed glass sample).

added. Thus, the addition of the dopants increase the CTE, most probably due to greater levels of disruption of the glass network. CTE data has been correlated with the cation field strength of glass modifiers (Pomeroy *et al.*, 2005). When a glass is heated through its glass transition temperature, the structural units are free to move and the volume of the glass increases at a faster rate than at temperatures below the glass transition temperature. This is reflected in Fig. 13 where a relative length increase over a small temperature difference (about 20°C) is observed. The point of inflection corresponding to the glass transition temperature (T_g) is marked on Fig. 13. The glass continues to expand at this rate until the dilatometric softening temperature T_D is reached. At this point, the glass begins to flow under the small load applied by the pushrod. Using correlations given by Wiesner and Bansal (2015), it is possible to use the T_g and T_D data obtained by dilatometry to develop a viscosity temperature curve using the Vogel–Fulcher–Tammann equation (Eq. 4). These authors assign viscosity values of $10^{12.6}$ and $10^{10.3}$ Pa s to T_g and T_D respectively.

When carrying out dilatometry of glasses it is also possible to determine if the glass sample is fully annealed. Fig. 14 shows schematic dilatometry curves for two samples of a rapidly cooled glass. One sample is fully annealed whilst the other is unannealed. It is seen that there is a temperature at which the two curves separate indicated by the arrow. Above this temperature the unannealed glass undergoes little strain until a temperature close to T_g is approached. This effect is discussed for a variety of glasses by Kaur *et al.* (2018). These authors note how extended annealing increase T_g values and densities. These changes are attributed to increased cross-linking of glasses during annealing. Thus, for borate glasses, annealing increased the number of tetrahedral linkages and for lead silicate glasses, a larger proportion of Q^3 species were evident after annealing.

Sometimes, perhaps reasonably often, discrepancies arise between T_g values measured by dilatometry and those measured by DSC or DTA. These discrepancies are most likely to arise from (1) the small load applied by the dilatometer inducing a volumetric and therefore linear dimensional change at lower temperatures than might be expected from DSC or DTA, and (2) poorly annealed

glasses undergoing greater amounts of pre- T_g relaxation in dilatometer systems due to the slower heating rates used (see [Shelby, 2005](#); [Naji et al., 2013](#)).

One final comment on dilatometry is the need to investigate the modes for standard modes of dilatometer usage. Perusal of the necessary US, European and International standards is advisable when measuring CTE values.

References

- Ali, M., Wani, B.N., Bharadwaj, S.R., 2009. Phase transition in Lamoxy type compounds. *Journal of Thermal Analysis and Calorimetry* 96, 463–468.
- Arii, T., Taguchi, T., Kishi, A., Ogawa, M., Sawada, Y., 2002. Thermal decomposition of cerium (III) acetate studied with sample-controlled thermogravimetric–mass spectrometry (SCTG–MS). *Journal of the European Ceramic Society* 22, 2283–2289.
- Bansal, N.P., Doremus, R.H., 1986. *Handbook of Glass Properties*. Orlando: Academic Press.
- Bundschuh, K., Schütze, M., Müller, C., Greil, P., Heider, W., 1995. Selection of materials for use at temperatures above 1500°C in oxidizing atmospheres. *Journal of the European Ceramic Society* 8, 2389–2391.
- Dollimore, D., 2003. Thermal analysis. In: Myers, R.A. (Ed.), *Encyclopedia of Physical Science and Technology*, third ed. Netherlands: Elsevier, pp. 591–612.
- Du, J., 2020. A differentiating approach to the master sintering curve analysis. *Ceramics International* 46, 6945–6950.
- Fernandes, R.G., Reis, R.M.C.V., Tobar, R.R., Zanotto, E.D., Ferreira, E.B., 2019. Simulation and experimental study of the particle size distribution and pore effect on the crystallization of glass powders. *Acta Materialia* 175, 130–139.
- Fernández-Rodríguez, L., Levy, D., Zayat, M., et al., 2021. Processing and luminescence of Eu/Dy-doped $\text{Sr}_2\text{MgSi}_2\text{O}_7$ glass-ceramics useful dilatometry and DTA data. *Journal of the European Ceramic Society* 41, 811–822.
- He, Y., 2004. Heat capacity, thermal conductivity, and thermal expansion of barium titanate-based ceramics. *Thermochimica Acta* 419, 135–141.
- Kaur, A., Khanna, A., Kaur, A., et al., 2018. Effects of annealing on density, glass transition temperature and structure of tellurite, silicate and borate glasses. *Journal of Non-Crystalline Solids* 500, 443–452.
- Kett, V., 2019. Thermal analysis unconventional techniques. In: Worsfold, P., Poole, C., Townshend, A., Miró, M. (Eds.), *Encyclopedia of Analytical Science*, third ed. Netherlands: Elsevier, pp. 33–42.
- Law, D., Zhou, D., 2017. Solid-State characterization and techniques. In: Qiu, Y., Chen, Y., Zhang, G., Yu, L., Mantri, R.V. (Eds.), *Developing Solid Oral Dosage Forms*, third ed. Cambridge, MA: Academic Press, pp. 59–84.
- Liu, Y., Chen, Z., Li, J., et al., 2020. 3D printing of ceramic cellular structures for potential nuclear fusion application. *Additive Manufacturing* 35, 101348.
- Maksimov, R.N., Shitov, V.A., Yurovskikh, A.S., 2018. Effect of rate-controlled sintering on characteristics of hot isostatically pressed transparent Yb-doped Lu_2O_3 ceramics. *Materials Letters* 211, 208–211.
- Marotta, A., Buri, A., Branda, F., Saiello, S., 1985. Nucleation in glass-forming systems. A DTA study. *Thermochimica Acta* 85, 231–234.
- Matusita, K., Sakka, S., 1980. Kinetic study of crystallization of glass by differential thermal analysis – Criterion on application of Kissinger plot. *Journal of Non-Crystalline Solids* 38–39, 741–746.
- Matusita, K., Sakka, S., 1981. Kinetic study on non-isothermal crystallization of glass by thermal analysis. *Bulletin of the Institute for Chemical Research* 59, 159–171.
- Moynihán, C.T., Lee, S.-K., Tatsumisago, M., Minami, T., 1996. Estimation of activation energies for structural relaxation and viscous flow from DTA and DSC experiments. *Thermochimica Acta* 280–281, 153–162.
- Naji, M., Piazza, F., Guimbretière, G., et al., 2013. Heating rate effect on the activation of viscoelastic relaxation in silicate glasses. *Physics Procedia* 48, 125–131.
- Pillai, S.K.C., Baron, B., Pomeroy, M.J., Hampshire, S., 2004. Effect of oxide dopants on densification, microstructure and mechanical properties of alumina-silicon carbide nanocomposite ceramics prepared by pressureless sintering. *Journal of the European Ceramic Society* 24, 3317–3326.
- Pomeroy, M.J., Ramesh, R., 1993. Understanding the morphological development of oxidation products formed on β -sialon materials with different z-values. In: Newcomb, S.B., Bennett, M.J. (Eds.), *Microscopy of Oxidation-2*. London: Institute of Materials Publishing, pp. 566–575.
- Pomeroy, M.J., Hampshire, S., 2008. Controlled crystallisation of a Y–Si–Al–O–N glass typical of grain boundary glasses formed in silicon nitride-based ceramics. *Journal of the Ceramic Society of Japan* 116, 722–726.
- Pomeroy, M.J., Nestor, E., Ramesh, R., Hampshire, S., 2005. Properties and crystallization of rare-earth Si–Al–O–N glasses containing mixed trivalent modifiers. *Journal of the American Ceramic Society* 88, 875–881.
- Pomeroy, M.J., O'Sullivan, D., Hampshire, S., Murtagh, M.J., 2011. Degradation resistance of cordierite diesel particulate filters to diesel fuel ash deposits. *Journal of the American Ceramic Society* 95, 746–753.
- Rafferty, A., Hill, R., Wood, D., 2000. Amorphous phase separation of ionomer glasses. *Journal of Materials Science* 35, 3863–3869.
- Ramesh, R., Nestor, E., Pomeroy, M.J., Hampshire, S., 1998. Classical and differential thermal analysis studies of the glass-ceramic transformation in a YSiAlON glass. *Journal of the American Ceramic Society* 81, 1285–1297.
- Ren, X., Shang, T., Wang, W., et al., 2019. Dynamic oxidation protective behaviors and mechanisms of HfB₂-20 wt% SiC composite coating for carbon materials. *Journal of the European Ceramic Society* 39, 1955–1964.
- Rodrigues, A.M., Cassar, D.R., Fokin, V.M., Zanotto, E.D., 2018. Crystal growth and viscous flow in barium disilicate glass. *Journal of Non-Crystalline Solids* 479, 55–61.
- Rouquerol, J., 2019. Thermal analysis sample-controlled techniques. In: Worsfold, P., Townshend, A., Poole, C., Miro, M. (Eds.), *Encyclopedia of Analytical Science*, third ed. Netherlands: Elsevier, pp. 17–32.
- Schawe, J.E.K., Hess, K.-U., 2019. The kinetics of the glass transition of silicate glass measured by fast scanning calorimetry. *Thermochimica Acta* 677, 85–90.
- Schick, C., 2016. *Calorimetry*. In: Hashmi, S. (Ed.), *Elsevier Reference Collection – Materials Science and Materials Engineering*. Netherlands: Elsevier.
- Shelby, J.E., 2005. *Introduction to Glass Science and Technology*, second ed. Cambridge: Royal Society of Chemistry.
- Storti, E., Hincinschi, C., Kortus, J., Aneziris, C.G., 2019. Synthesis and characterization of calcium zirconate nanofibers produced by electrospinning. *Journal of the European Ceramic Society* 39, 5338–5344.
- Tiefenbach, A., Wagner, S., Oberacker, R., Hoffmann, B., 2002. Measurement of the $t \rightarrow m$ and $m \rightarrow t$ transformations in Ce–TZP by dilatometry and impedance spectroscopy. *Journal of the European Ceramic Society* 22, 337–345.
- Togashi, M.M., Perdomo, C.P.F., Kiminami, R.H.G.A., 2020. Densification kinetics of nano-hematite using microwave assisted dilatometry. *Ceramics International* 46, 28546–28560.
- Wiesner, V.L., Bansal, N.P., 2015. Mechanical and thermal properties of calcium–magnesium aluminosilicate (CMAS) glass. *Journal of the European Ceramic Society* 35, 2907–2914.
- Wunderlich, B., 2001. Thermal analysis. In: Buschow, K.H.J., Cahn, R.W., Flemings, M.C., et al. (Eds.), *Encyclopedia of Materials: Science and technology*, second ed. Netherlands: Elsevier, pp. 9134–9141.
- Yue, Y.Z., Christiansen, J.D., Jensen, S.L., 2002. Determination of the fictive temperature for a hyperquenched glass. *Chemical Physics Letters* 357, 20–24.
- Zheng, Q., Zhang, Y., Montazerian, M., et al., 2019. Understanding glass through differential scanning calorimetry. *Chemical Reviews* 119, 7848–7939.
- Zheng, Q., Zheng, J., Solvang, M., Yue, Y., Mauro, J.C., 2020. Determining the liquidus viscosity of glass-forming liquids through differential scanning calorimetry. *Journal of the American Ceramic Society* 103, 6070–6074.

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High-Temperature Characterization of Glasses and Melts

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Introduction

The physical properties of oxide glasses and their melts at elevated temperatures are important for understanding high-temperature phenomena in the glass-melting process. High-quality flat glass was manufactured very efficiently using the float process in a bath of molten tin, a process invented by Pilkington and Bickerstaffe in 1953 (Hynd, 1984). This process enables the production of flat glass of the highest quality at thicknesses of 2–25 mm. Fig. 1 shows a schematic illustration of the float process (Achintha, 2016). In a glass-melting furnace, molten glass is formed by melting a mixture of several types of raw materials (e.g., SiO_2 , Na_2CO_3 , CaCO_3). To produce high-quality glass, it is essential to enhance the homogeneity of the glass components and remove bubbles from the melting furnace as much as possible because the inhomogeneity of glass (components and bubbles) has a negative influence on the appearance and properties of the glass materials. To consider the process of bubble removal from molten glass, the estimated velocity v_B of the rise of a bubble is expressed using Eq. (1) (Jucha *et al.*, 1982; Cable, 1984):

$$v_B = \frac{\rho g \chi^2}{12\eta} \quad (1)$$

where ρ and η are the density and viscosity of the molten oxide, respectively, and χ is the diameter of the bubble. Viscosity and density are essential in the elimination process of bubbles. In most molten glass, complete removal of bubbles takes time because glass-forming melts are highly viscous (e.g., $10^{0.5}$ – $10^{1.5}$ Pa s) even at temperatures higher than those of their liquidus (Bansal and Doremus, 1986).

Considering the float bath used in this process to control the thickness of the flat glass in the float process, understanding and estimating how the shape of the molten glass is manifested on the molten tin bath is necessary. Fig. 2 illustrates the force balance at the interface between the molten glass and the tin melt. Assuming equilibrium conditions, the thickness of molten glass (T_e) is given by Eqs. (2) and (3) (Hynd, 1984):

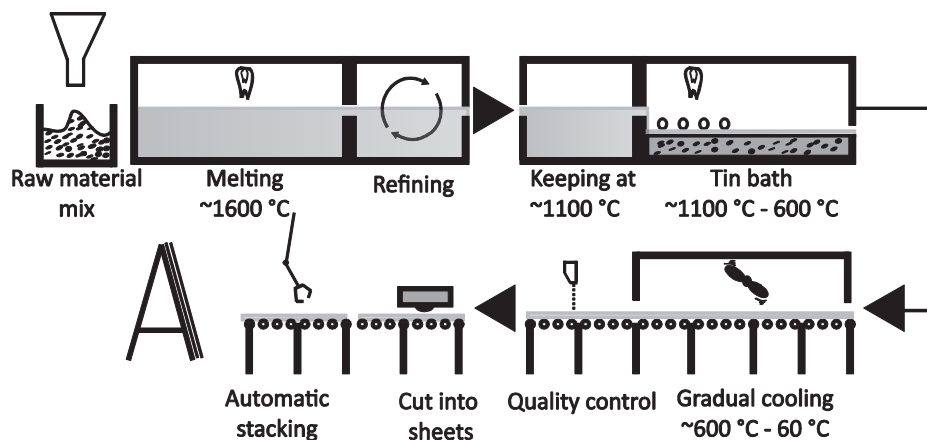


Fig. 1 Schematic of the production of float glass. Reproduced from Achintha, M., 2016. Chapter 5 – Sustainability of glass in construction. In: Khatib, J. (Ed.), Sustainability of Construction Materials, second ed. Cambridge: Woodhead Publishing, pp. 79–104.

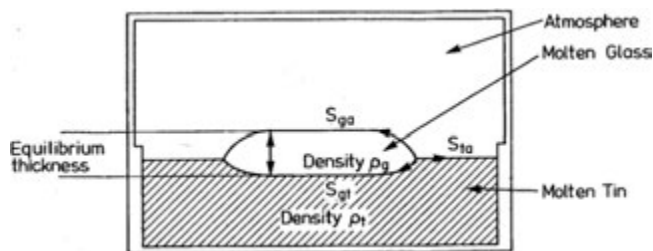


Fig. 2 Schematic of the equilibrium thickness where $S_{ga} = (\gamma_{ga})$: surface tension of molten glass (N m^{-1}), $S_{gt} = (\gamma_{gt})$: interfacial tension between molten glass and tin melt (N m^{-1}), and $S_{ta} = (\gamma_{ta})$: the surface tension of molten tin. Reproduced from Hynd, W.C., 1984. Flat glass manufacturing processes. In: Uhlmann, D.R., Kreidl, N.J. (Eds.), Glass: Science and Technology, Volume 2, Processing I. pp. 46–106.

$$T_e = \sqrt{(\gamma_{ga} + \gamma_{gt} - \gamma_{ta})/A} \quad (2)$$

$$A = g \left(\frac{\rho_g}{2} \right) \left(1 - \frac{\rho_g}{\rho_t} \right) \quad (3)$$

where γ_{ga} is the surface tension of the molten glass (N m^{-1}), γ_{gt} is the interfacial tension between the molten glass and tin melt (N m^{-1}), γ_{ta} is the surface tension of molten tin, ρ_g is the density of molten glass (kg m^{-3}), and ρ_t is the density of molten tin (kg m^{-3}). Although the float process is rarely operated in equilibrium mode, it is still important for engineers to understand the fundamentals of this phenomenon, for which the density and surface tension of molten glass are important physical properties.

Recently, vitrification has been used for the long-term storage of nuclear waste. In this process, hazardous waste is mixed with glass-forming components (e.g., borosilicate glass). The mixture is then melted in furnaces using joule heating. To control the melting process, the physical properties (e.g., viscosity, electrical conductivity, thermal conductivity) of their melts are very important. For example, the viscosity of molten glass was controlled within the range of 2–11 Pa s in a joule-heated waste melter (Bickford *et al.*, 1990). In other high-temperature industries, metallurgical processes use molten oxides as refining agents for metals, and in this process, the properties of molten oxides (i.e., slag) play important roles in improving the product quality and process efficiency (Mills *et al.*, 2014). In addition, molten oxides are found in nature as magma, and their properties are strongly related to the evolution and dynamics of the earth's surface and crust (Mysen and Richet, 2019). Techniques to measure the physical properties of oxide melts have been developed in the fields of material science, earth science, and fundamental physics over a long period of time. In this chapter, we explain the measurement techniques and the conventional procedure used to interpret the most fundamental properties, that is, viscosity, density, and surface tension, obtained at temperatures above those of their liquidus.

Viscosity

For a shear force applied to a melt, viscosity (η) is defined as a measure of the ratio of the force to the flow rate. Because the viscosity of molten oxides is highly sensitive to the melting temperature, the state of melts (i.e., characteristic temperature) is commonly characterized using the melt viscosity, for example, the glass transition temperature ($\eta \approx 10^{12}$ Pa s), softening point ($\eta \approx 10^{6.6}$ Pa s), and working point ($\eta \approx 10^3$ Pa s). These characteristic temperatures are essential knowledge when shaping and annealing glass products in glass industries. In glass-melting, η is normally controlled in the range of $10^{0.5}$ – $10^{1.5}$ Pa s (Martlew, 2005) because the viscosity directly influences several high-temperature phenomena, such as the flow behavior and reaction rate of molten oxides with refractory materials. In the present section, we particularly focus on viscosity measurement techniques at temperatures above those of their liquidus, where η is generally lower than 10^3 Pa s. The viscosity for lower temperature regions ($\eta > 10^3$ Pa s) has been discussed and summarized in books and papers (see further reading section). In addition, the conventional understanding of the characterizing procedures for viscosity data is shown.

Measurement Methods

To measure viscosity, an external force is applied to the melt. The measurements are then performed under dynamic conditions. Measurement techniques vary depending on the viscosity range, as the viscosity varies widely depending on the temperature and chemical composition. Here, we focus on the measurement technique, particularly for the lower viscosity range ($< 10^3$ Pa s) in which a conventional rotating cylinder method provides a reliable value. A sphere pulling method is also commonly used for this viscosity range (Shartsis and Spinner, 1951; Suzuki *et al.*, 2015). Recently, some container-less methods (levitation techniques) have been applied to measure the viscosity of oxide liquids. The rotating cylinder method and recent levitation techniques are explained in detail in the following sections.

Rotating cylinder method

Fig. 3 shows the principle of the rotating cylinder method. Two concentric cylinders (i.e., inner and outer cylinders) are prepared. The torque exerted on the inner cylinder is measured using a torque meter when one of the cylinders is rotated. Ideally, the viscosity should be as expressed by Eq. (4) (Mills, 1995):

$$\eta = \frac{M_t}{8\pi^2 v h} \left(\frac{1}{r_1^2} - \frac{1}{r_2^2} \right) \quad (4)$$

where M_t is the detected torque, v is the number of rotations per second, h and r_1 are the height and radius of the inner cylinder, respectively, and r_2 is the radius of the outer cylinder. Since Eq. (4) assumes infinitely long cylinders, the viscometer is commonly calibrated at room and elevated temperatures using reference materials (e.g., silicone oil). To calibrate the viscometer at elevated temperatures, some high-temperature reference materials have been produced by the National Institute of Standards and Technology (NIST), e.g., soda-lime silica (NIST standard reference material 710) and high boron glass (NIST standard reference material 717a). Similarly, the SRM2 standard-viscosity material (lithium aluminosilicate glass) has been used in the metallurgical research field (Mills, 1995). In general, the rotating cylinder method is applicable for a viscosity range of 10^{-1} – 10^8 Pa s (Martlew, 2005). However, the range strongly depends on the detection range of the torque meter as well as the dimensions of the inner and outer cylinders.

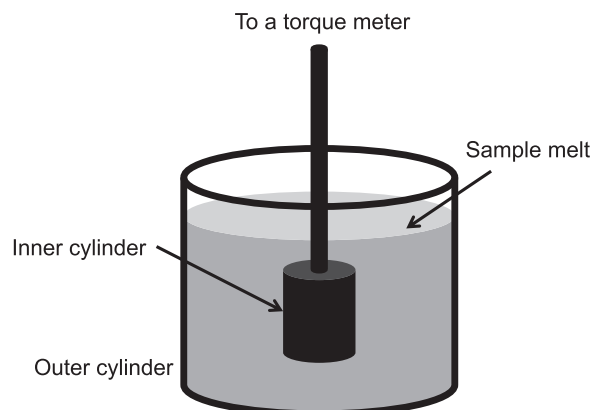


Fig. 3 Schematic of a typical setup of the inner and outer cylinders in the rotating cylinder method.

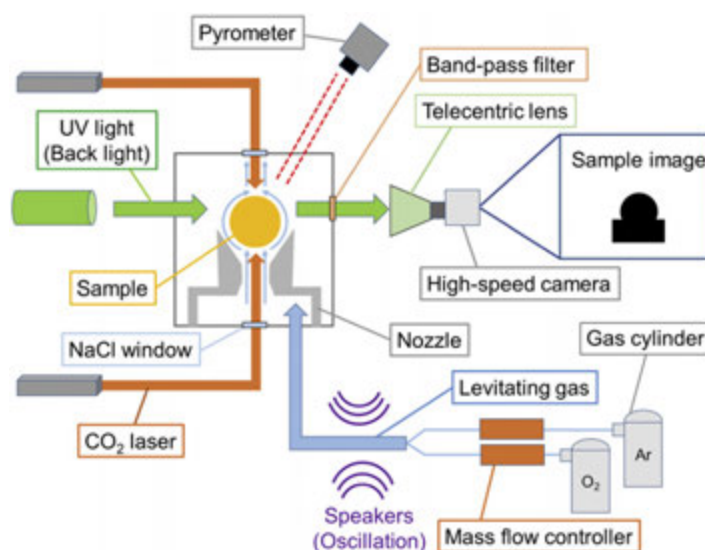


Fig. 4 Schematic of an experimental setup of viscosity measurement using aerodynamic levitation. Reproduced from Kondo, T., Muta, H., Kurosaki, K., *et al.*, 2019. Density and viscosity of liquid ZrO₂ measured by aerodynamic levitation technique. *Heliyon* 5, e20249.

Takeda *et al.* succeeded in applying this method to the lower viscosity range ($< 10^{-2}$ Pa s) by optimizing the shape of the inner and outer cylinders (Takeda *et al.*, 2020). In addition, the rotating cylinder method is advantageous for altering the shear rate in the viscosity measurement. As such, the method can be applied to both Newtonian and non-Newtonian fluids. In the field of metallurgy, the apparent viscosity during melt crystallization has been evaluated for industrial and scientific purposes (Harada *et al.*, 2018; Liu *et al.*, 2019; Saito *et al.*, 2009; Wright *et al.*, 2000). Another important aspect of performing reliable measurements is the selection of the appropriate contact material. The rotating cylinder method requires the contact materials to be sufficiently rigid to avoid deformation at elevated temperatures. Commonly, Pt–Rh alloys are used in oxidizing or intermediate conditions (e.g., Kim and Park, 2014; Saito *et al.*, 2003), and Mo, W, and graphite are used in reducing atmospheres (e.g., Chen *et al.*, 2014; Sukenaga *et al.*, 2020). Au is an appropriate contact material for TeO₂ containing system (Tokunaga *et al.*, 2010; Wilding *et al.*, 2016).

Levitation method

Although conventional container-based techniques (e.g., rotating cylinder method) are well-established and provide a reliable value of viscosity, the maximum temperature that can be examined is limited by the melting point of the contact materials. Levitation techniques are advantageous for measuring the viscosity of refractory melts at ultra-high temperatures (> 2200 K) without the need of a container that may be reactive to the sample melt. Sample levitations are commonly obtained using “aerodynamic” or “electrostatic” levitation with a CO₂ laser heating system (Langstaff *et al.*, 2013). Because viscosity is related to the damping behavior of an oscillating droplet, acoustic excitation must be applied to provide surface oscillation to the levitated melt using a frequency generator. Fig. 4 depicts the typical setup for viscosity measurement using aerodynamic levitation. The damping constant of the resonant oscillations of the droplet, Γ , is given by Eq. (5):

$$\Gamma = \frac{5}{\rho R^2} \eta, \quad (5)$$

where R is the radius of the oscillating sphere (sample melt), ρ is the density, and η is the viscosity. In practice, the sample droplet is acoustically excited. When the excitation is removed, the decay of the oscillation amplitude is obtained to determine Γ . The detailed procedure is explained in the literature (Langstaff *et al.*, 2013; Nakamura *et al.*, 2019). Levitation viscometry has been used for systems with high melting points ($> 1900\text{K}$), where the viscosities of refractory melts, such as Al_2O_3 (Langstaff *et al.*, 2013), ZrO_2 (Kondo *et al.*, 2019), $\text{CaO-Al}_2\text{O}_3$ (Nakamura *et al.*, 2019), and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ (Siafakas *et al.*, 2018a,b) have been reported. This method works well for samples with low viscosities ($< 0.1\text{ Pa s}$) and negligible sample evaporation rates.

Fig. 5 summarizes the viscosity measurement techniques with the viscosity range. By combining the levitation method with conventional container-based techniques, the applicable scope of viscosity measurement is expanding. Detailed information on other viscosity measurement techniques is presented in references (see further reading section).

Characterization Procedure of Viscosity Data

The viscosity of liquids exponentially increases with decreasing temperature. Typically, the logarithmic viscosity ($\log \eta$) is used to plot data against the reciprocal temperature. Fig. 6 depicts an example of the temperature dependence of the viscosity of a sodium silicate melt (Neuville, 2006). The liquidus temperature (T_l) and glass transition temperature (T_g) are important specific temperatures for categorizing the melt depending on their temperature range: liquid at T above their T_l , supercooled liquid ($T_g < T < T_l$), and glass ($T < T_g$). For viscosity data over a wide temperature range (i.e., from temperatures above that of the liquidus to temperatures close to the glass transition), the viscosity increases non-linearly with decreasing temperature (see Fig. 6(a)). Empirically, the Vogel–Fulcher–Tamann (VFT) equation, expressed in Eq. (6), reproduces the non-linear relationship using three fitting parameters: A_{VFT} , B_{VFT} , and C_{VFT} (Fulcher, 1925).

$$\log \eta = A_{\text{VFT}} + \frac{B_{\text{VFT}}}{T - C_{\text{VFT}}} \quad (6)$$

A_{VFT} , B_{VFT} , and C_{VFT} are the pre-exponential factor, pseudo-activation energy, and VFT-temperature, respectively (e.g., Giordano *et al.*, 2008). Although the physical interpretation of these fitting parameters (A_{VFT} , B_{VFT} , and C_{VFT}) remains to be understood, this equation is useful and commonly applied to express the temperature dependency of the viscosity over a wide temperature range. To understand the physical insight into the temperature dependence over a wide temperature range, several viscosity models have

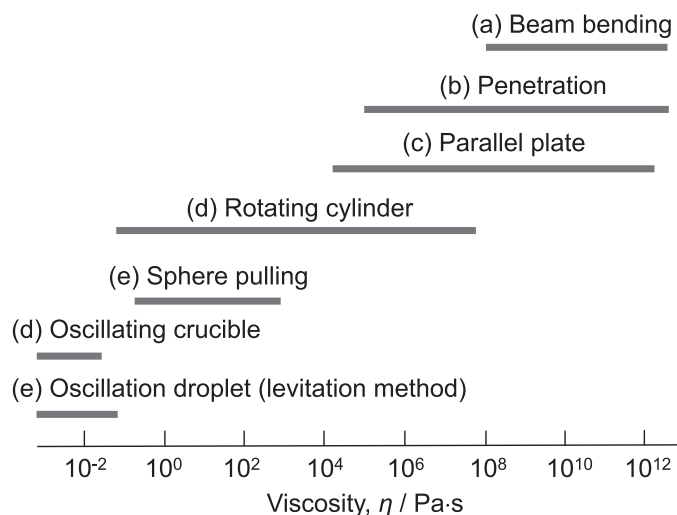


Fig. 5 Typical viscosity measurement techniques are shown with their conventional applicable viscosity range. The applicable viscosity ranges are drawn according to the corresponding reference papers: beam bending, penetration, rotating cylinder, parallel plate, sphere pulling, oscillating crucible, and oscillation droplet. Reproduced from Martlew, D., 2005. Viscosity of molten glasses. In: Pye, D., Joseph, I., Montenero, A. (Eds.), Properties of Glass-Forming Melts. Boca Raton: CRC Press. pp. 75–141. Kunugi, M., Ota, R., Yamate, T., 1996. A penetration viscometer for determining viscosity of glass. Journal of the Society of Materials Science, Japan 15, 567–571. Sakai, M., Shimizu, S., 2001. Indentation rheometry for glass-forming materials. Journal of Non-Crystalline Solids 282, 236–247. Gent, A.N., 1960. Theory of the parallel plate viscometer. British Journal of Applied Physics 11, 85–87. Neuville, D.R., Richet, P., 1991. Viscosity and mixing in molten (Ca, Mg) pyroxenes and garnets. Geochimica et Cosmochimica Acta 55, 1011–1019. Shartsis, L., Spinner, S., 1951. Viscosity and density of molten optical glasses. Journal of Research of the National Bureau of Standards 46, 177–194. Coe, I.M., Elwell, D., 1977. High-temperature oscillating crucible viscometer. Journal of Physics E: Scientific Instruments 10, 27–30. Siafakas, D., Matsushita, T., Hakamada, S., *et al.*, 2018a. Aerodynamic levitation and rotating bob methods and sources of systematic error. International Journal of Microgravity Science and applications 35 (350204), 350201–350208. Siafakas, D., Matsushita, T., Jarfors, A.E.W., Hakamada, S., Watanabe, M., 2018b. Viscosity of $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ slag with low silica – influence of $\text{CaO/Al}_2\text{O}_3$, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. ISIJ International 58, 2180–2185.

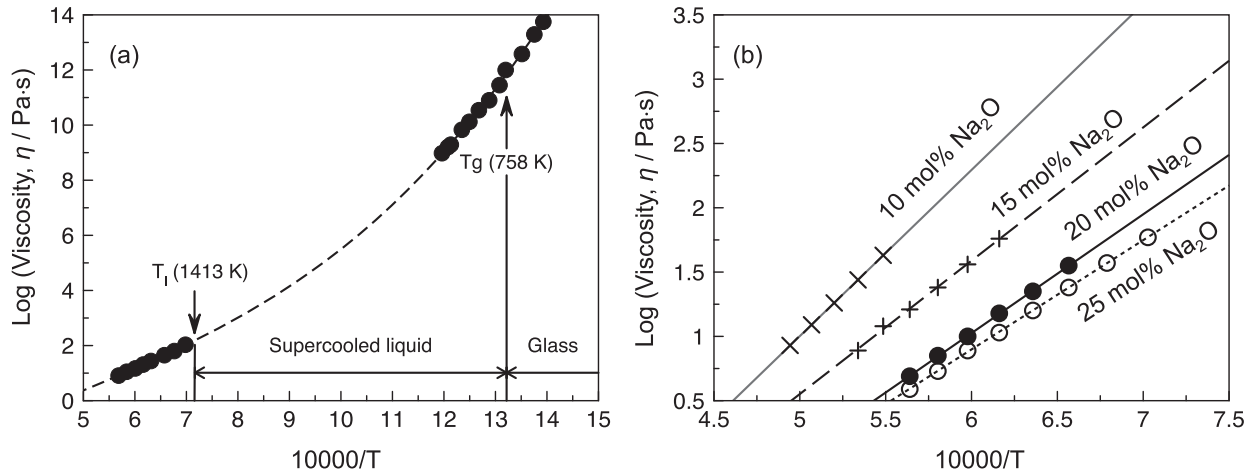


Fig. 6 (a) Viscosity of 33Na₂O-67SiO₂ (mol%) melt over a wide temperature range, as reported by (Neuville). (b) Viscosities of the Na₂O-SiO₂ binary system at temperatures above those of their liquidus. Data is obtained from Bockris *et al.* Reproduced from Neuville, D.R., 2006. Viscosity, structure and mixing in (Ca, Na) silicate melts. *Chemical Geology* 229, 28–41. Bockris, J.O.M., Mackenzie, J.D., Kitchener, J.A., 1955. Viscous flow in silica and binary liquid silicates. *Transactions of the Faraday Society* 51, 1734–1748.

been developed (Avramov and Milchev, 1988; Ikeda and Aniya, 2013; Mauro *et al.*, 2009). As a successful example, Adam and Gibbs proposed a model relating the relaxation time (i.e., viscosity) to the configurational entropy ($S_c(T)$) using Eqs. (7) and (8) (Adam and Gibbs, 1965):

$$\log_{10} \eta = A_e + \frac{B_e}{TS_c(T)} \quad (7)$$

$$S_c(T) = S_c(T_g) + \int_{T_g}^T \frac{C_p^{\text{conf}}}{T} dT \quad (8)$$

where A_e and B_e are constants for each sample composition and C_p^{conf} is the configurational heat capacity. C_p^{conf} is a measurable parameter. When C_p^{conf} is known for the target composition, the viscosity curve is fitted using three parameters: A_e , B_e , and $S_c(T_g)$. The configurational entropy of the glass, $S_c(T_g)$, is a meaningful parameter for understanding the glass structure (Neuville, 2006; Richet, 1984; Toplis *et al.*, 1997). Meanwhile, the mixing state of the chemically distinguishable units, bond distances, and bond angles are related to $S_c(T_g)$.

In the narrow temperature range at temperatures above their liquidus, $\log \eta$ linearly increases with decreasing temperature (see Fig. 6(b)). When $\log \eta$ is plotted against the reciprocal absolute temperature (T^{-1}), the slope can be related to the activation energy of viscous flow:

$$\log \eta = A_a + \frac{E_\eta}{2.303 \cdot R_g \cdot T} \quad (9)$$

where A_a is a composition-dependent constant, E_η is the activation energy of viscous flow, and R_g is the gas constant. However, the physical meaning of the activation energy is still under discussion. Toplis *et al.* (1997) analyzed the viscosity based on the Adam–Gibbs model and proposed that the viscosity in this region reflects the average bond strength of the melt. Overall, the viscosity at temperatures above their liquidus decreases through the depolymerization of silicate anions (i.e., an increase in the non-framework cations, such as alkali or alkaline-earth cations, see Fig. 6(b)). The viscosity of molten oxides has been measured for a wide range of compositions. These data are summarized in books and databases (see further reading section).

Density

In industries that commonly use high temperatures (e.g., glass making and metallurgical extractions), the melt density is an important property that is related to the phase separation process in multi-phase mixtures (liquid/liquid, liquid/solid, or liquid/gas). This value is also essential in simulating the density-driven liquid flow and thermal expansion of molten oxide in a melting furnace. In addition to its industrial importance, melt density is a good indicator of melt structure because the molar volume and atomic packing density are derived from melt density. It is well known that network forming cations (e.g., Si⁴⁺) prefer to exist as corner-sharing tetrahedra, which are commonly linked to a decrease in the atomic packing density (Kohara *et al.*, 2010; Zachariasen, 1932). Meanwhile, network modifiers (e.g., Ca²⁺, Na⁺) form the breakage region of the network structure, which normally has a higher packing density than the network structure because of the edge- or face-sharing local structure of modifier cations (Greaves, 1985; Warren, 1941). The density of oxide melts (and their glasses) is meaningful for understanding the structural roles

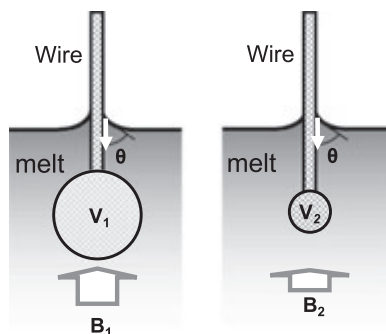


Fig. 7 Schematic of the principle of the double-bob Archimedean method, where θ represents the contact angle between the wire and the melt. The white arrows in the figure indicate the force exerted on the wire due to the surface tension of the melt.

of each oxide component in the melts as well as improving industrial processes. The density was measured using some well-established techniques that require contact materials. Recently, a container-less technique has been developed, which will expand the possibility of density measurements for more extreme conditions. In this section, the advantages and limitations of each measurement method are shown. A typical procedure for analyzing density data is also explained.

Measurement Methods

The liquid density, ρ , is simply defined as the ratio of the mass to the volume ($\rho = M/V$). Indeed, for a liquid at room temperature, it is not so difficult to measure its volume and mass. However, this is not the case for a high-temperature melt because the sample liquid needs to be melted using a furnace, where there are some limitations and difficulties in observing the volume and mass of the samples. Conventionally, the density of molten oxides has been evaluated using the Archimedean, sessile drop, or maximum bubble pressure (MBP) methods. Recently, levitation techniques (e.g., aerodynamic levitation, electrostatic levitation) have been applied to measure density. Here, the principle, characteristics, and limitations of the Archimedean, sessile drop, and levitation methods are discussed. The MBP method is used to measure the surface tension; however, the method allows us to estimate the density of the sample as a by-product. The details of the MBP method are explained in the section entitled “Surface Tension”.

Archimedean method

When an object is immersed in a liquid, the object assumes a buoyancy, which indicates the weight of the displaced liquid. This principle is known as the Archimedean method and is one of the best-established techniques to determine melt density. The concept of the Archimedean method is shown in Fig. 7.

The Archimedean method determines the melt density, ρ , by measuring the mass of a bob both in air and in the sample melt to calculate the buoyancy, B_i , whereas the volume of the bob, V_{bob} , is known. This concept is expressed by Eq. (10) (Keene and Mills, 1995):

$$\rho = \frac{B_i}{V_{\text{bob}}}, \quad (10)$$

More carefully, the surface tension of the melt is also applied to the wire that is used to suspend the bobs. To remove the effect of surface tension on the measured mass of the bob in the melts, two bobs with different sizes are used. This method is called the double-bob Archimedean method. The density of the melt is determined using Eq. (11) (Arman and Takebe, 2019; Bockris *et al.*, 1956):

$$\rho = \frac{B_1 - B_2}{V_1 - V_2}, \quad (11)$$

where B_1 and B_2 represent the buoyancies and V_1 and V_2 are the submerged volumes of the large and small bobs, respectively. The effect of thermal expansion for the bobs is given by Eq. (12):

$$V_1 - V_2 = (V_1' - V_2') \cdot (1 + 3\alpha \Delta T), \quad (12)$$

where V_1' and V_2' are the submerged volumes of the large and small bobs at room temperature and are determined using distilled water. Parameters α and ΔT are the linear expansion coefficient of the contact material and the difference between the examined temperature and room temperature, respectively. For the contact material, platinum group metals (e.g., Pt, Ir, Pt–Rh alloy) are appropriate for most molten oxides. Pt or Pt–Rh has typically been used at temperatures below 1873K. For the higher temperature range, Dingwell (1991) successfully measured the density up to 2200K using Ir contact materials. Mo and W perform better than Pt for systems containing high content of FeO (Biggar, 1970), whereas Mo, BN (or BN-lined graphite) is appropriate for oxynitride melts (Ali *et al.*, 2015; Hampshire and Pomeroy, 2008); however, these contact materials require lower oxygen partial pressures. Theoretically, this method works very well for most molten oxides. However, when the sample is very viscous (e.g., $\eta > 10$ Pa s), it is not easy to accurately measure the density without completely eliminating the convection flow in the crucible. Shartsis and Spinner (1951) evaluated the density of the melt with viscosity up to 500 Pa s using a counterbalanced sphere method, which is also based on the Archimedean principal.

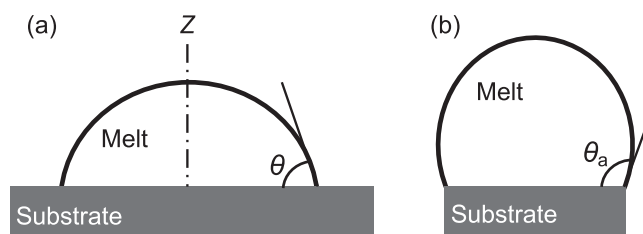


Fig. 8 Schematic of the principle of the (a) conventional and (b) constrained sessile drop methods. Parameters θ and θ_a show the equilibrated and apparent contact angles, respectively.

Sessile drop method

The sessile drop method is a standard method to determine a sample (liquid) shape on a substrate using optical observation. **Fig. 8(a)** shows a schematic illustration of the principle of the sessile drop measurement. The liquid shape is observed in the horizontal direction. Using a two-dimensional image of the liquid shape, the sample volume, V , is calculated from the rotational symmetry around the Z -axis. Therefore, for accurate measurements, the symmetry of the liquid shape should be carefully examined. Techniques for substrate rotation or observations from multiple directions have been developed for this purpose. The sessile drop method works even for more viscous melts ($\sim 10^{12}$ Pa s), as long as the liquid shape (i.e., volume) is clearly observed. However, it is necessary to find substrates that are less reactive and have poor wettability (i.e., contact angle is as high as possible) to the sample melts at elevated temperatures to improve measurement accuracy. Unfortunately, the contact angle of the molten oxide against less reactive materials (e.g., Pt, Rh, Pt–Rh, Mo, W) is not typically high enough ($< 90^\circ$) (Tashiro *et al.*, 2017; Volpe *et al.*, 1959) because the surface energies of these metals are high (> 1500 mN m $^{-1}$). The wettability of graphite (or boron nitride) by molten oxide is normally poor (contact angle $> 90^\circ$) (Eustathopoulos *et al.*, 1999); however, their reactivity to the samples should be carefully tested. Another possibility is the constrained sessile drop method (Duchesne and Hughes, 2017), which has been recently developed to increase the apparent contact angle with respect to the substrate for greater measurement accuracy (**Fig. 8(b)**); this would expand the applicability of the sessile drop method.

Levitation methods

As explained in the section on viscosity measurements, the advantages of levitation techniques are the maximum melting temperature (e.g., ~ 3500 K when using two 100 W CO $_2$ lasers (Kondo *et al.*, 2019)), avoidance of an interfacial reaction, and high degree of supercooling. Therefore, the levitation method has been especially successful for measurements in ultra-high temperature ranges (e.g., > 2200 K), where achieving accurate measurements using container-based methods is difficult owing to the challenge of finding appropriate contact materials to hold molten oxides at such high temperatures. Most molten oxides are levitated through magnetic (Kitamura *et al.*, 2000), electrostatic (Tamaru *et al.*, 2018), or aerodynamic (Nordine *et al.*, 2000; Rajavaram *et al.*, 2019) methods. To measure density by a levitation method, accurate measurement in a sample volume is essential. Electrostatic levitation has the advantage of accurate observation of the liquid shape because the sample is fully visible (Kohara *et al.*, 2014); in aerodynamic levitation, the sample is partly hidden because of a nozzle. However, in recent studies, techniques have been developed to improve the accuracy of estimating the shape of aerodynamically levitated samples (Nakamura *et al.*, 2019). More detailed information on the methodology and limitations of levitation methods are summarized in excellent review papers (e.g., Kargl *et al.*, 2015).

The measurement techniques should be appropriately selected depending on the sample properties, such as viscosity, reactivity against contact materials, and melting point. In particular, the viscosity of molten oxide changes by more than 12 orders of magnitude, depending on the temperature and composition. **Fig. 9** shows a change in the applicable techniques to determine the sample density as a function of melt viscosity. The double-bob Archimedean method enabled the reliable measurement of the liquid density for melt with relatively low viscosities (e.g., < 10 Pa s) as long as the convection flow in the crucible is sufficiently minimized. The double-bob Archimedean and MBP methods work for a similar viscosity range. For a more viscous liquid, the sessile drop method would function more optimally. Levitation methods theoretically enable the measurement of the sample density, regardless of the viscosity or melting point of the sample. However, it is necessary to carefully check the sample temperature and its homogeneity as well as the change in composition of the sample during the measurements because some of the components can easily evaporate from the melts.

Characterization Procedure for Density Data

The importance of density in industrial processes is described in the introduction. However, density is also a useful physical property for characterizing the melt structure, that is, the packing state of the melts. Since density depends on both the packing structure of the melt and the molecular weight of the components, it is converted into molar volume using Eq. (13) to characterize the melt structure.

$$V_m = \frac{\sum x_i \cdot M_i}{\rho}, \quad (13)$$

where x_i and M_i represent the molar fraction and molar weight (10^{-3} kg mol $^{-1}$), respectively, of component i . Alternatively, the

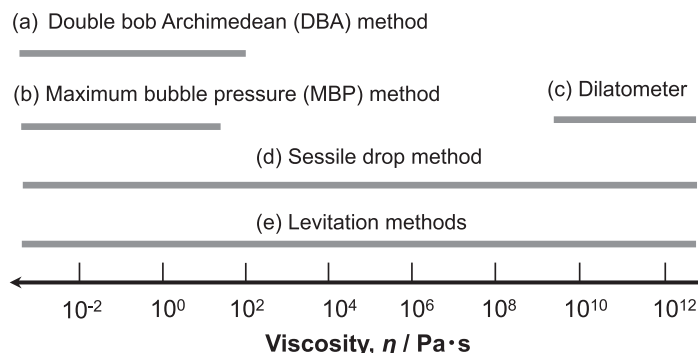


Fig. 9 Applicable viscosity ranges for melt density measurement techniques. (a), (b), and (c) were obtained from the literature. DBA: Conventional applicable range by the authors; MBP: Applicable range reported by Bradley Jr.; Dilatometer: Conventional applicable range by Mazurin. Reported by Bradley Jr, C.A., 1938. Measurement of surface tension of viscous liquids. *Journal of the American Ceramic Society* 21, 339–344. Mazurin, O.V., 2005. Density of glass melts. In: Pye, D., Joseph, I., Montenero, A. (Eds.), *Properties of glass forming melts*. Boca Raton: CRC Press, pp. 193–225.

atomic number density, n (m^{-3}), is derived from Eq. (14) using V_m :

$$n = \frac{N_A}{V_m}, \quad (14)$$

where N_A is Avogadro's number ($= 6.02 \times 10^{23}$). Theoretically, a more detailed packing structure could be described using the ionic packing fraction, V_p , which is estimated by Eq. (15):

$$V_p(\%) = \frac{\sum v_k \cdot m_k \cdot N_A}{V_m} \times 100, \quad (15)$$

where v_k and m_k are the ionic volume (m^3) and atomic fraction, respectively, of the ionic component k . To accurately estimate the V_p value, it is essential to accurately know the ionic volume, which would be obtained by X-ray or neutron scattering experiments. Recently, normalized number density has also been used to interpret the packing structure of oxide glasses and melts under high-pressure conditions (Salmon *et al.*, 2012; Wang *et al.*, 2014).

In the present section, the density of the binary alkali silicate system $\text{R}_2\text{O}-\text{SiO}_2$ ($\text{R} = \text{Li}, \text{Na}, \text{or K}$), a fundamental system used in industries that operate at high temperatures, is chosen as an example. Fig. 10(a) shows the density of binary alkali silicate systems reported by Bockris *et al.* (1956). The density decreases with the addition of all types of alkali oxides. To consider the melt structure, V_m was derived from the density data (Fig. 10(b)). V_m decreases with the addition of Li_2O , whereas V_m increases with increasing K_2O concentration. The additive effect of Na_2O on V_m is small. Similarly, n increases with increasing Li_2O concentration, indicating that Li_2O makes the structure dense (Fig. 10(c)). In the $\text{K}_2\text{O}-\text{SiO}_2$ system, the atomic distribution is sparser than that for $\text{Li}_2\text{O}-\text{SiO}_2$ or $\text{Na}_2\text{O}-\text{SiO}_2$ systems because the partial molar volume of potassium oxide ($\approx 50 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$) is larger than that of sodium oxide ($\approx 30 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$) (Yang *et al.*, 2019). V_m and n depend strongly on the size of alkali cations and open space in the network structure, while the size of the SiO_4 tetrahedron hardly changes depending on the type of alkali oxide (Saito *et al.*, 2016; Waseda and Suito, 1977). A detailed characterization of the three-dimensional structure of silicate melts is required to fully understand the change in V_m depending on the concentration and type of alkali cations. State-of-the-art approaches such as synchrotron X-ray scattering coupled with reverse Monte Carlo simulation would be helpful in revealing the packing state of the melt in detail (Kohara *et al.*, 2014).

Density measurements have been performed for many types of oxide systems, with density data available in papers, books, and databases (see further reading section).

Surface Tension

The atoms in the liquid bulk tend to satisfy their chemical interactions with their nearest neighbors, whereas surface atoms often lack neighboring atoms. The resulting unsaturated bonds at the surface lead to excess energy, which is the origin of surface tension. Because liquids tend to minimize their surface area to reduce excess energy γ , they should reflect the state of chemical bonds at the liquid surface; in other words, γ should increase with an increase in the number of unsaturated bonds. The dimension of γ is expressed by the ratio of energy to area (J m^{-2}); however, the unit (N m^{-1}) is more typically used as the dimension (because $1 \text{ J} = 1 \text{ N m}$). In industrial processes, surface tension is also an important physical property when we consider the phase-separating processes (e.g., gas/liquid, liquid/liquid, and liquid/solid) as well as the wetting and spreading behavior of molten oxides on a solid phase at elevated temperatures. Accordingly, knowing the γ of molten oxide is essential for understanding the structure of molten oxide around the surface as well as for controlling the high-temperature processes. In the present section for surface tension, the measurement techniques and interpretation of γ of molten oxides at temperatures above their liquidus are explained.

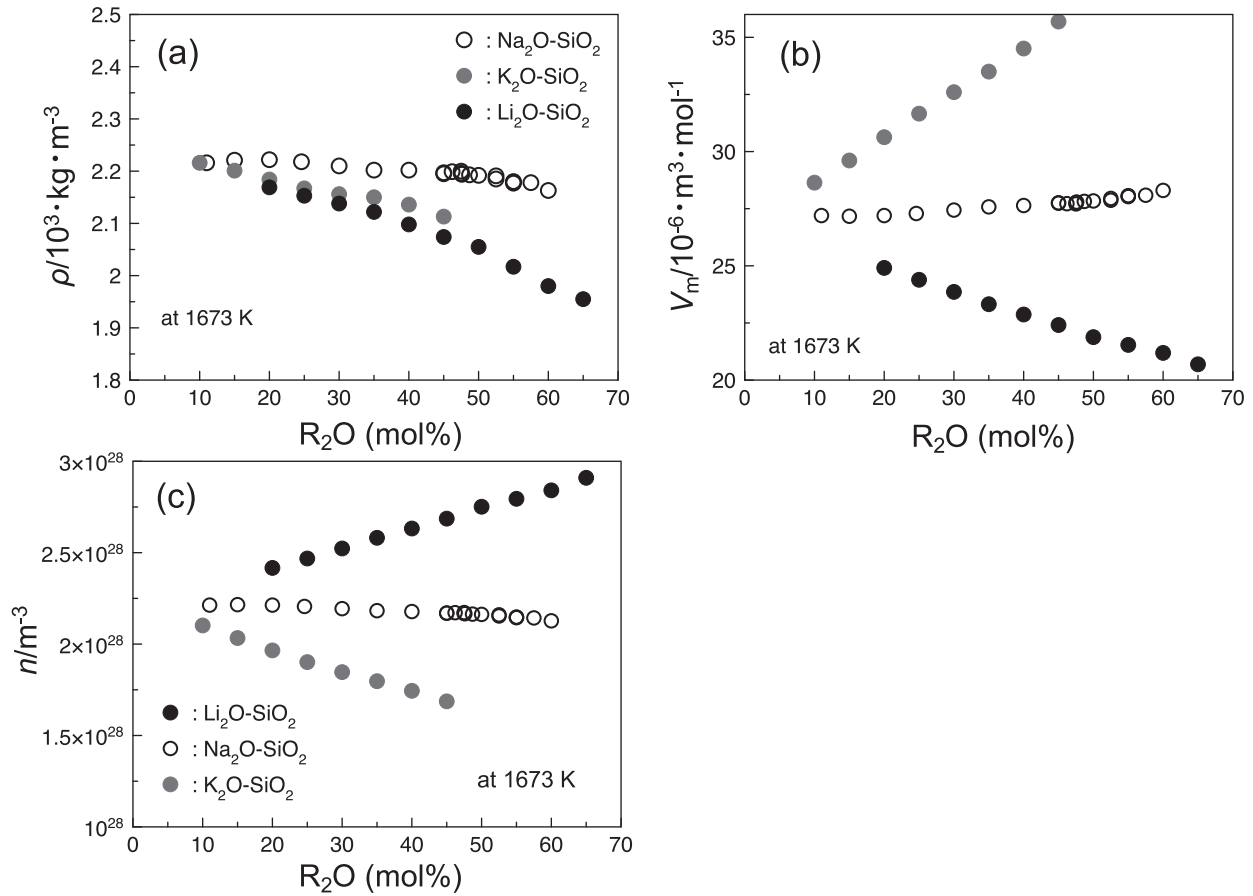


Fig. 10 Example of conversion of (a) density, ρ , data into (b) molar volume, V_m , or (c) number density, n , for binary alkali silicate melts. Original data from Bockris, J.O.M., Tomlinson, J.W., White, J.L., 1956. The structure of the liquid silicates: Partial molar volumes and expansivities. Transactions of the Faraday Society 52, 299–310.

Measurement Methods

Measurement techniques for liquid surface tension are composed of static and dynamic methods. Sessile or pendant drop methods are categorized as static methods, whereas ring methods (similar to the dipping cylinder method) or the MBP method are dynamic methods. Recently, levitation techniques have also been used to determine the surface tension. Because the ring method and MBP methods are frequently employed for molten oxides, we explain the details of these two conventional methods and recent levitation techniques for surface tension measurements.

Ring method

The ring method evaluates the surface tension, γ , by measuring the force required to detach a ring from the liquid surface. The principle of this method is similar to that of the dipping cylinder method (Babcock, 1940) and is illustrated in Fig. 11(a). The force has a maximum value ($w_{\max}$) when the contact angle θ is zero. Fig. 11(b) shows a typical example of evolution of the force value during the ring-pulling process. The γ parameter is expressed by Eq. (16) (Hwang *et al.*, 2012; Shimizu *et al.*, 2006):

$$\gamma = \frac{w_{\max} \cdot g}{4\pi R_0(1 + \alpha \Delta T)} \cdot S \quad (16)$$

where R_0 is the radius of the ring, α is the linear expansion coefficient of the ring material, ΔT is the difference between the room and examined temperature, and S is an empirical correction factor known as the Harkins and Jordan correction factor (Harkins and Jordan, 1930). S is a linear function of the ratio of the maximum force to the melt density ($w_{\max}/\rho$), which depends on the size and shape of the ring. In general, the relationship between S and $w_{\max}/\rho$ is determined using several types of reference materials (e.g., molten salts and room temperature liquids). The ρ and γ parameters of the reference materials should be known values (Hwang *et al.*, 2004). The principle of the ring method is simple and it enables us to measure γ accurately. A limitation of this method is that application to a highly viscous system (e.g., $\eta > 200$ Pa s) is difficult (Babcock, 1940). Moreover, this is also a container-based technique; thus, selecting an appropriate contact material is important for minimizing the reactivity of contact materials against a sample melt at the given temperatures.

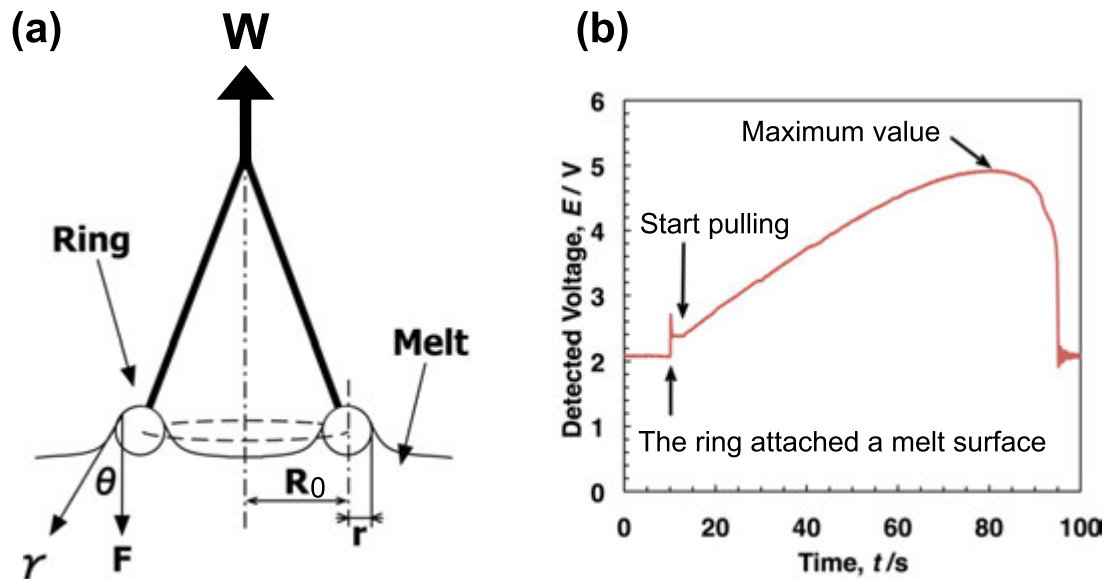


Fig. 11 (a) Schematic of the principle of the ring method. F depicts the force applied on the ring by the surface tension of the melt. (b) Evolution of detected electrical voltage by a strain gauge during the ring-pulling process where a calcium aluminosilicate melt sample was used. The detected voltage was linearly correlated with the force. (a) Redrawn from Saito, N., 2005. Fundamental Study on Liquid Phase Sintering Process of Silicon Nitride Ceramics. Doctoral dissertation. Kyushu University. (b) Redrawn from the authors' unpublished work.

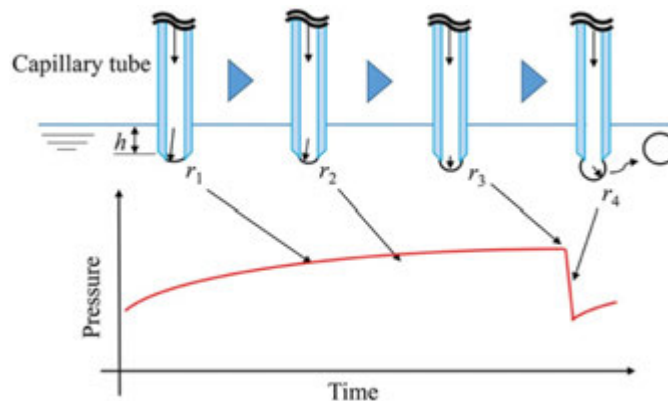


Fig. 12 Schematic for the principle of the MBP method. Figure is redrawn from Fukuta, M., Sumiyama, J., Motozawa, M., Yanagisawa, T., 2017. Surface tension measurement of oil/refrigerant mixture by maximum bubble pressure method. International Journal of Refrigeration 73, 125–133.

MBP method

Fig. 12 illustrates the principle of the MBP method. The MBP method evaluates the surface tension of the melt by monitoring the gas pressure $P_{\max}$, which is required for a bubble to break away from the tip of the capillary tube (commonly made of Pt or Ni) immersed in melts. The pressure in the capillary P is calculated by Eq. (17):

$$P = \rho gh + \frac{2\gamma}{r} \quad (17)$$

where ρ is the density of the melt, g is the gravitational acceleration, h is the immersed depth of the capillary, γ is the surface tension, and r is the radius of curvature of the bubbles. P has a maximum value, $P_{\max}$, when the bubble radius r is equal to the inner radius of the capillary (see **Fig. 12**). The detailed procedure is explained by [Takeda et al. \(2017\)](#). In addition to the ring method, the MBP method is a well-established technique for the low viscosity range ($\eta < 50$ Pa s) ([Bradley Jr., 1938](#)). For liquids with higher viscosities, static techniques (sessile drop or pendant drop method) should be used ([Ellefson and Taylor, 1938](#); [Kingery, 1959](#)). The static techniques are well summarized in textbooks (see further reading section).

Levitation technique

As explained in the “Viscosity” and “Density” sections, the levitation technique has expanded the applicable temperature range of the surface tension measurement. Rayleigh (1879) calculated the oscillation frequencies, ω_l , of a non-viscous, force-free liquid using Eq. (18) (Egry *et al.*, 2005, Langstaff *et al.*, 2013):

$$\omega_l^2 = l(l-1)(l+2) \frac{4\pi}{3} \frac{\gamma}{M} \quad (18)$$

where $l (\geq 2)$ is an integer and M is the mass of the droplet. For $l = 2$, ω_l has the lowest value, which is called the Rayleigh frequency. To measure ω_l , an acoustic oscillation generator has been typically used, as employed in the “viscosity” measurements (see Fig. 4). To measure the γ of molten oxides, several types of levitation techniques (e.g., aerodynamic levitator or electrostatic levitation techniques) have been used. In addition, γ has been reported for refractory melts (e.g., Al_2O_3 (Glorieux *et al.*, 2002)). Since Eq. (13) is only applicable for non-viscous systems, the levitation technique is difficult to apply to highly viscous melts; in addition, the applicable viscosity range of levitation techniques has not yet been reported in detail. As discussed for the viscosity and density measurement techniques, the measurement method for the melt surface tension also depends on the viscosity range of the melts. Fig. 13 illustrates the conventional applicable viscosity range of several types of measurement techniques for surface tension.

Interpretation of Melt Surface Tension

The surface tension, γ , of molten oxides depends on the structural difference between the bulk and the surface. Generally, the γ of a liquid increases as the bond strength and the number of unsaturated bonds at the liquid surface increase. Structural characterization techniques for high-temperature melts have been developed for Raman, NMR, and synchrotron X-ray spectroscopy and neutron scattering (e.g., Henderson *et al.*, 2014). However, understanding the surface structure of molten oxides remains difficult. Livey and Murray (1956) suggested that the surface of the molten oxides is mainly composed of oxygen atoms. This hypothesis has not been directly proven; however, it has been consistent with the surface tension of molten oxides. Boni and Derge (1956) related the γ of several types of molten pure oxides (i.e., single component) to the ionic potential (Z/r_i , r_i : ionic radius, Z : valence number), which is a measure of the charge density at the surface of the cations. Fig. 14 shows this relationship. Following the hypothesis of Livey and Murray, this trend should reflect the local structure of oxygen atoms around the melt surface. The surface tensions of monovalent or divalent metal oxides tend to increase with increasing ionic potential. This tendency can be explained by an increase in the bond strength between oxygen and the cation by the increasing Z/r_i when the number of unsaturated bonds is assumed to be comparable. It should also be noted that the surface tension of molten oxide for intermediate cations (e.g., Al^{3+}) is higher than that of framework cations (e.g., Si^{4+}). This phenomenon indicates that the surface oxygen atoms in an Al_2O_3 melt have a stronger tendency to lose their neighboring cations, compared with SiO_2 or B_2O_3 melts; these network liquids would satisfy the chemical bond at their melt surfaces more easily, as suggested by Kingery (1959). To understand the γ for multi-component systems (systems with more than two components), it is necessary to consider the presence of at least three types of oxygen atoms: bridging-, nonbridging-, and free-oxygen atoms. It has been reported that the γ of the four-component $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ melts increases with an increase in the number of nonbridging oxygens or the number of Al cations in the network structure (Sukenaga *et al.*, 2015). This phenomenon can be explained by the coordination structure of oxygen atoms (see Fig. 15). In the

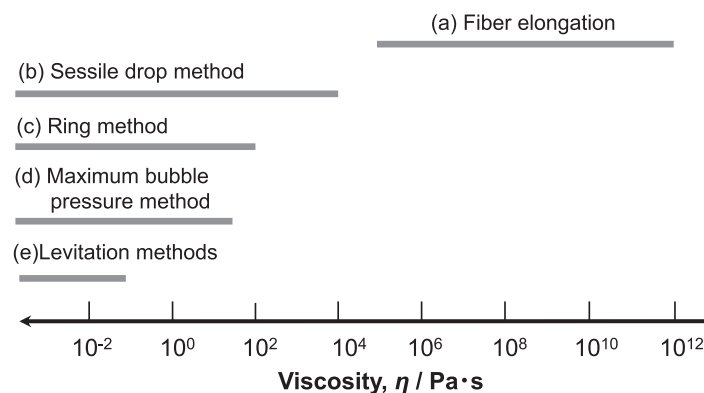


Fig. 13 Applicable viscosity ranges for surface tension measurement techniques. The typical viscosity ranges are displayed according to the following references: Fiber elongation, sessile drop conventional viscosity range, ring method, MBP, and levitation. Reproduced from Boyd, K., Ebendorff-Heidepriem, H., Monro, T.M., Munch, J., 2012. Surface tension and viscosity measurement of optical glasses using a scanning CO_2 laser. *Optical Materials Express* 2, 1101–1110. Babcock, C.L., 1940. Surface tension measurements on molten glass by a modified dipping cylinder method. *Journal of the American Ceramic Society* 23, 12–17. Bradley Jr, C.A., 1938. Measurement of surface tension of viscous liquids. *Journal of the American Ceramic Society* 21, 339–344. Siafakas, D., Matsushita, T., Hakamada, S., *et al.*, 2018a. Aerodynamic levitation and rotating bob methods and sources of systematic error. *International Journal of Microgravity Science and applications* 35 (350204), 350201–350208. Siafakas, D., Matsushita, T., Jarfors, A.E.W., Hakamada, S., Watanabe, M., 2018b. Viscosity of $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ slag with low silica – influence of $\text{CaO/Al}_2\text{O}_3$, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. *ISIJ International* 58, 2180–2185.

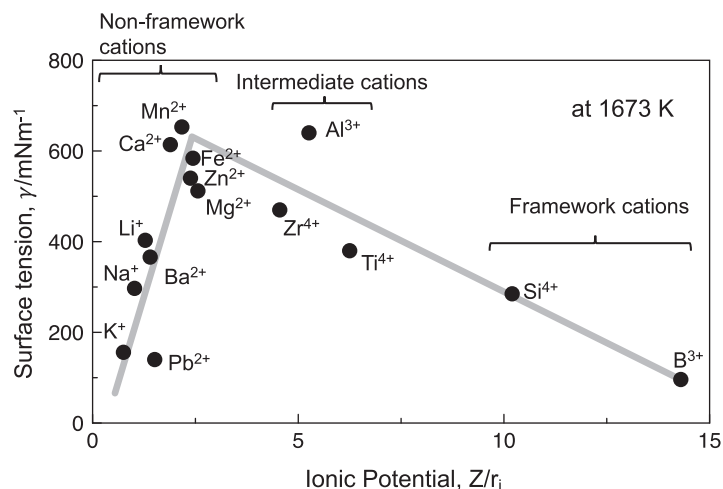


Fig. 14 Relationship between the surface tension and ionic potential of pure oxide melts at 1673K. The cationic species in the molten oxides are displayed. Figure is redrawn from Boni, R.E., Derge, G., 1956. Surface tensions of silicates. JOM 8, 53–59.

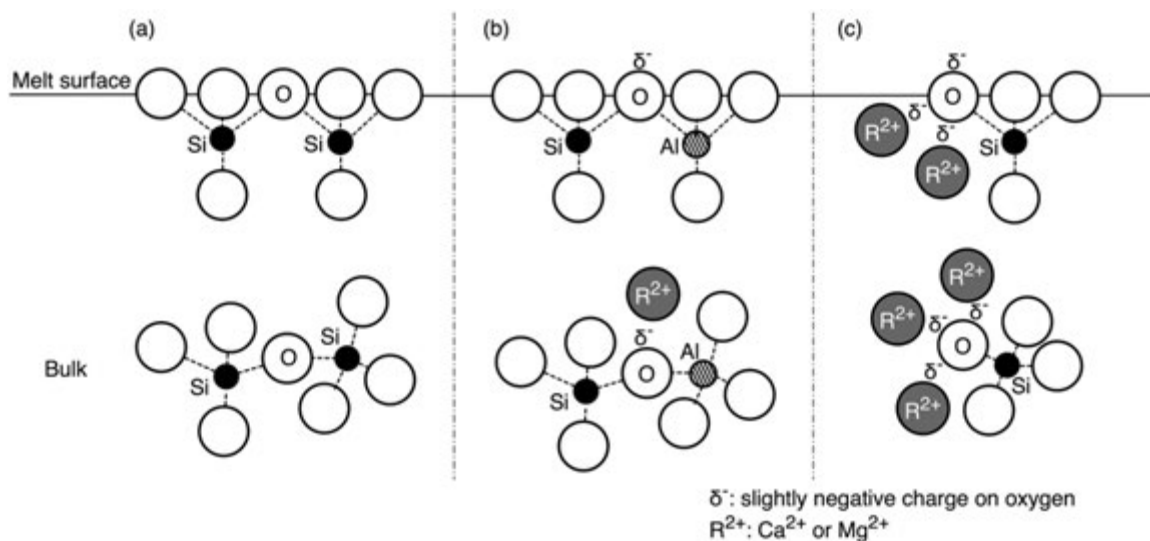


Fig. 15 Schematic illustrations of the local structure for three types of oxygen atoms in the bulk and at the melt surface. The Al coordination is assumed to be tetrahedral. The coordination numbers of (a) Si–O_{BO}–Si, (b) Si–O_{BO}–Al, and (c) Si–O_{NBO} are drawn as 2, 3 and 4, respectively. Figure is redrawn from Sukenaga, S., Higo, T., Shibata, H., Saito, N., Nakashima, K., 2015. Effect of CaO/SiO₂ ratio on surface tension of CaO–SiO₂–Al₂O₃–MgO melts. ISIJ International 55, 1299–1304.

bulk melt, a nonbridging oxygen (Si–O_{NBO}) and bridging oxygen between Si and Al atoms (Si–O_{BO}–Al) tend to have higher coordination number than that of a bridging oxygen between two Si atoms (Si–O_{BO}–Si). These oxygens with higher coordination number will have stronger tendency to lose their neighbors at the melt surface. To better understand γ for multicomponent oxide melts, characterization techniques for the surface structure should be developed in future studies.

Concluding Remarks and Further Reading

In the present chapter, we summarize the measurement techniques (including recent levitation techniques) and a typical procedure for the interpretation of three physical properties, viscosity, density, and surface tension of oxide melts, particularly at temperatures above their liquidus. Other physical properties, such as heat capacity, thermal and electrical conductivities, electrical capacitance, and diffusivity are also very important for controlling industrial processes and understanding the structure of melts at elevated temperatures. The authors believe that one of the important goals of the measurement of physical properties is to understand how each component is mixed together in the melts at elevated temperatures, because this understanding will directly

lead to an in-depth understanding of the melt structure and the establishment of a reliable estimation model for the properties. To achieve this, it is necessary to continue and expand these physical property measurements for a wide variety of compositions and temperature ranges. Recent structural analyses of molten oxides support this understanding (e.g., Alderman *et al.*, 2014; Florian *et al.*, 2018; Kanehashi and Stebbins, 2006; Maehara *et al.*, 2004). There are excellent texts and reviews that address how to measure and understand the properties of high-temperature melts. Detailed information on measurement techniques and the measured physical properties for a wide range of compositions can be found in the following references.

Measurement techniques and physical property data:

-Mills, K. C. (ed.). (1995). *Slag Atlas*. 2nd edition, Düsseldorf, Germany: Verein Deutscher Eisenhüttenleute (VDEh).

-Pye, L. D., Montenero, A. and Joseph, I. (eds.). (2005). Properties of glass-forming melts, Boca Raton: CRC press.

-Mills, K. C., Hayashi, M., Wang, L. and Watanabe, T. (2014). *The structure and properties of silicate slags*, in Seetharaman, S., McLean, A., Guthrie, R. and Seetharaman, S. (eds.) *Treatise on process metallurgy volume 1: process fundamentals*. 149–279, Oxford: Elsevier.

-Mazurin, O.V., Streltsina, M. V. and Shvaiko-Shvaikovskaya, T. P. (eds.). (1983). *Handbook of glass data, Physical Sciences data* 15, Amsterdam: Elsevier.

-Bansal, N. P. and Doremus, R. H. (eds.). (1986). *Handbook of Glass Properties*, (1986). Orlando: Academic press.

Physical meaning of the properties:

-Stebbins, J. F., McMillan, P. F. and Dingwell, D. B. (eds.). (1995). *Structure, dynamics and properties of silicate melts, Reviews in Mineralogy volume 32*, Berlin: De Gruyter.

-Mysen, B. O. and Richet, P. (eds.). (2019). *Silicate glasses and melts 2nd edition*, Amsterdam: Elsevier.

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References

- Achinta, M., 2016. Chapter 5 – Sustainability of glass in construction. In: Khatib, J. (Ed.), *Sustainability of Construction Materials*, second ed. Cambridge: Woodhead Publishing, pp. 79–104.
- Adam, G., Gibbs, J.H., 1965. On the temperature dependence of cooperative relaxation properties in glass-forming liquids. *The Journal of Chemical Physics* 43, 139–146.
- Alderman, O.L.G., Skinner, L.B., Benmore, C.J., Tamalonis, A., Weber, J.K.R., 2014. Structure of molten titanium dioxide. *Physical Review B* 90, 094204.
- Ali, S., Jonson, B., Pomeroy, M.J., Hampshire, S., 2015. Issues associated with the development of transparent oxynitride glasses. *Ceramics International* 41, 3345–3354.
- Arman, Takebe, H., 2019. Experimental study for measuring density of slag melts by an established Archimedean double-bob method. *IOP Conference Series: Materials Science and Engineering* 619.012036
- Avramov, I., Milchev, A., 1988. Effect of disorder on diffusion and viscosity in condensed systems. *Journal of Non-Crystalline Solids* 104, 253–260.
- Babcock, C.L., 1940. Surface tension measurements on molten glass by a modified dipping cylinder method. *Journal of the American Ceramic Society* 23, 12–17.
- Bansal, N.P., Doremus, R.H., 1986. Chapter 9 – Viscosity. In: Bansal, N., Doremus, R. (Eds.), *Handbook of Glass Properties*. San Diego: Academic Press, pp. 223–305.
- Bickford, D.F., Applewhite-Ramsey, A., Jantzen, C.M., Brown, K.G., 1990. Control of radioactive waste glass melter: I. Preliminary general limits at Savannah river. *Journal of the American Ceramic Society* 73, 2896–2902.
- Biggar, G.M., 1970. Molybdenum as a container for melts containing iron oxide. *Bulletin of American Ceramic Society* 49, 286–288.
- Bockris, J.O.M., Tomlinson, J.W., White, J.L., 1956. The structure of the liquid silicates: Partial molar volumes and expansivities. *Transactions of the Faraday Society* 52, 299–310.
- Boni, R.E., Derge, G., 1956. Surface tensions of silicates. *JOM* 8, 53–59.
- Bradley Jr, C.A., 1938. Measurement of surface tension of viscous liquids. *Journal of the American Ceramic Society* 21, 339–344.
- Cable, M., 1984. Principles of glass melting. In: Uhlmann, D.R., Kreidl, N.J. (Eds.), *Glass: Science and Technology*, Volume 2, Processing I., pp. 1–40.
- Chen, M., Zhang, D., Kou, M., Zhao, B., 2014. Viscosities of iron blast furnace slags. *ISIJ International* 54, 2025–2030.
- Dingwell, D.B., 1991. The density of titanium(IV) oxide liquid. *Journal of the American Ceramic Society* 74, 2718–2719.
- Duchesne, M.A., Hughes, R.W., 2017. Slag density and surface tension measurements by the constrained sessile drop method. *Fuel* 188, 173–181.
- Egry, I., Giffard, H., Schneider, S., 2005. The oscillating drop technique revisited. *Measurement Science and Technology* 16, 426–431.
- Ellefson, B.S., Taylor, N.W., 1938. Surface properties of fused salts and glasses: I. Sessile-drop method for determining surface tension and density of viscous liquids at high temperatures. *Journal of the American Ceramic Society* 21, 193–205.
- Eustathopoulos, N., Nicolas, M.G., Drevet, B., 1999. Chapter 9 – Wetting by glasses and salts. In: Eustathopoulos, N., Nicolas, G., Drevet, B. (Eds.), *Wettability at High Temperatures: Volume 3*, Pergamon Materials Series. Oxford: Pergamon, pp. 339–347.
- Florian, P., Novilov, A., Drewitt, J.W.E., *et al.*, 2018. Structure and dynamics of high-temperature strontium aluminosilicate melts. *Physical Chemistry Chemical Physics* 20, 27865–27877.
- Fukuta, M., Sumiyama, J., Motozawa, M., Yanagisawa, T., 2017. Surface tension measurement of oil/refrigerant mixture by maximum bubble pressure method. *International Journal of Refrigeration* 73, 125–133.
- Fulcher, G.S., 1925. Analysis of recent measurements of the viscosity of glasses. *Journal of the American Ceramic Society* 8, 339–355.
- Giordano, D., Russell, J.K., Dingwell, D.B., 2008. Viscosity of magmatic liquids: A model. *Earth and Planetary Science Letters* 271, 123–134.
- Glorieux, B., Millot, F., Rifflet, J.C., 2002. Surface tension of liquid alumina from contactless Techniques. *International Journal of Thermophysics* 23, 1249–1257.
- Greaves, G.N., 1985. EXAFS and the structure of glass. *Journal of Non-Crystalline Solids* 71, 203–217.
- Hampshire, S., Pomeroy, M.J., 2008. Oxynitride glasses. *International Journal of Applied Ceramic Technology* 5, 155–163.

- Harada, Y., Yamamura, H., Ueshima, Y., *et al.*, 2018. Simultaneous evaluation of viscous and crystallization behaviors of silicate melts by capacitance and viscosity measurements. *ISIJ International* 58, 1285–1292.
- Harkins, W.D., Jordan, H.F., 1930. A method for the determination of surface and interfacial tension from the maximum pull on a ring. *Journal of the American Chemical Society* 52, 1751–1772.
- Henderson, G., Neuville, D.R., Downs, R.T., 2014. Spectroscopic methods in mineralogy and materials science. In: Henderson, G., Neuville, D.R., Downs, R.T. (Eds.), *Reviews in Mineralogy & Geochemistry* 78. Washington DC: Mineralogical Society of America.
- Hwang, C., Fujino, S., Morinaga, K., 2004. Surface tension of $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ binary glass melts. *Journal of the Ceramic Society of Japan*, Supplement 112, S1200–S1205.
- Hwang, C., Ryu, B.K., Fujino, S., 2012. Surface tension of bismuth borosilicate melts. *Thermochimica Acta* 531, 70–74.
- Hynd, W.C., 1984. Flat glass manufacturing processes. In: Uhlmann, D.R., Kreidl, N.J. (Eds.), *Glass: Science and Technology*, Volume 2, Processing I., pp. 46–106.
- Ikedo, M., Aniya, M., 2013. Understanding the Vogel–Fulcher–Tammann law in terms of the bond strength–coordination number fluctuation model. *Journal of Non-Crystalline Solids* 371–372, 53–57.
- Jucha, R.B., Powers, D., McNeil, T., Subramanian, R.S., Cole, R., 1982. Bubble rise in glass melts. *Journal of the American Ceramic Society* 65, 289–292.
- Kanehashi, K., Stebbins, J.F., 2006. In situ high temperature ^{27}Al NMR study of structure and dynamics in a calcium aluminosilicate glass and melt. *Journal of Non-Crystalline Solids* 353, 4001–4010.
- Kargl, F., Yuan, C., Greaves, G.N., 2015. Aerodynamic levitation: thermophysical property measurements of liquid oxides. *International Journal of Microgravity Science and Application* 32, 320212.
- Keene, B.J., Mills, K.C., 1995. *Slag Atlas*. Germany: Verlag Stahl Eisen.
- Kim, T.S., Park, J., 2014. Structure–viscosity relationship of low-silica calcium aluminosilicate melts. *ISIJ International* 54, 2031–2038.
- Kingery, W.D., 1959. Surface tension of some liquid oxides and their temperature coefficients. *Journal of the American Ceramic Society* 42, 6–10.
- Kitamura, N., Makihara, M., Hamai, M., *et al.*, 2000. Containerless melting of glass by magnetic levitation method. *Japanese Journal of Applied Physics* 39, L324–L326.
- Kohara, S., Ohno, H., Takata, M., *et al.*, 2010. Lead silicate glasses: Binary network-former glasses with large amounts of free volume. *Physical Review B* 82.
- Kohara, S., Akola, J., Patrikeev, L., *et al.*, 2014. Atomic and electronic structures of an extremely fragile liquid. *Nature Communications* 5, 5892.
- Kondo, T., Muta, H., Kurosaki, K., *et al.*, 2019. Density and viscosity of liquid ZrO_2 measured by aerodynamic levitation technique. *Heliyon* 5, e02049.
- Langstaff, D., Gunn, M., Greaves, G.N., Marsing, A., Kargl, F., 2013. Aerodynamic levitator furnace for measuring thermophysical properties of refractory liquids. *Review of Scientific Instruments* 84, 124901.
- Liu, Z., Dekkers, R., Blanpain, B., Guo, M., 2019. Experimental study on the viscosity of stainless steelmaking slags. *ISIJ International* 59, 404–411.
- Livey, D.T., Murray, P., 1956. Surface energies of solid oxides and carbides. *Journal of the American Ceramic Society* 39, 363–372.
- Maehara, T., Yano, T., Shibata, S., Yamane, M., 2004. Structure and phase transformation of alkali silicate melts analyzed by Raman Spectroscopy. *Philosophical Magazine* 84, 3085–3099.
- Martlew, D., 2005. Viscosity of molten glasses. In: Pye, D., Joseph, I., Montenero, A. (Eds.), *Properties of Glass-Forming Melts*. Boca Raton: CRC Press, pp. 75–141.
- Mauro, J.C., Yue, Y., Ellison, A.J., Gupta, P.K., Allan, D.C., 2009. Viscosity of glass-forming liquids. *Proceedings of the National Academy of Sciences of the United States of America* 106, 19780.
- Mills, K.C., 1995. Viscosities of molten slags. In: Mills, K.C. (Ed.), *Slag Atlas*, second ed. Düsseldorf, Germany: Verein Deutscher Eisenhüttenleute (VDEh), pp. 349–401.
- Mills, K.C., Hayashi, M., Wang, L., Watanabe, T., 2014. Chapter 2.2 – The structure and properties of silicate slags. In: Seetharaman, S. (Ed.), *Treatise on Process Metallurgy*. Boston: Elsevier, pp. 149–286.
- Mysen, B., Richet, P., 2019. Chapter 1 – The discovery of silicate melts: an applied and geological perspective. In: Mysen, B., Richet, P. (Eds.), *Silicate Glasses and Melts*, second ed. Amsterdam: Elsevier, pp. 1–38.
- Nakamura, A., Hakamada, S., Mizuno, A., Watanabe, M., 2019. Density measurement of molten oxides of $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ system by aerodynamic levitated technique. *International Journal of Microgravity Science and Application* 34, 340404.
- Neuville, D.R., 2006. Viscosity, structure and mixing in (Ca, Na) silicate melts. *Chemical Geology* 229, 28–41.
- Nordine, P.C., Weber, J.K.R., Abadie, J.G., 2000. Properties of high-temperature melts using levitation. *Pure and Applied Chemistry* 72, 2127.
- Rajavaram, R., Kim, H., Park, J., *et al.*, 2019. Bridging between the physical properties: structure and density of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ melts at $\text{CaO/SiO}_2 = 1.3$ and different mole% of Al_2O_3 . *Ceramics International* 45, 19409–19414.
- Rayleigh, L., 1879. VI. On the capillary phenomena of jets. *Proceedings of the Royal Society of London* 29, 71–97.
- Richet, P., 1984. Viscosity and configurational entropy of silicate melts. *Geochimica et Cosmochimica Acta* 48, 471–483.
- Saito, N., Yoshimura, S., Haruki, S., *et al.*, 2009. Viscosity evaluation of $\text{CaO-SiO}_2\text{-R}_2\text{O}$ ($\text{R} = \text{Li, Na and K}$) based multi-phase fluxes. *Tetsu-to-Hagané* 95, 282–288.
- Saito, N., Hori, N., Nakashima, K., Mori, K., 2003. Viscosity of blast furnace type slags. *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science* 34, 509–516.
- Saito, Y., Yonemura, T., Masuno, A., *et al.*, 2016. Structural change of Na_2O -doped SiO_2 glasses by melting. *Journal of the Ceramic Society of Japan* 124, 717–720.
- Salmon, P.S., Drewitt, J.W.E., Whittaker, D.A.J., *et al.*, 2012. Density-driven structural transformations in network forming glasses: A high-pressure neutron diffraction study of GeO_2 glass up to 17.5 GPa. *Journal of Physics: Condensed Matter* 24, 415102.
- Shartsis, L., Spinner, S., 1951. Viscosity and density of molten optical glasses. *Journal of Research of the National Bureau of Standards* 46, 177–194.
- Shimizu, F., Tokunaga, F., Saito, N., Nakashima, N., 2006. Viscosity and surface tension of $\text{RE}_2\text{O}_3\text{-MgO-SiO}_2$ ($\text{RE} = \text{Y, Gd, Nd and La}$) melts. *ISIJ International* 46, 388–393.
- Siafakas, D., Matsushita, T., Hakamada, S., *et al.*, 2018a. Aerodynamic levitation and rotating bob methods and sources of systematic error. *International Journal of Microgravity Science and Applications* 35 (350204), 350201–350208.
- Siafakas, D., Matsushita, T., Jarfors, A.E.W., Hakamada, S., Watanabe, M., 2018b. Viscosity of $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ slag with low silica – influence of $\text{CaO/Al}_2\text{O}_3$, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. *ISIJ International* 58, 2180–2185.
- Sukenaga, S., Higo, T., Shibata, H., Saito, N., Nakashima, K., 2015. Effect of CaO/SiO_2 ratio on surface tension of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ melts. *ISIJ International* 55, 1299–1304.
- Sukenaga, S., Ogawa, M., Yanaba, Y., Ando, M., Shibata, H., 2020. Viscosity of Na-Si-O-N-F melts: Mixing effect of oxygen, nitrogen, and fluorine. *ISIJ International* 60 (12), 2794–2806.
- Suzuki, M., Hiramae, D., Tanaka, T., 2015. Development of viscometer based on single sphere pulling method for application to high temperature melts. *ISIJ International* 55, 1573–1580.
- Takeda, O., Yamada, M., Kawasaki, M., *et al.*, 2020. Development of wide-range viscometer and the viscosity measurement for $\text{SiO}_2\text{-Na}_2\text{O-NaF}$ System. *ISIJ International* 60, 590–596.
- Takeda, O., Iwamoto, H., Sakashita, R., Iseki, C., Zhu, H., 2017. Development of maximum bubble pressure method for surface tension measurement of high viscosity molten silicate. *International Journal of Thermophysics* 38, 109.
- Tamaru, H., Koyama, C., Saruwatari, H., *et al.*, 2018. Status of the electrostatic levitation furnace (ELF) in the ISS-KIBO. *Microgravity Science and Technology* 30, 643–651.
- Tashiro, M., Sukenaga, S., Shibata, H., 2017. Control of crystallization behaviour of supercooled liquid composed of lithium disilicate on platinum substrate. *Scientific Reports* 7, 6078.
- Tokunaga, H., Haruki, S., Sukenaga, S., Saito, N., Nakashima, K., 2010. Viscosity and refractive index of $\text{M}_2\text{O-TeO}_2$ ($\text{M} = \text{Li, Na and K}$) melts. *Journal of the Japan Institute of Metals and Materials* 74, 331–336.

- Toplis, M.J., Dingwell, D.B., Hess, K.-U., Lenci, T., 1997. Viscosity, fragility, and configurational entropy of melts along the join $\text{SiO}_2\text{-NaAlSiO}_4$. *American Mineralogist* 82, 979–990.
- Volpe, M.L., Fulrath, R.M., Pask, J.A., 1959. Fundamentals of glass-to-metal bonding: IV, Wettability of gold and platinum by molten sodium disilicate. *Journal of the American Ceramic Society* 42, 102–106.
- Wang, Y., Sakamaki, T., Skinner, L.B., *et al.*, 2014. Atomistic insight into viscosity and density of silicate melts under pressure. *Nature Communications* 5, 3241.
- Warren, B.E., 1941. Summary of work on atomic arrangement in glass. *Journal of the American Ceramic Society* 24, 256–261.
- Waseda, Y., Suito, H., 1977. The structure of molten alkali metal silicates. *Transactions of the Iron and Steel Institute of Japan* 17, 82–91.
- Wilding, M.C., Delaizir, G., Benmore, C.J., *et al.*, 2016. Structural studies of $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-TeO}_2$ glasses. *Journal of Non-Crystalline Solids* 451, 68–76.
- Wright, S., Zhang, L., Sun, S., Jahanshahi, S., 2000. Viscosity of a $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ melt containing spinel particles at 1646 K. *Metallurgical and Materials Transactions B* 31, 97–104.
- Yang, Y., Tokunaga, H., Ono, M., Hayashi, K., Mauro, J.C., 2019. Understanding the molar volume of alkali-alkaline earth-silicate glasses via Voronoi polyhedra analysis. *Scripta Materialia* 166, 1–5.
- Zachariasen, W.H., 1932. The atomic arrangement in glass. *Journal of the American Chemical Society* 54, 3841–3851.

Overview: Mechanical and Physical Properties and Property Testing of Ceramics and Glasses

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The properties of ceramic materials and glasses depend mainly on the types of atoms that compose them, their structural organization and the types of bonds between these atoms. Chemical bonds in ceramic and glassy materials are ionic and/or covalent. Such bonds are much stronger than metallic bonds, which explain, in general, why ceramics have particular properties. A key point is that metals are ductile and ceramics are brittle. This does not mean that the ceramic cannot withstand any stress, it means that on a given stress (critical stress), the failure is in general “catastrophic” (that is to say at the speed of sound). However, on the one hand this critical stress can be enormous and on the other hand there are many ways to improve the behavior of ceramic parts placed under aggressive loads.

Ceramics and glasses are used for numerous applications due to their wide range of special properties. In this section devoted to “Mechanical and Physical Properties and Property Testing of Ceramics and Glasses”, the following points will be described and discussed: elasticity, hardness, wear behavior (part A); flexural strength, toughness, crack growth, toughening, microstructure influence (part B); thermal behavior, creep, dislocations, corrosion (part C).

Part A: this sub-section comprises 3 chapters.

The first is devoted to the elastic or inelastic behavior of ceramics; the second describes in detail the hardness and the many methods commonly used to measure this quantity, finally the third chapter is devoted to the tribological behavior and to the wear resistance of ceramic-carbon composites.

Part B: In a first approach, it can be considered that ceramics and glasses follow the concept of linear mechanic of rupture. That means that the rupture of a ceramic or a glass will occur from an pre-existing defect located somewhere in the body or at its surface (it is called the critical defect). Under the effect of a stress concentrated around this defect, the defect size will increase at a given speed, as a function of the magnitude of the stress and of the environment. The two first chapters of this subsection deal with measurement, on the one hand of elastic modulus and tensile, flexural, compressive strength, on the other hand of fracture toughness. Then, one chapter concerns the increase of growth resistance as the crack extends (called R-curve behavior) and two chapters deal with the various aspects of the phenomenon of subcritical growth (basic relations, measurement and modeling). The three last chapters are devoted to examples as the transformation toughening with zirconia, as the mixed mode fracture or as the microstructural aspects on crack propagation.

Part C: historically, the first applications of technical ceramics were as refractory materials; this is why this subsection takes into account this important aspect (6 chapters). The three first chapters concerns thermal shock. After a general overview of thermal properties, thermal shock behavior is first discussed on the fundamental point of view introducing the thermal shock parameters; then through examining the thermal fatigue and the effect of the microstructure. Creep is also defined and presented both for oxide and for some non oxide ceramics (2 chapters). Then one chapter is devoted to movement of dislocations; finally, this section ends by 2 chapters concerning corrosion and degradation of ceramics and glasses, these last mostly in aqueous environment.

Elastic and Inelastic Behavior of Ceramics

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Introduction

Ceramics are generally considered as refractory materials resisting plastic deformation even at high temperature. In ceramics, we find elastic moduli, which are much higher than in metals. Moreover, ceramics and oxides generally own a low density. Therefore, the ratio between the modulus and the density, which is often searched for mechanical and structural applications, is generally very high. Some mechanical properties are summarized in [Table 1](#).

At room temperature, technical ceramics are generally brittle. As shown in [Table 1](#), their toughness hardly passes 5 MPa·m. In this case, zirconia owns a particular interest since the addition of yttria produces toughening levels unattained by other ceramics ([Marshall et al., 1983](#)).

However, limited plasticity appears in most ceramics at a temperature that can be defined as a brittle-to-ductile transition temperature. High temperature plastic deformation of fine-grained ceramics, such as Al_2O_3 , ZrO_2 , or Si_3N_4 , has been usually interpreted as due to grain boundary (GB) sliding ([Wakai et al. 1986](#); [Carry and Mocellin, 1987](#); [Duclos et al., 1989](#); [Boutz et al., 1994](#)).

In many cases, GB sliding is lubricated by an amorphous inter-granular phase, which results from the presence of sintering aids, and undergoes a glass transition at high temperature ([Rouxel and Wakai, 1993](#)). Extensive GB sliding without cavitation needs accommodation processes such as volume diffusion (Nabarro-Herring creep ([Herring, 1950](#))) or GB diffusion (Coble creep ([Coble, 1963](#))). Theoretical models have been developed to predict the values of parameters entering the standard equation for the creep rate

$$\dot{\epsilon}(\sigma, T) \approx \left(\frac{\sigma}{G}\right)^\eta \cdot \left(\frac{b}{d}\right)^p \cdot D_0 \cdot e^{-\frac{H}{RT}} \quad (1)$$

where G is the sliding modulus, b the Burgers vector, D_0 limit diffusion coefficient, σ the applied stress, n the stress exponent, d the mean grain size, p the grain size exponent, H the activation enthalpy and R gas constant.

Anelastic deformation i.e., reversible non-linear deformation precedes plastic deformation and consequently it may be the first manifestation of the brittle-to-ductile transition in ceramics. Mechanical spectroscopy ([Schaller et al., 2001](#)), is based on anelasticity ([Nowick and Berry, 1972](#)); it consists in measuring the internal friction i.e., the damping capacity or mechanical loss of materials. It is very sensitive to all microstructure changes, and it is well suited for studying a brittle-to-ductile transition, in which energy dissipation is involved. For instance in zirconia, GB sliding gives rise to a mechanical loss peak, which evolves in an exponential background at higher temperature ([Lakki et al., 1993](#)). The higher the amount of inter-granular glassy phase, the higher is the level of the exponential background and consequently the creep rate.

Anelasticity and Mechanical Spectroscopy

Anelasticity ([Nowick and Berry, 1972](#)) appears in the following simple experiment ([Fig. 1\(a\)](#)). A stress σ , of low amplitude, is applied abruptly to a specimen at time, $t = 0$, and held constant while the strain, ϵ , is recorded as a function of time.

It can be observed ([Fig. 1\(a\)](#)) that the instantaneous elastic strain, $\epsilon_e = J_u \sigma$, where J_u is the unrelaxed compliance, and the anelastic strain ϵ_a , increases with time from zero to an equilibrium value. When equilibrium is reached, $\epsilon = \epsilon_e + \epsilon_a^\infty = J_r \sigma$ where J_r is the relaxed compliance. This evolution from one equilibrium state to a new one, under an applied stress, is called anelastic relaxation, and may be defined by two parameters, the relaxation time τ and the relaxation strength Δ :

$$\Delta = \frac{\epsilon_a^\infty}{\epsilon_e} = \frac{J_r - J_u}{J_u} \quad (2)$$

If, the stress is removed after a certain delay, one can observe the instantaneous recovery of the elastic strain and, within the relaxation time τ , the recovery of the anelastic strain. In such an experiment, the strain is completely recoverable.

Table 1 Mechanical properties of some technical ceramics

	Young's Modulus [GPa]	Poisson's ratio	Density [Kg/dm ³]	Toughness [MPa·√m]
Al_2O_3	270–390	0.22–0.27	3.5–3.9	2.7–4.8
ZrO_2 (3%Y)	200–250	0.30–0.32	5.9–6.1	6.0–8.0
Si_3N_4	290–320	0.26–0.28	3.1–3.4	4.0–6.7
SiC	400–460	0.16–0.18	3.1–3.2	3.0–5.6

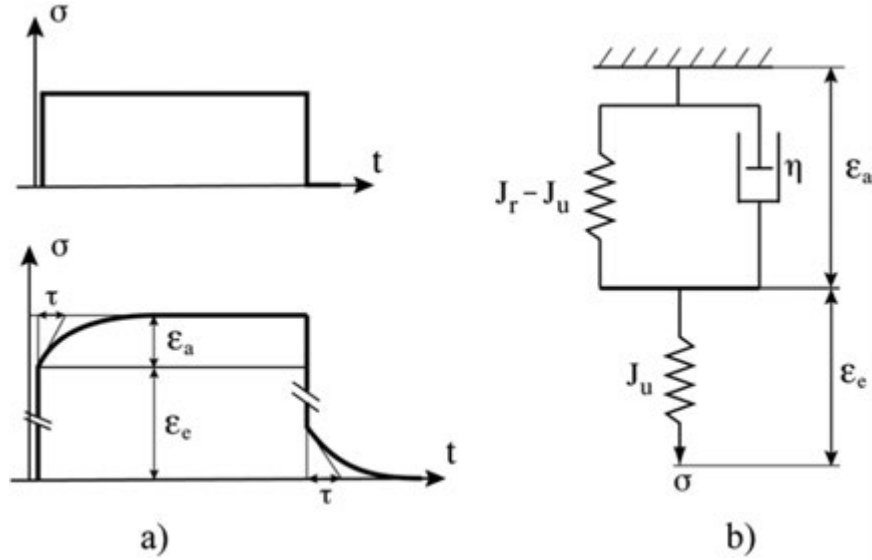


Fig. 1 (a) Elastic ϵ_e and anelastic ϵ_a strain of a solid submitted to stress σ . (b) Rheological model corresponding to the anelastic behavior of Fig. 1a.

From a microscopic point-of-view, anelastic strain can be interpreted as being due to the movements of structural defects (elastic dipoles, dislocations, interfaces, grain boundaries) from one equilibrium position defined at $\sigma = 0$ to another one defined at σ_0 . The relaxation strength, Δ , is then proportional to the concentration of defects, which are relaxing; the relaxation time τ accounting for their mobility.

From a rheological point-of-view, the solid can be represented by the model shown in Fig. 1(b). The spring " $J_r - J_u$ " in parallel with the dashpot of viscosity η is essential to the recoverable nature of the anelastic strain. If this spring does not operate, the anelastic strain does not reach an equilibrium value and then it is no longer completely recoverable: creep occurs.

The anelastic behavior in Fig. 1 is representative of the standard anelastic solid, the equation of which is:

$$\epsilon + \tau \cdot \dot{\epsilon} = J_r \cdot \sigma + \tau \cdot J_u \cdot \dot{\sigma} \quad (3)$$

Measurements performed as described in Fig. 1 are very delicate, and in practice, it is more convenient to use dynamic methods for measuring the relaxation parameters. If an alternated stress, of circular frequency ω , $\sigma = \sigma_0 \exp(i\omega t)$ is applied to the system, the linearity of the stress-strain relationships insures that strain ϵ is periodic with the same frequency: $\epsilon = \epsilon_0 \exp[i(\omega t - \phi)]$, where ϕ is the phase lag of strain behind stress (due to anelasticity). Introducing these expressions of σ and ϵ in Eq. (3) leads to the following relationship:

$$\epsilon = \left[\left(J_u + \frac{J_r - J_u}{1 + \omega^2 \tau^2} \right) - i \cdot \left(\frac{(J_r - J_u) \cdot \omega \tau}{1 + \omega^2 \tau^2} \right) \right] \cdot \sigma = [J_1(\omega) - iJ_2(\omega)] \cdot \sigma = J^*(\omega) \cdot \sigma \quad (4)$$

where J_1 and J_2 are, respectively, the real and the imaginary part of the complex compliance J^* .

In metals and ceramics $J_r - J_u \ll J_u$, and the mechanical loss angle ϕ is given by:

$$\tan \phi = \frac{J_2}{J_1} = \Delta \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (5)$$

and the variation of the dynamical compliance $\frac{\Delta J}{J}$ due to anelasticity by:

$$\frac{\delta J}{J} = \frac{J_1(\omega) - J_u}{J_u} = \Delta \frac{1}{1 + \omega^2 \tau^2} \quad (6)$$

Mechanical loss, $\tan \phi$, presents a maximum as a function of $\omega \tau$, centered at $\omega \tau = 1$. This maximum or peak gives us the relaxation strength, Δ , (height of the peak) and the relaxation time, τ , (position of the peak on the $\omega \tau$ axis). If several relaxation mechanisms are activated, the material exhibits a mechanical loss spectrum composed of damping peaks, which give information about the microstructure dynamics. Since, most of the relaxation mechanisms are thermally activated,

$$\tau = \tau_0 \cdot \exp(H/kT) \quad (7)$$

H being the activation enthalpy and τ_0 the limit relaxation time.

As a consequence, $\tan \phi$ can be also measured as a function of temperature holding ω constant and the curve $\tan(\phi) = \tan(\phi(T))$ is the mechanical loss spectrum described as a function of temperature. A maximum (peak) in the mechanical loss may appear at the frequency ω_p and temperature T_p under the condition that:

$$\omega_p \tau = \omega_p \tau_0 \cdot \exp\left(\frac{H}{kT_p}\right) = 1 \quad (8)$$

The activation enthalpy can be obtained by drawing an Arrhenius plot, in which $\ln \omega$ is reported as a function of the inverse of temperature (T_P^{-1}):

$$\ln \omega_p = -\ln \tau_0 - \frac{H}{k} \cdot \frac{1}{T_P} \quad (9)$$

The internal friction IF is defined as:

$$IF = \frac{1}{2\pi} \cdot \frac{W_{diss}}{W_{el}} \quad (10)$$

where W_{diss} is the energy dissipated in a volume unit during one cycle of vibration and W_{el} is the maximum stored elastic energy per unit volume.

$$W_{diss} = \oint \sigma \cdot d\varepsilon = \pi \cdot \sigma_0 \cdot \varepsilon_0 \cdot \sin \phi = \pi \cdot J_2 \sigma_0^2 \quad (11)$$

$$W_{el} = \int_0^{\sigma_0} \sigma \cdot d\varepsilon = \frac{1}{2} J_1 \sigma_0^2 \quad (12)$$

It follows immediately that:

$$IF = \tan \phi \quad (13)$$

Mechanical Spectrometer: Torsion Pendulum

For low frequency and particularly for high temperature the most commonly used apparatus for mechanical spectroscopy is the inverted torsion pendulum (Fig. 2, and (Gadaud *et al.*, 1990)). The sample, a wire or a plate (1), is placed in the center of a regulated furnace (2). The torsion excitation stress is applied to the pendulum axis by means of Helmholtz coils (3) acting on a permanent magnet fixed on the upper part of rod. Strain is measured by the deflection by a mirror of a laser beam (4) reflected onto a linear photo-detector (5). The whole apparatus is maintained under secondary vacuum (10^{-3} Pa) by a diffusion and a primary rotary pump.

Experimental Data

Two ceramics, differing by their microstructure (Fig. 3), which have been studied by mechanical spectroscopy are presented here as examples.

Fine-grained zirconia (3Y-TZP): fully tetragonal zirconia stabilized by 3 mol% of yttria) exhibits a microstructure of equiaxed grains with a mean diameter of 0.29 μm (Fig. 3(a)).

Silicon nitride (Si_3N_4) specimens exhibit a mixture of two kinds of grains: elongated and equi-axed (Fig. 3(b)). A relatively large volume fraction of glassy phase can be detected in these ceramics as inter-granular films or as pockets at the triple points.

Mechanical spectroscopy measurements were performed with a forced torsion pendulum as described in Fig. 2. With this apparatus, the mechanical loss angle ($\tan \Phi$) and the shear modulus (G) are obtained from the phase lag and the amplitude ratio between stress and strain, respectively. Measurements are performed under vacuum (10^{-3} Pa) as a function of temperature (300–1600K) at a fixed frequency, or as a function of frequency (10^{-3} –10 Hz) at fixed temperature.

Mechanical Spectroscopy of Zirconia

Fig. 4 shows a typical mechanical loss spectrum ($\tan \phi$ and elastic shear modulus $G = 1/J$) measured as a function of temperature in fine-grained zirconia (2Y-TZP): fully tetragonal zirconia stabilized by 2 mol% of yttria (Lakki *et al.*, 1993). The mechanical loss spectrum of TZP zirconia is composed of a damping peak at about 350K, associated with a modulus defect, and of an exponential increase in damping associated with a steep decrease in the shear modulus at high temperature.

Low Temperature Peak

The mechanical loss peak at 350K and the modulus variation occur as well in temperature measurements (with practically no hysteresis between heating and cooling curves (Fig. 5(a))), and in frequency measurements (Fig. 5(b)). They are, therefore, manifestations of the same relaxation phenomenon, which is found to be thermally activated. By using the data concerning the “frequency-temperature” peak locations, an Arrhenius plot can be drawn (Fig. 6).

The activation enthalpy, H_{act} , of this relaxation was found to be 0.97 ± 0.03 eV (89 kJ/mol) and the limit relaxation time, τ_0 , is equal $\approx 0.7 \cdot 10^{-14}$ s. These values characterize a point defect relaxation mechanism.

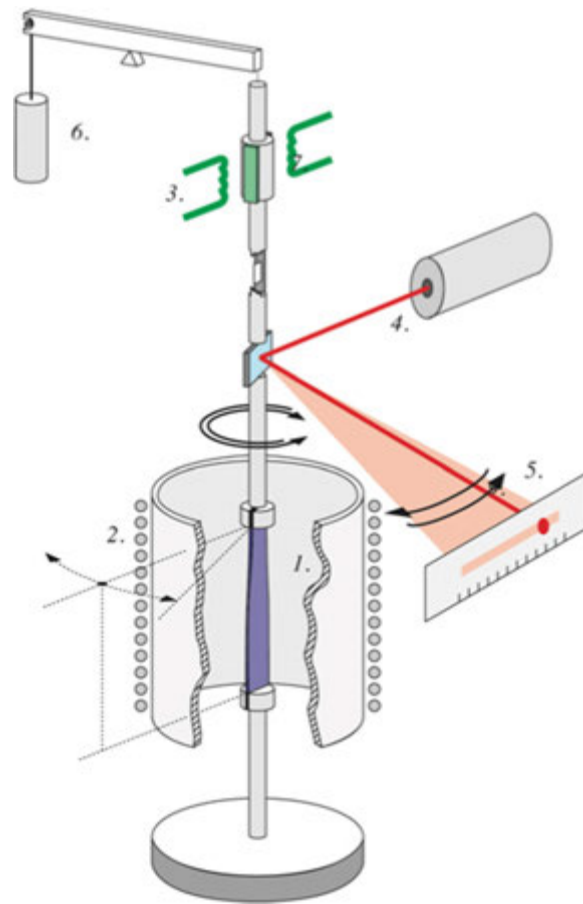


Fig. 2 Schematic drawing of an inverted forced torsion pendulum: (1) sample, (2) furnace, (3) excitation system “magnet- Helmholtz coils”, (4) laser and (5) photocells.

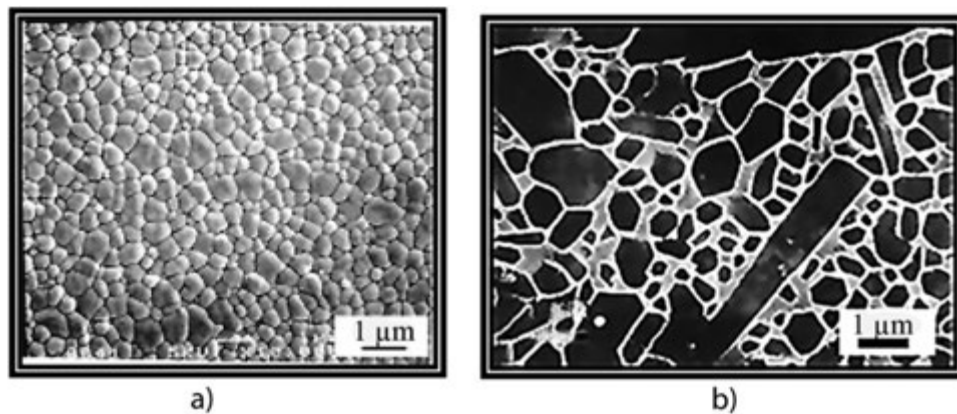


Fig. 3 (a) Granular microstructure of 3Y-TZP zirconia. (b) Microstructure silicon nitride with elongated and equiaxed grains (dark phase) surrounded by a glassy phase (white).

The current interpretation (Weller, 1994) invokes the reorientation of elastic dipoles of the type “oxygen vacancy-yttrium cation” under the influence of the applied stress (Fig. 7). Peak-broadening may be due to additional contributions of more complex clusters, e.g., two Y^{3+} ions and one O^{2-} vacancy. Since the elastic dipoles are at the same time electric dipoles, giving rise to a dielectric loss peak as well, this effect is important in the study of the ionic conductivity of zirconia.

In order to determine the origin of the high temperature damping, it is possible to compare the mechanical loss spectrum of the ceramic with the spectra of the components: grains and GBs. For zirconia, the comparison in Fig. 8 of the high temperature spectra of poly- and single-crystals shows clearly that the high temperature background is due to GBs.

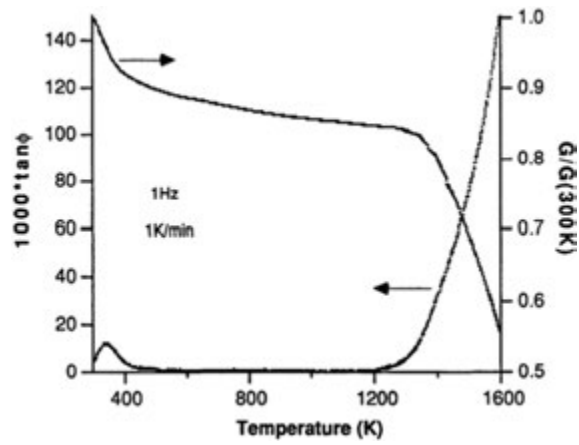


Fig. 4 Mechanical loss ($\tan \phi$) and elastic shear modulus (G) as functions of temperature in 2Y-TZP zirconia.

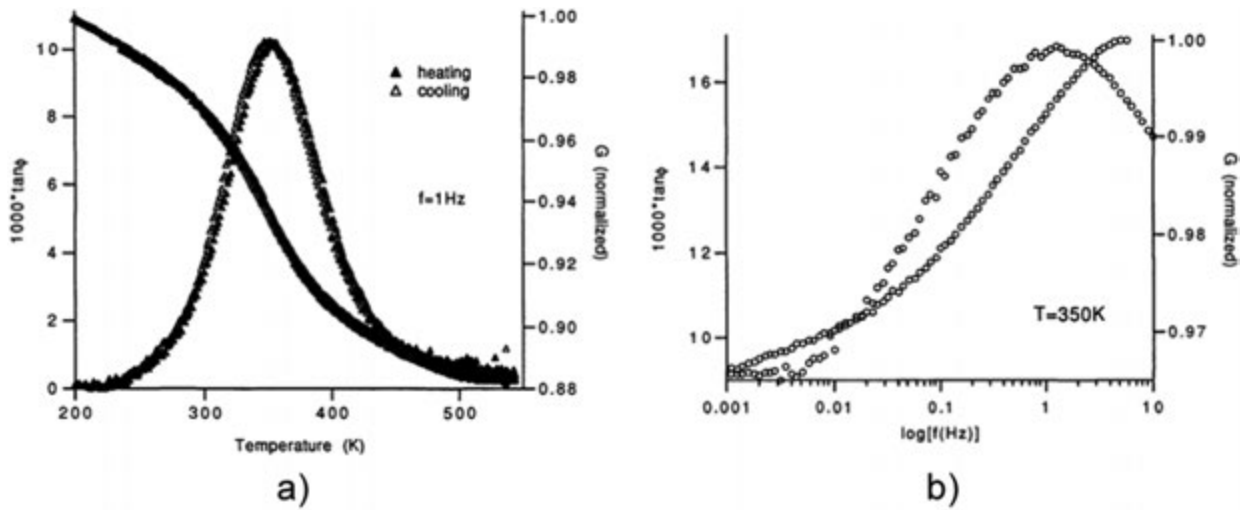


Fig. 5 Low temperature mechanical loss peak and modulus variation in zirconia. (a) as a function of temperature (measurements during heating and cooling) and (b) as a function of frequency.

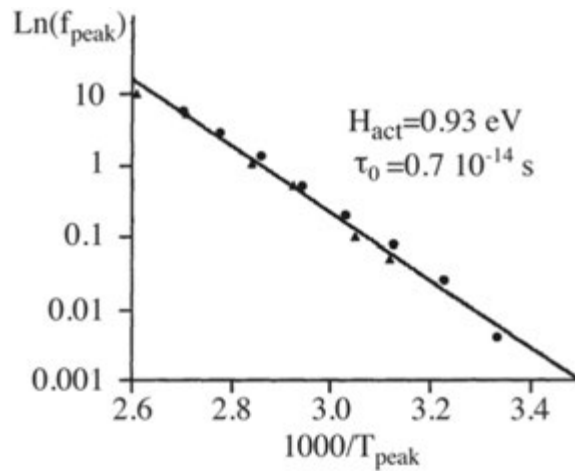


Fig. 6 Arrhenius plot from the "frequency-temperature" shifts of the low temperature peak in zirconia: $H_{\text{act}} = 0.93 \text{ eV}$ (89 kJ/mol), $\tau_0 \approx 0.7 \cdot 10^{-14} \text{ s}$.

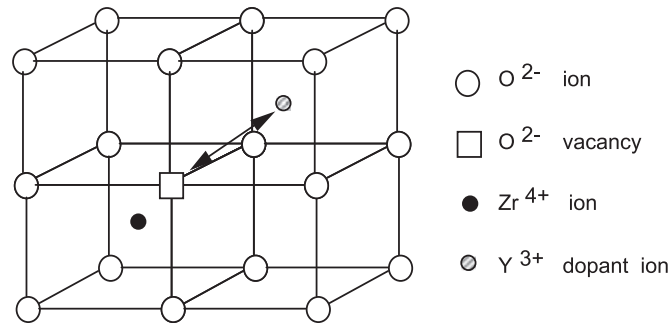


Fig. 7 Diagram of one-half the unit cell of zirconia, showing a substitutional Y-dopant cation forming an elastic and electric dipole with an oxygen-ion vacancy. Adapted from Nowick, A.S., 1985. The combining of dielectric and anelastic relaxation measurements in the study of point defects in insulating crystals J. Phys. Colloques 46 (C10), C10-507–C10-511.

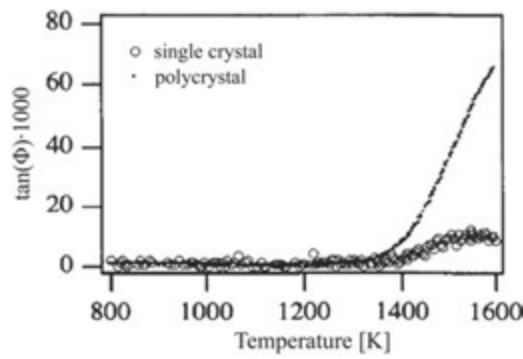


Fig. 8 Mechanical loss as a function of the temperature in a poly-(dots) and in a single-crystalline zirconia (markers).

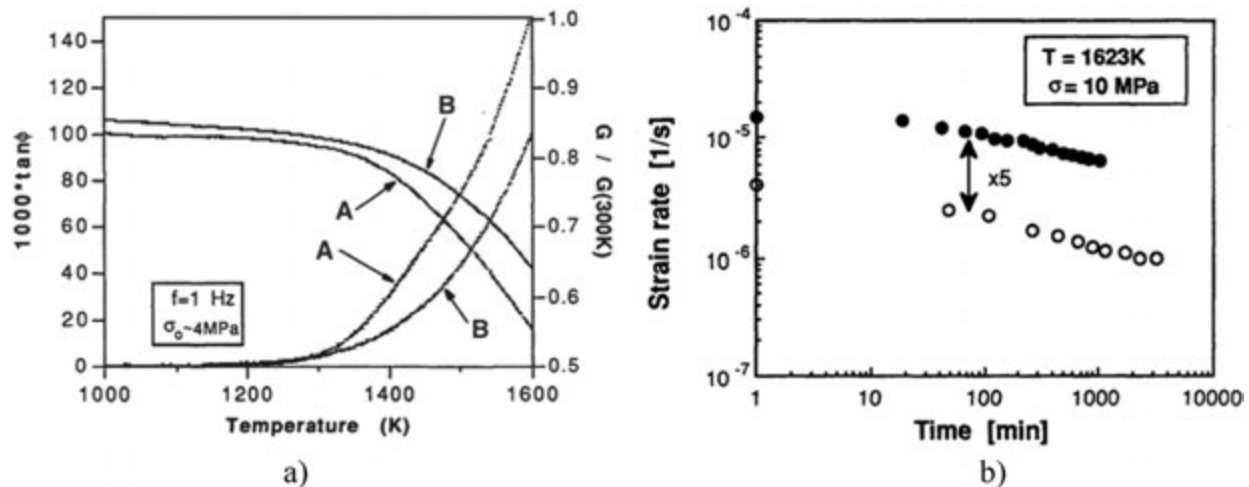


Fig. 9 Comparison of the high temperature behavior of two Y-TZP grades, A and B, which differ mainly in their impurity content: (a) Mechanical loss $\tan \Phi$ and shear modulus G as functions of temperature (frequency $f = 1$ Hz, heating rate 1 K/min). (b) Creep rate measured at 1623 K under a stress of 10 MPa as a function of time. Adapted from Lakki, A., Schaller, R., Nauer, M., Carry, C., 1993. High temperature superplastic creep and internal friction of yttria doped zirconia polycrystals. Acta Metall. Mater. 41, 2845–2853.

Fig. 9(a) displays the typical spectra of two zirconia grades A and B, which have almost the same grain size and differ only with respect to the impurity content (and therefore have a different amount of inter-granular glassy phase). The amplitude of the applied cyclic stress during measurements was of the order of 4 MPa.

Grade A (i.e., with the higher impurity content) shows a faster increase in the mechanical loss and a steeper modulus decrease than grade B. In parallel, grade A exhibits a higher strain rate during creep tests at 1623K in the low stress regime (10 MPa) than grade B (Fig. 9(b)).

The exponential increase in damping associated with the steep decrease in the shear modulus at high temperature accounts for the appearance of ductility in the ceramic material, i.e., a brittle-to-ductile transition. In fact, an exponential increase in $\tan(\phi)$ implies an increase in the anelastic strain, which does not reach an equilibrium value. This means that creep is occurring. The creep rate can be described by the classical Eq. (1):

$$\dot{\epsilon}(\sigma, T) \approx \left(\frac{\sigma}{G}\right)^n \cdot \left(\frac{b}{d}\right)^p \cdot D_0 \cdot e^{-\frac{H_{act}}{RT}}$$

Eq. (1) combined with Eqs. (10) to (13) can be used to calculate the internal friction IF or the mechanical loss $\tan(\phi)$,

$$\tan(\phi) = A \frac{G \cdot \sigma^{n-1}}{\omega \cdot d^p} \exp\left(-\frac{H_{act}}{kT}\right) \quad (14)$$

where G is the shear modulus, ω the circular frequency and A a material constant.

Eq. (14) has an exponential form, which fits well to the experimental results obtained in the high temperature domain where creep is enhanced. Plotting $\ln(\tan(\phi))$ as a function of $1/T$ leads to a straight line (Fig. 10), the slope of which would give the activation enthalpy.

In grade B, a value of $H_{act} = 162$ kJ/mol is obtained by this method. This value is much smaller than the activation enthalpy deduced from creep tests, which was of 620 kJ/mol (Nauer and Carry, 1990). This indicates that the above analysis is simplistic and leads to wrong quantitative values.

A better value for the activation enthalpy may be obtained from a method that is called Master Curve. It consists in shifting frequency spectra obtained in isothermal conditions in order to obtain a unique matching curve. The mechanical loss spectra obtained at different frequencies as a function of temperature are shown in Fig. 10(a). The value for the activation enthalpy is obtained from the Arrhenius plot (Fig. 10(b)) built from the "temperature-frequency" shifts of the mechanical loss spectra (Fig. 10(a)). The obtained value of 634 kJ/mol corresponds well to the one obtained in creep tests.

Grain Size Effect

The influence of the grain size on the mechanical loss spectra is shown in Fig. 11. Three samples with $d = 0.34, 0.69$ and $1.00 \mu\text{m}$ were measured. It is observed that the damping is inversely proportional to " d " as a first approximation. The deduced grain size exponent is found to be about 1. For all grain sizes, the (isothermal) spectra seem to be composed of a peak plus a background. Both the peak height and frequency position decrease with increasing the grain size.

All the above results show that there is a close correlation between the high temperature mechanical loss spectrum of zirconia and its creep behavior: similar values for the activation enthalpy and the grain size exponent. It has been observed that the mechanical loss increases linearly with stress in the low frequency (~ 10 mHz) and high temperature ($\sim 1600\text{K}$) regime for

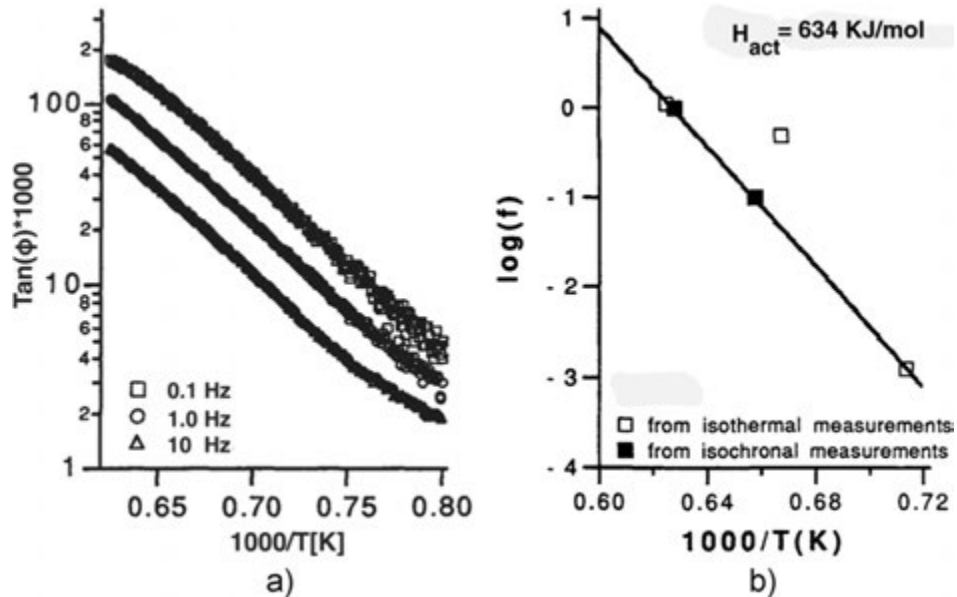


Fig. 10 (a) High temperature part of the mechanical loss spectrum of the B grade ($d = 0.34 \mu\text{m}$) as a function of temperature at 3 different frequencies. (b) Arrhenius plot for the high temperature part of the mechanical loss spectrum.

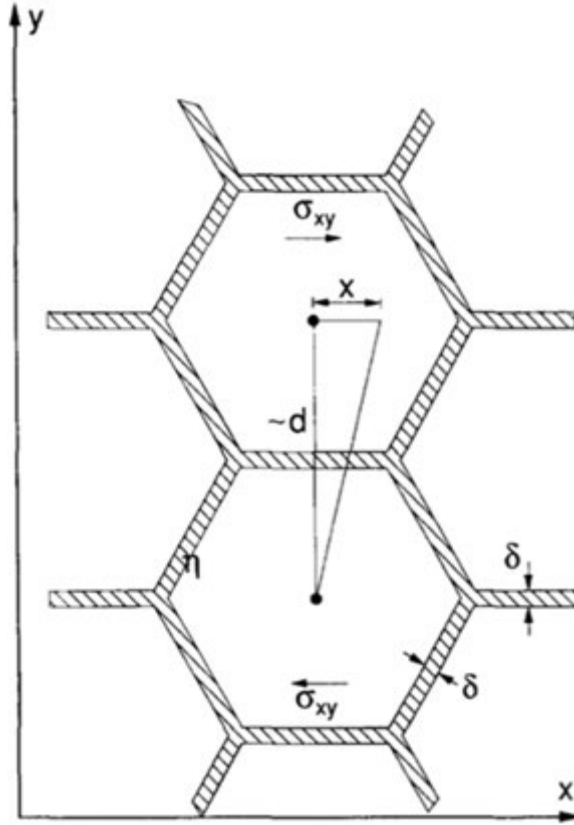


Fig. 11 Model of hexagonal grains separated by an inter-granular layer of viscosity η .

stresses higher than 2 MPa. This is in good agreement with Eq. (14) and with the value of the stress exponent $n \sim 2.4$ obtained in creep tests for stresses lower than 15 MPa (Nauer and Carry, 1990).

A theoretical model was developed by Lakki (1994) to account for the mechanical loss due to the relative sliding of grains of hexagonal shape (Fig. 12). If " u " is the relative displacement of two grains, τ the applied shear stress, η the interface viscosity, δ the inter-granular layer thickness and Ku the restoring force due to the limiting grains at triple junctions, the motion equation is:

$$\sigma = \frac{\eta}{\delta} \cdot \dot{u} + K \cdot u \quad (15)$$

The mechanical loss $\tan(\phi)$ is then directly obtained from the phase lag between stress τ and strain ε :

$$\varepsilon = \varepsilon_e + \varepsilon_a = \frac{\sigma}{G} + \frac{u}{d} \quad (16)$$

and, in the case of a harmonic stress, one obtains:

$$\tan(\phi) = \frac{G}{d} \cdot \frac{\omega \cdot \eta / \delta}{\left(\frac{KG}{d} + K^2\right) + (\omega \eta / \delta)^2} \quad (17)$$

$\tan \phi$ has the form of a peak with a maximum at

$$\omega_p = \frac{\delta}{\eta} \cdot \sqrt{\frac{KG}{d} + K^2} \quad (18)$$

However, the high temperature mechanical loss spectrum in zirconia does not exhibit a peak, but an exponential increase with temperature (Fig. 9).

In fact, isothermal measurements performed at 1600K show that the spectrum is composed of a peak and an exponential background at lower frequencies (Fig. 11).

It is possible to account for this spectrum by considering that the restoring force " Ku " is reduced at high temperature, where creep takes place. Assuming that K is proportional to the shear modulus $G(t) = \tau/\varepsilon(t)$, which decreases deeply at high temperature, one can calculate the theoretical spectra presented in Fig. 13(b).

The theoretical model by Lakki allows a good interpretation of the experimental results shown in Fig. 13(a): a grain boundary peak, which evolves into an exponential background at lower frequency. In Fig. 13(a), the finer the grains the higher the mechanical loss peak, in good agreement with Eq. (17). The transition from the peak to the exponential background is due to the decrease in the restoring force factor " K " due to the weakening of the triple points. The deformation is no more reversible, and creep occurs.

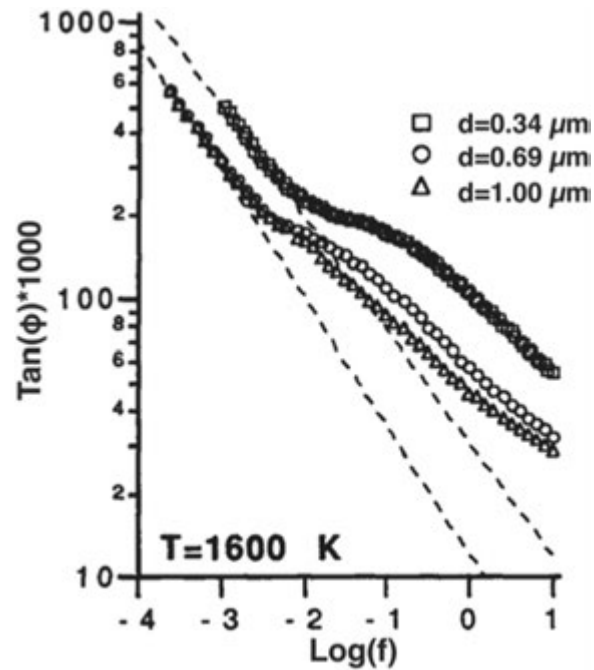


Fig. 12 Mechanical loss as a function of frequency, for zirconia of grade B, differing only in the grain size ($d = 0.34, 0.69$ and $1.00 \mu\text{m}$).

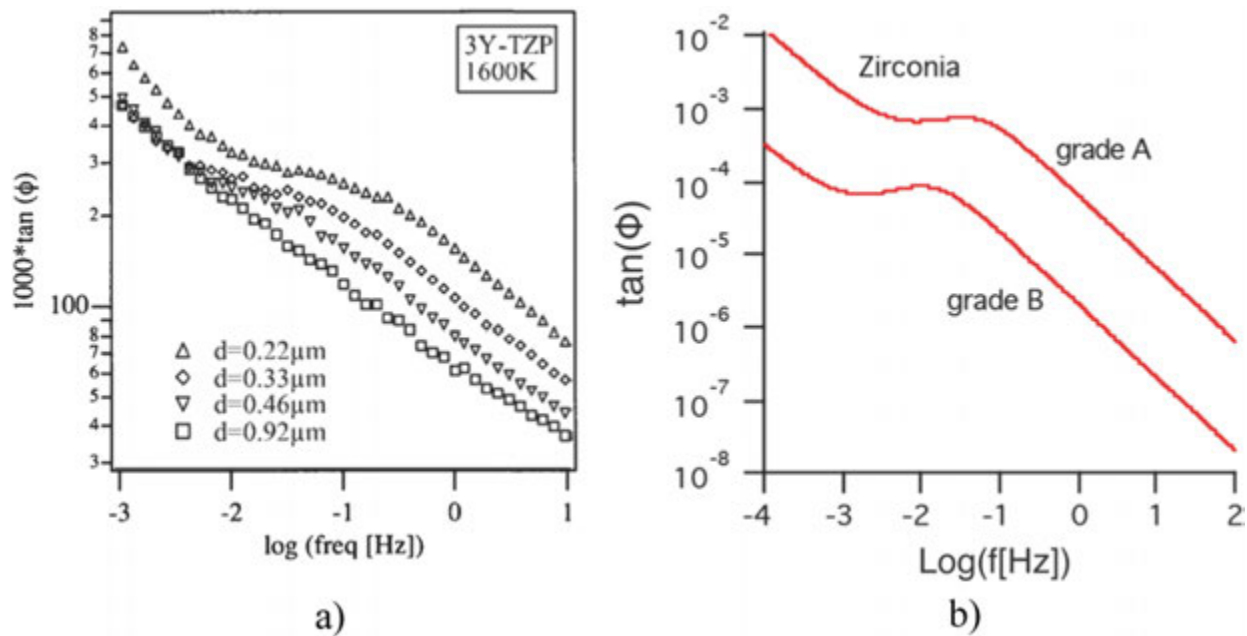


Fig. 13 (a) Mechanical loss spectra of 3Y-TZP zirconia measured at 1600K for different grain sizes d . (b) theoretical spectra calculated from Eq. (17) with a decrease of the restoring force K at high temperature.

As a conclusion, an increase in the creep resistance of fine grain ceramics needs to increase the restoring force, which hinders long range GB sliding resulting in a lower high temperature mechanical loss. Such an increase in creep resistance was achieved by Mazaheri *et al.* (2010), who reinforced fine grained zirconia with carbon nanotubes. It was shown that carbon nanotubes were located at the GBs and were able to limit considerably the sliding process. As a matter of fact, Fig. 14 shows that with additions of carbon nanotubes, the high temperature mechanical loss decreases (Fig. 14(a)) and so is the creep rate (Fig. 14(b)).

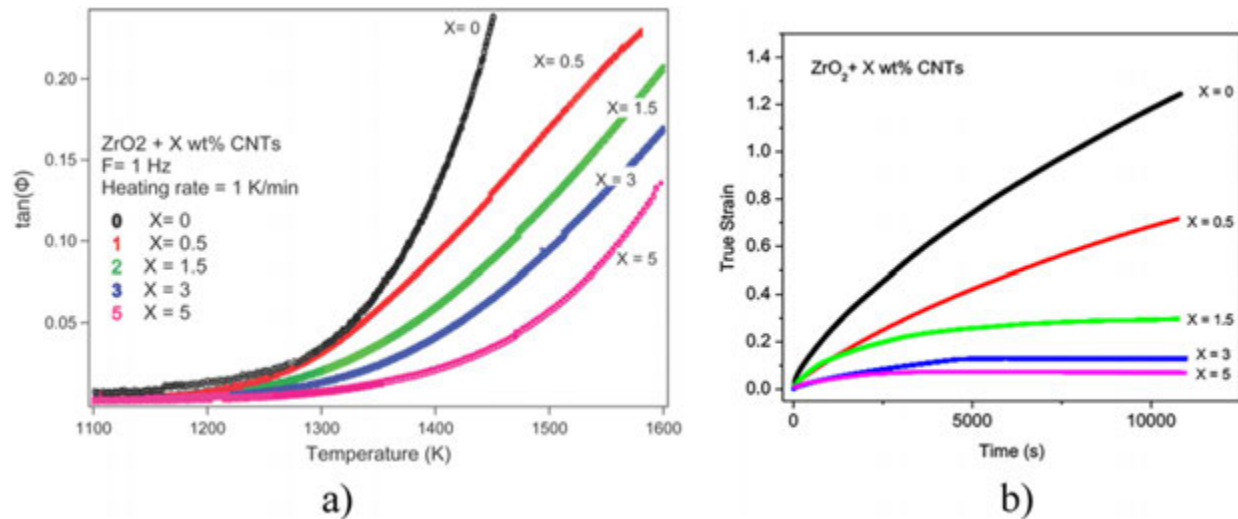


Fig. 14 (a) Mechanical loss spectra of 3Y-TZP zirconia reinforced with different amounts of carbon nanotubes (x wt%). (b) creep strain of 3Y-TZP zirconia reinforced with different amounts of carbon nanotubes (x wt%).

Mechanical Spectroscopy in Silicon Nitride

In silicon nitride (Si_3N_4), the sintering aids generate an important volume fraction of amorphous phase (YSiAlON glass). This phase is not only located as thin films between the grains, but also at the triple points where large glassy pockets have been observed.

The mechanical loss spectrum of Si_3N_4 shown in **Fig. 15** highly differs from the one of zirconia. The spectrum is composed of a mechanical loss peak located at around 1270K, which is superimposed on an exponential “background” and accompanied by a steep modulus decrease (curves 1 in **Fig. 15**).

The mechanical loss peak and the associated modulus anomaly disappear after thermal treatments, which enhance the crystallization of the glassy pockets (curves 2). This indicates that the peak is due to relaxations in the glassy pockets.

However, if the temperature does not exceed 1200K, the peak is stable and can be measured as a function of temperature under isothermal conditions (**Fig. 16(a)**). The peak is a relaxation peak, because it shifts in frequency when the temperature is modified.

An Arrhenius plot can be drawn (**Fig. 16(b)**) giving a value of 1117 kJ/mol for the activation enthalpy and $0.8 \cdot 10^{-47}$ s for the limit relaxation time.

It is possible to compare the spectrum of Si_3N_4 ceramic with the spectrum of one of the constituents, that is the glassy phase (**Fig. 17**). The mechanical loss in YSiAlON glass increases exponentially at the temperature where the peak is observed in silicon nitride. This increase in damping is due to the α -relaxation in a YSiAlON glass. The α -relaxation can be studied by measuring the real G_1 and imaginary component G_2 of the shear modulus G .

A relaxation peak is observed in the imaginary component G_2 (**Fig. 18**). The activation enthalpy of 1115 kJ/mol obtained from the shifts of the peak is the same as for the peak in Si_3N_4 . This confirms that the peak in Si_3N_4 is due to the α -relaxation in the glassy pockets (Donzel *et al.*, 1997). Near the glass transition temperature, the pockets in Si_3N_4 soften, but the ceramic skeleton remains elastic. As a consequence, the exponential background in Si_3N_4 (**Fig. 15**) is lower than in zirconia (**Fig. 9**), and the creep resistance of this ceramic is higher.

Mechanical Loss and Toughness

An exponential increase in mechanical loss at high temperature means a low creep resistance of the material, because the anelastic or microplastic strain has no limit. On the other hand, damping mechanisms are positive factors for improving toughness in hard and brittle materials. Since a mechanical loss peak is associated with a limited motion of structural defects, it cannot be associated with the onset of creep. It accounts for the ability of the material to dissipate locally a part of the vibration energy and hence to improve toughness by crack propagation blunting.

As an example, **Fig. 19(a)** shows the mechanical loss spectra of two grades of zircon (ZrSiO_4) (Carbonneau, 1997) differing by the content of the inter-granular glassy phase. **Fig. 19(b)** shows that a K_{Ic} maximum is observed only in the grade that exhibits a mechanical loss peak.

Since the mechanical loss accounts for energy dissipation in the solid, one can try to link it with the strain energy release rate G_{Ic} (Schaller and Fantozzi, 2001):

$$G_{Ic} = - \frac{dU}{h \cdot da} \quad (19)$$

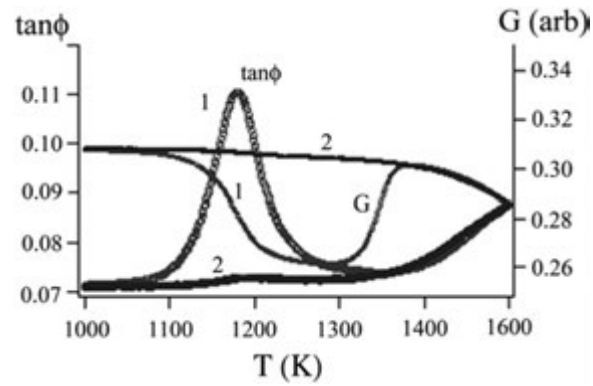


Fig. 15 Mechanical loss spectrum of Si_3N_4 as sintered (curves 1) and after annealing at 1600K, which leads to crystallization of the glassy phase at the triple points (curves 2). Adapted from Lakki, A., Schaller, R., Nauer, M., Carry, C., 1993. High temperature superplastic creep and internal friction of yttria doped zirconia polycrystals. *Acta Metall. Mater.* 41, 2845–2853.

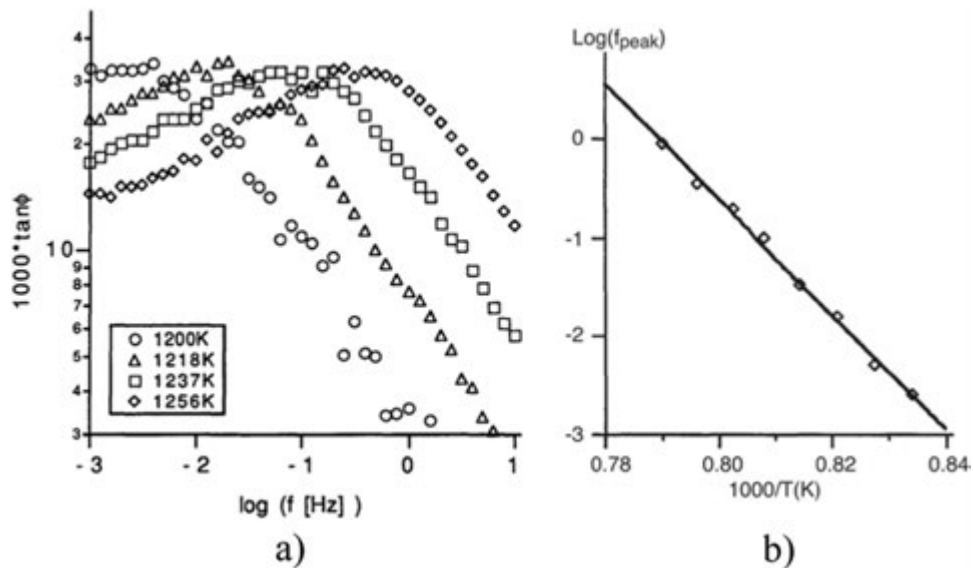


Fig. 16 (a) Mechanical loss peak in Si_3N_4 measured as a function of frequency at different temperatures. (b) Arrhenius plot associated with the relaxation peak observed in Si_3N_4 .

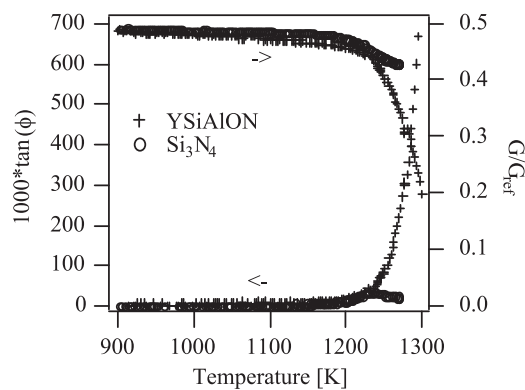


Fig. 17 Mechanical loss spectra of YSiAlON glass (a glass of the same composition as the pockets in Si_3N_4) and of Si_3N_4 ceramic.

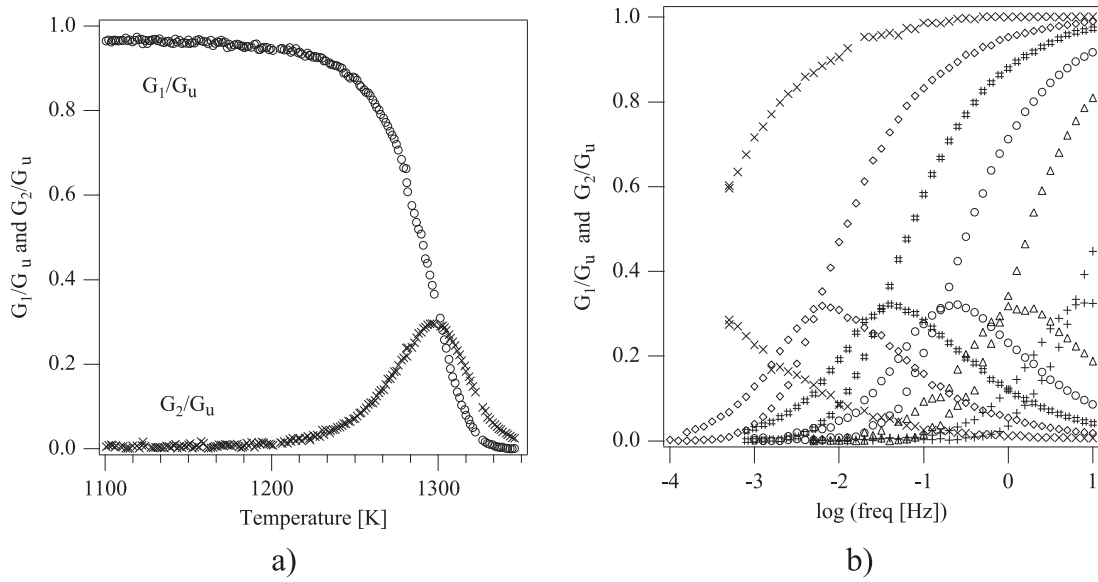


Fig. 18 Real G_1 and imaginary G_2 component of the shear modulus G in YSiAlON glass, as functions of temperature (a) and of frequency (b). The values are normalized with respect to the unrelaxed room temperature modulus G_u . Adapted from Donzel, L., Lakki, A., Schaller, R., 1997. Glass transition and α -relaxation in YSiAlON glasses and in Si_3N_4 ceramics studied by mechanical spectroscopy. Phil. Mag. A 76, 933–944.

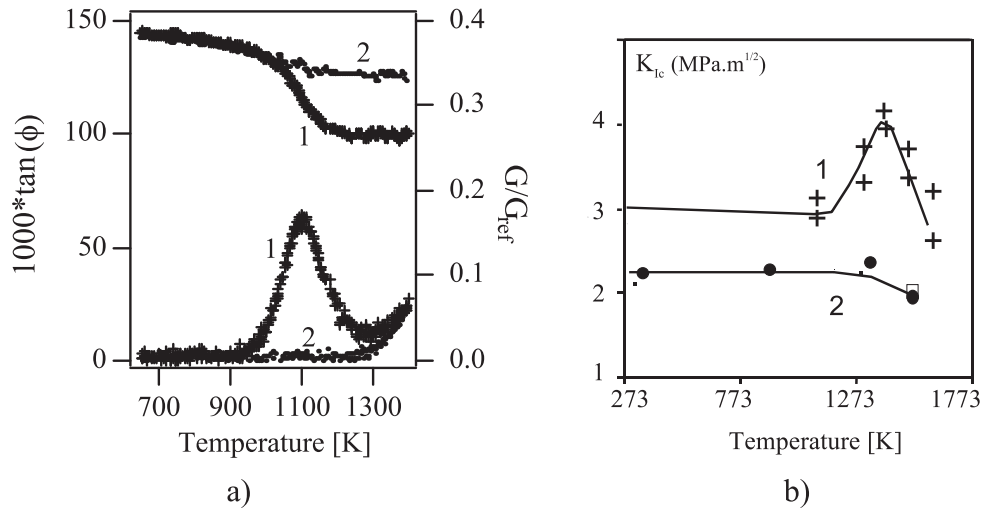


Fig. 19 (a) Mechanical loss ($\tan \Phi$) spectra and, (b) critical stress intensity factor K_{Ic} of two grades of zircon (ZrSiO_4). Grade A (curves 1) has a higher content of glassy phase than grade B (curves 2). Adapted from Schaller, R., 2000. Mechanical spectroscopy of the high-temperature brittle-to-ductile transition in ceramics and cermets. J. Alloys Compd. 310, 7–15. Carbonneau, X., 1997. Etude des propriétés thermomécaniques de mullite zircon et de zircon. PhD Thesis, INSA, Lyon, No 97 ISAL 0105.

where dU represents the potential energy release when the crack grows of “ da ”, the specimen thickness being of “ h ”. In brittle materials, an increase in the potential energy release ΔG_{Ic} can be due to an increase in the energy dissipation ΔW_{diss} in a volume V in front of the crack tip. When ΔW_{diss} is due to an internal friction mechanism, the eqs. (9) and (12) can be used for calculating ΔW_{diss} . Then:

$$\Delta G_{Ic} = -\frac{\Delta(dU)}{h \cdot da} = \frac{V \cdot \Delta W_{diss}}{h \cdot da} = \frac{2\pi \cdot V \cdot W_{el}}{h \cdot da} \cdot \Delta \tan(\phi) \quad (20)$$

where W_{el} is the maximum stored elastic energy per unit volume and $\Delta \tan \phi$ the increase in damping, respectively.

Supposing that the volume V is a cylinder of radius r and height h , which is translated of da when crack propagates, the increase ΔG_{Ic} of the strain energy release rate G is:

$$\Delta G_{Ic} = 4\pi \cdot r \cdot W_{el} \cdot \Delta \tan(\phi) \quad (21)$$

Taking into account the height of the mechanical loss peak $\Delta \tan(\phi)$ (Fig. 19(a)), and considering that crack propagation in zircon is enhanced under an applied stress of 200 MPa, one obtains $\Delta G_{Ic} = \sim 7\text{--}70 \text{ Jm}^{-2}$ depending on the value of the zone radius $r = \sim 0.1\text{--}1 \text{ mm}$ respectively. On the other hand, in the case of elastic materials, it is possible to derive ΔG_{Ic} from the increase in K_{Ic} associated with the toughness peak. One obtains $\Delta G_{Ic} = 32 \text{ Jm}^{-2}$, value of the same order of magnitude as the one predicted from mechanical loss peak. In fact, it is not evident to get a quantitative value of ΔG_{Ic} from the mechanical spectroscopy because of the estimation of the radius r of the dissipative zone, which has to be larger than the plastic zone considered in the models of fracture mechanics. However, from a qualitative point of view, it is clear that a mechanical loss peak is beneficial for toughness. For instance, it has been shown that the ability of Si_3N_4 to dissipate energy in the glassy phase decreases the strain accumulation under cyclic loading and consequently improves fatigue resistance (Roebben *et al.*, 1998).

Conclusions

Ceramics are generally considered as brittle materials. However, at relatively high temperatures, plastic yield can be observed defining a brittle-to-ductile transition. Such a transition, is often marked by a mechanical loss peak, which evolves into an exponential background at higher temperature. From the viewpoint of mechanical spectroscopy, the brittle-to-ductile transition can be decomposed into two stages: a brittle-to-“tough” transition associated with the relaxation peak and a “tough”-to-ductile transition associated with the exponential background. Structural ceramics have to be tough and creep resistant. In other words, they have to exhibit a mechanical loss peak with a low level of the high temperature background.

In the case of Si_3N_4 , it was shown that the mechanical loss peak was due to the α -relaxation in the pockets of YSiAlON type glass (Donzel *et al.*, 1997). Crystallization of these glassy pockets by thermal treatments led to an improved creep resistance (Besson *et al.*, 1998). Fine-grained zirconia presents a mechanical loss peak, which is not well resolved with respect to the exponential background. In these ceramics, the regular shape of the grains does not provide a strong restoring force in the GB sliding process and therefore extended creep can be observed. GB sliding is lubricated by amorphous intergranular films and anelastic relaxation is affected by the glass transition in these films. As these films are very stable, one way to limit GB sliding is to introduce hard particles or whiskers, for instance of SiC type or carbon nanotubes, at the triple points.

To conclude, the brittle-to-ductile transition in hard materials like ceramics or ceramic composites can be studied by mechanical spectroscopy. An appropriate strategy is to compare carefully the damping spectrum with the mechanical behavior determined by other techniques (creep tests, toughness tests). Moreover, transmission electron microscopy observations are of particular interest in modeling the damping mechanisms. Damping is important for toughness and for fatigue resistance of ceramics (Roebben *et al.*, 1996).

References

- Besson, J.L., Rouxel, T., Goursat, P., 1998. Ductility and creep resistance of a silicon nitride ceramic. *Scr. Mater.* 39, 1339–1343.
- Boutz, M.M.R., Winnubst, A.J.A., Burggraaf, A.J., Nauer, M., Carry, C., 1994. Low temperature superplastic flow of yttria stabilized tetragonal zirconia polycrystals. *J. Europ. Ceram. Soc.* 13, 103–111.
- Carbonneau, X., 1997. Etude des propriétés thermomécaniques de mullite zircone et de zircon. PhD Thesis, INSA, Lyon, No 97 ISAL 0105.
- Carry, C., Mocellin, A., 1987. Structural superplasticity in single phase crystalline ceramics. *Ceram. Int.* 13, 89–98.
- Coble, R.L., 1963. A model for boundary diffusion controlled creep in polycrystalline materials. *J. Appl. Phys.* 34, 1679–1682.
- Donzel, L., Lakki, A., Schaller, R., 1997. Glass transition and α -relaxation in YSiAlON glasses and in Si_3N_4 ceramics studied by mechanical spectroscopy. *Phil. Mag. A* 76, 933–944.
- Duclos, R., Crampon, J., Amana, B., 1989. Structural and topological study of superplasticity in zirconia polycrystals. *Acta Metall.* 37, 877–883.
- Gadaud, P., Guisolan, B., Kulik, K., Schaller, R., 1990. Apparatus for high-temperature internal friction differential measurements. *Rev. Sci. Instrum.* 61, 2671–2675.
- Herring, C., 1950. Diffusional viscosity of a polycrystalline solid. *J. Appl. Phys.* 21, 437–445.
- Lakki, A., 1994. Mechanical spectroscopy of fine-grained zirconia, alumina and silicon nitride. PhD Thesis, EPF – Lausanne, No 1266.
- Lakki, A., Schaller, R., Nauer, M., Carry, C., 1993. High temperature superplastic creep and internal friction of yttria doped zirconia polycrystals. *Acta Metall. Mater.* 41, 2845–2853.
- Marshall, D.B., Evans, A.G., Drory, M., 1983. Transformation toughening in ceramics. *Fract. Mech. Ceram.* 6 (190144), 289–307.
- Mazaheri, M., Mari, D., Schaller, R., 2010. High temperature mechanical spectroscopy of yttria stabilized zirconia reinforced with carbon nanotubes. *Phys. Status Solidi A* 207, 2456–2460.
- Nauer, M., Carry, C., 1990. Creep parameters of yttria doped zirconia materials and superplastic deformation mechanisms. *Scr. Metall. Mater.* 24, 1459–1463.
- Nowick, A.S., Berry, B.S., 1972. Anelastic Relaxation in Crystalline Solids. New York: Academic Press.
- Roebben, G., Donzel, L., Stemmer, S., *et al.*, 1998. Viscous energy dissipation at high temperatures in silicon nitride. *Acta Mater.* 46, 4711–4723.
- Roebben, G., Steen, M., Bressers, J., Van der Biest, O., 1996. Mechanical fatigue in monolithic non-transforming ceramics. *Prog. Mater. Sci.* 40, 265–331.
- Rouxel, T., Wakai, F., 1993. The brittle to ductile transition in a $\text{Si}_3\text{N}_4/\text{SiC}$ composite with a glassy grain boundary phase. *Acta Metall. Mater.* 41, 3203–3213.
- Schaller, R., Fantozzi, G., 2001. Study of the brittle-to-ductile transition in ceramics and cermets by mechanical spectroscopy. In: Bouchaud, E., Jeulin, D., Prioul, C., Roux, S. (Eds.), *Physical Aspects of Fracture*. Dordrecht, Boston, London: Kluwer Academic Publishers., pp. 111–121.
- Schaller, R., Fantozzi, G., Gremund, G., 2001. Mechanical Spectroscopy Q^{-1} 2001 With Applications to Materials Science (Materials Science Forum). 366–388. Trans Tech Publications.
- Wakai, F., Sakaguchi, S., Matsuno, Y., 1986. Superplasticity of yttria-stabilized tetragonal ZrO_2 polycrystals. *Adv. Ceram. Mater.* 1, 259–263.
- Weller, M., 1994. Mechanical loss measurements on yttria- and calcia-stabilized zirconia. *J. Alloys Compd.* 211/212, 66–70.

Indentation of Ceramics

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Introduction

One of the outstanding properties of ceramics is their high hardness, that is, they are resistant to permanent deformation produced by contact loads. Due to this property, there are many engineering applications where ceramics have a competitive advantage over metals. In fact, wear resistance and scratch resistance are a consequence of the high hardness and stiffness of ceramics, which translate in higher durability and performance. Therefore, applications such as ceramic bearings, cutting tools, grinding, motor components, or biomedical prosthesis require benefit from the high hardness of ceramics.

In addition, measuring hardness is a versatile and straightforward technique to assess mechanical properties of ceramics at local level. Hardness imprints are generated by inelastic mechanisms, which can be dislocation movement, twinning, phase transitions, densification or microcracking, depending on the material. Therefore, insights on these deformation mechanisms can be acquired by a simple hardness test, instead of a more complex, difficult to perform, mechanical tests. Moreover, hardness tests can be also probe other mechanical properties as well as plasticity: elasticity, fracture toughness, fatigue resistance, creep or impact, among others.

This chapter has the following structure. First, the hardness test using Vickers indenters is described. Then, a short review of the spherical indentation tests is presented. The third part introduces the nanoindentation test, on how it is used to measure hardness and Young's modulus, and the special precautions to be taken in case of testing ceramic materials. Further information is given on testing coatings, particles or grains, as well as porous ceramics and degraded surfaces. The last part covers the measurement of fracture toughness by indentation, the main formulas used, and the possible shortcomings of the technique.

Hardness Tests

Hardness is defined as the permanent deformation produced after indenting with a tip. Hardness tests were first developed as a fast and easy quality control test in the metal industry. For example, the name Vickers comes from the company Vickers Ltd, where it was first developed. As a consequence, there are many different hardness tests, based on the geometry of the indenter tip and the way load and/or penetration is measured. Most used ones are Brinell, Rockwell, Knoop and Vickers tests. All these tests, because of their industrial nature, use their own scales and have validity load ranges. It should also be mentioned that the Mohs scale from 1 to 10 using a series of benchmark minerals and putting the mineral in the scale on its ability to scrape the lower ranked minerals, is rarely used in scientific research, although it is the best known to the general public. This scale is more a qualitative test for scratch resistance, and, although being very intuitive, it does not provide consistent quantitative data. Because of the high hardness of ceramics, the main hardness test used in ceramics is by using Vickers indenters, and, in a minor extend, Knoop indenters. Berkovich indenters, which are similar to Vickers, are used in nanoindentation, as discussed later. The reason is because Vickers tests use sharp pyramidal tips, and, hence, produce inelastic deformation even at low loads and a measure can be done even at small loads.

In Vickers test, a four-side pyramidal diamond tip (68° angle) is pressed against a material with a known force P . After indentation, the diagonals of the imprint, d , are measured. Assuming perfect tip geometry, the area of contact (A_c) and the diagonal lengths can be related with

$$A_c = \frac{d^2}{2\sin(136^\circ/2)} \quad (1)$$

and, hence, the Vickers hardness is measured as:

$$H_V = \frac{P}{A_c} = 1.8544 \frac{P}{d^2} \quad (2)$$

In Vickers test, the load is measured in kgf and the diagonals in mm, and, consequently, units are, when reported, kgf/mm², or just in "Vickers number". A straightforward conversion into MPa can be done by multiplying the hardness value by 9.8 m/s². However, it has to be considered that Vickers hardness uses projected area, and therefore cannot be directly converted into a plastic stress. A more fundamental definition of hardness is Meyer's hardness that uses projected area instead with the same experimental setup. Discrepancies of 10% of hardness are then expected between both hardness tests. Meyer's hardness is used in instrumented indentation, and will be described with more detail later.

Values of hardness for ceramics vary between a few GPa for ionic bonded ceramics to even 50 GPa in case of boron nitride (Vepřek, 1999) or 100 GPa for diamond, the hardest material known, with typical values of advanced ceramics of 20 GPa for alumina, 23 GPa for SiC or 12 GPa for zirconia (Gallo *et al.*, 2019; Holleck, 1986). All these values have to be considered as

approximate, as the exact values depend strongly on the particular microstructure and, naturally, the processing route followed to produce the particular material to be tested (Rice *et al.*, 1994).

Spherical Contact

While sharp indentations are used to assess hardness because they produce inelastic deformation from the first moment of contact, indentations produced by blunt indenters produce an initial elastic contact which develops into elasto-plasticity at larger loads. This permits to study elastic regimes of the material as well as onset on inelastic deformation mechanisms, such as dislocation movement, micro-cracking or twinning. In addition, this type of contact is similar to the ones typically suffered during in-service conditions, where most contact loads are blunt in nature. The most used blunt indenters are spherical ones because it is easy to obtain spherical indenters (e.g., using bearing balls), the radius of curvature is known and there are no uncertainties in the first initial point with the ceramic. Consequently, we will only refer to spherical indenters for the rest of the chapter.

Spherical indentations are not self-similar, meaning that stresses will change upon load. This provide a methodology to activate different deformation mechanisms with different loads in a single test. At very low loads, the stress will be low and the contact will be elastic. Upon increasing loads, higher stresses will be generated underneath the indenter that will result in inelastic deformation, mainly by the shear stresses produced underneath the indenter. In addition, hoop stresses are produced around the indentation imprint, which can produce a crack in the material, even in full elastic regime. Therefore, spherical contact can produce damage in materials by generating inelastic deformation or by generating a crack in elastic regime.

Equations determining the stresses as a function of load were developed by Hertz in 1886 (Hertz, 1878). These equations shown that, when a sphere of radius R is pressed against a flat solid, the relationship between the contact radius (a) and the load (P) for small penetration depths equals to:

$$a^3 = \frac{3PR}{4E_{eff}} \quad (3)$$

where E_{eff} is the effective modulus between the sample and the indenter, which is defined as:

$$\frac{1}{E_{eff}} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i} \quad (4)$$

with the subscript i indicating the indenter material (for example, $E_i = 1140$ GPa and $\nu_i = 0.07$ for diamond, $E_i = 380$ GPa and $\nu_i = 0.28$ for alumina and $E_i = 450$ – 700 GPa and $\nu_i = 0.21$ – 0.24 for hard metal).

If the tested material has a radius of curvature (R_m), then instead of using the radius of the indentation sphere in the equations, the effective radius of curvature (R') has to be used:

$$\frac{1}{R'} = \frac{1}{R_m} + \frac{1}{R} \quad (5)$$

The mean pressure between the indenter and the material (p_0) is:

$$p_0 = \frac{P}{\pi a^2} = \frac{4E_{eff}}{3\pi} \left(\frac{a}{R} \right) \quad (6)$$

In the case of spherical indentation, by plotting p_0 against a/R , it is possible to display the stress-strain contact relationship. These types of curves are very useful to study the elastic range and the onset of inelastic deformation. However, they have to be treated with care when analysing the plastic region, as it cannot be directly compared with a uniaxial test.

The maximum tensile stress (σ_{tm}) is produced along the contact perimeter of the contact, and equals to:

$$\sigma_{tm} = \frac{1}{2}(1 - 2\nu)p_0 \quad (7)$$

The maximum shear stress (τ_m) is produced beneath the indentation axis at a depth close to $0.5a$, and equals to:

$$\tau_m = 0.46p_0 \quad (8)$$

In most materials, and according to the Tresca criterion, when the value of τ_m reaches a certain limit ($\tau_m = \sigma_y/2$ where σ_y is the yield strength of the material), the material will start to plastically flow and create a permanent deformation, making a transition from an elastic response to an elasto-plastic response. In hard ceramics, instead of plasticity, quasi-plastic damage can be produced.

If the contact is done at small scale, it is possible to activate dislocations at room temperate. Note that, because there are high hydrostatic stresses underneath the indenter, cracking may be hindered and the yield stress can be reached, activating the dislocation movement (Bull *et al.*, 2016; Gaillard *et al.*, 2006a,b; Page *et al.*, 1992; Tromas *et al.*, 2006). However, hard ceramics have high yield stress, and other inelastic deformation mechanisms may be activated before dislocation movement or twin formation are active.

Eqs. (8) and (9) summarize a competition between two stress components which will produce two different types of damage. One stress is tensile at the surface (Eq. 8), and the other is shear beneath the surface (Eq. 9). On the one hand, tensile stresses around the contact area will trigger grow of surface flaws around the indentation to produce a shallow ring crack which will then

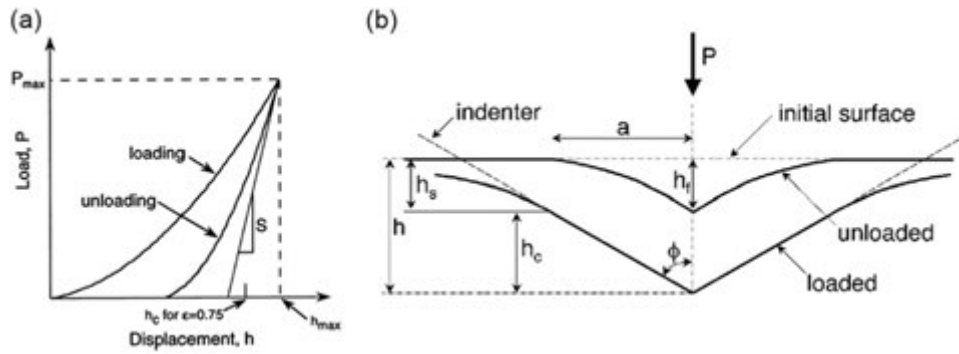


Fig. 1 (a) Typical load-unload curve of an indentation test. (b) Scheme of the indenter contact parameters and the residual imprint.

develop into a cone crack inside the material which will eventually arrest. Note that this is an extremely easy way of introducing a crack in a ceramic material without introducing further damage, which can be useful for studies of structural integrity.

On the other hand, quasi-plastic damage is produced by shear stresses underneath the surface at a depth around $0.5a$. This damage consists in microcracking of the material which will produce an inelastic deformation of the material, and a visible imprint in the surface (Lawn *et al.*, 1994).

These two types of damage are essentially controlled by the geometry of the indenter and the mechanical properties of the material. Indenting with a sphere of small radii will tend to produce quasi-plastic damage or plasticity, while spheres with large radii tend to produce cone cracking. Hard and brittle ceramics are more prone to cone cracking, while more ductile and tough ceramics will suffer quasi-plastic damage before cone cracking.

Therefore, ceramics as glass or porcelain will produce cone cracking, and tough ceramics as zirconia or ceramic composites will quasi-plastically deform. Ceramics such as SiC, Al_2O_3 or Si_3N_4 may present one type of damage or the other depending on the microstructure (particularly the grain size) and the type of indenter used.

Further information on the topic can be found in a devoted article of spherical contact of hard materials in the Comprehensive Hard Materials (Jiménez-Pique *et al.*, 2014a,b) as well as in several excellent reviews in the literature (Basu *et al.*, 2006; Fischer-Cripps and Collins, 1994; Ghaednia *et al.*, 2017; Lawn, 1998; Pathak and Kalidindi, 2015).

Nanoindentation

Instrumented indentation is similar to a hardness test, with the difference that the load and the displacement into the surface of the indenter are continuously measured during both loading and unloading parts of the test. Because of the high spatial resolutions achievable with most experimental equipment, the technique is also known as nanoindentation.

Nanoindentation is now a widespread technique to measure hardness and Young's modulus of materials. However, because of the small volumes probed, it is especially suited to probe coatings, surfaces or small microstructural features as grains, second phases, interfaces or damage surfaces. In addition, using other tips or loading methods, it allows measuring other relevant mechanical properties, as yield strength, creep, friction and, specially, fracturing toughness. Therefore, the technique is extremely versatile and provides a unique toolbox for probing microstructures of ceramics at extremely low scale.

Based on the analysis of the load (P)-displacement (h) curves it is possible to calculate the mechanical properties of the material. Fig. 1 presents an example of a P - h curve as well as the most relevant geometrical parameters used in the next section. The most used analysis used to extract both hardness and Young's modulus of the material is the one based on the work of Oliver and Pharr (1992), which it will be briefly reviewed here. The reader is referred to more extensive review papers in references (Fischer-Cripps, 2006, 2000; Golovin, 2008; Gouldstone *et al.*, 2007; Oliver and Pharr, 2010, 2004; Pharr, 1998; VanLandingham, 2003).

The Oliver and Pharr Method

The Oliver and Pharr method is now extensively used to measure Young's modulus and hardness of a variety of materials, and it is similar to the standard for instrumented indentation ISO 14577. The method is based on calculating the elastic unloading stiffness after fitting the unloading curve with a power law relation:

$$P = \alpha(h - h_f)^m \quad (9)$$

With α and m fitting parameters, and h_f the final depth. Stiffness is calculated as:

$$S = \left. \frac{dP}{dh} \right|_{h_{max}} \quad (10)$$

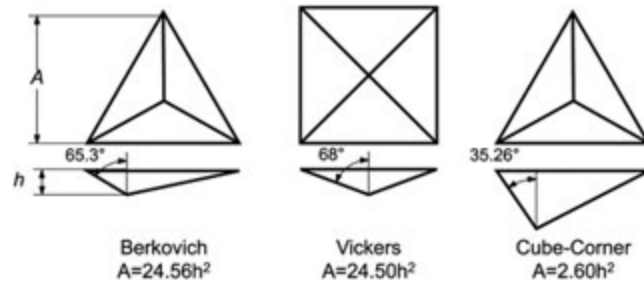


Fig. 2 Scheme of the most common sharp indentation tips, together with their most relevant geometrical parameters.

It has to be said that for hard materials, as ceramics, stiffness can also be estimated as the slope of the first points of the unloading curve without the necessity of adjusting the loading curve with the power law relationship. If stiffness is known, the contact depth (h_c) between the indenter and the sample at maximum load (P_{max} , h_{max}) can be calculated as:

$$h_c = h_{max} - \varepsilon \frac{P_{max}}{S} \quad (11)$$

Once the contact depth is known, the contact area $A(h_c)$ can be calculated. Note the dependency with h_c , as it is not a universal or constant value. This area will depend on the geometry of the indenter used. In nanoindentation testing, the most used indentation tip is a three-side Berkovich indenter, with its relationship between base and area similar to a Vickers tip. Reason for this is because all three-side pyramids end in a single point, while four-side pyramids may end in a vertex if they are not perfectly manufactured (they are not at nanometric level). **Fig. 2** presents a scheme of the most used tips. It has to be considered that tips, specially at low scales, are not perfect and the particular relationship between area and contact depth, $A(h_c)$, should be calibrated against a material with well-known properties (usually fused silica). The function will depend on the particular tip used as manufacturing of tips is not perfect, and will change as the indenter tip is worn with use. Once $A(h_c)$ is known, the hardness and Young's modulus are calculated as:

$$H = \frac{P_{max}}{A(h_c)} \quad (12)$$

and:

$$E_{eff} = \frac{\sqrt{\pi}}{2\beta} \frac{S}{\sqrt{A(h_c)}} \quad (13)$$

Being β a correction factor (usually 1.034) and E_{eff} defined in [Eq. \(4\)](#).

While this method extracts E and H at maximum applied load, acquiring single couple of values per test, it is possible to introduce small unloading cycles in the loading part. By measuring stiffness in the loading part, it is possible to measure H and E as the indenter penetrates the material. The exact way to do this depends on the particular nanoindentation instrument, and usually is different between instruments. This technique is of special interest when material properties change with penetration depth, as in case of coatings, particles or modified surfaces, however, it can be also used to understand elasto-plastic transitions at small scale.

In **Fig. 3**, a nanoindentation test on a single grain of a 3Y-TZP ceramic is presented. The P - h curve is presented, as well as the continuous measurement of both E and H with the continuous stiffness measurement technique. Observe as well that at small penetration depths ($h \approx 60$ nm), the tip is blunt and the contact behavior can be modeled as spherical Hertzian contact (dotted line). The departure from a perfectly sharp tip produces a decrease of apparent Young's modulus and hardness. The maximum in hardness corresponds to the maximum contact stress to generate deformation.

Nanoindentation of Ceramics

Regarding the particular case of ceramics testing by nanoindentation, there are some precautions to be taken. First of all, most advanced ceramics do have a large Young's modulus. This results in a stiff contact and, at sufficient high loads, this contact stiffness will be comparable to the frame stiffness of the testing machine, resulting in a convolution of both stiffness. This may yield erroneous values of both hardness and Young's modulus. While this problem is seldom noticed for compliant materials, it can be relevant for technical hard ceramics even at low loads. For example, nanoindentations in cubic boron nitride at depths as low as 1000 nm produce a contact stiffness in the order of magnitude of 10^6 N/m. Therefore, the frame stiffness of the machine has to be deconvoluted from the results, by measuring it against a material with well know properties (e.g., W single crystals) and subtracting it from the measured stiffness. It is important to use a different material for frame stiffness calibration than for tip shape calibration, as otherwise the measures will interfere with each other.

Another factor to be considered is the exact value of the correction factor β . This correction factor was introduced to account for the lack of axisymmetry of the Berkovich indenters, as well as the large lateral strains induced. In the original paper of [Oliver and](#)

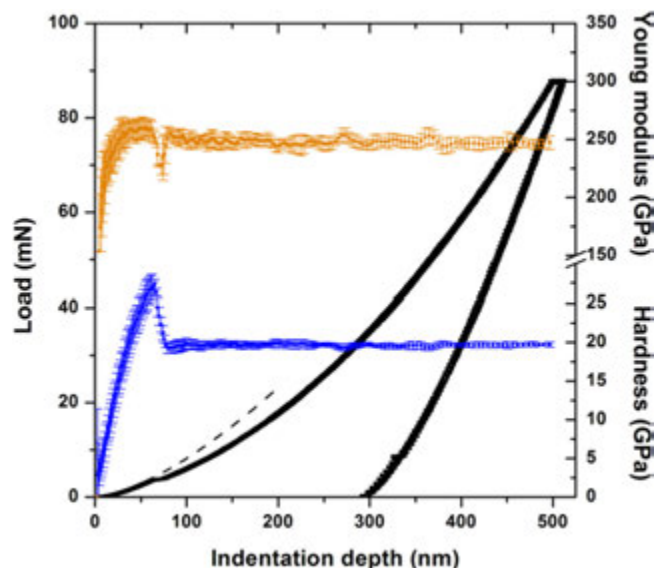


Fig. 3 Nanoindentation of a single grain of zirconia. Load displacement curves as well as hardness and Young's modulus obtained by continuous stiffness measurement are presented. Transition from Hertzian contact due to tip rounding occurs at around 60 nm. Reproduced with permission from Gaillard, Y., Anglada, M., Jimenez-Pique, E., 2009. Nanoindentation of yttria-doped zirconia: Effect of crystallographic structure on deformation mechanisms. *J. Mater. Res.* 24, 719–727. doi:10.1557/JMR.2009.0091.

Pharr (1992), the value of β was 1.034, and it is still a largely used quantity. However, there is still an open debate on the value of this correction, with proposed values ranging between 1 and approximately 1.3 (Cao *et al.*, 2007; Hay *et al.*, 1999; Larsson *et al.*, 1996; Xu and Li, 2008). Evenmore, this correction factor may not be universal, but dependent on the Poisson ratio of the indented material. For example Larsson *et al.* (1996) propose the following correction for the correction factor β :

$$\beta = 1.2304 \cdot (1 - 0.21\nu - 0.01\nu^2 - 0.41\nu^3) \quad (14)$$

Note that the value of the correction factor has an immediate consequence on the value of Young's modulus, and may yield higher values of Young's modulus than expected. For example, typical values of Young's modulus reported in the literature for zirconia ceramics (3Y-TZP) are around 240 GPa using the correction value of 1.034 (Cattani-Lorente *et al.*, 2016; Gaillard *et al.*, 2009; Rayón *et al.*, 2013). Use of a correction factor of 1.122 will yield values of 220 GPa instead, closer to the ones reported by other techniques.

Contact area in ceramic materials is normally well estimated with no pile up typical of softer materials as metals or polymers, but it is a good practice to observe the indentation imprints, specially to observe if microcracking, phase transformation, decohesion or other non-plastic events have taken place, which will, of course, produce inaccurate values of the mechanical properties.

As a final point, it is important to perform the measurements in a well-polished surface. If the tested surface is rough, this will result in a large scattering in the measured values and accordingly an uncertainty in the measured values. For ceramics, standard polishing with diamond paste until mirror finish should suffice for most measurements, without the need for extreme flatness required in other techniques (e.g., atomic force microscopy or EBSD).

Measuring the Intrinsic Properties of Coatings

Ceramic coatings are widely used in many industrial applications because of their wear resistance, chemical resistance and thermal properties. Applications range from hard coatings in the tool industry, to biomedical coatings or thermal protections. Because of the small thickness of the coatings, the best tool to measure the mechanical properties is by nanoindentation. However, and especially if the coating is thin, the measure can be a convolution of both the mechanical properties of the coating and the substrate. Deconvoluting the substrate-coating response is, therefore a requirement to properly measure the ceramic coatings.

The measurement of hardness is confined to the region of the plastic deformation. Although this volume varies for different materials; for ceramics, it is usually less than ten times the penetration depth, a little bit larger than the size of the diagonal of the indentation imprint, as a rule of thumb. Due to this, it is generally accepted that, if the penetration depth of the indentation is less than one tenth the thickness of the coating, the measured hardness is the true hardness of the coating. This is known as the "10% rule".

Fig. 4 presents cross-sections of a DLC coating on a hard metal. This coating was around 2000 nm thick. When an indentation was done up to 1000 nm maximum penetration depth, the substrate was also deformed and, consequently, the measured hardness was a combination of both substrate and coating. If the indentation was done until 100 nm maximum penetration depth, all deformation was constrained in the coating and the measured hardness value was the true coating hardness value.

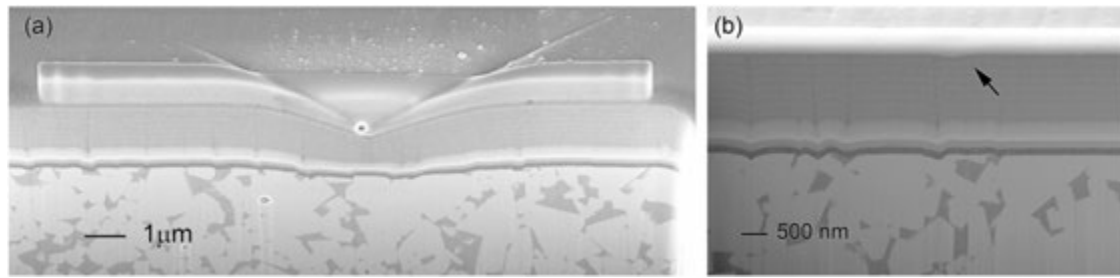


Fig. 4 Nanoindentations on a DLC coating on a cemented carbide. (a) When indenting up to 1000 nm maximum depth, both coating and substrate deform plastically. (b) At 100 nm maximum penetration depth, all plastic deformation is confined in the material. The residual imprint is indicated with an arrow.

If it is not possible to apply the 10% rule, there are several models to deconvolute the combined response of the experimental measurements in order to extract the hardness of the coating, assuming that the thickness of the coating is known as well as the mechanical properties of the substrate, adjusting through analytical formulas (Bhattacharya and Nix, 1991; Chicot and Lesage, 1995; Jönsson and Hogmark, 1984) or parametric adjustments (Korsunsky *et al.*, 1998; Puchi-Cabrera *et al.*, 2002).

In case of Young's modulus, the problem is similar, but with the difference that elastic fields are broader than plastic fields. This implies that when the material is indented a much larger volume of material is probed. As a consequence, the "10% rule" cannot be applied. That is, even if the penetration depth of the indentation is less than 10% of the coating thickness, the measured Young's modulus will be also affected by the elastic properties of the substrate. Only very shallow indentations (in the order of 1% of the coating thickness) are able to probe with reliability of the Young's modulus of the coating without the influence of the substrate. These shallow indentations are not easy to perform, and extremely sharp tips should be used to avoid tip rounding effects.

In this case, the use of models to extract the Young's modulus of the coating is recommended. There are several methods proposed in the literature (Bec *et al.*, 2006; Hay and Crawford, 2011; Jäger, 2002; Rar *et al.*, 2002; Saha and Nix, 2002), but most of them yield similar results if no large penetration depths are used and the differences in mechanical properties between coating and substrate are not extreme. Most of them are valid only for indentation depth below the coating thickness. In this sense, Fig. 5 presents the adjustment by different models of a nanoindentation of a 500 nm thick mullite coating on SiC (Botero *et al.*, 2012b). It can be seen how the produced results of the different models are similar, if the indentation is confined inside the coating. Once the indentation reaches the interface with the substrate, models diverge and fail.

Therefore, although use of various models to analyze experimental data is advised to generate robust results, use of a single model can yield good results. Even, in some cases, if the data comes from a continuous stiffness measurement and Young's modulus is measured continuously with penetration, a good estimation of the Young's modulus of the coating can be made just by extrapolating the measure of Young's modulus to zero penetration depth, as proposed in ISO 14577.

Measuring Single Grains

Measuring the mechanical properties of single grains or particles is especially relevant in ceramic composites such as alumina-zirconia, cermets or CBN composites, among others. In this case, the way to proceed to isolate the mechanical properties of a single particle is similar to the way coatings are measured, and numerical models may be used.

However, there are more uncertainties inherent to this type of measurement. First of all, the diameter of the indented particle at the surface may be known, but its exact depth is unknown. This depth may be measured by post-mortem cross-sectioning by, e.g., FIB, but it is experimentally cumbersome. Another way to proceed is to indent several particles and apply a thin film model to the average of the mechanical responses and the average of the particle diameter.

Another approach to follow, if one of the phases has known properties, is to perform a larger amount of nanoindentations at random. As the response will be a contribution of both phases, applying a rule of mixtures (Reuss and Voigt) will give upper and lower values of the second phases. This approach is similar to the massive nanoindentation approach described latter.

When applying thin film models in this context, it has to be taken into account that the elasto plastic properties will be affected by the whole matrix surrounding it. That is, not only the material below the particle may affect the response, as in the case of coatings, but also the surrounding material may have an effect, albeit small, in the mechanical response. In this case, a modified thin film model may be used to take this contribution explicitly into account, as the one proposed by (Botero *et al.*, 2012a) after the model of (Hay and Crawford, 2011).

Statistical Nanoindentation

Modern nanoindentation instruments have increased dramatically the speed of indentations, with current commercial instruments performing a single indent as fast as one per second. Previous generation of machines had speeds in the order of one indentation

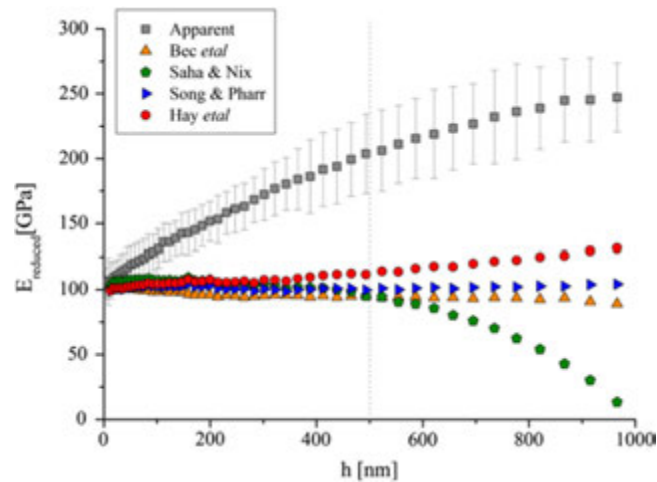


Fig. 5 Nanoindentation of a mullite coating on SiC. The coating thickness is indicated with a dotted line. The experimental data show an apparent Young's modulus that increase with depth, result of the convolution of the response of both the coating and substrate. Models proposed by (Bec *et al.*; Hay and Crawford; Rar *et al.*; Saha and Nix), are used to extract the Young's modulus of mullite ($E = 100$ GPa). Models produce similar results, but diverge when using data obtained for larger penetration depths than the coating thickness. Proposed by Bec, S., Tonck, A., Loubet, J.L., 2006. A simple guide to determine elastic properties of films on substrate from nanoindentation experiments. *Philos. Mag.* 86, 5347–5358. doi:10.1080/14786430600660856. Hay, J., Crawford, B., 2011. Measuring substrate-independent modulus of thin films. *J. Mater. Res.* 26, 727–738. doi:10.1557/jmr.2011.8. Rar, A., Song, H., Pharr, G.M., 2002. Assessment of new relation for the elastic compliance of a film-substrate system. *MRS Online Proc. Libr.* 695, 431–436. Saha, R., Nix, W.D., 2002. Effects of the substrate on the determination of thin film mechanical properties by nanoindentation. *Acta Mater.* 50 (1), 23–38. Reproduced with permission from Botero, C.A., Jiménez-Piqué, E., Seuba, J., *et al.*, 2012b. Mechanical behavior of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ films under nanoindentation. *Acta Mater.* 60, 5889–5899. doi:10.1016/j.actamat.2012.07.031.

per ten minutes. This high speed allows to produce a large amount of indentations in a reasonable amount of time, with the advantage of allowing for a statistical interpretation of the results obtained, especially when different phases exist in the material, as well as the possibility to generate property maps of a surface (Tromas *et al.*, 2010). This eliminates the necessity of selecting the phase of interest and the potentially laborious procedure as outlined before.

While there is many statistical techniques available, one of the most used ones is the method applied by Constantinides *et al.* (2003), Ulm *et al.* (2007). This method is based on assuming that the existing phases follow a Gaussian distribution of the values of hardness and Young's modulus. The method is relatively easy to perform, although it assumes that the scattering in properties is purely Gaussian.

As an example, Fig. 6 presents the results of statistical massive nanoindentation on a WC – cobalt hard metal (Roa *et al.*, 2015). It is seen how the technique is able to discern, not only between the metallic phase and the ceramic grains, but also on the differences on hardness on the prismatic and basal crystal orientations.

Porosity

Porosity is an important feature in ceramics, being this porosity made on purpose or as a consequence of processing. Even small amounts of porosity can influence the mechanical response under indentation. Understanding the effect of the porosity in this response is important not only to correct the results but also as a tool to quantify the amount of porosity in the material.

There are several formulas in the literature to account for the reduction of mechanical properties with porosity. For small amounts of porosity even a linear relationship is sometimes used, however it is more common to relate the change in properties with an exponential law. In case of Young's modulus, this reads as (He *et al.*, 2008; Amorós *et al.*, 2020):

$$E = E_0 \exp(-\gamma P) \quad (15)$$

Where E_0 is the elastic modulus of a pore-free material, P is the pore volume fraction and γ is an adjustment parameter.

If pores are not spherical, the formula proposed by Luo and Stevens can be used (Chintapalli *et al.*, 2012; Luo and Stevens, 1999, 1996):

$$E = E_0 \frac{1 - P}{1 + \alpha P} \quad (16)$$

Where α is a parameter that depends on the shape of the pores. This parameter is $\alpha = 1$ in case of spherical pores.

This model assume an elastic behavior of the pores, that is, the material does not collapse under indentation, and the shape of the pores remains the same after the test. Of course, for materials that are brittle or have a high amount of porosity this does not happen. In this case, more complex analysis have to be performed to deconvolute the effect of the porosity (Chen *et al.*, 2006; Ko *et al.*, 2006).

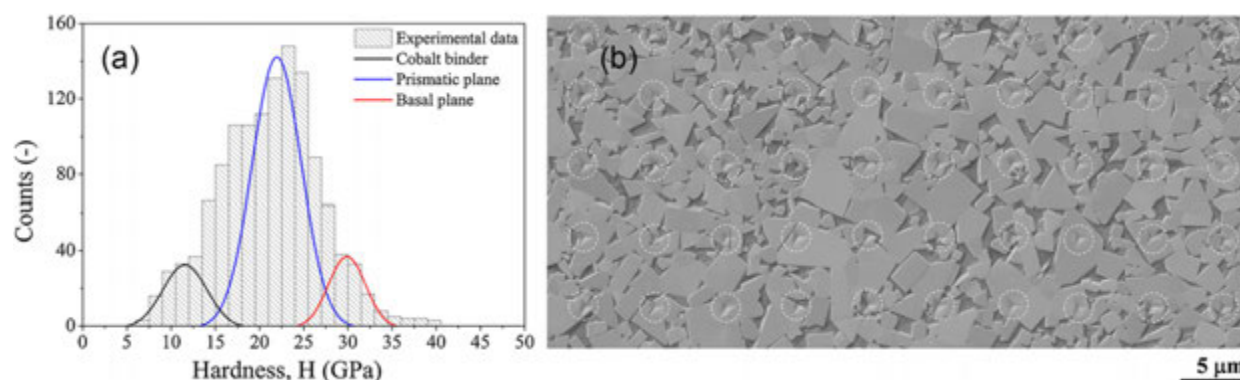


Fig. 6 Statistical nanoindentation on a WC-Co hard metal. A matrix of indentations is made and the data is latter treated to extract the mechanical properties of both orientations of WC gains as well as the cobalt phase. Reproduced with permission from Roa, J.J., Jimenez-Pique, E., Verge, C., *et al.*, 2015. Intrinsic hardness of constitutive phases in WC-Co composites: Nanoindentation testing, statistical analysis, WC crystal orientation effects and flow stress for the constrained metallic binder. *J. Eur. Ceram. Soc.* 35, 3419–3425. doi:10.1016/j.jeurceramsoc.2015.04.021.

Weak Interfaces

The same reasoning is applied to materials that have weak interfaces. This is specially the case of ceramic coatings with columnar structures, typical of PVD or CVD process, for example thermal barrier coatings for gas turbines. In this case, relative sliding between columns will result in an immediate drop in mechanical properties at shallow penetration depths (much earlier than reaching the 10% of the penetration depth) (Botero *et al.*, 2012a,b; Gaillard *et al.*, 2007, 2006a,b). This can be seen in Fig. 7 where the nanoindentation of top of an 8%Y₂O₃-ZrO₂ thermal barrier coating produced by EB-PVD and APS is presented. EB-PVD produces a columnar microstructure, while APS produces a splat-like microstructure. The coating is 200 μm thick, but elastic modulus decreases sharply even in the first stages of contact loading. For large penetration depths, the asymptotic value of *E* is 100 GPa. However, the Young's modulus of zirconia measured by nanoindentation is 240 GPa, which lowers to 190 GPa once the microporosity is taken into account. The sharp decrease of Young's modulus is then attributed to the weak interfaces between columns (EB-PVD) and splats (APS) that result in partial displacement between microstructural features.

A similar effect can be seen in Fig. 8, where Young's modulus vs. penetration depth of a columnar TiO₂ coating on silicon substrate is presented. In this case different glancing angles are used to produce slanted columns. Although column size and density were similar for the three angles presented, the incidence angle had a clear influence in the measured value.

Therefore, it is important to consider the possible weak interfaces in the material, as they will largely impact in the mechanical response. Understanding the precise deformation mechanisms is not trivial, and depends strongly on the type of material and the nature of the weak interfaces. Hence, it is usually necessary to perform further in-depth studies by microscopy techniques.

Degraded Surfaces

Upon service, materials may be subjected to degradation by many causes, including wear, corrosion, radiation or environment interactions. This mainly affects the surface of the material, changing its chemical composition, its crystallography, its plasticity or generating microcracking. This degraded surface has different mechanical properties of the rest of the bulk, and can have detrimental effects on the structural integrity and reliability of the material under service. Because it is generally well confined in the first microns of the surface, nanoindentation is especially suited to measure this degraded layer.

The approach generally used is to consider the degraded layer as a coating with different properties as the bulk material, and then applying the techniques and considerations described before for coatings (Afrasiabi and Kobayashi, 2013; Zheng *et al.*, 2019). However, it has to be taken into account that roughness may have increased during the degradation process and polishing may be necessary to produce data with higher reliability.

Fig. 9 presents the result of nanoindentation performed on zirconia (3Y-TZP) subjected to low temperature degradation (Botero *et al.*, 2015; Gaillard *et al.*, 2008; Muñoz-Tabares *et al.*, 2011a). During this degradation, the metastable tetragonal phase reverts to monoclinic phase, producing microcracking due to the slightly higher volume of the monoclinic phase. By indentation it is possible to measure the properties of the degraded layer as well as the thickness of the degradation surface as a function of the degradation time just by considering the degraded layer as a coating. Measuring the degradation by this technique has the advantage of probing a small volume, so spatial resolution is higher than other spectroscopic techniques.

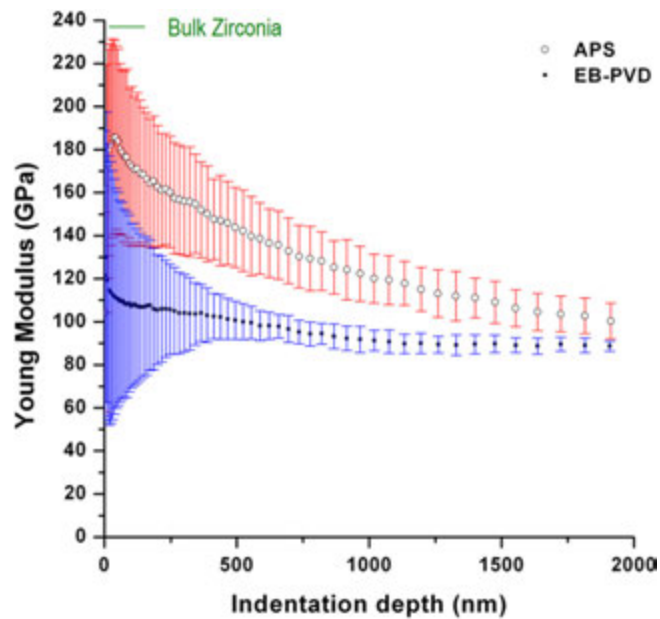


Fig. 7 Evolution of the Young's modulus as a function of the penetration depth of the indenter for APS and EB-PVD thermal barrier coatings. Weak interfaces in the microstructure produce a significant decrease in Young's modulus even at low penetration depths (below 1% of the coating thickness).

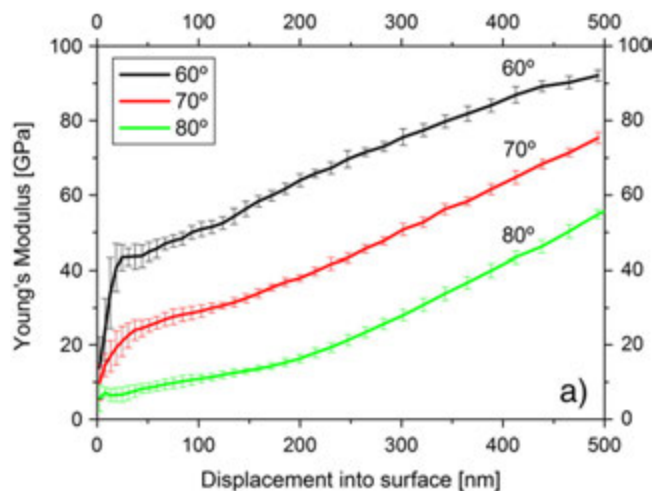


Fig. 8 Young's modulus of TiO_2 coating. While composition and density is similar, the different orientation of the columns produce a significant difference in the nanoindentation measurement. Reproduced with permission from Jiménez-Piqué, E., González-García, L., Rico, V.J., González-Elípe, A.R., 2014b. Nanoindentation of nanocolumnar TiO_2 thin films with single and stacked zig-zag layers. *Thin Solid Films* 550, 444–449. doi:10.1016/j.tsf.2013.10.022.

Fracture Toughness by Indentation

Indentation can also be used to estimate the fracture toughness of ceramics. Because of the high hardness of ceramics, upon application of load, the strain energy accumulated by the inelastic deformation can be released by fracture. This opens the door to measure fracture toughness in an easy way, without much sample preparation and in a local level (Lawn and Wilshaw, 1975; Leonardi *et al.*, 2009; Morrell, 2006; Ostojic and McPherson, 1987).

The method is based in measuring the lengths of the cracks produced at the vertex of the indentations at a given load. Vickers indenters are normally used at 50 kg load. Cube corner indenters are used in nanoindentation tests at smaller loads. Other indenters (e.g., Knoop) can also be used as well. Fig. 10 presents an image of cracks produced in different materials by cube corner nanoindentation.

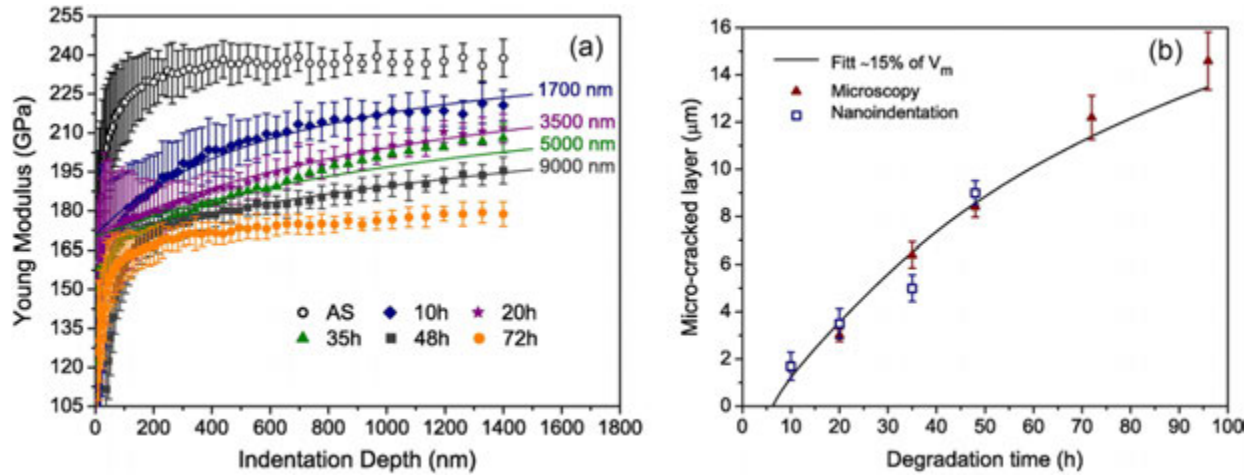


Fig. 9 (a) Nanoindentation of a low temperature degraded zirconia, up to 72 h in autoclave. Observe how the mechanical response diminish with degradation time. (b) By adjusting a thin-film model to the nanoindentation response, it is possible to evaluate the depth of the degradation, corroborated by micro-Raman microscopy and cross-section observations. Reproduced with permission from Muñoz-Tabares, J.A., Jiménez-Piqué, E., Anglada, M., 2011a. Subsurface evaluation of hydrothermal degradation of zirconia. *Acta Mater.* 59, 473–484. doi:10.1016/j.actamat.2010.09.047.

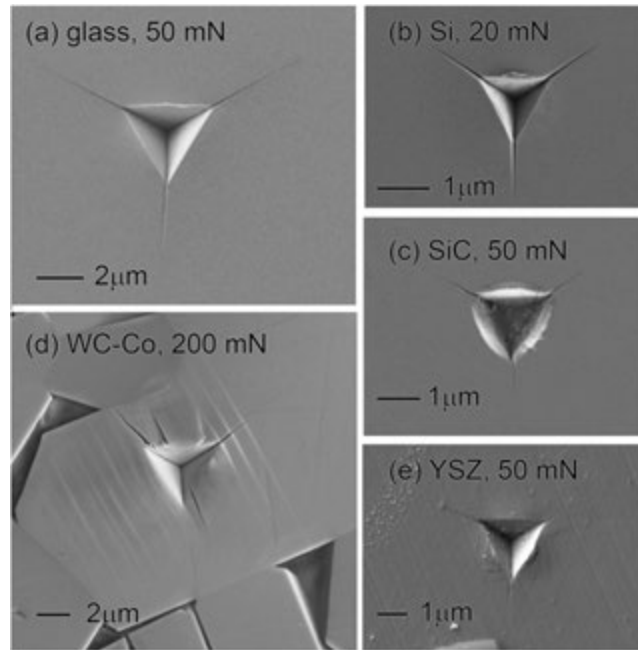


Fig. 10 Cube corner indentation, at different loads of (a) Soda-lime-glass, (b) Silicon single crystal, (c) Silicon Carbide single crystal (d) a WC grain of a hard metal, (e) YSZ single crystal. Observe how the cracks emanate from the vertex in the case (a) to (c), while deviations from the model occur in (d) and (e). Reproduced with permission from Cuadrado, N., Seuba, J., Casellas, D., Anglada, M., Jiménez-Piqué, E., 2015. Geometry of nanoindentation cube-corner cracks observed by FIB tomography: Implication for fracture resistance estimation. *J. Eur. Ceram. Soc.* 35, 2949–2955. doi:10.1016/j.jeurceramsoc.2015.03.031.

The most used formula to calculate fracture toughness is the one originally proposed by [Anstis et al. \(1981\)](#):

$$K_{Ic} = \xi \left(\frac{E}{H} \right)^{1/2} \frac{P}{c^{3/2}} \quad (17)$$

where E is the Young's modulus, H is the hardness, P is the indentation load and $2c$ is the total crack length (i.e., $c = l + a$, where l is the length of the crack from the indentation corner, and $2a$ is the indentation diagonal) and ξ is a material constant calibrated against materials with well-known fracture toughness, with a generally accepted value of $\xi = 0.016$. See [Fig. 11](#) for a graphical description of the geometric parameters.

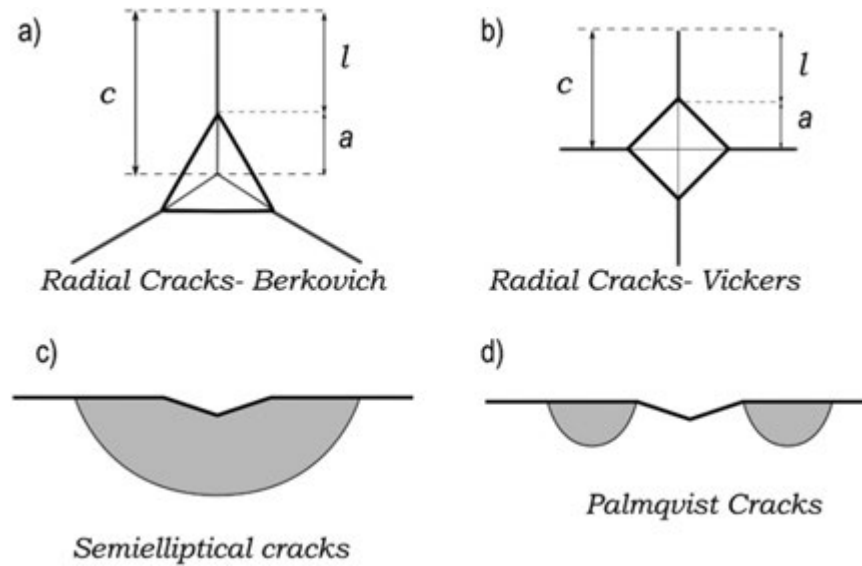


Fig. 11 (a) Scheme of a cube corner indentation with cracks. (b) Scheme of a cube corner indentation with cracks. (c) Cross section of an indentation that induces a semielliptical crack (d) Cross section of an indentation that induces a semielliptical crack. Reproduced with permission from Cuadrado, N., Seuba, J., Casellas, D., Anglada, M., Jiménez-Piqué, E., 2015. Geometry of nanoindentation cube-corner cracks observed by FIB tomography: Implication for fracture resistance estimation. *J. Eur. Ceram. Soc.* 35, 2949–2955. doi:10.1016/j.jeurceramsoc.2015.03.031.

The model assumes that the produced cracks are half-penny (semi-circular), and that no other energy dissipation is activated during indentation. In order to fulfill Anstis equation, the cracks have to be far away of the indentation to not be affected by the residual stresses, so the crack length has to be sufficient large to fulfill $c > 3a$.

The mechanism responsible of crack generation is as follows. Upon indentation, an inelastic deformation is generated under the indenter. This deformation is in compression, but induces tensile stresses in the surrounding volume. This tensile stresses ultimately generate a crack from the vertex which grows and ultimately arrest as the residual stresses decrease away from the indentation.

Fig. 12 presents an experimental FIB tomography of this process in soda lime glass. This tomography was done for cube corner indenters under nanoindentation but follows the same mechanisms as Vickers indentations (Cuadrado *et al.*, 2015). In this series of images, it is seen how a crack is produced underneath the indenter and propagates away of the indentation. The crack is alienated with the vertex of the indentation. As the load is increased, the length of these cracks is also increased. Observe as well that the cracks do not grow underneath the indenter, because in this region the residual stresses are compressive and, consequently, the stress intensity factor reverses sign and the crack cannot open. It is also interesting to point out that, although the indentation is performed in a well-behaved material, secondary cracks also appear.

It is important to understand that indentation can produce cracks with very different geometries, depending on the load and the type of material. A review of the shape of the cracks produced by indentation can be found in (Cook and Pharr, 1990).

There are other formulas to evaluate K_{Ic} in case other crack shapes are produced. If Palmqvist cracks are produced (see Fig. 11), the formula proposed by Laugier can be used:

$$K_{Ic} = \chi \left(\frac{l}{a} \right)^{-1/2} \left(\frac{E}{H} \right)^{2/3} \frac{P}{c^{3/2}} \quad (18)$$

Where χ is a material parameter equal to $\chi = 0.015$. However, the equation can be applied only as far as the ratio between crack length and indentation semi-diagonal are in a specific range [26]. The crack length should obey the requirement of $0.25a < l < 2.5a$. This type of Palmqvist cracks are typical of tough ceramics, with values in the order of 4–10 MPa m^{1/2}.

The same methodology can be used for nanoindentation tests. In order to induce cracking at lower loads, that is, in smaller regions of interest, a cube-corner indenter is used instead of Vickers or Berkovich indenters. The reason is that for this more acute tip, the residual stress generated by the deformed material underneath the nanoindentation imprint is larger, and, hence will produce cracking at much lower loads (in the order of mN for most brittle materials).

In case of cube-corner tips, the same formulas can be applied, but the material parameters ξ and χ have to be modified to $\xi = 0.026$ and $\chi = 0.057$, respectively (Cuadrado *et al.*, 2012).

There are several variations of these two equations, mainly on the value of the material parameter constant or the effect of the E/H ratio (Evans and Charles, 1976; Laugier, 1987; Ponton, 1985; Ponton and Rawlings, 1989) or the ellipticity of the cracks produced (Smith and Scattergood, 1992), as well as residual stress (Marshall and Lawn, 1977). In this case, assuming that the cracks are half-penny, the measured fracture toughness is affected by the surface residual stresses, as they will tend to close the crack and make it shorter (if compressive) or open it and, consequently, make it larger (if tensile):

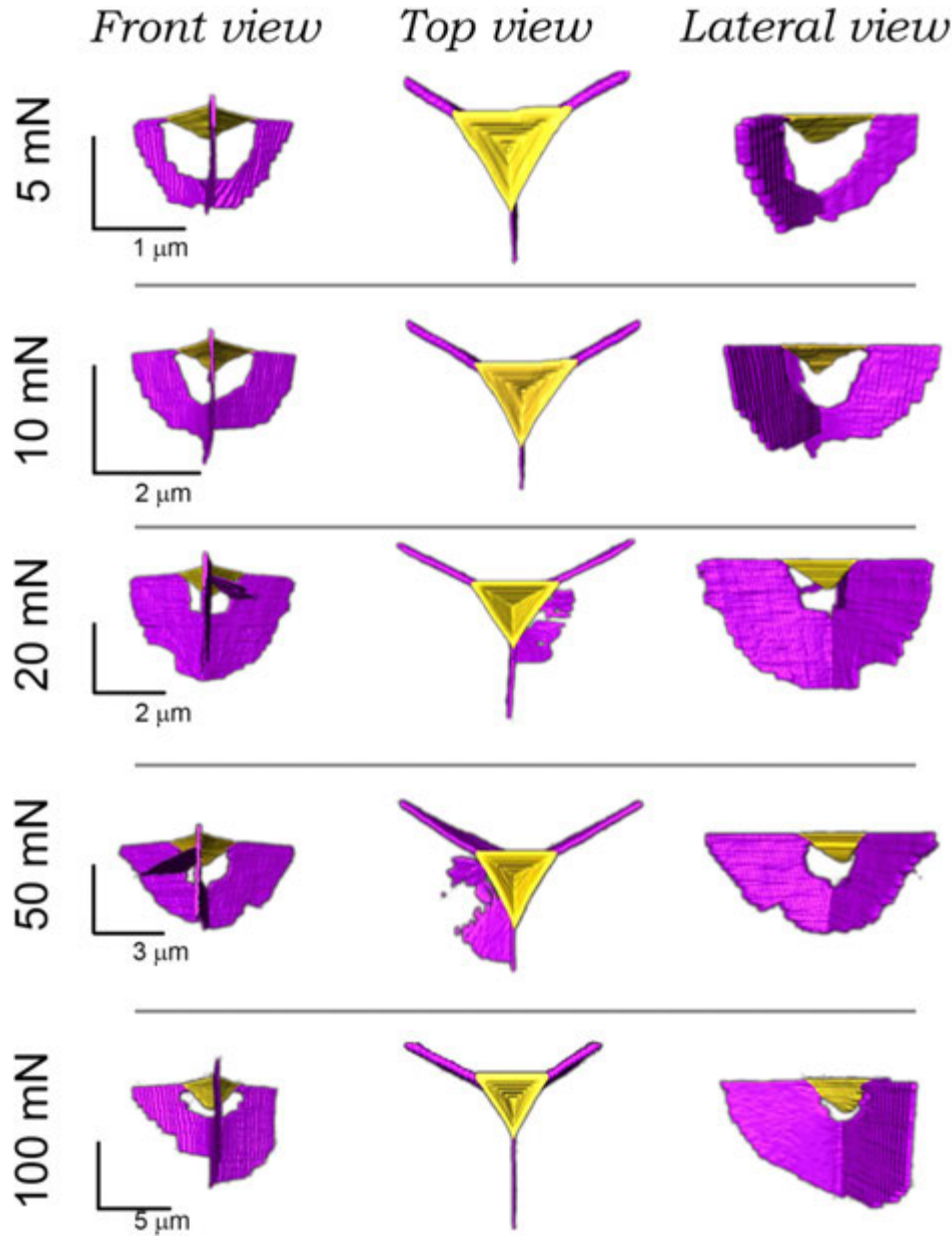


Fig. 12 Tomography of the cracks produced by cube-corner nanoindentations in soda-lime glass. Indentation imprints are colored in yellow, and cracks in magenta. Reproduced with permission from Cuadrado, N., Seuba, J., Casellas, D., Anglada, M., Jiménez-Piqué, E., 2015. Geometry of nanoindentation cube-corner cracks observed by FIB tomography: Implication for fracture resistance estimation. *J. Eur. Ceram. Soc.* 35, 2949–2955. doi:10.1016/j.jeurceramsoc.2015.03.031.

$$K_{Ic} = \xi \left(\frac{E}{H} \right)^{1/2} \frac{P}{c^{3/2}} + \psi \sigma_R \sqrt{c} \quad (19)$$

Where σ_R is the residual stress, and ψ is a geometric factor ($\psi = 1.29$ for a half-penny crack configuration). Observe how this formula provides a tool to measure residual stresses in the material, provided that the fracture toughness of the stress-free material is known (Pavon *et al.*, 2006). Fig. 13 shows an example of measurement of the residual stresses produced by grinding of 3YTZP (Muñoz-Tabares *et al.*, 2011b). In this case, for measuring the residual stress profile in depth, the ground surface was carefully polished away at a controlled depth while performing indentations at each step. As the material was removed, the cracks were becoming larger, indicating that the compressive residual stresses were decreasing with depth. Once the cracks are measured at each step, the residual stress profile can be quantified through formula (Eq.19).

In conclusion, indentation is a very powerful to estimate fracture toughness in ceramics. It is relatively easy to perform, especially compared to other techniques, where a crack of a given length has to be introduced in a sample of the material of

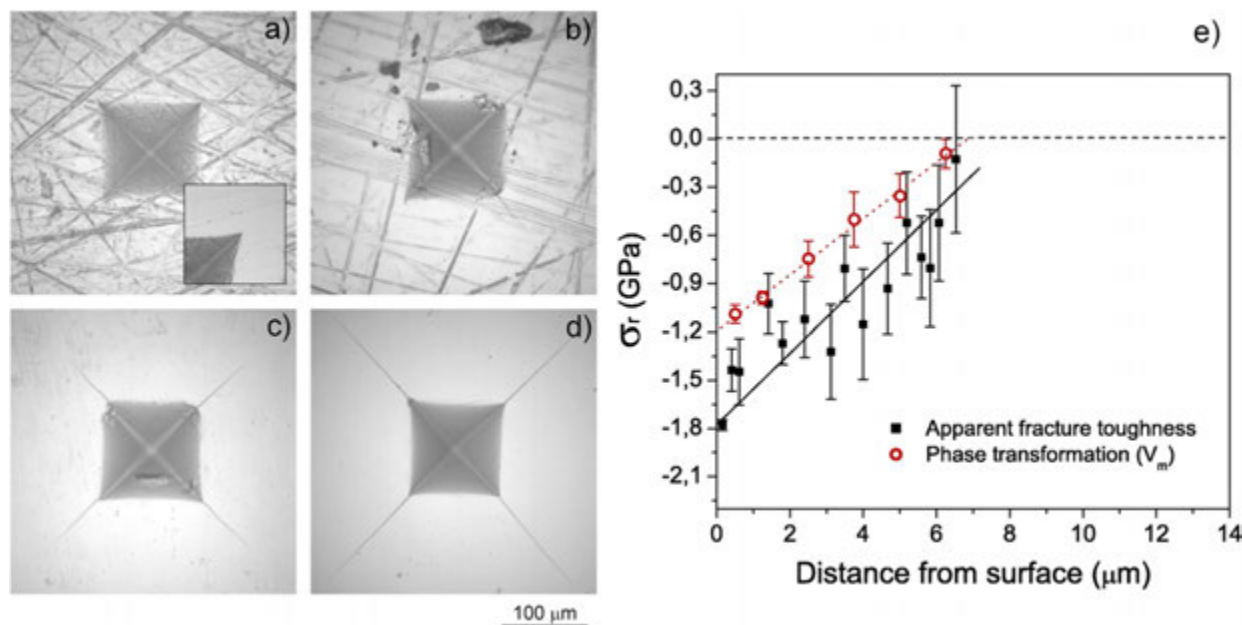


Fig. 13 Vickers indentations on ground zirconia. Residual stresses are calculated after measuring the crack lengths produced at different depths, available after controlled polishing (a–d). Residual stress calculation after formula (19) (e). Reproduced with permission from Muñoz-Tabares, J.A., Jimenez-Pique, E., Reyes-Gasga, J., Anglada, M., 2011b. Microstructural changes in ground 3Y-TZP and their effect on mechanical properties. *Acta Mater.* 59, 6670–6683. doi:10.1016/j.actamat.2011.07.024.

controlled geometry (for example single edge V-notched beams test). In addition, the indentation technique is local, so small volumes of interest can be measured, as grains, or stressed surfaces.

However, this method has received some criticism (Flanders *et al.*, 2003; Marshall *et al.*, 2015; Quinn and Bradt, 2007), as it often fails to provide a reliable value of fracture toughness. First of all, it has to be understood that what is really measuring the method is an indentation micro-fracture resistance of the material, which is translated into fracture toughness through the material parameters ξ and χ and the E/H relationship. Uncertainty in these values result in a not precise values of K_{Ic} .

Second, and most important, these models assume that the produced cracks have controlled geometries. However, not all materials behave that way. Some indentations in ceramic materials produce a variety of secondary cracks or bifurcation of cracks at the vertex of the tips or even spallation.

Third, the model assumes that the materials are isotropic and elasto-plastic. This means that it is not valid for porous ceramics or ceramic with weak interfaces that are able to dissipate energy by sliding. In fact, indenting a porous ceramic will produce little or no cracks at the vertex of the indentation imprint, but this does not imply that the fracture toughness is high (Melk *et al.*, 2015). Even more, indentation in highly transformable ceramics (as ceria-doped ceramics) may result in an overestimation of the real fracture toughness of this type of materials (Reveron *et al.*, 2017).

In conclusion, the method is versatile, easy to perform, and extremely good to probe small regions of the material. However, care has to be taken to be sure that all assumptions are met in order to measure with confidence fracture toughness. But, although an exact value of fracture toughness may not be measured, a good estimation can be provided, which can be extremely useful specially to compare similar materials.

Summary

Indentation is a very versatile, easy to implement and powerful tool to probe the mechanical properties of the surface of the ceramic materials, with local resolution. The use of different shapes of indenters allows testing different behaviors of the material. With instrumented indentation, the resolution and flexibility are further increased. In addition, indentation microfracture, if properly performed, permits the measurement of fracture toughness of ceramics.

Acknowledgments

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References

- Afrasiabi, A., Kobayashi, A., 2013. Hot corrosion control in plasma sprayed YSZ coating by alumina layer with evaluation of microstructure and nanoindentation data (H, E). *Vacuum* 88, 103–107. doi:10.1016/j.vacuum.2012.03.024.
- Amorós, J.L., Blasco, E., Moreno, A., Feliu, C., 2020. Mechanical properties obtained by nanoindentation of sintered zircon–glass matrix composites. *Ceram. Int.* 46, 10691–10695. doi:10.1016/j.ceramint.2020.01.075.
- Anstis, G.R., Chantikul, P., Lawn, B.R., Marshall, D.B., 1981. A critical evaluation of indentation techniques for measuring fracture toughness: I, Direct crack measurements. *J. Am. Ceram. Soc.* 64, 533–538.
- Basu, S., Moseson, A., Barsoum, M., 2006. On the determination of spherical nanoindentation stress-strain curves. *J. Mater. Sci.* 21, 2628–2637. doi:10.1557/JMR.2006.0324.
- Bec, S., Tonck, A., Loubet, J.L., 2006. A simple guide to determine elastic properties of films on substrate from nanoindentation experiments. *Philos. Mag.* 86, 5347–5358. doi:10.1080/14786430600660856.
- Bhattacharya, A.K., Nix, W.D., 1991. Finite element analysis of cone indentation. *Int. J. Solids Struct.* 27, 1047–1058. doi:10.1016/0020-7683(91)90100-T.
- Botero, C.A., Jiménez-Piqué, E., Baudín, C., Salán, N., Llanes, L., 2012a. Nanoindentation of $\text{Al}_2\text{O}_3/\text{Al}_2\text{TiO}_5$ composites: Small-scale mechanical properties of Al_2TiO_5 as reinforcement phase. *J. Eur. Ceram. Soc.* 32, 3723–3731. doi:10.1016/j.jeurceramsoc.2012.05.034.
- Botero, C.A., Jiménez-Piqué, E., Seuba, J., *et al.*, 2012b. Mechanical behavior of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ films under nanoindentation. *Acta Mater.* 60, 5889–5899. doi:10.1016/j.actamat.2012.07.031.
- Botero, C.A., Jiménez-Piqué, E., Martín, R., *et al.*, 2015. Influence of temperature and hard corrosion on the micro–nanomechanical behavior of protective mullite EBCs. *Int. J. Refract. Met. Hard Mater.* 49, 383–391. doi:10.1016/j.jrmhm.2014.09.025.
- Bull, S.J., Moharrami, N., Hainsworth, S.V., Page, T.F., 2016. The origins of chemomechanical effects in the low-load indentation hardness and tribology of ceramic materials. *J. Mater. Sci.* 51, 107–125. doi:10.1007/s10853-015-9412-3.
- Cao, Y.P., Dao, M., Lu, J., 2007. A precise correcting method for the study of the superhard material using nanoindentation tests. *J. Mater. Res.* 22, 1255–1264. doi:10.1557/jmr.2007.0150.
- Cattani-Lorente, M., Durual, S., Amez-Droz, M., Anselm Wiskott, H.W., Scherrer, S.S., 2016. Hydrothermal degradation of a 3Y-TZP translucent dental ceramic: A comparison of numerical predictions with experimental data after 2 years of aging. *Dent. Mater.* 32, 394–402. doi:10.1016/j.dental.2015.12.015.
- Chen, X., Xiang, Y., Vlassak, J.J., 2006. Novel technique for measuring the mechanical properties of porous materials by nanoindentation. *J. Mater. Res.* 21, 715–724. doi:10.1557/jmr.2006.0088.
- Chicot, D., Lesage, J., 1995. Absolute hardness of films and coatings. *Thin Solid Films* 254 (1–2), 123–130.
- Chintapalli, R.K., Jiménez-Piqué, E., Marro, F.G., *et al.*, 2012. Spherical instrumented indentation of porous nanocrystalline zirconia. *J. Eur. Ceram. Soc.* 32, 123–132. doi:10.1016/j.jeurceramsoc.2011.07.037.
- Constantinides, G., Ulm, F.-J., Van Vliet, K., 2003. On the use of nanoindentation for cementitious materials. *Mater. Struct.* 36, 191–196. doi:10.1007/bf02479557.
- Cook, R.F., Pharr, G.M., 1990. Direct observation and analysis of indentation cracking in glasses and ceramics. *J. Am. Ceram. Soc.* 73, 787–817. doi:10.1111/j.1151-2916.1990.tb05119.x.
- Cuadrado, N., Casellas, D., Anglada, M., Jiménez-Piqué, E., 2012. Evaluation of fracture toughness of small volumes by means of cube-corner nanoindentation. *Scr. Mater.* 66, 670–673. doi:10.1016/j.scriptamat.2012.01.033.
- Cuadrado, N., Seuba, J., Casellas, D., Anglada, M., Jiménez-Piqué, E., 2015. Geometry of nanoindentation cube-corner cracks observed by FIB tomography: Implication for fracture resistance estimation. *J. Eur. Ceram. Soc.* 35, 2949–2955. doi:10.1016/j.jeurceramsoc.2015.03.031.
- Evans, A.G., Charles, E.A., 1976. Fracture toughness determinations by indentation. *J. Am. Ceram. Soc.* 59, 7–8.
- Fischer-Cripps, A., 2000. A review of analysis methods for sub-micron indentation testing. *Vacuum* 58, 569–585.
- Fischer-Cripps, A., 2006. Critical review of analysis and interpretation of nanoindentation test data. *Surf. Coat. Technol.* 200, 4153–4165. doi:10.1016/j.surfcoat.2005.03.018.
- Fischer-Cripps, A.C., Collins, R.E., 1994. The probability of hertzian fracture. *J. Mater. Sci.* 29, 2216–2230. doi:10.1007/BF01154702.
- Flanders, L.A., Quinn, J.B., Wilson, O.C., Lloyd, I.K., 2003. Scratch hardness and chipping of dental ceramics under different environments. *Dent. Mater.* 19, 716–724. doi:10.1016/S0109-5641(03)00018-6.
- Gaillard, Y., Jiménez-Piqué, E., Anglada, M., 2006a. Scale dependence of the Young's modulus measured by nanoindentation in columnar YSZ EB-PVD thermal barriers coatings. *Philos. Mag.* 86, 5441–5451. doi:10.1080/14786430600778674.
- Gaillard, Y., Tomas, C., Woigard, J., 2006b. Quantitative analysis of dislocation pile-ups nucleated during nanoindentation in MgO. *Acta Mater.* 54, 1409–1417. doi:10.1016/j.actamat.2005.11.013.
- Gaillard, Y., Anglada, M., Jiménez-Piqué, E., 2009. Nanoindentation of yttria-doped zirconia: Effect of crystallographic structure on deformation mechanisms. *J. Mater. Res.* 24, 719–727. doi:10.1557/JMR.2009.0091.
- Gaillard, Y., Jiménez-Piqué, E., Bartsch, M., Anglada, M., 2007. Nucleation of shear bands on EB-PVD thermal barriers coatings under Hertzian indentations. *Key Eng. Mater.* 333, 277–280. doi:10.4028/www.scientific.net/KEM.333.277.
- Gaillard, Y., Jiménez-Piqué, E., Soldera, F., Mücklich, F., Anglada, M., 2008. Quantification of hydrothermal degradation in zirconia by nanoindentation. *Acta Mater.* 56, 4206–4216. doi:10.1016/j.actamat.2008.04.050.
- Gallo, L.S.A., Villas Boas, M.O.C., Rodrigues, A.C.M., Melo, F.C.L., Zanotto, E.D., 2019. Transparent glass-ceramics for ballistic protection: materials and challenges. *J. Mater. Res. Technol.* 8, 3357–3372. doi:10.1016/j.jmrt.2019.05.006.
- Ghaednia, H., Wang, X., Saha, S., *et al.*, 2017. A review of elastic-plastic contact mechanics. *Appl. Mech. Rev.* 69. doi:10.1115/1.4038187.
- Golovin, Y.I., 2008. Nanoindentation and mechanical properties of solids in submicrovolumes, thin near-surface layers, and films: A review. *Phys. Solid State* 50, 2205–2236.
- Gouldstone, A., Chollacoop, N., Dao, M., *et al.*, 2007. Indentation across size scales and disciplines: Recent developments in experimentation and modeling. *Acta Mater.* 55, 4015–4039. doi:10.1016/j.actamat.2006.08.044.
- Hay, J., Crawford, B., 2011. Measuring substrate-independent modulus of thin films. *J. Mater. Res.* 26, 727–738. doi:10.1557/jmr.2011.8.
- Hay, J.C., Bolshakov, A., Pharr, G.M., 1999. A critical examination of the fundamental relations used in the analysis of nanoindentation data. *J. Mater. Res.* 14, 2296–2305. doi:10.1016/j.matlet.2008.01.105.
- He, L.H., Standard, O.C., Huang, T.T.Y., Latella, B.A., Swain, M.V., 2008. Mechanical behaviour of porous hydroxyapatite. *Acta Biomater.* 4, 577–586. doi:10.1016/j.actbio.2007.11.002.
- Hertz, V.H.H., 1878. Die lieber die Berührung fester elastischer Körper. *J. für die Reine und Angew. Math.* 156–171.
- Holleck, H., 1986. Material selection for hard coatings. *J. Vac. Sci. Technol.* 4, 2661–2669. doi:10.1116/1.573700.
- Jäger, I.L., 2002. Comment on: "Effects of the substrate on the determination of thin films mechanical properties by nanoindentation" by Saha and Nix [Acta Mater 2002;50:23]. *Scr. Mater.* 47, 429–432. doi:10.1016/S1359-6462(02)00171-9.
- Jiménez-Piqué, E., Llanes, L., Anglada, M., 2014a. Resistance to contact deformation and damage of hard ceramics. In: Llanes, L., Mari, D. (Eds.), *Comprehensive Hard Materials*. Elsevier, pp. 367–383.
- Jiménez-Piqué, E., González-García, L., Rico, V.J., González-Elipe, A.R., 2014b. Nanoindentation of nanocolumnar TiO_2 thin films with single and stacked zig-zag layers. *Thin Solid Films* 550, 444–449. doi:10.1016/j.tsf.2013.10.022.
- Jönsson, B., Hogmark, S., 1984. Hardness measurements of thin films. *Thin Solid Films* 114, 257–269. doi:10.1016/0040-6090(84)90123-8.

- Ko, S., Lee, D., Jee, S., *et al.*, 2006. Mechanical properties and residual stress in porous anodic alumina structures. *Thin Solid Films* 515, 1932–1937. doi:10.1016/j.tsf.2006.07.169.
- Korsunsky, A.M., McGurk, M.R., Bull, S.J., Page, T.F., 1998. On the hardness of coated systems. *Surf. Coat. Technol.* 99, 171–183. doi:10.1016/S0257-8972(97)00522-7.
- Larsson, P.L., Giannakopoulos, A.E., Söderlund, E., Rowcliffe, D.J., Vestergaard, R., 1996. Analysis of Berkovich indentation. *Int. J. Solids Struct.* 33, 221–248. doi:10.1016/0020-7683(95)00033-7.
- Laugier, M.T., 1987. Palmqvist indentation toughness in WC-Co composites. *J. Mater. Sci. Lett.* 6, 897–900. doi:10.1007/BF01729862.
- Lawn, B., Wilshaw, R., 1975. Indentation fracture: Principles and applications. *J. Mater. Sci.* 10, 1049–1081. doi:10.1007/BF00823224.
- Lawn, B.R., 1998. Indentation of ceramics with spheres: A century after Hertz. *J. Am. Ceram. Soc.* 81, 1977–1994. doi:10.1111/j.1151-2916.1998.tb02580.x.
- Lawn, B.R., Padture, N.P., Cai, H., Guiberteau, F., 1994. Making ceramics “ductile”. *Science* 263, 1114–1116. doi:10.1126/science.263.5150.1114.
- Leonardi, A., Furgiuele, F., Syngellakis, S., Wood, R.J.K., 2009. Analytical approaches to stress intensity factor evaluation for indentation cracks. *J. Am. Ceram. Soc.* 92, 1093–1097. doi:10.1111/j.1551-2916.2009.03070.x.
- Luo, J., Stevens, R., 1996. Micromechanics of randomly oriented ellipsoidal inclusion composites. Part II: Elastic moduli. *J. Appl. Phys.* 79, 9057–9063. doi:10.1063/1.362639.
- Luo, J., Stevens, R., 1999. Porosity-dependence of elastic moduli and hardness of 3Y-TZP ceramics. *Ceram. Int.* 25, 281–286. doi:10.1016/S0272-8842(98)00037-6.
- Marshall, D.B., Lawn, B.R., 1977. An indentation technique for measuring stresses in tempered glass surfaces. *J. Am. Ceram. Soc.* 60, 86–87. doi:10.1111/j.1151-2916.1977.tb16106.x.
- Marshall, D.B., Cook, R.F., Padture, N.P., *et al.*, 2015. The compelling case for indentation as a functional exploratory and characterization tool. *J. Am. Ceram. Soc.* 98, 2671–2680. doi:10.1111/jace.13729.
- Melk, L., Roa Rovira, J.J., García-Marro, F., *et al.*, 2015. Nanoindentation and fracture toughness of nanostructured zirconia/multi-walled carbon nanotube composites. *Ceram. Int.* 41, 2453–2461. doi:10.1016/j.ceramint.2014.10.060.
- Morrell, R., 2006. Fracture toughness testing for advanced technical ceramics: Internationally agreed good practice. *Adv. Appl. Ceram.* 105, 88–98. doi:10.1179/174367606X84422.
- Muñoz-Tabares, J.A., Jimenez-Pique, E., Anglada, M., 2011a. Subsurface evaluation of hydrothermal degradation of zirconia. *Acta Mater.* 59, 473–484. doi:10.1016/j.actamat.2010.09.047.
- Muñoz-Tabares, J.A., Jimenez-Pique, E., Reyes-Gasga, J., Anglada, M., 2011b. Microstructural changes in ground 3Y-TZP and their effect on mechanical properties. *Acta Mater.* 59, 6670–6683. doi:10.1016/j.actamat.2011.07.024.
- Oliver, W.C., Pharr, G.M., 1992. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J. Mater. Res.* 7, 1564–1583.
- Oliver, W.C., Pharr, G.M., 2004. Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology. *J. Mater. Res.* 19, 3–20. doi:10.1557/jmr.2004.0002.
- Oliver, W.C., Pharr, G.M., 2010. Nanoindentation in materials research: Past, present, and future. *MRS Bull.* 35, 897–907. doi:10.1557/mrs2010.717.
- Ostojic, P., McPherson, R., 1987. A review of indentation fracture theory: Its development, principles and limitations. *Int. J. Fract.* 33, 297–312. doi:10.1007/BF00044418.
- Page, T.F., Oliver, W.C., McHargue, C.J., 1992. The deformation behavior of ceramic crystals subjected to very low load (nano)indentations. *J. Mater. Res.* 7, 450–473. doi:10.1557/JMR.1992.0450.
- Pathak, S., Kalidindi, S.R., 2015. Spherical nanoindentation stress-strain curves. *Mater. Sci. Eng. R Rep.* 91, 1–36. doi:10.1016/j.mser.2015.02.001.
- Pavon, J., Jimenez-Pique, E., Anglada, M., *et al.*, 2006. Stress–corrosion cracking by indentation techniques of a glass coating on $\text{Ti}_6\text{Al}_4\text{V}$ for biomedical applications. *J. Eur. Ceram. Soc.* 26, 1159–1169. doi:10.1016/j.jeurceramsoc.2005.01.045.
- Pharr, G.M., 1998. Measurement of mechanical properties by ultra-low load indentation. *Mater. Sci. Eng. A* 253, 151–159. doi:10.1016/S0921-5093(98)00724-2.
- Ponton, C.B., 1985. Vickers indentation fracture toughness test Part 1: Review of literature and formulation of standardised indentation toughness equations. *Mater. Sci. Technol.* 5, 865–872.
- Ponton, C.B., Rawlings, R.D., 1989. Vickers indentation fracture toughness test Part 2: application and critical evaluation of standardised indentation toughness equations. *Mater. Sci. Technol.* 5, 961–976. doi:10.1179/mst.1989.5.10.961.
- Puchi-Cabrera, E.S., Bernios, J.A., Teer, D.G., 2002. On the computation of the absolute hardness of thin solid films. *Surf. Coat. Technol.* 157 (2–3), 185–196.
- Quinn, G.D., Bradt, R.C., 2007. On the vickers indentation fracture toughness Test. *J. Am. Ceram. Soc.* 673–680. doi:10.1111/j.1551-2916.2006.01482.x.
- Rar, A., Song, H., Pharr, G.M., 2002. Assessment of new relation for the elastic compliance of a film–substrate system. *MRS Online Proc. Libr.* 695, 431–436.
- Rayón, E., Moreno, R., Alcázar, C., *et al.*, 2013. Enhanced hydrothermal resistance of Y-TZP ceramics through colloidal processing. *J. Am. Ceram. Soc.* 96, 1070–1076. doi:10.1111/jace.12225.
- Reveron, H., Fornabaio, M., Palmero, P., *et al.*, 2017. Towards long lasting zirconia-based composites for dental implants: Transformation induced plasticity and its consequence on ceramic reliability. *Acta Biomater.* 48, 423–432. doi:10.1016/j.actbio.2016.11.040.
- Rice, R.W., Wu, C.C., Boichelt, F., 1994. Hardness–grain-size relations in ceramics. *J. Am. Ceram. Soc.* 77, 2539–2553. doi:10.1111/j.1151-2916.1994.tb04641.x.
- Roa, J.J., Jimenez-Pique, E., Verge, C., *et al.*, 2015. Intrinsic hardness of constitutive phases in WC-Co composites: Nanoindentation testing, statistical analysis, WC crystal orientation effects and flow stress for the constrained metallic binder. *J. Eur. Ceram. Soc.* 35, 3419–3425. doi:10.1016/j.jeurceramsoc.2015.04.021.
- Saha, R., Nix, W.D., 2002. Effects of the substrate on the determination of thin film mechanical properties by nanoindentation. *Acta Materialia* 50 (1), 23–38.
- Smith, S.M., Scattergood, R.O., 1992. Crack-shape effects for indentation fracture toughness measurements. *J. Am. Ceram. Soc.* 75, 305–315. doi:10.1111/j.1151-2916.1992.tb08180.x.
- Tomas, C., Gaillard, Y., Woigard, J., 2006. Nucleation of dislocations during nanoindentation in MgO. *Philos. Mag.* 86, 5595–5606. doi:10.1080/14786430600690499.
- Tomas, C., Ouabadi, N., Gauthier-Brunet, V., Jaouen, M., Dubois, S., 2010. Mechanical properties of nanolaminate Ti_3SnC_2 carbide determined by nanohardness cartography. *J. Am. Ceram. Soc.* 93, 330–333. doi:10.1111/j.1551-2916.2009.03412.x.
- Ulm, F.J., Vandamme, M., Bobko, C., *et al.*, 2007. Statistical indentation techniques for hydrated nanocomposites: Concrete, bone, and shale. *J. Am. Ceram. Soc.* 90, 2677–2692. doi:10.1111/j.1551-2916.2007.02012.x.
- VanLandingham, M.R., 2003. Review of Instrumented Indentation. *J. Res. Natl. Inst. Stand. Technol.* 108, 249–265.
- Vepřek, S., 1999. The search for novel, superhard materials. *J. Vac. Sci. Technol.* 17, 2401–2420. doi:10.1116/1.581977.
- Xu, Z.H., Li, X., 2008. Effects of indenter geometry and material properties on the correction factor of Sneddon’s relationship for nanoindentation of elastic and elastic-plastic materials. *Acta Mater.* 56, 1399–1405. doi:10.1016/j.actamat.2007.11.030.
- Zheng, Y.F., Fargas, G., Besharatloo, H., *et al.*, 2019. Assessment of corrosion-induced changes on the mechanical integrity of cemented carbides at small length scales. *Int. J. Refract. Met. Hard Mater.* 84. doi:10.1016/j.jrmhm.2019.105033.

Contact Damage Resistance and Tribological Behavior of Ceramic/Carbon Nanostructure Composites

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Introduction

The development of ceramic matrix composites (CMCs) looks for improving the structural and/or functional properties of monolithic ceramics by adding fillers of distinct compositions (carbon, oxides, non-oxides...) and dimensions (nano/micro particles, fibers or whiskers, platelets...) to a ceramic matrix (Low, 2006). These CMCs exhibit, among others, great improvements in the fracture toughness or wear resistance, in the case of structural properties, or large increments in the electrical or thermal conductivities, when functional properties are investigated. Within CMCs, continuous carbon fibers reinforced silicon carbide (C/SiC) ceramic composites are one of the most studied due to their excellent properties (high toughness, good thermal shock and wear resistances, low friction...) that allows using them in high temperature advanced applications, for instance, as brake pads and disks in transportation or in thermal protection systems for aerospace vehicles (Krenkel and Berndt, 2005). Since the first C/SiC CMCs were manufactured in the 1980s, other promising carbon-based fillers were synthesized in the following decades, in particular, one-dimensional carbon nanotubes (CNTs), first described by Iijima (1991), and two-dimensional graphene, reported by Novoselov *et al.* (2004), who received the Nobel Prize in Physics in 2010 for their investigations in this carbon allotrope. These carbon nanostructures -nanotubes and graphene, CNs- attracted a great expectation since their discovery due to their outstanding electronic and physicochemical properties (Novoselov *et al.*, 2012; Popov, 2004), which could potentially enhance the performance of ceramics. The main difficulties to manufacture ceramic/CNs composites mainly are the dispersion of CNs into the matrix and the full densification of the CMCs avoiding the damage of the nanostructures at the high temperatures required during the sintering process. After some years of arduous investigations to mature the technology able to overcome these difficulties and develop the CNs composites, CMCs containing CNTs or graphene already led to remarkable improvements in numerous properties of ceramics (Azarniya *et al.*, 2017; Miranzo *et al.*, 2017). In this way, it is remarkable the development of toughened and highly electrical conducting ceramics.

At present, there is an increasing interest to improve the efficiency in industrial processes, minimizing the energy losses, as they are closely linked to economic and ecological issues. According to Holmberg *et al.* (2012), 28% of the fuel energy in passenger cars is employed to mitigate the undesirable friction phenomena occurred in the engine, transmission, and tires. These authors estimate a worldwide fuel savings of 117,000 MJ, economic savings of 174,000 M€, and reductions in CO₂ emissions of 290 MT if the friction losses are reduced by 18%. A similar study done in paper machines (Holmberg *et al.*, 2013), where the energy wasted due to the friction is in the range of 15–25%, concluded that a reduction in the next years of those numbers by 11% will also decisively contribute to minimize the greenhouse gas emissions, substantially saving money and electricity as well. Within this scenery and focused on the transportation field, one of the current approaches to reduce the fuel consumptions and the harmful emissions to the atmosphere is the development of gasoline direct injection (GDI) systems (Buri *et al.*, 2009), a challenging technology that requires high injection pressures -up to 80 MPa- but produces extensive wear of the GDI metallic parts. Therefore, the development of new materials with a better tribological response is of paramount importance and, in this sense, ceramic/CNs composites could have a decisive influence in these applications in the near future.

In this chapter, the friction behavior and wear resistance of oxide and non-oxide CMCs containing CNTs or graphene-based fillers are reviewed, describing the mechanisms that take place and the role played by CNs in the tribological response. The most common CNs fillers employed in bulk ceramic composites are multi-walled carbon nanotubes (MWCNTs), graphene nanoplatelets (GNPs) and graphene oxide sheets (GOs), which are thinner than GNPs but require a further reducing process (chemical or thermal, rGOs) to mostly recover the properties of graphene. Prior to go in depth on the tribological properties of ceramic/CNs composites, their contact damage resistances are also discussed. Despite this mechanical parameter is unusually analyzed when mechanical studies are performed, typically including hardness, fracture toughness, strength, etc., the contact damage resistance tests are relatively simple and fast, and provide important qualitative and preliminary information of the materials about their expected long- and short-crack behavior, machining performance or wear resistance.

It is important to remark that when the properties of different composites and reference materials are compared, their main microstructural characteristics, such as density, matrix grain size, crystalline phases, etc., must be similar; otherwise, it is quite complicate to elucidate the effect of the fillers in any property, as those microstructural parameters strongly affect the structural and functional properties of the materials.

Contact Damage Resistance of Ceramic/CNs Composites

Lawn's (1998) works were pioneering in the study of the contact damage resistance of ceramic materials employing Hertzian contact tests with spherical indenters and, in particular, the use of the bonding-interface technique. This technique easily allows

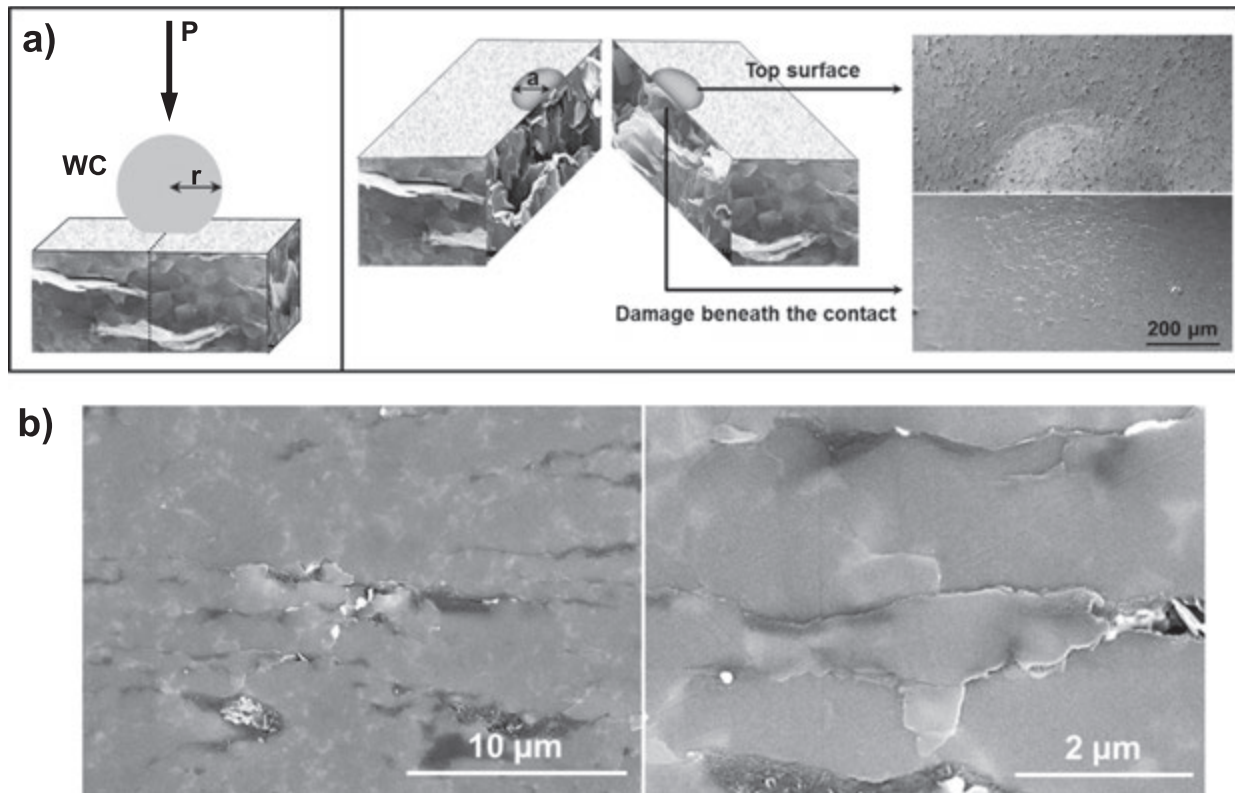


Fig. 1 (a) Scheme of the bonding interface configuration to observe top and cross-section surfaces at the Hertzian contact indentation. (b) Subsurface damage beneath the contact of SiC/5 vol% rGOs composite showing an array of mode II microcracks, parallel aligned to the tested surface, which come from the debonding of the SiC-rGO interphase. Adapted from Belmonte, M., Miranzo, P., Osendi, M.I., 2018. Contact damage resistant SiC/graphene nanofiller composites. *Journal of the European Ceramic Society* 38, 41–45.

investigating the damage beneath the contact surface. In essence, two polished half-specimens of the same material are glued face-to-face and, then, the top surface is ground and polished. Afterwards, WC indentations are performed at different loads in the bonded interface and, next, the glued specimens are separated by immersing them in acetone. Finally, the indented top surface and the cross-section beneath that surface are optically examined by Nomarski illumination (**Fig. 1(a)**). Distinct contact damage responses are observed depending on the microstructure of the ceramics. In this sense, homogenous monolithic materials with fine microstructures typically exhibit an elastic-brittle behavior where long well-defined Hertzian cone cracks are developed beneath the contact, which reduces the damage resistance. Conversely, heterogeneous materials, with a mixture of fine/equiaxed and large/elongated grains, present a quasi-ductile response, arresting, or at least limiting, the cone crack formation. In addition, the development of a subsurface damage zone with intergranular microcracks at the matrix-boundary phase interfaces is promoted. This behavior has been associated to the enhanced contact damage resistance of the material (Lawn *et al.*, 1994).

Nowadays, there are scarce works devoted to the contact damage resistance of ceramic/CNTs (Gonzalez-Julian *et al.*, 2011; Lee *et al.*, 2013; Wang *et al.*, 2004) and ceramic/graphene (Belmonte *et al.*, 2018; Roman-Manso *et al.*, 2014) composites. In the case of CNTs, Wang *et al.* (2004) reported well-defined cone cracks in the indented Al_2O_3 surface; while the absence of those cracks in the Al_2O_3 /10 vol% CNTs surface was indicative of a high-shear deformable response of the composite due to the presence of the nanotubes at the grain boundaries. As a consequence, the contact damage response enhanced, similarly to the heterogeneous ceramics described by Lawn *et al.* (1994). Comparable behavior was further confirmed by Gonzalez-Julian *et al.* (2011) in Si_3N_4 /5.3. vol% CNTs composites using the bonding interface technique. These authors observed in the cross-section of the CNTs composites shorter cone cracks than in the unfilled ceramics, as well as a quasi-plastic damage zone in which the weak interphase boundaries between Si_3N_4 and CNTs debonded due to a shear faulting process. As result, many mode II microcracks were formed, promoting the redistribution of the stress field under the indenter and limiting the formation of long cracks. This would also be indicative of enhanced fracture toughness and improved flaw tolerance.

In the case of graphene-based composites, Hertzian contact tests have been performed on SiC ceramics. Roman-Manso *et al.* (2014) found that the resistance to cone/ring cracking augmented in SiC materials due to the presence of multilayered graphene at grain boundaries. These graphene stacks, with a total content of ~ 4 vol%, were in situ grown into the ceramic material during its liquid-phase densification process by using the spark plasma sintering technique. Later, a deeper analysis of the short-crack endurance and contact damage resistance of SiC ceramics containing different graphene fillers (GNPs and rGOs) and amounts (up to 20 vol%) was carried out by Belmonte *et al.* (2018). According to these authors, the stress-strain curves obtained from the

indentation load and the radius of the imprints left on the top surface of the specimens showed a progressive deviation from the elastic-brittle response as GNPs content increased, which means that the composites were under a quasi-plastic deformation regime. Results from the bonded-interface tests evidenced huge differences in the damage resistance as a function of the graphene source and content. In particular, while monolithic SiC ceramics exhibited well-defined cone cracks beneath the contact zone, the progressive augment of GNPs concentration into the ceramics limited their propagation, associated to an increase in the fracture toughness and, especially, promoted the formation of a quasi-plastic damage zone. As described for ceramic/CNTs composites, the shear faulting process led to the matrix/graphene interface debonding and, consequently, abundant mode II microcracks were generated in the SiC/graphene composites (Fig. 1(b)), being more contact damage resistant than monolithic materials. However, the excessive formation of those microcracks for high GNPs contents (> 10 vol%) produced their coalescence and, hence, favored the substantial removal of material. In other words, its machinability would be enhanced during the grinding processes. The most interesting result of that work is the outstanding behavior of rGOs composites. These fillers, smaller and thinner than GNPs, completely avoided the cone crack formation and exhibited a contact damage response close to that of a ductile material, with an extensive quasi-plastic damage zone (see damage beneath the contact in Fig. 1(a)) where the redistribution of stresses was maximum through numerous short-microcracks that did not coalescence.

Therefore, the contact damage resistance of ceramics can be significantly enhanced by introducing CNTs or graphene-based fillers, which open new opportunities to use these composites in contact-mechanical applications, such as bearings, nozzles, face seal components or wear parts.

Tribological Response of Ceramic/CNTs Composites

The first well-described tribological study performed in ceramic/CNTs composites, in particular in $\text{Al}_2\text{O}_3/\text{MWCNTs}$, was published in by An *et al.* (2003) using a reciprocating ball-on-flat configuration. The dry tests at 25 N, with a Si_3N_4 ball as counterpart, concluded that the addition of 22 vol% of CNTs to an Al_2O_3 matrix reduced the friction coefficient in $\sim 40\%$ as compared to the monolithic ceramics. These authors explained this behavior based on the lubricating properties of the nanotubes and their rolling motion at the interface between both counterparts. This first work initiated a fruitful research line focused on the tribological characterization of ceramic/CNTs composites that extends until now. Some tribological reports on $\text{Al}_2\text{O}_3/\text{CNTs}$ materials followed in the next years (Ahmad *et al.*, 2010; Hvizdos *et al.*, 2012; Lee *et al.*, 2013; Lim *et al.*, 2005; Sharma *et al.*, 2019), and during that time other bulk ceramics filled with CNTs joined to the list, such as hydroxyapatite (HA) (Lahiri *et al.*, 2010; Zhao *et al.*, 2014), Si_3N_4 (Gonzalez-Julian *et al.*, 2011; Gonzalez-Julian *et al.*, 2014; Hvizdos *et al.*, 2012), yttria-stabilized zirconia (YSZ) -both tetragonal 3YSZ (Kasperski *et al.*, 2013; Melk *et al.*, 2015; Shin and Hong, 2012) and cubic 8YSZ (Lamnini *et al.*, 2019)-, SiC (Candelario *et al.*, 2016), SiO_2 (Sharma *et al.*, 2019), as well as Al_2O_3 (Balani *et al.*, 2008; Keshri and Agarwal, 2011) and TiO_2 (Wang *et al.*, 2018) coatings (c- Al_2O_3 and c- TiO_2). Most of these works were carried out employing a ball-on-disk geometry, dry testing conditions and loads from 1 to 60 N with a variety of counterparts (distinct ceramics and stainless steel). Besides, few studies also analyzed the tribological response of the composites under lubrication, such as isooctane, sea water or paraffin oil, looking for specific applications in GDI engines (Gonzalez-Julian *et al.*, 2011; Gonzalez-Julian *et al.*, 2014) or in marine environments (Keshri and Agarwal, 2011).

Table 1 collects tribological results reported for ceramic/CNTs composites. In general, CNTs lubricate the tribosystems and lead to significant decreases in the friction coefficient. Fig. 2(a) summarizes the highest friction coefficient reductions attained in ceramic/CNTs composites due to the incorporation of nanotubes. As it can be seen, the friction reductions and CNTs concentrations cover a wide range of values. Despite it is not easy to compare the tribological behavior of these composites due to its strong dependence with the microstructure of the tested materials and the selected tribological parameters, some ideas can be extracted. For instance, in $\text{Al}_2\text{O}_3/\text{CNTs}$ composites, one of the most studied materials, the best reported results in each work were always attained for composites containing the largest amount of nanotubes analyzed (up to 18–22 vol%, see Table 1). These data would suggest that the lubrication of the tribosystem only takes place when the concentration of nanotubes is elevated. As a matter of fact, Ahmad *et al.* (2010) reached the highest reduction in friction (80%) by adding ~ 18 vol% of MWCNTs (~ 3.9 and ~ 9.5 vol% were the other selected CNTs contents) when tested at 14 N. In the same way, for $\text{Si}_3\text{N}_4/\text{CNTs}$ (Gonzalez-Julian *et al.*, 2014; Hvizdos *et al.*, 2012) and YSZ/CNTs (Kasperski *et al.*, 2013; Lamnini *et al.*, 2019) composites with CNTs amounts in the range of 1.5–15.0 vol%, the lowest friction coefficients (50–75%) were always recorded at the maximum filler content studied (Table 1).

The lubricating capability of CNTs was not only demonstrated in dry tribosystems. For instance, isooctane lubricated $\text{Si}_3\text{N}_4/\text{CNTs}$ plates tested against Si_3N_4 balls up to 200 N (Gonzalez-Julian *et al.*, 2014) also evidenced a significant decrease of the friction coefficient (48%) thanks to the addition of 12 vol% of MWCNTs to the ceramic matrix.

The beginnings of the tribology in ceramic/graphene composites started in 2013, with the works on $\text{Si}_3\text{N}_4/\text{GNPs}$ composites by Hvizdos *et al.* (2013) and Belmonte *et al.* (2013), ten years after the work by An *et al.* (2003) in $\text{Al}_2\text{O}_3/\text{CNTs}$ composites. This delay comes from the later discovery of graphene compared with the nanotubes, although, conversely, the tribological experience acquired with the CNTs composites jointly with their excellent tribological results accelerated the investigations in graphene-based materials. In fact, nowadays, the number of reported works on tribology of ceramic/graphene composites (~ 90) is quite close to those published for ceramic/CNTs ones (~ 100). In spite of the friction results in those initial works on $\text{Si}_3\text{N}_4/\text{GNPs}$ were not very

Table 1 Maximum friction coefficient and wear rate reductions attained for ceramic/CNTs composites (the best CNTs content for those reductions when different amounts of fillers are used is included between parentheses)

Ceramic matrix	Filler content (vol%) ^a	Lubrication	Load (N)	Counterpart	Friction coefficient (filler vol%)	Wear rate (filler vol%)	References
Al ₂ O ₃	≤22	Dry	25	Si ₃ N ₄	↓40 (22 vol%)	↓45% (7.7 vol%)	An <i>et al.</i> (2003)
	≤21.3	Dry	25	Si ₃ N ₄	↓46 (21.3 vol%)	NA	Lim <i>et al.</i> (2005)
	≤18	Dry	14–35	Si ₃ N ₄	↓80 (18 vol%)	↓86% (18 vol%)	Ahmad <i>et al.</i> (2010)
	≤18	Dry	1–5	Al ₂ O ₃	↓60% (18 vol%)	↑ 3 orders (18 vol%)	Hvizdos <i>et al.</i> (2012)
	≤20	Dry	58.8	WC	↓38 (10 vol%)	↓92 (5 vol%)	Lee <i>et al.</i> (2013)
	≤5	Dry	9.8	Steel	NA	↓46% (3 vol%)	Sharma <i>et al.</i> (2019)
HA	~6	Dry	NA	Al ₂ O ₃	↓60%	↓66%	Lahiri <i>et al.</i> (2010)
	≤28.4	Dry	0.5–2.5	Steel	↓78% (28.4 vol%)	↓55% (28.4 vol%)	Zhao <i>et al.</i> (2014)
Si ₃ N ₄	≤15	Dry	1–5	Si ₃ N ₄	↓60% (15 vol%)	≈	Hvizdos <i>et al.</i> (2012)
	≤8.6	Isooctane	50–200	Si ₃ N ₄	↓40% (8.6 vol%)	↓80% (8.6 vol%)	Gonzalez-Julian <i>et al.</i> (2011)
	≤12	Isooctane	50–200	Si ₃ N ₄	↓48% (12 vol%)	↓87% (12 vol%)	Gonzalez-Julian <i>et al.</i> (2014)
3YSZ	≤3.4	Dry	5	Si ₃ N ₄	≈	↓93% (1 vol%)	Shin and Hong, 2012
	≤14	Dry	5, 10	Al ₂ O ₃	↓74 (14 vol%)	NA	Kasperski <i>et al.</i> (2013)
	≤5.8	Dry	5	ZrO ₂	↓33 (2.8 vol%)	↓83% (5.8 vol%)	Melk <i>et al.</i> (2015)
8YSZ	≤25	Dry	5	Si ₃ N ₄	↓22% (13.6 vol%)	↓ 3 orders (2.9 vol%)	Lamnini <i>et al.</i> (2019)
SiC	7	Paraffin oil	150	Si ₃ N ₄	NA	↓ 93%	Candelario <i>et al.</i> (2016)
SiO ₂	≤5	Dry	9.8	Steel	NA	↓64% (3 vol%)	Sharma <i>et al.</i> (2019)
c-Al ₂ O ₃	≤14.8	Dry	48	ZrO ₂	≈	↓ 1.5 orders (14.8 vol%)	Balani <i>et al.</i> (2008)
	≤14.8	Dry	30	Si ₃ N ₄	↓8% (14.8 vol%)	↓72% (14.8 vol%)	Keshri and Agarwal (2011)
	≤14.8	Sea water	30	Si ₃ N ₄	↓7% (14.8 vol%)	↓66% (14.8 vol%)	Keshri and Agarwal, (2011)
	≤14.8	873 K	30	Si ₃ N ₄	≈	↓76% (14.8 vol%)	Keshri and Agarwal, (2011)
c-TiO ₂	~6	Dry	20	ZrO ₂	↓37%	↓93.6%	Wang <i>et al.</i> (2018)

^aFor a better comparison, CNTs volume contents were employed and estimated if published data referred just to the weight percentage.

Abbreviation: NA, not available.

promising (friction coefficient decreased just 11% under isooctane lubrication (Belmonte *et al.*, 2013) or even kept invariable in dry conditions (Hvizdos *et al.*, 2013)), the wear results were quite remarkable (~60% improvement).

At present, Si₃N₄/GNPs composites (Balazsi *et al.*, 2017; Balko *et al.*, 2014; Belmonte *et al.*, 2013; Hvizdos *et al.*, 2013; Llorente *et al.*, 2019; Maros *et al.*, 2016; Rutkowski *et al.*, 2015; Tapasztó *et al.*, 2017) and Al₂O₃/(GNPs or rGOs) composites (Gutierrez-Gonzalez *et al.*, 2015; Hussainova *et al.*, 2016; Kim *et al.*, 2014; Sharma *et al.*, 2019; Yazdani *et al.*, 2015; Zhang *et al.*, 2016) are the most studied materials. In the last years other graphene composites, bulk and coatings (c-), based on SiC (Guo *et al.*, 2019; Llorente *et al.*, 2016; Llorente and Belmonte, 2018; Zhang *et al.*, 2018), B₄C (Sedlak *et al.*, 2017), 3YSZ (Gutierrez-Mora *et al.*, 2019; Zeng *et al.*, 2019), SiO₂ (Porwal *et al.*, 2014; Sharma *et al.*, 2019), c-ZrO₂ coatings (Li *et al.*, 2014), Y₂O₃-Al₂O₃-SiO₂ (c-YAS) coatings (Gomez-Gomez *et al.*, 2016) and CaSiO₃ (c-CS) (Xie *et al.*, 2014) coatings have been tested.

Fig. 2(b) represents the maximum friction coefficient reductions reported in ceramic/graphene composites. Interestingly, unlike CNTs composites where the most suitable filler contents scanned from ~5 to 22 vol%, in the case of graphene composites the filler amounts were below 10 vol%, reaching reductions in the friction that varied from negative values to up to 100%. The addition of lower filler contents in the case of GNPs or rGOs, as compared to CNTs, could be explained by its most effective dispersion into the ceramic matrix than in the case of the nanotubes, which easily agglomerate forming bundles and, hence, higher CNTs contents would be required to achieve similar contributions to the tribological performance. To shed some light about this fact, the friction coefficient reductions of the most interesting oxide (Al₂O₃) and non-oxide (Si₃N₄) ceramics containing both kinds of CNs fillers are compared in Fig. 3(a) and (b), respectively. Al₂O₃/CNs plot (Fig. 3(a)) clearly shows two groups of data: one related to graphene composites with filler contents ≤5 vol% and friction reductions around ~30%, and another one associated to CNTs composites, with nanotube contents between 10 to 22 vol% and friction reductions above 40% and up to 80%. The lack of results with larger graphene contents does not allow making a direct comparison of the friction behavior of these composites with that showed by CNTs ones, although both of them would be equivalent. However, that exercise can be done for Si₃N₄/CNs composites (Fig. 3(b)). If data with negligible or low reductions are not considered, no clear differences as a function of the kind of filler can be established, with overall friction reductions in the 40–60% interval. This suggests that the friction mechanisms would be similar, independently of the type of filler.

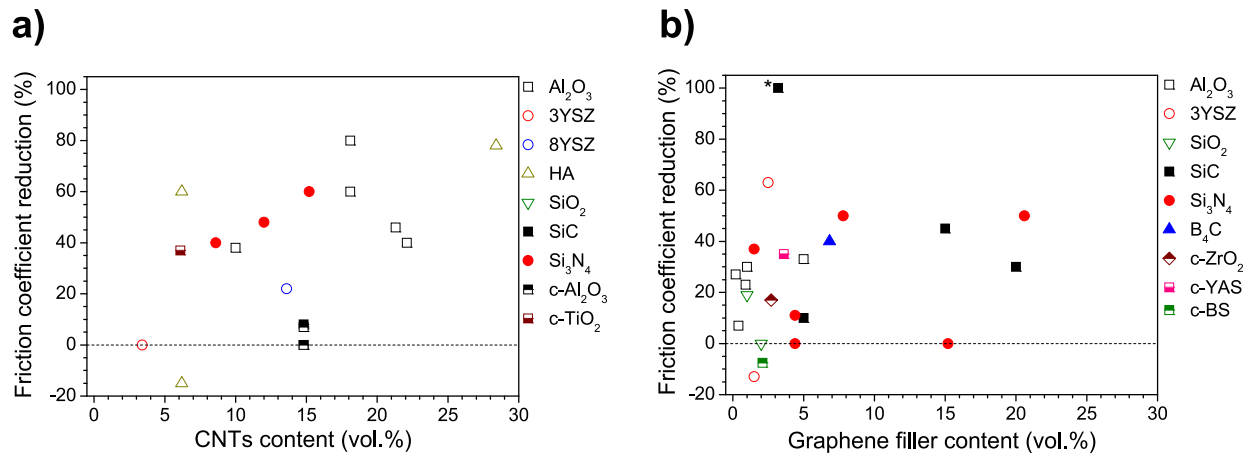


Fig. 2 Maximum reduction of the friction coefficient for ceramic/CNs composites as a function of CNTs (a) and graphene (b) fillers content. Plotted data correspond to the best value achieved for each individual work collected in [Tables 1](#) and [2](#). Oxide- and non-oxide-based ceramic composites are represented by empty and full symbols, while half-filled ones correspond to ceramic coatings (c-). An asterisk nearby a symbol indicates a reduction of the friction coefficient above one order of magnitude as compared to the corresponding reference material.

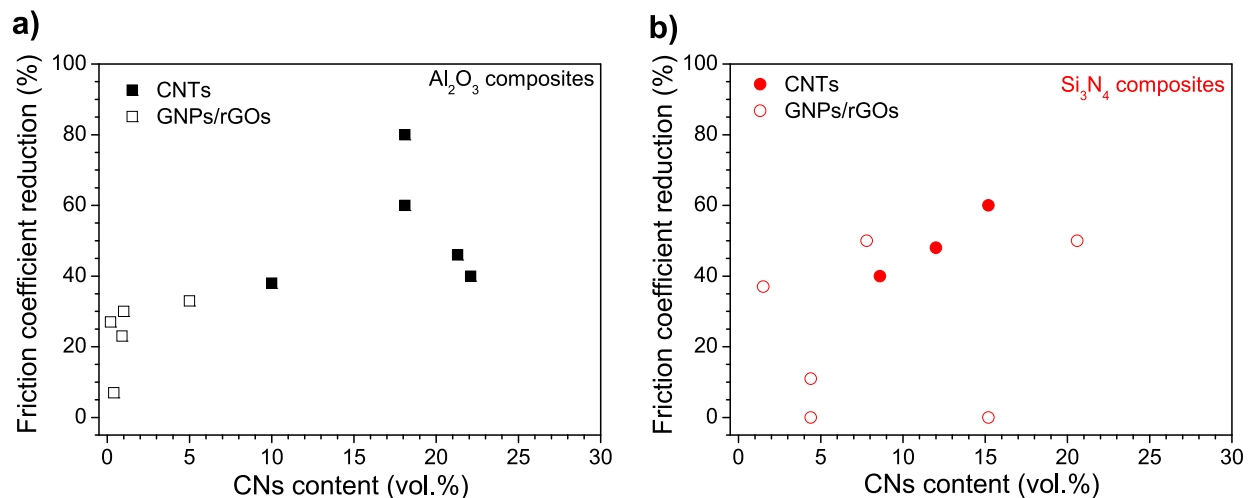


Fig. 3 Maximum reduction of the friction coefficient as a function of CNs content for: (a) Al_2O_3 /CNs and (b) Si_3N_4 /CNs composites. Plotted data correspond to the best value achieved for each individual work collected in [Tables 1](#) and [2](#). Full and empty symbols correspond to composites containing CNTs and graphene-based (GNPs or rGOs) fillers, respectively.

In general, when any material is tribologically tested at macro-scale (loads above 1 N), the friction evolution is on line recorded during the experiments and, afterwards, the wear volume is calculated by measuring the dimensions in 2D and/or 3D of the wear tracks. Less frequent is to use the wear loss parameter, which is estimated from differences in the specimen weight. The wear volume (W_V) or the wear rate (W_R), the latter assessed from the equation $W_R = W_V \cdot P^{-1} \cdot d^{-1}$, where P and d are the applied load and the tested distance, respectively, allow estimating the wear resistance performance of the materials. Most of works previously cited in the friction coefficient section also reported W_V or W_R data. Although the friction results achieved by adding CNs fillers to ceramic matrices are, in general, good enough, the wear response is much more encouraging. Actually, the majority of ceramic/CNs composites exhibit wear resistance improvements above 45% ([Fig. 4](#)), with numerous examples showing increases higher than 80%, and reaching in some cases W_R reductions close to two-three orders of magnitude for different ceramic composites and fillers (i.e., 8YSZ/2.9 vol% CNTs ([Lamnini et al., 2019](#)), 3YSZ/2.5 vol% GNPs ([Gutierrez-Mora et al., 2019](#)), and Si_3N_4 /7.8 vol% GNPs ([Tapasztó et al., 2017](#))). Authors relate this outstanding response to the formation of an adhered and continuous tribofilm based on CNs that protects against wear, and to the improvement in the mechanical properties of the composites as compared to the monolithic ceramics.

It is worth mentioning that a decrease in the friction coefficient for a specific ceramic composite and CNs filler content is not always synonym of a better wear resistance, or vice versa. In fact, when comparing data collected in [Tables 1](#) and [2](#) within the same

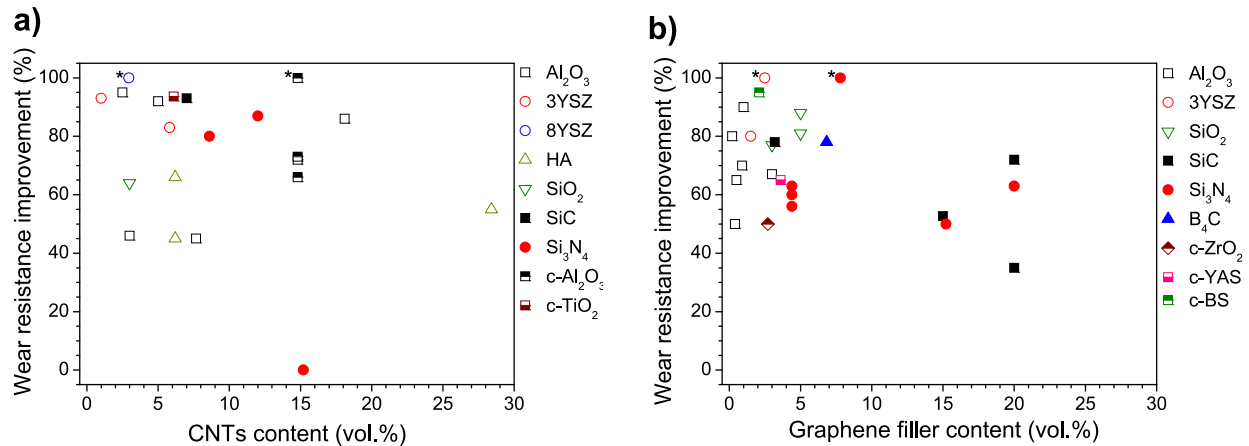


Fig. 4 Maximum improvement of the wear resistance for ceramic/CNs composites as a function of CNTs (a) and graphene-based (b) fillers content. Plotted data correspond to the best value achieved for each individual work collected in [Tables 1](#) and [2](#). Oxide- and non-oxide-based ceramic composites are represented by empty and full symbols, while half-filled ones correspond to ceramic coatings (c-). An asterisk nearby a symbol indicates a reduction of the wear resistance above one order of magnitude as compared to the corresponding reference material.

reported work, almost the half of the studies found that the best filler content for achieving the highest friction reductions did not match with the necessary CNs amount to promote the largest wear resistances. This trend has been observed for any ceramic matrix or type of filler and can be related to differences in the role played by CNs in the friction and wear mechanisms.

Friction and Wear Mechanisms in Ceramic/CNs Composites

There are many issues that affect the tribological response of materials. Some of them are related to the tribosystem, such as the testing conditions (load, lubrication, counterpart, speed...) and the third body (formed by all materials separating the counterparts such as debris, lubricants...); and some others are closely linked to the properties of the counterparts. The mechanical properties like hardness (H), elastic modulus (E), and fracture toughness (K_{IC}) stand out within this group, being especially important when fatigue and microfracture processes take place. Moreover, their impact on the wear response highly depends on the wear regime. While H and E have a decisive role in mild wear stages ([Hsu and Shen, 2004](#)); K_{IC} is extremely important for severe wear regimes ([Evans and Wilshaw, 1976](#)). The thermal conductivity of the materials can also influence the tribological performance, for instance, by dissipating the local heat at the tribocontacts, modifying the tribochemical conditions (i.e., oxidation), or reducing the thermal shock stresses and, hence, the cracks nucleation ([Hsu and Shen, 2004](#)). Finally, the electrical properties can contribute to some extent to the wear mechanisms. In this way, insulators could trap at the vacancies or grain boundaries the electrical charges generated during the motion of the counterparts, increasing the polarization energy and causing their dielectric breakdown and wear and, conversely, electrical conductors could easily release those charges and avoid this kind of wear ([Belmonte et al., 1996](#)). In the case of ceramic/CNs composites, carbon fillers improve many of these structural and functional properties ([Azamiya et al., 2017](#); [Miranzo et al., 2017](#)), although probably the key issue in the tribological process is the third body formation.

There is a general consensus within the tribology community that both CNTs and graphene-based fillers promote the decrease of the friction coefficient of ceramics due to their lubricating characteristics. In essence, CNs are pulled out from the composite during the tribotests and, then, crushed into debris due to the action of the microabrasion mechanism. Those debris are progressively compacted to form a self-lubricant carbon-rich tribofilm on the mated surfaces ([Fig. 5](#)). Sometimes, CNTs protruding from the composite surfaces have also been observed ([Ahmad et al., 2010](#)), which would act as lubricious rollers ([Fig. 6\(a\)](#)); whereas GNPs can be exfoliated into smaller and thinner flakes ([Belmonte et al., 2013](#)), contributing to the tribofilm ([Fig. 6\(b\)](#)).

According to [Wang et al. \(2018\)](#), there are four kinds of frictional effects of CNTs ([Fig. 7](#)): (1) tribo-protruding where CNTs are pulled-out from the composite surface and crushed; (2) tribo-reorientation of the lower aspect ratio CNTs that perpendicularly rotate to the sliding direction, a layout more effective to reduce the friction; (3) tribo-film, a lubricant layer formed by short and smeared CNTs and ceramic debris that substantially decrease friction and; (4) tribo-degradation of the CNTs due to the high shear forces attained during the whole test. These frictional effects can also be extended to GNPs, with maybe the unique exception of the tribo-reorientation.

[Belmonte et al. \(2013\)](#) employed for the first time the micro-Raman spectroscopy to investigate the tribofilm composition formed in Si_3N_4 /GNPs composites. CNs essentially exhibit three intense characteristic Raman bands: D ($\sim 1360 \text{ cm}^{-1}$), G ($\sim 1594 \text{ cm}^{-1}$) and 2D or G' ($\sim 2717 \text{ cm}^{-1}$). Moreover, if the ceramic matrix also has a clear Raman signature, the composition of the wear debris into the wear tracks could be established. [Fig. 8](#) illustrates how micro-Raman spectroscopy contributes to go in depth in the tribofilm characterization. In this example, the Raman spectrum points the main bands for SiC and GNPs in the

Table 2 Maximum friction coefficient and wear rate reductions attained for ceramic/graphene composites (the best graphene content for those reductions when different amounts of fillers are used is included between parentheses)

Ceramic matrix	Filler content (vol%) ^a	Lubrication	Load (N)	Counterpart	Friction coefficient (filler vol%)	Wear rate (filler vol%)	References
Si ₃ N ₄	4.4	Isooctane	50–200	Si ₃ N ₄	↓11%	↓56%	Belmonte <i>et al.</i> (2013)
	≤4.4	Dry	5	Si ₃ N ₄	≈	↓60% (4.4 vol%)	Hvizdos <i>et al.</i> (2013)
	≤4.4	Dry – 700°C	5	Si ₃ N ₄	↑	↓94% (1.5 vol%)	Balko <i>et al.</i> (2014)
	≤11.4	Dry	NA	NA	↓ (0.7 vol%)	↓ (1.5 vol%)	Rutkowski <i>et al.</i> (2015)
	≤4.4	Dry	40	Si ₃ N ₄ , SiC	↓37% (1.5 vol%)	↓63% (4.4 vol%)	Maros <i>et al.</i> (2016)
	≤15.2	Water	50	SiC	≈	↓50% (15.2 vol%)	Balazsi <i>et al.</i> (2017)
	≤7.8	Dry	5	Si ₃ N ₄	↓50% (7.8 vol%)	↓ 2 orders (7.8 vol%)	Tapasztó <i>et al.</i> (2017)
	≤20.6	Isooctane	50–180	Si ₃ N ₄	↓50% (20.6 vol%)	↓63% (20.6 vol%)	Llorente <i>et al.</i> (2019)
Al ₂ O ₃	≤1	Dry	25	WC	↓30% (1 vol%)	↓90% (1 vol%)	Kim <i>et al.</i> (2014)
	≤8.7	Dry	5–35	Si ₃ N ₄	↓23% (0.9 vol%)	↓70% (0.9 vol%)	Yazdani <i>et al.</i> (2015)
	0.4 (rGOs)	Dry	20	Al ₂ O ₃	↓7%	↓50%	Gutierrez-Gonzalez <i>et al.</i> (2015)
	≤5	Dry	40	Al ₂ O ₃	↓33% (5 vol%)	↓65% (0.5 vol%)	Zhang <i>et al.</i> (2016)
	≤2.9	Dry	0.98–4.9	Al ₂ O ₃	↓27% (0.2 vol%)	↓90% (0.2 vol%)	Hussainova <i>et al.</i> (2016)
	≤5	Dry	NA	Steel	NA	↓67% (3 vol%)	Sharma <i>et al.</i> (2019)
SiC	≤20 (rGOs 5%)	Dry	5	Si ₃ N ₄	↓10% (5 vol%)	↓72% (20 vol%)	Llorente <i>et al.</i> (2016)
	3.2	Water	50	SiC	↓ one order	↓78%	Zhang <i>et al.</i> (2018)
	≤20	Isooctane	50–180	Si ₃ N ₄	↓30% (20 vol%)	↓35% (20 vol%)	Llorente and Belmonte (2018)
	≤15	Dry	100	Si ₃ N ₄	↓45% (15 vol%)	↓53% (15 vol%)	Guo <i>et al.</i> (2019)
B ₄ C	≤6.83	Dry	5–50	SiC	↓40% (6.83 vol%)	↓78% (6.83 vol%)	Sedlak <i>et al.</i> (2017)
3YSZ	≤10	Dry	2–20	ZrO ₂	↓63% (2.5 vol%)	↓3 orders (2.5 vol%)	Gutierrez-Mora <i>et al.</i> (2019)
	≤1.5 (rGOs)	Dry	30	Si ₃ N ₄	↑13% (1.5 vol%)	↓80% (1.5 vol%)	Zeng <i>et al.</i> (2019)
SiO ₂	≤5	Dry	5	Al ₂ O ₃ , BS	↓19% (5 vol%)	↓88% (5 vol%)	Porwal <i>et al.</i> (2014)
	≤5	Dry	NA	Steel	≈	↓77% (3 vol%)	Sharma <i>et al.</i> (2019)
c-ZrO ₂	2.7	Dry	10–100	Al ₂ O ₃	↓14%	↓50%	Li <i>et al.</i> (2014)
c-YAS	≤3.6	Dry	5, 10	SS	↓35% (3.6 vol%)	↓65% (3.6 vol%)	Gomez-Gomez <i>et al.</i> (2016)
c-CS	≤5.6	Dry	10	SS	↑	↓95% (2.1 vol%)	Xie <i>et al.</i> (2014)

^aFor a better comparison, graphene volume contents were employed and estimated if published data referred just to the weight percentage. Fillers mostly correspond to GNPs. When using rGOs, the information is specified.

Abbreviation: BS, borosilicate; NA, not available; SS, stainless steel.

pristine SiC/GNPs composite (Fig. 8(a)). By selecting the most intense bands for the matrix and the filler, it was possible to create a false colored image (blue for SiC-TO band and red for G band) of the untested and tribological tested surfaces as a function of the GNPs content (Fig. 8(b)). In this tribosystem, the composite with the largest amount of GNPs was able to develop a uniform and continuous tribofilm (see differences between the images for untested and tested specimens in Fig. 8(b)) that was formed by some SiC debris and, especially, by carbonaceous material, which strongly contributed to reduce the friction (Llorente *et al.*, 2016). Furthermore, the intensity ratio between D and G bands (I_D/I_G) can be used to estimate the defects degree of CNs species and, in this way, an increase in I_D/I_G would correspond to more defective nanostructures. As Fig. 8(b) shows, I_D/I_G augmented after testing the materials due to the crushing and exfoliation processes of the pulled-out graphene stacks, being more extensive (higher I_D/I_G) when the complete tribofilm was formed. The exfoliation degree of GNPs was also studied by micro-Raman spectroscopy taking into account the intensity ratio between 2D and G bands (I_{2D}/I_G). In this case, an increment of this value would confirm a decrease in the number of layers forming the GNPs, or in other words, a higher exfoliation degree (Belmonte *et al.*, 2013). Actually, Raman maps of Si₃N₄/GNPs composites (Fig. 8(c)) evidence the presence on the worn surfaces of a considerably number of features with high I_{2D}/I_G values -in yellow color- as the tested load increased. Considering that the wear volume of this composite remained almost invariable with the load, this fact would support that GNPs are more exfoliated and highly contribute to the development of the tribofilm. Therefore, nowadays, micro-Raman spectroscopy has become into an essential tool for the tribological characterization of ceramic/CNs composites and numerous studies currently employ it.

Despite the tribofilm has also been observed when using external lubrication, its formation mechanism depends on the lubricating media. In this way, Al₂O₃/CNTs coatings tested against Si₃N₄ balls in sea water (Keshri and Agarwal, 2011) showed a reduced friction and higher wear resistance due to the formation of a SiO₂-rich protective layer coming from tribochemical reactions in the Si₃N₄ ball, a higher fracture toughness of CNT-reinforced coating, and the antifriction effect of sea water. In

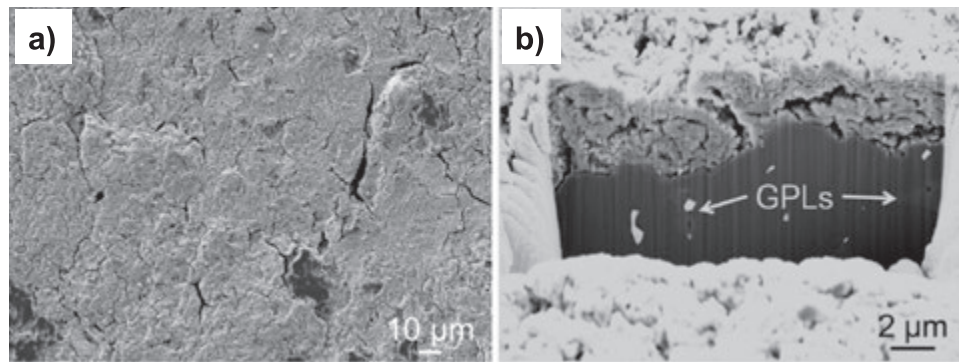


Fig. 5 Scanning electron micrographs of the tribolayer formed on $B_4C/6$ wt% GNPs composites after testing at 50 N: (a) top and (b) cross-section views showing a homogenous and compacted tribolayer with thickness around 2–3 μm . GPLs label corresponds to graphene platelets. Adapted from Sedlak, R., Kovalcikova, A., Balko, J., *et al.*, 2017. Effect of graphene platelets on tribological properties of boron carbide ceramic composites. *International Journal of Refractory Metals and Hard Materials* 65, 57–63.

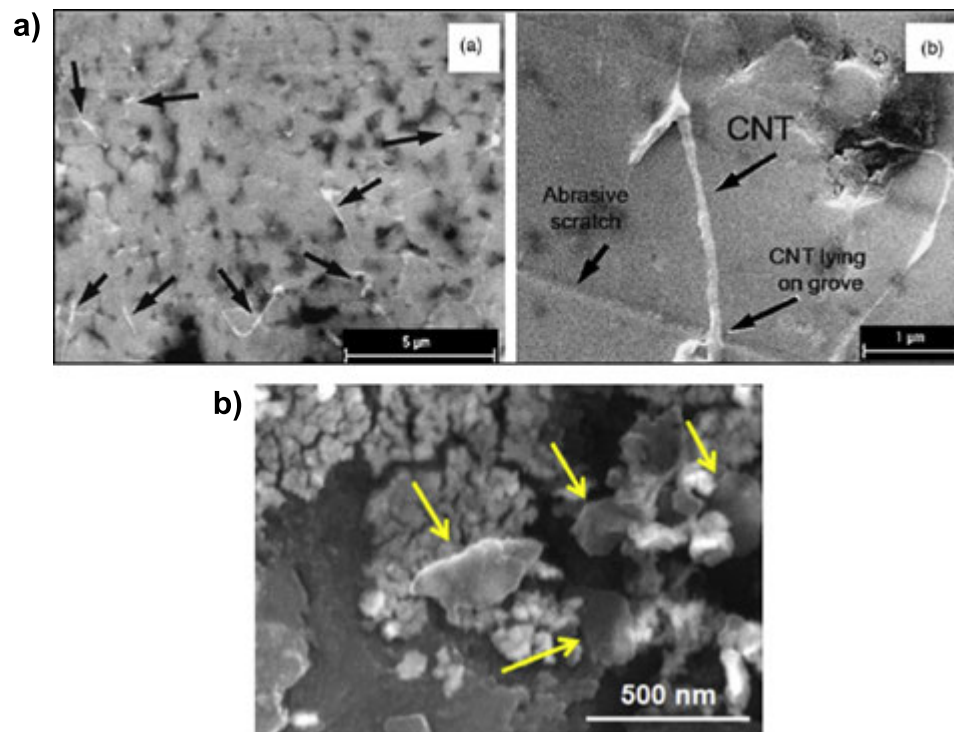


Fig. 6 Scanning electron micrographs of the worn $Al_2O_3/CNTs$ (a) and $Si_3N_4/GNPs$ surfaces (b) showing CNTs protruding from the composite and exfoliated GNPs-based debris, respectively. Adapted from Ahmad, I., Kennedy, A., Zhu, Y.Q., 2010. Wear resistant properties of multi-walled carbon nanotubes reinforced Al_2O_3 nanocomposites. *Wear* 269, 71–78. Belmonte, M., Ramirez, C., Gonzalez-Julian, J., *et al.*, 2013. The beneficial effect of graphene nanofillers on the tribological performance of ceramics. *Carbon* 61, 431–435.

$Si_3N_4/GNPs$ composites tested against SiC under water lubrication (Zhang *et al.*, 2018), the friction strongly decreased due to the combined effect of a carbon-containing surface layer and the stabilization of a water film between the counterparts. On the other hand, the decrease in the friction of isooctane lubricated $Si_3N_4/GNPs$ composites was attributed to the development of a double tribolayer (Llorente *et al.*, 2019). This tribolayer was formed by an inner thin transfer film containing isooctane and ultrafine wear debris, and an outer thick self-lubricant carbonaceous tribofilm coming from the pulling-out and crushing of GNPs and oxidized Si_3N_4 particles.

The wear resistance of a tribosystem is closely linked to the protection provided by the tribolayer and the mechanical properties of tested materials. In fact, the mechanical stresses attained at the tribocontact are the responsible for the destabilization and partial -or total- removal of that tribolayer, wearing the contact surfaces and reducing the wear resistance. Those mechanical stresses depend on many factors but are especially promoted under dry testing conditions, where severe wear usually occurs. In this way, an enhanced wear resistance is commonly attributed to the improved fracture toughness of CNs composites as compared to monolithic ceramics.

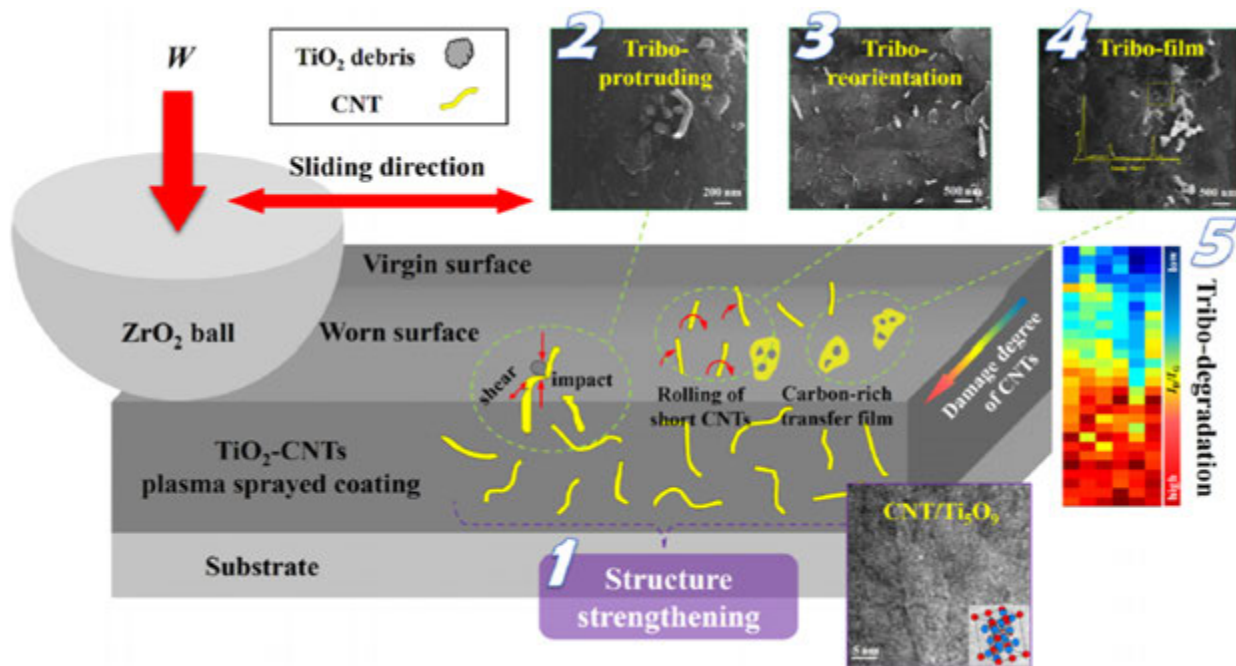


Fig. 7 Schematic illustrating the frictional effects of CNTs (tribo-protruding, tribo-reorientation, tribo-film, and tribo-degradation) on TiO_2/CNTs coatings. Adapted from Wang, H.-D., He, P.-F., Ma, G.-Z., *et al.*, 2018. Tribological behavior of plasma sprayed carbon nanotubes reinforced TiO_2 coatings. *Journal of the European Ceramic Society* 38, 3660–3672.

CNTs fillers arrest or limit the propagation of cracks developed beneath the tribocontact through the occurrence of toughening mechanisms such as crack deflection, bridging or branching (Ahmad *et al.*, 2010; Candelario *et al.*, 2016; Lamnini *et al.*, 2019). The micromechanical response and the contact damage resistance are also important, as the stress fields generated can be redistributed by the fillers located at the grain boundaries (Gonzalez-Julian *et al.*, 2011), restraining the formation of long cracks.

Hsu and Shen (2004) established that, under mild wear conditions, W_R of ceramics is inversely proportional to the product of H and E . Thus, considering that these mechanical parameters decrease with the CNTs additions in most of composites (Azamiya *et al.*, 2017; Miranzo *et al.*, 2017), a loss of the wear resistance in ceramic/CNTs composites would be expected. However, Llorente and Belmonte (2018) and Llorente *et al.* (2019) found that the development of an homogenous and well adhered lubricating carbon-based tribolayer on ceramic/GNPs surfaces was able to counterbalance the negative impact of their mechanical properties in the wear behavior. Actually, the wear resistance enhanced in $\text{Si}_3\text{N}_4/\text{GNPs}$ and SiC/GNPs composites until their respective tribolayers were destabilized due to an increment in the tensile stresses.

Nanotubes or Graphene?

One interesting question is to decide what kind of CNTs filler -nanotubes or graphene- is more attractive from the tribological point of view. Obviously, their dimensions (length/diameter for CNTs or thickness/lateral size for graphene) and number of layers (rolled or stacked) can modify the friction and wear responses of the CNTs composites. In addition, the only way to answer that question is to compare the same composites (composition, grain size, density, CNTs dispersion...) by replacing one filler by the same content of another one, and using identical testing conditions. Fig. 9 plots the steady state friction coefficient (Fig. 9(a)) and W_V (Fig. 9(b)) of $\text{Si}_3\text{N}_4/\text{MWCNTs}$ and $\text{Si}_3\text{N}_4/\text{GNPs}$ composites containing 3 wt% of fillers (~ 5 vol%). These materials were tested at different loads employing a reciprocating ball-on-plate configuration mated against Si_3N_4 balls under lubrication with isooctane. At first glance, CNTs provide a higher lubrication than GNPs, exhibiting a lower friction coefficient for all range of loads than the reference ceramics; while GNPs are able to reduce the friction of Si_3N_4 only at the maximum tested load. Interestingly, the friction curves for CNTs and GNPs composites are almost parallel but shifted to higher friction values in the latter material. It seems that nanotubes are easier pulled-out from the matrix than the nanoplatelets, quickly contributing to the development of a continuous lubricating tribolayer; whereas GNPs need more severe testing conditions to promote a similar mechanism. Both composites are more wear resistant than monolithic ceramics, all materials running under a mild wear regime ($W_R \sim 10^{-8} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$). Once more the tribolayer plays an active role in the wear behavior. While at low and intermediate loads a compacted and stabilized wear protecting tribolayer was formed on CNTs composite, limiting the wear compared to GNPs materials, at high loads that tribolayer became unstable for CNTs, GNPs composite being now that with the best wear performance. Moreover, its W_V value remained almost invariable with the load, which clearly reflects that the tribolayer is formed by the continuous exfoliation of pulled-out nanoplatelets. Lahiri *et al.* (2010) also

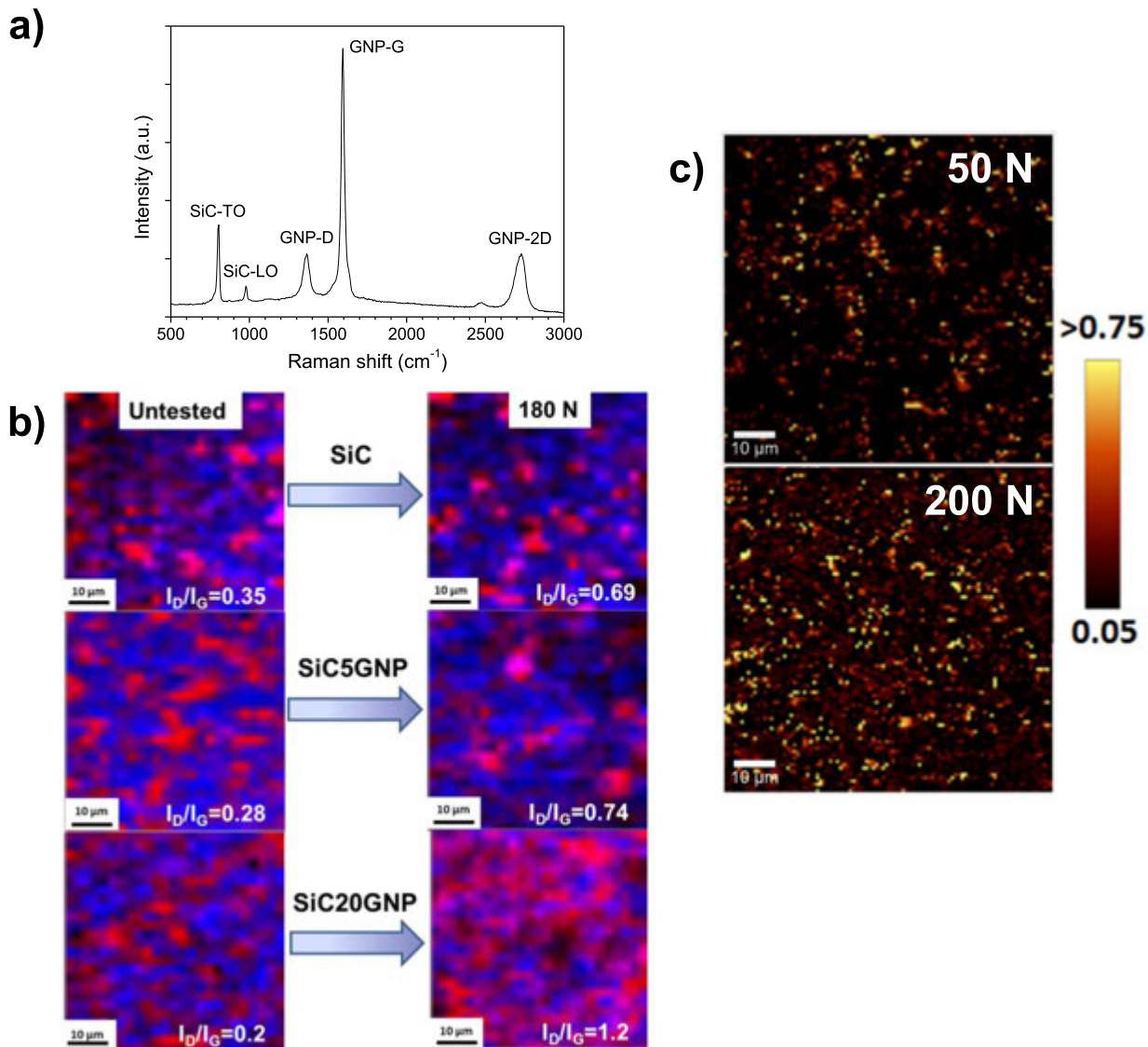


Fig. 8 Raman characterization of the tribolayer formed on ceramic/GNPs composites. (a) Raman spectrum of the untested SiC/GNPs composite with the main characteristic bands for SiC and GNPs, and (b) false colored Raman images for monolithic SiC and two composites containing 5 and 20 vol% of GNPs. The left hand column is for untested materials, while the right hand one is for tested surfaces. Features in blue and red are ascribed to SiC and GNPs. I_D/I_G values are also included for each image. (c) false colored Raman images representing I_{2D}/I_G in worn Si₃N₄/GNPs surfaces composites tested at 50 and 200 N. The bright yellow spots correspond to highly exfoliated GNPs (high I_{2D}/I_G values). Adapted from Belmonte, M., Ramirez, C., Gonzalez-Julian, J., *et al.*, 2013. The beneficial effect of graphene nanofillers on the tribological performance of ceramics. *Carbon* 61, 431–435. Llorente, J., Belmonte, M., 2018. Friction and wear behavior of silicon carbide/graphene composites under isooctane lubrication. *Journal of the European Ceramic Society* 38, 3441–3446.

observed that the shear stress level reached during the tests controls the tribological behavior. In that work, CNTs were removed from hydroxyapatite composites during macro-wear conditions, lubricating the system and reducing the friction but, conversely, using nano-wear parameters, the peeling action of the CNTs did not occur and the friction augmented.

Within the graphene-based category, GNPs and rGOs fillers can be distinguished. At present, there is just one work, reported by Llorente *et al.* (2016), where the effect of the graphene source on the tribological properties of ceramic/graphene composites was investigated. For the same volume content (5%), authors found better friction results of SiC/graphene composites when used GNPs instead rGOs. GNPs seem to be more easily removed, exfoliated, and crushed than rGOs, creating a compacted carbon-based tribolayer, which was not fully developed for rGOs. However, the wear resistances for both composites were very similar, slightly higher for rGOs. In this case, the lack of a well-formed tribolayer in rGOs composite was counteracted by its larger fracture toughness.

To conclude, both CNTs and GNPs tend to act as self-solid lubricants in ceramic/CNs composites through the formation of a carbonaceous-based tribolayer that can also protect against wear. The ability of each tribosystem to pull-out and crush the CNs into debris to create a stable tribolayer will depend on the testing conditions and properties of the materials, especially the

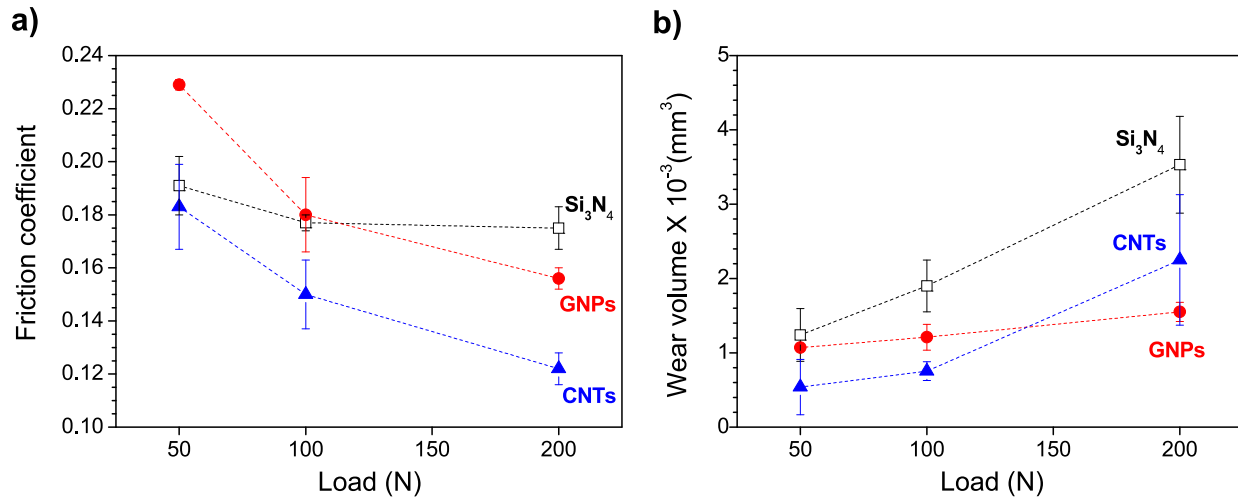


Fig. 9 Tribological behavior of Si₃N₄/CNs composites for the same filler (CNTs and GNPs) content (~5 vol%): (a) friction coefficient and (b) wear volume. Data replotted from Belmonte, M., Ramirez, C., Gonzalez-Julian, J., *et al.*, 2013. The beneficial effect of graphene nanofillers on the tribological performance of ceramics. Carbon 61, 431–435. Gonzalez-Julian, J., Schneider, J., Miranzo, P., Osendi, M.I., Belmonte, M., 2011. Enhanced tribological performance of silicon nitride-based materials by adding carbon nanotubes. Journal of the American Ceramic Society 94, 2542–2548.

mechanical ones. The wear response will depend on the balance between the stabilization of the tribolayer and the fracture toughness behavior, for severe wear regimes, or against the combination of hardness and elastic modulus, in the case of mild wear regimes commonly achieved for lubricated tribosystems. Finally, ceramic/CNs composites are very promising materials to be used under demanding tribological applications in many fields, from transportation to energy, including electronics or health.

References

- Ahmad, I., Kennedy, A., Zhu, Y.Q., 2010. Wear resistant properties of multi-walled carbon nanotubes reinforced Al₂O₃ nanocomposites. *Wear* 269, 71–78.
- An, J.-W., You, D.-H., Lim, D.-S., 2003. Tribological properties of hot-pressed alumina-CNT composites. *Wear* 255, 677–681.
- Azariya, A., Sovizi, S., Azariya, A., *et al.*, 2017. Physicomechanical properties of spark plasma sintered carbon nanotube-containing ceramic matrix nanocomposites. *Nanoscale* 9, 12779–12820.
- Balani, K., Harimkar, S.P., Keshri, A., *et al.*, 2008. Multiscale wear of plasma-sprayed carbon-nanotube-reinforced aluminum oxide nanocomposite coating. *Acta Materialia* 56, 5984–5994.
- Balazsi, C., Fogarassy, Z., Tapasztó, O., *et al.*, 2017. Si₃N₄/graphene nanocomposites for tribological application in aqueous environments prepared by attritor milling and hot pressing. *Journal of the European Ceramic Society* 37, 3797–3804.
- Balko, J., Hvizdos, P., Duszka, J., Balazsi, C., Gamcova, J., 2014. Wear damage of Si₃N₄-graphene nanocomposites at room and elevated temperatures. *Journal of the European Ceramic Society* 34, 3309–3317.
- Belmonte, M., Ramirez, C., Gonzalez-Julian, J., *et al.*, 2013. The beneficial effect of graphene nanofillers on the tribological performance of ceramics. *Carbon* 61, 431–435.
- Belmonte, M., Miranzo, P., Osendi, M.I., 2018. Contact damage resistant SiC/graphene nanofiller composites. *Journal of the European Ceramic Society* 38, 41–45.
- Belmonte, M., Jurado, J.R., Treheux, D., Miranzo, P., 1996. Role of triboelectrification mechanism in the wear behaviour of Al₂O₃-SiC platelet composites. *Wear* 199, 54–59.
- Buri, B., Busch, S., Kubach, H., Spicher, U., 2009. High injection pressures at the upper load limit of stratified operation in a DISI engine. *SAE International Journal of Engines* 2, 40–47.
- Candelario, V.M., Moreno, R., Guiberteau, F., Ortiz, A.L., 2016. Enhancing the sliding-wear resistance of SiC nanostructured ceramics by adding carbon nanotubes. *Journal of the European Ceramic Society* 36, 3083–3089.
- Evans, A.G., Wilshaw, T.R., 1976. Quasi-static solid particle damage in brittle solids.-I. Observations, analysis and implications. *Acta Metallurgica* 24, 939–956.
- Gomez-Gomez, A., Nistal, A., Garcia, E., *et al.*, 2016. The decisive role played by graphene nanoplatelets on improving the tribological performance of Y₂O₃-Al₂O₃-SiO₂ glass coatings. *Materials & Design* 112, 449–455.
- Gonzalez-Julian, J., Schneider, J., Miranzo, P., Osendi, M.I., Belmonte, M., 2011. Enhanced tribological performance of silicon nitride-based materials by adding carbon nanotubes. *Journal of the American Ceramic Society* 94, 2542–2548.
- Gonzalez-Julian, J., Datye, A., Wu, K.-H., Schneider, J., Belmonte, M., 2014. Robust and wear resistant in-situ carbon nanotube/Si₃N₄ nanocomposites with a high loading of nanotubes. *Carbon* 72, 338–347.
- Guo, X., Wang, R., Zheng, P., Lu, Z., Yang, H., 2019. Pressureless sintering of multilayer graphene reinforced silicon carbide ceramics for mechanical seals. *Advances in Applied Ceramics* 118, 409–417.
- Gutierrez-Gonzalez, C.F., Smirnov, A., Centeno, A., *et al.*, 2015. Wear behavior of graphene/alumina composite. *Ceramics International* 41, 7434–7438.
- Gutierrez-Mora, F., Morales-Rodriguez, M., Gallardo-Lopez, A., Poyato, R., 2019. Tribological behavior of graphene nanoplatelet reinforced 3YTZP composites. *Journal of the European Ceramic Society* 39, 1381–1388.
- Holmberg, K., Andersson, P., Erdemir, A., 2012. Global energy consumption due to friction in passenger cars. *Tribology International* 47, 221–234.
- Holmberg, K., Siilasto, R., Laitinen, T., Andersson, P., Jämsberg, A., 2013. Global energy consumption due to friction in paper machines. *Tribology International* 62, 58–77.
- Hsu, S.M., Shen, M., 2004. Wear prediction of ceramics. *Wear* 256, 867–878.
- Hussainova, I., Baronins, J., Drozdova, M., Antonov, M., 2016. Wear performance of hierarchically structured alumina reinforced by hybrid graphene encapsulated alumina nanofibres. *Wear* 368–369, 287–295.

- Hvizdos, P., Dusza, J., Balazsi, C., 2013. Tribological properties of Si_3N_4 -graphene nanocomposites. *Journal of the European Ceramic Society* 33, 2359–2364.
- Hvizdos, P., Puchy, V., Duszova, A., Dusza, J., Balazsi, C., 2012. Tribological and electrical properties of ceramic matrix composites with carbon nanotubes. *Ceramics International* 38, 5669–5676.
- Iijima, S., 1991. Helical microtubules of graphitic carbon. *Nature* 354, 56–58.
- Kasperski, A., Weibel, A., Alkattan, D., *et al.*, 2013. Microhardness and friction coefficient of multi-walled carbon nanotube-yttria-stabilized ZrO_2 composites prepared by spark plasma sintering. *Scripta Materialia* 69, 338–341.
- Keshri, A.K., Agarwal, A., 2011. Wear behavior of plasma-sprayed carbon nanotube-reinforced aluminum oxide coating in marine and high-temperature environments. *Journal of Thermal Spray Technology* 20, 1217–1230.
- Kim, H.J., Lee, S.-M., Oh, Y.-S., *et al.*, 2014. Unoxidized graphene/alumina nanocomposite: fracture- and wear-resistance effects of graphene on alumina matrix. *Scientific Reports* 4, 5176.
- Krenkel, W., Berndt, F., 2005. C/C-SiC composites for space applications and advanced friction systems. *Materials Science and Engineering A* 412, 177–181.
- Lahiri, D., Singh, V., Keshri, A.K., Seal, S., Agarwal, A., 2010. Carbon nanotube toughened hydroxyapatite by spark plasma sintering: microstructural evolution and multiscale tribological properties. *Carbon* 48, 3103–3120.
- Laminini, S., Balazsi, C., Balazsi, K., 2019. Wear mechanism of spark plasma sintered MWCNTs reinforced zirconia composites under dry sliding conditions. *Wear* 430–431, 280–289.
- Lawn, B.R., 1998. Indentation of ceramics with spheres: A century after Hertz. *Journal of the American Ceramic Society* 81, 1977–1994.
- Lawn, B.R., Padture, N.P., Cai, H., Guiberteau, F., 1994. Making ceramics ductile. *Science* 263, 1114–1116.
- Lee, K.-S., Jang, B.-K., Sakka, Y., 2013. Damage and wear resistance of Al_2O_3 -CNT nanocomposites fabricated by spark plasma sintering. *Journal of the Ceramic Society of Japan* 121, 867–872.
- Li, H.Q., Xie, Y.T., Li, K., *et al.*, 2014. Microstructure and wear behavior of graphene nanosheets-reinforced zirconia coating. *Ceramics International* 40, 12821–12829.
- Lim, D.-S., You, D.-H., Choi, H.-J., Lim, S.-H., Jang, H., 2005. Effect of CNT distribution on tribological behavior of alumina-CNT composites. *Wear* 259, 539–544.
- Llorente, J., Ramirez, C., Belmonte, M., 2019. High graphene fillers content for improving the tribological performance of silicon nitride-based ceramics. *Wear* 430–431, 183–190.
- Llorente, J., Roman-Manso, B., Miranzo, P., Belmonte, M., 2016. Tribological performance under dry sliding conditions of graphene/silicon carbide composites. *Journal of the European Ceramic Society* 36, 429–435.
- Llorente, J., Belmonte, M., 2018. Friction and wear behaviour of silicon carbide/graphene composites under isooctane lubrication. *Journal of the European Ceramic Society* 38, 3441–3446.
- Low, I.M., 2006. *Ceramic-Matrix Composites: Microstructure, Properties and Applications*. Cambridge: Woodhead Publishing.
- Maros, B.M., Nemeth, A.K., Karoly, Z., *et al.*, 2016. Tribological characterisation of silicon nitride/multilayer graphene nanocomposites produced by HIP and SPS technology. *Tribology International* 93, 269–281.
- Melk, L., Rovira, J.J.R., Antti, M.-L., Anglada, M., 2015. Coefficient of friction and wear resistance of zirconia-MWCNTs composites. *Ceramics International* 41, 459–468.
- Miranzo, P., Belmonte, M., Osendi, M.I., 2017. From bulk to cellular structures: A review on ceramic/graphene filler composites. *Journal of the European Ceramic Society* 37, 3649–3672.
- Novoselov, K.S., Geim, A.K., Morozov, S.V., *et al.*, 2004. Electric field effect in atomically thin carbon films. *Science* 306, 666–669.
- Novoselov, K.S., Falko, V.I., Colombo, L., *et al.*, 2012. A roadmap for graphene. *Nature* 490, 192–200.
- Popov, V.N., 2004. Carbon nanotubes: Properties and application. *Materials Science and Engineering R* 43, 61–102.
- Porwal, H., Tatarko, P., Saggarr, R., *et al.*, 2014. Tribological properties of silica-graphene nano-platelet composites. *Ceramics International* 40, 12067–12074.
- Roman-Manso, B., Sanchez-Gonzalez, E., Ortiz, A.L., *et al.*, 2014. Contact-mechanical properties at pre-creep temperatures of fine-grained graphene/SiC composites prepared in situ by spark-plasma sintering. *Journal of the European Ceramic Society* 34, 1433–1438.
- Rutkowski, P., Stobierski, L., Zientara, D., *et al.*, 2015. The influence of the graphene additive on mechanical properties and wear of hot-pressed Si_3N_4 matrix composites. *Journal of the European Ceramic Society* 35, 87–94.
- Sedlak, R., Kovalcikova, A., Balko, J., *et al.*, 2017. Effect of graphene platelets on tribological properties of boron carbide ceramic composites. *International Journal of Refractory Metals and Hard Materials* 65, 57–63.
- Sharma, N., Alam, S.N., Ray, B.C., Yadav, S., Biswas, K., 2019. Wear behavior of silica and alumina-based nanocomposites reinforced with multi walled carbon nanotubes and graphene nanoplatelets. *Wear* 418–419, 290–304.
- Shin, J.-H., Hong, S.-H., 2012. Microstructure and mechanical properties of single wall carbon nanotube reinforced yttria stabilized zirconia ceramics. *Materials Science & Engineering A* 556, 382–387.
- Tapasztó, O., Balko, J., Puchy, V., *et al.*, 2017. Highly wear-resistant and low friction Si_3N_4 composites by addition of graphene nanoplatelets approaching the 2D limit. *Scientific Reports* 7, 10087.
- Wang, H.-D., He, P.-F., Ma, G.-Z., *et al.*, 2018. Tribological behavior of plasma sprayed carbon nanotubes reinforced TiO_2 coatings. *Journal of the European Ceramic Society* 38, 3660–3672.
- Wang, X., Padture, N.P., Tanaka, H., 2004. Contact-damage-resistant ceramic/single-wall carbon nanotubes and ceramic/graphite composites. *Nature Materials* 3, 539–544.
- Xie, Y.T., Li, H.Q., Zhang, C., *et al.*, 2014. Graphene-reinforced calcium silicate coatings for load-bearing implants. *Biomedical Materials* 9, 025009.
- Yazdani, B., Xu, F., Ahmad, I., *et al.*, 2015. Tribological performance of graphene/carbon nanotube hybrid reinforced Al_2O_3 composites. *Scientific Reports* 5, 11579.
- Zeng, Z., Liu, Y., Guo, R., Li, K., 2019. Friction and wear behaviours of in situ reduced graphene oxide reinforced zirconia ceramic. *International Journal of Refractory Metals and Hard Materials* 79, 164–170.
- Zhang, C., Nieto, A., Agarwal, A., 2016. Ultrathin graphene tribofilm formation during wear of Al_2O_3 -graphene composites. *Nanomaterials and Energy* 5, 1–9.
- Zhang, W., Schröder, C., Schlüter, B., *et al.*, 2018. Effect of mechanochemically functionalized multilayer graphene on the tribological properties of silicon carbide/graphene nanocomposites in aqueous environment. *Tribology Letters* 66, 121.
- Zhao, Q., Shen, Y., Ji, M., *et al.*, 2014. Effect of carbon nanotube addition on friction coefficient of nanotubes/hydroxyapatite composites. *Journal of Industrial and Engineering Chemistry* 20, 544–548.

Methods of Determination of Young's Modulus and Tensile, Flexural and Compressive Strength

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General Introduction

This chapter aims at describing the main experimental methods used to determine critical mechanical parameters for ceramics: Young's modulus and fracture strength. The determination of fracture toughness, although a critical parameter for structural materials, will not be considered here.

Ceramic materials have stiff interatomic bonds and therefore high values of Young's modulus E (typically several hundreds of GPa), associated to high melting temperatures, these two properties being linearly correlated. This high stiffness explains that ceramic components show limited deformation when submitted to mechanical loadings. Glasses show Young's modulus ranging typically from 10 to 160 GPa (Rouxel, 2006). Ceramics and glasses can be found in their porous form in many multifunctional applications, with a total porosity fraction ranging from 0% to more than 90%. Young's modulus is in that case strongly dependent on the porosity fraction (Rice, 1998) and can be as low as 1 MPa of silica aerogels with porosity fraction above 90%. It is also worth mentioning concrete, as the largely used material in volume in the world, with a typical value of E of 30 GPa.

The fracture strength of ceramics is also high, typically of several hundreds of MPa in tension, and several GPa in compression in the case of dense ceramics. Ceramics and glasses usually show a linear elastic behavior until sudden fracture, at least at room temperature. The experimental scatter in fracture strength is relatively high as compared to ductile materials such as metals or polymers. This has a strong influence of the mechanical analysis for ceramic components in order to ensure a minimal probability of failure (Danzer *et al.*, 2008; Bermejo and Danzer, 2014). The porosity fraction has logically a deleterious influence of the fracture strength (Sanahuja *et al.*, 2010; Colombo *et al.*, 2013).

Determination of Young's Modulus

Definition

Elastic moduli link stresses and strains in the elastic domain, when no irreversible macroscopic deformation is noted, hence associated to small applied strains, typically below 0.1%. Young's modulus is defined as the ratio between axial (in the direction of solicitation) stress and axial strain in uniaxial tests, Poisson's ratio as the opposite of the ratio of lateral strain to axial strain. Shear modulus is the ratio of shear stress to shear strain in shear loadings. Bulk modulus is the ratio of hydrostatic pressure to hydrostatic volume variation in hydrostatic tests.

For isotropic materials, only two independent constant are needed to describe its entire elastic properties. Usually, Young's modulus E and Poisson's ratio ν are used, but bulk modulus K and shear modulus G are also commonly used. These latter moduli are related to the former one using the following equations:

$$K = \frac{E}{3(1-2\nu)}, G = \frac{E}{2(1+\nu)}, E = \frac{9KG}{G+3K} \text{ and } \nu = \frac{E}{2G} - 1$$

Fig. 1 illustrates the flexibility tensor (inverse of the stiffness tensor) for an isotropic material linking stress and strain tensors.

Ceramic based materials can be anisotropic, as in the case of composites (such as long fibers ceramic matrix composites), porous materials (3D printed structures, freeze-cast materials), or bio-inspired materials (nacre-like ceramics). They usually show an orthotropic behavior, with 3 different values of Young's modulus, Poisson's ratio and shear modulus in three orthotropic directions, and a total number of unknown engineering constants of 9. For transverse isotropic materials, the entire stiffness tensor can be determined with 5 parameters. Most of the experimental data of elastic modulus for anisotropic ceramic materials focus on the stiffer direction. Testing monocrystalline materials also leads to anisotropic behavior, possibility with more than 9 independent constants, depending on the nature of the ceramic. The readers are advised to refer to the classic book of Nye (1985), or to a composite design reference book (Tsai and Melo, 2015). It is always possible to average any anisotropic stiffness tensor to get isotropic parameters representative of an isotropic polycrystalline material. Experimental methods for the determination of elastic modulus mainly focus on the determination of E . For Poisson's ratio, values are usually between 0.25 and 0.3 for dense ceramics, for glasses a large range of value is noted (Greaves *et al.*, 2011).

This section on the determination of Young's modulus is divided into vibration methods and direct methods (static mechanical testing) to determine elastic modulus and especially the Young's modulus.

Vibration Methods

These methods give access to dynamic moduli, usually measured at high frequencies (typically above 1 kHz) and at a low associated strain. They are more accurate methods as compared to direct methods.

$$\begin{bmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \varepsilon_{33} \\ \varepsilon_{23} \\ \varepsilon_{13} \\ \varepsilon_{12} \end{bmatrix} = \begin{bmatrix} \frac{1}{E} & -\frac{\nu}{E} & -\frac{\nu}{E} & 0 & 0 & 0 \\ -\frac{\nu}{E} & \frac{1}{E} & -\frac{\nu}{E} & 0 & 0 & 0 \\ -\frac{\nu}{E} & -\frac{\nu}{E} & \frac{1}{E} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{2(1+\nu)}{E} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{2(1+\nu)}{E} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{2(1+\nu)}{E} \end{bmatrix} \begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{23} \\ \sigma_{13} \\ \sigma_{12} \end{bmatrix}$$

Fig. 1 Representation of the flexibility tensor for an isotropic material (components expressed as a function of Young's modulus E and Poisson's ratio ν). The stiffness tensor is the inverse of the flexibility tensor. Reminder: σ_{ij} and ε_{ij} are the stress and strain component respectively. If $i = j$, this corresponds to tension or compression for stresses, and dilatation/contraction for strains. If $i \neq j$, it corresponds to shear stresses and angle distortion for strains.

Ultrasonic propagation

This method is based on the measurement of longitudinal and transversal waves speed in the sample using piezoelectric transducers. Two methods exist: the transmission method where two transducers are used (one to excite, the other to detect waves), and the pulse echo method where the same transducer excites and detects the wave after reflection on the back face of the specimen. From the time record and the dimensions of the specimens, the calculation of the elastic moduli is possible.

For isotropic materials, the measure of longitudinal and transversal speeds gives access to the two independent constants describing the stiffness tensor of the material.

For Young's modulus determination:

$$E = \rho \left(\frac{3V_L^2 V_T^2 - 4V_T^4}{V_L^2 - V_T^2} \right)$$

with ρ bulk density in kg m^{-3} , and V_L and V_T wave speeds in m s^{-1} for longitudinal and transversal waves respectively.

For Poisson's ratio:

$$\nu = 0.5 \left(\frac{V_L^2 - 2V_T^2}{V_L^2 - V_T^2} \right)$$

The shear modulus is logically only related to the transverse wave speed: $G = \rho V_T^2$.

Anisotropic materials can also be characterized in terms of elastic moduli, depending on the ability to produce samples oriented along the different directions of symmetry. Wave propagation allows the determination of all components of the stiffness tensor of single crystals, whatever their crystalline symmetry (Watt and Peselnick, 1980). An estimation of an average stiffness of a dense and isotropic polycrystal can then be performed (Meille and Garboczi, 2001).

The method needs specimens with a well-defined geometry and a controlled surface state (need of two homogeneous, flat and parallel surfaces). The use of coupling agent or of a clamping system between transducers and sample ensures the good wave excitation of the sample. Testing small samples may be delicate as sensors are relatively large, typically 1 cm in diameter. Accuracy of the measure is usually of a few percent (EN843-2, 2005).

Free and forced vibration

In this method, a sample is submitted to an external solicitation, simply standing on a support in the case of free vibration, and suspended on wires for forced vibration. The typical frequency range lies from 0.1 to 100 kHz. As for the ultrasonic wave propagation, this method is accurate and well adapted to ceramics and glasses, usually showing limited damping at room temperature. The measure is based on the determination of the resonant frequency, related to samples moduli, dimensions and weight. The damping properties of a material can be characterized with this technique, either by measuring the width of the resonance peak for forced vibration, or by the analysis of decaying fundamental frequency for free vibration.

This measurement method needs samples with a well-defined geometry (bars are the most common, rods are also possible for flexion resonance) and smooth surfaces. A parallelism of the surfaces to approximately one hundredth of the corresponding sample's dimension is needed. Using flexion and torsion resonance, it is possible to determine Young's and shear modulus respectively. The Poisson's ratio can therefore be calculated from E and G . An important caution is necessary on the nature of vibration modes activated (mainly flexion versus torsion modes). The nodes for fundamental resonance in flexion are located at $0.224 l$ from each end of the sample, l being the sample length. For fundamental resonance in torsion, the nodes are located at mid-length and at mid-width of the sample (EN843-2, 2005).

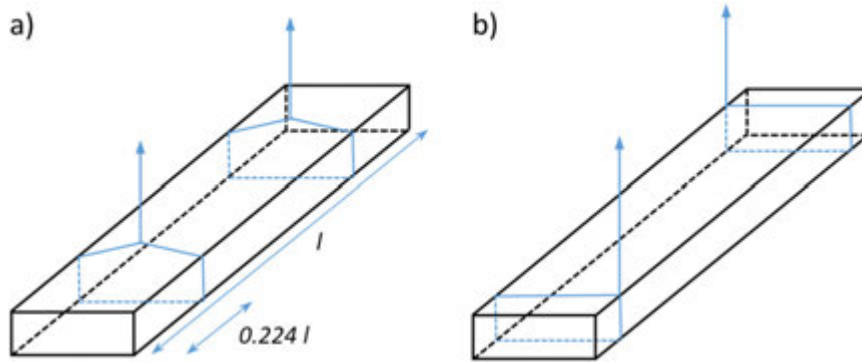


Fig. 2 Forced vibration method for the determination of elastic moduli, position of the wires used for excitation and for detection (a) flexural mode, (b) torsional mode.

For bars, a ratio of sample's length l to thickness h (in the direction of the flexural vibration) above 10 is recommended for flexion resonance, and above 20 for torsion resonance. In addition, a ratio of the length l on the width b should also be above 10. A ratio of width b to height h , b/h above 1.1 or below 0.9 is recommended to avoid confusion between vibration modes, typical values being $2.5 < b/h < 10$. It is therefore critical to pay attention in differencing b and h values when using the formulas.

Fig. 2 illustrates the testing specifications for flexion and torsion resonance for forced vibration.

Forced vibration

The sample is usually held by wires that drive and detect vibration. The wires must be positioned at the vibration nodes (see **Fig. 2**). For torsion resonance, the wires should be placed near the extremities, at the diagonally opposite corners. To ensure that a torsion mode is excited, possibly use a small microphone and move along the sample's length. The resonance should disappear at the center of the sample if it is torsional.

Impulse excitation method (free vibration)

The sample is supported at its nodes (i.e., at $0.224 l$ for bending mode, and at mid-length and mid-thickness for torsion mode) and mechanically excited by a light tap. The natural frequency of vibration is detected by a piezoelectric transducer or by a microphone. For flexion resonance, two parallel and compliant supports are located at the nodes and for torsion resonance at the center (specific support with a shape of a cross is usually supplied). The impact location should be at the centerpiece for flexion and at one corner of the sample for torsion. The position of the transducer should be either at the maximum vibration of the sample (near the ends, at mid-width for flexion and at a corner for torsion).

Apparatus for impulse excitation exist for high temperature up to 1500°C . The measure is also possible on disk shaped specimens (with a diameter to thickness ratio above 10). In that case, by exciting two different modes of vibration (symmetric mode and folding mode) can give access to the Poisson's ratio. If only one mode is activated and the Poisson's ratio is known, one can have access to the Young's modulus. Shear modulus can then be calculated, see (EN843-2, 2005) annex A for more details.

The same formulas for the calculation of moduli are used for both forced and free vibration techniques. For flexion resonance, the Young's modulus E is determined using equation:

$$E = 0.946 \left(\frac{mf^2}{b} \right) \left(\frac{l}{h} \right)^3 \left(1 + 6.585 \left(\frac{h}{l} \right)^2 \right)$$

with m mass of the sample, f resonance frequency of the fundamental mode, l , b and h length, width and height of the sample respectively. The last factor of the equation is a shape factor.

For torsional resonance, the equation to calculate the shear modulus G is (assuming $b > h$):

$$G = \left(\frac{4lmf^2}{bh} \right) \left(\frac{\frac{h}{b} + \frac{b}{h}}{4 \frac{h}{b} - 2.52 \left(\frac{h}{b} \right)^2 + 0.21 \left(\frac{h}{b} \right)^6} \right)$$

with f the resonant frequency in torsion, the other parameters being identical to the formula in flexion. The last factor in the equation is a shape factor.

Many other experimental methods exist to measure elastic properties, such as atomic force microscope AFM resonance or tapping modes, spectroscopy and diffusion / diffraction methods (Brillouin spectroscopy, neutrons and X-ray diffraction X-ray diffraction...). A detailed description of these techniques is beyond the scope of this chapter. The reading of the review paper by Angel *et al.* (2009) is recommended.

It is noteworthy to detail *resonant ultrasound spectroscopy (RUS)* as a complementary technique to those describe in this chapter. This technique is largely used in Earth sciences for the characterization of rocks. A sample is held between two piezoelectric sensors (a driver and a monitor), allowing the determination of different vibration frequencies in a single measure. Data reduction and

mode analysis usually take more time than the measure itself. This method is well adapted for anisotropic materials. To allow the determination of an anisotropic tensor with a single measurement, the sample needs to have a precise shape (sphere, or parallelepiped), polished surfaces, and being preferably dense. The sample characteristic size ranges typically from 1 mm to 1 cm. Measurements are possible up to 1500°C.

Direct Methods

These methods are based on the determination of the stress-strain linear relationship in a uniaxial mechanical test. They are largely used for determining elastic modulus, however they are not always adapted to ceramics due to the limited deformation to be measured, related to their high rigidity, and therefore to the difficulty to precisely measure the displacement of the sample.

General considerations

As mentioned here above, the determination of the displacement (and subsequently of the deformation) is particularly critical in the determination of elastic moduli on stiff specimens. The use of the crosshead displacement during mechanical tests is most of the time not precise enough to achieve a precise determination of E and it can lead to large errors in the elastic modulus determination. A proper displacement measurement can be made using:

- (1) Sensors, such as extensometers, LVDT (linear variable differential transducers), or strain gauges glued on sample's surface. These show a typical resolution 1 μm and less. Sensors for high temperature measurement exist, with alumina guides. It is also possible to use the crosshead displacement but only associated to a careful determination of the system stiffness (including contributions of the machine frame, the load cell, and the specific equipment) using a reference material with known elastic modulus.
- (2) Digital Image Correlation (Hild and Roux, 2006). This technique allows the characterization of the displacement field at the surface of samples during testing, using an appropriate measurement chain (video camera and objective), possibly at high temperature (Lepay et al., 2012). The calculation of the strain field is then possible from the displacement field. To improve the accuracy of the measurement, a regularization of the strain field can be used when known displacement fields corresponding to specific loading case are available. This is typically the case for tension/compression, flexion, and torsion. This enable to quantify the amount of rotation or of secondary bending in a tension test for example, and then to extract the relevant strain field corresponding to the pure tension loading.

The choice of a relevant load cell capacity is critical as the load values must lie in the measurement range of the cell, i.e., typically above 1% of the total capacity of the cell, this value being largely dependent on the cell quality.

For the stress and strain calculation, due to the high stiffness of ceramics and glasses, small deformation hypothesis is usually considered as valid. Engineering stresses and strains can be used instead of real stresses and strain. As shown hereafter, the main source of errors in the determination of elastic moduli and fracture stress, apart from the displacement measure, are the imperfections during testing.

Sample size

To test a representative elementary volume (REV), the rule of thumb is that the smallest dimension of the sample should be at least ten time the size to the largest heterogeneity of the material.

Uniaxial tension tests

This test implies a uniform axial solicitation, homogeneous in the central part of the sample, usually with a reduced cross-section, leading to an easy calculation of stresses and strains from the load and displacement values. The main concern is the possible imperfection during loading, mainly related to alignment issues. In that case, an additional bending moment can be applied to the sample. Therefore, an important care is necessary when designing a tensile test equipment. A more detailed description of the test is proposed in next section on the tensile fracture strength determination.

Using tensile test is certainly not the method to only measure E , due to the difficulty to run a well-controlled test. Tension tests are first carried out to determine tensile strength (see Section "Uniform Tests") and secondary to determine the Young's modulus.

Uniaxial compression tests

This test also leads to a uniform solicitation in the sample and therefore an easy determination of stress strain curves. However, experimental issues exist during uniaxial compression testing, mainly at the contact zones between top and bottom surfaces of the sample and the loading platens. As for uniaxial tension testing, more details on the experimental procedure are given in the compression strength determination (see Section "Uniform Tests").

A possible non-perfect parallelism of the top and bottom surfaces of the sample as well as the surface roughness always lead to stress concentrations that generate local irreversible damage. This results in non-linear behavior in the load – displacement curve. It is recommended to carefully prepare the samples and possibly to polished the surfaces in contact with the loading platens.

Running loading/unloading cycles in the elastic domain is the preferred method to estimate the slope of the stress strain curve, avoiding the influence of local damage and the non-perfect geometry of samples. This is particularly important for porous

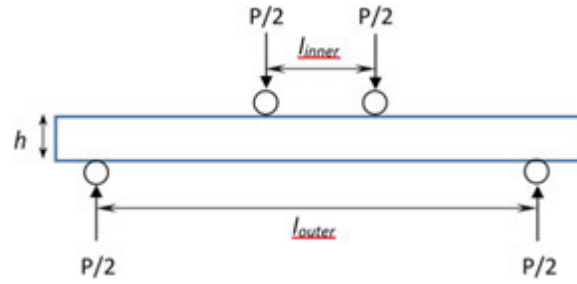


Fig. 3 Schematic representation of a 4 point bending test.

materials for which damage at the contact zone strongly influences the load-displacement curve. In that case, incorrect measurement of the slope of stress strain curve could lead to important errors in the determination of the Young's modulus, with a calculated value much smaller than the real one.

In some cases, the Young's modulus determined in compression may be smaller (typically 10% less) than the Young's modulus measured in tension. This is usually the case for micro-cracked materials (Lepay *et al.*, 2010; Belrhiti *et al.*, 2012; Bruno *et al.*, 2012). The material's behavior is then not perfectly elastic even though the macroscopic load-displacement curve appears linear. In such cases, the non-linear behavior is often more pronounced in tension tests (due to an easier opening of microcracks). The use of acoustic emission sensors to record elastic waves generated by local damage events is an efficient technique to define the stress or strain threshold above which damage is generated in the sample.

Bending tests

Flexion or bending testing is the preferred direct method to estimate the Young's modulus in ceramics and glasses, this for several reasons: no gripping of the samples unlike in tensile tests, no contact friction unlike in compression tests, and a rather large displacement of the sample (deflection) due to the low specimen stiffness in bending. However, experimental issues exist in bending, and the testing equipment should account for a non-perfect parallelism between top and bottom faces of bars (the most commonly used sample geometry).

The determination of the Young's modulus (as well as of the fracture stress, see Section "Determination of Fracture Strength") is based on the assumption of a symmetric behavior in tension and compression of the material, leading to a neutral axis located at mid-height of the sample. This assumption is considered to be valid for dense ceramics and glasses. For more details about the calculation of stresses and strains in bending, reference books such as Timoshenko (1955) are recommended. Here, only the formula to determine E is given. Fig. 3 illustrates a 4 point bending test configuration on a bar.

In the case of deflection measured at the center (mid-length) of the sample, E is given by:

$$E = \frac{\Delta P}{\Delta u} \frac{(l_{lower} - l_{upper}) (2l_{lower}^2 + 2l_{lower} \cdot l_{upper} - l_{upper}^2)}{8bh^3}$$

with u the deflection measured at the center of the specimen, P the applied load, l_{lower} and l_{upper} the distance between lower and upper rollers respectively, b the sample width, h the sample height. For 3 point bending, the equation is valid when considering $l_{upper} = 0$.

In the case of deflection measured on the loading points:

$$E = \frac{\Delta P}{\Delta u} \frac{(l_{lower} - l_{upper})^2 (l_{lower} + 2l_{upper})}{4bh^3}$$

with the same parameters as the previous equation.

The former equations are based on beam theory, and are valid under specific assumptions. In particular, the influence of shear stresses is neglected. This is considered as valid if the ratio of the lower span (or distance between lower rollers l_{lower}) to the sample's height, also referred as the slenderness, is large enough, typically above 8. If not, the additional deflection term caused by shear stresses as to be taken into account as it affects the Young's modulus determination. This influence can be taken into account by multiplying the Young's modulus determined without the influence of shear stresses by a factor χ :

$$\chi = 1 + \frac{(1 + \nu)h^2}{2l_{lower}^2 + 2l_{lower} \cdot l_{upper} - l_{upper}^2}$$

with the same parameters as the above equation, and ν the Poisson's ratio.

In case of large deflection during testing (for example for very thin samples or for a low stiffness material), the upper and lower roller distance may increase during the test, leading to a modification of the stress and strain in the material. In that case, possible friction may occur at the sample/roller interface. When testing materials that can damage under localized loading, wedging may occur below the rollers, affecting the measurement of the deflection. This effect is more pronounced with rollers of small diameter. A typical roller diameter of 3 mm is therefore recommended.

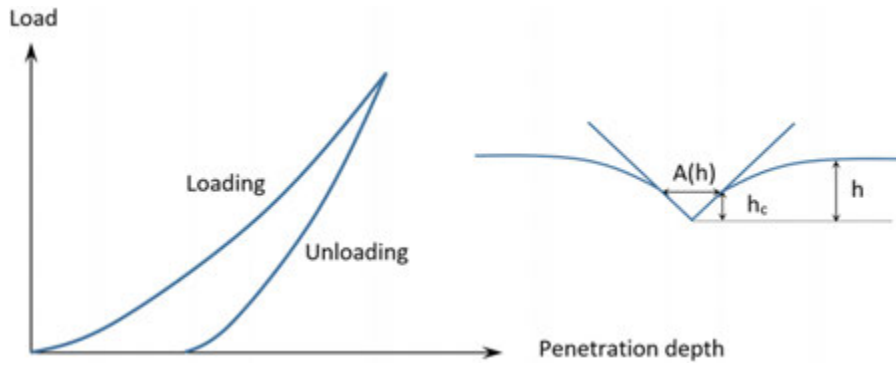


Fig. 4 Schematic representation of an instrumented indentation test, load – displacement curve and cross section of tip and sample during contact.

Corrections are proposed in literature to take into account these effects (Mitchell *et al.*, 2009). As an example, classical Hertz theory of elastic contact enables to correct the indentation influence of the roller (Quinn and Morrell, 1991; Munz and Fett, 1999). Identification of actual boundary conditions during testing is possible using regularized digital image correlation (Leplay *et al.*, 2010; Bouterf *et al.*, 2015).

The formulas given here above are also based on the hypothesis of symmetry between tension and compression stresses and strains in the sample, i.e., a neutral axis located at mid-height of the sample. If this is often respected during bending tests on dense ceramics and glasses, it is not the case for all materials, as in microcracked materials, stiffer under compression stresses that tend to close cracks than under tension stresses that tend to open them. In the case of a Young's modulus in tension lower than in compression, the neutral axis is not located at mid-height of the sample. Previous formulas for the determination of E are not valid anymore. Then, a precise determination of the position of the neutral axis is necessary, possibly using strain gages glued on the tensile and compressive faces of the sample (Simonin *et al.*, 2002) or digital image correlation. The calculation of the stress is then possible, for example if the stress-strain relationship in compression and tension is known (Leplay *et al.*, 2010).

Instrumented indentation

This direct technique is a local measure, allowing the determination of elastic properties in multiphase materials (as for cemented carbides or concrete (Velez *et al.*, 2001)), or in the presence of gradients of properties. It is also largely used in polycrystalline materials and glasses (Lawn, 1998; Rouxel *et al.*, 2010; Molnár *et al.*, 2016) as it enables to get properties from a small samples with no need of a well-controlled geometry. In addition, it can give a series of values on a single sample. Hardness determination by indentation is one of the most popular mechanical characterization method in Material Science. To get access to the elastic modulus, the indentation test must be instrumented, i.e., the load-displacement curve must be recorded during testing (Fig. 4).

In instrumented indentation testing, hardness is defined as the applied load to the projected contact area at maximum load, and elastic modulus can be estimated from the initial slope S of the unloading curve. The theoretical calculation is based on Sneddon work: (Fischer-Cripps, 2004)

$$S = \left(\frac{dP}{dh} \right)_{P_{\max}} = \frac{2\beta}{\sqrt{\pi}} E_r \sqrt{A(h_c)}$$

with P the applied load, h the penetration depth, h_c the contact depth, β a constant value depending of indenter geometry (1 for sphere and 1.012 for the Vickers), A the projected contact area of the tip and E_r the reduced Young's modulus.

The contact depth h_c is determined from the total penetration depth using different methods, such as Oliver & Pharr or Loubet methods (Oliver and Pharr, 1992; Bec *et al.*, 1996). The presence of sinking-in or pile-up around the indent has to be taken into account. Pile-up is usually observed in soft metals and more rarely on ceramics and glasses.

In Oliver & Pharr method, the contact depth h_c is calculated from the relation:

$$h_c = h_{\max} - \varepsilon \frac{P_{\max}}{S}$$

with $\varepsilon = 0.75$ for a Vickers/Berkovich tip and 0.72 for a sphere.

The reduced modulus E_r is determined using the following equation:

$$\frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu'^2}{E'}$$

with E and ν are respectively the Young's modulus and Poisson's ratio of the sample. E' and ν' being similar parameters for indenter's material. The values for the tip are usually well known, an assumption must be made on the Poisson's ratio of the tested material to estimate E .

The contact area is determined from the area function of the tip (defined as the projected contact area versus the penetration depth). For tips with a perfect geometry, $A(h_c)$ is calculated from the contact depth according to the following relations:

$$A = \pi a^2 = 2\pi R h_c - \pi h_c^2$$

for a spherical indenter of radius R

$$A = 4h_c^2 \tan^2 \theta = 24.5 h_c^2$$

for a Vickers or a Berkovich indenter.

Tips are usually pyramidal (Vickers and Berkovich being the most popular in instrumented indentation) or spherical. Spheres lead to a progressive setting of the tip / material contact and to a larger contact area at a given penetration depth, and therefore higher loads, as compared to sharp tip. Spherical tests are however more sensible to surface roughness since the penetration depth is lower.

A precise determination of the area function of the tip is necessary. Tests on calibrated fused silica is often used to identify the exact area function. Other corrections (frame compliance, thermal drift...) have to be made. The readers are encouraged to refer to reference books on this subject (Fischer-Cripps, 2004). An ISO standard is dedicated to instrumented indentation testing (ISO-14577, 2015).

Requirements on the sample for instrumented indentation are less conservative than for other mechanical tests, as no well-controlled geometry is needed, but only two flat and parallel surfaces. The surface state of the indented surface is critical as no reliable measurement is possible if the penetration depth is not at least three to five times larger than the root mean square (RMS) roughness (Miller *et al.*, 2008). The applied load must be high enough to avoid surface roughness influence and not too high to limit damage and cracking to ensure an elastic behavior during unloading. Continuous Stiffness Measurement (CSM) mode can be used to estimate the evolution of Young's modulus (and hardness) versus the penetration depth during the test.

Determination of Fracture Strength

A theoretical fracture strength of a perfect monocrystal can be calculated from the knowledge of its interatomic bounds. For cleavage fracture, this theoretical value approaches $E/7$, leading to tensile strength values above 10 GPa. Experimental values of tensile strength in ceramics and glasses are far below the theoretical strength, as the fracture originates from defects present in the material. Defects can be found in volume (related to fabrication: pores, impurities...) or at the surface (mainly related to fabrication and to sample preparation: machining, grinding, polishing). Guides for the fractography analysis are available (Quinn, 2007; EN843-6, 2009). The critical defect size, leading to the failure of a sample, can be calculated with the following formula:

$$a_c = \frac{1}{\pi} \left(\frac{K_{IC}}{\sigma_t} \right)^2$$

with K_{IC} the fracture toughness and σ_t the tensile fracture stress.

The determination of both parameters is therefore critical in the design of materials. For detailed studies on fracture mechanics of ceramics and on the design of ceramic component, specific references are recommended such as (Lawn, 1993; Danzer *et al.*, 2008).

For brittle materials like glasses and ceramics, a strong influence of the loading mode on the fracture strength is noted. The uniaxial compression strength is usually between five to ten times larger than the uniaxial tension strength. The choice of testing method for fracture strength determination is therefore of high importance and depends on the loading conditions in service, including manufacturing and handling. During service life, tension stresses are nearly always present (for example during machining, or due to residual stresses related to temperature gradients during processing or usage). Tension strength is usually the limiting strength for glasses and ceramics and is therefore a critical demand. However, in some applications such as the core of lightweight mineral boards for construction, the main solicitation is compressive.

In the following section, main different strength tests available for ceramics and glasses are listed according to their loading mode (uniform uniaxial loadings, non-uniform uniaxial loadings and multiaxial loadings). General recommendations for testing given in the previous section for the determination of elastic moduli (Section "Direct Methods") are also valid for strength determination. However, no measure of the specimen displacement is needed as fracture stress is calculated from fracture load and geometrical parameters.

The control of the test (either displacement-controlled or load-controlled) is not critical for purely elastic brittle material, as the fracture load is then easily identified as a drop in load at failure. This may be different for materials showing nonlinear behavior (for example due to local damage or plasticity). In that case, load-control testing is preferred to precisely determine the load at failure.

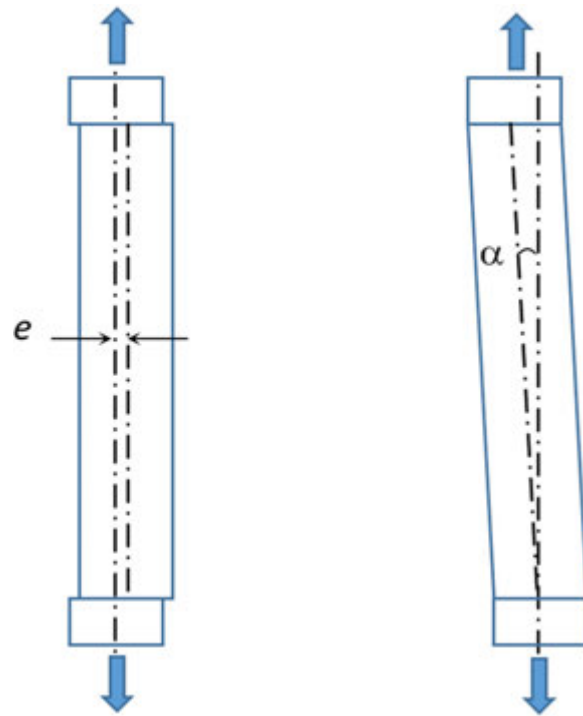


Fig. 5 Uniaxial tension testing: eccentricity e and misalignment α .

Uniform Tests

In such tests, the stress field is theoretically homogeneous in the sample, leading to a straightforward determination of the fracture strength, defined as the ratio of the fracture load to the cross-section area. However, imperfections during testing may influence the measured strength.

Uniaxial tension

It is the most adapted test to measure the tensile strength, however it is not commonly carried out on brittle materials due to the difficulty to avoid stress concentrations and secondary bending. Any imperfection during testing will tend to decrease the measured tensile strength.

Two main sources of imperfection in the tensile test are misalignment and eccentricity, as illustrated in [Fig. 5](#). To limit the misalignment two options exist, either using rigid fixations that should be perfectly aligned, or using equipment's allowing rotations (using universal/cardan joints) to ensure the best alignment. For sample gripping, two main options exist: either with glued tabs to limit damage in the holding part of the specimens, or direct mounting with half-shells to grip cylindrical specimens ([Hild et al., 1992](#)).

The use of samples with a perfectly controlled shape, usually dog-bone shaped, with a circular or a prismatic cross section, is also necessary. Samples with large cross section reduces eccentricity and facilitates the adjustment of grips ([Munz and Fett, 1999](#)). The zone with reduced cross-section has usually a length of 10 times the diameters for cylinders and at least 10 times the thickness for samples with prismatic cross section.

Strain gages glued on both sides of a flat rectangular tensile specimen enable to check the presence of a potential bending moment during testing ([Noguchi et al., 1990](#)). A correction of the fracture strength calculation is then possible, taking into account supplementary flexion ([Christ and Swanson, 1976](#); [Munz and Fett, 1999](#)). Digital image correlation monitoring during testing can also help to quantify test imperfections ([Leplay et al., 2010](#); [Bouterf et al., 2015](#)).

Uniaxial tension testing is usually performed on materials showing a non-linear behavior in tension such as concrete ([van Mier and van Vliet, 2002](#)) and thermostructural composites (ceramic matrix composites) ([Dalmaz et al., 1998](#)), as bending tests are usually preferred to estimate tensile strength for perfectly elastic materials up to failure.

Uniaxial compression

Under such loading conditions, ceramic samples can sustain very high stresses levels (several GPa) and therefore very high loads. Calculation of strength is straightforward as the ratio of fracture strength on the cross-section area. As noted for Young's modulus determination, compression testing seems easier to carry out than tension testing as the sample does not need to be gripped. This is only partially true as the friction at the interface between loading platens and sample can largely affect the fracture strength by generating unwanted local tension stresses. A possible flexion can also appear when testing rigid materials due to non-parallel

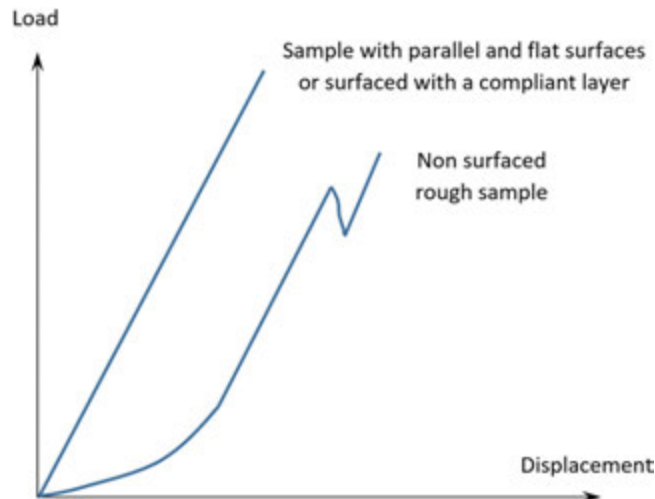


Fig. 6 Uniaxial compression testing, schematic representation of the influence of sample surface quality.

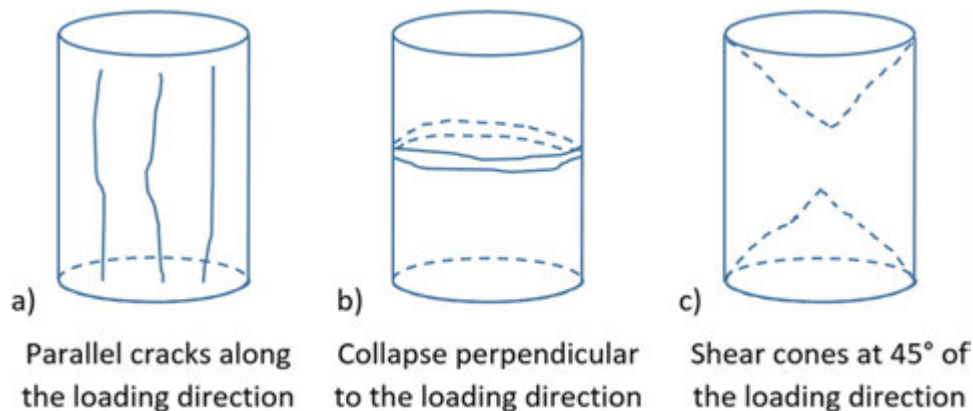


Fig. 7 Different fracture mode in uniaxial compression.

loading surfaces. The use of freely rotating upper platen (ball joint) is recommended, especially for all samples with non-perfectly parallel surfaces. It is also possible to surface treat the sample with a compliant material (wax, sulfur) to reduce friction, as commonly done in concrete. [Fig. 6](#) illustrates the influence of a non-perfect parallelism on load-displacement curve in uniaxial compression.

Sample geometry has an influence on the measured strength, and it is known in concrete testing that for a similar volume, testing cubes lead to higher strength than cylinders of 20% typically. Cylindrical samples, with an axisymmetric geometry, are preferred for uniaxial compression testing. A minimum aspect ratio (ratio of height on diameter) of two is needed to fully develop shear bands when testing frictional materials. The aspect ratio of samples should be below three to limit the risk of buckling during test. Therefore, cylinders with aspect ratios varying from two to three are most commonly used.

The observed fracture mode depends on the materials tested (see [Fig. 7](#)):

- For dense ceramics and glasses, brittle failure is noted with cracks oriented along solicitation direction (maximum tensile stresses) ([Sammis and Ashby, 1986](#)),
- For highly porous materials, there is a transition from brittle to cellular behavior with increasing porosity, with a progressive shortening of the sample by collapse of horizontal layers ([Meille et al., 2012](#)),
- For frictional materials (concrete, porous ceramics), shear induced damage is observed, with formation of shear bands with extensive cracking at 45° from the loading direction.

In scientific papers, it is recommended to show a typical experimental stress-strain curve and to describe the fracture mode observed in uniaxial compression test. A precise description of the surface preparation of the samples (polishing, control of the parallelism between top and bottom surfaces, presence of a compliant layer) is also necessary, as it may impact the fracture strength.

Non-Uniform Tests

Bending or flexion test

Bending test is by very far the mostly used testing method to determine the tensile strength of brittle materials, as the direct tension tests are difficult to carry out properly. Note that fracture strength as determined in bending tests can lead to different values than direct tensile tests (see Section "Parameters Influencing Strength").

Bending loading favors fracture from the sample surface loaded in tension (usually the bottom face, as illustrated in Fig. 3), highlighting the influence of surface defects. Note that in uniform tests, the location of defects (surface or bulk) does not affect the probability of failure of the sample. Flexion tests are usually under 3 points or 4 points configurations, with respectively one and two upper rollers. For fracture stress determination, 4 point bending is preferred as the zone between the upper rollers is submitted to the same stress state (constant bending moment). This latter test is therefore more adapted to the influence of the defect distribution on the fracture strength.

Experimental issues still exist in bending tests, especially in the case of a sample with non-parallel top and bottom surfaces. It is recommended to use a test equipment with a freely rotating upper platen. Additional imperfections during testing may arise from large deflection (change in the distance between sample/rollers contact points), from wrong span positioning, and from contact stresses at the loading points. For a detailed analysis of the influence of initial sample curvature, wrong spans, eccentric loading, and friction, the readers are recommended to refer to (Quinn and Morrell, 1991; EN843-1, 2007).

The ratio of the distance between the two lower rollers to the sample height, referred as slenderness, is usually above 8 to limit the influence of shear stresses influence. This is critical for Young's modulus determination as mentioned in the previous section, but shear stresses might also induce fracture at mid-height of the sample (where the shear stresses are maximal) in the case of specimens with weak interfaces (case of anisotropic materials: composites, laminates).

A large majority of bending tests are carried out on bars. The control of the surfaces parallelism is critical, chamfrains are also preferred to limit stress concentrations at the edges of the samples. The formula for determination of the tensile strength for bars is given by:

$$\sigma = \frac{3P(l_{\text{lower}} - l_{\text{upper}})}{2bh^2}$$

with P applied load, b sample width, h sample height, l_{lower} and l_{upper} the distances between lower and upper rollers respectively. In case of 3 point bending, the formula is valid with $l_{\text{upper}} = 0$.

Flexural tests on rods also exist, as processing cylindrical specimens may be convenient, as for example with glass rods, porcelains, or catalyst supports. A particular attention to the contacts stresses at the loading points is necessary, even with the use of curved rollers (Mitchell *et al.*, 2009). The fracture stress for cylindrical specimens is given by:

$$\sigma = \frac{8P(l_{\text{lower}} - l_{\text{upper}})}{\pi D^3}$$

with D sample diameter. The equation is valid for 3-point bending with $l_{\text{upper}} = 0$.

In any loading configuration, it is necessary to check the location of the failure section in the sample. It should lie between the two upper rollers for 4 points bending. If the fracture occurs always below the same upper roller, the testing equipment leads certainly not to the same applied load for the two upper rollers (it should be $P/2$ for both rollers). For 3 point bending, if fracture is noted at a distance from the upper roller, the calculation of the fracture stress should be corrected. This can be easily done as the tensile stress in the bottom face of the sample varies linearly from a maximum value below the upper roller to a zero value at the contact line with the lower rollers. Cracks initiation at the contact zone with rollers should also be carefully checked.

In case on non-purely elastic behavior (non-symmetry between tension and compression stresses due to microcracks propagation (Bruno *et al.*, 2012), tests at high temperature with viscous effect (Leplay *et al.*, 2012), or elasto-plastic behavior associated to phase transformation (Chevalier *et al.*, 2019)), the formulas to calculate the fracture strength are no longer valid. The knowledge of the stress repartition along the thickness of the sample is necessary to estimate the tensile stress in the specimen. Assumption on the compression and on the tension behavior are then necessary. Bending testing is therefore not always the preferred characterization method for tensile strength determination, and uniaxial tension testing may be more relevant.

Multiaxial Tests Used to Determine Tensile Strength

Brazilian test (diametral compression)

This test is an alternative option to estimate the tensile fracture strength of brittle materials using a uniaxial compressive loading on cylindrical specimens. It has been initially developed to determine the tensile strength of concrete and later adapted to ceramics (Wright, 1955; Marion and Johnstone, 1977; Munz and Fett, 1999). It is a standard test for tensile strength determination on cylindrical catalyst supports (ASTM-D4179, 2003; ASTM-D6175, 2003). The sample is set horizontally with loading direction along the diameter of the sample (no need to grip the sample, see Fig. 8(a)). A linear contact between sample and upper and lower platens is supposed, leading to very high contact stresses. A compliant material (small piece of cardboard or of lightweight wood) is often used at the contact between sample and platens. Initiation of fracture occurs by the propagation of a vertical crack at the center of the section of the sample. The stress repartition is not homogeneous, with axial stress (σ_1 in Fig. 7) varying from

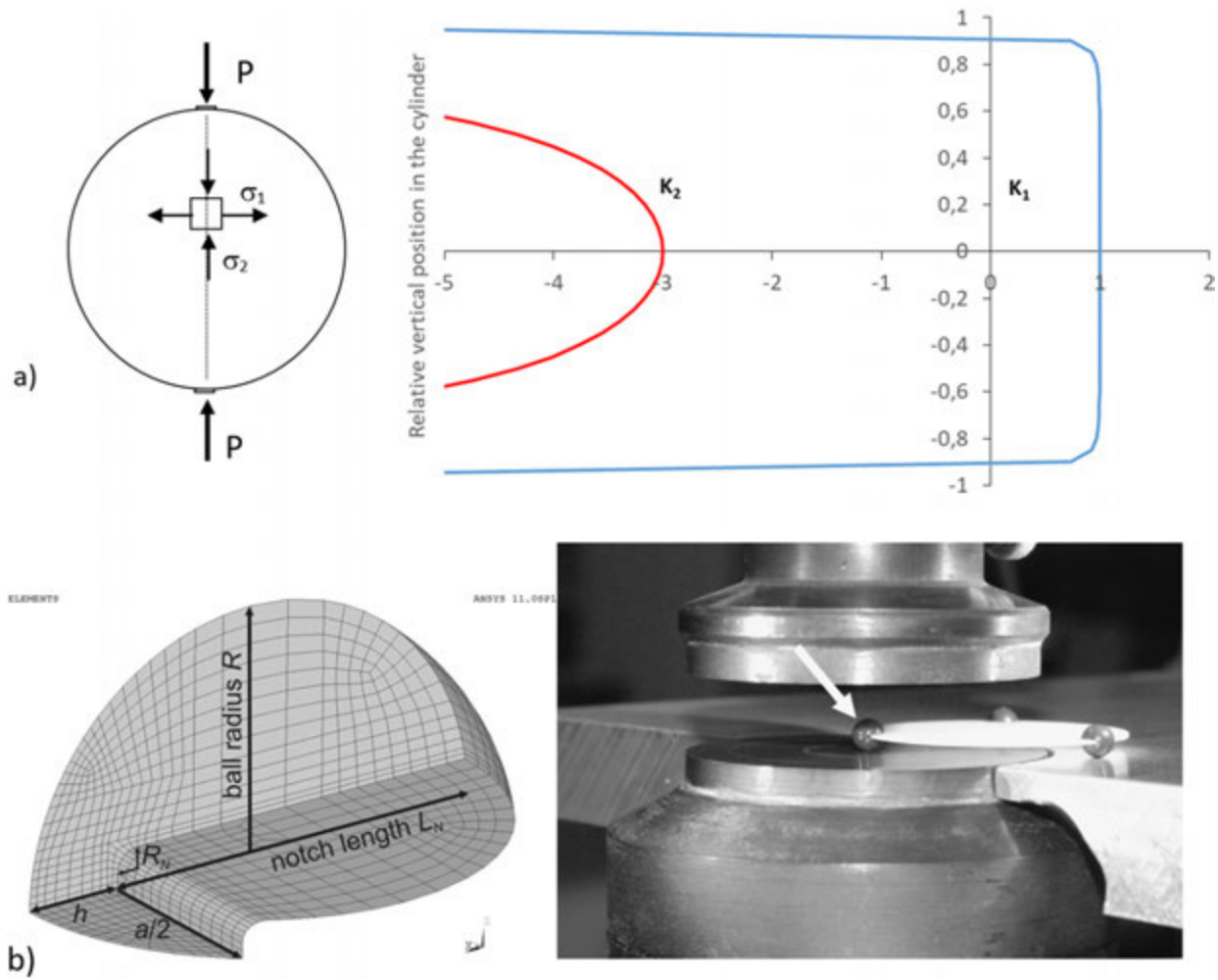


Fig. 8 (a) Illustration of the diametral compression test (Brazilian test) with evolution of K_1 and K_2 constants along the height of the sample and (b) geometrical parameter and illustration of the C-sphere test, from Supancic *et al.* Reproduced from Supancic, P., *et al.*, 2009. A new test to determine the tensile strength of brittle balls – The notched ball test. Journal of the European Ceramic Society 29 (12), 2447–2459. doi:10.1016/j.jeurceramsoc.2009.02.018.

compressive (at the contact points) to tensile, whereas transverse stresses (σ_2) are always compressive and are minimal at mi-height. General formulas for σ_1 and σ_2 are:

$$\sigma_1 = K_1 \cdot \frac{2}{\pi} \cdot \frac{P}{Dl}$$

$$\sigma_2 = K_2 \cdot \frac{2}{\pi} \cdot \frac{P}{Dl}$$

with P applied load, D sample diameter, l sample length, K_1 and K_2 constants.

On Fig. 8(a), the evolution of K_1 and K_2 is plotted along the height of the cylinder. Values at mi-height of the section, where the crack is initiated, lead to the following formulas for σ_1 (tensile stress, used for the tensile fracture strength calculation in brittle materials) and σ_2 (compressive stress):

$$\sigma_1 = \frac{2P}{\pi Dl}$$

$$\sigma_2 = \frac{-6P}{\pi Dl}$$

This test should not be used in case of large damage or densification in the sample near the contact lines as this would modify the calculated stress fields.

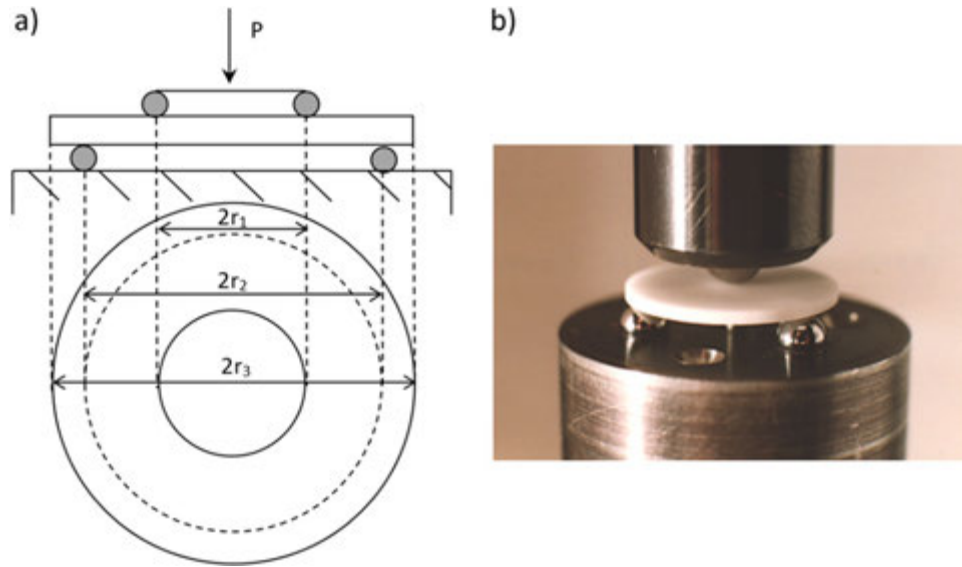


Fig. 9 (a) Schematic representation of ring on ring test with associated geometrical parameters, (b) illustration of a ball on 3 balls test (MATEIS, INSA Lyon).

C-Sphere test

This test has been initially developed to estimate the tensile strength of spherical samples (for example for balls used in ball-bearings). A slot is machined in a spherical sample and a uniaxial compression load is applied perpendicularly to the direction of the slot (see Fig. 8(b)). This solicitation is particularly adapted to test the influence of surface defects in spherical specimens, with a relative simple sample preparation. Test could be carried out on unnotched balls but the fracture occurs then at very high loads and any fractography of the sample is then impossible due to the disintegration of the sample after test (Wereszczak *et al.*, 2007). More recent work (Supancic *et al.*, 2009) has widened the use of this test, also referred as the notched ball test, considering variable notch shape and ball size. Note that a positioning aid to maintain the horizontal position of the notch during testing is helpful. The determination of tensile fracture in a C-sphere stress is done through a careful finite element (FE) analysis. The fracture stress can be computed with the following analytical formula:

$$\sigma = f_N \frac{6P}{h^2}$$

with P the applied load, h the ligament length and f_N a shape factor, depending on the relative notch length and width, the relative radius at the notch base, and the Poisson's ratio of the material, given in Supancic *et al.* (2009). A C-ring test also exists for determining strength for ring or tube-shaped components (EN843-7, 2007).

Biaxial bending

Biaxial bending is commonly used for tensile strength determination, due to the relative easiness to produce disk-shaped samples. Disks testing also limits cutting operation after pressing and sintering of ceramics as compared to bars testing. A major advantage of this procedure is to limit the influence of the edges of the sample, where machining may generate additional flaws, on contrary to 3 or 4 point bending tests. Biaxial tests are also more relevant for characterizing strength in the presence of residual thermal stresses, mostly biaxial in service application of ceramics components.

In a *ring-on-ring test*, a disk is supported on a ring and loaded by a concentric ring of smaller diameter, leading to a curvature of the sample and to biaxial bending (see Fig. 9(a)). The fracture strength is calculated as the maximum stress in the surface in tension (the surface in contact with the larger ring, usually the bottom face). In this test, radial and tangential stresses are identical (biaxial stress state), leading to a solicitation of the surface defects whatever their orientation. The determination of radial and tangential stresses in the tensile-loaded surface is given in (ISO-6474, 2011; ASTM-C1499, 2013) for $r < r_1$ where the stresses are maximum (expressions for $r > r_1$ are detailed in Munz and Fett (1999)):

$$\sigma_i = \frac{3P}{2\pi t^2} \left[(1 + \nu) \ln \left(\frac{r_2}{r_1} \right) + (1 - \nu) \left(\frac{r_2^2 - r_1^2}{2r_3^2} \right) \right]$$

i stands for radial and tangential directions

with P applied load, t sample thickness, r_1 loading ring radius, r_2 supporting ring radius, r_3 sample radius, and ν Poisson's ratio.

The equation is considered as valid if the disks are thin enough to limit shear stresses. It is usually recommended to have a support ring diameter at least 10 times the sample thickness. The failure of the sample should initiate from the tensile surface, where the formula is valid. Edge initiated failure should be removed from the analysis.

The limitation of the ring-on-ring test lies mainly in the need of a sample with parallel and flat surfaces, and with possible friction at the ring/sample contact line. The use of compliant layers to reduce friction effect is often made, especially for non-flat specimens.

Several adaptations to the ring on ring test have been proposed (ball on ring, ball on ring of balls, piston on three balls (Börger *et al.*, 2002; ISO-6872, 2015)), mainly to reduce friction effect and to be more tolerant to non-perfect parallel surfaces.

The *ball-on-three-balls (B3B) test* (Shetty *et al.*, 1980) a popular method to characterize the strength of ceramic components, for example on as sintered samples for production control. It has also been shown as particularly adapted to small specimens (Danzer *et al.*, 2007). A loading ball touches the disk-shape sample at the center of its top surface and the three supporting balls touch the disk on three points situated on a circle of radius R_a of its bottom surface (Fig. 9(b)). The calculation of the tensile stress is more difficult as compared to the ring-on-ring test due to the loss of axial symmetry, and extensive FE analysis is necessary. Analytic formulas are available to estimate the biaxial tensile stresses (Börger *et al.*, 2004):

$$\sigma = f \frac{P}{t^2}$$

with P the applied load, t the disk thickness and f a shape factor given by Börger *et al.* (2002), depending on R and t radius and thickness of the disk respectively, R_a radius of the circle defined by the contact points of three supporting balls, and constants varying with the Poisson's ratio of the tested material.

The formula is considered as valid for disk with thickness to radius ratios ranging from 0.05 to 0.6, limiting the risk of disk buckling (if too thin) and the risk of high contact loads at the ball / disk contact. Influence of test imperfections are discussed in Börger *et al.* (2004). The testing equipment should ensure a precise centering of loading and supporting spheres as well as allow ball rotation to reduce friction influence.

The *three balls-on-three balls (3B3B) test* has been developed from the B3B test to reduce the influence of loading stress spots and to increase the surface area tested (Fett *et al.*, 2007). Three loading balls and three supporting balls are used with two different configurations: loading and supporting spheres "in line", i.e., sphere centers located at the same polar angle, or loading or supporting spheres rotated by 60° .

For the "in line" configuration, with $R/R_1 = 2.25$ and $R_2/R_1 = 2$, R_1 being the radius of the loading sphere location circle and R_2 the radius of the supporting sphere location circle, the maximal tensile stress can be estimated by Fett *et al.* (2007):

$$\sigma = \frac{P}{t^2} \left(0.656 \left(\frac{t}{R_1} \right)^{-0.196} + 0.274 \left(\frac{t}{R_1} \right)^{-0.448} \nu \right)$$

with P applied load, t sample thickness, ν Poisson's ratio, and R_1 radius of the loading sphere location circle.

As the surface submitted to tensile stresses is larger than in B3B test, the average fracture strength as determined by 3B3B test is usually smaller than with B3B test.

Triaxial testing

It is possible to run triaxial tests on samples with three different principal stresses σ_{11} , σ_{22} , and σ_{33} (see Fig. 1). These are complex tests, rarely done on dense ceramics and glasses, but more common on rocks and soils, in order to determine a fracture criterion valid for any stress state. Triaxial tests were run on ceramics using internally pressurized tubes loaded axially in tension or compression (Ikeda and Igaki, 1984). Purely hydrostatic compression tests with three identical principal stresses, using either three manifolds, or pressurized fluid, or diamond anvil cells, lead to densification with absence of fracture, see for example (Keryvin *et al.*, 2014) on glass and (Bouterf, 2014) on porous ceramics.

Towards Small Scale Testing

Testing small samples is an increasing demand, as for example for electro ceramics components, for samples processed by complex methods (freeze-casting, magnetic assisted casting with a limited maximum size), or for explants of bio-ceramics or bio-glasses. A straightforward method for small scale testing is to miniaturize standard tests, for example the 4 points bending test (Lube *et al.*, 1997). The main limitation is this size reduction seems to be the influence of the contact stresses at the sample – roller interface. Using ceramic cylindrical rollers, the minimum distance between lower rollers is approximately 10 mm, corresponding to a typical sample size of $2 \times 2 \times 12 \text{ mm}^3$. A special care has to be brought to limit the roughness of samples with respect to roller diameter, the use of free rollers can also help to limit friction influence (Lube *et al.*, 1997). The B3B test is also well adapted for testing small samples.

To characterize the fracture strength at a smaller scale, micromechanics tests should be used on micro-specimens, usually in bending on cantilever beams or in compression on micropillars. Several approaches exist to fabricate such samples, such as FIB milling (Dehm *et al.*, 2018; Henry *et al.*, 2019a,b) (see Fig. 10), lithography (Gravier *et al.*, 2009), or micro electroerosion (Modica *et al.*, 2017). The typical samples dimensions are at the micron scale, ranging from 1 to 100 μm . Micromechanical testing offers the possibility to test inside grains, at grain boundaries, of thin layers. Strength values are usually very high as compared to standard specimen, typically of several GPa in tension, this being related to the small specimen size (Norton *et al.*, 2015; Henry *et al.*, 2019a,b).

Small scale testing is however highly demanding and requires electronic microscopy imaging for a precise measurement of geometrical parameters, numerical analysis to model the real loading conditions and the sample exact dimensions, and testing with micro or nanoindenters, ideally in situ. FIB milling may lead to ion implantation and amorphization, possibly modifying the

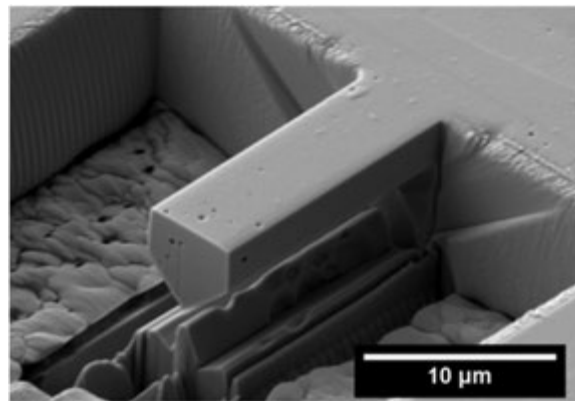


Fig. 10 FIB-milled cantilever beam, cubic zirconia. Reproduced from Henry, R., *et al.*, 2019a. Local fracture toughness measurements in polycrystalline cubic zirconia using micro-cantilever bending tests. *Mechanics of Materials* 136, 103086. doi:10.1016/j.mechmat.2019.103086. Henry, R., 2019b. Caractérisation locale des propriétés à la rupture du combustible irradié. PhD thesis, INSA Lyon.

Table 1 Central value of the Weibull distributions corresponding to a probability of failure of 63.2% and Weibull modulus measured on a polycrystalline alumina in 4-point bending, from Caravaca *et al.* Surface defects and residual stresses. Single plus (+) represents low, double plus (++) high, and null () absence

Test conditions	As received	Polished + annealed	Polished + annealed + sandblasted	Polished + annealed + sandblasted + annealed	Sandblasted
Surface defect	+		+	+	++
Residual stresses	++		+		++
σ_0 (MPa)	626	520	616	744	488
Weibull modulus	30	22	24	19	20

Note: Caravaca, C.F., *et al.*, 2018. Impact of sandblasting on the mechanical properties and aging resistance of alumina and zirconia based ceramics. *Journal of the European Ceramic Society* 38 (3), 915–925. doi:10.1016/j.jeurceramsoc.2017.10.050.

mechanical properties. The release of existing residual stresses during machining may also affect the mechanical parameters (Norton *et al.*, 2015). It is particularly the case for notch milling for testing fracture toughness, and less critical for fracture strength determination on un-notched samples.

Parameters Influencing Strength

Influence of sample preparation (polishing, annealing)

Sample preparation has a strong influence on strength, which appears to be rather logical as in many testing configurations (see bending), fracture initiates at the surface, where the tensile stresses are highest. A large influence of the presence of defects, of the surface roughness, and of residual stresses on the fracture strength and on its experimental distribution is found (Table 1). The sample preparation protocol before testing is therefore critical. One should choose sample preparation to have the closest sample state as compared to the in service conditions.

Test environment (temperature, presence of water)

At room temperature, fracture strength may be impacted by presence of water. Adsorbed water at the surface of samples and in the volume of porous samples reduces ionic and secondary (Van der Waals) bonds, and therefore decreases strength. This effect is largely referenced for ionic solids (gypsum, NaCl), glasses, and oxide ceramics, with possible slow crack growth due to stress corrosion (Wiederhorn, 1969, 1974). Local dissolution is also possible for ionic solids. It is recommended to control the storage conditions of samples, especially for materials with a high specific surface, as well as to control the temperature and relative humidity in the test rooms (or at least to mention the temperature and relative humidity in the test room in scientific papers).

High temperature testing of ceramics is critical as retaining high strength and rigidity at high temperature is an intrinsic characteristics of this class of materials. This can be done in oven with resistive heating and using magnetic susceptors heated by induction. A good control of the homogeneity of the temperature of the sample is necessary. The displacement measure for rigidity determination may be done with high temperature extensometers or using DIC. For glasses and ceramics, non-linear behavior is often more pronounced at high temperature than at room temperature due to viscous flow, leading to a possible anisotropy in tension-compression behavior. Therefore caution is required in the analysis of bending tests as the neutral axis may not be at mid-height of the sample.

Both water absorption and high temperature favor time-dependent effects in materials. Thus, strain rate, or stress rate, during testing may have an influence of the fracture strength (strength increases with the strain-rate), and therefore needs to be mentioned in the papers.

Statistical Analysis/Size Effect

As ceramics and glasses are brittle materials, their fracture strength is largely affected by the presence of defects and can show an important scatter. It is therefore necessary to characterize the strength in terms of probability of failure using a statistical analysis. This is not the objective of this chapter as many reference documents exist. Weibull or Gaussian distribution functions can be used for that purpose (Lu *et al.*, 2002; Gorjan and Ambrožič, 2012). The most largely used function is Weibull, based on the weakest link theory, and well adapted to describe the fracture of brittle materials. The identification of the Weibull parameters (σ_0 and m) is preferably done with the maximum likelihood method (EN843–5, 2007; Davies, 2017).

The influence of the sample size on strength, linked to the statistical distribution of defects, is important in brittle materials. The volume under tensile stresses has a strong influence on the fracture strength, the larger the volume, the higher the probability to find a critical defect and therefore the lower the strength. As already mentioned, the tensile stress repartition in a specimen is also dependent on the test used (uniaxial tension, uniaxial or multiaxial flexion). The quantification of the sample size effect for standard test methods is based on the calculation of an equivalent volume, or an equivalent surface, depending on whether the fracture initiates from volume or surface flaws. The equivalent volume V_E (or equivalent surface S_E) is that of a uniaxial tensile specimen which, when subjected to a tensile stress σ_m , has the same probability of fracture as a specimen of volume V (surface S) stressed at σ_m in the test method considered (Quinn and Quinn, 2010). Formulas to estimate the influence of the sample size for standard testing geometries (such as 3 point and 4 point bending, biaxial bending, C-sphere test) are available in literature (Quinn, 2003; Rödel *et al.*, 2009; Supancic *et al.*, 2009). For multiaxial tests, the principle of independent action is often considered to perform the calculation of the equivalent volume.

As limitations, the Weibull distribution was found not to be valid to describe the sample size effect for very small samples (Danzer, 2006), as well as for porous materials (Lu, Danzer and Fischer, 2004). Size effects also exists in compression (Bazant, 1997). As a general trend, the larger the specimen volume for a given loading configuration, the higher the stored elastic energy before failure, and the more brittle the behavior.

Conclusion

For a proper experimental determination of Young's modulus and fracture strength, a relevant testing method first need to be chosen. As many experimental methods exist, the choice depends on the application targeted for the material, on its environment conditions in service (temperature, relative humidity), and also on the capability to produce samples with a controlled geometry. One critical question to be asked before choosing the testing method is: what do I want to measure? Testing a material in the most representative conditions to be relevant with respect to the application is certainly an important point to keep in mind for that purpose.

Please note that this chapter does not present an exhaustive list of testing methods for brittle materials, but the mainly used ones. Many other exists or will be developed. Below are some general recommendations:

- (1) Young's modulus is an intrinsic value for a material, averaging the contributions of its microstructural features. Two main groups of measurement techniques exist: vibration (dynamic) or mechanical testing (quasi-static), also referred as direct methods. Dynamic methods are more accurate than direct testing. For static tests, a precise measurement of displacement is needed when testing rigid materials. The use of extensometers is often necessary, digital image correlation can also be well suited to characterize the displacement field in the specimens.
- (2) Fracture strength is not an intrinsic material property, as it largely depends on the loading mode and on the testing method. The stress field in the sample tends to favor fracture either from the surface or from the whole volume of the sample. Special care to the control of test protocol as well as to the assumptions made to calculate the stress is needed. As sample size, surface preparation, and environment conditions have a strong influence of the fracture strength, it is recommended to test samples with a size and a surface state representative of the service conditions, in a relevant environment.

As a final remark, in addition to the description of the test method in scientific papers, authors should also give precise information on sample size and surface preparation, on environment conditions during storage and testing. Showing typical load displacement curves with a description of the observed fracture mode is also necessary. This could be possibly done in supplementary information associated to scientific articles.

References

- Angel, R.J., *et al.*, 2009. Elasticity measurements on minerals: A review. *European Journal of Mineralogy* 21 (3), 525–550. doi:10.1127/0935-1221/2009/0021-1925.
 ASTM-C1499, 2013. Standard Test Method for Monotonic Equibiaxial Flexural Strength of Advanced Ceramics at Ambient Temperature. ASTM International. pp. 1–13. doi:10.1520/C1499-09R13.2.

- ASTM-D6175, 2003. Standard Test Method for Radial Crush Strength of Extruded Catalyst and Catalyst Carrier Particles. Philadelphia PA: ASTM international.
- ASTM-D4179, 2003. Standard Test Method for Single Pellet Crush Strength of Formed Catalyst Shapes. Philadelphia PA: ASTM international.
- Bazant, Z.P., 1997. Size effect in compression fracture: Splitting crack band propagation. *Journal of Engineering Mechanics* 2 (1981), 162–172.
- Bec, S., *et al.*, 1996. Improvements in the indentation method with a surface force apparatus. *Philosophical Magazine A* 74 (5), 1061–1072. doi:10.1080/01418619608239707.
- Belrhiti, Y., *et al.*, 2012. Application of optical methods to investigate the non-linear asymmetric behavior of ceramics exhibiting large strain to rupture by four-points bending test. *Journal of the European Ceramic Society* 32 (16), 4073–4081. doi:10.1016/j.jeurceramsoc.2012.06.016.
- Bermejo, R., Danzer, R., 2014. Chapter 2.09 – Mechanical characterization of ceramics: Designing with Brittle Materials. In: Sarin, V.K. (Ed.), *Comprehensive Hard Materials*, vol. 2. Elsevier, pp. 285–298. doi:10.1016/B978-0-08-096527-7.00028-3.
- Börger, A., Supancic, P., Danzer, R., 2002. The ball on three balls test for strength testing of brittle discs: Stress distribution in the disc. *Journal of the European Ceramic Society* 22 (9–10), 1425–1436. doi:10.1016/S0955-2219(01)00458-7.
- Börger, A., Supancic, P., Danzer, R., 2004. The ball on three balls test for strength testing of brittle discs: Part II: Analysis of possible errors in the strength determination. *Journal of the European Ceramic Society* 24 (10–11), 2917–2928. doi:10.1016/j.jeurceramsoc.2003.10.035.
- Bouterf, A., *et al.*, 2015. Damage law identification from full field displacement measurement: Application to four-point bending test for plasterboard. *European Journal of Mechanics, A/Solids* 49. doi:10.1016/j.euromechsol.2014.06.001.
- Bouterf, A., (2014) *Comportement mécanique de la plaque de plâtre étudié par tomographie et essais mécaniques in-situ*, <http://www.theses.fr>. Cachan, Ecole normale supérieure. Available at: <http://www.theses.fr/2014DENS0010> (accessed 11.12.19).
- Bruno, G., *et al.*, 2012. Connecting the macro and microstrain responses in technical porous ceramics. Part II: microcracking. *Journal of Materials Science* 47 (8), 3674–3689. doi:10.1007/s10853-011-6216-y.
- Chevalier, J., *et al.*, 2019. Forty years after the promise of ceramic steel?: Zirconia-based composites with a metal-like mechanical behavior. *Journal of the American Ceramic Society* 103 (3), doi:10.1111/jace.16903.
- Christ, B., Swanson, S., 1976. Alignments problems in the tensile test. *ASTM Journal of Testing and Evaluation* 4 (6), 405–417.
- Colombo, P., Dunand, D.C., Kumar, V., 2013. Porous materials: Less is more. *Journal of Materials Research* 28 (17), 2187–2190. doi:10.1557/jmr.2013.232.
- Dalmaz, A., *et al.*, 1998. Mechanical behavior and damage development during cyclic fatigue at high-temperature of a 2-5D carbonSiC composite. *Composites Science and Technology* 58 (5), 693–699. doi:10.1016/S0266-3538(97)00150-4.
- Danzer, R., 2006. Some notes on the correlation between fracture and defect statistics: Are Weibull statistics valid for very small specimens? *Journal of the European Ceramic Society* 26 (15), 3043–3049. doi:10.1016/j.jeurceramsoc.2005.08.021.
- Danzer, R., *et al.*, 2007. The ball on three balls test-Strength and failure analysis of different materials. *Journal of the European Ceramic Society* 27 (2–3), 1481–1485. doi:10.1016/j.jeurceramsoc.2006.05.034.
- Danzer, R., *et al.*, 2008. Fracture of ceramics. *Advanced Engineering Materials* 10 (4), 275–298. doi:10.1002/adem.200700347.
- Davies, I.J., 2017. Unbiased estimation of the Weibull scale parameter using linear least squares analysis. *Journal of the European Ceramic Society* 37 (8), 2973–2981. doi:10.1016/j.jeurceramsoc.2017.03.015.
- Dehm, G., *et al.*, 2018. Acta Materialia Overview on micro- and nanomechanical testing: New insights in interface plasticity and fracture at small length scales. *Acta Materialia* 142, 248–282. doi:10.1016/j.actamat.2017.06.019.
- EN843-1, 2017. Advanced Technical Ceramics – Mechanical Properties of Monolithic Ceramics at Room Temperature – Part 1: Determination of Flexural Strength.
- EN843-2, 2005. Advanced Technical Ceramics – Monolithic Ceramics. Mechanical Properties at Room Temperature. Part 2: Determination of Young's Modulus and Poisson's ratio.
- EN843-5, 2007. Advanced Technical Ceramics – Monolithic Ceramics. Mechanical Properties at Room Temperature. Part 5: Statistical Analysis.
- EN843-6, 2009. Advanced Technical Ceramics – Monolithic Ceramics. Mechanical Properties at Room Temperature. Part 6: Guide for fractographic Investigation.
- EN843-7, 2007. Advanced Technical Ceramics – Monolithic Ceramics. Mechanical Properties at Room Temperature. Part 7: C-Ring Test.
- Fett, T., *et al.*, 2007. A 3-balls-on-3-balls strength test for ceramic disks. *Journal of the European Ceramic Society* 27 (1), 1–12. doi:10.1016/j.jeurceramsoc.2006.02.033.
- Fischer-Cripps, A.C., 2004. *Nanoindentation*. Springer.
- Gorjan, L., Ambrožič, M., 2012. Bend strength of alumina ceramics: A comparison of Weibull statistics with other statistics based on very large experimental data set. *Journal of the European Ceramic Society* 32 (6), 1221–1227. doi:10.1016/j.jeurceramsoc.2011.12.010.
- Gravier, S., *et al.*, 2009. New on-chip nanomechanical testing laboratory – Applications to aluminum and polysilicon thin films. *Journal of Microelectromechanical Systems* 18 (3), 555–569. doi:10.1109/JMEMS.2009.2020380.
- Greaves, G.N., *et al.*, 2011. Poisson's ratio and modern materials. *Nature Materials* 10 (11), 823–837. doi:10.1038/nmat3134.
- Henry, R., *et al.*, 2019a. Local fracture toughness measurements in polycrystalline cubic zirconia using micro-cantilever bending tests. *Mechanics of Materials* 136, 103086. doi:10.1016/j.mechmat.2019.103086.
- Henry, R., 2019b. *Caractérisation locale des propriétés à la rupture du combustible irradié* PhD thesis, INSA Lyon.
- Hild, F., Roux, S., 2006. Digital image correlation: From displacement measurement to identification of elastic properties – A Review. *Strain* 42 (2), 69–80. doi:10.1111/j.1475-1305.2006.00258.x.
- Hild, F., Amar, E., Marquis, D., 1992. Stress heterogeneity effect on the strength of silicon nitride. *Journal of the American Ceramic Society* 75 (3), 700–702.
- Ikeda, K., Igaki, H., 1984. Fracture criterion for alumina ceramics subjected to triaxial stresses. *Journal of the American Ceramic Society* 67 (8), 538–554. doi:10.1111/j.1151-2916.1984.tb19166.x.
- ISO-14577, 2015. *Metallic Materials — Instrumented Indentation Test for Hardness and Materials Parameters — Part 1: Test Method*. CEN.
- ISO-6474, 2011. *Implants for Surgery — Ceramic Materials — Part 2: Composite Materials Based on a High Purity Alumina Matrix with Zirconia Reinforcement*. ISO. pp. 1–17.
- ISO-6872, 2015. *Dentistry — Ceramic Materials*.
- Keryvin, V., *et al.*, 2014. Constitutive modeling of the densification process in silica glass under hydrostatic compression. *Acta Materialia* 62 (1), 250–257. doi:10.1016/j.actamat.2013.07.067.
- Lawn, B., 1993. *Fracture of Brittle Solids*. Cambridge University Press. <http://dx.doi.org/10.1017/CBO9780511623127>
- Lawn, B.R., 1998. Indentation of ceramics with spheres: A century after Hertz. *Journal of the American Ceramic Society* 81 (1998), 1977–1994. doi:10.1111/j.1151-2916.1998.tb02580.x.
- Leplay, P., *et al.*, 2010. Damage law identification of a quasi brittle ceramic from a bending test using digital image correlation. *Journal of the European Ceramic Society* 30 (13), doi:10.1016/j.jeurceramsoc.2010.05.021.
- Leplay, P., *et al.*, 2012. Identification of asymmetric constitutive laws at high temperature based on digital image correlation. *Journal of the European Ceramic Society* 32 (15), doi:10.1016/j.jeurceramsoc.2012.03.024.
- Lu, C., Danzer, R., Fischer, F.D., 2002. Fracture statistics of brittle materials: Weibull or normal distribution. *Physical Review E – Statistical, Nonlinear, and Soft Matter Physics* 65 (6), 1–4. doi:10.1103/PhysRevE.65.067102.
- Lu, C., Danzer, R., Fischer, F.D., 2004. Scaling of fracture strength in ZnO: Effects of pore/grain-size interaction and porosity. *Journal of the European Ceramic Society* 24 (14), 3643–3651. doi:10.1016/j.jeurceramsoc.2003.12.001.
- Lube, T., Manner, M., Danzer, R., 1997. The miniaturisation of the 4-point-bend test. *Fatigue & Fracture of Engineering Materials & Structures* 20 (11), 1605–1616. doi:10.1111/j.1460-2695.1997.tb01514.x.
- Marion, R.H., Johnstone, J.K., 1977. Parametric study of the diametral compression test for ceramics. *American Ceramic Society Bulletin* 56 (11), 998–1002.

- Meille, S., *et al.*, 2012. Mechanical properties of porous ceramics in compression: On the transition between elastic, brittle, and cellular behavior. *Journal of the European Ceramic Society* 32 (15), 3959–3967. doi:10.1016/j.jeurceramsoc.2012.05.006.
- Meille, S., Garbozi, E.J., 2001. Linear elastic properties of 2D and 3D models of porous materials made from elongated objects. *Modelling and Simulation in Materials Science and Engineering* 9 (5), 371–390. doi:10.1088/0965-0393/9/5/303.
- Miller, M., *et al.*, 2008. Surface roughness criteria for cement paste nanoindentation. *Cement and Concrete Research* 38 (4), 467–476. doi:10.1016/j.cemconres.2007.11.014.
- Mitchell, M.R., *et al.*, 2009. Flexural strength of ceramic and glass rods. *Journal of Testing and Evaluation* 37 (3), 101649. doi:10.1520/jte101649.
- Modica, F., Marrocco, V., Fassi, I., 2017. Micro-Electro-Discharge Machining (Micro-EDM). Cham: Springer, pp. 149–173. http://dx.doi.org/10.1007/978-3-319-39651-4_6
- Molnár, G., *et al.*, 2016. Densification dependent yield criteria for sodium silicate glasses – An atomistic simulation approach. *Acta Materialia* 111, 129–137. doi:10.1016/j.actamat.2016.03.053.
- Munz, D., Fett, T., 1999. Ceramics: Mechanical properties, failure behaviour, materials selection. In: Hull, R., Jagadish, C., Kawazoe, Y., *et al.* (Eds.), *Springer Series in Materials Science*. Springer.
- Noguchi, K., *et al.*, 1990. Strength analysis of yttria-stabilized tetragonal zirconia polycrystals. *Journal of the American Ceramic Society* 76(197841).
- Norton, A.D., *et al.*, 2015. Microcantilever investigation of fracture toughness and subcritical crack growth on the scale of the microstructure in Al_2O_3 . *Journal of the European Ceramic Society* 35 (16), 4521–4533. doi:10.1016/j.jeurceramsoc.2015.08.023.
- Nye, J.F., 1985. *Physical Properties of Crystals*. Oxford University Press.
- Oliver, W.C., Pharr, G.M., 1992. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *Journal of Materials Research* 7 (6), 1564–1583. doi:10.1557/JMR.1992.1564.
- Quinn, G.D., 2007. Recommended Practice Guide. Gaithersburg, MD: NIST, doi:10.6028/NBS.SP.960-16.
- Quinn, G.D., 2003. Weibull strength scaling for standardized rectangular flexure specimens. *Journal of the American Ceramic Society* 86 (3).
- Quinn, G.D., Morrell, R., 1991. Design data for engineering ceramics: A review of the flexure test. *Journal of the American Ceramic Society* 74 (9), 2037–2066. doi:10.1111/j.1151-2916.1991.tb08259.x.
- Quinn, J.B., Quinn, G.D., 2010. A practical and systematic review of Weibull statistics for reporting strengths of dental materials. *Dental Materials* 26 (2), 135–147. doi:10.1016/j.dental.2009.09.006.
- Rice, R.W., 1998. *Porosity of Ceramics: Properties and Application*. CRC Press.
- Rödel, J., *et al.*, 2009. Development of a roadmap for advanced ceramics: 2010–2025. *Journal of the European Ceramic Society* 29 (9), 1549–1560. doi:10.1016/j.jeurceramsoc.2008.10.015.
- Rouxel, T., 2006. Elastic properties of glasses: A multiscale approach. *Comptes Rendus – Mécanique* 334 (12), 743–753. doi:10.1016/j.crme.2006.08.001.
- Rouxel, T., *et al.*, 2010. Indentation deformation mechanism in glass: Densification versus shear flow. *Journal of Applied Physics* 107 (9), 1–5. doi:10.1063/1.3407559.
- Sammis, C.G., Ashby, M.F., 1986. The failure of brittle porous solids under compressive stress states. *Acta Metallurgica* 34 (3), 511–526. doi:10.1016/0001-6160(86)90087-8.
- Sanahuja, J., *et al.*, 2010. Micromechanical explanation of elasticity and strength of gypsum: From elongated anisotropic crystals to isotropic porous polycrystals. *Journal of Engineering Mechanics* 136 (2), doi:10.1061/(ASCE)EM.1943-7889.0000072.
- Shetty, D.K., *et al.*, 1980. Biaxial flexure test for ceramics. *American Ceramic Society Bulletin* 52 (12), 1193–1197.
- Simonin, F., *et al.*, 2002. Room temperature quasi-brittle behaviour of an aluminous refractory concrete after firing. *Journal of the European Ceramic Society* 22 (2), 165–172. doi:10.1016/S0955-2219(01)00257-6.
- Supancic, P., *et al.*, 2009. A new test to determine the tensile strength of brittle balls – The notched ball test. *Journal of the European Ceramic Society* 29 (12), 2447–2459. doi:10.1016/j.jeurceramsoc.2009.02.018.
- Timoshenko, S., 1955. *Strength of Materials*. D. Van Nostrand Co.
- Tsai, S.W., Melo, J.D.D., 2015. *Composite Materials Design and Testing: Unlocking Mystery with Invariants*. Stanford: Stanford Aeronautics & Astronautics: JEC Group.
- van Mier, J.G., van Vliet, M.R., 2002. Uniaxial tension test for the determination of fracture parameters of concrete: State of the art. *Engineering Fracture Mechanics* 69 (2), 235–247. doi:10.1016/S0013-7944(01)00087-X.
- Velez, K., *et al.*, 2001. Determination by nanoindentation of elastic modulus and hardness of pure constituents of Portland cement clinker. *Cement and Concrete Research* 31 (4), 555–561. doi:10.1016/S0008-8846(00)00505-6.
- Watt, J.P., Peselnick, L., 1980. Clarification of the Hashin-Shtrikman bounds on the effective elastic moduli of polycrystals with hexagonal, trigonal, and tetragonal symmetries. *Journal of Applied Physics* 51 (3), 1525–1531. doi:10.1063/1.327804.
- Wereszczak, A.A., Kirkland, T.P., Jadaan, O.M., 2007. Strength measurement of ceramic spheres using a diametrically compressed “C-sphere” specimen. *Journal of the American Ceramic Society* 90 (6), 1843–1849. doi:10.1111/j.1551-2916.2007.01639.x.
- Wiederhorn, S.M., 1969. Fracture surface energy of glass. *Journal of the American Ceramic Society* 52 (2), 99–105. doi:10.1111/j.1151-2916.1969.tb13350.x.
- Wiederhorn, S.M., 1974. Subcritical crack growth in ceramics. In: Bradt, R.C., Hasselman, D.P.H., Lange, F.F. (Eds.), *Fracture Mechanics of Ceramics*. Boston, MA: Springer, pp. 613–646. http://dx.doi.org/10.1007/978-1-4615-7014-1_12
- Wright, P.J.F., 1955. Comments on an indirect tensile test on concrete cylinders. *Magazine of Concrete Research* 7 (20), 87–96. doi:10.1680/mac.1955.7.20.87.

Fracture Toughness Measurement

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Introduction

As structural materials, ceramics are characterized by their brittle failure behavior. The material property that is used as a measure to quantify this brittleness is the fracture toughness. Even though ceramics have a much lower fracture toughness than most metals, some are tougher and easier to use in demanding applications and some are more brittle and prone to failure. As they are intended to be used in load bearing applications, the fracture toughness – although it is usually not a design quantity – will be a guide for choosing appropriate materials. Increasing toughness is a prior objective in materials development, fracture toughness is a measure in material qualifications, material manufacturers want to give numbers in their data sheets. Apart from dictating the strength of a part, fracture toughness is also a relevant material property in many loading situations where ceramics are preferentially used, e.g., in wear situations or environments with high and/or changing temperatures.

In this chapter the basics behind the concept of the fracture toughness will be briefly outlined, standardized test methods will be introduced and it will be shown why the measurement of fracture toughness of ceramics is not straight forward. Standardized methods will be described and discussed in terms of material aspects, comparability across materials and methods and practical issues. Using recent examples, it will be shown how the concepts behind standardized methods have recently been applied to non-standardized specimen geometries or even components. Finally, a section will briefly discuss the use of indentation cracks for the investigation of fracture properties of ceramics.

Basic Principles

Linear Elastic Fracture Mechanics

Under applied stress, failure of ceramics is caused by small discontinuities in the volume or at the surface of components (Danzer *et al.*, 2008). For simplicity, they can be described as small cracks, and are usually termed flaws or defects. In a structure containing cracks, linear elastic fracture mechanics (Gross and Seelig, 2006) can be applied to derive a condition at which propagation of a crack is possible.

First ideas on conditions for crack propagation were described by Griffith (1920). He made a balance for an ideal elastic solid between the energy losses (change in elastic energy, work done by crack propagation) and the energy gains (energy necessary for creating new crack surfaces).

The concept was refined more than 30 years later by Irwin, who proposed the concept of linear elastic fracture mechanics (Irwin, 1958). In his theory all involved energy changes are strictly proportional to the change in crack surface. The strain energy release rate, G , describes all energy losses (elastic energies and work) and the critical strain energy release rate G_c is equal to the energy necessary to create the new fracture surface. Unstable fracture occurs if the energy losses exceed the gain in fracture energy:

$$G \geq G_c \quad (1)$$

For plane stress conditions and for mode-I loading it holds (Ashby and Jones, 1980):

$$G = K^2/E \quad (2)$$

with the stress intensity factor K

$$K = \sigma Y \sqrt{\pi a} \quad (3)$$

The critical strain energy release rate is related to the fracture toughness K_{Ic} by

$$G_c = K_{Ic}^2/E \quad (4)$$

For plane-strain conditions and mode I loading, which are most relevant when testing ceramics, E has to be replaced by $E' = E/(1 - \nu^2)$ (Gross and Seelig, 2006). E is Young's modulus, ν is Poisson's ratio and σ is the stress acting normal to the prospective crack plane in the un-cracked body. Y is a geometric factor, which takes the geometry of the crack, specimen and stress field into account. With this notation the well-known Griffith/Irwin criterion for brittle fracture can be defined:

$$K \geq K_{Ic} \quad (5)$$

In crack-opening mode, fracture occurs if the stress intensity at the tip of a crack with size a reaches the critical stress intensity K_{Ic} . This gives the relation between fracture stress σ_f , fracture toughness K_{Ic} and the size of the failure causing defect a :

$$\sigma_f Y \sqrt{\pi a} = K_{Ic} \quad (6)$$

Note that the above equations were derived for fast running cracks. Eq. (6) is the connection between the material property fracture toughness, the defect size, which is to a certain extent controllable through processing, and the strength, which is the actual design goal for components.

Microstructure and Environmental Effects on Crack Growth

The principles of linear fracture mechanics were derived for a continuum containing a crack with smooth, planar faces that cannot transfer forces. The fracture toughness is assumed to be independent of crack length. Ceramic materials deviate from this model in various ways: they consist of grains, cracks may propagate inter- or transgranularly leaving behind a more or less rough surface, friction may be present between crack faces, phase transformations may take place in the stress field ahead of a crack tip. This is the playground of materials development with the goal to enhance the fracture toughness of a material (Becher, 1991). Crack faces that cannot be separated easily due to bridging elements like coarse grains, whiskers or second phase particles result in an increasing resistance against crack propagation as the crack advances. A phase transformation in front of a crack that results in particles with an increased volume shields the crack tip from applied stresses and also increases the fracture toughness during crack growth. In such cases, where a material exhibits so-called R-curve behavior, the fracture toughness depends on the extent of advance which a crack has undergone before becoming critical. This amount differs for the test methods described here. An assessment, how R-curve behavior influences the measured fracture toughness value can be found in the Section "Standardized methods and R-curves". The measurement of fracture toughness as a function of crack advance poses additional challenges to the measurement technology, i.e., simultaneous capturing of crack advance and load during stable crack extension and requires specific test procedures. For a detailed treatise on this topic, the reader is referred to the paper by Munz (2007).

Ceramics, especially oxide ceramics, glasses and silicate-containing materials, are susceptible to environmentally assisted crack growth (Munz and Fett, 1999) which takes place at stress intensities below the critical one and is therefore called sub-critical crack growth (SCCG). It is chemically triggered (Michalske and Freiman, 1983) and/or thermally activated (Schoeck, 1990) and is extremely difficult to avoid. Depending on the experimental conditions it precedes every failure to a certain amount, the lower the stressing rate, the more. Consequently, the strength will be low when measured with a small stressing rate (long test duration) and high when measured with a high stressing rate (fast tests). Only in few ceramics the amount a crack has grown by this mechanism can be distinguished by fractography from the residual fast fracture surface (Swab and Quinn, 1998; Quinn, 2016). This has led to the conclusion that in ceramics the true critical stress intensity factor has to be the one for fast fracture.

R-Curve behavior and SCCG can lead to similar features in quantities that are acquired during a fracture mechanical test, e.g., load-displacement curves, so that they cannot be discerned. For a correct interpretation of fracture toughness test results or even the choice of a suitable testing method for a given material it is necessary to know at least if either of them may be present and how it may have influenced the test result.

Standardized Methods for the Measurement of Fracture Toughness of Ceramics

Eq. (6) provides a way to measure fracture toughness. If we have a crack with known size and shape fractured by a measured applied stress and know the geometry factor Y , the fracture toughness K_{Ic} can readily be computed. As for all mechanical testing procedures, care has to be taken, that the reality meets the fracture mechanical model, which is used to evaluate the test, as close as possible. Therefore, mandatory conditions for rigorous fracture toughness measurement are thus (Quinn and Salem, 2003; Morrell, 2006):

- (1) Fracture by fast crack propagation of,
- (2) A well defined crack in,
- (3) A well defined stress field, for which,
- (4) A well defined geometry factor Y is known.

Ideas how specimens and procedures that fulfill these conditions can be implemented have been laid down for metals in ASTM E399 (2017). Unfortunately, these are not applicable to ceramics for several reasons.

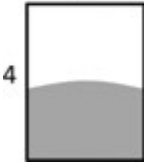
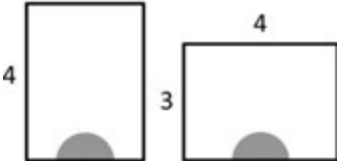
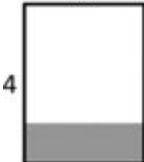
- (1) Ceramics are difficult and expensive to machine. It is relatively easy to grind pieces with flat faces, but it is difficult to drill holes or prepare cylinders.
- (2) Fatigue pre-cracking as suggested for metals does not work well for ceramics.
- (3) In many cases, only small material quantities are available for testing. Properties of ceramics depend on processing details. In many cases specimens have to be manufactured out of components.
- (4) The process zone in ceramics is small, so that the condition for small scale yielding also fulfilled for small specimens.

As a consequence, most standardized methods for fracture toughness measurement of ceramics use prismatic bars with a cross section of $W = 4 \text{ mm}$ and $b = 3 \text{ mm}$ and a length of approximately 45 mm which are flexure loaded in 4- or 3-point bending. ASTM C1421 (2018) allows for alternative dimensions for Chevron-notched bars. Pre-cracks or suitable notches are introduced into the prospective tensile surface of the bars by various methods. An overview of loading configuration, specimen dimensions and pre-crack shapes is given in Table 1, typical fracture surfaces are shown in Fig. 1.

Single-Edge Pre-Cracked Beam (SEPB) Method

For the single edge pre-cracked beam (SEPB) method which is standardized in ISO 15732 (2003) and ASTM C1421 (2018), a straight-through pre-crack with a relative depth a/W of $0.35 < a/W < 0.6$ is introduced. The specimen is then fractured in bending

Table 1 Overview of standardized specimens and loading geometries. In the leftmost column, the sketches of specimen cross-sections with the pre-crack and its configuration at fracture indicated in gray are shown. The numbers give the dimensions W and b in mm. The two other columns indicate the allowed loading configurations. L ... specimen length, 4P- x/y ... 4-point bending with support span x mm and loading span y mm, 3P- x mm ... 3-point bending with x mm support span.

Method	ISO, EN ISO	ASTM C1421
SEPB 	ISO 15732 $L \geq 35$ mm: 4P-30/10 mm $L \geq 45$ mm: 4P-40/20 mm $L \geq 18$ mm: 3P-16 mm $L \geq 35$ mm: 3P-30 mm $L \geq 45$ mm: 3P-40 mm	$20 \text{ mm} \leq L \leq 50 \text{ mm}$: 4P-16/8 mm to 4P-40/20 mm 3P-16 mm to 3P-40 mm
SCF 	EN ISO 18756 $L \geq 25$ mm: 4P-20/10 mm $L \geq 35$ mm: 4P-30/10 mm $L \geq 45$ mm: 4P-40/20 mm	$L \geq 25$ mm: 4P-20/10 mm $L \geq 45$ mm: 4P-40/20 mm
CNB 	ISO 24370 EN 14425-3:10 $L \geq 45$ mm: 4P-40/20 mm ISO 24370 allows for alternative geometries with certain geometrical restrictions	$L \geq 45$ mm: 4P-40/20 mm (two Chevron geometries) $W = 6$ mm, $b = 3$ mm, $L \geq 45$ mm: 3P-38 to 40 mm $W = 6.35$ mm, $b = 6.35$ mm, $L \geq 45$ mm: 4P-40/20 mm
SEVNB 	EN ISO 23146 $L \geq 35$ mm: 4P-20/10 mm $L \geq 45$ mm: 4P-40/20 mm $L \geq 35$ mm: 3P-30 mm $L \geq 45$ mm: 3P-40 mm	n.a.

with a rather fast loading rate in order to determine σ_f . The fracture test is generally conducted in a way that promotes unstable crack extension. The length of the pre-crack a is measured on the fracture surface, see Fig. 1(a). Specimens with pre-cracks of excessive uneven length or with pre-cracks that tilt or twist away from the ideal plane too much have to be rejected according to criteria specified in the standards.

The crucial point in this method is the introduction of the pre-crack. It is supposed to be driven into the specimen using indentation cracks or a shallow notch or a scratch as starter by a bridge-loading procedure, cf. Fig. 2. The gap in the upper block (the “bridge”) introduces a small tensile stress at the tip of the indentation starter cracks or the scratch. This leads to a pop-in of a longer crack, which is stopped by the overall compressive stress in the bar. There is no means to control the length of the pre-crack. Problems in generation of the pre-crack may occur in transformation toughened ceramics. In front of the indentation starter cracks or scratch a zone with compressive residual stresses may develop which inhibits the pop-in of the pre-crack. This is often expressed by extremely high loads that are necessary to achieve the pop-in. For tougher ceramics ($K_{Ic} > 4 \text{ MPam}^{0.5}$), the pre-cracking requires loads in the order of 8 kN to 25 kN (ISO 15732, 2003) while for the fracture test of the pre-cracked specimen itself, fracture loads are usually only 30 N to 150 N. In order to perform pre-cracking and the subsequent fracture test, two load cells with different maximum load range or even two different testing machines will have to be used to achieve the required accuracy of $\pm 1\%$ in force measurement.

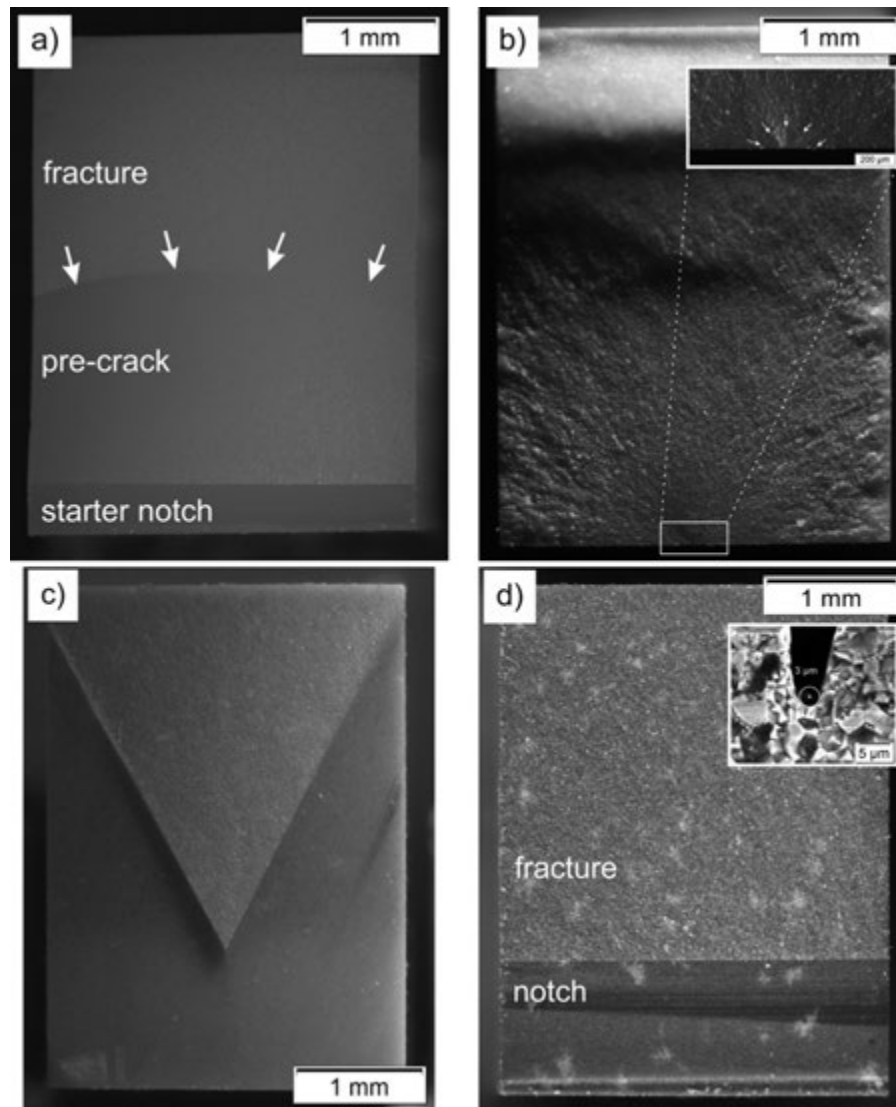


Fig. 1 Fracture surfaces of specimens tested with standardized methods. (a) single edge pre-cracked beam (SEPB), (b) surface crack in flexure (SCF), the insert shows details of the surface crack, (c) chevron notched beam (CNB), (d) single-edge V-notched beam (SEVNB), the insert shows the tip of a notch.

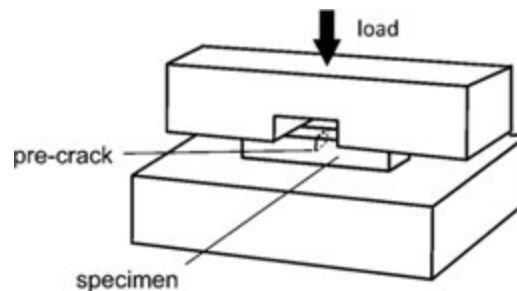


Fig. 2 Schematic of a 'bridge' device to obtain pre-cracks in SEPB specimens.

Surface Crack in Flexure (SCF) Method

This method is standardized in [ISO 18756 \(2005\)](#) and [ASTM C1421 \(2018\)](#). In this test a small semi-elliptical pre-crack is introduced into the bend bar using a Knoop indentation made with a load of typically 5 kg to 10 kg. In order to remove the residual stresses which are associated with the hardness imprint, a layer with a thickness of 4.5–5 times the indentation depth has

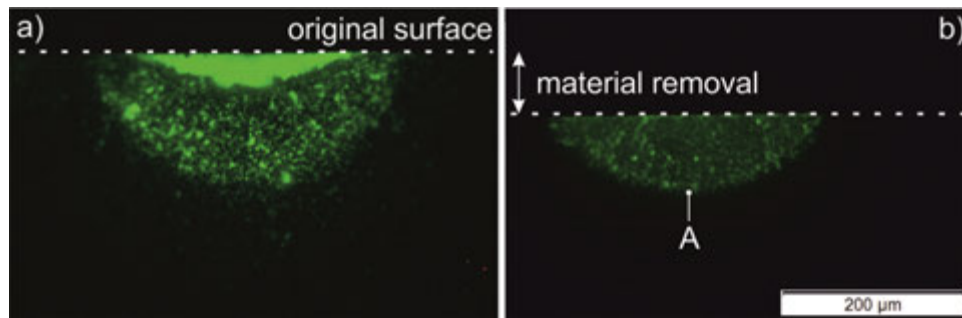


Fig. 3 Fracture surfaces of bend bars with Knoop indentation cracks impregnated with fluorescent penetration dye. (a) no material was ground off before the fracture test. The dashed line indicates the original specimen surface. (b) a ground-off crack, the dashed line indicates the new specimen surface. The deepest point, at which the maximum stress intensity will act, is indicated by A.

to be gently ground off the indented surface of the bar, see [Fig. 3](#). Then the bar is broken in a conventional 4-point bend test. The fracture toughness is calculated from the fracture stress σ_f of the bar, the crack depth, the surface crack length and the geometrical factor for semi-elliptical cracks derived by [Newman and Raju \(1981\)](#) for a Poisson's ratio of $\nu = 0.3$. The size of the pre-crack is measured on the fracture surface of the broken bar, see [Fig. 1\(b\)](#). In order to facilitate this, it is suggested to introduce the pre-crack with a slight twist or tilt with respect to the prospective fracture plane. While the generation of pre-cracks is straightforward but sometimes fails in transformation toughened materials, the identification of the pre-cracks on the fracture surfaces may be difficult, especially in coarse grained materials. Dye penetration procedures with inks (for light colored ceramics) or fluorescent dyes (for dark materials, [Fig. 3](#)) may facilitate this step.

Knoop indentations do not only generate the desired semi-elliptical surface breaking cracks but also cracks which run parallel to and below the surface – so called lateral cracks. They may be removed by the usual grinding procedure, but in some materials they are located at a depth beyond the ground-off layer ([Lube, 2001](#)). If they remain present in the specimens, the fracture toughness will be overestimated by up to 12% ([Quinn and Salem, 2003](#)). Checking the surface of the ground bars and possibly grinding off more material is a valid countermeasure.

The geometry factor for semi-elliptical surface cracks in a bend bar according to [Newman and Raju \(1981\)](#) depends on the size and shape of the crack and varies along its front and so does consequently the stress intensity. It is assumed that instable fracture starts at the point with the highest stress intensity. In order to satisfy the four prerequisites for good fracture toughness tests, it is desirable to get fracture from the deepest point of the crack front (point A in [Fig. 3\(b\)](#)). This is favored by shallow crack shapes, which in turn are generated by grinding off more material. As it is obvious from [Fig. 3](#), shallow cracks made in this way are no longer strictly semi-elliptical, they are truncated ellipses. This motivated a re-evaluation of the stress intensity factor for small surface cracks which also took into account values for Poisson's ratio different from $\nu = 0.3$. It turned out that a difference of several per cent may exist between the two solutions for specific geometries and Poisson's ratios ([Strobl et al., 2012a, 2018](#)). A study on glasses, where measurements made with the SEPB method and the SCF method were compared, showed that equal results could only be obtained when the new geometry factor for the correct Poisson's ratio was used ([Quinn and Swab, 2017](#)). The new geometry factors are available as fitted functions ([Strobl et al., 2012a, 2018](#)) or through an online tool ([Lehrstuhl für Struktur- und Funktionskeramik, 2020](#)).

Chevron-Notched Beam (CNB) Method

The method is standardized in [EN 14425-3 \(2010\)](#), [ISO 24370 \(2005\)](#), and [ASTM C1421 \(2018\)](#). Besides the preferred chevron shape, ISO 24370 allows for alternative geometries with certain restrictions, ASTM C1421 is even more flexible with three different possible cross sections and two different chevron shapes allowed for standard bend bars with a cross section of $3 \text{ mm} \times 4 \text{ mm}$. For this test method it is not necessary to produce a proper pre-crack. Instead, the bar is notched in a way that a chevron shaped ligament remains intact, [Fig. 1\(c\)](#). Upon loading a sharp crack starts to grow from the tip of the chevron. During further loading this cracks first grows stably because the cracked area gets disproportionately larger. During this crack growth the geometry factor for the crack decreases with increasing crack length. When it reaches a minimum, instable fracture of the specimen occurs. The fracture toughness is calculated from the specimen dimensions, the load at fracture and the minimal geometry factor which depends on the chevron geometry. No measurement of the crack length is necessary, but the existence of the stable crack growth has to be assured. Tests are only valid if the load-displacement-, load-time- or load-backface strain-plots recorded during the test show a behavior like to one depicted in [Fig. 4\(a\)](#) and [\(b\)](#). In [Fig. 4\(a\)](#), the deviation from linearity at P_i indicates stable crack growth before unstable fracture. Plots like the one shown in [Fig. 4\(b\)](#) are recorded, if the crack starts at a small overload, then pops in and finally grows stably until final fracture. Note that the pop-in load P_i may also be slightly higher than the final fracture load $P_{\max}$. Tests without any indication of stable crack growth which give plots like the one shown in [Fig. 4\(c\)](#) are invalid.

The preparation of chevron notches which fulfill the tight specifications given in the standards requires some practice and good equipment. Usually two separate cuts with precise depth through the cross section are necessary which have to be

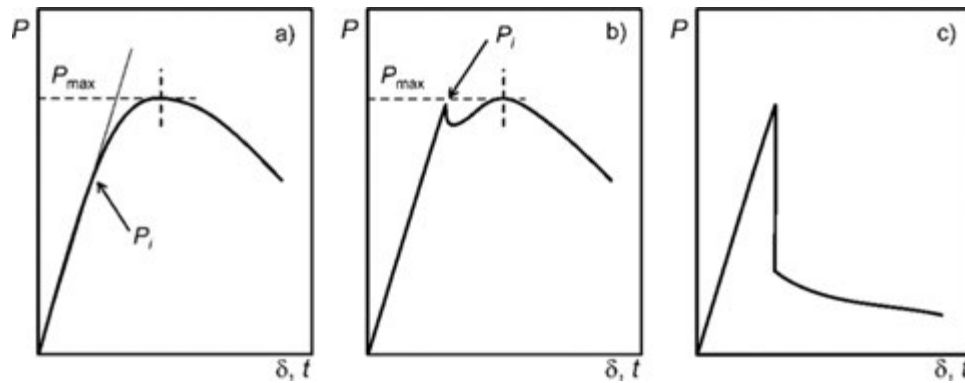


Fig. 4 Typical load-displacement (P - δ) or load-time (P - t) curves obtained during CNB tests. (a) stable crack growth, valid test (b) crack pop-in followed by stable crack growth, valid test, (c) unstable fracture, invalid test.

aligned within a narrow tolerance. The method can be applied to all ceramics because no complications regarding identification of crack lengths are to be expected. In transformation toughened ceramics and in materials with a high Young's modulus it may be difficult to obtain stable crack growth. A stiff testing system where most of the compliance is in the specimen eases the test procedure.

Single-Edge V-Notched (SEVNB) Method

The most recently standardized method is the single-edge V-notched beam method of ISO 23146 (2012). This method resembles the SEPB method in fracture test execution and calculation of the fracture toughness. Instead of the long, sharp pre-crack a slender notch is used. The fracture toughness is calculated from the stress at failure measured in a 3- or 4-point bend test, the depth of the notch and the corresponding geometry factor. The notch should have a relative depth a/W of $0.2 < a/W < 0.3$ and a notch root radius ρ which is smaller than the mean grain size of the tested material but in any case $\rho < 10 \mu\text{m}$. Such notches can be prepared by sharpening a saw cut with a razor blade and $1 \mu\text{m}$ diamond paste. With the use of a reciprocating machine notches can be cut directly into the smooth specimen surface using a coarse diamond grit. In fine grained materials notch root radii of $\rho \approx 2 \mu\text{m}$ can be obtained, see also Fig. 1(d).

Since a notch has a finite root radius the stress concentration at the notch root is always smaller than at a sharp crack with similar length. A higher load will be necessary to fracture the notched specimen. A fracture toughness test conducted with a notch instead of a sharp crack will therefore overestimate the fracture toughness, the more, the bigger the notch root radius is (Nishida *et al.*, 1994; Damani *et al.*, 1996). In order to measure a true value for the fracture toughness with notched specimens it has to be assured that the criterions (i) to (iv) mentioned above are fulfilled, i.e., that the notch behaves like a sharp crack. Model calculations were performed that assumed that a small sharp crack at the root of the notch is present. If the notch root radius is in the order of the crack length or smaller, this configuration behaves like a long sharp crack (Kübler *et al.*, 1999; Fett, 1999). In actual materials such small cracks are assumed to have the size of typical microstructural features (Damani *et al.*, 1996), for example the grain size. This leads to the conclusion that in order to perform a valid fracture toughness test (with only an insignificant overestimation of the true fracture toughness), the notch root radius has to be smaller than the mean grain size of the investigated material. This fact excludes that the method is applied to very fine grained materials or those in which not sharp notch can be made. In the ISO 23146 it is explicitly stated that the method must not be applied to Y-TZP.

In a round robin (Kübler, 1999) it could be shown that the method delivers consistent results in a variety of materials with suitable grain sizes. It is maybe the most robust method for inexperienced users and can be performed with very low scatter.

Comparison of the Standardized Methods

Studies to compare the results obtained with the SEPB, SCF and CNB methods show that they are equivalent for materials that show no R-curve behavior. The SEVNB method has been shown to only slightly overestimate the results (Quinn *et al.*, 2002). The National Institute of Standards and Technology (NIST) in the USA has developed a Standard Reference Material for fracture toughness (SRM 2100) (Quinn *et al.*, 2005) to provide a baseline for users to evaluate their procedures and equipment.

An overview of different aspects of the standardized methods is given in Table 2. It summarizes the experimental requirements, the necessary expertise and the effect that R-curve behavior and sub-critical crack growth as elucidated above may have on the performance of the methods. Another assessment of features of fracture toughness test methods and a guide to test method selection can be found in CEN/TS 14425-1 (2003).

Table 2 Comparison of standardized methods

	SEPB	SCF	CNB	SEVNB
experimental effort	medium to high	high	medium	low to medium
amount of experience needed	medium to high	high	low to medium	low
approximate crack length at fracture	1000–1500 μm	50–150 μm	several hundred μm	$\approx$ grain size
value on R-curve	saturation	increasing part	increasing part - saturation	begin
sensitive to SCCG	little	considerable	yes	possible
possibility to correct for SCCG effects	sometimes	sometimes	no	no
problematic materials	very tough, $K_{Ic} > 6 \text{ MPam}^{0.5}$	coarse grains, very tough (no indentation cracks)	high Young's modulus, transformation toughening	grain size $< 1 \mu\text{m}$, Y-TZP excluded

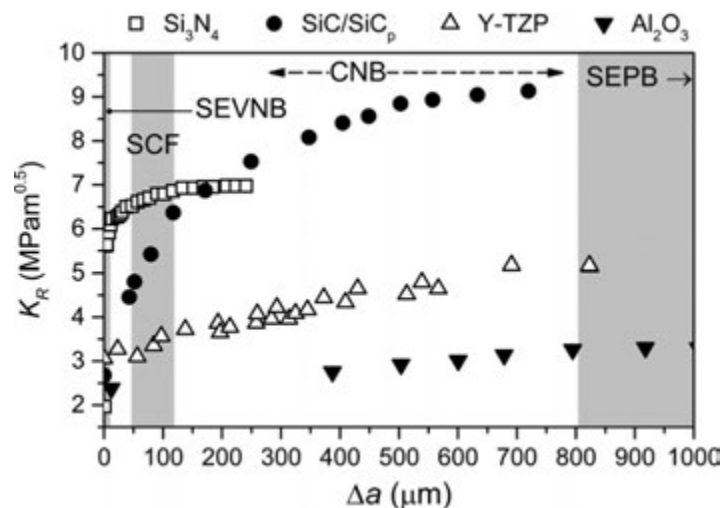


Fig. 5 R-curves for some ceramic materials and typical critical crack length ranges for standardized fracture toughness test methods. The R-curves are replotted from literature: Si_3N_4 , in-situ platelet reinforced SiC, 2.8Y-TZP and Al_2O_3 . Reproduced from Fünfschilling, S., Fett, T., Oberacker, R., *et al.*, 2010b. R curves from compliance and optical crack-length measurements. *Journal of the American Ceramic Society* 93, 2814–2821. Gilbert, C.J., Cao, J.J., de Jonghe, L.C., Ritchie, R.O., 1997. Crack growth resistance-curve behaviour in silicon carbide: Small versus long cracks. *Journal of the American Ceramic Society* 80, 2253–2261. Alcalá, J., Anglada, M., 1998. Indentation precracking of Y-TZP: Implications to R-curves and strength. *Materials Science and Engineering A245*, 267–276. Fett, T., Munz, D., Seidel, J., Stech, M., Rödel, J., 1996. Correlation between long and short crack R-curves in alumina using the crack opening displacement and fracture mechanical weight function approach. *Journal of the American Ceramic Society* 79, 1189–1196.

Standardized methods and R-curves

The four methods described so far work with distinctly different crack lengths at fracture. As already reported, they give equal numbers for K_{Ic} for fine grained and non-transforming ceramics (flat R-curve materials). The situation is different if materials are tested which show an effect of the crack length on fracture toughness. For such R-curve materials, considerable diverging numbers may be determined with different methods, cp. **Fig. 5**.

Pre-cracks used in the SEPB method are approximately 1000 μm to 1500 μm long. It can be expected, that with such measurements values near the saturation of R-curves will be determined. The SCF method uses rather small cracks in the range of 50 μm to 150 μm . For some materials with steeply rising R-Curves like self-reinforced silicon nitrides (Fünfschilling *et al.*, 2010b), the results will again be near the saturation value, but for other materials which have a more gently rising R-curve, intermediate values may be obtained. A variation of indentation load to produce pre-cracks of different size permits interference of a possible R-curve trend.

During CNB tests the crack grows stably by an unknown amount which depends on the specimen size and chevron shape (Munz and Fett, 1999). It can be expected that CNB results for R-curve-materials are K_R values somewhere in the rising part of the curve. In SEVNB tests it is assumed that instable fracture starts from a small crack with a size approximately equal to the grain size of the investigated material in front of the notch. SEVNB-fracture toughness will thus be near the start of the R-curve (Kübler, 1999).

Standardized methods and sub-critical crack growth

Sub-critical crack growth (SCCG) precedes every fracture to a certain amount and will therefore also influence fracture toughness measurements. It depends on the investigated material and its susceptibility to this behavior and the test method how to deal with this phenomenon.

SEPB tests can be performed with a variety of loading rates, depending on the applied standard procedure. If the test is conducted rather fast, i.e., with fracture occurring within a few seconds, the effect will be small, as shown even for glasses by Quinn *et al.* (Quinn and Swab, 2017). The same behavior can be observed for the SCF method. In some materials there is a chance that SCCG leaves behind a distinctly different fracture surface than instable, fast fracture (Swab and Quinn, 1998). In such cases the amount the pre-crack has grown by SCCG can be added to the pre-crack length when fracture toughness is evaluated. Some standards recommend performing tests at two significantly different loading speeds to gain insight into possible effect of SCCG on the measurement.

Cho *et al.* (2006) showed that generally, the SCF method is more sensitive to SCCG because at the same K the small crack in a SCF-specimen experiences a much larger relative change in crack length and thus in relative K_{Ic} than the long crack in a SEPB specimen.

CNB tests are often performed with low loading rate to facilitate stable crack propagation. This may just as well favor SCCG, which cannot be distinguished from the stable crack growth.

Alternative Pre-Cracking, Methods for Non-Standard Geometries, Components and Recent Developments

More Methods for Introducing Pre-Cracks or Notches

Other – non-standardised – ways to generate pre-cracks for SEPB tests have been reported. These methods have in common that the stress intensity at a given applied load has a maximum at a certain crack length. Crack advance beyond the maximum K requires an increase in load and is thus stable and controllable. This is shown schematically in Fig. 7. Two different ideas have been developed to achieve such K -trends. Fett *et al.* (2000, 2001) suggested to load a short starting notch by two pairs of rollers on each side of the notch as indicated in Fig. 6. The generated contact stress field drives the crack forward, for short crack lengths in an unstable and then in a stable way. Since a quantitative evaluation of the stress field and the geometry factor is provided, it is possible to control the length of the pre-crack by choosing a suitable applied load.

Sglavo *et al.* (Pancheri *et al.*, 1998; Sglavo *et al.*, 1999) suggested to “sandwich” the actual specimen between two metal plates and provided an analytical expression to calculate the stress intensity K as a function of crack length, elastic properties of the sandwich plates, and applied load. Even though simplifications were made in the theoretical analysis, the process is useful to obtain pre-cracks in a controlled way.

As becomes clear from Fig. 7, for both methods it is necessary to know an estimated value of the fracture toughness to predict the crack length at a specific applied load.

Recently studies have been made in which ultra-short pulsed laser ablation using pico- or femto-second lasers were used to obtain notches in various aluminas (Carlton *et al.*, 2016), 3Y-TZP (Turón-Vinas and Anglada, 2014) and silicon nitride (Turón-Vinas and Anglada, 2015). These notches are usually shallow ($\sim 50 \mu\text{m}$) and rather wide but have a small notch root radius. Fracture starts not directly at the notch root but at some kind of material specific damage that is induced in front of the notch. In Y-TZP it was a region of coalescent micro-cracks (Turón-Vinas and Anglada, 2014), in silicon nitride a damaged region containing extremely brittle phases and pores acted as starting crack (Turón-Vinas and Anglada, 2015). It is not clear if these pre-cracks fulfill the mandatory condition of being (ii) well-defined, further work will be necessary to properly assess the effect of the residual damage.

The viability of using focused ion beam milling to produce notches with extremely small tip radii made has been demonstrated by Fünfschilling *et al.* (2010a) on macroscopic specimens. This technique is predominantly used when fracture toughness is

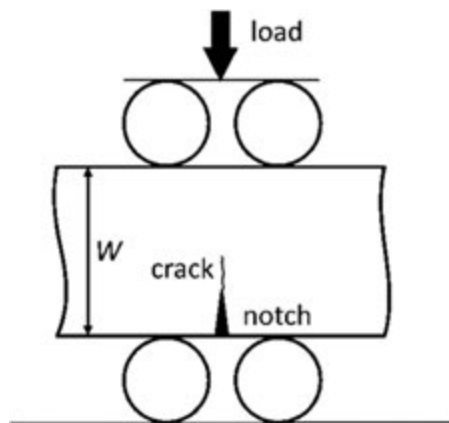


Fig. 6 Schematic of opposite roller loading of a notched bar as suggested by Fett *et al.* Reproduced from Fett, T., Munz, D., Thun, G., 2000. Strength and toughness test devices with opposite roller loading. *Engineering Fracture Mechanics* 29–38.

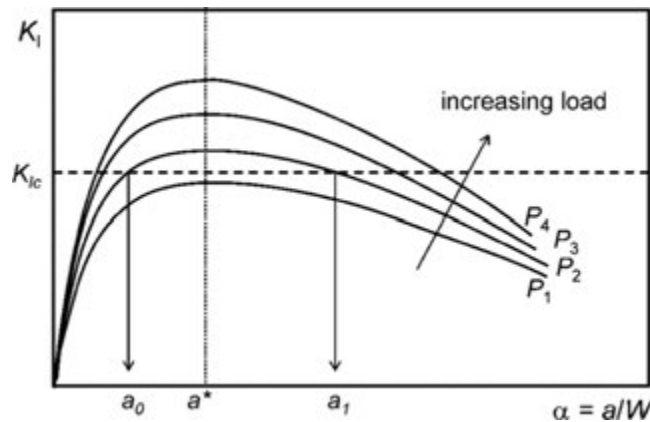


Fig. 7 Schematic of the trend of K as a function of crack length for opposite roller loading or sandwiched beams. In a material with the fracture toughness K_{Ic} (dashed line), a crack (or notch) with length a_1 will pop-in to length a_2 at a load P_2 . If the load is increased to P_3 and further, the crack will advance stably to the crack lengths given by the intersections of the K -curves with the line for K_{Ic} . Reproduced from Fett, T., Munz, D., Thun, G., 2000. Strength and toughness test devices with opposite roller loading. *Engineering Fracture Mechanics* 29–38. Pancheri, P., Bosetti, P., Dal Maschio, R., Sglavo, V.M., 1998. Production of sharp cracks in ceramic materials by three-point bending of sandwiched specimens. *Engineering Fracture Mechanics* 59, 447–456.

evaluated at the micro-scale using cantilever-beams with dimensions of only a few μm in the course of material investigation on the nano-scale (Cui and Vinci, 2017; Gruber *et al.*, 2018).

Testing of Specific Specimen Geometries or Components

Thin specimens, strips

New applications using very thin ceramics (fuel cells, electronic substrates or particulate filters) have led to the need to measure fracture toughness also on very thin ($0.2 \text{ mm} \leq b \leq 1 \text{ mm}$, $W = 4 \text{ mm}$, $36 \text{ mm} \leq L \leq 45 \text{ mm}$) specimens. In ISO 21113 (2018) variations of the SEPB method and the SEVNB method are standardized for such specimens. The adaptations mainly concern the procedures for pre-cracking, notching and assuring alignment of the specimens during the fracture test. In order to obtain the sharp pre-crack from a starter notch the specimen is glued onto a brass support bar with the tip of the notch slightly below the neutral axis of the support. During bending of the unit, a crack will pop-in. The specimen is then removed from the brass bar and fractured in bending. For the machining of notches, several thin specimens are glued together to form a wider unit which can be notched in a similar way to single bars.

Balls, small disks and plates

For quality control purposes and component development, fracture toughness testing techniques are required which can be applied directly to components, to (very small) specimens cut out of components or to typical specimens used in material development (small disks). Since the microstructure of ceramics sensitively depends on processing conditions, property gradients and inhomogeneity in components may occur (Strobl *et al.*, 2014b). Therefore it is useful to test fracture toughness of the critical areas.

The notched ball test (NBT) has been developed to determine the tensile surface strength of balls used in bearings. A deep, wide notch is cut into the equatorial plane of the ball, which is then compressed at its poles. This leads to a stress field in the surface region of the ball opposite of the root of the notch (Supancic *et al.*, 2009), see Fig. 8(a). This stress field can be used to load a pre-crack, which is made by a Knoop indentation, analogous to the SCF-method. Details like the determination of the geometric function and experimental details have been published (Strobl *et al.*, 2012b, 2014a), Fig. 8. It was shown that fracture toughness can be determined on balls as small as a few millimeters in diameter with an accuracy of a few per cent. This is similar to the typical scatter of fracture toughness results by standardized methods.

Many components appear as small disks or plates. Disc shaped parts are also common in material development. Meaningful strength tests for such of specimens are biaxial tests. For very small disks with diameters down to 2 mm the ball-on-three-balls (B3B) test has been established (Börger *et al.*, 2002, 2004) to complement other biaxial strength tests like the ring-on-ring test (ASTM C1499, 2019) at small dimensions. Again, modifications of the SCF method can be used to measure fracture toughness. This has been elaborated for the B3B-test (Rasche *et al.*, 2014; Strobl *et al.*, 2014c; Lube *et al.*, 2016). The Knoop indentation pre-crack is placed in the center of the specimen on the prospective tensile face, the plastic zone is polished off, Fig. 8(c). The test-piece is then strength tested with the loading ball immediately opposite the pre-crack. A fracture mechanical analysis for determining the geometry factor and the fracture toughness is available. Precise alignment of the pre-crack in the center of the disc is very important, but the technique does enable precise fracture toughness measurements (Belli *et al.*, 2018).

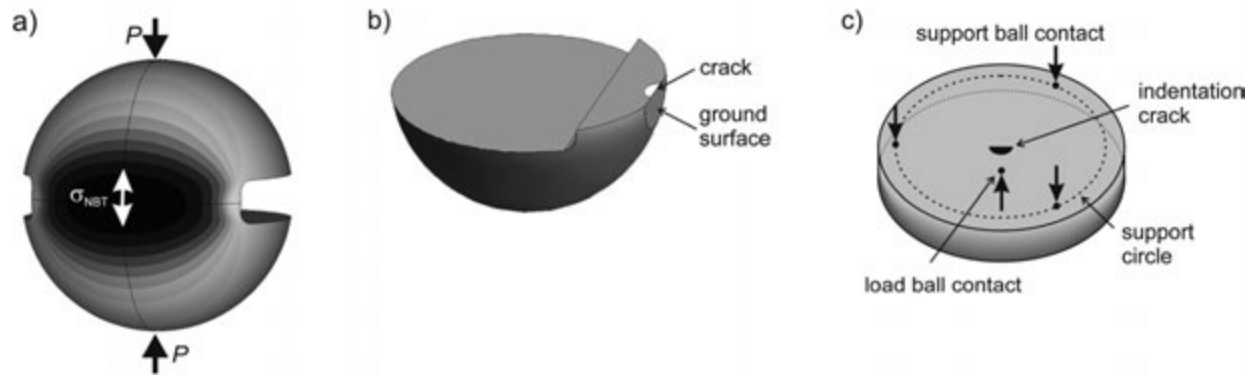


Fig. 8 Application of the SCF-method to components. (a) principle of the notched ball strength test, (b) schematic of a fractured notched ball with an semi-elliptical surface crack, (c) principle of the ball-on-three-balls fracture toughness test. The surface crack is introduced into the tensile side of the disc (the top side in this sketch). Reproduced from Supancic, P., Danzer, R., Witschnig, S., Polaczek, E., Morrell, R., 2009. A new test to determine the tensile strength of brittle balls – The notched ball test. *Journal of the European Ceramic Society* 29, 2447–2459. Strobl, S., Supancic, P., Lube, T., Danzer, R., 2012b. Toughness measurement on ball specimens, Part I: Theoretical analysis. *Journal of the European Ceramic Society* 32, 1163–1173. Strobl, S., Lube, T., Schöppl, O., 2014a. Toughness measurement on ball specimens. Part II: Experimental procedure and measurement uncertainties. *Journal of the European Ceramic Society* 34, 1881–1892. Lube, T., Rasche, S., Nindhia, T.G.T., 2016. B3B- K_{Ic} fracture toughness test – Geometric function formulae for semi-elliptical surface cracks in bi-axial bending. *Journal of the American Ceramic Society* 99, 249–256.

These examples show how established testing concepts can be transferred to other specimen geometries without sacrificing the basic principles of rigorous fracture toughness testing.

Other Methods: The Indentation Strength (IS) Method

Indentation cracks are perhaps the most simple way of generating pre-cracks on bend bars for fracture toughness measurements. However, if the residual stresses generated by the hardness indent are not removed, meaningful measurements are virtually impossible. This becomes obvious if the indentation-strength (IS) method is analyzed. For this method, a Vickers indentation pre-crack is introduced into a standard bend bar on the prospective tensile surface so that the diagonals are aligned parallel and perpendicular to the long axis of the bar. The bar is then fractured in bending and the fracture stress is determined. The fracture toughness is calculated from Young's modulus E , hardness H , the indentation load F and the fracture stress σ_f and a quantity η , which takes into account the residual stresses and the geometry factor of the crack.

$$K_{Ic} = \eta \left(\frac{E}{H} \right)^{1/8} \left(\sigma_f \cdot F^{1/3} \right)^{3/4} \quad (7)$$

The form of Eq. (7) has been derived by taking the combined loading of the crack by the residual stresses from the hardness indentation and the applied bending stress into account. This analysis shows that the indentation cracks grow to about 2.5 times their initial size during the bend test. Since neither the residual stresses nor the exact size of the crack at failure are known, the quantity η , which comprises the residual stress factor and the geometry factor Y can only be determined by experimental calibration Chantikul *et al.* (1981) to be $\eta = 0.59 \pm 0.12$. Strictly, conditions (iii) and (iv) are not satisfactory fulfilled for this test method. In a VAMAS round robin (Awaji *et al.*, 1990) the method was applied to a silicon nitride without R-curve behavior, among others. It turned out that the determined K_{Ic} was dependent on the indentation load, hence on the size of the pre-crack. This fact together with the large uncertainty of $\sim 20\%$ in η which directly transfers to an uncertainty in K_{Ic} , shows, that this method is not capable of delivering accurate values for the fracture toughness. Consequently it has not been standardized.

Indentation Fracture Resistance, The IF-Method

Instead of using an indentation crack as pre-crack in a strength test it seems to be even simpler to determine the fracture toughness directly from the lengths of the indentation crack. Unlike all other measurements reviewed so far in this contribution, this method uses arrested cracks – a fundamental difference, as pointed out by Quinn *et al.* (Quinn and Bradt, 2007).

Indentation cracks develop as a consequence of the wedging action which the irreversibly deformed zone around and under a hardness impression exerts. Apart from the two orthogonal half-penny cracks along the Vickers indentations diagonals, additional crack systems running parallel to the indented surface may be present (Cook and Pharr, 1990; Lube, 2001). The exact subsurface shape of the radiating cracks may depend on the indentation load (Pajares *et al.*, 1996) and the indented material. Relation between crack length and fracture toughness have been established using model descriptions of the loading and fracture toughness values

determined independently with different methods in order to find an empirical calibration constant. So far more than twenty different approaches have been published (a few can be found in the papers by Ponton *et al.* (Ponton and Rawlings, 1989a,b)). None of the relations works for all materials over a range of indentation forces and crack lengths.

Nevertheless the method seems to be so widespread and is believed to be indispensable for the investigation of small amounts of material that it was standardized for the measurement of a quantity called “indentation fracture resistance”. ISO 14627 (2012) is applicable to silicon nitrides for bearing balls, ISO 21618 (2019) is for all other monolithic and whisker or particle reinforced ceramics. In both standards it is explicitly noted – and shall be emphasized here – that the indentation fracture resistance “ $K_{I,IFR}$ ” is an estimate of a material’s resistance to cracking as introduced by an indenter and has correlations with wear resistance and rolling contact fatigue performance as well as machining processes, since these properties are governed by the resistance to crack extension in localized damage areas. By contrast, fracture toughness, K_{Isc} and K_{Ipb} are intrinsic properties of a material and are relevant to macroscopic and catastrophic fracture events with long cracks, rather than those phenomena caused by microscopic and successive damage accumulation associated with short cracks.” (ISO 21618, 2019).

It can be judged as beneficial that these two standards finally limit the range of applicable indentation loads to 20 kg and 10 kg (or 4.9 kg – only in ISO 21618), valid cracks and give defined procedures for the measurement of crack lengths and provide one single expression for the evaluation (Niihara *et al.*, 1982):

$$K_{I,IFR} = 0.000978 \left(\frac{E}{HV} \right)^{0.4} \left(\frac{F}{a^{1.5}} \right), \quad (8)$$

where HV is the Vickers hardness, F the indentation load in [N] and a the mean half surface crack length in [mm]. Along with the choice of the Eq. (8) goes the condition that only materials with a crack length to indent size ratio > 2.5 may be evaluated. Even if test circumstances are thus narrowed down and numbers measured on some ceramics fit proper SEVNB- or SCF-fracture toughness data, comparisons between different materials remain highly questionable. The method may appear to be quick and easy but it is still a subjective method.

Summary

Standardization of fracture toughness testing of ceramics has made a huge step forward in the last decade providing a wide choice of eligible methods. It has to be acknowledged that not all standardized methods work for all materials. Introduction and/or measurement of the pre-crack length on fracture surfaces is the major challenge.

The standardized methods work with pre-cracks that undergo different amounts of crack-growth before becoming critical. For materials exhibiting a rising crack resistance curve different methods may give different results. For a correct interpretation of a given fracture toughness value, the test method has to be known.

Since the properties of ceramic components are defined by the processing history it is favorable to machine specimens out of components. If this is not possible, standardized test methods may be adapted to be applicable to the components directly.

Arrested indentation cracks are useful to investigate the resistance to crack extension in localized damage areas but must not be used to measure the fracture toughness of ceramics.

References

- Ashby, M.F., Jones, D.R.H., 1980. Engineering Materials 1: An Introduction to Properties, Applications and Design. Oxford: Pergamon Press.
- ASTM C1421, 2018. Standard Test Methods for Determination of Fracture Toughness of Advanced Ceramics at Ambient Temperature, ASTM International, West Conshohocken, PA.
- ASTM C1499, 2019. Standard Test Method for Monotonic Equibiaxial Flexural Strength of Advanced Ceramics at Ambient Temperature, ASTM International, West Conshohocken, PA.
- ASTM E399, 2017. Standard Test Method for Linear-Elastic Plan-Strain Fracture Toughness K_{Ic} of Metallic Materials, ASTM International, West Conshohocken, PA.
- Awaji, H., Kon, J.-I., Okuda, H., 1990. The VAMAS Fracture Toughness Test Round Robin on Ceramics. Nagoya: Japan Fine Ceramics Centre.
- Becher, P.F., 1991. Microstructural design of toughened ceramics. *Journal of the American Ceramic Society* 74, 222–269.
- Belli, R., Wendler, M., Petschelt, A., Lube, T., Lohbauer, U., 2018. Fracture toughness testing of biomedical ceramic-based materials using beams, plates and discs. *Journal of the European Ceramic Society* 38, 5533–5544.
- Börger, A., Supancic, P., Danzer, R., 2002. The ball on three balls test for strength testing of brittle discs – Stress distribution in the disc. *Journal of the European Ceramic Society* 22, 1425–1436.
- Börger, A., Supancic, P., Danzer, R., 2004. The ball on three balls test for strength testing of brittle discs – Part II: Analysis of possible errors in the strength determination. *Journal of the European Ceramic Society* 24, 2917–2928.
- Carlton, H.D., Elmer, J.W., Freeman, D.C., *et al.*, 2016. Laser notching ceramics for reliable fracture toughness testing. *Journal of the European Ceramic Society* 36, 227–234.
- CEN/TS 14425-1, 2003. Advanced technical ceramics – Test methods for determination of fracture toughness of monolithic ceramics – Part 1: Guide to test method selection.
- Chantikul, P., Anstis, G.R., Lawn, B.R., Marshall, D.B., 1981. A critical evaluation of indentation techniques for measuring fracture toughness: II, Strength method. *Journal of the American Ceramic Society* 64, 539–543.
- Cho, S.J., Kim, J.C., Yoon, K.-J., *et al.*, 2006. Effect of loading rate and humidity in the fracture toughness testing of alumina. *Journal of the Korean Ceramic Society* 43, 4–9.
- Cook, R.F., Pharr, G.M., 1990. Direct observation and analysis of indentation cracking in glasses and ceramics. *Journal of the American Ceramic Society* 73, 787–817.
- Cui, F.Y., Vinci, R.P., 2017. A chevron-notched bowtie micro-beam bend test for fracture toughness measurement of brittle materials. *Scripta Materialia* 132, 53–57.
- Damani, R., Gstrein, R., Danzer, R., 1996. Critical notch root radius in SENB-S fracture toughness testing. *Journal of the European Ceramic Society* 16, 695–702.
- Danzer, R., Lube, T., Supancic, P., Damani, R., 2008. Fracture of ceramics. *Advanced Engineering Materials* 10, 275–298.
- EN 14425-3, 2010. Advanced technical ceramics – Test methods for determination of fracture toughness of monolithic ceramics – Part 3: Chevron notched beam (CNB) method.

- Fett, T., 1999. Estimated stress intensity factors for semi-elliptical cracks in front of narrow circular notches. *Engineering Fracture Mechanics* 64, 357–362.
- Fett, T., Munz, D., Thun, G., 2001. A toughness test device with opposite roller loading. *Engineering Fracture Mechanics* 68, 29–38.
- Fett, T., Munz, D., Thun, G., 2000. Strength and toughness test devices with opposite roller loading. *Engineering Fracture Mechanics* 29–38.
- Fünfschilling, S., Fett, T., Hoffmann, M.J., *et al.*, 2010a. Estimation of high-temperature R-curve for ceramics from strength measurements including specimens with focused ion beam notches. *Journal of the American Ceramic Society* 93, 2411–2414.
- Fünfschilling, S., Fett, T., Oberacker, R., *et al.*, 2010b. R curves from compliance and optical crack-length measurements. *Journal of the American Ceramic Society* 93, 2814–2821.
- Griffith, A.A., 1920. The phenomenon of rupture and flow in solids. *Philosophical Transactions of the Royal Society of London* A221, 163–198.
- Gross, D., Seelig, T., 2006. *Fracture Mechanics*. Berlin: Springer.
- Gruber, M., Konetschnik, R., Popov, M., *et al.*, 2018. Atomistic origins of the differences in anisotropic fracture behaviour of LiTaO₃ and LiNbO₃ single crystals. *Acta Materialia* 150, 373–380.
- Irwin, G.R., 1958. Fracture. In: Flügge, S. (Ed.), *Handbuch der Physik*. Berlin: Springer-Verlag.
- ISO 14627, 2012. Fine Ceramics (Advanced Ceramics, Advanced Technical Ceramics) – Test method for fracture resistance of silicon nitride materials for bearing balls at room temperature by indentation (IF) method, International Organization for Standardization.
- ISO 15732, 2003. Fine Ceramics (Advanced Ceramics, Advanced Technical Ceramics) – Test method for fracture toughness of monolithic ceramics at room temperature by single edge precracked beam (SEPB) method, International Organization for Standardization.
- ISO 18756, 2005. Fine ceramics (Advanced Ceramics, Advanced Technical Ceramics) – Determination of fracture toughness of monolithic ceramics at room temperature by the surface crack in flexure (SCF) method, International Organization for Standardization.
- ISO 21113, 2018. Fine Ceramics (Advanced Ceramics, Advanced Technical Ceramics) – Test method for fracture toughness of monolithic ceramics thin plates at room temperature, International Organization for Standardization.
- ISO 21618, 2019. Fine Ceramics (Advanced Ceramics, Advanced Technical Ceramics) – Test method for fracture resistance of monolithic ceramics at room temperature by indentation (IF) method, International Organization for Standardization.
- ISO 23146, 2012. Fine Ceramics (Advanced Ceramics, Advanced Technical Ceramics) – Test method for fracture toughness of monolithic ceramics - single-edge V-notch beam (SEVNB) method, International Organization for Standardization.
- ISO 24370, 2005. Fine Ceramics (Advanced Ceramics, Advanced Technical Ceramics) – Test method for fracture toughness of monolithic ceramics at room temperature by chevron-notched beam (CNB) method, International Organization for Standardization.
- Kübler, J., 1999. Fracture Toughness of Ceramics Using the SENVB Method: Round Robin, VAMAS Report No. 37, ESIS Document D2-99, EMPA, Swiss Federal Laboratories for Materials Testing and Research, Dübendorf.
- Kübler, J., Danzer, R., Fett, T., Damani, R., 1999. Notch Width - Theory and Model. In: KÜBLER, J. (ed.) *Fracture Toughness of Ceramics Using SEVNB Method Round Robin*. VAMAS Report No. 37, ESIS Document D2-99, EMPA, Swiss Federal Laboratories for Materials Testing and Research, Dübendorf.
- Lehrstuhl Für Struktur- und Funktionskeramik, 2020. Notched Ball Test (NBT) – Fracture Toughness Testing [Online]. Lehrstuhl für Struktur- und Funktionskeramik, Montanuniversität Leoben. Available: <https://www.isfk.at/de/958/> (accessed 15.3.2020).
- Lube, T., 2001. Indentation crack profiles in silicon nitride. *Journal of the European Ceramic Society* 21, 211–218.
- Lube, T., Rasche, S., Nindhia, T.G.T., 2016. B3B-KIc fracture toughness test – Geometric function formulae for semi-elliptical surface cracks in bi-axial bending. *Journal of the American Ceramic Society* 99, 249–256.
- Michalske, T.A., Freiman, S.W., 1983. A molecular mechanism for stress corrosion in vitreous silica. *Journal of the American Ceramic Society* 66, 284–288.
- Morrell, R., 2006. Fracture toughness testing for advanced technical ceramics: Internationally agreed good practice. *Advances in Applied Ceramics* 105, 88–98.
- Munz, D., 2007. What can we learn from R-Curve measurements? *Journal of the American Ceramic Society* 90, 1–15.
- Munz, D., Fett, T., 1999. *Ceramics*. Berlin, Heidelberg: Springer.
- Newman, J.C., Raju, I.S., 1981. An empirical stress-intensity factor equation for the surface crack. *Engineering Fracture Mechanics* 15, 185–192.
- Niihara, K., Morena, R., Hasselman, D.P.H., 1982. Evaluation of K_{Ic} of brittle solids by the indentation method with low crack-to-indent ratios. *Journal of Materials Science Letters* 1, 13–16.
- Nishida, T., Hanaki, Y., Pezzotti, G., 1994. Effect of notch-root radius on the fracture toughness of a fine-grained alumina. *Journal of the American Ceramic Society* 77, 606–608.
- Pajares, A., Guiberteau, F., Cumbreira, F.L., Steinbrech, R.W., Dominguez-Rodriguez, A., 1996. Analysis of kidney-shaped indentation cracks in 4Y-PSZ. *Acta Materialia* 44, 4387–4394.
- Pancheri, P., Bosetti, P., Dal Maschio, R., Sglavo, V.M., 1998. Production of sharp cracks in ceramic materials by three-point bending of sandwiched specimens. *Engineering Fracture Mechanics* 59, 447–456.
- Ponton, C.B., Rawlings, R.D., 1989a. Vickers indentation fracture toughness Test, Part 1: Review of literature and formulation of standardised indentation toughness equations. *Materials Science and Technology* 5, 865–871.
- Ponton, C.B., Rawlings, R.D., 1989b. Vickers Indentation Fracture Toughness Test, Part 2: application and Critical Evaluation of Standardised Indentation Toughness Equations. *Materials Science and Technology* 5, 961–976.
- Quinn, G.D., 2016. *Fractography of Ceramics and Glasses*. NIST.
- Quinn, G.D., Salem, J.A., 2003. Effect of lateral cracks on fracture toughness determined by the surfac-crack-in-flexure-method. *Journal of the American Ceramic Society* 85, 873–880.
- Quinn, G.D., Bradt, R.C., 2007. On the vickers indentation fracture test. *Journal of the American Ceramic Society* 90, 673–680.
- Quinn, G.D., Swab, J.J., 2017. Fracture toughness of glasses as measured by the SCF and SEPB methods. *Journal of the European Ceramic Society* 37, 4243–4257.
- Quinn, G.D., Xu, K., Gettings, R.J., Salem, J.A., Swab, J.J., 2002. Does anyone know the real fracture toughness? SRM 2100: the world's first ceramic fracture toughness reference material. In: Salem, J.A., Quinn, G.D., Jenkins, M.G. (Eds.), *Fracture Resistance Testing of Monolithic and Composite Brittle Materials*, ASTM STP 1409. West Conshohocken, PA: American Society for Testing and Materials.
- Quinn, G.D., Xu, K., Gettings, R., Salem, J.A., Swab, J.J., 2005. Standard reference material 2100: Fracture toughness of ceramics. In: Bradt, R.C., Munz, D., Sakai, M., White, K.W. (Eds.), *Fracture Mechanics of Ceramics*. Springer, pp. 499–529.
- Rasche, S., Strobl, S., Kuna, M., Bermejo, R., Lube, T., 2014. Determination of strength and fracture toughness of small ceramic discs using the small punch test and the ball-on-three-balls test. *Procedia Materials Science* 3, 961–966.
- Schoeck, G., 1990. Thermally activated crack propagation in brittle materials. *International Journal of Fracture* 44, 1–14.
- Sglavo, V.M., Bosetti, P., Trentini, E., Ceschini, M., 1999. Sandwiched-beam procedure for precracking brittle materials. *Journal of the American Ceramic Society* 82, 2269–2272.
- Strobl, S., Lube, T., Schöpl, O., 2014a. Toughness measurement on ball specimens. Part II: Experimental procedure and measurement uncertainties. *Journal of the European Ceramic Society* 34, 1881–1892.
- Strobl, S., Lube, T., Supancic, P., *et al.*, 2014b. Mechanical properties of silicon nitride rolling elements in dependence of size and shape. *Journal of the European Ceramic Society* 34, 4167–4176.
- Strobl, S., Supancic, P., Lube, T., Danzer, R., 2012a. Surface crack in tension or in bending – A reassessment of the newman and raju formula in respect to fracture toughness measurements in brittle materials. *Journal of the European Ceramic Society* 32, 1491–1501.

- Strobl, S., Supancic, P., Lube, T., Danzer, R., 2012b. Toughness measurement on ball specimens, Part I: Theoretical analysis. *Journal of the European Ceramic Society* 32, 1163–1173.
- Strobl, S., Supancic, P., Lube, T., Danzer, R., 2018. Corrigendum to “surface crack in tension or in bending – A reassessment of the newman and raju formula in respect to fracture toughness measurements in brittle materials” [*J. Eur. Ceram. Soc.* 32 (8) (2012) 1491–1501]. *Journal of the European Ceramic Society*. 355–358.
- Strobl, S., Rasche, S., Krautgasser, C., Sharova, E., Lube, T., 2014c. Fracture toughness testing of small ceramic discs and plates. *Journal of the European Ceramic Society* 34, 1637–1642.
- Supancic, P., Danzer, R., Witschnig, S., Polaczek, E., Morrell, R., 2009. A new test to determine the tensile strength of brittle balls – The notched ball test. *Journal of the European Ceramic Society* 29, 2447–2459.
- Swab, J.J., Quinn, G.D., 1998. Effect of precrack “halos” on fracture toughness determined by the surface crack in flexure method. *Journal of the American Ceramic Society* 81, 2261–2268.
- Turon-Vinas, M., Anglada, M., 2014. Fracture toughness of zirconia from a shallow notch produced by ultra-short pulsed laser ablation. *Journal of the European Ceramic Society* 34, 3865–3870.
- Turon-Vinas, M., Anglada, M., 2015. Assessment in Si₃N₄ of a new method for determining the fracture toughness from a surface notch micro-machined by ultra-short pulsed laser ablation. *Journal of the European Ceramic Society* 35, 1737–1741.

Relevant Websites

<https://www.isfk.at/de/958>

Montanuniversität Leoben.

Notched Ball Test (NBT) – Fracture Toughness Testing.

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Surface Crack in Flexure (SCF) – Fracture Toughness Testing.

R-Curve Behavior of Ceramics

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Basic Concepts on Fracture Mechanics

Ceramic materials fail by brittle fracture that originates at flaws, which can be generated during processing or in service. They are of different size and shape and they are distributed all through the material. Elastic fracture mechanics can be used to predict the strength when flaws are considered as very sharp cracks embedded in an elastic continuum. Cracks can propagate if the elastic energy released when they extend is larger than the energy necessary to create the new crack surfaces. The reader is referred to [Lawn \(1993\)](#) for background elastic fracture mechanics focused on ceramic materials.

The condition for fracture under a tensile stress acting perpendicular to the crack surface, that is, in mode I, can be also established in terms of the stress intensity factor, K_I , and the fracture toughness of the material, K_{Ic} . K_I describes the elastic stress field very near the crack tip and depends on the tensile stress, σ , the crack length, a , and the geometry of the specimen. Very often it can be written in a simple form,

$$K_I = \sigma Y \sqrt{\pi a} \quad (1)$$

In this expression Y is a geometrical factor which accounts for the loading mode, the geometry of the crack and of the specimen. Processing flaws in ceramic materials are generally very small in comparison to specimen dimensions, so that in this circumstance Y may be independent of the crack length. This is the case for a bulk small penny crack loaded in the direction perpendicular to the crack surface, where Y is equal to $2/\pi$ all along the crack front. K_{Ic} represents the critical value of K_I for which fracture occurs and it is in principle a material property. Therefore the fracture strength, σ_s , can be written as,

$$\sigma_s = \frac{K_{Ic}}{Y \sqrt{\pi a}} \quad (2)$$

This expression indicates that the fracture strength depends linearly on K_{Ic} and is inversely proportional to the square root of the crack length. It shows two possible strategies to increase the strength of ceramic materials, namely, increase the fracture toughness or decrease the defect size. From [Eq. \(2\)](#) it can be seen that the smallest strengths are associated with the largest flaws. Although specimens often contain many defects of different size, the strength will be determined by the larger crack size. On the other hand, if we know the strength of a specimen we can determine the minimum crack length or critical crack size for fracture. From [Eq. \(2\)](#) we obtain,

$$a_c = \frac{K_{Ic}^2}{\pi Y^2 \sigma_s^2} \quad (3)$$

In elastic fracture mechanics the strain release rate, G , is the energy available for unit of area of crack extension. Under plane strain in mode I, it is given by

$$G_I = \frac{K_I^2}{E} (1 - \nu^2) \quad (4)$$

where E is the Young modulus and ν the Poisson coefficient. Crack extension takes place when G reaches a critical value, G_{Ic} , which is the critical value for creating the unit surface of crack area. This is then related to the fracture toughness, K_{Ic} , by the above [Eq. \(4\)](#) at fracture,

$$G_{Ic} = \frac{K_{Ic}^2 (1 - \nu^2)}{E} \quad (5)$$

Units of G_I are energy per unit of area and are often expressed in kJm^{-2} while the units of K_I are stress per square root of length and it is often given in terms of $\text{MPa}\sqrt{\text{m}}$.

K_{Ic} and R-Curve Behavior

In the last section, K_{Ic} has been assumed to be a material parameter. However, in many structural ceramics the value of K_{Ic} depends on crack extension so that the fracture toughness cannot be considered to have a single value. In this situation, the material is characterized by a crack resistance curve ("R-curve") which represents the stress intensity factor that has to be applied by an external load for the onset and maintenance of crack extension. The R-curve behavior can be caused by several intrinsic effects as crack-face bridging, phase transformations, micro-cracking, etc. The effect of an increasing crack-resistance ("R-curve behavior") is commonly described by a function $K_R(\Delta a)$ in which K_R is the stress intensity factor necessary for crack propagation by an amount of Δa ([Fig. 1](#)). The R-curve is commonly obtained by inducing a long sharp crack and observing its stable extension as the stress intensity factor is increased until unstable fracture takes place. The condition for unstable fracture is now given by ([Anderson, 1995](#))

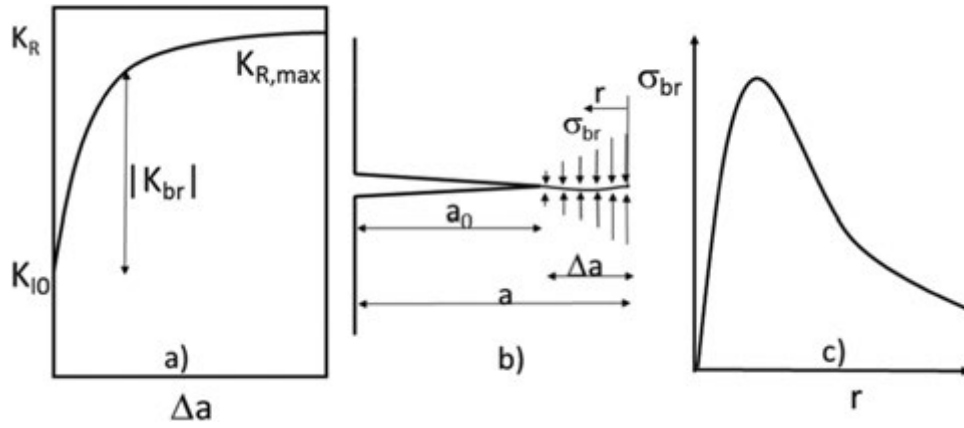


Fig. 1 (a) Schematic of an increasing crack growth resistance curve starting from the crack-tip toughness K_{I0} and exhibiting a saturation value $K_{R,max}$; (b) a crack in a ceramic material exhibiting crack surface interactions described by bridging stresses σ_{br} ; (c) distribution of bridging stresses versus distance to crack tip.

$$K = K_R \quad (6)$$

$$\frac{dK}{da} = \frac{dK_R}{da} \quad (7)$$

This means that for unstable fracture the functions K and K_R must have a common point where the tangents to both curves have the same value. The strength of a ceramic with R -curve behavior will be determined by the initial crack length as well as by the details of how much and how fast K_R increases with Δa .

Mechanisms Responsible for R -Curves

The critical stress intensity factor, K_{IC} (fracture toughness) of a ceramic that presents R -curve behavior is formally written as:

$$K_R = K_{IC} = K_{I0} + \Delta K_C \quad (8)$$

where K_{I0} is the intrinsic fracture toughness and ΔK_C the contribution from various crack-shielding mechanisms.

Grain Bridging

Coarse-grained materials present an R -curve effect which is caused by crack border interactions in the wake of an advancing crack (Swanson *et al.*, 1987). This fact has been proved experimentally in alumina with large grain size by re-notching experiments (Knehan and Steinbrech, 1982; Steinbrech *et al.*, 1983) and by in-situ observations under the electron microscope (Lathabai *et al.*, 1991). Then, the important mechanism for R -curve behavior is that of grains bridging the crack faces near the crack tip, that is, $\Delta K_C = |K_{br}|$ in Fig. 1.

In Fig. 2(a) friction bridging interaction by a friction force F is illustrated schematically. The crack face interactions localized at single grains can transfer loads which can be modeled in a more homogeneous way by the so-called bridging stresses σ_{br} that depend on the crack opening displacement δ . The bridging stresses shield the crack tip from the external loads as illustrated schematically in Fig. 2(b).

The bridging stresses depend on the crack opening displacement. When bridging is caused by friction effects, a simple relation between σ_{br} and δ is that proposed by Mai and Lawn (1987) and given in Eq. (9) in Table 1. Alternatively, another simple formulation of the bridging law is that of elastic bridging. In this event, bridges are assumed unbroken and can sustain a maximum stress, σ_0 (Eq. (10) of Table 1).

If it is assumed that the critical displacement for which the bridging stress vanishes, δ_c , follows the following function distribution density (Fett and Munz, 1993),

$$f(\delta_c) = \frac{1}{\delta_0} \left(\frac{\delta_c}{\delta_0} \right) \exp \left(-\frac{\delta_c}{\delta_0} \right) \quad (13)$$

Then, the macroscopically averaged bridging stress is given by:

$$\sigma_{br} = \int_0^\infty \sigma_{br} f(\delta_c) d\delta_c \quad (14)$$

The expressions obtained for the averaged bridging stresses for both bridging laws are given in Eqs. (11) and (12) of Table 1. Eqs. (10)–(13) are represented in Fig. 3.

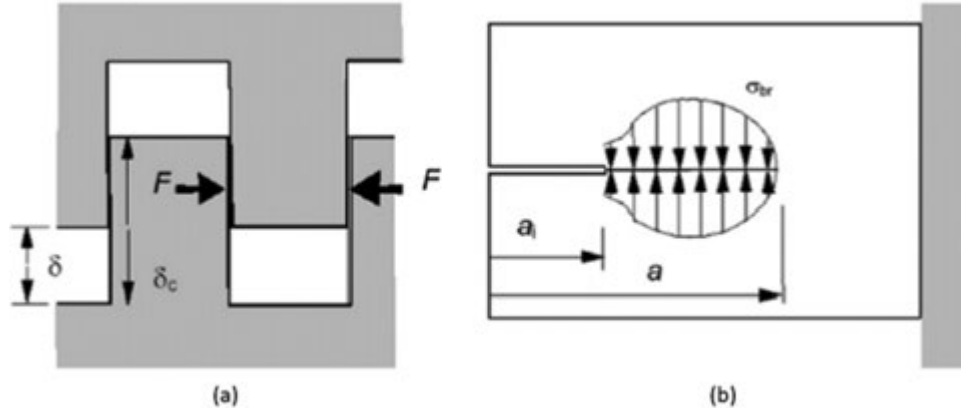


Fig. 2 Crack surface interactions due to bridging forces (schematic): (a) local bridging events, (b) continuous bridging stress distribution. Reprinted from Munz, D., Fett, T., 1999. *Ceramics, Mechanical Properties, Failure Behavior, Materials Selection*. Berlin: Springer with permission of Springer. All rights reserved.

Table 1 Simple models for the bridging stress laws and the corresponding averaged bridging stresses

Model	Friction bridging	Elastic bridging
Bridging stress law	$\sigma_{br} = \begin{cases} \sigma_0 \left[1 - \left(\frac{\delta}{\delta_c} \right) \right] & \frac{\delta}{\delta_c} \leq 1 \\ 0 & \frac{\delta}{\delta_c} > 1 \end{cases} \quad (9)$	$\sigma_{br} = \begin{cases} \sigma_0 \left(\frac{\delta}{\delta_c} \right) & \frac{\delta}{\delta_c} \leq 1 \\ 0 & \frac{\delta}{\delta_c} > 1 \end{cases} \quad (10)$
Averaged bridging stress	$\sigma_{br} = \sigma_0 \exp \left(-\frac{\delta}{\delta_0} \right) \quad (11)$	$\sigma_{br} = \sigma_0 \left(\frac{\delta}{\delta_0} \right) \exp \left(-\frac{\delta}{\delta_0} \right) \quad (12)$

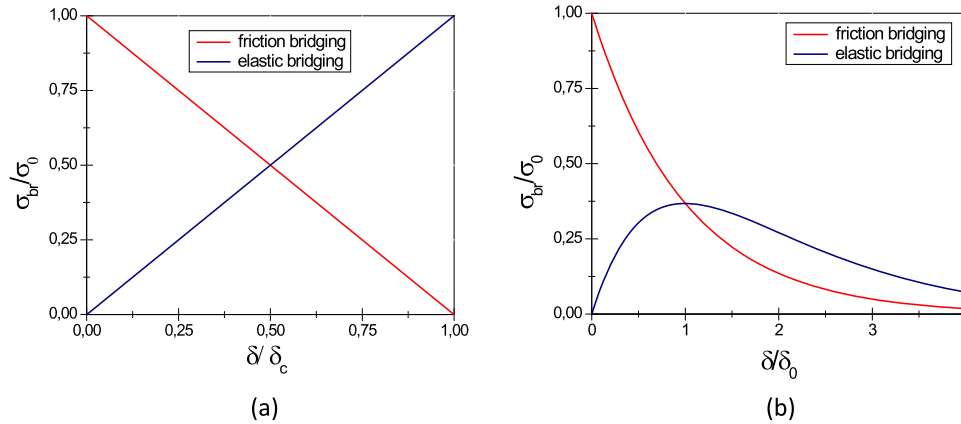


Fig. 3 Local (a) and global (b) bridging relations for friction and elastic bridging.

Phase Transformation Toughening in Zirconia Ceramics

In phase transformation zirconia ceramics, the main contribution to toughening is related to the stress activated t-m phase transformation in the crack tip process zone, where the stress reaches high values. The transformation is accompanied by an increase in volume which in turn creates a compressive strain field which opposes crack extension. If the transformation induces a strain ϵ^T in the unconstrained material, forces must be then applied on the contour of the transformed material in order to restore its original shape (Fig. 4). If the transformation is only dilatational, these forces are normal pressure inducing a tip shielding stress intensity factor. The maximum contribution to the toughness, ΔK_{CT} , resulting from the stress activated transformation is given by,

$$\Delta K_{CT} = \frac{\eta E^* \epsilon^T V_f w^{1/2}}{1 - \nu} \quad (15)$$

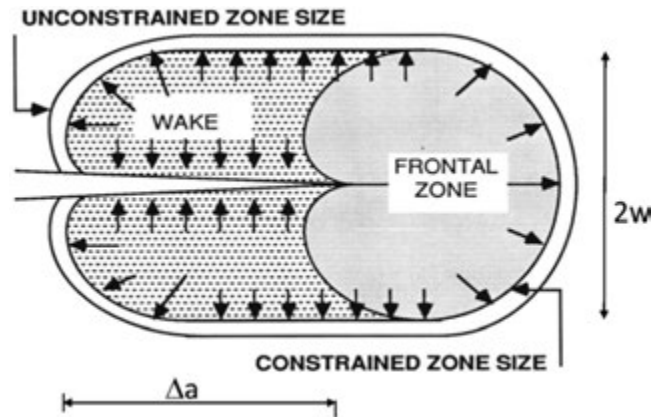


Fig. 4 Stresses in a dilatant transformation zone. The zone must be reduced in size from its unconstrained size to fit in the untransformed material. Once the zone extends behind the crack tip, stresses in the zone arise that are acting in a direction to close the crack. Reprinted from Green, D.J., Hannink, R.H.J., Swain, M.V., 1989. *Toughening of Ceramics*. Boca Raton: CRC Press with permission of CRC Press. All rights reserved.

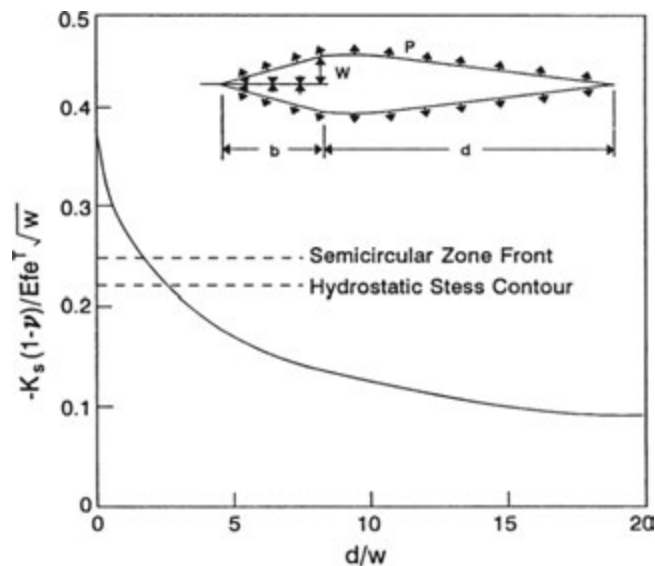


Fig. 5 Zone shape parameter η for Ce-TZP in terms of transformation aspect ratio d/w (see the insert) (Marshall, D.B., 1990. Crack shielding in ceria-partially-stabilized zirconia. *J. Am. Ceram. Soc.* 73, 3119–3121). The values of generally assumed transformation morphologies are indicated. Reprinted from Hannink, R.H.J., Swain, M.V., 1994. Progress in transformation toughening of ceramics. *Annu. Rev. Mater. Sci.* 24, 359–408 with permission of CRC. All rights reserved.

where η is a factor depending on the zone shape at the crack tip and on the nature of the stress field in that zone. Its value is equal to 0.22 for a pure dilatational transformation, V_f is the volume fraction transformed, w is the width of the transformation zone from the crack surface (i.e., the half-height of the zone) and ν is the Poisson coefficient (McMeeking and Evans, 1982). The matrix modulus E^* plays an important role in determining the effectiveness of the dilatational strain. For example, a stiffer matrix, such as Al_2O_3 ($E^* = 380$ GPa, $\nu = 0.2$), constrains the zirconia transformation more than does ZrO_2 ($E^* = 210$ GPa, $\nu = 0.3$) decreasing the extent of the transformation zone w , because of the high matrix E^* value that opposes the transformation. For a review of transformation toughening of zirconia ceramics see Hannink *et al.* (2000).

The transformation zone around the crack tip in Ce-TZP does not follow the nearly circular phase transformation zones which are found in MgO-doped zirconia, but typically extends some 10–20 times the zone width ahead of the cracks (Yu *et al.*, 1992). Although Eq. (15) still holds for the increase in toughness, the parameter η of this equation for Ce-TZP depends on the aspect ratio of the transformation zone (Fig. 5). For a 9 mol% Ce-TZP the transformation zones are shown in Fig. 6 for two sintering temperatures, 1400 and 1600°C, with resulting average tetragonal grain sizes of 0.9 and 2.5 μm , respectively (Rauchs *et al.*, 2002). At the lower sintering temperature the transformation zone is extremely narrow while at the higher temperature is wider and irregular in shape.

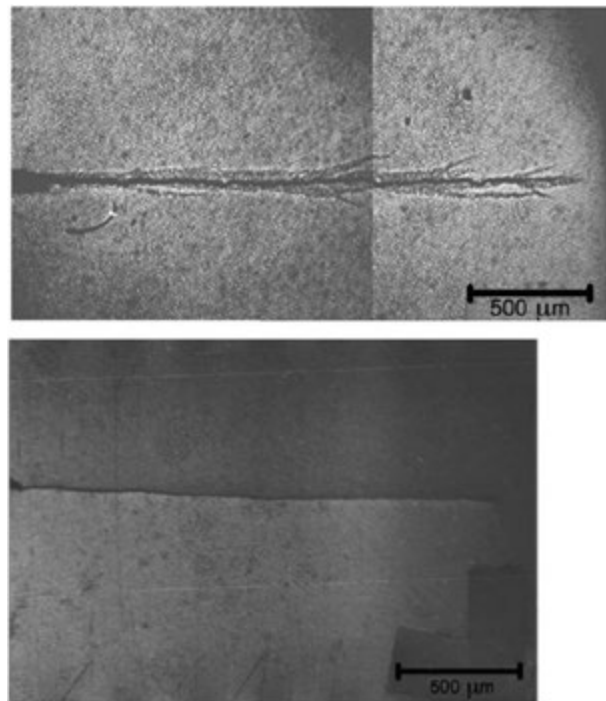


Fig. 6 Transformation shapes observed in 9 mol% Ce-TZP for two sintering temperatures: (a) top 1600°C, (b) bottom 1400°C with resulting average tetragonal grain sizes of 2.5 and 0.9 μm , respectively. Reprinted from Rauchs, G., Fett, T., Munz, D., 2002. *R*-curve behavior of 9Ce-TZP zirconia ceramics. Eng. Fract. Mech. 69, 389–401 with permission of Elsevier. All rights reserved.

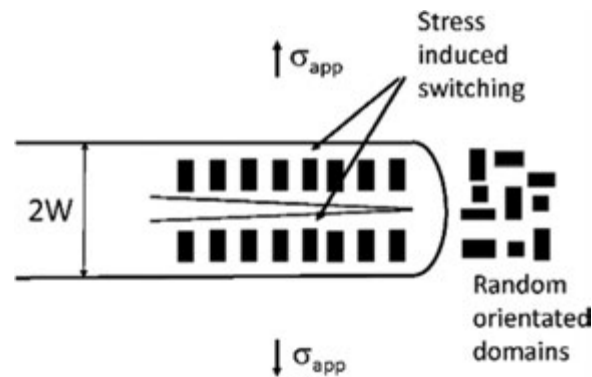


Fig. 7 Schematic illustration of the stress-induced domain switching in PZT.

Domain Switching in Piezoelectric Ceramics

Many materials have been studied as practical piezoelectric ceramics over the years. Most of them are still based on lead zirconate titanate ($\text{Pb}(\text{Zr,Ti})\text{O}_3$), which is a solid solution of PbZrO_3 and PbTiO_3 and it is referred as PZT. Most ferroelectric ceramics undergo a displacive structural phase transition from a high temperature prototype phase (often centrosymmetric) into one or more ferroelectric phases of lower symmetry. After cooling below the Curie temperature, the polarization of a ferroelectric polycrystal is zero because of the spontaneous polarization into domains, separated by domain boundaries, and with different polarization directions so that no net polarization results. The net polarization occurs when an electrical field is applied and the domains switch in the direction of the field, that is, the ceramic is poled. Switching of domains also takes place by the action of stress. If the stress applied is tensile, the polarization of the domains switch to the direction of the stress inducing a small increase in the length of the sample in this direction, while if the stress applied is compressive the domains switch in a direction with the polarization perpendicular to the stress resulting in a contraction of the sample. In a small zone very close to the crack tip (Fig. 7), the stress is high enough for switching the direction of the domains leading to non-linear deformation of the material inside this zone and a corresponding residual stress, similarly to the

stress activated phase transformation of zirconia, which increases when the crack extends (Chen and Lynch, 1998; Schneider and Heyer, 1999; dos Santos e Lucato *et al.*, 2000; Fett *et al.*, 2000a).

The effect of the applied stress on a poled ceramic will depend on the polling direction in front the crack tip. Thus, if the polling direction is the same as the applied tensile stress the effect will be small since few domains will switch to the stress direction as most of them are already oriented in this direction. On the contrary, if the polling direction is perpendicular to the applied stress, for example in the direction of the crack propagation direction, the domains will tend to switch in order to align with the stress field. This induces a strong anisotropy in the fracture toughness of poled piezoelectric ceramics as shown from experiments with Vickers or Knoop indentations cracks (Fett and Munz, 2000). This is mainly attributed to the different switching ability of domains lying in the crack tip stress field.

The highest plateau of *R*-curves of lead zirconate titanate in compact tension (CT) specimens is obtained when the polling direction is in the thickness direction (dos Santos e Lucato *et al.*, 2000). The lowest value is obtained when polling is in the direction of the applied stress, while for the unpoled material the toughness is between both values. By using specimens of different thickness and poled in the thickness direction, it has been concluded that the low coercive stress is responsible for the development of a large switching zone, which is of high relevance for the computation of the actual stress intensity factor at the crack tip and for the *R*-curve calculation (Fett *et al.*, 2005b; Njiwa *et al.*, 2006).

Microcrack Zone and Crack Deflection and Branching

Another toughening mechanism that involves crack-tip shielding is “microcrack toughening.” Microcracks can form in a zone close to the tip of large cracks in the grain boundaries of ceramics that contain localized residual stresses in a similar way as a stress-induced phase transformation zone forms (Buresch, 1978; Pabst *et al.*, 1978). Microcracks reduce the elastic modulus near the crack tip giving rise to shielding. Alternatively, in terms of energy considerations, by increasing the effective fracture surface, the effective critical energy release rate is also increased. As the crack extends, an increase of the damage zone will increase the fracture resistance. The formation of microcracks in the residual stress field could also give rise to a volume increase if the microcracks open. This effect can be formally treated by the transformation toughening equation of increase in fracture toughness. An increase in fracture toughness is expected since, as the crack extends, the microcracks enter the crack wake where dilation toughening will occur. Nevertheless, another effect specific to the formation of microcracks is that they degrade the material in front of the crack tip, so that the fracture toughness of this zone is lower than that of the non-microcracked ceramics. A mechanics model of microcrack toughening predicts the magnitude of microcrack toughening as well as the existence of *R*-curve effects (Evans and Faber, 2006). The toughening was attributed to both the elastic modulus diminution in the microcrack process zone and the dilatation induced by microcracking. The dilatational effect is potentially more substantial, as well as being the primary source of the *R*-curve. The analysis of the theoretical model also demonstrated that microcrack toughening is less potent than transformation toughening.

The mechanisms described so far act in the crack wake (that is, after crack extension commences) to resist crack propagation through crack-tip shielding mechanisms and they are referred to as extrinsic in contrast with those acting in front of the crack tip which as referred to as intrinsic. A potential increase in the crack growth resistance takes place when a crack bifurcates in two or more cracks since then the energy release rate is reduced because of the increase in crack surface. In ceramic laminates with strong interfaces a high increase in crack growth resistance is observed under compressive residual stresses perpendicular to the crack. In ceramic laminates with weak interfaces, a crack approaching the weak interface may be kinked along the interface which may result in a reduction of the crack driving force stopping the crack along the interface, so that applied stress intensity factor has to be increased to propagate the crack. The *R*-curves of ceramic laminates are described in Section “*R*-Curve in Ceramic Laminates”.

In general, several toughening mechanisms giving rise to *R*-curve behavior are simultaneously present. For example, the *in vitro* toughness of mineralized tissues illustrates the critical role of microstructure in the mechanisms of fracture at the macro-micro and nano-scales (Launey *et al.*, 2010). There is a mutual competition between extrinsic (crack-tip shielding) toughening mechanisms, which predominate at length scales at more than 1 μm , and intrinsic (plastic deformation) toughening mechanisms, which are active at length scales at primarily less than 1 μm (see Fig. 3 in Launey *et al.*, 2010). Distinct toughening mechanisms occur at each level of hierarchy. In these materials, the observed extrinsic mechanisms liable to contribute to *R*-curve behavior are microcracking, bridging by collagen fibers and uncracked ligaments and crack deflection due to crack–osteon interactions (Nalla *et al.*, 2003). However, in spite of the existence of different mechanisms, there is strong experimental evidence that crack bridging rather than constrained microcracking is dominant. The prime source of such bridging in human bone appears to be from the formation of uncracked ligaments in the crack wake, which are created either by the non-uniform advance of the crack front and/or by the imperfect linking of microcracks ahead of the crack tip with the main crack (Nalla *et al.*, 2005). High anisotropy in crack resistance curves in relation to the osteon direction is also present as can be appreciated in Zimmermann *et al.* (2015). It is also interesting to note that aging changes the *R*-curves of human bone resulting a decrease in the crack initiation toughness as well as in the crack-growth toughness, the latter being associated to higher osteon density and lack of uncracked ligaments bridges in aged tissue (Zimmermann *et al.*, 2011).

Determination of K_{Ic} and K_{R} Curves

Long Cracks

The principal procedure for the determination of K_{Ic} and K_R curves consists in the generation of a sharp long crack in a test specimen of simple geometry for which the stress intensity factor is very well known. From a test in which the load is recorded and

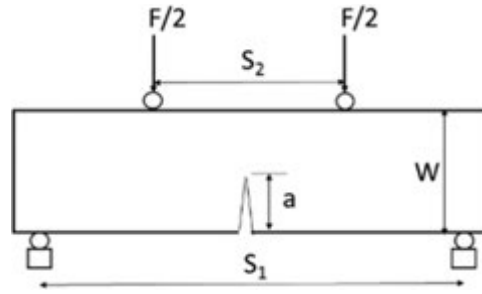


Fig. 8 Geometry for a four point bending specimen with and edge notch.

the crack length is directly observed with a travelling microscope, the applied stress intensity factor can be calculated and plotted in terms of the increase in crack length.

The test specimens most used are three and four point bending specimens with a thickness $B = 3$ mm and height $W = 4$. **Fig. 8** shows a four point bending specimens with the inner roller span, S_2 , of generally 20 mm, and the outer one, S_1 , of 40 mm. Three point bending specimens, that is, $S_2 = 0$ in **Fig. 8** and $S_1/W > 2.5$ are also used specially when there is limited material availability for testing. For both configurations the stress intensity factor can be formally written as:

$$K_I = \sigma \sqrt{a} Y \left(\frac{a}{W} \right) = \frac{F}{B \sqrt{W}} Y^* (a/W) \quad (16)$$

with

$$Y^* = \sqrt{\frac{a}{W}} Y \quad (17)$$

Expressions for Y^* for three and four point bending specimens can be found in [Rauchs et al. \(2002\)](#) and [Munz and Fett \(1999\)](#), respectively.

For the calculation of K_{IC} , the failure load and the crack length are introduced in [Eq. \(16\)](#). If the material exhibits crack resistance curve, the crack grows stably and the load and corresponding crack length at final fracture have to be determined. The two most used procedures are to measure in situ the crack growth at the specimen surface with an optical or electron microscope, or by an indirect method based on measuring the change in compliance, C , as the crack extends. In this occasion, the load point displacement, u , needs to be known accurately. From the slopes of partial unloading curves during crack growth the compliance ($C = u/F$) can be determined and from this the crack length ([Jelitto et al., 2007](#)).

In **Fig. 9** a very rigid bending test device is shown which was used for determining the R -curve in three-point bending with a roller span of 40 mm. The load and the load point displacement were simultaneously recorded and the crack length measured with a microscope. The crack length obtained via compliance was compared with the physical crack length visible on the surface. **Fig. 9** also displays the partial unloadings carried out during the test to measure the evolution of the compliance as the crack grows. The crack length can be obtained by previous calibration of compliance against that measured with test specimens of identical geometry with sharp saw cuts of specific lengths. The compliance can be also calculated by using an expression of C in terms of Y^* which can be obtained from the equation relating the energy release rate G_I with the compliance. For a plate of thickness B with a through-the thickness crack ([Anderson, 1995](#))

$$G_I = \frac{F^2}{2BW} \frac{dC}{d(a/W)} \quad (18)$$

By using this equation, the expression that results for the compliance in terms of $Y^*(a/W)$ is

$$C = C_0 + \frac{2}{BE'} \int_0^a Y^{*2}(\alpha') d\alpha' \quad (19)$$

C_0 is the compliance of the specimen in the absence of a crack or notch. From $\Delta C = C - C_0$, the normalized crack length a/W can be determined. Very often the compliance measured with actual cracks is lower than with saw cuts of the same length. The reason is the presence of bridging between the crack surfaces, which contributes to decrease the experimental compliance and can underestimate the length of the actual crack. In materials with strong R -curve behavior this effect can be important.

The Starting Notch for the Determination of Fracture Resistance

Another important point for measuring K_{IC} and K_R -curves is the need to use specimens with a very narrow notch. Usually narrow saw cuts induce notch tips radii too large for testing very fine grained ceramics. In this situation, a narrow V-notch is machined at the notch tip by using a razor blade with diamond paste ([Nishida et al., 1996](#); [Kübler, 1997](#)). In this way, the notch tip can be considerably sharpened inducing crack tip radii which sometimes can be smaller than 10 μm . However, the production of very sharp V-notches in a controlled manner is not straight forward.

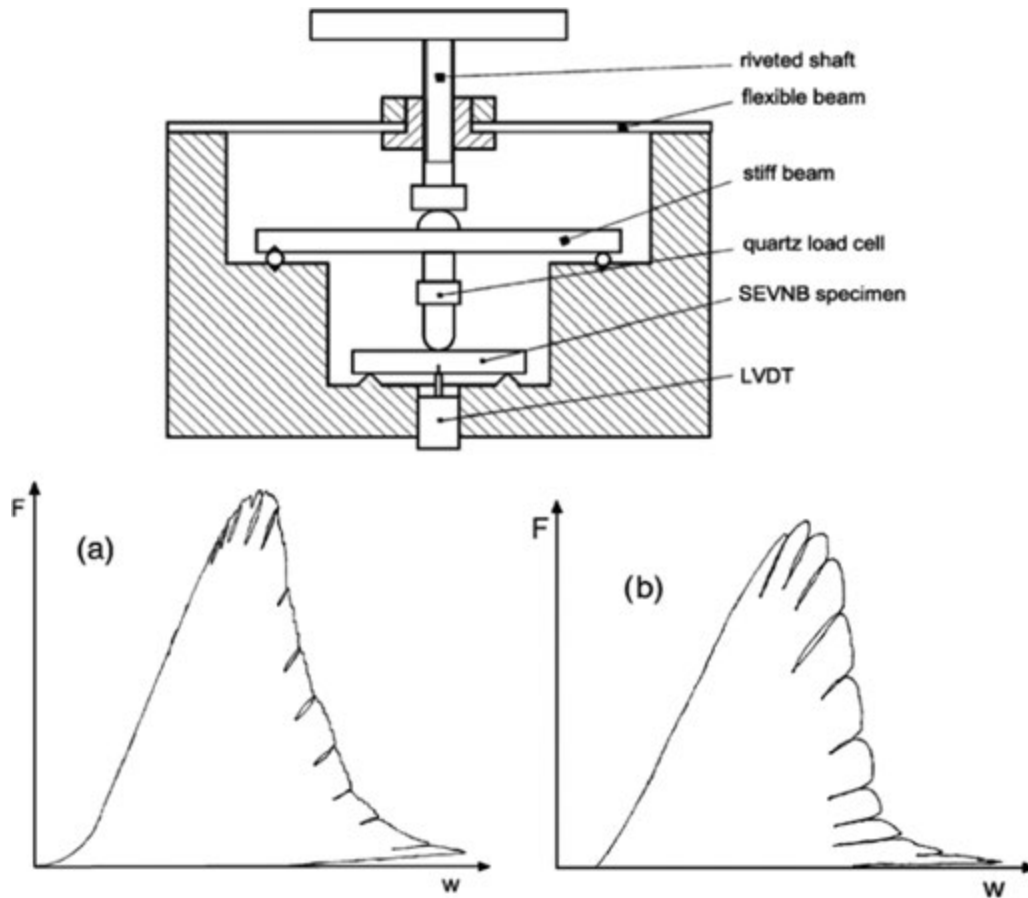


Fig. 9 At the top the rigid load rig used for the *R*-curve experiments. Bottom load-displacement diagram of 9 mol% Ce-TZP: (a) sintered at 1600°C with 2.5 μm grain size and (b) sintered at 1400°C with 0.9 μm grain size. Reprinted from Rauchs, G., Fett, T., Munz, D., 2002. *R*-curve behavior of 9Ce-TZP zirconia ceramics. *Eng. Fract. Mech.* 69, 389–401 with permission of Elsevier. All rights reserved.

Fett (1999) analyzed the stress intensity factor of a notch (with a tip radius R) and length a_0 with either an edge trough the thickness straight microcrack or a semicircular crack of length l in front of the notch tip. Microcracks are usually produced by the machining process and have dimensions typically in the range of 1–3 times the grain size (d). In coarse ceramics it is feasible that $l \sim 3d > R$ (Damani *et al.*, 1996), but as finer grain size ceramics are tested, this condition is more difficult to fulfill. For example, for 3Y-TZP, which is widely used for biomedical applications with an average grain size $d \sim 0.33 \mu\text{m}$ ($l \sim 1 \mu\text{m}$), R should be less than 1 μm , and this is not possible to achieve in practice by the method of the razor blade. Therefore, it may be not justified to take $a_0 + l$ for the crack length in the calculation of K_{Ic} or the K_R -curves. It is then expected that if K_{Ic} is measured from notches the value is overestimated since the stress field in front of a notch is more moderate than in front of a crack. This was shown in submicron grain size 3Y-TZP by testing a large number of samples with notch radii in the range 18 and 167 μm . The experimental values of K_{Ic} were strongly affected and ranged from 5.9 to 13.6 $\text{MPa m}^{1/2}$, respectively (Fischer *et al.*, 2008). For the correct determination of this property in submicron grain size ceramics, sharper starting V-notches are required.

A modified compliance method has been introduced for small cracks of length l emanating from the root of finite notches machined by the razor blade procedure, and it has been shown that the notch root radius, R , strongly affects the formally computed crack resistance curve (Fett *et al.*, 2008). Tests were performed on a silicon nitride with 5 wt% Y_2O_3 and 2 wt% MgO and with the modified compliance method it was shown how the initial true *R*-curve can be obtained from the data, finding a very steep *R*-curve with the saturation reached after only about 10 μm crack extension. An upper limit was found for the crack tip toughness of 3.6 $\text{MPa m}^{1/2}$, whereas the conventional procedure without considering the effect of the notch would yield an unrealistically high value of about 6.3 $\text{MPa m}^{1/2}$. The modified compliance method and the conventional procedure yield comparable results for $l > 2R$.

One method to machine very shallow single edge V notches on the surface of rectangular bending bars is by ultra-short pulsed laser ablation. In recent studies for the determination of K_{Ic} in 3Y-TZP (Turón-Vinas and Anglada, 2014) and Si_3N_4 (Turón-Vinas and Anglada, 2015) this technique was used. Fig. 10 shows the micro-notch with the microcracked zone in front of the micro-notch machined by ultra-short pulsed laser ablation. From these studies it was concluded that: (1) the technique is very suitable for measuring K_{Ic} in nanograin size specimens in which it is impossible to produce sharp notches with enough small tip

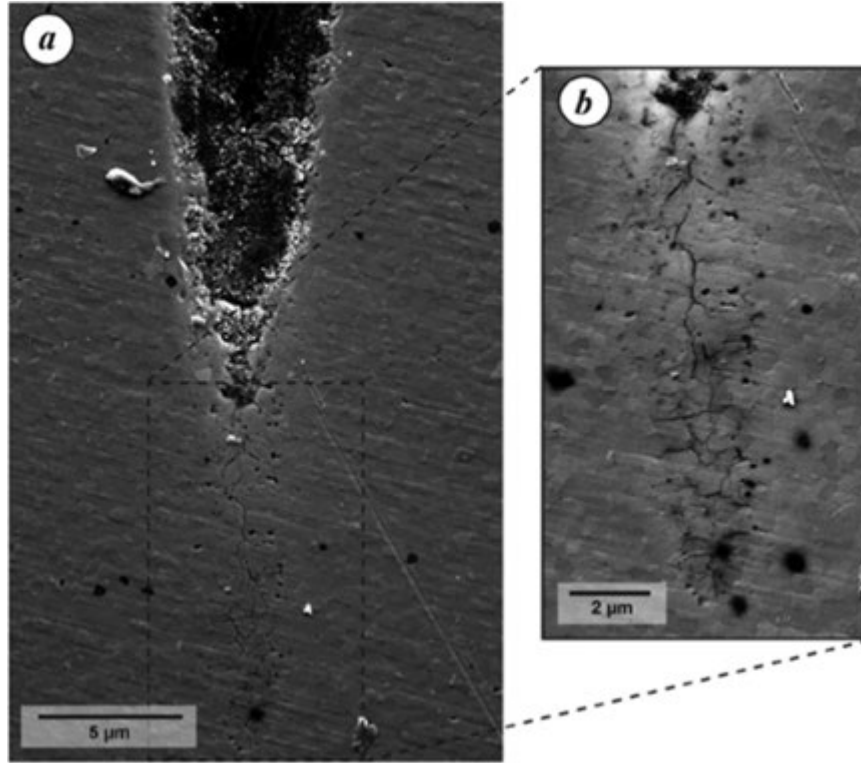


Fig. 10 (a) Micro-notch with tip radius below the micron induced by ultra-short pulsed laser ablation; (b) detail of the microcracked zone in front of the micronotch. Reprinted from Turon-Vinas, M., Anglada, M., 2014. Fracture toughness of zirconia from a shallow notch produced by ultra-short pulsed laser ablation. *J. Eur. Ceram. Soc.* 34, 3865–3870 with permission of Elsevier. All rights reserved.

radius by conventional methods; (2) although the notch tip radius induced by ultra-short pulsed laser ablation is of dimensions in the sub-micrometer range, the starting crack is the result of coalescence of very sharp microcracks induced by ultra-short pulsed laser ablation in front of the micro-notch tip; (3) the value obtained for K_{Ic} is inside the range of values quoted for 3Y-TZP and Si_3N_4 but rather in the lower values of the range.

K_R -Curves From Strength Measurements From Indentation Cracks

Measurements of the instability of long, well defined cracks are, in principle, of little relevance to the strength and reliability of ceramics. R -curves from cracks which are able to imitate service flaws are required for a sound design strategy with ceramics. In this sense, many R -curves have been evaluated from Vickers and Knoop indentation cracks (Lawn, 1993). During indentation, up to a maximum load, P , and during unloading, a crack system develops, where the details depend on the materials and on the maximum load. Three crack types are observed: radial cracks extending from the edges of the indentation at the surface, median cracks extending below the tip of the indentation, and lateral cracks parallel to the surface. In some occasions the radial and median cracks combine after unloading to semi-circular or semi-elliptical surface cracks. Compressive stresses are induced below the contact area after unloading while residual tensile stresses are produced away from the contact area. The model generally used to describe the stress intensity factor of the residual tensile stresses is that of an opening load at the crack center, whose magnitude is proportional to the indentation load. The residual stress intensity factor for a semi-circular crack is (Lawn, 1993)

$$K_r = \chi P c^{-3/2} \quad (20)$$

where c is the radius of the crack and χ is a constant which depends on the material. K_r decreases during crack extension until $K_r = K_R$. If an external stress is applied, the crack can grow in a stable manner to a new crack length for which the superposition of the applied and residual stress intensity factor equals the K_R -curve,

$$K_t = K_{appl} + K_r = Y \sigma \sqrt{c} + \chi P c^{-3/2} = K_R(c) \quad (21)$$

The fracture stress σ_c can be calculated by imposing the two conditions given in Eqs. (6) and (7). If $K_R(c)$, Y and χ were independent of c , a plot of $\log \sigma_c$ versus $\log P$ then leads to a straight line with slope of $-1/3$ (Chantikul et al., 1981). In materials with a rising crack growth resistance, the $\log \sigma_c - \log P$ curve has a slope that decreases with decreasing P (Lawn, 1993). For small indentation loads, failure does not occur anymore from indentation cracks since it originates from natural flaws. One important

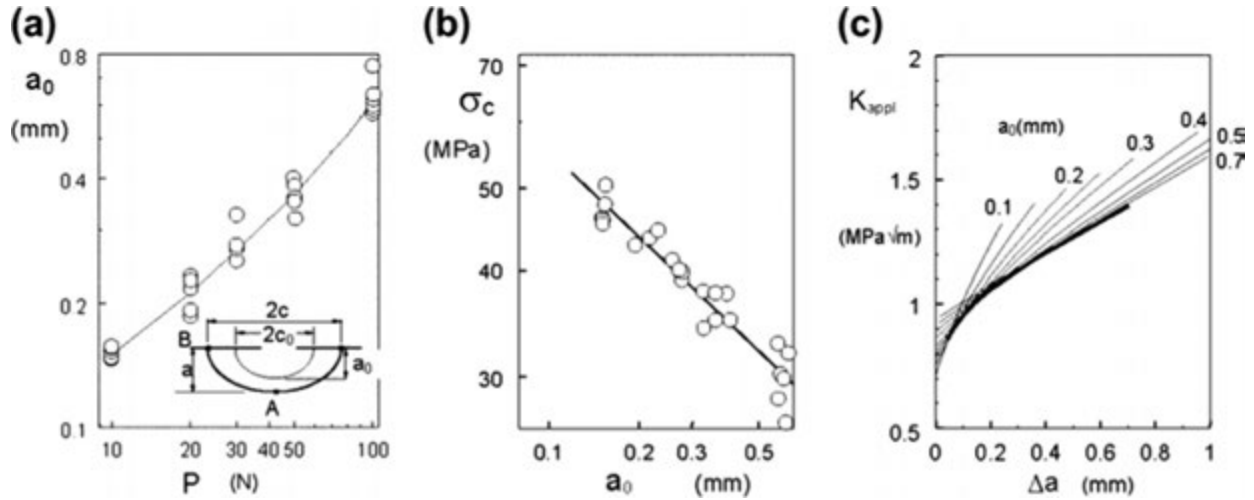


Fig. 11 First estimation of the R -curve, computed for fixed $a/c = 0.95$; (a) initial crack depths, (b) applied stress intensity factors for several initial crack depths (thin curves), (c) first estimation of the R -curve (thick curve). Reprinted from Fett, T., Munz, D., 2013. Fracture mechanics. In: Handbook of Advanced Ceramics. Elsevier. pp. 681–715 with permission of Elsevier. All rights reserved.

limitation of this method is that Y and χ need to be known and they must be constant during stable crack growth. The parameter χ depends on elastic modulus, E , and hardness, H (Lawn *et al.*, 1980):

$$\chi = \xi \left(\frac{E}{H} \right)^{\frac{1}{2}} \quad (22)$$

The value of the constant ξ often used is 0.016 which is the value proposed by Anstis *et al.* (1981). When an external stress is applied there is a reduction in K_r as shown for Vickers (Fett, 1995a), and Knoop (Fett and Rizzi, 2003) indentation cracks. Uncertainties in the residual stresses and the value of χ can be avoided by polishing away the elastic-plastic zone or annealing before testing in order to remove residual stresses. Nevertheless, care is needed to take into consideration the small change in the crack shape after polishing and any change induced during the annealing process on the microstructure at the crack tip or in the bridging stress between the crack surfaces.

One of the simpler methods for measuring the R -curve from indentation cracks consists on measuring the strength of tensile or bending specimens with surface Knoop indentation cracks induced with a range of indentation loads and with residual stresses removed by annealing. These cracks have an approximate semi-elliptical shape and the applied stress intensity factor changes along the crack front having different values at the deepest point (K_{IA}) and at the surface (K_{IB}), see Fig. 11(a). Then the crack starts to extend if $K_{IA}, K_{IB} > K_{I0}$, where K_{I0} is the intrinsic fracture toughness. Final fracture takes place after some stable crack extension at the deepest point, $\Delta a = a - a_0$, and at the surface, $\Delta c = c - c_0$. Then the conditions for final fracture (Eqs. (6) and (7)) applied to the surface and to the deepest point of the semi-circular crack are:

$$K_{IA} = K_{IR}(\Delta a), K_{IB} = K_{IR}(\Delta c) \quad (23)$$

$$\max \left(\frac{\partial(K_{IA} - K_{IR}(\Delta a))}{\partial a}, \frac{\partial(K_{IB} - K_{IR}(\Delta c))}{\partial a} \right) \geq 0 \quad (24)$$

Fett and Munz (2000) evaluated the R -curve under several simplifying assumptions: (1) the aspect ratio is fixed ($a/c = a_0/c_0 = \text{const.} = 0.95$) during crack extension; (2) the R -curve is independent of a_0 ; (3) the geometrical functions of the stress intensity factor at points A and B are identical and equal to their average value. The applied stress intensity factors computed with the measured strengths, σ_c , are given by Eq. (1). They are plotted for different values of a_0 in Fig. 11(c), with σ_c taken from Fig. 11(b). The resulting curves of K_{app} versus Δa are shown in Fig. 11(c) for each initial crack length. The R -curve resulting from the envelope condition is displayed as a thick line. It can be noticed that K_{IR} increases strongly with crack extension Δa . By dropping the assumption of a constant aspect ratio similar R -curve was obtained.

Stress Intensity Factor From Bridging Interactions

If the R -curve is produced by bridging stresses in the crack wake, these can be computed with the use of fracture mechanics weight functions and the experimental measurements of the R -curve. The specimen is loaded by an external load, which would lead to a stress distribution $\sigma_{appl}(x)$ at the location of the crack in the uncracked component (Fig. 12). The total stress is the sum of the applied stress, σ_{appl} , and the bridging stress, σ_{br} :

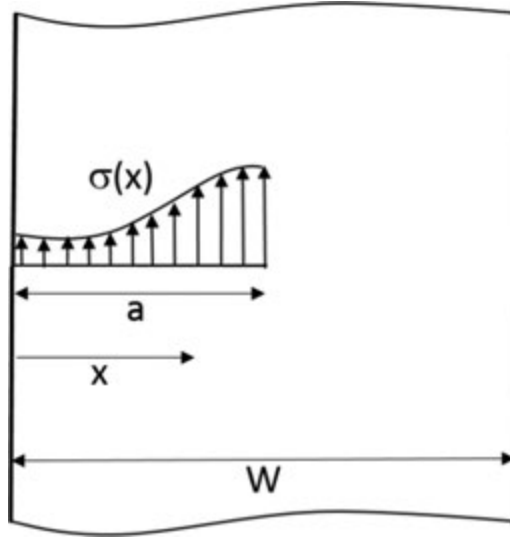


Fig. 12 Specimen with a crack with a bridging stress distribution.

$$\sigma(x) = \sigma_{appl}(x) + \sigma_{br}(x) \quad (25)$$

The bridging stress intensity factor, K_{br} , can be expressed in terms of the weight function, $h(x, a)$, which is a function of the crack length a and the coordinate x . Weight functions are used in fracture mechanics to calculate stress intensity factors because they are independent of the load applied and only depend on the geometry of the component. K_{br} in terms of $h(x, a)$ is given by

$$K_{br} = \int_0^a h(x, a) \sigma_{br}(x) dx \quad (26)$$

and for the applied stress intensity factor K_{Iappl} :

$$K_{Iappl} = \int_0^a h(x, a) \sigma_{appl}(x) dx \quad (27)$$

The weight functions are known for many types of test specimens and can be found in [Wu and Carlsson \(1991\)](#). The total stress intensity factor at the crack tip is then given as

$$K_{Itip} = K_{Iappl} + K_{Ibr} \quad (28)$$

In order to obtain σ_{br} and K_{Ibr} an expression for the total displacements of the crack surface, δ , can be derived by the existing relation between crack surface displacements, weight function and stress intensity factor for a given stress distribution $\sigma(x)$ ([Anderson, 1995](#)):

$$h = \frac{E'}{K_I} \frac{\partial \delta(x, a)}{\partial a} \quad (29)$$

E' is the elastic modulus in plain strain. Integration of this formula and applying [Eq. \(28\)](#) yields the crack surface displacements δ caused by the total stress σ of [Eq. \(25\)](#):

$$\delta(x) = \delta_{br}(x) + \delta_{app}(x) = \frac{1}{E'} \int_x^a h(x, a') \left[\int_0^{a'} h(a', x') (\sigma_{appl}(x') + \sigma_{br}(x')) dx' \right] da' \quad (30)$$

with

$$\delta_{br}(x) = \frac{1}{E'} \int_x^a h(x, a') \left[\int_0^{a'} h(a', x') \sigma_{br}(x') dx' \right] da' \quad (31)$$

$$\delta_{app}(x) = \frac{1}{E'} \int_x^a h(x, a') \left[\int_0^{a'} h(a', x') \sigma_{appl}(x') dx' \right] da' \quad (32)$$

where x is the coordinate of the point where the displacement is computed and x' is the location where the stress σ acts.

Determination of the Bridging Parameters From the K_R -Curves

A procedure that allows the bridging stresses to be determined from experimental R -curve was developed and applied to the R -curve of qcoarse-grained alumina ([Fett, 1995b](#); [Fett et al., 1995](#)). Later on, it was applied by [Fünfschilling et al. \(2009\)](#) to the

R-curves of silicon nitrides obtained by a high-resolution compliance method (Fett *et al.*, 2008). The procedure of the determination of the bridging stresses will be shown for these two silicon nitrides (Y₂O₃, MgO)-SN and (Al₂O₃, MgO)-SN which were consolidated in a two step sintering process.

The simplest approach to solve Eqs. (26)–(30) is to express the bridging law by a series expansion with respect to δ with unknown coefficients A_n ,

$$\sigma_{br}(\delta) = \sum_{n=0}^N A_n \delta^n \quad (33)$$

For a given arbitrary crack length, a , δ is first approximated by δ_{appl} . By using this value of δ , $\sigma_{br}(\delta)$ can be obtained from Eq. (33) with an arbitrarily chosen set of coefficients A_n . This first approximation for the bridging stress is then inserted in the integrand of Eq. (30), so that an improved solution for the total displacement is obtained. The procedure is then repeated by entering the δ -values in Eq. (33) for obtaining an improved bridging stress. The procedure is iterated until a certain state of convergence is reached. This part of the calculation forms the inner loop of a computer program. In the outer loop, the actual crack length is varied by $\Delta a = a - a_0$, and K_{br} is computed using Eq. (30). Then, from Eq. (28)

$$K_R = K_{lappl} = K_{ltip} - K_{lbr} \quad K_{lbr} < 0 \quad (34)$$

If this is repeated for a number of N crack length values, we obtain N computed K_R -values. A second iterative procedure is then applied in which the N coefficients are changed systematically until computed and measured K_R are identical (Fett *et al.*, 1995; Fünfschilling *et al.*, 2009). The results for the two silicon nitrides are plotted in Fig. 13. This method is computationally expensive, so that recently approximations have been developed that significantly reduce the computational time (Fünfschilling *et al.*, 2010). The crack tip displacement corresponding to the Irwin parabola is given by (Anderson, 1995)

$$\delta_{br,tip} = \sqrt{\frac{8 K_{br}}{\pi E}} \sqrt{a - x} \quad (35)$$

Eq. (35) is plotted in Fig. 13(d) for the same bridging stress intensity factor (dashed curve) as the exact solution given by Eq. (31) for $\Delta a = 100 \mu\text{m}$.

Effect of Specimen Geometry, Crack Size, and Type of Loading on the *R*-Curve

The *R*-curve is not a material property (Fett and Munz, 1990). It depends on the geometry of the component, the initial crack size, and the type of loading. This has been shown experimentally and by calculations using different type of specimens. Thus, the results of calculations of the bridging stress intensity factor using the same bridging relation are shown in Fig. 14 for different type of specimens (Fett *et al.*, 2000b).

The initial crack size also influences the *R*-curve as shown experimentally by Steinbrech *et al.*, 1990 in SENB specimens of Alumina (Fig. 15). Long initial cracks were produced by saw cutting, so that no wake or initial process zone was initially present.

Long and Small Cracks

R-curves for naturally small cracks are often different from those for macroscopic cracks, showing the trend of lower *R*-curves for small natural cracks. This is illustrated in Fig. 16 for Mg-doped zirconia and Alumina. The *R*-curves of small semielliptical surface flaws of silicon nitrides and carbides can be also different from those measured with long through-thickness cracks, particularly with regard to the initiation toughness and initial slope. For example, Li and Yamanis (1989) found that the *R*-curve in a Si₃N₄ ceramic using indentation-strength measurements rose more steeply than that measured from a double-cantilever beam specimen.

In silicon carbide, the *R*-curve behavior for small surface cracks and long through thickness cracks were studied in two SiC ceramics with sharply contrasting fracture properties (Gilbert *et al.*, 2005). The first was a commercial SiC (Hexoloy SA) that failed by transgranular cleavage without any evidence of crack shielding; the second one (referenced as ABC-SiC) had a microstructure formed by a network of plate-shaped grains with an amorphous grain-boundary film promoting debonding and crack deflection and resulting in toughening from a bridging generated *R*-curve. Hexoloy SA failed catastrophically at $K_{Ic} < 3 \text{ MPa m}^{1/2}$, while ABC-SiC exhibited much-improved flaw tolerance with significant rising *R*-curve behavior and a steady-state fracture toughness of $\sim 9 \text{ MPa m}^{1/2}$ after crack extension of $\sim 600 \mu\text{m}$. In ABC-SiC, however, the behavior of long and small cracks were very different for crack sizes extensions of less than $\sim 120 \mu\text{m}$, with the small-cracks showing much less crack-growth resistance; this effect was not observed in Hexoloy SA (Fig. 17).

According to Gilbert *et al.* (2005) this discrepancy in long- and small-crack *R*-curves at initial crack extensions was not caused by variation in the shape of the crack wake, but rather by the physically small nature of the crack, relative to grain size and local residual stress fluctuations. Fett *et al.* (1996) demonstrated that differences in the shape of the crack-opening profile for small surface cracks versus long through thickness cracks alters the initial slope of the *R*-curve, because of changes in the distribution of bridging tractions. However, according to Gilbert *et al.* (2005) these bridging tractions cannot explain the large decrease in initiation toughness and crack-growth resistance for small cracks compared to long cracks.

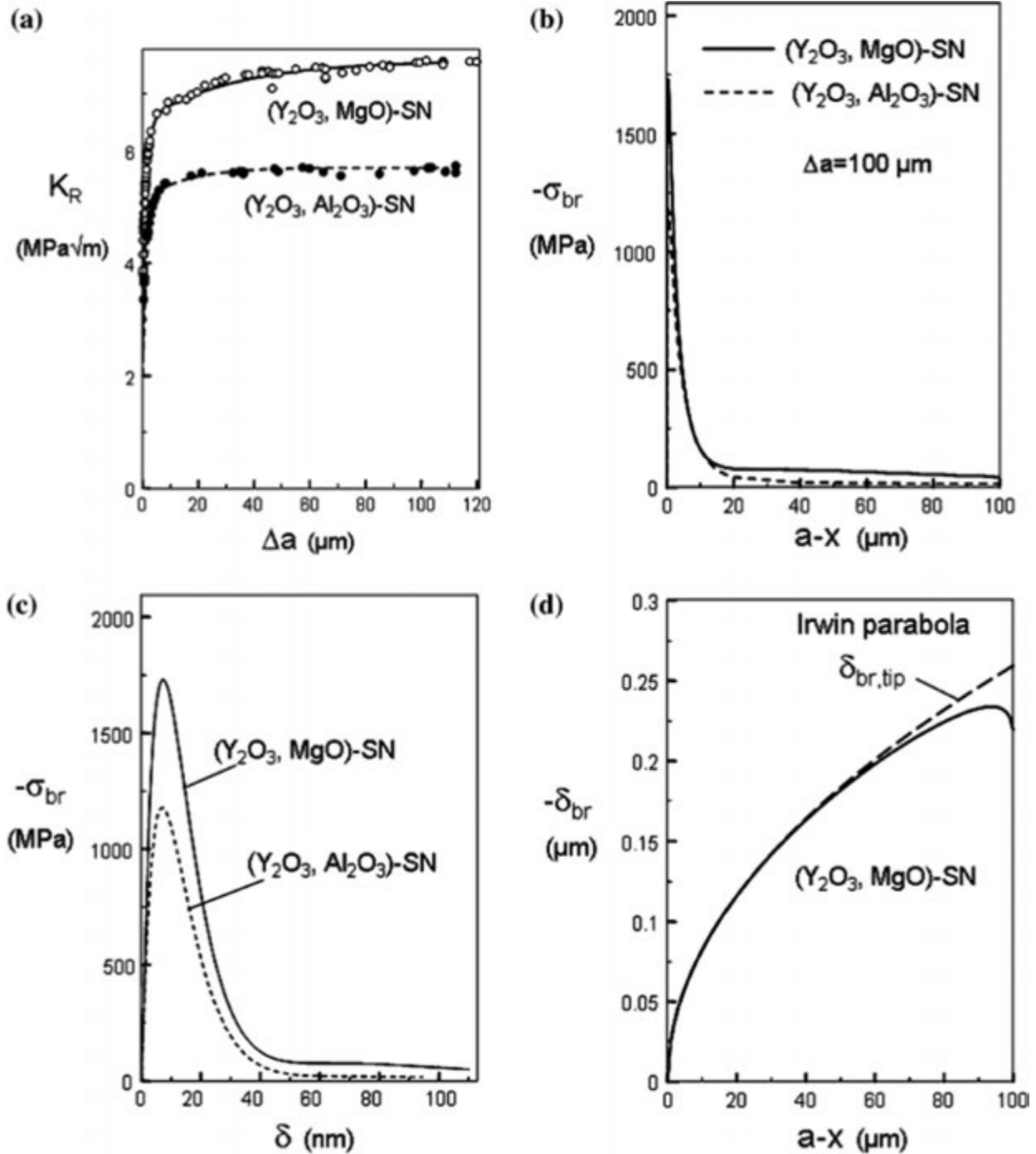


Fig. 13 (a) K_R -curve for the two Si₃N₄ ceramics; (b) bridging stress distribution over the length of a crack with $\Delta a = 100$ μm; (c) bridging stresses versus crack opening displacement; (d) bridging displacements from Eq. (31) (solid curve) and Irwin parabola according to Eq. (35) for the same bridging stress intensity factor (dashed curve) as the exact solution given by Eq. (31) for $\Delta a = 100$ μm. Reproduced from Fünfschilling, S., Fett, T., Hoffmann, M.J., *et al.*, 2009. Bridging stresses from *R*-curves of silicon nitrides. *J. Mater. Sci.* 44, 3900–3904.

Determination of Bridging Stresses

As can be seen from previous sections, crack bridging is an important mechanism for the crack propagation resistance. The *R*-curve depends on different factors such as specimen geometry, initial crack length, etc. Nevertheless, the bridging stress distribution as a function of crack opening displacement is widely believed to represent a true material property uninfluenced by sample geometry,

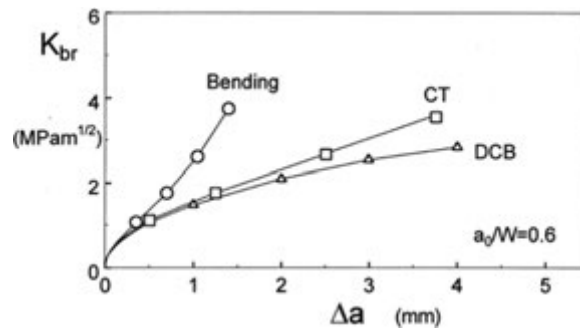


Fig. 14 Bridging stress intensity factor for bending, CT and DCB specimens. Reprinted from Fett, T., Munz, D., Geraghty, R.D., White, K.W., 2000b. Influence of specimen geometry and relative crack size on the *R*-curve. Eng. Fract. Mech. 66, 375–386 with permission of Elsevier. All rights reserved.

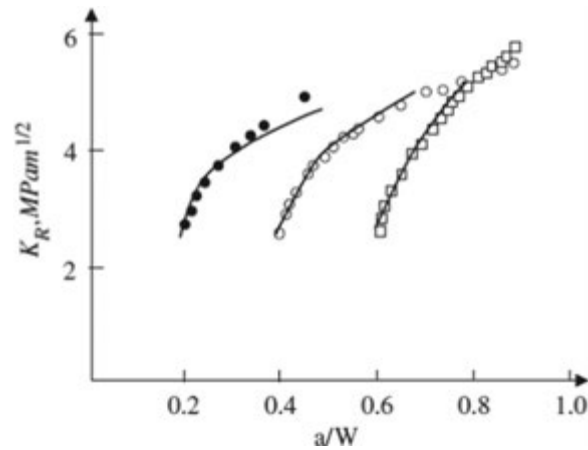


Fig. 15 Effect of initial crack length on *R* curve for an Al_2O_3 (experimental results of Steinbrech, R.W., Reichl, A., Schaarwächter, W., 1990. *R*-curve behavior of long cracks in Alumina. J. Am. Ceram. Soc. 73, 2009–2015). Reprinted from Munz, D., 2007. What can we learn from *R*-curve measurements? J. Am. Ceram. Soc. 90, 1–15 with The American Ceramic Society. All rights reserved.

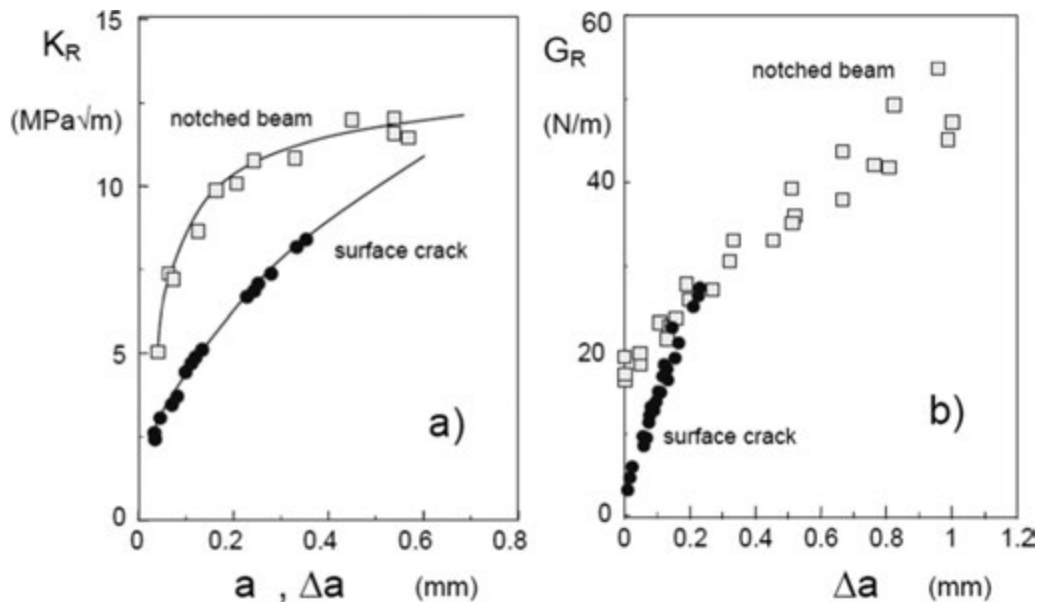


Fig. 16 *R*-curves for large and small cracks: (a) MgO doped zirconia; (b) Alumina. Reprinted from Marshall, D.B., Swain, M.V., 1988. Crack resistance curves in magnesia-partially-stabilized zirconia. J. Am. Ceram. Soc. 71, 399–404 and Steinbrech, R.W., Schmenkel, O., 1988. Crack resistance curves for surface cracks in alumina. J. Am. Ceram. Soc. 71, C271–C273, respectively, with permission of The American Ceramic Society. All rights reserved.

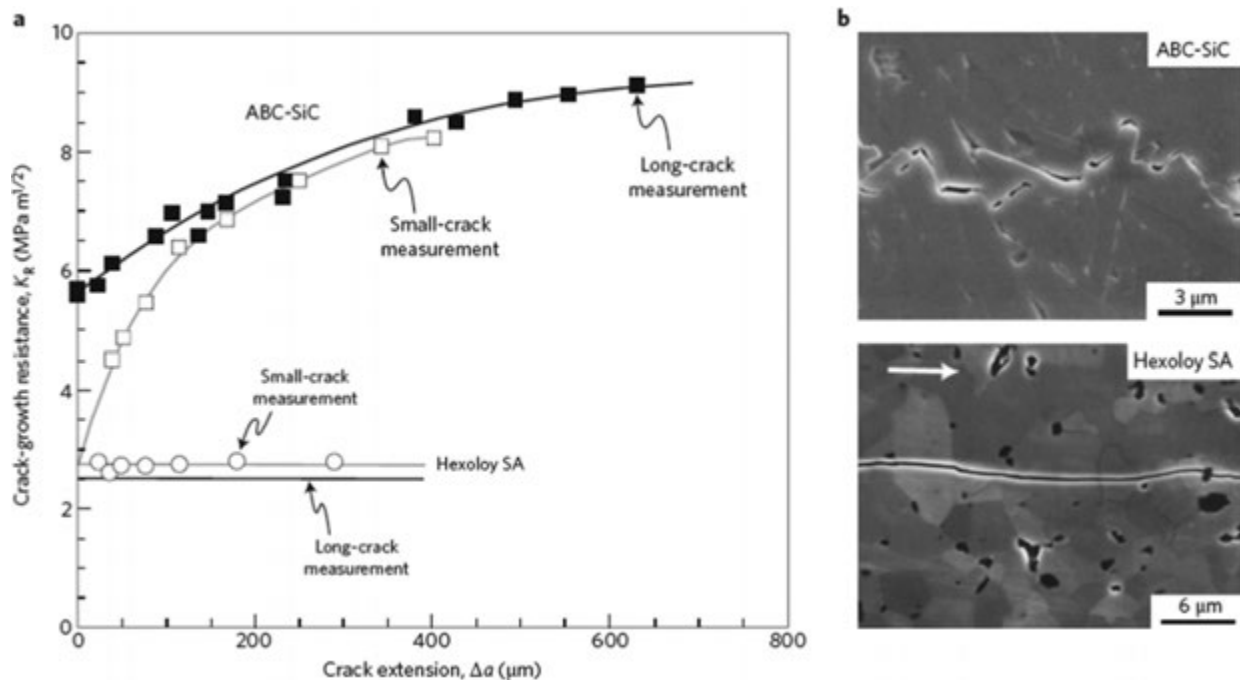


Fig. 17 (a) R -curves measured in Al, Si and B SiC (ABC-SiC, squares) with nanoscale glassy film along the grain boundaries and in commercial SiC Hexoloy (circles) using small and long cracks. (b) Intergranular fracture in ABC-SiC and transgranular fracture in SiC Hexoloy (Gilbert, C.J., Cao, J.J., Jonghe, L.C., Ritchie, R.O., 2005. Crack-growth resistance-curve behavior in silicon carbide: Small versus long cracks. *J. Am. Ceram. Soc.* 80, 2253–2261). Reproduced from Ritchie R.O., 2011. The conflicts between strength and toughness. *Nat. Mater.* 10, 817–822 with permission of Nature Materials. All rights reserved.

loading conditions, and other extrinsic factors (Greene *et al.*, 2012). A short description of existing methods for accurate measurement of the bridging stress distribution are presented below.

The Multi-Cutting Compliance Technique

The multi-cutting compliance technique is destructive and involves measuring the compliance after incremental saw cuts are made into the wake of a bridged crack (Hu *et al.*, 1991; Hu and Mai, 1992). It uses a diamond saw blade to incrementally cut away the crack wake while measuring the sample compliance via back-face strain gauges. Crack-opening profile measurements are also made and used along with the results of multi-cutting compliance experiments to obtain an estimate of the full bridging stress distribution. When the portion of crack wake eliminated is traction free, there is no change in compliance after cutting; conversely, if active bridges are removed from the crack wake by the saw blade, a corresponding increase in the sample compliance is expected. Thus, the extent of the grain-bridging zone behind the crack tip, L , may be determined by observing the notch length where the compliance begins to increase during the multi-cutting experiment. When the bridging-zone length is appreciably smaller than the sample size, the normalized grain-bridging stress distribution $\sigma_{br}(x)/\sigma_{max}$ can be obtained from the measured compliance during the multi-cutting experiment. σ_{max} is then determined by calculation of Eq. (35) by a least-squares fit to the experimental data of the measured bridged crack-opening profile. When L is of the order of the crack length the solution of Eq. (31) is facilitated by using an approximation (Wittmann and Hu, 1991; Kruzic *et al.*, 2004).

The Post-Fracture Tensile (PFT) Test

Hay and White (1993, 1995) developed the post-fracture tensile test (PFT) from cracked DCB specimens with the objective of determining directly the closure stress in terms of crack opening displacement. Small post fracture tensile specimens are machined by sectioning larger cracked ceramic specimens. These post fracture specimens are cut in such a way that they span the crack wake of the DCB specimen. Each one contains a portion of the original bridged through-thickness crack which can then be tensile tested. The separation between crack faces in the tensile test of the sliced specimens can be measured by using a laser interferometric displacement gauge. The wake stiffness and peak load capacity of the sliced specimens are measured, finding higher values for those closer to the crack tip. In alumina with coarse grain size the evaluation of the initial part of the R -curve combined with the results of post-fracture tensile tests allow the total bridging stress relation to be determined. The post fracture tensile tests provided the bridging stresses for larger displacements (Fett *et al.*, 2000c). One important limitation of this technique is the spatial resolution which is limited by the size of the width of the post fracture tensile specimens.

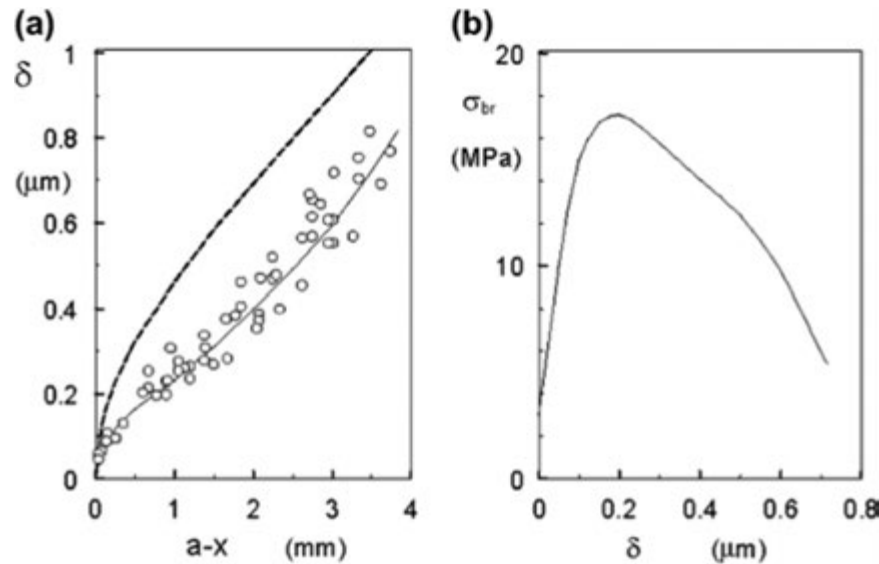


Fig. 18 (a) Crack profile δ for coarse-grained Al_2O_3 (symbols. Measured data, solid curve average dependency, dashed curve δ_{appi} ; (b) bridging stresses derived from (a)). Reproduced from Fett, T., Munz, D., Thun, G., 2000d. A method to estimate crack tip toughness from bending tests on pre-notched bars. J. Am. Ceram. Soc. 83, 421–423 with permission of the American Ceramic Society. All rights reserved.

Calculation of Bridging Stresses From Experimental Crack Profiles

A method to determine the bridging stress relation is based on the measurements of crack opening displacement (COD) during stable crack propagation (Fett *et al.*, 1994; Fett *et al.*, 2005a). The procedure is, in principle, based in Eq. (34) where the left-hand side is known as the result of the COD measurements. The bridging stress distribution $\sigma_{br}(x)$ is the magnitude to be found. The integral equation can be solved numerically. In Fig. 18(a) the experimental COD for coarse alumina is shown in terms of the distance to the crack tip as well as the COD that would exist for a given applied stress intensity factor ($K_{appl} = 3.75 \text{ MPa m}^{1/2}$) without bridging effects. The evaluation of these data via Eq. (34) yields the bridging stress law plotted in Fig. 18(b) (Fett *et al.*, 2000d).

Bridging Stresses From Raman and Fluorescent Spectroscopy

Fluorescent and Raman spectroscopy based methods can be used to measure bridging stresses in various ceramic base materials. Fluorescent spectroscopy has been used mainly in alumina because of the usual presence of Chromium as a substitution impurity. The optical fluorescence lines of Cr^{+3} are shifted by the stress from their stress-free position. The bridging stresses in the wake of the crack path were measured by fluorescence spectroscopy in large-grained alumina polycrystals (Pezzotti *et al.*, 1998). Frictional bridging stresses were $\approx 50 \text{ MPa}$, while unbroken ligaments between the crack faces were found to support tensile stresses up to $\approx 100 \text{ MPa}$. Average bridging stresses, either theoretically calculated from *R*-curve data or experimentally measured by fluorescence spectroscopy on frictional/bridging sites, were similar.

The peaks of the Raman spectrum are also sensitive to stress so that Raman spectroscopy has also been used for determining bridging stress profiles. In toughened Si_3N_4 with a remarkably rising *R*-curve behavior, using this technique tractions of the GPa order were determined during crack mouth opening experiments with unbroken acicular grains placed in the very neighborhood behind the advancing crack tip (within a crack length $0 < \Delta a < 100 \mu\text{m}$). Closure stresses up to values of several hundred MPa were measured in a zone up to several hundred microns behind the crack tip by friction of broken interfaces. Their magnitude averaged upon the frictional bridging zone, $100 < \Delta a < 800 \mu\text{m}$, was only 120 MPa, thus providing only a minor contribution to toughening. The crack bridging mechanism is then by far the main operative mechanism in Si_3N_4 on the microscopic scale (Pezzotti *et al.*, 1999a,b).

From the analysis of the bridging stresses measured by Greene *et al.* (2012) in Al_2O_3 and Si_3N_4 using spectroscopy methods, they conclude that spectroscopy methods only yield reliable bridging stress results if a reasonable through thickness volume of material is sampled. While 2.5% of the specimen thickness achieved using fluorescence spectroscopy appears adequate for Al_2O_3 , the 0.1%–0.2% of the sample thickness achieved using Raman spectroscopy for Si_3N_4 appears inadequate.

Calculation of Bridges Stresses From of COD in Vickers Cracks

The measurement of the *R*-curves from the crack tip opening displacement (COD) profile on Vickers indent cracks has some important advantages for determining the intrinsic crack-tip toughness, K_{I0} . These are the ease of producing indentation cracks and analyzing the COD in the microscope, and the fact that the COD measurements can be made on unloaded samples. They are also disadvantages since cracking patterns can vary for different ceramics (different crack shapes, presence of lateral cracking). When the

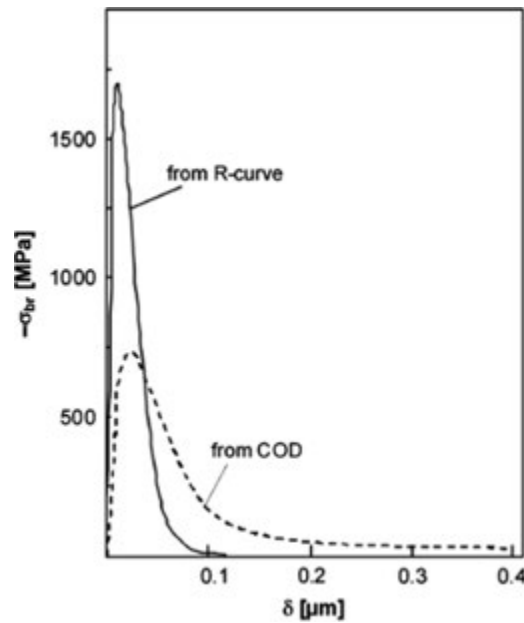


Fig. 19 Comparison of the bridging relations obtained from the *R*-curve (solid line) and the COD-evaluation (dashed line) in silicon nitride doped with MgO and Y₂O₃ (MgY-SN). Reproduced from Fünfschilling, S., Fett, T., Oberacker, R., *et al.*, 2011. Crack-tip toughness from Vickers crack-tip opening displacements for materials with strongly rising *R*-curves. *J. Am. Ceram. Soc.* 94, 1884–1892 with permission of the American Ceramic Society. All rights reserved.

bridges stresses are determined from COD measurements on Vickers cracks in materials with a very steep *R*-curve, the maximum value does not coincide with that calculated from the *R*-curve. For example, this value calculated from the *R*-curve in silicon nitride is about 1700 MPa at a crack tip distance of less than 2 μm, while from the COD measurements from Vickers cracks the maximal bridging stress value is calculated to be close to 750 MPa (Fig. 19). The main reason for the differences is that the *R*-curve reflects the bridging in the bulk material and COD curves reflect bridging at the surface where the thermal mismatch stresses must disappear in the direction normal to the surface. Consequently, debonding behavior at bridging crystals and frictional bridging effects must drastically be affected (Fünfschilling *et al.*, 2011).

R-Curve and Strength

Many engineering ceramics present *R*-curve behavior with fracture toughness increasing with crack extension. As a consequence, they show “flaw tolerance”, that is, the strength becomes less sensitive to initial flaw size relative to some conventional ceramics with single fracture toughness. The relation between initial flaw size, *R*-curve, and strength becomes not straightforward. In important technical strong ceramics, the strength depends of the first microns of crack extension of the *R*-curve, but the characterization of this part of the curve is challenging with macroscopic cracks. One reason is that if cracks are several millimeters in length significant toughening may be associated with the precrack. A second reason is that, if the cracks used for *R*-curve start from blunt notches they are overdriven and an unstable jump in crack length occurs until the crack extends more than the notch root radius. The result is that *R*-curves often begin at stress-intensity values well above the intrinsic toughness of single grains (Gilbert *et al.*, 2005). If the initial crack is of the order of the grain size, there are other factors that complicate the measurement of the initial part of the *R*-curve as, for example, the presence of local residual stresses from thermal expansion mismatch and the tendency towards a local not straight microcrack path (Kruzic *et al.*, 2008). All these effects are especially important in bridging ceramics such as Si₃N₄ in which the *R*-curves rise initially very steeply at short crack lengths relative to other bridging ceramics (Al₂O₃, SiC) giving them their exceptional strength and relative insensitivity to flaw size.

The relation between strength and initial part of the *R*-curve can be illustrated examining MgO–La₂O₃- and MgO–Lu₂O₃-doped ceramics (Kruzic *et al.*, 2008). The higher ionic radius of La with respect to Lu induces weaker grain-boundary adhesion and higher toughness for long cracks. However, the Lu-doped Si₃N₄ has higher strength, which can be explained by its steeper initial *R*-curve although its saturation toughness is lower than the La-doped material (Fig. 20).

R-Curve in Ceramic Laminates

Monolithic ceramics without *R*-curve behavior can still show this effect when they are processed as laminates composed by at least two different monolithic ceramics. A laminate can be formed by sintering layers of monolithic A with thickness t_A and monolithic

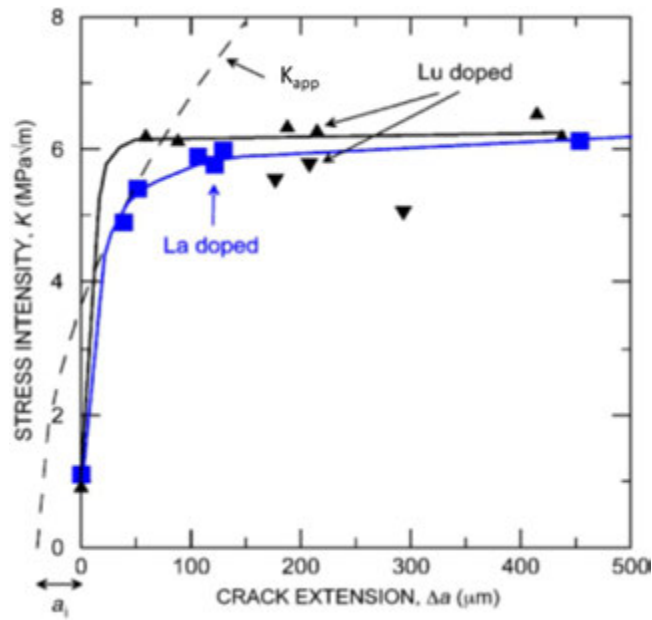


Fig. 20 Early *R*-curves for Lu and La-doped silicon nitrides. For small initial flaw sizes, a_i , the initial part of the *R*-curve determines the strength. K_{app} is plotted for $a_i = 540 \mu\text{m}$ and an applied stress of 510 MPa which is the predicted fracture strength for the La-doped Si_3N_4 at that flaw size. Reproduced from Kruzic, J.J., Satet, R.L., Hoffmann, M.J., Cannon, R.M., Ritchie, R.O., 2008. The utility of *R*-curves for understanding fracture toughness-strength relations in bridging ceramics. *J. Am. Ceram. Soc.* 91, 1986–1994 with permission of the American Ceramic Society. All rights reserved.

B layers with thickness t_B . Ceramic laminates can be classified in two types according to the interface between layers. For reviews on processing and mechanical characterization of laminates see, for example, Chan (1997), Minatto *et al.* (2014), Lube (2007), Sestakova *et al.* (2011) and Bermejo and Deluca (2013).

Those laminates with weak interfaces are inspired by biological structures such as mollusc shells formed by thin layers of calcium carbonate and tough polymers arranged in a hierarchical structure (Deville *et al.*, 2006). In the laboratory, the laminates with weak interfaces can be produced, for example, by combining thin layers with high porosity with thicker layers with low porosity (Blanks *et al.*, 1998; Davis *et al.*, 2000). In this example, neither chemical incompatibility nor differential shrinkage mismatch are produced so that residual stresses in the layers are avoided.

When a crack grows in a strong layer perpendicularly to a weak interface, it is kinked into the interface or weak layer and it is forced to grow as a delaminating crack. Eventually, the crack enters the strong layer and grows until arriving to the next weak interface where kinks again inducing delamination. This process is repeated again until final fracture.

The analysis of fracture of weak interface laminates is based on the criterion for crack deflection at an interface between two elastically dissimilar materials (He and Hutchinson, 1989). From this analysis, it comes out that the main requirements for designing strong laminates with weak interfaces are: (1) a high strength of the lamina of the A layer, (2) a high toughness of the very thin B-layer (or interface) to enhance the energy consumption for the propagation of the delamination cracks, but low enough to guarantee crack deflection, (3) for the same reason as (2), a low Young's modulus of the weak B-layers.

In terms of *R*-curve, it is more interesting to analyze laminates composed by two high strength monolithic ceramics, A and B, with different elastic and thermal properties. High residual biaxial stresses can arise in the laminate after sintering because of differential shrinkage if a strong interface is formed between layers.

To simplify the analysis of the *R*-curve of ceramic laminates with strong interfaces, the case of only two materials A and B will be considered together with a number of simplifying assumptions: (1) the laminate is described as an infinite plate and the influence of free surfaces is neglected; (2) the layer architecture is periodical and is mirror symmetrical with respect to the mid plane of the laminate; (3) the coefficients of thermal expansion of A and B are different, but the elastic properties are similar; (4) the thickness of the laminate is infinite. Under these assumptions, it can be shown (Oel and Fréchet, 1967) that the magnitude of the residual stresses, σ_A and σ_B , in an infinite thick laminate are approximately related by:

$$\frac{\sigma_A}{\sigma_B} = -\frac{t_B}{t_A} \quad (36)$$

To study the *R*-curve in these laminates we shall consider a short straight through-thickness edge crack of length a perpendicular to the layers (see Fig. 21). It is assumed that the applied stress is uniaxial and homogenous and perpendicular to the crack. The effect of the residual stress in the layers can be treated as an external stress which acts in addition to the applied stress. The condition for the initiation of fracture is then

$$K_{app} = K_C - K_{res}(a) \equiv K_R(a) \quad (37)$$

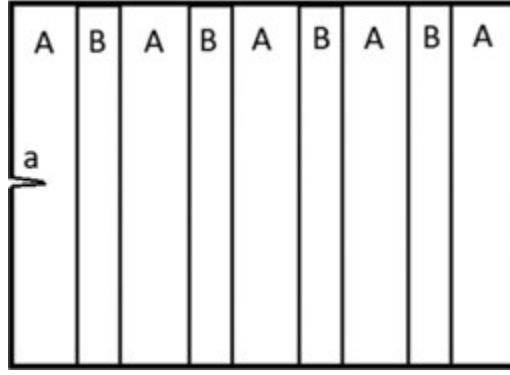


Fig. 21 Periodic multilayer architecture of alternating layers of materials A and B of thickness t_A and t_B respectively with a through-thickness edge crack of length a propagating perpendicular to the layers.

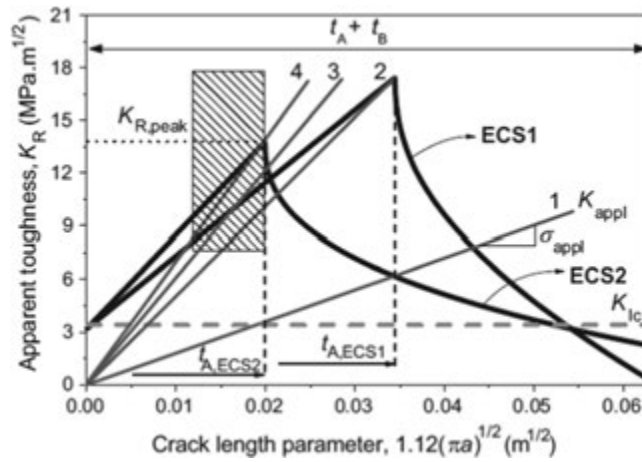


Fig. 22 Apparent *R*-curves ECS laminates characterized by $E = 390$ GPa, $\nu = 0.22$ and $\Delta\alpha = 1 \cdot 10^{-6} \text{ K}^{-1}$. $\sigma_0 = 590$ MPa and $t_A + t_B = 1$ mm. Two different values of t_B/t_A are considered: $t_B/t_A = 7/3$ (ECS1) and $9/1$ (ECS2). Reproduced from Bermejo, R., Deluca, M., 2013. Fracture mechanics. In: Handbook of Advanced Ceramics, second ed. Elsevier, pp. 733–751 with permission from Elsevier. All rights reserved.

where K_C is the fracture toughness of the monolithic ceramic and $K_{res}(a)$ is the stress intensity factor due to the residual stress which is negative for a compressive residual stress and positive for a tensile residual stress. For a layer with compressive residual stresses the effect is similar to the presence of crack tip shielding as described in previous sections, but, in this case, it is originated by the architecture and different expansion coefficients of the layers and not by the microstructure of both monolithic layers. If the residual stress is tensile, K_R will decrease with increasing crack extension. Finally, K_{app} is given by Eq. (1) with Y being constant and equal to 1.12 because of the assumption of infinite plate thickness.

The description of the crack shielding caused by residual stresses is simplified under the assumption that the elastic properties of materials A and B are equal since then $K_{res}(a)$ can be then determined using the weight function method (see Section “Stress Intensity Factor from Bridging Interactions”). The weight function method gives a very good approximation of the *R*-curve for laminates made of materials with similar elastic properties (E -moduli ratio less than 2). This condition is satisfied within the most common range of ceramic materials.

The *R*-curve that results depends on whether the external layer of the laminate is under compressive stresses (ECS) or tensile stresses (ICS). To illustrate the magnitude of the *R*-curve in ECS laminates we refer to the examples given in Sestakova et al. (2011) and Bermejo and Deluca (2013) where the values taken for the elastic properties of A and B materials are $E = 390$ GPa, $\nu = 0.22$ and $\Delta\alpha = 1 \cdot 10^{-6} \text{ K}^{-1}$ (the difference in thermal expansion coefficient). A new parameter σ_0 is defined as $\sigma_0 \equiv \sigma_A - \sigma_B$ and in the present example equals 590 MPa with $t_A + t_B = 1$ mm. The *R*-curves that result are shown in Fig. 22 for two ECS laminates with different t_B/t_A ratios, 7/3 (ECS1) and 9/1 (ECS2). In the thicker external A-layer (ECS2) the residual stress is lower and the corresponding *R*-curve at the interface reaches a lower value than in the thinner A-layer (ECS1) for which the residual compressive stress is higher.

From the curves shown in Fig. 22 for the first two layers, the maximum shielding is achieved at the first A/B interface, that is, when the crack length is equal to t_A . This peak value can be written as (Sestakova et al., 2011; Bermejo and Deluca, 2013):

$$K_{R, peak} = K_C - 1.12\sqrt{\pi t_A} \sigma_0 \frac{t_B}{t_A + t_B} \quad (38)$$

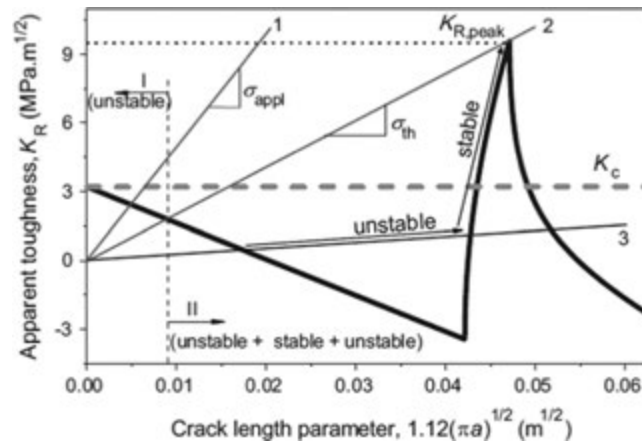


Fig. 23 Apparent toughness and strength in a typical ICS-laminate versus the crack size parameter. The curve corresponds to a laminate characterized by $\sigma_0 = +590$ MPa and $t_A + t_B = 1$ mm, whereas $t_B/t_A = 4/1$, $\sigma_A = 118$ MPa and $\sigma_B = -472$ MPa. Reproduced from Bermejo, R., Deluca, M., 2013. Fracture mechanics. In: Handbook of Advanced Ceramics, second ed. Elsevier, pp. 733–751 with permission from Elsevier. All rights reserved.

From this expression it can be shown that under the condition of $t_A + t_B = \text{constant}$, the maximum value of the R -curve is reached for $t_B/t_A = 2$ and this maximum increases with the value of $t_A + t_B$.

To examine the influence of the R -curves on the strength, we shall assume that main cracks are in the outer layer with dimensions in the usual range so that $1.12\sqrt{\pi a}$ is in the shaded bar of Fig. 22. The application of increasing external stresses induces stress intensity factors represented by the lines 1–4. It can be appreciated that the stress needed for fracture from the largest crack in the shaded area is given by the slope of line 3 for ECS1. By contrast, for the ECS2 laminate the fracture stress for the largest flaw in the same shaded area is given by the slope of line 4. We can see then that the laminate with the higher toughness is not the stronger one.

For ICS-laminates a similar analysis as for ECS can be carried out with the same simplifying assumptions as before. The apparent R -curve can be determined by the weight function method neglecting the difference in the elastic properties of the layers. Now the presence of a tensile residual stress in the outer A-layer produces a decreasing R -curve in this layer, which increases in the B-layer because of the presence of the compressive residual stress. The peak of the R -curve is reached in this case when $a = t_A + t_B$. The determination of this peak value in ICS laminates by the weight function method gives now a more complex expression. However, calculations show that, for $t_A + t_B = \text{constant}$, the maximum of the R -curve is achieved for $t_B/t_A = 0.25$. (Sestakova *et al.*, 2011; Bermejo and Deluca, 2013).

As can be seen in Fig. 23, the crack behavior depends on the crack size. For very small cracks in region I unstable crack propagation will take place (line 1) leading to catastrophic failure; however, cracks in region II will first pop in at the intersection of line 3 with the decreasing R -curve and then stop when the increasing part of the R -curve in B-layer is reached. If the stress is further increased, stable crack growth up to a length equal to $t_A + t_B$ occurs. Line 2 corresponds to the stress, where these cracks become unstable again and where catastrophic failure occurs. Line 2 determines a threshold for the strength of the laminate, which is given by:

$$\sigma_{th} = \frac{K_{R, peak}}{1.12\sqrt{\pi(t_A + t_B)}} \quad (39)$$

Finally, it should be noticed that although residual stresses are essential for increasing toughness, they can also induce a negative influence in the mechanical properties since they can also damage the sintered laminate in the form of tunnels cracks that may appear at the surface of the tensile layers if the residual stress is too high. Another type of defect are edge cracks which appear at the free edges of compression layers. These cracks compromise the strength and fracture toughness so that they should be taken into account in the design of ceramic laminates.

References

- Anderson, T.L., 1995. Fracture Mechanics, second ed. New York: CRC Press.
- Anstis, G.R., Chantikul, P., Lawn, B.R., Marshall, D.B., 1981. A critical evaluation of indentation techniques for measuring fracture toughness: i. Direct crack measurements. J. Am. Ceram. Soc. 64, 533–538.
- Bermejo, R., Deluca, M., 2013. Fracture mechanics. In: Handbook of Advanced Ceramics, second ed. Elsevier. pp. 733–751.
- Blanks, K.S., Kristofferson, A., Carlström, E., Clegg, W.J., 1998. Crack deflection in ceramic laminates using porous interlayers. J. Eur. Ceram. Soc. 18, 1945–1951.
- Buresch, F.E., 1978. A structure sensitive K_{IC} -value and its dependence on grain size distribution, density, and microcracking interaction. Fract. Mech. Ceram. 4, 835–847.
- Chan, H.M., 1997. Layered ceramics: Processing and mechanical behavior. Annu. Rev. Mater. Sci. 27, 249–282.
- Chantikul, P., Anstis, G.R., Lawn, B.R., Marshall, D.B., 1981. A critical evaluation of indentation techniques for measuring fracture toughness: ii, strength method. J. Am. Ceram. Soc. 64, 539–543.
- Chen, W., Lynch, C.S., 1998. A micro-electro-mechanical model for polarization switching of ferroelectric materials. Acta Mater. 46, 5303–5312.
- Damani, R.J., Gstrein, R., Danzer, R., 1996. Critical notch-root radius effect in SENB-S fracture toughness testing. J. Eur. Ceram. Soc. 16, 695–702.

- Davis, J.B., Kristoffersson, A., Carlström, E., Clegg, W.J., 2000. Fabrication and crack deflection in ceramic laminates with porous interlayers. *J. Am. Ceram. Soc.* 83, 2369–2374.
- Déville, S., Saiz, E., Nalla, R.K., Tomsia, A.P., 2006. Freezing as a path to build complex composites. *Science* 311, 515–518.
- dos Santos e Lucato, S.L., Lupascu, D.C., Rödel, J., 2000. Effect of poling direction on R-curve behavior in lead zirconate titanate. *J. Am. Ceram. Soc.* 83, 424–426.
- Evans, A.G., Faber, K.T., 2006. Crack-growth resistance of microcracking brittle materials. *J. Am. Ceram. Soc.* 67, 255–260.
- Fett, T., 1995a. An analysis of the residual stress intensity factor of Vickers indentation cracks. *Eng. Fract. Mech.* 52, 773–776.
- Fett, T., 1995b. Determination of bridging stresses and R-curves from load-displacement curves. *Eng. Fract. Mech.* 52, 803–810.
- Fett, T., 1999. Estimated stress intensity factors for semi-elliptical cracks in front of narrow circular notches. *Eng. Fract. Mech.* 64, 357–362.
- Fett, T., Munz, D., 1990. Influence of crack-surface interactions on stress intensity factor in ceramics. *J. Mater. Sci. Lett.* 9, 1403–1406.
- Fett, T., Munz, D., 1993. Evaluation of R-curve effects in ceramics 1. *Mater. Sci.* 28, 742–752.
- Fett, T., Munz, D., 2000. R-curve for a lead zirconate titanate ceramic obtained from tensile strength tests with Knoop-damaged specimens. *J. Am. Ceram. Soc.* 83, 3199–3201.
- Fett, T., Kamlah, M., Munz, D., Thun, G., 2000a. Strength of a PZT ceramic under different test conditions. In: Lynch, C.S. (Ed.), *Smart Structures and Materials 2000: Active Materials: Behaviour and Mechanics*, vol. 3992, pp. 197–208.
- Fett, T., Munz, D., Geraghty, R.D., White, K.W., 2000b. Influence of specimen geometry and relative crack size on the R-curve. *Eng. Fract. Mech.* 66, 375–386.
- Fett, T., Munz, D., Dai, X., White, K.W., 2000c. Bridging stress relation from a combined evaluation of the R-curve and post-fracture tensile test. *Int. J. Fract.* 104, 375–385.
- Fett, T., Munz, D., Thun, G., 2000d. A method to estimate crack tip toughness from bending tests on pre-notched bars. *J. Am. Ceram. Soc.* 83, 421–423.
- Fett, T., Munz, D., Kouna Njiwa, A.B., Rodel, J., Quinn, G.D., 2005a. Bridging stresses in sintered reaction bonded Si_3N_4 from COD measurements. *J. Eur. Ceram. Soc.* 25, 29–36.
- Fett, T., Njiwa, A.B.K., Rödel, J., 2005b. Shielding stresses for soft PZT. *Int. J. Fract.* 34, 151–159.
- Fett, T., Munz, D., Yu, C.-T., Kobayashi, A.S., 1994. Determination of bridging stresses in reinforced Al_2O_3 . *J. Am. Ceram. Soc.* 77, 3267–3269.
- Fett, T., Munz, D., Thun, G., Bahr, H.-A., 1995. Evaluation of bridging parameters in aluminas from R-curves by use of the fracture mechanical weight function. *J. Am. Ceram. Soc.* 78, 949–951.
- Fett, T., Munz, D., Seidel, J., Stech, M., Rodel, J., 1996. Correlation between long and short crack R-curves in alumina using the crack opening displacement and fracture mechanical weight function approach. *J. Am. Ceram. Soc.* 79, 1189–1196.
- Fett, T., Fünfschilling, S., Hoffmann, M.J., *et al.*, 2008. R-curve determination for the initial stage of crack extension in Si_3N_4 . *J. Am. Ceram. Soc.* 91, 3638–3642.
- Fett, T., Rizzi, G., 2003. Problems in fracture mechanics of indentation cracks. In: Report FZKA 6907 of Forschungszentrum Karlsruhe.
- Fischer, H., Waidich, A., Telle, R., 2008. Influence of preparation of ceramic SEVNB specimens on fracture toughness testing results. *Dent. Mater.* 24, 618–622.
- Fünfschilling, S., Fett, T., Gallops, S.E., *et al.*, 2010. First- and second-order approaches for the direct determination of bridging stresses from R-curves. *J. Eur. Ceram. Soc.* 30, 1229–1236.
- Fünfschilling, S., Fett, T., Hoffmann, M.J., *et al.*, 2009. Bridging stresses from R-curves of silicon nitrides. *J. Mater. Sci.* 44, 3900–3904.
- Fünfschilling, S., Fett, T., Oberacker, R., *et al.*, 2011. Crack-tip toughness from Vickers crack-tip opening displacements for materials with strongly rising R-curves. *J. Am. Ceram. Soc.* 94, 1884–1892.
- Gilbert, C.J., Cao, J.J., Jonghe, L.C., Ritchie, R.O., 2005. Crack-growth resistance-curve behavior in silicon carbide: Small versus long cracks. *J. Am. Ceram. Soc.* 80, 2253–2261.
- Greene, R.B., Gallops, S., Fünfschilling, S., *et al.*, 2012. A direct comparison of non-destructive techniques for determining bridging stress distributions. *J. Mech. Phys. Solids* 60, 1462–1477.
- Hannink, R.H.J., Kelly, P.M., Muddle, B.C., 2000. Transformation toughening in zirconia-containing ceramics. *J. Am. Ceram. Soc.* 83, 461–487.
- Hay, J.C., White, K.W., 1993. Grain-bridging mechanisms in monolithic alumina and spinel. *J. Am. Ceram. Soc.* 76, 1849–1854.
- Hay, J.C., White, K.W., 1995. Grain boundary phases and wake zone characterization in monolithic alumina. *J. Am. Ceram. Soc.* 78, 1025–1032.
- He, M.-Y., Hutchinson, J.W., 1989. Crack deflection at an interface between dissimilar elastic materials. *Int. J. Solids Struct.* 25, 1053–1067.
- Hu, X., Mai, Y.-W., 1992. Crack-bridging analysis for alumina ceramics under monotonic and cyclic loading. *J. Am. Ceram. Soc.* 75, 848–853.
- Hu, X.-Z., Lutz, E.H., Swain, M.V., 1991. Crack-tip-bridging stresses in ceramic materials. *J. Am. Ceram. Soc.* 74, 1828–1832.
- Jelitto, H., Felten, F., Swain, M.V., Balke, H., Schneider, G.A., 2007. Measurement of the total energy release rate for cracks in PZT under combined mechanical and electrical loading. *J. Appl. Mech.* 74, 1197–1211.
- Knehan, R., Steinbrech, R., 1982. Memory effects of crack resistance during slow crack growth in notched Al_2O_3 bend specimens. *J. Mater. Sci.* 1, 327–329.
- Kruzic, J.J., Cannon, R.M., Ritchie, R.O., 2004. Crack-size effects on cyclic and monotonic crack growth in polycrystalline alumina: Quantification of the role of grain bridging. *J. Am. Ceram. Soc.* 87, 93–103.
- Kruzic, J.J., Satet, R.L., Hoffmann, M.J., Cannon, R.M., Ritchie, R.O., 2008. The utility of R-curves for understanding fracture toughness-strength relations in bridging ceramics. *J. Am. Ceram. Soc.* 91, 1986–1994.
- Kübler, J., 1997. Fracture toughness using the SEVNB method: Preliminary results. *Ceram. Eng. Sci. Proc.* 18, 155–162.
- Lathabai, S., Rödel, J., Lawn, B.R., 1991. Cyclic fatigue from frictional degradation at bridging grains in alumina. *J. Am. Ceram. Soc.* 74, 1340–1348.
- Launey, M.E., Buehler, M.J., Ritchie, R.O., 2010. On the mechanistic origins of toughness in bone. *Annu. Rev. Mater. Res.* 40, 25–53.
- Lawn, B.R., 1993. *Fracture of Brittle Solids*, second ed. Cambridge: Cambridge University Press.
- Lawn, B.R., Evans, A.G., Marshall, D.B., 1980. Elastic/plastic indentation damage in ceramics: The median/radial crack system. *J. Am. Ceram. Soc.* 63, 574–581.
- Li, C.-W., Yamanis, J., 1989. Super-tough silicon nitride with R-curve behavior. *Ceram. Eng. Sci. Proc.* 10, 632–645.
- Lube, T., 2007. Mechanical properties of ceramic laminates. *Key Eng. Mater.* 333, 87–96.
- Mai, Y., Lawn, B.R., 1987. Crack-interface grain bridging as a fracture resistance mechanism in ceramics: II. Theoretical fracture mechanics model. *J. Am. Ceram. Soc.* 70, 289–294.
- McMeeking, R.M., Evans, A.G., 1982. Mechanics of transformation-toughening in brittle materials. *J. Am. Ceram. Soc.* 65, 242.
- Minatto, F.D., Milak, P., De Noni, A., Hotza, D., Montedo, O.R.K., 2014. Multilayered ceramic composites – A review. *Adv. Appl. Ceram.* 114, 127–138.
- Munz, D., Fett, T., 1999. *Ceramics, Mechanical Properties, Failure Behaviour, Materials Selection*. Berlin: Springer.
- Nalla, R.K., Kinney, J.H., Ritchie, R.O., 2003. Mechanistic fracture criteria for the failure of human cortical bone. *Nat. Mater.* 2, 164–168.
- Nalla, R.K., Kruzic, J.J., Kinney, J.H., Ritchie, R.O., 2005. Mechanistic aspects of fracture and R-curve behaviour in human cortical bone. *Biomaterials* 26, 217–231.
- Nishida, T., Pezzotti, G., Mangialardi, T., Paolini, A.E., 1996. Fracture mechanics evaluation of ceramics by stable crack propagation in bend bar specimens. *Fract. Mech. Ceram.* 11, 107–114.
- Njiwa, A.B.K., Fett, T., Lupascu, D.C., Rödel, J., 2006. Effect of geometry and electrical boundary conditions on R-curves for lead zirconate titanate ceramics. *Eng. Fract. Mech.* 73, 309–317.
- Oël, H.J., Fréchette, V.D., 1967. Stress distribution in multiphase systems: I Composites with planar interfaces. *J. Am. Ceram. Soc.* 50, 542–549.
- Pabst, R.F., Steeb, J., Claussen, N., 1978. Microcracking in a process zone and its relation to continuum fracture mechanics. *Fract. Mech. Ceram.* 4, 821–833.
- Pezzotti, G., Muraki, N., Maeda, N., Satou, K., Nishida, T., 1999a. In situ measurement of bridging stresses in toughened silicon nitride using Raman microprobe spectroscopy. *J. Am. Ceram. Soc.* 82, 1249–1256.
- Pezzotti, G., Suenobu, H., Nishida, T., 1999b. Measurement of microscopic bridging stresses in an alumina/molybdenum composite by in situ fluorescence spectroscopy. *J. Am. Ceram. Soc.* 82, 1257–1262.

- Pezzotti, G., Sbaizero, O., Sergio, V., *et al.*, 1998. In situ measurements of frictional bridging stresses in alumina using fluorescence spectroscopy. *J. Am. Ceram. Soc.* 81, 187–192.
- Rauchs, G., Fett, T., Munz, D., 2002. *R*-curve behaviour of 9Ce-TZP zirconia ceramics. *Eng. Fract. Mech.* 69, 389–401.
- Schneider, G.A., Heyer, V., 1999. Influence of the electric field on Vickers indentation crack growth in BaTiO₃. *J. Eur. Ceram. Soc.* 19, 1299–1306.
- Sestakova, L., Bermejo, R., Chlup, Z., Danzer, R., 2011. Strategies for fracture toughness, strength and reliability optimisation of ceramic-ceramic laminates. *Int. J. Mater. Res.* 102, 613–626.
- Steinbrech, R.W., Knehans, R., Schaanwächter, W., 1983. Increase of crack resistance during slow crack growth in Al₂O₃ bend specimens. *J. Mater. Sci.* 18, 265–270.
- Steinbrech, R.W., Reichl, A., Schaanwächter, W., 1990. *R*-curve behavior of long cracks in Alumina. *J. Am. Ceram. Soc.* 73, 2009–2015.
- Swanson, P.L., Fairbanks, C.J., Lawn, B.R., Mai, Y.-W., Hockey, B.J., 1987. Crack–interface grain bridging as a fracture resistance mechanism in ceramics: I experimental study on alumina. *J. Am. Ceram. Soc.* 70, 279–289.
- Turon-Vinas, M., Anglada, M., 2014. Fracture toughness of zirconia from a shallow notch produced by ultra-short pulsed laser ablation. *J. Eur. Ceram. Soc.* 34, 3865–3870.
- Turon-Vinas, M., Anglada, M., 2015. Assessment in Si₃N₄ of a new method for determining the fracture toughness from a surface notch micro-machined by ultra-short pulsed laser ablation. *J. Eur. Ceram. Soc.* 35, 1737–1741.
- Wittmann, F.H., Hu, X., 1991. Fracture process zone in cementitious materials. In: Bažant, Z.P. (Ed.), *Current Trends in Concrete Fracture Research*. Dordrecht: Springer.
- Wu, X.-R., Carlsson, J., 1991. *Weight Functions and Stress Intensity Factor Solutions*. Oxford: Pergamon Press.
- Yu, C.S., Shetty, D.K., Shaw, M.C., Marshall, D.B., 1992. Transformation zone shape effects on crack shielding in ceria-partially-stabilized zirconia (Ce-TZP)-alumina composites. *J. Am. Ceram. Soc.* 75, 2991–2994.
- Zimmermann, E.A., Busse, B., Ritchie, R.O., 2015. The fracture mechanics of human bone: Influence of disease and treatment. In: *BoneKey Reports* 4.
- Zimmermann, E.A., Schaible, E., Bale, H., *et al.*, 2011. Age-related changes in the plasticity and toughness of human cortical bone at multiple length scales. *Proc. Natl. Acad. Sci. USA* 108, 14416–14421.

Subcritical Crack Growth: Basic Relations and Experimental Evaluation

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Basic Relations

Crack Growth Law

Subcritical crack growth (SCCG), also called slow crack growth, occurs at a stress intensity factor below the fracture toughness, particularly in humid environment. It is governed by the stress intensity factor, K_I (in mode I loading), which is linked by a unique relation to the crack growth rate, v . For most ceramics and glasses, it is attributed to stress assisted corrosion at a crack tip, or any pre-existing defect in the material. This is the result of the combined effect of high stresses at the crack tip and the presence of water molecules (reducing surface energy at the crack tip) that induce crack propagation in a subcritical manner (Wiederhorn, 1967; Wiederhorn, 1974; Lawn, 1975; Michalske, 1983). As a general trend, SCCG is described on the basis of a crack velocity versus stress intensity factor (v - K_I) curve representation of which is shown in Fig. 1 in a log-log plot.

Below a threshold value, K_{I0} , there is typically negligible or no crack growth, which determines a safety range of the material use. Just beyond K_{I0} , three stages of crack propagation attributed to distinct mechanisms can be distinguished. In region I corresponding to low crack velocities, crack propagation is controlled by stress-assisted reaction kinetics at the crack tip. Region II corresponding to a constant crack velocity (plateau value), is controlled by the rate of transport of reactive species to crack tip. A slight ascending slope can also be observed in this region. Increasing K_I leads to high crack growth rates (region III) followed by unstable fracture, independent of the environment and controlled by the fracture toughness, K_{Ic} . Region I is of primary importance as it corresponds to the longest regime. In this region, the crack growth rate, v , is given by an empirical power-law relation (Wiederhorn, 1974; Munz and Fett, 1999) for most ceramics and glasses:

$$v = \frac{da}{dt} = AK_I^n = A^* \left(\frac{K_I}{K_{Ic}} \right)^n \quad (1)$$

where a is the crack size and t is time. A , A^* and n are parameters depending on the material, the temperature and the environment. Accurate determination of these parameters leads to lifetime prediction for ceramic components. n is known as the subcritical crack growth susceptibility coefficient. Its value is usually in the range 10–100 and the threshold K_{I0} may be around half the fracture toughness (Anglada, 2017). Comparison of the sensitivity to SCCG can be made using a normalized v - K_I/K_{Ic} diagram illustrated in Fig. 2 for different materials. The higher the slope of the diagram, i.e., the higher the K_{I0}/K_{Ic} ratio, the lower the sensitivity to SCCG by stress assisted corrosion. In this representation, very fine microstructures are considered to avoid microstructural effects (R-curve effects) which will be discussed below. It appears that the sensitivity to SCCG is strongly linked to the ionic fraction of the bond (Fig. 3): the higher the ionic fraction, the higher the intrinsic susceptibility to SCCG.

Glasses and oxide ceramics are particularly sensitive to SCCG as water molecules align to the cations at the crack tip surface, creating hydrogen bonding. An illustration of this reaction is given in Fig. 4 for zirconia. Reaction steps at the crack tip involve: (1) adsorption of water to Zr-O bond, (2) reaction involving simultaneous proton and electron transfer, and (3) formation of surface hydroxyls (De Aza et al., 2002).

Lifetimes Prediction

Under arbitrarily time-dependent stresses $\sigma(t)$, a general lifetime relation is obtained by integration of (1) considering the expression of the stress intensity factor ($K_I = \sigma Y(\pi a)^{1/2}$, where Y is a geometrical factor) (Munz and Fett, 1999).

$$\int_0^{t_f} \sigma(t)^n dt = B \sigma_c^{n-2} \left[1 - \left(\frac{\sigma_f}{\sigma_c} \right)^{n-2} \right] \quad (2)$$

B is related to the factor A in Eq. (1) by:

$$B = \frac{2}{AY^2(n-2)} K_{Ic}^{2-n} \quad (3)$$

t_f is time of fracture, (i.e., the time required for a flaw to grow from an initial length to the critical length for catastrophic crack propagation), σ_f is the fracture strength and σ_c is the inert strength (i.e., the strength in the absence of SCCG in an inert environment). Generally, $\sigma^{n-2} \ll \sigma_c^{n-2}$, and Eq. (2) can be simplified as follows:

$$\int_0^{t_f} \sigma(t)^n dt = B \sigma_c^{n-2} \quad (4)$$

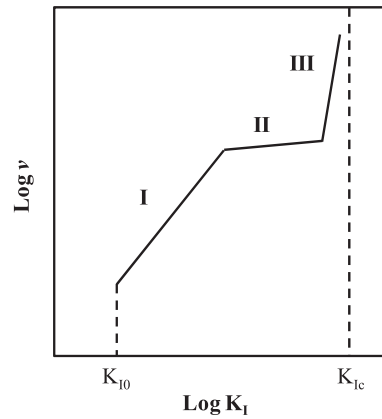


Fig. 1 Schematic of typical ν - K_I curve for glasses and ceramics. K_{I0} is the threshold of crack growth and K_{Ic} the fracture toughness.

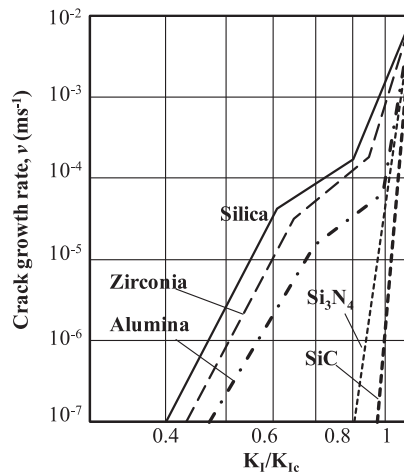


Fig. 2 Sensitivity to SCCG for different materials. From Chevalier, J., Fantozzi, G., 2005. Slow crack propagation in ceramics at the nano- and micro-scale: Effect of microstructure. In: Bradt, R.C., Munz, D., Sakai, M., White, K.W. (Eds.), *Fracture Mechanics of Ceramics*, vol. 14. New York: Springer, pp. 173–190.

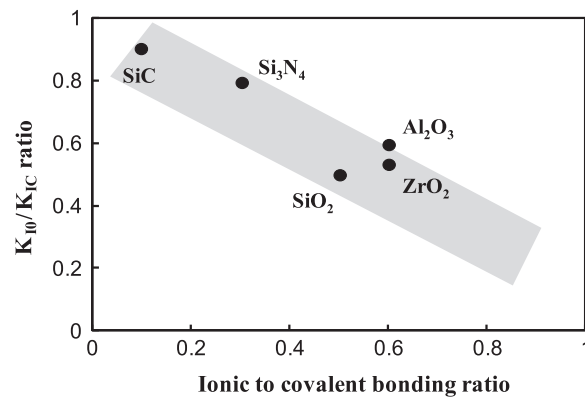


Fig. 3 Effect of the ionic fraction of the bond on the sensitivity to SCCG. From Chevalier, J., Deville, S., Fantozzi, G., *et al.*, 2005. Nanostructured ceramic oxides with a slow crack growth resistance close to covalent materials. *Nanoletters* 7, 1297–1301.

Under static loading (i.e., σ (t) constant), it becomes:

$$t_f = B\sigma_c^{n-2} \sigma^{-n} \left[1 - \left(\frac{\sigma}{\sigma_c} \right)^{n-2} \right] \quad (5)$$

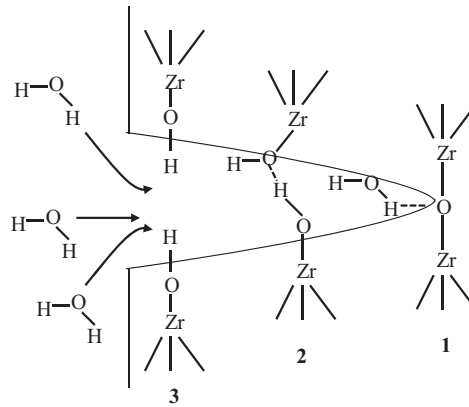


Fig. 4 Schematic representation of the reaction between water and Zr-O-Zr bonds at the crack tip. From De Aza, A.H., Chevalier, J., Fantozzi, G., Schehl, M., Torrecillas, R., 2002. Crack growth resistance of alumina, zirconia and zirconia toughened alumina ceramics for joint prostheses. *Biomaterials*, 23, 937–945.

Due to the high exponent n for glass and ceramic materials, the static lifetimes depend strongly on the applied stress. For long times, (5) can be simplified to:

$$t_f = B\sigma_c^{n-2} \sigma^{-n} \quad (6)$$

Direct Methods to Determine SCCG Parameters

Subcritical crack growth data can be obtained by direct methods, where crack velocity of macrocracks in the order of several mm is measured as a function of the stress intensity factor. The most common are double torsion (DT) (Evans, 1972; Williams and Evans, 1973; Fuller, 1979; Tait *et al.*, 1987), and double cantilever beam (DCB) (Freiman *et al.*, 1973; Champomier, 1979; Wiederhorn, 1974) as they allow stable crack growth which facilitates data acquisition.

Double Torsion Method

Specimen and loading configuration

The double torsion specimen consists of a plate containing a macrocrack, loaded symmetrically in bending to produce torsional deformation in the two plate halves (Fig. 5). An initial sharp crack is generally introduced by loading the specimen at a slow displacement rate. Sometimes, a groove is introduced along the length of the test specimen in order to control the crack path. However, it is not recommended as it leads to complicated stress field, the effects of which are not well understood. Crack path can be controlled without groove if the test specimen and the fixture are carefully aligned (Chevalier *et al.*, 1996).

Stress intensity factor

The determination of K_I is based on a compliance analysis considering that the deflection under the load-point, u , is caused by the elastic torsion of the two identical rectangular bars fixed at the crack-tip (Williams and Evans, 1973; Outwater *et al.*, 1974). Experimentally, it has been found for several materials that the compliance, C , defined as the ratio of load point displacement, u , to the applied load, P , varies linearly with the crack length a :

$$C = \frac{u}{P} = \alpha a + \beta \quad (7)$$

α and β are constants depending on the material properties.

For an applied load, P , the energy release rate, G , which represents the driving force for failure, is given by the following expression:

$$G = \frac{P^2}{2t} \left(\frac{dC}{da} \right) \quad (8)$$

where da is the increment of crack extension and t the thickness of the specimen.

Following Eq. (7), it becomes:

$$G = \frac{\alpha P^2}{2t} \quad (9)$$

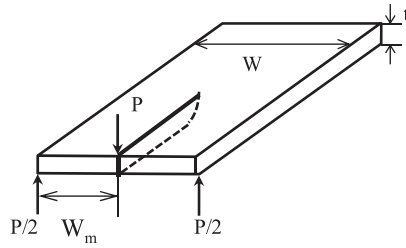


Fig. 5 Representation of the double torsion (DT) specimen.

For plane stress, the stress intensity factor K_I can be determined from:

$$K_I = \sqrt{2\mu(1+\nu)G} \quad (10)$$

where ν is the Poisson's ratio, and μ the elastic shear modulus.

Theoretical analysis of the compliance of the DT specimen (Williams and Evans, 1973) allows determination of α and finally the stress intensity factor as a linear function of load:

$$K_I = HP \quad (11)$$

with

$$H = \frac{W_m}{t^2} \left(\frac{3(1+\nu)}{W\Psi} \right)^{1/2} \quad (12)$$

where W and W_m are the width of the specimen and the moment arm respectively (Fig. 5), and $\psi(t/W)$ is a calibrating factor.

In the case of grooved DT specimens, the effective thickness, taking into account the groove depth, must be considered in the expression of K_I (Munz and Fett, 1999). It is to note that in this analysis, the stress intensity factor is independent of the crack length, which makes the DT testing very attractive. However it was found that the stress intensity factor could be a function of the crack length (Pletka and Wiederhorn, 1982; Chevalier *et al.*, 1996) and corrected expressions have been proposed to take into account this variation (Chevalier *et al.*, 1996; Ciccotti *et al.*, 2000; Shyam and Lara-Curzio, 2006; Becker *et al.*, 2011). This was particularly the case for alumina and zirconia materials for which the following corrected expression have been proposed (Chevalier *et al.*, 1996):

$$K_{I\text{cor}} = K_I(a/a_0)^{m/n} \quad (13)$$

where K_I is given by Eq. (11), a_0 is the notch length, $m = 6$ and $k = 32$ are constants for the test specimen geometry and the materials considered.

Crack growth rate

The crack growth rate during the double torsion test can be determined using three different methods: the constant loading test (Mckinney and Smith, 1973), the load relaxation and the constant displacement rate methods (Evans, 1972).

Constant loading test

In the constant loading tests, the sample is subjected to static loads for different durations and the crack growth rates are directly calculated as the ratio of the measured crack increment to loading time. This method allows to measure low velocities by applying the load over a long period of time.

Load relaxation test

In the relaxation test (Williams and Evans, 1973), the specimen is quickly loaded to just below the expected fracture load P_c (typically 90%–95% P_c), then the displacement of the loading point is kept constant during the experiment. The crack growth rate ($v = da/dt$) is determined assigning the load relaxation to the crack propagation. The time derivative of Eq. (7) leads to:

$$\frac{du}{dt} = (\alpha a + \beta) \frac{dP}{dt} + P\alpha \frac{da}{dt} \quad (14)$$

Introducing the load at the beginning or its final value at the end of the test and their associated crack lengths, it comes (u being constant in Eq. (7)):

$$P(\alpha a + \beta) = P_{i,f}(\alpha a_{i,f} + \beta) \quad (15)$$

where subscripts i and f denote reference measurements taken at the beginning or at the end of the test.

Considering Eq. (14), the crack growth rate can be determined from the instantaneous load, the corresponding load relaxation rate, and the initial or the final values of the load and the crack length as:

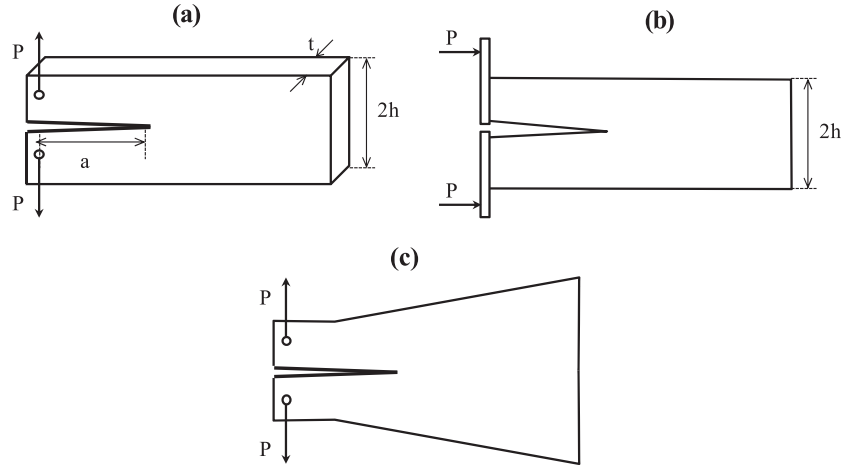


Fig. 6 Double-cantilever beam (DCB): (a) specimen with constant load, (b) specimen with constant moment, (c) modified tapered DCB specimen.

$$v(t) = \frac{da}{dt} = -\phi \frac{P_{i,f}}{P^2(t)} \left(a_{i,f} + \frac{\beta}{\alpha} \right) \left(\frac{dP}{dt} \right) \quad (16)$$

In practice, the constants α and β are obtained from a compliance calibration curve.

$\phi = t(da^2 + t^2)^{1/2}$ is a correction factor (Evans, 1972) to take into account the inclination of the crack front generally observed in DT specimens (Fig. 5).

Constant displacement rate method

In this method, the specimen is loaded at a constant displacement rate $\dot{u} = du/dt$. A steady state value of the load P (i.e., $dP/dt = 0$) is reached after a transient regime, which allows to calculate the crack growth from Eq. (14):

$$v = \frac{da}{dt} = \frac{\dot{u}}{P\alpha} \quad (17)$$

The whole v - K_I curve can be determined by performing tests at different values of the displacement rate, $\dot{u}$.

The principle advantage of the DT method is that the whole v - K_I curve can be obtained with a single specimen. Moreover, the possibility of indirect determination of the crack growth is practical for the investigation of the effects of temperature or environment on the v - K_I curve.

In practice, it is recommended to combine the relaxation method suitable for high crack growth rates ($> 10^{-7} \text{ m s}^{-1}$) with one of the two other techniques.

Double Cantilever Beam Method

A standard double cantilever beam (DCB) specimen (Fig. 6(a)) consists of a rectangular bar with a slit, loaded by applying symmetrical opening tensile loads at the ends of the beam. This enables the tensile opening mode (Mode I).

To obtain SCCG parameters, the specimen is subjected to different static loads and the crack extensions are directly measured to obtain the crack growth rates. The stress intensity factor is determined on the basis of analytically corrected compliances and measured crack lengths (Freiman *et al.*, 1973):

$$K_I = \frac{\sqrt{12aP}}{(1-v^2)^{1/2} t h^{3/2}} \left[\left(1 + \frac{\delta}{a} \right)^2 + \frac{1+v}{3} \left(\frac{h}{a} \right)^2 \right]^{1/2} \quad (18)$$

where P is the applied load, h is half the height of the specimen, t its thickness, δ is a characteristic length of the beam ($\delta \approx h/3$) and v is Poisson's ratio.

When grooved DCB specimens are used, t must be replaced by the effective thickness, corresponding to the width of the crack to account for the groove effect.

Modified specimens are also used to obtain a stress intensity factor independent on the crack length (Freiman *et al.*, 1973; Sakai and Bradt, 1993). This can be achieved by applying a constant moment rather than a constant load (Fig. 6(b)) or by using a tapered DCB specimen (Fig. 6(c)).

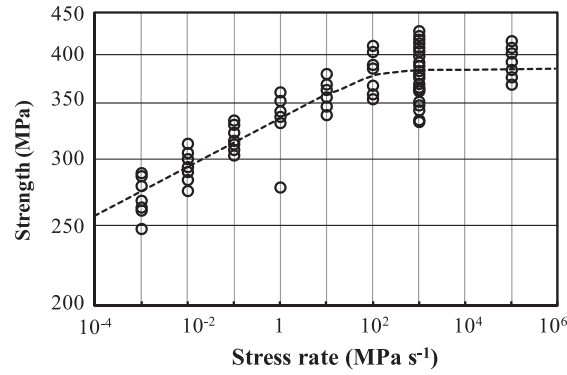


Fig. 7 Logarithmic plot of the strength versus the crack growth rate for a commercial Alumina. The dashed line corresponds to Eq. (19). From Lube, T., Baierl, R.G.A., 2011. Sub-critical crack growth in alumina – A comparison of different measurement and evaluation methods. *Berg Huettenmaenn Monatsh* 156, 450–456.

Indirect Methods to Determine SCCG Parameters

The crack propagation parameters can also be determined using indirect methods, based on the degradation of strength associated to SCCG (Evans, 1974; Wiederhorn, 1974; Ritter, 1978). These include constant stress (static test) and constant stress-rate (dynamic test) method. These methods present the advantage of being easy to conduct on specimens of very simple shape and do not require the measurement of a crack velocity or a crack length.

Dynamic Tests

In dynamic tests (ASTM C1368, 2006), specimens are loaded, generally in bending configuration under a constant stress rate, $\dot{\sigma}$, until fracture. Integration of Eq. (2) by introducing $d\sigma(t) = \dot{\sigma} t$, gives the following relation between the strength, σ_f , and the loading rate:

$$\sigma_f^{n+1} = B\sigma_c^{n-2} \dot{\sigma} (n+1) \left[1 - \left(\frac{\sigma_f}{\sigma_c} \right)^{n-2} \right] \quad (19)$$

For very high loading rates, σ_f tends towards the inert strength, σ_c , whereas for low loading rates, it follows asymptotically:

$$\sigma_f^{n+1} = B\sigma_c^{n-2} \dot{\sigma} (n+1) \quad (20)$$

The SCCG parameter, n , can be simply determined from the slope $(1/n+1)$ of the $\log(\sigma_f) - \log(\dot{\sigma})$ plot, determined within the validity range of Eq. (20). An example of such plot is displayed for a commercial Alumina (Lube and Baierl, 2011) in Fig. 7, where it can be seen that the effect of the stress rate is important at low stress rates while at very high values, the effect is negligible. The dashed line correspond to Eq. (19) with values of n and B respectively of 33.2 and $16705 \text{ (MPa)}^2 \text{ s}$.

The dynamic test is of short duration and it is easy to conduct with specimens containing natural flaws, similar to those present in structural parts. However, it requires a significant number of specimens and it only gives an average value of the different stages. Even in the case of a single stage, the presence of a threshold value or a too high loading rate could lead to erroneous results (Sudreau *et al.*, 1994).

Static Tests

Standard Procedure

In standard static tests, the specimen are tested under different constant applied loads and the results in terms of time to failure are plotted on a $\log(t_f)$ versus $\log(\sigma)$ diagram and analyzed using the common simplified formula (Eq. (6)) in its logarithmic form (Evans, 1974; Ritter, 1978):

$$\log(t_f) = -n \log(\sigma) + \log(B\sigma_c^{n-2}) \quad (21)$$

A linear regression analysis of this plot, allows to determine n (from the slope $-n$), then B (from the intercept).

Static tests allow measurements down to extremely low velocities as life times are much more influenced by the low crack growth rates than strengths used in dynamic tests. However, owing to the dispersion of the results, a lot of specimens are generally required for a fine analysis and accordingly, the procedure is of long duration.

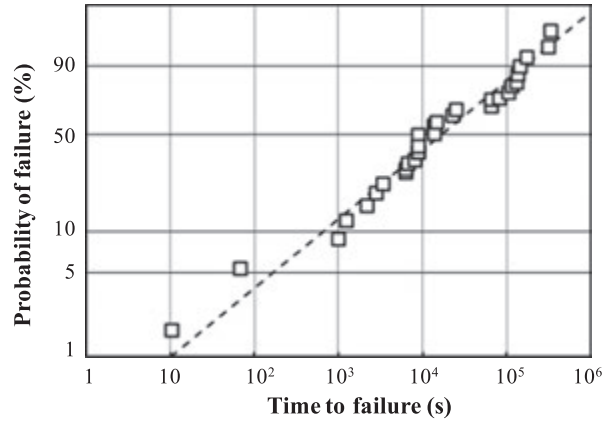


Fig. 8 Lifetimes distribution under static loading ($\sigma = 270$ MPa), determined for a commercial alumina. From Lube, T., Baierl, R.G.A., 2011. Sub-critical crack growth in alumina – A comparison of different measurement and evaluation methods. *Berg Huettenmaenn Monatsh* 156, 450–456.

Statistical Analysis

Ceramic materials, characterized by small values of Weibull modulus, show a large variability in inert strength (σ_c) and the time to failure (t_f), related to the scatter of the initial flaw sizes. A statistical analysis of the data is thus required for correct evaluation of SCCG parameters (Ritter, 1978; Jakus *et al.*, 1978; Peterlik, 1994; Pfingsten and Glien, 2006). Using the two parameter Weibull analysis (Weibull, 1951), the probability of failure for a given strength or time to failure (which are at equal failure probabilities) is obtained by expressing the inert strength in terms of its failure probability distribution:

$$P = 1 - \exp \left[- \left(\frac{\sigma_c}{\sigma_0} \right)^m \right] \quad (22)$$

where m and σ_0 are the Weibull parameters (respectively the Weibull modulus and the characteristic strength). From Eq. (22) we obtain:

$$\ln \ln \frac{1}{1-P} = m \ln \left(\frac{\sigma_c}{\sigma_0} \right) = m \ln \sigma_c - m \ln \sigma_0 \quad (23)$$

m is given by the slop of a regression line of the plot of this relation.

By using Eq. (6), Eq. (22) can be rewritten as:

$$P = 1 - \exp \left[- \left(\frac{t_f}{t_0} \right)^{m^*} \right] \quad (24)$$

with

$$m^* = \frac{m}{n-2} \quad (25)$$

and

$$t_0 = B \sigma_c^{n-2} \sigma^{-n} \quad (26)$$

m^* is obtained from the slop of linear regression of the logarithmic plot of Eq. (24):

$$\ln \ln \frac{1}{1-P} = m^* \ln t_f + m^* \ln \left(\frac{\sigma^n}{B} \right) - m \ln \sigma_0 \quad (27)$$

then the SCCG exponent, n , is deduced from Eq. (25).

Fig. 8 shows an example of life times distribution determined for a commercial alumina for which, it was found that $m^* = 0.554$ and $n = 32.7$, which is very close to that obtained by the dynamic tests (Lube and Baierl, 2011).

General comments

In the procedures and examples described above, a shape of the ν - K_I curve is presupposed (Eq. (1)) and the tests are performed with samples containing natural flaws. Fett and Munz (1985) have proposed a modified analysis which presents the main advantage of not requiring any prerequisite on the sub-critical crack law. Static tests can also be performed with indentation cracks for which the initial sizes can be measured (Gupta and Jubb, 1981; Fett *et al.*, 1988). Indentation controlled surface cracks allow the determination of the SCCG parameters with a single applied load and a limited number of specimens (Olagnon *et al.*, 1994). They also can be used to evaluate the slow-crack-growth behavior at elevated temperature (Mendiratta and Petrovic, 1978) or to

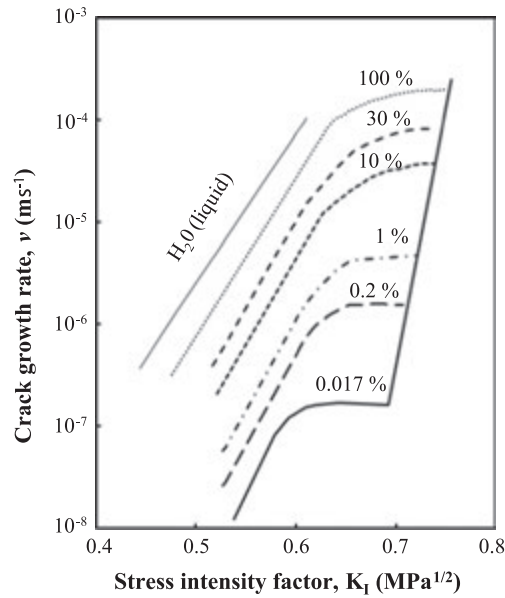


Fig. 9 Effect of humidity on SCCG in a soda-lime glass. From Wiederhorn, S.M., 1974. Subcritical crack growth in ceramics. In: Bradt, R.C., Hasselman, D.P.H., Lange, F.F. (Eds.), *Fracture Mechanics of Ceramics*. New York: Plenum, pp. 613–646.

determine the threshold stress intensity factor on the basis of the decay of the residual indentation stresses over time (Marx *et al.*, 2004; Garmendia *et al.*, 2011).

Instead of the commonly used bending tests on rectangular bars, the SCCG parameters are increasingly determined using biaxial flexural tests (Krohn *et al.*, 2002; Gonzaga *et al.*, 2011; Bermejo *et al.*, 2013; Bakken *et al.*, 2018) due to their easy use. For example, the ball-on-three-balls test is detailed in (Bermejo, 2020), where a methodology is presented to model the crack growth rate law of brittle materials in various environments.

Typical ν - K_I Curves for Glasses

SCCG behavior of glasses depends on many parameters, the more important of which are composition, environment and temperature (Gy, 2003; Jones, 2008; Ciccotti, 2009). The dependence of these parameters can generally be fitted by the expression (Wiederhorn, 1967):

$$\nu = D \left(\frac{p}{p_0} \right)^{n'} \exp \left(- \frac{\Delta E_a - b K_I}{RT} \right) \quad (28)$$

where p is the partial pressure of the vapor phase in the atmosphere, p_0 is the total atmospheric pressure and R the gas constant; D , n' , ΔE_a and b are adjustable parameters corresponding to the dependence on the glass composition.

The value of the n exponent (Eq. (1)) varies within a wide range, for example between 12 and 50 for silicate glasses (Evans and Wiederhorn, 1974). Fig. 9 illustrates the effect of humidity on SCCG in a soda-lime glass for which the three stages of propagation were observed. Increasing the amount of water in the environment shifts region I towards lower K_I values, without changing the slope n , and region II towards higher crack growth rates.

Fig. 10 shows examples of ν - K_I curves obtained by the DCB method for glasses with different compositions (Wiederhorn and Bolz, 1970). For soda-lime silicate and borosilicate glasses, deviation from Eq. (1) was observed with threshold values respectively of 0.26 MPam^{1/2} and 0.34 MPam^{1/2}. The last value is similar to that obtained from lifetime measurements by Fett *et al.* (1991). The threshold was observed in other glasses for which it was shown that the position of the threshold depends strongly on the pH (Simmons and Freiman, 1981; Gehrke *et al.*, 1991). It was suggested that the effect of the composition on SCCG in glasses have their origin in the nature of the chemical bonding of these materials and the ability of these bonds to resist separation by mechanical and chemical forces (Wiederhorn, 1991). Moreover, Michalske and Bunker (Michalske and Bunker, 1987) proposed that the molecule size affects crack tip reactivity and thus the SCCG behavior of glasses.

The effect of temperature on the ν - K_I curve is shown in Fig. 11 for a soda-lime glass tested in water in which only the stage I was observed (Wiederhorn and Bolz, 1970). Increasing the temperature increases the crack growth rate at a fixed stress intensity factor, as a consequence of the thermal activation of the stress corrosion process having an exponential dependence with the inverse temperature, $1/T$ (Eq. (28)). Such behavior was also observed in a phosphate glass for which the three regions of stress corrosion were observed at ambient temperature (Crichton *et al.*, 1999).

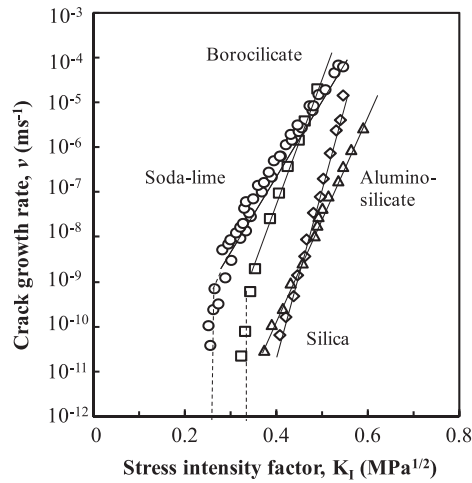


Fig. 10 Effect of the composition on v - K_I curves of glass. From Wiederhorn, S.M., Bolz, L.H., 1970. Stress corrosion and static fatigue of glass. *Journal of the American Ceramic Society* 53, 543–548.

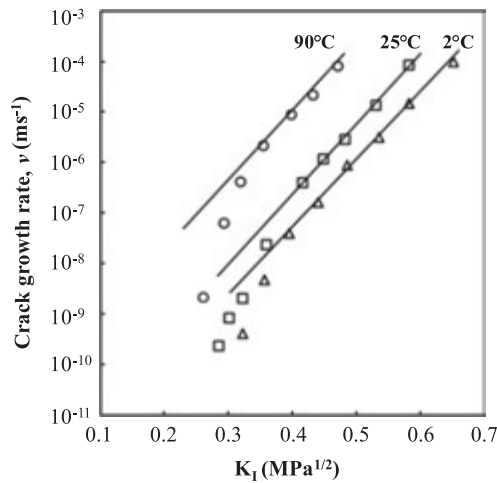


Fig. 11 Effect of temperature on the v - K_I curve for a soda-lime glass tested in water. From Wiederhorn, S.M., Bolz, L.H., 1970. Stress corrosion and static fatigue of glass. *Journal of the American Ceramic Society* 53, 543–548.

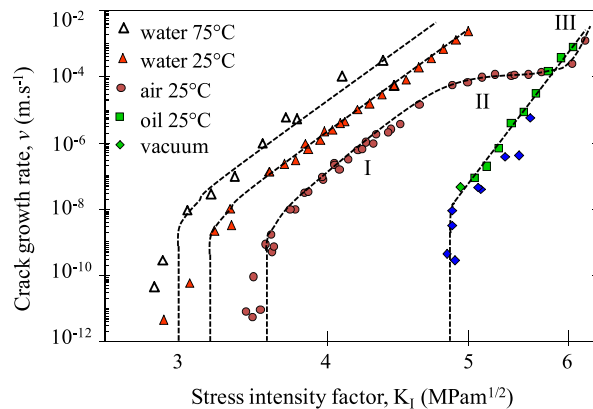


Fig. 12 v - K_I curves of YTZP zirconia determined with DT specimens in different media, both with the constant-stress and the load relaxation methods. From Chevalier, J., Fantozzi, G., 2005. Slow crack propagation in ceramics at the nano- and micro-scale: Effect of microstructure. In: Bradt, R.C., Munz, D., Sakai, M., White, K.W. (Eds.), *Fracture Mechanics of Ceramics*, vol. 14. New York: Springer, pp. 173–190.

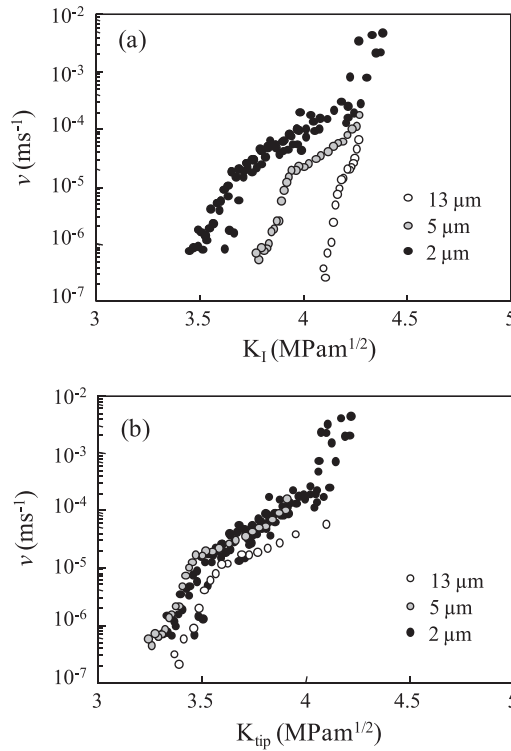


Fig. 13 v - K_I curves for alumina with different grain sizes obtained by the DT method (a) and corresponding intrinsic v - K_{tip} curve (b). From Chevalier, J., Fantozzi, G., 2005. Slow crack propagation in ceramics at the nano- and micro-scale: Effect of microstructure. In: Bradt, R.C., Munz, D., Sakai, M., White, K.W. (Eds.), *Fracture Mechanics of Ceramics*, vol. 14. New York: Springer, pp. 173–190.

Characterization and understanding of SCCG of glasses is crucial not only for their applications in bulk form, but also because they are often present at the grain boundaries of polycrystalline ceramics. Their sensitivity to stress-induced corrosion directly affects the subcritical crack-growth behavior of these materials as it was shown for alumina (Barinov *et al.*, 1998; Ramalingam *et al.*, 2011; Bakken *et al.*, 2018) and silicon nitride (Bhatnagar *et al.*, 2000; Jacobs and Chen, 1994).

Typical v - K_I Curves for Polycrystalline Ceramics

Effect of Environment and Temperature

Examples of v - K_I curves with typical pattern of SCCG due to stress corrosion are shown for different environments and temperatures in Fig. 12 for a polycrystalline YTZP zirconia doped with 3 mol% of Y_2O_3 (Chevalier and Fantozzi, 2005). The results show the presence of a threshold under vacuum, water and air conditions, below which no propagation occurs. In water, only the stage I appears and under vacuum or silicon oil where no water molecules are present, only the stage III occurs for a stress intensity factor near K_{IC} . Due to the thermal activation of SCCG (Eq. (28)), increasing the temperature shifts region I towards higher K_I values as for glasses.

Carbides and nitrides, characterized by a low fraction ionic bonding, are relatively insensitive to SCCG at ambient. However, it was shown that they exhibit slow crack propagation at high temperatures (Evans and Lange, 1975; Choi *et al.*, 1998; Lube and Dusza, 2007).

Microstructural Effects

For polycrystalline ceramics, the microstructure plays a major role which requires a careful interpretation on the v - K_I curves obtained experimentally, particularly for reinforced materials for which the crack growth resistance increases with crack growth (R-curve effect). In this case, the crack growth curve is progressively shifted to lower velocities as crack resistance increases. Depending on the crack length measurement with respect to the rising part of the R-curve, either a complete shift or a higher slope can be obtained (Chevalier and Fantozzi, 2005). The most important toughening mechanisms in ceramics are grain bridging and transformation toughening, which act as crack-shielding mechanisms due to closure tractions in the wake of a propagating crack (Knehan *et al.*, 1983; Heuer, 1987; Evans, 1990; Fantozzi and Saâdaoui, 2014). Due to the crack shielding associated with the reinforcement, the effective crack tip stress intensity factor, K_{tip} , corresponding to the driving force for crack growth may be expressed as follow:

$$K_{tip} = K_I - K_{sh} \quad (29)$$

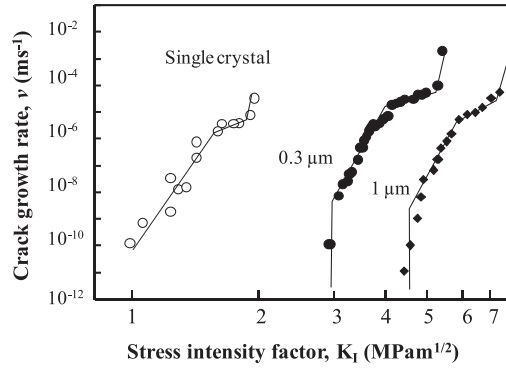


Fig. 14 v - K_I curves of polycrystalline YTZP zirconia ceramics with too different grain sizes (0.3 and 1 μm), compared to that of a zirconia single crystal for which no transformation toughening occurs. From Chevalier, J., Fantozzi, G., 2005. Slow crack propagation in ceramics at the nano- and micro-scale: Effect of microstructure. In: Bradt, R.C., Munz, D., Sakai, M., White, K.W. (Eds.), *Fracture Mechanics Of Ceramics*, vol. 14. New York: Springer, pp. 173–190.

where K_I is the applied stress intensity factor and K_{sh} is the shielding contribution due to the microstructure.

Influence of grain bridging

Grain bridging, occurs in monolithic ceramics, such as alumina (Marshall *et al.*, 1983; Steinbrech *et al.*, 1990; Swanson *et al.*, 1987) and silicon nitride (Li *et al.*, 1992). It arises from elastic and interfacial frictional stresses that act to reduce the crack opening. Its magnitude is controlled by microstructural parameters such as grain size and morphology (aspect ratio). Increasing the shielding effect of bridging during crack propagation, enhances the threshold of crack propagation and the apparent stress intensity factor, K_I (Eq. (29)) during sub-critical crack growth (Ebrahimi *et al.*, 2000; El Attaoui *et al.*, 2005). An example of such effect is illustrated in Fig. 13(a) for alumina with v - K_I curves obtained by the relaxation method under DT loading. The higher the grain size, the higher the slope of stage I and the apparent threshold value K_{I0} , defined as the minimum applied stress intensity factor that leads to measurable crack propagation. This is related to the increase of the shielding effect of grain bridging with the grain size (Chantikul *et al.*, 1990; Kovar *et al.*, 2000). This also explains the convergence of the v - K_I curves at high crack growth rate corresponding to the beginning of the relaxation test from small crack lengths, for which bridging interactions are not yet fully developed.

Crack shielding is an extrinsic mechanism that occurs at the crack wake. Considering the stress intensity factor at the crack tip by the subtraction of the shielding effect (Eq. (29)) leads to an intrinsic v - $K_{I_{tip}}$ curve independent of the grain size and only dependent of the chemical bonds broken at the crack tip (Fig. 13(b)).

It is to not that extrinsic mechanism could not be totally effective for real short cracks. For example, Munz and Fett (1999) showed that a crack velocity decrease could be observed at the beginning of the propagation of small cracks in alumina.

Effect of phase transformation toughening

Transformation toughening which may occur in zirconia based ceramics is due to a stress-induced martensitic transformation of tetragonal zirconia grains or particles to the monoclinic phase ahead of a propagating crack. During crack propagation, the volume increase ($\sim 5\%$) accompanying the transformation, creates compressive stresses that shield the crack tip from the applied stress (Marshall *et al.*, 1983; Hannink *et al.*, 2000). The shielding stress intensity factor is proportional to the applied one (McMeeking and Evans, 1982):

$$K_{sh} = C_{sh} \cdot K_I \quad (30)$$

where C_{sh} is a parameter which increases with the material transformability.

If we assume that the intrinsic mechanism of SCCG is given by:

$$v = A_0 K_{I_{tip}}^n \quad (31)$$

then, the experimentally determined v - K_I law in the presence of transformable zirconia particles is:

$$v = A_0 (1 - C_{sh})^n K_I^n = A K_I^n \quad (32)$$

This means that the effect of transformation toughening on slow crack growth is to shift the v - K_I curve towards high stress intensity factors, preserving the value of the n exponent. This is illustrated in Fig. 14 showing v - K_I curves of polycrystalline YTZP zirconia ceramics with different grain sizes, compared to that of a zirconia single crystal for which crack shielding does not occur. Increasing the grain size leads to a shift of the SCCG curve towards higher stress intensity factors, expressing an increase of crack resistance due to higher transformability. At the same time, the curves run parallel, with a slope corresponding to intrinsic zirconia n exponent (Chevalier and Fantozzi, 2005).

Zirconia-toughened alumina (ZTA) composites show improvement in SCCG resistance, compared to a fine grain alumina or zirconia. This is illustrated in Fig. 15 showing v - K_I curves of two ZTA composites corresponding to different reinforcement

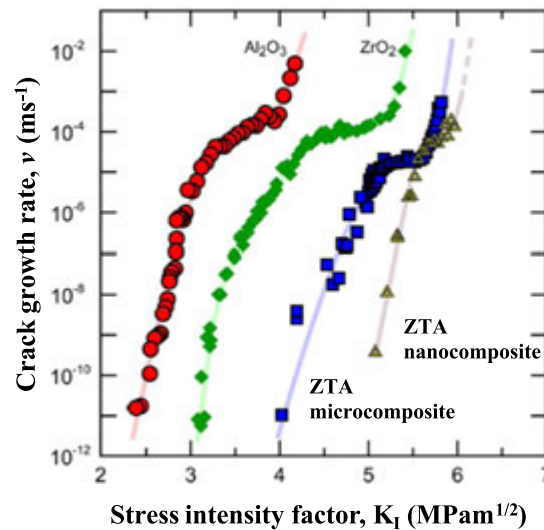


Fig. 15 Comparison of ν - K_I curves for fine grain alumina and zirconia, a microcomposite ZTA and a nanocomposite ZTA. From Chevalier, J., Taddei, P., Gremillard, L., *et al.*, 2011. Reliability assessment in advanced nanocomposite materials for orthopaedic applications. *Journal of the Mechanical Behavior of Biomedical Materials* 4, 303–314.

strategies (Chevalier *et al.*, 2005; De Aza *et al.*, 2003): a micro-composite containing 10 vol% of zirconia with an optimized particles size (100–600 nm) and a nanocomposite containing a small amount (1.7 vol%) of zirconia nanoparticles (< 100 nm). The micro-composite offers two main advantages. Primarily, crack propagation occurs through the alumina matrix which has a lower susceptibility to stress assisted corrosion than zirconia. Second, transformation toughening by zirconia particles shifts the ν - K_I curve towards higher K_I values while preserving the slope of the alumina curve. For the nanocomposite, no transformation toughening occurs, since the particles are too small to transform even at the crack tip. For this material, both the toughness and the threshold are significantly increased. This is attributed to a compressive residual stress field in the alumina matrix, which retards the crack front opening when an external stress is applied. The relative effect of the residual stress intensity factor is higher for lower applied stress intensity factors. Thus, the ν - K_I curve of the nanocomposite exhibits a high slope, close to that of covalent ceramics, (Chevalier *et al.*, 2005), implying a lower sensitivity to delayed failure. It is to note that unlike extrinsic mechanism (as grain bridging or transformation toughening operating at the crack wake), the intrinsic reinforcement by compressive residual stresses operating on a scale smaller than the one of the matrix microstructure, can be applied to real cracks under any loading condition.

Concluding Remarks

In this chapter, the basic relations governing the subcritical crack growth and experimental methods to evaluate this phenomenon in glasses and ceramic materials have been presented. This review is not exhaustive as it is only focused on the most important case of mode I loading, considering a power law relationship between the crack growth rate, ν , and the stress intensity factor, K_I . It has been shown that SCCG parameters, the knowledge of which is crucial for life time prediction for components under loading, can be determined from either crack growth data (direct methods) or from strength data (indirect methods). Both types of methods have proper advantages and drawbacks, and attention should be paid to the interpretation of their experimental results, particularly in the case of polycrystalline ceramics. For these materials, SCCG can be analyzed considering (1) the intrinsic response of the atomic bounds to stress assisted corrosion and (2) the influence of extrinsic microstructural effects which dependent on the amount of reinforcement. Examples of such microstructural effects are given in the case of crack bridging and transformation toughening, but other mechanisms such as micro-cracking and residual stresses may also occur and influence the ν - K_I curves.

References

- Anglada, M., 2017. Assessment of mechanical properties of ceramic materials. In: Palmero, P., De Barra, E., Cambier, F. (Eds.), *Advances in Ceramic Biomaterials: Materials, Devices and Challenges*. Duxford: Woodhead Publishing, pp. 83–109.
- ASTM C1368, 2006. Standard Test Method for Determination of Slow Crack Growth Parameters of Advanced Ceramics by Constant Stress-Rate Flexural Testing at Ambient Temperature. West Conshohocken: American Society for Testing Materials.
- Bakken, A., Wagner, S., Hoffmann, M.J., *et al.*, 2018. Biaxial strength and slow crack growth in porous alumina with silica sintering aid. *Journal of the European Ceramic Society* 38, 665–670.
- Barinov, S.M., Ivanov, N.V., Orlov, S.V., Shevchenko, V.J., 1998. Dynamic fatigue of alumina ceramics in water-containing environment. *Ceramics International* 24, 421–425.
- Becker, T.H., Marrow, T.J., Tait, R.B., 2011. An evaluation of the double torsion technique. *Experimental Mechanics* 51, 1511–1526.

- Bermejo, R., Supancic, P., Krautgasser, C., Morrell, R., Danzer, R., 2013. Subcritical crack growth in low temperature co-fired ceramics under biaxial loading. *Engineering Fracture Mechanics* 100, 108–121.
- Bermejo, R., 2020. Subcritical Crackgrowth: Modelling of the v-K Curve in Different Environments. Chapter 12119 in *Encyclopedia of Materials: Technical Ceramics and Glasses*, Elsevier.
- Bhatnagar, A., Hoffman, M.J., Dauskardt, R.H., 2000. Fracture and subcritical crack-growth behavior of Y-Si-Al-O-N glasses and Si_3N_4 ceramics. *Journal of the American Ceramic Society* 83, 585–596.
- Championier, F.P., 1979. Crack propagation measurements on glass: A comparison between double torsion and double cantilever beam specimens. In: Freiman, S.W. (Ed.), *Fracture Mechanics Applied to Brittle Materials*. ASTM STP 678. Philadelphia, PA: American Society for Testing and Materials, pp. 60–72.
- Chantikul, P., Bennison, S.J., Lawn, B.R., 1990. Role of grain size in the strength and R-curve properties of alumina. *Journal of the American Ceramic Society* 73, 2419–2427.
- Chevalier, J., Fantozzi, G., 2005. Slow crack propagation in ceramics at the nano- and micro-scale: Effect of microstructure. In: Bradt, R.C., Munz, D., Sakai, M., White, K.W. (Eds.), *Fracture Mechanics of Ceramics*, vol. 14. New York: Springer, pp. 173–190.
- Chevalier, J., Deville, S., Fantozzi, G., *et al.*, 2005. Nanostructured ceramic oxides with a slow crack growth resistance close to covalent materials. *Nanoletters* 7, 1297–1301.
- Chevalier, J., Saâdaoui, M., Olagnon, C., Fantozzi, G., 1996. Double torsion testing a 3Y-TZP ceramic. *Ceramics International* 22, 171–177.
- Choi, S.R., Salem, J.A., Nemeth, N.N., 1998. High-temperature slow crack growth of silicon carbide determined by constant-stress-rate and constant-stress testing. *Journal of Materials Science* 33, 1325–1332.
- Ciccotti, M., 2009. Stress-corrosion mechanisms in silicate glasses. *Journal of Physics D: Applied Physics* 42, 18. (214006).
- Ciccotti, M., Negri, N., Sassi, L., Gonzato, G., Mulargia, F., 2000. The double torsion loading configuration for fracture propagation: An improved methodology for the load relaxation at constant displacement. *International Journal of Rock Mechanics & Mining Sciences* 37, 1103–1113.
- Crichton, S.N., Tomozawa, M., Hayden, J.S., Suratwala, T.I., Campbell, J.H., 1999. Subcritical crack growth in a phosphate laser glass. *Journal of the American Ceramic Society* 82, 3097–3104.
- De Aza, A.H., Chevalier, J., Fantozzi, G., Schehl, M., Torrecillas, R., 2002. Crack growth resistance of alumina/zirconia and zirconia toughened alumina ceramics for joint prostheses. *Biomaterials* 23, 937–945.
- De Aza, A.H., Chevalier, J., Fantozzi, G., Schehl, M., Torrecillas, R., 2003. Slow crack growth behavior of zirconia-toughened alumina ceramics processed by different methods. *Journal of the American Ceramic Society* 86, 115–120.
- Ebrahimi, M.E., Chevalier, J., Fantozzi, G., 2000. Slow crack-growth behaviour of alumina ceramics. *Journal of Materials Research* 15, 142–147.
- El Attaoui, H., Saâdaoui, M., Chevalier, J., Fantozzi, G., 2005. Quantitative analysis of crack shielding degradation during cyclic fatigue of alumina. *Journal of the American Ceramic Society* 88, 172–178.
- Evans, A.G., 1972. A method for evaluating the time-dependent failure characteristics of brittle materials and its applications to polycrystalline alumina. *Journal of Materials Science* 7, 1137–1146.
- Evans, A.G., 1974. Slow crack growth in brittle materials under dynamic loading conditions. *International Journal of Fracture* 10, 251–259.
- Evans, A.G., 1990. Perspective on the development of high-toughness ceramics. *Journal of the American Ceramic Society* 73, 187–206.
- Evans, A.G., Wiederhorn, S.M., 1974. Proof testing of ceramic materials – An analytical basis for failure prediction. *International Journal of Fracture* 10, 379–392.
- Evans, A.G., Lange, F.F., 1975. Crack propagation and fracture in silicon carbide. *Journal of Materials Science* 10, 1659–1664.
- Fantozzi, G., Saâdaoui, M., 2014. Toughness, fatigue and thermal shock of ceramics: Microstructural effects. In: Sarin, V.K., Llanes, L., Mari, D. (Eds.), *Comprehensive Hard Materials* 1. Amsterdam: Elsevier, pp. 299–319.
- Fett, T., Munz, D., 1985. Determination of v-KI curves by a modified evaluation of lifetime measurements in static bending tests. *Journal of the American Ceramic Society* 68, C-213–C-215.
- Fett, T., Munz, D., Keller, K., 1988. Determination of subcritical crack growth on glass in water from lifetime measurements on Knoop-cracked specimens. *Journal of Materials Science* 23, 798–803.
- Fett, T., Germerdonk, K., Grossmoller, A., Keller, K., Munz, D., 1991. Subcritical crack growth and threshold in borosilicate glass. *Journal of Materials Science* 26, 253–257.
- Freiman, W., Mulville, D.R., Mast, P.W., 1973. Crack propagation studies in brittle materials. *Journal of Materials Science* 8, 1527–1533.
- Fuller, E.R., 1979. An evaluation of double-torsion testing-analysis. In: Freiman, S.W. (Ed.), *Fracture Mechanics Applied to Brittle Materials*. ASTM STP 678. Philadelphia, PA: American Society for Testing and Materials, pp. 3–18.
- Garmendia, N., Grandjean, S., Chevalier, J., *et al.*, 2011. Zirconia–multiwall carbon nanotubes dense nano-composites with an unusual balance between crack and ageing resistance. *Journal of the European Ceramic Society* 31, 1009–1014.
- Gehrke, E., Ullner, C., Hahnert, M., 1991. Fatigue limit and crack arrest in alkali-containing silicate glasses. *Journal of Materials Science* 26, 5445–5455.
- Gonzaga, C.C., Cesar, P.F., Miranda Jr., W.G., Yoshimura, H.N., 2011. Slow crack growth and reliability of dental ceramics. *Dent. Mater.* 2 (7), 394–406.
- Gupta, P.K., Jubb, N.J., 1981. Post-indentation slow growth of radial cracks in glasses. *Journal of the American Ceramic Society* 64, C-112–C-114.
- Gy, R., 2003. Stress corrosion of silicate glass: A review. *Journal of Non-Crystalline Solids* 316, 1–11.
- Hannink, R.H.J., Kelly, P.M., Muddle, B.C., 2000. Transformation toughening in zirconia-containing ceramics. *Journal of the American Ceramic Society* 83, 461–487.
- Heuer, A.H., 1987. Transformation toughening in ZrO_2 -containing ceramics. *Journal of the American Ceramic Society* 70, 689–698.
- Jacobs, D.S., Chen, I.W., 1994. Mechanical and environmental factors in the cyclic and static fatigue of silicon nitride. *Journal of the American Ceramic Society* 77, 1153–1161.
- Jakus, K., Coyne, D.C., Ritter, J.E., 1978. Analysis of fatigue data for lifetime predictions for ceramic materials. *Journal of Materials Science* 13, 2071–2080.
- Jones, H.R., 2008. Environment induced crack growth of ceramics and glasses. In: Shipilov, Jones, S.A.R.H., Olive, J.M., Rebak, R.B. (Eds.), *Environment-Induced Cracking of Materials: Chemistry, Mechanics and Mechanisms*. Amsterdam: Elsevier, pp. 449–466.
- Knehans, R., Steinbrech, R., Schaarwachter, W., 1983. Increase of crack resistance during slow crack growth in Al_2O_3 bend specimens. *Journal of Materials Science* 18, 265–270.
- Kovar, D., Bennison, S.J., Ready, M.J., 2000. Crack stability and strength variability in alumina ceramics with rising toughness-curve behavior. *Acta Materialia* 48, 565–578.
- Krohn, M.H., Hellmann, J.R., Shelleman, D.L., Pantano, C.G., Sakoske, G.E., 2002. Biaxial flexure strength and dynamic fatigue of soda–lime–silica float glass. *Journal of the American Ceramic Society* 85, 1777–1782.
- Lawn, B.R., 1975. An atomistic model of kinetic crack growth in brittle solids. *Journal of Materials Science* 10, 469–480.
- Li, C.W., Lee, D.J., Lui, S.C., 1992. R-curve behaviour and strength for in-situ reinforced silicon nitrides with different microstructures. *Journal of the American Ceramic Society* 75, 1777–1785.
- Lube, T., Duszka, J., 2007. A silicon nitride reference material – A testing program of ESIS TC6. *Journal of the European Ceramic Society* 27, 1203–1209.
- Lube, T., Baiert, R.G.A., 2011. Sub-critical crack growth in alumina – A comparison of different measurement and evaluation methods. *Berg Huettenmaenn Monatsh* 156, 450–456.
- Marshall, D.B., Evans, A.G., Drory, M., 1983. Transformation toughening in ceramics. In: Bradt, R.C., Evans, A.G., Hasselman, D.P.H., Lange, F.E. (Eds.), *Fracture Mechanics of Ceramic* 6. New York: Plenum Press, pp. 289–307.
- Marx, R., Jungwirth, F., Walter, P.O., 2004. Threshold intensity factors as lower boundaries for crack propagation in ceramics. *BioMedical Engineering OnLine* 3.41(9).
- McKinney, H.R., Smith, H.L., 1973. Method of studying subcritical cracking of opaque materials. *Journal of the American Ceramic Society* 5, 30–32.
- McMeeking, R.M., Evans, A.G., 1982. Mechanisms of transformation toughening in brittle materials. *Journal of the American Ceramic Society* 65, 242–246.
- Mendiratta, M.G., Petrovic, J.J., 1978. Slow crack growth from controlled surface flaws in hot-pressed Si_3N_4 . *Journal of the American Ceramic Society* 61, 226–230.

- Michalske, T.A., 1983. The stress corrosion limit: Its measurement and implications. In: Bradt, R.C., Evans, A.G., Hasselman, D.P.H., Lange, F.F. (Eds.), *Fracture Mechanics of Ceramics 5*. New York: Plenum Press, pp. 277–289.
- Michalske, T.A., Bunker, B.C., 1987. Steric effects in stress corrosion fracture of Glass. *Journal of the American Ceramic Society* 70, 780–784.
- Munz, D., Fett, T., 1999. *Ceramics: Mechanical Properties, Failure Behaviour, Materials Selection*. Berlin; Heidelberg: Springer.
- Olagnon, C., Chevalier, J., Sudreau, F., Fantozzi, G., 1994. A new approach for slow crack growth measurements. *Journal of the European Ceramic Society* 14, 327–335.
- Outwater, J., Murphy, M., Kumble, R., Berry, J., 1974. Double torsion technique as a universal fracture toughness test method. In: Paris, P., Irwin, G. (Eds.), *Fracture Toughness and Slow-Stable Cracking*. West Conshohocken, PA: ASTM International, pp. 127–138.
- Peterlik, H., 1994. Comparison of evaluation procedures for the subcritical crack growth parameter n . *Journal of the European Ceramic Society* 13, 509–519.
- Pfingsten, T., Glien, K., 2006. Statistical analysis of slow crack growth experiments. *Journal of the European Ceramic Society* 26, 3061–3065.
- Pletka, B.J., Wiederhorn, S.M., 1982. A comparison of failure predictions by strength and fracture mechanics techniques. *Journal of Materials Science* 17, 1247–1268.
- Ramalingam, S., Reimanis, I.V., Fuller, E.R., Haftel, J.D., 2011. Slow crack growth behavior of zirconia-toughened alumina and alumina using the dynamic fatigue indentation technique. *Journal of the American Ceramic Society* 94, 576–583.
- Ritter, J.E., 1978. Engineering design and fatigue failure of brittle materials. In: Bradt, R.C., Hasselman, D.P.H., Lange, F.F. (Eds.), *Fracture Mechanics of Ceramics*. New York and London: Plenum, pp. 667–686.
- Sakai, M., Bradt, R.C., 1993. Fracture toughness testing of brittle materials. *International Materials Reviews* 38, 53–78.
- Shyam, A., Lara-Curzio, E., 2006. The double-torsion testing technique for determination of fracture toughness and slow crack growth behavior of materials: A review. *Journal of Materials Science* 41, 4093–4104.
- Simmons, C.J., Freiman, S.W., 1981. Effect of corrosion processes on subcritical crack growth in glass. *Journal of the American Ceramic Society* 64, 683–686.
- Steinbrech, R.W., Reichl, A., Schaarwachter, W., 1990. R-Curve behaviour of long cracks in alumina. *Journal of the American Ceramic Society* 73, 2009–2015.
- Sudreau, F., Olagnon, C., Fantozzi, G., 1994. Lifetime prediction of ceramics: Importance of the test method. *Ceramics International* 20, 125–135.
- Swanson, P.L., Fairbanks, C.J., Lawn, B.R., Mai, Y.-W., Hockey, B.J., 1987. Crack-interface grain bridging as a fracture resistance mechanism in ceramics: I, experimental study on alumina. *Journal of the American Ceramic Society* 70, 279–289.
- Tait, R.B., Fry, P.R., Garrett, G.G., 1987. Review and evaluation of the double-torsion technique for fracture toughness and fatigue testing of brittle materials. *Experimental Mechanics* 27, 14–22.
- Weibull, W.A., 1951. A statistical distribution function of wide applicability. *Journal of Applied Mechanics* 18, 293–297.
- Wiederhorn, S.M., 1967. Influence of water vapour on crack propagation in soda-lime glass. *Journal of the American Ceramic Society* 50, 407–414.
- Wiederhorn, S.M., 1974. Subcritical crack growth in ceramics. In: Bradt, R.C., Hasselman, D.P.H., Lange, F.F. (Eds.), *Fracture Mechanics of Ceramics*. New York: Plenum, pp. 613–646.
- Wiederhorn, S.M., 1991. Subcritical crack growth. In: Brook, R.J. (Ed.), *Concise Encyclopedia of Advanced Ceramic Materials*. Oxford: Bergamon press, pp. 461–466.
- Wiederhorn, S.M., Bolz, L.H., 1970. Stress corrosion and static fatigue of glass. *Journal of the American Ceramic Society* 53, 543–548.
- Williams, D.P., Evans, A.G., 1973. A simple method for studying slow crack growth. *Journal of Testing and Evaluation* 1, 264–270.

Subcritical Crack Growth: Modeling of the v-K Curve in Different Environments

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Introduction

Many glasses and ceramic materials suffer for subcritical crack growth (SCCG), which enables the stable growth of cracks under an applied load. At ambient and moderate temperatures it is probably the most important damage mechanism for these materials (Gurney, 1947; Wiederhorn, 1967, 1974; Evans, 1974; Danzer, 1993; EN 843-3, 1996; Danzer *et al.*, 2008). It causes a reduction of strength with time under load and, as a consequence, a significant reduction in the load bearing capability of glass- and ceramic-based (brittle) components. SCCG has been recognized as an important limiting factor for their reliability and lifetime. SCCG is strongly promoted by environments with high moisture content (Wiederhorn, 1974) and by elevated temperatures. The basic aspects of this phenomenon are discussed in detail by Saadaoui (2020).

In terms of linear elastic fracture mechanics, cracks may propagate (with a certain velocity, v) for an applied stress intensity factor, $K_I = \sigma Y \sqrt{\pi a}$, lower than the fracture toughness of the material, K_{Ic} (Munz and Fett, 1999). σ is the tensile stress applied perpendicular to the crack plane, Y a geometric factor and a the size of the crack. For most ceramics and glasses, the crack growth rate, v , in the technically relevant velocity region (namely between 10^{-12} and 10^{-5} m s $^{-1}$), also defined as Region I (*reaction-rate controlled region*, see (Wiederhorn, 1974)) can be described by the empirical power-law relation (Wiederhorn, 1967; Evans, 1974):

$$v = \frac{da}{dt} = v_0 \cdot \left(\frac{K_I}{K_{Ic}} \right)^n \quad (1)$$

where t is the time, n is the SCCG exponent and v_0 is a material constant (i.e., critical crack growth velocity) for the particular testing conditions (e.g., environment, temperature). Depending on the crack growth rate and testing conditions different mechanisms of SCCG may take place, which are ascribed to different slopes in a double log plot of the v - K_I curve (Wiederhorn, 1967). Many different ideas on mechanisms for SCCG can be found in the literature, which range from thermally assisted breaking of bonds at the crack tip (Schoeck, 1990), stress enhanced corrosion (Wiederhorn, 1974), hydrolysis of silica bonds to diffusion of water within the crack or the development of a diffusion zone around the crack tip which causes a decrease of the fracture toughness (Wiederhorn *et al.*, 2011). In general the parameter n is used as an indicator for the mechanism but a clear understanding of the physical principles of SCCG is still lacking (Freiman *et al.*, 2009). Among the different models of crack growth, a direct chemical attack of the environment on the crack tip seems to have the strongest experimental support (Michalske and Freiman, 1983) – at least in silicate containing materials. Note that in the regime I very high values of the SCCG exponent n (e.g., around 30) are often reported in the literature (Munz and Fett, 1999). In regime III these values may even become much larger (around 200).

In order to obtain crack propagation data, and thus assess the susceptibility of a material to SCCG, both direct and indirect methods may be employed (Wiederhorn, 1974). With direct methods the crack velocity is measured as a function of the stress intensity factor by direct observation of the crack growth increment on fracture mechanics type specimens (e.g., double cantilever specimen, double torsion specimen) having long cracks. With indirect methods the growth of internal defects (which are described as cracks) causes a degradation of strength. One indirect method which is already standardized is based on strength measurements at different stress rates in a given environment (Fett and Munz, 1990). The different stress rates cause different testing times. In longer lasting tests more time for the crack growth exists and the strength is reduced. This is used to determine the underlying crack growth parameters. It can be assumed that for design purposes the indirect methods deliver more relevant data than direct methods, since they are based on the behavior of real small material defects (which are typical fracture origins in components) and not on artificially made long cracks.

The strength of glasses and ceramics scatter. This is caused by the fact that in each smooth specimen the size of the fracture origin is different, as described by the Weibull theory (Danzer, 1992; Danzer *et al.*, 2001; Danzer, 2006). This large scatter of strength data in combination with the high values of the SCCG exponent makes the measurement laborious. The reliable measurement of a characteristic (or mean) strength needs the testing of many specimens. Several sets of tests at different loading rates have to be employed.

This problem becomes even worse if the testing procedure is not very accurate. The frequently used strength tests for glasses and ceramics (e.g., flexural beam tests or ring on ring tests) are not very precise and measurement uncertainties up to 10% (and even more for small specimens) have been reported (Lube *et al.*, 1997). This makes the determination of a high SCCG exponent even more difficult and the requirement of large data sets even stronger (Bermejo *et al.*, 2012b). For these reasons a much more precise biaxial strength testing method – the ball on three balls test – is proposed in this chapter, which may reduce the number of specimens needed for an accurate measurement dramatically. Another advantage of the B3B test is that the testing is easy and quick to perform.

As an example for the advantages of the use of the ball on three balls test to determine SCCG parameters, the mechanical room temperature strength of a glass-ceramic composite was evaluated to characterize the sub-critical crack growth behavior in this

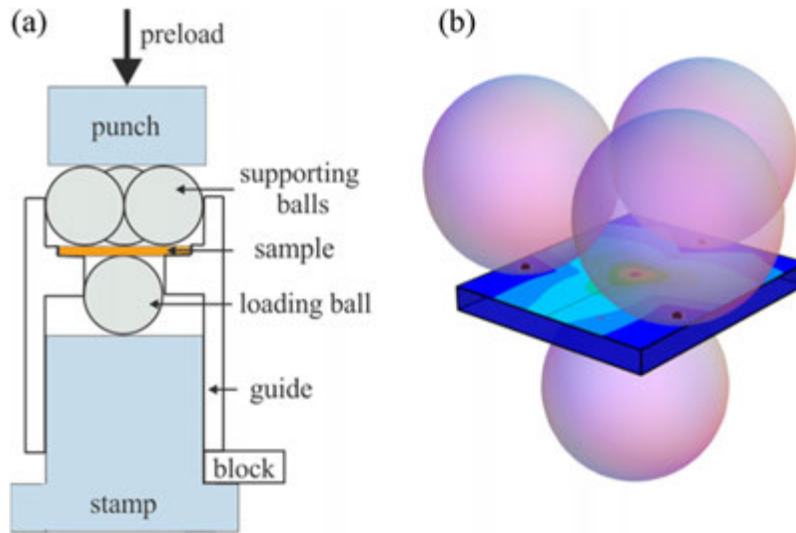


Fig. 1 (a) Schematic of the ball-on-three-balls testing jig; (b) stress distribution in a plate during biaxial loading. The maximal stress is concentrated in the center of the specimen.

material. Different loading conditions (i.e., from 0.01 to 200 MPa s⁻¹) and environments (i.e., water, air and silicone oil) with low and high relative humidity respectively were selected aiming to reproduce possible loading scenarios during service. Measurement of inert strength was attempted in argon at a very high stress rate. Based on the experimental strength results a model for the SCCG was derived for low and high humidity testing conditions using a double and a single power-law v-K relation, respectively, which could characterize the crack propagation behavior in different environments.

Experimental Evidence of Slow Crack Growth

Reference Material and Geometry

The substrate (glass-ceramic) employed to fabricate the LTCC specimens of study is made of approx. 50% of Al₂O₃ as filler and 50% of several glasses containing Ca, Na, Si, K, B, and Al, where the crystallization degree after sintering exceeds 90%. Microstructural characterization of the bulk material can be found elsewhere (Bermejo *et al.*, 2013). For the biaxial strength measurements samples of “as-received” rectangular plate specimens of dimension ca. 11.0 × 9.6 × 0.4 mm³ were used. For statistical significance, between 10 and 30 specimens were tested for each condition.

Experimental Evaluation of Biaxial Strength

The biaxial strength (maximum failure stress) was determined using the ball-on-three-balls test. The specimen was symmetrically supported by three balls on one side and loaded by a fourth ball on the opposite face (see Fig. 1). The loading balls had a radius of 4 mm resulting in a support radius of ~4.6 mm. A pre-load of 7 N was applied to hold the specimen in the fixture. More details on the testing methodology can be found in previous publications (Börger *et al.*, 2002, 2004; Danzer *et al.*, 2006, 2007). The tests were conducted under displacement control at different cross-head speeds (i.e., 0.0001 mm min⁻¹, 0.001 mm min⁻¹, 0.01 mm min⁻¹, 0.1 mm min⁻¹, and 2 mm min⁻¹) using a universal testing machine (ZWICK Z010, Zwick/Roell, Ulm, Germany). The corresponding stress rates were calculated from the load-displacement curves, ranging from approx. 0.01 MPa s⁻¹ to 200 MPa s⁻¹. The flexural strength was determined in every case from the maximum tensile stress ($\sigma_{\max}$) in the specimen during loading, given by:

$$\sigma_{\max} = f \cdot \frac{P}{d^2} \quad (2)$$

with P [N] the maximum load at failure, d [mm] the plate thickness, and f a dimensionless factor which depends on the geometry of the specimen, the Poisson's ratio of the tested material and details of the load transfer from the jig into the specimen (Danzer *et al.*, 2006). In order to determine the f factor a FEM analysis was performed using ANSYS 14.0 for this geometry (ANSYS, 2011), assuming isotropic elastic properties for the material, giving as a result: $f = 3.3 - 29.9 \cdot (d/L) + 187.8 \cdot (d/L)^2$. Where $L = 11$ mm is the width of the specimen. This factor f is valid for $0.4 < d < 0.5$ mm, for a Poisson ratio $\nu = 0.2$. The factor f for disc-shaped geometries can be accessed at “See Relevant Website section”.

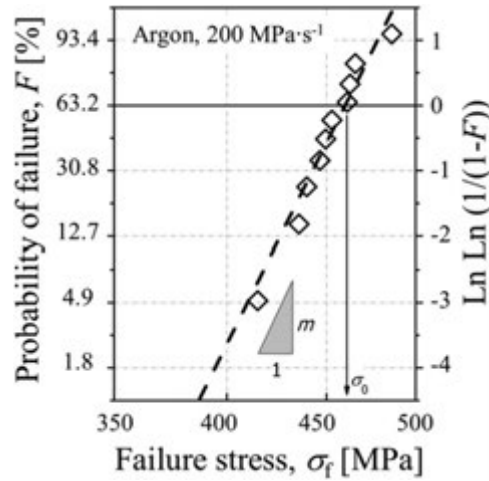


Fig. 2 Weibull diagram of the strength of LTCC specimens tested in argon at $200 \text{ MPa} \cdot \text{s}^{-1}$ (near-inert conditions). The dashed line represents the best fit of the data using the maximum likelihood method.

Biaxial Strength Results in Different Environments

The biaxial strength of LTCC specimens tested under several stressing rates (i.e., 0.01, 0.1, 1, 10, and $200 \text{ MPa} \cdot \text{s}^{-1}$) in different environments (i.e., silicone oil, air with 40% RH, and water) was measured on samples containing between 10 and 30 specimens. The “inert” strength was measured in argon at high speed rate ($200 \text{ MPa} \cdot \text{s}^{-1}$). As an example, the biaxial strength distribution in argon is represented in **Fig. 2** in a Weibull diagram, where the failure stress, σ_f (calculated for every specimen according to Eq. (2)) is plotted versus the probability of failure, F . From the measured failure strength distribution the Weibull parameters, σ_0 and m , were calculated according to EN-843-5 (EN 843-5, 1997). The dashed line represents the best fit of the strength data using the maximum likelihood method. It can be observed that the failure stress values follow a Weibull distribution, which reflects the flaw size distribution in the sample (Danzon, 1992). All ten tested specimens failed at surface flaws located at the tensile surface. Fractographic evidences can be found elsewhere (Bermejo *et al.*, 2013). The characteristic flexural inert strength, σ_{inert} , at room temperature resulted in 460 MPa with a 90% confidence interval (CI) of 449–472 MPa. The Weibull modulus, m , was 26; the limits of the 90% confidence interval for m ranged from 15 to 35. Such a high Weibull modulus indicates a narrow critical flaw size distribution in the tested specimens. Moreover, it also indicates the accuracy of the measurements: (see (Bermejo *et al.*, 2012b) for more details).

In **Fig. 3** the strength data for each set is (log-log) plotted versus the stressing rate, tested in the three environments; the inert strength is also presented for comparison. The characteristic strength and Weibull modulus for each sample as well as the corresponding 90% confidence intervals (error bars in **Fig. 3**) can be found in (Bermejo *et al.*, 2013). From **Fig. 3** different slopes in the stress-stress rate curves can be seen, especially comparing humid environments (e.g., air or water) with dry conditions (i.e., silicone oil). For the cases of air and water, assuming a single power-law to describe the v-K behavior, a SCCG parameter n ranging between 30 and 35 can be obtained (Bermejo *et al.*, 2013). However, the behavior in silicone oil cannot be fitted using a single power-law. Based on the experimental evidences shown in **Fig. 3**, it can be observed how - depending on the stress rate - two different crack growth mechanisms may be taken place. In order to understand the SCCG in dry environments (i.e., silicone oil in our case), a new model for crack growth must be implemented, taking into account different regions in the v-K curve, namely Region I and II. The procedure to model the v-K behavior in different regions, based on strength – stress rate measurements, will be developed in the next section.

Modeling of Subcritical Crack Growth in Different Environments

Modeling the effect of SCCG by using a general crack growth law is based on the Griffith criterion, which predicts that fast fracture occurs when the stress intensity factor is equal or exceeds the fracture toughness of the material:

$$K_I \geq K_{Ic} \quad (3)$$

The stress intensity factor is usually given by

$$K_I = Y \cdot \sigma \cdot \sqrt{\pi \cdot a} \quad (4)$$

while the critical stress intensity factor under inert conditions is defined by:

$$K_{Ic} = Y \cdot \sigma_{\text{inert}} \cdot \sqrt{\pi \cdot a_i} \quad (5)$$

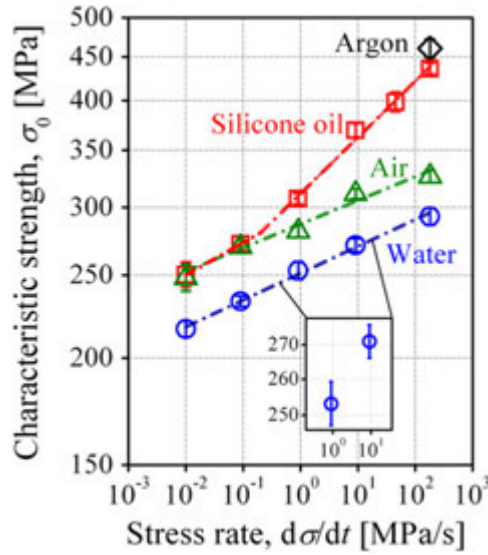


Fig. 3 Characteristic strength as a function of the stressing rate (i.e., from 0.01 to 200 MPa · s⁻¹) in different environments (i.e., oil (□), 40%RH (Δ) and water (○)) presented as log σ₀ vs. log dσ/dt. The inert strength (◇) measured in argon is also shown as reference. The close-up shows the 90% CI of strength of two samples measured in water.

where σ_i is the inert strength and a_i the initial crack length (for this investigation, σ_{inert} was set to 460 MPa and, accordingly, a_i calculated with Eq. (3) yields ~5 μm (assuming Y ~ 1, and K_{Ic} = 2 MPa · m^{1/2})).

By introducing dimensionless quantities, $\hat{K}_I = K_I/K_{Ic}$ and $\hat{\sigma} = \sigma/\sigma_{inert}$, a general evolution equation for the stress intensity factor can be derived:

$$\frac{d\hat{K}_I}{dt} = \frac{\partial \hat{K}_I}{\partial \hat{\sigma}} \times \frac{d\hat{\sigma}}{dt} + \frac{\partial \hat{K}_I}{\partial a} \times \frac{da}{dt} = \hat{K}_I \hat{\sigma} \times \frac{d\hat{\sigma}}{dt} + \frac{\hat{\sigma}^2}{\hat{K}_I} \frac{1}{2a_i} \times \frac{da}{dt} \quad (6)$$

For constant stress rate experiments, as conducted in this investigation (i.e., $\frac{d\hat{\sigma}}{dt} = \dot{\sigma}/\sigma_{inert}$), Eq. (6) reduces to:

$$\frac{d\hat{K}_I}{dt} = \frac{\hat{K}_I}{t} + \frac{1}{\hat{K}_I} \left(\frac{\dot{\sigma}}{\sigma_{inert}} \right) t^2 \frac{1}{2a_{c,0}} \times \frac{da}{dt} \quad (7)$$

Substituting the crack growth rate associated with Region I, i.e., $da/dt = v_0(\hat{K}_I)^n$, into Eq. (7) we obtain a Bernoulli differential equation (i.e., $y'(t) = P(t)y + Q(t)y^n$) on $\hat{K}_I$, with t as independent variable:

$$\frac{d\hat{K}_I}{dt} = \frac{\hat{K}_I}{t} + \left(\frac{\dot{\sigma}}{\sigma_{inert}} \right) t^2 \frac{v_0}{2a_{c,0}} \hat{K}_I^{n-1} \quad (8)$$

This differential equation can be solved even analytically in the case of a single power-law type crack growth behavior, as derived in (Supancic and Schöpf, 2012), resulting in:

$$\hat{K}_I = \frac{\dot{\sigma}}{\sigma_{inert}} \cdot t \cdot \left(1 - \frac{n-2}{n+1} \cdot \frac{v_0}{2a_{inert}} \cdot \left(\frac{\dot{\sigma}}{\sigma_i} \right)^n \cdot t^{n+1} \right)^{-1/(n-2)} \quad (9)$$

The time to fracture, i.e., $t = t_f$ can be calculated from Eq. (9) when $\hat{K}_I$ reaches 1. Then, for a given applied stress rate, $\dot{\sigma}$, the corresponding failure stress value is given by the applied stress at the time of fracture, i.e., $\sigma = \dot{\sigma} \cdot t_f$.

Based on the experimental results in air and in water (i.e., characteristic strength vs. stress rate) Eq. (9) can be solved to best fit the parameters n and v_0 when fracture occurs (i.e. for $\hat{K}_I=1$), for different stress rates (i.e., taking $\dot{\sigma}$ as independent variable). This is plotted in Fig. 4(a) along with the experimental strength data in both environments. The best fit for these data is obtained for $n \sim 35$ and $v_0 \sim 0.5 \text{ m} \cdot \text{s}^{-1}$ for air and $n \sim 31$ and $v_0 \sim 7 \text{ m} \cdot \text{s}^{-1}$ for water. Using these parameters, the v-K curve for this material can be obtained, as shown in Fig. 4(b). It can be inferred from this figure that for a given K_I/K_{Ic} the crack growth rate in water may be more than 2 orders or magnitude larger compared to the rate in ambient air. A direct consequence is a significant reduction of the lifetime of this material in water (see more details in (Bermejo et al., 2013)). We caution the reader that a difference between $n = 35$ and $n = 31$ may not be significant, due to the error in determining the n -exponent from strength – stress rate measurements, as has been analyzed elsewhere (Krautgasser et al., 2017).

In order to model the crack growth behavior in silicone oil, a single power law could not account for the change of slope as found experimentally in the strength–stress rate tests (see Fig. 3). In an attempt to explain and rationalize the crack growth rate, v , as function of the applied stress intensity factor, K , in silicone oil, a double power law was implemented into Eq. (7) for da/dt , according to:

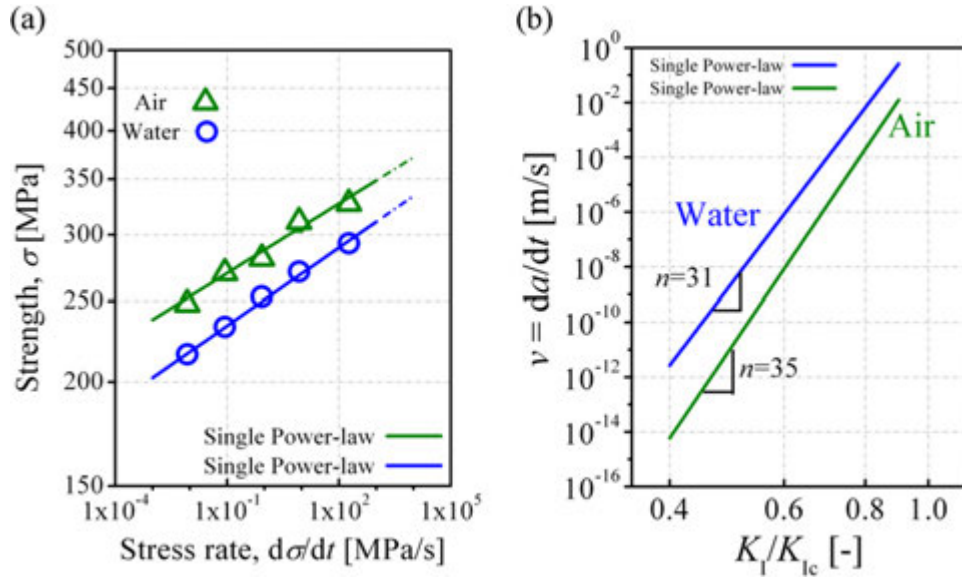


Fig. 4 (a) Characteristic strength as a function of the stress rate (i.e., from 0.01 to 200 MPa s⁻¹) in water (○) and in air (△) presented as log σ_0 vs. log $d\sigma/dt$. The best fit is based on a single power law to describe the SCCG behavior. (b) v-K curve for water and air based on the parameters estimated from the strength-stress rate experiments.

$$v(K_I) = \frac{da}{dt} = \begin{cases} v \cdot \left(\frac{K_I}{K_{Ic}}\right)^n & K_I < K_T \\ v_1 \cdot \left(\frac{K_I}{K_{Ic}}\right)^{n_1} & K_I \geq K_T \end{cases} \quad (10)$$

Eq. (10) introduces five parameters into Eq. (9), i.e., v , n , v_1 , n_1 , and K_T , where four of them are independent parameters. The parameter v_1 can be expressed as: $v_1 = v \cdot (K_T/K_{Ic})^{(n-n_1)}$. The parameter K_T is defined as “transition stress intensity factor” indicating the continuous transition between both crack growth regions, with different SCCG exponents, n and n_1 , respectively.

Now Eq. (7) can be solved in an analogous way and the evolution of $\dot{K}_I$ with time can be obtained. Solving for $\dot{K}_I = 1$, for different stress rates, the parameters v , n , v_1 , n_1 , and K_T can be found which best fit the experimental data in silicone oil. Note that a system of at least four equations is needed to determine the four independent parameters, thus experimental data from four different stress rates are required. Since the region corresponding to low stress rates in oil and in air show the same trend (see Fig. 3) the parameters v and n that describe Region I can be taken as those calculated for ambient air, i.e., $v \sim 0.5$ m s⁻¹ and $n \sim 35$. Thus, the best fit for oil is shown in Fig. 5(a) along with the experimental data. It can be seen how the model tends to a plateau region corresponding to the inert strength, measured in argon (see Fig. 2). However, this has not been measured with experiments yet.

Once the SCCG parameters for silicone oil have been obtained, the v-K curve (as given by Eq. (10)) for LTCC in silicone oil can be built up, as shown in Fig. 5(b). The relationship between log strength vs. log stress rate leads to a kink which is related to the change in the crack growth mechanism occurring in the material during loading. At relatively low stress intensity factors, a *reaction-rate-controlled region* (hydrolysis of Si-O bonds) dominates the crack growth rate (defined as $v = da/dt$ (Wiederhorn, 1967)). At intermediate stress intensity factors the crack growth rate decreases to a level limited by the rate of diffusion of water molecules to the crack tip, and thus a *transport-controlled region* governs the growth rate in the v-K curve (Wiederhorn, 1967). The resulting parameters to describe SCCG of this material in silicon oil may change in a different environment (e.g., argon) and can be also be affected by temperature.

Significance of the Ball-on-Three-Balls Testing Method for SCCG

Several methods can be used to determine the biaxial strength of ceramic-based materials. Recent works on LTCC have employed the ball-on-ring (BOR) test (Dannheim et al., 2004) or the ring-on-ring (ROR) test (Tandon et al., 2007) on bulk specimens, showing the effect of the loading rate and environmental conditions on the mechanical strength. These methods induce a maximal biaxial stress distribution in the center of the specimen and avoid the influence of edge effects. However, it has been shown that, during testing, small geometric inaccuracies (e.g., for the case of “as-sintered” specimens) can lead to an undefined load transfer from the rings to the specimen and thus may cause large uncertainties in the determined strength, as has been observed in (Morrell et al., 1999). Measurement uncertainties (MUs) up to $\pm 10\%$ have been reported. This problem is specially enhanced when testing small specimens (Lube et al., 1997). Other testing methods such as the pin-on-three-balls (POB) technique may be used to avoid

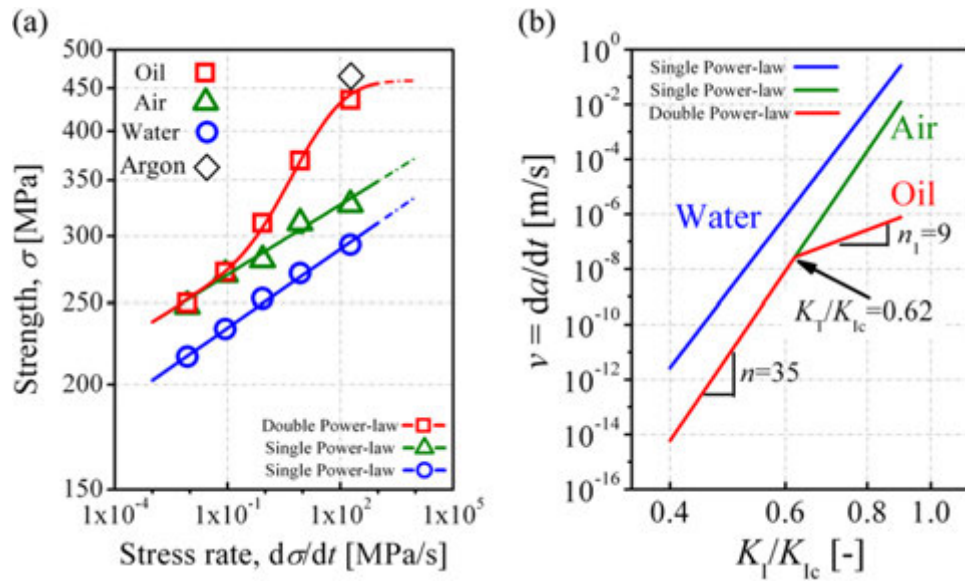


Fig. 5 (a) Characteristic strength as a function of the stressing rate (i.e., from 0.01 to 200 MPa s⁻¹) in water (○), in air (△), in silicone oil (□), and in argon (◇), presented as log σ_0 vs. log $d\sigma/dt$. The best fit in oil is based on a double power law to describe the SCCG behavior. (b) v-K curve for water, air and oil based on the parameters estimated from the strength-stress rate experiments. A “kink” in the oil curve can be observed, indicating different SCCG mechanisms acting at the crack tip.

slight imperfections in the sintered plate (Wachtman *et al.*, 1972), but there remain uncertainties about the loading under a flat-ended pin. Such uncertainties are much reduced when a modified version of this loading configuration, the ball-on-three-balls (B3B) test, is used (Börger *et al.*, 2002, 2004). Therefore, the effect of loading conditions, environment and/or surface features on the strength of such components may be better discerned using the B3B method, as has been reported elsewhere (Bermejo *et al.*, 2009, 2011, 2012a). In Fig. 3 a close-up shows the 90% CI of strength corresponding to two samples tested at different stress rates (i.e., at approx. 1 and 10 MPa s⁻¹). The narrow confidence interval for every testing condition represented by the scatter bars in Fig. 3 is not only a direct consequence of the high Weibull modulus of the material, but also of the high accuracy of the testing method. In a previous work using Monte Carlo simulations, it was demonstrated that MUs of the strength measurement of each specimen might mask the inherent scatter of the material strength (Bermejo *et al.*, 2012b). Measuring the scatter of the strength distribution is only possible if the MUs of the measuring technique are much smaller than the former. Such large MU may be in the range of the scatter of the strength. It has been shown in (Bermejo *et al.*, 2012b) that probably, under these conditions, a Weibull modulus of about $m = 15$ would be determined, whereas the “real” modulus should be $m = 30$ or higher. In our experiments using the B3B technique, the experimental MUs are much less than 1% and an accurate determination of the strength distribution (in particular of the Weibull modulus m) is possible. This testing method largely reduces uncertainties in the load transfer (e.g., due to lack of parallelism between both specimen sides) which might lead to under- or overestimation of the fracture load in the test.

In addition, the use of the B3B method, as inferred from Fig. 3, could allow discerning small differences in strength between samples tested in slightly different environments. Furthermore, as reported in this work, it was possible to observe the similar strength values in oil and in air for low stressing rates, which might have been mistaken by scatter using other testing procedures. In the experimental work presented in this chapter as reference, more than 400 specimens were tested, which also demonstrates the ease and cost efficiency of the B3B test as indirect method, and is therefore recommended for characterizing the SCCG behavior of brittle materials.

Summary and Conclusions

The strength of brittle materials may be strongly affected by the environment and loading conditions in which the material is subject to mechanical stress. This is caused by the subcritical growth of cracks (SCCG) during loading, a mechanism activated by the prolonged presence of humidity at the specimen’s surface loaded under tension.

A methodology based on indirect (biaxial) strength measurements using the Ball-on-three-Balls (B3B) test in distinct environments has been employed to model the subcritical crack growth behavior (v-K curve) in brittle materials. For illustrative purposes, experimental results on a Low Temperature Co-fired Ceramic (i.e., glass-ceramic composite) reference material have been utilized to quantify such effects on strength. Whereas high strength values can be reached during high-rate testing in “quasi-inert” environment (e.g., argon), up to a 50% lower strength values have been measured on specimens immersed in water tested

for longer time periods. In addition, due to the high measurement accuracy of the B3B test, constant stress rate experiments in a relative dry environment (i.e., silicon oil) have shown for the first time evidence of two different crack growth mechanisms taking place during mechanical loading. It is shown how a double power-law for the crack growth rate (i.e., v - K curves) can describe the experimental results in dry environments. This approach might be also employed to describe the SCCG behavior of other functional ceramic-based materials and can be also useful to predict lifetime of components.

References

- ANSYS, 2011. ANSYS Release 14.0. Available at: www.ansys.com.
- Bermejo, R., Kraleva, I., Antoni, M., Supancic, P., Morrell, R., 2009. Influence of internal architectures on the fracture response of LTCC components. *Key Engineering Materials* 409, 275–278.
- Bermejo, R., Supancic, P., Aldrian, F., Danzer, R., 2012a. Experimental approach to assess the effect of metallization on the strength of functional ceramic components. *Scripta Materialia* 66, 546–549.
- Bermejo, R., Supancic, P., Danzer, R., 2012b. Influence of measurement uncertainties on the determination of the Weibull distribution. *Journal of the European Ceramic Society* 32, 251–255.
- Bermejo, R., Supancic, P., Kraleva, I., Morrell, R., Danzer, R., 2011. Strength reliability of 3D low temperature co-fired multilayer ceramics under biaxial loading. *Journal of the European Ceramic Society* 31, 745–753.
- Bermejo, R., Supancic, P., Krautgasser, C., Morrell, R., Danzer, R., 2013. Subcritical crack growth in low temperature co-fired ceramics under biaxial loading. *Engineering Fracture Mechanics* 100, 108–121.
- Börger, A., Supancic, P., Danzer, R., 2002. The ball on three balls test for strength testing of brittle discs: stress distribution in the disc. *Journal of the European Ceramic Society* 22, 1425–1436.
- Börger, A., Supancic, P., Danzer, R., 2004. The ball on three balls test for strength testing of brittle discs – Part II: Analysis of possible errors in the strength determination. *Journal of the European Ceramic Society* 24, 2917–2928.
- Dannheim, H., Schmid, U., Roosen, A., 2004. Lifetime prediction for mechanically stressed low temperature co-fired ceramics. *Journal of the European Ceramic Society* 24, 2187–2192.
- Danzer, R., 1992. A general strength distribution function for brittle materials. *Journal of the European Ceramic Society* 10, 461–472.
- Danzer, R., 1993. *Ceramics: Mechanical Performance and Lifetime Prediction*. In: Cahn, R.W., Brook, R. (Eds.), *Encyclopedia of Materials Science and Engineering*. Oxford: Pergamon Press.
- Danzer, R., 2006. Some notes on the correlation between fracture and defect statistics: Are Weibull statistics valid for very small specimens? *Journal of the European Ceramic Society* 26, 3043–3049.
- Danzer, R., Harrer, W., Supancic, P., *et al.*, 2007. The ball on three balls test – Strength and failure analysis of different materials. *Journal of the European Ceramic Society* 27, 1481–1485.
- Danzer, R., Lube, T., Supancic, P., 2001. Monte Carlo simulations of strength distributions of brittle materials – Type of distribution, specimen and sample size. *Zeitschrift Fur Metallkunde* 92, 773–783.
- Danzer, R., Lube, T., Supancic, P., Damani, R., 2008. Fracture of advanced ceramics. *Advanced Engineering Materials* 10, 275–298.
- Danzer, R., Supancic, P., Harrer, W., 2006. Biaxial tensile strength test for brittle rectangular plates. *Journal of the Ceramic Society of Japan* 114, 1054–1060.
- EN 843-3, 1996. *Advanced Technical Ceramics, Monolithic Ceramics, Mechanical Properties at Room Temperature – Part 3: Determination of subcritical crack growth parameters from constant stressing rate flexural strength tests*.
- EN 843-5, 1997. *Advanced technical ceramics – Monolithic ceramics – Mechanical tests at room temperature – Part 5: Statistical analysis*.
- Evans, A.G., 1974. Slow crack growth in brittle materials under dynamic loading conditions. *International Journal of Fracture* 10, 251–259.
- Fett, T., Munz, D., 1990. Evaluation of subcritical crack extension under constant loading. *Journal of the European Ceramic Society* 6, 67–72.
- Freiman, S.W., Wiederhorn, S.M., Mecholsky, J.J., 2009. Environmentally enhanced fracture of glass: A historical perspective. *Journal of the American Ceramic Society* 92, 1371–1382.
- Gurney, C., 1947. Delayed fracture in glass. *Proceedings of the Physical Society* 59, 169–185.
- Krautgasser, C., Bermejo, R., Supancic, P., Danzer, R., 2017. Influence of the scatter of strength and of measurement uncertainties on the determination of the subcritical crack growth exponent in ceramics and glasses. *Journal of the European Ceramic Society* 37, 1873–1878.
- Lube, T., Manner, M., Danzer, R., 1997. The miniaturisation of the 4-point bend-test. *Fatigue and Fracture of Engineering Materials and Structures* 20, 1605–1616.
- Michalske, T.A., Freiman, S.W., 1983. A molecular mechanism for stress corrosion in vitreous silica. *Journal of the American Ceramic Society* 66, 284–288.
- Morrell, R., McCormick, N., Bevan, J., Lodeiro, M., Margetson, J., 1999. Biaxial disc flexure – Modulus and strength testing. *British Ceramic Proceedings* 59, 31–44.
- Munz, D., Fett, T., 1999. *Ceramics: Mechanical Properties, Failure Behaviour, Materials Selection*. Berlin: Springer.
- Saâdaoui, M., 2020. Chapter 12109 – Subcritical crack growth: Basic relations and experimental evaluation. *Encyclopedia of Materials: Technical Ceramics and Glasses*, Elsevier.
- Schoeck, G., 1990. Thermally activated crack propagation in brittle materials. *International Journal of Fracture* 44, 1–44.
- Supancic, P., Schöpf, H., 2012. Exact implementation of subcritical crack growth into a Weibullian strength distribution under constant stress rate conditions. *Journal of the European Ceramic Society* 32, 4031–4040.
- Tandon, R., Newton, C.S., Monroe, S.L., Glass, S.J., Roth, C.J., 2007. Sub-critical crack growth behavior of a low-temperature co-fired ceramic. *Journal of the American Ceramic Society* 90, 1527–1533.
- Wachtman, J.B., Capps, W., Mandel, J., 1972. Biaxial flexure tests of ceramic substrates. *Journal of Materials* 7, 188–194.
- Wiederhorn, S.M., 1967. Influence of water vapour on crack propagation in soda-lime glass. *Journal of the American Ceramic Society* 50, 407–414.
- Wiederhorn, S.M., 1974. Subcritical crack growth in ceramics. In: Bradt, R.C., Hasselman, D.P.H., Lange, F.F. (Eds.), *Fracture Mechanics of Ceramics*. New York: Plenum.
- Wiederhorn, S.M., Fett, T., Rizzi, G., *et al.*, 2011. Effect of water penetration on the strength and toughness of silica glass. *Journal of The American Ceramic Society* 94, s196–s203.

Relevant Website

www.isfk.at/de/960/

Montanuniversität Leoben » B3B (strength test).

Ceramics: Transformation Toughening

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Constrained Transformation

Upon cooling from high temperature, pure zirconia undergoes two phase transformations, from cubic (c) to tetragonal (t) crystal structure at $\sim 2367^\circ\text{C}$ and from tetragonal to monoclinic (m) structure at $\sim 1170^\circ\text{C}$. The toughening mechanism, which is similar to that occurring in TRIP (transformation induced plasticity) steels (Zackay *et al.*, 1967), was first reported by Garvie *et al.* (1975). The t–m transformation is martensitic, i.e., diffusionless, and is accompanied by a large shear strain ($\sim 9\%$) and volume increase ($\sim 4\%$). In many practical cases the net shear strain is reduced or eliminated by twinning or by the formation of several variants and is often accompanied by microcracks, which in certain circumstances can lead to an additional fracture toughening contribution (Evans, 1984). Both t and m transformation temperatures can be reduced by alloying with other oxides (e.g., MgO , Y_2O_3 , CaO , Ce_2O_3 , or other rare-earth oxides) that form solid solutions with ZrO_2 .

The t–m transformation temperature can also be reduced by mechanical constraint that opposes the accompanying shape and volume changes. The thermodynamics of the phase transformation for a particle of ZrO_2 embedded in an elastic matrix then involves a balance of two terms: a decrease in chemical free energy accompanying the transformation and an increase in elastic strain energy in both the particle and the matrix. The magnitude of the former increases with decreasing temperature, while the latter is, to first order, independent of temperature. If the magnitude of the strain energy term is sufficiently large, the transformation can be suppressed to cryogenic temperatures. The strain energy can be increased or decreased by the action of a remotely applied stress field (the interaction energy in the analyses of Eshelby (1957)) and the transformation temperature correspondingly changed.

Experimental observations indicate the existence of a size effect in the t–m transformation, which is key to designing toughened microstructures. For a given system of embedded ZrO_2 particles at a given temperature, there exists a critical particle size above which all particles transform spontaneously to the monoclinic phase, and below which the tetragonal phase is stable. The critical particle size decreases with decreasing temperature. Since both of the energy terms mentioned above scale with volume, the existence of a size effect requires either an additional energy term that scales differently with size, or that the transformation be controlled by a nucleation barrier.

Several possibilities exist for energy terms that scale with particle surface area (localized strain energy associated with terminations of twins, as observed in monoclinic particles, and differences in interfacial energies between the matrix and the t or m phases). However, evidence exists for nucleation control in some cases that is dependent on strain concentrations associated either with second phase particles, as in the case of the δ -phase ($\text{Mg}_2\text{Zr}_5\text{O}_{12}$) in magnesia–partial stabilized zirconia (Mg-PSZ) (Hannink *et al.*, 1994) or with the shape of the ZrO_2 particle itself. In the absence of definitive experiments to distinguish these possibilities, the critical conditions for the onset of the t–m transformation remain the least well understood aspect of the transformation and of the associated theoretical predictions of transformation toughening.

Although the martensitic t–m transformation is reversible, hysteresis is observed during temperature cycling, i.e., the martensitic start temperature (M_s) for the forward transformation is lower than the temperature for the reverse transformation (A_s). Hysteresis is also usually observed in experiments involving isothermal stress-induced transformation. Among the potential causes of hysteresis is the formation of microcracks around transformed particles (stabilization by relief of strain energy) or the effect of nucleation steps in the forward and reverse directions.

Toughening Mechanism

Transformation toughening requires a microstructure containing stabilized t- ZrO_2 particles with M_s near or below ambient temperature. The toughening involves the formation of a zone surrounding a growing crack in which the t–m transformation is induced by the concentrated stresses near the crack tip (Figure 1). The transformation strains give rise to closure stresses on the crack, or, in terms of the fracture mechanics formulation, a negative stress intensity factor, K_T , which superimposes on the remotely applied stress intensity factor, K_a , thus opposing further crack growth. In this way the measured fracture toughness is increased by a crack shielding mechanism, while the fundamental brittle bond rupture processes at the crack tip are unchanged.

The contribution of the transform strain to toughening is dependent on the location of the transformed particle relative to the crack tip. For example, in the case of a net dilatational transformation strain, a particle located ahead of the crack (at $\theta < 60^\circ$ in Figure 1(b)) causes additional tensile stresses ahead of the crack tip (and thus reduced toughening), while a particle behind the crack tip (at $\theta > 60^\circ$ in Figure 1(b)) causes compressive stress. This implies that, to achieve effective toughening, the reverse m–t

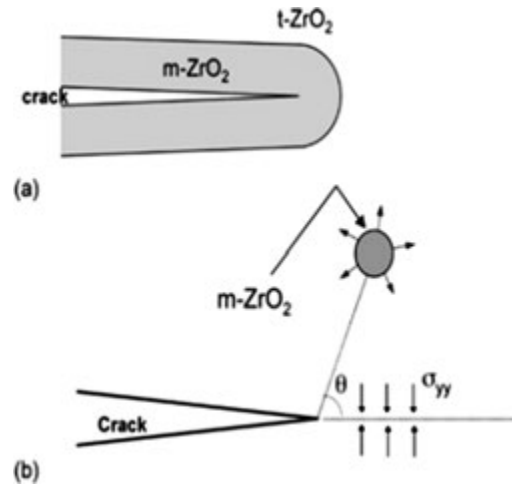


Figure 1 Schematics of transformation toughening: (a) well-developed transformation zone surrounding crack; (b) effect of individual transformed particle on stresses ahead of crack tip.

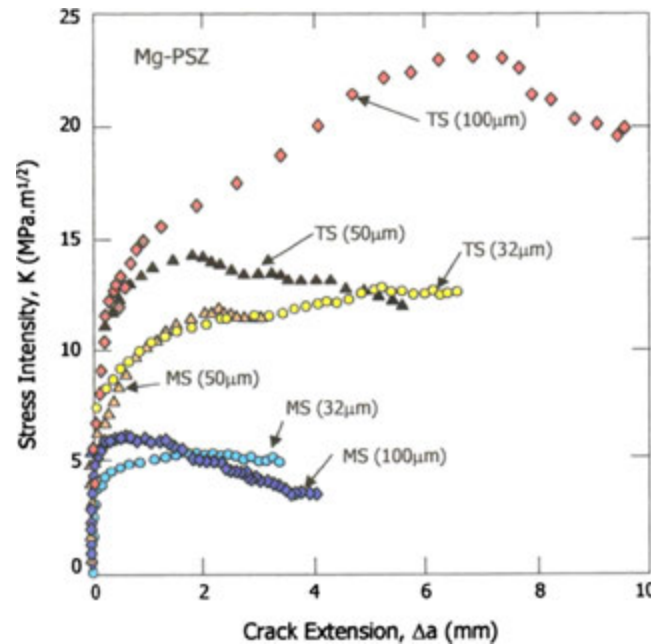


Figure 2 R-curve behavior (stress intensity versus crack extension) of two differently aged Mg-PSZ materials, MS (Maximum Strength) and TS (Thermal Shock) grades with the same composition as a function of grain size (Haffman *et al.*, 1993).

transformation should not occur upon removal of the crack-tip stress field, so that a wake of transformed material develops as the crack grows, as indicated in Figure 1(a). A second implication is that the toughening effect for a pre-existing crack will initially increase as the crack grows and the wake develops, before approaching a steady state condition (i.e., R-curve behavior). The effect on R-curve behavior through the influence of heat treatment control of grain size and precipitate size and form is shown for a Mg-PSZ alloy in Figure 2 (Haffman *et al.*, 1993).

The boundary of the transformation zone is determined by the critical stress required to induce the t-m transformation. This stress and, thus, the zone width and the degree of toughening are sensitive to temperature as well as microstructure. The optimum toughening is achieved when the critical stress is small, i.e., when the ambient temperature is above but close to the M_s temperature. This requirement also defines one of the limitations on the application of this toughening mechanism since, although large toughness increases are possible, the mechanism is effective only over a small range of temperatures.

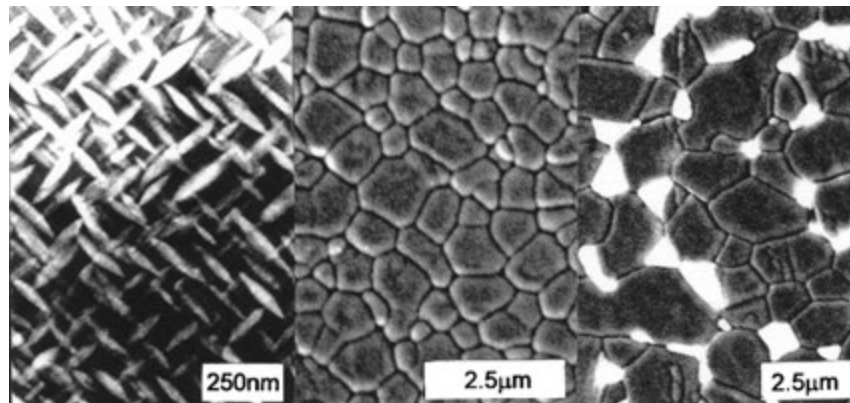


Figure 3 Microstructures of the three most common forms of transformation-toughened ceramics from L to R: Mg-PSZ, Y-TZP (yttria-tetragonal zirconia polycrystals) and ZTA (zirconia-toughened alumina).

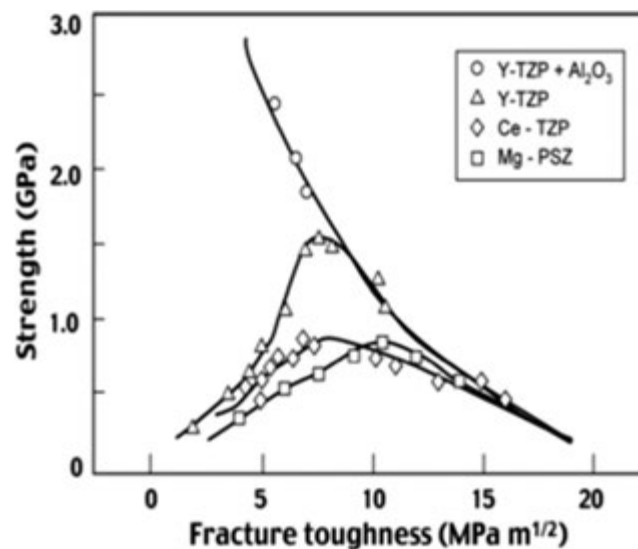


Figure 4 Measured strengths and toughnesses for several series of transformation-toughened ceramics (adapted from Swain, 1985).

Microstructures and Properties of Transformation-Toughened Ceramics

While many transformation-toughened microstructures have been investigated, those developed commercially are of three distinct types, **Figure 3**.

- (i) Partially stabilized zirconia (PSZ) consists of coherent $t\text{-ZrO}_2$ precipitates in a matrix of cubic zirconia. The precipitated microstructure is developed by adding a stabilizing solute (MgO , CaO , or Y_2O_3) at concentrations smaller than needed for full stabilization of the cubic phase, sintering at high temperature ($\sim 1600\text{--}1800^\circ\text{C}$) in the cubic phase field, generally resulting in large $c\text{-ZrO}_2$ grains ($\sim 35\text{--}100\ \mu\text{m}$), and heat treating during cooling in the temperature range $\sim 1100\text{--}1500^\circ\text{C}$ to nucleate and grow the precipitates. In Mg-PSZ the precipitates are oblate spheroids with optimum dimensions $\sim 50 \times 200\ \text{nm}$.
- (ii) Tetragonal zirconia polycrystals (TZP) consist of a matrix of fine-grained ($0.1\text{--}1\ \mu\text{m}$), predominantly single-phase $t\text{-ZrO}_2$ with additions of Y_2O_3 , Ce_2O_3 , or other rare-earth oxides. Sintering is carried out in the single-phase $t\text{-ZrO}_2$ field at temperatures in the range $\sim 1300\text{--}1500^\circ\text{C}$ for alloys containing 1.5–3.5 mol.% Y_2O_3 .
- (iii) Zirconia-toughened ceramics (ZTC) consist of $t\text{-ZrO}_2$ particles dispersed (usually intergranularly) in a matrix of another ceramic such as alumina (Al_2O_3) or mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). A small amount of Y_2O_3 is usually added to the ZrO_2 particles to stabilize the t -phase. The critical particle size is usually between ~ 0.5 and $1\ \mu\text{m}$ depending on the amount of Y_2O_3 additive and the matrix.

Zirconia-toughened materials have the highest strengths ($>2\ \text{GPa}$) and toughnesses ($>15\ \text{MPa m}^{1/2}$) of any polycrystalline ceramics. However, the highest strengths and toughnesses are not found in the same materials (**Figure 4**). In each of the systems

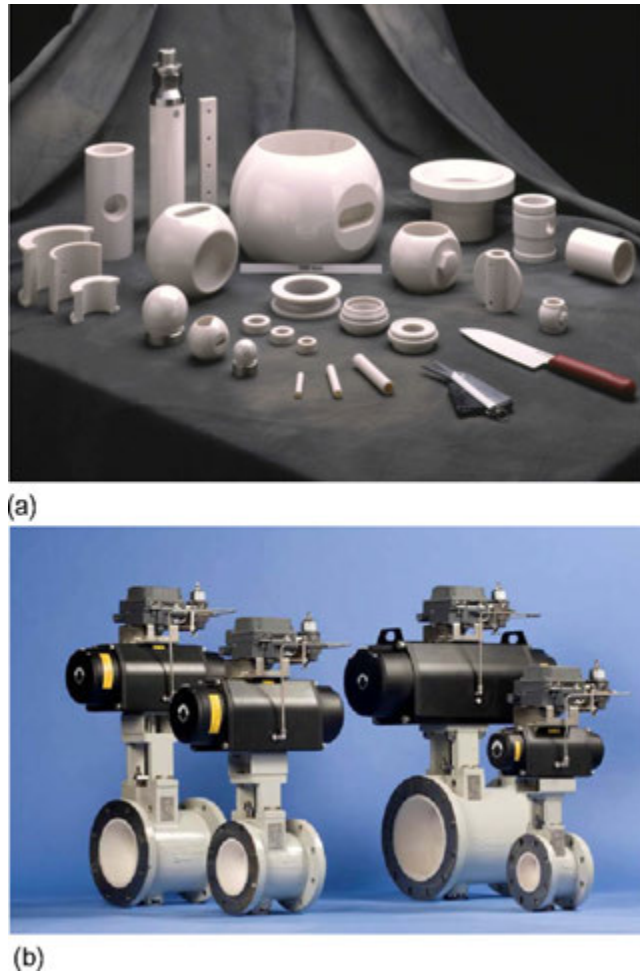


Figure 5 (a) Components of transformation-toughened zirconia (Mg-PSZ and Y-TZP), (b) A series of remotely controlled Z-valves with PSZ liners and valves (courtesy Morgan Technical Ceramics Pty Ltd).

described above the fracture toughness, for given stabilizing solute content, can be varied by adjusting the heat treatment to change the critical stress for transformation, and in most cases the strength is maximum at an intermediate toughness. In the materials with the highest toughness (Mg-PSZ and Ce-TZP) the critical stress for transformation is ~ 500 MPa and transformation zones with widths up to about 1 mm have been observed around well-developed cracks. However, the transformation stress apparently places an upper limit on the strength of the material, for even in the absence of pre-existing cracks, bands of transformation induced by the applied stress lead to failure. The materials with the highest strengths (Y-TZP and zirconia-toughened alumina) have lower toughnesses ($\sim 5\text{--}8$ MPa $\text{m}^{1/2}$) and correspondingly smaller zone widths (< 10 μm).

Additional improvements in properties can be gained by surface grinding. The t-m transformation is induced within a layer near the surface by localized grinding stresses, resulting in a layer of residual compressive stress. The compressive stress inhibits crack initiation and can improve strength, wear resistance, and thermal shock resistance.

Theoretical Understanding of Transformation Toughening

A weight-function method has been used to calculate the reduction in stress intensity factor, K_T , (i.e., the toughness increase) in terms of the distribution of transformation strains surrounding the crack (McMeeking and Evans, 1982). When the transformation strain, e^T , and volume fraction, v_f , of transformed particles are uniform within the zone, K_T is given by

$$K_T = \eta E^* e^T V_f h^{1/2} \quad [1]$$

where E^* is an effective elastic constant, h is a characteristic dimension of the transformed zone, and η is a parameter (with values

in the range ~ 0.22 – 1) that depends on the nature of the transformation strains and the shape of the zone near the crack tip. An equivalent result has been derived from a fracture mechanics energy balance analysis. The result in eqn [1] can be generalized by linear superposition to include effects of nonuniform strain distributions and volume fractions within the transformation zone, which can arise from statistical distributions of M_s temperatures or subcritical transformations.

Experimental measurements indicate that transformation strains generally are nonuniform. Moreover, since ν_f usually decreases monotonically with distance from the crack, the toughening is larger (by a factor of two or more) than it would be for a uniform zone with the same average transformation strain (or ν_f).

In general, the shape of the frontal boundary of the transformation zone and the net transformation strain cannot be predicted *a priori*: both are affected by microstructural characteristics and autocatalytic transformation effects that vary in different systems. Observations indicate that the frontal zone boundary in Mg-PSZ is similar to that defined by a critical hydrostatic stress, while the net strain is close to hydrostatic dilation (i.e., shear strains relieved by twinning). In contrast, the frontal zone in Ce-TZP materials extends in a wedge shape ahead of the crack for a distance about ten times further than in Mg-PSZ.

Applications

Transformation-toughened zirconia has found widespread industrial application as an engineering ceramic, mostly making use of its resistance to wear, chemical inertness, low friction, high hardness and stiffness, and relatively high thermal expansion coefficient (which is closer to metals than those of most other ceramics). Applications of Mg-PSZ include: tooling for the metal forming industry (hot and cold forming dies, can-closure rollers, capstans, draw plugs, and plungers); food processing (homogenizing-pump parts); mineral, gas, and oil treatment (bearings, valves, vortex finders, orifice inserts, spigots, and spools); and the paper, chemical, and manufacturing industries (autoclave nozzles, glue transfer rollers, battery component tooling, and valves). Y-TZP is used for biological applications such as hip-ball replacements, dental implants, industrial cutters, knives, and scissors, as well as golf club inserts. Zirconia-toughened alumina is used for its higher hardness and stiffness in cutting tool tips, high-performance seals and wear parts in engines, and in the mining industry. Typical components made of Mg-PSZ and Y-TZP is shown in **Figures 5(a)** and **(b)**.

References

- Eshelby, J.D., 1957. Determination of the elastic field of an ellipsoidal inclusion and related problems. *Proc. R. Soc. London A* 241, 376–396.
- Evans A.G., 1984. Toughening Mechanism in Zirconia Alloys *Advances in Ceramics* 2, vol. 12, pp. 193–211, The American Ceramic Society Inc.
- Garvie, R.C., Hannink, R.H.J., Pascoe, R.T., 1975. Ceramic steel? *Nature* 258, 703–704.
- Haffman, M.J., Dauskardt, R.H., Mai, Y.W., Richie, R.O., 1993. A review of the mechanics and mechanism of cyclic fatigue-crack propagation in transformation toughened ceramics. In: Zirconia, V. (Ed.), *Science and Technology*. Lancaster, PA: Technomic, pp. 321–338.
- Hannink, R.H.J., Howard, C.J., Kisis, E.H., Swain, M.V., 1994. Relationship between fracture toughness and phase assemblage in Mg-PSZ. *J. Am. Ceram. Soc.* 77, 571–579.
- McMeeking, R.M., Evans, A.G., 1982. Mechanics of transformation toughening in brittle materials. *J. Am. Ceram. Soc.* 65, 242–246.
- Swain, M.V., 1985. Inelastic deformation of Mg-PSZ and its significance for strength–toughness relationship of zirconia-toughened ceramics. *Acta Metall.* 33, 2083–2091.
- Zackay, V.F., Parker, E.R., Farh, D., Busch, R., 1967. The enhancement of ductility in high-strength steels. *ASM Trans. Quart.* 60 (2), 252–259.

Further Reading

- Evans, A.G., Cannon, R.M., 1986. Toughening of brittle solids by martensitic transformations. *Acta Metall.* 34, 761–800.
- Green, D.J., Hannink, R.H.J., Swain, M.V., 1989. *Transformation Toughening of Ceramics*. Boca Raton, FL: CRC Press.
- Hannink, R.H.J., Kelly, P.M., Muddle, B.C., 2000. Transformation toughening in zirconia-containing ceramics. *J. Am. Ceram. Soc.* 83, 461–487.
- Heuer, A.H., Lange, F.F., Swain, M.V., Evans, A.G., 1986. Transformation toughening: An overview. *J. Am. Ceram. Soc.* 69, i–iv. (entire issue devoted to papers on transformation toughening).
- Kelly, P.M., Rose, L.R.F., 2001. The martensitic transformation in ceramics – Its role in transformation toughening. *Progr. Mater. Sci.* 47, 463–557.
- Marshall, D.B., Shaw, M., Dauskardt, R.H., *et al.*, 1990. Crack tip transformation zones in toughened zirconia. *J. Am. Ceram. Soc.* 73, 2659–2666.

Mixed-Mode Fracture and Microstructural Aspects of Crack Propagation

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Introduction

Since prehistoric times, ceramic materials have been a constant companion for mankind. It was invented and re-invented in almost all cultures in all continents. Its uses ranged from humble everyday dinnerware to artful Greek and Chinese vases. Ceramic materials, due to their thermal resistance and mechanical properties, were used in many applications, like insulators, refractories for steel fabrication, etc. More recently, ceramic products have been used in extensive and sophisticated applications that include thermal protection for aircraft engines, ultrasonic transducers, multilayer capacitors and applications for dental and medical fields. But, since nothing is perfect, the main disadvantage of ceramic materials is their brittleness, which can cause catastrophic failure of the ceramic component, without prior warning. Despite their brittleness, nowadays, advanced technical ceramics constitute the support of an ample variety of important products. Ceramic compositions, with special characteristics, are continuously being developed to satisfy the demands of new high technology applications, among them: magnetic, optical and high-temperature ceramics, high-strength products, piezoelectrics, dielectrics, semiconductors, spark plugs, heat engines, aerospace applications, solid oxide fuel cells, hip and knee replacements in the human body, dental ceramic prosthetic, etc. To this day, progress continues with developments in nanotechnology and novel processing routes.

Ceramics mechanical behavior have other disadvantages, such as: (1) large scatter of strength caused by the statistical distribution of the flaw size and the flaw location and (2) subcritical crack extension that could cause failure under constant or cyclic loading during the operation of a component. Good performance in mechanical behavior of ceramic components is directly influenced by a large number of factors. Material parameters like composition, microstructure features (phases distribution, pore size, grain size, cracks, surface condition), crystal or amorphous structure, internal strains and specimen shape and size are such factors, but also some environmental parameters like temperature, atmosphere, strain rate, static or cyclic fatigue, type of stress (uniaxial, biaxial, etc.). With so many factors in play, there is a high degree of complexity of the mechanical phenomena of advanced ceramics and glasses and all should be considered when designing the components.

The most important obstacle for a design methodology for a ceramic component is the absence of a definitive mechanical parameter analogous to the yield strength in metals. Many efforts and studies had been dedicated to characterize fracture process of ceramic materials using the fracture strength parameter but, as mentioned before, failure in ceramics depends on many variables. Even with the most detailed and careful design, the ceramic material could fail due to the extension of processing defects such as pores, inclusions, or cracks. Occult, and probably undetectable, defects can lead to catastrophic failure. Therefore, any successful application of ceramics will require a carefully designed strategy for minimizing the occurrence and propagation of cracks that may lead to catastrophic failures. To achieve this, knowledge of how materials fail is a must. The understanding of fracture mechanics plays a main role in the design and the use of ceramic materials, even more where the component would be subjected to significant stresses. Fracture mechanics framework provides a rational, cost effective, approach to the development of a practical design methodology for ceramic materials since it is a strong tool to study: (1) Maximum (or safe) load limit to operate structural components, (2) Safe period of operation under a given load, (3) Detection of possible imminent failure and (4) Post-mortem fracture analysis.

Generally speaking, materials fail in three manners: brittle, quasi-brittle and ductile fractures, with the vast majority of ceramic materials prone to suffer brittle fracture. Early works on fracture mechanics were devoted to the study of brittle fracture in a homogeneous and isotropic body. Griffith's thermodynamic derivations (Griffith, 1920) from Inglis' report (Inglis, 1913) showed a condition for unstable crack growth in brittle materials like glass. Studies by Orowan (1949) provided some insights into the role of cracks and plasticity in fracture. Irwin (1958) developed an important engineering concept for a driving force parameter, called the "stress intensity factor". Williams (1956) and Paris and Erdogan (1963) made contributions for the crack-tip fields under linear elastic mechanics conditions and fatigue, respectively. Later studies led to the development of fracture mechanics approaches for elastic-plastic and fully plastic conditions with Wells' work (crack-tip opening displacement) (Wells, 1961), Rice's study (J integral) (Rice, 1968) and McClintock's research (characterization of the crack driving force under fully plastic conditions) (McClintock *et al.*, 1995). All these developments are covered in conventional texts of fracture mechanics. It is important to highlight that most of the current knowledge about fracture mechanics come from studies on metallic materials, and that the over-emphasis on the differences between structural metals and ceramics had, possibly, delayed the use of ceramics as valuable structural materials. However, since the mid-70s, there has been a substantial research effort to deepening the body of knowledge of the fracture behavior of ceramic materials (Anderson, 2017).

As a model for a material, Irwin's stress intensity factors are especially useful for engineering applications, since it characterizes the stress field near the crack tip. In this model, there are three primary modes that define the orientation of a crack relative to the loading: (1) "the opening mode", where displacement discontinuity is perpendicular to the plane of the crack; (2) "the sliding mode", in which the displacement discontinuity is in the plane and parallel to the direction of the crack; and (3) "the tearing mode", where the displacement discontinuity is perpendicular to the plane of the material and in the plane of the crack (See Fig. 1). The stress concentration at the crack tip is designated by the stress intensity factors K_I , K_{II} and K_{III} . The subscripts represent the direction of load

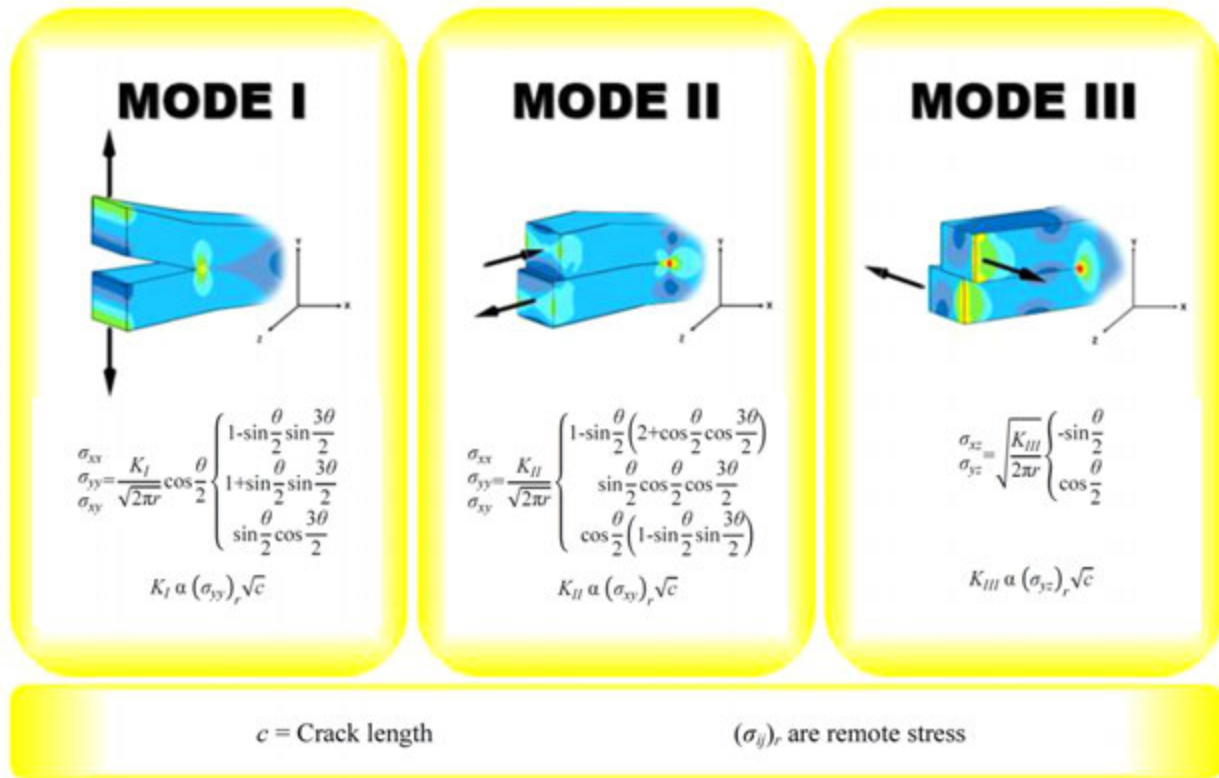


Fig. 1 Modes of loading respect to crack orientation.

application with respect to the position of the crack. It is also defined the critical stress intensity which indicates when the crack will propagate and lead to fracture, and it is known as the “fracture toughness”. The higher the fracture toughness, the more difficult will be to initiate and propagate a crack (Anderson, 2017). Mode I is the most frequently reported in the literature and stress analysis solutions for K_I for a variety of crack locations within simple geometries have been extensively presented. Also, estimations of K_{Ic} from experimental data for a diversity of materials have been produced.

The theoretical model behind the definition of K_I assumes that the direction of crack growth is known, so that the defining equations (See Fig. 1) could only be useful when the load is applied normal to the crack and in such a way that the crack propagates in a self-similar manner. In practice, nonalignment of loads pertaining to crack orientation is the case, so the crack tip stress field involves the combination of three stress intensity factors (K_I , K_{II} and K_{III}) and it is no longer governed solely by mode I stress loading. Additionally, the direction of crack initiation is unknown and depends on combinations of K_I , K_{II} and K_{III} that satisfy some fracture criteria. Actually, modes II and III do not occur separately, but always in combination with mode I, e.g., I-II, or I-III or I-II-III. Obviously, the understanding and management of the combined modes is more complex than that presented in the studies carried out for mode I, but in the industry, the mixed-mode fracture and the mixed-mode crack growth are recognized more as the rule than as the exception, i.e., the applied loadings usually do not coincide with the orthogonal K_I - K_{II} - K_{III} space. While there are many excellent books and articles about fracture mechanics, just a handful of them deal with the mixed-mode fracture topic, and most present studies made on metals (Anderson, 2017). This is understandable, since many of the more conventional fracture criteria (maximum normal stress, critical stress intensity factor or energy release rate, etc.) that have been successful when applied to simpler crack problems, are inadequate, and often invalid, for more complex situations like those of the mixed-mode fracture process. Since most ceramic structural applications involve a combination of tensile (mode I) and shear (mode II) loading conditions, the knowledge of mixed-mode fracture behavior of ceramics is necessary for furthering the use of these materials in more applications. In this context, the present chapter is based on the published current knowledge for mixed-mode fracture and microstructural issues of crack propagation in ceramics and glasses.

Mixed-Mode Fracture Criteria

The practical importance of fracture mechanics studies relies on the prediction of crack growth, which, in turn, is based on answering two questions: When the crack will start to grow? and What direction will the crack follow?. It is well known, in a homogeneous isotropic material, crack propagation is collinear under pure mode I loading. In that case, either Irwin’s stress intensity factor theory

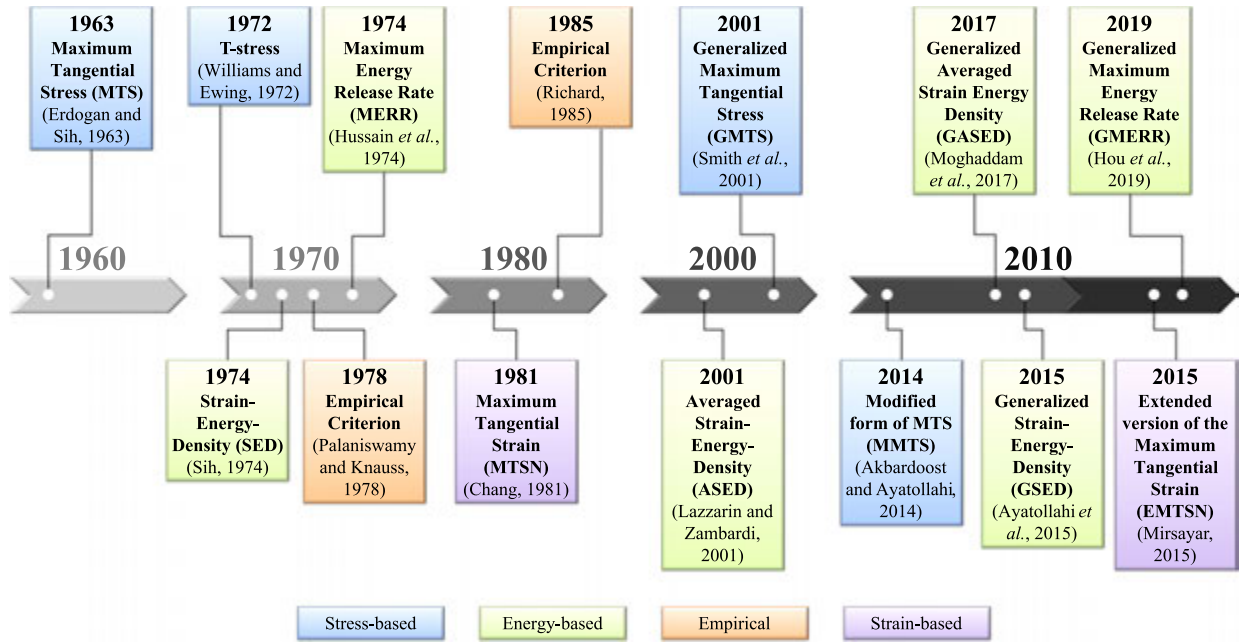


Fig. 2 Timeline of mixed-mode fracture criteria. The colors represent a classification accordingly to the supporting argument.

(K_I) or Griffith's energy release theory (G_I) could be used to establish the fracture criterion. But, under general mixed-mode conditions, the stress field at the crack tip is much more complicated to study, due to the interaction of loadings; the crack will no longer grow in its original direction and pertinent fracture criteria are needed to predict mixed mode crack extension.

Even though the earliest fracture criteria were established before 1924, it was not until the mid-60s that appeared a report on mixed-mode loading. [Erdogan and Sih \(1963\)](#) were the first to study the crack extension of brittle material under mixed-mode I/II loading and developed the maximum-stress theory, that states that a crack emerges perpendicularly to the maximum tangential stress at the crack-tip. [Williams and Ewing \(1972\)](#) produced an improved correlation for the angle of fracture by the inclusion of a non-regular term for the stress distribution around the crack tip. [Smith *et al.* \(2001\)](#) described a generalized maximum tensile stress (MTS) criterion with which a more rigorous prediction of the crack initiation angle was obtained. A decade later, at mid-70s, [Sih \(1974\)](#) proposed the minimum-strain energy density criterion or S-criterion, which states that direction of crack threshold coincides with the direction having minimum strain energy density and the crack will grow when the strain energy density reaches a critical value (S_{cr}). As with the maximum-stress theory, various researchers proposed different criteria based on the S-criterion. By the same time, [Hussain *et al.* \(1974\)](#), introduced the G-criterion based on the Griffith energy principle, assuming that, under mixed-mode loading, the crack will grow along its own original plane and that the crack initiation happens at the direction of the maximum of the energy release rate. Since then, many fracture criteria in mixed-mode loading have been published. In general, most of the reported criteria could be classified in four categories: stress-based, energy-based, strain-based and empirical. In [Fig. 2](#) some of the mixed-mode fracture criteria found in the literature are summarized and grouped within this classification.

It is not appropriate to say that one criterion is definitely superior to another. Analysts are still perplexed with selecting an appropriate fracture criterion because it requires much discernment and judgment. Criteria which often appeared valid for idealized situations are quickly discredited in practice in the face of more complex physical phenomena. Furthermore, the assertion of generality should not be on an agreement between theory and experiment for a few simple examples. Due to the lack of globally accepted fracture criteria, the determination of the structure damage, due to material failure, is still under intensive research. From a practical viewpoint, the need for a fracture criterion that can treat real situations is apparent.

Almost all of the proposed mixed-mode fracture criteria were based on linear elastic fracture mechanics (LEFM) and most only involve a combination of mode I/II loading conditions. LEFM assumes a negligible amount of plastic deformation around the crack tip, so that elastic stresses and strains can be used to determine the mechanical behavior of the specimen. According to [Williams \(1956\)](#), in the Cartesian coordinate system (See [Fig. 3\(a\)](#)) the elastic stress field around the crack tip may be expressed as a set of infinite series expansions presented in [Eq. \(1\)](#):

$$\begin{Bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \tau_{xy} \end{Bmatrix} = \frac{1}{\sqrt{2\pi r}} \begin{bmatrix} \cos \frac{\theta}{2} - \frac{1}{2} \sin \theta \sin \frac{3\theta}{2} & -2 \sin \frac{\theta}{2} + \frac{1}{2} \sin \theta \cos \frac{3\theta}{2} \\ \cos \frac{\theta}{2} + \frac{1}{2} \sin \theta \sin \frac{3\theta}{2} & \frac{1}{2} \sin \theta \cos \frac{3\theta}{2} \\ \frac{1}{2} \sin \theta \cos \frac{3\theta}{2} & \left(\cos \frac{\theta}{2} - \frac{1}{2} \sin \theta \sin \frac{3\theta}{2} \right) \end{bmatrix} \times \begin{Bmatrix} K_I \\ K_{II} \end{Bmatrix} + \begin{bmatrix} T \\ 0 \\ 0 \end{bmatrix} + \begin{Bmatrix} O(r^{1/2}) \\ O(r^{1/2}) \\ O(r^{1/2}) \end{Bmatrix} \quad (1)$$

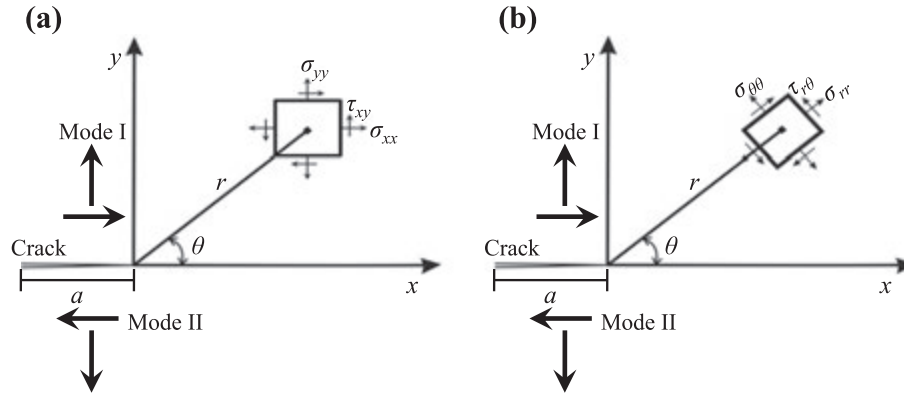


Fig. 3 Elastic stresses around the crack tip in the: (a) Cartesian coordinate system, and; (b) Polar coordinate system.

where r and θ are the conventional crack tip coordinates and σ_{xx} , σ_{yy} , and τ_{xy} represent the stresses. The first term of the right side of Eq. (1) is singular and depends on the mode I and mode II stress intensity factors (SIFs) K_I and K_{II} . The other two terms of the right side of Eq. (1) are non-singular. The first non-singular term, called “ T -stress”, enters only in σ_{xx} , the parallel-to-the-crack component of stress, and is independent of the distance from the crack tip. The higher order terms in the series expansion $O(r^{1/2})$ are often considered to be negligible near the crack tip. In the polar coordinate system (See Fig. 3(b)), the Williams’ series expansions can be written as:

$$\sigma_{\theta\theta} = \frac{1}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left[K_I \cos^2 \frac{\theta}{2} - \frac{3}{2} K_{II} \sin \theta \right] + T \sin^2 \theta + O(r^{1/2}) \quad (2)$$

$$\sigma_{rr} = \frac{1}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left[K_I \left(1 + \sin^2 \frac{\theta}{2} \right) + K_{II} \left(\frac{3}{2} \sin \theta - 2 \tan \frac{\theta}{2} \right) \right] + T \cos^2 \theta + O(r^{1/2}) \quad (3)$$

$$\tau_{r\theta} = \frac{1}{2\sqrt{2\pi r}} \cos \frac{\theta}{2} [K_I \sin \theta + K_{II} (3 \cos \theta - 1)] - T \sin \theta \cos \theta + O(r^{1/2}) \quad (4)$$

where $\sigma_{\theta\theta}$, σ_{rr} and $\tau_{r\theta}$ are the polar stresses. The crack tip parameters K_I , K_{II} , and T are known functions of the external loads and depend on the geometry and loading configurations, as such, then can vary considerably for different specimens. Analytical, experimental and numerical methods are three major techniques for calculating the crack tip parameters (Anderson, 2017). According to Ayatollahi and Aliha (2007), for complicated geometry and loading conditions, the finite element technique has proved to be an useful and comprehensive tool for determining the crack tip parameters.

Maximum Tangential Stress Criterion

Erdogan and Sih (1963) stated two hypotheses for the extension of cracks in a brittle material under slowly applied plane loads: (1) crack extension starts at its tip in radial direction, and; (2) crack extension starts in the plane perpendicular to the direction of greatest tension. These hypotheses imply that the crack will start to grow from the tip in the direction along which the tangential stress $\sigma_{\theta\theta}$, is maximum and the shear stress $\tau_{r\theta}$, is zero. Subsequently, the maximum tangential stress (MTS) criterion suggests that, for a brittle material, crack propagation initiates along the direction θ_0 of maximum tangential stress around the crack tip (See Fig. 4). It is important to note that when the stress intensity at pre-existing crack tip increases to a certain level, the crack (with a half-length, a) (See Fig. 4) will extend a small length, $\bar{a}$, to form a branch crack along the direction θ_0 . In case of initiation of fracture, instead of fracture propagation, the length of $\bar{a}$ can be assumed to shrink to zero. It indicates that the stresses around the tip of branch crack are approximately equal to the stresses (such as $\sigma_{\theta\theta}$ and $\tau_{r\theta}$) at the tip of original crack with a direction $\theta = \theta_0$. Therefore, the angle θ_0 can be found by solving Eq. (5):

$$\frac{\partial \sigma_{\theta\theta}}{\partial \theta} = 0 \Rightarrow \theta = \theta_0 \quad (5)$$

Erdogan and Sih’s MTS criterion (Erdogan and Sih, 1963) ignores the contribution of the non-singular stress term, T -stress, and the higher order terms $O(r^{1/2})$ of the Williams’ model (Eqs. (1)–(4)). Hence, from Eqs. (2) and (5), θ_0 is determined by solving Eq. (6):

$$K_I \sin \theta_0 + K_{II} (3 \cos \theta_0 - 1) = 0 \quad (6)$$

Plugging the value of θ_0 in Eq. (2), the conditions for the onset of crack propagation can be found, as in Eq. (7):

$$\cos \frac{\theta_0}{2} \left[K_I \cos^2 \frac{\theta_0}{2} - \frac{3}{2} K_{II} \sin \theta_0 \right] = \text{constant} = \sqrt{2\pi r_c} (\sigma_{\theta\theta})_c \quad (7)$$

where r_c is the critical radius from the crack tip and $(\sigma_{\theta\theta})_c$ is the critical value of the tangential stress at the critical radius r_c , material properties that are assumed to be independent of the geometry of specimen and loading configuration. Eqs. (6) and (7) describe

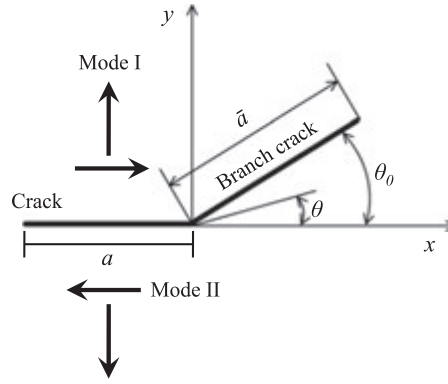


Fig. 4 Geometry for the branch crack.

the MTS criterion where mixed mode I/II fracture is predicted for any geometry in which K_I and K_{II} are known. For pure mode I (K_{II} and θ_0 are equal to zero), K_I at fracture can be replaced by the mode I fracture toughness K_{Ic} , that is also a material property, and Eq. (7) reduces to:

$$\sqrt{2\pi r_c}(\sigma_{\theta\theta})_c = K_{Ic} \quad (8)$$

As mentioned earlier, in mixed mode I/II conditions, the crack growth is not in the same plane as the initial crack. For this case, the T -stress contributes to the tangential stress (along the direction of initiation of crack growth) and hence influences the apparent mixed mode fracture toughness. Smith *et al.* (2001) re-examined the role of the T -stress in brittle fracture for linear elastic materials and proposed the generalized MTS criterion (GMTS). GMTS takes into account the effects of both, the singular terms and the T -stress term, in the tangential stress around the crack tip. Retaining both the singular terms and the T -stress in Eqs. (2)–(4), the MTS criterion, θ_0 is determined by solving Eq. (9):

$$[K_I \sin \theta_0 + K_{II}(3 \cos \theta_0 - 1)] - \gamma \sin \frac{\theta_0}{2} \cos \theta_0 = 0 \quad (9)$$

where:

$$\gamma = 16(T\sqrt{2\pi r_c})/3 = 16(B\alpha K_{eff})/3 \quad (10)$$

$$B = (T\sqrt{\pi a})/K_{eff} \quad (11)$$

$$\alpha = \sqrt{2r_c/a} \quad (12)$$

$$K_{eff} = \sqrt{(K_I^2 + K_{II}^2)} \quad (13)$$

B is often called the biaxiality ratio, since it is equal to the ratio of T -stress to the effective stress intensity factor (K_{eff}), α is the dimensionless form of the critical radius from the crack tip, a is the crack length (semi-crack length for center cracks and the crack length for edge-cracks). Therefore, the conditions for the onset of crack propagation are giving by:

$$\cos \frac{\theta_0}{2} \left[K_I \cos^2 \frac{\theta_0}{2} - \frac{3}{2} K_{II} \sin \theta_0 \right] = K_{Ic} - T\sqrt{2\pi r_c} \sin^2 \theta_0 \quad (14)$$

or, in term of the biaxiality ratio, B :

$$\cos \frac{\theta_0}{2} \left[K_I \cos^2 \frac{\theta_0}{2} - \frac{3}{2} K_{II} \sin \theta_0 \right] = -B\alpha K_{eff} \sin^2 \theta_0 + K_{Ic} \quad (15)$$

Using this criterion, the direction and the onset of fracture initiation can be predicted for any combination of the crack tip parameters K_I , K_{II} and T . Smith *et al.* (2001) also defined the mixity parameter M^e given in Eq. (16):

$$M^e = \frac{2}{\pi} \tan^{-1} \left(\frac{K_I}{K_{II}} \right) \quad (16)$$

The value of M^e is one for pure mode I and zero for pure mode II. Usually, it is shown that positive T reduces the apparent fracture toughness in mixed mode loading and a negative T increases it (Smith *et al.*, 2001). In 2014, Akbardoost and Ayatollahi (2014) proposed a modified form of MTS (MMTS) criterion which takes into account the effects of three non-singular stress terms (T , A_3 and B_3) in addition to the singular terms (SIFs). A_3 and B_3 are constant coefficients of the third terms in the Williams series expansion for the tangential stress component, $\sigma_{\theta\theta}$, around the crack tip that now can be written as:

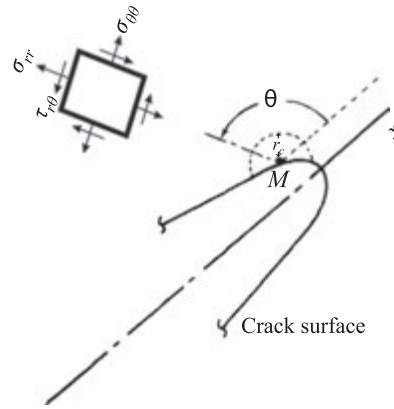


Fig. 5 Location of the maximum surface tangential strain, point M, and its stress element.

$$\begin{aligned} \sigma_{\theta\theta} = & \frac{3}{4} \frac{K_I}{\sqrt{2\pi r}} \left(\cos \frac{\theta}{2} + \frac{1}{3} \cos \frac{3\theta}{2} \right) + T \sin^2 \theta + \frac{15}{4} \sqrt{r} A_3 \left(\cos \frac{\theta}{2} - \frac{1}{5} \cos \frac{5\theta}{2} \right) - \frac{3}{4} \frac{K_{II}}{\sqrt{2\pi r}} \left(\sin \frac{\theta}{2} + \sin \frac{3\theta}{2} \right) \\ & - \frac{15}{4} \sqrt{r} B_3 \left(\sin \frac{\theta}{2} - \sin \frac{5\theta}{2} \right) + O(r) \end{aligned} \quad (17)$$

The fracture parameters K_I , K_{II} , T , A_3 and B_3 are known and depend on the geometry and loading conditions of the test specimen and their magnitudes may vary over a wide range for different test samples. The MMTS criterion ignores the remaining terms of the series expansion represented by $O(r)$. Similar to MTS and GMTS criterion, using Eqs. (2) and (17), an expression for θ_0 can be obtained in order to predict the mixed mode I/II fracture resistance. The predicted curves using MMTS criterion, based on a more accurate equation in which higher order terms of Williams expansion are taken into account, show better agreement with reported experimental results than other conventional criteria.

Maximum Tangential Strain Criterion

Chang (1981) modified the maximum-normal-strain theory of St-Venant and applied it to the study of the angled crack problem. This modified criterion, called maximum tangential strain (MTSN) criterion, states: (1) Crack extension starts from the location of the maximum surface tangential strain (point M in Fig. 5), along a direction θ equal to θ_0 , at which the circumferential strain $\varepsilon_{\theta\theta}$, on a circular arc of (small) radius r_c from point M, reaches a maximum value with respect to θ , and; (b) Fracture is imminent when the maximum strain $\varepsilon_{\theta\theta}$, at the distance r_c from point M, reaches a critical value ε_F . These statements are equivalent to Eqs. (18)–(19) below.

$$\left. \frac{\partial \varepsilon_{\theta\theta}}{\partial \theta} \right|_{r=r_c; \theta=\theta_0} = 0 \quad (18)$$

$$\left. \frac{\partial^2 \varepsilon_{\theta\theta}}{\partial \theta^2} \right|_{r=r_c; \theta=\theta_0} < 0 \quad (19)$$

$$(\varepsilon_{\theta\theta})_c = \varepsilon_F = \sigma_F / E \quad (20)$$

where σ_F is the tensile fracture strength and E is Young's modulus of the material. The critical distance r_c could be considered as damaged zone around the crack tip which is a material property. The linear elastic relationship between the tangential strain and stress components is given by Eq. (21):

$$\varepsilon_{\theta\theta} = \frac{1}{E} (\sigma_{\theta\theta} - \nu \sigma_{rr}) \quad (21)$$

where ν is the Poisson's ratio and $\sigma_{\theta\theta}$ and σ_{rr} are the tangential and radial components of the stress field polar coordinate system, respectively. The MTSN criterion claims that fracture initiation depends not only on the geometry and boundary conditions but also on the Poisson's ratio, ν , of the material. It is clear from Eq. (21) that predictions based on MTSN criterion will coincide with those made with MTS criterion when $\nu = 0$. Substituting Eqs. (2) and (3) into Eq. (21), and taking into account only the singular stress terms (associated with the K_I and K_{II}), the conventional MTSN could be represented by Eqs. (22) and (23):

$$\frac{K_I}{E\sqrt{2\pi r_c}} \{f'_{\theta\theta,1}(\theta_0) - \nu \times f'_{rr,1}(\theta_0)\} + \frac{K_{II}}{E\sqrt{2\pi r_c}} \{f'_{\theta\theta,2}(\theta_0) - \nu \times f'_{rr,2}(\theta_0)\} = 0 \quad (22)$$

$$\frac{K_I}{E\sqrt{2\pi r_c}} \{f_{\theta\theta,1}(\theta_0) - \nu \times f_{rr,1}(\theta_0)\} + \frac{K_{II}}{E\sqrt{2\pi r_c}} \{f_{\theta\theta,2}(\theta_0) - \nu \times f_{rr,2}(\theta_0)\} = \varepsilon_F = \sigma_F/E \quad (23)$$

where

$$f'_{ij,n}(\theta_0) = \frac{\partial}{\partial \theta} [f_{ij,n}(\theta)] \Big|_{\theta=\theta_0} \quad (24)$$

and $(i, j) \equiv (r, \theta)$ are the polar coordinates with the origin at the crack tip and the functions $f_{ij,n}(\theta)$ [$ij \equiv r, \theta; n \equiv 1$ (mode I, opening), 2 (mode II, sliding)] are given by Eqs. (25)–(28):

$$f_{rr,1}(\theta) = \frac{1}{4} \left(5\cos\frac{\theta}{2} - \cos\frac{3\theta}{2} \right) \quad (25)$$

$$f_{rr,2}(\theta) = \frac{1}{4} \left(-5\sin\frac{\theta}{2} + 6\sin\frac{3\theta}{2} \right) \quad (26)$$

$$f_{\theta\theta,1}(\theta) = \frac{1}{4} \left(3\cos\frac{\theta}{2} + \cos\frac{3\theta}{2} \right) \quad (27)$$

$$f_{\theta\theta,2}(\theta) = \frac{1}{4} \left(-3\sin\frac{\theta}{2} - \sin\frac{3\theta}{2} \right) \quad (28)$$

Fracture initiation angle, θ_0 , obtained from Eq. (22), is used to find the onset conditions of fracture when the left-hand side of the Eq. (23) reaches the tensile fracture strength. Mirsayar (2015) modified the MTSN criterion and proposed the extended version of the maximum tangential strain (EMTSN), retaining singular stress terms and adding the T -stress into Eq. (21). Hence, Eqs. (22) and (23) can be written as:

$$\frac{K_I}{E\sqrt{2\pi r_c}} \{f'_{\theta\theta,1}(\theta_0) - \nu \times f'_{rr,1}(\theta_0)\} + \frac{K_{II}}{E\sqrt{2\pi r_c}} \{f'_{\theta\theta,2}(\theta_0) - \nu \times f'_{rr,2}(\theta_0)\} + (1 + \nu) \frac{T}{E} \sin(2\theta_0) = 0 \quad (29)$$

$$\frac{K_I}{E\sqrt{2\pi r_c}} \{f_{\theta\theta,1}(\theta_0) - \nu \times f_{rr,1}(\theta_0)\} + \frac{K_{II}}{E\sqrt{2\pi r_c}} \{f_{\theta\theta,2}(\theta_0) - \nu \times f_{rr,2}(\theta_0)\} + \frac{T}{E} [\sin^2(\theta_0) - \nu \cos^2(\theta_0)] = \sigma_F/E \quad (30)$$

or, in term of biaxiality ratio, B (Eq. (11)):

$$K_I \{f_{\theta\theta,1}(\theta_0) - \nu \times f_{rr,1}(\theta_0)\} + K_{II} \{f_{\theta\theta,2}(\theta_0) - \nu \times f_{rr,2}(\theta_0)\} = \sigma_F \sqrt{2\pi r_c} - B\alpha K_{eff} [\sin^2(\theta_0) - \nu \cos^2(\theta_0)] \quad (31)$$

In Eq. (30), the first non-singular tangential strain term in the left hand of the equation, corresponding to parameter T , is called “tangential T -strain”. This tangential T -strain is equal to the well-known T -stress, defined by Williams (1956). Radial and shear components are associated within the tangential T -strain term and, normally, they are determined by finite element analysis. Finally, Mirsayar (2015) defined the parameter K_{Ic}^* , identified as “generalized fracture toughness”, as in Eq. (32), that takes into account the effect of both Poisson’s ratio and specimen geometry ($B\alpha$) in calculation of the mode I fracture toughness.

$$K_{Ic}^* = \frac{\sigma_F \sqrt{2\pi r_c}}{1 - \nu(1 + B\alpha)} \quad (32)$$

Energy-Based Criteria

Maximum energy release rate criterion

Hussain *et al.* (1974) proposed the maximum energy release rate (MERR) criterion, for which the fracture takes place from the crack tip along the direction (θ_0) of maximum energy release rate. Departing from Griffith’s energy release theory, they computed the energy release rate G for combined mode I and mode II under plane stress conditions as:

$$G = \frac{1}{E} (K_I^2 + K_{II}^2) \quad (33)$$

where K_I and K_{II} are the SIFs for mode I and mode II, respectively; and E is the Young’s modulus of the material. Eq. (33) was obtained by assuming that the crack, under combined loading, moves along its own initial plane. Unfortunately, the crack extension is not collinear, for a crack subjected to either skew-symmetric loads or combined loads. Hence, an equation that would give the energy release rate for an arbitrary direction of crack propagation is necessary for applying the Griffith-Irwin energy release rate criterion to cracks under combined loads. When the fracture initiation takes place running apart from the original crack, in the direction $\theta = \theta_0$, the energy release rate for the branch crack, G_θ , can be obtained from Eq. (34):

$$G_\theta = \frac{2\pi r}{E'} (\sigma_{\theta\theta}^2 + \tau_{r\theta}^2) \quad (34)$$

where E' equals E for plane stress condition, or $[E/(1 - \nu^2)]$ for plane strain condition, with E and ν the Young’s modulus and Poisson’s ratio, respectively. According to MERR criterion when the energy release rate along the direction θ_0 and at a critical distance r_c from the crack tip reaches its critical value, the crack initiation will take place along the fracture initiation angle θ_0 . Therefore, the fracture initiation angle θ_0 can be determined by solving the following equations:

$$\left. \frac{\partial G_\theta}{\partial \theta} \right|_{r=r_c; \theta=\theta_0} = 0 \quad (35)$$

$$\left. \frac{\partial^2 G_\theta}{\partial \theta^2} \right|_{r=r_c; \theta=\theta_0} < 0 \quad (36)$$

If the energy release rate due to the initiation of a branch crack only depends on the stress state before fracture begins, Eqs. (2) and (4) can be used to rewrite Eq. (34) (ignoring the high order term $O(r^{1/2})$), and the energy release rate G_θ can be obtained as:

$$G_\theta = \frac{1}{E'} \left[B_1 K_I^2 + B_2 K_{II}^2 + B_3 K_I K_{II} + B_4 \sqrt{2\pi r} K_I T + B_5 \sqrt{2\pi r} K_{II} T + B_6 (2\pi r) T^2 \right] \quad (37)$$

where

$$B_1 = \frac{1}{4} (\cos \theta + 1)^2 \quad (38)$$

$$B_2 = -3 \sin^4 \frac{\theta}{2} + 2 \sin^2 \frac{\theta}{2} + 1 \quad (39)$$

$$B_3 = -\frac{1}{2} \sin(2\theta) - \sin \theta \quad (40)$$

$$B_4 = -4 \cos^5 \frac{\theta}{2} + 4 \cos^3 \frac{\theta}{2} \quad (41)$$

$$B_5 = 4 \sin^5 \frac{\theta}{2} - 4 \sin^3 \frac{\theta}{2} \quad (42)$$

$$B_6 = \sin^2 \theta \quad (43)$$

Eq. (37) for G_θ into Eq. (35), gives θ_0 as the solution of Eq. (44):

$$C_1 K_I^2 + C_2 K_{II}^2 + C_3 K_I K_{II} + C_4 \sqrt{2\pi r_c} K_I T + C_5 \sqrt{2\pi r_c} K_{II} T + C_6 (2\pi r_c) T^2 = 0 \quad (44)$$

in which

$$C_1 = -\frac{1}{4} \sin(2\theta_0) - \frac{1}{2} \sin \theta_0 \quad (45)$$

$$C_2 = \frac{3}{4} \sin(2\theta_0) - \frac{1}{2} \sin \theta_0 \quad (46)$$

$$C_3 = -2 \cos^2 \theta_0 - \cos \theta_0 + 1 \quad (47)$$

$$C_4 = 10 \sin^5 \frac{\theta_0}{2} - 14 \sin^3 \frac{\theta_0}{2} + 4 \sin \frac{\theta_0}{2} \quad (48)$$

$$C_5 = 10 \cos^5 \frac{\theta_0}{2} - 20 \cos^3 \frac{\theta_0}{2} + 8 \cos \frac{\theta_0}{2} \quad (49)$$

$$C_6 = \sin(2\theta_0) \quad (50)$$

When the energy release rate at the crack tip reaches a critical value, the crack starts to grow. At this time:

$$G_\theta = G_{\theta c} \quad (51)$$

where $G_{\theta c}$ is the critical value of the energy release rate at the critical distance r_c along the direction $\theta = \theta_0$. Combining the Eqs. (37) and (51), the following equation can be obtained:

$$G_{\theta c} = \frac{1}{E'} \left[B_1 K_I^2 + B_2 K_{II}^2 + B_3 K_I K_{II} + B_4 \sqrt{2\pi r_c} K_I T + B_5 \sqrt{2\pi r_c} K_{II} T + B_6 (2\pi r_c) T^2 \right] \quad (52)$$

For pure mode I when K_{II} and θ_0 are equal to zero, K_I at fracture can be replaced by the mode I fracture toughness K_{Ic} , that is a material property, and Eq. (52) reduces to:

$$G_{\theta c} = \frac{1}{E'} K_{Ic}^2 \quad (53)$$

Therefore, Eq. (52) can be rewritten as:

$$K_{Ic}^2 = B_1 K_I^2 + B_2 K_{II}^2 + B_3 K_I K_{II} + B_4 \sqrt{2\pi r_c} K_I T + B_5 \sqrt{2\pi r_c} K_{II} T + B_6 (2\pi r_c) T^2 \quad (54)$$

Eqs. (44) and (54) can be used to predict the initiation of the mixed mode I/II crack and the model is called "generalized maximum energy release rate criterion" (GMERR), proposed by Hou *et al.* (2019) as an improvement of the conventional MERR criterion, in consideration to the important role that T -stress plays in the fracture analysis of the materials under mixed mode loading. It is, also, a way to avoid the overestimating or underestimating of the fracture initiation angles and fracture resistances.

Strain-energy-density criterion

The search for a quantity that would provide a description of the direction of crack growth under mixed mode I/II conditions, as well as a measure of the intrinsic property of the material, led to model the energy concentrated in the crack tip region where fracture may take place. Sih (1974) modeled the strain-energy density distribution around the crack tip by considering that the strain energy stored dW , in the element dA for a plane elasticity problem can be found from:

$$\frac{dW}{dA} = \frac{1}{2\mu} \left[\frac{\kappa+1}{8} (\sigma_{rr} + \sigma_{\theta\theta})^2 - \sigma_{rr}\sigma_{\theta\theta} + \tau_{r\theta}^2 \right] \quad (55)$$

where $\sigma_{\theta\theta}$, σ_{rr} and $\tau_{r\theta}$ are the polar stresses, μ is the modulus of rigidity or shear modulus equal to $[E/2(1+\nu)]$ and κ is an elastic constant that equals $(3-4\nu)$ or $[(3-\nu)/(1+\nu)]$ for the plane strain or for plane stress problems, respectively. Therefore, the strain energy density factor, S , which represents the strength of the elastic energy field in the vicinity of the crack tip can be defined as:

$$S = r \frac{dW}{dA} = \frac{r}{2\mu} \left[\frac{\kappa+1}{8} (\sigma_{rr} + \sigma_{\theta\theta})^2 - \sigma_{rr}\sigma_{\theta\theta} + \tau_{r\theta}^2 \right] \quad (56)$$

Sih (1974) proposed the strain-energy-density (SED) criterion, that consider as hypotheses for crack initiation in a two-dimensional stress field that: (1) The initial crack growth takes place in the direction along $\theta = \theta_0$ which the strain-energy-density factor possesses a stationary (minimum), and; (2) Crack initiation occurs when the strain-energy-density factor reaches a critical value, S_{cr} . This criterion represented by:

$$\left. \frac{\partial S}{\partial \theta} \right|_{r=r_c; \theta=\theta_0} = 0 \quad (57)$$

$$\left. \frac{\partial^2 S}{\partial \theta^2} \right|_{r=r_c; \theta=\theta_0} > 0 \quad (58)$$

$$S = S_{cr} \text{ for } \theta = \theta_0 \text{ and } r = r_c \quad (59)$$

By replacing the stress components from Eqs. (2), (3) and (4) into Eq. (56), the strain energy density factor S , can be written as:

$$S = a_1 K_I^2 + a_2 K_{II}^2 + a_3 K_I K_{II} + a_4 K_I T + a_5 K_{II} T + a_6 T^2 \quad (60)$$

where

$$a_1 = \frac{1}{16\pi\mu} (\kappa - \cos\theta)(1 + \cos\theta) \quad (61)$$

$$a_2 = \frac{1}{16\pi\mu} [\kappa(1 - \cos\theta) + \cos\theta(1 + 3\cos\theta)] \quad (62)$$

$$a_3 = \frac{1}{8\pi\mu} \sin\theta [2\cos\theta - (\kappa - 1)] \quad (63)$$

$$a_4 = \frac{\sqrt{2r}}{8\sqrt{\pi\mu}} \cos\frac{\theta}{2} [\cos(2\theta) - \cos\theta + (\kappa - 1)] \quad (64)$$

$$a_5 = -\frac{\sqrt{2r}}{8\sqrt{\pi\mu}} \sin\frac{\theta}{2} [\cos(2\theta) + \cos\theta + (\kappa + 1)] \quad (65)$$

$$a_6 = \frac{(\kappa + 1)r}{16\mu} \quad (66)$$

Substituting the Eq. (60) into Eq. (57), the angle θ_0 can be found from:

$$c_1 K_I^2 + c_2 K_{II}^2 + c_3 K_I K_{II} + c_4 (B\alpha K_{eff}) K_I + c_5 (B\alpha K_{eff}) K_{II} + c_6 (B\alpha K_{eff})^2 = 0 \quad (67)$$

in which

$$c_1 = \frac{1}{16\pi\mu} \sin\theta_0 (2\cos\theta_0 - \kappa + 1) \quad (68)$$

$$c_2 = -\frac{1}{16\pi\mu} \sin\theta_0 (6\cos\theta_0 - \kappa + 1) \quad (69)$$

$$c_3 = \frac{1}{8\pi\mu} [2\cos(2\theta_0) - (\kappa - 1)\cos\theta_0] \quad (70)$$

$$c_4 = -\frac{1}{16\pi\mu} \sin\frac{\theta_0}{2} \left\{ 5[\cos(2\theta_0) + \cos\theta_0] + (\kappa + 1) \right\} \quad (71)$$

$$c_5 = -\frac{1}{16\pi\mu} \cos\frac{\theta_0}{2} \left\{ 5[\cos(2\theta_0) - \cos\theta_0] + (\kappa + 3) \right\} \quad (72)$$

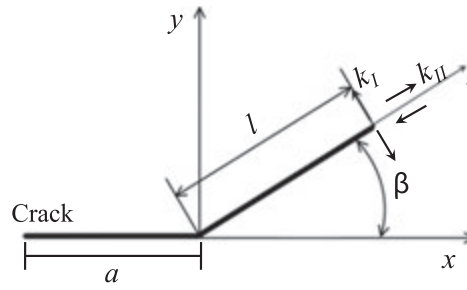


Fig. 6 Geometry of kinked crack.

$$c_6 = 0 \quad (73)$$

As before, B is the biaxiality ratio of Eq. (11), α is the dimensionless form of the critical radius from the crack tip and K_{eff} is the effective stress intensity factor. By substituting the angle of crack growth (θ_0) into Eq. (60), the onset of crack propagation can be determined. Brittle fracture takes place when the SED factor reaches its critical value S_{cr} . According to Sih (1974), there is a direct relation between S_{cr} and mode I fracture toughness K_{Ic} as:

$$S_{cr} = \frac{1}{8\pi\mu} (\kappa - 1) K_{Ic}^2 \quad (74)$$

Conventional SED criterion only considers the singular terms of Williams' expansion. Ayatollahi *et al.* (2015) introduced the effect of T-stress in addition to the stress intensity factors K_I and K_{II} that are already present in the conventional SED criterion and developed the model called the generalized strain energy density (GSED) criterion, as described in the Eqs. (60) and (67). The advantage of the generalized SED criterion relative to the conventional SED criterion is more noticeable in cracked components that have significant value of T-stress under mixed mode loading and for materials that possess large critical distances.

Other criterion based on strain-density-energy were proposed by Lazzarin and Zambardi (2001) and Moghaddam *et al.* (2017). In Lazzarin and Zambardi (2001), the averaged strain energy density (ASED) criterion in order to predict the mixed mode I/II fracture resistance of brittle and quasi-brittle materials is proposed. This criterion utilizes the deformation energy averaged in a control volume of radius r_c to estimate the fracture load for both cracked and notched specimens. In crack problems, the control volume has a circular shape and its radius r_c is a material property. Brittle fracture takes place when the averaged value of the deformation energy inside the control volume reaches a critical value (also a material property). To obtain the average value of strain energy density around the crack tip finite element analysis is used. In Moghaddam *et al.* (2017) a modified energy-based model called the generalized averaged strain energy density (GASED) criterion is proposed. It considers the effect of T-stress in addition to the stress intensity factors K_I and K_{II} in the Williams' series expansion when calculating the strain energy density averaged in a control volume around the crack tip.

Empirical Criterion

The three criteria reviewed in the sections above, although different in their approaches, result in very similar predictions for both the directions of crack extensions and the critical conditions of loading for mixed mode fracture. These theoretical predictions can also be fitted very closely with the empirical function of the equation proposed by Palaniswamy and Knauss (1978):

$$\left(\frac{K_I}{K_{Ic}}\right) + \frac{3}{2} \left(\frac{K_{II}}{K_{Ic}}\right)^2 = 1 \quad (75)$$

where K_I and K_{II} are the mode I and mode II SIFs; and K_{Ic} is the mode I fracture toughness. Under mixed mode I/II loading, Cotterell and Rice (1980) suggested that a crack may extend in a plane deviating from the original by kinking. Such a kink of length, l , with a sudden change of the original direction by an angle, β , is shown in Fig. 6.

According to Bilby *et al.* (1978) and Cotterell and Rice (1980), the local mixed-mode stress intensity factors k_I and k_{II} can be computed from the singular stress field produced ahead of the original (unkinked) crack as:

$$K_I = c_{11}K_I + c_{12}K_{II} \quad (76)$$

$$K_{II} = c_{21}K_I + c_{22}K_{II} \quad (77)$$

where

$$C_{11} = \cos^3\left(\frac{\beta}{2}\right) \quad (78)$$

$$C_{12} = -3\sin\left(\frac{\beta}{2}\right)\cos^2\left(\frac{\beta}{2}\right) - \frac{1}{3}\sin^3\left(\frac{\beta}{2}\right) \quad (79)$$

$$C_{21} = \sin\left(\frac{\beta}{2}\right) \cos^2\left(\frac{\beta}{2}\right) \quad (80)$$

$$C_{22} = \cos\left(\frac{\beta}{2}\right) \left[1 - 3\sin^2\left(\frac{\beta}{2}\right)\right] + \frac{1}{6}\sin^2\left(\frac{4\beta}{5}\right) \quad (81)$$

For the limit case $K_{II} \ll K_I$ ($K_{II}/K_I \rightarrow 0$), expansion of Eqs. (78) and (79) can be obtained and an approximation of k_I can be found from:

$$K_I = \left(1 - \frac{3}{8}\beta^2\right)K_I - \left(\frac{3}{2}\beta\right)K_{II} \quad (82)$$

The maximum value of k_I results from solving:

$$\frac{dk_I}{d\beta} = 0 \quad (83)$$

and thus,

$$\beta = -2\frac{K_{II}}{K_I} \quad (84)$$

Substituting Eq. (84) into Eq. (82) and assuming the failure will occur if k_I reaches the value K_{Ic} ($k_I = K_{Ic}$), Eq. (85) can be obtained:

$$K_I^2 - K_{Ic}K_I + \frac{3}{2}K_{II}^2 = 0 \quad (85)$$

Solving the quadratic equation and simplifying:

$$K_I = \frac{1}{2}K_{Ic} \left[1 \pm \sqrt{1 - 6\left(\frac{K_{II}}{K_{Ic}}\right)^2}\right] \cong \frac{1}{2}K_{Ic} \left\{1 \pm \left[1 - 3\left(\frac{K_{II}}{K_{Ic}}\right)^2\right]\right\} \rightarrow \left(\frac{K_I}{K_{Ic}}\right) + \frac{3}{2}\left(\frac{K_{II}}{K_{Ic}}\right)^2 = 1; \text{ with } \beta = -2\frac{K_{II}}{K_I} \quad (86)$$

and, thus, the empirical criterion, proposed by Palaniswamy and Knauss (1978), is finally obtained. For the limit case $K_{II} \gg K_I$ ($K_{II}/K_I \rightarrow \infty$), it is necessary to deduce the maximum value of the function C_{12} :

$$\max[C_{12}] = C_{12}(\beta_{\max}) = 1.2247 \quad (87)$$

therefore

$$\beta_{\max} \cong -1.33(-76^\circ) \quad (88)$$

The value of the crack deflection angle under pure mode II loading obtained by this empirical criterion ($\beta_{\max} = -76^\circ$) is close to the values calculated using MTS criterion ($\theta_0 = -70.5^\circ$) (Erdogan and Sih, 1963) and SED criterion ($\theta_0 = -79.2^\circ$, with $\nu = 0.22$) (Sih, 1974). Richard (1985) proposed an empirical criterion with the form:

$$\left(\frac{K_I}{K_{Ic}}\right)^u + \left(\alpha\frac{K_{II}}{K_{Ic}}\right)^v = 1 \quad (89)$$

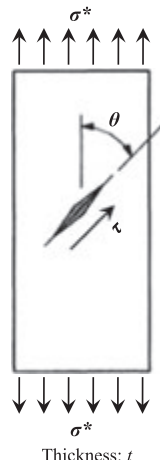
where u and v are exponents that could be varied in order to obtain a reasonably good fit to the experimental data and α is the relation between mode I fracture toughness K_{Ic} and mode II fracture toughness K_{IIc} ($\alpha = K_{Ic}/K_{IIc}$). When $u = 1$, $v = 2$ and $\alpha = \sqrt{3}/2 = 1.2247$, the Richard's criterion is exactly the empirical criterion proposed by Palaniswamy and Knauss (1978) (Eq. 75), and the value of the coefficient α is in agreement with the limit case $K_{II} \gg K_I$, as can be seen from Eq. (86).

Testing in Mixed-Mode Fracture

It is widely recognized that catastrophic fracture can be initiated in structural ceramic components at cracks or preexisting flaws which are oriented at arbitrary angles to the far-field loading directions or subjected to multiaxial stresses. According to Suresh *et al.* (1990), the efficient and safe design of advanced ceramics for potential structural applications inevitably requires the development of fracture data and failure criteria for combinations of mode I (tensile opening), mode II (in-plane shear), or mode III (tearing) loading. Several studies had been conducted on mixed-mode fracture of ceramic materials, but, unfortunately, conflicting experimental results have generated controversy and discussions on the validity of multiaxial test data and failure criteria.

This begins with a suitable fracture test specimen, that should have some benefits such as simple configuration, inexpensive preparation method, ease of loading set-up and ability of providing full loading conditions ranging from pure mode I to pure mode II (Pirmohammad and Mengharpey, 2018). For the determination of combined mode I/II fracture initiation resistance in ceramics, researchers have been employed various fracture test specimens for conducting mixed mode I/II experiments, among them it is worth to mention: inclined Knoop surface flaw in bending bars (Petrovic *et al.*, 1975; Petrovic and Mendiratta, 1976; Munz and Fett, 1999), Oblique Edge Notched Beam (OENB) (Fett *et al.*, 1995), Single Edge Notched Beam (SENB) (Fett *et al.*, 1995; Xeidakis *et al.*, 1996; Paulino and Kim, 2004), Brazilian Disc specimen (BD) (Shetty *et al.*, 1983, 1986, 1987; Shetty, 1987; Atahan *et al.*, 2005), Compact Shear specimen (CS) (Hoyniak and Conway, 1979; Marsavina *et al.*, 2017), Single Edge Crack (SEC)

Table 1 Resume of fracture test specimens for conducting mixed mode I/II experiments and loading conditions

Fracture test specimen	Geometry	Observations
Inclined Knoop surface flaw	 Thickness: t	– A single Knoop surface flaw, with a depth a and a surface length $2c$, is placed on the tensile surface at an orientation angle θ with respect to the specimen length axis. The externally applied uniaxial stress σ^* (performed with a 4-point bending test) gives rise to a stress normal to the crack and a shear stress τ in the crack plane: $\sigma_{n(x)} = \sigma^*_{(x)} \sin^2 \theta \quad (90)$ $\tau_{(x)} = \sigma^*_{(x)} \sin \theta \cos \theta \quad (91)$

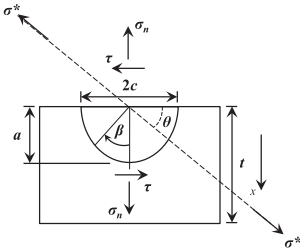
In a bending test σ^* decreases linearly with the distance from the surface. The Knoop crack was assumed to be a semi-circular crack, which is nearly in agreement with experimental results, and the decrease of σ^* was neglected ($a/t \ll 1$). The stress intensity factors used were for a crack in an infinite body where surface effects are ignored:

$$K_I = \left(2\sqrt{a/\pi} \right) \sigma_n \quad (92)$$

$$K_{II} = \left(\frac{4}{2-v} \sqrt{a/\pi} \right) \tau \sin \beta \quad (93)$$

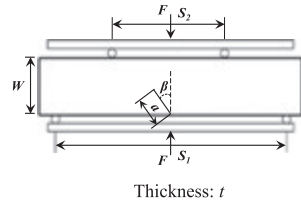
$$K_{III} = \left[\frac{4(1-v)}{2-v} \sqrt{a/\pi} \right] \tau \cos \beta \quad (94)$$

(Petrovic *et al.*, 1975; Petrovic and Mendiratta, 1976; Munz and Fett, 1999)



At the depth of the flaw ($\beta = 0^\circ$), only modes I and III are present, giving the stress intensity factors K_I and K_{III} with $K_{II} = 0$. The value of K_{III} is maximum at this site. At the surface of the flaw ($\beta = 90^\circ$), only modes I and II operate, leading to the stress intensity factors K_I and K_{II} with $K_{III} = 0$. The value of K_{II} is maximum at this site. For intermediate locations along the flaw periphery, all 3 displacement modes are present.

OENB (Oblique Edge Notched Beam)



– The oblique edge-crack plate in four-point bending can be used for the determination of fracture toughness under mixed-mode condition. The stress intensity factors, K_I and K_{II} , are given by

$$K_I = \sigma Y_I \sqrt{\pi a} \quad (95)$$

$$K_{II} = \sigma Y_{II} \sqrt{\pi a} \quad (96)$$

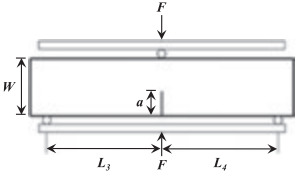
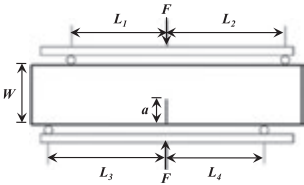
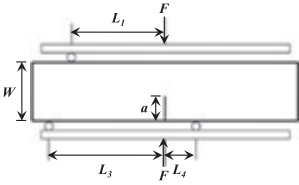
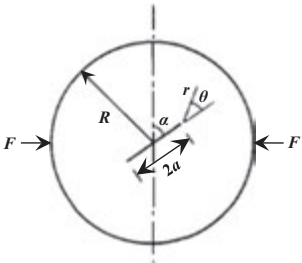
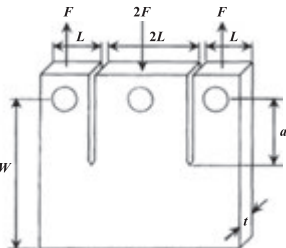
$$\sigma = \frac{3S_1 - S_2}{2tW^2} F \quad (97)$$

where t is the specimen thickness and Y_I , Y_{II} are geometric functions based on the influence of the crack length a/W and the angle β .

(Continued)

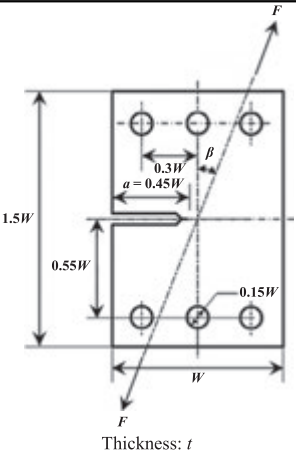
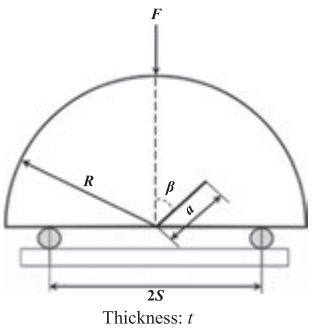
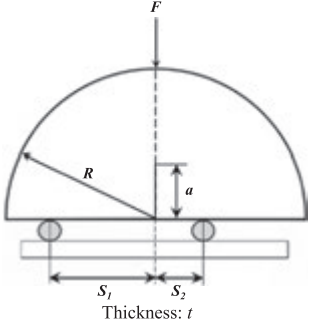
(Fett *et al.*, 1995)

Table 1 Continued

Fracture test specimen	Geometry	Observations
SENB (Single Edge Notched Beam)	– Three-point bending configuration for pure mode I ($L_3=L_4$; $K_{II}/K_I = 0$)  Thickness: t – Asymmetric four-point bending (AFPB) configuration for pure mode II ($L_1=L_4 < L_2=L_3$; $K_{II}/K_I \rightarrow \infty$)  Thickness: t	– Simple and effective method. Easy to introduce the notch. – Different bending configurations (three-point bending and asymmetric four-point bending) are necessary to change the mode of fracture from pure mode I (tensile) to pure mode II (shear). – The stress analysis of the beam (determination of K_I and K_{II}) is usually determined by a suitable finite element computer program.
(Fett <i>et al.</i> , 1995; Xeidakis <i>et al.</i> , 1996; Paulino and Kim, 2004)	– Three-point bending configuration for mixed mode loading ($L_1 \neq L_3 \neq L_4$). For example, if $L_4 = \frac{1}{4}L_3 = \frac{1}{3}L_1$; $K_{II}/K_I = 0.33$.  Thickness: t	
BD (Brazilian Disc)	 Thickness: t	– A centrally cracked disc is subjected to diametral compression. By changing the inclination of the notch with respect to the loading direction (α), it is possible to change the mode of fracture from pure mode I (tensile) to pure mode II (shear). – The resulting through-cracks can be analyzed precisely for K_I and K_{II} by available solutions. Better predictions can be obtained including the second order non-singular terms in the expressions for the crack-tip stresses (T-stress). Likewise, a finite element analysis can be used to determine SIFs and T-stress values.
CS (Compact Shear)		– Use in the determination of pure mode II fracture toughness. K_{II} is usually determined by a finite element analysis.

(Continued)

Table 1 Continued

Fracture test specimen	Geometry	Observations
SEC (Single Edge Crack)	 Thickness: t	– The single edge crack (SEC) specimen with Arcan grips can produce from pure mode I to pure mode II only by changing the loading angle, β. The loading angle are $\beta = 0^\circ$ and $\beta = 90^\circ$ for mode I test and mode II test, respectively. Mixed mode loading conditions can be obtained with $0^\circ \leq \beta \leq 90^\circ$. Stress intensity factors solutions can be achieved by finite element analysis.
SCB (semi-circular bend specimen)	 Thickness: t	– The SCB specimen is a semi-circle of radius R containing an edge crack of length, a. The crack makes an angle β relative to the vertical direction. The specimen is placed on two bottom supports of distance $2S$ and is loaded by the vertical load F. When the specimen is subjected to three-point bending, depending on $(a/R, S/R, \beta)$ various combinations of modes I and II are obtained. When $\beta = 0^\circ$ the specimen is subjected to pure mode I (opening mode) independent of a/R and S/R. By increasing the angle β, the mode II (or sliding mode) contribution in the crack deformation is increased. Pure mode II takes place in a specific angle β depending on a/R and S/R. SIFs and T-stress can be calculated using a finite element method.
ASCB (asymmetric semicircular bend specimen)	 Thickness: t	– The asymmetric semi-circular bend (ASCB) specimen is used to perform mode I, mode II and mixed mode fracture toughness tests. This semi-circular specimen with radius R, which contains an edge crack of length a oriented normal to the specimen edge, loaded with a three-point bend fixture, was proved to give a wide range of mixed modes from pure mode I ($S_1 = S_2$) to pure mode II ($S_1 \neq S_2$). SIFs and T-stress can be calculated using a finite element method.

(Marsavina *et al.*, 2015, 2017), Semi-Circular Bend specimen (SCB) (Ayatollahi *et al.*, 2006) and Asymmetric Semi-Circular Bend specimen (ASCB) (Ayatollahi *et al.*, 2011; Negru *et al.*, 2013; Marsavina *et al.*, 2015). **Table 1** summarizes the schematic of some testing configurations for mixed-mode loading evaluations, as well as some comments about them.

A significant source of uncertainty in the experimental measurement of intrinsic mixed-mode fracture toughness in ceramics, is the experimental problem of introducing a “sharp” pre-crack prior to the mixed-mode fracture test. In most experimental studies,

the Knoop microhardness indentation technique is used to produce small, controlled surface flaws. This simple technique has the advantage that indented flaws could be taken as strength-limiting defects in structural ceramics. However, it is evident that the generation of residual stresses, due to plastic deformation at the root of the indentation, can markedly influence subsequent fracture. Other source of uncertainty arises from the possibility of frictional sliding between the faces of the crack, especially in coarse-grained microstructures and materials which exhibit pronounced resistance curves (Suresh *et al.*, 1990; Tikare and Choi, 1993). It is then expected that the length of the pre-crack, introduced in the test specimen prior to the mixed-mode experiment, can have a decisive effect on the measured toughness. Therefore, information about mixed-mode fracture initiation toughness, gathered from laboratory test specimens containing long pre-cracks, may lead to dangerously non-conservative guidelines for design against multiaxial fracture in structural ceramic components containing small internal flaws (Anderson, 2017).

Microstructural Effects During Mixed-Mode Fracture

The understanding of the mechanical behavior of ceramics has improved considerably as a direct result of the application of fracture mechanics to ceramics. These concepts have been applied successfully to glasses, mainly because the microstructure is usually defect-free and almost featureless down to the atomic scale and the fracture process can be modeled in an isotropic continuum. In contrast, polycrystalline ceramic materials are not microstructurally homogeneous and the variations in properties as a consequence of fabrication technique, defect distributions and anisotropy have to be taken into account. Different microstructural parameters present in polycrystalline materials like grain and pore size distribution, grain and pore morphology, grain-boundary interactions and phase distribution become significant on the crack propagation mechanism and the determination of the stress intensity factors. For example, preexisting pores would act as stress concentrators which might lead to more vulnerability to further crack growth. Moreover, the mode of crack propagation (transgranular and/or intergranular path) in polycrystalline materials depends on the normalized grain strength, normalized grain toughness and the presence of toughening mechanisms in the process zone (e.g., grain bridging or transformation toughening) which can reduce the stress intensity at the crack tip.

Despite its importance, there is not much literature about the microstructural influences on the mixed mode failure. In the study of mixed-mode fracture of ceramic materials, there is considerable heterogeneity among the investigations. For starters and factors to be considered are different types of ceramic materials (e.g., glasses, polycrystalline and monocrystalline ceramics), various kind of specimens and load configurations (e.g., three-point bending, asymmetric four-point bending, diametral compression, semi-circular bending, asymmetric semi-circular bending and Arcan test) and diverse types of cracks and notches (e.g., indentation surface flaws, edge-notch, central-crack and edge-crack). So, nowadays no conclusive results are found concerning the superiority of any given test for establishing a possible relationship between the best fitting fracture criterion and the microstructure of the materials. Nevertheless, it is important to mention that some microstructural effects are consistent between studies, for example polycrystalline ceramics exhibit higher normalized mode II fracture toughness than glasses due to crack-surface resistance from grain interlocking and abrasion, and fine-grained ceramic materials exhibit more reproducible mixed-mode data and fit better to brittle fracture theories when precracks are long enough to be free of the influence of the notch-tip field.

A propagating crack will follow the path of least resistance, i.e., maximum driving force, and if the material is isotropic and homogeneous, the crack will propagate to maximize the energy release rate, as occurs in glass. In contrast, the driving force for crack propagation will be reduced if there is any interaction between the growing crack and the microstructure that could absorb part of the energy available at the crack tip stress field. This is the case of toughened ceramics. When a specimen is tested in pure mode I loading, the crack propagates in its original direction, but in mixed-mode loading, the crack kinks out of the plane (Anderson, 2017). Thus, an important characteristic that allow to detect mixed loading conditions failure in a material is the presence of a crack deflection in the fracture surface. Two types of deflection can be observed: (1) tilting of the crack about an axis parallel to the crack-front and (2) twisting about an axis normal to the crack-front. The overall deflection process is manifested as roughness of the final fracture surface. Also, it has been reported an increase of fracture toughness that will depend on the twist component, the volume fraction and the shape of the particles (Green *et al.*, 2018). An important microstructural observation during brittle fracture is to determine the process zone, which is the area around the crack tip inside the material that is damaged due to localized large strains. In ceramic materials, the process zone is an area containing numerous microcracks. As the applied load is increased, the microcracks get denser until the zone is saturated, and the brittle failure commences. Some studies have reported an empirical relationship between the grain size of the material and the size of the process zone (Ayatollahi and Aliha, 2011; Ghouli *et al.*, 2018).

Fractography as post-mortem analysis of fracture surfaces is a powerful tool to evaluate fracture of glasses and ceramics. It could be used to identify the cause of failure and provide information about loading conditions. It is well known that fracture surfaces of brittle materials, like glass, will display 3 distinctive zones: (1) "the fracture mirror", defined as a relatively smooth region surrounding the fracture origin, (2) "the mist" which is the area with tiny local crack perturbations surrounding the origin and (3) "the hackle", defined by a region with out-of-plane perturbations as "fingers". An important factor of fractography studies is pattern recognition (Anderson, 2017). Unlike the case of mode I loading, it has been reported that when the glass is tested under mixed-mode loading, specifically in modes I/II, "the mist zone" does not form around glass fracture mirrors and the boundary is comprised of a "lance hackle zone" that is very similar to twist hackle. However, the size of the mirror region is not altered by the

mixed-mode loading conditions. These observations have a practical approach to distinguish between pure tension fracture surface (mode I) from a mixed-mode situation (Quinn, 2016).

Some microstructural effects described in the literature on glasses and ceramic materials, evaluated under mixed-mode fracture conditions, are:

- Studies on borosilicate glass revealed crack branching, primarily due to the formation of mixed-mode stresses at the crack tip during generation of the initial fracture. The crack branching pattern was analyzed, using fractal methods, and it was found variations of the fractal dimension depending on the stress level and the loading configurations (Chen *et al.*, 2015; DeLellis *et al.*, 2020).
- Fractography evaluations of soda-lime-silica glass and mica glass ceramics under mixed-mode I/II loading revealed absence of the mist region and the presence of twist-hackle markings in the fracture surface, as mentioned before, which could be used to identify surfaces of brittle materials that fail in combined mode loading. Also, the angles of branching could provide information about the state and direction of stress application (Freiman and Mecholsky, 2019).
- Texturized dental lithium disilicate (LS2) glass-ceramics, tested under combined mode-I and mode-II loading, showed an anisotropic fracture behavior, in which the crack path was redirected by the microstructure for long extensions of crack growth before reorienting toward the angle dictated by the fracture criterion. In this case, it was presumed an underlying competition between the energetically favorable path, induced by the microstructural texturization, governing the initial portion of crack growth, and the global mechanical driving force, leading the rest of the crack trajectory (Belli *et al.*, 2017).
- Mixed-mode fracture of hot-pressed Si_3N_4 was conducted using inclined indentation surface flaws in bending and large crack geometries in combined tension/torsion. Mixed-mode I/II fracture behavior of surface flaws was significantly different from that of large cracks. Surface flaws response was best described by coplanar fracture and strain energy density criteria, while large cracks behavior was best illustrated by non-coplanar fracture and maximum stress criteria. These findings suggest that shear resistance effects operate to reduce the effective value of the mode II stress intensity factor. To improve agreement between theory and experimental data, it was proposed a modified form of mode II stress intensity factor considering ratio of crack opening displacement (*COD*) to crack surface asperity height (*d*), where *d* is a function of material grain size. Results suggest that ceramics with high elastic moduli and large grain sizes may be the most susceptible to shear resistance effects (Petrovic, 1985). Tikare and Choi (1993) proposed that the toughening mechanism for silicon nitride materials, in mode I loading, is crack deflection by pullout of long needle-shaped grains, as well as crack bridging in the crack wake. Under combined mode I/II and pure mode II loading, the same toughening mechanisms are operative.
- Suresh *et al.* (1990) evaluated polycrystalline Al_2O_3 under mixed-mode I/II and I/III loading conditions. The mode of failure in both pure mode I and pure mode II loading was, predominantly, intergranular with sporadic transgranular cleavage. A similar failure mechanism was observed on the combined mode I/II fracture surfaces. In contrast, pure mode III fracture surface exhibits intergranular fracture as well as debris particles, flat transgranular facets, spanning tens of grains and abrasion marks produced by the severe frictional sliding between fracture surfaces. Combined mode I/III fracture exhibits similar trends. Additionally, it was observed that fine-grained polycrystalline alumina ceramic showed more reproducible mixed-mode toughness values in comparison to coarse-grained microstructure. Fine-grained microstructure minimizes possible crack bridging and microscopic deflections in crack path which might enhance frictional locking between the fracture surface asperities under near mode II loading conditions.
- Singh and Shetty (1989) evaluated CeO_2 -TZP materials and found that intergranular fracture was the predominant failure mode when the specimens were subjected to pure mode I loading. On the contrary, when the mode of failure was preponderantly pure mode II loading it was found to be transgranular. Also, it was found an increased mode II fracture toughness attributed to grain interlocking and abrasion observed by fractography techniques of fracture surfaces. Equivalent results were found by Ghoul *et al.* (2018).

Summary

Nowadays, most of mixed-mode loading evaluations performed in glasses and ceramic materials are conducted on biomaterials and structural products. After what was presented in this up-to-date review, it is clear the need for both a deep the state-of-the-art (including Mode III) studies that will bring standardized testing methods, and the inclusion of advanced analysis techniques (software and finite element analysis) that will achieve better adjustments between theoretical models and experimental data.

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References

- Akbardoost, J., Ayatollahi, M.R., 2014. Experimental analysis of mixed mode crack propagation in brittle rocks: The effect of non-singular terms. *Engineering Fracture Mechanics* 129, 77–89.
- Anderson, T.L., 2017. *Fracture Mechanics*, CRC Press.
- Atahan, H.N., *et al.*, 2005. Mode I and mixed mode fracture studies in brittle materials using the Brazilian disc specimen. *Materials and Structures* 38 (277), 305–312.

- Ayatollahi, M.R., Aliha, M.R.M., 2007. Wide range data for crack tip parameters in two disc-type specimens under mixed mode loading. *Computational Materials Science* 38 (4), 660–670.
- Ayatollahi, M.R., Aliha, M.R.M., 2011. Fracture analysis of some ceramics under mixed mode loading. *Journal of the American Ceramic Society* 94 (2), 561–569.
- Ayatollahi, M.R., Aliha, M.R.M., Hassani, M.M., 2006. Mixed mode brittle fracture in PMMA – An experimental study using SCB specimens. *Materials Science and Engineering A* 417 (1–2), 348–356.
- Ayatollahi, M.R., Aliha, M.R.M., Saghaei, H., 2011. An improved semi-circular bend specimen for investigating mixed mode brittle fracture. *Engineering Fracture Mechanics* 78 (1), 110–123.
- Ayatollahi, M.R., Moghaddam, M.R., Berto, F., 2015. A generalized strain energy density criterion for mixed mode fracture analysis in brittle and quasi-brittle materials. *Theoretical and Applied Fracture Mechanics* 79, 70–76.
- Belli, R., *et al.*, 2017. Mixed-mode fracture toughness of texturized LS2 glass-ceramics using the three-point bending with eccentric notch test. *Dental Materials* 33 (12), 1473–1477.
- Bilby, B.A., Cardew, G.E., Howard, I.C., 1978. Stress intensity factors at the tips of kinked and forked cracks. In *Analysis and Mechanics*. Elsevier. pp. 197–200.
- Chang, K.J., 1981. On the maximum strain criterion – A new approach to the angled crack problem. *Engineering Fracture Mechanics* 14 (1), 107–124.
- Chen, C.H., *et al.*, 2015. Crack front segmentation and facet coarsening in mixed-mode fracture. *Physical Review Letters* 115 (26), 1–5.
- Cotterell, B., Rice, J.R., 1980. Slightly curved or kinked cracks. *International Journal of Fracture* 16 (2), 155–169.
- DeLellis, D.P., *et al.*, 2020. A fractal analysis of crack branching in borosilicate glass. *Journal of the American Ceramic Society* 103 (9), 5283–5290.
- Erdogan, F., Sih, G.C., 1963. On the crack extension in plates under plane loading and transverse shear. *Journal of Basic Engineering* 85 (4), 519–525.
- Fett, T., *et al.*, 1995. Fracture tests for ceramics under mode-I, mode-II and mixed-mode loading. *Journal of the European Ceramic Society* 15 (4), 307–312.
- Freiman, S.W., Mecholsky, J.J., 2019. *The Fracture of Brittle Materials: Testing and Analysis*. John Wiley & Sons, Inc.
- Ghoul, S., Ayatollahi, M.R., Bushroa, A.R., 2018. Fracture characterization of ceria partially stabilized zirconia using the GMTSN criterion. *Engineering Fracture Mechanics* 199, 647–657.
- Green, D.J., Hannink, R.H.J., Swain, M.V., 2018. *Transformation Toughening of Ceramics*. CRC Press.
- Griffith, A.A., 1920. The phenomena of rupture and flow in solids. *Philosophical Transactions of the Royal Society of London. Series A, Containing Papers of a Mathematical or Physical Character* 221 (1921), 163–198.
- Hou, C., *et al.*, 2019. A generalized maximum energy release rate criterion for mixed mode fracture analysis of brittle and quasi-brittle materials. *Theoretical and Applied Fracture Mechanics* 100, 78–85.
- Hoyniak, D., Conway, J.C., 1979. Finite element analysis of the compact shear specimen. *Engineering Fracture Mechanics* 12 (2), 301–306.
- Hussain, M., Pu, S., Underwood, J., 1974. Strain energy release rate for a crack under combined mode I and mode II. In: Irwin, G. (Ed.), *Fracture Analysis: Proceedings of the 1973 National Symposium on Fracture Mechanics, Part II*. ASTM International, pp. 2–28.
- Inglis, C.E., 1913. Stresses in a plate due to the presence of cracks and sharp corners. *Transactions of the Institute of Naval Architects* 55, 219–241.
- Irwin, G.R., 1958. Fracture, in elasticity and plasticity/Elastizität und Plastizität. *Handbuch der Physik/Encyclopedia of Physics*. 551–590.
- Lazzarin, P., Zambardi, R., 2001. A finite-volume-energy based approach to predict the static and fatigue behavior of components with sharp V-shaped notches. *International Journal of Fracture* 112, 275–298.
- Marsavina, L., *et al.*, 2015. Shear and mode II fracture of PUR foams. *Engineering Failure Analysis* 58, 465–476.
- Marsavina, L., *et al.*, 2017. An engineering approach to predict mixed mode fracture of PUR foams based on ASED and micromechanical modelling. *Theoretical and Applied Fracture Mechanics* 91, 148–154.
- McClintock, F.A., Kim, Y.J., Parks, D.M., 1995. A criterion for plane strain, fully plastic, quasi-steady crack growth. *International Journal of Fracture* 72 (3), 197–221.
- Mirsayar, M.M., 2015. Mixed mode fracture analysis using extended maximum tangential strain criterion. *Materials & Design* 86, 941–947.
- Moghaddam, R.M., Ayatollahi, M.R., Berto, F., 2017. Mixed mode fracture analysis using generalized averaged strain energy density criterion for linear elastic materials. *International Journal of Solids and Structures* 120, 137–145.
- Munz, D., Fett, T., 1999. *Ceramics – Mechanical Properties, Failure Behaviour, Materials Selection*. Munz, D., Fett, T. (Eds.), Berlin; Heidelberg: Springer Berlin Heidelberg. (Springer Series in Materials Science).
- Negru, R., *et al.*, 2013. Investigation of mixed mode I/II brittle fracture using ASCB specimen. *International Journal of Fracture* 181 (1), 155–161.
- Orowan, E., 1949. Fracture and strength of solids. *Reports on Progress in Physics* 12 (1), 185–232.
- Palaniswamy, K., Knauss, W.G., 1978. On the problem of crack extension in brittle solids under general loading. In *Mechanics Today*. Elsevier. pp. 87–148.
- Paris, P., Erdogan, F., 1963. A critical analysis of crack propagation laws. *Journal of Basic Engineering* 85 (4), 528–533.
- Paulino, G.H., Kim, J.H., 2004. A new approach to compute T-stress in functionally graded materials by means of the interaction integral method. *Engineering Fracture Mechanics* 71 (13–14), 1907–1950.
- Petrovic, J.J., *et al.*, 1975. Controlled surface flaws in hot-pressed Si_3N_4 . *Journal of the American Ceramic Society* 58 (3–4), 113–116.
- Petrovic, J.J., 1985. Mixed-mode fracture of hot-pressed Si_3N_4 . *Journal of the American Ceramic Society* 68 (6), 348–355.
- Petrovic, J.J., Mendiratta, M.G., 1976. Mixed-mode fracture from controlled surface flaws in hot-pressed Si_3N_4 . *Journal of the American Ceramic Society* 59 (3–4), 163–167.
- Pirmohammad, S., Mengharpey, M.H., 2018. A new mixed mode I/II fracture test specimen: Numerical and experimental studies. *Theoretical and Applied Fracture Mechanics* 97, 204–214.
- Quinn, G.D., 2016. *Fractography of Ceramics and Glasses*. National Institute of Standards and Technology.
- Rice, J.R., 1968. A path independent integral and the approximate analysis of strain concentration by notches and cracks. *Journal of Applied Mechanics* 35, 379–386.
- Richard, H.A., 1985. Prediction of fracture of cracks subjected to combined tensile and shear loads. *VDI Research Report*, 631/85.
- Shetty, D.K., 1987. Mixed-mode fracture criteria for reliability analysis and design with structural ceramics. *Journal of Engineering for Gas Turbines and Power* 109 (3), 282–289.
- Shetty, D.K., Rosenfield, A.R., Duckworth, W.H., 1983. Crack branching in ceramic disks subjected to biaxial flexure. *Journal of the American Ceramic Society* 66 (1), C-10–C-12.
- Shetty, D.K., Rosenfield, A.R., Duckworth, W.H., 1986. Mixed-mode fracture of ceramics in diametral compression. *Journal of the American Ceramic Society* 69 (6), 437–443.
- Shetty, D.K., Rosenfield, A.R., Duckworth, W.H., 1987. Mixed-mode fracture in biaxial stress state: Application of the diametral-compression (Brazilian disk) test. *Engineering Fracture Mechanics* 26 (6), 825–840.
- Sih, G.C., 1974. Strain-energy-density factor applied to mixed mode crack problems. *International Journal of Fracture* 10 (3), 305–321.
- Singh, D., Shetty, D.K., 1989. Fracture toughness of polycrystalline ceramics in combined mode I and mode II loading. *Journal of the American Ceramic Society* 72 (1), 78–84.
- Smith, D.J., Ayatollahi, M.R., Pavier, M.J., 2001. The role of T-stress in brittle fracture for linear elastic materials under mixed-mode loading. *Fatigue & Fracture of Engineering Materials & Structures* 24 (2), 137–150.
- Suresh, S., *et al.*, 1990. Mixed-mode fracture toughness of ceramic materials. *Journal of the American Ceramic Society* 73 (5), 1257–1267.
- Tikare, V., Choi, S.R., 1993. Combined mode I and mode II fracture of monolithic ceramics. *Journal of the American Ceramic Society* 76 (9), 2265–2272.
- Wells, A.A., 1961. Unstable crack propagation in metals: Cleavage and fast fracture. *Proceedings of the Crack Propagation Symposium* 1, 210–230.
- Williams, J.G., Ewing, P.D., 1972. Fracture under complex stress – The angled crack problem. *International Journal of Fracture Mechanics* 8 (4), 441–446.
- Williams, M.L., 1956. On the stress distribution at the base of a stationary crack. *Journal of Applied Mechanics* 24 (1), 109–114.
- Xeidakis, G.S., *et al.*, 1996. Crack growth in a mixed-mode loading on marble beams under three point bending. *International Journal of Fracture* 79 (2), 197–208.

Further Reading

- ASTM C1145-19, 2019. Standard Terminology of Advanced Ceramics. West Conshohocken, PA: ASTM International.
- ASTM C1322-15, 2019. Standard Practice for Fractography and Characterization of Fracture Origins in Advanced Ceramics. 2019. West Conshohocken, PA: ASTM International.
- Basu, B., 2017. Mechanical properties of biomaterials. In: Basu, B. (Ed.), *Biomaterials for Musculoskeletal Regeneration*. Springer Nature Singapore Private Limited, pp. 175–222.
- Richard, H.A., Sander, M., 2016. Fatigue crack growth. In: Barber, J.R., Klarbring, A. (Eds.), *Solid Mechanics and Its Applications*. Springer International Publishing.
- Zehnder, A.T., 2012. *Fracture Mechanics, Lecture Notes in Applied and Computational Mechanics*. Pfeiffer, F., Wriggers, P. (Eds.), Springer Science + Business Media B.V.

R-Ratio and Microstructure Effects

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Introduction

Materials from any moving device or component are subjected to the risk of fatigue failure due to the growth of preexisting flaws, or cracks originated by the operating conditions. If the loading is below the material strength and occurs just once, it will, probably, not represent a risk of failure. Nevertheless, in real-world service, ceramic devices are frequently bearing small loads recurrently. Each repetition of a load could provoke progressive crack propagation generating, eventually, a crack-length long enough to induce failure of the component. In this case, it is common that failure is not preceded by large plastic deformation, even in ductile materials, rendering it more difficult to detect component damage under recurrent loads. Consequently, this phenomenon greatly increases the possibility of catastrophic failure at stress levels considerably below the strength of the material. For this reason, it is decisive to understand the behavior of ceramic materials under cyclic loading conditions.

It has been extensively documented the term “fatigue” to identify the deterioration of a material exposed to ongoing loading repetitions for sustained periods of service. In this process, the recurrent loading could be static or cyclic, and there are excellent textbooks dedicated to both topics (“Further Reading”). Here, special emphasis will be placed on cyclic fatigue. A basic distinction, though, should be made between “cyclic fatigue”, dependent on the cyclic nature of loading, and the “static fatigue” which is a constant-stress phenomenon.

Another relevant indication is the well-documented behavior of ceramics, known as the “slow-crack-growth” which generates an increase of the applied stress intensity factor until failure is reached. This subcritical crack propagation mechanism, in most cases, involves a stress-assisted reaction in liquid-containing environments that provokes dissolution at the crack tip of the amorphous phases. This mechanism is denoted as “delayed failure”, “stress corrosion” or “static fatigue”. Even though both terms could be confusing, what should be remembered is that despite the origin of the stress, when cyclic loading is applied, fatigue damage may result (Further Reading).

From this point forward, the term “fatigue” will be used to refer to “cyclic fatigue” or “mechanical fatigue”. The phenomenon is directly evaluated by the following stress parameters: minimum stress (σ_{min}), maximum stress (σ_{max}), stress amplitude (σ_a), stress range ($\Delta\sigma$), mean stress (σ_m), and the period (T), which correlates to one cycle or alternation of load and is associated to the number of stress cycles (N) and time (t), as shown in the following equations:

$$\sigma_a = \frac{\sigma_{max} - \sigma_{min}}{2} \quad (1)$$

$$\Delta\sigma = \sigma_{max} - \sigma_{min} = 2\sigma_a \quad (2)$$

$$\sigma_m = \frac{\sigma_{max} + \sigma_{min}}{2} \quad (3)$$

$$t = NT \quad (4)$$

Another important descriptor of the cyclic fatigue is the “R-ratio” (R) defined in Eq. (5)

$$R = \frac{\sigma_{min}}{\sigma_{max}} \quad (5)$$

The R -ratio could also be described in terms of stress intensities factors (K), a well-known parameter described in the literature (“Further Reading”). The stress intensity factor for the cyclic loading ($K(t)$) is associated with the applied load ($\sigma(t)$), a geometric factor (Y), and the length of the crack (a), by the widely known Eq. (6)

$$K(t) = \sigma(t)\sqrt{\pi a}Y \quad (6)$$

At this point, it is important to remember that subscript I is added to the stress intensity factor (K) to indicate that crack opening is occurring under mode I loading, i.e., pure tension across the crack face. Other ways to apply stress to cracks, as defined by Irwin (1958), are mode II (in-plane shear) and mode III (out-plane shear). However, the predominant situation for ceramics and glasses is mode I loading, so when no aperture mode is designated, mode I should be assumed. Thus, when a device is working under mode I cycling loading, the stress intensity factor could be re-written, for a time varying stress, $\sigma(t)$, as in Eq. (7):

$$K_I(t) = \sigma(t)\sqrt{\pi a}Y_I \quad (7)$$

Hence, $K_I(t)$, maximum and minimum, could be determined as in Eqs. (8) and (9)

$$K_{max} = \sigma_{max}\sqrt{\pi a}Y \quad (8)$$

$$K_{min} = \sigma_{min}\sqrt{\pi a}Y \quad (9)$$

in which (K_{max}) and (K_{min}) are the maximum and minimum values of stresses in cyclic loading, respectively. From Eqs. (8) and (9) it is clear that the R -ratio can be written as $R = \frac{K_{min}}{K_{max}}$. Furthermore, the cyclic stress intensity factor (ΔK) for a given cyclic loading with constant amplitude, could be defined by Eq. (10):

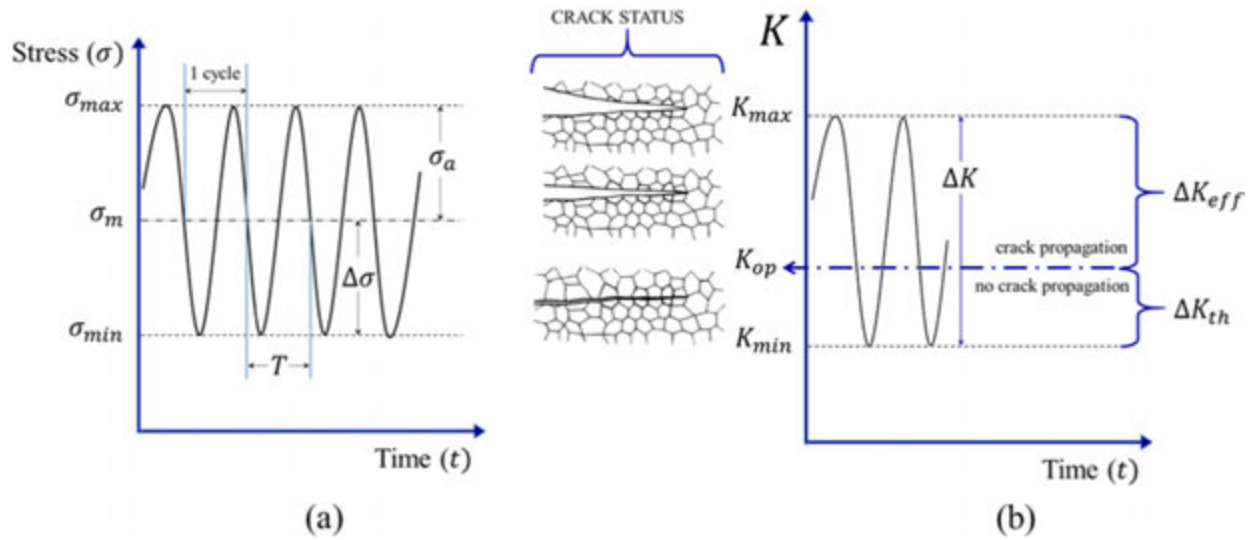


Fig. 1 Parameters associated to cyclic fatigue: (a) descriptors of cyclic loading and (b) Elber's approach to cycling loading.

$$\Delta K = K_{max} - K_{min} = (\sigma_{max} - \sigma_{min})\sqrt{\pi a Y} \quad (10)$$

Finally, a relationship between the cyclic stress intensity factor (ΔK) and the R -ratio (R) for cyclic fatigue phenomenon is exhibited in Eq. (11):

$$\Delta K = (1 - R)K_{max} \quad (11)$$

Another basic concept from linear elastic fracture mechanics (LEFM) should be considered: when a crack reaches a critical size, it becomes unstable and it propagates; then, K turns into K_{IC} or "fracture toughness". In addition, when the cyclic stress intensity factor reaches a critical level, i.e., K_{max} is equivalent to K_{IC} , then, Eq. (11) becomes Eq. (12) (Rösler *et al.*, 2007):

$$\Delta K_{IC} = (1 - R)K_{IC} \quad (12)$$

An important approach for cyclic stress loading, first proposed by Elber (1970), is referred to as the "crack closure" effect. He described material's behavior associated with opening and closing of cracks under cyclic loads. Paradoxically, the "crack closure" process is the incomplete closure of the crack during the unloading part of the cyclic fatigue. For this reason, some authors have suggested the name of "residual crack opening", which seems phenomenologically more appropriate than the "crack closure". Anyhow, since Elber, various researchers have found that, effectively, the "crack-closure" happens during crack propagation of a material subjected to cyclic fatigue. During the discharge cycle, a zone in compression close to the crack tip remains, creating a "crack-closure effect". The partial or insufficient closure of the edges of the crack makes an irreversible strain of the crack surfaces. Subsequently, during the loading cycle, this deformation allows debris to locate inside the crack, preventing complete closure of the crack, and promotes, at some point, the advance of the crack opening (Anderson, 2017). Elber defined K_{op} as the "crack opening stress intensity factor", and the ΔK_{eff} has the "effective cyclic stress intensity factor", which corresponds to the loading beyond which the crack is completely opened. The relationship is expressed in Eq. (13) (Richard and Sander, 2016).

$$\Delta K_{eff} = K_{max} - K_{op} \quad (13)$$

Another relevant parameter for cycling loading is the "fatigue-crack-growth threshold" (ΔK_{th}) that determines the limits for crack propagation, i.e., the crack will propagate if the cyclic stress intensity factor exceeds the fatigue-crack-growth threshold value ($\Delta K \geq \Delta K_{th}$). The threshold parameter is characterized by Eq. (14) (Rösler *et al.*, 2007):

$$\Delta K_{th} = K_{op} - K_{min} = (1 - R)K_{op} \quad (14)$$

Fig. 1 illustrates parameters associated with cyclic fatigue at constant amplitude, in Fig. 1(a) detailed descriptors of the cyclic loading while Fig. 1(b) shows crack propagation parameters.

Cyclic Fatigue Evaluation and R -Ratio Effect

Despite the importance of failure by cycling loading for certain applications, literature about evaluation of ceramics under these conditions is not abundant. Several reasons could account for this fact, such as the large number of samples required to obtain a reliable predictor of failure, the number of competing theories and unanswered questions in the field, among others. In any case, fatigue phenomenon is, in general, characterized by two approaches: (1) the well-known $S - N$ diagrams in which applied stress is plotted against the number of cycles and (2) the fatigue crack growth rate curves (FCGR), where crack growth rate is exhibited as a function of the stress intensity factor. Both cases will be addressed below.

Stress-Cycles Curves

The most common tool to evaluate fatigue phenomenon for materials are the so-called $S - N$ curves or Wöhler plots. These are diagrams representing the applied cyclic stress versus the number of cycles to failure. In the $S - N$ diagrams, the stress can be logarithmically or linearly represented while the number of cycles to failure will always be in logarithmic scale. To obtain these curves, a sample is cyclically loaded at a particular stress level, and the number of cycles to failure is registered. After several tests, recorded data is presented in a graph like the one shown in Fig. 2. Two distinctive regions are described for $S - N$ curves: low-cycle fatigue (LCF) field, where the number of cycles to failure is below 10^4 , and the high-cycle fatigue (HCF) area where the number of cycles exceed this value (Further Reading).

Dependence of stress with the number of cycles is quite clear in Wöhler diagrams: as the number of cycles increases, the applied stress supported by specimens is lower. Two distinguishing fatigue degradation patterns have been reported: some ceramics, like material A in Fig. 2, exhibit an horizontal asymptote which is associated with a parameter named “fatigue limit”, “fatigue strength” or “endurance limit” ($\Delta\sigma_0$). The endurance limit implies that from this level of stress and below, failure will not occur under a large number of stress-cycles. In other words, even if there is an increasing number of cycles, the stress range for failure will be, approximately, the same. Another behavior is the one displayed for material B in Fig. 2, which presents ongoing degradation while increasing the number of cyclic loading (Rösler *et al.*, 2007; Taylor, 2007; Pelleg, 2014).

Obviously, variations in the applied stresses will produce modifications of R -ratio that, accordingly, will generate changes in the Wöhler diagrams, as displayed in Fig. 3. It can be observed a downward shift of the curve when the R -ratio is increased, i.e., as its value is augmented, the failure of the component will occur at lower applied stress, for the same number of fatigue cycles (Taylor, 2007).

Fig. 4 exhibits several $S - N$ curves of ceramic materials compiled from different bibliographic sources. Two major trends could be identified: (1) those materials that behave as described in Section “Stress-Cycles Curves”, i.e., materials that follow the typical

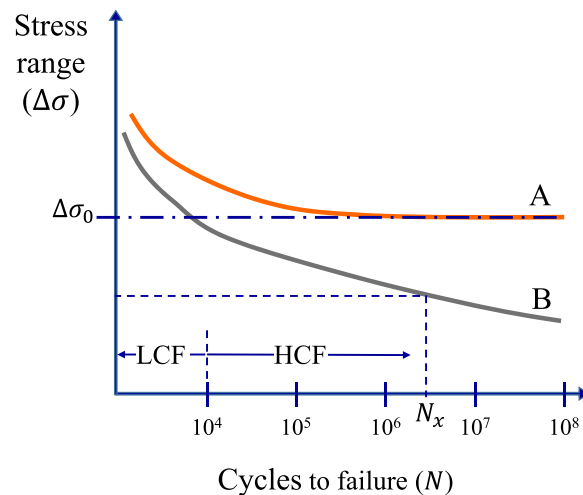


Fig. 2 Typical $S - N$ curves with endurance level and low-cycle and high-cycle zones.

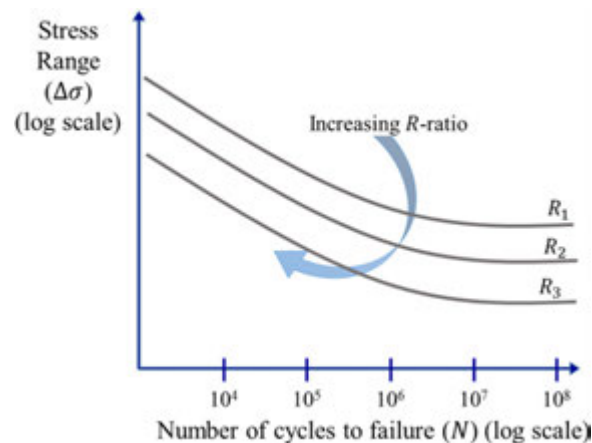


Fig. 3 Effect of R -ratio in $S - N$ curves.

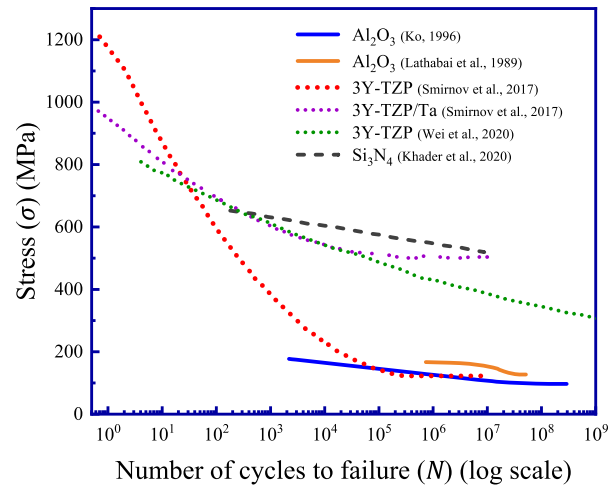


Fig. 4 $S - N$ curves of some ceramics from several references.

$S - N$ curve; this is the case of composites and zirconia-based materials (3Y-TZP and 3Y-TZP/Ta), and (2) compounds with a linear behavior that is almost asymptotical to horizontal axis, which is the case of alumina and silicon nitride. It must be mentioned that Fig. 4 was constructed with data from various references, therefore, comparison of similar compounds is not straight forward. Data from different studies come with variations in: tests conditions (with or without indentation, humidity, etc), raw materials (grain size, commercial, etc.) and testing methods (flexural, rotary bending, etc.). In any case, all the materials shown in Fig. 4 have been used for many years within engineering components subjected to cyclic loading conditions, due to their good performance, high stress resistance, and other factors, such as cost and raw materials availability.

$S - N$ diagrams are very useful to study fatigue behavior but they require a large number of samples to obtain a representative graph. In this context, Goodman representations is a good approach to overcome the problem of high number of tests. Goodman graphs are created by plotting the stress amplitude versus the mean stress over a specified number of cycles. A continuous line is drawn between fatigue strength (σ_e) at $R = -1$, at mean stress equal to zero, and tensile strength (σ_u) at zero stress amplitude with $R = 1$. This results in a negative slope given by the expression displayed in Eq. (15) (Pelleg, 2014):

$$\sigma_a = \sigma_e \left[1 - \frac{\sigma_m}{\sigma_u} \right] \quad (15)$$

Any combination of amplitude and mean stress in this line will have the same fatigue life. Usually, the area below the curve is associated with conditions where the material should not fail, as shown in Fig. 5(b). The area outside the shaded triangle represents the probability of the occurrence of fatigue failure. As can be seen in Fig. 5(a), different R -ratios can be represented in the same diagram, and clearly, each one of them will modify the safe region of the component. The integers next to the symbols indicate the number of samples tested (Pelleg, 2014). Even though the Goodman diagram is widely used for metallic materials, some researchers had reported Goodman graphs for ceramic materials. Fig. 5(a) outlines the Goodman plots for 3Y-TZP (Liu and Chen, 1991a) and for Si_3N_4 (Soma et al., 1988; Masuda et al., 1990). In Fig. 5, the square and the circular dots allude to the experimental values for 3Y-TZP and Si_3N_4 , sequentially. The empty forms represent failed specimens under specific conditions, while the filled ones did not fail during the test.

Fatigue Crack Growth Rate Curves (FCGR Curves)

To study the relationship between fatigue crack-growth rate and R -ratio, it is necessary to point out that when a crack is subjected to fatigue by loading in pure mode I , propagation will occur in the initial direction of the crack, and the advance will continue, under the right conditions ($\Delta K \geq \Delta K_{op}$), as the load cycles are augmented. Thus, the mean crack-growth rate, within a time interval ($\Delta a / \Delta N$), will be associated with changes in crack length (Δa) per variations in cycle numbers (ΔN).

When ΔN tends to zero ($\Delta N \rightarrow 0$), the crack-growth rate will be equivalent to the slope (da/dN) of the crack length curve (a) versus the number of cycles (N), as shown in Fig. 6. Consequently, the crack growth rate accelerates exponentially with an increasing number of load cycles, for loading at constant amplitude. Therefore, as seen in Fig. 6, at constant R -ratio, the load applied to a cracked component generates a variation on the $a - N$ curve and, ergo, on the crack growth rate. Under greater loads ($\sigma_1 < \sigma_2 < \sigma_3$), the crack growth rate increases, and it becomes unstable at shorter crack lengths (Richard and Sander, 2016). Likewise, it is observed that with increasing R ($R_1 < R_2 < R_3$), the crack length also raises; consequently, the slope becomes steeper, which is associated with a higher crack propagation rate. Microscopical observation is the most common method to measure the crack length, among other techniques. Typically, studied samples consisted of edge-notched three- and four-point bending bars, compact tension specimens, double-cantilever beam samples and sometimes, double torsion probes (Munz and Fett, 2001).

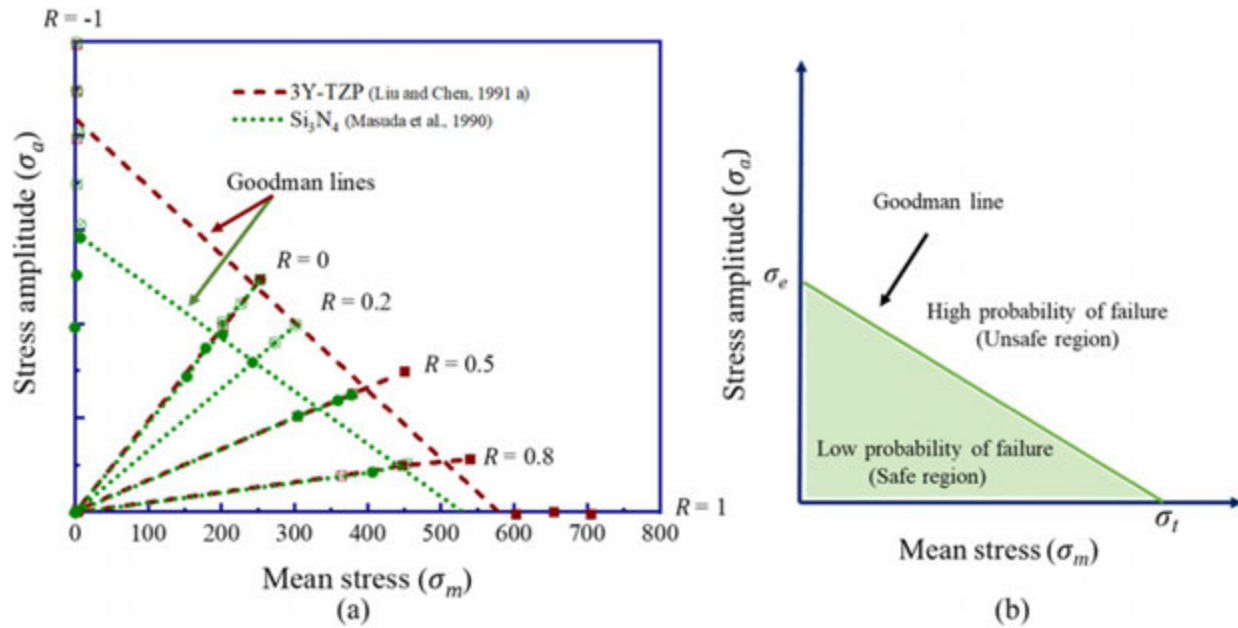


Fig. 5 Goodman diagrams for ceramic materials from various references.

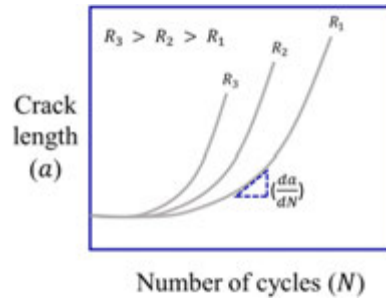


Fig. 6 Effect of R -ratio on fatigue crack-growth rate.

Normally, the crack-growth rate is found experimentally and is used to represent the fatigue crack growth behavior in a log-log plot of da/dN versus ΔK , which is a sigmoidal curve containing three distinctive regions (see Fig. 7). In this type of graph, two asymptotes can be observed: one for low ΔK values previously named ΔK_{th} or “fatigue-crack-growth threshold”, below which the crack will not grow; and one for the upper limit ΔK_{IC} where crack propagation becomes unstable, leading to fatigue failure. It is well documented that ceramic materials fracture in brittle manners with little or no signs of plastic deformation. Therefore, fracture origin is surrounded by a smooth area, called the mirror, and by rougher regions named the mist and the hackle. The sizes of these regions are proportional to σ^2 , where σ denotes the stress in an uncracked body at the position of the origin of fracture (Danzer *et al.*, 2008) (“Further Reading”).

The stages of crack growth rate associated with damage evolution are the following:

- (1) Stage I (crack initiation): consists of the development of microstructural damage such as microcracks, which will grow and eventually unite to form a dominant crack. Much of a component life can be spent at this stage if the conditions of the component are adequate.
- (2) Stage II (linear crack propagation): in this region, the dominant crack will grow stably under repeated applied loads at a rate following a power-law.
- (3) Stage III (unstable crack propagation): here, the crack has grown to a point where it becomes unstable, thereby accelerating, even more, the propagation of the crack, exposing the component to catastrophic failure.

In the linear region of the log-log plot in Fig. 7 (Stage II), the crack-growth rate follows the so-called “Paris law” (Paris and Erdogan, 1963), their empirical power-law relationship is shown in Eq. (16)

$$\frac{da}{dN} = C\Delta K^m, \quad (16)$$

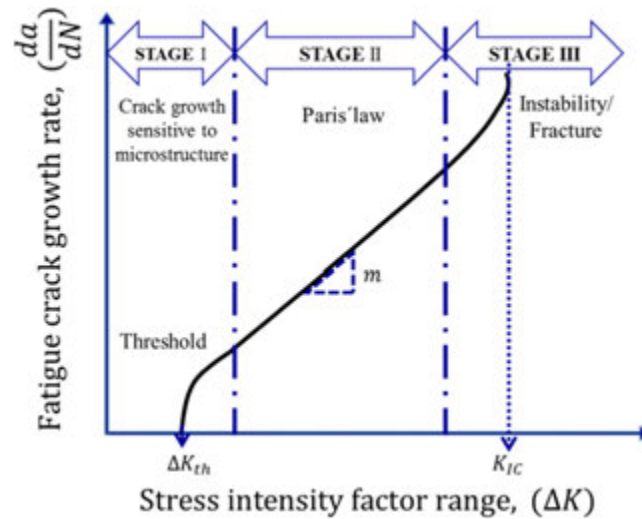


Fig. 7 Typical log fatigue crack-growth behavior (FCGR curve).

where $\frac{da}{dN}$ represents the crack-growth rate, C is a constant depending on the material and the R -ratio, m is an exponent associated with the material's nature, and ΔK the cyclic stress intensity factor whose general definition is in the Eq. (11) ("Further Reading").

It has been found that the Paris exponent (m) for ductile metals takes values about 2–4, while for polymers it is ~ 10 . For brittle materials, such as ceramics the m -values are much larger, in the order of 10–100 (Kruzic et al., 2018). Thus, mechanistically, there are important differences between metals and ceramic materials. Experimental observations have demonstrated that crack-advance in ceramics is identical for cycling and for monotonic loadings, i.e., strongly dependent on stress intensity factor at the crack-tip (K_I). So, the stress intensity factor leading to fatigue failure (K_{max}) should be considered for ceramics in the empirical Paris law. In other words, the distinction between m values, for metals and ceramics, imply that crack-growth rates in ceramic materials will rely on K_{max} while metals will be more sensitive to ΔK . Some researchers modified Paris's empirical statement using Walker's model, which was originally designed for metallic materials. In this way, another observational growth-rate relationship that explicitly incorporates the effect of K_{max} , was developed. The modified relation is shown in Eq. (17): (Liu and Chen, 1991a; Dauskardt et al., 1992; Ritchie, 2003).

$$\frac{da}{dN} = C' (K_{max})^n (\Delta K)^p, \quad (17)$$

where, C' , n , and p are constants defined by $C' = C (1 - R)^n$ and $m = (n + p)$. Also, from Eq. (11) $K_{max} = \frac{\Delta K}{(1-R)}$; and hence, re-writing crack-growth rate in terms of R -ratio, the relation becomes: (Dauskardt et al., 1992; Ritchie, 2003)

$$\frac{da}{dN} = \frac{C'}{(1-R)^n} (\Delta K)^{(n+p)}. \quad (18)$$

This model has been reported to describe R -ratio effects of cyclic fatigue in technological ceramics like SiC-whisker-reinforced alumina composites in which the exponents n and p are ~ 10 and 5, respectively (Dauskardt et al., 1992). Another study for yttria-stabilized tetragonal zirconia polycrystal material (3Y-TZP) revealed m -value ~ 24 (Liu and Chen, 1991b). Equation (18) had been used for identifying dominant stress parameters under fatigue failure and, accordingly, to discriminate possible mechanisms for crack advance. For instance, it has been described that high values of m -exponent, in ceramics, are associated with extrinsic mechanisms conducting to fracture under cyclic loading, and it is characterized by higher n -exponent than p -exponent. On the contrary, in metals, frequently occurs a dominant dependence of ΔK , as a consequence of intrinsic mechanisms for crack propagation and weaker variation with K_{max} ; thus, p -exponent has larger values than n -values (Ritchie, 2003).

Another relevant consideration is the effect of R -ratio on typical log-log fatigue curves. It is shown in Fig. 8 how variations in R -values displace the sigmoidal fatigue curve. According to Eq. (14), there is a linear relationship between ΔK_{th} and the stress ratio, R -ratio, which can be seen in Fig. 8, i.e., the fatigue-crack-growth threshold is decreased when R -ratio values are increased. Accordingly, in the intermediate zone (stage II), the log-log curve goes towards higher values of da/dN , which means that the crack-growth rate accelerates as R increases. It is also evident from the graph in Fig. 8, that R -value influence is more pronounced at high and low crack-growth rate ranges, zones I and III, respectively; yet, the effect is less sensitive on the linear region (stage II). In summary, if R -ratio increases, so do the crack growth rate, and it lowers both the fatigue threshold (ΔK_{th}) and the allowed cyclical stress intensity factor (ΔK_{IC}) (Rösler et al., 2007; Taylor, 2007; Huang and Moan, 2007; Richard and Sander, 2016; Perez, 2004). It is worth mentioning that intensity factors, including ΔK_{th} , are sensitive to many parameters like grain size, Young's modulus, and others. So, it is common to find scattered results even within the same class of material. Still, the equations are useful in estimating the order of magnitude of the threshold. Some models have been proposed to indicate the influence of R -ratio on the fatigue crack-growth threshold value (ΔK_{th}), but they have been designed and tested for metallic materials (Rösler et al., 2007; Richard and

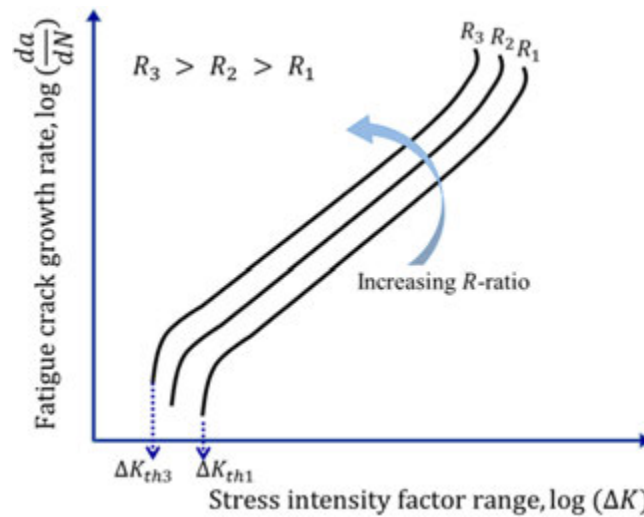


Fig. 8 Effect of R -ratio on fatigue crack growth rate curves.

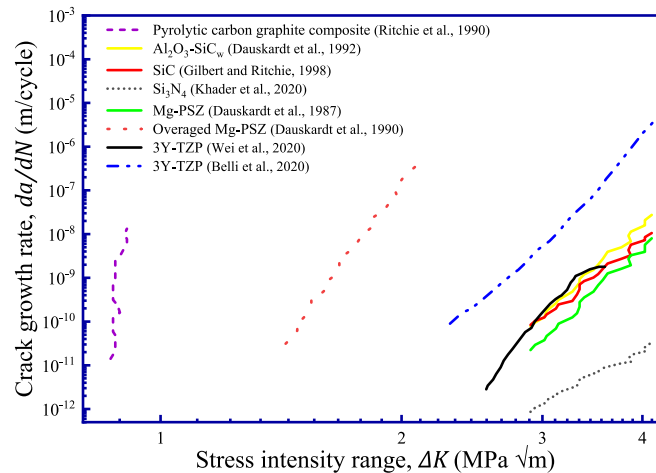


Fig. 9 Crack-growth curves (FCGR curves) of different ceramic materials.

Sander, 2016). Nevertheless, it would be interesting, in the near future, to apply them in ceramics, in the same way other empirical models had been adapted in the past.

Fig. 9 shows representative da/dN curves for various ceramic materials. It is clearly detected, in the graph, the characteristic steep slopes of large values of Paris's exponent (m) for this type of compounds. Higher slopes are associated with small crack initiation zones and with accelerated crack growth in the propagation field. This behavior reflects the gradual and slow deterioration of fatigue resistance due to cyclical loading; thus, for ceramic materials, crack initiation and propagation regions are not as distinguishable as they are for metals. In metallic devices, there is a clear differentiation, kind of inflection point, indicating meaningful crack length over long periods before the material reaches the critical value for failure that allows detecting the crack during regular inspection procedures (Rösler et al., 2007).

Crack Growth Mechanisms During Cycling Loading

Several crack propagation mechanisms have been reported for metals and for ceramic materials, specific for each one of them. In metallic materials, crack propagation is dominated by intrinsic mechanisms like plasticity-induced closure, roughness-induced closure, oxide-induced closure, closure induced by a viscous fluid, and transformation-induced closure. Intrinsic mechanisms imply that crack advance happens from the damage process in the crack-tip field, being particular to cyclic loading. On the other hand, crack advance, in ceramic materials, is managed by extrinsic mechanisms like crack deviations, generation of inelastic zones around the cracks, or by crack interactions due to sliding, bridging, and wedging phenomena, described later. Extrinsic mechanisms usually involve crack propagation ahead of the crack tip in a similar manner as that for monotonic loading. It has

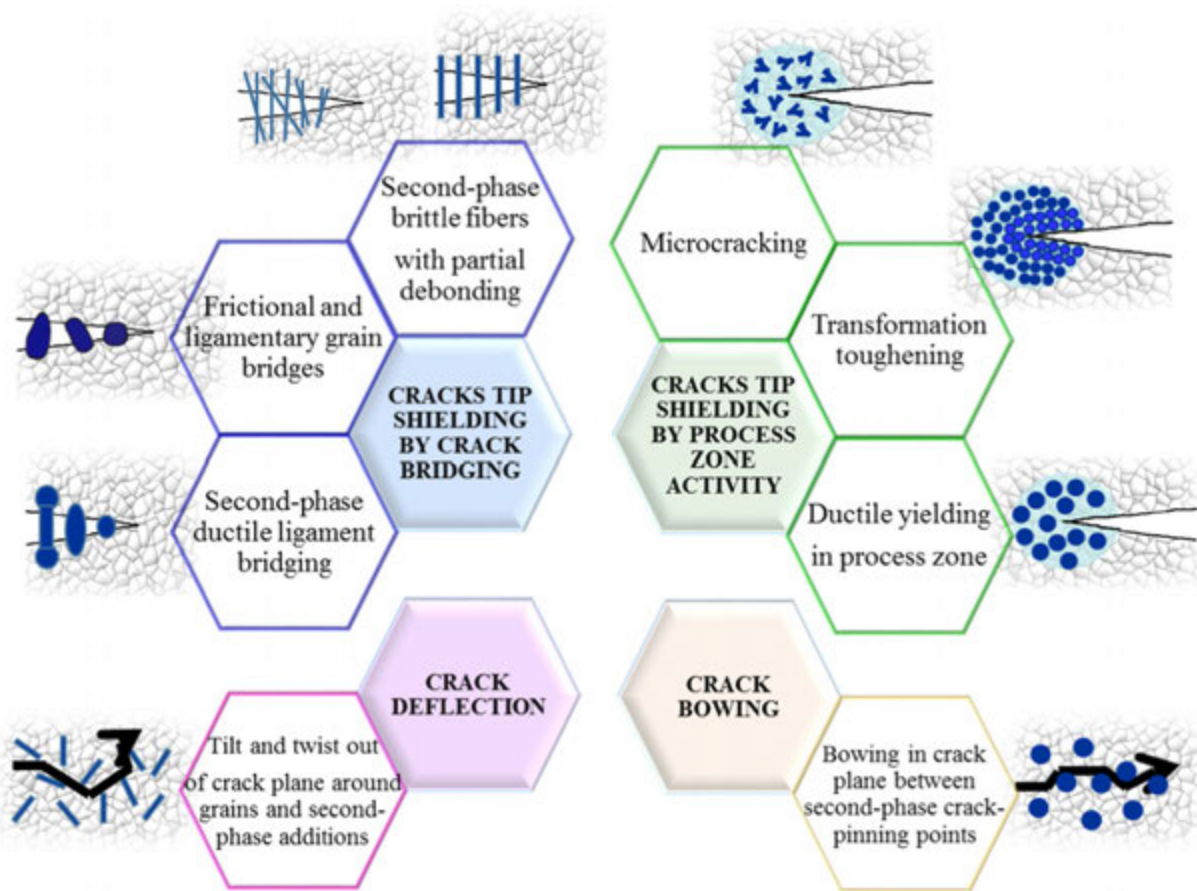


Fig. 10 Schematic illustrations of toughening mechanisms in ceramic materials.

been reported that an important issue of the cyclic crack growth in ceramics is the degradation of the crack-tip shielding, specifically in high-toughened ceramic materials (Ritchie, 2003).

The propagation of cracks in metals is a phenomenon that has been exhaustively studied and it is associated with the movement of dislocation and consequent plastic deformation that occurs at the crack tip ("Further Reading"). However, for ceramics materials, the plastic strain is highly restricted at low temperatures, so cracks cannot grow through this mechanism. For this reason, it was believed that fatigue did not affect ceramics, until some investigations, carried out in the last decades revealed that some ceramic materials can fail due to the propagation of cracks under cyclic loading. In particular, it was described that extrinsic mechanisms, designed to increase toughening in the material, were responsible for reducing the driving force of crack growth when applying fluctuating stresses in the crack faces. Some of these mechanisms are illustrated in Fig. 10 (Rösler *et al.*, 2007; Casellas *et al.*, 1999; Ritchie, 2003).

As mention before, in the case of intrinsic crack propagation mechanisms in metallic materials the predominant term from the modified Paris's empirical law (see Eq. 16), is ΔK , i.e., $n \ll p$. Thus, in the intermediate range (stage II), expressing growth rates in terms of ΔK , will linearize the load-ratio dependence. On the contrary, in ceramic materials, the dominant term is K_{max} , i.e., $p \ll n$; so, normalization is achieved by characterizing the growth rates as a function of K_{max} . This distinctive difference is represented in Fig. 11.

Although many efforts have been made to explain the mechanisms of cyclic fatigue in various ceramics and glasses, some aspects remain unclear. One of the first studies conducted on cyclic loading of ceramic materials was the one done by Evans and Fuller (1974). They evaluated glass and porcelain and showed that crack growth does not significantly increase by the effect of cyclic fatigue. In that work, it was concluded that degradation was primarily due to static slow crack growth mechanism and mechanical fatigue was considered of minor significance in these materials (Evans and Fuller, 1974). Later on, other authors reported that advanced ceramics with a pronounced R-curve effect appear to have higher sensitivity to cyclic loads (Dauskardt *et al.*, 1987; Lathabai *et al.*, 1989; Grathwohl and Liu, 1991; Kishimoto, 1991). For instance, Dauskardt *et al.*, demonstrated the influence of cyclic loading on magnesium partially stabilized zirconia samples (Mg-PSZ). Their results, based on changes in the crack-growth rate, reported that, under cyclic loading conditions, crack propagation values were by 8 orders of magnitude above the expected value for static loading conditions. Furthermore, crack propagation happened at stresses below the threshold value reported for static fatigue (Dauskardt *et al.*, 1987; Steffen *et al.*, 1991).

Until today, cyclic fatigue failure has been shown in several structural ceramics including various zirconia composites, alumina, silicon nitride, and silicon carbide, among others. While strong toughened ceramics appears to be very vulnerable to cyclic fatigue degradation, in

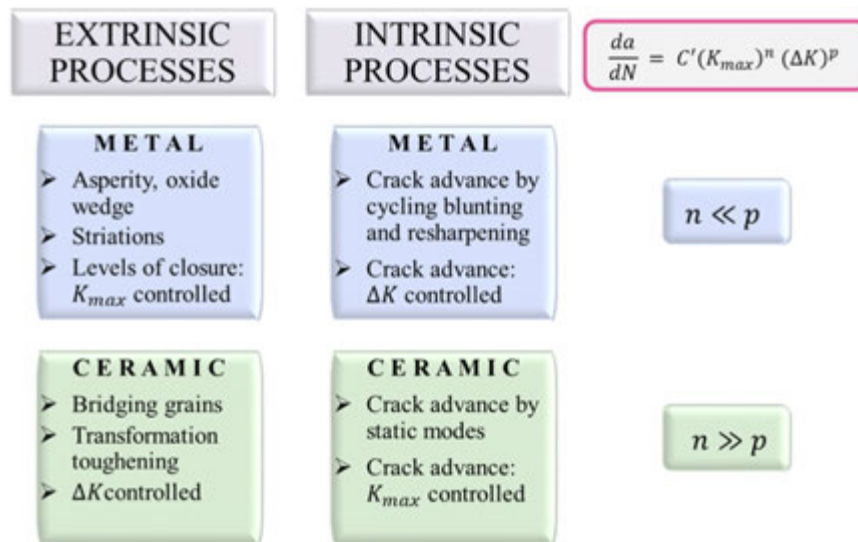


Fig. 11 Illustrative diagram of the intrinsic and extrinsic mechanisms involved in cyclic fatigue-crack growth in metals and ceramics. Adapted from Ritchie, R., 2003. Cyclic loading and fatigue: Fatigue of brittle materials. In: Milne, I., Ritchie, R., Karihaloo, B. (Eds.), *Comprehensive Structural Integrity*. Oxford: Elsevier, pp. 359–376.

what is seemingly to be a contradictory fact, glasses and un-toughened ceramic materials are mainly not affected by cyclic fatigue. Indeed, in ceramic materials, the cyclic loading acts to diminish the shielding in the crack wake. Common degradation processes of extrinsic mechanisms described in the literature for ceramic materials are: (1) Crack bridging, that occurs when non-fracture obstacles (such as grains, precipitates, fibers, whiskers, among others) that act as ligaments opposing aperture of the fissure, are left behind in the propagation of the crack. Then, repeated opening and closing of crack surfaces under cyclic loads causes them to rub against each other and induces dissipating energy, wearing the surfaces of the crack, and, eventually, reducing the crack bridging effect. (2) Deviation of cracks in grain boundaries, which can also generate a similar effect than crack bridging. (3) Transformation toughening, such as in partially stabilized zirconia, where phase transformations arise near the crack-tip. The phenomenon has associated volume increments at the crack tip upon the destabilization of the tetragonal phase, so compressive stresses are generated and induce closure of the crack. This effect is also related to the formation of microcracks near the crack tip (Rösler *et al.*, 2007; Casellas *et al.*, 1999; Cotterell, 2010).

Ample studies have been dedicated to monolithic non-transforming ceramics in which the toughening is primarily due to grain bridging in the wake of the propagating crack. Evaluated materials include several qualities of alumina, Si_3N_4 , SiC, and aluminum titanate, in which the grain-bridging mechanism is the microstructural basis of the fatigue failure. This behavior is attributed to a degradation of the grain-bridging zone associated with frictional wear at the grain matrix interface, that enhance the crack-tip driving force locally (Gilbert *et al.*, 1995; Jacobs and Chen, 1995; Li and Guin, 1995; Bermudo *et al.*, 1997; Huh and Song, 1998; Huh *et al.*, 2000; Han *et al.*, 2001; Sonsino, 2003; Kruzic *et al.*, 2004; El Attaoui *et al.*, 2005; Kruzic *et al.*, 2005; El Attaoui *et al.*, 2006; Matsudaira *et al.*, 2009). Another paramount toughened ceramics that exhibit mechanical degradation under fluctuating loads are zirconia-based composites. Materials with transformation toughening like magnesia-partially-stabilized zirconia (Mg-PSZ), yttria-tetragonal zirconia polycrystal (Y-TZP), ceria-tetragonal zirconia polycrystal (9Ce-TZP), and others, where phase transformation occur near the crack tip, and cyclic fatigue damage is attributed to the formation of microcracks in the vicinity of the crack tip (Dauskardt *et al.*, 1987; Grathwohl and Liu, 1991; Hoffman and Mai, 1995; Hoffman *et al.*, 1996; Schmitt *et al.*, 1996; Chevalier *et al.*, 1999).

An interesting study conducted by Casellas *et al.*, evaluated alumina, zirconia-toughened-alumina (ZTA) and mullite by cyclic fatigue at constant amplitude. They reported that the following extrinsic mechanisms for toughening are susceptible to fatigue degradation: (1) Deviation of crack's path due to interaction with second-phase particles or grains requiring higher stress levels to maintain crack propagation, (2) Grain bridging by non-fractured obstacles (3) Energy dissipation process by microcracking and (4) Development of compressive stresses related to volumetric changes by transformation toughening.

A singular outcome from this research was that alumina and ZTA suffer degradation when subjected to cyclic fatigue but mullite did not present damage under the same testing conditions. Thus, it was confirmed that advanced ceramics with increased toughening are more prone to suffer deterioration under cyclic loading due to deterioration of shielding mechanisms at the crack-tip (Casellas *et al.*, 1999).

Cyclic Fatigue Phenomenon (*R*-Ratio) and Microstructural Effect

Dependence of physical and mechanical properties on microstructure is well known in materials science. The vast amount of experimental results suggests that resistance of the materials to the initiation and propagation of fatigue crack are significantly influenced by multiple microstructural factors. To mention a few: interatomic bonds linked to material stiffness; presence and

nature of precipitates/inclusions and distances between them; surface roughness; porosities; and grain size (François, 1989). Analogous to R , the microstructural parameters have a profound influence on stages I and III of the crack growth curve, as represented in Fig. 7, and a less pronounced impact in region II (Perez, 2004). It should be noted that when more than one parameter is modified simultaneously, the incidence of these factors on fatigue resistance is unpredictable. There may be synergistic or antagonistic effects, depending on particular conditions of test and material nature.

In ceramic materials, the morphology of cyclic fatigue fracture surfaces is almost identical to that obtained under monotonic loads, except for one subtle detail, which is the presence of small debris particles on the fracture surfaces. Furthermore, it has been reported that the crack propagation path and crack growth mechanism are indistinguishable under static or cyclic fatigue processes (Ritchie, 2003; Ritchie and Dauskardt, 1991; Quinn, 2016). The configuration of the crack wake surface is determined by the inter- or transgranular fracture mode. Fractographic and in-situ crack-path evaluations from the majority of studies claim that fatigue fracture in ceramics is intergranular. This represents a discontinuous process depending on relative orientation of the grain boundaries and microstructural homogeneity of the material. The subcritical crack propagation in the intergranular path occurs along the grain boundaries by the creation, growth and coalescence of microcracks in front of the crack tip. Clearly, the process of intergranular fracture will happen in materials where the intergranular phases are weaker than the grains. Also, some pull-out of grains from the bulk of the material and relaxation of residual stress could happen due to intergranular crack propagation.

However, the process described above does not represent the whole picture, Kawakubo and Komeya (1987) referred to a fatigue failure that consisted of intergranular crack propagation with partial transgranular path at perpendicular elongated crystals of sintered Si_3N_4 (Kawakubo and Komeya, 1987). Another study reported a fine-grained Si_3N_4 with transgranular propagation generating a flat fracture surface that did not present accelerated fatigue failure (Horibe and Hirahara, 1991). A singular evaluation, conducted on hard porcelain, revealed transgranular crack path after cyclic loading, basically due to heterogeneous microstructure (amorphous matrix, crystalline grains and porosities) (Maity *et al.*, 1994). In conclusion, there is not one single path for crack growth; it will depend on the specific microstructural features of each material. This fact was confirmed by a very interesting study conducted by Mutoh *et al.* (1993) on the fatigue crack growth rate (cyclic and static) of five ceramic materials: Si_3N_4 , Al_2O_3 , TiB_2 , SiC and ZrO_2 . Evaluations of the morphologies of the fractures surface revealed the following: (1) materials with predominantly intergranular fatigue-cracking exhibit microcracking at the crack tip with formation of bridging elements in the crack wake, but the bridging units located behind the crack tip tends to be broken; cyclic loading provokes degradation of shielding effect at the crack tip. (2) materials with mostly transgranular fatigue-cracking exhibit crack growth rate identical under static and cyclic loading conditions. A summary of these observations is presented in Table 1. (Mutoh *et al.*, 1993).

As expected, in cyclic fatigue studies, one of the most reported microstructural features is grain size, which significantly influences fatigue resistance in ceramic materials. An interesting approach could be to consider the empirical Hall-Petch relation where the mechanical resistance is inversely proportional to the square root of grain size. Even though the relationship is widely used in metallic materials, it has also been reported valid for ceramic materials like zirconia composites and magnesium aluminate spinel, specifically in hardness measurements (François, 1989; Pelleg, 2014). In any case, this empirical concept could be used over the cyclic fatigue resistance since fine-grained microstructures exhibit superior fatigue properties over coarse-grained materials, assuming all other microstructural features are kept, approximately, fixed. In this context, the research of Grathwohl and Liu (1991), confirms this approach. They evaluated the effect of grain size on fatigue resistance for tetragonal zirconia material stabilized with ceria (9Ce-TZP). Three different grain sizes were studied (1.0, 1.5 and 2.7 μm) and the results were presented as stress-failure time curves (useful life). It was determined that stress required to produce fatigue failure decreased with increasing grain size, regardless of magnitude of R -ratio (See Fig. 12). In the same work, an important microstructural observation was that fatigue samples with larger grain sizes evidenced higher degree of transcrystalline fracture probably due to the tetragonal to monoclinic transformation within the grains for this 9Ce-TZP ceramic material. (Grathwohl and Liu, 1991; Pelleg, 2014).

Notable appreciation from Fig. 12 is the comparison of the material under static or cyclic loading. It is revealed for 9Ce-TZP that under static loads, failure times are about 2 or 3 orders of magnitude higher than for cyclic loading, at the same stress level (Grathwohl and Liu, 1991). This fact has been recognized by other studies, like the one conducted by Dauskardt *et al.* (1990), that reported crack growth improvements up to 8 orders of magnitude by cyclic fatigue compared to static loading for an evaluation done in partially stabilized zirconia with magnesium oxide (Mg-PSZ).

Table 1 Morphologies of the fracture surfaces under cyclic fatigue

Material	Fracture path
Si_3N_4	Intergranular
SiC	Transgranular
TiB_2	Intergranular and transgranular
ZrO_2	Transgranular
Al_2O_3	Intergranular and transgranular

Adapted from Mutoh, Y., Takahashi, M., Takeuchi, M., 1993. A molecular interpretation of stress corrosion in silica. In: Hong, Y. (Ed.), *Fatigue and Fracture of Engineering Materials and Structures*, vol. 16 (8). Wiley. pp. 875–890.

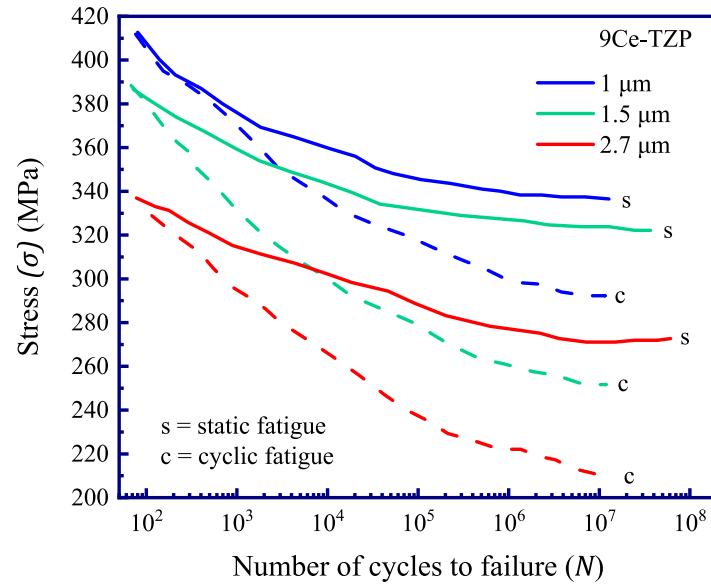


Fig. 12 Effect of grain size in fatigue test for 9Ce-TZP materials. Results from cyclic and static fatigue. Adapted from Grathwohl, G., Liu, T., 1991. Crack resistance and fatigue of transforming ceramics: II, CeO₂-Stabilized Tetragonal ZrO₂. *Journal of the American Ceramic Society* 74 (12), 3028–3034.

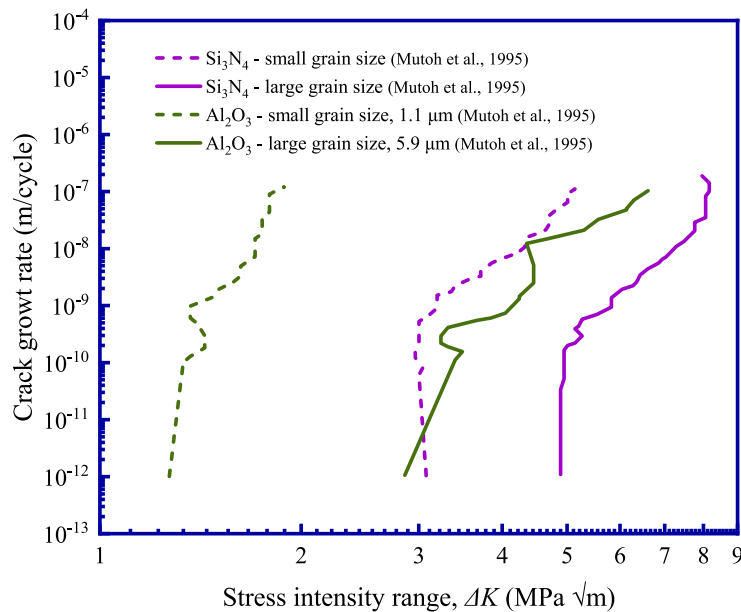


Fig. 13 Effect of grain size in crack growth rate for Si₃N₄ and Al₂O₃. Adapted from Mutoh, Y., Hansson, Y.T., Takahashi, M., 1995. Effect of grain size on fatigue crack growth in silicon nitride and alumina. In: Bradt, R., Brookes, C., Routbort, J. (Eds.), *Plastic Deformation of Ceramics*. New York: Springer, pp. 653–666.

On the other hand, microstructural effects on cyclic loading is not a simple issue and dependence of fatigue crack propagation threshold on the grain size, for instance, is a little more complex situation. In this regard, a study was conducted on two ceramic materials (Si₃N₄ and Al₂O₃) with different grain sizes (designated as “small” and “large”). In **Fig. 13**, the results of crack propagation rate as a function of ΔK , are presented. For coarse-grained Si₃N₄ (see **Fig. 13**) higher threshold value (ΔK_{th}) and lower crack propagation rate (da/dN) were found, compared to the values of finer Si₃N₄. Specifically, the threshold value increased from 2.9 MPa^{1/2} for the small grain to 4.7 MPa^{1/2} for the large grain size material. Similar behavior was observed in alumina. Possible explanations for this behavior could be: (1) incomplete crack closure during unloading due to high degree of roughness in the crack surface that will generate increments in the closing load, i.e., (K_{op}), and, consequently, it will increase (ΔK_{th}) according to Eq. (14), and (2) raise of the grain bridging effect, which is a very important crack-tip shielding mechanism, due to higher grain sizes in the material. It has also been reported that materials with intergranular fracture, like the one from this study, show an increasing R-curve behavior with increasing grain size (Mutoh *et al.*, 1995; Gilbert and Ritchie, 1997).

In conclusion, there is a need for systematic investigations of cyclic fatigue for a large group of ceramic materials. Some reported results could be applied only to a particular kind of ceramic material and they could not be considered as common characteristics of ceramics. Furthermore, other aspects such as variable amplitude of the cycling loading, high temperature fatigue and thermal fatigue are interesting topics to examine but they are beyond the scope of the present article. In any case, systematic studies are required for a better understanding of fatigue crack-growth phenomena.

Cyclic Fatigue (R-ratio) and Ceramic and Glasses Applications

Through the years, enhanced properties of advanced ceramics have introduced them into new fields of applications including environmental uses, energy, biomaterials composites, intelligent materials, and so on. Proper functioning of materials in these areas must take into account operating conditions that could promote cyclic fatigue of ceramic devices. In this regard, it is handy to remember the evaluation of advanced ceramics under cyclic loading conditions: alumina, silicon nitride, lead zirconate titanate, and zirconia-based materials, are prone to undergo accelerated degradation, while ceramics like soda-lime glass, porcelain, silicon carbide, mullite, lead titanate, and α -alumina, are not. This susceptibility to cyclical fatigue is associated with deterioration of shielding mechanisms, mainly bridging and weakening for microcracking, which allows crack propagation reactivation (Evans and Fuller, 1974; Kishimoto, 1991; Guiu *et al.*, 1991; Liu and Chen, 1991a; Ritchie and Dauskardt, 1991; Horibe and Choi, 1994; Casellas *et al.*, 1999).

Thus, to conclude the present article, it is worthwhile to mention some practical applications and studies related to engineering ceramics subjected to cyclic loading. One example is the use of alumina in automobile spark plugs and hip joint replacements (Sômiya *et al.*, 2003; Matizambuka, 2018). A very important field of development is the utilization of zirconia-based compounds with different oxide stabilizers for dental restorations, particularly in dental pieces such as crowns or bridges. Other outstanding applications for zirconia-based materials are components for the aerospace industry, cutting and drilling tools and biomedical implants. Latest research in this area reported materials that include metallic ductile phase in the matrix of zirconia composite (ZrO_2 -Ta) to increase fracture toughness, tolerance to damage and fatigue performance (Dauskardt *et al.*, 1990; Grathwohl and Liu, 1991; Guiu *et al.*, 1991; Liu and Chen, 1991a; Schmitt *et al.*, 1996; Anglada *et al.*, 2002; Delgado *et al.*, 2003; Chevalier *et al.*, 2007; Wang *et al.*, 2014; Smimov *et al.*, 2017; Gjurin *et al.*, 2018; Matizambuka, 2018; Belli *et al.*, 2020; Chevalier *et al.*, 2020; Wei *et al.*, 2020).

Another relevant ceramic is silicon nitride for its excellent properties. This type of compounds is employed for engine and turbine components, such as turbocharger rotors or bearings, valves and cutting tools in industrial environments. Nowadays, it is common to find them as refractory materials, exposed to temperature fluctuations during production cycles, inducing cyclical thermomechanical loads. Recent study has described the use of silicon-based material as spring material for aggressive high-temperature conditions, in combination with humid environments under cyclic loads. Even though, thermal fatigue is out of the scope of this article, it should be considered for future fatigue studies (Ritchie and Dauskardt, 1991; Jacobs and Chen, 1995; Bermudo *et al.*, 1997; Sômiya, 2013; Andreev *et al.*, 2018; Khader *et al.*, 2020).

Finally, a paramount material that has caught attention for several years is the lead zirconate titanate (PZT). This material is attractive as ferroelectric ceramic and even now is being studied for the electric voltage effect generated under cyclic loads over long periods (Kishimoto, 1991; Weitzing *et al.*, 1999; Okayasu and Ogawa, 2020). Although it is out of the scope of this article, it is advisable to consider, in the forthcoming times, the cyclic fatigue of ferroelectric and piezoelectric ceramics, mainly in electric and electronic devices. This is an interesting closed-related field of study that will enhance the knowledge of the fatigue behavior of ceramics under cyclic loads.

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References

- Anderson, T., 2017. *Fracture Mechanics Fundamentals*, fourth ed. Boca Raton: CRC Press.
- Andreev, K., Tadaiona, V., Kostera, J., Verstryngbe, E., 2018. Cyclic fatigue of silica refractories – Effect of test method on failure process. *Journal of the European Ceramic Society* 37 (4), 1811–1819.
- Anglada, M., Alcalá, J., Fernández, R., Llanes, L., Casellas, D., 2002. *Fracture Mechanics of Ceramics*. In: Bradt, R., Munz, D., Sakai, M., Shevchenko, V., White, K. (Eds.), vol. 13: Crack – Microstructure Interaction, R-Curve Behavior, Environmental Effects in Fracture, and Standardization. Springer, pp. 255–272.
- Belli, R., Loher, C., Petschelt, A., *et al.*, 2020. Low-temperature degradation increases the cyclic fatigue resistance of 3Y-TZP in bending. *Dental Materials* 36 (8), 1086–1095.
- Bermudo, J., Osendi, M., Li, M., Reece, M., 1997. Cyclic fatigue behavior of silicon nitride materials. *Journal of the European Ceramic Society* 17, 1855–1860.
- Casellas, D., Nagl, M., Vélez, M., Anglada, M., 1999. Determinación de la presencia de fatiga mecánica en materiales cerámicos. *Boletín de la Sociedad Española de Cerámica y Vidrio* 38 (2), 101–110.
- Chevalier, J., Olagnon, C., Fantozzi, G., 1999. Crack propagation and fatigue in zirconia-based composites. *Composites: Part A – Applied Science and Manufacturing* 30 (4), 525–530.
- Chevalier, J., Gremillard, L., Deville, S., 2007. Low-temperature degradation of zirconia and implications for biomedical implants. *Annual Review of Materials Research* 37, 1–32.

- Chevalier, J., Liens, A., Reveron, H., *et al.*, 2020. Forty years after the promise of «ceramic steel?»: Zirconia-based composites with a metal-like mechanical behavior. *Journal of the American Ceramic Society* 103 (3), 1482–1513.
- Cotterell, B., 2010. *Fracture and Life*. Singapore: World Scientific Publishing.
- Danzer, R., Lube, T., Supancic, P., Damani, R., 2008. Fracture of Ceramics. *Advanced Engineering Materials* 10 (4), 275–298. (Special Issue: Heat Transfer in Cellular and Composite Materials).
- Dauskardt, R., Yu, W., Ritchie, R., 1987. Fatigue crack propagation in transformation-toughened zirconia ceramic. *Journal of the American Ceramic Society* 70 (10), 248–252.
- Dauskardt, R., Marshall, D., Ritchie, R., 1990. Cyclic fatigue-crack propagation in magnesia-partially-stabilized zirconia ceramics. *Journal of the American Ceramic Society* 73 (4), 893–903.
- Dauskardt, R., James, M., Porter, J., Ritchie, R., 1992. Cyclic fatigue-crack growth in a SiC-whisker-reinforced alumina ceramic composite: Long- and Small-Crack Behavior. *Journal of the American Ceramic Society* 75 (4), 759–771.
- Delgado, J., Morejón, L., Martínez, S., Gil, J., 2003. Cerámicas de circonia para aplicaciones biomédicas. *Sociedad Ibérica de Biomecánica y Biomateriales* 11, 46–52.
- El Attaoui, H., Saâdaoui, M., 2005. Quantitative analysis of crack shielding degradation during cyclic fatigue of alumina. *Journal of the American Ceramic Society* 88 (1), 172–178.
- El Attaoui, Saâdaoui, M., Chevalier, J., Fantozzi, G., 2006. Crack propagation behavior of alumina with different grain sizes under static and cyclic fatigue. *Key Engineering Materials* 317–318, 449–452.
- Elber, W., 1970. Fatigue crack closure under cyclic tension. *Engineering Fracture Mechanics* 2 (1), 37–44.
- Evans, A., Fuller, E., 1974. Crack propagation in ceramic materials under cyclic loading conditions. *Metallurgical Transactions* 5, 27–33.
- François, D., 1989. The influence of the microstructure on fatigue. In: Moura, C., Guerra, L. (Eds.), *Advances in Fatigue Science and Technology*. Dordrecht: Kluwer Academic, pp. 23–76.
- Gilbert, C., Ritchie, R., 1997. Mechanisms of Cyclic Fatigue-Crack Propagation in a Fine-Grained Alumina Ceramic: The Role of Crack Closure. *Fatigue and Fracture of Engineering Materials and Structures* 20 (10), 1453–1466.
- Gilbert, C., Petrány, R., Ritchie, R., Dauskardt, R., Steinbrech, R., 1995. Cyclic fatigue in monolithic alumina: mechanisms for crack advance promoted by frictional wear of grain bridges. *Journal of Materials Science* 30, 643–654.
- Gjurić, S., Özcan, M., Oblak, C., 2018. Zirconia ceramic fixed partial dentures after cyclic fatigue tests and clinical evaluation: A systematic review. *Advances in Applied Ceramics: Structural, Functional and Bioceramics* 118 (1), 1–8.
- Grathwohl, G., Liu, T., 1991. Crack resistance and fatigue of transforming ceramics: II, CeO₂-Stabilized Tetragonal ZrO₂. *Journal of the American Ceramic Society* 74 (12), 3028–3034.
- Guiu, F., Reece, M., Vaughan, A., 1991. Cyclic fatigue of ceramics. *Journal of Materials Science* 26, 3275–3286.
- Han, Y., Kim, D., Gilbert, C., Ritchie, R., 2001. Cyclic fatigue–crack propagation behavior in silicon carbide: Long- and small-crack behavior. *Journal of the American Ceramic Society* 84 (3), 551–554.
- Hoffman, M., Mai, Y., 1995. Crack-tip degradation processes observed during in situ cyclic fatigue of partially stabilized zirconia. *Journal of the American Ceramic Society* 78 (10), 2801–2810.
- Hoffman, M., Wakayama, S., Kishi, T., Mai, Y., Kawahara, M., 1996. Crack closure during cyclic fatigue in Mg-PSZ ceramic as detected by acoustic emissions. *Materials Science Forum* 210–213, 487–494.
- Horibe, S., Hirahara, R., 1991. Cyclic fatigue of ceramic materials: Influence of crack path and fatigue mechanisms. *Acta Metallurgica Materialia* 29 (6), 1309–1317.
- Horibe, S., Choi, G., 1994. Cyclic fatigue in ceramics: Mechanisms and effects of microstructure and environment. In: Sômiya, S., Doyama, M., Hasegawa, M., Agata, Y. (Eds.), *Advanced Materials '93, I: A. Ceramics, Powders, Corrosion and Advanced Processing*. Transactions of the Materials Research Society of Japan. pp. 929–935.
- Huang, X., Moan, T., 2007. Improved modeling of the effect of R-ratio on crack growth rate. *International Journal of Fatigue* 29, 591–602.
- Huh, Y., Song, J., 1998. Cyclic fatigue crack growth and closure behaviour in alumina ceramics. *Fatigue and Fracture of Engineering Materials and Structures* 21 (12), 1575–1587.
- Huh, Y., Yoon, K., Cho, S., Song, J., 2000. Behavior of cyclic fatigue crack growth for SiC ceramics. *Key Engineering Materials* 183–187 (187), 1249.
- Irwin, G., 1958. Fracture. In: Flügge, S. (Ed.), *Encyclopedia of Physics - Volume 6: Elasticity and Plasticity*. Verlag: Springer, pp. 551–590.
- Jacobs, D., Chen, I., 1995. Cyclic fatigue in ceramics: A balance between crack shielding accumulation and degradation. *Journal of the American Ceramic Society* 78 (3), 513–515.
- Kawakubo, T., Komeya, K., 1987. Static and cyclic fatigue behavior of a sintered silicon nitride at room temperature. *Journal of the American Ceramic Society* 70 (6), 400–405.
- Khader, I., Koplin, C., Schröder, C., *et al.*, 2020. Characterization of a silicon nitride ceramic material for ceramic springs. *Journal of the European Ceramic Society* 40 (10), 3541–3554.
- Kishimoto, H., 1991. Cyclic Fatigue in Ceramics. *Japan Society of Mechanical Engineers International Journal* 34 (4), 393–403.
- Kruzic, J., Cannon, R., Ritchie, R., 2004. Crack-size effects on cyclic and monotonic crack growth in polycrystalline alumina: Quantification of the role of grain bridging. *Journal of the American Ceramic Society* 87 (1), 93–103.
- Kruzic, J., Cannon, R., Ager III, J., Ritchie, R., 2005. Fatigue threshold R-curves for predicting reliability of ceramics under cyclic loading. *Acta Materialia* 53 (9), 2595–2605.
- Kruzic, J., Arsecularatne, J., Tanaka, C., Hoffman, M., Cesar, P., 2018. Recent advances in understanding the fatigue and wear behavior of dental composites and ceramics. *Journal of the Mechanical Behavior of Biomedical Materials* 88, 504–533.
- Lathabai, S., Mai, Y., Lawn, B., 1989. Cyclic fatigue behavior of an alumina ceramic with crack-resistance characteristics. *Journal of the American Ceramic Society* 72 (9), 1760–1763.
- Li, M., Guiu, F., 1995. Subcritical fatigue crack growth in alumina—II. Crack bridging and cyclic fatigue mechanisms. *Acta Metallurgica et Materialia* 43 (5), 1871–1884.
- Liu, S., Chen, I., 1991a. Fatigue of yttria-stabilized zirconia: I, Fatigue damage, fracture origins, and lifetime prediction. *Journal of the American Ceramic Society* 74 (6), 1197–1205.
- Liu, S., Chen, I., 1991b. Fatigue of yttria-stabilized zirconia: II, Fatigue damage, fracture origins, and lifetime prediction. *Journal of the American Ceramic Society* 74 (6), 1197–1205.
- Maity, S., Chaudhuri, J., Sarkar, B., 1994. Cyclic fatigue behaviour of porcelain under repeated impact. *Journal Transactions of the Indian Ceramic Society* 53 (1), 1–7.
- Masuda, M., Soma, T., Matsui, M., 1990. Cyclic fatigue behavior of Si₃N₄ ceramics. *Journal of the European Ceramic Society* 6, 253–258.
- Matizamhuka, W., 2018. Advanced ceramics — The new frontier in modern-day technology: Part I. *Nature Journal of the Southern African Institute of Mining and Metallurgy* 118, 757–764.
- Matsudaira, T., Matsumura, Y., Kitaoka, S., Awaji, H., 2009. Effect of microstructure on the fatigue behavior of aluminum titanate ceramics. *Journal of Materials Science* 44, 1622–1632.
- Munz, D., Fett, T., 2001. *Ceramics Mechanical Properties, Failure Behaviour, Materials Selection*, second ed. Heidelberg: Springer.
- Mutoh, Y., Takahashi, M., Takeuchi, M., 1993. A molecular interpretation of stress corrosion in silica. In: Hong, Y. (Ed.), *Fatigue and Fracture of Engineering Materials and Structures*, vol. 16. Wiley, pp. 875–890.
- Mutoh, Y., Miyashita, Y., Hansson, T., Takahashi, M., 1995. Effect of grain size on fatigue crack growth in silicon nitride and alumina. In: Bradt, R., Brookes, C., Routbort, J. (Eds.), *Plastic Deformation of Ceramics*. New York: Springer, pp. 653–666.
- Okayasu, M., Ogawa, T., 2020. Failure characteristics of PZT ceramic during cyclic loading. *Journal of Electronics Materials* 49, 5534–5541.
- Paris, P., Erdogan, F., 1963. A critical analysis of crack propagation laws. *Journal of Basic Engineering* 85 (4), 528–533.

- Pelleg, J., 2014. Mechanical Properties of Ceramics. Cham: Springer.
- Perez, N., 2004. Fracture Mechanics. Boston: Kluwer academic.
- Quinn, G., 2016. Fractography of Ceramics and Glasses. Gaithersburg: National Institute at Standards and Technology.
- Richard, H., Sander, M., 2016. Fatigue Crack Growth: detect — Assess — Avoid. Cham: Springer.
- Ritchie, R., 2003. Cyclic loading and fatigue: Fatigue of brittle materials. In: Milne, I., Ritchie, R., Karihaloo, B. (Eds.), Comprehensive Structural Integrity. Oxford: Elsevier, pp. 359–376.
- Ritchie, R., Dauskardt, R., 1991. Cyclic fatigue of ceramics: A fracture mechanics approach to subcritical crack growth and life prediction. *Journal of the Ceramic Society of Japan* 99 (10), 1047–1062.
- Rösler, J., Harders, H., Bäker, M., 2007. Mechanical Behaviour of Engineering Materials. Heidelberg: Springer.
- Schmitt, R., Fett, T., Munz, D., 1996. Cyclic fatigue of zirconia. *Fatigue and Fracture of Engineering Materials and Structures* 19 (12), 1411–1420.
- Smirnov, A., Beltrán, J., Rodriguez-Suarez, T., *et al.*, 2017. Unprecedented simultaneous enhancement in damage tolerance and fatigue resistance of zirconia/Ta composites. *Scientific Reports* 7, 1–13.
- Soma, T., Masuda, M., Matsui, M., Oda, I., 1988. Cyclic fatigue testing of ceramic materials. *International Journal of High Technology Ceramics* 4, 289–299.
- Sōmiya, S., 2013. Handbook of Advanced Ceramics: Materials, Applications, Processing and Properties. London: Academic Press.
- Sōmiya, S., Aldinger, F., Claussen, N., *et al.*, 2003. Handbook of Advanced Ceramics – Volume 2: Processing and their Applications. London: Elsevier.
- Sonsino, C., 2003. Fatigue design of structural ceramic parts by the example of automotive intake and exhaust valves. *International Journal of Fatigue* 25, 107–116.
- Steffen, A., Dauskardt, R., Ritchie, R., 1991. Cyclic fatigue life and crack-growth behavior of microstructurally small cracks in magnesia-partially-stabilized zirconia ceramics. *Journal of the American Ceramic Society* 74 (6), 1259–1268.
- Taylor, D., 2007. The Theory of Critical Distances: A New Perspective in Fracture Mechanics. London: Elsevier.
- Wang, R., Lu, C., Wang, G., Zhang, D., 2014. Influence of cyclic loading on the fracture toughness and load bearing capacities of all-ceramic crowns. *International Journal of Oral Science* 6 (2), 99–104.
- Wei, C., Gong, X., Xie, C., *et al.*, 2020. In vitro cyclic fatigue and hydrothermal aging lifetime assessment of yttria-stabilized zirconia dental ceramics. *Journal of the European Ceramic Society* 40 (13), 4647–4654.
- Weitzing, H., Schneider, G., Steffens, J., Hammer, M., Hoffmann, M., 1999. Cyclic fatigue due to electric loading in ferroelectric ceramics. *Journal of the European Ceramic Society* 19, 1333–1337.

Further Reading

- Gilbert, C., Ritchie, R., 1998. On the quantification of bridging tractions during subcritical crack growth under monotonic and cyclic fatigue loading in a grain-bridging silicon carbide ceramic. *Acta Materialia* 46 (2), 609–616.
- Ko, H., 1996. Fatigue behavior of sintered Al_2O_3 under rotary bending and static fatigue. In: Bradt, R., Hasselman, D., Munz, D., Sakai, M., Shevcheko, V. (Eds.), *Fracture Mechanics of Ceramics – Volume 12: Fatigue, Composites, and High-Temperature Behavior*. New York: Springer, pp. 15–29.
- Ritchie, R., Dauskardt, R., Yu, W., Brendzel, A., 1990. Cyclic fatigue-crack propagation, stress-corrosion, and fracture-toughness behavior in pyrolytic carbon-coated graphite for prosthetic heart valve applications. *Journal of Biomedical Materials Research* 24 (2), 189–206.

Thermal Properties of Ceramic Materials

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Introduction

Ceramic materials constitute one of the very important classes of material that mankind exploits in the modern world. The abilities of ceramic materials to control heat exchange and resist high temperatures explain why they are used in the building, cooking, electronics, aerospace, transport, and energy sectors. In such working situations the thermal properties become of prime importance. These are essentially heat capacity, thermal expansion and thermal conductivity. Though related parameters such as thermal diffusivity can be considered, the present contribution focuses on these three properties.

In this context, the notions of temperature and heat energy can be introduced. Starting from the zero'th law of thermodynamics, temperature is a parameter which determines whether a system is in thermal equilibrium with another system. At the microscopic scale, temperature corresponds to a measure of the average energy or thermal agitation of the atoms. Heat is then a form of energy associated with the movement of individual atoms or molecules of a body (gas, liquid, or solid) and is defined from the first law of thermodynamics as energy in transit due to a difference in temperature. Heat capacity refers to the heat energy required to increase the temperature of a body and, in experimental conditions of constant volume, is related to the change in internal energy. For a typical ceramic material, the internal energy U expresses itself in the form of atomic vibrations. At higher temperature a larger amplitude of vibrations occurs corresponding to higher internal energy.

If two systems are at different temperatures then heat transfer can take place by conduction, convection or radiation. According to the second law of thermodynamics, heat flows from the hot body to the cold body or surroundings. The focus here will be on conduction in the solid state which can be described for heat flow in one dimension down a thermal gradient by Fourier's law

$$\Phi = -\lambda A \frac{dT}{dx} \quad (1)$$

where Φ is heat flow in W, A is the cross sectional area, T is temperature, and x is a position coordinate within the solid body. In the case of a homogeneous isotropic solid, λ corresponds to a constant of proportionality in Eq. (1) known as the thermal conductivity. In a ceramic material the heat energy is carried by the atomic vibrations which determine λ .

Thermal expansion or contraction can also be related to the nature of atomic vibrations in the solid. Increase in volume of a solid at higher temperature can be explained by the increased amplitude of vibrations about an average position. But since in the interatomic pair potential the repulsion and attraction terms are not symmetric, the average atomic separation increases for the larger amplitude vibrations at high temperature.

Given the importance of atomic vibrations for all three properties, the first section discusses lattice vibrations in a crystalline solid.

Lattice Vibrations

Consider a single atom vibrating in a solid (Fig. 1). If it is connected to the surrounding atoms with a force constant equivalent to Young's modulus, the natural vibration frequency is of the order of 5×10^{12} Hz.

This is equivalent to frequencies in the infrared. But the stimulation of vibrations in a crystalline solid involves a much wider range of frequencies from sound waves at low frequencies below 1 kHz up to the THz region. This is because the solid is a multi-atom system. It is conveniently treated as a continuum.

Consider now a line of atoms connected by springs representing the chemical bonds. Propagation of a vibration takes place in the form of an elastic wave described, for example, by a cosine function:

$$u(x, t) = u_0 \cos(qx - \omega t) \quad (2)$$

where ω is the radial frequency and $q = \frac{2\pi}{\Lambda}$ is proportional to the inverse of the wavelength Λ .

Two types of waves can be identified:

- Transverse waves where atoms move at 90° to the propagation direction,
- Longitudinal waves where atoms move in the same direction as the propagation direction.

For a given elastic wave propagation direction, two transverse polarizations at 90° to each other and one longitudinal polarization are required to describe the movement of an atom in any direction in space (i.e., the description is complete).

So the vibrational modes of the crystal can be described in the form of elastic waves each with a characteristic wavelength and frequency. Two questions can then be asked:

- (1) How many vibrational modes (or different waves) exist?

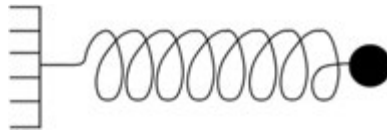


Fig. 1 Simple representation of a single atom vibrating in a solid.

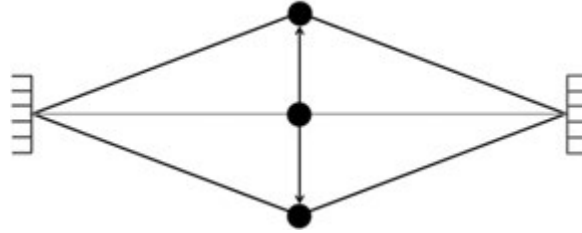


Fig. 2 Single particle on a tight string.

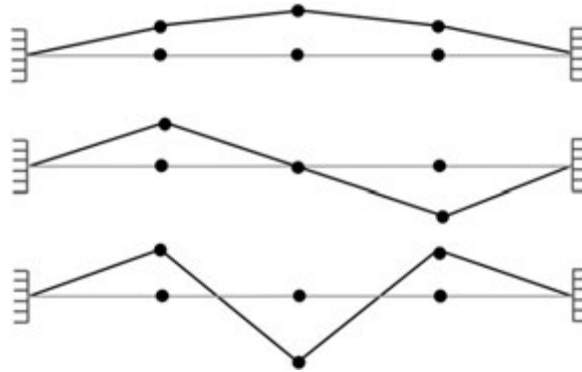


Fig. 3 Three particles on a string – different vibration modes.

Consider identical atoms in a line oscillating in the form of transverse standing waves. By analogy to a particle on a string of length L , a system with one free atom has one mode of oscillation with wavelength $2L$ and a characteristic frequency (Fig. 2).

Now consider three atoms in the line (or three particles on a string). Three different modes of oscillation with wavelengths: $2L$, L , $2/3 L$ can be identified (Fig. 3).

So each new atom adds a new mode of oscillation. For N atoms, there will be N modes of oscillation. If the three types of polarization are then taken into account this gives for a crystal with N atoms a total of $3N$ modes of vibration.

(2) What is the relation between wavelength and frequency?

Consider a crystal of identical atoms with cubic symmetry. The atoms on a line, each separated by distance a , are connected with bonds represented by springs which obey Hooke's law. When an atom is displaced from its equilibrium position (u_s), the restoring force is proportional to the displacement distance. The equation of motion can be written:

$$M \frac{d^2 u_s}{dt^2} = \sum_p K_p (u_{s+p} - u_s) \quad (3)$$

where each atom has mass M , K_p is the force constant on atom s due to the relative displacement between atoms $s+p$ and s . With simplifications this has solution:

$$\omega = \left(\frac{4K_1}{M} \right)^{1/2} \left| \sin \left(\frac{1}{2} qa \right) \right| \quad (4)$$

where K_1 is the nearest neighbor force constant and q is the inverse wavelength (Kittel, 1976). Eq. (4) describes theoretically the dispersion relation between frequency and inverse wavelength for what are known as acoustic vibrations. In this type of vibration the atoms (even if of different type) move in phase with each other. The physically useful solutions are found in the

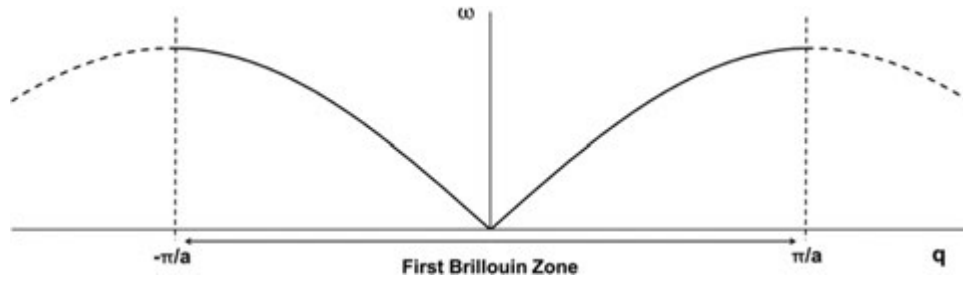


Fig. 4 Dispersion relation in the first Brillouin zone for a simple system with identical atoms.

range $-\pi/a < q < +\pi/a$; known as the Brillouin zone (Fig. 4). At low frequency, the wavelength is long (small value of q). At high frequency (q tends to $\frac{\pi}{a}$), the wavelength is short and approaches the interatomic distance, a .

In fact the derivative (slope) of the dispersion relation $\frac{d\omega}{dq} = v_g$ is the group velocity of the elastic waves or close to the origin, the speed of sound in the crystal. This is an important factor for heat conduction through the crystal.

Finally, we should consider what happens to the vibrational possibilities of the solid when the crystal structure (unit cell) involves two or more different atoms, as in the case of MgO. The result is that the dispersion relation develops new branches at high frequency called optical branches. These vibrations are more complex than acoustic vibrations because the different atom types vibrate in opposition of phase. Though the optical branches have important effects, especially for infrared absorption, the present discussion can be restricted to the acoustic branches with respect to heat capacity and thermal conductivity.

Heat Capacity

Heat energy is defined from the 1st law of thermodynamics given by:

$$\Delta U = Q + W \quad (5)$$

where ΔU is the internal energy change, Q is the heat transferred to system and W is the work done on the system. The first law expresses the conservation of energy in a process and allows the notion of heat capacity to be introduced. Heat capacity is defined by the heat energy required to increase the temperature of a body by 1K according to the experimental conditions of constant volume or constant pressure. For constant volume

$$C_V = \left(\frac{dQ}{dT} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (6)$$

where T is temperature, U is the internal energy and subscript V refers to constant volume.

For a system at constant pressure (example: solid in a chamber with a controlled pressure but no control on volume):

$$C_P = \left(\frac{dQ}{dT} \right)_P = \left(\frac{\partial H}{\partial T} \right)_P \quad (7)$$

where H is the enthalpy and subscript P refers to constant pressure.

For solids $C_P \approx C_V$ except at high temperature. So C_V can be calculated which is easier and C_P is measured corresponding to real experimental conditions. We focus on the internal energy U of a solid. Starting at a minimum energy state (the ground state) at absolute zero ($T = 0$ K), the increase of internal energy with temperature is expressed in different ways:

- Atomic vibrations,
- Excitation of electrons to higher energy levels,
- Formation of defects, which increases the disorder of the solid.

If the solid is electrically insulating, like many ceramics and glasses, there are very few available conduction electrons. So the major contribution to the internal energy comes from the atomic vibrations. This allows a simple but very useful model as a first approximation to be developed.

High Temperature Limit of Heat Capacity (or Classical Model)

Consider an atom in a crystal lattice (solid) which can move in one direction. This is a 1 dimensional simple harmonic oscillator (like a ball on a spring). For vibration in 1 direction, from the equipartition theorem, there is:

- $\frac{1}{2} k_B T$ of average kinetic energy (due to particle speed).
- $\frac{1}{2} k_B T$ of average potential energy (stored energy).

where k_B is Boltzmann's constant. As the atom vibrates to and fro these energy modes are continually exchanging. The total average energy for the atom is then the sum, i.e., $k_B T$. However in a solid an atom moves in 3 dimensions. So we require three orthogonal directions (x, y, z) to describe its movement completely. Since each direction has an energy of $k_B T/\text{atom}$, the total average energy is $3k_B T/\text{atom}$.

For N atoms in the solid the energy content is:

$$U = 3Nk_B T \quad (8)$$

So the heat capacity is:

$$C_V = \frac{dU}{dT} = 3Nk_B \quad (9)$$

which is just a constant value (invariant with temperature). This result can be used to illustrate another important point. As listed below heat capacity comes in different forms.

Heat capacity	per unit mass	$[\text{JK}^{-1} \text{kg}^{-1}]$	$C = \frac{1}{m} \frac{dQ}{dT}$ where m is the sample mass
	per unit volume	$[\text{JK}^{-1} \text{m}^{-3}]$	
	per mole	$[\text{JK}^{-1} \text{mole}^{-1}]$	
	per g – atom	$[\text{JK}^{-1} \text{g – atom}^{-1}]$	

In each case to calculate C_V with Eq. (9) it is necessary to count the number of atoms in the unit of a kg , m^3 , mole or g-atom . As an example, 1 g-atom contains N_A atoms where N_A is Avogadro's number (6.02×10^{23}). So the heat capacity per g-atom is approximately $25 \text{ J K}^{-1} \text{g-atom}^{-1}$ and this is independent of the type of solid (Kingery *et al.*, 1976).

In fact Eq. (9) is a good approximation of the high temperature behavior of many crystalline solids but does not describe the lower temperature behavior. Experimentally as temperature tends to absolute zero ($T = 0 \text{ K}$), the heat capacity decreases to zero. So what is missing? It is the collective nature of atomic vibrations in the form of elastic waves which has not been taken into account. The simple classical model considered each atom as moving individually without affecting the neighbors. In fact as the solid is cooled, it contracts with shortening of the atom-atom nearest neighbor distances. If one atom moves, it pushes or pulls its neighbors. So instead of adding up the energies of each atom, the Debye model is based on the sum (or in practice the integral) of the energies of these collective vibrations.

Debye Model

In the standard treatment made in solid state physics textbooks (Kittel, 1976) a number of simplifications are made: first a monatomic solid with cubic symmetry is considered with N atoms contained in a volume V . All the elastic waves are assumed to move with the same speed (of sound), i.e., the dispersion relation is linear (called the Debye approximation: $\omega = v_0 k$). Then the energy of each elastic wave is quantified: $\xi = (n + \frac{1}{2})\hbar\omega$, where $\hbar\omega$ is the smallest interval of energy called a phonon by analogy to the photon.

Instead of counting up the energy of all the atoms, the energies of all the possible elastic waves (vibrational possibilities of solid) are counted up to a maximum limiting frequency, called the Debye frequency (ω_D). This yields the well known Debye expression for heat capacity.

$$C_V = 9Nk_B \left(\frac{T}{\theta_D} \right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (10)$$

where $x = \frac{\hbar\omega}{k_B T}$, $x_D = \frac{\theta_D}{T}$, and $\theta_D = \frac{\hbar v_0}{k_B} \left(\frac{6\pi^2 N}{V} \right)^{1/3}$ is the Debye temperature.

Plotting this relation yields a heat capacity starting at 0 at $T = 0 \text{ K}$ which increases with T (Fig. 5). However at high temperature C_V then approaches a constant value. This high temperature limit is the same value as that predicted by the simple classical model. In the low temperature regime, close to $T = 0 \text{ K}$, C follows a dependence $\propto \left(\frac{T}{\theta_D} \right)^3$. This describes all the main features of heat capacity as a function of temperature. And though most solids are not quite as simple as the monatomic cubic crystal, Debye's model predicts values close to experimental data (Kingery *et al.*, 1976).

In practice the temperature dependence of heat capacity for a solid is described by a polynomial relation with a set of empirical coefficients. This is illustrated in the following example for alumina ceramic.

Example

Suppose we wish to calculate how much energy a furnace must supply to heat up alumina to a firing temperature of 1800 K (close to 1500°C).

The heat capacity per unit mass over this range can be described by a polynomial relation:

$$C = \frac{1}{M} \left[a + bT + \frac{d}{T^2} \right] \quad (11)$$

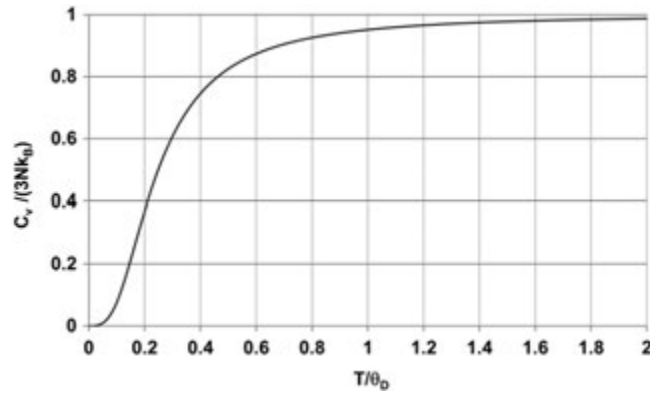


Fig. 5 Debye model – Heat capacity per $3 NK_B$ as a function of temperature (T/θ_D).

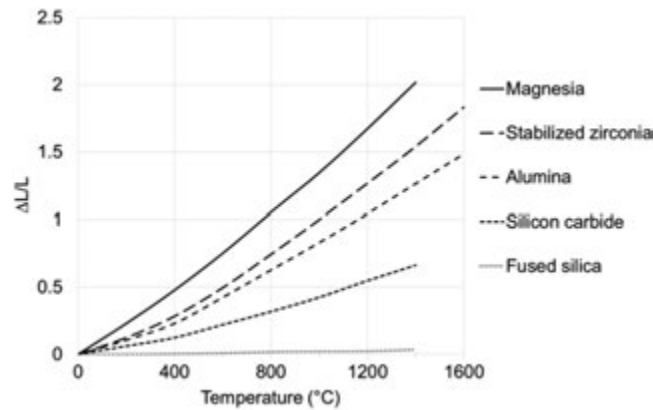


Fig. 6 Thermal expansion of ceramics. Data from Kingery, W.D., Bowen, H.K., Uhlmann, D.R., 1976. Introduction to Ceramics, second ed. New York: John Wiley and Sons.

where a , b , d are empirical coefficients ($a = 117.487$, $b = 10.376 \times 10^{-3}$, $d = -3.711 \times 10^6$ for alumina) found in a thermochemical data handbook (Knacke *et al.*, 1991) and M is the molar mass.

The energy change is obtained by integrating the polynomial relation in Eq. (11)

$$\Delta E = \int_{300}^{1800} C(T) dT = \frac{1}{M} \left[aT + \frac{bT^2}{2} - \frac{d}{T} \right]_{300}^{1800} \quad (12)$$

$$\Delta E \simeq 1.79 \text{ MJ kg}^{-1}$$

Thermal Expansion

Linear thermal expansion of a solid is characterized by measurements of length (dimension), denoted by l , as a function of temperature. Some typical curves for ceramic materials, which can be considered as macroscopically isotropic, are given in Fig. 6.

The expansion results from the asymmetry of the interatomic pair potential where the repulsion term is stronger than the attraction term holding the atoms in the solid together. The coefficient of thermal expansion (α) is then given by:

$$\alpha = \frac{1}{l_0} \frac{dl}{dT} \quad (13)$$

where l_0 is the reference length chosen at a convenient temperature such as 0°C . The coefficient α increases with temperature but, similarly to heat capacity, tends towards an asymptotic value as shown in Fig. 7.

In fact, the average separation distance of atoms at a given temperature is determined by the energy of the atomic vibrations. So similar trends in the coefficient of thermal expansion and heat capacity can be explained by the role of atomic vibrations.

In practice, thermal expansion coefficients are often evaluated as average values between 0°C and 1000°C ($\bar{\alpha}$). Thus a useful approximation for length l is given by:

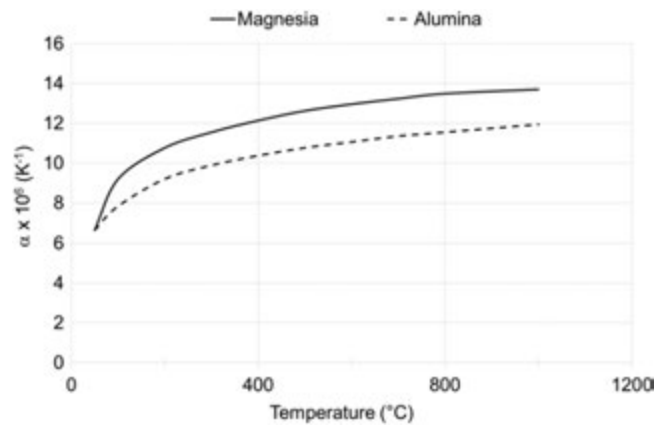


Fig. 7 Coefficients of thermal expansion for alumina and magnesia. Data from Kingery, W.D., Bowen, H.K., Uhlmann, D.R., 1976. Introduction to Ceramics, second ed. New York: John Wiley and Sons.

Table 1 Mean thermal expansion coefficients between 0°C and 1000°C for some ceramic materials

Material	Average linear thermal expansion coefficient ($\bar{\alpha}$ with units K^{-1})
Alumina	8.8×10^{-6}
Magnesia	13.5×10^{-6}
Mullite	5.3×10^{-6}
Stabilized zirconia	10.0×10^{-6}
Silicon Carbide	4.7×10^{-6}
Diamond	3.5×10^{-6}

Note: Data from Kingery, W.D., Bowen, H.K., Uhlmann, D.R., 1976. Introduction to Ceramics, second ed. New York: John Wiley and Sons.

$$l = l_0(1 + \bar{\alpha}T) \quad (14)$$

where T is in °C. For larger temperature ranges or greater accuracy, polynomial relations are used as given in the Handbook of Physics and Chemistry (Rumble, 2018):

$$l = l_0(1 + aT + bT^2 + cT^3 \dots) \quad (15)$$

where a , b , c are empirical coefficients and T is in °C.

One can also consider the coefficient of volume expansion (β) given by

$$\beta = \frac{1}{V_0} \frac{dV}{dT} \quad (16)$$

where V is the volume of the solid and V_0 is the volume at 0°C. For isotropic expansion

$$\bar{\beta} \approx 3\bar{\alpha} \quad (17)$$

provides a useful approximation.

Average values for linear thermal expansion coefficient of some well known ceramic materials measured for a temperature change between 0°C and 1000°C are given in Table 1 (Kingery *et al.*, 1976).

They can be compared to values for metals like copper of $16.6 \times 10^{-6} K^{-1}$ or aluminum of $25 \times 10^{-6} K^{-1}$. It can be noted that solids with strong covalent bonding such as diamond or silicon carbide exhibit small values of linear thermal expansion coefficient. The role of bond strength in a solid is also revealed by the relation of crystal symmetry to linear thermal expansion coefficients measured along the different crystal axes. Some relevant examples are given in Table 2.

The case of graphite is a good illustration with strong anisotropic thermal expansion due to the weak bonding between graphite planes compared to the bonds within the plane.

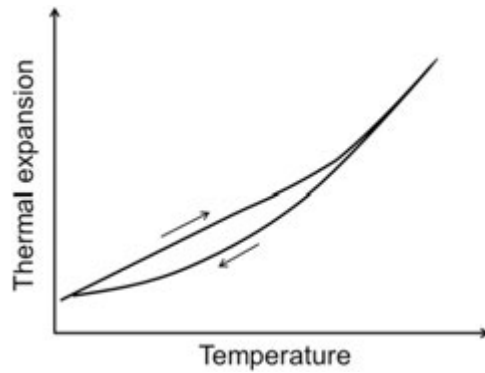
Anisotropic thermal expansion of individual grains has another consequence. If the polycrystalline matrix of a sintered ceramic consists essentially of random orientations, cooling down to room temperature after firing will yield stresses. For a significant difference in coefficients along the crystal axes combined with large grains, this can result in microcracking (Kingery *et al.*, 1976). Such behavior is revealed by hysteresis in the dilatometric curve of Fig. 8.

One solution to avoid this consists of careful powder preparation and processing to limit grain size. For example, alumina ceramics, made with an average grain size of less than 10 μm , do not exhibit microcracks.

Table 2 Thermal expansion coefficients measured perpendicular and parallel to the c-axis

Crystalline Solid	α measured normal to the c-axis (units K^{-1})	α measured along the c-axis (units K^{-1})
Alumina (Sapphire)	8.3×10^{-6}	9.0×10^{-6}
Silica (Quartz)	14.0×10^{-6}	9.0×10^{-6}
Graphite	1.0×10^{-6}	27×10^{-6}
Aluminum Titanate	-2.6×10^{-6}	11.5×10^{-6}
Titania	6.8×10^{-6}	8.3×10^{-6}

Note: Data from Kingery, W.D., Bowen, H.K., Uhlmann, D.R., 1976. Introduction to Ceramics, second ed. New York: John Wiley and Sons.

**Fig. 8** Dilatometric heating and cooling curve with hysteresis due to microcracking.

Intrinsic Thermal Conductivity

Heat conduction through an isotropic solid is proportional to the thermal gradient applied across it, described by Fourier's law as given in Eq. (1). In a dielectric solid (like most ceramics) where there are no mobile electrons, this heat is carried by the atomic vibrations discussed earlier. Imagine these vibrations traveling in different directions through the solid. Sometimes they collide setting off new vibrations in new directions with new energies (called 3 phonon or 4 phonon processes). This behavior is like that of a gas and so we consider the vibrations as a gas of "phonons". From kinetic theory the thermal conductivity of an ideal gas can be described with the relation:

$$\lambda = \frac{1}{3} C \bar{v} l \quad (18)$$

where C is the volume heat capacity, $\bar{v}$ is the root mean square speed of the gas molecules and l is the mean free path of a molecule between collisions.

In a somewhat similar way the thermal conductivity of the phonon gas is described by

$$\lambda = \frac{1}{3} \int_0^{\omega_D} c(\omega) v(\omega) l(\omega) d\omega \quad (19)$$

where c , v and l refer to heat capacity, group velocity and mean free path of the lattice vibrations. These are all dependent on frequency (ω) and with the integral we add up all the acoustic vibrational contributions from low or sonic frequencies up to the Debye frequency in the THz region. The Debye frequency marks the highest frequency which can be excited.

Two important questions can then be asked about thermal conductivity.

- (1) How does it vary with temperature for a crystalline inorganic non-metallic solid?
- (2) How does it vary between different types of solid such as crystalline and amorphous solids?

The following examples help to give some answers.

Example 1

Consider the thermal conductivity of an alumina single crystal (sapphire) measured as a function of temperature. In fact most crystalline dielectric solids follow the general behavior of a peak value in λ at low temperature at about 20 K and notably a progressive decrease as temperature is increased to about 1000°C (Fig. 9).

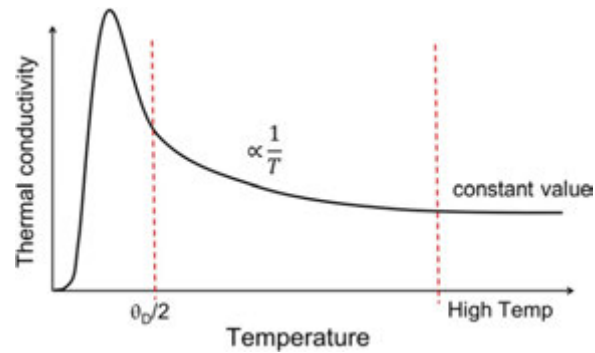


Fig. 9 Thermal conductivity as a function of temperature for a crystalline solid.

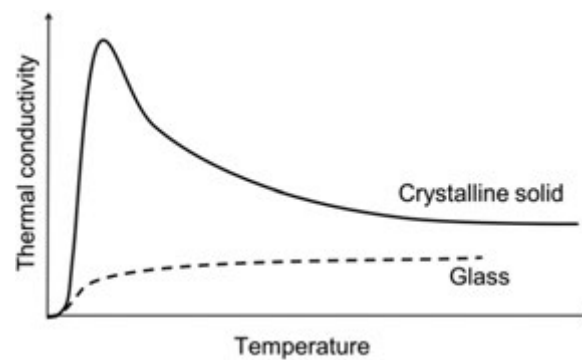


Fig. 10 Schematic of thermal conductivity as a function of temperature for a crystalline solid compared to a glass such as two different forms of silica.

We must examine the three parameters c , v and l found in the integral of Eq. (19). Since the propagation speed of the vibrations only decreases slightly as temperature is increased, in a first approximation, $v(\omega)$ is considered as a constant. At the lowest temperatures (left hand side of the peak value), the mean free path of the lattice vibrations is of the order of the sample size (i.e., mm). The principal controlling variable is the heat capacity which follows T^3 behavior as mentioned in the previous section. This explains why at absolute zero ($T = 0\text{K}$), the thermal conductivity tends to zero because there are no excited vibrations to carry heat.

As T increases, the heat capacity asymptotically approaches a constant value (above room temperature). This means for the high temperature side of the peak, the principal controlling factor is the mean free path. In essence as more lattice vibrations are stimulated at higher temperature, they mutually interfere; thus shortening the mean free path. At 1000°C the mean free path approaches the interatomic distance of less than 1 nm. This explains the dramatic decrease in thermal conductivity for single crystal alumina (sapphire) from $5000\text{ W m}^{-1}\text{ K}^{-1}$ at low temperature (about 20 K) to typically less than $7\text{ W m}^{-1}\text{ K}^{-1}$ at 1000°C (Kingery *et al.*, 1976); i.e., almost 3 orders of magnitude. At room temperature a single crystal of alumina (Sapphire) exhibits a typical value of $36\text{ W m}^{-1}\text{ K}^{-1}$ (Popov *et al.*, 2011).

Example 2

The role of the mean free path can be illustrated in another way when two forms of silica are compared. These are:

- (a) Crystalline solid (quartz),
- (b) A glass.

The thermal conductivity of quartz is greater than glass for all temperatures (Fig. 10). This is essentially due to a difference in mean free paths. In a glass, the mean free path for propagation of vibrations is restrained to approximately the interatomic distance due to the lack of order in the structure (disordered solid). Thus the thermal conductivity of a glass, typically close to $1\text{ W m}^{-1}\text{ K}^{-1}$, actually increases slightly with temperature, following the variation of the heat capacity. It can also be seen how at high temperature the conductivity curve of quartz approaches that of a glass – because the mean free path tends towards the interatomic distance.

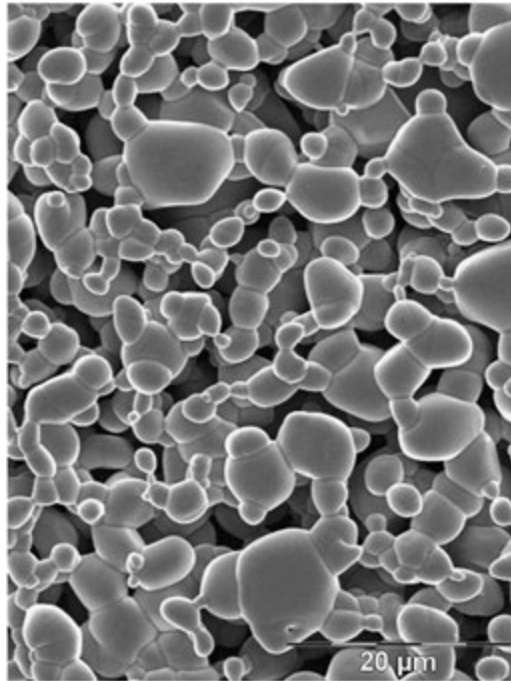


Fig. 11 Pores, grains and grain boundaries in tin oxide ceramic.

This section has emphasized the role of the mean free path of atomic vibrations in the intrinsic thermal conductivity of a material. In the final section modulation of this value by the microstructure to yield an overall (or effective) thermal conductivity for the ceramic materials is discussed.

Influence of Microstructure on Thermal Properties

Compared to a single crystal, ceramic materials are characterized by the presence of grain boundaries and pores (Fig. 11). In the case of a composite material, the ceramic is also constituted by a mixture of solid phases, each one with its own properties. So the question to ask is: What is the effect of this microstructure on the heat capacity and thermal conductivity? These microstructural factors are examined in the order:

- Grain boundaries,
- Pores,
- Mixture of solid phases.

Heat Capacity

The heat capacity of a dielectric solid is essentially controlled by the atomic vibrations and depends on the number of atoms contained in the chosen unit of study (a mole, a kg, or a m^3). Though increased disorder will increase the internal energy, the effect of a grain boundary on heat capacity can be neglected since there is virtually no change in the number of atoms in the mole, the kg, or the m^3 .

Using the same approach, the presence of porosity in the ceramic material does not change the number of atoms in a kg of solid. Therefore the heat capacity per unit mass (specific heat denoted by C) of dense alumina is the same as that of porous alumina. In contrast the heat capacity per unit volume of porous alumina (ρC with units $\text{J K}^{-1} \text{m}^{-3}$) is less than that of dense alumina because there are fewer atoms in 1 m^3 of the material. This is exploited in furnace design when rapid heating or cooling is required. Furnaces can be made of very porous refractories with small values of heat capacity per unit volume.

Ceramic materials, such as many refractories, often present a mixture of two or more solid phases. In such a case an average value (C_{av}) representing the material can be calculated using the rule of mixtures:

$$C_{\text{av}} = m_1 c_1 + m_2 c_2 \quad (20)$$

where m_1 , m_2 are the mass fractions and c_1 , c_2 are the specific heat values of phases 1 and 2. The rule of mixtures (or Neumann-Kopp rule) also offers a valuable approximation in the case of an unknown phase providing it can be broken down into constituents with known specific heat values. This can avoid the need to make delicate experimental measurements.

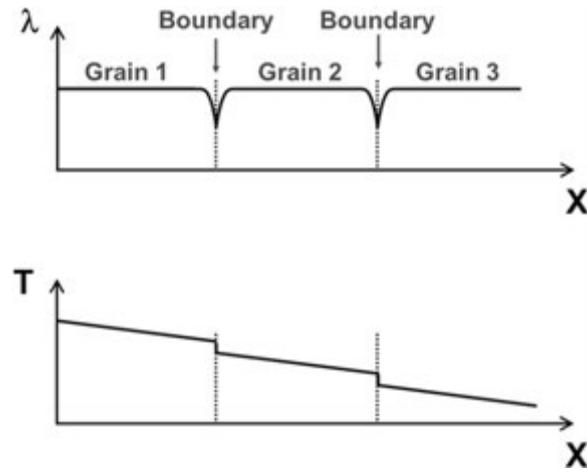


Fig. 12 Schematic of local thermal conductivity and temperature variation for three grains in the heat flow path.

Thermal Conductivity

The effects of microstructure are particularly significant for the thermal conductivity. First consider heat transfer by conduction across grain boundaries. The presence of local disorder in the grain boundary region increases the scattering of the lattice vibrations, yielding a local decrease in thermal conductivity. Thus interfacial thermal resistances can be attributed to the grain boundaries which act as additional series resistances in the heat flow path to those of the grains (Smith *et al.*, 2003). Due to the pronounced temperature drops occurring in conditions of steady state heat flow, illustrated in Fig. 12, the interfacial resistances are also called Kapitza resistances.

The thermal conductivity of the dense polycrystalline ceramic can now be described by the expression:

$$\frac{1}{\lambda_{\text{poly}}} = \frac{1}{\lambda_{\text{grain}}} + nR_{\text{int}} \quad (21)$$

where n is the number of grain boundaries per unit length of heat flow path (or inverse grain size) and R_{int} is the grain boundary thermal resistance. Typical values for R_{int} are in the range $0.5\text{--}1.0 \times 10^{-8} \text{ m}^2 \text{ K W}^{-1}$ depending on the material (Smith *et al.*, 2003, 2018, 2013).

As an example single crystal alumina (or sapphire) has a thermal conductivity of $36 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature. In its polycrystalline form, alumina with an average grain size of $1 \mu\text{m}$ yields a value of λ_{poly} close to $30 \text{ W m}^{-1} \text{ K}^{-1}$ and with an even smaller average grain size of $0.5 \mu\text{m}$, the effective thermal conductivity of dense alumina is less than $25 \text{ W m}^{-1} \text{ K}^{-1}$ (Smith *et al.*, 2018).

So smaller grain size of a ceramic reduces its effective thermal conductivity. Though, that said, the effect is less significant for insulating materials like stabilized zirconia where the thermal resistance of the grains is predominant.

The role of porosity on the effective thermal conductivity (λ) of a ceramic is now examined. Theoretically, the effective thermal conductivity can be predicted using a 2-phase mixture approach with a choice of analytical relations differing by the geometrical simplifications which have been made (Fig. 13).

For small amounts of porosity $v_p < 15\%$, the pores are typically closed, and well isolated from each other. This can be approximated by a spherical void centered in a solid cube as described by the Maxwell-Eucken relation:

$$\lambda = \lambda_s \frac{\lambda_p + 2\lambda_s + 2v_p(\lambda_p - \lambda_s)}{\lambda_p + 2\lambda_s - v_p(\lambda_p - \lambda_s)} \quad (22)$$

where λ_s is the solid phase thermal conductivity, λ_p is the pore thermal conductivity and v_p is the pore volume fraction.

In fact in this range, most relations yield predictions which are close to each other as shown in Fig. 13 (Smith *et al.*, 2013).

For pore volume fraction $> 15\%$, typically the pores are connected or “open”. In this case, the pore phase blocks the heat transfer more effectively due to the spatial distribution and this can be described by Landauer’s relation based on effective medium theory (Landauer, 1952):

$$\lambda = \frac{1}{4} \left[\lambda_p(3v_p - 1) + \lambda_s(2 - 3v_p) + \left([\lambda_p(3v_p - 1) + \lambda_s(2 - 3v_p)]^2 + 8\lambda_s\lambda_p \right)^{1/2} \right] \quad (23)$$

A very nice agreement to Landauer’s relation is given by measurements of the thermal conductivity of porous zirconia ceramics made with latex pore formers as can be seen in Fig. 14 (Nait-Ali *et al.*, 2006).

Then as a final example of very porous materials, kaolin based foams present pore volume fractions upto 95% with large semi-closed pores as shown in Fig. 15 (Bourret *et al.*, 2013).

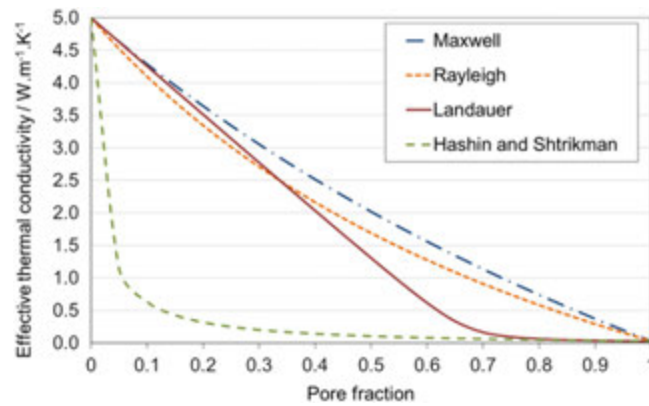


Fig. 13 Analytical relations describing thermal conductivity as a function of pore volume fraction for a porous solid. These are the Maxwell - Eucken (blue), the Rayleigh (orange), the Landauer (brown) relations and the lower Hashin-Shtrikman bound (gray). The solid phase conductivity has been fixed with a value of $\lambda_s = 5 \text{ W m}^{-1} \text{ K}^{-1}$.

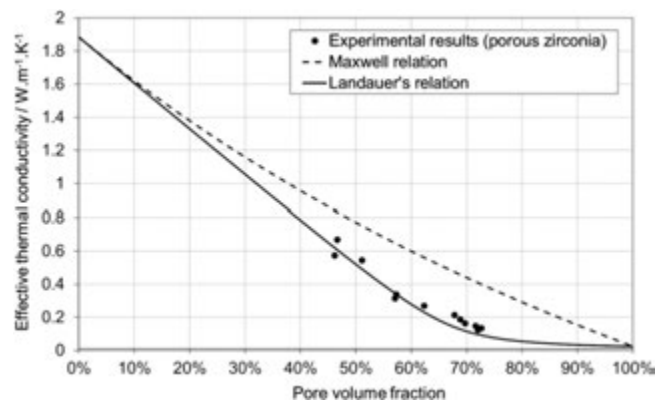


Fig. 14 Effective thermal conductivity as a function of pore volume fraction for porous zirconia ceramics. Experimental values compared to predictions by the Maxwell-Eucken and Landauer relations.

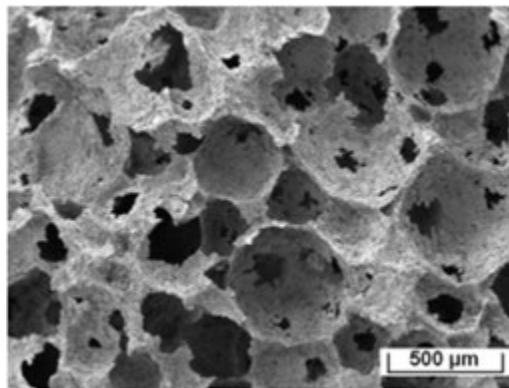


Fig. 15 Microstructure of very porous kaolin based ceramics.

These in fact yield experimental conductivity values close to the Hashin - Shtrikman upper bound, which is equivalent to the Maxwell - Eucken relation. The comparison between prediction and experiment is presented in [Fig. 16](#). With 95% porosity, the conductivity is close to $50 \text{ mW m}^{-1} \text{ K}^{-1}$, just twice the thermal conductivity of air ([Bourret et al., 2013](#)).

As a final word, this approach of phase mixture relations can also be extended to mixtures of solid phases as found in composite materials such as many refractories.

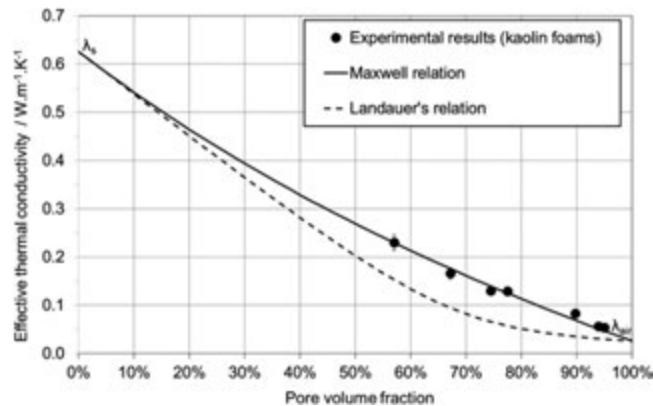


Fig. 16 Effective thermal conductivity as a function of pore volume fraction for porous kaolin based ceramics. Experimental values compared to predictions by the Maxwell-Eucken and Landauer relations.

Conclusions

The thermal properties of a ceramic material are determined essentially by its atomic vibrations. Heat capacity for a crystalline solid can be related to the derivative with respect to temperature of the internal energy. The internal energy is dominated by the contribution of the lattice vibrations. Thermal expansion results from the asymmetry of the interatomic pair potential. Thus at higher temperature, larger amplitude vibrations yield an increase in average atomic separation. Finally, with application of a thermal gradient across a polycrystalline ceramic material, the majority of heat is carried by lattice vibrations. This intrinsic thermal conductivity can be significantly modulated at the macroscopic scale by the ceramic microstructure due to the presence of pores and grain boundaries.

References

- Bourret, J., Tessier-Doyen, N., Nait-Ali, B., *et al.*, 2013. Effect of the pore volume fraction on the thermal conductivity and mechanical properties of kaolin based foams. *J. Eur. Ceram. Soc.* 33, 1487–1493.
- Kingery, W.D., Bowen, H.K., Uhlmann, D.R., 1976. *Introduction to Ceramics*, second ed. New York: John Wiley and Sons.
- Kittel, C., 1976. *Introduction to Solid State Physics*, fifth ed. New York: John Wiley and Sons.
- Knacke, O., Kubaschewski, O., Hesselmann, K., 1991. *Thermochemical Properties of Inorganic Substances*, second ed. Berlin: Springer Verlag.
- Landauer, R., 1952. The electrical resistance of binary metallic mixtures. *J. Appl. Phys.* 21, 779–784.
- Nait-Ali, B., Haberkorn, K., Vesteghem, H., Absi, J., Smith, D.S., 2006. Thermal conductivity of highly porous zirconia. *J. Eur. Ceram. Soc.* 26, 3567–3574.
- Popov, P.A., Solomennik, V.D., Belyaev, P.V., Lytvynov, L.A., Puzikov, V.M., 2011. Thermal conductivity of pure and Cr³⁺ and Ti³⁺ doped Al₂O₃ crystals in 50–300 K temperature range. *Funct. Mater.* 18, 476–480.
- Rumble, J., 2018. *CRC Handbook of Chemistry and Physics*, ninety ninth ed. London: Taylor & Francis Ltd.
- Smith, D.S., Alzina, A., Bourret, J., *et al.*, 2013. Thermal conductivity of porous materials. *J. Mater. Res.* 28, 2260–2271.
- Smith, D.S., Fayette, S., Grandjean, S., *et al.*, 2003. Thermal resistance of grain boundaries in alumina ceramics and refractories. *J. Am. Ceram. Soc.* 86, 105–111.
- Smith, D.S., Puech, F., Nait-Ali, B., Alzina, A., Honda, S., 2018. Grain boundary thermal resistance and finite grain size effects for heat conduction through porous polycrystalline alumina. *Int. J. Heat and Mass Transfer* 121, 1273–1280.

Thermal Shock Behavior of Ceramics: Fundamentals and Thermal Shock Resistance Parameters

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Introduction

Most applications of ceramics materials involve temperature gradients that vary over time. These gradients produce differential deformations in the components and, consequently, stresses (i.e., thermal stresses). If the stresses created exceed the fracture strength of the material, degradation or even complete failure occurs. Together with corrosion and abrasion, failure due to thermal stresses is one of the main mechanisms of degradation of many ceramic parts in service.

It is said that a body is subjected to thermal shock when the surrounding temperature changes sharply. The simplest example, found frequently in everyday life, is the case of a ceramic part that is cooled rapidly from a temperature, T_0 , to a temperature, T_f . The surface will tend to contract and its contraction will be prevented from the interior that is at a higher temperature. Therefore, surface tensile stresses develop and they might lead to fracture. The case in which the rate of temperature variation is infinite is the easiest case to deal with theoretically and, at the same time, the most extreme. The conclusions derived from this approach, modulated, are applicable to situations of milder temperature changes.

In this article, the general aspects of thermal stresses and fracture are discussed. It has been chosen to refer classical works that established the physics and mechanics of the problem during the second half of last century. The main material properties involved in the response to thermal shock and their relative influence are described in terms of the so-called *thermal shock parameters*. First, the two classic approaches to the problem of thermal shock resistance of brittle materials – thermoelastic approach and energy balance criterion – and the associated parameters are reviewed. Subsequently, the *Unified theory of Hasselman* and the derived parameters are discussed.

Finally, values of the properties involved in the thermal shock resistance of different materials are reported and the classification of ceramic materials in terms of the thermal shock parameters in order to check their suitability for different applications is discussed.

Thermal Stresses

Polycrystalline ceramics with non-textured microstructures can be considered at the macroscopic level as homogeneous and isotropic. Therefore, the magnitude of the expansion or contraction that a ceramic component undergoes when its temperature increases or decreases can be characterized by the coefficient of linear thermal expansion, α , determined from the unidirectional expansion suffered by an elongated specimen.

If a bar of length, L , and free ends is heated or cooled with a temperature increment, $\Delta T = T_f - T_0$, it will expand or contract for a length, $\Delta L = L_f - L_0$, given by Eq. (1):

$$\Delta L = \alpha \cdot L_0 \cdot \Delta T \quad (1)$$

The magnitude of ΔL varies depending on the material. For example, for 1 m long bars cooled from 125°C to room temperature (25°C), ΔL would be ≈ 0.5 and 13.5×10^{-4} m for silica glass and a magnesia refractory, respectively.

If the bar is prevented from deformation, it will be subjected to stresses which level is given by Hook's law (Eq. (2)):

$$\sigma = E \cdot \varepsilon = E \cdot \alpha \cdot \Delta T \quad (2)$$

Where:

$$\varepsilon = \frac{\Delta L}{L_0} \quad (3)$$

is the strain.

When the temperature of the surroundings of a component changes abruptly, an uneven temperature distribution is created across it. Then, a distribution of stresses arises due to incompatibilities between deformations originating in different areas of the piece. The simplest case is that of a thin plate of infinite length subjected to sudden cooling or heating from its surface (Fig. 1).

If the surface is instantly cooled from the temperature T_0 to T_f , a temperature profile develops such that, at the first instant, the surface is at T_f and the center of the plate at T_0 (Fig. 1(a)). The surface tends to contract, which is prevented by the interior, so a stress distribution is created that changes from compression to tension from the center of the plate to the surface. If the plate heats up instantly, the sign of the stresses is reversed (Fig. 1(b)).

Kingery (1959) and Kingery *et al.* (1976) summarized solutions for thermal stresses that develop due to sudden cooling in different simple geometric configurations. In cases where the temperature variation is instantaneous, the maximum surface tension can be described by expressions given by Eq. (4):

$$\sigma = C \cdot \frac{E \cdot \alpha}{(1 - \nu)} \cdot \Delta T \quad (4)$$

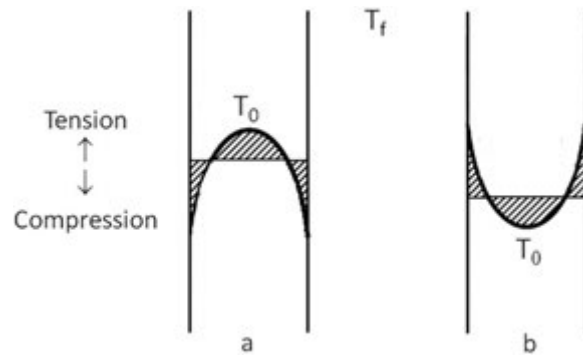


Fig. 1 Thin plate of infinite length subjected to a sudden temperature change from its surface. T_0 : initial temperature, T_f : final temperature. (a) Cooling. (b) Heating.

where C is a dimensionless factor that includes all the geometrical terms, ν is the Poisson's coefficient and $(1-\nu)$ accounts for the biaxial stress state.

In practice, temperature variations are not instantaneous, so the stresses created are lower than those calculated from Eq. (4) and vary over time. In the case where the coefficient of heat transmission between the surface of the specimen and the environment, h , is constant, the magnitude of the stresses can be expressed in terms of a dimensionless parameter called the Biot modulus (Eq. (5)) (Kingery, 1959; Hasselman, 1970):

$$\beta = \frac{\alpha \cdot h}{K} \quad (5)$$

where α is a characteristic dimension of the body in the direction of the maximum temperature gradient and K is the thermal conductivity of the material.

The maximum surface tension is reached after a certain time interval has elapsed, the greater the smaller the Biot modulus, and it is given by:

$$\sigma = \frac{E \cdot \alpha}{(1-\nu)} \cdot \Delta T \cdot f(\beta) \quad (6)$$

In general, $f(\beta)$ is a complicated function of the Biot modulus; however, different authors have established approximations for low values of the Biot modulus ($\beta < 5$) – i.e., low heat transmission, small parts or high thermal conductivity of the material. The general expression is given by Eq. (7) (Kingery, 1955; Hasselman, 1963a):

$$\frac{1}{f(\beta)} = A + \frac{B}{\beta} \quad (7)$$

where A and B are dimensionless constants.

The effect of Biot modulus is exemplified in Fig. 2, in which the maximum stress reached in a refractory lining is plotted as a function of time for two different values of β . It is important to emphasize that the stresses developed by a fixed temperature variation – i.e., the severity of the conditions to which a component is subjected – depend on the properties of the material, the heat transfer mechanism, the geometry of the component and the thermal gradient. The actual maximum stress is lower and it develops after longer times for lower β – i.e., low heat transfer to the environment, small characteristic dimension and higher thermal conductivity of the material.

As can be concluded from the above discussion, the level of thermal stresses developed in a ceramic component depends on the properties of the material, the conditions of heat transfer (magnitude and speed of temperature variation), and geometric factors (shape and size of the piece, orientation against the thermal gradient). Therefore, it is impossible to evaluate the thermal shock resistance of a material using a single property or test satisfactory for all conditions.

Variation of the Properties Due to Thermal Shock

When the stresses originated in a body by thermal shock equal or exceed the fracture strength of the material, σ_f , degradation by cracking occurs. Such degradation is reflected in the material properties, elastic, electrical, thermal, etc., and, especially, strength.

The general behavior of brittle materials subjected to sudden cooling of different severities, ΔT , is schematically represented in Fig. 3.

This graph shows the variation of strength of the material and summarizes both the classic experiments performed on alumina materials (Davidge and Tappin, 1967; Ainsworth and Moore, 1969) and subsequent experiments on various types of dense structural ceramic materials (e.g., Coppola and Bradt, 1973; Konsztowicz, 1990; Sato et al., 1987) and refractories (e.g., Maity et al., 1997). In these

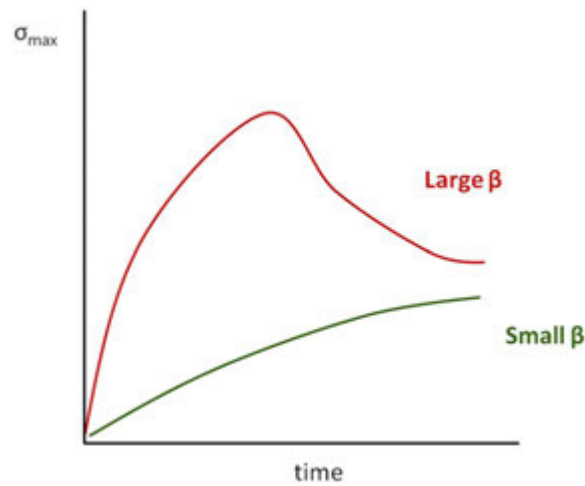


Fig. 2 Maximum stress reached in a refractory lining as a function of time for two different values of the Biot modulus, β .

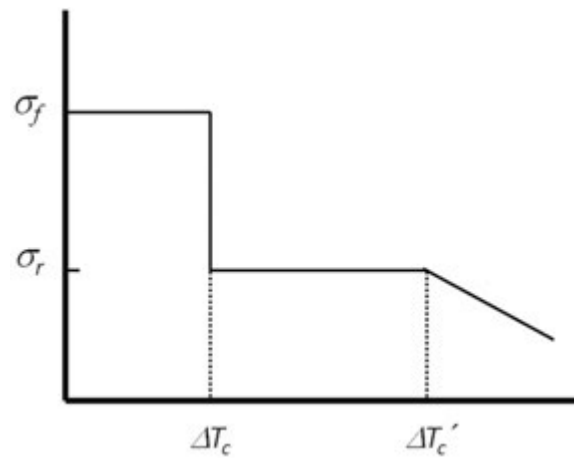


Fig. 3 General behavior of brittle materials subjected to sudden cooling as a function of the temperature difference, ΔT . ΔT_c and $\Delta T'_c$: minimum temperature differences for propagation of short and long cracks, respectively. σ_f and σ_r : Strength of the material before and after sudden degradation by thermal shock, respectively.

experiments, nominally identical specimens are subjected to cooling of increasing intensity and the strength is determined in flexure. Several regions are observed in the graph:

- (1) The strength of the specimens subjected to temperature variations of magnitude equal to or less than ΔT_c is the same as that of the untested specimens, σ_f .
- (2) The strength values of most specimens subjected to thermal shock of intensities close to ΔT_c , σ_r , are much lower than the original ones.
- (3) The increase in the intensity of the thermal shock from ΔT_c to $\Delta T'_c$ does not imply further degradation of the material.
- (4) From $\Delta T'_c$, strength experiences a gradual decrease as the severity of the shock increases.

From this figure, it is clear that there are two fundamental aspects to consider when dealing with the problem of thermal shock resistance. On the one hand, the beginning of the fracture for a ΔT_c and, on the other, the degree of propagation of the cracks once the fracture begins, which determines the degradation suffered by the material – i.e., difference between σ_f and σ_r .

Classic Models

Fracture under the sole effect of thermal shock occurs in absence of external body forces. Therefore, the only energy available for crack propagation is the elastic energy due to the thermal stresses build up in the body by the temperature change, which is finite. This fact makes the analysis of thermal shock different from the typical analysis of fracture in ceramic bodies subjected to constant applied stress.

The classic models that describe the thermal shock resistance of brittle materials are based on the simplification of the thermal state and the geometry of the body and provide parameters that weigh the relative effect of the intrinsic properties of the materials on the behavior – start and propagation of cracks – against temperature variations (Kingery, 1955, 1959; Kingery *et al.*, 1976; Hasselman, 1963a,b, 1969, 1970, 1971).

In essence there are two types of approach to the problem: the study of the beginning of the fracture, based on the results of the thermoelastic theory, and the study of the degree of damage suffered by the material due to the propagation of the cracks, from an energy balance criterion. The Hasselman (1969, 1971) Unified Theory encompasses both approaches and makes it possible to completely predict the behavior plotted in Fig. 3.

Thermoelastic Approach

The thermoelastic approach is essentially based on the calculation of the stresses created in a component or structure subjected to given thermal conditions. The criterion is that fracture occurs if the stresses created exceed the fracture strength of the material. This type of approach allows predicting which solicitations lead to fracture of the component or structure as a function of the properties of the material. Classical works collecting analytical expressions for the surface and volume stresses created in pieces of simple geometry (disks, spheres, etc.) subjected to thermal solicitations are those by Hasselman (1970) and Kingery (1955).

Resistance to thermal shock is defined as the minimum solicitation – temperature difference, rate of temperature change, etc. – required to develop a thermal stress equal to the fracture strength of the material. As discussed above, in the case of simple geometric shapes cooled through a certain, ΔT , the thermal stress created has the general form of Eq. (4), for infinite rate of temperature variation ($h = \infty$) and of Eq. (6) for mild conditions. Then, the fracture criterion is the minimum temperature interval, ΔT_c , that raises thermal stresses equal to the strength of the material.

In the case of $h = \infty$, from Eq. (4):

$$\Delta T_c = \frac{1}{C} \cdot \sigma_f \cdot \frac{(1 - \nu)}{E \cdot \alpha} \quad (8)$$

Different authors have proposed approximations that simplify Eq. (7) and give proportionality relationships between $f(\beta)$ and β . In such cases, for mild conditions of temperature variations, with $h = \text{constant}$, the critical temperature interval is given by Eq. (9):

$$\Delta T_c = \frac{1}{C'} \cdot \sigma_f \cdot \frac{(1 - \nu)}{E \cdot \alpha} \cdot \frac{K}{h \cdot a} \quad (9)$$

Where C' is a dimensionless constant.

The material properties included in Eqs. (8) and (9) can be grouped in two parameters called *thermal shock resistance parameters* for the initiation of fracture:

$$R = \sigma_f \cdot \frac{(1 - \nu)}{E \cdot \alpha} \quad \text{for } h = \infty \quad (10)$$

$$R' = \sigma_f \cdot \frac{(1 - \nu)}{E \cdot \alpha} \cdot K = K \cdot R \quad \text{for } h = \text{cte} \neq \infty \quad (10')$$

Energy Balance Criterion

In many cases, the working conditions are severe enough to produce fracture; therefore, it is necessary to know the degree of damage that the material will experience due to the fracture. This problem was studied by Hasselman (1963b) using results previously obtained by Kingery (1955) and an energy balance criterion.

When a solid is subjected to a sudden temperature change, non-compatible dimensional changes from different parts of the solid give rise to stresses within it and, consequently, to an increase in the strain energy. This strain energy is the only energy available for crack propagation. For ΔT_c the cracks in the body will grow absorbing the strain energy accumulated in it, converting the strain energy in surface energy. The final size of the cracks is dependent on their initial size and the number of cracks that propagate.

Even though it is not possible to perform an exact energy balance during the propagation of the cracks, it can be assumed the area of the new surfaces created to be proportional to the energy available for propagation, i.e., the strain energy.

The model used by Hasselman is a sphere of radius b with N identical cracks whose surface undergoes a sudden increase in temperature. It is assumed that cracks do not interact during propagation. The conclusions, in terms of material properties, can be generalized to other geometries using dimensional analysis.

At the point of fracture, the elastic energy accumulated in the piece is given by Eq. (11):

$$W_e = B \cdot \sigma_f^2 \cdot \frac{(1 - \nu) \cdot V}{E} \quad (11)$$

where V is the volume of the piece and B is a dimensionless constant.

The surface energy necessary to propagate N cracks through an area A is given by Eq. (12):

$$W_f = 2 \cdot A \cdot G \quad (12)$$

where G is the surface fracture energy required to produce unit area of crack surface. By matching Eqs. (11) and (12), it is possible to know the area through which the cracks would propagate (Eq. (13)):

$$A = B' \cdot \frac{\sigma_f^2 \cdot (1 - \nu) \cdot V}{N \cdot E \cdot G} \quad (13)$$

The area A would be minimized when the elastic energy – proportional to σ_f^2/E – is minimized and the effective surface energy and the number of cracks are maximized.

Therefore, the material properties can be grouped in the *thermal shock parameters for damage*, R''' and R'''' , whose maximization will minimize, damage (Eqs. (14) and (15)):

$$R''' = \frac{E}{\sigma_f^2 \cdot (1 - \nu)} \quad (14)$$

$$R'''' = \frac{E \cdot G}{\sigma_f^2 \cdot (1 - \nu)} \quad (15)$$

In order to maximize R''' and R'''' it would be necessary to maximize the Young's modulus while minimizing the fracture strength, which is somehow contradictory because in general strength and Young's modulus present similar trends when the microstructure is changed. This is why materials subjected to severe thermal shocks, sufficient to begin fracture, should present high values of the fracture energy.

Unified Theory of Hasselman

From the results of the thermoelastic theory, it is possible to predict the existence and evaluate the magnitude of the critical temperature interval, ΔT_c , or minimum temperature difference that causes the fracture of the material in Fig. 3. Moreover, the classical energy balance approach predicts the sudden degradation from σ_f to σ_r and evaluates the degree of damage suffered by the body. However, none of these two approaches has the remaining sections of the curve of Fig. 3 – range of ΔT originating the same degradation, additional critical temperature interval, $\Delta T_c'$, and gradual increase in the degree of damage for shocks of intensity greater than $\Delta T_c'$.

Hasselman's (1969, 1971) Unified Theory encompasses both the moment of initiation of fracture and the associated damage and allows to completely predicting the behavior of a brittle material under thermal shock shown in Fig. 3. The approach of this theory, based on a criterion of minimum energy, is similar to the one used by Griffith to study the fracture of brittle solids (Griffith, 1921).

In the first paper (Hasselman, 1969), the historical one, Hasselman takes as a model a body with N circular cracks per unit volume, which is prevented from contracting because its surfaces are rigidly held and which is cooled evenly. This model is the one that maximizes the severity because all the points of the body are subjected to a triaxial state of thermal stresses.

The two-dimensional model proposed by Hasselman (1971) is shown in Fig. 4. It is a plate infinite in the X direction of a brittle material containing N cracks of length, $2l$, per unit area. The plate is cooled uniformly while its deformation in the Y direction is prevented. This model is closer to the actual conditions of thermal shock because it can be assimilated to the surface of a suddenly cooled body. In addition, its mathematical treatment is simpler and the conclusions are similar to those of the original model.

It is assumed that fracture of the plate occurs by the simultaneous propagation of the N cracks when the temperature increment reaches, ΔT_c , and that the cracks do not interact.

The equilibrium state of an elastic body subjected to external forces is one in which the energy of the entire system is minimal. To use this theorem when studying the fracture of real solids, it is necessary to consider, in addition to the variation in elastic energy, the increase in energy involved in the creation of two new surfaces.

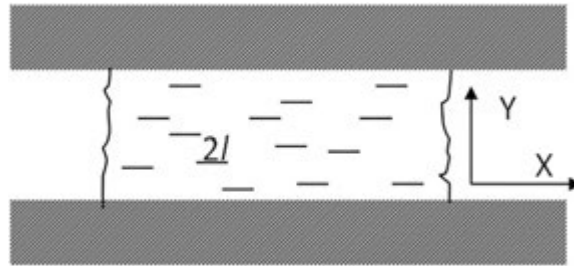


Fig. 4 The two-dimensional model used by Hasselman in 1971 (Hasselman, 1971). A plate infinite in the X direction of a brittle material containing N cracks of length, $2l$, per unit area. Deformation in the Y direction is prevented.

The Young's modulus of the cracked plate, E_{eff} , is given by (Eq. (16)):

$$E_{eff} = \frac{E}{(1 + 2\pi \cdot N \cdot l^2)} \quad (16)$$

where E is the Young's modulus of the material without cracks.

The elastic energy in the plate when it is uniformly cooled a temperature interval, ΔT , is given by (Eq. (17)):

$$W_e = \frac{\alpha^2 \cdot (\Delta T)^2 \cdot E}{2 \cdot (1 + 2\pi \cdot N \cdot l^2)} \quad (17)$$

The surface energy due to the presence of the cracks is (Eq. (18)):

$$W_s = 4 \cdot G \cdot l \cdot N \quad (18)$$

where G is the surface fracture energy required to produce unit length of crack. In the three dimensional model, G is the surface fracture energy required to produce unit area of crack surface, in the same way as in the energy balance criterion.

The total energy of the cooled cracked plate is given by (Eq. (19)):

$$W = \frac{\alpha^2 \cdot (\Delta T)^2 \cdot E}{2 \cdot (1 + 2\pi \cdot N \cdot l^2)} + 4 \cdot G \cdot l \cdot N \quad (19)$$

Thermal requirement for fracture onset

Cracks will be unstable whenever their growth diminishes the energy of the system ($dW/dl \leq 0$). The condition $dW/dl = 0$ allows determining the critical temperature interval (Eq. (20)):

$$\Delta T_c = \left(\frac{2 \cdot G}{\pi \cdot l \cdot \alpha^2 \cdot E} \right)^{\frac{1}{2}} \cdot (1 + 2\pi \cdot l^2) \quad (20)$$

The relationships between the critical temperature interval and the crack length are plotted in Fig. 5(a) (solid lines) for plates with two different crack densities.

For a given value of ΔT_{c0} , crack instability occurs between two values of crack length. The minimum value, l_0 , is coincident for both crack densities while the maximum one, l_1 and l_2 , is smaller for materials with higher crack densities. These observations can be quantitatively derived by using the approximations of short ($2\pi l \ll 1$) and long ($2\pi l \gg 1$) cracks, as described below.

The approximation of short cracks leads to a critical temperature interval independent of the density of cracks:

$$\Delta T_c = \left(\frac{2 \cdot G}{\pi \cdot l \cdot \alpha^2 \cdot E} \right)^{\frac{1}{2}} \quad (21)$$

while for long cracks, the critical temperature interval, $\Delta T'_c$, is a function of the density of cracks, N :

$$\Delta T'_c = \left(\frac{8 \cdot \pi \cdot G \cdot N^2 \cdot l^3}{\alpha^2 \cdot E} \right)^{\frac{1}{2}} \quad (22)$$

Taking into account the Griffith (1921) criterion for crack instability (Eq. (23)), it is possible to evaluate the relative effect of material properties on, $\Delta T'_c$ in the same way as for the previously discussed approaches. The bidimensional model leads to (Eq. (24)):

$$\sigma_f \approx \left(\frac{G \cdot E}{l} \right)^{\frac{1}{2}} \quad (23)$$

$$\Delta T_c \approx \frac{\sigma_f}{\alpha \cdot E} \quad (24)$$

And, in the tridimensional model:

$$\Delta T_c \approx \sigma_f \cdot \frac{(1 - \nu)}{\alpha \cdot E} = R \quad (25)$$

For long cracks, considering just the material properties involved in Eq. (22), it is possible to define this new thermal shock parameter that will optimize the behavior of materials with long cracks:

$$R_{st} = \left(\frac{G}{\alpha^2 \cdot E} \right)^{\frac{1}{2}} \quad (26)$$

Regions of crack instability

As plotted in Fig. 5(a), the $\Delta T - l$ plane is divided in two zones of stability and instability, delimited by the curve $dW/dl = 0$. The region of crack instability is larger for materials with low crack densities. As discussed above, for a given ΔT_{c0} , the fracture of the plates takes place if the size of the cracks is between two values of l . The minimum crack size, l_0 , that would result in the fracture of

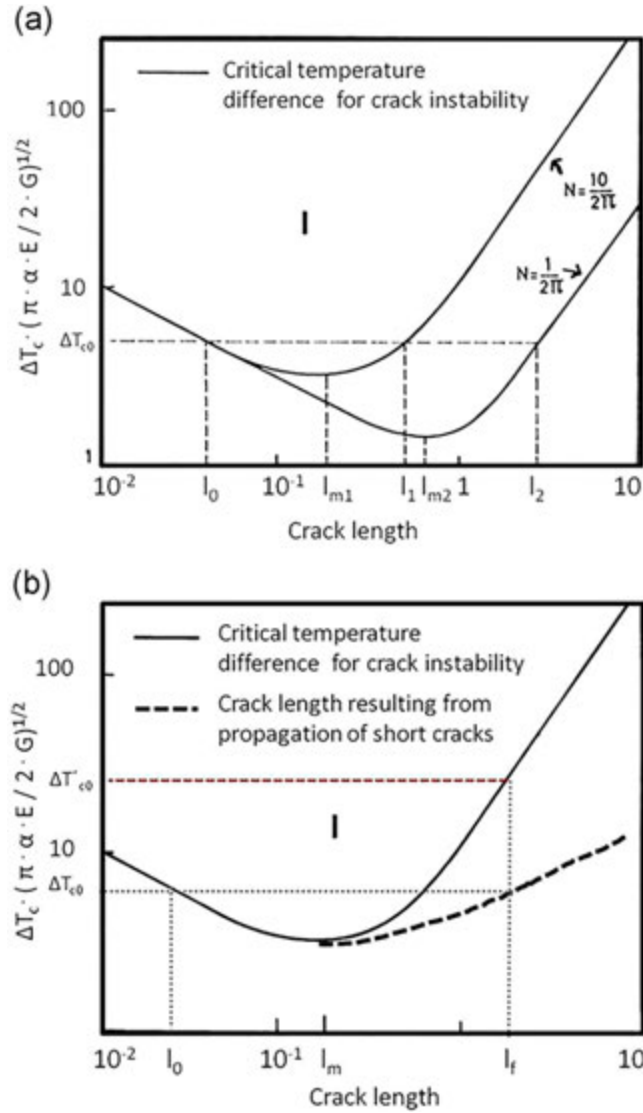


Fig. 5 Main results from the Unified theory of Hasselman (Hasselman (1969, 1971)). (a) Normalized critical temperature interval vs crack length (solid lines) for plates with two different crack densities, N . I: instability. (b) Normalized critical temperature interval vs crack length (solid lines) for a plate with $N=10/2\pi$. When initially short cracks, $l_0 < l_m$, reach the region of instability, they propagate kinetically to reach l_f .

the plates is the same for both crack densities. However, the maximum crack size for instability for higher crack density, l_1 , is smaller than for lower crack density, l_2 .

Propagation of the cracks

Eq. (20) is not sufficient to completely describe crack propagation. The sign of d^2W/dl^2 determines the type of propagation the cracks, quasi-static ($d^2W/dl^2 > 0$) or kinetic ($d^2W/dl^2 < 0$); the limit is given by:

$$l_m = (6 \cdot \pi \cdot N)^{\frac{1}{2}} \quad (27)$$

Cracks with size $l_0 > l_m$ propagate in a quasi-static manner while when $l_0 < l_m$ the cracks propagate kinetically.

Degree of damage

When initially short cracks, $l_0 < l_m$, reach the region of instability, they propagate rapidly while the temperature changes just an infinitesimal. In order to determine the crack length after propagation, it is possible to assume that cracks extend until all the energy released is converted into crack surface energy. This is done by setting the difference between elastic energies for initial and final crack lengths equal to the difference between surfaces energies (Eq. (28)):

$$W_e(l_0) - W_e(l_f) = W_s(l_f) - W_s(l_0) \quad (28)$$

This allows the calculation of the final crack sizes, l_f , plotted in Fig. 5(b) with a dotted line.

Eq. (21) allows getting the value of the final size of short cracks after the kinetic propagation (Eq. (29)):

$$l_f = (4 \cdot \pi \cdot l_0)^{-1} \quad (29)$$

Applying the Griffith model, as above:

$$l_f \approx \frac{\sigma_f^2}{G \cdot E} \quad (30)$$

And for the tridimensional model, the final crack surface, S_f :

$$S_f \approx \frac{\sigma_f^2 \cdot (1 - \nu)}{G \cdot E} \quad (31)$$

Summary

In summary, the Hasselman model allows to obtain, from a single expression that encompasses the sum of elastic and surface energies (Eq. (19)), the following solutions:

- (1) Thermal condition for fracture onset, ΔT_c , that is, critical temperature difference for the propagation of short cracks. The parameter that maximizes ΔT_c (Eq. (25)) is the same as that obtained in the thermoelastic approach, R (Eq. (10)). The dimensional equation of this parameter is:

$$[R] = T \quad (32)$$

Therefore, its physical meaning is clear; the critical temperature difference is proportional to R .

- (2) Degree of kinetic propagation of short cracks. As shown in Eq. (31), the final size S_f is inversely proportional to the surface energy necessary for crack propagation, G , and directly proportional to the accumulated elastic energy (σ_f^2/E). In order to minimize S_f , it is necessary to maximize the same relationships between the properties of the material given by parameters R''' (Eq. (14)) and R'''' (Eq. (15)).

The dimensional equation of R'''' is:

$$[R'''''] = L \quad (33)$$

due to the fact that in the proportionality between the area through which the crack is spread and R'''' there is an effect of the microstructure of the material that is not included in this parameter:

$$S_f^{-1} = f(N, l_0) \cdot R'''' \quad (34)$$

- (3) The novelty of Hasselman's theory as compared to the thermoelastic theory and the energetic balance approach is that it allows explaining the behavior of long cracks ($l > l_m$). These cracks might be preexisting in the material or consequence of the kinetic propagation of short cracks. The parameter, R_{st} (Eq. (26)) maximizes the minimum temperature interval required to propagate long cracks, $\Delta T'_c$. However, simplification of Eq. (22) gives:

$$\Delta T'_c = f(N, l_0) \cdot R_{st} \quad (35)$$

Therefore, the parameter R_{st} also lacks of straightforward physical meaning, revealed by its dimensional equation:

$$[R_{st}] = T \cdot L^{\frac{1}{2}} \quad (36)$$

The conclusions of Hasselman's theory allow explaining the general behavior of materials subjected to thermal shock plotted in Fig. 3.

As discussed above for the thermoelastic approach, both parameters, R and R_{st} , will be modulated by the thermal conductivity of the material for mild conditions of heat transfer.

Selection of Materials

Before discussing the potential of the thermal shock resistance parameters for the selection of ceramics, it is important to remark a main result of the Unified Theory of Hasselman that is not included in the parameters. As described above, thermal shock fracture occurs in absence of external body forces. Therefore, the only energy available for crack propagation is the elastic energy accumulated in the body due to the constrained dimensional changes associated to the temperature change, ΔT . For ΔT_c , the cracks in the body propagate by transforming the elastic energy in surface energy until the former one is consumed. As the elastic energy is finite, the final crack length depends on the initial one and the density of cracks (Fig. 5), thus, ceramics with a large number of small defects degrade less than those with a small number of defects. This fact is currently applied for the development of thermal shock tolerant materials for applications such as kiln lining and furniture, thermal barrier coatings or crucibles for metal casting.

Characteristic values of the properties of materials involved in their response to thermal shock and the thermal shock resistance parameters associated are summarized in Tables 1–3. Structural ceramics suitable for high temperature applications are considered. The classical division between oxide and non-oxide technical ceramics and refractories is used for clarity. Simplified parameters not including the dependence on Poisson's ratio are considered.

Table 1 Properties involved in the response to thermal shock of non-oxide technical ceramics and the corresponding calculated Hasselman's parameters

	SiC^a		$Si_3N_4^b$
	Sintered	HP and HIP	
Density (% of T.D)	97	> 99	> 99
Young's Modulus (GPa)	430	440–450	320
Bending Strength (MPa)	400	640	500–1300
Thermal expansion coefficient ($\times 10^{-6} K^{-1}$)	4.1	3.8	3.1
Thermal conductivity ($W m^{-1} K^{-1}$)	130	120–130	105–170
G ($J m^{-2}$) ^c	25	28	78–313
K_{IC} (MPa $m^{1/2}$)	3.5	3.5	5–10
R (K)	227	378	504–1310
R' ($\times 10^3 W m^{-1}$)	30	47	53–223
R''' ($m \times 10^{-3}$)	2.7	1.1	0.2–1.3
R'''' (m)	68	30	59–100
R_{st} ($m^{1/2}K$)	1.9	2.1	5–10

^aKriegesmann (2014).^bProperties highly variable, dependent on the relative amount of crystalline phases, α and β and microstructure (Hampshire, 2016).^c $G = G_c = K_{IC}^2/E$.**Table 2** Properties involved in the response to thermal shock of oxide technical ceramics and the corresponding calculated Hasselman's parameters. Y-TZP and c-ZrO₂: Y₂O₃ stabilized tetragonal and cubic ZrO₂, respectively. ZT30Z: composite ZrTiO₄/ZrO₂

	$Al_2O_3^a$	$Al_2SiO_5^b$	Y-TZP	c-ZrO ₂	ZrTiO ₄	ZT30Z	$Al_2TiO_5^c$	$Mg_2Al_4Si_5O_{18}$
Density (% of T.D)	≥ 99	97–98	> 99	> 99	94	> 99	–	–
Young's Modulus (GPa)	405	195–206	220 ^d	220 ^d	136 ^e	155 ^f	13–15	130 ^g
Bending Strength (MPa)	360–450	227	1040 ^h	276 ⁱ	120 ^j	270 ^k	10–20	110 ^g
Thermal expansion coefficient ($\times 10^{-6} K^{-1}$)	8.4–9.1	4.1	10.6 ^l	10.6 ^m	8.1 ^{l,n}	8.7 ^o	1–1.5	2.6 ^p
Thermal conductivity ($W m^{-1} K^{-1}$)	130	7.5	–	2 ^q	1.7 ^l	1.7 ^l	–	–
G ($J m^{-2}$)	24 ^r	14 ^s	291 ^t	–	–	34 ^k	–	–
K_{IC} (MPa $m^{1/2}$)	2.5 ^r	0.88 ^s	8	–	–	2.3 ^k	–	1.7 ^u
R (K)	115	277	446	118	109	200	1071	325
R' ($\times 10^3 W m^{-1}$)	15	2	–	237	185	340	–	–
R''' (m)	71	54	60	–	–	73	–	238
R_{st} ($m^{1/2}K$)	1	4.2	3.4	–	–	1.7	–	5

^aUribe and Baudín (2003), Mezquita *et al.* (2001), Baudín (2014). Sintered.^bBurgos-Montes *et al.* (2010), Mezquita *et al.* (2001), García-Prieto and Baudín (2012).^cMilosevski *et al.* (1995).^dSelçuk and Atkinson (1997).^eLópez-López *et al.* (2012b).^fLópez-López *et al.* (2013).^gHayashi *et al.* (1993).^hStevens and Scheneider (1991).ⁱDonzel and Roberts (2000).^jLópez-López (2012).^kLópez-López *et al.* (2015).^lLópez-López *et al.* (2009).^mTerblanche (1989).ⁿLópez-López *et al.* (2012a).^oLópez-López *et al.* (2012c).^pChotard *et al.* (2008).^qWinter and Clarke (2006).^rGarcía-Prieto and Baudín (2010). Stable fracture tests.^sGarcía-Prieto and Baudín (2012). Stable fracture tests.^t $G = G_c = K_{IC}^2/E$.^uCamerucci *et al.* (2001).

Table 3 Properties involved in the response to thermal shock of commercial refractories and the corresponding calculated Hasselman's parameters

	Fused silica ^a	Magnesia	Magnesia-graphite	High alumina	
				Brick ^b (60–72 wt% Al ₂ O ₃)	Castable (62–74 wt% Al ₂ O ₃)
Apparent porosity (%)	14–20	15 ^c	< 2 ^d		
Young's Modulus (GPa)	6–20	40–106 ^{c,e}	10–20 ^d	4–8	36–50 ^{f,g}
Bending strength (MPa)	< 5	7–15 ^{c,e}	8–16 ^d	11–23	10–13 ^{f,g}
Thermal expansion coefficient ($\times 10^{-6}\text{K}^{-1}$)	0.1–1.3	13–14 ^{c,e}	3–4 ^e	6–7	6 ^f
Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	1.1–1.5	–	–	–	–
G (J m^{-2}) ^h	–	–	–	40–140	188–220 ^{f,g}
K _{IC} (MPa ^{1/2})	–	–	–	–	–
R (K)	500	11	229	31	46
R' ($\times 10^3 \text{ Wm}^{-1}$)	600	–	–	–	–
R'''' (m)	–	–	–	230–1000	1500–1900
R _{st} (m ^{1/2} K)	–	–	–	4–7	11–13

^aAndreev *et al.* (2019).^bSemler *et al.* (1991).^cDai *et al.* (2017).^dBaudin *et al.* (1999a,b).^eBaudin (2001), Zhu *et al.* (2017).^fRibeiro *et al.* (2016).^gGarcía-Prieto *et al.* (2015).^hG = 2 γ_{wof} , γ_{wof} = work of fracture from Nakayama (1965).

Thermal expansion values are mainly determined by the phase composition of the materials, thus, values for oxide technical ceramics are similar to those of oxide refractories. Fused silica refractories present extremely low thermal expansion while MgO-graphite bricks have low thermal expansion as compared to magnesia bricks.

In general, technical ceramics present higher Young's modulus and strength than refractories while the latter have high fracture energies, especially the modern refractory castables with optimized microstructural design.

Non oxide ceramics are covalent bonded ceramics which results in high thermal conductivity and low values of thermal expansion, only mullite, cordierite and, especially, aluminum titanate, from the oxides present also low thermal expansion. The latter also has extremely low Young's modulus. The extremely low values of α and E for aluminum titanate materials are due to microcracking during cooling from the sintering temperature due to thermal expansion anisotropy, therefore, aluminum titanate materials present also very low strength. Zirconium titanate has also high thermal expansion anisotropy; therefore, zirconium titanate materials and its composites with zirconia also present some microcracking and associated low E.

In general, fracture of covalent materials is brittle because they cannot deform under stresses. Another characteristic related to the covalent bonding is the difficulty of sintering, which sometime requires additives, then, resulting properties are highly dependent on processing. In the case of Si₃N₄, optimization of processing can lead to a special microstructure made of β -Si₃N₄ tabular grains that present high resistance to crack propagation (self-reinforced Si₃N₄).

In Fig. 6 values of the thermal shock resistance parameters R and R_{st} (Tables 1–3) are plotted for the different materials.

In general, technical ceramics present much higher values of R (Fig. 6(a)) than refractories because they have higher strength, which make them materials appropriate for applications in which no cracking of the material is allowed, such as cutting tools for metal machining. Y-TZP is the oxide with most resistance to cracking by thermal shock because of its unique fracture behavior. In spite of its extremely low strength, aluminum titanate and fused silica refractories can be used in applications that require high thermal shock resistance, such as crucibles for metal cast, due to their low thermal expansion. The high thermal conductivity of non-oxides makes them as ideal materials for applications that involve high thermal shocks such as metal machining with lubricants, as revealed by the high values of R' (Table 1).

As revealed by the differences in the values of R''', 1–2 orders of magnitude higher for refractories (Table 3) than for technical ceramics (Tables 1 and 2), degradation of refractories once thermal shock fracture starts is less severe than that of the high strength technical ceramics. From these later, only cordierite presents especially high damage resistance, due to its low strength that leads to very low elastic energy available for cracking.

The parameter R_{st} that maximizes the resistance of materials to the propagation of long cracks, is similar to R'''' in that both parameters weight the relative effects of the fracture energy, G, and the elastic energy, represented by $\alpha^2 E$ in R_{st} (Eq. (26)) and σ_f^2/E in R'''' (Eq. (15)). The case of self-reinforced Si₃N₄ is special because it combines very high strength and fracture energy.

As discussed for R''', values of R_{st} plotted in Fig. 6(b) show how refractories, and especially the well-designed modern castables, are adequate for severe thermal shock conditions in which fracture initiation cannot be avoided. In fact, refractories are successfully used in all basic industries that involve thermal cycling at high temperatures: steelmaking, energy, cement, waste incineration, etc.

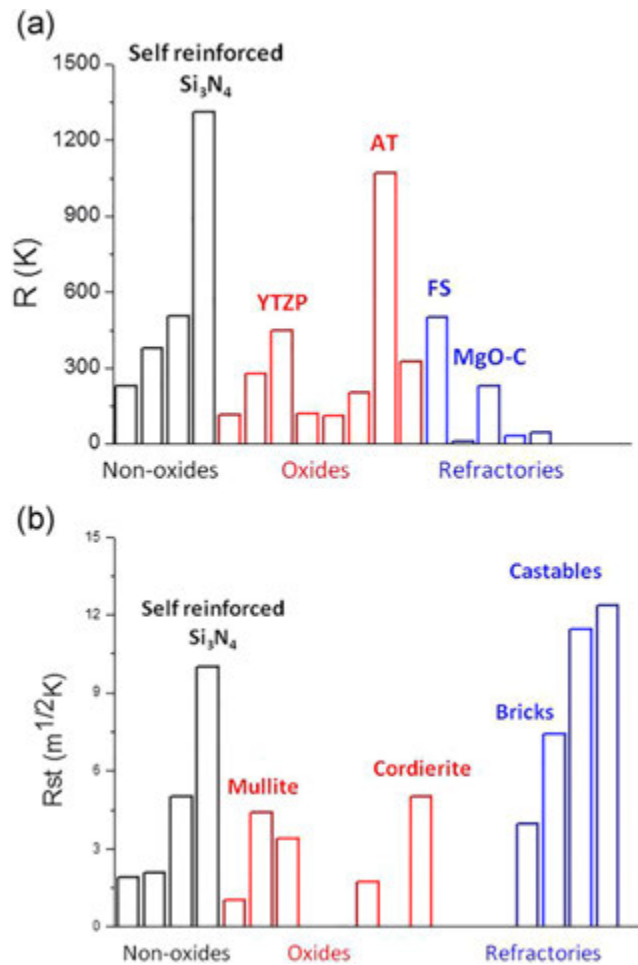


Fig. 6 Characteristic values of the thermal shock resistance parameters for the indicated materials (Tables 1–3). (a) Parameter R (Eq. (10)). YTZP: Y_2O_3 (3 mol%)-stabilized ZrO_2 ; AT: Aluminum titanate; FS: Fused silica. (b) Parameter R_{st} (Eq. (26)).

Final Remarks

The general aspects of thermal stresses and fracture have been discussed. A main straightforward conclusion is that the level of stresses created in a structure or component due to temperature changes is a function, not only of the thermal solicitations imposed, but also of the surface state, a number of material properties and geometrical factors. Therefore, the response to temperature variations is not an intrinsic property of the materials, such as the modulus of elasticity or the specific heat. It is not possible to think about one single experiment for characterizing the response of materials under all thermal solicitations.

The thermal shock parameters derived from classical works, that analyze the effect of the main material properties involved in the response to thermal shock and their relative influence, are useful to predict the relative performance of materials under specific temperature variations. Nevertheless, the effect of the microstructural factor, qualitatively analyzed by Hasselman in terms of the density of defects, should be quantitatively described in order to predict the actual behavior of the materials. Moreover, the simplifying assumption of calculating crack extension from the available elastic energy and a constant value of surface energy might not be valid for the new ceramics designed to develop toughening mechanisms during crack propagation.

References

- Ainsworth, J., Moore, R.E., 1969. Fracture behavior of thermally shocked aluminum oxide. *Journal of the American Ceramic Society* 52, 628–629.
- Andreev, K., Tadaion, V., Zhu, Q., *et al.*, 2019. Thermal and mechanical cyclic tests and fracture mechanics parameters as indicators of thermal shock resistance – Case study on silica refractories. *Journal of the European Ceramic Society* 39, 1650–1659.
- Baudin, C., 2001. High temperature mechanical behavior of magnesia-graphite based refractories. In: Bennett, J.P., Smith, J.D. (Eds.), *Fundamentals of Refractory Technology*, Ceramic Transactions 125. USA: The American Ceramic Society Inc., pp. 73–92.
- Baudin, C., 2014. Processing of alumina and corresponding composites. In: Sarin, V.K., Llanes, L., Mari, D. (Eds.), *Comprehensive Hard Materials*. The Netherlands: Elsevier, pp. 31–72.

- Baudin, C., Alvarez, C., Moore, R.E., 1999a. Influence of chemical reactions in magnesia-graphite refractories, Part I: Effects on texture and high temperature mechanical properties. *Journal of the American Ceramic Society* 82, 529–538.
- Baudin, C., Alvarez, C., Moore, R.E., 1999b. Influence of chemical reactions in magnesia-graphite refractories, Part II: Effects of graphite and aluminum contents in generic products. *Journal of the American Ceramic Society* 82, 3539–3548.
- Burgos-Montes, O., Moreno, R., Baudin, C., 2010. Effect of mullite additions on the fracture mode of alumina. *Journal of the European Ceramic Society* 30, 857–863.
- Camerucci, M.A., Urretavizcaya, G., Cavalieri, A.L., 2001. Mechanical behaviour of cordierite and cordierite-mullite materials evaluated by indentation techniques. *Journal of the European Ceramic Society* 21, 1195–1204.
- Chotard, T., Soro, J., Lemerrier, H., Huger, M., Gault, C., 2008. High temperature characterization of cordierite-mullite refractory by ultrasonic means. *Journal of the European Ceramic Society* 28, 2129–2135.
- Coppola, J.A., Bradt, R.C., 1973. Thermal-shock damage in SiC. *Journal of the American Ceramic Society* 56, 14–518.
- Dai, Y., Gruber, D., Harmuth, H., 2017. Determination of the fracture behaviour of MgO-refractories using multi-cycle wedge splitting test and digital image correlation. *Journal of the European Ceramic Society* 37, 5035–5043.
- Davidge, R.W., Tappin, G., 1967. Thermal shock and fracture in ceramics. *Transactions of the British Ceramic Society* 66, 405–422.
- Donzel, L., Roberts, S.G., 2000. Microstructure and mechanical properties of cubic zirconia (8YSZ)/SiC nanocomposites. *Journal of the European Ceramic Society* 20, 2457–2462.
- García-Prieto, A., Baudin, C., 2010. Crack mouth opening displacement controlled fracture tests of brittle ceramics. *Journal of the European Ceramic Society* 30, 3297–3302.
- García-Prieto, A., Baudin, C., 2012. Influence of experimental variables on fracture toughness determined on SEVNB in three points bending. Mullite a case study. *Journal of the European Ceramic Society* 32, 4241–4248.
- García-Prieto, A., Dos Ramos-Lotito, M., Gutiérrez-Campos, D., Pena, P., Baudin, C., 2015. Influence of microstructural characteristics on fracture toughness of refractory materials. *Journal of the European Ceramic Society* 35, 1955–1970.
- Griffith, A.A., 1921. Phenomena of rupture and flow in solids. *Philosophical Transactions of the Royal Society of London. Series A* 221, 163–198.
- Hampshire, S., 2016. Silicon nitride ceramics. In: Tatsuki, O., Mrityunjay, S. (Eds.), *Engineered Ceramics: Current Status and Future Prospects*. USA: The American Ceramic Society and John Wiley & Sons, pp. 79–97.
- Hasselmann, D.P.H., 1963a. Thermal shock by radiation heating. *Journal of the American Ceramic Society* 46, 229–234.
- Hasselmann, D.P.H., 1963b. Elastic energy and surface energy as design criteria for thermal shock. *Journal of the American Ceramic Society* 46, 535–540.
- Hasselmann, D.P.H., 1969. Unified theory of thermal shock fracture initiation and crack propagation in brittle ceramics. *Journal of the American Ceramic Society* 52, 600–604.
- Hasselmann, D.P.H., 1970. Thermal stress resistance parameters for brittle refractory ceramics: A compendium. *American Ceramic Society Bulletin* 49, 1033–1037.
- Hasselmann, D.P.H., 1971. Thermal stress crack stability and propagation in severe environments. In: *Ceramics in Severe Environments, Materials Science and Research*, 5. USA: Plenum Press, pp. 89–103.
- Hayashi, K., Yamada, T., Okamoto, Y., Nishikawa, T., 1993. Mechanical properties of glass and polycrystalline ceramic with cordierite composition. *Journal of the Ceramic Society of Japan* 10, 1264–1267.
- Kingery, W.D., 1955. Factors affecting thermal stress resistance of ceramic materials. *Journal of the American Ceramic Society* 38, 3–15.
- Kingery, W.D., 1959. Thermal stress resistance. In *Property Measurements at High Temperature*. USA: John Wiley and Sons Inc., pp. 185–215.
- Kingery, W.D., Bowen, H.K., Uhlman, D.R., 1976. Chapter 6. Thermal and compositional stresses. In: *Introduction to Ceramics*, second ed., USA: John Wiley and Sons Inc., pp. 816–844.
- Konsztowicz, K.J., 1990. Crack growth and acoustic emission in ceramics during thermal shock. *Journal of the American Ceramic Society* 73, 502–508.
- Kriegesmann, J., 2014. Processing of silicon carbide-based ceramics. In: Sarin, V.K., Llanes, L., Mari, D. (Eds.), *Comprehensive Hard Materials*. The Netherlands: Elsevier, pp. 89–175.
- López-López, E., 2012. Formación In-Situ de Estructuras Tenaces en el Sistema ZrO_2 - TiO_2 (PhD Thesis). Spain: Universidad Autónoma de Madrid.
- López-López, E., Baudin, C., Moreno, R., 2009. Thermal expansion of zirconia-zirconium titanate materials obtained by slip casting of mixtures of YTZP- TiO_2 . *Journal of the European Ceramic Society* 29, 3219–3225.
- López-López, E., Baudin, C., Moreno, R., *et al.*, 2012a. Structural characterization of bulk $ZrTiO_4$ and its potential for thermal shock applications. *Journal of the European Ceramic Society* 32, 299–306.
- López-López, E., Erauw, J.P., Moreno, R., Baudin, C., Cambier, F., 2012b. Elastic behaviour of zirconium titanate bulk materials at room and high temperature. *Journal of the European Ceramic Society* 32, 4083–4089.
- López-López, E., Erauw, J.P., Moreno, R., Cambier, F., Baudin, C., 2013. Elastic behaviour of zirconium titanate-zirconia bulk composite materials at room and high temperature. *Journal of the European Ceramic Society* 33, 3195–3200.
- López-López, E., Moreno, R., Baudin, C., 2015. Fracture strength and fracture toughness of zirconium titanate-zirconia bulk composite materials. *Journal of the European Ceramic Society* 35, 277–283.
- López-López, E., Santacruz, I., Leon-Reina, L., *et al.*, 2012c. Reaction sintered zirconium titanate-zirconia bulk materials from $3Y_2O_3$ -stabilized zirconia and TiO_2 . Phase composition and their potential for thermal shock applications. *Journal of the European Ceramic Society* 32, 1205–1211.
- Maity, S., Mukhopadhyay, T.K., Sarkar, B.K., 1997. Strength of sillimanite sand reinforced porcelain subject to thermal shock. *Journal of the European Ceramic Society* 17, 749–752.
- Mezquita, S., Uribe, R., Moreno, R., Baudin, C., 2001. Influence of mullite additions on thermal shock resistance of dense alumina materials. Part II: Thermal properties and thermal shock behaviour. *British Ceramics Transactions* 100, 246–250.
- Milosevski, M., Ondracek, O., Milisevska, R., Spaseska, D., Dimeska, A., 1995. Thermal expansion and mechanical properties of Al_2TiO_5 - SiO_2 system. *Advanced Science and Technology*. 1875–1882.
- Nakayama, J., 1965. Direct measurement of fracture energies of brittle heterogeneous materials. *Journal of the American Ceramic Society* 48, 583–587.
- Ribeiro, G.C., Resende, W.S., Rodrigues, J.A., Ribeiro, S., 2016. Thermal shock resistance of a refractory castable containing andalusite aggregate. *Ceramics International* 42, 19167–19171.
- Sato, T., Fukushima, T., Endo, T., Shimada, M., 1987. Thermal shock resistance of yttria-doped tetragonal zirconia polycrystals: Effect solvent in quenching test. *Journal of Materials Science* 6, 1287–1290.
- Selçuk, A., Atkinson, A., 1997. Elastic properties of ceramics oxides used in solid oxide fuel cells (SOFC). *Journal of the European Ceramic Society* 17, 1523–1532.
- Semler Jr., C.E., Hawisher, T.H., Bradt, R.C., 1991. Thermal shock of alumina refractories: Damage resistance parameters and the ribbon test. *American ceramic Society Bulletin* 60 (7), 724–729.
- Stevens, R., Schneider Jr., S.J., 1991. Engineering properties of zirconia. In: *Engineered Materials Handbook 4*. USA: ASM International, pp. 775–786.
- Terblanche, S.P., 1989. Thermal-expansion coefficients of yttria-stabilized cubic zirconias. *Journal of Applied Crystallography* 22, 283–284.
- Uribe, R., Baudin, C., 2003. Influence of a dispersion of aluminum titanate particles of controlled size on the thermal shock resistance of alumina. *Journal of the American Ceramic Society* 86, 846–850.
- Winter, M.R., Clarke, D.R., 2006. Thermal conductivity of yttria-stabilized zirconia-hafnia solid solutions. *Acta Materialia* 54, 5051–5059.
- Zhu, T., Li, Y., Sang, S., Xie, Z., 2017. Mechanical behavior and thermal shock resistance of MgO-C refractories: Influence of graphite content. *Ceramics International* 43, 7177–7183.

Thermal Shock and Thermal Fatigue Behavior of Ceramics: Microstructural Effects

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Introduction

The thermal shock degradation of ceramic materials is commonly evaluated from quenching experiments, generally in water, and the measurement of the retained strength, σ_R (Baudin, 2020). σ_R remains constant until the applied temperature difference, ΔT , reaches a critical value, ΔT_c , and then decreases above this value. From Hasselman's classical approach (Hasselman, 1969, 1978), brittle materials are classified into two categories: low strength materials resistant to thermal shock damage for which the retained strength decreases gradually (Fig. 1(a)) and high strength materials resistant to crack initiation, for which it decreases instantaneously (Fig. 1(b)). Hence, the dilemma with ceramic materials is to design microstructures that exhibit both high strength and high thermal-shock damage resistance. More refined fracture mechanics approach in terms of stress intensity factor (SIF) or energy release rate (Evans and Charles, 1977; Swain, 1990; Pompe, 1993; Bahr *et al.*, 1993; Schneider, 1991) was developed, allowing to take into account the transient character of thermal shock and the toughness behavior of the material.

In this article, the mechanical approach will be presented and used to discuss the strength degradation of ceramic materials under thermal shock. A special focus will be put on the microstructural effects, in particular the possibility to obtain an optimal state between resistance to crack initiation and resistance to crack propagation under thermal shock (Fig. 1(c)), by increasing the crack growth resistance (R-curve behavior). The basic concepts of thermal fatigue will also be presented with examples of typical behaviors.

Fracture Mechanics of Thermal Shock

Due to the transient nature and the complexity of the thermal shock, associated crack propagation is difficult to capture with available experimental techniques. Numerical simulations and modeling are increasingly used (Schneider and Petzow, 1993; Schneider, 1991; Saâdaoui and Fantozzi, 1998; Collins and Rowcliffe, 2000; Li *et al.*, 2013) to determine thermal stresses and induced stress intensity factors in order to understand material response and predict crack initiation and crack growth under thermal shock conditions.

Transient Thermal Stresses

It is important to take into account the time dependence of induced stresses, which arises from the temperature gradient and the resulting strain differences between the surface and the bulk. Under thermal shock loading, the temperature field can be obtained from the equation of transient heat conduction:

$$\frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(\lambda \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(\lambda \frac{\partial T}{\partial z} \right) = \rho C \frac{\partial T}{\partial t} \quad (1)$$

where t is time, ρ is the material density, C its specific heat and λ its thermal conductivity.

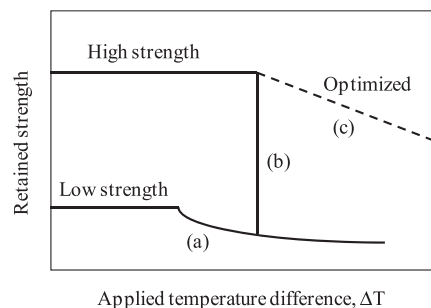


Fig. 1 Illustration of the strength degradation under thermal shock for (a) low-strength and (b) high-strength materials and (c) optimized microstructures.

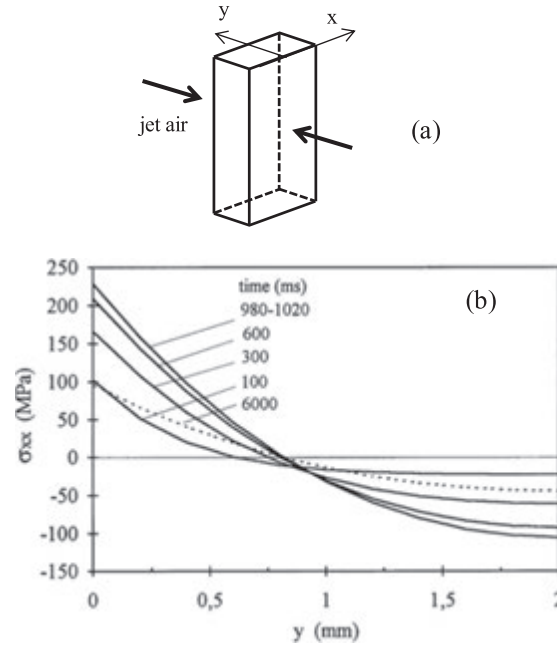


Fig. 2 Illustration of an alumina sample (thickness 4 mm) submitted to thermal shock with a jet air at a critical applied temperature difference, $\Delta T_c = 845\text{K}$ (a) and the resulting transient normal stresses σ_{xx} at the median plane ($x = 0$) (b). From Saâdaoui, M., Fantozzi, G., 1998. Crack growth resistance under thermal shock loading of alumina. Materials Science and Engineering A247, 142–151.

In the case of quenching with a constant heat transfer coefficient h , the boundary condition at the surface of the body is:

$$\frac{\partial T}{\partial n} = \frac{h}{\lambda} (T_e - T_s) \quad (2)$$

where $\vec{n}$ is the outward normal of the surface, T_e is the temperature of the quenching medium and T_s the surface temperature. The thermal stress can be calculated as follows:

$$\sigma(y, t) = \frac{E\alpha}{1-\nu} (T(y, t) - T^*) \quad (3)$$

where E is the Young's modulus, α is the thermal expansion coefficient, ν the Poisson ratio and T^* is the temperature at the point where the thermal strain is zero.

An example of the time dependence of the thermal stresses is shown in Fig. 2 for rectangular alumina samples subjected to thermal shock by the application of two jets of pulsed air to the largest faces (Saâdaoui and Fantozzi, 1998). It can be seen that tensile stresses are generated in the surface region ($y = 0$) while the middle region ($y = 2$ mm) is subjected to compressive stresses. Figs. 2 and 3 show that the tensile stress at the surface increases rapidly up to about 1 s, then decreases after a maximum value. In this case, a peak of acoustic emission was observed when the maximum surface stress is reached and was correlated to the appearance of a large surface crack.

Crack Propagation Analysis

From the fracture mechanics point of view, the thermal shock strength degradation of ceramic materials is a consequence of the propagation of preexisting cracks or defects when subjected to sufficiently severe thermal shocks. For an extending surface crack with a length a , the applied thermal shock stress intensity factor, K_{TS} , can be determined at any time from the transitional thermal stresses using the weight function method (Pertroski and Achenbach, 1978; Tsai and Ma, 1992; Wu, 1993):

$$K_{TS}(a, t) = \int_0^a \sigma(x) h(x, a) dx \quad (4)$$

where x is the coordinate with the origin at the surface and $h(a, x)$ is the weight function independent of the stress.

The crack extension can be described by a diagram representing K_{TS} as a function of crack length, a , and time (Swain, 1990; Schneider, 1991), a schematic illustration of which is shown in Fig. 4, for an applied temperature difference larger than the critical value. As the thermal shock is a transient phenomena, K_{TS} increases with time for a given crack length, displays a peak value and then decreases. At a fixed time, K_{TS} passes through a maximum and all the curves have a common envelope which allows anticipating crack propagation modes and arrest, depending on the material behavior and thermal shock conditions.

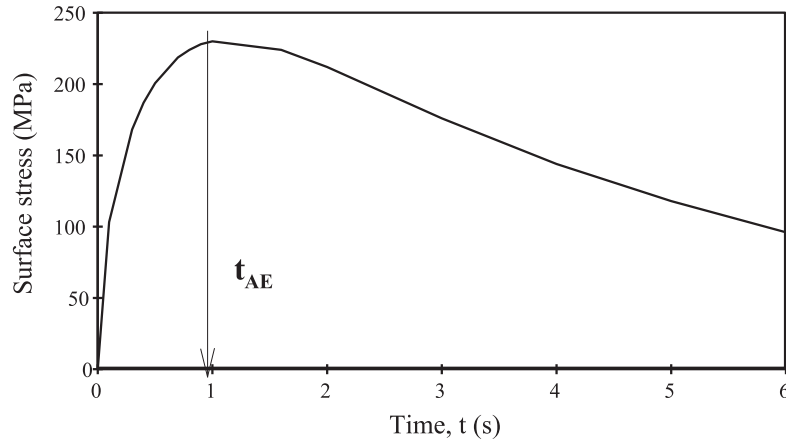


Fig. 3 Variation with time of the tensile surface stress corresponding to conditions of Fig. 2. Apeak of acoustic emission was observed when the maximum surface stress is reached ($t = t_{AE}$).

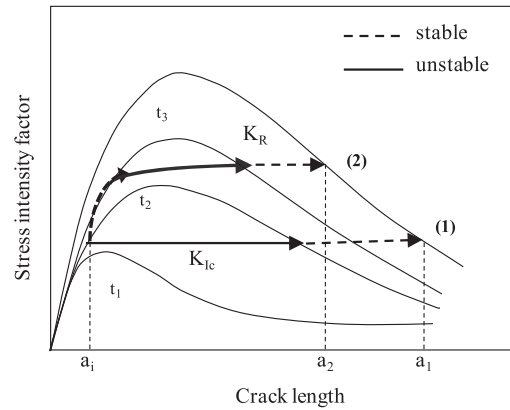


Fig. 4 Illustration of crack growth under thermal shock loading for a material with a constant toughness, K_{IC} (curve 1) and a rising R-curve behavior (curve 2) where K_R is the crack growth resistance in terms of stress intensity factor.

A crack with an initial length a_i will extend following stable or unstable sequences depending on the toughness behavior. For a material with a constant toughness, K_{IC} , the crack propagation follows two stages (Fig. 4, curve (1)). The propagation is first unstable under the conditions:

$$K_{TS} = K_{IC} \quad (5a)$$

$$dK_{TS}/da > 0 \quad (5b)$$

then becomes stable with:

$$K_{TS} = K_{IC} \quad (6a)$$

$$dK_{TS}/da < 0 \quad (6b)$$

A crack arrest occurs with a final crack length, a_1 , determined by the envelope curve.

The crack propagation criterion can also be expressed by the energy release rate, G , using time-dependent G-curves (Bahr *et al.*, 1987). The different sequences of stable and unstable crack growth have been observed by Schneider *et al.* during model thermal loading experiments of ceramic disks by lamp irradiation (Schneider *et al.*, 1993). Their relative importance depend on material properties and thermal loading conditions, in particular the applied temperature difference (Schneider, 1991).

Ceramic materials with particular microstructures exhibit stress shielding effects due to reinforcement mechanisms as grain bridging (Steinbrech *et al.*, 1990; Vekinis *et al.*, 1990; Li *et al.*, 1992) or transformation toughening (Evans, 1990; Hannink *et al.*, 2000). Thus, their toughness increases with the crack length and the fracture behavior is described by a crack growth resistance curve (R-curve). In this case, the crack propagation under thermal shock is generally characterized by three consecutive stages (Fig. 4, curve (2)). The onset of crack propagation occurs when the applied thermal shock SIF, K_{TS} reaches the crack growth resistance, K_R :

$$K_{TS} = K_R \quad (7)$$

If the R-curve is steep enough, the crack extension is first stable as:

$$\frac{dK_{TS}}{da} < \frac{dK_R}{da} \quad (8)$$

and becomes unstable when:

$$\frac{dK_{TS}}{da} > \frac{dK_R}{da} \quad (9)$$

For large crack lengths, the extension becomes again stable as $dK_{TS}/da < 0$, thus the condition in Eq. (8) is always satisfied.

It can be seen that for the R curve material, the final crack length a_2 , is lower than that obtained with the constant toughness material (a_1), which leads to higher retained strength. Based on these theoretical considerations, an optimal state between resistance to crack initiation and resistance to crack propagation (Fig. 1(c)) is possible to obtain by increasing the crack growth resistance (R curve behavior). For quantitative analysis, suitable R curves under thermal shock conditions have to be considered as they are generally different from those determined under mechanical loading (Bahr *et al.*, 1993; Saâdaoui and Fantozzi, 1998).

It is to note that for ceramic materials, multiple cracking under thermal shock is usually observed experimentally (Gupta, 1972; Mignard *et al.*, 1995). Bahr *et al.* (1986) extended the above fracture mechanics approach to multiple cracking which was also simulated considering different models as in Jin and Fen (2009) and Li *et al.* (2013).

Microstructural Effects on Thermal Shock Resistance

On the basis of the fracture mechanical analysis, improvements in the resistance to thermal shock of ceramic materials can be obtained by tailoring their microstructures (Fantozzi and Saâdaoui, 2014) in order to improve their crack growth resistance (R-curve). For alumina, known to exhibit R curve behavior due to crack shielding by grain bridging, Steinbrech (1992) showed that the retained strength after thermal shock increases linearly with the slope of the R curve, due to the increase of the shielding effect with the grain size. For Si_3N_4 ceramics, it has been shown that the thermal shock resistance can be enhanced by coarsening and elongating the microstructure, via the influence on toughness and R-curve behavior (Hoffmann *et al.*, 1993; Lee *et al.*, 2002). Controlled grain coarsening, inducing a high crack growth resistance, allows maintaining a high initial strength, which decreases gradually after thermal shock, compared to the typical catastrophic strength loss observed in a fine grain material (Fig. 5).

Improvement in thermal shock resistance over a single phase ceramic material can be achieved by the incorporation of a second phase particles as for ZrO_2 reinforced Al_2O_3 , (Becher, 1981; Swain, 1990), SiC reinforced Si_3N_4 (Kovalcikova *et al.*, 2009), and BN reinforced Si_3N_4 (Lutz and Swain, 1992). For example, Becher (1981) showed that incorporating zirconia particles in alumina increases the critical temperature difference and allows to obtain materials with high initial strength, which exhibit only moderate degradation after thermal shock. This can be attributed to the non-linear stress-strain and R-curve behavior of these composites as suggested by Swain (1990). Lutz *et al.* (1991) have shown that the thermal shock behavior of high strength alumina-zirconia composites can be significantly modified by incorporating pressure zones in a duplex structure that induces crack growth resistance. The authors used a power function ($K_R \propto a^\tau$ the logarithmic slope of which is an indication of the importance of the R curve behavior): $\tau = 0$ corresponds to constant toughness and $\tau > 0$ indicates pronounced R curve behavior the intensity of which increases with τ . Fig. 6 shows that the thermal shock strength degradation is significantly decreased for the duplex ceramics with pronounced R curve behavior.

Ceramic materials with pronounced R-curve behavior and minimal thermal shock degradation often exhibit nonlinear stress-strain behavior attributed to stress induced microcracking or transformation toughening in ZrO_2 containing ceramics (Lutz, 1993;

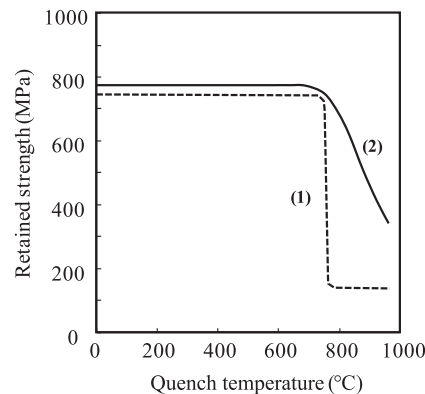


Fig. 5 Thermal shock behavior of Si_3N_4 ceramics: (1) fine grain size and (2) optimally coarsened microstructure. From Hoffmann, M.J., Schneider, G.A., Petzow, G., 1993. The potential of Si_3N_4 for thermal shock applications. In: Schneider, G.A., Petzow, G. (Eds.), Thermal Shock and Thermal Fatigue Behaviour of Advanced Ceramics. Dordrecht: Kluwer Academic Publishers, pp. 49–58.

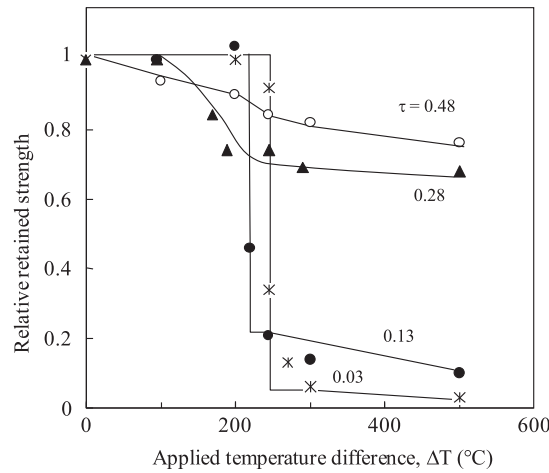


Fig. 6 Relative retained strength for duplex alumina-zirconia duplex composites as a function of the amplitude of the R curve: $\tau = 0$ corresponds to a material with a constant toughness (flat R curve) and $\tau > 0$ corresponds to R curve effect the intensity of which increases with τ . From Lutz, E.H., Swain, M.V., Claussen, N., 1991. Thermal shock behaviour of duplex ceramics. *Journal of the American Ceramic Society* 74, 19–24.

Swain, 1990). During the nonlinear deformation, the Young's modulus of a material decreases according to the expression (Gogotsi *et al.*, 1978):

$$E(\varepsilon) = E_0[1 - \omega(\varepsilon)] \quad (10)$$

where $\omega(\varepsilon)$ is an increasing function with strain.

This induces a reduction of the elastic modulus of the material and hence, a reduction of the elastic energy available for crack propagation under thermal shock.

Other reinforcement strategies that allow to enhance the thermal shock resistance, compared to monolithic ceramics, include whiskers reinforcement (Tiegs and Becher, 1987), ductile reinforcement (Aldridge and Yeomans, 1998; Jin and Batra, 1999) and fiber reinforcement (Wang and Singh, 1994; Singh and Wang, 1995). Excellent thermal shock resistance can be reached due to crack bridging by the reinforcing phase that increases the crack growth resistance and prevents coalescence of the cracks present in the matrix into critical flaws.

The concept of functional grading or multilayered architectural design of ceramic materials has attracted considerable interest, as ceramic composites with layered structure may exhibit high work of fracture and non-catastrophic failure behavior (Lugovy *et al.*, 2005; Bermejo *et al.*, 2006, 2008). High thermal shock resistance can be reached in these materials due to the formation of surface compressive residual stresses, as reported for alumina-zirconia (Bermejo *et al.*, 2005) and $\text{ZrB}_2\text{-SiC}$ (Zhou *et al.*, 2016) laminate composites and a Sialon- Si_3N_4 graded composite (Zheng *et al.*, 2012). These compressive stresses shield the crack tip from the applied thermal stresses during thermal shock and thus decrease the driving force for crack propagation. Moreover, Vandeperre *et al.* (2011) showed that the presence of deflecting weak interlayers enhanced the thermal shock resistance of alumina-zirconia laminate composites, as they increase the resistance to the penetration of a crack under thermal shock loading, compared to laminates in which cracks are not deflected for monolithic ceramics.

Thermal Fatigue

Thermal fatigue i.e., fatigue caused by a thermally induced stress is an important phenomenon that can limit the lifetime of ceramic components. Conversely to thermal shock, thermal fatigue has not been intensively studied. An important problem is the result scattering that asks to realize a large number of experiments. Moreover, the precise stress field is difficult to evaluate because of the transient nature and the number of involved parameters.

Fundamental Aspects

Thermal fatigue experiments are generally conducted by heating a specimen and subsequently quenching it in water or air. The damage is evaluated by measuring a characteristic property of the material, as the elastic modulus or the mechanical strength, after successive thermal shock cycles. The measurement of the elastic modulus is a non-destructive test that allows to rely its decrease to the nucleation and the propagation of cracks in the ceramic. Furthermore, the elastic modulus is sensitive to the entire ensemble of cracks whereas the measurement of mechanical strength is rather sensitive to the largest crack and is a destructive test (Case *et al.*, 1993).

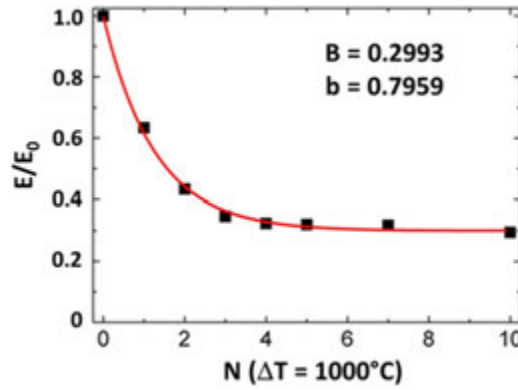


Fig. 7 Evolution of the elastic modulus as a function of the number of quenching tests for $\Delta T = 1000^\circ\text{C}$ for a zircon-mullite composite. From Rendtorff, N.M., Garrido, L.B., Aglietti, E.F., 2011. Thermal shock resistance and fatigue of zircon-mullite composite materials. *Ceramics International* 37, 1427–1434.

An example of the evolution of the elastic modulus during thermal fatigue for a zircon-mullite composite is shown in **Fig. 7** (Rendtorff *et al.*, 2011). The thermal fatigue induced modulus decrease can be described by the following empirical equation:

$$E/E_0 = B + (1 - B) \exp(-bN) \quad (11)$$

where E is the elastic modulus after N thermal cycles at a fixed ΔT (quench temperature difference), E_0 is the elastic modulus before quenching in water (microcrack free material), B is a saturation parameter and b is a rate parameter.

The parameter B corresponds to the steady state value of the elastic modulus obtained after a certain number of thermal cycles and b corresponds to the rate at which the thermally fatigued specimen reaches saturation. A higher B and a lower b represent better thermal fatigue behaviors.

Similar evolution is also obtained for the mechanical strength or the internal friction of thermally fatigued ceramics (Case *et al.*, 1993; Lee and Case, 1989). Internal friction is more sensitive to the microcrack damage than elastic modulus due to the rubbing of opposing crack faces leading to frictional energy dissipation.

Moreover, the thermal fatigue behavior of a brittle material can be investigated by measuring the critical number of thermal shock cycles (lifetime), N_c , required to provoke the failure of specimens submitted to a thermal fatigue with a temperature difference, ΔT . Kamiya and Kamigaito (1976) have made a prediction of the thermal fatigue life by application of fracture mechanics based on subcritical crack growth under thermally induced stresses. The crack growth rate da/dt can be described by the following power law:

$$da/dt = AK_I^n \quad (12)$$

where a is the crack length, K_I is the stress intensity factor, A and n are material constants which depend on the environment. K_I can be expressed as:

$$K_I = \sigma_{th} Y a^{1/2} \quad (13)$$

where σ_{th} is the stress characteristic of the thermal shock (generally the maximum stress on the specimen surface), Y is a configuration coefficient dependent on the crack and sample shapes.

The thermal stress, σ_{th} , is a function of time and temperature difference and can be expressed by the following relation:

$$\sigma_{th} = \Delta T f(t) \quad (14)$$

where $f(t)$ is a function of time.

By combining Eq. (14) with Eqs. (12) and (13), the differential Eq. (12) describing the crack propagation becomes:

$$da/dt = A \Delta T^n f^n(t) Y^n a^{n/2} \quad (15)$$

Assuming that Y is independent of a , the integration of Eq. (15) over the total crack propagation (assuming $a_f^{-n} \ll a_i^{-n}$ with a_i and a_f corresponding respectively to the initial and the final crack lengths) allows to determine the lifetime of the ceramic, N_c :

$$(a_i)^{\frac{2-n}{2}} = \frac{n-2}{2} N_c A \Delta T^n Y^n \int_0^{t_c} f^n(t) dt \quad (16)$$

where t_c is the cycle duration.

Generally, the crack growth parameter n can be determined for ceramics having the same initial crack length a_i from the measurement of N_c for a series of applied temperature differences ΔT (from Eq. (16)):

$$N_c/N'_c = (\Delta T'/\Delta T)^n \quad (17)$$

where N'_c is the critical number of thermal cycles corresponding to a temperature difference $\Delta T'$.

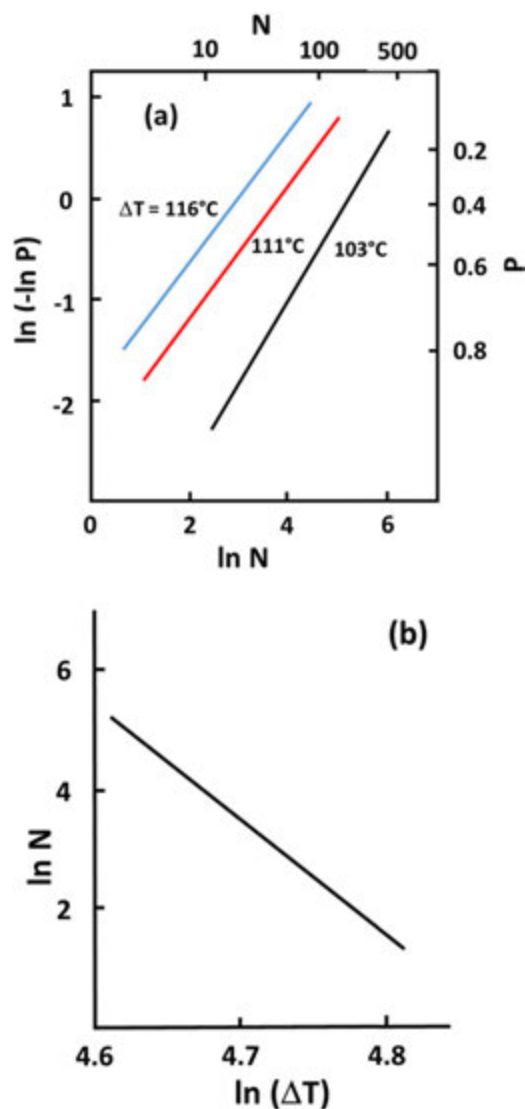


Fig. 8 (a) Survival probability, P , versus thermal fatigue life N_c , (b) N_c versus ΔT for yttria-stabilized zirconia. From Kamiya, N., Kamigaito, O., 1976. Prediction of thermal fatigue life of ceramics. *Journal of Materials Science* 14, 573–582.

However, ceramics exhibit different initial crack lengths and the Eq. (17) must be applied for the median or mean values of the critical number of thermal cycles (or for a common survival probability) as suggested by Kamiya and Kamigaito (1976). An example of such analysis applied to yttria-stabilized zirconia is given by Fig. 8. The survival probability, P , under the thermal shock cycle is given by Weibull statistics and the plot of $\ln(-\ln P)$ versus the thermal fatigue life, N_c , gives a straight line for a given value of ΔT , the slope of which is equal to m/n , where m is the Weibull modulus. The n value can be determined according to Eq. (17) by plotting $\ln N$ versus $\ln(\Delta T)$ for a given value of survival probability (Fig. 8(b)). The determined m value is about 15 and the n value is about 20.

The plot of $\log N_c$ versus $\log a_i$ can be fitted by a straight line (Eq. (16)) with a slope equal to $2/(n-2)$. The A parameter can be determined from the evolution of the thermal stress σ_{th} and the configuration coefficient Y . For example, this analysis was applied to an homogeneous alumina ceramic with a fine grain size of 3 μm (Saadaoui *et al.*, 1999). The thermal fatigue experiments were carried out by using bars with controlled indentation flaws. The indented samples were heated and cooled (with a temperature difference of 830°C) by two jets of pulsed air as shown in Fig. 2(a). The critical thermal cycle number, N_c , determined by acoustic emission is plotted as a function of the initial crack length, a_i , in Fig. 9. There is a significant scattering but a decrease of N_c with increasing crack length is observed. Above a limit value of a_i ($= 120 \mu\text{m}$), unstable crack growth occurs during the first cycle (when the fracture toughness K_{IC} is reached). The plot of $\log N_c$ versus $\log a_i$ can be fitted by a straight line with a slope equal to $2/(n-2)$, from which a value of $n = 18$ was obtained.

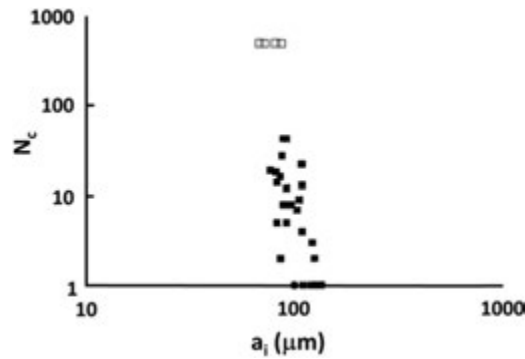


Fig. 9 Critical number of thermal cycles versus the initial crack length. From Saâdaoui, M., Olagnon, C., Fantozzi, G., 1999. Thermal fatigue of alumina: Comparison with mechanical data and life time prediction. *Ceramics International* 25, 497–504.

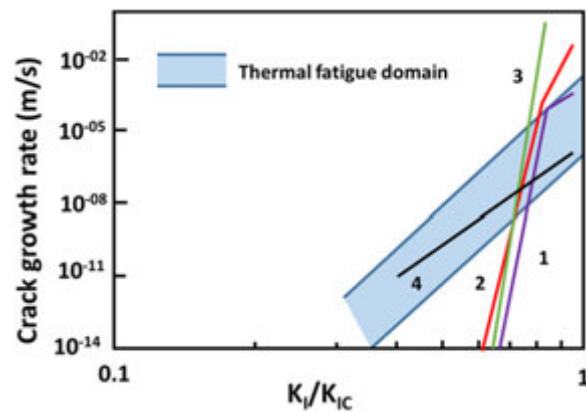


Fig. 10 Thermal fatigue domain compared to the subcritical crack growth laws obtained under mechanical loading: Double torsion at 20°C (curve 1); Double torsion at 800°C (curve 2); Dynamic fatigue at 800°C (curve 3); Double torsion at 20°C, cyclic loading (curve 4). From Saâdaoui, M., Olagnon, C., Fantozzi, G., 1999. Thermal fatigue of alumina: Comparison with mechanical data and life time prediction. *Ceramics International* 25, 497–504.

The A parameter is determined from the knowledge of the thermal stress and the configuration coefficient Y is calculated by finite element. Thus the crack growth rate under thermal loading is obtained (Fig. 10). The crack growth rates under mechanical loading (measured by double torsion and dynamic fatigue methods) are equally shown.

The crack growth rate under thermal loading is higher than under static isothermal loading in a large domain of stress intensity factor and it is close to that observed under mechanical cyclic loading. Thus, the lifetime prediction under thermal fatigue cannot be deduced from the slow crack growth obtained from monotonic mechanical loading as for glass (Fett *et al.*, 1991). Cyclic fatigue effects as well as temperature variation must be taken into account. The physical mechanisms intervening during the thermal loading need to be specified and the R-curve effect should be taken in consideration.

Microstructural Effects

In order to increase the thermal fatigue resistance of ceramics, different reinforcement mechanisms can be used improving the mechanical strength, toughness and thermal shock parameters (Fantozzi and Saâdaoui, 2014). This is illustrated by some examples which will be developed below.

Rendtorff *et al.* (2011) have studied the thermal fatigue behavior of zircon-mullite composites with different compositions and dense microstructures as shown in Fig. 11. Two composites denoted ZM15 and ZM45 contain respectively 82 and 46 wt% of zircon (middle gray), 14 and 44 wt% of mullite (dark gray), and 4 and 10 wt% of zirconia (white). Increasing the fracture toughness K_{IC} from 2.04 (for ZM15) to 2.72 MPa m^{1/2} (for ZM45) increases the thermal shock parameter R_{st} from 1.43 (for ZM15) to 2.72 (for ZM45).

It was shown that a clear correlation is obtained between the B parameter (Eq. (11)) and the thermal shock parameter, R_{st} (Fig. 12) which characterizes the behavior of ceramics with long cracks under severe thermal stresses (Baudin, 2020):

$$R_{st} = \left(\frac{G}{\alpha^2 E} \right)^{\frac{1}{2}} = \frac{K_{IC}}{(2\alpha E)^{\frac{1}{2}}} \quad (18)$$

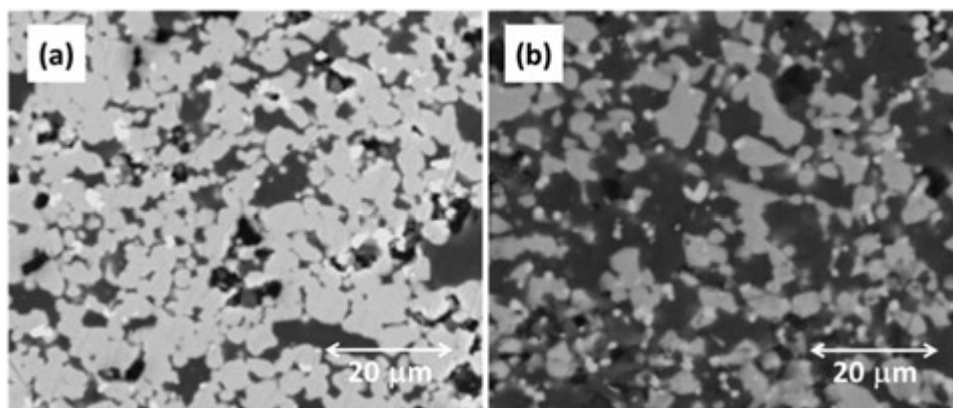


Fig. 11 Typical microstructures of Zircon-Mullite composites ZM15 (A) and ZM45 (B). From Rendtorff, N.M., Garrido, L.B., Aglietti, E.F., 2011. Thermal shock resistance and fatigue of zircon-mullite composite materials. *Ceramics International* 37, 1427–1434.

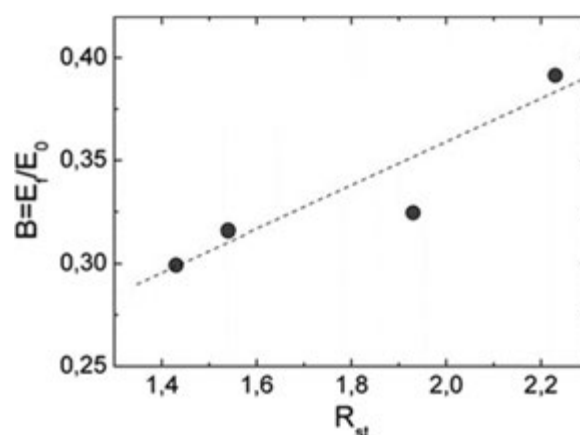


Fig. 12 Relation between the saturation parameter B with the thermal shock parameter R_{st} . From Rendtorff, N.M., Garrido, L.B., Aglietti, E.F., 2011. Thermal shock resistance and fatigue of zircon-mullite composite materials. *Ceramics International* 37, 1427–1434.

where, G is the fracture surface energy, α is the linear thermal expansion coefficient and K_{IC} is the fracture toughness.

The same correlation has been observed by Tian *et al.* (2008) for Si_3N_4 -TiC nano-composites. The microstructures of monolithic Si_3N_4 and Si_3N_4 -TiC nano-composites consist of spherical grains (~ 100 nm) reinforced with TiC particles for the composite ($\sim$ less than 1 μm). The crack growth versus the number of thermal cycles of water-quenched samples with a temperature difference $\Delta T = 600^\circ C$ is shown in Fig. 13 for the monolithic ceramic and for a nano-composite containing 10 wt% TiC. The crack propagation of the nano-composite is clearly lower than the monolithic one. This is linked to the strengthening and to the toughening of the nano-composite, due to the crack-tip bridging and to the crack deflection by the TiC particles as shown by Fig. 14. The fracture toughness is an important factor to evaluate the thermal shock resistance of ceramics as shown by the preceding examples and an appropriate microstructure allows to optimize the thermal shock and thermal fatigue resistance.

The thermal fatigue behavior of oxide/oxide ceramic matrix composites has been recently studied by Yang *et al.* (2019) by following the evolution of the elastic modulus. The composite consists of $0^\circ/90^\circ$ woven Nextel 610 fibers (99% α -alumina) in an alumina (85 wt%)- 3YSZ (15 wt%) porous matrix. Fig. 15 shows the decrease of the elastic modulus as a function of the number of cycles for different applied thermal shock temperatures (the thermal shock test was performed by heating the specimen up to the thermal shock temperature and quenching in water) and for two directions: 0° (warp bundles) and 90° (weft bundles). This decrease of elastic modulus is due to nucleation and propagation of micro-cracks in the matrix, the fibers being not damaged.

Thermal shock and thermal fatigue resistance of Sialon- Si_3N_4 graded composite ceramic materials have been studied by Zheng *et al.* (2012). Thermal fatigue tests were performed by using an indentation-quench method. Five Vickers indents were introduced on the wide surfaces of the polished samples with dimensions of 3 mm x 4 mm x 35 mm. The indented samples were heated in a high temperature furnace for 20 min and then dropped into $20^\circ C$ water. The length of cracks (defined as the distance from the center of the indent to the crack tip) was measured after thermal shock. The Sialon- Si_3N_4 graded composite fabricated by hot pressing were made of five-layered graded materials with symmetrical structure. The first layer (ST10) of the composite named

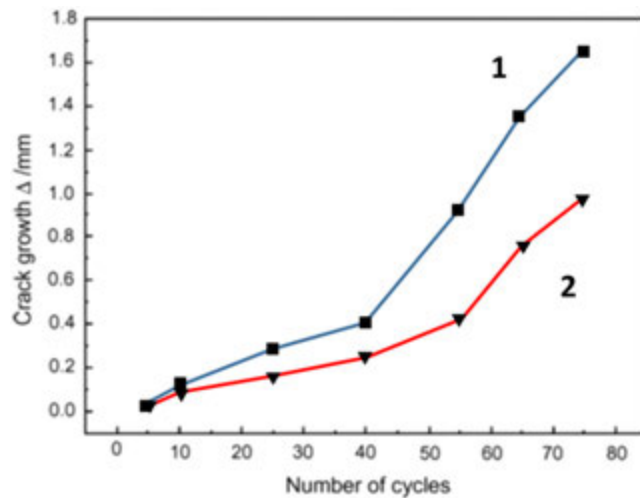


Fig. 13 Crack growth as a function of the number of thermal cycles for a temperature difference $\Delta T = 600^\circ\text{C}$ for a monolithic Si_3N_4 ceramic (1) and a nano-composite with 10 wt% TiC (2). From Tian, C., Liu, N., Lu, M., 2008. Thermal shock and thermal fatigue behavior of Si_3N_4 -TiC nano-composites. *International Journal of Refractory Metals and Hard Materials* 26, 478–484.

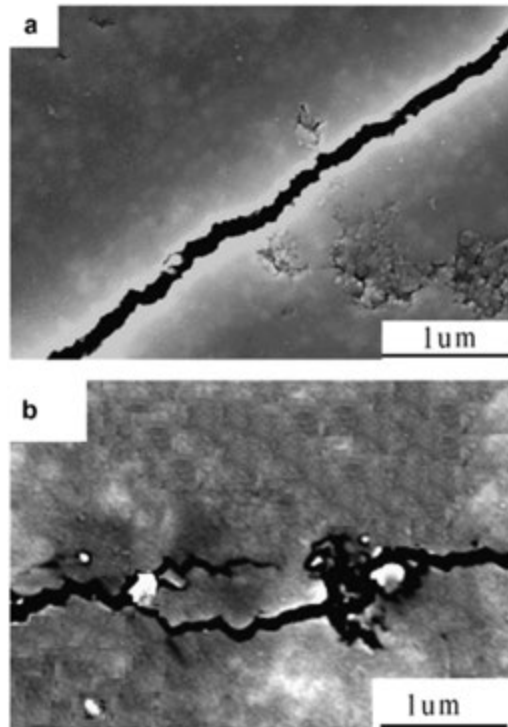


Fig. 14 Propagation path of crack after thermal shock for a monolithic ceramic (a) and a nano-composite (b). From Tian, C., Liu, N., Lu, M., 2008. Thermal shock and thermal fatigue behavior of Si_3N_4 -TiC nano-composites. *International Journal of Refractory Metals and Hard Materials* 26, 478–484.

GSS1 is constituted of the major phases $\beta\text{-Si}_3\text{N}_4$ and $\text{TiC}_{0.7}\text{N}_{0.3}$ whereas the first layer (SAAT10) of the composite named GSS2 corresponds to the β -Sialon phase. The second and third layers of the composites are the same.

Several toughening mechanisms intervene for the surface layer of the composites such as reinforcement by intergranular and transgranular TiCN particles, crack deflection and twin structure. The TiCN particles deflect the crack to travel through a tortuous path and participate to an increase of the fracture energy. Therefore, the graded ceramic composites exhibit higher mechanical properties: the flexural strength σ_f is 980 MPa (for the GSS1 composite) and 810 MPa (for the GSS2 composite) and the fracture toughness of the surface layer is 9.54 and 9.33 $\text{MPa m}^{1/2}$ respectively. Fig. 16 shows the crack extension as a function of the number of cycles for a thermal shock $\Delta T = 400^\circ\text{C}$ for the composites and the homogeneous ceramics. The crack growth in

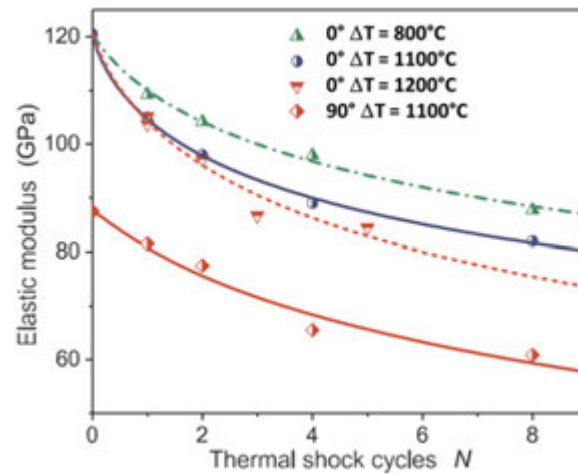


Fig. 15 Elastic modulus as a function of the number of thermal shock cycles for the oxide/oxide ceramic matrix composites for two orientations 0° and 90° and different applied temperature differences ΔT . From Yang, Z., Yuan, H., Markert, B., 2019. Representation of micro-structural evolution and thermo-mechanical damage in thermal shocked oxide/oxide ceramic matrix composites. *International Journal of Fatigue* 126, 122–129.

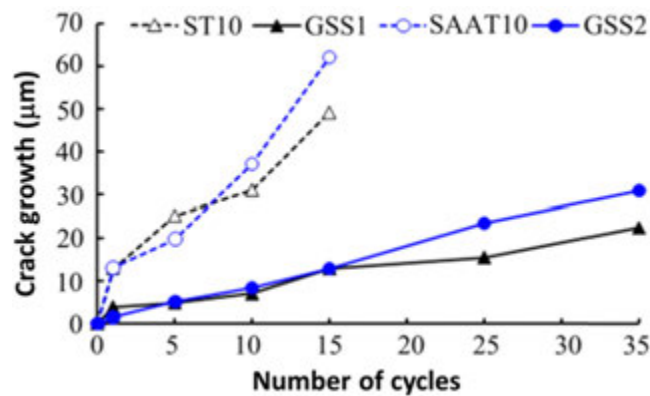


Fig. 16 Crack extension versus the number of cycles for graded composites (GSS1 and GSS2 curves) and homogeneous ceramics (ST10 and SAAT10 curves) at $\Delta T = 400^\circ\text{C}$. From Zheng, G., Zhao, J., Jia, C., *et al.*, 2012. Thermal shock and thermal fatigue resistance of Sialon– Si_3N_4 graded composite ceramic materials. *International Journal of Refractory Metals and Hard Materials* 35, 55–61.

the graded ceramic composites is much lower than in the homogeneous ceramics. Thus, the thermal fatigue resistance of the graded ceramic composites is higher than the homogeneous ceramic one. This increase may be linked to the increase of flexural strength and fracture toughness of the surface layer compared to the homogeneous ceramic. Furthermore, compressive residual stresses appear at the surface layer of the graded composites due to the difference of the thermal expansion coefficient which is higher at the center compared to the surface. These compressive stresses counteract the tensile stresses generated during the thermal shock.

References

- Aldridge, M., Yeomans, J.A., 1998. The thermal shock behaviour of ductile particle toughened alumina composites. *Journal of the European Ceramic Society* 19, 1769–1775.
- Bahr, H.A., Balke, H., Kuna, M., Liesk, H., 1987. Fracture analysis of a single edge cracked strip under thermal shock. *Theoretical and Applied Fracture Mechanics* 8, 33–39.
- Bahr, H.A., Fett, T., Hahn, I., Munz, D., Pflugbeil, I., 1993. Fracture mechanics treatment of thermal shock and the effect of bridging stresses. In: Schneider, G.A., Petzow, G. (Eds.), *Thermal Shock and Thermal Fatigue Behaviour of Advanced Ceramics*. Dordrecht: Kluwer Academic Publishers, pp. 105–117.
- Bahr, H.A., Fischer, G., Weiss, H.J., 1986. Thermal-shock crack patterns explained by single and multiple crack propagation. *Journal of Materials Science* 21, 2716–2720.
- Baudin, C., 2020. Thermal shock behavior of ceramics: Fundamentals and thermal shock resistance parameters. In: *Encyclopedia of Materials: Technical Ceramics and Glasses*. Oxford: Elsevier.
- Becher, P.F., 1981. Transient thermal stress behavior in ZrO_2 -toughened. *Journal of the American Ceramic Society* 64, 37–A1239.
- Bermejo, R., Llanes, L., Anglada, M., Supancic, P., Lube, T., 2005. Thermal shock behavior of an $\text{Al}_2\text{O}_3/\text{ZrO}_2$ multilayered ceramic with residual stresses due to phase transformations. *Key Engineering Materials* 290, 191–198.

- Bermejo, R., Pascual, J., Lube, T., Danzer, R., 2008. Optimal strength and toughness of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ laminates designed with external or internal compressive layers. *Journal of the European Ceramic Society* 28, 1575–1583.
- Bermejo, R., Torres, Y., Sanchez-Herencia, A.J., *et al.*, 2006. Residual stresses, strength and toughness of laminates with different layer thickness ratios. *Acta Materialia* 54, 4745–4757.
- Case, E.D., Kim, K., Lee, W.J., 1993. Cyclic thermal shock in SiC whisker reinforced alumina and in other ceramic systems. In: Schneider, G.A., Petzow, G. (Eds.), *Thermal Shock and Thermal Fatigue Behaviour of Advanced Ceramics*. Dordrecht: Kluwer Academic Publishers, pp. 393–406.
- Collins, M., Rowcliffe, D., 2000. Analysis and prediction of thermal shock in brittle materials. *Acta materialia* 48, 1655–1665.
- Evans, A.G., Charles, E.A., 1977. Structural integrity in severe thermal environments. *Journal of the American Ceramic Society* 60, 22–28.
- Evans, A.G., 1990. Perspective on the development of high-toughness ceramics. *Journal of the American Ceramic Society* 73, 187–206.
- Fantozzi, G., Saadaoui, M., 2014. Toughness, fatigue and thermal shock of ceramics: Microstructural effects. In: Sarin, V.K., Llanes, L., Mari, D. (Eds.), *Comprehensive Hard Materials* 1. Amsterdam: Elsevier, pp. 299–319.
- Fett, T., Keller, K., Munz, D., 1991. Subcritical crack growth in borosilicate glass under thermal fatigue. *Theoretical Applied Fracture Mechanics* 16, 27–34.
- Gogotsi, G.A., Grushevsky, Y.L., Strelov, K.K., 1978. The significance of non-elastic deformation in the fracture of heterogeneous ceramic materials. *Ceramurgia International* 4, 113–118.
- Gupta, T.K., 1972. Strength degradation and crack propagation in thermally shocked Al_2O_3 . *Journal of the American Ceramic Society* 55, 249–253.
- Hannink, R.H.J., Kelly, P.M., Muddle, B.C., 2000. Transformation toughening in zirconia-containing ceramics. *Journal of the American Ceramic Society* 83, 461–487.
- Hasselman, D.P.H., 1969. United theory of thermal shock fracture initiation and crack propagation in brittle ceramics. *Journal of the American Ceramic Society* 52, 600–604.
- Hasselman, D.P.H., 1978. Figures-of-merit for the thermal stress resistance of high-temperature brittle materials: A review. *Ceramurgia International* 4, 147–150.
- Hoffmann, M.J., Schneider, G.A., Petzow, G., 1993. The potential of Si_3N_4 for thermal shock applications. In: Schneider, G.A., Petzow, G. (Eds.), *Thermal Shock and Thermal Fatigue Behaviour of Advanced Ceramics*. Dordrecht: Kluwer Academic Publishers, pp. 49–58.
- Jin, Z.H., Batra, R.C., 1999. Thermal shock cracking in a metal-particle-reinforced ceramic matrix composite. *Engineering Fracture Mechanics* 62, 339–350.
- Jin, Z.H., Fen, Y.Z., 2009. An array of parallel edge cracks with alternating lengths in a strip subjected to a thermal shock. *Journal of Thermal Stresses* 32, 431–447.
- Kamiya, N., Kamigaito, O., 1976. Prediction of thermal fatigue life of ceramics. *Journal of Materials Science* 14, 573–582.
- Kovalcikova, A., Duszaj, S., Sajgalik, P., 2009. Thermal shock resistance and fracture toughness of liquid-phase-sintered SiC-based ceramics. *Journal of the European Ceramic Society* 29, 2387–2394.
- Lee, W.J., Case, E.D., 1989. Cyclic thermal shock in SiC-whisker-reinforced alumina composite. *Materials Science and Engineering A* 119, 113–126.
- Lee, S.K., Moretti, J.D., J. Readey, M.J., Lawn, B.R., 2002. Thermal shock resistance of silicon nitrides using an indentation-quench test. *Journal of the American Ceramic Society* 85, 279–281.
- Li, C.W., Lee, D.J., Lui, S.C., 1992. R-curve behaviour and strength for in-situ reinforced silicon nitrides with different microstructures. *Journal of the American Ceramic Society* 75, 1777–1785.
- Li, J., Song, F., Jiang, C., 2013. Direct numerical simulations on crack formation in ceramic materials under thermal shock by using a non-local fracture model. *Journal of the European Ceramic Society* 33, 2677–2687.
- Lugovy, M., Slyunyayev, V., Orlovskaya, N., *et al.*, 2005. Apparent fracture toughness of Si_3N_4 -based laminates with residual compressive or tensile stresses in surface layers. *Acta Materialia* 53, 289–296.
- Lutz, E.H., 1993. Interrelation between flaw resistance, R-curve behavior, thermal shock strength degradation and stress-strain behavior of ceramics. In: Schneider, G.A., Petzow, G. (Eds.), *Thermal Shock and Thermal Fatigue Behavior of Advanced Ceramics*. Dordrecht: Kluwer Academic Publishers, pp. 75–85.
- Lutz, E.H., Swain, M.V., Claussen, N., 1991. Thermal shock behaviour of duplex ceramics. *Journal of the American Ceramic Society* 74, 19–24.
- Lutz, E.H., Swain, M.V., 1992. Fracture toughness and thermal shock behavior of silicon nitride-boron nitride ceramics. *Journal of the American Ceramic Society* 75, 67–70.
- Mignard, F., Olagnon, C., Fantozzi, G., 1995. Acoustic emission monitoring of damage evaluation in ceramics submitted to thermal shock. *Journal of the European Ceramic Society* 15, 651–653.
- Pertroski, H.J., Achenbach, J.D., 1978. Computation of the weight function from a stress intensity factor. *Engineering Fracture Mechanics* 10, 257–266.
- Pompe, W.E., 1993. Thermal shock behavior of ceramic materials – Modeling and measurement. In: Schneider, G.A., Petzow, G. (Eds.), *Thermal Shock and Thermal Fatigue Behaviour of ADVANCED Ceramics*. Dordrecht: Kluwer Academic Publishers, pp. 3–14.
- Rendtorff, N.M., Garrido, L.B., Aglietti, E.F., 2011. Thermal shock resistance and fatigue of zircon-mullite composite materials. *Ceramics International* 37, 1427–1434.
- Saadaoui, M., Fantozzi, G., 1998. Crack growth resistance under thermal shock loading of alumina. *Materials Science and Engineering: A* 247, 142–151.
- Saadaoui, M., Olagnon, C., Fantozzi, G., 1999. Thermal fatigue of alumina: Comparison with mechanical data and life time prediction. *Ceramics International* 25, 497–504.
- Schneider, G.A., 1991. Thermal shock criteria for ceramics. *Ceramics International* 17, 325–333.
- Schneider, G.A., Magerl, F., Hahn, I., Petzow, G., 1993. In situ observations of unstable and stable crack propagation and R-curve behavior in thermally loaded disks. In: Schneider, G.A., Petzow, G. (Eds.), *Thermal Shock and Thermal Fatigue Behaviour of Advanced Ceramics*. Dordrecht: Kluwer Academic Publishers, pp. 229–244.
- Schneider, G.A., Petzow, G., 1993. *Thermal Shock and Thermal Fatigue Behavior of Advanced Ceramics*. Dordrecht: Kluwer Academic Publishers.
- Singh, R.N., Wang, H., 1995. Thermal shock behavior of fiber-reinforced ceramic matrix composites. *Composites Engineering* 5, 1287–1297.
- Steinbrech, R.W., 1992. R curve behavior of ceramics. In: Bradt, R.C., Hasselman, D.P.H., Munz, D., Sakai, M., Shevchenko, V.Y. (Eds.), *Fracture Mechanics of Ceramics* 9. New York: Plenum Press, pp. 187–208.
- Steinbrech, R.W., Reichl, A., Schaarwachter, W., 1990. R-curve behavior of long cracks in alumina. *Journal of the American Ceramic Society* 73, 2009–2015.
- Swain, M.V., 1990. R-curve behavior and thermal shock resistance of ceramics. *Journal of the American Ceramic Society* 73, 621–628.
- Tian, C., Liu, N., Lu, M., 2008. Thermal shock and thermal fatigue behavior of $\text{Si}_3\text{N}_4\text{-TiC}$ nano-composites. *International Journal of Refractory Metals and Hard Materials* 26, 478–484.
- Tiegs, T.N., Becher, P.F., 1987. Thermal shock behavior of an alumina-SiC whisker composite. *Journal of the American Ceramic Society* 70, C109–C111.
- Tsai, C.H., Ma, C.C., 1992. Thermal weight function of cracked bodies subjected to thermal loading. *Engineering Fracture Mechanics* 41, 27–40.
- Vandeperre, L.C., Kristofferson, A., Carlstrom, E., Clegg, W.J., 2011. Thermal shock of layered ceramic structures with crack-deflecting interfaces. *Journal of the American Ceramic Society* 84, 104–110.
- Vekinis, G., Ashby, M.F., Beaumont, P.W.R., 1990. R-curve behavior of alumina ceramics. *Acta Metallurgica et Materialia* 38, 1151–1162.
- Wang, H., Singh, R.N., 1994. Thermal shock behaviour of ceramics and ceramic composites. *International Materials Reviews* 39, 228–244.
- Wu, X.R., 1993. Application of weight function method for crack analysis in thermal stress fields. In: Schneider, G.A., Petzow, G. (Eds.), *Thermal Shock and Thermal Fatigue Behaviour of Advanced Ceramics*. Dordrecht: Kluwer Academic Publishers, pp. 119–141.
- Yang, Z., Yuan, H., Markert, B., 2019. Representation of micro-structural evolution and thermo-mechanical damage in thermal shocked oxide/oxide ceramic matrix composites. *International Journal of Fatigue* 126, 122–129.
- Zheng, G., Zhao, J., Jia, C., *et al.*, 2012. Thermal shock and thermal fatigue resistance of SiAlon-Si₃N₄ graded composite ceramic materials. *International Journal of Refractory Metals and Hard Materials* 35, 55–61.
- Zhou, P., Fan, Y., Wang, P., Chen, J., 2016. The indentation thermal shock behavior of laminated ZrB₂-SiC ceramics with strong interfaces. *Ceramics International* 42, 17489–17496.

Creep Behavior of Ceramics

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Phenomenological Aspects

At high temperatures, under a constant stress, plastic deformation called creep occurs and the creep strain as a function of time depends on the applied stress σ and on the temperature T . Typical creep curves can be generally reported into three stages as shown in **Fig. 1**:

- A primary stage where the creep rate decreases with time.
- A secondary stage called steady-state stage where the creep rate is almost constant.
- A tertiary stage where the creep rate increases strongly up to the failure (formation of cracks or voids).

These three stages are not independent because creep is a continuous phenomenon. Under low applied stress, the third stage can disappear and under high stress, the secondary stage can be replaced by an inflexion point. Usually, only the steady-state stage is considered. This steady-state stage is not always observed and very often the minimum creep rate is taken into account to study the creep behavior of ceramics.

Most creep models predict a dependence of creep rate on the temperature, stress and microstructure according to the general Norton relationship:

$$\dot{\epsilon} = \frac{AD}{kT} \frac{\sigma^n}{d^m} \quad (1)$$

A = material constant (which depends on the creep mechanism, see Section "Creep Mechanisms")

D = diffusion coefficient = $D_0 \exp(-Q/RT)$, D_0 = constant, R = gas constant, Q = activation energy, T = absolute temperature.

k = Boltzman's constant.

d = grain size.

σ = applied stress.

m and n = grain size and stress exponents, respectively.

m , n , and Q depend on the creep mechanism pertaining during creep.

Theoretically, the creep mechanisms can be identified by determining the exponents m and n . But very often, two (or more) creep mechanisms can occur simultaneously or sequentially and a complete analysis of the strain-stress relation cannot be analyzed by using a single exponent value.

The dominant creep mechanisms controlling the creep behavior depend on structures, microstructures, and stress regimes.

Of particular importance are the mode of loading and the testing method used for the creep characterization. Tensile tests are the most relevant test type for a homogeneous stress but are difficult and expensive to conduct. Alternatively, compressive tests are often conducted because they utilize a simpler load application system. Bending tests are also easy to conduct, are inexpensive and are very often used although the stress state is not homogeneous.

Creep Mechanisms

At sufficiently high temperatures, (above half of the melting point), the creep of materials can be governed by several mechanisms: the non-conservative motion of dislocations (recovery creep), the pure transport of matter (diffusional creep), or by grain boundary sliding accommodated by transport of matter.

Recovery Creep

For the non-conservative motion of dislocations, the different mechanisms describing recovery creep are derived from the Orowan equation:

$$\dot{\epsilon} = \rho_m b v_m \quad (2)$$

where ρ_m is the density of mobile dislocations, b is the Burgers vector and v_m is the velocity of dislocations that is controlled by climb and given by σD , see **Table 1** which shows the different models derived from microscopic observation (**Poirier, 1976**).

In 1957, Harper-Dorn observed that in materials with saturation of dislocations, ρ_m is constant and $\dot{\epsilon} \sim \sigma D$. If the deformation is due to pure climb (Nabarro model), $\dot{\epsilon} \propto D \sigma^3$. In the rest of models the deformation is due to the glide of dislocation and the strain rate is controlled by the climb as illustrated by the Weertman model depicted in **Fig. 2**.

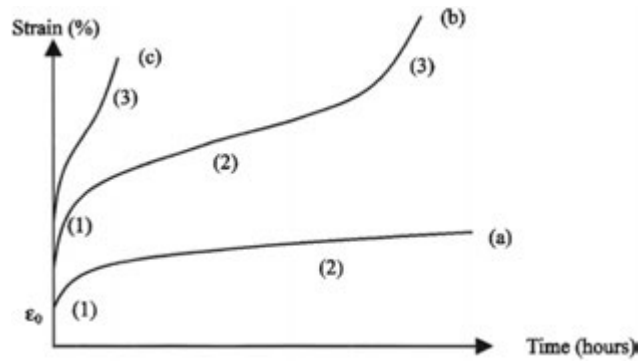


Fig. 1 Typical creep curves at constant stress: (a) two stages (1) and (2) at low temperature or low stress, (b) three creep stages (1 – 3), (c) at high temperature or high stress. From Fantozzi, G., Chevalier, J., Olagnon, C., Chermant, J.L., 2000. Creep of ceramic matrix composites. Chapter 7: Carbon/carbon, cement, and ceramic matrix composites. In: Warren, R. (Ed.), *Comprehensive Composite Materials*, vol. 4. Oxford: Elsevier.

Table 1 Different recovery creep models

ρ_m	L	d	v_m		$\dot{\epsilon}$	Model
$\frac{ML^2}{d}$	$(Md)^{-1/2}$	σ^{-1}	σD	$M = \text{cte}$	$D\sigma^{4.5}$	Weertman 1968
L^{-2}	σ^{-1}	L	σD		$D\sigma^3$	Nabarro 1967
$\frac{ML^2}{d}$	$(Md)^{-1/2}$	σ^{-1}	σD	$M = \frac{\rho_m}{d}$	$D\sigma^3$	Weertman 1972
$\frac{a\sigma^2}{L}$		σ^{-1}	σD	$a = \text{cte}$	$D\sigma^4$	Blum 1971
$\frac{N}{HL}$	$\sigma^{-2/3}$	$\frac{H}{N}$	$N\sigma D$	$H \propto \sigma^{-1}$ $H \propto \sigma L$	$D\sigma^3$ $D\sigma^4$	Weertman 1972
Cte			σD		$D\sigma$	Harper-Dorn 1957

Note: In the table, L is the size of the dislocation network, M is the density of Frank–Read sources, d is the climb distance, a is the width of dislocations, N is the number of dislocations pile-up, and H is the mean distance of dislocations in the pile-up.

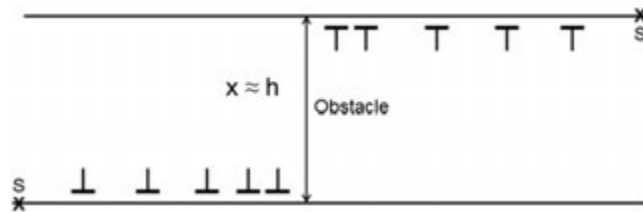


Fig. 2 The Weertman creep model for recovery creep.

The backstress due to the dislocation pile-up on the sources S and S' cancel the external applied stress and the sources cannot emit any more dislocations; the dislocations at the head of the pile-up recombine by climb, the backstress decreases and the sources can emit new dislocations. Thus, the strain (ϵ) is produced by the glide of the new dislocations and the strain rate ($\dot{\epsilon}$) is controlled by the dislocation climb at the point of pile-up.

In general:

$$\dot{\epsilon} \propto \sigma^n D \quad (3)$$

with $n \geq 3$. This picture gives rise to the so-called natural power law model and it is always possible to find an ad-hoc model to adjust the stress exponent to the experimental values.

For a compound (monolithic ceramic) $A_\alpha B_\beta$, D is given by the molecular diffusion coefficient D_{mol} (Philibert, 1982).

$$D_{\text{mol}} = \frac{D_A D_B}{\alpha D_B + \beta D_A} \quad (4)$$

D_A and D_B can be expressed by the corresponding expression:

$$D_A^{eff} = D_A^l + 10 \left(\frac{\sigma}{\mu} \right)^2 D_A^p + \frac{\pi \delta}{d} D_A^{Gb} \quad (5)$$

In this expression, l is lattice, p is pipe diffusion, Gb is grain boundary, δ is the grain boundary thickness and the superscript indicates the path for diffusion, the prefactor of D_x^p and D_x^{Gb} are taken as $10 \left(\frac{\sigma}{\mu} \right)^2$ and $\frac{\pi \delta}{d}$ respectively (Ashby and Frost, 1975). The same treatment can be applied for the species B.

From Eqs. (3) and (4), it can be concluded that the rate-controlling process for creep is the motion of the slowest diffusing species along the easiest path.

Diffusional Creep

Regarding diffusional creep, the deformation is due to pure transport of matter and it is generally produced at high temperature $T \geq \frac{T_M}{2}$ (T_M is the melting temperature) and low non-isostatic stress field. According to the ideas of Nabarro (1948) and modified by Herring (1950), the equilibrium concentrations of vacancies differ, depending of the orientation of the surfaces or interfaces where they can be generated or annihilated. The difference in vacancy concentration produces a flux proportional to the gradient of chemical potential which gives rise to a mass flow. The transport can take place in the lattice (Nabarro–Herring) or along the grain boundary (Coble). As previously explained, for a compound A_xB_y , the molecular diffusion coefficient D_{mol} is written as in Eq. (4), and D_A^{eff} will be given by Eq. (6):

$$D_A^{eff} = D_A^l + \frac{\pi \delta}{d} D_A^{Gb} \quad (6)$$

and similar treatment applies to B.

The gradient of chemical potential is of the order of $\sigma \Omega / L$ (Ω is the atomic volume and L is the mean grain size) and then the mass flux $J \propto D^l \sigma / kTL$ and the number of atoms transported per unit of time and per face (L^2) is $\Phi \approx JL^2$ producing a volume change per face and unit time of $\Delta V = J\Omega L^2$ distributed over L^2 or a change in length $J\Omega$ per unit time and so a strain rate:

$$\dot{\epsilon} = \frac{1}{L} \frac{dL}{dt} = \frac{1}{L} J\Omega \quad (7)$$

In the following L is replaced by d (grain size). When the flux of vacancies is along the bulk, the strain rate is written:

$$\dot{\epsilon} = B \frac{D^l \sigma \Omega}{kT d^2} \quad (8)$$

In 1963, Coble considers that the mass flow can occurs along the grain boundary and then the strain rate will be:

$$\dot{\epsilon} = C \frac{\sigma \Omega D^{Gb} \delta}{d^3 kT} \quad (9)$$

The constants B and C depend on the grain shape factor and the applied stress system and in general $B \approx 13$ and $C \approx 24$. For details see Philibert (1982).

In general the viscous flow can comprise of both volume and grain boundary mass flow can contribute to the mass transport and then the strain rate is:

$$\dot{\epsilon} = A \frac{\sigma \Omega}{d^2 kT} \left(D^l + \frac{\pi \delta D^{Gb}}{d} \right) \quad (10)$$

with A being a dimensionless constant.

Assuming a grain boundary thickness (δ) of 1 nm, the term $\frac{\pi \delta}{d}$ in Eq. (10) can vary by several orders of magnitude depending on the grain size. Therefore, depending on the activation energies of the diffusion coefficients, D^l can be smaller than D^{Gb} multiplied by the term $\frac{\pi \delta}{d}$ and, consequently, diffusion through the lattice will be rate controlling. However, when the grain size decreases, this inequality can change, and the grain boundary diffusion can be rate controlling. This can be summarized from the Fig. 3 (Dominguez-Rodriguez *et al.*, 2010).

As it can be observed in the figure, the dashed lines (3) and (4) stand for the effective grain boundary diffusion coefficient $\frac{\pi \delta}{d} D^{Gb}$ for nanometric (30 nm) and micrometric (1 μ m) grain sizes, respectively. T_1 and T_2 correspond to the transition temperature for lattice to grain boundary diffusion for the two ranges of grain size. Below T_2 diffusion along grain boundary controls plasticity, although no plasticity is expected under these conditions. In nanometric specimens, such a transition can occur below T_1 , when grain boundary diffusion can be expected.

Grain Boundary Sliding

In diffusional creep in order to maintain cohesion between the grains, grain boundary sliding (GBS) occurs as shown in Fig. 4. This type of GBS is termed as "Lifshitz" GBS.

A different picture arises when GBS is responsible for the deformation, as shown in Fig. 5.

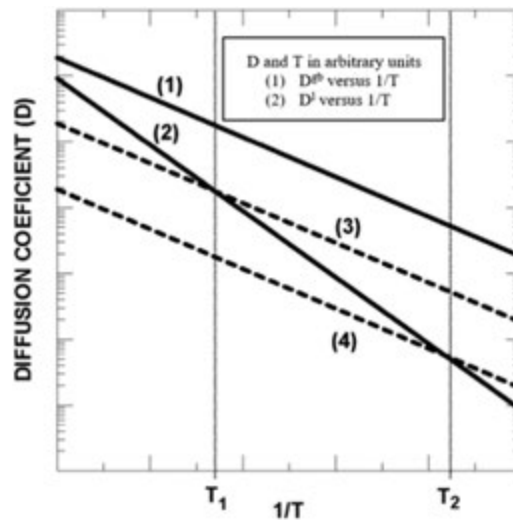


Fig. 3 Schematic plots of the diffusion coefficients versus inverse of temperature. The solid lines 1 and 2 correspond to a hypothetical grain boundary D^{gb} , and lattice diffusion coefficient D^l respectively. The dashed lines correspond to D^{gb} at 30 nm and 1 μm grain sizes, respectively. From Dominguez-Rodriguez, A., Gomez-Garcia, D., Castillo-Rodriguez, M., Zapata, E., Chaim, R., 2010. Superplasticity in nanoceramics: Achievements and open questions. *International Journal of Materials Research* 101, 1215–1221.

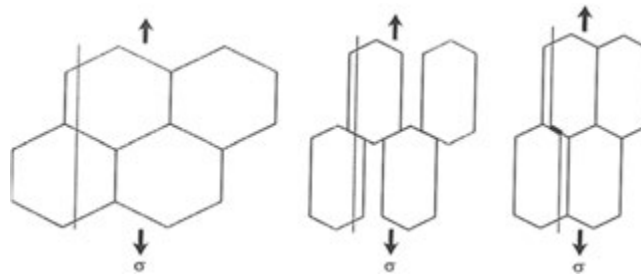


Fig. 4 Schema of the Lifshitz GBS. The thick line shows the GBS after deformation.

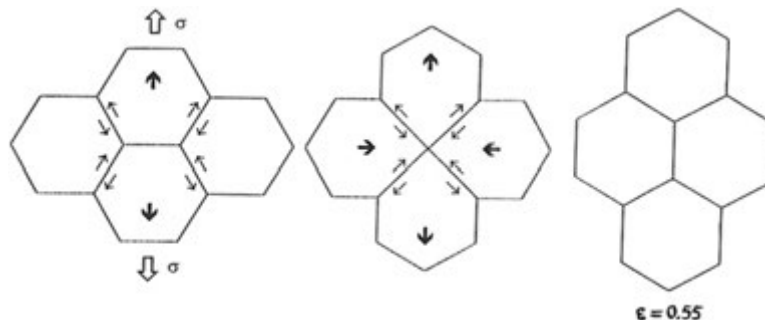


Fig. 5 Schema of the Rachinger GBS showing that the grain shape remains constant after deformation. From Ashby, M.F., Verrall, R.A., 1973. Diffusion-accommodated flow and superplasticity. *Acta Metallurgica* 21, 149–163.

In order to release stresses created during GBS, deformation is to be accompanied by intergranular slip throughout adjacent grains, by localized slip adjacent to the boundaries or by diffusional processes involving point defect migration. Sometimes, formation of triple point follows and the opening-up of cracks at the triple points can also accommodate GBS; however, as soon as there is coalescence of voids or cracks, the material fails and that happens at not so-large deformations. This type of GBS, accommodated by the process described above, is termed as 'Rachinger grain boundary sliding'. When this occurs, the average grain size and shape remain unchanged after large deformation values being the main feature of this regime.

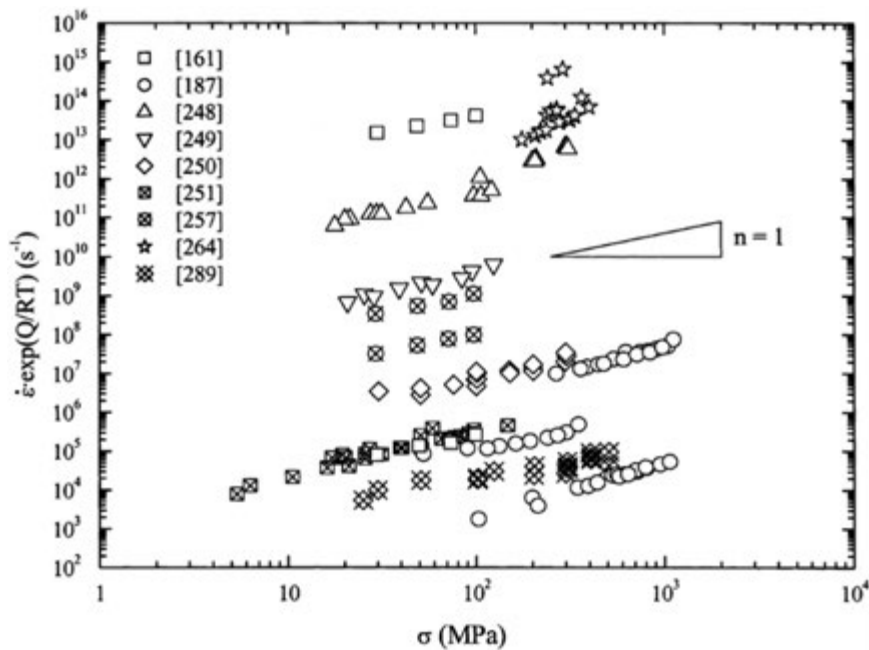


Fig. 6 Experimental temperature-compensated strain rates vs stress plots for compressive creep of silicon nitride-based ceramics. The stress exponent $n = 1$ is shown for comparison. From Melendez-Martinez, J.J., Dominguez-Rodriguez, A., 2004. Creep of silicon nitride. *Progress in Materials Science* 49, 19–107.

Creep of Monolithic Ceramics and Deformation Maps

Creep of Monolithic Ceramics

Ceramics can be classified into oxide ceramics and non-oxide ceramics. In the first class, Al_2O_3 has been studied more extensively than any other ceramics. In the case of non-oxide ceramics, SiC and Si_3N_4 are the most extensively studied.

Al_2O_3 is a stoichiometric ceramic and small amount of impurities can dramatically change the mechanical behavior. At high temperatures, the creep equation is a function of the diffusion coefficients of the species controlling the plasticity and it has been shown (Heuer, 2008) that there is a very high scatter in these values and as a consequence, of the creep parameters. The creep rate depends on the grain size, the purity and the composition of the glassy phase eventually present in grain boundaries. The values obtained experimentally for m , n , and Q are $0 < m < 3$, $0.7 < n < 3.3$ and $295 < Q < 840 \text{ kJ mol}^{-1}$ (Chevalier *et al.*, 1997). A large number of mechanisms can correspond to the obtained values for m and n exponents. Furthermore, two or more mechanisms can occur simultaneously. For alumina, the possible mechanisms are the following: lattice mechanism (dislocation creep), diffusion creep (Nabarro–Herring and Coble creep), grain boundary sliding, cavitation creep and microcracking. Some data concerning creep of alumina will be presented in Figs. 15, 16, and 18.

For non-oxide ceramics, a review article (Melendez-Martinez and Dominguez-Rodriguez, 2004) showed creep data for Si_3N_4 . In this ceramic, the creep data depend on whether the ceramic is deformed under compression or under tension. In order to avoid confusion, only the values under compression are represented (Fig. 6). The references shown in Fig. 6 can be obtained in the article (Melendez-Martinez and Dominguez-Rodriguez, 2004).

Silicon nitride ceramics are a very complex system with generally more than one phase. No model accounts for the experimental results with a complete success and it is difficult to determine the creep mechanisms. Creep is due to a series of mechanisms occurring simultaneously. Compression creep occurs by grain boundary sliding, accommodated by solution-precipitation. Tensile creep is influenced by cavitation. The presence of secondary glassy phases differently influences the creep behavior under compression and under tension.

Deformation Maps

It is useful to have a procedure to summarize, at a glance, for a given polycrystalline material, information about the range of dominance of the mechanisms controlling plasticity. A good review of deformation maps can be found in the book from Frost and Ashby (1982).

In order to construct a map, it is necessary to perform creep tests for a well-defined ceramic. However, the maps are critically dependent on the microstructure of the specimen under study. This fact implies that a same material can exhibit quite different maps as a function of differences in their microstructures. A good example is shown when compared the deformation maps in NiO

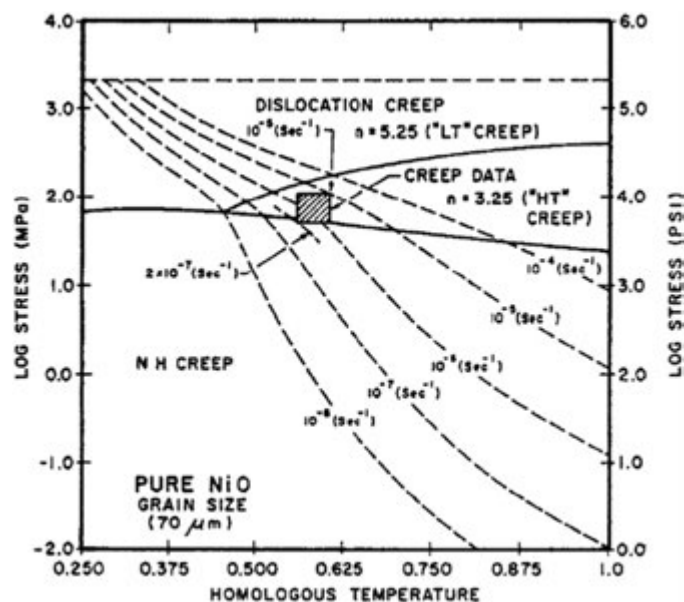


Fig. 7 Deformation map for NiO with grain size of 70 μm . From Krishnamachari, V., Notis, M.R., 1977. High temperature deformation of polycrystalline NiO and CoO. *Acta Metallurgica* 25, 1307–1313.

for grain size of 70 μm (**Fig. 7**) (Krishnamachari and Notis, 1977) and for NiO with grain size of 9 μm (Jimenez-Melendo *et al.*, 1986) (**Fig. 8**). In the latter map, there are three data sets (a, b, and c) corresponding to the creep data for different authors as explained in Jimenez-Melendo *et al.* (1986).

Superplasticity

Superplasticity is macroscopically defined as the ability of a polycrystalline material to exhibit large elongations at elevated temperatures and relatively low stresses. This is commonly found in a wide range of materials from metals to ceramics when the grain size is small enough: a few micrometers in the case of metals and less than a micron for ceramics. The first observation of superplasticity was reported in a 3 mol% yttria-stabilized tetragonal zirconia polycrystal ceramic (Y-TZP) with a grain size of 0.4 μm and deformed at 1450°C and $3 \times 10^{-4} \text{ s}^{-1}$ (Wakai *et al.*, 1986) (**Fig. 9**).

On a microscopic scale, a superplastically deformed polycrystal is characterized by its microstructure, i.e., grain size and form factor, almost unchanged after deformation, and it is generally accepted that these features are mainly achieved through grain boundary sliding. Clear evidence of grain boundary sliding during ceramic superplasticity can be observed in **Fig. 10**, which shows the relative motion of grains during deformation of Y-TZP (Duclos, 2004). It can be observed how two small grains, initially separated by two larger grains in contact, become nearer and nearer and finally the larger grains are separated. Several examples of switching events are also shown in the same reference (Duclos, 2004). As shown in **Fig. 10**, superplasticity occurs not only in tension, even though the polycrystal is deformed in compression, or in three- or four-point bending conditions, as long as GBS is the primary process (Dominguez-Rodriguez *et al.*, 2006).

Since the structure and the nature of the grain boundaries can be profoundly modified by segregation or glassy phases, the accommodation processes which control the strain rate of superplasticity are also affected by segregation and second phases. In the case of segregation, several important factors can be recognized: the ionic radius of the impurities, their charge, the binding energy between the host atoms and the impurities. In the case of secondary phase, it may act as a “lubricant” so that the viscous movement of the glassy phases constitutes an accommodation mechanism for grain boundary sliding.

As it was already explained, cavitation can be discarded as an accommodation mechanism for superplasticity, since the strain-to-failure afforded by this mechanism is rather small. Another important point is concerned with the activation of dislocations; as indicated in Castaing *et al.* (1989) and Dominguez-Rodriguez *et al.* (2013). For zirconia, the stresses needed to activate dislocations in cubic zirconia single crystals (170–300 MPa), as well as in tetragonal yttria stabilized zirconia single crystals (400 MPa) when deformed at 1400°C and strain rates $\sim 10^{-5} \text{ s}^{-1}$ are a factor of 20–40 times greater than in Y-TZP deformed under the same experimental conditions. It is easy to believe that dislocations cannot be activated in this system for the conditions under which superplasticity is studied. In addition, neither a sample of Y-TZP deformed by tension in the superplastic regime and cooled down under load to avoid the recovery of dislocations, or another sample quenched after deformation show no dislocation activity (Dominguez-Rodriguez *et al.*, 2013); so the activity of dislocations can also be discarded as an accommodation mechanism for superplasticity. Therefore, only the flow of point defects and solution-precipitation mechanisms are important. Depending on

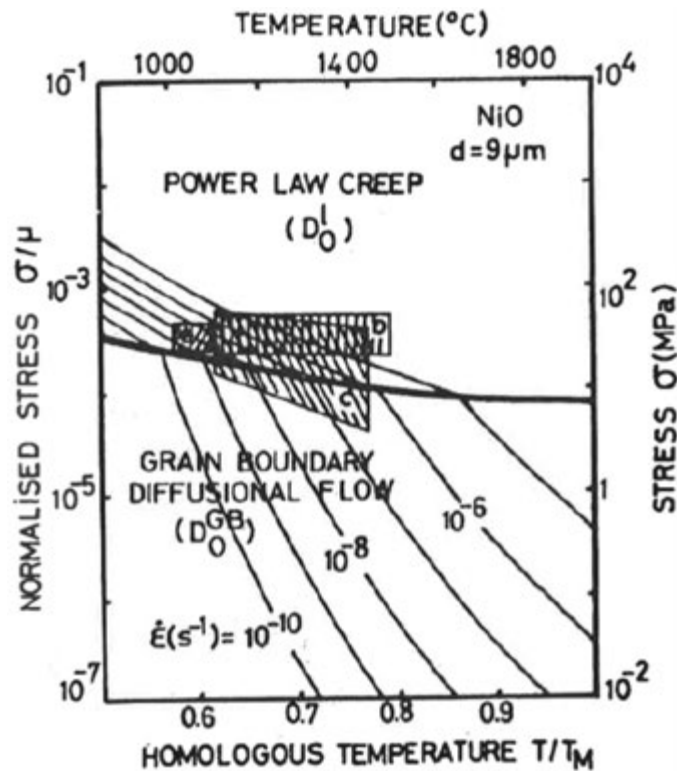


Fig. 8 Deformation map for NiO with grain size of 9 μm . From Jimenez-Melendo, M., Dominguez-Rodriguez, A., Castaing, J., Marquez, R., 1986. Diffusion and creep: Application to deformation maps on NiO. *Scripta Metallurgica* 20, 739–742.



Fig. 9 As-received and tensile-deformed specimens superplastic yttria tetragonal zirconia polycrystals (YTZP), as displayed in Wakai *et al.* Reproduced from Wakai, F., Sakaguchi, S.S., Matsuno, Y., 1986. Superplasticity of yttria-stabilized tetragonal ZrO_2 polycrystals. *Advanced Ceramic Materials* 1, 259–263. Courtesy of Prof. Wakai.

which of these factors dominates during deformation, the accommodation mechanism may be regarded as the flow of point defects or solution–precipitation.

GBS Accommodated by the Diffusional Flow of Point Defects

This type of mechanism is due to a non-uniform flow of point defects: Their fundamental topological features are that the grains in the polycrystals change their neighbors and almost do not change their shape after large deformation. It was modeled in the first instance by Ashby and Verrall (1973) (thereafter A–V). The model considers a group of four grains deformed at constant pressure and stress (Fig. 5). During this flow, four irreversible processes take place:

- (1) Diffusive process by which grains temporarily change shape.
- (2) Grain or phase boundaries are sinks and sources of point defects.
- (3) Grain boundary sliding.
- (4) Fluctuations of boundary area.

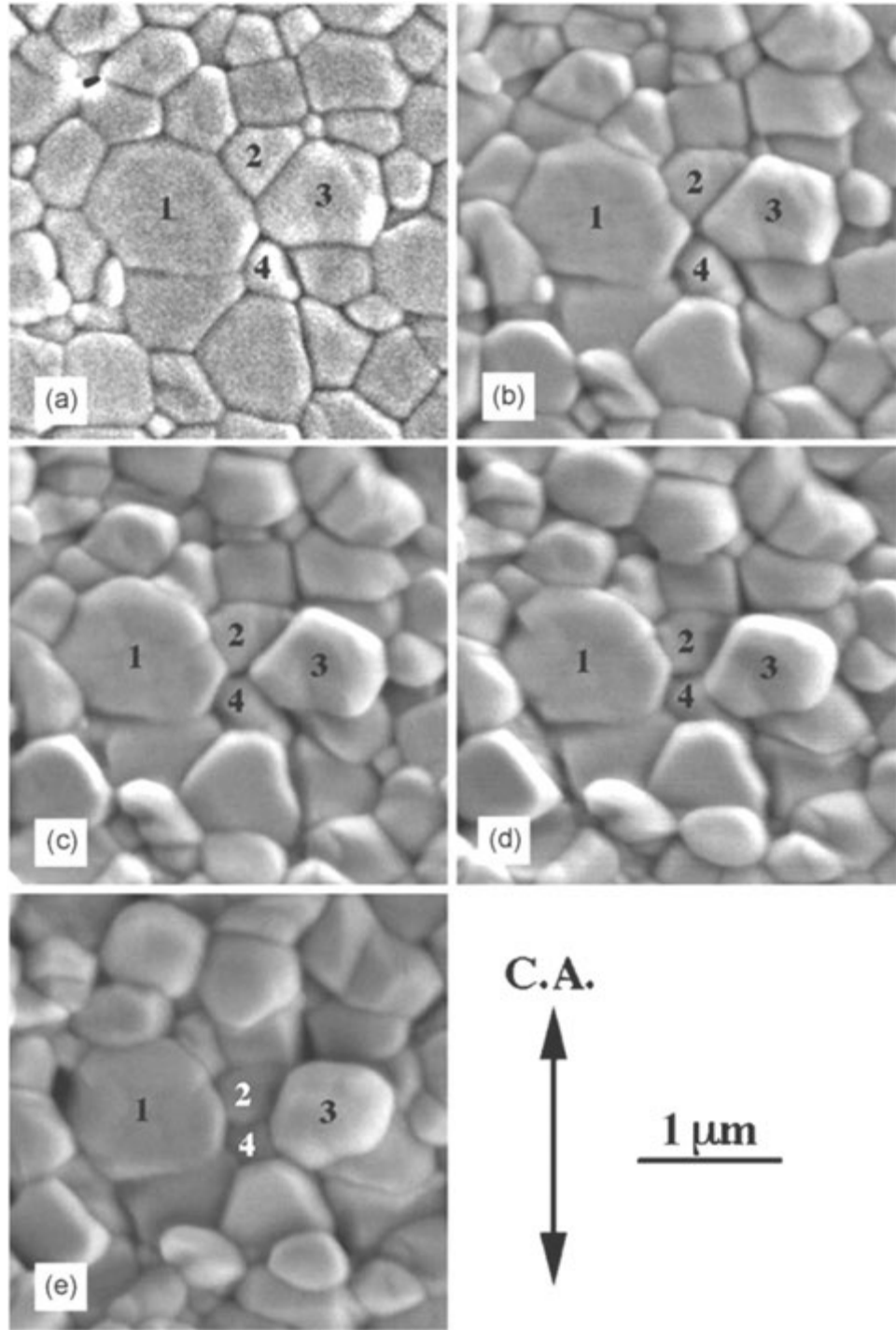


Fig. 10 Experimental evidence of grain boundary sliding with microstructural invariance in superplastic YTZP. The arrow indicates the compression axis. Courtesy of Prof. Duclos.

By considering the entropy change in these four processes, the constitutive equation of the A-V model, when lattice and grain boundary diffusion are taking into account, is written:

$$\dot{\epsilon} = \frac{100\Omega}{kTd^2} \left(\sigma - \frac{0.72\gamma}{d} \right) D^l \left(1 + \frac{3\delta D^{Gb}}{dD^l} \right) \quad (10)$$

where $\frac{0.72\gamma}{d}$ is a threshold stress for the grain-switching event and γ is the grain boundary free energy.

It is clear that many studies on MgO, Al₂O₃, and UO₂ show a linear relationship between strain rate and stress which is explained in terms of diffusional models even though the measured strain rates are some orders of magnitude different from that predicted by creep models (Burton, 1977). This discrepancy is usually put down to different impurity levels or, in some cases, to the experimental technique used, e.g., in bending beam experiments. This relationship is not valid when segregation at grain boundaries occurs as in Y-TZP where a large number of studies have been performed (Jimenez-Melendo *et al.*, 1998; Jimenez-Melendo and Dominguez-Rodriguez, 1998) with a big scatter in the value of n , which ranged between 2 and 5. Probably the most plausible explanation is that the threshold stress in the A-V model ($\frac{0.72\gamma}{d}$) is not valid in Y-TZP. In Y-TZP γ is $\sim 0.15 \text{ Jm}^{-2}$ and for a grain size of $0.3 \mu\text{m}$, σ_0 is 0.3 MPa much smaller than the values found experimentally, which ranged between 3 and 9 MPa (Dominguez-Rodriguez *et al.*, 2013). In Y-TZP, the threshold stress has been obtained experimentally (Dominguez-Rodriguez *et al.*, 1998a,c) as:

$$\sigma_0 = 5 \times 10^{-4} \frac{\exp\left(\frac{120 \text{ kJ/mol}}{RT}\right)}{d} \quad (11)$$

When the threshold stress is introduced into the creep equation, the stress exponent is 2, identical to that found in metals when lattice diffusion is the rate controlling mechanism (Jimenez-Melendo and Dominguez-Rodriguez, 1998).

Solution-Precipitation Model

In the case of solution-precipitation, the secondary phase melts at temperatures lower than the matrix and, provided that the crystals are at least partially soluble in the glassy phase, creep may take place by Fig. 11:

- solution of the crystal in the liquid phase at grain boundaries under compression,
- diffusion along the liquid phase, and
- precipitation of the crystalline materials at grain boundaries under traction.

The solution precipitation model was first proposed by Raj and Chyung (1981), modified by Wakai (1994), and finally the divergence of the creep parameters in Wakai (1994) was solved by Melendez-Martinez *et al.* (2004), detailed consideration of the precipitation or solution of the crystalline material at the line defects which present as kinks in the step formed at the grain boundaries. The modified model predicts stress exponent deviating slightly from $n = 1$ as found experimentally (Melendez-Martinez *et al.*, 2002).

Applications of Superplasticity

The increasing applications of advanced ceramics in technical areas including aerospace, energy, electronics, etc., often require complex shapes to be manufactured at low prices. The extensive potential applications, together with the possibility of processing dense high-ductility ceramics with controlled microstructures, have been the driving force for the appearance of applications such as sheet forming, blowing, stamping, forging, and joining.

A good example of superplastic forming of different ceramics can be found in the first figure of Chen and Xue (1990). In this figure, flat 1 mm thick disks of Si₃N₄, 2Y-TZP:Al₂O₃, 2Y-TZP:Mullite, and 2Y-TZP + 0.3% doped with Mn, Fe, Co, Cu, and Zn, were stretched with a 6.5 mm radius punch at temperatures and forming times depending of the ceramics.

Sinter forging is a promising technique because densification and net-shaping are achieved simultaneously (Venkatachari and Raj, 1987). This technique avoids cavities and voids because sinter forging is achieved by compression producing an enhancement of strength in ceramics, Kondo *et al.* (1999) being a good example of the high strength and high fracture toughness that can be achieved in a sinter forged Si₃N₄.

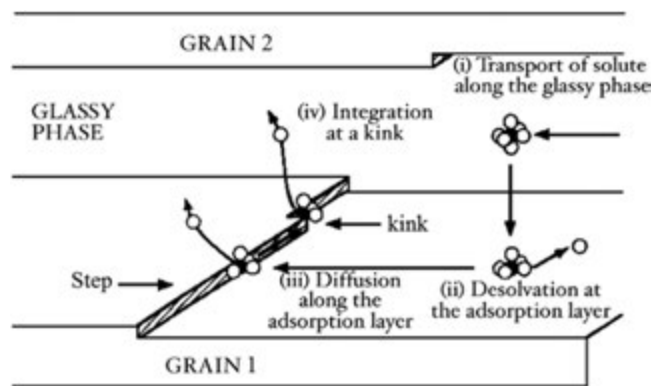


Fig. 11 Schematic representation of the solution-precipitation mechanism in Wakai step model. From Melendez-Martinez, J.J., Dominguez-Rodriguez, A., 2004. Creep of silicon nitride. *Progress in Materials Science* 49, 19–107.

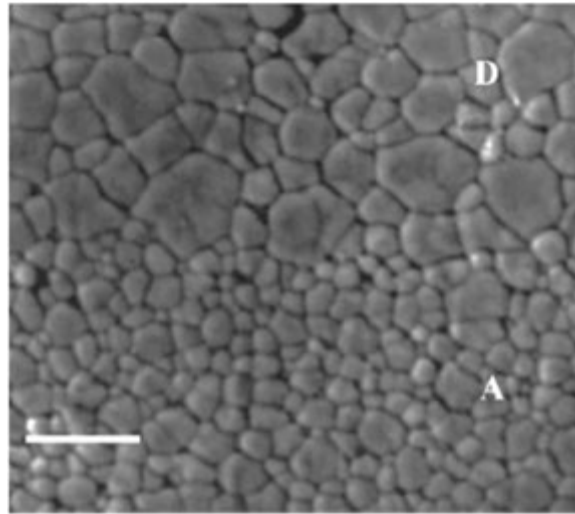


Fig. 12 SEM picture of the two pieces joined with different grain sizes (0.3 and 1 μm). The bar is 2 μm . From Dominguez-Rodriguez, A., Pique, E., Jimenez-Melendo, M., 1998b. Processing of multilayer of Y-TZP by superplastic flow. Scripta Materialia 39, 21–25.

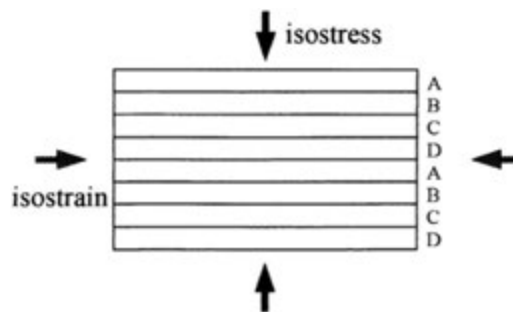


Fig. 13 Scheme of the two types of compression test performed to produce the junction (isostress) and to check the strength of the junction (isostrain). From Dominguez-Rodriguez, A., Pique, E., Jimenez-Melendo, M., 1998b. Processing of multilayer of Y-TZP by superplastic flow. Scripta Materialia 39, 21–25.

As previously mentioned, it is now accepted that GBS accompanied by solution precipitation diffusional process are the mechanisms controlling superplasticity. These can start to be deployed as a novel technique to join ceramics, which takes advantage of both processes (Ye and Dominguez-Rodriguez, 1995; Dominguez-Rodriguez *et al.*, 1998a,c). When two parts in contact are superplastically deformed, the grains of one part interpenetrate those of the other, producing a rapid and perfect junction of both parts. The superplasticity does not mean that the materials need to be deformed over 100%. As soon as the material is deformed in the superplastic regime (GBS), which happens for $\epsilon > 2\%$, the junction can be achieved. A good example can be observed in Fig. 12.

Based on the mechanism controlling the superplastic behavior of fine-grained ceramics and that the creep resistance is proportional to the grain size, these two concepts have been used to join zirconia layers of different compositions and/or grain sizes to obtain a multilayer composite with a clean and strong interface and heterogeneous mechanical behavior depending on the stress application (Dominguez-Rodriguez *et al.*, 1998b).

Fully dense 3 mol% Y-TZP material 0.5 mm thick and with grain size of 0.3 μm , 0.5 μm , 0.8 μm , and 1.0 μm were joined as described in Dominguez-Rodriguez *et al.* (1998b). The composites obtained were deformed with the applied stress perpendicular to the interfaces “isostress test” and with the applied stress parallel to the interfaces “isostrain test” as indicated in Fig. 13.

These results have interesting implications in the design of materials with complex forms, for low and high temperature applications. For example, at room temperature, a short-crack ceramic (ceramic with small grain size and tough) can be superplastically joined to a long-crack ceramic (ceramic with big grain size and wear resistant) to obtain a tough and wear resistant ceramic composite. At high temperature, for the “isostress test”, the layer with the smaller grain size will control the mechanical behavior, whereas for the “isostrain test” is the layer with bigger grain size will control mechanical behavior.

For the isostrain case, where the strain and the strain rate are the same for each phase, the stress for this configuration, can be modulated by changing the volume fraction and the grain size of the different layers, details can be found in

Dominguez-Rodriguez *et al.* (1998b). This technique allows designing materials with complex shapes or Functional Gradient Materials (FGM) with anisotropic mechanical properties at low as well as high temperature.

As a final remark, it can be concluded that superplastic flow can be used to join heterogeneous zirconia layers with different mechanical properties with strong and clean interfaces junctions. As a broader implication of this work, such superplastic joining could be effectively employed to design multilayered ceramic composites for structural applications at low and high temperatures.

Future Trends in Superplastic Ceramics

- In the immediate future, the main focus in ceramic superplasticity will be the search for the right conditions to achieve “High Strain Rate Superplasticity” (HSRS) ($\dot{\epsilon} \geq 10^{-2} \text{ s}^{-1}$).

Although this phenomenon has been demonstrated in several ceramic compounds and several controlling inputs have been outlined to achieve it, we are still far from elucidating how to control this process systematically. Gaining fundamental control over HSRS can be expected to broaden the range of the applications for such ceramics.

- Improvements in ceramic powder processing technology, the routine preparation of high-purity and the new techniques for the processing of these powders such as HIP, SPS, microwave furnace, etc., will be the driving forces for a future study on nanoceramics, opening up new phenomena, and new applications.
- Finally, the future complete comprehension of superplasticity will demand a clear elucidation and justification of the basic equations describing this phenomenon. At this point, simulations at microscopic as well as mesoscopic levels may emerge as a useful tool.

Creep Behavior of Ceramic Matrix Composites

The effect of the following different types of reinforcement on the creep behavior of composites will be considered: particles reinforcement, nano-reinforcement, whisker, carbon nanotube or graphene reinforcement and continuous fiber reinforcement.

Particle Reinforced Composites

The creep behavior of particle reinforced composites has been studied by many researchers, some examples results of which will be presented. Various particle reinforcements have been added to alumina matrices. Fig. 14 shows the stress dependence of the strain rate of alumina and zirconia toughened alumina (ZTA) containing 10 vol% of zirconia. The zirconia particles ($0.5 \mu\text{m}$) are homogeneously dispersed at grain junctions between alumina grains. Both materials have the same grain size ($\sim 2 \mu\text{m}$). The addition of zirconia particles does not lead to an improvement of the creep resistance. The stress exponent $n \sim 2.5$ is similar for the matrix and the composite. Creep of alumina is controlled by grain boundary sliding (GBS) accommodated by grain boundary diffusion with the formation of cavities. The microstructures observed after creep show the presence of small cavities at the triple grain junctions and along the grain boundaries (Fig. 15).

The effect of SiC platelet reinforcement (diameter $25\text{--}45 \mu\text{m}$, aspect ratio ~ 10) on the creep behavior of alumina is shown in Fig. 16. The creep resistance is increased by more than one order of magnitude. The stress exponent of the composites ($n = 2.5$) is higher than for monolithic alumina ($n = 1.5$). The decrease of the creep rate is due to unloading of alumina grains due to load transfer from the matrix to the platelets.

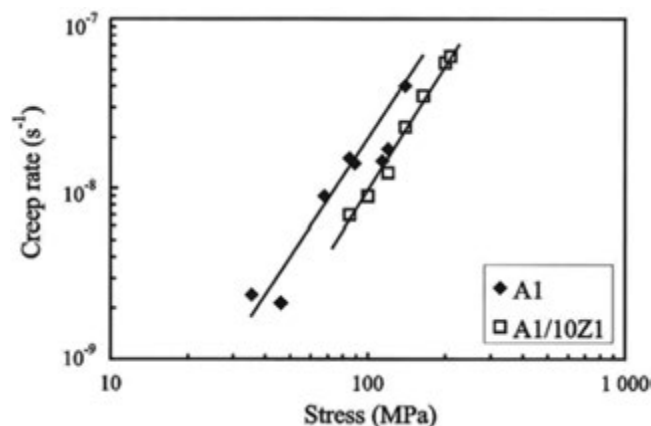


Fig. 14 Stress dependence of the strain rate in bending of alumina and a ZTA composite at 1473K. From Fantozzi, G., Chevalier, J., Olagnon, C., Chermant, J.L., 2000. Creep of ceramic matrix composites. Chapter 7: Carbon/carbon, cement, and ceramic matrix composites. In: Warren, R. (Ed.), Comprehensive Composite Materials, vol. 4. Oxford: Elsevier.

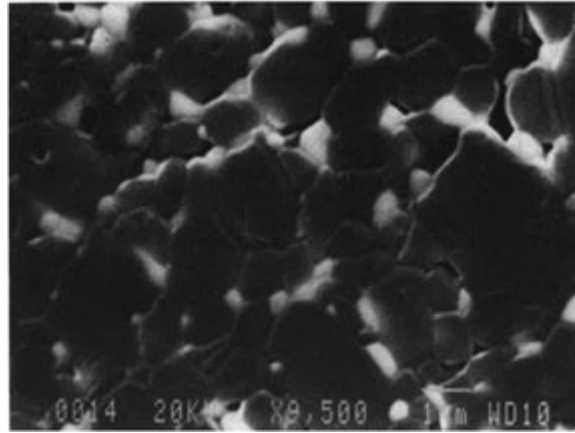


Fig. 15 Microstructure of a ZTA composite after creep at 1473K. From Fantozzi, G., Chevalier, J., Olagnon, C., Chermant, J.L., 2000. Creep of ceramic matrix composites. Chapter 7: Carbon/carbon, cement, and ceramic matrix composites. In: Warren, R. (Ed.), *Comprehensive Composite Materials*, vol. 4. Oxford: Elsevier.

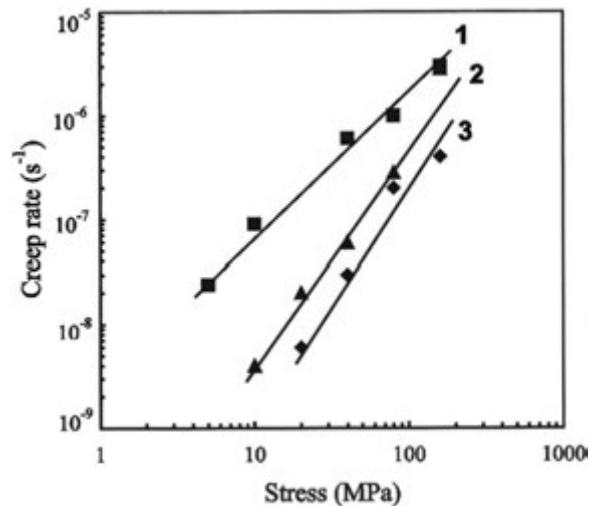


Fig. 16 Stress dependence of compression creep rate of alumina-SiC platelet composites at 1623K : (1) alumina; (2) alumina + 10 vol% SiC_p; alumina + 20 vol% SiC_p. From Fantozzi, G., Chevalier, J., Olagnon, C., Chermant, J.L., 2000. Creep of ceramic matrix composites. Chapter 7: Carbon/carbon, cement, and ceramic matrix composites. In: Warren, R. (Ed.), *Comprehensive Composite Materials*, vol. 4. Oxford: Elsevier.

Another example concerns the zircon-based composites. Due to the presence of an intergranular glassy phase, zircon exhibits a low creep resistance. The creep mechanism of zircon is GBS which can be prevented by second phase interlocking and glassy phase modification (amount and viscosity). Composites reinforced with 9 wt% alumina can show a strong increase of the creep resistance (3 orders of magnitude).

The creep behavior of Si₃N₄ reinforced with particles or platelets has been studied by several authors (Fantozzi *et al.*, 2000). The creep resistance depends on the presence and the composition of grain boundary phase (glassy or crystalline phase). The reinforcement is essentially due to a load transfer from the matrix to the platelet or particle.

Nanocomposites

Nanocomposites are composed of micro-sized matrix grains with nano-sized reinforcing particles. Ohji *et al.* (1994) have studied the creep behavior of an alumina reinforced by 17 vol% SiC nanoparticles (average particle size ~ 100 nm). The SiC particles were located within the alumina grains (~ 2 µm) and along the grain boundaries. The nanocomposites exhibit a higher creep resistance (Fig. 17) compared to alumina (the failure strain was 0.5% against 4% for alumina). After creep, very few cavities, and microcracks are observed for the nanocomposites, in contrast to pure alumina. The creep rate with the addition of the nanoparticles is three to

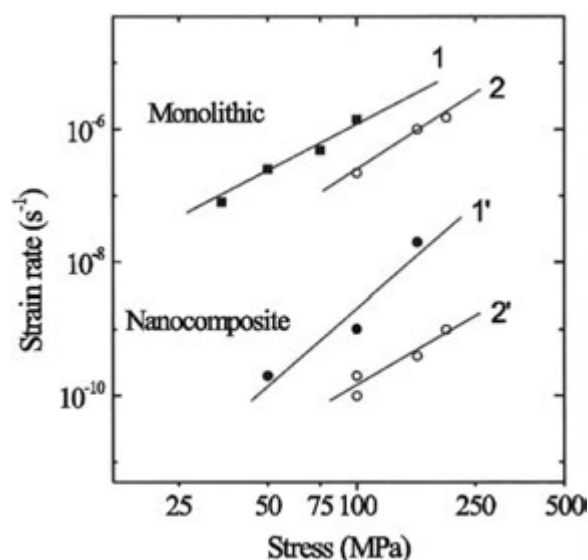


Fig. 17 Stress dependence of strain rate in tension (curves 1 and 1') or flexure (curves 2 and 2') of alumina and nanocomposite at 1473K. From Fantozzi, G., Chevalier, J., Olagnon, C., Chermant, J.L., 2000. Creep of ceramic matrix composites. Chapter 7: Carbon/carbon, cement, and ceramic matrix composites. In: Warren, R. (Ed.), *Comprehensive Composite Materials*, vol. 4. Oxford: Elsevier.

four orders of magnitude lower than for alumina with the same grain size. The stress exponent measured for the nanocomposite ($n = 3.1$) in tension is higher than for alumina ($n = 2.2$).

The role of the SiC nanoparticles is difficult to specify, but a rotation of intergranular nanoparticles occurs that “plunge” into the alumina matrix as shown by Ohji *et al.* (1994) and provokes the formation of small cavities around the particles. This process leads to a particle pinning of the grain boundaries and to hindrance of GBS and so to a significant increase in creep resistance. The presence of SiC nanoparticles can also modify the chemistry of grain boundaries and decrease the boundary diffusivity leading to a reduction of cavity formation. The enhancement of grain boundary cohesion by SiC nanoparticles inhibits GBS and provokes plastic deformation by dislocation motion. This can explain the high n values measured for the nanocomposites, values consistent with creep mechanisms involving dislocation glide or climb.

The creep behavior of nanocomposites with a Si_3N_4 matrix reinforced by SiC nanoparticles has been studied by several authors (Fantozzi *et al.*, 2000). The nanocomposites exhibit a good creep resistance due to an increase in grain interlocking by SiC nanoparticles.

Whisker, Carbon Nanotube, and Graphene Reinforced Composites

First, the case of SiC whiskers (SiC_w) reinforced alumina will be considered. The creep rate of alumina is strongly reduced by the addition of SiC_w (more than two orders of magnitude lower) as shown by Fig. 18. The decrease depends on the whisker content, size and shape and on the matrix grain size. The stress exponent n (~ 2) is similar to that of alumina except at high temperature where n increases (~ 7 to 8). As shown by De Arellano-Lopez *et al.* (1990), these high n values obtained by using flexural creep tests are related to the stress gradient from tension to compression. Smaller values (~ 2) are obtained by compression tests.

The improvement of the creep resistance can be attributed to the inhibition of GBS by the pinning and locking action of the whiskers located along the grain boundaries. This can explain the important difference in strain to failure observed for alumina ($> 3\%$) and for the composites ($< 0.5\%$) as shown by Fig. 18. The high stress exponent observed at high temperature can be linked to creep cavitation at matrix-interfaces. The whiskers act as stress concentration sites leading to more extensive cavitation and cracking.

Similar enhancement in creep resistance is observed for other composite matrices (Fantozzi *et al.*, 2000).

Secondly, creep in carbon nanotube (CNT) reinforced ceramic composites will be examined. As mentioned by Castillo-Rodriguez *et al.* (2018), the influence of incorporation of CNTs in ceramic composites is not clear. Indeed, Mazaheri *et al.* (2011) have shown that CNTs/nanostructured 3Y-TZP zirconia composites exhibit a significant reduction of creep strain but other authors found that CNTs enhance GBS and do not act as reinforcement phases. Mazaheri *et al.* consider that the higher creep resistance of the CNTs/3Y-TZP composites is due to the pinning effect of CNTs blocking GBS. It must be mentioned that the creep behavior considered by Mazaheri *et al.* took place at very low stress (6 MPa) whereas for most of studies the considered creep stress range is much higher (10–400 MPa).

Recent results (Gopalan and Choskhi, 2018; Castillo-Rodriguez *et al.*, 2018) show that the creep resistance at high stress is not influenced by the addition of CNTs to an alumina matrix (Fig. 19). For the same matrix grain size (0.5 μm), the stress exponent

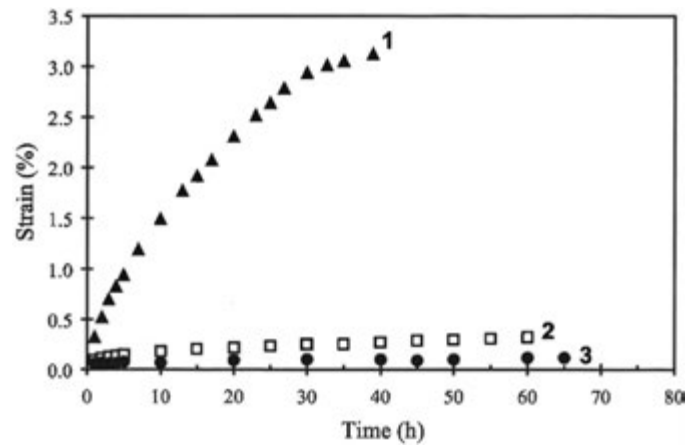


Fig. 18 Flexural creep curve for alumina and SiC_w-alumina composites at 1473K and 100 MPa under air: (1) alumina; (2) 12 vol% SiC_w; (3) 30 vol% SiC_w. From Fantozzi, G., Chevalier, J., Olagnon, C., Chermant, J.L., 2000. Creep of ceramic matrix composites. Chapter 7: Carbon/carbon, cement, and ceramic matrix composites. In: Warren, R. (Ed.), *Comprehensive Composite Materials*, vol. 4. Oxford: Elsevier.

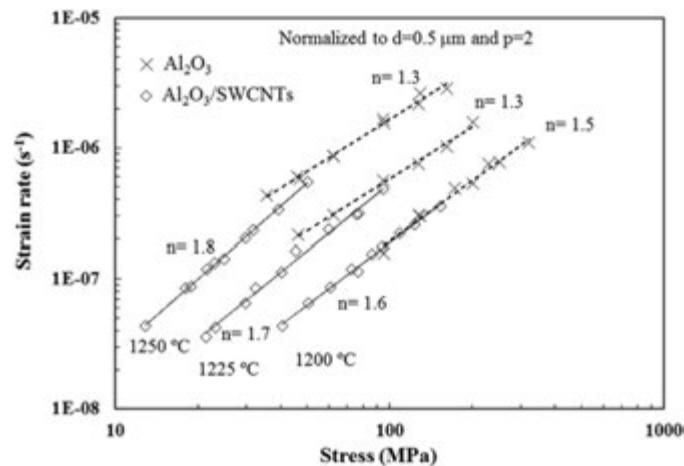


Fig. 19 Strain rate–stress curves for alumina and CNT-alumina nanocomposites tested at different temperatures. From Castillo-Rodriguez, M., Munoz, A., Dominguez-Rodriguez, A., 2018. Creep study on alumina and alumina/SWCNT nanocomposites. *Journal of The European Ceramic Society* 38, 5497–5502.

and the activation energy of alumina and CNT-alumina composites are very similar. The GBS accommodated by lattice diffusion (Nabarro–Herring type), is the predominant creep mechanism.

Thirdly, the creep behavior of graphene oxide-reinforced alumina (or zirconia) composites was recently studied by Cano-Crespo *et al.* (2017, 2018). Graphene-reinforced zirconia composites do not exhibit an improvement of the creep resistance compared to monolithic zirconia. The dominant effect of graphene is a lubricant effect increasing the grain boundary mobility. Concerning graphene-reinforced alumina composites, the creep resistance is improved compared to alumina at intermediate temperatures whereas at high temperatures there is no reinforcement. The dominant creep mechanism is GBS accommodated by diffusion and the creep parameters for the composites are similar to those of pure alumina.

Long Fiber Reinforced Composites

Long fiber ceramic composites often reinforced with SiC Nicalon fibers have been studied either with a glass-ceramic matrix or a crystalline ceramic matrix (Fantozzi *et al.*, 2000). The creep processes in these composites are complex and cannot be treated by conventional creep models. Several models have been proposed for continuous ceramic fiber-reinforced CMCs, first based on the rule of mixtures, then on the shear-lag model and then based on damage mechanics. These models must take into account the stress redistribution between fibers and matrix occurring during creep and the processes of damage accumulation. This stress redistribution between the composite constituents depends on the creep mismatch ratio (CMR) defined on the ratio of the fiber creep rate to that of the matrix. CMR is time, stress and temperature dependent.

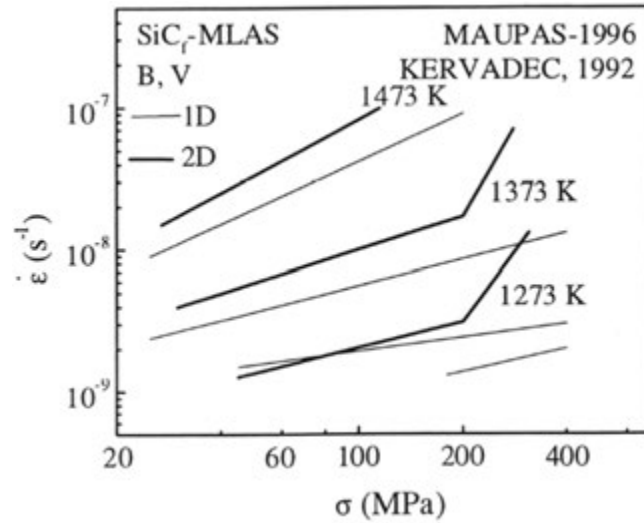


Fig. 20 Creep rates versus stress for $\text{SiC}_f\text{-MLAS}$ composite. B: bending test, V: vacuum for two architectures (1D and 2D). From Fantozzi, G., Chevalier, J., Olagnon, C., Chermant, J.L., 2000. Creep of ceramic matrix composites. Chapter 7: Carbon/carbon, cement, and ceramic matrix composites. In: Warren, R. (Ed.), *Comprehensive Composite Materials*, vol. 4. Oxford: Elsevier.

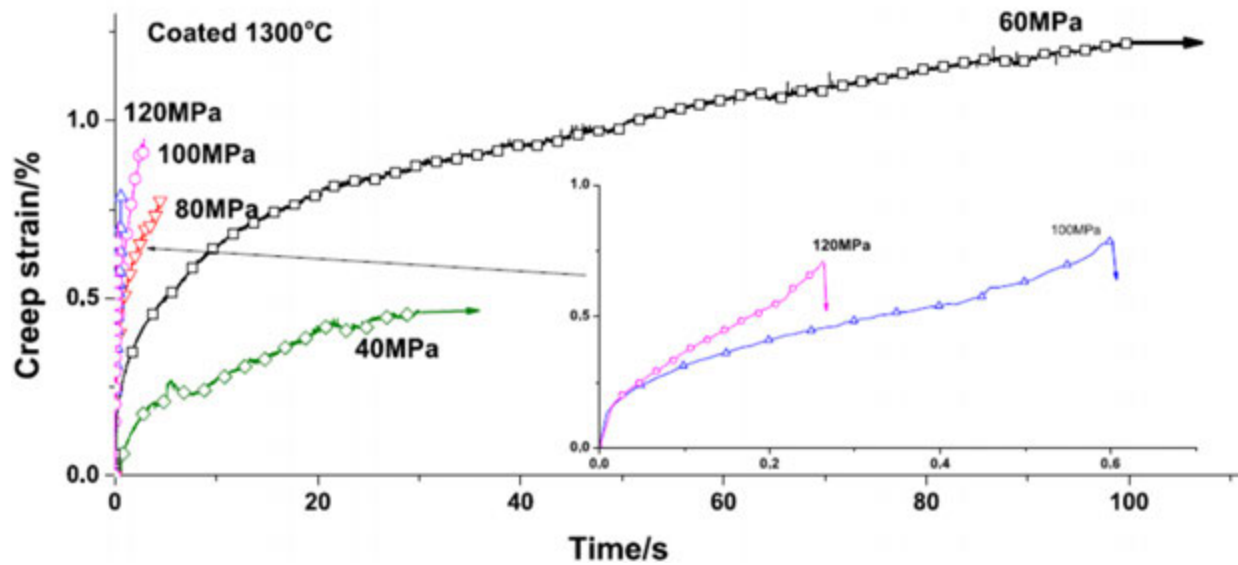


Fig. 21 Tensile creep strain versus time tested at 1300°C for coated specimen. From Jing, X., Yang, X., Shi, D., Niu, H., 2017. Tensile creep behavior of three-dimensional four-step braided SiC/SiC composite at elevated temperature. *Ceramics International* 43, 6721–6729.

When $\text{CMR} < 1$, the matrix has a higher creep rate than the fibers and there is a transfer from the matrix to the fibers, which controls the deformation and the rupture of the composites. The stress in fiber ceramics increases and fiber breakage occurs. This is also the case with glass-ceramic matrix composites.

An example of creep behavior for a glass-ceramic matrix composite is given in Fig. 20. $\text{SiC}_f\text{-MLAS}$ composites (magnesium-lithium aluminosilicate + Nicalon NLM 202 SiC fibers) were studied by three-point bending under vacuum for two architectures 1-D unidirectional orientation and bi-directional orientation $(0-90^\circ)_6$, between 1173K and 1473K and at stresses from 25 to 400 MPa. For the 1-D architecture, only one domain is observed for the creep rate versus stress curves whereas two domains are observed for the 2D architecture. The initial loading affects the creep behavior if the stress exceeds the linearity stress limit. The shear stresses drive the matrix microcracking and thus the sequence of the creep stages.

When $\text{CMR} > 1$, case of composites with very creep resistant matrices (ceramic matrices), a load transfer from the fiber to the matrix occurs, the matrix stress increase can lead to microcracking. The creep behavior is dominated by matrix properties. An example of such behavior is given by Fig. 21. Jing *et al.* (2017) which shows the tensile creep strain versus time curves for a SiC_f (Nicalon)/ SiC composite (coated with an environmental barrier coating) at 1300°C in air. The creep resistance of the porous

matrix is low. The stress exponent deduced from these results is close to 1 and similar to the Nicalon fibers (Newtonian-type viscous flow), the creep of the composites being controlled by the fiber creep.

The same observations have been made by Morscher (2010) on a 2D-woven SiC/SiC composite at 1315°C under air, the dominant factors controlling creep and rupture behavior of the composite are creep and rupture of the fibers.

Furthermore, the creep behavior of long fiber reinforced composites depends not only on the creep properties of constituents but also on their textile structures. This creep behavior is also strongly influenced by the oxidation resistance of the constituents (fiber, interface and matrix), which limits the composite lifetime at high temperature in air. The oxidation embrittlement propagates through matrix microcracking. Several oxygen diffusion barriers can be used to protect the composites against oxidation: glass sealant, SiBC matrix, coatings (Jing *et al.*, 2017). The oxide-oxide composites with high oxidation resistance at elevated temperatures can be considered if creep resistant fibers are developed.

References

- Ashby, M.F., Frost, H.J., 1975. The kinetics of inelastic deformation above 0°K. In: Argon, A.S. (Ed.), *Constitutive Equations in Plasticity*. Cambridge: The MIT Press.
- Ashby, M.F., Verrall, R.A., 1973. Diffusion-accommodated flow and superplasticity. *Acta Metallurgica* 21, 149–163.
- Burton, B., 1977. *Diffusional Creep of Polycrystalline Materials in Diffusion and Defect Monograph Series* (No. 5). Trans Tech Publications.
- Cano-Crespo, R., Moshtaghioun, B.M., Gomez-Garcia, D., Dominguez-Rodriguez, A., Moreno, R., 2017. High temperature creep of carbon nanofiber-reinforced and graphene oxide-reinforced alumina composites sintered by spark plasma sintering. *Ceramics International* 43, 7136–7141.
- Cano-Crespo, R., Moshtaghioun, B.M., Gomez-Garcia, D., Moreno, R., Dominguez-Rodriguez, A., 2018. Graphene or carbon nanofiber-reinforced zirconia composites: Are they really worthwhile for structural applications? *Journal of The European Ceramic Society* 38, 3994–4002.
- Castaing, J., Monty, M., Dominguez-Rodriguez, A., 1989. Diffusion in binary oxides and its relation to high temperature creep. *Defect & Diffusion Forum* 64/65, 139–156.
- Castillo-Rodriguez, M., Munoz, A., Dominguez-Rodriguez, A., 2018. Creep study on alumina and alumina/SWCNT nanocomposites. *Journal of The European Ceramic Society* 38, 5497–5502.
- Chen, I.-W., Xue, L.A., 1990. Development of superplastic structural ceramics. *Journal of the American Ceramic Society* 73, 2585–2609.
- Chevalier, J., Olagnon, C., Fantozzi, G., Gros, H., 1997. Creep behavior of alumina, zirconia and zirconia-toughened alumina. *Journal of the European Ceramic Society* 17, 859–964.
- De Arellano-Lopez, A.R., Cumbra, F.L., Dominguez-Rodriguez, A., Goretti, K.C., Routbort, J.L., 1990. Compressive creep of SiC-whisker-reinforced Al_2O_3 . *Journal of the American Ceramic Society* 73, 1297–1300.
- Dominguez-Rodriguez, A., Bravo-Leon, A., Ye, J.D., Jimenez-Melendo, M., 1998c. Grain size and temperature dependence of the threshold stress for superplastic deformation in yttria-stabilized zirconia polycrystals. *Material Science and Engineering A* 247, 97–101.
- Dominguez-Rodriguez, A., Gomez-Garcia, D., Castillo-Rodriguez, M., Zapata, E., Chaim, R., 2010. Superplasticity in nanoceramics: Achievements and open questions. *International Journal of Materials Research* 101, 1215–1221.
- Dominguez-Rodriguez, A., Gomez-Garcia, D., Wakai, F., 2006. *Superplastic Ceramic Composites in Ceramic Matrix Composites: Microstructure, Properties, and Application*. Low, I.M. (Ed.), Cambridge: Woodhead Publishing Limited.
- Dominguez-Rodriguez, A., Gomez-Garcia, D., Wakai, F., 2013. High temperature plasticity in yttria stabilized tetragonal zirconia polycrystals (Y-TZP). *International Materials Reviews* 58, 399–417.
- Dominguez-Rodriguez, A., Guiberteau, F., Jimenez-Melendo, M., 1998a. Heterogeneous junction of YTZP by superplastic flow. *Journal Material Research* 13, 1631–1636.
- Dominguez-Rodriguez, A., Pique, E., Jimenez-Melendo, M., 1998b. Processing of multilayer of Y-TZP by superplastic flow. *Scripta Materialia* 39, 21–25.
- Duclos, R., 2004. Direct observation of grain rearrangement during superplastic creep of a fine-grained zirconia. *Journal of the European Ceramic Society* 24, 3103–3110.
- Fantozzi, G., Chevalier, J., Olagnon, C., Chermant, J.L., 2000. Creep of ceramic matrix composites. Chapter 7: Carbon/carbon, cement, and ceramic matrix composites. In: Warren, R. (Ed.), *Comprehensive Composite Materials*, vol. 4. Oxford: Elsevier.
- Frost, H.J., Ashby, M.F., 1982. *Deformation-Mechanism Maps*. Pergamon Press.
- Gopalan, H., Choskhi, A.H., 2018. Creep in alumina and carbon nanotube reinforced alumina composites. *Materials Science and Engineering A* 731, 561–568.
- Herring, C., 1950. Diffusional viscosity of a polycrystalline solid. *Journal of Applied Physics* 21, 437–444.
- Heuer, A.H., 2008. Oxygen and aluminum diffusion in Al_2O_3 : How much do we really understand? *Journal of the European Ceramic Society* 28, 1495–1507.
- Jimenez-Melendo, M., Dominguez-Rodriguez, A., Bravo-Leon, A., 1998. Superplastic flow of fine-grained yttria-stabilized zirconia polycrystals: Constitutive equation and deformation mechanisms. *Journal of the American Ceramic Society* 81, 2761–2776.
- Jimenez-Melendo, M., Dominguez-Rodriguez, A., Castaing, J., Marquez, R., 1986. Diffusion and creep: Application to deformation maps on NiO. *Scripta Metallurgica* 20, 739–742.
- Jimenez-Melendo, M., Dominguez-Rodriguez, A., 1998. Like-metal superplasticity of fine-grained Y_2O_3 -stabilized zirconia ceramics. *Philosophical Magazine A* 79, 1591–1608.
- Jing, X., Yang, X., Shi, D., Niu, H., 2017. Tensile creep behavior of three-dimensional four-step braided SiC/SiC composite at elevated temperature. *Ceramics International* 43, 6721–6729.
- Kondo, N., Suzuki, Y., Ohji, T., 1999. Superplastic sinter-forging of silicon nitride with anisotropic microstructure formation. *Journal of the American Ceramic Society* 82, 1067–1069.
- Krishnamachari, V., Notis, M.R., 1977. High temperature deformation of polycrystalline NiO and CoO. *Acta Metallurgica* 25, 1307–1313.
- Mazaheri, M., Mari, D., Hesabi, Z.R., Schaller, R., Fantozzi, G., 2011. Multi-walled carbon nanotube/nanostructures zirconia composites: Outstanding mechanical properties in a wide range of temperature. *Composite Science and Technology* 71, 939–945.
- Melendez-Martinez, J.J., Dominguez-Rodriguez, A., 2004. Creep of silicon nitride. *Progress in Materials Science* 49, 19–107.
- Melendez-Martinez, J.J., Gomez-Garcia, D., Dominguez-Rodriguez, A., 2004. A critical analysis and a recent improvement of the two-dimensional model for solution-precipitation creep: Application to silicon nitride ceramics. *Philosophical Magazine* 84, 2305–2316.
- Melendez-Martinez, J.J., Jimenez-Melendo, M., Dominguez-Rodriguez, A., Wötting, G., 2002. Creep behavior of two sintered silicon nitride ceramics. *Journal of the European Ceramic Society* 22, 2495–2499.
- Morscher, G., 2010. Tensile creep and rupture of 2D-woven SiC/SiC composites for high temperature applications. *Journal of the European Ceramic Society* 30, 2209–2221.
- Nabarro, F.R.N., 1948. Deformation of Crystals by the Motion of Single Ions. In *Report of a Conference on Strength of Solids*. London: The Physical Society, p. 75.
- Ohji, T., Nakahira, A., Hirano, T., Niihara, K., 1994. Tensile creep behavior of alumina/silicon carbide nanocomposite. *Journal of the American Ceramic Society* 77, 3259–3262.
- Philibert, J., 1982. Creep and diffusion. In: Petot-Ervas, G., Matzke, H.J., Monty, C. (Eds.), *Transport in Nonstoichiometric Compounds*. North-Holland.

- Poirier, J.P., 1976. Plasticité à haute température des solides cristallins. Paris: Eyrolles.
- Raj, R., Chyung, C.K., 1981. Solution-precipitation creep in glass ceramics. *Acta Metallurgica* 29, 159–166.
- Venkatachari, K.R., Raj, R., 1987. Enhancement of strength through sinter forging. *Journal of the American Ceramic Society* 70, 514–520.
- Wakai, F., S. Sakaguchi, S., Matsuno, Y., 1986. Superplasticity of yttria-stabilized tetragonal ZrO_2 polycrystals. *Advanced Ceramic Materials* 1, 259–263.
- Wakai, F., 1994. Step model of solution-precipitation creep. *Acta Materialia* 42, 1163–1172.
- Ye, J., Dominguez-Rodriguez, A., 1995. Joining of Y-TZP parts. *Scripta Metallurgica et Materialia* 33, 441–445.

Nonoxide Ceramics, Creep and Creep Rupture of: Silicon Nitrides and Silicon Carbides

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Processing and Creep of Silicon Nitride

Commercial Si_3N_4 is normally made by liquid-phase sintering at temperatures between 1800 and 2000 °C. Rare-earth oxides, Al_2O_3 , and MgO are used as sintering aids. These react with the silica normally present on the surface of the silicon nitride grains to produce an intergranular silicate phase that aids sintering. Hot isostatic pressing (HIPing) or high-pressure nitrogen, 1–8 MPa, is used to prevent decomposition of the Si_3N_4 at these temperatures. Microstructural studies on liquid-phase sintered Si_3N_4 show that a silicate phase wets almost all of the grains of Si_3N_4 . An amorphous silicate layer, about 1 nm thick, separates the grains of Si_3N_4 . The silicate phase in multigrain junctions partially devitrifies at 1200–1400 °C, forming a variety of crystalline phases. Because the sintering aid softens at a lower temperature than the Si_3N_4 grains, creep depends on the refractoriness and amount of the sintering aids. Compositions containing only rare-earth oxides are the most creep resistant. The addition of Al_2O_3 or alkaline earth oxides lowers both the sintering temperature and the creep resistance. However, these are necessary to improve toughness or wear resistance and so are used even though creep behavior is degraded.

Studies on commercial grades of silicon nitride indicate that the mechanisms of creep in tension and compression are different. In compression, the creep rate is a power function of the applied stress, with a stress exponent close to unity. The creep mechanism is believed to be due to solution-precipitation, in which Si_3N_4 dissolves into the silicate phase at areas on the grains where compressive stresses are high. The Si_3N_4 then diffuses through the silicate phase and reprecipitates on Si_3N_4 grains where stresses on the grains are very much lower or where the stresses are tensile in character. In tension, the creep rate depends exponentially on the applied stress (Figure 1), and is primarily a consequence of cavity formation and the flow of the silicate phase away from the cavitation site. For the same magnitude of applied stress and temperature, creep in tension can be hundreds of times greater than creep in compression. Meléndez-Martínez and Domínguez-Rodríguez (2004) and Moreira da Silva *et al.* (2010) indicate the importance of the nature of the second silicate phase, with the latter clearly endorsing the work of others relating to the realization of lower creep rates when the second (grain boundary) phase is a crystalline silicate rather than a vitreous one.

Processing and Creep of Silicon Carbide

Solid-state sintering of SiC through the use of sintering aids such as boron (or aluminum) and carbon produce grades of SiC with very high creep resistance. These elements modify grain boundary and surface energies, and enhance volume diffusion rates to favor densification of SiC. Carbon also converts SiO_2 to SiC to hinder the formation of glass at grain boundaries. In these materials, the SiC grains are in direct crystalline contact; there is no second phase at the grain boundaries. Hence, molecular processes that control solid-state sintering, i.e., grain boundary and bulk diffusion, also control the compressive creep of sintered SiC. Large-grain-size SiC (made by chemical vapor deposition) retards diffusional creep. Then, dislocation motion controls the creep process.

High-density silicon carbides can be made at lower temperatures by reaction bonding SiC grains with silicon. Because they are made by the infiltration of molten silicon into carbonized, partially bonded SiC, all grades of reaction-bonded SiC consist of an interconnected structure of silicon and SiC, in which the grains of SiC are directly bonded. Residual silicon fills the remaining structure. Reaction-bonded SiC is impermeable to oxygen and, hence, resistant to internal oxidation at high temperatures.

The mechanical behavior of reaction-bonded SiC depends on the amount of metallic silicon in the microstructure. With less than 10% of silicon by volume, substantial bonding occurs between the grains. Creep occurs by the deformation of the SiC, which is the same mechanism of creep as occurs in the solid-state sintered material. However, in the absence of sintering aids to enhance diffusion, creep rates of the reaction-bonded material can be less than that of the sintered material (Figure 2).

As the volume fraction of silicon is increased, less SiC is available to bond the SiC grains together. The decreased bonding between SiC grains permits these bonds to rupture as creep commences. The SiC grains slide over one another and the deformation of the silicon that accompanies the sliding process then controls creep. Because silicon deforms more readily than SiC, reaction-bonded SiC with large volume fractions of silicon is less creep resistant than sintered SiC (Figure 2). Like liquid-phase sintered Si_3N_4 , tensile creep of reaction-bonded SiC can be hundreds of times faster than compressive creep. Here too, the difference in behavior is a consequence of cavity formation during tensile creep.

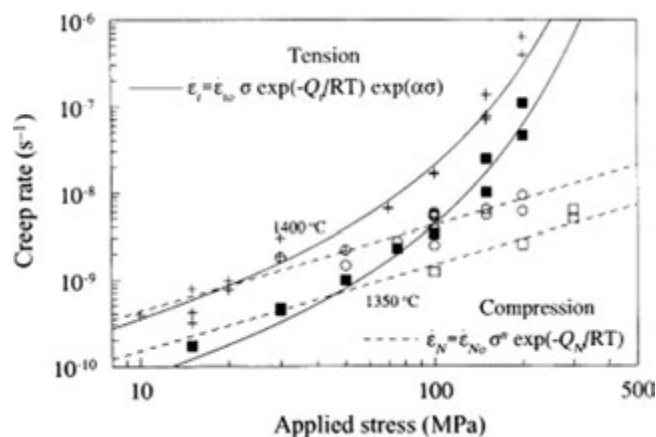


Figure 1 Tensile and compressive creep behavior of silicon nitride (data taken from Yoon *et al.*, 2000).

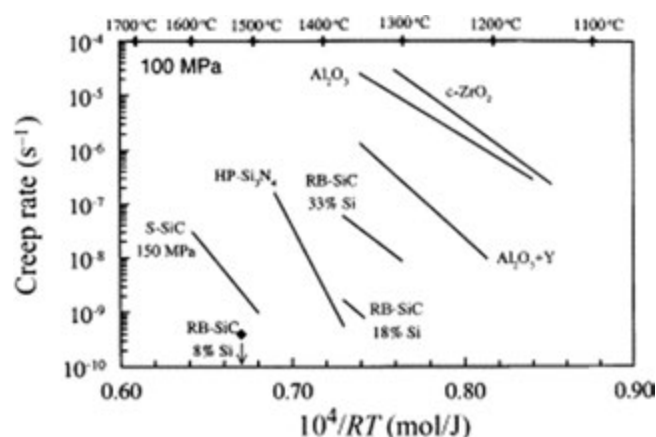


Figure 2 Comparison of secondary creep rates for covalent (SiC and Si₃N₄) and ionic (Al₂O₃ and ZrO₂) materials: HP, hot pressed; RB, reaction bonded; S, sintered (data for SiC and Si₃N₄ taken from Wiederhorn *et al.* (1999), for Al₂O₃ and ZrO₂ from French *et al.* (1994)).

Creep Rupture of Silicon Nitride and Silicon Carbide

Little is known of the mechanism of failure of Si₃N₄ and SiC at creep temperatures. The final stages of failure always involve the growth of a macroscopic crack; however, the defects that cause failure at room temperature and at high temperature are not necessarily the same. Experimental studies are still needed to clarify the mechanisms of failure. However, for all structural ceramics, a logarithmic plot of creep rate vs. failure time fits a straight line, or a set of straight lines depending on temperature. Therefore, higher creep resistance leads to an improved lifetime. This finding has determined the main direction of research and development to produce better high-temperature commercial grades of Si₃N₄.

For additional information on creep of Si₃N₄ and SiC, readers should consult the review articles by Davis and Carter (1988), Hynes and Doremus (1996), Luecke and Wiederhorn (1999), Wiederhorn *et al.* (1999), Meléndez-Martínez and Domínguez-Rodríguez (2004), and Ramírez-Rico and Martínez-Fernández (2014).

References

- Davis, R.F., Carter Jr., C.H., 1988. A review of creep in silicon nitride and silicon carbide. In: Saito, S. (Ed.), *Advanced Ceramics*. Oxford: Oxford University Press, pp. 95–125.
- French, J.D., Zhao, Jh., Harmer, M.P., Chan, H.M., Miller, G.A., 1994. Creep of duplex microstructures. *J. Am. Ceram. Soc.* 77 (11), 2857–2865.
- Hynes, A., Doremus, R., 1996. Theories of creep in ceramics. *Crit. Rev. Solid State* 21 (2), 129–187.
- Luecke, W.E., Wiederhorn, S.M., 1999. A new model for tensile creep of silicon nitride. *J. Am. Ceram. Soc.* 82 (10), 2769–2778.
- Meléndez-Martínez, J.J., Domínguez-Rodríguez, A., 2004. Creep of silicon nitride. *Prog. Mater. Sci.* 49 (1), 19–107.

- Moreira da Silva, C.R., Pereira Reis, D.A., dos Santos, C., 2010. Creep of heat treated silicon nitride with neodymium and yttrium oxides additions. *Materials Science and Engineering: A* 527 (26), 6893–6898.
- Ramírez-Rico, J., Martínez-Fernández, J., 2014. High-temperature mechanical behavior of hard ceramics. *Comprehensive Hard Materials* 2, 321–343.
- Wiederhorn, S.M., Hockey, B.J., French, J.D., 1999. Mechanisms of deformation of silicon nitride and silicon carbide at high temperatures. *J. Eur. Ceram. Soc.* 19, 2273–2284.
- Yoon, K.J., Wiederhorn, S.M., Luecke, W.E., 2000. Comparison of tensile and compressive creep behavior in silicon nitride. *J. Am. Ceram. Soc.* 83, 2017–2022.

Further Readings

- Koyanagi, T., Shimoda, K., Kondo, S., *et al.*, 2014. Irradiation creep of nano-powder sintered silicon carbide at low neutron fluences. *J. Nuclear Mater.* 455 (1–3), 73–80.
- Shankar, V., Was, G.S., 2011. Proton irradiation creep of beta-silicon carbide. *J. Nuclear Mater.* 418 (1–3), 198–206.

Dislocations in Ceramic Materials

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Introduction

Ceramics are based on compounds of high thermodynamic stability, with strong chemical bonds having dominant ionic or covalent character. This leads to specific characteristics, namely ceramics are generally brittle and very resistant to corrosion. Ceramic bodies are constituted of small crystalline grains (sizes of 1 μm or larger) mixed with glassy phases, in amounts which depend on the materials, the processing and the applications. At high temperatures, they are easy to deform because grain boundary sliding becomes an important mechanism; some grain deformation is required to accommodate local strains, which can be achieved, in particular, by dislocation motion. At intermediate temperatures, the fracture toughness of crystalline ceramic materials can be increased by dislocations generated at crack tips. These two examples show the importance of dislocations for mechanical applications of ceramics. The corresponding market is still small compared to that of electronic and optical ceramics, where dislocations have not attracted much attention in spite of their influence on the performance of devices. Following studies in metals and semiconductors, dislocations in ceramics have been the object of many investigations. In this article, we summarize the features which explain why they have motivated basic research efforts and we illustrate the acquired knowledge by selecting examples on a number of compounds (NiO, zirconia, Al_2O_3 , SiC, Si_3N_4 , superconductors).

General Features

Dislocations in ceramics share many aspects with those in metals and semiconductors in explaining plastic deformation properties. However, most ceramic materials have low-symmetry crystal structures with large unit cells, producing a number of consequences regarding dislocations, as reviewed by Bretheau *et al.* (1979) and Mitchell and Heuer (2004). The Burgers vectors b can be as large as 1.5–2 nm, with correspondingly several extra half-planes inserted for edge dislocations. This calls for a complexity in the dislocation of core configurations (hollow cores, broken bonds, nature of atoms, position of slip plane, etc.), as well as for jogs and kinks along the line which has to be addressed. The elastic energy of such dislocations can be very large; taking μb^2 (μ being the elastic shear modulus, between 100 GPa and 200 GPa) as the energy per repeat distance along the line, typical values are 22 eV for NiO, 100 eV for basal slip in $\alpha\text{-Al}_2\text{O}_3$, and 600 eV for $\text{Y}_3\text{Fe}_5\text{O}_{12}$ or $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (GGG), compared to less than 5 eV for f.c.c. metals ($1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$). An immediate consequence is that dislocation dissociation is expected in order to decrease the amount of elastic energy stored in deformed crystals. This dissociation has been observed in many cases, with stacking faults in the glide plane (Fig. 1), and also out of the glide plane (Fig. 2), generally when high temperatures and large point defect concentrations make diffusivity fast enough for the climb of partial dislocations. The dissociation by climb in spinels has been first reviewed by Bretheau *et al.* (1979). Later, Veyssi re (1988) suggested that climb dissociation, by considerably reducing the mobility of dislocations in MgAl_2O_4 , explains the anomaly in the variation of the CRSS (critical resolved shear stress) with temperature that he observed for single crystals deformed under hydrostatic pressure between 20 C and 1000 C. In various cases, no dissociation was observed, although many properties (very strong thermal activation of the flow stress, violation of Schmid's

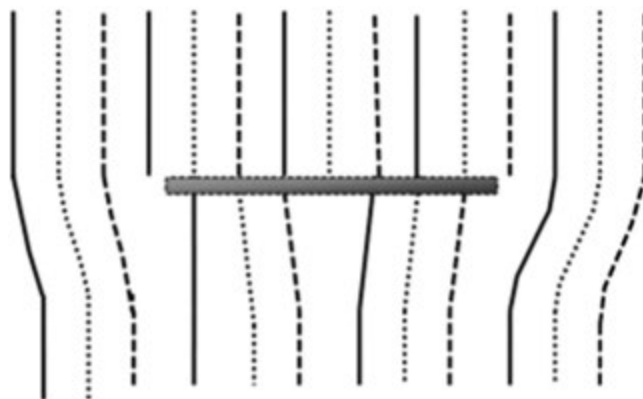


Fig. 1 Schematic representation on an edge dislocation dissociated by glide into three collinear partials: the stacking fault is indicated by the gray area. This corresponds to a $\langle 1 - 010 \rangle$ dislocation activated for prism plane slip in sapphire; an edge dislocation is formed by inserting three different layers. For the sake of simplicity, the distances between the partials have been reduced to unrealistic small values of the order of $1/3 \langle 1 - 010 \rangle$. Reproduced from Lagerlof, K.P.D., Mitchell, T.E., Heuer, A.H., *et al.*, 1984. Stacking fault in sapphire ($\alpha\text{-Al}_2\text{O}_3$). *Acta Metall.* 32, 97–105.

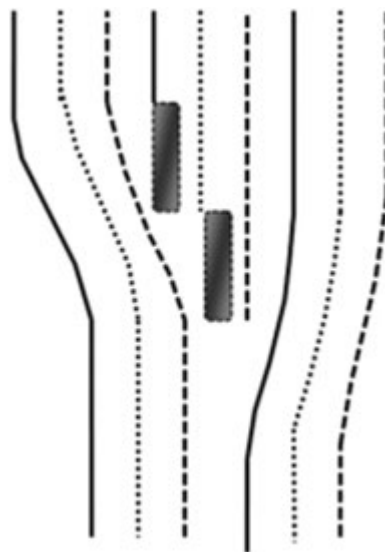


Fig. 2 The dislocation in Fig. 1 is dissociated by climb of the partials. Two stacking faults appear which are indicated by the gray areas. This figure corresponds to one of the three possible climb configurations for prism plane slip dislocations in sapphire. Reproduced from Lagerlof, K.P.D., Mitchell, T.E., Heuer, A.H., *et al.*, 1984. Stacking fault in sapphire (α -Al₂O₃). *Acta Metall.* 32, 97–105.

law, etc.) lead to the assumption of core extension below the detection limit of transmission electron microscopy (TEM). In the complex structures of ceramics, several possibilities may also exist as regards the atomic configuration of the glide plan. Depending on the location of the shear, the core structures of dislocations can be as different as the resultant glide properties (dissociation, Peierls stresses (see Section “Brittle Compounds”). Then although the same glide system is activated, different mechanisms can be operative, depending of the shear location which in turn may depend on stress and temperature (see, e.g., Duesbery and Joos, 1996).

Plastic deformation occurs when dislocations glide and multiply in given planes, the characteristics determining the easiest plane follow well-established rules, such as electrostatic interactions, for example, in cubic zirconia (Dominguez Rodriguez *et al.*, 1991) or low elastic energy, especially in extremely anisotropic crystals such as TeO₂ (Peter *et al.*, 1986). Among exceptions, one finds α -Al₂O₃ (see Section “Ductile Compounds”) where the observation of slip on the prism plane is unexpected in view of the energies required for dislocation glide (Heuer *et al.*, 1998). Finally, there may be crystallographic constraints on glide behavior, due to low symmetry, which make glide in the positive and negative slip direction (i.e., along $+b$ and $-b$) different; this is the situation for slip on the system (0001) $\langle 011-0 \rangle$ in α -Al₂O₃ (Castaing *et al.*, 1997).

The first cause for the brittleness of ceramics is that the number of slip systems is insufficient for the deformation of polycrystals, even for materials such as MgO, NiO, etc., which have a cubic crystal structure. When the temperature is increased, plastic anisotropy is decreased and atomic diffusion is effective, thus allowing plastic deformation. A second cause for the brittleness is the covalent character of the chemical bonds in most ceramic materials; this is associated with large Peierls stresses, or lattice friction, which impedes dislocation glide at low temperature. Even single-crystal specimens fracture before plastic deformation, a behavior which is common to semiconductors as well. Brittle/ductile transitions have been observed at 800°C for cubic zirconia single crystals (Marrow *et al.*, 1994) and around 1000°C for α -Al₂O₃ sapphire (Kim and Roberts, 1994). Fracture can be suppressed by the use of hydrostatic pressure, which induces plasticity in alumina well below 1000°C (Castaing *et al.*, 2000). Experiments of this kind have promoted the development of new models to explain the thermal activation of dislocation glide based on the formation of kink pairs and kink motion with large lattice friction (Mitchell and Heuer, 2004; Castillo Rodriguez *et al.*, 2007). In the following, we give examples to illustrate these general features about dislocations in ceramic materials.

Cubic Crystals

Ductile Compounds

There have been many investigations of dislocations and plasticity in ionic crystals such as LiF, NaCl, MgO, CaF₂, etc.; these materials have been available as single crystals for decades and they show extensive ductility, as reviewed by Castaing (1981). Slip occurs along the $\{11-0\} \langle 110 \rangle$ system which can be activated in compression along $\langle 001 \rangle$. It has been activated at temperatures as low as 4.2 K for NaCl type oxides, for example, CoO (Dominguez Rodriguez, *et al.*, 1988) and NiO (Jimenez Melendo *et al.*, 1992), with CRSS around 100 MPa at 4.2K. This unusual ductility for ceramic materials can be ascribed with the highly ionic chemical bonds in these compounds, with the absence of strong obstacles to dislocation glide. When the compression axis is parallel to $\langle 111 \rangle$, glide on $\{11-0\} \langle 110 \rangle$ is prevented from being activated, and dislocations can glide in the

secondary slip system $\{0\ 0\ 1\} \langle 110 \rangle$. The plastic anisotropy can be very large, with ratios of the CRSS for $\{0\ 0\ 1\}$ slip to that for $\{11\ 0\}$ slip reaching values as large as fifty in MgO around 300°C (Foitzik *et al.*, 1989). This is consistent with the fact that dislocations in compounds with the NaCl structure are dissociated on $\{11\ 0\}$ but not on $\{0\ 0\ 1\}$ planes, with the exception of PbS (Foitzik *et al.*, 1989). However, there is no clear observation of such dissociation using weak beam TEM (with its limit of detection around 2 nm) (Foitzik *et al.*, 1989). Dislocations have been observed by high-resolution TEM in several oxides, including SrTiO₃, MgO, CoO, and NiO, where extension of the cores was detected (Takeuchi *et al.*, 1989).

Atomistic simulations of dislocation properties have been performed showing results in agreement with experimental facts (Castaing, 1981). No dislocation dissociation has been found under normal conditions. Core energies and Peierls stresses have been calculated for several materials, with Peierls stress values around 60–70 MPa for MgO. Atomistic simulations have also enabled the elucidation of mechanisms such as diffusion along the dislocation core in MgO (Rabier and Puls, 1985) and dislocation-point defect interactions in NiO (Rabier *et al.*, 1990). Nickel vacancies, which are associated with nonstoichiometry in NiO, could be present in higher concentrations on edge dislocations and lead to a very defective core, with consequences to their glide mobility. Recently, TEM techniques are now available to probe non-stoichiometry on dislocation cores (Jia *et al.*, 2005), but such measurements have not been reported for NiO.

Brittle Compounds

Several oxides (e.g., Cu₂O, UO₂, MgAl₂O₄, Y₂O₃) are brittle at low temperatures but show extensive plasticity at high temperatures (Bretheau *et al.*, 1979); many of them have non compact cubic structures and are largely covalently bonded, which is at the origin of their brittleness. Yttria stabilized cubic zirconia (ZrO₂ with more than 9 mol% Y₂O₃) is another example of a ceramic material which has been studied in detail; although it is brittle below 800°C in bending (Marrow *et al.*, 1994), single crystals have been deformed in compression down to 500°C at normal pressures (0.1 MPa) and down to 250°C under 0.4 GPa hydrostatic pressure, with flow stresses around 700 MPa and 3000 MPa, respectively. The work on dislocations and plasticity in zirconia has been reviewed by Messerschmidt *et al.* (1997, 1998). Cubic zirconia has the CaF₂ crystal structure and deforms by glide of $1/2 \langle 110 \rangle$ dislocations with $\{0\ 0\ 1\}$ as the primary glide plane; $\{1\ 1\ 1\}$ and $\{1\ 1\ 0\}$ planes can also be activated, the plastic anisotropy disappearing above 1400°C. This behavior is similar to that of CaF₂ single crystals, for which the CRSS decreases in the order $\{1\ 1\ 0\} > \{1\ 1\ 1\} > \{1\ 0\ 0\}$, Schmid's law for these slip planes being obeyed in all cases, as revealed by tests along five compression axes (Munoz *et al.*, 1994). The large amount of point defects in zirconia, due to yttria, does not affect the choice of the slip plane. However, yttria hardens zirconia; at 1400°C, the flow stress of single crystals increases from 200 MPa to 350 MPa when the concentration of Y₂O₃ increases from 9 mol% to 22 mol% (Messerschmidt *et al.*, 1998). At $T > 1400^\circ\text{C}$, although solute drag and recovery play important role, yttria continues to harden zirconia crystals (Gomez Garcia *et al.*, 1997). Detailed examinations of the dislocation structure by TEM have permitted elucidation of some of the mechanisms controlling the rate of deformation. Dislocation dissociation has not been found; the violation of Schmid's law for $\{0\ 0\ 1\}$ slip, around 400°C under hydrostatic pressure, is probably due to a core extension smaller than the limit of detection of the experimental techniques.

The case of partially stabilized zirconia (ZrO₂ with less than 8 mol% Y₂O₃) has also been studied in detail and reviewed by Messerschmidt *et al.* (1997). For 3–6 mol% Y₂O₃, tetragonal precipitates (*t*-ZrO₂) appear, with morphologies at 1600°C that depend on the annealing time (Martinez Fernandez *et al.*, 1995). These precipitates harden single crystals as they develop with time, the flow stress increasing above 300 MPa. The hardening has been explained by the classical models, namely dislocations cutting the precipitates where they must glide as pairs of $1/2 \langle 110 \rangle$ partials separated by a stacking fault or creation of Orowan loops around precipitates, the balance between the two mechanisms depending on the sizes and spacings of the precipitates.

Cubic perovskite structure materials are of great interest because of their presence in the earth lower mantle and because of their numerous uses in electronic ceramics; they can be plastically deformed at high temperatures. It was surprising to discover that SrTiO₃ could be deformed down to 43K at normal pressure with a gap in ductility between 1000K and 1200–1400K (Gumbsch *et al.*, 2001; Brunner, 2006). This behavior has been ascribed to modifications of the dislocation core structure with the temperature. This has been confirmed recently by atomistic calculations (Hirel *et al.*, 2016) showing a change in the core structure from glissile glide-dissociated into a sessile, climb-dissociated configuration at high temperature.

The garnet structure can be used to exemplify the consequences of large strain energies of dislocations on the plastic behavior of ceramics. This structure can be regarded as a b.c.c. one with a large unit cell parameter, usually $a_0 > 1.2$ nm, with a noncompact distorted oxygen sublattice (Rabier *et al.*, 1976). As a consequence, the smallest Burgers vector $1/2 \langle 111 \rangle$ has a magnitude larger than 1.0 nm. Although these Burgers vector can dissociate according to the reaction: $1/2 \langle 111 \rangle \rightarrow 1/4 \langle 111 \rangle + 1/4 \langle 111 \rangle$, the strain energy of a dissociated configuration is still very high as compared to metals.

High-temperature deformation of Gd₃Ga₅O₁₂ (GGG) ($T_M = 1780^\circ\text{C}$, $a_0 = 1.237$ nm, $|b| = 1.07$ nm) in the temperature range 1300–1500°C ($0.79\text{--}0.92T_M$) has been investigated by creep as well as at constant strain rate in air as a function of compression xxqaxis $\langle 100 \rangle$ and $\langle 110 \rangle$. The observed glide planes are $\{110\}$, $\{112\}$, $\{123\}$ similar to those observed in b.c.c. metals (Garem *et al.*, 1982).

The activated glide systems depend on the orientation of compression axis and the slip system with the highest Schmid factor is not always activated. This observed violation of the Schmid law is analogous to what is found in b.c.c. metals at low temperature (see Dislocations in Metals and Metallic Alloys) and as in b.c.c. metals, long straight screw segments were found in GGG belonging to Frank–Read sources in samples deformed at a constant strain rate (Rabier and Garem, 1984).

In a 'low-temperature deformation b.c.c. metal mechanism', the screw dislocations located along a threefold axis are weakly dissociated into a nonplanar sessile configuration. Dislocation glide occurs if the applied force is sufficient to transform this sessile configuration into a glissile planar one by recombination of the partials. The energy needed to recombine the dislocation core is of the order of μb^3 . For b.c.c. metals, there is a transition temperature between the sessile core screw dislocations controlling deformation and a high-temperature regime where they do not play any role. The transition temperature is a function of μb^3 (Kubin, 1976) and it has been shown that the sessile core structure of screw dislocations controls the plastic properties for values of the ratio $KT/\mu b^3$ lower than 5×10^{-3} .

At the melting temperature the large values of the dislocation strain energies in GGG yield for the ratio $kT/\mu b^3$ respectively 2.7×10^{-4} ($b = 1/2 \langle 111 \rangle$) and 2×10^{-3} ($b = 14 \langle 111 \rangle$) which are lower than the critical value for b.c.c. metals. This shows that a dissociation recombination mechanism is expected to control plastic properties of GGG up to the melting point. The threefold dissociation mechanisms, usually observed for metals only at low temperature, are to be considered also at high temperature for materials with large Burgers vectors although such mechanisms can be hindered by diffusion processes.

Low Symmetry Crystals

α -Alumina

Sapphire, which is the single-crystalline form of α -Al₂O₃, as well as alumina ceramics have wide-ranging applications. Its crystal structure can be described using a rhombohedral unit cell with threefold symmetry; the description using a hexagonal unit cell is convenient, but can induce incorrect ideas on atomistic mechanisms (Heuer *et al.*, 1998). Deformation of alumina single crystals has received considerable interest because it is a model material for many low-symmetry minerals. Sapphire is brittle in bending below 1030–1100°C (Kim and Roberts, 1994). It can be deformed in compression by $(0\ 0\ 0\ 1) \langle 2 - 110 \rangle$ basal slip above 890°C at normal pressure, with adequate crystalline orientations to avoid rhombohedral twinning; twinning can be activated at 900–1100°C under shear stresses between 10 MPa and 60 MPa, dislocations being strong obstacles to twin extension (Castaing *et al.*, 2002). The shortest Burgers vector is $1/3 \langle 2 - 110 \rangle$ ($b = 0.475$ nm). The secondary system is $\{12 - 10\} \langle 1 - 010 \rangle$ prism plane slip, which is unexpected because its Burgers vector ($b = 0.822$ nm) is longer than three other repeat distances in the structure (Heuer *et al.*, 1998), and glide on prism planes can, in principle, occur along the same direction as in the basal plane. At 1400°C or above, Cadoz *et al.* (1982) found by TEM that $\langle 1 - 010 \rangle$ dislocations gliding in $\{12 - 10\}$ decompose into two $1/3 \langle 2 - 110 \rangle$ basal dislocations, especially for large deformations (shear stresses above 100 MPa). At small strains, the microstructure consists of prism plane slip dislocations which are dissociated into three collinear partials with Burgers vectors of the type $1/3 \langle 1 - 010 \rangle$ (Fig. 2). This dissociation corresponds to a decrease in energy equivalent to that resulting from the decomposition into two basal slip dislocations (Lagerlof *et al.*, 1984). For specimens deformed at 1400°C, climb dissociation has been observed by TEM both for $1/3 \langle 2 - 110 \rangle$ basal slip dislocations (into $1/3 \langle 1 - 010 \rangle$ and $13 \langle 1 - 100 \rangle$) and for $\langle 1 - 010 \rangle$ prism plane slip dislocations (Fig. 2), with distances between partials of 8 nm and 30 nm, respectively (Lagerlof *et al.*, 1984). This corresponds to dislocation configurations with energies lower than those for glide dissociation (Fig. 1), and is facilitated by high-temperature diffusion. In both cases, the stacking fault planes are distinct from the $(0\ 0\ 0\ 1)$ basal plane. This agrees with the fact that the stacking fault energies in sapphire are low on the prism planes; values between $0.1\ \text{J m}^{-2}$ and $0.2\ \text{J m}^{-2}$ are deduced from TEM in agreement with computed values (Jhon *et al.*, 2005). On the basal plane, the stacking fault energy is only available from computations that give high values ($\approx 2\ \text{J m}^{-2}$) (Heuer *et al.*, 1998). Although climb dissociation has been largely observed in alumina, no anomaly has been found for the variations of the CRSS with temperature, either for basal slip, or for prism plane slip, contrary to the situation for other materials (Veyssi re, 1988).

Below 1000°C alumina ceramics and single crystals have been plastically deformed under 1.5 GPa hydrostatic pressures (Lagerlof *et al.*, 1994; Castaing *et al.*, 2000); CRSS values as high as 3000 MPa were obtained for prism plane slip at 200°C. For basal slip orientations, extensive twinning was obtained below 800°C, including basal twinning which had not been observed previously after mechanical tests (Castaing *et al.*, 2004). This discovery stimulated a new understanding of basal slip and twinning based on the glide of $1/3 \langle 101 - 0 \rangle$ partial dislocations on an electrically neutral plane within the puckered Al ion array. This leaves half of the Al ions on the surfaces of the two half-crystals gliding on each other, rather than all the Al ions on one half, as suggested by the misleading use of the hexagonal unit cell (Heuer *et al.*, 1998). This is particularly true for the basal twinning mechanism, where complicated models involving several types of dislocations have been suggested in the past by many authors. The new model merely requires the glide of $1/3[101 - 0]$ partials on every other $(0\ 0\ 0\ 1)$ basal plane. This, in turn, can be accomplished by a Frank–Read type source involving only partials which jump from one plane to the next available plane after the emission of one loop (Heuer *et al.*, 1998). Indeed, such sources have been observed by TEM (Fig. 3) supporting the new understanding for basal slip and twinning (He *et al.*, 2002).

At low temperature, slip dislocations on the prism plane have been found to dissociate by glide (Fig. 1). The fact that prism plane slip becomes easier than basal slip below 600°C, under hydrostatic pressure, and the strong thermal activation of dislocation glide, have suggested that the cores of the rate controlling dislocations are extended. However, weak-beam TEM of basal slip dislocations never revealed any core extension (Lagerlof *et al.*, 1994). High-resolution TEM on basal slip dislocations has confirmed the already observed climb dissociation with a distance of 4.7 nm between the two partials (Nakamura *et al.*, 2002); no perfect dislocation or glide dissociation was found. A molecular-dynamic simulation of a basal slip dislocation does not give any



Fig. 3 Weak-beam TEM of a prism plane slip dislocation in sapphire dissociated into three partials lying in a basal twin boundary. This feature is a source for basal twinning. Sapphire was deformed at 700°C under a stress of 1095 MPa. Reproduced from He, A., Lagerlof, K.P.D., Castaing, J., Heuer, A.H., 2002. Considerations of the double cross slip mechanism for basal and rhombohedral twinning in sapphire. *Philos. Mag. A* 82, 2855–2867, with permission from Taylor & Francis Ltd., <http://www.tandf.co.uk/journals>.

indication of glide dissociation (Bodur *et al.*, 2005). The Peierls mechanism has also been invoked to explain the different dislocation glide mobilities for the two kinds of slip, and to calculate curves of CRSS versus temperature which are consistent with experimental data (Mitchell and Heuer, 2004). Because of difficulties with fitting parameters, more elaborate models (Mitchell *et al.*, 2003) have been used to achieve satisfactory descriptions of the experimental data (Castillo Rodriguez *et al.*, 2007).

Dislocation motion has been found to be enhanced by the presence of hydrogen, inducing a large softening for the deformation of sapphire and alumina ceramics below 1000°C; this is analogous to the well-known hydrolytic weakening of quartz (Castaing *et al.*, 2000). The influence of impurities (Mg, Ti, Cr) has also been studied (Mitchell and Heuer, 2004); for rubies with various Cr concentrations, basal slip is still dominated by the Peierls mechanism (Castillo Rodriguez *et al.*, 2007).

Silicon Carbide

Silicon carbide has two different types of applications. First, its excellent properties above 1000°C make it largely used as a structural ceramic. Second, SiC is a semiconductor with a bandgap of 2.4 eV or more, which can be included in high-power devices for use at temperatures much higher than conventional semiconductors. Silicon carbide is the only compound that forms in the Si–C phase diagram; it exists in more than 200 polytypes or stacking arrangements along the direction of close packing. There is one cubic polytype named β -SiC, corresponding to the stacking of three different layers, like other compounds with the zinc blende structure; for this reason, it is also named 3C-SiC. The noncubic polytypes are named collectively α -SiC. They have hexagonal (H) or rhombohedral (R) symmetry and are also named using the number of stacked layers along the close packing direction (Pirouz and Yang, 1993; Hong *et al.*, 2000). The most common polytypes are 4H-SiC and 6H-SiC which have become recently available as single crystals. In addition to the mechanical properties, the polytypic transformations are directly influenced by dislocations. The great variety of SiC ceramic materials explains the large number of investigations; we focus here on single-crystal studies.

Fujita *et al.* (1987) deformed 6H-SiC single crystals oriented for basal slip. The CRSS decreased from 70 MPa at 1100°C to about 10 MPa at 1600–1800°C; these stresses are remarkably small for a compound which is a major component of SiC structural ceramics. TEM examination of the deformed specimens revealed large numbers of $1/3 \langle 2 - 110 \rangle$ dislocations dissociated into $1/3 \langle 1 - 010 \rangle$ and $1/3 \langle 1 - 100 \rangle$ partials with large separations, indicating a low-energy stacking fault (2.5 mJ m^{-2}) (Maeda *et al.*, 1988). This opens the possibility for the glide of single partial dislocations, with an applied shear stress of 14 MPa providing enough mechanical work to generate stacking faults. Recently, Samant and Pirouz (1998) performed similar compression-deformation experiments on 4H-SiC and 6H-SiC between 550°C and 1300°C. The CRSS increases sharply below 700°C where 6H-SiC becomes stronger than 4H-SiC (the CRSSs are 450 MPa and 235 MPa respectively, at 550°C); below 1100°C, the deformation of both polytypes takes place by nucleation and glide of partial dislocations alone. However, there is no clear explanation for the difference of strengths between 4H-SiC and 6H-SiC. Hong *et al.* (2000) found that the dissociation widths of dislocations introduced at 1300°C are quite different in the two polytypes, giving stacking fault energies of 2.9 mJ m^{-2} for 6H-SiC, in agreement with Maeda *et al.* (1988), and 14.7 mJ m^{-2} for 4H-SiC; the difference can be explained on the basis of the crystal structures. Similar types of observations were made on Al doped α -SiC deformed at 1950°C; dissociated dislocations were found

on the basal planes of 4H-SiC grains and a stacking fault energy of 14 mJ m^{-2} was deduced, in agreement with the value found for single crystals (Duval-Riviere and Vicens, 1994).

The existence of numerous polytypes and the easy movement of single partial dislocations, due to the low stacking-fault energies, suggest that the two phenomena are linked and that the polytypic transformation can be a consequence of partial dislocation glide, as suggested by the TEM observations of deformed α -SiC ceramics by Duval-Riviere and Vicens (1994). Pirouz and Yang (1993) describe the transformation mechanism whereby a partial dislocation changes the stacking sequence. If a second partial glides on a basal plane parallel to the first one, this can create a lamella of a new polytype. The partial dislocations can be created by a Frank–Read source, with the modification that after emitting the first partial, a second identical one cannot glide on the faulted plane; instead it has to cross-slip to the next available plane. After transformation of the crystal from one polytype to another, a residual dislocation is left on the cross-slip plane, that is, parallel to the $[0\ 0\ 0\ 1]$ axis in α -SiC. Pirouz and Yang (1993) demonstrated that this mechanism was operative by deforming a properly oriented 6H-SiC crystal, which was transformed into the 3C phase by compression at 1100°C and 1400°C . Similar ideas have been used to design mechanisms for twinning in various crystals, in particular for basal twinning in sapphire (see Section “Ductile Compounds”). The properties of partial dislocation Frank–Read sources are also taken into account to explain the brittle to ductile transition in SiC. Indeed, brittleness is associated with the occurrence of deformation microstructures built with numerous extended stacking faults (Pirouz *et al.*, 2003). It is postulated that, at low temperature, the ‘trailing’ partial eliminating the stacking faults associated to the dissociation of a perfect $1/3\ \langle 2 - 110 \rangle$ dislocations cannot be nucleated. Since the Frank–Read source cannot emit a second partial in the same plane, the source shuts, hence the brittle behavior.

Different types of dislocations gliding in the $(0\ 0\ 0\ 1)$ plane (or $(1\ 1\ 1)$ plane for 3C material) have been recognized in relation to their core structure. The extra half-planes can end at the dislocation cores on carbon or a silicon rows. In addition, as in cubic semiconductors, the shearing can take place between widely separated planes (shuffle set) or between closest planes (glide set). The dislocations in those planes can be either perfect, having an expected low Peierls potential (the shuffle set) or dissociated, having an expected high Peierls potential (the glide set). Experimentally the signature of the glide set is the observation of dissociated dislocations although no clear evidence has been put forward up to now of the actual core location.

In a given set, Si and C core have been distinguished using the LACBED TEM technique. It has been shown that the partial dislocations in 4H and 6H which yield to the formation of large extended stacking faults below the brittle to ductile transition temperature are usually Si ones which appear as the partials with the highest velocity (Pirouz *et al.*, 2001). The results of these observations are in disagreement with *ab initio* computations where the C partial is shown to have the highest velocity.

Applying a confining pressure, higher stresses than those usually investigated in 4H-SiC can be reached (Demenet *et al.*, 2005). The deformation microstructures are built not only with dissociated dislocations but also with perfect dislocations which are expected to be nucleated in the shuffle set. This has been also observed after nano indentation tests at room temperature (Texier *et al.*, 2013). Other experiments report that other type of perfect dislocations can be found below the BDT in the prismatic or first order pyramidal plane which suggests that dislocation nucleation can occur in those planes before cross slipping in the basal plane (Mussi *et al.*, 2006; Mussi *et al.*, 2007). More experiments are needed to understand the relation between dislocation nucleation mechanism, the core structure of dislocations and the brittle-to-ductile transition. Note also that in SiC 4H of electronic quality, the effect of electronic doping has been evidenced on dislocation mobilities, an effect similar to that obtained in elemental semiconductors (Demenet *et al.*, 2011).

Nitrides

There has been considerable work done on nitrides. Here, we consider a couple of them which are being increasingly used for various types of applications. Silicon nitride Si_3N_4 ceramics are well suited for structural applications such as heat exchangers or gas turbines; they are used commercially for car turbochargers. Aluminum nitride, AlN, has very good heat conduction, which is excellent for electronic substrates. The system AlN-GaN-InN provides unique possibilities for optoelectronic devices with band gaps between 2 eV and 6 eV; blue and green light emitting diodes (LEDs) are commercially available and are based on GaN containing various amounts of In or Al (Ponce and Bour, 1997). They are generally grown by chemical vapor deposition of epitaxial layers on $(0\ 0\ 0\ 1)$ sapphire substrates. Very surprisingly, the active layers of these LEDs contain dislocations in densities as high as 10^{10} cm^{-2} , which is more than six orders of magnitude greater than in other conventional semiconductor devices. The light efficiency of these GaN-based LEDs is remarkably insensitive to the presence of dislocations (Ponce and Bour, 1997).

There have been only a few attempts to introduce dislocations in AlN by plastic deformation. Audurier *et al.* (1998) deformed AlN ceramics by compression between room temperature and 800°C under 1 GPa hydrostatic pressure; the applied uniaxial stresses reached almost 4000 MPa. TEM observations have shown that both $(0\ 0\ 0\ 1)\ \langle 2 - 110 \rangle$ basal slip and $\{1 - 010\}\ \langle 12 - 10 \rangle$ prism plane slip have been activated. AlN has the hexagonal wurtzite structure; $1/3\ \langle 12 - 10 \rangle$, which is the shortest repeat distance (0.31 nm), is the Burgers vector. In the basal plane only screw dislocations, with the three $1/3\ \langle 2 - 110 \rangle$ Burgers vectors, are observed by TEM. This suggests that the Peierls stress on these dislocations is large. The configurations in the prism plane slip are more diverse. There are many reactions and cross-slip events, which are expected for multiple slip in a polycrystal. Prism plane slip could be easier than basal slip. Dislocation dissociation has not been observed by weak-beam TEM. These preliminary observations on AlN do not coincide with those made on homoepitaxial GaN layers by Ponce *et al.* (1996); they found three Burgers vectors, namely $1/3\ \langle 12 - 10 \rangle$, $1/3\ \langle 1 - 1 - 23 \rangle$, and $[0\ 0\ 0\ 1]$, and considerable evidence for dissociation. The mechanism of dislocation multiplication during epitaxial growth has not yet been elucidated.

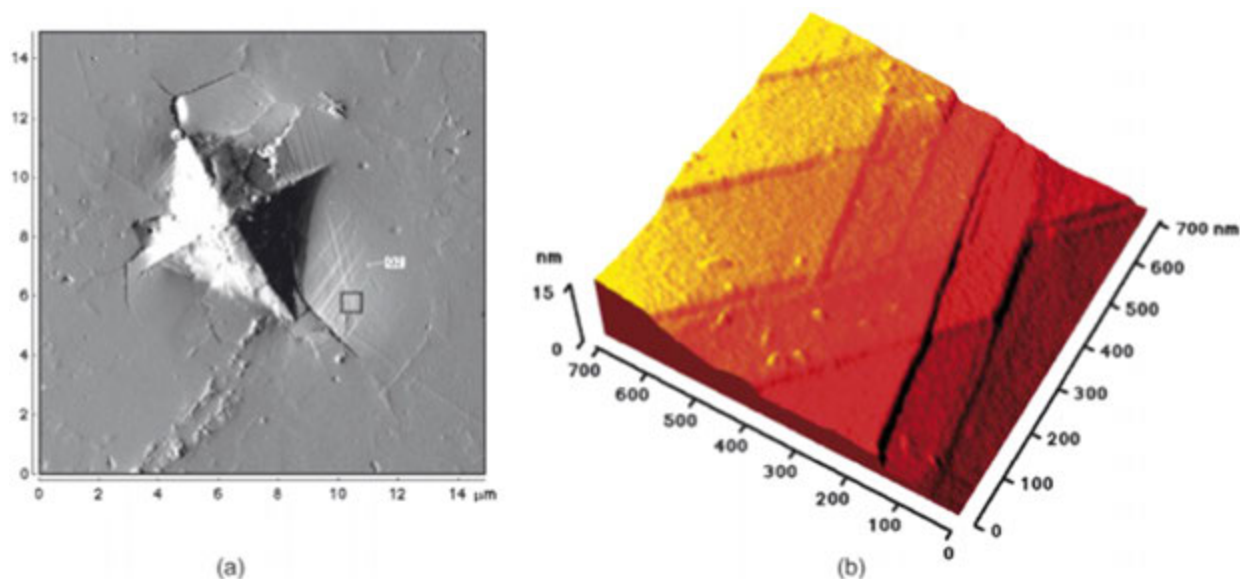


Fig. 4 AFM images of glide lines in β - Si_3N_4 indented at room temperature. (a) General view, (b) enlargement of the surrounded area in (a). Step heights correspond to the output of a few dislocations with $[0\ 0\ 0\ 1]$ Burgers vectors. Reproduced from Milhet, X., Girard, J.C., Demenet, J.L., Rabier, J., 2001. Characterization of room temperature plastic deformation of β - Si_3N_4 by atomic force microscopy and transmission electron microscopy. *Philos. Mag. A* 81, 623–629, reprinted by permission of Taylor & Francis Ltd., <http://www.informaworld.com>.

Silicon nitride ceramics are generally mixtures of Si_3N_4 and glasses which result from the oxides (MgO , Al_2O_3 , etc.) added during processing to promote densification. The softening of the glass phase has probably prevented the observation of dislocations after high-temperature deformation of silicon nitride. Milhet *et al.* (1999) have used compression tests at 850°C under 1 GPa hydrostatic pressure to induce dislocations in Si_3N_4 grains of sintered ceramics. The specimen failed at a uniaxial stress of 2850 MPa. Thin foils for TEM were prepared from regions near the cracks generated by the mechanical test. The dislocations in the microstructure had $[0\ 0\ 0\ 1]$ Burgers vectors. They were generally screw in character and in the form of elongated loops, from which it was concluded that the mobility of screws were smaller than that of edges due to differences in the Peierls stress. The two $\{1\ 010\}$ and $\{12\ 10\}$ planes have been suggested as glide planes. Extension of the dislocation core in the six possible slip planes has been suspected. Dislocations have been observed in grains of the high-temperature β - Si_3N_4 phase, possibly because β - Si_3N_4 is softer than α - Si_3N_4 or possibly because β -type grains are bigger than α -type grains and therefore easier to find for TEM examination. The crystal structure of β - Si_3N_4 can be represented using hexagonal unit cells with dimensions $a = 0.77\text{ nm}$ and $c = 0.29\text{ nm}$, $[0\ 0\ 0\ 1]$ being indeed the shortest repeat distance. The unit cell of the α -phase is also hexagonal, with c being twice that for the β -phase: c dislocations have consequently higher strain energies in the α -phase than in the β phase.

Although these compounds were considered to be brittle at room temperature, dislocations motion has been found to occur during indentation tests conducted at room temperature on β - Si_3N_4 . This was probed by using atomic force microscopy (AFM) a technique able to evidence slip lines with an excellent resolution (see Fig. 4). Such images were used to characterize glide lines corresponding to the emergence of a few dislocations as well as cross-slip (Milhet *et al.*, 2001).

From these various studies, it is clear that dislocations in silicon nitrides can contribute to plasticity more than what is usually thought. There is still a lot to learn about dislocations in these compounds.

Superconductors

The discovery in 1986 of superconductors with high critical transition temperatures promoted intense research activity on these compounds and great expectations for applications. However, many limitations have appeared, mostly because of the chemical instability and the brittleness of the compounds. The best-known of those so-called high- T_c superconductors is certainly $\text{YBa}_2\text{Cu}_3\text{O}_7$ whose high temperature phase $\text{YBa}_2\text{Cu}_3\text{O}_6$ is not superconducting so that an oxygenation step is required after high-temperature annealing. Furthermore, $\text{YBa}_2\text{Cu}_3\text{O}_7$ is unstable as compared to $\text{YBa}_2\text{Cu}_4\text{O}_8$, so that additional CuO atomic layers are easily nucleated in the material. The challenge is to reach critical currents in superconductors that are as high as possible. Dislocations are interesting defects for high- T_c materials. Indeed, differently from usual “low- T_c ” superconductors, high- T_c materials possess low correlation lengths, which are of the order of the core extension length of dislocations. Then single dislocations are potential pinning centers for vortices. The microstructures of those materials are usually complex, built with a variety of extended defects (Fig. 5) but can be modified by various thermomechanical treatments. In this context, Sandiumenge *et al.* (2000) have reviewed the different ways to optimize flux pinning in textured $\text{YBa}_2\text{Cu}_3\text{O}_7$ or similar compounds.

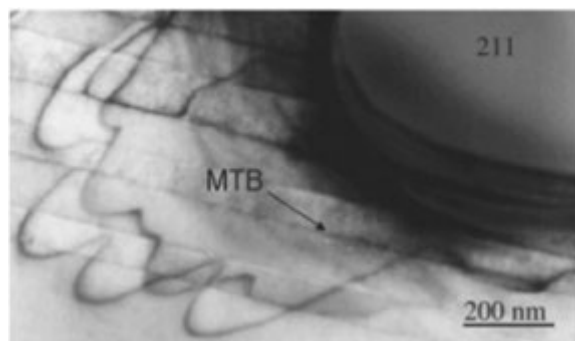


Fig. 5 TEM image of the as-grown microstructure of a melt textured grown $\text{YBa}_2\text{Cu}_3\text{O}_7$: mirror twin boundaries (MTB), dislocations interacting with MTB, second phase inclusion 211 $\text{Y}_2\text{Ba}_1\text{Cu}_1\text{O}_5$. Picture: courtesy of Plain J.

Rabier *et al.* (1993) were able to deform polycrystals under hydrostatic pressure in the superconducting phase; dislocations were usually not dissociated. If, in addition to room-temperature deformation, the specimens are subjected to a thermal treatment (900°C for 24 h, cooled and maintained at 450°C for 4 h, in air), the dislocation structure is completely changed, with very large dissociation widths associated to additional CuO layer, that is, a “nonstoichiometric dissociation”. This shows that dislocations act as nuclei for CuO precipitation. Conventional high-temperature deformation in the ductile regime tends to degrade the superconducting performance, with a decrease in critical current, even after annealing in oxygen to restore the superconducting phase (Vilalta *et al.*, 1997). Other processes were studied to create dislocations in the superconducting phase in order to avoid the oxygenation step and preventing crack nucleation: cold isostatic pressing (CIP) and annealing under high oxygen pressure (HOP). CIP yields to dislocation multiplication at elastic discontinuities in the solid resulting in increases in the critical current (Martinez *et al.*, 1999). Using HOP (Plain *et al.*, 2002a), it is possible to monitor the dislocation density and improve the critical current densities (Plain *et al.*, 2002b). This dislocation engineering process relies upon the instability of the material versus $\text{YBa}_2\text{Cu}_4\text{O}_8$ so that the microstructures after HOP annealing are built with partial dislocations bounding a nonstoichiometric stacking fault. It was possible to probe the effect of partial dislocations and the associated stacking faults on the critical current. It is shown that the pinning efficiency is maximum when the stacking fault surface is minimum and the length of the partial dislocations maximum. Indeed, dislocations act as point pinning centers, whereas stacking faults lead to diminish the coherence length along the vortices. The optimum in critical current density was realized when the ratio dislocation length over stacking fault surface is maximum.

In all these microstructures obtained, dislocations are found to be located in the (0 0 1) easy glide plane, as well as the nonstoichiometric stacking faults while the ideal orientation for flux pinning is perpendicular to it. Compounds with Nd, instead of Y, have been shown to have glide planes perpendicular to (0 0 1) (Sandiumenge *et al.*, 1998); they could be more convenient for vortices pinning by dislocations.

Conclusions

Dislocation multiplication can occur in ceramic materials by the application of stresses. We have examined here a number of typical cases, but have not covered the whole field. Other important materials have received attention, such as UO_2 , Cu_2O , quartz, garnets, etc. The questions raised by dislocations in ceramics are very close to those concerning the dislocations responsible for the deformation of rocks and minerals. These types of studies have benefited from those performed on dislocations in metals and in semiconductors. However, there are various specific questions which are still unsolved. For instance, the energies of dislocations in ceramic materials are so large that they have to be decreased by dissociation, observed by TEM, or by core extensions. Climb dissociation has been found more frequently than in any other classes of materials. This is probably due to the high temperatures necessary to activate dislocation motion; atomic diffusion also increases at such temperatures. Climb dissociation does not have always a well-understood influence on the plastic properties of ceramic materials. There are many examples where extension of the core is suspected and not observed directly. Up to date TEM techniques such as high-resolution TEM and STEM equipped with aberration correctors have to be used extensively and coupled with atomistic simulations in order to shed new light on the properties of dislocations in ceramics.

Acknowledgments

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References

- Audurier, V., Demenet, J.L., Rabier, J., 1998. AlN plastic deformation between room temperature and 800°C; Dislocation substructure observations. *Philos. Mag. A* 77, 825–842.
- Bodur, C.T., Chang, J., Argon, A.S., 2005. Molecular dynamics simulation of basal and pyramidal system edge dislocations in sapphire. *J. Eur. Ceram. Soc.* 25, 1431–1439.
- Brethreau, T., Castaing, J., Rabier, J., Veyssière, P., 1979. Dislocation motion and high temperature plasticity of binary and ternary oxides. *Adv. Phys.* 28, 829–1014.
- Brunner, D., 2006. Low-temperature plasticity and flow-stress behavior of strontium titanate single crystals. *Acta Mater.* 54, 4999–5011.
- Cadoz, J., Castaing, J., Phillips, D.S., Heuer, A.H., Mitchell, T.E., 1982. Work hardening and recovery in sapphire (α -Al₂O₃) undergoing prism plane deformation. *Acta Metall.* 30, 2205–2218.
- Castaing, J., 1981. Plasticité et dislocations dans les cristaux ioniques. *Ann. Phys. Fr.* 6, 195–221.
- Castaing, J., Munoz, A., Dominguez Rodriguez, A., 2002. Hardening of rhombohedral twinning in sapphire (α -Al₂O₃) by basal slip dislocations. *Philos. Mag. A* 82, 1419–1431.
- Castaing, J., Munoz, A., Gomez Garcia, D., Dominguez Rodriguez, A., 1997. Basal slip in sapphire (α -Al₂O₃). *Mater. Sci. Eng. A* 223, 121–125.
- Castaing, J., Kronenberg, A.K., Kirby, S.H., Mitchell, T.E., 2000. Hydrogen defects in α -Al₂O₃ and water weakening of sapphire and alumina ceramics between 600 and 1000°C-II mechanical properties. *Acta Mater.* 48, 1495–1504.
- Castaing, J., He, A., Lagerlof, K.P.D., Heuer, A.H., 2004. Deformation of sapphire by basal slip and basal twinning below 700°C. *Philos. Mag.* 84, 1113–1125.
- Castillo Rodriguez, M., Munoz, A., Castaing, J., Veyssière, P., Dominguez Rodriguez, A., 2007. Chromium hardening and Peierls mechanism for basal slip in sapphire (α -Al₂O₃) at temperatures between 900°C and 1500°C. *J. Eur. Ceram. Soc.* 27, 1113–1125.
- Demenet, J.L., Milhet, X., Rabier, J., 2005. TEM observations of the coexistence of perfect and dissociated dislocations in SiC under high stress. *Phys. Status Solidi ((c))* 202, 1987–1991.
- Demenet, J.L., Amer, M., Mussi, A., Rabier, J., 2011. Effect of electronic doping on the plasticity of homoepitaxial 4H-SiC single crystals, *Journal of Physics: Conference Series* 281, 012003/1–012003/4.
- Dominguez Rodriguez, A., Heuer, A.H., Castaing, J., 1991. Dislocations and the mechanical properties of stabilized ZrO₂. *Radiat. Eff. Def. Solids* 119–121, 759–769.
- Dominguez Rodriguez, A., Castaing, J., Koizumi, H., Suzuki, T., 1988. Plastic deformation down to 4.2K of CoO single crystals and TEM observation of dislocations, *Revue Phys. Rev. Phys. Appl.* 23, 1361–1368.
- Duesbery, M.S., Joos, B., 1996. Dislocation motion in silicon: The shuffle-glide controversy. *Philos. Mag. Lett.* 74, 253–258.
- Duval-Riviere, M.L., Vicens, J., 1994. Polytype transformation and gliding behavior in polycrystalline α -SiC deformed by compression at high temperatures. *Philos. Mag. A* 69, 451–470.
- Foitzik, A., Skrotzki, W., Haasen, P., 1989. Correlation between microstructure, dislocation dissociation and plastic anisotropy in ionic crystals. *Mater. Sci. Eng. A* 113, 399–407.
- Fujita, S., Maeda, K., Hyodo, S., 1987. Dislocation glide motion in 6H-SiC single crystals subjected to high temperature deformation. *Philos. Mag. A* 55, 203–215.
- Garem, H., Rabier, J., Veyssière, P., 1982. Slip systems in gadolinium gallium garnet single crystals. *J. Mater. Sci.* 17, 878–884.
- Gomez Garcia, D., Martinez Fernandez, J., Dominguez Rodriguez, A., Castaing, J., 1997. Mechanisms of high temperature creep of fully stabilized zirconia single crystals as a function of the yttria content. *J. Am. Ceram. Soc.* 80, 1668–1672.
- Gumbsch, P., Taeri-Baghdarani, S., Brunner, D., Sigle, W., Ruhle, M., 2001. Plasticity and inverse brittle-to-ductile transition in strontium titanate. *Phys. Rev. Lett.* 87, 085505/1–085505/14.
- He, A., Lagerlof, K.P.D., Castaing, J., Heuer, A.H., 2002. Considerations of the double cross slip mechanism for basal and rhombohedral twinning in sapphire. *Philos. Mag. A* 82, 2855–2867.
- Heuer, A.H., Lagerlof, K.P.D., Castaing, J., 1998. Slip and twinning dislocations in sapphire (α -Al₂O₃). *Philos. Mag. A* 78, 747–763.
- Hirel, P., Carrez, P., Cordier, P., 2016. From glissile to sessile: Effect of temperature on <110> dislocations in perovskite materials. *Scripta Mater.* 120, 67–70. doi:10.1016/j.scriptamat.2016.04.001.
- Hong, M.H., Samant, A.V., Pirouz, P., 2000. Stacking fault energy of 6H-SiC and 4H-SiC single crystals. *Philos. Mag. A* 80, 919–935.
- Jhon, M.H., Glaeser, A.M., Chrzan, D.C., 2005. Computational study of stacking faults in sapphire using total energy methods. *Phys. Rev. B* 71, 214101/1–214101/5.
- Jia, C.L., Thust, A., Urban, K., 2005. Atomic-scale analysis of the oxygen configuration at a SrTiO₃ dislocation core. *Phys. Rev. Lett.* 95, 225506/1–225506/14.
- Jimenez Melendo, M., Riviere, J.P., Suzuki, T., *et al.*, 1992. Deformation of NiO single crystals below room temperature: Dislocation configurations. *J. Mater. Sci.* 27, 3589–3593.
- Kim, H.S., Roberts, S.G., 1994. The brittle ductile transition and dislocation mobility in sapphire. *J. Am. Ceram. Soc.* 77, 3099–3104.
- Kubin, L.P., 1976. Déformation plastique et microscopie électronique des métaux et alliages de structure cubique centre. *J. Microsc. Spectrosc. Electron* 1, 585.
- Lagerlof, K.P.D., Mitchell, T.E., Heuer, A.H., *et al.*, 1984. Stacking fault in sapphire (α -Al₂O₃). *Acta Metall.* 32, 97–105.
- Lagerlof, K.P.D., Heuer, A.H., Castaing, J., Riviere, J.P., 1994. Slip and twinning in sapphire (α -Al₂O₃). *J. Am. Ceram. Soc.* 77, 385–397.
- Maeda, K., Suzuki, K., Fujita, S., Ichihara, M., Hyodo, S., 1988. Defects in plastically deformed 6H-SiC single crystals studied by TEM. *Philos. Mag. A* 57, 573–592.
- Marrow, T.J., Roberts, S.G., Pearce Higgins, A.K., 1994. The brittle ductile transition in cubic stabilized zirconia. *J. Eur. Ceram. Soc.* 14, 447–453.
- Martinez, B., Sandiumenge, F., Puig, T., *et al.*, 1999. Enhanced critical currents in melt textured YBa₂Cu₃O₇ by cold isostatic pressing. *Appl. Phys. Lett.* 74, 73–75.
- Martinez Fernandez, J., Jimenez Melendo, M., Dominguez Rodriguez, A., *et al.*, 1995. High temperature precipitation hardening in Y₂O₃ partially stabilized ZrO₂ (Y-PSZ) single crystals—III effect of solute composition and orientation on the hardening. *Acta Metall. Mater.* 43, 2469–2484.
- Messerschmidt, U., Baufeld, B., Baither, D., 1998. Plastic deformation of cubic zirconia single crystals. *Key Eng. Mater.* 153–154, 143–182.
- Messerschmidt, U., Baither, D., Baufeld, B., Bartsch, M., 1997. Plastic deformation of zirconia single crystals: A review. *Mater. Sci. Eng. A* 233, 61–74.
- Milhet, X., Demenet, J.L., Rabier, J., 1999. Glide dislocations in β silicon nitride. *Philos. Mag. Lett.* 79, 19–24.
- Milhet, X., Girard, J.C., Demenet, J.L., Rabier, J., 2001. Characterization of room temperature plastic deformation of β Si₃N₄ by atomic force microscopy and transmission electron microscopy. *Philos. Mag. A* 81, 623–629.
- Mitchell, T.E., Heuer, A.H., 2004. Chapter 68 – Dislocations and mechanical properties of ceramics. In: Nabarro, F.R.N., Hirth, J.P. (Eds.), *Dislocations in Solids* 12. Amsterdam: Elsevier B.V.
- Mitchell, T.E., Anderson, P.M., Baskes, M.I., *et al.*, 2003. Nucleation of kink pairs on partial dislocations: A new model for solution hardening and softening. *Philos. Mag.* 83, 1329–1346.
- Munoz, A., Dominguez Rodriguez, A., Castaing, J., 1994. Slip systems and plastic anisotropy in CaF₂. *J. Mater. Sci.* 29, 6207–6211.
- Mussi, A., Demenet, J.L., Rabier, J., 2006. TEM study of defects generated in 4H-SiC by micro indentation on the prismatic plane. *Philos. Mag. Lett.* 86 (9), 561–568. doi:10.1080/09500830600930198.
- Mussi, A., Rabier, J., Thilly, L., Demenet, J.L., 2007. Plasticity mechanisms in 4H-silicon carbide near and below the brittle-to-ductile transition. *Phys. Status Solidi ((c))* 4, 2929–2933. doi:10.1002/pssc.200675438.
- Nakamura, A., Yamamoto, T., Ikuhara, Y., 2002. Direct observation of basal dislocation in sapphire by HRTEM. *Acta Mater.* 50, 101–108.
- Peter, A., Fries, E., Janszky, J., Castaing, J., 1986. Dislocations in paratellurite TeO₂: Elastic energies and plastic deformation. *Rev. Phys. Appl.* 21, 289–298.
- Pirouz, P., Yang, J.W., 1993. Polytypic transformations in SiC: The role of TEM. *Ultramicroscopy* 51, 189–214.
- Pirouz, P., Demenet, J.-L., Hong, M.H., 2001. On the transition temperature in the plasticity and fracture of semiconductors. *Philos. Mag. A* 81, 1207–1227.
- Pirouz, P., Zhang, M., Demenet, J.-L., Hobgood, H.M., 2003. Yield and fracture properties of the wide band-gap semiconductor 4H-SiC. *J. Appl. Phys.* 93, 3279–3290.

- Plain, J., Sandiumenge, F., Obradors, X., Rabier, J., 2002a. Microstructural influence on critical currents and irreversibility line in melt textured $\text{YBa}_2\text{Cu}_3\text{O}_{7-\text{Y}}$ re-annealed at high oxygen pressure. *Phys. Rev. B* 65, 104526/1–104526/10.
- Plain, J., Sandiumenge, F., Rabier, J., Denanot, M.F., Obradors, X., 2002b. Dislocation substructures and phase stability of melt textured $\text{YBa}_2\text{Cu}_3\text{O}_{7-\text{Y}}/\text{Y}_2\text{BaCuO}_5$ composites at high oxygen pressure. *Philos. Mag. A* 82, 337–348.
- Ponce, F.A., Bour, D.P., 1997. Nitride-based semiconductors for blue and green light-emitting devices. *Nature* 386, 351–359.
- Ponce, F.A., Cherns, D., Young, W.T., Steeds, J.W., 1996. Characterization of dislocations in GaN by transmission electron diffraction and microscopy techniques. *Appl. Phys. Lett.* 69, 770–772.
- Rabier, J., Garem, H., 1984. Plastic deformation of oxides with garnet structure. In: Tressler, R.E., Bradt, R.C. (Eds.), *Deformation of Ceramic Materials II*. New York: Plenum Press, pp. 187–198.
- Rabier, J., Puls, M.P., 1985. Atomistic model calculations of pipe-diffusion mechanisms in MgO. *Philos. Mag. A* 52, 461–473.
- Rabier, J., Veyssière, P., Grilhé, J., 1976. Possibility of stacking faults and dissociation of dislocations in the garnet structure. *Phys. Status Solidi. A* 35, 259–268.
- Rabier, J., Soullard, J., Puls, M.P., 1990. Atomistic calculations of point defect interactions with an edge dislocation in NiO. *Philos. Mag. A* 61, 99–108.
- Rabier, J., Tall, P.D., Denanot, M.F., 1993. On the dissociation of dislocations in $\text{YBa}_2\text{Cu}_3\text{O}_7$. *Philos. Mag. A* 67, 1021–1035.
- Samant, A.V., Pirouz, P., 1998. Activation parameters for dislocation glide in α -SiC. *Int. J. Refract. Met. Hard Mater.* 16, 277–289.
- Sandiumenge, F., Vilalta, N., Rabier, J., Obradors, X., 1998. Three dimensional dislocation substructure in melt textured $\text{NdBa}_2\text{Cu}_3\text{O}_7$ superconductor. *Appl. Phys. Lett.* 73.2660
- Sandiumenge, F., Puig, T., Rabier, J., Plain, J., Obradors, X., 2000. Optimization of flux pinning in bulk melt textured 1-2-3 superconductors: Bringing dislocations under control. *Adv. Mater.* 12, 375–381.
- Takeuchi, S., Suzuki, K., Ichihara, M., Suzuki, T., 1989. High resolution electron microscopy of core structure of dislocations in oxide ceramics. *Jpn. J. Appl. Phys.* 2, 17–24.
- Texier, M., De Luca, A., Pichaud, B., *et al.*, 2013. Evidence of perfect dislocations' glide in nanoindented 4H-SiC. *J. Phys. Conf. Ser.* 471. 012013. doi:10.1088/1742-6596/471/1/01201.
- Veyssière, P., 1988. Dislocation core effects in plasticity. *Rev. Phys. Appl.* 23, 431–443.
- Vilalta, N., Sandiumenge, F., Rabier, J., Denanot, M.F., Obradors, X., 1997. Evolution of the microstructure, during high temperature creep and oxygenation in directionally solidified $\text{YBa}_2\text{Cu}_3\text{O}_7$. *Philos. Mag. A* 76, 837.

Corrosion of Ceramics in Aqueous Environments

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The term “corrosion” is defined for ceramics as well as for metallic or polymeric materials as a local or large-area reaction of a material with a surrounding medium, which can lead to degradation of the material or component up to its destruction. Corrosion stability is therefore not a property of the material per se, but a property of the system and requires not only the specification of the material but also the specification of the respective conditions (e.g., medium, temperature, pressure, flow conditions, additional mechanical and tribological load) (ISO, 2020; Clark and Zito, 1992; McCauley, 1995; Brevier *Technische Keramik*, 2020; Nickel and Gogotsi, 2000; Schilm and Herrmann, 2010; Herrmann and Klemm, 2014; Herrmann, 2013a; Frankel *et al.*, 2018; Chevalier *et al.*, 2009; Clark *et al.*, 1976; Paul, 1977). Textbooks therefore usually list the corrosion resistance for standard conditions. For special applications it must be decided whether these conditions can be transferred or whether separate corrosion investigations are necessary.

To assess the corrosion behavior of a ceramic in advance, it is necessary to evaluate its stability against aqueous media from both thermodynamic and kinetic points of view. While thermodynamics provides basic information about the possibility (Gibbs free energy of reaction $\Delta G_{\text{reaction}} < 0$) or impossibility of a corrosive attack ($\Delta G_{\text{reaction}} \gg 0$), kinetic considerations provide information about the rate of the reaction. For example, the thermodynamic instability of Al_2O_3 ceramics in acids is countered by a very low dissolution rate, which is responsible for an extremely slow corrosive attack. This makes high-purity corundum ceramics stable in these media.

To understand the corrosion behavior, it is advantageous to divide ceramics into two main groups:

- Solid state sintered materials with high purity and low content of secondary phases (high purity Al_2O_3 ; ZrO_2 ; SiC , TiO_2 , YAG, spinel) and
- Liquid phase sintered or infiltrated ceramics with a higher proportion of grain boundary phase (silicon nitride ceramics (Si_3N_4); liquid phase sintered SiC (LPSSiC); AlN ; porcelain; Al_2O_3 with glass phase, silicon infiltrated silicon carbide (SiSiC), cermets; WC/Co).

Fig. 1 shows microstructures of one representative of each of these two groups and additionally the picture of a reactive infiltrated material.

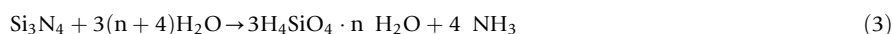
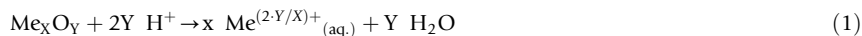
The processes taking place during corrosion in liquids in both types of ceramics are shown schematically in **Fig. 2**.

In contrast to the solid state sintered materials, the liquid phase sintered materials have an amorphous, partially crystalline, or crystalline grain boundary phase, which normally forms a three-dimensional skeleton. This means that the corrosive attack can damage the material to great depths if the grain boundary phase is less stable than the main phase. Therefore, the properties of the grain boundary phase often determine the corrosion stability of liquid phase sintered ceramics. Small changes in the amount and composition of the grain boundary phase can therefore cause strong changes in the corrosion stability.

Fig. 3 demonstrates the strong reduction in corrosion stability with increasing amount of grain boundary phase (increasing amounts of SiO_2) for corundum ceramics. **Fig. 4** shows the change in mass as a function of time for Si_3N_4 -ceramics with different additive compositions, i.e., different grain boundary compositions. It is shown that the choice of additives can change the stability of the ceramics by several orders of magnitude.

In contrast, the solid state sintered ceramics show only minimal segregations of impurities or dopants at the grain boundaries. These segregations do not form a three dimensional network and therefore the difference in chemical stability of the impurities has a minor impact on the overall corrosion behavior, but could result in local enhanced corrosion pitting (see below) and could be a reason for strength reduction.

Compared to metals, in which corrosion takes place via redox reactions with locally separated cathodic and anodic reactions and local electrical currents flow, the corrosion of ceramics is generally not characterized by any change in the oxidation state of the components involved (exception e.g., SiC and other carbides). The reactions taking place are acid-base reactions (Eq. (1)), hydration of metal oxides (Eq. (2)) or the hydrolysis of covalent bonds (Eq. (3)).



These processes are comparable to the dissolution of passivating protective layers on metals. Therefore, compared to metallic materials, technical ceramics are usually more corrosion resistant.

The amount of corrosion is often determined as mass change per unit area, thickness of the corroded or removed layer, or as the accumulation of individual components in the eluate as a function of time. (McCauley, 1995; Nickel and Gogotsi, 2000; Schilm and Herrmann, 2010; ISO, 2006; Galuskova *et al.*, 2014; Striegler *et al.*, 2018).

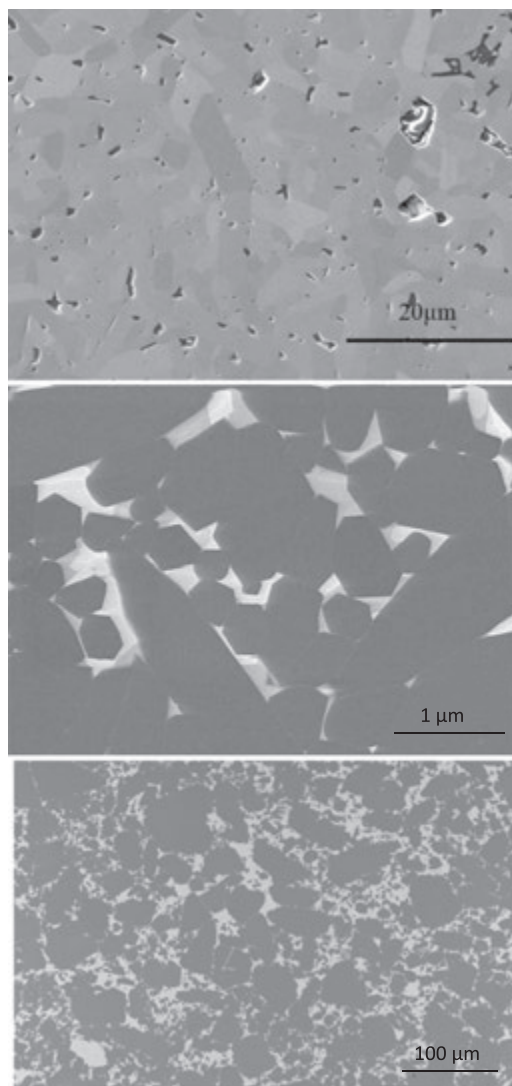


Fig. 1 (a) Microstructure of solid state sintered silicon carbide (SSiC) (locally isolated pores and black inclusions (carbon and boron carbide) are visible), (b) Liquid phase sintered Si_3N_4 ceramics, the white area is the grain boundary phase forming a three-dimensional network, (c) Silicon infiltrated silicon carbide (SiSiC), the white phase is elemental Si forming a three-dimensional network around SiC (gray).

The most powerful method is the determination of the residual strength in combination with analysis of the fracture surfaces. In addition to the rate of integral corrosion, conclusions can also be drawn about locally increased corrosion (pitting) and the reduction of strength due to corrosion. This is important because structural materials are often subjected to mechanical stress in addition to chemical attack. However, this is also the most expensive method because a high number of samples is necessary. The methods are summarized in (Nickel and Gogotsi, 2000; Schilm and Herrmann, 2010; ISO, 2006) and Table 1.

As a rule, several reactions or mass transport processes are involved in a corrosive attack, which depend in different ways on the surrounding parameters (e.g., temperature, concentration ratios in the corrosive medium, composition and the quantity of the grain boundary phase). The superposition of these individual processes often results in complex time dependencies of the corrosion processes, which are determined by the slowest, and thus rate-determining process. (Clark and Zoitos, 1992; McCauley, 1995; Nickel and Gogotsi, 2000; Herrmann and Klemm, 2014; Frankel *et al.*, 2018).

Fig. 5 schematically shows three typical dependencies of corrosion processes as a function of time.

The typical time dependencies of corrosion processes are:

- linear dependence on time for interface-controlled processes. The corrosion depth X can be calculated by the equation

$$X = K t + C \text{ with } K = K_0 e^{\frac{-E}{RT}} \quad (4)$$

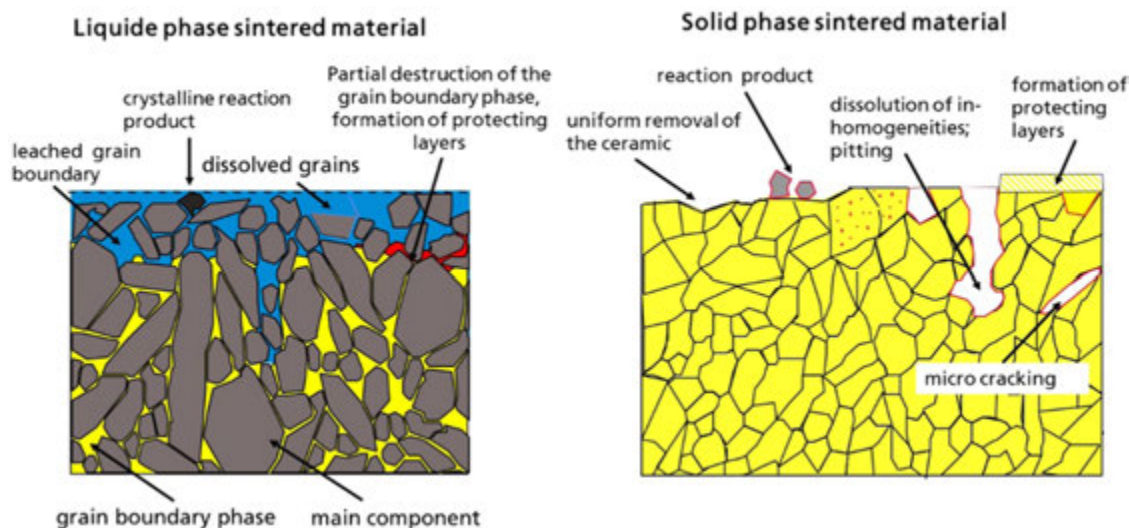


Fig. 2 Schematic view of the corrosion processes taking place in liquid phase sintered materials (a) and solid state sintered materials (b). After Schilm, J., Herrmann, M., 2010. Korrosion in wässrigen Medien. In: Kollenberg, W. (Ed.), Technische Keramik, 2. Auflage. Essen: Vulkan Verlag, pp. 102–106.

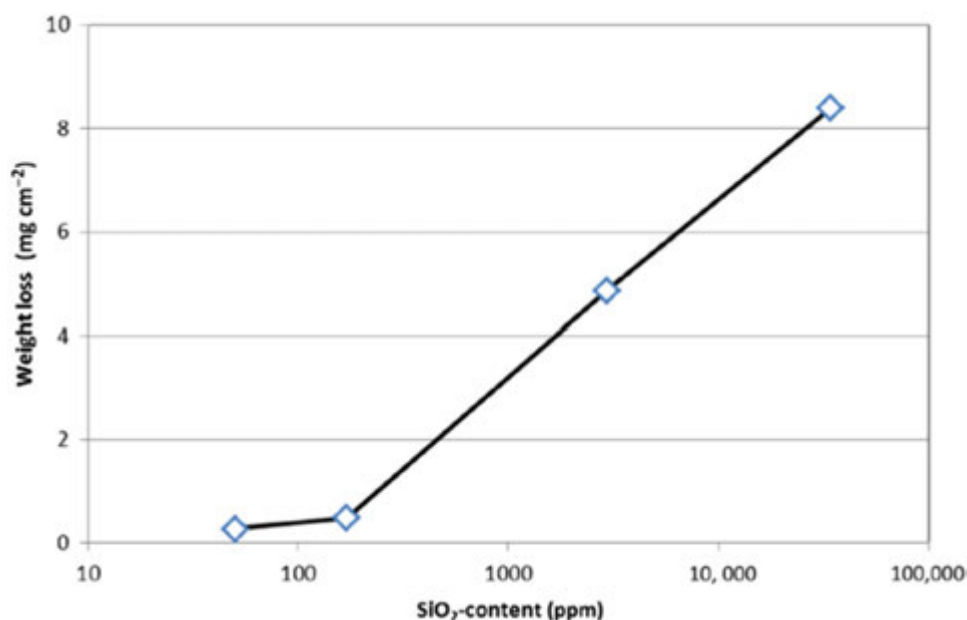


Fig. 3 Mass losses of corundum ceramics depending on the SiO_2 content (corrosion conditions: 1N HCl 150°C, 96 h). Reproduced from Herrmann, M., Klemm, H., 2014. Corrosion of ceramic materials. In: Comprehensive Hard Materials, second ed. Newnes, pp. 413–446.

with K – reaction constant, which may additionally depend on the concentration of the reacting species. t – time, E – activation energy and R – general gas constant and T – temperature, C is a constant that adds up initial surface effects, or corrosion up to time $t = 0$ (e.g., during heating up).

- parabolic dependence on the time takes place when diffusion processes determine the rate.

$$X^2 = K t + C \text{ with } K = K_0 e^{\frac{-E}{RT}} \quad (5)$$

(designation analogous to Eq. (4)).

- If additional passivation reactions occur, the reaction slows down over time even more than in the diffusion-controlled process. Such passivation takes place by precipitation of solid phases which are deposited in the corroded ceramic or on its surface, which can lead to the formation of highly protective layers (Figs. 5 and 2).

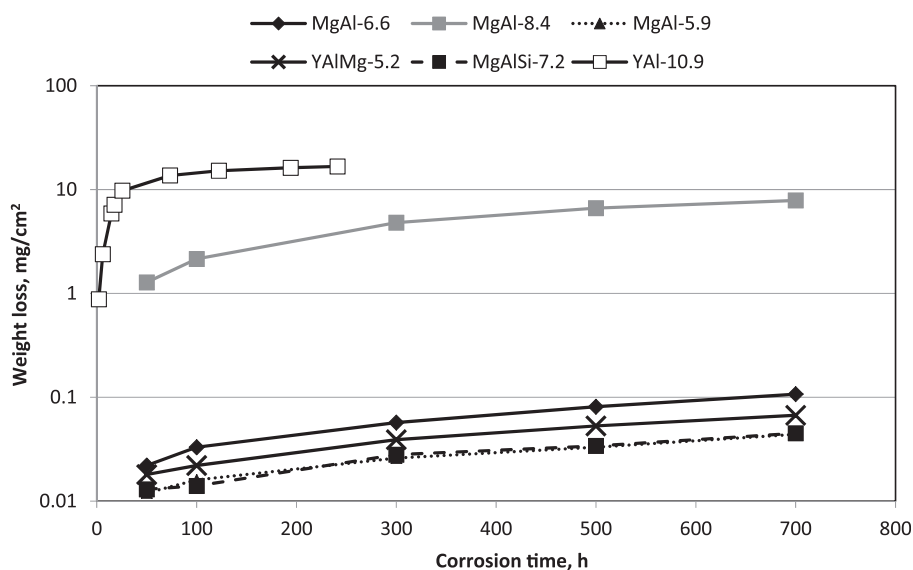


Fig. 4 Corrosion of Si_3N_4 ceramics with different kind and amount of additives in 0.5 mol/l H_2SO_4 and 90°C (the labeling shows the kind of additives (Mg: MgO , Al: Al_2O_3 , Y: Y_2O_3 , Si: SiO_2) and the number corresponds to the volume percentage content). Reproduced from Herrmann, M., Klemm, H., 2014. Corrosion of ceramic materials. In: Comprehensive Hard Materials, second ed. Newnes, pp. 413–446.

Table 1 Overview of assessment methods

Nr	Evaluation procedure	Comment	Examples
1	Strength change	Expensive, as many samples are required per condition; must be coupled with determination of the strength in order to determine defects and thickness of the corrosion layer (fractography)	Suitable for all materials
2	Depth of penetration (Depth of damage)	Suitable for all types of corrosion; Preparation of polished cross sections required (dye penetration test can be useful); sometimes corrosion depth can be determined at fracture surfaces (method1)	Si_3N_4 ; Al_2O_3 ; SiC, WC/Co, Cermets
3	Change of test piece size (layer thickness)	Often unsuitable, because not accurate enough, removal by corrosion must be $> 5 \mu\text{m}$, suitable for growing layers, but then analysis of cross sections/fracture surfaces necessary	Glasses Oxidation processes of non-oxides
4	Specific mass change	Suitable for surface corrosion, for interpretation the analysis of the damage depth is useful. Is influenced by the sample geometry (shrinking core effect)	Si_3N_4 ; SiC Not suitable for ZrO_2 materials
5	Change of the composition of the corrosion medium	Suitable for corrosion with solution processes especially for liquid phase sintered materials	Not suitable for ZrO_2 -materials
6	Phase change	Standard for ZrO_2 materials, (e.g., for medical materials ISO 13356:2015)	ZrO_2 -materials (TZP, PSZ)
7	Change of the surface morphology	Suitable for understanding the corrosion mechanisms in the initial phase; (use of polished surfaces)	Liquid phase sintered materials; SiSiC

Note: Reproduced from Clark, E.D., Zitois, B.K., 1992. Corrosion of Glass, Ceramics and Ceramic Superconductors. Park Ridge New Jersey, USA: Noyes Publications. McCauley, R.A., 1995. Corrosion of Ceramics. New York: Marcel Dekker, Inc. Brevier Technische Keramik, 2020. Informationszentrum Technische Keramik Verband der Keramischen Industrie e.V. Verlag Hans Carl 90411 Nürnberg. Available at: http://www.keramverband.de/brevier_dt/brevier.htm. Nickel, K.G., Gogotsi, Y.G., 2000. Corrosion of Hard Materials. In Handbook of Ceramic Hard Materials. Wiley-VCH. pp. 140–182. Schilm, J., Herrmann, M., 2010. Korrosion in wässrigen Medien. In: Kollenberg, W. (Ed.), Technische Keramik. 2. Auflage, S. Essen: Vulkan Verlag, pp. 102–106. Chevalier, J., Gremillard, L., Virkar, A.V., Clarke, D.R., 2009. The tetragonal–monoclinic transformation in zirconia: Lessons learned and future trends. J. Am. Ceram. Soc. 92,1901–1920. doi:10.1111/j.15512916.2009.03278.x. ISO, 2006. Advanced technical ceramics – Monolithic ceramics – Part 1: General practice for undertaking corrosion tests; German version ISO EN 12923-1:2006. Galuskova, D., Galusek, D., Sajgalik, P., 2014. Evaluation of corrosion of engineering ceramics by atomic emission spectrometry in inductively coupled plasma. Ceramics-Silikaty 58 (1), 39–45. Striegler, M., Matthey, B., Mühle, U., Michaelis, A., Herrmann, M., 2018. Corrosion resistance of silicon infiltrated silicon carbide (SiSiC). Ceram. Int. 44, 10111–10118. doi:10.1016/j.ceramint.2018.02.229. Galuskova, D., Hnatko, M., Galusek, D., Sajgalik, P., 2011a. Corrosion of structural ceramics under sub-critical conditions in aqueous sodium chloride solution and in deionized water. Part II: Dissolution of Al_2O_3 -based ceramics. J. Am. Ceram. Soc. 94, 3044–3052. Galuskova, D., Hnatko, M., Galusek, D., Sajgalik, P., 2011b. Corrosion of structural ceramics under subcritical conditions in aqueous sodium chloride solution and in deionized water. Part I: Dissolution of Si_3N_4 -based ceramics. J. Am. Ceram. Soc. 94, 3035–3043. doi:10.1016/j.matchar.2011.01.012.

- The rate of corrosion can also be controlled by diffusion in the surrounding media or slow down due to enrichment of the solved species in the solution. This results in more complex reaction kinetics (Clark and Zitois, 1992; McCauley, 1995; Nickel and Gogotsi, 2000; Frankel et al., 2018; Herrmann, 2013b).

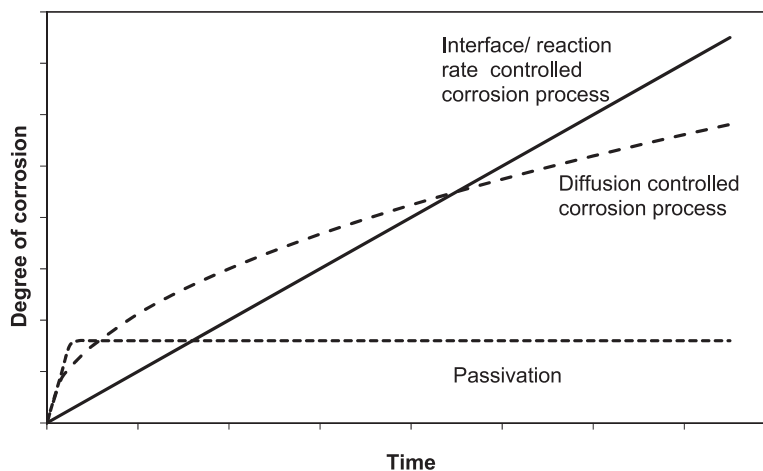


Fig. 5 Schematic view of the different corrosion kinetics. Reproduced from Herrmann, M., Klemm, H., 2014. Corrosion of ceramic materials. In: Comprehensive Hard Materials, second ed. Newnes, pp. 413–446.

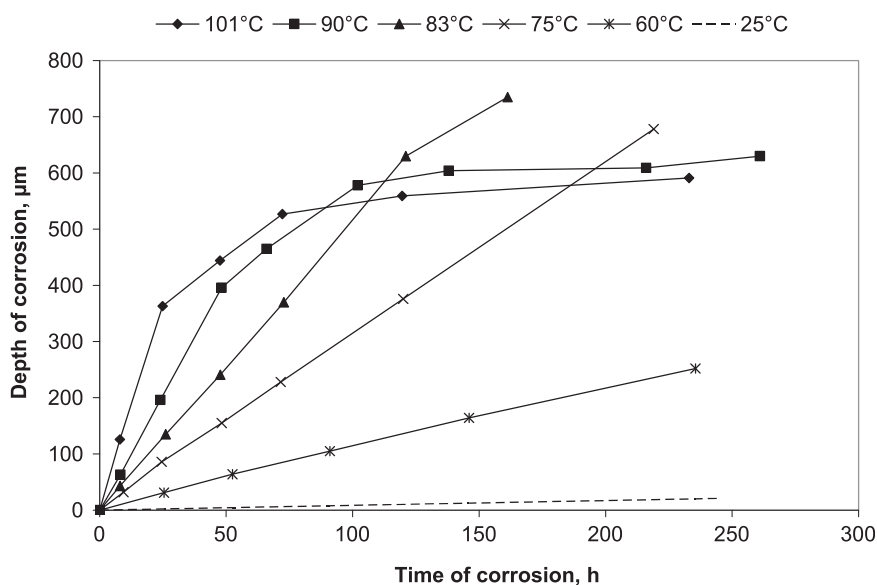


Fig. 6 Time dependence of the thickness of the corrosion layer on a Si_3N_4 -ceramic as a function of temperature in 0.5 mol/l H_2SO_4 (Si_3N_4 -material with 6 wt% Y_2O_3 and 4 wt% Al_2O_3). Reproduced from Herrmann, M., Klemm, H., 2014. Corrosion of ceramic materials. In: Comprehensive Hard Materials, second ed. Newnes, pp. 413–446.

For plate like shapes of the samples or under the condition that the corrosion depth is low in comparison to the sample dimensions, the Eqs. (4) and (5) can also be used for describing the mass change as a function of time. In other cases, the geometry must be considered (shrinking core effect) (Herrmann, 2013b; Schilm, 2004).

Knowing the activation energy, the result determined at higher temperatures can be extrapolated to lower temperature. This allows the prediction of the long-term behavior of a component based on the laboratory experiments. The precondition for such extrapolation is, that the mechanism does not change.

The mechanism can depend on the composition of the material and on the corrosion conditions. Fig. 6 shows an example of Si_3N_4 ceramics. An increase in temperature of only a few K changes the mechanism of corrosion in 0.5 mol H_2SO_4 from an interface-controlled reaction at $T < 75^\circ\text{C}$ to passivation of the ceramic after an initial starting period at $T > 83^\circ\text{C}$. The passivation is caused by the formation of SiO_2 rich deposits in the leached grain boundaries. The result of the mechanism change is that the sample corroded at a higher temperature (e.g., 90°C) is attacked less than the sample corroded at 75°C for corrosion times > 200 h. (Herrmann and Klemm, 2014; Herrmann, 2013b; Schilm, 2004) The example shows that kinetics are sometimes very complex and therefore, the prediction of the behavior over long periods of time requires a precise determination of the mechanism.

In addition, the corrosion behavior often depends strongly on the concentration of the reagents. Fig. 7 shows the dependence of the corrosion of a Si_3N_4 ceramic as a function of the concentration of H_2SO_4 . The data reveal that in concentrated and dilute H_2SO_4 the

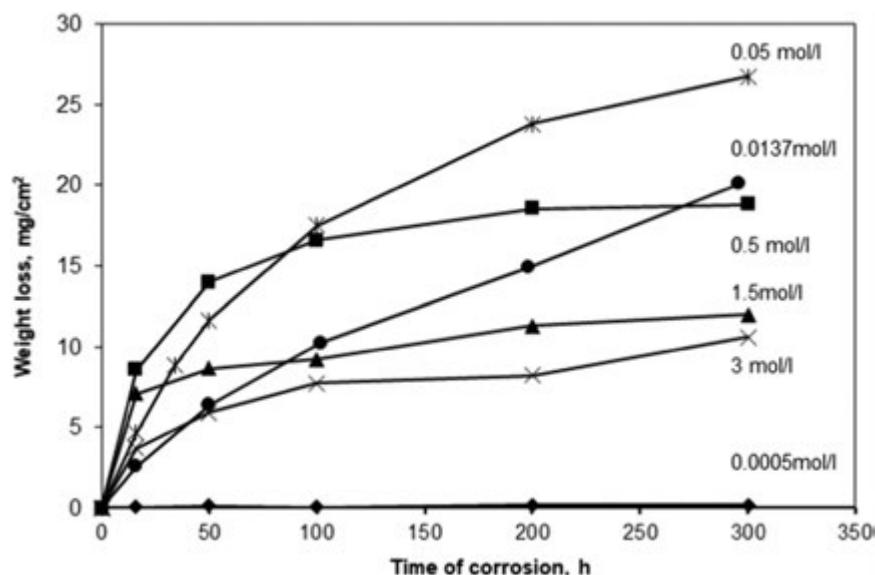


Fig. 7 Time dependence of weight loss on corrosion time for a Si_3N_4 material with 6 wt% Y_2O_3 and 4 wt% Al_2O_3 in H_2SO_4 with different concentrations at 90°C (concentrations given in the diagram). Reproduced from Herrmann, M., Klemm, H., 2014. Corrosion of ceramic materials. In: Comprehensive Hard Materials, second ed. Newnes, pp. 413–446.

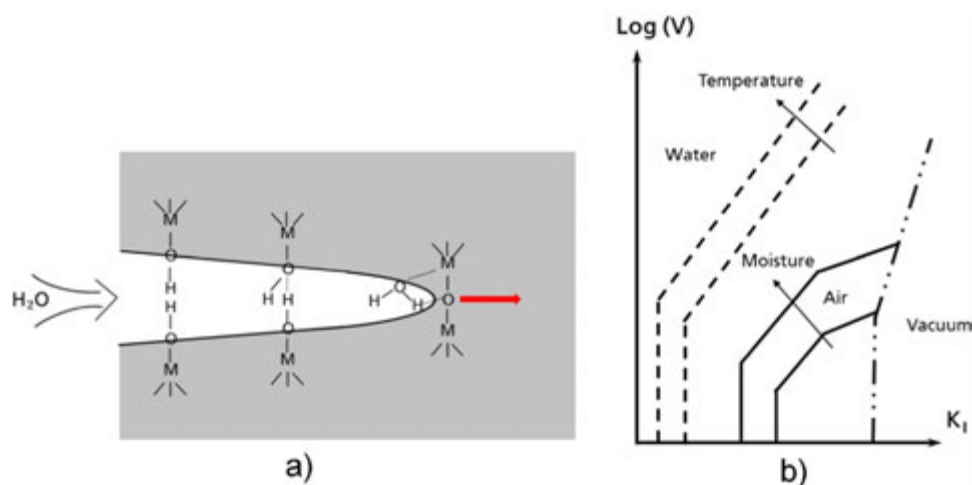


Fig. 8 Increase of the subcritical crack growth rate of ceramics by chemical reactions with water. (a) schematic illustration of the interaction with H_2O , which leads to increased breaking of the bonds in the ceramic and thus to increased subcritical crack growth (M- metal e.g., Al, Zr). (b) Schematic illustration of the dependence of the logarithm of the crack growth rate on the stress intensity factor and the surrounding media. Adapted from Aza, A.H., Chevalier, J., Fantozzi, G., 2002. Crack growth resistance of alumina, zirconia and zirconia toughened alumina ceramics for joint prostheses. *Biomaterials* 23, 937–945.

attack is much less than in acids of medium concentration. The higher stability in concentrated acids is due to the low solubility of SiO_2 from the grain boundary phase in these media. This leads to a passivation by the formation of poorly soluble SiO_2 layers. Similar behavior was observed for alumina ceramics (Herrmann and Klemm, 2014; Herrmann, 2013b; Schilm, 2004; Sato *et al.*, 1991).

Besides the integral corrosion stability, local corrosion plays a decisive role. Such local damage of the ceramic is called pitting. It is enhanced corrosion at inhomogeneities of the material and essentially determines the strength of the materials after corrosion (residual strength), since defects close to the surface are rapidly increased. The reduction in strength is particularly intensive in the initial phase of corrosion and is strongly influenced by local inhomogeneities, pores or other defects existing in the material. (Herrmann and Klemm, 2014; Herrmann, 2013a; Striegler *et al.*, 2018; Herrmann, 2013b; Schilm, 2004).

Since ceramic components are usually not only chemically stressed but also tribologically or mechanically stressed, the determination of the residual strength is of great importance for the selection of materials for specific applications.

Mechanical stress below the critical stress, which leads to fracture, can lead to failure after a certain time. The reason is the subcritical growth of existing defects. This subcritical crack growth is intensified by load and corrosion (Freiman *et al.*, 2009; Aza *et al.*, 2002; Barsoum, 2003). This is shown schematically in Fig. 8(a). Even moisture increases the subcritical crack growth in

Table 2 Stabilities of different technical ceramics in aqueous solutions

Material	Medium	Stability	Notes
Al ₂ O ₃ (> 99.9%)	H ₂ SO ₄ ; HCl; < 100°C NaOH; H ₂ O ≤ 100–200°C	high	Stability could be influenced by impurity content
Al ₂ O ₃ (< 99.9%)	H ₂ SO ₄ ; HCl, NaOH, H ₂ O	Lower than pure Al ₂ O ₃	Corrosion resistance is determined by the composition of the grain boundary phase. SiO ₂ in the material reduces the stability
ZrO ₂ CSZ (8Y-SZ)	H ₂ SO ₄ > RT H ₂ O (including hydro-thermal conditions and water vapor)	high	Show a very low solubility in the media, the cubic phase does not transform
ZrO ₂ Y-TZP	H ₂ SO ₄ > RT H ₂ O > 100°C	Low, medium	Degradation of the ceramic material occurs due to stress caused by a corrosion-related transformation to monoclinic ZrO ₂
Mg-PSZ Ce-TZP	H ₂ SO ₄ > RT H ₂ O < 200°C	higher than Y-TZP	Material is much less prone to degradation than Y-TZP
ZTA (10–15 wt% ZrO ₂)	H ₂ SO ₄ ; NaOH < 100°C H ₂ O > 200°C	high medium	Material exhibits almost no degradation if it is free of SiO ₂ Degradation of the ceramic material occurs due to stress which is caused by a corrosion-related transformation to monoclinic ZrO ₂
SiC	acid; bases HF Electrochemical attack possible	high	Depends on the conductivity of the material
SiSiC	acids HF bases, hydrothermal	high low low	In acid passivation of Si by SiO ₂ formation Dissolution of free silicon Dissolution of free silicon
LPSSiC	acid; bases hydrothermal	medium or high	Corrosion resistance is strongly dependent upon the composition and distribution of the grain boundary phase and defects
Si ₃ N ₄	concentrated HCl, HNO ₃ , H ₂ SO ₄ diluted acids, bases	high stability high or low	SiO ₂ surface layer formation results in passivation Stability depends on the amount and composition of the grain boundary phase
	H ₂ O < 200°C HF	very low medium/low	Dissolution of grains and grain boundary phase occurs Stability depends on the amount and composition of the grain boundary phase
	H ₂ O > 200–250°C		Increased dissolution of Si ₃ N ₄ grains occurs
WC/Co/Cermets	acids	low	Dissolution of the metallic binder Ni containing materials more stable than Co containing systems
	electrochemical Corrosion	low, medium	Dissolution of the binder in acidic solutions and WC in basic solutions

Note: After Schilm, J., Herrmann, M., 2010. Korrosion in wässrigen Medien. In: Kollenberg, W. (Ed.), Technische Keramik, 2. Auflage. Essen: Vulkan Verlag, pp. 102–106. Herrmann, M., Klemm, H., 2014. Corrosion of ceramic materials. In: Comprehensive Hard Materials, second ed. Newnes, pp. 413–446.

comparison to inert conditions (Fig. 8(b)). The effect is more intensive in aqueous solutions and at elevated temperatures. The local chemical corrosion at the crack tip can increase the crack growth rate by several orders of magnitude, which leads to a drastic reduction in service life. The subcritical crack growth depends on the material and the microstructure, whereby oxide ceramics tend to have a stronger tendency to subcritical crack growth than SiC- and Si₃N₄-ceramics.

The influence of superimposing wear and corrosion is still not investigated in detail due to the wide range of possible parameters. In general, the wear reduces the corrosion resistance.

Table 2 provides a rough overview of the corrosion behavior of various important technical ceramics. As was explained before, the intensity of the corrosive attack can vary greatly depending on the composition, especially the grain boundary phase.

The Fig. 9 gives a comparison of the change of strength as a function of the corrosion conditions for different materials.

In the following paragraphs, some corrosion aspects for the individual ceramics will be dealt with briefly.

Corundum Ceramics (Clark and Zoitos, 1992; Herrmann and Klemm, 2014; Galuskova *et al.*, 2011a,b; Mikeska *et al.*, 2000; Mikeska, 1999)

High-purity corundum ceramics have a high chemical stability in most media. An indication of the high stability is the unchanged strength independent of the corrosion conditions. If the ceramic contains grain boundary phases, these can have a

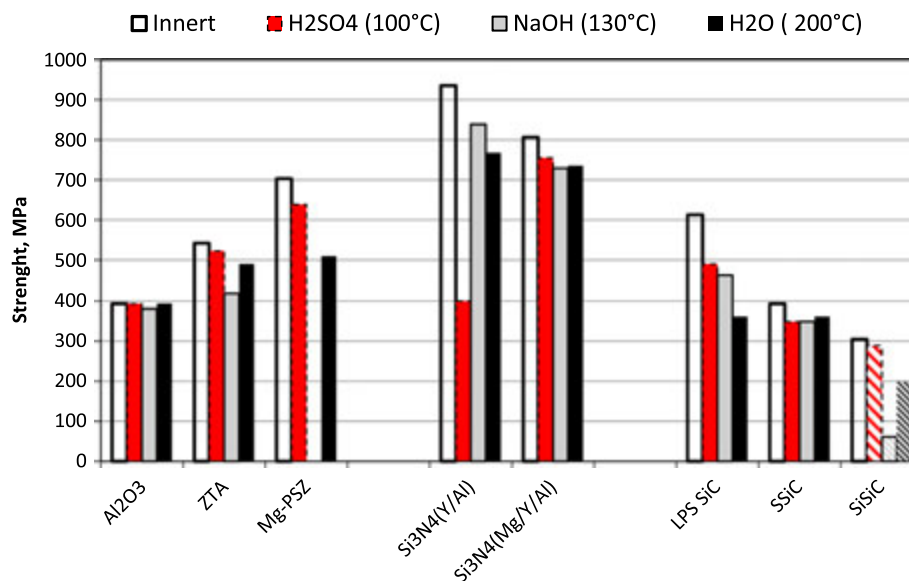


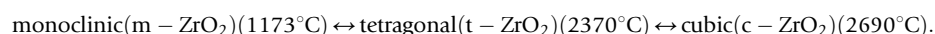
Fig. 9 Residual strength of different ceramics after 200 h corrosion in 1 mol NaOH (130°C) and 0.5 Mol/l H₂SO₄ (100°C) and under hydrothermal conditions in water at 200°C (SiSiC (silicon infiltrated SiC) was measured at 90°C. The hydrothermal corrosion of SiSiC at 200°C resulted in destroyed samples). Data from Herrmann, M., Klemm, H., 2014. Corrosion of ceramic materials. In: Comprehensive Hard Materials, second ed. Newnes, pp. 413–446. Striegler, M., Matthey, B., Mühle, U., Michaelis, A., Herrmann, M., 2018. Corrosion resistance of silicon infiltrated silicon carbide (SiSiC). *Ceram. Int.* 44, 10111–10118. doi:10.1016/j.ceramint.2018.02.229. Herrmann, M., Kluge, E., Rödel, C., McKie, A., van Staden, F., 2014a. Corrosion behaviour of silicon carbide diamond composite materials in aqueous solutions. *J. Europ. Ceram. Soc.* 34, 2143–2151.

strong influence on the chemical stability (Fig. 3). Silicate grain boundaries typically show low stability in mineral acids. The formation of crystalline Mg- or Ca-containing aluminates as secondary phases leads to a much lower damage during corrosion. Therefore, when assessing corundum materials that contain 0.5%–20% of silicates (Herrmann and Klemm, 2014; Galuskova *et al.*, 2011a,b; Mikeska *et al.*, 2000; Mikeska, 1999), the chemical composition of the secondary phases must always be taken into account.

Porous membranes usually consist of transition aluminas, which have a lower stability in comparison to corundum. In addition, the high surface of such filter materials influences the stability (Dong *et al.*, 2011).

ZrO₂ ceramics (Chevalier *et al.*, 2009; Aza *et al.*, 2002; Lawson, 1995; Lughi and Sergo, 2010; Keuper *et al.*, 2013)

ZrO₂ has 3 different modifications at normal pressure, which transform into each other:



The transformations are accompanied by a change in volume, which has a strong effect on the behavior of the ceramics (transformation toughening). The cubic and tetragonal modification can be stabilized with different amounts of rare earth or alkaline earth oxides. Based on the composition and the phases different classes of ceramics are formed which have different properties.

Cubic stabilized zirconia (CSZ) or fully stabilized zirconia (FSZ) is based on the cubic phase and often contains 8 mol% Y₂O₃ (8YSZ). Cubic ZrO₂ is very stable in aqueous media due to its low solubility up to high temperatures. Therefore, only extremely small mass changes occur during the ageing process. However, it has a relative low strength.

The ZrO₂ ceramics materials with high strength and toughness are TZP – *Tetragonal Zirconia Polycrystal*, PSZ – *Partially Stabilized Zirconia*. They are based on the metastable tetragonal phase. The corrosion stability of these ceramics is not primarily linked to the dissolution of ZrO₂. The stability is related to the stability of the metastable tetragonal phase. In hot acids, bases and under hydrothermal conditions a chemically induced transformation of the metastable tetragonal ZrO₂ grains (*t*-ZrO₂) into the monoclinic phase (*m*-ZrO₂) takes place. The destabilization is caused by the diffusion of water or OH-ions into the *t*-ZrO₂ grains (oxygen vacancies in the lattice) (Chevalier *et al.*, 2009; Lawson, 1995; Lughi and Sergo, 2010; Keuper *et al.*, 2013; Johannes and Schneider, 2012). The phase transformation results in volume increase. The resulting stresses lead to the formation of micro-crack systems, which accelerate corrosion and, in the final consequence, lead to a disintegration of the ceramic. The mechanism of phase transformation, which is on the one hand intended to increase the toughness of the materials, leads to low temperature aging, i.e., the destruction of the ceramic in hot water based solutions and especially under hydrothermal conditions. This is particularly important for medical applications, e.g., in the dental field. For this reason, attempts have been made to increase the stability through various material modifications. Fig. 10 gives an indication.

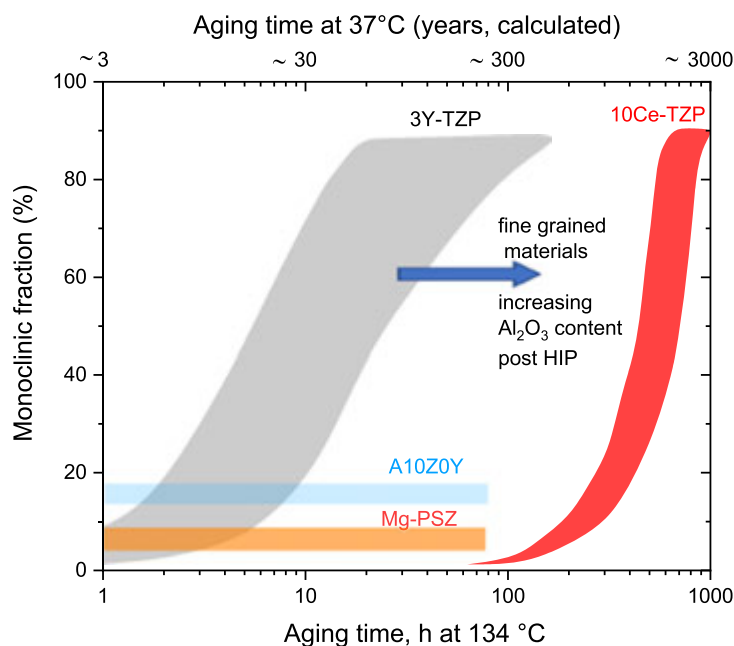


Fig. 10 Content of the monoclinic zirconia phase after ageing in steam at 134°C as a function of time and extrapolation to the degree of conversion at 37°C using activation energy (10Ce-TZP CeO₂ stabilized TZP, A10Z0Y – Zirconia toughened alumina (ZTA) with 10% unstabilized ZrO₂. The thickness of the corroded layer (m-ZrO₂-content) in 3YTZP ceramics depends linearly on time. Adapted from Chevalier, J., Gremillard, L., Virkar, A.V., Clarke, D.R., 2009. The tetragonal–monoclinic transformation in zirconia: Lessons learned and future trends. *J. Am. Ceram. Soc.* 92, 1901–1920. doi:10.1111/j.15512916.2009.03278.x. Keuper, M., Eder, K., Berthold, C., Nickel, K.G., 2013. Direct evidence for continuous linear kinetics in the lowtemperature degradation of Y-TZP. *Acta Biomater.* 9, 4826–4835.

CeO₂ doped TZP or Mg-partially stabilized ZrO₂ (Mg-PSZ), which show a lower transformation rate $t\text{-ZrO}_2 \rightarrow m\text{-ZrO}_2$ under the same conditions, are correspondingly more corrosion resistant (Chevalier *et al.*, 2009). The degradation of strength is moderate in hot H₂SO₄ and under hydrothermal conditions. (Fig. 9).

The healing of defects or small pores in Y-TZP-ceramics by post HIP processes increases the resistance significantly too. A reduction of the ZrO₂ grain size or the addition of Al₂O₃ also increases the chemical stability of the materials (Johannes and Schneider, 2012).

The stability of zirconia toughened materials (like zirconia toughened alumina (ZTA)) strongly depends on the amount of zirconia, the concentration of the stabilizer and distribution of the ZrO₂. The stability depends on the ability of the matrix to withstand the stresses caused by the transformation. Sometimes the strength of the material even increases due to the compression surface stresses generated by the chemically induced phase transformation.

Si₃N₄ ceramics (Herrmann and Klemm, 2014; Herrmann, 2013b; Schilm, 2004; Galuskova *et al.*, 2011a,b)

The stability of Si₃N₄ ceramics (see microstructure in Fig. 1(b)) depends very much on the composition of the grain boundary phase. The stability in acids can vary by several orders of magnitude depending on the composition of the grain boundary phase (Fig. 4). In concentrated alkaline solutions at elevated temperatures and under hydrothermal conditions > 200°C, SiO₂ passive layers on the Si₃N₄ grains dissolve, making the ceramic unstable. (Herrmann, 2013b).

Most commercial materials sintered with Y₂O₃ and Al₂O₃ additives show good stability in water and alkaline solutions, but lower stability in hot acids. This instability can be minimized by a specific design of the grain boundary phase (Fig. 4) (Herrmann, 2013b; Schilm, 2004). The corrosion stability of Si₃N₄ and Sialon ceramics is summarized in (Herrmann, 2013b; Schilm, 2004).

In media containing hydrofluoric acid, Si₃N₄ ceramics, like most ceramics containing Si, are not stable, as the formation of soluble SiF₆²⁻ complexes destroys the typical SiO₂-passivation layer and therefore dissolve the Si₃N₄ grains. The only exception is SSiC. (Herrmann, 2013b; Schilm, 2004; Mikeska *et al.*, 2000; Schmalzried and Schwetz, 2010).

The corrosion behavior of silicate ceramics is like that of Si₃N₄ ceramics. The corrosion in acids, bases and under hydrothermal conditions is mainly determined by the quantity and composition of the grain boundary phase. The stability of the grain boundary phase could be predicted by the results of glass corrosion (Clark and Zito, 1992; Clark *et al.*, 1976; Paul, 1977). In HF solutions the main components dissolve. Therefore, in HF containing solutions the stability is low.

SiC ceramics

(Schmalzried and Schwetz, 2010; Meschke and Kailer, 2004; Kitaoka *et al.*, 1994; Presser *et al.*, 2009; Gogotsi, 1994; Sydow *et al.*, 2010; Herrmann *et al.*, 2015; Striegler *et al.*, 2018).

Solid state sintered SiC ceramics (SSiC) (see microstructure in Fig. 1(a)) are the ceramics which are typically used when universal chemical resistance in aqueous media is required (e.g., bearings and seals of chemical pumps). SSiC shows a high chemical stability even in hydrofluoric acid (Schmalzried and Schwetz, 2010). Due to the good tribological properties and the high corrosion resistance, SSiC is used as bearing and sealing material (Schmalzried and Schwetz, 2010; Meschke and Kailer, 2004; Presser et al., 2009).

The SiC reacts under hydrothermal conditions in different ways:

In the temperature range of 100–200°C it reacts in water predominantly according to (Kitaoka et al., 1994)



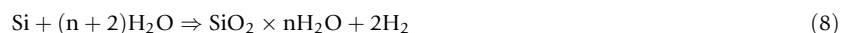
and partially



Additionally, at 300°C, C₂H₆ (less than 1% of the amount of H₂), CO₂ and CO were observed in the gas phase indicating different reaction mechanisms. In the presence of dissolved oxygen in the water CO₂ and CO were dominant reaction products. Reaction (6) is a redox reaction whereas reaction (7) is simple hydrolysis. It has been shown, that by hydrothermal corrosion carbon layers can be formed on SiC and different carbides and metal carbide layers are formed by a treatment of MAX phases (Gogotsi, 1994; Anasori et al., 2017).

It can be stated that of all the common structural ceramic materials, solid state sintered silicon carbide (SSiC) has a universal stability in various media (Fig. 9). For this reason, and because of its favorable tribological properties, SiC is widely used for highly stressed bearings and seals (Herrmann, 2013a; Schmalzried and Schwetz, 2010; Presser et al., 2009).

Silicon infiltrated SiC ceramics (SiSiC) (see microstructure in Fig. 1(c)) are used for seals and bearings, partly because of their good tribological properties and low production costs for large components. However, SiSiC has a low stability in HF as well as in alkaline solutions and under hydrothermal conditions, as the free Si is dissolved by reaction



The formed SiO₂ has an increased solubility as silicates in alkaline solutions and as silicic acid under hydrothermal conditions.

The dissolution of the 3-dimensional network of Si is the reason for the observed strength reduction (Fig. 9).

The stability of *liquid phase sintered SiC (LPSSiC)* is determined by the oxide grain boundary phases formed. They are nearly fully crystallized (usually Y₃Al₅O₁₂; Al₂O₃, YAlO₃; and/or Y₄Al₂O₉) and are quite stable in acids and bases of medium concentration. However, the corrosion stability is somewhat lower than for SSiC. The formation of pits results in the reduction of strength (Fig. 9). (Herrmann and Klemm, 2014; Herrmann, 2013a; Schmalzried and Schwetz, 2010). Therefore, retention of the properties under corrosive conditions relates to minimization of defects (segregation of additives and pores).

Conductive ceramics such as SiC, other carbides or electrically conductive composite ceramics (e.g., Al₂O₃/TiC; Si₃N₄/SiC, Si₃N₄/TiN) may be subject to electrochemical corrosion in addition to pure chemical corrosion. These processes are very similar to the electrochemical corrosion processes of metals. However, the corrosion current densities are usually much lower (Sydow et al., 2010; Herrmann et al., 2015). The investigation of the electrochemical corrosion of SSiC ceramics revealed that in H₂SO₄ the reaction



is the dominant electrochemical reaction (Herrmann et al., 2014b).

Such electrochemical corrosion can cause corrosion under conditions where the material is otherwise stable. For example, local corrosion of SiC mechanical seals has been observed in deionized water. (Meschke and Kailer, 2004).

Conclusions

Overall, the corrosion behavior of ceramic materials in aqueous solutions is well understood. Modeling at different levels from atomic level to macro kinetics promises to deepen the understanding in the future (Frankel et al., 2018; Moras et al., 2011; Philippe and Vincent, 2017).

The existing knowledge can be used for the selection of materials for different applications. However, the corrosion behavior of the materials strongly depends on the existence and composition of small amounts of impurities, grain boundary phases (e.g., Si₃N₄; Al₂O₃-ceramics), grain size or dopants of the main component (especially ZrO₂ ceramic (TZP)) and the environmental conditions. The corrosion behavior is affected by superimposed tribological or mechanical load. Therefore, a careful selection of the materials for a given application must be carried out.

References

- Anasori, B., Lukatskaya, M., Gogotsi, Y., 2017. 2D metal carbides and nitrides (MXenes) for energy storage. *Nat. Rev. Mater.* 2 (2017), 16098. doi:10.1038/natrevmats.2016.98.
- Aza, A.H., Chevalier, J., Fantozzi, G., 2002. Crack growth resistance of alumina, zirconia and zirconia toughened alumina ceramics for joint prostheses. *Biomaterials* 23, 937–945.
- Barsoum, M., 2003. *Fundamentals of Ceramics*. Bristol and Philadelphia: Institute of Physics Publishing.
- Brevier Technische Keramik, ed., 2020. Informationszentrum Technische Keramik Verband der Keramischen Industrie e.V. Verlag Hans Carl 90411 Nürnberg. Available at: http://www.keramverband.de/brevier_dt/brevier.htm.

- Chevalier, J., Gremillard, L., Virkar, A.V., Clarke, D.R., 2009. The tetragonal–monoclinic transformation in zirconia: Lessons learned and future trends. *J. Am. Ceram. Soc.* 92, 1901–1920. doi:10.1111/j.15512916.2009.03278.x.
- Clark, E.D., Zito, B.K., 1992. *Corrosion of Glass, Ceramics and Ceramic Superconductors*. Park Ridge New Jersey, USA: Noyes Publications.
- Clark, D.E., Dillmore, M.F., Ethridge, E.C., Hench, L.L., 1976. Aqueous corrosion of soda-silica and soda-lime-silica glass. *J. Am. Ceram. Soc.* 59, 62–65.
- Dong, Y.C., Lin, B., Zhou, J., *et al.*, 2011. Corrosion resistance characterization of porous alumina membrane supports. *Material Characterization* 62, 409–418.
- Frankel, G.S., Vienna, J.D., Lian, J., *et al.*, 2018. A comparative review of the aqueous corrosion of glasses, crystalline ceramics, and metals. *npj Mater. Degrad.* 2 (15). doi:10.1038/s41529-018-0037-2.
- Freiman, S.W., Wiederhorn, S.M., Mecholsky, J.J., 2009. Environmentally enhanced fracture of glass: A historical perspective. *J. Am. Ceram. Soc.* 92, 1371–1382.
- Galuskova, D., Galusek, D., Sajgalik, P., 2014. Evaluation of corrosion of engineering ceramics by atomic emission spectrometry in inductively coupled plasma. *Ceramics-Silikaty* 58 (1), 39–45.
- Galuskova, D., Hnatko, M., Galusek, D., Sajgalik, P., 2011a. Corrosion of structural ceramics under sub-critical conditions in aqueous sodium chloride solution and in deionized water. Part II: Dissolution of Al_2O_3 -based ceramics. *J. Am. Ceram. Soc.* 94, 3044–3052.
- Galuskova, D., Hnatko, M., Galusek, D., Sajgalik, P., 2011b. Corrosion of structural ceramics under subcritical conditions in aqueous sodium chloride solution and in deionized water. Part I: Dissolution of Si_3N_4 -based ceramics. *J. Am. Ceram. Soc.* 94, 3035–3043. doi:10.1016/j.matchar.2011.01.012.
- Gogotsi, Y.G., 1994. Hydrothermale Korrosion von SiC – Betrachtung der schädlichen und nützlichen Aspekte in Keramik in Wissenschaft und Praxis. In: Telle, R. (Ed.), *Korrosion und Verschleiß von keramischen Werkstoffen*, pp. 114–122. FoB DKG.
- Herrmann, M., 2013a. Ceramic Bearings and seals. In: Somiya, S. (Ed), *Handbook of Advanced Ceramics: Materials, Applications, Processing and Properties*, second ed. Academic Press, pp 301–328.
- Herrmann, M., 2013b. Corrosion of silicon nitride materials in aqueous solutions. *J. Am. Ceram. Soc.* 96, 3009–3022.
- Herrmann, M., Klemm, H., 2014. Corrosion of ceramic materials. In: *Comprehensive Hard Materials*, second ed. Newnes, pp 413–446.
- Herrmann, M., Kluge, E., Rödel, C., McKie, A., van Staden, F., 2014a. Corrosion behaviour of silicon carbide diamond composite materials in aqueous solutions. *J. Europ. Ceram. Soc.* 34, 2143–2151.
- Herrmann, M., Sempf, K., Schneider, M., *et al.*, 2014b. Electrochemical corrosion of silicon carbide ceramics in H_2SO_4 . *J. Europ. Ceram. Soc.* 34, 229–235.
- Herrmann, M., Sempf, K., Kremmer, K., *et al.*, 2015. Electrochemical corrosion of silicon infiltrated silicon carbide ceramics in aqueous solutions. *Ceram. Int.* 41, 4422–4429.
- ISO, 2020. Corrosion of metals and alloys – Vocabulary; Trilingual version EN ISO 8044:2020.
- ISO, 2006. Advanced technical ceramics – Monolithic ceramics – Part 1: General practice for undertaking corrosion tests; German version ISO EN 12923-1:2006.
- Johannes, M., Schneider, J., 2012. Processing of nanostructured zirconia composite ceramics with high aging resistance. *J. Cer. Sci. Tech.* 3, 151–158.
- Keuper, M., Eder, K., Berthold, C., Nickel, K.G., 2013. Direct evidence for continuous linear kinetics in the lowtemperature degradation of Y-TZP. *Acta Biomater.* 9, 4826–4835.
- Kitaoka, S., Toshidhide, T., Toshio, K., Yamaguchi, Y., Kashiwagi, K., 1994. Tribological characteristics of SiC ceramics in high temperature and high pressure water. *J. Am. Ceram. Soc.* 77, 1851–1856.
- Lawson, S., 1995. Environmental degradation of zirconia ceramics. *J. Europ. Ceram. Soc.* 15, 485–502.
- Lughi, V., Sergio, V., 2010. Low temperature degradation – Aging- of zirconia: A critical review of the relevant aspects in dentistry. *Dental Mater.* 26, 807–820.
- McCauley, R.A., 1995. *Corrosion of Ceramics*. New York: Marcel Dekker, Inc.
- Meschke, F., Kailer, A., 2004. Electrically driven cold water corrosion of SiC. *Ceram. Forum Int.* 81, E19–E22.
- Mikeska, K.R., 1999. Corrosion of alumina in aqueous hydrofluoric acid. *J. Am. Ceram. Soc.* 82, 3561–3566.
- Mikeska, K.R., Bennison, S., Grise, S., 2000. Corrosion of ceramics in aqueous hydrofluoric acid. *J. Am. Ceram. Soc.* 83, 1160–1164.
- Moras, G., Pastewka, L., Gumbsch, P., *et al.*, 2011. Formation and oxidation of linear carbon chains and their role in the wear of carbon materials. *Tribol. Lett.* 44, 355. doi:10.1007/s11249-011-9864-9.
- Nickel, K.G., Gogotsi, Y.G., 2000. Corrosion of Hard Materials. In *Handbook of Ceramic Hard Materials*. Wiley-VCH. pp. 140–182.
- Paul, A., 1977. Chemical durability of glasses; a thermodynamical approach. *J. Mat. Sci.* 12, 2246–2268.
- Philippe, M., Vincent, M., 2017. Atomic level characterization in corrosion studies. *Philos. Trans. R. Soc. A* 37520, 160414. doi:10.1098/rsta.2016.0414.
- Presser, V., Nickel, K.G., Krummhauser, O., Kailer, A., 2009. A model for wet silicon carbide tribo-corrosion. *Wear* 267, 168–176.
- Sato, T., Sato, S., Okuwaki, A., 1991. Corrosion behavior of alumina ceramics in caustic alkaline solutions at high temperatures. *J. Am. Ceram. Soc.* 74, 3081–3084.
- Schilm, J., 2004. PhD IKTS/TU BAFKorrosionsverhalten von Siliciumnitridkeramiken in Säuren.
- Schilm, J., Herrmann, M., 2010. Korrosion in wässrigen Medien. In: Kollenberg, W. (Ed.), *Technische Keramik*, 2. Auflage Essen: Vulkan Verlag, pp. 102–106.
- Schmalzried, C., Schwetz, K.A., 2010. Silicon carbide and boron carbide based hard materials. In: Riedel, R., Chen, I.W. (Eds.), *Ceramic Science and Technology*. Wiley VCH, pp. 131–225.
- Striegler, M., Matthey, B., Mühle, U., Michaelis, A., Herrmann, M., 2018. Corrosion resistance of silicon infiltrated silicon carbide (SiSiC). *Ceram. Int.* 44, 10111–10118. doi:10.1016/j.ceramint.2018.02.229.
- Sydow, U., Schneider, M., Herrmann, M., Kleebe, H.-J., Michaelis, A., 2010. Electrochemical Corrosion of Silicon Carbide Ceramics Part 1: Electrochemical Investigation of sintered Silicon Carbide (SSiC). *Mater. Corros.* 61, 657–664.

Corrosion and Degradation of Glass

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Introduction

Chemical degradation of glass-based materials is often considered unimportant, mainly due to the fact, that glass is generally perceived as very durable material. Highly corrosion resistant glass-based materials are utilized as coatings (glazes and enamels) for corrosion protection of less durable materials, notably metals. They also serve as inert matrices for storing dangerous waste, both chemical or radioactive. On the other hand, degradation of glass, either through direct corrosion in various environments (e.g., dishwashing in large gastronomy, as the most palpable example), or weathering when exposed to elements, causes significant losses to glass producers and users. Leaching of components of glass to liquid content stored in container glass vessels might impair the safety of food, beverages, and above all drugs and medicals. Controlled dissolution of some specific glass compositions facilitates its use in the human body as a biomaterial, replacing both hard (bones) and soft (cartilage) tissues. All these applications require a deep understanding of the mechanisms responsible for glass degradation, and detailed knowledge of the influence of glass composition and structure on its dissolution in various agents, at a molecular level.

Corrosion

All materials in contact with various types of environments show a certain degree of interaction. Interactions resulting in the degradation of mechanical and physical properties or appearance of a material have a negative impact on the usability of the material in the long run. Corrosion can therefore be defined as physical and chemical changes in a material caused by interactions with the environment in which the material is used. For the three main groups of materials, i.e., metals, glass (including ceramics), and polymers, the degradation mechanisms differ. Unlike metals, glass is perceived as chemically highly resistant at low temperatures ($<100^{\circ}\text{C}$), and corrosion occurs mostly at elevated temperatures or in contact with aggressive, mostly aqueous, environments.

The term glass corrosion is then applied for a complex interaction between a glass surface and a corrosive medium (in most cases an aqueous solution). As a consequence, irreversible changes both to glass and to the solution occur.

Corrosion can be classified using several parameters: the way of the attack, the site of the attack, and the medium in which the material is used or to which it is exposed. The classification of individual parameters is schematically shown in [Table 1](#) (Nickel, 1997).

Basic classification of the type of corrosion distinguishes between active and passive corrosion. In the active form, a glass in contact with the corrosive environment is gradually lost, by dissolving in a liquid corrosion environment which is accompanied by a change in the size and weight of the sample.

The passive form involves processes where the glass reacts with a corrosive environment to form a new condensed phase covering its surface. Weight gain or positive change in sample size is observed. The new phase can slow down the corrosion process over time (surface passivation), but there are also cases where the newly formed layer does not prevent further attack of the corrosive medium (Riedel, 2000).

In terms of location of the corrosion attack, the glass, as a phase-homogeneous material, is characterized by external corrosion, where the surface is usually attacked evenly, and the material is either evenly dissolved or a uniform layer of corrosive products is formed. The process becomes more complex if grain boundaries or a secondary phase in the form of finely dispersed particles (e.g., in glass-ceramics)

Table 1 Classification schemes of corrosion

Weight and volume change	Negative	Active corrosion	
	Positive	Passive corrosion (layer of corrosion products is formed)	Slows down corrosion (protective role) Does not affect corrosion rate
Physical-chemical conditions of corrosion medium	Solution (e.g., acid)		
	Melt	Metal Ionic liquid	Hot corrosion Salts/slugs Silicate melts
	Gas		Hot gas corrosion
Location of the corrosion attack	Whole surface		
	Localized	Random places Secondary phases Grain boundaries	

are present in the material, each phase reacting differently with the environment: in this case, localized attack and uneven corrosion of the glass matrix may occur.

Significant differences in the corrosion behavior of individual materials are caused by the variability of the corrosive environment. Corrosive behavior is thus not a property of the material as such, but that of the whole system material – corrosive medium. Therefore, there exists no standard, generally applicable procedure to evaluate the corrosive behavior of glass, just as it is not possible to devise a generally applicable corrosion mechanism to glasses of various compositions and exposed to various environments. The chemical resistance of glass is thus affected by the glass itself and the conditions to which the glass is exposed. The procedures for evaluation of various types of glass under various conditions are specified in a number of norms and standards (DIN 52289: 1998–09, 1998; DIN-EN 12875–2, 2002; ISO 10629:1996, 1996; ISO 20492:2008, 2008; ISO, 4794:1982, 1982; ISO, 8424:1996, 1996).

Corrosion Media

The variability of corrosive environments is so large that any attempts to classify corrosion behavior entirely from the point of view of the individual environment were bound to fail. The most commonly used scheme classifies the corrosive media according to their physical state. Relatively large attention has been paid to the corrosion of various types of materials in hot gases, but this environment is usually irrelevant for the corrosion of glass. Ambient air, which is relevant for the degradation of glass by weathering, is also a corrosive environment. In this case, the primary corrosive agent is moisture containing dissolved oxygen, but sulfur compounds (SO_2 , SO_3) and sodium chloride, which is often present in the air, especially in coastal areas, also contribute to corrosion. A diluted sulfuric acid solution in the form of acid rain is a source of corrosion in industrial areas.

The most relevant and most frequently investigated media for glass corrosion are liquids, i.e., aqueous solutions (acids, bases or solutions of inorganic salts), (Callister, 2005; Tressler and McNallan, 1990; Schilm *et al.*, 2007). In terms of its corrosion characteristics, the aqueous environment is extremely diverse. Natural water usually contains dissolved oxygen and other minerals, some of which determine the hardness of the water. Seawater is generally more aggressive than freshwater, containing approximately 3.5 wt% of salts (mainly sodium chloride) as well as some other minerals and organic substances (Herrmann *et al.*, 2000).

Thermodynamic Equilibrium in the System Glass-Liquid

Chemical thermodynamics deals with chemical changes that take place in a system glass-liquid corrosion medium, such as changes in the composition of the corrosive medium, changes in the molar amount of the individual components in the system as a result of chemical reactions, and transitions of the components between phases, and the composition of the corrosive medium after reaching equilibrium.

All chemical reactions tend to reach equilibrium, i.e., each system tries to reach the state with the lowest energy, which is accompanied by a decrease in the value of the total Gibbs energy G of the system. The Gibbs energy is then a function of the extent of the reaction ξ , i.e., $G = G(\xi)$. The Gibbs energy of any substance or phase in a system depends on a number of factors, temperature, pressure, and composition, in particular. This dependence is described by Eq. (1) (Stumm and Morgan, 1996; Oelkers *et al.*, 2009):

$$dG = Vdp - SdT + \sum_{i=1}^k \mu_i dn_i \quad (1)$$

where V is volume, p is pressure, S is entropy, T is thermodynamic temperature and μ_i and n_i represent the chemical potential and concentration of the i -th component, respectively. If we consider a system at a constant temperature and pressure, the first two terms on the right side of the equation are equal to zero. From the mass balance equations, it applies that $dn_i = v_i d\xi$. Then:

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \sum_{i=1}^k v_i \mu_i = \Delta_r G_m, \quad (2)$$

where v_i represents the stoichiometric coefficient of component i . The equilibrium state of the system, i.e., the state with the smallest value of Gibbs energy, is characterized by the equilibrium value of the extent of the reaction $\xi = \xi_{\text{eq}}$, for which $\Delta_r G_m = 0$.

To illustrate the dissolution of a glass containing components B, where B represents cationic components, and A stands for anionic components, we can use, similarly to the dissolution of ionic compounds or minerals, a dissociation reaction (Eq. 3):



Where indices s and aq represent solid and liquid phases, respectively. The distribution of components in equilibrium can be then described as follows:

$$K_c = \frac{a(B_{aq}^{n+})a(A_{aq}^{n-})}{a_{BA}} \quad (4)$$

where a_i is the activity of the respective ion in solution and a_{BA} is the activity of the solid phase. Based on the definition of the

standard state, the activity of the solid phase is equal to 1; K_c is then equal to the solubility product K_s . In the case of a substance with complex stoichiometry, the equilibrium constant is generally expressed as $K = \prod a_i^{v_i}$, where v_i is the stoichiometric coefficient of the ion i in the formula of the solid. When we replace the chemical potential μ_i with the activity a_i , the expression for the Gibbs energy change takes the form:

$$\Delta_r G_m = \sum_{i=1}^k v_i \mu_i^o + RT \ln \prod_{i=1}^k a_i^{v_i} \quad (5)$$

where the first term on the right side of the equation represents the standard Gibbs energy. The activity of the components i in the system at a certain moment is expressed by the quantity Q , defined as $Q = \prod_i a_i^{v_i}$.

After reaching equilibrium, when $\Delta_r G_m = 0$, the numerical value of Q is identical with the equilibrium constant K . Then:

$$\Delta G_m^o = -RT \ln K \quad (6)$$

$$\Delta_r G_m = RT \ln \frac{Q}{K} \quad (7)$$

Comparing the values of Q and K provides information on whether the system is unsaturated ($\Delta_r G_m < 0$, the glass dissolves in liquid medium), in equilibrium ($\Delta_r G_m = 0$), or supersaturated ($\Delta_r G_m > 0$), and precipitation of reaction products at glass surface if favored, Schott *et al.* (2009).

The thermodynamic approach to the chemical durability of glass is based on a thermodynamic description of the solution with dissolved constituents of glass. We can define the Gibbs energy of formation of glass from elements G_{GL} as a difference between the Gibbs energy of formation of isocompositional polycrystalline system G_C and G_{vit} – the energy difference between the polycrystalline and the vitreous state. If we denote the energy state of an aqueous system containing dissolved glass constituents G_{GLaq} , we obtain the driving force of glass corrosion as ΔG_{hydr}

$$\Delta G_{hydr} = G_{GLaq} - G_{GL} \quad (8)$$

where the value ΔG_{hydr} is the quantitative representation of glass durability (Conradt, 2018). In terms of thermodynamic states, the glass corrosion at temperature T can be described by the sequence $\text{Glass}(T) + \text{aq.soln.}(T) \rightarrow \text{aq.species}(T)$ (Conradt *et al.*, 1999). The quantity ΔG_{hydr} is then influenced by the composition of glass, the energies of the formation of glass and its aqueous solution, and the temperature dependencies of the associated processes.

The rate of glass dissolution is influenced by temperature. According to Arrhenius Eq. (9), the rate constant changes with temperature exponentially:

$$k = A \cdot \exp\left(-\frac{E_A}{RT}\right) \quad (9)$$

where k is the reaction rate constant, and A is the empirical pre-exponential factor. The overall dissolution of glass is usually described through the dissolution of the rate-controlling species, which in silicate glasses is usually silica. Silicon atoms have to pass through an energetically unfavorable transient state, creating an activated complex characterized by the activation energy E_A . The activation energy represents the energy barrier that must be overcome for dissolution to occur. By logarithmizing the expression (Eq. 9) takes the form (Eq. 10):

$$\ln k = \ln A - E_A/RT \quad (10)$$

The $\ln k$ dependence on $1/T$ is linear, with the slope defined by (Eq. 11):

$$\frac{d \log k}{d(1/T)} = \frac{-E_A}{2.303R} \quad (11)$$

Diffusion processes in the liquid phase are characterized by low E_A values in the range of a few kJ mol^{-1} . The values in the range of about 80 kJ mol^{-1} are typical for surface reactions, while values of several hundred kJ mol^{-1} are associated with recrystallization processes (White, 1992). Based on the determined values of activation energies, we can infer the dissolution mechanisms. Some typical values of activation energies for chemical and transport processes are given in Table 2 (Appelo and Postma, 2005).

Table 2 Values of activation energies for chemical transport processes related to glass dissolution

Process	E_a (kJ mol^{-1})
Photochemical reactions	15 (10–30)
Diffusion in water	20
Dissolution and precipitation	60 (20–80)
Biochemical reactions	63 (50–75)
Solid state diffusion	500 (200–650)

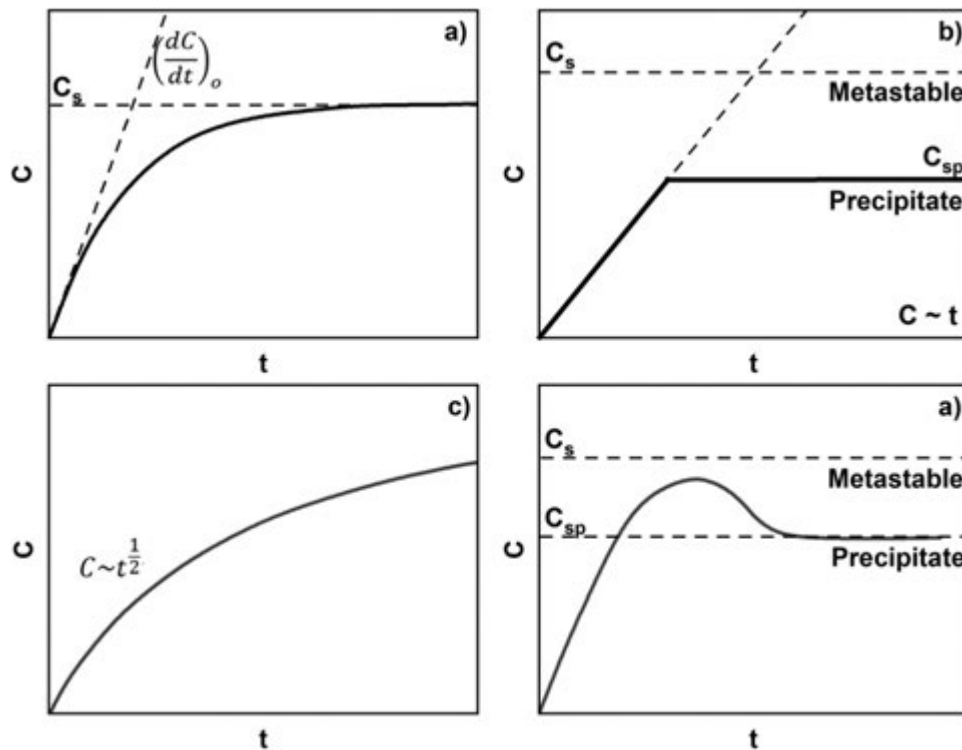


Fig. 1 Curves describing the rate of ion transfer into solution for different dissolution mechanisms. (A) Solid equilibrates with the solution when the saturation concentration of C_s is achieved. (B) Linear kinetic dependence interrupted by formation of a precipitated phase. (C) Diffusion controlled (parabolic) dissolution kinetics. (D) Dissolution slowed by the formation of a precipitated phase.

Kinetics of Glass Corrosion

When modeling the kinetics of the corrosion process and determining the kinetic constants, we usually assume a steady-state and constant activity of the corrosion factor in the environment and an infinite amount of corroded material. A corrosion rate is then defined as a loss of matter per surface area and time.

The transport of ions from the glass to the solution can be schematically described by the curves shown in Fig. 1. If the glass is in contact with the corrosion medium, it gradually becomes saturated with respect to the content of the ionic components. The amount of dissolved material and the concentration of dissolved components increase with time. The dissolution rate slows over time and stops when the concentration of dissolved components reaches an equilibrium concentration. Heterogeneous and homogeneous reactions take place at the glass-corrosion medium interface. Any such reaction is characterized by the following steps:

- (1) Transport of reactants to the surface of the solid.
- (2) Adsorption of reactants.
- (3) Chemical reactions between adsorbed components and surface.
- (4) Desorption of reaction products.
- (5) Transport of reaction products into the volume of the corrosive medium.

The dissolution rate itself can be quantified according to the type of rate-controlling process. These are usually classified as follows (Giess, 1963; Sharp *et al.*, 1966; Berehta, 1984):

- (1) Film diffusion control (reaction rate controlled by the flow velocity of the solution),
- (2) Surface control (rate control by an energy barrier, e.g., an activated complex, in the surface),
- (3) Pore diffusion control (rate control by diffusion through a growing layer),
- (4) Nucleation and crystallization rate control (i.e., the formation of a new secondary phase in the vicinity of the dissolving phase).

During active corrosion under steady-state conditions, the material is lost by decomposition or dissolution. The flow of mass from corroded material can be expressed by Eq. (8):

$$J = k_r c_i \quad (12)$$

where J is the mass flow, k_r the reaction coefficient, and c_i the concentration of dissolved component i at the interface. For first-order reactions under steady-state conditions, the dependence is linear. The diffusion-controlled kinetics is then described by Fick's first law. At equilibrium, the concentration gradient does not change, the thickness of the diffusion layer remains constant, and the

flow J is also constant. The weight loss (Δx) of the dissolving material will change linearly with time t :

$$\Delta x = k_t t \quad (13)$$

where k_t is the rate constant (g s^{-1}).

In the case of passive corrosion accompanied by the formation of a layer of reaction products, the situation is more complex. A more or less porous layer of precipitated or re-mineralized secondary phases forms on top of the residual glass. The layer either acts as a diffusion barrier or controls the elemental concentrations in the solution at the interface to the residual glass. In the simplest case, the corrosion is controlled by chemical reaction. If the reaction proceeds slowly compared to the flow of reagents to the reaction site, the concentration of solute at the interface is as high as its concentration in the surrounding corrosive medium. In this case, for a given temperature, the linear time dependence of the mass change is observed, following Eq. (13). The term Δx is positive and represents the growth of the layer of reaction products accompanied by weight increase.

Another case is a homogeneously growing single-phase layer that allows slow transport of the corrosive medium to the corroded material by diffusion. Steady-state means that the thickness of the diffusion layer increases with time, while the absolute value of the concentration gradient remains constant. In this situation we also apply the first Fick's law, with the equation assuming a parabolic form, where k_p is the rate constant (Eq. 14):

$$(\Delta x)^2 = k_p t \quad (14)$$

Another case of passive corrosion is represented by the situation where the reaction products that form on the glass surface completely block the access of the corrosive agent, resulting in a rapid reduction in the surface area available for chemical reactions. The process is described by a logarithmic dependence (Eq. 15):

$$\Delta x = k_t t + k_{\log} \log t \quad (15)$$

with the logarithmic rate constant $k_{\log}$. If the corrosion is controlled by diffusion through the passivating layer and the crystallized phase completely blocks the corrosive agent or its diffusion coefficient is much smaller than that of the original layer, the effective cross-section for transporting the corrosive agent decreases rapidly.

However, in real life, the situation is more complex, and the dissolution rates of glass are influenced by numerous parameters (temperature, pH, the chemical composition of an aqueous system, and a solid phase), which are in most cases time-dependent. The concepts originally developed in geochemical literature were adopted to glass corrosion by a number of authors, e.g., Grambow (1985), Advocat *et al.* (1990), Bourcier *et al.* (1990), Grambow (1992), Helebrant (1997), and McGrail *et al.* (1997). In its most general form, the corrosion rate can be expressed by Eq. (16) (Conradt, 2008):

$$r = r_+ f(i) \left(1 - \frac{I_p}{I_{ps}} \right) \quad (16)$$

With the symbols denoting the following quantities: r - corrosion rate, r_+ - a forward rate, and $f(i)$ a term summarizing the effects of dissolved species i on the dissolution rate. The term $1 - I_p/I_{ps}$ expresses the degree of saturation of the solution in terms of the respective ion activity product I_{ps} with the index s denoting saturation. The forward rate r_+ is expressed as (Advocat *et al.*, 1990):

$$r_+ = X \cdot e^{\left(-\frac{E_A}{RT}\right)} e^{\left(-\frac{\Delta G_h}{RT}\right)} \quad (17)$$

where X is a constant, E_A the activation energy (for silicate glasses usually around 80 kJ/mol (Scholze, 1990)), and ΔG_h is the Gibbs energy of hydration.

Due to the lack of experimental data on the nature and time dependence of precipitated layer thickness, the mathematical description of its formation is mostly based on a semi-empirical approach. The precipitation can take place either by back precipitation of the species dissolved from glass (e.g., during the dissolution of glass in deionized water) or by precipitation of the species originally contained in the corrosion medium (e.g., during the dissolution of bioactive glasses in simulated body fluids). In both cases, two mechanisms of precipitated layer formation can be considered: (a) the activity products of dissolved ions exceed their solubility products, and new phases are formed by precipitation from the solution. The second mechanism assumes a direct reaction of ions in a sub-surface zone (Fig. 2) at the glass-liquid interface. For both mechanisms, the rate of precipitation is assumed to be directly proportional to the rate of dissolution (Conradt, 2008). The precipitation rate R_p can be expressed as a function of supersaturation with respect to precipitated compounds (Eq. (18), Mann *et al.*, 1989):

$$R_p = k_p \left[\left(\frac{I_p}{K_s} \right)^{\frac{1}{j}} - 1 \right]^n \quad (18)$$

Where i is the exponent reflecting the precipitation mechanism, K_s is the solubility product, and j the number of ions in the precipitated compound. The thickness h of the precipitated layer can be described by Eq. (19) (Helebrant, 1997):

$$h = h_n \left(1 - e^{-\frac{k_h}{t}} \right) \quad (19)$$

where h_n represents is the final layer thickness and k_h represents a rate constant.

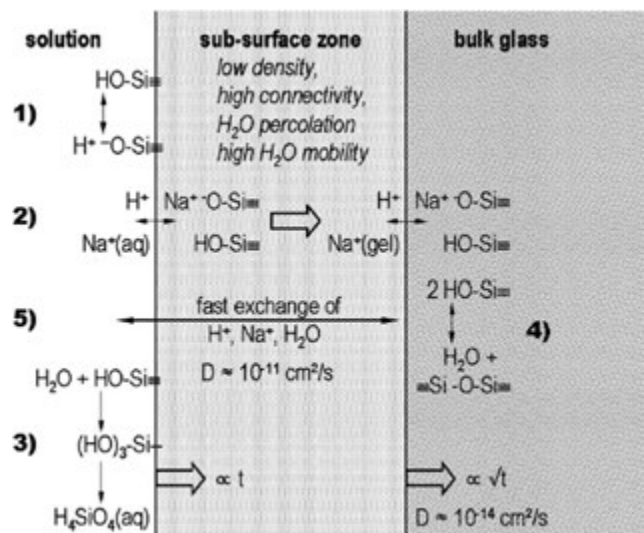


Fig. 2 Subsurface zone in a sodium silicate glass and related phenomena: (1) instantaneously established electrochemical surface equilibrium; (2) ion exchange; (3) cleavage of silica bonds; (4) condensation of silanol groups (gel formation); (5) fast exchange of metal ions, protons, and molecular water. Reproduced from Conradt, R., 2008. Chemical durability of oxide glasses in aqueous solutions: A review. *Journal of the American Ceramic Society* 91, 728–735.

Parameters Influencing the Corrosion of Glass

As mentioned above, corrosion of glass is a process influenced by many parameters, which are specific for any particular system glass-corrosion environment. For the sake of simplicity, in this section we will focus on the systems most relevant from a practical point of view, i.e., oxide (and in most cases silicate) glasses exposed to an aqueous environment. The parameters influencing the corrosion of glass can be attributed to the properties of corroded material (the composition and structure of glass, its surface finish), the characteristics of the corrosion medium (pH, ionic strength, presence of buffers), and the conditions of corrosion process (temperature, surface area to solution volume ratio, static versus dynamic conditions).

The dissolution rate and corrosion mechanisms of glasses critically depend also on the quality of the corroded surface and the formation and presence of corrosion and gel layers, and the layers of reaction products formed in the process of corrosion. Mechanical surface damage by e.g., grinding or polishing can become an initiation point of corrosion and its penetration into the depth of the material.

Characteristics of the Corrosion Medium

In general, the silicate glasses are most stable in slightly acidic, neutral, or slightly basic environment (pH ~ 4–8), less stable in strong acids, and poorly corrosion resistant in strongly basic solutions.

The ionic strength, i.e., the presence of dissolved ionic salts has a significant influence on the elementary mechanisms of corrosion. For example, a 1 M NaCl solution at the neutral pH accelerates the corrosion rate of silicate glasses in the same manner as a 1 M solution of HCl (Conradt, 2018). The presence of alkali ions in a solution significantly increases the number of surface charges in the weakly acidic or neutral solutions, thus enhancing the glass dissolution rate. This must be considered especially during *in vitro* tests of bioactive glasses, as the physiological fluids in the human body contain approximately 9 g L⁻¹ of NaCl.

Buffers in corrosion solutions not only maintain the pH at a constant level but also interfere with elemental mechanisms of glass dissolution. Moreover, the pH in a bulk of the corrosion medium might significantly differ from the pH at the liquid/glass interface since some products of glass dissolution, e.g., siliceous acid, also act as buffers.

Conditions of the Corrosion Process

Temperature is a parameter that critically influences the corrosion and dissolution of glass in aqueous media. The activation energy of dissolution of a silicate glass in aqueous media usually ranges between 60 and 80 kJ mol⁻¹, which means that the increase of temperature by 10K increases the reaction rate by a factor of 2.3 (Oelkers *et al.*, 2009). The change of temperature also affects thermochemical equilibria (solubilities), thus influencing the formation of layers of corrosion products.

In addition to temperature, corrosion/dissolution of glass is influenced also by the ratio of the surface of the material to the volume of the corrosive medium A/V . With other parameters constant, the A/V parameter significantly influences the rate of glass dissolution (Kamizono *et al.*, 1989; Fillet *et al.*, 1986). Under laboratory conditions, the A/V ratio for monolithic samples usually ranges from 0.001 cm⁻¹ to 100 cm⁻¹. When the area of the sample is large with respect to the volume of the corrosive medium

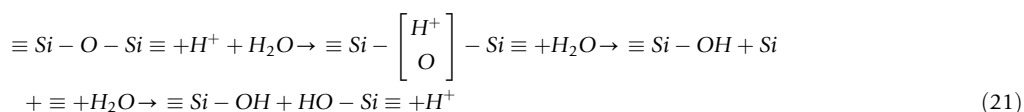
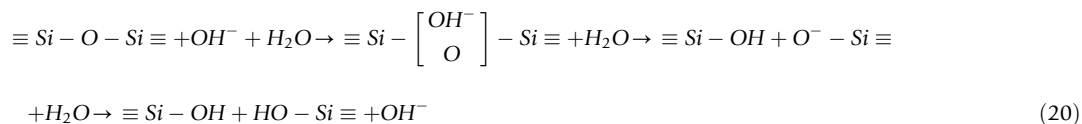
($A/V > 10 \text{ cm}^{-1}$), supersaturation of the corrosive solution by the components leached out of the materials can be achieved relatively quickly. This situation is common if the chemical/corrosion resistance of glass is tested under static conditions (i.e., without the exchange of the corrosive medium). This experimental arrangement is mainly used for the identification and analysis of the formed corrosion products and simulation of long-term action of the corrosion process. Due to the saturation effect, the surface of the monitored samples under static conditions is usually less degraded than in the samples tested at lower A/V values, or under a dynamic (flow-through) arrangement of the corrosion test.

Molecular Mechanism of Glass Corrosion in Aqueous Media

Depending on the conditions, water, even distilled water, becomes an aggressive corrosive agent. Due to the strong polarity of the O–H bonds and the bent shape, the water molecule has a strongly polar character: as the glass interacts with water, the solvent molecules cluster around ions on the glass surface so that the positive poles of dipoles seek proximity to anions and negative poles center over cations. The ions are electrostatically attracted outwards from the glass surface: as a result, the attractive forces between the ions are substantially weakened. More often, however, chemical bonds of the donor-acceptor type are formed between cations and water molecules during hydration, and complexes of metal ions with water molecules are formed (Gažo, 1981). Inter-molecular (i.e., adsorption) interactions are among the most common chemical reactions that occur when a glass surface comes into contact with water as a solvent. These include surface complexation reactions (e.g., hydrolysis) as well as electrical interactions on the surface.

When silica-based glasses are exposed to an aqueous environment, several processes are usually considered. An electrochemical equilibrium is established first, within a very short period of time at the order of magnitude of a few tens of milliseconds (Bauke, 1985).

Subsequently, sodium ions are mobilized by excess charge resulting from protons entering the electron cloud of oxygen atoms at the glass surface, forming $\equiv\text{Si-OH}$ groups immediately. The glass (silica) matrix is then dissolved: silicon atoms go through a transition, energetically unfavorable state, forming activated complexes. The nature of these states depends on the surface charge equilibrium, influenced by the pH (Oelkers *et al.*, 2009). The two different types of transient states in the basic and acidic environment are described by Eqs. 20 and 21, respectively:

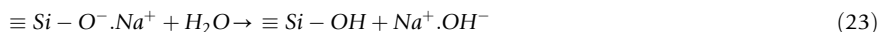


In both cases siloxane bonds $\equiv\text{Si-O-Si}\equiv$ are split into two silanol groups $\equiv\text{Si-OH}$ (Eq. 22).



After splitting all siloxane bonds of a SiO_4 tetrahedron, silica dissolves as siliceous acid. The amount of silica released to the solution depends on the coverage of the glass surface by charges, which is strongly influenced by the pH of the system. Regardless of the dissolution mechanism, a new thermodynamic equilibrium is established within the solution.

Subsequently, dynamic back and forth recombination reactions increase the connectivity of the glass structure and generate interstitial water molecules (Oelkers *et al.*, 2009; Scholze, 1959). This process is strongly influenced by the presence of glass modifiers, especially Na. Some studies conclude that the reaction described by the Eq. (22) is more relevant for the generation of OH groups in the glass structure than the reaction between molecular water and siloxane bonds (Eq. (23)), Behrens and Stuke (2003):



If Na^+ is later leached from the glass structure, the remaining matrix cannot contain such high amounts of OH^- groups, and condensation of molecular water in the glass structure occurs (Smets and Lommen, 1981). The subsurface zone is thus converted to a gel, consisting of a percolating SiO_2 network and H_2O molecules (Conradt, 2008). An exchange of ions and water molecules then continues between the gel zone and the solution. Finally, the outermost layer condenses to a dense silica network. The structural compaction results from condensation of initially formed silanol groups yielding a network with enhanced connectivity (Casey *et al.*, 1993; Portal and Sempere, 2003), and rendering a water-exposed glass surface more corrosion resistant than the original surface of the as-produced glass.

As a result of the processes described above, a subsurface layer with a chemical composition different from that of the bulk glass (not to be mixed with the formation of a layer of reaction products precipitating at the surface of glass due to supersaturation of corrosion media) forms at the contact between the liquid and the glass surface (Fig. 2, Conradt, 2008). Starting from the solution/glass interface, the layer consists of a transition zone, a zone with approximately constant water content, and a transition zone to the bulk (Scholze, 1975). Well established local chemical equilibria are characteristic for the subsurface zone. The depletion of elements from the zone does not follow the categories of a network former versus a network modifier, but rather their elemental solubilities in water. In some cases, crystalline precipitates may form in the subsurface zone (Portal and Sempere, 2003).

Structure, Composition, and Corrosion of Glass

The rate of glass degradation is often related to the network connectivity of its structure. It has been — at least partially successfully — applied for predicting degradation rate and hence, the bioactivity of a range of bioactive glasses (Hill and Brauer, 2011). This approach, however, requires reliable information on glass structure expressed in terms of an average number of bridging oxygens in the glass structure. This can be relatively reliably assessed for silicate glasses but runs into problems if additional network formers, e.g., phosphorus or boron with complex structural functions are present.

An alternative thermodynamical approach based on the works of Paul (1982) and Grambow (1992) has been therefore proposed. The approach is based on three assumptions: (1) the forward rate of the rate-controlling elementary step is temperature and pH-dependent; (2) the reaction turnover dependent Gibbs energy of hydration of glass, ΔG_{hydr} , accounts for glass composition effects; (3) the solubility product of the rate-controlling species (for silicate glasses usually SiO_2) is considered (Conradt, 2001). However, the solubility of amorphous silica is significantly influenced by the aqueous environment. Moreover, the traditional thermodynamic approach, which considers the ΔG_{hydr} as a parameter accounting for glass degradation, does not account for the effect of glass composition in an appropriate way. The ΔG_{hydr} is often calculated from the weighted contributions of hydration reactions of individual species, assuming that glass is a physical mixture of oxides and metasilicates, and to a great extent ignoring the glass structure as we understand it today (Conradt, 2001). The main problem is related to the fact, that with this attitude a glass must be considered an extremely non-ideal mixture of its oxide components, and requires consideration of mixing, structural and configurational effects. These difficulties can be overcome by the constitutional approach, based on the work of e.g., Shakhmatkin *et al.* (1994), who described glass as a mixture of its constitutional phases. In this case, the main constitutional problem is the determination of the crystalline reference state (C_R) of the glass. For a simple system, this information is contained directly in the respective phase diagram. For a more complex, multi-component, system a predominant ternary or quaternary oxide system is determined first. The constitutional phases from this system are then considered as major mineral phases in the system. The molar amounts of the phases are calculated from the composition of glass, and the thermodynamic quantities are determined. It has been confirmed that this approach correctly accounts for glass composition and yields significantly improved values of ΔG_{hydr} as a major parameter influencing the hydrolytic resistance of glass. However, many glasses exhibit a strong pH dependence of their degradation behavior, which cannot be explained merely on the basis of the ΔG_{hydr} values. These findings are usually interpreted through the coverage of glass surface by charged groups, expressed in terms of a surface coverage factor θ :

$$\theta \approx \sum_j \frac{k_j c_j}{1 + k_j c_j} \quad (24)$$

with k_j representing the adsorption of the charged species j , where $j = \text{H}^+, \text{OH}^-, \text{R}^+, \dots$, and c_j standing for its concentration. The pH dependence of the rates of degradation of glass is then determined by both ΔG_{hydr} and $\log \theta$.

Conclusions

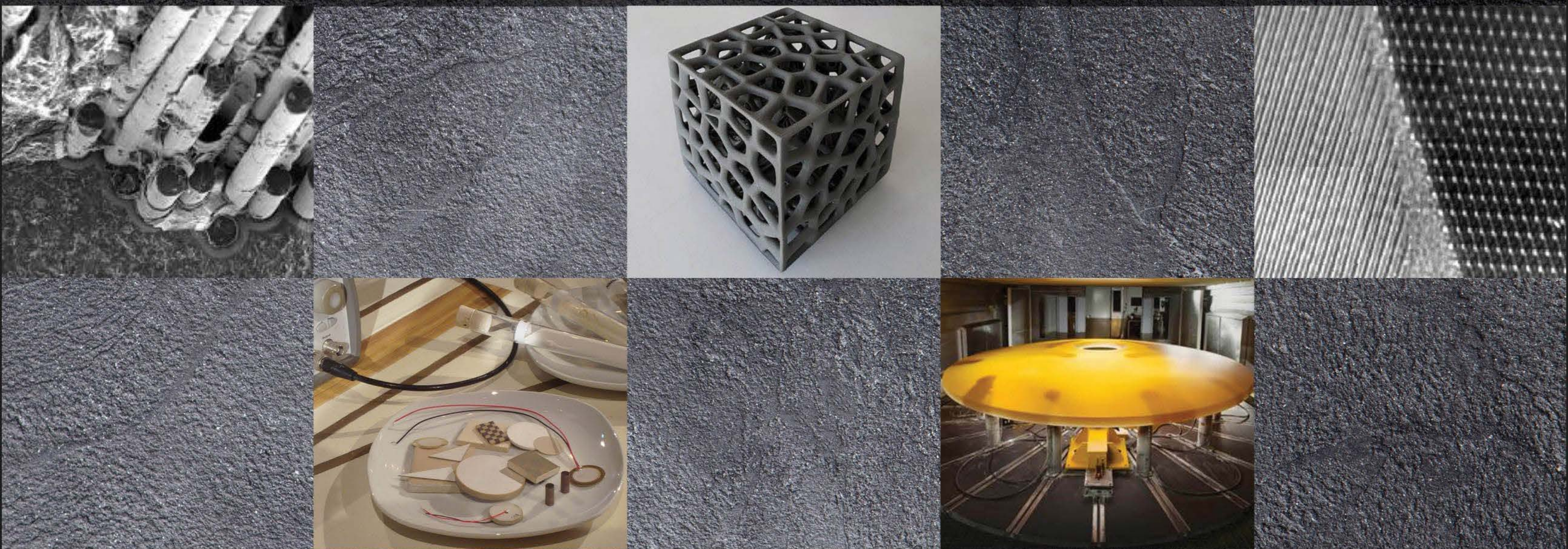
Corrosion and chemical degradation of glass are the processes, which markedly deteriorate the properties of glass products and limit their use. Due to a broad variety of glass compositions, and variability of corrosion environments, there exists no unified methodology of evaluation of glass corrosion properties, nor is there a possibility to describe the degradation of all types of glasses by a well defined and generally valid model with reliable predictive capacity. A constitutional approach describing glass as a mixture of its mineral constituents was found to provide a reliable estimation of degradation properties of several industrially relevant silicate glasses. Irrespective of the approach applied, any glass corrosion model relies on an adequate description of the adsorption equilibria established at the surface of glass exposed to an aqueous environment, correct determination of the Gibbs energy of formation of glass from elements and the Gibbs energy of formation of the aqueous system. The coverage of glass surface exposed to aqueous media by charged species, including H^+ and OH^- , is a key parameter for pH dependence of the rate of degradation.

References

- Advocat, T., Crovisier, J.-L., Fritz, B., Vernaz, E., 1990. Thermokinetic model of borosilicate dissolution: Contextual affinity. *Materials Resesearch Symposium Proceedings* 13, 214–248.
- Appelo, C.A.J., Postma, D., 2005. *Geochemistry, Groundwater and Pollution*, second ed. Leiden: A.A. Balkema Publishers.
- Baucke, F.G.K., 1985. The glass electrode. *Applied electrochemistry of glass surfaces. Journal of Non-Crystalline Solids* 73, 215–231.
- Behrens, H., Stuke, A., 2003. Quantification of HO contents in silicate glasses using IR spectroscopy – A calibration based on hydrous glasses analyzed by Karl–Fischer titration. *Glass Science and Technology* 76, 176–189.
- Berekta, J., 1984. Kinetic analysis of solid-state reactions between powdered reactants. *Journal of the American Ceramic Society* 67, 615–620.
- Bourcier, W.L., Pfeiffer, D.W., Knauss, K.G., McKeegan, K.D., Smith, D.K., 1990. A kinetic model for borosilicate glass dissolution based on the dissolution affinity of a surface alteration layer. *Materials Resesearch Symposium Proceedings* 176, 209–216.
- Callister Jr., W.D., 2005. *Materials Science and Engineering*. Weinheim: Wiley-VCH Verlag GmbH.
- Casey, W.H., Westrich, H.R., Banfield, J.F., Ferruzzi, G., Arnold, G.W., 1993. Leaching and reconstruction at the surfaces of dissolving chain-silicate minerals. *Nature* 366, 253–256.
- Conradt, R., 2001. A proposition for an improved theoretical treatment of the corrosion of multi-component glasses. *Journal of Nuclear Materials* 298, 19–26.
- Conradt, R., 2008. Chemical durability of oxide glasses in aqueous solutions: A review. *Journal of the American Ceramic Society* 91, 728–735.
- Conradt, R., 2018. Chemical durability of glasses. In: Takada, A., Parker, J., Durán, A., Bange, K. (Eds.), *Teaching Glass Better. International Commission on Glass*.
- Conradt, R., Bach, H., Krause, D. (Eds.), 1999. *Analysis of the Composition and Structure of Glass and Glass Ceramics*. Berlin: Springer.
- DIN 52289: 1998-09, 1998. *Road Vehicles – Safety Glazing Materials – Determination of the Chemical Resistance*.
- DIN-EN 12875-2, 2002. *Mechanical Dishwashing Resistance of Utensils – Part 2: Inspection of Non-Metallic Articles*.
- Fillet, S., Vernaz, E., Nogues, J.L., Jacquet-Francillon, N., 1986. Leaching of actinides from the French LWR reference glass. *Materials Research Society Symposia Proceedings* 50, 211–218.
- Gažo, J., 1981. *Inorganic Chemistry*. Bratislava: Alfa SNTL.
- Giess, E.A., 1963. Equations and tables for analyzing solid-state reaction kinetics. *Journal of the American Ceramic Society* 46, 374–376.
- Grambow, B., 1985. A general rate equation for nuclear waste glass corrosion. *Materials Resesearch Symposium Proceedings* 26, 15–27.
- Grambow, B., 1992. Geochemical approach to glass dissolution. In: Clark, D.E., Zaitos, B.K. (Eds.), *Corrosion of Glass, Ceramics, and Ceramic Superconductors*. Park Ridge: Noyes Publications, pp. 153–217.
- Helebrant, A., 1997. Kinetics of corrosion of silicate glasses in aqueous solutions. *Ceramics-Silikáty* 41, 147–151.
- Herrmann, M., Klemm, H., Schubert, C., 2000. Silicon nitride based hard materials. In: Riedel, R. (Ed.), *Handbook of Ceramic Hard Materials*. Weinheim: Wiley-VCH. 747.
- Hill, R., Brauer, D., 2011. Predicting the bioactivity of glasses using the network connectivity or split network models. *Journal of Non-Crystalline Solids* 357, 3884–3887.
- ISO 10629:1996, 1996. *Raw Optical Glass – Resistance to Attack by Aqueous Alkaline Solutions at 50°C – Test Method and Classification*.
- ISO 20492:2008, 2008. *Glass in Buildings – Insulating Glass – Part 1: Durability of Edge Seals by Climate Tests*.
- ISO 4794:1982, 1982. *Laboratory Glassware – Methods for Assessing the Chemical Resistance of Enamels Used for Colour Coding and Colour Marking*.
- ISO 8424:1996, 1996. *Raw Optical Glass – Resistance to Attack by Aqueous Acidic Solutions at 25°C – Test Method and Classification*.
- Kamizono, H., Clark, D.E., Lodding, A.R., 1989. Accelerated leach tests of SRL-165 high-level waste glass in deionized water: Solution analyses and supplemental SIMS analyses. *Journal of Nuclear Science and Technology* 26, 441–448.
- Mann, S., Webb, J., Williams, R.J.P., 1989. *Biomineralization*. Weinheim: VCH Verlagsgesellschaft.
- McGrail, B.P., Ebert, W., Bakel, A.J., Peeler, D.K., 1997. Measurement of kinetic rate law parameters on a Na–Ca–Al borosilicate glass for low-activity waste. *Materials Research Symposium Proceedings* 249, 175–189.
- Nickel, K.G., 1997. Corrosion of non-oxide ceramics. *Ceramics International* 23, 127–133.
- Oelkers, E.H., Bénéth, P., Pokrovsky, G.S., 2009. Thermodynamic databases for water-rock interaction. *Reviews in Mineralogy & Geochemistry* 70, 1–46.
- Paul, A., 1982. *Chemistry of Glasses*. London: Chapman and Hall.
- Portal, S., Sempere, R., 2003. Study of alkali silicate glass corrosion using spectroscopy ellipsometry and secondary ion mass spectroscopy. *Physics and Chemistry of Glasses* 44, 303–307.
- Riedel, R., 2000. *Handbook of Ceramic Hard Materials*. Weinheim: Wiley-VCH Verlag GmbH.
- Schilm, J., Herrmann, M., Michael, G., 2007. Corrosion of Si_3N_4 -ceramics in aqueous solutions. Part II: Corrosion mechanisms in acids as a function of concentration, temperature and composition. *Journal of the European Ceramic Society* 27, 3573–3588.
- Scholze, H., 1959. The incorporation of water in glasses (in German). *Glastechnische Berichte* 32, 81–88.
- Scholze, H., 1975. Significance of the leached layer for the chemical durability: Investigation with soda–lime–silica glass. *Glastechnische Berichte* 58, 116–124.
- Scholze, H., 1990. *Glass – Nature, Structure, and Properties*, English ed. Berlin: Springer Verlag.
- Schott, J., Pokrovsky, O.S., Oelkers, E.H., 2009. The link between mineral dissolution/precipitation kinetics and solution chemistry. *Reviews in Mineralogy & Geochemistry* 70, 207–258.
- Shakhmatkin, B.A., Vedishcheva, N.M., Schultz, M.M., Wright, A.C., 1994. The thermodynamic properties of oxide glasses and glass-forming liquids and their chemical structure. *Journal of Non-Crystalline Solids* 177, 249–256.
- Sharp, J.H., Brindley, G.W., Narahari Achar, B.N., 1966. Numerical data for some commonly used solid state reaction equations. *Journal of the American Ceramic Society* 49, 379–382.
- Smets, B.M.J., Lommen, T.P.A., 1981. SIMS and XPS investigation of the leaching of glasses. *Verres Refractories* 35, 84–90.
- Stumm, W., Morgan, J.J., 1996. *Aquatic Chemistry*, third ed. New York: John Wiley & Sons, Inc.
- Tressler, R.E., McNallan, M., 1990. *Corrosion and Corrosive Degradation of Ceramics*. Boston: Martin Nijhoff.
- White, W.B., 1992. *Theory of Corrosion of Glass and Ceramics*. Park Ridge: Notes Publications.

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CONTENT OF VOLUME 2

List of Contributors for Volume 2	ix
Content of All Volumes	xiii

VOLUME 2

Overview: Oxide Ceramics and Non-oxide Ceramics <i>Stuart Hampshire and Michael Pomeroy</i>	1
Structural and Thermostructural Ceramics <i>Jon Binner and Tammanna SRC Murthy</i>	3
Alumina, Structure and Properties <i>Carmen Baudín</i>	25
Low Thermal Expansion Ceramic and Glass-Ceramic Materials <i>Pascal Pilate and Florimond Delobel</i>	47
Mullite: Structure and Properties <i>Gi��le L Lecomte-Nana and Aghiles Hammas</i>	59
Aluminum Titanate, Structure and Properties <i>Salvador Bueno and Carmen Baudín</i>	76
Zirconia Ceramics, Structure and Properties <i>Anne Leriche, Francis Cambier, and Helen Reveron</i>	93
Si ₃ N ₄ -Ceramics: An Introduction <i>MJ Hoffmann</i>	105
Si ₃ N ₄ Ceramics, Structure and Properties <i>Monika Tatarkov��, Peter Tatarko, and Pavol ��ajgal��k</i>	109
SiAlONs and the Representation of Phase Relationships <i>Stuart Hampshire</i>	119
Si-Al-O-N Ceramics, Structure and Properties <i>Ali ��elik and Servet Turan</i>	128
Aluminum Nitride and AlON Ceramics, Structure and Properties of <i>JW McCauley</i>	144
SiC Ceramics, Structure, Processing and Properties <i>Young-Wook Kim and Rohit Malik</i>	150
High Thermal Conductivity Ceramics <i>Mikito Kitayama</i>	165
MAX Phases, Structure, Processing, and Properties <i>Nick Goossens, Bensu Tunca, Thomas Lapauw, Konstantina Lambrinou, and Jozef Vleugels</i>	182
ZrB ₂ , HfB ₂ , OsB ₂ and IrB ₂ Boride Ceramics: Processing, Structure, and Properties <i>Nina Orlovskaya, Holden Hyer, Yongho Sohn, Mykola Lugovy, Gurdial Blugan, Thomas Graule, Jakob Kuebler, Sergey Yarmolenko, Jagannathan Sankar, and Michael J Reece</i>	200

Directionally-Solidified Eutectic Oxide Ceramics <i>VM Orera[†] and J Llorca</i>	216
Overview: High-Performance Ceramics and Ceramic Composites <i>Michael Pomeroy</i>	225
Ceramic Matrix Composites With Roughly Equiaxed Reinforcements: Microstructure and Mechanical Behavior <i>Gilbert Fantozzi and Jérôme Chevalier</i>	227
Nanoscale Ceramic Composites <i>GS Thompson and MP Harmer</i>	240
Ceramic Matrix Graphene and Carbon Nanotube Composites <i>Katalin Balázsi, Mónika Furkó, and Csaba Balázsi</i>	243
Short Fiber Ceramic Matrix Composites (SF-CMCs) <i>Walter Krenkel, Stefan Flauder, and Georg Puchas</i>	260
Glass and Glass-Ceramic Matrix Composites for Advanced Applications: Part I: Properties and Manufacturing Technologies <i>Dino Boccaccini, Maria Cannio, Enrico Bernardo, and Aldo R Boccaccini</i>	277
Glass and Glass-Ceramic Matrix Composites for Advanced Applications: Part II: Applications <i>Dino Boccaccini, Maria Cannio, Enrico Bernardo, and Aldo R Boccaccini</i>	288
High Performance Fibers <i>AR Bunsell</i>	304
Spun (Slurry and Sol–Gel) Ceramic Fibers <i>DM Wilson</i>	314
Ceramic Matrix Fiber Composites <i>Francis Rebillat</i>	317
Ultra-High Temperature Ceramic Matrix Composites <i>Luca Zoli, Diletta Sciti, Antonio Vinci, Pietro Galizia, Frédéric Monteverde, Simone Failla, and Laura Silvestroni</i>	340
Carbon-Matrix Composites <i>Deborah DL Chung</i>	353
Ceramics in Space Applications <i>Barry Twomey, Daithí de Faoite, Kevin AJ Doherty, and Kenneth T Stanton</i>	359
Porous Ceramics for Energy Applications <i>Andreas Kaiser, Bhaskar R Sudireddy, and Farid Akhtar</i>	380
Joining of Advanced Ceramics <i>John A Fernie and Kevin M Knowles</i>	393
Abrasives <i>Jean-André Alary</i>	406
Wear and Erosion Resistant Ceramic Materials <i>Pavol Hvizdoš</i>	416
Wear and Erosion Resistant Ceramic Coatings <i>František Lofaj and Marián Mikula</i>	425
Oxidation and Corrosion of Non-oxide Ceramics <i>NS Jacobson and EJ Opila</i>	440
Overview: Glass and Glass Ceramics <i>Stuart Hampshire</i>	445

[†]Deceased.

The Glassy State <i>Maziar Montazerian and Edgar D Zanotto</i>	448
Glasses: Alkali and Alkaline-Earth Silicates <i>Benjamin JA Moulton and Grant S Henderson</i>	462
Soda-Lime-Silica Glasses <i>Russell J Hand</i>	483
Glasses: Aluminosilicates <i>Laurent Cormier</i>	496
Borosilicate Glasses <i>Yuanzheng Yue, Manzila I Tuheen, and Jincheng Du</i>	519
Glasses: Chalcogenides <i>Myungkoo Kang and Kathleen A Richardson</i>	540
Glasses: Oxynitride Glass Formation and Structure <i>Stuart Hampshire</i>	555
Glasses: Oxynitride Glass Properties and Crystallization <i>Stuart Hampshire</i>	569
Glasses: Phosphates <i>Andrea Moguš-Milanković, Ana Šantić, and Luka Pavić</i>	580
Halide Glasses <i>Marcel Poulain</i>	591
Glass: Annealing and Tempering <i>Mathieu Hubert and Peter J Lezzi</i>	623
Glass: Chemical and Thermal Strengthening <i>Ali Talimian and Vincenzo M Sglavo</i>	632
Properties of Glass Materials <i>M Hasanuzzaman, A Rafferty, M Sajjia, and A-G Olabi</i>	647
Optical Glass: Challenges From Optical Design <i>Ulrich Fotheringham, Martin Letz, Uwe Petzold, Simone Ritter, and Yvonne Menke-Berg</i>	658
Glass Fibers <i>KK Chawla</i>	676
Glass: Optical Fibers – Manufacture and Properties <i>Conleth D Hussey</i>	681
Glasses: Sol–Gel Methods: An Introduction <i>T Woignier and J Phalippou</i>	689
Glasses and Glass-Ceramics Prepared by Sol–Gel <i>María E Cruz, Yolanda Castro, and Alicia Durán</i>	695
Glass-Ceramics and Their Applications <i>Maurice Gonon and Florian Dupla</i>	709
Glass Reactive Sintering <i>Acacio Rincon Romero, Hamada Elsayed, Jozef Kraxner, and Enrico Bernardo</i>	728
Glasses and Glass-Ceramics as Sealing Materials <i>María J Pascual</i>	746
Glasses and Glass-Ceramics for Nuclear Waste Immobilization <i>Daniel Caurant and Odile Majérus</i>	762

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CONTENT OF ALL VOLUMES

List of Contributors for Volume	ix
Editor Biographies	xxiii
Preface	xxv

VOLUME 1

Overview: Manufacture of Ceramics and Microstructural Developments in Ceramics <i>Francis Cambier and Anne Leriche</i>	1
Synthesis of Oxide and Non-Oxide Advanced Ceramics <i>Prashant N Kumta</i>	2
Synthesis of Ceramic Powders by Wet Chemical Routes <i>Paola Palmero</i>	27
Self-Propagating High-Temperature Synthesis <i>Jerzy Lis</i>	40
Hydrothermal Synthesis <i>Ender Suvaci and Emel Özel</i>	59
Ultrasonic Sprayed Aerosol for Ultrafine Ceramic Powder Synthesis <i>Sylvie Foucaud and Yann Leconte</i>	69
Calcination and Phase Transformations <i>Gary L Messing</i>	83
Preceramic Polymers as Precursors of Advanced Ceramics: The Polymer-Derived Ceramics (PDCs) Route <i>Yuji Iwamoto, Günter Motz, Emanuel Ionescu, and Samuel Bernard</i>	93
Organic Additives in Ceramic Processing <i>Anne Aimable and Thierry Chartier</i>	103
Powder Mixing and Grinding Processes for Ceramics <i>David Houivet and Jérôme Bernard</i>	112
Powder Granulation and Compaction <i>Michele Dondi</i>	136
Colloid Casting Processes: Slip Casting, Centrifugal Casting, and Gel Casting <i>Nur S Yüzbaşı and Thomas Graule</i>	146
Processing of Ceramics by Direct Coagulation Casting <i>Margarida Almeida and Joaquim M Vieira</i>	154
Extrusion <i>Stuart Blackburn and Marcin Szymiczek</i>	162
Ceramic Injection Molding <i>Moritz v Witzleben and Tassilo Moritz</i>	179

Tape Casting and Lamination <i>Eric R Twiname</i>	189
Freeze Casting <i>Dominique Hautcoeur</i>	195
Additive Manufacturing <i>Andrea Zocca, Giorgia Franchin, Paolo Colombo, and Jens Günster</i>	203
Green Machining of Ceramics <i>Fabrice Petit</i>	222
Screen Printing <i>Danjela Kuscser</i>	227
Sintering of Ceramics: An Overview <i>Anne Leriche, Francis Cambier, and Stuart Hampshire</i>	233
Solid-State Sintering <i>John E Blendell and Wolfgang Rheinheimer</i>	249
Liquid Phase Sintering: Fundamentals <i>Suk-Joong L Kang</i>	258
Viscous Sintering <i>George W Scherer</i>	265
Hot Pressing and Hot Isostatic Pressing <i>Mathias Herrmann and Jan Räthel</i>	270
Reaction Sintering <i>Carmen Baudín</i>	278
Flash Sintering and Other Rapid Sintering Techniques <i>David Salamon</i>	286
Spark Plasma Sintering <i>Umberto Anselmi-Tamburini</i>	294
Cold Sintering and Hydrothermal Sintering <i>Graziella Goglio, Arnaud Ndayishimiye, Catherine Elissalde, and Clive A Randall</i>	311
Microwave Sintering of Ceramics <i>Jean-Marc Chaix</i>	327
Porous Ceramics Processing <i>Manabu Fukushima, Akihiro Shimamura, Paolo Colombo, Hideki Hyuga, Tatsuki Ohji, and Yu-ichi Yoshizawa</i>	342
Porous Ceramics Including Fibrous Insulation, Structure and Properties of <i>M Fukushima, T Ohji, P Colombo, and Y-I Yoshizawa</i>	346
Control of the Microstructure in Ceramics <i>Anne Leriche, Stuart Hampshire, and Francis Cambier</i>	349
Templated Grain Growth of Textured Ceramics <i>Gary L Messing</i>	367
Functionally Graded Ceramics <i>Omer Van der Biest and Achim Neubrand</i>	374
Transparent Ceramics: Materials, Processing, Properties and Applications <i>Marc Rubat du Merac</i>	399
Geopolymers and Geopolymer-Derived Composites <i>Waltraud M Kriven</i>	424

Overview: Characterization and Modelling of Ceramics and Glasses <i>Michael Pomeroy and Stuart Hampshire</i>	439
Ceramic Genomics: Total Bond Order Density <i>Wai-Yim Ching</i>	441
Predictive Modeling of Ceramic Materials <i>Sarah Guerin, Syed AM Tofail, and Damien Thompson</i>	475
Molecular Dynamics Simulations of Glass Structure <i>Mattias Edén</i>	481
Computation of Phase Diagrams for Ceramics <i>Sara Serena, Angel Caballero, Antonio H de Aza, and Maria A Sainz</i>	498
Characterization of Ceramic Powders <i>Martin J Murtagh and Navin Venugopal</i>	517
Amorphous Materials: Vibrational Spectroscopy <i>PF McMillan</i>	530
MAS NMR Analysis of Ceramics and Glasses <i>Yajie Gao</i>	536
X-Ray Powder Diffraction <i>Scott T Mixture</i>	549
Case Studies in the X-ray Diffraction of Ceramics <i>Maurice Gonon</i>	560
Introduction to Transmission Electron Microscopy; The Basics <i>Ann-Katrin Fetzer, Maximilian Trapp, Stefan Lauterbach, and Hans-Joachim Kleebe</i>	578
High Resolution Analytical Electron Microscopy of Ceramics and Glasses <i>Jennifer Cookman, Michele Conroy, and Ursel Bangert</i>	600
Introduction to Three Dimensional Electron Crystallography <i>Andrew Stewart and Ute Kolb</i>	618
Preparation of Ceramic, Glass-Ceramic and Glasses for Microstructural Examination <i>Michael J Pomeroy</i>	634
Scanning Electron Microscopy for Ceramics and Glasses <i>Michael J Pomeroy</i>	651
Fractography: Brittle Materials <i>John J Mecholsky, Jr.</i>	662
Thermal Analysis Techniques for Technical Ceramics and Glasses <i>Michael J Pomeroy</i>	676
High-Temperature Characterization of Glasses and Melts <i>Sohei Sukenaga and Hiroyuki Shibata</i>	689
Overview: Mechanical and Physical Properties and Property Testing of Ceramics and Glasses <i>Anne Leriche and Francis Cambier</i>	704
Elastic and Inelastic Behavior of Ceramics <i>Daniele Mari and Robert Schaller</i>	705
Indentation of Ceramics <i>Emilio Jiménez-Piqué</i>	718
Contact Damage Resistance and Tribological Behavior of Ceramic/Carbon Nanostructure Composites <i>Manuel Belmonte</i>	733

Methods of Determination of Young's Modulus and Tensile, Flexural and Compressive Strength <i>Sylvain Meille</i>	745
Fracture Toughness Measurement <i>Tanja Lube</i>	762
R-Curve Behavior of Ceramics <i>Marc J Anglada</i>	775
Subcritical Crack Growth: Basic Relations and Experimental Evaluation <i>Malika Saâdaoui</i>	797
Subcritical Crack Growth: Modeling of the v-K Curve in Different Environments <i>Raul Bermejo</i>	811
Ceramics: Transformation Toughening <i>DB Marshall and RHJ Hannink</i>	818
Mixed-Mode Fracture and Microstructural Aspects of Crack Propagation <i>Delia Gutiérrez-Campos and Yuk Ming X Hung-Hung</i>	823
R-Ratio and Microstructure Effects <i>Delia Gutiérrez-Campos, Eliana Pinto-González, and Elvira Saab-Llatas</i>	841
Thermal Properties of Ceramic Materials <i>David S Smith and Benoît Naït-Ali</i>	855
Thermal Shock Behavior of Ceramics: Fundamentals and Thermal Shock Resistance Parameters <i>Carmen Baudín</i>	867
Thermal Shock and Thermal Fatigue Behavior of Ceramics: Microstructural Effects <i>Gilbert Fantozzi and Malika Saâdaoui</i>	879
Creep Behavior of Ceramics <i>Gilbert Fantozzi and Arturo Dominguez-Rodriguez</i>	891
Nonoxide Ceramics, Creep and Creep Rupture of: Silicon Nitrides and Silicon Carbides <i>SM Wiederhorn</i>	908
Dislocations in Ceramic Materials <i>Jacques Rabier</i>	911
Corrosion of Ceramics in Aqueous Environments <i>Mathias Herrmann</i>	921
Corrosion and Degradation of Glass <i>Dagmar Galusková and Dušan Galusek</i>	932

VOLUME 2

Overview: Oxide Ceramics and Non-oxide Ceramics <i>Stuart Hampshire and Michael Pomeroy</i>	1
Structural and Thermostructural Ceramics <i>Jon Binner and Tammana SRC Murthy</i>	3
Alumina, Structure and Properties <i>Carmen Baudín</i>	25
Low Thermal Expansion Ceramic and Glass-Ceramic Materials <i>Pascal Pilate and Florimond Delobel</i>	47

Mullite: Structure and Properties <i>Gi��le L Lecomte-Nana and Aghiles Hammas</i>	59
Aluminum Titanate, Structure and Properties <i>Salvador Bueno and Carmen Baud��n</i>	76
Zirconia Ceramics, Structure and Properties <i>Anne Leriche, Francis Cambier, and Helen Reveron</i>	93
Si ₃ N ₄ -Ceramics: An Introduction <i>MJ Hoffmann</i>	105
Si ₃ N ₄ Ceramics, Structure and Properties <i>Monika Tatarkov��, Peter Tatarko, and Pavol ��ajgal��k</i>	109
SiALONs and the Representation of Phase Relationships <i>Stuart Hampshire</i>	119
Si-Al-O-N Ceramics, Structure and Properties <i>Ali ��elik and Servet Turan</i>	128
Aluminum Nitride and ALON Ceramics, Structure and Properties of <i>JW McCauley</i>	144
SiC Ceramics, Structure, Processing and Properties <i>Young-Wook Kim and Rohit Malik</i>	150
High Thermal Conductivity Ceramics <i>Mikito Kitayama</i>	165
MAX Phases, Structure, Processing, and Properties <i>Nick Goossens, Bensu Tunca, Thomas Lapauw, Konstantina Lambrinou, and Jozef Vleugels</i>	182
ZrB ₂ , HfB ₂ , OsB ₂ and IrB ₂ Boride Ceramics: Processing, Structure, and Properties <i>Nina Orlovskaya, Holden Hyer, Yongho Sohn, Mykola Lugovy, Gurdial Blugan, Thomas Graule, Jakob Kuebler, Sergey Yarmolenko, Jagannathan Sankar, and Michael J Reece</i>	200
Directionally-Solidified Eutectic Oxide Ceramics <i>VM Orera^{��} and J Llorca</i>	216
Overview: High-Performance Ceramics and Ceramic Composites <i>Michael Pomeroy</i>	225
Ceramic Matrix Composites With Roughly Equiaxed Reinforcements: Microstructure and Mechanical Behavior <i>Gilbert Fantozzi and J��r��me Chevalier</i>	227
Nanoscale Ceramic Composites <i>GS Thompson and MP Harmer</i>	240
Ceramic Matrix Graphene and Carbon Nanotube Composites <i>Katalin Bal��zsi, M��nika Furk��, and Csaba Bal��zsi</i>	243
Short Fiber Ceramic Matrix Composites (SF-CMCs) <i>Walter Krenkel, Stefan Flauder, and Georg Puchas</i>	260
Glass and Glass-Ceramic Matrix Composites for Advanced Applications: Part I: Properties and Manufacturing Technologies <i>Dino Boccaccini, Maria Cannio, Enrico Bernardo, and Aldo R Boccaccini</i>	277
Glass and Glass-Ceramic Matrix Composites for Advanced Applications: Part II: Applications <i>Dino Boccaccini, Maria Cannio, Enrico Bernardo, and Aldo R Boccaccini</i>	288

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High Performance Fibers <i>AR Bunsell</i>	304
Spun (Slurry and Sol–Gel) Ceramic Fibers <i>DM Wilson</i>	314
Ceramic Matrix Fiber Composites <i>Francis Rebillat</i>	317
Ultra-High Temperature Ceramic Matrix Composites <i>Luca Zoli, Diletta Sciti, Antonio Vinci, Pietro Galizia, Frédéric Monteverde, Simone Failla, and Laura Silvestroni</i>	340
Carbon-Matrix Composites <i>Deborah DL Chung</i>	353
Ceramics in Space Applications <i>Barry Twomey, Daithi de Faoite, Kevin AJ Doherty, and Kenneth T Stanton</i>	359
Porous Ceramics for Energy Applications <i>Andreas Kaiser, Bhaskar R Sudireddy, and Farid Akhtar</i>	380
Joining of Advanced Ceramics <i>John A Fernie and Kevin M Knowles</i>	393
Abrasives <i>Jean-André Alary</i>	406
Wear and Erosion Resistant Ceramic Materials <i>Pavol Hvizdoš</i>	416
Wear and Erosion Resistant Ceramic Coatings <i>František Lofaj and Marián Mikula</i>	425
Oxidation and Corrosion of Non-oxide Ceramics <i>NS Jacobson and EJ Opila</i>	440
Overview: Glass and Glass Ceramics <i>Stuart Hampshire</i>	445
The Glassy State <i>Maziar Montazerian and Edgar D Zanutto</i>	448
Glasses: Alkali and Alkaline-Earth Silicates <i>Benjamin JA Moulton and Grant S Henderson</i>	462
Soda-Lime-Silica Glasses <i>Russell J Hand</i>	483
Glasses: Aluminosilicates <i>Laurent Cormier</i>	496
Borosilicate Glasses <i>Yuanzheng Yue, Manzila I Tuheen, and Jincheng Du</i>	519
Glasses: Chalcogenides <i>Myungkoo Kang and Kathleen A Richardson</i>	540
Glasses: Oxynitride Glass Formation and Structure <i>Stuart Hampshire</i>	555
Glasses: Oxynitride Glass Properties and Crystallization <i>Stuart Hampshire</i>	569
Glasses: Phosphates <i>Andrea Moguš-Milanković, Ana Šantić, and Luka Pavić</i>	580

Halide Glasses <i>Marcel Poulain</i>	591
Glass: Annealing and Tempering <i>Mathieu Hubert and Peter J Lezzi</i>	623
Glass: Chemical and Thermal Strengthening <i>Ali Talimian and Vincenzo M Sglavo</i>	632
Properties of Glass Materials <i>M Hasanuzzaman, A Rafferty, M Sajjia, and A-G Olabi</i>	647
Optical Glass: Challenges From Optical Design <i>Ulrich Fotheringham, Martin Letz, Uwe Petzold, Simone Ritter, and Yvonne Menke-Berg</i>	658
Glass Fibers <i>KK Chawla</i>	676
Glass: Optical Fibers – Manufacture and Properties <i>Conleth D Hussey</i>	681
Glasses: Sol–Gel Methods: An Introduction <i>T Woignier and J Phalippou</i>	689
Glasses and Glass-Ceramics Prepared by Sol–Gel <i>María E Cruz, Yolanda Castro, and Alicia Durán</i>	695
Glass-Ceramics and Their Applications <i>Maurice Gonon and Florian Dupla</i>	709
Glass Reactive Sintering <i>Acacio Rincon Romero, Hamada Elsayed, Jozef Kraxner, and Enrico Bernardo</i>	728
Glasses and Glass-Ceramics as Sealing Materials <i>María J Pascual</i>	746
Glasses and Glass-Ceramics for Nuclear Waste Immobilization <i>Daniel Caurant and Odile Majérus</i>	762

VOLUME 3

Overview: Electroceramics and Ceramics and Glasses in Energy Generation and Storage <i>Carmen Galassi</i>	1
Photovoltaics: Advanced Inorganic Materials <i>Abdelilah Slaoui and Reuben T Collins</i>	5
Ion Conducting Materials: Superionic Conductors and Solid-State Ionics <i>Junichi Kawamura</i>	17
Development, Structure, and Mechanical Properties of Sulfide Solid Electrolytes <i>Koji Ohara, Atsushi Sakuda, and Akitoshi Hayashi</i>	38
Solid Oxide Fuel Cells <i>Alessandra Sanson and Angela Gondolini</i>	49
Laser Processing of Energy Storage Materials <i>Heungsoo Kim and Alberto Piqué</i>	59
Aluminum, Gallium, and Indium Nitrides <i>Qilin Hua, Bei Ma, and Weiguo Hu</i>	74
Novel Nitride Phosphors <i>M Bettinelli</i>	84

Phosphors: VUV Excitation <i>Jean-Claude Krupa and AZMS Rahman</i>	89
Silicon Carbide Electronic Devices <i>PG Neudeck and GK Sujan</i>	93
Scintillator Crystals <i>D Klimm</i>	103
Ceramics for Laser Technologies <i>Jan Hostaša</i>	110
Ceramic Sensors for Industrial Applications <i>David Degler, Frank Allmendinger, and Nicolae Barsan</i>	125
Pyroelectric Crystals, Ceramics, and Thin Films for IR Sensors <i>Roger W Whatmore</i>	139
Superconducting Materials <i>Peter Majewski</i>	151
Superconductors: Borocarbides <i>Günter Fuchs, Karl-Hartmut Müller, and Vladimir N Narozhnyi</i>	162
The RABiTS Approach for Second Generation (2G) High Temperature Superconductors <i>Martin W Rupich</i>	174
Ferrite Ceramics at Microwave Frequencies: Applications and Characterization <i>Jean-Luc Mattei, Alexis Chevalier, and Vincent Laur</i>	183
Ferrite Magnets: Properties and Applications <i>Jean-Marie Le Breton</i>	206
Ferrites <i>PJ van der Zaag</i>	217
Multiferroic Composites <i>Xianfeng Liang, Huaihao Chen, Cheng Tu, Zhaoqiang Chu, Cunzheng Dong, Yifan He, Yuyi Wei, Yuan Gao, Hwaider Lin, and Nian X Sun</i>	225
Zinc-Oxide-Based Electronics and Photonics <i>David J Rogers, Ferechteh H Teherani, Eric V Sandana, and Philippe Bove</i>	241
Varistor Electrical Properties: Microstructural Effects <i>Zumret Topcagic and Thomas E Tsovilis</i>	254
Latest Trend of ZnO Multilayer Ceramic Varistors <i>Eiichi Koga, Yoshiko Higashi, and Michio Matsuoka</i>	272
Dielectric, Ferroelectric, Antiferroelectric, Relaxor, Piezoelectric Ceramics: Definitions and Main Applications <i>Floriana Craciun</i>	281
Electroceramics: Modeling of Sintering, Microstructure Evolution and Functional Properties <i>Constantin Hutanu, Vlad Alexandru Lukacs, and Liliana Mitoseriu</i>	295
BaTiO ₃ -Based Ceramics: Fundamentals, Properties and Applications <i>Vincenzo Buscaglia, Maria Teresa Buscaglia, and Giovanna Canu</i>	311
The PZT System <i>Florian Jean and Christian Courtois</i>	345
Lead-Free Piezoelectric Ceramics <i>Barbara Malič, Mojca Otoničar, Kristian Radan, and Jurij Koruza</i>	358

Electrostrictive Ceramics and Their Applications <i>Simone Santucci and Vincenzo Esposito</i>	369
Low-Loss Ceramics in Mobile Communications <i>K Wakino, H Tamura, and GK Sujan</i>	375
Small-Scale Energy Harvesting Devices for Smart Electronics <i>Sumanta Kumar Karan, Rammohan Sriramdas, Min-Gyu Kang, Yongke Yan, and Shashank Priya</i>	391
Multilayer Ceramic Actuators <i>K Uchino</i>	426
Multilayer Glass–Ceramic/Ceramic Composite Substrates <i>Jobin Varghese, Nina Joseph, and Heli Jantunen</i>	437
Functional Ceramics through Novel Chemical Approaches <i>K Kato, Y Torii, and G Majumdar</i>	452
Overview: Bioceramics and Bioreactive Glasses <i>Anne Leriche and Francis Cambier</i>	458
Bone as a Material: Lessons From Nature <i>Laura M O'Sullivan and Laoise M McNamara</i>	459
Overview of Substitutes for Bone Replacement: Natural and Synthetic Products <i>Nicolas Somers and Marie Lasgorceix</i>	473
New Trends in Ceramics for Orthopedics <i>Laurent Gremillard and Jérôme Chevalier</i>	493
New Trends in Ceramics for Dentistry <i>Paola Palmero</i>	501
Oxide Ceramics for Biomedical Applications <i>Corrado Piconi and Anna Tampieri</i>	511
Non-Oxide Ceramics as Biomaterials <i>Stuart Hampshire</i>	526
Carbon in Biomedical Engineering <i>Jill S Kawalec</i>	533
Yttria-Stabilized Zirconia as a Biomaterial: From Orthopedic Towards Dental Applications <i>Helen Reveron and Jérôme Chevalier</i>	540
ZTA Ceramics for Biomedical Applications <i>Frank Kern, Paola Palmero, and Wolfgang Burger</i>	553
Phosphates <i>David Grossin</i>	567
Apatitic and Tricalcic Calcium Phosphate-Based Bioceramics: Overview and Perspectives <i>Christophe Drouet and Christèle Combes</i>	575
Calcium Phosphates in Biomedical Engineering <i>Maria Canillas, Antonio H de Aza, and Miguel A Rodríguez</i>	595
Bioceramics in Regenerative Medicine <i>Simone Sprio, Anna Tampieri, Massimiliano Dapporto, Michele Iafisco, and Monica Montesi</i>	601
Bioactive Glasses and Glass-Ceramics <i>Francesco Baino</i>	614
Calcium Phosphate Cements <i>Aoife Culliton and Eamonn De Barra</i>	624

Bone Regeneration With Ceramics Scaffold <i>Vida Strasser and Maja Dutour Sikirić</i>	646
Advanced Processes for the Design of Customized Ceramic Medical Devices <i>Eric Champion and Patricia Pascaud-Mathieu</i>	662
Bioactive and Biodegradable Polymer-Based Composites <i>Lukas Gritsch and Aldo R Boccaccini</i>	674
Surface Treatment of Bioceramics <i>Nicolas Somers and Marie Lasgorceix</i>	701
Chemical Functionalization of Calcium Phosphate Bioceramic Surfaces <i>Chantal Damia, Amandine Magnaudeix, and Betty Laverdet</i>	716
Thermally Sprayed Materials for Biomedical Applications <i>Andreas Killinger and Rainer Gadow</i>	732
Design of Tissue Engineering Scaffold by Means of Mathematical Modeling <i>Stefan Scheiner</i>	750
Unconventional, Nature-Inspired Approaches to Develop Bioceramics for Regenerative Medicine <i>Anna Tampieri, Simone Sprio, Monica Sandri, Elisabetta Campodoni, Andrea Ruffini, Laura Mengozzi, and Silvia Panseri</i>	758
Assessment of Mechanical Properties of Bioceramics <i>Gilbert Fantozzi</i>	772
Mechanical Properties of Dental Ceramics <i>Fei Zhang and Jozef Vleugels</i>	784
Biological Assessment of Bioceramics: In Vitro and In Vivo Tests <i>Maria H Fernandes and Pedro de Sousa Gomes</i>	798
Zirconia Ceramics: Clinical and Biological Aspects in Dentistry <i>Andraž Kocjan, Tadej Mirt, Ralf-Joachim Kohal, Zhijian Shen, and Peter Jevnikar</i>	817
Subject Index	832

Overview: Oxide Ceramics and Non-oxide Ceramics

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Structural ceramics have been under development for many decades and many are now used in a wide range of advanced technological applications where high wear resistance and/or high temperatures combined with chemical stability are required. So as a result of these developments there is a range of ceramic materials available which are classified according to their chemistry: oxides, carbides, nitrides and borides, which are reviewed in the various chapters which follow.

The first chapter gives a complete overview of these structural and thermostructural ceramics, introducing the different groups above and their performance in major applications which enhance component life, increase efficiency of existing processes, reduce energy consumption or improve environmental impact. The different synthesis methods for these ceramics are introduced and their consolidation by different sintering techniques and how these lead to microstructural development that enhances their particular special properties.

The next chapter deals with Alumina ceramics which have the largest share of the world ceramics market. The crystalline structure and properties of single-crystal α -Al₂O₃ are described followed by the fabrication processes for alumina materials. Raw materials are available at relatively low cost and alumina components with wide ranges of shapes and sizes and controlled microstructure can be fabricated by pressureless sintering. A review of properties follows including hardness and stiffness, wear resistance, chemical inertness and associated corrosion resistance and strength, all of which can be retained at high temperature. They are excellent electrical insulators and can be made translucent or even transparent depending on grain size. Chemical inertness allows alumina to be used in biological environments. The main applications are described on the basis of the required properties.

The next chapter introduces ceramics and glass-ceramics which have low thermal expansion, materials which are of interest for applications which need dimension stability during temperature variation or special thermomechanical behavior such as a high thermal shock resistance. Some theoretical considerations are presented which explain the origin of low thermal expansion and its importance. An overview is given of ceramic and glass-ceramics which are well known for their low thermal expansion, such as silica, cordierite, aluminum titanate, zirconyl phosphate and NZP, and various glass-ceramics. Their main characteristics, fabrication processes and current or potential applications are outlined.

The wide technological applicability of mullite ceramics is reviewed in the next chapter. An overview of mullites is given, outlining mineralogy and crystal structure, their stability and composition, the main processing routes to form ceramics and the relevant typical final properties such as high thermal stability, low thermal expansion and conductivity, together with suitable strength and fracture toughness which, combined, give mullite its excellent thermal shock resistance. Finally applications in both traditional and advanced ceramics are described.

The main special characteristic of aluminum titanate (AT), a very low overall thermal expansion coefficient, is outlined in the next chapter. The strong anisotropy in the thermal expansion of its crystallographic directions is explained, as well as the causes of microcracking observed in AT. These features promote excellent thermal shock resistance but at the expense of strength. The structure, properties and applications of AT are summarized, together with a review of processing routes and technological applications. The inclusion of AT in the design of ceramic composite materials for structural applications is discussed whereby different toughening mechanisms operate in both monolithic and laminated alumina-based structures with different AT contents.

The next chapter reviews the crystallographic, physical and chemical properties of zirconia. Developed since the 1980s following the discovery of stabilization at room temperature of its high temperature phases, zirconia has continued to fascinate scientists and technologists by its particular characteristics of its solid solutions with other oxides leading to occurrence of mechanical toughening behavior (through manipulation of the tetragonal-monoclinic phase transformation) and special ionic conduction processes (in its cubic form). An outline is given of how the microstructure can be engineered such that very high fracture strength or high toughness can be generated. A section is given on wear, cutting, thermal barrier coatings, ionically conductive and biomedical applications.

The next two chapters are concerned with silicon nitride ceramics, the first providing an introduction to this major non-oxide ceramic. An overview is given of crystal structures and processing, whereby most silicon nitride ceramics are prepared by using α -rich Si₃N₄ powders with oxide additives which allow liquid formation and the transformation during sintering from α - to β -Si₃N₄. The microstructural development of growth of elongated β grains with high aspect ratios is described along with the characteristics of the intergranular films formed from the liquid phase which depend on additive chemistry. The microstructure-property relationships are discussed. The second contribution expands on this, showing that the properties are not only pre-determined by the intrinsic properties of Si₃N₄ single crystals, but also strongly depend on the size, orientation and volume fraction of the Si₃N₄ grains, as well as the chemistry and volume fraction of grain boundary phases. This means that properties of Si₃N₄ ceramics such as superior fracture toughness and high thermal conductivity can be significantly improved by tailoring the microstructure such that it can be used in automotive engine parts, heat exchangers, pump seals, ball bearings, cutting tools and ceramic armor as well as potential use in electronic and biomedical applications.

Related to silicon nitride are SiAlON ceramics which are solid solutions whereby Al and O substitute for Si and N in the α - and β - Si_3N_4 crystal structures and extra cations can be accommodated in the α -phase. An introduction to α - and β -SiAlONs and the representation of the Si-Al-O-N and related M-Si-Al-O-N systems, including the Jänecke prism, is given in the next chapter. The accompanying chapter explains how easier densification provided by oxide additives results in alpha/beta-SiAlON composites with lower glass content grain boundaries and better high temperature properties. An overview of the properties of SiAlON ceramics is given and how they are controlled by parameters such as phase ratio, solubility of Al and O ions in the Si_3N_4 structures, type of rare-earth additive used and crystallization of grain boundary phase(s). A brief section on applications is included describing structure-property-performance relationships in SiAlON ceramics.

Related to the SiAlONs is ALON, which can be thought of as a nitrogen-stabilized cubic aluminum oxide, and this is the subject of the next chapter which details both AlN and ALON, their crystal chemistry and the phase equilibria for the pseudo-binary Al_2O_3 -AlN system. Processing of AlN and ALON are described; small amounts of additives (rare earth oxides) are typically utilized to achieve fully dense, pore-free material and examples of microstructural development are presented. Properties are outlined, especially the high thermal conductivity for AlN. Carbothermal reduction enhances sintering of ALON and yields a transparent ceramic which makes it suitable for use in impact resistant windows or as an upconversion material (if Er and Yb oxides are used as sintering aids).

The next chapter reviews the scientific research and technological advances in SiC ceramics and discusses their current status in terms of the structure, processing methods, properties, and applications. The different crystal structures (polytypes) found for SiC are outlined. An overview follows of various processing techniques for SiC including pressureless sintering, gas pressure sintering (GPS), hot pressing, spark plasma sintering (SPS), reaction bonding (RBSC), recrystallization, chemical vapor deposition (CVD), and hot isostatic pressing (HIP). Examples of different microstructures are presented. Further discussion deals with the capability of different processing techniques to achieve high fracture energy, reduced flaw size, fine grain microstructure, and high density, which are prerequisites for achieving excellent mechanical properties. This includes details on their microstructure, porosity, and grain boundary chemistry, which in turn depend on the starting composition and processing technique. Finally, many of the most important structural and functional applications of SiC are outlined.

Because of emphasis in modern society on energy and environment-related issues, the latest power electronic devices need ceramic substrates with high thermal conductivity. In the next chapter, the developments of representative high thermal conductivity ceramics, silicon carbide, aluminum nitride and silicon nitride, are reviewed. In each case, intrinsic thermal conductivity is described followed by the basic ceramic processing techniques used and a discussion of the fundamental understanding of factors influencing and enhancing thermal conductivity, such as sintering additives and microstructural development.

The next chapter provides an introduction to MAX phases, or $\text{M}_{n+1}\text{A}_n\text{X}_n$ phases, which are a family of compounds within the class of complex or double carbides or nitrides where "M" refers to an early transition metal, "A" to an A-group element, "X" can be C and/or N and "n" is an integer (commonly 1, 2 or 3). It focuses on their multi-element nano-layered structure with atomic planes of A-atoms interleaving rock salt-structured $[\text{M}_6\text{C}]$ -octahedra, which form the basis for their unique set of both ceramic- and metal-like properties. Following an in-depth presentation on crystal structures, topics covered include processing of powders, thin film and bulk material synthesis, and an outline of their attractive properties.

The penultimate chapter in this section reviews Structure, Processing and Properties of Boride Ceramics: ZrB_2 , HfB_2 , OsB_2 and IrB_2 . Selected studies are described on synthesis of ReB_2 type hexagonal OsB_2 and IrB_2 powders by mechanochemistry of their precursor elements and their crystal structures are compared with commercial ZrB_2 and HfB_2 powders. All the borides have been densified using Spark Plasma Sintering (SPS) and densification, phase composition, microstructure analysis along with mechanical properties by nanoindentation of these diborides are presented.

The final chapter reviews Directionally Solidified Eutectic (DSE) Oxide Ceramics which consist of cubic zirconia, perovskite, or garnet phases of micron or nanometer size, dispersed in a continuous sapphire single crystalline phase grown from the melt. The combination of the outstanding creep behavior of Al_2O_3 along its c-axis with a huge amount of clean and strong grain boundaries, characteristic of the eutectic solids, results in a new set of ceramic oxides with excellent creep behavior and good mechanical properties up to 1700°C , even in corrosive environments. DSE ceramic oxides are thus envisaged as ultra-high temperature functional and structural materials.

In summary, the common theme throughout all of these chapters above is the composition-structure/microstructure-properties relationships.

Structural and Thermostructural Ceramics

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Introduction

It is generally recognized that the progress of human civilization is intimately connected with the availability and development of two major resources – materials and energy. What is perhaps less appreciated is the inextricable relation between materials development and energy generation (Murthy, 2004). This interdependence has been continuously growing and it is engineering materials that hold the key to the large-scale production of energy from renewable energy sources, which reduces the CO₂ footprint. Besides safe operations, high efficiency energy production and transport are key areas of research in the world today (Binner *et al.*, 2020; Murthy, 2012). These can be realised by future technologies such as wind and wave power, second generation concentrated solar power generation, generation IV nuclear fission and fusion reactors, as well as for other applications ranging from aerospace through to hypersonic and re-entry space vehicles. Many of these technologies are conceptually ready to be demonstrated but are not currently capable of being realised at the industrial scale due to limitations in obtaining appropriate materials (Krenkel *et al.*, 2006). Amongst the engineering structural materials, advanced ceramics, including the oxides, borides, carbides, nitrides and silicides, have received widespread attention over the past few decades and are suitable for many engineering applications.

Ceramics can be classified very broadly into structural, functional and bio-ceramics based on the type of application; however this chapter only discusses structural ceramics for room, high and ultra-high temperature applications; this will include discussing how the properties depend on the chemistry and nature of the bonding. In terms of processing, unlike metals and alloys where component size, shape and properties can all be tuned using post-processes such as mechanical working (e.g., rolling, forging and extrusion) or heat treatments, the synthesis and consolidation of ceramics are less straight forward. Hence it is important to select at the start the appropriate combination of synthesis and consolidation methods in order to obtain the required properties for ceramics and their composites and thus a range of different types of synthesis routes and consolidation methods are described herein. Since structure, texture and properties are all related to each other, important microstructural characterization techniques are also described for different types of ceramics and composites, albeit there is currently limited data available on texture effects for structural and thermostructural ceramics. Performance evaluation can be largely determined based on mechanical and physical properties and so key properties for structural applications are described, including thermal properties such as thermal conductivity, coefficient of thermal expansion (CTE), creep and thermal shock resistance, oxidation and ablation resistance.

Classification and Properties

Advanced structural ceramics have attracted attention in the scientific community for many decades. Compared with metals, ceramics have much higher hardness and service temperatures, often > 1200°C and, in some specific cases, up to around 3000°C. From this perspective, ceramics have advantageous properties, such as refractoriness, strength retention at elevated temperatures, high melting points, wear resistance and chemical inertness. As a result of such an attractive combination of properties, ceramics are considered as candidate materials for many structural applications at both room and elevated temperatures. The widespread use of ceramics has been limited, however, by their inherent brittleness and the difficulties associated with their fabrication, which typically demand very high temperatures and, for non-oxide ceramics, controlled atmospheres (Murthy, 2020a).

Classification of ceramics can be achieved in several different ways, for example, based on chemistry, properties or applications, Fig. 1. This chapter focuses on structural and thermostructural ceramics, which are defined by their applications in a wide variety of environments including wear, erosion, corrosion, ablation, high temperatures and irradiation, amongst others and including combinations of all of them. In general, the primary properties of structural/thermostructural ceramics are classified as physical, mechanical, thermal and nuclear; values are compared for different ceramics in Table 1. Many of the properties possessed by ceramics are associated with their “mixed” bonding, a combination of covalent and ionic and, sometimes, metallic. They consist of arrays of interconnected atoms; there are no discrete molecules. The majority of ceramics are compounds of metals or metalloids (B, Si) and non-metals (O, N, C). It is worth noting here that many of the important properties of ceramics are actually superior to many structural metals and alloys, including, for example, density (they are generally lower), melting point (they are generally higher), strength (generally higher but with brittle failure) and CTE (generally lower) as shown in Table 1. As just one example, the density of silicon carbide is $\sim 3.2 \text{ g cm}^{-3}$, which is around half of many structural metals and alloys, whilst its maximum use temperature, in non-oxidizing environments (which metals also generally need) can be as high as 1700°C. The reason that the majority of ceramics are brittle is due to the mixed ionic-covalent bonding that holds the constituent atoms together. According to the von Mises criterion, a minimum of five independent active slip systems is required for deformation/ductility (Basu and Balani, 2011) and since ceramics do not have these at room temperature, they are fundamentally brittle. Note that this is not always true at elevated temperatures, where there can be limited examples of plasticity. Ceramics are also much stronger in compression than

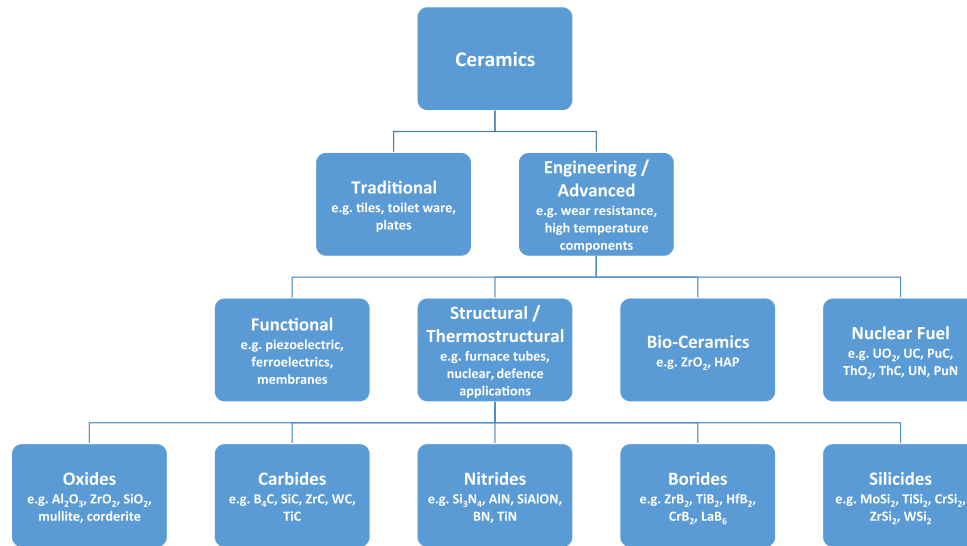


Fig. 1 Broad classification of ceramics based on type of applications.

in tension, whereas metals have comparable tensile and compressive strengths; this difference is important when ceramics are used for load-bearing applications (Kingery *et al.*, 1976).

A large number of ceramics are also stable in both harsh chemical and thermal environments. The need for high performance materials for energy, aerospace, automotive and industrial components that can operate in aggressive environments such as corrosive/ablative atmospheres, high or ultra-high temperatures, irradiation and erosion has led to a surge in research and development into the structural/thermostructural ceramics and their composites. Although most applications do not exceed, say, 1500°C, there are an increasing number of applications, including re-entry space vehicles and hypersonic platforms, that are required to operate at temperatures of up to 3000°C and the ultra-high temperature ceramics, primarily transition metal carbides, borides and their composites, are candidates for these applications (Murthy, 2020b).

As well as the ceramics themselves, there are a range of composites that are based on reinforcing the host matrix, allowing these ceramics to be classified into six groups based on their microstructures, Fig. 2. More details on the microstructural aspects of these ceramics are discussed in the microstructure section; suffice it to say here that the use of reinforcement can significantly increase the toughness of these materials, adding this property to the generally very beneficial properties possessed by monolithic structural and thermostructural ceramics.

Applications

Ceramics are often used in preference to metals for one or more reasons, including, typically, to allow performance under more demanding conditions in order to enhance component life or safety, or to increase the efficiency of an existing process or reduce fuel consumption, especially for the transport sector, and, more recently, to reduce global warming. A variety of applications where structural and thermostructural ceramics and their composites are used are discussed below:

1. *Wear resistance and tribological applications:* The key properties for these applications are hardness, hot hardness, high melting point, elastic modulus, chemical inertness and corrosion resistance. As a result, applications include such items as: cutting tools, drills, thread guides, extrusion dies, wear tiles, grinding media, ball bearings and hybrid bearings (ceramic balls enclosed in a steel race), amongst many others. Whilst many of these applications are used extensively throughout a wide range of different industrial sectors, some are quite “high profile”, for example, hybrid bearings were used in the turbo pumps of the space shuttle main engines (Binner *et al.*, 2020).

Alumina, Al_2O_3 , has the highest hardness (up to 23 GPa) amongst the oxides and is also one of the cheaper advanced ceramics and so it is used extensively for its wear, erosion and impact resistance (Abyzov, 2019a). Silicon carbide, SiC (hardness up to 30 GPa), and boron carbide, B_4C (hardness up to 37 GPa and third hardest material after diamond and cubic BN), are both harder than the hardest oxides and are therefore used in large tonnages as abrasives in grinding wheels, cutting wheels, lapping media, etc. (Suri *et al.*, 2010). Tungsten carbide-cobalt, WC-Co-based cermets are commercially available for crushing and grinding applications, whilst the friction and wear properties of Al_2O_3 , zirconia, ZrO_2 , and SiC have been shown to be very useful for cryo-tribological applications (Guha and Basu, 2010). Ceramic balls for ball bearings are commercially available with diameters from 4 mm to as large as 20–30 mm and can be made from Al_2O_3 , ZrO_2 , SiC, B_4C , WC, silicon nitride, Si_3N_4 , and SiAlON, the latter being an “alloy” of Al_2O_3 and Si_3N_4 . ZrO_2 -based ceramics are increasingly being favored for applications ranging from kitchen knives to large industrial slitting knives, to room temperature metal extrusion and drawing dies. Other carbides, e.g., titanium carbide, TiC-based cermets are also used extensively as cutting tools.

Table 1 Important physical, mechanical, thermal and nuclear properties of selected structural/thermostructural ceramics

Property	Physical			Mechanical				Thermal				Nuclear
Material	Cryst.	Density/ gcm ⁻³	Elect. res./μs2- cm	Hardness/ GPa	Fracture toughness/ MPam ^{1/2}	Flex. Str./ MPa	E/GPa	M. pt. ^o C	Therm. Cond./ Wm ⁻¹ K ⁻¹	CTE/10 ⁻⁶ K ⁻¹	Thermal shock resistance/K	Σ/(thermal) barns
<i>Oxides</i>												
Al ₂ O ₃	Hex. Rhom.	3.96–3.97	10 ²⁰	14–23	1.5–4.2	330	275–380	2054	27–30	7.2–9.6	92	0.093
ZrO ₂	Cubic Tetra. Mono.	5.56–5.75	10 ⁴ –10 ⁸	10–15	2.8–8.2	400–600	97–207	2681–2847	2–8	7.0–13.5	223	0.062
Cr ₂ O ₃	Hex. Rhom.	5.21–5.22	–	29	3.9	178–400	> 103	2330	10–33	7.5	277	1.240
Mullite	Ortho.	2.80	10 ¹⁹	11	2.2–2.6	270	145–220	1880	3–5	5.0–5.7	213	0.083
TiO ₂	Tetra. Ortho.	3.84–4.25	10 ¹⁹ –10 ²⁴	7	2.5	140	283	1825–1855	3–9	7.1–11.0	40	2.034
<i>Carbides</i>												
B ₄ C	Rhom.	2.52	10 ⁶	28–37	3.0–3.5	300	445–470	2350–2450	16–28	5.0	106	608.001
SiC	Hex.	3.10–3.21	10 ⁻⁴ –10 ²	22–30	4.6	610	410–469	2700–2797	78–490	3.0–4.7	267	0.085
ZrC	Cubic	6.56–6.73	20–75	19–29	–	790–870	195–482	3400–3532	20.5	2.3–5.0	515	0.094
WC	Hex.	15.30–15.70	53–80	13–22	–	480–800	641–696	2800–2870	100–121	4.0–7.3	134	9.202
TiC	Cubic	4.94	180–250	30–32	–	100–230	448–451	2940–3065	17–21	7.7	39	3.052
HfC	Cubic	12.20–12.76	109	18–25	–	350–470	352	3000–3900	–	6.60	144	52.002
<i>Nitrides</i>												
RBSN	Hex.	3.19	10–10 ⁹	16	1.5–8.5	150–200	120–130	1900–2173	7–43	2.3–3.5	797	1.163
SSN	Hex.	3.20	10–10 ⁹	15–20	5.0–8.5	1000–1200	300–330	2173	30–43	3.0–3.5	974	1.163
SiAlON	Hex.	3.20–3.30	–	–	6.0–8.0	750–950	300	–	15–22	3.0–3.7	622	0.899
AlN	Hex.	3.26	> 10 ⁸	12	4.5	235–370	260–350	2227–2230	50–180	4.4–5.7	151	1.072
BN	Cubic Hex.	3.48	10 ¹⁸ –10 ²⁰	45–49	–	30–80	150	2730–3027	20–33	1.0–6.0	133	380.955
		2.27	–	–	–	–	–	20–100	–	–	–	–
TiN	Cubic	5.43	–	19	–	–	–	2930–3290	29	9.4	–	4.005
ZrN	Cubic	7.09	–	15	–	–	390	2960	–	–	–	1.047
<i>Borides</i>												
TiB ₂	Hex.	4.38–4.52	10–30	25–35	5.0–7.0	700–1000	560	3225	60–120	7.3	187	508.700
ZrB ₂	Hex.	6.10–6.17	9.2	22–26	4.0 – 6.0	300	300–350	3245	20–58	6.8	99	506.728
HfB ₂	Hex.	10.50–11.21	11	21–28	–	350	500	3100–3380	104	6.3	84	541.333
NbB ₂	Hex.	6.80–6.97	–	18–19	–	420	505	2290–2900	–	7.7	83	507.050
TaB ₂	Hex.	11.20–12.50	–	25	4.5	555	550	3040–3140	–	8.2	95	513.500
CrB ₂	Hex.	5.22	30	11–20	3.5	600	211	2200	32	10.5	214	507.700
<i>Silicides</i>												
MoSi ₂	Tetra.	6.23–6.30	21–37	9–13	1.9–5.9	317	242–440	1900–2050	29–221	6.5–10.4	93	0.977
TiSi ₂	Ortho.	4.00–4.15	15–123	8–10	2.0–3.0	–	250	1500–1540	–	10.4	–	2.144
CrSi ₂	Hex.	4.60–4.91	70000	11	–	–	355	1477–1490	10	7.4–9.2	–	1.144
ZrSi ₂	–	4.88	–	–	–	–	–	1620	–	–	–	0.172
WSi ₂	Tetra.	9.30–14.52	50–60	7–10	3.7	–	312–468	2160–2324	–	5.0–16.3	–	6.244
HfSi ₂	Ortho.	7.60	–	–	–	–	–	1700	–	–	–	34.777

Note: Mono: Monoclinic; Rhom: Rhombohedral; Hex: Hexagonal; Ortho: Orthorhombic; Tetra: Tetragonal; Σ: Thermal Neutron absorption cross section, E – Youngs modulus; RBSN-Reaction bonded silicon nitride; SSN-Fully dense sintered silicon nitride.

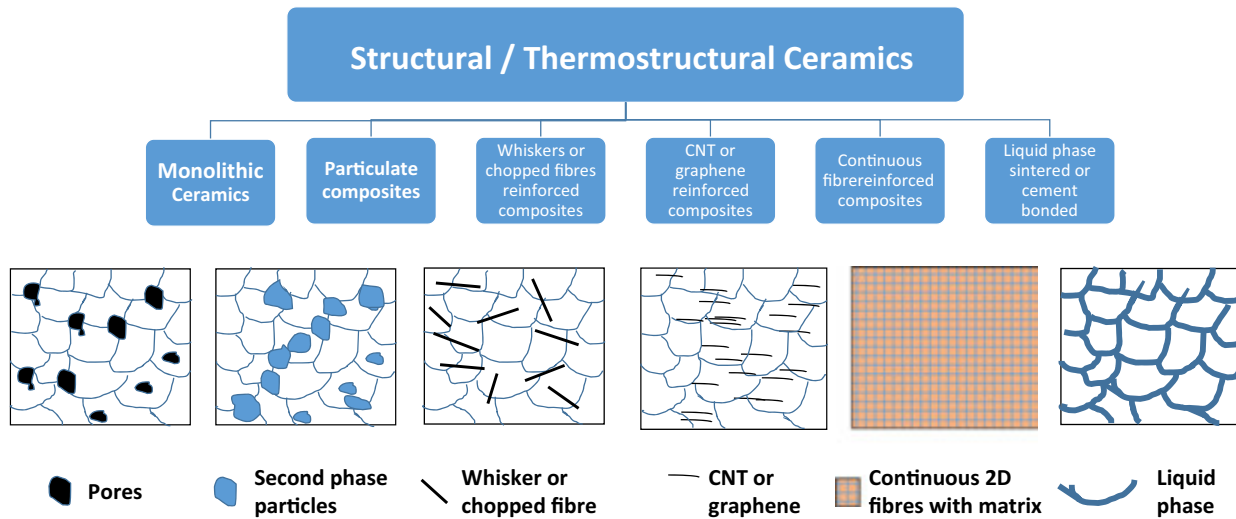


Fig. 2 Classification of structural/thermostructural ceramics based on their microstructures.

2. *Automobile and other metal-based industries:* The key properties for these applications are refractoriness, hardness, high melting point, chemical inertness and liquid metal corrosion resistance since applications include widespread uses as refractories for steel and nonferrous metals/alloy-making industries, including heating elements, roller hearths, thermocouple tubes and rollers for glass annealing kilns. Alumina, silica, magnesia, mullite, zirconia, cordierite and spinel are widely used refractories for different temperatures and conditions due to their high melting points $> 1800^{\circ}\text{C}$ (Table 1). In addition, ceramics find applications in electrical/thermal insulation, tubes, sheaths, molten metal crucibles and thermowell tubes in the steel refinement process. There are also increasing applications in automobile valves, exhaust systems, gears, valve guides & seals, engine tappets, turbocharger rotors, seals and bearings involving fluid and gas transport, which typically operate under quite corrosive conditions. Ceramics are also used for extrusion dies, cylinder liners, evaporation boats for vapor coating of aluminum, electrodes in Hall-Heroult cells, alkali metal thermoelectric converters and electric discharge machining (EDM) (Abyzov, 2019a,b). Commercial springs made of Si_3N_4 , which has a high elastic modulus of up to 330 GPa, Table 1, are also now available (Hampshire, 2007, 2008).
3. *Ceramic based coatings:* The key properties for these applications are hardness, high melting point, chemical inertness, wear, corrosion and ablation resistance with a wide range of applications including thermal barrier coatings (TBC), environmental barrier coatings (EBC), wear resistant coatings and corrosion resistant coatings. In addition, coatings are often used in the production and repair of a wide range of service components, including turbine blades, exhaust manifolds, nuclear equipment, valve and pump parts, grinding rollers, heat exchangers, jet engine parts, evaporators, chemical processing equipment and parts that are exposed to marine and other demanding environments (Abyzov, 2019a). Coatings are frequently made from carbides, nitrides, silicides, silicates and/or borides with coating thicknesses normally ranging between 1 and 50 μm , depending on the requirements of the application and the deposition process used (Krenkel *et al.*, 2006). Thicker coatings, e.g., in the millimeter range, can be applied by techniques such as thermal spraying but are limited in chemistry, compatibility with the substrate properties (e.g., thermal expansion, etc.), adhesion and cohesion (Basu and Balani, 2011). In recent years there has been a major focus on developing EBCs for the aerospace industry and other applications, with four different generations having been developed. The most recent, 4th generation, which mainly consists of rare earth silicates with oxide ceramics (zirconia & alumina), can withstand at least 1500°C (Krenkel *et al.*, 2006).
4. *Defense applications:* The key properties for these applications are high hardness, the Hugoniot Elastic Limit (HEL), wear resistance, lightweight and low thermal expansion coefficient, with a primary application being armor, whether for personnel, helicopter or tank and with transparent armor being used for windows (Suri *et al.*, 2010). In addition, ceramics are used for radar transparent missile nose cones and for hypervelocity platforms, e.g., missiles and rockets (Binner *et al.*, 2020). Over more than three decades, ballistic performance and dynamic behavior studies have been performed on a range of ceramics, including aluminum nitride, AlN , Al_2O_3 , B_4C , SiC , titanium diboride, TiB_2 , WC and ZrO_2 . Among these, B_4C in particular is used at the commercial scale for body armor due to its low density, 2.52 g cm^{-3} , and high HEL. Fully sintered silica is used for missile cones, whilst the ultra-high temperature ceramics and their composites are being extensively researched for hypervelocity applications (Binner *et al.*, 2020).
5. *Nuclear Applications:* The key properties for these applications are a low neutron absorption cross section for structural applications, a high neutron absorption cross section for control rod/shielding applications and irradiation resistance for both. Applications range from neutron absorbers, control rods and neutron shielding materials, fuel rod cladding tubes, irradiation shields for different types of sensors, reactor core components and structural materials for generation IV nuclear reactors. There are also a number of structural components and coatings used in fusion reactors, especially first wall and tokamak divertors. SiC and ZrC are both candidate structural materials in high temperature nuclear reactors due to their resistance to irradiation damage and low neutron absorption cross section (~ 0.9 barns), whilst B_4C is one of the most important materials for nuclear reactor applications. It is used as a control rod material for nuclear reactors due to the presence of the neutron absorbing ^{10}B isotope in natural boron and a resulting high neutron absorption cross section of ~ 600 barns (Florez *et al.*, 2020; Subramanian *et al.*, 2010).

6. *High and ultra-high temperature applications:* The key properties for these applications are a high melting point, thermal conductivity and wear resistance, a low coefficient of thermal expansion, excellent corrosion and/or ablation resistance as well as strength retention at elevated temperatures, good thermal shock resistance and, for some applications, low mass. The components (and their oxidized products if applicable) should be stable as solid phases at elevated temperatures, which can potentially be $\geq 2000^\circ\text{C}$. These structural and thermostructural ceramics are used for a range of aerospace and aeronautical applications, such as engine parts, including high pressure turbine shrouds, exhaust nozzles, combustor liners, turbine blades and vanes, rocket motors, bearing seals, plasma arc electrodes, heaters and igniters, leading edges, nose caps, and, for the highest temperature applications where operating temperatures can exceed 3000°C , hypersonic and scramjet platforms (Binner *et al.*, 2020; Paul *et al.*, 2016, 2014; Rubio *et al.*, 2018). Carbides and borides of Zr, Hf and Ta are the candidate materials for these applications due to their high melting points of $> 3000^\circ\text{C}$, low CTE of $\sim 10^{-6} \text{ K}^{-1}$ and good thermal shock resistance, Table 1.

Synthesis

A variety of synthesis methods have been explored by researchers around the world based on the requirements of the application, i.e. the properties desired, and the need for commercial viability, e.g., the quantities required (Fahrenholtz *et al.*, 2016; Sonber *et al.*, 2013). The successful application of ceramic components starts with the careful selection and optimization of the initial raw materials, i.e., the powder chemistry, purity, particle shape, size and its distribution, its specific surface area, degree of homogeneity, and, not least, its cost. All this necessitates choosing the right synthesis method, some of which are summarized in Table 2 (Murthy, 2020a; Sonber *et al.*, 2013). Subsequently, this is followed by a need to select the appropriate green forming and densification route; both the latter are discussed in the section on densification/consolidation.

Chemical methods

Many of the minerals that can be processed into oxide ceramics are naturally occurring in the earth's crust. They are extracted from the associated gangue by one or more of a range of mineral processing steps that are typically selected to deliver the required quantity with the required purity and particle size (Abyzov, 2019a). As one example, alumina is almost always obtained using the Bayer process, which involves extraction from bauxite – a mineral that mainly consists of the hydrated forms of Al_2O_3 , including gibbsite ($\text{Al}(\text{OH})_3$), boehmite and diasporite (Abyzov, 2019a). The bauxite ore is crushed and treated with strongly alkaline solutions of $\text{Na}(\text{OH})$ and $\text{Ca}(\text{OH})_2$. In the first stage, the aluminum hydroxides are converted into sodium aluminate NaAlO_2 and the silica present is also dissolved, whilst the CaO , Fe_2O_3 and TiO_2 impurities remain as part of an insoluble residue, which can be easily removed. The silica is subsequently also removed by slow heating, which causes a $\text{Na}_2\text{Si}(\text{OH})_6$ precipitate to form. The remaining clear solution of $\text{NaAl}(\text{OH})_4$ is cooled, diluted with water and neutralized with carbon dioxide. As a result, aluminum trihydrate, $\text{Al}(\text{OH})_3$, is selectively precipitated from the solution without any dissolved silica residues. The $\text{Al}(\text{OH})_3$ is calcined to yield anhydrous Al_2O_3 , the quality of which varies quite significantly depending on the baking conditions. At low temperatures ($300\text{--}800^\circ\text{C}$), metastable, transitional crystalline forms of Al_2O_3 are formed (e.g., δ , γ , η , κ , χ and θ - Al_2O_3), whilst higher temperatures, e.g., $1000\text{--}1300^\circ\text{C}$, yield α - Al_2O_3 , or corundum (Abyzov, 2019a). The main impurity in Al_2O_3 produced by the Bayer process is sodium, which is one of the worst contaminants for alumina ceramics and, if present in too large quantities limits the number of technical applications. This was one of the major issues in the early days of advanced ceramics, when demand for the material was too low to justify removing enough of the sodium. However, these days halogen-containing compounds such as BCl_3 are used to remove the sodium in the form of volatile NaCl by evaporation. The crystallite size of the α - Al_2O_3 typically varies from 0.5 to $10 \mu\text{m}$, with higher baking temperatures yielding coarser alumina (Abyzov, 2019a). These days, the drive is very much towards finer particle sizes since these yield finer grain sizes in the final ceramics, which can lead to superior properties such as strength though at the expense of a more expensive powder.

Other chemical methods to obtain oxide powders include hydroxide coprecipitation (Abyzov, 2019b), alkoxide hydrolysis, gel precipitation microemulsion, sol-gel (Xiong *et al.*, 2017), gas phase reaction and hydrothermal synthesis (Dell'agli & Mascolo, 2000). The first and last of these methods are currently exploited in large scale commercial production, whilst the others are typically either used for small scale production or are still in the laboratory. The co-precipitation method can be used, for example, to synthesize homogeneously distributed Y_2O_3 -doped ZrO_2 powders. The process involves using ammonia to leach ZrOCl_2 and $\text{YCl}_3/\text{Y}(\text{NO}_3)_3$ solution. A co-precipitation route has also been used to produce, nano crystalline, ZrO_2 by using KOH as precipitating agent (Ramachandran *et al.*, 2018). Hydrothermal synthesis is simple and cheap and is typically used to form nano crystalline and agglomerate-free oxide or mixed oxide powders at relatively low temperatures. For example, fine ZrO_2 - Y_2O_3 solid solutions have been prepared by using the precursors of zirconia gel, crystalline Y_2O_3 and Na_2CO_3 and NaOH solutions at a temperature of 110°C . A high pH value was obtained due to the hydrolysis of the Na_2CO_3 , often called a mineralizer, which helped to structurally rearrange the zirconia gel during the crystallization enabling the production of nano-sized particles (Dell'agli & Mascolo, 2000).

Indeed, a significant recent trend has been to find synthesis routes that will yield nanostructured powders since these can yield enhanced properties, not just increased strength but also transparency or other specialist properties in some cases. The sol-gel technique is a much investigated route to synthesize nanoparticles using a range of different precursors (Kumar *et al.*, 2015) since it requires low temperatures and has proven to be flexible and less complex compared to other routes for nanoparticle synthesis. The initial step is typically to convert the precursor material, often chlorides or metal alkoxides, into a colloidal solution, known as a sol, usually via hydrolysis. The latter is then converted, often via dehydration, into a gel, which is made up of discrete particles. The limitations of the sol-gel method are its expensive raw materials, the often poor yield and the fact that the processes involved are

Table 2 Important chemical reactions involved in the different types of synthesis of non-oxide structural/thermostructural ceramics

Type of synthesis reaction	Reaction number
I. Direct elemental/solid state reaction method	
$M_{(s)} + 2B_{(s)} \rightarrow MB_{2(s)}$	(1)
$M_{(s)} + C_{(s)} \rightarrow MC_{(s)}$	(2)
$M_{(s)} + 2Si_{(s)} \rightarrow MSi_{2(s)}$	(3)
$MH_{2(s)} + 2B_{(s)} \rightarrow MB_{2(s)} + H_{2(g)}$ (modified elemental reaction)	(4)
$MH_{2(s)} + C_{(s)} \rightarrow MC_{(s)} + H_{2(g)}$ (modified elemental reaction)	(5)
$MH_{2(s)} + 2Si_{(s)} \rightarrow MSi_{2(s)} + H_{2(g)}$ (modified elemental reaction)	(6)
$2M_{(s)} + Si_{(s)} + B_4C_{(s)} \rightarrow 2MB_{2(s)} + SiC_{(s)}$ (appropriate for making composite powders)	(7)
$8M_{(s)} + 1.5Si_{(s)} + 2B_4C_{(s)} + 3.5C_{(s)} \rightarrow 4MB_{2(s)} + 1.5SiC_{(s)} + 4MC_{(s)}$ (appropriate for making composite powders)	(8)
$M_{(s)} + 2Si_{(s)} + Mo_{(s)} + 2B_{(s)} \rightarrow MB_{2(s)} + MoSi_{2(s)}$ (appropriate for making composite powders)	(9)
$M_{(s)} + 2Si_{(s)} + Mo_{(s)} + C_{(s)} \rightarrow MC_{(s)} + MoSi_{2(s)}$ (appropriate for making composite powders)	(10)
$2M_{(s)} + 2Si_{(s)} + Mo_{(s)} + 2B_{(s)} + C_{(s)} \rightarrow MB_{2(s)} + MC_{(s)} + MoSi_{2(s)}$ (appropriate for making composite powders)	(11)
$3M_{(s)} + 2BN_{(s)} \rightarrow MB_{2(s)} + 2MN_{(s)}$ (appropriate for making composite powders)	(12)
$4M_{(s)} + Si_3N_{4(s)} + 3B_4C_{(s)} \rightarrow 4MB_{2(s)} + 3SiC_{(s)} + 4BN_{(s)}$ (appropriate for making composite powders)	(13)
$3M_{(s)} + B_4C_{(s)} \rightarrow 2MB_{2(s)} + MC_{(s)}$ (appropriate for making composite powders)	(14)
$10M_{(s)} + Si_3N_{4(s)} + 3B_4C_{(s)} \rightarrow 6MB_{2(s)} + 3SiC_{(s)} + 4MN_{(s)}$ (appropriate for making composite powders)	(15)
II. Oxide reduction methods	
a. Carbothermic	
$MO_{2(s)} + B_2O_{3(l)} + 5C_{(s)} \rightarrow MB_{2(s)} + 5CO_{(g)}$	(16)
$MO_{2(s)} + 3C_{(s)} \rightarrow MC_{(s)} + 2CO_{(g)}$	(17)
b. Carbothermic in the presence of Boron carbide	
$2MO_{2(s)} + B_4C_{(s)} + 3C_{(s)} \rightarrow 2MB_{2(s)} + 4CO_{(g)}$	(18)
c. Borothermic	
$3MO_{2(s)} + 10B_{(s)} \rightarrow 3MB_{2(s)} + 2B_2O_{3(l/g)}$	(19)
d. Carbo and borothermic reduction	
$7MO_{2(s)} + 5B_4C_{(s)} \rightarrow 7MB_{2(s)} + 3B_2O_{3(l/g)} + 5CO_{(g)}$	(20)
e. Metallothermic reduction	
$3MO_{2(s)} + 3B_2O_{3(l)} + 10Al_{(l)} \rightarrow 3MB_{2(s)} + 5Al_2O_{3(s)}$	(21)
$MO_{2(s)} + B_2O_{3(l)} + 5Mg_{(l)} \rightarrow MB_{2(s)} + 5MgO_{(s)}$	(22)
f. Silicothermic reduction	
$MO_{2(s)} + 2Si_{(s)} \rightarrow MSi_{2(s)} + 4SiO_{(g)}$	(23)
g. Other reduction methods	
$MO_{2(s)} + B_2O_{3(s)} \xrightarrow{a} MB_{2(s)} + 5/2O_{2(g)}$	(24)
III. Chloride reduction/chemical synthesis methods	
$MCl_{4(g)} + 2BCl_{3(g)} + 5H_{2(s)} \rightarrow MB_{2(s)} + 10HCl_{(g)}$	(25)
$2MCl_{4(g)} + 8LiBH_{4(g)} \rightarrow 2MB_{2(s)} + 2B_2H_{6(g)} + 10H_{2(g)} + 8LiCl_{(g)}$	(26)
$MCl_{4(g)} + 2NaBH_{4(g)} \rightarrow MB_{2(s)} + 2NaCl_{(s)} + 4H_{2(g)} + Cl_{2(g)}$	(27)
IV. Displacement reaction method (suitable for making composite powders)	
$MC_{(s)} + 6B_{(s)} \rightarrow MB_{2(s)} + B_4C_{(s)}$	(28)
$2MC_{(s)} + B_4C_{(s)} + 3Si_{(s)} \rightarrow 2MB_{2(s)} + 3SiC_{(s)}$	(29)
$MN_{(s)} + B_{(s)} \rightarrow MB_{2(s)} + BN_{(s)}$	(30)
$4MN_{(s)} + 3B_4C_{(s)} + 3Si_{(s)} \rightarrow 4MB_{2(s)} + 3SiC_{(s)} + 4BN_{(s)}$	(31)

^ain the presence of catalyst 'CaO+CaF₂'; 'M' - Refractory/transition/rare earth metal, 's' - solid, 'l' - liquid, 'g' - gas, 'O' - oxygen, 'C' - carbon, 'N' - nitrogen.

often slow and energy-intensive, particularly for large scale production. Nevertheless, the method has been used for producing Al₂O₃, SiO₂, TiO₂, rare earth oxides and metal silicates, amongst other oxides (Kumar *et al.*, 2015).

Non-oxide ceramics are also produced by the sol-gel method, although they are not as easy to achieve. As just one example, nanocrystalline ZrC has been prepared by using zirconium *n*-propoxide and furfuryl alcohol as the precursors with a block copolymer P123 (Pluronic P123 is a symmetric triblock copolymer comprising poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) in an alternating linear fashion, PEO-PPO-PEO) surfactant being used to achieve intimate mixing (Mallick *et al.*, 2016). Formation of ZrC starts at 1250°C and full conversion takes place at 1450°C but requires an argon atmosphere.

Direct elemental, self-propagating high temperature synthesis (SHS), mechanical alloying and shock-wave reaction methods

All these methods are typically used to produce non-oxide ceramics. The direct elemental reaction method represents the reaction between the respective metallic and/or non-metallic elements to form the desired ceramic, for example Ti, Zr, Hf, Nb are directly reacted with elemental carbon, boron or silicon in the stoichiometric ratio to form the respective carbides, borides or silicides

(SiC, TiC, ZrC, TiB₂, ZrB₂, HfB₂, MoSi₂, TiSi₂, ZrSi₂) at elevated temperature in a vacuum or inert atmosphere as shown in reactions 1–3 in Table 2. The advantages of this method are the ability to obtain highly pure and stoichiometric/near-stoichiometric products with fine particle/crystal sizes. However, this method requires expensive and pyrophoric-natured elemental powders, which, in turn, need extensive care to handle and store. For example, the synthesis of boron carbide from its elements is expensive due to the high cost of elemental boron and hence is employed for specialized nuclear applications only, such as B¹⁰-enriched or very pure/near-stoichiometric B₄C. Since the latter is in equilibrium with free carbon and is the only boundary between B_nC and B_nC + C (where 4 < n < 10), the synthesis of B₄C without free carbon is extremely difficult. With a view to producing B₄C, however, various experiments have been reported in which the B/C ratio was varied from 4.0 to 4.6 (Sonber *et al.*, 2013; Suri *et al.*, 2010). Whilst the B₄C phase could be obtained when the B/C ratio was 4.0, i.e., stoichiometric, the boron-rich B₈C phase was also present with the higher B/C ratios. Similarly, single phase niobium diboride, NbB₂, powder has been prepared by direct reaction of Nb and amorphous B powders (Murthy, 2020a) whilst molybdenum disilicide, MoSi₂, was synthesized from its elements using stoichiometric amounts of pure Mo (> 99.7%) and Si (> 99%) in a moderate vacuum of 0.1 Pa up to a temperature of 1400°C. Metal hydrides can also be used as starting materials instead of expensive elemental metals as per the reactions 4–6 in Table 2 to obtain similar purity products. Moreover, this approach can also produce composite powders, as per reactions 7–15 in Table 2. Nano-crystalline ZrC, for example, has been prepared by fast exothermic solid state metathesis reactions between CaC₂ and ZrCl₄ (Mallick *et al.*, 2016).

Self-propagating high-temperature synthesis (SHS) is an energy efficient method that can create phase pure, non-oxide ceramic powders in seconds via highly exothermic reactions of a reactant mixture. The temperature of the combustion can be extremely high, up to ~5000K, whilst the rate of wave propagation can be very rapid, e.g., 25 cm s⁻¹ (Mallick *et al.*, 2016). The key additional benefit of this method is the ability to obtain high purity, porous products due to the evaporation of the volatile impurities – the porous nature makes the crushing and grinding operations much easier leading to fine powders that contain few impurities from the grinding media. As an example, ZrC prepared by the SHS process using ball milled Al, Zr and C powders, the latter in the form of nano-sized carbon black. During the reaction, a metastable ZrAl₃ phase was formed and the heat released by this reaction was utilized to form the ZrC (Mallick *et al.*, 2016). ~26 nm TiB₂ powder has been produced via an SHS process using 20 wt% NaCl as a diluent (Gadaky *et al.*, 2014) whilst ZrB₂ has been formed from the elemental powders via a thermodynamically favorable reaction; $\Delta G_{2000K} - 279.6 \text{ kJ mol}^{-1}$. ZrB₂-based cermets were also prepared by the SHS route using ZrO₂, B₂O₃ and excess Al as reactants together with Fe₂O₃. Meanwhile ZrB₂-ZrC composite powders were synthesized by a mechanical activation-assisted SHS process using a mixture of Zr, B and C powders (Sonber *et al.*, 2013).

Mechanical alloying (MA) is a solid-state powder processing technique involving high energy ball milling, often for prolonged durations. Submicron-sized TiB₂ powder has been prepared from a mixture of Ti and B powders (Hwang and Lee, 2002). It was reported that the size of the metal powder and the heat of formation of the boride greatly affected the mechanical alloying time, whilst leading to fine boride compound powders. The room temperature MA of B–C mixtures in planetary ball mills for prolonged duration, which was said to activate the powders, was followed by an annealing heat treatment that lead to B₄C powders, which were subsequently densified by spark plasma sintering to yield 95% pure boron carbide ceramics (Heian *et al.*, 2004). Spark plasma synthesis is a process in which a pulsed high DC current is passed through the charge mixture, which is contained in a cavity, along with the simultaneous application of uniaxial pressure. In this process for B₄C, the start and completion of formation were reported at 1000 and 1200°C respectively. Finally, ZrB₂ with a crystallite size of ~75 nm was also prepared successfully by mechanical alloying of ZrO₂, B₂O₃ and Mg for 15 h (Sonber *et al.*, 2013).

Finally, the shock wave (SW) technique is based on achieving very high heating and cooling rates along with a simultaneous high pressure. This is accomplished by placing the reactants inside a steel container, which, in turn, is placed inside a steel tube. An electric detonator is placed between a container and the tube to initiate an explosive detonation that occurs in micro to milliseconds. After the resulting shock treatment, the samples were recovered by shaving off the steel container with a lathe (Suri *et al.*, 2010). This approach is suitable for the preparation of crystals of non-equilibrium phases that are hard to be produced under conditions of thermal equilibrium. The approach has been used to synthesize boron carbide from amorphous boron and graphite powder using trimethylenetrinitramine as the detonator. The resultant product exhibited several different morphologies, such as filaments, distorted ellipsoids, plates and nano-sized polyhedron particles.

Oxide reduction methods (carbothermic, borothermic, metallothermic and silicothermic)

Carbothermal reduction of the corresponding transition or refractory metal oxides emerged as an economical production route and continues to be the most popular method for the synthesis of commercial carbide and boride powders as per reactions 16–18 in Table 2. The resulting powders typically contain oxygen and excess carbon as impurities (up to 1%) along with other metallic impurities that are present in the starting raw materials. For example, commercial ZrB₂ is produced from naturally occurring zircon ores, which usually contain Hf as an impurity. In addition, although it is possible to reduce some impurities, particularly carbon and oxygen, to ppm level by an appropriate high temperature vacuum treatment, impurities, including the reintroduction of oxygen, can be picked up during grinding, both from the media used and the atmosphere (Fahrenholtz *et al.*, 2016). Although this route is commercially viable, all process parameters have to be carefully optimized to yield both the desired phase and the required particle size. Other metal oxide reduction methods such as borothermic, metallothermic and silicothermic reduction processes, though far less common, are also attractive for commercial production of some non-oxide ceramics at the industrial scale, as shown in Table 2, reactions 16–24. A few case studies are summarized below.

B₄C powder has been synthesized at 1200°C by the carbothermal reduction of boric acid with petroleum coke and also by the magnesiothermic reduction of B₂O₃ or alkali Na₂B₄O₇ in the presence of carbon at 1650–1700°C (Gunnewiek *et al.*, 2017). The addition of metallic sulfates, which act as a catalyst, allows the temperature to be reduced to as low as 700°C. Nano ZrC powder with only 0.1 wt% O₂ impurity was synthesized by the reduction of ZrO₂ with carbon in an argon atmosphere at 1800°C (Mallick *et al.*, 2016) whilst pure WC nanopowder, ~7 nm particle size, was prepared by the mechanical solid-state reduction of WO₃ and Mg followed by the solid-state reaction of W and C using high-energy ball milling (HEBM).

ZrB₂ powder is typically synthesized as per reaction 18 in Table 2 at a temperature of > 1800°C in a dynamic vacuum or inert atmosphere; the former yields faster kinetics and results in a higher purity product (Murthy, 2020a). The borothermal reduction of ZrO₂ can yield pure ZrB₂ at temperatures higher than 1600°C, though the method is not economic for commercial production as it involves the volatilization of expensive boron in the form of boron oxide (Sonber *et al.*, 2013). The carbothermal reduction of zirconia and boric acid with carbon has also been used to synthesize ZrB₂ whiskers. Meanwhile, ZrB₂, TiB₂ and HfB₂ powders have all been synthesized by the borothermal reaction between the respective metal dioxides and elemental boron in the range 1000–1750°C under vacuum (Jung *et al.*, 2012). The morphology and particle size of the powders was strongly influenced by the synthesis temperature; a faceted morphology and diameter of ~0.15 µm was reported between 1000 and 1200°C whilst a spherical morphology with a particle size of ~0.66 µm was observed at > 1500°C. Guo and Zhang (2009) reported that they generally formed ZrC along with ZrB₂ when using additions of boron carbide during the reduction; however they obtained single phase ZrB₂ by using an excess of 20–25 wt% B₄C; this will have covered for the volatilization of the boron.

The metallothermic reduction of ZrO₂ and B₂O₃ (as for all of these processes, excess B₂O₃ is required) involves the use of cheap raw materials and is self-sustainable due to its exothermic, self-propagating high temperature synthesis, nature. Generally, magnesium, aluminum, calcium, sodium or silicon are used as reducing agents for metallothermic reductions; of these magnesium is usually preferred due to the relative ease of leaching out its oxide form from the product. During this process, the complete consumption of the reactants has to be ensured, especially the ZrO₂ since it is very difficult to remove any excess from the product by leaching or dissolution due to its refractory nature (Sonber *et al.*, 2013). Aluminum was used as the reducing agent for the preparation of ZrB₂-Al₂O₃ composite powders as per reaction 21 in Table 2. Several different precursor mixtures have been used during the synthesis of TiB₂ by carbothermic reduction, including the mixed oxides of boron and titanium, the reduction of titanium oxide by mixtures of boron carbide and carbon, and the reduction of the mixed oxides by metals, including aluminum, silicon and magnesium (Fahrenholtz *et al.*, 2016). Meanwhile HfB₂ has also been synthesized by borothermic reduction, carbothermic and metallothermic reduction (Murthy, 2020a; Sonber *et al.*, 2013). NbB₂ has been prepared by borothermic reduction of Nb₂O₅ in a vacuum and also by melting a mixture of Nb₂O₅ and B in an argon plasma arc (Yeh and Chen, 2006). CrB₂ and other refractory metal borides have also been synthesized by a range of different reduction methods as per the reactions 16–24 in Table 2.

Gas phase reactions and other methods of synthesis

Other methods of synthesis include gas phase, solution-based, molten salt electrolysis and polymer-precursor methods. These approaches generally enable the production of ultra-fine powders with very high purity, but suffer from the limitations of being expensive with low productivity and often involving the handling of toxic or explosive gases or solutions.

The solution-based methods involve intimate contact between the reactants in a liquid state and hence require only low temperatures (Sonber *et al.*, 2013). ~200 nm ZrB₂ powders with a specific surface area of 32 m²g⁻¹ were prepared by using inorganic-organic hybrid precursors of zirconium oxychloride (ZrOCl₂·8H₂O), boric acid and phenolic resin as sources of zirconia, boron oxide and carbon respectively at the relatively low temperature of 1500°C. ZrB₂ has also been synthesized using zirconium *n*-propoxide refluxed with 2,4-pentanedione to form zirconium diketonate. This compound further hydrolyzed in a controllable fashion to form a zirconia precursor that, with boric acid and phenol-formaldehyde, was concentrated, dried, pyrolyzed at 800–1100°C, and then carbothermally reduced at 1150–1800°C to yield spherical particles of 200–600 nm ZrB₂ (Murthy, 2020a). Even finer, 5–100 nm, TiB₂ has been prepared using a solution phase reaction between NaBH₄ and TiCl₄, followed by annealing the amorphous precursor obtained at 900–1100°C (Khoshshima *et al.*, 2020).

Various non-oxide ceramics have been synthesized by the molten salt electrolysis method (Sonber *et al.*, 2013). ZrB₂ was deposited from a solution of ZrO₂ and B₂O₃ dissolved in molten Na₃AlF₆ at 1020°C on nickel cathodes using a graphite anode. The resultant ZrB₂ was reported to be scaly/dendritic and non-adherent. ZrB₂ has also deposited on nickel cathodes from cryolite-alumina melts containing zirconium and boron oxide. Meanwhile CrB₂ nanorods were prepared via a reduction-boronation route at 650°C in a molten salt of anhydrous aluminum trichloride using an autoclave. Many other rare earth hexaborides have also been prepared using the molten salt electrolysis method (Berchmans *et al.*, 2010).

The polymer precursor method for synthesizing of non-oxide ceramics is typically performed by dispersing a metal oxide in a boron carbide-polymeric precursor. On heating, the mixture results in the in-situ generation of boron carbide and carbon, which provide the source of B and C, followed by a reaction to produce the non-oxide ceramics by reduction of the appropriate metal oxide. The desired characteristics of the polymer are that it should contain the required elements to form the intended non-oxide ceramic compound by the reduction of the metal oxide but also be stable and “processable”. Dinitrile polymers are one of the examples which have the required characteristics and provide a good yield when used to form borides from the condensation polymerization of deca-borane (Sonber *et al.*, 2013). Crystalline ZrB₂ has been prepared by dispersing ZrO₂ into polymer precursor decaborane dicyanopentane polymer (-B₁₀H₁₂-NC-(CH₂)₅-CN-)_x and pyrolysing at 1450°C (Forsthoefer and Sneddon, 2004). Displacement reactions are another common method used for the in-situ synthesis of ceramics and composites powders as per reactions 28–31, Table 2. These reactions offer the same advantages as direct synthesis reactions, viz., low temperature

requirements, high purity and control of particle morphology, but often use less costly or more stable precursors. HfB_2 powders containing 22 vol% SiC and 5 vol% ZrC were synthesized below 1200°C from a mixture of Hf, Si and B_4C (Forsthoefel and Sneddon, 2004).

The nitridation reaction can be used to synthesize nitride ceramics, for example, porous solid reaction bonded silicon nitride (RBSN) is formed by reacting silicon powder with nitrogen gas at $> 1000^\circ\text{C}$. The porous solid can then be ground into a fine powder using standard milling techniques. Chemical vapor deposition can also be used to deposit nitride coatings by reacting metal chlorides, e.g., silicon tetrachloride, with ammonia. The product, in this case silicon nitride, Si_3N_4 , is usually obtained in an amorphous state, but it can be crystallized by a heat treatment at a higher temperature such as $\sim 1300^\circ\text{C}$. The carbothermal reduction of metal oxides with carbon in the presence of high pressure nitrogen also yields nitride powders. For example, Si_3N_4 can also be obtained by reducing SiO_2 with petroleum or active coke in a nitrogen atmosphere. The process requires excess carbon in order to ensure complete reduction of the SiO_2 . Any residual carbon is subsequently burned off at temperatures of $\geq 550^\circ\text{C}$. SiO and SiC can also be formed during this process unless the composition and temperature are carefully controlled (Hampshire, 2007, 2008).

Densification/Consolidation

A number of different fabrication methods are listed in Table 3, each with a representative schematic and the advantages and limitations of each method are also outlined. Sintering can be accomplished via pressureless sintering – typically used for the oxide-based materials, or, more commonly, by using external pressure (e.g., hot pressing, hot isostatic pressing or spark plasma sintering). There are also a range of newer techniques, including microwave sintering and flash sintering where the use of conventional furnaces is replaced by alternative energy sources.

The pressure-based approaches are often used for the non-oxides since pressureless sintering rarely yields a sufficiently high density due to the high melting point, strong covalent bonding and low intrinsic self-diffusivity of the ceramics (Fahrenholtz *et al.*, 2014). Higher temperatures can be used for densification by pressureless sintering techniques, but this tends to lead to exaggerated grain growth, which results in poor mechanical properties due to the formation of micro cracks at the grain boundaries (Suri *et al.*, 2010). In addition, non-oxide ceramic powder surfaces are always contaminated with surface oxides, which promote surface diffusion and evaporation condensation mechanisms (Basu *et al.*, 2006). To achieve high densities whilst inhibiting abnormal grain growth, it has been recommended that the total oxygen content of the powder must be limited to ≤ 0.5 wt% or strong reducing additives need to be used to remove the surface oxides (Murthy, 2012). Other possible solutions to overcome these limitations include using nanosized starting powders, or using reactive sintering, liquid phase sintering, cement-bonded sintering as well as the pressure-assisted sintering techniques mentioned above. Sintering additives can enhance the densification and hence properties of the end product due to one or more mechanisms, including (1) the formation of a liquid phase at the sintering temperature (liquid phase sintering), (2) the reduction of the surface oxides, (3) an increase in the defect concentration due to chemical reactions (reactive sintering) or (4) the stabilization of high temperature phases (Murthy, 2020a; Sonber *et al.*, 2013). A range of additives have been exploited to improve the sinterability and properties of the non-oxide structural ceramics, including metallic additions, e.g., Ni, Fe, Cu, Co, Ti, and non-metallic, e.g., Y_2O_3 , CeO_2 , AlN, MoSi_2 , CrSi_2 , WSi_2 , TiSi_2 , SiC, Si_3N_4 , CrB_2 , B_4C , TaC, CNT, graphene (Alexander *et al.*, 2018; Binner *et al.*, 2020; Suri *et al.*, 2010). The choice of sinter additive is very important as they can also influence the mechanical, thermal, nuclear and oxidation properties.

Historically, the use of hot pressing or spark plasma sintering to create CMCs has typically resulted in damage to the continuous fibers due to the high sintering temperatures and pressures required. Hence, other non-sintering approaches such as polymer impregnation and pyrolysis (PIP), reactive melt infiltration (RMI) and chemical vapor infiltration (CVI) are also commonly adopted for fabricating CMCs (Binner *et al.*, 2020). The most commonly used approaches are reviewed below.

Pressureless sintering

Pressureless sintering is a very simple and economical technique to consolidate green components. The operation is carried out in two steps: (1) making the green compacts, which need to have sufficient handling strength, via one of many different approaches, including dry powder compaction, wet forming routes such as slip casting or plastic forming routes such as injection molding and then (2) densifying the green bodies by sintering at the required temperature in an appropriate atmosphere. Heating can be done in a resistance heating furnace or, less commonly, in an induction furnace; the latter is suitable for conductive/semi-conductive ceramics or else graphite/SiC susceptors can be used (Murthy, 2020a; Suri *et al.*, 2010). Multi wall carbon nano tubes (MWCNT)- Al_2O_3 composites, for example, have been prepared by pressureless sintering for 1–2 h at 1500–1600°C in argon though the final densities were reported to be poor (Akin and Goller, 2015). Similar work by sintering for 2 h at 1700°C in argon were reported to achieve a density of $\sim 99\%$ of theoretical (Akin and Goller, 2015). Silicon nitride powder compacts have been sintered at 1750–1900°C under a 0.1 MPa nitrogen atmosphere (Hampshire, 2007, 2008), with a relative density of $\sim 85\%$ being achieved whilst only 78% dense samples were obtained for monolithic ZrB_2 after 2 h at 2050°C (Sonber and Suri, 2011). In contrast, $\sim 98\%$ dense ZrB_2 was achieved by pressureless sintering at 2150°C for 9 h (Ma *et al.*, 2015). In the case of HfC, a maximum density of 90% of theoretical was reported after pressureless sintering for 2 h at 2760°C (Liu *et al.*, 2013) whilst 93.1% density was reported for TiB_2 after sintering at for 2 h 2150°C in argon and 93% density was achieved for CrB_2 after 6 h at 1850°C under vacuum. The use of liquid phase sintering additives can result in higher densities; ZrB_2 – SiC – MoSi_2 composites achieved 98.7% relative density after pressureless sintering for only 1 h at 2150°C (Mashhadi *et al.*, 2016).

Table 3 Densification/consolidation methods of structural/thermostructural ceramics by different methods

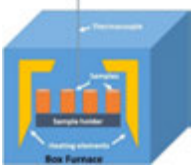
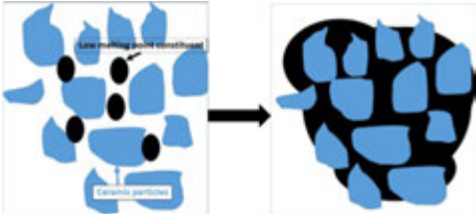
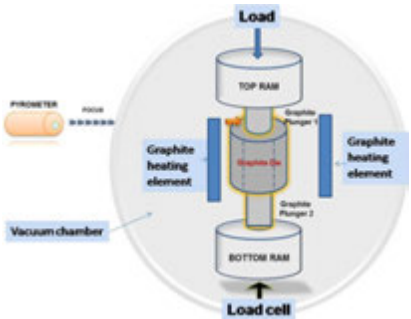
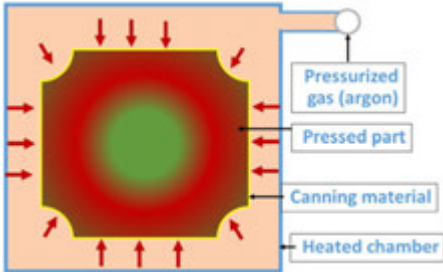
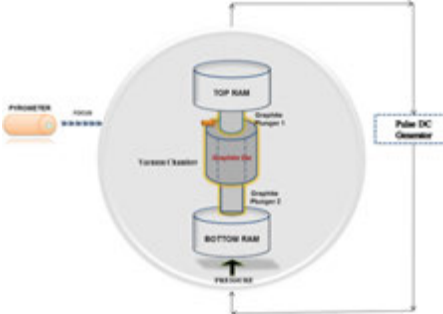
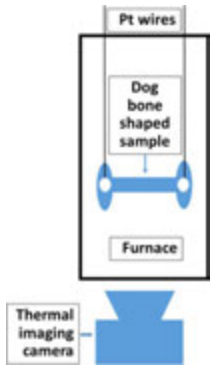
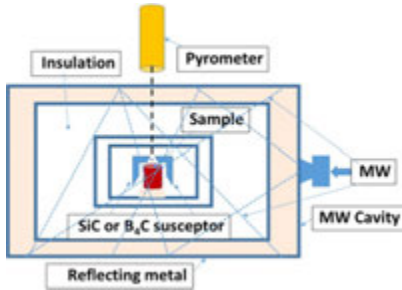
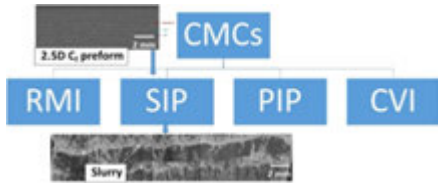
Type of method	Schematic/Mechanism	Advantages	Limitations
Pressureless sintering		● Fabrication of near net shape components which will drastically reduce expensive machining operations. ● Simple process and more economical	● It is extremely difficult to prepare sound dense shapes of non-oxide ceramics due to low self-diffusivity coefficient
Liquid phase/ Cement bonded/ Reactive sintering	 Rearrangement → Dissolution & Reprecipitation → Solid state Sintering → Grain growth	● Lower sintering temperature ● Fast densification ● High final densities and resulting microstructures often providing mechanical or physical material properties superior to solid state sintered materials	● High distortion ● Deterioration of mechanical properties due to the solidification of brittle/noncrystalline phases along grain boundaries and/or grain growth during sintering, Not suitable for high-temperature applications; ● This technique can be used only for a limited combination of materials
Hot Pressing (HP)	 [reprinted with permission from Handbook of Advanced Ceramics and Composites, Springer Nature Switzerland AG, 2019]	● High density achievable ● Grain growth can be minimised ● Often lower temperatures and time required compared to PS ● Apparatus is the same can be used for the PS or LPS ● Different 2D shapes can be manufactured ● Superior microstructures compared to PS	● Near-net shape components are not achievable ● Expensive initial investment, tooling materials and maintenance costs ● For CMCs: Matrix-fibre interaction and fibre degradation due to high temperature and pressure
Hot Isostatic pressing (HIP)		● High density achievable ● Grain growth can be minimised ● Often lower temperatures and time required compared to PS, HP ● Superior microstructures compared to PS & HP ● Near-net shapes are possible	● Equipment is more expensive than conventional HP and pressureless furnaces ● Usually works with high pressure ● Selection of suitable canning material ● For CMCs: Matrix-fibre interaction and fibre degradation due to high temperature and pressure
Spark plasma sintering (SPS)	 [reprinted with permission from Elsevier: Figure 4 in Sairam <i>et al.</i>, 2014. Influence of spark plasma sintering parameters on densification and mechanical properties of boron carbide. International Journal of Refractory Metals and Hard Materials 42, 185–192.]	● High density achievable ● Grain growth can be avoided ● Relatively low temperatures and time required compared to PS, HP ● Superior microstructures compared to PS & HP	● Near-net shape components are not achievable ● Expensive initial investment, tooling materials and maintenance costs ● For CMCs: Matrix-fibre interaction and fibre degradation due to high temperature and pressure

Table 3 Continued

Type of method	Schematic/Mechanism	Advantages	Limitations
Flash Sintering		● Rapid consolidation of ceramic powders ● Near theoretical density whilst retaining homogeneous fine grained microstructures ● Much lower temperatures than conventional	● Relatively new technique, demonstrated to only for lab scale ● Reproducibility ● Specialised equipment and expertise required ● Proven for only a few ceramics ● Near net shape is not feasible with the current technology
Microwave Sintering (MW)		● Uniform and rapid heating since the energy is directly coupled into the specimen rather than being conducted into the specimen from an external heat source like conventional resistance heating systems. ● Faster heating than conventional methods (PS, HP, HIP)	● Size limitation due to limited depth of penetration ● Compatible for only a limited materials
Ceramic Matrix composites (CMC) – continuous fibre reinforced composites		<u>RMI</u> ● A near fully dense matrix ● Processing time is short ● Relatively cheap <u>SIP</u> ● Cheap, quick and easy ● Simple procedure to introduce a slurry to a fibrous substrate ● Properties of the slurry are easily tuneable based on the chemicals used <u>PIP</u> ● Composition of the ceramic deposit is highly versatile due to chemistry of precursor ● A large degree of control of the physical properties of the precursor is obtainable again by tailoring the chemistry of the precursor ● Simple procedure <u>CVI</u> ● High purity, nano size, near stoichiometric deposition is possible ● Low temperature process, thus fibre damage can be avoided ● Intricate shapes can be prepared without damaging the continuous fibres	<u>RMI</u> ● Required high temperatures ● The exothermic nature of the reaction between constituents can increase the temperatures locally, causing more damage of the fibres (Liquid metal corrosion) ● Residual metallic phases, which have relatively low oxidation resistance and a lower melting point than the ceramic phases present. This metallic phase can lead to accelerated creep, crack propagation <u>SIP</u> ● Homogeneous penetration of large preforms is difficult ● Stable suspensions of dense ceramic particles are hard to make; possible issue with respect to scalability ● Issues exist with clogging the surface of preforms with ceramic particles <u>PIP</u> ● Low yields of ceramic from precursor will require many cycles of infiltration and pyrolysis

(Continued)

Table 3 Continued

Type of method	Schematic/Mechanism	Advantages	Limitations
			• The matrix will always be porous and micro-cracked, due to the escape of gaseous by-products and volumetric shrinkage from precursor to ceramic • Reactive chemicals and repeated heat treatments can cause fibre degradation or damage
			CVI
			• Processing times of industrial scale CVI is currently very long, on the order of 2–3 months, due to isothermal heating rates and premature surface porosity closure that requires the process to be stopped a number of times • Large energy input is required due to the extended process times • Corrosive by-products require special safety precautions, expensive equipment and maintenance costs are subsequently high • It is very difficult to obtain fully dense composites; densities of ~90% of theoretical are therefore typical

CVI – chemical vapour infiltration, PIP – precursor infiltration and pyrolysis, RMI – reactive melt infiltration, SIP – slurry impregnation process.

Hot pressing (HP)

Hot pressing is the most commonly used technique for fabricating dense, non-oxide monolithic ceramics and their composites (Suri *et al.*, 2010). During hot pressing, temperature and pressure are simultaneously applied to the powder compact contained in a die. Heating is usually achieved using induction coils and a graphite die, whilst the pressure is often applied hydraulically. Under the application of pressure, the contact points between particles develop a very high stress, increasing the local diffusion rates. As for all forms of densification, the particle size, temperature, pressure, heating rate and holding time all influence the density and microstructure of the hot pressed compacts whilst a controlled atmosphere is required for the non-oxides. Carbides, borides and silicides are often hot pressed under vacuum or an inert gas such as argon whilst the nitrides are generally densified under a nitrogen atmosphere. Often, the pressure is applied when the maximum sintering temperature is reached, though it can be increased at intervals as the temperature increases. As examples of the densities achieved via hot pressing, 90% of theoretical was obtained for Fe-Al₂O₃-(4–6 wt%) CNT composites by hot pressing for 15 min at 1500°C under 43 MPa (Akin and Goller, 2015); this compares favorably with what could be achieved by pressureless sintering. Fully dense Si₃N₄ was produced by hot pressing for 1 h at 1850°C and 23 MPa with magnesia as the additive (Hakeem *et al.*, 2014; Hampshire, 2007, 2008) whilst fully dense ZrB₂ required 1 h at 1900°C and 32 MPa (Chamberlain *et al.*, 2004). In contrast, only 80% of theoretical density was achieved by hot pressing HfB₂ for 2 h at 1850°C and 35 MPa, though CrB₂ has been reported to be fully dense by hot pressing for 2 h at 1700°C and 35 MPa (Bedse *et al.*, 2015; Sonber *et al.*, 2010). Further improvement in densification, as well as properties of the resulting non-oxide ceramics, have been reported after the addition of sintering additives such as metal or non-metal particles, including Nb, EuB₆ and MoSi₂, amongst others (Murthy, 2020a; Sonber *et al.*, 2013).

Spark plasma sintering (SPS)

SPS is a relatively new technique compared to hot pressing, although the approach is not intrinsically different. Typically, the powder to be consolidated is placed in a graphite die assembly, similar to that for a hot press, and then the heating source consists of passing a pulsed or direct current through the conductive die (Murthy, 2020a; Sairam *et al.*, 2014). A schematic is shown in Table 3. Note that the temperature is typically measured on the die surface, which will be much lower than the actual sample

temperature, the difference depending on factors such as the size of the die, the level of vacuum and the insulation used. The primary advantage of SPS over hot pressing is the very fast rate of heating achieved; this helps to achieve higher densities by the phenomenon of “fast firing” (Ji *et al.*, 2017); this particularly helps with retaining finer grain sizes, especially with finer powders that are more sinter-active (Hu *et al.*, 2020).

The densification mechanism during SPS has been debated and many theories and models are discussed in the literature (Hu *et al.*, 2020). Some of the key points are summarized here. One argument is that the current passes primarily through the die and it is the resulting very fast heating rate that leads to the higher densification achieved under similar conditions – or the ability to use lower temperatures/pressures and/or shorter times (Hu *et al.*, 2020). An alternative argument is that the driving force for densification is provided by the current passing through the powder, generating electrical discharges that activate the particle surfaces by evaporation of the oxide film (non-oxide ceramic particle surfaces are always contaminated with oxygen) and impurities (Ji *et al.*, 2017). Subsequently, bonding is accomplished by resistance heating at the contact points between the activated particles in the presence of high pressure. The time and temperature required for consolidation are lowered due to the combination of high current density and high shear, which leads to localized heating and plastic deformation at the interparticle contact points. The rapid sintering, which ideally lasts for less than a few minutes, prevents grain growth and allows the grain size to be not much larger than the original particle size (Hu *et al.*, 2020; Ji *et al.*, 2017). In terms of what has been achieved, nano- Al_2O_3 and nano- TiO_2 powders have been consolidated using SPS in just 3 mins at 1150°C and 63 MPa (Saheb *et al.*, 2019). Similarly, Al_2O_3 + (6–15 wt%) SWCNT (single walled carbon nanotubes) composites were densified after 3 mins at 1150–1200°C and 63 MPa (Akin and Goller, 2015). Fully dense nano SiAlON ceramics with a BaO additive required 30 mins at 1400°C and 50 MPa (Hakeem *et al.*, 2014) whilst fully dense AlN ceramics were prepared in 15–30 min at 1500–1600°C and 30–40 MPa and >98% dense Si_3N_4 ceramics required 5 min at 1500°C and 20 MPa (Belmonte *et al.*, 2010). Whilst higher temperatures are required for ceramics such as ZrB_2 , full density was obtained after just 3 mins at 1900°C and 50 MPa; the heating rate was 200–300°C min⁻¹ (Guo *et al.*, 2008). Conventional SPS was used to obtain 99% dense ZrB_2 –20% SiC composites in 5 mins at 2000°C and 20 MPa, whilst the combination of SPS with reactive sintering for the same composite was achieved using Zr, Si and B_4C in 9 mins at just 1400°C and 30 MPa (Zhao *et al.*, 2009). Finally, HfB_2 –20% SiC composites were densified to near theoretical density in 10 mins at 1850°C and 30 MPa using conventional SPS, whilst achieving 98.4% dense chromium diboride required 15 mins at 1900°C and 70 MPa (Mahesh *et al.*, 2015; Nisar and Balani, 2017).

Microwave sintering (MW)

Microwave sintering is a potential alternative to conventional densification techniques. In microwave sintering, heating of the ceramic powder compact is achieved by absorption of microwaves within the material to be sintered, although it should be noted that not all ceramics are good absorbers of microwaves. Ceramics such as zirconia, silicon carbide, zirconium and hafnium diboride do absorb microwaves whilst others, such as alumina or silicon nitride are largely transparent until the temperature reaches around 1000°C or higher (Oghbaei and Mirzaee, 2010). For ceramics that do absorb microwaves, the approach offers the potential advantage of rapid heating since the energy is directly coupled into the specimen, rather than being conducted into the specimen from an external heat source such as conventional resistance heating systems. Since the ceramic is the hottest part of the system, subsequent heat losses from the surface can result in an inverse temperature profile, i.e., the center of the body is hotter than the surface. This can offer significant advantages, especially for materials where there is a need to maintain a gas phase in contact with the powder particles as they sinter, for example, during the microwave reaction sintering of silicon metal powder into silicon nitride (Luo *et al.*, 2020). In general, the rapid nature of the sintering and the so-called “microwave effect” (where the ceramic densifies at a lower temperature and/or in a faster time than with conventional sintering) can result in finer microstructures for microwave sintered materials (Oghbaei and Mirzaee, 2010). This phenomenon has been rigorously investigated using hybrid sintering systems and found to be a consistent result (Wang *et al.*, 2006). As a result, research has shown microwave sintering can take <20% of the time required with conventional gas or electrically heated furnaces for similar products – and hence use only 20% of the energy (Bhattacharya and Tanmay, 2016).

Although many ceramics have been sintered successfully using purely microwave energy (Bhattacharya and Tanmay, 2016), there is evidence that a hybrid approach that combines microwaves and conventional energy can result in superior results (Binner *et al.*, 2008). Whilst most work focuses on using 2.45 GHz, there have been some attempts to use 28 GHz, though the depth of penetration is smaller, limiting the size of the samples (Luo *et al.*, 2020). Most work has focused on the densification of oxides; however non-oxides can also be successfully sintered, though a controlled atmosphere is also required. For example, TiB_2 has been rapidly sintered to >90% of theoretical in ≤ 30 mins at 1900–2100°C using 6 kW of 2.45 GHz microwave heating. A comparison with conventional sintering indicated that microwave sintering of TiB_2 + 3 wt% CrB_2 occurred at a temperature 200°C lower and yielded significantly improved hardness, grain size and fracture toughness.

Although as indicated above, not all ceramics absorb microwaves at room temperature, most will do so at elevated temperature. Thus, high purity alumina, which is transparent to microwaves at room temperature, will start to couple at typically >1000°C. It is therefore not unknown for additives to be introduced into ceramics that will absorb the microwaves at low temperature, knowing that once the temperature of the material gets high enough, the whole of the material will begin to absorb in its own right. For example, ZrB_2 + SiC composite has been fully densified at 1850°C, with the SiC providing the initial microwave absorption (Sharma and Karunakar, 2019).

Liquid phase sintering (LPS)

Like solid state sintering, liquid phase sintering is a densification mechanism rather than a sintering approach and hence can be used in combination with any of the other techniques described above (Kang, 2005). It is mentioned here in its own right because it is an

approach that is often used for the non-oxide ceramics that form the basis of many structural and thermostructural ceramics. It involves designing the ceramic's composition so that there is typically 5%–10% of liquid at the sintering temperature; this allows the ceramic particles to rearrange and, as importantly, for the atoms to dissolve, diffuse down concentration gradients and then reprecipitate at different points in the microstructure. This accelerates the densification process considerably compared to solid state sintering, though it can result in glassy grain boundary phases after the liquid present at the sintering temperature cools (Kang, 2005). As a result, liquid phase sintering is often used for densifying ceramics that are hard to densify by solid state sintering, e.g., the non-oxides. As an example, the addition of Mo to the TiC–Ni system decreases the contact angle from 30° to 0° (German *et al.*, 2009), allowing sintering to obtain the dense component. Like all silicon-based non-oxides, Si_3N_4 powder particles are contaminated with surface silica layers so additives such as MgO and Y_2O_3 will react with the silica and some of the nitride itself at the sintering temperature to form an oxynitride liquid that promotes liquid phase sintering. In addition, the equiaxed α - Si_3N_4 dissolves in the liquid and is precipitated as the acicular β - Si_3N_4 , which yields an interlocked microstructure that offers a higher toughness (Hampshire, 2007, 2008; Hampshire *et al.*, 1978).

Non-sintering based techniques

There are a number of densification techniques that do not rely on sintering; they are generally used for the densification of ceramic matrix composites, CMCs. Examples include reactive melt infiltration (RMI), precursor infiltration and pyrolysis (PIP) and chemical vapor infiltration (CVI). Each of these will be very briefly described in turn.

RMI is the introduction of molten metal, typically Si, Zr or Ti, into a porous ceramic fiber preform where it reacts in-situ with either a pre-matrix carbon or boron phase to form the desired ceramic compound, typically with a high matrix density (Binner *et al.*, 2020). This technique was industrialized for the mass production of SiC_f/SiC CMCs by General Electric for their advanced civilian aerospace engines (GE Aviation Fired up on CMCs, 2015). These CMCs were the first to be used commercially in the civil aviation industry on General Electric's CFM LEAP engines that were launched in 2016. Work on the formation of ultra-high temperature CMCs (UHTCMCs) based on ZrB_2 has also been undertaken using RMI by DLR (Johnson, Gasch and Stackpoole, 2009).

PIP is initially a green-forming procedure in which a liquid chemical precursor is impregnated into a reinforcement phase and then subsequently pyrolyzed at elevated temperatures. The pyrolysis reaction yields the required ceramic product, which is retained within the preform body (Binner *et al.*, 2020). Whilst very successful, the evolution of gaseous by-products and the consequent volume shrinkage as the precursor converts to the ceramic means that the process must be performed iteratively many times, often a dozen or more, until a matrix of the desired density is achieved. Once again, the process has been used for SiC , ZrB_2 , ZrC , HfC and HfB_2 ceramic based composites (Zhao *et al.*, 2017).

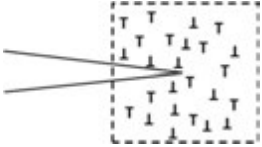
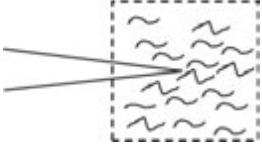
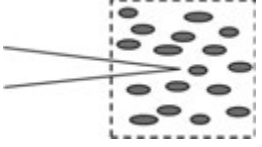
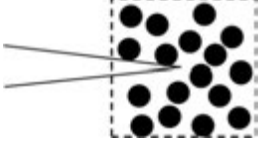
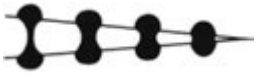
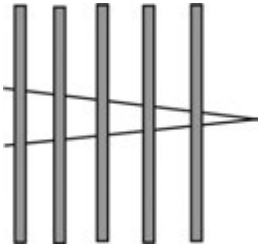
CVI is a well-established technique for the fabrication of fiber-reinforced ceramic matrix composites (FRCMCs) and, again, particularly for SiC_f/SiC CMCs (Vignoles, 1992). The main benefit is its ability to produce materials with attractive mechanical properties at relatively low processing temperatures, typically $\sim 1000^\circ\text{C}$, whilst avoiding the use of pressure, which reduces fiber stress and damage. CVI is a near-net shape process, which aids the production of irregular-shaped components for a wide range of applications. During CVI a gas flows through a porous body, typically a ceramic fiber preform and, on being heated, it breaks down to yield a solid, the desired ceramic. This is deposited within the pore network and so densifies the composite. It is an intrinsically slow process, however (it can take many hundreds of hours), and therefore the product can be very expensive. Among the different variations developed to overcome these limitations, the use of microwave or radio frequency energy to heat the fiber preform yields the inverse thermal gradient profile mentioned above that causes the preform to be densified from the inside out. This greatly reduces the process times, whilst retaining all of the advantages of the CVI process. SiC_f/SiC composites have been produced using microwave heating in approximately an order of magnitude less time than required conventionally (Porter, 2020), whilst carbon fiber reinforced ZrB_2 - and ZrC -based composites have been prepared in $\sim 40\times$ less time using RF-accelerated CVI (Binner *et al.*, 2020).

Microstructure

Microstructure plays a crucial role in determining the properties of the material and is, in turn, controlled by the quality of the starting powder, which is controlled by the synthesis method, the green forming route and the densification method. The microstructures of structural ceramics and composites can be classified into 6 different categories, these are presented in Fig. 2. Monolithic ceramics are conventionally assumed to have an absence of secondary phases and hence consist of the grains of the ceramic plus any porosity, if present. Additional phases can be added to ceramics in either small or large quantities for one or a combination of reasons; these include enhancing (1) densification, (2) the mechanical, physical or thermal properties, including properties such as the wear resistance, (3) the oxidation and/or ablation resistance and (4) inhibiting the grain growth. The role of secondary phases on densification could be either to enhance the lattice or grain boundary diffusion, or the formation of a liquid phase, see the earlier discussion in the section on Liquid Phase Sintering (LPS). The presence of secondary phases can also enhance the toughness of materials, for example by arresting crack propagation as shown in Table 4; more details of the different toughening mechanisms are provided below in the form of a few case studies on the microstructures of structural ceramics and composites.

Over the past few decades, considerable work has been focused on the production of monolithic ceramics with high strength and toughness. This has examined a number of options, including refining the grain structure (Kingery *et al.*, 1976) and exploiting the opportunities available from zirconia toughening (Wang and Stevens, 1989), particularly from yttria doped zirconia. One option for the latter is yttria stabilized tetragonal zirconia polycrystalline (Y-TZP) ceramics. They are well regarded as strong

Table 4 Typical toughening mechanisms reported in ceramics and its composites

Mechanism	Schematic	Details with examples
Dislocation cloud		Dislocation toughening mechanism usually seen in metals and alloy systems by localised plasticity at the crack tip. In the case of oxide ceramics with predominantly ionic bonding, the dislocations cannot glide on all possible slip planes, involving displacements of ions, in order to maintain the charge neutrality. For non-oxide ceramics with predominantly covalent bonds, dislocation movement is restricted due to directional bonding with an inherent rigid bond network. The dislocation core width of ceramics is narrower than that in metals/alloys, leading to the requirement of high Poirier–Nabarro stress for dislocation glide.
Microcrack cloud		This mechanism can be seen in monolithic ceramics, where the microcracks can act as crack arrestors. The crack tip stress is absorbed by the micro cracks and as a result the primary crack does not propagate further.
Phase transformation		Transition from tetragonal to monoclinic zirconia, in the crack tip stress field involves volume expansion. In a constrained microstructure, this will result in compressive stress on the crack faces, leading to closure of the crack tip. Good examples are given in the sections on Microstructure and Mechanical and Physical Properties.
Crack deflections		Crack deflection is mostly observed in composites containing particulates, whiskers, or fibers as the second phase. Essentially, the crack path is increased as the crack bypasses around the hard or rigid second phase, and the model of Faber and Evans (1983) predicts that the maximum increment in crack deflection induced toughening can be realized in composites with around 30 vol% particulate reinforcement. The particle size, shape and distribution of second-phase particles will influence on the toughness increment.
Grain interlock		This mechanism is similar to the bridging mechanism as explained under whisker and fibre reinforced mechanisms. It is usually observed in the presence of hard second phase particles in metal matrix composites (MMC) such as ODS steels, carbide or boride dispersed Al matrix composites.
Ductile metal second phase bridging		This mechanism is usually observed in liquid metal sintered, cement bonded composites and cermets. In the crack tip stress field, the ductile flow of metallic particles leading to bridging of crack faces reduces the available driving force for crack propagation. The toughness of WC–Co cermets therefore is reduced with lower Co content. From the material-development point of view, a critical amount of Co is required to facilitate liquid phase sintering and the balance of hardness and toughness requires tailoring of the Co content.
Whisker/chopped fibre reinforcement		In whisker-reinforced composites with random whisker alignment, crack bridging also takes place but to a lower extent than fibre toughening. Such bridging also involves whisker pull out and the toughness increment depends on the volume fraction of whiskers.
Continuous fibre reinforcement		This type of toughening is realized in continuous fibre reinforced composites (CMCs). For example, both SiC matrix and SiC fibres are inherently brittle. However, the toughness of SiC/SiC _f composites can be very high and the underlying mechanisms involve crack bridging due to fibre–crack interaction. Such interaction in composites under externally applied tensile stress essentially involves matrix–fibre debonding or matrix micro cracking in the crack wake of the matrix crack or mode I crack, crack deflection at the interface, fibre pull out, and, finally, crack bridging. The combination of these mechanisms essentially results in the nonlinear stress–strain tensile response of the composite, leading to damage-tolerant behaviour. This toughening mechanism is superior to earlier ones; as a result higher toughness could be seen in properly designed CMCs.

candidates for structural applications due to their excellent strength (700–1200 MPa) and reasonable fracture toughness (up to $10 \text{ MPa m}^{1/2}$) in addition to good chemical inertness (Basha *et al.*, 2020). The high toughness of zirconia monoliths comes from the stress induced transformation of the tetragonal (t) phase to the monoclinic (m) phase in the stress field of propagating cracks, a concept that is widely known as transformation toughening, schematically shown in Table 4. Basic microstructural requirements for the effective contribution from transformation toughening is the maximum retention of the tetragonal phase at the application temperature with sufficient transformability to m-ZrO₂ in the stress fields of crack tips. Since the discovery of the concept of transformation toughening in the 1970s, this approach has also been successfully utilized to toughen other ceramic microstructures, for example, extensive efforts have been put into increasing the toughness of alumina by adding zirconia, a class of materials known as zirconia-toughened alumina (ZTA) (Basha *et al.*, 2020).

ZTA and other particle reinforced ceramics, for example SiC_p-reinforced alumina, offer a viable, and relatively cost-effective option, for developing ceramics with improved combinations of mechanical properties, e.g., hardness, strength and toughness. For example, whilst dense alumina with a submicron grain size can be obtained using a fine alumina powder, standard pressureless sintering techniques and relatively low sintering temperatures, the addition of 5 wt% ZrO₂ reduces the mean grain size from 0.5 to 0.7 μm to between 0.4–0.55 μm , whilst still yielding a relative density of 99.0%–99.7% (Abyzov, 2019b). The resulting toughness is described in the next section on “Mechanical and Physical Properties”.

Liquid phase sintered Si₃N₄ ceramic's microstructural features are also very interesting from a toughness perspective (Hampshire, 2008). As indicated previously in the section on LPS, every powder particle of silicon nitride is surrounded by a very thin surface layer of silica. This can react with oxide additives and some of the nitride itself at the sintering temperature to form an oxynitride liquid that promotes densification by solution-precipitation. The equiaxed α -Si₃N₄ dissolves in the liquid and is subsequently precipitated as β -Si₃N₄, which grows in the form of prismatic, hexagonal rod-like crystals that eventually impinge on each other forming an interlocked microstructure, whilst the liquid cools to form an intergranular, usually glass, phase. Well known additives for Si₃N₄ are MgO, Y₂O₃, Al₂O₃ and various rare earth oxides. The amount of additive initially introduced determines the quantity and chemistry of the glass phase and this affects properties such as fracture toughness, ambient and high temperature strengths, creep resistance and oxidation resistance (Hampshire, 2007, 2008). Toughness values as high as 7–10 MPa m^{1/2} have been achieved (Hampshire, 2007).

The highest toughness values for ceramic materials are achieved by reinforcing them with continuous fibers, together with a suitable interface between the matrix and fiber (Tülümen *et al.*, 2019). Continuous fiber CMCs can be made by stacking 2 dimensional (2D) layers, needling the layers to create what are known as 2.5D composites, or by weaving 3D fabrics, performance, and price, increasing in that order. CMCs include carbon fiber/carbon (C_f/C) – though not everyone considers these to be CMCs, C_f/silicon carbide (C_f/SiC), SiC_f/SiC and oxide fiber/oxide (ox_f/ox). More recently, there has been extensive development of ultra-high temperature ceramics and these have also been reinforced, usually with carbon fibers (Sciti *et al.*, 2018). For all fiber-reinforced CMCs, to achieve the required toughness the matrix/reinforcement bond strength must be sufficiently weak to allow relaxation of the stress field at the crack tip and bridging of the matrix cracks by the reinforcement (Parlier *et al.*, 2011). There are 3 approaches, as shown in Fig. 3 (Tülümen *et al.*, 2019). For dense matrix CMCs (e.g., SiC_f/SiC), a low cohesion coating is applied to the fibers before the matrix is formed yielding Weak Interface Composites, WICs, and toughening mechanisms such as crack-deflection, crack-bridging & fiber pullout – though the coating can be vulnerable to oxidation at high temps. The second approach is to form Weak Matrix Composites, WMCs (e.g., ox_f/ox), which have a porous matrix; their reduced stiffness allows

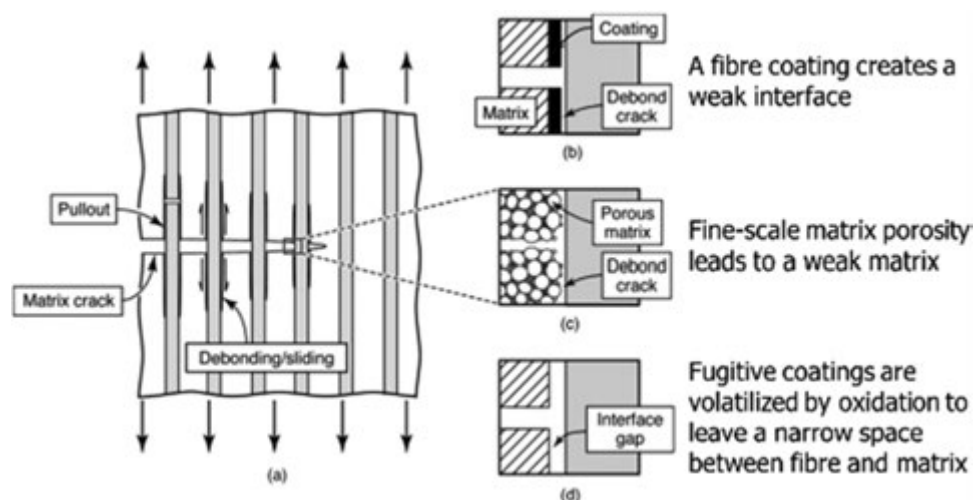


Fig. 3 Reinforcement mechanisms for continuous-fiber ceramic composites. Reproduced from Tülümen, H.M., Hanemann, T., Piotter, V., Stenzel, D., 2019. Investigation of feedstock preparation for injection. Molding of oxide – Oxide ceramic composites. Journal of Manufacturing and Materials Processing 3 (1), 9. <https://www.mdpi.com/2504-4494/3/1/9>.

damage-tolerant behavior but also yields inherent permeability and low strength, wear resistance & thermal conductivity. The third, fugitive coating, approach is less common.

Mechanical and Physical Properties

Ceramics, because of their ionic and/or covalent bonding, have a combination of useful thermo-mechanical properties (high elastic modulus, hardness and strength), excellent corrosion and ablation resistance together with low specific densities. In many structural and tribological applications at room and high temperatures, even in aggressive environments such as irradiation and ablation, ceramics are recognized as having great potential to replace existing materials (Kingery *et al.*, 1976). As implied in the section on Microstructure above, one of the most critical properties, however, is the fracture toughness, which is generally low. A value of around 3–3.5 MPa m^{1/2} is normal for most monolithic advanced ceramics, such as alumina, though as has been shown this can be increased to a value of ~25 MPa m^{1/2} for fiber-reinforced CMCs (Binner *et al.*, 2020).

Toughening mechanisms have been broadly classified into two categories, one involving a process zone around the crack tip, the other related to the bridging of crack faces by reinforcements, which can include particles, whiskers and fibers. The different toughening mechanisms, with associated schematics, are shown in Table 4. The phase transformation mechanism can be seen in the tetragonal phase-stabilized zirconia composites, whilst crack deflection, crack bridging and grain interlock mechanisms are applicable in particulate reinforced composites. Residual grain boundary secondary phases, whether arising from glasses after liquid phase sintering, cements from cementitious bonding or ductile metals from RMI-based processes, can help to bridge cracks, Table 4. Other crack bridging mechanisms also occur in whisker, graphene, chopped fiber and continuous fiber-reinforced composites; the latter also benefit from the fiber pull out mechanism (Binner *et al.*, 2020; Faber, 1997). The latter in particular can contribute to the very high values of toughness (for ceramics) in continuous fiber reinforced composites mentioned in the paragraph above. Important mechanical and physical properties of various structural & thermostructural ceramics are summarized in Table 1, whilst a few case studies are described below.

Addition of 0.3 vol% SWCNTs to Al₂O₃ resulted in retention of alumina's high hardness, 21 GPa, and a fracture toughness of ~5.5 MPa m^{1/2} due to crack bridging and crack deflection mechanisms. The enhanced toughness over monolithic alumina was also explained by the positive effect of an improved matrix/CNT connectivity with the formation of an internal "bamboo" morphology (Akin and Goller, 2015). The electrical conductivity values of the composites were measured as 1050 and 3345 S m⁻¹ for 5.7 and 15 vol% SWCNTs, respectively. These were considered to be very good and were explained by the SWCNTs remaining in contact with each other in the matrix during the SPS densification process, which was performed at relatively low temperature and with a short holding time. The addition of TiB₂ to both Al₂O₃ and B₄C matrices increased their hardness, strength and fracture toughness (Skorokhod and Krstic, 2000). Furthermore, the addition of TiB₂, TiN or TiC can also be used to obtain electro conductive materials, as well as enhanced toughness, when incorporated into Al₂O₃ and Si₃N₄ matrices. These composites can be shaped by electro discharge machining (EDM), allowing the manufacture of complex-shaped components, which has greatly increased the number of industrial applications for these materials (Bilal *et al.*, 2019).

As mentioned earlier, toughening of ceramics by the incorporation of zirconia particulates is well known; in high elastic modulus ceramics such as alumina it is achieved by transformation toughening whilst in elastically softer materials such as zinc oxide the mechanism is based on microcracking – though the latter also reduces the strength (Basha *et al.*, 2020). Values of toughness obtainable with the transformation toughening mechanism, e.g., for ZTA, are typically up to about 10–12 MPa m^{1/2}. This is slightly better than the values for whisker-reinforced composites, e.g., Al₂O₃/SiC_w composites (typically 8–9 MPa m^{1/2}), which are, in turn, better than those for particle-reinforced composites, e.g., Al₂O₃/SiC_p composites (typically 4–6 MPa m^{1/2}) (Abyzov, 2019a). There are also a number of what are effectively "zirconia toughened zirconias", including partially stabilized zirconia (PSZ) and tetragonal zirconia polycrystals (TZPs). There are many reports on them, e.g., (Basu and Balani, 2011), and their toughness values can be as high as 15–25 MPa m^{1/2} for PSZ and 20–30 MPa for TZP (Lin and Duh, 2003), though the precise value obtained is somewhat dependent on the sintering parameters and hence the microstructure. For example, transformation toughness is dependent on grain size and hence the transformability of the tetragonal phase, with the highest toughness being measured at a tetragonal grain size of 1.9 µm (Lin and Duh, 2003). Impurities also play a role on the mechanical properties, for example, 3Y-TZPs sintered using starting powders with a higher impurity content (Daiichi grade; Al₂O₃ 0.72 wt%; SiO₂ 0.08 wt%) exhibited a higher indentation toughness compared with the value for a higher purity ceramic (Tosoh grade; Al₂O₃ <0.005 wt%; SiO₂ 0.007 wt%) (Moradkhani *et al.*, 2019). The quantity of the secondary phase also influences the mechanical properties, for example the fracture toughness of a Y-TZP increased nonlinearly with decreasing yttria content from 2.5 to 2.0 mol %, with a maximum value of 20 MPa m^{1/2} for the 2Y-TZP, although this again will depend on the grain size. An analysis of the effect of yttria content on the properties of nano zirconia has been undertaken (Binner *et al.*, 2011) and it showed that higher yttria content zirconia ceramics also offer some interesting resistance to hydrothermal ageing, albeit at the expense of lower toughness values.

Whilst a 0.5 µm grained B₄C ceramic was reported to have a hardness, flexural strength and fracture toughness of 27 GPa, ~200 MPa and 3.1 MPa m^{1/2} respectively, addition of 3–5 wt% of carbon and TiO₂ played an important role in eliminating the surface oxide layer and also forming the reaction product of TiB₂, thereby resulting in superior mechanical properties such as hardness – 34 GPa, flexural strength – 630 MPa and fracture toughness – 5.1 MPa m^{1/2} (Suri *et al.*, 2010).

Hardness, fracture toughness and flexural strength of refractory borides of TiB₂ and ZrB₂ are reported in the range of 15–25 GPa, 3–6 MPa m^{1/2} and 300–600 MPa respectively. However, the addition of up to 5 vol% Si-based sintering additives (e.g., SiC, Si₃N₄ or silicides) enhances the sintered density of the materials, leading to enhanced mechanical properties of 30 GPa, 6–9 MPa m^{1/2} and 600–800 MPa respectively (Golla *et al.*, 2020).

Thermal Properties

Properties such as thermal conductivity, coefficient of thermal expansion (CTE), and resistance to creep, oxidation, thermal shock and ablation are all important for thermostructural ceramics. Some typical values for selective monolithic ceramics are listed in [Table 1](#), though they are significantly influenced by the presence of porosity and secondary phases. In general, a low CTE and high thermal conductivity are desired for thermostructural ceramics. From [Table 1](#), it is very clear that non-oxide ceramics, especially carbides and borides, have higher thermal conductivities than oxide ceramics and this is a useful property for distributing heat. Hence, the carbides and borides of Zr, Hf and Ta, which also have ultra-high melting points, are under consideration for use in aerospace and other applications where extreme temperature resistance is desired ([Binner et al., 2020](#)). They are also the basis behind the C_f-reinforced UHTCMCs, though it should be noted that continuous fiber reinforced composites usually exhibit anisotropy, especially in their thermal conductivity and CTE.

In general, UHTCs and UHTCMCs need to have a small CTE because a large value can cause instability on the local surface at high temperature as a result of an imbalance in internal thermal stresses. The CTE of the monolithic UHTCs can be affected by the presence of doped secondary phases such as MoSi₂, TaSi₂, ZrSi₂ and SiC. For example, doping with SiC significantly reduced the CTE of HfC and TaC because of the lower CTE of SiC; whilst doping with TaSi₂ or MoSi₂ caused only a minor change in value. Another example is that the addition of 30 vol% SiC to ZrB₂ resulted in a decrease in CTE, however only at higher temperatures (1300–1675K), whilst at lower temperatures (300–1300K) this effect was not observed ([Binner et al., 2020](#)).

Thermal conductivity, κ , is a strong function of temperature and secondary phases. For example, the incorporation of CNTs to ceramics enhances their thermal conductivities since the value for individual MWCNTs and SWCNTs are 3000 Wm⁻¹ K⁻¹ and 6000 Wm⁻¹ K⁻¹ respectively at room temperature ([Akin and Goller, 2015](#)). Addition of MoSi₂ into ZrB₂ leads to a decrease in thermal conductivity, whilst 5–30 vol% SiC increases it ([Binner et al., 2020](#)). On the other hand, increasing temperature causes the thermal conductivity of borides to decrease whilst that of carbides increases ([Golla et al., 2020](#)).

Creep and thermal shock resistance are also important high temperature properties for structural applications. Whilst monolithic ceramics generally have good creep resistance due to their high melting points, especially for non-oxide ceramics, the presence of secondary phases, particularly glassy phases such as those that can remain after liquid phase sintering, can decrease the creep resistance. For example, commercially produced Al₂O₃ powders typically contain impurities such as silica, calcia, magnesia, soda and potassium oxide. These form liquids during sintering that can promote the formation of a more dense ceramic, but reduce the high temperature mechanical properties, including strength, creep and thermal shock resistance, by forming glassy grain boundary phases ([Abyzov, 2019a](#)). Similar results can be found for liquid phase sintered silicon nitride-based ceramics (β -SiAlON); however by carrying out a post-sintering heat treatment at ~1350°C the creep resistance can be improved. The heat treatment allows the matrix and grain-boundary glass phase to react to yield a slightly modified β -composition and a crystalline yttrium aluminum garnet, Y₃Al₅O₁₂ phase ([Hampshire, 2008](#)). This material has excellent creep resistance and is the strongest SiAlON ceramic compared to Si₃N₄. Creep behavior is also dependent on both intergranular film and triple point viscosities and hence doping larger RE cations into silicon nitride or SiAlON can enhance the creep resistance by enhancing the viscosity of these liquid films at elevated temperatures ([Hampshire, 2008](#)).

In many applications ceramics are exposed to thermomechanical stresses because of transient thermal conditions such as a sudden change in temperature, for example in a high temperature furnace or a gas turbine engine ([Singh and Wang, 1995](#)). When a material is subjected to a thermal transient of suddenly decreasing temperature (ΔT), e.g., in a quench test, the surface of the material is placed under a tensile stress and the interior under a compressive stress. Under these conditions, ceramics are susceptible to catastrophic failure, known as thermal shock, because of their brittleness, relatively low thermal conductivity and high Young's modulus of elasticity. A number of thermal shock resistance parameters, denoted R, have been developed that indicate the maximum allowable temperature difference to which a body can be subjected without the initiation of fracture under a range of different thermal conditions ([Li et al., 2014](#)). The most common version of R is that shown below, which represents the maximum allowable heat flux a body can take before fracture initiates under steady heat flow conditions, or the maximum allowable temperature difference to which a body can be subjected without the initiation of fracture under mild transient thermal shock conditions ([Kingery et al., 1976](#)):

$$\Delta T_c = \frac{\sigma_t(1 - \nu)}{\alpha E} = R$$

where σ_t is the tensile strength, ν Poisson's ratio, α coefficient of thermal expansion, E Young's modulus. The R values presented in [Table 1](#) are calculated using the above equation. The change in the coefficient of thermal expansion (α) has the most profound effect, whilst a change in the thermal conductivity (κ) has a relatively smaller influence ([Singh and Wang, 1995](#)).

Continuous fiber reinforced ceramic matrix composites (CMCs) possess superior resistance to thermal shock damage than monolithic ceramics; however matrix cracking can still be induced by thermomechanical stresses produced during thermal shock, leading to the onset of damage, which, in turn, can decrease the strength and elastic modulus of the composite ([Arai et al., 2019](#)). These matrix cracks can grow during cyclic thermal shock loading ([Singh and Wang, 1995](#)). The extent of the damage is limited by the presence of the continuous reinforcing fibers, which generally means that the catastrophic failure typical of a monolithic ceramic is avoided, although the extent of the thermal shock resistance is dependent on several factors including the strength of the fiber-matrix interface. Too strong or too weak an interface means that the extent of damage protection is reduced, so a weakly-bonded interface is required to achieve the required crack deflection and crack bridging ([Singh and Wang, 1995](#)). It follows that

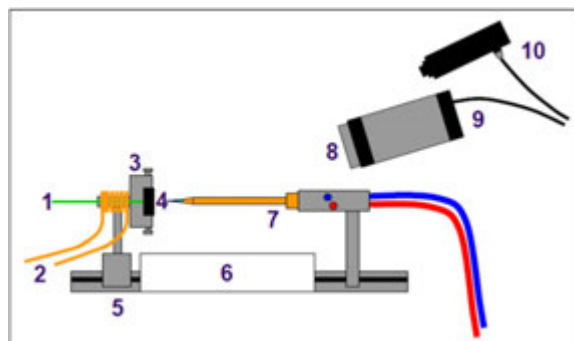


Fig. 4 Typical Oxyacetylene (OAT)/oxypropylene torch (OPT) test facility at University of Birmingham (1) Back face thermocouple, (2) water cooling, (3) sample holder, (4) sample, (5) sample guide, (6) protective insulation, (7) oxyacetylene torch, (8) neutral density filter, (9) thermal imaging camera and (10) 2 color pyrometer. Reprinted with permission from Elsevier, Paula, A., Venugopala, S., Binner, J.G.P., 2013. UHTC-carbon fiber composites: Preparation, oxyacetylene torch testing and characterization. *Journal of the European Ceramic Society* 33, 423–432.

any process that affects these mechanisms, such as degradation of the fiber-matrix interfacial properties, e.g., through oxidation, will also degrade the thermal shock resistance of the CMCs (Singh and Wang, 1995).

Whilst mentioning the oxidation resistance of thermostructural ceramics and their composites, it can be significantly enhanced by appropriate compositional design so that it leads to the formation of a surface layer of immiscible, multicomponent glass (Murthy, 2020b). The resulting increased liquidus temperatures and viscosities, as well as decreased oxygen diffusivities in the immiscible glasses, are considered responsible for the observed improvement in the oxidation resistance of the composites. It is therefore beneficial to optimize the type and quantity of glass-forming elements present in the ceramics, typically by incorporation of appropriate additives. However, in doing so, it is important to balance the resulting enhanced oxidation resistance with the material's other properties, including mechanical, physical and thermal, to best suit the particular application. As has already been shown, the incorporation of glassy secondary phases can reduce high temperature properties such as strength and creep resistance.

Over the past decade, researchers around the world have investigated the oxidation behavior of a range of thermostructural ceramics, including TiB_2 , CrB_2 , ZrB_2 , HfB_2 , SiC , ZrC , HfC and TaC amongst others (Binner *et al.*, 2020; Sonber *et al.*, 2014). Modification of the chemical composition of the oxide surface layer, leading to a decreased inward diffusion of oxygen, is one of the ways of controlling the oxidation resistance of non-oxide ceramics. This modification can be accomplished by either changing the bulk composition or by applying suitable coatings. The addition of silica formers or rare earth elements, notably silicides, SiC , Si_3N_4 , Ti_3SiC_2 , Y, La, Eu, Ce and Yb, can reduce the oxidation rate through the formation of a more stable borosilicate glass/rare earth (RE) oxide up to $\sim 1600^\circ\text{C}$ (for Si formers) and $> 2000^\circ\text{C}$ (for RE oxides). Several groups have studied the effects of SiC additions on the behavior of borides or carbides when exposed to air at elevated temperatures (Fahrenholtz *et al.*, 2007). It is known that borate and silicate glasses containing transition/rare earth oxides show a strong tendency to phase separate as a result of immiscibility in the phase diagram. Systems exhibiting such immiscibility are characterized by steeply rising liquidus temperatures and increased viscosity. As demonstrated by the Stokes-Einstein relationship (Murthy, 2020b), the latter decreases the oxygen diffusion rate through the oxide surface scale, since the diffusivity is inversely proportional to viscosity. Another potential benefit of increased viscosity, as well as increased liquidus temperature, is the suppression of boria/silica evaporation from the glass (Binner *et al.*, 2020).

With the increasing interest in ultra-high temperature ceramics and composites, materials that withstand temperatures up to and indeed above 3000°C , for aerospace applications such as hypersonic vehicles, testing the oxidation/ablation resistance using oxyacetylene torches (OAT) and oxypropylene torches (OPT) is increasing. OAT testing can reach temperatures up to $\sim 3000^\circ\text{C}$ and heat fluxes up to $\sim 17 \text{ MW m}^{-2}$, whilst the equivalent figures for the OPT test are $\sim 2500^\circ\text{C}$ and $\sim 6 \text{ MW m}^{-2}$ (Binner *et al.*, 2020). A typical OAT/OPT test schematic is shown in Fig. 4 and a video clip of a typical test can be found *here*. Interestingly, the gas velocity for both systems, which has been directly measured, were very similar at Mach ~ 0.6 . The flames involved can also be manipulated by varying the gas chemistry to be oxidizing, reducing or neutral and the distance between the flame and the sample and the angle the flame makes on contact with the sample can all be varied (Binner *et al.*, 2020). As an aside, it is interesting to note that the rapid oxidation of borides and carbides at $\sim 600^\circ\text{C}$ results in the formation of B_2O_3 or CO/CO_2 respectively. Whilst the latter are gases and hence are evolved immediately, the former melts first and only evaporates at $\sim 1000^\circ\text{C}$. This is believed to explain the result that ZrB_2 and HfB_2 both develop a more protective oxide coating than ZrC or HfC ; the oxide scale on the latter has a strong tendency to spall off whilst that on the borides typically remains attached (Binner *et al.*, 2020).

Summary and Outlook

The interest in structural/thermostructural ceramics and their composites arise due to their combination of high hardness, strength (including high temperature and creep strength), elastic modulus and wear resistance, together with good thermal shock, corrosion and ablation resistance and a relatively low specific gravity. Toughness is also relatively high in the composites, though it is

generally much lower in the monolithic ceramics. Whilst there are many applications for these materials in a wide variety of environments, including wear, erosion, corrosion, ablation, high temperatures and irradiation, amongst others and including combinations of all of them, further applications are often limited by their relatively high costs compared to other types of materials (Binner *et al.*, 2020; Murthy, 2012). The latter arise due to the complexity of the processing required, usually combined with the need to use high temperatures and, for the non-oxide ceramics, controlled atmospheres. Ongoing research and development is contributing to both the formation of materials with enhanced properties and the creation of lower cost processing and hence the range of applications for these ceramics is increasing.

Whilst oxide ceramics are generally obtained from minerals using what essentially amount to purification processes, non-oxide ceramics need to be synthesized from synthetic precursors in controlled atmospheres at high temperatures due to their high melting points and low self-diffusivity coefficient (Abyzov, 2019a). Both types of ceramic are fabricated, however, using similar green forming routes and subsequent densification by sintering. For oxides, however, the latter is generally done pressureless, whilst non-oxides need elevated pressure, typically involving hot pressing, hot isostatic pressing or, more recently, spark plasma sintering. This makes the densification of the non-oxides much more expensive. A major world-wide research effort is focused on both reducing the fundamental costs associated with manufacturing these materials as well as trying to improve the energy efficiency to make the processes more sustainable.

Oxide ceramics have generally good chemical and corrosion resistance, including towards molten metals, and, therefore, find many applications as containment materials, e.g. crucibles, tubes and refractories for molten metals, glass and high temperature furnaces. Oxides, particularly alumina, also display good erosion and wear resistance so they are also used as coatings for wear tiles, liners and grinding media. Alumina also has the advantage that its precursor material, bauxite, is relatively abundant, which helps to keep the ceramic relatively cheap. Non-oxide ceramics generally display high thermal conductivities, low thermal expansion coefficients combined with high hardnesses, melting points and stiffnesses. Whilst they have been explored for high temperature applications for several decades, very recently, the borides and carbides have also been extensively explored in terms of their potential for ultra-high temperature applications, including rocket nozzles and leading edges. The borides and carbides are also considered for a range of nuclear reactor applications (Krenkel *et al.*, 2006). The neutron absorption cross section should be low for reactor structural components and high for shielding, control/safety rod applications. Borides and B_4C are the potential neutron absorbers; hence these materials are widely used for control rod applications in commercial nuclear power reactors. ZrC and WC are the choice for first wall materials in fusion reactors. With lower cost manufacture, ideally with further enhanced properties, the number of applications for all these ceramics could increase significantly.

It is a well-known fact, however, that all monolithic ceramics, not just the structural and thermostructural ceramics, suffer from poor fracture toughness. Values in the range 3–6 MPa m^{1/2} are common; these are at least an order of magnitude lower than even relatively poor toughness metals. The addition of a secondary phase in the form of ceramic or metal particulates, whiskers (though these are not permitted everywhere in the world) or chopped fibers can all lead to higher toughness values, particularly for zirconia-based ceramics. However, the greatest increases in toughness arise when continuous fiber reinforcement is used. The latter ceramic matrix composites (CMCs) are a rapidly evolving and growing technical field with a very wide range of applications across the aerospace, defense, energy, medical and transport sectors as a result of their superior mechanical and physical properties. Continuous fiber CMCs combine the advantages of the high temperature properties of the matrix phase with a high flaw tolerance (Binner *et al.*, 2020). As a result, these composites offer pseudo-ductility behavior due to a range of mechanisms, though implicit in these mechanisms is the assumption that the matrix cracks are bridged to some degree by the fibers. Historically, the use of pressure-based sintering routes to create CMCs has typically resulted in coarse microstructures and damage to the continuous fibers due to the high sintering temperatures required. Without the use of an appropriate interfacial layer, the components are brittle. However, the high density achieved yields good strengths and reduces the risk of oxidative attack of the fibers (and matrix). Other methods such as precursor impregnation and pyrolysis (PIP), reactive melt infiltration (RMI) and chemical vapor infiltration (CVI) are also commonly used techniques for fabricating CMCs (Binner *et al.*, 2020), though each has their own advantages and disadvantages. Very recently, research into ultra-high temperature ceramic matrix composites (UHTCMCs) has led to materials that have potential for applications in aerospace (e.g. rocket nozzles and leading edges), high temperature nuclear fission and fusion reactors as well as concentrated solar power receiver materials.

Appendix A Supplementary Material

Supplementary data associated with this chapter can be found in the online version at doi:10.1016/B978-0-12-818542-1.00067-9.

References

- Abyzov, A.M., 2019a. Aluminum oxide and alumina ceramics (Review). Part 1. Properties of Al_2O_3 and commercial production of dispersed Al_2O_3 . *Refractories and Industrial Ceramics* 60 (1), 24–32.
- Abyzov, A.M., 2019b. Aluminum oxide and alumina ceramics (Review). Part 2. Foreign manufacturers of alumina ceramics. *Technologies and Research In The Field Of Alumina Ceramics* 1. *Refractories and Industrial Ceramics* 60 (1), 33–42.

- Akin, I., Goller, G., 2015. Spark plasma sintering of zirconia-toughened alumina composites and ultra-high temperature ceramics reinforced with carbon nanotubes. In: Brahim, A. (Ed.), *Research and Innovation in Carbon Nanotube-Based Composites*. Hong Kong: The World Academic Publishing Co. Ltd, pp. 85–101.
- Alexander, R., *et al.*, 2018. Effect of graphene nano-platelet reinforcement on the mechanical properties of hot pressed boron carbide based composite. *Ceramics International* 44 (8), 9830–9838.
- Arai, Y., Inoue, R., Goto, K., Kogo, Y., 2019. Carbon fiber reinforced ultra-high temperature ceramic matrix composites: A review. *Ceramics International* 45 (12), 14481–14489.
- Basha, M.M., *et al.*, 2020. A review on synthesis of zirconia toughened alumina (ZTA) for cutting tool applications. *Materials Today Proceedings* 26, 534–541.
- Basu, B., Balani, K., 2011. *Advanced Structural Ceramics*. Hoboken, NJ: John Wiley & Sons, Inc. <http://doi.wiley.com/10.1002/9781118037300>.
- Basu, B., Raju, G.B., Suri, A.K., 2006. Processing and properties of monolithic TiB₂ based materials. *International Materials Reviews* 51 (6), 352–374.
- Bedse, R.D., Sonber, J.K., Sairam, K., *et al.*, 2015. Processing and characterization of CrB₂-based novel composites. *High Temperature Materials and Processes* 34 (7), 683–687.
- Belmonte, M., González-Julián, J., Miranzo, P., Osendi, M.I., 2010. Spark plasma sintering: A powerful tool to develop new silicon nitride-based materials. *Journal of the European Ceramic Society* 30 (14), 2937–2946.
- Berchmans, L.J., *et al.*, 2010. Electrosynthesis of Samarium hexaboride using tetra borate melt. *Ionics* 16 (9), 833–838.
- Bhattacharya, M., Tanmay, B., A review on the susceptor assisted microwave processing of materials. *Energy* 97, 306–338.
- Bilal, A., Jahan, M.P., Talamona, D., Perveen, A., 2019. Electro-discharge machining of ceramics: A Review. *Micromachines* 10 (10), 1–41.
- Binner, J., Annaporani, K., Paul, A., *et al.*, 2008. Dense nanostructured zirconia by two stage conventional/hybrid microwave sintering. *Journal of the European Ceramic Society* 28, 973–977.
- Binner, J., Porter, M., Baker, B., Zou, J., *et al.*, 2020. Selection, PProcessing, Properties And Applications Of Ultra-high Temperature Ceramic Matrix Composites, UHTCMCs – A review. *International Materials Reviews* 65 (7), 389–444.
- Binner, J., Vaidyanathan, B., Paul, A., Annaporani, K., Raghupathy, B., 2011. Compositional effects in nanostructured yttria partially stabilized zirconia. *International Journal of Applied Ceramic Technology* 8 (4), 766–782.
- Chamberlain, A.L., Fahrenholtz, W.G., Hilmas, G.E., Ellerby, D.T., 2004. High-strength zirconium diboride-based ceramics. *Journal of the American Ceramic Society* 87 (6), 1170–1172.
- Dell'aghi, G., Mascolo, G., 2000. Hydrothermal synthesis of ZrO₂-Y₂O₃ solid solutions at low temperature. *Journal of the European Ceramic Society* 20 (2), 139–145.
- Faber, K.T., 1997. Ceramic composite interfaces: Properties and design. *Annual Review of Materials Science* 27 (1), 499–524.
- Faber, K.T., Evans, A.G., 1983. Crack deflection processes—I. Theory. *Acta Metallurgica* 31 (4), 565–576.
- Fahrenholtz, W.G., Binner, J., Zou, J., 2016. Synthesis of ultra-refractory transition metal diboride compounds. *Journal of Materials Research* 31 (18), 2757–2772.
- Fahrenholtz, W.G., Hilmas, G.E., Talmy, I.G., Zaykowski, J.A., 2007. Refractory diborides of zirconium and hafnium. *Journal of the American Ceramic Society* 90 (5), 1347–1364.
- Fahrenholtz, W.G., Wuchina, E.J., Lee, W.E., Zhou, Y. (Eds.), 2014. *Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications*. Hoboken, NJ: John Wiley & Sons, Inc.
- Florez, R., *et al.*, 2020. The irradiation response of ZrC ceramics under 10 MeV Au³⁺ ion irradiation at 800°C. *Journal of the European Ceramic Society* 40 (5), 1791–1800.
- Forsthoefel, K., Sneddon, L.G., 2004. Precursor routes to group 4 metal borides, and metal boride/carbide and metal boride/nitride composites. *Journal of Materials Science* 39 (19), 6043–6049.
- Gadarkary, S., Khanra, A.K., Veerababu, R., 2014. Production of nanocrystalline TiB₂ powder through self-propagating high temperature synthesis (SHS) of TiO₂-H₃BO₃-Mg mixture. *Advances in Applied Ceramics* 113 (7), 419–426.
- GE Aviation Fired up on CMCs, 2015. Available at: <https://www.geaviation.com/press-release/other-news-information/ge-aviation-fired-cmc>.
- German, R.M., Suri, P., Park, S.J., 2009. Review: Liquid phase sintering. *Journal of Materials Science* 44 (1), 1–39.
- Golla, B.R., Mukhopadhyay, A., Basu, B., Thimmappa, S.K., 2020. Review on ultra high temperature boride ceramics. *Progress in Materials Science* 111, 100651.
- Guha, T.K., Basu, B., 2010. Microfracture and limited tribochemical wear of silicon carbide during high speed sliding in cryogenic environment. *Journal of the American Ceramic Society* 93 (6), 1764–1773.
- Gunnewiek, R.F.K., Souto, P.M., Kiminami, R.H.G.A., 2017. Synthesis of nanocrystalline boron carbide by direct microwave carbothermal reduction of boric acid. *Journal of Nanomaterials* 8.
- Guo, S.Q., Nishimura, T., Kagawa, Y., Yang, J.M., 2008. Spark plasma sintering of zirconium diborides. *Journal of the American Ceramic Society* 91 (9), 2848–2855.
- Guo, W.-M., Zhang, G.-J., 2009. Reaction processes and characterization of ZrB₂ powder prepared by boro/carbothermal reduction of ZrO₂ in vacuum. *Journal of the American Ceramic Society* 92 (1), 264–267.
- Hakeem, A.S., *et al.*, 2014. Development and processing of SiAlON nano-ceramics by spark plasma sintering. *Advances in Science and Technology* 89, 63–69.
- Hampshire, S., 2007. Silicon nitride ceramics – Review of structure, processing and properties. *Journal of Achievements in Materials and Manufacturing Engineering* 24 (1), 43–50.
- Hampshire, S., 2008. Silicon Nitride Ceramics. In: Ralph, B., Xiao, P. (Eds.), *Advances in Ceramic Materials*. Materials Science Forum 606. Switzerland: Trans Tech Publications, pp. 27–41.
- Hampshire, S., Park, H.K., Thompson, D.P., Jack, K.H., 1978. α -sialon ceramics. *Nature* 274 (31 August), 880–882.
- Heian, E.M., Khalsa, S.K., Yamamoto, T., Ohyanagi, M., 2004. Synthesis of dense, high-defect-concentration B₄C through mechanical activation and field assisted combustion. *Journal of the American Ceramic Society* 87 (5), 779–783.
- Hu, Z.-Y., *et al.*, 2020. A review of multi-physical fields induced phenomena and effects in spark plasma sintering: Fundamentals and applications. *Materials & Design* 191, 108662.
- Hwang, Y., Lee, J.K., 2002. Preparation of TiB₂ powders by mechanical alloying. *Materials Letters* 54 (1), 1–7.
- Ji, W., *et al.*, 2017. Ultra-fast firing: Effect of heating rate on sintering of 3YSZ, with and without an electric field. *Journal of the European Ceramic Society* 37, 2547–2551.
- Johnson, S., Gasch, M., Stackpole, M., 2009. Assessment of the State of the Art of Ultra High Temperature Ceramics. Moffett Field, CA: NASA Ames Research Center Report. <https://ntrs.nasa.gov/search.jsp?R=20090035833>.
- Jung, E.Y., Kim, J.H., Jung, S.H., Choi, S.C., 2012. Synthesis of ZrB₂ powders by carbothermal and borothermal reduction. *Journal of Alloys and Compounds* 538, 164–168.
- Kang, S.-J.L., 2005. Basis of liquid phase sintering. In: Kang, S.-J.L. (Ed.), *Sintering*. Oxford: Butterworth-Heinemann, pp. 199–203.
- Khoshima, S., Altıntaş, Z., Burkhardt, U., *et al.*, 2020. CoB-TiB₂ crystalline powders: Synthesis, microstructural analysis and their utilization as reinforcement agent. *Advanced Powder Technology* 31 (7), 2964–2972.
- Kingery, W.D., Bowen, H.K., Uhlmann, D.R., 1976. *Introduction to Ceramics*, second ed. New York: Wiley.
- Krenkel, W., Naslain, R., Schneider, H. (Eds.), 2006. *High Temperature Ceramic Matrix Composites*. Weinheim: Wiley-VCH Verlag GmbH & Co.
- Kumar, A., Yadav, N., Bhatt, M., *et al.*, 2015. Sol-gel derived nanomaterials and it's applications: A review. *Research Journal of Chemical Sciences* 5 (12), 98–105.
- Li, K., Wang, D., Chen, H., Guo, L., 2014. Normalized evaluation of thermal shock resistance for ceramic materials. *Journal of Advanced Ceramics* 3 (3), 250–258.
- Lin, J.-D., Duh, J.-G., 2003. Fracture toughness and hardness of ceria- and yttria-doped tetragonal zirconia ceramics. *Materials Chemistry and Physics* 78 (1), 253–261.
- Liu, J.-X., Huang, X., Zhang, G.-J., 2013. Pressureless sintering of hafnium carbide-silicon carbide ceramics. *Journal of the American Ceramic Society* 96 (6), 1751–1756.
- Luo, T., *et al.*, 2020. Efficient preparation of Si₃N₄ by microwave treatment of solar-grade waste silicon powder. *ACS Omega* 5 (11), 5834–5843.
- Ma, H.-B., *et al.*, 2015. Pressureless sintering, mechanical properties and oxidation behavior of ZrB₂ ceramics doped with B₄C. *Journal of the European Ceramic Society* 35 (10), 2699–2705.

- Mahesh, B., *et al.*, 2015. Sinterability studies of monolithic chromium diboride (CrB₂) by spark plasma sintering. *International Journal of Refractory Metals and Hard Materials* 52, 66–69.
- Mallick, A.R., Chakraborty, S., Das, P.K., 2016. Synthesis and consolidation of ZrC based ceramics: A review. *Reviews on Advanced Materials Science* 44 (2), 109–133.
- Mashhadi, M., Shambuli, M., Safi, S., 2016. Effect of MoSi₂ addition and particle size of SiC on pressureless sintering behavior and mechanical properties of ZrB₂–SiC–MoSi₂ composites. *Journal of Materials Research and Technology* 5 (3), 200–205.
- Moradkhani, A., Baharvandi, H., Naserifar, A., 2019. Fracture toughness of 3Y-TZP dental ceramics by using vickers indentation fracture and SELNB methods. *Journal of the Korean Ceramic Society* 56 (1), 37–48.
- Murthy, T.S.R.C., 2004. Development and Characterization Of TiB₂ Based Materials For High Temperature Applications. (Masters thesis). India: IIT-Kanpur. https://archive.org/stream/in.ernet.dli.2015.199211/2015.199211.Development-And-Characterization-Of-TiB2-Based-Materials-For-High-Temperature-Applications_djvu.txt.
- Murthy, T.S.R.C., 2012. Effect of Sinter Additives on the Consolidation and Properties of Titanium Diboride Composites. (Ph.D. thesis). Homi Bhabha National Institute. <http://www.hbni.ac.in/phdthesis/engg/ENGG01200704007.pdf>.
- Murthy, T.S.R.C., 2020a. Boron-based ceramics and composites for nuclear and space applications: Synthesis and consolidation. In: Mahajan, Y., Johnson, R. (Eds.), *Handbook of Advanced Ceramics and Composites*. Switzerland: Springer International Publishing, pp. 1–36.
- Murthy, T.S.R.C., 2020b. Role of rare earth oxide particles on the oxidation behaviour of silicon carbide coated 2.5D carbon fibre preforms. *Open Ceramics* 2 (100018), 1–12.
- Nisar, A., Balani, K., 2017. Phase and microstructural correlation of spark plasma sintered HfB₂–ZrB₂ based ultra-high temperature ceramic composites. *Coatings* 7 (8), 110.
- Oghbaei, M., Mirzaee, O., 2010. Microwave versus conventional sintering: A review of fundamentals, advantages and applications. *Journal of Alloys and Compounds* 494 (1–2), 175–189.
- Parlier, M., Valle, R., Perrière, L., Lartigue-Korinek, S., Mazerolles, L., 2011. Potential of directionally solidified eutectic ceramics for high temperature applications. *Aerospace Lab Journal AL03–07* (3), 75–87. <https://aerospacelab.onera.fr/sites/www.aerospacelab-journal.org/files/AL3-07.pdf>.
- Paul, A., *et al.*, 2016. Heat flux mapping of oxyacetylene flames and their use to characterise C_f–HfB₂ composites. *Advances in Applied Ceramics* 115 (3), 158–165.
- Paul, A., Binner, J., Vaidhyanathan, B., 2014. UHTC composites for hypersonic applications. In: Fahrenholtz, W.G., Wuchina, E.J., Lee, W.E., Zhou, Y. (Eds.), *Ultra-High Temperature Ceramics*. Hoboken, NJ: John Wiley & Sons, Inc, pp. 144–166.
- Porter, M., 2020. High-Temperature Ceramic Matrix Composites Prepared via Microwave Energy Enhanced Chemical Vapour Infiltration. (Ph.D. thesis). University of Birmingham.
- Ramachandran, M., Subadevi, R., Liu, W.-R., Sivakumar, M., 2018. Facile synthesis and characterization of ZrO₂ nanoparticles via modified co-precipitation method. *Journal of Nanoscience and Nanotechnology* 18, 368–373.
- Rubio, V., Ramanujam, P., Binner, J., 2018. Ultra-high temperature ceramic composite. *Advances in Applied Ceramics* 117 (sup1), 56–61.
- Saheb, N., Hayat, U., Hassan, S.F., 2019. Recent advances and future prospects in spark plasma sintered alumina hybrid nanocomposites. *Nanomaterials* 9 (1607), 1–43.
- Sairam, K., *et al.*, 2014. Influence of spark plasma sintering parameters on densification and mechanical properties of boron carbide. *International Journal of Refractory Metals and Hard Materials* 42, 185–192.
- Sciti, D., *et al.*, 2018. Introduction to H2020 Project C 3 HARME – Next generation ceramic composites for combustion harsh environment and space. *Advances in Applied Ceramics* 117 (sup1), 70–75.
- Sharma, A., Karunakar, D.B., 2019. Development and investigation of densification behavior of ZrB₂–SiC composites through microwave sintering. *Materials Research Express* 6 (10), 105072.
- Singh, R.N., Wang, H., 1995. Thermal shock behavior of fiber-reinforced ceramic matrix composites. *Composites Engineering* 5 (10–11), 1287–1297.
- Skorokhod, V., Krstic, V.D., 2000. High strength-high toughness B₄C–TiB₂ composites. *Journal of Materials Science Letters* 19, 237–239.
- Sonber, J.K., *et al.*, 2010. Investigations on synthesis of HfB₂ and development of a new composite with TiSi₂. *International Journal of Refractory Metals and Hard Materials* 28 (2), 201–210.
- Sonber, J.K., *et al.*, 2014. Effect of WSi₂ addition on densification and properties of ZrB₂. *Advances in Applied Ceramics* 113 (2), 114–119.
- Sonber, J.K., Suri, A.K., 2011. Synthesis and consolidation of zirconium diboride: Review. *Advances in Applied Ceramics* 110 (6), 321–334.
- Sonber, J.K., Murthy, T.S.R.C., Subramanian, C., Fotedar, R.K., *et al.*, 2013. Synthesis, densification and characterization of boron carbide. *Transactions of the Indian Ceramic Society* 72 (2), 100–107.
- Sonber, J.K., Murthy, T.S.R.C., Subramanian, C., Hubli, R.C., *et al.*, 2013. Chapter 6 – Processing methods for ultra high temperature ceramics. In: Low, I.M., Sakka, Y., Hu, C.F. (Eds.), *MAX Phases and Ultra-High Temperature Ceramics for Extreme Environments*. Hershey, PA: IGI Global, pp. 180–202.
- Subramanian, C., Suri, A.K., Murthy, T.S.R.C., 2010. Development of Boron-Based Materials for Nuclear Applications. *BARC Newsletter* 313, 6–7.
- Suri, A.K., Subramanian, C., Sonber, J.K., Murthy, T.S.R.C., 2010. Synthesis and consolidation of boron carbide: A review. *International Materials Reviews* 55 (1), 4–40.
- Tülümen, H.M., Hanemann, T., Piottier, V., Stenzel, D., 2019. Investigation of feedstock preparation for injection. *Molding of oxide – Oxide ceramic composites*. *Journal of Manufacturing and Materials Processing* 3 (1), 9.
- Vignoles, G.L., 1992. Atomic relaxation and dynamical generation of ordered and disordered chemical vapour infiltration (CVI) SiC polytypes. *Journal of Crystal Growth* 118 (3–4), 430–438.
- Wang, J., *et al.*, 2006. Evidence for the microwave effect during hybrid sintering. *Journal of the American Ceramic Society* 89 (6), 1977–1984.
- Wang, J., Stevens, R., 1989. Review: Zirconia-toughened alumina (ZTA) ceramics. *Journal of Materials Science* 24, 3421–3440.
- Xiong, Z.-B., *et al.*, 2017. Magnetic iron-cerium-tungsten mixed oxide pellets prepared through citric acid sol-gel process assisted by microwave irradiation for selective catalytic reduction of NO with NH₃. *Powder Technology* 319, 19–25.
- Yeh, C.L., Chen, W.H., 2006. Preparation of niobium borides NbB and NbB₂ by self-propagating combustion synthesis. *Journal of Alloys and Compounds* 420 (1–2), 111–116.
- Zhao, X., *et al.*, 2017. Improved ablation resistance of C/SiC–ZrB₂ composites via polymer precursor impregnation and pyrolysis. *Ceramics International* 43 (15), 12480–12489.
- Zhao, Y., *et al.*, 2009. Effect of holding time and pressure on properties of ZrB₂–SiC composite fabricated by the spark plasma sintering reactive synthesis method. *International Journal of Refractory Metals and Hard Materials* 27 (1), 177–180.

Alumina, Structure and Properties

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Introduction

Alumina materials are a family of ceramics whose principal constituent is α -aluminum oxide (α -Al₂O₃), known as alumina in the ceramic sector. On a weight basis, these materials have the largest share of the ceramics world market.

Alumina is the ceramic material most extensively studied both from theoretical and practical stand points. There exist several reviews about alumina materials – properties, production and uses – (Gitzen, 1970; Dörre and Hübner, 1984; Kingery, 1984; Hart, 1990; Briggs, 2007; Doremus, 2008; Riley, 2009), on which this chapter relies to summarize the basic aspects of alumina materials. It adds to the previous publications by dealing with new developments and trends that were just proposed as possibilities in some of these reviews. More recently, processing and processing-related properties of alumina materials have been reviewed (Baudín, 2014a) and new and future applications were extensively analyzed in a comprehensive book dealing with the engineering of alumina ceramics (Ruy, 2019).

Etymology of the name alumina comes from the mineral alum (KAl(SO₄)₂ · 12H₂O), used since the years 3000 BCE in medicine, alchemy, and industry. First patents on commercial applications of single-phase alumina date from the beginning of the 20th century. For instance, an early German patent describes the production of alumina dies for drawing wires (General Electric Company, 1913) and the first British Patent (Thomson-Houston Company, 1913) deals with components for wear-resistant applications such as tools, bearings, dies, and drills.

Widespread commercial applications of alumina came later, in the 1930s, when alumina started to be used for various applications such as crucibles for corrosive liquids, cutting tools for metal machining and high voltage electrical insulators. The requirements of increasing temperatures of the combustion aeroengines during the period preceding World War II led to the need for electrical insulators capable of withstanding higher temperatures. The first large scale use was in spark plug insulators, constituted by 90–95 wt% aluminum oxide and glass formed by liquid-phase sintering aids.

The widespread usefulness of alumina is due to a variety of properties such as high melting point (2054°C), high chemical stability in different environments, hardness, strength, abrasion resistance, electrical resistance and transparency. A huge research effort was dedicated to alumina since the 1950s, leading to numerous new applications of advanced materials in technologies that were emerging during the last quarter of the 20th century.

Alumina materials present a wide range of compositions from nearly 100% aluminum oxide with trace elements used as sintering additives or associated impurities to materials containing up to 20 wt% of other constituents. In most cases, aluminosilicates are present in the materials as glass. Materials with amounts of glass up to 10 wt% are considered as alumina ceramics while those with larger amounts are included in the group of alumina porcelains.

The microstructures of advanced alumina materials consist of small, normally ≤ 30 μ m, aluminum oxide grains strongly bonded across grain boundaries. Small amounts of glass might be present in the form of very thin films at the grain boundaries (1–2 nm). Those ceramics containing aluminosilicates usually have glass forming pockets at triple points and grain boundaries. Commercial aluminas for more highly demanding applications such as hip joints for arthroplasty or cutting tools have typical grain sizes under 5 μ m.

In **Table 1**, the main commercial applications of alumina materials and the properties required for the envisaged application are summarized.

As a single-crystal, alumina is prized as gemstones (sapphire or ruby, depending on the impurities) and for special applications such as watch bearings. Moreover, some high grade glass substitutes are made of single-crystal alumina (artificial sapphire). In coarse polycrystalline form, alumina is the major constituent of high grade shaped and unshaped refractory materials. In the form of powder and grids, alumina is used as grinding and abrasive media. In the form of whiskers and fibers, alumina is used for low-thermal-mass furnace insulation and metal reinforcement. Porous sintered aluminas are used as catalyst supports for chemical processes. Alumina-based materials with different alumina contents (from around 88 to more than 99.5 wt%) and micrometer grain sizes are used for a wide range of applications requiring specific mechanical, chemical, electrical, optical and biomedical characteristics.

Structural applications of alumina at room temperature are based on the combination of hardness, wear resistance, and corrosion resistance that alumina provides. Room temperature applications include wear parts in medical engineering (prostheses for hip and knee joints), in process plants (pump components and valve faces, lining of pipework), and in mechanical engineering (bearings and valves). Alumina pieces of different shapes and sizes are currently used as textile guides.

Alumina presents also high refractoriness; that is, high melting point and retention of structural integrity at high temperature. Due to its high refractoriness, one of the most successful applications of alumina is in cutting tools for high speed machining of metals, which have experienced a huge development since their commercial introduction in the early 1950s.

Applications of alumina in components for engines are limited by its low thermal shock resistance as compared to that of non-oxide ceramics.

Table 1 Commercial applications of alumina materials and the related properties

	<i>Applications</i>	<i>Primary property</i>	<i>Other properties</i>
Single crystal	Gemstones	Esthetics	Mechanical stability at room temperature
	Glass substitutes	Translucency/Transparency	Hardness and stiffness up to 1000°C
	Special applications (e.g., watch bearings)	Hardness and stiffness	
Grains	Abrasives	Hardness	
	Aggregates for unshaped refractories		
Shaped: Polycrystalline	Shaped refractories	Chemical inertness at high temperature	Hardness and stiffness at high temperature
	Catalyst supports for chemical processes	Porosity and chemical inertness	Dimensional stability
	Mechanical engineering (e.g., bearings and valves)	Wear resistance at room temperature	Chemical inertness at room temperature
	Process plants (pumps, valves, pipeworks...)		
	Cutting tools for metals	Wear resistance up to 1200°C	Hardness and stiffness at high temperature
			Chemical inertness
	Wear resistant parts (mining, textile, paper, food ...)	Wear resistance	
	Medical engineering (e.g., total prostheses for hip joints)	Biocompatibility	Wear resistance at room temperature
	Feedthroughs for bionic implants	Biocompatibility and bioinertness	Stiffness and strength
		High electrical resistivity	
	High voltage spark plug insulators (> 80 to 95% alumina)	Electrical resistivity at high temperature	Strength
			Chemical inertness
	Substrates for semiconductor and microelectronics industry	Electrical resistivity	Dimensional stability
			Low loss tangent (High frequency applications)
	Armor	Resistance to impact	
	Glass substitutes	Translucency/Transparency	Hardness and stiffness up to 1000°C

The optical properties of alumina together with its structural stability make it an ideal substitute for glass in harsh environments.

As reported by [Ruy \(2019\)](#), from an economic point of view, the most significant applications for alumina are as substrates in the semiconductor and microelectronics industry and in medicine. Alumina is one of the most satisfactory materials for bearings for arthroplasty due to its biocompatibility and its high wear resistance. The high electrical resistivity together with biocompatibility and bioinertness and dimensional stability makes alumina the ideal material for feedthroughs in bionic implants, which has meant a true revolution in the sector of implantable bionics.

Apart from the specific properties of alumina, there are two factors that contribute to the wide use of alumina ceramics for advanced applications: the availability of raw materials and the possibility of sintering high purity alumina ceramics to full density.

The attractive technological properties of alumina ceramics are due to the properties of their main component, α -Al₂O₃, which are determined by its crystalline structure and the nature of the bonds.

This chapter deals with high purity (>95 wt%) and fine grain size ($\leq 30 \mu\text{m}$) wear resistant alumina ceramics, thus, alumina porcelains, and refractories will not be addressed. Zirconia toughened alumina (ZTA) will also be considered when discussing alumina as a biomaterial. First, the thermodynamics of Al₂O₃ will be analyzed. Then, the crystalline structure and the related properties of single-crystal α -Al₂O₃ will be discussed. Then, the main processes for the production of alumina materials with controlled microstructure will be summarized. The properties and applications of alumina materials will then be discussed in relation to those of single-crystal α -Al₂O₃ and microstructure. Last, the most recent and future applications of alumina materials will be summarized.

Thermodynamic Stability

As stated by [Brewer \(1953\)](#) in his exhaustive review, from a thermodynamic stand point, α -Al₂O₃ is one of the most stable of the metal oxides. This fact is clearly demonstrated by the large negative Gibbs energy of formation from the metal, ΔG_T , according to:



Where ΔG_T values range from -1590 to -945 kJ/mol from $T = 273\text{K}$ to $T = 2273\text{K}$ (calculations using the program Outokumpu 1993). This high thermodynamic stability is responsible for the absence of natural deposits of free Al.

Dissociation of Al_2O_3 to two sub-oxides, Al_2O and AlO , has been reported to take place at high temperature and low oxygen partial pressures (Brewer, 1953; Brewer and Searcy, 1951) according to:



However, even though both reactions present a negative Gibbs energy, the corresponding equilibrium constants are extremely low, e.g., at 1773K, $K = 2.76 \times 10^{-30}$ and 4.56×10^{-24} for reactions (2) and (3), respectively, (calculations using the program Outokumpu 1993). Therefore, alumina experiences extremely low weight losses in vacuum, even at high temperatures, e.g., $\approx 10^{-6}$ – 10^{-5} kg/m²·s in the temperature interval 1973–2273K (Harper, 2001).

Even though the fusion temperature of alumina is very high, liquids can be formed at the lower temperatures of the invariant points associated with impurities. Some examples of liquid forming temperatures (Levin *et al.*, 1964) are those corresponding to the systems Al_2O_3 – SiO_2 (1590°C: mullite-tridymite), Al_2O_3 – SiO_2 – CaO (1170°C: pseudowollastonite-tridymite-anorthite), Al_2O_3 – MgO – SiO_2 (1355°C: protoenstatite-cordierite-tridymite), Al_2O_3 – SiO_2 – K_2O (689°C: quartz-potash feldspar – $\text{K}_2\text{Si}_4\text{O}_9$, 990°C: leucite-mullite-cristobalite) and Al_2O_3 – SiO_2 – Na_2O (720°C: quartz-albite-anorthite). Some of these impurities can be used as sintering aids to increase the final density and/or reduce the sintering temperature of polycrystalline alumina materials. However, they remain at the grain boundaries in the sintered material, most often in glass form, and are detrimental for the high temperature structural integrity of the materials. In the same way, the chemical inertness of α - Al_2O_3 makes materials with above 99% alumina resistant to chemical corrosion by liquids – acidic, caustic, and saline – while silicate impurities dramatically reduce corrosion resistance.

Single-Crystal Aluminum Oxide

Crystalline Structure

The main constituent of alumina ceramics is α - Al_2O_3 , which is the only crystalline form of pure aluminum oxide at ambient pressure throughout the whole temperature range up to the melting point (2054°C). It is important to remark that β -alumina and γ -alumina are not different polymorphs of Al_2O_3 , as such confusing nomenclature would suggest. β -alumina is sodium aluminum oxide of composition $\text{Na}_2\text{O} \cdot x\text{Al}_2\text{O}_3$ ($x = 5$ –12) while γ -alumina powders are poorly crystallized hydrated aluminum oxide powders. The crystalline phase α - Al_2O_3 is called corundum and, in the single-crystal form, corundum is called sapphire.

The crystalline structure of α - Al_2O_3 – hexagonal structure, D_{3h}^6 space group – is described in several sources (e.g., Deer *et al.*, 1992; Brook, 1991); (See Relevant Websites section).

This crystal lattice can be described by planes of hexagonal close packed oxygen ions (Fig. 1(a)) that leave octahedrally coordinated sites which are occupied by Al^{3+} ions. The radius of the O^{2-} ion (140 pm) is larger than that of Al^{3+} (50 pm). Only two thirds of the sites are filled by Al^{3+} ions due to the 2:3 at. proportions in Al_2O_3 (Fig. 1(b) and (c)). Thus, the Al^{3+} ions are

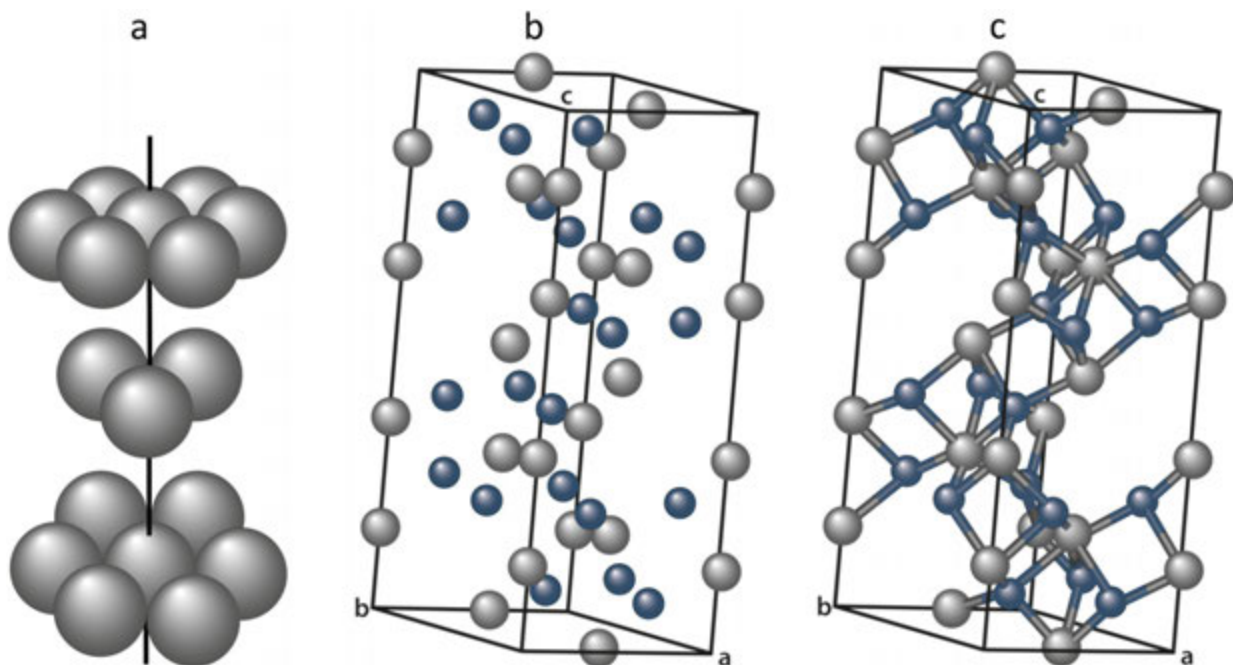


Fig. 1 Crystalline structure of sapphire. Gray: oxygen atoms; blue: aluminum atoms. (a) Planes of hexagonal close packed oxygen ions. (b) Ideal structure showing the atom distribution. (c) Ideal structure showing the atom distribution and the O–Al bonds.

bonded to 6 oxygen forming AlO_6 octahedrons. Each such octahedron shares a face with one on the upper and one on the lower layers. The real structure is not symmetrical as polarization is produced when the small cations with large charges occupy the interstices. Then, three O^{2-} are closer to each Al^{3+} than the other three and the octahedrons are distorted, the mean aluminum-oxygen distance being 192 pm. The measured *a* and *c* lattice parameters are 476 pm and 1299 pm, respectively, giving a theoretical density for the single-crystal of 3990 kg m^{-3} (Powder X Ray diffraction file ASTM42-1468).

Aluminum oxide is considered to be ionic, constituted by Al^{3+} and O^{2-} ions; however, its bonds have some covalent character (Sousa *et al.*, 1993). As the share of ionic character to the bond is 63%, there is a highly covalent contribution to the bond strength, which is high.

As with all non-cubic materials, aluminum oxide presents anisotropy in properties at the crystalline level which is higher in ionic oxides due to partial polarization. Properties of sapphire are determined by the close packed and anisotropic crystalline structure and the high energy bonding, as discussed below.

Elastic and Mechanical Properties

The most direct measurements of the bond strength of single-crystals are the elastic constants. Values of the single-crystal compliances (*C_{ij}*) and stiffnesses (*S_{ij}*) determined by different authors were collected by Bradt and Scott (1990) who found that values determined by different authors from 1960 were coincident. Anisotropy in Young's modulus for sapphire is lower than for other oxides. The difference between the values of Young's modulus in directions parallel (430 GPa) and perpendicular (465 GPa) to the *c* axis is small and a minimum value occurs in an intermediate direction (380 GPa). As shown in Fig. 2, this small anisotropy in Young's modulus is maintained at high temperature, where a minimal decrease occurs from room temperature up to 1000°C. The decrease of stiffness with temperature is due to the increase in atomic displacements originated by atomic vibrations and the associated reduction in bond strength.

In addition to the high Young's modulus, the high bond strength in the close-packed crystal structure of $\alpha\text{-Al}_2\text{O}_3$ is reflected in the fact that sapphire is one of the hardest materials, with a hardness of 9 on the Mohs scale (non-linear, 1: talc, 10: diamond) and Vickers hardness up to 30 GPa, depending on the orientation (Ryshkewitch and Richerson, 1985).

In terms of comparison, only some non oxide ceramics present higher Young's modulus, *E*, and hardness, *H*, values than $\alpha\text{-Al}_2\text{O}_3$. For instance, values of $H = 61 \pm 1 \text{ GPa}$ and $E = 1070 \pm 30 \text{ GPa}$ have been determined by nanoindentation on the (111) plane of single-crystals of cubic BN (Deura *et al.*, 2018). In the case of SiC, which is considered a hard material, values of Knoop microindentation (100 g) hardness between 22 and 30 GPa for $\alpha\text{-SiC}$ (Shaffer, 1964) and between 27 and 30 GPa for $\beta\text{-SiC}$ (Shaffer, 1964), depending on orientation, have been reported.

Sapphire can experience plastic deformation depending on the temperature and the stress history (Jones and Tressler, 1991).

Deformation of sapphire fibers is linear up to temperatures above 1600°C for most orientations. For instance, sapphire fibers oriented such that the basal (0001) plane is perpendicular to the fiber axis possess high deformation resistance due to the extreme anisotropy of the sapphire crystal structure, resulting in few slip systems available to be activated. Also, the high covalent contribution to the alumina bond strength further increases the Peierls force needed to initiate slip.

Dislocation glide in sapphire occurs at high temperature (Bradt and Scott, 1990). Basal slip on the close-packed oxygen planes is the most common. Below 1600°C, plastic flow occurs by slip on the basal plane (0001) in the $[\bar{1}\bar{1}20]$ direction both in tension and compression in the temperature range of 900–2000°C, depending on the applied stress, as first identified by Watchman and Maxwell (1957). The second most common slip system is on the prism plane ($\bar{1}2\bar{1}0$) in the $[\bar{1}010]$ direction.

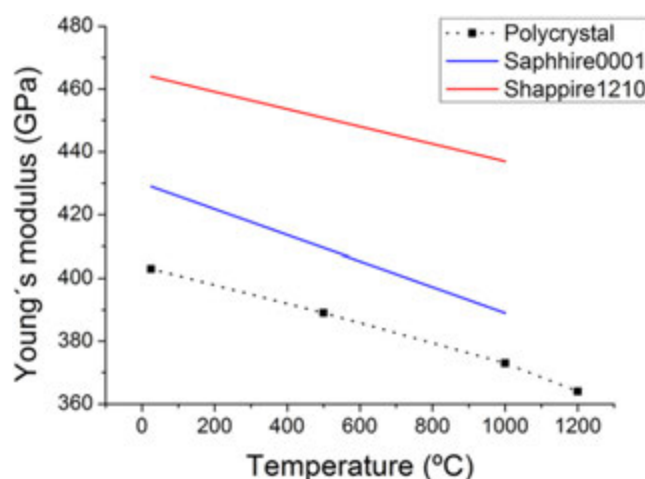


Fig. 2 Young's modulus of $\alpha\text{-Al}_2\text{O}_3$ as a function of temperature. Data for a dense (>99% of T.D.) alumina material and for single-crystal in the indicated crystalline planes, (0001) and ($\bar{1}2\bar{1}0$). Plotted from Gitzen, W.H., 1970. Alumina as a ceramic material American Ceramic Society Special Publication No. 4. Ohio, USA: The American Ceramic Society. Bradt, R.C., Scott, W.D., 1990. Mechanical properties of alumina In: Hart, L.D. (Ed.), Alumina Chemicals Science and Technology Handbook. USA: The American Ceramic Society Inc, pp. 23–39.

The fracture behavior of alumina single-crystals has been extensively studied over many years because of its technological interest in the crushing of single-crystal grains of alumina abrasives and the fabrication of jewelry. Crack propagation in sapphire occurs as cleavage on specific crystallographic planes, being the rhombohedral R plane ($\bar{1}012$), the one which cleaves more easily at room temperature and the basal plane (0001) the most difficult to cleave (Bradt and Scott, 1990). Wiederhorn and colleagues (Wiederhorn, 1969; Wiederhorn *et al.*, 1973) measured a surface energy of 6 Jm^{-2} for the former one and estimated that of the later one to be higher than 40 Jm^{-2} . Iwasa and Bradt (1984) reported K_{IC} values of 2.4 ± 0.1 and $4.5 \pm 0.3 \text{ MPam}^{1/2}$ for ($\bar{1}012$) and (0001), respectively. The easiness of cleavage of plane ($\bar{1}012$) is due to the large array of vacant cation lattice sites parallel to this plane. Wiederhorn attributed the high resistance of the basal plane to cleavage to a lack of charge neutrality in this plane.

Iwasa and Bradt (1984) studied the effect of temperature on K_{IC} of different crystallographic planes, from room temperature up to 1400°C . The temperature increase affected differently the different planes. The plane for which the effect was more severe was (0001) for which K_{IC} at 800°C was about one quarter of the value at room temperature and increased for higher temperatures revealing plastic deformation. This phenomenon was also detected for the plane ($10\bar{1}2$).

Sapphire presents relatively high strengths that are lower than its theoretical strength, calculated using the simplest relationship ($\sigma_t \approx 0.1 \cdot E = 38\text{--}46 \text{ GPa}$). Room temperature bending strengths of $400\text{--}700 \text{ MPa}$ and tensile strengths of 500 MPa , depending on orientation and surface imperfections, are common (Brook, 1991; Riley, 2009). Moreover, values up to 7 GPa have been reported for flame polished artificial sapphire rods (Brook, 1991; Watchman and Maxwell, 1959) which are increased up to 11 GPa for thin filaments. Recent data for microcantilever beams ($10\text{--}30 \mu\text{m}$ long, width and depth $2\text{--}5 \mu\text{m}$), machined by FIB and tested in a nanoindenter, range from 10 to 13 GPa for monocrystals.

In agreement with the variations of Young's modulus and K_{IC} , classical works on tensile properties of sapphire filaments reported changes of strength with temperature. Reported strength values for sapphire filaments grown in the direction of the c axis follow non-monotonous dependence on temperature (Shahinian, 1971). A significant decrease from room temperature down to around 500°C was attributed to brittle fracture while an increase from this temperature up to 1000°C was explained by microplastic deformation at stress concentrations. Bayer and Cooper (1969) measured the tensile strength of sapphire filaments of diverse origins and orientations and found a decrease of strength from room temperature up to 1000°C that could be associated with brittle fracture. From around 1200°C , strength experienced a slight increase in agreement with the occurrence of plastic deformation processes. More recently, flexural strength determination in sapphire for high temperature pressure sensors showed a decrease of about 6% for every increase of 100°C from 750 MPa at room temperature to 350 MPa at 1200°C (Guo *et al.*, 2018).

Thermal and Functional Properties

Thermal and functional properties of single-crystal $\alpha\text{-Al}_2\text{O}_3$ present slight anisotropy due to the anisotropy of the crystal structure.

$\alpha\text{-Al}_2\text{O}_3$ exhibits a relatively low crystalline average thermal expansion coefficient, $\alpha \approx 8.7 \times 10^{-6} \text{ K}^{-1}$ between 25 and 1000°C (Taylor, 1984). However, there is a perceptible larger thermal expansion coefficient parallel to, rather than perpendicular to, the c axis, $\alpha \approx 9.2$ and $8.4 \times 10^{-6} \text{ K}^{-1}$ between $25\text{--}1000^\circ\text{C}$, in the parallel and perpendicular directions, respectively (Taylor, 1984). This thermal expansion anisotropy is responsible for the development of stresses in polycrystalline alumina materials when cooling from the sintering temperature. As will be discussed, manipulation of microstructure in order to control the effect of the thermal stresses is the main way for optimizing the fracture behavior of alumina materials.

In nonmetallic solids, heat is transported by phonons (i.e., lattice vibrations). Thermal conductivity is determined by the mean free path of phonons which, in turn, is dependent on temperature, phonon-phonon interactions and scattering by lattice defects. Reported values of thermal conductivity of sapphire are highly dependent on the fabrication method because of the strong effect of defects, in particular, those derived from impurities. Also this property is slightly anisotropic, being higher in the direction parallel to the c axis than in the direction perpendicular, e.g., (See Relevant Websites section) for commercial optical sapphire at room temperature $K = 25.8$ and 23.0 W/mK in directions parallel and perpendicular, respectively. Values of average thermal conductivity of sapphire as a function of temperature have been summarized and discussed by Doremus (2008) and are plotted in Fig. 3. At very low temperatures ($\leq 40 \text{ K}$) the mean free path of phonons is determined by specimen dimensions because scattering occurs from the specimen surfaces, and the thermal conductivity is very high. From 40 K , conductivity decreases sharply due to the increase of phonon-phonon interactions. Above 1073 K (800°C), the mean free path is of the order of lattice distances and it becomes constant with temperature. Thermal conductivity of around 40 W/mK at room temperature makes sapphire a relatively good thermal conductor.

The electrical properties of sapphire were extensively reviewed and analyzed by Gitzen (1970) and, more recently, by Doremus (2008). Values of the electrical properties of sapphire are shown in Table 2. The electrical resistivity is one of the highest of all known materials while the dielectric loss tangent is among the lowest.

Sapphire is well known as an optical material because of its excellent transmittance. Sapphire, together with Mg-Al spinel and aluminum oxynitride (ALON®) transmit from about $5 \mu\text{m}$ in the infrared to at least as far as $\approx 0.2 \mu\text{m}$ in the ultraviolet. As sapphire is mechanically stronger, thinner sapphire windows, with the associated increase in transmittance, are required. As in the case of other properties analyzed in this chapter, sapphire presents anisotropy in the refractive index. Comprehensive data on the optical properties of sapphire can be found in the classical book by Gitzen (1970). Synthetic sapphire windows are used in both high pressure and vacuum chambers for spectroscopy, watch faces, barcode scanners due to its resistance to scratching. Due to the high temperature stability it is also used in windows of laser tubes and, to a lesser extent, small dimension tubes ($1\text{--}10 \text{ cm}$) of sapphire are used as vapor-tight envelopes in sodium vapor lamps due to its excellent corrosion resistance.

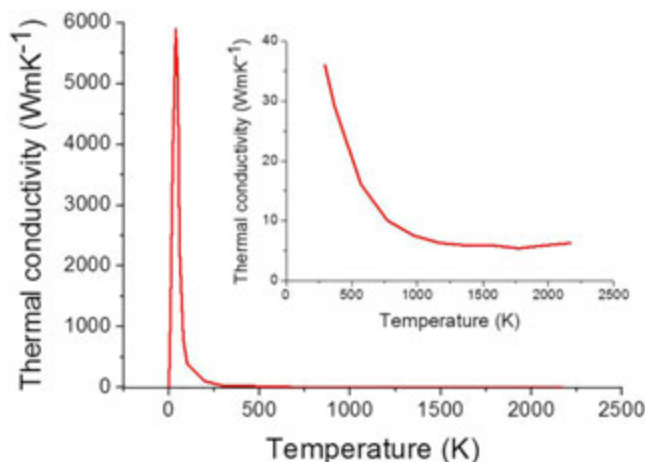


Fig. 3 Thermal conductivity of sapphire as a function of temperature. Plotted from Doremus, R.H., 2008. Chapter 1: Alumina. In: Shackelford, J.F., Doremus, R.H. (Eds.), *Ceramic and Glass Materials: Structure, Properties and Processing*. USA: Springer, pp. 1–26.

Table 2 Electrical properties at room temperature of ceramics for insulating components^a

Material	Electrical resistivity $\Omega \cdot m$	Loss tangent, $\tan(\delta)$, at 50 Hz
Sapphire ^b	10^{14}	
Alumina 99.5%	10^{12}	0.0002
Alumina 96%	10^{12}	0.0005
Porcelain	10^{10}	0.025
BeO	10^{12}	0.001
AlN	10^{12}	0.0005–0.001
BaAl ₂ Si ₂ O ₈	10^{12}	0.01

^aData from Ruy (2019).

^bData from Riley (2009).

Properties – Summary

From a thermodynamic stand point, α -Al₂O₃ is one of the most stable of the metal oxides and its melting point is high.

Single-crystal α -Al₂O₃ presents very interesting mechanical properties such as high stiffness and hardness which are maintained at relatively high temperatures but it lacks toughness. It has a relatively high thermal conductivity for an oxide. From the stand point of electrical properties, it is an excellent insulator because of its high resistivity and low dielectric loss. Also sapphire has excellent optical transparency.

Most of the work on the development of alumina materials has been devoted to take advantage of the desired properties of the single-crystals by controlling the microstructure. High purity aluminas with controlled grain sizes have been developed for advanced applications in different fields as will be discussed in the following sections. In particular, the thermal expansion anisotropy has been used as the basis for toughness increases.

Production of Alumina

Aluminum is the third most common element in the Earth's crust (≈ 8 wt%), after oxygen and silicon, with enough economically available reserves to supply at least another 300 years of current demand (International Aluminum Institute 2019, See Relevant Websites section).

However, because of its chemical reactivity it is mostly found in its oxidized form (approx. 250 different minerals exist) and it almost never occurs in purely metallic form.

As a natural mineral alumina, α -Al₂O₃, is rare and it is called corundum. Even rarer is the single-crystal form, sapphire, which is usually slightly colored due to metallic impurities (Ni and Mg give yellow and Ti gives blue) and ruby, which contains a small amount of Cr (≈ 1 wt%).

The most prominent group of aluminum containing minerals is that of the aluminosilicates, and the products of their weathering, the clays. With regards to aluminum production, the aluminum hydroxides represent the most important compounds. Pure anhydrous Al₂O₃ forms two hydrates: Al₂O₃·H₂O (AlO(OH)) and Al₂O₃·3H₂O (Al(OH)₃). Each of these compounds has two

crystalline forms, α and γ and a specific name (diaspore: α - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, boehmite: γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, bayerite: α - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and gibbsite or hydrargillite: γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$).

Most alumina grades are originally manufactured from mineral sources. The most significant advancement in terms of raw materials has been the development of chemical routes to fabricate high purity powders with controlled particle sizes.

Small particle size ($\approx 1 \mu\text{m}$ or less) and high purity ($> 99.5\%$) powders are required for the production of high strength and hardness advanced alumina ceramics. For structural applications, especially involving high temperature, and optical and electrical applications, extremely high purity aluminum oxide is needed. In particular, liquid forming agents such as SiO_2 , Na_2O , CaO , etc. should be avoided.

Industrial Processes

The main raw material for alumina is bauxite (named after Les Baux-en-Provence in France), a mixture of the oxide hydrates and clays (aluminosilicates). Impurities are mostly oxides such as SiO_2 and TiO_2 and small amounts (ppm) of the strategic compound Ga_2O_3 and iron oxides which occur as weathering products of low iron and silica bedrock in tropical climatic conditions. The most common mineral constituent of bauxite is gibbsite. Detailed descriptions of bauxite mineralogy are included in a number of text books, e.g., Wells (1984) and summaries can be found in several revisions, e.g., Doremus (1984). Evolution of gibbsite with temperature has been recently studied by neutron thermodiffraction (Rivas Mercury *et al.*, 2006). Deposits of bauxite exist around the world; the largest ones are found in China, Guinea, Australia, Brazil, and Jamaica.

Purification of bauxite to fabricate aluminum and, to a lesser extent, alumina, is done by the Bayer process. Bauxite consumption per ton of alumina has increased in recent years (from around 2.7 tons in 2005) due to declining quality of bauxite resources and now three tons of bauxite are required to produce one ton of alumina and two tons of alumina are required for the production of one ton of primary aluminum metal. However, the energy efficiency of the Bayer process has improved over that period (International Aluminum Institute 2019, See Relevant Websites section).

Fig. 4(a) shows the geographical share of alumina production in 2018 recognized by the International Aluminum Institute; most alumina was produced in China. The major part of alumina is used for the production of aluminum whereas a small part goes to the alumina chemicals industry (Fig. 4(b)). Nevertheless, the alumina chemicals industry has become a global enterprise in

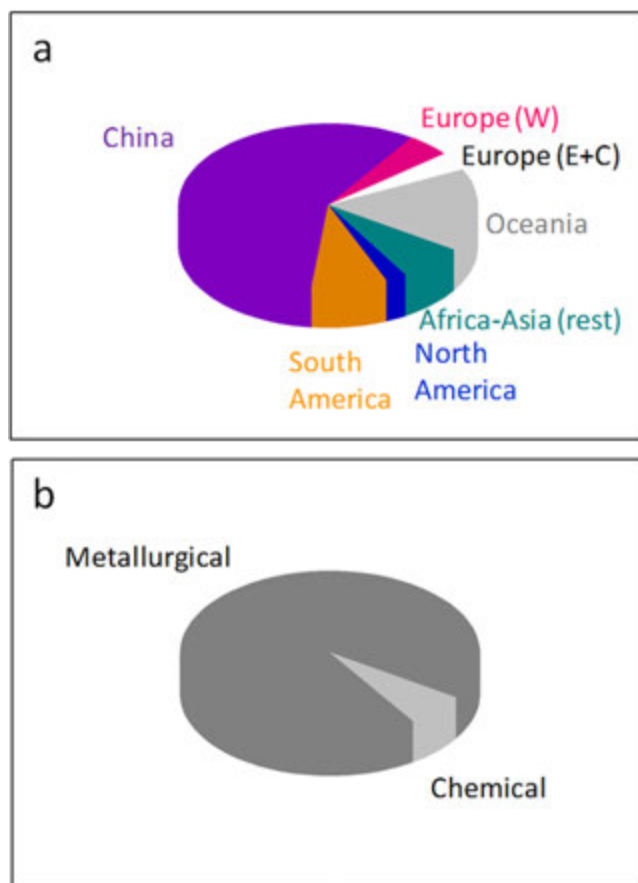


Fig. 4 Alumina production by weight in 2018. Total: 64.336 million tons (a) Geographical share. E + C: Eastern and Central; W: West; rest: non-China (b) Metallurgical (Al production) and chemical (Al_2O_3 production) share. <http://www.world-aluminum.org/statistics/alumina-production/#data>.

which most of the world's major aluminum firms participate. Most applications of alumina chemical products are in the field of ceramics, including refractories, cements and abrasives.

The Bayer process starts by dissolving crushed bauxite in sodium hydroxide under pressure at 300°C to form a supersaturated solution of sodium aluminate at normal conditions of pressure and temperature. The insoluble oxides are then removed and the hydrated aluminum oxide is precipitated as gibbsite by seeding, more frequently, or as metastable bayerite by reduction of pH by carbon dioxide. The precipitated low temperature forms, γ -alumina, are then washed and subsequently dehydrated at 1000–1200°C to fully convert into the stable α -alumina phase. This material is named calcined alumina and typically contains 0.1–0.5 wt% of sodium and calcium oxides. Powders calcined at intermediate temperatures, usually called reactive aluminas, are mixtures of α -Al₂O₃ and transition aluminas. The coarse aggregates made of large alumina single-crystals for the refractory industry (fused alumina) are obtained by fusing and casting reactive alumina powders and crushing the obtained material. Also it can be graded to be used for grinding and abrasives.

The sizes of powders required for the fabrication of high performance ceramics are in the range of microns (μm) while the calcined agglomerates have sizes up to $\approx 100 \mu\text{m}$, even though the sizes of the primary crystals can be smaller than $1 \mu\text{m}$. Therefore, the calcined agglomerates have to be milled down to obtain uniform sized, small particles. A major objective of the calcination step is to obtain soft agglomerates in order to avoid the expensive and polluting process of intensive milling as much as possible. The other main characteristic of the calcined aluminas is the presence of up to 0.5 wt% Na₂O as mentioned above. Low soda calcined aluminas are considered when the Na₂O is lower than 0.05 wt%. Typical specifications of calcined aluminas are given by [Riley \(2009\)](#).

High Purity Alumina Powders

High purity alumina powders with controlled size distributions and reactivity are required for advanced applications. New processes for obtaining high purity powders have been developed since the late 1980s. The most common are based on the decomposition in air of aluminum containing salts such as ammonium aluminum sulfate, (NH₄)₂SO₄·Al₂(SO₄)₃·12H₂O, or aluminum hydroxides. The obtained transition aluminas are then converted into α -alumina by heating at temperatures over 1000°C, which also promotes the growth of the α -alumina particles and the formation of hard agglomerates. Since the early uses of alumina, different ways have been proposed to reduce the temperature of treatment in order to limit the formation of agglomerates. Different additives such as metal oxides ([Messing *et al.*, 1988](#); [Xue and Chen, 1992](#); [Wakao and Hibino, 1962](#)), α -alumina seeds ([Kumagai and Messing, 1985](#); [Messing *et al.*, 1988](#); [Rajendran, 1994](#); [Yoshizawa and Saito, 1996](#); [Yoshizawa *et al.*, 2004](#)), liquid-phase formers ([Shelleman and Messing, 1988](#)), and different organic and non-organic compounds ([Xue and Chen, 1992](#); [Rajendran, 1994](#); [Wu *et al.*, 2002](#)) as well as high energy ball milling ([Tonej *et al.*, 1994](#); [Wang *et al.*, 2005](#)) have proven to be effective to reduce the α -alumina transformation temperature. The hydrolysis of aluminum alkoxide has also been proposed to obtain high purity alumina ([Fujiwara *et al.*, 2007](#)). All these processes are relatively expensive and produce only small quantities of powders that are used only for specific advanced technology applications.

Since the late 1990s, a huge effort has been devoted to fabricate not only high purity but also extremely fine grain aluminas ($\approx 100 \text{ nm}$). In this sense, direct processing of the nanosized and high specific surface transition aluminas to fabricate the bulk material was proposed. [Bowen and Carry \(2002\)](#) published a comprehensive review on colloidal processing of nanoparticles where most issues about the processing of transition aluminas are discussed. Due to the wide potential applications of monohydrates – boehmite (γ -AlOOH), diasporite (α -AlOOH) and pseudoboehmite – as precursors of aluminas for advanced applications such as orthopedic or dental materials, a growing research effort has been focused on their synthesis in recent years, e.g., [Hai *et al.* \(2018\)](#).

Processing of Alumina Materials

One of the consequences of the high melting point of ceramics and, in particular of alumina, is that materials are generally fabricated from powders and not from fused mixtures. Consequently, the general fabrication process includes the processing of the powders to reach a shaped powder form, usually named the green body, and then followed by thermal treatment. The word sintering is used to describe the various phenomena that occur during the thermal treatment ([Leriche *et al.*, 2020](#)).

When the powder compact is heated to a suitable temperature at which the mass transport mechanisms are operative, the porous compact shrinks as a result of the initial misfit of the particles. Apart from shrinkage, grain growth occurs during the process. In some cases, reaction between the constituents occurs which might aid or impede shrinkage. This latter process is fundamental when the sintering aids are needed.

Processing of advanced alumina ceramics has been recently reviewed in a focused encyclopedia chapter ([Baudín, 2014a](#)) and by [Ruy \(2019\)](#). The main issues that determine the properties of alumina materials are summarized in the following sections.

Thermal Stresses

One main issue of single-phase polycrystalline alumina materials are the thermal stresses which originate when cooling from the sintering temperature due to the thermal expansion anisotropy of single-crystal α -Al₂O₃. Different authors have discussed the importance of thermal expansion anisotropy on alumina materials (e.g., [Blendell and Coble, 1982](#)).

The stress level depends on the particular relative orientation of the grain boundaries and they can also arise due to thermal expansion mismatch between the alumina grains and grain boundary impurity phases. Once the stress level reaches the strength of the material, microcracking is favorable if the elastic energy is sufficient to create two new surfaces. Then, for grain sizes above a critical one, microcracking and even complete failure of the component might occur.

In the case of the alumina ceramics with small grain sizes ($< 30 \mu\text{m}$) considered here, the thermal stresses usually remain as residual stresses in the sintered materials and are partially responsible for the dependence of properties such as hardness, fracture toughness and strength on grain size because they add to the externally applied stresses (Mussler *et al.*, 1982; Rice *et al.*, 1981; Bueno and Baudín, 2006a; Bueno *et al.*, 2008; García-Prieto and Baudín, 2010).

The residual stresses created in single-phase polycrystalline aluminum oxide and in composites as a result of its constrained anisotropic thermal contraction can be measured with the technique of piezospectroscopy using the fluorescence from trace Cr^{3+} impurities (Ma and Clarke, 1994; de Portu *et al.*, 2006). Ma and Clarke (1984) claimed that over the range of grain sizes from 2–16 μm the residual stresses exhibit a dependence on grain size consistent with the prediction of the Evans-Clarke model of thermal stress relaxation by grain boundary diffusion when cooling from 1400°C.

Green Processing

Due to the high cost of machining hard materials such as alumina following sintering, near net shape fabrication methods, and green machining are preferable routes.

Green machining after isostatic pressing is used routinely to fabricate insulators. The extreme geometrical requirements for hip and knee implants require intermediate and final machining and final polishing and two or three stage sintering.

The packing structure of the green body determines the development of the microstructure during sintering. In order to obtain high quality materials, the control of the shape forming processes is of prime importance. In order to avoid defects in the green state, dispersion of the powders to bring them into the state that allows the use of the different shaping methods available is needed.

The sintering of submicronic and high purity (99.5%) aluminum oxide powders to near full density (99% of theoretical) was first reported by Cahoon and Cristensen (1956). Nowadays, processing of high performance alumina materials with relative densities close to 100% and controlled grain sizes, using high purity sub-micrometric and nanosized powders (average diameters from $< 50 \text{ nm}$ up to $0.6 \mu\text{m}$) commercially available since the late eighties, is possible. In principle, the fine particle size together with the increased particle curvature would increase the driving force for solid state sintering, reducing the required temperature and, consequently, limiting grain growth. However, fine particles have a larger tendency to agglomerate. Agglomeration hinders locally homogeneous densification as explained first by Lange (1984) and confirmed later for finer raw materials by Xue and Chen (1990). Therefore, the agglomerates in the green body evolve towards differential sintered density areas consisting of large particles or particle assemblies surrounded by low density zones. In order to achieve real benefit from the use of sub-micrometric powders, the relationships between sintering temperature, sintered density, and grain size as a function of spatial homogeneity and grain interfaces have to be known and handled.

A number of different approaches such as dry (preferentially cold isostatic) pressing and various wet shaping methods followed by pressureless sintering have turned out to be applicable not only for obtaining small samples with submicrometer microstructures but also for providing larger sintered corundum components with grain sizes of 0.5–0.6 μm at relative densities $> 99.5\%$ (e.g., Krell *et al.*, 2003).

Tapecasting is used for manufacturing thin-film and thick-film insulator substrates for microchips, thick-film devices, and micro-feedthroughs for bionics.

Ceramic injection molding (CIM) has long been considered the most appropriate green processing method for high-precision alumina components. High technology components that require high-dimensional precision and shape complexity fabricated by CIM include cochlear bionic feedthroughs and slurry pump components.

The main drawback of green processing methods such as tape casting and CIM that require organic binders is the debinding stage that, apart from the time and energy consumption involved, has the risk of causing cracking, especially for bulk pieces fabricated by CIM.

In order to obtain ceramic components with appropriate shapes for specific applications, different additive manufacturing (AM), also known as 3D printing (3DP), techniques are being developed. These techniques are based on the fabrication of the components layer-by-layer, which provides shape flexibility with reduced time and cost, allowing increased customization of products. A recent review on AM techniques for ceramics has been published by Hitesh *et al.* (2019). AM are considered niche technologies, in particular, it has been proposed to fabricate alumina complex shapes to be used as packages for sensors or electronics for room or high temperatures. Examples of the versatility of 3D technologies for shaping alumina components are shown in Fig. 5, in which pure alumina parts fabricated by lithography based ceramic manufacturing (Schwentenwein and Homa, 2014) are shown.

Many applications of materials would benefit from properties similar to those of the single-crystals. When sufficiently large single-crystals or specific shapes are needed, texture-engineered ceramics lead to property values ranging between those of single-crystals and isotropic bulk ceramics. For instance, textured alumina materials might present increased transparency (Pringuet *et al.*, 2016). An updated review of textured ceramics was published by Messing *et al.* (2017).

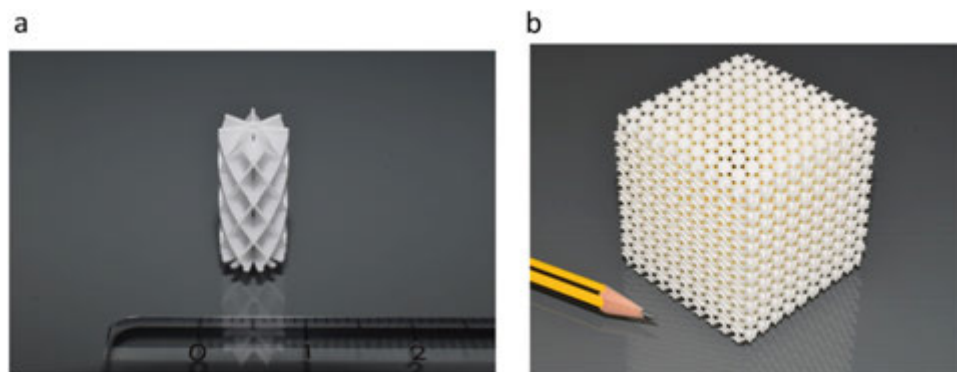


Fig. 5 Examples of the shape versatility of additive manufacturing techniques. Alumina parts produced by lithography based ceramic manufacturing (LCM) and sintered at 1600°C. By kind permission of Lithoz GmbH.

Sintering

The sintering of dense bodies from relatively pure (>99 wt%) alumina powders has received more attention than that of any other single oxide system. In fact, it was considered as a model system for the analysis of conventional sintering of ceramics including the effect of additives, and of the sintering of ceramics under pressure.

Diffusion of the aluminum and oxygen ions is slow at temperatures below 1000°C. However, both ions diffuse at higher temperatures (>1300°C) allowing the solid state sintering of alumina materials which is the most used process to fabricate alumina parts. In general, it is agreed that diffusion of both aluminum and oxygen occurs by a vacancy mechanism. However, suitable doping is needed for oxygen diffusion. Basic parameters for solid state sintering of alumina were already known in the early 1960s (Coble *et al.*, 1984; Phillips and Shiue, 1984; Coble, 1961, 1962; Shaw and Brook, 1986). Several articles reviewing early knowledge on alumina sintering can be found in Kingery (1984). The contributions to two *International Conferences on Science and Technology of Alumina* are published in two special issues of the Journal of the American Ceramic Society (French and Heuer, 1994; Elsässer *et al.*, 2003), the first of the issues dedicated to R.L. Coble, one of the greatest researchers in alumina who set up the basis for the understanding of sintering mechanisms in alumina materials (Handwerker *et al.*, 1994). The issue from 2003 is especially devoted to the advancements in diffusion and grain growth.

Two main processes occur during solid state sintering: shrinkage (or densification) and coarsening. Surface diffusion, grain boundary diffusion and lattice (or volume) diffusion are the main mechanisms for material transfer. Only the last two lead to shrinkage whereas surface diffusion increases the interparticle contacts and decreases the surface curvature, eliminating smaller grains and reducing the sintering activity. Some additives can decrease the temperature needed for these processes to take place.

Nowadays it is generally agreed that densification in pure and relatively fine (≈ 0.5 – $1\ \mu\text{m}$) alumina powders at moderate to high temperature is controlled by lattice diffusion of the Al^{3+} cations, with an activation energy $Q = 580\ \text{kJ/mol}$ (Rahaman, 2008). However, some work, dealing mainly with fine grained powders, found sintering parameters compatible with grain boundary diffusion (Bernard-Granger *et al.*, 2007). Moreover, sintering of nanoparticles presents specific characteristics due to the extremely high initial specific surface area.

Coarsening in alumina is dominated by surface diffusion with activation energies in the range 230–280 kJ/mol. In fact, in most ceramics grain growth is controlled by drag of the attached porosity, the pores moving by surface diffusion of atoms (Harmer and Brook, 1981).

Kinetic field diagrams can be used to identify mechanisms interacting with shrinkage in order to establish improved temperature cycles for alumina sintering (Raether and Schulze, 2009).

In the conventional sintering process, the green body is subjected to the thermal treatment in absence of other effects. Since the early 1960s, existing technology permits fabrication of dense alumina pieces by pressureless sintering with MgO (Phillips and Shiue, 1984; Coble, 1961, 1962; Shaw and Brook, 1986) or liquid forming additives such as CaSiO_3 or SiO_2 (Phillips and Shiue, 1984).

Pure alumina is susceptible to exaggerated grain growth of a fraction of grains during pressureless sintering. As a consequence, wide distributions of grain sizes and isolated pores trapped within the largest grains are present in the microstructure. The additions of small amounts ($\approx 0.5\ \text{wt}\%$) of MgO allow control of alumina grain growth and MgO-doped alumina can undergo normal grain growth to large sizes ($> 20\ \mu\text{m}$) without pore trapping inside the grains.

CaSiO_3 and SiO_2 doped materials undergo liquid-phase sintering which enhances anisotropic grain growth (Rödel and Glaeser, 1990; Song and Coble, 1990; Gavrillov *et al.*, 2003). Small amounts of titania (TiO_2) can be used as agents for enhancement of alumina sintering and grain growth (Powers and Glaeser, 1997; Chi *et al.*, 2003; Bueno and Baudín, 2006b). Calcium additions above the solubility limit also enhance elongated growth of alumina grains (Sánchez Herencia *et al.*, 2000; Jung and Baik, 2003; Altay and Gülgün, 2003).

Further aid for compact densification during sintering is the use of hydrogen or water rich atmospheres to enhance the diffusion of the gas trapped in the closed pores during the final stages of sintering (Coble, 1962). Fast firing of alumina doped with $\approx 200\ \text{ppm}$ of MgO at 1850°C during 10 min led to a dense and fine grained alumina material (Harmer and Brook, 1981).

A sintering schedule including a high temperature short step followed by a long low temperature step was used to reach relatively high density ($\approx 98.8\%$) keeping the size of the grains under $1\text{ }\mu\text{m}$, about 60% lower than that obtained for conventionally sintered alumina of the same density (Bodisova *et al.*, 2007).

In principle, ceramic nanopowders would permit the use of low sintering temperatures thus keeping small grain sizes in the sintered body (Chaim *et al.*, 2008). The main criterion for achieving high levels of sintering is to start with a high density and homogeneous green body, which is not evident when dealing with nanoparticles due to their high specific surface areas. Specific forming methods for very fine powders have been developed, especially for transition aluminas. Nevertheless, the need to produce real nanostructures for improving the mechanical performance of ceramics is limited to very special conditions, and most technical advances require controlled and dense submicrometer microstructures rather than nanostructures. Furthermore, the use of submicronic powders ($\approx 200\text{ nm}$) and the substitution of dry iso-pressing by a colloidal pressing approach to improve the particle coordination of green bodies can lead to a decrease of the sintering temperature by $200\text{--}250^\circ\text{C}$ (Yu and Lange, 2010; Tallon *et al.*, 2010).

When applying pressure during sintering, shrinkage is accelerated by enhanced pressure generated at the contacts between the grains by the external pressure. However, there is no acceleration of the grain growth because there is no increase of pressure gradient across the grain boundary (Coble and Ellis, 1963). Since the early 1960s, existing technology permits fabrication of fine grained dense pieces by hot-pressing of undoped powders (Phillips and Shiue, 1984; Vasilos and Spriggs, 1963).

Pressure assisted sintering of alumina is usually done uniaxially (usually named hot pressing, HP) by applying directly the pressure to the powder using a graphite die. However, special shapes such as femoral heads cannot be fabricated by uniaxial pressing and isostatically applied pressure is necessary. Originally hot pressing and hot isostatic pressing were only used for high added value components because they were rather expensive techniques limited to small scale production. Since the 1990s, alumina-based cutting tool inserts are routinely fabricated using high temperature pressing at reasonable cost (Bocanegra-Bernal, 2004; Whitney, 1994).

Other techniques of thermal treatment are at the R + D stage and alumina is routinely used as model material. Electric current activated/assisted sintering (ECAS) is a growing class of versatile techniques in which mechanical pressure is combined with electric and thermal fields to enhance interparticle bonding and densification. An updated review on these techniques has been published by Sakka and Grasso (2019). In the case of single-phase ceramics, the specific sintering conditions allow the preservation of initial powder grain size or nanostructure and improvement of the bonding strength. In particular, it has been demonstrated that spark plasma sintering (SPS) or, better named electrical field assisted sintering, is useful for the efficient densification of submicronic alumina ceramics.

Microwave sintering is based on the coupling of the material with the electric field, absorbing the electrical energy in its bulk and transforming it into heat. The coupling behavior depends on the dielectric loss factor of the material which, in the case of pure alumina is very low, thus, it strongly depends on doping elements and impurities. A systematic study on microwave sintering of alumina has been reported by Croquesel *et al.* (2016).

Properties of Alumina Materials

As previously stated, most of the work on the development of alumina materials has been devoted to take advantage of the desired properties of the single-crystals by controlling the microstructure. Porosity and low density grain boundary phases lead to density values of alumina materials lower than those of sapphire.

Nowadays, high purity alumina polycrystalline materials with controlled microstructure – grain sizes and shapes, grain boundaries, porosity – for advanced applications are available.

Elastic and Mechanical Properties

Hardness and creep

As described above, alumina single-crystals are among the hardest oxides. Accordingly, alumina materials present high hardness, which is one of its most important properties for the industry. Typical values for fine grained and dense ($\approx 99\%$ of T.D.) aluminas are around 20 GPa . By comparison, hardness of commercial mullite and tetragonal zirconia (YTZP) materials are $10\text{--}11$ and 12 GPa , respectively. Grain boundary amorphous phases and porosity decrease hardness. Cr_2O_3 doping leads to formation of a solid solution with Al_2O_3 at the grain boundaries which increases the hardness of alumina materials (Bradt, 1967; Ghate *et al.*, 1975).

Hardness measurements are carried out by pushing an indenter into the surface of the materials. Therefore, the distribution of stresses under the indenter is complex and deformation under it is not purely plastic, especially in ceramics with residual stresses such as alumina materials in which cracking might occur. The hardness of alumina materials increases as grain size decreases from $5\text{ }\mu\text{m}$ down to $0.5\text{ }\mu\text{m}$. On the one hand, there is an increasing limitation of microplastic deformation by movement of dislocations and twins (Krell, 1995, 1996). On the other hand, large-grain materials tend to present grain boundary microcracking under localized loads with associated lowering of hardness; a decrease of Vickers hardness from 20 to 17 GPa for an increase of average grain size from ≈ 1 to $\approx 5.5\text{ }\mu\text{m}$ has been reported (Bueno and Baudín, 2006a). In the sub-micrometer range the favorable influence of small grain size decreases because of a growing (and counter-acting) influence of the network of grain boundaries. In fact, nanomaterials exhibit an increasing tendency to microplasticity. Consequently, in order to maintain the desirable high hardness of alumina, grain size should be kept above 100 nm .

Alpert *et al.* (1988) measured hardness as a function of temperature (20–1000°C) for different aluminas, including sapphire and polycrystalline aluminas containing different amounts of second phase. For all materials, they reported a steady decrease in hardness with increasing temperature according to the semi-empirical equation:

$$H = H_0 \cdot (1 - T/T_0) \quad (4)$$

With $H_0 \approx 23$ GPa for sapphire and pure aluminas and $H_0 \approx 16$ –18 GPa for aluminas containing grain boundary amorphous phases. This behavior conformed to a thermally activated slip process, limited by Peierls stresses. At low temperature, the hardness of materials with secondary phases was lower than that of pure alumina, consistent with the softening of the boundary phases. At high temperatures ($\geq 800^\circ\text{C}$) hardness values of all materials were similar, indicating that deformation was controlled predominantly by the Al_2O_3 .

Polycrystalline aluminas experience permanent plastic deformation under load at high temperature (creep). As in the case of other properties, the creep behavior of alumina has been studied more extensively than that of any other crystalline solid, ceramic or metal. Classical studies proposed diffusional creep as the rate-controlling process. A recent review on creep data for over 40 different aluminas (Ruano *et al.*, 2003) concluded that the dominant deformation mechanism in creep of fine-grained alumina is grain boundary sliding (GBS) accommodated by slip. The metallographic evidence for this mechanism is that the initially equiaxed alumina grains remain equiaxed even after extensive deformation, which is incompatible with diffusional creep. The slip accommodation process is related to the sequential steps of dislocation glide and climb. Pure and dense aluminas present high resistance to creep under relatively high stresses (> 20 MPa) up to temperatures over 1200°C .

Elastic properties

Uncracked fine grained alumina materials under load present the typical behavior of brittle materials which is characterized by the absence of significant plastic deformation being linear elastic up to the point of fracture. The relationship between strain and stress is determined by the elastic properties: Youngs modulus, shear modulus and Poissons ratio, from which only two are independent. The elastic properties are determined by porosity and secondary phases. Typical room temperature values of the elastic properties of fine grained and dense alumina materials fabricated by conventional sintering are summarized in Table 3.

Corresponding with the high stiffness of single-crystal $\alpha\text{-Al}_2\text{O}_3$, elastic properties of polycrystalline alumina materials are high compared with other oxides. By comparison, Youngs modulus of ZrO_2 stabilized with 3 mol% of Y_2O_3 (YTZP; Gurauskis *et al.*, 2006) and mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$; Burgos-Montes *et al.*, 2010) are 200–230 GPa.

For uncracked materials, Youngs modulus decreases with density but it is not affected by grain size (Table 3). These observations are common for different alumina materials. Reported Young's modulus values for pure ($> 99\%$), fine grained (2–6 μm) and dense ($\geq 98\%$ of theoretical) alumina ceramics range from 380 to 410 GPa for conventionally sintered materials and up to 400–450 GPa for the optimized hot-pressed and hot-isostatically pressed aluminas. The elastic properties are determined by porosity. As reviewed by Rice (1998) for a number of oxides and, in particular, for alumina, the log-log plot of the relative Youngs modulus, E/E_0 , versus volume fraction porosity, P , up to around 60%, gives a straight line the slope of which, b , depends on pore geometry. The simplest equation that was initially fitted empirically (Spriggs, 1961), is given by:

$$E = E_0 \cdot \exp(-bP) \quad (5)$$

The same kind of relationship is found for the shear modulus. Such relationships are in agreement with the minimum solids area (MSA) models for different pore geometries.

Values of b for E , and the shear modulus, G , reviewed by Rice are shown in Table 4. The value of b is associated with a given fabrication technique because it is determined by the geometry of the pores and the distribution of the continuous phase and porosity.

Youngs modulus of alumina materials decreases slightly with temperature up to temperatures between 900 – 1200°C , depending on the presence and nature of grain boundary phases. Above these temperatures, irreversible plastic deformation starts due to grain boundary sliding which, in most cases, is due to viscous flow of the boundary phase. For the high purity material (data are plotted in Fig. 2), the decrease is slight up to 1200°C , following the classical relationship for common oxides: decrease $\approx 1\%$ every 100°C increase, between room temperature and the softening temperature (Watchman and Lam, 1959; Watchman *et al.*, 2009).

Table 3 Typical room temperature values of elastic properties and strength of fine grained and dense polycrystalline alumina produced by conventional sintering

Reference	Average grain size (SD) μm	Density (SD) % of theoretical	Youngs modulus (SD) GPa	Shear modulus (SD) GPa	Poissons ratio	Strength (SD), 4pb MPa
^a	1 (0.7)	98.8 (0.5)	405 (5)	126 (1)	0.223 (0.004)	480 (32)
^b	3.5 (0.3)	98.1 (0.3)	379 (8)	–	–	456 (29)
	5.5 (0.6)	98.1 (0.5)	375 (6)	–	–	349 (31)

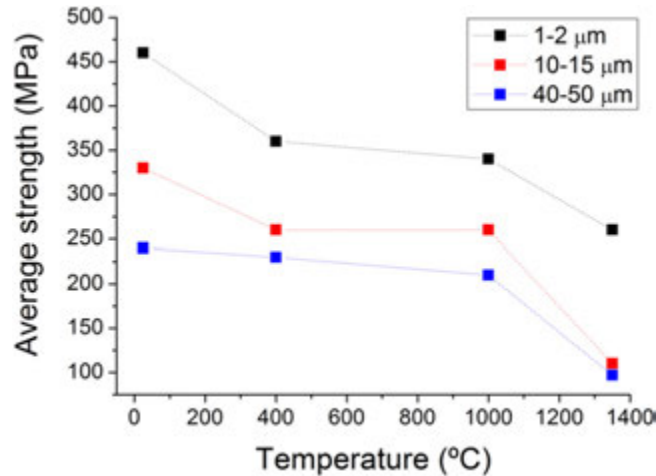
^aBurgos-Montes *et al.* (2010).

^bBueno *et al.* (2008).

Table 4 Values of the parameter b (Eq. (5)) for elastic properties and strength for oxides fabricated using different processing methods

Property	Processing method			
	Extrusion	Uniaxial pressing	Isostatic pressing	Hot pressing
Youngs modulus, E	2.3	3.6 ± 0.8	4.0 ± 1.2	4.5 ± 0.7
Shear modulus, G	2.2	3.2 ± 0.9	3.9 ± 1.3	4.3 ± 0.6
Strength, σ_f	5.1 ± 2.3	4.1 ± 1.1		5.8 ± 1.5

Note: Rice, R.W., 1998. Porosity of Ceramics, vol. 12. USA: Marcel Dekker Inc.

**Fig. 6** Average strength of polycrystalline aluminas of the indicated grain sizes as a function of temperature. (Spriggs *et al.*, 1964).

Fracture

Brittle behavior is characteristic of alumina because the stress level at which fracture starts is determined by the presence of defects which act as stress concentrators leading to catastrophic failure in the material. Thus, the strength of alumina materials is an extremely variable property, which depends on the distribution of defects present at the surface and internally. Descriptions of brittle fracture can be found in different text books (e.g., Jayatilaka, 1979), a review of structural ceramics with specific examples dealing with alumina materials is published in Bueno and Baudin (2007).

Values of strength of polycrystalline aluminas are lower than those of sapphire and are determined by the material defects as well as the surface state and testing conditions. Typical room temperature values of four-point bending strength of fine grained and dense alumina materials fabricated by conventional sintering are summarized in Table 3.

Apart from specific surface or internal flaws introduced in the material during processing (intrinsic flaws) or machining (extrinsic flaws), grain boundaries are weak microstructural features due to lower density of atoms, concentration of impurities and residual stresses that, depending on their sign, might add to the externally applied stress. Therefore, strength of alumina materials decreases as grain size increases. Fig. 6 summarizes the classical work by Spriggs *et al.* (1964) on the variation of strength with grain size for high purity (99.9%) and dense (98% of T.D.) aluminas processed by hot pressing.

Pores are one of the most characteristic intrinsic defects. Strength values of alumina materials, σ_f , follow the same kind of relationship with porosity, P , and strength of the fully dense material, σ_{f0} , as with Youngs modulus (Eq. (5)), as expected from the MSA models:

$$\sigma_f = \sigma_{f0} \cdot \exp(-bP) \quad (6)$$

Values of b for strength of materials processed differently are given in Table 4. Ceramics do not have uniquely defined failure strengths. Instead a range of strength values are found because of the presence of strength-controlling defects of different sizes which follow a probabilistic distribution proposed by Weibull. Such a distribution implies that the measured values are dependent on the effective volume of specimen subjected to stress. Smaller specimens give higher values - this can be visualized by the fact that the presence of larger defects is less probable. Therefore, testing of small specimens such as microcantilever beams gives strength values determined by the intrinsic microstructural parameters. Microcantilever beams of alumina poly-crystals gave strength values about 5 GPa and presented intergranular fracture usually initiated at the grain boundaries (Yahya and Todd, 2012).

When the material was doped with 0.01% C, the fracture mode changed to transgranular and strength values (≈ 8 GPa) were almost double those obtained for pure alumina.

As occurred with the elastic properties, strength values experience also slight decreases with temperature up to a certain point from which a sharp decrease occurs (Fig. 6). When the material contains a significant amount of residual glass, strength determined at relatively low deformation rates might increase near the glass transition temperature (Gitzen, 1970).

A wide range of fracture energy and fracture toughness values of alumina materials are observed depending on the materials and their processing – composition, grain size and porosity – and also testing technique. Since the initial systematic studies done by Claussen *et al.* (1982), the dependence on grain size and test technique in the case of high purity aluminas has been partially attributed to toughening mechanisms. Toughening mechanisms identified in alumina are crack deflection, microcracking, crack bridging and, for extremely large grain sizes, crack branching. Such mechanisms are mainly due to the presence of residual stresses and therefore, highly dependent on grain size. This is revealed by the greater roughness of the fracture surfaces of the larger grain size aluminas. Table 5 summarizes toughness parameters, determined in flexure tests, for dense alumina materials with relatively small grain sizes. For fine grained materials ($d_{50} \approx 2\text{--}8\ \mu\text{m}$) K_{IC} values from 2 to 6 MPa m^{1/2}, K_{I0} values around 2–2.5 MPa m^{1/2} and specific fracture energy values from 10 to 20 J/m² are found. All K_{IC} values are higher than those reported for alumina single-crystals. For similar testing geometries, values determined using semistable and stable fracture tests are lower ($\approx 35\%$) than those

Table 5 Toughness parameters for polycrystalline aluminas determined in flexure tests. D: density, G_A : average grain size, γ : specific fracture energy ($2\gamma = G$), ρ : notch radius

Reference	D (% of T.D.)	G_A (μm)	K_{IC} (MPa m ^{1/2})	G_{IC} (J/m ²)	γ (J/m ²)
Palmero <i>et al.</i> (2014)	> 3.90	< 7	5.5 (0.2) ^a , $K_{I0} = 2.5$ (0.2) ^a Air		
Bueno <i>et al.</i> (2008)	98.1 (0.3)	3.5 (0.3)	2.9; 2.8 ^b	20.4; 19.6 ^b	10.5; 9.8 ^b
	98.1 (0.5)	5.5 (0.6)	3.2 (0.1) ^c	26.2 (0.7) ^c	20.1 (2.0) ^c
García-Prieto and Baudín (2010)	98.1 (0.3)	3.5 (0.3)	2.5 (0.2) ^c	16.4 (2.3) ^c	7.0 (0.3) ^c
Rahaman <i>et al.</i> (2007)	> 3.97	1–5	4–5, $K_{I0} = 2.0\text{--}2.5$ Air		
de Aza <i>et al.</i> (2002)	~ 99	1.7	4.2 (0.2) ^a , $K_{I0} = 2.5$ (0.2) ^a Air		
Ebrahimi <i>et al.</i> (2000)	99.2	1.9	4.3 ^a , $K_{I0} = 3.5^a$ Air, $K_{I0} = 4^a$ Silicone oil		
		4.8	4.3 ^a , $K_{I0} = 3.7^a$ Air		
	99.5	12.7	4.3 ^a , $K_{I0} = 4.1^a$ Air		
Sbaizero <i>et al.</i> (1998)	99	3	$\sim 3^b$		20 ^b
Damani <i>et al.</i> (1996)	Low	10	2.8 ^d $\rho < 9\ \mu\text{m}$		
			3.0 ^d $\rho \sim 25\ \mu\text{m}$		
			3.5 ^d $\rho \sim 67\ \mu\text{m}$		
			3.9 ^d $\rho \sim 92\ \mu\text{m}$		
Mai and Lawn (1987)		50			20 ^e
Mussler <i>et al.</i> (1982)	> 95	< 5	4–6 ^d $\rho = 40\text{--}70\ \mu\text{m}$		
		6–30	4–4.5 ^d $\rho = 40\text{--}70\ \mu\text{m}$		
	< 95	2–50	3.8–5.8 ^{b,f}		
Claussen <i>et al.</i> (1982)		1			50 ^d
		20			20 ^d
Rice <i>et al.</i> (1981)		3.5–20			27–36 ^d
					33–40 ^b
					38–47 ^a
					38–48 ^e
					35–70 ^e
Freiman <i>et al.</i> (1973)		4	3.2; 3.7 ^{a,e}		17; 19 ^{a,e}
		7	3.0		20
		8	3.7		18
		20	4.7; 4.9		32; 35; 44
		35	4.1		22

^aDouble torsion.

^bSingle edge vee-notched bending. Unstable/Semistable fracture.

^cSingle edge vee-notched bending. Stable fracture.

^dSingle edge notched beam. Unstable fracture.

^eDouble cantilever beam

^fIndentation/strength in bending

reported for aluminas with similar grain sizes determined from unstable fracture tests because unstable crack extension implies additional energy consumption as compared to the stable one. Also larger notch radius leads to higher K_{IC} . It is well known that double torsion tests always give the highest values as compared to other methods, as observed for alumina.

There are differences between the values of the crack-tip toughness, K_{I0} , reported. For similar testing conditions, this fact can be attributed to differences in fracture mode of aluminas with different microstructures, as total toughness would be the sum of contributions of intergranular grain boundary fracture, cleavage across the easy fracture planes of the single-crystals and the increase in fracture surface due to deflection (Seidel and Rödel, 1997). In fact, reported K_{I0} values determined in air using microcantilever beams notched by focused ion beam (FIB) for individual alumina grain boundaries ($K_{I0} = 0.7 \pm 0.2 \text{ MPa m}^{1/2}$) and grain cleavage ($K_{I0} = 1.5 \pm 0.3 \text{ MPa m}^{1/2}$) are lower than those shown in Table 4 for polycrystalline materials (Norton et al., 2015).

A significant amount of transgranular fracture (20%), independent of the grain size of the material, was reported by Seidel and Rödel (1997) whereas only the largest grains ($> 5 \mu\text{m}$) presented transgranular fracture in the fine-grained alumina tested by Bueno et al. (2008). Additionally, K_{I0} depends on the testing environment because of the possibility of slow crack growth (SCG) in polycrystalline alumina ceramics, which was first reported by Freiman et al. (1973). The basic mechanism for SCG is the stress assisted corrosion by environmental species (especially water) at the crack tip bonds. The group of Chevalier, from INSA (Lyon), has extensively studied the phenomenon of SCG in high purity alumina ceramics used for total hip arthroplasty (Chevalier and Gremillard, 2008; de Aza et al., 2002; Palmero et al., 2014) and found that it is an extremely slow process in air, with crack growth velocities around 10^{-10} m/s for K_I values slightly above K_{I0} ($\approx 2.5 \text{ MPa m}^{1/2}$, Table 5).

As seen in Table 5, values of specific fracture energy for fine grained ($\approx 10 \text{ J/m}^2$) and coarse grained ($\approx 20 \text{ J/m}^2$) materials are both higher than that reported by Wiederhorn et al. (Wiederhorn, 1969; Wiederhorn et al., 1973) for the preferred cleavage plane in alumina single-crystals at room temperature (6 J/m^2). Even in the absence of significant toughening mechanisms, the fracture energies of poly-crystals are higher than those for single-crystals due to the contribution of intergranular fracture, in the same way as crack tip toughness values in poly-crystals are higher than those at the easy cleavage planes.

The similarity between the G_{IC} and 2γ for fine grained alumina (García-Prieto and Baudín, 2010) reveal the absence of significant crack-size dependent toughening phenomena. On the contrary, for the coarse grained alumina, 2γ is much higher ($\approx 55\%$) than G_{IC} revealing toughening processes (Bueno et al., 2008).

The main drawback of the early initial alumina materials was their brittleness and associated lack of strength reliability. The mechanical behavior of alumina materials has constantly improved since the 1960s. The relationship between the fracture strength, σ_f , the critical stress intensity factor in mode I, K_{IC} , and the defect size, a , is given by the fracture criterion:

$$\sigma_f = \frac{K_{IC}}{Y\sqrt{a}} \quad (7)$$

where Y is a geometric constant. Taking into account this relationship, the two possible ways for improving the mechanical behavior are the control (minimization) of defect size and shape distributions and the increase of toughness.

Regarding the control of the distribution of defects, efforts have been directed towards the decrease of the sizes of the microstructural parameters and the homogenization of the microstructure. Actions have included the increase of the purity and the homogenization and decrease of the particle size of the raw materials, the addition of dopants to control grain size as well as the use of advanced sintering techniques. The development of alumina materials for metal machining and seals as well as for biomedical and optical applications has been the driver of such improvements.

The adequate manipulation of the crystalline thermal expansion anisotropy can lead to increased toughness due to crack deflection, crack branching and microcracking during the fracture process acting as toughening mechanisms.

Wear

Wear is the process of removal of surface material through contact with another moving phase or material. It involves a number of different processes: abrasion, sliding, erosion, cutting, and grinding. There is no single property or test that can predict the response to wear of materials under any environment, this response being the result of a combination of material properties and environment. In general, wear resistance requires high hardness, strength and toughness together with chemical inertness in the considered environment. When lubricants or intermittent wear processes are involved, the material should be resistant to thermal shock. In addition, specific microstructural properties are required to minimize the volume loss by wear. High porosity makes a ceramic friable and, thus, low porosity ceramics are required. Intergranular fracture is dominant in the case of anisotropic materials such as alumina and, thus, small grain size is also needed to minimize volume loss. Also, large grains detached from the alumina surface might contribute to third body wear. In the case of sliding wear, the coefficient of friction between the surfaces in contact should be as low as possible.

Wear rates and wear mechanisms are affected, not only by the material characteristics, but also by the severity of the surface contacts. Under sliding wear pure alumina materials experience sharp transitions between initial mild wear and severe wear (Rainforth, 2004). Mild wear is characterized by material removal by plastic grooving and accumulation of subsurface damage. Damage accumulation leads to the increase of internal stresses resulting in grain boundary cracking and grain pull-out, which is known as severe wear. Transition between mild and severe wear occurs after longer times when lower loads and aluminas with smaller grain sizes are involved.

As already described, the crystal structure of alumina is formed by planes of hexagonal close packed oxygen ions that leave octahedrally coordinated sites which are occupied by Al^{3+} ions. As only two thirds of the sites are filled by Al^{3+} , there are available unsaturated oxygen ions in the structure. In wet environments, alumina materials are capable of chemisorption of water molecules, or carboxylic acid molecules through van der Waals bonding. These bonds are stable up to 200°C and create protective layers that reduce the coefficient of friction and, consequently, the sliding wear of alumina materials (Baudín, 2014b; Rainforth, 2004). This represents a significant advantage for alumina bearings or pump components in wet environments.

As observed by Yahya and Todd (2012), the addition of trace amounts of carbon to alumina changes the fracture mode to transgranular and, as a consequence, the resistance to abrasion wear increases by a factor of 2.7 compared with pure alumina of approximately the same grain size.

Thermal Properties

The thermal conductivity of polycrystalline alumina is determined by the high thermal conductivity of sapphire and modified by porosity and impurities. These latter are responsible for the nature and distribution of the second phases and, therefore, for the characteristics of the grain boundaries. The thermal conductivity of alumina is high for an oxide. By comparison, thermal conductivity of dense mullite between room temperature and 400°C is lower than $8 \text{ W}(\text{mK})^{-1}$ while for alumina it ranges from $\approx 30 \text{ W}(\text{mK})^{-1}$ at room temperature to $\approx 15 \text{ W}(\text{mK})^{-1}$ at 400°C (Mezquita *et al.*, 2001). Thermal conductivity decreases as the impurity content increases. Examples of values of room temperature values for commercial aluminas in $\text{W}(\text{mK})^{-1}$ are: 33.0 for extremely pure alumina (min 99.9%) of density 3.92 g/cm^3 , 27.5 for a 98.5% purity alumina of density 3.80 g/cm^3 , and 16.0 for a 85% alumina of density 3.42 g/cm^3 (See Relevant Websites section).

The effect of the anisotropy in thermal expansion of sapphire is not reflected in the thermal expansion of polycrystalline aluminas unless the microstructure is textured. The thermal expansion coefficient is intermediate for an oxide material. By comparison, the average thermal expansion between $25\text{--}800^\circ\text{C}$ for mullite and alumina (Burgos-Montes *et al.*, 2010) are: ≈ 4.1 and $8.4 \times 10^{-6} \text{ K}^{-1}$, respectively, while for magnesia materials it is $\approx 13.5 \times 10^{-6} \text{ K}^{-1}$ (Lee and Rainforth, 1994). The thermal expansion coefficient is mainly determined by the major phase, thus, it is not affected by porosity or the presence of minor secondary phases.

Functional Properties

Electrical

The first commercial uses of alumina ceramics were in electrical applications. Research on electrical properties of alumina was initiated in the 1930s; since then, a wide range of different results have been reported. Updated reviews on electrical properties of alumina can be found in Doremus (2008) and Ruy (2019).

Alumina, as with most ceramics, is an ionic conductor at intermediate temperatures, but shows no ionic conduction at room temperature. Electron conduction occurs in alumina at temperatures over 1200°C .

Alumina materials are well known because of their high electrical resistivity at room temperature which corresponds with the high electrical resistivity of sapphire. It decreases sharply with decreasing grain size, being orders of magnitude lower for polycrystalline alumina than for sapphire (Table 2). Variation of this property with impurities is different depending on their nature.

Even low alumina grades (85% purity) present high direct current resistivity, $\approx 10^{12} \Omega \cdot \text{m}$. Other ceramics with such high resistivity are AlN, BeO, BN, and $\text{BaAl}_2\text{Si}_2\text{O}_8$ (celsian) (Table 2). However, they present drawbacks as compared to alumina: BeO is expensive and toxic, AlN and BN are expensive and, in order to attain high density, have to be hot pressed in controlled atmosphere, and $\text{BaAl}_2\text{Si}_2\text{O}_8$ is a feldspar mineral that is not widely available with controlled properties.

A dopant is a trace impurity added to a crystal lattice to alter its properties. In semiconductor terminology, dopants are known as “acceptors” (electron acceptors) or “donors” (electron donors). When Al, with three valence electrons, is doped with Ti, with four valence electrons, Ti becomes a “donor” dopant and forms a net negative charge in the alumina lattice, “n-type” region, impeding ionic conductivity. Mg, with two valence ions, is an “acceptor” dopant and forms a net positive charge in the alumina lattice, “p-type” region, enhancing ionic conductivity. For instance, doping pure single-crystal alumina with 430 ppm Ti enhanced its resistivity by four orders of magnitude, while doping it with 10 ppm Mg reduced its resistivity by two orders of magnitude (Ruy, 2019). In the same way, Na and the alkali metals reduce resistivity even more strongly than divalent metals such as Mg.

The other electric property of interest of alumina is the high dielectric loss or AC loss tangent, $\tan(\delta)$. This property measures the efficiency of an insulator in high-frequency electromagnetic fields. Low values of this property are necessary in high-frequency applications such as thick-film microelectronics in microwave technology and microwave-transparent windows in microwave generators. Alumina presents very low loss tangent as compared to other electrical ceramics (Table 2). As for optimum electrical resistivity, the alkali content is critical for the loss tangent and, thus, high purity aluminas are needed.

Optical

As a consequence of the properties of $\alpha\text{-Al}_2\text{O}_3$ single-crystals, alumina ceramics might be transparent in different wavelength ranges. Transparent polycrystalline ceramics such as alumina that possess a unique combination of properties – high-temperature dimensional and chemical stability, hardness, strength, and corrosion resistance – are in great demand in high-tech industries,

such as nanophotonics, opto-electronics, (laser technology, radiative heat transfer), aerospace engineering, and safety systems (transparent armor). The main advantages of ceramics over single-crystals are: low production costs, compositional flexibility, possibility of fabricating articles with different shapes (including complex geometries), and large dimensional sizes.

Detailed analysis of the effect of different microstructural and external parameters on the optical behavior of polycrystalline ceramics can be found in the works of [Krell et al. \(2009\)](#) and [Kachaev et al. \(2016\)](#).

Transparent ceramics have a number of different absorbing and scattering centers, such as grain boundaries, impurities, different phases, porosity, oxygen vacancies, and birefringence for noncubic materials such as alumina. Porosity is the most degrading factor for transparency of ceramics. Residual grain boundary phases due to impurities whose refractive index differs from that of the alumina grains reduce the transparency as a result of light scattering. Also, due to the anisotropy of the refractive index of sapphire, the size of the crystals strongly affects the scattering of light. External factors such as the thickness of the component and the quality of the surface treatment also affect transparency. The development of transparent polycrystalline aluminas has required the availability of pure raw materials and the establishment of processing methods to reach high purity and high density fine grain materials. Processing of polycrystalline aluminas for optical applications has been reviewed by [Baudín \(2014a\)](#).

In principle, full density to over 99.9999% of theoretical and grain size refinement below 100 nm will change the dominant light-scattering mechanism in alumina, allowing the material to become transparent. However, to reach such a microstructure would require the use of nanosized powders that tend to agglomerate and experience very large shrinkage during sintering, and even the smallest defect would have to be avoided during the green processing ([Messing and Stevenson, 2008](#)). Optimized green processing methods together with special sintering procedures such as HIP, HP, SPS and high pressure SPS, or combinations of pressureless sintering or vacuum sintering followed by HP or HIP, have allowed the production of materials with submicrometric grain sizes (0.34–0.60 μm) and porosities lower than 0.05% with in-line transmissions in the range 50%–79% depending on processing and surface preparation (e.g., [Krell and Klimke, 2006](#); [Mata-Osoro et al., 2012](#); [Drdlikova et al., 2019](#); [Ratzker et al., 2019](#)). High transmittance is also obtained in alumina with a highly-oriented (104) microstructure processed using an A-plane single-crystal sapphire as template ([Yanga et al., 2019](#)).

Present and Future of Alumina

As has been described throughout, alumina materials with controlled composition and microstructure have unique combinations of properties retained at high temperature – hardness and stiffness, wear resistance, chemical inertness and associated corrosion resistance and sufficient strength; they also present excellent electrical insulating properties and, when fully dense, they can be translucent and even transparent depending on grain size and porosity. The chemical inertness of alumina also allows its use in biological environments, biocompatibility being one of the most valuable properties of alumina.

In addition to such a unique set of properties, alumina raw materials are available at relatively low cost, even the high grade powders with controlled purity and particle characteristics. Moreover, alumina components with wide ranges of shapes and sizes and controlled microstructure can be fabricated by pressureless sintering.

As described in the introduction, widespread commercial applications of alumina commenced from the 1930s. Many of the uses that were incipient at that time are now routine ones and have extended to a wide range of applications. This is the case for wear resistant parts in different industries – mining, textile, food and beverage, papermaking, wood – and of components in corrosive industrial environments – crucibles, tubes, pumps, seals, etc. In particular, alumina and alumina-based tool tips for metal machining are extensively used since the second half of the 20th century. Such applications, that are possible due to the combination high wear and corrosion resistances of alumina and at relatively low cost, were already widespread when [Doremus \(2008\)](#) stated: “These predictions are speculative, but the most promising new applications of alumina will probably be in electronic circuits, optical components and biomaterials”. Nowadays, alumina is a fundamental material for advanced optical, electronic and biological applications in technologies that were emerging at the beginning of the 21st century.

Alumina is the ideal substitute for glass in harsh environments due to its optical properties, together with dimensional stability, chemical inertness and resistance to wear. Optimization of the microstructures - by reducing the grain sizes to the sub-micrometric scale and further density increases – has permitted the evolution from the translucent aluminas used in high pressure sodium vapor lamp tubes to the transparent ones to be used in lasers, health care, armor, high pressure metal halide lamps and electrical devices.

The combination of high electrical resistivity and low dielectric loss with other properties such as dimensional and chemical stability up to 1700°C, high corrosion resistance, sufficient strength and low cost relative to other ceramics with comparable electrical resistivity, makes alumina the most used ceramic as an insulator, as reviewed by [Ruy \(2019\)](#). The first electrical use of alumina was in macro-insulators: spark plug insulators and power transmission systems. Nowadays, alumina is used as a major constituent of insulating substrates in microelectronics because of its dimensional stability and relatively high thermal conductivity together with thermal expansion coefficient similar to Si. Such application started in the 1980s and experienced a dramatic increase together with the rise of the electronics industry. Alumina is also used as an electrical insulating feedthrough seal in advanced electrical devices where dimensional and chemical stability are required. Regarding insulating applications, it is important to highlight that the biological compatibility and inertness of alumina has allowed the development of a whole family of bionic implants – pacemakers, eye, ear implants ... – with alumina feedthroughs. This industry that started in the second half of the 1980s is now a \$25000 million industry in which alumina is the only material for feedthroughs ([Ruy, 2019](#)).

The high wear resistance of alumina and its inertness that makes the alumina wear particles non-toxic are the main drivers for the success of alumina bearings for arthroplasty since the turn of the 21st century, when ceramic arthroplasty was considered only

as a research activity. Currently, the total number of hip bearing components implanted annually in the world is approaching one million, with 55% of them involving alumina (40% alumina-polyethylene and 15% alumina-alumina (Ruy, 2019)).

The requirements and evolution of biomaterials and, in particular, ceramics for arthroplasty have been analyzed in several reviews (Chevalier and Gremillard, 2008; Huet *et al.*, 2011; Hu and Yoon, 2018; Ruy, 2019).

The alumina hip bearings introduced in the 1970s lacked reliability due to unexpected fracture. Processing improvements together with microstructural design has led to alumina materials with high strength and hardness, decreasing dramatically the incidence of fracture. Fig. 7 shows ceramic bearings commercialized by a leading producer of ceramic bearings for arthroplasty, CeramTec, and their microstructures are shown in Fig. 8. Values of the technological properties are summarized in Table 6. For single-phase alumina,

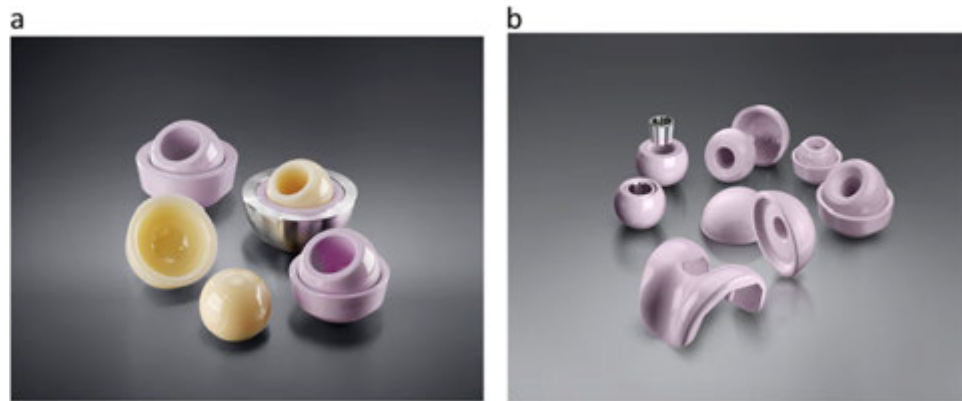


Fig. 7 Ceramic bearings for arthroplasty manufactured by CeramTec GmbH. With kind permission of CeramTec under the creative Commons License CC BY-ND 3.0. (a) Bearings for total hip arthroplasty (THA). Pure alumina (ivory) and ZTA (pink) hip femoral heads and acetabular cups. Monoblock acetabular cups of alumina and ZTA and a modular cup with ZTA liner and stainless steel (gray) shell are shown. (b) ZTA bearings for arthroplasty. Femoral heads and cups for THA, half sphere for hip resurfacing and a femoral replacement for knee arthroplasty are shown.

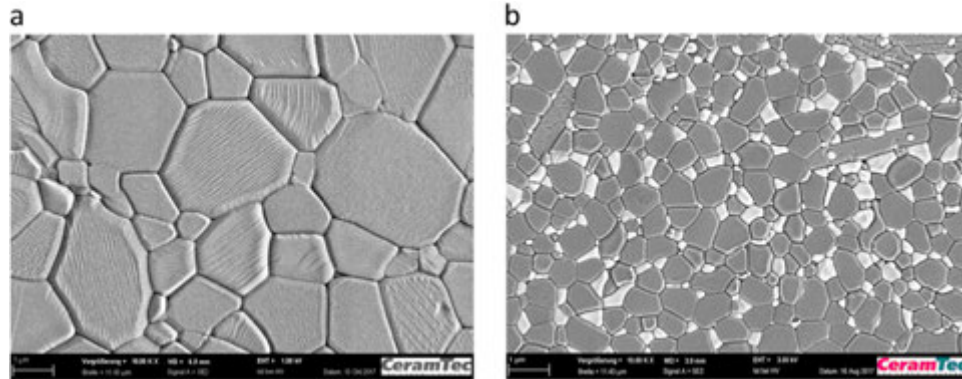


Fig. 8 Microstructure of ceramic bearings for arthroplasty manufactured by CeramTec GmbH. Scanning electron microscopy of polished and thermally etched surfaces. With kind permission of CeramTec under the creative Commons License CC BY-ND 3.0. (a) BIOLOX(R) forte. Pure alumina material (b) BIOLOX(R) delta. ZTA. Zirconia (white) toughened alumina (gray).

Table 6 Evolution of alumina-based materials for arthroplasty manufactured by CeramTec GmbH

Material	Year	Fracture toughness ($\text{MPa} \cdot \text{m}^{1/2}$)	Average strength (MPa)	Hardness (GPa)	Failure rate of hip bearings (%)
Alumina	1970s	3.5	> 300	17.7	
BioloX	≥ 1974	4	400	20	
BioloX forte	≥ 1995	4.5	≈ 630	20	0.022 ^a
BioloX delta (ZTA)	> 2003	6.5	≈ 1390	19	< 0.001 ^a

^ahttps://www.ceramtec.com/files/mt_bioloX_forte_delta_comparison_en.pdf.

Note: Piconi, C., Porporati, A.A., 2016. Bioinert ceramics: Zirconia and alumina. In: Antoniac, I. (Ed.), Handbook of Bioceramics and Biocomposites. Cham: Springer. doi:10.1007/978-3-319-12460-5_4.

the improvement of the microstructure from the initial materials to that of the third generation ones (Fig. 8(a)) led to higher strength and hardness values and associated dramatic decrease in the failure rate. The high strength of the zirconia toughened alumina (ZTA) material is primarily due to transformation toughening by zirconia particles. Also, ≈ 3 vol% of strontium aluminate platelets (up to 3 μm in length) nucleated in situ provide toughening by crack bridging and crack deflection. Even though this material has slightly lower hardness, the strength increase is sufficient to assure high wear resistance. The failure rate of ZTA hip bearings is extremely low. The extremely good properties of ZTA allow its use in more demanding applications such as knee replacement.

As follows from what has been described and discussed here, there is currently a variety of $\alpha\text{-Al}_2\text{O}_3$ materials used in a wide range of advanced high technology applications. Such materials, that possess unique combinations of properties in the materials world, have been possible by taking advantage of the intrinsic properties of $\alpha\text{-Al}_2\text{O}_3$ single-crystal by manipulating and controlling the final microstructure. Most probably, further research will open up still unimagined possibilities for alumina materials.

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References

- Alpert, C.P., Chan, H.M., Bennison, S.J., Lawn, B., 1988. Temperature dependence of hardness of alumina-based ceramics. *Journal of the American Ceramic Society* 71, C-371–C-373.
- Altay, A., Gülgün, M.A., 2003. Microstructural evolution of calcium-doped α -alumina. *Journal of the American Ceramic Society* 86, 623–629.
- Baudin, C., 2014a. Processing of alumina and corresponding composites. In: Sarin, V.K. (Ed.), *Comprehensive Hard Materials*, Volume 2: Ceramics. The Netherlands: Elsevier, pp. 31–72. [L. Llanes & D. Mari (Vol. Eds.)].
- Baudin, C., Tricoteaux, A., Joire, H., 2014b. Improved resistance of alumina to mild wear by aluminium titanate additions. *Journal of the European Ceramic Society* 34, 69–80.
- Bayer, P.D., Cooper, R.E., 1969. The tensile strength of sapphire whiskers at elevated temperatures. *Journal of Materials Science* 4, 15–20.
- Bernard-Granger, G., Guizard, C., Addad, A., 2007. Sintering of ultrapure α -alumina powder; I. Densification, grain growth and sintering path. *Journal of Materials Science* 42, 6316–6324.
- Blendell, J.E., Coble, R.L., 1982. Measurement of stress due to thermal expansion anisotropy in Al_2O_3 . *Journal of the American Ceramic Society* 65, 174–178.
- Bocanegra-Bernal, M.H., 2004. Review. Hot Isostatic Pressing (HIP) technology and its applications to metals and ceramics. *Journal of Materials Science* 39, 6399–6420.
- Bodisova, K., Sajgalik, P., Galusek, D., Svancarek, P., 2007. Two-stage sintering of alumina with submicrometer grain size. *Journal of the American Ceramic Society* 90, 330–332.
- Bowen, P., Carry, C., 2002. From powders to sintered pieces: forming, transformations and sintering of nanostructured ceramic oxides. *Powder Technology* 128, 248–255.
- Bradt, R.C., Scott, W.D., 1990. Mechanical properties of alumina. In: Hart, L.D. (Ed.), *Alumina Chemicals Science and Technology Handbook*. USA: The American Ceramic Society Inc, pp. 23–39.
- Bradt, R.C., 1967. Cr_2O_3 solid solution hardening of Al_2O_3 . *Journal of the American Ceramic Society* 50, 54–55.
- Brewer, L., 1953. The thermodynamic properties of the oxides and their vaporization processes. *Chemical Reviews* 52, 1–75.
- Brewer, L., Searcy, A.W., 1951. The gaseous species of the $\text{Al-Al}_2\text{O}_3$ system. *Journal of the American Chemical Society* 73, 5308–5314.
- Briggs, J., 2007. *Engineering ceramics in Europe and the USA*. Worcester UK: Menwith Wood.
- Brook, R., 1991. *Concise Encyclopedia of Advanced Ceramic Materials*. Oxford, GB: Pergamon Press.
- Bueno, S., Baudin, C., 2006a. Instrumented Vickers microindentation of alumina-based materials. *Journal of Materials Research* 21, 161–173.
- Bueno, S., Baudin, C., 2006b. In situ developed laminates with large microstructural differences between layers of similar composition. *Journal of Materials Science* 21, 3695–3700.
- Bueno, S., Baudin, C., 2007. Mechanical behavior of structural ceramics. *Boletín de la Sociedad Española de Cerámica y Vidrio* 46, 103–118.
- Bueno, S., Berger, M.H., Moreno, R., Baudin, C., 2008. Fracture behaviour of microcrack-free alumina–aluminium titanate ceramics with second phase nanoparticles at alumina grain boundaries. *Journal of the European Ceramic Society* 28, 1961–1971.
- Burgos-Montes, O., Moreno, R., Baudin, C., 2010. Effect of mullite additions on the fracture mode of alumina. *Journal of the European Ceramic Society* 30, 857–863.
- Cahoon, H.P., Cristensen, C.J., 1956. Sintering and grain-growth of alpha-alumina. *Journal of the American Ceramic Society* 39, 337–344.
- Chaim, R., Levin, M.m., Shlayer, A., Estournes, C., 2008. Sintering and densification of nanocrystalline ceramic oxide powders: A review. *Advances in Applied Ceramics* 107, 159–168.
- Chevalier, J., Gremillard, L., 2008. Ceramics for medical applications: A picture for the next 20 years. *Journal of the European Ceramic Society* 29, 1245–1255.
- Chi, M., Gu, H., Wang, X., Wang, P., 2003. Evidence of bilevel solubility in the bimodal microstructure of TiO_2 -doped alumina. *Journal of the American Ceramic Society* 86, 1953–1955.
- Claussen, N., Mussler, B., Swain, M.V., 1982. Grain-size dependence of fracture energy in ceramics. *Journal of the American Ceramic Society* 65, C-14–C-16.
- Coble, R.L., 1961. Sintering crystalline solids: II. Experimental test of diffusion models in powder compacts. *Journal of Applied Physics* 32, 793–799.
- Coble, R.L., 1962. Sintering of alumina: effect of atmospheres. *Journal of the American Ceramic Society* 45, 123–128.
- Coble, R.L., Ellis, J.S., 1963. Hot-pressing alumina – Mechanisms of material transport. *Journal of the American Ceramic Society* 46, 438–441.
- Coble, R.L., Song, H., Brook, R.J., Hendwerker, C.A., Dynys, J.M., 1984. In: Kingery, W.D. (Ed.), *Structure and Properties of MgO and Al_2O_3 Ceramics*. Ohio, USA: The American Ceramic Society, pp. 839–852. [1984].
- Croquesel, J., Bouvard, D., Chaix, J.M., et al., 2016. Direct microwave sintering of pure alumina in a single mode cavity: Grain size and phase transformation effects. *Acta Materialia* 116, 53–62.
- Damani, R., Gstrein, R., Danzer, R., 1996. Critical notch-root radius effect in SENB-S fracture toughness testing. *Journal of the European Ceramic Society* 16, 695–702.
- de Aza, A.H., Chevalier, J., Fantozzi, G., Schehl, M., Torrecillas, R., 2002. Crack growth resistance of alumina, zirconia and zirconia toughened alumina ceramics for joint prostheses. *Biomaterials* 23, 937–945.

- de Portu, G., Bueno, S., Micele, L., Baudin, C., Pezzotti, G., 2006. Piezo-spectroscopic characterization of alumina-aluminium titanate laminates. *Journal of the European Ceramic Society* 26, 2699–2705.
- Deer, W.A., Howie, R.A., Zussman, J., 1992. *An Introduction to The Rock-forming Minerals*, second ed. United Kingdom: Longman Scientific and Technical.
- Deura, M., Kutsukake, K., Ohno, Y., Yonenaga, I., Taniguchi, T., 2018. Mechanical properties of cubic-BN(111) bulk single crystal evaluated by nanoindentation. *Physica Status Solidi B – Basic Solid State Physics* 255, 1700473.
- Doremus, R.H., 1984. Chapter 2: Alumina-silica system. In: Chermisinoff, N.P. (Ed.), *Handbook of Ceramics and Composites*. Vol. 1: Synthesis and properties. New York, USA: Marcel Dekker, pp. 23–34.
- Doremus, R.H., 2008. Chapter 1: Alumina. In: Shackelford, J.F., Doremus, R.H. (Eds.), *Ceramic and Glass Materials: Structure, Properties and Processing*. USA: Springer, pp. 1–26.
- Dörre, E., Hübner, H., 1984. *Alumina: Processing, Properties and Applications*. Berlin, Germany: Springer-Verlag.
- Drdlikova, K., Maca, K., Slama, M., Drdlik, D., 2019. *Journal of the American Ceramic Society* 102, 7137–7144.
- Ebrahimi, M.E., Chevalier, J., Fantozzi, G., 2000. Slow crack-growth behavior of alumina ceramics. *Journal of Materials Research* 15, 142–147.
- Elsässer, C., Heuer, A.H., Rühle, M., Wiederhorn, S.M. (Eds.), 2003. Special topical issue: Alumina. *Journal of the American Ceramic Society* 86 (4).
- Freiman, S.W., McKinney, K.R., Smith, H.L., 1973. Slow crack growth in polycrystalline ceramics. In: Bradt, R.C., Hasselman, D.P.H., Lang, F.F. (Eds.), *Fracture Mechanics of Ceramics*, vol. 2. USA: Plenum Press, pp. 659–676.
- French, R.H., Heuer, A.H. (Eds.), 1994. *Science of alumina*. *Journal of the American Ceramic Society* 77 (2).
- Fujiwara, S., Tamura, Y., Maki, H., Azuma, N., Takeuchi, Y., 2007. Development of new high-purity alumina. *Sumitomo Kagaku* 2007-I, 1–10.
- García-Prieto, A., Baudin, C., 2010. Crack mouth opening displacement controlled fracture tests of brittle ceramics. *Journal of the European Ceramic Society* 30, 3297–3302.
- Gavrilov, K.L., Bennisson, S.J., Mikeska, K.R., Levi-Setti, R., 2003. Role of magnesia and silica in alumina microstructure evolution. *Journal of Materials Science* 38, 3965–3972.
- Ghate, B.B., Smith, W.C., Kim, C.H., Hasselman, D.P.H., Kane, G.E., 1975. Effect of chromia alloying on machining performance of alumina cutting tools. *American Ceramic Society Bulletin* 54, 210–215.
- Gitzen, W.H., 1970. Alumina as a ceramic material. In *American Ceramic Society Special Publication No. 4*. Ohio, USA: The American Ceramic Society.
- Guo, Y.J., Lu, F., Zhang, L., *et al.*, 2018. Properties of ceramic substrate materials for high-temperature pressure sensors for operation above 1000°C. *Advances in Materials Science and Engineering* 2018.ID 2317295).
- Gurauskis, J., Sánchez-Herencia, A.J., Baudin, C., 2006. Al₂O₃/Y-TZP and Y-TZP materials fabricated by stacking layers obtained by aqueous tape casting. *Journal of the European Ceramic Society* 26, 1489–1496.
- Hai, C., Zhang, L., Zhou, Y., *et al.*, 2018. Phase transformation and morphology evolution characteristics of hydrothermally prepared boehmite particles. *Journal of Inorganic and Organometallic Polymers and Materials* 28, 643–650.
- Handwerker, C.A., Cannon, R.M., French, R.H., 1994. Robert L. Coble: A Retrospective. *Journal of the American Ceramic Society* 77, 293–297.
- Harmer, M.P., Brook, R.J., 1981. Fast firing- microstructural benefits. *Transactions and Journal of the British Ceramic Society* 80, 147–148.
- Harper, C.A., 2001. *Handbook of ceramic, glasses and diamonds*. New York: McGraw-Hill.
- Hart, L.D., 1990. *Alumina Chemicals: Science and Technology Handbook*. USA: The American Ceramic Society.
- Hitesh, D., Sheng-Jen, H., Jia-Chang, W., 2019. Review of additive manufacturing methods for high-performance ceramic materials. *The International Journal of Advanced Manufacturing Technology* 103, 2627–2647.
- Hu, C.Y., Yoon, T.-R., 2018. Recent updates for biomaterials used in total hip arthroplasty. *Biomaterials Research* 22, 33.
- Huet, R., Sakona, A., Kurtz, S.M., 2011. Strength and reliability of alumina ceramic femoral heads: Review of design, testing, and retrieval analysis. *Journal of the Mechanical Behavior of Biomedical Materials* 4, 476–483.
- Iwasa, M., Bradt, R.C., 1984. Fracture toughness of single-crystal alumina. In: Kingery, W.D. (Ed.), *In Structure and properties of MgO and Al₂O₃ ceramics*. Ohio, USA: The American Ceramic Society, pp. 767–779. [1984].
- Jayatilaka, A.S., 1979. *Fracture of Engineering Brittle Materials*. UK: Applied Science Publishers Ltd.
- Jones, L.E., Tressler, R.E., 1991. The high temperature creep behavior of oxides and oxide fibers. NASA Contractor Report. 187060.
- Jung, J., Baik, S., 2003. Abnormal grain growth of alumina: CaO effect. *Journal of the American Ceramic Society* 86, 644–649.
- Kachaev, A.A., Grashchenkov, D.V., Lebedeva, Yu.E., Solntsev St., S., Khasanov, O.L., 2016. Optically transparent ceramic (Review). *Glass and Ceramics* 73, 117–123.
- Kingery, W.D., 1984. *Structure and Properties of MgO and Al₂O₃ Ceramics*. Ohio, USA: The American Ceramic Society.
- Krell, A., 1995. Grain size dependence of hardness in dense submicrometer alumina. *Journal of the American Ceramic Society* 78, 1118–1120.
- Krell, A., 1996. Improved hardness and hierarchic influences on wear in submicron sintered alumina. *Materials Science and Engineering A* 209, 156–163.
- Krell, A., Blank, P., Ma, H., *et al.*, 2003. Transparent sintered corundum with high hardness and strength. *Journal of the American Ceramic Society* 86, 12–18.
- Krell, A., Klimke, J., 2006. Effects of the homogeneity of particle coordination on solid-state sintering of transparent alumina. *Journal of the American Ceramic Society* 89, 1985–1992.
- Krell, A., Hutzler, T., Klimke, J., 2009. Transmission physics and consequences for materials selection, manufacturing, and applications. *Journal of the European Ceramic Society* 29, 207–221.
- Kumagai, M., Messing, G.L., 1985. Controlled transformation and sintering of a boehmite sol-gel by α -alumina seeding. *Journal of the American Ceramic Society* 68, 500–505.
- Lange, F.F., 1984. Sinterability of agglomerated powders. *Journal of the American Ceramic Society* 67, 83–89.
- Lee, W.E., Rainforth, W.M., 1994. *Refractory materials*. In *Ceramic Microstructures: Property Control by Processing*. UK: Chapman & Hall, pp. 470–488.
- Leriche, A., Cambier, F., Hampshire, S., 2020. Sintering of ceramics. In *Reference Module in Materials Science and Materials Engineering*. Elsevier. doi:10.1016/B978-0-12-803581-8.12083-1.
- Levin, E.M., Robbins, C.R., McMurde, H.F., 1964. *Phase Diagrams for Ceramists*. Ohio, USA: The American Ceramic Society.
- Ma, Q., Clarke, D.R., 1994. Piezospectroscopic determination of residual stresses in polycrystalline alumina. *Journal of the American Ceramic Society* 77, 298–302.
- Mai, Y.-W., Lawn, B.R., 1987. Crack-interface grain bridging as a fracture resistance mechanism in ceramics: II. Theoretical fracture mechanics model. *Journal of the American Ceramic Society* 70, 289–294.
- Mata-Osoro, G., Moya, Pecharrómán, J.C., 2012. Transparent alumina by vacuum sintering. *Journal of the European Ceramic Society* 32, 2925–2933.
- Messing, G.L., Shelleman, R.A., McArdle, J.L., 1988. Controlled chemical nucleation of alpha alumina transformation. In: Taylor, D. (Ed.), *Science of Ceramics* 14. Stoke-on-Trent, GB: The Institute of Ceramics, pp. 101–106.
- Messing, G.L., Stevenson, A.J., 2008. Toward pore-free ceramics. *Science* 322, 383–384.
- Messing, G.L., Poterala, S., Chang, Y., *et al.*, 2017. Texture-engineered ceramics – Property enhancements through crystallographic tailoring. *Journal of Material Research* 32, 3219–3241.
- Mezquita, S., Uribe, R., Moreno, R., Baudin, C., 2001. Influence of mullite additions on thermal shock resistance of dense alumina materials. Part II: thermal properties and thermal shock behavior. *British Ceramic Transactions* 100, 246–250.
- Mussler, B., Swain, M.V., Claussen, N., 1982. Dependence of fracture toughness of alumina on grain size and test technique. *Journal of the American Ceramic Society* 65, 566–572.
- Norton, A.D., Falco, S., Young, N., Severs, J., Todd, R.I., 2015. Microcantilever investigation of fracture toughness and subcritical crack growth on the scale of the microstructure in Al₂O₃. *Journal of the European Ceramic Society* 35, 4521–4533.

- Palmero, P., Montanaro, L., Reveron, H., Chevalier, J., 2014. Review: surface coating of oxide powders: A new synthesis method to process biomedical grade nano-composites. *Materials* 7, 5012–5037.
- Phillips, D.S., Shiue, Y.R., 1984. Grain-boundary microstructures in alumina ceramics. In: Kingery, W.D. (Ed.), *Structure and Properties of MgO and Al₂O₃ Ceramics*. Ohio, USA: The American Ceramic Society, pp. 357–367.
- Piconi, C., Porporati, A.A., 2016. Bioinert ceramics: Zirconia and alumina. In: Antoniac, I. (Ed.), *Handbook of Bioceramics and Biocomposites*. Cham: Springer. doi:10.1007/978-3-319-12460-5_4.
- Powers, J.D., Glaeser, A.M., 1997. Titanium effects on sintering and grain boundary mobility of alumina. *Ceramic Engineering and Science Proceedings* 18, 617–622.
- Pringuet, A., Takahashi, T., Baba, S., *et al.*, 2016. Fabrication of transparent grain-oriented polycrystalline alumina by colloidal processing. *Journal of the American Ceramic Society* 99, 3217–3219.
- Raether, F., Schulze, H.P., 2009. Investigation of sintering mechanisms of alumina using kinetic field and master sintering diagrams. *Journal of the European Ceramic Society* 29, 2225–2234.
- Rahaman, M.N., 2008. *Sintering of Ceramics*. Florida, USA: CRC Press.
- Rahaman, M.N., Yao, A., Sonny Bal, B., Garino, J.P., Ries, M.D., 2007. Ceramics for prosthetic hip and knee joint replacement. *Journal of the American Ceramic Society* 90, 956–988.
- Rainforth, W.M., 2004. The wear behaviour of oxide ceramics – A review. *Journal of Materials Science* 39, 6705–6721.
- Rajendran, S., 1994. Production of ultrafine alpha alumina powders and fabrication of fine grained strong ceramics. *Journal of Materials Science* 29, 5664–5672.
- Ratzker, B., Wagner, A., Sokol, M., *et al.*, 2019. Optical and mechanical properties of transparent alumina fabricated by high-pressure spark plasma sintering. *Journal of the European Ceramic Society* 39, 2712–2719.
- Rice, R.W., Freiman, S.W., Becher, P.F., 1981. Grain-size dependence of fracture energy in ceramics: I. Experiment. *Journal of the American Ceramic Society* 64, 345–350.
- Rice, R.W., 1998. *Porosity of Ceramics*. vol. 12. USA: Marcel Dekker Inc.
- Riley, F.L., 2009. *Structural ceramics*. In *Fundamentals and Case Studies*. Cambridge, UK: Cambridge University Press.
- Rivas Mercury, J.M., Pena, P., de Aza, A.H., Sheptyakov, D., Turrillas, X., 2006. On the decomposition of synthetic gibbsite studied by neutron thermogravimetry. *Journal of the American Ceramic Society* 89, 3728–3733.
- Rödel, J., Glaeser, A.M., 1990. Anisotropy of grain growth in alumina. *Journal of the American Ceramic Society* 73, 3292–3301.
- Ruano, O.A., Wadsworth, J., Sherby, O.D., 2003. Deformation of fine-grained alumina by grain boundary sliding accommodated by slip. *Acta Materialia* 5, 3617–3634.
- Ruy, A., 2019. *Alumina Ceramics. Biomedical and Clinical Applications*. The Netherlands: Woodhead Publishing, Elsevier.
- Ryshkewitch, E., Richerson, D.W., 1985. *Oxide Ceramics: Physical Chemistry and Technology*, second ed. Florida, USA: Academic Press.
- Sánchez Herencia, A.J., Moreno, R., Baudin, C., 2000. Fracture behavior of alumina-calcium hexaluminate composites obtained by colloidal processing. *Journal of the European Ceramic Society* 20, 2575–2583.
- Sakka, Y., Grasso, S., 2019. Pulsed electrodischarged pressure sintering and flash sintering, a review. *Materials Today-Proceedings* 16, 14–24.
- Sbaizero, O., Pezzotti, G., Nishida, T., 1998. Fracture Energy and R-Curve Behaviour of Al₂O₃/Mo Composites. *Acta Materialia* 46, 681–687.
- Seidel, J., Rödel, J., 1997. Measurement of crack tip toughness in alumina as a function of grain size. *Journal of the American Ceramic Society* 80, 433–438.
- Shaffer, P.T.B., 1964. Effect of crystal orientation on hardness of silicon carbide. *Journal of the American Ceramic Society* 47, 466.
- Shahinian, P., 1971. High-temperature strength of sapphire filament. *Journal of the American Ceramic Society* 54, 67–68.
- Shaw, N.J., Brook, R.J., 1986. Structure and grain coarsening during the sintering of alumina. *Journal of the American Ceramic Society* 69, 107–110.
- Shellemen, R.A., Messing, G.L., 1988. Liquid-phase-assisted transformation of seeded γ -alumina. *Journal of the American Ceramic Society* 71, 317–322.
- Song, H., Coble, R.L., 1990. Origin and growth kinetics of platelike abnormal grains in liquid-phase-sintered alumina. *Journal of the American Ceramic Society* 73, 2077–2085.
- Sousa, C., Illas, F., Pacchioni, G., 1993. Can corundum be described as an ionic oxide? *Journal of Chemical Physics* 99, 6818–6823.
- Spriggs, R.M., 1961. Expression for effect of porosity on elastic modulus of polycrystalline refractory materials, particularly aluminum oxide. *Journal of The American Ceramic Society* 44, 628–629.
- Spriggs, R.M., Mitchell, J.B., Vasilos, T., 1964. Mechanical properties of pure, dense aluminum oxide as a function of temperature and grain size. *Journal of the American Ceramic Society* 47, 323–327.
- Schwentenwein, M., Homa, J., 2014. Additive manufacturing of dense alumina ceramics. *International Journal of Applied Ceramic Technology* 2014, 1–7.
- Tallon, C., Limacher, M., Franks, G.V., 2010. Effect of particle size on the shaping of ceramics by slip casting. *Journal of the European Ceramic Society* 30, 2819–2826.
- Taylor, D., 1984. Thermal expansion data: III. Sesquioxides, M₂O₃ with the corundum and the A-, B- and C-M₂O₃. *British Ceramic Transactions and Journal* 83, 92–98.
- Tonejc, A., Stubiaar, M., Tonejc, A.M., *et al.*, 1994. Transformation of γ -AlOOH (boehmite) and Al(OH)₃ (gibbsite) to α -Al₂O₃ (corundum) induced by high energy ball milling. *Journal of Materials Science Letters* 13, 519–520.
- Vasilos, T., Spriggs, R.M., 1963. Pressure sintering: Mechanisms and microstructures for alumina and magnesia. *Journal of the American Ceramic Society* 46, 493–496.
- Wakao, Y., Hibino, T., 1962. Effect of metallic oxides on α -transformation of alumina. *Nagoya Kogyo Gijutsu Shikennijo Hokoku* 11, 588–595.
- Wang, Y., Suryanarayana, C., An, L., 2005. Phase transformation in nanometersized γ -alumina by mechanical milling. *Journal of the American Ceramic Society* 88, 780–783.
- Watchman, J.B., Maxwell, L.H., 1957. Plastic deformation of ceramic-oxide single crystals II. *Journal of the American Ceramic Society* 40, 377–385.
- Watchman, J.B., Lam Jr, D.G., 1959. Young's modulus of various refractory materials as a function of temperature. *Journal of the American Ceramic Society* 42, 254–260.
- Watchman, J.B., Maxwell, L.H., 1959. Strength of single crystal sapphire and ruby as a function of temperature and orientation. *Journal of the American Ceramic Society* 42, 432–453.
- Watchman, J.B., Cannon, W.R., Matthewson, M.J., 2009. *Mechanical Properties of Ceramics*, second ed. USA: John Wiley & Sons Inc.
- Wells, A.F., 1984. *Structural Inorganic Chemistry*. Oxford, GB: Oxford University Press.
- Whitney, E.D., 1994. *Ceramic Cutting Tools. Materials, Development and Performance*. Florida, USA: Noyes Publications.
- Wiederhorn, S.M., 1969. Fracture of sapphire. *Journal of the American Ceramic Society* 52, 485–491.
- Wiederhorn, S.M., Hockey, B.J., Roberts, D.E., 1973. Effect of temperature on the fracture of sapphire. *Philosophical Magazine* 28, 783–796.
- Wu, Y., Zhang, Y., Pezzotti, G., Guo, J., 2002. Influence of AlF₃ and ZnF₂ on the phase transformation of gamma to alpha alumina. *Materials Letters* 52, 366–369.
- Xue, L.A., Chen, I.-W., 1990. Deformation and grain growth of low-temperature-sintered high-purity alumina. *Journal of the American Ceramic Society* 73, 3518–3521.
- Xue, L.A., Chen, I.-W., 1992. Influence of additives on γ - to α -transformation of alumina. *Journal of Materials Science Letters* 11, 443–445.
- Yahya, N.A., Todd, R.I., 2012. Influence of C doping on the fracture mode and abrasive wear of Al₂O₃. *Journal of the European Ceramic Society* 32, 4003–4007.
- Yanga, Q., Wanga, H., Chen, S., Zhang, L., Xua, S., 2019. Highly-oriented (104) polycrystalline α -Al₂O₃ transparent ceramics prepared by a templated grain growth method. *Journal of the European Ceramic Society* 39, 1721–1724.
- Yoshizawa, Y., Saito, F., 1996. Formation of α -Al₂O₃ from Al(OH)₃ in the presence of seed particles and its sinterability. *Journal of the Ceramic Society of Japan* 104, 867–871.
- Yoshizawa, Y., Hirao, K., Kanzaki, S., 2004. Fabrication of low cost fine-grained alumina powders by seeding for high performance sintered bodies. *Journal of the European Ceramic Society* 24, 325–330.
- Yu, B.C., Lange, F.F., 2010. Shape forming alumina slurries via colloidal isopressing. *Journal of the European Ceramic Society* 30, 2795–2803.

Further Reading

- Lagerlof, K.P.D., Heuer, A.H., Castaing, J., Rivière, J.P., Mitchell, T.E., 1994. Slip and twinning in sapphire (α -Al₂O₃). *Journal of the American Ceramic Society* 77, 385–397.
- Liu, P., Yi, H., Zhou, G., Zhang, J., Wang, S., 2015. HIP and pressureless sintering of transparent alumina shaped by magnetic field assisted slip casting. *Optical Materials Experimental* 5, 441–447.
- Soh, K.H., Kolos, E., Ruys, A.J., 2015. Foamed high porosity alumina for use as a bone tissue scaffold. *Ceramics International* 41, 1031–1047.

Relevant Websites

- <https://www.coorstek.com/media/4235/advanced-alumina.pdf>
Advanced Alumina.
01023K.
CoorsTek.
- <http://primary.world-aluminium.org/aluminium-facts/raw-materials/>
Aluminium for Future Generations.
Raw Materials.
- <http://valleydesign.com/sappprop.htm>
Properties of Sapphire Wafers, Sapphire Thermal Conductivity.
- <https://icsd.fiz-karlsruhe.de/display/details.xhtml>
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Low Thermal Expansion Ceramic and Glass-Ceramic Materials

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Introduction

Low thermal expansion ceramic materials are of special interest for applications which require dimensional stability versus temperature and mainly a high resistance to thermal shock and thermal gradients. During a thermal shock, the sudden variation of temperature induces a temperature gradient between the surface and the bulk of the material. The difference in thermal expansion induces a stress which could initiate the fracture of a brittle material. In many applications, materials are submitted to a constant high temperature difference between their two faces, during a long time. The induced stresses may also lead to material degradation.

For example, during fast cooling, the resistance to failure initiation could be related to the first parameter of thermal shock resistance R' (Kingery, 1955):

$$R' = \frac{\sigma_f}{\alpha E}$$

where σ_f is the strength, α is the thermal expansion coefficient and E is the elastic modulus (Young modulus). It is possible to optimize R' by altering the different parameters (increasing σ_f , decreasing α and/or E). However, it is obvious that materials with very low - near zero - thermal expansion exhibit superb resistance to thermal shock and gradients.

There exists a family of oxide ceramic materials which exhibit a low thermal expansion coefficient. Most of them are well known and already used in various applications such as refractory materials (metal working, coke ovens, etc.), automobiles, domestic cookware, etc.

Thermal expansion

The heating of a crystallographic lattice induces an expansion which is due to the increase of the atomic vibration amplitude around their average position. Another rule is that heating leads to more symmetric lattice. For example, in the tetragonal structure, the c/a ratio, where a and c are the length of the lattice parameters, decreases with increasing temperature (Darnell, 1963; Evans *et al.*, 1980; Son *et al.*, 2019).

The thermal expansion coefficient α (TEC) is defined as (Collins and White, 1964):

$$\alpha = \frac{\Delta L}{L_0} \frac{1}{\Delta T}$$

where ΔL is the difference between the length (L) of the material at the temperature T and the initial length (L_0) of the material at the initial temperature (T_0), ΔT is the temperature variation ($T - T_0$). The measurement unit of the TEC is given in K^{-1} . Some examples of TEC of ceramic materials are given in Table 1 and compared with that of a steel material (Carvill, 1993; Routschka and Granitzki, 2000).

The intrinsic value of the thermal expansion coefficient closely depends on the strength of the chemical bonds but also on the crystalline structure. For example, in a cubic lattice, the TEC is the same in the three directions, and the volume coefficient can be approximated by $\alpha_v = 3 \alpha_l$, where α_l is the linear coefficient. Nevertheless, during heating of asymmetric lattices, the atomic vibrations lead to a more symmetric network and the thermal expansion changes with the direction. In some crystals with high anisotropy, this may induce stress and strain, leading to a negative expansion along one axis and a very low or negative average volume expansion.

Moreover, in polycrystalline materials, the macroscopic thermal expansion coefficient value may be linked to the grain size (Kuszyk and Bradt, 1973; Parker and Rice, 1989). In the case of very high crystalline anisotropy expansion, TEC decreases when the grain size increases, as reported in Fig. 1 (Parker and Rice, 1989). This phenomenon is also associated with a hysteresis whose intensity increases when expansion decreases shown in Fig. 2 (Ohya *et al.*, 2017).

The presence of a hysteresis can be explained by material microcracking. After material heating, during cooling, the thermal expansion anisotropy locally induces stresses at the grain boundaries and leads to cracking. This phenomenon only appears when grain size is higher than a size which is called "critical grain size".

Cleveland and Bradt (1978) demonstrated that the critical grain size may be estimated from the equation:

$$(g_s)_{cr} = 14.4 \frac{\gamma_f}{E \Delta \alpha_{max}^2 \Delta T^2}$$

where γ_f is the energy of crack propagation, E is the elastic modulus, $\Delta \alpha_{max}$ is the highest difference of thermal expansion coefficient and ΔT is the temperature difference during the cooling.

Table 1 Average thermal expansion coefficient of some ceramic materials

Material	Linear TEC α (0–1000°C, $K^{-1} \times 10^{-6}$)
Al ₂ O ₃	8.8
MgO	13.5
Mullite (3Al ₂ O ₃ · 2SiO ₂)	5.3
Vitreous silica (SiO ₂)	0.5
Steel (Carvill, 1993)	10.4–12.4

Note: Routschka, G., Granitzki, K.-E., 2000. Refractory ceramics. Ullmann's Encyclopedia of Industrial Chemistry Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA.

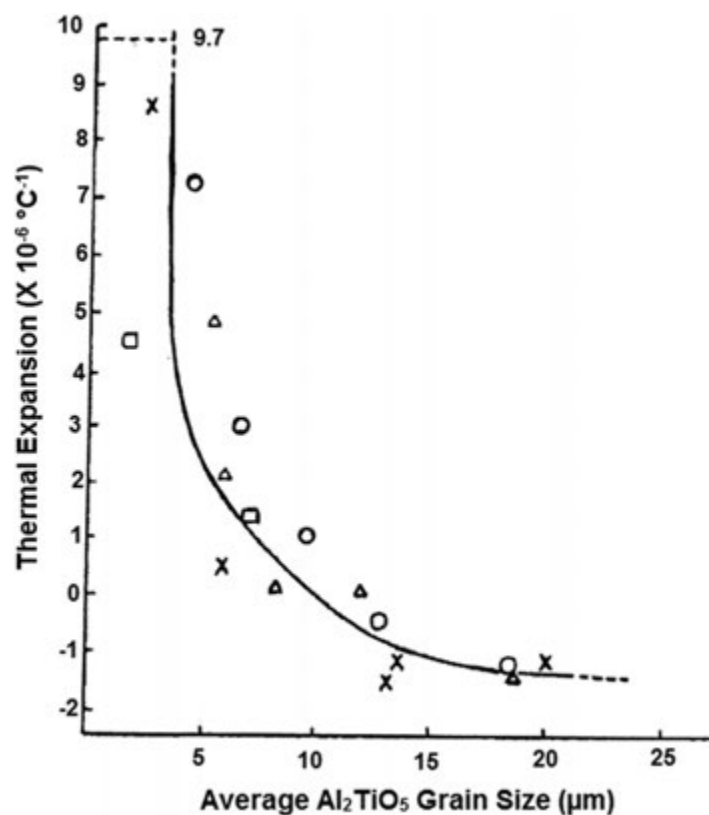


Fig. 1 Thermal expansion coefficient of polycrystalline aluminum titanate as a function of grain size. Reproduced from Parker, F.J., Rice, R.W., 1989. Correlation between grain size and thermal expansion for aluminum titanate materials. *Journal of the American Ceramic Society* 72 (12), 2364–2366. doi:10.1111/j.1151-2916.1989.tb06091.x.

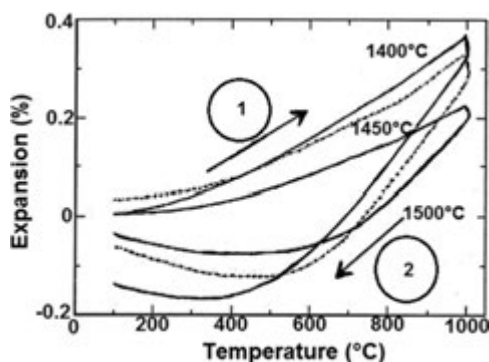


Fig. 2 Thermal expansion of a fired MgO-Y₂O₃-doped Al₂TiO₅ material. Reproduced from Ohya, Y., *et al.*, 2017. Thermal expansion and mechanical properties of self-reinforced aluminum titanate ceramics with elongated grains. *Journal of the European Ceramic Society* 37 (4), 1673–1680. doi:10.1016/j.jeurceramsoc.2016.11.037.

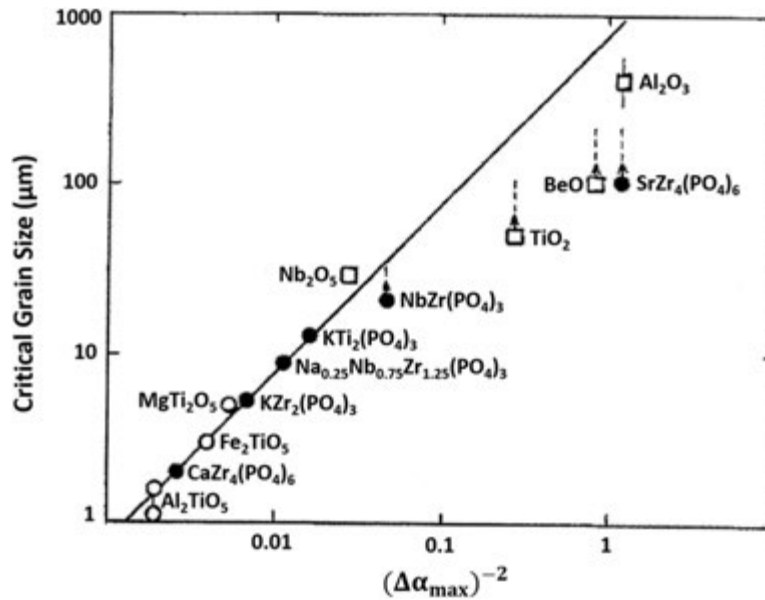


Fig. 3 Variation of critical grain size with inverse square of maximal thermal expansion difference for $\text{NaZr}_2(\text{PO}_4)_3$ family of materials (●), pseudobrookite oxides (○) and other materials (□). Reproduced from Yamai, I., Ota, T., 1993. Grain size-microcracking relation for $\text{NaZr}_2(\text{PO}_4)_3$ family ceramics. *Journal of the American Ceramic Society* 76 (2), 487–491. doi:10.1111/j.1151-2916.1993.tb03811.x. Cleveland, J.J., Bradt, R.C., 1978. Grain size/microcracking relations for pseudobrookite oxides. *Journal of the American Ceramic Society* 61 (11–12), 478–481. doi:10.1111/j.1151-2916.1978.tb16121.x. Rice, R.W., Pohanka, R.C., 1979. Grain-size dependence of spontaneous cracking in ceramics. *Journal of the American Ceramic Society* 62 (11–12), 559–563. doi:10.1111/j.1151-2916.1979.tb12730.x.

This equation is generally simplified to give the relation (Yamai and Ota, 1993):

$$(g_s)_{cr} \sim \frac{1}{\Delta\alpha_{\max}^2}$$

The latter has been demonstrated for many materials, as reported in Fig. 3 (Cleveland and Bradt, 1978; Rice and Pohanka, 1979; Yamai and Ota, 1993).

For most materials, it is possible to control the microstructure and to avoid the appearance of microcracking during the fabrication process (firing). However, when the critical grain size is very small, for example in the case of aluminum titanate, it is very difficult, even impossible, to obtain materials without any microcracks.

The microcracks appear in the material during the fabrication process, in particular during cooling after the first heating (sintering). During reheating (first part of Fig. 2) at low temperature, two phenomena contribute to material shrinkage: grain expansion in the cracks and crack healing. Therefore, at the macroscopic level, the thermal expansion is lower than the intrinsic one. It may be very low (after firing at 1400°C), near zero (after firing at 1450°C) or even negative (after firing at 1500°C). At high temperature, microcracks are closed, the slope of the expansion versus temperature curve thus increases and the thermal expansion coefficient is close to the intrinsic one. During cooling, the material shrinks with a high average thermal expansion and the “cooling” curve is “located” below the heating curve (second step of Fig. 2). When the temperature difference is sufficient, microcracking starts and compensates the natural shrinkage. Finally, the two curves join at the initial temperature.

Moreover, microcracking is inevitably associated with a decrease in the mechanical properties such as elastic modulus and strength. Indeed, Cleveland and Bradt (1978) demonstrated that grain-boundary cracking linked to the increase of grain size, results in many properties changes (e.g., decreases) in the material (Fig. 4).

Ceramic Materials

Silica

Silica ceramic materials are mainly manufactured from pure quartzites and quartz (Brunk, 2000, 2001). Silica is used to manufacture “classical” silica bricks which are well known as refractory materials for some special applications. During the fabrication process, the crushed raw materials are pressed and fired at high temperature between 1400 and 1500°C. The β -quartz from the raw materials is transformed to a mixture of α -cristobalite and α -tridymite with some residual quartz. This transformation is associated with volume changes (4%–5%) (Brunk, 2000; Routschka and Granitzki, 2000). Moreover, during cooling and further reheating, the material exhibits very large and sharp volume variations due to polymorphic transformations between high (α) and low crystallographic phases (β). Table 2 presents the mineralogical modifications and associated volume changes of silica as a function

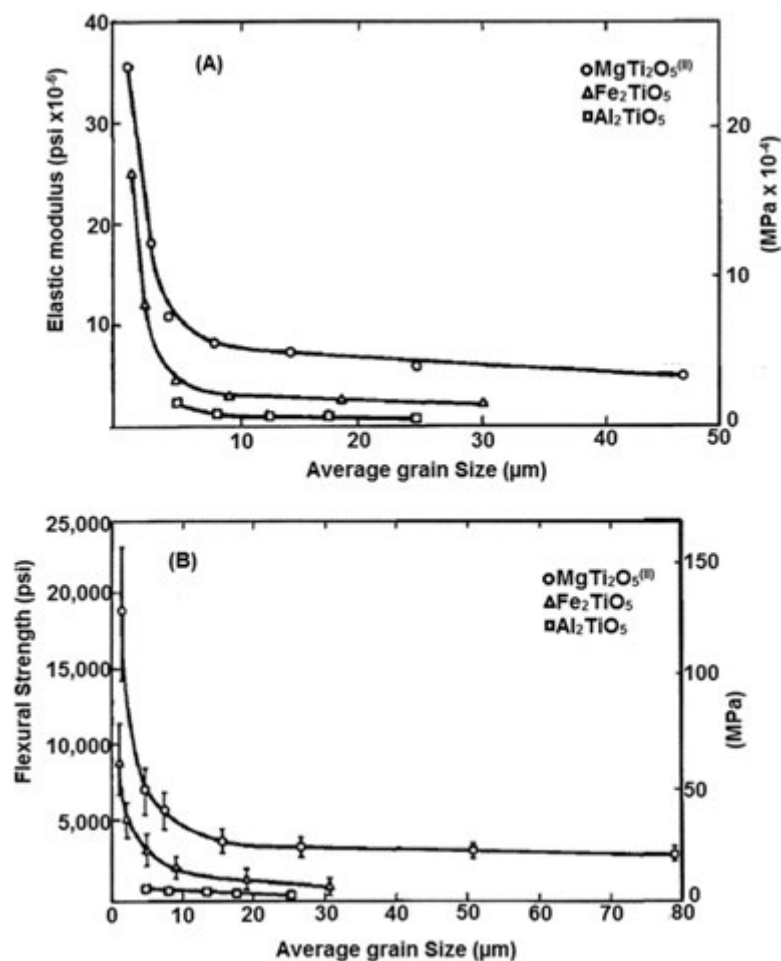


Fig. 4 Variation of (A) elastic modulus and (B) flexural strength with grain size. Reproduced from Cleveland, J.J., Bradt, R.C., 1978. Grain size/microcracking relations for pseudobrookite oxides. *Journal of the American Ceramic Society* 61 (11–12), 478–481. doi:10.1111/j.1151-2916.1978.tb16121.x.

Table 2 Modification and volume changes of SiO_2

Modification changes $\leftrightarrow$ reversible, $\rightarrow$ irreversible	Transformation temperature ($^{\circ}\text{C}$)	Volume change (%)
$\beta \leftrightarrow \alpha$ -quartz	573	0.8–1.3
α -quartz $\rightarrow$ α -cristobalite	1250 ($\approx 1050^a$)	17.4
$\beta \leftrightarrow \alpha$ -cristobalite	≈ 260	2–2.8
α -quartz $\rightarrow$ α -tridymite ^a	≈ 870	14.4
$\gamma \leftrightarrow \beta \leftrightarrow \alpha$ -tridymite ^a	117–163	0.5
α -tridymite $\rightarrow$ α -cristobalite ^a	1470	0
α -cristobalite $\rightarrow$ melt	1713 ± 10	–
α -tridymite $\rightarrow$ melt ^b	1610 ± 10	–
Fused silica $\rightarrow$ α -cristobalite	Above $\approx 1150^a$	≈ 0.9

^aIn presence of impurities.

^bRapid heating.

Note: Brunk, F., 2001. Silica refractories. *InterCeram: International Ceramic Review* 27–30.

of the transformation temperature (Brunk, 2001). Fig. 5 (Brunk, 2000) shows the usual thermal expansion curve of silica bricks resulting from the overlapping and combination of the three single phase curves (Pereira *et al.*, 2014). At low temperature, the material exhibits a very large expansion between room temperature and 600°C . Both during heating and cooling, the materials are very sensitive to thermal shock in this range of temperature. Below 600°C , the installation must be heated and cooled slowly and very carefully. Above 600°C and up to 1400°C , the curve is flat, the thermal expansion is very low and the resistance to thermal shock and gradients is very high. The main verification of this characteristic is the building of coke oven walls which have to

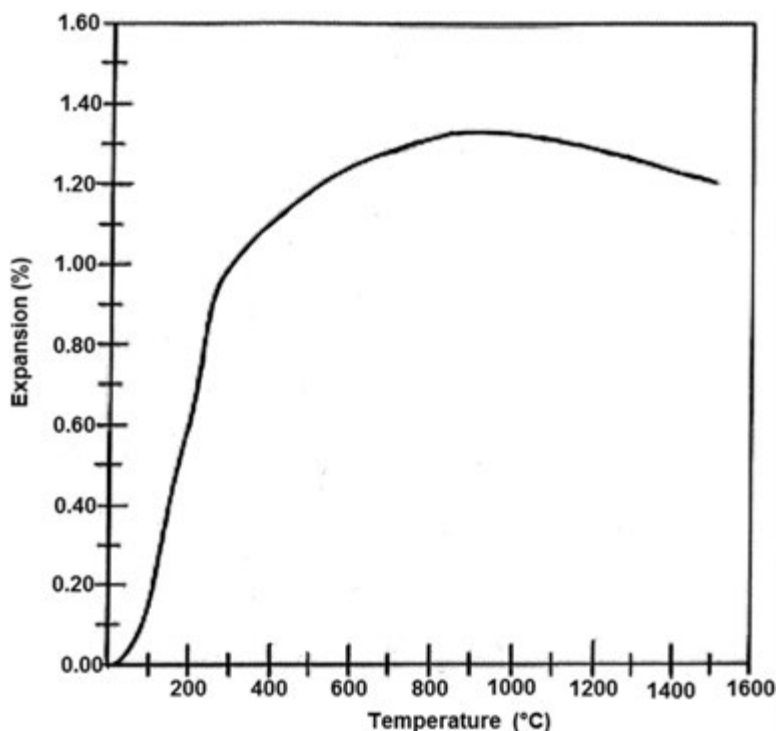


Fig. 5 Thermal dilatation of silica coke oven brick. Reproduced from Brunk, F., 2000. Silica bricks for modern coke oven batteries. *Coke Making International* 12 (2), 37–40.

sustain a high temperature difference between the “firing side” (1400–1450°C) and the “coke side” (1000–1100°C) (Brunk, 2000; Andreev *et al.*, 2017). Silica bricks are also used for glass furnace crowns (Brunk, 2001; Postrach *et al.*, 2009) and also as checker bricks in the top of the blast furnace stoves where sudden temperature differences regularly occur (Schneider *et al.*, 1986; Brunk, 2001; Manivasakan *et al.*, 2010).

Silica melting in electric arc furnaces allows production of “fused” (“amorphous” or “vitreous”) silica. Fused blocks are crushed and the resulting granular material is used to manufacture pressed or slip-cast refractory materials (Routschka and Granitzki, 2000). Materials are either unfired (hydraulically or chemically bonded) or fired at low temperature to avoid or to limit crystallization of cristobalite (Table 2). Fused silica material exhibits a very small, near zero, thermal expansion coefficient: $\alpha \approx 0.6 \times 10^{-6} \text{ K}^{-1}$ (Routschka and Granitzki, 2000). Therefore, fused silica is practically insensitive to thermal shock. However, there are restrictions concerning the temperature in service. From 1150°C, it crystallizes and transforms into cristobalite with polymorphic transformations which inhibit the technical applications of fused silica above this temperature (Table 2). In some cases, hot repair for example, the small expansion (high thermal shock resistance) is only used during installation, bricks transforming in service. Vitreous silica products are used for hot repairs in glass furnaces and coke ovens, where bricks are directly introduced in hot parts without any preheating (Robyn and Deschepper, 1985; Brunk, 2001). Fused silica rollers, are used to transport warm glass panels at the end of the float glass furnace and to convey steel strip inside furnaces at 1100°C. Fused silica is also used for the manufacture of crucibles for silicon melting (Yamahara *et al.*, 2001). Further applications include ladle shrouds and submerged entry nozzles for steel continuous casting. Fused silica materials are also foreseen for a fast “first heating” of coke ovens (Andreev *et al.*, 2017). Due to the low thermal expansion, low thermal conductivity and excellent abrasion resistance of fused silica grains, products of silica could also be used in aerospace applications, for thermal protection systems (Criss, 1991; Mishra *et al.*, 2010). Fused silica castables are used to cast dies for the hot forming of titania and for brazing honeycomb high speed aircraft structures. This material is also used to protect metal structures on launch pads (Criss, 1991). The ceramic tiles of the reusable surface insulation (RSI) of the space shuttle were mainly composed of high purity amorphous silica fibers (Buckley, Strouhal and Gangler, 1981; Korb, 1981; Buckley, 1995; Sziroczak and Smith, 2016).

Cordierite

Cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$), is a ternary compound in the alumina-silica-magnesia system (Keith and Schairer, 1952; Smart and Glasser, 1981). Cordierite materials are generally obtained by solid-state reaction sintering of a mixture of a magnesia precursor (talc, soapstone, magnesium carbonate or chlorite) with alumina and clay (kaolin) powders, at a temperature between 1350°C and 1400°C (Yamuna, 2004). A cordierite chamotte (prefired grains) can be also added to the original composition to limit shrinkage during sintering (Routschka and Granitzki, 2000). The melting temperature of pure cordierite is about 1460°C

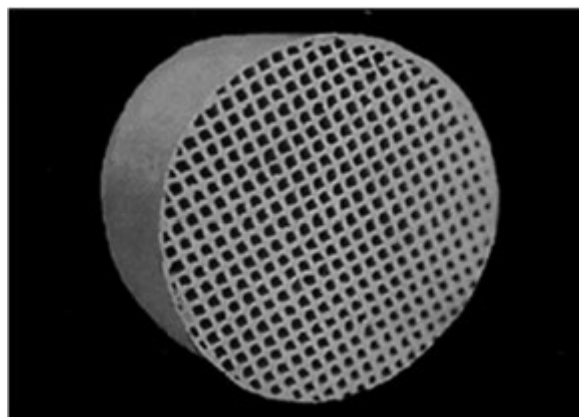


Fig. 6 Kaolin-based cordierite catalyst supports included in ceramic honeycomb or monolith type catalyst converter. Reproduced from Heisler, H., 1995. *Advanced Engine Technology*. London: Arnold. Yamuna, A., 2004. Kaolin-based cordierite for pollution control. *Journal of the European Ceramic Society* 24 (1), 65–73. doi:10.1016/S0955-2219(03)00269-3.

(Camerucci *et al.*, 2003). However, due to the proximity of a low melting temperature (1350–1400°C) in the phase diagram, the maximum recommended use temperature is generally lower than 1350°C, depending on the composition and impurities. Cordierite exhibits a low reversible thermal expansion ($\alpha \approx 2.16 \times 10^{-6} \text{ K}^{-1}$) which ensures a very good thermal shock resistance ($\Delta T > 350\text{K}$) (Ikawa *et al.*, 1986; Vepa and Umarji, 1993; Costa Oliveira and Cruz Fernandes, 2002).

Pure cordierite is used in technical ceramic and refractory materials. Its numerous properties (high thermal and chemical stability, good thermal shock resistance and low thermal expansion coefficient) allows alumina to be replaced by cordierite materials for many applications. In the refractory field, this material is often associated with another mineral – generally mullite or in some cases alumina – to improve its refractoriness and mechanical properties (Ibrahim *et al.*, 1995; Chlup *et al.*, 2005; Ariyajinno and Thiansem, 2018). For materials presenting low cordierite content, cordierite can be considered as an additive which allows improvement of the thermal shock resistance.

The main application of cordierite ceramic is as the catalyst support for car exhaust gas purification and as a diesel exhaust gas particle filter. The material consists of a honeycomb structure which is obtained from the extrusion of a plastic mix as shown in Fig. 6 (Heisler, 1995; Yamuna, 2004).

Refractory applications of cordierite materials are kiln furniture, linings for kiln cars, electrical insulators and supports for electrical resistance and heating elements. Cordierite is also used for technical stoneware and porcelain (Chowdhury *et al.*, 2007).

Aluminum Titanate (Tialite)

Tialite or aluminum titanate (Al_2TiO_5) presents the crystalline structure of the pseudobrookite type, with general formula A_2BO_5 , where A is a trivalent cation and B is a tetravalent one. Tialite monocrystal exhibits a high thermal expansion anisotropy, respectively $\alpha_a = 1.18 \times 10^{-6} \text{ K}^{-1}$, $\alpha_b = 1.94 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_c = -0.26 \times 10^{-6} \text{ K}^{-1}$, that leads to an average calculated thermal expansion coefficient of $9.4 \times 10^{-6} \text{ K}^{-1}$ (Zhien *et al.*, 1996). Moreover, due to a very small critical grain size (1–2 μm), all aluminum titanate materials contain microcracks and exhibit a resulting low, near zero or negative thermal expansion (Fig. 1). Also due to microcracking, the expansion curve versus temperature exhibits a hysteresis (Fig. 2), and mechanical properties of this material are low, generally lower than 50 MPa (Wohlfrohm *et al.*, 1992; de Arenas, 2012). Aluminum titanate can be produced by different chemical routes and calcination, but the most conventional method is the solid-state reaction of fine alumina (Al_2O_3) and titanium oxide (TiO_2) powders at a temperature higher than 1300°C (Freudenberg and Mocellin, 1990; Tilloca, 1991; Segadães *et al.*, 1997). Pre-reacted tialite is sintered at a temperature between 1400 and 1500°C. Tialite material can also be obtained by reaction sintering: shaped alumina and titanium oxide powders are heated at a sufficient temperature allowing both reaction and sintering (Buscaglia *et al.*, 1994; de Arenas, 2012). From the chemical point of view, the tialite material is the only stable compound in the Al_2O_3 - TiO_2 system at temperatures higher than 1280°C (Segadães *et al.*, 1998). Practically, it is unstable between 800 and 1280°C (Buscaglia *et al.*, 1994; Segadães *et al.*, 1998). Some additions can improve the stability. For example, the addition of magnesia (MgO) is generally used to promote solid solution with higher chemical stability (Wohlfrohm *et al.*, 1990; Buscaglia *et al.*, 1994). A small quantity (<3%) of silica leads to a small amount of liquid phase during sintering and a slight increase of the mechanical properties which partially compensates the effect of microcracking (Yoleva *et al.*, 2010). The presence of additives in the tialite, as well as their content, also modifies the value of the thermal expansion coefficient (Morishima *et al.*, 1987; Wohlfrohm *et al.*, 1990; Tilloca, 1991; Zhien *et al.*, 1996; Yoleva *et al.*, 2009, 2010; de Arenas, 2012).

Besides a very good thermal shock resistance, tialite exhibits a low wettability with molten metals. A main application is in the non-ferrous metals foundry and especially for aluminum smelting and casting: as crucibles, pouring spouts, riser tubes, ladles, etc. (Takabatake, 1978; Alecu *et al.*, 2002; Ewais *et al.*, 2017). Recently, a group of researchers even demonstrated the possibility to use aluminum titanate in the automotive sector as a filter for light duty diesel applications (Boger *et al.*, 2011).

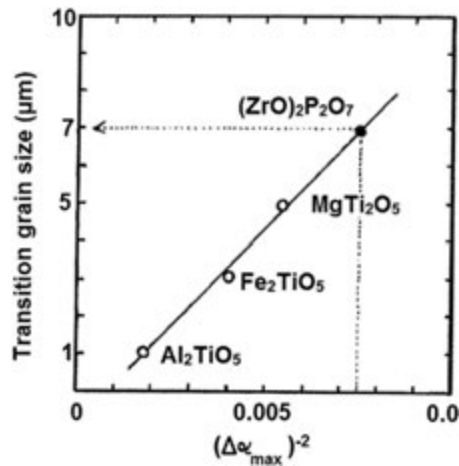


Fig. 7 Comparison of transition grain size as a function of thermal expansion anisotropy. Reproduced from Yamai, I., Oota, T., 1985. Low-thermal-expansion polycrystalline zirconyl phosphate ceramic. *Journal of the American Ceramic Society* 68 (5), 273–278. doi:10.1111/j.1151-2916.1985.tb15321.x.

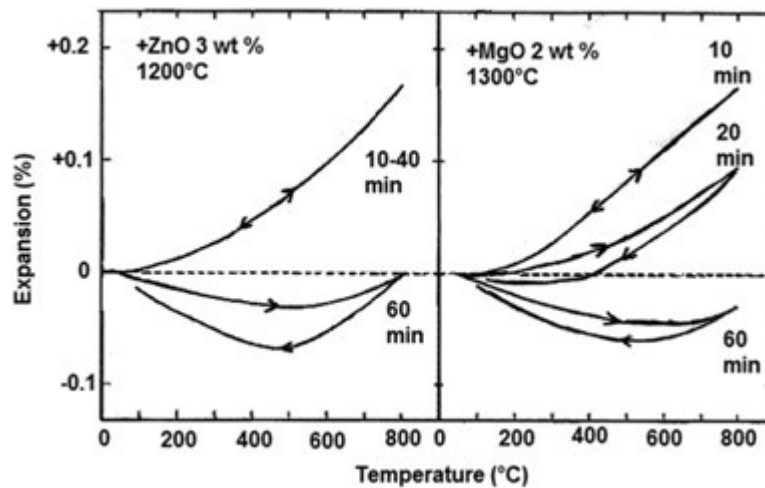


Fig. 8 Variation of thermal expansion with sintering time for zirconyl phosphate containing different additives. Reproduced from Yamai, I., Oota, T., 1985. Low-thermal-expansion polycrystalline zirconyl phosphate ceramic. *Journal of the American Ceramic Society* 68 (5), 273–278. doi:10.1111/j.1151-2916.1985.tb15321.x.

Zirconyl Phosphate and NZP Materials

Zirconyl phosphate

Zirconyl pyrophosphate $(\text{ZrO})_2\text{P}_2\text{O}_7$ exhibits a high thermal expansion anisotropy ($\alpha_a = 3.6 \times 10^{-6} \text{ K}^{-1}$, $\alpha_b = -5 \times 10^{-6} \text{ K}^{-1}$, $\alpha_c = 6.4 \times 10^{-6} \text{ K}^{-1}$) and thus a low average resulting thermal expansion: $1.7 \times 10^{-6} \text{ K}^{-1}$ (Yamai and Oota, 1985; Pilate and Tirlocq, 1994; Pilate *et al.*, 1998). Zirconyl phosphate powder can be obtained from a chemical process followed by a calcination. Final materials are obtained from a classical ceramic process including shaping and sintering at high temperature. Due to its very difficult densification, the sintering of zirconyl phosphate requires a firing temperature near that of decomposition (1600°C). However, the addition of an additive, such as MgO or ZnO, allows this temperature to be reduced to between 1250 and 1300°C by the formation of a liquid phase (Yamai and Oota, 1985; Pilate and Tirlocq, 1994).

Contrary to aluminum titanate, the critical grain size of zirconyl phosphate is relatively high: $G_{cr} \approx 7 \mu\text{m}$ as reported in Figs. 7 and 3 (Yamai and Oota, 1985; Yamai and Ota, 1993). Therefore, it is easy to synthesize a material without any microcracking or with near theoretical thermal expansion as can be seen in Fig. 8 (Yamai and Oota, 1985). Depending on the sintering conditions (additives, temperature and time), Fig. 8 shows it is possible to obtain materials from positive to negative thermal expansion and with or without hysteresis of the thermal expansion curve (Yamai and Oota, 1985).

Zirconyl phosphate is stable up to 1600°C . Dense materials can withstand severe thermal shock with temperature difference higher than 500K . However, heating to a temperature higher than 1200°C leads to an exaggerated grain growth with appearance of defects (microcracking) and a decrease of mechanical properties. This can be hindered by addition of inhibitors such as silica which allows a material to be obtained with higher microstructure stability (Yamai and Oota, 1985; Yamai and Ota, 1987).

Table 3 Thermal expansion and critical grain size of $\text{NaZr}_2(\text{PO}_4)_3$ family of materials

$\text{NaZr}_2(\text{PO}_4)_3$ family	Thermal expansion coefficient ($\text{K}^{-1} \times 10^{-6}$) ^a				
	α_a	α_c	α_{avg} ^b	$\Delta\alpha_{max}$	G_{cr} (μm)
$\text{KZr}_2(\text{PO}_4)_3$	− 4.4	+ 7.6	− 0.4	12.0	5.5
$\text{KTi}_2(\text{PO}_4)_3$	0.0	+ 7.8	+ 2.6	7.8	13
$\text{CaZr}_4(\text{PO}_4)_6$	− 4.8	+ 14.3	+ 1.6	19.1	2.0
$\text{SrZr}_4(\text{PO}_4)_6$	+ 2.6	+ 1.7	+ 2.3	0.9	> 50
$\text{Na}_{0.25}\text{Nb}_{0.75}\text{Zr}_{1.25}(\text{PO}_4)_3$	− 3.4	+ 6.0	− 0.3	9.4	9.0
$\text{NbZr}(\text{PO}_4)_3$	− 3.4	+ 1.2	− 1.9	4.6	21

^aAverage from room temperature to 1200°C.^b α_{avg} was calculated by $\alpha_{avg} = (\alpha_a + \alpha_c)/3$ (Pet'kov and Asabina, 2004).

Note: Oota, T., Yamai, I., 1986. Thermal expansion behavior of $\text{NaZr}_2(\text{PO}_4)_3$ type compounds. Journal of the American Ceramic Society 69 (1), 1–6. doi:10.1111/j.1151-2916.1986.tb04682.x. Yamai, I., Ota, T., Jin, P., 1988. Low-thermal-expansion ceramics of $\text{Na}_{1-x}\text{Nb}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ System Journal of the Ceramic Society of Japan 96 (1118), 1019–1024. doi:10.2109/jcersj.96.1019. Ota, T., Jin I., 1989. Yamai Low thermal expansion and low thermal expansion anisotropy ceramic of $\text{Sr}_{0.5}\text{Zr}_{1.5}(\text{PO}_4)_3$ system. Journal of Materials Science 24 (12), 4239–4245. doi:10.1007/BF00544493. Yamai, I., Ota, T., 1992. Thermal expansion of homogeneous and gradient solid solutions in the system $\text{KZr}_2(\text{PO}_4)_3\text{KTi}_2(\text{PO}_4)_3$ Journal of the American Ceramic Society 75 (8), 2276–2282. doi:10.1111/j.1151-2916.1992.tb04495.x.

Due to its high temperature of decomposition (higher than that of cordierite), zirconyl phosphate is a good candidate for applications as a heat-resistant material. It should be noted that its low strength does not allow its use as a structural material (Omori *et al.*, 1992). Zirconyl phosphate materials could be used for applications which require excellent thermal shock resistance and heat resistance (Watanabe and Ohashi, 1989; Limaye, 1996). Moreover, it seems to be attractive for use as mineral ion exchangers for waste treatment (Baetslé and Pelsmaekers, 1961).

NZP materials

NZP products are also materials based on zirconium phosphate. They are based on the main product with chemical formula: NaZr_2PO_4 . The ions Zr^{4+} and P^{5+} can be substituted to obtain products such as: $\text{Na}_{1+x}\text{Zr}(\text{Si}_x\text{P}_{3-x})\text{O}_{12}$, $\text{Na}_{1-x}\text{Nb}_x\text{Zr}_{2-x}(\text{PO}_4)_3$, $\text{Na}_{1+2x}\text{MgZr}_{2-x}(\text{PO}_4)_3$, etc. (Oota and Yamai, 1986; Yamai *et al.*, 1988; Ota *et al.*, 1989; Yamai and Ota, 1992; Pet'kov and Asabina, 2004; Miyazaki *et al.*, 2008).

These materials also exhibit high thermal expansion differences. The expansion difference and the critical grain size depend on the nature and the level of ionic substitutions (Table 3) which leads to crystallographic modifications (Oota and Yamai, 1986; Yamai *et al.*, 1988; Ota *et al.*, 1989; Yamai and Ota, 1992). Table 3 shows that NZP materials exhibit a very large range of thermal expansion anisotropy and critical grain size (Oota and Yamai, 1986; Yamai *et al.*, 1988; Ota *et al.*, 1989; Yamai and Ota, 1992).

Due to their low thermal expansion and high ionic substitutions capacity, NZP materials are especially attractive for many applications such as fast ionic conductors, devices requiring good thermal shock resistance and catalyst supports in automobiles (Agrawal *et al.*, 1991, 1996; Limaye, 1996). These materials are also attractive as host ceramic for nuclear waste immobilization (Scheetz *et al.*, 1994) or as protective coatings for thermal barrier protection (Limaye *et al.*, 1989; Brown *et al.*, 1992; Breval *et al.*, 2000).

Glass-Ceramic Materials

Glass-ceramics are obtained from reheating of special glasses, usually at two different nucleation and growth temperatures, inducing the crystallization of micro-crystals. Resulting materials consist of micro-crystals dispersed in a glassy bonding phase (Stookey, 1960; Donald, 1993; Beall and Pinckney, 2004). They are very interesting materials because they combine both glass properties (optical, zero porosity) and ceramic properties (mechanical, thermal). These properties mainly depend on the crystal nature. The crystallization of low thermal expansion compounds allows materials to be obtained with low average thermal expansion and therefore products exhibit a good thermal shock resistance. Another advantage of a low thermal expansion is the very high dimensional stability with respect to the temperature.

Cordierite

Glass-ceramics are produced whose micro-crystals are cordierite (Rudolph *et al.*, 1991; Chowdhury *et al.*, 2007). For example, Corning® Pyroceram® is a cordierite (see above) type glass-ceramic. It is a strong material, with a high thermal conductivity and a low dielectric constant (Rudolph *et al.*, 1991). Although its thermal expansion coefficient is not very low ($5.7 \times 10^{-6} \text{ K}^{-1}$ in the range 25–300°C), it can withstand high thermal shock. It is also transparent to radar (Orlova *et al.*, 2015). Main uses of cordierite glass-ceramic are as cook ware, tactical missile nosecones, antenna windows, radomes, solid wave guides and hydrospace systems (Beall, 2009; Orlova *et al.*, 2015).



Fig. 9 LAS glass-ceramic cook top panel manufactured by Corning.

LAS Compounds

The $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (LAS) system contains two different stable ternary compounds: β -eucryptite (LAS 1-1-2) and β -spodumene (LAS 1-1-4) (Nordmann and Cheng, 1997; Rebouças *et al.*, 2019). A solid solution exists between β -eucryptite and β -spodumene, and between β -spodumene and silica (up to 1-1-10).

β -eucryptite exhibits a high anisotropy of thermal expansion and a highly negative expansion along the c axis ($\alpha_a = 7.8 \times 10^{-6} \text{ K}^{-1}$, $\alpha_c = -17.5 \times 10^{-6} \text{ K}^{-1}$, from room temperature to 1100°C) (Schulz, 1974). β -spodumene exhibits a low positive expansion along the a axis ($0.9 \times 10^{-6} \text{ K}^{-1}$) which decreases with silica content of the solid solution (up to $0.3 \times 10^{-6} \text{ K}^{-1}$) (Ostertag *et al.*, 1968). The β -eucryptite – β -spodumene solid solution exhibits an average negative thermal expansion (Xia *et al.*, 2012). After crystallization, LAS glass-ceramics contain both spodumene and eucryptite. The control of the crystallization step allows materials to be obtained with thermal expansion coefficients ranging from 0 to $13 \times 10^{-6} \text{ K}^{-1}$. The control of the fabrication process also leads to materials transparent to visible and infrared light. LAS glass-ceramics are used for domestic (cook top panel (Fig. 9), stove windows, cookware) and technical applications (advanced optics for telescope mirror) (Bach, 1995; Pannhorst, 2004; Xiao *et al.*, 2011; Buchner *et al.*, 2013; Kleebusch *et al.*, 2018).

Pollucite

Pollucite, of formula $\text{CsAlSi}_2\text{O}_6$ (Beger and Buerger, 1967), is the most refractory silicate. Its melting point is higher than 1900°C (Bedard *et al.*, 1992; Morena, 1992). At 200°C , this material exhibits an allotropic transformation with a volume discontinuity, but at higher temperature, the thermal expansion is low. The thermal expansion coefficient ranges between 0 and $2 \times 10^{-6} \text{ K}^{-1}$ (Richerson and Hummel, 1972; Kobayashi *et al.*, 1997). The sintering of pollucite could only be performed at temperatures higher than 1700°C (He and Jia, 2013). High densification can be obtained from 1650°C by hot pressing. More recent researches demonstrate the possibility to develop highly dense pollucite at very low-temperature: 1200°C by the use of a geopolymer precursor (He and Jia, 2013) and even temperatures lower than 1000°C by the sintering of the Cs-exchanged form of Na, Ca-LTA type of zeolite (Omerašević *et al.*, 2016). Pollucite is used as a zeolite material, in particular in the field of nuclear applications, thanks to its high capacity to retain a large amount of Cs when it is immersed in a fluid phase (Gatta *et al.*, 2009). It could also be attractive as an additive for the improvement of refractoriness of glass-ceramics for us in high temperature applications. For example, glass-ceramics containing pollucite are used as preform cores in the making of hollow metal castings for aeronautic applications which require the use of very high temperature alloys (super alloys of nickel and cobalt base) (Beall and Rittler, 1973).

Celsian

Celsian (BAS, $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is the only compound of the ternary $\text{BaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (Levin and McMurdie, 1975; Drummond, 1990). This material exhibits a crystallographic change at 1590°C from monoclinic to hexagonal (hexacelsian) crystalline structure. The latter polymorph is then stable from 1590°C to the melting point of Celsian (1760°C) (Lin and Foster, 1968; Hoghooghi *et al.*, 2005). However, hexacelsian could be the first phase which appears during the synthesis and it could remain metastable at room temperature (Schmutzler and Sandhage, 1995; Lee and Aswath, 2000). It exhibits a volume change (3%–4%) at 300°C with a rapid structural change from β -hexacelsian (hexagonal) to α -hexacelsian (orthorhombic) (Schmutzler and Sandhage, 1995). Because it does not present any structural modifications, the most interesting phase is the monoclinic one (Schmutzler and Sandhage, 1995).

This crystalline structure can be promoted by high temperature heating, or use of additives such as SrO which forms SAS ($\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). BAS reacts with SAS to form a solid solution (Bansal, 1998). Partial substitution of BaO by SrO allows the monoclinic phase to stabilize up to above 1600°C (Long-González *et al.*, 2010). Moreover, the addition of mineralizers such as Li_2O , MgO, CaO, NaF and TiO_2 generally enhances the hexacelsian to celsian transformation (Lee and Aswath, 2003). Celsian can be synthesized through a solid-state process and can be densified at temperatures close to 1580°C. Its strength can be up to 100–120 MPa depending on the composition (Bansal, 1998; Sedghi and Dadashian, 2015). Celsian materials are attractive due to their high refractoriness and their low thermal expansion coefficient ($2.29 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$, 20–1000°C) (Hoghooghi *et al.*, 2005). It can also be exploited in glass-ceramic materials, radar nose cones, electrical insulators, porcelain, enamel, high-temperature electromagnetic windows (radomes) and matrix material in ceramic composites for thermostructural applications (Miller, 1976; Lansmann and Jansen, 2001; Hoghooghi *et al.*, 2005; Amritphale *et al.*, 2007; Sedghi and Dadashian, 2015).

References

- Agrawal, D.K., 1996. NZP: A new family of low thermal expansion ceramics. *Transactions of the Indian Ceramic Society* 55 (1). 1–8. doi:10.1080/0371750X.1996.10804741.
- Agrawal, D.K., Huang, C.-Y., McKinstry, H.A., 1991. NZP: A new family of low-thermal expansion materials. *International Journal of Thermophysics* 12 (4). 697–710. doi:10.1007/BF00534225.
- Alecu, I.D., *et al.*, 2002. New developments in aluminium titanate ceramics and refractories. *Key Engineering Ceramics* 206, 1705–1710.
- Amritphale, S.S., *et al.*, 2007. Development of celsian ceramics from fly ash useful for X-ray radiation-shielding application. *Journal of the European Ceramic Society* 27 (16). 4639–4647. doi:10.1016/j.jeurceramsoc.2007.03.034.
- Andreev, K., *et al.*, 2017. Refractories for coke oven wall – Operator's perspective. *BHM Berg- und Hüttenmännische Monatshefte* 162 (1). 20–27. doi:10.1007/s00501-016-0563-6.
- Ariyajinno, N., Thiansem, S., 2018. Characterization and properties of cordierite – Mullite refractories from raw materials and Narathiwat clay (in Thailand). *Materials Today: Proceedings* 5 (6). 13948–13953. doi:10.1016/j.matpr.2018.02.045.
- Bach, H., 1995. *Low Thermal Expansion Glass Ceramics*. Schott Series on Glass and Glass Ceramics. Berlin, Heidelberg: Springer. <http://dx.doi.org/10.1007/978-3-662-03083-7>.
- Baetslé, L., Pelsmaekers, J., 1961. Ion exchange properties of zirconyl phosphates – I: Contribution to the structure of zirconyl phosphates. *Journal of Inorganic and Nuclear Chemistry* 21 (1–2). 124–132. doi:10.1016/0022-1902(61)80420-X.
- Bansal, N.P., 1998. Solid state synthesis and properties of monoclinic celsian. *Journal of Materials Science* 33 (19). 4711–4715. doi:10.1023/A:1004484903436.
- Beall, G.H., 2009. Refractory glass-ceramics based on alkaline earth aluminosilicates. *Journal of the European Ceramic Society* 29 (7). 1211–1219. doi:10.1016/j.jeurceramsoc.2008.08.010.
- Beall, G.H., Pinckney, L.R., 2004. Nanophase glass-ceramics. *Journal of the American Ceramic Society* 82 (1). 5–16. doi:10.1111/j.1151-2916.1999.tb01716.x.
- Beall, G., Rittler, H., 1973. Glass-ceramics containing pollucite. Google Patents.
- Bedard, R.L., Broach, R.W., Flanigen, E.M., 1992. Leucite-pollucite glass ceramics: A new family of refractory materials with adjustable thermal-expansion. *MRS Proceedings* 271. 581doi:10.1557/PROC-271-581.
- Beger, R.M., Buerger, M.J., 1967. The crystal structure of the mineral pollucite. *Proceedings of the National Academy of Sciences* 58 (3). 853–854. doi:10.1073/pnas.58.3.853.
- Boger, T., *et al.*, 2011. Next Generation Aluminum Titanate Filter for Light Duty Diesel Applications. SAE International.
- Brevai, E., McKinstry, H.A., Agrawal, D.K., 2000. New [NZP] materials for protection coatings. Tailoring of thermal expansion. *Journal of Materials Science* 35 (13). 3359–3364. doi:10.1023/A:1004828917908.
- Brown, J. *et al.*, 1992. Ceramic materials with low thermal conductivity and low coefficients of thermal expansion. Google Patents.
- Brunk, F., 2000. Silica bricks for modern coke oven batteries. *Coke Making International* 12 (2). 37–40.
- Brunk, F., 2001. Silica refractories. *InterCeram: International Ceramic Review*. 27–30.
- Buchner, S., *et al.*, 2013. Comparison of the mechanical and tribological properties of a sintered low expansion $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass-ceramic and a commercial cooktop plate. *Glass* 54 (6). 211–217.
- Buckley, J., 1995. No-Draft Slip-Casting With Low CTE Materials. 1995. Sterling Publications Ltd. pp. 46–47.
- Buckley, J.D., Strouhal, G., Gangler, J.J., 1981. Early development of ceramic fiber insulation for the space shuttle. *The Bulletin of the American Ceramic Society* 60 (11).
- Buscaglia, V., *et al.*, 1994. Reaction sintering of aluminium titanate: I – Effect of MgO addition. *Journal of the European Ceramic Society* 13 (5). 411–417. doi:10.1016/0955-2219(94)90018-3.
- Camerucci, M.A., Urretavizcaya, G., Cavalieri, A.L., 2003. Sintering of cordierite based materials. *Ceramics International* 29 (2). 159–168. doi:10.1016/S0272-8842(02)00100-1.
- Carvill, J., 1993. Engineering materials. In *Mechanical Engineer's Data Handbook*. Elsevier. pp. 218–266. doi:10.1016/B978-0-08-051135-1.50011-X.
- Chlup, Z., *et al.*, 2005. Thermal shock resistance of cordierite-mullite refractory composites. *Key Engineering Materials* 290, 260–263. doi:10.4028/www.scientific.net/KEM.290.260.
- Chowdhury, A., *et al.*, 2007. Synthesis, properties and applications of cordierite ceramics. *InterCeram: International Ceramic Review* 56, 98–102.
- Cleveland, J.J., Bradt, R.C., 1978. Grain size/microcracking relations for pseudobrookite oxides. *Journal of the American Ceramic Society* 61 (11–12). 478–481. doi:10.1111/j.1151-2916.1978.tb16121.x.
- Collins, J.G., White, G.K., 1964. Chapter IX – Thermal expansion of solids. In *Progress in Low Temperature Physics*. Elsevier. pp. 450–479. 10.1016/S0079-6417(08)60157-2
- Costa Oliveira, F.A., Cruz Fernandes, J., 2002. Mechanical and thermal behaviour of cordierite-zirconia composites. *Ceramics International* 28 (1). 79–91. doi:10.1016/S0272-8842(01)00061-X.
- Criss, G.H., 1991. Fused silica refractories for industrial applications. *Materials Science Forum* 34–36, 689–694. doi:10.4028/www.scientific.net/MSF.34-36.689.
- Darnell, F.J., 1963. Temperature dependence of lattice parameters for Gd, Dy, and Ho. *Physical Review* 130 (5). 1825–1828. doi:10.1103/PhysRev.130.1825.
- de Arenas, I.B., 2012. Chapter 22 – Reactive sintering of aluminum titanate. In: Lakshmanan, A. (Ed.), *Sintering of Ceramics-New Emerging Techniques*. IntechOpen.
- Donald, I.W., 1993. Preparation, properties and chemistry of glass- and glass-ceramic-to-metal seals and coatings. *Journal of Materials Science* 28 (11). 2841–2886. doi:10.1007/BF00354689.
- Drummond, C.H., 1990. Glass formation and crystallization in high-temperature glass-ceramics and Si_3N_4 . *Journal of Non-Crystalline Solids* 123 (1–3). 114–128. doi:10.1016/0022-3093(90)90778-K.
- Evans, D.L., *et al.*, 1980. Thermal expansions and chemical modifications of cordierite. *Journal of the American Ceramic Society* 63 (11–12). 629–634. doi:10.1111/j.1151-2916.1980.tb09850.x.
- Ewaïs, E.M.M., Besisa, N.H.A., Ahmed, A., 2017. Aluminum titanate based ceramics from aluminum sludge waste. *Ceramics International* 43 (13). 10277–10287. doi:10.1016/j.ceramint.2017.05.057.
- Freudenberg, B., Mocellin, A., 1990. Aluminium titanate formation by solid state reaction of Al_2O_3 and TiO_2 single crystals. *Journal of Materials Science* 25 (8). 3701–3708. doi:10.1007/BF00575408.
- Gatta, G.D., *et al.*, 2009. On the crystal structure and crystal chemistry of pollucite, $(\text{Cs},\text{Na})_{16}\text{Al}_{16}\text{Si}_{32}\text{O}_{96} \cdot n\text{H}_2\text{O}$: A natural microporous material of interest in nuclear technology. *American Mineralogist* 94 (11–12). 1560–1568. doi:10.2138/am.2009.3237.

- He, P., Jia, D., 2013. Low-temperature sintered pollucite ceramic from geopolymer precursor using synthetic metakaolin. *Journal of Materials Science* 48 (4). 1812–1818. doi:10.1007/s10853-012-6944-7.
- Heisler, H., 1995. *Advanced Engine Technology*. London: Arnold.
- Hoghooghi, B., *et al.*, 2005. Microstructural development, densification, and hot pressing of celsian ceramics from ion-exchanged zeolite precursors. *Journal of the American Ceramic Society* 81 (4). 845–852. doi:10.1111/j.1151-2916.1998.tb02418.x.
- Ibrahim, D.M., *et al.*, 1995. Cordierite-mullite refractories. *Ceramics International* 21 (4). 265–269. doi:10.1016/0272-8842(95)99792-A.
- Ikawa, H., *et al.*, 1986. Crystal structures and mechanism of thermal expansion of high cordierite and its solid solutions. *Journal of the American Ceramic Society* 69 (6). 492–498. doi:10.1111/j.1151-2916.1986.tb07451.x.
- Keith, M.L., Schairer, J.F., 1952. The stability field of sapphirine in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$. *The Journal of Geology* 60 (2). 181–186. doi:10.1086/625947.
- Kingery, W.D., 1955. Factors affecting thermal stress resistance of ceramic materials. *Journal of the American Ceramic Society* 38 (1). 3–15. doi:10.1111/j.1151-2916.1955.tb14545.x.
- Kleebusch, E., *et al.*, 2018. The effect of TiO_2 on nucleation and crystallization of a $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ glass investigated by XANES and STEM. *Scientific Reports* 8 (1). 2929. doi:10.1038/s41598-018-21227-x.
- Kobayashi, H., Yanase, I., Mitamura, T., 1997. A new model for the pollucite thermal expansion mechanism. *Journal of the American Ceramic Society* 80 (8). 2161–2164. doi:10.1111/j.1151-2916.1997.tb03104.x.
- Korb, L.J., 1981. The shuttle orbiter thermal protection system. *Ceramic Bulletin*. 1188–1193.
- Kuszyk, J.A., Bradt, R.C., 1973. Influence of grain size on effects of thermal expansion anisotropy in MgTi_2O_5 . *Journal of the American Ceramic Society* 56 (8). 420–423. doi:10.1111/j.1151-2916.1973.tb12714.x.
- Lansmann, V., Jansen, M., 2001. Application of the glass-ceramic process for the fabrication of whisker reinforced celsian-composites. *Journal of Materials Science* 36 (6). 1531–1538. doi:10.1023/A:101756116431.
- Lee, K.-T., Aswath, P.B., 2000. Synthesis of hexacelsian barium aluminosilicate by a solid-state process. *Journal of the American Ceramic Society* 83 (12). 2907–2912. doi:10.1111/j.1151-2916.2000.tb01659.x.
- Lee, K.-T., Aswath, P.B., 2003. Role of mineralizers on the hexacelsian to celsian transformation in the barium aluminosilicate (BAS) system. *Materials Science and Engineering: A* 352 (1–2). 1–7. doi:10.1016/S0921-5093(02)00118-1.
- Levin, E.M., McMurdie, H.F., 1975. Phase diagrams for ceramists, 1975 supplement.
- Limaye, S.Y., *et al.*, 1989. Low expansion ceramic. Available at: <https://patents.google.com/patent/US4801566A/en> (accessed 12.08.19).
- Limaye, S.Y., 1996. Ultra low thermal expansion, highly thermal shock resistant ceramic. Google Patents.
- Lin, H.C., Foster, W.R., 1968. Studies in the system $\text{BaO-Al}_2\text{O}_3\text{-SiO}_2$ I. The polymorphism of celsian. *American Mineralogist: Journal of Earth and Planetary Materials* 53 (1–2). 134–144.
- Long-González, D., *et al.*, 2010. Synthesis of monoclinic celsian from coal fly ash by using a one-step solid-state reaction process. *Ceramics International* 36 (2). 661–672. doi:10.1016/j.ceramint.2009.10.008.
- Manivasakan, P., *et al.*, 2010. Effect of TiO_2 nanoparticles on properties of silica refractory: Effect of TiO_2 nanoparticles on silica refractory. *Journal of the American Ceramic Society* 93 (8). 2236–2243. doi:10.1111/j.1551-2916.2010.03727.x.
- Miller, D.M., 1976. Refractory celsian glass-ceramics. Google Patents.
- Mishra, S., Mitra, R., Vijayakumar, M., 2010. Structure–property correlation in cellular silica processed through hydrophobized fused silica powder for aerospace application. *Journal of Alloys and Compounds* 504 (1). 76–82. doi:10.1016/j.jallcom.2010.05.056.
- Miyazaki, H., *et al.*, 2008. Thermal expansion of $\text{NaZr}_2(\text{PO}_4)_3$ family ceramics in a low-temperature range. *Japanese Journal of Applied Physics* 47 (9). 7262–7265. doi:10.1143/JJAP.47.7262.
- Morena, R.M., 1992. Preparation of pollucite ceramics. Google Patents.
- Morishima, H., *et al.*, 1987. Synthesis of aluminium titanate-mullite composite having high thermal shock resistance. *Journal of Materials Science Letters* 6 (4). 389–390.
- Nordmann, A., Cheng, Y.-B., 1997. Crystallization behaviour and microstructural evolution of a $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ glass derived from spodumene mineral. *Journal of Materials Science* 32 (1). 83–89. doi:10.1023/A:1018519030791.
- Ohya, Y., *et al.*, 2017. Thermal expansion and mechanical properties of self-reinforced aluminum titanate ceramics with elongated grains. *Journal of the European Ceramic Society* 37 (4). 1673–1680. doi:10.1016/j.jeurceramsoc.2016.11.037.
- Omerasević, M., *et al.*, 2016. Safe trapping of cesium into pollucite structure by hot-pressing method. *Journal of Nuclear Materials* 474. 35–44. doi:10.1016/j.jnucmat.2016.03.006.
- Omori, M., *et al.*, 1992. Thermal and dielectric properties of zirconyl phosphate compact. *Journal of Materials Science* 27 (2). 408–412. doi:10.1007/BF00543930.
- Oota, T., Yamai, I., 1986. Thermal expansion behavior of $\text{NaZr}_2(\text{PO}_4)_3$ type compounds. *Journal of the American Ceramic Society* 69 (1). 1–6. doi:10.1111/j.1151-2916.1986.tb04682.x.
- Orlova, L.A., *et al.*, 2015. Recent advances in radio transparent glass-ceramic materials based on high-temperature aluminosilicate systems. *Russian Journal of Inorganic Chemistry* 60 (13). 1692–1707. doi:10.1134/S0036023615130045.
- Ostertag, W., Fischer, G.R., Williams, J.P., 1968. Thermal expansion of synthetic β -spodumene and β -spodumene-silica solid solutions. *Journal of the American Ceramic Society* 51 (11). 651–654. doi:10.1111/j.1151-2916.1968.tb12638.x.
- Ota, T., Jin, P., Yamai, I., 1989. Low thermal expansion and low thermal expansion anisotropy ceramic of $\text{Sr}_{0.5}\text{Zr}_{1.5}(\text{PO}_4)_3$ system. *Journal of Materials Science* 24 (12). 4239–4245. doi:10.1007/BF00544493.
- Pannhorst, W., 2004. Recent developments for commercial applications of low thermal expansion glass ceramics. *Glass Technology - European Journal of Glass Science and Technology Part A* 45, 51–53.
- Parker, F.J., Rice, R.W., 1989. Correlation between grain size and thermal expansion for aluminum titanate materials. *Journal of the American Ceramic Society* 72 (12). 2364–2366. doi:10.1111/j.1151-2916.1989.tb06091.x.
- Pereira, A.H.A., *et al.*, 2014. A study about the contribution of the α - β phase transition of quartz to thermal cycle damage of a refractory used in fluidized catalytic cracking units. *Cerâmica* 60, 449–456.
- Pet'kov, V.I., Asabina, E.A., 2004. Thermophysical properties of NZP ceramics (A Review). *Glass and Ceramics* 61 (7/8). 233–239. doi:10.1023/B:GLAC.0000048353.42467.0a.
- Pilate, P., Tirloq, J., 1994. Liquid phase sintering and characterization of thermal shock resistant zirconyl phosphate materials. *Silicates Industriels* 59 (11–12). 321–325.
- Pilate, P., Cambier, F., Tirloq, J., 1998. Synthesis and characterisation of zirconyl phosphate based composites. *Silicates Industriels* 63 (1–2). 7–11.
- Postrach, S., *et al.*, 2009. State-of-the-art refractory linings for float glass furnaces. *Refractories World Forum* 1 (2). 80–83.
- Rebouças, L.B., *et al.*, 2019. Characterization of $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ glass-ceramics produced from a Brazilian spodumene concentrate. *Cerâmica* 65 (375). 366–377. doi:10.1590/0366-69132019653752699.
- Rice, R.W., Pohanka, R.C., 1979. Grain-size dependence of spontaneous cracking in ceramics. *Journal of the American Ceramic Society* 62 (11–12). 559–563. doi:10.1111/j.1151-2916.1979.tb12730.x.
- Richerson, D.W., Hummel, F.A., 1972. Synthesis and thermal expansion of polycrystalline cesium minerals. *Journal of the American Ceramic Society* 55 (5). 269–273. doi:10.1111/j.1151-2916.1972.tb11278.x.
- Robyn, P., Deschepper, P., 1985. Adding to silica refractory structures. Available at: <https://patents.google.com/patent/US4542888A/en> (accessed 30.10.19).
- Routshchka, G., Granitzki, K.-E., 2000. Refractory ceramics. In *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA.
- Rudolph, T., *et al.*, 1991. Microstructural development of a P_2O_5 -modified cordierite glass ceramic during sintering. *Glastech. Ber* 64 (8). 141–147.
- Scheetz, B.E., *et al.*, 1994. Sodium zirconium phosphate (NZP) as a host structure for nuclear waste immobilization: A review. *Waste Management* 14 (6). 489–505. doi:10.1016/0956-053X(94)90133-3.

- Schmutzler, H.J., Sandhage, K.H., 1995. Transformation of Ba-Al-Si precursors to celsian by high-temperature oxidation and annealing. *Metallurgical and Materials Transactions B* 26 (1). 135–148. doi:10.1007/BF02648986.
- Schneider, H., Majdic, A., Vasudevan, R., 1986. Kinetics of the quartz-cristobalite transformation in refractory-grade silica materials. *Materials Science Forum* 7, 91–102. doi:10.4028/www.scientific.net/MSF.7.91.
- Schulz, H., 1974. Thermal expansion of Beta eucryptite. *Journal of the American Ceramic Society* 57 (7). 313–318. doi:10.1111/j.1151-2916.1974.tb10909.x.
- Sedghi, A., Dadashian, S., 2015. Solid state synthesis of celsian barium aluminosilicate by a multistep firing technique. *Advances in Materials and Processing Technologies* 1 (3–4). 484–492. doi:10.1080/2374068X.2015.1128172.
- Segadaes, A.M., Morelli, M.M., Kiminami, R.H.G.A., 1997. Combustion synthesis of aluminium titanate: Thermal stability. *Key Engineering Materials* 132–136, 209–212. doi:10.4028/www.scientific.net/KEM.132-136.209.
- Segadaes, A.M., Morelli, M.R., Kiminami, R.G.A., 1998. Combustion synthesis of aluminium titanate. *Journal of the European Ceramic Society* 18 (7). 771–781. doi:10.1016/S0955-2219(98)00004-1.
- Smart, R.M., Glasser, F.P., 1981. The subsolidus phase equilibria and melting temperatures of $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ compositions. *Ceramics International* 7 (3). 90–97. doi:10.1016/0272-8842(81)90003-1.
- Son, M.-A., *et al.*, 2019. Structural origin of negative thermal expansion of cordierite honeycomb ceramics and crystal phase evolution with sintering temperature. *Journal of the European Ceramic Society* 39 (7). 2484–2492. doi:10.1016/j.jeurceramsoc.2019.02.017.
- Stokey, S.D., 1960. Method of making ceramics and product thereof. Google Patents.
- Sziroczak, D., Smith, H., 2016. A review of design issues specific to hypersonic flight vehicles. *Progress in Aerospace Sciences* 84, 1–28.
- Takabatake, M., 1978. Aluminum titanate composition being stable at high temperature. Google Patents.
- Tilloc, G., 1991. Thermal stabilization of aluminium titanate and properties of aluminium titanate solid solutions. *Journal of Materials Science* 26 (10). 2809–2814.
- Vepa, S.S.V.S.S., Umarji, A.M., 1993. Effect of substitution of Ca on thermal expansion of cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$). *Journal of the American Ceramic Society* 76 (7). 1873–1876. doi:10.1111/j.1151-2916.1993.tb06664.x.
- Watanabe, K., Ohashi, T., 1989. Heat resisting low expansion zirconyl phosphate-zircon composite. Google Patents.
- Wohlfromm, H., *et al.*, 1992. Al_2TiO_5 formation in alumina/titania multilayer composites. *Journal of the American Ceramic Society* 75 (12). 3473–3476. doi:10.1111/j.1151-2916.1992.tb04453.x.
- Wohlfromm, H., Moya, J.S., Pena, P., 1990. Effect of ZrSiO_2 and MgO additions on reaction sintering and properties of Al_2TiO_5 -based materials. *Journal of Materials Science* 25 (8). 3753–3764. doi:10.1007/BF00575415.
- Xia, L., *et al.*, 2012. Nearly zero thermal expansion of β -spodumene glass ceramics prepared by sol-gel and hot pressing method. *Ceramics International* 38 (6). 5315–5318. doi:10.1016/j.ceramint.2012.03.004.
- Xiao, Z., *et al.*, 2011. Microstructure and properties of $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-P}_2\text{O}_5$ glass-ceramics. *Open Materials Science Journal* 5, 45–50.
- Yamahara, K., *et al.*, 2001. Surface of silica glass reacting with silicon melt: Effect of Raw Materials for Silica Crucibles. *Japanese Journal of Applied Physics* 40 (Part 1, 3A). 1178–1182. doi:10.1143/JJAP.40.1178.
- Yamai, I., Ota, T., 1985. Low-thermal-expansion polycrystalline zirconyl phosphate ceramic. *Journal of the American Ceramic Society* 68 (5). 273–278. doi:10.1111/j.1151-2916.1985.tb15321.x.
- Yamai, I., Ota, T., 1987. Low-thermal-expansion polycrystalline zirconyl phosphate ceramic: Solid-solution and microcracking-related properties. *Journal of the American Ceramic Society* 70 (8). 585–590. doi:10.1111/j.1151-2916.1987.tb05711.x.
- Yamai, I., Ota, T., 1992. Thermal expansion of homogeneous and gradient solid solutions in the system $\text{KZr}_2(\text{PO}_4)_3\text{-KTi}_2(\text{PO}_4)_3$. *Journal of the American Ceramic Society* 75 (8). 2276–2282. doi:10.1111/j.1151-2916.1992.tb04495.x.
- Yamai, I., Ota, T., 1993. Grain size-microcracking relation for $\text{NaZr}_2(\text{PO}_4)_3$ family ceramics. *Journal of the American Ceramic Society* 76 (2). 487–491. doi:10.1111/j.1151-2916.1993.tb03811.x.
- Yamai, I., Ota, T., Jin, P., 1988. Low-thermal-expansion ceramics of $\text{Na}_{1-x}\text{Nb}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ System. *Journal of the Ceramic Society of Japan* 96 (1118). 1019–1024. doi:10.2109/jcersj.96.1019.
- Yamuna, A., 2004. Kaolin-based cordierite for pollution control. *Journal of the European Ceramic Society* 24 (1). 65–73. doi:10.1016/S0955-2219(03)00269-3.
- Yoleva, A., *et al.*, 2010. Effect of SiO_2 addition on thermal hysteresis of aluminum titanate. *Journal of the University of Chemical Technology and Metallurgy* 45 (3). 269–274.
- Yoleva, A., Hristov, V., Djambazov, S., 2009. Aluminum titanate ceramic with mullite addition. *Ceramics-Silikáty* 53 (1).
- Zhien, L., Qingmin, Z., Jianjun, Y., 1996. The effects of additives on the properties and structure of hot-pressed aluminium titanate ceramics. *Journal of Materials Science* 31 (1). 90–94. doi:10.1007/BF00355131.

Relevant Websites

- <https://www.final-materials.com/gb/52-aluminium-titanate-al2tio5>
Aluminium titanate Al_2TiO_5 .
Final Advanced Materials
- https://www.ceramtec.com/files/ct_alutit_aluminum_titanate_en.pdf
Aluminium Titanate ALUTIT.
CeramTec.
The Ceramic Experts.
- <https://nishimuraac.com/458>
Aluminum Titanate crucible.
- <https://www.corning.com/worldwide/en.html>
Corning.
Materials Science Technology and Innovation.
- <https://www.vesuvius.com/en/our-solutions/fr-fr/iron-and-steel/steel-finishing/electrical-steel.html>
Electrical Steel.
Vesuvius.
- https://www.castablerefractory.com/hot_blast_stove_refractory/silica-bricks-hot-blast-stove.html
Silica Bricks for Hot Blast Stove.
Rongsheng Refractory.
- <http://www.cncunse.com/refractroy-material-hot-blast-stove/silica-brick.html>
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Mullite: Structure and Properties

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Introduction

Silica and alumina are the most used oxides to manufacture ceramic materials, devoted to everyday life or to more technical or functional applications. Within this binary system, mullite occurs as the predominant defined composition, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, exhibiting a congruent melting under atmospheric pressure (Duval *et al.*, 2008; Schneider *et al.*, 2015). The term mullite originates from the Isle of Mull in Scotland (Fig. 1(a)) where the mineral was first discovered by Bowen and Greig (1924). The naturally occurring mullite is found in very few deposits due to the very atypical and harsh conditions (high temperature and low pressure) required for its formation. The main deposits are located in Scotland (Isle of Mull), in Germany (Eifel mountains), etc. In these deposits, mullite resulted from the interactions of superheated magma with alumina-rich sediments, the high temperature metamorphic rocks of the sanidinite facies or the lightning impacts in sandstones leading to aluminosilicate lechatelierite glasses. An illustration of the shape of naturally occurring mullite is provided in Fig. 1(b). Due to the scarcity of mullite deposits, most mullite or mullite-based products are synthesized. The starting materials commonly used to manufacture mullite products are widely abundant on earth, namely: bauxite, kyanite, silica and aluminosilicate materials (kaolin, sillimanite, andalusite, etc).

Mullite has the following general chemical formula $\text{Al}_2^{\text{VI}}(\text{Si}_{2-2x}^{\text{IV}}\text{Al}_{2+2x}^{\text{IV}})\text{O}_{10-x}$ or $\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$, where x can vary between 0.2 and 0.9 (corresponding to the range 55–90 mol% or 71–96 wt% of Al_2O_3 respectively) (Fischer *et al.*, 1996). In the first formula, $\text{Al}_2^{\text{VI}}(\text{Si}_{2-2x}^{\text{IV}}\text{Al}_{2+2x}^{\text{IV}})\text{O}_{10-x}$, IV and VI represent the tetrahedral and octahedral locations, respectively, of these cations in the structure of mullites. Accordingly, mullite can be considered as a solid solution within the binary system alumina-silica, whereby the value of x tends to increase with increasing temperature. The most common form of mullite in ceramics is the 3:2 mullite ($x = 0.25$, corresponding to 72 wt% of Al_2O_3). 2:1 mullite can also be obtained in some cases and corresponds to $x = 0.4$ (Aksay *et al.*, 1991; Aryal *et al.*, 2012; Klar *et al.*, 2017). Nevertheless, depending on the starting reagents, the processing route and the sintering temperature, the final mullite phase can be tuned in agreement with the target application. The phases corresponding to $x = 0$ (Al_2SiO_5), namely kyanite, sillimanite and andalusite have not been considered since they tend to form at higher pressure (Belnou, 2002; Duval *et al.*, 2008) (>10 kPa) compared to mullite in the binary system alumina-silica. Nevertheless, these phases are widely abundant and are used as starting materials to produce mullite. Techniques such as sol-gel, hydrolysis, and precipitation, plasma processing and sintering have been used to produce synthetic mullite and mullite-based materials. The great interest of mullite products relies on its good stability (thermal shock, corrosion and chemical resistance) and on the low coefficient of thermal expansion of mullite that promotes its use in high temperature (refractory) and coating (protection against corrosion and oxidation) applications. Almost 5000 papers (including articles and reviews, among which 350 open access papers) have been published in the last century on mullites. Fig. 2 shows the evolution of the number of publications for each year since 1920. Indeed, the top five authors that have been working on mullites are: Schneider H.; Schmücker M.; Moya J-S.; Liu J.; and Pitak N.V. (source = scopus). Indeed from 1920 to 1970, less than 10 papers were published each year and then a significant increase is observed up to 2000 due to the technological advances and industrial development of mullite-based products. In years that are more recent, the research activities on mullites tend to be stable with the number of publications close to 200 each year.

The aim is to present a review on topics related to: (1) the structure and stability of mullite phases; (2) the processing routes to manufacture mullite products; (3) the main properties and applications of mullites.

Crystallography and Stability

Phase Diagram of Mullite

Most ceramics are multicomponent materials and the most stable phase at any temperature will be the one with the lowest free energy, G (Carter and Norton, 2007). Nevertheless, phase diagrams are one of the most important sources of information for the development of ceramic materials. It can be described as a map of the equilibrium phases associated with various combinations of temperature, pressure, and composition. Understanding the phase diagram of a given system is quite useful to understand solidification processes, characterization of compounds, and phases, and for understanding the chemical reactions involving multiple components at different temperatures. Alumina and silica are components of many commercial ceramics and important minerals such as silica, semi-silica, fireclay, low alumina, mullite, high alumina, and corundum; therefore, the phase diagram is one of the most important of all oxide pairs. Shepherd *et al.* (1909) and Bowen and Greig (1924) published the first Al_2O_3 – SiO_2 equilibrium phase diagram. The equilibrium diagram of this system is illustrated in Fig. 3, which shows the composition in weight percent and temperature in degrees Celsius.

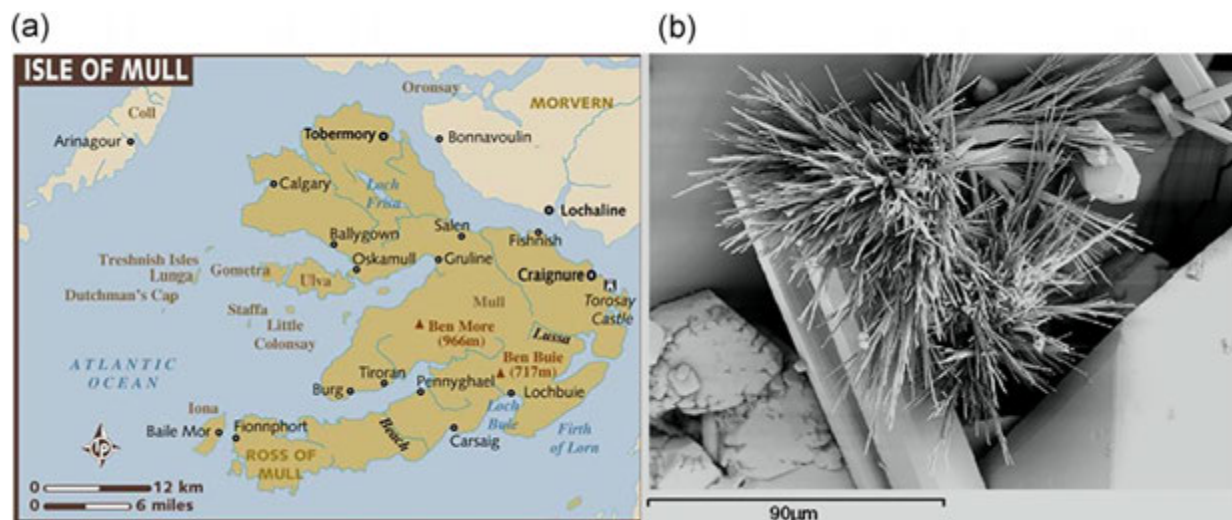


Fig. 1 (a) location of Isle of Mull (Scotland) where mullite was discovered and (b) micrograph of naturally occurring mullite from the Eifel mountains (Germany). Reproduced from Schneider, H., Schreuer, J., Hildmann, B., 2008. Structure and properties of mullite-A review. *J. Eur. Ceram. Soc.* 28, 329–344. doi:10.1016/j.jeurceramsoc.2007.03.017.

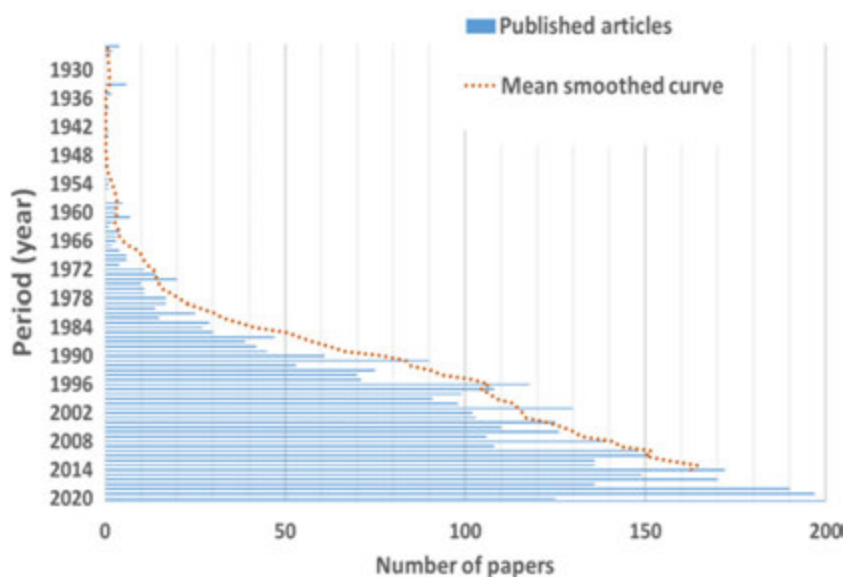


Fig. 2 Illustration of the growing interest in mullites from the number of published papers over a century (from 1920 to 2020).

According to the result obtained by Bowen and Greig on both natural sillimanite and with a mixture of Al_2O_3 and SiO_2 in the ratio 1:1, when heated to a high temperature and cooled slowly, good corundum crystals were formed. However, in subsequent studies of phase equilibria in the system Al_2O_3 – SiO_2 the 3:2 compound, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, is formed and referred to as mullite. However, as can be seen from the diagram of Fig. 3, there are two eutectics in the system: one between cristobalite and mullite at $\sim 1595^\circ\text{C}$ and the other at $\sim 1840^\circ\text{C}$ between mullite and corundum. As can be seen from the diagram, mullite takes a limited amount of alumina into solid solution. Indeed, within the limited solid solution domain, 3:2 mullite is a phase of alumina and silica with the composition $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ with 72 wt% of alumina, while 2:1 mullite corresponds to the formula $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ with 78 wt% of alumina. In specimens prepared with alumina and quartz in the ratio 3:2, homogeneous aggregates of crystals of only one kind (mullite) were obtained at all temperatures up to 1810°C , where melting began. A slight excess of silica caused the formation of some cristobalite below 1545°C and a small amount of glass (from liquid) above 1545°C .

The Al_2O_3 – SiO_2 phase diagram can be used to explain the “classes” of alumina-silica brick in terms of generalized “refractoriness”. These classes are given in Table 1 along with comments on the use of the products (Schacht, 2004).

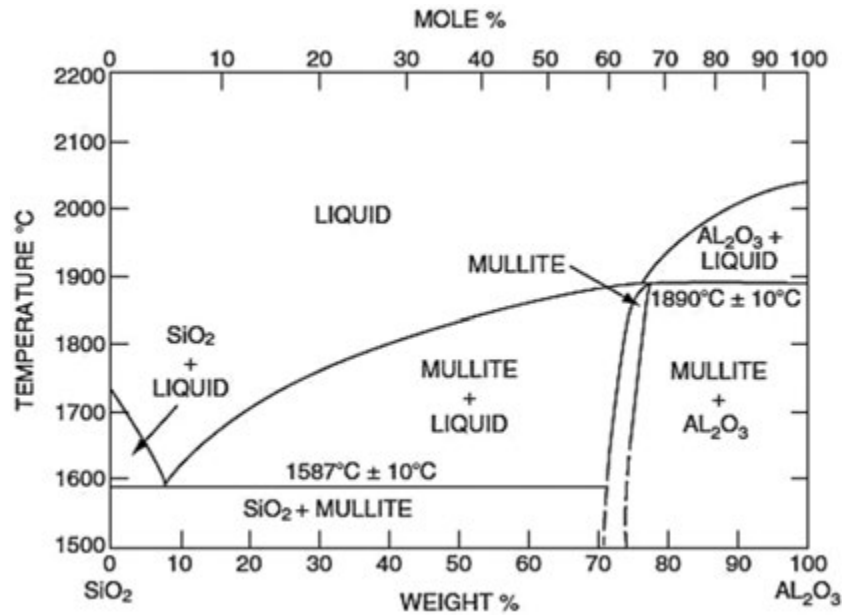


Fig. 3 Phase diagram for the Al_2O_3 - SiO_2 system. Reproduced from Carter, C.B., Norton, M.G., 2007. Ceramic Materials: Science and Engineering. Springer.

Table 1 Classes of alumina-silica brick explained in terms of the Al_2O_3 - SiO_2 phase equilibrium diagram

Al_2O_3 range in most standards	Common terminology for phases	General performance in the absence of slag corrosion or alkali attack conditions
Less than 50% Al_2O_3	Fireclay (Chamotte) Phases on phase diagram: mullite and glass (can contain "free SiO_2 ")	Usually made from 100% fireclay Highest-quality grades usable to about 1600°C ("super-duty" brick)
50% Al_2O_3 or 60% Al_2O_3	Sillimanite, andalusite, or kyanite Phases on phase diagram: Major phase—mullite and minor phase—glass (can contain "free SiO_2 ")	Cannot be made from 100% clay since clays do not contain sufficient Al_2O_3 . Made from 60% alumina minerals and contain some fireclay. Can be made with bauxite and clay. Can be used in excess of 1700°C
70% Al_2O_3	Mullite Phases on phase diagram: Major phase—mullite. Products made with bauxite contain corundum, mullite and glass	Made either from "bauxitic clay" or calcined bauxite and Clay. Can be used in excess of 1750°C
80% Al_2O_3 and 85% Al_2O_3	Bauxite Phases on phase diagram: The major phase is corundum, with a minor quantity of mullite and glass	Made from calcined bauxite. Usually used in aluminum contact refractories
90% Al_2O_3	Alumina Phases on phase diagram: The major phase is corundum, with a substantial minor quantity of mullite and glass. Bricks for molten iron contact usually contain fused Al_2O_3 for enhanced abrasion resistance	Made from tabular and/or fused synthetic (Bayer process) alumina aggregates. Can be used in excess of 1800°C

Note: Schacht, C., 2004. Refractories Handbook, first ed. Boca Raton: CRC Press.

Structure and Crystallography of Mullite

The understanding of the structures of mullite is consequently an area of increasing importance and attraction to many researchers in the field of ceramic materials. The mullite crystallization arises between 900 and 1000°C and within this interval of temperature, mullite is found to be weakly crystalline. Some authors point out the formation of a spinel-like transitory phase also, which is associated with the broad X-ray pattern between 20° and 30° in 2θ (for $\text{Cu K}_{\alpha 1}$ radiation). In contrast, in the temperature range 1100 – 1250°C , mullite development occurs predominantly at the cost of disappearance of the broad X-ray pattern due to the spinel phase. The intensity of the mullite XRD peak is therefore increased from 1100°C . At about 1200°C and above, increases in both intensity and crystallinity of mullite are significantly marked. Splitting of the 0.341 and 0.338 nm peak (corresponding to (120) and (210) crystallographic planes respectively) is enhanced, while the other XRD lines become well resolved and similar to the standard pattern of mullite (Chakraborty, 2014). Typical structures of mullite are shown in Fig. 4.

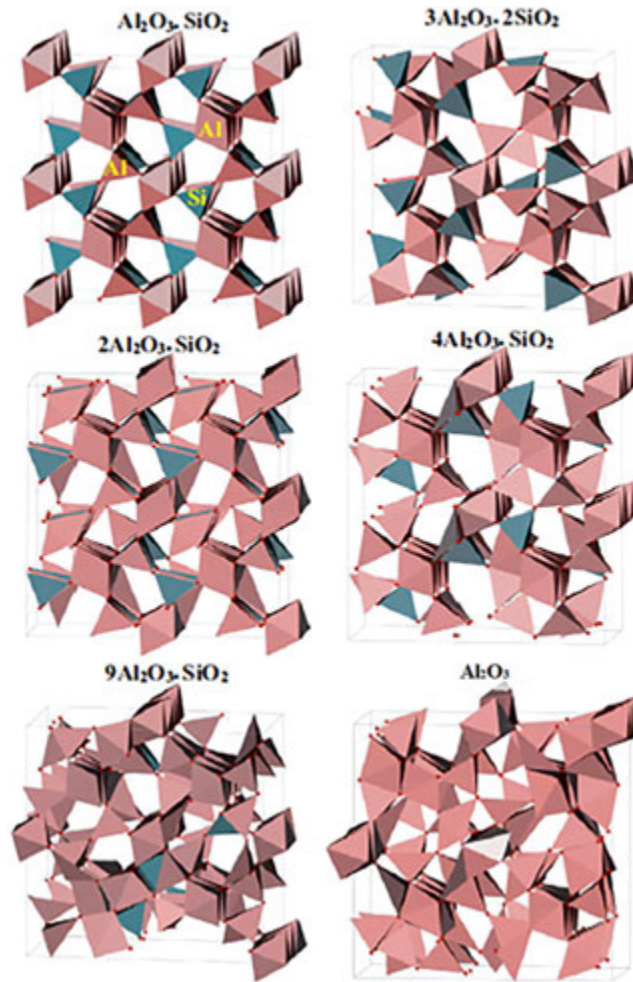


Fig. 4 Different Structural models obtained from the chemical formula $\text{Al}_2(\text{Al}_{2+2x}\text{Si}_{2-2x})\text{O}_{10-x}$, with $x = 0-1$. Reproduced from Aryal, S., Rulis, P., Ching, W., 2012. Mechanical properties and electronic structure of mullite phases using first-principles modeling. *J. Am. Ceram. Soc.* 95, 2075–2088.

The structure of mullite consists of chains of slightly distorted Al-O octahedra which run parallel to the *c*-axis of the orthorhombic unit cell. These chains are linked by discontinuous double chains of Al-O and Si-O tetrahedra with randomly distributed aluminum and silicon atoms (Fig. 5(a) and (b)). The backbone of the mullite structure consists of linear chains of edge-connected AlO_6 octahedra reinforced by TO_4 tetrahedra. Some of the Si ions are replaced by Al according to Eq. (1). The oxygen vacancy causes the neighboring (Al,Si) O_4 tetrahedra chain to contract and to form an Al-O bridge, as indicated by the ions shown in Fig. 5(c).



However, it is generally assumed that in mullite structure there are two types of tetrahedral sites, noted (T) and (T*). The first position (T) is in a regular environment, while the tetrahedron which surrounds the second (T*) is deformed due to the presence of an oxygen atom O^* common to three tetrahedra. The change in stoichiometry 2:1 to 3:2 is achieved by the departure of an oxygen atom in position O (3) which links two tetrahedral units.

The crystal structure of 3:2 mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is orthorhombic with the space group *Pbam* and unit cell dimensions $a = 7.533 \text{ \AA}$, $b = 7.686 \text{ \AA}$ and $c = 2.8864 \text{ \AA}$ (stoichiometric composition) (Lenz *et al.*, 2019). Table 2 illustrates the summarized structural parameters of different mullite phases compared to phases with $x = 0$ (spinel) and $x = 1$ (sillimanite, andalusite and kyanite) (Burnham, 1963; Angel *et al.*, 1991; Digne *et al.*, 2004; Schneider *et al.*, 2008).

Processing of Mullite

Different types of mullite can be obtained depending on the synthesis procedures. We can consider the three conventional processing routes for mullite, namely: (1) sintering, (2) melting and (3) chemical routes. In addition, plasma processing is used in order to achieve specific additional performance for the final product (oxides or non-oxides) coated with mullite.

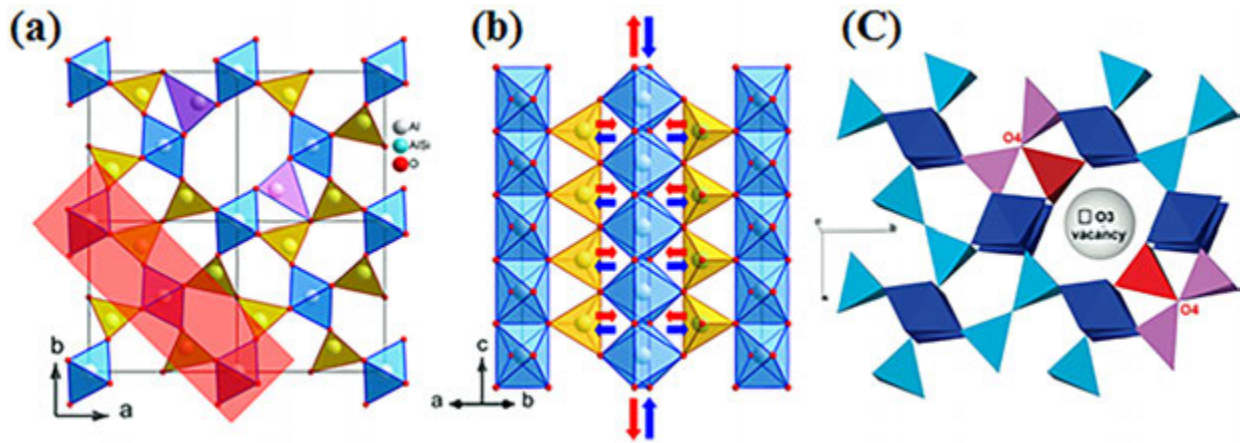


Fig. 5 Crystal structure of mullite. (a) View parallel to [001], the shaded area is shown in (b) from a different angle. (b) View parallel to the [110] direction; Red and blue arrows indicate movement of atoms under tensional and compressional stresses, respectively. (c) Polyhedral representations of mullite structure; Si^{4+} is partially replaced by Al^{3+} , requiring the formation of O3 vacancies (large white semitransparent sphere). Reproduced from (b) Schneider, H., Fischer, R.X., Schreuer, J., 2015. Mullite: Crystal structure and related properties. *J. Am. Ceram. Soc.* 98, 2948–2967. doi:10.1111/jace.13817. (c) Birkenstock, J., Petříček, V., Pedersen, B., Schneider, H., Fischer, R.X., 2015. The modulated average structure of mullite. *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.* 71, 358–368. doi:10.1107/S205252061500757X.

Table 2 Unit cell parameters and space groups for mullite phases, sillimanite, andalusite, kyanite and γ -alumina (spinel phase). The value of x is related to the formula $\text{Al}_2(\text{Al}_{2+2x}\text{Si}_{2-2x})\text{O}_{10-x}$.

		Mineral	Space group	Unit cell parameters			References
				a (Å)	b (Å)	c (Å)	
Value for x	0	Sillimanite	$Pbnm$	7.486	7.675	5.775	Burnham (1963)
	0.25	3:2-Mullite	$Pbam$	7.533	7.686	2.8864	Angel <i>et al.</i> (1991)
	0.4	2:1-Mullite	$Pbam$	7.588	7.688	2.8895	Schneider <i>et al.</i> (2008)
	0	Kyanite	$P\bar{1}$	7.1262	7.8520	5.5724	Burnham (1963)
	0	Andalusite	$Pnnm$	7.77942	7.8985	5.559	Burnham and Buerger (1961)
	–	γ -Alumina	$Fd\bar{3}m$	5.587	8.413	8.068	Digne <i>et al.</i> (2004)

1. The sintering route

In this type of processing, solid-state reactions govern the formation of mullite, and tend to lead to the production of 3:2 mullite phase. The sintering route is widely used in the ceramic industry, based on mixtures of bauxite, kaolin and/or kyanite (Carter and Norton, 2007). Such homogeneous mixtures are sintered at temperature up to 1600°C and the final products can obtain between 85 and 90 wt% of 3:2 mullite. Andalusite and sillimanite can also be used instead of kyanite (Birkenstock *et al.*, 2015) in cost-effective methods (using sillimanite beach sand). The use of a small amount of TiO_2 or ZrO_2 can improve the densification and/or final properties of sintered mullite products. The addition of 2–4 wt% of TiO_2 tends to lower the densification temperature of mullite produced by the sintering method, since the maximum bulk density can be reached in the range 1450–1500°C (instead of 1600°C without TiO_2 addition). Such improvement depends on the purity and composition of the starting powders; the more the silica content, the less wt% of added TiO_2 is needed. The densifying interactions in the presence of TiO_2 are:

- An increase of the cation mobility due to the formation of vacancies while substituting Al^{3+} by Ti^{4+} ;
- The occurrence of a liquid phase at the firing temperature, that enhances the diffusion of reactants, particle rearrangement and therefore the removal of porosity from grain boundaries.

The starting particle size distribution, specific surface area and milling time of the batches have a significant influence on the densification temperature and the final properties (such as flexural strength) of sintered mullite products (Birkenstock *et al.*, 2015).

2. The melting route – Fused mullite

Fused mullite is obtained through the crystallization of alumino-silicate melts. In this case, 2:1 mullite is promoted. In the fusing process, it is necessary to mix the correct amount of alumina and kaolin and fuse them in an electric-arc furnace at about 1750°C or higher temperatures. With this process, a product can be obtained with more than 95% of mullite, and the remainder

will be a mixture of alumina and glass (Burnham, 1963). In general, the starting materials for fused-mullite exhibit very low impurity levels. The crystallization of mullite is obtained from the aluminum silicate melts previously cast into ingot molds (cooling of the bath or by Czochralski crystal growth techniques). The cooling rate controls the Al_2O_3 content of the bulk: higher quenching leads to Al_2O_3 -rich mullites.

3. The chemical route

The heat-treatments of organic and/or inorganic precursors are referred to as the chemical route and the obtained mullites are called chemical mullites. These type of mullites are extremely rich in Al_2O_3 and the composition depends mostly on the starting materials. In general, with the sol-gel method, the type of starting precursors can lead to mullites through a single-phase system or by reaction of a diphasic SiO_2 and Al_2O_3 mixture (Lee *et al.*, 2008). Three types of sol-gel precursors have been defined by Schneider *et al.* (1993) regarding the final mullite morphology and stoichiometry. Type I precursors, which are amorphous in the starting preparation, tend to lead to mullite single phase at 980°C . Type II precursors which are based on pseudo-boehmite and non-crystalline silica mixtures lead to the formation of spinel at 400°C and finally to mullite above 1250°C . Type III precursors, which are amorphous in the starting preparation, give rise to a partial conversion into spinel phase near to 980°C and finally to the crystallization of mullite above 1100°C . A combination of sol-gel and solution combustion synthesis (SCS) can also be used to produce mullites or doped mullites. SCS is a chemical route whereby an exothermic redox reaction is performed between an oxidizer (a metal nitrate in general) and an organic fuel reducing agent (urea, glycine, hydrazides, etc.). For the SCS method, the solution is obtained by mixing soluble reagents and an external heat supply is provided in order to promote the ignition of the mixture, leading to the self-sustained reaction. The advantage of combining SCS and a sol-gel method is to ensure a good mixture of the starting materials (allowing also to incorporate a large variety of foreign cations). In addition, the synthesis temperatures of as-prepared mullite powders are reduced (Schneider *et al.*, 1993).

4. Plasma processing and others

Mullite coatings are very interesting for applications as environmental barrier coatings (EBCs) and/or as thermal barrier coatings (TBCs) on metal components. They can be applied on oxide and non-oxide ceramics substrates as well. Mullite barriers act by forming layers of SiO_2 bonds at the interface with the substrates that prevent them from damage due to water or vapor containing atmospheres or corrosive environments at elevated temperatures. These mullite coatings are also known to possess adequate wear or scar resistance properties. Various deposition techniques can be used for processing mullite coatings, namely: chemical vapor deposition (CVD), physical vapor deposition (PVD), flame spraying and air plasma spraying (APS) techniques. The plasma spraying technique appears to be very efficient compared to other methods for producing mullite coatings, regarding the related cost saving and fast coating synthesis (Mekap *et al.*, 2019).

Beside mullite coatings, some studies are focused on the fabrication of highly textured or fiber mullite components. The acicular or needle-like shape can be used to develop ceramic products exhibiting highly anisotropic properties, like mechanical strength, and/or thermal conductivity. Thanks to the needle-like structure of some mullite phases, the preferred orientation along a direction or a plane can be controlled. Topotactic growth of mullite crystals has been reported in literature and offers an interesting route to control the microstructure and final properties of sintered ceramic products (Lecomte and Blanchart, 2006; Deniel *et al.*, 2010; Boussois *et al.*, 2013; Lecomte-Nana *et al.*, 2013). The shape of mullite will have a significant influence on the properties during use. Fig. 6 shows the typical morphology that can be obtained regarding the processing conditions.

Properties and Applications

Properties of Mullite Ceramics

The following sections will emphasize the properties of mullite materials which are relevant for a wide field of its applications. As previously mentioned, interest is still growing for mullite-based materials due to their high-temperature properties such as high thermal stability even in harsh oxidizing environments, low thermal expansion coefficient (CTE) and thermal conductivity that enhances the thermal shock resistance and allows low creep rates (Schneider *et al.*, 2015). Table 3 summarizes some physical properties of mullite compared with those of alumina, sillimanite and kyanite.

Mechanical properties

Depending on the synthesis route, mullite materials also contain a certain amount of residual liquid as glassy phases. Softening temperature and viscosity of these residual amorphous phases dramatically depend on their composition. These characteristics and the distribution of the glassy phase will strongly influence the mechanical properties of mullite products. Typical values of some mechanical properties are provided in Table 3 (Kind *et al.*, 2010; Sarkar, 2016). At room temperature, the higher the alumina content in mullites, the higher are the mechanical resistances. The presence of pores and glassy phases (or other impurities) tend to decrease the mechanical strength of mullite products. In addition, the incorporation of foreign cations in the structure of mullite could significantly improve these mechanical properties. It should be noted that these mechanical properties increase with temperature (Table 4). However it can be noted that high values of fracture toughness and flexural strength are obtained at 1200°C compared to 22°C , which is mainly due to the low porosity of mullite phases (Hammas *et al.*, 2020). Indeed, at 1200°C fracture

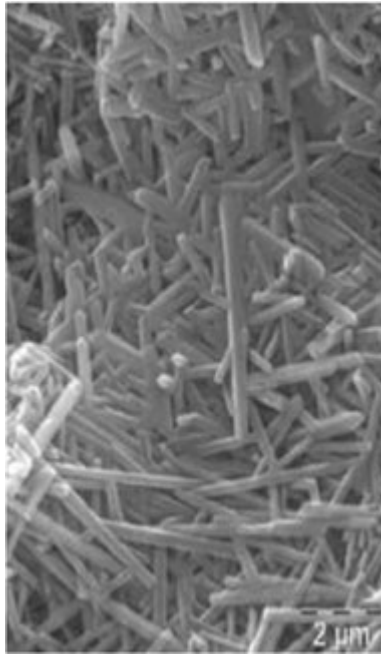


Fig. 6 Example of mullite crystal morphology (elongated needle-like shape).

Table 3 Physical properties of mullite and aluminosilicate phases

Phase	Melting temperature ($^{\circ}\text{C}$)	Elastic modulus (GPa)	Modulus of rupture (MPa)	Hardness (GPa)	Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	Specific gravity
Sillimanite	/	/	/		1 – 6.7 at 1200 $^{\circ}\text{C}$	3.23 – 3.27
3:2-Mullite	1810	150	160	6 – 7.5		3.16
Kyanite	/	297–405	/	4.5–5		3.56–3.66
Andalusite	1740 ?	/	/	6.5 – 7.5		3.12–3.16
$\gamma\text{-Al}_2\text{O}_3$	2040	286	152–800	8	8–38	3.6

Note: Kind, M., Martin, H., Stephan, P., *et al.*, 2010. VDI Heat Atlas. Berlin: Springer-Verlag. Sarkar, R., 2016. Refractory Technology: Fundamentals and Applications, first ed. Boca Raton: CRC Press.

Table 4 Values of fracture toughness (K_{Ic}), fracture strength (σ_f), flexural strength, Young's modulus and microhardness for 3:2 mullite at different temperatures

T ($^{\circ}\text{C}$)	K_{Ic} ($\text{MPa}\cdot\text{m}^{1/2}$)	σ_f (MPa)	Flexural strength (MPa)	Microhardness (GPa)	Density (g/cm^3)
22	2.5 ± 0.5		186	15	2.82–3.10
1000				10	
1200	3.6 ± 0.1	260 ± 15	500		
1300	3.5 ± 0.2	200 ± 20			
1400	3.3 ± 0.2	120 ± 25	360		

Note: Schneider, H., Schreuer, J., Hildmann, B., 2008. Structure and properties of mullite-A review. J. Eur. Ceram. Soc. 28, 329–344. doi:[10.1016/j.jeurceramsoc.2007.03.017](https://doi.org/10.1016/j.jeurceramsoc.2007.03.017). Lee, W.E., Souza, G.P., McConville, C.J., Tarvornpanich, T., Iqbal, Y., 2008. Mullite formation in clays and clay-derived vitreous ceramics. J. Eur. Ceram. Soc. 28, 465–471. doi:[10.1016/j.jeurceramsoc.2007.03.009](https://doi.org/10.1016/j.jeurceramsoc.2007.03.009).

toughness and flexural strength are equal to $3.6 \text{ MPa m}^{1/2}$ and 500 MPa, respectively. The latter increase could result from the network of glassy phase and hard inclusions that contribute to arrest and dissipate fracture lines caused by mechanical or thermal stresses (the cracks would require more energy to propagate catastrophically through the ceramic body).

The mechanical properties of mullite ceramics, synthesized under different conditions, were studied by several authors. Liu *et al.* (2020) synthesized mullite ceramics from coal gangue and high alumina refractory solid wastes by using the solid-state

Table 5 Electrical and thermal properties of 3:2 mullite-based insulators

Coefficient of thermal expansion (10^{-6} K^{-1})	Dielectric constant (ϵ) at 1 MHz	Dielectric loss ($\tan\delta$) at 1 MHz	Thermal conductivity ($\text{W m}^{-1} \text{ K}^{-1}$)
3.7–5.3	5.4–6.8	0.003	4–6.7

Note: Harper, C.A., 1993. *Electronic Materials and Processes Handbook*. New York: McGraw-Hill. Shackelford, J.F., 2016. *Introduction to Materials Science for Engineers*, eighth ed. London: Pearson.

reaction method. This study realized the resource utilization of coal gangue and aluminum wastes, and had certain guiding significance for the resource utilization of other wastes of similar components. The best values of fracture toughness and bending strength of the mullite ceramics prepared in this work were close to $1.82 \text{ MPa m}^{1/2}$ and 71.76 MPa respectively. It was shown that mullite ceramics from the powders exhibited a needle-like interweaving microstructure, after sintering at 1500°C for 3 h and offered good application prospects. Krenzel *et al.* (2019) studied the correlation between different physical properties and thermo-mechanical properties of mullite ceramics. Consequently, they concluded that the elastic properties of the hot isostatically pressed mullite (HIPed) material were very close to the corresponding properties of single crystal mullite, for example, the Young's modulus of single crystal mullite is 221.5 GPa and that of HIPed Al_2O_3 -rich mullite equal to 222.5 GPa .

Over the previous decades, preparation of mullite ceramic foams from fly ash had drawn increasing attention due to environmentally friendly features, which could promote the comprehensive utilization of resources (Chen *et al.*, 2019; Dong *et al.*, 2019; Li *et al.*, 2019; Chen *et al.*, 2020a). Chen *et al.* (2020a,b) improved the mechanical properties of mullite ceramic foams prepared by vacuum infiltration using andalusite, sillimanite and kyanite slurries. Poor mechanical strength (compressive strength equal to 1.5 MPa) and thermal shock resistance (low residual strength) were obtained for such mullite ceramic foams (heated at 1400°C) when kyanite slurries were used as infiltration slurries. However, the mechanical strength and residual strength ratio of the mullite ceramic foams treated with andalusite infiltration slurries reached 2.59 MPa and 49.9% .

Electrical and thermal properties

Besides the excellent mechanical properties at high temperature, mullite ceramics are widely used in electrical insulation and dielectric applications (MacKenzie *et al.*, 2008; Sanad *et al.*, 2014), thanks to their thermal and electrical properties (Table 5) (Harper, 1993; Shackelford, 2016). Recent research investigations indicated that porous mullite ceramics are the most suitable materials for thermal insulation (Gong *et al.*, 2013; Kalemtaş *et al.*, 2018; Zhang *et al.*, 2020).

For example, Zhang *et al.* (2020) prepared nanofibrous porous ceramics by the gel-casting method. The as-obtained mullite material presented low thermal conductivity ($0.0597 \text{ W m}^{-1} \text{ K}^{-1}$) which is recommended for thermal insulation materials. In addition, Kalemtaş *et al.* (2018) prepared layered porous mullite ceramics via the polymeric sponge method: by using a commercial-grade kaolin source as raw material, a three-layer porous specimen was obtained from this study as shown in Fig. 7 with the three colored arrows. This method comprises three steps: (1) the impregnation of a polymeric sponge which exhibits the desired pore size and distribution; (2) the drying of the obtained material; and finally (3) heat treatment is carried out in order to achieve the designed porous ceramic body (the polymeric sponge is burnt out). It was concluded from this work that the obtained ceramic material appeared suitable for applications in the field of heat insulators.

Optical properties

The optical properties of ceramics are naturally affected either directly or indirectly by several factors such as the constituent elements constituting the ceramic, the crystalline symmetry, the microstructure of the ceramic, and changes in the external field. Taking optical transmittance as an example of the optical and physical properties of a transparent ceramic, this depends on the surface roughness due to the degree of polishing of the ceramic surface, and the optical transmittance changes when the scattering of light is different (Sōmiya *et al.*, 2003). Some results obtained from selected studies on optical properties of mullites are presented in Table 6 (Li *et al.*, 2019; Chen *et al.*, 2020a,b). Indeed, Schneider *et al.* (1993) studied the optical transmittance of pressureless-sintered and hot isostatically pressed mullite ceramics in the near infrared (NIR), visible light (VIS), and in the ultraviolet (UV) spectral ranges. They concluded from this work that optically translucent mullite was found suitable for optical windows in the VIS and NIR ranges, particularly at high temperatures. On the other hand, Seong *et al.* (2007) synthesized and examined the optical properties of single-crystalline mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) nanowires using the chloride vapor transport (CVT) process. It was reported that the mullite nanowires could offer good opportunities for highly toughened ceramic, metal, and polymer composites. Islam *et al.* (2017) doped mullite with a very small amount of 0.1 M Er^{3+} in order to study its effects on optical device applications. Consequently, the experimental result revealed that Er^{3+} doped mullite matrix is beneficial for optical applications at room temperature.

Application and use of Mullite Ceramics

Regarding the aforementioned properties of mullites (see Tables 2–4), manufactured mullites products are found in widely distributed low cost applications as well as in technical or particular high added value applications. Accordingly, the literature contains a large number of papers dealing with the fabrication, characterization, and the use of mullite ceramics. This includes

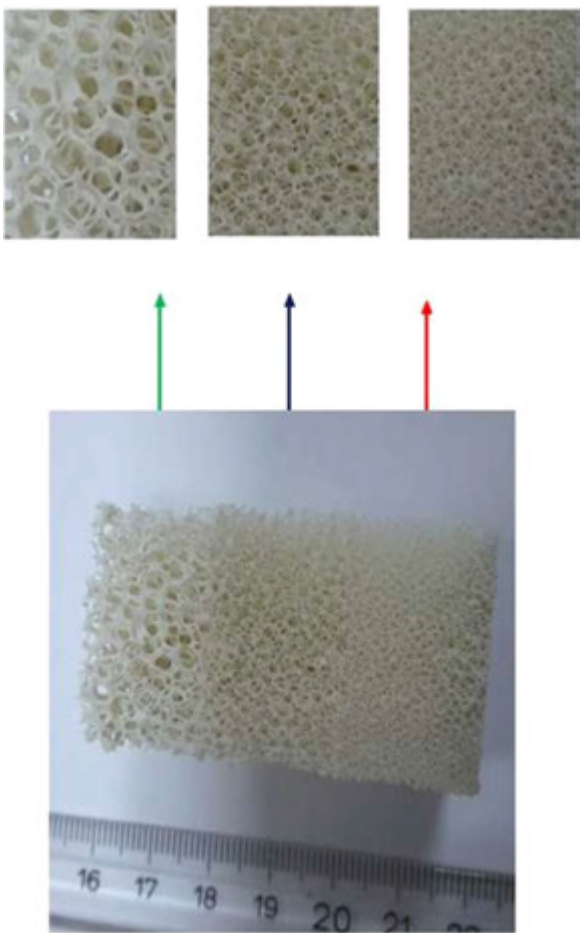


Fig. 7 Macroscopical image of the porous layered specimen fabricated at 1400°C for 5 h. Reproduced from Kalemtaş, A., Özey, N., Aytekin Aydin, M.T., 2018. Processing of layered porous mullite ceramics. J. Aust. Ceram. Soc. 54, 545–555. doi:10.1007/s41779-018-0183-6.

Table 6 Summary of optical transmittances for various mullite products

Type of mullite product	Optical transmittance (%)	Utilization
Pressureless-sintered mullite	20	Optical window material at elevated temperatures
HIPed mullite	VIS (– 40%) and NIR (– 80%).	Optical window material at elevated temperatures
Nanowire mullite	/	highly toughened ceramic, metal, and polymer composites
Er-doped mullite	70	optical applications at room temperature.

Note: Chen, S., Cai, W.-H., Wu, J.-M., *et al.*, 2020a. Porous mullite ceramics with a fully closed-cell structure fabricated by direct coagulation casting using fly ash hollow spheres/kaolin suspension. *Ceram. Int.* 46, 17508–17513. Chen, R., Hei, D., Wang, Y., Li, S., Jia, W., 2020b. Effects of different kinds of sillimanite minerals on the properties of mullite ceramic foams. *Mater. Res. Express* 6, 125203. Li, C., Zhou, Y., Tian, Y., *et al.*, 2019. Preparation and characterization of mullite whisker reinforced ceramics made from coal fly ash. *Ceram. Int.* 45, 5613–5616.

traditional technical products such as porcelain, tableware, and refractories, but also advanced materials such as heat exchangers, filters, catalytic converters, substrates, electronic packaging devices, components for optical systems and turbine engines and heat shields (for details, see the following sections).

Traditional mullite ceramics

Pottery and whitewares

Whitewares are traditional ceramic materials which generally make up pottery and porcelain. The raw materials traditionally used in whiteware production mainly are kaolin and/or kaolin clay, quartz, and feldspars. Generally, mullite (3Al₂O₃ · 2SiO₂) is one of the most stable constituents developed in related refractory products and pottery (Mishra and Ningthoujam, 2017). Fig. 8(a) illustrates a mullite pouring cup fabricated by Schaefer Industrial Ceramics, USA. Lee and Iqbal (2001) examined the

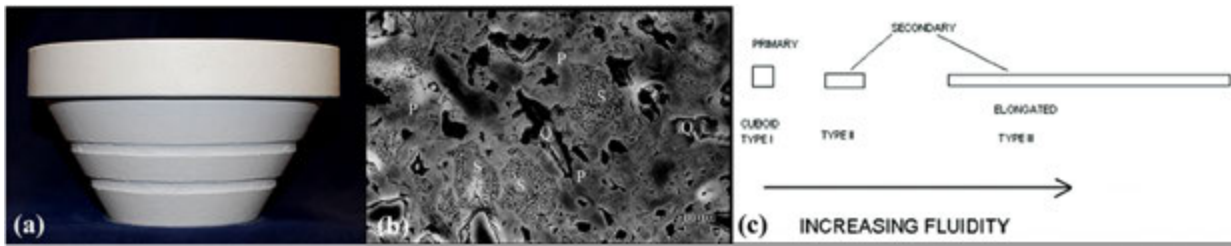


Fig. 8 (a) Mullite Pouring Cups fabricated by Schaefer Industrial Ceramics, USA; (b) Micrograph showing (P) primary and (S) secondary mullite and (Q) Quartz. (c) Schematic diagram of mullite morphologies in porcelains. Reproduced from (c) Lee, W.E., Iqbal, Y., 2001. Influence of mixing on mullite formation in porcelain. *J. Eur. Ceram. Soc.* 21, 2583–2586.

Table 7 Physical properties of mullite-based refractories sintered between 1200 and 1500°C

Refractory	Flexural/Compressive strength (MPa)	Coefficient of thermal expansion ($10^{-6} K^{-1}$)	Thermal conductivity ($W m^{-1} K^{-1}$) at 1200°C
Mullite	30 – 100 (3-points bending)	5.0 – 5.7	≈ 4
Mullite-corundum	60 – 160 (biaxial)		0.3
Mullite-cordierite	180 (compressive)	≈ 4.5	0.06

Note: Kind, M., Martin, H., Stephan, P., *et al.*, 2010. VDI Heat Atlas. Berlin: Springer-Verlag. Sarkar, R., 2016. Refractory Technology: Fundamentals and Applications, first ed. Boca Raton: CRC Press.

microstructural features and the importance of mixing on the nature of the mullite formation and morphologies in porcelain under heat treatments and these are shown in [Fig. 8\(b\)](#) and [\(c\)](#). It was indicated that various forms of mullite occurred in porcelains:

(1) primary (P) mullite (close to 2:1 mullite) which was obtained by decomposition of pure kaolinite under heat treatment at 1000 and 1200°C; (2) secondary (S) mullite (close to 3:2 mullite) which was formed by the reaction of feldspar with clay or clay and quartz (Q); and (3) tertiary mullite which seemed to precipitate from an alumina-rich liquid obtained by dissolution of alumina filler.

[Deutou *et al.* \(2020\)](#) investigated the ability of kyanite particles to control the mullitization process and hinder feldspar vitrification during the sintering of microporous porcelain. Therefore, microporous mullite with multimodal pore size distribution was successfully designed by using kyanite that acted to hinder vitrification at relatively low temperature and improve crystallization between 1200 and 1350°C. Consequently, in this range of temperature, optimum interconnectivity, lower average pore size (1.54 μm), higher specific pore area and elastic modulus (> 20 GPa) were achieved as a result of the control of the mullite grain growth and optimum densification and packing of acicular, fibrous and secondary mullite developed.

[Sanz *et al.* \(2018\)](#) studied the crystalline phases of the mullite content in whiteware, which was obtained by sintering of two different industrial kaolins. The main conclusion of this work was related to the evidence of increasing mullite content in the crystalline fraction of the produced porcelains after faster firing in both blends. The composition of the mullite approaches the stoichiometric composition 3:2, similar to that of mullite in stoneware produced from illite-kaolinite compositions, from thermal transformations of kaolin and from sintered mullite at temperatures of $\sim 1300^\circ C$. In contrast there are no significant changes in the average Al_2O_3 contents (near the stoichiometric composition (3:2)) of the mullites.

In addition, [Sirilar *et al.* \(2019\)](#) examined the different properties of mullite formation and glaze-body fit of sanitary ware bodies, by using pottery stone from Lampang, Thailand as a substitute for kaolin, feldspar, and silica. The results of this study showed that the crystal structure and the improvement of mechanical properties of the body mainly resulted from a higher amount of mullite content. It has been indicated that the sample with 37.7–20.7–41.6 of clay-quartz-feldspar ratio and pottery stone as substitute for 100% silica, sintered at 1200°C exhibited 9.27% total shrinkage, 0.17% water absorption, and 60 MPa flexural strength. In addition, linear thermal expansion and thermal expansion coefficient were lower at 0.34 and $7.07 \times 10^{-6} K^{-1}$, respectively.

Refractories

Refractories (see [Sarkar, 2016](#)) are the products used for any high-temperature processing to insulate the system, to introduce erosion–corrosion–abrasion resistances against the process conditions, and are made mainly from non-metallic minerals. However, diverse requirements may arise from application temperatures, atmospheric conditions that prevail during the processing, mechanical, thermal, chemical, abrading and wear conditions, and so on. Therefore, many of the refractory materials have been developed to meet specific service conditions of particular high temperature processing conditions. To meet this wide variety of application conditions, different classes of refractory materials ([Sarkar, 2016](#)) are required and are being developed as time progresses.

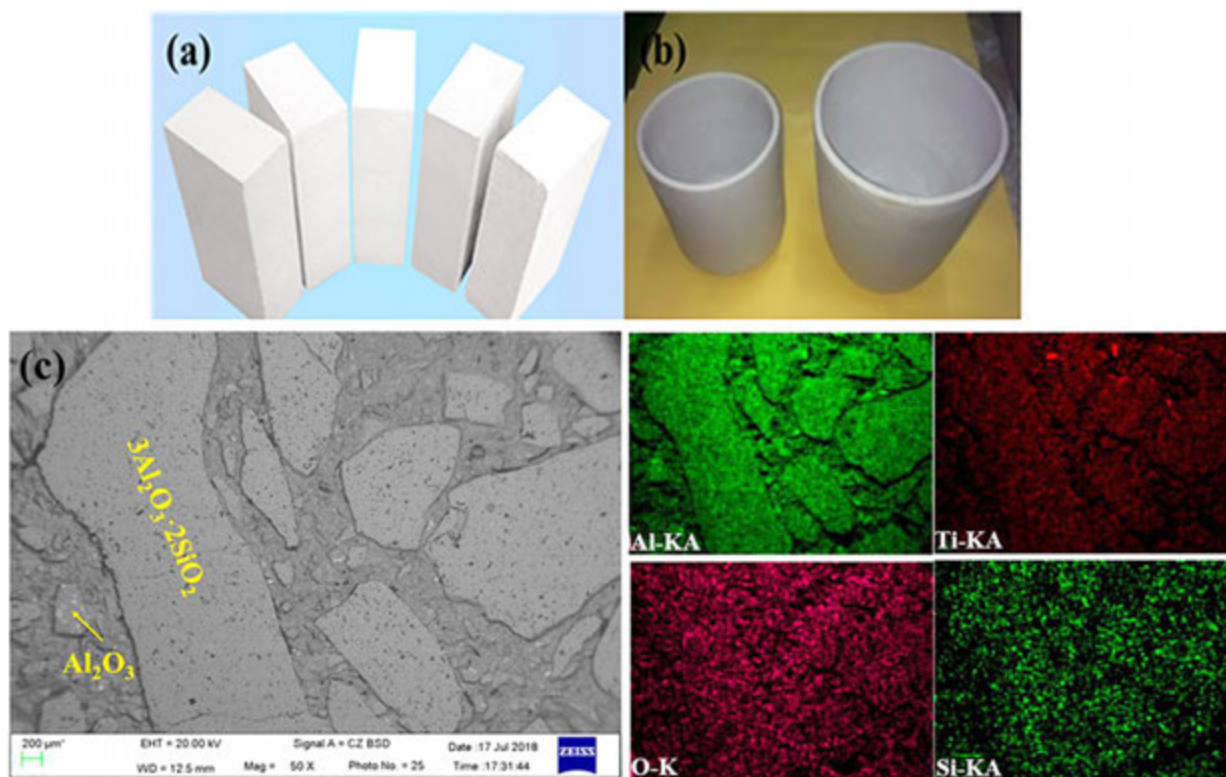


Fig. 9 (a) Mullite bricks and (b) crucible fabricated by Zhengzhou Shennan Refractory China and Kumar Ceramics Private Limited, West Bengal, India, respectively; (c) SEM morphology of mullite brick. Reproduced from Yao, S., Zhou, H., Wu, S., *et al.*, 2020. Microstructure and physical properties of a mullite brick in blast furnace hearth: Influence of temperature. *Ironmaking & Steelmaking: Processes, Products and Applications*, vol. 3. Taylor and Francis pp. 1–7.

In general, the major components of refractories can be represented using the binary Al_2O_3 – SiO_2 phase diagram. However, among of all alumina-silica refractories, mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), with 71.8 wt% Al_2O_3 , has many advantageous properties, which make it an important material for many industrial fields, its several physical properties indicated in [Table 7](#). In addition, synthetic mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) is also used as a raw material for some special alumina refractories, produced by the sintering process or melting. In the process, the initial materials are kaolinitic clay, pyrophyllite ($\text{Si}_4\text{Al}_2\text{O}_{10}(\text{OH})_2$), and muscovite ($\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$), which are enriched in alumina in order to meet the required composition of mullite by the addition of calcined Al_2O_3 ([Sarkar, 2016](#)).

The technology of alumina-silica brick is relatively simplified. However, mullite bricks were primarily used as blast furnace hearth lining materials that feature several advantageous properties ([Fig. 9\(a\)](#)). [Yao *et al.* \(2020\)](#) studied the microstructure and physical properties of a mullite brick under different heat treatments (1150, 1350, and 1500°C for 10 h). From the results of this study, the main composition of mullite brick was reported as mullite and corundum (Al_2O_3) ([Fig. 9\(c\)](#)). The chemical composition of these bricks was reported as mainly constituted by Al_2O_3 (71.46 wt%), SiO_2 (21.76 wt%) with small content of TiO_2 (2.44 wt%). Consequently, there is a minor change in the phase compositions after heat treatments. Although the temperature had no effect on the micro-morphology of the mullite aggregate, it directly affected the microstructure of the mullite matrix. With the increase in temperature, the degree of bonding of fine grains was higher and the bonding phase became smooth in the matrix. In addition, the bonding phase formed between aggregate and matrix was gradually widened and reinforced with the increase in temperature.

Also, crucibles made from mullite refractory have received much attention in recent times ([Fig. 9\(b\)](#)). The mullite-based crucibles are usually synthesized from mixtures of clay minerals and bauxite, aluminum hydroxide or alumina. Kaolinite is the clay mineral most commonly used ([Schneider and Komarneni, 2006](#)). [Martín-Torres *et al.* \(2008\)](#) reported different features of mullite-based crucibles such as processing technology, microstructure and phase analysis. In this work, mullite crystalline phase was synthesized by sintering quartz-tempered kaolinite to temperatures above 1300°C, with primary mullite developing in most of the glass and highly acicular secondary mullite growing in regions fluxed by feldspars. The resulting crucibles indicated superior material properties, including high-temperature strength, creep and thermal shock resistance, and thermal and chemical refractoriness. These trends explained their outstanding success in the international market for applications from at least 1300°C.

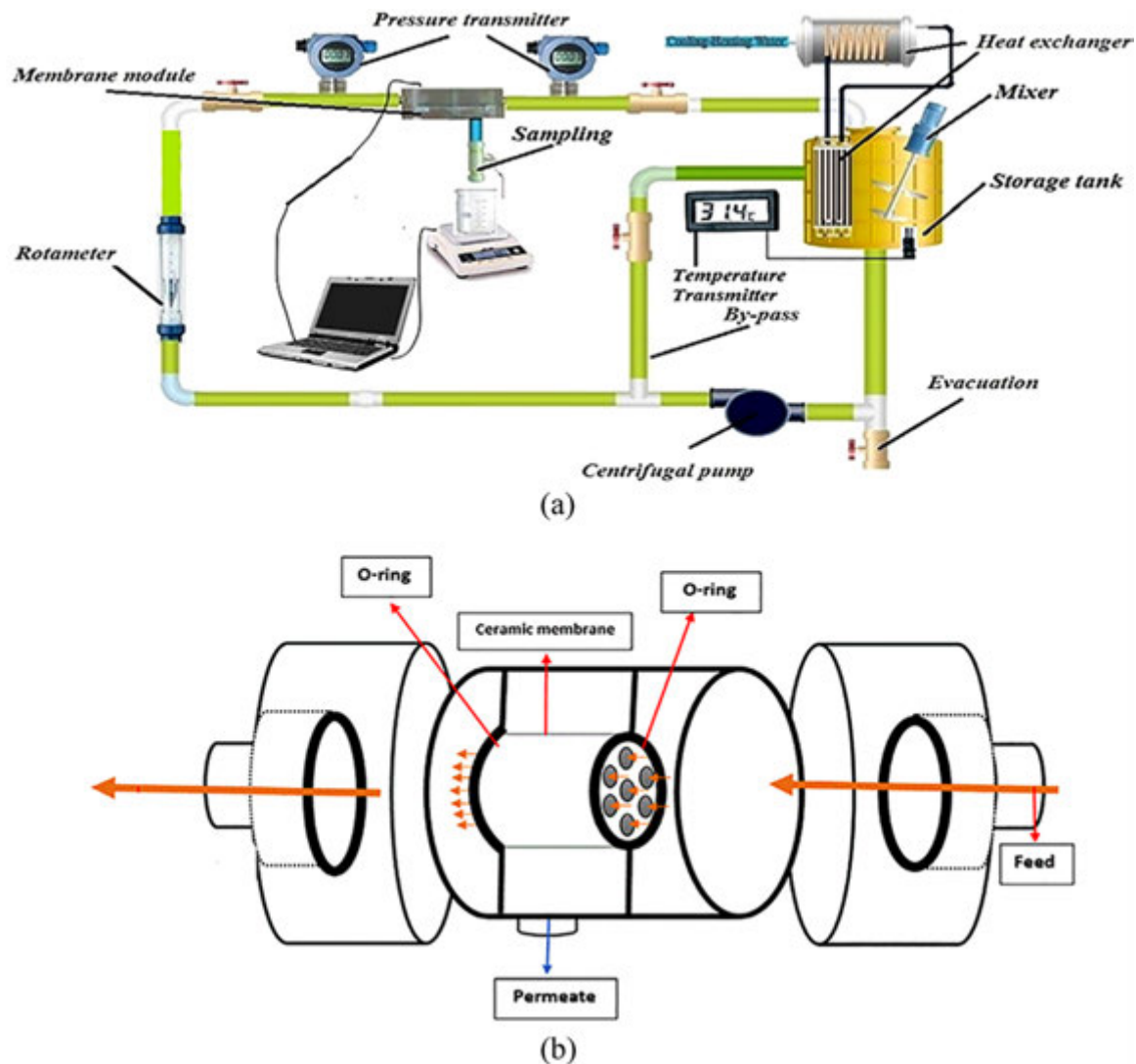


Fig. 10 (a) Experimental setup and (b) membrane module for preparation of ceramic monolith microfilters using kaolinitic clay. Reproduced from (b) Arzani, M., Mahdavi, H.R., Sheikhi, M., Mohammadi, T., Bakhtiari, O., 2018. Ceramic monolith as microfiltration membrane: Preparation, characterization and performance evaluation. *Appl. Clay Sci.* 161, 456–463.

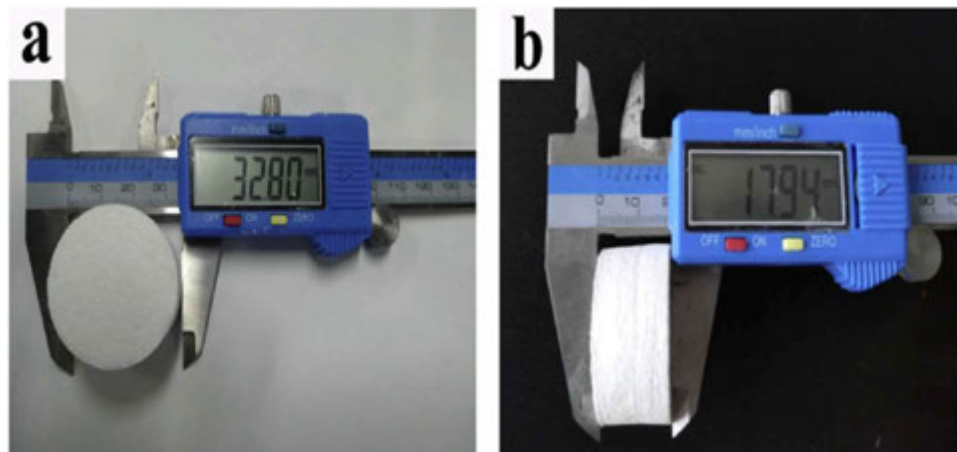


Fig. 11 The dimensions of the final product made of mullite fibrous ceramics processed by infiltration and in situ pyrolysis of organic precursors followed by sintering at 1500°C for 2 h in air. Reproduced from Zhu, W., Guo, A., Xue, Y., *et al.*, 2019. Mechanical evaluations of mullite fibrous ceramics processed by filtration and in situ pyrolysis of organic precursor. *J. Eur. Ceram. Soc.* 39, 1329–1335.

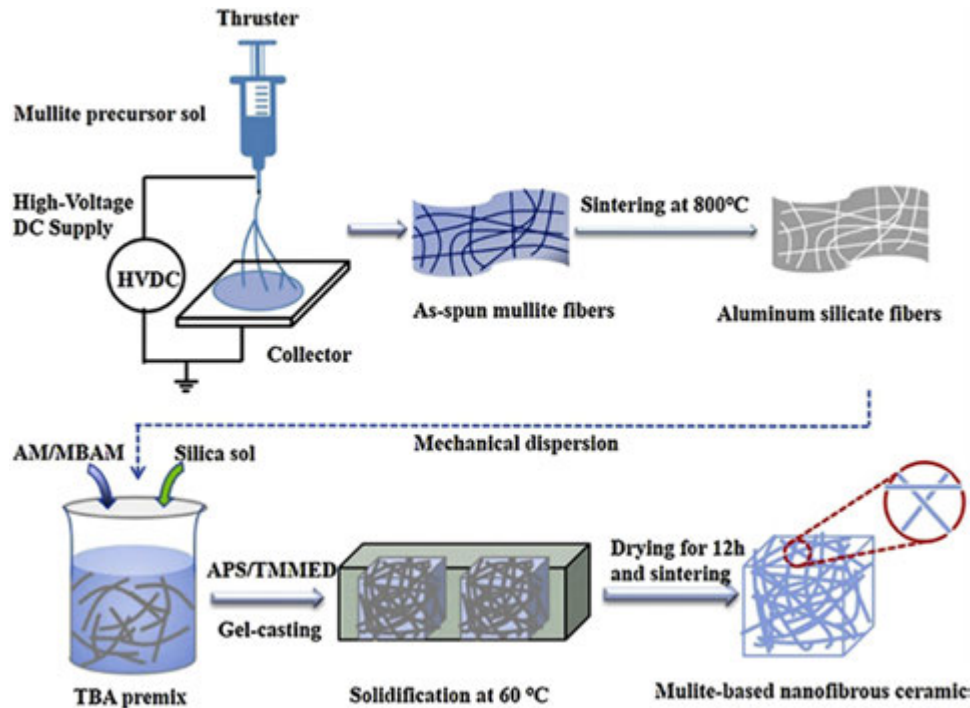


Fig. 12 The mullite nanofibrous porous ceramics manufacturing process flow chart. Reproduced from Zhang, Y., Wu, Y., Yang, X., *et al.*, 2020. High-strength thermal insulating mullite nanofibrous porous ceramics. *J. Eur. Ceram. Soc.* 40, 2090–2096.

Advanced mullite ceramics

Advanced ceramics or engineered ceramics, also previously called industrial ceramics, are various inorganic chemical compounds, not necessarily oxides and silicates, that exhibit improved physical and chemical properties and can be grouped according to their field of application: electrical (e.g., semiconductors, insulators, dielectrics, piezoelectrics and pyroelectrics, and superconductors), optical (e.g., phosphors, lasing crystals, mirrors, and reflectors), magnetics (e.g., permanent magnets), and structural ceramics (Cardarelli, 2018). However, besides the traditional use of mullite as a clay product, for which it is credited with giving superior properties for traditional ceramics, it has become a strong candidate for use as an advanced structural, optical, and functional ceramic in recent decades.

Monolithic mullite ceramics

Monolithic ceramic materials, as typical brittle materials, possess very limited plastic deformation capability (Sōmiya *et al.*, 2003). The characteristics of monolithic mullite ceramics are influenced by the amount, size, and distribution of mullite, and by the occurrence of coexisting phases and porosity (Schneider *et al.*, 2015). Liu *et al.* (2020) investigated the influence of sintering temperature (1200–1500°C) on the microstructural and mechanical properties of monolithic mullite ceramics. In this work, three kinds of mullite powders, including micro-, submicron, and nano-powders, were obtained through physical or chemical methods, and the fabrication of monolithic mullite ceramics with the use of these powders as raw materials were studied. They found that the mullite ceramic produced using submicron-powder became fully dense after being sintered at 1200°C, and exhibited a high flexural strength of 254.7 MPa and fracture toughness of 2.9 MPa m^{1/2}, indicating that low-temperature densification of mullite ceramics could be achieved by enhancing the sintering activity of the mullite powder. Li *et al.* (2016) prepared hierarchical porous mullite monoliths via a sol-gel process accompanied by phase separation. In this process, three different silicon sources are used, hypotoxic tetraethylorthosilicate (TEOS), nontoxic aqueous colloidal silica (Aq), and tetramethoxysilane (TMOS). Consequently, it was found that the relative crystallinity is highest in the TEOS system, and lowest in the aqueous colloidal silica system. In addition, Arzani *et al.* (2018) prepared ceramic monolith microfilters (MF), using kaolinitic clay, for the purification of solid-liquid wastewater. The experimental setup and the membrane module are represented in Fig. 10(a) and (b), respectively. The membrane prepared at a sintering temperature of 1150°C and 5 h dwell time, presented specific properties such as permeation flux of 80.9 kg m⁻² h⁻¹ and NTU rejection of 89.8%, mechanical strength of 5.8 MPa, 49.3% porosity and pore size of 1.2 μm. This material could be used for treating solid-liquid wastewaters.

Mullite fibers

Generally, mullite fibers are widely used in industrial ceramics due to their excellent creep resistance at high temperature, good thermal and chemical stability, low thermal expansion coefficient and good dielectric properties (Schneider and Komarneni, 2006). Zhu *et al.*

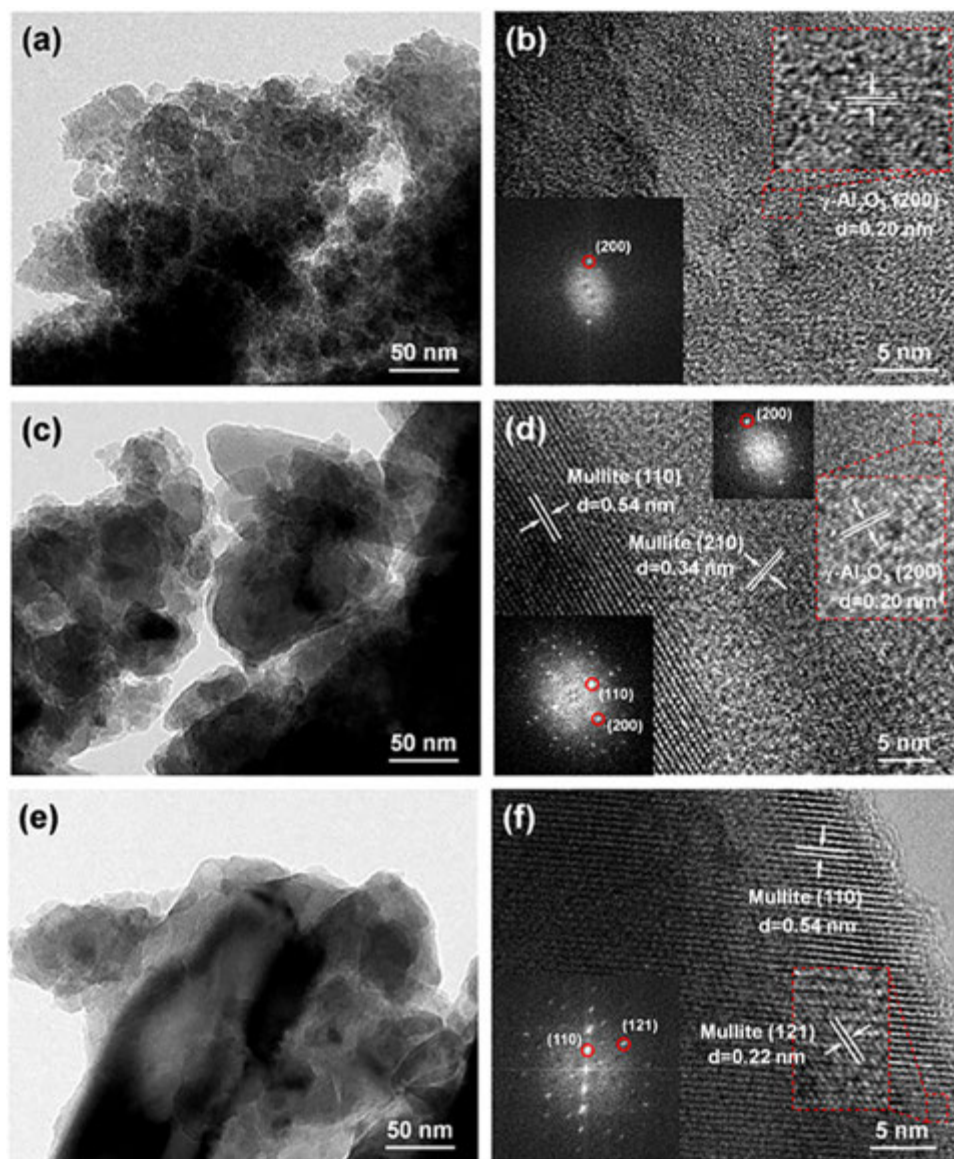


Fig. 13 TEM and HRTEM descriptions of the diphasic mullite fibers sintered at (a, b) 1000°C, (c, d) 1200°C and (e, f) 1400°C. Reproduced from Gao, Y., Liu, W., Song, X., *et al.*, 2019. Preparation, characterization and mechanical properties of continuous mullite fibers derived from the diphasic sol-gel route. *J. Sol-Gel Sci. Technol.* 92, 75–83.

(2019) studied different properties of porous and nanofibrous mullite fiber-based ceramics. The specimens shown in Fig. 11 are typical mullite fibrous ceramics processed by infiltration and in situ pyrolysis of organic precursors (dimethyl silicone oil and rubber) followed by sintering at 1500°C for 2 h in air atmosphere. Their diameter and thickness were 33 ± 0.5 mm and 20 ± 0.5 mm, respectively. From this work (Zhu *et al.*, 2019), highly porous mullite fiber-based ceramics with a three-dimensional cross structure were successfully designed and fabricated by a filtration method. Polysiloxane binder was introduced in the bonding system in order to analyze the thermal migration of silica sol and to form more stable nodes in the skeleton. The results showed that all specimens recorded high porosity (74.1%–80.9%), low density (0.554 g/cm^3 to 0.608 g/cm^3) and relatively low thermal conductivity ($<0.14 \text{ W m}^{-1} \text{ K}^{-1}$).

In addition, the fabrication of mullite nanofibrous porous ceramics was investigated using a gel-casting method, in order to further increase the strength of the mullite fibrous ceramics (Zhu *et al.*, 2019); the manufacture flow chart of the mullite nanofibrous porous ceramics is shown in Fig. 12. It has been concluded that mullite nanofibrous porous ceramics exhibit a higher compressive strength (0.837 MPa) compared to that of mullite micron-fibrous porous ceramics (0.515 MPa) with density values of 0.202 and 0.266 g/cm^3 , respectively. From this study, the obtained materials that present the best combination of mechanical and thermal properties can be regarded as potential high-temperature thermal insulators in various thermal protection systems.

Continuous mullite fibers have also attracted considerable attention because of their range of applications such as insulators, filters, catalysts, etc. or as reinforcements for ceramic matrix composites (CMCs). Gao *et al.* (2019) fabricated continuous mullite

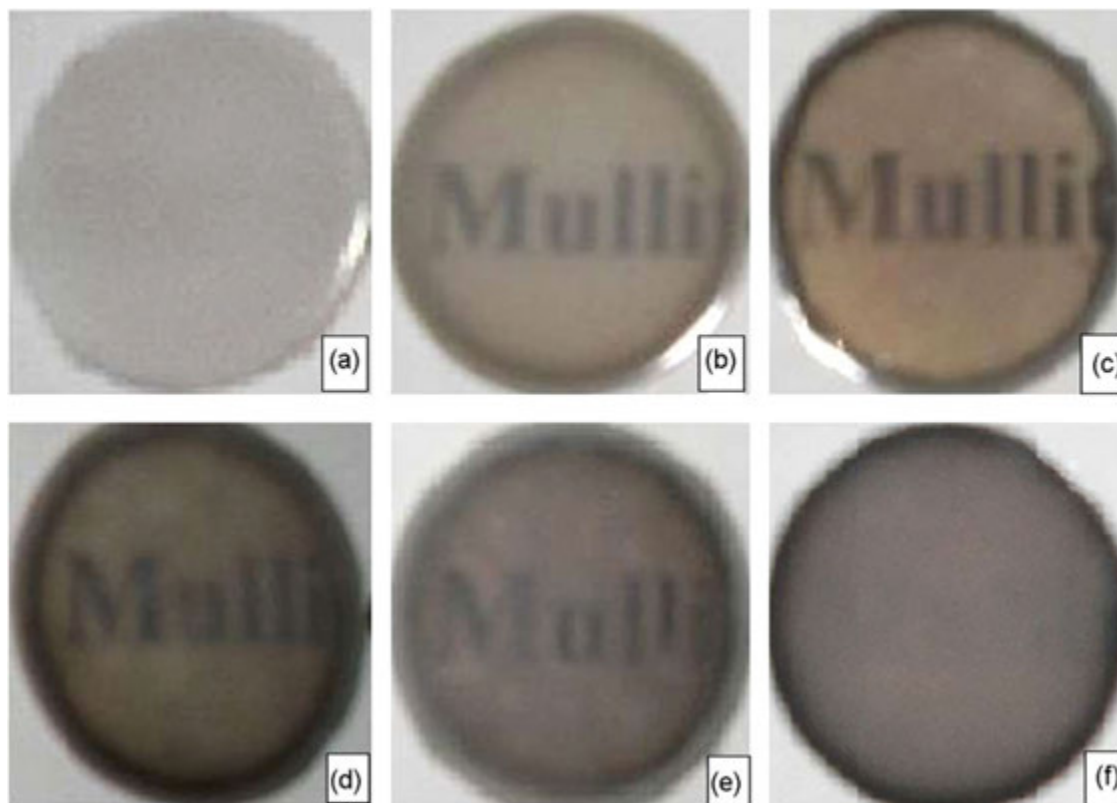


Fig. 14 Appearance of sintered mullite ceramic: samples (a)–(d) sintered at 1450°C for 10 min and the precursors calcined at: (a) 800°C, (b) 1000°C, (c) 1100°C, (d) 1400°C. Samples (e) and (f) sintered at 1500°C and at 1550°C, respectively, after precursors calcined at 1000°C. Reproduced from Zhang, G., Wang, Y., Fu, Z., *et al.*, 2009. Transparent mullite ceramic from single-phase gel by spark plasma sintering. *J. Eur. Ceram. Soc.* 29, 2705–2711.

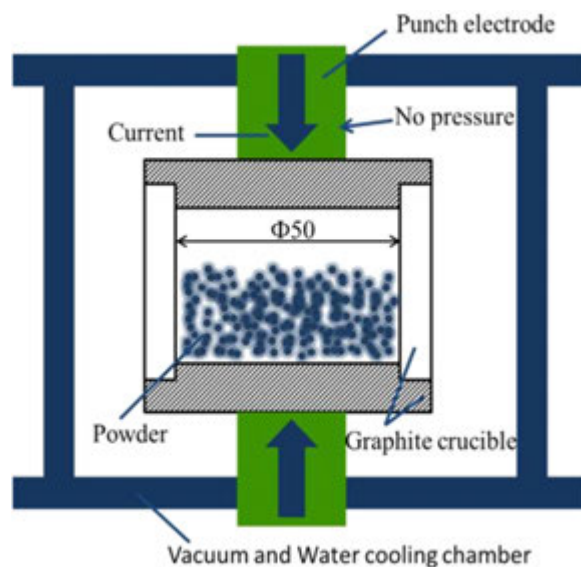


Fig. 15 Schematic illustration of the graphite die used for spark plasma sintering of mullite ceramic powders.

fibers via the diphasic sol-gel route. Aluminum isopropoxide (AIP) and aluminum nitrate (AN) as the alumina sources and colloidal silica as the silica source were the starting materials in this study. According to the TEM and HRTEM results ([Fig. 13](#)), it is noted that the crystal grain sizes increased considerably at higher temperatures. Consequently, at 1000°C ([Fig. 13\(b\)](#)), the formed

γ -Al₂O₃ grains with sizes smaller than 15 nm were delimited by amorphous silica and showed crystallographic orientation in the (200) crystal plane. At 1200°C (Fig. 13(d)) the fibers were composed of mullite grains, γ -Al₂O₃ grains and amorphous SiO₂. Therefore, the mullite grains with sizes ranging from 10 to 50 nm mainly grew in the directions of the (110) and (210) crystal faces and the inlaid tiny γ -Al₂O₃ grains still showed crystallographic orientation in the (200) crystal plane. After sintering at 1400°C, the sizes of mullite grains were larger than 200 nm. Fig. 13(f) indicated that the grains grew in the directions of the (110) and (121) crystal faces. Regarding the results of this study, it was suggested that the as-prepared fibers are ideal candidates as reinforcements for ceramics and have promising application in the field of thermal storage.

Transparent mullite ceramics

Transparent ceramics may represent a topic of interest for many ceramists and also for people outside this community, like laser, lighting, or military optical systems developers (Goldstein *et al.*, 2020). Recently, many ceramics have been reclassified as transparent materials, and the mechanisms that make them transparent have also gradually become clearer (Somiya *et al.*, 2003). Exhibiting optical transparency and other highly desirable properties such as a low thermal expansion coefficient, high strength, and a good thermal shock resistance, mullite can be useful as an ideal optical window material at elevated temperatures (Xiao *et al.*, 2020). Zhang *et al.* (2009) fabricated transparent mullite ceramics via spark plasma sintering (SPS) from monophasic precursors. In this work, the effect of the heat treatments, precursor powders, and sintering parameters on the mullite ceramics were studied. Results showed that the as-sintered samples without any additive, exhibited relative bulk density of above 97.5% and an infrared transmittance of 75%–82% in the wavelength range of 2.5–4.3 μ m. The heat treatments of the precursor powders below 1000°C were unfavorable for the complete elimination of -OH, H₂O, and organic compounds, which had negative effects on the optical properties of the final material. In contrast, the increase of the sintering temperature above 1450°C resulted in the decrease of the transmittance of sintered specimens due to elongated grain growth (Zhang *et al.*, 2009). Fig. 14 shows samples which were sintered at 1450°C for 10 min after calcination at (a) 800, (b) 1000, (c) 1100 and (d) 1400°C. In addition, the samples shown in Fig. 14(e) and (f) were previously calcined at 1000°C then sintered at 1500 and 1550°C, respectively. According to these trends, it was suggested that the best calcination range is 1000°C < T < 1400°C in order to ensure the total removal of organics and avoid the occurrence of low powder surface areas and hard agglomerates (both of which are unfavorable for packing, namely when calcining at 1400°C).

Ren *et al.* (2015) synthesized mullite nano-powders from precursor materials using the sol-gel process and pulsed current heating. In addition, infrared transparent mullite ceramics were obtained by the spark plasma sintering method shown schematically in Fig. 15. From this study, a mullite ceramic was achieved with the following properties: infrared transmittance between 83% and 88% in the wavelength range from 2.5 to 4 μ m, fine grain size of 200 nm, hardness and toughness values equal to 17.82 GPa and 3.6 MPa m^{1/2}, respectively.

Summary

This chapter has reviewed various details regarding mullites, from the crystal structure to synthesis methods and to the final properties and applications. Indeed, these aluminosilicates appear to be very attractive for improving ceramic microstructures and physical/chemical properties for everyday life products as well as for new technology trends and environmental issues. Some clarification on the crystallization relationships with starting phases need to be investigated for the mullite solid solutions. In addition, the implementation of other processing methods including additive manufacturing are open research and development topics for mullite-based materials.

References

- Aksay, I.A., Dabbs, D.M., Sarikaya, M., 1991. Mullite for structural, electronic, and optical applications. *J. Am. Ceram. Soc.* 74, 2343–2358. doi:10.1111/j.1151-2916.1991.tb06768.x.
- Angel, R.J., McMullan, R.K., Prewitt, C.T., 1991. Substructure and superstructure of mullite by neutron diffraction. *Am. Mineral.* 76, 332–342.
- Aryal, S., Rulis, P., Ching, W., 2012. Mechanical properties and electronic structure of mullite phases using first-principles modeling. *J. Am. Ceram. Soc.* 95, 2075–2088.
- Arzani, M., Mahdavi, H.R., Sheikhi, M., Mohammadi, T., Bakhtiari, O., 2018. Ceramic monolith as microfiltration membrane: Preparation, characterization and performance evaluation. *Appl. Clay Sci.* 161, 456–463.
- Belnou, F., 2002. Mullitisation et inhibition du retrait dans des systèmes multioxydes alumine-zircon et porcelaine alumineuse. These Docteurat. Ecole Nationale Supérieure des Mines de Saint-Etienne et de L'institut National Polytechnique de Grenoble.
- Birkenstock, J., Petříček, V., Pedersen, B., Schneider, H., Fischer, R.X., 2015. The modulated average structure of mullite. *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.* 71, 358–368. doi:10.1107/S205252061500757X.
- Boussois, K., Deniel, S., Tessier-Doyen, N., *et al.*, 2013. Characterization of textured ceramics containing mullite from phyllosilicates. *Ceram. Int.* 39, 5327–5333. doi:10.1016/j.ceramint.2012.12.038.
- Bowen, N.L., Greig, J.W., 1924. The system: Al₂O₃-SiO₂. *J. Am. Ceram. Soc.* 7, 238–254.
- Burnham, C.W., Buerger, M.J., 1961. Refinement of the crystal structure of andalusite. *Zeitschrift Für Krist. Mater.* 115, 269–290.
- Burnham, C.W., 1963. Refinement of the crystal structure of kyanite. *Zeitschrift für Krist. Mater.* 118, 337–360.
- Cardarelli, F., 2018. *Materials Handbook*, third ed. Springer.
- Carter, C.B., Norton, M.G., 2007. *Ceramic Materials: Science and Engineering*. Springer.
- Chakraborty, A.K., 2014. *Phase Transformation of Kaolinite Clay*. Springer. doi:10.1007/978-81-322-1154-9.
- Chen, A.-N., Gao, F., Li, M., *et al.*, 2019. Mullite ceramic foams with controlled pore structures and low thermal conductivity prepared by SLS using core-shell structured polyamide12/FAHSS composites. *Ceram. Int.* 45, 15538–15546.

- Chen, S., Cai, W.-H., Wu, J.-M., *et al.*, 2020a. Porous mullite ceramics with a fully closed-cell structure fabricated by direct coagulation casting using fly ash hollow spheres/kaolin suspension. *Ceram. Int.* 46, 17508–17513.
- Chen, R., Hei, D., Wang, Y., Li, S., Jia, W., 2020b. Effects of different kinds of sillimanite minerals on the properties of mullite ceramic foams. *Mater. Res. Express* 6, 125203.
- Deniel, S., Tessier-Doyen, N., Dublanche-Tixier, C., Chateigner, D., Blanchart, P., 2010. Processing and characterization of textured mullite ceramics from phyllosilicates. *J. Eur. Ceram. Soc.* 30, 2427–2434.
- Deutou, J.N.G., Zounedou, N., Kaze, R.C., *et al.*, 2020. Semi-vitrified porous kyanite mullite ceramics: Young modulus, microstructure and pore size evolution. *SN Appl. Sci.* 2, 1–12.
- Digne, M., Sautet, P., Raybaud, P., Euzen, P., Toulhoat, H., 2004. Use of DFT to achieve a rational understanding of acid–basic properties of γ -alumina surfaces. *J. Catal.* 226, 54–68.
- Dong, L., Ruan, Z., Chen, Y., Li, J., Luo, L., 2019. Fabrication, microstructure and physico-mechanical properties of highly porous acicular mullite ceramic foams by freeze casting method. *Mater. Res. Express* 6, 115091.
- Duval, D.J., Risbud, S.H., Shackelford, J.F., 2008. Mullite. In: Duval, D.J., Shackelford, J.F. (Eds.), *Ceramic and Glass Materials: Structure, Properties and Processing*. Switzerland: Springer, pp. 27–39.
- Fischer, R.X., Schneider, H., Voll, D., 1996. Formation of aluminum rich 9:1 mullite and its transformation to low alumina mullite upon heating. *J. Eur. Ceram. Soc.* 16, 109–113.
- Gao, Y., Liu, W., Song, X., *et al.*, 2019. Preparation, characterization and mechanical properties of continuous mullite fibers derived from the diphasic sol-gel route. *J. Sol-Gel Sci. Technol.* 92, 75–83.
- Goldstein, A., Krell, A., Burshtein, Z., 2020. *Transparent Ceramics: Materials, Engineering, and Applications*. John Wiley & Sons.
- Gong, L., Wang, Y., Cheng, X., Zhang, R., Zhang, H., 2013. Thermal conductivity of highly porous mullite materials. *Int. J. Heat Mass Transf.* 67, 253–259.
- Hammam, A., Lecomte-Nana, G., Daou, I., Zibouche, F., 2020. Sintering and final properties of kaolinite-magnesite tapes for the manufacture of cordierite-mullite ceramics. *Int. J. Appl. Ceram. Technol.* 17, 2265–2276. doi:10.1111/ijac.13568.
- Harper, C.A., 1993. *Electronic Materials and Processes Handbook*. New York: McGraw-Hill.
- Islam, S., Bidin, N., Riaz, S., Naseem, S., Sanagi, M.M., 2017. Low temperature sol-gel based erbium doped mullite nanoparticles: Structural and optical properties. *J. Taiwan Inst. Chem. Eng.* 70, 366–373.
- Kalemtaş, A., Özey, N., Aytekin Aydin, M.T., 2018. Processing of layered porous mullite ceramics. *J. Aust. Ceram. Soc.* 54, 545–555. doi:10.1007/s41779-018-0183-6.
- Kind, M., Martin, H., Stephan, P., *et al.*, 2010. *VDI Heat Atlas*. Berlin: Springer-Verlag.
- Klar, P.B., De La Pinta, N., Lopez, G.A., *et al.*, 2017. Ordered vacancy distribution in 2/1 mullite: A superspace model. *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.* 73, 377–388. doi:10.1107/S2052520617001652.
- Krenzel, T.F., Schreuer, J., Laubner, D., Cichocki, M., Schneider, H., 2019. Thermo-mechanical properties of mullite ceramics: New data. *J. Am. Ceram. Soc.* 102, 416–426.
- Lecomte, G., Blanchart, P., 2006. Textured mullite at muscovite–kaolinite interface. *J. Mater. Sci.* 41, 4937–4943.
- Lecomte-Nana, G., Mokrani, A., Tessier-Doyen, N., Boussois, K., Goure-Doubi, H., 2013. Texturation of model clay materials using tape casting and freezing. *Ceram. Int.* 39, 9047–9053. doi:10.1016/j.ceramint.2013.04.108.
- Lee, W.E., Iqbal, Y., 2001. Influence of mixing on mullite formation in porcelain. *J. Eur. Ceram. Soc.* 21, 2583–2586.
- Lee, W.E., Souza, G.P., McConville, C.J., Tarvornpanich, T., Iqbal, Y., 2008. Mullite formation in clays and clay-derived vitreous ceramics. *J. Eur. Ceram. Soc.* 28, 465–471. doi:10.1016/j.jeurceramsoc.2007.03.009.
- Lenz, S., Birkenstock, J., Fischer, L.A., *et al.*, 2019. Natural mullites: Chemical composition, crystal structure, and optical properties. *Eur. J. Mineral.* 31, 353–367.
- Li, C., Zhou, Y., Tian, Y., *et al.*, 2019. Preparation and characterization of mullite whisker reinforced ceramics made from coal fly ash. *Ceram. Int.* 45, 5613–5616.
- Li, J., Zhao, T., Li, F., *et al.*, 2016. A comparative study on the synthesis mechanism and microstructural development of hierarchical porous mullite monoliths obtained by the sol-gel process with three different silicon sources. *Ceram. Int.* 42, 4806–4818.
- Liu, D., Gui, K., Long, J., *et al.*, 2020. Low-temperature densification and mechanical properties of monolithic mullite ceramic. *Ceram. Int.* 46, 12329–12334. doi:10.1016/j.ceramint.2020.01.282.
- MacKenzie, K.J.D., Dougherty, T., Barrel, J., 2008. The electronic properties of complex oxides of bismuth with the mullite structure. *J. Eur. Ceram. Soc.* 28, 499–504.
- Martín-Torres, M., Freestone, I.C., Hunt, A., Rehren, T., 2008. Mass-produced mullite crucibles in medieval Europe: Manufacture and material properties. *J. Am. Ceram. Soc.* 91, 2071–2074.
- Mekap, A., Sahoo, R.K., Das, A., *et al.*, 2019. Two-step plasma mediated synthesis of mullite and sillimanite powder and their suspensive spray coating on stainless steel. *Surf. Coatings Technol.* 372, 103–110.
- Mishra, R., Ningthoujam, R.S., 2017. Chapter 11 – High-temperature ceramics. In: Tyagi, A.K., Banerjee, S. (Eds.), *Materials Under Extreme Conditions: Recent Trends and Future Prospects*. Amsterdam: Elsevier, pp. 377–409. doi:10.1016/B978-0-12-801300-7.00011-5.
- Ren, L., Fu, Z., Wang, Y., *et al.*, 2015. Fabrication of transparent mullite ceramic by spark plasma sintering from powders synthesized via sol-gel process combined with pulse current heating. *Mater. Des.* 83, 753–759.
- Sanad, M.M.S., Rashad, M.M., Abdel-Aal, E.A., El-Shahat, M.F., Powers, K., 2014. Optical and electrical properties of Y^{3+} ion substituted orthorhombic mullite $Y(x)Al(6-x)Si_2O_{13}$ nanoparticles. *J. Mater. Sci. Mater. Electron.* 25, 2487–2493.
- Sanz, A., Bastida, J., Caballero, A., Kojdecki, M., 2018. X-ray diffraction Warren–Averbach mullite analysis in whiteware porcelains: influence of kaolin raw material. *Clay Miner.* 53, 471–485.
- Sarkar, R., 2016. *Refractory Technology: Fundamentals and Applications*, first ed. Boca Raton: CRC Press.
- Schacht, C., 2004. *Refractories Handbook*, first ed. Boca Raton: CRC Press.
- Schneider, H., Komarneni, S., 2006. Mullite. Weinheim: Wiley-VCH.
- Schneider, H., Schreuer, J., Hildmann, B., 2008. Structure and properties of mullite-A review. *J. Eur. Ceram. Soc.* 28, 329–344. doi:10.1016/j.jeurceramsoc.2007.03.017.
- Schneider, H., Fischer, R.X., Schreuer, J., 2015. Mullite: Crystal structure and related properties. *J. Am. Ceram. Soc.* 98, 2948–2967. doi:10.1111/jace.13817.
- Schneider, H., Saruhan, B., Voll, D., Merwin, L., Sebal, A., 1993. Mullite precursor phases. *J. Eur. Ceram. Soc.* 11, 87–94.
- Seong, H., Kim, U., Kim, M., *et al.*, 2007. Synthesis and optical properties of mullite nanowires. *J. Am. Ceram. Soc.* 90, 1937–1939.
- Shackelford, J.F., 2016. *Introduction to Materials Science for Engineers*, eighth ed. London: Pearson.
- Shepherd, E.S., Rankin, G.A., Wright, F.E., 1909. The binary systems of alumina with silica, lime and magnesia. *Am. J. Sci.* 28, 293.
- Sirilar, P., Srisukhumbowornchai, N., Thanakijkasem, P., Sirisoonthorn, S., Klein, G., 2019. Influence of Lampang pottery stone: Local materials in Thailand on CQF ratio, key properties, mullite formation and glaze-body fit of vitreous ceramic sanitary ware. *J. Aust. Ceram. Soc.* 55, 1153–1160.
- Sõmiya, S., Aldinger, A., Claussen, N., *et al.*, 2003. *Handbook of Advanced Ceramics: Materials Science, Processing and their Applications*. vol. 2. Amsterdam: Elsevier.
- Xiao, Z., Yu, S., Li, Y., *et al.*, 2020. Materials development and potential applications of transparent ceramics: A review. *Mater. Sci. Eng. R: Reports* 28, 100518.
- Yao, S., Zhou, H., Wu, S., *et al.*, 2020. Microstructure and physical properties of a mullite brick in blast furnace hearth: Influence of temperature. In: *Ironmaking & Steelmaking: Processes, Products and Applications*, vol. 3. Taylor and Francis, pp. 1–7.
- Zhang, G., Wang, Y., Fu, Z., *et al.*, 2009. Transparent mullite ceramic from single-phase gel by spark plasma sintering. *J. Eur. Ceram. Soc.* 29, 2705–2711.
- Zhang, Y., Wu, Y., Yang, X., *et al.*, 2020. High-strength thermal insulating mullite nanofibrous porous ceramics. *J. Eur. Ceram. Soc.* 40, 2090–2096.
- Zhu, W., Guo, A., Xue, Y., *et al.*, 2019. Mechanical evaluations of mullite fibrous ceramics processed by filtration and in situ pyrolysis of organic precursor. *J. Eur. Ceram. Soc.* 39, 1329–1335.

Aluminum Titanate, Structure and Properties

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Introduction

Aluminum titanate (Al_2TiO_5 , hereinafter AT) ceramics are synthetic materials which, owing to the high melting point of AT, low thermal conductivity, low thermal expansion and excellent thermal shock resistance, have a high technological interest. AT ceramics are usually prepared by reactive sintering of alumina (Al_2O_3) and titania (TiO_2) powders, forming a compound of stoichiometric proportions.

AT ceramics are commercially classified as a specialized material commonly used in extreme temperature conditions and found mostly in the non-ferrous molten metal industry, especially in aluminum foundries. They are also used as components of internal combustion engines, exhaust port liners, crucibles for metallurgy and thermal barriers.

The microstructure of AT ceramics, the main feature of which is microcracking along the grain boundaries, strongly determines their main properties. Microcracking occurs during cooling from the sintering temperature, owing to the unusual extreme anisotropy in thermal expansion of the orthorhombic $\beta\text{-Al}_2\text{TiO}_5$ single-crystal. The presence of these microcracks leads to technologically desirable properties such as low thermal expansion and thermal diffusivity of polycrystalline $\beta\text{-Al}_2\text{TiO}_5$ materials. However, many potential applications of these materials are limited due to their moderate to low strength values. Consequently, huge efforts have been, and still are, devoted to the improvement of the mechanical behavior of aluminum titanate materials through composition and microstructural control (solid solutions, grain size and shape control, secondary phases and AT-based monolithic and laminated composites).

In previous reviews (Wohlfromm, 1991; Barrios de Arenas, 2012; Thomas and Stevens, 1989a,b; Kim and Gauckler, 2012) different aspects of AT such as structure, properties, synthesis from reaction sintering of alumina and titania powders and thermal stability have been outlined. The relevance and applications of materials with almost zero thermal expansion due to microcracking and which are, consequently, highly resistant to thermal shock have also been described (Papitha *et al.*, 2014; Mandal *et al.*, 2017; Kim, 2010). Moreover, the extraordinary thermo-mechanical behavior of AT has led to the inclusion of this compound in composite materials with structural applications (Morishima *et al.*, 1986; Padture *et al.*, 1993a; Runyan and Bennison, 1991; Yano *et al.*, 1992). Successful application of aluminum titanate materials is determined by the ability to control the microcracking phenomena, together with the ability to manage the decomposition behavior.

The aim of this chapter is to update the available information, especially with respect to the technological interest of aluminum titanate materials, with an additional focus on improving their mechanical performance through the design of ceramic composites. In this sense, the strategy of developing laminated structures, combining layers of high strength brittle materials such as alumina with layers with a high content of AT, with a significant presence of microcracks, is shown as an effective approach to increase toughness (fracture energy) of these structures (Bueno and Baudín, 2007, 2009).

$\text{Al}_2\text{O}_3 - \text{TiO}_2$ Phase Equilibrium Diagram

The $\text{Al}_2\text{O}_3 - \text{TiO}_2$ phase equilibrium relationships can be described by a simple binary system that has been studied by different authors (Lang *et al.*, 1952; Freudenberg, 1987). The main features of the $\text{Al}_2\text{O}_3 - \text{TiO}_2$ phase equilibrium are summarized in Fig. 1, which displays the stability regions with Al_2TiO_5 as the only intermediate compound, and the existence of two eutectics: between Al_2TiO_5 and Al_2O_3 and between Al_2TiO_5 and TiO_2 . Due to the high AT melting point (in this system no liquid phase appears under 1705°C) the usefulness for the design of refractory materials is evident. In agreement with the equilibrium diagram proposed by Lang *et al.* (1952), Fig. 1 shows that there are two polymorphic forms of aluminum titanate, $\alpha\text{-Al}_2\text{TiO}_5$ (stable between 1860 and 1820°C) and $\beta\text{-Al}_2\text{TiO}_5$ (stable between 1820 and $\approx 1280^\circ\text{C}$).

The transformation from β to $\alpha\text{-Al}_2\text{TiO}_5$ is spontaneous and completely reversible. Below approximately 1280°C , aluminum titanate is unstable and decomposes by eutectoid reaction into $\alpha\text{-Al}_2\text{O}_3$ and rutile- TiO_2 , according to reaction (1) (Buscaglia *et al.*, 1994b):



although there is a kinetic inhibition for such a decomposition which depends on grain size and the incorporation of stabilizing phases (Pohlmann *et al.*, 1975). It is known that some additives (MgO , Fe_2O_3 , SiO_2 , ZrO_2) are able to influence both the thermal stability and the microstructure of aluminum titanate (Kim, 2010; Nagano *et al.*, 1999).

Freudenberg and Mocellin (1987) based on subsequent contributions to the $\text{Al}_2\text{O}_3 - \text{TiO}_2$ diagram, proposed $\beta\text{-Al}_2\text{TiO}_5$ as the only stable compound in the system with a decomposition temperature of $1280 \pm 1^\circ\text{C}$, and described the regions of solid solutions plotted in Fig. 1. The solubility of Al_2O_3 in TiO_2 is about an order of magnitude greater than the solubility of TiO_2 in Al_2O_3 . The solubility of both Al_2O_3 and TiO_2 in Al_2TiO_5 is practically negligible; that is, aluminum titanate can be considered a stoichiometric compound; however, this statement is correct only in an oxidizing atmosphere.

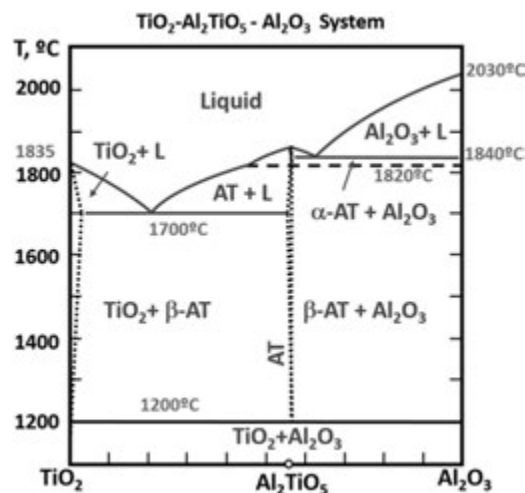


Fig. 1 Phase equilibrium diagram of the $\text{Al}_2\text{O}_3 - \text{TiO}_2$ system Adapted from Freudenberg, B., Mocellin, A., 1987. Aluminum titanate formation by solid-state reaction of fine Al_2O_3 and TiO_2 powders. *Journal of the American Ceramic Society* 70 (1), 33–38. doi:10.1111/j.1151-2916.1987.tb04849.x. The solid solution regions of Al_2O_3 in TiO_2 and negligible solubility of both TiO_2 and Al_2O_3 in AT have also been plotted.

More recently, [Berger and Sayir \(2008\)](#) and [Ilatovskaia et al. \(2017\)](#) discussed a high temperature phase, $\text{Al}_6\text{Ti}_2\text{O}_{13}$, that is not an allotropic form of AT, as described by [Lang et al. \(1952\)](#). This compound would participate as an intermediary phase in the eutectic reaction $\text{L} \rightarrow \text{Al}_6\text{Ti}_2\text{O}_{13} + \text{Al}_2\text{TiO}_5$ instead of $\text{L} \rightarrow \text{Al}_2\text{TiO}_5 + \text{Al}_2\text{O}_3$. In addition, the peritectic reaction $\text{L} + \text{Al}_2\text{O}_3 \rightarrow \text{Al}_2\text{TiO}_5$ at 1850°C is also described ([Ilatovskaia et al., 2017](#)).

The thermal instability of Al_2TiO_5 is one of its disadvantages ([Kim, 2010](#)). Several additives have been employed that demonstrated certain efficiency for stabilizing microstructures ([Wohlfrohm, 1991](#); [Rezaie et al., 2009](#)).

Aluminum Titanate Single-Crystals

Crystalline Structure

Al_2TiO_5 crystallizes in a base-centered orthorhombic structure with the *Cmcm* space group. Although some authors assign a *Bbmm* or *Ccmm* space group, these space groups are identical to *Cmcm* except for an interchange of the *a*, *b* and *c* axes. An elemental cell contains 4 formula units, and this results in a theoretical density of 3.702 g cm^{-3} ([Holcombe and Coffey, 1973](#)). The review by [Thomas and Stevens \(1989a\)](#) highlighted as more significant the cell parameters analyzed by [Austin and Schwartz \(1953\)](#) and [Morosin and Lynch \(1972\)](#).

[Austin and Schwartz \(1953\)](#) showed that aluminum titanate is isomorphic with pseudobrookite, Fe_2TiO_5 (**Fig. 2**). This compound gives the name to a group of complex oxides that can be described by the formula A_2BO_5 (where A is a trivalent ion and B is a tetravalent one), which crystallize with this same structure. In the Al_2TiO_5 structure, each Al^{3+} or Ti^{4+} cation are found in octahedral sites surrounded by oxygen. The double chains of distorted octahedra are parallel to the *c* axis. The degree of distortion increases with the difference between the radii of the cations and, thus, is much greater in Al_2TiO_5 than, for example, in Fe_2TiO_5 or Mg_2TiO_5 , due to the small ionic radius of Al^{3+} ([Wohlfrohm, 1991](#)). As will be discussed later, this degree of distortion of the structure can be related to thermal expansion, enthalpy of formation, and compound stability.

On the other hand, in Al_2TiO_5 there is no preference for the two metallic sites present in the structure (Al^{3+} and Ti^{4+}) that are distributed in the network completely randomly. This behavior contrasts with that of the isomorph Fe_2TiO_5 , in which there is a tendency of Fe^{3+} towards the sites of less distortion. [Ohya et al. \(2017\)](#) point out that this random distribution of cations leads to maximum entropy giving rise to the structure of TA becoming stable at high temperature (above 1280°C) despite the fact that the reaction of AT formation from the mixture of corundum and rutile is endothermic.

Thermal Expansion

Pseudobrookite-type oxides are characterized by a strong anisotropy in thermal expansion, expressed as the difference between the coefficients of expansion of the crystallographic axes with the highest and lowest thermal expansion, $\Delta\alpha = \alpha_{\text{max}} - \alpha_{\text{min}}$. In **Table 1** it is observed that the expansion is very large in the direction of the *c* axis, which corresponds to the direction of double chains of distorted octahedra, moderate in the *b* axis, and negative in the *a* axis. The strong expansion in the *b* and *c* directions has been related to the tendency of oxygen atoms to move towards a position of less distortion with increasing temperature. In addition, the maximum distortion of the octahedra in the pseudobrookite isomorph series (with Al, Ga, and Fe as the trivalent cation) also corresponds to the maximum anisotropy. ([Wohlfrohm, 1991](#); [Bayer, 1971, 1973](#)).

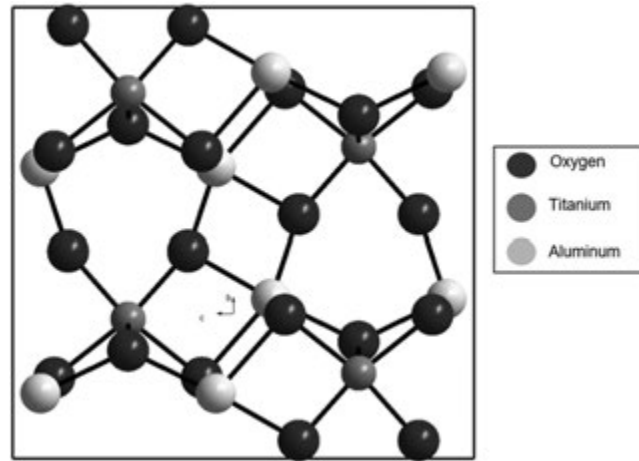


Fig. 2 Crystal structure of Pseudobrookite. Modified from Wikimedia Commons, 2009.

Table 1 Thermal expansion coefficient in aluminum titanate single crystals and polycrystalline materials

Thermal Expansion Coefficient along Crystallographic axes ($\times 10^{-6}\text{K}^{-1}$)	
$\alpha_{a20-520}/\alpha_{a20-1000}$	– 2.9/3.0
$\alpha_{b20-520}/\alpha_{b20-1000}$	10.3/11.8
$\alpha_{c20-520}/\alpha_{c20-1000}$	20.1/21.8
Thermal Expansion Anisotropy ($\times 10^{-6}\text{K}^{-1}$)	
$\Delta\alpha_{20-520}/\Delta\alpha_{20-1000}$	23.0/24.8
Average Crystallographic Thermal Expansion Coefficient ($\times 10^{-6}\text{K}^{-1}$)	
$\bar{\alpha}_{20-520}/\bar{\alpha}_{20-1000}$	9.2/10.2
Macroscopic Thermal Expansion Coefficient ($\times 10^{-6}\text{K}^{-1}$)	
$\alpha_{20-1000}$	1.0/1.5
$\alpha_{20-1000}$	1.5/1.7

As **Table 1** shows, the high crystallographic thermal expansion in the direction of the c axis is not noticeable in the average crystalline coefficient of expansion, $\bar{\alpha}$, which is of the order of magnitude of those of common oxides. There is usually a direct and simple relationship between the macroscopic coefficient of materials, α , and the crystallographic ones. In the case of polycrystalline materials free of texture, that is, with a statistical distribution of crystal orientations, α generally coincides with the average of the coefficients corresponding to the crystallographic axes, $\bar{\alpha}$. However, in **Table 1** it is seen that this is not the case for Al_2TiO_5 . As will be discussed later, the macroscopic coefficient of thermal expansion, α , of AT materials is much lower than $\bar{\alpha}$, and, below 1000°C , it can even be smaller than the average thermal expansion coefficient of silica glass between 20 and 1000°C , $\alpha_{20-1000^\circ\text{C}} = 0.5 \cdot 10^{-6}\text{K}^{-1}$ (Fernández Navarro, 2003).

Fabrication of AT Materials

Aluminum titanate materials can be manufactured from previously synthesized aluminum titanate powder (Padture *et al.*, 1993a; Runyan and Bennison, 1991; Uribe and Baudín, 2003) or from alumina and titania mixtures that produce aluminum titanate by reaction sintering of the mixtures (Bartolomé *et al.*, 1996; Okamura *et al.*, 1989). Fabrication from previously synthesized aluminum titanate powders is significantly more expensive as it implies, not only the previous reaction, but also the grinding and milling of the synthesized powders and their sintering at relatively high temperatures ($> 1300^\circ\text{C}$). On the contrary, the processing of materials in one step, using reaction sintering of alumina and titania, is more interesting in terms of process costs and energy savings. Moreover, the potential contamination of the powders by milling is avoided.

Reaction Sintering of Alumina and Titania Powders

As described above, ($\text{Al}_2\text{O}_3 - \text{TiO}_2$ phase equilibrium diagram) AT is a stoichiometric compound in an oxidizing atmosphere, consisting of one mole of alumina, Al_2O_3 , and one mole of titania, TiO_2 , according to the solid state reaction described by:



This solid-state reaction of titania and alumina is thermodynamically favorable above 1280°C (Freudenberg and Mocellin, 1987, 1988; Kato *et al.*, 1980). This is an endothermic reaction and only the positive contribution of the entropic term due to the random cations distribution makes the existence of AT at high temperature feasible. Thus, as collected and analyzed by Wohlfromm (1991) the molar free energy for the reaction (ΔG°) corresponds to:

$$\Delta G^\circ = \Delta H^\circ - \Delta S^\circ \cdot T = 17000 - 10.95 \cdot T (\text{J} \cdot \text{mol}^{-1}) \quad (3)$$

Where ΔH° and ΔS° are the enthalpy and the standard molar entropy of the reaction and T is the temperature in K. This expression reflects values of free energy of formation considerably lower than those of most ceramic oxides (e.g.: G_T for Al_2O_3 ranges from -1590 to -945 kJ mol for temperatures, $T = 273$ to 2273 K (See Baudin, 2021, this Encyclopedia "Alumina, Structure and Properties").

The solid state formation reaction of Al_2TiO_5 , from the equimolar mixture of alumina and titania powders has been studied by various researchers: (Uribe and Baudín, 2000; Freudenberg and Mocellin, 1987, 1988; Thomas and Stevens, 1989d; Buscaglia *et al.*, 1996b). In general, in all the works it is established that this reaction involves nucleation and growth processes that occur completely in the solid state, with a rapid initial advance of the reaction and a later, slower reaction phase, controlled by the diffusion of a single or various species. However, the identification of nucleation sites for AT has not led to conclusive results.

Nucleation of Al_2TiO_5 not only involves the energy necessary for the creation of a new surface, but also requires additional elastic energy that overcomes the elastic constraint exerted by the unreacted matrix of particles of alumina and titania on the Al_2TiO_5 grains in formation. This is because the formation of AT from Al_2O_3 and TiO_2 produces a volumetric expansion of $\approx 11\%$ (taking into account the theoretical densities from the XRD files of 3.99 g cm^{-3} for $\alpha\text{-Al}_2\text{O}_3$, ASTM: 42-1468, 4.25 for TiO_2 -rutile, ASTM: 21-1276, and 3.70 g cm^{-3} for $\beta\text{-Al}_2\text{TiO}_5$, ASTM: 26-0040).

Most of the works on the reactive sintering of Al_2TiO_5 from the equimolar mixture of TiO_2 and Al_2O_3 powders of different nature (particle size, purity level, ... etc.) describe that the microstructure of the formed Al_2TiO_5 is characterized by a matrix of porous cells of Al_2TiO_5 , separated by cracks, which in many cases contain inclusions of Al_2O_3 and TiO_2 . These investigations cite as basic references the works by Freudenberg and Mocellin (1987, 1988). These authors focus their research on studies on compacts prepared from equimolar mixtures of fine alumina powders ($d_{50} < 0.4 \mu\text{m}$) and fine ($d_{50} < 1.5 \mu\text{m}$) or coarse ($d_{50} < 13 \mu\text{m}$) powders of titania, subjected to treatments of up to 100 h over a wide range of temperatures. Thus, they determined the existence of two types of nucleation and growth as a function of the temperature range. At low temperature ($T < 1327^\circ\text{C}$) they identified two stages of evolution of the reaction: a first nucleation and growth characterized by a limited number of "easy nucleation" sites and the isolated growth of Al_2TiO_5 cells within a porous matrix of non-reacted Al_2O_3 and TiO_2 particles. Formed Al_2TiO_5 cells are equally porous and inside there are inclusions of Al_2O_3 and TiO_2 . The growth of these Al_2TiO_5 cells progresses until the sample volume is completely occupied and, from that moment, the Al_2TiO_5 formation reaction continues in a second stage at much lower speeds, with a significant percentage of the initial unreacted oxides within the Al_2TiO_5 cells remaining in the final compacts. The kinetic data of the first stage are adjusted to an Avrami model that assumes the initial presence of all nuclei and their three-dimensional growth at constant speed (Hulbert, 1967) which would agree that the random nucleation sites of the Al_2TiO_5 cells correspond to impurities. On the other hand, at high temperature ($T > 1427^\circ\text{C}$), almost instantaneous nucleation and growth occurs throughout the compact.

Therefore, Freudenberg and Mocellin (1987, 1988) concluded that nucleation and growth depend on the treatment temperature and attributed it to the elastic energy barrier that exists for the formation of Al_2TiO_5 , due to the increase in volume implied by the formation of this phase. At high temperature, the driving force of chemical origin for the formation of the Al_2TiO_5 is sufficient to overcome this barrier. On the contrary, at low temperature the elastic energy barrier can only be surpassed in the "easy nucleation sites" that constitute the discontinuities of the material. Likewise, they observed that, at low temperature, the limited nucleation allows the existence of metastable diffusion pairs of the type $\text{Al}_2\text{TiO}_5/\text{TiO}_2/\text{Al}_2\text{O}_3$ where TiO_2 exerts a double function as a reagent and fast path for the diffusion of Al in the first stage of the reaction. At high temperature, rapid nucleation leads to $\text{Al}_2\text{O}_3/\text{Al}_2\text{TiO}_5/\text{TiO}_2$. Consequently, due to the slow transport of the initial oxides through the Al_2TiO_5 cells, the growth rate of Al_2TiO_5 by diffusion is apparently slower at high temperatures.

With regard to the densification of these materials, during the first minutes of the heat treatment, when only 1% of the sample is reacted, practically 80%–90% of the final density is reached. In fact, the densification process comes to a halt when $\approx 10\%$ is reacted.

Concerning the control of the microstructure of the materials manufactured by reactive sintering, Buscaglia *et al.* (1994a,b, 1995, 1996a,b,c) conclude that the nature of the alumina powders used in the reaction determines the microstructural evolution of the formed Al_2TiO_5 . On the one hand, by decreasing the diameter of the alumina particles, the size of the Al_2TiO_5 cells increases ($0.8 \mu\text{m Al}_2\text{O}_3$ – $100 \mu\text{m Al}_2\text{TiO}_5$ versus $0.3 \mu\text{m Al}_2\text{O}_3$ – $400 \mu\text{m Al}_2\text{TiO}_5$) and, on the other, the presence of MgO in the initial oxide mixture reduces the size of the Al_2TiO_5 cells ($\approx 200 \mu\text{m}$ without MgO versus $\approx 20 \mu\text{m}$ with MgO). In the case of the observations of Wohlfromm (1991) on compacts prepared from equimolar mixtures of fine powders, the size of the formed Al_2TiO_5 cells is influenced by the heat treatment speed, noting that, although the size of the Al_2TiO_5 cells can be reduced using fast heating rates, this type of treatment is detrimental to the degree of reaction.

In general, aluminum titanate commercial components such as crucibles, tubes, plates, spacers, etc. (Ceramtec®), are fabricated by reaction sintering. As will be discussed below, industrial processes usually lead to incomplete reaction of the powders and commercial materials present a huge variability of microstructures with different amounts of unreacted minor phases. The particular microstructure developed depends on the presence of the stable $\text{Al}_2\text{O}_3/\text{Al}_2\text{TiO}_5/\text{TiO}_2$ structures the formation of which is determined by the characteristics of the starting powders (size, specific surface area and impurities) and the thermal cycle.

AT Powder Synthesis

The potential of aluminum titanate materials as advanced ceramics led to the development of a number of chemical methods involving solution chemistry or vapor phase reactions for the development of high purity powders with controlled size and high specific surface area during the last century. Extensive description of these methods can be found in the work by [Thomas and Stevens \(1989c\)](#).

Most works deal with the fabrication of AT powders by co-precipitation of alkoxide solutions and subsequent thermal treatments. The controlled hydrolysis of the single alkoxides to coat either γ - Al_2O_3 or TiO_2 dispersed particles has also been proposed ([Brugger and Mocellin, 1986](#)) and also that of hydrolysis of titanium isopropoxide in a dispersed alumina sol ([Okamura et al., 1989](#)). Other methods include reaction of aerosols ([Ingebrethsen et al., 1983](#)), the direct evaporation of the solvent ([Hori and Kurita, 1985](#)) from aqueous solutions ([Kato et al., 1978](#)) and reaction of Al_2O_3 and TiO_2 mixtures prepared by chemical vapor deposition (CVD) ([Hori and Kurita, 1985](#)).

Sol-gel processing ([Vioux, 1997](#)) can also lower the temperature for the synthesis of aluminum titanate. Formation of AT at $\sim 600^\circ\text{C}$ can be achieved via non-hydrolytic synthesis ([Andrianainarivelo et al., 1997](#)) and at around 800°C by a synthesis with alkoxides stabilized with acetyl-acetone ([Bonhomme-Courty et al., 1994](#)). Also acid-catalyzed solutions of aluminum and titanium alkoxides have been used to synthesize Al_2TiO_5 films at around 700°C ([Innocenzi et al., 2005](#)). The formation of aluminum titanate at these low temperatures is attributed to a diffusion-limited crystallization process, which takes place in conditions of high homogeneity at the molecular level reached in the material ([Lange et al., 1994](#)).

In general, powders fabricated by all these methods are pure and present good and fast sinterability, as opposition to rather slow conventional reaction sintering from oxides. The main drawback is price and the difficulty for scaling up due to the relatively small batches that can be prepared.

Novel Processing Methods

Different investigations on new synthesis and shaping methods contemplate the study of the behavior of aluminum titanate or of its main precursors (Al_2O_3 and TiO_2) to obtain materials due to their special combination of thermo-mechanical properties. In this sense, additive manufacturing through directed laser deposition (DLD) of alumina-titania mixtures ([Wu et al., 2019](#)) gave rise to ceramic composites in the alumina – aluminum titanate system in variable proportions, observing a crack suppression effect in most of the obtained materials depending on initial titania amount. Crack-free structures with a continuous matrix phase formed of Al_2TiO_5 successfully reached maximum cross-sectional dimension of 30 mm and maximum length of 150 mm ([Niu et al., 2019](#)).

Flash sintering and SPS experiments have also been performed on Al_2O_3 and TiO_2 nanopowder mixtures ([Jha et al., 2016](#); [Yang et al., 2009a](#)) allowing the preparation of bulk ceramic materials with high relative densities in a few minutes. The flash sintering tests also made it possible to identify that the reaction sintering process occurs in two stages, with an initial densification of the starting powders and, then, the AT formation reaction, which takes place at temperatures below the nominal equilibrium phase transformation temperature of 1280°C ([Jha et al., 2016](#); [Borrell et al., 2013](#)).

On the other hand, in the general context of developing environmentally sustainable manufacturing routes, in the case of aluminum titanate materials, the following possibilities have been described: synthesis by reactive sintering from Al-sludge waste and rutile ore as rich sources of alumina and titania instead of pure commercial powders ([Ewais et al., 2017](#)) and the use of a solar furnace to obtain AT granular materials ([Gulamova et al., 2018](#)).

Properties of AT Materials

Table 2 summarizes the main properties of AT compiled from the scientific literature and different industrial suppliers. As already described, the main aspect that determines the special characteristics is the AT crystallographic structure and the strong anisotropy in the coefficient of thermal expansion between its crystallographic directions, which gives rise to the development of high thermal stresses during cooling from the fabrication temperature that are the origins of microcracking. This microstructural characteristic determines all the technological properties of aluminum titanate materials, such as their low thermal conductivity and diffusivity and Young's

Table 2 Main physicochemical and mechanical properties of Al_2TiO_5 materials

Property	Al_2TiO_5
CAS no	12004-39-6
Appearance	Light yellow, gray or white powder
Molecular weight (g mol^{-1})	181.83
Bulk density (g cm^{-3})	3.20 – 3.68
Melting Point ($^\circ\text{C}$)	1860
Young's Modulus, E (GPa)	10 – 20
Vickers Hardness, H_v (GPa)	5
Bending strength, σ (MPa)	4 – 40
Thermal Conductivity, k ($\text{W m}^{-1} \text{K}^{-1}$)	1.5 – 2.5

modulus and, especially, their extremely low thermal expansion coefficient and associated excellent thermal shock resistance. However, the major drawback associated with microcracking is the low strength of AT materials. (Nagano *et al.*, 1999; Ohya *et al.*, 1987).

The main goal in the fabrication of AT components is to achieve a microstructure with a relatively fine microcrack network so as to produce low thermal expansion and sufficient strength.

Microcracking; Critical Grain Size

The microstructural development of aluminum titanate materials is determined by the thermal expansion mismatch between contiguous AT grains of different orientation due to the pronounced crystalline thermal expansion anisotropy. Their fabrication, by reaction sintering of Al_2O_3 and TiO_2 mixtures or solid state sintering of AT powders, requires thermal treatments at temperatures high enough to allow mass transport. Then, any thermal expansion mismatch can be accommodated by mass transport at such temperatures. Contrarily, when the sintered compacts are cooled below the temperatures at which mass transport mechanisms are allowed, the thermal expansion mismatch cannot be accommodated and gives rise to the so-called thermal stresses. Such stresses can initiate microcracking or remain as residual stresses in the cooled materials.

All non-cubic crystalline structures present a certain degree of thermal expansion anisotropy. The formation of microcracks in non-cubic polycrystals due to thermal stresses originated by the thermal expansion mismatch depends on the grain size. According to energy criteria, there is a critical grain size below which the formation of microcracks is inhibited (Kuszyk and Bradt, 1973; Ohya *et al.*, 1987). In general, for pseudobrookites, a critical grain size of around 2–5 μm has been determined (Cleveland and Bradt, 1978) significantly lower than that in $\alpha\text{-Al}_2\text{O}_3$ ($\sim 400 \mu\text{m}$) (Rice and Pohanka, 1979).

For the critical grain size of aluminum titanate, there are values in the literature in the range 1–4 μm . The dispersion of these values is probably due to the different criteria used to determine the critical size. For example, Ohya *et al.* (1987) determined a critical size by the abrupt change in mechanical resistance as a function of grain size, while Parker and Rice (1989) made use of the increase in the coefficient of thermal expansion. In summary, it is an effective critical grain size, that is, the minimum grain size necessary for a sufficient amount of microcracks to occur to produce a significant effect on the properties of the material.

During processing AT ceramics, the starting composition and characteristics of the powder raw materials and the temperature and duration of the sintering thermal treatment are key factors that lead to different microcracked microstructures. As an example, Fig. 3 shows two characteristic microstructures of commercial AT materials. Both materials have aluminum titanate as the major phase and rutile as a minor phase (white in the SEM micrographs), while in material (b) alumina traces were also detected. Material (a) consists of relatively small AT regions and a high density of small cracks as compared to material (b), with a lower density of larger cracks and larger AT regions.

The main way to control these cracks and defects is by introducing additives to AT. Different authors point that the addition of dopants such as MgO , or Fe_2O_3 , which are isomorphous with the mineral pseudobrookite, limits microcracking in AT materials (Maki and Suzuki, 2013; Kornaus *et al.*, 2019). Another possibility for controlling the microcracking phenomenon is to add suitable second-phase particles like Al_2O_3 , ZrO_2 or mullite (Sarkar *et al.*, 2015, 2016). Sintering temperature also has an inversely proportional relationship with the mechanical properties and thermal expansion coefficient, in which an increase in the former causes a reduction in the latter properties (Li *et al.*, 1995).

Thermal Expansion and Thermal Diffusivity

As stated previously, the macroscopic coefficient of thermal expansion, α , of AT materials is much lower than the average crystallographic CTE, $\bar{\alpha}$, and it is highly dependent on composition, grain size, thermal history, etc. Buessem and Lange

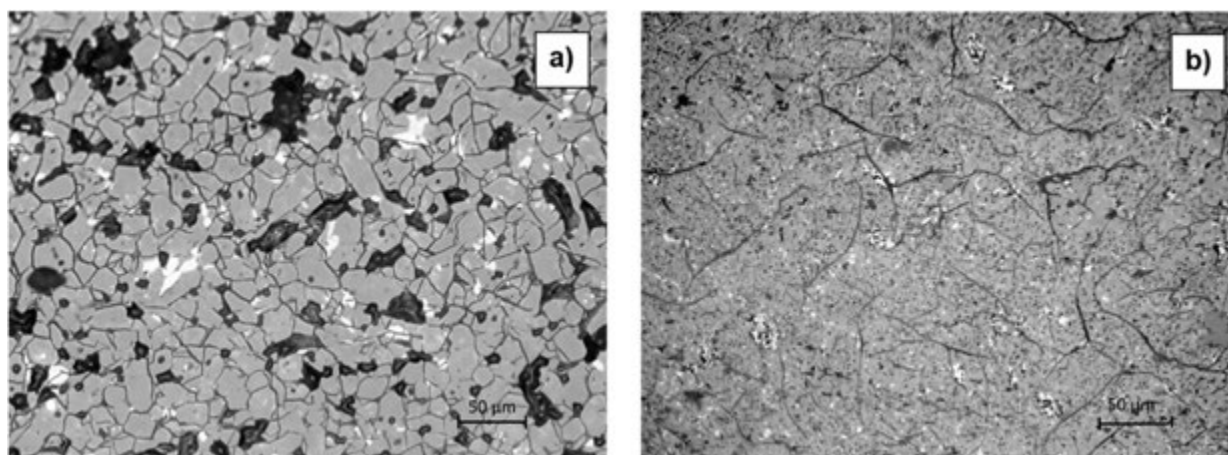


Fig. 3 Characteristic microstructures of commercial aluminum titanate materials. Extensive microcracking is observed. Both materials have aluminum titanate as major phase (gray) and rutile as minor phase (white). In material (b) alumina traces were also detected by XRD.

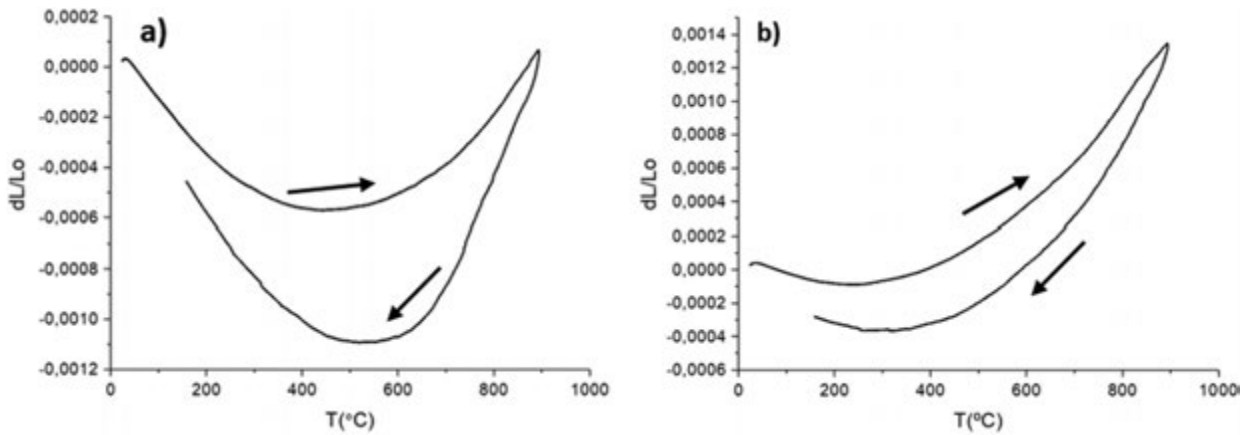


Fig. 4 Characteristic curves of thermal expansion of two AT materials whose microstructures are shown in Fig. 3. The hysteresis between the heating and cooling treatments is observed.

(1966) were the first researchers that performed a careful analysis on the effect of microcracks due to the thermal expansion anisotropy on the properties of AT, in particular, in the thermal expansion coefficient. Lately, this subject has been investigated by a number of researchers (Bruno *et al.*, 2010; Kim and Cao, 2002; Giordano *et al.*, 2002; Kim and Kim, 2004; Ohya *et al.*, 2017).

As shown in Table 1, AT materials have much lower coefficients of thermal expansion than the crystallographic average. Moreover, the expansion behavior presents strong hysteresis between heating and cooling, as shown in the characteristic thermal expansion curves Fig. 4 of the commercial materials whose microstructures are shown in Fig. 3. Material (a), with a high amount of smaller microcracks presents lower overall thermal expansion and higher thermal expansion hysteresis than material (b), with lower density of larger microcracks. The observed hysteresis is appreciable even in thermal cycles between room temperature and 400°C, and the hysteresis area increases progressively with the maximum temperature of the treatment.

The microstructural origin of the thermal expansion behavior of AT polycrystals can be described as follows. At room temperature, sintered Al_2TiO_5 bodies contain remarkable amounts of microcracks at the grain contacts. Most of them are perpendicular to the crystallographic axes with the highest coefficients of expansion, *b* and *c*, while the grain-grain contacts perpendicular to the axis, *a*, remain intact. Such microstructural features explain the thermal expansion curves of AT materials, according to the scheme of Fig. 5, by reversible micro-processes of recombination of microcracks (crack healing during heating) and formation of microcracks (microcracking during cooling).

When heating Al_2TiO_5 ceramics that already contain a certain amount of microcracks, the crystallites expand on a microscopic scale in directions *b* and *c*, filling the volume of microcracks, and contract in direction *a*; As a consequence, the piece does not initially experience any dimensional change or may even undergo a slight contraction (first section during heating in Fig. 4). From about 300–400°C the body begins to expand and the coefficient of expansion increases gradually. This section of the expansion curve becomes controlled by the expansion of the recombined material according to the crystallographic expansion coefficients. During cooling, the body contracts until it reaches a minimum of the curve where, as Wright (1972) demonstrated by acoustic emission, the formation of microcracks occurs again, typically between 300 and 700°C, and the body expands again (last cooling section, Fig. 4) due to microcracking. Therefore, the specific U-shape of macroscopic dilation versus temperature curve in AT ceramics gives a clear indication of the temperature at which thermal microcracks can be considered healed and the material expands like a compact body (Bruno *et al.*, 2010). The particular shape of each thermal expansion curve in Fig. 4 is due to the microstructural differences of each material, which translate into a different length and density of microcracks as noted in the previous section.

Regarding the insulating capacity of AT materials, they can be considered good thermal insulators as a consequence of the presence of microcracks, which hinder the flow of heat via conduction. These materials present thermal conductivities, *K*, at room temperature, of around $1.5\text{--}2.5 \text{ W m}^{-1} \text{ K}^{-1}$ (Kolomeitsev *et al.*, 1981) and thermal diffusivities, *a*, of $0.3\text{--}0.6 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$ (one order of magnitude less than alumina). When the dependence of the thermal diffusivity with temperature is evaluated, it is observed that AT materials present an anomalous behavior (as noted previously for the coefficient of thermal expansion). Thus, the curve of thermal diffusivity versus temperature shows a hysteresis between heating and cooling, detecting a tendency of thermal diffusivity to increase with temperature (Siebenbeck *et al.*, 1976). Again, the microcracking and crack healing processes are responsible for this behavior. That is, the microstructural factors predominate over the intrinsic properties, making it impossible to extrapolate the physical properties of the single crystal to the polycrystalline material.

In addition, it should be noted that, despite the increase in diffusivity and thermal conductivity with temperature, aluminum titanate ceramics maintain an excellent thermal insulation capacity up to 1000°C (Wohlfrohm, 1991).

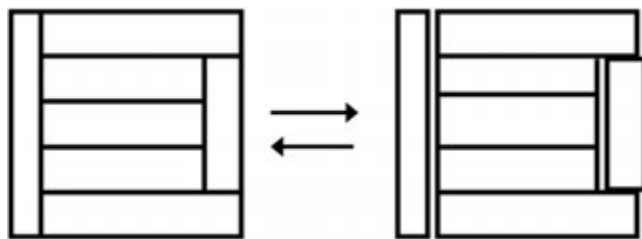


Fig. 5 Schematic representation of reversible microstructural changes during heating (crack healing) and cooling (crack opening). Modified from Wohlfrohm, H., 1991. Preparación por sinterización reactiva y estudio del comportamiento mecánico y térmico de materiales de titanato de aluminio (Doctoral thesis). Facultad de Ciencias. Universidad Autónoma de Madrid.

Elastic and Mechanical Behavior

Aluminum titanate ceramics are promising materials for different engineering applications because of their excellent thermal shock resistance and chemical inertness. In this sense, the guarantee of reliability has become an important requirement for AT ceramics because of their significantly low mechanical strength compared with general structural ceramics as result of the presence of microcracks along the grain boundaries. (Bruno *et al.*, 2013; Matsudaira *et al.*, 2009).

Room temperature

As a consequence of the presence of microcracks, a pure AT material with a grain size greater than the critical one for microcracking has a Young's modulus, E , ~ 10 – 20 GPa (Cleveland and Bradt, 1978), that is an order of magnitude less than the values generally found in ceramic materials. This value increases slightly, for the same grain size, in the presence of additives that enter into solid solution reducing the anisotropy of thermal expansion (Fe_2O_3 , MgO) (Maki and Suzuki, 2016; Ohya *et al.*, 2017).

With regard to hardness, AT is a relatively soft material within ceramics, with a value of 6 on the Mohs scale (such as feldspars) (Bhattacharyya and Sen, 1965) and a Vickers hardness of 5 GPa ($\text{HV} = 500$) (Dworak and Fingerle, 1987).

The mechanical strength of aluminum titanate is also a function of the grain size and the thermal history of the material. Due to the presence of microcracks, the bending strength of commercial materials usually varies between 20 and 40 MPa (Wohlfrohm, 1991). In the case of compression tests this value increased by a factor of 10–20 (Freudenberg *et al.*, 1989). It is of great interest that in these flexural and compression tests the stress-strain curves present a non-linear character, without a catastrophic failure of the material. That is, it could be treated as a behavior that is far from linear-elastic, so some authors qualify this behavior as “pseudoplastic” (Wohlfrohm, 1991) or anelasticity (Bruno *et al.*, 2013). Due to the density of microcracks, this behavior allows achievement of very high deformations for a ceramic material (up to 2% in bending and 0.8% in compression). The works by Babelot *et al.* (2011) and Chen *et al.* (2019) use the concept of “flexible” ceramic to refer to this behavior in the nonlinear stress-strain curves and propose mimicking the microstructure of natural flexible minerals like itacolumite.

The non-linear character of the stress-strain curves shows a dependence between the resistance to the propagation of a crack and the crack size. That is, there is an R-curve behavior in which the resistance to crack growth increases with its size (flaw tolerant behavior). Thus, Hamano *et al.* (1985) and Sakai and Osamu (1987) showed small increases in toughness during crack propagation in AT materials, contrary to what is observed in very brittle materials. This inelastic contribution is produced by irreversible processes such as grain bridging through the lips of the crack. Furthermore, the model of Fu and Evans (1982) analyzes the interaction of the stress field of a crack with the thermoelastic residual stresses produced by the anisotropy of thermal expansion. This model explains the strong influence of grain size on the toughness of pseudobrookites. Fine-grained materials, free of microcracks, would not present reinforcement and would be completely brittle. From a certain grain size, the formation of microcracks occurs in the process zone induced by the stress field of the main crack. This process consumes energy and produces the shielding of the main crack, which is equivalent to an increase in toughness. For grain sizes greater than the critical one, a spontaneous formation of microcracks that coalesce takes place and, consequently, a decrease in toughness occurs. Fu and Evans (1982) estimated that this microcracking reinforcement develops from a grain size of approximately 0.4 times the critical grain size for spontaneous microcracking.

Effect of temperature

Uncommon in a ceramic material is the significant increase in Young's modulus with temperature (Freudenberg *et al.*, 1989; Ohya *et al.*, 1988). Young's modulus is maximum (around three times the value at room temperature) at $\sim 900^\circ\text{C}$. There is also a hysteresis between heating and cooling, indicating that the same processes of recombination (crack healing) and formation of microcracks that determine thermal expansion are also responsible for the variation of Young's modulus with temperature.

In a similar way to what happens with Young's modulus, strength increases with temperature up to approximately 1200°C (Freudenberg *et al.*, 1989; Ohya *et al.*, 1988; Kolomeitsev *et al.*, 1981; Kim *et al.*, 2014; Papitha *et al.*, 2014).

Table 3 Decomposition ratio (wt%) of AT in alumina-aluminum titanate monolithic composites treated at 900, 1000 and 1150°C for 4 h with heating and cooling rates of 5°C min⁻¹

Annealing treatment – 4 h	Specimens sintered at 1450°C – 2 h			Specimens sintered at 1550°C – 3 h		
	900°C	1000°C	1150°C	900°C	1000°C	1150°C
Alumina + 10 wt%AT	Traces	9	100	Traces	7	100
Alumina + 30 wt%AT	Traces	21	100	Traces	22	100
Alumina + 40 wt%AT	Traces	22	100	Traces	21	100

Thermal Stability

Aluminum titanate is classically produced by heating a combination of alumina and titania up to a temperature above 1350°C at atmospheric pressure. However, pure synthesized AT is thermally unstable below 1280°C. Therefore, it tends to decompose, through a eutectoid reaction, into alumina and titania during cooling from sintering treatments, which would render the material useless for industrial applications. However, at temperatures below 800–900°C there is a kinetic inhibition of this decomposition (Buscaglia and Nanni, 1998).

Different authors have reviewed and analyzed the main strategies to control or delay the AT thermal decomposition (Wohlfromm, 1991; Barrios de Arenas, 2012; Pratapa *et al.*, 2011). In the first place, as has been commented on throughout this chapter, there is a dependence between the degree of thermal stability of the material and its history throughout processing: forming pressure, atmosphere and temperature of the thermal treatment and, on the final grain size of the material (Wohlfromm, 1991; Naghizadeh *et al.*, 2009). Secondly, there is a general agreement on improving AT stability through the formation of solid solutions by doping with oxide additives such as magnesium oxide (MgO) and ferric oxide (Fe₂O₃) which are isomorphous with the pseudobrookite structures, and thus form solid solutions with AT (Buscaglia *et al.*, 1996a,c; Ishitsuka *et al.*, 1987; Korim, 2009).

This thermodynamic stabilization is related to the material's decreased decomposition temperature during cooling (MgTi₂O₅ and Fe₂TiO₅) decompose below 700 and 565°C, whereas AT decomposes at 1280°C. This is explained by the smaller differences between the ionic radii of Fe, Mg and Ti, which produces a lower degree of distortion of the octahedra that form the structure. The improved stabilization in the solid solutions is also due to increased entropy caused by cation mixing disorder (Kim and Gauckler, 2012). Among other possible stabilizing oxides, SiO₂ has been studied to a greater extent, with limited solubility in AT (Ishitsuka *et al.*, 1987). An important note in mixing additives is that they should not significantly decrease the aluminum titanate properties. Small additions (≤ 3–5 wt%) are usually incorporated with the aim of forming aluminum titanate solid solutions.

In the case of alumina-aluminum titanate composite materials with improved toughness presented in the following section, a higher decomposition has been determined than in single-phase AT materials, due to the action of the alumina particles as nucleation points for the decomposition reaction (Uribe, 2001). In the literature, maximum values of decomposition rate are reported at temperatures between 1000°C and 1200°C, with peak values between 1100°C and 1150°C (Buscaglia and Nanni, 1998; Uribe, 2001), while below 800–900°C the materials can be considered stable. Therefore, a study of the decomposition in the materials is necessary in order to determine their maximum application time and temperature. Based on these observations, the AT decomposition study was carried out in samples of alumina-aluminum titanate composite monoliths (with volumetric proportions of AT particles in the range 10–40 vol%) treated at 900, 1000 and 1150°C for 4 h (Table 3). It was observed that in the samples treated at 900°C there was no decomposition, while in the samples treated at 1150°C the decomposition was total in 4 h. For the treatment at 1000°C, moderate decomposition (~ 10–20 wt%) is shown.

These values show a good agreement with results obtained by other authors (Uribe, 2001) where a decomposition of 15 wt% has been found in alumina materials with 10 vol% of aluminum titanate, treated at 1000°C for 4 h.

AT-Based Materials

As discussed above, microcracked aluminum titanate materials present desirable properties; however, their use in critical structural applications is limited due to lack of strength. The typical ceramic processing approach of strengthening a material by reducing its grain size in order to limit microcracking on cooling would succeed in strengthening aluminum titanate. However, it is inherently accompanied by an undesirable increase in thermal expansion, thermal conductivity and Young's modulus. Moreover, the control of grain growth in reaction sintered AT materials is complicated because of the specific characteristics of the reaction process.

Solid Solutions in Aluminum Titanate

Efforts have been devoted to decreasing the thermal expansion anisotropy of the aluminum titanate crystals by doping to form solid solutions and increase strength values (Thomas and Stevens, 1989b; Maki and Suzuki, 2016; Ishitsuka *et al.*, 1987; Korim, 2009; Guedes-Silva *et al.*, 2016; Rezaie *et al.*, 2009).

Recently, as an example, [Ohya et al. \(2017\)](#) have investigated the co-doping of MgO with Y_2O_3 , La_2O_3 and Nb_2O_5 to fabricate aluminum titanate ceramics that possess both low thermal expansion coefficients and excellent mechanical properties. The best results were found for Mg-Y co-doping. In this respect, a material with average thermal expansion between room temperature and 1000°C similar to that of the undoped material ($\sim 3 \times 10^{-6}\text{K}^{-1}$) and strength ~ 60 MPa was developed by sintering at intermediate temperature (1450°C). Increasing the sintering temperature to 1500°C significantly decreased the thermal expansion coefficient ($\sim 0.7 \times 10^{-6}\text{K}^{-1}$) but was associated with a sharp decrease in strength (~ 17 MPa).

Strengthened AT Materials With Enhanced Structural Integrity

Different ceramic composites with aluminum titanate as one of the major phases have been proposed ([Basnet et al., 2017](#); [Luo et al., 2015](#); [Xu et al., 2015](#)). The aim is to exploit the excellent resistance to thermal shock of aluminum titanate in applications such as thermal barrier coatings, exhaust filter components for diesel engines and high temperature ceramic substrates with improved mechanical properties. Such approach has been successful for dense AT ([Violini et al., 2018](#); [Parker, 1990](#)) or porous materials containing zirconium titanate ([Sarkar et al., 2015](#)), which present increased structural integrity while maintaining low, or even negative, thermal expansion coefficients. In the same way, [Zhao et al. \(2016\)](#) reported strengthened aluminum titanate reinforced by calcium dialuminate with thermal expansion similar to that of the matrix. Porous aluminum titanate materials with mullite additions up to 50 vol% ([Sarkar et al., 2016](#); [Xu et al., 2015](#)) also present enhanced structural integrity even though they experience increased thermal expansion especially for the highest mullite contents.

Materials Reinforced by Aluminum Titanate

An important field of research during the last years has been that of developing composites with aluminum titanate as second phase, in order to improve the mechanical behavior of the matrix by manipulating the thermal stresses associated with the thermal expansion behavior of this phase. It is well known that thermal expansion mismatch between the matrix and the dispersed phases might lead to different toughening mechanisms, i.e., crack deflection, crack branching, crack bridging and microcracking. Un-cracked composites based on this approach present thermal expansion behavior similar to that of the matrices, with lower average coefficients as function of the composition (e.g., [Uribe and Baudín, 2003](#)) and the microcracked ones present thermal expansion hysteresis associated with the presence of microcracks ([de Portu et al., 2006](#)).

[Morishima et al. \(1986\)](#) and [Yano et al. \(1992\)](#) reported that only relatively large additions of AT (> 63 vol%) led to significant increases in the thermal shock resistance of mullite and that such additions were associated with sharp strength decreases due to microcracking. [Kucuk and Boyraz \(2019\)](#) did not find any beneficial effect of aluminum titanate on the mechanical behavior of yttria stabilized zirconia.

The most investigated system is that of alumina-aluminum titanate. In this system, materials present extremely different mechanical behaviors as a function of the length scale in the microstructure because such scale determines the main toughening mechanisms ([Park et al., 2003](#)). As an example, in fine grained materials of alumina with 10 vol% of aluminum titanate, microcracking was identified as the main toughening mechanism in alumina matrices with AT nanoparticles at the grain boundaries ([Bueno et al., 2008](#)) and crack bridging for those matrices with a uniform dispersion of micrometric AT particles ([Uribe and Baudín, 2003](#)). The same conclusions were reached later by [Sobhani et al. \(2016\)](#) for materials with higher content of AT.

[Wang et al.](#) have investigated a series of dense ([Wang et al., 2009](#); [Yang et al., 2009a](#); [Wang et al., 2005](#)) and porous ([Yang et al., 2009b](#)) alumina-aluminum titanate composites with micro and nano-scale microstructures. Such composites presented relatively high strength, especially the nanostructured composite, with 426 MPa compared to 222 MPa for the composite with micro-scale microstructure, and both showed good wear resistance ([Sharma and Dogan, 2019](#); [Wang et al., 2005, 2009](#)), especially the one with the micro-scale microstructure ([Wang et al., 2009](#)).

Characteristic examples of monolithic materials and laminates developed in the alumina-aluminum titanate system are described in the sections which follow. Colloidal shaping methods allow the fabrication of homogeneous monolithic materials with a wide range of microstructures ([Bueno et al., 2004](#)) and laminated materials consisting of layers of very different microstructures ([Bueno and Baudín, 2006](#); [Bueno et al., 2011](#)).

Monolithic Alumina-Aluminum Titanate Composites

Due to the thermal expansion mismatch between aluminum titanate ([Taylor, 1987](#)) and alumina ($\alpha_{a25-1000^\circ\text{C}} = 8.4 \cdot 10^{-6}\text{K}^{-1}$, $\alpha_{c25-1000^\circ\text{C}} = 9.2 \cdot 10^{-6}\text{K}^{-1}$) ([Taylor, 1984](#)) high residual stresses between the grains can arise in alumina-AT composite materials during cooling from the sintering temperature, depending on their crystallographic orientation. Specifically, in the orientations in which the aluminum titanate grains present a lower coefficient of expansion than the alumina grains, they are subjected to compressive stresses and, as a consequence, can act as crack bridging sites during fracture ([Padture et al., 1993a](#); [Runyan and Bennison, 1991](#)). The extreme local stresses that develop in these compounds can also generate microcracks during cooling or during material loading and, therefore, the grain size of the materials has to be controlled below the critical size so that generalized failure does not occur.

This critical size has been evaluated ([Uribe and Baudín, 2003](#)) by means of a simple energy approximation, at $6.4 \mu\text{m}$, for the formation of circumferential cracks around the tensile grains of aluminum titanate, and at $2.2 \mu\text{m}$ for the formation of radial

cracks from the grains of aluminum titanate subjected to compression. These values are in agreement with the experimental results of Padture *et al.* (1993a,b). The level of cracking depends on the number of grains that contribute and, therefore, their size and the volume fraction of aluminum titanate. Thus, in compounds with AT contents of 10–40 vol%, a gradual decrease in fracture stress is observed from ~ 300 MPa, for average grain sizes of $2\text{ }\mu\text{m}$, to a drastic drop ($\sim 20\text{--}30$ MPa) for average grain sizes of the order of $4\text{--}7\text{ }\mu\text{m}$ (depending on the volumetric content of AT) (Padture *et al.*, 1993b).

In addition to microcracking and crack bridging as toughening mechanisms in alumina-AT composites, crack branching and crack deflection are also identified in the alumina materials with 30 and 40 vol% of AT described below. These materials were manufactured by a colloidal route (slip casting) from aqueous alumina and titania suspensions and sintered with 2 h dwell at 1450°C and 3 h dwell at 1550°C . In all these composites the mean sizes of the aluminum titanate grains (Table 4) were in the order of or higher than the critical value, thus explaining the presence of microcracks in the as sintered state (Fig. 6(a)) that propagates preferentially along grain boundaries and gives rise to non-linear load-displacement curves (Fig. 6(b)).

Table 4 Main properties of Alumina-30 vol%AT and Alumina-40 vol%AT ceramic composites sintered at 1450°C and 1550°C . G: grain size, $\alpha_{25-850^\circ\text{C}}$: average thermal expansion coefficient between 25 and 850°C , σ_f : 3-point bending strength, γ_{WOF} : work of fracture. A: Alumina, AT: Aluminum titanate; sd: standard deviation

	G_A (sd) μm	G_{AT} (sd) μm	$\alpha_{25-850^\circ\text{C}}$ (sd) 10^{-6}K^{-1}	σ_f (sd) MPa	γ_{WOF} (sd) J/m^2
1450°C					
Alumina + 30 wt%AT	2.3 (0.2)	2.2 (0.2)	5.6 (0.4)	94 (10)	57.4 (3.9)
Alumina + 40 wt%AT	2.5 (0.1)	2.7 (0.3)	4.7 (0.4)	83 (2)	35.9 (3.2)
1550°C					
Alumina + 30 wt%AT	3.0 (0.2)	2.9 (0.3)	4.4 (0.5)	76 (4)	37.6 (2.5)
Alumina + 40 wt%AT	3.2 (0.4)	3.2 (0.2)	3.9 (0.4)	61 (1)	33.1 (0.7)

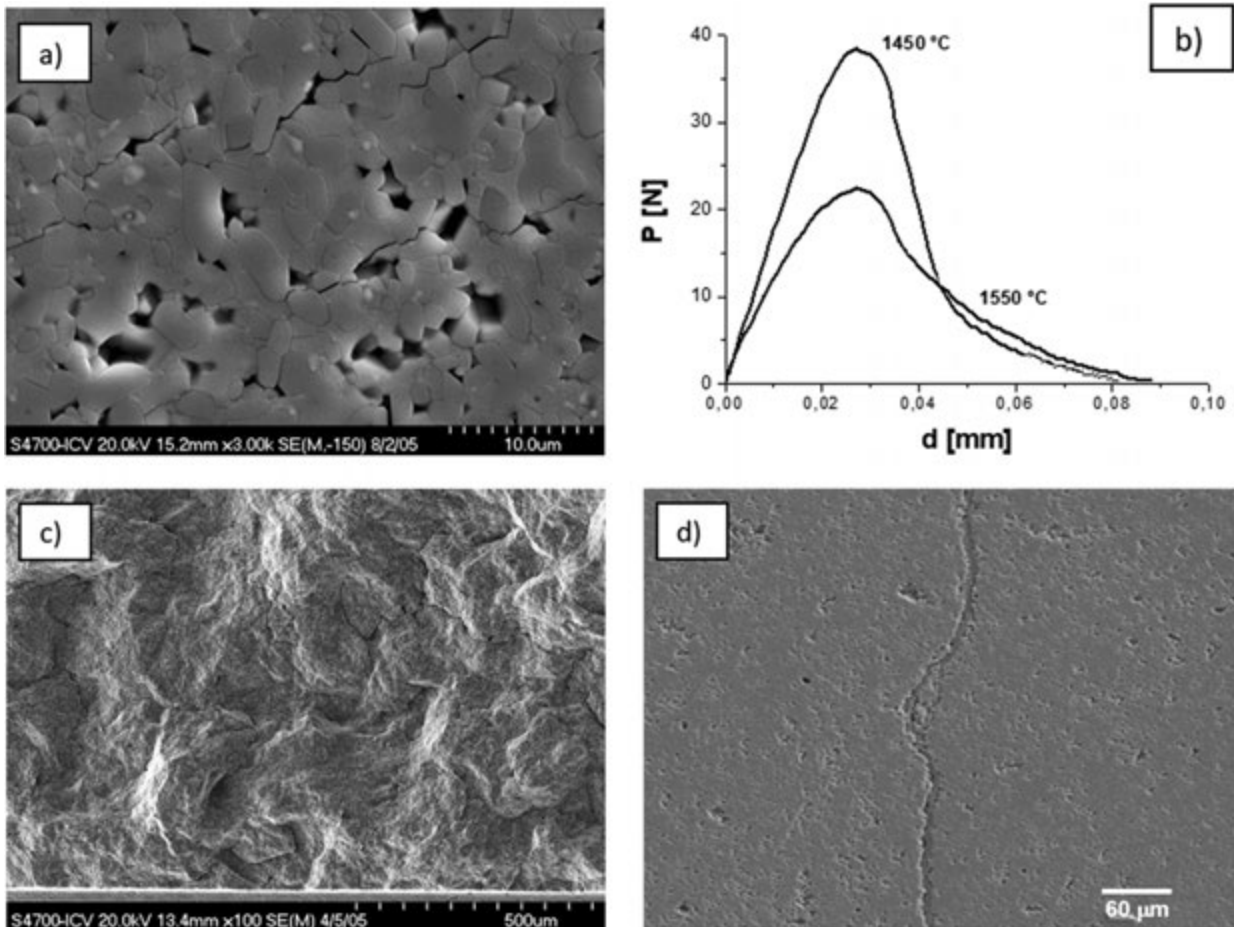


Fig. 6 Characteristic microstructural and fracture features of alumina-30 vol%AT and alumina-40 vol%AT composites sintered at 1450 and 1550°C . (a) As sintered microstructure (b) Non-linear load-displacement curve of notched specimens (c) Fracture surface displaying numerous crack deflections (d) Crack branching detail in the crack profile of notched specimens.

The macroscopic features of the fracture surfaces and crack path (Fig. 6(c) and (d)) are conditioned by the relatively long cracks already presented in the as-sintered materials. The main crack diverts and branches by the interaction with the pre-existing cracks leading to crack profiles like that shown in Fig. 6(d), where portions of material not fractured remained trapped along the wake of the propagating crack.

Thermomechanical characterization of these alumina-AT materials in Table 4 shows values of the coefficient of thermal expansion and of the work of fracture in the order described for pure AT materials stabilized by doping (Ohya *et al.*, 2017) but with superior strength values.

Structural Layered Composites

The development of laminated ceramic materials emerged as a design strategy to minimize the inherent brittleness and unreliability of ceramic materials during fracture. Some of the designs used for ceramic laminates are those that introduce flaw-tolerant inner layers and have strong interfaces between them and the outer layers of higher strength (Chan, 1997; Clegg, 1998; Lawn *et al.*, 2002). Another group of designed ceramic laminates is that of layers joined by weak interfaces to initiate crack deflection (Chan, 1997; Clegg, 1998; Tomaszewski *et al.*, 2007; Zhang *et al.*, 2004) to reach high toughness values. Such materials present graceful fracture under loads perpendicular to the layers due to their high capability for crack deflection and delamination along the weak interfaces.

Bueno and colleagues (Bueno *et al.*, 2005; Bueno and Baudín, 2006, 2007, 2009) have developed alumina-aluminum titanate based laminates designed to combine high crack deflection capability with strong interfaces. They consisted of relatively stiff and brittle external layers with microcracked internal layers, with moderate AT contents, to produce multiple crack deflection and/or branching. The most important difference between these laminated structures and other laminates with high capability for crack

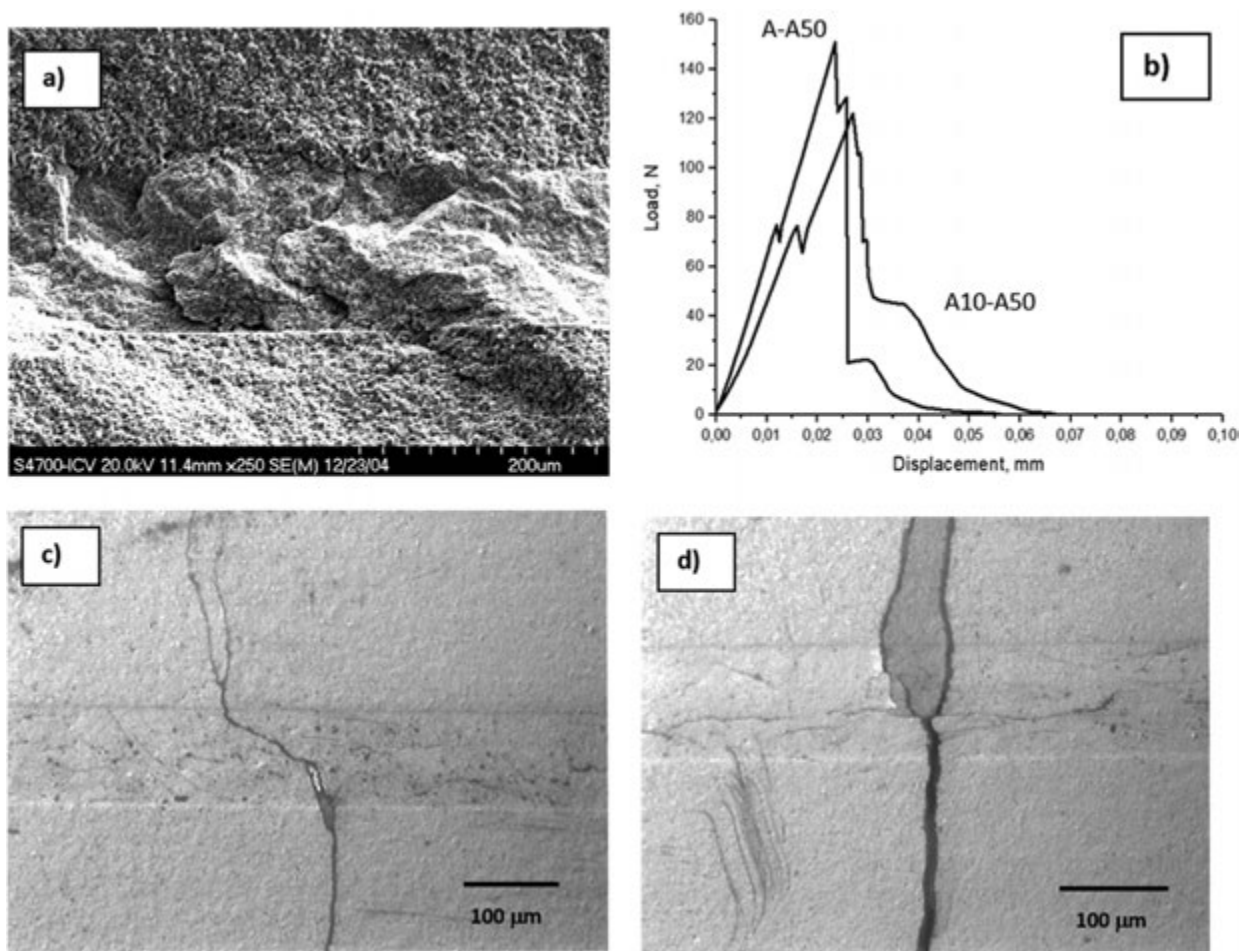


Fig. 7 Characteristic fracture features of alumina-aluminum titanate based laminates. Thin internal layers in the micrographs are formed by highly microcracked alumina-50 vol%AT composite. (a) Detail of fracture surface in an internal layer (b) Graceful failure in load-displacement curve of notched specimens (c) Crack profile in a notched specimen showing main crack deflection by interacting with microcracks in the internal layers. (d) Crack profile of a notched specimen showing branching of the main propagating crack by interacting with microcracks in the internal layers.

deflection is that in these ones delamination occurred at the microstructural level and, thus, delamination lengths were limited and delamination did not lead to the loss of structural integrity.

The behavior of laminated structures with relatively highly microcracked thin internal layers containing 50 vol% of AT is now presented. These laminates had stiff and brittle surface layers of alumina or alumina + 10 vol% AT and were sintered for 2 h dwell at 1450°C. Characteristic fracture features of the tested specimens are shown in Fig. 7. In all specimens, the internal A50 layers were well defined and showed multiple fracture planes (Fig. 7(a)). It is clear from the aspect of the A50 layers in the fracture surfaces that the main crack experienced multiple deflections and branching due to its interaction with the microstructure of the weak and thin internal layers. Such processes led to crack arrest and re-initiation at the internal thin layers and thus to the graceful failure presented by the load-displacement curves (Fig. 7(b)) as can also be inferred from the crack profile observed in the lateral surfaces (Fig. 7(c) and (d)). Work of fracture values of these laminated structures were in the order of 100–120 J m⁻², superior to those described for alumina-AT monoliths in Table 4.

Technological Interest

Summarizing the main considerations from the previous sections, aluminum titanate materials have high melting point, chemical inertness and excellent resistance to thermal shock due to their low coefficient of thermal expansion. Furthermore, the presence of microcracks also leads to low thermal conductivity. Therefore, one of the main uses of these materials is aimed at applications where thermal insulation is required (Mandal *et al.*, 2017; Stingl *et al.*, 1986). However, such applications are limited because microcracking is associated to strength values an order of magnitude lower than the typical values of ceramic materials (~15–20 MPa). Aluminum titanate is also important for ceramic industry due to its good chemical resistance and, in this way, aluminum titanate is a suitable material for various technological applications such as foundry parts or catalytic converters for motor vehicles (Barrios de Arenas, 2012).

Refractories

Aluminum titanate is commercially considered a specialized material for extreme temperature conditions and found mostly in the non-ferrous molten metal industry, especially in aluminum foundries. Some specific applications in this field are: nozzles, casting molds, crucibles, spacers, mold joints, flow rods, retainer rings, riser tubes, feeders or dosing tubes among many other components or devices for the treatment of molten metals (Ceramtec®). In addition, the poor wettability of aluminum titanate with molten metals is another of the properties that makes it ideal for use in foundry technology and metallurgical melting (Ceramtec®, Cumi®, Kyocera®). On the other hand, it must also be added to this exceptional behavior that the thermal conductivity is in the range 1–2 W m K⁻¹ for refractory ceramics based on AT. This low thermal conductivity saves energy, giving rise to energy-efficient processes, increased process reliability, reduced freeze-offs and improved yield levels (Cumi®). It is also remarkable that the outstanding chemical and abrasive resistance of AT ensure high melt purity and, thus, prevents metal adhesion, simplifies cleaning, increases service life, does not contaminate the melt and enhances product quality and plant efficiency. When compared to competing materials like calcium silicate and fused silica, components manufactured using aluminum titanate have significantly longer service life (Ceramtec®).

To all these characteristics it must also be added that microcrack healing during heating AT ceramics increases strength with increase in temperature, which further favors, if required, the high chemical resistance of these materials.

Advanced Engineering Applications

AT also demonstrates great versatility for specific engineering applications. In particular, the exceptional thermal behavior of AT makes it a good option for substrates in catalytic converters for motors, spacing rings of catalytic reactors, vehicle emissions control, diesel particulate filters, high-temperature flue gas filtration supports and thermal insulation liners (Li *et al.*, 1995; Kim, 2010; Adler and Petasch, 2013).

In particular, several investigations have been undertaken regarding the use of AT materials for the development of diesel particulate filters (DPF) (Brodnik and Faber, 2019; Chen *et al.*, 2020; Kim, 2010; Millo *et al.*, 2015; Papitha *et al.*, 2014). Since 2009 wall flow DPFs have been adopted for all European passenger cars, in order to comply with the PM (Particulate Matter) EU5 emissions limits. Silicon carbide and cordierite filters are commonly used for this application, but dense AT with engineered porosity is an interesting ceramic material for DPF due to its very low thermal expansion coefficient and thermal shock resistance in combination with high refractoriness and melting point. Main results showed that aluminum titanate and cordierite, compared to silicon carbide, can give significant advantages in terms of price, thermal expansion and in reducing the temperature loss through the DPF (Kim, 2010). However, increased regeneration frequency of AT and cordierite leads to significant penalties in terms of fuel consumption and oil life compared to silicon carbide. However, this gap could be partially overcome by adopting specific regeneration strategies (Millo *et al.*, 2015).

Another new application for aluminum titanate is its use in solid oxide fuel cells (SOFC) (Welander *et al.*, 2019, 2018; McCleary and Amendola, 2018; Law and Sofie, 2011; Hunt *et al.*, 2018; Welander *et al.*, 2018; McCleary and Amendola, 2018; Law

and Sofie, 2011; Hunt *et al.*, 2018). Aluminum titanate has been incorporated in the standard SOFC anode, the Ni-YSZ cermet, in order to prevent anode degradation and improve mechanical properties and cell performance.

Other minor applications refer to the use of AT as a biomaterial for bone repair (Kalita and Somani, 2010), as a catalyst (Almerindo *et al.*, 2016) or even as a photoactive material (Trung *et al.*, 2019).

Summary

In general, AT materials have to compromise between demands for a low macroscopic thermal expansion coefficient and high strength and, thus, in spite of the fact that microcracking would limit the strength, it has a positive effect of decreasing thermal expansion coefficient. In this way AT materials become especially resilient to thermal shock stresses.

Different processing and design strategies are being evaluated to increase the strength of AT materials without sacrificing the properties that make aluminum titanate unique. These possibilities range from the development of solid solutions to the formation of flaw-tolerant laminated structures, including the design of composites with other ceramic compounds.

This improvement in properties increases the chances of success of AT materials for advanced engineering applications that are already being investigated, apart from their traditional use as a refractory material.

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References

- Adler, J., Petasch, U., 2013. Particulate filters. In: Somiya, S. (Ed.), *Handbook of Advanced Ceramics: Materials, Applications, Processing, and Properties*, second ed. Academic press, pp. 585–606.
- Almerindo, G.I., *et al.*, 2016. Propanolysis of methyl paraoxon in the presence of aluminum-titanate-supported erbium oxide. *Journal of Physical Chemistry C* 120 (39), 22323–22329. doi:10.1021/acs.jpcc.6b06085.
- Andrianainarivelo, M., Corriu, R.J.P., Leclercq, D., Mutin, P., Vioux, A., 1997. Nonhydrolytic sol–gel process: Aluminum titanate gels. *Chemistry of Materials* 9, 1098–1102.
- Austin, A.E., Schwartz, C.M., 1953. The crystal structure of aluminium titanate. *Acta Crystallographica* 6, 812–813.
- Babelot, C., Guignard, A., Huger, M., *et al.*, 2011. Preparation and thermomechanical characterisation of aluminum titanate flexible ceramics. *Journal of Materials Science* 46 (5), 1211–1219. doi:10.1007/s10853-010-4897-2.
- Barrios de Arenas, I.B., 2012. Chapter 22 – Reactive sintering of aluminum titanate. In: Lakshmanan, A. (Ed.), *Sintering of Ceramics – New Emerging Techniques*. InTechOpen, pp. 501–526. doi:10.5772/34366.
- Bartolomé, J., Requena, J., Moya, J.S., Li, M., Guiu, F., 1996. Cyclic fatigue crack growth resistance of $\text{Al}_2\text{O}_3\text{-Al}_2\text{TiO}_5$ composites. *Acta Materialia* 44, 1361–1370.
- Basnet, B., Sarkar, N., Park, J., Mazumder, S., Kim, I., 2017. $\text{Al}_2\text{O}_3\text{-TiO}_2\text{-ZrO}_2\text{-SiO}_2$ based porous ceramics from particle-stabilized wet foam. *Journal of Advanced Ceramics* 6 (2), 129–138. doi:10.1007/s40145-017-0225-5.
- Bayer, G., 1971. Thermal expansion characteristics and stability of pseudobrookite-type compounds, Me_2O_3 . *Journal of the Less-Common Metals* 24, 129–138.
- Bayer, G., 1973. Thermal expansion anisotropy of oxide compounds. *Proceedings of the British Ceramic Society* 22, 39–53.
- Berger, M.H., Sayir, A., 2008. Directional solidification of $\text{Al}_2\text{O}_3\text{-Al}_2\text{TiO}_5$ system. *Journal of the European Ceramic Society* 28 (12), 2411–2419. doi:10.1016/j.jeurceramsoc.2008.03.005.
- Bhattacharyya, B.N., Sen, S., 1965. Aluminium titanate – Formation and properties. *Glass and Ceramic Bulletin* 12 (3), 92–103.
- Bonhomme-Courty, L., Lequeux, N., Mussotte, S., Boch, P., 1994. Preparation of $\text{Al}_2\text{TiO}_5\text{-ZrO}_2$ mixed powders via Sol–Gel Process. *Journal of Sol–Gel Science and Technology* 2, 371–375.
- Borrell, A., Salvador, M.D., Rocha, V.G., *et al.*, 2013. Enhanced properties of alumina-aluminium titanate composites obtained by spark plasma reaction-sintering of slip cast green bodies. *Composites Part B-Engineering* 47, 255–259. doi:10.1016/j.compositesb.2012.11.010.
- Brodnik, N.R., Faber, K.T., 2019. Out-of-plane mechanical characterization of acicular mullite and aluminum titanate diesel particulate filters. *International Journal of Applied Ceramic Technology* 16 (3), 1173–1183. doi:10.1111/ijac.13161.
- Brugger, P.A., Mocellini, A., 1986. Preparation of composite $\text{Al}_2\text{O}_3\text{-TiO}_2$ particles from organometallic precursors and transformations during heating. *Journal of Materials Science* 21, 4431–4435.
- Bruno, G., Efremov, A., Wheaton, B., *et al.*, 2010. Micro- and macroscopic thermal expansion of stabilized aluminum titanate. *Journal of the European Ceramic Society* 30 (12), 2555–2562. doi:10.1016/j.jeurceramsoc.2010.04.038.
- Bruno, G., Kilali, Y., Efremov, A.M., 2013. Impact of the non-linear character of the compressive stress-strain curves on thermal and mechanical properties of porous microcracked ceramics. *Journal of the European Ceramic Society* 33 (2), 211–219. doi:10.1016/j.jeurceramsoc.2012.09.004.
- Bueno, S., Baudín, C., 2006. In situ developed laminates with large microstructural differences between layers of similar composition. *Journal of Materials Science* 41 (12), 3695–3700. doi:10.1007/s10853-006-6088-8.
- Bueno, S., Baudín, C., 2007. Layered materials with high strength and flaw tolerance based on alumina and aluminium titanate. *Journal of the European Ceramic Society* 27 (2–3), 1455–1462. doi:10.1016/j.jeurceramsoc.2006.05.054.
- Bueno, S., Baudín, C., 2009. Design and processing of a ceramic laminate with high toughness and strong interfaces. *Composites Part A Applied Science and Manufacturing* 40 (2), 137–143. doi:10.1016/j.compositesa.2008.10.012.
- Bueno, S., Moreno, R., Baudín, C., 2004. Reaction sintered $\text{Al}_2\text{O}_3\text{-Al}_2\text{TiO}_5$ microcrack-free composites obtained by colloidal filtration. *Journal of the European Ceramic Society* 24 (9), doi:10.1016/j.jeurceramsoc.2003.08.015.
- Bueno, S., Moreno, R., Baudín, C., 2005. Design and processing of $\text{Al}_2\text{O}_3\text{-Al}_2\text{TiO}_5$ layered structures. *Journal of the European Ceramic Society* 25 (6), 847–856. doi:10.1016/j.jeurceramsoc.2004.05.001.
- Bueno, S., Micele, L., Melandri, C., *et al.*, 2011. Improved wear behaviour of alumina-aluminium titanate laminates with low residual stresses and large grained interfaces. *Journal of the European Ceramic Society* 31 (4), 475–483. doi:10.1016/j.jeurceramsoc.2010.11.002.

- Bueno, S., Berger, M.-H., Moreno, R., Baudin, C., 2008. Fracture behaviour of microcrack-free alumina-aluminium titanate ceramics with second phase nanoparticles at alumina grain boundaries. *Journal of the European Ceramic Society* 28 (10), 1961–1971. doi:10.1016/j.jeurceramsoc.2008.01.017.
- Buessens, W.R., Lange, F.F., 1966. Residual stresses in anisotropic ceramics. *Intereram* 15 (3), 229–231.
- Buscaglia, V., Nanni, P., 1998. Decomposition of Al_2TiO_5 and $\text{Al}_{2(1-x)}\text{Mg}_x\text{Ti}_{(1+x)}\text{O}_5$ ceramics. *Journal of the American Ceramic Society* 81 (10), 2645–2653.
- Buscaglia, V., Battilana, G., Leoni, M., Nanni, P., 1996a. Decomposition of Al_2TiO_5 - MgTi_2O_5 solid solutions: A thermodynamic approach. *Journal of Materials Science* 31, 5009–5016.
- Buscaglia, V., Delfrate, M.A., Leoni, M., Bottino, C., 1996b. The effect of MgAl_2O_4 on the formation kinetics of Al_2TiO_5 from Al_2O_3 and TiO_2 fine powders. *Journal of Materials Science* 31, 1715–1724.
- Buscaglia, V., Delfrate, M.A., Leoni, M., Bottino, C., Nanni, P., 1996c. The effect of MgAl_2O_4 on the formation kinetics of Al_2TiO_5 from Al_2O_3 and TiO_2 fine powders. *Journal of Materials Science* 31, 1715–1724.
- Buscaglia, V., Nanni, P., Battilana, G., Aliprandi, G., Carry, C., 1994a. Reaction sintering of aluminium titanate: I Effect of MgO addition. *Journal of the European Ceramic Society* 13, 411–417.
- Buscaglia, V., Nanni, P., Battilana, G., Aliprandi, G., Carry, C., 1994b. Reaction sintering of aluminium titanate: II Effect of different Alumina powders. *Journal of the European Ceramic Society* 13, 419–426.
- Buscaglia, V., Delfrate, M.A., Nanni, P., Leoni, M., Bottino, C., 1995. Factors affecting microstructure evolution during reaction sintering of Al_2TiO_5 ceramics. *Advances in Science and Technology Research* 3C, 1867–1874.
- Chan, H.M., 1997. Layered ceramics: Processing and mechanical behavior. *Annual Review of Materials Research* 27, 249–282.
- Chen, C., Müller, B.R., Prinz, C., *et al.*, 2020. The correlation between porosity characteristics and the crystallographic texture in extruded stabilized aluminium titanate for diesel particulate filter applications. *Journal of the European Ceramic Society* 40 (4), 1592–1601. doi:10.1016/j.jeurceramsoc.2019.11.076.
- Chen, W., Shui, A., Wang, C., *et al.*, 2019. Preparation of aluminium titanate flexible ceramic by solid-phase sintering and its mechanical behavior. *Journal of Alloys and Compounds* 777, 119–126. doi:10.1016/j.jallcom.2018.09.317.
- Clegg, W.J., 1998. Design of ceramics laminates for structural applications. *Materials Science and Technology* 14 (6), 483–495.
- Cleveland, J.J., Bradt, R.C., 1978. Grain size microcracking relations for pseudo-brookite oxides. *Journal of the American Ceramic Society* 61 (11–1), 478–481. doi:10.1111/j.1151-2916.1978.tb16121.x.
- de Portu, G., Bueno, S., Micele, L., *et al.*, 2006. Piezo-spectroscopic characterization of alumina-aluminium titanate laminates. *Journal of the European Ceramic Society* 26 (13), 2699–2705. doi:10.1016/j.jeurceramsoc.2005.07.060.
- Dworak, W., Fingerle, D., 1987. Ceramic materials for engines. *British Ceramic Transactions* 86 (6), 170–178.
- Ewais, E.M.M., Besisa, N.H.A., Ahmed, A., 2017. Aluminum titanate based ceramics from aluminum sludge waste. *Ceramics International* 43 (13), 10277–10287. doi:10.1016/j.ceramint.2017.05.057.
- Fernández Navarro, J.M., 2003. Dilatación térmica (Chapter 12) in *El vidrio: constitución, fabricación, propiedades*. Madrid: CSIC.
- Freudenberg, B., 1987. Etude de la réaction à l'état solide: $\text{Al}_2\text{O}_3 + \text{TiO}_2 \rightarrow \text{Al}_2\text{TiO}_5$ (Doctoral thesis). Lausanne: Ecole Polytechnique.
- Freudenberg, B., Mocellin, A., 1987. Aluminum titanate formation by solid-state reaction of fine Al_2O_3 and TiO_2 powders. *Journal of the American Ceramic Society* 70 (1), 33–38. doi:10.1111/j.1151-2916.1987.tb04849.x.
- Freudenberg, B., Mocellin, A., 1988. Aluminum titanate formation by solid-state reaction of coarse Al_2O_3 and TiO_2 powders. *Journal of the American Ceramic Society* 71 (1), 22–28. doi:10.1111/j.1151-2916.1988.tb05755.x.
- Freudenberg, B., Lindner, H.A., Gugel, E., Thometzek, P., 1989. Thermomechanical properties of aluminium titanate ceramic between 20 and 1000°C. In: de With, G., Terpstra, R.A., Metselaar, R. (Eds.), *Euroceramics (Proc. 1st ECERS Conference)* 2. Maastricht: Elsevier, pp. 2.64–2.72.
- Fu, Y., Evans, A.G., 1982. Microcrack zone formation in single phase polycrystals. *Acta Metallurgica* 30, 1619–1625.
- Giordano, L., Viviani, M., Bottino, C., *et al.*, 2002. Microstructure and thermal expansion of Al_2TiO_5 - MgTi_2O_5 solid solutions obtained by reaction sintering. *Journal of the European Ceramic Society* 22 (11), 1811–1822. doi:10.1016/S0955-2219(01)00503-9.
- Guedes-Silva, C.C., de Souza Carvalho, F., Ferreira, T., Genova, L.A., 2016. Formation of aluminum titanate with small additions of MgO and SiO_2 . *Materials Research* 19 (2), 384–388. doi:10.1590/1980-5373-MR-2015-0498.
- Gulamova, D.D., Bakhronov, K.N., Bobokulov, S.K., Turdiev, Z.S., 2018. Ceramics based on aluminum titanate synthesized by using solar energy. *Refractories and Industrial Ceramics* 59 (2), 194–198. doi:10.1007/s11148-018-0205-5.
- Hamano, K., Ohya, Y., Nakagawa, Z., 1985. Crack propagation resistance of aluminum titanate ceramics. *International Journal of High Technology Ceramics* 1, 129–137.
- Holcombe, C.E., Coffey, A.L., 1973. Calculated X-ray powder diffraction data for β - Al_2TiO_5 . *Journal of the American Ceramic Society* 56 (4), 220–221.
- Hori, S., Kurita, R., 1985. Sintering of CVD aluminium oxide - Titanium dioxide powders. *International Journal of High Technology Ceramics* 1, 59.
- Hulbert, S.F., 1967. Models for solid-state reactions in powdered compacts: A review. *Journal of the British Ceramic Society* 6, 11–20.
- Hunt, C., Zachariasen, M., Driscoll, D., *et al.*, 2018. Degradation rate quantification of solid oxide fuel cell performance with and without Al_2TiO_5 addition. *International Journal of Hydrogen Energy* 43 (32), 15531–15536. doi:10.1016/j.ijhydene.2018.06.115.
- Ilatovskaia, M., Savinykh, G., Fabrichnaya, O., 2017. Thermodynamic description of the Ti-Al-O system based on experimental data. *Journal of Phase Equilibria and Diffusion* 38 (3), 175–184. doi:10.1007/s11669-016-0509-4.
- Ingebretsen, B.J., Matijevic, E., Parth, R.E., 1983. Preparation of uniform colloidal dispersions by chemical reactions in aerosols: iii. Mixed titania/alumina colloidal spheres. *Journal of Colloid and Interface Science* 95, 228–239.
- Innocenzi, P., Martucci, A., Armelao, L., 2005. Sol-gel synthesis of β - Al_2TiO_5 thin films at low temperature. *Journal of the European Ceramic Society* 25, 3587–3591.
- Ishitsuka, M., Sato, T., Endo, T., Shimada, M., 1987. Synthesis and thermal stability of aluminum titanate solid solutions. *Journal of the American Ceramic Society* 70, 69–71.
- Jha, S.K., Lebrun, J.M., Raj, R., 2016. Phase transformation in the alumina-titania system during flash sintering experiments. *Journal of the European Ceramic Society* 36 (3), 733–739. doi:10.1016/j.jeurceramsoc.2015.10.006.
- Kalita, S.J., Soman, V., 2010. Al_2TiO_5 - Al_2O_3 - TiO_2 nanocomposite: Structure, mechanical property and bioactivity studies. *Materials Research Bulletin* 45 (12), 1803–1810. doi:10.1016/j.materresbull.2010.09.017.
- Kato, E., Daimon, K., Kobayashi, Y., 1978. Factors affecting decomposition rate of Al_2TiO_5 . *Journal of the Ceramic Society of Japan* 86 (12), 626–631.
- Kato, E., Daimon, K., Takahashi, J., 1980. Decomposition temperature of β - Al_2TiO_5 . *Journal of the American Ceramic Society* 63 (5–6), 355–356.
- Kim, D., Kim, H.-J., Kim, H.-T., *et al.*, 2014. Mechanical properties of Al_2TiO_5 ceramics for high temperature application. *Current Nanoscience* 10 (1), 154–158. doi:10.2174/1573413709666131109005012.
- Kim, I.J., 2010. Thermal stability of Al_2TiO_5 ceramics for new diesel particulate filter applications-a literature review. *Journal of Ceramic Processing Research* 11 (4), 411–418.
- Kim, I.J., Cao, G., 2002. Low thermal expansion behavior and thermal durability of ZrTiO_4 - Al_2TiO_5 - Fe_2O_3 ceramics between 750 and 1400°C. *Journal of the European Ceramic Society* 22 (14–15), 2627–2632.
- Kim, I.J., Kim, H.C., 2004. Zero level thermal expansion materials based on ZrTiO_4 - Al_2TiO_5 ceramics synthesized by reaction sintering. *Journal of Ceramic Processing Research* 5 (4), 308–312.
- Kim, I.J., Gauckler, L.G., 2012. Formation, decomposition and thermal stability of Al_2TiO_5 ceramics. *Journal of Ceramic Science and Technology* 3 (2), 49–60. doi:10.4416/JCST2011-00049.
- Kolomeitsev, V.V., Suvorov, S.A., Makarov, V.N., Denisov, D.E., 1981. Synthesis, sintering, and properties of aluminum titanate. *Refractories* 22, 446–452.
- Korim, T., 2009. Effect of Mg^{2+} and Fe^{3+} -ions on formation mechanism of aluminium titanate. *Ceramics International* 35 (4), 1671–1675. doi:10.1016/j.ceramint.2008.07.017.

- Kornaus, K., Lach, R., Szumera, M., *et al.*, 2019. Synthesis of aluminium titanate by means of isostructural heterogeneous nucleation. *Journal of the European Ceramic Society* 39 (7), 2535–2544. doi:10.1016/j.jeurceramsoc.2019.02.021.
- Kucuk, I., Boyraz, T., 2019. Structural and mechanical characterization of mullite and aluminium titanate reinforced yttria stabilized zirconia ceramic composites. *Journal of Ceramic Processing Research* 20 (1), 73–79.
- Kuszyk, J., Bradt, R.C., 1973. Influence of grain size on effects of thermal expansion anisotropy in Mg_2TiO_5 . *Journal of the American Chemical Society* 56 (8), 420–423.
- Lang, S.M., Fillmore, C.L., Maxwell, L.H., 1952. The system Beryllia-alumina-titania: Phase relations and general physical properties of three-component porcelains. *Journal of Research of the National Institute of Standards and Technology* 48 (4), 301–321.
- Lange, F.F., Balmer, M.L., Levi, C.G., 1994. Diffusion limited crystallization and phase partitioning in ZrO_2 -metal oxide binary systems. *Journal of Sol-Gel Science and Technology* 2, 317–321.
- Law, C.H., Sofie, S.W., 2011. Anchoring of infiltrated nickel electro-catalyst by addition of aluminum titanate. *Journal of the Electrochemical Society* 158 (9), B1137–B1141. doi:10.1149/1.3610226.
- Lawn, B.R., Deng, Y., Miranda, P., *et al.*, 2002. Overview: Damage in brittle layer structures from concentrated loads. *Journal of Materials Research* 17 (2), 3019–3036.
- Li, W.S., Li, Y.G., Li, H.R., *et al.*, 1995. Aluminum titanate ceramics and their application in exhaust pipes for engines. In: Fu, X.R., Yan, D.S., Shi, S.X. (Eds.), *Ceramic Materials and Components For Engines - Proceedings of the 5th International Symposium*. World Scientific, pp. 759–762.
- Luo, X., Xie, Z., Zheng, L., *et al.*, 2015. Effect of adding $\text{Cr}_2\text{O}_3/\text{Fe}_2\text{O}_3$ on aluminum titanate properties. *Refractories and Industrial Ceramics* 56 (4), 337–343. doi:10.1007/s11148-015-9844-y.
- Maki, R.S.S., Suzuki, Y., 2013. Microstructure and mechanical properties of MgO -doped Al_2TiO_5 prepared by reactive sintering. *Journal of the Ceramic Society Of Japan* 121 (1415), 568–571. doi:10.2109/jcersj2.121.568.
- Maki, R.S.S., Suzuki, Y., 2016. Mechanical strength and electrical conductivity of reactively-sintered pseudobrookite-type Al_2TiO_5 - MgTi_2O_5 solid solutions. *Journal of the Ceramic Society of Japan* 124 (1), 1–6. doi:10.2109/jcersj2.15098.
- Mandal, S., Chatakonda, S.K., Chatterjee, A., Rao, S.S., 2017. CUMITHERM (R) – A state-of-the-art zero expansion ceramics and its applications. *Journal of Siberian Federal University-Chemistry* 10 (4), 465–476. doi:10.17516/1998-2836-0041.
- Matsudaira, T., Matsumura, Y., Kitaoka, S., Awaji, H., 2009. Effect of microstructure on the fatigue behavior of aluminum titanate ceramics. *Journal of Materials Science* 44 (6), 1622–1632. doi:10.1007/s10853-008-3228-3.
- McCleary, M., Amendola, R., 2018. Reduction kinetics of undoped and aluminum titanate (Al_2TiO_5) doped NiO -YSZ solid oxide fuel cell anodes. *Ceramics International* 44 (13), 15557–15564. doi:10.1016/j.ceramint.2018.05.218.
- Millo, F., Andreato, M., Rafigh, M., *et al.*, 2015. Impact on vehicle fuel economy of the soot loading on diesel particulate filters made of different substrate materials. *Energy* 86, 19–30. doi:10.1016/j.energy.2015.03.076.
- Morishima, H., Kato, Z., Uematsu, K., Saito, K., 1986. Development of aluminium titanate-mullite composite having high thermal shock resistance. *Journal of the American Chemical Society* 69 (10), C226–C227.
- Morosin, B., Lynch, R.W., 1972. Structure studies on Al_2TiO_5 at room temperature and at 600°C . *Acta Crystallographica B* 28, 1040–1046.
- Nagano, M., Nagashima, S., Maeda, H., Kato, A., 1999. Sintering behavior of Al_2TiO_5 base ceramics and their thermal properties. *Ceramics International* 25 (8), 681–687. doi:10.1016/S0272-8842(98)00083-2.
- Naghizadeh, R., Rezaie, H.R., Golestani-fard, F., 2009. The influence of composition, cooling rate and atmosphere on the synthesis and thermal stability of aluminum titanate. *Materials Science And Engineering B-Advanced Functional Solid-State Materials* 157 (1–3), 20–25. doi:10.1016/j.mseb.2008.12.002.
- Niu, F., Wu, D., Huang, Y., *et al.*, 2019. Direct additive manufacturing of large-sized crack-free alumina/aluminum titanate composite ceramics by directed laser deposition. *Rapid Prototyping Journal* 25 (8), 1370–1378. doi:10.1108/RPJ-08-2018-0215.
- Ohya, Y., Yamamoto, S., Ban, T., Tanaka, M., Kitaoka, S., 2017. Thermal expansion and mechanical properties of self-reinforced aluminum titanate ceramics with elongated grains. *Journal of the European Ceramic Society* 37 (4), 1673–1680. doi:10.1016/j.jeurceramsoc.2016.11.037.
- Ohya, Y., Nakagawa, Z.E., Hamano, K., 1987. Grain-boundary microcracking due to thermal-expansion anisotropy in aluminum titanate ceramics. *Journal of the American Ceramic Society* 70 (8), C184–C186.
- Ohya, Y., Nakagawa, Z., Hamano, K., 1988. Crack healing and bending strength of aluminum titanate ceramics at high temperature. *Journal of the American Ceramic Society* 71 (5), C232–C233.
- Ohya, Y., Kawauchi, Y., Ban, T., 2017. Cation distribution of pseudobrookite-type titanates and their phase stability. *Journal of the Ceramic Society of Japan* 125 (9), 695–700. doi:10.2109/jcersj2.17086.
- Okamura, H., Barringer, E.A., Bowen, H.K., 1989. Preparation and sintering of narrow-sized Al_2O_3 - TiO_2 composite powders. *Journal of Materials Science* 24, 1867–1880.
- Padture, N.P., Bennison, S.J., Chan, H.M., 1993a. Flaw-tolerance and crack-resistance properties of alumina-aluminum titanate composites with tailored microstructures. *Journal of the American Ceramic Society* 76 (9), 2312–2320.
- Padture, N.P., Runyan, J.L., Bennison, S.J., Braun, L.M., Lawn, B.R., 1993b. Model for toughness curves in two-phase ceramics: II, Microstructural variables. *Journal of the American Ceramic Society* 76 (9), 2241–2247.
- Papitha, R., Suresh, M.D., Dibakar, D., Johnson, R., 2014. High-temperature flexural strength and thermal stability of near zero expanding doped aluminum titanate ceramics for diesel particulate filters applications. *International Journal of Applied Ceramic Technology* 11 (4), 773–782. doi:10.1111/ijac.12092.
- Park, S.Y., Jung, S.W., Chung, Y.B., 2003. The effect of starting powder on the microstructure development of alumina-aluminum titanate composites. *Ceramics International* 29 (6), 707–712. doi:10.1016/S0272-8842(02)00221-3.
- Parker, F.J., 1990. Al_2TiO_5 - ZrTiO_4 - ZrO_2 composites: A new family of low-thermal-expansion ceramics. *Journal of the American Ceramic Society* 73 (4), 929–932.
- Parker, F.J., Rice, R.W., 1989. Correlation between grain size and thermal expansion for aluminum titanate materials. *Journal of the American Ceramic Society* 72 (12), 2364–2366.
- Pohlmann, H.J., Schricker, K., Schüller, K.H., 1975. Untersuchung an Werkstoffen im System Al_2O_3 - TiO_2 - SiO_2 . *Berichte der Deutschen Keramischen Gesellschaft* 52 (6), 179–183.
- Pratapa, S., Umaroh, K., Weddakarti, E., 2011. Microstructural and decomposition rate studies of periclase-added aluminum titanate-corundum functionally-graded materials. *Materials Letters* 65 (5), 854–856. doi:10.1016/j.matlet.2010.11.072.
- Rezaie, H.R., Naghizadeh, R., Farrokhnia, N., Arabi, S., 2009. The effect of Fe_2O_3 addition on tialite formation. *Ceramics International* 35 (2), 679–684. doi:10.1016/j.ceramint.2008.02.009.
- Rice, R.W., Pohanka, R.C., 1979. Grain-size dependence of spontaneous cracking in ceramics. *Journal of the American Ceramic Society* 62 (11–12), 559–563.
- Runyan, J.L., Bennison, S.J., 1991. Fabrication of flaw-tolerant Aluminum-titanate-reinforced Alumina. *Journal of the European Ceramic Society* 7, 93–99.
- Sakai, M., Osamu, S., 1987. R-Curve behavior of an Al_2TiO_5 refractory. In: *Proceedings of the 2nd International Conference on Refractories*, Tokyo, Japan.
- Sarkar, N., Park, J.G., Mazumber, S., *et al.*, 2015. Processing of particle stabilized Al_2TiO_5 - ZrTiO_4 foam to porous ceramics. *Journal of the European Ceramic Society* 35 (14), 3969–3976. doi:10.1016/j.jeurceramsoc.2015.07.004.
- Sarkar, N., Lee, J.S., Park, J.G., *et al.*, 2016. Mechanical and thermal properties of highly porous Al_2TiO_5 -Mullite ceramics. *Ceramics International* 42 (2), 3548–3555. doi:10.1016/j.ceramint.2015.11.002.
- Sharma, M., Dogan, N., 2019. Comparison of dissolution kinetics of nonmetallic inclusions in steel-making slag. In: Nakano, J., Pistorius, P.C., Tamerler, C., *et al.* (Eds.), *Advanced Real Time Imaging II: Cutting-Edge Techniques In Materials Science Studies*. (Minerals Metals & Materials Series). Springer, pp. 119–127. doi:10.1007/978-3-030-06143-2_12.

- Siebenbeck, H.J., Cleveland, J.J., Hasselman, D.P.H., Bradt, R.C., 1976. Thermal diffusivities of microcracked polycrystalline ceramics. In: Fulrath, R.M., Pask, J.A. (Eds.), *Ceramic Microstructures* '76. Boulder, CO: Westview Press, pp. 753–762.
- Sobhani, M., Ebadzadeh, T., Rahimipour, M.R., 2016. A comparison study on the R-curve behavior of alumina/aluminum titanate composites prepared with different TiO₂ powders. *Theoretical and Applied Fracture Mechanics* 85 (B), 159–163. doi:10.1016/j.tafmec.2016.01.005.
- Stingl, P., Heinrich, J., Huber, J., 1986. Properties and application of aluminium titanate components. In: *Proceedings of the 2nd International Symposium on Ceramic Materials and Components for Engines*. pp. 369–379. Ed. W. Bunk & H. Hausnes, Germany.
- Taylor, D., 1984. Thermal expansion data: III. Sesquioxides, M₂O₃ with the Corundum and the A-, B- and C-M₂O₃ structures. *British Ceramic Transactions and Journal* 83, 92–98.
- Taylor, D., 1987. Thermal expansion data, XI. Complex oxides, A₂BO₅, and the garnets. *British Ceramic Transactions and Journal* 86 (1), 1–6.
- Thomas, H.A.J., Stevens, R., 1989a. Aluminum titanate – A literature-review. Part 1: Microcracking Phenomena. *British Ceramic Transactions and Journal* 88 (4), 144–151.
- Thomas, H.A.J., Stevens, R., 1989b. Aluminum titanate – A literature review. Part 2: Engineering properties and thermal stability. *British Ceramic Transactions and Journal* 88, 184–190.
- Thomas, H.A.J., Stevens, R., 1989c. Aluminum titanate – A literature review. Part 3: Preparation of powders. *British Ceramic Transactions and Journal* 88, 229–233.
- Thomas, H.A.J., Stevens, R., 1989d. Microstructure development during the reaction sintering of Alumina and Titania to produce Aluminum Titanate. In: Stevens, R., Taylor, D. (Eds.), *Brit. Cer. Proc. No. 42, Complex Microstructures*. The Institute of Ceramics, Stoke-on-Trent, pp. 117–122.
- Tomaszewski, H., Weglarz, H., Wajler, A., Boniecki, M., Kalinski, D., 2007. Multilayer ceramic composites with high failure resistance. *Journal of the European Ceramic Society* 27 (2–3), 1373–1377.
- Trung, N.D., Ha, A., Tri, N., *et al.*, 2019. A low temperature fabrication and photoactivity of Al₂TiO₅ in cinnamic acid degradation. *Materials Transactions* 60 (9), 2022–2027. doi:10.2320/matertrans.M2019076.
- Uribe, R., 2001. Desarrollo de materiales estructurales de alúmina-titanato de aluminio con alta resistencia al choque térmico (Doctoral thesis). Facultad de Ciencias. Universidad Autónoma de Madrid.
- Uribe, R., Baudin, C., 2000. Formación de titanato de aluminio por reacción en estado sólido de alúmina y titania. *Boletín de la Sociedad Española de Cerámica y Vidrio* 39 (2), 221–228. doi:10.3989/cyv.2000.v39.i2.867.
- Uribe, R., Baudin, C., 2003. Influence of a dispersion of aluminum titanate particles of controlled size on the thermal shock resistance of alumina. *Journal of the American Ceramic Society* 86 (5), 846–850.
- Violini, M.A., Hernandez, M.F., Gauna, M.R., *et al.*, 2018. Low (and negative) thermal expansion Al₂TiO₅ materials and Al₂TiO₅ - 3Al₂O₃ - 2SiO₂ - ZrTiO₄ composite materials. Processing, initial zircon proportion effect, and properties. *Ceramics International* 44 (17), 21470–21477. doi:10.1016/j.ceramint.2018.08.208.
- Vioux, A., 1997. Nonhydrolytic sol–gel routes to oxides. *Chemistry of Materials* 9, 2292–2299.
- Wang, X.T., Padture, N.P., Tanaka, H., Ortiz, A.L., 2005. Wear-resistant ultra-fine-grained ceramics. *Acta Materialia* 53, 271–277.
- Wang, Y., Yang, Y., Zhao, Y., *et al.*, 2009. Sliding wear behaviors of in situ alumina/aluminum titanate ceramic composites. *Wear* 266 (11–12), 1051–1057. doi:10.1016/j.wear.2008.11.006.
- Welander, M.M., Zachariasen, M.S., Sofie, S.W., Walker, R.A., 2018. Enhancing Ni-YSZ anode resilience to environmental redox stress with aluminum titanate secondary phases. *ACS Applied Energy Materials* 1 (11), 6295–6302. doi:10.1021/acsaem.8b01288.
- Welander, M.M., Zachariasen, M.S., Sofie, S.W., Walker, R.A., 2019. Mitigating carbon formation with Al₂TiO₅-enhanced solid oxide fuel cell anodes. *Journal Of Physical Chemistry C* 123 (18), 11406–11413. doi:10.1021/acs.jpcc.9b00964.
- Wohlfromm, H., 1991. Preparación por sinterización reactiva y estudio del comportamiento mecánico y térmico de materiales de titanato de aluminio (Doctoral thesis). Facultad de Ciencias. Universidad Autónoma de Madrid.
- Wright, R.E., 1972. Acoustic emission of aluminum titanate. *Journal of the American Ceramic Society* 55 (1), 54–57.
- Wu, D., Huang, Y., Niu, F., *et al.*, 2019. Effects of TiO₂ doping on microstructure and properties of directed laser deposition alumina/aluminum titanate composites. *Virtual and Physical Prototyping* 14 (4), 371–381. doi:10.1080/17452759.2019.1622987.
- Xu, G., Zhao, H., Cui, H.Z., *et al.*, 2015. Stability, microstructure and mechanical properties of (Al,Fe)₍₂₎TiO₅ porous ceramic reinforced by in-situ mullite. *Journal of the Ceramic Society of Japan* 123 (1435), 156–159. doi:10.2109/jcersj2.123.156.
- Yang, Y., Wang, Y., Tian, W., *et al.*, 2009a. In situ alumina/aluminum titanate bulk ceramic composites prepared by SPS from different structured composite powders. *Journal of Alloys and Compounds* 481 (1–2), 858–862. doi:10.1016/j.jallcom.2009.03.129.
- Yang, Y., Wang, Y., Tian, W., *et al.*, 2009b. In situ porous alumina/aluminum titanate ceramic composite prepared by spark plasma sintering from nanostructured powders. *Scripta Materialia* 60 (7), 578–581. doi:10.1016/j.scriptamat.2008.12.016.
- Yano, T., Kiyohara, M., Otsuka, N., 1992. Thermal and mechanical properties of aluminium titanate - mullite composites-effects of aluminum titanate particle size. *Journal of the Ceramic Society of Japan* 100 (4), 487–492.
- Zhang, J.X., Jiang, D.L., Qin, S.Y., Huang, Z.R., 2004. Fracture behavior of laminated SiC composites. *Ceramics International* 30, 697–703.
- Zhao, G., Bai, Y., Qiao, L., 2016. Aluminum titanate-calcium dialuminate composites with low thermal expansion and high strength. *Journal of Alloys and Compounds* 656, 1–4. doi:10.1016/j.jallcom.2015.09.237.

Relevant Websites

- <https://www.ceramtec.com/alutit/>
Advanced Ceramics for Foundry Technology.
- <https://www.kyocera-precision.com/materials/aluminum-titanate/>
Aluminum titanate.
- <https://www.americanelements.com/aluminum-titanate-12004-39-6>
Aluminum Titanate — AMERICAN ELEMENTS®.
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- <https://www.cumi-murugappa.com/ceramics/ic/materials/aluminum-titanate/Materials>.

Zirconia Ceramics, Structure and Properties

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Introduction

Zirconia (Zirconium oxide, ZrO_2), the oxide of zirconium metal, occurs as a natural mineral and is formed in igneous rocks such as schists, gneiss, granites, and syenites. Zirconia was first identified by the German chemist Martin Heinrich in 1789 (cited by [Klaproth, 1958](#)) as a reaction product of heating zirconium. In 1892, a more abundant source was discovered in the mineral baddeleyite (80%–98% of zirconia) (cited by [Audley, 1917](#)) from which a relatively pure zirconia can be prepared. Baddeleyite contains small amounts of silica and iron as impurities. In this form it is concentrated in the tailings of the uranium and copper deposits found at Palabora, South Africa. All deposits of zirconia also contain a small percentage of hafnium, separation of which can only be achieved by sophisticated chemical processing such as occurs in ion exchange columns. Other main sources of the oxide are in Northern Russia. Zirconia is also extensively recovered from zircon (the zirconium orthosilicate: ZrSiO_4), which is found in several areas of the world as beach sand. The relatively pure oxide, containing hafnia (<2%) is found in nature as comparatively large particles (>1 mm) of monoclinic phase, which has been formed over a long period of time by hydrothermal dissolution and precipitation.

The monoclinic form is thermodynamically stable at room temperature but transforms reversibly to the tetragonal crystallographic system on heating above 1170°C, the transformation being accompanied by a decrease in volume of approximately 4%–5%. Conversely, the transformation from tetragonal to monoclinic on cooling shows a volume increase, occurs at high speed and is used to develop extraordinary properties in zirconia-based engineering ceramics. The crystal structures are unusual in that the structure becomes more symmetric on heating; thus, the monoclinic form (space group $P2_1/c$) first transforms to the tetragonal form (space group $P4_2/nmc$) and at 2370°C to the cubic fluorite phase (space group $Fm\bar{3}m$) ([Fig. 1](#)). Intermediate between the tetragonal and the cubic crystal, several high-pressure orthorhombic forms have also been detected ([Bouvier et al., 2000](#)). Use of pure zirconia in applications is not feasible due to the large volume change of the tetragonal to monoclinic phase transformation that leads to the disintegration of sintered parts during cooling. The problem has been alleviated by alloying zirconia with other oxides that stabilize tetragonal and/or cubic phases down to room temperature, thus preventing the tetragonal to monoclinic transformation. Since this discovery, many conferences and books have been devoted to the science and technology of zirconia ([Heuer and Hobbs, 1981](#); [Claussen et al., 1984](#); [Somiya et al., 1988](#); [Badwal et al., 1993](#)).

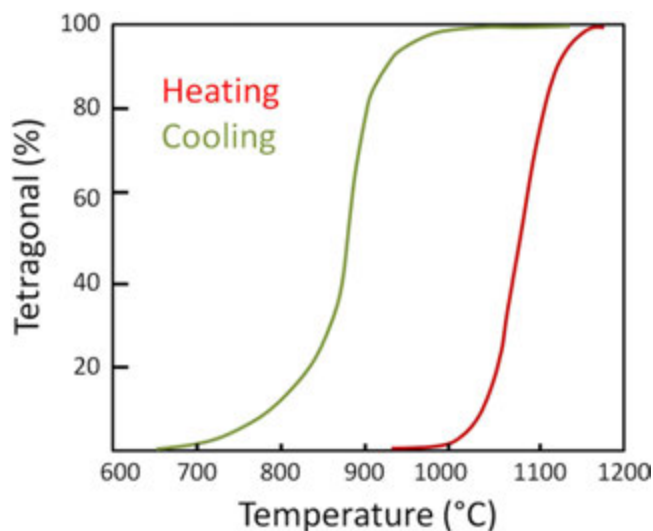


Fig. 1 The crystal structures of zirconia showing the effect of temperature, stabilizer addition and temperature hysteresis for transformations. Adapted from Ricca, C., Ringued, A., Cassir, M., Adamo, C., Labat, F., 2015. A comprehensive DFT investigation of bulk and low-index surfaces of ZrO_2 polymorphs. *J. Comput. Chem.* 36, 9–21.

The relationships between the crystallographic phases are best shown diagrammatically, where it can be seen that the symmetry increases with temperature and stabilizer content (Fig. 1).

The higher temperature phases may thus be stabilized by the addition into solid solution of specific cubic oxides. Additives, also known as stabilizers, such as CaO, MgO, Y_2O_3 and CeO_2 , in which the cations have a similar ionic radius to Zr and sufficient solid solubility, will, when incorporated into the monoclinic phase, first stabilize the tetragonal form and with further addition, the cubic phase. There are many elements in the periodic table which satisfy the radius criterion, but only a few have sufficient solid solubility so that the most efficient stabilizers are limited to several rare-earth elements. Factors other than the simple radius ratio which might contribute to cubic stability include the development of increased covalent bonding and the generation of sufficient oxygen vacancies to accommodate eightfold coordination of the oxygen ion sites.

Tetragonal-Monoclinic Phase Transformation

The tetragonal phase of zirconia exists over a temperature range. On cooling below 950°C , it transforms to the monoclinic phase. The transformation occurs by a diffusionless shear process at high speed (near sonic velocity), with a thermal hysteresis developed between the heating and cooling cycles (Fig. 2). The transformation is akin to that of the martensitic transformation which occurs when steel is quenched from its austenitic phase. In addition, it has been demonstrated that the transformation is dependent on the particle size of the components, finer particles transforming at a lower temperature than coarser particles.

The martensitic nature of the transformation has been confirmed by transmission electron microscopy when extensive shear in the form of twin generation has been observed (Leriché, 1986) (Fig. 3). In zirconia, three different crystallographic correspondences exist

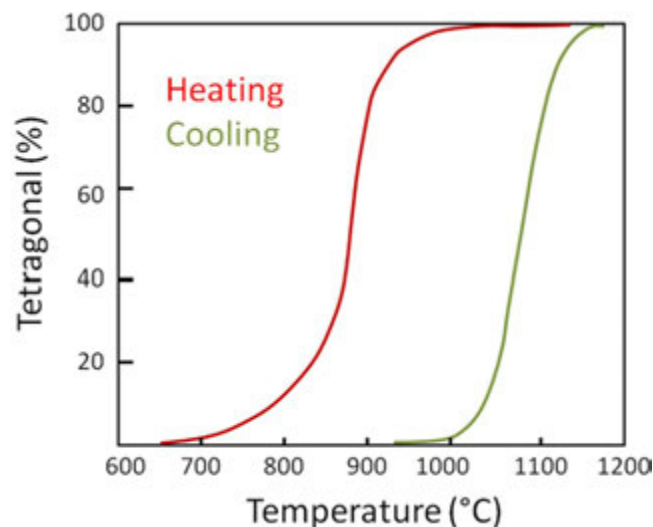


Fig. 2 Temperature hysteresis for the monoclinic-tetragonal transformation of pure zirconia.



Fig. 3 Transmission electron micrograph in dark field, showing transformed (tetragonal - monoclinic) zirconia particle. The transformed phase (zirconia particle in a mullite matrix) consists of narrow twins, indicative of a martensitic shear type transformation. Reproduced from Leriché, A., 1986. Influence of Mullite-Zirconia Composites Processing Parameters on Their Microstructure. (Ph.D. thesis). Belgium: University of Mons. (in French).

between the parent (tetragonal) and the product (monoclinic) phase, called ABC, BCA and CAB, which imply that the lattice parameters of the tetragonal phase (a_t , b_t , c_t) change into (a_m , b_m , c_m), (b_m , c_m , a_m) and (c_m , a_m , b_m), respectively. Each of these lattice correspondences may occur along two different habit planes, leading to six different configurations. For each, the volume change or dilatation component of transformation strain is around 5% and the shear strain is around 16%, which is 3 or 4 times larger than the dilatational component (Kelly and Francis Rose, 2002; Chevalier *et al.*, 2009).

A thermodynamic analysis of the nucleation and growth of the monoclinic martensite phase has been made to explain the effect of particle size on phase stability. A key issue has been that of nucleation of the martensite platelets and evidence for both homogeneous and heterogeneous nucleation is available. For the polycrystalline ceramic systems of technological interest, the importance of stress raising sites and of strain energy is well established. The availability of a martensitic transformation in zirconia has allowed the development of a range of transformation toughened ceramics, which not only improve the toughness of the host but also allow remarkable increases in strength. Furthermore, the process also leads to the development of stress-induced compressive surface stresses which for the first time allow ceramics to become more tolerant to surface flaws.

These toughening phenomena will be described below.

Stress-Induced Transformation Toughening

When heated above $\sim 1170^\circ\text{C}$, monoclinic zirconia transforms to the tetragonal phase. On cooling, the tetragonal-monoclinic transformation should take place with a significant volume increase. However, if the ZrO_2 is in the form of finely divided particles (below a critical size of ~ 20 nm), or has a constraining pressure exerted on it by the matrix, then the zirconia particle can be retained in the tetragonal state as a metastable phase. Such metastable tetragonal crystals can be introduced into suitable matrix materials such as alumina during the initial stages of fabrication or they are formed in-situ from cubic solid solutions by applying secondary heat treatment after sintering, as in the case of Mg-PSZ (see below). As previously mentioned, the tetragonal phase can also be retained at room temperature in zirconia ceramics by adding stabilizing oxides, such as yttria (Y_2O_3) or ceria (CeO_2). Tetragonal zirconia polycrystalline (TZP) materials exhibit nearly 100% tetragonal phase and are often designated with a prefix to denote the stabilizing cation and its content, for example 3Y-TZP represents a 3 mol% Y_2O_3 stabilized zirconia.

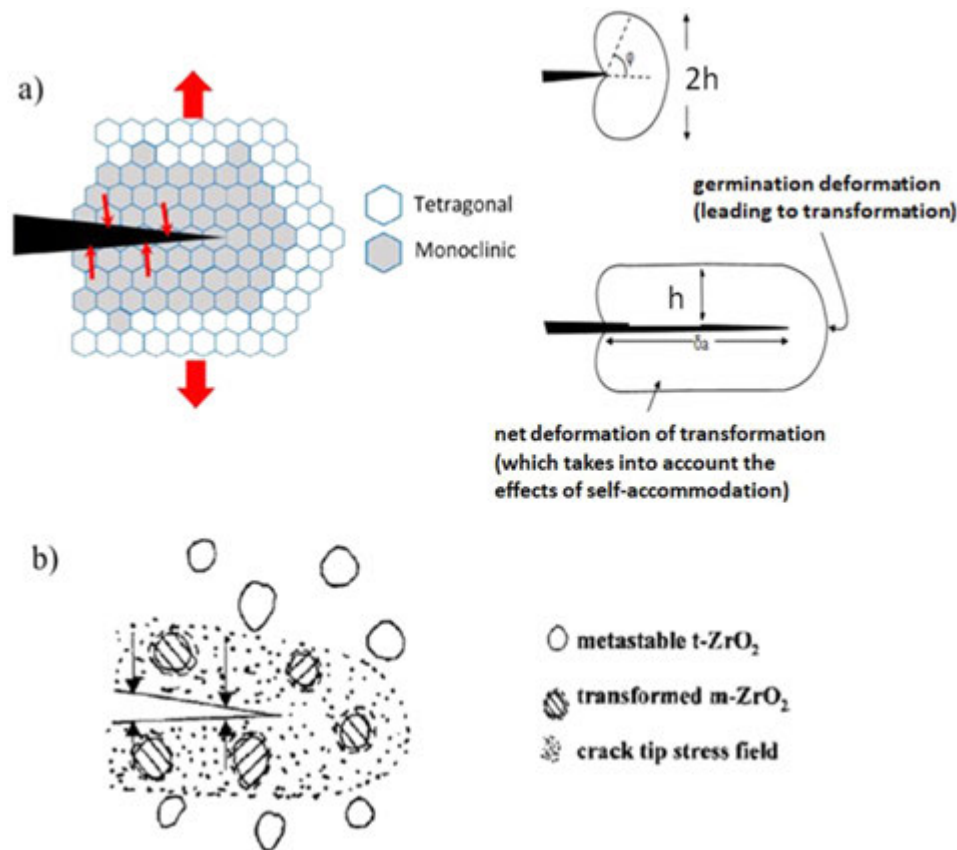


Fig. 4 Diagrammatic representation of the transformation toughening process in the region of an opening crack tip (a) in polycrystalline TZP zirconia and (b) in ceramics containing tetragonal particles. Reproduced from (a) Palmero, P., Montanaro, L., Reveron, H., Chevalier, J., 2014. Review: Surface coating of oxide powders: A new synthesis method to process biomedical grade nano-composites. *Materials* 7, 5012–5037. (b) Jin, X.-J., 2005. Martensitic transformation in zirconia containing ceramics and its applications. *Curr. Opin. Solid State Mater. Sci.* 9 (6), 313–318.

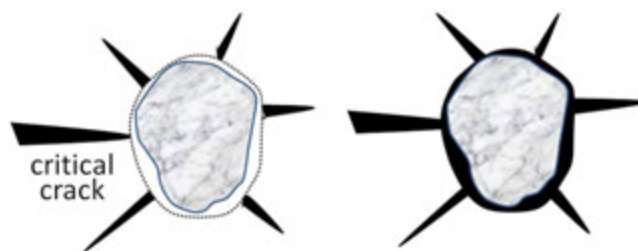


Fig. 5 Diagram showing how the presence of microcracking around a spontaneously transformed ZrO_2 particle has caused bifurcation and deflection of a growing critical crack, thereby toughening the host material.

The martensitic tetragonal to monoclinic transformation can be induced by cooling, by external loading and in some ceramics spontaneously if they are put in contact with water. The stress-induced transformation enhances the toughness of zirconia ceramics. In TZP, the transformation toughening process occurs when metastable retained tetragonal grains transform to their monoclinic form in the tensile stress field created around a propagating crack (Fig. 4(a)). In the case of tetragonal particles dispersed in a matrix, if a crack is made to extend under a stress, then tensile stresses are generated around and ahead of the crack tip. When the stresses are large enough and released on the metastable tetragonal zirconia particles, the particles transform to the monoclinic phase (Fig. 4(b)). The tetragonal to monoclinic transformation occurs at a given stress (critical transformation stress) and implies a volume increase, typically 4%–5%. The volume expansion generates large compressive stresses in the process zone around the crack tip. This reduces the local crack tip stress intensity and hence the driving force for crack propagation, so increasing the effective toughness of the ceramic. A critical size range exists within which the metastable tetragonal particles can be induced to transform. Below this range, the particles cannot transform and above it they transform spontaneously. The size range depends on factors such as the degree of matrix constraint, the degree of substitutional stabilization, and the shape and distribution of the zirconia particles.

Microcrack Toughening

Microcracks can be readily introduced into a ceramic matrix (cubic zirconia or another ceramic such as alumina) by the incorporation of the transformable tetragonal phase. Spontaneous transformation on cooling through the transformation temperature results in a large volume increase (4%) which cannot be accommodated by elastic strains and consequently results in the development of microcracks (Fig. 5). These can be used to deflect a primary crack enhancing the toughness and/or the thermal shock resistance in the process. Provided the microcracks are small compared with the primary crack, then they would have a minimal effect on the fracture strength. Optimum conditions arise when the microcracks are small enough to deflect the primary crack but are too small or too few to link up and increase the effective length of the critical crack.

Similarly, the maximum toughness is reached when the number of cracks is at a maximum such that deflection occurs but not a linking up of adjacent microcracks. The situation is generally obtained with 10%–15% of the material in the form of transformed monoclinic particles.

Phase Relationships

Extensive literature exists on the phase equilibria of zirconia. Many binary and ternary systems have been investigated in detail, in particular, $\text{ZrO}_2\text{-MgO}$, $\text{ZrO}_2\text{-CaO}$, $\text{ZrO}_2\text{-Y}_2\text{O}_3$, and $\text{ZrO}_2\text{-rare-earth oxide(s)}$. Substitution is dependent on compatible ionic size and in addition the electrical neutrality must be maintained in conjunction with the substitution. Thus, ions having a different valency must be compensated for with an appropriate number of anion or cation vacant sites in the modified crystal. The condition for Mg^{2+} substitution for Zr^{4+} is:



Where Mg_{Zr}'' represents a zirconium site occupied by magnesium (double-charged negatively), O_0 represents an oxygen site occupied by oxygen (neutral) and $\text{V}_{\text{O}}^{\bullet\bullet}$ a vacancy on an oxygen site (double-charged positively).

Stabilization is considered to be helped by the creation of oxygen vacancies which effect a distortion of the tetragonal and monoclinic unit cells to the more symmetric cubic symmetry.

The high melting points and low cation mobility of the constituents constrain the development of equilibrium conditions, which makes for experimental difficulties, notably the extensive time required for accurate determination of the precise limit of the phase fields, particularly those at medium and low temperatures.

It is noticeable that the addition of the second component has the effect of reducing the transformation temperature of the monoclinic transformation. A further feature of interest is the increase with temperature of the compositional range of the tetragonal phase field, which will as a consequence allow heat treatment and phase separation, subsequent to a primary sintering cycle, in the process enhancing the properties of the sintered ceramic.

ZrO₂-MgO

The ZrO₂-MgO system has been used extensively and the phase diagram given in Fig. 6 is widely accepted. Of particular interest to technological applications is the presence of a region above 1400°C consisting of a mixed cubic and tetragonal phase. At lower temperature in the range 1200–1400°C, the monoclinic phase is stable, by virtue of a decomposition reaction, when the cubic phase breaks down to form the tetragonal phase and free MgO.

Manipulation of this region of the phase diagram has allowed the development of strong tough engineering ceramics designated as partially stabilized zirconia (PSZ) based on the principle of transformation toughening. The structure developed consists of large (> 50 μm) grains of cubic matrix containing a uniform dispersion of lenticular tetragonal phase (Fig. 7). The properties of Mg-PSZ are summarized in Table 1.

Generally, commercial ZrO₂-MgO materials are produced within a limited composition range of 8–10 mol% MgO. The first commercial zirconia-based product appeared in 1928 and was a MgO-stabilized ZrO₂ crucible for metal melts. Today, magnesia-stabilized zirconia is available both partially and fully stabilized for applications including structural ceramics for turbine blades, anti-ballistic and armor ceramics and ionically conductive uses.

ZrO₂-Y₂O₃

Although Y₂O₃ and ZrO₂ have different space groups, the arrangement of the ions is similar with only a small shift in the atomic positions. Thus, the solubility limit of Y₂O₃ in both the monoclinic and tetragonal phases is relatively high, giving extensive tetragonal and cubic solid solution phase fields in the phase diagram. The extended range of the tetragonal phase field has

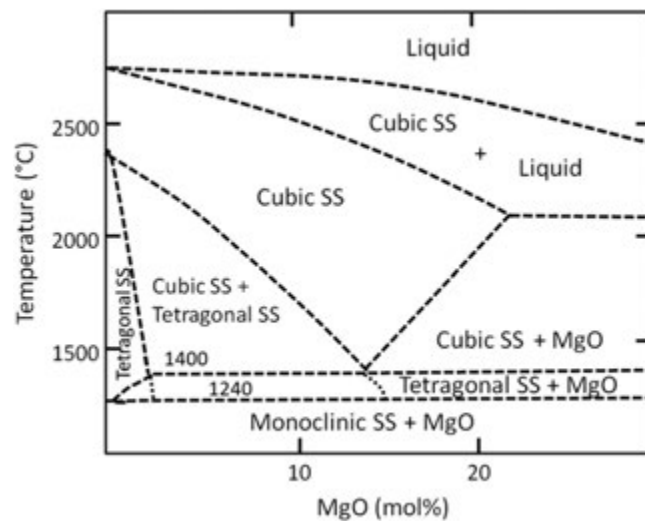


Fig. 6 Equilibrium phase diagram for ZrO₂-MgO. Adapted from Grain, C., 1967. Phase relations in the ZrO₂-MgO system. *J. Am. Ceram. Soc.* 50, 6, 288–290.

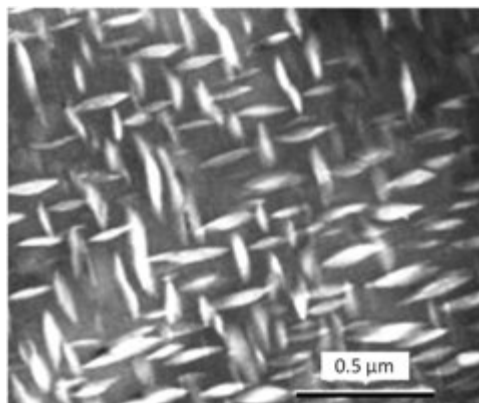
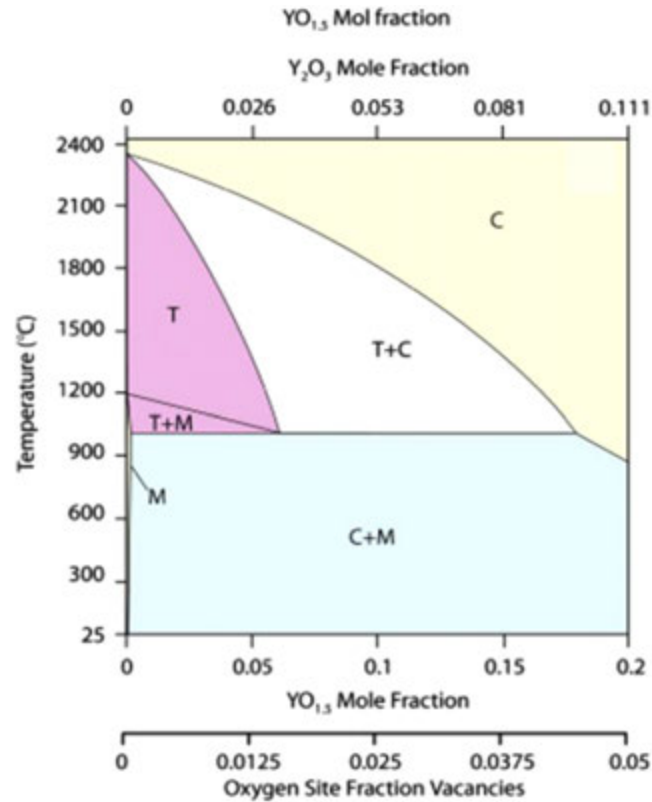


Fig. 7 Transmission electron micrograph of a heat treated Mg-PSZ showing the phase separation of the lenticular tetragonal phase (light phase) from the matrix of the cubic phase stabilized with a higher MgO content. Reproduced from Stevens, R., 1986. *An Introduction to Zirconia*, second ed. London, England: Magnesium Elektron Ltd. (Magnesium Elektron Publication No 113).

Table 1 Comparison of zirconia ceramic properties

Ceramic	Toughness ($\text{MPa m}^{1/2}$)	Flexural strength (MPa)	Weibull modulus	Grain size (μm)	Hardness (GPa)
Mg-PSZ	5	600	–	50	12
Y-TZP	7–12	1000–1200	8	0.3	12–14
Ce-TZP	15–20	400–600	20	2–3	8–10

**Fig. 8** Equilibrium phase diagrams for $\text{ZrO}_2\text{-Y}_2\text{O}_3$. Reproduced from Lakiza, S., Fabrichnaya, O., Zinkevich, M., Aldinger, F., 2006. On the phase relations in the $\text{ZrO}_2\text{-YO}_{1.5}\text{-AlO}_{1.5}$ System. *J. Alloy. Compd.* 420, 237–245.

considerable importance in the transformation toughening of commercial ceramics. The equilibrium phase diagram $\text{ZrO}_2\text{-YO}_{1.5}$ presented in Fig. 8 shows that from a thermodynamic point of view, the tetragonal phase should not exist at low temperature even in the presence of yttria: a mix of monoclinic and cubic solid solutions are expected. However, from a kinetic point of view, since at the eutectoid temperature (near 1000°C) the diffusion of yttrium ions in the tetragonal structure is very low, it is very easy to retain the tetragonal phase until room temperature. To give a more precise idea, the time required for Y^{3+} to migrate 150 nm would be 10^7 seconds (several months!) (Kilo *et al.*, 2000).

Thus, the addition of yttria to zirconia has two significant effects. It extends the range of the tetragonal phase field and also has the effect of lowering the temperature at which the tetragonal-monoclinic transformation takes place. Moreover, the Zr^{4+} substitution by a trivalent cation generates oxygen vacancies for maintaining the charge neutrality. Oxygen vacancies are responsible for the phenomenon of Low Temperature Degradation (LTD) or aging in the presence of moisture. This enables the fabrication of dense zirconia polycrystalline ceramics consisting of nearly 100% tetragonal phase (TZP) (Fig. 9). Typically, at 2.5–3 mol% Y_2O_3 the material produced is stable at room temperature providing it has a sufficiently small grain size. Materials based on these compositions are fabricated commercially and have found widespread use in markets involving cutting and wear applications, where the materials have proved superior to any available alternative metal or ceramic. From early 1990s, 3Y-TZP was used in orthopedics for the fabrication of femoral heads for total hip arthroplasty until 2001, when more than 400 failures of zirconia heads were reported, associated with an accelerated aging issue. Since then, Y-TZP ceramics are used in the dental field for manufacturing implants, abutments, crowns and bridges. Due to the phase transformation toughening mechanism, 3Y-TZP ceramics exhibit outstanding mechanical properties (i.e., strength >1000 MPa and toughness ~ 6 $\text{MPa m}^{1/2}$).

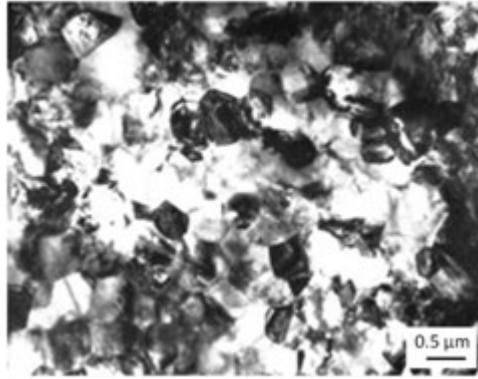


Fig. 9 Transmission electron micrograph showing the fine grained metastable tetragonal phase of TZP, stabilized with yttria. Reproduced from Stevens, R., 1986. An Introduction to Zirconia, second ed. London, England: Magnesium Elektron Ltd. (Magnesium Elektron Publication No 113).

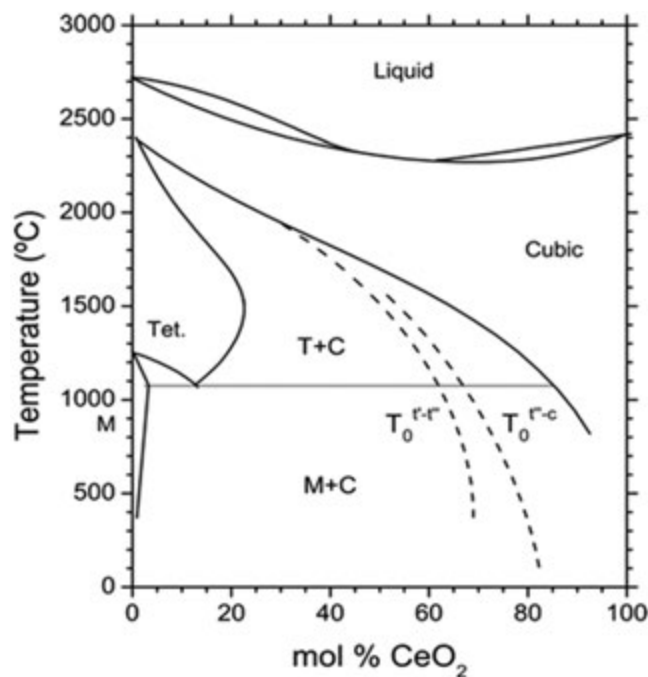


Fig. 10 Equilibrium phase diagrams for $\text{ZrO}_2\text{-CeO}_2$. Adapted from Huang, S., Li, L., Vleugels, J., Wang, P., Van der Biest, O., 2003. Thermodynamic prediction of the non stoichiometric phase $\text{Zr}_{11-x}\text{Ce}_x\text{O}_{2-x}$ in the $\text{ZrO}_2\text{-CeO}_{1.5}\text{-CeO}_2$ system. J. Eur. Ceram. Soc. 23 (1), 99–106.

$\text{ZrO}_2\text{-CeO}_2$

In the case of ceria stabilization, the Zr^{4+} substitution by an isovalent cation does not generate oxygen vacancies since the neutrality of the crystal is not compromised. However, the number of oxygen atoms surrounding the Zr^{4+} will be reduced due to the longer chemical bond for Ce-O than for Zr-O leading to tetragonal stabilization. For stabilizing zirconia with ceria, relatively high quantities of this oxide are necessary, at least 10 mol% as illustrated in Fig. 10. As cerium presents 2 oxidation states (+2 and +4), only 6 mol% will be necessary to stabilize the tetragonal phase in the case of sintering materials under reducing atmosphere, favorable to Ce^{2+} (Zhu, 1994).

Contrary to 3Y-TZP ceramics which exhibits relatively moderate toughness ($\sim 6 \text{ MPa m}^{1/2}$) but impressive strength ($> 1000 \text{ MPa}$), Ce-TZP ceramics containing 10–12 mol% CeO_2 present much higher toughness ($15\text{--}20 \text{ MPa m}^{1/2}$) but lower strength (typically 600 MPa). This behavior is due to the larger grain size obtained in ceria-stabilized ceramics after sintering ($> 1.5\text{--}2.0 \mu\text{m}$), compared to that of 3Y-TZP ($< 300 \text{ nm}$). The Ce-TZP ceramics distinguish also from 3Y-TZP by a lower transformation critical stress (around 300 MPa), a higher t-m transformation temperature and a larger process zone (around $100\text{--}200 \mu\text{m}$ instead of a few μm in 3Y-TZP) (Shimozono *et al.*, 2006; Grathwohl and Liu, 1991). Because the tetragonal stabilization is not due to oxygen vacancies as for Y-TZP, Ce-TZP possesses higher stability in the presence of water.

Table 1 presents a comparison of the different zirconia ceramic properties.

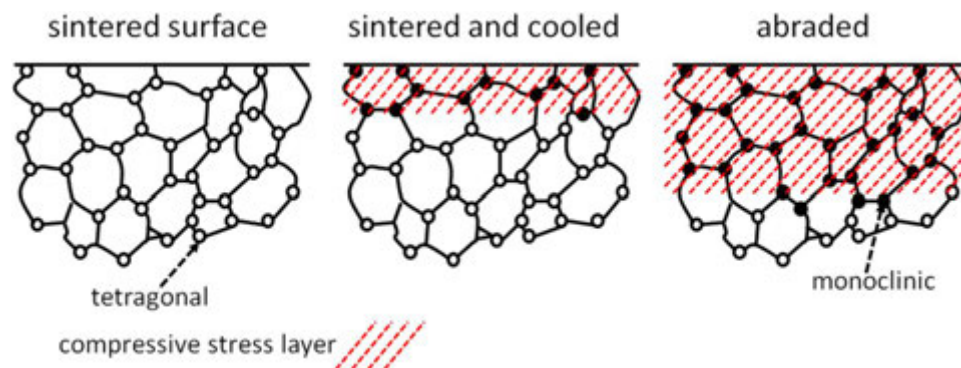


Fig. 11 Diagram of a section through a free surface at (a) the sintering temperature. On cooling, particles of ZrO_2 near the surface (b) transform due to reduced constraint, developing a compressive stress in the matrix. The thickness of this compressively stressed layer can be increased (c) by abrasion or machining. Adapted from Stevens, R., 1986. *An Introduction to Zirconia*, second ed. London, England: Magnesium Elektron Ltd. (Magnesium Elektron Publication No 113).

It is important to note that this transformation toughening diminishes as the temperature increases because t-m transformation disappears above the phase transition temperature. Therefore, the PSZ and TZP are not high temperature materials. This strength reduction at higher temperatures can be compensated by adding other particles which will replace the transformation toughening by other mechanisms.

Compressive Surface Layers

Compressive surface layers are developed in zirconia based transformation toughened ceramics as a result of the spontaneous transformation of particles of tetragonal zirconia situated in or near the surface (Fig. 11). The easier transformation arises from the lack of hydrostatic constraint near the free surface, in the manner shown in Fig. 11.

A considerable increase in the fracture strength can be obtained by the generation of a large compressive surface stress. Furthermore, the magnitude of the surface stress can be increased considerably by any process such as grinding which generates stresses of a sufficient level internally to trigger the tetragonal - monoclinic transformation at greater than normal depths. The magnitude of the strengthening effect is dependent on the severity of grinding and transformation to the monoclinic phase can take place to depths of 100 μm . It is apparent that this phenomenon is only practical when the depth of the transformed layer is larger than the critical flaw size but small in comparison with the overall cross-section of the ceramic. The effect is of great significance in engineering components since for the first time a ceramic is available, which, when abraded or impacted as might happen to a component in manufacture or service, is stronger after the “damage” event than before it occurred.

Aging of Zirconia Ceramics (LTD)

The tetragonal to monoclinic transformation which is responsible for the toughening (when induced by stresses around propagating cracks in the volume) can also have a negative impact if it takes place spontaneously at the surface, a phenomenon known as Low Temperature Degradation. As a consequence, microcracking, grain pull-out and an increase of the surface roughness appear. In the worst case, it leads to premature failures, as was the case with the 3Y-TZP femoral head ruptures in 2001. This catastrophic episode of failures led to the prohibition of using Y-TZP ceramics in orthopedic applications (Chevalier *et al.*, 2009). Fig. 12 presents the model proposed by Yoshimura *et al.* (1987) to explain the stress increase which will trigger the t-m phase transformation, by water chemisorption and as-formed hydroxyl diffusion from the surface to the bulk. This diffusion would be favored by the presence of oxygen vacancies, especially numerous in Y-TZP ceramics. Fig. 13 illustrates the aging phenomenon showing the t-m nucleation in a surface grain, its propagation to the neighboring grains and the resulting microfissuration (Chevalier, 2006).

As the aging phenomenon is directly linked to oxygen vacancies created when stabilizing with cations of valence $< +4$ (e.g., with calcium, magnesium and yttrium addition), ceria-stabilized zirconia, owing to the tetravalent nature of cerium, possesses excellent aging resistance. Fig. 14 presents the results of accelerated aging kinetic assays performed in an autoclave at 134°C under 2 bars to simulate aging at 37°C for the 3-TZP and 10 Ce-TZP ceramics which confirms the excellent aging resistance of Ce doped zirconia (Chevalier *et al.*, 2009).

Synthesis of Doped Zirconia Powders for Ceramic Processing

The commercial grades of zirconia are produced by a number of routes, usually involving zircon as a precursor. Zircon is broken down into its constituents, ZrO_2 and SiO_2 , either chemically, by the addition of an aggressive alkali (NaOH , CaO), or by heating

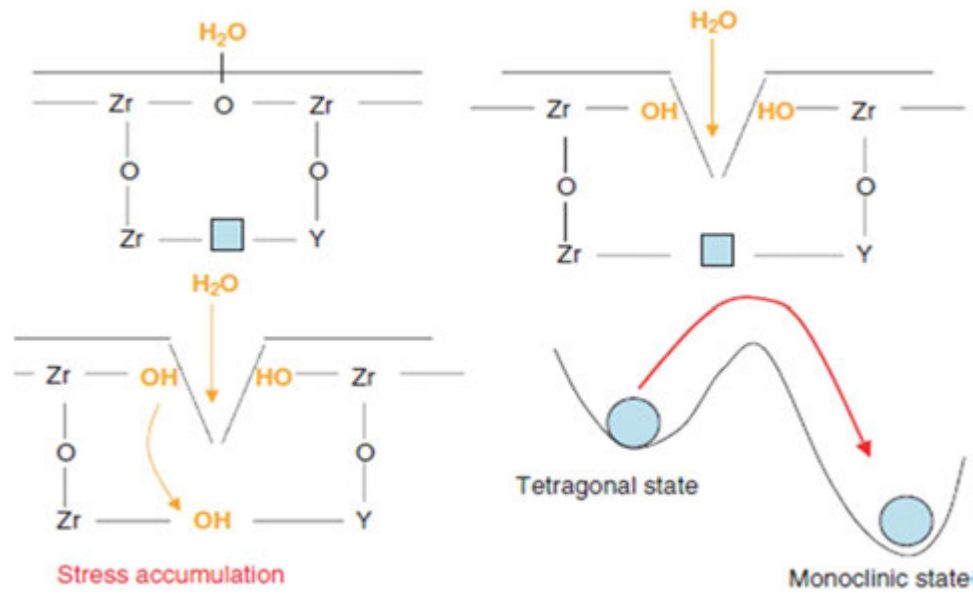


Fig. 12 Model describing the stress increase provoked by water chemisorption and hydroxyl diffusion into the network. Adapted from Yoshimura, M., Noma, T., Kawabata, K., Somiya, S., 1987. Role of water on the degradation process of Y-TZP. *J. Mater. Sci. Lett.* 6, 465–467.

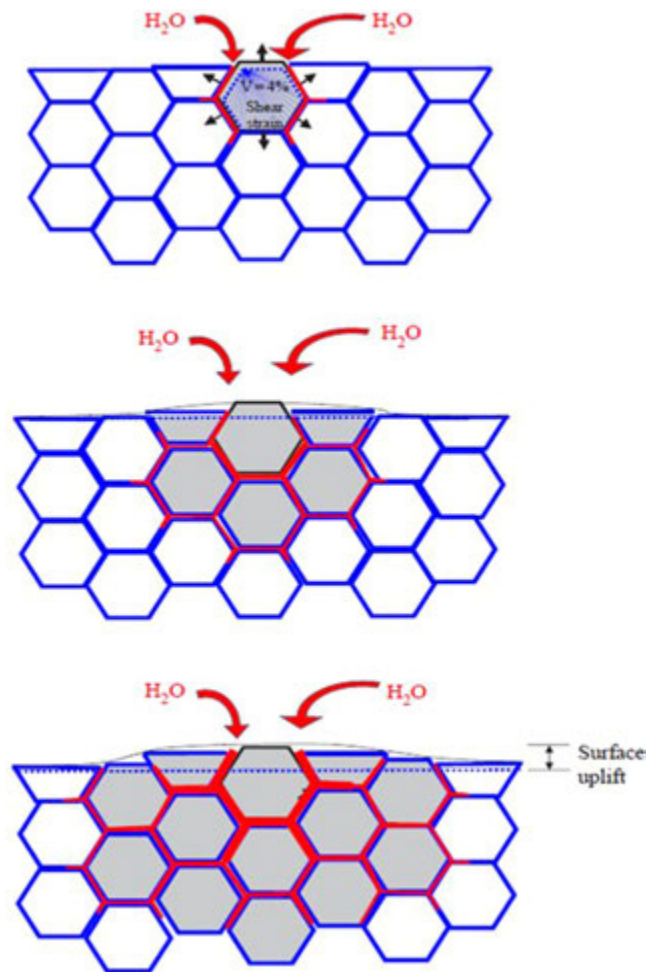


Fig. 13 Schematic representation of zirconia aging. Adapted from Chevalier, J., 2006. What future for zirconia as a biomaterial? *Biomaterials* 27, 535–543.

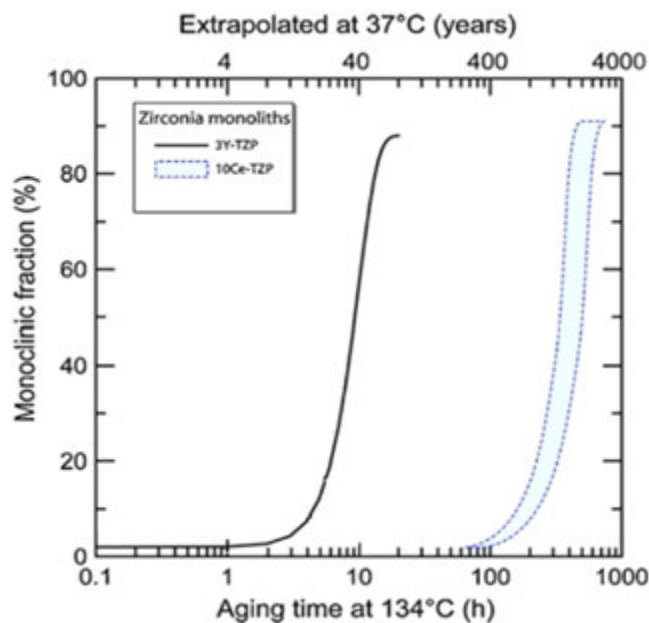


Fig. 14 Aging accelerated assays (134°C, 2 bars) for 3Y-TZP and 10Ce-TZP. Adapted from Chevalier, J., Gremillard, L., Virkar, A.V., Clarke, D.R., 2009. The tetragonal-monoclinic transformation in zirconia: Lessons learned and future trends. *J. Am. Ceram. Soc.* 92, 1901–1920.

to a high temperature, when the zircon dissociates into its constituent phases and separation occurs. The zirconia can then be removed by dissolution in sulfuric acid and is subsequently precipitated. The rate of reaction is governed by the particle sizes of the component phases and these are carefully controlled. Similarly, the morphology of the phases can have an influence on the process. Both these factors can be influenced by the processing temperature and the rate of cooling.

The zirconia can then be precipitated from solution when the variables employed control the nature of the precipitate, in particular, the size and morphology of the primary particles and the agglomerates. Calcination of the precipitate will then reduce the surface area of the powder and decrease its “reactivity”, but the primary structure of the particles and agglomerate will be retained. Thus, the powder manufacturing route will control the basic powder parameters of interest to the ceramist. Generally, the most active powders are produced by the sol-gel route, but due to their fine crystallite and particle size (they are often amorphous), these can be difficult to handle and shape prior to sintering. At the industrial level, micron-sized granules made of nanometric zirconia powders are employed. The powders which have gained greatest commercial acceptance are those which demonstrate sufficient surface area ($6\text{--}15\text{ m}^2\text{ g}^{-1}$) to enable sintering at relatively low temperatures but which have a macro-structure and shape which enables them to be easily handled (granule size $5\text{--}150\text{ }\mu\text{m}$).

Further improvement in the quality of powders is dependent on chemical homogeneity. In practice this is best achieved by the coprecipitation of the constituent oxides from a mixed solution. This is accomplished by titrating an acid solution of the soluble salts into a bath of aqueous ammonia. The mixed oxide is then washed several times and calcined in the temperature range $800\text{--}1000^\circ\text{C}$ to give a sinterable powder which is chemically homogeneous at an atomic level. To improve the handling characteristics, the powder is often granulated and it can be formed by a number of methods (e.g., spray drying).

Applications of Zirconia

Zirconia exhibits a number of desirable properties, notably high elastic modulus and hardness, a high melting point, a low friction coefficient and outstanding corrosion resistance. The microstructure can also be engineered such that very high fracture strength ($>1.5\text{ GPa}$) or high toughness ($>20\text{ MPa m}^{1/2}$) can be generated. Therefore, the material has found application in many markets particularly in wear, cutting, thermal barrier coatings, ionically conductive and biomedical applications (Palmero *et al.*, 2015). The traditional applications of zirconia have been in refractories for the glass industry, as color hosts in the pottery decoration industry, and as a component in many of the electronic ceramics available. In the following sections, two application fields of zirconia are outlined.

Refractories

The very high melting point and outstanding chemical resistance of zirconia make it a prime candidate for refractory applications where extreme conditions are experienced. It is a candidate material for components which are subject to high thermal shock, high

temperature and a corrosive environment such as a sliding gate valve in a continuous casting steel plant or in the nozzles and stoppers of transfer ladles. The superior performance of zirconia containing ceramics is believed to be due to the generation of a distribution of microcracks which can arrest the propagation of larger flaws generated as a consequence of thermal stresses. In this way the refractory although not having particularly high strength, has a superior crack stopping ability and is able to find applications in areas where the integrity of the structure is all important.

Stabilized zirconia has also been fabricated in the form of polycrystalline fibers for use as a thermal insulation blanket and this has a maximum temperature of $> 2100^{\circ}\text{C}$. In this temperature range the main heat transfer medium is radiative and the purpose of the fibers is to retain mechanical integrity, aided by the exceptional chemical stability of zirconia in conjunction with its high melting point.

A similar application in somewhat more arduous conditions occurs when thermal barriers are deposited on gas turbine engines using a plasma spray deposition process. Zirconia, as well as having the required thermal insulation properties, also has a thermal expansion coefficient close to that of the nickel based alloy substrate, thus minimizing breakdown due to stress generation arising from thermal cycling. An intermediate layer of nickel, chromium, aluminum, yttrium bond coat is often utilized to enhance the life of the coating. The most suitable composition is in the range 6–8 mol% Y_2O_3 and as would be expected with rapidly cooled material, the structure is non equilibrium, consisting of a mixture of cubic, non transformable tetragonal, and monoclinic phases. The whole structure is held together with a glassy bonding phase and interspersed with a network of fine randomly oriented microcracks. Use of this technology is now well established in stationary applications such as flame tubes and the technique is being further developed for rotating components.

Zirconia Electrolytes

The cubic phase has the fluorite structure in the stabilized systems based on $(\text{CaO}, \text{MgO}, \text{Y}_2\text{O}_3)\text{-ZrO}_2$ within specific compositional ranges. The void space generated by the presence of an oxygen ion vacancy is considered to be larger than for the corresponding Zr^{4+} vacancy and since the solute cations are of lower vacancy than zirconia, then there are many more of them. This accounts for the high ionic conductivity of the electrolyte to the oxygen species and its use as the membrane in oxygen sensors. These are commercially available for applications such as combustion control, atmosphere control, and monitoring oxygen content in metals.

A difference in oxygen partial pressure ($p = p_1 - p_2$) results in an electromotive force (EMF) being generated across the porous platinum electrodes according to the Nernst equation:

$$E = \frac{RT}{4F} \frac{p_2 \text{O}_2}{p_1 \text{O}_2} t \ln(p \text{O}_2) \quad (2)$$

For ionic conductivity $t = 1$ and the EMF generated is given by:

$$E = \frac{RT}{4F} \ln \frac{p_1 \text{O}_2}{p_2 \text{O}_2} \quad (3)$$

All measurements are based on the premise that thermodynamic equilibrium is present and that the kinetics of the electrode processes are sufficiently rapid that correct voltages are measured. The equation predicts that the EMF is dependent on temperature, which has been confirmed in many laboratories. On the basis of this, several important devices, such as oxygen sensors (Fig. 15) and monitors, oxygen pumps, and combined heat and electricity generating fuel cells are manufactured and are commercially available.

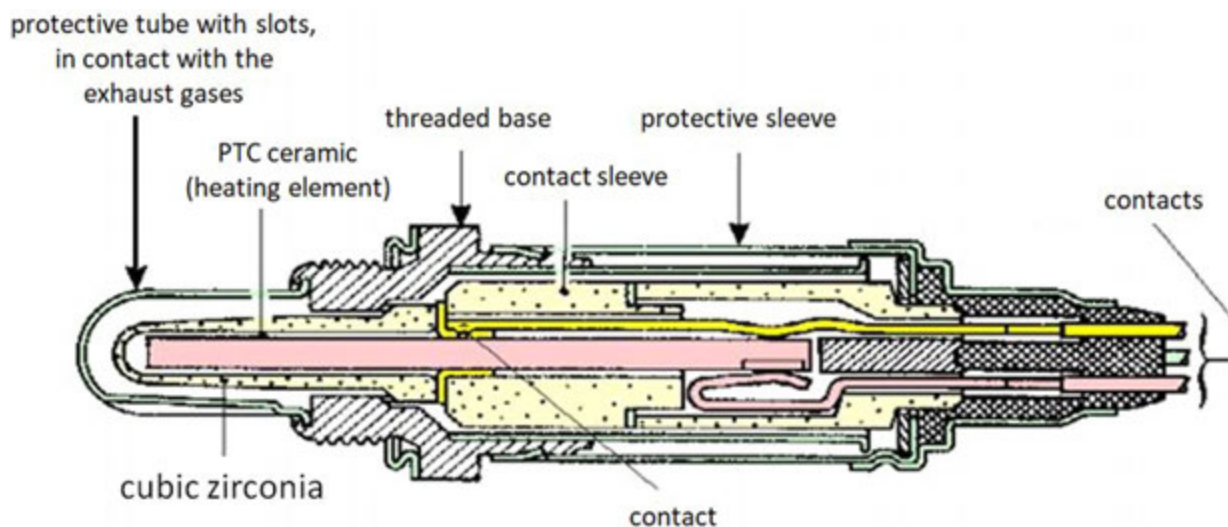


Fig. 15 Schema of a Lambda sensor. Adapted from Bosch.

Summary

Zirconia exhibits three crystallographic phases at atmospheric pressure: monoclinic, tetragonal and cubic. By alloying zirconia with oxides which are cubic at room temperature (i.e., MgO, CaO, Y₂O₃, CeO₂, etc.), it is possible to stabilize the zirconia cubic phase at room temperature. If the amount of cubic addition is too low, metastable tetragonal phase is obtained. The presence of these 2 phases governs the properties of the resulting material. Indeed, on the one hand cubic zirconia is an ionic conductor, being at the origin of electro-ceramics applications (sensor, actuator); on the other hand, the transformation under stress of metastable tetragonal zirconia into monoclinic phase is at the origin of the well known “transformation toughening” phenomenon leading to huge increase of mechanical properties, particularly fracture toughness, for bulk zirconia (PSZ, TZP) and for composites (e.g., ZTA).

Since the 1980s, new zirconia and zirconia based materials have been developed and applied to many more and various fields. The exceptional wear and corrosion resistance explain why seals in valves, chemical and slurry pumps are made of zirconia. As oxygen sensors, doped zirconia is used for fuel-air regulation in automobile engines. Zirconia particles are also used as reinforcing inclusions in ceramic matrices. The best known are alumina-zirconia composites which have superior strength, toughness and wear resistance when compared to conventional alumina and are used as cutting tools and in hip and knee prostheses. More recently, zirconia based nanocomposites have also been developed for biomedical applications (dental implants and other devices) combining several toughening mechanisms like t-m transformation, microcracking but also crack deviation due to the presence of elongated secondary phases (Palmero *et al.*, 2015; Chevalier *et al.*, 2020; Fornabairo *et al.*, 2017).

References

- Audley, J.A., 1917. The use of zirconia as a refractory material. *Nature* 99 (2488), 375–376.
- Badwal, S.P.S., Bannister, M.J., Hannink, R.H.J. (Eds.), 1993. *Science and Technology of Zirconia V*. Lancaster, PA: Technomic.
- Bouvier, P., Djurado, E., Lucazeau, G., Le Bihan, T., 2000. High-pressure structural evolution of undoped tetragonal nanocrystalline zirconia. *Phys. Rev. B* 62 (13), 8731–8737.
- Chevalier, J., 2006. What future for zirconia as a biomaterial? *Biomaterials* 27, 535–543.
- Chevalier, J., Gremillard, L., Virkar, A.V., Clarke, D.R., 2009. The tetragonal-monoclinic transformation in zirconia: Lessons learned and future trends. *J. Am. Ceram. Soc.* 92, 1901–1920.
- Chevalier, J., Liens, A., Reveron, H., *et al.*, 2020. Forty years after the promise of <<ceramic steel?>>: Zirconia-based composites with a metal-like mechanical behavior. *J. Am. Ceram. Soc.* 103, 3, 1482–1513.
- Claussen, N., Ruhle, M., Heuer, A.H. (Eds.), 1984. *Science and technology of zirconia II*. Advances in Ceramics vol. 12, Westerville, OH: American Ceramic Society.
- Fornabairo, M., Reveron, H., Adolfsson, E., *et al.*, 2017. Design and development of dental ceramics: Examples of current innovations and future concepts. In: Palmero, P., De Barra, E., Cambier, F. (Eds.), *Advances in Ceramic Biomaterials: Materials, Devices and Challenges*. Woodhead Publishing Series in Biomaterials, pp. 355–389. (ISBN: 978-0-08-100881-2).
- Grathwohl, G., Liu, T., 1991. Crack resistance and fatigue of transforming ceramics: II, CeO₂ stabilized tetragonal ZrO₂. *J. Am. Ceram. Soc.* 74 (1), 3028–3034.
- Heuer, H., Hobbs, L.W. (Eds.), 1981. *Science and technology of zirconia I*. Advances in Ceramics vol. 3, Westerville, OH: American Ceramic Society.
- Kelly, P.M., Francis Rose, L.R., 2002. The martensitic transformation in ceramics-its role in transformation toughening. *Prog. Mater. Sci.* 47, 463–557.
- Kilo, M., Bocharadt, G., Lesage, B., *et al.*, 2000. Cation transport in yttrine stabilized cubic zirconia: ⁹⁶Zr tracer diffusion in (Zr_xY_{1-x})O_{(2-x)/2} single crystals with 0.15 <x> 0.48. *J. Eur. Ceram. Soc.* 20, 2069–2077.
- Klaproth, M.H., 1958. Ein deutscher Apotheker und Chemiker, sein Weg und seine Leistung, Couverture. Georg Edmund Dann, Akademie-Verlag. 1743–1817.
- Leriche, A., 1986. Influence of Mullite-Zirconia Composites Processing Parameters on Their Microstructure (Ph.D. thesis). Belgium: University of Mons, (in French).
- Palmero, P., Fornabairo, M., Montanaro, L., *et al.*, 2015. Towards long lasting zirconia-based composites for dental implants. Part I: innovative synthesis, microstructural characterization and in vitro stability. *Biomaterials* 50, 38–46.
- Shimozono, T., Ikeda, J., Pezzotti, G., 2006. Evaluation of transformation zone around propagating cracks in zirconia biomaterials using Raman microprobe spectroscopy. *Key Eng. Mater.* 311, 1207–1210.
- Somiya, S., Yamamoto, N., Hanagida, H. (Eds.), 1988. *Science and technology of zirconia III*. Advances in Ceramics vol. 24, Westerville, OH: American Ceramic Society.
- Yoshimura, M., Noma, T., Kawabata, K., Somiya, S., 1987. Role of water on the degradation process of Y-TZP. *J. Mater. Sci. Lett.* 6, 465–467.
- Zhu, H.Y., 1994. CeO_{1.5}-stabilized tetragonal ZrO₂. *J. Mater. Sci.* 29, 4351–4356.

Si₃N₄-Ceramics: An Introduction

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Silicon nitride ceramics are composite materials, consisting of Si₃N₄ grains embedded in a matrix of amorphous or partially devitrified glass. They represent a whole class of materials with various properties depending on the volume fraction and composition of the grain-boundary phase as well as on the size and morphology of the Si₃N₄ grains. The microstructure is usually characterized by elongated grains surrounded by a fine-grained matrix. Since the elongated grains grow during the densification process, the resulting type of microstructure has been labeled as either self-reinforced or *in situ* toughened. Due to the self-reinforced microstructure, silicon nitride ceramics can exhibit an exceptionally high strength and toughness and make them interesting as structural components for numerous applications in engines and turbines. A steadily growing field of application is the use-as-wear parts in ball bearings and pumps, and they are widely used as cutting tools for the machining of cast iron (Chen *et al.*, 1993; Hoffmann and Petzow, 1994a). Relatively high thermal conductivities combined with a high strength for certain types of silicon nitride ceramics can also open new markets for electronic applications (Hirao *et al.*, 2001). More recently silicon nitride ceramics are discussed as potential materials for orthopedic applications, such as prosthetic hip and knee joints (Bal and Rahaman, 2012).

Crystal Structures

Silicon nitride has a density of 3180 kg m⁻³. During heating, it decomposes into liquid silicon and nitrogen gas at 1877 °C. The basic structural units are highly covalent bonded SiN₄ tetrahedra. They can be linked together in different ways to form three different modifications. The most stable phase is denoted as β-Si₃N₄ and crystallizes in the hexagonal space group P6₃. The α-Si₃N₄ also has hexagonal symmetry (P31c), but it is metastable and forms only at lower temperatures. A high-pressure modification with cubic symmetry has been discovered by Zerr *et al.* (1999). There is some evidence that α-Si₃N₄ is indeed a defect structure with a minor replacement of nitrogen atoms by oxygen atoms (Jack, 1976). The two forms cannot be transformed one to the other by a displacive transformation and a reconstructive process is necessary, usually in the presence of a liquid phase. The exact nature of the phase transformation is still not known. Both Si₃N₄ modifications can form solid solutions with Al₂O₃.

Processing and Microstructural Development

In general, silicon nitride ceramics are manufactured by standard powder metallurgical routes. The powder compacts are prepared by cold pressing, slip casting, or injection molding. Two basic types of silicon nitride ceramics are known: sintered silicon nitrides (SSN), and reaction-bonded silicon nitrides (RBSN). RBSN are prepared from silicon powder compacts, which are nitridated at 1100–1450 °C in a nitrogen atmosphere, usually under atmospheric pressure. The temperature–time program of the exothermic reaction depends on the geometry of the components and the particle size of the silicon powder. The final product shows a high porosity and, therefore a low strength, which limits the range of applications (Ziegler *et al.*, 1987). SSN are prepared from silicon nitride powder compacts. Due to the highly covalent bonding of the silicon nitride, densification can only be obtained by liquid-phase sintering using metal oxides such as MgO, Al₂O₃, Y₂O₃, or rare earth as sintering additives.

Most of the sintered silicon nitride ceramics are prepared by using α-rich Si₃N₄ powders which transform during sintering into β-Si₃N₄. The β-modification forms elongated grains if there is no pronounced grain impingement. The grain-growth anisotropy with the fast growth direction parallel to the crystallographic *c*-axis leads to a needle-like grain morphology with aspect ratios of up to 10, similar to whiskers. Grain anisotropy is strongly related to the additives used for densification. High-resolution and analytical transmission electron microscopy clearly indicates that growth sites for the attachment of silicon and nitrogen at the prism planes are blocked by rare earth ions (Shibata *et al.*, 2004; Winkelmann *et al.*, 2005). Thereby, the number of adsorbed rare earth atoms scales with the binding energy and is high for large atoms such as lanthanum (strong adsorption) and low for smaller atoms such as lutetium (minor adsorption) (Painter *et al.*, 2004). The adsorption of rare earth ions at the prism planes do not only influence growth anisotropy, but also has a strong impact on the mechanical properties.

A typical microstructure of an *in situ* toughened sintered silicon nitride ceramic is shown in Figure 1. By using pressure-assisted densification methods with pressures between 10 MPa (gas-pressure sintering) and 100 MPa (hot isostatic pressing), the sintering temperature could be raised above the decomposition temperature of silicon nitride and complete densification could be achieved even with small amounts of additives (2 vol.%) (Hoffmann *et al.*, 1999). Higher sintering temperatures also promote grain growth and an increase of the volume fraction of elongated grains. The second effect of an applied pressure is the reduction of the critical flaw size in the final product, which gives in an improvement in strength and reliability (Satet *et al.*, 2006).

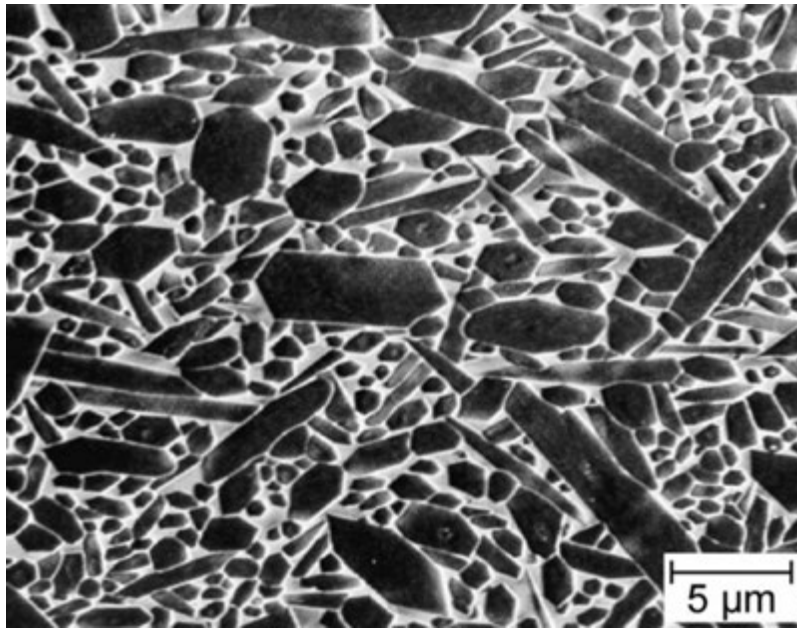


Figure 1 Scanning electron micrograph of a plasma-etched silicon nitride microstructure. The dark particles are silicon nitride grains and the bright phase is the amorphous grain boundary.

An alternative manufacturing method for silicon nitride ceramics is based on a combination of the RBSN and SSN processes. The initial powder compacts consist of silicon powder and sintering additives. The silicon powder is first nitridated and subsequently postdensified at temperatures between 1750 and 1850 °C. The final product is denoted as SRBSN; it has a similar microstructure to the sintered silicon nitride ceramics (SSN) and comparable properties (Lee *et al.*, 2000).

One of the main features of a SSN microstructure is the formation of intergranular grain boundary films of a constant thickness at two-grain junctions between adjacent grains, as shown in Figure 2. The equilibrium film thickness is determined by the additive composition and varies between 1 and 2 nm. The intergranular films are always amorphous, whereas pockets at multigrain junctions could be crystallized (Kleebe *et al.*, 1992). High-temperature resistant silicon nitride materials mostly have crystallized multigrain junctions, while materials for applications in the temperature range below 1000 °C often reveal a completely amorphous grain-boundary phase.

The properties of the intergranular films that are controlled by the adsorption of rare earth elements at the prism planes, have a strong impact on the strength and toughness at room temperature, since *in situ* reinforcement not only requires high aspect ratio grains, but also a tailored interfacial strength to activate toughening mechanisms upon failure. There seems to be a contradiction between the development of high-strength or high-toughness materials and high-temperature resistant ceramics due to the fact that the intergranular film is on one hand responsible for the exceptional properties at lower temperatures, but on the other hand it limits the properties at temperatures above the softening point of the film. Indeed, high-temperature resistant silicon nitrides only reveal an intermediate strength and toughness level.

Mechanical Properties

Toughening in silicon nitride ceramics with a high volume fraction of elongated grains and a tailored interface between the glass matrix and the grains is attributed to crack-wake mechanisms. For structural applications, the fracture conditions will typically be governed by the presence of small flaws or defects present either in the as-sintered component or generated under in-service stresses. Because toughening mechanisms develop and become increasingly effective as a small crack extends and interacts further with the microstructure, the fracture resistance increases with crack size giving rise to so-called R-curve behavior. The rate of increase of the fracture resistance (steepness of the R-curve) with the initial extension of a small crack is quite important for catastrophic failure characteristics as the fracture-origin defects are typically below 30 μm in size for these type of materials (Becher, 1991; Kruzic *et al.*, 2008). More recent results revealed that the toughness of silicon nitrides increases from 2–3 MPa m^{1/2} to about 5–8 MPa m^{1/2} within the first 20 μm of crack extension. This steep increase is attributed to elastic bridges without debonding which requires an intermediate interfacial strength. Toughening mechanisms such as elastic bridging with debonding, frictional bridging or grain pull-out which rely on weaker interfaces do not significantly contribute to fracture resistance (Fünfschilling *et al.*, 2011).

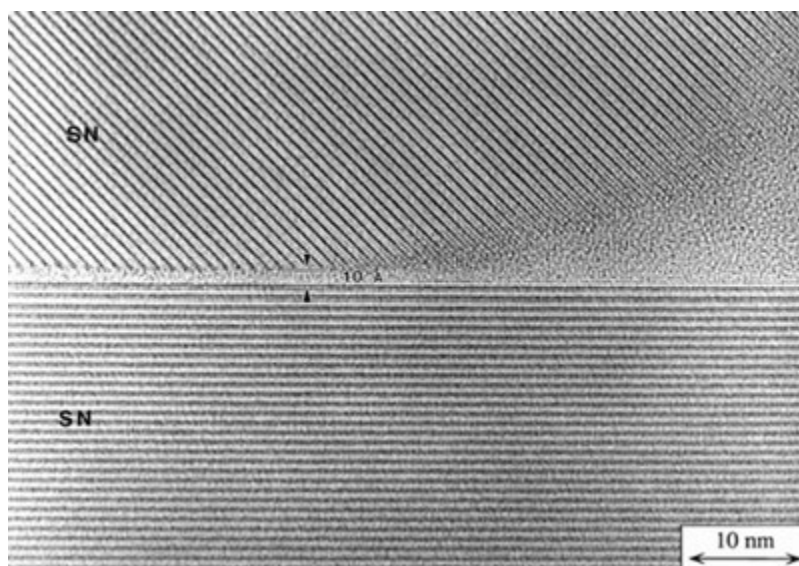


Figure 2 High-resolution transmission electron micrograph of an intergranular grain boundary film of 1 nm thickness between two parallel silicon nitride grains (left side), with a transition to an amorphous multigrain junction on the right side.

Since fine-grained silicon nitrides exhibit a very steep R-curve with a maximum toughness up to $7\text{--}8 \text{ MPa m}^{1/2}$, a high strength up to 1400 MPa with a Weibull modulus between 20 and 30 could be obtained. However, there is significant strength degradation at temperatures above 1000 °C, when the intergranular films start to soften. Materials developed for high-temperature applications have a lower mean bending strength between 600 and 800 MPa, and crystallized multigrain junctions. The best high-temperature-resistant silicon nitrides can be used up to 1400 °C for several hundred hours without damage by oxidation or creep (Lofaj *et al.*, 2002). A further advantage of silicon nitride, in comparison to other structural ceramics, is the relatively high thermal shock resistance due to the low thermal expansion coefficient of $\sim 3 \times 10^{-6} \text{ K}^{-1}$. This means that high-strength silicon nitride ceramics can withstand temperature differences of more than 800 °C.

Conclusions

Silicon nitride ceramics have several excellent properties and clear advantages over other structural materials, but many potential applications are still not realized. A breakthrough in their use is inhibited not only by the high costs of the components for the automotive market, but also by the lack of knowledge of potential users which type of silicon nitride ceramic would fulfill best the demands during service: A silicon nitride developed as cutting tool to machine cast iron may not be the best materials solution as component in lubricated sliding systems or as component in gas turbines. However, the relatively complex interrelationships between the size and morphology of the Si₃N₄ grains, chemical composition and distribution of the grain-boundary phase offers a wide variety to tailor the microstructure and the resulting properties to meet the requirements of engineers for specific applications.

References

- Bal, B.S., Rahaman, M.N., 2012. Orthopedic applications of silicon nitride ceramics. *Acta Biomater.* 8, 2889–2898.
- Becher, P.F., 1991. Microstructural design of toughened ceramics. *J. Am. Ceram. Soc.* 74 (12), 1050–1061.
- Chen, I.W., Becher, P.F., Mitomo, M., Petzow, G., Yen, T.-S. (Eds.), 1993. *Silicon Nitride Ceramics – Scientific and Technological Advances*. MRS Symposium Proceedings, vol. 287. Pittsburgh, PA: Materials Research Society.
- Fünfschilling, S., Fett, T., Hoffmann, M.J., *et al.*, 2011. Mechanisms of toughening in silicon nitrides: The roles of crack bridging and microstructure. *Acta Mater.* 59, 3978–3989.
- Hirao, K., Watari, K., Hayashi, H., Kitayama, M., 2001. High thermal conductivity silicon nitride ceramic. *MRS Bull.* 26, 451–455.
- Hoffmann, M.J., Geyer, A., Oberacker, R., 1999. Potential of the sinter-HIP-technique for the development of high-temperature resistant Si₃N₄-ceramics. *J. Euro. Ceram. Soc.* 19, 2359–2366.
- Hoffmann, M.J., Petzow, G., 1994a. Tailoring of mechanical properties of Si₃N₄ ceramics. In *NATO ASI Series E*. Dordrecht: Kluwer.
- Jack, K.H., 1976. Review of Sialons and related nitrogen ceramics. *J. Mater. Sci.* 11, 1135–1158.
- Kleebe, H.-J., Hoffmann, M.J., Rühle, M., 1992. Influence of secondary phase chemistry on grain-boundary film thickness in silicon nitride. *Z. Metallkd.* 83 (8), 610.
- Kruzic, J.J., Satet, R.L., Hoffmann, M.J., Cannon, R.M., Ritchie, R.O., 2008. The utility of R-curves for understanding fracture toughness-strength relations in bridging ceramics. *J. Am. Ceram. Soc.* 91, 1986–1994.
- Lee, B.-T., Yoo, J.-H., Kim, H.-D., 2000. Microstructural characterization of GPSed-RBSN and GPSed-Si₃N₄ ceramics. *Mater. Trans.* 41, 312–331.
- Lofaj, F., Wiederhorn, S.M., Long, G.G., *et al.*, 2002. Non-cavitation tensile creep in Lu-doped silicon nitride. *J. Euro. Ceram. Soc.* 22, 2479–2487.
- Painter, G.S., Becher, P.F., Shelton, W.A., Satet, R.L., Hoffmann, M.J., 2004. First-principles study of rare-earth effects on grain growth and microstructure in β -Si₃N₄ ceramics. *Phys. Rev. B* 70, 144108.

- Satet, R.L., Hoffmann, M.J., Cannon, R.M., 2006. Experimental evidence of the impact of rare-earth elements on particle growth and mechanical behaviour of silicon nitride. *Mater. Sci. Eng. A* 422, 66–76.
- Shibata, N., Pennycook, S.J., Gosnell, T.R., *et al.*, 2004. Observation of rare-earth segregation in silicon nitride ceramics at subnanometre dimensions. *Nature* 428, 730–733.
- Winkelman, G.B., Dwyer, C., Hudson, T.S., *et al.*, 2005. Three-dimensional organization of rare-earth atoms at grain boundaries in silicon nitride. *Appl. Phys. Lett.* 87, 061911.
- Zerr, A., Miehe, G., Serghiou, G., *et al.*, 1999. Synthesis of cubic silicon nitride. *Nature* 400, 340–342.
- Ziegler, G., Heinrich, J., Wötting, G., 1987. Review relationships between processing, microstructure and properties of dense and reaction-bonded silicon nitride. *J. Mater. Sci.* 22, 3041–3086.

Further Reading

- Hoffmann, M.J., Petzow, G., 1994b. Tailored microstructures of silicon nitride ceramics. *Pure Appl. Chem.* 66 (9), 1807–1817.

Si₃N₄ Ceramics, Structure and Properties

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Silicon nitride (Si₃N₄) based ceramics are polycrystalline, composite materials, which consist of minimum two phases, i.e., silicon nitride grains and grain boundary phases. The individual silicon nitride grains are single crystals of one of the three possible crystallographic modifications of silicon nitride, α -, β -, or γ -Si₃N₄. On the other hand, the grain boundary phases are either amorphous or partially crystalline, and are formed during liquid phase sintering of starting silicon nitride powder. Therefore, the properties of the sintered Si₃N₄-based ceramics are not only pre-determined by the intrinsic properties of Si₃N₄ single crystals, but they strongly depend on the size, orientation and volume fraction of the Si₃N₄ grains, as well as the chemistry, and volume fraction of grain boundary phases. This all means that the properties of Si₃N₄ ceramics can be significantly improved by tailoring the microstructure.

Extensive research over the past five decades has significantly improved the mechanical and thermal properties of silicon nitride ceramics. Si₃N₄ ceramics with superior mechanical properties and high thermal conductivity may be obtained by the use of high-purity sub-micron powders, and careful selection of sintering aids. Due to its excellent combination of properties, such as low bulk density, low thermal expansion coefficient, good mechanical properties at high temperatures, high thermal shock resistance and resistance to chemical attack, and good tribological properties, Si₃N₄ can be used in a variety of structural applications, such as automotive engine parts, heat exchangers, pump seal parts, ball bearings, cutting tools and ceramic armors. In the last two decades, the use of silicon nitride has been broadened towards the electronic and biological, mainly orthopedic applications.

Single crystals of Si₃N₄

Structure

Si₃N₄ occurs in two crystalline phases at ambient pressure: α - and β -Si₃N₄. Both polymorphs have a hexagonal structure, but different stacking sequences: ABCD in α -Si₃N₄, while ABAB in β -Si₃N₄. Both modifications consist of SiN₄ tetrahedra, in which a Si atom lies at the center of a tetrahedron, and four N atoms at each corner. The SiN₄ tetrahedra are joined by sharing corners in such a way that each N is common to three tetrahedra. The idealized structure of β -Si₃N₄ has hexagonal symmetry with the space group either $P6_3$ (noncentrosymmetric) or $P6_3/m$ (centrosymmetric), while the idealized α -Si₃N₄ structure has trigonal symmetry of space group $P3_1C$ (Riley, 2000; Hardie and Jack, 1957).

The unit cell dimensions of the single crystals are listed in Table 1. A summary of the reported values from the individual works can be found in (Wang *et al.*, 1996). For β -Si₃N₄, the standard deviation is 0.005 Å and 0.004 Å for the *a*- and *c*-axis dimensions, while it is 0.014 Å and 0.008 Å for α -Si₃N₄. The greater deviation for α -Si₃N₄ is caused by a partial replacement of nitrogen in the N (1) site with oxygen (oxynitride), while the β -phase is a pure silicon nitride.

The α -phase is metastable (low temperature) modification of Si₃N₄, which always transforms into the β -phase (high temperature modification) at high temperatures. This transformation requires a lattice reconstruction that cannot occur by a displacive transformation, but can occur via solution-precipitation process above 1400°C or by vapor phase process above 1600°C (Zhu and Sakka, 2008). The reverse β to α transformation has never been observed (Riley, 2000). Therefore, β -Si₃N₄ is the major form used in Si₃N₄ ceramics.

A third polymorph of Si₃N₄, cubic phase with spinel structure (γ -Si₃N₄) was discovered in 1999 by synthesis at pressures above 15 GPa and temperatures exceeding 1700°C (Zerr *et al.*, 1999). The cubic Si₃N₄ spinel phase of space group $Fd-3m$ ($z = 8$) contains two different constituting units, i.e., SiN₄ tetrahedra and SiN₆ octahedra in a 1:2 ratio. Thus, the cubic phase may be better described as Si[Si₂N₄] instead of Si₃N₄.

Properties

A summary of the properties of single crystals of silicon nitride is given in Table 2. Similar to the unit-cell dimensions, the density of silicon nitride also slightly varies, depending on the real structure of Si₃N₄, but the list of all available data can be found in (Wang *et al.*, 1996). The density of γ -Si₃N₄ exceeds that of hexagonal structures by around 20%, due to a significantly closer atomic packing in the crystal structure.

The longer stacking sequence in α -Si₃N₄ results in its higher hardness when compared to β -Si₃N₄, however, the hardness of the cubic γ -Si₃N₄ is significantly higher than that of hexagonal phases. The hardness of both α -Si₃N₄ and β -Si₃N₄ is significantly anisotropic (Chakraborty and Mukerji, 1982). Recently, the effect of crystal orientation on nanohardness and indentation modulus of silicon nitride was studied by nanoindentation. The {10 $\bar{1}$ 0 [0001]} slip system was found to have the most significant effect on hardness anisotropy of β -Si₃N₄ (Csanádi *et al.*, 2016).

Table 1 Unit-cell dimensions of three modifications of silicon nitride, α -, β -, and γ -Si₃N₄

Crystallographic modification of Si ₃ N ₄	<i>a</i> -lattice parameter (Å)	<i>c</i> -lattice parameter (Å)
α -Si ₃ N ₄	7.818(3) (Kato <i>et al.</i> , 1975)	5.591(4) (Kato <i>et al.</i> , 1975)
β -Si ₃ N ₄	7.595(1) (Grun, 1979)	2.9023(6) (Grun, 1979)
γ -Si ₃ N ₄	7.7381(2) (Zerr <i>et al.</i> , 1999)	–

Table 2 Properties of all three known crystal modifications of Si₃N₄, α -, β - and γ -phase

Property	α -Si ₃ N ₄	β -Si ₃ N ₄	γ -Si ₃ N ₄
Density (calculated) [g cm ⁻³]	3.150–3.178 (Wang <i>et al.</i> , 1996)	3.213–3.214 (Wang <i>et al.</i> , 1996)	3.93 (Zerr <i>et al.</i> , 1999)
Hardness; prismatic plane (direction $\parallel$ to the <i>c</i> -axis) [GPa]	51.76 (HV0.1)–33.06 (HV0.5) (Chakraborty and Mukerji 1982)	36.96 (HV0.1)–21.36 (HV0.5) (Chakraborty and Mukerji 1982)	30–43 (HV0.5) (Zerr <i>et al.</i> , 2002)
Hardness; basal plane (direction $\perp$ to the <i>c</i> -axis) [GPa]	38.59 (HV0.1)–25.55 (HV0.5) (Chakraborty and Mukerji 1982)	20.43 (HV0.1)–14.45 (HV0.5) (Chakraborty and Mukerji 1982)	
Tensile strength (calculated)	up to $\sim$ 51 (Ogata <i>et al.</i> , 2004)	up to $\sim$ 57 (Ogata <i>et al.</i> , 2004)	$\sim$ 45 (Kocer <i>et al.</i> , 2003)
Bulk modulus (calculated) [GPa]	257–263 (Ogata <i>et al.</i> , 2004)	225–292 (Ogata <i>et al.</i> , 2004)	290 (Zerr <i>et al.</i> , 2002)
Shear modulus (calculated) [GPa]	132 (Ogata <i>et al.</i> , 2004)	112–116 (Ogata <i>et al.</i> , 2004)	258–261 (Zerr <i>et al.</i> , 2002)
Thermal conductivity (calculated) (direction $\parallel$ to the <i>c</i> -axis) [W m ⁻¹ K ⁻¹]	170 (Hirosaki <i>et al.</i> , 2002)	225 (Hirosaki <i>et al.</i> , 2002)	80 (Morelli and Heremans 2002)
Thermal conductivity (calculated) (direction $\perp$ to the <i>c</i> -axis) [K ⁻¹]	105 (Hirosaki <i>et al.</i> , 2002)	450 (Hirosaki <i>et al.</i> , 2002)	
Coefficient of thermal expansion (direction $\parallel$ to the <i>c</i> -axis) [K ⁻¹]	3.61×10^{-6} (Henderson and Taylor 1975)	3.72×10^{-6} (Henderson and Taylor 1975)	3.89×10^{-6} (Jiang <i>et al.</i> , 2002)
Coefficient of thermal expansion (direction $\perp$ to the <i>c</i> -axis) [K ⁻¹]	3.70×10^{-6} (Henderson and Taylor 1975)	3.23×10^{-6} (Henderson and Taylor 1975)	

Contrary to the hardness, fracture toughness is relatively isotropic, but both significantly decrease with increasing temperature (Reimanis *et al.*, 1996). The ab initio calculations also showed that the tensile strength of an β -Si₃N₄ crystal is the highest among all of three modifications of Si₃N₄ (Ogata *et al.*, 2004).

The coefficient of thermal expansion as well as the thermal conductivity of both α - and β -phases are also anisotropic, but the anisotropy is more significant in the case of β -phase. The coefficient of thermal expansion of the γ -phase is the highest among of all three configurations. On the other hand, the intrinsic thermal conductivity of β -Si₃N₄ is clearly the highest, while the other two structures have thermal conductivity at a very similar level.

Preparation

Two major crystal structure of Si₃N₄, hexagonal α - and β -phases, attracted main attention of the researchers to develop and investigate single crystals. The single crystals were produced either by the CVD process (mainly α -Si₃N₄) (Kijima *et al.*, 1974) or by the growth from Si melts (mainly β -Si₃N₄) (Inomata and Yamane, 1974). When the silicon melt contains a small amount of Fe ($\sim$ 1 wt%), α -Si₃N₄ single crystals could be grown along with β -Si₃N₄ single crystals (Chakraborty and Mukerji, 1980). However, the size of the single crystals was usually limited to the dimensions of several hundred μ m up to several mm (Reimanis *et al.*, 1996).

With the beginning of the era of one dimensional nanostructured materials, the research on the preparation of Si₃N₄ single crystals shifted towards the development of Si₃N₄ single crystal nanobelts (Yang *et al.*, 2005a), nanowires (Yang *et al.*, 2005b) or whiskers (Yang *et al.*, 2004). The materials are usually only a few nm thick, but their length can be from several hundred μ m up to several tens of mm. A variety of synthesis techniques have been used to produce these materials, including chemical vapor deposition, direct nitridation, carbothermal reduction, and laser and plasma synthesis. Such 1D materials are promising candidates for matrix enhancement of composites in aerospace applications, metallurgy industry, and aviation and military hardware. They are also wide-band gap semiconductors and can be introduced to nano-devices to tailor electronic and optical properties (Yang *et al.*, 2004). This is currently the most promising utilization of silicon nitride single crystals, as the manufacturing of large-scale single crystals is very difficult. On the other hand, the excellent properties of Si₃N₄ single crystals are exploited in its polycrystalline form (sintered Si₃N₄), in which the individual grains of Si₃N₄ (α - or β -phase single crystals) are embedded in a matrix of amorphous or partially crystalline phase.

Polycrystalline Si₃N₄

Silicon nitride is mostly produced from α -Si₃N₄ powder, which is transformed to β solid solution during liquid phase sintering via the solution-precipitation process. Due to the low self-diffusion coefficient of Si₃N₄ and the highly covalent Si–N bonds, densification requires the use of sintering additives. The additives form a liquid phase during sintering at high temperatures by their reactions with SiO₂ or oxynitrides, which are always present on the surface of Si₃N₄ powders. The presence of a liquid phase significantly facilitates the densification of silicon nitride. Upon cooling, the liquid solidifies to form amorphous or partially crystallized oxynitride glassy phases at the grain boundaries of Si₃N₄ grains (single crystals) (Hampshire and Pomeroy, 2012).

Preparation of silicon nitride has mainly been conducted using so-called conventional sintering techniques, such as hot pressing (HP), gas pressure sintering (GPS), hot isostatic pressing (HIP), and pressureless sintering (PS). More recently, unconventional sintering techniques, such as spark plasma sintering (SPS) and microwave sintering (MS) have attracted attention due to their advantages over conventional sintering techniques, such as reduced sintering time and temperature, possibility to produce a unique microstructure that would not be possible to achieve using conventional routes. The SPS technique can enhance the sinterability of Si₃N₄ with controlled grain growth and phase transformation at reduced temperatures (Nishimura *et al.*, 1995; Belmonte *et al.*, 2010). The activation energy for phase transformation using the SPS process is much higher than for the conventional process, such as HP (Suganuma *et al.*, 2003). A homogenous Si₃N₄ nanomaterial with an average grain size as low as 70 nm can be prepared by SPS (Xu *et al.*, 2005). Similarly, the significantly enhanced densification and phase transformation were observed when microwave heating was applied during processing of Si₃N₄ (Zhang *et al.*, 1992). The α - β transformation occurs at lower temperature ($\sim 1500^\circ\text{C}$) than in the case of conventional techniques ($\sim 1750^\circ\text{C}$), due to lower viscosity of grain-boundary glassy phase caused by selective localized heating of microwaves (Chockalingam and Earl, 2010).

Regardless of the sintering technique used, densification of sintered Si₃N₄ always consists of the same steps, including formation of liquid phase, solution-precipitation process, grain growth, solidification and partial crystallization of the grain boundary phase. Therefore, common characteristics of microstructure development of Si₃N₄ and their relations to the final properties will be discussed in the next sections.

Development of Si₃N₄ Microstructure

The evolution of microstructure of Si₃N₄ is mainly controlled by the starting Si₃N₄ powder, type and amount of sintering additives, and sintering parameters. This all significantly affects the α - β transformation during sintering, and the final microstructure of Si₃N₄. The β -phase grows on the nuclei, which are the result of heterogeneous nucleation, as homogenous nucleation does not play an important role (Šajgalík and Galusek, 1993).

The starting powder usually contains different amounts of α and β phases, but mainly α -rich powders are used. The number of β -Si₃N₄ (pre-existing β -grains) determines the number of elongated β -Si₃N₄ in the final microstructure. A small amount results in a large interparticle distance between β -grains, thus the grains are able to grow during sintering without significant impingement by other grains (Šajgalík and Galusek, 1993). During sintering, the metastable α -phase and the subcritical β -phase ($< 0.5\ \mu\text{m}$) dissolve in the liquid due to their higher chemical potential, and then re-precipitate on the larger pre-existing β -grains (Petzow and Herrmann, 2002). The largest β -grains dominate the grain growth process and establish the fraction of large, elongated grains in the final microstructure (Becher *et al.*, 1998).

On the other hand, if the starting mixture contains a large amount of β -phase ($> 30\ \text{vol}\%$), the driving force for the solution-precipitation process is much smaller (Petzow and Herrmann, 2002). In this case, the final microstructure will consist of fine, equiaxed grains. Similarly, the equiaxed β -Si₃N₄ microstructure can be produced when the starting powder consists only of β -phase (Becher, 1991).

Fig. 1 shows an example of two microstructures of Si₃N₄, which were obtained after SPS sintering of the same starting powder mixture of Si₃N₄:Y₂O₃:Al₂O₃ (93:5:2 wt%) at different temperatures (1600°C versus 1750°C). The amount of α -Si₃N₄ in the initial

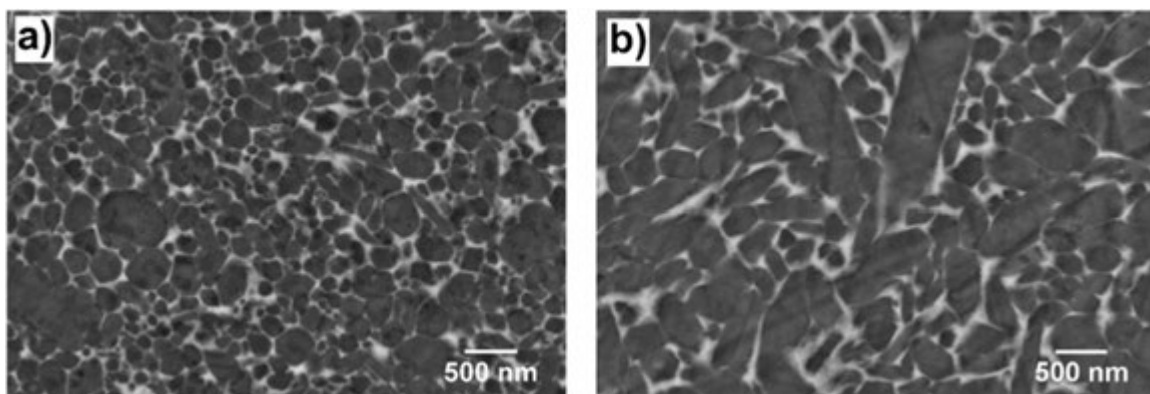


Fig. 1 Typical equiaxed microstructure of silicon nitride with a high content (82%) of the α -phase (a), and fully transformed microstructure (100% β -phase) consisting of the elongated grains (b).

Si₃N₄ powder was > 95%. The sintering at a lower temperature resulted in a microstructure with more equiaxed grains (Fig. 1(a)), while the increase in the temperature led to a significant increase of the number of large elongated β -Si₃N₄ grains (Fig. 1(b)). Indeed, the Rietveld analysis of the XRD data confirmed that only a small amount of the β -phase was present in the first case (18% β -Si₃N₄), while the complete transformation (100% β -Si₃N₄) occurred during sintering at 1750°C.

It is generally accepted that prismatic planes of the hexagonal grains of Si₃N₄ are more stable when compared to basal planes. The hexagonal crystals grow preferentially along the c-axis direction to form elongated, needle-like grain morphology. This is related to the Si₃N₄ crystal structure, in which it is energetically more favorable for a surface nucleus to attach to a basal plane than to a prismatic plane. The growth mechanism is diffusion controlled for the basal plane, while the growth rate is determined by the formation of surface nuclei on the prismatic planes. Therefore, the growth rate of the basal plane is much faster (along the c-axis) than that of prismatic planes (Petzow and Herrmann, 2002; Satet *et al.*, 2006). One of the main factors of elongated grain formation is the viscosity of the liquid phase formed during sintering (Becher *et al.*, 2008). The liquid with higher viscosity hinders both the heterogeneous nucleation and material transport, which promotes the preferential growth of the pre-existing β -grains and formation of β -Si₃N₄ grains with a higher aspect ratio (Bressiani *et al.*, 1999).

Grain boundary phases of Si₃N₄

Upon cooling from sintering temperature, a liquid solidifies in the form of an amorphous or a partially crystalline phase at the grain boundaries of Si₃N₄. Therefore, the type and amount of sintering additives not only improve densification, but also pre-determine the chemistry and quantity of the resulting grain boundary (GB) phases.

Very often, post-sintering heat treatment is necessary for devitrification of the GB phase, as an amorphous phase is not in an equilibrium condition according to the phase diagram. However, HRTEM analysis revealed that the devitrification of the glassy phase is not completed even after heat treatment (Liu and Nemat-Nasser, 1998). A residual glass remains at the tip of each triple junction, along with the amorphous film between two Si₃N₄ grains, or between Si₃N₄ and a crystalline secondary phase. The thickness of the amorphous phase (~ 0.5–3 nm) depends on the temperature, additive composition and impurities of the starting powder (Petzow and Herrmann, 2002), but does not depend on the amount of the sintering additives used (Hampshire and Pomeroy, 2012). The description of the manner of crystallization of the GB phases is described in (Liu and Nemat-Nasser, 1998).

Effect of rare-earth oxides on the microstructure development of Si₃N₄

The type of sintering additives strongly affects the viscosity of a liquid phase by altering the glass composition, which determines the diffusion rates of silicon and nitrogen, and thereby the grain growth rate. Initially, silicon nitride was sintered using additives, such as MgO, Al₂O₃, Y₂O₃ or their mixtures. Later, rare earth (RE) oxides (RE₂O₃) attracted attention, mainly due to their refractory nature (enhancing the high temperature properties), but also due to their significant effect on the microstructure development, which can be tailored by the use of different RE-based oxides. The effect of RE oxides on the microstructural development of Si₃N₄ is related to the different viscosities of RE-containing glassy phases at sintering temperatures, which significantly increase with a decreasing ionic radius of RE³⁺ (i.e., from La to Lu) (Becher and Ferber, 2004; Hampshire and Pomeroy, 2004).

The RE₂O₃ additives control the rates of $\alpha \rightarrow \beta$ phase transformation, the grain growth anisotropy, and the aspect ratio of β -Si₃N₄ grains (Satet and Hoffman, 2005). The activation energy for $\alpha \rightarrow \beta$ transformation is higher when a larger ionic radius RE is considered, which results in the slower phase transformation at the same annealing temperature when compared to the RE with a smaller ionic radius (Kitayama *et al.*, 2006). In addition, the temperatures of initiation and completion of the phase transformation decrease with a decreasing ionic radius of RE (Becher *et al.*, 2010).

The role of RE₂O₃ additives during liquid phase sintering of Si₃N₄ is changed when some other oxides are added to the composition. The effect of La₂O₃ versus Lu₂O₃ in a system with low viscosity (in combination with MgO, or Al₂O₃) is opposite of that observed for a high viscosity system (in combination with SiO₂). The detailed explanation can be found in Becher *et al.* (2010). This was clearly experimentally confirmed as for the Si₃N₄ system with the RE₂O₃ and MgO additives (low viscosity system) the aspect ratio of β -Si₃N₄ grains increased with increasing RE³⁺ in the RE₂O₃ additives (Satet and Hoffman, 2005). On the other hand, the aspect ratio of β -Si₃N₄ grains increased with decreasing RE³⁺ for the Si₃N₄ composition with the RE₂O₃ and SiO₂ as the only additives (Lojanová *et al.*, 2010; Tatarko *et al.*, 2010).

Self-reinforced microstructure of Si₃N₄

Self-reinforced β -Si₃N₄ microstructure is an analog to a whisker-reinforced microstructure, in which the elongated rod-like grains (which are similar to whiskers) toughen the materials (Becher *et al.*, 1998). Such reinforcement is possible due to the fact that the growth rate of β -grains along the c-axis significantly exceeds the growth rate of the grains in the direction perpendicular to the c-axis direction.

The formation of elongated β -Si₃N₄ grains with a high aspect ratio can be controlled by the addition of appropriate sintering additives as they would alter the viscosity of the liquid during sintering, thereby modifying the diffusion rates of Si and N. The size and the number of elongated grains in the final microstructure can also be affected by the α/β ratio of the starting powder (the fraction of β -Si₃N₄ in the powder) (Becher *et al.*, 1998; Šajgalík *et al.*, 1995). A broad size distribution leads to abnormal grain growth. On the contrary, when a narrow particle size distribution of β -grains is used, a material with rather homogenous microstructure will be formed. The use of a rather higher temperature (in the range of 1800–2000°C) will help to develop a self-reinforced microstructure, due to the fact that a mass transport at the grain boundaries will be enhanced. The effect of the presence of the β -phase in the starting powder can even be enhanced by the use of elongated β -seeds in the starting powder. The larger the

seeding particles, a significant distinct bimodal size distribution microstructure can be obtained (Becher *et al.*, 1998). This type of elongated β -morphology is typical of dense Si₃N₄ prepared from α -Si₃N₄ rich starting powders and is very important for the improvement of mechanical properties.

Textured microstructure of Si₃N₄

Superior properties of silicon nitride can be achieved by the formation of a textured microstructure, in which the elongated β -Si₃N₄ grains are oriented. The textured Si₃N₄ can be manufactured by various techniques, such as hot pressing, hot forging, sinter forging, templated grain growth, and strong magnetic field alignment. Details, including theoretical models and review of the research works, can be found in Zhu and Sakka (2008). In the case of high temperature processes (hot pressing, hot forging, or sinter forging), a textured microstructure is formed due to the rotation of elongated β -Si₃N₄ grains induced by a uniaxial stress applied during sintering or forging, followed by their preferential growth along the c-axis direction. On the other hand, the templated grain growth technique relies on the abnormal epitaxial growth of β -Si₃N₄ grains on the initially oriented β -Si₃N₄ seeds (or template) by the consumption of the fine-grained matrix during sintering.

Highly textured silicon nitride can be prepared by slip casting (Zhu and Sakka, 2008) or gel casting (Yang *et al.*, 2014) in a strong magnetic field of $> 6T$. When a strong magnetic field is applied, the Si₃N₄ crystals will become oriented during the slurry forming process. This technique relies on the fact that when diamagnetic or paramagnetic particles with anisotropic magnetic susceptibility are suspended in a liquid medium and placed in a magnetic field, they will rotate to an angle to minimize the system energy. Due to the higher magnetic susceptibility of silicon nitride crystals in the a-, b- directions than that of the c-axis direction ($\chi_{a,b} > \chi_c$), the Si₃N₄ crystals will be aligned with their a-, b-axes parallel to the magnetic field. In order to align the c-axis of Si₃N₄, rotating magnetic field must be used during slip casting. The β -Si₃N₄ crystals exhibit stronger texturing ability than the α -Si₃N₄ due to their higher anisotropic magnetic susceptibility when compared to the α -phase (Zhu and Sakka, 2008). The use of β -Si₃N₄ in the starting powder may enhance the degree of orientation and form a microstructure with more significant bimodal grain size distribution.

Properties of Polycrystalline Si₃N₄

Room temperature mechanical properties

Room temperature mechanical properties of Si₃N₄ mainly depend on the microstructure of the material (α/β ratio, grain size, amount and chemistry of GB phases), which can be controlled by the amount and/or type of sintering additives, as well as by the densification and sintering conditions used. As an example, Table 3 demonstrates how significantly the mechanical properties of Si₃N₄ can vary when the same starting mixture is sintered at two different temperatures, resulting in a different α/β ratio in the final microstructures. The starting mixture of Si₃N₄:Y₂O₃:Al₂O₃ = 93:5:2 wt% was sintered by SPS at different temperatures (1600°C and 1750°C), while using the same mechanical pressure of 50 MPa and the dwell time of 7 min. In both cases, the GB phases were amorphous, so the effect of different chemistry of the GB phase can be neglected. On the other hand, the α/β ratio significantly changed, as the sintering at 1600°C led to a limited α/β transformation (only 18% of β -Si₃N₄), while the α -phase fully transformed into the β -phase when sintered at 1750°C (100% of β -Si₃N₄). The representative microstructures of both materials are shown in Fig. 1. In agreement with the α -phase having the higher hardness, the hardness of the Si₃N₄ with majority of α -grains is higher by ~ 3 GPa than that of Si₃N₄ with 100% β -Si₃N₄ grains. On the other hand, the positive effect of the presence of elongated β -Si₃N₄ is clearly observed for the strength and fracture toughness of Si₃N₄ (Table 3).

Hardness

Hardness of silicon nitride mainly depends on the phase transformation of Si₃N₄ because of the significant difference between the hardness of α - and β -phases (see Section “Properties”). Generally, the material with a higher amount of α -Si₃N₄ exhibits a higher hardness when compared to the material with majority of β -Si₃N₄. Hardness of β -Si₃N₄ increases with a decreasing amount of grain boundary phase as well as with a decreasing grain diameter. Usually, the hardness of β -Si₃N₄ is at the level of ~ 12 GPa for a material with coarse grained microstructure and/or a high additive content, while it reaches a value of ~ 20 GPa for the material with a fine grained microstructure and/or low additive content (Petzow and Herrmann, 2002).

Table 3 Mechanical properties of the same material composition (Si₃N₄:Y₂O₃:Al₂O₃) sintered at different temperatures (1600°C and 1750°C) by SPS, resulting in a different α/β ratio

The amount of β -Si ₃ N ₄ phase	18% β -Si ₃ N ₄ grains	100% β -Si ₃ N ₄ grains
Grain size [nm]	165 $\pm$ 77	235 $\pm$ 131
Aspect ratio of grains	1.7 $\pm$ 0.6	2.0 $\pm$ 0.9
Young's modulus [GPa]	317 $\pm$ 1	290 $\pm$ 1
HV5 [GPa]	18.1 $\pm$ 0.7	15.0 $\pm$ 0.3
Flexural strength [MPa]	424 $\pm$ 97	736 $\pm$ 36
Fracture toughness (Chevron notch) [MPa m ^{1/2}]	3.1 $\pm$ 0.1	5.5 $\pm$ 0.3

The hardness of Si₃N₄ can also be affected by the chemistry of GB phases. It was shown that the hardness of Si₃N₄ (HV1) increases with a decreasing cation radius of RE³⁺ in RE₂O₃ (e.g., when La is replaced with Lu) from ~ 17 GPa to ~ 15.4 GPa (Lojanová *et al.*, 2010). This is due to the fact that the presence of a RE element with the smaller cation size increases cationic field strength of the glassy phase, which in turn increases the hardness of the whole Si₃N₄ body.

Strength

Flexural strength of fully dense Si₃N₄ varies in the range of 800–1400 MPa, depending on the presence of processing defects, such as pores, inclusions, agglomerates, etc. (Petzow and Herrmann, 2002). Si₃N₄ with a fine, submicrometer grained microstructure reaches the highest fracture strength of more than 1000 MPa. Generally, the strength decreases as the grain size increases. However, the increase of the strength with increasing grain size was observed for the self-reinforced microstructure, in which the flexural strength can be as high as ~ 1100 MPa (Becher *et al.*, 1998). When the large, elongated grains do not come into contact with each other and are dispersed uniformly in the fine equiaxial grained matrix, the strength of Si₃N₄ is not reduced. The large grains or a cluster of large grains act as fracture flaws, which significantly deteriorate the strength of Si₃N₄ (Hirotsaki *et al.*, 1993).

By developing the textured Si₃N₄, the strength can be maximized in one direction, usually in the direction perpendicular to the grain alignment (to the c-axis of Si₃N₄). The superior strength of Si₃N₄ was observed when the textured microstructure was prepared using seeding and tape casting (1100 MPa) (Hirao *et al.*, 1995), seeding and extrusion techniques (1400 MPa) (Teshima *et al.*, 1999), or sinter-forging method (2100 MPa) (Kondo *et al.*, 1999).

The strength of sintered Si₃N₄ also depends on the chemistry of GB phases. The bending strength of Si₃N₄ increases with a decreasing ionic radius of RE³⁺ in the GB phase. This was observed for both the fully amorphous RE-based GB phase (from ~ 880 MPa for La-containing GB phase to 1050 MPa for Lu-containing GB phase) (Satet and Hoffman, 2005) and crystalline RE₂Si₂O₇ type of GB phases (from ~ 520 MPa for La-based GB phase to ~ 700 MPa for Lu-based GB phase) (Tatarko *et al.*, 2010). The decrease in the strength caused by the use of a RE with larger RE³⁺ can be explained by the decrease in grain-GB interfacial strength with an increasing size of RE³⁺. Weak interfaces could induce a growth of natural flaws to a critical size at lower loads, resulting in a lower bulk strength (Satet and Hoffman, 2005).

Fracture toughness

A relatively low fracture toughness of sintered Si₃N₄ was initially a major barrier to the wide structural application of Si₃N₄. Therefore, the improvement of fracture toughness and the development of self-reinforced microstructures have been the two most investigated areas in the silicon nitride research field. Typical monolithic silicon nitride ceramics fabricated using α-Si₃N₄ raw powder exhibits fracture toughness in the range of 3–6 MPa m^{1/2}. The fracture toughness can be increased to 8–14 MPa m^{1/2} for self-reinforced Si₃N₄.

Fracture toughness of Si₃N₄ depends mainly on the shape and size of grains and the composition of the grain boundary phases. The dominant toughening mechanisms are controlled by the diameter and volume fraction of the large elongated grains (Tatarko *et al.*, 2010; Šajgalík *et al.*, 1995). Pull-out and elastic bridging were most frequently observed in the fine-grained microstructure with tailored, needle-like β-Si₃N₄ grains with diameters of < 1 μm. On the other hand, crack deflection was the main toughening mechanism observed in Si₃N₄ with coarse-grained microstructures having grains with diameters of > 1 μm. Silicon nitride with a microstructure having the highest volume fraction of grains with aspect ratio > 4 shows the highest fracture toughness of > 8 MPa m^{1/2} (Šajgalík *et al.*, 1995).

The presence of large elongated β-Si₃N₄ grains in the microstructure is essential for the improvement of fracture toughness, but still does not guarantee the occurrence of the toughening mechanisms. One of the critical issues in microstructural design of Si₃N₄ is to control the debonding at the interface between the β-Si₃N₄ and the intergranular glassy phase to enable crack deflection and crack bridging (Becher *et al.*, 1998). The interfacial debonding strongly depends on the chemistry of GB phases, which is directly determined by the composition of the sintering additives used. It was clearly demonstrated that the fracture toughness of silicon nitride increases with increasing Y/Al and O/N ratios in the additives, due to the enhanced interfacial debonding (Sun *et al.*, 1998). Similarly, RE elements also affect the interfacial bonding strength of silicon nitride. Their role is different when some other additives are simultaneously used, as described in the case of microstructure development (Section “Effect of Rare-Earth Oxides on the Microstructure Development of Si₃N₄”). For the low viscosity system (RE₂O₃ + MgO or Al₂O₃) and/or amorphous GB phases, the fracture toughness of silicon nitride increases with an increasing size of RE³⁺ (when Lu is replaced with La) from 5.5 MPa m^{1/2} to 7.2 MPa m^{1/2} (Satet and Hoffman, 2005). On the other hand, for the high viscosity system (RE₂O₃ + SiO₂) and crystalline GB phases, the fracture toughness of silicon nitride shows the opposite behavior, as it increases with a decreasing size of RE³⁺ (when La is replaced with Lu) from ~ 4.7 MPa m^{1/2} to ~ 7 MPa m^{1/2} (Tatarko *et al.*, 2010).

As with the strength of silicon nitride, the fracture toughness can also be significantly improved by the texturing of the microstructure, which exceeds the level of 10 MPa m^{1/2} and can reach up to ~ 14 MPa m^{1/2} for the textured Si₃N₄ developed using seeding and tape casting or seeding and extrusion techniques, respectively (Hirao *et al.*, 1995; Teshima *et al.*, 1999).

High temperature mechanical properties

At temperatures above 1000°C, the softening of the GB phases occurs, which significantly affects the high temperature properties of silicon nitride. Therefore, GB chemistry, effective viscosity and volume fraction of the GB phases will control the high temperature behavior of Si₃N₄, such as oxidation and creep resistance.

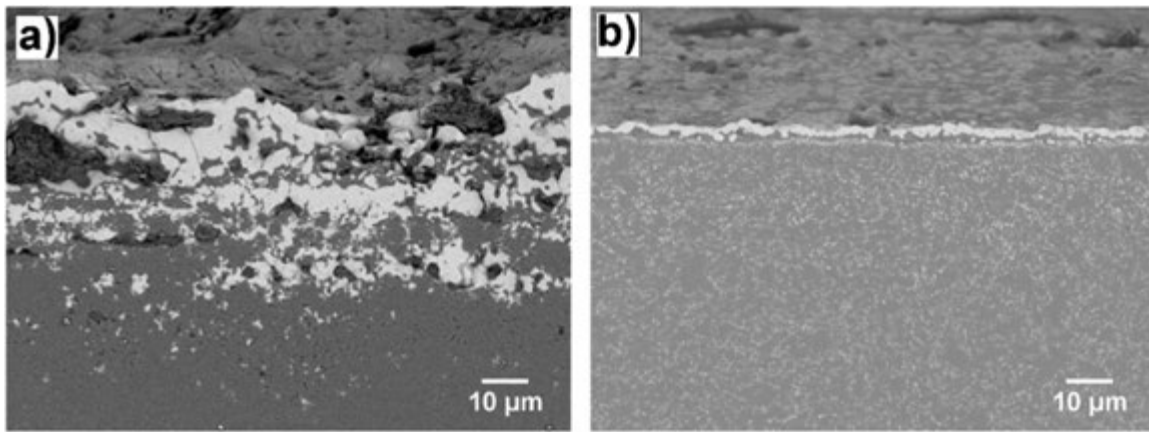


Fig. 2 Back-scattered SEM images of cross sections of Si₃N₄ with La₂O₃ (a) or with Lu₂O₃ (b) after the oxidation test at 1400°C for ~ 200 h.

Oxidation resistance

When pure silicon nitride is exposed at high temperatures (above 1000°C) in oxidizing atmosphere, a layer of pure silica (SiO₂) is formed on its surface. The diffusion of oxygen through the SiO₂ layer is the rate-controlling step, leading to a parabolic oxidation kinetic (Klemm, 2010). When Si₃N₄ contains sintering additives, some additional crystalline and/or amorphous silicates are formed in the SiO₂ layer. These phases weaken the pure SiO₂ layer, which results in the higher oxygen diffusion through the layer into the ceramic body when compared to the materials without additives (Klemm, 2010). In the case of Si₃N₄ with additives, both the inward diffusion of oxygen and the outward diffusion of cations of additives and nitrogen result in the formation of a compositional gradient in the material beneath the oxide layer (Cinibulk *et al.*, 1992). To relax this chemical gradient, the diffusion of cations of additives to the surface occurs, which is followed up by the evolution of a higher amount of gaseous reaction products, causing the formation of bubbles on the surface layer (Klemm, 2010).

In order to improve the oxidation resistance of multiphase silicon nitride, the following requirements are necessary (Andrews and Riley, 1989):

- (1) Minimum quantity of intergranular phases.
- (2) Presence of additives with low mobility of their cations.
- (3) Presence of crystalline GB phases.
- (4) During oxidation, a high eutectic temperature composition in the system: oxidation product/SiO₂ must be formed.

The oxidation resistance of Si₃N₄ can be associated well with the refractoriness of the GB phases, i.e., it is inversely related to the eutectic temperature in the system. The refractory nature of GB phases mainly determines the diffusion rate of cations and anions along the residual amorphous GB phase. Due to the greater cation field strength, the more refractory GB phases are expected for Si₃N₄ sintered with RE oxides having a smaller cation size of RE³⁺ (Cinibulk *et al.*, 1992; Tatarko *et al.*, 2013). Fig. 2 shows back-scattered SEM images of cross sections of the oxidation layer for Si₃N₄ with La₂O₃ (Fig. 2(a)) and Si₃N₄ with Lu₂O₃ (Fig. 2(b)). A significantly greater amount of La³⁺ diffused into the surface layer when compared to the Lu³⁺ cations. This confirms that the highly refractory Lu₂O₃-SiO₂ composition significantly hinders the diffusion of cations towards the surface layer, thereby improving the oxidation resistance of Si₃N₄. On the other hand, the greater mobility of additive cations leads to the formation of a zone depleted by RE cations, in which the grain boundaries between the Si₃N₄ grains are completely free of the former GB phase (La³⁺ cations).

Creep resistance

Creep deformation mostly takes place at the grain boundaries, therefore, the viscosity and refractory nature of GB phases again play an important role in improving the creep resistance of Si₃N₄.

The creep deformation in Si₃N₄ can occur either via so called “cavitation” or “non-cavitation” (viscous flow or solution-precipitation process) creep. In most of the sintered Si₃N₄ materials, particularly in high-viscosity systems, cavity formation is not observed after creep deformation. This suggests that only volume-conservative mechanisms, such as viscous flow, grain boundary sliding and solution-precipitation processes are occurring. The grain boundary sliding is an integral part of the viscous flow. The viscous flow can occur due to the decreased viscosity of the GB phase at high temperatures. Under the effect of an external stress at high temperatures, the grains approach each other (grain boundary sliding), so the GB phase is squeezed out or flows away from the area between the grains. Viscous flow creep cannot be the main controlling mechanism, but it is rather considered as a transient process responsible for the primary creep regime, up to about 1% strain (Meléndez-Martínez and Domínguez-Rodríguez, 2004). Apparently, the only possible mechanism to rationalize the deformation process of silicon nitride with highly refractory GB phase is the solution-precipitation process (Lofaj and Wiederhorn, 2009).

Since in most silicon nitride systems the glass melts at lower temperatures than those at which diffusion becomes significant, the Si₃N₄ crystals dissolve in the liquid phase at the grain boundaries subjected to compression. The dissolved matter then diffuses along the liquid phase and finally precipitates at the grain boundaries subjected to tension (Lofaj and Wiederhorn, 2009; Meléndez-Martínez and Domínguez-Rodríguez, 2004). Either the dissolution of the crystals or the diffusion of matter is the rate-controlling step, whichever is slower. In principle, the process is analogous to the solution-precipitation process during densification of silicon nitride.

Functional properties

Thermal conductivity

As a highly covalent compound, Si₃N₄ transports heat primarily by phonons at room temperature. The experimentally measured thermal conductivity of sintered polycrystalline Si₃N₄ is much lower than the predicted values (up to 450 W m⁻¹ K⁻¹ in the c-axis direction, see the Section “Properties”), and in most cases it lies between 60–90 W m⁻¹ K⁻¹ (Duan *et al.*, 2019; Kim *et al.*, 2017; Hu *et al.*, 2016; Zhu and Sakka, 2008). This is caused by the presence of GB phases with a rather low thermal conductivity (< 5 W m⁻¹ K⁻¹), and lattice defects in Si₃N₄ grains (impurity atoms, vacancies, dislocations, stacking faults, etc.), which can induce phonon scattering, resulting in the decrease of thermal conductivity. One of the main problematic impurities is oxygen, as the solution of oxygen in Si₃N₄ is relatively high and it generates vacancies at the Si sites in the Si₃N₄ lattice (Zhou *et al.*, 2015). Therefore, the use of a Si₃N₄ powder with a very low oxygen impurity content is essential for the preparation of Si₃N₄ with high thermal conductivities. Indeed, the highest ever reported value, experimentally measured for polycrystalline Si₃N₄, was 177 W m⁻¹ K⁻¹. This was obtained due to a significant reduction in the oxygen impurity content, as well as enhanced grain growth during post-sintering (Zhou *et al.*, 2015). Due to the intrinsic anisotropic thermal conductivity of Si₃N₄ grains, a highly anisotropic silicon nitride (~ 66%) can be prepared by texturing using HIP, in which the thermal conductivity is 155 and 52 W m⁻¹ K⁻¹ in the c-axis and a,b-axes directions, respectively (Watari *et al.*, 1999).

This all confirms that Si₃N₄ can reach almost as high thermal conductivity as AlN (~ 200 W m⁻¹ K⁻¹), while exhibiting significantly higher fracture toughness and strength when compared to AlN. Therefore, silicon nitride shows potential to replace AlN as a ceramic substrate for the next generation power devices.

Biological properties

Nowadays, silicon nitride is intensively investigated in the biomedical fields owing to its interesting biological properties. Reaction bonded Si₃N₄ was the first type of silicon nitride ever used in a human clinical trial as anterior lumbar interbody fusion in 1986 (Sorrell *et al.*, 2004). Since 2008, silicon nitride has been used as a fusion cage for arthrodesis of the cervical and thoracolumbar spine (Taylor *et al.*, 2010). At the present time, Si₃N₄-based materials are under development to be used as bearings components of prosthetic hip and knee joints, as spinal reconstruction devices and as inner parts of dental implants.

Silicon nitride is a bioinert, non-cytotoxic material, and its biocompatibility was already experimentally confirmed (Bal and Rahaman, 2012). Si₃N₄ is visible on plain radiographs as a partially radiolucent material and is non-magnetic, which allows an accurate view of the implant during surgical procedure and in postoperative evaluation on magnetic resonance imaging. Silicon nitride is more resistant to bacterial biofilm formation, colonization and growth (Gorth *et al.*, 2012), and has better osseointegration (Webster *et al.*, 2012), when compared to medical-grade PEEK (polyether ether ketone) and titanium implants. The wear rates of prototype Si₃N₄ total hip bearings against Si₃N₄ acetabular bearings are comparable to those of Al₂O₃-Al₂O₃ wear rates, which are the lowest of any orthopedic bearing (Bal *et al.*, 2009). Moreover, the in vivo environment should be even more favorable, since human synovial fluid is an excellent lubricant.

The current research in biological field is focused on the improvement of bioactivity of Si₃N₄ with the aim to promote faster and stronger silicon nitride osseointegration. This can be achieved either by coating of the Si₃N₄ surface with a hydroxyapatite layer (Precnerová *et al.*, 2015), or introducing a bioactive phase into the Si₃N₄ body, or using various surface treatments to produce a silica-rich or N-rich composition (Pezzotti, 2019; Hnatko *et al.*, 2020), which can influence the response of cells, tissues, and bacteria in vivo.

References

- Andrews, P., Riley, F.L., 1989. The microstructure and composition of oxide films formed during high temperature oxidation of a sintered silicon nitride. *Journal of the American Ceramic Society* 5, 245–256.
- Bal, B.S., Rahaman, M.N., 2012. Orthopedic applications of silicon nitride ceramics. *Acta Biomaterialia* 8, 2889–2898.
- Bal, B.S., Khandkar, A., Lakshminarayanan, R., *et al.*, 2009. Fabrication and testing of silicon nitride bearings in total hip arthroplasty. *Journal of Arthroplasty* 24, 110–116.
- Becher, P.F., 1991. Microstructural design of toughened ceramics. *Journal of the American Ceramic Society* 74, 255–269.
- Becher, P.F., Ferber, M.K., 2004. Temperature-dependent viscosity of SiREAl-based glasses as a function of N:O and RE:Al ratios (RE = La, Gd, Y, and Lu). *Journal of the American Ceramic Society* 87, 1274–1279.
- Becher, P.F., Sun, E.Y., Plucknett, K.P., *et al.*, 1998. Microstructural design of silicon nitride with improved fracture toughness: I, Effects of grain shape and size. *Journal of the American Ceramic Society* 81, 2821–2830.
- Becher, P.F., Shibata, N., Painter, G.S., *et al.*, 2010. Observations on the influence of secondary Me oxide additives (Me = Si, Al, Mg) on the microstructural evolution and mechanical behavior of silicon nitride ceramics containing RE₂O₃ (RE = La, Gd, Lu). *Journal of the American Ceramic Society* 93, 570–580.
- Becher, P.F., Painter, G.S., Shibata, N., Waters, S.B., Lin, H.T., 2008. Effect of rare-earth (RE) intergranular adsorption on the phase transformation, microstructure evolution, and mechanical properties in silicon nitride with RE₂O₃+MgO additives: RE = La, Gd, Lu. *Journal of the American Ceramic Society* 91, 2328–2336.

- Belmonte, M., Gunzález-Julián, J., Miranzo, P., Osendi, M.I., 2010. Spark plasma sintering: A powerful tool to develop new silicon nitride-based materials. *Journal of the European Ceramic Society* 30, 2937–2946.
- Bressiani, J.C., Izhevskiy, V., Bressiani, A.H.A., 1999. Development of the microstructure of silicon nitride based ceramics. *Materials Research* 2, 165–172.
- Chakraborty, D., Mukerji, J., 1980. Characterization of silicon nitride single crystals and polycrystalline reaction sintered silicon nitride by microhardness measurements. *Journal of Materials Science* 15, 3051–3056.
- Chakraborty, D., Mukerji, J., 1982. Effect of crystal orientation, structure and dimension on Vickers microhardness anisotropy of β -, α -Si₃N₄, α -SiO₂ and α -SiC single crystals. *Materials Research Bulletin* 17, 843–849.
- Chockalingam, S., Earl, D.A., 2010. Microwave sintering of Si₃N₄ with LiYO₂ and ZrO₂ as sintering additives. *Materials & Design* 31, 1559–1562.
- Cinibulk, M.K., Thomas, G., Johnson, S.M., 1992. Oxidation behavior of rare-earth disilicate-silicon nitride ceramics. *Journal of the American Ceramic Society* 75, 2044–2049.
- Csanádi, T., Németh, D., Dusza, J., Lenčič, Z., Šajgalík, P., 2016. Nanoindentation induced deformation anisotropy in β -Si₃N₄ ceramic crystals. *Journal of the European Ceramic Society* 36, 3059–3066.
- Duan, Y., Zhang, J., Li, X., *et al.*, 2019. High thermal conductivity silicon nitride ceramics prepared by pressureless sintering with ternary sintering additives. *International Journal of Applied Technology* 16, 1399–1406.
- Gorth, D.J., Puckett, S., Ercan, B., *et al.*, 2012. Decreased bacteria activity on Si₃N₄ surfaces compared with PEEK or titanium. *International Journal of Nanomedicine* 7, 4829–4840.
- Grun, R., 1979. The crystal structure of β -Si₃N₄: Structural and stability considerations between α - and β -Si₃N₄. *Acta Crystallographica B* 35, 800–804.
- Hampshire, S., Pomeroy, M.J., 2004. Effect of composition on viscosities of rare earth oxynitride glasses. *Journal of Non-Crystalline Solids* 344, 1–7.
- Hampshire, S., Pomeroy, M.J., 2012. Grain boundary glasses in silicon nitride: a review of chemistry, properties and crystallisation. *Journal of the European Ceramic Society* 32, 1925–1932.
- Hardie, D., Jack, K.H., 1957. Crystal structures of silicon nitride. *Nature* 180, 332–333.
- Henderson, C., Taylor, D., 1975. Thermal expansion of the nitrides and oxynitrides of silicon in relation to their structures. *Transactions and Journal of the British Ceramic Society* 74, 49–53.
- Hirao, K., Ohashi, M., Brito, M.E., Kanzaki, S., 1995. Processing strategy for producing highly anisotropic silicon nitride. *Journal of the American Ceramic Society* 78, 1687–1690.
- Hirosaki, N., Akimune, Y., Mitomo, M., 1993. Effect of grain growth of β -silicon nitride on strength, weibull modulus, and fracture toughness. *Journal of the American Ceramic Society* 76, 1892–1894.
- Hirosaki, N., Ogata, S., Kocer, C., Kitagawa, H., Nakamura, Y., 2002. Molecular dynamics calculation of the ideal thermal conductivity of single crystal α - and β -Si₃N₄. *Physical Review B* 65, 1–11.
- Hnatko, M., Hičák, M., Labudová, M., *et al.*, 2020. Bioactive silicon nitride by surface thermal treatment. *Journal of the European Ceramic Society* 40, 1848–1858.
- Hu, F., Zhao, L., Xie, Z.P., 2016. Silicon nitride ceramics with high thermal conductivity and excellent mechanical properties fabricated with MgF₂ sintering aid and post-sintering heat treatment. *Journal of Ceramic Science and Technology* 7, 423–428.
- Inomata, Y., Yamane, T., 1974. β -Si₃N₄ single crystals grown from Si melts. *Journal of Crystal Growth* 21, 317–318.
- Jiang, J.Z., Lindelov, H., Gerward, L., *et al.*, 2002. Compressibility and thermal expansion of cubic silicon nitride. *Physical Review B* 65, 161202.
- Kato, K., Inoue, Z., Kijima, K., Kawada, I., Tanaka, H., 1975. Structural approach to the problem of oxygen content in alpha silicon nitride. *Journal of the American Ceramic Society* 58, 90–91.
- Kijima, K., Seteka, N., Tanaka, H., 1974. Preparation of silicon nitride single crystals by chemical vapor deposition. *Journal of Crystal Growth* 24/25, 183–187.
- Kim, J.M., Ko, S.I., Kim, H.N., *et al.*, 2017. Effects of microstructure and intergranular glassy phases on thermal conductivity of silicon nitride. *Ceramic International* 43, 5441–5449.
- Kitayama, M., Hirao, K., Kanzaki, S., 2006. Effect of rare-earth oxide additives on the phase transformation rates of Si₃N₄. *Journal of the American Ceramic Society* 89, 2612–2618.
- Klemm, H., 2010. Silicon nitride for high-temperature applications. *Journal of the American Ceramic Society* 93, 1501–1522.
- Kocer, C., Hirosaki, N., Ogata, S., 2003. Ab initio calculation of the ideal tensile and shear strength of cubic silicon nitride. *Physical Review B* 67, 035210.
- Kondo, N., Suzuki, Y., Ohji, T., 1999. Superplastic sinter-forging of silicon nitride with anisotropic microstructure formation. *Journal of the American Ceramic Society* 82, 1067–1069.
- Liu, M., Nemat-Nasser, S., 1998. The microstructure and boundary phase of in-situ reinforced silicon nitride. *Materials Science and Engineering A* 254, 242–252.
- Lofaj, F., Wiederhorn, S.M., 2009. Creep processes in silicon nitride ceramics. *Journal of Ceramic Processing Research* 10, 269–277.
- Lojanová, Š., Tatarko, P., Chlup, Z., *et al.*, 2010. Rare-earth element doped Si₃N₄/SiC micro/nano-composites – RT and HT mechanical properties. *Journal of the European Ceramic Society* 30, 1931–1944.
- Meléndez-Martínez, J.J., Domínguez-Rodríguez, A., 2004. Creep of silicon nitride. *Progress in Materials Science* 49, 19–107.
- Morelli, D.T., Heremans, J.P., 2002. Thermal conductivity of germanium, silicon, and carbon nitride. *Applied Physics Letters* 81, 5126–5128.
- Nishimura, T., Mitomo, M., Hirotsuru, H., Kawahara, M., 1995. Fabrication of silicon-nitride nano-ceramics by spark plasma sintering. *Journal of Materials Science Letters* 14, 1046–1047.
- Ogata, S., Hirosaki, N., Kocer, C., Shibutani, Y., 2004. A comparative ab initio study of the "ideal" strength of single crystal α - and β -Si₃N₄. *Acta Materialia* 52, 233–238.
- Petzow, G., Herrmann, M., 2002. *Silicon Nitride Ceramics in High Performance Non-Oxide Ceramics II*. Berlin Heidelberg: Springer, pp. 46–166. (ISBN: 978-3-540-43132-9).
- Pezzotti, G., 2019. Silicon nitride: A bioceramics with a gift. *ACS Appl. Mater. Interfaces* 11, 26619–26636.
- Precnerová, M., Bodišová, K., Frajkorová, F., *et al.*, 2015. In vitro bioactivity of silicon nitride-hydroxyapatite composites. *Ceramics International* 41, 8100–8108.
- Reimanis, I.E., Suematsu, H., Petrovic, J.J., Mitchell, T.E., 1996. Mechanical properties of single-crystal α -Si₃N₄. *Journal of the American Ceramic Society* 79, 2065–2073.
- Riley, F.L., 2000. Silicon nitride and related materials. *Journal of the American Ceramic Society* 83, 245–265.
- Šajgalík, P., Galusek, D., 1993. α/β phase transformation of silicon nitride: Homogenous and heterogenous nucleation. *Journal of Materials Science Letters* 12, 1937–1939.
- Šajgalík, P., Dusza, J., Hoffmann, M.J., 1995. Relationship between microstructure, toughening mechanisms, and fracture toughness of reinforced silicon nitride ceramics. *Journal of the American Ceramic Society* 78, 2619–2624.
- Satet, R.L., Hoffmann, M.J., 2005. Influence of the rare-earth element on the mechanical properties of RE-Mg-bearing silicon nitride. *Journal of the American Ceramic Society* 88, 2485–2490.
- Satet, R.L., Hoffmann, M.J., Cannon, R.M., 2006. Experimental evidence of the impact of rare-earth elements on particle growth and mechanical behaviour of silicon nitride. *Materials Science and Engineering A* 422, 66–76.
- Sorrell, C.C., Hardcastle, P.H., Druitt, R.K., Howlett, C.R., McCartney, E.R., 2004. Results of 15-year clinical study of reaction bonded silicon nitride intervertebral spacers. In: *Proceeding of the 7th World Biomaterials Congress*. pp. 18–72.
- Suganuma, M., Kitagawa, Y., Wada, S., Murayama, N., 2003. Pulsed electric current sintering of silicon nitride. *Journal of the American Ceramic Society* 86, 387–394.
- Sun, E.Y., Becher, P.F., Plucknett, K.P., *et al.*, 1998. Microstructural design of silicon nitride with improved fracture toughness: II, Effects of yttria and alumina additives. *Journal of the American Ceramic Society* 81, 2831–2840.
- Tatarko, P., Lojanová, Š., Dusza, J., Šajgalík, P., 2010. Influence of various rare-earth oxide additives on microstructure and mechanical properties of silicon nitride based nanocomposites. *Materials Science and Engineering A* 527, 4771–4778.

- Tatarko, P., Kašiarová, M., Dusza, J., Šajgalik, P., 2013. Influence of rare-earth oxide additives on the oxidation resistance of Si₃N₄-SiC nanocomposites. *Journal of the European Ceramic Society* 33, 2259–2268.
- Taylor, R.M., Bernero, J.P., Patel, A.A., Brodke, D.S., Khandkar, A.C., 2010. Silicon nitride – A new material for spinal implants. *The Journal of Bone and Joint Surgery-British* 92 (Suppl. I), 133.
- Teshima, H., Hirao, K., Toriyama, M., Kanzaki, S., 1999. Fabrication and mechanical properties of silicon nitride ceramics with unidirectionally oriented rodlike grains. *Journal of the Ceramic Society of Japan* 107, 1216–1220.
- Wang, C.-M., Pan, X., Rühle, M., Riley, F.L., Mitomo, M., 1996. Review – Silicon nitride crystal structure and observations of lattice defects. *Journal of Materials Science* 31, 5281–5298.
- Watari, K., Hirao, K., Brito, M.E., Toriyama, M., Kanzaki, S., 1999. Hot isostatic pressing to increase thermal conductivity of Si₃N₄ ceramics. *Journal of Materials Research* 14, 1538–1541.
- Webster, T.J., Patel, A.A., Rahaman, M.N., Bal, B.S., 2012. Anti-infective and osteointegration properties of silicon nitride, poly(ether ether ketone), and titanium implants. *Acta Biomaterialia* 8, 4447–4454.
- Xu, X., Nishimura, T., Hirotsaki, N., *et al.*, 2005. New strategies for preparing nanosized silicon nitride ceramics. *Journal of the American Ceramic Society* 88, 934–937.
- Yang, W., Xie, Z., Li, J., *et al.*, 2004. Growth of platelike and branch single-crystalline Si₃N₄ whiskers. *Solid State Communications* 132, 263–268.
- Yang, W., Zhang, L., Xie, Z., *et al.*, 2005a. Growth and optical properties of ultra-long single-crystalline α -Si₃N₄ nanobelts. *Applied Physics A* 80, 1419–1423.
- Yang, W., Xie, Z., Li, J., *et al.*, 2005b. Ultra-long single-crystalline α -Si₃N₄ nanowires: Derived from a polymeric precursor. *Journal of the American Ceramic Society* 88, 1647–1650.
- Yang, Z., Yu, J., Deng, K., *et al.*, 2014. Fabrication of textured Si₃N₄ ceramics with β -Si₃N₄ powders as raw material by gel-casting under strong magnetic field. *Materials Letters* 135, 218–221.
- Zerr, A., Miehe, G., Serghiou, G., *et al.*, 1999. Synthesis of cubic silicon nitride. *Nature* 400, 340–342.
- Zerr, A., Kempf, M., Schwarz, M., *et al.*, 2002. Elastic moduli and hardness of cubic silicon nitride. *Journal of the American Ceramic Society* 85, 86–90.
- Zhang, J., Cao, L., Xia, F., 1992. Microwave sintering of Si₃N₄ ceramics. *Materials Research Society Symposium Proceedings* 269, 329–334.
- Zhou, Y., Hyuga, H., Kusano, D., *et al.*, 2015. Development of high-thermal-conductivity silicon nitride ceramics. *Journal of Asian Ceramic Societies* 3, 221–229.
- Zhu, X., Sakka, Y., 2008. Textured silicon nitride: Processing and anisotropic properties. *Science and Technology of Advanced Materials* 9, 033001.

SiAlONs and the Representation of Phase Relationships

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Introduction

Silicon nitride is a generic term that is used to describe a family of materials based on silicon nitride (Si_3N_4) but fabricated using different methods which give their names to the type of silicon nitride. Silicon nitride as a ceramic was first developed in the 1950s for use as thermocouple tubes, crucibles for molten metals and also rocket nozzles (Collins and Gerby, 1955). This type of material was formed by nitriding silicon powder compacts in the temperature range 1100–1450°C and was later termed reaction-bonded silicon nitride (RBSN) (Parr *et al.*, 1960).

Sintering of silicon nitride is quite difficult because self-diffusivity is low and species only become sufficiently mobile for sintering at temperatures where the decomposition of silicon nitride commences ($> 1850^\circ\text{C}$) (Riley, 2000). To promote densification, sintering additives, such as yttria and alumina (Sun *et al.*, 1998), are mixed with $\alpha\text{-Si}_3\text{N}_4$ powder which has layers of silica on its particle surfaces. The oxides react with this silica and some of the nitride itself at sintering temperatures to form an oxynitride liquid which promotes liquid phase sintering and densification by solution-diffusion-precipitation (Hampshire and Jack, 1981; Riley, 2000; Lange, 2006; Hampshire, 2009). The $\alpha\text{-Si}_3\text{N}_4$ dissolves in the liquid and is precipitated as $\beta\text{-Si}_3\text{N}_4$ which grows in the longitudinal direction as prismatic hexagonal rod-like crystals that eventually impinge on each other forming an interlocked microstructure. The liquid cools as an intergranular phase, usually a glass, according to the following:



Various rare earth (RE) oxides, with either alumina or MgO, have also been investigated (Becher *et al.*, 1998; Satet *et al.*, 2006; Becher *et al.*, 2010) as sintering additives and this allows the development of different types of microstructures and, hence, properties by modifying the chemistry of the sintering liquid phase. The types and amounts of additives used for sintering determine the nature and quantity of the resulting grain boundary phase which has a significant effect on materials properties. One significant milestone was the discovery of the SiAlONs (Jack, 1973, 1976; Thompson, 2002).

SiAlONs

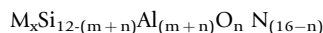
SiAlONs are solid solutions based on the α - and β -silicon nitride structures in both of which the Si atoms lie at the center of Si-N₄ tetrahedra, joined at the corners to form 8-membered Si-N puckered rings which join in turn to form sheets perpendicular to the *c*-axis. In β -silicon nitride the sheets are stacked periodically ABABABAB, with large diameter channels parallel to the *c*-axis. In α the stacking sequence is ABCDABCD with the CD sheets rotated with respect to AB by 180° about the *c*-axis. The rotation creates 2 large interstices in the unit cell (in place of the channels in β) capable of accommodating metal cations.

β' -SiAlON is formed when oxygen (O^{2-}) replaces nitrogen (N^{3-}) in the $\beta\text{-Si}_6\text{N}_8$ structure while, at the same time, silicon (Si^{4+}) is replaced by aluminum (Al^{3+}) to maintain overall charge neutrality (Oyama and Kamigaito, 1971; Jack and Wilson, 1972). The β' -SiAlON solid solution composition is:



retaining the 6:8 metal: non-metal ratio of $\beta\text{-Si}_6\text{N}_8$, with *z* values in the range 0–4.2. The single-phase β' -sialon still requires a sintering additive such as Y_2O_3 in order to densify the ceramic (Ekström and Nygren, 1992). Microstructures are similar to $\beta\text{-Si}_3\text{N}_4$ with elongated hexagonal grains of β' -sialon but a reduced amount of intergranular glass phase.

α -SiAlONs (α') are based on the $\alpha\text{-Si}_{12}\text{N}_{16}$ unit cell with general composition (Hampshire *et al.*, 1978):



In α' -SiAlON, partial replacement of Si^{4+} by Al^{3+} occurs if, at the same time, charge compensation is effected by the accommodation of other ions, $\text{M} = \text{Li}^+, \text{Ca}^{2+}, \text{Y}^{3+}$ or rare earth lanthanide ions (RE^{3+}), in the two interstitial sites (*x*) in the unit cell. $x = m/v$ where *v* is the valence of the M cation, and *x* should be a value between 0.3 and 2 (the maximum value because of 2 interstitial sites per unit cell). As with β' , Y_2O_3 is used as a densification aid but also provides Y^{3+} ions for stabilization of α' . Other oxides where the cation can be accommodated in the α' -SiAlON structure are also used as sintering additives (Mandal, 1999).

Unlike Si_3N_4 , where $\beta\text{-Si}_3\text{N}_4$ is the main stable phase after sintering, the two SiAlON phases, α' and β' can coexist depending on the sintering additives used. Therefore, there are more variables to be used as design parameters for SiAlON ceramics and the amount of α' -SiAlON can be varied from 0% to 100% continuously and the type and amount of intergranular phase can also be modified by using mixed additives (Mandal *et al.*, 1999). These are usually combinations of CaO and two rare earth lanthanide oxides which allow more easier densification but on subsequent heat treatment, the final properties of the SiAlON ceramics can be tailored so that when high hardness is needed, α' -SiAlON content is increased and when higher toughness is required, then

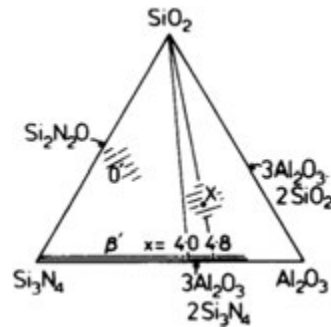


Fig. 1 Phase Relationships in the SiO_2 - Si_3N_4 - Al_2O_3 system at 1700°C . After Jack, K.H., 1973. Nitrogen ceramics (17th Mellor Memorial Lecture). Transactions and Journal of the British Ceramic Society 72, 376–384.

additive chemistry is changed to give predominantly β' -SiALON (Mandal, 1999). These ceramics are already available as cutting tools or refractories and are being developed as wear parts (Çelik and Turan, 2021).

An initial challenge was how to represent phase relationships in complex systems involving nitrides and oxides. The phases formed when a mixture of alumina and normal silicon nitride powder is sintered cannot simply be represented on a binary Si_3N_4 - Al_2O_3 diagram since there is also SiO_2 present on the silicon nitride. Jack (1973) presented the ternary SiO_2 - Si_3N_4 - Al_2O_3 shown in Fig. 1 with the composition of β -SiALON along the Si_3N_4 - Al_2O_3 join. In addition to forming β -SiALON, another phase was discovered referred to as "X", so-called because its structure was unknown initially, which lies on a line between Si_3N_4 and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). Fig. 1 also shows an area marked O' which is $\text{Si}_2\text{N}_2\text{O}$ with partial replacement of Si and N by Al and O (Jack, 1973).

The x value given along the Si_3N_4 - Al_2O_3 join refers to the formula for β -SiALON which was thought to be correct at the time. Because x-ray analysis showed only one single-phase crystalline product, it was concluded, on the basis of limited chemical analyses, that the β' composition was:

$$\text{Si}_{6-3x/4}\text{Al}_{2x/3}\text{O}_x\text{N}_{8-x}$$

This formula satisfies valency balance requirements. However, further research (Jack, 1976; Lewis *et al.*, 1977) showed that compositions along the Si_3N_4 - Al_2O_3 join also contained some glass phase and that the β -SiALON phase range extended from Si_3N_4 towards Al_2O_3 consistent with the "z" formula:

$$\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$$

The question then was how to represent these more complex systems.

Representation of the Si-Al-O-N System

In view of the compositions which had been investigated, it was necessary to consider the complete (quaternary) Si_3N_4 - AlN - Al_2O_3 - SiO_2 system. Gauckler *et al.* (1975) and Jack (1976) both proposed adoption of the following representation of the Si-Al-O-N and related systems based on equivalent concentrations.

The Si-Al-O-N system has 4 component elements and so can be represented as a regular tetrahedron as shown in Fig. 2, each of the vertices of which represent one atom (or gram-atom) of the respective elements. It can be seen that the condensed phases: Si_3N_4 , AlN , Al_2O_3 , SiO_2 , lie at the corners of a quadrilateral, no two opposite sides of which are parallel. For example, Si_3N_4 (with 7 atoms in total) lies at a point $3/7$ along the edge from N to Si; AlN lies at a point $1/2$ along the edge from N to Al; Al_2O_3 lies at a point $3/5$ along the edge from Al to O; SiO_2 lies at a point $2/3$ along the edge from Si to O. This makes it inconvenient for plotting compositions and for representation of the phase relationships in the "normal" way for a phase diagram. A much simpler representation is obtained by expressing concentrations in "equivalents" instead of atoms or gram-atoms.

If each corner of the tetrahedron represents one equivalent of an element and, because one equivalent of any element or compound always reacts with one equivalent of any other species, the compositions of the phases Si_3N_4 , AlN , Al_2O_3 and SiO_2 , expressed in equivalents, are located at the mid-points of the edges of the tetrahedron as shown in Fig. 3 and the quadrilateral becomes a square.

A different approach gives the same conclusion. Effectively the composition of any condensed phase in the Si-Al-O-N system is determined by only two variables which can be plotted perpendicular to each other. This is the same as for reciprocal salt pairs (Findlay, 1927; Zernicke, 1955) which consist of two or three cations and two anions. The compositions are expressed in equivalent percent (eq.%) of cations and anions instead of atomic, molar or weight percentages (Gauckler *et al.*, 1975; Jack, 1976).

Thus, the four-component Si-Al-O-N system (Jack, 1976) is a square plane which has, as components, the oxides and nitrides of silicon and aluminum as shown in Fig. 4. In this system, it is convenient to let the bottom left hand corner of the square represent one mole of Si_3N_4 with 12 +ve and 12 -ve valencies. The other corners of the square represent Al_4N_4 , Al_4O_6 and Si_3O_6 . In going from left to right, 3Si^{4+} is gradually replaced by 4Al^{3+} and from bottom to top 4N^{3-} is replaced by 6O^{2-} . Any point in the square represents a combination of 12 positive and 12 negative valence units. The cations and anions are thus treated

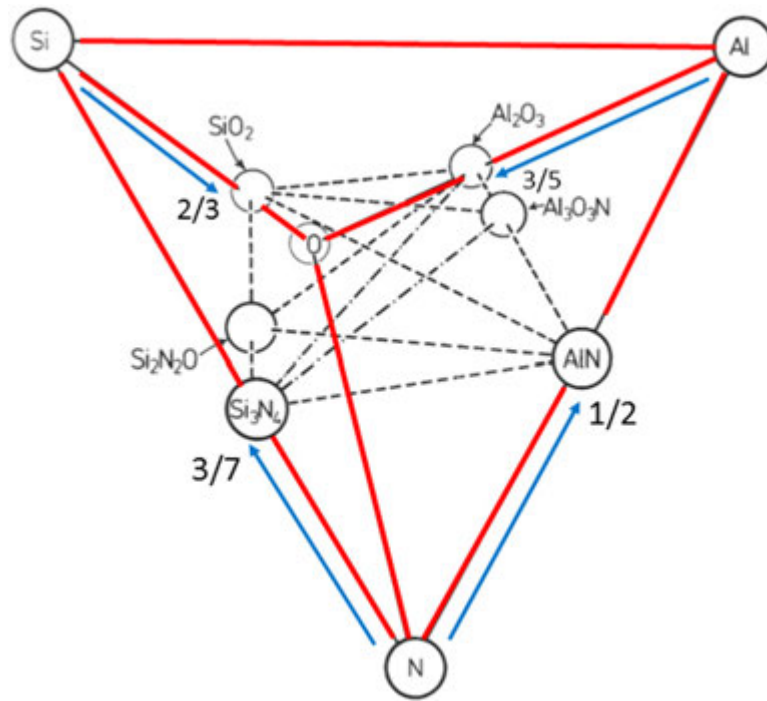


Fig. 2 The tetrahedral representation of the Si-Al-O-N system. Adapted from Jack, K.H., 1976. Review: Sialons and related nitrogen ceramics. *Journal of Materials Science* 11, 1135–1158.

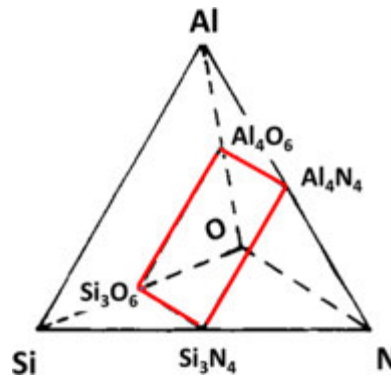


Fig. 3 The quaternary $\text{Si}_3\text{N}_4\text{-Al}_4\text{N}_4\text{-Al}_4\text{O}_6\text{-Si}_3\text{O}_6$ system in equivalent % is a square. Adapted from Tien, T.-Y., 1995. Chapter 4 – Use of phase diagrams in the study of silicon nitride ceramics In: Alper, A.M. (Ed.), *Phase Diagrams in Advanced Ceramics*. Elsevier, pp. 127–156.

separately. The concentrations can be expressed as equivalent percentages (eq.%) of either cations or anions as follows:

$$\text{equivalent percentage (eq.\%) Si} = (4[\text{Si}] \times 100) / (4[\text{Si}] + 3[\text{Al}]) \quad (2)$$

where [Si] and [Al] are, respectively, the atomic concentrations of Si and Al in any composition and 4 and 3 are their respective normal valencies.

$$\text{equivalent \% (eq.\%) Al} = 100 - \text{eq.\% Si} \quad (3)$$

For the anions:

$$\text{equivalent \% (eq.\%) of nitrogen} = (3[\text{N}] \times 100) / (2[\text{O}] + 3[\text{N}]) \quad (4)$$

where [O] and [N] are, respectively, the atomic concentrations of oxygen and nitrogen within any composition and 3 and 2 are their respective valencies.

$$\text{equivalent \% (eq.\%) oxygen} = 100 - \text{eq.\% N} \quad (5)$$

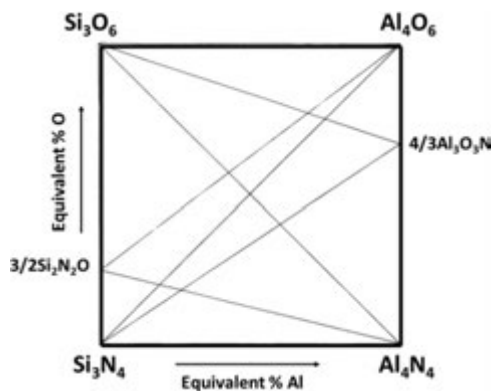


Fig. 4 The square representation of the Si-Al-O-N system. Adapted from Jack, K.H., 1976. Review: Sialons and related nitrogen ceramics. *Journal of Materials Science* 11, 1135–1158.

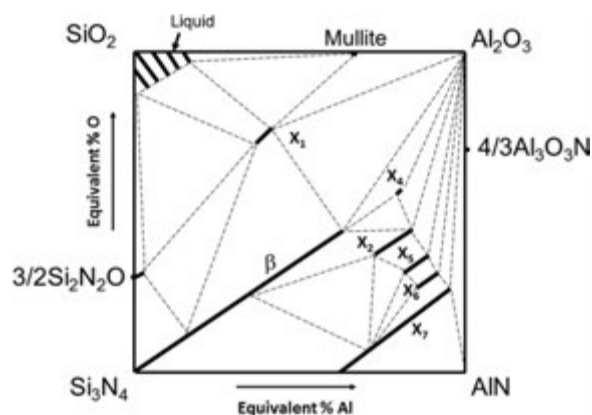


Fig. 5 The Si_3N_4 -AlN- Al_2O_3 - SiO_2 system at 1760°C. Adapted from Gauckler, L.J., Lukas, H.L., Petzow, G., 1975. Contribution to the phase diagram Si_3N_4 -AlN- Al_2O_3 - SiO_2 . *Journal of the American Ceramic Society* 58, 346–347.

Phases in the Si-Al-O-N System

The first diagram to use this approach for the Si_3N_4 -AlN- Al_2O_3 - SiO_2 system was presented by Gauckler *et al.* (1975) and a modified version of this is shown in Fig. 5. It gives the phases and their compositions after hot-pressing powder mixtures at 1760°C and is considered as a behavior diagram rather than an equilibrium phase diagram. The β' -SiAlON extends from the Si_3N_4 corner towards the composition $\text{Al}_2\text{O}_3\cdot\text{AlN}$ consistent with the “z” formula (Lewis *et al.*, 1977). A phase X_1 occurs in the region between $\text{Si}_2\text{N}_2\text{O}$ and mullite which is the same phase found by Jack (1973). Other phases labeled X_4 , X_2 , X_5 , X_6 , X_7 , were reported with compositions in the AlN-rich corner of the system.

Jack (1976) also used the approach of equivalent concentrations and published a different diagram for the Si_3N_4 - Al_4N_4 - Al_4O_6 - Si_3O_6 system at 1700°C shown in Fig. 6. As with the previous diagram by Gauckler *et al.* (1975), β' -SiAlON extends from the Si_3N_4 corner towards $\text{Al}_3\text{O}_3\text{N}$ with a range of compositions: $\beta'\text{-Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ where $z = 0$ is Si_3N_4 and the limit of solid solution is approximately $\beta'_{z=4.2}$. Silicon oxynitride, $\text{Si}_2\text{N}_2\text{O}$ also has a limited range of solid solution (marked O') with partial replacement of Si and N by Al and O. The liquid region at 1700°C in the SiO_2 -rich corner is quite extensive. Other phases in this system are X-phase and sialon polytypoids (8H, 15R, 12H, 21R, 27R and 2H⁰) with structures based on that of 2H wurtzite-type AlN (Roebuck and Thompson, 1977; Thompson *et al.*, 1983).

Sialon X-Phase

Sialon X-phase is triclinic with a unit cell containing, ideally, six $\text{Si}_3\text{Al}_6\text{O}_{12}\text{N}_2$ units. Its crystal structure consists of alternate chains of octahedra and tetrahedra, as in mullite, linked to form sheets that are stacked parallel and joined together by a network of tetrahedra, some units of which resemble those of the Si_6N_8 cell in $\beta\text{-Si}_3\text{N}_4$. The description of the X-phase as a “nitrogen mullite” is therefore not inappropriate. It melts congruently at 1725°C and its existence in “low” and “high” modifications is due to the very high incidence of stacking faults in the latter when it crystallizes rapidly from the supercooled melt (Thompson and Korgul, 1983).

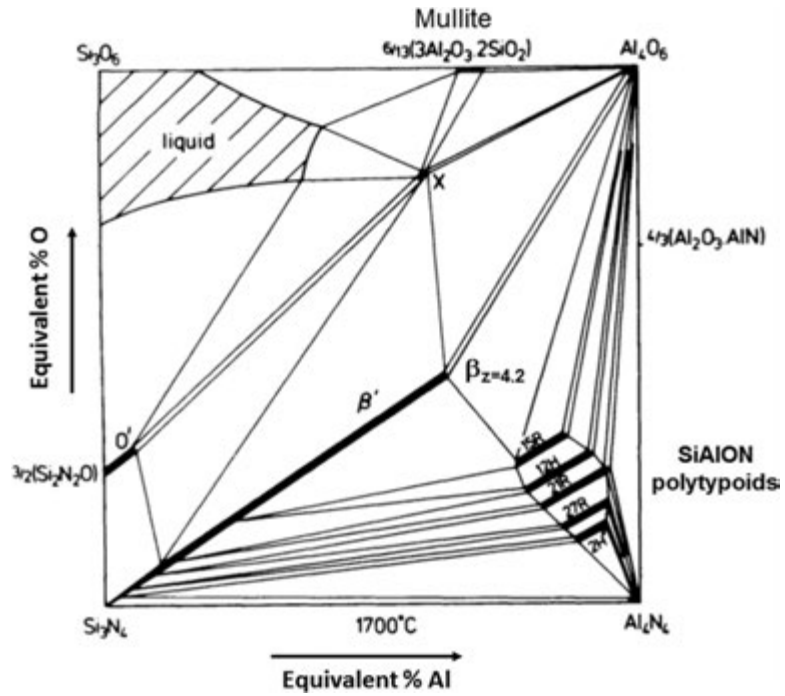


Fig. 6 The Si_3N_4 - Al_4N_4 - Al_4O_6 - Si_3O_6 system at 1700°C . Adapted from Jack, K.H., 1991. Sialons. In: Brook, R.J. (Ed.), Concise Encyclopedia of Advanced Ceramic Materials. Elsevier, pp. 411–416.

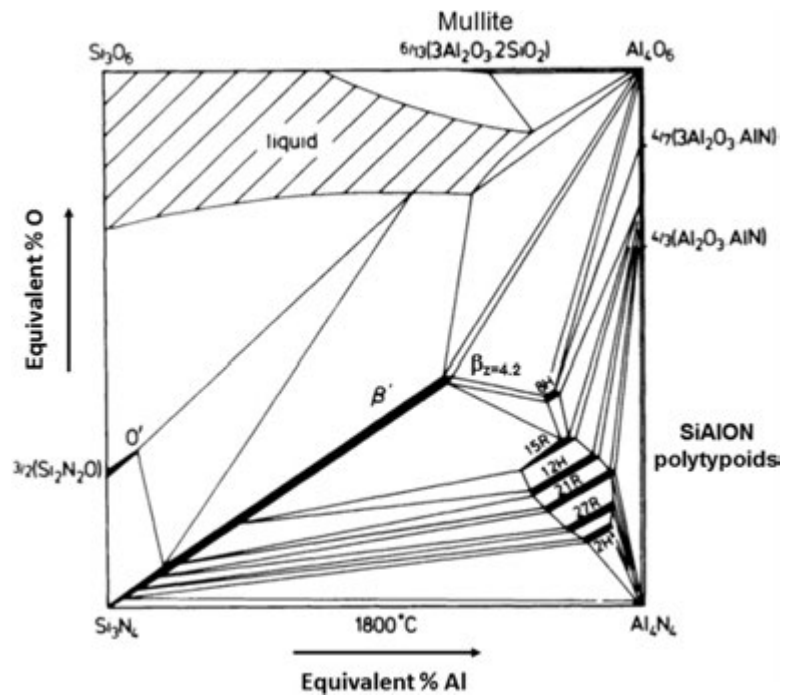


Fig. 7. The Si_3N_4 - Al_4N_4 - Al_4O_6 - Si_3O_6 system at 1800°C . Adapted from Jack, K.H., 1991. Sialons. In: Brook, R.J. (Ed.), Concise Encyclopedia of Advanced Ceramic Materials. Elsevier, pp. 411–416.

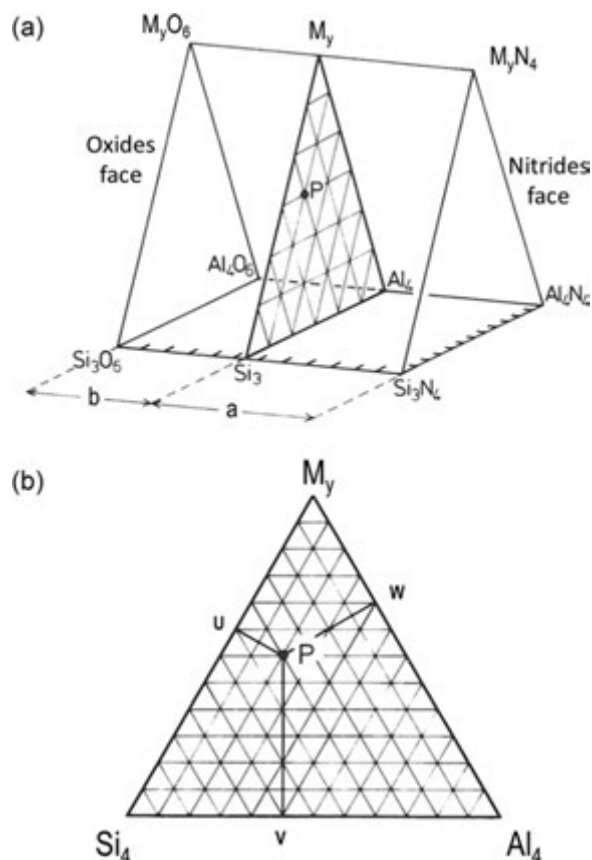


Fig. 8 (a) The Jänecke prism representation of the M -Si-Al-O-N – M_yN_4 – M_yO_6 – Si_3N_4 – Al_4N_4 – Al_4O_6 – Si_3O_5 – system (M = 3rd cation), e.g., Mg, Ca, Y, RE (rare earth lanthanide). The distance, a , of any point P from the nitrides face represents the concentration ratio in equivalents of $O/(N + O) = [a/(a + b)]$; (b) Triangular vertical plane in the Jänecke prism with constant O:N ratio. Sides of the triangle are scaled in equivalent units of cations.

Sialon Polytypoids

Compositions in the Si-Al-O-N system between β' -sialon and the Al_4N_4 corner (see Fig. 6) show six phases with structures based on that of wurtzite-type AlN (Thompson *et al.*, 1983). They are a series of polytypoids, similar to the many polytypes of SiC (Kim and Malik, 2021) in that they exhibit changes in structural stacking in one dimension only, but differing from them in that the structures are directly related to their compositions M_mX_{m+1} , where m has values 4, 5, 6, 7, 9 and 11; the polytypoids have either hexagonal (H) or rhombohedral (R) unit cells described by the respective Ramsdell (1947) symbols 8H, 15R, 12H, 21R, 27R and $2H^d$, the latter being a disordered 2H structure. There are n double layers MX stacked along the c dimension of the unit cell, where n is the Ramsdell numeral and where $n_H = 2m$, $n_R = 3m$. Each block of m layers of wurtzite-type tetrahedra contains an inserted single layer of octahedra and, midway between these octahedral layers, metal atoms are shared between two adjacent layers of tetrahedra to give an MX_2 unit (Thompson *et al.*, 1983). Although x-ray methods do not distinguish between silicon and aluminum or between oxygen and nitrogen, there is little doubt that the layers of octahedra consist of aluminum coordinated by 6 oxygens.

Further Research on the Si-Al-O-N System

The Si_3N_4 – Al_4N_4 – Al_4O_6 – Si_3O_5 diagram based on research at the University of Newcastle upon Tyne, UK (Jack, 1976, 1986, 1991) has evolved over time. Fig. 6 at 1700°C does not include the 8H polytypoid (see above) which was confirmed by further research at higher temperatures as can be seen in Fig. 7 at 1800°C. It appears that the phase relationships change between 1700 and 1800°C. At both temperatures all of the polytypoid phases are in equilibrium with different β' -SiAlON compositions. The area of liquid phase becomes more extensive at 1800°C covering the X-phase composition and therefore the melting point of X-phase is below this temperature.

Any sialon composition can be produced in several ways. For example, β' -SiAlON with $z = 1$ may be prepared from different powder mixes, such as Si_3N_4 –AlN– Al_2O_3 , Si_3N_4 –AlN– SiO_2 , Si_3N_4 – SiO_2 –21R, etc., provided that allowance is made for the surface oxides that are always present on the nitrides. There are advantages in using preprepared polytypoids in place of AlN since they are less easily hydrolyzed and can be used as finer, more reactive powders to give a more homogeneous product (Jack, 1991).

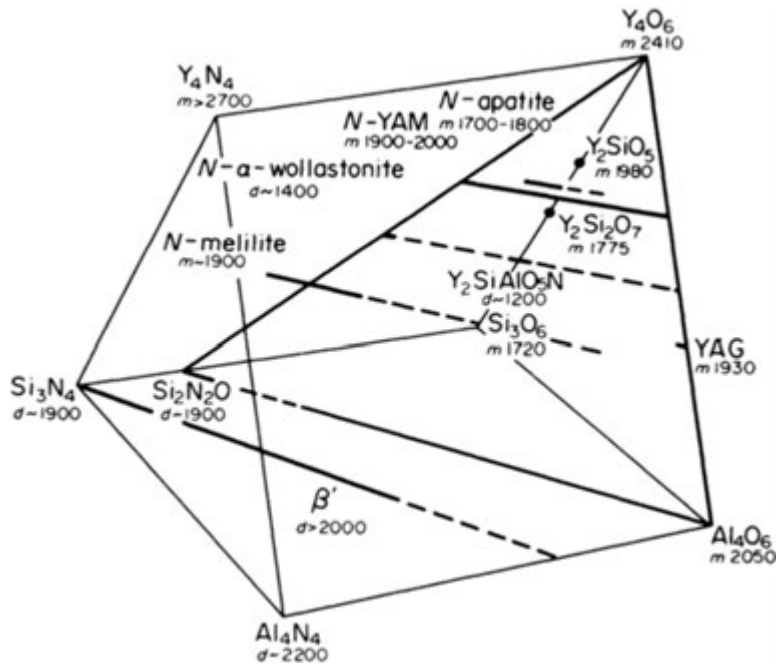


Fig. 9 The Y_4N_4 - Y_4O_6 - Si_3N_4 - Al_4N_4 - Al_4O_6 - Si_3O_6 system showing the various crystalline phases in the Y-Si-O-N system extending into the Jänecke prism. After Jack, K.H., 1991. Sialons. In: Brook, R.J. (Ed.), Concise Encyclopedia of Advanced Ceramic Materials. Elsevier, pp. 411–416.

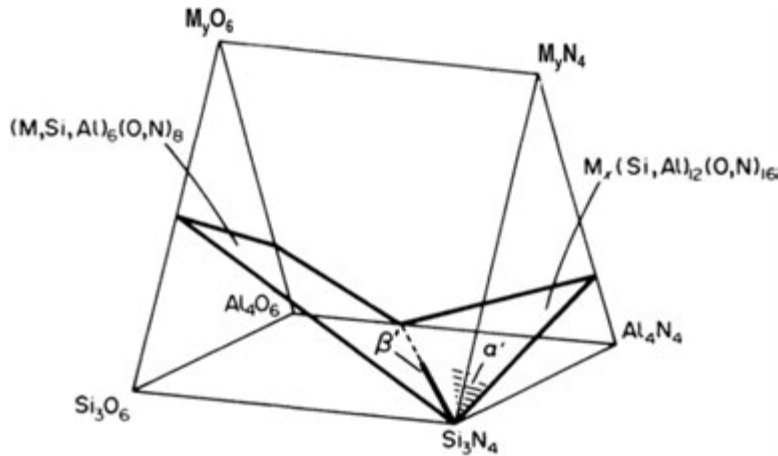


Fig. 10 Relationship between α' and β' -sialon phase regions on two planes in the M_yN_4 - M_yO_6 - Si_3N_4 - Al_4N_4 - Al_4O_6 - Si_3O_6 Jänecke prism with general compositions: $(M,Si,Al)_6(O,N)_8$ and $M_x(Si,Al)_{12}(O,N)_{16}$ (M = 3rd cation, e.g., Mg, Ca, Y, RE (rare earth lanthanide)). Adapted from Jack, K.H., 1991. Sialons. In: Brook, R.J. (Ed.), Concise Encyclopedia of Advanced Ceramic Materials. Elsevier, pp. 411–416.

Representation of M-Si-Al-O-N Systems

Pressureless sintering of β -SiAlON can be achieved to near theoretical density but this still requires the use of an oxide additive such as MgO, Y_2O_3 or RE_2O_3 , where RE is a rare earth lanthanide element. To interpret the reactions and phase relationships that occur when a third cation is introduced, it is necessary to consider the representation of M-Si-Al-O-N systems, where M is a third cation with fixed valency. In this case, the apparent five components are effectively reduced to four and any composition is defined by only three independent variables. In the classification by Zernicke (1955) this is a “quaternary system of the third kind” and is represented by Jänecke’s triangular prism (Jänecke, 1907) shown in Fig. 8(a) for any M-Si-Al-O-N system. This is based on the Si_3N_4 - Al_4N_4 - Al_4O_6 - Si_3O_6 square of Fig. 4 with the third cation M with valency v_M in equivalent units in the third dimension:

$$\text{equivalent \% (eq.\%) of } M = (v_M[M] \times 100) / (4[Si] + 3[Al] + v_M[M]) \quad (6)$$

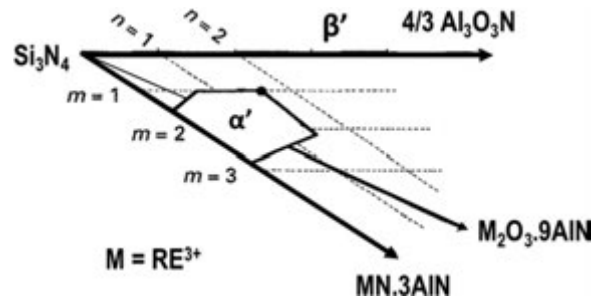


Fig. 11 The (α' -plane) or the Si_3N_4 - $4/3(\text{Al}_3\text{O}_3\text{N})$ - MN.3AlN plane where $\text{M} = \text{Y}^{3+}$ or RE^{3+} . The region of α' -sialon formation is based on data for $\text{Y}-\alpha'$ -SiAlON from Sun, W.Y., Tien, T.Y., Yen, T.S., 1991. Solubility limits of α' -sialon solid solutions in the system Si, Al, Y/N, O. *Journal of the American Ceramic Society* 74, 2547–2550. Adapted from Mandal, H., 1999. New developments in α -SiAlON ceramics. *Journal of the European Ceramic Society* 19, 2349–2357.

The front (right) triangular face of the Jänecke prism represents nitrides and the rear (left) face the oxides. Any vertical plane within the prism has a constant N:O ratio. As shown in Fig. 8(a), the distance, a , of any point P from the nitrides face represents the concentration ratio in equivalents of $\text{O}/(\text{N} + \text{O}) = [a/(a + b)]$. In the triangular vertical plane containing point P (Fig. 8(b)), the cation concentrations, in equivalents, are represented in the usual way for a ternary system. Any point in the prism, as with the Si-Al-O-N square, represents a combination of 12 positive and 12 negative valencies and so the edges of the prism can be scaled in valency units (Fig. 8(b)). The point P thus has a composition in valency units of:

$$\text{M}^{6+} + \text{Si}^{4+} + \text{Al}^{3+} + \text{O}^{6-} - \text{N}^{5-}$$

and in atomic units:

$$\text{M}_{6/_{\text{vm}}} \text{Si}_{1.0} \text{Al}_{0.67} \text{O}_{3.3} \text{N}_{1.8}$$

When Y_2O_3 is used as the sintering additive for Si_3N_4 or β' -SiAlON, a grain boundary glass is usually formed. However, a number of other crystalline phases can be formed either during sintering or by crystallizing the grain boundary glass phases in these ceramics. Fig. 9 shows the Y-Si-Al-O-N system (Jack, 1991) and the various crystalline phases that exist. In the Si_3N_4 - 4YN - $2\text{Y}_2\text{O}_3$ - 3SiO_2 sub-system (square back face of the prism), there are four Y-Si-O-N phases (Thompson, 1989): N-apatite, N-YAM, N-wollastonite and N-melilite and all of these phases extend into the Y-Si-Al-O-N prism. Not shown on this diagram is the range of compositions for α' -SiAlON containing Y.

Representation of M-Si-Al-O-N systems with α' -SiAlON

As outlined earlier, the general composition for α' -SiAlON (Hampshire *et al.*, 1978) is:

$$\text{M}_x\text{Si}_{12-(m+n)}\text{Al}_{(m+n)}\text{O}_n\text{N}_{(16-n)}$$

where M is Li, Mg, Ca, Y, Sc and rare earth lanthanides except La, Ce, Pr and Eu (Ekström and Nygren, 1992; Mandal, 1999). An important advantage of α' -SiAlONs is that the amount of intergranular phase is reduced by the transient liquid phase being absorbed into the α' -SiAlON crystal phase during sintering. However, complete densification can only be achieved either by hot pressing or HIPing.

α and β -sialon phases are completely compatible and α -sialon/ β -sialon composites have received increasing attention because of their easier fabrication compared with Si_3N_4 ceramics; by varying the starting composition using an appropriate mixture of nitrides and oxides and the heating and cooling cycle during sintering it was possible to vary the α/β phase ratio and particle morphology to tailor material properties for particular applications (Ekström and Nygren, 1992). Fig. 10 illustrates the relationship between α and β -sialon phase regions (Jack, 1991) on two planes in the M-Si-Al-O-N Jänecke prism with general compositions:

$$(\text{M,Si,Al})_6(\text{O,N})_8 \text{ and } \text{M}_x(\text{Si,Al})_{12}(\text{O,N})_{16}$$

The first one represents compositions with 3:4 stoichiometry (as for β) in which M cations substitute for Si or Al whereas the second has variable stoichiometry depending on the level of solubility (x) of the cation M into, for example, α -sialon with a fixed cation:anion ratio of $(\text{Si,Al}):(\text{O,N}) = 3:4$. This plane is referred to in many publications as the α' -plane (Jack, 1991; Shen and Nygren, 1997; Mandal, 1999; Rosenflanz and Chen, 1999).

Fig. 11 shows the α -SiAlON stability region on the $\text{M}_x(\text{Si,Al})_{12}(\text{O,N})_{16}$ (α' -plane) or more correctly the Si_3N_4 - $4/3(\text{Al}_3\text{O}_3\text{N})$ - MN.3AlN plane where $\text{M} = \text{Y}$ or RE (Shen and Nygren, 1997; Mandal, 1999; Rosenflanz and Chen, 1999). The extent of this region increases with decreasing size of the RE cation as well increasing temperature.

The phase composition and microstructure of α - and α - β -sialon ceramics are greatly affected by post sintering heat treatment procedures at lower temperatures (1300–1600°C) when rare earth oxides are used as sintering additives (Mandal *et al.*, 1993). The α -sialon phase is only stable at high temperatures and transforms to β -sialon plus other crystalline or vitreous phases. The ease with which this transformation proceeds decreases with increasing atomic number of the rare earth cation.

One advantage of α -SiAlONs is high hardness whereas fracture toughness is quite low relative to β -sialon (Mandal, 1999). The possibility to change the ratio of hard α -SiAlON to tough β -SiAlON by altering the composition makes α/β -SiAlON ceramics unique for applications in wear parts and cutting tools for metal machining operations. Because of the advancements in manufacturing technology and the possibility for close control of microstructure, novel α/β -SiAlON milling tools have been developed and commercialized (Çelik and Turan, 2021).

References

- Becher, P.F., Sun, E.Y., Plucknett, K.P., *et al.*, 1998. Microstructural design of silicon nitride with improved fracture toughness: I, Effects of grain size and shape. *Journal of the American Ceramic Society* 81, 2821–2830.
- Becher, P.F., Shibata, N., Painter, G.S., *et al.*, 2010. Observations on the influence of secondary Me oxide additives (Me = Si, Al, Mg) on the microstructural evolution and mechanical behavior of silicon nitride ceramics containing RE_2O_3 (RE = La, Gd, Lu). *Journal of the American Ceramic Society* 93 (2), 570–580.
- Çelik, A., Turan, S., 2021. Si-Al-O-N ceramics, structure and properties. In: Pomeroy, M.J. (Ed.), *Encyclopedia of Materials: Technical Ceramics and Glasses*. Elsevier.
- Collins, J.F., Gerby, R.W., 1955. New refractory uses for silicon nitride reported. *Journal of Metals* 7, 612–615.
- Ekström, T., Nygren, M., 1992. SiAlON ceramics. *Journal of the American Ceramic Society* 75, 259–276.
- Findlay, A., 1927. The phase rule and its applications, sixth ed. London: Longmans Green.
- Gauckler, L.J., Lukas, H.L., Petzow, G., 1975. Contribution to the phase diagram Si_3N_4 – AlN – Al_2O_3 – SiO_2 . *Journal of the American Ceramic Society* 58, 346–347.
- Hampshire, S., 2009. Silicon nitride ceramics. *Materials Science Forum* 606, 27–41.
- Hampshire, S., Jack, K.H., 1981. The kinetics of densification and phase transformation in nitrogen ceramics. *Proceedings of the British Ceramic Society* 31, 37–49.
- Hampshire, S., Park, H.K., Thompson, D.P., Jack, K.H., 1978. α -sialon ceramics. *Nature* 274, 880–882.
- Jack, K.H., 1973. Nitrogen ceramics (17th Mellor Memorial Lecture). *Transactions and Journal of the British Ceramic Society* 72, 376–384.
- Jack, K.H., 1976. Review: Sialons and related nitrogen ceramics. *Journal of Materials Science* 11, 1135–1158.
- Jack, K.H., 1986. Sialons: A study in materials development. In: Hampshire, S. (Ed.), *Non-Oxide Technical and Engineering Ceramics*. London: Elsevier Applied Science, pp. 1–30.
- Jack, K.H., 1991. Sialons. In: Brook, R.J. (Ed.), *Concise Encyclopedia of Advanced Ceramic Materials*. Elsevier, pp. 411–416.
- Jack, K.H., Wilson, W.I., 1972. Ceramics based on the Si-Al-O-N and related systems. *Nature Physical Sciences* 238 (80), 28–29.
- Jänecke, E., 1907. Über eine Darstellungsform der van't Hoff'schen Untersuchungen über ozeanische Salzablagerungen III. *Zeitschrift für Anorganische und Allgemeine Chemie* 53, 319–326.
- Kim, Y.-W., Malik, R., 2021. SiC ceramics, structure, processing and properties. In: Pomeroy, M.J. (Ed.), *Encyclopedia of Materials: Technical Ceramics and Glasses*. Elsevier. [This volume].
- Lange, F.F., 2006. The sophistication of ceramic science through silicon nitride studies. *Journal of the Ceramic Society of Japan* 114, 873–879.
- Lewis, M.H., Powell, B.D., Drew, P., *et al.*, 1977. The formation of single-phase Si-Al-O-N ceramics. *Journal of Materials Science* 12, 61–74.
- Mandal, H., 1999. New developments in α -SiAlON ceramics. *Journal of the European Ceramic Society* 19, 2349–2357.
- Mandal, H., Thompson, D.P., Ekström, T., 1993. Reversible $\alpha \leftrightarrow \beta$ SiAlON transformation in heat treated sialon ceramics. *Journal of the European Ceramic Society* 12, 421–429.
- Mandal, H., Hoffmann, M.J., Thompson, D.P., Jack, K.H., 1999. $\alpha \leftrightarrow \beta$ phase transformation in multi-cation doped α -sialon ceramics. *Advances in Science and Technology* 13, 137–144.
- Oyama, Y., Kamigaito, O., 1971. Solid solubility of some oxides in Si_3N_4 . *Japanese Journal of Applied Physics* 10, 1637.
- Parr, N.L., Martin, G.F., May, E.R.W., 1960. Preparation, microstructure, and mechanical properties of silicon nitride. In: Popper, P. (Ed.), *Special Ceramics 1*. London: Heywood, pp. 102–135.
- Ramsdell, L.S., 1947. Studies on silicon carbide. *American Mineralogist* 32, 64–82.
- Riley, F.L., 2000. Silicon nitride and related materials. *Journal of the American Ceramic Society* 83 (2), 245–265.
- Roebuck, P., Thompson, D.P., 1977. In: Glasser, F.P., Potter, P.E. (Eds.), *High Temperature Chemistry of Inorganic and Ceramic Materials*. London: The Chemical Society, pp. 222–228.
- Rosenflanz, A., Chen, I.-W., 1999. Kinetics of phase transformations in SiAlON ceramics: I. Effects of cation size, composition and temperature. *Journal of the European Ceramic Society* 19, 2325–2335.
- Satet, R.L., Hoffmann, M.J., Cannon, R.M., 2006. Experimental evidence of the impact of rare-earth elements on particle growth and mechanical behaviour of silicon nitride. *Materials Science & Engineering A* 422, 66–76.
- Shen, Z., Nygren, M., 1997. On the extension of the α -SiAlON phase area in yttrium and rare-earth doped systems. *Journal of the European Ceramic Society* 17, 1639–1645.
- Sun, E.Y., Becher, P.F., Plucknett, K.P., *et al.*, 1998. Microstructural design of silicon nitride with improved fracture toughness: II, Effects of yttria and alumina additives. *Journal of the American Ceramic Society* 81, 2831–2840.
- Thompson, D.P., 1989. The crystal chemistry of nitrogen ceramics. *Materials Science Forum* 47, 21–42.
- Thompson, D.P., 2002. Materials Science – Cooking up Tougher Ceramics. *Nature* 417, (237).
- Thompson, D.P., Korgul, P., 1983. Sialon X-phase. In: Riley, F.L. (Ed.), *Progress in Nitrogen Ceramics* 65. Dordrecht: Martinus Nijhoff (Springer), pp. 375–380. [NATO ASI Series (Series E: Applied Sciences)].
- Thompson, D.P., Korgul, P., Hendry, A., 1983. The structural characterisation of sialon polytypoids. In: Riley, F.L. (Ed.), *Progress in Nitrogen Ceramics* 65. Dordrecht: Martinus Nijhoff (Springer), pp. 61–74. [NATO ASI Series (Series E: Applied Sciences)].
- Zernicke, J., 1955. *Chemical Phase Theory*. Deventer: Kluwer.

Si-Al-O-N Ceramics, Structure and Properties

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Introduction

SiAlONs, isostructural with Si_3N_4 , are ceramic alloys obtained by the replacement of silicon and nitrogen by aluminum, oxygen, and rare-earth (RE) cations in the crystal structure of silicon nitride (Rosenflanz, 1999; Izhevskiy *et al.*, 2000). While Si_3N_4 was discovered at the beginning of 20th century (Cao and Metselaar, 1991), partially dense Si_3N_4 ceramics were only developed in the 1950s for refractory applications such as thermocouple tubes, crucibles for molten metals and nozzles (Collins and Gerby, 1955). Dense silicon nitride was only developed in the 1960s and required the use of oxide additives to provide conditions for liquid phase sintering under applied pressure. The discovery of SiAlON ceramics was reported later in the early 1970s (Oyama and Kamigaito, 1971; Jack, 1973; Jack and Wilson, 1972). Due to their high strength, hardness, fracture toughness, corrosion and oxidation resistance, thermal shock resistance and refractoriness, Si_3N_4 and SiAlON ceramics are unique materials for applications such as cutting tools, bearings, turbochargers, engine valves and other wear resistant parts (Rosenflanz, 1999), used under aggressive conditions (Collins and Gerby, 1955; Sage and Histed, 1961; Parr, 1960). The properties and applications of both Si_3N_4 and SiAlON ceramics strongly depend on the technological development in effective densification techniques as well as starting powder quality. While high strength covalent bonds between Si^{4+} and N^{3-} give a remarkably high hardness to Si_3N_4 ceramics, self-diffusion of these ions makes these ceramics difficult to sinter without using sintering additives (Deeley *et al.*, 1961; Mitomo and Tajima, 1991). Therefore, the application of pressure assisted sintering techniques such as hot pressing (HP) (Yu *et al.*, 2017; Babini *et al.*, 1980; Bowen *et al.*, 1978; Kossowsky, 1973; Prochazka and Rocco, 1978; Wada *et al.*, 1999), gas pressure sintering (GPS) (Biswas and Riley, 2001; Hwang *et al.*, 1997; Mitomo *et al.*, 1990; Mitomo and Uenosono, 1992) and spark plasma sintering (SPS) (Wada *et al.*, 1999; Lukianova and Ivanov, 2018; Ratzker *et al.*, 2018; Lukianova *et al.*, 2017; Suganuma *et al.*, 2003) are required to obtain fully dense structures with minimum sintering additives. Thus, the solubility of Al and O as well as RE elements in the Si_3N_4 crystal structure brings a considerable advantage to SiAlONs over Si_3N_4 due to easier pressureless densification without diminishing high temperature properties (Rosenflanz, 1999).

Si_3N_4 has two major phases known as α and β , which have high hardness and toughness, respectively. Normally, α - Si_3N_4 is considered the low temperature form of Si_3N_4 (Cao and Metselaar, 1991) and a reconstructive transformation to β - Si_3N_4 occurs in the range 1400–1800°C (Cao and Metselaar, 1991; Evans and Sharp, 1971). Therefore, only the β modification exists in conventionally sintered Si_3N_4 ceramics. On the other hand, stabilization of α -SiAlON phase during sintering by proper selection of RE cations (Mandal, 1999; Ekström, 1992; Söderlund and Ekström, 1990) can be possible and is another advantage of SiAlONs compared to Si_3N_4 ceramics. Consequently, thermodynamically stable hard α -SiAlON (α') and tough β -SiAlON (β') phases can be present simultaneously, which means that optimum mechanical properties for a specific application can be designed by altering the α/β -SiAlON ratio (Kumar *et al.*, 2009).

The sintering oxides such as Y_2O_3 , Al_2O_3 , Yb_2O_3 , etc. react with nitrogen and SiO_2 , which always exists on the surface of Si_3N_4 powder particles, and form a liquid phase during sintering which is carried out in a N_2 gas atmosphere (Cinibulk *et al.*, 1992a; Ziegler *et al.*, 1987; Becher *et al.*, 1996). This liquid phase facilitates the densification and phase transformation during sintering and then solidifies as an amorphous phase around the Si_3N_4 grains (Drew and Lewis, 1974). It is well known that this amorphous phase starts to soften at temperatures around 1000°C, and deteriorates high temperature properties (Cinibulk *et al.*, 1992a; Lichvár *et al.*, 2007). Although crystallization of the grain boundary phase by a post sintering heat treatment, depending on the type and the composition of RE elements used as additives for Si_3N_4 , was reported in several studies (Lichvár *et al.*, 2007; Lee and Hilmas, 1989; Tsuge *et al.*, 1975; Weston *et al.*, 1978), the control of the crystallization of grain boundary phases is much easier for SiAlON ceramics thanks to high amounts of RE oxides. Therefore, SiAlON ceramics with superior high temperature mechanical and chemical properties can be fabricated by controlling grain boundary crystallization.

As stated above, SiAlONs are unique engineering ceramics, properties of which can be designed by controlling the α'/β' phase ratio, type of the RE additive system, “z” value of β -SiAlON (see below) indicating the solubility of Al_2O_3 in Si_3N_4 , and crystallinity of grain boundary phase. These parameters are shown schematically in Fig. 1. Here the aim is to explain and correlate the mechanical, thermal, and optical/electrical behavior of SiAlON ceramics with its corresponding structural parameters. Moreover, a brief section on applications is included in the last part to make clear structure-property-performance relationships in SiAlON ceramics.

Structure and Phases of SiAlON Ceramics

Si_3N_4 has two major polymorphs designated as α and β (Hardie and Jack, 1957) and a cubic spinel modification (γ) synthesized by application of high temperature and mechanical pressure above 15 GPa (Zerr *et al.*, 1999; Schwarz *et al.*, 2000). The crystallographic

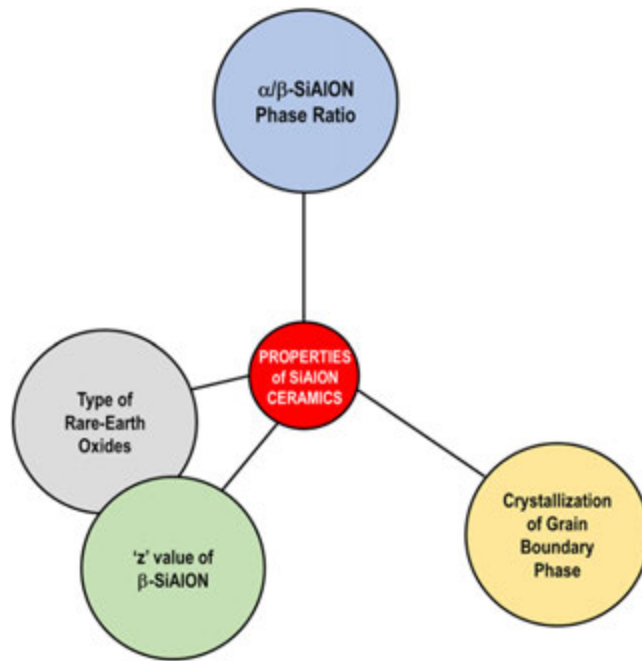


Fig. 1 The structural parameters effective on the properties of SiAlON ceramics.

structure of α ($\text{Si}_{12}\text{N}_{16}$) and β (Si_6N_8) modifications are shown in **Fig. 2** (Legut *et al.*, 2014). β - Si_3N_4 is isostructural with Be_2SiO_4 (phenacite), in which oxygen and beryllium atoms are replaced by nitrogen and silicon, respectively (Hampshire, 2007). The total structure is formed by the combination of covalently bonded SiN_4 tetrahedra and each nitrogen at the corners is shared by three tetrahedra. The tetrahedra are linked with one edge parallel and one edge perpendicular to the (0001) plane in the hexagonal structure (Schwarz *et al.*, 2000). Both phases are characterized by planar structures parallel to the basal plane. Si-N planes in β - Si_3N_4 are stacked in a sequence of ABABAB..., with large diameter channels parallel to the c -axis, while the planes in α - Si_3N_4 repeat in every four layers stacked as ABCDABCD.... with the CD layers rotated with respect to AB by 180° about the c -axis. This blocks off the continuous channels resulting in two large interstices per unit cell capable of accommodating metal (Me) cations. Therefore, the length of the c -axis of α - Si_3N_4 is twice that of the β phase (Legut *et al.*, 2014).

SiAlONs exist as α -SiAlON (α') and β -SiAlON (β'), which are isostructural with α and β silicon nitride phases, respectively. β' -SiAlONs are obtained by the replacement of Si atoms by Al in the β - Si_6N_8 crystal structure. In order to maintain the charge neutrality, equivalent numbers of N should be substituted by O atoms. This replacement of Si and N with Al and O is illustrated by the general formula of $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$, where " z " can be altered from 0 to 4.2 (Izhevskiy *et al.*, 2000; Mandal, 1999; Gauckler *et al.*, 1975; Jack, 1981; Ekström *et al.*, 1989). The stability region of β -SiAlON is narrow and lies on the Si_3N_4 -(Al_2O_3 , AlN) tie line in the phase diagram of Al_2O_3 - Si_3N_4 - SiO_2 -AlN given in **Fig. 3(a)** (Qin *et al.*, 2018; Bergman *et al.*, 1991; Mackenzie *et al.*, 1998). In the case of α -SiAlON, the stability region for α' is seen on the Si_3N_4 - $4/3(\text{Al}_2\text{O}_3$, AlN)-MeN.3AlN plane in the Me-Si-Al-O-N phase diagram (Janecke prism) shown in **Fig. 3(b)** (Me = Li, Mg, Ca, Y, RE) (Hampshire *et al.*, 1978; Thompson, 1989; Rosenflanz and Chen, 1999). The extent of this region increases with decreasing size of the Me cation (Rosenflanz and Chen, 1999; Shen *et al.*, 1997; Shen and Nygren, 1997) as well as increasing the temperature (Rosenflanz and Chen, 1999). The valency compensation is required due to the solubility of Me cations in the interstitial sites in the crystal structure. α -SiAlON, based on the α - $\text{Si}_{12}\text{N}_{16}$ crystal structure, is represented by the general formula:



where Me represents cations such as Mg, Ca, Y, Sm, Yb, etc., $x = m/v$ where v is the valency of the Me cation, and x should be a value between 0.3 and 2 (the maximum value because of 2 interstitial sites per unit cell). In α -SiAlON, the lattice strain is high due to the longer Al-N bonds ($\sim 1.87 \text{ \AA}$) replaced with Si-N bonds ($\sim 1.74 \text{ \AA}$), and this strain limits the value of m . Higher n values (more oxygen) in the formula also results in a tendency for α -SiAlON to be unstable and to formation of β -SiAlON (Mandal, 1999).

Mechanical Properties of SiAlON Ceramics

Ceramics have many advantages, such as high hardness, high wear resistance and chemical stability at high temperatures, over metallic materials for specific high temperature applications. However, they are susceptible to impact loads due to their strong ionic and/or directional covalent bonding. Although the brittle nature of ceramics limits their utilization, there are some methods

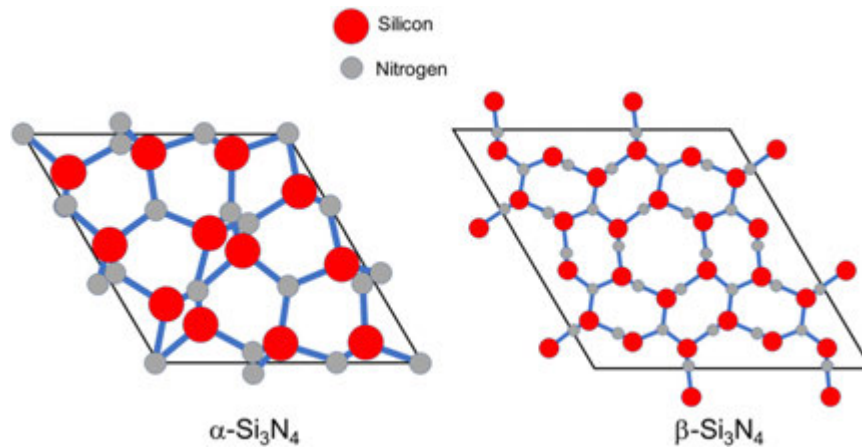


Fig. 2 Crystal structure of $\alpha\text{-Si}_3\text{N}_4$ and $\beta\text{-Si}_3\text{N}_4$ viewed along their crystallographic c-axes. For the β phase the $2 \times 2 \times 1$ supercell is shown. Adapted from Legut, D., Wdowik, U.D., Kurtyka, P., 2014. Vibrational and dielectric properties of $\alpha\text{-Si}_3\text{N}_4$ from density functional theory. Materials Chemistry and Physics 147, 42–49.

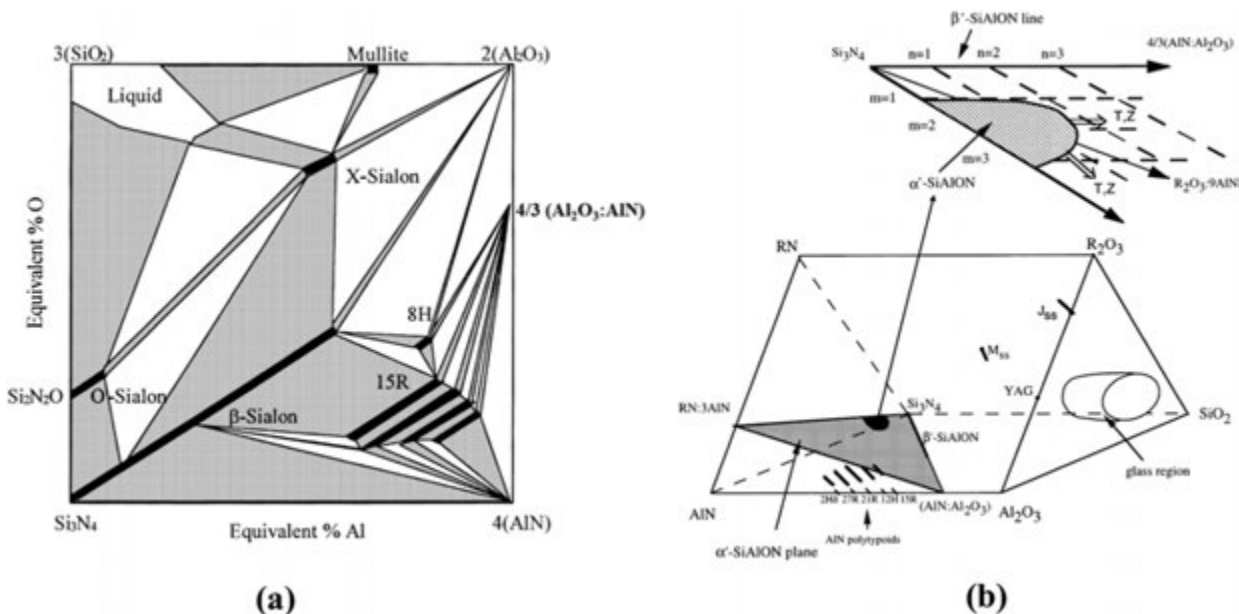


Fig. 3 (a) $\text{Al}_2\text{O}_3\text{-Si}_3\text{N}_4\text{-SiO}_2\text{-AlN}$ phase diagram at 1700°C and (b) stability region of $\alpha\text{-SiAlON}$ on the $\text{Si}_3\text{N}_4\text{-}4/3(\text{Al}_2\text{O}_3\cdot\text{AlN})\text{-MeN.3AlN}$ plane in the Janecke prism. Reproduced from (a) Mackenzie, K.J., Sheppard, C.M., Barris, G.C., *et al.*, 1998. Kinetics and mechanism of thermal oxidation of SiAlON ceramic powders. *Thermochimica Acta* 318, 91–100. (b) Rosenflanz, A., Chen, I.-W., 1999. Kinetics of phase transformations in SiAlON ceramics: I. Effects of cation size, composition and temperature. *Journal of the European Ceramic Society* 19, 2325–2335.

to improve the resistance to propagation of a micro-crack by various mechanisms such as crack deflection, bridging, bowing, shielding etc. (Pelleg, 2014; Wachtman *et al.*, 2009). With the possibility to change the β and α phase content by slightly altering the composition, hardness and toughness of SiAlON ceramics can be designed for a specific application. While $\alpha\text{-SiAlON}$ is 40% harder than β -phase thanks to its 4 layers repetitive crystallographic structure (Ekström and Nygren, 1992), the rod-like grain morphology of $\beta\text{-SiAlON}$ grains (Satet *et al.*, 2006) gives the ability to deflect and to bridge a propagating crack as illustrated in Fig. 4, which shows the representative microstructure of an $\alpha/\beta\text{-SiAlON}$ ceramic. In the corresponding back-scattered electron (BE) SEM image, $\beta\text{-SiAlON}$ phase is seen as large dark gray rod-like grains, $\alpha\text{-SiAlON}$ phase appears as equiaxed and finer and light gray grains due to the partial solubility of high atomic number RE elements in the $\alpha\text{-Si}_3\text{N}_4$ crystal lattice. The sub-micron size white dots distributed throughout the structure are the grain boundary oxynitride crystalline/amorphous phase. When a crack starts to propagate along its path, it encircles the grain bridges. On the other hand, the frictional force between a grain and its surroundings may still provide a closure force on the crack surface. If grains are rod-like as in β , frictional bridging is remarkably effective for fracture resistance (Wachtman *et al.*, 2009). The crack bridging is expressed as the main toughening mechanism in alumina (Knehans and Steinbrech, 1982) and Si_3N_4 (Rödel, 1992; Becher, 1991) ceramics.

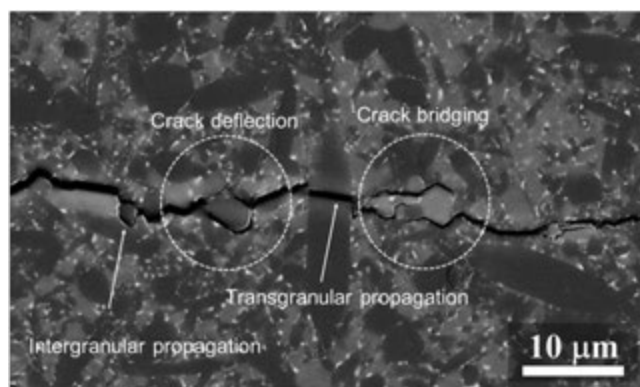


Fig. 4 A crack propagation profile in the microstructure of a representative α/β -SiAlON ceramic. Reproduced from Çelik, A., 2013. The Performance of SiAlON Ceramics on Drilling Operations of Carbon Fiber Reinforced Polymer Composites. (Doctoral thesis). Eskişehir: Anadolu University.

β - Si_3N_4 /SiAlON grains grow with the geometry of a hexagonal prism with pyramidal ends which are called basal planes. According to the periodic bond chain (PBC) theory (Krämer *et al.*, 1994), the growth perpendicular to the basal planes in a gas phase (porosity) is energetically favored and results in anisotropy. On the other hand, this model does not consider the atoms other than silicon and nitrogen adsorbed on the prismatic and basal planes and not applicable to the materials with high anisotropy (Satet *et al.*, 2006). In the case of Si_3N_4 or SiAlON, RE oxides, alumina and silica form an oxynitride grain boundary liquid phase which surrounds the nucleated grains during sintering. Results obtained by experimental studies explain the effect of grain boundary phase composition on the degree of anisotropic growth in Si_3N_4 /SiAlON ceramics and hence properties. Anisotropy is the result of the difference in growth rate of basal and prismatic planes (Hoffmann and Holzer, 2003) and fracture toughness increases with the increase in aspect ratio of the grains (Ye *et al.*, 2020) in which is related to the ionic radius of the RE element (Satet *et al.*, 2006; Becher *et al.*, 2008; Krämer *et al.*, 1993; Satet and Hoffmann, 2004; Satet and Hoffmann, 2005). For example, the dependency of anisotropic grain growth on RE addition is clearly shown by the fact that elongated grains with an aspect ratio of 8:1 can be obtained by La_2O_3 addition whereas relatively shorter grains (aspect ratio of 2:1) are observed by the addition of Lu_2O_3 (Becher *et al.*, 2008).

It is obvious that a bimodal microstructure consisting of elongated grains in a fine matrix results in toughening of Si_3N_4 and SiAlON ceramics because of crack deflection and crack bridging by larger elongated grains (Becher *et al.*, 1995). While β -phase already showed anisotropic growth as outlined above, further studies were undertaken to attempt to form α -SiAlON phase with elongated grains by (1) controlling grain boundary chemistry (Chen *et al.*, 2002; He *et al.*, 2011; Santos *et al.*, 2004; Zenotchkine *et al.*, 2003), (2) introducing seeds for external nucleation sites for elongated α grains (Kim *et al.*, 2000; Shuba and Chen, 2002; Zenotchkine *et al.*, 2002) and (3) application of heat treatment (Kurama *et al.*, 2002; Ye *et al.*, 2003; Ye *et al.*, 2004). Similar to the growth of β phase, the aspect ratio of α -SiAlON grains also increases with the ionic radius of RE elements in the composition. This can be attributed to the change in viscosity of the grain boundary glassy phase (Shelby and Kohli, 1990; Hampshire and Pomeroy, 2004) as well as the stability of α -SiAlON as a function of the dopant ion radius. If the RE element is too large to enter the interstitial sites in the α - Si_3N_4 structure, mass transfer and, therefore, driving force for grain growth becomes relatively low (Chen *et al.*, 2002). This results in large differences in the growth rates of basal and prismatic planes.

The utilizing of seed crystals with an exact composition is another method for obtaining elongated α -SiAlON grains. The number of elongated grains has a linear relationship with the amount of seed crystals. On the other hand, a similar relationship may not be observed in fracture toughness because of the reduction of the aspect ratio of the elongated grains with further seeding (Kim *et al.*, 2000). Moreover, a microstructure with very large elongated α -SiAlON grains gives rise to formation of stress points and reduction in strength of the overall material (Shuba and Chen, 2002). Therefore, the addition of seed crystals in small amounts (1–8 wt%) is suggested to optimize the mechanical properties.

A post heat treatment after sintering is generally performed to crystallize the amorphous grain boundary phase, but it also can increase α -SiAlON grain aspect ratio. On the other hand, crystallization of grain boundary phases can cause a considerable increase in interfacial bond strength for the systems containing excess amounts of rare-earth oxides. Thus, fracture toughness of SiAlON ceramics can decrease due to change in fracture mode from inter- to transgranular, which inhibits toughening mechanisms (Ye *et al.*, 2003). A similar effect is also observed for Al-O bonds replaced by Si-N (decreasing z value of β -SiAlON) (Becher, 1991; Sun *et al.*, 1998, 1999). The bond strength at the β -SiAlON-oxynitride glass interface is determined by the concentration of Al and O atoms. If z value increases up to 0.2, the number of strong chemical bonds at the interface increases rapidly, and the debonding becomes more difficult which results in an increase in the number of transgranular fractures. This leads to a further remarkable reduction in fracture toughness (Sun *et al.*, 1998). The further increase of z value from 0.3 to 1.1 results in a slight decrease of fracture toughness of SiAlON ceramics (Acikbas and Kara, 2017).

To conclude, room temperature mechanical properties of SiAlON ceramics strongly depend on (1) the α/β -SiAlON phase ratio, (2) the number and aspect ratio of elongated α and β -SiAlON grains in the microstructure, which is strongly influenced by the type

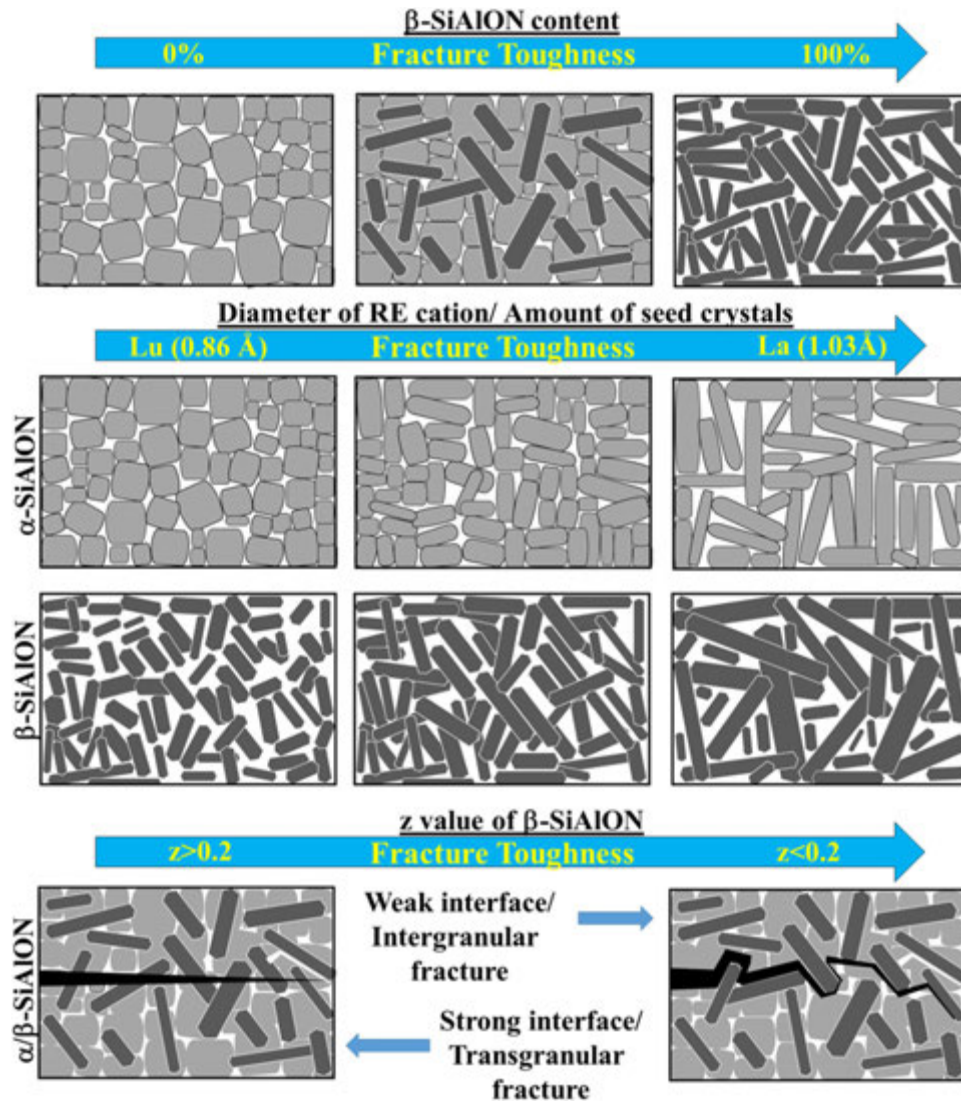


Fig. 5 Schematic illustration of the effect of various parameters on the fracture toughness of SiAlON ceramics.

of the RE elements and the bond strength of the SiAlON-grain boundary phase interface, on which the crystallinity of the grain boundary phase and z value of β -SiAlON are significant. A summary of these parameters controlling the mechanical properties of SiAlON ceramics is illustrated in Fig. 5.

Thermal Properties of SiAlON Ceramics

SiAlON ceramics are mainly utilized in applications at high temperatures such as cutting tools for high speed machining of metals, refractories for non-ferrous molten metals, wire drawing dies and welding pin locaters (De Faoite *et al.*, 2012). It is, therefore, critically important to determine the thermal properties of SiAlON ceramics. Within this section, the high temperature behavior of SiAlON ceramics and the key parameters are discussed.

Thermal Conductivity

As a successful cutting tool material for high-speed machining of cast irons and Ni-based high temperature alloys, the dispatch of heat from the SiAlON tool face is a critical issue since the excess heat accumulated on the surface results in temperature localization which in turn activates diffusion processes between tool and metal atoms and, thus, wear of the tool material. With a relatively simple structure in comparison to SiAlONs, the thermal conductivity of Si_3N_4 was reported as between $100\text{--}180 \text{ W m}^{-1} \text{ K}^{-1}$ (Hayashi *et al.*, 2001; Zhu *et al.*, 2006, 2007; Yokota and Ibukiyama, 2003b; Kim *et al.*, 2017) by experimental results, while it can

theoretically reach $170 \text{ W m}^{-1} \text{ K}^{-1}$ and $450 \text{ W m}^{-1} \text{ K}^{-1}$ along a- and c-axis directions, respectively (Hirosaki *et al.*, 2002). The reasons for much lower thermal conductivity of Si_3N_4 ceramics than the theoretical values were attributed to factors causing the scattering of phonons (lattice vibrations) such as the presence of amorphous grain boundary phases with very low thermal conductivity ($1 \text{ W m}^{-1} \text{ K}^{-1}$) (Zhu *et al.*, 2007; Kim *et al.*, 2017; Kitayama *et al.*, 1999), impurities, vacancies, etc. (Kitayama *et al.*, 2000; Yokota and Ibukiyama, 2003a).

SiAlONs are solid solutions obtained by the introduction of different atoms into the α and β Si_3N_4 crystal structures. Therefore, it is normal to see much lower thermal conductivity for SiAlON ceramics due to these foreign atoms as well as the presence of both α and β phases together. As with the mechanical properties, the thermal conductivity in SiAlON ceramics strongly depends on the amount and composition of each phase (α , β and grain boundary phase) and microstructural properties such as grain size, amount of grain boundary phase, grain size distribution and elongation of grains. The ratio of α/β -phases is one of the most important factors affecting the thermal conductivity. An inverse relationship between α -SiAlON phase content and thermal conductivity of an α/β -SiAlON composite was reported (Liu *et al.*, 1995). This is related to the differences in crystallographic structures of α and β phases. In the β -SiAlON structure, SiN_4 tetrahedra are linked together to form tunnel (channel) structure (Fig. 2). On the other hand, this tunnel structure does not exist in α -SiAlON due to the presence of the additional glide plane, which behaves as a defect (Kohatsu and McCauley, 1974) and results in the formation of the interstitial sites in which the RE and other cations are accommodated. Thus, the higher degree of asymmetry and complexity of the crystal structure of α -SiAlON reduces the phonon mean free path (Liu *et al.*, 1995). Since different RE elements from Lu^{3+} to Nd^{3+} (Redington *et al.*, 1991) can be incorporated into the α -SiAlON structure, the thermal conductivity of α -phase stabilized with different additives is expected to show some minor variation. The α -SiAlON ceramics prepared by utilizing single dopants and smaller cations such as Lu^{3+} , Yb^{3+} , etc. have higher thermal conductivities due to less phonon scattering by smaller elements and the simplicity of the crystal structure (Kushan *et al.*, 2007).

The thermal conductivity of Si_3N_4 ceramics is very sensitive to lattice oxygen content and remarkably reduces even at low oxygen concentrations ($z < 0.03$) (Kusano *et al.*, 2014). Similarly, the z value of β -SiAlON is the other main determinant in reducing thermal conductivity, apart from α -phase content and the type of RE elements. In commercial α/β -SiAlON ceramics, β -phase generally has a z value in the range ~ 0.2 -1 whereas $z = 0$ for Si_3N_4 ceramics. The increase in lattice defects with the replacement of Al-O bonds for Si-N bonds results in more phonon scattering and, accordingly, lower thermal conductivity (Yi *et al.*, 2014; Dong *et al.*, 2012). Finally, the crystallization of grain boundary phase is also an influencing factor on thermal conductivity of SiAlON ceramics. Generally, amorphous materials show lower thermal conductivity and diffusivity than crystalline counterparts in a specific composition because of higher phonon scattering. Therefore, crystallization of the grain boundary phase by application of post sintering heat treatment results in slightly higher thermal conductivity (Bentsen *et al.*, 1984).

Thermal Shock Resistance

Ceramics are susceptible to catastrophic fracture under severe thermal transient conditions. The ability to survive against sudden temperature differences is defined as "thermal shock resistance" (Li *et al.*, 2015). In simple terms, the thermal shock resistance parameter, R' , is the maximum allowable temperature difference ΔT_c to which a ceramic can be subjected without initiation of fracture:

$$R' = \Delta T_c = \frac{\sigma_f(1 - \nu)}{\alpha E} k \quad (1)$$

It is controlled by the fracture strength (σ_f), thermal expansion coefficient (α), elastic modulus (E) and thermal conductivity (k) of the material (Manson and Smith, 1955). Increase in σ_f and k and decrease in α improves the thermal shock resistance of brittle ceramics. The thermal shock resistance of SiAlONs is remarkable thanks to their relatively high fracture strength and thermal conductivity among structural ceramics and is of great importance especially for refractory and cutting tool applications (Pettersson *et al.*, 2002). However, there are limited number of studies performed to analyze the effect of structural parameters on the thermal shock resistance of monolithic SiAlON ceramics (Li *et al.*, 2015; Pettersson *et al.*, 2002; Lee *et al.*, 1989; Liu *et al.*, 2010; Pettersson *et al.*, 2001; Ye *et al.*, 2010; Zheng *et al.*, 2012). The thermal shock resistance of β -SiAlON is strongly influenced by microstructural and mechanical properties. The change in fracture mode from transgranular to intergranular with decreasing z value results in better thermal shock resistance. Moreover, utilizing higher quantities of sintering additives and higher sintering temperature results in formation of more elongated β grains, which in turn gives higher fracture toughness β -SiAlON ceramics and, therefore, higher thermal shock resistance (Pettersson *et al.*, 2002). For quenching cycles in which the temperature difference is above 1000°C , the thermal oxidation can provide a positive effect on the closure of the thermal cracks. As a result of the oxidation of SiAlON grains, viscous products can fill the tip of the micro-cracks and make the propagation more difficult (Liu *et al.*, 2010).

Another approach is to reinforce SiAlON ceramics in terms of fracture toughness by the addition of other ceramics in particulate (Tian *et al.*, 2011; Acikbas *et al.*, 2014) or platelet shape (Tian *et al.*, 2019). For example, addition of 25 wt% TiN to an α/β -SiAlON improves the thermal conductivity and fracture toughness as well as thermal shock resistance of the matrix considerably (Acikbas *et al.*, 2014).

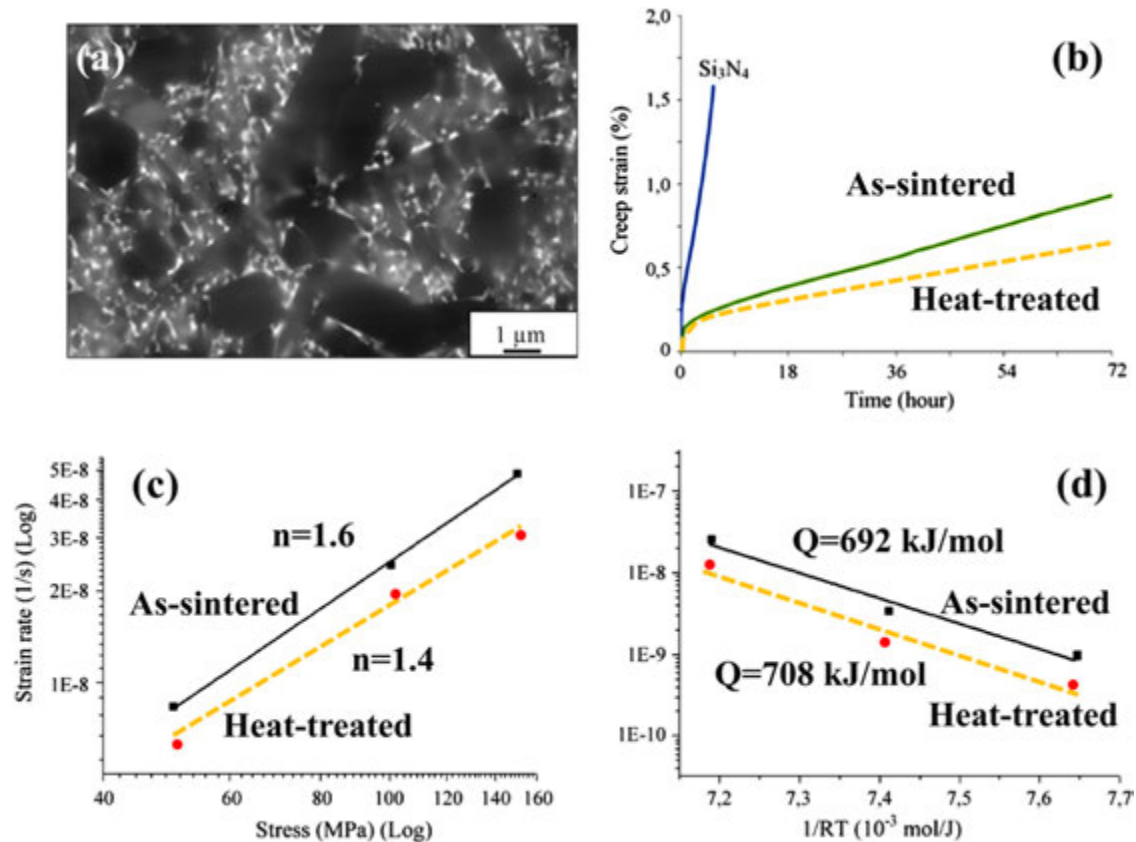


Fig. 6 (a) Microstructure of (Y-Sm-Ca) multi-doped α/β -SiAlON ceramic (b) comparative creep strain-time curves of as-sintered and heat-treated ceramics together with Si_3N_4 ($T = 1400^\circ\text{C}$, $\sigma = 100 \text{ MPa}$), (c) stress and (d) temperature dependence of strain rate of as-sintered and heat-treated SiAlON ceramics. Adapted from Uludağ, A., Turan, D., 2011. High temperature bending creep behavior of a multi-cation doped α/β -SiAlON composite. *Ceramics International* 37, 921–926. Turan, D., Uludag, A., Turan, S., 2019. Effect of heat treatment on the creep behavior of α/β SiAlON sintered with multication oxide sintering additives. *International Journal of Applied Ceramic Technology* 16, 404–409.

Creep Behavior of SiAlON Ceramics

Creep is defined as time dependent deformation of a material under stress at high temperature and is considered a good representation for high temperature behavior of SiAlON ceramics utilized especially as tools for metal machining operations. The creep tests are generally performed by the application of static load on the material in tension or compression at high temperature. At the end of the test, a typical strain-time graph with three distinct regions is obtained. In the first region (primary creep), strain rate gradually decreases. Then, the rate becomes constant in a secondary creep region, and, finally, a rapid increase is observed in the tertiary creep region prior to fracture (Fox and Hellmann, 2008). In the case of Si_3N_4 and SiAlON ceramics, the tertiary creep region is not observed due to the brittle nature of Si_3N_4 based ceramics (Menon *et al.*, 1994; Luecke *et al.*, 1995; Wereszczak *et al.*, 1999).

The creep resistance of SiAlON ceramics is controlled by microstructural features such as α/β phase ratio, morphology of the grains, grain size, grain boundary phase composition and structure (Fox and Hellmann, 2008; Fox *et al.*, 2006). An improved creep resistance of α -SiAlON can be obtained by reducing the grain boundary phase via incorporation of additive elements into the crystal structure (Rosenflanz, 2002). On the other hand, β -SiAlON phase shows better creep resistance than α -SiAlON thanks to its more elongated grain structure, which hinders grain boundary sliding (Wereszczak *et al.*, 1998). While the effect of grain size is less pronounced, the chemistry of the grain boundary phase is a much more influencing factor on the creep performance of Si_3N_4 -based ceramics (Wiederhorn *et al.*, 2004).

The type of RE oxides used for liquid phase sintering of SiAlON ceramics has a strong effect on the creep resistance of SiAlON ceramics since it determines the viscosity of the grain boundary phase at high temperatures. The smaller the cation, the higher the viscosity, which results in reduced grain boundary sliding and, thus, improved creep resistance. The effect of viscosity of the grain boundary phase can also be seen in the strain rate-time curve in which a slowly decreasing rate rather than a steady-state creep rate is generally observed for Si_3N_4 /SiAlON ceramics. The decreasing rate is attributed to the gradual increase in viscosity of the grain boundary phase due to the partial crystallization and oxidation during creep (Cinibulk *et al.*, 1992b). Accordingly, the crystallization of the grain boundary phase is as important as grain boundary composition on creep resistance. A good example is the differences in creep behaviors of as-sintered (Turan *et al.*, 2019) and subsequently heat treated α/β -SiAlON ceramic (Turan *et al.*, 2019) prepared

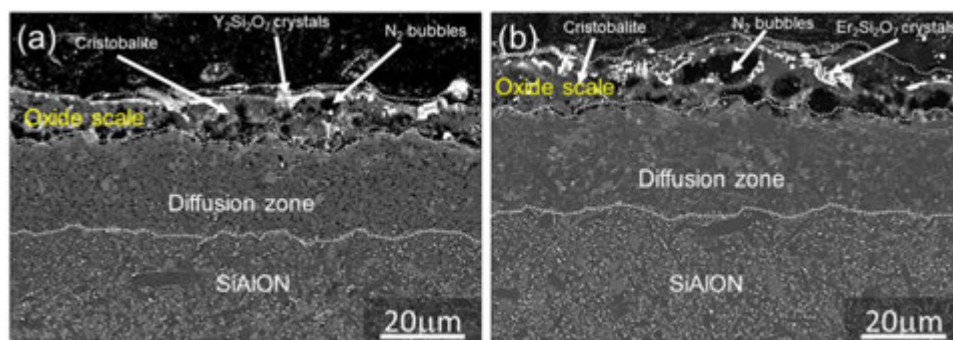


Fig. 7 Cross-section scanning electron micrographs of (a) Y- and (b) Er-doped α/β -SiAlON ceramics oxidized at 1350°C for 2 h. Reproduced from Çelik, A., 2019. Oxidation behavior of Y_2O_3 and Er_2O_3 -doped- α/β -SiAlON ceramics. Akademik Platform Mühendislik ve Fen Bilimleri Dergisi 7, 381–388.

with Y^{3+} as the main dopant and small amounts of Sm^{3+} and Ca^{2+} . The as-sintered ceramic has a considerable amount of crystalline grain boundary phase in the form of melilite ($Ln_2Si_{3-x}Al_xO_{3+x}N_{4-x}$) as shown in Fig. 6(a). Therefore, the creep resistance of this ceramic is observed to be much higher than Si_3N_4 as shown in Fig. 6(b). After a post heat treatment performed at 1600°C for 2 h, the crystallization of melilite phase at the triple pockets and grain boundaries is enhanced which provides an improvement in creep resistance (Uludağ and Turan, 2011; Turan et al., 2019). The stress exponent (n) gives an indication of creep mechanisms in SiAlON ceramics such as viscous flow, grain boundary sliding, cavitation, etc. and was determined as 1.6 and 1.4 for as-sintered and heat treated SiAlON ceramics, respectively, as shown in Fig. 6(c). These values show that the main creep mechanism for SiAlON under bending stress is grain boundary sliding. The activation energies indicating the creep resistances were also calculated as 692 kJ/mol and 708 kJ/mol for the corresponding ceramics as shown in Fig. 6(d).

Oxidation Behavior and Chemical Stability of SiAlON Ceramics

Oxidation is one of the main problems not only for SiAlON ceramics, but also for the other non-oxide ceramics utilized in high temperature applications under normal atmospheric conditions. It is well known that the oxidation resistance of SiAlON ceramics depends on the individual parameters influencing the properties of α , β and grain boundary phases. In addition to these parameters, it should be noted that insufficient densification after sintering also has a detrimental effect on the oxidation resistance (Hou et al., 2012). Only 2% lower densification of β -SiAlON ceramics results in a considerable reduction in oxidation resistance. For β phase, the z value in the general formula of $Si_{6-z}Al_zO_{2.5}N_{8-z}$, indicating the solubility of Al and O atoms in crystal structure of β - Si_3N_4 , is known to have a significant effect on the properties including oxidation resistance. The formation of crystalline and/or amorphous oxide products as a result of oxidation reactions is affected by the amount and viscosity of the grain boundary phase and also the z value of β -SiAlON (Lewis and Barnard, 1980; Pomeroy and Hampshire, 1985). While the oxidation kinetics for SiAlON ceramics generally obey a parabolic rate law (Shimada et al., 1998; Singhal, 1976), some deviation occurs with the change in z value of β -SiAlON which directly determines the type of oxidation products. The increase in the crystallization of oxide products with increasing z value can be assumed as a positive effect due to the formation of a more durable layer against inward diffusion of oxygen, but this layer also prevents outward diffusion of gas products (especially N_2), which results in formation of bubbles in the oxide scale and, thus, discontinuity. After formation of bubbles and cracks in the oxide scale, the diffusion becomes severe again. Consequently, the oxidation kinetic is slower for lower z values due to the formation of a more continuous protective oxide scale (Yi et al., 2010).

The oxidation resistance of α -SiAlON is higher than that of β -phase due to lower amount of grain boundary phase in the final microstructure as a result of incorporation of dopant cations into the α -SiAlON structure. The formation of cristobalite and mullite in the oxide scale is independent from the RE elements for α -SiAlON ceramics. These two crystalline phases are good protective barriers for inward diffusion of oxygen in the oxide layer and outward diffusion of dopants through grain boundaries. However, after crystallization of rare-earth containing silicates and aluminates, the protective nature of the scale is changed, unavoidably. The types of crystalline phases formed is the main determinant of the oxidation resistance of α -SiAlON ceramics and this is controlled by the dopants (Yu et al., 2004; Nordberg et al., 1998; Çelik, 2019). It is possible to conclude that improved oxidation resistance can be obtained for α -SiAlON ceramics containing rare-earth cations such as Y^{3+} , Yb^{3+} , Er^{3+} , etc., which leave oxygen-rich grain boundary phases after sintering (Bergman et al., 1991; Mackenzie et al., 1998). These ceramics experience silicate crystallization in the oxide scale during oxidation reactions. If the oxide scale consists mainly of aluminate crystals, as in the case of Sm^{3+} and Nd^{3+} , then the oxide scale also has large bubbles, indicating N_2 gas evaporation from oxidation of the grain boundary phase, which is generally nitrogen-rich melilite. The easy removal of gas bubbles also indicates a much lower viscosity silicate liquid phase is present (Mackenzie et al., 1998). Representative scanning electron micrographs of Y- and Er-doped α/β -SiAlON ceramics after oxidation tests performed at 1350°C for 2 h are shown in Fig. 7 (Çelik, 2019). The larger amount of bubble formation for the Er-doped sample is attributed to the higher degree of crystallization of the grain boundary phase in the form of melilite. The

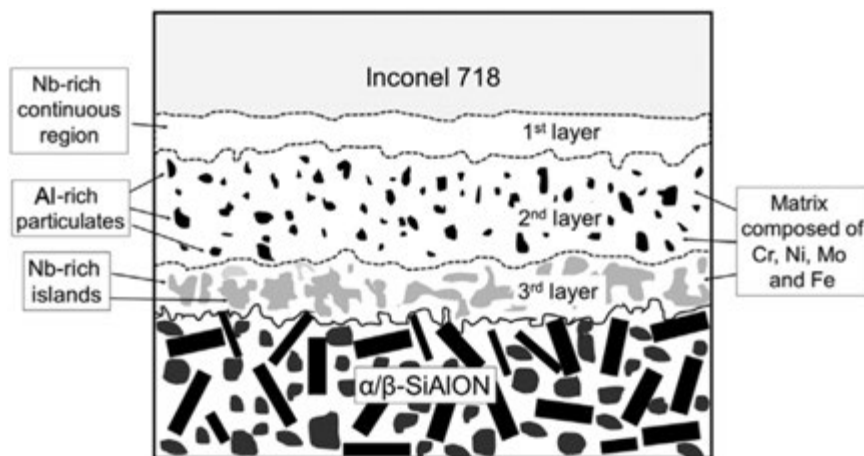


Fig. 8 Schematic illustration of the structure of the diffusion interface between SiAlON and Inconel 718 alloy. Reproduced from Çelik, A., 2018. Dopant-dependent diffusion behavior of SiAlON ceramics against Inconel 718 superalloy. *Ceramics International* 44, 17440–17446.

utilization of alkali and alkaline earth oxides rather than RE oxides gives rise to formation of low eutectic liquids and foam-like oxide scales on the surface of the oxidized ceramics. Due to the rapid diffusion of oxygen and other elements through this foam-like scale, a severe oxidation of α -SiAlON ceramics doped with alkaline oxides is observed (Yu *et al.*, 2004; Liu *et al.*, 2017).

Because SiAlONs are generally used as refractory parts and cutting tools in metallurgical and machining industries, respectively, the chemical stability of these ceramics against metals at high temperatures needs to be taken into consideration. When Si_3N_4 based ceramics are in contact with ferrous molten alloys such as steel, solid solution of Si in Fe occurs and various silicides, Fe_3Si , Fe_5Si_3 and FeSi are formed as a result of severe corrosion (Shimoo *et al.*, 1997; Křestán *et al.*, 2007). A similar diffusion-based reaction between SiAlON and steel is also observed due to the high tool-chip contact length in machining operations of steel with SiAlON cutting tools (Buljan and Wayne, 1989). Therefore, chemical resistance is one of the main parameters for tool selection for machining of alloys containing high amounts of Fe. The other class of metals, which cannot be machined with SiAlON tools is titanium and its alloys due to chemical incompatibility of highly reactive Ti and the elements present in SiAlON tools (Tunckan *et al.*, 2013, 2019). In this case, the formation of complex Ti-Si-N compounds at the interface inhibits the utilization of SiAlON ceramics for machining of Ti-based alloys. The chemical stability of SiAlON tools also plays an important role in high speed machining of Ni-based superalloys. Since there are too many elements available in both SiAlONs and superalloys, the diffusion process is quite complicated. In Fig. 8, a schematic illustration of the interface between a SiAlON and Inconel 718 alloy is shown in which three distinct layers are formed because of severe competitive diffusion from each side (Çelik, 2018). The thickness of the diffusion zone depends more on the crystallinity of the grain boundary phase rather than parameters related to the α and β phases such as α/β ratio, z value, aspect ratio, etc.

Optical Properties of SiAlON Ceramics

From the simultaneous discovery in Japan (Oyama and Kamigaito, 1971) and in England (Jack and Wilson, 1972) of β -SiAlON and that of α -SiAlON (Hampshire *et al.*, 1978), to date SiAlON ceramics are well known as impressive materials for structural applications due to their unique thermo-mechanical properties controlled by their structural parameters. Chronologically, β -SiAlON was first obtained as optically transparent with 50% of infrared transmittance (Mitomo *et al.*, 1982), and then absorption spectra of RE doped α -SiAlONs were reported at the end of 1990s (Shen *et al.*, 1997; Karunaratne *et al.*, 1996). The factors which are effective for the optical transmission of polycrystalline materials are divided into two categories: (1) intrinsic factors such as bond strength and vibrational energy of the bonds and (2) extrinsic factors such as porosity, impurities, grain boundary phases, etc. (Fox, 2002). Therefore, obtaining full densification after sintering, reducing the amount of grain boundary phases as much as possible and keeping the microstructure uniform and more equiaxed are necessary to eliminate the external factors (Joshi *et al.*, 2012). Besides equiaxed grain shape, selective dissolution of RE ions from the grain boundary phase into the crystal structure gives a considerable advantage to α -SiAlON ceramics in terms of reduction of grain boundary phase and makes it a suitable material for applications in which optical transparency is required. In α -SiAlON ceramics, distribution, size and shape of grains, amount of secondary amorphous and crystalline phases are the characteristic factors which affect optical transmittance. These factors are directly related to the type of metal cation in SiAlON systems (Su *et al.*, 2004b). In contrast to improved fracture resistance by using the large RE elements for elongation of α and/or β -SiAlON grains, the aim here is to obtain more equiaxed grains and stabilization of α phase with smaller size cations (Joshi *et al.*, 2012; Su *et al.*, 2004b). Moreover, sample thickness (Su *et al.*, 2004c), distribution of rare earth elements in α -SiAlON grains (Su *et al.*, 2004a), and carbon contamination arising from

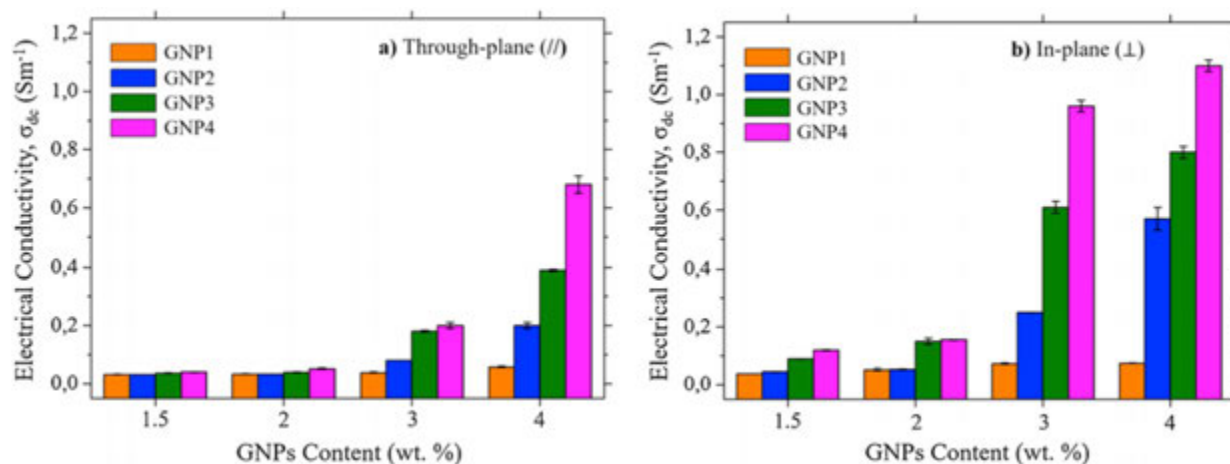


Fig. 9 Electrical conductivity differences between SiAlON-GNPs composites in the (a) through-plane (//) and (b) in-plane (⊥) directions at the same GNPs contents. Reproduced from Baskut, S., Turan, S., 2020. The effect of different GNPs addition on the electrical conductivities and percolation thresholds of the SiAlON matrix composites. *Journal of the European Ceramic Society* 40, 1159–1167.

the sintering environment during hot pressing (Chen *et al.*, 2005), also have considerable effects on the transparency of α -SiAlON ceramics.

Phosphors are high purity inorganic materials that emit light when exposed to various excitation sources such as photons, electrons or an electrical field. These materials are used as field emission displays, fluorescent lamps, cathode-ray tubes, etc. (Blasse and Grabmaier, 1994; Xie *et al.*, 2002). A luminescent material is composed of a host lattice and small amounts of impurity ions with a luminescent property (Joshi *et al.*, 2012). The inorganic phosphors based on RE doped oxynitride ceramics are popular as host materials due to their nontoxicity, thermal stability, and luminescence properties (Höppe *et al.*, 2000; Uheda *et al.*, 2000; Jansen and Letschert, 2000). Among these oxynitrides, hexagonal α -SiAlON is one of the most attractive materials for optical luminescence applications due to its suitable crystal structure for anti-stokes photoluminescence compared with cubic crystals (Krämer *et al.*, 2004; Suyver *et al.*, 2006; Joshi *et al.*, 2015). On the other hand, detailed TEM investigations revealed that not only α -phase but also β -SiAlON has the ability to incorporate some RE elements, such as Yb and Ce, in its crystal structure (Yurdakul *et al.*, 2011). This gives potential applications for α/β -SiAlON ceramics as luminescent materials in which the emission color depends on the luminescence cation. The yellow-emitting Ca-SiAlON:Eu²⁺ is attracting great attention because it can be used to create warm white LEDs (Blasse and Grabmaier, 1994; Xie *et al.*, 2016, 2006, 2004). The green-emitting Mg-SiAlON:Er³⁺ phosphors have potential applications in windows for solar cells (Yurdakul *et al.*, 2011).

Electrical Properties of SiAlON Ceramics

The electrical conductivity of SiAlON ceramics is very low due to absence of charge carrier free electrons and/or ions (Thorp and Sharif, 1976; Ukyo *et al.*, 1979; Mitomo and Uemura, 1981). Therefore, the application of SiAlON ceramics related to electrical properties is restricted to insulator materials. However, there is still a strong demand for electrically conductive SiAlON ceramics because of their outstanding thermo-mechanical properties which make SiAlONs suitable for a wide range of electrical applications such as glow-plugs, heaters, igniters, etc. (Ayas *et al.*, 2008). Although much higher electrical conductivity can be obtained by doping of α -SiAlON ceramics with Li (1000 times higher than that of pure SiAlON) (Sharif *et al.*, 1981), the general approach to improve the conductivity of SiAlONs is the addition of conductive secondary phases such as TiN (Ayas *et al.*, 2008; Bellosi *et al.*, 1992), TiCN (Ayas and Kara, 2011), SiC (Kim *et al.*, 1998; Yamada and Kamiya, 1999) as well as graphene (Baskut *et al.*, 2018; Baskut and Turan, 2020). A good example for the efficiency of different graphene-nanoplatelets (GNPs) (GNP1-GNP4) as electroconductive reinforcement phases is given in Fig. 9 (Baskut and Turan, 2020). While the electrical conductivity of pure SiAlON ceramic is around 10^{-9} S m⁻¹, the conductivity of the ceramic composite is drastically increased with the addition of only 1.5 wt% GNPs. It is also observed in Fig. 9 that the SiAlON-GNPs composites have a remarkable anisotropy in electrical conductivity values due to the vertical alignment of GNPs to the pressing direction during spark plasma sintering (SPS).

Applications of SiAlON Ceramics

The application of SiAlON ceramics is increasing gradually due to technological progress on the synthesis of high purity raw starting powders as well as efficient sintering techniques such as hot pressing, gas pressure sintering and spark plasma sintering, etc. Fig. 10 shows images of some structural SiAlON products used mainly as relatively low temperature wear resistant parts (attritor



Fig. 10 Representative images of SiAlON wear parts, solid milling cutters and turning inserts used in structural applications (photo courtesy of MDA Advanced Ceramics Co.).

mill arms for fine milling of ceramic slurries, pipe bending rollers, etc.) and cutting tools for metal machining operations. The possibility to change the ratio of hard α -SiAlON to tough β -SiAlON by altering the composition makes α/β -SiAlON ceramics unique for wear parts utilized at relatively low temperature applications. The wear of SiAlON ceramics in such applications is directly related to the tribological behavior of these materials which has been the subject of various research investigations (Kumar *et al.*, 2009; Jones *et al.*, 2003; Kurama *et al.*, 2009; Sun *et al.*, 2017). The general results in these studies proved that the amount of β -SiAlON phase, the crystallization of grain boundary phase and z value are critical factors influencing the total amount of wear. The difficulties of manufacturing large parts with complicated geometries (Fig. 10) is the major problem for commercializing of SiAlON wear resistant components.

The main utilization of SiAlON ceramic inserts is the high speed turning of cast irons at cutting speeds up to 1000 m/min. (Mandal *et al.*, 2003; Bitterlich *et al.*, 2008; Tu *et al.*, 2016; Bitterlich and Friederich, 2007; Acikbas *et al.*, 2012). The application of high cutting speeds is related to the discontinuous chip formation due to the relatively brittle nature of cast iron during cutting operations. On the other hand, use of SiAlON inserts for turning of ferrous metals is constrained by the ductility of the metal part. Therefore, steels as a more ductile version of cast iron cannot be machined with SiAlON inserts because of the high chemical interaction between tool and workpiece at high cutting speeds. Since the oxidation resistance and chemical stability of SiAlON ceramics can be improved by adjusting the optimum z value of β -SiAlON and the amount of α -SiAlON in α/β -SiAlON ceramics, it is possible to create successful turning/milling inserts for high speed machining of Ni-based high temperature alloys (Hao *et al.*, 2017; Sun *et al.*, 2020; Tian *et al.*, 2013; Zheng *et al.*, 2010). Because of the advancements in manufacturing technology and the possibility for close control of microstructure, novel α/β -SiAlON milling tools have been developed and commercialized (Fig. 10). The key point in this application is to increase the cutting zone temperature intentionally by performing the operation at ultra-high cutting speeds (above 600 m/min.) to soften the superalloy part. As a result of softening of the workpiece, the mechanical stress acting on the tool is reduced, and catastrophic fracture is prevented (Çelik *et al.*, 2017; Finkeldei *et al.*, 2019; Dang *et al.*, 2020; Ming *et al.*, 2020; Huang *et al.*, 2020). Since high temperature is required in the cutting zone for this mechanism, SiAlON tools can only be applicable in machining operations of deformable metallic materials in which the loads acting on the tool face are more uniform. The machining of non-metallic anisotropic materials such as fiber reinforced polymer composites is not possible with SiAlON tools because of the cyclic cutting loads resulting from the anisotropy, which causes propagation of microcracks and, therefore, severe microchipping of the tool cutting edge (Çelik *et al.*, 2015a,b).

Apart from refractory parts for metallurgical applications, SiAlON ceramics are being developed as optical luminescence components such as light emitting diodes (LEDs), fluorescent lamps, X-ray detectors, etc. The relative performance of an Er-doped α -SiAlON ceramic as a high temperature sensor was investigated and superior thermal and chemical stability was attained compared with chalcogenide and fluoride glass-based optical temperature sensors; a maximum operating temperature of 1273K, the highest temperature measurement via FIR technique in optical thermometry, was achieved (Kshetri *et al.*, 2020). Moreover, the biocompatibility of SiAlON ceramics has also been examined in a series of studies (Li *et al.*, 2020; Xie *et al.*, 2019; Zhang *et al.*, 2020a,b). With promising

results from these studies on the compatibility with bone-cell cultures, SiAlON based ceramics can be highlighted as potential bone restorative bioceramics in the near future.

References

- Acikbas, N.C., Kara, F., 2017. The effect of z value on intergranular phase crystallization of α/β -SiAlON-TiN composites. *Journal of the European Ceramic Society* 37, 923–930.
- Acikbas, N.C., Yurdakul, H., Mandal, H., *et al.*, 2012. Effect of sintering conditions and heat treatment on the properties, microstructure and machining performance of α - β -SiAlON ceramics. *Journal of the European Ceramic Society* 32, 1321–1327.
- Acikbas, N.C., Tegmen, S., Ozcan, S., Acikbas, G., 2014. Thermal shock behaviour of α : β -sialon–tin composites. *Ceramics International* 40, 3611–3618.
- Ayas, E., Kara, A., 2011. Novel electrically conductive α - β SiAlON/TiCN composites. *Journal of the European Ceramic Society* 31, 903–911.
- Ayas, E., Kara, A., Kara, F., 2008. A novel approach for preparing electrically conductive α/β SiAlON-TiN composites by spark plasma sintering. *Journal of the Ceramic Society of Japan* 116, 812–814.
- Babini, G., Bellosi, A., Vincenzini, P., 1980. Hot pressing of silicon nitride with ceria additions. *Ceramurgia International* 6, 91–98.
- Baskut, S., Turan, S., 2020. The effect of different GNPs addition on the electrical conductivities and percolation thresholds of the SiAlON matrix composites. *Journal of the European Ceramic Society* 40, 1159–1167.
- Baskut, S., Cinar, A., Seyhan, A.T., Turan, S., 2018. Tailoring the properties of spark plasma sintered SiAlON containing graphene nanoplatelets by using different exfoliation and size reduction techniques: Anisotropic electrical properties. *Journal of the European Ceramic Society* 38, 3787–3792.
- Becher, A.P., Sun, E., Hsueh, C.-H., *et al.*, 1996. Debonding of interfaces between beta-silicon nitride whiskers and Si-Al-Y oxynitride glasses. *Acta Materialia* 44, 3881–3893.
- Becher, P.F., 1991. Microstructural design of toughened ceramics. *Journal of the American Ceramic Society* 74, 255–269.
- Becher, P.F., Hwang, S.-L., Hsueh, C.-H., 1995. Using microstructure to attack the brittle nature of silicon nitride ceramics. *MRS Bulletin* 20, 23–27.
- Becher, P.F., Painter, G.S., Shibata, N., Waters, S.B., Lin, H.T., 2008. Effects of rare-earth (RE) intergranular adsorption on the phase transformation, microstructure evolution, and mechanical properties in silicon nitride with $\text{RE}_2\text{O}_3 + \text{MgO}$ additives: RE=La, Gd, and Lu. *Journal of the American Ceramic Society* 91, 2328–2336.
- Bellosi, A., Guicciardi, S., Tampieri, A., 1992. Development and characterization of electroconductive Si_3N_4 -TiN composites. *Journal of the European Ceramic Society* 9, 83–93.
- Bentsen, L.D., Hasselman, D., Tien, T.Y., 1984. Effect of crystallization of the grain-boundary phase on the thermal diffusivity of a SiAlON ceramic. *Journal of the American Ceramic Society* 67, c85–c86.
- Bergman, B., Ekström, T., Micski, A., 1991. The Si-Al-O-N system at temperatures of 1700–1775°C. *Journal of the European Ceramic Society* 8, 141–151.
- Biswas, S., Riley, F., 2001. Gas pressure sintering of silicon nitride – Current status. *Materials Chemistry and Physics* 67, 175–179.
- Bitterlich, B., Friederich, K., 2007. Particle-reinforced SiAlONs for cutting tools. *Materials Science Forum* 554, 129–134.
- Bitterlich, B., Bitsch, S., Friederich, K., 2008. SiAlON based ceramic cutting tools. *Journal of the European Ceramic Society* 28, 989–994.
- Blasse, G., Grabmaier, B., 1994. *Luminescence Materials*. Berlin: Springer-Verlag.
- Bowen, L., Weston, R.J., Carruthers, T., Brook, R., 1978. Hot-pressing and the α - β phase transformation in silicon nitride. *Journal of Materials Science* 13, 341–350.
- Buljan, S.-T., Wayne, S.F., 1989. Wear and design of ceramic cutting tool materials. *Wear* 133, 309–321.
- Cao, G., Metselaar, R., 1991. α -SiAlON ceramics: A review. *Chemistry of Materials* 3, 242–252.
- Çelik, A., 2018. Dopant-dependent diffusion behavior of SiAlON ceramics against Inconel 718 superalloy. *Ceramics International* 44, 17440–17446.
- Çelik, A., 2019. Oxidation behavior of Y_2O_3 and Er_2O_3 -doped- α/β -SiAlON ceramics. *Akademik Platform Mühendislik ve Fen Bilimleri Dergisi* 7, 381–388.
- Çelik, A., Lazoglu, I., Kara, A., Kara, F., 2015a. Investigation on the performance of SiAlON ceramic drills on aerospace grade CFRP composites. *Journal of Materials Processing Technology* 223, 39–47.
- Çelik, A., Lazoglu, I., Kara, A., Kara, F., 2015b. Wear on SiAlON ceramic tools in drilling of aerospace grade CFRP composites. *Wear* 338, 11–21.
- Çelik, A., Alağaç, M.S., Turan, S., Kara, A., Kara, F., 2017. Wear behavior of solid SiAlON milling tools during high speed milling of Inconel 718. *Wear* 378, 58–67.
- Chen, W.W., Sun, W.Y., Wang, P.L., *et al.*, 2002. Control of microstructures in α -SiAlON ceramics. *Journal of the American Ceramic Society* 85, 276–278.
- Chen, W.W., Su, X.L., Wang, P.L., *et al.*, 2005. Optical properties of Gd- α -SiAlON ceramics: Effect of carbon contamination. *Journal of the American Ceramic Society* 88, 2304–2306.
- Cinibulk, M.K., Thomas, G., Johnson, S.M., 1992a. Oxidation behavior of rare-earth disilicate–silicon nitride ceramics. *Journal of the American Ceramic Society* 75, 2044–2049.
- Cinibulk, M.K., Thomas, G., Johnson, S.M., 1992b. Strength and creep behavior of rare-earth disilicate–silicon nitride ceramics. *Journal of the American Ceramic Society* 75, 2050–2055.
- Collins, J., Gerby, R., 1955. New refractory uses for silicon nitride reported. *JOM* 7, 612–615.
- Dang, J., Zhang, H., Ming, W., An, Q., Chen, M., 2020. New observations on wear characteristics of solid $\text{Al}_2\text{O}_3/\text{Si}_3\text{N}_4$ ceramic tool in high speed milling of additive manufactured Ti6Al4V. *Ceramics International* 46, 5876–5886.
- De Faoite, D., Browne, D.J., Chang-Díaz, F.R., Stanton, K.T., 2012. A review of the processing, composition, and temperature-dependent mechanical and thermal properties of dielectric technical ceramics. *Journal of Materials Science* 47, 4211–4235.
- Deeley, G.G., Herbert, J.M., Moore, N.C., 1961. Dense silicon nitride. *Powder Metallurgy* 4, 145–151.
- Dong, P., Wang, X., Zhang, M., Seshadri, S., 2012. Conductivity properties of β -SiAlON ceramics. *Science China Technological Sciences* 55, 2409–2415.
- Drew, P., Lewis, M., 1974. The microstructures of silicon nitride ceramics during hot-pressing transformations. *Journal of Materials Science* 9, 261–269.
- Ekström, T., 1992. SiAlON ceramics sintered with yttria and rare earth oxides. In: Chen, I.W., Becher, P.F., Mitomo, M., Petzow, G., Yen, T.-S. (Eds.), *Silicon Nitride Ceramics – Scientific and Technological Advances*, Materials Research Society Symposium Proceedings 287. MRS Online Proceedings Library Archive, pp. 121–132.
- Ekström, T., Nygren, M., 1992. SiAlON ceramics. *Journal of the American Ceramic Society* 75, 259–276.
- Ekström, T., Käll, P.-O., Nygren, M., Olsson, P.-O., 1989. Dense single-phase β -SiAlON ceramics by glass-encapsulated hot isostatic pressing. *Journal of Materials Science* 24, 1853–1861.
- Evans, A., Sharp, J., 1971. Microstructural studies on silicon nitride. *Journal of Materials Science* 6, 1292–1302.
- Finkeldei, D., Sexauer, M., Bleicher, F., 2019. End milling of Inconel 718 using solid Si_3N_4 ceramic cutting tools. *Procedia CIRP* 81, 1131–1135.
- Fox, K., Hellmann, J., Dickey, E., *et al.*, 2006. Impression and compression creep of SiAlON ceramics. *Journal of the American Ceramic Society* 89, 2555–2563.
- Fox, K.M., Hellmann, J.R., 2008. Microstructure and creep behavior of silicon nitride and SiAlONs. *International Journal of Applied Ceramic Technology* 5, 138–154.
- Fox, M., 2002. *Optical Properties of Solids*. Oxford: OUP.
- Gaukler, L., Lukas, H., Petzow, G., 1975. Contribution to the phase diagram Si_3N_4 -AlN- Al_2O_3 - SiO_2 . *Journal of the American Ceramic Society* 58, 346–347.
- Hampshire, S., 2007. Silicon nitride ceramics – Review of structure, processing and properties. *Journal of Achievements in Materials and Manufacturing Engineering* 24, 43–50.
- Hampshire, S., Pomeroy, M.J., 2004. Effect of composition on viscosities of rare earth oxynitride glasses. *Journal of Non-crystalline Solids* 344, 1–7.
- Hampshire, S., Park, H., Thompson, D.P., Jack, K.H., 1978. α -SiAlON ceramics. *Nature* 274, 880–882.

- Hao, Z., Fan, Y., Lin, J., Ji, F., Liu, X., 2017. New observations on wear mechanism of self-reinforced SiAlON ceramic tool in milling of Inconel 718. *Archives of Civil and Mechanical Engineering* 17, 467–474.
- Hardie, D., Jack, K.H., 1957. Crystal structures of silicon nitride. *Nature* 180, 332–333.
- Hayashi, H., Hirao, K., Toriyama, M., Kanzaki, S., Itatani, K., 2001. MgSiN₂ addition as a means of increasing the thermal conductivity of β -silicon nitride. *Journal of the American Ceramic Society* 84, 3060–3062.
- He, W., Liu, Q., Zhong, H., 2011. Composition controlled microstructure and mechanical properties of Yb/Lu co-doped SiAlON. *Materials Science and Engineering A* 528, 8359–8364.
- Hirosaki, N., Ogata, S., Kocer, C., Kitagawa, H., Nakamura, Y., 2002. Molecular dynamics calculation of the ideal thermal conductivity of single-crystal α - and β -Si₃N₄. *Physical Review B* 65, 134110.
- Hoffmann, M.J., Holzer, S., 2003. Processing and microstructural evolution of rare earth containing SiAlONs. *Key Engineering Materials* 237, 141–148.
- Höppe, H.A., Lutz, H., Morys, P., Schnick, W., Seilmeier, A., 2000. Luminescence in Eu²⁺-doped Ba₂Si₃N₈: Fluorescence, thermoluminescence, and upconversion. *Journal of Physics and Chemistry of Solids* 61, 2001–2006.
- Hou, X., Lu, X., Peng, B., *et al.*, 2012. A new approach to interpreting the parabolic and non-parabolic oxidation behaviour of hot-pressed β -SiAlON ceramics. *Corrosion Science* 58, 278–283.
- Huang, X., Zou, F., Ming, W., *et al.*, 2020. Wear mechanisms and effects of monolithic SiAlON ceramic tools in side milling of superalloy FGH96. *Ceramics International* 46, 26813–26822.
- Hwang, S.L., Becher, P.F., Lin, H.T., 1997. Desintering process in the gas-pressure sintering of silicon nitride. *Journal of the American Ceramic Society* 80, 329–335.
- Izhevskiy, V.A., Genova, L.A., Bressiani, J.C., Aldinger, F., 2000. Progress in SiAlON ceramics. *Journal of the European Ceramic Society* 20, 2275–2295.
- Jack, K.H., 1973. Solid solubility of alumina in silicon nitride. *Transactions and Journal of the British Ceramic Society* 72, 376–378.
- Jack, K.H., 1981. The significance of structure and phase equilibria in the development of silicon nitride and SiAlON ceramics. In: Carlsson, R., Karlsson, S. (Eds.), *Science of Ceramics* 11. Gothenburg: Swedish Ceramic Society, pp. 125–131.
- Jack, K.H., Wilson, W., 1972. Ceramics based on the Si-Al-ON and related systems. *Nature Physical Science* 238, 28–29.
- Jansen, M., Letschert, H.-P., 2000. Inorganic yellow-red pigments without toxic metals. *Nature* 404, 980–982.
- Jones, M.I., Hirao, K., Hyuga, H., Yamauchi, Y., Kanzaki, S., 2003. Wear properties of Y- α/β composite SiAlON ceramics. *Journal of the European Ceramic Society* 23, 1743–1750.
- Joshi, B., Lee, H.H., Wang, H., *et al.*, 2012. The effect of different rare earth oxides on mechanical and optical properties of hot pressed α/β -SiAlON ceramics. *Journal of the European Ceramic Society* 32, 3603–3610.
- Joshi, B., Kshetri, Y.K., Adhikari, R., Lee, S.W., 2015. IR to visible upconversion luminescence of transparent (Mg, Er)- α -SiAlON ceramics. *Ceramics International* 41, 6455–6462.
- Karunaratne, B., Lumby, R., Lewis, M., 1996. Rare-earth-doped α' -SiAlON ceramics with novel optical properties. *Journal of Materials Research* 11, 2790–2794.
- Kim, J., Rosenflanz, A., Chen, I.W., 2000. Microstructure control of in-situ-toughened α -SiAlON Ceramics. *Journal of the American Ceramic Society* 83, 1819–1821.
- Kim, J.-M., Ko, S.-I., Kim, H.-N., *et al.*, 2017. Effects of microstructure and intergranular glassy phases on thermal conductivity of silicon nitride. *Ceramics International* 43, 5441–5449.
- Kim, W., Taya, M., Yamada, K., Kamiya, N., 1998. Percolation study on electrical resistivity of SiC/Si₃N₄ composites with segregated distribution. *Journal of Applied Physics* 83, 2593–2598.
- Kitayama, M., Hirao, K., Tsuge, A., *et al.*, 2000. Thermal conductivity of β -Si₃N₄: II, Effect of lattice oxygen. *Journal of the American Ceramic Society* 83, 1985–1992.
- Kitayama, M., Hirao, K., Toriyama, M., Kanzaki, S., 1999. Thermal conductivity of β -Si₃N₄: I, Effects of various microstructural factors. *Journal of the American Ceramic Society* 82, 3105–3112.
- Knehans, R., Steinbrech, R., 1982. Memory effect of crack resistance during slow crack growth in notched Al₂O₃ bend specimens. *Journal of Materials Science Letters* 1 (8), 327–329.
- Kohatsu, I., Mccauley, J.W., 1974. Re-examination of the crystal structure of α -Si₃N₄. *Materials Research Bulletin* 9, 917–920.
- Kossowsky, R., 1973. The microstructure of hot-pressed silicon-nitride. *Journal of Materials Science* 8, 1603–1615.
- Krämer, K.W., Biner, D., Frei, G., *et al.*, 2004. Hexagonal sodium yttrium fluoride based green and blue emitting upconversion phosphors. *Chemistry of Materials* 16, 1244–1251.
- Krämer, M., Hoffmann, M.J., Petzow, G., 1993. Grain growth studies of silicon nitride dispersed in an oxynitride glass. *Journal of the American Ceramic Society* 76, 2778–2784.
- Krämer, M., Wittmüss, D., Küppers, H., Hoffman, M., Petzow, G., 1994. Relations between crystal structure and growth morphology of β -Si₃N₄. *Journal of Crystal Growth* 140, 157–166.
- Křestian, J., Pritula, O., Smrčok, Ľ., *et al.*, 2007. Corrosion of β -SiAlON-based ceramics by molten steel. *Journal of the European Ceramic Society* 27, 2137–2143.
- Kshetri, Y.K., Kamiyama, T., Torii, S., *et al.*, 2020. Electronic structure, thermodynamic stability and high-temperature sensing properties of Er- α -SiAlON ceramics. *Scientific Reports* 10, 1–13.
- Kumar, R., Acikbas, N.C., Kara, F., Mandal, H., Basu, B., 2009. Microstructure – Mechanical properties – Wear resistance relationship of SiAlON ceramics. *Metallurgical and Materials Transactions A* 40, 2319–2332.
- Kurama, S., Herrmann, M., Mandal, H., 2002. The effect of processing conditions, amount of additives and composition on the microstructures and mechanical properties of α -SiAlON ceramics. *Journal of the European Ceramic Society* 22, 109–119.
- Kurama, S., Schulz, I., Herrmann, M., 2009. Wear behaviour of α - and α/β -SiAlON ceramics stabilized with Nd₂O₃ and Y₂O₃. *Journal of the European Ceramic Society* 29, 155–162.
- Kusano, D., Hyuga, H., Zhou, Y., Hirao, K., 2014. Effect of aluminum content on mechanical properties and thermal conductivities of sintered reaction-bonded silicon nitride. *International Journal of Applied Ceramic Technology* 11, 534–542.
- Kushan, S.R., Uzun, I., Dogan, B., Mandal, H., 2007. Experimental and finite element study of the thermal conductivity of α -SiAlON ceramics. *Journal of the American Ceramic Society* 90, 3902–3907.
- Lee, H.L., Lim, H.J., Kim, S., Lee, H.B., 1989. Thermomechanical properties of β -SiAlON synthesized from kaolin. *Journal of the American Ceramic Society* 72, 1458–1461.
- Lee, W.E., Hilmas, G.E., 1989. Microstructural changes in β -silicon nitride grains upon crystallizing the grain-boundary glass. *Journal of the American Ceramic Society* 72, 1931–1937.
- Legut, D., Wdowik, U.D., Kurtyka, P., 2014. Vibrational and dielectric properties of α -Si₃N₄ from density functional theory. *Materials Chemistry and Physics* 147, 42–49.
- Lewis, M., Barnard, P., 1980. Oxidation mechanisms in Si-Al-ON ceramics. *Journal of Materials Science* 15, 443–448.
- Li, M., Zhang, L., Zhang, C., *et al.*, 2020. Effect of Y₂O₃ on the physical properties and biocompatibility of β -SiAlON ceramics. *Ceramics International* 46, 23427–23432.
- Li, Y., Yu, H., Jin, H., *et al.*, 2015. Fast heating thermal shock test for β -SiAlON with molten metals as heating medium. *Ceramics International* 41, 6117–6121.
- Lichvár, P., Šajgalík, P., Liška, M., Galusek, D., 2007. CaO–SiO₂–Al₂O₃–Y₂O₃ glasses as model grain boundary phases for Si₃N₄ ceramics. *Journal of the European Ceramic Society* 27, 429–436.
- Liu, C.F., Ye, F., Zhou, Y., Huang, Y.D., Zhou, J.M., 2010. Thermal shock behavior of Nd-doped α -SiAlON ceramics. *Key Engineering Materials* 434–435, 130–133.
- Liu, D.M., Chen, C.J., Lee, R.R.R., 1995. Thermal diffusivity/conductivity in SiAlON ceramics. *Journal of Applied Physics* 77, 494–496.

- Liu, J., Ma, C., Du, H., Tu, G., 2017. The preparation and oxidation behavior of Ca-doped α -SiAlON ceramic with elongated grains. *Journal of Alloys and Compounds* 722, 400–405.
- Luecke, W.E., Wiederhorn, S.M., Hockey, B.J., Krause Jr, R.F., Long, G.G., 1995. Cavitation contributes substantially to tensile creep in silicon nitride. *Journal of the American Ceramic Society* 78, 2085–2096.
- Lukianova, O., Ivanov, O., 2018. The effect of Al_2O_3 -MgO additives on the microstructure of spark plasma sintered silicon nitride. *Ceramics International* 44, 390–393.
- Lukianova, O., Novikov, V.Y., Parkhomenko, A., Sirota, V., Krasilnikov, V., 2017. Microstructure of spark plasma-sintered silicon nitride ceramics. *Nanoscale Research Letters* 12, 293.
- Mackenzie, K.J., Sheppard, C.M., Barris, G.C., *et al.*, 1998. Kinetics and mechanism of thermal oxidation of SiAlON ceramic powders. *Thermochimica Acta* 318, 91–100.
- Mandal, H., 1999. New developments in α -SiAlON ceramics. *Journal of the European Ceramic Society* 19, 2349–2357.
- Mandal, H., Kara, F., Turan, S., Kara, A., 2003. Novel SiAlON ceramics for cutting tool applications. *Key Engineering Materials* 237, 193–202.
- Manson, S., Smith, R., 1955. Theory of thermal shock resistance of brittle materials based on Weibull's statistical theory of strength. *Journal of the American Ceramic Society* 38, 18–27.
- Menon, M.N., Fang, H.T., Wu, D.C., Jenkins, M.G., Ferber, M.K., 1994. Creep and stress rupture behavior of an advanced silicon nitride: Part II, creep rate behavior. *Journal of the American Ceramic Society* 77, 1228–1234.
- Ming, W., Huang, X., Ji, M., *et al.*, 2020. Analysis of cutting responses of SiAlON ceramic tools in high-speed milling of FGH96 superalloys. *Ceramics International* 47 (1), 552–554.
- Mitomo, M., Uemura, Y., 1981. Electrical conductivity of α -SiAlON ceramics. *Journal of Materials Science* 16, 552–554.
- Mitomo, M., Tajima, Y., 1991. Sintering, properties and applications of silicon nitride and SiAlON ceramics. *Journal of the Ceramic Society of Japan* 99, 1014–1025.
- Mitomo, M., Uenosono, S., 1992. Microstructural development during gas-pressure sintering of α -silicon nitride. *Journal of the American Ceramic Society* 75, 103–107.
- Mitomo, M., Moriyoshi, Y., Sakai, T., Ohsaka, T., Kobayashi, M., 1982. Translucent β -SiAlON ceramics. *Journal of Materials Science Letters* 1, 25–26.
- Mitomo, M., Tsutsumi, M., Tanaka, H., Uenosono, S., Saito, F., 1990. Grain growth during gas-pressure sintering of β -silicon nitride. *Journal of the American Ceramic Society* 73, 2441–2445.
- Nordberg, L.O., Nygren, M., Käll, P.O., Shen, Z., 1998. Stability and oxidation properties of RE- α -SiAlON ceramics (RE = Y, Nd, Sm, Yb). *Journal of the American Ceramic Society* 81, 1461–1470.
- Oyama, Y., Kamigaito, O., 1971. Solid solubility of some oxides in Si_3N_4 . *Japanese Journal of Applied Physics* 10, 1637.
- Parr, N., 1960. Silicon nitride. A new ceramic for high temperature engineering and other applications. *Research* 13.
- Pelleg, J., 2014. *Mechanical Properties of Ceramics*. Springer Science and Business.
- Pettersson, P., Shen, Z., Johnsson, M., Nygren, M., 2001. Thermal shock resistance of α/β -SiAlON ceramic composites. *Journal of the European Ceramic Society* 21, 999–1005.
- Pettersson, P., Shen, Z., Johnsson, M., Nygren, M., 2002. Thermal shock properties of β -SiAlON ceramics. *Journal of the European Ceramic Society* 22, 1357–1365.
- Pomeroy, M.J., Hampshire, S., 1985. Oxidation processes in a high substitution β -SiAlON. *Materials Chemistry and Physics* 13, 437–448.
- Prochazka, S., Rocco, W.A., 1978. High-pressure hot-pressing of silicon nitride powders. In: Palmour, H., Davis, R.F., Hare, T.M. (Eds.), *Processing of Crystalline Ceramics* 11. Boston, MA: Springer, pp. 615–625.
- Qin, H., Li, Y., Long, M., *et al.*, 2018. In situ synthesis mechanism of 15R-SiAlON reinforced Al_2O_3 refractories by Fe-Si liquid phase sintering. *Journal of the American Ceramic Society* 101, 1870–1879.
- Ratzker, B., Sokol, M., Kalabukhov, S., Frage, N., 2018. High-pressure spark plasma sintering of silicon nitride with LiF additive. *Journal of the European Ceramic Society* 38, 1271–1277.
- Redington, M., O'Reilly, K., Hampshire, S., 1991. On the relationships between composition and cell dimensions in α -SiAlONs. *Journal of Materials Science Letters* 10, 1228–1231.
- Rödel, J., 1992. Interaction between crack deflection and crack bridging. *Journal of the European Ceramic Society* 10, 143–150.
- Rosenflanz, A., 1999. Silicon nitride and SiAlON ceramics. *Current Opinion in Solid State and Materials Science* 4, 453–459.
- Rosenflanz, A., 2002. Glass-reduced SiAlONs with improved creep and oxidation resistance. *Journal of the American Ceramic Society* 85, 2379–2381.
- Rosenflanz, A., Chen, I.-W., 1999. Kinetics of phase transformations in SiAlON ceramics: I. Effects of cation size, composition and temperature. *Journal of the European Ceramic Society* 19, 2325–2335.
- Sage, A., Histed, J., 1961. Applications of silicon nitride. *Powder Metallurgy* 4, 196–212.
- Santos, C., Strecker, K., Ribeiro, S., *et al.*, 2004. α -SiAlON ceramics with elongated grain morphology using an alternative sintering additive. *Materials Letters* 58, 1792–1796.
- Satet, R., Hoffmann, M., 2004. Grain growth anisotropy of β -silicon nitride in rare-earth doped oxynitride glasses. *Journal of the European Ceramic Society* 24, 3437–3445.
- Satet, R.L., Hoffmann, M.J., 2005. Influence of the rare-earth element on the mechanical properties of RE-Mg-bearing silicon nitride. *Journal of the American Ceramic Society* 88, 2485–2490.
- Satet, R.L., Hoffmann, M.J., Cannon, R.M., 2006. Experimental evidence of the impact of rare-earth elements on particle growth and mechanical behaviour of silicon nitride. *Materials Science and Engineering A* 422, 66–76.
- Schwarz, M., Mieke, G., Zerr, A., *et al.*, 2000. Spinel- Si_3N_4 : Multi-anvil press synthesis and structural refinement. *Advanced Materials* 12, 883–887.
- Sharif, R., Thorp, J., Kavanagh, S., 1981. Some electrical characteristics of lithium and yttrium SiAlONs. *Journal of Materials Science* 16, 211–220.
- Shelby, J.E., Kohli, J.T., 1990. Rare-earth aluminosilicate glasses. *Journal of the American Ceramic Society* 73, 39–42.
- Shen, Z., Nygren, M., 1997. On the extension of the α -SiAlON phase area in yttrium and rare-earth doped systems. *Journal of the European Ceramic Society* 17, 1639–1645.
- Shen, Z., Nygren, M., Halenius, U., 1997. Absorption spectra of rare-earth-doped α -SiAlON ceramics. *Journal of Materials Science Letters* 16, 263–266.
- Shimada, S., Aoki, T., Kiyono, H., Mackenzie, K.J., 1998. Early-stage thermal oxidation of carbothermal β -SiAlON powder. *Journal of the American Ceramic Society* 81, 266–268.
- Shimoo, T., Yamasaki, T., Okamura, K., 1997. Interaction of Si_3N_4 with carbonyl iron under nitrogen or argon atmosphere. *Journal of the Ceramic Society of Japan* 105, 734–739.
- Shuba, R., Chen, I.W., 2002. Effect of seeding on the microstructure and mechanical properties of α -SiAlON: II, Ca- α -SiAlON. *Journal of the American Ceramic Society* 85, 1260–1267.
- Singhal, S.C., 1976. Thermodynamics and kinetics of oxidation of hot-pressed silicon nitride. *Journal of Materials Science* 11, 500–509.
- Söderlund, E., Ekström, T., 1990. Pressureless sintering of Y_2O_3 - CeO_2 -doped SiAlONs. *Journal of Materials Science* 25, 4815–4821.
- Su, X., Wang, P., Chen, W., *et al.*, 2004a. Effects of composition and thermal treatment on infrared transmission of Dy- α -SiAlON. *Journal of the European Ceramic Society* 24, 2869–2877.
- Su, X., Wang, P., Chen, W., *et al.*, 2004b. Optical properties of SPS-ed Y-and (Dy, Y)- α -SiAlON ceramics. *Journal of Materials Science* 39, 6257–6262.
- Su, X., Wang, P., Chen, W., *et al.*, 2004c. Translucent α -SiAlON ceramics by hot pressing. *Journal of the American Ceramic Society* 87, 730–732.
- Suganuma, M., Kitagawa, Y., Wada, S., Murayama, N., 2003. Pulsed electric current sintering of silicon nitride. *Journal of the American Ceramic Society* 86, 387–394.
- Sun, E., Becher, P., Hsueh, C.-H., *et al.*, 1999. Debonding behavior between β - Si_3N_4 whiskers and oxynitride glasses with or without an epitaxial β -SiAlON interfacial layer. *Acta Materialia* 47, 2777–2785.
- Sun, E.Y., Becher, P.F., Plucknett, K.P., *et al.*, 1998. Microstructural design of silicon nitride with improved fracture toughness: II, Effects of yttria and alumina additives. *Journal of the American Ceramic Society* 81, 2831–2840.
- Sun, J., Huang, S., Ding, H., Chen, W., 2020. Cutting performance and wear mechanism of SiAlON ceramic tools in high speed face milling GH4099. *Ceramics International* 46, 1621–1630.

- Sun, Q., Yang, J., Yin, B., *et al.*, 2017. Dry sliding wear behavior of β -SiAlON ceramics at wide range temperature from 25 to 800°C. *Journal of the European Ceramic Society* 37, 4505–4513.
- Suyver, J.F., Grimm, J., Van Veen, M., *et al.*, 2006. Upconversion spectroscopy and properties of NaYF₄ doped with Er³⁺, Tm³⁺ and/or Yb³⁺. *Journal of Luminescence* 117, 1–12.
- Thompson, D.P., 1989. The crystal chemistry of nitrogen ceramics. *Materials Science Forum* 47, 21–42.
- Thorpe, J., Sharif, R., 1976. Electrical conductivity in hot-pressed nitrogen ceramics. *Journal of Materials Science* 11, 1494–1500.
- Tian, C., Jiang, H., Liu, N., 2011. Thermal shock behavior of Si₃N₄-TiN nano-composites. *International Journal of Refractory Metals and Hard Materials* 29, 14–20.
- Tian, X., Zhao, J., Zhao, J., Gong, Z., Dong, Y., 2013. Effect of cutting speed on cutting forces and wear mechanisms in high-speed face milling of Inconel 718 with SiAlON ceramic tools. *The International Journal of Advanced Manufacturing Technology* 69, 2669–2678.
- Tian, Z., Yang, Y., Wang, Y., *et al.*, 2019. Thermal shock resistance of rare-earth doped in-situ SiAlON reinforced h-BN matrix ceramics under vacuum thermal cycling. *Ceramics International* 45, 20121–20127.
- Tsuge, A., Nishida, K., Komatsu, M., 1975. Effect of crystallizing the grain-boundary glass phase on the high-temperature strength of hot-pressed Si₃N₄ containing Y₂O₃. *Journal of the American Ceramic Society* 58, 323–326.
- Tu, G., Wu, S., Liu, J., Long, Y., Wang, B., 2016. Cutting performance and wear mechanisms of SiAlON ceramic cutting tools at high speed dry turning of gray cast iron. *International Journal of Refractory Metals and Hard Materials* 54, 330–334.
- Tunckan, O., Yurdakul, H., Turan, S., 2013. Identification and quantification of reaction phases at Si₃N₄-Ti interfaces by using analytical transmission electron microscopy techniques. *Ceramics International* 39, 1087–1095.
- Tunckan, O., Yurdakul, H., Turan, S., 2019. Unveiling the reaction products in heat treated Si₃N₄-Ti joined ceramics by transmission electron microscopy. *Journal of Advanced Ceramics* 8, 500–508.
- Turan, D., Uludag, A., Turan, S., 2019. Effect of heat treatment on the creep behavior of α/β SiAlON sintered with multication oxide sintering additives. *International Journal of Applied Ceramic Technology* 16, 404–409.
- Uheda, K., Takizawa, H., Endo, T., *et al.*, 2000. Synthesis and luminescent property of Eu³⁺-doped LaSi₃N₅ phosphor. *Journal of Luminescence* 87, 967–969.
- Ukyo, Y., Goto, K., Inomata, Y., 1979. Ionic conductivity of the system Si-Al-O-N from 850° to 1400°C. *Journal of the American Ceramic Society* 62, 410–413.
- Uludağ, A., Turan, D., 2011. High temperature bending creep behavior of a multi-cation doped α/β -SiAlON composite. *Ceramics International* 37, 921–926.
- Wachtman, J.B., Cannon, W.R., Mathewson, M.J., 2009. *Mechanical Properties of Ceramics*. John Wiley and Sons.
- Wada, S., Suganuma, M., Kitagawa, Y., Murayama, N., 1999. Comparison between pulse electric current sintering and hot pressing of silicon nitride ceramics. *Journal of the Ceramic Society of Japan* 107, 887–890.
- Wereszczak, A., Kirkland, T., Ferber, M., Watkins, T., Yeckley, R., 1998. The effects of residual α phase on the 1370°C creep performance of yttria-doped HIPed silicon nitride. *Journal of Materials Science* 33, 2053–2060.
- Wereszczak, A.A., Ferber, M.K., Kirkland, T.P., *et al.*, 1999. Asymmetric tensile and compressive creep deformation of hot-isostatically-pressed Y₂O₃-doped-Si₃N₄. *Journal of the European Ceramic Society* 19, 227–237.
- Weston, J., Pratt, P., Steele, B., 1978. Crystallization of grain boundary phases in hot-pressed silicon nitride materials. *Journal of Materials Science* 13, 2137–2146.
- Wiederhorn, S.M., De Arellano Lopez, A.R., Luecke, W.E., *et al.*, 2004. Influence of grain size on the tensile creep behavior of ytterbium-containing silicon nitride. *Journal of the American Ceramic Society* 87, 421–430.
- Xie, H., Zhang, L., Xu, E., *et al.*, 2019. SiAlON-Al₂O₃ ceramics as potential biomaterials. *Ceramics International* 45, 16809–16813.
- Xie, R.J., Mitomo, M., Uheda, K., Xu, F.F., Akimune, Y., 2002. Preparation and luminescence spectra of calcium- and rare-earth (R = Eu, Tb, and Pr)-codoped α -SiAlON ceramics. *Journal of the American Ceramic Society* 85, 1229–1234.
- Xie, R.-J., Hirosaki, N., Mitomo, M., *et al.*, 2004. Optical properties of Eu²⁺ in α -SiAlON. *The Journal of Physical Chemistry B* 108, 12027–12031.
- Xie, R.-J., Li, Y.Q., Hirosaki, N., Yamamoto, H., 2016. *Nitride Phosphors and Solid-state Lighting*. Boca Raton, FL: CRC Press.
- Xie, R.-J., Hirosaki, N., Mitomo, M., Takahashi, K., Sakuma, K., 2006. Highly efficient white-light-emitting diodes fabricated with short-wavelength yellow oxynitride phosphors. *Applied Physics Letters* 88, 101104.
- Yamada, K., Kamiya, N., 1999. High temperature mechanical properties of Si₃N₄-MoSi₂ and Si₃N₄-SiC composites with network structures of second phases. *Materials Science and Engineering A* 261, 270–277.
- Ye, C., Ru, H., Qin, Z., *et al.*, 2020. Silicon nitride composites with magnesia and alumina additives: Toughening mechanisms and mechanical properties. *Materials Science and Engineering A* 779, 139140.
- Ye, F., Hoffmann, M.J., Holzer, S., Iwasa, M., 2004. Microstructural development of Y- $\alpha/(\beta)$ -SiAlONs after post heat-treatment and its effect on mechanical properties. *Ceramics International* 30, 229–238.
- Ye, F., Zhang, L., Liu, C., Zhang, H., 2010. Thermal shock resistance of in situ toughened α -SiAlONs with barium aluminosilicate as an additive sintered by SPS. *Materials Science and Engineering A* 527, 6368–6371.
- Ye, F., Hoffmann, M.J., Holzer, S., Zhou, Y., Iwasa, M., 2003. Effect of the amount of additives and post-heat treatment on the microstructure and mechanical properties of yttrium- α -SiAlON Ceramics. *Journal of the American Ceramic Society* 86, 2136–2142.
- Yi, X., Zhang, W., Akiyama, T., 2014. Thermal conductivity of β -SiAlONs prepared by a combination of combustion synthesis and spark plasma sintering. *Thermochimica Acta* 576, 56–59.
- Yi, X., Yamauchi, A., Kurokawa, K., Akiyama, T., 2010. Oxidation of β -SiAlONs prepared by a combination of combustion synthesis and spark plasma sintering. *Corrosion Science* 52, 1738–1745.
- Yokota, H., Ibukiyama, M., 2003a. Effect of lattice impurities on the thermal conductivity of β -Si₃N₄. *Journal of the European Ceramic Society* 23, 55–60.
- Yokota, H., Ibukiyama, M., 2003b. Microstructure tailoring for high thermal conductivity of β -Si₃N₄ ceramics. *Journal of the American Ceramic Society* 86, 197–199.
- Yu, J., Du, H., Shuba, R., Chen, I.-W., 2004. Dopant-dependent oxidation behavior of α -SiAlON ceramics. *Journal of Materials Science* 39, 4855–4860.
- Yu, J.-J., Guo, W.-M., Sun, S.-K., Lin, H.-T., Wang, C.-Y., 2017. Graded Si₃N₄ ceramics with hard surface and tough core by two-step hot pressing. *Ceramics International* 43, 7948–7950.
- Yurdakul, H., Idrobo, J.C., Pennycook, S.J., Turan, S., 2011. Towards atomic scale engineering of rare-earth-doped SiAlON ceramics through aberration-corrected scanning transmission electron microscopy. *Scripta Materialia* 65, 656–659.
- Zenotchkine, M., Shuba, R., Chen, I.W., 2003. Effect of seeding on the microstructure and mechanical properties of α -SiAlON: III, Comparison of modifying cations. *Journal of the American Ceramic Society* 86, 1168–1175.
- Zenotchkine, M., Shuba, R., Kim, J.S., Chen, I.W., 2002. Effect of seeding on the microstructure and mechanical properties of α -SiAlON: I, Y-SiAlON. *Journal of the American Ceramic Society* 85, 1254–1259.
- Zerr, A., Miehke, G., Serghiou, G., *et al.*, 1999. Synthesis of cubic silicon nitride. *Nature* 400, 340–342.
- Zhang, L., Liu, X., Li, M., *et al.*, 2020a. Feasibility of SiAlON-Si₃N₄ composite ceramic as a potential bone repairing material. *Ceramics International* 46, 1760–1765.
- Zhang, L., Zhang, C., Xu, E., *et al.*, 2020b. Effect of ZrO₂ on the physicochemical properties and biological properties of β -SiAlON-ZrO₂ composite ceramics. *Ceramics International* 47 (1), 1244–1252.
- Zheng, G., Zhao, J., Jia, C., *et al.*, 2012. Thermal shock and thermal fatigue resistance of SiAlON-Si₃N₄ graded composite ceramic materials. *International Journal of Refractory Metals and Hard Materials* 35, 55–61.

- Zheng, G.M., Zhao, J., Song, X.Y., Yan, C.Q., Li, Y.E., 2010. Ultra high speed turning of Inconel 718 with SiAlON ceramic tools. *Advanced Materials Research* 126–128, 653–657.
- Zhu, X., Zhou, Y., Hirao, K., Lenčič, Z., 2006. Processing and thermal conductivity of sintered reaction-bonded silicon nitride. I: Effect of Si powder characteristics. *Journal of the American Ceramic Society* 89, 3331–3339.
- Zhu, X., Zhou, Y., Hirao, K., Lenčič, Z., 2007. Processing and thermal conductivity of sintered reaction-bonded silicon nitride: (II) effects of magnesium compound and yttria additives. *Journal of the American Ceramic Society* 90, 1684–1692.
- Ziegler, G., Heinrich, J., Wötting, G., 1987. Relationships between processing, microstructure and properties of dense and reaction-bonded silicon nitride. *Journal of Materials Science* 22, 3041–3086.

Aluminum Nitride and AlON Ceramics, Structure and Properties of

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Phase Equilibria and Crystal Chemistry

Substitution of nitrogen for oxygen in Al_2O_3 or, conversely, substitution of oxygen into AlN stabilizes new phases with significantly different crystal structures and symmetry (space group): $\alpha\text{-Al}_2\text{O}_3 = R\bar{3}c$, AlON = $Fd\bar{3}m$, and AlN = $P6_3mc$ – rhombohedral, cubic, and hexagonal, respectively. AlON can be thought of as a nitrogen-stabilized cubic aluminum oxide. It has many properties comparable to $\alpha\text{-Al}_2\text{O}_3$, but because of its cubic crystal structure, fully dense, polycrystalline bodies can be completely transparent if processed properly (McCauley and Corbin, 1979). Other properties, like dielectric loss tangent, can be extremely low because of the lack of thermal expansion-induced residual strain at grain boundaries. AlN is an intriguing material because of its theoretical thermal conductivity of about $320 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature – extremely high for a dielectric material and comparable or higher than many metals. Excellent reviews for AlN can be found in Dugger (1975), Sheppard (1990), and Prohaska and Miller (1990); for AlON in Corbin (1989); and for polycrystalline α -alumina in Munro (1997).

Figure 1 illustrates the proposed phase-equilibrium diagram for the pseudobinary Al_2O_3 –AlN composition join determined experimentally by McCauley *et al.* (1988). In a series of papers (Willems *et al.*, 1992a,b; Dumitrescu and Sundman, 1995; Qiu and Metselaar, 1997), the thermodynamics of AlON have been worked out and the phase relations calculated, confirming the main aspects of the experimental diagram. Tabary and Servant (1998) have also reassessed the phase relationships in this system. Fukuyama *et al.* (1999), using plasma arc melting to produce AlON powder, seem to have confirmed the vapor–liquid relationship in the extreme temperature region. Besides the three primary phases, there are also many intermediate phases. Among these are the following.

AlON– Al_2O_3 region:

- $13\text{Al}_2\text{O}_3:1\text{AlN} = \phi\text{-Al}_2\text{O}_3$ (Michel, 1972)
- $9\text{Al}_2\text{O}_3:1\text{AlN} = \delta\text{-Al}_2\text{O}_3$ (Long and Foster, 1961; Lefebvre *et al.*, 1972; Tabary and Servant, 1999b)
- $10\text{Al}_2\text{O}_3:2\text{AlN} = \zeta\text{-Al}_2\text{O}_3$ or $\phi'\text{-Al}_2\text{O}_3$ (Long and Foster, 1961; Michel, 1972); $\text{Al}_{22}\text{O}_{30}\text{N}_2 = \text{AlON}'$ or ϕ' (McCauley, 1978; Tabary and Servant, 1999b)

AlON region:

- $9\text{Al}_2\text{O}_3:5\text{AlN} - \text{Al}_{23}\text{O}_{27}\text{N}_5 = \text{AlON}$ (McCauley, 1978; Tabary and Servant, 1999a)

AlN polytypoids (Corbin, 1989; Tabary and Servant, 1999a; Tabary *et al.*, 2000):

- $1\text{Al}_2\text{O}_3:4\text{AlN} = 12\text{H}$
- $1\text{Al}_2\text{O}_3:5\text{AlN} = 21\text{R}$
- $1\text{Al}_2\text{O}_3:7\text{AlN} = 27\text{R}$ (Krishnan *et al.*, 1985)
- $1\text{Al}_2\text{O}_3:14\text{AlN} = 32\text{H}$ (Krishnan *et al.*, 1985)

Other polytypoids have also been identified: 8H, 15R, 16H, 33R, 24H, 39R, but the phase equilibria have not yet been clarified. Tabary and Servant (1999a) and Tabary *et al.* (2000) have carried out fairly detailed microstructural characterization of the polytypoids in this system. Figure 2 (McCauley *et al.*, 1988) summarizes selected phase equilibria, bonding, and atomic structure changes in this system. The bonding changes from primarily ionic in $\alpha\text{-Al}_2\text{O}_3$ to covalent in AlN. The electronegativities of aluminum = 1.5, oxygen = 3.5, and nitrogen = 3.0 result in predicted ionic character of $\alpha\text{-Al}_2\text{O}_3$ at 63%, AlN at 43%, and AlON at about 56% (Pauling, 1963). With a magnesium electronegativity of 1.2, MgAl_2O_4 has a predicted ionic character of about 68%. Structurally, the substitution of oxygen into AlN or nitrogen into Al_2O_3 destabilizes the parent structures with the resulting formation of modulated structures. Conceptually, nitrogen substitution into Al_2O_3 causes a local charge imbalance on the substituted nitrogen. This can be reduced by a shift in anion coordination around aluminum from six to four, driving the $\alpha\text{-Al}_2\text{O}_3$ -based phase toward a spinel (MgAl_2O_4) type structure, where the cations are distributed between octahedral and tetrahedral coordination.

This has been confirmed by crystal structure analysis of AlON, first by Goursat *et al.* (1981) and more recently by Tabary and Servant (1999a), confirming the predictive model of McCauley (1978). Basically, in the spinel unit cell, there are 8 aluminum cations in tetrahedral sites, and 15 aluminum and one vacancy in the 16 octahedral sites. The model proposed by McCauley (1978), which assumes a constant number (32) of anions in a spinel unit cell, has been worked out that has successfully been used to describe and account for the unconventional (seemingly nonstoichiometric) composition of both the AlON ($N=5$) and the ϕ' ($N=2$) phases: the model assumes the formula $\text{Al}_{(64+x)/3}\text{Cation Vacancy}_{(8-x)/3}\text{O}_{(32-x)}\text{N}_x$. Table 1 lists the various compositions

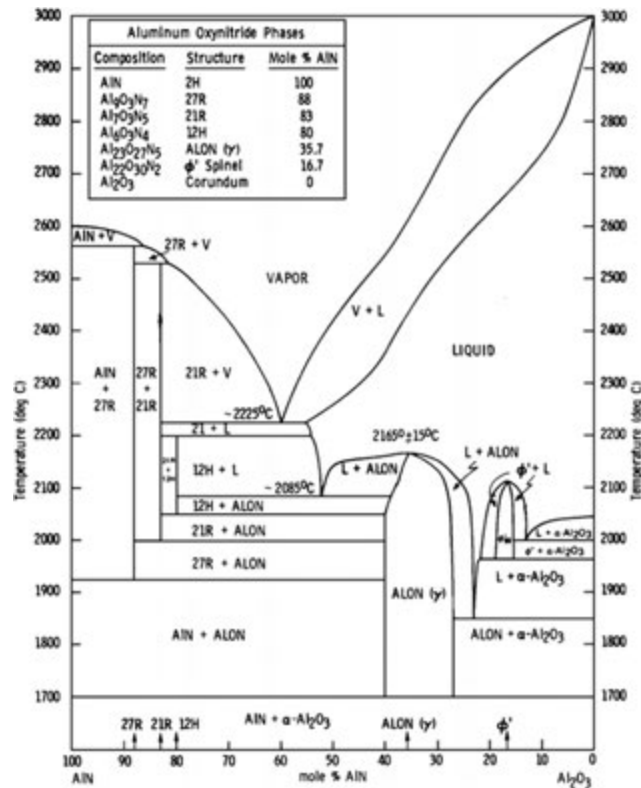


Figure 1 Proposed experimental phase-equilibrium diagram for the pseudobinary Al_2O_3 -AlN composition join at one atmosphere of flowing nitrogen (after McCauley and Corbin, 1983).

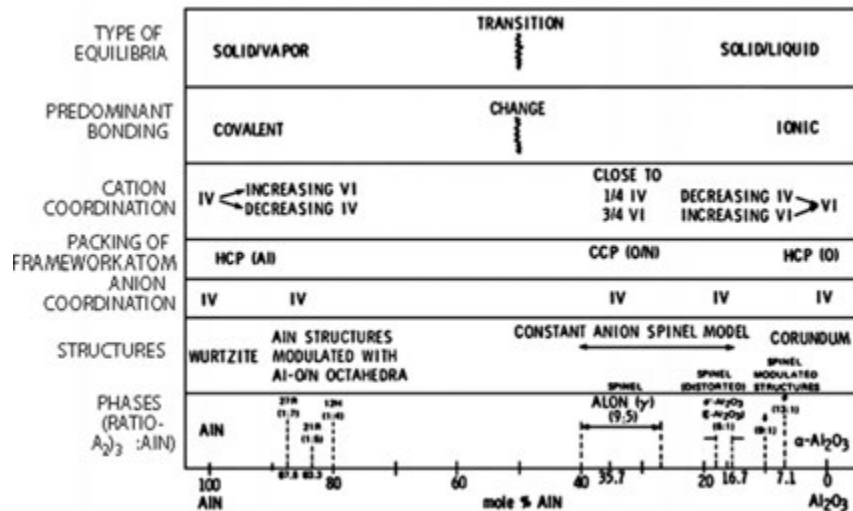


Figure 2 Crystal chemistry relationships in the Al_2O_3 -AlN system (after McCauley and Corbin, 1983).

predicted by this model from $N=0$ to $N=11$. The 'normal' spinel composition ($N=8$) does not seem to be a stable phase, whereas ALON ($N=5$) and ϕ' ($N=2$) are seemingly stable, stoichiometric phases, verified by many investigators. Yamaguchi and Yanagida (1959) were the first investigators to propose that nitrogen additions to Al_2O_3 would stabilize a spinel-type material. As indicated in Figure 2, AlN has the hexagonal, wurtzite structure, where aluminum is tetrahedrally coordinated with nitrogen. The substitution of oxygen for nitrogen in the wurtzite AlN structure results in structural irregularities (Dorignac *et al.*, 1994) and the

Table 1 Stoichiometries calculated from the constant anion model

<i>N</i>	<i>O</i>	<i>Al</i>	<i>Interstitials</i>	<i>Vacancies</i>	<i>AlN (mol%)</i>
11 ^a	21	25.00	1.00	^b	61.1
10	22	24.67	0.67	^b	57.7
9	23	24.33	0.33	^b	54.0
8 ^a	24	24.00	0	0	50.0 Normal
7	25	23.67	^b	0.33	45.7
6	26	23.33	^b	0.67	40.9
5 ^a	27	23.00	^b	1.00	35.7 AlON (γ)
4	28	22.67	^b	1.33	30.0
3	29	22.33	^b	1.67	23.7
2 ^a	30	22.00	^b	2.00	16.7 AlON' (ϕ')
1	31	21.67	^b	2.33	8.8
0	32	21.33	^b	2.67	0

^aStoichiometric compounds.^bIntegral numbers of atoms.

Source: McCauley (1978).

formation of many polytype-like (polytypoid) phases; this is apparently different than SiC which has a vast array of polytypes. However, Ueno *et al.* (1992) and Xia *et al.* (1993) have confirmed that at pressures of about 16–20 GPa, AlN transforms into an octahedrally coordinated rocksalt structure (O_h^5). Augmentation of this analysis of bonding and structure, including MAS-NMR data is given by McCauley *et al.* (2009).

Processing and Microstructures of AlN and AlON

AlN powder can be produced by nitridation of aluminum metal powder or also by the reduction of alumina with admixed fine carbon particles in the presence of nitrogen or ammonia. AlON can be produced by the simple reaction of Al_2O_3 with AlN in nitrogen or by the carbothermal reduction of Al_2O_3 + carbon mixtures (Yawes *et al.*, 1997a; Yawes *et al.*, 1997b; Ish-Shalom, 1982).

Even though AlN is hexagonal, it can be sintered into translucent, almost transparent polycrystalline ceramics (Kuramoto and Taniguchi, 1984; Kuramoto *et al.*, 1989). Coble (1962) demonstrated similar results for α - Al_2O_3 , called Lucalox by the General Electric Company. Both of these materials can never be truly transparent in polycrystalline bodies because of their anisotropic optical properties or birefringence. Note, however, that materials with grain sizes significantly smaller than the wavelength of light could possibly be transparent. AlON, however, being optically isotropic, can be produced in completely transparent ceramic bodies (McCauley and Corbin, 1979). Raytheon Corporation manufactures AlON in sizes up to about $30 \times 30 \times 0.6$ cm for special high-performance applications, including transparent armor and radar windows and domes.

Figure 3 illustrates typical microstructures of AlN (Kuramoto and Taniguchi, 1984; Kuramoto *et al.*, 1989), AlON, and Lucalox. Of course, there are many variations of these microstructures, including grain size, shape, porosity, etc. The microstructure of AlON is hard to resolve optically, because the lack of residual stress at the grain boundaries prevents the polishing treatment from preferentially eroding the boundaries for better contrast. See McCauley *et al.* (1988) for a comprehensive review of microstructures in the Al_2O_3 –AlN system, focusing on the AlON', AlON, and polytypoid regions.

Both pressureless sintering and hot pressing have been used to produce pore-free, fully dense AlN and AlON ceramics. Small amounts of additives (MgO in Al_2O_3 , and CaO and rare earth compounds in AlN) are typically utilized to achieve fully dense, pore-free material. Various chemical-vapor-deposition techniques (e.g., Irene *et al.*, 1975; Silvestri *et al.*, 1975) can be used to produce $Al_xO_yN_z$ films. The effect of oxygen on the sintering and hot pressing of AlN has been studied extensively (Sakai and Iwata, 1977; Sakai *et al.*, 1978). It has been recently shown by Liu *et al.* (2013) that carbothermal reduction can enhance sintering and yield transparent AlON ceramics. Lui *et al.* (2013) also draw attention to other densification aids yielding transparent AlON ceramics. Several investigators have also studied the hot pressing of Al_2O_3 –AlN powder mixtures and determined the resulting properties; however, the formation of the various polytypoids makes the interpretation of their results difficult (Turpin-Launay, *et al.* 1983; Shimpo *et al.*, 1992; Sakai, 1978a,b, 1981a,b); Figure 3(b) is an example of a mixed-phase microstructure.

Sakai (1978a, 1981a,b) has reported on the room- and high-temperature flexural strength of AlN– Al_2O_3 materials in the 0–70 mol% Al_2O_3 region. The final products contained variable amounts of AlN polytypoids. Shimpo *et al.* (1992) investigated the properties of pure AlON as compared to AlON–BN composite materials. In a more comprehensive study, Turpin-Launay *et al.* (1983) and Launay *et al.* (1984) investigated the properties of materials in the AlN– Al_2O_3 system by both reactive hot pressing and reaction sintering; they have referred to these materials as ALUMINALON. Significant variations in hardness, flexure strength, and fracture toughness were observed. The friction, wear resistance, and other mechanical properties of the ALUMINALON family of materials were systematically studied by Trabelsi *et al.* (1987). Since this time, the cubic Al_3O_3N phase has seen commercialization (ALONTM) as impact resistant windows transparent to visible and IR radiation (McCauley *et al.*, 2009).

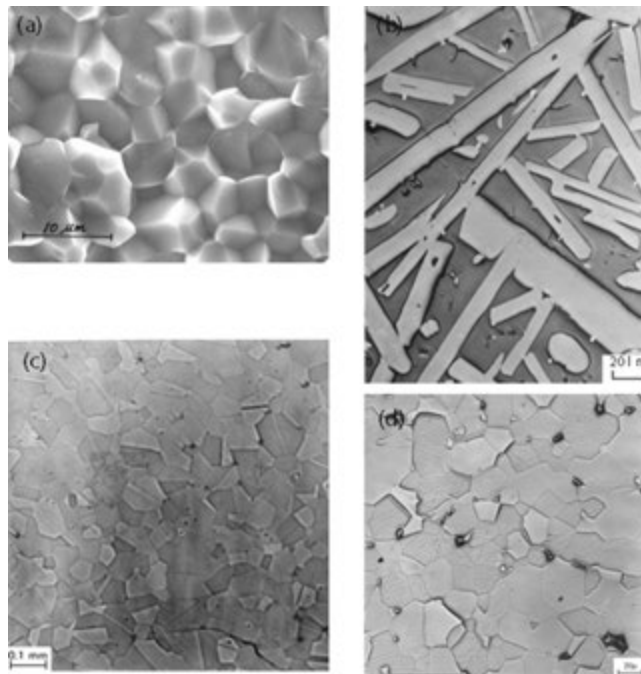


Figure 3 Representative microstructures of (a) AlN, (b) AlON/polytypoid mixture, (c) AlON, and (d) Al₂O₃.

Table 2 Representative properties of polycrystalline AlN, AlON, and α -Al₂O₃

Property	AlN	AlON ^a	α -Al ₂ O ₃
Density (g cm ⁻³)	3.26	3.711	3.98
Hardness (GPa)	12	13.8	15
Young's modulus (GPa)	308	307–320	416
Flexure strength (MPa)	400	228–307	380
Compressive strength (GPa)	1.5–4.0	NA	1.3–4.0
Fracture toughness (MPa ^{1/2})	3.0–4.0	2.4–2.9	3.5
Bulk modulus (GPa)	200	206–214	257
Shear modulus (GPa)	127–130	123–128	150–169
Poisson's ratio	0.23–0.24	0.25	0.23
Thermal conductivity (W m ⁻¹ °C ⁻¹)	180–220	9.4–10.3	33
Coefficient of expansion (°C ⁻¹) (× 10 ⁻⁶ °C ⁻¹) (25–1000 °C)	5.6	7.6	8.1
Melting temperature °C	Sublimes	2165	2050
Electrical band gap (eV)	6	6.2	9.9
Dielectric constant (eV) 1 MHz	8.9	8.56	9.9 ^b
Dielectric constant (eV) 7 GHz	8.2	8.6	9.9
Dielectric loss 1 MHz	0.001	0.0005	0.002
Dielectric loss 7 GHz	0.002	0.0002	
Refractive index (at 0.55 μm) n or n_o	2.23	1.785	1.768
Refractive index n_e	2.17		1.76
IR cut off (μm)	6.3	5.2	6
Longitudinal sound velocity (km s ⁻¹)	10.7–10.8	10.13–10.3	9.0–11.0
Hugoniot elastic limit (GPa)	7.0–9.4	10.5–10.9	5.0–14.0

^a35.7 mol% AlN material.

^bSapphire dielectric constants: parallel to c axis = 9.39; perpendicular to c axis = 11.58.

Source: Harris (1999).

Properties of AlN and AlON

AlN is a high band gap (about 6.2 eV) dielectric material with a very high thermal conductivity. Slack (1973) estimated the thermal conductivity of a single crystal to be about 320 W m⁻¹ K⁻¹ at 300 K. Since that time, there has been a great deal of effort in

attempting to produce ceramics that approach this value for a variety of high-performance substrate and packaging applications in microelectronics and high-power devices (Ichinose, 1988; Sheppard, 1990). It also has excellent molten-metal corrosion resistance and stability at high temperatures. Extensive high-temperature creep and compressive strength measurements have been carried out on AlN (e.g., Masson *et al.*, 1994). It is also very interesting to note that Heard and Cline (1980) have reported a brittle–ductile transformation in AlN at 0.55 GPa confining pressure; Al₂O₃ does not seem to exhibit this transformation up to a confining pressure of 1.25 GPa. AlON has not been studied in this way yet.

AlON has not been studied as extensively as AlN or α -Al₂O₃. The elastic properties have been worked out by Graham *et al.* (1988), the thermomechanical properties by Quinn *et al.* (1984) and Swab *et al.* (1999), dielectric properties by Westphal and the optical properties by Tropf and Thomas (1991). Kim and Richards (1985) investigated the electrical conductivity of AlON. Neutron irradiation studies are detailed by Jeanne *et al.* (1987). Goursat *et al.* (1976, 1981) have carried out extensive studies on the oxidation of AlON-based materials at high temperature. Table 2 summarizes a variety of representative properties for AlN, AlON, and α -Al₂O₃.

The transparency of AlON to light of various wavelengths makes it suitable as an upconversion material. Thus, if the AlON is densified using erbium and ytterbium as densifying aids, near IR wavelengths can be dissociated into optical wavelengths in both the green and red visible region (Su *et al.*, 2015) due to the double quantum yield associated with Er–Yb interactions. Liu *et al.* (2013) also draw attention to rare earth doped AlON R–G–B emitters using laser excitation as well as rare earth doped AlON being possible materials for the phosphor-converted white LEDs. Thus, AlON appears to have potential use in luminescent materials, as well as in impact resistant windows.

References

- Coble, R. L., 1962. US Patent 3026210.
- Corbin, N.D., 1989. Aluminum oxynitride spinel: A review. *J. Eur. Ceram. Soc.* 5, 143–154.
- Dorignac, D., Mazel, A., Kihn, Y., *et al.*, 1994. Transmission electron microscopy studies of AlN. *J. Eur. Ceram. Soc.* 14, 345–353.
- Dugger, C.O., 1975. The Single Crystal Synthesis and Some Properties of Aluminum Nitride, AFCRL-TR-75-0486. Hanscom AFB, MA: Air Force Cambridge Research Laboratories.
- Dumitrescu, L., Sundman, B., 1995. A thermodynamic reassessment of the Si–Al–O–N system. *J. Eur. Ceram. Soc.* 15, 239–247.
- Fukuyama, H., Nakao, W., Susa, M., Nagata, K., 1999. New synthetic method of forming aluminum oxynitride by plasma arc melting. *J. Am. Ceram. Soc.* 82, 1381–1387.
- Goursat, P., Billy, M., Goeuriot, P., *et al.*, 1981. Contribution a l'etude du systeme Al/O/N II: Retention d'azote dans les produits d'oxydation de l'oxynitride d'aluminium γ . *Mater. Chem.* 6, 81–94.
- Goursat, P., Goeuriot, P., Billy, M., 1976. Contribution a l'etude du systeme Al/O/N I – reactivite de l'oxynitride d'aluminium γ . *Mater. Chem.* 1, 131–149.
- Graham, E.K., Munly, W.C., McCauley, J.W., Corbin, N.D., 1988. Elastic properties of polycrystalline aluminum oxynitride spinel and their dependence on pressure, temperature, and composition. *J. Am. Ceram. Soc.* 71, 807–812.
- Harris, D.C., 1999. *Materials for Infrared Windows and Domes*. Bellingham, WA: SPIE Optical Engineering Press.
- Heard, H.C., Cline, C.F., 1980. Mechanical behavior of polycrystalline BeO, Al₂O₃ and AlN at high pressures. *J. Mater. Sci.* 15, 1889–1897.
- Ichinose, N., 1988. Aluminum nitride ceramics for substrates ceramic developments. *Mater. Sci. Forum* 34–6, 663–667.
- Irene, E.A., Silvestri, V.J., Woolhouse, G.R., 1975. Some properties of chemically vapor deposited films of Al₂O₃N₂ on silicon. *J. Electron. Mater.* 4, 409–427.
- Ish-Shalom, M., 1982. Formation of aluminum oxynitride by carbothermal reduction of aluminum oxide in nitrogen. *J. Mater. Sci. Lett.* 1, 147–149.
- Jeanne, A., Labbe, J.C., Lefort, P., Roult, G., 1987. Behavior of aluminum oxynitride under fast neutron irradiation. In: Vincenzini, P. (Ed.), *High Tech Ceramics*. Amsterdam: Elsevier, pp. 2981–2988.
- Kim, I., Richards, V.L., 1985. High-temperature electrical conductivity of aluminum oxynitride spinel. *J. Am. Ceram. Soc.* 68, C210.
- Krishnan, K.M., Rai, R.S., Thomas, G., Corbin, N.D., McCauley, J.W., 1985. Characterization of long-period polytypoid structures in the Al₂O₃–AlN system. *MRS Proc.* 60, 211–218.
- Kuramoto, N., Taniguchi, H., 1984. Transparent AlN ceramic. *J. Mater. Sci. Lett.* 3, 471–474.
- Kuramoto, N., Taniguchi, H., Aso, I., 1989. Development of translucent aluminum nitride ceramics. *Ceram. Bull.* 68, 883–887.
- Launay, D., Orange, G., Goeuriot, P., Thevenot, F., Fantozzi, G., 1984. Reaction-sintering of an Al₂O₃–AlON composite: determination of mechanical properties. *J. Mater. Sci. Lett.* 3, 890–892.
- Lefebvre, A., Gilles, J.C., Collongues, R., 1972. Antiphases periodiques dans un spinelles nonstoechiometrique (9Al₂O₃–AlN) prepare a haute temperature. *MRS Bull.* 7, 557–566.
- Long, G., Foster, L.M., 1961. Crystal phases in the system Al₂O₃–AlN. *J. Am. Ceram. Soc.* 44, 255–258.
- Liu, X.J., Chen, F., Zhang, F., *et al.*, 2013. Hard transparent AlON ceramic for visible/IR windows. *Int. J. Refract. Metals Hard Mater.* 39, 38–43.
- Masson, I., Feiereisen, J.P., Michel, J.P., George, A., Mocellin, A., 1994. High-temperature compressive tests of aluminum nitride: Mechanical properties and microstructure. *J. Eur. Ceram. Soc.* 355–363.
- McCauley, J.W., 1978. A simple model for aluminum oxynitride spinels. *J. Am. Ceram. Soc.* 61, 372–373.
- McCauley, J.W., Corbin, N.D., 1979. Phase relations and reaction sintering of transparent cubic aluminum oxynitride spinel (AlN). *J. Am. Ceram. Soc.* 62, 476–479.
- McCauley, J.W., Corbin, N.D., 1983. High temperature reactions and microstructures in the Al₂O₃–AlN system. In: Riley, F.L. (Ed.), *Progress in Nitrogen Ceramics*. The Netherlands: Nijhoff Dordrecht, pp. 111–118.
- McCauley, J.W., Krishnan, K.M., Rai, R.S., *et al.*, 1988. Anion-controlled microstructures in the Al₂O₃–AlN system. In: Park, J., Evans, A. (Eds.), *Ceramic Microstructures* 86. New York: Plenum, pp. 577–590.
- McCauley, J.W., Patel, P.L., Chen, M., *et al.*, 2009. AlON: A brief history of its emergence and evolution. *J. Europ. Ceram. Soc.* 29 (2), 223–236.
- Michel, D., 1972. Contribution a l'etude de phenomenes d'ordonnement de defaults dans les monocristaux de materiaux refractaires a base d'alumine et de zircone. *Rev. Int. Haute Temp. Refract.* 9, 225–242.
- Munro, R.G., 1997. Evaluated material properties for a sintered α -alumina. *J. Am. Ceram. Soc.* 80, 1919–1928.
- Pauling, L., 1963. *The Nature of the Chemical Bond*. Ithaca, NY: Cornell University Press, pp. 88–102.
- Prohaska, G.W., Miller, G.R., 1990. Aluminum nitride: A review of the knowledge base for physical property development. *MRS Symp. Proc.* 167, 215–227.
- Qiu, C., Metselaar, R., 1997. Phase relations in the aluminum carbide–aluminum nitride–aluminum oxide system. *J. Am. Ceram. Soc.* 80, 2013–2020.
- Quinn, G.D., Corbin, N.D., McCauley, J.W., 1984. Thermomechanical properties of aluminum oxynitride spinel. *J. Am. Ceram. Soc.* 63, 723–729.

- Sakai, T., 1978a. Hot-pressing of the AlN–Al₂O₃ system. *Yogyo-Kyokai-Shi* 88, 37–42.
- Sakai, T., 1978b. Effect of oxygen composition on flexural strength of hot-pressed AlN. *J. Am. Ceram. Soc.* 61, 460–461.
- Sakai, T., 1981a. Hot-pressed oxynitrides in the system AlN–Al₂O₃, sintering – Theory and practice. *Mater. Sci. Monogr.* 14, 591–596.
- Sakai, T., 1981b. High-temperature strength of AlN hot-pressed with Al₂O₃ additions. *J. Am. Ceram. Soc.* 64, 135–136.
- Sakai, T., Iwata, M., 1977. Effect of oxygen on sintering of AlN. *J. Mater. Sci.* 12, 1659–1665.
- Sakai, T., Kuriyama, M., Inukai, T., Kizima, L.M., 1978. Effect of oxygen impurity on the sintering and the thermal conductivity of AlN polycrystal. *Yogyo-Kyokai-Shi* 86, 30–35.
- Sheppard, L.M., 1990. Aluminum nitride: A versatile but challenging material. *Ceram. Bull.* 69, 1801–1812.
- Shimpo, A., Ide, H., Ueki, M., 1992. AlON and its composite ceramics. *J. Ceram. Soc. Jpn.* 100, 504–508.
- Silvestri, V.J., Irene, E.A., Zirinsky, S., Kuptsis, A., 1975. Chemical vapor deposition of Al_xO_yN_z films. *J. Electron. Mater.* 4, 429–444.
- Slack, G.A., 1973. Nonmetallic crystals with high thermal conductivity. *J. Phys. Chem. Solids* 34, 321–335.
- Su, M., Zhou, Y., Wang, K., Huang, D., Xu, W., Cao, Y., 2015. Effect of Yb³⁺ concentration on upconversion luminescence of AlON: Er³⁺ phosphors. *J. Rare Earths* 33 (3), 227–230.
- Swab, J., LaSalvia, J.C., Gilde, G.A., Patel, P., Motyka, M.J., 1999. Transparent armor ceramics: AlON and spinel. *Ceram. Eng. Sci. Proc.* 20, 79–86.
- Tabary, P., Servant, C., 1998. Thermodynamic reassessment of the AlN–Al₂O₃ system. *Calphad* 22, 179–201.
- Tabary, P., Servant, C., 1999a. Crystalline and microstructure of the AlN–Al₂O₃ section in the Al–N–O system I. Polytypes and γ -AlON spinel phase. *J. Appl. Crystallogr.* 32, 241–252.
- Tabary, P., Servant, C., 1999b. Crystalline and microstructure of the AlN–Al₂O₃ section in the Al–N–O system II. ϕ' and δ -AlON spinel phases. *J. Appl. Crystallogr.* 32, 253–272.
- Tabary, P., Servant, C., Alary, J.A., 2000. Microstructure and phase transformations in the AlN–Al₂O₃ pseudo-binary system. *J. Eur. Ceram. Soc.* 20, 913–926.
- Trabelsi, R., Treheux, D., Goeuriot-Launay, D., *et al.*, 1987. Friction, wear resistance, and mechanical properties of an alumina- γ -aluminum oxynitride composite (Aluminalon). In: Vincenzini, P. (Ed.), *High Tech Ceramics*. Amsterdam: Elsevier, pp. 2683–2695.
- Tropf, W.J., Thomas, M.E., 1991. Aluminum oxynitride (AlON) spinel. In: Palik, E.D. (Ed.), *Handbook of Optical Constants of Solids II*. New York: Academic Press, pp. 777–787.
- Turpin-Launay, D., Thevenot, F., Delvoe, F., Boch, P., 1983. Reactive hot-pressing of γ -aluminum oxynitride. In: Vincenzini, P. (Ed.), *Ceramic Powders*. Amsterdam: Elsevier, pp. 891–897.
- Ueno, M., Onodera, A., Shimomura, O., Takemura, K., 1992. X-ray observation of the structural phase transition of aluminum nitride under high pressure. *Phys. Rev. B* 45, 10123–10126.
- Willems, H.X., Hendrix, M.M.R.M., Metselaar, R., de With, G., 1992a. Thermodynamics of AlON I: Stability at lower temperatures. *J. Eur. Ceram. Soc.* 10, 327–337.
- Willems, H.X., Hendrix, M.M.R.M., Metselaar, R., de With, G., 1992b. Thermodynamics of AlON II: Phase relations. *J. Eur. Ceram. Soc.* 10, 339–346.
- Xia, Q., Xia, H., Ruoff, L., 1993. Pressure-induced rocksalt phase of aluminum nitride: A metastable structure at ambient condition. *J. Appl. Phys.* 73, 8198–8200.
- Yamaguchi, G., Yanagida, H., 1959. Study on the reductive spinel – A new spinel formula AlN–Al₂O₃ instead of the previous one Al₃O₄. *Bull. Chem. Soc. Jpn.* 32, 1264–1265.
- Yawes, L., Nan, L., Runzhang, Y., 1997a. Effect of raw materials on carbothermal reduction synthesis of γ -aluminum oxynitride spinel powder. *Sci. Sinter.* 29, 95–103.
- Yawes, L., Nan, L., Runzhang, Y., 1997b. The formation and stability of γ -aluminum oxynitride spinel in the carbothermal reduction and reaction sintering processes. *J. Mater. Sci.* 32, 979–982.

Further Reading

- Buhr, H., Muller, G., Wiggers, H., 1991. Phase composition, oxygen content, and thermal conductivity of AlN(Y₂O₃) ceramics. *J. Am. Ceram. Soc.* 74, 718–723.
- Cazamias, J.U., Fiske, P.S., Bless, S.J., 2000. Shock properties of AlON. In: Staudhammer, K.P., Murr, L.E., Meyers, M.A. (Eds.), *Fundamental Issues and Applications of Shock-wave and High Strain-Rate Phenomena*. Amsterdam: Elsevier, pp. 181–188.
- Cormack, A., 1989. Intrinsic disorder in aluminum nitride. *J. Am. Ceram. Soc.* 72, 1730–1732.
- Hartnett, T.M., Maguire, E.A., Gentilman, R.L., Corbin, N.D., McCauley, J.W., 1982. Aluminum oxynitride spinel (AlON) – A new optical and multimode window material. *Ceram. Eng. Sci. Proc.* 3, 67–76.
- Holmquist, T.J., Rajendram, A.M., Templeton, D.W., Bishoi, K.D., 1989. A Ceramic Armor Materials Database, TARDEC Technical Report No. 13754. US Army Tank-Automotive Research, Development, and Engineering Center, Warren, MI.
- Huseby, I.C., 1983. Synthesis and characterization of a high-purity AlN powder. *J. Am. Ceram. Soc.* 66, 217–220.
- Iwamoto, Y., Kuibira, A., Sugiura, I., Tsubaki, J., 1992. Effects of powder properties on thermal conductivity of aluminum nitride. *J. Eur. Ceram. Soc.* 100, 652–656.
- Shafer, P.T.B., Mroz, T.J., 1992. *Handbook of Advanced Ceramic Materials*. Buffalo, NY: Advanced Refractory Technologies, Inc.
- Tabary, P., Servant, C., Guymont, M., 1999. High-resolution transmission electron microscopy study of the ϕ' and δ -AlON spinel phases of the pseudo-binary section of AlN–Al₂O₃. *J. Appl. Crystallogr.* 32, 755–760.
- Willems, H.X., de With, G., Metselaar, R., 1993. Thermodynamics of AlON III: Stabilization of AlON with MgO. *J. Eur. Ceram. Soc.* 12, 43–49.

SiC Ceramics, Structure, Processing and Properties

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Introduction

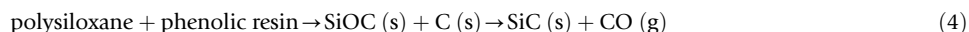
Silicon carbide (SiC), also known as carborundum, is an important non-oxide ceramic that exhibits unique properties, such as high temperature strength; resistance to wear, corrosion, and oxidation; tunable thermal and electrical properties; thermal shock resistance; amenable toughness, and a high hardness. Moissanite is an extremely rare mineral of SiC in earth's crust. In industries, it is produced by the Acheson process by reacting high-purity sand with low-sulfur coke at 2200–2500°C via the following reaction:



The high temperature employed in the Acheson process favors the formation of α -SiC (hexagonal crystal structure), a thermodynamically stable, high-temperature phase of SiC. By contrast, the cubic phase, β -SiC, is synthesized by the following vapor phase reactions at 1200–1600°C:



Nano-sized β -SiC powders can be synthesized by pyrolyzing preceramic polymers at 1500°C in an inert atmosphere via the following reaction (Kim *et al.*, 2009):



This chapter summarizes the academic and technological advances in SiC ceramics and discusses their current status in terms of the structure; processing methods; properties including mechanical, electrical, thermal, magnetic, and optical properties; and applications. The processing and properties of SiC-based composites, thin films, and porous ceramics are excluded.

Structure

The fundamental structural unit of SiC is either CSi_4 or SiC_4 , where the central atom (C/S) is bonded to four adjacent atoms (S/C) in a tetrahedral coordination (Izhevskiy *et al.*, 2000). SiC exhibits polymorphism and has more than 250 known polytypes (Cheung, 2006). It is customary to designate all the cubic polytypes as β -SiC, and all the non-cubic structures (hexagonal and rhombohedral) as α -SiC. All the polytypes can be described in a general hexagonal axis system, wherein a particular polytype is described by a SiC bilayer stacking sequence along the c-axis of the hexagonal system. As shown in Fig. 1, the SiC polytypes differ from each other with respect to the stacking sequence of the SiC bilayers. For instance, if the stacking sequence is of the ABCABC... type, then it is referred to as 3C-SiC. Similarly, the stacking sequences of ABCBABC... and ABCACB... are known as 4H and 6H, respectively. Some important properties of the major SiC polytypes are listed in Table 1.

Processing

SiC ceramics can be fabricated by various processing techniques, such as pressureless sintering, gas pressure sintering (GPS), hot pressing, spark plasma sintering (SPS), reaction bonded SiC (RBSC), recrystallization, chemical vapor deposition (CVD), and hot isostatic pressing (HIP). A brief discussion of these processing methodologies is given below.

Pressureless Sintering

SiC is a highly covalently bonded compound. Therefore, it is difficult to densify it without sintering additives. SiC can be sintered via solid-state sintering with the aid of B and C or B_4C and C, which drastically improve its shrinkage kinetics (Prochazka and Popper, 1975). Alternatively, liquid-phase sintering can be performed using metal oxides or mixtures of metal oxides and metal nitride, such as Al_2O_3 and Y_2O_3 (Mulla and Krstic, 1994; Kim *et al.*, 1998) and Al_2O_3 - Y_2O_3 -AlN (Kim *et al.*, 2017a). The oxides react with SiO_2 , which is typically present at the surface of SiC particles, to form an oxide melt and increase the densification. Solid-state sintering of SiC is typically performed at temperatures of approximately 2050–2200°C and results in moderate mechanical properties (flexural strength of 250–450 MPa and fracture toughness of 2.5–4 $\text{MPa m}^{1/2}$). By contrast, liquid-phase sintering of SiC can be achieved at relatively lower temperatures ($\leq 2000^\circ\text{C}$) (Eom *et al.*, 2016; Kim and Kim, 2019). Thus, the interest in liquid-phase-sintered SiC (LPS-SiC) has grown continually owing to its superior mechanical properties relative to those of solid-state-sintered SiC (SSS-SiC) and its cost-effectiveness.

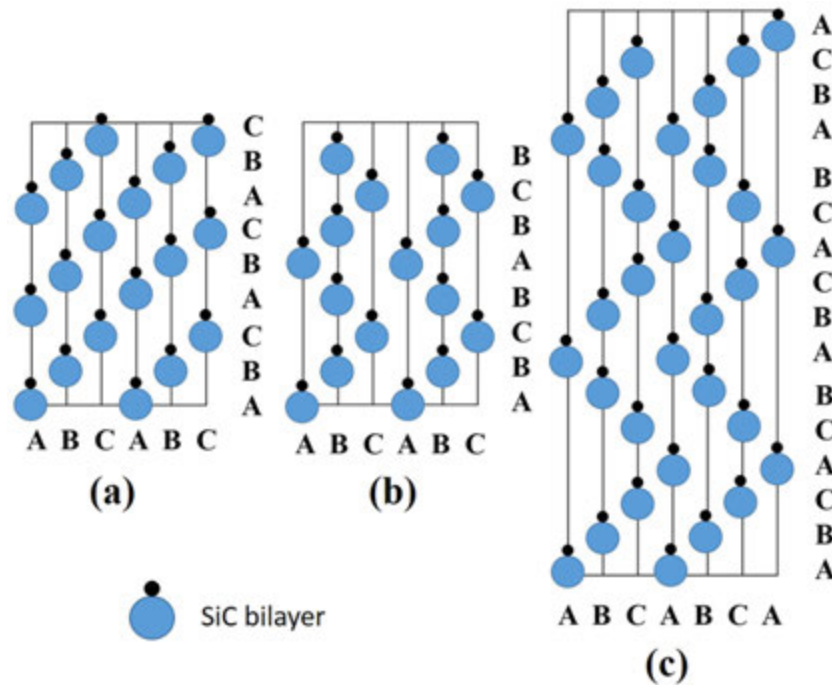


Fig. 1 SiC polytypes: (a) 3C, (b) 4H, and (c) 6H. Modified from Morkoc, H., Strite, S., Gao, G.N., *et al.*, 1994. Large-band-gap SiC, III-V nitride, and II-VI ZnSe-based semiconductor device technologies. *Journal of Applied Physics* 76, 1363–1398.

Table 1 Properties of major SiC polytypes

Polytype	3C	4H	6H
Crystal structure	Zinc blende (cubic)	Wurtzite	Wurtzite
Lattice	Face-centered cubic	Hexagonal	Hexagonal
Symmetry group	F-43m	$P6_3mc$	$P6_3mc$
Lattice constant (Å)	4.35890	3.08100, 10.06100	3.08065, 15.11740
Density (g cm^{-3})	3.216	3.220	3.215
Bandgap (eV)	2.390	3.263	3.023
Bulk modulus (GPa) (300K)	250	220	220

Note: Schneer, C.J., 1955. Polymorphism in one dimension. *Acta Crystallographica* 8, 279–285. Goldberg, Y., Levinstein, M.E., Rumyantsev, S.L., 2001. Chapter – 5 Silicon carbide (SiC). In: Levinstein, M.E., Rumyantsev, S.L., Shur, M.S. (Eds.), *Properties of Advanced Semiconductor Materials: GaN, AlN, SiC, BN, SiC, SiGe*. New York: John Wiley & Sons, Inc, pp. 93–148. Anon1, 1977. Powder Diffraction File, Card No. 29–1127. Joint Committee on Powder Diffraction Standards. Swarthmore, PA. Anon2, 1977. Powder Diffraction File, Card No. 29–1129. Joint Committee on Powder Diffraction Standards. Swarthmore, PA. Anon3, 1997. Powder Diffraction File, Card No. 72–0018. Joint Committee on Powder Diffraction Standards. Swarthmore, PA.

A typical microstructure of an LPS-SiC ceramic with a ternary additive system ($\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-CaO}$) is shown in **Fig. 2(a)** (Eom *et al.*, 2016). A unique characteristic of the microstructure of LPS-SiC ceramics is a core/rim structure, formed by grain growth via solution-reprecipitation during sintering. By contrast, the typical microstructure of SSS-SiC shown in **Fig. 2(b)** (Kim *et al.*, 2013b) lacks a core/rim structure, and SSS-SiC ceramics fracture transgranularly.

The factors affecting the densification behavior of SiC ceramics include impurities (C and SiO_2) and the polytype of the SiC powders, sintering atmosphere, and sintering additive composition. The influence of carbon and SiO_2 impurities present in the starting powders on the densification of SiC ceramics is two-fold. In the case of solid-state sintering of SiC ceramics, the presence of a moderate amount of free C is beneficial because it reacts with SiO_2 , removing it from the surface of the SiC particles (Kim *et al.*, 1995c). By contrast, it is detrimental to liquid-phase sintering because of its tendency to react with oxide additives and liberate gaseous products during sintering (Kim *et al.*, 1995c, 1996). The presence of SiO_2 impurity in SiC powders is disadvantageous in solid-state sintering because it liberates gaseous CO by reacting with the free carbon. However, it is beneficial in liquid-phase sintering because it promotes the formation of a liquid phase with other oxide additives and enhances densification (Kim *et al.*, 1996).

The polytype of the starting SiC powders does not have a significant influence on the densification behavior of SiC ceramics; however, it affects the final microstructure following sintering. In LPS-SiC ceramics, the α -SiC starting powders lead to equiaxed grains, whereas β -SiC starting powders lead to elongated grains because of the $\beta \rightarrow \alpha$ transformation of SiC during sintering (Kim *et al.*, 1998; Nader *et al.*, 1999). By contrast, the microstructure of SSS-SiC ceramics is predominantly influenced by the sintering

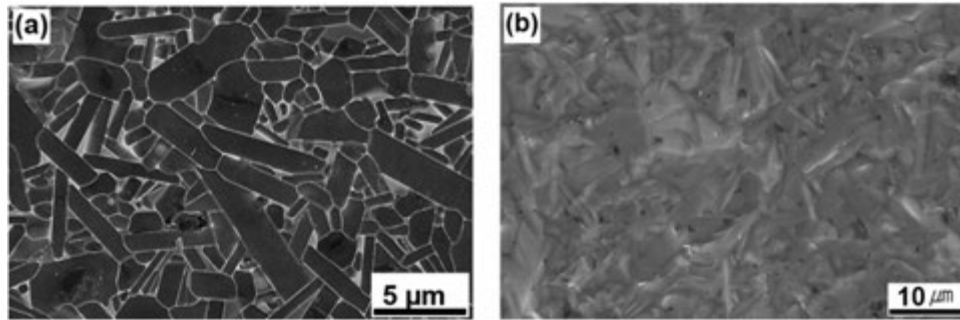


Fig. 2 Typical microstructures of (a) liquid-phase sintered SiC ceramics and (b) solid state sintered SiC ceramics. Reproduced from (a) Eom, J.H., Seo, Y.K., Kim, Y.W., 2016. Mechanical and thermal properties of pressureless sintered silicon carbide ceramics with alumina-yttria-calcia. *Journal of the American Ceramic Society* 99, 1735–1741. (b) Kim, K.J., Lim, K.Y., Kim, Y.W., 2013b. Control of electrical resistivity in silicon carbide ceramics sintered with aluminum nitride and yttria. *Journal of the American Ceramic Society* 96, 3463–3469.

temperature. When the sintering temperature exceeds a critical temperature, exaggerated grain growth is frequently observed because of $3C \rightarrow 6H$ and/or $6H \rightarrow 4H$ phase transformations of SiC (Williams *et al.*, 1984).

Atmosphere significantly influences the sintering behavior of SiC ceramics. The following effects are reported in SSS-SiC ceramics densified with B and C:

- (1) Argon and vacuum atmospheres are effective in the densification of SiC ceramics via solid-state sintering (Prochazka and Popper, 1975; Ness and Rafaniello, 1994).
- (2) A CO partial pressure of 6.5×10^{-4} MPa does not significantly inhibit densification. However, a CO pressure of 2.5×10^{-3} MPa noticeably inhibits the densification of SiC, and a pressure of 0.1 MPa CO stops the densification of SiC because of the removal of boron present in the sintered body (Prochazka *et al.*, 1979).
- (3) A nitrogen-containing atmosphere retards both the grain growth and densification of SiC ceramics (Prochazka *et al.*, 1979).

The following effects are known in LPS-SiC ceramics with metal oxide additives or metal oxide-AlN mixtures:

- (1) An argon atmosphere is extremely effective in the densification of LPS-SiC ceramics when the liquid phase does not contain nitrogen (Eom *et al.*, 2015).
- (2) A nitrogen atmosphere is more effective than argon when the liquid phase contains nitrogen, e.g., oxynitride or oxycarbonitride liquids that cool to form grain boundary glasses, because a nitrogen atmosphere stabilizes a N-containing liquid phase at high temperatures (Kim and Mitomo, 1999). A nitrogen atmosphere also leads to the growth of N-doped SiC ceramics by dissolution into the liquid phase, resulting in electrically conductive SiC ceramics (Fig. 3; Kim *et al.*, 2015b).
- (3) A vacuum atmosphere is detrimental in the densification of LPS-SiC ceramics because of the accelerated evaporation of the liquid phase during sintering.

The additives in the sintering of LPS-SiC ceramics can be regarded as not only densification aids, but also as key elements for functionality. This is because the electrical, thermal, and mechanical properties are influenced by the composition of the additives as well as the microstructure of the resulting ceramics (Lee *et al.*, 2001a,b; Eom *et al.*, 2015; Jang *et al.*, 2016). Not only for achieving a successful densification of SiC but also for realizing functionality in LPS-SiC ceramics, much effort has been expended to determine new additive compositions because the pressureless sintering of SiC ceramics is preferred for a cost-effective production of the corresponding parts. Thus, various additive systems such as binary, ternary, and quaternary systems have been investigated for a pressureless sintering of SiC ceramics. The additive composition, sintering conditions, and sintered density of pressureless sintered SiC ceramics are listed in Table 2. The relative sintered densities of pressureless sintered SiC ceramics for a binary, ternary, and quaternary additive system are in the ranges 97.0%–99.9%, 96.0%–99.4%, and 96.7%–98.8%, respectively, depending on the additive composition, additive content, and sintering conditions (Table 2). A typical microstructure of a pressureless sintered SiC is shown in Fig. 4(a).

Hot Pressing

SiC ceramics can be densified to near-theoretical densities by hot pressing. During hot pressing, the material transport is accelerated by a plastic flow, and particle rearrangement is performed by the application of a high pressure (10–40 MPa) and diffusion at a high temperature (1700–2000°C). Additionally, the application of pressure helps in reducing the required sintering temperature for densification and inhibits the grain growth. Fig. 4(b) shows a typical microstructure of a monolithic SiC sintered to a high relative density (97.5%) when hot pressed at 1750°C at 20 MPa for 15 min under an Ar atmosphere using fine β -SiC and Al_2O_3 - Y_2O_3 -CaO (sintering additives) as the starting materials (Kim *et al.*, 1995b). However, owing to the uniaxial application of pressure, only simple shapes with anisotropic properties can be sintered by hot pressing. To obtain full densification at low temperatures ($\leq 2000^\circ\text{C}$) and a short holding time (1–6 h), liquid-forming additives such as Al-compounds, RE oxides, and alkaline earth oxides are frequently used (Kim *et al.*, 1997; Lee *et al.*, 2001a,b; Kim *et al.*, 2004; Cho *et al.*, 2018; Malik *et al.*, 2018, 2019). An important advantage of hot pressing

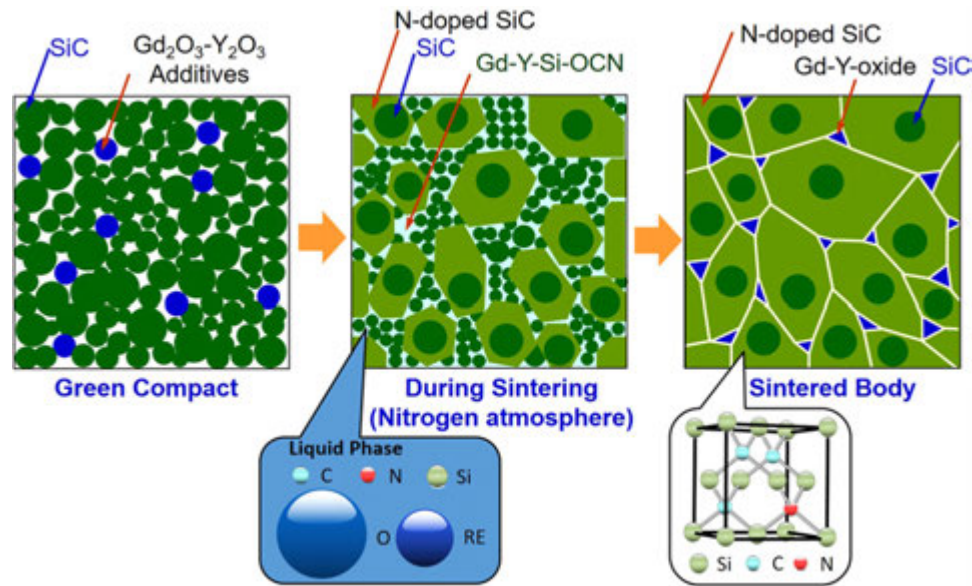


Fig. 3 Schematic illustration of nitrogen-doping mechanism via solution-precipitation in SiC ceramics sintered with $\text{Gd}_2\text{O}_3\text{-Y}_2\text{O}_3$ in a nitrogen atmosphere. Reproduced from Kim, Y.W., Cho, T.Y., Kim, K.J., 2015b. Effect of grain growth on electrical properties of silicon carbide ceramics sintered with gadolinia and yttria. *Journal of the European Ceramic Society* 35, 4137–4142.

Table 2 Sintered density of pressureless sintered LPS-SiC ceramics

Additive system	Sintering additives	Processing conditions	Sintered density (%)	References
Binary	6 vol% $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$	1850°C/5 min/Ar	97	Mulla and Krstic (1991)
	6 mol% $\text{Al}_2\text{O}_3\text{-Gd}_2\text{O}_3$	1950°C/1 h/Ar	98	Chen (1996)
	16.2 wt% $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$	1950°C/3 h/Ar	97.3	Kim <i>et al.</i> (1998)
	17 wt% $\text{Al}_2\text{O}_3\text{-Y}_3\text{Al}_5\text{O}_{12}$	1950°C/3 h/Ar	98	Baud <i>et al.</i> (2003)
	7 wt% $\text{Al}_2\text{O}_3\text{-CeO}_2$	1840°C/1 h/Ar	99.1	Liang <i>et al.</i> (2014a)
	7 wt% $\text{Al}_2\text{O}_3\text{-Er}_2\text{O}_3$	1880°C/1 h/Ar	98	Liang <i>et al.</i> (2016)
	10 vol% $\text{AlN-Yb}_2\text{O}_3$	2000°C/2 h/Ar	99.5	Santos and Ribeiro (2018)
	10 vol% $\text{AlN-Y}_2\text{O}_3$	1900°C/2 h/ N_2	99.9	Kim <i>et al.</i> (2019b)
Ternary	10 wt% $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-MgO}$	1950°C/2 h/Ar	96	Gubernat <i>et al.</i> (2007)
	12 wt% $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-TiO}_2$	1920°C/0.5 h/Ar	99.2	Liang <i>et al.</i> (2014b)
	3 vol% $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-AlN}$	1900°C/1 h/Ar	99.4	Eom <i>et al.</i> (2015)
	9 wt% $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-CaO}$	1850°C/2 h/Ar	99	Eom <i>et al.</i> (2016)
	6.5 vol% $\text{Y}_2\text{O}_3\text{-Sc}_2\text{O}_3\text{-AlN}$	1950°C/6 h/ N_2	98.6	Cho <i>et al.</i> (2016)
	3 vol% $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-AlN}$	1900°C/1 h/Ar	97.0	Kim <i>et al.</i> (2017a)
Quaternary	9.07 wt% $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-SrO-CaO}$	1900°C/2 h/Ar	96.7	Seo <i>et al.</i> (2018)
	9 wt% $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-MgO-CaO}$	1800°C/2 h/Ar	98.8	Kim and Kim (2019)
	3.87 wt% $\text{AlN-Y}_2\text{O}_3\text{-Sc}_2\text{O}_3\text{-MgO}$	1850°C/2 h/Ar	98.3	Kim <i>et al.</i> (2019a)

over the conventional pressureless sintering is the reduced amount of sintering additives, which improves the high-temperature strength and the thermal and electrical properties.

Gas Pressure Sintering

GPS is used to prevent the decomposition of the nitride additives added for the densification of SiC (Biswas *et al.*, 2001). AlN-containing sintering additives are extensively used for the low-temperature densification of SiC. However, the decomposition of an AlN additive with the evolution of gaseous products is detrimental to the densification of SiC. To avoid this problem, AlN in combination with RE oxides can be used to sinter SiC under a nitrogen pressure (Biswas *et al.*, 2001, 2005). An α -SiC compact containing 10 vol% $\text{AlN-Y}_2\text{O}_3$ as the sintering additives can be completely densified by the GPS at 1950°C under a nitrogen pressure of 10 MPa for 1 h (Biswas *et al.*, 2001). A typical microstructure of a gas-pressure-sintered SiC is shown in Fig. 4(c).

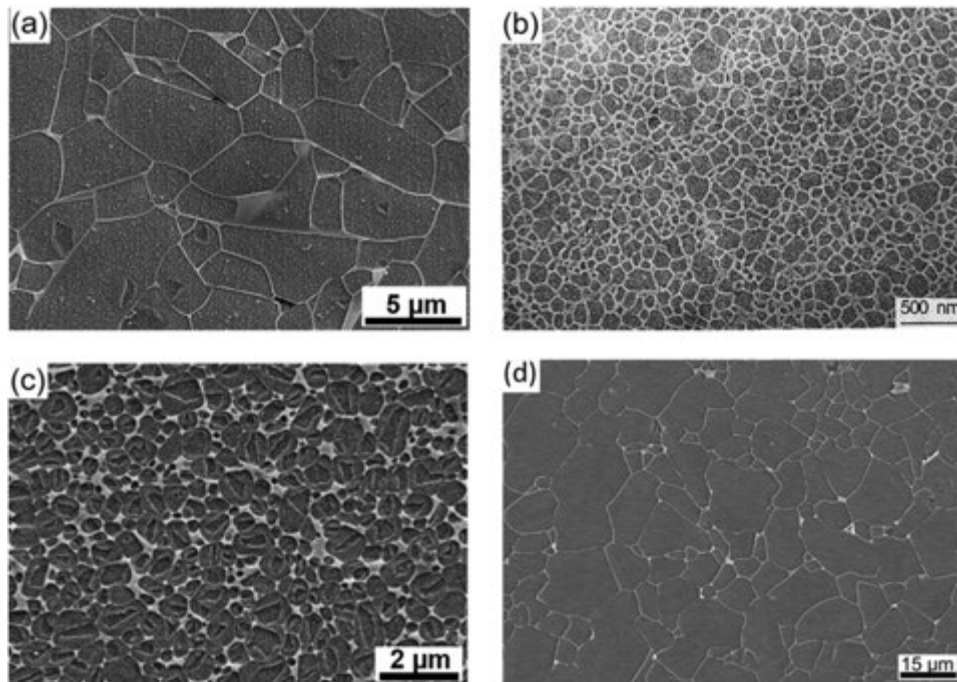


Fig. 4 Typical microstructures of (a) pressureless sintered SiC with $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-Sc}_2\text{O}_3\text{-MgO}$ at 1950°C for 2 h in Ar atmosphere, (b) hot pressed SiC with $\text{Y}_2\text{O}_3\text{-Sc}_2\text{O}_3$ at 1850°C for 2 h in N_2 atmosphere, (c) gas pressure sintered SiC with $\text{AlN-Y}_2\text{O}_3$ at 2050°C for 1 h under 10 MPa of N_2 atmosphere, and (d) spark plasma sintered SiC with $\text{Y}_2\text{O}_3\text{-Sc}_2\text{O}_3$ at 2050°C for 6 h at 60 MPa in N_2 atmosphere. Reproduced from (a) Kim, H.M., Kim, Y.W., Lim, K.Y., 2019a. Pressureless sintered silicon carbide matrix with a new quaternary additive for fully ceramic microencapsulated fuels. *Journal of the European Ceramic Society* 39, 3971–3980. (b) Kim, Y.W., Mitomo, M., Hirotsuru, H., 1995b. Grain growth and fracture toughness of fine-grained silicon carbide ceramics. *Journal of the American Ceramic Society* 78, 3145–3148. (c) Rixecker, G., Biswas, K., Rosinus, A., *et al.*, 2002. Fracture properties of SiC ceramics with oxynitride additives. *Journal of the European Ceramic Society* 22, 2669–2675. (d) Seo, Y.K., Kim, Y.K., Nishimura, T., Seo, W.S., 2017. High thermal conductivity of spark plasma sintered silicon carbide ceramics with yttria and Scandia. *Journal of the American Ceramic Society* 100, 1290–1294.

Spark Plasma Sintering

SPS, also known as field-assisted sintering technique (FAST) or pulsed electric current sintering (PECS), is a rapid sintering method that can densify ceramics within a few minutes compared to the several hours taken by hot pressing and pressureless sintering to achieve the same sintered density (Tamari *et al.*, 1995; Barick *et al.*, 2016). The heating in SPS is obtained by the joule heating of the graphite die and powder compact if it is conducting. The internal characteristic of heat generation compared to that of external heating in conventional sintering methods facilitates an extremely high heating or cooling rate of 500 K/min. Such high heating/cooling rates provide a technical advantage of rapid heating of the powder compact to the final sintering temperature while avoiding the loss of grain boundaries. The presence of a high grain boundary area at the sintering temperature facilitates the rapid densification of the powder compact via grain-boundary diffusion. However, the poor thermal conductivity of a ceramic powder compact limits the sample size owing to the thermal shock issues. Regardless, SPS can provide a fully dense ultrafine microstructure, which is difficult to obtain using pressureless sintering and hot pressing. For instance, SiC nanopowders synthesized by mechanical alloying could be successfully densified via SPS to a relative density of 98% with an average particle size of less than 100 nm when sintered at 1700°C for 10 min at a load of 40 MPa in vacuum atmosphere (Yamamoto *et al.*, 2005). A typical microstructure of SPS-SiC is shown in Fig. 4(d).

Reaction-Bonded SiC

Reaction bonding is an economical route to fabricate dense SiC ceramics suitable for use in wear resistance applications and hostile environments (Ness and Page, 1986; Chiang, 1991). RBSC ceramics are prepared by the reactive infiltration of molten Si into a macroporous SiC–C preform. The infiltrated Si reacts with the carbon and generates β -SiC. Thus, the resulting microstructure consists of the initially added α -SiC particles (3–30 μm), in situ synthesized β -SiC, and residual Si. Owing to the low-temperature synthesis ($\sim 1550\text{--}1650^\circ\text{C}$), short time, near net shape fabrication, and no requirement of expensive sintering additives, this fabrication process is highly cost-effective. However, the presence of residual Si (5–15 vol%) in the microstructure renders the RBSC susceptible to corrosion and poor mechanical properties at high temperatures. Fig. 5(a) shows a typical microstructure of an RBSC ceramic infiltrated with molten Si, exhibiting a dense microstructure without the grain growth of SiC.

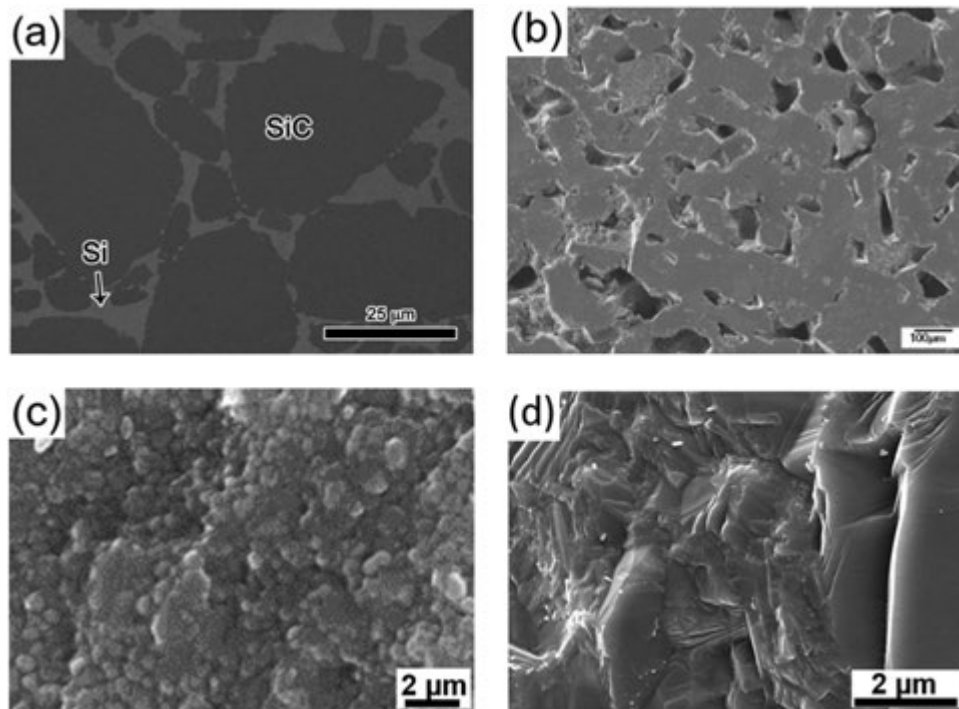


Fig. 5 Typical microstructures of (a) reaction bonded SiC sintered at 1850°C for 90 min in vacuum, (b) recrystallized SiC sintered at 2400°C for 20 min in argon atmosphere, (c) hot isostatically pressed SiC ceramic processed at 1600°C for 1 h under 350 MPa, and (d) CVD-SiC. Reproduced from (a) Hsu, C.Y., Zhang, Y., Xie, Y., *et al.*, 2019. In-situ measurement of SiC/Si interfacial tensile strength of reaction bonded SiC/Si composite. *Composite Part B* 175, 107116. (b) Guo, W., Xiao, H., Xie, W., *et al.*, 2012. A new design for preparation of high performance recrystallized silicon carbide. *Ceramics International* 38, 2475–2481. (c) Vaßen, R., Stover, D., 2001. Processing and properties of nanophase non-oxide ceramics. *Materials Science and Engineering A* 301, 59–68.

Recrystallized SiC

Recrystallized SiC is a high-temperature structural material with a high purity in the absence of any sintering additives or secondary phases (Kriegesmann, 2004; Guo *et al.*, 2012; Kim *et al.*, 2012c). Such a material is sintered at 2200–2400°C in argon or vacuum by the evaporation–condensation mechanism, and in Ar, it retains its useful mechanical properties up to 2000°C. However, its extensive use is restricted by its residual porosity (~15%) and poor mechanical properties. The porosity and pore structure are amenable via the sintering temperature and initial SiC particle size. Fig. 5(b) shows a typical microstructure of a recrystallized SiC sintered at 2400°C for 20 min in an argon atmosphere.

Other Processing Techniques

HIP is a densification process that involves the simultaneous application of isostatic pressure (200–300 MPa) and temperature (1500–2000°C). HIP ensures: (1) low-temperature (~1500°C) densification of SiC and (2) improved mechanical properties owing to the removal of the residual flaws and porosity by the synergistic effect of the extremely high pressure and temperature. The nano-SiC powder (20 nm) synthesized via laser-assisted pyrolysis can be densified to near-theoretical density without appreciable grain growth when it is hot isostatically pressed at 1500°C for 4 h under an isostatic pressure of 350 MPa (Vaßen *et al.*, 1996). A typical microstructure of hot isostatically pressed SiC is shown in Fig. 5(c).

The CVD method can be used to fabricate high-purity β -SiC monolithic ceramics with a near theoretical density (Gulden, 1969; Drieux *et al.*, 2016). This method facilitates the simultaneous synthesis and densification of in-situ synthesized β -SiC via the pyrolysis of the precursor gases, such as methyltrichlorosilane, at 1200–1800°C. The microstructure exhibits columnar grains of several microns in size. Fig. 5(d) depicts the microstructure of highly dense coarse grained SiC ceramic synthesized via CVD.

Properties

Mechanical Properties

Room-temperature mechanical properties

The mechanical properties of SiC ceramics are governed by their microstructure, fracture energy, flaw size, porosity, and grain boundary chemistry, which in turn depend on the starting composition and processing technique. This section deals with the

Table 3 Room temperature mechanical properties of polycrystalline SiC ceramics

Sintering method	Sintering additives	Processing conditions	Sintered density (%)	Mechanical properties			References
				Flexural strength (MPa)	Fracture toughness (MPa m ^{1/2})	Hard-ness (GPa)	
Pressure-less sintering	16.2 wt% Al ₂ O ₃ -Y ₂ O ₃	1950°C/3 h/Ar	95.1–97.3	321–477	4.4–6.8	–	Kim <i>et al.</i> (1998)
	10 wt% Al ₂ O ₃ -Y ₂ O ₃	1950°C/1 h/Ar	98	625	7.5	–	She and Ueno (1999)
	7 wt% Al ₂ O ₃ -CeO ₂	1840°C/1 h/Ar	99.1	437 ^a	4.6	23	Liang <i>et al.</i> (2014a)
	10 vol% AlN-Yb ₂ O ₃	2000°C/2 h/Ar	99.5	638	3.4	–	Santos and Ribeiro (2018)
	10 wt% Al ₂ O ₃ -Y ₂ O ₃ -MgO	1950°C/2 h/Ar	96	455	5.9	22	Gubernat <i>et al.</i> (2007)
	3 vol% Al ₂ O ₃ -Y ₂ O ₃ -AlN	1900°C/1 h/Ar	99.4	425	6.9	–	Eom <i>et al.</i> (2015)
	9 wt% Al ₂ O ₃ -Y ₂ O ₃ -CaO	1850°C/2 h/Ar	99	628	5.3	29.1	Eom <i>et al.</i> (2016)
	6.5 vol% Y ₂ O ₃ -Sc ₂ O ₃ -AlN	1950°C/6 h/N ₂	98.6	509	4.1	27.2	Cho <i>et al.</i> (2016)
	9.07 wt% Al ₂ O ₃ -Y ₂ O ₃ -SrO-CaO	1900°C/2 h/Ar	96.7	457.3	5.0	–	Seo <i>et al.</i> (2018)
	9 wt% Al ₂ O ₃ -Y ₂ O ₃ -MgO-CaO	1800°C/2 h/Ar	98.8	346.8	5.2	29.3	Kim and Kim (2019)
	3.87 wt% AlN-Y ₂ O ₃ -Sc ₂ O ₃ -MgO	1850°C/2 h/Ar	98.3	510	6.9	24.7	Kim <i>et al.</i> (2019a)
Hot pressing	10 wt% Y-Mg-Si-Al-O-N glass	1900°C/3 h /Ar/20 MPa	98.7	847	3.5	–	Kim and Mitomo (1999)
	10 wt% Al ₂ O ₃ -Y ₂ O ₃ -CaO	2000°C/4 h /Ar/25 MPa	98.3	500	7.5	–	Kim <i>et al.</i> (2002)
	2 vol% Y ₂ O ₃ -Sc ₂ O ₃	2000°C/3 h /N ₂ /40 MPa	98.9	546	4.2	–	Kim <i>et al.</i> (2015a)
	2.98 wt% Y ₂ O ₃	2000°C/3 h/N ₂ /40 MPa	99.1	586	3.4	–	Seo <i>et al.</i> (2016a,b)
	2 vol% Y ₂ O ₃ -Sc ₂ O ₃	2000°C/3 h/N ₂ /40 MPa	98.9	546	4.2	28.5	Malik <i>et al.</i> (2018)
SPS	7 wt% Al ₂ O ₃ -Y ₂ O ₃	1800°C/5 min/40 MPa	98	850 ^a	3.4	22	Tamari <i>et al.</i> (1995)
	–	1700°C/10 min/40 MPa	98	520	3.6	21	Yamamoto <i>et al.</i> (2005)
	1 wt% B ₄ C – 3 wt% C	1500°C/5 min/Ar/50 MPa	97.7	–	3.3	27	Barick <i>et al.</i> (2016)
GPS	10 vol% Al ₂ O ₃ -Y ₂ O ₃	2010°C/1 h/10 MPa-N ₂ pressure	100	467	4.9	–	Biswas <i>et al.</i> (2001)
	2 mol% Gd ₂ O ₃ -Ho ₂ O ₃	2000°C/1 h/10 MPa-N ₂ pressure	99.5	–	3.5	21	Biswas <i>et al.</i> (2005)
Reaction bonded SiC	17 wt% MoSi ₂	2050°C/20 min/vacuum	98	410	–	–	Lim <i>et al.</i> (1989)
	16.5 vol% Si	1450°C/1 h /vacuum	100	162	–	20	Meyers <i>et al.</i> (2018)
Recrystallized SiC	–	2400°C /20 min	93	162.3	–	–	Guo <i>et al.</i> (2012)
CVD	–	1400°C/1 h /vacuum	98.7	950	–	–	Gulden (1969)
HIP	–	1500°C/3–4 h/350 MPa	99	580 ^a	2.9	24	Vaßen <i>et al.</i> (1996)

^a3-point bending method.

Table 4 High temperature flexural strength of polycrystalline SiC ceramics

Sintering method	Sintering additives	Processing conditions	Sintered density (%)	Flexural strength (MPa)/Temperature (°C)/Atmosphere	References
Hot pressing	10 vol% AlN-Sc ₂ O ₃	2000°C/6 h/N ₂ /25 MPa	99.2	620/1600/N ₂	Kim <i>et al.</i> (2005)
	10 vol% AlN-Lu ₂ O ₃	2000°C/6 h/N ₂ /25 MPa	97.5	596/1600/N ₂	Kim <i>et al.</i> (2007)
	1 wt% AlN-Lu ₂ O ₃	2050°C/6 h/N ₂ /40 MPa	98.5	633/1600/N ₂	Lim <i>et al.</i> (2013)
	1 vol% Y ₂ O ₃ -Sc ₂ O ₃	2050°C/6 h/N ₂ /40 MPa	99.9	501/1600/N ₂	Seo <i>et al.</i> (2016a,b)
	2000 ppm Y ₂ O ₃	2200°C/6 h/N ₂ /40 MPa	99.9	981/2000/ N ₂	Kim <i>et al.</i> (2017c)
CVD	–	1400°C/1 h/vacuum	98.7	869/1400	Gulden (1969)

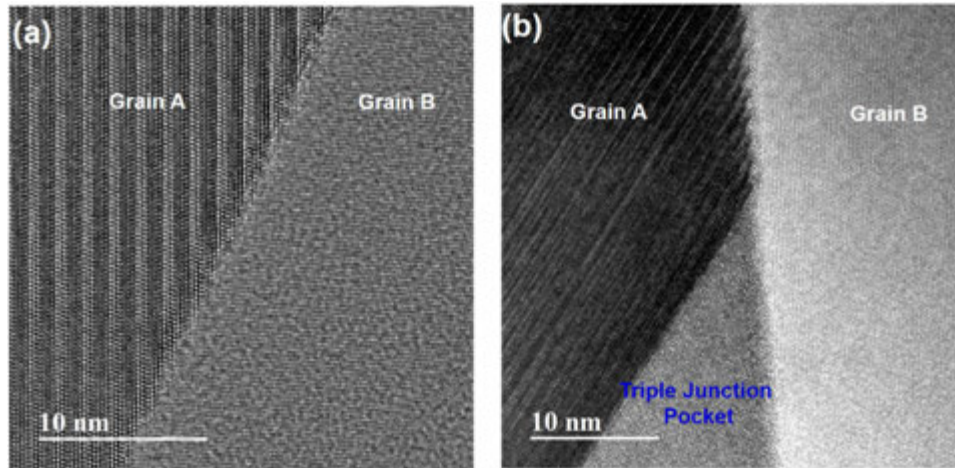


Fig. 6 HRTEM micrographs revealing (a) a clean homophase boundary (SiC/SiC) without amorphous intergranular films and (b) a heterophase boundary (SiC/junction phase). Reproduced from Kim, Y.W., Jang, S.H., Nishimura, T., Choi, S.Y., Kim, S.D., 2017c. Microstructure and high-temperature strength of silicon carbide with 2000 ppm yttria. *Journal of the European Ceramic Society* 37, 4449–4455.

capability of different processing techniques for achieving a high fracture energy, reduced flaw size, fine grain microstructure, and high density, which are a prerequisite for achieving excellent mechanical properties. **Table 3** lists room-temperature (RT) flexural strength, fracture toughness, and hardness of SiC ceramics obtained using various processing techniques. The typical ranges of the RT flexural strength, fracture toughness, and hardness of the monolithic SiC ceramics are 321–950 MPa, 2.9–7.5 MPa m^{1/2}, and 20.0–29.3 GPa, respectively.

High-temperature strength

LPS-SiC ceramics possess excellent mechanical properties at RT and can be processed at temperatures below those for SSS-SiC. However, the high-temperature strength of LPS-SiC is often limited by the softening of the intergranular films (Kim *et al.*, 2005; Seo *et al.*, 2016a,b). Therefore, continued studies were directed toward developing high-refractory intergranular films with various combinations of sintering additives (Kim *et al.*, 2007; Lim *et al.*, 2013). **Table 4** summarizes the high-temperature flexural strengths of hot-pressed SiC and CVD-SiC. As is evident from the table, a few AlN-RE (RE=Sc, Lu) oxide systems exhibit RT strength retention up to 1600°C. A SiC ceramic sintered at 2200°C with 2000 ppm yttria showed an extremely high strength of 981 MPa at 2000°C, which was 74% higher than its RT strength. This excellent strength at 2000°C was attributed to the strengthening effect of the plastic deformation and clean boundaries (Fig. 6; Kim *et al.*, 2017c). A CVD-SiC showed an excellent strength of 869 MPa at 1400°C, which is 91% of its RT strength. This excellent strength is attributed to the absence of amorphous intergranular films. In summary, monolithic SiC with a coarse microstructure in the absence of impurities and amorphous films at the grain boundary will show high strength retention at elevated temperatures.

Electrical Properties

SiC is an electrical semiconductor with a wide bandgap. The electrical resistivity of monocrystalline SiC at RT ranges from 5.3×10^{-3} to 3×10^{11} Ω cm, depending on the dopant type and concentration (Table 5). In contrast, the RT electrical resistivity of polycrystalline SiC ceramics ranges between 3.5×10^{-3} and 3×10^{13} Ω cm depending on the additive composition and microstructure (Table 6). The critical factors affecting the electrical conductivity of LPS-SiC ceramics include the SiC polytype, grain boundary structure, soluble atoms, porosity, and grain size (Kim *et al.*, 2019d).

Table 5 Electrical resistivity of single crystalline SiC

Polytype	Dopant	Electrical resistivity (RT) (Ω cm)	References
4H	No doping	10^3	Augustine <i>et al.</i> (2000)
6H	No doping	10^2 – 10^3	Hobgood <i>et al.</i> (1995)
4H	Al	8×10^{-2}	Heera <i>et al.</i> (2006)
6H	Al	10^{-2}	Wirth <i>et al.</i> (1999)
4H	N	5.3×10^{-3}	Onoue <i>et al.</i> (1996)
6H	V	3×10^{11}	Rasp <i>et al.</i> (2003)

Table 6 Electrical resistivity of polycrystalline SiC ceramics

Sintering additives	Processing conditions	Electrical resistivity (RT) (Ω cm)	References
5 wt% Y_2O_3 (yttrium nitrate)	Hot-pressing, 2050°C/40 MPa/6 h/ N_2	3.5×10^{-3}	Kim <i>et al.</i> (2011)
12.6 wt% Y_2O_3	Hot-pressing, 2050°C/40 MPa/6 h/ N_2	7.0×10^{-3}	Kim <i>et al.</i> (2012a)
6.5 wt% AlN- Y_2O_3	Hot-pressing, 2050°C/20 MPa/6 h/ N_2	1.4×10^{-2}	Kim <i>et al.</i> (2013b)
2 vol% Y_2O_3 - Lu_2O_3	Hot-pressing, 2000°C/40 MPa/3 h/ N_2	1.5×10^{-2}	Jang <i>et al.</i> (2016)
1 wt% AlN- Nd_2O_3	Hot-pressing, 2050°C/20 MPa/12 h/ N_2	1.5×10^{-2}	Kim <i>et al.</i> (2012b)
1 wt% AlN- Sc_2O_3	Hot-pressing, 2050°C/20 MPa/12 h/ N_2	2.0×10^{-2}	Kim <i>et al.</i> (2012b)
0.5 wt% AlN- Y_2O_3	Hot-pressing, 2050°C/40 MPa/6 h/ N_2	4.3×10^{-2}	Lim <i>et al.</i> (2014)
2 vol% Y_2O_3 - Gd_2O_3	Hot-pressing, 2000°C/40 MPa/3 h/ N_2	5.6×10^{-2}	Jang <i>et al.</i> (2016)
2 wt% AlN- Er_2O_3	Hot-pressing, 2050°C/40 MPa/6 h/ N_2	8.1×10^{-2}	Lim <i>et al.</i> (2011)
1 wt% AlN- Dy_2O_3	Hot-pressing, 2050°C/40 MPa/6 h/ N_2	1.0×10^{-1}	Lim <i>et al.</i> (2012)
0.5 wt% AlN- Lu_2O_3	Hot-pressing, 2050°C/40 MPa/6 h/ N_2	1.5×10^{-1}	Lim <i>et al.</i> (2014)
6.5 vol% AlN- Y_2O_3 - Sc_2O_3	Pressureless Sintering, 1950°C/6 h/ N_2	6.7×10^{-1}	Cho <i>et al.</i> (2016)
2 wt% AlN	Hot-pressing, 2050°C/20 MPa/2 h/ N_2	1.0×10^3	Kim <i>et al.</i> (2013b)
3 vol% AlN- $Y_3Al_5O_{12}$	Pressureless Sintering, 1900°C/2 h/Ar	10^2 – 10^7	Siegelin <i>et al.</i> (2003)
10 vol% Al_2O_3 - Y_2O_3	Hot-pressing, 1900°C/30 MPa/1 h/Ar	1.8×10^8	Kim <i>et al.</i> (2014a)
3 vol% AlN- Y_2O_3 - V_2O_5	Hot-pressing, 1900°C/30 MPa/1 h/Ar	2.0×10^8	Kim <i>et al.</i> (2014a)
10 wt% Al_2O_3 - Y_2O_3	Hot-pressing, 1925°C/0.5 h/Ar $\rightarrow$ Gas Pressure Sintering, 1925°C/80 bar/1 h/Ar	1.0×10^{11}	Can <i>et al.</i> (2007)
3 vol% AlN- Al_2O_3 - Y_2O_5	Pressureless Sintering, 1900°C/1 h/Ar	1.2×10^{13}	Kim <i>et al.</i> (2017a,b)
1 wt% Be	Hot-pressing, 2040°C/20 MPa/1 h	3×10^{13}	Takeda <i>et al.</i> (1987)

Until now, over 250 SiC polytypes have been reported (Ramsdell, 1945; Cheung, 2006). Each SiC polytype exhibits different electrical properties owing to differences in the stacking sequence and bandgap. Among them, 3C-SiC (β -SiC) and 6H-SiC (α -SiC) powders are the most widely available polytypes at present. Generally, the LPS-SiC ceramics processed from β -SiC powder show a lower electrical resistivity (3.5×10^{-3} – 3.4Ω cm) (Zhan *et al.*, 2001; Kim *et al.*, 2011, 2015b) than those processed from α -SiC (5.4 – $1.2 \times 10^{13} \Omega$ cm) (Koumoto *et al.*, 1987; Cho *et al.*, 2016; Kim *et al.*, 2017a). Specifically, the electrical resistivity values of the LPS-SiC ceramics sintered with AlN- Y_2O_3 - Sc_2O_3 are $6.7 \times 10^{-1} \Omega$ cm and 5.4Ω cm when β -SiC and α -SiC are used as the starting powders, respectively (Cho *et al.*, 2016). In most cases, although the $\beta \rightarrow \alpha$ phase transformation of SiC partially occurs during sintering (Cho *et al.*, 2016; Jang *et al.*, 2016), the β -SiC starting powder typically leads to a lower electrical resistivity than that of the α -SiC powder under the same sintering conditions. This is because of the smaller bandgap of 3C-SiC (2.4 eV) and lower ionization energy of the nitrogen donors in 3C-SiC (~ 60 meV) compared to those in 6H-SiC (3.0 eV and 100–155 meV) (Ikeda *et al.*, 1980; Iwata *et al.*, 2003).

The electrical resistivity of the LPS-SiC ceramics is affected by the grain boundary structure. LPS-SiC ceramics with clean SiC/SiC grain boundaries exhibit lower electrical resistivities than those with amorphous intergranular films at the SiC/SiC boundaries. Specifically, polycrystalline SiC ceramics, containing amorphous grain boundary films at the SiC/SiC boundaries, have electrical resistivities of the order of 10^{10} – $10^{13} \Omega$ cm at RT (Kim *et al.*, 2014a; Liang *et al.*, 2015; Kim *et al.*, 2017a). By contrast, polycrystalline SiC ceramics, which possess clean SiC/SiC boundaries (i.e., no amorphous films), show significantly low electrical resistivities of the order of 10^{-2} – $10^0 \Omega$ cm at RT (Kim *et al.*, 2012c; Lim *et al.*, 2013; Kim *et al.*, 2017c).

Dopants act as acceptors or donors in the SiC lattice. The ability to dope the SiC lattice is limited by the solid solubility limit. The soluble atoms in the SiC lattice include Al, B, Ga, Sc, N, P, Be, O, and V (Ikeda *et al.*, 1980; Tajima and Kingery, 1982; Takeda *et al.*, 1987; Persson *et al.*, 1999; Wirth *et al.*, 1999; Laube *et al.*, 2002; Tamulaitis *et al.*, 2004; Heera *et al.*, 2006; Racka *et al.*, 2015). Al, B, Ga, and Sc act as p-type dopants, whereas N and P act as n-type dopants in the SiC lattice (Kim *et al.*, 2019d). However, Be, O, and V tend to create deep levels within the bandgap, which can capture carriers, leading to a semi-insulating or insulating SiC (Takeda *et al.*, 1987; Ventra and Pantelides, 2000; Tamulaitis *et al.*, 2004). Because the sintering additives and sintering atmosphere often contain n- or p-type dopants, e.g., Al_2O_3 , AlN, B, B_4C , and Sc_2O_3 as

additives and nitrogen as the sintering atmosphere, the dopant atoms are incorporated into the SiC lattice during the grain growth via a solution-reprecipitation mechanism. Typical examples are N-doping of the SiC grains during the sintering of SiC ceramics with $\text{Y}_2\text{O}_3\text{--Gd}_2\text{O}_3$ additives in a nitrogen atmosphere (Fig. 3) (Kim *et al.*, 2015b) and Al doping during the sintering of SiC ceramics with $\text{AlN--Y}_2\text{O}_3$ additives in a nitrogen atmosphere (Kim *et al.*, 2013b). Thus, the careful selection of the sintering additive composition and sintering atmosphere is important for achieving the desired electrical resistivity in LPS-SiC ceramics.

Porous LPS-SiC ceramics show a substantially higher electrical resistivity than the dense LPS-SiC ceramics (Zhan *et al.*, 2001; Ihle *et al.*, 2006). For example, the electrical resistivity of the SiC ceramics increased from 0.10 to 1.41 $\Omega\text{ cm}$ with increasing porosity from 38.8% to 42.2% when SiC was sintered with $\text{Al}_2\text{O}_3\text{--Y}_2\text{O}_3$ additives (Ihle *et al.*, 2006).

The LPS-SiC ceramics exhibited a tendency of increasing resistivity with decreasing grain size because of the grain boundary scattering of the carriers. Specifically, a LPS-SiC ceramic with an average grain size of 3.5 μm showed a higher electrical resistivity ($5.2 \times 10^{-2} \Omega\text{ cm}$) than that with an average grain size of 5.5 μm ($8.9 \times 10^{-3} \Omega\text{ cm}$) at RT (Kim *et al.*, 2015b). However, a deviation from the above trend was also observed when the $\beta \rightarrow \alpha$ phase transformation of SiC occurred simultaneously with the grain growth in LPS-SiC ceramics (Kim *et al.*, 2019d).

Thermal Properties

As a covalently-bonded compound, SiC transports heat primarily via phonons at RT (Kim *et al.*, 2014b). The intrinsic thermal conductivities of 6H and 4H (N-doped) single crystals are reported as 490 W(m K)^{-1} and 342 W(m K)^{-1} at RT, respectively (Slack, 1964; Wei *et al.*, 2013). However, the thermal conductivity values of polycrystalline SiC ceramics are much lower than the intrinsic values because of the defects in the SiC grains and grain boundaries. There is a wide variation in the reported thermal conductivity data of polycrystalline SiC ceramics (32–262 W(m K)^{-1}), depending on the composition and quantity of the sintering additives (Table 7). The most detrimental element is Al because Al creates additional silicon vacancies in the SiC lattice according to the following defect equation: $\text{Al}_2\text{O}_3 \rightarrow 2\text{Al}_{\text{Si}} + 3\text{O}_{\text{C}} + \text{V}_{\text{Si}}^{\bullet\bullet}$ (Zhou *et al.*, 2003; Kim and Kim, 2019). These vacancies cause phonon scattering and reduce the thermal conductivity. Thus, a LPS-SiC with Al-containing additives revealed a conductivity of 32–83 W(m K)^{-1} (Zhan *et al.*, 2002; Sigl, 2003; Zhou *et al.*, 2003; Eom *et al.*, 2016; Seo *et al.*, 2018; Kim *et al.*, 2019a), whereas the LPS-SiC ceramics sintered with $\text{Y}_2\text{O}_3\text{--RE}_2\text{O}_3$ (RE = Sc, Lu, Gd, Sm, La) exhibited a conductivity of 181–262 W(m K)^{-1} (Zhou *et al.*, 2003; Kim *et al.*, 2014b; Jang *et al.*, 2016; Cho and Kim, 2017; Seo *et al.*, 2017). Another critical impurity in the SiC lattice is oxygen because oxygen generates additional silicon vacancies therein according to the following defect equation: $\text{SiO}_2 \rightarrow \text{Si}_{\text{Si}} + 2\text{O}_{\text{C}} + \text{V}_{\text{Si}}^{\bullet\bullet}$ (Cho and Kim, 2017). As shown in Fig. 7, the thermal conductivity increases with decreasing lattice oxygen content in LPS-SiC ceramics without Al-containing additives. The data in the circle were reported from those of the LPS-SiC ceramics sintered with Al-containing additives. It is clear that the addition of Al-containing additives leads to much lower thermal conductivities than those with additive compositions without Al compounds by the increased phonon scattering at Si vacancies. The thermal conductivity of the SiC ceramics sintered with Al-containing additives was insensitive to the lattice oxygen content. These results confirm that Al incorporation in the SiC lattice is more detrimental to oxygen incorporation for improving the thermal conductivity of the LPS-SiC ceramics.

Table 7 Thermal conductivity of polycrystalline SiC ceramics

Sintering additives	Processing conditions	Thermal conductivity (RT) ($\text{Wm}^{-1}\text{K}^{-1}$)	References
10 wt% $\text{Al}_2\text{O}_3\text{--Y}_2\text{O}_3\text{--CaO}$	Hot-pressing, 1750°C/25 MPa/40 min/Ar	32	Zhan <i>et al.</i> (2002)
3.87 wt% $\text{AlN--Y}_2\text{O}_3\text{--Sc}_2\text{O}_3\text{--MgO}$	Pressureless sintering, 1850°C/2 h /Ar	67	Kim <i>et al.</i> (2019a)
5 vol% $\text{Al}_2\text{O}_3\text{--Y}_2\text{O}_3$	Hot-pressing, 2000°C/40 MPa/2 h/Ar	71	Zhou <i>et al.</i> (2003)
9 wt% $\text{Al}_2\text{O}_3\text{--Y}_2\text{O}_3\text{--CaO}$	Pressureless sintering, 1850°C/2 h /Ar	80	Eom <i>et al.</i> (2016)
9 wt% $\text{Al}_2\text{O}_3\text{--Y}_2\text{O}_3\text{--CaO--SrO}$	Pressureless sintering, 1900°C/2 h /Ar	82	Seo <i>et al.</i> (2018)
3 vol% $\text{Y}_3\text{Al}_5\text{O}_{12}\text{--AlN}$	Pressureless sintering, 1970°C/0.5 h /Ar	83	Sigl (2003)
9 wt% $\text{Al}_2\text{O}_3\text{--Y}_2\text{O}_3\text{--MgO--CaO}$	Pressureless sintering, 1850°C/2 h/Ar	83	Kim and Kim (2019)
1.87 wt% $\text{Y}_2\text{O}_3\text{--Sc}_2\text{O}_3\text{--MgO}$	Hot-pressing, 1850°C/30 MPa/2 h/ N_2	99	Kim <i>et al.</i> (2019c)
1.87 wt% $\text{Y}_2\text{O}_3\text{--Sc}_2\text{O}_3\text{--MgO}$	Hot-pressing, 1850°C/30 MPa/2 h/Ar	114	Kim <i>et al.</i> (2019c)
2 vol% Y_2O_3	Hot-pressing, 2000°C/40 MPa/3 h/ N_2	178	Jang <i>et al.</i> (2016)
2 vol% $\text{Y}_2\text{O}_3\text{--Lu}_2\text{O}_3$	Hot-pressing, 2000°C/40 MPa/3 h/ N_2	181	Jang <i>et al.</i> (2016)
0.4 wt% B + 0.4 wt% C	Pressureless sintering, 2150°C/1 h/Ar → Annealing, 1950°C/4 h/Ar	192	Li <i>et al.</i> (2014)
2 vol% $\text{Y}_2\text{O}_3\text{--Sm}_2\text{O}_3$	Hot-pressing, 2000°C/40 MPa/3 h/ N_2	198	Jang <i>et al.</i> (2016)
5 vol% $\text{La}_2\text{O}_3\text{--Y}_2\text{O}_3$	Hot-pressing, 2000°C/40 MPa/2 h/Ar → Annealing, 2000°C/4 h/Ar	211	Zhou <i>et al.</i> (2003)
3 vol% $\text{Gd}_2\text{O}_3\text{--Y}_2\text{O}_3$	Hot-pressing, 2000°C/40 MPa/12 h/Ar	225	Cho and Kim (2017)
1 vol% $\text{Y}_2\text{O}_3\text{--Sc}_2\text{O}_3$	Hot-pressing, 2050°C/40 MPa/6 h/ N_2	234	Kim <i>et al.</i> (2014b)
0.79 vol% $\text{Y}_2\text{O}_3\text{--Sc}_2\text{O}_3$	Spark plasma sintering, 2050°C/60 MPa/6 h/ N_2	262	Seo <i>et al.</i> (2017)

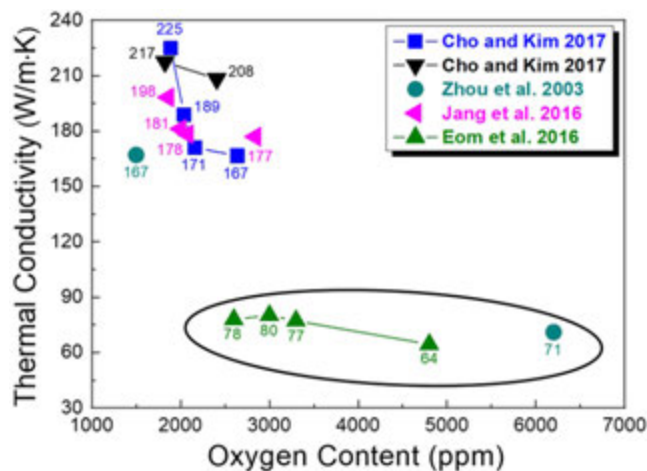


Fig. 7 Effect of the lattice oxygen content on the thermal conductivity of LPS-SiC ceramics. Literature data were also plotted for comparison. Reproduced from Cho, T.Y., Kim, Y.W., 2017. Effect of grain growth on the thermal conductivity of liquid-phase sintered silicon carbide ceramics. *Journal of the European Ceramic Society* 37, 3475–3481.

The thermal conductivity of SSS-SiC depends on the amount of boron and carbon additives and microstructure. By optimizing these, a thermal conductivity of $192 \text{ Wm}^{-1} \text{ K}^{-1}$ was obtained in SSS-SiC ceramics sintered with 0.4 wt% boron and 0.4 wt% carbon (Li *et al.*, 2014).

Other Properties

Concerning optical properties, β -SiC has important applications such as in domes and windows in armor, hypersonic missiles, and thermal control for thin-disc lasers. Transparent β -SiC was successfully fabricated by the pyrolysis of methyltrichlorosilane in a hot-wall, low-pressure CVD reactor exhibiting excellent transmittance ($\sim 60\%$) in the wavelength range of $0.5\text{--}6 \mu\text{m}$ (Goela *et al.*, 1993). Optical transparency in pure cubic SiC (99.9997%) was attributed to the columnar grains grown parallel to the $\langle 111 \rangle$ direction, absence of twins, stacking faults, and low densities of dislocations (Kim *et al.*, 1995a).

SiC-based magnetic semiconductors are potential materials for high-temperature and high-frequency magnetic devices owing to their high thermal stability and high thermal conductivity. Liu and Wang (2018) synthesized tunable SiC powders via microwave heating, which exhibited a high saturated magnetization (M_s , 0.9 emu/g, 300K) attributed to the existence of point defects in the SiC lattice and interface between the SiC and SiO_x . Furthermore, dilute magnetic semiconductors (DMS) are promising candidates for spintronics where transition metals such as Sc, Ti, V, Cr, Mn, Fe, Co, and Ni with partially filled d states can be doped for transforming spin-frustrated semiconductors (like SiC) to a ferromagnetic phase. Vanadium-doped SiC nanowires fabricated via CVD exhibited a mixture of the diamagnetic phase (VC and non-doped β -SiC) and ferromagnetic or paramagnetic phase (V-doped SiC) owing to the low solubility of V in SiC (Seong *et al.*, 2009). Fe-doped bulk SiC fabricated by hot-pressing exhibited ferromagnetic hysteresis at RT (Kim and Kim, 2012).

Applications

The important applications of SiC can be broadly divided into two categories: structural and functional applications. The structural applications include abrasives, car disc brakes, car clutches, armor plates in bulletproof vests, kiln furniture, sand blasting nozzles, automotive water pump seals, bearings, mechanical seals, and extrusion dies. In the manufacturing industry, SiC is widely used in machining processes such as grinding, honing, water-jet cutting and sandblasting. Cutting tools made of SiC whisker-reinforced alumina are commercially available in the market. In the automobile industry, carbon-reinforced SiC disc brakes are used in high-performance cars owing to their lower weight, high temperature stability, and high thermal conductivity. In the semiconductor industry, various SiC parts such as focus rings, wafer boats, tubes, susceptors, and dummy wafers are widely used for semiconductor processing. In the astronomy industry, SiC mirrors are much desirable owing to their low thermal expansion coefficient, high hardness, rigidity, and thermal conductivity. In foundries, SiC crucibles are used to hold molten metals (Peter *et al.*, 2011). Porous SiC ceramics are used as diesel particulate filters (O'Sullivan *et al.*, 2004), molten metal filters, membranes for water purification (Kim *et al.*, 2017b) and gas separation, and hot-gas filters. In steel production, SiC is used as a fuel to increase the tap temperature and adjust the Si and C content. In the nuclear industry, SiC is being developed as a matrix material for tristructural isotropic (TRISO) fuel particles to provide multiple barriers to fission products, conduct heat, high temperature stability, radiation damage resistance, and oxidation resistance against high-temperature steam (Kim *et al.*, 2019a). SiC fiber is

used as a reinforcement for SiC matrix composites, which are used as turbine components, such as turbine shrouds, combustors, nozzles, and combustor liners (Steibel, 2019).

The functional applications of SiC include varistors, light-emitting diodes (LEDs), and semiconductor devices. SiC-semiconductor-based power devices such as JFETs and MOSFETs are already commercialized exhibiting advantages like a fast response, high temperature, and high-voltage applications. SiC is an important LED component that is used as a substrate for growing GaN devices and a heat spreader in high-power LEDs (Stringfellow, 1998). SiC fibers ($\sim 15 \mu\text{m}$) are widely used in thin-film pyrometry to measure high flame temperatures in the range of 800–2500K (Maun *et al.*, 2007). SiC-based heating elements are widely used in the melting of glass, non-ferrous metals, and heat treatment of metals (Deshmukh, 2005).

Summary

SiC is an important ceramic material that is widely used in automotive, steel, electronic, astronomy, semiconductor, and nuclear industries owing to its unique set of properties such as high temperature strength, resistance to wear and corrosion, tunable thermal and electrical properties, thermal shock resistance, amenable toughness, and high hardness. Structurally SiC exhibits more than 250 polymorphs, among which all the cubic polytypes are referred to as β -SiC, and all the non-cubic structures (hexagonal and rhombohedral) are known as α -SiC. Hexagonal SiC is synthesized via the Acheson process, whereas cubic SiC is synthesized via vapor-phase reactions and the pyrolysis of polymeric precursors.

Owing to the high covalent bonding nature and low self-diffusivity, SiC is difficult to densify without sintering additives. B- and C-additives are used for solid-state sintering at 2050–2200°C, whereas liquid-phase sintering, facilitated by the use of various lower-temperature liquid-forming additives (oxides and nitrides), can be achieved at $\leq 2000^\circ\text{C}$. Contrary to pressureless sintering, hot pressing requires less additives for densification, thus facilitating improved high-temperature strengths and thermal and electrical properties. Spark plasma sintering can be employed to develop fully dense ultrafine microstructures, providing improved strength and hardness. Gas pressure sintering is advantageous for nitride additive systems because it prevents the decomposition of nitride additives at high temperatures by applying a nitrogen overpressure ($\sim 10 \text{ MPa}$). Reaction-bonded SiC offers an economical route to fabricate dense SiC ceramics that exhibit attractive mechanical properties at RT; however, their maximum application temperature is restricted by the presence of residual Si, which melts at 1414°C. Recrystallized SiC is widely used for making kiln furniture because it can retain its useful mechanical properties up to 2000°C in an inert atmosphere. CVD and HIP are expensive methods to fabricate high-purity and highly dense SiC ceramics suitable for high-temperature and functional applications sensitive to the impurity concentration.

The typical flexural strength, fracture toughness, and hardness of SiC ceramics at RT are 321–950 MPa, 2.9–7.5 MPa $\text{m}^{1/2}$, and 20.0–29.3 GPa, respectively. The best high temperature strength reported in LPS-SiC lies in the range of 500–600 MPa at $\sim 1600^\circ\text{C}$. The electrical resistivity at RT of monocrystalline and polycrystalline SiC lie in the ranges 5.3×10^{-3} – $3 \times 10^{11} \Omega \text{ cm}$ and 3.5×10^{-3} – $3 \times 10^{13} \Omega \text{ cm}$, respectively, depending on the dopant type and concentration in the monocrystalline SiC and additive composition and microstructure in the polycrystalline SiC. Depending on the composition and quantity of the sintering additives, the reported thermal conductivity data of the polycrystalline SiC ceramics varies from 32 to 262 $\text{W}(\text{m K})^{-1}$ at RT. SiC ceramics also exhibit attractive optical properties that have applications such as domes and windows in armor, hypersonic missiles, and thermal control for thin disc lasers. SiC-based magnetic semiconductors are established as potential materials for high-temperature and high-frequency magnetic devices owing to their high thermal stability and high thermal conductivity.

References

- Augustine, G., Balakrishna, V., Brandt, C.D., 2000. Growth and characterization of high-purity SiC single crystals. *Journal of Crystal Growth* 211, 339–342.
- Barick, P., Chakravarty, D., Saha, B.P., Mitra, R., Joshi, S.V., 2016. Effect of pressure and temperature on densification, microstructure and mechanical properties of spark plasma sintered silicon carbide processed with β -silicon carbide nanopowder and sintering additives. *Ceramics International* 42, 3836–3848.
- Baud, S., Thevenot, F., Chatillon, C., 2003. High temperature sintering of SiC with oxide additives: IV. Powder beds and the influence of vaporization on the behavior of SiC compacts. *Journal of the European Ceramic Society* 23, 29–36.
- Biswas, K., Rixecker, G., Wiedmann, I., *et al.*, 2001. Liquid phase sintering and microstructure-property relationships of silicon carbide ceramics with oxynitride additives. *Materials Chemistry and Physics* 67, 180–191.
- Biswas, K., Rixecker, G., Aldinger, F., 2005. Gas pressure sintering of SiC sintered with rare-earth-(III)-oxides and their mechanical properties. *Ceramics International* 31, 703–711.
- Can, A., McLachlan, D.S., Sauti, G., Herrmann, M., 2007. Relationships between microstructure and electrical properties of liquid-phase sintered silicon carbide materials using impedance spectroscopy. *Journal of the European Ceramic Society* 27, 1361–1363.
- Chen, Z., 1996. Effects of gadolinia and alumina addition on the densification and toughening of silicon carbide. *Journal of the American Ceramic Society* 79, 530–532.
- Cheung, R., 2006. *Silicon Carbide Microelectromechanical Systems for Harsh Environments*. London: Imperial College press.
- Chiang, Y.M., 1991. Reaction formed silicon carbide. *Materials Science and Engineering A* 144, 63–74.
- Cho, T.Y., Kim, Y.W., 2017. Effect of grain growth on the thermal conductivity of liquid-phase sintered silicon carbide ceramics. *Journal of the European Ceramic Society* 37, 3475–3481.
- Cho, T.Y., Kim, Y.W., Kim, K.J., 2016. Thermal, electrical, and mechanical properties of pressureless sintered silicon carbide ceramics with yttria-scandia-aluminum nitride. *Journal of the European Ceramic Society* 36, 2659–2665.
- Cho, T.Y., Malik, R., Kim, Y.W., Kim, K.J., 2018. Electrical and mechanical properties of pressureless sintered SiC-Ti₂CN composites. *Journal of European Ceramic Society* 38, 3064–3072.

- Deshmukh, Y.V., 2005. *Industrial Heating: Principles, Techniques, Materials, Applications and Design*. Boca Raton, FL: CRC Press.
- Drieux, P., Chollon, G., Jacques, S., 2016. Synthesis and characterization of monolithic CVD-SiC tubes. *Journal of European Ceramic Society* 36, 1873–1883.
- Eom, J.H., Seo, Y.K., Kim, Y.W., 2016. Mechanical and thermal properties of pressureless sintered silicon carbide ceramics with alumina-yttria-calcia. *Journal of the American Ceramic Society* 99, 1735–1741.
- Eom, J.H., Seo, Y.K., Kim, Y.W., Lee, S.J., 2015. Effect of additive composition on mechanical properties of pressureless sintered silicon carbide ceramics sintered with alumina, aluminum nitride, and yttria. *Metals and Materials International* 21, 525–530.
- Goela, J.S., Burns, L.E., Taylor, R.L., 1993. Transparent chemical vapor deposited β -SiC. *Applied Physics Letters* 64, 131–133.
- Gubernat, A., Stobierski, L., Labaj, P., 2007. Microstructure and mechanical properties of silicon carbide pressureless sintered with oxide additives. *Journal of the European Ceramic Society* 27, 781–789.
- Gulden, T.D., 1969. Mechanical properties of polycrystalline β -SiC. *Journal of the American Ceramic Society* 52, 585–590.
- Guo, W., Xiao, H., Xie, W., *et al.*, 2012. A new design for preparation of high performance recrystallized silicon carbide. *Ceramics International* 38, 2475–2481.
- Heera, V., Madhusoodanan, K.N., Skorupa, W., Dubois, C., Romanus, H., 2006. A comparative study of the electrical properties of heavily Al implanted, single crystalline and nanocrystalline SiC. *Journal of Applied Physics* 99, 123716.
- Hobgood, H.M., Glass, R.C., Augustine, G., *et al.*, 1995. Semi-insulating 6H-SiC grown by physical vapor transport. *Applied Physics Letters* 66, 1364–1366.
- Ihle, J., Martin, H.P., Herrmann, M., *et al.*, 2006. The influence of porosity on the electrical properties of liquid-phase sintered silicon carbide. *International Journal Materials Research* 97, 649–656.
- Ikeda, M., Matsunami, H., Tanaka, T., 1980. Site effect on the impurity levels in 4H, 6H, and 15R SiC. *Physical Review B* 22, 2842–2854.
- Iwata, H.P., Lindelfelt, U., Oberg, S., Briddon, P.R., 2003. Stacking faults in silicon carbide. *Physica B* 340–342, 165–170.
- Izhevskiy, V.A., Genova, L.A., Bressiani, J.C., Bressiani, H.A., 2000. Review article: Silicon carbide. Structure, properties and processing. *Ceramica* 46, 4–13.
- Jang, S.H., Kim, Y.W., Kim, K.J., Lee, S.J., Lim, K.Y., 2016. Effects of Y_2O_3 - RE_2O_3 ($RE = Sm, Gd, Lu$) additives on electrical and thermal properties of silicon carbide ceramics. *Journal of the American Ceramic Society* 99, 265–272.
- Kim, H.M., Kim, Y.W., 2019. Low temperature pressureless sintering of silicon carbide ceramics with alumina-yttria-magnesia-calcia. *Journal of the Ceramic Society of Japan* 127, 207–214.
- Kim, H.M., Kim, Y.W., Lim, K.Y., 2019a. Pressureless sintered silicon carbide matrix with a new quaternary additive for fully ceramic microencapsulated fuels. *Journal of the European Ceramic Society* 39, 3971–3980.
- Kim, Y.H., Kim, Y.W., Kim, K.J., 2019b. Electrically conductive SiC ceramics processed by pressureless sintering. *International Journal of Applied Ceramic Technology* 16, 843–849.
- Kim, Y.H., Kim, Y.W., Lim, K.Y., Lee, S.J., 2019c. Mechanical and thermal properties of silicon carbide ceramics with yttria-scandia-magnesia. *Journal of the European Ceramic Society* 39, 144–149.
- Kim, Y.W., Kim, Y.H., Kim, K.J., 2019d. Electrical properties of liquid-phase sintered silicon carbide ceramics: A review. *Critical Reviews in Solid State and Materials Sciences* 45, 66–84.
- Kim, K.J., Kim, Y.W., 2012. Fe doping and magnetic properties of zincblende SiC ceramics. *Journal of the European Ceramic Society* 32, 1149–1155.
- Kim, K.J., Lim, K.Y., Kim, Y.W., 2012a. Influence of Y_2O_3 addition on electrical properties of β -SiC ceramics sintered in nitrogen atmosphere. *Journal of the European Ceramic Society* 32, 4401–4406.
- Kim, Y., Min, K., Shim, J., Kim, D.J., 2012b. Formation of porous SiC ceramics via recrystallization. *Journal of the European Ceramic Society* 32, 3611–3615.
- Kim, Y.W., Lim, K.Y., Kim, K.J., 2012c. Electrical resistivity of silicon carbide ceramics sintered with 1 wt% aluminum nitride and rare earth oxide. *Journal of the European Ceramic Society* 32, 4427–4434.
- Kim, K.J., Lee, S., Lee, J.H., *et al.*, 2009. Structural and optical characteristics of crystalline silicon carbide nanoparticles synthesized by carbothermal reduction. *Journal of the American Ceramic Society* 92, 424–428.
- Kim, K.J., Lim, K.Y., Kim, Y.W., 2013a. Control of electrical resistivity in silicon carbide ceramics sintered with aluminum nitride and yttria. *Journal of the American Ceramic Society* 96, 3463–3469.
- Kim, K.J., Lim, K.Y., Kim, Y.W., Kim, H.C., 2013b. Temperature dependence of electrical resistivity (4–300K) in aluminum- and boron-doped SiC ceramics. *Journal of the American Ceramic Society* 96, 2525–2530.
- Kim, K.J., Lim, K.Y., Kim, Y.W., Lee, M.J., Seo, W.S., 2014a. Electrical resistivity of α -SiC ceramics with Al_2O_3 or AlN additives. *Journal of the European Ceramic Society* 34, 1695–1701.
- Kim, Y.W., Lim, K.Y., Seo, W.S., 2014b. Microstructure and thermal conductivity of silicon carbide with yttria and scandia. *Journal of the American Ceramic Society* 97, 923–928.
- Kim, K.M., Jang, S.H., Kim, W.Y., Seo, W.S., 2015a. Thermal and Mechanical properties of SiC-TiC_{0.5}N_{0.5} composites. *Journal of the American Ceramic Society* 98, 616–623.
- Kim, Y.W., Cho, T.Y., Kim, K.J., 2015b. Effect of grain growth on electrical properties of silicon carbide ceramics sintered with gadolinia and yttria. *Journal of the European Ceramic Society* 35, 4137–4142.
- Kim, K.J., Eom, J.H., Kim, Y.W., *et al.*, 2017a. Highly resistive SiC ceramics sintered with Al_2O_3 -AlN- Y_2O_3 additions. *Ceramics International* 43, 5343–5346.
- Kim, S.C., Kim, Y.W., Song, I.H., 2017b. Processing and properties of glass-bonded silicon carbide membrane supports. *Journal of the European Ceramic Society* 37, 1225–1232.
- Kim, Y.W., Jang, S.H., Nishimura, T., Choi, S.Y., Kim, S.D., 2017c. Microstructure and high-temperature strength of silicon carbide with 2000 ppm yttria. *Journal of the European Ceramic Society* 37, 4449–4455.
- Kim, Y., Zangvil, A., Goela, J.S., Taylor, R.L., 1995a. Microstructure comparison of transparent and opaque CVD SiC. *Journal of American Ceramic Society* 78, 1571–1579.
- Kim, Y.W., Mitomo, M., Hirotsuru, H., 1995b. Grain growth and fracture toughness of fine-grained silicon carbide ceramics. *Journal of the American Ceramic Society* 78, 3145–3148.
- Kim, Y.W., Tanaka, H., Mitomo, M., Otani, S., 1995c. Influence of powder characteristics on liquid phase sintering of silicon carbide. *Journal of the Ceramic Society of Japan* 103, 257–261.
- Kim, Y.W., Mitomo, M., 1999. Fine-grained silicon carbide ceramics with oxynitride glass. *Journal of the American Ceramic Society* 82, 2731–2736.
- Kim, Y.W., Mitomo, M., Lee, J.G., 1996. Influence of silica content on liquid phase sintering of silicon carbide with yttrium-aluminum garnet. *Journal of the Ceramic Society of Japan* 104, 816–818.
- Kim, Y.W., Mitomo, M., Hirotsuru, H., 1997. Microstructural development of silicon carbide containing large seed grains. *Journal of the American Ceramic Society* 80, 99–105.
- Kim, Y.W., Lee, S.G., Mitomo, M., 2002. Microstructural development of liquid phase sintered silicon carbide during annealing with uniaxial pressure. *Journal of the European Ceramic Society* 22, 1031–1037.
- Kim, Y.W., Mitomo, M., Emoto, H., Lee, J.G., 1998. Effect of initial α -phase content on microstructure and mechanical properties of sintered silicon carbide. *Journal of the American Ceramic Society* 81, 3136–3140.
- Kim, Y.W., Lee, S.H., Nishimura, T., Mitomo, M., 2005. Heat-resistant silicon carbide with aluminum nitride and scandium oxide. *Acta Materialia* 53, 4701–4708.
- Kim, Y.W., Lee, Y., Mitomo, M., Choi, H.J., Lee, J.G., 2004. Fabrication and mechanical properties of silicon carbide-silicon nitride composites with oxynitride glass. *Journal of the American Ceramic Society* 82, 1058–1060.
- Kim, Y.W., Chun, Y.S., Nishimura, T., Mitomo, M., Lee, Y.H., 2007. High-temperature strength of silicon carbide sintered with rare earth oxide and aluminium nitride. *Acta Materialia* 55, 727–736.

- Kim, Y.W., Kim, K.J., Kim, H.C., Cho, N.H., Lim, K.Y., 2011. Electrodischarge-machinable silicon carbide ceramics sintered with yttrium nitrate. *Journal of the American Ceramic Society* 94, 991–993.
- Koumoto, K., Shimohigoshi, M., Takeda, S., Yanagida, H., 1987. Thermoelectric energy conversion by porous SiC ceramics. *Journal of Materials Science* 6, 1453–1455.
- Kriegesmann, J., 2004. Microstructure control during consolidation of fine grained recrystallized silicon carbide. *Key Engineering Materials* 264–268, 2199–2202.
- Laube, M., Schmid, F., Pensl, G., *et al.*, 2002. Electrical activation of high concentrations of N^{+} and P^{+} ions implanted into 4H-SiC. *Journal of Applied Physics* 92, 549–554.
- Lee, S.G., Kim, Y.W., Mitomo, M., 2001a. Relationship between microstructure and fracture toughness of toughened silicon carbide ceramics. *Journal of the American Ceramic Society* 84, 1347–1353.
- Lee, S.G., Shim, W.H., Kim, J.Y., Kim, Y.W., Kwon, W.T., 2001b. Effect of sintering-additive composition of fracture toughness of liquid-phase-sintered SiC ceramics. *Journal of Materials Science Letters* 20, 143–146.
- Li, Y., Yin, J., Wu, H., *et al.*, 2014. High thermal conductivity in pressureless densified SiC ceramics with ultra-low contents of additives derived from novel boron-carbon sources. *Journal of the European Ceramic Society* 34, 2591–2595.
- Liang, H., Yao, X., Deng, H., *et al.*, 2015. High electrical resistivity of spark plasma sintered SiC ceramics with Al_2O_3 and Er_2O_3 as sintering additives. *Journal of the European Ceramic Society* 35, 399–403.
- Liang, H., Yao, X., Zhang, J., Liu, X., Huang, Z., 2014a. Low temperature pressureless sintering of α -SiC with Al_2O_3 and CeO_2 as additives. *Journal of the European Ceramic Society* 34, 831–835.
- Liang, H., Yao, X., Zhang, H., Liu, X., Huang, Z., 2014b. In situ toughening of pressureless liquid phase sintered α -SiC by using TiO_2 . *Ceramics International* 40, 10699–10704.
- Liang, H., Yao, X., Huang, Z., Zeng, Y., Su, B., 2016. Effect of sintering techniques on the microstructure of liquid-phase-sintered SiC ceramics. *Journal of the European Ceramic Society* 36, 1863–1871.
- Lim, C.B., Yano, T., Iseki, T., 1989. Microstructure and mechanical properties of RB-SiC/MoSi₂ composite. *Journal of Material Science* 24, 4144–4151.
- Lim, K.Y., Kim, Y.W., Kim, K.J., 2012. Influence of powder characteristics on the electrical resistivity of SiC ceramics. *Journal of the Ceramic Society of Japan* 120, 251–255.
- Lim, K.Y., Kim, Y.W., Kim, K.J., 2014. Electrical properties of SiC ceramics sintered with 0.5 wt% AlN-RE₂O₃ (RE=Y, Nd, Lu). *Ceramics International* 40, 8885–8890.
- Lim, K.Y., Kim, Y.W., Kim, K.J., Yu, J.H., 2011. Effect of in situ-synthesized nano-size SiC addition on density and electrical resistivity of liquid-phase sintered silicon carbide ceramics. *Journal of the Ceramic Society of Japan* 119, 965–967.
- Lim, K.Y., Kim, Y.W., Nishimura, T., Seo, W.S., 2013. High temperature strength of silicon carbide sintered with 1 wt% aluminum nitride and lutetium oxide. *Journal of the European Ceramic Society* 33, 345–350.
- Liu, S., Wang, J., 2018. Tunable magnetic properties of SiC obtained by microwave heating. *Journal of Alloys and Compounds* 731, 369–374.
- Malik, R., Kim, H.Y., Kim, Y.W., Kim, K.J., 2018. Grain-growth-induced high electrical conductivity in SiC-BN composites. *Ceramics International* 44, 16394–16399.
- Malik, R., Jang, S.H., Kim, Y.W., Nishimura, T., 2019. Mechanical properties of silicon carbide-in situ zirconium carbonitride composites. *International Journal of Applied Ceramic Technology* 16, 1304–1313.
- Maun, J.D., Sunderland, P.B., Urban, D.L., 2007. Thin-filament pyrometry with a digital still camera. *Applied Optics* 46, 483–488.
- Meyers, S., Leersnijder, L.D., Vlegels, J., Kruth, J.P., 2018. Direct laser sintering of reaction bonded silicon carbide with low residual silicon content. *Journal of the European Ceramic Society* 38, 3709–3717.
- Mulla, M.A., Krstic, V.D., 1991. Low-temperature pressureless sintering of β -Silicon carbide with aluminum oxide and yttrium oxide additions. *American Ceramic Society Bulletin* 70, 439–443.
- Mulla, M.A., Krstic, V.D., 1994. Pressureless sintering of β -SiC with Al_2O_3 additions. *Journal of Materials Science* 29, 934–938.
- Nader, M., Aldinger, F., Hoffmann, M.J., 1999. Influence of the α/β -SiC phase transformation on microstructural development and mechanical properties of liquid phase sintered silicon carbide. *Journal of Materials Science* 34, 1197–1204.
- Ness, E.A., Rafaniello, W., 1994. Origin of density gradients in sintered β -silicon carbide parts. *Journal of the American Ceramic Society* 77, 2879–2884.
- Ness, J.N., Page, T.F., 1986. Microstructural evolution in reaction-bonded silicon carbide. *Journal of Materials Science* 21, 1377–1397.
- O'Sullivan, D., Pomeroy, M.J., Hampshire, S., Murtagh, M.J., 2004. Degradation resistance of silicon carbide diesel particulate filters to diesel fuel ash deposits. *Journal of Materials Research* 19, 2913–2921.
- Onoue, K., Nishikawa, T., Katsuno, M., Ohtani, N., 1996. Nitrogen incorporation kinetics during the sublimation growth of 6H and 4H SiC. *Japanese Journal of Applied Physics* 35, 2240–2243.
- Persson, C., Lindefelt, U., Sernelius, B.E., 1999. Doping-induced effects on the band structure in n-type 3C-, 2H-, 4H-, 6H-SiC, and Si. *Physical Review B* 60, 16479–16493.
- Peter, F., Kimoto, T., Ley, L., Pensl, G., 2011. *Silicon Carbide: Volume 1: Growth, Defects, and Novel Applications*. Hoboken, NJ: John Wiley & Sons.
- Prochazka, S., 1975. The role of boron and carbon in the sintering of silicon carbide. In: Popper, P. (Ed.), *Special Ceramics 6*. Stoke-on-Trent: The British Ceramic Research Association, pp. 171–181.
- Prochazka, S., Johnson, C.A., Giddings, R.A., 1979. Atmosphere effects in sintering of silicon carbide. In: Somya, S., Saito, S. (Eds.), *Proceedings of International Symposium on Factors in Densification and Sintering of Oxide and Non-oxide Ceramics*. Tokyo: Gakajutsu Bunken Fukyu-kai, pp. 366–381.
- Racka, K., Avdonin, A., Sochacki, M., *et al.*, 2015. Magnetic, optical and electrical characterization of SiC doped with scandium during the PVT growth. *Journal of Crystal Growth* 413, 86–93.
- Ramsdell, L.S., 1945. Studies on silicon carbide. *American Mineralogist* 32, 64–82.
- Rasp, M., Straubinger, T.L., Schmitt, E., *et al.*, 2003. PVT growth of p-type and semi-insulating 2 inch 6H-SiC crystals. *Materials Science Forum* 433–436, 55–58.
- Santos, A.C., Ribeiro, S., 2018. Liquid phase sintering and characterization of SiC ceramics. *Ceramics International* 44, 11048–11059.
- Seo, Y.K., Eom, J.H., Kim, Y.W., 2018. Process-tolerant pressureless-sintered silicon carbide ceramics with alumina-ytria-calcia-strontia. *Journal of the European Ceramic Society* 38, 445–452.
- Seo, Y.K., Kim, K.Y., Kim, K.J., Seo, W.S., 2016a. Electrically conductive SiC-BN composite. *Journal of the European Ceramic Society* 36, 3879–3887.
- Seo, Y.K., Kim, K.Y., Nishimura, T., Seo, W.S., 2016b. High-temperature strength of a thermally conductive silicon carbide ceramic sintered with yttria and scandia. *Journal of the European Ceramic Society* 36, 3755–3760.
- Seo, Y.K., Kim, Y.K., Nishimura, T., Seo, W.S., 2017. High thermal conductivity of spark plasma sintered silicon carbide ceramics with yttria and scandia. *Journal of the American Ceramic Society* 100, 1290–1294.
- Seong, H.K., Park, T.E., Lee, S.C., 2009. Magnetic properties of vanadium-doped silicon carbide nanowires. *Metals and Materials International* 15, 107–111.
- She, J.H., Ueno, K., 1999. Densification behavior and mechanical properties of pressureless-sintered silicon carbide ceramics with alumina and yttria additions. *Materials Chemistry and Physics* 59, 139–142.
- Siegelein, F., Kleebe, H.J., Sigl, L.S., 2003. Interface characteristics affecting electrical properties of Y-doped SiC. *Journal of Materials Research* 18, 2608–2617.
- Sigl, L.S., 2003. Thermal conductivity of liquid phase sintered silicon carbide. *Journal of the European Ceramic Society* 23, 1115–1122.
- Slack, G.A., 1964. Thermal conductivity of pure and impure silicon, silicon carbide, and diamond. *Journal of Applied Physics* 35, 3460–3466.
- Steibel, J., 2019. Ceramic matrix composites taking flight at GE Aviation. *American Ceramic Society Bulletin* 98, 30–33.
- Stringfellow, G.B., 1998. *High Brightness Light Emitting Diodes*. Cambridge, MA: Academic Press.
- Tajima, Y., Kingery, W.D., 1982. Solid solubility of aluminum and boron in silicon carbide. *Journal of the American Ceramic Society* 65, C-27–C-29.

- Takeda, Y., Nakamura, K., Maeda, K., Matsushita, Y., 1987. Effects of elemental additives on electrical resistivity of silicon carbide ceramics. *Journal of the American Ceramic Society* 70, C-266–C-267.
- Tamari, N., Tanaka, T., Tanaka, K., *et al.*, 1995. Effect of spark plasma sintering on densification and mechanical properties of silicon carbide. *Journal of the Ceramic Society of Japan* 103, 740–742.
- Tamulaitis, G., Yilmaz, I., Shur, M.S., Anderson, T., Gaska, R., 2004. Carrier lifetime in conductive and vanadium-doped 6H-SiC substrates. *Applied Physics Letters* 84, 335–337.
- Vaßen, R., Kaiser, A., Förster, J., Buchkremer, H.P., Stover, D., 1996. Densification of ultrafine SiC powders. *Journal of Materials Science* 31, 3623–3637.
- Ventra, M.D., Pantelides, S.T., 2000. Oxygen stability, diffusion, and precipitation in SiC: Implications for thin-film oxidation. *Journal of Electronic Materials* 29, 353–358.
- Wei, R., Song, S., Yang, K., *et al.*, 2013. Thermal conductivity of 4H-SiC single crystals. *Journal of Applied Physics* 113, 053503.
- Williams, R.M., Juterbock, B.N., Peters, C.R., Whalen, T.J., 1984. Forming and sintering of B- and C-doped α - and β -SiC. *Journal of the American Ceramic Society* 67, C-62–C-64.
- Wirth, H., Panknin, D., Skorupa, W., Niemann, E., 1999. Efficient p-type doping of 6H-SiC: Flash-lamp annealing after aluminum implantation. *Applied Physics Letters* 74, 979–981.
- Yamamoto, T.A., Kondou, T., Kodera, Y., *et al.*, 2005. Mechanical properties of β -SiC fabricated by spark plasma sintering. *Journal of Materials Engineering and Performance* 14, 460–466.
- Zhan, G.D., Mitomo, M., Mukherjee, A.K., 2002. Effects of heat treatment and sintering additives on thermal conductivity and electrical resistivity in fine-grained SiC ceramics. *Journal of Materials Research* 17, 2327–2333.
- Zhan, G.D., Mitomo, M., Xie, R.J., Mukherjee, A.K., 2001. Thermal and electrical properties in plasma-activation-sintered silicon carbide with rare-earth-oxide additives. *Journal of the American Ceramic Society* 84, 2448–2450.
- Zhou, Y., Hirao, K., Yamauchi, Y., Kanzaki, S., 2003. Effects of rare-earth oxide and alumina additives on thermal conductivity of liquid-phase-sintered silicon carbide. *Journal of Materials Research* 18, 1854–1862.

High Thermal Conductivity Ceramics

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Introduction

High thermal conductivity ceramics have drawn much attention due to energy and environment-related issues after the beginning of the 21st century. In order to reduce the emission of carbon dioxide, energy sources need to shift from fossil fuel to renewable energy sources like solar, wind and hydrogen power generations, in which so-called power modules are necessarily used to convert and control electric power. Power electronic devices are key technologies for this purpose, and also, they will be widely used for electric vehicles in the near future according to the world-wide trend for the replacement of fossil fuels towards electric power. Thermal dissipation has been always one of the critical issues for semiconductor devices, since they must be cooled to avoid thermal runaway and resultant failure of devices. Thus, ceramic substrates have been utilized for high-power electronic devices such as switching devices, oscillating devices, semiconductor lasers and LED lighting. Large thermal stresses induced by large electrical power has been posing great challenges for the assembly of the devices (Yamagiwa, 2010), especially for brittle ceramic substrates that provide functions of electrical insulation and heat dissipation.

High thermal conductivity ceramics are also used for heat exchangers, which are widely used in highly efficient modern power plants with cogeneration systems, combustion furnaces, chemical and petrochemical plants. The world-wide trends for energy saving should accelerate the use of ceramic heat exchangers for these applications, in which the materials must have durability at high temperature, in corrosive environments and under high thermal stress as well as high thermal conductivity.

Table 1 summarizes selected properties of commercial engineering ceramics. For more than half a century, aluminum oxide (Al_2O_3) has been an ideal ceramic material for semiconductor packaging and substrates for electronic circuits with excellent electrical properties and relatively low production cost. In the 1980s, strong demands mentioned above pushed the development of high thermal conductivity aluminum nitride (AlN) that was reported to have high intrinsic thermal conductivity (Slack, 1973, 1987) about 10 times higher than Al_2O_3 . In the 21st century, the demand for more efficient control of electric power and the advancement toward higher voltage, larger current, greater power density, is poised to be accelerated with the replacement of silicon by the wide-band gap semiconductors (silicon carbide and gallium nitride), which are able to operate at much higher temperatures than silicon. However, the thermal expansion coefficient differential between wiring materials, such as Cu, and AlN substrate yield large thermal stresses that cause cracks after thermal cycle tests due to the poor mechanical properties of AlN ceramics (Yamagiwa, 2010), and this also makes the machining process for through-holes difficult. Moreover, large dielectric dispersion around ~ 1 GHz (Nakayama *et al.*, 1996) and degradation of electric resistance at temperatures greater than 200°C (Naba, 2012) were reported for AlN ceramics, which accelerated the development of high thermal conductivity silicon nitride (Si_3N_4) ceramics that inherently possess excellent mechanical properties, much better than AlN, due to the interlocking of rod-like β - Si_3N_4 crystals within the microstructure (Becher, 1991) and intrinsic thermal conductivity as high as AlN (Haggerty and Lightfoot, 1995). Although silicon carbide (SiC) ceramics were known to have even higher intrinsic thermal conductivity than AlN (Slack, 1973), its electrical properties are basically those of a semiconductor, which would make its application as electrical circuit substrates very difficult; however, its excellent thermal and chemical stability as well as low thermal expansion coefficient make it a suitable material for heat exchangers.

Fig. 1 demonstrates how the thermal conductivities of AlN and SiC ceramics have advanced during the past 50 years after the prediction of their high intrinsic values by Slack in 1973 and that of Si_3N_4 by Haggerty and Lightfoot (1995). In this chapter, the intrinsic thermal conductivities of high thermal conductivity materials are first reviewed. Then, technological advancements for improving the thermal conductivities of AlN, SiC and Si_3N_4 ceramics will be separately reviewed in detail, followed by a short summary. High thermal conductivity ceramics were reviewed by Watari (2001) and therefore this we mainly focuses on the advancements in the 21st century.

Table 1 Properties of engineering ceramics^a

Materials	Density (gcm^{-3})	Bending strength (MPa)	Fracture toughness ($\text{MPa}\sqrt{\text{m}}$)	Thermal expansion coefficient (10^{-6} K^{-1})	Thermal conductivity ($\text{W m}^{-1} \text{ K}^{-1}$)	Dielectric strength (kV mm^{-1})	Resistivity (Ωm)	Relative permittivity
SiC	3.1	450–540	2–5	3.7	60–200	–	10^5 – 10^8	9–10
AlN	3.3	220–310	3–3.5	4.6	67–150	14–16	$> 10^{12}$	6–8.5
Si_3N_4	3.2	600–750	6.5–7.5	2.7–3.4	27–54	12–18	$> 10^{12}$	7–9
Al_2O_3	3.9	300–400	3.5–4	7–8	18–24	10–18	$> 10^{12}$	9–10
ZrO_2	6.0	750–1000	4–8	10–11	3	11–13	10^{11} – 10^{12}	28–33
SiO_2	2.2	67–69	–	0.51–0.58	1.38	25–40	10^{14}	3.7–8

^aCHARACTERISTICS OF KYOCERA FINE CERAMICS, <https://global.kyocera.com/prdct/fc/product/pdf/material.pdf>.

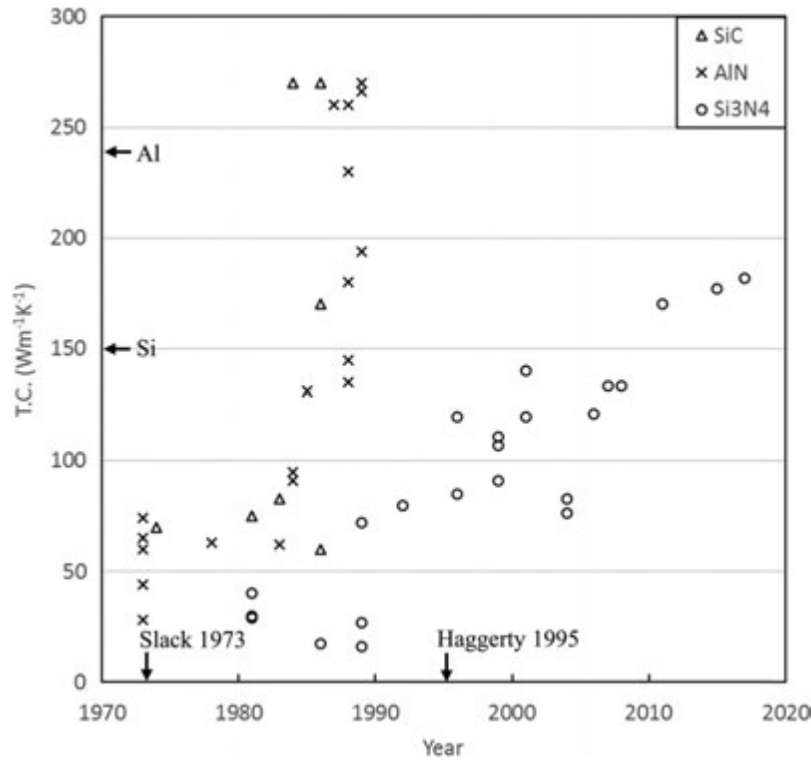


Fig. 1 Advancement of thermal conductivities of AlN and SiC ceramics during the past 50 years after the prediction of their high intrinsic values and that of Si_3N_4 . Adapted from Slack, G.A., 1973. Nonmetallic crystals with high thermal conductivity. *Journal of Physics Chemistry of Solids* 34, 321–335. Haggerty, J.S., Lightfoot, A., 1995. Opportunities for enhancing the thermal conductivity of SiC and Si_3N_4 ceramics through improved processing. *Ceramic Engineering & Science Proceedings* 16, 475–487.

Intrinsic Thermal Conductivities

Silver has the highest thermal conductivity of any metal at room temperature where its thermal conductivity, κ , is $427 \text{ W m}^{-1} \text{ K}^{-1}$. For copper, the value is $398 \text{ W m}^{-1} \text{ K}^{-1}$. In metals, the heat is carried primarily by electrons, while in non-metals it is carried primarily by phonons, the quantum mechanical description of a lattice vibration. For example, diamond exhibits κ value as high as $2000 \text{ W m}^{-1} \text{ K}^{-1}$ exceeding those of silver and copper. Those crystals for which κ at room temperature exceeds $100 \text{ W m}^{-1} \text{ K}^{-1}$ were considered to possess high thermal conductivity, and those of simple adamantane (diamond-like) compounds were investigated (Slack, 1973).

As an example for the effects of temperature on the thermal conductivity, that of a large, high-purity CVD-SiC single crystal (Slack, 1964) is shown in Fig. 2 (Haggerty and Lightfoot, 1995) along with its estimated intrinsic behavior (Kingery *et al.*, 1976). From 0K, the thermal conductivity increases rapidly with temperature, reaches a maximum value at approximately 55, then decreases with increasing temperature. For temperatures less than several hundred degrees Celsius, heat transfer is dominated by phonon transport and thermal conductivity (κ) is given by:

$$\kappa = \frac{1}{3} C_v v \lambda_{\text{effective}} \quad (1)$$

where C_v is the heat capacity of a unit volume, v is the phonon velocity, and $\lambda_{\text{effective}}$ is the effective phonon mean free path (Kingery *et al.*, 1976). The overall effect of temperature on κ is defined by the temperature dependencies of the individual terms. Fig. 2 also shows the effect of temperature on the intrinsic mean free path, which was analyzed for the high and low temperature domains that are defined in terms of the Debye temperature, θ_D . Between the temperature corresponding to the maximum conductivity and $T = 1/6 \cdot \theta_D$, the low temperature mean free path decreases exponentially with temperature, making κ proportional to $\exp(\text{constant} \cdot \theta_D \cdot T^{-1})$. At high temperature, $T \geq \theta_D$, the Peierls' adaptation of the Debye model predicts that:

$$\kappa = B \bar{M} \delta \theta_D^3 T^{-1} \gamma^{-2} \quad (2)$$

where B = some constant, $\bar{M}$ = average mass of an atom in the crystal, δ^3 = average volume occupied by one atom of the crystal (volume of a unit cell divided by n , the number of atoms in a primitive cell), and γ = Grüneisen's constant (Slack, 1973). This derivation gives the experimentally observed T^{-1} dependence. Between these two regimes, the conductivities of intrinsic materials generally change progressively between these limiting behaviors.

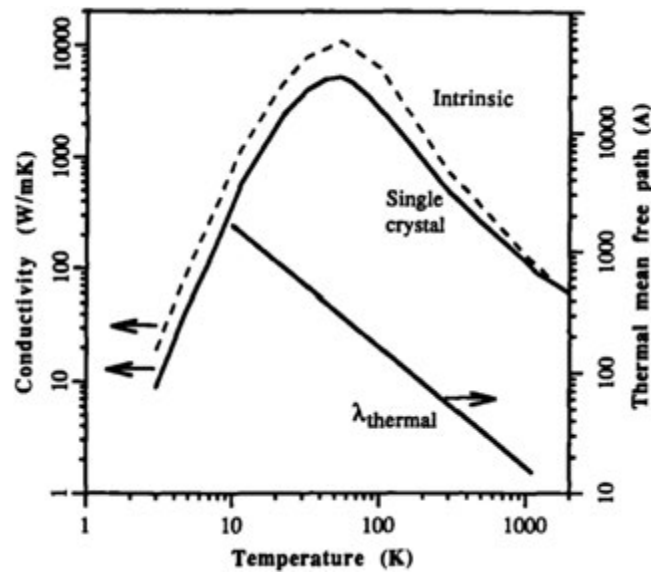


Fig. 2 Thermal conductivity data for a high purity α -SiC single crystal (solid line) as well as the projected intrinsic behavior (dashed line). Also shown are thermal mean free paths in SiC defined by intrinsic thermal effects. Adapted from Slack, G.A., 1964. Thermal conductivity of pure and impure silicon, silicon carbide, and diamond. *Journal of Applied Physics* 35, 3460–3466. Kingery, W.D., Bowen, H.K., Uhlmann, D.R., 1976. *Introduction to Ceramics*, second ed. New York: John Wiley & Sons, p. 615.

Table 2 Parameters affecting thermal conductivity κ , κ_{int} : intrinsic κ at room temperature calculated according to Eq. (2), and κ_{exp} : the highest κ at room temperature experimentally determined, of some adamantane compounds and silicon nitride

Crystals	θ (K)	$\bar{M}$ (g)	n	δ (10^{-10} m)	γ	$M\delta\theta^3$ (g m K ³)	κ_{in} (W m ⁻¹ K ⁻¹)	κ_{pc} (W m ⁻¹ K ⁻¹)
Diamond	2240	12.01	8	1.780	1.3	24.07	2000	400
BN	1750	12.41	8	1.810	—	12.02	760	290
SiC	1185	20.05	8	2.180	0.76	7.25	490	270
BeO	1280	12.51	8	1.900	—	4.99	370	—
BP	975	20.89	8	2.270	—	4.39	360	—
AlN	950	20.49	8	2.186	0.77	3.84	319	270
Si ₃ N ₄	1100	20.05	28	2.180	0.72	5.8	200 or 320	182
Si	648	28.09	8	2.715	—	2.07	156	—
GaN	525	41.86	8	2.245	—	1.36	130	—

Source: $\bar{M}$ = average mass of an atom in the crystal, δ^3 = average volume occupied by one atom of the crystal (volume of a unit cell divided by n , the number of atoms in a primitive cell), and γ = Grüneisen's constant.

Table 2 summarizes the parameters affecting κ , κ_{int} : intrinsic κ at room temperature calculated according to Eq. (2), and κ_{exp} : the highest κ at room temperature experimentally determined, of adamantane compounds and selected ceramic materials with high κ . These parameters imply four conditions of high κ materials as follows:

- (1) Low atomic mass,
- (2) Strong interatomic bonding,
- (3) Simple crystal structure, and
- (4) Low anharmonicity.

Conditions (1) and (2) mean high θ_D , condition (3) means low n , and condition (4) means small γ . Thus, simple adamantane crystals composed of elements with low atomic mass are the representative high κ materials as shown in **Table 2**. One exception in this table would be Si₃N₄ with $n = 28$. As is true of Y₂O₃, which exhibits an anomalously high conductivity, it appears that the primitive cell of Si₃N₄ should be approximated as an ensemble of smaller cells having different spatial orientations. For Si₃N₄, possible effective values of n are 14 and 7, which yield κ_{int} at room temperature, ~ 200 and ~ 320 W m⁻¹ K⁻¹, respectively (Haggerty and Lightfoot, 1995).

Imperfections in the crystal lattice resulting from impurity atoms, interstitials, vacancies, dislocations, twins, crystallographic disorder, etc., all increase anharmonicity in the vibrational modes (Touloukian *et al.*, 1970). As with intrinsic thermal effects, the

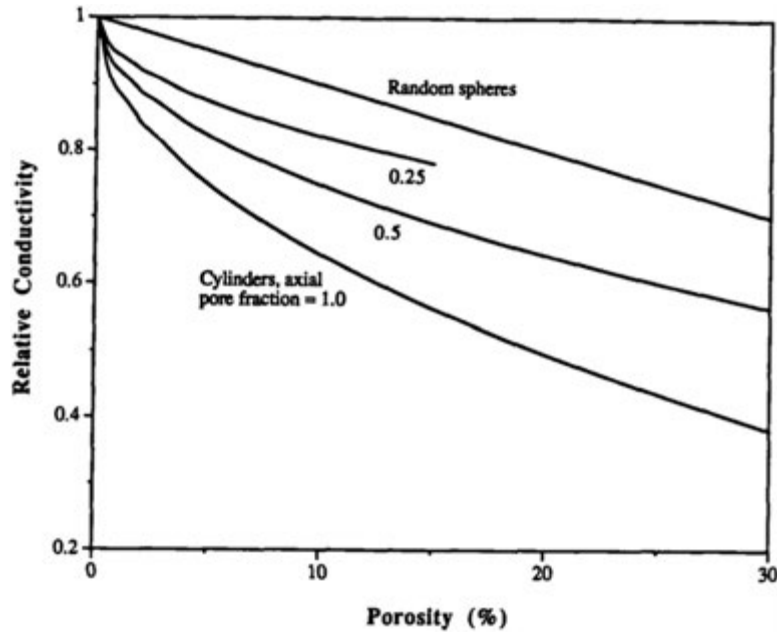


Fig. 3 Normalized low temperature thermal conductivities as a function of porosity for randomly distributed, uniform diameter, spherical pores (upper curve), and square ordered arrays of cylindrical pores whose axes are perpendicular to the direction of heat flow (pore lengths = 25%, 50% and 100% of sample length).

anharmonicities reduce the thermal conductivity by reducing the effective phonon mean free path. The effect of defects on the effective mean free path is given by:

$$\frac{1}{\lambda_{\text{effective}}} = \frac{1}{\lambda_{\text{thermal}}} + \frac{1}{\lambda_{\text{impurity}}} + \frac{1}{\lambda_{\text{defect}}} + \text{etc.} \quad (3)$$

where λ_{thermal} is the thermal mean free path, $\lambda_{\text{impurity}}$ is the mean free path defined by impurities, and λ_{defect} is the mean free path defined by defects other than impurities. In a crystalline lattice, the value of $\lambda_{\text{impurity}}$ is approximated by the distance between impurity atoms $\sim (\text{number per volume})^{-1/3}$. For example, 1 vol% solute impurity atoms are spaced $\sim 10 \text{ \AA}$ for SiC, which is smaller than the thermal mean free path for temperatures below 1600K as shown in Fig. 2 (Haggerty and Lightfoot, 1995). As summarized in Table 2, significant discrepancies in κ_{int} and κ_{exp} are confirmed, which are mainly due to the existence of impurities in these crystals. It was pointed out that the dominant impurity was oxygen in AlN (Slack, 1973) as was true in Si_3N_4 (Kitayama *et al.*, 1999c), which will be discussed in detail as well as the other impurity effects on thermal conductivity in SiC later below.

The effects of pores on the thermal conductivity of solids are extraordinarily complex in detail, however two models (Russell, 1935; Loeb, 1954) adequately describe the effects of uniform pores on the thermal conductivity of dielectric materials containing up to 60% porosity. The Russell model treats only spherical pores; however, it includes both radiation and the conductivity of the gas phase which can become significant in materials having open pore structures when used at high gas pressures. The Loeb model treats both spherical and cylindrical pores having arbitrary aspect ratios. However, in Loeb's model, heat transport across pores is assumed to occur only by radiation. Despite fundamental differences, both models predict values that agree closely with measured values for temperatures up to 900°C in dielectrics having porosity levels up to 60% (Francl and Kingery, 1954). In agreement with experimental observations, the calculated conductivity shown in Fig. 3 (Haggerty and Lightfoot, 1995) decreases proportionally with increasing concentration of spherical pores.

Silicon Carbide

Since it is very difficult to obtain dense SiC ceramics due to its strong covalent bonding, the use of applied pressure during sintering and the addition of effective sintering additives were the keys to obtain dense ceramics. Initial research on SiC ceramics employed hot-pressing (HP) for fabricating dense SiC ceramics. An extensive study of different sintering aids suggested that Al (either in elemental form or as an oxide) would result in a high density ($> 98\%$ of theoretical) material (Alliegro *et al.*, 1956), and the densification behaviors using Al_2O_3 as a sintering additive were studied in detail by Lange (1975). The pressureless sintering (PLS) of sub-micron SiC powder using B and C as sintering additives successfully fabricated dense SiC ceramics at more than 2100°C (Prochazka, 1974). Liquid-phase sintering using Al_2O_3 and Y_2O_3 as sintering additives lowered the HP temperature to 2000°C for obtaining dense SiC ceramics (Cutler and Jackson, 1988). Finally, the PLS of high purity B-doped sub-micron SiC powder successfully fabricated dense SiC ceramics at 2000°C using BeO as a sintering additive (Yasutomi *et al.*, 1995).

Table 3 Development of high thermal conductivity SiC ceramics

Year	κ ($\text{W m}^{-1}\text{K}^{-1}$)	Sintering additives	Sintering method ^a	Sintering temperature ($^{\circ}\text{C}$)	Sintering time (hr)	References
1974	70	B ₄ C + C	PLS	2100		Prochazka (1974)
1981	75	B + C	HP	1950–2100	0.25	Rafaniello <i>et al.</i> (1981)
1983	83	–	HP	2100		Bentsen <i>et al.</i> (1983)
1983	270	BeO	HP	2050	1	Takeda <i>et al.</i> (1983)
1986	270	BeO	HP	2050	1	Takeda <i>et al.</i> (1986)
	170	B				
	60	Al				
1988	150	B ₄ C + C	PLS	2200	0.5	Takeda (1988)
	70	BeO + B ₄ C + C				
1995	270	BeO + B	PLS	2000	1	Yasutomi <i>et al.</i> (1995)
	230	BeO				
1996	90	Al ₂ O ₃ -Y ₂ O ₃	HP	2000	2	Liu and Lin (1996)
1997	185	Al ₂ O ₃	HP	2050	5	Kinoshita and Munekawa (1997)

^aSintering methods abbreviations: HP, Hot-pressing; PLS, Pressure-less sintering.

Table 3 chronologically arranges the development of high thermal conductivity SiC ceramics including sintering aids, sintering methods and conditions and resultant κ values reported, which demonstrates that the type of sintering additives remarkably affects the κ values of dense SiC. The highest κ of about $270 \text{ W m}^{-1} \text{ K}^{-1}$ was obtained when BeO was employed (Takeda *et al.*, 1986); however much lower κ values were reported for other sintering additives: $170 \text{ W m}^{-1} \text{ K}^{-1}$ for B addition (Takeda *et al.*, 1986), $60 \text{ W m}^{-1} \text{ K}^{-1}$ for Al addition (Takeda *et al.*, 1986), $120\text{--}235 \text{ W m}^{-1} \text{ K}^{-1}$ for Al₂O₃ addition (Kinoshita and Munekawa, 1997) and $75\text{--}90 \text{ W m}^{-1} \text{ K}^{-1}$ for Al₂O₃-Y₂O₃ addition (Liu and Lin, 1996). These differences were reasonably explained by the solid solubilities of these elements in the SiC crystal lattice (Takeda, 1988). The solid solubility of Be was reported to be $\sim 8 \times 10^{18} \text{ cm}^{-3}$, which was much less than those of B and Al: 1×10^{20} and $1 \times 10^{21} \text{ cm}^{-3}$, respectively (Vodakov and Mokhov, 1973). Therefore, it can be concluded that the κ enhancement of SiC ceramics, as shown in Fig. 1, is primarily attributed to the optimization of sintering additives. However, it should be noted that the resistivities of SiC ceramics sintered with B and C were as low as of the order of $10^2 \Omega \cdot \text{m}$. Although the addition of BeO increases the resistivities to the order of $10^{10} \Omega \cdot \text{m}$, the electrical properties of these SiC ceramics were found to show the typical behavior of a varistor (Takeda, 1988).

The effect of phase development of SiC polytypes on the conductivity of ceramics should be noted. Works by Sakai and Aikawa (1988) and Liu and Lin (1996) reported that the conductivity of SiC decreases appreciably with increasing fraction of 4H SiC. However, a detailed relationship between the conductivity of SiC ceramics and phase content of 4H, 8H, 15R, etc., has not yet been clarified. The polytype 3C SiC, which has a cubic structure, is postulated to have the highest thermal conductivity among the SiC polytypes because of its highly symmetric crystal structure. SiC ceramics consisting of a large amount of 3C were fabricated by pressureless sintering of B-doped 3C-SiC powders with BeO addition (Yasutomi *et al.*, 1995) and this material was reported to have a κ value of $230 \text{ W m}^{-1} \text{ K}^{-1}$. Since the relative density of this material was 94%, further enhancement of the conductivity would be expected on full densification.

Aluminum Nitride

As well as SiC, initial research employed hot-pressing (HP) for fabricating dense AlN ceramics. The lattice oxygen was already found to be the main impurity that decreased the thermal conductivity of AlN ceramics (Slack, 1973; Sakai *et al.*, 1978), and the maximum solid solubility of oxygen in AlN at about 2000°C has been reported to be $2 \times 10^{21} \text{ cm}^{-3}$ (1.6 wt%) (Slack, 1973). Extensive studies of different sintering aids suggested that alkaline-earth oxides and rare-earth oxides were effective sintering additives for pressureless sintering (PLS) of AlN (Komeya *et al.*, 1981, 1982). These sintering additives form the liquid phase by the eutectic reactions between AlN, sintering additives and Al₂O₃ that normally presents as a surface film on AlN particles. These sintering additives are not only beneficial for promoting densification via the liquid phase sintering process, but they also enhance κ .

Table 4 chronologically shows the development of high thermal conductivity AlN ceramics including sintering aids, sintering methods and conditions and resultant κ values reported between 1973 and 1997. Initial works reported that the κ values of AlN ceramics densified by HP without any additives were limited to $74 \text{ W m}^{-1} \text{ K}^{-1}$ (Slack, 1973; Sakai *et al.*, 1978; Bentsen *et al.*, 1983). After the discovery of effective sintering additives for AlN (Komeya *et al.*, 1981, 1982), the κ values of AlN ceramics were drastically improved; however the developments were step by step as follows:

Table 4 Development of high thermal conductivity AlN ceramics

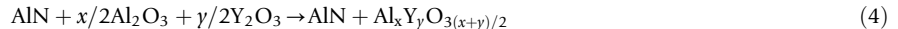
Year	κ ($\text{Wm}^{-1}\text{K}^{-1}$)	Sintering additives	Sintering method ^a	Sintering temperature ($^{\circ}\text{C}$)	Sintering time (hr)	References
1973	28–74	no	HP	1900	–	Slack (1973)
1978	63	no	HP	2000	2	Sakai <i>et al.</i> (1978)
1983	62	no	HP	1700	–	Bentsen <i>et al.</i> (1983)
1984	91	CaO	HP	2000	3	Kuramoto and Taniguchi (1984)
	95		PLS	1900	3	
1985	131	CaO	PLS	1800	3	Kuramoto <i>et al.</i> (1985)
1986	165	Y_2O_3	PLS	1800	–	Shinozaki and Tsuge (1986)
1987	255	Y_2O_3	PLS	1900	96	Horiguchi <i>et al.</i> (1987)
1988	135	CaO	HP	1800	2	Kurokawa <i>et al.</i> (1988)
	145	Y_2O_3				
	180	CaC ₂				
1988	230	CaO	PLS	1900	6	Fujimoto and Ueda (1988)
1988	260	Y_2O_3	PLS	1900	96	Ueno and Horiguchi (1989)
1989	194	Y_2O_3	PLS	1850	1.7	Virkar <i>et al.</i> (1989)
1989	266	Y_2O_3	PLS	1900	24	Okamoto <i>et al.</i> (1989)
1989	270	Y_2O_3	PLS	1977	96	Horiguchi and Ueno (1989)
1994	250	Y_2O_3 + Tr. Met.	PLS	1850	48	Kasori <i>et al.</i> (1994)
1997	246	Y_2O_3	PLS	1950	16.7	Jackson <i>et al.</i> (1997)

^aSintering methods abbreviations: HP, Hot-pressing; PLS, Pressureless sintering.

- (1) With the same amount of 0.5 wt% CaO, PLS gave higher κ values than HP (Kuramoto and Taniguchi, 1984; Kuramoto *et al.*, 1985),
- (2) Commercial high purity submicron AlN powders with low oxygen content (1.0 wt%) were synthesized by the carbothermal-reduction and nitridation of Al_2O_3 , and enabled the fabrication of translucent AlN ceramics by PLS with 1.0 wt% CaO (Kuramoto *et al.*, 1985),
- (3) Although the addition of about 1 wt% CaO or Y_2O_3 was enough to densify AlN ceramics, it was found that the further addition of sintering additives, depending on the oxygen content of raw AlN powders, drastically improved the conductivity, which was determined by the composition of the grain boundary phases (Shinozaki and Tsuge, 1986),
- (4) During the heat-treatments of AlN ceramics in the reducing N_2 atmosphere, which were achieved by: (a) using CaC_2 addition (Kurokawa *et al.*, 1988), (b) mixing CF_4 gas (Fujimoto and Ueda, 1988) and (c) heat-treatment in a graphite sagger (Okamoto *et al.*, 1989), the grain-boundary phases containing higher oxygen content migrate to the surface of AlN specimens resulting in lower oxygen content inside the specimens.

Following these developments, the highest κ value, $270 \text{ W m}^{-1} \text{ K}^{-1}$, was finally achieved for AlN ceramics (Horiguchi and Ueno, 1989), which is about 85% of the intrinsic κ of AlN crystals (Slack, 1987).

Thermodynamic, kinetic and microstructural effects of oxygen removal on the thermal conductivity of AlN ceramics were discussed by Virkar *et al.* (1989), Buhr *et al.* (1991) and Jackson *et al.* (1997). In the case of Y_2O_3 addition, a possible reaction during firing is considered as follows,



Oxygen atoms dissolved in the AlN grains diffuse to grain-boundaries, in order to produce stable Al-Y-O compounds. If their free energies of formation are sufficiently low, the grain-boundary phases trap oxygen impurities, and the concentration of oxygen impurity in the AlN grain would be reduced significantly. The different yttrium aluminates, $\text{Y}_4\text{Al}_2\text{O}_9$ (YAM), YAlO_3 (YAP) and $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) phases are stable at high temperature. Fig. 4 shows a quaternary phase diagram for the system: $\text{Al}_4\text{N}_4\text{-Al}_4\text{O}_6\text{-Y}_4\text{O}_6\text{-Y}_4\text{N}_4$. The activity of Al_2O_3 in the three phase fields may be deduced from the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ pseudobinary (Adylov *et al.*, 1988). With increasing amounts of Y_2O_3 , the grain-boundary phase changes from YAG to YAP to YAM, the lattice oxygen content decreases, and hence, the thermal resistivity decreases linearly as shown in Fig. 5 (Buhr *et al.*, 1991). When both YAP and YAM phases were present (field III), the highest thermal conductivity was achieved (Jackson *et al.*, 1997).

During the heat-treatment under the reducing N_2 atmosphere, the following reactions were identified (Okamoto *et al.*, 1989);



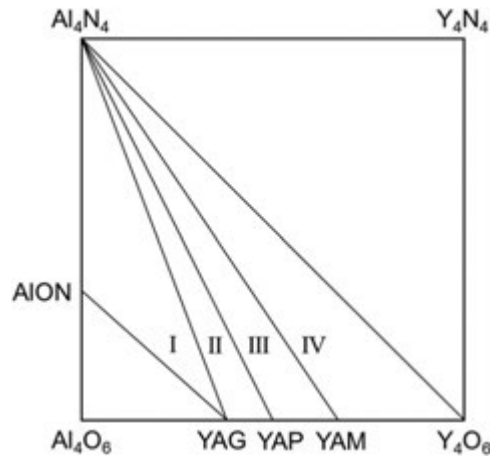


Fig. 4 Quaternary phase diagram for the system: $\text{Al}_4\text{N}_4\text{-Al}_4\text{O}_6\text{-Y}_4\text{O}_6\text{-Y}_4\text{N}_4$. The $\text{Y}_4\text{Al}_2\text{O}_9$, YAlO_3 and $\text{Y}_3\text{Al}_5\text{O}_{12}$ phases are designated as YAM, YAP and YAG, respectively. Fields I, II, III and IV designate AlN-AION-YAG , AlN-YAG-YAP , AlN-YAP-YAM and $\text{AlN-YAM-Y}_2\text{O}_3$ pseudo-ternary systems, respectively.

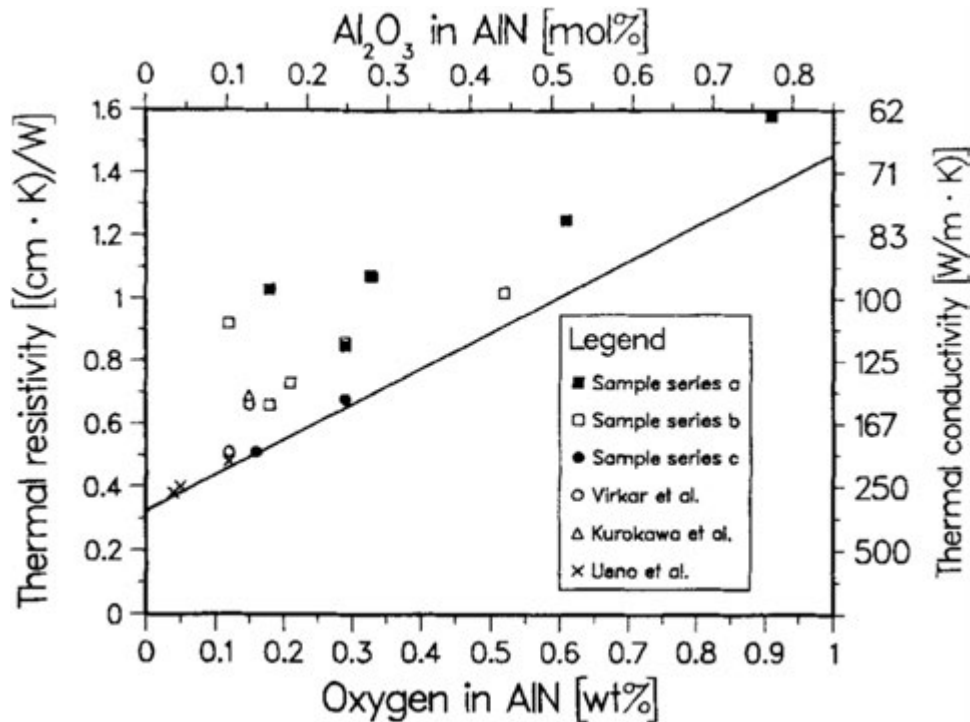


Fig. 5 Thermal resistivity at room temperature as a function of the oxygen content in the AlN lattice. Line represents correlation in single-phase AlN ceramics. Sample series a, b and c represent sintering conditions. Series a and b are AlN with Y_2O_3 contents in the range from 0.2 to 8 wt%; for series a and b, respectively, samples sintered at 1750 and 1790°C, using heating rates of 30 and 16 K/min, sintering time = 1 and 3 hrs. Series c are additional samples with Y_2O_3 contents of 1 and 5 wt% sintered under slightly different conditions. Adapted from Slack, G.A., 1973. Nonmetallic crystals with high thermal conductivity. *Journal of Physics Chemistry of Solids* 34, 321–335.

The initial grain-boundary phase, YAM, which existed mainly as a grain boundary film, was decomposed to Y_2O_3 according to Eq. (6) and migrated to the triple junctions in conjunction with grain growth as shown in Fig. 6 (Okamoto *et al.*, 1989). In addition to the compositional change of the grain boundary phases, their morphological change associated with grain growth further enhanced the κ values of AlN ceramics from $199 \text{ W m}^{-1} \text{ K}^{-1}$ to $266 \text{ W m}^{-1} \text{ K}^{-1}$ during heat-treatment at 1900°C for (a) 1 h and (b) 24 h, respectively. The grain-boundary phase migrated to the surface of AlN specimens and finally YN was formed on the specimen surface (Yagi *et al.*, 1989).

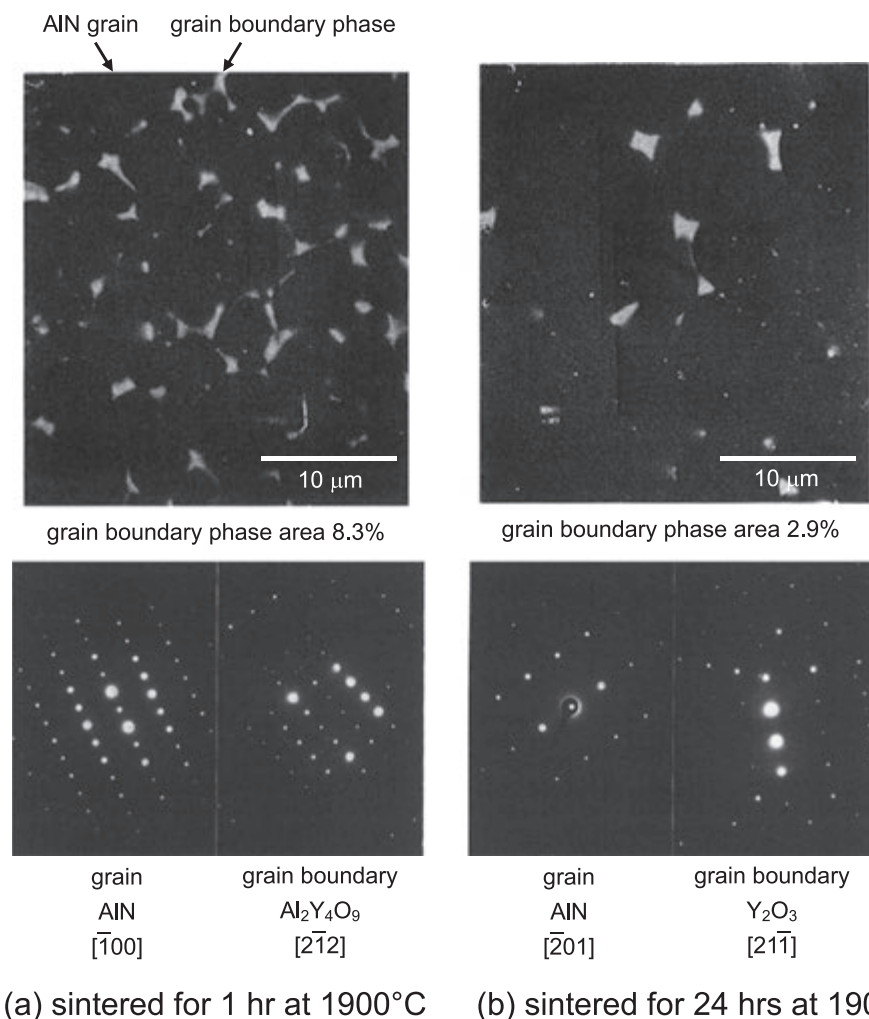


Fig. 6 SEM photographs of polished surface (upper row) and TEM electron diffraction patterns (lower row) of AlN ceramics sintered at 1900°C for (a) 1 h and (b) 24 h, respectively.

Effects of transition-metal compounds on the thermal conductivity of AlN sintered with 3 wt% Y_2O_3 were studied, and it was found that the thermal conductivity was influenced by oxygen release from the transition metal oxides, but not by the existence of transition-metal compounds, TiN, ZrN, TaC NbC, and W, all within 0.3 wt% (Kasori *et al.*, 1994). Effects of a variety of lanthanide oxide additives were also investigated, and no significant difference was observed between Y_2O_3 and Ln_2O_3 ($\text{Ln} = \text{La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb}$ and Lu) except $\text{Ln} = \text{Ce}$ and Eu which significantly deteriorated densification (Jackson *et al.*, 1997).

Silicon Nitride

In Silicon Nitride (Si_3N_4), there are two stable crystalline structures designated as α and β . Both structures consist of SiN_4 tetrahedra forming a corner-shared three-dimensional network with the characteristic (0001) plane of a hexagonal unit cell with a similar a -dimension but with the c -dimension of α about twice that of β . However, the stacking of the planes are different: in β the sheets are stacked periodically ABABABAB, with large diameter channels parallel to the c -axis; in α the stacking sequence is ABCDABCD with the CD sheets rotated with respect to AB by 180° about the c -axis (Hardie and Jack, 1957). As with SiC and AlN, due to the low self-diffusion coefficients, sintering additives must be used for densifying Si_3N_4 ceramics. It was first found that Si_3N_4 powder could be densified completely by hot-pressing with a second phase additive, MgO (Deeley *et al.*, 1961). It was suggested that MgO reacted with SiO_2 that is normally present on the surface of Si_3N_4 particles to form a magnesium silicate liquid phase at $>1550^\circ\text{C}$ (Terwilliger and Lange, 1974). Later it was shown that the liquid phase is an oxynitride liquid and promotes not only densification, but also the α to β phase transformation (Hampshire and Jack, 1981; Kitayama *et al.*, 1998b). Commercial Si_3N_4 powders mainly consist of α - Si_3N_4 and a small amount of β : the α - Si_3N_4 dissolves into the liquid phase during sintering and precipitates onto β - Si_3N_4 , which develops the interlocking microstructure of elongated β - Si_3N_4 grains and enhances the fracture toughness of this material (Lange, 1973) through the crack-bridging mechanism (Becher, 1991). Since the early research,

Table 5 Development of high thermal conductivity Si_3N_4 ceramics

Year	κ ($\text{W m}^{-1}\text{K}^{-1}$)	Sintering additives	Sintering method ^a	Sintering temperature ($^{\circ}\text{C}$)	Sintering time (hr)	References
1981	40	MgO	HP	1700	3	Ziegler and Hasselman (1981)
1981	30	MgO	HP	1900	1	Tsukuma <i>et al.</i> (1981)
	29	no				
1986	17	no	RB	1480	–	Hayashi <i>et al.</i> (1986)
1989	16	Al_2O_3	HIP	1750	1	Watari <i>et al.</i> (1989)
	27	$\text{Al}_2\text{O}_3 + \text{Y}_2\text{O}_3$				
	72	Y_2O_3				
1992	80	–	GPS	–	–	Li <i>et al.</i> (1992)
1996	120	$\text{Y}_2\text{O}_3 + \text{Nd}_2\text{O}_3$	GPS	2000	4	Hirosaki <i>et al.</i> (1996a)
1996	121 ^b	Y_2O_3	HP + GPS	1900	66	Hirao <i>et al.</i> (1996)
	60 ^b					
1999	155 ^c	Y_2O_3	HP + HIP	2500	2	Watari <i>et al.</i> (1999)
	52 ^c					
1999	162 ^d	$\text{Y}_2\text{O}_3 + \text{Nd}_2\text{O}_3$	GPS + HIP	2200	16	Akimune <i>et al.</i> (1999)
	85 ^d					
2001	122	$\text{Yb}_2\text{O}_3 + \text{MgO}$	GPS	1950	48	Hayashi <i>et al.</i> (2001a)
2001	140	$\text{Yb}_2\text{O}_3 + \text{MgSiN}_2$	GPS	1950	48	Hayashi <i>et al.</i> (2001b)
2004	83	$\text{Yb}_2\text{O}_3 + \text{MgO}$	SRBSN	1900	6	Zhu <i>et al.</i> (2004)
	76	$\text{Y}_2\text{O}_3 + \text{MgO}$				
2006	121	$\text{Y}_2\text{O}_3 + \text{MgSiN}_2$	SRBSN	1900	12	Zhu <i>et al.</i> (2006)
2007	133	$\text{Y}_2\text{O}_3 + \text{MgO}$	SRBSN	1900	24	Zhu <i>et al.</i> (2007)
2008	133	$\text{Y}_2\text{O}_3 + \text{MgO}$	SRBSN	1900	24	Zhou <i>et al.</i> (2008)
2011	170	$\text{Y}_2\text{O}_3 + \text{MgO}$	SRBSN	1900	60	Zhou <i>et al.</i> (2011)
2015	177	$\text{Y}_2\text{O}_3 + \text{MgO}$	SRBSN	1900	60	Zhou <i>et al.</i> (2015)
2017	182	$\text{Y}_2\text{O}_3 + \text{MgO}$	SRBSN	1900	60	Hirao <i>et al.</i> (2017)
2019	156	$\text{Y}_2\text{O}_3 + \text{MgO}$	SRBSN	1900	24	Zhou <i>et al.</i> (2019)
2020	114	$\text{ZrSi}_2 + \text{MgO}$	GPS	1900	12	Wang <i>et al.</i> (2020a)
2020	123	$\text{YH}_2 + \text{MgO}$	GPS	1900	12	Wang <i>et al.</i> (2020b)
2020	117	$\text{ZrSi}_2 + \text{MgSiN}_2$	GPS	1900	12	Wang <i>et al.</i> (2020c)

^aSintering methods abbreviations: HP, Hot-pressing; RB, Reaction-bonding; HIP, Hot-isostatic-pressing; GPS, Gas-pressure-sintering; and SRBSN, Sintering of reaction-bonded silicon nitride.

^bTape-casting made thermal conductivity anisotropic. An averaged value, $(121 + 75 + 60)/3 \approx 85$ ($\text{W m}^{-1}\text{K}^{-1}$), is plotted in Fig. 1.

^cTape-casting made thermal conductivity anisotropic. An averaged value, $(155 + 67 + 52)/3 \approx 91$ ($\text{W m}^{-1}\text{K}^{-1}$), is plotted in Fig. 1.

^dExtrusion molding made thermal conductivity anisotropic. An averaged value, $(162 + 85 + 85)/3 \approx 111$ ($\text{W m}^{-1}\text{K}^{-1}$), is plotted in Fig. 1.

numerous studies have been conducted, and alkaline-earth oxides, Al_2O_3 , and rare-earth oxides including Y_2O_3 and lanthanide oxides were found to be effective sintering additives for Si_3N_4 (Negita 1985a,b; Tsuge *et al.*, 1989). After sintering, the liquid phase remains at triple points or along the matrix grain boundaries as a glassy phase or crystalline phases, the volume fractions of which are typically up to 10%.

Table 5 shows chronologically the development of high thermal conductivity Si_3N_4 ceramics including sintering aids, sintering methods and conditions and resultant κ values reported. Initial works reported that the κ values of Si_3N_4 ceramics densified by HP with MgO were limited to $40 \text{ W m}^{-1}\text{K}^{-1}$ (Ziegler and Hasselman, 1981; Tsukuma *et al.*, 1981). The reaction-bonding (RB) technique initially produced Si_3N_4 ceramics with a κ value as low as $17 \text{ W m}^{-1}\text{K}^{-1}$ due to high porosity (Hayashi *et al.*, 1986). It is well recognized that the use of Al_2O_3 , one of the most beneficial sintering additives for Si_3N_4 , considerably lowers thermal conductivity (Watari *et al.*, 1989) because Al_2O_3 reacts with Si_3N_4 to form the solid solution of $\beta\text{-Si}_3\text{N}_4$, $\beta\text{-Sialon}$, which has the chemical formula, $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ ($0 < z < 4.2$). Thus, alkaline-earth oxides and rare-earth oxides including Y_2O_3 and lanthanide oxides (Watari, 2001), which had no solid solubility in the Si_3N_4 crystal lattice, were solely used or combined to form the eutectic mixtures for lowering the sintering temperature, because Si_3N_4 decomposes at elevated temperature $> 1850^{\circ}\text{C}$ under normal pressure (Greskovich and Prochazka, 1981). In addition, pressure-assisted sintering methods such as hot-pressing (HP), hot-isostatic pressing (HIP) and, especially, gas-pressure sintering (GPS) (Mitomo and Uenosono, 1991) to suppress the thermal

decomposition of Si_3N_4 were basically used for fabricating dense Si_3N_4 ceramics. Commercial Si_3N_4 ceramics fabricated by GPS achieved high thermal conductivity of $\sim 80 \text{ W m}^{-1} \text{ K}^{-1}$ (Li *et al.*, 1992).

As in the case of AlN ceramics, the development of high thermal conductivity Si_3N_4 ceramics was step by step as follows:

- (1) A silicon-imide thermal decomposition method provided high-purity, fine $\alpha\text{-Si}_3\text{N}_4$ powders (Yamada, 1993), which reduced firing temperature for densification, and increased the conductivity of sintered materials.
- (2) Grain growth of $\beta\text{-Si}_3\text{N}_4$ promoted by prolonged annealing time or extremely high annealing temperature through the solution-precipitation process in the liquid phase (Kitayama *et al.*, 1998a) to form purified $\beta\text{-Si}_3\text{N}_4$ grains, which effectively improved thermal conductivity beyond $100 \text{ W m}^{-1} \text{ K}^{-1}$ (Hirosaki *et al.*, 1993; Hirao *et al.*, 1996; Watari *et al.*, 1999; Akimune *et al.*, 1999; Hayashi *et al.*, 2001a).
- (3) Using non-oxide sintering additives, the native SiO_2 on the raw Si_3N_4 particles were effectively removed to enhance thermal conductivity to $140 \text{ W m}^{-1} \text{ K}^{-1}$ (Hayashi *et al.*, 2001b).
- (4) Development of a new sintering process, sintering of reaction-bonded silicon nitride (SRBSN), initially using Si powder with low oxygen content (0.28 wt%) as a starting material which further improved thermal conductivity (Zhu *et al.*, 2004, 2006, 2007; Zhou *et al.*, 2008, 2011, 2019). The highest thermal conductivity reported for $\beta\text{-Si}_3\text{N}_4$ ceramics was finally achieved up to $182 \text{ W m}^{-1} \text{ K}^{-1}$ after the post-sintering at 1900°C for 60 hrs and subsequent slow cooling at a rate of $0.2^\circ\text{C min}^{-1}$ maintaining its excellent mechanical properties, bending strength of 720 MPa and fracture toughness of $11 \text{ MPa m}^{1/2}$ (Hirao *et al.*, 2017).

In the second stage, high-purity $\beta\text{-Si}_3\text{N}_4$ seed crystals (Hirao *et al.*, 1993) were added to the raw fine $\alpha\text{-Si}_3\text{N}_4$ powder, and subsequent tape-casting or extrusion molding processes rendered the grains arranged in one direction. Through the Ostwald ripening process, the seed crystals preferentially were grown to give textured microstructure composed of large rod-like $\beta\text{-Si}_3\text{N}_4$ crystals in a fine matrix, which achieved the anisotropic thermal conductivity of $120\text{--}162 \text{ W m}^{-1} \text{ K}^{-1}$ parallel to the rod-like crystals and $52\text{--}85 \text{ W m}^{-1} \text{ K}^{-1}$ perpendicular to them; however, the average values in the three directions were limited to $85\text{--}111 \text{ W m}^{-1} \text{ K}^{-1}$ (Hirao *et al.*, 1996; Watari *et al.*, 1999; Akimune *et al.*, 1999) even though the prolonged annealing times or extremely high temperatures would certainly increase the production cost of this material. This became the strong motivation for searching the fundamental understanding about the thermal conductivity of $\beta\text{-Si}_3\text{N}_4$ ceramics (Kitayama *et al.*, 1999a,b, 2000, 2001), which are briefly described in the following sub-sections.

Effect of Microstructure

Based on experimental results, Hirosaki *et al.* (1996a,b) stressed the possibility that the amount of grain boundary film that was directly related to grain size might have a significant influence on the thermal conductivity of $\beta\text{-Si}_3\text{N}_4$. This is because the grain boundary phases in Si_3N_4 ceramics are mainly composed of a SiO_2 -rich oxynitride glassy phase with thermal conductivity as low as $\sim 0.5\text{--}1 \text{ W m}^{-1} \text{ K}^{-1}$, which is much lower than those of the crystalline grain boundary phases in AlN ceramics in the range $2.5\text{--}13 \text{ W m}^{-1} \text{ K}^{-1}$ (Jackson *et al.*, 1997).

Buhr and Müller (1993) treated the thermal conductivity of AlN using simple cubic models with thin grain boundary films, and with or without the continuous network of secondary phases along grain edges. Calculated thermal conductivities were in good agreement with the measured values of AlN sintered bodies with the two types of microstructures mentioned above (Buhr and Müller, 1993; Kim *et al.*, 1996). Due to the isotropic grain shape of AlN, simple cubic models successfully simulated the thermal conductivity of this material. Although the grain boundary film thickness was taken into account in their model, grain anisotropy was not considered so that it is not applicable to $\beta\text{-Si}_3\text{N}_4$ with highly anisotropic grain shape. The strong faceting tendency of the liquid phase sintered Si_3N_4 further complicated the modeling of the thermal conductivity of $\beta\text{-Si}_3\text{N}_4$. Even though the distance between two crystals is in equilibrium (typically 1–2 nm) at some parts of the crystals (Clarke and Thomas, 1977), other parts should have much larger distances due to the faceting of the prismatic planes of $\beta\text{-Si}_3\text{N}_4$ because the two elongated grains are generally not parallel but inclined to each other as in Fig. 7 (Kitayama *et al.*, 1999b). The parts of grain boundaries pointed to by open arrows are very thin and would have the equilibrium grain boundary thickness. In contrast, the other parts pointed to by filled arrows have much larger width than those pointed to by open arrows due to the faceting of the prismatic planes of $\beta\text{-Si}_3\text{N}_4$, which was referred to as the “thick film” in contrast to the thin film in equilibrium. Calculations based on a simple modified Wiener’s model (Wiener, 1904) for thermal conductivity of a composite material predicted that the thermal conductivity of $\beta\text{-Si}_3\text{N}_4$ quickly decreased as the grain boundary film thickness increased in a range of a few tenths of a nanometer, and also that it steeply increased initially with the increase of grain size, and then reached almost constant values as shown in Fig. 8. Theoretically and experimentally, it was demonstrated that mere grain growth would have little effect for improving the thermal conductivity of $\beta\text{-Si}_3\text{N}_4$ (Kitayama *et al.*, 1999b).

Effect of the Lattice Oxygen

Until the end of the 20th century, it was not known whether oxygen dissolved in the $\beta\text{-Si}_3\text{N}_4$ crystal lattice and, if so, how much, although several oxygen contents in the $\alpha\text{-Si}_3\text{N}_4$ crystal lattice were reported: 0.31–0.53 wt% for those prepared by the nitridation of silicon (Edwards *et al.*, 1974) and 0.05–0.30 wt% for those prepared by chemical vapor deposition (Priest *et al.*, 1973; Kijima *et al.*, 1975), for example. Two kinds of pure $\beta\text{-Si}_3\text{N}_4$ crystal powders were prepared by heat treatment of $\alpha\text{-Si}_3\text{N}_4$ powder with sintering additives of $\text{Y}_2\text{O}_3\text{:SiO}_2 = 1\text{:}2$ and $2\text{:}1$ molar ratios. After the secondary phase was removed through acid treatments, their

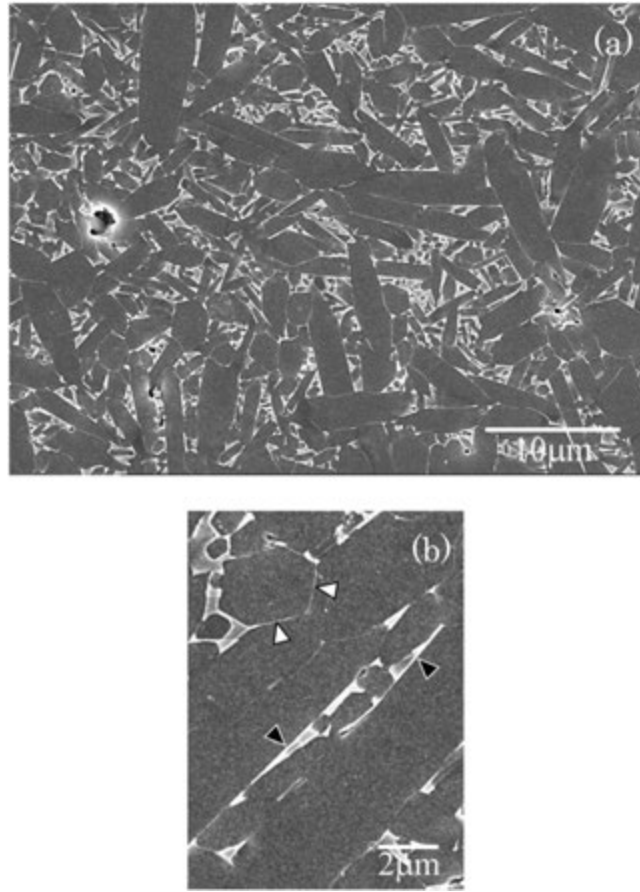


Fig. 7 SEM photographs of β - Si_3N_4 fabricated by hot-pressing at 1800°C for 2 h and subsequent heat-treatment at 1850°C for 4 h: (a) polished and etched plane parallel to hot-pressed surface, and (b) enlarged image of (a). Note that parts of grain boundary indicated by open arrows are very thin with equilibrium thickness, and those indicated by filled arrows are much wider because of faceting of prismatic planes of β - Si_3N_4 .

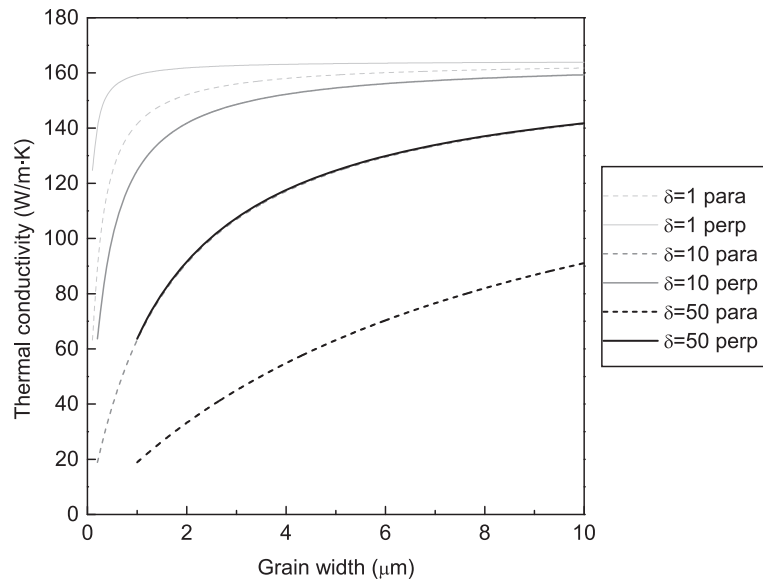


Fig. 8 Effect of grain size on the thermal conductivity of β - Si_3N_4 with various grain-boundary film thickness $\delta = 1, 10$ and 50 nm. Calculations were performed using the aspect ratio $= 5$ and the volume fraction of grain boundary phase $= 6\%$. 'Para' and 'Perp' mean thermal conductivities parallel and perpendicular, respectively, to the hot-press direction.

oxygen contents were determined by the hot-gas extraction method (Thomas and Müller, 1991) giving 0.258 and 0.158 wt%, respectively, which were comparable to α - Si_3N_4 as well as AlN (Kitayama *et al.*, 1999c).

As described in the previous section, the ratio of Y_2O_3 and Al_2O_3 in the grain boundary phase was crucial for controlling the lattice oxygen content, and hence, the thermal conductivity of AlN ceramics (Buhr *et al.*, 1991). Thus, it was readily expected that the ratio of Y_2O_3 and SiO_2 derived from the oxygen impurities in the raw powder would control the lattice oxygen content, and hence, the thermal conductivity of β - Si_3N_4 ceramics. Commercial α - Si_3N_4 powder (oxygen content 0.84 wt%) was mixed with Y_2O_3 and SiO_2 powders using the molar ratios of $\text{Si}_3\text{N}_4\text{:Y}_2\text{O}_3\text{:SiO}_2 = 40\text{:}1\text{:}2, 40\text{:}2\text{:}1, 40\text{:}2.5\text{:}0.5$ and $40\text{:}3\text{:}0$, designated Y1, Y2, Y3 and Y4, respectively. After CIPing, powder compacts were hot-pressed at 1800°C for 2 hrs and subsequently annealed at 1850°C for 4 hrs under a nitrogen pressure of 1 MPa. Considering oxygen impurity contained in the raw α - Si_3N_4 powder, corrected $\text{Y}_2\text{O}_3/\text{SiO}_2$ ratios were 0.289, 0.807, 1.267 and 2.029 for Y1, Y2, Y3 and Y4. The grain boundary phases in these specimens were identified using XRD, and it was confirmed that Y1 was in the phase field I, Y2 was in the phase field II, and Y3 and Y4 were in the phase field III shown in Fig. 9 (Kitayama *et al.*, 2000). It was found that a significant increase in thermal conductivity takes place at the critical ratio $\text{Y}_2\text{O}_3/\text{SiO}_2 = 1$ as shown in Fig. 10, which closely correlated to the oxygen contents of 0.400, 0.185, 0.064 and 0.058 wt% for the specimens Y1, Y2, Y3 and Y4, respectively. Thus, it was concluded that the phase composition of the grain boundary dictated the lattice oxygen content of β - Si_3N_4 , and that there was an

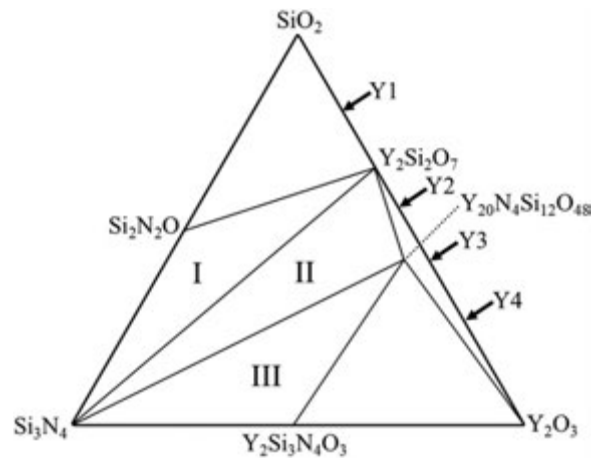


Fig. 9 $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-SiO}_2$ phase diagram at 1850°C , constructed schematically from the XRD phase-identification result. $\text{Y}_2\text{O}_3/\text{SiO}_2$ ratios of samples Y1-Y4 are indicated by arrows.

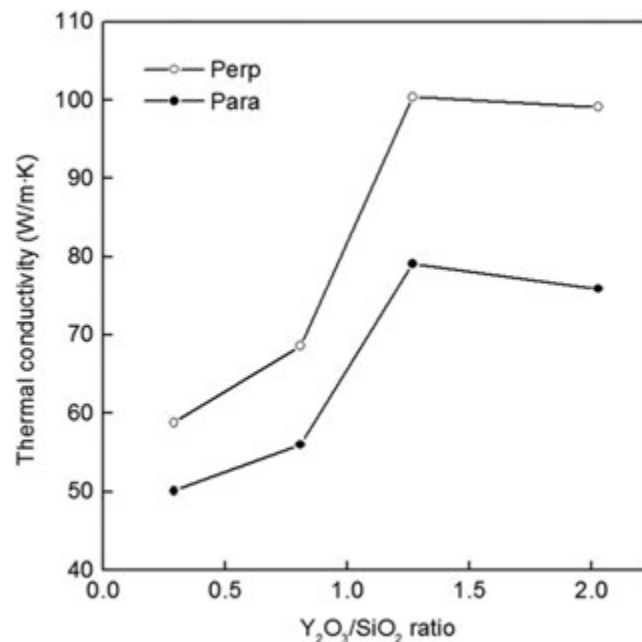


Fig. 10 Relationship between the $\text{Y}_2\text{O}_3/\text{SiO}_2$ ratios and thermal conductivities of samples Y1-Y4.

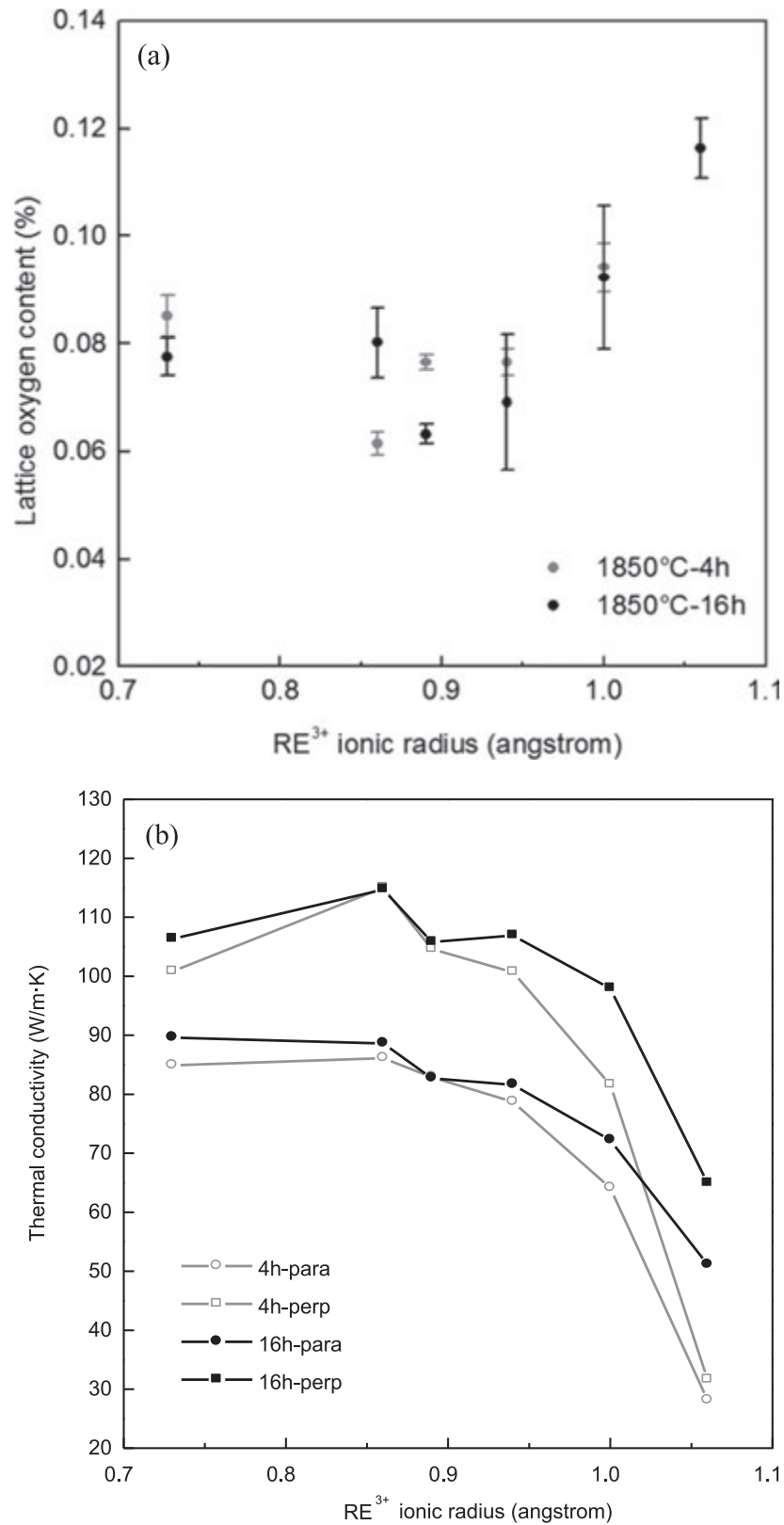


Fig. 11 Relationships between ionic radii of rare-earth oxide additives and (a) the lattice oxygen contents and (b) thermal conductivities of β -Si₃N₄ annealed at 1850°C for 4 and 16 hrs. 'Para' and 'Perp' mean thermal conductivities parallel and perpendicular, respectively, to the hot-press direction.

optimum amount of Y_2O_3 addition, depending on the amount of oxygen impurity in the raw Si_3N_4 powder, to achieve the highest thermal conductivity in β - Si_3N_4 just as in the case of AlN ceramics.

Effect of Rare-earth Oxide Additives

Rare-earth elements including Sc, Y and lanthanides (Ln) have a common ionic valence z of $+3$ and are known to be the most electro-positive elements. Thus, it was suggested that they are suitable sintering additives for Si_3N_4 (Negita, 1985a,b). Because the ionic radius r of lanthanide elements continuously decreases with increasing atomic number – known as the lanthanide contraction – the cationic field strength z/r^2 also continuously changes with the atomic number, which causes substantial variations in the thermal and physical properties of Ln-Si-(Al)-O-N glasses (Shelby and Kohli, 1990; Tanabe *et al.*, 1992; Ohashi *et al.*, 1995; Ramesh *et al.*, 1997). These glasses are similar to the grain boundary amorphous phases in Si_3N_4 ceramics sintered with rare-earth oxide additives, and thus, they should affect various properties of Si_3N_4 ceramics themselves. It was observed that the mean aspect ratio of β grains at the end of the α to β phase transformation was proportional to the ionic radius of the rare-earth elements (Hoffmann, 1994), and also that rare-earth elements strongly influenced grain growth behavior not only during the phase transformation but also during the Ostwald ripening (Kitayama *et al.*, 1999c). These works clearly demonstrated that rare-earth oxide additives significantly affected the grain growth behavior of Si_3N_4 during and after the phase transformation, which would influence the purification kinetics of the β - Si_3N_4 crystal lattice that proceed via the solution-precipitation mechanism through the liquid phase. Although a series of different rare-earth oxide additives had no significant effect on thermal conductivity of AlN (Jackson *et al.*, 1997), there were significant differences for β - Si_3N_4 (Kitayama *et al.*, 2001).

Commercial α - Si_3N_4 powder (oxygen content 0.84 wt%) was mixed with RE_2O_3 powders ($RE = La, Nd, Gd, Y, Yb$, and Sc) using the molar ratios of $Si_3N_4:RE_2O_3 = 20:1:2$. After CIPing, powder compacts were hot-pressed at $1800^\circ C$ for 2 hrs and subsequently annealed at $1850^\circ C$ for 4 and 16 hrs under a nitrogen pressure of 1 MPa. Only a sample sintered with La_2O_3 at $1850^\circ C$ for 4hrs contained a significant amount of the α -phase, and none of the other samples contained α -phase. In addition to the amorphous grain boundary phase, a variety of crystalline phases were observed for different rare-earth oxide additives. For Sc_2O_3 , only Sc_2SiO_5 ($RE_2O_3:SiO_2 = 1:1$) was identified. For La_2O_3 , both $La_{20}N_4Si_{12}O_{48}$ ($RE_2O_3:SiO_2 = 10:9$) and La_2SiO_5 ($RE_2O_3:SiO_2 = 1:1$) were identified. For Nd_2O_3 , both $Nd_2Si_3O_3N_4$ ($RE_2O_3:SiO_2 = 1:0$) and $Nd_4Si_3O_{12}$ ($RE_2O_3:SiO_2 = 2:3$) were identified. For Y_2O_3 and Gd_2O_3 , both $RE_{20}N_4Si_{12}O_{48}$ ($RE_2O_3:SiO_2 = 10:9$) and $RE_2Si_3O_3N_4$ ($RE_2O_3:SiO_2 = 1:0$) were identified. For Yb_2O_3 , only $Yb_4Si_2N_2O_7$ ($RE_2O_3:SiO_2 = 4:1$) was identified. Evidently, grain size markedly increased as the ionic radius of the rare-earths decreased from La to Nd to Gd, and reached almost a constant level at lower ionic radius. Relationships between ionic radii of rare-earths from the oxide additives and lattice oxygen contents (Fig. 11(a)), and also thermal conductivities (Fig. 11(b)) demonstrated that thermal conductivity showed a good inverse correlation with lattice oxygen content. Thus, unlike AlN, the ionic radius of the particular rare-earth element significantly influenced the phase transformation kinetics (Kitayama *et al.*, 2006), grain growth behavior, grain boundary phase, lattice oxygen content and hence thermal conductivity of β - Si_3N_4 , which was reasonably explained by the different interfacial adsorption behaviors of rare-earth ions (Urakami *et al.*, 2017).

Summary

As described in the introduction, the world-wide trend for power electronics has created a strong demand for high thermal conductivity ceramics. After the prediction made by Slack (1973), the thermal conductivities of SiC and AlN ceramics were improved very significantly. However, no further developments occurred after 1990 as shown in Fig. 1, at which point they had reached about 55% and 85%, respectively, of their intrinsic values. Although there is still room for improvement in SiC, the demand had ceased probably due to the fact that its electrical properties were those of a semiconductor, which renders it unsuitable for application as a substrate material for electronic circuits.

The thermal conductivity of AlN ceramics had reached almost its maximum value; however, its poor mechanical properties had restricted its industrial application. Thus, an alternative high thermal conductivity ceramic candidate with excellent mechanical properties, Si_3N_4 , has been actively developed after the prediction made by Haggerty and Lightfoot (1995). However, the improvement of its thermal conductivity was found to be much more difficult than for AlN mainly due to the amorphous grain boundary phase and the strong faceting nature of the β - Si_3N_4 crystal. Although the recent advancement of high thermal conductivity Si_3N_4 ceramics by the new SRBSN technique using Si powder with low oxygen content as a raw material achieved about 57% of its intrinsic thermal conductivity, assuming the value of $320 \text{ Wm}^{-1} \text{ K}^{-1}$, this achievement still depended on prolonged annealing time at high temperature, which would certainly increase the production cost of this material. Since there is still room for further improvement in Si_3N_4 , efforts for fabricating high thermal conductivity Si_3N_4 ceramics, using lower temperatures and shorter duration for annealing, have been on-going through the optimization of the SRBSN technique (Zhou *et al.*, 2019). Finally, other possibilities are being explored using non-oxide sintering additives such as $ZrSi_2$ (Wang *et al.*, 2020a), YH_2 (Wang *et al.*, 2020b) and $ZrSi_2$ - $MgSiN_2$ (Wang *et al.*, 2020c) as shown in Table 5.

References

- Adylov, G.T., Voronov, G.V., Mansurova, E.P., Sigalov, L.M., Urazaeva, E.M., 1988. Yttrium oxide–alumina system above 1473K. *Journal of Inorganic Chemistry* 33, 1062–1063.
- Akimune, Y., Munakata, F., Matsuo, K., *et al.*, 1999. Raman spectroscopic analysis of structural defects in hot isostatically pressed silicon nitride. *Journal of the Ceramic Society of Japan* 107, 339–342.
- Alliegro, R.A., Coffin, L.B., Tinklepaugh, J.R., 1956. Pressure-sintered silicon carbide. *Journal of the American Ceramic Society* 39, 386–389.
- Becher, P.F., 1991. Microstructural design of toughened ceramics. *Journal of the American Ceramic Society* 74, 255–269.
- Bentsen, L.D., Haselman, D.P.H., Ruh, R., 1983. Effect of hot-pressing temperature on the thermal diffusivity/conductivity of SiC/AlN composites. *Journal of the American Ceramic Society* 66, C40–C41.
- Buhr, H., Müller, G., 1993. Microstructure and thermal conductivity of AlN (Y_2O_3) ceramics sintered in different atmospheres. *Journal of the European Ceramic Society* 12, 271–277.
- Buhr, H., Müller, G., Wiggers, H., *et al.*, 1991. Phase composition, oxygen content, and thermal conductivity of AlN (Y_2O_3) ceramics. *Journal of the American Ceramic Society* 74, 718–723.
- Clarke, D.R., Thomas, G., 1977. Grain boundary phases in hot-pressed MgO fluxed silicon nitride. *Journal of the American Ceramic Society* 60, 491–495.
- Cutler, R.A., Jackson, T.B., 1988. In: Tenney, V.J. (Ed.), *Proceedings of the 3rd International Symposium on Ceramic Materials and Components for Engines*. Columbus, OH: American Ceramic Society, pp. 309–318. [Las Vegas, NV].
- Deeley, G.G., Herbert, J.M., Moore, N.C., 1961. Dense silicon nitride. *Powder Metallurgy* 8, 145–151.
- Edwards, A.J., Elias, D.P., Lindley, M.W., Atkinson, A., Moulson, A.J., 1974. Oxygen content of reaction-bonded α -silicon nitride. *Journal of Materials Science* 9, 516–517.
- Franci, J., Kingery, W.D., 1954. Thermal conductivity: IX, experimental investigation of effect of porosity on thermal conductivity. *Journal of the American Ceramic Society* 37, 99–107.
- Fujimoto, M., Ueda, S., 1988. Effect of annealing in CF_4 gas atmosphere on thermal conductivity of AlN ceramics. *Journal of the Ceramic Society of Japan* 96, 1210–1213.
- Greskovich, C., Prochazka, S., 1981. Stability of Si_3N_4 and liquid phase(s) during sintering. *Journal of the American Ceramic Society* 64, C96–C97.
- Haggerty, J.S., Lightfoot, A., 1995. Opportunities for enhancing the thermal conductivity of SiC and Si_3N_4 ceramics through improved processing. *Ceramic Engineering & Science Proceedings* 16, 475–487.
- Hampshire, S., Jack, K.H., 1981. The kinetics of densification and phase transformation in nitrogen ceramics. *Proceedings of the British Ceramic Society* 31, 37–49.
- Hardie, D., Jack, K.H., 1957. Crystal structures of silicon nitride. *Nature* 180, 332–335.
- Hayashi, H., Hirao, K., Kitayama, M., Yamauchi, Y., Kanzaki, S., 2001a. Effect of oxygen content on thermal conductivity of sintered silicon nitride. *Journal of the Ceramic Society of Japan* 109, 1046–1050.
- Hayashi, H., Hirao, K., Toriyama, M., Kanzaki, S., 2001b. MgSiN₂ addition as a means of increasing the thermal conductivity of β -silicon nitride. *Journal of the American Ceramic Society* 84, 3060–3062.
- Hayashi, K., Tsujimoto, S., Nishikawa, T., Imamura, Y., 1986. Thermal conductivity of reaction bonded Si_3N_4 . *Journal of the Ceramic Society of Japan* 94, 595–600.
- Hirao, K., Tsuge, M., Brito, M.E., Kanzaki, S., 1993. Preparation of rod-like β - Si_3N_4 single-crystal particles. *Journal of the Ceramic Society of Japan* 101, 1078–1080.
- Hirao, K., Watari, K., Brito, M.E., Toriyama, M., Kanzaki, S., 1996. High thermal conductivity in silicon nitride with anisotropic microstructure. *Journal of the American Ceramic Society* 79, 2485–2488.
- Hirao, K., Zhou, Y., Miyazaki, H., Hyuga, H., 2017. *Journal of the Japanese Society of Powder Metallurgy* 64, 439–444.
- Hirosaki, N., Akimune, Y., Mitomo, M., 1993. Microstructural design by selective grain growth of β - Si_3N_4 . In: Chen, I.W., Becher, P.F., Mitomo, M., Petzow, G., Yen, T.-S. (Eds.), *Silicon Nitride Ceramics - Scientific and Technological Advances*, Materials Research Society Symposium Proceedings 287. Pittsburgh, USA: MRS, pp. 405–410.
- Hirosaki, N., Okamoto, Y., Ando, M., Munakata, F., Akimune, Y., 1996a. Thermal conductivity of gas-pressure-sintered silicon nitride. *Journal of the American Ceramic Society* 79, 2878–2882.
- Hirosaki, N., Okamoto, Y., Ando, M., Munakata, F., Akimune, Y., 1996b. Effect of grain growth on the thermal conductivity of silicon nitride. *Journal of the Ceramic Society of Japan* 104, 49–53.
- Hoffmann, M.J., 1994. Analysis of microstructural development and mechanical properties of Si_3N_4 ceramics. In: Hoffmann, M.J., Petzow, G. (Eds.), *Tailoring of Mechanical Properties of Si_3N_4 Ceramics*. Dordrecht, The Netherlands: Kluwer Academic Publishers, pp. 59–72.
- Horiguchi, F., Kasori, A., Ueno, K., Tsuge, A., 1987. In: *Proceedings of the Annual Meeting of the Ceramic Society of Japan*, p. 969. Nagoya, Japan.
- Horiguchi, A., Ueno, F., 1989. In: De With, G., Terpstra, R.A., Metselaar, R. (Eds.), *EuroCeramics 1, Proceedings of 1st European Ceramic Society Conference*. London, New York: Elsevier Applied Science, p. 387.
- Jackson, T.B., Virkar, A.V., More, K.L., Dinwiddie, R.B., Cutler, R.A., 1997. High-thermal-conductivity aluminum nitride ceramics: The effect of thermodynamic, kinetic, and microstructural factors. *Journal of the American Ceramic Society* 80, 1421–1435.
- Kasori, M., Ueno, F., Tsuge, A., 1994. Effect of transition-metal additions on the properties of AlN. *Journal of the American Ceramic Society* 77, 1991–2000.
- Kijima, K., Kato, K., Inoue, Z., Tanaka, H., 1975. Oxygen content of α - Si_3N_4 single crystals. *Journal of Materials Science* 10, 362–363.
- Kim, W.-J., Kim, D.K., Kim, C.H., 1996. Morphological effect of second phase on the thermal conductivity of AlN ceramics. *Journal of the American Ceramic Society* 79, 1066–1072.
- Kingery, W.D., Bowen, H.K., Uhlmann, D.R., 1976. *Introduction to Ceramics*, second ed. New York: John Wiley & Sons, p. 615.
- Kinoshita, T., Munekawa, S., 1997. Effect of grain boundary segregation on thermal conductivity of hot-pressed silicon carbide. *Acta Materialia* 45, 2001–2012.
- Kitayama, M., Hirao, K., Kanzaki, S., 2006. Effects of rare-earth oxide additives on the phase transformation rates of Si_3N_4 . *Journal of the American Ceramic Society* 89, 2612–2618.
- Kitayama, M., Hirao, K., Toriyama, M., Kanzaki, S., 1998a. Modeling and simulation of grain growth in β - Si_3N_4 : I. Anisotropic Ostwald ripening. *Acta Materialia* 46, 6541–6550.
- Kitayama, M., Hirao, K., Toriyama, M., Kanzaki, S., 1998b. Modeling and simulation of grain growth in Si_3N_4 : II. The α - β transformation. *Acta Materialia* 46, 6551–6557.
- Kitayama, M., Hirao, K., Toriyama, M., Kanzaki, S., 1999a. Control of β - Si_3N_4 crystal morphology and its mechanism (Part 2): Effect of lanthanide additives. *Journal of the Ceramic Society of Japan* 107, 995–1000.
- Kitayama, M., Hirao, K., Toriyama, M., Kanzaki, S., 1999b. Thermal conductivity of β - Si_3N_4 – I. Effects of various microstructural factors. *Journal of the American Ceramic Society* 82, 3105–3112.
- Kitayama, M., Hirao, K., Toriyama, M., Kanzaki, S., 1999c. Oxygen content in β - Si_3N_4 crystal lattice. *Journal of the American Ceramic Society* 82, 3263–3265.
- Kitayama, M., Hirao, K., Tsuge, A., *et al.*, 2000. Thermal conductivity of β - Si_3N_4 – II. Effect of lattice oxygen. *Journal of the American Ceramic Society* 83, 1985–1992.
- Kitayama, M., Hirao, K., Watari, K., Toriyama, M., Kanzaki, S., 2001. Thermal conductivity of β - Si_3N_4 – III. Effects of rare-earth oxide additives. *Journal of the American Ceramic Society* 84, 353–358.
- Komeya, K., Inoue, H., Tsuge, A., 1981. Effect of various additives on sintering of aluminum nitride. *Journal of the Ceramic Society of Japan* 89, 330–336.
- Komeya, K., Tsuge, A., Inoue, H., Ohta, H., 1982. Effect of $CaCO_3$ addition on the sintering of AlN. *Journal of Materials Science Letters* 1, 325–326.
- Kuramoto, N., Taniguchi, H., 1984. Transparent AlN ceramics. *Journal of Materials Science Letters* 3, 471–474.

- Kuramoto, N., Taniguchi, H., Numata, Y., Aso, I., 1985. Sintering process of translucent AlN and effect of impurities on thermal conductivity of AlN ceramics. *Journal of the Ceramic Society of Japan* 93, 517–522.
- Kurokawa, Y., Utsumi, K., Takamizawa, H., 1988. Development and microstructural characterization of high-thermal-conductivity aluminum nitride ceramics. *Journal of the American Ceramic Society* 71, 588–594.
- Lange, F.F., 1973. Relation between strength, fracture energy, and microstructure of hot-pressed Si_3N_4 . *Journal of the American Ceramic Society* 56, 518–522.
- Lange, F.F., 1975. Hot-pressing behavior of silicon carbide powder with additions of aluminium oxide. *Journal of Materials Science* 10, 314–320.
- Liu, D.-M., Lin, B.-W., 1996. Thermal conductivity of hot-pressed silicon carbide. *Ceramics International* 22, 407–414.
- Li, C.W., Yamanis, J., Whalen, P.J., Gasdaska, C.J., Ballard, C.P., 1992. Properties of in situ reinforced silicon nitride ceramics. In: Hodge, E., Ishizaki, K. (Eds.), *Pressure Effects on Materials Processing and Design*. Materials Research Society Symposium Proceedings 251. Pittsburgh, USA: MRS, pp. 103–111.
- Loeb, A.L., 1954. Thermal conductivity: VIII. A theory of thermal conductivity of porous materials. *Journal of the American Ceramic Society* 37, 96–99.
- Mitomo, M., Uenosono, S., 1991. Gas pressure sintering of β -silicon nitride. *Journal of Materials Science* 26, 3940–3944.
- Naba, T., 2012. Trends in silicon nitride substrate with high thermal conductivity for power module. *Bulletin of the Ceramic Society of Japan* 47, 38–41.
- Nakayama, A., Nambu, S., Inagaki, M., Miyauchi, M., Itoh, N., 1996. Dielectric dispersion of polycrystalline aluminum nitride at microwave frequencies. *Journal of the American Ceramic Society* 79, 1453–1456.
- Negita, K., 1985a. Ionic radii and electronegativities of effective sintering aids for Si_3N_4 ceramics. *Journal of Materials Science Letters* 4, 417–418.
- Negita, K., 1985b. Effective sintering aids for Si_3N_4 ceramics. *Journal of Materials Science Letters* 4, 755–758.
- Ohashi, M., Nakamura, K., Hirao, K., Kanzaki, S., Hampshire, S., 1995. Formation and properties of Ln-Si-O-N glasses (Ln = lanthanides or Y). *Journal of the American Ceramic Society* 78, 71–76.
- Okamoto, M., Arakawa, H., Ohashi, M., Ogihara, S., 1989. Effect of microstructure on thermal conductivity of AlN ceramics. *Journal of the Ceramic Society of Japan* 97, 1478–1485.
- Priest, H.F., Burns, F.C., Priest, G.L., Skaar, E.C., 1973. Oxygen content of alpha silicon nitride. *Journal of the American Ceramic Society* 56, 395. [395].
- Prochazka, S., 1974. Sintering of SiC ceramics. In: Burke, J.J., Gorum, A.E., Katz, R.N. (Eds.), *Ceramics for High-Performance Applications*. Chestnut Hill, MA, USA: Brook Hill Publ. Co, pp. 239–252.
- Rafaniello, W., Cho, K., Virkar, A.V., 1981. Fabrication and characterization of SiC-AlN alloys. *Journal of Materials Science* 16, 3479–3488.
- Ramesh, R., Nestor, E., Pomeroy, M.J., Hampshire, S., 1997. Formation of Ln-Si-Al-O-N glasses and their properties. *Journal of the European Ceramic Society* 17, 1933–1939.
- Russell, H.W., 1935. Principles of heat flow in porous insulators. *Journal of the American Ceramic Society* 18, 1–5.
- Sakai, T., Aikawa, T., 1988. Phase transformation and thermal conductivity of hot-pressed silicon carbide containing alumina and carbon. *Journal of the American Ceramic Society* 71, C7–C9.
- Sakai, T., Kuriyama, M., Inukai, T., Kizima, T., 1978. Effect of the oxygen impurity on the sintering and the thermal conductivity of AlN polycrystal. *Journal of the Ceramic Society of Japan* 86, 174–179.
- Shelby, J.E., Kohli, J.T., 1990. Rare-earth aluminosilicate glasses. *Journal of the American Ceramic Society* 73, 39–42.
- Shinozaki, K., Tsuge, A., 1986. Characterization techniques of ceramics II.5 Development of high thermal conductivity aluminum nitride (AlN). *Ceramics Japan* 21, 1130–1135.
- Slack, G.A., 1964. Thermal conductivity of pure and impure silicon, silicon carbide, and diamond. *Journal of Applied Physics* 35, 3460–3466.
- Slack, G.A., 1973. Nonmetallic crystals with high thermal conductivity. *Journal of Physics Chemistry of Solids* 34, 321–335.
- Slack, G.A., 1987. The intrinsic thermal conductivity of AlN. *Journal of Physics Chemistry of Solids* 48, 641–647.
- Takeda, Y., 1988. Development of high-thermal-conductive SiC ceramics. *American Ceramic Society Bulletin* 67, 1961–1963.
- Takeda, Y., Nakamura, K., Maeda, K., Ura, M., 1986. Effects of elemental additives on densification, microstructure, strength, and thermal conductivity of silicon carbide ceramics. *Advanced Ceramic Materials* 1, 162–165.
- Takeda, Y., Usami, K., Nakamura, K., *et al.*, 1983. Grain-boundary structure of highly resistive sic ceramics with high thermal conductivity. In: Yan, M.F., Heuer, A.H. (Eds.), *Advances in Ceramics, Vol. 7 – Additives and Interfaces in Electronic Ceramics*. Columbus, OH, USA: American Ceramic Society, pp. 253–259.
- Tanabe, S., Hirao, K., Soga, N., 1992. Elastic properties and molar volume of rare-earth aluminosilicate glasses. *Journal of the American Ceramic Society* 75, 503–506.
- Terwilliger, G.R., Lange, F.F., 1974. Hot-pressing behavior of Si_3N_4 . *Journal of the American Ceramic Society* 57, 25–29.
- Thomas, A., Müller, G., 1991. Determination of the concentration of oxygen dissolved in the AlN lattice by hot gas extraction from AlN ceramics. *Journal of the European Ceramic Society* 8, 11–19.
- Touloukian, Y.S., Powell, R.W., Ho, C.Y., Klemens, P.G., 1970. *Thermophysical Properties of Matter Volume 2: Thermal Conductivity: Nonmetallic Solids*. New York-Washington: IFI/Plenum.
- Tsuge, A., Inoue, H., Nishida, K., 1989. Grain-boundary phase crystallization of silicon nitride with material loss during heat treatment. *Journal of the American Ceramic Society* 72, 2014–2016.
- Tsukuma, K., Shimada, M., Koizumi, M., 1981. Thermal conductivity and microhardness of Si_3N_4 with and without additives. *American Ceramic Society Bulletin* 60, 910–912.
- Ueno, F., Horiguchi, A., 1989. *EuroCeramics. 1*. Amsterdam: Elsevier, pp. 383–387.
- Urakami, R., Sato, Y., Ogushi, M., *et al.*, 2017. Phase transformation and interface segregation behavior in Si_3N_4 ceramics sintered with $\text{La}_2\text{O}_3\text{-Lu}_2\text{O}_3$ mixed additive. *Journal of the American Ceramic Society* 100, 1231–1240.
- Virkar, A.V., Jackson, T.B., Cutler, R.A., 1989. Thermodynamic and kinetic effects of oxygen removal on the thermal conductivity of aluminum nitride. *Journal of the American Ceramic Society* 72, 2031–2042.
- Vodakov, Y.A., Mokhov, E.N., 1973. Diffusion and solubility of impurities in silicon carbide. In: Marshall, R.C., Faust, Jr., J.W., Ryan, C.E. (Eds.), *Silicon Carbide-1973, Proceedings of the 3rd International SiC Conference*. Columbia, SC, USA: University of South Carolina Press, pp. 508–519.
- Wang, W., Yao, D., Chen, H., *et al.*, 2020a. $\text{ZrSi}_2\text{-MgO}$ as novel additives for high thermal conductivity of $\beta\text{-Si}_3\text{N}_4$ ceramics. *Journal of the American Ceramic Society* 103, 2090–2100.
- Wang, W., Yao, D., Liang, H., *et al.*, 2020b. Improved thermal conductivity of $\beta\text{-Si}_3\text{N}_4$ ceramics by lowering $\text{SiO}_2/\text{Y}_2\text{O}_3$ ratio using YH_2 as sintering additive. *Journal of the American Ceramic Society* 103, 5567–5572.
- Wang, W., Yao, D., Liang, H., *et al.*, 2020c. Effect of the binary nonoxide additives on the densification behavior and thermal conductivity of Si_3N_4 ceramics. *Journal of the American Ceramic Society* 103, 5891–5899.
- Watari, K., 2001. High thermal conductivity non-oxide ceramics. *Journal of the Ceramic Society of Japan* 109, S7–S16.
- Watari, K., Hirao, K., Brito, M.E., Toriyama, M., Kanzaki, S., 1999. Processing of high thermal conductivity Si_3N_4 . *Journal of Materials Research* 14, 1538–1541.
- Watari, K., Seki, Y., Ishizaki, K., 1989. Temperature dependence of thermal coefficients for HIPped silicon nitride. *Journal of the Ceramic Society of Japan* 97, 174–181.
- Wiener, O., 1904. Lamellare Doppelbrechung. *Physikalische Zeitschrift* 5, 332–338.
- Yagi, T., Shinozaki, K., Mizutani, N., Kato, M., Sawada, Y., 1989. Migration of grain boundary phases in AlN ceramics by heating in reduced atmosphere. *Journal of the Ceramic Society of Japan* 97, 1372–1378.
- Yamada, T., 1993. Preparation and evaluation of sinterable silicon nitride powder by imide decomposition method. *American Ceramic Society Bulletin* 72, 99–106.
- Yamagiwa, M., 2010. Packaging technologies of power module for hybrid electric vehicles and electric vehicles (recent developments and future issues). *Bulletin of the Ceramic Society of Japan* 45, 432–437.
- Yasutomi, Y., Miyata, M., Sawai, Y., Kondo, J., 1995. Effect of BeO on the sintering and properties of boron-doped high-purity SiC ceramics. *Journal of the Ceramic Society of Japan* 103, 374–380.

- Zhou, Y., Hyuga, H., Kusano, D., Matsunaga, C., Hirao, K., 2019. Effects of yttria and magnesia on densification and thermal conductivity of sintered reaction-bonded silicon nitrides. *Journal of the American Ceramic Society* 102, 1579–1588.
- Zhou, Y., Hyuga, H., Kusano, D., Yoshizawa, Y., Hirao, K., 2011. A tough silicon nitride ceramic with high thermal conductivity. *Advanced Materials* 23, 4563–4567.
- Zhou, Y., Hyuga, H., Kusano, D., *et al.*, 2015. Development of high-thermal-conductivity silicon nitride ceramics. *Journal of Asian Ceramic Societies* 3, 221–229.
- Zhou, Y., Zhu, X.-W., Hirao, K., Lences, Z., 2008. Sintered reaction-bonded silicon nitride ceramic with high thermal conductivity and high strength. *International Journal of Applied Ceramic Technology* 5, 119–126.
- Zhu, X.-W., Zhou, Y., Hirao, K., 2004. Effect of sintering additive composition on the processing and thermal conductivity of sintered reaction-bonded silicon nitride. *Journal of the American Ceramic Society* 87, 1398–1400.
- Zhu, X.-W., Zhou, Y., Hirao, K., Lences, Z., 2006. Processing and thermal conductivity of sintered reaction-bonded silicon nitride: (I) Effects of Si powder characteristics. *Journal of the American Ceramic Society* 89, 3331–3339.
- Zhu, X.-W., Zhou, Y., Hirao, K., Lences, Z., 2007. Processing and thermal conductivity of sintered reaction-bonded silicon nitride: (II) Effects of magnesium compound and yttria additives. *Journal of the American Ceramic Society* 90, 1684–1692.
- Ziegler, G., Hasselman, D.P.H., 1981. Effect of phase composition and microstructure on the thermal diffusivity of silicon nitride. *Journal of Materials Science* 16, 495–503.

MAX Phases, Structure, Processing, and Properties

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Historical Overview

The MAX or $M_{n+1}AX_n$ phases are a family of compounds within the class of complex or double carbides or nitrides where “M” refers to an early transition metal, “A” to an A-group element, “X” can be C and/or N and “n” is an integer (commonly 1, 2 or 3) as described in Barsoum (2013). Based on the integer n, the MAX phases can be subcategorized into 211, 312 and 413 structures, respectively. New compounds and possible M and A elements are still being discovered and, hence, this family is expanding every month. At the moment, over 155 ternary MAX phase compounds have been experimentally reported, as recently summarized by Sokol *et al.* (2019). This number increases considerably when solid solutions are taken into account.

The name “MAX phase” was introduced around the year 2000 (Barsoum, 2000; Barsoum and El-Raghy, 2001). However, the history of these phases goes back to the early 1950s. To the best of our knowledge, in the first report on these phases, Bloom and Grant (1950) observed the “Cr₂AlC” phase in a Cr-Al-C mixture in an attempt to synthesize the binary CrC. About 10 years later, Kudielka and Rohde (1960) described the crystal structure of a ternary carbide Ti₂SC, observed in steel, reporting that Ti could be replaced by Zr. In the beginning of the 1960s, a systematic study by Jeitschko, Nowotny and Benesovsky revealed that Cr₂AlC and Ti₂SC along with about 30 other ternary transition metal (T) carbides form a set of isomorphous compounds with the general structure “T₂MX,” which they grouped as H(agg)-phases (Nowotny *et al.*, 1964; Jeitschko *et al.*, 1963, 1964a,b,c). Apart from the H-phases, the group of Nowotny also identified two related compounds, i.e., Ti₃SiC₂ (Jeitschko and Nowotny, 1967) and Ti₃GeC₂ (Wolfsgruber *et al.*, 1967). Except for the crystallographic description of these phases, little was known about their properties. Barsoum and El-Raghy (1996) reported on the “remarkable ceramic: Ti₃SiC₂” and demonstrated the attractive properties of this laminated ternary carbide. With the discovery of Ti₄AlN₃ (Barsoum *et al.*, 2004), they concluded that all these phases could be grouped under the formula unit “M_{n+1}AX_n.” Since 2000, “MAX phase” is the common name used to refer to this family of carbides, although some exceptions exist, such as the TAX (Zhou *et al.*, 2013) or T₂MX (Hug, 2006) phases.

Not all combinations of M, A and X elements indicated in Fig. 1 are possible. The elements with a hatched background, i.e., Fe, Cu, Zn, Y, Sb, W and all lanthanides, are actually only reported in solid solutions. On the other hand, some elemental combinations can form several MAX phase orders, e.g., Ti₂GeC, Ti₃GeC₂ and Ti₄GeC₃ are known to exist in the Ti-Ge-C system (Högberg *et al.*, 2005a). From this family of MAX phases, a few ternary combinations have been investigated more extensively, i.e., Ti₃SiC₂, Ti₂AlC, Ti₃AlC₂ and Cr₂AlC. The reason, therefore, is the possibility to synthesize these carbide materials in a nearly phase-pure bulk form using a relative simple process. A first chemically out-of-plane ordered (o-MAX) quaternary 312 (M',M'')₃AlC₂ MAX phase, i.e., (Cr_{2/3},Ti_{1/3})₃AlC₂, was reported in Liu *et al.* (2014). In-plane ordering (i-MAX) was observed in (Mo_{2/3},Sc_{1/3})₂AlC by Tao *et al.* (2017); by Dahlqvist *et al.* (2017); and by Dahlqvist *et al.* (2018). Besides alloying on the M site, alloying on the A (Li *et al.*, 2020) and X (Manoun and Saxena, 2007; Cabioch *et al.*, 2012) sites is also possible. Very recently, the first high entropy MAX (HE-MAX) phase, (Ti_{0.35}Zr_{0.12}Nb_{0.21}Hf_{0.12}Al_{0.19})₂Al_{0.81}C, was reported by Bao *et al.* (2020).

The chemical etching and exfoliating or selective de-intercalation of the MAX phases results in MXenes, which have attracted a tremendous interest since the first report of Naguib *et al.* (2011). Anasori and Gogotsi (2019) contains a detailed overview of the progress in MXene synthesis, characterization and applications.

Structure of $M_{n+1}AX_n$ Phases

Ternary MAX Phases

The $M_{n+1}AX_n$ phases are known to be “nanolaminated solids” and exactly this layered nature provides them with a set of salient properties. The crystal structure of the $M_{n+1}AX_n$ phases is characterized by a hexagonal, anisotropic unit cell of space group 194 (P6₃/mmc) consisting of two formula units. For the three common $M_{n+1}AX_n$ phase types or orders, i.e., 211, 312 and 413, these unit cells are shown in Fig. 2(a)–(c), revealing the origin of the layered structure: n [M₆X]-octahedra are interleaved with an atomic layer of A, where the M-atoms form a trigonal prismatic unit with the A-element in the center. Splitting the lattice this way, the MAX structure is composed of two building blocks: (1) the M₆X-octahedra that are structured in the rock-salt (NaCl-type) configuration and (2) the trigonal prismatic M₆A-units that have an hexagonal closed packing structure (Etzkorn *et al.*, 2007a; Etzkorn *et al.*, 2009; Hug *et al.*, 2005; Hug, 2006). For example, the unit cell of the 211 type is composed of two of each of these building blocks.

In order to completely determine the structure, three lattice parameters have to be refined: the dimensions of the unit cell, *a* and *c*, and the relative height *z_M* of the M-atom with respect to the central layer of carbon, as shown in Figs. 2 and 3. The canonical position of the latter is at 1/12 (0.0833), which corresponds to an equal spacing of the M- and A-planes. The 312 type comprises

Mn+1AnX																													
1A																8A													
1 H 1.00794																	2 He 4.002602												
2A																													
3 Li 6.941	4 Be 9.012182																												
11 Na 22.989769		12 Mg 24.3050																											
19 K 39.0983		20 Ca 40.078		3B	4B	5B	6B	7B	8B		1B	2B	3A	4A	5A	6A	7A	10											
37 Rb 85.4678		38 Sr 87.62		21 Sc 44.955912	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938045	26 Fe 55.845	27 Co 58.933195	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.38	5 B 10.811	6 C 12.0107	7 N 14.0067	8 O 15.9994	9 F 18.9984032	18 Ar 39.948										
55 Cs 132.9054519		56 Ba 137.327		Lanthanides	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.96	43 Tc [98]	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 107.8682	13 Al 26.9815386	14 Si 28.0855	15 P 30.973762	16 S 32.065	17 Cl 35.453	36 Kr 83.798										
87 Fr 223		88 Ra [226]		Actinides	57-71	72 Hf 178.43	73 Ta 180.94718	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.084	79 Au 196.966569	31 Ga 69.723	32 Ge 72.64	33 As 74.92160	34 Se 78.96	35 Br 79.904	54 Xe 131.293										
118 Uuo [294]		117 Uus [294]		116 Uuh [294]	115 Uup [290]	114 Uuq [289]	113 Uut [286]	112 Uub [285]	111 Rg [272]	110 Ds [271]	109 Mt [268]	108 Hs [270]	107 Bh [272]	106 Sg [271]	105 Db [269]	104 Rf [267]	89-103	86 Rn [222]	53 I 126.90447										
Lanthanides																													
57 La 138.90547		58 Ce 140.116		59 Pr 140.90768		60 Nd 144.242		61 Pm [145]		62 Sm 150.36		63 Eu 151.964		64 Gd 157.25		65 Tb 158.92535		66 Dy 162.500		67 Ho 164.93032		68 Er 167.259		69 Tm 168.93421		70 Yb 173.054		71 Lu 174.967	
Actinides																													
89 Ac [227]		90 Th 232.03806		91 Pa 231.03688		92 U 238.02891		93 Np [237]		94 Pu [244]		95 Am [243]		96 Cm [247]		97 Bk [247]		98 Cf [251]		99 Es [252]		100 Fm [257]		101 Md [258]		102 No [259]		103 Lr [262]	

Fig. 1 The different M, A and X elements that have been reported in ternary MAX phases. The hatched elements are only reported in quaternary systems.

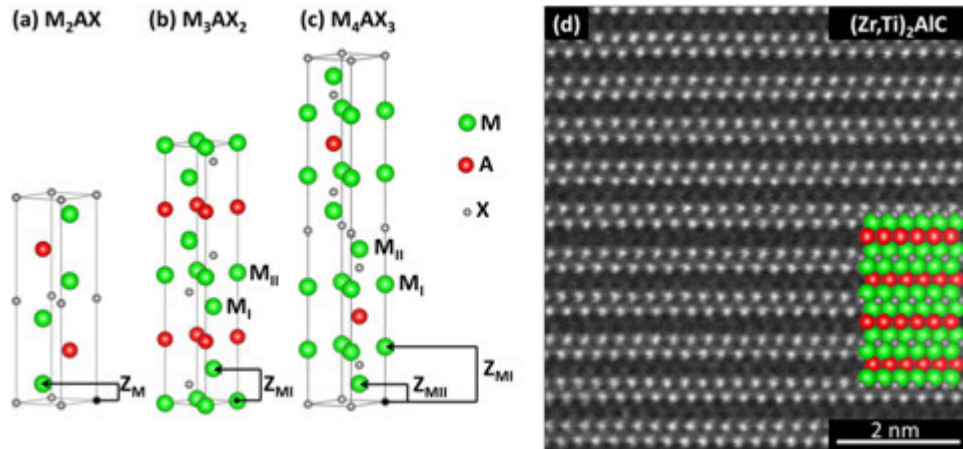


Fig. 2 Unit cells of (a) M_2AX , (b) M_3AX_2 and (c) M_4AX_3 and (d) a high-resolution STEM image along the $[1\bar{2}10]$ -direction of $(Zr,Ti)_2AlC$.

two M_6X -units that are present between each A-layer, resulting in two non-equivalent M-sites: the M_I -site close to the A-layer and the central M_{II} -site, which is only bonded to M and X. For this type, there are four free variables: a , c , z_X and z_{M_I} . In a similar fashion, the 413 type has five free variables, due to two non-equivalent M- and X-sites (Etzkorn *et al.*, 2007a). Table 1 gives an overview of the atomic positions for the three most common MAX phase orders: 211, 312 (α -312) and 413 (α -413). Of the latter two types, polymorphs exist that involve a shearing of A-layers (β -312 and γ -413) (Wang *et al.*, 2004; He *et al.*, 2011) or restructuring of the MX-block (β -413) (Eklund *et al.*, 2007).

The laminated structure can be visualized clearly using high-resolution transmission scanning electron microscopy (HRSTEM) when looking along the $[1\bar{2}10]$ direction, as illustrated for $(Zr,Ti)_2AlC$ in Fig. 2(d). The M-atoms form a zigzag pattern where the A-layer acts as mirror plane, similar as observed in $(MC)_nAl_3C_2$ and $(MC)_n[Al(Si)]_4C_3$ phases. However, a fundamental difference with the latter is the absence of bonds between A and X. The X atoms are only connected to M-atoms where the M–X bonding is significantly stronger than the M–A bonding (Medvedeva *et al.*, 1998; Zhang and Wang, 2007). The MAX phase bonds are achieved

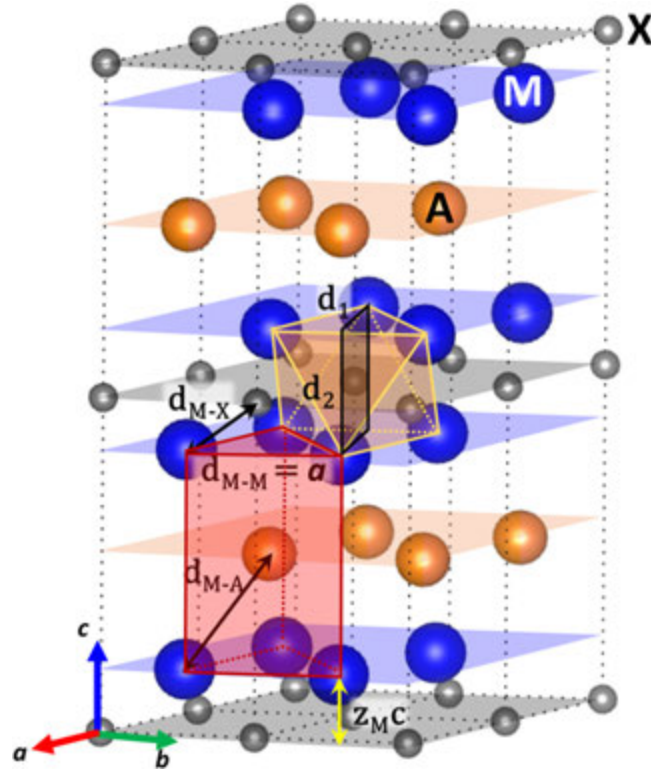


Fig. 3 M_2AX crystallographic parameters with an M_6X octahedron indicated in orange and an M_6A trigonal prism indicated in red.

Table 1 Lattice description with idealized coordinates for M_2AX , α - M_3AX_2 and α - M_4AX_3

M_2AX					M_3AX_2					M_4AX_3				
	Wyckoff	x	y	z		Wyckoff	x	y	z		Wyckoff	x	y	z
A	2c	1/3	2/3	3/12	2b	0	0	4/16	2c	1/3	2/3	5/20		
M_I	4f	2/3	1/3	1/12	4f	1/3	2/3	2/16	4e	0	0	3/20		
M_{II}					2a	0	0	0	4f	1/3	2/3	1/20		
X_I	2a	0	0	0	4f	2/3	1/3	1/16	4f	2/3	1/3	2/20		
X_{II}									2a	0	0	0		

by hybridization of the M-atom d-states with the X- and A-atom p-states (Hug, 2006; Magnuson *et al.*, 2007), where the M–X bond in the MAX phases shows similar characteristics to the M–X bonds in the corresponding binary carbides. When considering the two building blocks of the 211 type, some steric effect is observed after Kanoun *et al.* (2009). Both the octahedron and the trigonal prism (see Fig. 3) are distorted due to the fact that the M-atom is commonly not on the canonical position and the c/a -ratio deviates from the ideal packing ($c/a = 2\sqrt{6}$) (Hug *et al.*, 2005; Hug, 2006). The distortion of the cubic octahedron, o_d , can be expressed as:

$$o_d = \frac{d_1}{d_2} = \frac{\sqrt{3}}{2\sqrt{4z_M^2\left(\frac{c}{a}\right)^2 + \frac{1}{12}}} \quad (1)$$

And the distortion parameter of the trigonal prism, p_d , is given by:

$$p_d = \frac{d_{M-M}}{d_{M-A}} = \frac{1}{\sqrt{\frac{1}{3} + \left(\frac{1}{4} - z_M\right)^2\left(\frac{c}{a}\right)^2}} \quad (2)$$

For the ideal case, the distortion parameters are equal to 1. In addition, they are known to vary with temperature as Jaouen *et al.* (2013) reported for Cr_2AlC , and are also significantly affected by the chemical composition according to Cabioch *et al.* (2013). However, no direct connection between o_d , p_d and the intrinsic stability of a MAX phase compound has been established, but a correlation between the atomic radii of the M and A elements towards stable MAX phases was proposed by Lapauw *et al.* (2018b). Small M-atoms combine better with small A-atoms and large M-atoms with large A-atoms. This “match” in atomic radii between

M and A can be used as a practical guideline for the synthesis of solid solution MAX phases. The concept of double solid solution $(M', M'')_2(A', A'')C$ was found advantageous in terms of MAX phase synthesis and purity (see Section “Solid Solutions and Ordered MAX Phases”).

Apart from the 3 common MAX phase types, some other rather exceptional structures have been reported. Most of them are grouped by [Hu et al. \(2013\)](#). A first set comprises $M_{n+1}AX_n$ -like structures with $n > 3$, e.g., Ta_6AlC_5 by [Lin et al. \(2006\)](#) and Ti_7SnC_6 by [Zhang et al. \(2009\)](#). These structures were detected during HRTEM investigations in the Ta-Al-C and Ti-Sn-C systems, respectively. However, no significant amount of “phase-pure” material has been reported yet and, therefore, they are not considered as distinct phases ([Eklund et al., 2010](#)). Another set consists of the “hybrid” orders $M_5A_2C_3$ and $M_7A_2C_5$ that are a combination of a 312 atomic stacking sequence with a 211 and 413 order, respectively. These structures have been reported by [Palmquist et al. \(2004\)](#), [Högborg et al. \(2005a\)](#), [Zhou et al. \(2008\)](#), [Scabarozi et al. \(2011\)](#), [Lane et al. \(2012\)](#), [Wang et al. \(2012\)](#) for several systems, e.g., $Ti_5A_2C_3$ with $A = Si, Ge$ and Al . The unit cell consists of three formula units and has been observed over significant distances resulting in clear associated peaks in the XRD pattern.

Another important point to address is the X-element content in the MAX phases. Most of the phases are reported as (near-) stoichiometric compounds, although some reports on sub-stoichiometric X are found in literature, especially 413 phases. The experimentally observed deficiency of N in $Ti_4AlN_{3-\delta}$ is reported to stabilize the structure by [Barsoum et al. \(2000\)](#) and by [Music et al. \(2005\)](#). Also for V_4AlC_{3-x} ([Etzkorn et al., 2007b](#)) and Nb_4AlC_{3-x} ([Zhang et al., 2015b](#)), C-vacancies have been reported, mainly on the central, C_{II} -site (Wyckoff 2a). For the latter, a transition from an ordered (o - $Nb_4AlC_3 - Nb_{12}Al_3C_8$) to disordered Nb_4AlC_{3-x} around $1400^\circ C$ was observed. This is not surprising since the main unit in the 413 types is the M_6X octahedron, identical with the NaCl-type binary carbides. This observation is also true for the corresponding binary carbides, which can be significantly sub-stoichiometric.

Solid Solutions and Ordered MAX Phases

The exploration of quaternary (or higher) systems that crystallize in the MAX structure already started in the 1960s with [Reiffenstein et al. \(1966\)](#), looking merely at the interchangeability of the atoms on the M-site. Nevertheless, the investigation of quaternary and more complex MAX phase based structures is a very active research topic today, in particular due to the fact that they can serve as base material for the synthesis of unique 2D-carbide materials, MXenes, as demonstrated by [Tao et al. \(2017\)](#).

Single-site and double-site solid solutions

[Naguib et al. \(2014\)](#) provide a list of reported MAX phase solid solutions up to 2014, including 34 systems with substitutional solid solutions on the M, A and X-site, whereas the more recent overview by [Sokol et al. \(2019\)](#) contains already 29 $(M', M'')_{n+1}AX_n$ and 15 $M_{n+1}(A', A'')X_n$ single-site solution MAX phases. One of the reasons of interest is the possibility of synthesizing compounds for which one or both of the end-members do not exist, i.e., the elements with the hatched background in [Fig. 1](#). This can even lead to the incorporation of unconventional M- or A-elements such as W ([Yang et al., 2014](#); [Lai et al., 2017](#)) or Fe ([Lin et al., 2016](#)).

The addition of a fourth element can also be beneficial to improve the phase purity of the material, such as the addition of Al to Ti_3SiC_2 in order to avoid the formation of TiC ([Zhu et al., 2004](#)). The addition of a fifth element, targeting the formation of $(M', M'')_{n+1}(A', A'')X_n$ double solid solutions was successfully explored to synthesize near-phase pure MAX phase ceramics. As an example, although Zr_2AlC , Zr_3AlC_2 and Hf_2AlC/Hf_3AlC_2 can be synthesized, as respectively reported by [Lapauw et al. \(2016a,b,c\)](#), it is always present in combination with ZrC/HfC and Zr-Al/Hf-Al intermetallics. Judicious alloying on both M and A sites, however, allowed to produce near-phase pure ($> 99\%$) $(Zr, Nb)_2(Al, Sn)C$ ([Lapauw et al., 2018b](#)) and $(Zr, Ti)_2(Al, Sn)C$ ([Tunca et al., 2019](#)) ceramics. In a similar approach ([Griseri et al., 2020](#)), the $(Ta_{1-x}Hf_x)_4AlC_3$ and $(Ta_{1-x}Nb_x)_4AlC_3$ MAX phase content could be substantially increased by the addition of Sn to form $(Ta_{1-x}Hf_x)_4(Al_{0.5}Sn_{0.5})C_3$ and $(Ta_{1-x}Nb_x)_4(Al_{0.5}Sn_{0.5})C_3$ double solid solutions. Moreover, alloying ternary MAX phases allows tuning of some properties, like the coefficient of thermal expansion (CTE) of $Cr_2(Al, Ge)C$ ([Cabioch et al., 2013](#)), improving the high temperature stability of $(Ti, Zr)_3SiC_2$ ([Wan et al., 2010](#)), increasing the hardness of $(Ti, V)_2AlC$ ([Meng et al., 2005](#)), increasing the toughness, high temperature stiffness and thermal stability of $(Nb, Zr)_4AlC_3$ ([Lapauw et al., 2016d](#)) or altering the magnetic properties of $(Cr, Mn)_2AlC$ ([Mockute et al., 2014](#)) and $V_2(Sn, A)C$ ($A = Fe, Co, Ni, Mn$) ([Li et al., 2020](#)).

In terms of crystal structure, alloying directly affects the lattice parameters a and c . They obey Vegard's law, as proposed by [Vegard \(1921\)](#), meaning that the variation of a and c is linearly dependent on the amount of dopant. However, the effects on a and c can be different, changing the anisotropy of the unit cell and the distortion factors α_d and ρ_d ([Cabioch et al., 2013](#)). The evolution of the other free variable, z_M , in the 211 type, depends on which element is partially replaced. In the case of $(Ti, Nb)_2AlC$, an M-site solid solution, [Hug et al. \(2005\)](#) showed that each M-element would have a different z_M . For $Cr_2(Al, Ge)C$, an A-site solid solution, [Cabioch et al. \(2013\)](#) showed that z_M increased linearly with increasing Al-content. For all the structures listed by [Naguib et al. \(2014\)](#), a statistical distribution of the host and solute atoms was assumed.

o-MAX phases

[Liu et al. \(2014\)](#) demonstrated the synthesis of Cr_2TiAlC_2 , showing a special type of ordering. The Cr-atoms preferentially occupy M_I -sites adjacent to the A-layers, while the Ti-atoms are positioned on the M_{II} -sites in the middle of the MX-block. [Caspi et al. \(2015\)](#)

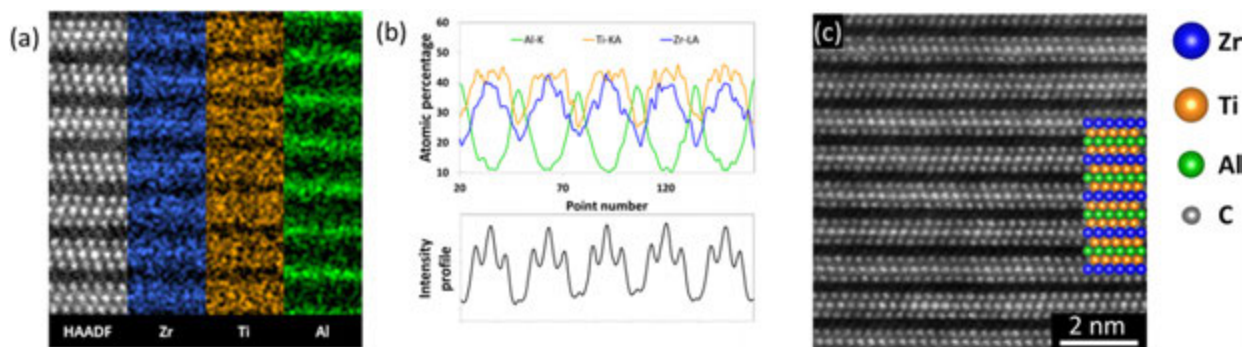


Fig. 4 (a) EDS-mapping, (b) EDS line scan intensity along the c-direction and (c) HRSTEM image of the solid solution o-MAX phase $(\text{Zr}_{1/3}\text{Ti}_{2/3})_3\text{AlC}_2$.

described the same ordering in the M-atom positions for Cr_2VAlC_2 and $\text{Cr}_2\text{V}_2\text{AlC}_3$. These structures are referred to as o-MAX phases; out-of-plane ordered quaternary $(\text{M}', \text{M}'')_3\text{AX}_2$ or $(\text{M}', \text{M}'')_4\text{AX}_3$ MAX phases with a unique ordering of the M layers, such that two M' layers sandwich either one or two layers of M'' within each M–X block, where M' and M'' are early transition metals. Similarly, $(\text{Mo}_2\text{Ti})\text{AlC}$, $(\text{Mo}, \text{Ti})_2\text{AlC}_3$, $(\text{Mo}_2\text{Sc})\text{AlC}_2$ and $(\text{Ti}_2\text{Zr})\text{AlC}_2$ have been subsequently reported as o-MAX phases by [Anasori et al. \(2014\)](#), [Anasori et al. \(2015a\)](#), [Meshkian et al. \(2017\)](#) and [Tunca et al. \(2019\)](#), respectively. Interestingly, all identified o-MAX phases up to now contain Al as the A-element and C as the X-element. Since no high phase purity bulk o-MAX ceramics have been reported yet, their intrinsic material properties are still unknown.

The fully ordered atomic stacking sequence of $(\text{Zr}_{1/3}\text{Ti}_{2/3})_3\text{AlC}_2$ is shown in [Fig. 4](#). Two main factors responsible for ordering were already addressed by [Hume-Rothery \(1950\)](#), i.e., a clear difference in electronegativity (χ) and in covalent radii. For both factors, the ordering is consistent in all ordered MAX phases so far reported. It appears that the M-element with the smallest atomic radius ($\text{Cr} < \text{V} < \text{Mo} < \text{Ti} < \text{Zr} < \text{Sc}$) and the highest χ ($\text{Mo} > \text{Cr} > \text{V} > \text{Ti} > \text{Sc} > \text{Zr}$) is positioned in the outer-layers of the M_I – M_II – M_I “sandwich” (312 type) or M_I – M_II – M_II – M_I “sandwich” (413 type) next to the A-element layer, whereas the larger and less electronegative M-element is positioned inside the “sandwich” structure on the M_II -sites ([Tunca et al., 2017](#)). For most of the observed ordered systems, one or even both of the end members are not stable and they should be differentiated from the random solid solution. A unique exception is $(\text{Zr}_{1/3}\text{Ti}_{2/3})_3\text{AlC}_2$, which can claim the double label of solid solution and ordered phase ([Tunca et al., 2017](#)).

Different types of ordering have been reported by [Tao et al. \(2016\)](#). A first type was observed during the thin film deposition of $(\text{Mn}, \text{V})_3\text{GaC}_2$, where the different M-elements tend to cluster in separate M_3C_2 -blocks forming an alternated pattern of V-rich M_3C_2 -layers with Mn-rich M_3C_2 -layers interleaved by a plane of Ga-atoms.

i-MAX phases

The discovery of $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ revealed a new type of ordering, the so-called i-MAX phase. This MAX phase compound has a 211 stoichiometry and exhibits an in-plane order of the M-elements. In “conventional” 211-type MAX structures, there is only one M-site which is statistically occupied by the different M-elements in $(\text{M}', \text{M}'')_2\text{AX}$ solid solutions. The description of the i-MAX crystal structure consists of a more complex unit cell, extended in-plane along a and b , with non-equivalent M-sites where the monoclinic (space group 15 – $\text{C}2/c$) and orthorhombic (space group 63 – Cmcm) descriptions show equal stability. Next to $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$, $(\text{V}_{2/3}\text{Zr}_{1/3})_2\text{AlC}$, $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlC}$ and $(\text{Cr}_{2/3}\text{Zr}_{1/3})_2\text{AlC}$ have been identified as i-MAX phases by [Dahlqvist et al. \(2017\)](#) and [Chen et al. \(2018\)](#). The structure of $(\text{Cr}_{2/3}\text{Zr}_{1/3})_2\text{AlC}$ is displayed in [Fig. 5](#). HRSTEM and selected area electron diffraction (SAED) reveal the atomic stacking sequence along the $[110]$ and $[100]$ zone axes of the monoclinic structure. This structure was discovered by a close interplay of experimental synthesis and characterization followed by a computational assessment of the stability using density functional theory (DFT).

Due to the possibility of making the attractive MXene 2D-derivative, the theoretical possibility to form ordered MAX phases has been predicted for 24 structures by [Anasori et al. \(2015b\)](#). In these calculations, two important parameters have to be considered: the formation enthalpy (ΔH_cp) of these phases should be lower than for all other competing phases, underlying the importance of including all possible phases, even hypothetical phases ([Dahlqvist et al., 2010](#); [Tao et al., 2017](#)). The second parameter is the order-to-disorder transition temperature (T_disorder), which takes into account the configurational entropy ([Dahlqvist and Rosen, 2015](#)). Above T_disorder , the disordered structure is most favorable. In order to experimentally obtain an ordered structure, it is suggested that T_disorder should be higher than the synthesis temperature.

[Sokol et al. \(2019\)](#) provides an overview of about 30 i-MAX phases that have already been discovered, including rare-earth containing phases, which have been reported for the first time by [Tao et al. \(2019\)](#). Interestingly, all identified i-MAX phases have been synthesized with Al or Ga as the A-element, and C as the X-element. Since no high phase purity bulk i-MAX ceramics have been reported yet, their intrinsic material properties are still unknown.

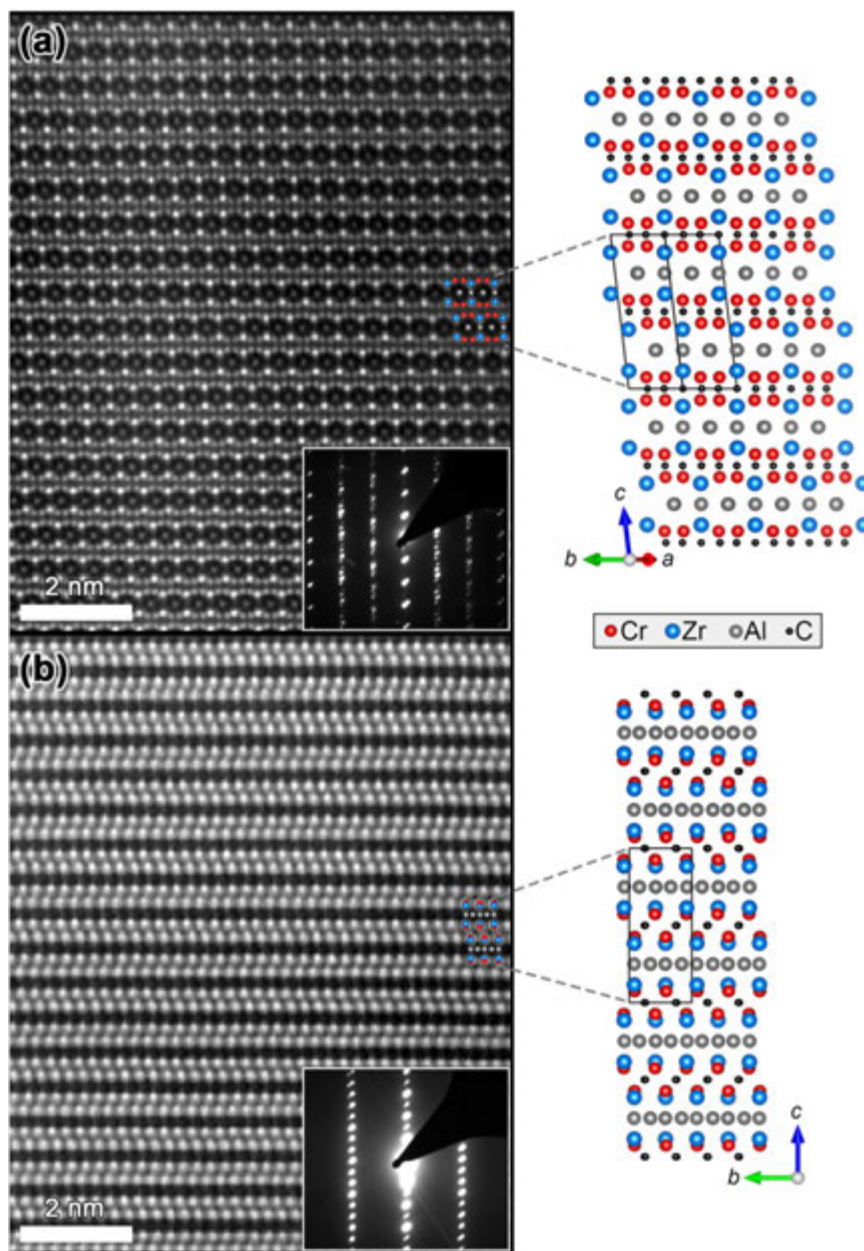


Fig. 5 The atomic stacking sequence of the i-MAX $(\text{Cr}_{2/3}\text{Zr}_{1/3})_2\text{AlC}$ by STEM along the (a) $[110]$ and (b) $[100]$ zone axes with corresponding SAED patterns. Cr, Zr, Al and C atoms are depicted by the red, blue, gray and black spheres, respectively. Reprinted with permission from Chen, L., Dahlgqvist, M., Lapauw, T., *et al.*, 2018. Theoretical prediction and synthesis of $(\text{Cr}_{2/3}\text{Zr}_{1/3})_2\text{AlC}$ i-MAX phase. *Inorganic Chemistry* 57, 6237–6244. Copyright (2018) American Chemical Society.

MAX Phase Synthesis

Synthesis Methods

Regarding the synthesis of MAX phase ceramics, it should be highlighted that there are very few commercial MAX phase powder sources available at present and limited to the Ti_3SiC_2 , Ti_2AlC , Ti_3AlC_2 , V_2AlC and Nb_2AlC compositions, whereas bulk MAX phase ceramics, as far as we know, are not available on the market at present. MAX phase synthesis can be divided into powder, bulk, and thin film synthesis.

MAX phase powders

Amongst the powder production routes are self-propagating high temperature synthesis (SHS) (Yeh and Yang, 2013) used for the Maxthal® 211 and 312 production, microwave synthesis (Hamm *et al.*, 2016) and via molten salts (Tian *et al.*, 2008). MAX phase powders can be obtained by molten salt synthesis from elemental powders. Ti_2AlC , Ti_3AlC_2 , Cr_2AlC and other phases, for example, can be obtained in molten KBr (Dash *et al.*, 2019), Cr_2AlC can be synthesized in NaCl/KCl mixtures (Tian *et al.*, 2008), and Ti_2AlC and Ti_3AlC_2 powder can be produced in molten NaCl and/or KCl (Galvin *et al.*, 2018; Yang *et al.*, 2019). Electrosynthesis of MAX phase powder from an oxide/carbon precursor in molten salt is also possible. Ti_3AlC_2 powder can be made from a $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{C}$ precursor pellet (cathode) at 900°C and 3.1 V in molten CaCl_2 (Li *et al.*, 2018), whereas Cr_2AlC powder can be obtained from a $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{C}$ precursor pellet (cathode) at 700°C and 3 V in molten NaCl- CaCl_2 (Abdelkader, 2016). MAX phase powder can alternatively be obtained by comminution of bulk material processed by reactive synthesis.

MAX phase coatings

From the thin film perspective, mainly three types of deposition techniques have been used: physical vapor deposition (PVD) via elemental dc sputtering (Högborg *et al.*, 2005b), cathodic arc deposition (Rosen *et al.*, 2007) or magnetron sputtering (Walter *et al.*, 2006; Furgeaud *et al.*, 2019) and chemical vapor deposition (CVD) (Pickering *et al.*, 2000), as well as solid-state reaction synthesis between thin films or at a film-bulk interface (Eklund *et al.*, 2017). A comprehensive review on MAX phase thin films is provided by Eklund *et al.*, (2010). Of special interest is the synthesis of new MAX phase coatings by a thermal substitution reaction of a Ti_3SiC_2 coating with noble metals like Au and Ir forming Ti_3AuC_2 , $\text{Ti}_3\text{Au}_2\text{C}_2$ and Ti_3IrC_2 coatings (Fashandi *et al.*, 2017).

Comparing bulk and thin film processing, some clear differences can be identified. Primarily, the synthesis temperature is different. MAX phase formation occurs at significantly lower temperatures in case of thin films, e.g., PVD of Cr_2AlC at 450°C (Eklund *et al.*, 2010), whereas a temperature in the range of 1200–1400°C is reported for bulk synthesis by Wang and Zhou (2010). The difference is caused by the additional energetic flux originating from the atomic bombardment. A second difference is the thermodynamic state of the formed material. For most bulk techniques, a near-equilibrium state is considered. Hence, the produced MAX phases are assumed to be more stable than the competing phases. For some thin film processes, MAX phase compounds marked as “meta-stable,” such as Ti_4SiC_3 (Palmquist *et al.*, 2004), Ti_4GeC_3 (Högborg *et al.*, 2005a) and Ti_3SnC_2 (Högborg *et al.*, 2006), could be deposited. These MAX phases are considered intrinsically stable in terms of the Cauchy-Born criterion, but are difficult to synthesize in bulk where the formation of Ti_4SiC_3 is only observed using a very specific technique (Istomin *et al.*, 2016) or in the case of Ti_3SnC_2 by including some specific additives (Dubois *et al.*, 2007). Similarly, Ingason *et al.* (2013) reported the thin film synthesis of the magnetic MAX phase Mn_2GaC . Despite the interest in magnetic MAX phases, Mn_2GaC has not been synthesized in bulk to date.

MAX phase bulk ceramics

Bulk processing of MAX phase ceramics is predominantly achieved by powder metallurgy and requires an intimate contact between the starting powder constituents. These methods include conventional (CS) or microwave sintering under protective atmosphere (Hamm *et al.*, 2016; Wang *et al.*, 2014), hot isostatic pressing (HIP) (Barsoum and El-Raghy, 1996), hot pressing (HP) (Hu, Li *et al.*, 2007), spark plasma sintering (SPS) (Tian *et al.*, 2007a), single crystal growth (Etzkorn *et al.*, 2009), and mechanical alloying (MA) Li and Zhai (2005). The synthesis protocols of the most common layered carbide and nitride MAX phases were reviewed by Haemers *et al.* (2020). Bulk synthesis techniques can be subdivided in processes that follow a pressureless synthesis route (e.g., CS and SHS), and others that are associated with pressure-assisted sintering techniques (e.g., HIP, HP and SPS). The latter group seems more successful in terms of being able to synthesize the different members of the MAX phase family, especially considering the higher orders. Nb_4AlC_3 has only been reported by HP or SPS synthesis. $\text{M}_{n+1}\text{AX}_n$ phases with a higher n require a higher formation temperature compared to MAX phases with a smaller M_{n+1}X_n layer in the same ternary system. Hence, it is possible to obtain Ti_3AlC_2 , Nb_4AlC_3 and Ta_4AlC_3 by annealing the 211-phase containing materials in the corresponding ternary systems (Eklund *et al.*, 2010). However, at high temperature, MAX phase decomposition occurs as a competing reaction:



The weakest bond in the MAX phases is the M–A bond, which is also the first one to break at elevated temperature, followed by outward diffusion of the A-element. One of the advantages of the pressure-assisted techniques lies in the fact that the material is encapsulated in a die/punch system (HP and SPS) or metal capsule (HIP) that minimizes the loss of the A-element. This claim is supported by Lu and Zhou (2010), where the ternary powder mixture is embedded in Al_4C_3 , which significantly improved the amount of Ti_3AlC_2 formed during pressureless sintering.

As basis for the discussion of the various synthesis routes and the different process parameters, the ternary Ti–Al–C system is selected, since it contains two of the most investigated MAX phases, i.e., Ti_2AlC and Ti_3AlC_2 . The most economical way to produce MAX phases is by self-propagating high temperature synthesis (SHS), as it is time and energy effective, requires limited infrastructure and can be performed on an industrial scale. The formation of MAX phase compounds is exothermal and can be self-sustainable. The powder bed is ignited and a reaction front propagates through the powder bed converting the starting powder into the reaction products. A high MAX phase content can be obtained in this way, but there are often competing phases present, such as TiC (Liu *et al.*, 2007). This method commonly uses pure elemental powders as starting material. Other combinations have been reported, such as a mixture of M-oxides, Al and Al_4C_3 to form $(\text{Ti,V})_2\text{AlC}$ solid solution and Al_2O_3 by aluminothermal

reduction of the M-oxides (Yeh and Yang, 2013). This method is commercially viable, but control of the process and, hence, the final product is limited. Moreover, only a limited number, mainly 211 types, of MAX phases synthesized by SHS have been reported, and an additional densification step is required to produce mechanical components.

Conventional sintering provides better process control and is used for several MAX phase systems. A powder compact composed of the elemental powders is heated under a protective atmosphere or in vacuum and held for a certain amount of time. This method is also cost effective and easily facilitates upscaling. It has been successfully employed for several ternary and quaternary MAX phases, for instance by Liu *et al.* (2007); Naguib *et al.* (2014); Meshkian *et al.* (2017). Pressureless sintering can be preceded by mechanical alloying (MA). Nechiche *et al.* (2017) introduced Cu as an element into the Ti_3AlC_2 structure by MA in combination with pressureless sintering. Additionally, microwaves can be used as an alternative heat source. Ti_2AlN MAX phase grains were observed to grow in a preferred orientation upon microwave sintering, but the mechanism behind this is not fully understood (Liu *et al.*, 2015).

Reactive hot pressing and hot isostatic pressing have been reported numerous times for the Ti-Al-C system and are excellent techniques to synthesize high purity, dense Ti_2AlC and Ti_3AlC_2 on a lab-scale. The important process parameters are the chemistry of the starting powders and their stoichiometric ratio, sintering temperature (commonly in the 1200–1500°C range), dwell time (0.5–16 h), pressure (30–70 MPa) and, optionally, a heat treatment at lower temperature. As starting powder, elemental powders are the most obvious choice, but also binary compounds, such as TiC_x , Al_4C_3 and TiH_2 , are used (Zou *et al.*, 2006, 2007). The latter acts as Ti-source as it is more economical and less pyrophoric compared to fine pure Ti powder (Li *et al.*, 2013b). The hydride dehydrogenates in situ around 600°C. Al_4C_3 is reported as an effective Al and C source in several Ti-Al-C MAX phase synthesis reports. However, due to the hygroscopic nature of this carbide, Al_2O_3 is reported as a parasitic phase in the final product (Tzenov and Barsoum, 2000). The main limitations of HP and HIP are the rather slow processing cycles in combination with a limited amount of material per run which makes these techniques, especially HIP, rather costly. The speed of the process can be increased using SPS (also known as PDS or FAST) due to higher heating and cooling rates and short dwell times of only a few minutes. Moreover, the reported SPS synthesis temperatures are generally 50–200°C lower compared with hot pressing. For instance, Yang *et al.* (2009) reported the synthesis of dense Ti_3AlC_2 by combining mechanical alloying (MA) and SPS at 1050°C. It is unclear whether this difference with more conventional HP or HIP can be related to the nature of the process, enhanced diffusion due to the current flow, or whether it is just an artefact of the way the temperature is measured.

Formation and Dissociation Mechanisms

So far, a single generally valid formation mechanism has not been identified for the family of MAX phases. Nevertheless, some reports try to clarify the formation of specific MAX phases starting from elemental powders. Considering the reported reaction pathways for some 211 carbide structures, such as Ti_2AlC by Pietzka and Schuster (1994) and Low (2012), Ti_2SnC by Li *et al.* (2006), Cr_2AlC by Tian *et al.* (2007b) and Nb_2AlC by Hu *et al.* (2012), a similar sequence can be identified. After melting the A-element, M_xA_y -intermetallics are formed. These tend to evolve from an A-rich intermetallic phase towards a more M-containing compound. The next step differs for Ti and Nb compared to Cr. Ti and Nb intermetallics react with C resulting in a binary MC_x or at higher temperature in the formation of another complex ternary carbide, i.e., Ti_3AlC or $\text{Nb}_3\text{Al}_2\text{C}$. In the case of Cr-intermetallics, C directly reacts with the intermetallic forming the 211 structure (Tian *et al.*, 2007b):



For $\text{M} = \text{Ti}$ or Nb , the reported C-source in the MAX phase-forming reaction is commonly the binary or ternary carbide (Li *et al.*, 2006; Hu *et al.*, 2012; Low, 2012; Lapauw *et al.*, 2016a):



The formation reactions in these four systems give a first idea on how the M_2AX phases can be synthesized. However, a few remarks should be added to these straightforward reactions. First of all, regarding the X source, even for the systems presented above, MAX phase synthesis has been reported starting from alternative carbon sources in the starting powder, such as Cr_3C_2 or Al_4C_3 (Tzenov and Barsoum, 2000; Lin *et al.*, 2007), which will most likely modify the reaction path. If $\text{X} = \text{N}$, the starting powders are MN_x , or when $\text{A} = \text{Al}$, AlN has also been used by Procopio *et al.* (2000). Secondly, these reaction paths are based on interrupted sintering experiments and constitute a good approximation. However, they are still a simplification of the local reaction front where nucleation and growth take place. Additionally, the effect of impurities should not be underestimated. They can hinder the formation or destabilize certain MAX phases. Tzenov *et al.* (2000) reported that the presence of 1% of Fe or V impurities in Ti-Si-C starting powder causes noticeable Ti_3SiC_2 MAX phase dissociation and, hence, TiC_x formation. On the other hand, Nowotny (1972) already noted the importance of the presence of impurities and stated that: “minute amounts of other non-metal elements (N, O, H, etc.) are sometimes able to stabilize carbide structures, which either do not exist or cannot be prepared in the absence of these impurities.” Although not frequently reported upon, impurities likely play a very important role in the (non-) formation of MAX phases. Although not soluble in the MAX phase itself, the addition of Fe, Co or Ni assisted in the formation of

Ti_3SnC_2 , Zr_3SnC_2 and Hf_3SnC_2 MAX phases, whereas their 211 Ti_2SnC , Zr_2SnC and Hf_2SnC equivalents were formed in the undoped M-Sn-C mixtures (Lapauw *et al.*, 2017).

Most of the 312 and 413 MAX phases can be obtained by heat treating their corresponding 211 phase. In this regard, Lane *et al.* studied the transition in the Ti-Al-C system. They observed a change from a 211 to a 523 atomic stacking sequence by the outward diffusion of Al and rearrangement of the $\text{Ti}_{n+1}\text{C}_n$ blocks. This topotactic transformation is reported by Lane *et al.* (2012) as an intermediate step in the conversion towards Ti_3AlC_2 and eventually TiC_x . Finally, Ti_3SiC_2 is in this respect particular as no 211 structure exists. The in situ formation of this MAX phase structure by SHS of a Ti, SiC and C powder mixture was captured in an ultra-high-speed neutron diffraction study. Just before the MAX phase formation, a single NaCl-structured material was observed. This was postulated by Riley *et al.* (2002) to be TiC with Si in solid solution, out of which Ti_3SiC_2 can grow. A similar reaction principle was observed by Abdulkadhim *et al.* (2011) during magnetron sputtering of Ti, Al and C by direct formation of MAX phases by Al intercalation into TiC_x ($0.4 \leq x \leq 1$).

The opposite reaction occurs for most MAX phases when heated above a certain temperature. As indicated by reaction (3), the MAX phases dissociate and transform into MC_x where the A-element melts or sublimates. The remaining M_{n+1}X_n structure relaxes and de-twinning of these slabs form $\text{TiC}_{0.67}$ (Emmerlich *et al.*, 2007). The dissociation reaction is limited by the outward diffusion of the A element (Pang *et al.*, 2010). Apart from thermal degradation, the presence of impurities can lower the stability of certain MAX phases and cause the presence of MX compounds (Tzenov *et al.*, 2000).

Attractive Properties of the MAX Phases

The systematic study of MAX phase properties started when Barsoum and El-Raghy (1996) revealed the fascinating properties of Ti_3SiC_2 . The extraordinary combination of a high fracture toughness, excellent oxidation and corrosion resistance, good high temperature stability and machinability formed the driving force in MAX phase research. A short overview of these five properties is given below, starting with what was labeled a “Mechanical Wonder” in Barsoum (2000).

Fracture Toughness and Damage Tolerance

Ceramic materials are generally associated with a brittle mechanical behavior. They lack energy absorbing mechanisms, such as dislocation motion in metals. Therefore, most ceramics have a low resistance to crack propagation and correspondingly have a modest fracture toughness (K_{IC}). In most engineering applications, however, this property is a prerequisite for the design of a structural component, hence, limiting the use of ceramic materials. One of the unique features of MAX phase materials is the presence of additional energy absorbing mechanisms, which can make them multiple times more tough than their corresponding binary carbides. The damage tolerant mechanisms are related to their nano-layered nature, but cannot be explained solely by this structure. As Barsoum (2013) pointed out, several other laminated materials exist that have a relatively low fracture toughness, such as graphite and MoS_2 . In the MAX phases, additional toughening mechanisms are present, including dislocation

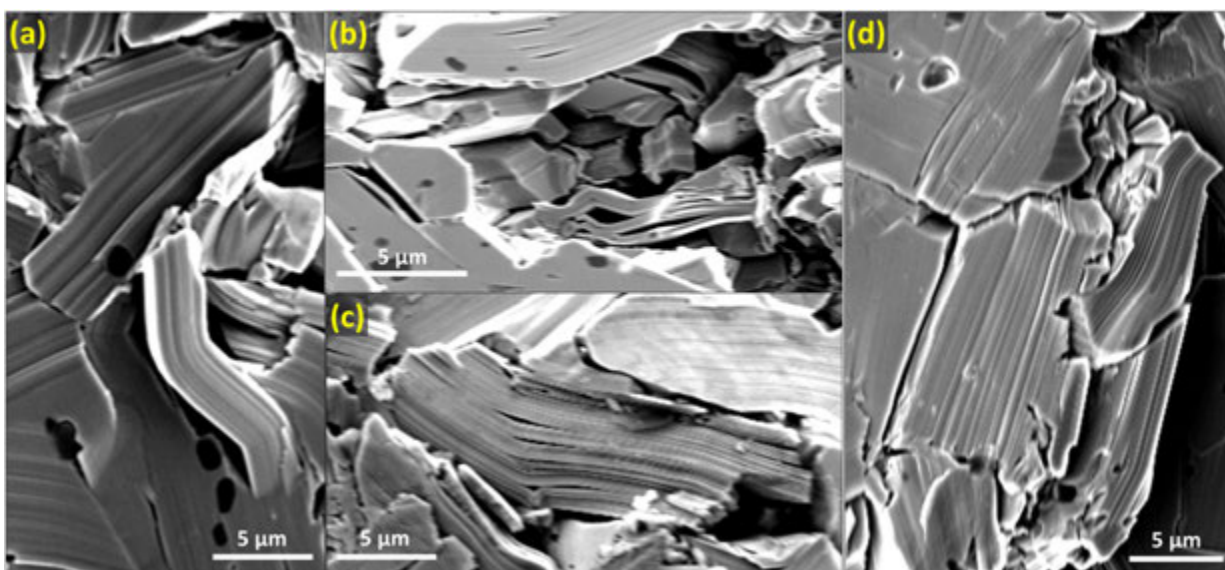


Fig. 6 Toughening deformation mechanisms in MAX phases: (a) kinking, (b) delamination, and (c) shearing of individual Nb_4AlC_3 platelets that allow crack bridging. Additionally, Nb_4AlC_3 undergoes (d) intergranular cracking.

multiplication and motion in the basal plane, crack deflection and bridging, delamination, kink boundaries and plastically deformable bridge ligaments. An illustration of a heavily deformed bridge ligament is shown in Fig. 6(a).

Of particular interest are the different ways on how to make optimal use of these toughening mechanisms. Grain alignment was found to be a very useful method to further improve fracture toughness. One way to realize this is by slip casting a MAX phase powder suspension in a strong magnetic field (12 T) and subsequently densifying the green compact by SPS. This method was successfully employed for Nb₄AlC₃, Ti₃SiC₂ and Ti₃AlC₂ (Hu *et al.*, 2011a,b,d; Zhang *et al.*, 2015a). The MAX phases are susceptible to a strong magnetic field due to their anisotropic unit cell. The *c*-axis tends to align parallel to the magnetic field. A record K_{IC} value of $17.9 \pm 5.2 \text{ MPa m}^{1/2}$ was measured on highly textured Nb₄AlC₃ loaded perpendicular to the basal plane. The concomitant flexural strength was 1.2 GPa, which indicates that grain alignment caused an overall improved mechanical behavior. The fracture toughness recorded in the perpendicular direction was $11.5 \pm 1.4 \text{ MPa m}^{1/2}$, which is still significantly higher than $7.1 \text{ MPa m}^{1/2}$ for Nb₄AlC₃ with randomly oriented grains. This improved mechanical behavior was explained by the additional crack deflection induced by the stacked platelet-like microstructure. This results in a zigzag pattern caused by crack deflection. It should be mentioned that the value of $17.9 \text{ MPa m}^{1/2}$ was measured on a material with about 15 vol% of Al₂O₃. As reported in Hu *et al.* (2011c), these oxide particles also act as crack deflectors and improve the fracture toughness. They repeated the grain alignment procedure followed by SPS for Nb₄AlC₃ material with 3 vol% Al₂O₃, which resulted in a K_{IC} of $14.1 \text{ MPa m}^{1/2}$ and $9.3 \text{ MPa m}^{1/2}$ parallel and perpendicular to the *c*-axis, respectively. These lower values clearly illustrate that the secondary oxide particles can enhance the fracture toughness. Texturing of MAX phases is also possible by plastic deformation of fully dense bulk material at elevated temperature, as demonstrated in Lapauw *et al.* (2016e) by spark plasma deformation of hot pressed Ti₃SiC₂, Ti₃AlC₂/Ti₂AlC, Nb₄AlC₃ and (Nb_{0.85},Zr_{0.15})₄AlC₃ or by SPS of milled pressureless sintered Cr₂AlC, as shown by Duan *et al.* (2015).

Oxidation Resistance and Crack Healing

A second attractive aspect of some MAX phases is their excellent oxidation resistance. The stability of the material in oxidative environments relies on the formation of a well-adherent protective oxide layer that shields the underlying material. MAX phase compounds known for their good oxidation resistance (i.e., stable above 1000°C) are Ti₃SiC₂, Ti₂AlC, Ti₃AlC₂ and Cr₂AlC. Ti₃SiC₂ forms a duplex oxide layer with an outer rutile (TiO₂) layer followed by a mixture of TiO₂ and silica (SiO₂), which shows a stable oxidation behavior up to about 1100°C (Barsoum *et al.*, 1997; Sun *et al.*, 2001). The three other compounds mainly rely on the formation of a stable α -Al₂O₃ layer. A comprehensive review of their oxidation behavior is given by Tallman *et al.* (2013), where Ti₂AlC is reported as the most oxidation-resistant MAX phase. The oxide layer is well-adherent up to 1350°C due to the excellent match in coefficient of thermal expansion (CTE) between alumina and Ti₂AlC. Thin Al₂O₃ scales of 15 μm have been reported after 8000 thermal cycles by Sundberg *et al.* (2004). The oxidation process of Ti₃AlC₂ is similar, but this MAX phase has a lower amount of Al that makes the formation of a continuous α -Al₂O₃ layer less probable and increases the oxidation rate. Nevertheless, a stable oxidation behavior was observed up to 1300°C by Wang and Zhou (2003). Cr₂AlC has the same Al-content as Ti₂AlC and a slower oxidation rate than Ti₂AlC below 1200°C. During oxidation however, this MAX phase forms a Cr₇C₃ layer underneath the Al₂O₃ layer with poor oxidation resistance (Lee *et al.*, 2007). This unique feature, i.e., the fact that Cr₂AlC is the only MAX phase forming a binary carbide layer underneath, makes Cr₂AlC prone to oxidation in case of damage of the alumina layer. Moreover, the thermal expansion of Cr₂AlC is significantly higher than for alumina. These facts limit its applicability (Tallman *et al.*, 2013). Doping the MAX phases or creating solid solutions was found to be beneficial for improving the oxidation resistance of MAX phases, such as Ti₃(Al,Si)C by Nb, Ti₃SiC₂ by Al, Nb₂AlC by Ti, and Nb₄AlC₃ by Ti addition reported, respectively, by Zheng *et al.* (2011), Zhang *et al.* (2004), Salama *et al.* (2003) and Gu *et al.* (2016). Although not a MAX phase, an improved oxidation resistance of Zr₂(AlSi)₄C₅ was reported by Lu *et al.* (2011) by replacing 20 at% Zr with Ti.

The study of the oxidation behavior of MAX phases in the Ti-Al-C system has revealed their ability to “heal” cracks. This healing consists of a heat treatment of Ti₂AlC or Ti₃AlC₂ in oxidative environment that fills the crack with TiO₂ and Al₂O₃ oxidation products, thereby (partially) restoring the strength of the material (Song *et al.*, 2008; Yang *et al.*, 2011). A similar behavior was observed for Cr₂AlC by Li *et al.* (2013a). Farle *et al.* (2015) carried out a study aimed at identifying other MAX phases suitable for this kind of self-healing behavior. They listed a set of thermodynamic and mechanical requirements based on which they selected some potential candidate self-healing MAX phases, including V₂AlC, Ti₃SiC₂ and Zr₂AlC. Li *et al.* (2016) and Li *et al.* (2017) demonstrated the healing of thermal shock-induced cracks in Ti₂SnC. They showed a restored strength after treatment in air where the large cracks were filled with TiO₂ and SnO₂ and the smaller cracks with metallic Sn. Crack healing is an added value for all materials subject to mechanical load. The Ti₂SnC example shows this behavior can also be observed for A-elements different from the most-commonly studied Al and Si.

Corrosion Resistance in Liquid Metals

MAX phase research for select applications in Gen-IV lead-cooled fast reactors (LFRs) demands the compatibility of the candidate structural/functional MAX phase-based materials with the heavy liquid metal (HLM) primary coolant, such as lead (Pb) and lead-bismuth eutectic (LBE). Under service conditions where conventional stainless steels suffer heavily from dissolution corrosion

Table 2 Overview of liquid Pb and LBE exposure studies of MAX phases in literature

MAX phase	LBE/Pb	T (°C)	Time (kh)	C ₀ (wt%)	Flow	Interaction	References
Ti ₃ SiC ₂	LBE	700	1	5 × 10 ⁻⁶	Static	No interaction	Rivai and Takahashi (2008)
	LBE	550/650	3	10 ⁻⁶ /10 ⁻⁸	Static	TiO ₂ (rutile)	Heinzel <i>et al.</i> (2009)
	LBE	550/650/ 700	1/3/5/10	10 ⁻⁶ /10 ⁻⁸	Static	TiO ₂ (rutile), local surface disintegration	Heinzel <i>et al.</i> (2016)
	Pb	650/800	1	10 ^{-12^a}	NC	No interaction	Barnes <i>et al.</i> (2008)
	Pb	550/600 750	0.5/2/4	10 ⁻⁶ /10 ⁻⁸	Static	TiO ₂ (rutile) formation	Heinzel <i>et al.</i> (2009)
	Pb	500	2	10 ⁻⁶	1 m s ⁻¹	Thin oxide layer	Uttili <i>et al.</i> (2011)
	LBE	500	3.5	10 ⁻¹⁰	Static	No interaction	Lapauw <i>et al.</i> (2019)
Ti ₂ AlC	LBE	550/650 700	1/3/5/10	10 ⁻⁶ /10 ⁻⁸	Static	TiO ₂ (rutile) & Al ₂ O ₃ formation (C ₀ = 10 ⁻⁶) Dissolution of secondary phases (C ₀ = 10 ⁻⁸ , T = 650, 750°C)	Heinzel <i>et al.</i> (2016)
	Pb	650/800	1	10 ^{-12^a}	NC	No interaction	Barnes <i>et al.</i> (2008)
	LBE	500	3.5	10 ⁻¹⁰	Static	No interaction	Lapauw <i>et al.</i> (2019)
Ti ₃ AlC ₂	LBE	500	3.5	10 ⁻¹⁰	Static	local GB penetration	Lapauw <i>et al.</i> (2019)
(Ti,Nb) ₂ AlC	LBE	500	3.5	10 ⁻¹⁰	Static	No interaction	Lapauw <i>et al.</i> (2019)
Nb ₂ AlC	LBE	500	3.5	10 ⁻¹⁰	Static	No interaction	Lapauw <i>et al.</i> (2019)
Nb ₄ AlC ₃	LBE	500	3.5	10 ⁻¹⁰	Static	No interaction	Lapauw <i>et al.</i> (2019)
(Nb _{0.85} Zr _{0.15}) ₄ AlC ₃	LBE	500	1	~10 ⁻¹¹ 5 × 10 ⁻⁹	Static ~8 m s ⁻¹	No interaction 3–4 μm Nb ₂ O ₅ -based scale	Lapauw <i>et al.</i> (2019)
Zr ₂ AlC	LBE	500	1	~10 ⁻¹¹	Static	LBE ingress into MAX phase, Zr ₂ (Al,Bi,Pb)C formation	Lapauw <i>et al.</i> (2019)
				5 × 10 ⁻⁹	~8 m s ⁻¹	Mild ZrO ₂ formation	
Zr ₃ AlC ₂	LBE	500	1	~10 ⁻¹¹	Static	LBE ingress into MAX phase Zr ₃ (Al,Bi,Pb)C ₂ formation	Lapauw <i>et al.</i> (2019)
				5 × 10 ⁻⁹	~8 m s ⁻¹	Severe ZrO ₂ formation	
(Zr _{0.8} Ti _{0.2}) ₂ AlC & (Zr _{0.8} Ti _{0.2}) ₃ AlC ₂	LBE	500	1	~10 ⁻¹¹	Static	LBE ingress into MAX phase, dissolution of intermetallic (Zr _{0.8} Ti _{0.2}) _{n+1} (Al,Pb,Bi)C _n formation	Lapauw <i>et al.</i> (2019)
Ti ₂ SnC	LBE	500	1	~10 ⁻¹¹	Static	LBE ingress through GBs Secondary Sn phase at GBs attacked	Lapauw <i>et al.</i> (2019)

^aIt indicates a calculated value for C₀.

Note: Adapted from Lapauw, T., Tunca, B., Joris, J., *et al.*, 2019. Interaction of M_{n+1}AX_n phases with oxygen-poor, static and fast-flowing liquid lead-bismuth eutectic. Journal of Nuclear Materials 520, 258–272. Copyright (2019), with permission from Elsevier.

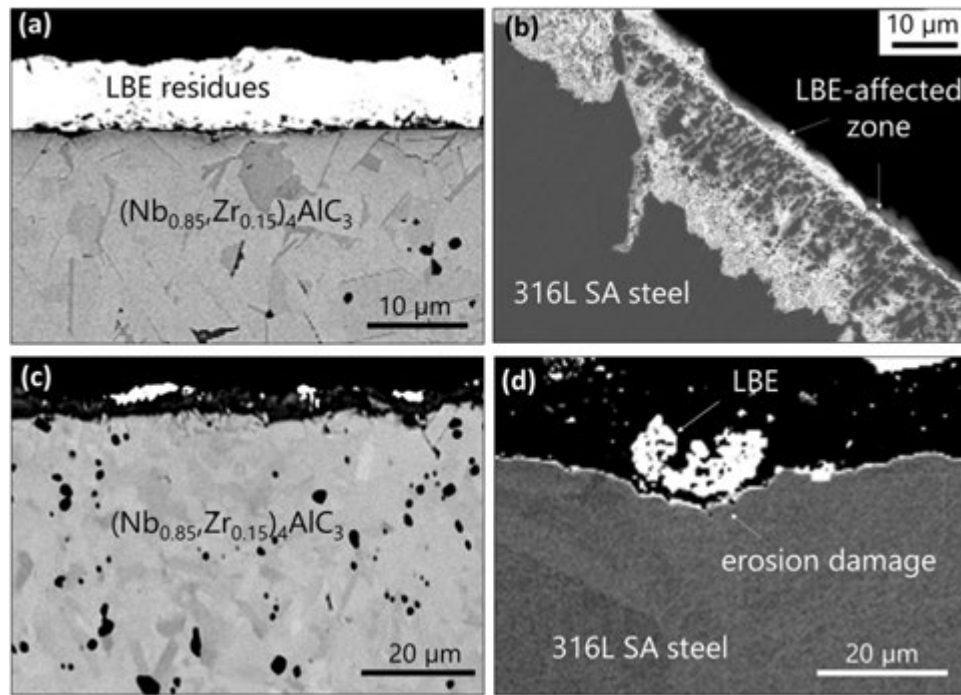


Fig. 7 Materials exposed to oxygen-poor, static LBE at 500°C for 1000 h: (a) $(\text{Nb}_{0.85}\text{Zr}_{0.15})_4\text{AlC}_3$ MAX phase solid solution, (b) 316L SA (solution annealed) stainless steel. Materials exposed to oxygen-poor, fast-flowing LBE at 500°C for 1000 h: (c) $(\text{Nb}_{0.85}\text{Zr}_{0.15})_4\text{AlC}_3$ MAX phase solid solution, (d) 316L SA stainless steel.

(Lambrinou *et al.*, 2017), e.g., high temperatures ($>450^\circ\text{C}$) and low HLM oxygen concentration ($C_{\text{O}} < 10^{-8}$ mass%), most MAX phases remain inert in contact with liquid LBE.

The liquid metal corrosion (LMC) resistance of the MAX phases is an appealing property that made them stand out as candidate materials for Gen-IV LFRs. The liquid Pb and LBE interaction experiments that have been reported in literature are summarized in [Table 2](#). Commercially available MAX phase ceramics, i.e., Maxthal® 312 (Ti_3SiC_2 and TiC) and Maxthal® 211 (Ti_2AlC , Ti_3AlC_2 and TiAl), were exposed to liquid Pb and LBE at reactor-relevant temperature ranges in order to assess their compatibility with these HLM coolants. No major corrosion effects were observed that could jeopardize the structural integrity of the MAX phase component. The most severe interaction with the HLM was the dissolution of the remaining TiAl phase in the Ti_2AlC ceramic, which resulted in LBE ingress into the material bulk (Heinzel *et al.*, 2016). Thin rutile TiO_2 formation was observed on Ti_3SiC_2 . Lapauw *et al.* (2019) reported on the stability of 11 MAX phase ceramics in oxygen-poor ($C_{\text{O}} \leq 2.2 \times 10^{-10}$ mass%) liquid LBE at 500°C for 1000–3500 h. In static LBE exposure tests, Maxthal® 312, Maxthal® 211, $(\text{Ti,Nb})_2\text{AlC}$, Nb_2AlC , Nb_4AlC_3 and $(\text{Nb}_{0.85}\text{Zr}_{0.15})_4\text{AlC}_3$ did not show any interaction with the HLM. It was concluded that these MAX phase ceramics were either intrinsically resistant to LBE attack or were passivated by a nanometric Al_2O_3 or SiO_2 oxide scale, as it is known that both Al_2O_3 and SiO_2 are stable at $C_{\text{O}} < 10^{-15}$ mass% at 500°C in liquid LBE (Schroer and Konys, 2007).

LBE interaction was observed in Ti_2SnC , where the competing Sn phase was dissolved by LBE that was found at the grain boundaries (Lapauw *et al.*, 2019). The susceptibility of competing phases that are rich in the A-element was also shown by Heinzel *et al.* (2016), who reported the dissolution of the TiAl phase present in Ti_2AlC . These findings indicate the importance of phase purity on the LMC resistance of MAX phases. The most severe interaction was observed in Zr-rich MAX phases (Zr_2AlC , Zr_3AlC_2 , $(\text{Zr}_{0.8}\text{Ti}_{0.2})_{n+1}\text{AlC}_n$) exposed to static liquid LBE (Lapauw *et al.*, 2019). Local LBE interaction was found only with the MAX phase grains, while the surface integrity of the ceramic was maintained. Attacked Zr-rich MAX phase grains were in-situ transformed into $\text{Zr}(\text{Ti})_{n+1}(\text{Al,Bi,Pb})\text{C}_n$ MAX phase solid solutions (Tunca *et al.*, 2020). The LBE dissolution attack of the intermetallic phases in the $(\text{Zr}_{0.8}\text{Ti}_{0.2})_{n+1}\text{AlC}_n$ ceramic was also observed. Lapauw *et al.* (2019) also reported that tests conducted for 1000 h at 500°C in oxygen-poor ($C_{\text{O}} \approx 5 \times 10^{-9}$ mass%), fast-flowing ($v \approx 8 \text{ m s}^{-1}$) liquid LBE resulted in 3–4 μm thick Nb_2O_5 -based oxide scale formation on $(\text{Nb}_{0.85}\text{Zr}_{0.15})_4\text{AlC}_3$. While both Zr_2AlC and Zr_3AlC_2 formed porous ZrO_2 layers, oxidation was milder in Zr_2AlC . Under fast-flowing LBE conditions, no signs of erosion or erosion/corrosion were observed in the MAX phase ceramics. Solution-annealed 316L stainless steels tested as reference structural material in the same experiment showed erosion damage (Fig. 7).

Stability at Elevated Temperature

Transition metal carbides are known as refractory carbides, due to their excellent high temperature strength. The MAX phases are reported to have a good stability at elevated temperature. Primarily, this thermal stability can be interpreted in terms of phase

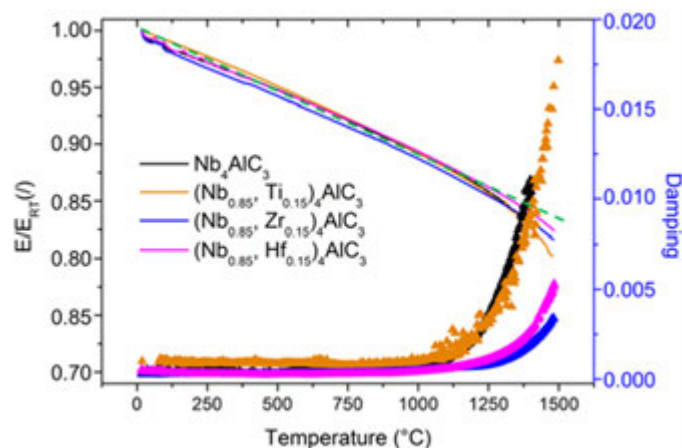


Fig. 8 Temperature dependence of the normalized Young's modulus and mechanical damping for $(\text{Nb}_{0.85}\text{M}_{0.15})_4\text{AlC}_3$ with $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ compared to unalloyed Nb_4AlC_3 . Reprinted from Lapauw, T., Swarnakar, A.K., Tunca, B., Lambrinou, K., Vleugels, J., 2018a. Nanolaminated ternary carbide (MAX phase) materials for high temperature applications. *International Journal of Refractory Metals and Hard Materials* 72, 51–55. Copyright (2018), with permission from Elsevier.

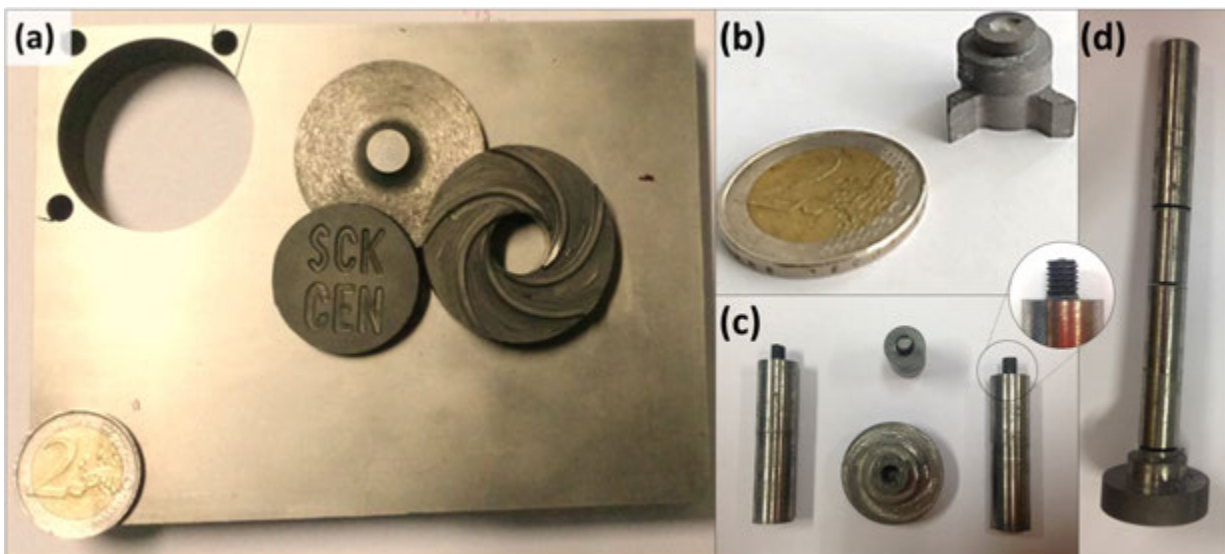


Fig. 9 (a) $(\text{Nb}_{0.85}\text{Zr}_{0.15})_4\text{AlC}_3$ MAX phase tile ($14 \times 13 \times 2 \text{ cm}^2$) produced in an industrial-size hot press, demonstrating the scalability of the adopted powder metallurgical processing approach. Milled impeller component parts machined out of a blank that was wire-EDM out of the master tile. (b) Custom-made impeller made of Cr_2AlC for a stirred batch reactor. (c) and (d) Turned Cr_2AlC assembly with threaded interconnects.

stability. As mentioned in Section “Formation and Dissociation Mechanisms,” the MAX phases dissociate at elevated temperatures and the exact dissociation temperature can vary roughly between 1000 and 1700°C, depending on the specific MAX phase and the environmental conditions. An overview of the different parameters controlling the decomposition and degradation of Ti-based MAX phases was published by Low (2019). The thermal decomposition of Ta_4AlC_3 is addressed in Griseri *et al.* (2019).

Another point of interest is the response of the MAX phases to mechanical loads at high temperature. The knowledge of this mechanical behavior is mainly based on experiments with Ti_3SiC_2 , complemented with some reports on Ti_3GeC_2 and Al-containing phases. A detailed overview is provided by Barsoum (2013). In general, the MAX phases have a brittle-to-plastic transition temperature (BPTT). Below the BPTT, their mechanical response is almost temperature-independent and they fail in a brittle way. Above the BPTT, the MAX phases can be plastically deformed and the plastic behavior becomes more pronounced at higher temperature as well as lower stress (σ) and strain rate ($\dot{\epsilon}$) (Barsoum *et al.*, 2001; Radovic *et al.*, 2002; Sun *et al.*, 2006). The activation of additional dislocation slip systems above the BPTT can be ruled out as explanation for the observed behavior, as the reported fracture toughness above the BPTT drops significantly (Wan *et al.*, 2008). The mechanism that is most likely responsible for the observed behavior is delamination and/or grain boundary decohesion (Barsoum, 2013). The temperature where softening of the grain boundaries and the brittle-to-plastic transition occurs can be measured by evaluating the stiffness as a function of

temperature. A drastic decrease in E-modulus indicates the transition towards the plastic regime (Radovic *et al.*, 2002). This transition also determines the temperature at which MAX phase components lose their load-bearing capacity and is, therefore, of interest when envisaging structural applications at elevated temperature. The ternary MAX phase that has been reported to have the best high temperature stability is Nb₄AlC₃. The evolution of the Young's modulus as a function of temperature has been reported by Hu *et al.* (2008), comparing Nb₄AlC₃ to the lower-order Nb₂AlC and Ta_{n+1}AlC_n phases. Nb₄AlC₃ clearly outpaced the other MAX phases, a fact that is also reflected in the mechanical damping. A linear decrease in stiffness was maintained until around 1400°C. Alloying Nb₄AlC₃ with Zr or Hf even further enhances the high-temperature stability (Lapauw *et al.*, 2016d, 2018a) Fig. 8.

Machinability

An important technological attribute regarding the production and shaping of components is the machinability of MAX phase compounds. They can be machined using conventional high-speed tool steel and hardmetal tools and, therefore, shaping of the MAX phases can be done using conventional machining processes such as milling, turning and drilling. A crucial prerequisite for machining is high phase purity, since parasitic carbide or oxide phases are detrimental to the tools. Some examples of MAX phase components are presented in Fig. 9. This shape flexibility is definitely one of the MAX phase assets that makes these ceramics stand out as compared to binary and other ternary transition metal carbides. The machinability is often compared to that of graphite. Barsoum *et al.* (2001) use the analogy with ice: “M_{n+1}AX_n compounds do not machine as one would scoop ice cream (as in metals), but rather as one would shave ice, i.e., by breaking off tiny microscopic flakes.” Since the MAX phases are good electrical conductors, they can also be machined using electrical discharge machining (EDM). This technique is less sensitive to the presence of competing, conductive phases, e.g., binary carbides, and still allows a high degree of shape flexibility.

Summary

This survey aimed at providing a short introduction to the MAX phases, of which the nano-layered structure leads to unusual combinations of properties. One of the most intriguing points is that some combinations of M, A and X elements are stable in the MAX phase structure, whereas other chemically similar M, A and X combinations do not form a MAX phase compound. Although one would expect a close crystallographic relation with the corresponding binary carbides/nitrides, the absence of a “Hägg-ian” rule similar to that holding for the transition metal carbides/nitrides opens up the possibility to still discover new ternary and quaternary or even multi-element MAX phases with similar or even improved properties. Despite the tremendous amount of newly discovered MAX phases, like o-MAX, i-MAX, HE-MAX, and double solid solution MAX phases, there are very few commercial MAX phase powder sources available at present and limited to the Ti₃SiC₂, Ti₂AlC, Ti₃AlC₂, V₂AlC and Nb₂AlC compositions. Bulk MAX phase ceramics, as far as we know, are not available on the market at present. Moreover, no high phase purity has been reported yet for ordered o-MAX or i-MAX ceramics, and their intrinsic material properties are still unknown. Despite the extremely interesting properties, such as damage tolerance, crack healing, oxidation resistance, relatively high temperature stability, liquid metal corrosion resistance, irradiation tolerance and machinability of some MAX phase compositions, most of the research on the MAX phases nowadays focuses on MXene synthesis, i.e., 2D transition metal carbides or nitrides synthesized by etching the A-element out of the MAX phase.

References

- Abdelkader, A.M., 2016. Molten salts electrochemical synthesis of Cr₂AlC. *Journal of the European Ceramic Society* 36, 33–42.
- Abdulkadhim, A., Takahashi, T., Music, D., Munnik, F., Schneider, J.M., 2011. MAX phase formation by intercalation upon annealing of TiC_x/Al (0.4 ≤ x ≤ 1) bilayer thin films. *Acta Materialia* 59, 6168–6175.
- Anasori, B., Gogotsi, Y. (Eds.), 2019. 2D Metal Carbides and Nitrides (MXenes). Springer International Publishing.
- Anasori, B., Halim, J., Lu, J., *et al.*, 2014. Mo₂TiAlC₂: A new ordered layered ternary carbide. *Scripta Materialia* 101, 5–7.
- Anasori, B., Dahlgvist, M., Halim, J., *et al.*, 2015a. Experimental and theoretical characterization of ordered MAX phases Mo₂TiAlC₂ and Mo₂Ti₂AlC₃. *Journal of Applied Physics* 118, 094304.
- Anasori, B., Xie, Y., Beidaghi, M., *et al.*, 2015b. Two-dimensional, ordered, double transition metals carbides (MXenes). *ACS Nano* 9, 9507–9516.
- Bao, W., Wang, X.G., Ding, H., *et al.*, 2020. High-entropy M₂AlC-MC (M = Ti, Zr, Hf, Nb, Ta) composite: Synthesis and microstructures. *Scripta Materialia* 183, 33–38.
- Barnes, L.A., Dietz Rago, N.L., Leibowitz, L., 2008. Corrosion of ternary carbides by molten lead. *Journal of Nuclear Materials* 373, 424–428.
- Barsoum, M.W., 2000. The M_{n+1}AX_n phases: A new class of solids: thermodynamically stable nanolaminates. *Progress in Solid State Chemistry* 28, 201–281.
- Barsoum, M.W., 2013. MAX Phases: Properties of Machinable Ternary Carbides and Nitrides. Wiley-VCH Verlag GmbH & Co.
- Barsoum, M.W., El-Raghy, T., 1996. Synthesis and characterization of a remarkable ceramic: Ti₃SiC₂. *Journal of the American Ceramic Society* 79, 1953–1956.
- Barsoum, M.W., El-Raghy, T., 2001. The MAX phases: Unique new carbide and nitride materials ternary ceramics turn out to be surprisingly soft and machinable, yet also heat-tolerant, strong and lightweight. *American Scientist* 89, 334–343.
- Barsoum, M.W., El-Raghy, T., Ogbuji, L.U.J.T., 1997. Oxidation of Ti₃SiC₂ in air. *Journal of the Electrochemical Society* 144, 2508–2516.
- Barsoum, M.W., Rawn, C.J., El-Raghy, T., *et al.*, 2000. Thermal properties of Ti₄AlN₃. *Journal of Applied Physics* 87, 8407–8414.
- Barsoum, M.W., Farber, L., Levin, I., *et al.*, 2004. High-resolution transmission electron microscopy of Ti₄AlN₃, or Ti₃Al₂N₂ revisited. *Journal of the American Ceramic Society* 82, 2545–2547.
- Barsoum, M.W., Radovic, M., Finkel, P., El-Raghy, T., 2001. Ti₃SiC₂ and ice. *Applied Physics Letters* 79, 479–481.
- Bloom, D.S., Grant, N.J., 1950. The system Cr-C. *Journal of Metals* 188, 41–46.

- Cabioch, T., Eklund, P., Mauchamp, V., Jaouen, M., 2012. Structural investigation of substoichiometry and solid solution effects in $\text{Ti}_2\text{Al}(\text{C}_x\text{N}_{1-x})_y$ compounds. *Journal of the European Ceramic Society* 32, 1803–1811.
- Cabioch, T., Eklund, P., Mauchamp, V., Jaouen, M., Barsoum, M.W., 2013. Tailoring of the thermal expansion of $\text{Cr}_2(\text{Al}_x\text{Ge}_{1-x})\text{C}$ phases. *Journal of the European Ceramic Society* 33, 897–904.
- Caspi, E.N., Chartier, P., Porcher, F., Damay, F., Cabioch, T., 2015. Ordering of (Cr,V) layers in nanolamellar $(\text{Cr}_{0.5}\text{V}_{0.5})_{n+1}\text{AlC}_n$ compounds. *Materials Research Letters* 3, 100–106.
- Chen, L., Dahlqvist, M., Lapauw, T., *et al.*, 2018. Theoretical prediction and synthesis of $(\text{Cr}_{2/3}\text{Zr}_{1/3})_2\text{AlC}$ i-MAX phase. *Inorganic Chemistry* 57, 6237–6244.
- Dahlqvist, M., Rosen, J., 2015. Order and disorder in quaternary atomic laminates from first-principles calculations. *Physical Chemistry Chemical Physics* 17, 31810–31821.
- Dahlqvist, M., Alling, B., Rosen, J., 2010. Stability trends of MAX phases from first principles. *Physical Review B. Condensed Matter and Materials Physics* 81, 220102.
- Dahlqvist, M., Lu, J., Meshkian, R., *et al.*, 2017. Prediction and synthesis of a family of atomic laminate phase with Kagomé-like and in-plane chemical ordering. *Science Advances* 3, 1–10.
- Dahlqvist, M., Petruhins, A., Lu, J., Hultman, L., Rosen, J., 2018. Origin of chemically ordered atomic laminates (i-MAX): Expanding the elemental space by a theoretical/experimental approach. *ACS Nano* 12, 7761–7770.
- Dash, A., Vassen, R., Guillon, O., Gonzalez-Julian, J., 2019. Molten salt shielded synthesis of oxidation prone materials in air. *Nature Materials* 18, 465–470.
- Duan, X., Shen, L., Jia, D., *et al.*, 2015. Synthesis of high-purity, isotropic or textured Cr_2AlC bulk ceramics by spark plasma sintering of pressure-less sintered powders. *Journal of the European Ceramic Society* 35, 1393–1400.
- Dubois, S., Cabioch, T., Chartier, P., Gauthier, V., Jaouen, M., 2007. A new ternary nanolaminate carbide: Ti_3SnC_2 . *Journal of the American Ceramic Society* 90, 2642–2644.
- Eklund, P., Palmqvist, J.P., Höwing, J., *et al.*, 2007. Ta_4AlC_3 : Phase determination, polymorphism and deformation. *Acta Materialia* 55, 4723–4729.
- Eklund, P., Rosen, J., Persson, P.O.Å., 2017. 2D derivative MXene: An overview from a thin-film perspective. *Journal of Physics D: Applied Physics* 50, 113001.
- Eklund, P., Beckers, M., Jansson, U., Högborg, H., Hultman, L., 2010. The $\text{M}_{n+1}\text{AX}_n$ phases: Materials science and thin-film processing. *Thin Solid Films* 518, 1851–1878.
- Emmerlich, J., Music, D., Eklund, P., *et al.*, 2007. Thermal stability of Ti_3SiC_2 thin films. *Acta Materialia* 55, 1479–1488.
- Etzkorn, J., Ade, M., Hillebrecht, H., 2007a. Ta_3AlC_2 and Ta_4AlC_3 – Single-crystal investigations of two new ternary carbides of tantalum synthesized by the molten metal technique. *Inorganic Chemistry* 46, 1410–1418.
- Etzkorn, J., Ade, M., Hillebrecht, H., 2007b. V_2AlC , V_4AlC_3-x ($x \approx 0.31$), and $\text{V}_{12}\text{Al}_3\text{C}_6$: synthesis, crystal growth, structure, and superstructure. *Inorganic Chemistry* 46, 7646–7653.
- Etzkorn, J., Ade, M., Kotzot, D., Kleczek, M., Hillebrecht, H., 2009. Ti_2GaC , Ti_4GaC_3 and Cr_2GaC – Synthesis, crystal growth and structure analysis of Ga-containing MAX-phases $\text{M}_{n+1}\text{GaC}_n$ with $\text{M}=\text{Ti}, \text{Cr}$ and $n=1, 3$. *Journal of Solid State Chemistry* 182, 995–1002.
- Farle, A.S., Kwakernaak, C., van der Zwaag, S., Sloof, W.G., 2015. A conceptual study into the potential of $\text{M}_{n+1}\text{AX}_n$ -phase ceramics for self-healing of crack damage. *Journal of the European Ceramic Society* 35, 37–45.
- Fashandi, H., Dahlqvist, M., Lu, J., *et al.*, 2017. Synthesis of Ti_3AuC_2 , $\text{Ti}_3\text{Au}_2\text{C}_2$ and Ti_3IrC_2 by noble metal substitution reaction in Ti_3SiC_2 for high-temperature-stable ohmic contacts to SiC. *Nature Materials* 16, 814–819.
- Furgeaud, C., Brenet, F., Nicolai, J., 2019. Multi-scale study of Ti_3SiC_2 thin film growth mechanism obtained by magnetron sputtering. *Materialia* 7, 100369.
- Galvin, T., Hyatt, N.C., Rainforth, W.M., Reaney, I.M., Shepherd, D., 2018. Molten salt synthesis of MAX phases in the Ti-Al-C system. *Journal of the European Ceramic Society* 38, 4585–4589.
- Griseri, M., Tunca, B., Lapauw, T., *et al.*, 2019. Synthesis, properties and thermal decomposition of the Ta_4AlC_3 MAX phase. *Journal of the European Ceramic Society* 39, 2973–2981.
- Griseri, M., Tunca, B., Huang, S., *et al.*, 2020. Ta-based 413 and 211 MAX phase solid solutions with Hf and Nb. *Journal of the European Ceramic Society* 40, 1829–1838.
- Gu, J., Pan, L., Yang, J., *et al.*, 2016. Mechanical properties and oxidation behavior of Ti-doped Nb_4AlC_3 . *Journal of the European Ceramic Society* 36, 1001–1008.
- Haemers, J., Gusmão, R., Sofer, Z., 2020. Synthesis protocols of the most common layered carbide and nitride MAX phases. *Small Methods* 4, 1900780.
- Hamm, C.M., Schäfer, T., Zhang, H., Birkel, C.S., 2016. Non-conventional synthesis of the 413 MAX phase V_4AlC_3 . *Zeitschrift für Anorganische und Allgemeine Chemie* 642, 1397–1401.
- He, X., Bai, Y., Zhu, C., Barsoum, M.W., 2011. Polymorphism of newly discovered Ti_4GaC_3 : A first-principles study. *Acta Materialia* 59, 5523–5533.
- Heinzel, A., Müller, G., Weisenburger, A., 2009. Compatibility of Ti_3SiC_2 with liquid Pb and PbBi containing oxygen. *Journal of Nuclear Materials* 392, 255–258.
- Heinzel, A., Weisenburger, A., Müller, G., 2016. Long-term corrosion tests of Ti_3SiC_2 and Ti_2AlC_2 in oxygen containing LBE at temperatures up to 700°C. *Journal of Nuclear Materials* 482, 114–123.
- Högborg, H., Hultman, L., Emmerlich, J., *et al.*, 2005b. Growth and characterization of MAX-phase thin films. *Surface and Coatings Technology* 193, 6–10.
- Högborg, H., Emmerlich, J., Eklund, P., *et al.*, 2006. Growth and property characterization of epitaxial MAX-phase thin films from the $\text{Ti}_{n+1}(\text{Si},\text{Ge},\text{Sn})\text{C}_n$ system. *Advances in Science and Technology* 45, 2648–2655.
- Högborg, H., Eklund, P., Emmerlich, J., Birch, J., Hultman, L., 2005a. Epitaxial Ti_2GeC , Ti_3GeC_2 , and Ti_4GeC_3 MAX-phase thin films grown by magnetron sputtering. *Journal of Materials Research* 20, 779–782.
- Hu, C., Li, F., Zhang, J., *et al.*, 2007. Nb_4AlC_3 : A new compound belonging to the MAX phases. *Scripta Materialia* 57, 893–896.
- Hu, C., Li, F., He, L., *et al.*, 2008. In situ reaction synthesis, electrical and thermal, and mechanical properties of Nb_4AlC_3 . *Journal of the American Ceramic Society* 91, 2258–2263.
- Hu, C., Sakka, Y., Grasso, S., *et al.*, 2011a. Shell-like nanolayered Nb_4AlC_3 ceramic with high strength and toughness. *Scripta Materialia* 64, 765–768.
- Hu, C., Sakka, Y., Nishimura, T., *et al.*, 2011c. Physical and mechanical properties of highly textured polycrystalline Nb_4AlC_3 ceramic. *Science and Technology of Advanced Materials* 12, 044603.
- Hu, C., Huang, Q., Bao, Y., Zhou, Y., 2012. Sintering and properties of Nb_4AlC_3 ceramic. In: Lakshmanan, A. (Ed.), *Sintering of Ceramics – New Emerging Techniques*, first ed. Intech Open Limited, pp. 141–158.
- Hu, C., Sakka, Y., Grasso, S., Suzuki, T., Tanaka, H., 2011b. Tailoring Ti_3SiC_2 ceramic via a strong magnetic field alignment method followed by spark plasma sintering. *Journal of the American Ceramic Society* 94, 742–748.
- Hu, C., Sakka, Y., Tanaka, H., Nishimura, T., Grasso, S., 2011d. Fabrication of textured Nb_4AlC_3 ceramic by slip casting in a strong magnetic field and spark plasma sintering. *Journal of the American Ceramic Society* 94, 410–415.
- Hu, C., Zhang, H., Li, F., Huang, Q., Bao, Y., 2013. New phases' discovery in MAX family. *International Journal of Refractory Metals and Hard Materials* 36, 300–312.
- Hug, G., 2006. Electronic structures of and composition gaps among the ternary carbides Ti_2MC . *Physical Review B* 74, 184113.
- Hug, G., Jaouen, M., Barsoum, M.W., 2005. X-ray absorption spectroscopy, EELS, and full-potential augmented plane wave study of the electronic structure of Ti_2AlC , Ti_2AlN , Nb_2AlC and $(\text{Ti}_{0.5}\text{Nb}_{0.5})_2\text{AlC}$. *Physical Review B* 71, 024105.
- Hume-Rothery, W., 1950. *The Structure of Metals and Alloys*, second ed. The Institute of Metals.
- Ingason, A.S., Petruhins, A., Dahlqvist, M., *et al.*, 2013. A nanolaminated magnetic phase: Mn_2GaC . *Materials Research Letters* 2, 89–93.
- Istomin, P., Istomina, E., Nadutkin, A., Grass, V., Presniakov, M., 2016. Synthesis of a bulk Ti_4SiC_3 MAX phase by reduction of TiO_2 with SiC. *Inorganic Chemistry* 55, 11050–11056.
- Jaouen, M., Chartier, P., Cabioch, T., *et al.*, 2013. Invar like behavior of the Cr_2AlC MAX phase at low temperature. *Journal of the American Ceramic Society* 96, 3872–3876.
- Jeitschko, W., Nowotny, H., 1967. Die Kristallstruktur von Ti_3SiC_2 – ein neuer Komplexcarbidge-Typ. *Monatshefte für Chemie – Chemical Monthly* 98, 329–337.
- Jeitschko, W., Nowotny, H., Benesovsky, F., 1963. Kohlenstoffhaltige ternäre Verbindungen (H-Phase). *Monatshefte für Chemie – Chemical Monthly* 94, 672–676.

- Jeitschko, W., Nowotny, H., Benesovsky, F., 1964a. Carbides of formula T_2MC . *Journal of the Less Common Metals* 7, 133–138.
- Jeitschko, W., Nowotny, H., Benesovsky, F., 1964b. Die H-Phasen Ti_2TiC , Ti_2PbC , Nb_2InC , Nb_2SnC und Ta_2GaC . *Monatshefte für Chemie und verwandte Teile Andere Wissenschaften* 95, 431–435.
- Jeitschko, W., Nowotny, H., Benesovsky, F., 1964c. Die H-Phasen: Ti_2CdC , Ti_2GaC , Ti_2ZrC , Ti_2InC , Zr_2InC und Nb_2GaC . *Monatshefte für Chemie und verwandte Teile Andere Wissenschaften* 95, 178–179.
- Kanoun, M.B., Goumri-Said, S., Jaouen, M., 2009. Steric effect on the M site of nanolaminate $M(2)SnC$ ($M = Ti, Zr, Hf$ and Nb). *Journal of Physics: Condensed Matter* 21, 045404.
- Kudielka, H., Rohde, H., 1960. Strukturuntersuchungen an Carbosulfiden von Titan und Zirkon. *Zeitschrift für Kristallographie* 114, 447–456.
- Lai, C.C., Petruhins, A., Lu, J., *et al.*, 2017. Thermally induced substitutional reaction of Fe into Mo_2GaC thin films. *Materials Research Letters* 5, 533–539.
- Lambrinou, K., Charalampopoulou, E., Van der Donck, T., Delville, R., Schryvers, S., 2017. Dissolution corrosion of 316L austenitic stainless steels in contact with static liquid lead-bismuth eutectic (LBE) at 500°C. *Journal of Nuclear Materials* 490, 9–27.
- Lane, N.J., Naguib, M., Lu, J., Hultman, L., Barsoum, M.W., 2012. Structure of a new bulk $Ti_5Al_2C_3$ MAX phase produced by the topotactic transformation of Ti_2AlC . *Journal of the European Ceramic Society* 32, 3485–3491.
- Lapauw, T., Halim, J., Lu, J., *et al.*, 2016a. Synthesis of the novel Zr_3AlC_2 MAX phase. *Journal of the European Ceramic Society* 36, 943–947.
- Lapauw, T., Lambrinou, K., Cabioch, T., *et al.*, 2016b. Synthesis of the new MAX phase Zr_2AlC . *Journal of the European Ceramic Society* 36, 1847–1853.
- Lapauw, T., Tunca, B., Cabioch, T., *et al.*, 2016c. Synthesis of MAX phases in the Hf-Al-C system. *Inorganic Chemistry* 55, 10922–10927.
- Lapauw, T., Tytko, D., Vanmeensel, K., 2016d. $(Nb_xZr_{1-x})_4AlC_3$ MAX phase solid solutions: Processing, mechanical properties, and density functional theory calculations. *Inorganic Chemistry* 55, 5445–5452.
- Lapauw, T., Tunca, B., Potashnikov, D., *et al.*, 2018b. The double solid solution $(Zr,Nb)_2(Al,Sn)C$ MAX phase: A steric stability approach. *Scientific Reports* 8, 12801.
- Lapauw, T., Tunca, B., Joris, J., *et al.*, 2019. Interaction of $M_{n+1}AX_n$ phases with oxygen-poor, static and fast-flowing liquid lead-bismuth eutectic. *Journal of Nuclear Materials* 520, 258–272.
- Lapauw, T., Vanmeensel, K., Lambrinou, K., Vleugels, J., 2016e. A new method to texture dense $M_{n+1}AX_n$ ceramics by spark plasma deformation. *Scripta Materialia* 111, 98–101.
- Lapauw, T., Tunca, B., Cabioch, T., Vleugels, J., Lambrinou, K., 2017. Reactive spark plasma sintering of Ti_3SnC_2 , Zr_3SnC_2 and Hf_3SnC_2 using Fe, Co or Ni additives. *Journal of the European Ceramic Society* 37, 4539–4545.
- Lapauw, T., Swarnakar, A.K., Tunca, B., Lambrinou, K., Vleugels, J., 2018a. Nanolaminated ternary carbide (MAX phase) materials for high temperature applications. *International Journal of Refractory Metals and Hard Materials* 72, 51–55.
- Lee, D.B., Nguyen, T.D., Han, J.H., Park, S.W., 2007. Oxidation of Cr_2AlC at 1300°C in air. *Corrosion Science* 49, 3926–3934.
- Li, L., Zhou, A., Xu, L., Li, Z., Wang, L., 2013b. Synthesis of high pure Ti_3AlC_2 and Ti_2AlC powders from TiH_2 powders as Ti source by tube furnace. *Journal of Wuhan University of Technology – Materials Science Edition* 28, 882–887.
- Li, S., Zhai, H., 2005. Synthesis and reaction mechanism of Ti_3SiC_2 by mechanical alloying of elemental Ti, Si and C powders. *Journal of the American Ceramic Society* 88, 2092–2098.
- Li, S., Xiao, L., Song, G., *et al.*, 2013a. Oxidation and crack healing behavior of a fine-grained Cr_2AlC ceramic. *Journal of the American Ceramic Society* 96, 892–899.
- Li, S., Bei, G., Chen, X., *et al.*, 2016. Crack healing induced electrical and mechanical properties recovery in a Ti_2SnC ceramic. *Journal of the European Ceramic Society* 36, 25–32.
- Li, S., Zou, X., Xiong, X., *et al.*, 2018. Electrosynthesis of Ti_3AlC_2 from oxides/carbon precursor in molten calcium chloride. *Journal of Alloys and Compounds* 735, 1901–1907.
- Li, S., Bei, G., Zhai, X., Zhou, Y., 2006. High-temperature reaction using Ti/Sn/C and Ti/Sn/TiC powder compacts. *Journal of the American Ceramic Society* 89, 3617–3623.
- Li, S., Zhang, L., Yu, W., Zhou, Y., 2017. Precipitation induced crack healing in a Ti_2SnC ceramic in vacuum. *Ceramics International* 43, 6963–6966.
- Li, Y., Lu, J., Li, M., *et al.*, 2020. Multielemental single-atom-thick A layers in nanolaminated $V_2(Sn,1)C$ ($A = Fe, Co, Ni, Mn$) for tailoring magnetic properties. In: Rao, C.N.R. (Ed.), *Proceedings of the National Academy of Sciences of the United States of America*. National Academy of Sciences, pp. 820–825.
- Lin, S., Huang, Y., Zu, L., *et al.*, 2016. Alloying effects on structural, magnetic, and electrical/thermal transport properties in MAX-phase $Cr_{2-x}M_xGeC$ ($M = Ti, V, Mn, Fe$, and Mo). *Journal of Alloys and Compounds* 680, 452–461.
- Lin, Z.J., Li, M.S., Wang, J.Y., Zhou, Y.C., 2007. High-temperature oxidation and hot corrosion of Cr_2AlC . *Acta Materialia* 55, 6182–6191.
- Lin, Z.J., Zhuo, M., Zhou, Y., Li, M., Wang, J., 2006. Microstructures and theoretical bulk modulus of layered ternary tantalum aluminum carbides. *Journal of the American Ceramic Society* 89, 3765–3769.
- Liu, G., Chen, K., Zhou, H., *et al.*, 2007. Layered growth of Ti_2AlC and Ti_3AlC_2 in combustion synthesis. *Materials Letters* 61, 779–784.
- Liu, W., Qiu, C., Zhou, J., *et al.*, 2015. Fabrication of Ti_2AlN ceramics with orientation growth behavior by the microwave sintering method. *Journal of the European Ceramic Society* 35, 1385–1391.
- Liu, Z., Wu, E., Wang, J., *et al.*, 2014. Crystal structure and formation mechanism of $(Cr_{2/3}Ti_{1/3})_3AlC_2$ MAX phase. *Acta Materialia* 73, 186–193.
- Low, I.M., 2012. *Advances in Science and Technology of $Mn + 1AX_n$ Phases*. Elsevier.
- Low, I.M., 2019. An overview of parameters controlling the decomposition and degradation of Ti-based $M_{n+1}AX_n$ phases. *Materials* 12, 473–484.
- Lu, X., Zhou, Y., 2010. Pressureless sintering and properties of Ti_3AlC_2 . *International Journal of Applied Ceramic Technology* 7, 744–751.
- Lu, X., Xiang, H., He, L., Sun, L., Zhou, Y., 2011. Effect of Ti dopant on the mechanical properties and oxidation behavior of $Zr_2[Al(Si)]_4C_5$ ceramics. *Journal of the American Ceramic Society* 94, 1872–1877.
- Magnuson, M., Mattesini, M., Li, S., *et al.*, 2007. Bonding mechanism in the nitrides Ti_2AlN and TiN : An experimental and theoretical investigation. *Physical Review B* 76, 195127.
- Manoun, B., Saxena, S.K., 2007. Synthesis and compressibility of $Ti_3(Al,Sn_{0.2})C_2$ and $Ti_3(C_{0.5}N_{0.5})_2$. *Journal of Applied Physics* 101, 113523.
- Medvedeva, N.I., Novikov, D.L., Ivanovsky, A.L., Kuznetsov, M.V., Freeman, A.J., 1998. Electronic properties of Ti_3SiC_2 -based solid solutions. *Physical Review B* 58, 16042–16050.
- Meng, F.L., Zhou, Y.C., Wang, J.Y., 2005. Strengthening of Ti_2AlC by substituting Ti with V. *Scripta Materialia* 53, 1369–1372.
- Meshkian, R., Tao, Q., Dahlqvist, M., *et al.*, 2017. Theoretical stability and materials synthesis of a chemically ordered MAX phase, Mo_2ScAlC_2 , and its two-dimensional derivative Mo_2ScC_2 MXene. *Acta Materialia* 125, 476–480.
- Mockute, A., Persson, P.O.Å., Magnus, F., *et al.*, 2014. Synthesis and characterization of arc deposited magnetic $(Cr,Mn)_2AlC$ MAX phase films. *Physica Status Solidi – Rapid Research Letters* 8, 420–423.
- Music, D., Ahuja, R., Schneider, J.M., 2005. Theoretical study of nitrogen vacancies in Ti_4AlN_3 . *Applied Physics Letters* 86, 031911.
- Naguib, M., Kurtoglu, M., Presser, V., *et al.*, 2011. Two-dimensional nanocrystals produced by exfoliation of Ti_3AlC_2 . *Advanced Materials* 23, 4248–4253.
- Naguib, M., Bentzel, G.W., Shah, J., *et al.*, 2014. New solid solution MAX phases: $(Ti_{0.5}V_{0.5})_3AlC_2$, $(Nb_{0.5}V_{0.5})_2AlC$, $(Nb_{0.5}V_{0.5})_4AlC_3$ and $(Nb_{0.8}Zr_{0.2})_2AlC$. *Materials Research Letters* 2, 233–240.
- Nechiche, M., Gauthier-Brunet, V., Mauchamp, V., *et al.*, 2017. Synthesis and characterization of a new $(Ti_{1-x}Cu_x)(Al,Cu)_2C_2$ MAX phase solid solution. *Journal of the European Ceramic Society* 37, 459–466.
- Nowotny, H., 1972. Crystal chemistry of complex carbides and related compounds. *Angewandte Chemie International Edition in English* 11, 906–915.
- Nowotny, H., Jeitschko, W., Benesovsky, F., 1964. Neue Komplexcarbide und -nitride, ihre Beziehung zu Hartstoffphasen. *Planseeberichte für Pulvermetallurgie* 12, 31–43.

- Palmquist, J.P., Li, S., Persson, P.O.Å., *et al.*, 2004. $M_{n+1}AX_n$ phases in the Ti-Si-C system studied by thin-film synthesis and ab initio calculations. *Physical Review B* 70, 165401.
- Pang, W.K., Low, I.M., Sun, Z.M., 2010. In situ high-temperature diffraction study of the thermal dissociation of Ti_3AlC_2 in vacuum. *Journal of the American Ceramic Society* 93, 2871–2876.
- Pickering, E., Lackey, W.J., Crain, S., 2000. CVD of Ti_3SiC_2 . *Chemical Vapor Deposition* 6, 289–295.
- Pietzka, M.A., Schuster, J.C., 1994. Summary of constitutional data on the aluminum-carbon-titanium system. *Journal of Phase Equilibria* 15, 392–400.
- Procopio, A., El-Raghy, T., Barsoum, M.W., 2000. Synthesis of Ti_4AlN_3 and phase equilibria in the Ti-Al-N system. *Metallurgical and Materials Transaction A* 31, 373–378.
- Radovic, M., Barsoum, M.W., El-Raghy, T., Wiederhorn, S.M., Luecke, W.E., 2002. Effect of temperature, strain rate and grain size on the mechanical response of Ti_3SiC_2 in tension. *Acta Materialia* 50, 1297–1306.
- Reiffenstein, E., Nowotny, H., Benesovsky, F., 1966. Strukturchemische und magnetochemische Untersuchungen an Komplexcarbiden. *Monatshefte für Chemie und Verwandte Teile Anderer Wissenschaften* 97, 1428–1436.
- Riley, D.P., Kisi, E.H., Hansen, T.C., Hewat, A.W., 2002. Self-propagating high-temperature synthesis of Ti_3SiC_2 : I, ultra-high-speed neutron diffraction study of the reaction mechanism. *Journal of the American Ceramic Society* 85, 2417–2424.
- Rivai, A.K., Takahashi, M., 2008. Compatibility of surface-coated steels, refractory metals and ceramics to high temperature lead-bismuth eutectic. *Progress in Nuclear Energy* 50, 560–566.
- Rosen, J., Ryves, L., Persson, P.O.Å., Bilek, M.M.M., 2007. Deposition of epitaxial Ti_2AlC thin films by pulsed cathodic arc. *Journal of Applied Physics* 101, 056101.
- Salama, I., El-Raghy, T., Barsoum, M.W., 2003. Oxidation of Nb_2AlC and $(Ti,Nb)_2AlC$ in air. *Journal of the Electrochemical Society* 150, C152–C158.
- Scabarozzi, T.H., Hettinger, J.D., Lofland, S.E., *et al.*, 2011. Epitaxial growth and electrical-transport properties of $Ti_7Si_2C_5$ thin films synthesized by reactive sputter-deposition. *Scripta Materialia* 65, 811–814.
- Schroer, C., Konyas, J., 2007. Physical Chemistry of Corrosion and Oxygen Control in Liquid Lead and Lead-Bismuth Eutectic. *Forschungszentrum Karlsruhe*.
- Sokol, M., Natu, V., Kota, S., Barsoum, M.W., 2019. On the chemical diversity of the MAX phases. *Trends in Chemistry Special Issue Part Two: Big Questions in Chemistry* 1, 143–274.
- Song, G.M., Pei, Y.T., Sloof, W.G., *et al.*, 2008. Oxidation-induced crack healing in Ti_3AlC_2 ceramics. *Scripta Materialia* 58, 13–16.
- Sun, Z.M., Zhou, Y., Li, M., 2001. Oxidation behaviour of Ti_3SiC_2 -based ceramic at 900–1300°C in air. *Corrosion Science* 43, 1095–1109.
- Sun, Z.M., Hashimoto, H., Zhang, Z.F., Yang, S.L., Tada, S., 2006. Synthesis and characterization of a metallic ceramic material – Ti_3SiC_2 . *Materials Transactions* 47, 170–174.
- Sundberg, M., Malmqvist, G., Magnusson, A., El-Raghy, T., 2004. Alumina forming high temperature silicides and carbides. *Ceramics International* 30, 1899–1904.
- Tallman, D.J., Anasori, B., Barsoum, M.W., 2013. A critical review of the oxidation of Ti_2AlC , Ti_3AlC_2 and Cr_2AlC in air. *Materials Research Letters* 1, 115–125.
- Tao, Q., Salikhov, R., Mochalko, A., *et al.*, 2016. Thin film synthesis and characterization of a chemically ordered magnetic nanolaminate $(V,Mn)_3GaC_2$. *APL Materials* 4, 086109.
- Tao, Q., Dahlqvist, M., Lu, J., *et al.*, 2017. Two-dimensional $Mo_{1.33}C$ MXene with divacancy ordering prepared from parent 3D laminate with in-plane chemical ordering. *Nature Communications* 8, 14949.
- Tao, Q., Lu, J., Dahlqvist, M., *et al.*, 2019. Atomically layered and ordered rare-earth i-MAX phases: A new class of magnetic quaternary compounds. *Chemistry of Materials* 31, 2476–2485.
- Tian, W., Vanmeensel, K., Wang, P., *et al.*, 2007a. Synthesis and characterization of Cr_2AlC ceramics prepared by spark plasma sintering. *Materials Letters* 61, 4442–4445.
- Tian, W., Wang, P., Kan, Y., *et al.*, 2007b. Phase formation sequence of Cr_2AlC ceramics starting from Cr-Al-C powders. *Materials Science and Engineering: A* 443, 229–234.
- Tian, W., Wang, P., Kan, Y., Zhang, G., 2008. Cr_2AlC powders prepared by molten salt method. *Journal of Alloys and Compounds* 461, L5–L10.
- Tunca, B., Lapauw, T., Karakulina, O.M., *et al.*, 2017. Synthesis of MAX phases in the Zr-Ti-Al-C system. *Inorganic Chemistry* 56, 3489–3498.
- Tunca, B., Lapauw, T., Delville, R., *et al.*, 2019. Synthesis and characterization of double solid solution $(Zr,Ti)_2(Al,Sn)C$ MAX phase ceramics. *Inorganic Chemistry* 58, 6669–6683.
- Tunca, B., Lapauw, T., Callaert, C., *et al.*, 2020. Compatibility of Zr_2AlC MAX phase-based ceramics with oxygen-poor, static liquid lead-bismuth eutectic. *Corrosion Science* 171, 108704.
- Tzenov, N., Barsoum, M.W., El-Raghy, T., 2000. Influence of small amounts of Fe and V on the synthesis and stability of Ti_3SiC_2 . *Journal of the European Ceramic Society* 20, 801–806.
- Tzenov, N.V., Barsoum, M.W., 2000. Synthesis and characterization of Ti_3AlC_2 . *Journal of the American Ceramic Society* 83, 825–832.
- Uitili, M., Agostini, M., Coccoluto, G., Lorenzini, E., 2011. Ti_3SiC_2 as a candidate material for lead cooled fast reactor. *Nuclear Engineering and Design* 241, 1295–1300.
- Vegard, L., 1921. Die Konstitution der Mischkristalle und die Raumfüllung der Atome. *Zeitschrift für Physik* 5, 17–26.
- Walter, C., Sigumonrong, D.P., El-Raghy, T., Schneider, J.M., 2006. Towards large area deposition of Cr_2AlC on steel. *Thin Solid Films* 515, 389–393.
- Wan, D.T., He, L., Zheng, L., *et al.*, 2010. A new method to improve the high-temperature mechanical properties of Ti_3SiC_2 by substituting Ti with Zr, Hf or Nb. *Journal of the American Ceramic Society* 93, 1749–1753.
- Wan, D.T., Meng, F.L., Zhou, Y.C., Bao, Y.W., Chen, J.X., 2008. Effect of grain size, notch width, and testing temperature on the fracture toughness of $Ti_3Si(Al)C_2$ and Ti_3AlC_2 using the chevron-notched beam (CNB) method. *Journal of the European Ceramic Society* 28, 663–669.
- Wang, Q., Hu, C., Cai, S., *et al.*, 2014. Synthesis of high-purity Ti_3SiC_2 by microwave sintering. *International Journal of Applied Ceramic Technology* 11, 911–918.
- Wang, X., Zhang, H., Zheng, L., *et al.*, 2012. $Ti_5Al_2C_3$: A new ternary carbide belonging to MAX phases in the Ti-Al-C system. *Journal of the American Ceramic Society* 95, 1508–1510.
- Wang, X.H., Zhou, Y.C., 2003. Oxidation behavior of Ti_3AlC_2 at 1000–1400°C in air. *Corrosion Science* 45, 891–907.
- Wang, X.H., Zhou, Y.C., 2010. Layered machinable and electrically conductive Ti_2AlC and Ti_3AlC_2 ceramics: A review. *Journal of Materials Science & Technology* 26, 385–416.
- Wang, Z., Zha, C.S., Barsoum, M.W., 2004. Compressibility and pressure-induced phase transformation of Ti_3GeC_2 . *Applied Physics Letters* 85, 3453–3455.
- Wolfsgruber, H., Nowotny, H., Benesovsky, F., 1967. Die Kristallstruktur von Ti_3GeC_2 . *Monatshefte für Chemie und verwandte Teile Anderer Wissenschaften* 98, 2403–2405.
- Yang, C., Wang, F., Zhu, J., *et al.*, 2014. Synthesis, microstructure and mechanical properties of $(Ti,W)_3AlC_2/Al_2O_3$ composites by in situ reactive hot pressing. *Materials Science and Engineering: A* 610, 154–160.
- Yang, C., Jin, S.Z., Liang, B.Y., Jia, S.S., 2009. Low-temperature synthesis of high-purity Ti_3AlC_2 by MA-SPS technique. *Journal of the European Ceramic Society* 29, 181–185.
- Yang, H.J., Pei, Y.T., Rao, J.C., *et al.*, 2011. High temperature healing of Ti_2AlC : On the origin of inhomogeneous oxide scale. *Scripta Materialia* 65, 135–138.
- Yang, L.X., Wang, Y., Zhang, H.L., Liu, H.J., Zeng, C.L., 2019. A simple method for the synthesis of nanosized Ti_3AlC_2 powder in NaCl-KCl molten salt. *Materials Research Letters* 7, 361–367.
- Yeh, C.L., Yang, W.J., 2013. Formation of MAX solid solutions $(Ti,V)_2AlC$ and $(Cr,V)_2AlC$ with Al_2O_3 addition by SHS involving aluminothermic reduction. *Ceramics International* 39, 7537–7544.
- Zhang, H., Hu, T., Wang, X., *et al.*, 2015b. Discovery of carbon-vacancy ordering in Nb_4AlC_{3-x} under the guidance of first-principles calculations. *Scientific Reports* 5, 14192.
- Zhang, H.B., Hu, C.F., Sato, K., *et al.*, 2015a. Tailoring Ti_3AlC_2 ceramic with high anisotropic physical and mechanical properties. *Journal of the European Ceramic Society* 35, 393–397.
- Zhang, H.B., Zhou, Y.C., Bao, Y.W., Li, M.S., 2004. Improving the oxidation resistance of Ti_3SiC_2 by forming a $Ti_3Si_{0.9}Al_{0.1}C_2$ solid solution. *Acta Materialia* 52, 3631–3637.
- Zhang, H.Z., Wang, S.Q., 2007. First-principles study of Ti_3AC_2 ($A = Si, Al$) (001) surfaces. *Acta Materialia* 55, 4645–4655.
- Zhang, J., Liu, B., Wang, J.Y., Zhou, Y.C., 2009. Low-temperature instability of Ti_2SnC : A combined transmission electron microscopy, differential scanning calorimetry, and x-ray diffraction investigations. *Journal of Materials Research* 24, 39–49.

- Zheng, L.L., Sun, L.C., Li, M.S., Zhou, Y.C., 2011. Improving the high-temperature oxidation resistance of $\text{Ti}_3(\text{SiAl})\text{C}_2$ by Nb-doping. *Journal of the American Ceramic Society* 94, 3579–3586.
- Zhou, Y.C., Meng, F., Zhang, J., 2008. New MAX-phase compounds in the V-Cr-Al-C system. *Journal of the American Ceramic Society* 91, 1357–1360.
- Zhou, Y.C., He, L.F., Lin, Z.J., Wang, J.Y., 2013. Synthesis and structure-property relationships of a new family of layered carbides in Zr-Al(Si)-C and Hf-Al(Si)-C systems. *Journal of the European Ceramic Society* 33, 2831–2865.
- Zhu, J., Mei, B., Xu, X., Liu, J., 2004. Synthesis of single-phase polycrystalline Ti_3SiC_2 and Ti_3AlC_2 by hot pressing with the assistance of metallic Al or Si. *Materials Letters* 58, 588–592.
- Zou, Y., Sun, Z.M., Tada, S., Hashimoto, H., 2006. Synthesis reactions for Ti_3AlC_2 through pulse discharge sintering $\text{Ti}/\text{Al}_4\text{C}_3/\text{TiC}$ powder mixture. *Scripta Materialia* 55, 767–770.
- Zou, Y., Sun, Z.M., Tada, S., Hashimoto, H., 2007. Rapid synthesis of single-phase Ti_3AlC_2 through pulse discharge sintering a $\text{TiH}_2/\text{Al}/\text{TiC}$ powder mixture. *Scripta Materialia* 56, 725–728.

ZrB₂, HfB₂, OsB₂ and IrB₂ Boride Ceramics: Processing, Structure, and Properties

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Introduction

Like carbon, boron forms strong covalent bonds with its three valence electrons. But being electron deficient, it cannot form 3D networks with two-center covalent bonding alone (Mori, 2008). Boron is a metalloid, so although its bonding electrons favor metallic behavior, they are strongly localized and insulating states emerge (Oganov *et al.*, 2009; Zhai *et al.*, 2014). Boron tends to form clusters in which B₁₂ icosahedra or cubo-octahedra are common structural units (Wiberg *et al.*, 2001; Greenwood and Earnshaw, 1997; Gogotsi and Andrievski, 1999; Higashi, 2000). Within the B-clusters, the valence electron density is high, so boron-rich solids feature strong covalent bonding and correspondingly high melting point, high hardness, low compressibility, yet light weight and low coefficient of thermal expansion. These properties make X-borides good candidates for use in applications involving extreme conditions where other materials fail, including: abrasives; cutting tools; lightweight armor; fiber reinforcement; neutron shielding; nuclear reactor control rods; sand-blaster nozzles; turbines blades; thermal protection systems (TPS) for rockets; electron emitting cathodes for electron microscopy; thermocouples; thermoelectrics; and many other amazing applications (Nabhani, 2001; Orton and Scuderi, 1998; Monteverde and Savino, 2012).

Boron has high affinity for transition- and rare-earth metals, which form many interesting borides. These include metallic B (Häussermann *et al.*, 2003); binary compounds: B₄C, ZrB₂, HfB₂, MgB₂, TiB₂, AlB₂, ReB₂, OsB_{1.1}, AuB₂, Os₂B₃, OsB₂, RhB₂, RuB₂, PtB₂, IrB₂, CrB₄, MnB₄, WB₄, LaB₆, SiB₆, CeB₆, PrB₆, NbB₆, ZrB₁₂, HfB₁₂, AlB₁₂, YB₁₂, YB₆₆ (Thevenot and Roy, 1991; Sonber and Suri, 2011; Wuchina *et al.*, 2004; Buzea and Yamashita, 2001; Basu *et al.*, 2006; Xiao-Lin *et al.*, 2006; Liang and Zhang, 2007; Stuparević and Živković, 2004; Hebbache *et al.*, 2006; Gou *et al.*, 2006; Wang *et al.*, 2012; Gou *et al.*, 2012); ternary compounds: AlMgB₁₄, ErAlB₁₄, AlCrB₁₄ (Muthu *et al.*, 2008; Liu *et al.*, 2013; Roberts *et al.*, 2009); and many other B compounds (Gu *et al.*, 2008; Weinberger *et al.*, 2009; Rau and Latini, 2009; Ivanovskii, 2012; Lazar *et al.*, 2009). Metal atoms provide additional electrons that stabilize structures, resulting in new properties. When M is a rare earth, adding even small amounts of C, N, or Si leads to complex ternaries, like MB_{15.5}CN, MB₂₂C₂N, MB_{28.5}C₄, MB₁₈Si₅. Although most borides are *p*-type conductors or semiconductors (Mori and Nishimura, 2006), homologous M-B-C(N) borides are *n*-type conductors (Mori, 2008). Very few borides have a band gap above 2 eV (Peditakis *et al.*, 2010; Hubert *et al.*, 1998), so most are darkly colored or opaque and unsuitable for optical applications.

Borides are attracting great interest (Kaner *et al.*, 2009; Chung *et al.*, 2008; Chen *et al.*, 2006; Aydin and Simsek, 2009) due to the demand for high-performance materials (Cutler, 1991). ReB₂, OsB₂, IrB₂, RuB₂, CrB₄, WB₄, IrB₂, IrB_{1.1}, IrB_{1.35} and related borides with remarkable properties were reported by: Xie *et al.* (2015a), Suh *et al.* (2007), Živković and Stuparević (2005) and Deligoz *et al.* (2012). ReB₂, OsB₂, and IrB_x received special attention for their extreme stiffness and incompressibility, which results from the high B-B and M-B bond covalency (Xie, 2014; Levine *et al.*, 2008; La Placa and Post, 1962). ReB₂-type hexagonal OsB₂ that exhibits ultra-high hardness (31 ± 9 GPa) and Young's modulus (574 ± 112 GPa), a ReB₂-type IrB₂ and IrB monophase were reported by: Xie *et al.* (2015b, 2014a,b), Orlovskaya *et al.* (2018, 2014) and Xie *et al.* (2015c, 2016a,b). Nanoindentation of OsB₂ revealed a reversible "pop-in" event during loading and unloading, which evidences a previously unknown high-pressure AlB₂-type OsB₂ phase. Upon heating, *hex*-OsB₂ exhibits a *negative* thermo-chemical expansion in the crystallographic *a*-direction (Xie *et al.*, 2014a,b). This points to a super-hard, stiff OsB₂ phase with unexpected thermal and mechanical behavior (Levine *et al.*, 2009; Knappschneider *et al.*, 2013). Yet, the properties of recently synthesized IrB₂, IrB (Xie *et al.*, 2016a, 2015c; Orlovskaya *et al.*, 2014), and many other binary and ternary compounds remain completely unexplored (Kempter and Fries, 1961). Here we report on the processing, structure, and properties of ZrB₂, HfB₂, OsB₂ and IrB₂ diboride ceramics.

Processing of ZrB₂, HfB₂, OsB₂, and IrB₂ Ceramics

All four diboride compounds reported are hard to synthesize and require high temperature sintering under pressure. ZrB₂ and HfB₂ ceramics can be sintered using commercially available powders; however, OsB₂ and IrB₂ powders are not available on the market and have to be synthesized using available techniques. One of the techniques reported for the synthesis of OsB₂ and IrB₂ powder composites is high energy ball milling or mechanochemistry (Ivanov and Suryanarayana, 2000). A special milling process is usually employed using mills where high axial and shear forces are produced by frequent ball impact events, which fracture the particles followed by solid state diffusion reactions leading to the formation of the target compounds. Shear stress and strain play a major role in the mechanochemical synthesis as the shear strength of many compounds is much lower in comparison with their

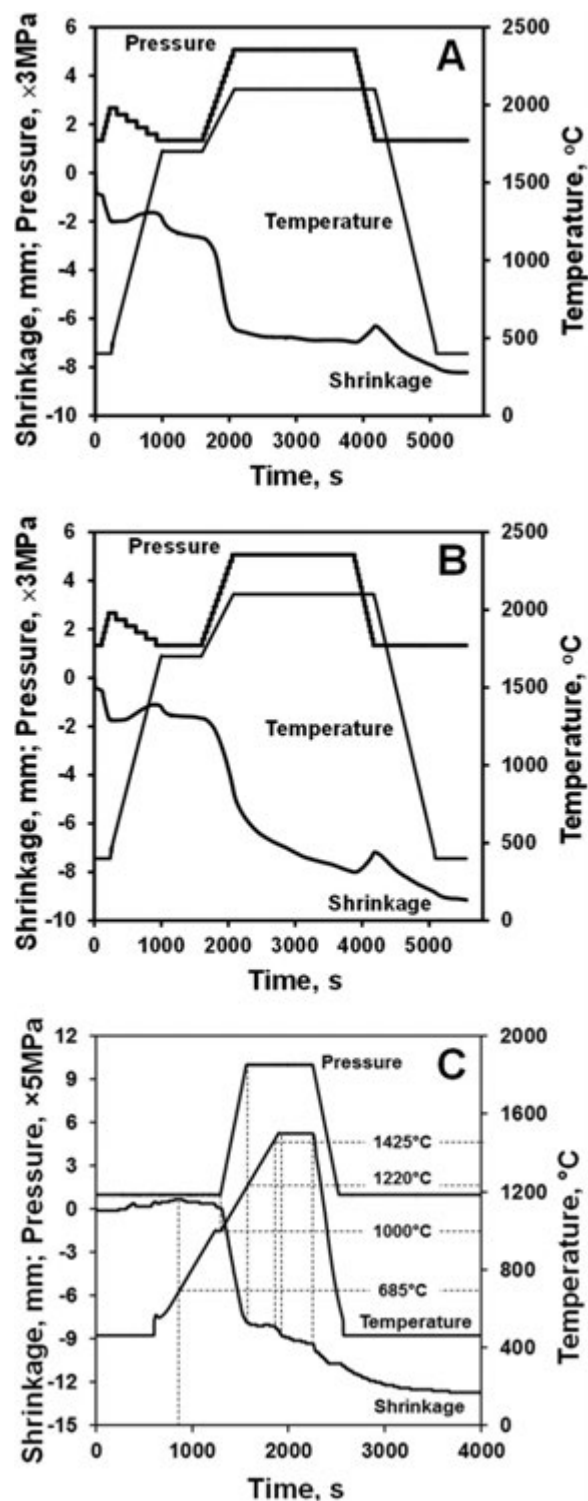


Fig. 1 Sintering regimes used for the densification of ZrB₂, HfB₂, and OsB₂ powders. Temperature, pressure, and shrinkage data as a function of time during spark plasma sintering are presented. (A) ZrB₂; (B) HfB₂; (C) OsB₂. Reproduced from Xie, Z., Lugovy, M., Orlovskaya, N., *et al.*, 2015b. Hexagonal OsB₂: Sintering, microstructure and mechanical properties *Journal of Alloys and Compounds* 634, 168–178.

compressive uniaxial strength. Therefore, if shear deformation is present, the solid-state synthesis could be favored over those techniques where only axial or hydrostatic pressure are acting alone. The level of applied axial and shear stresses present during mechanochemical synthesis was estimated by Xie *et al.* (2016a). These stresses result in plastic deformation of nanoparticles at the atomic level, which is very important to facilitate solid state chemical reactions using mechanochemistry.

Table 1 Microstructure parameters for OsB₂ after SPS

Composition	Grain size, μm	Porosity, %
ZrB ₂	18.52 ± 10.45	3
HfB ₂	2.75 ± 1.28	8.87
OsB ₂	0.56 ± 0.26	26.9

Mechanochemical high energy ball milling was used to synthesize ReB₂-type hexagonal OsB₂ and IrB₂ compounds (Orlovskaya *et al.*, 2018, 2014). Mechanochemical synthesis involving milling of Os and Ir metal powders with elemental B powders for extended period of time using WC media and balls allowed the production of the hexagonal OsB₂ and IrB₂ metastable high pressure phases for the first time (Xie *et al.*, 2014b, 2016a). Therefore, the mechanochemical approach was successfully used to synthesize previously unknown metastable OsB₂ and IrB₂ phases, which cannot be easily processed by other available means.

Spark Plasma Sintering has become a very popular sintering technique, where electric current activated sintering is used to sinter hard to densify materials, such as borides (Munir *et al.*, 2006). The SPS technique is used to densify powders under simultaneous application of an electric current and pressure. During this process, powders are packed in a graphite die and heating is conducted by passing a pulsed DC current through the die and, if sufficiently electrically conductive, the powders. This process coincides with the application of uniaxial pressure to the powders using graphite punches. Both high heating rates, electric currents, and application of pressure play a significant role in fast densification of the ceramics by SPS (Munir *et al.*, 2006; Dudina *et al.*, 2019). The advantages of SPS compared to pressureless sintering or hot pressing include shorter dwell time, lower sintering temperature and improved mechanical and physical properties of materials consolidated using the SPS technique.

SPS has been used to densify boride ceramics, such as ZrB₂ and HfB₂. The typical sintering conditions used for densifying ZrB₂ included heating rate of 100–150°C min⁻¹ and pressure of 15–100 MPa with a dwell of 5–35 min at temperatures between 1900 and 2100°C. In addition to the conventional SPS technique for processing of boride ceramics, the recently developed Flash Spark Plasma Sintering technique was used to densify borides. Grasso *et al.* (2014) achieved densification of pure ZrB₂ to above 95% relative density using a very rapid heating rate (4000°C min⁻¹), very short processing time (35 s) and temperature range 2100–2200°C.

The commercially available ZrB₂ and HfB₂ powders were sintered using SPS (SPS machine FCT HPD 25; FCT Systeme GmbH, Rauenstein, Germany). The sintering of both compounds was performed under identical processing conditions of 2100°C, heating rate of 100°C min⁻¹, 35 min dwell time and 15 MPa applied pressure (Fig. 1(A)). From the shrinkage plots, it can be seen that the densification behavior of ZrB₂ and HfB₂ are very different. Originally, upon heating from room temperature the equipment exhibits a small expansion, but when the pressure is increased from the initial minimum pressure, both materials shrink in a similar way. However, while the 15 MPa max pressure and 2100°C max temperature are reached at the same time, the shrinkage of the two powders behave differently. ZrB₂ experiences a sharp densification, with the shrinkage decreasing dramatically once the temperature and pressure reach their maximum (Fig. 1(A)). During the dwell time of 35 min there is very little further densification, which is indicative that ZrB₂ is fully dense or contains very little porosity. In fact, the densification of the ceramics suggests that during the dwell time ZrB₂ might experience significant grain growth behavior and that the dwell time during sintering of ZrB₂ at 2100°C might need to be shorter than 35 min to produce materials with fine grains. Unlike ZrB₂, HfB₂ did not densify completely by the time the temperature and pressure reached their maximums at 2100°C and 15 MPa, respectively (Fig. 1(B)). HfB₂ continued shrinking throughout the 35 min of the dwell time and, in fact, never reached the complete densification stage. Therefore, based on its shrinkage behavior, it was expected that a certain amount of porosity could be found and smaller grain size would be retained at the end of SPS processing of HfB₂.

The mechanochemically synthesized hexagonal OsB₂ powder was sintered using Spark Plasma Sintering (SPS) (SPS 25–10, Thermal Technologies, CA). The sintering of the powder packed in the graphite die was performed at 1500°C, 50 MPa for 5 min with heating and loading rates of 47°C min⁻¹ and 10 MPa min⁻¹ respectively. The sintering behavior of OsB₂ in terms of both temperature and pressure, along with a shrinkage plot, are shown in Fig. 1(C). As can be seen, at the beginning of the temperature increase, a small expansion of the material is observed up to 685°C; however when temperature exceeded 685°C, the slow shrinkage of OsB₂ became evident. At 1000°C a uniaxial pressure was applied, reaching 50 MPa at 1220°C, which resulted in a significant densification of the powder. Upon further temperature increase, a small shrinkage was further observed in the 1425–1500°C temperature range, followed by slow densification during a 5 min isothermal dwell at 1500°C. As the shrinkage did not stop during the isothermal dwell, it was apparent that the material did not fully densify and porosity was expected. Upon cooling, the shrinkage of the material continued, mainly due to temperature decrease. Therefore, by using the chosen sintering conditions, an incomplete densification of h-OsB₂ occurred and rather porous bulk material was produced (Xie *et al.*, 2015b). The porosity, phase composition and grain size of OsB₂ after SPS is given in Table 1. While ZrB₂, HfB₂, and OsB₂ were densified using SPS, to date IrB₂ and mixture of other Ir-B phases have not been sintered; their sintering behavior will be investigated in future work.

Table 2 The lattice parameters of all of the hexagonal ZrB₂, HfB₂, OsB₂ and IrB₂ phases

Composition	Space Group	Lattice parameters, Å		
		<i>a</i>	<i>c</i>	<i>a/c</i>
ZrB ₂	<i>P6₃/mmm</i>	3.17	3.53	0.898
HfB ₂	<i>P6₃/mmm</i>	3.14	3.48	0.902
OsB ₂	<i>P6₃/mmc</i>	2.916	7.376	0.395
IrB ₂	<i>P6₃/mmc</i>	2.926	7.543	0.388

Structure of ZrB₂, HfB₂, OsB₂, and IrB₂ Ceramics

Crystal Structure

The characterization of ZrB₂, HfB₂, OsB₂ and IrB₂ borides was performed to determine their crystal structure and phase composition using X-ray diffraction, and microstructure using X-ray diffraction as well as SEM coupled with EBSD and TEM coupled with SAED. Room temperature X-ray diffraction was used to determine the crystal symmetry, unit cell, and the lattice parameters of hexagonal ZrB₂, HfB₂, OsB₂ and IrB₂ diboride ceramics. Selected measurements were also performed at high temperature under inert, oxidizing and reducing atmospheres (Ar, N₂, air, O₂ or vacuum) by XRD to determine how environmental conditions affect the stability of the ZrB₂, OsB₂ and IrB₂ diboride ceramics (Xie *et al.*, 2015a, 2016b). It was determined that ZrB₂, HfB₂, OsB₂ and IrB₂ ceramics all have the hexagonal symmetry. However, it was determined that ZrB₂ and HfB₂ crystallize in the *P6₃/mmm* space group (Lawson *et al.*, 2011), while OsB₂ and IrB₂ crystallize in the *P6₃/mmc* space group (Xie *et al.*, 2014b). It was reported that at room temperature ZrB₂ and HfB₂ have lattice parameters, respectively, of *a* = 3.17 Å and *c* = 3.53 Å; and *a* = 3.14 Å and *c* = 3.48 Å, while those for OsB₂ and IrB₂ are *a* = 2.916 Å and *c* = 7.376 Å; and *a* = 2.926 Å and *c* = 7.543 Å, respectively. The *a/c* ratio was rather large for ZrB₂ and HfB₂ ceramics; however both OsB₂ and IrB₂ compounds had significantly lower *a/c* ratio (Table 2). It was also determined that ZrB₂ did not contain any detectable secondary phases, HfB₂ and OsB₂ contained small amounts of related secondary phases, while newly discovered IrB₂ was a secondary phase itself in the mixture of related secondary phases of IrB_{1.35} and IrB. The phase composition of ZrB₂, HfB₂, OsB₂, and IrB₂ compounds is shown in Table 3.

The X-ray diffraction patterns of hexagonal *P6₃/mmm* space group ZrB₂ and HfB₂ ceramics sintered at 2100°C using Spark Plasma Sintering are shown in Fig. 2. As can be seen from Fig. 2, ZrB₂ is phase pure, while HfB₂ after sintering contains a small amount of the monoboride HfB with cubic space group and lattice parameter *a* = 4.63 Å and monoclinic HfO₂ phase with *P2₁/a* space group and lattice parameters *a* = 5.29 Å; *b* = 5.16 Å; *c* = 5.14 Å. Unlike ZrB₂ and HfB₂, OsB₂ was crystallized into hexagonal *P6₃/mmc* space group lattice after high energy ball milling and a schematic presentation of this metastable ReB₂-type OsB₂ crystal structure is shown in Fig. 3. This structure consists of alternating layers of hexagonally arranged osmium and boron. Boron forms infinite sheets consisting of 6-membered rings in a chair configuration (Xie *et al.*, 2014b). This hexagonal ReB₂-type OsB₂ structure was predicted to have high bulk and shear moduli, *i.e.*, an improved hardness, due to the shortened Os-Os bonds as compared to the thermodynamically stable orthorhombic OsB₂ (Orlovskaya *et al.*, 2018).

An X-ray diffraction pattern of IrB₂ and related phases of Ir-B ceramics is shown in Fig. 4. A mixture of three Ir-B phases was reported, where IrB₂ diboride and IrB monoboride were reported to exist as minor phases in the batch with the IrB_{1.35} structure (Xie *et al.*, 2016a), similar to the reported hexagonal OsB₂ (Xie *et al.*, 2014b). A previously non-reported ReB₂-type IrB₂ structure as well as a new orthorhombic iridium monoboride (IrB) structure have been discovered in this work for the first time. The lattice parameters of all hexagonal ZrB₂, HfB₂, OsB₂ and IrB₂ phases are presented in Table 2.

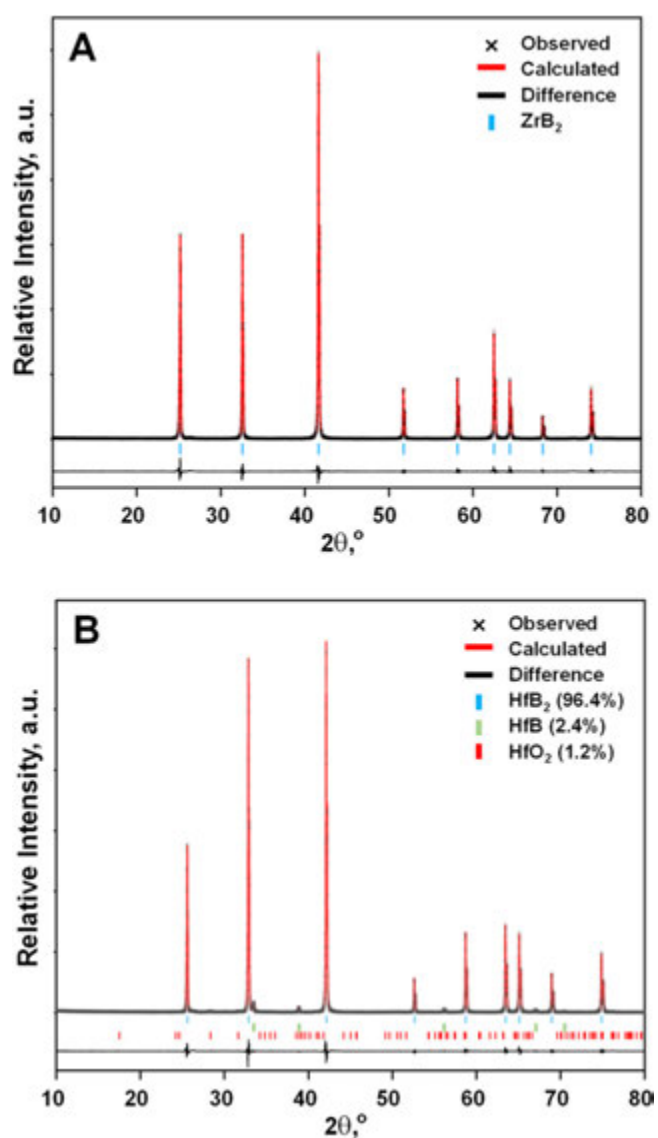
Microstructure

The microstructures of ZrB₂ and HfB₂ ceramics are shown in Fig. 5. While the same sintering conditions (2100°C, 15 MPa, 35 min dwell time) were used for processing of both ceramics, the sintering behavior of these two materials was very different, resulting in different mechanisms of grain growth, porosity, and even formation of texture during densification. The band contrast images of the microstructure revealed that ZrB₂ was well sintered, contained low porosity (<3%) and had an average grain size of 18.52 μm ± 10.45 μm. Apparently, significant solid state diffusion had occurred during sintering of ZrB₂ that was responsible for grain growth and complete densification. Texture also resulted as the sintering occurred under a uniaxial stress. The pole figures for ZrB₂ (Fig. 5(E)) show the presence of texture, thus making ZrB₂ ceramics slightly anisotropic after processing by SPS, where the basal (0001) planes were oriented perpendicular to the direction of the applied stress. Therefore, ZrB₂ exhibited some degree of anisotropy after densification.

Unlike ZrB₂, HfB₂ exhibited very different sintering behavior. While ZrB₂ was much more easy to densify and achieve full density, which was accompanied by significant grain growth, HfB₂ densified very differently under the same (2100°C, 15 MPa, and 35 min dwell time) sintering conditions as ZrB₂. It was not possible to fully sinter HfB₂ and it had a significant amount of porosity (up to 9%) and its average grain size was 2.75 μm ± 1.28 μm after densification. From such a difference, it might be concluded that solid state diffusion is much more limited in HfB₂, leading to significant residual porosity and much smaller average grain size, compared with ZrB₂. Also, no preferred crystallographic orientation was found to form after sintering, such that effectively

Table 3 The phase composition of processed ZrB₂, HfB₂, OsB₂, and IrB₂ compounds

Compound	Phases	Weight %
ZrB ₂	ReB ₂ -type ZrB ₂	100
HfB ₂	ReB ₂ -type HfB ₂	96.58
	HfB	2.32
	HfO ₂	1.1
OsB ₂	<i>h</i> -OsB ₂	80
	<i>o</i> -OsB ₂	20
IrB ₂	IrB _{1.35}	76.2
	ReB ₂ -type IrB ₂	7.7
	<i>o</i> -IrB	16.1

**Fig. 2** XRD refinement of ZrB₂ and HfB₂ samples after spark plasma sintering. (A) ZrB₂; (B) HfB₂.

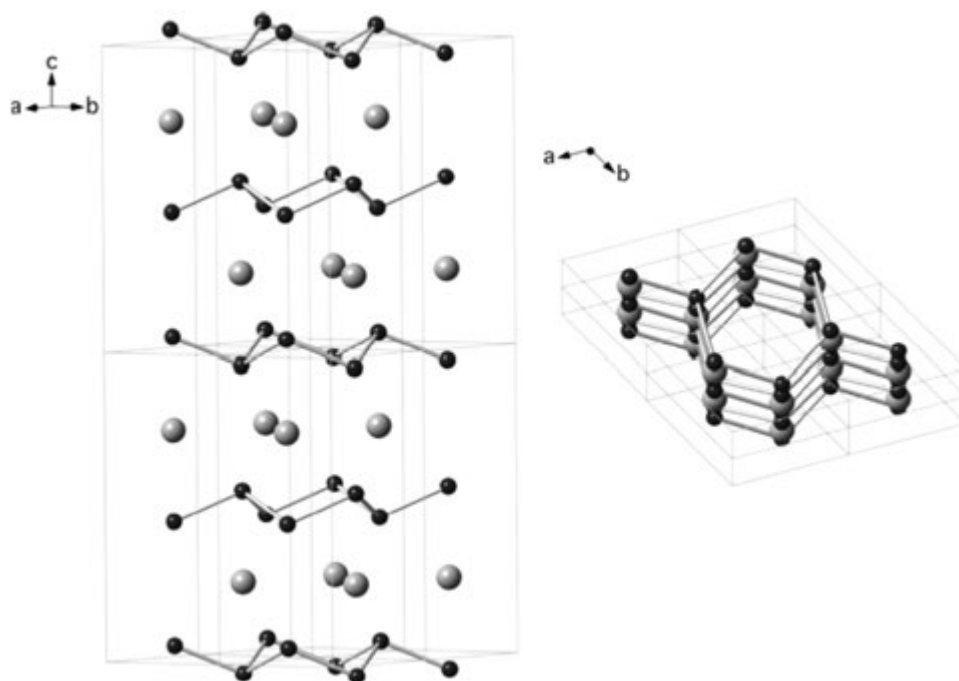


Fig. 3 Schematic representation of the crystal structure of ReB₂-type hexagonal OsB₂. The osmium atoms are the larger gray spheres, and boron atoms are the smaller black spheres. Reproduced from Xie, Z., Graule, M., Orlovskaya, N., *et al.*, 2014b. Novel high pressure hexagonal OsB₂ by mechanochemistry. *Journal of Solid State Chemistry* 215, 16–21.

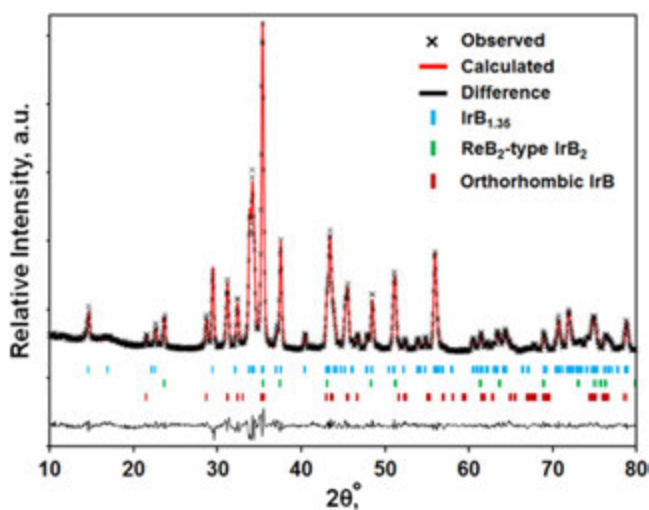


Fig. 4 XRD refinement of Ir-B powder mixture after 30 h of high energy ball milling and 48 h of annealing showing phases present. Reproduced from Xie, Z., Blair, R., Orlovskaya, N., *et al.*, 2016a. In search of the elusive IrB₂: Can mechanochemistry help? *Journal of Solid State Chemistry* 233, 108–119.

sintered HfB₂ was fully isotropic, despite the applied pressure used during sintering by SPS (**Fig. 5(F)**). The pole figures of HfB₂ indicated the absence of texture, thus showing this ceramic to be fully isotropic.

ZrB₂ and HfB₂ ceramics are both well-known and well characterized materials, and their powders are available from commercial vendors. It is impossible to source OsB₂ from commercial companies. Therefore, the powder of this compound was synthesized using mechanochemistry (Ivanov and Suryanarayana, 2000). As mechanochemistry employs high normal and deviatoric stresses accompanied by elevated temperatures during milling of Os and B powders, the process leads to the formation of metastable ReB₂-type hexagonal OsB₂, which was reported by Xie *et al.* (2014b). It was also possible to retain its hexagonal structure after densification at 1500°C by SPS. After such high temperature sintering, 80% of OsB₂ was retained as the hexagonal *P63/mmc* space group structure, while 20% was converted into the thermodynamically more stable orthorhombic OsB₂. The densification was not complete at this temperature, as shrinkage of the material was not completed (**Fig. 1(C)**), resulting in high

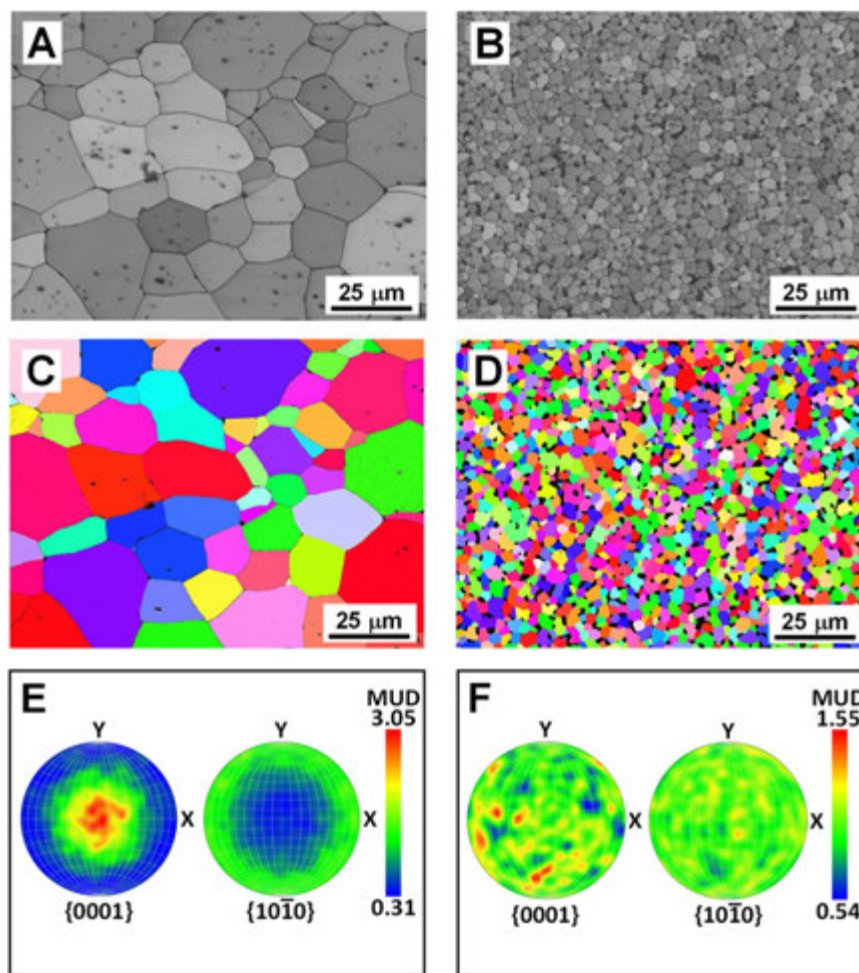


Fig. 5 SEM images (A), (B), EBSD grain orientation maps (C), (D), and pole figures (E), (F) of sintered ZrB₂ (A), (C), (E) and HfB₂ (B), (D), (F) ceramics.

residual porosity ($\sim 27\%$) and a relatively small submicron grain size after densification. The porosity and grain size of OsB₂ ceramics are listed in [Table 1](#). Electron backscatter diffraction (EBSD) was used to identify the structure of OsB₂ after sintering and, very similar to the X-ray analysis data, it was identified that 77.3 wt% of the grains belonged to the ReB₂-type OsB₂, while the remaining 22.7 wt% were identified as orthorhombic OsB₂ ([Fig. 6](#)). Some areas on the map ([Fig. 6\(A\)](#)), apparent as a black phase, were identified either as pores or as the rhombohedral boron (B) phase; however, it was not possible to index B due to a lack of signal and the limiting sensitivity of the equipment. The grain orientation of OsB₂ is shown in [Fig. 6](#), where no texture is possible to identify. Scanning Transmission Electron Microscopy (STEM) was also employed to analyze the OsB₂ ceramic structure after SPS and the micrographs of individual grains with hexagonal and orthorhombic structure are shown in [Fig. 7](#) along with their selected area diffraction patterns. The hexagonal grain, shown in [Fig. 7](#), exhibits the presence of well-defined linear defects, which could be either dislocations or even tiny microcracks present along the length of the grain. The presence of these defects is an indication of the brittle nature of OsB₂, since such defects might easily facilitate the brittle failure of the grain and be responsible for high overall brittleness of the OsB₂.

While it was possible to synthesize almost phase pure non-equilibrium ReB₂-type hexagonal OsB₂ and even partially retain this phase after high temperature sintering, only a small fraction of hexagonal IrB₂ phase was synthesized and retained after high energy ball milling of Ir and B powders ([Xie et al., 2016a](#)). The major phase was the thermodynamically stable IrB_{1.35} phase; however, small quantities of ReB₂-type IrB₂ phase were also detected along with IrB monoboride. A STEM micrograph of Ir-B particles after 30 h of milling and 48 h of annealing at 1050°C *in vacuo* (~ 7 Pa) are presented in [Fig. 8](#). The micrograph shows a mixture of different Ir-B phases, such as pure B, IrB_{1.35}, IrB and IrB₂ as shown in [Fig. 8\(A\)](#), where the ReB₂-type hexagonal IrB₂ structure was found among the particles shown in [Fig. 8\(A\)](#). The corresponding bright and dark field STEM images of the hexagonal IrB₂ phase oriented in the [100] direction are shown in [Fig. 8\(B\)](#) and [\(C\)](#), respectively. In addition to 30 h of high energy ball milling and 48 h of high temperature annealing at 1050°C *in vacuo*, a mixture of Ir and B nanoparticles was also milled for 90 h under similar high energy ball milling conditions ([Xie et al., 2016a](#)). A HRTEM image of a hexagonal IrB₂ nanoparticle is shown in [Fig. 9](#), where a Fourier transform (FFT) pattern shows the orientation of this particle in the [121] direction. Annealing for 72 h at

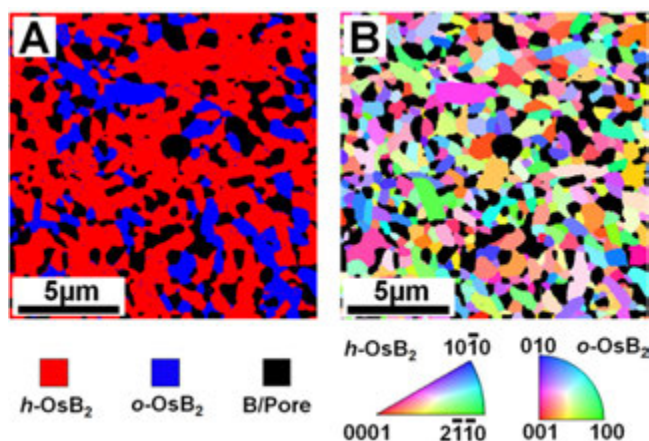


Fig. 6 EBSD phase map (A) and grain orientation map (B) of sintered OsB₂ ceramics, where the crystal structure-type (A) as well as crystallographic orientation of each individual OsB₂ grain (B) can be identified. Xie, Z., Lugovy, M., Orlovskaya, N., *et al.*, 2015b. Hexagonal OsB₂: Sintering, microstructure and mechanical properties *Journal of Alloys and Compounds* 634, 168–178.

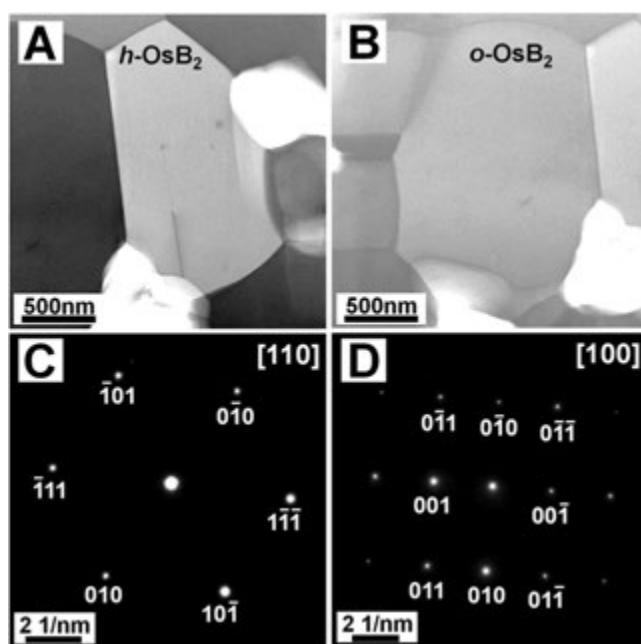


Fig. 7 TEM micrographs of hexagonal (A) and orthorhombic (B) OsB₂ grains with the corresponding electron diffraction patterns ((C) and (D), respectively). Reproduced from Xie, Z., Lugovy, M., Orlovskaya, N., *et al.*, 2015b. Hexagonal OsB₂: Sintering, microstructure and mechanical properties *Journal of Alloys and Compounds* 634, 168–178.

1050°C *in vacuo* of the Ir-B phases resulted in Ir atom segregation from the IrB₂ lattice along disoriented defective domains (Fig. 10). STEM and HAADF STEM images are presented in Fig. 10(A) and (B). Magnified images of selected lattice fringes of IrB₂ are shown in Fig. 10(C)–(E). The magnification is identical for the (C), (D) and (E) images. This segregation of Ir atoms along the disordered domains resulted in the formation of rows of single Ir atoms as well as Ir segregation into separate clusters, which might be important for use of this material as an active Ir based catalyst (Xie *et al.*, 2015c).

Nanoindentation of ZrB₂, HfB₂ and OsB₂ Ceramics

Methodology

Nanoindentation of ZrB₂ and HfB₂ ceramics was performed using a Hysitron TI Premier machine equipped with a Berkovich diamond tip at the University of Central Florida (UCF), Orlando, USA. A total of 25 indents were produced on the polished

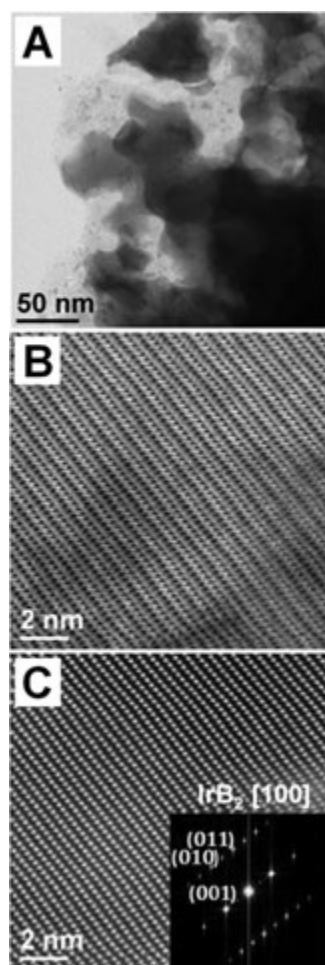


Fig. 8 STEM of the Ir and B mixture after 30 h of ball milling and 48 h of annealing (A). The corresponding bright and dark field STEM images of the hexagonal IrB_2 phase oriented in $[100]$ direction are shown in HRSTEM ((B) and (C), respectively). Reproduced from Xie, Z., Blair, R., Orlovskaya, N., *et al.*, 2016a. In search of the elusive IrB_2 : Can mechanochemistry help? *Journal of Solid State Chemistry* 233, 108–119.

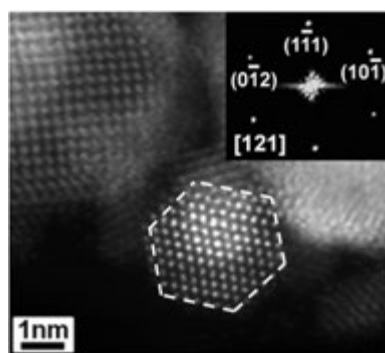


Fig. 9 HRTEM image of ReB_2 type hexagonal IrB_2 structure. Insert shows fast Fourier transform pattern of IrB_2 . Reproduced from Xie, Z., Terracciano, A., Cullen, D.A., Blair, R., Orlovskaya, N., 2015c. High temperature Ir segregation in Ir-B ceramics: Effect of oxygen presence on Stability of IrB_2 and other Ir-B phases. *Advances in Applied Ceramics* 114, 429–435.

surfaces of ZrB_2 and HfB_2 samples using a maximum load of 9.5 mN, which was held for 3 s at the maximum load between loading and unloading in load control mode. Nanoindentation of OsB_2 ceramic was performed using a Hysitron TI 950 nanoindenter equipped with a spheroconical diamond tip featuring a radius of 0.222 μm at Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland. The 50 nanoindentations were performed in displacement control mode with a maximum depth of penetration of 70 nm. The Oliver and Pharr method (Oliver and Pharr, 1992; Pharr *et al.*, 1992) was used to

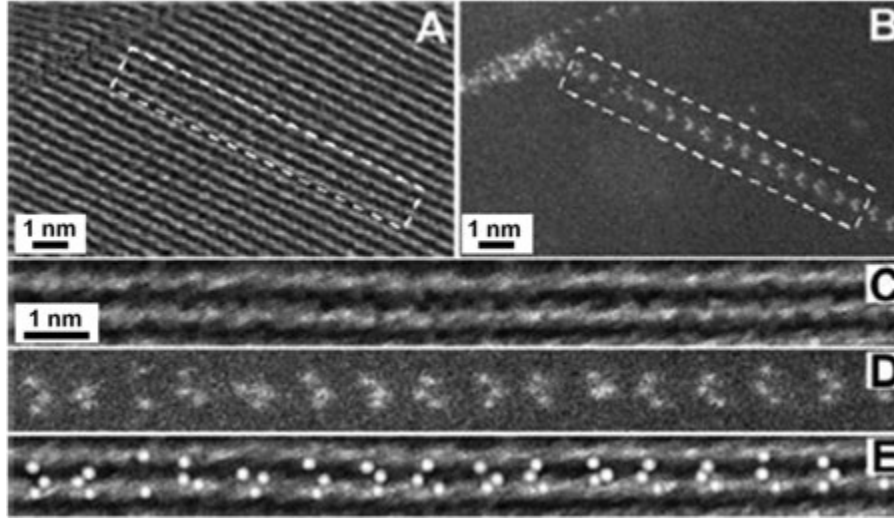


Fig. 10 Ir atoms segregated in IrB₂ along defect domains in the lattice. (A) STEM, (B) HAADF STEM, (C)–(E) magnified images of selected lattice fringes of IrB₂. The magnification is identical for the (C), (D) and (E) images. Reproduced from Xie, Z., Terracciano, A., Cullen, D.A., Blair, R., Orlovskaya, N., 2015c. High temperature Ir segregation in Ir-B ceramics: Effect of oxygen presence on Stability of IrB₂ and other Ir-B phases. *Advances in Applied Ceramics* 114, 429–435.

calculate the hardness and Young's modulus of ZrB₂, HfB₂ and OsB₂, assuming the diamond indenter and sample to be an elastically isotropic solid. The reduced modulus values, calculated for the diamond indenter – specimen system, is defined as:

$$\frac{1}{E_r} = \frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_i^2}{E_i} \quad (1)$$

where ν is the Poisson's ratio, E is the Young's modulus, and the subscripts s and i refer to the specimen and the indenter, respectively. From the unloading part of the load-displacement curve the effective E_r can be estimated as:

$$E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}} \quad (2)$$

where S is taken as the slope of the unloading curve at the beginning of unloading and A is the projected contact area. A is determined from a nanoindenter area function $A(h_c)$, where h_c is the distance from the contour of contact to the maximum penetration depth. The following expression was proposed for the computation of h_c (Oliver and Pharr, 1992):

$$h_c = h - \frac{3P}{4S} \quad (3)$$

where h and P are the displacement and the load from measured nanoindentation diagram. It was determined that the area function $A(h_c)$ can be presented by the following equations:

$$A(h_c) = C_0 h_c^2 + C_1 h_c + C_2 h_c^{1/2} + C_3 h_c^{1/4} + C_4 h_c^{1/8} + C_5 h_c^{1/16} \quad (4a)$$

$$A(h_c) = -3.14 h_c^2 + 1397 h_c [\text{nm}^2] \quad (4b)$$

for Berkovich and spheroconical diamond nanoindenters, respectively.

Note that C_0 , C_1 , C_2 , C_3 , C_4 , and C_5 are the coefficients determined for a given Berkovich indenter from a series of indents at various contact depths in a sample of known elastic modulus (typically fused quartz), and $C_0 = 24.5$ for an ideal Berkovich probe. The hardness of the material was determined using the following standard equation:

$$H = \frac{P}{A} \quad (5)$$

where P is the maximum load of nanoindentation, A can be found using Eq. (4) or from a SEM image of the corresponding impression.

The mean contact pressure was calculated for a Berkovich tip indenter as (Kuliev et al., 2020):

$$p_i = \frac{P_i}{A_i} \quad (6)$$

where P_i is the current indentation load on the load – indenter displacement diagram (P_i may be taken directly from indentation data points); A_i is the contact area that may be determined by using the area function:

$$A_i = C_0 (h_c)_i^2 + C_1 (h_c)_i + C_2 (h_c)_i^{1/2} + C_3 (h_c)_i^{1/4} + C_4 (h_c)_i^{1/8} + C_5 (h_c)_i^{1/16} \quad (7)$$

where $(h_c)_i$ is the contact depth corresponding to P_i which can be calculated as:

$$(h_c)_i = h_i - (h_e)_i \quad (8)$$

Table 4 Mechanical properties of ZrB₂, HfB₂, and OsB₂ by nanoindentation

Composition Indenter	ZrB ₂ Berkovich	HfB ₂ Berkovich	OsB ₂ Spheroconical
<i>H</i> , GPa	43 ± 3	34 ± 11	31 ± 9
<i>E_r</i> , GPa	349 ± 8	322 ± 48	446 ± 87
Poisson ratio	0.12	0.13	0.18
<i>E</i> , GPa	494 ± 11	440 ± 66	574 ± 112
<i>I_E</i>	0.12	0.11	0.05
<i>I_D</i>	0.29	0.3	0.45
Pop-in	No	Yes	Yes

where h_i is the total measured indenter displacement corresponding to P_i (h_i may be taken directly from indentation data points); $(h_e)_i$ is the corresponding elastic deflection (Novikov *et al.*, 1996; Oliver and Pharr, 1992; Sneddon, 1965):

$$(h_e)_i = (h_e)_{\max} \sqrt{\frac{P_i}{P_{\max}}} = \varepsilon \frac{P_{\max}}{S} \sqrt{\frac{P_i}{P_{\max}}} \quad (9)$$

where $(h_e)_{\max}$ is the elastic deflection at maximum load $P_{\max}$ of the indentation diagram; S is the slope at the beginning of the unloading portion of the indentation diagram which is the unloading stiffness; ε is a constant that depends on the indenter's geometry ($\varepsilon=0.75$ for Berkovich indenter). After calculation the mean contact pressure can be plotted against the contact depth.

From the contact area A for spherical indentation the radius of contact for certain h and P can be calculated as:

$$a = \sqrt{\frac{A}{\pi}} \quad (10)$$

Once the radius is calculated, then the following equations were used for conversion of load-displacement into indentation stress-indentation strain plots (Pathak *et al.*, 2008):

$$\sigma_{\text{ind}} = \frac{P}{\pi a^2} \quad (11)$$

and

$$\varepsilon_{\text{ind}} = \frac{4}{3\pi} \frac{h}{a} \quad (12)$$

By converting load-displacement data into indentation stress-indentation strain plots, the elastic part:

$$\sigma_{\text{ind}} = E_r \varepsilon_{\text{ind}} \quad (13)$$

of the loading segment of the nanoindentation diagram can be revealed as well as a yield point, where the deviation from linear behavior and the onset of plastic deformation can be visualized.

The material can be also characterized by elasticity and ductility indices. The elasticity index is defined as (Xie *et al.*, 2015b):

$$I_E = H/E_r \quad (14)$$

where H is the hardness and E_r is the reduced modulus (Sakai, 1999; Malzbender, 2003; Chen and Bull, 2006). The elasticity indices of the most brittle ceramics range from 0.3 to 0.05 and of ductile metals from 0.005 to 0.001 (Sakai, 1999; Malzbender, 2003). The indentation ductility index is defined as follows (Sakai, 1999):

$$I_D = \frac{U_r}{U_t} = \frac{h_r}{h_{\max}}, \quad (15)$$

where U_r is the consumed energy for creating the residual impression, U_t is the total work at maximum load, h_r is the residual depth of indentation as measured from the load-displacement diagram after complete unloading, $h_{\max}$ is the maximum depth of indentation at maximum load. The ductility index must be 1 for a purely plastic (purely ductile) body without elastic recovery during unloading and 0 for a purely elastic body exhibiting a complete unloading recovery in an elastic manner. With the increase in the elasticity index, the ductility index decreases from 1 to 0 (Sakai, 1999).

Hardness, Young's Modulus, Indentation Stress – Indentation Strain Behavior, Elasticity and Ductility Indices of ZrB₂, HfB₂ and OsB₂

The average hardness and Young's modulus values of ZrB₂ were measured to be 43 ± 3 GPa and 494 ± 11 GPa, respectively (Table 4). Such high values of hardness and elastic modulus can be explained by the very high density/short bond lengths of ZrB₂. A typical load-displacement nanoindentation diagram of ZrB₂ is shown in Fig. 11(A), and almost identical deformation behavior was observed for all indentations. One characteristic feature of all these diagrams is the lack of any discontinuities both upon loading and upon unloading during nanoindentation. On conversion of load-displacement plots into a mean contact pressure - indentation contact depth diagram (Fig. 11(B)) the maximum mean contact pressure was in the range of 47–51 GPa,

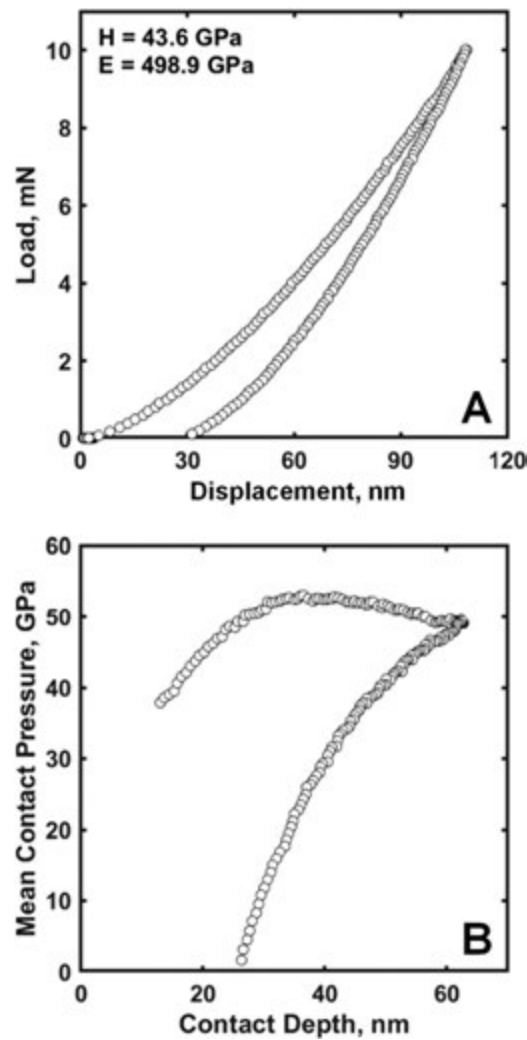


Fig. 11 Nanoindentation load-displacement (A) and mean contact pressure-contact depth (B) curves for ZrB₂ during loading and unloading.

which related very well to the average hardness value of ZrB₂. Elasticity and ductility indices of ZrB₂ ceramics were also calculated (Table 4).

The average hardness and Young's modulus values of HfB₂ were measured to be 34 ± 11 GPa and 440 ± 66 GPa. While these are still considered to be very high values of mechanical properties for HfB₂, they are lower than those reported for ZrB₂. Such lower values can possibly be explained by the presence of porosity in the sample but also by the intrinsic behavior of HfB₂. A typical load-displacement nanoindentation diagram of HfB₂ is shown in Fig. 12(A) and the corresponding mean contact pressure – contact depth diagram is shown in Fig. 12(B). Unlike ZrB₂, the deformation behavior of HfB₂ during nanoindentation was characterized by the presence of “pop-in” events during loading. These “pop-ins” were almost always present and they characterized a small mean contact pressure drop, possibly due to crack formation and propagation to relieve tensile stress at the corners of the Berkovich indents during indentation. The maximum mean contact pressure was in the range of 38–41 GPa, which again, similar to the ZrB₂ values, represents very well the average hardness values of HfB₂. The mean contact pressure values measured both for ZrB₂ and HfB₂ are above the average hardness values measured by dividing maximum load by the contact area of impressions. Elasticity and ductility indices of HfB₂ ceramics were also calculated and they are presented in Table 4.

The average hardness and Young's modulus values of OsB₂ were measured to be 31 ± 9 GPa and 574 ± 112 GPa, respectively. This newly identified hexagonal OsB₂ material exhibited quite high hardness and very high stiffness, which corresponds very well with high valence electron density present in this compound (Xie *et al.*, 2015b; Chung *et al.*, 2008). The typical load-displacement nanoindentation diagram of OsB₂ is shown in Fig. 13(A). As can be seen, “pop-in” events are present during the loading portion of the deformation plot. It was found that out of all 50 load-displacement deformation plots, 36 of them featured “pop-in” events at the loading portion of the plots. The “pop-in” events are present even more prominently, when load displacement diagrams are recalculated into indentation stress – indentation strain plots (Fig. 13(B)). From Fig. 13(B) it can

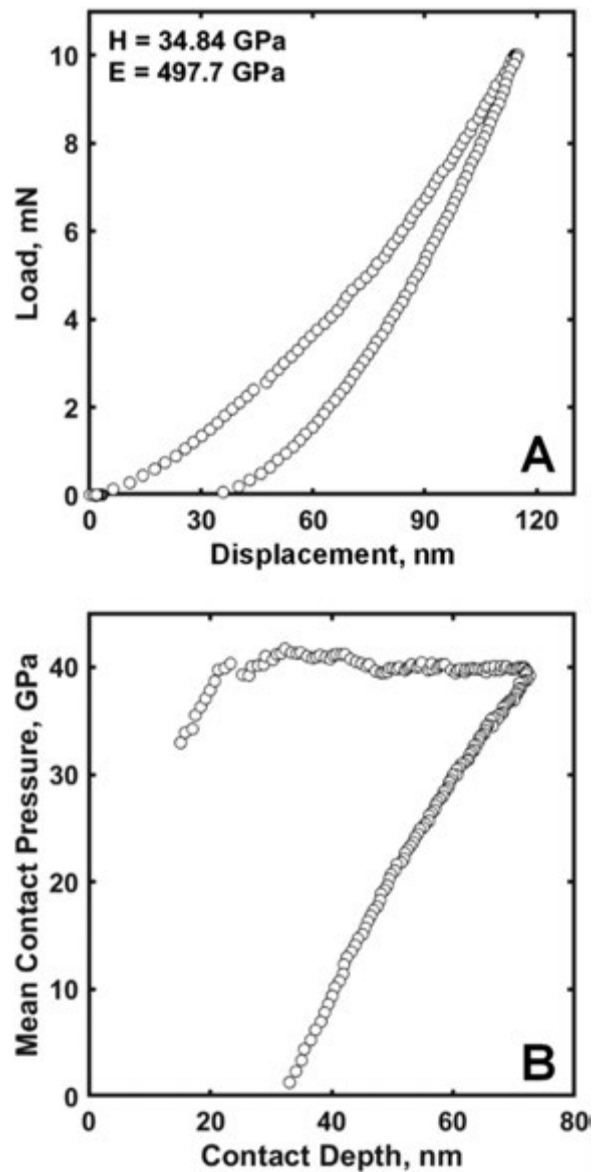


Fig. 12 Nanoindentation load-displacement (A) and mean contact pressure-contact depth (B) curves for HfB₂ during loading and unloading.

be seen that a very high stress level existed below the spheroconical diamond indenter during indentation, and thus such conversion makes it possible to see the indentation deformation behavior of OsB₂ during contact loading. The “yield” stress could also be estimated from such indentation stress – indentation strain diagrams and for OsB₂ an example of “yield” stress equal to 20 GPa evaluated from the diagram is shown in Fig. 13(B). The average “yield” stress value calculated using all 36 indentation plots was equal to 23 ± 7 GPa. The nanoindentation experiments indicated that OsB₂ phases are relatively hard and rather stiff with high yield stress values, as determined by their hardness, Young’s modulus, “yield” stress, and indentation stress – indentation strain deformation behavior.

The elasticity and ductility indices of ZrB₂, HfB₂ and OsB₂ ceramics were calculated according to Eqs. (14) and (15). The results of the calculation are presented in Table 4. The computed elasticity index I_E was high and equal to 0.12 and 0.11 for ZrB₂ and HfB₂ ceramics, respectively, while it was significantly lower and equal to 0.05 for OsB₂. The computed ductility index I_D was equal to 0.29 and 0.30 for ZrB₂ and HfB₂, respectively; however the value was higher and equal to 0.45 for OsB₂. For comparison, the I_E of Al₂O₃, SiC and Si₃N₄ ceramics are equal to 0.08, 0.13, and 0.175, respectively, and their I_D values are equal to 0.68, 0.57, and 0.59, respectively (Sakai, 1999). For glass, I_E and I_D are equal to 0.19 and 0.54, respectively. Thus, the elasticity indices of ZrB₂ and HfB₂ are very close in values to those of SiC ceramics, but the I_E of OsB₂ is located in the lower range for all materials. Ductility indices of all three diboride ceramics are much lower, in comparison even with a glass. Such low values of both indices of ZrB₂, HfB₂ and OsB₂ reflect the highly brittle nature of these ceramics.

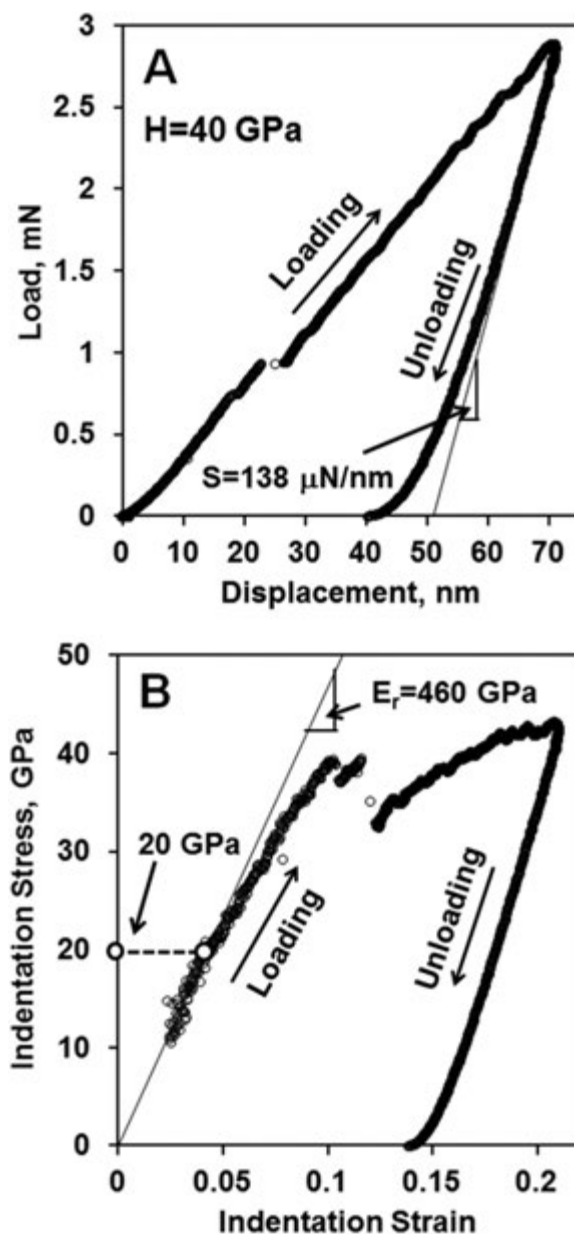


Fig. 13 Load-displacement (A) and recalculated indentation stress – indentation strain (B) diagrams produced by nanoindentation of polished OsB₂ surface where “pop-in” events were present during the loading portion of the load-displacement curve. Reproduced from Xie, Z., Lugovy, M., Orlovskaya, N., *et al.*, 2015b. Hexagonal OsB₂: Sintering, microstructure and mechanical properties *Journal of Alloys and Compounds* 634, 168–178.

Summary

The processing, structure, and properties of ZrB₂, HfB₂, OsB₂, and IrB₂ diboride ceramics have been presented. While ZrB₂ and HfB₂ powders are commercially available, OsB₂ and IrB₂ have been synthesized by mechanochemistry for the first time. ZrB₂, HfB₂, and OsB₂ can be densified using the Spark Plasma Sintering technique. Almost fully dense ZrB₂ was sintered at 2100°C, 15 MPa and 35 min dwell time; however densification of HfB₂ under the same conditions was limited and ~9% of porosity was retained after sintering. Such difference indicates that ZrB₂ is easier to sinter in comparison with HfB₂. An attempt to sinter hexagonal OsB₂ was successful; however only ~80% of hexagonal OsB₂ was retained after sintering at 1500°C, 50 MPa and 5 min dwell time, while the other ~20% was transformed into the thermodynamically stable orthorhombic OsB₂ phase. OsB₂ also contained a high amount of porosity (~27%), and thus more work on the optimization of the sintering conditions is required to achieve fully dense hexagonal OsB₂.

All four diboride compounds were studied by X-ray diffraction to determine their phase composition and lattice parameters. It was found that only ZrB₂ is a phase pure material with no secondary phase found, while HfB₂ contained HfB monoboride and HfO₂ as minor secondary phases. OsB₂ after sintering contained a mixture of the metastable hexagonal and thermodynamically

stable orthorhombic phases; however, the hexagonal ReB₂ type IrB₂ was not a major phase in a mixture of Ir-B phases, and only constituted 7.7 wt%, while the thermodynamically stable IrB_{1.35} was the major phase with an amount equal to 76.2 wt% with the rest of the mixture present as orthorhombic IrB monoboride. The microstructure of all four diborides were investigated by SEM, EBSD, and TEM techniques.

The mechanical properties, such as hardness, Young's modulus, indentation deformation behavior, and elasticity and ductility indices of ZrB₂, HfB₂, and OsB₂ ceramics were studied by nanoindentation. All three ceramics exhibited high hardness, which varied from 31 ± 9 GPa for OsB₂ to 43 ± 3 GPa for ZrB₂. Indeed, their Young's modulus values were also very high: 574 ± 112 GPa for OsB₂, 494 ± 11 GPa for ZrB₂, and 440 ± 66 GPa for HfB₂. It was found that ZrB₂ does not exhibit any "pop-in" events during loading and unloading, thus showing that this material is able to accommodate severe plastic deformation caused by nanoindentation using the sharp Berkovich indenter without microcracking or a phase transition. However both HfB₂ and, especially, OsB₂ experienced "pop-ins" during loading, which were most likely caused by microcracking due to appearance of high stresses. All three diboride compounds showed a very brittle nature as indicated by their elasticity and ductility indices. The mechanical behavior of IrB₂ and other Ir – B phases will be studied in the future, where purer IrB₂ powder will be synthesized and sintered using Spark Plasma Sintering or other relevant techniques.

References

- Aydin, S., Simsek, M., 2009. First-principles calculations of MnB₂, TcB₂, and ReB₂ within the ReB₂-type structure. *Physical Review B* 80, 134107.
- Basu, B., Raju, G.B., Suri, A.K., 2006. Processing and properties of monolithic TiB₂ based materials. *International Materials Reviews* 51 (6), 352–374.
- Buzea, C., Yamashita, T., 2001. Review of the superconducting properties of MgB₂. *Superconductor Science and Technology* 14 (11), R115.
- Chen, J., Bull, S.J., 2006. A critical examination of the relationship between plastic deformation zone size and Young's modulus to hardness ratio in indentation testing. *Journal of Materials Research* 21, 2617–2627.
- Chen, Z.Y., Xiang, H.J., Yang, J., Hou, J.G., Zhu, Q., 2006. Structural and electronic properties of OsB₂: A hard metallic material. *Physical Review B* 74 (1), 012102.
- Chung, H.-Y., Weinberger, M., Yang, J.-M., Tolbert, S., Kaner, R., 2008. Correlation between hardness and elastic moduli of the ultraincompressible transition metal diborides RuB₂, OsB₂, and ReB₂. *Applied Physics Letters* 92, 261904.
- Cutler, R.A., 1991. Engineering properties of borides. In: Schneider, S.J. (Ed.), *Ceramics and Glasses. Engineering Materials Handbook*, vol. 4. Materials Park, OH: ASM International, pp. 787–803.
- Deligoz, E., Colakoglu, K., Ciftci, Y.O., 2012. Lattice dynamical and thermodynamical properties of ReB₂, RuB₂, and OsB₂ compounds in the ReB₂ structure. *Chinese Physics B* 21 (10), 106301.
- Dudina, D.V., Bokhonov, B.B., Olevsky, E.A., 2019. Fabrication of porous materials by spark plasma sintering: A review. *Materials* 12 (3), 541.
- Gogotsi, Y.G., Andrievski, R.A., 1999. *Materials Science Of Carbides, Nitrides and Borides*. St. Petersburg, Russia: Kluwer Academic Publishers, (NATO Science Partnership Sub-Series: 3).
- Gou, H., Hou, L., Zhang, J., *et al.*, 2006. First-principles study of low compressibility osmium borides. *Applied Physics Letters* 88, 221904.
- Gou, H., Li, Z., Niu, H., *et al.*, 2012. Unusual rigidity and ideal strength of CrB₄ and MnB₄. *Applied Physics Letters* 100 (11), 111907.
- Grasso, S., Saunders, T., Porwal, H., *et al.*, 2014. Flash spark plasma sintering (FSPS) of pure ZrB₂. *Journal of the American Ceramic Society* 97 (8), 2405–2408.
- Greenwood, N.N., Earnshaw, A., 1997. *Chemistry of the Elements*. Burlington, MA: Elsevier Butterworth–Heinemann.
- Gu, Q., Krauss, G., Steurer, W., 2008. Transition metal borides: Superhard versus ultra-incompressible. *Advanced Materials* 20 (19), 3620–3626.
- Häussermann, U., Simak, S.I., Ahuja, R., Johansson, B., 2003. Metal-nonmetal transition in the boron group elements. *Physical Review Letters* 90 (6), 065701.
- Hebbache, M., Stuparević, L., Živković, D., 2006. A new superhard material: Osmium diboride OsB₂. *Solid State Communications* 139 (5), 227–231.
- Higashi, I., 2000. Crystal Chemistry of α -AlB₁₂ and γ -AlB₁₂. *Journal of Solid State Chemistry* 154, 168–176.
- Hubert, H., Garvie, L.A.J., Devouard, B., *et al.*, 1998. High-pressure, high-temperature synthesis and characterization of boron suboxide (B₂O₃). *Chemistry of Materials* 10 (6), 1530–1537.
- Ivanov, E., Suryanarayana, C., 2000. Materials and process design through mechanochemical routes. *Journal of Materials Synthesis and Processing* 8 (3–4), 235–244.
- Ivanovskii, A.L., 2012. Mechanical and electronic properties of diborides of transition 3d–5d metals from first principles: Toward search of novel ultra-incompressible and superhard materials. *Progress in Materials Science* 57 (1), 184–228.
- Kaner, R.B., Tolbert, S.H., Kavner, A., *et al.*, 2009. Rhenium boride compounds and uses thereof, Patent Application No. US 2009/0274897 A1.
- Kempton, C.P., Fries, R.J., 1961. Crystallography of the Ru-B and Os-B systems. *The Journal of Chemical Physics* 34 (6), 1994–1995.
- Knappschneider, A., Litterscheid, C., Dzyvenko, D., *et al.*, 2013. Possible superhardness of CrB₄. *Inorganic Chemistry* 52 (2), 540–542.
- Kuliev, R., Orlovskaya, N., Hyer, H., *et al.*, 2020. Spark plasma sintered B₄C – Structural, thermal, electrical and mechanical properties. *Materials* 13 (7), 1612.
- La Placa, S.J., Post, B., 1962. The crystal structure of rhenium diboride. *Acta Crystallographica* 15 (2), 97–99.
- Lawson, J.W., Bauschlicher Jr, C.W., Daw, M.S., 2011. Ab initio computations of electronic, mechanical, and thermal properties of ZrB₂ and HfB₂. *Journal of the American Ceramic Society* 94 (10), 3494–3499.
- Lazar, P., Chen, X.-Q., Podlousky, R., 2009. First-principles modeling of hardness in transition-metal diborides. *Physical Review B* 80, 012103.
- Levine, J.B., Nguyen, S.L., Rasool, H.I., *et al.*, 2008. Preparation and properties of metallic, superhard rhenium diboride crystals. *Journal of the American Chemical Society* 130 (50), 16953–16958.
- Levine, J.B., Tolbert, S.H., Kaner, R.B., 2009. Advancements in the search for superhard ultra-incompressible metal borides. *Advanced Functional Materials* 19, 3519–3533.
- Liang, Y., Zhang, B., 2007. Mechanical and electronic properties of superhard ReB₂. *Physical Review B* 76 (13), 132101.
- Liu, W., Wu, Y.-T., Mao, S.-H., *et al.*, 2013. Field-activated, pressure-assisted synthesis of ultra-hard, super-abrasive AlMgB₁₄. *Journal of Materials Engineering and Performance* 22 (4), 983–987.
- Malzbender, J., 2003. Comment on hardness definitions. *Journal of the European Ceramic Society* 23, 1355–1359.
- Monteverde, F., Savino, R., 2012. ZrB₂ – SiC sharp leading edges in high enthalpy supersonic flows. *Journal of the American Ceramic Society* 95, 2282–2289.
- Mori, T., 2008. Higher borides. In: Gschneidner, K.A., Bünzli, J.-C.G., Pecharsky, V.K. (Eds.), *Handbook on the physics and chemistry of rare earths*, first ed., V. 38. Elsevier, pp. 105–173.
- Mori, T., Nishimura, T., 2006. Thermoelectric properties of homologous p- and n-type boron-rich borides. *Journal of Solid State Chemistry* 179, 2908–2915.
- Munir, Z.A., Anselmi-Tamburini, U., Ohyanagi, M., 2006. The effect of electric field and pressure on the synthesis and consolidation of materials: a review of the spark plasma sintering method. *Journal of Materials Science* 41 (3), 763–777.
- Muthu, D.V.S., Chen, B., Cook, B.A., Kruger, M.B., 2008. Effects of sample preparation on the mechanical properties of AlMgB₁₄. *High Pressure Research* 28, 63–68.
- Nabhani, F., 2001. Wear mechanisms of ultra-hard cutting tools materials. *Journal of Materials Processing Technology* 115, 402–412.

- Novikov, N.V., Dub, S.N., Milman, Y.V., Gridneva, I.V., Chugunova, S.I., 1996. Application of nanoindentation method to study a semiconductor-metal phase transformation in silicon. *Journal of Superhard Materials* 18 (3), 32–40.
- Oganov, A.R., Chen, J., Gatti, C., *et al.*, 2009. Ionic high-pressure form of elemental boron. *Nature* 457, 863–867.
- Oliver, W.C., Pharr, G.M., 1992. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *Journal of Materials Research* 7, 1564–1583.
- Orlovskaya, N., Xie, Z., Blair, R.G., 2014. Mechanochemical synthesis and applications of new IrB₂ and IrB powders. U.S. Provisional Patent, Serial No.: 62/069,299.
- Orlovskaya, N., Xie, Z., Blair, R., 2018. Mechanochemical synthesis of hexagonal OsB₂. US Patent 9 926 204 B2.
- Orton, G., Scuderi, L., 1998. A hypersonic cruiser concept for the 21st century. In: *Proceedings of the AIAA and SAE, World Aviation Conference*.
- Pathak, S., Kalidindi, S.R., Klemen, C., Orlovskaya, N., 2008. Analyzing indentation stress-strain response of LaGaO₃ single crystals using spherical indenters. *Journal of the European Ceramic Society* 28, 2213–2220.
- Pediaditakis, A., Schroeder, M., Sagawe, V., Ludwig, T., Hillebrecht, H., 2010. Binary boron-rich borides of magnesium: Single-crystal investigations and properties of MgB₇ and the new boride Mg_(~5)B₍₄₄₎. *Inorganic Chemistry* 49, 10882–10893.
- Pharr, G., Oliver, W., Brotzen, F., 1992. On the generality of the relationship among contact stiffness, contact area and elastic modulus during indentation. *Journal of Materials Research* 7, 613–617.
- Rau, J.V., Latini, A., 2009. New hard and superhard materials: Rhb_{1.1} and IrB_{1.35}. *Chemistry of Materials* 21 (8), 1407–1409.
- Roberts, D., Zhao, J., Munir, Z., 2009. Mechanism of reactive sintering of MgAlB₁₄ by pulse electric current. *International Journal of Refractory Metals & Hard Materials* 27, 556–563.
- Sakai, M., 1999. The Meyer hardness: A measure for plasticity? *Journal of Materials Research* 14, 3630–3639.
- Sneddon, I.N., 1965. The relation between load and penetration in the axisymmetric Boussinesq problem for a punch of arbitrary profile. *International Journal of Engineering Science* 3, 47–57.
- Sonber, J.K., Suri, A.K., 2011. Synthesis and consolidation of zirconium diboride: Review. *Advances in Applied Ceramics* 110 (6), 321–334.
- Stuparević, L., Živković, D., 2004. Phase diagram investigation and thermodynamic study of Os-B system. *Journal of Thermal Analysis and Calorimetry* 76 (3), 975–983.
- Suh, B.J., Zong, X., Singh, Y., Niazi, A., Johnston, D.C., 2007. ¹¹B NMR in the layered diborides OsB₂ and RuB₂. *Physical Review B* 76, 144511.
- Thevenot, F., Roy, P.R., 1991. A Review on Boron Carbide. Switzerland: Trans Tech Publications.
- Wang, D.Y., Wang, B., Wang, Y.X., 2012. New crystal structures of IrB and IrB₂: First-principles calculations. *The Journal of Physical Chemistry C* 116 (41), 21961–21966.
- Weinberger, M.B., Levine, J.B., Chung, H.-Y., *et al.*, 2009. Incompressibility and hardness of solid solution transition metal diborides: Os_{1-x}Ru_xB₂. *Chemistry of Materials* 21 (9), 1915–1921.
- Wiberg, N., Holleman, A.F., Wiberg, E., 2001. *Inorganic Chemistry*. San Diego, CA: Academic Press.
- Wuchina, E., Opeka, M., Causey, S., *et al.*, 2004. Designing for ultrahigh-temperature applications: The mechanical and thermal properties of HfB₂, HfC_x, HfN_x and α -Hf(N). *Journal of Materials Science* 39 (19), 5939–5949.
- Xiao-Lin, Z., Ke, L., Xiang-Rong, C., Jun, Z., 2006. Structural and thermodynamic properties of AlB₂ compound. *Chinese Physics* 15 (12), 3014.
- Xie, Z., 2014. Rhenium, osmium and iridium diborides by mechanochemistry: Synthesis, structure, thermal stability and mechanical properties. PhD Thesis, University of Central Florida.
- Xie, Z., Blair, R., Orlovskaya, N., *et al.*, 2016a. In search of the elusive IrB₂: Can mechanochemistry help? *Journal of Solid State Chemistry* 233, 108–119.
- Xie, Z., Blair, R., Orlovskaya, N., *et al.*, 2016b. Oxygen interaction with hexagonal OsB₂ at high temperature. *Journal of the American Ceramic Society* 99, 4057–4065.
- Xie, Z., Blair, R., Orlovskaya, N., Cullen, D., Payzant, E.A., 2014a. Thermal stability of hexagonal OsB₂. *Journal of Solid State Chemistry* 219 (01), 210–219.
- Xie, Z., Graule, M., Orlovskaya, N., *et al.*, 2014b. Novel high pressure hexagonal OsB₂ by mechanochemistry. *Journal of Solid State Chemistry* 215, 16–21.
- Xie, Z., Blair, R., Orlovskaya, N., Payzant, E.A., 2015a. Hexagonal OsB₂ reduction upon heating in H₂ containing environment. *Advances in Applied Ceramics* 114 (2), 114–120.
- Xie, Z., Lugovy, M., Orlovskaya, N., *et al.*, 2015b. Hexagonal OsB₂: Sintering, microstructure and mechanical properties. *Journal of Alloys and Compounds* 634, 168–178.
- Xie, Z., Terracciano, A., Cullen, D.A., Blair, R., Orlovskaya, N., 2015c. High temperature Ir segregation in Ir-B ceramics: Effect of oxygen presence on Stability of IrB₂ and other Ir-B phases. *Advances in Applied Ceramics* 114, 429–435.
- Zhai, H.-J., Zhao, Y.-F., Li, W.-L., *et al.*, 2014. Observation of an all-boron fullerene. *Nature Chemistry* 6, 727–731.
- Živković, D., Stuparević, L., 2005. Calculation of thermodynamic properties in the Ir-B system based on the known phase diagram. *Materials and Geoenvironment* 52 (2), 463–468.

Directionally-Solidified Eutectic Oxide Ceramics

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Excellent chemical stability in oxidizing atmospheres makes ceramic oxides suitable for high-temperature structural applications. However, the poor strength retention, creep resistance, and the presence of low melting point intergranular phases deteriorate the mechanical behavior of conventional ceramics above 1100 °C. Alternatively, single-crystal oxides present superior creep resistance up to 1500 °C but their strength is sometimes impaired due to slow crack growth. These limitations can be successfully eliminated in the directionally-solidified eutectic (DSE) ceramics grown from melt. DSE ceramic oxides are envisaged as ultra-high-temperature functional and structural materials, which may find use in structural applications, photonics, electronic devices, and magnetic applications and also as structured substrates (Llorca and Orera, 2006; Merino *et al.*, 2003).

This is the case for the sapphire-based $\text{Al}_2\text{O}_3/\text{c-ZrO}_2$, $\text{Al}_2\text{O}_3/\text{Y}_3\text{Al}_5\text{O}_{12}/\text{YSZ}$, $\text{Al}_2\text{O}_3/(\text{RE})\text{AP}$ (RE (rare earth) = Sm, Eu, Gd), and $\text{Al}_2\text{O}_3/(\text{RE})\text{AG}$ (RE = Sm–Lu, Y) eutectics. These systems consist of cubic zirconia, perovskite, or garnet phases of micron or nanometer size, dispersed into the continuous sapphire single crystalline phase. The combination of the outstanding creep behavior of Al_2O_3 along its *c*-axis with a huge amount of clean and strong grain boundaries, characteristic of the eutectic solids, results in a new set of ceramic oxides with excellent creep behavior and good mechanical properties up to 1700 °C even in corrosive environments. This makes sapphire-based eutectics useful in the fields of aeronautics and aerospace, gas turbines, and power generation industries (Waku *et al.*, 1997).

The present article briefly reviews these DSE oxides and also some spinel- $(\text{MgAl}_2\text{O}_4)$ and ZrO_2 -based eutectics under the light of recent developments. The emphasis is on the relationships between growth parameters and microstructure, hence on the influence of the microstructure in the mechanical properties of these compounds.

Oxide Eutectics: Composition Microstructure and Preparation

Microstructure

Eutectics grown from the melt give rise to homogeneous, highly-structured dense materials. The basic microstructure of a regular eutectic consists of nonfaceted phases either single-crystal rods or lamellae embedded in a single-crystal matrix as depicted in Figures 1 and 2. In the simplest case of isotropic surface energy, fibers instead of lamellae are found for volume fractions of the minority phase less than 28%. When the fusion entropy is high, the eutectic microstructure is complex because the growth interface cannot deviate from certain crystal orientations and faceted phases are produced (Hunt and Jackson, 1966). In the DSE oxides described in this article, simple regular microstructures are an exception more than a rule. The tendency of Al_2O_3 to develop facets leads to complex microstructure morphologies where cells with degenerated lamellae or rod eutectic structures are usually interspersed in regular regions in the same sample (Orera and Peña, 2012).

The most favorable situation from the point of view of mechanical properties and high-temperature stability (Peña *et al.*, 2002) is when the phases are continuously entangled in a three-dimensional interpenetrating (TDI) network as depicted in Figure 3. This homogeneous and fine microstructure free of grain boundaries are produced under low solidification rates for which the growth mode is more co-operative. In contrast with metallic eutectics, TDI microstructures are also found in faceted/faceted oxide systems. In case of facets, the microstructure exhibits the aspect of Figure 4 referred to in the literature as Chinese Script (CS) microstructure. Recently, superplastic behavior has been observed in some nanofibrillar directionally-solidified ternary eutectic oxides grown at high growth rates (Pastor *et al.*, 2013).

The microstructure size is growth-rate dependent. In the simple, nonfaceted/nonfaceted regular eutectics, the interphase spacing λ depends on the solidification rate R as $\lambda^2 \cdot R = C$, where C is known as the interphase spacing law constant. In the case of DSE oxides, the microstructure size always decreases with increasing growth rate. For eutectics with simple regular or TDI microstructures, the solidification rate rule still holds. Interphase spacing is typically in the 0.2–10 μm range. The composition, melting temperature, and C -value for the oxide eutectics covered in this article are given in Table 1. The physical properties of the component phases are summarized in Table 2.

Preparation

For homogeneous growth, large axial thermal gradients are usually needed to keep micro- and macroscopically flat solid–liquid interfaces during growth, thus preventing cellular growth (Ashbrook, 1977). Among the different directional solidification

[†]This chapter is dedicated to the memory of Víctor Manuel Orera Clemente.

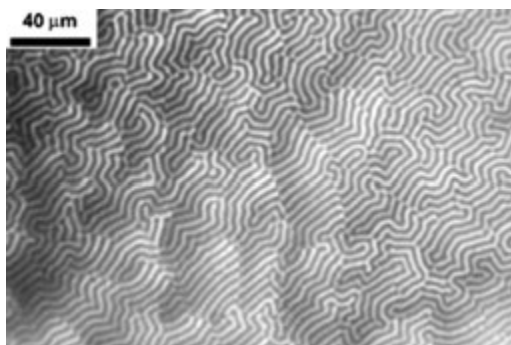


Figure 1 Optical microscope image of the lamellar eutectic microstructure of a CaSZ/CaZrO₃ DSE. The bright phase is the YSZ.

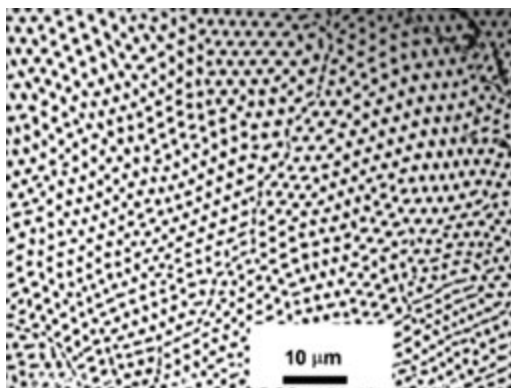


Figure 2 Scanning electron microscope (SEM) image of the fibrous eutectic microstructure of a MgO/MgSZ DSE. The dark phase is MgO.

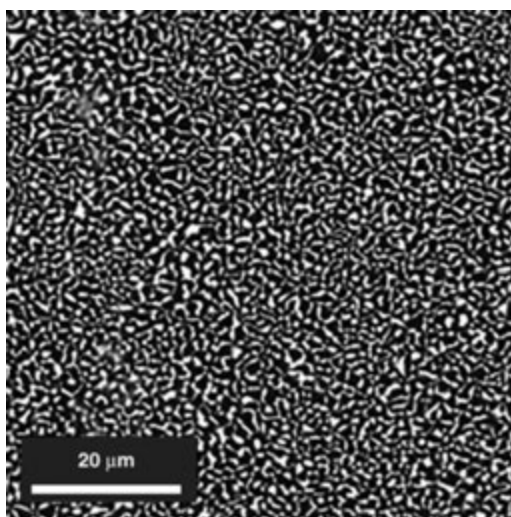


Figure 3 TDI microstructure typical of Al₂O₃/YSZ eutectic solidified at low growth speed (10 mm h⁻¹). The bright phase is YSZ (SEM image).

procedures to grow oxide ceramic eutectics (Stubican and Bradt, 1981), the Bridgman method uses relatively low thermal gradients ($< 10^2$ K cm⁻¹) and low growth rates (< 100 mm h⁻¹) resulting in bulk samples with interphase spacing larger than 1 μm. Micro-pulling down (μ -PD), Stepanov, and edge-defined film growth (EFG) methods with thermal gradients of the order of 10^3 K cm⁻¹ allow the growth of shaped samples at relatively high growth rates (up to a few m h⁻¹). Processing techniques based on floating zone are crucibleless methods in which a relatively small amount of sample volume is melted by the action of lasers, or r.f. or light waves. Thermal gradients can be very large, up to 10^4 K cm⁻¹, allowing fast growing rates in the coupled growth regime. These

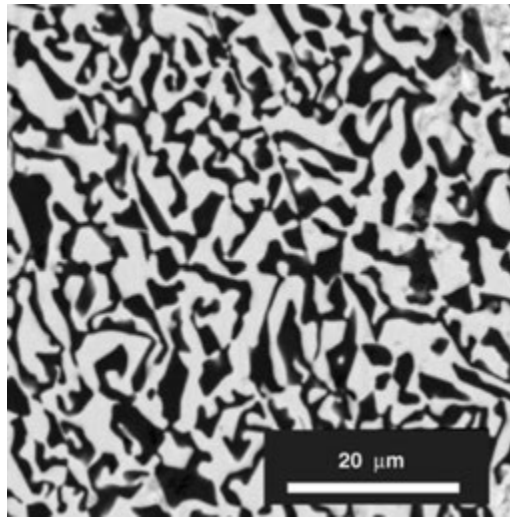


Figure 4 Chinese Script microstructure characteristic of $\text{Al}_2\text{O}_3/\text{YAG}$ DSE grown at 25 mm h^{-1} . The bright phase is YAG (SEM image).

Table 1 Component phases, melting point, eutectic composition, and C -value for some oxide eutectics

Components	Melting point (K)	Composition (%wt)	% Volume minor phase	C ($\mu\text{m}^3 \text{s}^{-1}$)
$\text{YSZ}^a/\text{Al}_2\text{O}_3$	2135	42 YSZ + 58 Al_2O_3	32.7 YSZ	11
$\text{Al}_2\text{O}_3/\text{Y}_3\text{Al}_5\text{O}_{12}$	2100	33.5 Y_2O_3 + 66.5 Al_2O_3	45 Al_2O_3	100
$\text{CaZrO}_3/\text{CaSZ}^b$	2525	23.5 CaO + 76.5 ZrO_2	41 CaSZ	400
MgO/MgSZ^c	2445	27 MgO + 73 ZrO_2	28 MgO	50
$\text{Al}_2\text{O}_3/\text{Er}_3\text{Al}_5\text{O}_{12}$	2075	52.5 Al_2O_3 + 47.5 Er_2O_3	42.5 Al_2O_3	120
$\text{Al}_2\text{O}_3/\text{EuAlO}_3$	1985	46.5 Al_2O_3 + 53.5 Eu_2O_3	44 Al_2O_3	
$\text{Al}_2\text{O}_3/\text{GdAlO}_3$	2015	47 Al_2O_3 + 53 Gd_2O_3	48 Al_2O_3	6.3
$\text{MgAl}_2\text{O}_4/\text{MgO}$	2270	45 MgO + 55 Al_2O_3	23.5 MgO	150
$\text{Al}_2\text{O}_3/\text{Er}_3\text{Al}_5\text{O}_{12}/\text{ErSZ}$	1990	45 Al_2O_3 + 39.7 Er_2O_3 + 15.3 ZrO_2	21 ErSZ	53
$\text{YSZ}/\text{NiAl}_2\text{O}_4$	2270	54 NiAl_2O_4 + 46 YSZ	39 YSZ	8
CaSZ/NiO	2115	61 NiO + 39 CaSZ	44 CaSZ	32.5
CaSZ/CoO	2025	64 CoO + 36 CaSZ	38.5 CaSZ	25
CeO_2/NiO	1925	50.3 NiO + 49.7 CeO_2	48 CeO_2	36
CeO_2/CoO	1925	66.5 CoO + 33.5 CeO_2	31.5 CeO_2	41
CaF_2/MgO	1625	10 MgO + 90 CaF_2	9 MgO	68
$\text{Al}_2\text{O}_3/\text{Y}_3\text{Al}_5\text{O}_{12}/\text{YSZ}$	1990	54 Al_2O_3 + 27 Y_2O_3 + 19 ZrO_2	18 YSZ	70
$\text{Mn}_3\text{O}_4/\text{YMnSZ}$	1800	75 Mn_2O_3 + 25 YSZ	21 YMnSZ	7.15

^aTetragonal or cubic stabilized zirconia.

^bCalcium stabilized zirconia $\text{Ca}_{0.25}\text{Zr}_{0.75}\text{O}_{1.75}$.

^cMagnesium stabilized zirconia $\text{Mg}_{0.2}\text{Zr}_{0.8}\text{O}_{1.8}$.

methods are suitable to grow fibers down to tens of microns in diameter. Some interesting variations of the laser float zone method (LFZ) have been recently reported, which take advantage of laser spots in the form of narrow lines to produce directional solidified eutectic plates up to 0.5 mm in thickness (Orera *et al.*, 2012). This latter method is very promising for coatings and surface processing (Larrea *et al.*, 2002, 2005).

Crystallography

In eutectics the single-crystal phases grow along well-defined crystallographic directions generally corresponding to interfacial energy minima. Nevertheless, in most of the DSE oxides presented here, relationships among the crystallographic orientations do not necessarily correspond to surfaces of lowest interfacial energy. In fact, the large fusion entropy and anisotropy of Al_2O_3 enhance the contribution of growth kinetics in developing the interfaces. The growth-rate dependence of the microstructure morphology can be roughly understood as follows. At low growth rates, a planar solidification front is formed and coupled growth results in homogeneous eutectic TDI microstructures. As the growth-rate increases, colonies with ordered eutectic structures in the

Table 2 Crystallographic and physical properties of individual component phases

Compound	Symmetry ^a	Space group	Density (g cc ⁻¹)	Melting point T _m (K)	Thermal expansion ($\times 10^6$ K ⁻¹) ^b
α -Al ₂ O ₃	R	R $\bar{3}$ c	3.987	2327	8.8 $\parallel$ to <i>c</i> -axis 7.9 $\perp$ to <i>c</i> -axis
Y ₃ Al ₅ O ₁₂ (YAG)	C	Ia $\bar{3}$ d	4.554	2210	8.9
Er ₃ Al ₅ O ₁₂ (ErAG)	C	Ia $\bar{3}$ d	6.432	2235	
EuAlO ₃ (EuAP)	O	Pbnm	7.246	2320	
GdAlO ₃ (GdAP)	O	Pbnm	7.443	2342	
MgO	C	Fm $\bar{3}$ m	3.583	3105	13
Y _{0.16} Zr _{0.84} O _{1.92} (YSZ) ^c	C	Fm $\bar{3}$ m	5.94	3110	10.6
CaZrO ₃	O	Pcmn	4.82	2825	15.1 $\parallel$ to <i>a</i> -axis 10.9 $\parallel$ to <i>b</i> -axis 4.9 $\parallel$ to <i>c</i> -axis
MgAl ₂ O ₄	C	Fd $\bar{3}$ m	3.577	2408	8.8

^aAbbreviations used for symmetry: C, cubic; R, rhombohedral; O, orthorhombic.

^bAveraged values 25–1000 °C.

^cStabilizer type and amount can alter values of stabilized zirconia.

center start to develop. Finally, eutectics grown at very high growth rates show a cellular structure comprising very elongated cells parallel to the growth axis. The microstructure within the cells consists of very fine TDI resulting from the co-operative growth of both phases, as in the rods grown at low rates. Multiple orientation relationships have been reported for these systems, which can be, to some extent, modified by appropriate changes of the growth parameters. This is the case, for example, of Al₂O₃–YAG (Table 3).

The mutual orientation of the component phases has a marked influence on the residual stresses, microstructure morphology, stability, and mechanical properties of the material. This is the case for some simple DSE oxides such as MgO/MgSZ, MgAl₂O₄/MgO, and CaZrO₃/CaSZ although in the latter the relative orientation between lamellae may accommodate some misalignment (see Table 3).

Mechanical Properties

The properties of primary importance for high-temperature applications are the resistance to chemical and thermochemical corruptions, the maximum operating temperature, mechanical properties such as stiffness, toughness and hardness, thermal conductivity and expansion, and density. Impact, erosion, wear resistance, as well as creep resistance are also important for some applications. The components of the DSE oxides described in this article (crystalline sapphire, oxide perovskites, oxide garnets, spinel, and zirconia) are among the best high-temperature materials for oxidizing ambient. The decrease of the melting point of DSE oxides (see Table 1) is fully compensated by the increase in strength and creep resistance due to the presence of large surface fraction of clean, strong interfaces as well as by the lack of susceptibility to stress corrosion cracking. Table 4 summarizes some relevant mechanical properties of DSE oxides. The best mechanical properties at ambient and elevated temperatures are found in the binary Al₂O₃–YAG and the pseudo-binary Al₂O₃–ZrO₂(Y₂O₃) systems and are described in detail below.

Al₂O₃–YAG

This eutectic presents an excellent potential as structural material for high-temperature applications in oxidizing environments due to (1) the good creep resistance of both phases, (2) the strong interfacial bonding between the eutectic domains, (3) their interpenetrating morphology which impedes free dislocation motion in each phase, (4) the absence of amorphous phases at the interfaces, and (5) its inherent microstructural and chemical stability up to temperatures very close to the eutectic point. Matson and Hecht (1999), Waku *et al.* (2001), and Pastor *et al.* (2004) have measured the strength at ambient temperatures in eutectics with domain thickness, λ , in the range 0.2 to 25 μ m and their results are compiled in Figure 5. The strength is proportional to $1/\sqrt{\lambda}$, indicating that the critical defects responsible for brittle fracture depend on the size of the eutectic domains. In fact, when the critical defects are semicircular surface cracks with a radius equal to λ , the eutectic tensile and flexure strength, σ_u , is given by (according to fracture mechanics)

$$\sigma_u = \frac{\sqrt{\pi} K_C}{2 \sqrt{\lambda}} \quad [1]$$

Table 3 Microstructure and crystallography of DSE oxides

Eutectic	Microstructure	Solidification direction	Orientation relationships
YSZ/Al ₂ O ₃ ^a	CR and TDI	$(\bar{1}10\bar{2})_A$ $(\bar{1}10)_Z$	$(\bar{1}10\bar{2})_A \parallel (\bar{1}10)_Z$ $[02\bar{2}1]_A \parallel [111]_Z$
YSZ/Al ₂ O ₃ ^a	Fibrous (YSZ) in Colonies	$[0001]_A$ $\langle 001 \rangle_Z$ or $\langle 123 \rangle_Z$	$(0001)_A \parallel (010)_Z$ $[2\bar{1}\bar{1}0]_A \parallel [010]_Z$ $[01\bar{1}0]_A \parallel [001]_Z$
Al ₂ O ₃ /Y ₃ Al ₅ O ₁₂ ^a	CR and ChS	$(155)_{YAG}$, $(0001)_A$	$(0001)_A \parallel (111)_{YAG}$ $(0001)_A \parallel [1\bar{2}1]_{YAG}$ $(0101)_A \parallel (011)_{YAG}$ $[1120]_A \parallel [211]_{YAG}$
CaZrO ₃ /CaSZ ^b	Lamellar	$\approx [112]_{CaSZ}$ $\approx [101]_{CaZO}$	$\approx (100)_{CaSZ} \parallel (011)_{CaZO}$ $\approx (010)_{CaSZ} \parallel (100)_{CaZO}$
MgO/MgSZ	Fibrous (MgO)	$[111]_{MgO}$ $[111]_{MgSZ}$	$(hkl)_{MgO} \parallel (hkl)_{MgSZ}$
Al ₂ O ₃ /Er ₃ Al ₅ O ₁₂ ^a	CR and TDI	$\approx c\text{-axis Al}_2\text{O}_3$ $\approx [110]_{ErAG}$	
Al ₂ O ₃ /GdAlO ₃	CR and ChS	$\approx \langle 10\bar{1}4 \rangle$ $\approx \langle 111 \rangle$	
MgAl ₂ O ₄ /MgO	Fibrous (MgO)	$[111]_{MgO}$ $[111]_{Spinel}$	$(hkl)_{MgO} \parallel (hkl)_{Spinel}$
Al ₂ O ₃ /Y ₃ Al ₅ O ₁₂ /YSZ ^a	CR and TDI	$[001]_{YAG}$ $[\bar{1}2\bar{1}6]_{Al_2O_3}$ $[001]_{YSZ}$	

^aThe solidification direction and orientation relationships are strongly dependent on growth conditions.

^bSome misalignment between adjacent lamellae has been reported. Abbreviations CR, complex regular; TDI, three-dimensional interlocking (interpenetrating); ChS, Chinese script morphology.

Table 4 Flexural strength σ_f and toughness K_{IC} of DSE eutectics

Components	σ_f (GPa) at 300 K	σ_f (GPa) at the temperature indicated	K_{IC} MPa m ^{1/2}
YSZ/Al ₂ O ₃	1.55	0.9 (1600 K)	5–7.8
Al ₂ O ₃ /Y ₃ Al ₅ O ₁₂	1.9	1.7 (1700 K)	2.0
CaZrO ₃ /CaSZ	0.22		
MgO/MgSZ	0.3		
Al ₂ O ₃ /Er ₃ Al ₅ O ₁₂	2.7	2.7 (1600 K)	1.9
Al ₂ O ₃ /EuAlO ₃		0.32 (1775 K) [†]	
Al ₂ O ₃ /GdAlO ₃		0.28 (1775 K) [†]	
MgAl ₂ O ₄ /MgO		0.2 (1875)	
Al ₂ O ₃ /Y ₃ Al ₅ O ₁₂ /YSZ	4.0	2.5 (1450)	3.3

[†]Tensile strength.

where K_{IC} is the fracture toughness. The linear fit to the experimental results in Figure 5 is obtained with $K_{IC} = 1.6 \text{ MPa m}^{1/2}$, and this value is only marginally lower than the ambient temperature fracture toughness of Al₂O₃-YAG, which is close to $2 \text{ MPa m}^{1/2}$, and independent of the orientation and domain size (Ochiai et al., 2001; Pastor et al., 2004). Of course, the moderate toughness of the eutectic is also its Achilles' heel for, any chemical or mechanical processes that induce surface damage, may degrade the strength considerably.

The flexure strength of the Al₂O₃-YAG eutectics has been measured as a function of temperature in air and in Ar (Waku et al., 2001; Pastor et al., 2004). Average values, together with the corresponding standard errors, are plotted in Figure 6. The eutectics with large domain size maintained their flexure strength up to 1900 K, very close to the eutectic temperature of 2100 K. Eutectics with an average domain size of 1 μm and below suffer from a significant reduction in the strength at temperatures above 1700 K due to homogeneous microstructure coarsening. In addition, Matson and Hecht (1999) reported that the tensile strength of small diameter fibers shows a marked reduction in strength after annealing in air at moderate temperatures (above 1400 K). The fracture of Al₂O₃-YAG fibers at high-temperature, or after annealing, was controlled by the nucleation of defects, which developed as a result of a reaction between the eutectic components and silica-containing dust and dirt particles from the environment. The eutectics are extremely flaw-sensitive because of their poor fracture toughness and the localized coarsening of the microstructure

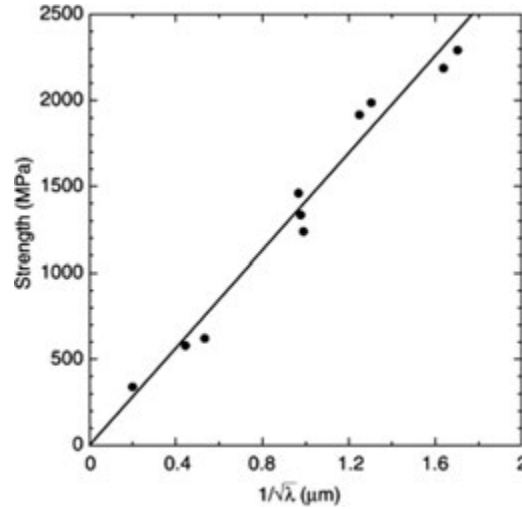


Figure 5 Strength of Al_2O_3 -YAG DSE at ambient temperature as a function of the thickness, λ , of eutectic domain.

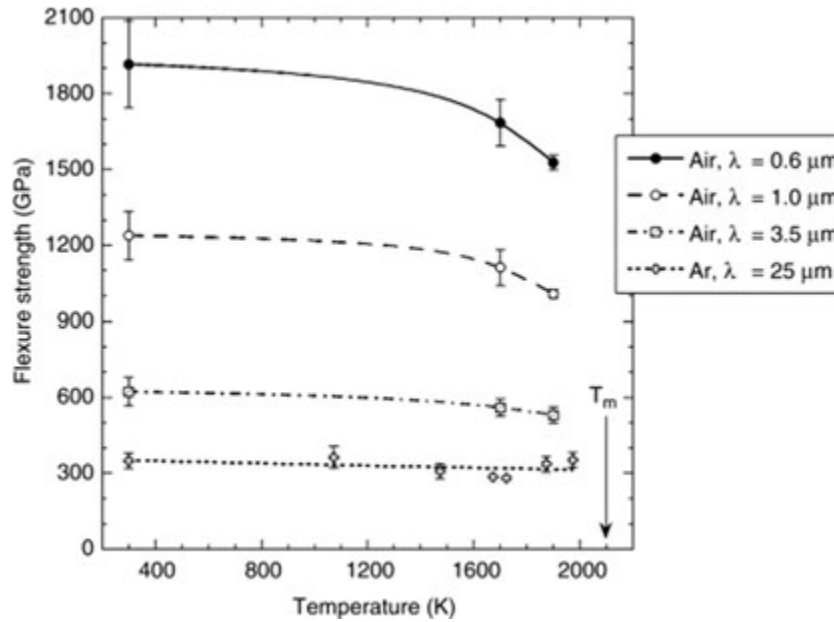


Figure 6 Flexure strength of Al_2O_3 -YAG DSE as a function of temperature. The legend indicates the environment used for the test and the thickness of the eutectic domain in the microstructure.

due to the reaction of the eutectic oxides with the environment is responsible for the degradation of the tensile properties, which is the most noticeable in fibers with a large specific surface.

The creep resistance of coarse-grained and single-crystal Al_2O_3 -YAG eutectics along the solidification direction in air was measured by Parthasarathy *et al.* (1993) and Harada *et al.* (2004). The minimum creep rate, $\dot{\epsilon}$, is plotted in Figure 7 as a function of the applied stress, σ , and both sets of experiments (in single-crystal and coarse-grained DSE) indicate that the eutectic creep follows a power-law relationship as

$$\dot{\epsilon} = A\sigma^n \exp\left(-\frac{Q}{RT}\right) \quad [2]$$

where T is the absolute test temperature, n the stress exponent, and Q the activation energy of the physical mechanism responsible for creep deformation. The stress exponents are in the range 5–6 for both materials at temperatures above 1800 K and the activation energies are in the range 650–800 kJ mol^{-1} in the coarse-grained material and slightly higher (800–1000 kJ mol^{-1}) in the single-crystal eutectic. These results are compatible with creep deformation controlled by dislocation motion in each phase

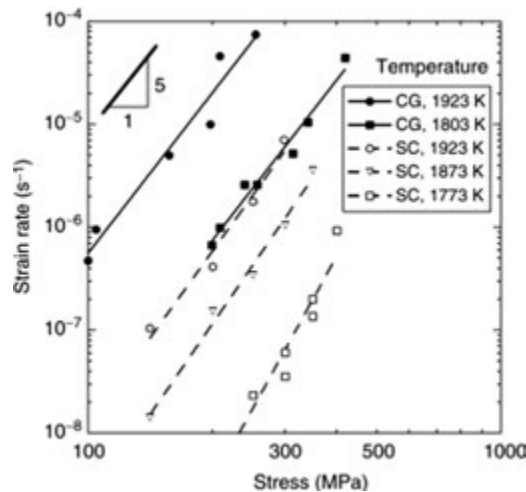


Figure 7 Minimum creep rate as a function of the applied stress in Al_2O_3 -YAG DSE with coarse-grained (CG) and single-crystal (SC) microstructure.

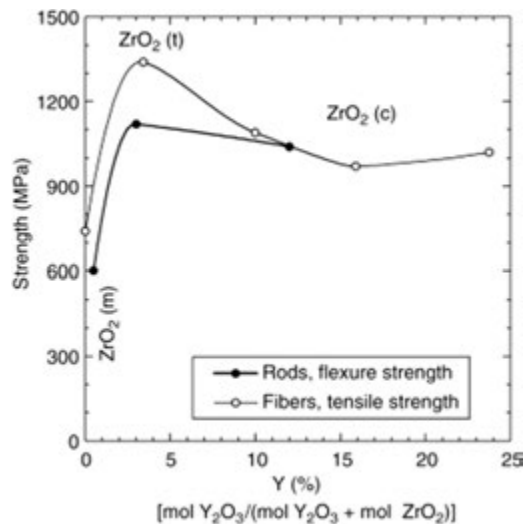


Figure 8 Ambient temperature strength of Al_2O_3 - $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ DSE rods and fibers as a function of the yttria content expressed by $Y = \text{mol of } \text{Y}_2\text{O}_3 / (\text{mol } \text{ZrO}_2 + \text{mol } \text{Y}_2\text{O}_3)$.

induced by lattice diffusion in the single-crystal eutectic, and this assumption was supported by transmission electron microscopy studies showing evidence of dislocation activity in both phases, particularly in Al_2O_3 .

Al_2O_3 - $\text{ZrO}_2(\text{Y}_2\text{O}_3)$

The ambient temperature strength of Al_2O_3 -YAG is essentially a function of the domain thickness, whereas that of Al_2O_3 - $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ depends primarily on (1) the Y_2O_3 content, which controls the structure of the polymorphic variant of zirconia within the eutectic together with the residual stresses and (2) on the spatial distribution of both phases, which varies with the growth rate.

The effect of the Y_2O_3 content on the ambient temperature strength has been studied in hypo-eutectic Al_2O_3 - $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ fibers (Farmer and Sayir, 2002) and eutectic Al_2O_3 - $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ rods (Llorca et al., 2004). The results of these investigations are plotted in Figure 8, where Y stands for the mol% of Y_2O_3 dissolved in the $\text{ZrO}_2 + \text{Y}_2\text{O}_3$ phase. The poorest mechanical properties are always found in the yttria-free samples, where zirconia has transformed from tetragonal to monoclinic upon cooling from the processing temperature. The volumetric change associated with the transformation generates large tensile residual stresses in the Al_2O_3 continuous phase, and impaired the eutectic strength. Tetragonal ZrO_2 is found in the eutectics with $Y \approx 3\%$ as the tetragonal to monoclinic transformation is completely suppressed by yttria. As a result, the thermo-elastic residual stresses

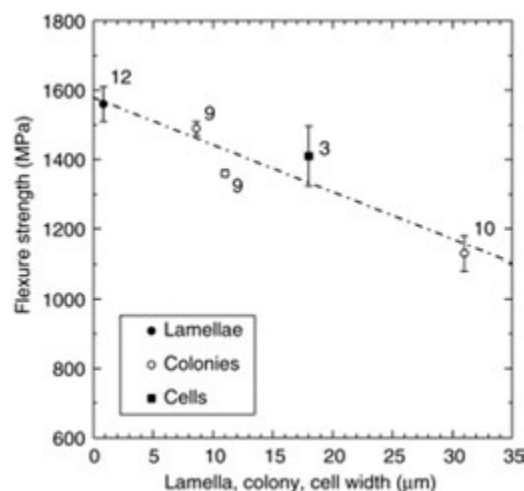


Figure 9 Influence of the microstructure morphology on the flexure strength of $\text{Al}_2\text{O}_3\text{-ZrO}_2(\text{Y}_2\text{O}_3)$ DSE rods. The number beside each experimental point indicates the yttria content expressed in Y(%).

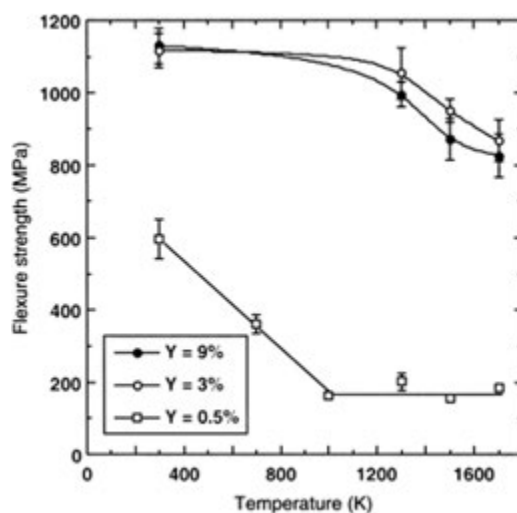


Figure 10 Flexure strength of $\text{Al}_2\text{O}_3\text{-ZrO}_2(\text{Y}_2\text{O}_3)$ DSE rods as a function of temperature.

generated upon cooling are compressive in the Al_2O_3 phase and the strength is almost doubled with respect to the yttria-free samples. Further increase in the yttria content leads to the stabilization of the cubic ZrO_2 phase in the eutectic. The thermal expansion coefficients of tetragonal and cubic ZrO_2 being very similar, the thermal residual stresses do not vary significantly as the yttria content increases above $Y=3\%$.

The intercolony and intercellular regions contained coarse ZrO_2 particles of irregular shape, as well as cracks and pores, and their thickness increases with the yttria content due to the segregation of this oxide to the intercolony and intercellular regions during solidification. The flexure strength of $\text{Al}_2\text{O}_3\text{-ZrO}_2(\text{Y}_2\text{O}_3)$ DSE with various microstructures and $Y \approx 3\%$ is plotted in [Figure 9](#) as a function of the width perpendicular to the growth axis of the relevant feature, either lamellae, cells, or colonies, that characterizes the microstructure. The highest strength is measured in the eutectics made up by a fine dispersion of ZrO_2 lamellae within the continuous Al_2O_3 matrix, while materials with colony or cell structure attain lower strengths which decrease with the cell or colony width ([Peña et al., 2006](#)). The critical defects, promoting fracture in the eutectics with cell and colony morphologies, are localized at the intercellular and intercolony regions ([Pastor et al., 2008](#)).

The strength retention at high-temperature of $\text{Al}_2\text{O}_3\text{-ZrO}_2(\text{Y}_2\text{O}_3)$ DSE has been measured by [Llorca et al. \(2004\)](#) and [Pastor et al. \(2001\)](#), and the average flexure strength is plotted in [Figure 10](#) for three eutectics with different Y_2O_3 contents. The materials which contain ZrO_2 in either tetragonal ($Y=3\%$) or cubic ($Y=9\%$) form do not experience any noticeable degradation up to 1300 K retaining up to 70–80% of the ambient temperature strength at 1700 K. This excellent high-temperature behavior is similar to that found in $\text{Al}_2\text{O}_3\text{-YAG}$, although the strength reduction starts at lower temperatures because the ZrO_2 resistance to plastic deformation is lower than that of YAG. On the contrary, the eutectic with monoclinic ZrO_2 experiences a marked degradation in

strength at very low temperature accompanied by the appearance of longitudinal cracks in the fracture surfaces. These cracks are generated by the build-up of tensile residual stresses in the ZrO_2 phase resulting from the differences in the thermal expansion coefficients of monoclinic ZrO_2 and Al_2O_3 as well as from the negative volumetric strain in the ZrO_2 when the martensitic transformation is reversed.

Summary

Directionally-solidified eutectic ceramic oxides are a family of *in situ* composite materials with a homogeneous and stable microstructure, whose morphology and size can be tailored by processing. Their hardness and strength at ambient temperature are comparable to or even better than those obtained in conventional structural ceramics. Additionally, due to the presence of large amounts of clean, strong interfaces and to the homogeneity of the microstructure, DSE maintains the mechanical properties up to temperatures very close to the eutectic point even in oxidizing environments. As compared with other ceramic oxides, DSE oxides show good thermal shock resistance and fracture toughness, although they do not attain the outstanding values measured in some carbides and borides. The most interesting DSE oxides for structural applications are those containing corundum, in particular Al_2O_3 -YAG and Al_2O_3 -YSZ, which offer excellent strength retention and creep resistance in the range 1400–1600 °C. Good mechanization and fabrication efficiency of structural components as compared with sintered engineering ceramics make these materials very promising candidates for high-temperature structural applications in oxidizing environments.

References

- Ashbrook, R.L., 1977. Directionally solidified ceramic eutectics. *J. Am. Ceram. Soc.* 60, 428–435.
- Farmer, S.C., Sayir, A., 2002. Tensile strength and microstructure of Al_2O_3 - ZrO_2 hypo-eutectic fibers. *Eng. Fract. Mech.* 69, 1015–1024.
- Harada, Y., Suzuki, T., Hirano, K., Waku, Y., 2004. Ultra-high temperature compressive creep behaviour of an in-situ Al_2O_3 single crystal/YAG eutectic composite. *J. Eur. Ceram. Soc.* 24, 2215–2222.
- Hunt, J.D., Jackson, K.A., 1966. Binary eutectic solidification. *Trans. AIME.* 236, 843–852.
- Larrea, A., de la Fuente, G.F., Merino, R.I., Orera, V.M., 2002. ZrO_2 - Al_2O_3 eutectic plates produced by laser zone melting. *J. Eur. Ceram. Soc.* 22, 191–198.
- Larrea, A., Orera, V.M., Merino, R.I., Peña, J.I., 2005. Microstructure and mechanical properties of Al_2O_3 -YSZ and Al_2O_3 -YAG directionally solidified eutectic plates. *J. Eur. Ceram. Soc.* 25, 1419–1429.
- Llorca, J., Orera, V.M., 2006. Directionally solidified eutectic ceramic oxides. *Prog. Mat. Sci.* 51, 711–809.
- Llorca, J., Pastor, J.Y., Poza, P., *et al.*, 2004. Influence of the Y_2O_3 content and temperature on the mechanical properties of melt-grown Al_2O_3 - ZrO_2 eutectics. *J. Am. Ceram. Soc.* 87 (4), 633–639.
- Matson, L.E., Hecht, N., 1999. Microstructural stability and mechanical properties of directionally solidified alumina/YAG eutectic monofilaments. *J. Eur. Ceram. Soc.* 19, 2487–2501.
- Merino, R.I., Peña, J.I., Larrea, A., de la Fuente, G.F., Orera, V.M., 2003. Melt grown composite ceramics obtained by directional solidification structural and functional applications. *Recent Res. Devel. Mat. Sci.* 4, 1–24.
- Ochiai, S., Ueda, T., Sato, K., *et al.*, 2001. Deformation and fracture behaviour of an Al_2O_3 /YAG composite from room temperature to 2023 K. *Comp. Sci. Tech.* 61, 2117–2128.
- Orera, V.M., Peña, J.I., 2012. Directional solidification. In: Bansal, N.P., Boccaccini, A.R. (Eds.), *Ceramics and Composites Processing Methods*. Hoboken, New Jersey: John Wiley & Sons, Inc., pp. 417–457. ISBN 978-0-470-55344-2, Chapter 12.
- Orera, V.M., Peña, J.I., Oliete, P.B., Merino, R.I., Larrea, A., 2012. Growth of eutectic ceramic structures by directional solidification methods. *J. Cryst. Growth* 360 (2012), 99–104.
- Parthasarathy, T.A., Mah, T.I., Matson, L.E., 1993. Deformation behavior of an $\text{Al}_2\text{O}_3/\text{Y}_3\text{Al}_5\text{O}_{12}$ eutectic composite in comparison with sapphire and YAG. *J. Am. Ceram. Soc.* 76 (1), 29–32.
- Pastor, J.Y., Llorca, J., Martín, A., Peña, J.I., Oliete, P.B., 2008. Fracture toughness and strength of Al_2O_3 - $\text{Y}_3\text{Al}_5\text{O}_{12}$ and Al_2O_3 - $\text{Y}_3\text{Al}_5\text{O}_{12}$ - ZrO_2 directionally solidified eutectic oxides up to 1900 K. *J. Eur. Ceram. Soc.* 28, 2345–2351.
- Pastor, J.Y., Llorca, J., Salazar, A., Peña, J.I., 2004. Mechanical properties of melt-grown alumina – YAG eutectics up to 1900 K. *J. Am. Ceram. Soc.* 88 (6), 1488–1495.
- Pastor, J.Y., Martín, A., Molina-Aldareguía, J.M., *et al.*, 2013. Superplastic deformation of directionally solidified nanofibrillar Al_2O_3 - $\text{Y}_3\text{Al}_5\text{O}_{12}$ - ZrO_2 eutectics. *J. Eur. Ceram. Soc.* 33, 2579–2586.
- Pastor, J.Y., Poza, P., Llorca, J., *et al.*, 2001. Mechanical properties of directionally solidified Al_2O_3 - ZrO_2 (Y_2O_3) eutectics. *Mater. Sci. Eng.* A308, 241–249.
- Peña, J.I., Larsson, M., Merino, R.I., *et al.*, 2006. Processing, microstructure and mechanical properties of directionally-solidified Al_2O_3 - $\text{Y}_3\text{Al}_5\text{O}_{12}$ - ZrO_2 ternary eutectics. *J. Eur. Ceram. Soc.* 26, 3113–3121.
- Peña, J.I., Merino, R.I., Harlan, N.R., *et al.*, 2002. Microstructure of Y_2O_3 doped Al_2O_3 - ZrO_2 eutectics grown by the laser floating zone method. *J. Eur. Ceram. Soc.* 22, 2595–2602.
- Stubican, V.S., Bradt, R.C., 1981. Eutectic solidification in ceramic systems. *Ann. Rev. Mater. Sci.* 11, 267–297.
- Waku, Y., Nakagawa, N., Ohtsubo, H., Mitani, A., Shimizu, K., 2001. Fracture and deformation behaviour of melt growth composites at very high temperature. *J. Mater. Sci.* 36, 1585–1594.
- Waku, Y., Nakagawa, N., Wakamoto, T., *et al.*, 1997. A ductile ceramic eutectic composite with high strength at 1.873 K. *Nature* 389, 49–52.

Overview: High-Performance Ceramics and Ceramic Composites

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This section is devoted to ceramic matrix composites (CMC) and ceramics for use aggressive environments, as well as joining of ceramics. The composites part begins with a chapter by Fantozzi and Chevalier which provides an excellent overview of reinforcement mechanisms in ceramics: transformation toughening, microcracking, crack deflection and crack bridging as well as whisker reinforcement. The chapter then goes on to review the state of the art knowledge of zirconia toughened composites, whisker composites, particle and platelet reinforced composites and finally carbon nanotube and graphene reinforced ceramic composites. For each type of composite, Fantozzi and Chevalier outline improvements in mechanical properties e.g., toughness, hardness, modulus, creep resistance induced by introducing reinforcements into a ceramic matrix. In addition, they indicate the mechanisms by which the mechanical properties are improved. The chapter by Thompson and Harmer describes alumina-silicon carbide nanoparticle composites. The chapter gives an excellent background to the development of nanocomposites and how the addition levels of SiC particles control the grain structure and grain size distribution of an alumina matrix. This chapter then goes on to report strengths of up to 1500 MPa realized by alumina-silicon carbide nanocomposites as well as toughness increases. Thompson and Harmer's chapter also shows how nanoparticle reinforcement reduces creep rates and typically changes fracture paths from intergranular for monolithic alumina to transgranular for the nanocomposite. This change of fracture path is related to improved wear and erosion resistance. Balázs *et al.* continue the theme of nanocomposites. However, the work they review is based upon a silicon nitride matrix reinforced with carbon nanotubes or graphene. Their chapter gives good insight into the processing of such nanocomposites without comminution of the nanostructured carbon reinforcements. Having looked at processing, the chapter then gives a very good overview of how the reinforcements are integrated into the matrix from transmission and scanning electron microscopy examination, as well as how they induce crack deflection. The chapter then goes on to look at the property improvements afforded by carbon nanostructure reinforcements, noting the importance of avoiding reinforcement agglomeration during processing. Agglomerates act as defects, inducing lower strengths for example, whereas well distributed carbon nanostructures act as reinforcements, increasing strength and indeed toughness. Following the papers on fine scale reinforcements, the chapter by Krenkel *et al.* increases the scale of reinforcement to the chopped or short fiber scale. Having addressed the mechanisms of short fiber reinforcement, including fiber/matrix interfacial debonding and matrix/fiber load transfer, the chapter is then able to show the importance of short fiber aspect ratio. One clear advantage of short fiber reinforcements is that the resulting composites are generally anisotropic. Krenkel *et al.* then review estimations of ceramic matrix composite strength and stiffness parameters before looking at how non-oxide CMCs are fabricated and used as well as reviewing their properties. The chapter finishes by looking at manufacturing routes, properties and applications of oxide matrix CMCs. Throughout it is made clear that short fiber CMCs cannot compete with long fiber CMCs in terms of strength and stiffness. However, the relative ease of fabricating complex components from short fiber CMCs means that they are used in high volume throughput components e.g., automobile brake disks.

Two chapters by Boccaccini *et al.* follow, the first of which describes the constitution of glass and glass ceramic matrix composites with particulate, whisker, platelet, chopped fiber, and continuous fiber reinforcements. As with the chapters by Fantozzi and Chevalier and Krenkel *et al.* toughening and strengthening mechanisms are discussed. The complexities associated with manufacture are discussed and typical manufacturing routes described. These routes include powder technology, infiltration of preforms via a number of precursors e.g., slurries, sol-gel/colloidal routes and polymers followed by debinding/pyrolysis steps and finally a pressureless sintering or pressure aided densification step yields a high density product. Boccaccini *et al.* also review the more recent use of 3D additive manufacturing routes. In their chapter on applications, Boccaccini *et al.* review the use of the various types of glass/glass ceramic matrix composites for aerospace, solid oxide fuel cell, biomedical, electronic substrate and structural applications.

The final five chapters in the sub-section on composites relate to continuous fiber composites, although the penultimate one discusses some elements of short fiber composites for ultra-high temperatures. They begin with the paper by Bunsell on high performance fibers, which is an excellent review of fiber manufacture and properties. The phenomenal property values for fibers become wholly evident to the reader. Thus, for example, Bunsell quotes strengths of more than 2.5 GPa for glass fibers as well as strains to failure of up to 5.3%. Bunsell also reviews carbon fibers, oxide fibers and silicon carbide fibers. The chapter by Wilson extends that of Bunsell with respect to spun oxide fibers. Wilson's chapter looks in depth at the production of alumina fibers via sol-gel and spinning routes. The resulting fibers have considerably higher strengths (up to 3 GPa) than alumina monoliths, as might be expected. Rebillet's chapter on long (continuous) fiber CMCs starts out with an excellent description of the various fiber woven architectures which fiber preforms can assume. It then explains how it is possible to achieve non-linear elastic behavior with this type of composite and deals with the importance of the interphase between the fiber and matrix in controlling this. Having explained the development of superior mechanical properties in long fiber composites, Rebillet goes on to cover the many various ways by which fiber preforms are infiltrated and inter-fiber spaces filled by a ceramic matrix material. In doing so, Rebillet is careful to look at how processing conditions require suitable control, in order to ensure that impregnation extends through the total thickness of the layered-up fiber assemblies. The chapter by Zoli *et al.*, which is devoted to ultra-high temperature ceramic matrix composites (UHTCMCs),

extends that of Rebillat by looking at other matrix types such as borides rather than SiC, to facilitate ultra-high temperature usage. This chapter reviews the fabrication of UHTCMCs without any sintering step by the use of polymer infiltration and pyrolysis, repeated impregnation by slurries and precursor gases (e.g., hafnium containing gases) as well as infiltration by molten but reactive silicides or metal – copper alloys which convert in the presence of carbon or boron to a ceramic matrix and a liquid metal which is expelled to the surface. The chapter then covers the manufacturing of materials with a sintering step and describes in detail the types of considerations which must be taken into account to achieve good densification with little or no fiber degradation. Zoli *et al.* also address ultra-high temperature short fiber UHTCMCs in this part. Having looked at functionally graded UHTCMCs Zoli *et al.* describe the benefits of adopting functionally graded composites with varying reinforcement contents. This approach, they show, increases toughness as well as reducing potential unwanted post-sintering residual stresses, which arise in long fiber UHTCMCs with a singular reinforcement content. The chapter concludes with sections on mechanical properties of UHTCMCs and their thermal-ablative resistance. In the final chapter in this sub-section, Chung's contribution deals with C/C composites. This chapter describes the constitution of C/C composites, how they are fabricated and their significant advantage as far as maximum use temperature in vacuum or argon is concerned (up to 2000°C). Chung draws attention to the need for SiC coatings if the C/C material is to be used in oxidizing environments. Thermal expansion mismatch between matrix and fiber carbons also causes a degradation of properties at high temperatures. In general, though the properties quoted for a commercial C/C composite by Chung appear modest, the fact that these properties can be maintained to very high > 2000°C gives such materials the potential to be used in very high temperature applications e.g., aerospace. Chung also draws attention to the self-monitoring and self-powering capability of C/C materials as well as their important ability to provide electromagnetic shielding.

Having looked at high performance ceramic CMCs, Section 8 then looks at the application of materials in space applications. The chapter by Twomey *et al.* documents the various requirements for the application of ceramic materials in space. Typical application areas are: propulsion systems for spacecraft, structures for launchers and spacecraft, thermal protection systems and substrates for space optics. The application range is quite significant, as is the range of ceramic materials used in space applications as Twomey *et al.* summarize and explain very well. This chapter also indicates the move towards space commercialization and thus the potential increase in use of ceramics in space. Although not specifically mentioned in the chapter by Kaiser *et al.* their coverage of gas purification and solid oxide cells are additional aerospace applications of ceramics. That said, the chapter by Kaiser *et al.* is devoted to porous ceramics for energy applications and covers catalysts, solid oxide cells and ceramic membranes for liquid and gas separation. In addition to describing the technologies and typical requirements of these applications, Kaiser *et al.* also describe typical manufacturing routes for relevant components. They then finally discuss structure-property relationships for ceramics employed in the three application areas concerned. In many instances, it is necessary to bond ceramic components to other ceramic components or metallic components. Fernie and Knowles review the various methods of bonding available. The chapter looks at mechanical methods, friction/ultrasonic methods and diffusion bonding for joining, as well as glass to metal sealing and bonding. Adhesive bonding, soldering and brazing are also reviewed. Importantly, joint design and testing are also topics dealt with by Fernie and Knowles.

The remainder of Section 8 looks at specific uses of ceramics in relatively aggressive environments. The chapter by Alary is a review of ceramic abrasives from an Industrial viewpoint. The abrasives market (including raw grits, abrasive tool bits and assembled abrasive tools) is of the order of 10 B€. Thus, manufacturing routes of abrasives are well developed as is the technology with over 50,000 patents being filed per annum. Alary discusses the properties required for abrasives and indicates how in addition to hardness, brittleness and friability are important. He also indicates how abrasive grits are classified by size. Alary describes typical fabrication processes for abrasive grits and draws attention to sol-gel processing which yields submicron grits and is a hot development topic. It is clearly pointed out in this chapter that the selection of an abrasive type, and indeed tool, requires a holistic approach with all application and abrasive property factors being taken into account. Ceramic materials for wear resistance are then reviewed by Hvizdoš. Having described the methods by which wear resistance is characterized, Hvizdoš discusses the wear properties of various oxide and non-oxide ceramic materials. More particularly, his chapter appraises the improvements in wear behavior, if the ceramic materials are reinforced with carbon nanostructures. These are primarily due to the development of a tribolayer affording a lower coefficient of friction. The formation of tribolayers is also important in the wear behavior of silicon nitride and sialons. Hvizdoš also discusses the wear behavior of silicon carbide, boron carbide, boride and high entropy ceramics. Lofaj and Mikula's chapter covers wear resistant ceramic coatings. Following an excellent explanation of tribology, wear mechanisms and erosion, Lofaj and Mikula discuss the importance of hardness to modulus (H/E) ratio as a "rule of thumb" indicator of wear resistance and how a composite approach to wear resistant coatings enables both hardness and modulus to be manipulated to obtain required H/E ratios. Lofaj and Mikula give an excellent and highly detailed review of coating methods as well as how nanostructured coatings can be developed on substrate surfaces. Concluding Section 8, is an important chapter by Jacobson and Opila on the oxidation and corrosion of non-oxide ceramics. This chapter deals in the main with silica forming materials (e.g., Si₃N₄, SiC) in oxygen, carbon dioxide and water vapor. The authors outline how water vapor accelerates oxidation rates of silica formers as it reacts with the silica to form non-protective volatile oxidation products. The adverse effects of sodium salts (often found in gas turbines) on the oxidation of silica formers is also discussed and attributed to the formation of low viscosity sodium silicate oxidation products. Jacobson and Opila also cover active oxidation of silica formers. Having looked at the oxidation of SiC-SiC composites, the chapter addresses the state of development of protective coatings; outlining their requirements and indicating some environmental barriers of use. The chapter concludes by addressing the oxidation of ultra-high temperature ceramics.

Ceramic Matrix Composites With Roughly Equiaxed Reinforcements: Microstructure and Mechanical Behavior

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Introduction

The main goal of ceramic matrix composites is to obtain ceramic-based materials with improved mechanical properties, especially toughness and/or strength and creep resistance. For this purpose, several reinforcement mechanisms can be used (Fantozzi and Chevalier, 2001) including phase transformation, microcracking, crack deflection, crack bridging, and fiber or whisker reinforcement.

These mechanisms will first be briefly presented. Then the application of these mechanisms on particle, whisker, carbon nanotube, graphene, and platelet-reinforced composites will be described.

General Background on Reinforcement Mechanisms in Ceramics

Transformation Toughening

Increases in strength and toughness can be obtained in ceramics that undergo a stress-induced transformation (Green *et al.*, 1989). The case of ceramics containing zirconia particles that present a tetragonal to monoclinic phase transformation is the most spectacular. By using an addition of Y_2O_3 , CeO_2 – other ions or even with the presence of a surrounding matrix with different thermomechanical properties (e.g., alumina) – zirconia can be kept in a metastable tetragonal-solid solution at room temperature. Under the effect of an applied stress, a martensitic tetragonal (t) to monoclinic (m) transformation may take place in the vicinity of the crack, which is associated with a volume increase and a shear strain that impede the crack opening and therefore lead to an increase of toughness. This increase is given by (Evans, 1984):

$$\Delta K_c^t = \frac{\eta e^T V h^{1/2}}{(1 - \nu)} \quad (1)$$

where η is a factor depending on the shape of the transformation zone around the crack, h its width, E the effective Young's modulus of the material, V the volume fraction of transformed particles, e^T the unconstrained transformation strain, and ν is Poisson's ratio.

The zone width and the volume fraction of transformable particles depend on the microstructure and especially on the grain size of the material and the dopant (e.g., Y_2O_3 or CeO_2) content, via the critical stress for transformation, σ_c . The higher the grain size (or the lower the dopant content) is, the lower is σ_c , thus the higher the volume fraction of transformed particles; however, when the grain size becomes higher than a critical size, d_c , spontaneous transformation occurs upon cooling and most grains are already transformed before crack propagation. There is therefore an optimum grain size/dopant content/zirconia content in the composite, for which transformation toughening is the most efficient.

Microcracking

When the size of the particles is greater than the critical size d_c , microcracking arises, which leads to a decrease in the strength of the material (Evans, 1984). However, if the particle size is smaller than the critical size, microcracks need additional stress to be induced that can be provided by the applied load. For efficient reinforcement, the microcracking must be confined in a process zone in front of the crack tip. The particle size must be as close as possible to the critical size to induce significant toughening, while preserving strength.

Crack Deflection

Cracks can be deviated either by the stress fields present around particles or by hard particles of higher resistance. This mechanism leads to a nonplanar crack, subjected to a mixed fracture mode. The analysis has been carried out for spherical, rod, and disc shaped particles for isotropic composite materials (Evans, 1984). In the case of discs and rods, the influence of the aspect ratio has been investigated. High deflection and therefore high toughening are obtained with rods with a high aspect ratio for a volume fraction of about 10%–20%.

This analysis has also been extended to the case of rods randomly oriented in planes in order to simulate transverse isotropic whisker-like composites. A more significant reinforcement can be obtained by crack deflection for this more specific case.

Crack Bridging

Such a reinforcement occurs when a crack meets a reinforcement particle without breaking it. The unbroken ligament exerts a bridging stress on the crack surfaces that counteracts the crack opening and thus reduces the stress intensity factor (Becher and Rose, 1994).

The toughening reinforcement is given by:

$$\Delta K_c^b = 2 \left(\frac{V_f \sigma \mu u_c}{1 - \nu} \right)^{1/2} \quad (2)$$

where V_f is the volume fraction of ligaments, σ the closing stress applied to the ligaments, μ the shear modulus, and u_c the crack opening at the end of the bridging zone.

The reinforcement depends on ligament density and the stress exerted by the ligaments, as well as on the crack opening. The reinforcement must exhibit a high strength in order to exert the highest possible stress and must be of large dimension in order to bridge over a large crack opening.

Whisker (Short Fiber, Carbon Nanotube, or Graphene) Reinforcement

The analysis of toughening by whisker reinforcement has been reviewed by Becher and Rose (1994). They consider uniaxially aligned whiskers. The analysis of reinforcement by whiskers is close to that developed for crack bridging. However, debonding of the whisker–matrix interface, and consequent friction at the interface, are generally taken into account. When whisker–matrix interface debonding occurs, the bridging stress supported by the whisker is reduced and a large bridging zone appears.

The energy dissipated by friction is given by:

$$\Delta G^f = \frac{V_f (\sigma_f^w)^3 r}{GE^w \tau_0} \quad (3)$$

where σ^w , E^w , r , and V_f are, respectively, the strength, the Young's modulus, the radius, and the volume fraction of whiskers, and τ_0 the interfacial shear stress.

The fracture energy increases as the interfacial shear stress decreases (i.e., when more interface debonding occurs). Furthermore, after whisker failure, whisker pull-out can contribute to additional toughening.

In the case of short fibers, carbon nanotubes, or graphenes, the same dependence of the fracture energy is observed: Low fiber (or reinforcement)–matrix adhesion and high fiber (or reinforcement) strength are needed in order to obtain matrix microcracking and fiber (or reinforcement) pull-out with friction and energy absorption.

Mechanical Properties of Zirconia-Toughened Composites

As shown in Section "Transformation Toughening", the fracture toughness increase is due to the $t \rightarrow m$ transformation of zirconia particles and needs the retention of $t\text{-ZrO}_2$ after sintering and cooling. This retention can be obtained by using several types of microstructures (Claussen, 1984). In all cases, the grain size of zirconia particles must be lower than the critical size d_c required for the spontaneous $t \rightarrow m$ without any stress, but sufficient enough to transform under stresses. Zirconia can be found in the form of tetragonal zirconia polycrystal (TZP) stabilized in the tetragonal symmetry by an addition of different oxides (e.g., cerium (Ce-TZP) or yttrium (Y-TZP) oxides). Zirconia can also exist in the form of tetragonal precipitates in a cubic matrix. An example is that of magnesia partially stabilized zirconia (Mg-PSZ), which is a composite structure of two phases (tetragonal precipitates in a cubic matrix). Zirconia particles can also be dispersed in a ceramic matrix other than ZrO_2 : These materials are called ZrO_2 -dispersed ceramics. An example of such a composite is ZrO_2 -toughened alumina (ZTA) of which a microstructure is shown in Fig. 1.

Effect of Size and Amount of Zirconia Particles on Toughening

Toughness improvement is related to the tetragonal particle size. In the case of partially stabilized zirconia (PSZ) the precipitate size depends on the annealing (sometimes referred as 'aging') conditions after sintering and solution treatment. A dramatic drop-off in toughness occurs when the precipitate size is just above the critical size d_c : the $t \rightarrow m$ transformation becomes spontaneous during cooling and the amount of tetragonal precipitates available for transformation decreases. Spontaneous transformation during cooling, especially if generalized to the entire composite, has to be avoided. Fig. 1 represents a ZTA composite where the zirconia grain size has been optimized in size (below d_c but above a certain size to induce transformation under stress at the crack tip) and distribution (as narrow as possible) in order to obtain the largest amount of transformation toughening (Chevalier et al., 2000).

Eq. (1) predicts that the toughness increment due to the $t \rightarrow m$ transformation depends on the volume fraction of transforming particles. This is actually observed (Becher and Rose, 1994) when care is taken to control the tetragonal particles content. If during processing, monoclinic particles or stable (nontransforming) particles are obtained, the transformation toughening contribution decreases. Hence, fracture toughness presents a maximum with increasing volume fraction of zirconia particles. The maximum occurs at higher volume fraction with smaller particle size. This behavior is due to local tensile thermal stresses that provoke

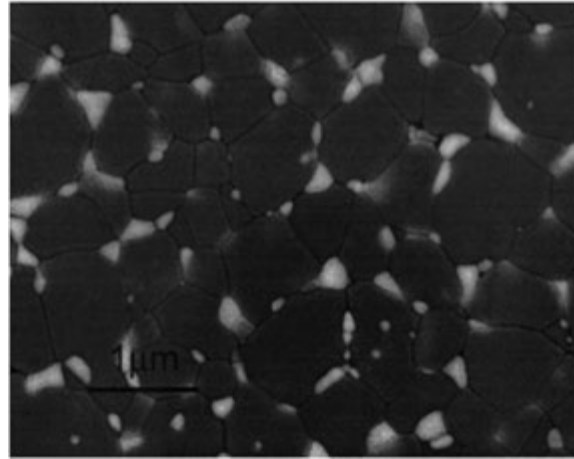


Fig. 1 Microstructure of a zirconia (10 vol%)-toughened alumina. Zirconia appears as the bright phase in back-scattered scanning electron microscope observation. From Encyclopedia of Materials: Science and Technology, Elsevier, 2001.

Table 1 Fracture energy of ZrO₂-toughened alumina ceramics

Composition	A	A5Z	A10Z	A15Z	A20Z	A20Z1Y	A20Z2Y	A20Z3Y	A45Z3Y
ZrO ₂ (vol%)	0	5	10	15	20	20	20	20	45
Y ₂ O ₃ (mol%)	0	0	0	0	0	1	2	3	3
PS materials									
G _c (J m ⁻²)	41	86	80	95	98	88	120	72	390
Qr (%)	0	98	48	20	15	33	95	98	96
HP materials									
G _c (J m ⁻²)	50	160	250	115	102	117	270	194	576
Qr (%)	0	96	82	23	7	30	97	100	99

Note: From Encyclopedia of Materials: Science and Technology, Elsevier, 2001.

Abbreviation: PS, pressureless sintered, HP, hot-pressed.

spontaneous transformation of the zirconia particles during cooling, decreasing the tetragonal phase content. Maximum toughness occurs for a volume fraction of particles corresponding to thermal stresses (that increase with the volume fraction of ZrO₂) reaching the critical stress σ_c . In this case, another contribution to toughening due to ZrO₂ particles that have spontaneously transformed is microcracking in the stress field around the monoclinic particles. Fracture energy (G_c) values for different pressureless sintered (PS) or hot-pressed (HP) ZTA compositions have been measured (Fantozzi and Orange, 1986; Table 1). For PS composites, G_c is nearly constant up to 15 vol% ZrO₂ whereas, for HP materials, G_c shows a maximum near 10 vol% ZrO₂.

The observed increase in G_c in PS materials and to 10% ZrO₂ in HP materials can be attributed mainly to the stress-induced transformation-toughening mechanism as indicated by the relative amount to tetragonal phase Qr and as predicted by Eq. (1).

Above 15 vol% pure ZrO₂, the relative amount of tetragonal phase is considerably reduced and microcracking toughening becomes the effective mechanism. However, the microcracking toughening is not as energy dissipative as transformation toughening, thus toughness is lower and strength is often affected. This latter effect is thus generally avoided in practical terms, and most of industrial zirconia-toughened ceramics rely on phase transformation during crack propagation.

Effect of Solute Content and Temperature

With stabilizing agent additions, the initial tetragonal phase content increases (Table 1), which is reflected by an increase of the critical size d_c . Consequently, the stress-induced phase transformation toughening effect becomes preponderant over microcracking toughening and the fracture energy increases up to 2 mol% Y₂O₃. For higher Y₂O₃ content, the critical stress σ_c required to initiate the transformation increases and the tetragonal phase becomes too stable to induce transformation toughening (G_c decreases).

Because the critical stress σ_c increases with yttria content and the thermal stresses augment with the volume fraction of ZrO₂, the volume fraction of particles corresponding to maximum toughness increases also as a function of yttria content.

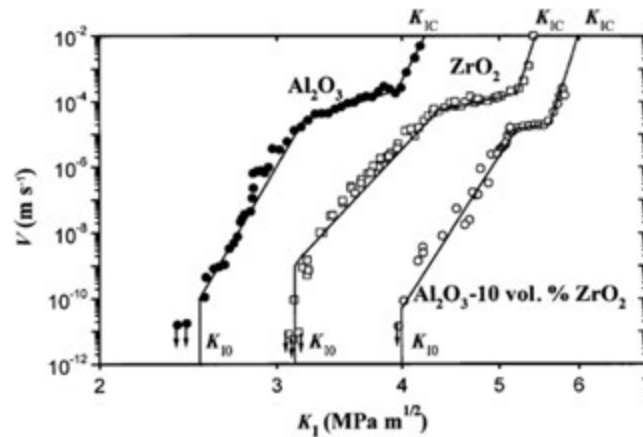


Fig. 2 Crack velocity versus stress intensity factor K_I in alumina, zirconia (Y-tetragonal zirconia polycrystal) and ZrO_2 -toughened alumina (10 vol% ZrO_2). From Encyclopedia of Materials: Science and Technology, Elsevier, 2001.

Fracture toughness decreases as temperature increases, σ_c increases. The reinforcement becomes negligible when temperature reaches about 600°C, the critical temperature at which the $t \rightarrow m$ transformation is no longer effective.

When the preponderant toughening mechanism is microcracking (e.g., the composite A20Z without stabilizing addition, in Table 1), toughening becomes independent of temperature.

Zirconia particles have also been added to reinforce other ceramic matrices. The preceding general features can be applied; however, toughening mechanisms are more complex (Green *et al.*, 1989).

Creep and Fatigue Behaviors of Zirconia-Toughened Composites

The creep behavior of zirconia-reinforced ceramics has been described by Fantozzi *et al.* (2000). The addition of zirconia particles does not improve the creep resistance, creep being essentially controlled by grain boundary sliding (GBS) in the matrix.

The static fatigue behavior of ZTA composites was studied at room temperature (Chevalier *et al.*, 2000). Fig. 2 shows the slow crack growth behavior of a reinforced alumina under static loading. For comparison, the results obtained for alumina and yttria-stabilized polycrystalline tetragonal zirconia (3Y-TZP) are also included.

Crack propagation is controlled by stress corrosion by water at the crack tip. Clearly, the slow crack growth resistance is increased for the ZTA composite, because the overall $V-K_I$ (crack velocity versus stress intensity factor) curve is shifted toward high stress intensity factors for the composite. A threshold K_{I0} below which no propagation occurs is observed in the three ceramics. The threshold K_{I0} is higher for the alumina composite compared to alumina or TZP. This result is very significant (e.g., for bioceramics applications such as hip joints) where the resistance to slow crack growth is detrimental. This explains, in part (some other factors also play a role in the overall reliability of a component), why current femoral heads are often made of ZTA ceramics (e.g., Biolox Delta®) (Chevalier *et al.*, 2009).

Cyclic loading promotes crack growth rate and leads to a decrease of the threshold stress. The fatigue behavior can be described as stress corrosion propagation associated with toughening degradation (as shown by Chevalier *et al.*, 1999). Several toughening mechanisms can intervene (e.g., transformation toughening, bridging, microcracking). Similar observations have been made on PSZ composites by Dauskardt *et al.* (1990). Nevertheless, ZTA composites still offer a better cyclic resistance than alumina monoliths or even 3Y-TZP.

Properties of Whisker Composites

Whiskers (W) were among the first reinforcements proposed in ceramic composites to improve toughness by crack deflection and bridging. Being strongly anisotropic, different composite textures can be observed depending on the processing route used to produce the composite. The reduction of densification induced by the whiskers has led to the use of hot pressing (HP), which produces a microstructure in which the whiskers are randomly oriented within a plane. This is also the case when the slip-casting route is used. Isotropic bodies can be obtained by powder preparation followed with pressureless or hot isostatic pressing.

The structural anisotropy can be observed on the microstructure and by toughness and strength measurements. An increase of both toughness and strength of about 50% has been measured in $SiC(W)-Al_2O_3$ composites when the crack plane was perpendicular to the whisker plane (Becher and Wei, 1984). Whiskers have been incorporated in alumina, silicon nitride, and to a lesser extent in mullite, zirconia, glass, or other matrices (Bradley *et al.*, 1988).

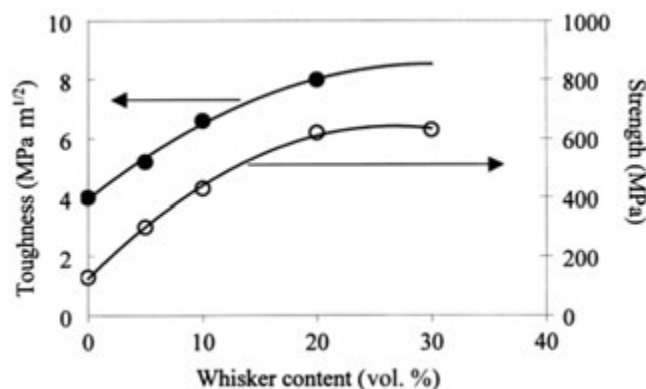


Fig. 3 Fracture toughness and flexural strength of whisker-reinforced alumina as a function of whisker content. From Encyclopedia of Materials: Science and Technology, Elsevier, 2001.

SiC(W)–Alumina Composites

Spectacular reinforcements by whiskers have been obtained in the case of alumina, with concomitant increases of both toughness and strength (Fig. 3). Toughness values higher than $10 \text{ MPa m}^{1/2}$ have been recorded for 20–30 vol% whisker content. Such composites have been made with small diameter whiskers ($0.3\text{--}0.6 \mu\text{m}$). The achievement of a similar strengthening depends on the whisker dispersion in the matrix and on the densification of the composite. In order to reach theoretical density, the composites are generally hot pressed. Fig. 3 shows the evolution of both toughness and flexural strength of alumina matrix composites with the SiC(W) addition.

As predicted by Eq. (3), higher toughening is obtained with increasing whisker diameter, strength, and volume content, and with decreasing the frictional interfacial shear stress.

However, due to the thermal expansion mismatch of SiC and Al_2O_3 , a too large whisker diameter induces matrix microcracking, reducing strength. Optimum results have been obtained with whisker diameters lower than $1 \mu\text{m}$ (Fantozzi and Olagnon, 1993).

The main toughening mechanisms are crack deflection and crack bridging. Reinforcement is observed up to about 1000°C .

SiC(W)–Other Matrices Composites

Whiskers have been incorporated in silicon nitride, mullite, zirconia, and glass (Becher and Rose, 1994). In the case of a Si_3N_4 matrix, the results were disappointing: The reinforcement is less significant than for alumina. This is due to the different microstructures observed for Si_3N_4 : Equiaxed or elongated grains depending on the sintering conditions and sintering aids. Toughness values of about $10 \text{ MPa m}^{1/2}$ have been observed. For other matrices, the toughness increase is lower.

In order to improve toughness further, various toughening processes can be combined: Whisker reinforcement, transformation toughening, and matrix microstructural-grain size effect. Either additive or coupled contributions can be obtained and multiple toughening mechanisms provide significant increase in fracture resistance: Values of $10 \text{ MPa m}^{1/2}$ have been observed for mullite reinforced by 20 vol% of SiC(W) and 20 vol% of $t\text{-ZrO}_2$ and toughness higher than $13 \text{ MPa m}^{1/2}$ has been achieved for ZTA reinforced with 20 vol% of SiC(W).

Creep Behavior

Most creep studies of these materials have been performed on whisker-reinforced alumina but other matrices such as Si_3N_4 , ZrO_2 , and mullite have also been studied (Fantozzi *et al.*, 2000).

The creep rate of alumina is reduced by the additional SiC(W), as shown by Fig. 4. This decrease depends significantly on the whisker content, size, and shape, on the presence of densification additives, and on the matrix grain size. The steady state creep rates of the alumina composites are two orders of magnitude lower than that of monolithic alumina. GBS, accommodated by diffusion processes, is the dominant mechanism responsible for the creep behavior of the composites. The addition of whiskers limits GBS, the whiskers acting as hard intergranular particles. For high whisker content ($> 30 \text{ vol}\%$), creep resistance is degraded, creep cavitation being enhanced. Similar enhancement in creep resistance is observed for mullite. However, reinforced Si_3N_4 , ZTA, or ZrO_2 do not show improvement in creep resistance.

Particle- and Platelet-reinforced Composites

Under this classification, only particles or platelets experiencing no transformation are considered.

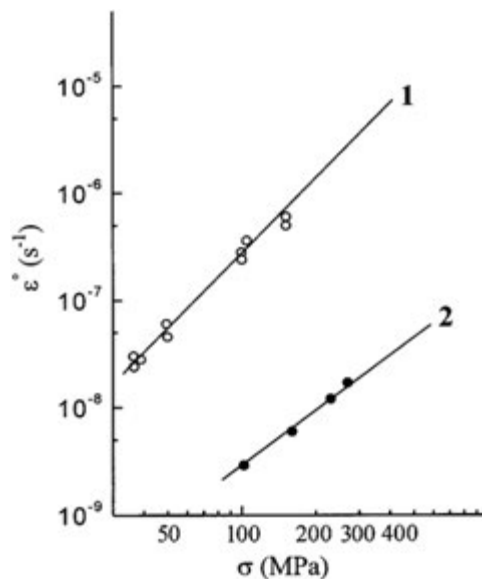


Fig. 4 Stress dependence of the steady creep rate in flexure of alumina (1) and 20 vol% SiC (W) composite (2) at 1473K. From Encyclopedia of Materials: Science and Technology, Elsevier, 2001.

The concept is similar to that of whisker composites, but with lower potential toughening. However, this type of composites has the advantage of being processed by conventional methods. The development of such composites was primarily focused on tribological applications with a double target: Improving both toughness and hardness.

The reinforcement of alumina by SiC, TiC, BN, and TiN; of silicon carbide by TiB₂, TiC, and AlN; and of silicon nitride by SiC and TiC has been investigated (Fantozzi and Olagnon, 1993).

The residual stress due to thermal mismatch is an important parameter controlling toughening. When the thermal expansion coefficient of particles is lower than that of the matrix, composites are likely to experience microcrack toughening whereas in the opposite case, toughening will be mostly due to crack particle interaction.

A good example of toughening by microcracking has been observed in SiC–Al₂O₃ composites: A maximum in toughness occurs as a function of the particle contents. Highest toughening is obtained with the smallest particles but a strength degradation is observed for large-sized particles, due to the formation of large cracks.

In the case of Si₃N₄ reinforced with SiC, the highest fracture energy has been obtained with the coarse particles, crack deflection being responsible for toughening without microcracking.

Thus no general law between the toughness and the particle size can be stated since values observed strongly depend on the toughening mechanism. The reinforcement by particles can lead to values of 5–6 MPa m^{1/2} for toughness.

SiC or Al₂O₃ platelets have been incorporated into Si₃N₄, alumina, mullite, and TZP matrices. Toughening is due to crack deflection and crack bridging, with some pull-out. In the case of Si₃N₄, spectacular toughening has been observed with 30% SiC platelets (14 MPa m^{1/2}), but this was accompanied by a strength reduction. A special mention must be made with regard to nanocomposites (Niihara, 1991). The reinforcing nanosized particles are either inter- or intragranular. Indeed, room-temperature and high-temperature strengths are significantly improved in nanocomposites, although fracture toughness is only modestly increased. The particles bridging and the decrease of flaw sizes could be the essential strengthening mechanisms.

The creep behavior of particle or platelet-reinforced composites has been studied for different matrices (alumina, mullite, Si₃N₄) (Fantozzi *et al.*, 2000). In the case of alumina composites, the increase of creep resistance is lower than that observed with the whisker composites (one order of magnitude). On the other hand, alumina/silicon carbide nanocomposites present an excellent creep resistance: The creep rate is reduced by two to three orders of magnitude in comparison with alumina. The SiC nanoparticles hinder GBS and provoke a large improvement in creep resistance.

Improvement of creep resistance in other matrices for particle or platelet composites is also observed but is generally low. However, excellent creep resistance is obtained for mullite–zirconia composites and Si₃N₄ composites.

Mechanical Properties of Carbon Nanotube- and Graphene-Reinforced-Based Ceramic Composites

Carbon nanotubes, and more recently graphene nanoplatelets or graphene oxide nanosheets, have attracted a lot of attention in the materials science community to improve targeted properties such as wear resistance, conductivity and above all mechanical resistance. Thanks to the exceptional mechanical properties (very high modulus and strength) and electrical conductivity of carbon

nanotubes (CNTs) and graphene, fabrication of ceramics reinforced with CNTs and graphene presents a great interest in order to obtain tough and electric conductive ceramic composites (Ahmad *et al.*, 2015; Markandan *et al.*, 2017; Porwal *et al.*, 2013). Graphene is an interesting alternative to CNTs because it exhibits a large specific surface area and a homogeneous distribution in the matrix. The two types of reinforcements will be successively considered. Note that other types of graphene-based materials can be considered, or even other platelet-like reinforcements (e.g., boron nitride nanosheets). The fundamental mechanisms of toughening are quite similar to the ones described below.

Carbon Nanotube-Reinforced Ceramic Composites

The majority of composites are reinforced by using multiwalled CNTs (MWCNTs) against single-walls CNTs (SWCNTs). A good homogeneous dispersion of CNTs within the matrix must be obtained. This is detailed, for example, by Ahmad *et al.* (2015). A homogeneous dispersion is obtained only for the low CNT concentration (<2 wt%), agglomeration being observed for higher concentration. Furthermore, CNTs hinder the densification during sintering and the CNT-reinforced ceramics are very often sintered with a pressure-assisted process like spark plasma sintering (SPS) or hot pressing (HP) in order to obtain high density and good mechanical properties. This also preserves the quality of the CNTs.

Many studies show that higher fracture toughness are obtained for CNT-reinforced ceramics with MWCNTs and lower CNT addition (<2 wt%). Some authors have found the same fracture toughness than the matrix whereas others have even observed a decrease of fracture toughness (Lamnini *et al.*, 2019; Bocanegra-Bernal *et al.*, 2016).

It must be noted that the fracture toughness is measured with different techniques such as indentation fracture (IF) or single-edge notch beam (SENB) and single-edge V-notch beam (SEVNB). The validity of different methods of measurement is always controversial but the SENB or SEVNB methods are generally considered as more consistent and accurate. However, IF should be considered (with care) for comparison and evolution purposes.

Regarding hardness, very often it decreases with the addition of NTCs. This decrease can be related to the density decrease, the agglomeration of CNTs or to the presence of soft phases along the grain boundaries (Shin *et al.*, 2018). An increase of hardness can be observed for the composites, which is attributed to the reduction of grain size.

Three typical examples of reinforcement by CNTs will be subsequently addressed.

The first one concerns the reinforcement of alumina matrix by SWCNTs (Shin *et al.*, 2018). A homogeneous dispersion of SWCNTs and nearly full densification were achieved by SPS. The variation of the elastic modulus is shown in Fig. 5: The elastic modulus decreases with increasing the CNT content. This decrease is linked to the density decrease. The evolution of hardness and IF toughness is described in Fig. 6. Although grain size is decreasing, the hardness decreases due to a decrease of the density and an agglomeration of CNTs. The fracture toughness is slightly increasing as a function of CNT content from 3.7 MPa m^{1/2} for monolithic alumina to 4.2 MPa m^{1/2} for 1 wt% SWCNT addition. The flexural strength measured by three-point bending test increases with increasing the CNT content except for 1 wt% due to the decrease in density and CNT agglomerates.

The toughening mechanisms occurring in the composites are crack deflection, crack branching, and crack bridging.

The second example corresponds to nanostructured high purity 3 mol% yttria-stabilized zirconia (3YSZ) reinforced by MWCNTs. Full-dense nanostructured composites (98%) without damage of NTCs (Mazaheri *et al.*, 2011) were processed by SPS

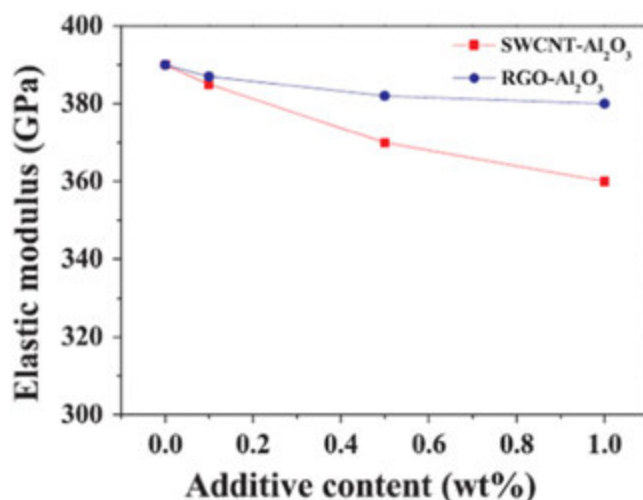


Fig. 5 Elastic modulus of single-wall carbon nanotube-reinforced (and reduced graphene oxide-reinforced) alumina composites. From Shin, J.H., Choi, J., Kim, M., Hong, S.H., 2018. Comparative study on carbon nanotube- and reduced graphene oxide-reinforced alumina ceramic composites. *Ceramics International* 44, 8350–8357.

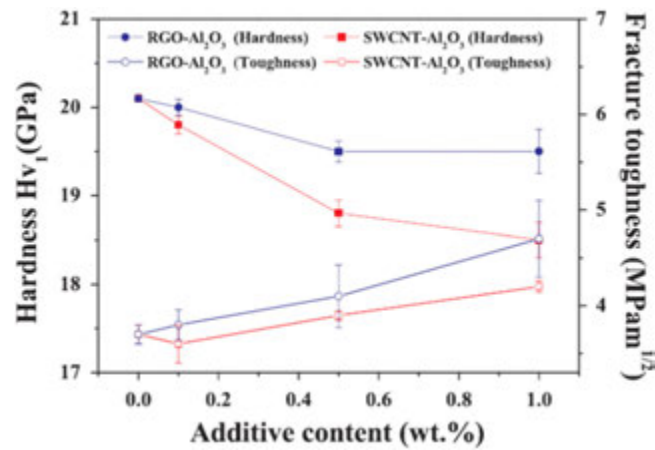


Fig. 6 Vickers hardness and indentation fracture toughness of single-wall carbon nanotube-reinforced (and reduced graphene oxide-reinforced) alumina composites. From Shin, J.H., Choi, J., Kim, M., Hong, S.H., 2018. Comparative study on carbon nanotube- and reduced graphene oxide-reinforced alumina ceramic composites. *Ceramics International* 44, 8350–8357.

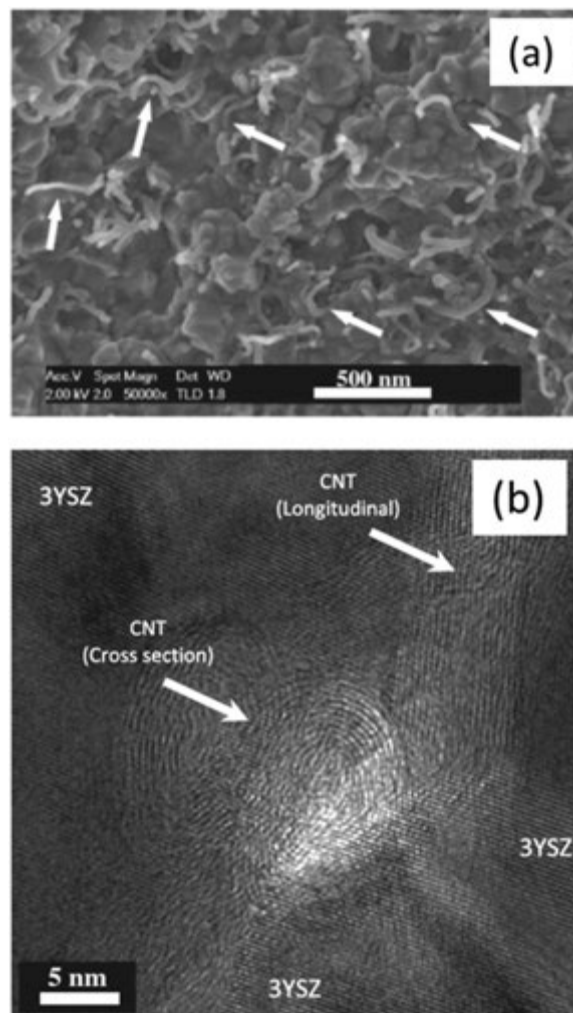


Fig. 7 Scanning electron microscopy picture of fractured surface of 3YSZ/5 wt% carbon nanotube (a) and high resolution-transmission electron microscopy of interface between multiwalled carbon nanotubes and zirconia grains (b). From Mazaheri, M., Mari, D., Hesabi, Z.R., Schaller, R., Fantozzi, G., 2011. Multi-walled carbon nanotube/nanostructured zirconia composites: Outstanding mechanical properties in a wide range of temperature. *Composites Science and Technology* 71, 939–945.

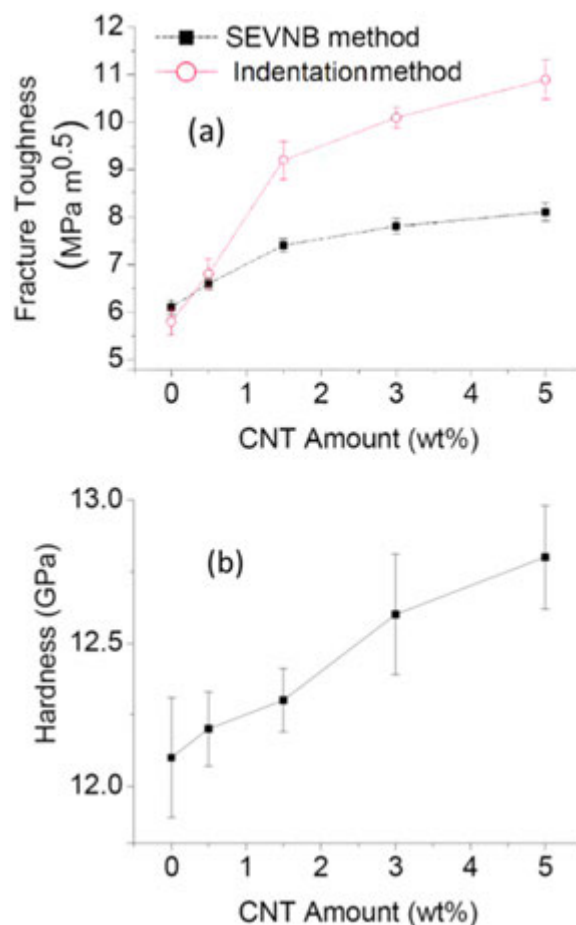


Fig. 8 Fracture toughness (a) and Vickers hardness (b) as a function of carbon nanotubes wt%. From Mazaheri, M., Mari, D., Hesabi, Z.R., Schaller, R., Fantozzi, G., 2011. Multi-walled carbon nanotube/nanostructured zirconia composites: Outstanding mechanical properties in a wide range of temperature. *Composites Science and Technology* 71, 939–945.

(the grain size is about 100 nm). No evidence of CNT damage and agglomeration can be observed up to 5 wt% CNT content. MWCNTs reduce grain growth because they pin grain boundaries.

Fig. 7(a) shows a scanning electron microscopy (SEM) image of a fracture surface of 3YSZ/5 wt% CNT. A homogeneous distribution of MWCNTs in nanostructured zirconia matrix is observed and CNT pull-out is apparent. The high resolution transmission electron microscopy (TEM) image shows clean interfaces between MWCNTs and zirconia grains (**Fig. 7(b)**). The evolution of the fracture toughness (measured by two methods IF and SEVNB) and Vickers hardness is shown in **Fig. 8** as a function of the MWCNT content. A significant increase of toughness with increasing CNT content and a slight increase of hardness are observed (**Fig. 8(a)**). To ensure that the reinforcement is not due to phase transformation toughening but is due to the effect of CNTs, it was verified that the stress-induced monoclinic phase decreases with the increase of CNT content due to the decreasing grain size. Thus the reinforcement can only be attributed to CNTs.

The toughening mechanisms frequently reported for the reinforcement are pull-out, crack deflection and crack bridging. **Fig. 9** shows the MWCNTs are stretched between crack faces of the indentation-induced crack with the occurrence of crack bridging, crack deflection and CNT pull-out (**Fig. 9(b)**).

Nanotubes are flexible and are not embedded within the matrix grains and are present especially along the grain boundaries. The length of emerging CNTs on the fracture surface is short (< 200 nm) and therefore the energy dissipation for debonding is negligible as suggested by [Mukhopadhyay et al. \(2010\)](#). Furthermore, as shown by **Fig. 7(b)**, a strong interface between CNT and matrix is observed that does not allow pull-out and that leads to a higher elastic modulus of the composites compared to the monolithic zirconia one.

A possible mechanism responsible for both toughening and strengthening is thus the uncoiling and stretching of NTCs producing crack bridging as shown by **Fig. 9(b)**, leading to fracture work and energy dissipation. It can be also noticed a pinning effect of CNTs that inhibit GBS and creep at high temperature.

The last example concerns the toughening of nanostructured MWCNT/SiC composites sintered by SPS without sintering additives ([Lanfant et al., 2019](#)). CNTs have a negative effect on the densification and leads to a decrease of grain size with

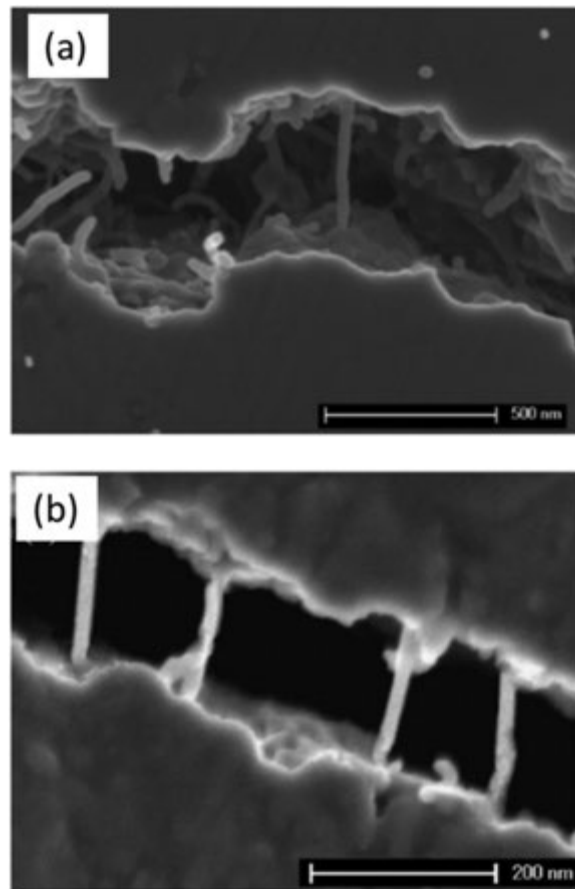


Fig. 9 Scanning electron microscopy picture of indentation-induced crack on the surface of 3YSZ/5 wt% carbon nanotubes. From Mazaheri, M., Mari, D., Hesabi, Z.R., Schaller, R., Fantozzi, G., 2011. Multi-walled carbon nanotube/nanostructured zirconia composites: Outstanding mechanical properties in a wide range of temperature. *Composites Science and Technology* 71, 939–945.

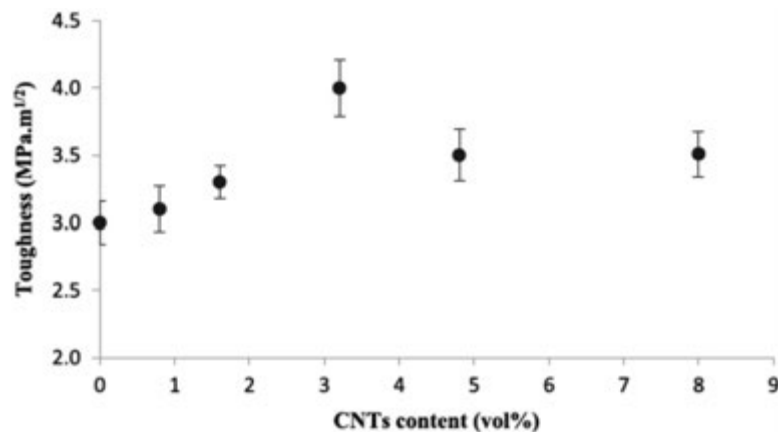


Fig. 10 Evolution of toughness of the SiC composites as a function of carbon nanotubes content. From Lanfant, B., Leconte, Y., Debski, N., *et al.*, 2019. Mechanical, thermal and electrical properties of nanostructured CNTs/SiC composites. *Ceramics International* 45, 2566–2575.

increasing CNT content. However, it is possible to achieve nanostructured composites with a relative density of 97% for 3 vol% of CNTs. A beneficial effect of CNTs on the mechanical properties is obtained. Vickers hardness was increased up to 2560 Hv (for 3 vol% of CNTs) instead of 2080 Hv for the SiC matrix. The evolution of fracture toughness estimated by IF as a function of CNT content is shown in Fig. 10. Up to 3.2 vol% of CNTs, a clear increase of toughness is observed and a toughness of 4 MPa m^{1/2} is reached. Then a small decrease is observed for CNT content higher than 3.2 vol%. The SEM observations of fracture surfaces

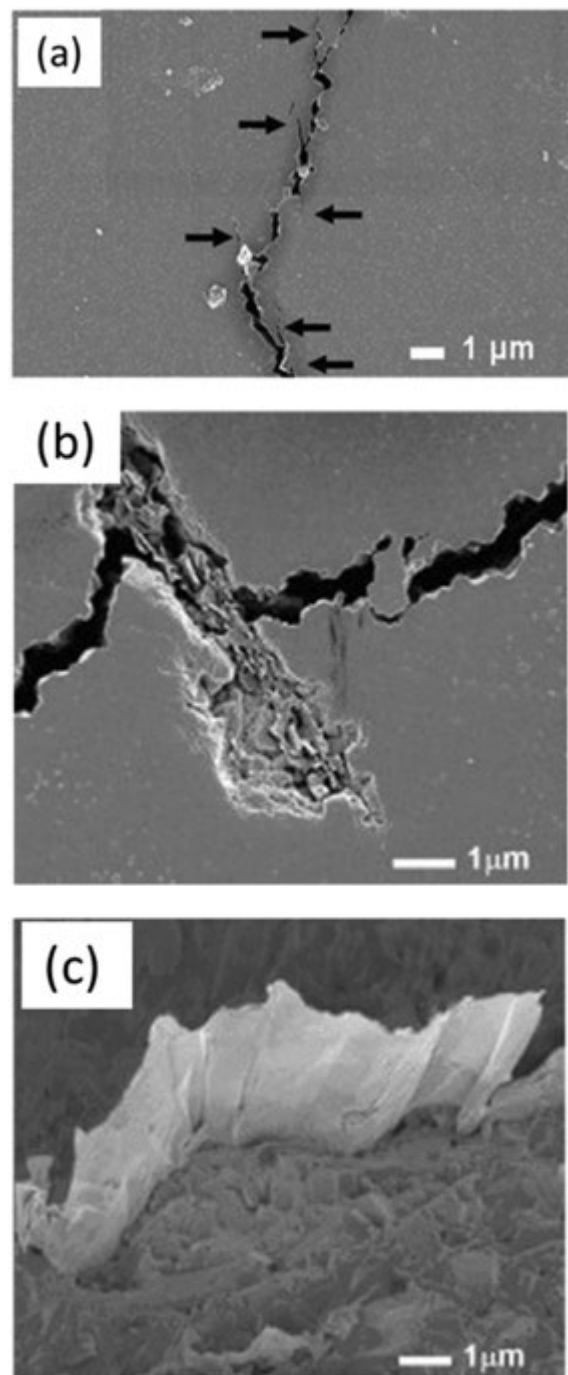


Fig. 11 Toughening mechanisms by graphene platelet in Si₃N₄ composites: Crack branching (a), crack bridging, (b) and pull-out (c). From Kvetkova, L., Duszova, A., Hvizdos, P., *et al.*, 2012. Fracture toughness and toughening mechanisms in graphene platelet reinforced Si₃N₄ composites. *Scripta Materiala* 66, 793–796.

show the bridging and the pull-out of CNTs, mechanisms improving toughness. For higher content than 3.2 vol%, toughness is decreasing due to the presence of CNT bundles in the composites.

In summary, CNTs allow to improve the mechanical behavior of CNT-reinforced ceramic composites, especially fracture toughness. Furthermore, CNTs can act as lubricant leading to wear resistant materials, decreasing the friction coefficient. They can also lead to conductive materials, which is positive for some applications as well as for electro-machining.

Graphene-Reinforced Ceramic Composites

Graphene presents similar electrical, mechanical, and thermal properties to CNTs (Ahmad *et al.*, 2015; Markandan *et al.*, 2017; Porwal *et al.*, 2013). Graphene exhibits a higher specific area and can be more easily dispersed into a matrix without formation of tangles compared to CNTs. Powder processing used for graphenes-reinforced ceramic composites is very similar to that used for CNTs, and the same sintering techniques with application of pressure are used.

Many authors have reported an improvement of mechanical properties of ceramics by addition of graphene. An example of increase of IF toughness of alumina with addition of reduced graphene oxide (RGO) is shown in Fig. 6: The fracture toughness increases up to 4.7 MPa m^{1/2} for 1 wt% RGO addition. The elastic modulus and hardness of RGO-reinforced composites are decreased with RGO addition, the relative density being slightly higher (Figs. 5 and 6). This decrease can be linked to the sliding feature and low elastic modulus of RGO.

The toughening mechanisms reported for the reinforcement by graphene are similar to mechanisms observed for CNTs: Pull-out, crack deflection, crack branching, and crack bridging.

Fig. 11 shows these different mechanisms observed by Kvetkova *et al.* (2012) in graphene platelet (GPL)-reinforced Si₃N₄ composites. The IF toughness of the composites is increased from 6.9 MPa m^{1/2} for the matrix up to 9.9 MPa m^{1/2} for a composite reinforced with 1 wt% GPL addition. Fig. 11(a) shows crack branching linked to the interaction of the propagating crack and smaller GPLs – with the occurrence of secondary cracks. Crack deflection is observed upon crack interaction with larger GPLs. Fig. 11(b) shows crack bridging by larger GPLs and Fig. 11(c) pull-out by a large GPL. It can be noticed that the energy required for the pull-out of graphene sheet is more important than for NTCs due to sheet wrapping and larger contact area between GPL and matrix grains. The interface nature plays a significant role in the toughening compared to CNTs.

Conclusion

Monolithic ceramics can be toughened with roughly equiaxed reinforcements primarily to increase toughness, strength, creep resistance, and fatigue behavior. A wide variety of approaches can be used to reinforce ceramics: Toughness values can be increased from 2–4 MPa m^{1/2} for monolithic ceramics to about 15 MPa m^{1/2} for composites with an optimized microstructure. Special care must be taken in terms of choice of compositions and processing, since there is generally a maximum in mechanical properties (corresponding to an optimum in terms of toughening) before a quite strong decrease occurs. In any case, good dispersion of the reinforcement is absolutely mandatory.

References

- Ahmad, I., Yazdani, B., Zhu, Y., 2015. Recent advances on carbon nanotubes and graphene reinforced ceramics nanocomposites. *Nanomaterials* 5, 90–114.
- Becher, P.F., Rose, L.R.F., 1994. Chapter 8. Toughening mechanisms in ceramic systems. In: Swain, M.V. (Ed.), *Materials Science and Technology: Structure and Properties of Ceramics*, vol. 11. Weinheim: VCH.
- Becher, P.F., Wei, G.C., 1984. Toughening behavior in SiC-whisker-reinforced alumina. *Journal of the American Ceramic Society* 67, C-267–C-269.
- Bocanegra-Bernal, M.H., Dominguez-Rios, C., Echeberria, I., *et al.*, 2016. Spark plasma sintering of multi-, single/double- and single-walled carbon nanotube-reinforced alumina composites: Is it justifiable the effort to reinforce them. *Ceramics International* 42, 2054–2062.
- Bradley, R.A., Clark, D.E., Larsen, D.C., Stiegler, J.O., 1988. *Whisker- and Fiber-Toughened Ceramics*. Materials Park, OH: ASM International.
- Chevalier, J., De Aza, A., Fantozzi, G., Schehl, M., Torrecillas, R., 2000. Extending the lifetime of ceramic orthopedic implants. *Advanced Materials* 12, 1619–1621.
- Chevalier, J., Gremillard, L., Virkar, A.V., Clarke, D.R., 2009. The tetragonal-monoclinic transformation in zirconia: Lessons learned and future trends. *Journal of the American Ceramic Society* 92, 1901–1920.
- Chevalier, J., Olagnon, C., Fantozzi, G., 1999. Subcritical crack growth in 3Y-TZP ceramics: Static and cyclic fatigue. *Journal of the American Ceramic Society* 82, 3129–3138.
- Claussen, N., 1984. Microstructural design of zirconia-toughened ceramics. In: Claussen, N., Rühle, M., Heuer, A.H. (Eds.), *Advances in Ceramics: Science and Technology of Zirconia II*, vol. 12. Columbus, OH: American Ceramic Society, pp. 325–351.
- Dauskardt, R.H., Marshall, D.B., Ritchie, R.O., 1990. Cyclic fatigue-crack propagation in magnesia-partially-stabilized zirconia ceramics. *Journal of the American Ceramic Society* 73, 893–903.
- Evans, A.G., 1984. Toughening mechanism in zirconia alloys. In: Claussen, N., Rühle, M., Heuer, A.H. (Eds.), *Advances in Ceramics: Science and Technology of Zirconia II* 12. Columbus, OH: American Ceramic Society, pp. 193–212.
- Fantozzi, G., Chevalier, J., 2001. Ceramic matrix composites with roughly equiaxed reinforcements: Microstructure and mechanical behavior. In *Encyclopedia of Materials: Science and Technology*. Oxford: Elsevier, pp. 1066–1072.
- Fantozzi, G., Chevalier, J., Olagnon, C., Chermant, J.L., 2000. Chapter 7. Carbon/carbon, cement and ceramic matrix composites. Creep of ceramic matrix composites. In: Warren, R. (Ed.), *Comprehensive Composite Materials*, vol. 4. Oxford: Elsevier.
- Fantozzi, G., Olagnon, C., 1993. Chapter 5. Ceramic matrix composites. In: Chou, T.W. (Ed.), *Materials Science and Technology: Structure and Properties of Composites*, vol. 13. Weinheim: VCH.
- Fantozzi, G., Orange, G., 1986. Thermomechanical properties of zirconia-toughened alumina materials. In: Moya, J.S., de Aza, S. (Eds.), *Proceedings Processing of Advanced Ceramics*. Arganda del Rey: Sociedad Espanola de Ceramica y Vidrio, pp. 187–215.
- Green, D.J., Hannink, R.H.J., Swain, M.V., 1989. *Transformation Toughening of Ceramics*. Boca Raton, FL: CRC Press.
- Kvetkova, L., Duszova, A., Hvizdos, P., *et al.*, 2012. Fracture toughness and toughening mechanisms in graphene platelet reinforced Si₃N₄ composites. *Scripta Materiala* 66, 793–796.
- Lamini, S., Karoly, Z., Bodis, E., Balazsi, K., Balazsi, C., 2019. Influence of structure on the hardness and the toughening mechanism of the sintered 8YSZ/MWCNTs composites. *Ceramics International* 45, 5058–5065.
- Lanfani, B., Leconte, Y., Debski, N., *et al.*, 2019. Mechanical, thermal and electrical properties of nanostructured CNTs/SiC composites. *Ceramics International* 45, 2566–2575.

- Markandan, K., Chin, J.K., Tan, M.T.T., 2017. Recent progress in graphene based ceramic composites: A review. *Journal of Materials Research* 32, 84–106.
- Mazaheri, M., Mari, D., Hesabi, Z.R., Schaller, R., Fantozzi, G., 2011. Multi-walled carbon nanotube/nanostructured zirconia composites: Outstanding mechanical properties in a wide range of temperature. *Composites Science and Technology* 71, 939–945.
- Mukhopadhyay, A., Chu, B.T.T., Green, M.L.H., Todd, R.I., 2010. Understanding the mechanical reinforcement of uniformly dispersed multiwalled carbon nanotubes in alumina-borosilicate glass ceramic. *Acta Materialia* 58, 2685–2697.
- Niihara, K., 1991. New design concept of structural ceramics-ceramic nano-composites. *Journal of the Ceramic Society of Japan* 99, 974–982.
- Porwal, H., Grasso, S., Reece, M.J., 2013. Review of graphene-ceramic matrix composites. *Advance in Applied Ceramics* 112, 443–454.
- Shin, J.H., Choi, J., Kim, M., Hong, S.H., 2018. Comparative study on carbon nanotube- and reduced graphene oxide-reinforced alumina ceramic composites. *Ceramics International* 44, 8350–8357.

Nanoscale Ceramic Composites

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Processing and Microstructure of Al_2O_3 -SiC Nanocomposites

Al_2O_3 -SiC nanocomposites are produced using standard ceramic processing techniques. Matrix and second-phase powders are typically comilled in an organic medium to achieve a uniform dispersion of second phase throughout the matrix. After milling, the nanocomposite powder is dried and then densified using pressureless sintering or hot pressing. Relative to that of monolithic Al_2O_3 , densification in the nanocomposite is strongly inhibited by the presence of particles on grain boundaries, which reduce the rate of grain-boundary diffusion. As a result, the sintering conditions necessary to achieve full densification are strongly dependent on the amount of second phase, with the sintering temperature increasing significantly with the second-phase volume fraction. While monolithic Al_2O_3 can be pressureless sintered to near-theoretical density at 1400 °C, a temperature of 1775 °C is necessary for full densification in a nanocomposite of Al_2O_3 containing 5 vol.% SiC (Stearns *et al.*, 1992). In fact, no study has shown that full density can be achieved using pressureless sintering in a nanocomposite containing more than 5 vol.% SiC. The difficulties of densification in the nanocomposite can be alleviated by hot pressing. During hot pressing, an applied pressure increases the driving force for densification, allowing dense nanocomposites to be manufactured at lower temperatures (e.g., 1500 °C for 5 vol.% SiC) and with higher volume fractions of second phase (e.g., 20 vol.% SiC at a temperature of 1675 °C) (Stearns and Harmer, 1996).

The processing steps used to produce nanocomposites have a significant effect on their microstructures and properties. It is well known that the properties of the nanocomposite are strongly dependent on the second-phase dispersion (Stearns *et al.*, 1992). Specifically, a uniform dispersion of second phase is critical to obtaining superior properties in the nanocomposite relative to the monolith. Unfortunately, the spatial distribution of the second phase has been shown to be very sensitive to the processing conditions used, indicating that small changes in processing can lead to significant differences in the properties of the nanocomposite.

The microstructures of nanocomposites produced using the above technique are also strongly dependent on the amount of second phase present. In nanocomposites with a high volume fraction of second phase (>5 vol.%), matrix grains are equiaxed with a narrow size distribution, and second-phase particles are uniformly distributed among the matrix grains. An example of this type of microstructure (5 vol.% SiC in Al_2O_3) can be seen in Figure 1. On the contrary, in samples with a low volume fraction of second phase, the grain-size distribution of matrix grains may be significantly wider and in extreme cases, abnormal grains may be present.

As shown in Figure 1, second-phase particles in the nanocomposite are either located on grain boundaries (intergranular) or inside grains (intragranular). As will be discussed later, the location of particles with respect to grain boundaries plays the paramount role in the improvement of the properties of the nanocomposite over the monolith (Xu *et al.*, 1997). In particular, intragranular particles are believed to be responsible for the superior room-temperature properties of the nanocomposite, while the intergranular particles are believed to be responsible for its superior high-temperature properties. Intergranular particles also significantly increase the microstructural stability of the nanocomposite. The interaction of particles with grain boundaries strongly inhibits matrix grain growth which would normally take place at high temperatures. Figure 2 shows SiC particles inhibiting grain growth in the nanocomposite by pinning migrating grain boundaries. The relative proportions of intra- and intergranular particles is strongly related to the matrix grain size in the Al_2O_3 -SiC system, with the percentage of intergranular particles decreasing significantly with the grain size. For example, approximately 70% of particles are expected to be intergranular for a grain size of 1 μm , whereas 25% of particles are expected to be intergranular for a grain size of 5 μm (Stearns and Harmer, 1996).

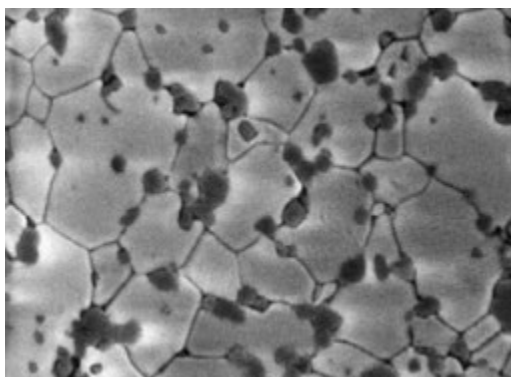


Figure 1 Scanning-electron-microscope image of the microstructure of a Al_2O_3 -5 vol.% SiC nanocomposite showing the presence of both intergranular and intragranular particles.

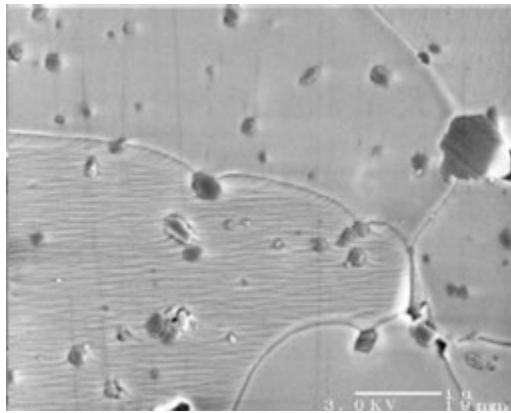


Figure 2 Scanning-electron-microscope image of SiC particles (5 vol.%) inhibiting grain growth by pinning migrating Al₂O₃ grain boundaries.

Room-Temperature Properties of Al₂O₃-SiC Nanocomposites

The superior mechanical properties of Al₂O₃-SiC nanocomposites at room temperature were first shown by Niihara, who found that the addition of 5 vol.% of 300 nm SiC particles to Al₂O₃ increased the strength from 380 to 1100 MPa (Niihara and Nakahira, 1988). Furthermore, it was shown that a simple annealing treatment at 1300 °C for 1 hour in argon gas subsequently increased the strength of the nanocomposites to over 1500 MPa. Niihara reported that the addition of the SiC particles also resulted in a significant increase in the fracture toughness, from 3.8 to 4.7 MPam^{1/2}. The superior properties of Al₂O₃-SiC nanocomposites over monolithic Al₂O₃ have been confirmed by a number of researchers, although none of these improvements have been as dramatic as those reported by Niihara (Zhao *et al.*, 1993; Borsa *et al.*, 1995; Jang *et al.*, 1996).

While the superior properties of the nanocomposite are well documented, the mechanisms responsible for the improvement in properties are still unclear. Proposed strengthening and toughening mechanisms for the unannealed nanocomposite include the reduction in critical flaw size due to the development of intragranular particle-induced subgrain boundaries, the attraction of intergranular cracks into matrix grains by residual tensile hoop stresses which arise due to the large thermal-expansion mismatch between Al₂O₃ and SiC, and the formation of a surface layer of compressive stresses during machining. The subsequent increase in strength and toughness after annealing has been attributed to the healing of surface flaws and the retainment of machining-induced compressive surface stresses, both the result of a slower stress relaxation behavior in the nanocomposite (Thompson *et al.*, 1995).

In addition to having improved strength and toughness relative to monolithic Al₂O₃, Al₂O₃-SiC nanocomposites also have superior wear properties. The improved wear properties are the result of a change in fracture mode which occurs when the concentration of the SiC second phase is greater than ~4 vol.%. While monolithic Al₂O₃ exhibits predominantly intergranular fracture, the large thermal-expansion mismatch between Al₂O₃ and SiC results in an apparent strengthening of Al₂O₃ grain boundaries, causing the nanocomposite to fracture transgranularly. As a result, grains in Al₂O₃-SiC nanocomposites are worn away slowly, in contrast to monolithic Al₂O₃ where wear typically involves the removal of entire grains due to the relatively weak interface at grain boundaries. The effect of the change in fracture mode on the wear properties of the nanocomposite is dramatic. In one study, the wet erosive wear rate of a 5 vol.% SiC nanocomposite was measured to be one-third that of monolithic Al₂O₃ with the same grain size (Walker *et al.*, 1994). Furthermore, the lack of grain pullout in the nanocomposite allows a higher-quality surface finish to be prepared (and retained during wear) than is possible with monolithic Al₂O₃.

High-Temperature Properties of Al₂O₃-SiC Nanocomposites

In addition to its superior room-temperature properties, Al₂O₃-SiC nanocomposite also possesses superior high-temperature properties. The superior strength and toughness of the nanocomposite at room temperature are retained as high as 1000 °C (Niihara and Nakahira, 1988). Furthermore, studies have shown that at higher temperatures, the creep resistance of Al₂O₃ is increased significantly by the presence of SiC particles (Ohji *et al.*, 1995; Thompson *et al.*, 1997). As shown in Figure 3, the creep rate of Al₂O₃ containing 5 vol.% SiC (150 nm) is 2–3 orders of magnitude lower than that of monolithic Al₂O₃ at temperatures as high as 1300 °C. In addition, the creep life of the nanocomposite is more than an order of magnitude longer than in the monolith. Unfortunately, the failure strain of the nanocomposite is lower than that of Al₂O₃ due to the nucleation of cavities at intergranular particles. The improved creep resistance of Al₂O₃-SiC has been attributed to a number of mechanisms. These mechanisms include a reduction in the rate of grain-boundary diffusion due to the presence of intergranular particles; an inhibition of shape-accommodation processes necessary for creep to occur, such as grain-boundary sliding and migration; and a reduction of the intrinsic grain-boundary diffusivity of Al₂O₃ by silicon cation contamination. The dominant mechanism responsible for the improved creep behavior of the nanocomposite is unknown.

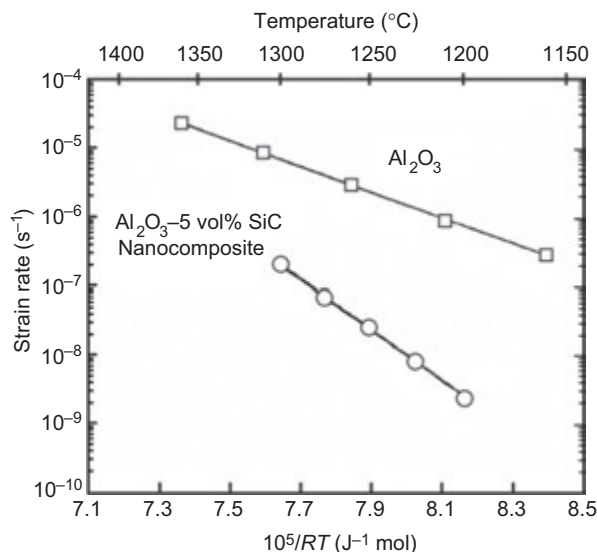


Figure 3 Plot of creep strain rate as a function of temperature for monolithic Al_2O_3 and Al_2O_3 -5 vol.% SiC nanocomposites (after Thompson *et al.*, 1997).

Concluding Remarks

Ceramic nanocomposites are relatively new materials which appear to have promise. In particular, Al_2O_3 containing nano-sized SiC second-phase particles has been shown to possess both room- and high-temperature properties which are superior to monolithic Al_2O_3 . These properties, which include higher strength and toughness, increased wear resistance, lower creep rates at elevated temperatures, and excellent microstructural stability, make nanocomposites an attractive alternative to monolithic ceramics for many structural applications.

References

- Borsa, C.E., Jiao, S., Todd, R.I., Brook, R.J., 1995. Processing and properties of $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites. *J. Microsc.* 177 (3), 305–312.
- Jang, B.-K., Enoki, M., Kishi, T., Lee, S.-H., Oh, H.-K., 1996. Fracture behavior and toughening of alumina-based composites fabricated by microstructural control. In: Bradt, R. C., Munz, D., Sakai, M., Ya Shevchenko, V. (Eds.), *Fracture Mechanics of Ceramics*. New York: Plenum, pp. 371–382.
- Niihara, K., Nakahira, A., 1988. Strengthening of oxide ceramics by SiC and Si_3N_4 dispersions. In *Proceedings 3rd International Symposium Ceramic Materials and Components for Engines*. Westerville, OH: The American Ceramic Society, pp. 919–926.
- Ohji, T., Nakahira, A., Hirano, T., Niihara, K., 1995. Tensile creep behavior of alumina/silicon carbide nanocomposite. *J. Am. Ceram. Soc.* 77 (12), 3259–3263.
- Stearns, L.C., Harmer, M.P., 1996. Particle-inhibited grain growth in Al_2O_3 -SiC: I. experimental results. *J. Am. Ceram. Soc.* 79 (12), 3013–3019.
- Stearns, L.C., Zhao, J., Harmer, M.P., 1992. Processing and microstructure development in Al_2O_3 -SiC "nanocomposites." *J. Eur. Ceram. Soc.* 10 (6), 473–477.
- Thompson, A.M., Chan, H.M., Harmer, M.P., 1995. Crack healing and stress relaxation in Al_2O_3 -SiC "nanocomposites." *J. Am. Ceram. Soc.* 78 (3), 567–571.
- Thompson, A.M., Chan, H.M., Harmer, M.P., 1997. Tensile creep of alumina-silicon carbide "nanocomposites." *J. Am. Ceram. Soc.* 80 (9), 2221–2228.
- Walker, C.N., Borsa, C.E., Todd, R.I., Davidge, R.W., Brook, R.J., 1994. Fabrication, characterisation and properties of alumina-matrix nanocomposites. *Br. Ceram. Proc.* 53, 249–264.
- Xu, Y., Zangvil, A., SiC, A. Kerber, 1997. Nanoparticle-reinforced Al_2O_3 matrix composites: Role of intra- and intergranular particles. *J. Eur. Ceram. Soc.* 17, 921–928.
- Zhao, J., Stearns, L.C., Harmer, M.P., Chan, H.M., Miller, G.A., 1993. Mechanical behavior of alumina-silicon carbide "nanocomposites." *J. Am. Ceram. Soc.* 76 (2), 503–510.

Further Reading

- Jiao, S., Jenkins, M.L., Davidge, R.W., 1997. Electron microscopy of crack/particle interactions in $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites. *J. Microsc.* 185 (2), 259–264.
- Niihara, K., 1991. New design concept of structural ceramics: Ceramic nanocomposites. Centennial Memorial Issue of the Ceramic Society of Japan 99 (10), 974–982.
- Niihara, K., Nakahira, A., 1990. Particulate-strengthened oxide nanocomposites. In: Vincenzini, P. (Ed.), *Advanced Structural Inorganic Composites*. London: Elsevier, pp. 637–664.
- Niihara, K., Nakahira, A., Sasaki, G., Hirabayashi, M., 1989. Development of strong Al_2O_3 -SiC composites. In: *Materials Research Society Symposium Proceedings International Meeting on Advanced Materials*. vol. 4 Materials Research Society, Warrendale, PA. pp. 129–134.

Ceramic Matrix Graphene and Carbon Nanotube Composites

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Introduction

Development of new materials with extreme mechanical, thermal and electrical properties is of technological interest. Silicon nitride based ceramics are well-known as low density materials with high strength and toughness, thus they are ideal candidates for several structural applications, even at high temperatures. By in-situ tailoring processes, the mechanical properties may be improved through the formation of tough interlocking microstructures (Shen *et al.*, 2002; Thompson, 2002). Depending on processing route, micro/nano or nano/nano type microstructures can be synthesized (Bhaduri and Bhaduri, 1998). Many recently developed preparation routes exist to produce ceramic matrix composites with superior technological characteristics (Papakonstantinou *et al.*, 2001). Although diamond and graphite have been well known for centuries, nanosized allotropes of carbon such as fullerenes, nanotubes and lastly graphene have been only discovered recently. Monolayer graphene is a one atom thick sheet composed of hexagonal structures of carbon atoms, however graphene samples with two or more layers are also being investigated with equal interest. This two dimensional material is characterized by exceptional electrical, mechanical and thermal properties (Balandin *et al.*, 2008; Geim and Novoselov, 2007; Rao *et al.*, 2009; Segal, 2009; Soldano *et al.*, 2010). Researchers have proved that electrons can move ballistically in graphene layers with a mobility exceeding $200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Moreover, graphene has unique thermal conductivities (up to $5300 \text{ W m}^{-1} \text{ K}^{-1}$) and it has superior mechanical properties with a Young's modulus of approximately 1.0 TPa. Interestingly, despite their non-perfect structure, even suspended graphene oxide sheets retain a Young's modulus of almost 0.25 TPa. Therefore, it is expected that the addition of graphene based materials will significantly improve the properties of different matrices, such as polymer, metal and ceramic (Ramanathan *et al.*, 2008).

In the last few years there are increasing numbers of reports on the use of graphene in ceramics. Fan *et al.* (2010) have prepared graphene nanosheet reinforced alumina matrix composites. The electrical conductivity of that composite outperforms the conductivity of the Al_2O_3 /carbon nanotube composites. The research on ceramic composites with incorporated carbon-based fillers has mainly focused on carbon nanotubes (CNTs) at the beginning of the 21st century. In the first decade, various CNT-reinforced ceramic systems have been developed and improved properties of these composite materials have been reported in a large number of works. It has been reported that a significant increase in bending strength and fracture toughness has been achieved in CNT reinforced alumina matrix composites (Ahmad *et al.*, 2010; Xia *et al.*, 2004; Yamamoto *et al.*, 2008; Zhan *et al.*, 2003). On the contrary, other researchers have not found such increases in toughness, but have noted significantly improved contact-damage resistance for these composites (Wang *et al.*, 2004). Considerable increases in electrical conductivity have been achieved in carbon nanofibers-zirconia composites (Dusza *et al.*, 2009) and CNT reinforced silicon nitride matrix composites (Gonzalez-Julian *et al.*, 2011; Tatami *et al.*, 2005; Yoshio *et al.*, 2011). In addition, the carbon nanotubes can influence the thermal conductivity (Corral *et al.*, 2011) and the friction coefficient (Hvizdos *et al.*, 2011) of silicon nitride composites. It has also been shown that with carbon nanostructure (CNT, graphene) incorporation into ceramic matrices, new emerging technologies can be foreseen and established (Fényi *et al.*, 2008a; Maleka *et al.*, 2011; Ramirez *et al.*, 2011; Balázs, 2012).

From an electrical point of view, ceramic matrix materials (e.g., alumina, silicon nitride) are regarded as typically insulator materials. The carbon additives, such as carbon nanotube (CNT) and graphene (GR) can drastically change the electric properties of the composites (Balázs *et al.*, 2005a; Kónya *et al.*, 2002; McLachlan *et al.*, 1990; Thostenson *et al.*, 2001). Analysis of the resistance measurements, changes in electric nature as a function of the type and concentration of the carbon additive can be determined. Indeed, carbon addition influenced mainly the electric properties, e.g., insulator – conductor transition (Fényi *et al.*, 2008b).

Definition of Composite, Nanocomposite Material

A composite consists of at least two different materials with significantly different physical or chemical properties. The definition of nanocomposite material has broadened significantly to encompass a large variety of systems such as one-dimensional, two-dimensional, three-dimensional and amorphous materials, made of distinctly dissimilar components and mixed at the nanometer scale (Niihara, 1991). Reducing the sizes of structural features in materials leads to a significant increase in the portion of surface/interface atoms. The surface/interface energies essentially control the properties of a solid, thus interfaces provide a means of introducing non-homogeneity into a material. This non-homogeneity can result in significant modification to both thermal and mechanical properties of the composites. Thus, selective mixing of materials with a highly tailored morphology with high percentage of interface area, leads to composite materials with enhanced properties.

The properties of composite materials depend not only on the properties of their individual components, but also on their morphology and interfacial characteristics. Nanocomposites find their use in various applications because of the improvements in the properties over the simpler structures. Some advantages can be summarized as:

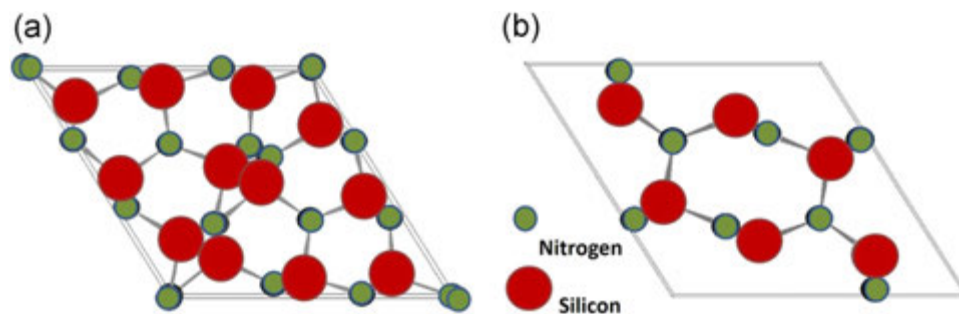


Fig. 1 Schematic diagram of silicon nitride. (a) α - Si_3N_4 , (b) β - Si_3N_4 .

- (1) Improved mechanical properties e.g., strength, modulus and dimensional stability.
- (2) Decreased permeability to gases, water and hydrocarbons.
- (3) Higher thermal stability and heat distortion temperatures.
- (4) Higher flame retardancy and reduced smoke emissions.
- (5) Higher chemical resistance.
- (6) Smoother surface appearance.
- (7) Higher electrical conductivity.

Starting Materials for Composite Preparation

Silicon Nitride (Si_3N_4)

Two crystalline modifications of silicon nitride are widely known and researched. **Fig. 1** shows a schematic diagram of the α - Si_3N_4 (**Fig. 1(a)**) and β - Si_3N_4 (**Fig. 1(b)**) phases. Both structures are made up of tetrahedra containing one silicon atom in the center and four nitrogen atoms at the corners. They are covalently bonded to each other. The crystal structure of the α and β phases is hexagonal. The difference between the a unit cell parameter is not very significant (for α - Si_3N_4 $a = 7.818 \text{ \AA}$, and for β - Si_3N_4 $a = 7.608 \text{ \AA}$) (Villars and Calvert, 1986). However, along the longitudinal axis (c -axis), the unit cell c dimension of the α -phase ($5.591 \text{ \AA}$) is about twice that of the β -phase ($2.911 \text{ \AA}$) (Villars and Calvert, 1986).

α - Si_3N_4 ceramics typically have an equiaxed structure. In contrast, β - Si_3N_4 ceramics have elongated, needle-shaped grains which are less hard than α - Si_3N_4 . Due to its rod-like shape, the material may have an inhibitory effect on crack propagation, and thus the material containing β - Si_3N_4 has a higher toughness than the material containing only α - Si_3N_4 . The alpha and beta phases are similar in that some of the Si atoms can be replaced by Al and some of the N atoms can be replaced by O, this material is called SiALON (Hampshire *et al.*, 1978).

During the sintering of Si_3N_4 ceramics, oxide additives react with silica present on the Si_3N_4 particles to form an oxynitride liquid. The α silicon nitride dissolves in the sintering liquid and is transformed into the β form. The $\alpha \rightarrow \beta$ transformation features seem to be independent of the amount of additive. Ruzjukevics and Ishizaki (1993) reported $\alpha \rightarrow \beta$ transformation at about 1750°C during sintering of α - Si_3N_4 with 3%, 5% and 7% YAlO_3 as sintering aid. Yang *et al.* (2000) found complete transformation during sintering at about 1700°C for different compositions ($2.5\% \text{ Y}_2\text{O}_3 + 1.0\% \text{ Al}_2\text{O}_3$, $5.0\% \text{ Y}_2\text{O}_3 + 2.0\% \text{ Al}_2\text{O}_3$ and $10.0\% \text{ Y}_2\text{O}_3 + 4.0\% \text{ Al}_2\text{O}_3$) of the same additive system studied by Lee *et al.* (1990). Similar results have been found for various amounts of the same additive system (Hampshire and Jack, 1981). Hampshire and Jack (1981) reported a phase transformation activation energy in the presence of a liquid phase close to 405 kJ mol^{-1} , which is near the Si–N bond energy (435 kJ mol^{-1}). Suematsu *et al.* (1997) reported 500 kJ mol^{-1} for the phase transformation activation energy in a ceramic doped with Y_2O_3 and MgO. When the phase transformation accompanies densification and/or grain growth, the identification of the activation energy with specific kinetic processes is not easy, since there are various concurrent phenomena taking place.

Carbon Nanotubes (CNTs)

It is known that the carbon atoms of a single (graphene) sheet of graphite form a planar honeycomb lattice, in which each atom is connected through a strong chemical bond to three neighboring atoms. Because of these strong bonds, the basal-plane elastic modulus of graphite is one of the largest of any known material. The high elastic modulus, tensile strength, electrical and thermal conductivity of carbon nanotubes make them very attractive for ceramic-based composite applications. There are two main types of carbon nanotubes (CNTs): single-wall carbon nanotubes (SWCNTs) (**Fig. 2(a)**) and multi-wall carbon nanotubes (MWCNTs) (**Fig. 2(b)**). SWCNTs are characterized by high stiffness, high resistance to damage from physical forces. Three types of idealized carbon nanotube architectures exist depending on the folding versions of the basic graphene layer, which determines the arrangement of hexagons around the circumference: armchair, zigzag, or chiral. The electrical conductivity is highly sensitive to a slight change of helicity, which may cause a change of behavior between metallic and semiconducting states. There has been considerable practical interest in the

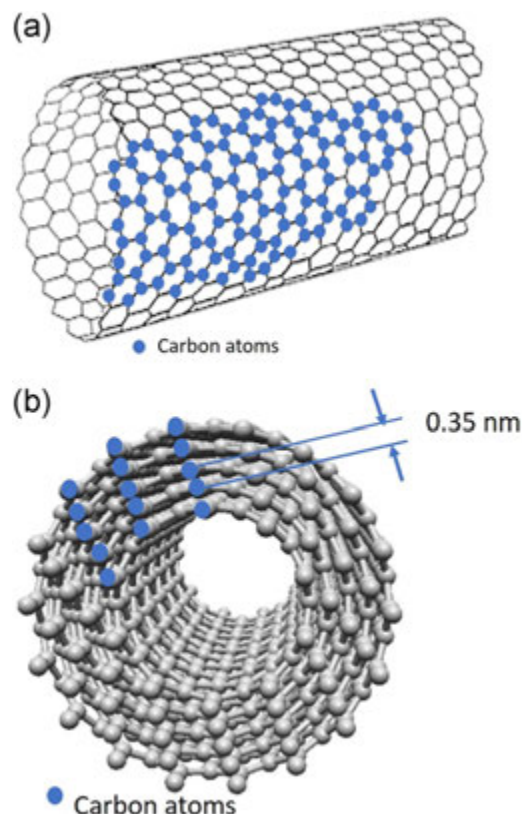


Fig. 2 Schematic illustration of carbon nanotube. (a) single-wall carbon nanotube (SWCNT), (b) multi-wall carbon nanotube (MWCNT).

conductivity of CNTs. Their conductivity has been observed to be a function of their chirality (degree of twist), as well as their diameter. Conductivity in MWCNTs is quite complex. Some types of “armchair”-structured CNTs appear to conduct better than other metallic CNTs (Arato and Balázs, 2008). Carbon nanotubes offer significant advantages over many existing materials due to their exceptional mechanical, electronic, and chemical properties, such as a specific electrical conductivity of $10^{-4} \Omega \text{ cm}$; a maximum current load of $10^{13} \text{ A cm}^{-2}$; a thermal conductivity of $2000\text{--}6000 \text{ W m}^{-1} \text{ K}^{-1}$; Young’s modulus of 1 TPa; and tensile strength of 30 GPa (Journet *et al.*, 1997; Thostenson *et al.*, 2001; Yu *et al.*, 2000).

Iijima (1991) developed a new, novel form of carbon, later named multi-walled carbon nanotube (MWCNT), by arc evaporation of graphite in the first instance. The discovered structure consisted of concentric graphene cylinders, and the diameter of each multi-walled tube was about 10 nm. Two other groups prepared single-wall carbon nanotubes (SWCNT), in which the diameter of each single-walled tube was 1 nm (Bethune *et al.*, 1993; Iijima and Ichlhashi, 1993). To date, several manufacturing technologies are available to prepare carbon nanotubes, such as high-pressure CO conversion (HiPCO) (Nikolaev *et al.*, 1999), pulsed-laser vaporization (PLV), chemical vapor deposition (CVD), and carbon arc synthesis (CA) (Huang *et al.*, 1998; Ren *et al.*, 1998, 1999). Promising approaches have been taken with CVD technologies, providing a method viable for industrial scale production of nanotubes. High purity CNT, both single-walled and multi-walled, can be obtained by reorganization of fragmented carbon fractions within a plasma environment created by arc discharge (Bethune *et al.*, 1993; Iijima and Ichlhashi, 1993; Journet *et al.*, 1997) or laser flash evaporation.

Graphene, Multilayered Graphene (MLG)

Generally, graphene is a one atom depth, two dimensional layer and usually exists as a film (Fig. 3(a)). Nevertheless, the gradually growing interest in graphene production has led to the creation of various graphene forms that can be used for unique purposes. These forms include chemical vapor deposited graphene (CVD), graphene oxide flakes (GO), reduced graphene oxide powders (rGO) graphene nanoplates (GNPs) and multilayer graphene powders (MLG) or few-layer graphene (FLG). Monolayer GO flakes can be obtained by chemical exfoliation of graphite (Hirata *et al.*, 2004). Graphene films are currently produced by chemical vapor deposition on metallic substrates. Chemical vapor deposition is an industrially relevant manufacturing method because it can produce large-area films that can be deposited onto a wide variety of substrates (Gall *et al.*, 1995, 1997; Novoselov *et al.*, 2004). The GO flakes are heavily functionalized by oxygen-containing groups such as epoxy, hydroxyl, carbonyl and carboxylic acid groups, and they form very stable dispersions in water. However, they are electrically insulating. On the other hand, GNPs are electrically conductive and predominantly hydrophobic. GNPs can be manufactured as a free-standing, powder-like material and

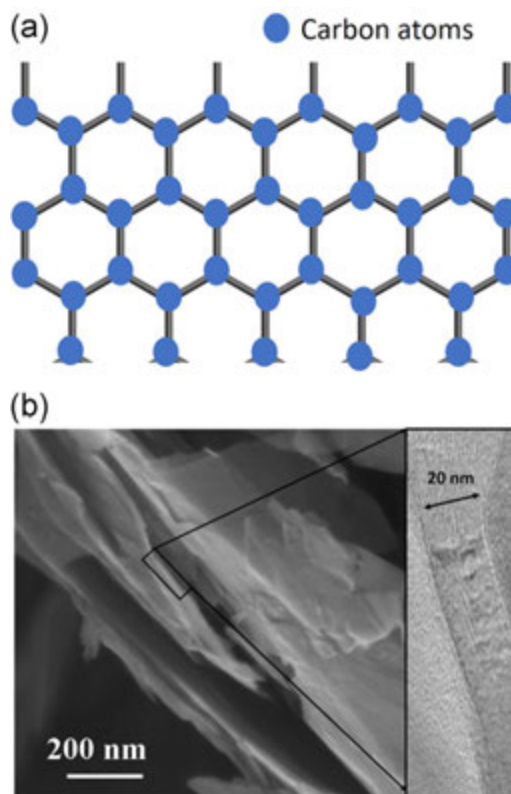


Fig. 3 Structure of graphene. (a) Schematic view of graphene single layer, (b) SEM images of MLG.

in large quantities and can act as a multifunctional additive. They are mostly obtained by exfoliation of graphite. For conciseness, we will focus on mainly the preparation and characterization of the MLGs and GNPs.

The different types of multilayer or few-layer graphene may be used as reinforcement materials for ceramic matrices. The quick and easy method for large-scale preparation of multilayer graphene (MLG) is the high efficiency attritor milling (**Fig. 3(b)**) (Kun *et al.*, 2011). For many industrial applications, using this process can be a simple and efficient way for graphene production.

The starting materials used in experiments were synthetic graphite powder and deionized water or ethanol without further purification. The graphite was milled in a high efficiency attritor mill (Union Process, type 01-HD/HDDM) equipped with zirconia disks and grinding media (diameter of 1 mm) in a 750 mL silicon nitride tank. The milling carried out with different rotation speeds (mild: 600 or intensive: 4000 rpm) for different times (5, 6 or 10 h). Finally, the milled suspension was dried and sieved through a filter with mesh size of 100 μm (Kun *et al.*, 2012).

Ceramic Matrix Composites (CMCs)

Ceramic Matrix Composites With Reinforcing Phase

The most common methods for processing nanocomposites are mechanical alloying powder processing methods followed by different sintering techniques (Samal and Smrutisikha, 2008). Mechanical alloying occurs as a result of repeated breaking up and joining of the component particles which can prepare highly metastable structures such as amorphous alloys and nanocomposite structures with high flexibility. Scaling up of synthesized materials to industrial quantities is easily achieved in this process, but purity and homogeneity of the structures produced remains a challenge. In addition to the erosion and agglomeration, high-energy milling can stimulate chemical reactions that are induced by the transfer of mechanical energy, which can influence the milling process and the properties of the product. Powder processing methods can also be used to fabricate ceramic matrices. The small diameter and large aspect ratio of the nanotubes could make it difficult to obtain a good distribution of the two phases prior to sintering or hot pressing. Using conventional milling techniques can improve the homogeneity of samples, especially with the use of low to moderate nanotube volume fractions.

Four main sintering methods are widely used: GPS (gas pressure sintering), HIP (hot isostatic pressing), HP (hot pressing) and SPS (spark plasma sintering). A discussion on the HIP and SPS techniques will be given in more detail. Tatami *et al.* (2005) prepared a Si_3N_4 composite by ball milling in ethanol (Tatami *et al.*, 2005; Yoshio *et al.*, 2011). Fine high-purity powders of Si_3N_4 , Y_2O_3 , Al_2O_3 , AlN , and TiO_2 were used as raw materials. The multiwall carbon nanotubes used in this study had diameters of

60 nm and lengths of 6 μm . CNTs and a dispersant were added to ethanol. Ball milling was carried out at 110 rpm for 48 h using 5 mm zirconia balls to mix the powders. The powder mixtures were obtained by evaporating the ethanol. 4 wt% paraffin and 2 wt% Bis(2-ethylhexyl) were added as the binder and lubricant, respectively, to make granules by sieving the mixed powder using a nylon mesh with openings of 250 μm . The granules were molded by uniaxial pressing at 50 MPa, followed by cold isostatic pressing at 200 MPa. The organic binder was eliminated at 500°C for 3 h at 4 L min^{-1} N_2 flow. After dewaxing, the green bodies were fired at 1700, 1750, and 1800°C for 2 h in 0.9 MPa N_2 using a gas pressure sintering (GPS) furnace. To complete the densification, the gas pressure sintered samples were subjected to hot isostatic pressing (HIP) at 1700°C for 1 h under 100 MPa N_2 .

These results showed that the relative density of the CNT dispersed Si_3N_4 ceramics was higher than 90% except for the sample containing less than 1 wt% of CNTs and fired at a temperature of 1800°C. It was confirmed that CNTs exist in the samples with a higher density. The pullout length of CNTs on the fracture surface of samples fired at higher temperatures was shorter because of the degradation of the CNTs. By TEM observation, CNTs were found to exist in the grain boundary in the Si_3N_4 ceramics, and their diameter was found to be almost the same as that of raw CNTs. Electrical conductivity was exhibited in the samples containing more than 1 wt% CNTs though the sample containing only 0.5 wt% CNTs was an insulator. The electrical conductivities of the samples increased with increase in the firing temperature, which was explained by the grain growth of $\beta\text{-Si}_3\text{N}_4$. The bending strength of the samples with 1 wt% of CNTs was as high as that of samples without CNTs. Thus, CNT-dispersed Si_3N_4 ceramics having both electrical conductivity and a higher bending strength were obtained by controlling the quantity of CNTs and the firing temperature.

Pasupuleti *et al.* (2008) prepared a Si_3N_4 composite by ball milling in polyethylene containers. 90 wt% micron sized silicon nitride and conventional 6 wt% Al_2O_3 , 4 wt% Y_2O_3 , and 1 wt% ZrO_2 (total of 11 wt%) sintering aids were used for sample preparation. A batch of CNT- Si_3N_4 composite was prepared with 1 wt% MWCNTs as nano-additions and with identical sintering aids as the base line material. Arc grown multi walled carbon nanotubes were selected for incorporation into silicon nitride. The powder batches were ball milled inside a polyethylene container for 24 h. The slurries were dried and sieved through a 325 mesh screen. The powders were placed inside a graphite die. Uniaxial hot-pressing was performed under a nitrogen atmosphere at 1750°C for 1 h. A pressure of 30 MPa was applied.

It was shown that CNT additions cause a refinement of the microstructure, leading to a finer grain size as well as increased acicularity of grains. Densification is not seriously impacted by the CNT additions. There is a slight loss of hardness but a substantial gain in toughness due to the CNTs. Silicon nitrides with CNT additions showed a classic toughening behavior with a sharp rise in the crack growth resistance with crack length followed by a plateau. Crack propagation paths through the microstructure show evidence of crack-path deflection as a toughening mechanism. Fracture surfaces show the presence of CNTs thus indicating crack-bridging and CNT pullout as toughening mechanisms. The hot-pressing conditions used in this study have clearly allowed a good proportion of the CNTs to survive and enhance the toughness and toughening behavior of this CNT-silicon nitride composite.

Corral *et al.* (2008) investigated the effect of SWNTs on the electrical and thermal properties of Si_3N_4 after densification using spark plasma sintering (SPS). All of the nanocomposite and monolith specimens were made from powders that were dispersed using colloidal processing methods followed by SPS. 90 wt% Si_3N_4 powders and 10 wt% sintering additives (Y_2O_3 , MgO and Al_2O_3) were used in sample preparation. Commercially available SWNTs in powder form and purified to less than 2-wt% residual metal catalyst were used as received. The nanocomposites made in this study each contain a mixture of 1-, 2-, and 6-vol% well-dispersed single and bundled SWNTs. A cationic surfactant, cetyltrimethylammonium bromide (CTAB) was used as a dispersant throughout this study. They used SPS to densify nanocomposites using a maximum pulse current of 5000 A and maximum pulse voltage of 10 V. The pulse cycle was 12 ms on and 2 ms off with a heating rate of 200°C min^{-1} . The temperature was monitored on the surface of the die wall using optical pyrometry. An external pressure of 25 kN was applied as the powders were heated inside a graphite die lined with graphite foil to prevent surface reactions between the powder and the inner die wall. A vacuum of 10^{-2} Torr was used and sintering occurred under vacuum.

The use of only 2 vol% SWNTs additions resulted in a decrease of the room temperature thermal conductivity by 62% compared to the monolith and increasing the addition to 6 vol% SWNTs transformed the insulating ceramic into a metallic electrical conductor (92 S m^{-1}). It was found that densification of the nanocomposites was inhibited with increasing SWNT concentration, however the phase transformation from α - to $\beta\text{-Si}_3\text{N}_4$ was not. After SPS, they found evidence of SWNT survival in addition to sintering induced defects detected by monitoring SWNT peak intensity ratios using Raman spectroscopy. Their results showed that by densifying by SPS, SWNTs can be used to effectively increase electrical conductivity and lower thermal conductivity of Si_3N_4 due to electrical transport enhancement and thermal scattering of phonons by SWNTs.

Gonzalez-Julian *et al.* (2011) studied the Si_3N_4 /MWCNTs composites prepared by SPS and containing 0.9–8.6 vol% MWCNTs. CVD synthesized MWCNTs of 30 nm diameter and 1–5 μm length were thoroughly mixed with Si_3N_4 plus liquid forming sintering additives, 2 wt% of Al_2O_3 and 5 wt% of Y_2O_3 . Compositions were spark plasma sintered at 1585°C for 5 min in vacuum (6 Pa), applying a pressure of 50 MPa.

A balance was observed between semiconductor and metallic-like conduction mechanisms, the proportions of which depend on both the temperature and the MWCNTs content. The metallic-type conduction was associated with charge transport along the nanotube shells whereas the semiconductor behavior is linked to hopping conduction across nanotube–nanotube contacts and across intrinsic defect clusters within the nanotubes separating metallic domains. When the MWCNTs network is close to the percolation threshold (0.9 vol% composite), inter-nanotubes hopping or tunneling mechanisms become the rate limiting steps for charge transport. Once this concentration was surpassed the contribution of defect clusters within nanotubes in the highly conductive paths competes with the above mechanism.

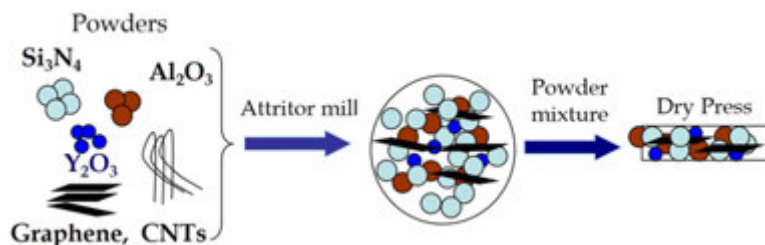


Fig. 4 Schematic illustration of starting powder mixtures.

Graphene is a favored additive reinforcing phase for ceramic matrix composite development. Nano-scaled graphene platelets of several desired size ranges (e.g., length and width of approximately 0.05–10 μm and thickness of approximately 1–10 nm) demonstrate exceptionally high thermal and electrical conductivity and an exceptional combination of mechanical properties. Typically there are three methods used for the preparation of graphene platelets: micromechanical exfoliation, epitaxial growth of graphene film and chemical processing (Bhuyan *et al.*, 2016). Kun *et al.* (2011, 2012) used the attritor milling of graphite powder for multilayered graphene preparation and its distribution in ceramic matrices. Recently, conducting ceramic composites were fabricated by the in-situ formation of graphene-like layers (Weibel *et al.*, 2018). In particular, an aluminosilicate/graphene composite with an in-plane conductivity of 700 S m^{-1} was obtained by carbonization of polyaniline layers (Capková *et al.*, 2014). Likewise, SiC/graphene composites with $\sigma \approx 100 \text{ S m}^{-1}$ (~ 6 orders of magnitude larger than monolithic SiC ceramics) were obtained by growing epitaxial multilayers of graphene in-situ at the SiC grain boundaries during the spark plasma sintering (SPS) process (Miranzo *et al.*, 2013). Recently a very interesting point raised by a new ceramic/graphene design is that graphene is not used as a conventional ‘reinforcement’ but rather to engineer a fine network of relatively weak interfaces that provide improved electrical conductivity and fracture resistance (Picot *et al.*, 2017). The response depends not only on the chemistry but also on the topology (roughness) of the interfaces at the nano-scale. These results underline the need to look at alternative approaches in the way we design and build practical composites using nanomaterials and that these approaches will need to integrate mechanical and functional response. The latter is probably the most interesting possibility opened by these new layered nanomaterials and a path to generate a step change in the field of structural, multifunctional materials.

Preparation of Carbon Nanotubes- and Graphene-Containing Ceramic Matrix Composites

Powder technology methods were used for these ceramic matrix composite preparations (Fig. 4). The ceramic starting powders were Si₃N₄ (SN-ESP, UBE, Japan), Al₂O₃ (A16, Alcoa, USA), and Y₂O₃ (grade C, H. C. Starck, Germany). For composite processing, multi-walled carbon nanotubes (MWCNTs) and multilayered graphene (MLG) were added into the base ceramic with different concentrations (Fig. 5) (Balázs *et al.*, 2003, 2005b, 2006, 2007).

A stable, applicable processing technology for CNT/ceramic composites has to control the homogeneous distribution of nanotubes during powder mixing and shaping and preserve their amount and topology in the course of heat treatments.

The homogeneity of a powder mixture can be significantly improved by using very intensive milling. A new attritor mill (01-HD/HDDM, Union Process, USA) is being used, which operates at a high speed of 4000 rpm. Milling for 3–5 h with this equipment significantly changed the size and morphology of the powder mixture constituents. Spark plasma sintering (next to flash sintering) is a technique that has been successful in the research on nanoceramics. It was observed that this method decreases the sintering temperature, impeding the degradation of nanotubes and the Oswald ripening (excess growth) of matrix particles/grains.

Hot isostatic pressing (HIP) was performed at 1700°C in high purity nitrogen atmosphere in an ABRA-made HIP apparatus and 20 MPa for 3 h. Gas pressure sintering (GPS) can be done in the same HIP apparatus. Several temperature-time runs were tested, with a high temperature of 1750°C and a nitrogen pressure of 1.5 MPa. Hot pressing (HP) was used at 1700°C, 50 MPa in nitrogen for 1 h.

The dimensions of specimens after full densification (and cutting, polishing) were $3.5 \times 5 \times 50 \text{ mm}$. Before mechanical testing, all surfaces of the samples were finely ground on a diamond wheel, and then the edges polished.

In the case of SPS methods, the ceramic powder can be annealed at lower temperatures and for much shorter times than in other sintering processes (e.g., hot pressing, hot isostatic pressing, and pressureless sintering) and allows the fabrication of fully dense ceramics and composites with a nanocrystalline microstructure.

A key factor of a stable processing technology is prevention of degradation of nanotubes during sintering. The temperature of conventional sintering procedures is rather high for silicon nitride ceramics (1700–1800°C). These high temperatures are disadvantageous because the size of nanograins increases, a part of carbon nanotubes transforms to graphite, and a certain amount of carbon is lost at the surface and via open pores. The main difference between SPS and hot pressing is the simultaneous application of a pulsed current in the former, which generates electrical discharges (Groza, 1998). The electrical discharges do not densify powders and therefore, additional energy is required to increase the final density. This extra energy may be mechanical due to the applied pressure and thermal energy generated by electrical discharge. Electrical current activation has been applied in the plasma assisted sintering (PAS) process – developed in Japan in the 1960s – followed by today’s widely used spark plasma sintering method (Groza, 1998). The principle of SPS is based on the application of a pulsed DC current through and around the specimen. Conduction along the die is important, but it basically represents ohmic heating.

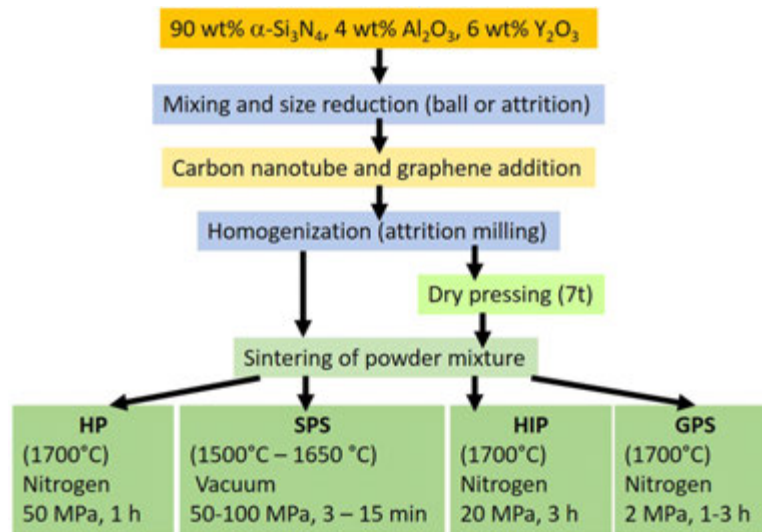


Fig. 5 Schematic diagram of steps of ceramic matrix composite preparation.

Table 1 Summarized data of apparent densities of carbon nanotube and graphene added Si_3N_4 composites prepared by different sintering methods

Sintering method	Additive	GPS	HIP	SPS	HP
		density (g/cm^3)			
Carbon nanotube	0 wt%	3.15	3.19	3.23	3.41
	1 wt%	2.807	3.028	3.17	–
	3 wt%	2.653	2.752	3.23	–
	5 wt%	2.240	2.245	–	–
Graphene	1 wt%	2.78	2.84	3.19	3.36
	3 wt%	2.62	2.589	3.174	3.37
	5 wt%	–	2.49	2.71	3.42

Silicon nitride composites containing carbon nanotubes and graphene have been produced by spark plasma sintering in vacuum (Dr. Sinter 2050 SPS, FCT HP D10-SD) (Balázsi *et al.*, 2005b, 2013). The powder precursors were loaded in cylindrical carbon dies with an inner diameter of 10 mm. The samples were heated via a pulsed DC current that assured $100^\circ\text{C}/\text{min}$ heating rate for all of the experiments. The temperature was automatically raised to 600°C over a period of 3 min, and from this point onward it was monitored and regulated by an optical pyrometer focused on the surface of the die. A uniaxial pressure of either 50 MPa or 100 MPa was applied from the start to the end of the sintering cycle. Short holding times were applied, from 3 to 5 min. The setup allows a cooling rate of about $400^\circ\text{C}/\text{min}$ in the temperature range $1650\text{--}1000^\circ\text{C}$.

Structure of CNTs- and Graphene-Containing Ceramic Matrix Composites

The selection of the ceramic matrix and amount of the reinforcing phase is a fundamental step. Thus, the Si_3N_4 matrix, which is more dense, is responsible for the mechanical strength of the final sintered composite, whereas the secondary reinforcing phase (carbon nanotube, graphene) determines the toughness and work of fracture. These non-oxide materials usually have much higher fusion temperatures than the matrix and do not dissolve in the liquid present during sintering. This means that the addition of any sort of nanoparticle/nanotube carbon phase is likely to significantly decrease the rate of sintering (Table 1).

A plausible explanation of this effect is to suppose that the added carbon phase located between ceramic particles hinders the generation and growth of interparticle contacts. Microstructural observations have confirmed that the carbon reinforcing phase has been located in pores between grains of the ceramic matrix, independent of sintering method (Figs. 6 and 7).

The $\text{Si}_3\text{N}_4/\text{MWCNT}$ composites studied consisted of Si_3N_4 grains with average size $300\text{--}500$ nm and multi-wall carbon nanotubes with diameter around 20 nm and lengths of a few microns (Fig. 6). For the three different densification processes, GPS, HIP, SPS, there is evidence for the presence of MWCNTs after sintering (Balázsi *et al.*, 2003, 2005a, 2013). The short sintering time with low pressure resulted in residual porosity in the Si_3N_4 composite. Web-like connected MWCNTs can be found in some areas, but

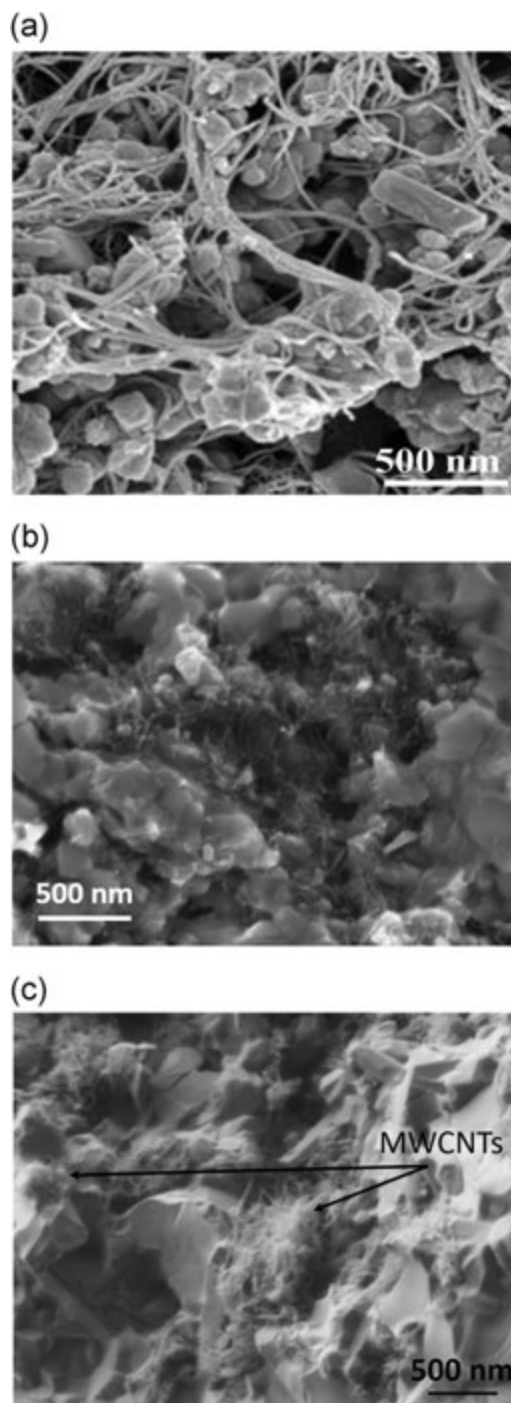


Fig. 6 Structural observation of $\text{Si}_3\text{N}_4/3$ wt% MWCNTs sintered by different methods. (a) GPS, (b) HIP, (c) SPS.

individual MWCNTs, properly attached to Si_3N_4 surfaces can also be observed (Fig. 6(a)). The ceramic grains along with the attached CNTs can be observed in the fracture surface of the HIP sintered composite (Fig. 6(b)). The ten times higher pressure and longer sintering time decreased the porosity and increased the density of the composite (Table 1). SPS can enhance the sinterability of Si_3N_4 producing dense materials with controlled grain growth. In SPS sintered composites, higher density was achieved (Table 1) with Si_3N_4 grains of average size 500 nm and MWCNT agglomerations between the ceramic grains (Fig. 6(c)) were observed.

In the case of graphene addition, various sintering methods such as hot pressing (HP), HIP and SPS may be used for sintering of final composites (Kun *et al.*, 2012; Balázs *et al.*, 2017; Tapasztó *et al.*, 2016).

One of the problematic issues of composite preparation is to improve the homogeneity of the dispersion of reinforcing phases (Fig. 8). Increasing milling time and ultrasonic agitation of powder mixtures can solve this problem. Highly efficient milling processes have a

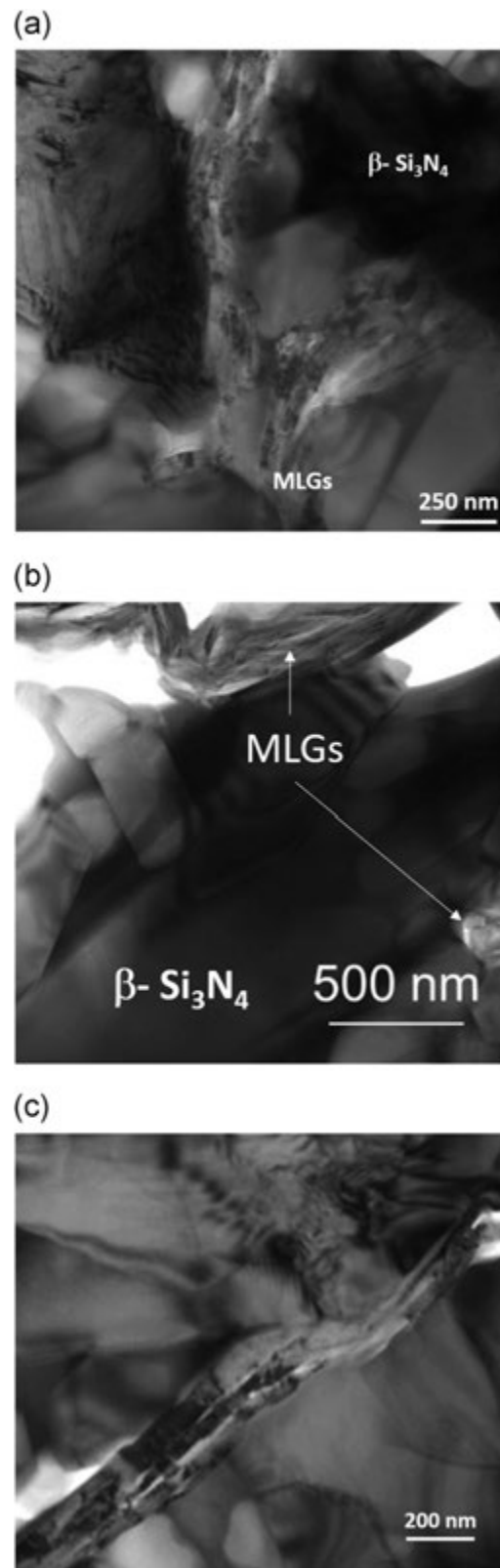


Fig. 7 Structural observation of $\text{Si}_3\text{N}_4/3 \text{ wt\% MLGs}$ sintered by different methods. (a) HP, (b) HIP, (c) SPS.

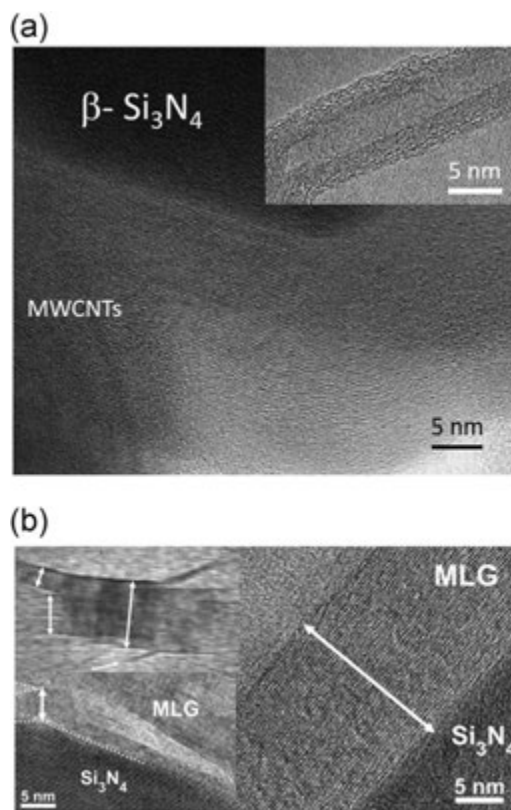


Fig. 8 High resolution TEM images of sintered Si_3N_4 composites. (a) with MWCNTs, (b) with MLG additive.

double effect on structure; homogenization of the base powders and size reduction. In the case of Si_3N_4 composites containing MWCNT (**Fig. 8(a)**) or MLG (**Fig. 8(b)**), some structural defects after milling and sintering were observed (Kun *et al.*, 2012).

On the other hand, phase transformation of final composites occurred during the sintering process. The type of sintering, holding time and pressure have an effect on the α - Si_3N_4 matrix. The α - Si_3N_4 particles dissolved in the existing liquid phase and subsequently new β - Si_3N_4 nuclei were formed (Peng *et al.*, 2009). The higher carbon nanotube and graphene content may block the total phase transformation of Si_3N_4 (**Fig. 9**). The liquid phase is needed for the α - β phase transformation, which occurs by the dissolution of fine α -phase starting powder and subsequent precipitation of the β -phase (Riley, 2004). Sintering additives (mainly oxides) need to be added to assist the densification process through "liquid phase sintering" (Krstic and Krstic, 2012). In the case of Si_3N_4 , the best known system is a combination of Y_2O_3 and Al_2O_3 (Krstic and Krstic, 2012).

The phase transformations that may occur during processing of ceramic matrix composites are shown in **Fig. 9**. Phase analysis of composites revealed that the transformation α to β - Si_3N_4 was completed after HIP and HP sintering, where mainly the main lines of β - Si_3N_4 can be observed (**Fig. 9(a)** and **(b)**). In the case of GPS or SPS the α to β - Si_3N_4 transformation is not finished, therefore the main lines of both α and β - Si_3N_4 may be observed after sintering (**Fig. 9(a)** and **(b)**). It is known that during sintering the oxide additives react with oxidized surface layers on silicon nitride powders to form an eutectic liquid at high temperature. As a concurrent process by increasing the holding time of sintering the α to β - Si_3N_4 transformation is beginning, it is also known that the SPS is working with enhanced electrical field, rapid heating and very short sintering time. Due to these facts SPS can enhance the sinterability of Si_3N_4 producing dense materials with controlled grain growth (Belmonte *et al.*, 2010). The addition of the electrical conductive carbon phase to ceramic matrix modified the shrinkage behavior during sintering process. XRD measurements confirmed the ZrO_2 contamination from milling, where intensive milling at high speed (5000 rpm) was applied (**Fig. 9(a)** and **(b)**). In the literature there are several works where ZrO_2 is intentionally used as sintering aid (Pasupuleti *et al.*, 2008) or is added to matrix as a toughening agent (Sayyadi-Shahraki *et al.*, 2019). The line of (002) of carbon on XRD is supporting the results of microstructural investigations which show the presence of MWCNT (**Fig. 9(a)**) and MLG (**Fig. 9(b)**) after sintering.

Mechanical Properties of CNTs- and Graphene-Containing Ceramic Matrix Composites

Control of the mechanical properties of Si_3N_4 based composites is possible via the modification of their composition and processing conditions, knowing how the microstructure peculiarities can influence the mechanical behavior.

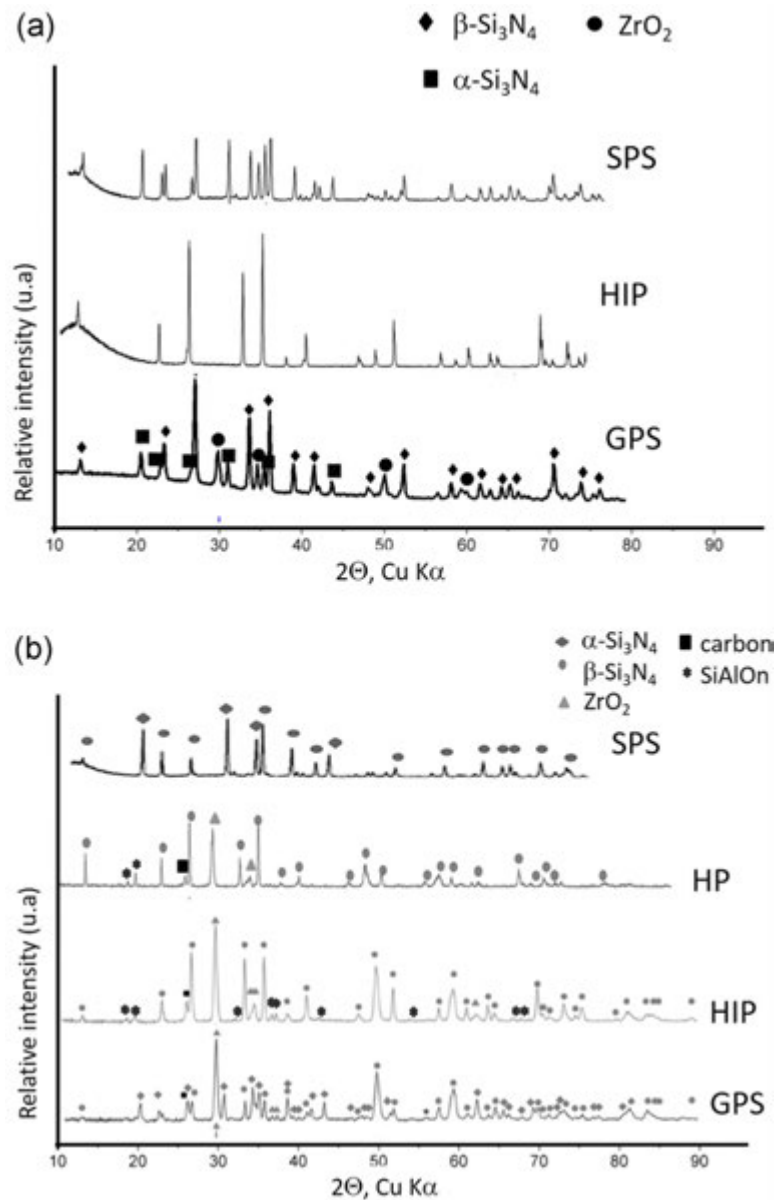


Fig. 9 Phase analysis of Si_3N_4 based composites. (a) MWCNT reinforce phase, MLG additive.

The determination of the hardness allows useful qualitative conclusions to be made regarding the mechanical properties of ceramic composites (Fig. 10(a)). It is one of the most economical characterization methods, since this can be carried out with little effort on small sintered sample.

Si_3N_4 ceramic matrix composites containing carbon nanotubes and graphene have hardness values between 11 and 19 GPa (Balázsi *et al.*, 2013, 2017; Kvetková *et al.*, 2012; Kovalčíková *et al.*, 2012) depending on the sintering method and amount of reinforcing phase. The highest hardness of the composite compared to the monolithic material is mainly dependent on the residual porosity that remains in the material after sintering and good homogenization of the reinforcing phase. Together with the porosity, clusters of MWCNTs or MLGs are characteristic processing defects present in the materials and have been presented and discussed in all of the other work dealing with similar composites. This indicates that there are some persistent difficulties in the preparation of defect free carbon nanotubes or graphene reinforced ceramic composites. Reducing such defects has the potential for the improvement of their functional and mechanical properties.

The MWCNTs and graphene play a favorable role by bridging the cracks, healing the crack openings as is proved by the crack morphology. In the case of Si_3N_4 /MWCNTs the width of crack openings are substantially smaller as compared to “pure” Si_3N_4 . On the other hand, the formation of MWCNT agglomerations (Fig. 6) and graphene agglomerations (Fig. 7) caused hardness to decrease by increasing porosity.

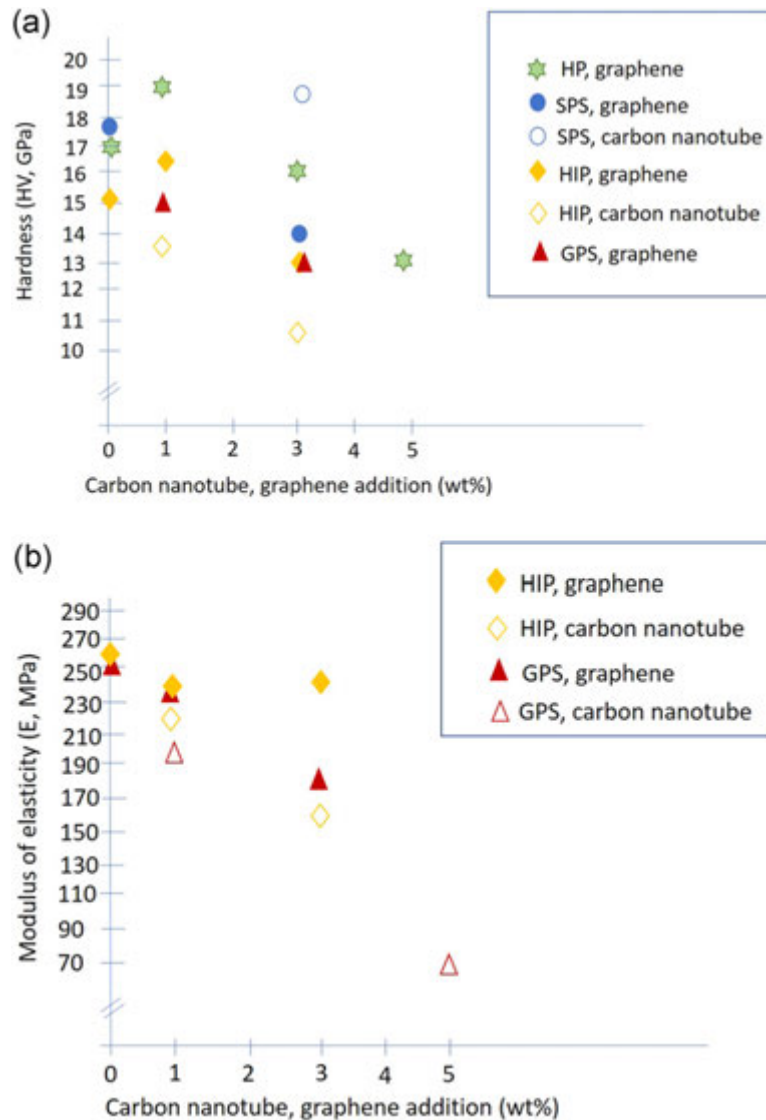


Fig. 10 Comparison of the mechanical properties of carbon nanotube and graphene added Si_3N_4 based composites prepared by various sintering technology. (a) hardness, (b) modulus of elasticity.

The modulus of elasticity (E) is one of the essential parameters in the study of advanced material mechanics. Its values for ceramic matrix composites with graphene addition showed higher values compared to composites with carbon nanotubes independent of the sintering method applied (Fig. 10(b)). In all cases, the reference Si_3N_4 without any second phase addition has the highest degree of densification related to the highest modulus value (Fig. 10(b)). It is known that the porosity due to reinforcing phase addition to the brittle matrix can have significant influence on mechanical properties. The better homogenization of graphene sheets caused lower porosities and finally higher strength values compared with agglomerated carbon nanotube reinforcing phases.

3-point bend strength data show a similar tendency, but higher values resulted for composites containing graphene compared with those containing carbon nanotubes (Fig. 11). All composites showed the same tendency. As a result of applying a higher pressure (20 MPa, in the case of HIP) a higher densification level, and a strength increase by 100% from an average level of 300 MPa to 600 MPa can be realized in the case of 1% CNT addition (Balázsi *et al.*, 2007).

Interestingly, contrary to CNTs, graphene addition has a beneficial role in the re-arrangement of grains during sintering at low nitrogen pressure (2 MPa, in the case of GPS) which at the end of sintering results in more dense structures with higher 3-point bending strengths as shown in Fig. 11(a).

In the case of Si_3N_4 , the reinforcing mechanism by adding second phase particles is introducing residual stresses induced by a different coefficient of thermal expansion (CTE) for the matrix (Gogotsi, 1994). The compressive residual stresses close cracks, while tensile residual stresses deflect stress. The residual stresses at the grain boundaries caused by different CTE between Si_3N_4 grains and grain boundary phase enhance crack deflection. The fracture toughness of Si_3N_4 ceramics increased almost linearly from

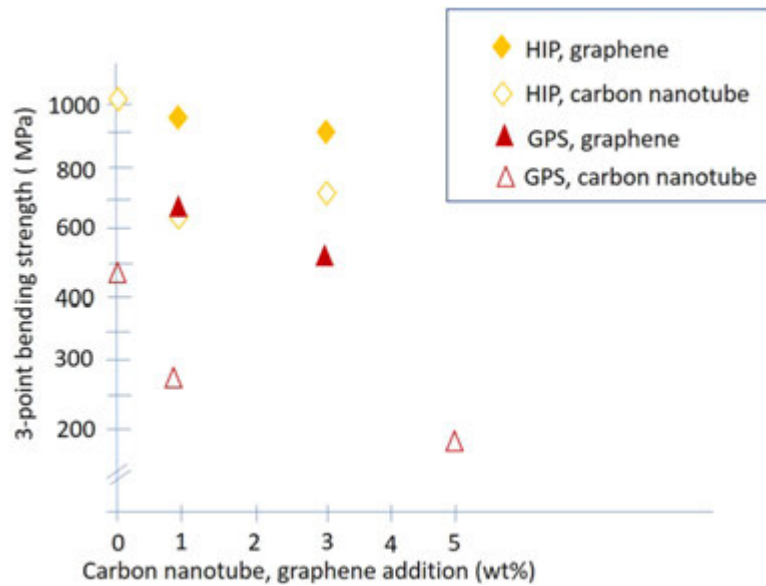


Fig. 11 Comparison of the 3-point bending strength of carbon nanotube and graphene added Si_3N_4 based composites prepared by various sintering technology.

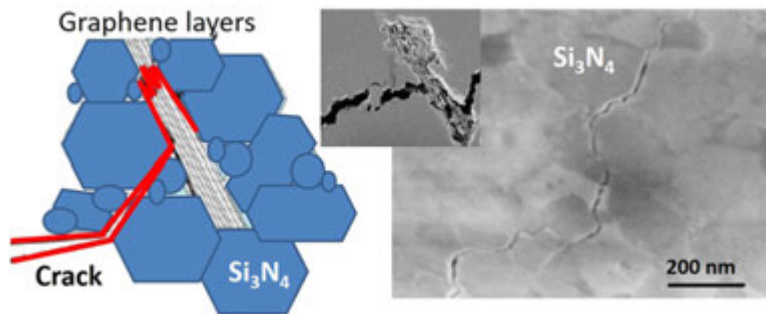


Fig. 12 Crack deflection mechanism in graphene added Si_3N_4 ceramics.

4 to 5–6 $\text{MPa m}^{1/2}$ when a phase with higher CTE crystallizes at the grain boundaries (Peterson and Tien, 1995). Thus, the introduction of carbon nanotube or graphene reinforcing phase with higher CTE toughened the final Si_3N_4 composite. The basic mechanism of crack deflection in the Si_3N_4 composite containing graphene is shown schematically in Fig. 12. The indentation fracture toughness of the composites containing carbon nanotubes or graphene are significantly higher compared to the monolithic silicon nitride, with the highest value of 9.9 $\text{MPa m}^{1/2}$ for graphene reinforcing phase (Kvetková et al., 2012).

The observed differences in the mechanical properties of the samples prepared by different sintering methods have complex processes at their origin. Two factors could be named with important roles in the properties of the resulting composites:

- (1) The effect of different sintering methods on the phase transformation of the silicon nitride matrix, which is clearly reflected also in the final phase composition of the samples (SPS sintered samples mainly consist of $\alpha\text{-Si}_3\text{N}_4$, while HIP and HP sintered samples predominantly contain $\beta\text{-Si}_3\text{N}_4$ grains).
- (2) The effect of holding times at high temperatures on the structure (degradation) of the carbon reinforcing phase. It is known that both carbon nanotubes and graphene can be damaged during long exposures to high temperatures, whereupon their intrinsic mechanical properties can substantially decay. In this sense, the fast heating rates and short holding times of the SPS method are expected to better preserve the excellent mechanical properties of the filler phase.

Tribological Properties of Ceramic Matrix Composites

Significantly decreasing the friction coefficient is essential for reducing the losses in moving and rotating parts, while increasing the wear resistance improves the durability and lifetime of the components. In all such applications, Si_3N_4 materials will have to face the challenge of friction and wear damage.

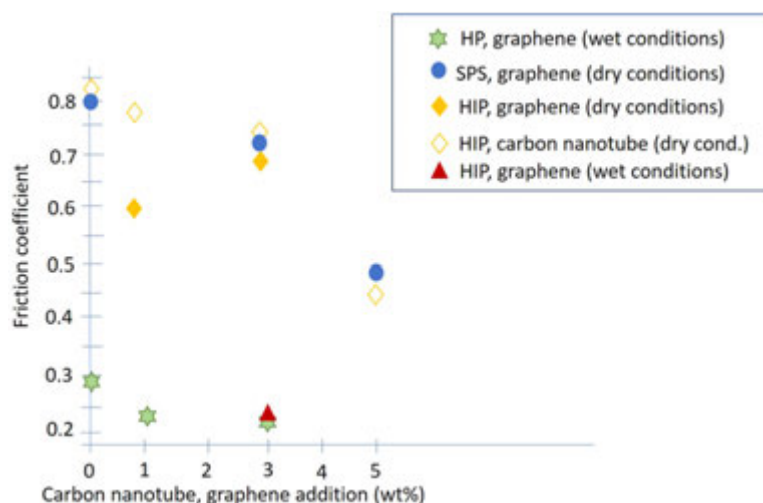


Fig. 13 Friction coefficient of carbon nanotube and graphene added Si₃N₄ matrix composites.

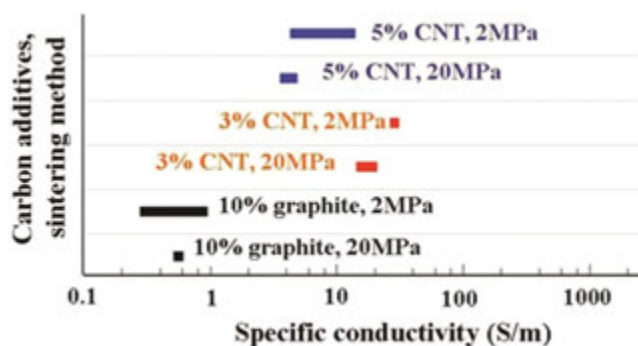


Fig. 14 The specific conductivity of nanocomposites with different carbon additions and sintering method.

The friction behavior of the Si₃N₄ with different MWCNT and graphene additions tested under dry and wet conditions against SiC rings is shown in Fig. 13. For all investigated material combinations a decrease in friction coefficient is clearly visible with increasing reinforcing phase content.

In the case of HP and HIP sintered composites the morphological appearance of the worn surfaces showed that more stable and coherent tribofilms developed in the wear track. This provided better lubrication at the contact points under wet conditions. SPS sintering effectively improved the tribological performance of the Si₃N₄ composites by preserving the harder α -Si₃N₄ structure of the initial ceramic powder to a great extent.

The values for friction coefficients under wet conditions are in the range of 0.3–0.15 compared to between 0.45 and 0.83 under dry conditions (Balázs *et al.*, 2017; Hvizdoš *et al.*, 2012, 2013).

The lower friction coefficients during wet conditions may be related to the typical wear patterns for ceramic materials in water, i.e., tribochemical wear and some traces of surface microfracture and fatigue (Balázs *et al.*, 2017). It was demonstrated that graphene is preserved on the tribo-surface even after severe tribochemical wear. Consequently, at higher graphene content larger presence of multilayer graphene in the wear debris. As it was shown by (Belmonte *et al.*, 2013) the wear behavior in graphene added composites is controlled by the continuous supply during severe wear process of the exfoliated graphene flakes that are present in lubricating tribofilm well adhered to the surface.

Even though the SPS or HIP provided higher friction coefficients for reference samples the CNT or graphene beneficial role to decrease the friction coefficients during dry conditions might be observed on Fig. 11. By 5 wt% CNT or graphene addition, a 60% reduction in friction coefficient is achieved.

Carbon nanotubes and graphene contribute significantly to the decrease of friction coefficient. Increasing the amount of carbon phase has beneficial role showing lower frictional response of Si₃N₄ ceramic composites.

Electrical Conductivity of Ceramic Matrix Composites

Silicon nitride ceramics are insulators, with a specific conductivity of about $10^{-12} \text{ S m}^{-1}$. The examined composites can be grouped into insulator and conductor types as identified from four point DC resistance measurements. Si_3N_4 matrix composites can be considered as insulators because their resistance was not measurable (10 M Ω measurement limit). The percolation threshold was observed in composites with 3 wt% and 5 wt% MWCNT and 10 wt% for graphite (as reference) (Fényi *et al.*, 2008b). The specific conductivity range of the composites according to type, amounts of additives, sintering technique and type of ceramic matrix is shown in Fig. 14.

As for conductivity, the matrix does not take part in the charge transport, however it may modify the topology of the conductive phase. Composites with graphite additives (for comparison) have the worst electrical conductivity because of the size and shape of the mixed graphite grains (Fényi *et al.*, 2008a, 2009). In the case of lower values of MWCNT additives with better homogenization, the higher conductivity was observed (Fig. 14). In this structure, the nodules only few current paths maybe involved in conductivity process because of the nodulation of the MWCNTs. In case of higher MWCNT content, the homogenous distribution of reinforcing phase was not realized (Fényi *et al.*, 2008b), MWCNTs agglomerated in porosities and due to this, they are not connected (Fig. 6). Furthermore the crystallization and grain growth of β - Si_3N_4 grains may inhibit the bridging of MWCNTs (Fig. 6).

Conclusions

Silicon nitride (Si_3N_4) based ceramics are well-known as low density materials with high strength and toughness. Silicon nitride, known as a typical dielectric material, is an ideal candidate for several structural applications, even at high temperatures. The addition of graphene or carbon nanotubes to silicon nitride to create ceramic nanocomposites gives rise to promising applications in a wide range of fields such as electronics, biomedical aids, membranes, flexible wearable sensors and actuators. This chapter shows how the use of different reinforcing phases and sintering methods affects microstructure and as a result, mechanical properties, electrical conductivity and friction coefficients of the final silicon nitride nanocomposites.

The main important conclusions that can be drawn are:

- (1) A key factor of a stable nanocomposite processing technology is the prevention of the degradation of carbon nanotubes and graphene during the sintering process.
- (2) The selection of the ceramic matrix and quality assurance of the reinforcing phase is a fundamental step because the secondary reinforcing phases (carbon nanotube, graphene) and their quality determine the toughness and work of fracture.
- (3) One of the problematic issues in composite preparation is the improvement of the homogeneity of the dispersion of reinforcing phases within the ceramic matrix. Agglomeration of CNTs and graphene cause porosity increase which in turn decrease the strength by initiation of flaws. Increasing milling time and ultrasonic agitation of the powder mixtures can solve this problem.
- (4) Two factors have important role for the resulting composites; the effect of different sintering kinetics on the phase transformation of the silicon nitride matrix and the effect of degradation of the carbon reinforcing phase.
- (5) The more lengthy HIP and HP sintering processes allow completion of the α to β - Si_3N_4 transformation compared to SPS where the α - Si_3N_4 was preserved due to working with enhanced electrical field, rapid heating and very short sintering times.
- (6) The highest hardness of the nanocomposites compared to the monolithic material is mainly dependent on the residual porosity that remains in the material after the sintering and good homogenization of the reinforcing phase.
- (7) Modulus of elasticity of ceramic matrix composites with graphene addition showed higher values compared to composites with carbon nanotubes independent of the sintering method applied.
- (8) Graphene addition has a beneficial role in the re-arrangement of grains during sintering at low nitrogen pressure (2 MPa, in the case of GPS) which at the end of sintering results in more dense structures with higher 3-point bending strengths than for CNT addition.
- (9) The introduction of carbon nanotube or graphene reinforcing phases with higher coefficients of thermal expansion toughen the final Si_3N_4 matrix composite.
- (10) Carbon nanotubes and graphene contribute significantly to the decrease of friction coefficient. Increasing the amount of carbon phase has beneficial role showing lower frictional response of Si_3N_4 ceramic composites.
- (11) The specific conductivity range of the CNT added composites processed by GPS or HIP can reach 10 S m^{-1} which allows processing by electrical-discharge machining (EDM).

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References

- Ahmad, I., Kennedy, A., Zhu, Y.Q., 2010. Carbon nanotubes toughened aluminium oxide nanocomposites. *Journal of the European Ceramic Society* 30, 865–873.
- Arato, P., Balázs, C., 2008. Chapter 47 – Carbon nanotubes in silicon nitride. In: Tseng, T.-Y., Nalwa, H.S. (Eds.), *Handbook of Nanoceramics and their Based Nanodevices*. Chicago: American Scientific Publishers, pp. 1–20.
- Balandin, A.A., Ghosh, S., Bao, W., *et al.*, 2008. Superior thermal conductivity of single-layer graphene. *Nano Letters* 8, 902–907.
- Balázs, C., 2012. Silicon nitride composites with different nanocarbon additives. *Journal of the Korean Ceramic Society* 49, 352–362.
- Balázs, C., Wéber, F., Kövér, Z.S., *et al.*, 2005a. Development of preparation processes for CNT/Si₃N₄ composites. *Key Engineering Materials* 290, 135–141.
- Balázs, C., Shen, Z., Konya, Z., *et al.*, 2005b. Processing of carbon nanotube reinforced silicon nitride composites by spark plasma sintering. *Composites Science and Technology* 65, 727–733.
- Balázs, C., Weber, F., Kover, Z., *et al.*, 2006. Application of carbon nanotubes to silicon nitride matrix reinforcements: Engineering aspects of nanomaterials and technologies. *Current Applied Physics* 6, 124–130.
- Balázs, C., Czigany, Z., Weber, F., *et al.*, 2007. Silicon nitride – Carbon nanotube composites. *Materials Science Forum* 554, 123–128.
- Balázs, C., Tapasztó, O., Károly, Z., *et al.*, 2013. Structural and mechanical properties of milled Si₃N₄/CNTs composites by spark plasma sintering method. *Materials Science Forum* 729, 31–36.
- Balázs, C., Fogarassy, Z.S., Tapasztó, O., *et al.*, 2017. Si₃N₄/graphene nanocomposites for tribological application in aqueous environments prepared by attritor milling and hot pressing. *Journal of the European Ceramic Society* 37, 3797–3804.
- Balázs, C., Konya, Z., Weber, F., Biro, L.P., Arato, P., 2003. Preparation and characterization of carbon nanotube reinforced silicon nitride composites. *Materials Science & Engineering C* 23, 1133–1137.
- Belmonte, M., Ramirez, C., Gonzalez-Julian, J., *et al.*, 2013. The beneficial effect of graphene nanofillers on the tribological performance of ceramics. *Carbon* 61, 431–435.
- Belmonte, M., Gonzalez-Julian, J., Miranzo, P., Osendi, M.I., 2010. Spark plasma sintering: A powerful tool to develop new silicon nitride-based materials. *Journal of the European Ceramic Society* 30, 2937–2946.
- Bethune, D.S., Kiang, C.I.I., De, Vries, *et al.*, 1993. Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls. *Nature* 363, 605–607.
- Bhaduri, S., Bhaduri, S.B., 1998. Recent developments in ceramic nanocomposites. *Journal of the Minerals, Metals & Materials Society* 50, 44–50.
- Bhuyan, S.A., Uddin, N., Islam, M., Bipasha, F.A., Hossain, S.S., 2016. Synthesis of graphene. *International Nano Letters* 6, 65–83.
- Capková, P., Matějka, V., Tokarský, J., *et al.*, 2014. Electrically conductive aluminosilicate/graphene nanocomposite. *Journal of the European Ceramic Society* 13, 3111–3117.
- Corral, E.L., Cesarano, J., Shyam, A., *et al.*, 2008. Engineered nanostructures for multifunctional single-walled carbon nanotube reinforced silicon nitride nanocomposites. *Journal of the American Ceramic Society* 91, 3129–3137.
- Corral, E.L., Wang, H., Garay, J., Munir, Z., Barrera, E.V., 2011. Effect of single-walled carbon nanotubes on thermal and electrical properties of silicon nitride processed using spark plasma sintering. *Journal of the European Ceramic Society* 31, 391–400.
- Dusza, J., Blugan, G., Morgiel, J., *et al.*, 2009. Hot pressed and spark plasma sintered zirconia/carbon nanofiber composites. *Journal of the European Ceramic Society* 29, 3177–3184.
- Fan, Y., Wang, L., Lib, J., *et al.*, 2010. Preparation and electrical properties of graphene nanosheet/Al₂O₃ composites. *Carbon* 48, 1743–1749.
- Fényi, B., Koszor, O., Balázs, C., 2008a. Ceramic based nanocomposites for functional applications. *Nano* 3, 323–328.
- Fényi, B., Arató, P., Wéber, F., Hegman, N., Balázs, C., 2008b. Electrical examination of silicon nitride – Carbon composites. *Materials Science Forum* 589, 203–208.
- Fényi, B., Hegman, N., Szemmelweis, K., Balázs, C., 2009. Impedance changes and carbon stability during the heat treatment of Si₃N₄ – Carbon composites. *Key Engineering Materials* 409, 365–368.
- Gall, N.R., Rut'Kov, E.V., Tontogode, A.Y., 1995. Influence of surface carbon on the formation of silicon-refractory metal interfaces. *Thin Solid Films* 266, 229–233.
- Gall, N.R., Rut'Kov, E.V., Tontogode, A.Y., 1997. Two dimensional graphite films on metals and their intercalation. *International Journal of Modern Physics B* 11, 1865–1911.
- Geim, A.K., Novoselov, K.S., 2007. The rise of graphene. *Nature Materials* 6, 183–191.
- Gogotsi, Y.G., 1994. Particulate silicon nitride-based composites. *Journal of Materials Science* 29, 2541–2556.
- Gonzalez-Julian, J., Iglesias, Y., Caballero, A.C., *et al.*, 2011. Multi-scale electrical response of silicon nitride/multiwalled carbon nanotubes composites. *Composites Science and Technology* 71, 60–66.
- Groza, J.R., 1998. Field-activated sintering. In: Samal, P.K., Newkirk, J.W. (Eds.), *ASM Materials Handbook*, vol. 7. Materials Park, OH: ASM International, pp. 583–589.
- Hampshire, S., Jack, K.H., 1981. Special ceramics. *Proceedings of the British Ceramic Society* 31, 37.
- Hampshire, S., Park, H.K., Thompson, D.P., Jack, K.H., 1978. α' -Sialon ceramics. *Nature* 274, 880–882.
- Hirata, M., Gotou, T., Horiuchi, S., Fujiwara, M., Ohba, M., 2004. Thin film particles of graphene oxide 1: High-yield synthesis and flexibility of the particles. *Carbon* 42, 2929–2937.
- Huang, Z.P., Xu, J.W., Ren, Z.F., *et al.*, 1998. Growth of highly oriented carbon nanotubes by plasma-enhanced hot filament chemical vapor deposition. *Applied Physics Letters* 73, 3845–3847.
- Hvizdoš, P., Duszová, A., Puchy, V., *et al.*, 2011. Wear behavior of ZrO₂-CNF and Si₃N₄-CNT nanocomposites. *Key Engineering Materials* 465, 495–498.
- Hvizdoš, P., Dusza, J., Balázs, C., 2013. Tribological properties of Si₃N₄-graphene nanocomposites. *Journal of the European Ceramic Society* 33, 2359–2364.
- Hvizdoš, P., Puchy, V., Duszová, A., Balázs, C., Dusza, J., 2012. Tribological and electrical properties of ceramic matrix composites with carbon nanotubes. *Ceramics International* 38, 5669–5676.
- Iijima, S., 1991. Synthesis of carbon nanotubes. *Nature* 354, 56–58.
- Iijima, S., Ichihashi, T., 1993. Single-shell carbon nanotubes of 1-nm diameter. *Nature* 363, 603–605.
- Journet, C., Maser, W.K., Bernier, P., *et al.*, 1997. Large-scale production of single-walled carbon nanotubes by the electric-arc technique. *Nature* 388, 756–758.
- Kónya, Z., Vesselenyi, I., Niesz, K., *et al.*, 2002. Large scale production of short functionalized carbon nanotubes. *Chemical Physics Letters* 360, 429–435.
- Kovalčíková, A., Balázs, C., Dusza, J., Tapasztó, O., 2012. Mechanical properties and electrical conductivity in a carbon nanotube reinforced silicon nitride composite. *Ceramics International* 38, 527–533.
- Krstic, Z., Krstic, V.D., 2012. Silicon nitride: the engineering material of the future. *Journal of Materials Science* 47, 535–552.
- Kun, P., Wéber, F., Balázs, C., 2011. Preparation and examination of multilayer graphene nanosheets by exfoliation of graphite in high efficient attritor mill. *Central European Journal of Chemistry* 9, 47–51.
- Kun, P., Tapasztó, O., Weber, F., Balázs, C., 2012. Determination of structural and mechanical properties of multilayer graphene added silicon nitride based composites. *Ceramics International* 38, 211–216.
- Kvetková, L., Duszová, A., Hvizdoš, P., *et al.*, 2012. Fracture toughness and toughening mechanisms in graphene platelet reinforced Si₃N₄ composites. *Scripta Materialia* 66, 793–796.
- Lee, D.D., Kang, S.J.L., Petzow, G., Yoon, D.N., 1990. Effect of α to β (β') phase transition on the sintering of silicon nitride ceramics. *Journal of the American Ceramic Society* 73, 767–769.
- Maleka, O., González-Julian, J., Vleugels, J., *et al.*, 2011. Carbon nanofillers for machining insulating ceramics. *Materials Today* 14, 496–501.
- McLachlan, D.S., Blaszkiewicz, M.B., Newman, R.E., 1990. Electrical resistivity of composites. *Journal of the American Ceramic Society* 73, 2187–2203.

- Miranzo, P., Ramirez, C., Román-Manso, B., Belmonte, M., 2013. In situ processing of electrically conducting graphene/SiC nanocomposites. *Journal of the European Ceramic Society* 33, 1665–1674.
- Niihara, K., 1991. New design concept for structural ceramics – Ceramic nanocomposites. *Journal of the Ceramic Society of Japan* 99, 974–982.
- Nikolaev, P., Bronikowski, M.J., Bradley, *et al.*, 1999. Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide. *Chemical Physics Letters* 313, 91–97.
- Novoselov, S., Geim, A.K., Morozov, S.V., *et al.*, 2004. Electric field effect in atomically thin carbon films. *Science* 306, 666–669.
- Papakonstantinou, C.G., Balaguru, P., Lyon, R.E., 2001. Comparative study of high temperature composites. *Composites Part B: Engineering* 32, 637–649.
- Pasupuleti, S., Peddetti, R., Santhanam, S., *et al.*, 2008. Toughening behavior in a carbon nanotube reinforced silicon nitride composite. *Materials Science and Engineering A* 491, 224–229.
- Peng, G.H., Li, X.G., Liang, M., *et al.*, 2009. Spark plasma sintered high hardness α/β Si_3N_4 composites with MgSiN_2 as additives. *Scripta Materialia* 61, 347–350.
- Peterson, I.M., Tien, T.Y., 1995. Effect of grain boundary thermal expansion coefficient on the fracture toughness in silicon nitride. *Journal of the American Ceramic Society* 78, 2345–2352.
- Picot, O.T., Rocha, V.R., Ferraro, C., *et al.*, 2017. Using graphene networks to build bioinspired self-monitoring ceramics. *Nature Communications* 8, 14425.
- Ramanathan, T., Abdala, A.A., Stankovich, S., *et al.*, 2008. Functionalized graphene sheets for polymer nanocomposites. *Nature Nanotechnology* 3, 327–331.
- Ramirez, C., Garzon, L., Miranzo, P., Osendi, M.I., Ocal, C., 2011. Electrical conductivity maps in graphene nanoplatelet/silicon nitride composites using conducting scanning force microscopy. *Carbon* 49, 3873–3880.
- Rao, C.N.R., Sood, A.K., Subrahmanyam, K.S., Govindaraj, A., 2009. Graphene: The new two-dimensional nanomaterial. *Angewandte Chemie* 48, 7752–7777.
- Ren, Z.F., Huang, Z.P., Xu, J.W., *et al.*, 1998. Synthesis of large arrays of well-aligned carbon nanotubes on glass. *Science* 282, 1105–1107.
- Ren, Z.F., Huang, Z.P., Xu, J.W., *et al.*, 1999. Growth of a single freestanding multiwall carbon nanotube on each nanonickel dot. *Applied Physics Letters* 75, 1086–1088.
- Riley, F.L., 2004. Silicon nitride and related materials. *Journal of the American Ceramic Society* 83, 245–265.
- Ruzjukiev, A., Ishizaki, K., 1993. Sintering of silicon nitride with YAlO_3 additive. *Journal of the American Ceramic Society* 76, 2373–2375.
- Samal, S.S., Smrutisikha, B., 2008. Carbon nanotube reinforced ceramic matrix composites – A review. *Journal of the Minerals, Metals, and Materials Society* 7, 355–370.
- Sayyadi-Shahraki, A., Mahdi Rafiaei, S., Ghadami, S., Nekouee, K.A., 2019. Densification and mechanical properties of spark plasma sintered $\text{Si}_3\text{N}_4/\text{ZrO}_2$ nano-composites. *Journal of Alloys and Compounds* 776, 798–806.
- Segal, M., 2009. Selling graphene by the ton. *Nature Nanotechnology* 4, 612–614.
- Shen, Z., Zhao, Z., Peng, H., Nygren, M., 2002. Formation of tough interlocking microstructures in silicon nitride ceramics by dynamic ripening. *Nature* 417, 266–269.
- Soldano, C., Mahmood, A., Dujardin, E., 2010. Production properties and potential of graphene. *Carbon* 48, 2127–2150.
- Suematsu, H., Mitomo, M., Mitchell, T.E., *et al.*, 1997. The α – β transformation in silicon nitride single crystals. *Journal of the American Ceramic Society* 80, 615–620.
- Tapasztó, O., Tapasztó, L., Lemmel, H., *et al.*, 2016. High orientation degree of graphene nanoplatelets in silicon nitride composites prepared by spark plasma sintering. *Ceramics International* 42, 1002–1006.
- Tatami, J., Katashima, T., Komeya, K., Meguro, T., Wakihara, T., 2005. Electrically conductive CNT-dispersed silicon nitride ceramics. *Journal of the American Ceramic Society* 88, 2889–2893.
- Thompson, D.P., 2002. Materials science: Cooking up tougher ceramics. *Nature* 417, 237.
- Thostenson, E.T., Ren, Z., Chou, T.W., 2001. Advances in the science and technology of carbon nanotubes and their composites: a review. *Composites Science and Technology* 61, 1899–1912.
- Villars, P., Calvert, L.D., 1986. *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*. vol. 3. Metals Park, OH: American Society for Metals.
- Wang, X., Padture, N.P., Tanaka, H., 2004. Contact-damage resistant ceramic/single-wall carbon nanotubes and ceramic/graphite composites. *Nature Materials* 3, 539–544.
- Weibel, A., Mesguich, D., Chevallier, G., Flahaut, E., Laurent, C., 2018. Fast and easy preparation of few-layered-graphene/magnesia powders for strong, hard and electrically conducting composites. *Carbon* 136, 270–279.
- Xia, Z., Riester, L., Curtin, W.A., Li, H., *et al.*, 2004. Direct observation of toughening mechanisms in carbon nanotube ceramic matrix composites. *Acta Materialia* 52, 931–944.
- Yamamoto, G., Omori, M., Hashida, T., Kimura, H., 2008. A novel structure for carbon nanotube reinforced alumina composites with improved mechanical properties. *Nanotechnology* 19, 1–7.
- Yang, J.F., Ohji, T., Niihara, K., 2000. Influence of yttria–alumina content on sintering behavior and microstructure of silicon nitride ceramics. *Journal of the American Ceramic Society* 83, 2094–2096.
- Yoshio, S., Tatami, J., Wakihara, T., *et al.*, 2011. Effect of CNT quantity and sintering temperature on electrical and mechanical properties of CNT-dispersed Si_3N_4 ceramics. *Journal of the Ceramic Society of Japan* 119, 70–75.
- Yu, M.F., Files, B.S., Arepalli, S., Ruoff, R.S., 2000. Tensile loading of ropes of single wall carbon nanotubes and their mechanical properties. *Physical Review Letters* 84, 5552–5555.
- Zhan, G.D., Kuntz, J.D., Wan, J., Mukherjee, A.K., 2003. Single-wall carbon nanotubes as attractive toughening agents in alumina-based nanocomposites. *Nature Materials* 61 (2), 38–42.

Short Fiber Ceramic Matrix Composites (SF-CMCs)

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Introduction

Reinforcing ceramics with fibers allows them to overcome their brittleness and induce fracture toughness in the material and damage tolerance to the ceramic component. In many cases, the fibers will provide sufficient mechanical properties even if their length is far smaller than the dimension of the component, offering technological advantages in terms of near-net shape producibility and/or economical benefits compared to continuous fibers. Short fibers or chopped fiber bundles are typically produced by cutting long fibers or rovings to lengths from several millimeters to few centimeters. In comparison with polymeric or metallic matrices, the minimum fiber length for the reinforcement of ceramic matrices is typically one order of magnitude higher and is mostly defined rather by empirical knowledge than theoretical concepts. Short fiber ceramic matrix composites have been developed both as non-oxide matrix composites with ceramic or carbon fiber reinforcements as well as oxide matrix composites in which non-oxide or oxide fibers are incorporated in an oxide matrix.

The need to use short fibers in composites with brittle ceramic matrices can be driven by a multiplicity of motivations. Of course, there is the economical aspect of cost reduction by replacing long fibers and 2D-fabrics with short fibers as well as the application of certain near-net shape fabrication methods (Zuber and Heidenreich, 2006). The main objective for short fiber reinforced CMCs is the adjustment of structural and functional properties in the final composite. Compared with the properties of the pristine ceramic matrix material, the fiber addition in the final composite can lead to:

- (1) Improved damage tolerance, often accompanied by an increased strain-to-failure.
- (2) Increased tensile strength for comparable weak or porous matrices (Slosarczyk *et al.*, 2000).
- (3) Increased resistance against creep (Pachalis *et al.*, 1990).
- (4) Adjusted thermal expansion and thermal conductivity e.g., for a low coefficient of thermal expansion (CTE) and high thermal conductivity in the composite (Krödel *et al.*, 2002; Song *et al.*, 2003).
- (5) An appropriate frictional performance (Krenkel *et al.*, 2002).
- (6) Tailored absorption behavior of electromagnetic waves (Cao *et al.*, 2010).

Some prevalent applications of short fiber CMCs benefit from the combination of damage tolerance with the inherent properties of the ceramic constituents, like high melting point, hardness, oxidation resistance, and high resistance against thermal shock, rendering them very suitable for the use in environments with high thermo-mechanical loads.

Before discussing the principles of influencing effects of the short fibers on the desired composite properties, we have to address the state of the short fibers within the composite. The short fibers can occur in the matrix either as distributed single fibers, or more commonly as distributed short fiber bundles, due to their cutting from fiber rovings with a distinctive filament number. In contrast to continuous fiber reinforced CMCs, which are often derived from rovings or from fabrics with a 2D fiber orientation, resulting in a high anisotropy, it is easier to achieve quasi-isotropic properties in one plane with short fiber reinforced CMCs. This is due to the random orientation of short fiber bundles during fabrication methods like compression molding. The primary parameters, which have a decisive impact on the composite properties, and also determine the possible mechanisms of action of the reinforcement in the composites are: the inherent material properties of the constituents (e.g., quantities of stiffness, Poisson's ratio and CTE), the fiber volume content, the length of the short fibers or short fiber bundles, the diameter of the fibers, the aspect ratio of a single fiber defined by the length divided by the diameter, the fiber orientation from random to orientated, and the bonding strength between fibers and matrix as well as their origin (chemical and/or physical bonding).

Mechanisms of Short Fiber Reinforcement

In contrast to the existing comprehensive models and understandings about the mechanical behavior and properties of continuous fiber reinforced CMCs (Evans and Zok, 1994), only a few consistent models exist for short fiber CMCs. Most of the existing insights and model conceptions for short fiber CMCs are based upon empirical approaches and are often limited to a single CMC material class or to specific short fiber orientations and hence are far away from general applicability. It has to be pointed out, that the majority of theories for the estimation and prediction of properties of short fiber CMCs, and their interdependence from structure, were originally derived for composites with polymeric or metallic matrices and fibers. Some model boundary conditions for these can be in accordance with the conditions prevailing in distinctive short fiber CMC materials and could therefore be used as a first estimation of properties and their relation with structure and composition.

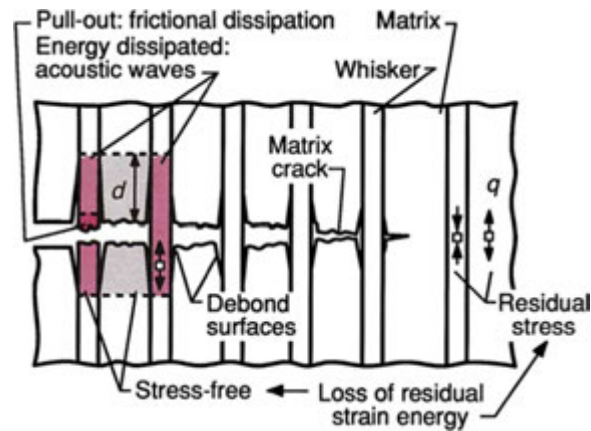


Fig. 1 Schematic of the toughening mechanisms stress shielding, crack bridging, pull-out, crack deflection and debonding. From Evans, A.G., 1990. Perspective on the development of high-toughness ceramics. *Journal of the American Ceramic Society* 73, 187–206. Copyright John Wiley & Sons, Inc.

Damage Tolerance and Extrinsic Toughness

The achievement of a damage-tolerant material behavior, in terms of an extrinsic toughening (Launey and Ritchie, 2009), is one of the most pronounced endeavors for short fiber CMCs. Mechanisms of extrinsic toughening, such as stress shielding of crack bridging fibers and fiber pull-out, take effect after a prolonged crack growth and occur in the wake of the crack tip. In contrast to the intrinsic toughness of a material, which determines the initial resistance against crack growth due to mechanisms within or ahead of the crack tip, the extrinsic toughening often leads to a higher resistance against the crack growth with increasing damage and crack extension.

The fiber reinforcement often enables an increase of the total strain-to-failure of the composite above the level of the brittle fiber and matrix. Due to the fiber reinforcement, different energy dissipating mechanisms can occur during failure. Stress shielding by fibers in front of a crack transfers stress from a crack within the matrix to the fiber with a higher modulus of elasticity and strength, thereby reducing the stress intensity of the crack in the matrix. If the fibers induce residual stress fields in their adjacent regions within the matrix, a crack can be deflected or branched, causing it to meander around the fibers. This deflection can also occur directly at the fiber/matrix-interface. If a crack is deflected around a sufficiently strong fiber, the crack can be elongated, while the fiber is still bridging the gap. For this purpose, the fiber needs to be long enough to span the crack. With further elongation the fiber can break somewhere away from the crack opening and the remaining fiber fragment can be pulled-out, thereby dissipating energy by frictional sliding. Fig. 1 sums up principle models of toughening mechanisms.

Except for the stress shielding by fibers and the crack branching, debonding of fiber and matrix is a prerequisite for all toughening mechanisms, such as crack deflection at the fiber matrix interface, crack bridging and pull-out of fibers from the matrix during proceeding crack growth. In order for debonding to occur, a sufficient bonding between fiber and matrix is necessary. If the bonding is too low, this will only cause the fibers to act as flaws in the matrix and no load transfer appears. A sufficiently strong bond between fiber and matrix can be achieved with the choice of processing, constituents, and/or fiber coatings, leading to the adjustment of the suitable interface design or weak matrices in the case of porous or gradient matrices (Zok, 2006; Koch *et al.*, 2008). The capacity of pull-out and friction mechanisms is dependent on the fiber length, resulting in a toughness increase for short fiber reinforced CMCs, which is often less pronounced than for continuous fiber reinforced CMCs. The boundary conditions for fiber pull-out depend on the embedded fiber length, the shear strength, the ratio of the elastic moduli of fiber and matrix, and the stress distribution within the fiber (Lawrence, 1972). This theoretical concept can predict the situation, in which a fiber of minimum length will be pulled-out of the matrix instead of breaking without any pull-out. If a short fiber CMC with unidirectional (UD) fiber alignment has an optimum fiber length, so that all the fibers in a crack will be pulled-out instead of fracturing, the toughening effect by the pull-out mechanism can be greater than for long fiber reinforcement of the same material (Budiansky and Cui, 1995). Of course, the strength of the continuous reinforced material will always be higher.

The quantitative estimation of toughness values for a given short fiber composite is intricate, as the amount of the single toughening effects and their contribution to the total composite toughness is difficult to determine. An approach for the calculation of the toughness values for the pull-out and the fiber bridging mechanisms of short fiber reinforced ceramics is presented by (Becher, 1991) considering the determination of the pull-out length regarding (Budiansky *et al.*, 1986). Despite the fact, that the necessary calculated pull-out length of 26 μm was satisfied with carbon fibers longer than 100 μm in a silicon nitride matrix, and a desired pull-out mechanism could be found, damage tolerance and quasi-ductility was not observed in the final composite (Herzog *et al.*, 2007). Hence, there is no guaranty, that the activation of one or more principal toughening mechanisms will lead to a damage tolerance of the material.

The influence of interface debonding, matrix cracking stress and frictional conditions between fiber and matrix on the overall toughness of composites can be modeled for the special case of unidirectional short fiber reinforcements (Budiansky *et al.*, 1995). A model with a probabilistic approach describes the toughness of short fiber CMCs with aligned or randomly oriented fibers with

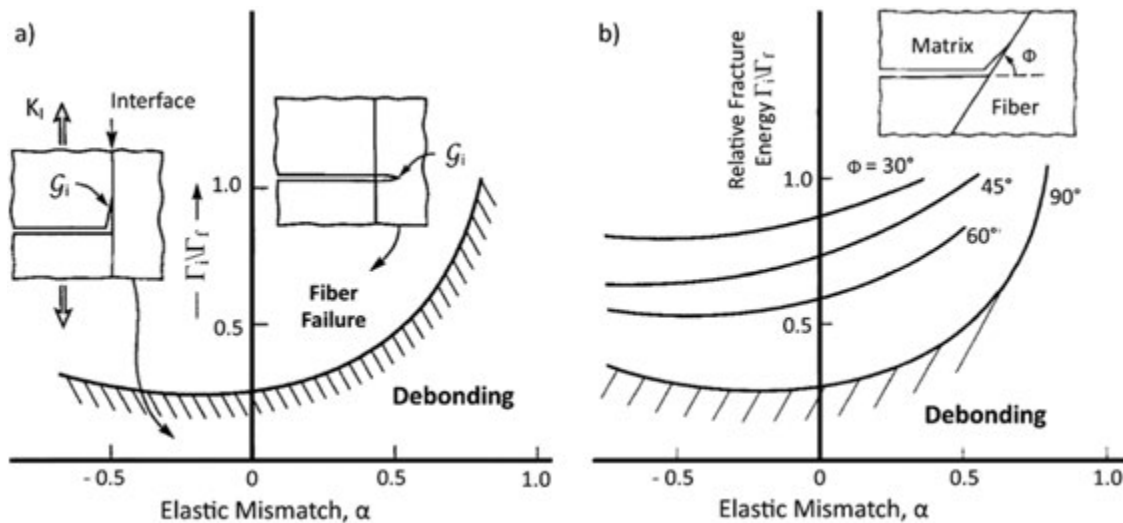


Fig. 2 Criteria for fiber cracking or debonding depending on (a) the relation of interface (i) and fiber (f) fracture energy and the elastic mismatch and (b) the inclination of the crack to the fiber. From Evans, A.G., He, M.Y., Hutchinson, J.W., 1989. Interface debonding and fiber cracking in brittle matrix composites. *Journal of the American Ceramic Society* 72, 2300–2303. Copyright John Wiley & Sons, Inc.

regard to the pull-out effect, the fiber shape parameter, the fiber inclination, and the fiber strength distribution (Suemasu *et al.*, 2001). Too much inclination between the fibers and the crack leads to fiber breakage instead of pull-out, thus, the toughness for randomly oriented short fiber composites was found to be lower compared to unidirectionally aligned short fiber reinforced composites.

Debonding of Fiber and Matrix

The behavior of a crack in the interface region between the matrix and the fiber plays an important role in the performance of the composite. The debonding process is a requirement for most toughening mechanisms. If a matrix crack, driven by an external load, is propagating towards the fiber, it could either penetrate or bypass the fiber. To bypass, a debonding between fiber and matrix is necessary. The debonding can occur as a failure in the interface, the coating, or the matrix itself. The principal debonding conditions and their mechanisms are well understood and extensive models are available. A first approach explains the debonding between two elastic and isotropic materials by means of an energy release rate criterion of a deflection or penetration of the crack (He and Hutchinson, 1989). It also includes the influence of different angles between the crack, the interface, and the load direction. Beside this general approach for the coupling of two materials, a model for brittle matrix composites was evolved to describe the conditions for debonding or fiber cracking based on a fracture energy criterion of interface and fiber (Evans *et al.*, 1989). The schemes for debonding conditions are depicted in Fig. 2, and consider the elastic mismatch of fiber and interface as well as the inclining of fiber, crack, and load direction. Hence, it is a very powerful tool for material design and development in order to adjust the right combination of fiber and matrix, fiber coating, or interface design. The model shows, that debonding appears more readily, if a crack perpendicular to the load direction approaches a fiber with an axis not perpendicular to the fiber. The smaller the angle between fiber and crack, the easier the debonding. Furthermore, if the crack approaches the fiber at a smaller angle, the debonding can occur at a higher ratio of interface fracture energy to fiber fracture energy. In addition, a smaller angle between crack and fiber can also affect the failure mode of the fibers, which can lead to kinking instead of rupture. This has consequences for short fiber reinforced CMCs, as the fiber distribution function and the load direction become crucial for the overall material behavior. The debonding condition in the short fiber CMC can become a function of the spatial orientation of the single fibers and fiber bundles within the material and therefore, the enabled toughening mechanisms related to debonding become a function of position and orientation itself.

Advanced debonding models make it possible to account for residual stresses within the composite, which are quite common for CMCs. It is possible to extend the fracture energy criterion with the integration of friction after debonding, which is caused by residual compressive stresses in the composite between fiber and matrix (Hutchinson and Jensen, 1990). If residual tensile stresses between fiber and matrix are present, debonding can lead to a state free of friction after interface debonding (Charalambides and Evans, 1989). The fiber debonding conditions can also be evaluated under combined mechanical and thermal loads, at which the residual stresses arise from a change of temperature (Charalambides, 1990). The last three models should be considered in the assessment of damage tolerance due to fiber pull-out, as the influences of friction and residual stresses play a key role for the amount of energy absorption. Although the general conditions for debonding in CMCs with a weak matrix are addressed partly by the consideration of elastic mismatch in the model of Evans, He, and Hutchinson (Evans *et al.*, 1989), a more

emphasized description was derived for debonding conditions predominant in weak matrix CMCs with strong interfacial bonding (Tu *et al.*, 1996).

Load Transfer Between Matrix and Fiber

The load transfer from a stressed matrix to the fiber is treated with different assumptions leading to so called shear lag models. Models for short fiber reinforced CMCs are only of limited practical use, since the desired mechanism of debonding is not addressed in the existing models and most of the model assumptions are far away from the conditions apparent in short fiber CMCs under load. For example, most of the shear lag models consider an alignment of the external load, shear load from matrix to fiber, fiber orientation and the axial fiber load. This arrangement will be rare in real short fiber CMC materials. Hence, the shear lag models with their simplified approaches provide only basic insights in intricate problems.

The linear elastic shear lag model assumes, that there is only a load transfer from the matrix to the fiber via shear load with a perfect bonding between fiber and matrix, no radial stresses due to clamping forces or elastic mismatch, no load transfer at the fiber ends, and the modulus of the fiber is greater than that of the matrix (Cox, 1952). This model can be used to calculate the axial stress distribution within the fiber and the interfacial shear stress between matrix and fiber. The axial fiber stress will increase from both fiber ends with a hyperbolic function and reach a maximum in the middle of the fiber. The shear stresses within the matrix start from zero in the middle of the fiber and increase inhomogeneously and steeply towards the fiber ends. With the additional assumption of a constant shear load over the whole fiber length, the elastic-plastic model can derive a critical aspect ratio for the maximum exploitation of the fiber strength (Kelly and Tyson, 1965). The constant shear load was initially an interpretation of a given yield strength for metal matrix composites. For the case of CMCs it was assumed that the constant shear load for this model could be the constant friction state between fiber and matrix. A constant shear load assumption leads to a linear increase of axial fiber stress from the fiber ends towards the fiber middle. This axial stress can attain the maximum fiber strength level ($\sigma_{\text{fiber,max}}$), if the fiber aspect ratio ($\frac{l}{d}$) is high enough to transfer an external load via the known and constant shear strength (τ_i). Hence, it would be possible to derive a critical aspect ratio or a critical fiber length (l), which would take full use of the maximum fiber strength, if the diameter (d) of the fiber is set for a known fiber and interface shear strength (Eq. 1). If the aspect ratio is smaller, the maximum axial stress in the fiber will be below fiber strength.

$$\left(\frac{l}{d}\right)_{\text{crit}} = \frac{\sigma_{\text{fiber,max}}}{2 \cdot \tau_i} \quad (1)$$

This model can be used to estimate pull-out or breakage of fibers and is often the prerequisite to derive models for the estimation of stiffness, strength and toughness in composites.

The application of the shear lag model to short fiber reinforced polymer composites leads to the experimental validation of strength dependency from fiber length and critical fiber lengths in the range of a few hundred μm (Fu and Lauke, 1996). However, the practical applicability for CMC materials seems questionable. A calculation for a CMC with an oxide fiber reinforcement of Nextel™610 with a fiber strength of 3300 MPa and a diameter of 12 μm (Wilson and Visser, 2001) within an oxide matrix and an interface shear strength of 2–12 MPa (Weaver *et al.*, 2006) leads to critical fiber lengths of 1.7–10 mm. The experimental determination of the critical fiber length in short carbon fiber reinforced carbon using a double lap joint method leads to a value of 52 mm (Heim *et al.*, 2013). These values are up to two orders of magnitude greater than those for polymer matrix composites. An obvious change of bending strength was not observed for short carbon fiber reinforced SiC composites, if the fiber lengths were varied from 10 to 40 mm (Zuber and Heidenreich, 2006) or 6–24 mm (Liensdorf *et al.*, 2019).

Further developments of shear lag models try to refine the explanatory power with the coverage of more and more practical constraints. The load transfer from matrix to the fiber across the fiber ends can be considered for aligned short fiber composites, leading to a refinement of stress fields in fiber and interface (Fukuda and Chou, 1981). The inclusion of residual stresses and matrix cracking for unidirectional continuous fiber reinforced CMCs under tensile load, allows a better approximation of stress distribution as well as the estimation of debonding lengths (Lee and Daniels, 1992; Daniels *et al.*, 1993). Some attempts also account for residual axial stresses caused by thermal mismatch for short fiber reinforced CMCs (Hsueh and Becher, 1996). A refinement of axial stresses of the fiber in dependency of the aspect ratio could be achieved, but radial stresses were also not considered in this modified shear lag model. A critical assessment for the use of shear lag models for unidirectional composites states that it is a sufficient analytical tool to estimate axial stresses for axisymmetric stress states (Nairn, 1997). However, the predictions of shear stresses and energy release rates are of low accuracy and the associated errors are strongly dependent on the ratio of the fiber and matrix Young's moduli. The shear lag approach is also not applicable to low fiber volume contents (Nairn, 1997).

Estimate Composite Strength

Compared to obtaining an increased damage tolerance and toughness by incorporating short fibers into a matrix, the goal to increase the strength is only a secondary intention. To achieve a strength increase with short fiber reinforcement, the strength of the fibers has to be much higher than the strength of the matrix and strong fiber matrix bonding is needed. Following this approach leads to a brittle composite. With this assumption, the load transfer could be estimated with existing shear lag models, meaning an

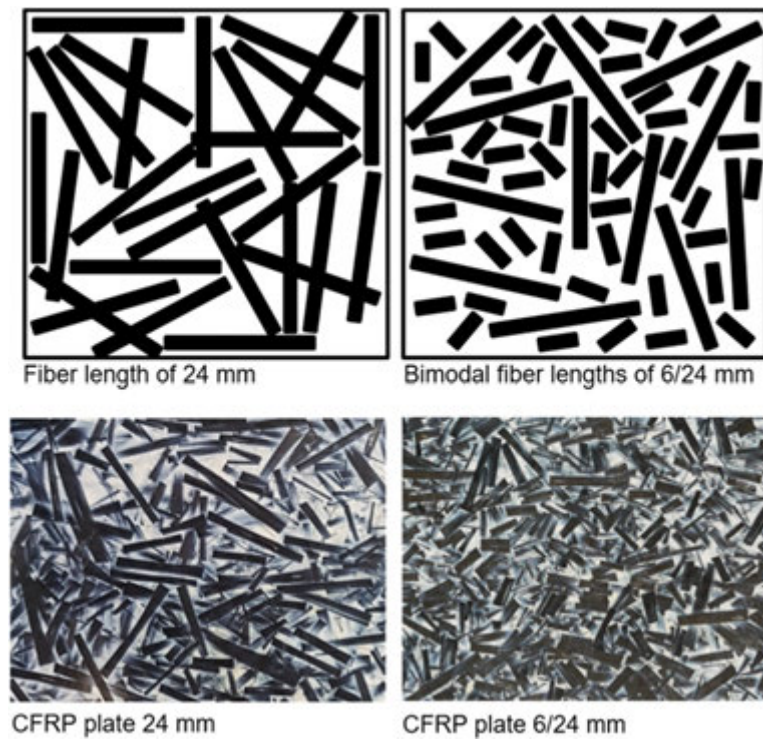


Fig. 3 Mono-modal (fiber length 24 mm) and bi-modal (fiber lengths 6 and 24 mm) fiber distributions in a short fiber CFRP composite prior to pyrolysis. Reproduced from Liensdorf, T., Langhof, N., Krenkel, W., 2019. Mechanical properties of PEEK-derived C/SiC composites with different fiber lengths. *Advanced Engineering Materials* 21 (5), 1800835. Copyright Wiley-VCH GmbH.

increasing fiber length leads to improved utilization of the fiber strength and therefore, a higher composite strength. The models for the estimation of the strength of unidirectional aligned short fiber composites show a dependency from fiber volume fraction, fiber aspect ratio and the ratio of the modulus of elasticity (Chen, 1971). Existing models for brittle polymeric matrix composites can predict the stress strain curve and matrix cracking for short aligned fibers according to the maximum strain hypothesis (Chen and Tucker, 1984). The strength estimation for randomly oriented fibers can be made via quasi-isotropic laminate theory following the maximum stress criterion (Hahn, 1975) or maximum strain criterion (Halpin and Kardos, 1978). The mentioned models, however, were not derived for CMC materials and did not consider the debonding aspects for the majority of CMCs with an intended damage-tolerant behavior. Nevertheless, it was shown that the calculated strength values for a damage-tolerant short carbon fiber reinforced $\text{ZrB}_2\text{-SiC}$ composite agreed well with the measured values (Yang *et al.*, 2010). For this purpose, the maximum strain criterion was applied and the decrease of strength from 502 to 445 MPa due to the addition of 20 vol% of randomly oriented carbon fibers was forecast with a strength value of 452 MPa. For 20 vol% short carbon fiber reinforced TiC, it was also possible to calculate the composite strength with a simplified rule of mixtures approach considering the fiber orientation and the fiber strength degradation during the fabrication (Song *et al.*, 2002). In this connection, the predicted flexural strength of 627 MPa was in good accordance with the measured value of 593 MPa.

Estimate Stiffness Quantities

A first approximation for the stiffness behavior can be deduced from general composite models. The stiffness values increase with increasing fiber volume content following certain rules of mixtures within upper and lower bonds. For aligned short fibers, the modulus of elasticity in the fiber direction is strongly influenced by the aspect ratio of the fibers, whereas the Poisson's ratio, the modulus of elasticity perpendicular to the fiber orientation, and the shear modulus are not sensitive to the aspect ratio (Halpin, 1969). For in-plane randomly oriented fibers the laminated plate theory for quasi-isotropic laminates can be applied. The stiffness increases with increasing aspect ratio of the fiber until a threshold, which strongly depends on the relation of the Young's moduli of fiber and matrix, is reached (Halpin and Pagano, 1969).

The lack of reliable analytical models designed specifically for short fiber CMCs leads to the development of better approximations for each individual material via simulation and finite element methods. The elastic properties for C/C-SiC for example, can be numerically modeled with a mesoscale approach considering the size, shape, and orientation of fiber bundles, leading to an agreement of calculated Young's and shear moduli with measured values of a bending test (Airolidi *et al.*, 2013).

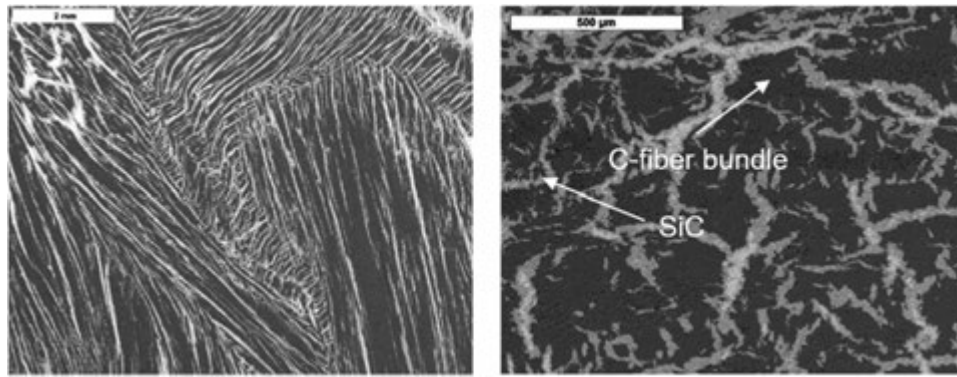


Fig. 4 SEM micrographs of the surface (left) and the cross section (right) of a SF-CMC material (C/C-SiC).

Non-Oxide CMCs

Non-oxide ceramic matrix composites comprise mainly the materials carbon and silicon carbide and are abbreviated as C/C, C/SiC, C/C-SiC or SiC/SiC, depending whether the reinforcing fiber is carbon or SiC. In some special cases, for example for hypersonic applications, ultra-high temperature ceramics (UHTCs) like ZrB_2 or HfB_2 are used as main constituent of the matrix materials (Guo *et al.*, 2013; Sha *et al.*, 2015, 2016). Principally, various processing routes exist to infiltrate the fiber preform with the matrix or with a matrix precursor. Conventional powder-based techniques which are used for fabricating monolithic ceramics are mostly not suitable and rather unconventional techniques are applied to avoid damage to the fibers. They can be distinguished between the impregnation either by a gas phase (chemical vapor infiltration, CVI) or by a liquid phase infiltration (Liquid Silicon Infiltration, LSI or Polymer Infiltration and Pyrolysis, PIP). The CVI process needs a stable and stiff fiber architecture such as a fiber preform, and therefore only the LSI and the PIP process are commonly used for the manufacture of short fiber reinforced composites. SiC fibers are up to two orders of magnitude more expensive than carbon fibers and their use as short fibers is therefore limited to special applications (Sciti *et al.*, 2011). As a result, talking about short fiber reinforced non-oxide CMCs usually means referring to C/SiC or C/C-SiC composites.

Most publications and applications of SF-CMCs refer to the LSI process. This technique is based on the impregnation of porous carbon/carbon composites by molten silicon and the reaction of the metallic melt with the carbon to form the silicon carbide matrix. Therefore, this process belongs to the reactive melt infiltration processes (RMI). The fiber preform with its interconnecting network of cracks and pores is infiltrated under vacuum applying only capillary forces and at temperatures at least beyond the melting point of silicon (1415°C). The high reactivity and the exothermal reaction between carbon and silicon require a sophisticated fiber coating or the preservation of dense fiber bundles prior to the infiltration.

The initial step of the process is the fabrication of a carbon fiber reinforced plastic (CFRP) composite with polymeric matrices of high carbon yield. Normally, commercially available resins, such as thermosets (e.g., phenolics) or thermoplastics (e.g., Polyetheretherketone, PEEK) are used to fabricate laminates by compression molding (Krenkel *et al.*, 2002) or other common CFRP techniques like transfer molding (Ahmad *et al.*, 2020) or injection molding (Müller-Köhn *et al.*, 2020). The latter two technologies suffer from the drawback that the chopped fibers are further shortened considerably by the shear forces in the extruder during the compounding and injection step and that the fiber bundles cannot be preserved, resulting in single fibers with a length of only some few hundred μm . In contrast, the compression molding process allows the chopped fibers to maintain their original length (mm to cm), as well as maintaining the integrity of the bundles over the total CFRP forming process.

In order to reach a high fiber volume content as well as a homogenous fiber distribution, different fiber lengths can be combined to form the reinforcement. Fig. 3 depicts schematic diagrams and the corresponding microstructures of CFRP composites with a mono-modal fiber distribution of fibers with a length of 24 mm, and a bi-modal fiber distribution of fibers with 6 and 24 mm in length, respectively. The bi-modal fiber preform results in a more quasi-isotropic in-plane fiber orientation with a higher fiber volume content of 35% in comparison with the mono-modal fiber preform.

After curing or solidifying the matrix, the composites are pyrolysed under inert conditions (e.g., nitrogen or vacuum) at temperatures beyond 900°C to convert the polymeric matrix to amorphous carbon. The pyrolysis of the CFRP composite leads to a volumetric contraction of about 50% of the neat polymer. As this contraction of the polymer is hindered by the embedded fibers, the macroscopic shrinkage of the composite during pyrolysis is considerably lower. The shrinkage impediment is dependent on the fiber alignment and on the fiber/matrix bonding in the interphase. In the direction of the fiber orientation the macroscopic shrinkage is close to zero with the result that the matrix contraction leads to a microscopical network of cracks within the resulting C/C composite. The fiber/matrix bonding strength plays an important role for the crack formation. It can be modified by a fiber coating (e.g., pyC) or by a thermal pretreatment of the carbon fibers in order to adapt the functional groups on the carbon fiber surfaces. The latter method is often used due to its easy and cheap approach in contrast to the fiber coating process and is described well in the literature (Sha *et al.*, 2017; Liensdorf *et al.*, 2019). In general, the higher the fiber/matrix bondings the higher the tendency to preserve and form dense fiber bundles, comprising hundreds of filaments, interconnected with a translaminar crack

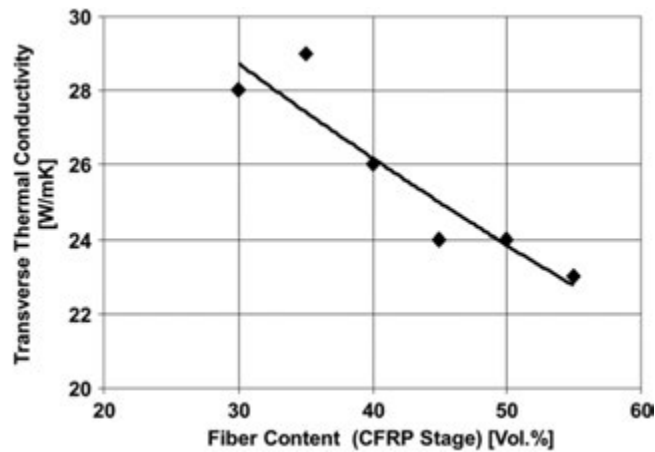


Fig. 5 Transverse thermal conductivity of C/C-SiC composites with 40 mm chopped fibers versus fiber volume content in the CFRP stage. Reproduced from Krenkel, W., Heidenreich, B., Renz, R., 2002. C/C-SiC composites for advanced friction systems. *Advanced Engineering Materials* 4, 427–436. Copyright Wiley-VCH GmbH.

system. These microcracks represent the open porosity of the C/C composite which is subsequently infiltrated with molten silicon to form the silicon carbide matrix (Krenkel, 2004, 2005, 2008; Krenkel *et al.*, 2002; Krenkel and Berndt, 2005).

After the siliconizing step, the resulting C/C-SiC composite comprises short carbon fiber bundles, embedded in a multi-phase matrix of carbon, silicon carbide and residual silicon. The density is between 2 and 2.5 g cm⁻³ with an open porosity of up to 5%. **Fig. 4** shows a typical cross-section and a top view of a short fiber CMC with fiber lengths between 6 and 40 mm.

The fiber/matrix interphase and the resulting bonding forces are affected by the type of carbon fiber. Guo *et al.* compared pitch and PAN derived fibers with lengths of 6 mm and reported that the flexural strength of pitch-based C/C-SiC composites was higher at room as well as at high temperature (800°C). Also, the thermal conductivity was higher compared to PAN fiber C/C-SiC and increased with the fiber volume content of the composite (Guo *et al.*, 2012). For PAN fibers with low thermal conductivity, the relationship between transverse thermal conductivity is vice versa: The higher the fiber volume content, the lower the thermal conductivity as lower fiber contents result in a higher amount of SiC in the matrix which shows a higher thermal conductivity than the fibers (Krenkel *et al.*, 2002). **Fig. 5** shows this correlation for C/C-SiC composites with 40 mm chopped fibers, referred to the fiber volume content in the intermediate CFRP stage.

Besides the fiber volume content, the length and the orientation of the fibers to the loading direction are the most important influences on the mechanical and thermophysical properties of SF-CMCs. In an experimental study with 6 mm carbon fibers, Hausherr *et al.* reported an increase of 50% in flexural strength and of 80% in stiffness, if the loading occurs in direction of the fiber alignment, compared with randomly oriented fibers (Hausherr *et al.*, 2015). **Table 1** summarizes the relationship between the fiber alignment and the loading direction and shows, that the mean value of different unidirectional reinforced SF-CMCs with angles between 0° and 90° to the load direction is very similar to the flexural strength of a randomly oriented, isotropic reinforced SF-CMC with the same fibers.

In contrast to continuous fiber reinforced CMCs no international standard exists for testing SF-CMCs in terms of dependence on the fiber orientation and fiber length. Studies of Shi *et al.* with C/C-SiC composites showed, that the flexural testing of SF-CMC should be conducted with a four point bending set-up rather than with a three point configuration (Shi *et al.*, 2015). It is recommended, that the width of flexural test coupons should be triple the fiber length and the span-to-thickness ratio should be 10. For longer fibers (10 mm and more) the width should be twice the fiber length and the span-to-thickness ratio should be at least six (Shi *et al.*, 2017).

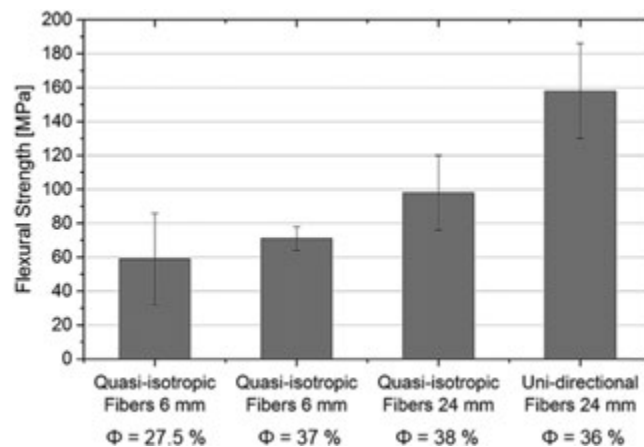
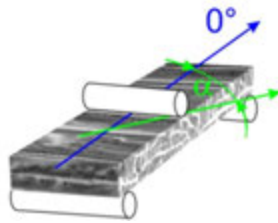
Fig. 6 depicts the influence of fiber volume content, fiber length and fiber orientation on the mechanical properties of a C/C-SiC composite. Whereas higher fiber contents increase the flexural strength slightly, longer fibers (24 mm instead of 6 mm length) show a more pronounced increase of the strength level. In the case where all fibers are aligned in one direction (unidirectional reinforcement), this short fiber UD-composite shows much better properties compared to randomly oriented composites with a quasi-isotropic behavior.

Compared with continuous fiber reinforced composites the mechanical properties of short fiber reinforced composites are somewhat lower. **Fig. 7** shows the flexural strength, the strain-to-failure and the Young's modulus of a mono-modal reinforcement of C/C-SiC with fibers of 6, 12 and 24 mm in length. As for all short fiber reinforcements, the scatter in the property data is higher in comparison to 2D reinforcements, for example fabrics. The values in general are in the range of 100 MPa for the flexural strength, 30 GPa for the Young's modulus and 0.5% strain-to-failure. These properties are also achieved with a bi-modal short fiber reinforcement (**Fig. 8**) with the combination of 6 and 12 mm fibers, 6 and 24 mm as well as 12 and 24 mm fibers, combined with a more homogenous microstructure (Liensdorf *et al.*, 2019).

As for all CMCs, the conventional determination of the Mode I fracture toughness does not correctly describe the quasi-ductile behavior of the composites. Typically, the fracture toughness K_{IC} is on the same level as that of SiC or other monolithic engineering

Table 1 Influence of fiber orientation on the mechanical RT-properties of SF-C/C-SiC (fiber length 6mm) (Hausherr, Eitel, Krenkel, 2015)

Short Fibers (6mm)	Fiber Orientation α								Isotropic
	0°	15°	30°	45°	60°	75°	90°	Mean Value	
Flexural Strength [MPa]	67	62	48	43	30	28	25	44	45,6
Young's Modulus [GPa]	45	40	30	25	22	19	16	28	25
Strain [%]	0,17	0,16	0,17	n.a.	0,17	0,16	0,16	0,16	0,17

**Fig. 6** Dependence of fiber length, fiber content and fiber orientation on the mechanical properties of SF-C/C-SiC composites.

ceramics. Inoue *et al.* measured K_{IC} values of about $4 \text{ MPa}\sqrt{\text{m}}$ and Sha *et al.* of up to $7.6 \text{ MPa}\sqrt{\text{m}}$ (Inoue *et al.*, 2013; Sha *et al.*, 2017). However, the damage-tolerant behavior of these composites is much better than these properties imply. Fig. 9 shows the typical fracture surface of a C/C-SiC composite reinforced with 24 mm long fibers, which had been thermally pretreated at 700°C to reduce the fiber/matrix bonding at the interface.

The current most important applications of short fiber reinforced CMCs are brake disks for high-performance cars (Krenkel and Thébault, 2014). More than 200,000 C/C-SiC brake disks are produced annually in increasing numbers, corresponding to a production volume of approximately 1000 tons of SF-CMC every year. Compounds of chopped fiber rovings and powdery phenolic resins are mixed, filled in a mold with a geometry similar to the desired shape of the disk and subsequently compression molded, pyrolysed and siliconized. Applying a bi-modal fiber distribution, very complex and thin-walled designs of internally ventilated rotors are manufactured in a near-net shape process (Fig. 10). In comparison with metallic rotors the low density of this type of SF-CMC (below 2.5 g cm^{-3}) results in weight savings of up to 50% of the braking system of a passenger car.

Oxide CMCs

The reinforcing short fibers for oxide matrices can be either oxide or non-oxide. The following description of the current status of oxide matrix composites will concentrate on polycrystalline fibers and will forego all whisker-reinforced materials, although whiskers can reach similar dimensions as some of the short fibers described.

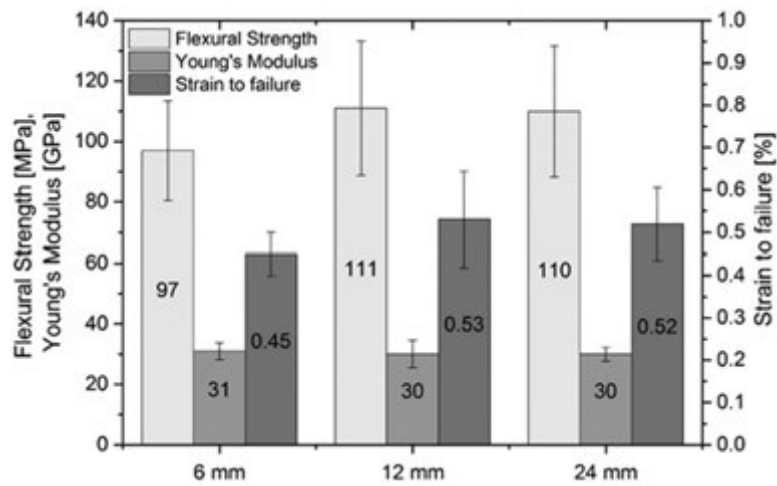


Fig. 7 Mechanical properties of mono-modal reinforced short fiber CMCs. Reproduced from Liensdorf, T., Langhof, N., Krenkel, W., 2019. Mechanical properties of PEEK-derived C/SiC composites with different fiber lengths. *Advanced Engineering Materials* 21 (5), 1800835. Copyright Wiley-VCH GmbH.

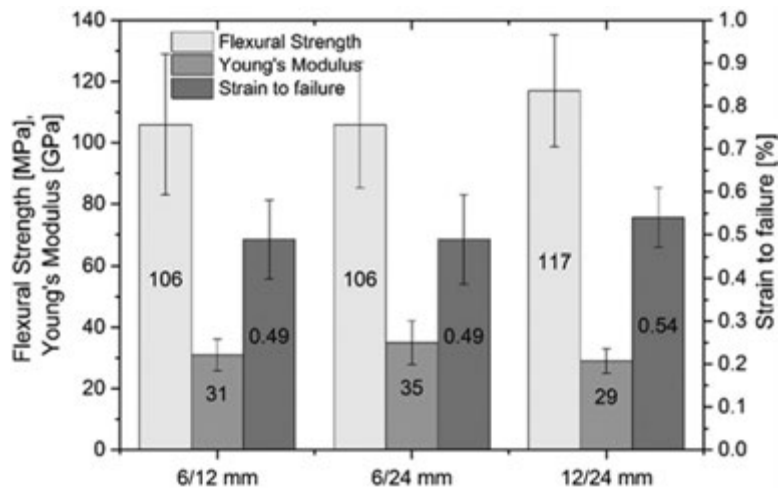


Fig. 8 Mechanical properties of bi-modal reinforced short fiber CMCs. Reproduced from Liensdorf, T., Langhof, N., Krenkel, W., 2019. Mechanical properties of PEEK-derived C/SiC composites with different fiber lengths. *Advanced Engineering Materials* 21 (5), 1800835. Copyright Wiley-VCH GmbH.

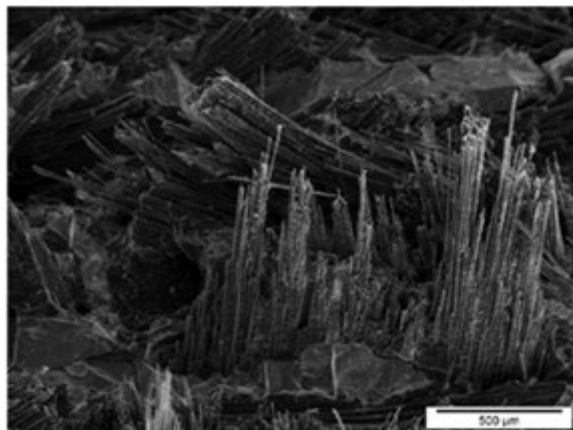


Fig. 9 SEM micrograph of the fracture surface of C/C-SiC (24 mm chopped and pretreated fibers). Reproduced from Liensdorf, T., Langhof, N., Krenkel, W., 2019. Mechanical properties of PEEK-derived C/SiC composites with different fiber lengths. *Advanced Engineering Materials* 21 (5), 1800835. Copyright Wiley-VCH GmbH.



Fig. 10 Ventilated carbon/ceramic brake disk for passenger cars. Courtesy of Audi AG.

Non-Oxide Fiber Reinforcements

An overview of oxide matrices reinforced with non-oxide short fibers is shown in [Table 2](#). The most commonly used non-oxide fibers for the reinforcement of oxide matrices are carbon fibers with diameters in the range of 5 μm to 13 μm . All described non oxide fiber/oxide matrix composites, with the exception of the ones produced by ([Langhans and Roeder, 1992](#)), include at least one pressing step during fabrication, which indicates the desire to obtain a dense matrix. Since all of the manufacturing techniques for non-oxide fiber/oxide matrix composites in the literature contain at least either a pressing step or an extrusion step and some even contain an additional milling step, the initial fiber length is shortened and the actual fiber length in the composite is considerably smaller. This final length is more likely to be in a similar range as the 20–150 μm described by ([Dorner-Reisel et al., 2004](#)) and the length distributions with fiber lengths less than 280 μm and 180 μm reported by ([Ye et al., 2008](#)).

The reinforcement of biocompatible as well as bioactive matrices such as calcium phosphate ([Park and Vasilos, 1997](#)) and hydroxyapatite ([Slosarczyk et al., 2000](#); [Dorner-Reisel et al., 2004](#)) with short carbon fibers was motivated by improving the mechanical properties of the matrix materials for possible applications as implants. The enhancement of mechanical properties was also the objective for the reinforcement of alumina ([Jia et al., 2018](#)), BAS ([Ye et al., 2008](#); [Ma et al., 2009](#)), β -SiAlON ([Demir, 2012](#)) as well as alkali-lime-silica glass ([Langhans and Roeder, 1992](#)) with carbon and/or silicon carbide short fibers. In contrast to this, alumina was reinforced by small amounts of carbon fibers (0.1 wt%–0.5 wt%) in order to influence its mechanical as well as its dielectric properties ([Huang et al., 2012, 2013, 2014](#)). The reinforcement of silica with 20 wt% carbon fibers by [Cao et al.](#) was pursued exclusively with regard to the improvement of the dielectric properties ([Cao et al., 2010](#)).

Due to the relatively dense matrices, the mechanical properties such as flexural strength and fracture toughness of reinforced matrices improved for most of the materials compared with unreinforced matrices, despite the short fiber length. One notable exception is the work of [Huang et al. \(2012\)](#), where the strength and hardness was decreased slightly by the introduction of carbon fibers into the matrix. This was attributed to big grains and a non-uniform grain size distribution as well as to less strong interfacial fiber/matrix bonds ([Huang et al., 2013](#)).

Extensive studies on the reinforcement of Pyrex glass, and also of soda-lime glass, lithia alumino-silicate glass-ceramic, alumina and magnesia with carbon fibers were carried out by ([Sambell et al., 1972](#)), while others concentrated just on the reinforcement of Pyrex glass with carbon fibers ([Phillips, 1972](#); [Phillips et al., 1972](#)).

Oxide Fiber Reinforcement

A summary of all-oxide short fiber reinforced CMCs is presented in [Table 3](#). Generally, one can distinguish three types of short oxide fiber/oxide matrix composites, based on the type of reinforcing fiber. These are.

- (1) Glass or silica (quartz) fibers ([Mishra et al., 2008](#); [Mishra et al., 2009](#); [Yunus et al., 2017](#)).
- (2) Low performance thermal insulation fibers, which include amongst others Saffil®, Denka®, Fiberfrax® and Zircar®; fibers ([Boussois et al., 2014](#); [Hua et al., 2013](#); [Liu et al., 1998](#); [Naskar et al., 2004](#); [Naskar et al., 2009](#); [Özkal and Uçar, 2010](#); [Papargyri et al., 2003](#); [Russell-Floyd et al., 1993](#); [Sambell et al., 1972](#); [Sheldon and Lewis, 1976](#); [Wang et al., 1991](#); [Yunus et al., 2017](#)).

Table 2 Literature survey summary of non-oxide short fiber reinforced oxide matrices

Matrix	Fiber	Fiber content	Initial fiber length	Fiber diameter	Reference
Al ₂ O ₃	C	0.22–0.44 wt%	1–3 mm	7.8 μm	Huang <i>et al.</i> (2012)
Al ₂ O ₃	C	0.1–0.3 wt%	2–4 mm	5–7 μm	Huang <i>et al.</i> (2013)
Al ₂ O ₃	C	0.1–0.5 wt%	2 mm	5–7 μm	Huang <i>et al.</i> (2014)
Al ₂ O ₃	C	5–15 vol%	2 mm	7 μm	Jia <i>et al.</i> (2018)
Ca ₃ (PO ₄) ₂	C	5 vol%			Park and Vasilos (1997)
Hydroxyapatite	C	20 vol%		8–9 μm 12–13 μm	Slosarczyk <i>et al.</i> (2000)
Hydroxyapatite	C	20 vol%	20–150 μm (milled)	5 μm	Dorner-Reisel <i>et al.</i> (2004)
SiO ₂ , Feldspar, Kaolin clay	C	0.25–1 wt%	1 mm	7 μm	Yunus <i>et al.</i> (2017)
SiO ₂	C	20 wt%	1 mm	7 μm	Cao <i>et al.</i> (2010)
Glasses, Glass-ceramics, Al ₂ O ₃ , MgO	C	5–40 vol%		8 μm	Sambell <i>et al.</i> (1972)
BAS	C	20–40 vol%	3–5 mm	6–8 μm	Ye <i>et al.</i> (2008)
Pyrex-Glass	C	19.8–57.1 vol%		8 μm	Phillips (1972)
Pyrex-Glass	C	22.9–59.5 vol%		8 μm	Phillips <i>et al.</i> (1972)
BAS + Si ₃ N ₄	C	20 vol%	2–4 mm	7 μm	Ma <i>et al.</i> (2009)
	SiC	20 vol%	2–4 mm	12 μm	
β-SiAlON	SiC	5–15 vol%	1–2 mm	14 μm	Demir (2012)
Alkali-lime-silica glass	SiC	5–30 vol%	1 mm	15 μm	Langhans and Roeder (1992)

- (3) High performance fibers, for example the DuPont™ FP, ALMAX™ and Nextel™ fibers, although only the Nextel™ fibers are commercially available today (Böttcher *et al.*, 2019; De With and Corbijn, 1989; Knepper *et al.*, 1997, 1998; Tülümen *et al.*, 2017).

It is noteworthy, that, in contrast to the non-oxide reinforcements, the fiber diameters used for oxide fiber/oxide matrix composites vary to a larger degree, namely from 3 μm to 20 μm. With diameters less than 5 μm, some of the low cost thermal insulation fibers might even be harmful to the human respiratory tract/system. Their matching CTE as well as their low thermal conductivity were the reasons, why glass (Mishra *et al.*, 2008) and silica (Mishra *et al.*, 2009) short fibers were investigated for the reinforcement of ceramic silica foams as thermal protection systems for space applications. The challenge of dispersing these 20–25 mm short fibers at a relatively high content of 10 wt% was addressed in both of these publications.

A comparative study on the properties of continuous as well as short fiber reinforced composites, prepared by a freeze gelation route, reported the influence of porosity on the mechanical properties of short oxide fiber/oxide matrix composites (Russell-Floyd *et al.*, 1993).

Yunus *et al.* used a SLA 3DP process to produce silica/Feldspar/Kaolin + Ball clay matrix composites reinforced with either carbon, silica or alumina fibers (Yunus *et al.*, 2017). They investigated the mechanical properties on unreinforced and reinforced matrices, as well as the influence of fiber orientation. The alignment of the fibers as well as the increase of the fiber content led to an increase of the mechanical properties.

For the same reason as (Slosarczyk *et al.*, 2000; Dorner-Reisel *et al.*, 2004) used short carbon fibers for the reinforcement of hydroxyapatite, short alumina fibers of the type ALMAX™ (Knepper *et al.*, 1997, 1998) and DuPont™ FP (De With and Corbijn, 1989) were used, having the additional advantage of being bio-compatible.

The only reports of using a short fiber preform instead of short fibers and subsequent forming steps are by Naskar *et al.* (2004) and Naskar *et al.* (2009). They used a vacuum-infiltration process to infiltrate fiber preforms with different matrix-forming sols (zirconia-yttria, alumina-zirconia, alumina, alumina-silica) and investigated the influence of different numbers of infiltration cycles as well as of varying sintering temperatures. The highest flexural strength obtained in these studies was 31.1 MPa, by a zirconia-yttria-sol infiltrated alumina short fiber preform with four infiltration cycles and sintered at 1400°C (Naskar *et al.*, 2009). No account of the porosity of the samples and its influence on the mechanical behavior was given.

As for the non-oxide fiber/oxide matrix composites, most of the literature in Table 2 on glass, silica and thermal insulation fiber reinforced oxide matrix composites describes the decrease of mechanical performance with increasing porosity and therefore aspires to reach dense ceramics. Notable exceptions are given in the work of Sheldon and Lewis (1976), Mishra *et al.* (2008) and Mishra *et al.* (2009). But whereas the desired high porosity in the work of Mishra *et al.* (2008) and Mishra *et al.* (2009) was mostly due to the ceramic foam structure while the struts and cell walls, which contain the fibers, were desired to be dense, the work of Sheldon and Lewis (1976) investigated the fiber reinforcement of porous mullite ceramics for implant applications with the preservation of the porous structure in mind.

All of the literature mentioned above strives for a dense matrix, except Sheldon and Lewis (1976). However, the most common concept for all-oxide CMCs nowadays is the weak matrix concept (WMC), which describes a quasi-ductile fracture behavior

Table 3 Literature survey summary of oxide short fiber reinforced oxide matrices

Matrix	Fiber	Fiber content	Initial fiber length	Fiber diameter	Reference
Fused SiO ₂	E-Glass	1–10 wt%	20–25 mm	10 μm	Mishra <i>et al.</i> (2008)
Fused SiO ₂	E-Glass, SiO ₂ (quartz)	10 wt%	ca. 20 mm	10 μm	Mishra <i>et al.</i> (2009)
SiO ₂	Al ₂ O ₃ -SiO ₂	5–30 vol%			Russell-Floyd <i>et al.</i> (1993)
Mullite	Al ₂ O ₃ -SiO ₂	≤ 33 vol%			Sheldon and Lewis (1976)
Clay-Kaolin	Al ₂ O ₃ -SiO ₂	2–6 wt%		< 10 μm	Özkal and Uçar (2010)
NiFe ₂ O ₄	ZrO ₂	3 wt%	5–6 mm	8–10 μm	Hua <i>et al.</i> (2013)
MgO	ZrO ₂	10–20 vol%	> 10 mm	4 μm	Sambell <i>et al.</i> (1972)
SiO ₂ , Feldspar, Kaolin + Ball clay	Al ₂ O ₃ , SiO ₂	2.5–10 wt%	2.7–3.2 mm	2.5–3 μm	Yunus <i>et al.</i> (2017)
SiO ₂	Al ₂ O ₃	8.1–25.4 vol%	3.4 mm	3 μm	Liu <i>et al.</i> (1998)
Kaolin	Al ₂ O ₃	3 vol%	125 μm	3 μm	Boussois <i>et al.</i> (2014)
Mullite (Saffil)	Al ₂ O ₃	5–30 vol%	50–100 μm	5–10 μm	Wang <i>et al.</i> (1991)
ZrO ₂ -Y ₂ O ₃ , Al ₂ O ₃ -ZrO ₂ , Al ₂ O ₃ , Al ₂ O ₃ -SiO ₂	Al ₂ O ₃ (preform)	30 vol%	200–250 μm	3–7 μm	Naskar <i>et al.</i> (2009)
ZrO ₂ -Y ₂ O ₃ , Al ₂ O ₃ -ZrO ₂ , Al ₂ O ₃ , Al ₂ O ₃ -SiO ₂	Mullite (preform)	15 vol%		3–8 μm	Naskar <i>et al.</i> (2004)
Kaolin clay	Mullite	9.7 vol%	10–200 μm	5 μm	Papargyri <i>et al.</i> (2003)
	α-Al ₂ O ₃	4.7–14 vol%	10–200 μm	5 μm	
	γ-Al ₂ O ₃	4.5–14.7 vol%	50–200 μm	3.4 μm	
Hydroxyapatite	Al ₂ O ₃	10–30 vol%	1 mm	20 μm	De With and Corbijn (1989)
Hydroxyapatite	Al ₂ O ₃	10–20 vol%	0.3–0.5 mm	10 μm	Knepper <i>et al.</i> (1998)
Hydroxyapatite	Al ₂ O ₃	10–20 vol%	0.3–0.7 mm	10 μm	Knepper <i>et al.</i> (1997)
Al ₂ O ₃	Al ₂ O ₃ (Nextel™610)	10–30 vol%	22–368 μm 45–422 μm (post-CIM)	11–13 μm	Böttcher <i>et al.</i> (2019)
Al ₂ O ₃	Al ₂ O ₃ (Nextel™610)	0–50 vol%	3.2 mm	11–13 μm	Piotter <i>et al.</i> (2019)
Al ₂ O ₃	Al ₂ O ₃ (Nextel™610)	0–100 vol%	3.2 mm	11–13 μm	Tülümen <i>et al.</i> (2017)
Al ₂ O ₃	Al ₂ O ₃ (Nextel™610)	0–50 vol%	3.2 mm 50–500 μm in feedstock	11–13 μm	Tülümen <i>et al.</i> (2019)
Al ₂ O ₃ -ZrO ₂	Al ₂ O ₃ (Nextel™610)	20–40 vol%	14 mm (in the CMC)	11–13 μm	Winkelbauer <i>et al.</i> (2021)

derived from a porous matrix in combination with reinforcing fibers (Levi *et al.*, 1999; Zok, 2006). The only commercially available high performance oxide fibers today are the Nextel™ fibers 610 (α-alumina) and 720 (α-alumina-mullite). In the following, the different fabrication techniques for short fiber reinforced oxide matrix composites, based on Nextel™ fibers and designed according to the weak matrix concept, are described exemplarily.

Ceramic Injection Molding

Ceramic injection molding (CIM) is a common process for the production of complex ceramic components. By the introduction of Nextel™610 α-alumina fibers in the feedstock, it is possible to manufacture short fiber reinforced oxide matrix composites (Tülümen *et al.*, 2017; Piotter *et al.*, 2019; Tülümen *et al.*, 2019; Böttcher *et al.*, 2019). During the CIM process, the fibers are broken and oriented, so that the composite contains single short fibers of highly varying length with a preferred orientation in an oxide matrix. Both works do not depict the fracture behavior of the resulting composites in detail, but Böttcher *et al.* (2019) mention that the desired damage-tolerant fracture behavior was not obtained. This is most likely attributed to the separation of the fiber bundles into single fibers, as well as to the short length of the fibers.

For highly porous and therefore weak matrices, a critical fiber length in the range of millimeters as well as a minimum fiber volume content is necessary in order to assure a contribution of the fibers towards the matrix strength and to obtain a damage-tolerant fracture behavior. By the usage of fiber bundles with a length of several mm, instead of single fibers, both issues can be solved.

Impregnation of Short Fiber Preforms

A process for the fabrication of an oxide short fiber bundle preform, which comprises the arrangement of dry fiber bundles, followed by an infiltration with a binder and its stabilization by curing in a compacted state, was developed by Wamser *et al.* (2013). After a subsequent infiltration step of the fiber bundle preform with a ceramic slurry and an additional sintering step above 1200°C, an oxide short fiber reinforced oxide ceramic matrix composite was obtained. A thus prepared

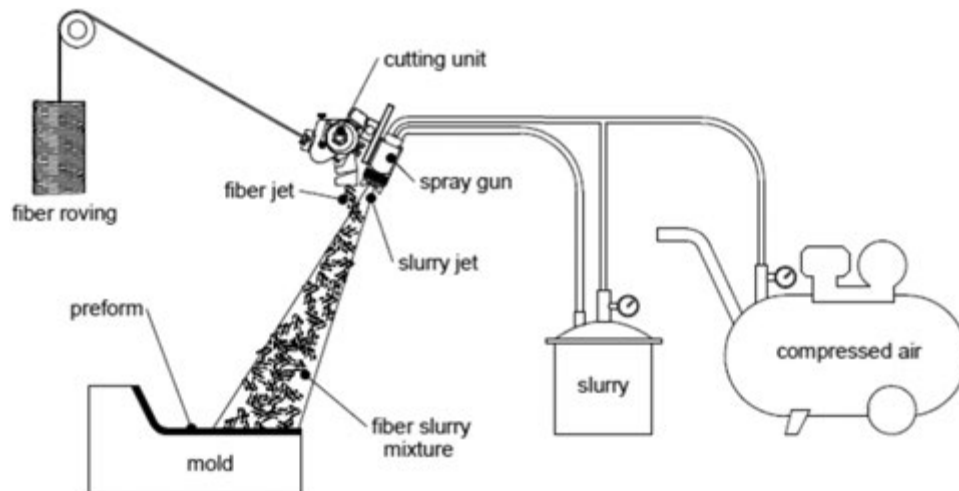


Fig. 11 Schematic depiction of the fiber spraying process.

alumina composite reinforced with 6 mm Nextel™610 short fiber bundles exhibited a flexural strength of up to 90 MPa with a damage-tolerant fracture behavior.

Fiber Spraying Process

Based on common fiber spraying processes for glass fiber reinforced plastic (GFRP) and carbon fiber reinforced plastic (CFRP), a short fiber spraying process for the manufacturing of oxide short fiber bundle/oxide matrix composites has been developed (Knohl *et al.*, 2017b). A schematic depiction of the fiber spraying process is shown in Fig. 11. In contrast to GFRP and CFRP, the preservation of the fiber bundles during the spraying process is of paramount importance. In order to achieve this, the fiber bundles are infiltrated in flight with a low viscosity slurry and are subsequently deposited on the mold surface.

Due to the usage of an alcoholic compound with hygroscopic properties, e.g., glycerol, the water content of the slurry can be adjusted in a similar way to that used by Krenkel *et al.* (2014), Wamser *et al.* (2016), Knohl *et al.* (2017a) and Puchas *et al.* (2020), which yields a pre-impregnated fiber preform (prepreg) with a defined tack ready for lamination. As fiber reinforcements, 14 mm long Nextel™610 10,000 denier (den) fiber bundles with 2550 single filaments were used, while the matrix consisted of alumina and zirconia. By using the fiber spraying process, Nextel™610/Al₂O₃-ZrO₂ composites with a fiber volume content of about 21%, an apparent porosity of 40 vol% and a flexural strength of up to 120 MPa were fabricated. The mechanical properties in xy-plane are not entirely isotropic, because there is a slightly preferred fiber bundle orientation. A typical stress-strain-curve of a three point bending test for these short fiber bundle reinforced composites is shown in Fig. 12(a) and a representative microstructure of the cross-section is presented in Fig. 12(b).

In comparison, a 2D fabric-reinforced Nextel™610/Al₂O₃-ZrO₂ composite with a fiber volume content of 28% had an average flexural strength in 0° of 237 MPa, whereas in 45° to the fiber orientation it exhibited only an average flexural strength of 70 MPa (Puchas and Krenkel, 2018). Therefore, it can be concluded, that the nearly isotropic flexural strength of short fiber bundle reinforced composites is higher than the off-axis flexural strength of 2D fabric reinforced composites, based on identical matrices and fiber type. A feasibility study proved the aptitude of the fiber spraying process for primary forming as well as for shaping, i.e. one can either fabricate flat prepregs to form a more complex component by lamination, or one can fabricate more complex components in a single step by directly spraying on to a complex mold or in a cavity.

Current research focuses on the automation of the fiber spraying process (Fig. 13) and to gain a deeper understanding of the mechanical behavior of short fiber bundle reinforced composites (Schmidt *et al.*, 2020). For this purpose, the mechanical properties of an unidirectional continuous fiber reinforced composite were compared with 14 mm short fiber reinforced composites, which were fabricated by manual lay-up, as well as with one sprayed composite with 14 mm fiber bundles. The short fiber reinforcements were UD, quasi-isotropic (0°/90°/ + 45°/ - 45°)_s, ±45°, randomly oriented and sprayed. The properties of the obtained composites are shown in Table 4.

The average flexural strength of the continuous fiber reinforced UD sample was more than three times higher than that of the 14 mm short fiber bundle reinforced UD sample, with 580 MPa to 163 MPa, respectively. Not surprisingly, the lowest strength was obtained by the “± 45°” composite with an average of 47 MPa, since none of the fiber bundles are oriented parallel to the loading direction.

The fiber orientations of the composites “randomly oriented”, “quasi-isotropic” and “sprayed” were more or less isotropic. The “sprayed” composite showed the highest average flexural strength with 90 MPa, albeit having only about half the fiber volume content of the sample “quasi-isotropic” with an average of 78 MPa. The lower strength of the sample “randomly oriented”, namely 62 MPa, can be attributed to the random lay-up of the short fiber bundles, which amounted in the formation of macropores in the

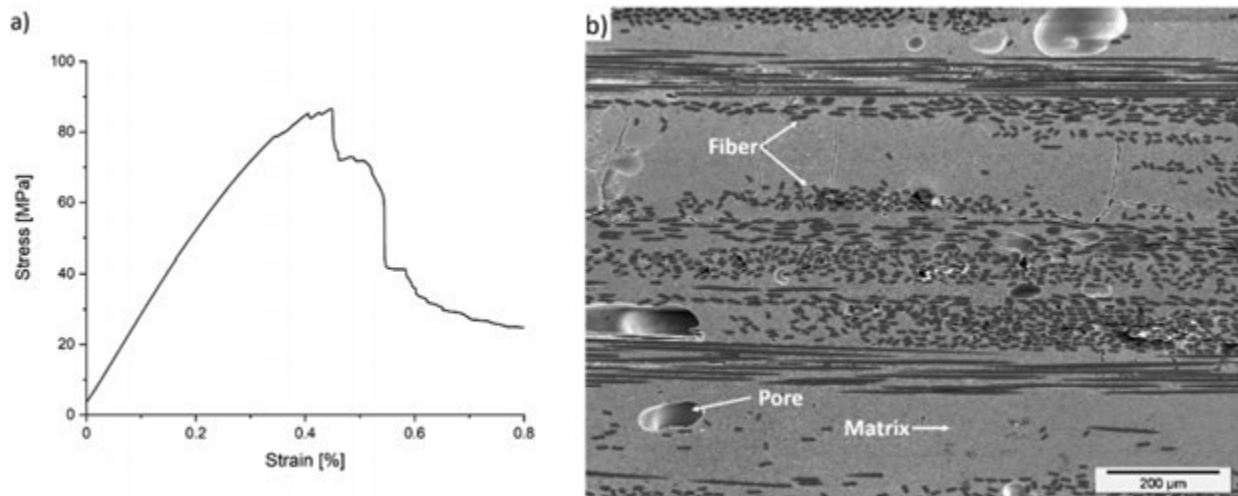


Fig. 12 Typical stress-strain-curve for short fiber bundle-reinforced composites (a) and typical microstructure of all-oxide composites (b).

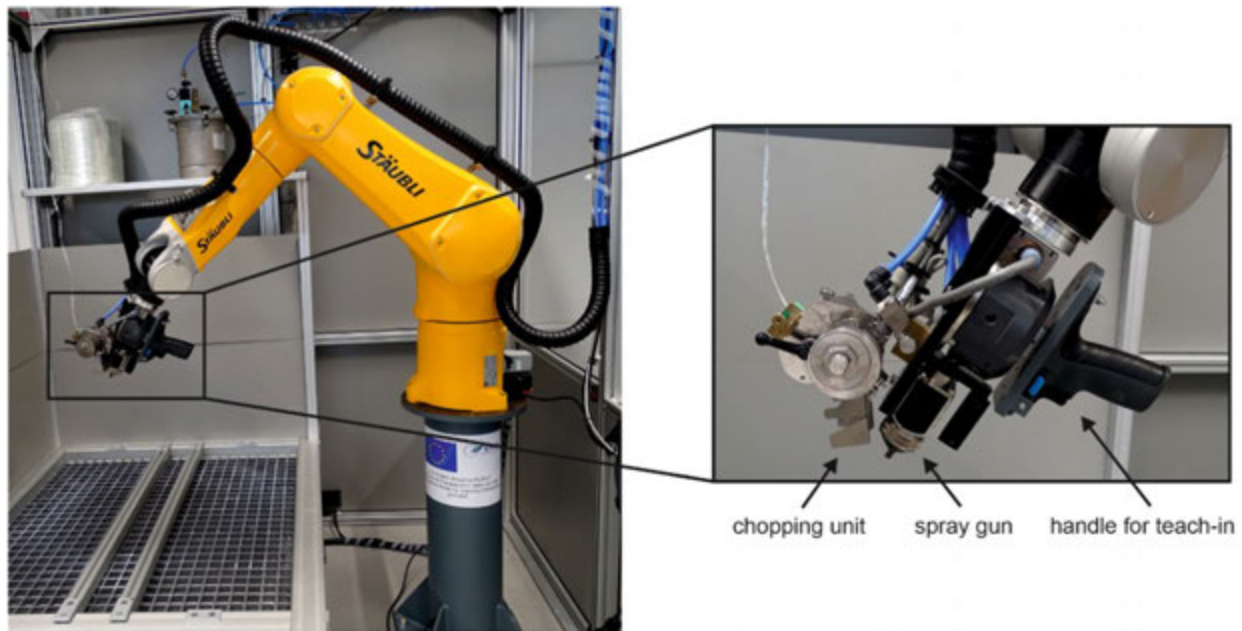


Fig. 13 Device for an automated fiber spraying process.

Table 4 Properties of one continuous fiber and several 14 mm short fiber reinforced oxide composites

	<i>Flexural strength [MPa]</i>	<i>Strain [%]</i>	<i>Young's modulus [GPa]</i>	<i>Fiber volume content [%]</i>	<i>Porosity [%]</i>
Continuous fiber (0°)	580 ± 63	0.48 ± 0.05	125 ± 5	39.7	30
14 mm (0°)	163 ± 17	0.18 ± 0.02	105 ± 6	40.3	32
14 mm sprayed	90 ± 19	0.46 ± 0.13	25 ± 2	21.3	40
14 mm (quasiisotropic)	78 ± 12	0.15 ± 0.02	63 ± 8	39.5	32
14 mm randomly oriented	62 ± 12	0.20 ± 0.03	38 ± 6	36.5	37
14 mm (± 45°)	47 ± 5	0.23 ± 0.04	28 ± 2	40.7	30

composite. These are detrimental to the mechanical properties and their formation is verifiable by comparing the fiber volume content and the porosity of the samples “quasi-isotropic” and “randomly oriented”. While the fiber volume content of the sample “randomly oriented” is only 3% lower, the porosity is 5% higher. This is only achievable if macropores are formed. Representative stress-strain-curves of all manually prepared samples are presented in [Fig. 14](#).

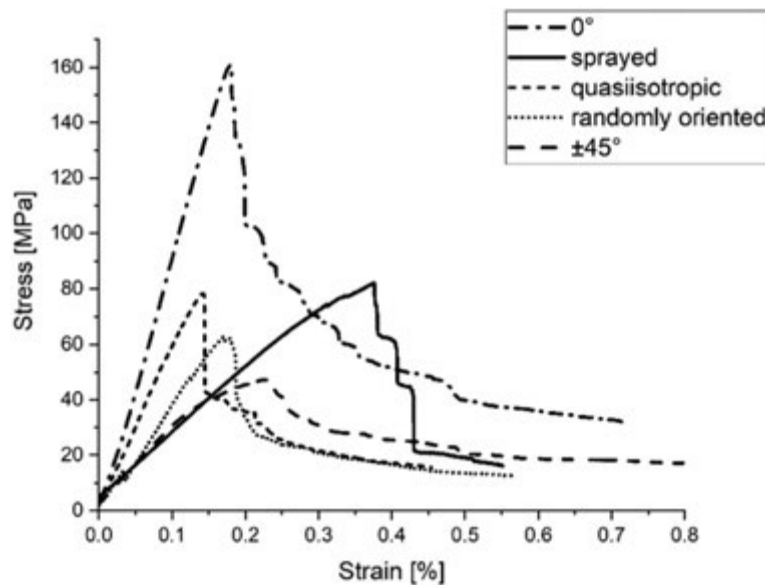


Fig. 14 Representative stress-strain-curves (from three point bending tests) of 14 mm short fiber bundle reinforced oxide composites.

In addition to the advantage of being able to produce complex CMC structures by fiber spraying in a single step, the use of short fiber bundles drastically reduces the material costs. At a constant fiber volume content, the costs can be reduced by 26%, comparing 3000 denier fabrics with 3000 denier short fiber bundles and up to 60%, comparing 3000 denier fabrics with 10,000 denier short fiber bundles (Lincoln *et al.*, 2017).

Summary

Short and chopped fibers have been successfully incorporated as discontinuous reinforcing phases in oxide as well as non-oxide matrices. Mostly, the addition of short fibers is used for the ease of manufacturing near-net shaped components without any scrap compared to continuous fibers. Up to now, economical and technological requirements dominate the choice of fiber length and fiber type. In order to act as a reinforcing phase, a minimum fiber length of several millimeters is necessary as well as fiber coatings or well preserved fiber bundles. Although less pronounced in comparison with continuous fibers, toughening mechanisms such as fiber/matrix interface debonding, crack deflection, fiber bridging or even fiber pull-out occur in many fiber-matrix combinations. The strain-to-failure, fracture toughness and Weibull moduli are improved in general, compared to the monolithic matrix. Carbon fiber reinforced SiC composites are currently the most developed SF-CMCs, but also carbon fiber reinforced UHTCs and all-oxide CMCs show an advanced development status. Emerging areas still remain in the theoretical description of the toughening mechanisms, the target-oriented fiber alignment, the automation of the manufacture processes and the applicability of additive manufacturing methods.

References

- Ahmad, H., Stiller, J., Päßler, E., *et al.*, 2020. Properties of C/C-SiC composites produced via transfer moulding and inner siliconization. *International Journal of Applied Ceramic Technology* 17, 2137–2146.
- Airolidi, A., Di Landro, L., Sirna, M., Iavarone, P., Sala, G., 2013. Development of a numerical mesoscale material model for short fibre-reinforced ceramics matrix composites. *Journal of Materials Science* 48, 1646–1659.
- Becher, P.F., 1991. Microstructural design of toughened ceramics. *Journal of the American Ceramic Society* 74, 255–269.
- Böttcher, M., Nestler, D., Stiller, J., Kroll, L., 2019. Injection moulding of oxide ceramic matrix composites: Comparing two feedstocks. *Key Engineering Materials* 809, 140–147.
- Boussois, K., Tessier-Doyen, N., Blanchart, P., 2014. High-toughness silicate ceramic. *Journal of the European Ceramic Society* 34, 119–126.
- Budiansky, B., Cui, Y.L., 1995. Toughening of ceramics by short aligned fibers. *Mechanics of Materials* 21, 139–146.
- Budiansky, B., Hutchinson, J.W., Evans, A.G., 1986. Matrix fracture in fiber-reinforced ceramics. *Journal of the Mechanics and Physics of Solids* 34, 167–189.
- Budiansky, B., Evans, A.G., Hutchinson, J.W., 1995. Fiber-matrix debonding effects on cracking in aligned fiber ceramic composites. *International Journal of Solids and Structures* 32, 315–328.
- Cao, M.-S., Song, W.-L., Hou, Z.-L., Wen, B., Yuan, J., 2010. The effects of temperature and frequency on the dielectric properties, electromagnetic interference shielding and microwave-absorption of short carbon fiber/silica composites. *Carbon* 48, 788–796.
- Charalambides, P.G., Evans, A.G., 1989. Debonding properties of residually stressed brittle-matrix composites. *Journal of the American Ceramic Society* 72, 746–753.
- Charalambides, P.G., 1990. Fiber debonding in residually stressed brittle-matrix composites. *Journal of the American Ceramic Society* 73, 1674–1680.
- Chen, C.Y., Tucker III, C.L., 1984. Mechanical property predictions for short fiber/brittle matrix composites. *Journal of Reinforced Plastics and Composites* 3, 120–129.

- Chen, P.E., 1971. Strength properties of discontinuous fiber composites. *Polymer Engineering and Science* 11, 51–56.
- Cox, H.L., 1952. The elasticity and strength of paper and other fibrous materials. *British Journal of Applied Physics* 3, 72–79.
- Daniels, I.M., Anastassopoulos, G., Lee, J.-W., 1993. The behavior of ceramic matrix fiber composites under longitudinal loading. *Composites Science and Technology* 46, 105–113.
- De With, G., Corbijn, A.J., 1989. Metal fibre reinforced hydroxy-apatite ceramic. *Journal of Materials Science* 24, 3411–3415.
- Demir, A., 2012. Effect of Nicalon SiC fibre heat treatment on short fibre reinforced β -sialon ceramics. *Journal of the European Ceramic Society* 32, 1405–1411.
- Dörner-Reisel, A., Bertho, K., Neubauer, R., *et al.*, 2004. Unreinforced and carbon fiber reinforced hydroxyapatite: Resistance against microabrasion. *Journal of the European Ceramic Society* 24, 2131–2139.
- Evans, A.G., Zok, F.W., 1994. The physics and mechanics of fibre-reinforced brittle matrix composites. *Journal of Materials Science* 29, 3857–3896.
- Evans, A.G., He, M.Y., Hutchinson, J.W., 1989. Interface debonding and fiber cracking in brittle matrix composites. *Journal of the American Ceramic Society* 72, 2300–2303.
- Fu, S.-Y., Lauke, B., 1996. Effects of fiber length and fiber orientation distributions on the tensile strength of short-fiber-reinforced polymers. *Composites Science and Technology* 56, 1179–1190.
- Fukuda, H., Chou, T.-W., 1981. An advanced shear-lag model applicable to discontinuous fiber composites. *Journal of Composite Materials* 15, 79–91.
- Guo, S., Nishimura, T., Kagawa, Y., 2012. Mechanical properties of short carbon fiber-reinforced SiC-matrix composites and correlation to fibers. *Key Engineering Materials* 512–515, 798–803.
- Guo, S., Naito, K., Kagawa, Y., 2013. Mechanical and physical behaviors of short pitch-based carbon fiber-reinforced HfB₂-SiC matrix composites. *Ceramics International* 39, 1567–1574.
- Hahn, H.T., 1975. On approximations for strength of random fiber composites. *Journal of Composite Materials* 9, 316–326.
- Halpin, J.C., 1969. Stiffness and expansion estimates for oriented short fiber composites. *Journal of Composite Materials* 3, 732–734.
- Halpin, J.C., Pagano, N.J., 1969. The laminate approximation for randomly oriented fibrous composites. *Journal of Composite Materials* 3, 720–724.
- Halpin, J.C., Kardos, J.L., 1978. Strength of discontinuous reinforced composites: I. Fiber reinforced composites. *Polymer Engineering and Science* 18, 496–504.
- Hausherr, J.-M., Eitel, M., Krenkel, W., 2015. Determination of material properties for short fibre reinforced C/C-SiC. *MATEC Web of Conferences* 29, 00005.
- He, M.Y., Hutchinson, J.W., 1989. Crack deflection at an interface between dissimilar elastic materials. *International Journal of Solids and Structures* 25, 1053–1067.
- Heim, D., Hartmann, M., Neumayer, J., *et al.*, 2013. Novel method for determination of critical fiber length in short fiber carbon/carbon composites by double lap joint. *Composites Part B Engineering* 54, 365–370.
- Herzog, A., Woetting, G., Vogt, U.F., 2007. Short-fibre-reinforced reaction-bonded silicon nitride (RBSN) by precursor route: Processing and properties. *Journal of the European Ceramic Society* 27, 3561–3572.
- Hsueh, C.-H., Becher, P.F., 1996. Residual thermal stresses in ceramic composites, Part II: With short fibers. *Materials Science and Engineering A* 212, 29–35.
- Hua, Z., Yao, G., Ma, J., Zhang, M., 2013. Fabrication and mechanical properties of short ZrO₂ fiber reinforced NiFe₂O₄ matrix composites. *Ceramics International* 39, 3699–3708.
- Huang, S., Zhou, W., Wei, P., *et al.*, 2013. Short-carbon-fiber reinforced alumina ceramic with improved mechanical property and dielectric property in the Ku-band. *Physica Status Solidi A* 210, 1944–1949.
- Huang, S., Zhou, W., Luo, F., Wei, P., Zhu, D., 2014. Mechanical and dielectric properties of short carbon fiber reinforced Al₂O₃ composites with MgO additive. *Ceramics International* 40, 2785–2791.
- Huang, Z., Zhou, W., Ma, R., *et al.*, 2012. Dielectric and mechanical properties of hot-pressed sintered C_s/Al₂O₃ ceramic composites. *International Journal of Applied Ceramic Technology* 9, 413–420.
- Hutchinson, J.W., Jensen, H.M., 1990. Models of fiber debonding and pullout in brittle composites with friction. *Mechanics of Materials* 9, 139–163.
- Inoue, R., Yang, J.M., Kakisawa, H., Kagawa, Y., 2013. Mode I fracture toughness of short carbon fiber-dispersed SiC matrix composite fabricated by melt infiltration process. *Ceramics International* 39, 8341–8346.
- Jia, J., Liu, D., Gao, C., Ji, G., Guo, T., 2018. Preparation and mechanical properties of short carbon fibers reinforced α -Al₂O₃-based composites. *Ceramics International* 44, 19345–19351.
- Kelly, A., Tyson, W.R., 1965. Tensile properties of fibre-reinforced metals: Copper/tungsten and copper/molybdenum. *Journal of the Mechanics and Physics of Solids* 13, 329–350.
- Knepper, M., Moricca, S., Milthorpe, B.K., 1997. Stability of hydroxyapatite while processing short-fibre reinforced hydroxyapatite ceramics. *Biomaterials* 18, 1523–1529.
- Knepper, M., Milthorpe, B.K., Moricca, S., 1998. Interdiffusion in short-fibre reinforced hydroxyapatite ceramics. *Journal of Materials Science: Materials in Medicine* 9, 589–596.
- Knohl, S., Krenkel, W., Puchas, G., Wamser, T., 2017a. Ceramic composite materials and method for producing same. Patent No. US20190210930A1.
- Knohl, S., Wamser, T., Martin, B., Krenkel, W., 2017b. Verfahren zur Herstellung eines Zwischenprodukts für die Fertigung eines faserverstärkten Bauteils sowie Vorrichtung zu dessen Durchführung. Patent No. DE102017008180A1.
- Koch, D., Tushkev, K., Grathwohl, G., 2008. Ceramic fiber composites: Experimental analysis and modeling of mechanical properties. *Composites Science and Technology* 68, 1165–1172.
- Krenkel, W., 2004. Carbon fiber reinforced CMC for high-performance structures. *International Journal of Applied Ceramic Technology* 1, 188–200.
- Krenkel, W., 2005. Carbon fibre reinforced silicon carbide composites (C/SiC, C/C-SiC). In: Bansal, N.P. (Ed.), *Handbook of Ceramic Composites*. Boston: Kluwer Academic Publishers, pp. 117–148.
- Krenkel, W., 2008. *Ceramic Matrix Composites*. Weinheim: WILEY-VCH.
- Krenkel, W., Berndt, F., 2005. C/C-SiC composites for space applications and advanced friction systems. *Materials Science and Engineering A* 412, 177–181.
- Krenkel, W., Thébaud, J.G., 2014. Ceramic matrix composites for friction applications. In: Bansal, N.P., Lamon, J. (Eds.), *Ceramic Matrix Composites: Materials, Modeling and Technology*. Hoboken: Wiley, pp. 647–671.
- Krenkel, W., Heidenreich, B., Renz, R., 2002. C/C-SiC composites for advanced friction systems. *Advanced Engineering Materials* 4, 427–436.
- Krenkel, W., Wamser, T., Scheler, S., 2014. Ceramic matrix composites and processes for their production. Patent No. WO2016016388A1.
- Krödel, M., Kutter, G.S., Deyerler, M., Pailer, N., 2002. Short carbon-fiber reinforced ceramic - Cesci® - for optomechanical applications. *Proceedings of the Society of Photo-optical Instrumentation Engineers ((SPIE))* 4771, 230–242.
- Langhans, K., Roeder, E., 1992. Manufacture of short-fibre reinforced glasses by extrusion and examinations regarding their structure and their mechanical properties. *Glastechnische Berichte* 65, 103–111.
- Launey, M.E., Ritchie, R.O., 2009. On the fracture toughness of advanced materials. *Advanced Materials* 21, 2103–2110.
- Lawrence, P., 1972. Some theoretical considerations of fibre pull-out from an elastic matrix. *Journal of Materials Science* 7, 1–6.
- Lee, J.-W., Daniels, I.M., 1992. Deformation and failure of longitudinally loaded brittle-matrix composites. In: Grimes, G.C. (Ed.), *Composite Materials Testing and Design*, vol. 10. Philadelphia: ASTM, pp. 204–221.
- Levi, C.G., Zok, F.W., Yang, J.-Y., Mattoni, M., Löfvander, J.P.A., 1999. Microstructural design of stable porous matrices for all-oxide ceramic composites. *Zeitschrift für Metallkunde* 90, 1037–1047.
- Liensdorf, T., Langhof, N., Krenkel, W., 2019. Mechanical properties of PEEK-derived C/SiC composites with different fiber lengths. *Advanced Engineering Materials* 21 (5), 1800835.

- Lincoln, J., Jackson, B., Barnes, A., Beaver, A.R., Visser, L., 2017. Oxide-oxide ceramic matrix composites – Enabling widespread industry adoption. In: Singh, M., Ohji, T., Dong, S., *et al.* (Eds.), *Advances in High Temperature Ceramic Matrix Composites and Materials for Sustainable Development*, Ceramic Transactions, Volume CCLXXIII, first ed., 263. Hoboken: Wiley, pp. 401–412.
- Liu, H.-K., Kuo, W.-S., Lin, B.-H., 1998. Pressure infiltration of sol/gel processed short fibre ceramic matrix composites. *Journal of Materials Science* 33, 2095–2101.
- Ma, J., Ye, F., Liu, L., Zhang, H., 2009. Processing and mechanical properties of short fibers/Si₃N₄ reinforced BaO · Al₂O₃ · 2SiO₂ ceramic matrix composites. *Materials Science and Engineering: A* 520, 158–161.
- Mishra, S., Mitra, R., Vijayakumar, M., 2008. A novel route for the dispersion of fibers for the preparation of fiber reinforced porous ceramics. *Materials Letters* 62, 2025–2028.
- Mishra, S., Mitra, R., Vijayakumar, M., 2009. Structure and properties of short fibre reinforced silica matrix composite foams. *Ceramics International* 35, 3111–3116.
- Müller-Köhn, A., Ahlhelm, M., Neubrand, A., *et al.*, 2020. Fabrication of short-fibre reinforced SiCN by injection moulding of pre-ceramic polymers. *Ceramic forum international/Berichte* 97 (7–8), 46–52.
- Nairn, J.A., 1997. On the use of shear-lag methods for analysis of stress transfer in unidirectional composites. *Mechanics of Materials* 26, 63–80.
- Naskar, M.K., Basu, K., Chatterjee, M., 2009. Sol-gel approach to near-net-shape oxide-oxide composites reinforced with short alumina fibres – The effect of crystallization. *Ceramics International* 35, 3073–3079.
- Naskar, M.K., Chatterjee, M., Dey, A., Basu, K., 2004. Effects of processing parameters on the fabrication of near-net-shape fibre reinforced oxide ceramic matrix composites via sol-gel route. *Ceramics International* 30, 257–265.
- Özkal, B., Uçar, T., 2010. Effect of fiber-matrix integration on the fracture behavior of aluminosilicate fiber reinforced clay-kaolin matrix composites. *Key Engineering Materials* 417–418, 549–552.
- Pachalis, J.R., Kim, J., Chou, T.-W., 1990. Modeling of creep of aligned short-fiber reinforced ceramic composites. *Composites Science and Technology* 37, 329–346.
- Papargyri, S.A., Cooke, R.G., Papargyris, D.A., *et al.*, 2003. Mechanical properties of short oxide fibre- kaolin clay matrix composites. *British Ceramic Transactions* 102, 193–203.
- Park, K., Vasilos, T., 1997. Characteristics of carbon fibre-reinforced calcium phosphate composites by hot pressing. *Journal of Materials Science Letters* 16, 985–987.
- Phillips, D.C., 1972. The fracture energy of carbon-fibre reinforced glass. *Journal of Materials Science* 7, 1175–1191.
- Phillips, D.C., Sambell, R.A.J., Bowen, D.H., 1972. The mechanical properties of carbon fibre reinforced pyrex glass. *Journal of Materials Science* 7, 1454–1464.
- Piotter, V., Tueluemen, M., Hanemann, T., Hoffmann, M., Ehreiser, B., 2019. Powder injection molding of oxide ceramic CMC. *Key Engineering Materials* 809, 148–152.
- Puchas, G., Krenkel, W., 2018. Neuartige Herstellungsverfahren für oxidkeramische Faserverbundwerkstoffe. *dIALOG: Materialwissenschaft und Werkstofftechnik* 2018 (1), 34–41.
- Puchas, G., Möckel, S., Krenkel, W., 2020. Novel prepreg manufacturing process for oxide fiber composites. *Journal of the European Ceramic Society* 40, 5930–5941.
- Russell-Floyd, R.S., Harris, B., Cooke, R.G., *et al.*, 1993. Application of sol-gel processing techniques for the manufacture of fiber-reinforced ceramics. *Journal of the American Ceramic Society* 76, 2635–2643.
- Sambell, R.A.J., Bowen, D.H., Phillips, D.C., 1972. Carbon fibre composites with ceramic and glass matrices Part 1: Discontinuous fibers. *Journal of Materials Science* 7, 663–675.
- Schmidt, E., Winkelbauer, J., Puchas, G., Henrich, D., Krenkel, W., 2020. Robot-based fiber spray process for small batch production. In: Schüppstuhl, T., Tracht, K., Henrich, D. (Eds.), *Annals of Scientific Society for Assembly, Handling and Industrial Robotics*. Berlin Heidelberg: Springer, pp. 295–305.
- Sciti, D., Guicciardi, S., Silvestroni, L., 2011. SiC chopped fibers reinforced ZrB₂: Effect of the sintering aid. *Scripta Materialia* 64, 769–772.
- Sha, J.J., Li, J., Wang, S.H., *et al.*, 2016. Improved microstructure and fracture properties of short carbon fiber-toughened ZrB₂-based UHTC composites via colloidal process. *International Journal of Refractory Metals and Hard Materials* 60, 68–74.
- Sha, J.J., Li, J., Lv, Z.Z., *et al.*, 2017. ZrB₂-based composites toughened by as-received and heat-treated short carbon fibers. *Journal of the European Ceramic Society* 37, 549–558.
- Sha, J.J., Li, J., Wang, S.H., Zhang, Z.F., Dai, J.X., 2015. Toughening effect of short carbon fibers in the ZrB₂-ZrSi₂ ceramic composites. *Materials and Design* 75, 160–165.
- Sheldon, D.A., Lewis, D., 1976. Fabrication and proper ties of a ceramic fiber-ceramic matrix composite. *Journal of the American Ceramic Society* 59, 372–374.
- Shi, Y., Koch, D., Hausherr, J.M., Neubrand, A., 2015. Influence of specimen geometry and surface quality on the bending strength of short fiber-reinforced C/SiC. *Materials Science Forum* 825–826, 249–255.
- Shi, Y., Hausherr, J.-M., Hoffmann, H., Koch, D., 2017. Inspection of geometry influence and fiber orientation to characteristic value for short fiber reinforced ceramic matrix composite under bending load. *Journal of the European Ceramic Society* 37, 1291–1303.
- Slosarczyk, A., Klisch, M., Blazewicz, M., *et al.*, 2000. Hot pressed hydroxyapatite-carbon fibre composites. *Journal of the European Ceramic Society* 20, 1397–1402.
- Song, G.-M., Wu, Y., Li, Q., 2002. Elevated temperature strength and thermal shock behavior of hot-pressed carbon fiber reinforced TiC composites. *Journal of the European Ceramic Society* 22, 559–566.
- Song, G.-M., Zhou, Y., Kang, S.J.L., 2003. Experimental description of thermomechanical properties of carbon fiber-reinforced TiC matrix composites. *Materials and Design* 24, 639–646.
- Suemasu, H., Kondo, A., Itatani, K., Nozue, A., 2001. A probabilistic approach to the toughening mechanism in short-fiber-reinforced ceramic-matrix composites. *Composites Science and Technology* 61, 281–288.
- Tu, W.-C., Lange, F.F., Evans, A.G., 1996. Concept for a damage-tolerant ceramic composite with “Strong” interfaces. *Journal of the American Ceramic Society* 79, 417–424.
- Tülümen, H.M., Hanemann, T., Piotter, V., Stenzel, D., 2019. Investigation of feedstock preparation for injection molding of oxide-oxide ceramic composites. *Journal of Manufacturing and Materials Processing* 3 (1), 9.
- Tülümen, M., Hanemann, T., Hoffmann, M.J., Oberacker, R., Piotter, V., 2017. Process development for the ceramic injection molding of oxide chopped fiber reinforced aluminum oxide. *Key Engineering Materials* 742, 231–237.
- Wamser, T., Puchas, G., Krenkel, W., 2016. Keramische Verbundwerkstoffe und Verfahren zu ihrer Herstellung. Patent No. DE102016007652A1.
- Wamser, T., Scheler, S., Krenkel W., 2013. Method for the production of an oxide ceramic composite material and fiber preform. Patent No. EP2848599B1.
- Wang, J., Piramoon, M.R., Ponton, C.B., Marquis, P.M., 1991. A study in short alumina fibre-reinforced mullite composites. *British Ceramics Transactions* 90, 105–111.
- Weaver, J.H., Rannou, J., Mattoni, M.A., Zok, F.W., 2006. Interface properties in a porous-matrix oxide composite. *Journal of the American Ceramic Society* 89, 2869–2873.
- Wilson, D.M., Visser, L.R., 2001. High performance oxide fibers for metal and ceramic composites. *Composites: Part A* 32, 1143–1153.
- Winkelbauer, J., Puchas, G., Krenkel, W., 2021. Short fiber reinforced oxide fiber composites. Manuscript in progress.
- Yang, F., Zhang, X., Han, J., Diu, S., 2010. Analysis of the mechanical properties in short carbon fiber-toughened ZrB₂-SiC ultra-high temperature ceramic. *Journal of Composite Materials* 44, 953–961.
- Ye, F., Liu, L., Huang, L., 2008. Fabrication and mechanical properties of carbon short fiber reinforced barium aluminosilicate glass-ceramic matrix composites. *Composites Science and Technology* 68, 1710–1717.
- Yunus, D.E., He, R., Shi, W., Kaya, O., Liu, Y., 2017. Short fiber reinforced 3d printed ceramic composite with shear induced alignment. *Ceramics International* 43, 11766–11772.
- Zok, F.W., 2006. Developments in oxide fiber composites. *Journal of the American Ceramic Society* 89, 3309–3324.
- Zuber, C., Heidenreich, B., 2006. Development of a net shape manufacturing method for ventilated brake discs in single piece design. *Materialwissenschaft und Werkstofftechnik* 37, 301–308.

Glass and Glass-Ceramic Matrix Composites for Advanced Applications: Part I: Properties and Manufacturing Technologies

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Introduction

Ceramic matrix composites (CMCs) continue to attract attention for several engineering applications based on the highly attractive combination of properties they offer, such as high stiffness, fracture toughness and corrosion resistance together with a new range of functionalities for specific applications (Chawla, 2019) (Fig. 1). It is well-known that composites are a combination of two materials with different but complementary physical and chemical properties. Composites are designed to obtain better properties than ordinary (one-phase) materials due to effective interaction between the constituents.

Within the wide spectrum of CMCs, glass and glass-ceramic matrix composites (GMCs and GCMCs, respectively) represent a very important class of materials, since they offer attractive properties for a range of specific applications in which other materials cannot be used or are difficult to be applied. Regarding GMCs, due to the intrinsically low fracture toughness of the glass matrices ($< 1 \text{ MPa m}^{0.5}$), the reinforcement must be able to provide a significant improvement in the resistance to crack propagation, effectively acting as toughening elements (Boccaccini, 2006). On the other hand, glasses also have several unique characteristics that favor their application as matrices in some specific fields, e.g., its low viscosity at temperatures of 800–1400°C makes it possible to manufacture the material at substantially lower densification temperatures and with more intricate shapes than is possible with polycrystalline ceramics. Moreover lower processing temperatures lead to reduction of the possible degradation of the filler (reinforcement) in the course of composite fabrication (Chainikova *et al.*, 2014).

GCMCs use glass-ceramic materials as matrices taking advantage of their higher mechanical properties compared to glasses. Glass-ceramics are a special group of materials whereby a glass matrix is crystallized to different crystalline phases under carefully controlled heat-treatment conditions (Allix and Cormier, 2019; Kothiyal *et al.*, 2012).

The chapter aims at giving an up-to-date overview of glass and glass-ceramic matrix composites employed for advanced applications. It has evolved from previous overviews on the same topic (Boccaccini, 2006; Roether and Boccaccini, 2006), however with considerably updated information. General aspects of composite properties, e.g., mechanical behavior, thermal shock resistance and chemical stability to aggressive agents are presented. Part I of the chapter includes three sections. The first section provides a classification of the matrices and reinforcements used for GMCs and GCMCs highlighting the main

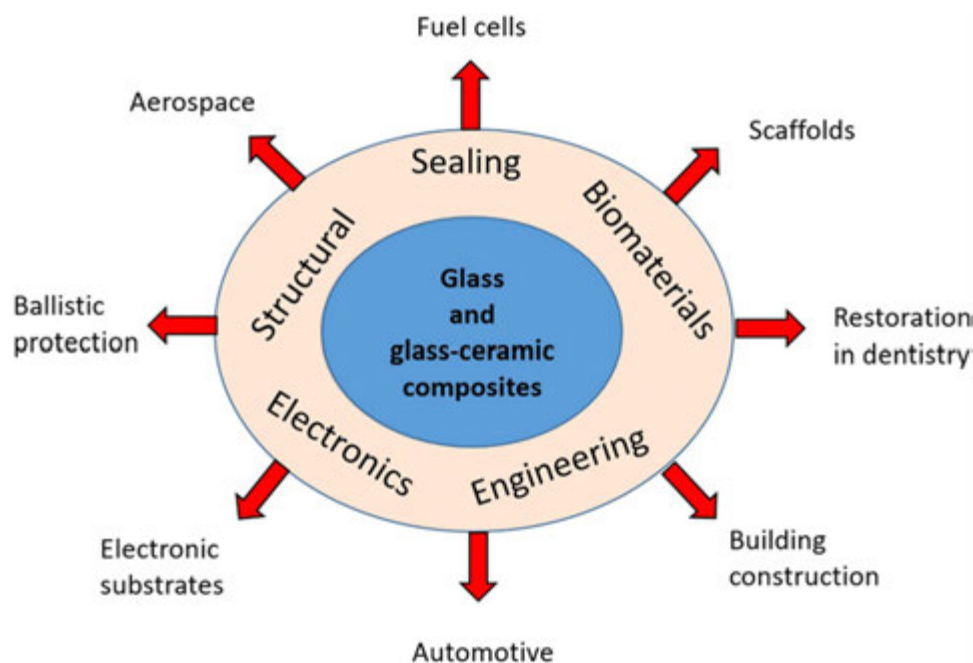


Fig. 1 Main application fields of glass and glass-ceramic matrix composites.

characteristics/properties of these materials. This section deals with the design and formulations of such composites adopted to achieve the required standard for various applications. Properties such as thermal expansion coefficient, chemical stability, density and mechanical resistance are discussed. Toughening mechanisms in GMCs and GCMCs are covered in the following section while the third section will consider the typical manufacturing processes for GMCs and GCMCs. Part II reviews the most important fields of application of this kind of composite materials. Previous work concerning applications of GMCs and GCMCs in aerospace, medicine, solid oxide fuel cells (SOFCs), electronic devices and in structural composites is presented and discussed.

Composite Constituents

The Matrices: Glasses and Glass-Ceramics

Glasses are non-crystalline (amorphous) solids, typically transparent or translucent, obtained by rapid cooling of a melt to room temperature, which as result of the increase of viscosity exhibits the mechanical properties of a solid (Shackelford and Doremus, 2008). The production of glasses involves three types of oxides, which are called formers, fluxes, and stabilizers (Musgraves *et al.*, 2019; Bansal and Doremus, 2013). Most technical glasses are based on silica (SiO_2) as glass former oxide.

Considering the glass production worldwide, soda-lime glasses represent most (approximately 90%) of the production (Musgraves *et al.*, 2019), taking into account that pure silica, due to its elevated melting temperature (1723°C), is challenging to produce and difficult to shape in technically relevant structures (Bansal and Doremus, 2013). For this reason, “soda”, or sodium carbonate (Na_2CO_3), is added to lower the glass-transition temperature (Bansal and Doremus, 2013). However, soda makes the glass water-soluble, which is usually undesirable. To avoid the increase of glass solubility following the addition of sodium carbonate, “lime” (CaO) is incorporated to provide better chemical durability. Other glass formers used to produce technical glasses are boric oxide (B_2O_3) and phosphorus pentoxide (P_2O_5). An important class of technical silicate glasses are borosilicate glasses which are based on silica and boron trioxide as glass-formers. Borosilicate glasses show very low coefficients of thermal expansion ($\approx 3 \times 10^{-6} \text{ K}^{-1}$ at 20°C), which make them resistant to thermal shock in comparison to other glasses such as soda-lime glass (Musgraves *et al.*, 2019). Borosilicate glasses are used in numerous industrial sectors, including electronics, cookware, laboratory ware and scientific equipment as well as in optics, aquarium heaters, and thermal protection systems. Special properties of borosilicate glasses include high strength, chemical durability and heat resistance (Madheshiya *et al.*, 2018) which has enabled their use in very special applications as for example in the coating of the thermal insulation tiles on the Space Shuttle (Space Shuttle Orbiter Systems, 1988). Furthermore, borosilicate glasses are used for immobilization of radioactive wastes (Zhu *et al.*, 2020) and as glass tubing in TIG welding torch nozzles (Muñoz-Sánchez and Cabezas, 2018). Given their outstanding thermo-mechanical properties, borosilicate glasses are interesting matrices to develop GMCs (Boccaccini *et al.*, 1994).

Glasses show intermediate values of elastic modulus, normally in the range of 60–90 GPa, while the elastic modulus of typical reinforcements, especially fibers, is usually higher than 200 GPa (Bernardo, 2011). This difference in stiffness between matrix and reinforcement is relevant for the design of GMCs, since this elastic mismatch determines if effective load transfer may occur between the matrix and the reinforcement (Bernardo, 2011). In contrast, for polycrystalline CMCs, a load transfer mechanism is less effective because the values of elastic modulus of matrix and reinforcement are similar.

The properties of glasses such as their characteristic temperatures or the thermal expansion coefficients may be changed by adjusting their chemical composition. In fact, tailored and well-designed compositions are crucial to convert glass matrices into glass-ceramics matrices: densification and crystallization of a glassy matrix lead to the achievement of higher creep resistance and higher elastic modulus (Bernardo, 2011; Bansal and Doremus, 2013). Other properties lead to materials with extended functionalities: the transparency enables the use of glasses in optical applications (Zhang *et al.*, 2006; Calvez, 2014), the doping with rare earth elements may lead to semiconducting behavior, permitting their use in electronics (Dey *et al.*, 2016), antibacterial properties enable their use in the biomaterials sector (Nakamura *et al.*, 2021) and chemical inertness motivates their use as safe matrices for inclusion of hazardous wastes (Pace *et al.*, 2005).

Each glass exhibits a characteristic softening point, which depends on its composition: glasses can deform and flow when their viscosity decreases at moderately high temperatures. In this state, they can infiltrate fiber assemblies without causing mechanical damage, thus facilitating composite fabrication. Glass matrices can achieve full density, especially if the processing is carried out by application of hot pressing of glass powders mixed with the reinforcing phase (Bansal and Doremus, 2013). Furthermore, glasses are considered economically attractive. This is because the cost of the raw materials employed to manufacture glass matrices are relatively low and the materials are widely available, especially in the case of glasses of silicate compositions. Moreover, it should be noted that recycling generates a large amount of crushed glass. In this case, the production of glass matrices is cost-effective since neither refining of a glass melt nor annealing are usually needed (Kothiyal *et al.*, 2012; Musgraves *et al.*, 2019).

A particular class of glasses are bioactive glasses, developed for the first time by Hench *et al.* in 1969 (Hench, 2006), representing a group of bioreactive materials that are able to bond to bone tissue in physiological environment. These amorphous silicate-based materials have the potential to interact with the human body establishing a bond to bone and/or repairing damaged bone and soft tissues (Ratner, 2019). The main constituents of standard silicate bioactive glasses are SiO_2 , CaO , P_2O_5 , and Na_2O , in proportions different from those of stable soda-lime silica glasses used in non-biologic applications. Bioactive glasses can be transformed into glass-ceramics by changes in the starting formulations and by addition of nucleating agents, inducing the

formation of crystals within the glass matrix during sintering. Furthermore, several studies have shown the fabrication of bioactive glass-based GMCs by the addition of different ceramic fillers.

Glass-ceramics

Glass-ceramics (GCs) derive from the crystallization of a glass, implying the formation of several crystalline phases within a matrix of residual amorphous material. The resulting structure combines the properties of glasses with the benefits of crystalline phases (Deubener *et al.*, 2018; Karmakar, 2017). Briefly, the glass is subjected to a thermal treatment that induces nucleation and crystallization of crystals in the remaining glass (Allix and Cormier, 2019). Glass-ceramics range from transparent to opaque depending on the amount of crystalline and glassy phases. Modifying the chemical compositions and the heat treatment schedules, the properties of glass-ceramics may be tuned to satisfy demanding requirements in several applications. The combination of knowledge about glass-ceramic systems and experimental data available in literature plays a key role in the design of GC matrices with the correct glassy and crystalline phase contents to achieve the desired properties and final product quality. The constituting chemical elements and their percentage in the composition regulate the glass-ceramic properties (Pannhorst, 1997). The compositions are tailored by adding to the base (parent) glass specific mineralizers or oxides able to give finely dispersed crystalline phases upon controlled thermal treatments. Holand and Beall (2012) classified glass-ceramic materials based on their chemical composition, as alkaline and alkaline earth silicates, aluminosilicates, fluorosilicates, silicophosphates, iron silicates, and phosphates. Another useful classification of glass-ceramics divides them into oxide and non-oxide categories (Holand and Beall, 2012; Karmakar, 2017). Oxide glass-ceramics include silicate, phosphate, borate and materials based on GeO_2 .

A wide variety of glass-ceramic materials is available with different microstructures and properties, which are associated with the combination of amorphous and crystalline phase properties. To attain specific properties, the right combination of chemical composition and an optimal heat treatment cycle to favor the process of nucleation and crystal growth are required (Holand and Beall, 2012). In general, some glass-ceramics can present almost close to zero coefficient of thermal expansion, high fracture toughness, high resistance toward impact and other unique characteristics (Bach, 2005). Glass-ceramics resulting from the crystallization of β -eucryptite and β -spodumene, as an example, are characterized by low coefficients of thermal expansion (CTE) (Bach, 2005; Arcaro *et al.*, 2017). Such low CTE glass-ceramics are materials of choice for applications that require resistance to very rapid temperature changes (high thermal shock resistance), including heat exchangers, household cookers, cutting tools and precision optical instruments (Arcaro *et al.*, 2017). Another interesting family of glass-ceramics involves those based on perovskites and spinel structures (Dugué *et al.*, 2019). These show a satisfying refractoriness, good optical, electrical and mechanical properties which make them useful for example as constituents of solar panels, screens with liquid crystal display and magnetic disks (Manzani *et al.*, 2019; Walas *et al.*, 2019; Tarafder *et al.*, 2016). Mullite crystallization offers the possibility of producing materials with high chemical resistance and high temperature capability (Fathi and Johnson, 2016; Duminis *et al.*, 2017). High mechanical resistance can be achieved also by the crystallization of canasite (Fu *et al.*, 2017). Sometimes it is difficult to control functionally opposite properties such as a high workability with sufficient hardness, a high chemical resistance in an environment rich in alkaline elements/oxides or turning an inert glass-ceramic into a bioactive glass (Holand and Beall, 2012). GCs can also be used for waste encapsulation (Rawlings *et al.*, 2006; Stoch *et al.*, 2018; McCloy and Goel, 2017). Glass-ceramic materials can be also manufactured from rocks, e.g., basaltic rocks, to obtain high chemical and wear resistance materials. In general, GCs are outstanding systems for the development of matrices for composites.

The Reinforcements

Ceramic particles, chopped fibers, whiskers and platelets are the most commonly used discontinuous reinforcements in glass and glass-ceramic matrices (Roether and Boccaccini, 2006). As particulate reinforcing phases, alumina, SiC, silica, zirconia, titania, mullite, silicon nitride, cordierite, chromia, boron nitride, aluminum nitride and thoria particles have been used (Arcaro *et al.*, 2017; Roether and Boccaccini, 2006). For example, zirconia particles have been utilized in glass and glass-ceramic matrices to improve their mechanical properties. The effects of zirconia particles on densification, flexural strength and fracture toughness of GCs have been reported for lithium aluminosilicate (LAS) GCs (Choi and Ahn, 1997), for mica-based GCs (Montazerian *et al.*, 2008a) and for mica-apatite compositions (Montazerian *et al.*, 2008b). The reinforcement of apatite-wollastonite GCs with alumina particles is reported in (Park *et al.*, 2010), which led to an interesting system for biomedical applications, especially for the repair and replacement of natural bone.

Metallic second phases as nickel particles or stainless steel chopped fibers have been also investigated as reinforcing phases in glass and GC matrix composites where specially the plastic deformation of the metallic phase is used to impart increased fracture toughness to the brittle matrices. Typical metals reported in literature and used as reinforcement in GMCs and GCMCs are stainless steel and other alloys (e.g., Fe-Ni-Co) as well as elemental metals such as Ag, Al, Au, Cu, Fe, Mo, Nb, Ni, Ti, Pb, and V and intermetallics (e.g., Ni_3Al). Metallic inclusions in the form of particles, flakes, wires and fibers have been used in GMCs and GCMCs (Roether and Boccaccini, 2006; Riaz *et al.*, 2020; Rai *et al.*, 2020; Miller and Misture, 2010).

Dispersion-reinforced composites, despite the limited enhancement in fracture toughness they provide with respect to fiber-reinforced GMCs and GCMCs, are used in several industrial applications due to their low-cost manufacturing and the possibility to develop complex mixtures with different functionalities (Roether and Boccaccini, 2006).

The use of long (continuous) fibers to reinforce glass and glass-ceramic matrices was first proposed more than 50 years ago, as discussed elsewhere (Boccaccini, 2006). Fibrous reinforcements (mainly carbon and SiC fibers) can strengthen the glass/glass ceramic

matrix leading to a remarkable improvement of the fracture strength and toughness in comparison to the unreinforced matrices. The use of fibers, in fact, allows the development of composites with enhanced fracture toughness (of up to 30 MPa m^{1/2}) and outstanding fracture tolerance at service temperatures up to about 1500°C (depending on the type of matrix) (Bernardo, 2011). GMCs and GCMCs with continuous fiber reinforcement have been proposed for structural applications in energy conversion systems and in the automotive and aerospace sectors as they are lightweight materials with high thermal capability and stiffness. Such composites find applications also in ballistic protection panels, in chemical plants, metallurgical processes, thermal protection, precision and micro-engineering and special machinery.

The incorporation of second phases in glasses and glass-ceramics has been also explored to obtain composites with specific functionalities, e.g., such composites were not only developed with the purpose to improve the mechanical properties of the matrix. Some examples of such functional composites are: GMCs for multilayer ceramic circuit boards in microelectronic packages (El-Kheshen *et al.*, 2009; Marques *et al.*, 2010), thick film resistors (Li *et al.*, 2018; Totokawa *et al.*, 2009), GMCs and GCMCs containing ferroelectric phases (e.g., lead zirconate titanate, barium titanate) (Liu *et al.*, 2014; Harizanova *et al.*, 2020; Rahangdale and Deshpande, 2019), semi-conductor nanoparticles (e.g., CdS, ZnSe, etc.) (Yuryeva *et al.*, 2020; Han *et al.*, 2018; Xue *et al.*, 2020; Janbandhu *et al.*, 2019a,b), ZnO-glass composite varistors (Feng *et al.*, 2020; Biswas *et al.*, 2019), silica composites incorporating carbon particles (Ott *et al.*, 2020), metallic nanoparticles/nanoclusters and a variety of other GMCs for optical (Li *et al.*, 2019; Veber *et al.*, 2019; Wei *et al.*, 2019), biomedical (Menazea and Abdelghany, 2020), decoration (Rostampour and Eavani, 2020) and high-dielectric strength applications (Fuentes *et al.*, 2019; Liu *et al.*, 2019; Prabhu *et al.*, 2020). Moreover cordierite GCMCs (Jiang *et al.*, 2019) and oxynitride GMCs (Baron *et al.*, 2000) incorporating SiC nanoparticles (5–10 vol%) have been developed. More recently, carbon nanotubes have been used as reinforcing elements in GMCs and GCMCs (Ramasamy *et al.*, 2019; Patil *et al.*, 2020), including fused silica (Okawara *et al.*, 2019), borosilicate glass (Boccaccini *et al.*, 2007, 2005; Thomas *et al.*, 2009; Chu *et al.*, 2008) and cordierite glass-ceramic (Salahi *et al.*, 2019) matrices. GMCs have been also developed incorporating organic phases in order to achieve novel functional properties (Avetissov *et al.*, 2018; Roether and Boccaccini, 2006).

Laminated reinforced composites are especially designed to increase the impact resistance and/or the flexural strength. For example, glass-ceramic substrates based on the LiO₂-ZrO₂-SiO₂-Al₂O₃ (LZSA) system have been manufactured by laminated object manufacturing (LOM) for microelectronic packages using water-based cast tapes (Gomes *et al.*, 2011). Other applications include the fabrication of laminated bilayers of lithium ion conducting glass-ceramics and polymer electrolytes for the development of composite solid electrolytes for Li ion batteries (Tenhaeff *et al.*, 2012).

Analysis of the literature indicates that, in general, GCMCs with discontinuous reinforcing phases have an important advantage over GMCs reinforced with continuous fibers: low cost of raw materials and simple production methods (Chainikova *et al.*, 2014) even if the increase in mechanical properties is not as pronounced as for continuous fiber reinforcement. Indeed in recent years there has been an increase in the development of GMC and GCMC systems with discontinuous phases aiming at obtaining systems with specific functional properties (Chainikova *et al.*, 2014).

Toughening Mechanisms in GMC and GCMC

In GMCs and GCMCs, like in most ceramic matrix composites, the interactions between cracks and the dispersed phase are basically intended to increase the fracture toughness (K_{IC}). A reduction in the scattering of strength data is achieved, however, only if cracks encounter a progressive resistance to their propagation, according to a substantial dissipation of fracture energy (Evans, 1990). Numerous previous studies have considered toughening mechanisms in GMCs and GCMCs, as summarized in this section.

In a GMC an increase of critical value of the strain energy release rate (G_c) ($G_c \sim K_{IC}^2/E$, with E being the elastic modulus) may arise from the bowing of a crack front between dispersed particles in a matrix, as found when Ni and alumina particles are dispersed in glass matrices (Stett and Fulrath, 1968; Lange, 1971). However, the effect of inclusions is improved if the crack front deviates from the original plane, in a condition of ‘crack deflection’, according to a system of internal stresses. These stresses are caused by the thermo-elastic mismatch between constituents, upon the cooling of composites from the manufacturing temperature. The out-of-plane deflections are enhanced especially when inclusions with high aspect ratio are used, such as whiskers (Gadkaree and Chyung, 1986) (Ye *et al.*, 2001) or disc-shaped Al₂O₃ or SiC mono-crystals (platelets) (Chaim and Talanker, 1995) (Verma *et al.*, 1995; Ye *et al.*, 2003; Boccaccini, 1994; Boccaccini and Trusty, 1996; Todd *et al.*, 1999).

A much more substantial dissipation of fracture energy derives from the inclusion of continuous, aligned fibers (Nicolais *et al.*, 2012) (see Table 1; Bernardo, 2011) by means of a careful control of the matrix-fiber interface. In fact, a too weak interface would not allow any load transfer, while a too strong interface would induce some toughening only by crack deflection.

Debonding of fibers, when a crack approaches fibers, implies remarkable energy dissipation by itself; the dissipation being further enhanced when fibers are partially pulled out. The amount of energy involved in debonding and pull-out is proportional to the strength of the fiber and to the so-called *critical length* (l_c) (Matthews and Rawlings, 1994), given by the equation:

$$l_c = \frac{\sigma_{f, fail} \cdot D}{2\tau}$$

where $\sigma_{f, fail}$ is the fiber failure stress, D is the fiber diameter and τ is the interfacial shear stress. The excellent fracture toughness of about 35 MPa m^{0.5}, accompanied by a bending strength exceeding 800 MPa (Nicolais *et al.*, 2012), found for example in carbon fiber-reinforced glasses, basically derives from the suitable interfacial bonding (low interfacial shear stress, long critical length).

Table 1 Examples of fibrous reinforcements for glass and glass-ceramic matrix composites

Material	Diameter (μm)	Density (g/cm^3)	E (GPa)	Ultimate tensile stress (GPa)	Thermal expansion coefficient (10^{-6} K^{-1})
B monofilament	100–200	2.5	400	2.75	4.7
SiC monofilament	140	3.3	425	3.45	4.4
Carbon yarn	7–10	1.7–2.0	200–700	1.4–5.5	–0.4 to –1.8
Thornel 300 ^a [39 vol%]			234 [127]	2.93 [0.71]	
HM ^a [54 vol%]			350 [180]	2.70 [0.62]	
GY-70 ^a [58 vol%]			516 [275]	2.07 [0.68]	
P-100 ^a [54 vol%]			654 [332]	2.07 [0.68]	
SiC yarn (Nicalon, Nippon Carbon Co., Japan)	10–15	2.55	190	2.4	3.1
FP alumina yarn (Du Pont, Wilmington DE)	20	3.9	380	1.4	5.7
Alumino-silicate yarn (Nextel 312, 3M Co., St. Paul, MN)	10	2.5	150	1.7	

^aExamples of fibers introduced in unidirectional carbon-fiber-reinforced borosilicate glass matrix composites; between square brackets are reported the fiber loading and the composite properties, in terms of elastic modulus and ultimate tensile strength.

Interestingly, the relatively weak glass-carbon bonding also explains the success of polymer-derived SiC fibers as reinforcing elements in borosilicate glass (Prewo and Brennan, 1980) and lithium alumino-silicate (LAS) GC matrices (Brennan and Prewo, 1982; Prewo, 1986, 1987). A thin (10–50 nm) carbonaceous layer, promoting a significant fiber pull-out effect, is the result of a solid-state reaction between SiC and oxygen from the glass matrix during the composite fabrication process.

Another phenomenon implying substantial energy dissipation is the plastic deformation of metal inclusions, ideally forming ductile ligaments in the proximity of the crack tip. Although widely studied in the context of GMCs and GCMCs (Green *et al.*, 1979; Powell *et al.*, 1980; Biswas, 1980; Krstic *et al.*, 1981; Waku *et al.*, 1997; Dlouhy *et al.*, 1997), this particular toughening mechanism has significant technological and theoretical constraints, to be effective. To prevent the melting of inclusions, composites should be manufactured with glasses with relatively low sintering temperatures, such as calcium-phosphate glasses (enabling also low temperature crystallization, for glass-ceramic matrices), or PbO and ZnO-rich solder glasses (Pernot and Rogier, 1993; Vaidya and Subramanian, 1990; Claxton *et al.*, 2002). To prevent crack deflection, the differences in terms of both thermal expansion coefficient and elastic modulus of the constituents should be minimized (Krstic *et al.*, 1981). Finally, to prevent debonding, the glass-metal interface should be strong, which is typically achieved by promoting the surface oxidation of metal particles (Krstic *et al.*, 1981; Bernardo *et al.*, 2003).

Even considering the mentioned constraints, Al inclusions were found to lead to a remarkable effect (toughness and critical energy release rate exceeding $6 \text{ MPa m}^{0.5}$ and 600 J m^{-2} , respectively) (Krstic *et al.*, 1981). The toughening was not particularly enhanced by the replacement of particles with short fibers, or ribbons (Vaidya and Subramanian, 1990). On the contrary, more spectacular effects were found with long stainless steel and Ni-based alloy filaments or with stainless steel bidimensional mats in glass and glass-ceramic matrices (work of fracture up to 50 kJ m^{-2}) (Donald and Metcalfe, 1996; Boccaccini *et al.*, 1997).

A final, very important dissipative phenomenon corresponds to the transformation of a secondary phase, as found in ceramic composites embedding metastable tetragonal zirconia nano-crystals. The latter phase was effectively introduced in both sol-gel derived glasses (Nogami and Tomozawa, 1986) and more conventional calcium phospho-silicate glasses crystallizing to mica and mica-apatite (Montazerian *et al.*, 2008b). In these systems, the crack propagation is hindered by compressive stresses around the same crack front, in turn induced by the tetragonal-to-monoclinic transformation – with volumetric expansion – of the zirconia inclusions. Composites exhibiting fracture toughness values up to $5 \text{ MPa m}^{0.5}$ have been developed. Less substantial effects may arise from other inclusion transformation mechanisms, such as the stress-induced alignment of polarization domains in piezo-electric particles, as found for PZT (lead zirconate titanate) particles embedded in a lead containing glass (Boccaccini and Pearce, 2003).

Manufacturing Techniques

GMCs and GCMCs are characterized by the relatively straightforward manufacturing technologies required for their production (Boccaccini, 2006). An important advantage of glass and glass-ceramic matrices is that their processing temperatures are considerable lower than those required for polycrystalline ceramics. The capacity of glass to flow (much like polymeric resins) at moderate temperatures is exploited in different fabrication strategies to produce GMCs and GCMCs.

Powder Technology

Powder technology is one of the most extensively employed techniques for the manufacturing of GMCs and GCMCs because it is a simple and economically efficient method which permits the use of standard processes used in the ceramic industry: mixing of

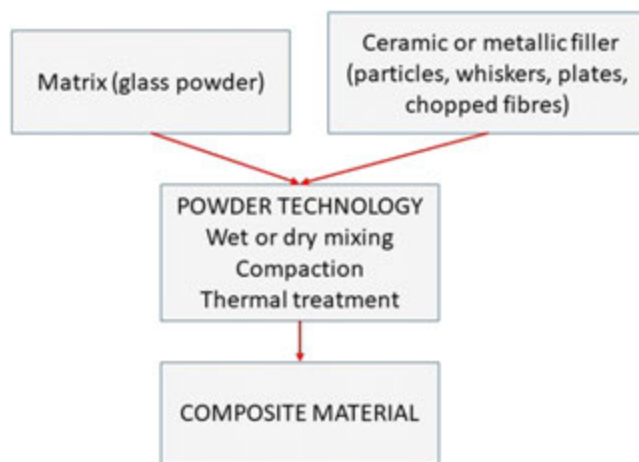


Fig. 2 Manufacturing steps in the powder technology process for fabrication of GMCs and GCMCs.

powders, compaction and sintering. The main steps of the process are shown schematically in [Fig. 2](#) ([Chainikova et al., 2014](#); [Roether and Boccaccini, 2006](#)). A non-homogeneous distribution of the dispersed phase due to the agglomeration of filler particles may lead to structural defects, such as voids and cracks ([Chainikova et al., 2014](#)). To avoid this, it is important to adjust the granulometric composition of the powders and to use wet mixing in aqueous or organic solvents with addition of suitable binders (e.g., polyvinyl alcohol) and the simultaneous application of ultrasonic or magnetic agitation to break up agglomerates. From an economic point of view, the simplest process includes sintering without compaction of the powder mixture at temperatures in the range from T_g to T_f of the glass matrix. In this case, the composite is densified via softening of the glass phase by the viscous flow mechanism. However, this method can be used only at low filler contents (up to 15%) ([Chainikova et al., 2014](#)). [Eberstein et al. \(2009\)](#) used $\alpha\text{-Al}_2\text{O}_3$ particles as rigid inclusions in alumo-borosilicate glass preparing composites via softening of the glass phase by the viscous-flow mechanism. An improved processing method for fabricating multiwalled carbon nanotube/GC nanocomposites based on vanadium doped silicate glass matrices has also been reported ([Giovanardi et al., 2010](#)).

Hot-pressing allows to obtain a higher degree of densification at high filler content (up to 90%) ([Chainikova et al., 2014](#)), because densification occurs under pressure (between 5 and 20 MPa) in a mold. Hot pressing is, however, a relatively expensive method and shows limitations when intricate geometric composite shapes are required ([Chainikova et al., 2014](#)).

Slurry Infiltration and Hot-Pressing

One of the most used approaches for manufacturing fiber-reinforced GMCs and GCMCs is based on the hot-pressing of powder infiltrated fiber preforms or fabric lay-ups. Individual fibers (or fiber tows) and fiber bodies are usually coated by matrix powder using a slurry (slurry dipping method). The slurry is composed of the glass powder, an organic binder, and a liquid carrier which is usually water, alcohol or a mixture of both. The design of the slurry is a key step in this fabrication process as it will impact the quality of the “green body” (e.g., the material before densification heat treatment). The development of the slurry must include the optimization of the powder content, particle size distribution, type and amount of binder, as well as proper selection of the liquid. For example, using a glass powder with particle size smaller than the fiber diameter will lead to better impregnation of the fiber bodies and thus it will reduce residual porosity. The infiltration of particles into fiber mats can be further improved by adding wetting agents to the slurry. Densification occurs during the hot-pressing stage when temperature is high enough to enable viscous flow of the glass particles into the pores between individual fibers. Hot-pressing enables the application of uniaxial pressures (in the range 10–20 MPa) to facilitate viscous flow after the temperature has reached the softening point of the glass, leading to highly dense (almost pore free) GMCs and GCMCs. Hot-pressing has been a common technique employed to fabricate borosilicate GMCs reinforced with SiC (Nicalon® type) fibers ([Boccaccini, 2006](#)). In the case that a glass-ceramic matrix is needed, a crystallization thermal treatment of the glass matrix after densification can be performed. [Xia et al. \(2018\)](#) reported the manufacturing of laminated $\text{SiC}_{\text{NW}}\text{-C}_f/\text{LAS}$ matrix composites by this method. Recently, a series of carbon fiber reinforced lithium aluminosilicate GC matrix composites (C_f/LAS) has been produced by the slurry infiltration coupled with hot pressing method ([Xia et al., 2015](#); [Ma, et al., 2020](#); [Wang et al., 2019](#)).

Sol-Gel, Colloidal Routes and Electrophoretic Deposition

The sol-gel method has been used to develop silicate matrices starting from metal alkoxide solutions or colloidal sols as precursors ([Boccaccini, 2006](#)). The precursors are hydrolyzed, polymerized into gels, and subsequently dried and heat-treated to obtain silicate glasses. For fabrication of composites (fiber reinforced) the fibers are immersed in a sol to deposit a thin silica gel layer on the fiber surfaces. A heat treatment at temperatures in the range 100–200°C is first required to remove the liquid from the gel and a second heat-treatment at higher temperatures (300–500°C) is necessary to burn out organic residues. Multiple infiltration cycles

may be required to achieve sufficient densification after which the composite sample is dried and heat-treated at high temperatures to obtain the final glass or glass-ceramic matrix.

The densification can occur by pressureless sintering or by hot-pressing. There are several advantages of the sol-gel method over powder processing (slurry infiltration) that can be highlighted. Thus, better fiber infiltration can be achieved that can facilitate densification even by pressureless sintering or by applying lower hot-pressing temperatures. This less aggressive fabrication process will have an extra beneficial effect as it will limit structural damage to fibers (Boccaccini, 2006). The sol-gel processing method is also advantageous when complex fiber structures are used as reinforcement as it enables a more effective infiltration of such fiber preforms that powder based slurry infiltration. The sol-gel method has some drawbacks however, in particular due to the large shrinkage that sol-gel derived matrices exhibit due to the presence of liquid in the starting green structure which must be removed in the drying and densification stages. Such large shrinkage usually leads to the development of microcracks which are detrimental to the mechanical properties of the resulting glass matrices. In addition, the sol-gel technique requires a large number of infiltration/drying cycles as mentioned above, which makes the process time-consuming and expensive. Sol-gel processing has been reported in the fabrication of borosilicate, and lithium- (LAS), magnesium- (MAS), barium- (BAS), calcium- (CAS) and sodium- aluminosilicate matrices (Boccaccini, 2006). Wang *et al.* (2011) report the manufacturing of $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$ glass/ CaSiO_3 (CBS/CS) matrix composites via sol-gel processing routes. Moreover, porous composites based on Si_3N_4 and sol-gel derived BG have been fabricated and characterized (Frajkorová *et al.*, 2015). The sol-gel based fabrication of bioactive GCMCs for dental applications is presented by Chatzistavrou *et al.* (2012), showing the development of microporous GCs for applications as coatings for dental ceramics.

Electrophoretic deposition (EPD) has been shown to be a versatile and attractive technique to infiltrate fiber preforms with nanoparticles of the matrix material for fabricating composites (Boccaccini *et al.*, 2001). After EPD infiltration of fiber preforms, pressureless sintering or hot-pressing is employed to densify the matrices and thus obtain mechanically robust composites. Numerous GMCs and GCMCs incorporating 2-dimensional fiber mats as reinforcement have been fabricated by EPD over the years (Boccaccini, 2006). More recently, EPD of mesoporous bioactive glass on glass-ceramic foam scaffolds for bone tissue engineering has been introduced (Fiorilli *et al.*, 2015).

Polymer Infiltration and Pyrolysis (PIP)

In the PIP process, a fiber preform is combined with an organic material that can be converted to a ceramic on heat treatment (pyrolysis). Usually fiber preforms are infiltrated multiple times with a liquid organic precursor that can be converted by pyrolysis to a ceramic. Instead of a conventional thermoset resin (e.g., epoxy) used to make polymer matrix composites, an organometallic polymer is used. Usually multiple and time consuming infiltration and pyrolysis cycles are required to obtain dense composites, which results in a relatively expensive process. Silicon oxycarbide glasses and glass-ceramic materials (SiOC) have been reported for advanced structural and functional applications (Stabler *et al.*, 2018). The chemical and phase compositions of SiOC glasses and glass-ceramics obtained by PIP strongly depend on the heat treatment parameters such as pyrolysis temperature, heating rate, dwell time and atmosphere. Three-dimensional braided carbon fiber reinforced silicon oxycarbide composites have been developed by multiple polysiloxane impregnation and pyrolysis cycles (Ma *et al.*, 2005). Moreover, basalt fiber reinforced SiOC-matrix composites have been also manufactured by PIP (Weichand and Gadow, 2015). Additive manufacturing techniques have been also developed showing high potential for the processing of polysiloxanes to fabricate complex-shaped and miniaturized parts.

Powder-Bed-Based Technologies: 3-D Printing and Selective Laser Treatment

Powder-based indirect additive manufacturing technologies involve the sequential deposit of thin layers of powder, followed by applying selective laser treatments or by ink-jetting a liquid binder (Cannio *et al.*, 2019). Three-dimensional printing (3DP) is a powder based additive manufacturing (AM) method which is commonly used to fabricate complex structures (Sun *et al.*, 2017). Post-processing including binder removal and sintering is required. In comparison to other AM technologies, such as fused deposition modeling (FDM) and stereolithography (SL), 3DP can be applied to a variety of materials. For example, 3DP has been applied to obtain hydroxyapatite/apatite-wollastonite GCMCs (Suwanprateeb *et al.*, 2009) and 13–93 bioactive glass-hydroxyapatite (HAp) composites (Winkel *et al.*, 2012). In another study, the powder-based three-dimensional (3D)-printing of wollastonite (CaSiO_3)-based silicate bioceramic parts has been described (Zocca *et al.*, 2015).

Alternative Fabrication Methods

Other techniques suggested to fabricate complex shaped GMC and GCMC articles are the matrix transfer molding and injection molding techniques (Bernardo, 2011). In the first method, fibers are wound on a mandrel inserted in a shell and glass is forced to fill the gap between the mandrel and the shell wall. This technique is suitable to manufacture thin-walled hollow tubes and similar shapes. In the injection molding method, glass powders, usually mixed with chopped fibers, are injected at high temperature into a mold cavity by applying uniaxial pressure. The technique leads to composites containing uniaxial oriented fibers. However the resulting composites are not particularly strong since the fiber orientation cannot be sufficiently controlled.

Another high temperature processing method for manufacturing unidirectional fiber reinforced GMCs in rod shape is pultrusion (Roether and Boccaccini, 2006). Glass impregnated fibers are passed through the nozzle of a crucible filled with molten glass. Possible degradation of the fibers is reduced by reducing the time of exposure to the molten glass. Another related processing technique for the manufacturing of rods or cylinders is extrusion (Roether and Boccaccini, 2006). In recent papers, extrusion has also been employed for the fabrication of transparent glass-ceramics functionalized by dispersed crystals (Liu *et al.*, 2018).

The sintering of GCMCs by microwave heating to improve the densification process has also been reported in literature (Chainikova *et al.*, 2014). Data reporting the sintering of SiO₂ powders, silicate gels, glass nanopowders, calcium-zirconium-silicate GCs, multilayer cordierite substrates and GCMCs based on glasses reinforced with SiC fibers or SiC whiskers have been presented (Chainikova *et al.*, 2014; Minay *et al.*, 2004).

Spark Plasma Sintering (SPS) has been shown to lead to high density GCMCs, increasing the mechanical properties of the resulting materials, compared with most standard hot-pressing techniques (Chainikova *et al.*, 2014). The SPS method has been tested in the fabrication of GCMCs based on BAS matrices (Ye *et al.*, 2008; Liu *et al.*, 2010), bioactive glasses (Jia *et al.*, 2011; Porwal *et al.*, 2015) and other silicate materials. Even if SPS is an important approach to obtain GCMCs from simple to complex shapes with full densification in a short time, SPS based synthesis as an alternative route to develop GMCs and GCMCs is still in its infancy.

Final Remarks

This chapter has summarized the field of glass and glass-ceramic matrix composites in its evolution in the last years covering the most popular matrices and reinforcements investigated and key properties achieved. GMCs and GCMCs have been fabricated by traditional techniques such as powder technology, slurry infiltration and sol-gel processing, with densification usually achieved by pressureless sintering or hot-pressing methods, but it is worth highlighting the introduction of novel methodologies such as electrophoretic deposition, SPS and 3D printing.

References

- Allix, M., Cormier, L., 2019. Crystallization and Glass-Ceramics. Springer Handbooks. Springer. pp. 113–167.
- Arcaro, S., Nieto, M.I., Moreno, R., *et al.*, 2017. LZS/Al₂O₃ glass-ceramic composites sintered by fast firing. *Mater. Res.* 20 (2), 84–91.
- Avetissov, I.C., Petrova, O.B., Anurova, M.O., *et al.*, 2018. Mechanical and optical properties of hybrid materials based on inorganic glass matrix and organic metal complex phosphors. *J. Phys. Conf. Ser.* 1045, 1–7.
- Bach, H. (Ed.), 2005. Low Thermal Expansion Glass Ceramics. Springer International Publishing.
- Bansal, N.P., Doremus, R.H., 2013. Handbook of Glass Properties. Elsevier.
- Baron, B., *et al.*, 2000. Fracture of oxynitride glasses and SiC particulate composites. *Mater. Sci. Forum* 325, 295–302.
- Bernardo, E., 2011. Glass matrix composite. In *Wiley Encyclopedia of Composites*. Hoboken, NJ: John Wiley & Sons, Inc.
- Bernardo, E., Scarinci, G., Hreglich, S., 2003. Mechanical properties of metal-particulate lead-silicate glass matrix composites obtained by means of powder technology. *J. Eur. Ceram. Soc.* 23, 1819–1827.
- Biswas, D., Ningthemcha, R.K.N., Das, A.S., Singh, L.S., 2019. Structural characterization and electrical conductivity analysis of MoO₃-SeO₂-ZnO semiconducting glass nanocomposites. *J. Non. Cryst. Solids* 515, 21–33.
- Biswas, D.R., 1980. Strength and fracture toughness of indented glass-nickel compacts. *J. Mater. Sci.* 15, 1696–1700.
- Boccaccini, A.R., 1994. Sintering of glass matrix composites containing Al₂O₃ platelet inclusions. *J. Mater. Sci.* 29, 4273–4278.
- Boccaccini, A.R., 2006. Continuous fibre reinforced glass and glass-ceramic matrix composites. In *Handbook of Ceramic Composites*. US: Springer, pp. 461–484.
- Boccaccini, A.R., Trusty, P.A., 1996. Toughening and strengthening of glass by Al₂O₃ platelets. *J. Mater. Sci. Lett.* 15, 60–63.
- Boccaccini, A.R., Pearce, D.H., 2003. Toughening of glass by a piezoelectric secondary phase. *J. Am. Ceram. Soc.* 86, 180–182.
- Boccaccini, A.R., Ondracek, G., Syhre, C., 1994. Borosilicate glass matrix composites reinforced with short metal fibres. *Glas. Sci. Technol.* 67, 16–20.
- Boccaccini, A.R., Ovenstone, J., Trusty, P.A., 1997. Fabrication of woven metal fibre reinforced glass matrix composites. *Appl. Compos. Mater.* 4, 145–155.
- Boccaccini, A.R., Kaya, C., Chawla, K.K., 2001. Use of electrophoretic deposition in the processing of fibre reinforced ceramic and glass matrix composites: A review. *Compos. Part A Appl. Sci. Manuf.* 32, 997–1006.
- Boccaccini, A.R., Acevedo, D.R., Brusatin, G., Colombo, P., 2005. Borosilicate glass matrix composites containing multi-wall carbon nanotubes. *J. Eur. Ceram. Soc.* 25, 1515–1523.
- Boccaccini, A.R., Thomas, B.J.C., Brusatin, G., Colombo, P., 2007. Mechanical and electrical properties of hot-pressed borosilicate glass matrix composites containing multi-wall carbon nanotubes. *J. Mater. Sci.* 42, 2030–2036.
- Brennan, J.J., Prew, K.M., 1982. Silicon carbide fibre reinforced glass-ceramic matrix composites exhibiting high strength and toughness. *J. Mater. Sci.* 17, 2371–2383.
- Calvez, L., 2014. Chapter 10 – Transparent chalcogenide glass-ceramics. In: Adam, J.L., Zhang, X. (Eds.), *Chalcogenide Glasses: Preparation, Properties and Applications*. Woodhead Publishing Ltd., pp. 310–330.
- Cannio, M., Boccaccini, D.N., Taurino, R., *et al.*, 2019. Digital printing of glass-ceramic glazes. In: Vincenzini, P. (Ed.), *Ceramics in Modern Technologies 1*. Techna Group Srl, pp. 129–137.
- Chaim, R., Talanker, V., 1995. Microstructure and mechanical properties of SiC platelet/cordierite glass-ceramic composites. *J. Am. Ceram. Soc.* 78, 166–172.
- Chainikova, A.S., Orlova, L.A., Popovich, N.V., Lebedeva, Y.E., Solntsev, S.S., 2014. Tendencies in the development of the technology of composite materials based on glass/glass-ceramic matrices and discrete fillers. *Russ. J. Appl. Chem.* 87, 1201–1209.
- Chatzistavrou, X., Tsigkou, O., Amin, H.D., *et al.*, 2012. Sol-gel based fabrication and characterization of new bioactive glass-ceramic composites for dental applications. *J. Eur. Ceram. Soc.* 32 (12), 3051–3061.
- Chawla, K.K., 2019. Ceramic matrix composites. In *Composite Materials*. Cham: Springer International Publishing, pp. 251–296.
- Choi, S.Y., Ahn, J.M., 1997. Viscous sintering and mechanical properties of 3Y-TZP-reinforced LAS glass-ceramic composites. *J. Am. Ceram. Soc.* 80 (12), 2982–2986.

- Chu, B.T.T., Tobias, G., Salzmann, C.G., *et al.*, 2008. Fabrication of carbon-nanotube-reinforced glass-ceramic nanocomposites by ultrasonic in situ sol-gel processing. *J. Mater. Chem.* 18, 5344–5349.
- Claxton, E., Taylor, B.A., Rawlings, R.D., 2002. Processing and properties of a bioactive glass-ceramic reinforced with ductile silver particles. *J. Mater. Sci.* 37, 3725–3732.
- Deubener, J., Allix, M., Davis, M.J., *et al.*, 2018. Updated definition of glass-ceramics. *J. Non. Cryst. Solids* 501, 3–10.
- Dey, C., Molla, A.R., Karmakar, B., 2016. Chapter 12 – Semiconductor glass nanocomposites: Preparation, properties and applications. In: Karmakar, B., Rademann, K., Stepanov, A. (Eds.), *Glass Nanocomposites: Synthesis, Properties and Applications*. William Andrew, pp. 279–297.
- Dlouhy, I., Reinisch, M., Boccaccini, A.R., Knott, J.F., 1997. Fracture characteristics of borosilicate glasses reinforced by metallic particles. *Fatigue Fract. Eng. Mater. Struct.* 20, 1235–1253.
- Donald, I.W., Metcalfe, B.L., 1996. The preparation, properties and applications of some glass-coated metal filaments prepared by the Taylor-wire process. *J. Mater. Sci.* 31, 1139–1149.
- Dugué, A., Dymshits, O., Cormier, L., *et al.*, 2019. Structural transformations and spectroscopic properties of Ni-doped magnesium aluminosilicate glass-ceramics nucleated by a mixture of TiO₂ and ZrO₂ for broadband near-IR light emission. *J. Alloy. Compd.* 780, 137–146.
- Duminis, T., Shahid, S., Hill, R.G., 2017. Apatite glass-ceramics: A review. *Front. Mater.* 3, 59.
- Eberstein, M., Reinsch, S., Müller, R., Deubener, J., Schiller, W.A., 2009. Sintering of glass matrix composites with small rigid inclusions. *J. Eur. Ceram. Soc.* 29 (12), 2469–2479.
- El-Kheshen, A.A., Zawrah, M.F., Awaad, M., 2009. Densification, phase composition, and properties of borosilicate glass composites containing nano-alumina and titania. *J. Mater. Sci. Mater. Electron.* 20, 637–643.
- Evans, A.G., 1990. Perspective on the development of high-toughness ceramics. *J. Am. Ceram. Soc.* 73 (2), 187–206.
- Fathi, H.M., Johnson, A., 2016. The effect of TiO₂ concentration on properties of apatite-mullite glass-ceramics for dental use. *Dent. Mater.* 32, 311–322.
- Feng, X., Lv, Y., Zhang, L., *et al.*, 2020. High performance of low-temperature-cofired ceramic with Al₂O₃/BN biphasic ceramics based on B₂O₃–Bi₂O₃–SiO₂–ZnO glass. *Adv. Eng. Mater.* 22 (5), 1901486.
- Fiorilli, S., Bairo, F., Cauda, V., *et al.*, 2015. Electrophoretic deposition of mesoporous bioactive glass on glass-ceramic foam scaffolds for bone tissue engineering. *J. Mater. Sci. Mater. Med.* 26, 21.
- Frajkorová, F., Bodišová, K., Boháč, M., Bartoničková, E., Sedláček, J., 2015. Preparation and characterisation of porous composite biomaterials based on silicon nitride and bioglass. *Ceram. Int.* 41, 9770–9778.
- Fu, Q., Beall, G.H., Smith, C.M., 2017. Nature-inspired design of strong, tough glass-ceramics. *MRS Bull.* 42 (3), 220–225.
- Fuertes, V., Cabrera, M.J., Soares, J., *et al.*, 2019. Microstructural study of dielectric breakdown in glass-ceramics insulators. *J. Eur. Ceram. Soc.* 39, 376–383.
- Gadkaree, K.P., Chyung, K., 1986. Silicon carbide whisker-reinforced glass and glass-ceramic composites. *Am. Ceram. Soc. Bull.* 65, 370–376.
- Giovanardi, R., Montorsi, M., Ori, G., *et al.*, 2010. Microstructural characterisation and electrical properties of multiwalled carbon nanotubes/glass-ceramic nanocomposites. *J. Mater. Chem.* 20, 308–313.
- Gomes, C., Travitzky, N., Greil, P., *et al.*, 2011. Laminated object manufacturing of LZSA glass-ceramics. *Rapid Prototyp. J.* 17 (6), 424–428.
- Green, D.J., Nicholson, P.S., Embury, J.D., 1979. Fracture of a brittle particulate composite – Part 1. Experimental aspects. *J. Mater. Sci.* 14, 1413–1420.
- Han, K., Im, W., Bin, Heo, J., Chung, W.J., 2018. Compositional dependency of Cd-S-Se quantum dots within silicate glass on color conversion for a white LED. *J. Am. Ceram. Soc.* 102 (4), 1703–1709.
- Harizanova, R., Slavov, S., Vladislavova, L., *et al.*, 2020. Barium titanate containing glass-ceramics – The effect of phase composition and microstructure on dielectric properties. *Ceram. Int.* 46 (15), 24585–24591.
- Hench, L.L., 2006. The story of bioglass®. *J. Mater. Sci. Mater. Med.* 17, 967–978.
- Holand, W., Beall, G.H., 2012. *Glass Ceramic Technology*, second ed. John Wiley & Sons, Inc.
- Janbandhu, S.Y., Joshi, A., Munishwar, S.R., Gedam, R.S., 2019a. CdS/TiO₂ heterojunction in glass matrix: Synthesis, characterization, and application as an improved photocatalyst. *Appl. Surf. Sci.* 497, 143758.
- Janbandhu, S.Y., Munishwar, S.R., Sukhadeve, G.K., Gedam, R.S., 2019b. Effect of annealing time on optical properties of CdS QDs containing glasses and their application for degradation of methyl orange dye. *Mater. Charact.* 152, 230–238.
- Jia, Z., Zhang, J., Jia, C., Nie, J., Chu, K., 2011. Preparation and characterization of mechanical properties of carbon nanotube/45S5Bioglass composites for biologic applications. *Mater. Sci. Eng. A* 528, 1553–1557.
- Jiang, Q., *et al.*, 2019. Strong and tough glass with self-dispersed nanoparticles via solidification. *Adv. Mater.* 31, 1901803.
- Karmakar, B., 2017. *Functional Glasses and Glass-Ceramics, Processing, Properties, and Applications*. Elsevier.
- Kothiyal, G.P., Ananthanarayanan, A., Dey, G.K., 2012. Glass and glass-ceramics. In: Banerjee, S., Tyagi, A.K. (Eds.), *Functional Materials*. USA: Elsevier, pp. 323–376.
- Krstic, V.V., Nicholson, P.S., Hoagland, R.G., 1981. Toughening of glasses by metallic particles. *J. Am. Ceram. Soc.* 64, 499–504.
- Lange, F.F., 1971. Fracture energy and strength behavior of a sodium borosilicate glass-Al₂O₃ composite system. *J. Am. Ceram. Soc.* 54, 614–620.
- Li, D., Lin, W., Jiang, N., Wang, C., Li, C., 2019. Optical limiting property of gold nanorods/ormosil gel glass composites. *Opt. Commun.* 437, 363–366.
- Li, H., Ou, J., Wen, M., Guan, X., 2018. Thick-film resistors on glass ceramic substrates as smart strain sensing aggregates for SHM. In: Sohn, H. (Ed.), *Sensors and Smart Structures Technologies for Civil, Mechanical, and Aerospace Systems 10598*. SPIE(46).
- Liu, L., Ye, F., Zhou, Y., Zhang, Z., 2010. Microstructure compatibility and its effect on the mechanical properties of the α -SiC/ β -Si₃N₄ co-reinforced barium aluminosilicate glass ceramic matrix composites. *Scr. Mater.* 63, 166–169.
- Liu, S., Shen, B., Hao, H., Zhai, J., 2019. Glass-ceramic dielectric materials with high energy density and ultra-fast discharge speed for high power energy storage applications. *J. Mater. Chem. C* 7 (48), 15118–15135.
- Liu, X., Pu, Y., Li, P., Wu, T., Gao, P., 2014. Influence of different nucleating agent additives on phase structure and ferroelectric properties of SrO-BaO-Nb₂O₅-CaO-SiO₂-B₂O₃ glass-ceramics. *J. Mater. Sci. Mater. Electron.* 25, 3044–3051.
- Liu, X., Zhou, J., Zhou, S., Yue, Y., Qiu, J., 2018. Transparent glass-ceramics functionalized by dispersed crystals. *Prog. Mater. Sci.* 97 (8), 38–96.
- Ma, H., Wu, X., Xia, L., *et al.*, 2020. Friction and wear behavior of carbon fiber reinforced lithium aluminosilicate composites sliding against GCr15 steel. *Friction* 8, 1063–1072.
- Ma, Q.S., *et al.*, 2005. Effects of pyrolysis processes on microstructure and mechanical properties of Cf/Si-O-C composites fabricated by preceramic polymer pyrolysis. *Ceram. Int.* 31 (2005), 305–314. doi:10.1016/j.ceramint.2004.05.021.
- Madheshiya, A., Gautam, C., Upadhyay, S., 2018. Preparation, optical and electrical properties of bismuth substituted lead titanate borosilicate glass and glass ceramics. *J. Non. Cryst. Solids* 502, 118–127.
- Manzani, D., Souza Junior, J.B., Reyna, A.S., *et al.*, 2019. Phosphotellurite glass and glass-ceramics with high TeO₂ contents: Thermal, structural and optical properties. *Dalton Trans.* 48, 6261–6272.
- Marques, V.M.F., Tulyaganov, D.U., Kothiyal, G.P., Ferreira, J.M.F., 2010. The effect of TiO₂ and P₂O₅ on densification behavior and properties of anortite-diopside glass-ceramic substrates. *J. Electroceramics* 25, 38–44.
- Matthews, F.L., Rawlings, R.D., 1994. *Composite Materials: Engineering and Science*. London: Chapman & Hall.
- McCloy, J.S., Goel, A., 2017. Glass-ceramics for nuclear-waste immobilization. *MRS Bull.* 42, 233–238.
- Menazea, A.A., Abdelghany, A.M., 2020. Precipitation of silver nanoparticle within silicate glassy matrix via Nd:YAG laser for biomedical applications. *Radiat. Phys. Chem.* 174, 108958.

- Miller, M.E., Mixture, S.T., 2010. Stoichiometric (Ni,Mg)-cordierite glass-ceramics. *J. Am. Ceram. Soc.* 93, 1018–1025.
- Minay, E.J., Boccaccini, A.R., Veronesi, P., Cannillo, V., Leonelli, C., 2004. Processing of novel glass matrix composites by microwave heating. *J. Mater. Process. Technol.* 155–156, 1749–1755.
- Montazerian, M., Alizadeh, P., Eftekhari Yekta, B., 2008a. Pressureless sintering and mechanical properties of mica glass-ceramic/Y-PSZ composite. *J. Eur. Ceram. Soc.* 28 (14), 2687–2692.
- Montazerian, M., Alizadeh, P., Eftekhari Yekta, B., 2008b. Processing and properties of a mica-apatite glass-ceramic reinforced with Y-PSZ particles. *J. Eur. Ceram. Soc.* 28 (14), 2693–2699.
- Muñoz-Sánchez, B.N., Cabezas, M.G., 2018. Borosilicate nozzles manufactured by reproducible fire shaping. *J. Mater. Process. Technol.* 261, 173–183.
- Musgraves, J.D., Hu, J., Calvez, L. (Eds.), 2019. *Handbook of Glass*. Springer Handbooks.
- Nakamura, J., Sugawara-Narutaki, A., Ohtsuki, C., 2021. Bioactive ceramics: Past and future. In *Bioceramics*. Elsevier, pp. 377–388.
- Nicolais, L., Borzacchiello, A., Lee, S.M., 2012. *Wiley Encyclopedia of Composites*, 5 Volume Set. Wiley.
- Nogami, M., Tomozawa, M., 1986. ZrO₂-transformation-toughened glass-ceramics prepared by the sol-gel process from metal alkoxides. *J. Am. Ceram. Soc.* 69, 99–102.
- Okawara, S., Kudo, M., Miyamori, M., *et al.*, 2019. Second-harmonic generation from supported carbon nanotube films grown by chemical vapor deposition on fused silica. *Jpn. J. Appl. Phys.* 58, 032006.
- Ott, A., Rogg, S., Lauterbach, S., *et al.*, 2020. Novel 0D-nanocarbon-silica ceramic composites: Sol-gel synthesis and high-temperature evolution. *Dalton Trans.* 49, 7144–7154.
- Pace, S., Cannillo, V., Wu, J., *et al.*, 2005. Processing glass-pyrochlore composites for nuclear waste encapsulation. *J. Nucl. Mater.* 341, 12–18.
- Pannhorst, W., 1997. Glass ceramics: State-of-the-art. *J. Non. Cryst. Solids* 219, 198–204.
- Park, J., You, S.H., Shin, D.W., Ozturk, A., 2010. Tribological behavior of alumina-added apatite-wollastonite glass-ceramics in simulated body fluid. *Mater. Chem. Phys.* 124, 113–119.
- Patil, S.P., Shendye, P., Markert, B., 2020. Molecular dynamics simulations of silica aerogel nanocomposites reinforced by glass fibers, graphene sheets and carbon nanotubes: A comparison study on mechanical properties. *Compos. Part B Eng.* 190.107884.
- Pernot, F., Rogier, R., 1993. Mechanical properties of phosphate glass-ceramic-316 L stainless steel composites. *J. Mater. Sci.* 28, 6676–6682.
- Porwal, H., Estili, M., Grünwald, A., *et al.*, 2015. 45S5 Bioglass®-MWCNT composite: Processing and bioactivity. *J. Mater. Sci. Mater. Med.* 26 (6), 199.
- Powell, B.R., Youngblood, G.E., Hasselman, D.P.H., Bentsen, L.D., 1980. Effect of thermal expansion mismatch on the thermal diffusivity of glass-Ni composites. *J. Am. Ceram. Soc.* 63, 581–586.
- Prabhu, N.S., Vignesh, K.R., Bhardwaj, S., *et al.*, 2020. Correlative exploration of structural and dielectric properties with Er₂O₃ addition in BaO–ZnO–LiF–B₂O₃ glasses. *J. Alloy. Compd.* 832, 154996.
- Prew, K.M., 1986. Tension and flexural strength of silicon carbide fibre-reinforced glass ceramics. *J. Mater. Sci.* 21, 3590–3600.
- Prew, K.M., 1987. Fatigue and stress rupture of silicon carbide fibre-reinforced glass-ceramics. *J. Mater. Sci.* 22, 2695–2701.
- Prew, K.M., Brennan, J.J., 1980. High-strength silicon carbide fibre-reinforced glass-matrix composites. *J. Mater. Sci.* 15, 463–468.
- Rahangdale, V.U., Deshpande, V.K., 2019. Lead-zirconate-titanate based glass and glass-ceramics: Preparation, physical, dielectric and ferroelectric properties. *Materials Today: Proceedings* 29 (3), 866–871.
- Rai, P., Chaturvedi, R.K., Mishra, A., Kumar, V., Singh, V.K., 2020. To develop biodegradable Mg-based metal ceramic composites as bone implant material. *Bull. Mater. Sci.* 43, 1–6.
- Ramasamy, D.L., Puhakka, V., Doshi, B., Iftikhar, S., Sillanpää, M., 2019. Fabrication of carbon nanotubes reinforced silica composites with improved rare earth elements adsorption performance. *Chem. Eng. J.* 365, 291–304.
- Ratner, B.D., 2019. Biomaterials: Been there, done that, and evolving into the future. *Annu. Rev. Biomed. Eng.* 21, 171–191.
- Rawlings, R.D., Wu, J.P., Boccaccini, A.R., 2006. Glass-ceramics: Their production from wastes – A review. *J. Mater. Sci.* 41 (3), 733–761.
- Riaz, M., Zia, R., Fatima, F., Bashir, F., Hussain, T., 2020. Characterization, bioactivity and antimicrobial properties of a metal-ceramic composite for bone regeneration. *Ceram. Int.* 46, 16663–16669.
- Roether, J.A., Boccaccini, A.R., 2006. Dispersion-Reinforced Glass and Glass-Ceramic Matrix Composites. In *Handbook of Ceramic Composites*. US: Springer, pp. 485–509.
- Rostampour, M., Eavani, S., 2020. Synthesis and characterization of the novel nano composite pigments using CoWO₄ on different silica sources: A comparative study. *Powder Technol.* 363, 86–94.
- Salahi, E., Ebadzadeh, T., Faeghinia, A., 2019. Investigation of MWCNTs addition on mechanical properties of cordierite glass-ceramic composites. *Int. J. Mater. Res.* 110, 174–177.
- Shackelford, J.F., Doremus, R.H., 2008. *Ceramic and Glass Materials: Structure, Properties and Processing*. US: Springer.
- Space Shuttle Orbiter Systems, 1988. Available at: https://science.ksc.nasa.gov/shuttle/technology/sts-newsref/sts_sys.html (accessed 29.09.2020).
- Stabler, C., *et al.*, 2018. Silicon oxycarbide glasses and glass-ceramics: “All-rounder” materials for advanced structural and functional applications. *J. Am. Ceram. Soc.* 101, 4817–4856.
- Stett, M.A., Fulrath, R.M., 1968. Strengthening by chemical bonding in brittle matrix composite. *J. Am. Ceram. Soc.* 51, 599–600.
- Stoch, P., Ciecierska, M., Stoch, A., Kuterasiński, Ł., Krakowiak, I., 2018. Immobilization of hospital waste incineration ashes in glass-ceramic composites. *Ceram. Int.* 44, 728–734.
- Sun, C., Tian, X., Wang, L., *et al.*, 2017. Effect of particle size gradation on the performance of glass-ceramic 3D printing process. *Ceram. Int.* 43 (1), 578–584.
- Suwanprateeb, J., Sanngam, R., Suvannapruk, W., Panyathanmaporn, T., 2009. Mechanical and in vitro performance of apatite-wollastonite glass ceramic reinforced hydroxyapatite composite fabricated by 3D-printing. *J. Mater. Sci. Mater. Med.* 20 (6), 1281–1289.
- Tarafder, A., Molla, A.R., Karmakar, B., 2016. Advanced glass-ceramic nanocomposites for structural, photonic, and optoelectronic applications. In: Karmakar, B., Rademann, K., Stepanov, A.L. (Eds.), *Glass Nanocomposites: Synthesis, Properties and Applications*. Elsevier, pp. 299–338.
- Tenhaff, W.E., Perry, K.A., Dudney, N.J., 2012. Impedance characterization of Li ion transport at the interface between laminated ceramic and polymeric electrolytes. *J. Electrochem. Soc.* 159, A2118.
- Thomas, B.J.C., Shaffer, M.S.P., Boccaccini, A.R., 2009. Sol-gel route to carbon nanotube borosilicate glass composites. *Compos. Part A Appl. Sci. Manuf.* 40, 837–845.
- Todd, R.I., Boccaccini, A.R., Sinclair, R., Yaltee, R.B., Young, R.J., 1999. Thermal residual stresses and their toughening effect in Al₂O₃ platelet reinforced glass. *Acta Mater.* 47, 3233–3240.
- Totokawa, M., Yamashita, S., Morikawa, K., *et al.*, 2009. Microanalyses on the RuO₂ particle-glass matrix interface in thick-film resistors with piezoresistive effects. *Int. J. Appl. Ceram. Technol.* 6, 195–204.
- Vaidya, R.U., Subramanian, K.N., 1990. Metallic glass ribbon-reinforced glass-ceramic matrix composites. *J. Mater. Sci.* 25, 3291–3296.
- Veber, A., Lu, Z., Vermillan, M., *et al.*, 2019. Nano-structured optical fibers made of glass-ceramics, and phase separated and metallic particle-containing glasses. *Fibers* 7.105.
- Verma, A.R.B., Murthy, V.S.R., Murty, G.S., 1995. Microstructure and compressive strength of SiC-platelet-reinforced borosilicate composites. *J. Am. Ceram. Soc.* 78, 2732–2736.
- Waku, Y., Suzuki, M., Oda, Y., Kohtoku, Y., 1997. Improving the fracture toughness of MgO–Al₂O₃–SiO₂ glass/molybdenum composites by the microdispersion of flaky molybdenum particles. *J. Mater. Sci.* 32, 4549–4557.
- Walas, M., Lisowska, M., Lewandowski, T., *et al.*, 2019. From structure to luminescence investigation of oxyfluoride transparent glasses and glass-ceramics doped with Eu³⁺/Dy³⁺ ions. *J. Alloy. Compd.* 806, 1410–1418.
- Wang, C., Xia, L., Zhong, B., *et al.*, 2019. Fabrication and mechanical properties of carbon fibers/lithium aluminosilicate ceramic matrix composites reinforced by in-situ growth SiC nanowires. *J. Eur. Ceram. Soc.* 39, 4625–4633.

- Wang, M., Zuo, R., Meng, W., Liu, Y., 2011. Sol-gel derived $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$ glass/ CaSiO_3 ceramic composites: Processing and electrical properties. *J. Mater. Sci. Mater. Electron.* 22, 843–848. doi:10.1007/s10854-010-0223-7.
- Wei, Y., Ebendorff-Heidepriem, H., Zhao, J. Tim, 2019. Recent advances in hybrid optical materials: Integrating nanoparticles within a glass matrix. *Adv. Opt. Mater.* 7, 1900702.
- Weichand, P., Gadow, R., 2015. Basalt fibre reinforced SiOC-matrix composites: Manufacturing technologies and characterisation. *J. Eur. Ceram. Soc.* 35 (14), 4025–4030.
- Winkel, A., Meszaros, R., Reinsch, S., *et al.*, 2012. Sintering of 3D-printed glass/HAp composites. *J. Am. Ceram. Soc.* 95 (11), 3387–3393.
- Xia, L., Zhong, B., Zhang, T., *et al.*, 2015. Effect of boron doping on the thermal properties of carbon fibers reinforced lithium aluminosilicate matrix composites. *J. Eur. Ceram. Soc.* 35 (9), 2555–2562.
- Xia, L., Zhang, X., Yang, Y., *et al.*, 2018. Enhanced electromagnetic wave absorption properties of laminated SiCNW-Cf/lithium–aluminum–silicate (LAS) composites. *J. Alloy. Compd.* 748, 154–162.
- Xue, J., Wang, X., Jeong, J.H., Yan, X., 2020. Fabrication, photoluminescence and applications of quantum dots embedded glass ceramics. *Chem. Eng. J.* 383, 123082.
- Ye, F., Gu, J.C., Zhou, Y., Iwasa, M., 2003. Synthesis of $\text{BaAl}_2\text{Si}_2\text{O}_8$ glass-ceramic by a sol-gel method and the fabrication of SiCp/ $\text{BaAl}_2\text{Si}_2\text{O}_8$ composites. *J. Eur. Ceram. Soc.* 23, 2203–2209.
- Ye, F., Liu, L., Zhang, J., Meng, Q., 2008. Synthesis of 30 wt%BAS/ Si_3N_4 composite by spark plasma sintering. *Compos. Sci. Technol.* 68, 1073–1079.
- Ye, F., Zhou, Y., Lei, T.C., Yang, J.M., Zhang, L.T., 2001. Microstructure and mechanical properties of barium aluminosilicate glass-ceramic matrix composites reinforced with SiC whiskers. *J. Mater. Sci.* 36, 2575–2580.
- Yuryeva, T.V., Malykhin, S.A., Kudryavtsev, A.A., *et al.*, 2020. CdZnSse crystals synthesized in silicate glass: Structure, cathodoluminescence, band gap, discovery in historical glass, and possible applications in contemporary technology. *Mater. Res. Bull.* 123, 110704.
- Zhang, X.H., Calvez, L., Seznec, V., *et al.*, 2006. Infrared transmitting glasses and glass-ceramics. *J. Non. Cryst. Solids* 352 (23–25), 2411–2415.
- Zhu, H., Wang, F., Liao, Q., Zhu, Y., 2020. Synthesis and characterization of zirconolite-sodium borosilicate glass-ceramics for nuclear waste immobilization. *J. Nucl. Mater.* 532, 152026.
- Zocca, A., Elsayed, H., Bernardo, E., *et al.*, 2015. 3D-printed silicate porous bioceramics using a non-sacrificial preceramic polymer binder. *Biofabrication* 7 (2), 025008.

Glass and Glass-Ceramic Matrix Composites for Advanced Applications:

Part II: Applications

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Applications of Glass and Glass-Ceramic Matrix Composites

Table 1 gives a summary of selected studies from the literature giving a short description of the manufacturing processes and properties of common glass matrix composites (GMCs) and glass-ceramic matrix composites (GCMCs) for various application fields. In the following paragraphs the typical applications of GMCs and GCMCs are discussed in more detail.

Aerospace

Advanced glass and glass-ceramic matrix composite materials have been developed for applications in the aerospace field. These materials should ensure reliability and their manufacturing processes must result in accuracy and precision of dimensions. Brakes, flaps, windows, lenses, panels, fuel components and sensors (speedometers, thermometers and altimeters) incorporate an specific amount of glass and glass composite materials (ElanTechnology, 2020). Other interesting structural applications include thermal protection systems in rocket exhaust cones, insulating tiles for space vehicles (e.g., the former space shuttle), missile nose cones and engine components (Wang *et al.*, 2017). Additionally, glass frit sealing is used to protect components against humidity and gas degradation. Hence being lightweight and having high temperature resistance, electrical insulation, high energy of ablation, resistance to corrosion, chemical stability, wear resistance, and ability to withstand vibration, are the typical properties that make these materials efficient and appealing for aerospace applications.

Mica glass-ceramics are well-known machinable ceramics, which exhibit zero porosity and, in general, are excellent insulators at high voltages, various frequencies and high temperatures. Mica GCs can be machined to complicated shapes and precision parts with ordinary metal-working tools. Their relatively high CTE matches those of most metals and sealing glasses (Zanotto, 2010). These unique properties of mica glass-ceramics make them suitable for use in different high-performance applications, including the manufacturing of aerospace components (Zanotto, 2010). Nevertheless these glass-ceramics suffer from their low hardness and insufficient mechanical strength (Montazerian *et al.*, 2008a). Many different methods can be applied to improve the mechanical properties of mica glass-ceramics, for example, through the addition of second rigid and strong phases forming GCMCs. However, this could lead to a reduction of the machinability of the material (Alizadeh *et al.*, 2008), unless the reinforcement phase itself has suitability for machining. The addition of other rigid and strong second crystalline phases such as fibers, whiskers and particles to the glass matrix can be effective. For example, different amounts of partially stabilized zirconia particles have been added to the starting composition to improve the mechanical properties (Montazerian *et al.*, 2008b; Gali, 2019; Ghaffari *et al.*, 2012).

The lithium aluminosilicate glass-ceramic family is one of the most studied systems to prepare materials with very low CTE. Eucryptite and spodumene are the most used and studied phases with these characteristics (García-Moreno *et al.*, 2011). Materials with a very low CTE are of great interest in aerospace applications (García-Moreno *et al.*, 2011). LAS glass-ceramics were originally developed for use in mirrors and mirror mounts of astronomical telescopes (Zanotto, 2010). However, LAS materials exhibit high brittleness. GCMCs of the aforementioned LAS matrix and a second phase of dispersed submicron alumina have been fabricated (García-Moreno *et al.*, 2011). Fig. 1(a) reports the investigated compositions, having different LAS/Al₂O₃ ratios, while Fig. 1(b) and (c) show FE-SEM images of the TLAS1 and TLAS2 compositions, respectively. The results obtained validated the possibility of designing composites with a very low CTE (e.g., the composites comprising 15.65 wt% alumina and 84.35 wt% of eucryptite gave the closest to zero CTE value) as well as improved mechanical properties.

The microwave heating of LAS GCs incorporating graphene has been reported (Benavente *et al.*, 2020). The composite exhibited high dielectric loss factor. García-Moreno *et al.* (2010) reported the pressureless sintering (conventional sintering) of LAS-nSiC nanocomposite with improved mechanical properties and excellent expansion behavior, which was achieved by means of controlling the crystallization of the matrix during sintering. In addition, LAS GCs reinforced with carbon nanofibres and alumina for controlled-thermal-expansion materials are reported in (Borrell *et al.*, 2012).

α -SiC/ β -Si₃N₄ co-reinforced barium aluminosilicate (BaAl₂Si₂O₈) (BAS) GCMCs have been prepared (Liu *et al.*, 2010). BAS has a very high melting point ($\sim 1760^\circ\text{C}$) and it can be used as a hot section component in propulsion systems after being reinforced with whiskers (Ye *et al.*, 2001), fibers (Bansal and Eldridge, 1998), platelets (Ye *et al.*, 2003b) or particles (Ma *et al.*, 2010). Indeed numerous studies have been reported on SiC particle and in situ β -Si₃N₄ grain-reinforcement of BAS GCMCs. Such composites achieved high chemical erosion resistance, good oxidation and thermal shock resistance and superior mechanical properties (Liu *et al.*, 2010). It has been demonstrated that SiC-reinforced BAS composites exhibit higher hardness and elastic moduli than β -Si₃N₄-reinforced BAS composites (Liu *et al.*, 2010). On the other hand, β -Si₃N₄-reinforced BAS composites were reported to

Table 1 Examples of applications with manufacturing process and properties of glass and glass-ceramic matrix composites

Application field	Matrix material composition	Reinforcement	Manufacturing process	Main properties			References
				Mechanical properties	Physical properties	Thermal properties	
Aerospace							
Retaining rings at hinge points, frame corners, spacers, reflectors and cavities in laser assemblies, electronics/semiconductors, precision coil formers, high voltage insulators	Mica-diopside machinable glass-ceramics	Y-PSZ powder	Powder technology (pressureless sintering) (Montazerian <i>et al.</i> , 2008a)	s_f^a : 50.91 $\pm$ 10.50 (matix) (Montazerian <i>et al.</i> , 2008a) s_f : 132.47 $\pm$ 13.8 MPa (composite with 15 wt% Y-PSZ) (Montazerian <i>et al.</i> , 2008a) K_{IC}^b : 0.8 $\pm$ 0.08 (Montazerian <i>et al.</i> , 2008a), 0.8 $\pm$ 0.2 (Gali <i>et al.</i> , 2018) (matrix) K_{IC}^c : 1.36 $\pm$ 0.07 (composite with 15 wt% Y-PSZ) (Montazerian <i>et al.</i> , 2008a), 3.6 $\pm$ 0.2 (composite with 20 wt% YSZ) (Gali <i>et al.</i> , 2018) HV ^d : 2.62 $\pm$ 0.36 (Montazerian <i>et al.</i> , 2008a), 2.0 $\pm$ 0.3 (Gali <i>et al.</i> , 2018) (matrix) HV: 4.35 $\pm$ 0.64 (composite with 15 wt% Y-PSZ) (Montazerian <i>et al.</i> , 2008a), 9.2 $\pm$ 0.5 (composite with 20 wt% YSZ) (Gali <i>et al.</i> , 2018) E^d : 73 $\pm$ 1.0 (matrix) (Gali <i>et al.</i> , 2018), E: 125 $\pm$ 5.0 (composite with 20 wt% YSZ) (Gali <i>et al.</i> , 2018)	Relative density (%): 97.2% (matrix) (Montazerian <i>et al.</i> , 2008a) — 92.4 (composite with 15 wt% Y-PSZ) (Montazerian <i>et al.</i> , 2008a)	CTE ^e : 5.07 $\pm$ 0.19 (composite with 20 wt% YSZ) (Gali, 2019)	(Montazerian <i>et al.</i> , 2008a) (Gali, 2019) (Ghaffari <i>et al.</i> , 2012) (Gali <i>et al.</i> , 2018)
Mirrors and mirror mounts of astronomical telescopes	Lithium aluminosilicate glass-ceramic family (LAS) with eucryptite and spodumene as main crystalline phases	Alumina	Pressureless conventional sintering and SPS	s_f : 163.8 $\pm$ 6.1 (Composite TLAS5 (84.35% LAS, 15.65 Al ₂ O ₃ Taimei)	Relative density (%): 98.8 (Composite TLAS5 (84.35% LAS, 15.65 Al ₂ O ₃ Taimei)	CTE (–150–450°C): –0.14 CTE (25–450°C): 0.56 (Composite TLAS5 (84.35% LAS, 15.65 Al ₂ O ₃ Taimei)	(García-Mor-eno <i>et al.</i> , 2011)
Mirrors and mirror mounts of astronomical telescopes	LAS	LAS + 20 vol% CNFs	SPS	s_f : 164.5 $\pm$ 5.4 K_{IC} : 2.28 $\pm$ 0.10	Relative density (%): 99.7	CTE (–150 to 450°C) –0.69 $\pm$ 0.05 CTE (25 to 450°C) –0.32 $\pm$ 0.05	(García-Mor-eno <i>et al.</i> , 2010)
Hot section component in propulsion systems	Barium aluminosilicate (BaAl ₂ Si ₂ O ₈)	α -SiC/ β -Si ₃ N ₄	SPS	s_f : between 493 $\pm$ 41 and 809 $\pm$ 55 K_{IC} : between 4.2 $\pm$ 0.7 and 7.9 $\pm$ 0.9 HV: between 12.2 $\pm$ 0.5 and 17.8 $\pm$ 0.6	All the compositions reached densities >99% of their theoretical		(Liu <i>et al.</i> , 2010)
SOFCs							
Sealings	BaO, Al ₂ O ₃ , SiO ₂ , CaO, TiO ₂ , ZrO ₂ , MgO, La ₂ O ₃ and B ₂ O ₃	Different ceramic fibers	Wet mixing	Good adhesion with the steel	–	–	(Haeng <i>et al.</i> , 2005)
Sealings	BaO, CaO, SiO ₂	20 wt% Ag particles and small amounts of Al ₂ O ₃ , B ₂ O ₃ , V ₂ O ₅ and ZnO	Wet mixing. Sealant deposition by screen printing.	Fracture stress 55 $\pm$ 6 MPa at room temperature; 25 MPa at 700°C and 7 MPa at 800°C			(Wei <i>et al.</i> , 2015)

(Continued)

Table 1 Continued

Application field	Matrix material composition	Reinforcement	Manufacturing process	Main properties			References
				Mechanical properties	Physical properties	Thermal properties	
Sealings	40% B ₂ O ₃ , 10% Al ₂ O ₃ , 20% MgO, 20% CaO and 10% BaO–SrO for the Ba and Sr-compositions	YSZ powder (5 and 20 wt%)	Wet mixing and cold pressing	–		CTE Ba ₂ SiO ₃ glass composites: 9.7; pure Ba ₂ SiO ₃ glass: 9.4 CTE Sr ₂ SiO ₃ glass composites: 9.4; pure Sr ₂ SiO ₃ glass: 9.4	(Brochu <i>et al.</i> , 2006)
Sealings	BaO–CaO–Al ₂ O ₃ –B ₂ O ₃ –SiO ₂ (BCABS)	Al ₂ O ₃	Wet mixing and cold pressing	–	–	CTE : 10.5 ± 0.2	(Huang <i>et al.</i> , 2018)
Biomaterials							
Restorative dentistry: dentin bonding; inlays and onlays	Lithium disilicate base glass with a composition of 31 mol% Li ₂ O, 62 mol% SiO ₂ , 2 mol% ZnO, 3 mol% K ₂ O, 1 mol% CaO and 1 mol%, P ₂ O ₅	3Y-TZP (0, 5 wt%, 10 wt%, 15 wt%, 20 wt% and 30 wt%, respectively)	Wet mixing and hot-pressing at 800°C, 30 MPa for 1 h in vacuum	σ_f : 310 ± 42 (glass-ceramic) K_{IC} : 2.2 ± 0.3 (glass-ceramic) σ_f : 340 ± 38 (composite with 15 wt% of 3Y-TZP) K_{IC} : 3.5 ± 0.3	–	–	(Huang <i>et al.</i> , 2014)
Restorative dentistry: dentin bonding; inlays and onlays	Lithium silicate glass-ceramic (SiO ₂ , Li ₂ O, K ₂ O, P ₂ O ₅ , Al ₂ O ₃ , CeO ₂ , pigments) (Vita Suprinity)	Zirconia reinforcement (≈10% by weight)	Commercial manufacturing process not reported	σ_f : 443.63 ± 38.90 K_{IC} : 2.31 ± 0.17 HV: 6.53 ± 0.49 E: 70.44 ± 1.97 B ¹ : 2.84 ± 0.26	–	–	(Chen <i>et al.</i> , 2020)
Dental crowns and inlays. Implants	Mica-apatite glass-ceramic. Parent glass: CaO–SiO ₂ –P ₂ O ₅ –MgO glass system	5, 10 and 15 wt% Y-PSZ powder	Wet mixing and pressureless sintering	σ_f : 109.37 ± 18.31 (glass-ceramic) K_{IC} : 0.85 ± 0.09 (glass-ceramic) HV: 3.25 ± 0.59 (glass-ceramic) σ_f : 132.27 ± 14.30 (composite with 10 wt% of 3Y-TZP) K_{IC} : 1.44 ± 0.16 HV: 4.48 ± 0.82 HV: 0.35	Relative density (%): Parent glass: 96% Composite with 5 wt% Y-PSZ: 95% Composite with 10 wt% Y-PSZ: 94% Composite with 15 wt% Y-PSZ: 92%	–	(Montazerian <i>et al.</i> , 2008b)
Dental restoration	Bioactive glass 58S (60 wt%)	Leucite based feldspathic porcelain (40 wt%)	Cold uniaxial pressing		–	CTE: 8.8 Ts: 715°C	(Chatzistavrou <i>et al.</i> , 2012)
Ti-based porous scaffolds to promote bone or tissue ingrowth into pores and provide biological anchorage	45S5 Bioglass (45% SiO ₂ , 24.5% Na ₂ O, 24.5 CaO, 6% P ₂ O ₅)	10 wt% Titanium (<45 µm)	Mechanical alloying process with hard steel balls for 15 h and then uniaxially pressed at compacting pressure of 600 MPa	E: 110 K_{IC} : 1.75 HV: 620	Relative density (%): 91.0		(Huan <i>et al.</i> , 2011)

Bone tissue engineering	Bioglass of composition: 45.0 SiO ₂ –24.5 Na ₂ O–24.5 CaO–6.0 P ₂ O ₅ in wt%	Si ₃ N ₄ powder (0–30% weight)	Wet mixing in isopropanol, uniaxially pressed at 100 MPa, free sintered at 980°C	HV: Si ₃ N ₄ -0 0.34 Si ₃ N ₄ -10 1.19 Si ₃ N ₄ -30 1.15 K _{IC} : Si ₃ N ₄ -0 1.28 Si ₃ N ₄ -10 0.99 Si ₃ N ₄ -30 1.05	Relative density (%): Si ₃ N ₄ -0 52.5 Si ₃ N ₄ -10 60.3 Si ₃ N ₄ -30 65.7 Density (g cm ⁻³) Porosity overall Si ₃ N ₄ -0 1.7 47.5 Si ₃ N ₄ -10 1.9 39.7 Si ₃ N ₄ -30 2.0 34.3	–	(Frajkorová <i>et al.</i> , 2015)
Bio-active and electrically conductive scaffolds for bone tissue engineering	Bioglass ®45S5	Graphene nano-platelets (1, 3 and 5 vol%)	Powder mixtures using colloidal processing route (acetone and DI water) and powder processing. Densification by SPS at 600°C with a 2 min dwell time and 70 MPa pressure	–	Electrical conductivity BG-GNP at 3 and 5 vol%: 3 and 13 S/m, respectively (about 9 order magnitude increase compared to pure BG)	–	(Porwal <i>et al.</i> , 2014)
Bio-active and electrically conductive scaffolds for bone tissue engineering	Bioglass ®45S5	Graphene nano-platelets (0, 0.1, 0.5, and 1 wt%)	Colloidal process using dimethylformamide (DMF) Sintering at 550°C for 3 min by SPS with pressure of 50 MPa	BG0.5 showed the highest values of E: 90.6 HV: 5.82 K _{IC} : 1.2	BG0.5 shows: -the lowest friction coefficient 0.59 -the smallest specific wear rate of 1.75 × 10 ⁻¹⁴ m ³ /Nm, (decrement of 21.3% in friction coefficient and 62.0% in specific wear rate compared with BG0)	–	(Li <i>et al.</i> , 2017)
Effect of incorpo-rating MWCNTs on osteoblast-like cells	Bioglass ®45S5	MWCNT (6.35 wt%)	Colloidal processing plus SPS at 550°C with a 2 min dwelltime, 70 MPa pressure and in a vacuum environment	–	Bulk density (g/cm ³) BG 2.72 BG-MWCNTs (6.35 wt%) 2.64 Relative density (%): BG 100 BG-MWCNTs (6.35 wt%) 98.9 Electrical conductivity (S/m) BG 6.13 10 ⁻⁸ BG-MWCNTs (6.35 wt%) 6.5 10 ⁻¹	–	(Porwal <i>et al.</i> , 2015)
<i>Electronic substrates</i> Microelectronics packaging substraes	Borosilicate glass (80 wt% SiO ₂ , 13 wt% B ₂ O ₃ , 4 wt% Na ₂ O, 2 wt% Al ₂ O ₃ , 0.5 wt% K ₂ O, and 0.2 wt% CaO	10, 20, 30, 40, and 50 wt% of Li-Na-K-feldspar	Powder technology and uniaxially semi-dry pressing at 50 MPa. Sintering at 850°C for 2 h in electric furnace	HV: 7.2 GPa (highest value for composite containing 50 wt% feldspar) K _{IC} : 2.51 (highest for composite containing 50 wt% feldspar) The range of obtained values of fracture toughness is 2.1–2.51	Apparent porosity: 2.68–2.91% Bulk density: 2.17–2.40 g/cm ³	CTE: 5.62 (lowest value for composite containing 50 wt% feldspar) Dielectric constant: 5.40	(Zawrah <i>et al.</i> , 2017)

(Continued)

Table 1 Continued

Application field	Matrix material composition	Reinforcement	Manufacturing process	Main properties			References
				Mechanical properties	Physical properties	Thermal properties	
Microelectronics packaging substrate	Borosilicate glass SiO ₂ (73.5%), B ₂ O ₃ (23.5%), Li ₂ O (1.5%) and Al ₂ O ₃ (1.5%)	Zn-titanate (ceramic/ borosilicate glass in 10/0, 9/1, 7/3 and 5/5ratios)	Powder technology Samples casted in discs at 20 KN using PVA (7% in solution) as binder. Sintering temperatures from 1000 to 1300°C		Bulk density (g/cm ³): Glass addition (wt%) 0 4.35 10 4.04 30 3.54 50 2.56 Dielectric constant (ε', 800 kHz at 298K): Glass addition (wt%) 0 213.36 10 10.27 30 2.37 50 16.46	–	(Morsi <i>et al.</i> , 2019)
RF modules and wireless communication devices	Borate glass La ₂ O ₃ 20 mol% B ₂ O ₃ 60 mol% TiO ₂ 20 mol%	Conventional BNT (BaO–Nd ₂ O ₃ –TiO ₂) ceramic	Low-temperature co-fired ceramic (LTCC) Sintering temperature from 750 to 900°C	–	Apparent density from 4.0 to 4.2 g/cm ³ at increasing sintering T: lower values than that of pure ceramic material (5.6 g/cm ³). Porosity: 15.1 at 750°C 15.6 at 800°C 5.1 at 850°C 8.9 at 900°C Maximum density: 2.8 g/cm ³ for 15 wt% of glass at 950°C Apparent density: LBS 2.4 g/cm ³ lower than forsterite (3.04 g/cm ³)	CTE: 7.4 Dielectric constant ε _r For pure ceramic: 90 For composite: 18.4 at 750°C 18.1 at 800°C 19.9 at 850°C 19.6 at 900°C	(Jung <i>et al.</i> , 2005)
In LTCC applications	B ₂ O ₃ , Li ₂ CO ₃ , SiO ₂ (LBS): 0.5–20 wt%	Mg ₂ SiO ₄ forsterite:	Wet mixing in water. Sintering temperature in the range 950–1500°C	–	Relative density: from 99.7 to 97 with increasing AlN content	Dielectric constant ε _r : Mg ₂ SiO ₄ : 7.1 (1 MHz) and 5.1(7 GHz) Mg ₂ SiO ₄ + 15%LBS: 6.9 (1 MHz) and 5 (7 GHz)	(Sasikala <i>et al.</i> , 2008)
Micro-electronic packaging	Glass composition wt%: 16MgO, 26Al ₂ O ₃ , 53SiO ₂ , 0–5.0 B ₂ O ₃ plus P ₂ O ₅ , 0–5 Bi ₂ O ₃	AlN: 20, 40 and 50 vol%	Wet mixing in ethanol. Hot pressing at 40 MPa for 30 min, T= 1000°C	Strength decreases from 212 MPa (in 40 vol% AlN) to 206 MPa K _{IC} : 1.27 MPa m ^{1/2} for the pure cordierite glass–ceramics matrix to 3.05 MPa m ^{1/2} with 40 vol% AlN	Relative density: from 99.7 to 97 with increasing AlN content	Thermal conductivity from 2 to 6.5 Wm ^{–1} K ^{–1}	(Chen and Liu, 2007)
Structural applications From the microelectronic industry to precision optics, especially in the applications requiring dimensional stability and size precision	Lithium aluminosilicate glass ceramics (LAS) in the form of β-spodumene (Li ₂ O–Al ₂ O ₃ –4SiO ₂)	PAN-based carbon fibers diameter of 6–8 μm. Carbon fiber content: approximate 35–40 vol%	LAS sol by a sol-gel method. Slurry prepared by mixing H ₃ BO ₃ (less than 0.05 mm) powder with the LAS sol through ball milling. Carbon fiber tows were impregnated. Composites prepared by stacking the fiber sheets into a graphite mould and hot-pressing with 10 MPa at 1350°C for 0.5 h under vacuum condition	Room temperature: s _f : 640 K _{IC} : 19.9	–	–	(Xia <i>et al.</i> , 2015)

High temperature structural applications	BaAl ₂ Si ₂ O ₈ (BAS) glass-ceramic	Dense short silicon carbide (SiC _{st}) and carbon fibers (C _{st}). Formulations: 20C _{st} /BAS, 20C _{st} 30SN/BAS, 20SiC _{st} 30SN/BAS	Wet milling and hot-pressing in graphite dies at 1600 °C for 1 h under a pressure of 20 MPa in a nitrogen atmosphere	20 vol%SiC _{st} + 30 vol%Si ₃ N ₄ /BAS composite: s _f : 296.63 K _{IC} : 4.48 271% and 149% compared to the pure BAS matrix, respectively 20 vol%C _{st} + 30 vol%Si ₃ N ₄ /BAS composite: s _f : 216.2 K _{IC} : 3.27 171% and 82% compared to the pure BAS matrix, respectively 30 vol% C _{st} /BAS: s _f : 201 K _{IC} : 3.39 Increase of 127% and 92%, respectively, compared to the pure BAS matrix 30 vol% C _{st} /BAS: s _f : 256 K _{IC} : 3.45 BAS monoliths: s _f : 86.7 ± 13.3 K _{IC} : 1.75 ± 0.13 E: 92.8 ± 8.9 BN30 (composite): s _f : 193.5 ± 6.2 K _{IC} : 2.57 ± 0.05 E: 77.8 ± 4.7 BAS monoliths: s _f : 84 ± 8 K _{IC} : 1.22 ± 0.05 10 vol%MWNT/BAS: s _f : 245 ± 11 K _{IC} : 2.97 ± 0.10	Relative density (%): 97–99%	Radial CTE between room and 900 °C: BAS matrix: 8 C _{st} reinforced composites: 8 ~ 12 SiC _{st} reinforced composites: 3.4	(Ma <i>et al.</i> , 2009)
Electronic packaging, structural components and nuclear shielding	BAS: BaSi ₂ Al ₂ O ₈ and BSAS: 0.75BaO-0.25SrO-Al ₂ O ₃ -2SiO ₂	Carbon fibers, diameter of 6–8 μm, cut to a length of 3–5 mm. Content: 0–40 (vol%)	Wet mixing in ethanol and hot-pressing in graphite dies at 1300–1600 °C for 1 h under a pressure of 35 MPa in a nitrogen atmosphere	30 vol% C _{st} /BAS: s _f : 201 K _{IC} : 3.39 Increase of 127% and 92%, respectively, compared to the pure BAS matrix 30 vol% C _{st} /BAS: s _f : 256 K _{IC} : 3.45 BAS monoliths: s _f : 86.7 ± 13.3 K _{IC} : 1.75 ± 0.13 E: 92.8 ± 8.9 BN30 (composite): s _f : 193.5 ± 6.2 K _{IC} : 2.57 ± 0.05 E: 77.8 ± 4.7 BAS monoliths: s _f : 84 ± 8 K _{IC} : 1.22 ± 0.05 10 vol%MWNT/BAS: s _f : 245 ± 11 K _{IC} : 2.97 ± 0.10	Relative density (%) > 95%	CTE: Pure BSAS celsian: 5.28 Pure BAS hexacelsian: 8.0 BSAS composite (30 vol% C _{st}): 1.63 BAS composite (30 vol% C _{st}): 3.5	(Ye <i>et al.</i> , 2008)
Radome, microelectronic packaging and high temperature conditions	Barium aluminosilicate (BaAl ₂ Si ₂ O ₈ , BAS)	Hexagonal boron nitride (BN). Content: 10–50 wt%	Wet-milling in alcohol. Sintering at 1500 °C for 60 min with a heating/cooling rate of 20 °C/min under a pressure of 10 MPa in nitrogen atmosphere	BAS monoliths: s _f : 86.7 ± 13.3 K _{IC} : 1.75 ± 0.13 E: 92.8 ± 8.9 BN30 (composite): s _f : 193.5 ± 6.2 K _{IC} : 2.57 ± 0.05 E: 77.8 ± 4.7 BAS monoliths: s _f : 84 ± 8 K _{IC} : 1.22 ± 0.05 10 vol%MWNT/BAS: s _f : 245 ± 11 K _{IC} : 2.97 ± 0.10	Density (g/cm ³): BAS monoliths: 3.31 BN30 (composite): 2.77	CTE: Pure BAS hexacelsian: 8.0 BAS composite (30 vol% BN): 2–2.7	(Li <i>et al.</i> , 2019)
General structural applications	Barium aluminosilicate (BAS)	MWNTs, 60–100 nm in diameter and 5–15 μm in length (from 5 to 15 vol%)	Wet mixing in ethyl alcohol. Hot-pressing in graphite dies at 1600 °C for 1 h under a pressure of 20 MPa in a nitrogen atmosphere	BAS monoliths: s _f : 84 ± 8 K _{IC} : 1.22 ± 0.05 10 vol%MWNT/BAS: s _f : 245 ± 11 K _{IC} : 2.97 ± 0.10	Relative density (%): BAS: 100 5 vol%MWNT/BAS: 100 10 vol%MWNT/BAS: 100 15 vol%MWNT/BAS: 97	–	(Ye <i>et al.</i> , 2006)

^aBending strength, s_f, (MPa).^bThermal expansion coefficient, CTE, (10^{−6}/°C).^cFracture toughness (indentation), K_{IC}, (MPa m^{1/2}).^dVickers micro-hardness, HV, (GPa).^eElastic modulus, E, (GPa).^fBrittleness index, B, (μm^{−1/2}).

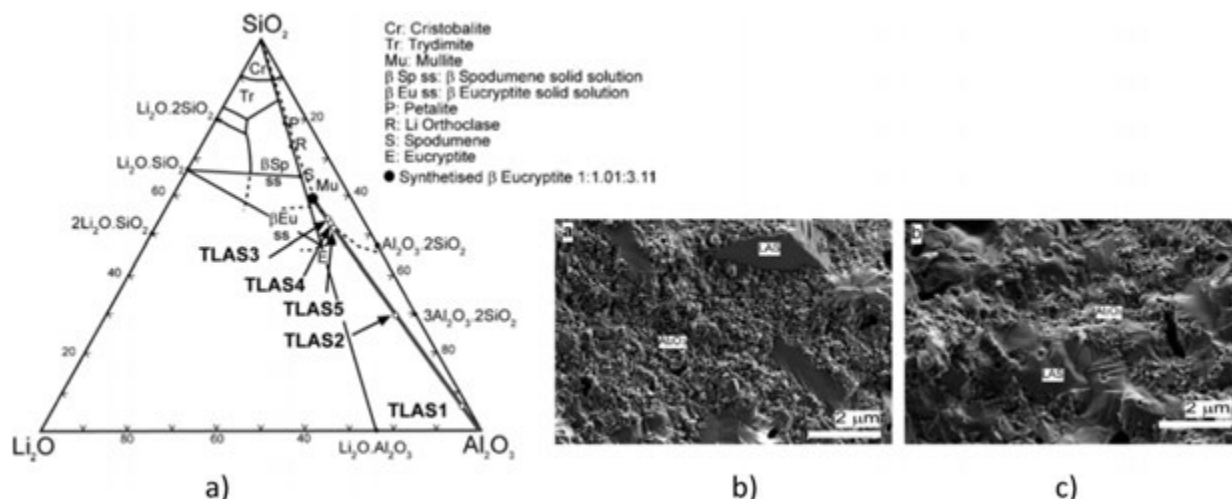


Fig. 1 (a) Composition of alumina-LAS composites, (b) and (c) FE-SEM scanning electron microscopy images of fracture surfaces of (a) TLAS1 and (b) TLAS2, respectively. Reproduced from García-Moreno, O., Borrell, A., Bittmann, B., Fernández, A., Torrecillas, R., 2011. Alumina reinforced eucryptite ceramics: Very low thermal expansion material with improved mechanical properties. *J. Eur. Ceram. Soc.* 31 (9), 1641–1648, with permission of Elsevier Ltd.

exhibit higher flexure strength and fracture toughness, due to better load transfer and crack bridging mechanisms provided by the highly elongated β - Si_3N_4 grains. Thus, in the work of Liu *et al.* (2010), in order to obtain all the above mentioned properties in one composite, a co-addition of SiC and Si_3N_4 to the BAS matrix was intended. However, the effort to develop superior ternary phase composites to maximize the reinforcing effects by simultaneous addition of α -SiC and β - Si_3N_4 was only partially successful because the growth of β - Si_3N_4 grains was reduced by the presence of α -SiC, and thus the reinforcing effect of the inclusions was decreased (Liu *et al.*, 2010).

A multifunctional high-temperature GCMC containing aluminosilicate reinforcing fillers has been also developed (Solntsev, 2011). The composites were successfully tested for erosion resistance in aircraft engine jets (Solntsev, 2011).

The resistance of GCs to withstand ultra-high temperatures (i.e., above 2000°C) without significant damage in a strongly oxidative and ablative environment allows their use for extreme applications like the propulsion of rockets for hypersonic flight. Ultra-high temperature ceramic (UHTC) filled composites can be formed, for example, when GCs are used as matrices to protect carbon fibers (C_f) effectively protecting C_f/C matrix composites from oxidation by forming oxides with high melting points during application (Makurunje *et al.*, 2017). A coating that prevents oxygen permeation should be free of defects, continuous, and have a low rate of oxygen diffusion. Ren *et al.* (2014) developed several multiphase TaB_2 based GC coatings for C_f/C composites. It was found that the oxides of Ta-based boride/carbide in a borosilicate glass matrix increased the viscosity of the in-situ formed Ta-Si-O glass, reducing oxygen diffusion and therefore increasing the overall oxidation resistance of the C_f/C composites. Walker and Corral (2014) proved that the formation of ZrO_2 - SiO_2 GC coatings on C-C composite was responsible for enhanced oxidation protection. In the work of Li *et al.* (2018), a TaSi_2 - MoSi_2 - ZrO_2 -borosilicate glass (TMZG) coating was prepared on a carbon fiber-reinforced porous silicon oxycarbide (SiCO) composite for thermal protection.

SiC-fiber reinforced barium osumilite (barium-magnesium-aluminum silicate (BMAS)) GCMCs have been also developed for high temperature (T) applications (Dassios *et al.*, 2013). Infrared thermography (IRT) and acoustic emission (AE), two major non-destructive methodologies for evaluating damage in ceramic matrix composites (CMCs) for aerospace applications, have been used to characterize SiC-fiber reinforced BMAS laminates, confirming the suitability of such GCMC systems for aerospace technologies.

Solid Oxide Fuel Cells (SOFCs)

A common approach in the field of solid oxide fuel cells and batteries is the addition of powders and second phase materials (particles, fibers), in particular ZrO_2 , Al_2O_3 , yttria-stabilized zirconia (YSZ) or mixtures of these oxides, to develop ceramics with complex microstructures (containing two or more phases) via reaction sintering, with the aim of improving specific properties. For example it is a usual approach to use such composite systems to tailor the CTE in order to match the CTE values of all components in the SOFC stack, to enhance the mechanical and insulating properties of the final products and to achieve the required gas tightness.

Different glasses and glass-ceramics enriched with the inclusion of second phases to improve specific properties in SOFC technology have been reported. For example, compositions particularly suitable for solid oxide fuel cell sealants, based on glass matrices and different volume fractions of ceramic fibers have been reported in a US patent (Haeng *et al.*, 2005). Briefly, an organic component containing a porous ceramic fiber, a filler, a hardener and a plasticizer were added to a glass matrix in the system

$\text{BaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CaO-TiO}_2\text{-ZrO}_2\text{-MgO-La}_2\text{O}_3\text{-B}_2\text{O}_3$. This addition of ceramic fibers can be used to avoid the undesired viscous flow of the glass matrix at high T. The patent (Russel *et al.*, 2010) describes the manufacturing of a glass seal with ZrO_2 and Al_2O_3 ceramic fibers in a mixture of both these oxides in different contents (1–60 wt% with respect to the GC matrix). A latex binder was added to the slurries to facilitate the extrusion of the composite. Finally, the green sealant was thermally treated to achieve densification of the structure during the SOFC stack assembly process. Moreover, a SOFC design having a glass composite seal has been reported (Anthony *et al.*, 2009). This glass composite seal includes fibers, powders, and/or beads of zirconium oxide, aluminum oxide, and YSZ to achieve the desired properties. The presence of a residual glass in the sealant is important to impart geometrical stability and to guarantee the required performance of the self-healing seal. Interesting designs of sealants for SOFCs with glass fibers or particle addition have been presented (Gross *et al.*, 2011; Zhao *et al.*, 2011; Le *et al.*, 2006; Taniguchi *et al.*, 2000; Lee *et al.*, 2007) and the performance of such composite sealants in terms of mechanical and sealing properties has been investigated. The results suggest that the fracture strength depends on the type and amount of the glass fiber used in the composite. Furthermore, the leakage rate was found to be related to the mechanical strength. Timurkutluk *et al.* (2019), for example, employed glass fibers and demonstrated that structures showing high bonding strength values can be obtained when a single glass fiber layer is located between two GC layers. Therefore glass fibers can be conveniently used as reinforcements for GCMC materials based on their relatively high strength, low density and low cost. The reinforced composites obtained will exhibit superior joining strength and high temperature sealing performance if the type of glass fiber is carefully selected. As suggested by Timurkutluk *et al.* (2019), further studies are required to investigate the influence of the addition of glass fibers on the kinetics of crystallization and the formation of new crystalline phases to better understand the effect of CTE mismatch between the fibers and other components of the SOFC. Fig. 2 shows a schematic diagram of a SOFC stack and a SEM cross-sectional image of the sealant in the design of Timurkutluk *et al.* (2019). Wei *et al.* (2015) improved the mechanical properties of a sealant in the BaO-CaO-SiO_2 ternary system by adding Ag particles and small concentrations of Al_2O_3 , B_2O_3 , V_2O_5 and ZnO. The tests performed on the annealed Ag reinforced GC sealant showed a lower average fracture stress and higher creep resistance compared to the as-sintered sealant: this positive effect on the mechanical behavior of the investigated composite was reported to be due to the incorporation and uniform distribution of Ag particles in the matrix and the reduction of the glassy phase during annealing.

Some attempts have been also made to establish the potential of natural silica sand, instead of commercially expensive materials, to be used as a future SOFC sealant (Hidayat *et al.*, 2017). The manufacturing process starts with a first step in which sand is washed, ball-milled and then heated at 1000°C for 1 h. Finally, the obtained powder is mixed with alumina powder at different percentages and treated at 1150°C and 1250°C . The main phases in the $\text{SiO}_2/\text{Al}_2\text{O}_3/\text{CaSiO}_3$ composite are cristobalite (SiO_2) and wollastonite (CaSiO_3) with alumina (Al_2O_3) inclusions. The results suggest that the similarity of the CTE with the one of other stack components means that the material is attractive for use as sealant in SOFCs.

In a related study, Brochu *et al.* (2006) investigated the feasibility of adding YSZ powders to modify the crystallization, microstructure and properties (CTE, wettability) of two borate glasses containing Ba and Sr, respectively, used as sealants in electrolyte supported SOFCs. It was found that Ba-containing glass reacted with YSZ to form BaZrO_3 which led to a significant reduction of CTE. On the other hand, the reaction between the Sr-containing glass and YSZ during heating led to the formation of strontium zirconate. The measured CTE due to a change in composition of the remaining glassy phase was close to the CTE of the YSZ additive. A related glass composite sealing system based on the addition of Al_2O_3 to BCABS glass has been reported, where crystallization kinetics and long-term thermal stability of the glass were investigated (Huang *et al.*, 2018). In other work, based on a Ba free composition, the incorporation of aluminum nitride (AlN) into borosilicate glasses and glass-ceramics was investigated with the aim of improving the sealing performance by forming borosilicate GCMCs (Li *et al.*, 2019b). The experiments performed

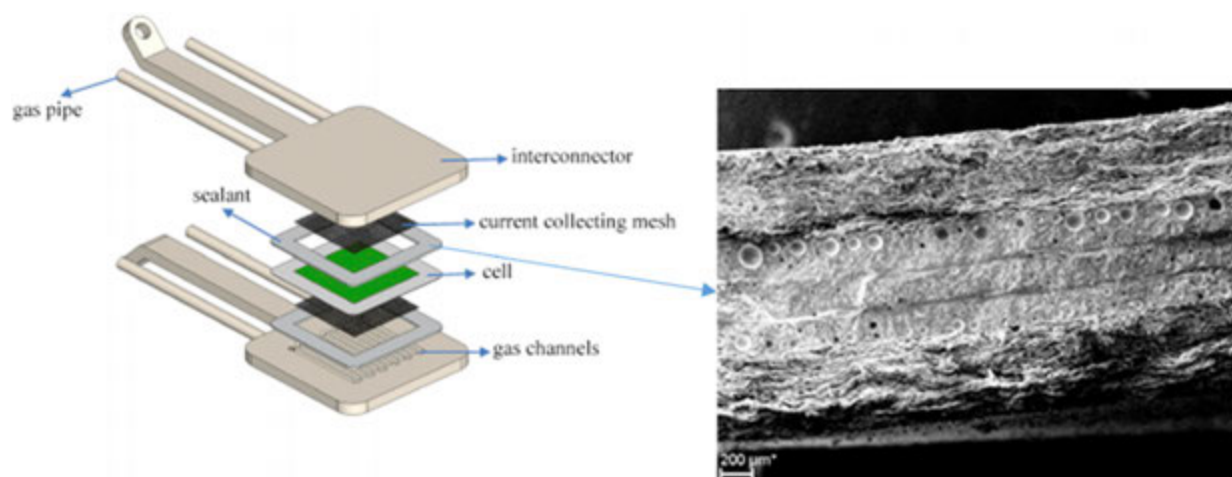


Fig. 2 Schematic presentation of a SOFC stack and a SEM cross-sectional microstructural image of the sealant in one of the investigated SOFC designs. Reproduced from Timurkutluk, B., Altan, T., Celik, S., Timurkutluk, C., Palaci, Y., 2019. Glass fiber reinforced sealants for solid oxide fuel cells. *Int. J. Hydrog. Energy* 44 (33), 18308–18318, with permission from Elsevier Ltd. (TBC).

indicated that AlN doping reduced the electrical conductivity and the composites exhibited a significant enhancement of thermal and chemical compatibility with the Y_2O_3 - ZrO_2 electrolyte.

Biomaterials

Biomaterials include those materials able to directly interact with biological systems, replace and/or repair tissues and organs or restore the function of tissues in the body (Ratner, 2019). Therefore, these materials must exhibit a range of optimized properties, i.e., chemical stability or controlled degradability, mechanical and biological properties, which depend on the functions they will have in contact with the biological system (Ratner, 2019). In this section, we take into consideration bioactive glass and glass-ceramic composites reported in literature and used in medical applications such as bone substitution and repair, dental restoration, implants, tissue engineering and drug delivery devices (Crovace *et al.*, 2016). Glass-ceramics for dental application can be divided into the following two main groups: restorative and bioactive (Montazerian and Zanotto, 2017). Most restorative dental glass-ceramics are used in the restoration and reconstruction of teeth because they are inert and biocompatible. Bioactive dental glass-ceramics, on the other hand, play an important role in the stimulation of biological reactions at the material/tissue interface. Even though bioactive glasses are characterized by outstanding bioactive properties, they suffer from low mechanical strength and low fracture toughness (Hench and Jones, 2015). In fact the bending strength of dense bioactive glass is close to 70 MPa and the fracture toughness K_{IC} shows values of $\sim 0.5 \text{ MPa m}^{1/2}$, which limit the fields of applications (Hench and Jones, 2015). To solve this issue and improve the mechanical performance of bioactive glasses and GCs, many studies have been conducted aiming at the development of bioactive GMCs and GCMCs.

Glass-ceramics for dental restoration need to satisfy distinctive requirements such as translucency and color, specific high strength, wear, toughness and Young's modulus together with a good compatibility with the oral cavity similar to those of natural teeth (Rampf and Höland, 2019). Recent developments have considered the addition of particles, fibers and also the use of advanced technologies, such as in sintering, molding and machining applying CAD/CAM or 3D printing, to manufacture novel dental materials (Galante *et al.*, 2019). The main glass-ceramic materials used in dental restoration applications are: (1) leucite-, (2) mica- (SiO_2 - Al_2O_3 - MgO - K_2O - B_2O_3 -F) based and (3) lithium disilicate-based glass-ceramics. Many works in the literature have shown that incorporation of ZrO_2 particles into matrices of lithium disilicate (Huang *et al.*, 2014), silicate (Chen *et al.*, 2020; Elsaka and Elnaghy, 2016) and mica (Gali, 2019; Yang *et al.*, 2011; Montazerian *et al.*, 2008a) is an effective method to enhance the mechanical properties of glass-ceramic matrices. In fact, ZrO_2 can induce transformation toughening and has crack deflection toughening effects. This is because the phase transition in ZrO_2 grains causes an expansion in the volume of the ZrO_2 particles leading to compressive stresses or to the formation of microcracks around the main crack. This behavior leads to a consumption of the energy of the main crack and as a consequence to an increase of the fracture resistance of the glass-ceramic (Apel *et al.*, 2007; Yang *et al.*, 2011). Another study (Huang *et al.*, 2014) has shown that the amount of ZrO_2 plays an important role in the improvement of the strengthening effect in disilicate GCMCs. However when the content of ZrO_2 particles was above 15–20 wt% manufacturing problems appeared (Chen *et al.*, 2020). In another study, Elsaka *et al.* (Elsaka and Elnaghy, 2016) developed a ZrO_2 -reinforced lithium silicate glass-ceramic with improved value of fracture toughness and flexural strength with respect to those of the lithium silicate GC matrix. Leucite glass-ceramics are usually fabricated by the controlled crystallization of leucite in the same ternary phase system (SiO_2 - Al_2O_3 - K_2O) as the conventional feldspathic porcelains, but with a higher amount of K_2O ($\sim 12 \text{ wt\%}$).

Chatzistavrou *et al.* (2012) have reported the fabrication of bioactive GCMCs for dental applications via a sol-gel process. The fabrication involved mixing commercial high fusing leucite based feldspathic porcelain powder (particle size 20–63 μm) with sol-gel derived bioactive glass. The sol-gel process was applied to obtain homogenous porous-free coatings on the surface of dental ceramic substrates creating bioactive coatings with strong bonding at the interface. In the work of Kumar *et al.* (2016) the effect of Al_2O_3 on leucite based bioactive glass ceramic composite for dental veneering was investigated. Composites containing alumina reinforcement exhibited higher flexural strength than that of pure leucite GCs.

Some bioactive materials, such as Bioglass® 45S5 (BG), can bond to bone and soft tissues (Syed *et al.*, 2019). In addition, bioactive glasses are characterized by a high biocompatibility, outstanding bioactive behavior and, in some compositions, antibacterial properties (Syed *et al.*, 2019). The drawback of BGs is their poor mechanical properties, which worsen in the case of porous BGs, used for example in applications as bone tissue engineering scaffolds. Indeed many studies have been performed to improve the mechanical characteristics of BG-based scaffolds tailoring crystallization and altering the composition of classical BGs with the inclusion of second phases in the form of ceramic or metallic particles and fibers, as well as graphene, carbon nanotubes and apatite crystals (Rizwan *et al.*, 2017). These composites may have a wide range of potential applications for hard (bones and teeth) and soft tissue engineering (Rizwan *et al.*, 2017). In particular, to utilize the outstanding bone-bonding ability of BGs, composites with biocompatible metals, such as stainless steel (SS) 316-L fibers and magnesium alloys, have been prepared (Huan *et al.*, 2010; Ducheyen and Hench, 1982; Schepers *et al.*, 1989). The Mg alloy ZK-30 has been used to reinforce BG matrices to improve its bone-bonding ability and to increase the resistance against corrosion in physiological fluids (Huan *et al.*, 2010, 2011). Moreover, Jurczyk *et al.* (2011) reported the fabrication of Titanium–10 wt% 45S5 BG nanocomposites for biomedical applications. Synthetic hydroxyapatite (HA) or tricalcium phosphate (β -TCP)-BG composites have been also extensively proposed (Rizwan *et al.*, 2017). Demirkiran *et al.* (2011) studied the bioactivity and biomineralization performance of HA composites with additions of up to 25 wt% of BG. BG was shown to act as sintering aid, promoting the occurrence of a minor β -TCP phase in the HA matrix. A significant increase in the mechanical properties was also observed by increasing the BG content up to 25 wt%.

Bellucci *et al.* (2013) developed a new hydroxyapatite-based BG biocomposite for bone replacement. The resulting composites could be sintered at a relatively low temperature (800°C) due to the use of a new glass with a reduced tendency to crystallize compared to 45S5 BG. The manufacturing of 3D-printed glass/HAp composites has been also reported (Winkel *et al.*, 2012). Furthermore, Schickle *et al.* (2011) fabricated a BG composite with 40 wt% β -TCP and studied its biocompatibility. The combination of bioinert and bioactive materials to produce bioceramic composites has been also investigated for bone tissue engineering applications. Si_3N_4 is a bioinert ceramic that can be combined with BGs to improve biocompatibility. BG acts also as sintering aid in the sintering process of Si_3N_4 . Frajkorová *et al.* (2015) developed and characterized porous composites based on Si_3N_4 containing sol-gel derived BGs. Amaral *et al.* (2002, 2007) fabricated and characterized Si_3N_4 -BG composites (30 wt% BG) for applications in hip and knee joint implants, using hot pressing between 1300°C and 1500°C. Furthermore, graphene and carbon nanotubes (CNTs) have been employed to develop composites in combination with BGs aiming at improving their mechanical properties and bioactivity (Xie and Cerruti, 2015). Porwal *et al.* (2014) fabricated BG matrix composites containing 0–5 vol% graphene nanoplatelets (GNP) by using spark plasma sintering (SPS) at 600°C and 70 MPa for 2 min. The BG-graphene composite showed high bioactivity, improved electrical conductivity and high density (99%). Similar composites were reported by Li *et al.* (2017). In addition, Porwal *et al.* fabricated a 45S5 BG-MWCNT (multi-walled carbon nanotubes) composites (Porwal *et al.*, 2015). SPS was used as it enabled fast sintering of the matrix to minimize damage of the MWCNT structure. The BG-MWCNT composites exhibited high electrical conductivity, about 8 orders of magnitude higher than that of the matrix, with the addition of 6.35 wt% of MWCNTs. The steps followed for preparation of the powder mixture to fabricate BG-MWCNT composites are illustrated in Fig. 3.

Finally, it must be mentioned that preceramic polymers, especially in the form of silicone resins, have a distinctive advantage to use advanced shaping technologies, including additive manufacturing, for the synthesis of bioceramics. Calcite (CaCO_3), a widely-recognized bioactive material, may be easily included in silicone-based pastes used in direct ink writing of reticulated scaffolds. The thermo-oxidative decomposition of the silicone polymer to obtain a ceramic matrix, if performed below 650°C, does not lead to the degradation of calcite particles (Fiocco *et al.*, 2017). Analogous thermal treatments, for example conducted in inert (N_2) atmosphere, bring additional opportunities, with the transformation of the silicone into amorphous silica embedding nano-dispersed pyrolytic carbon (Elsayed *et al.*, 2018). Such carbon phase may be found even by processing at higher temperatures, at which an extensive silicone-filler interaction occurs, leading to the formation of Ca silicate and Ca-Mg silicate crystals (Fiocco *et al.*, 2018). Carbon inclusions are very promising in making the composites sensitive to photothermal effects (heating induced by absorption of infrared radiation), that could be exploited in bone tissue engineering applications for the sterilization of scaffolds before implantation or for thermal ablation therapy of bone tumors (Fu *et al.*, 2020; Zhu *et al.*, 2020).

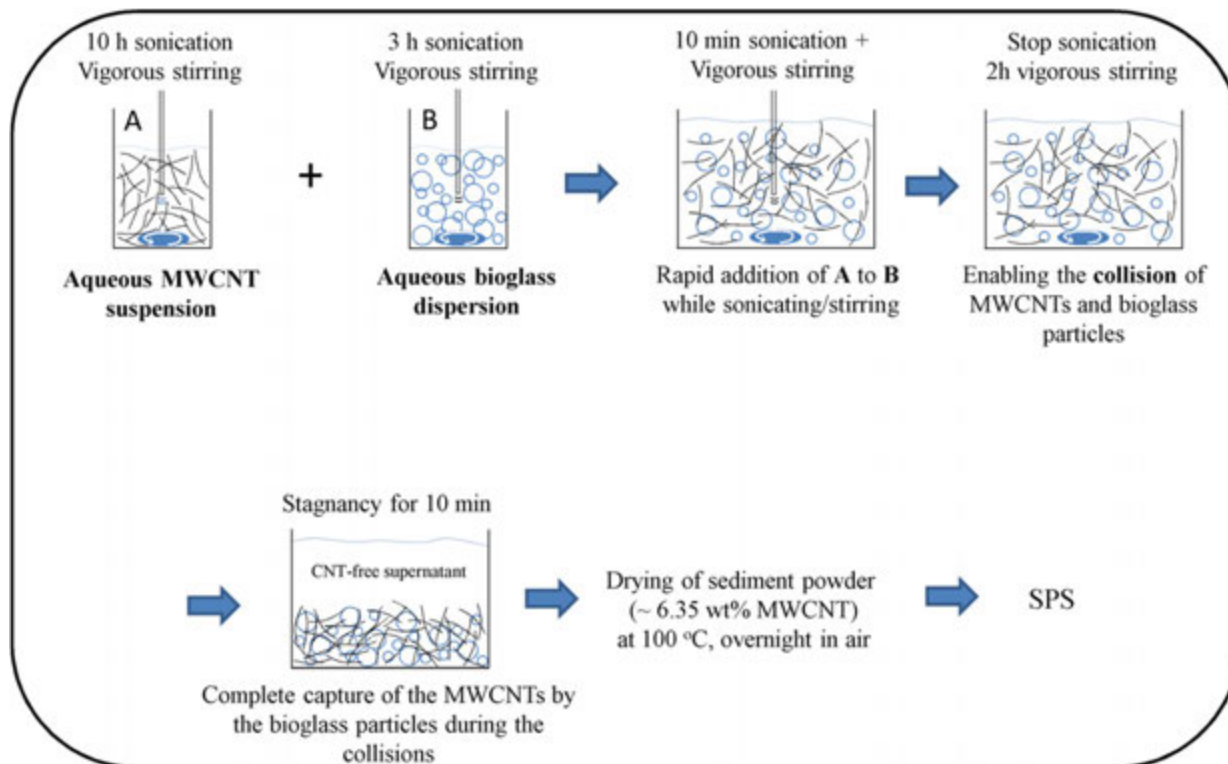


Fig. 3 Schematic diagram showing the processing steps involved in the fabrication of BG-MWCNT composites. Reproduced from Porwal, H., Estili, M., Grünewald, A., *et al.*, 2015. 45S5 Bioglass[®]-MWCNT composite: Processing and bioactivity. *J. Mater. Sci. Mater. Med.* 26 (6), 199, with permission of Springer Science + Business Media New York.

Electronic Substrates

GMCs and GCMCs are considered important materials for electronic applications, for example to make microelectronic packaging substrates (Zawrah *et al.*, 2017). They must have low dielectric constant and low CTE ($\leq 8\text{--}12 \times 10^{-6} \text{ K}^{-1}$) (Susan *et al.*, 1992). In addition such substrates are designed to be useful for integrated circuits (IC) because they can be densified at relatively low temperatures. The use of glass or glass-ceramic matrices lowers the sintering temperature and allows the co-firing with low resistance conductors such as gold and copper (Zawrah *et al.*, 2017). In the work of Zawrah *et al.* (2017), Li-Na-K containing feldspar was added to borosilicate glass to fabricate GMCs for electronic substrate applications. The results revealed that the combination of Li-Na-K feldspar and borosilicate glass led to composites exhibiting the required electrical properties (dielectric constant ~ 5) and thermal expansion ($\leq 8\text{--}12 \times 10^{-6} \text{ K}^{-1}$) suitable for electronic applications. Morsi *et al.* (2019) fabricated composite materials based on Zn-titanate and borosilicate glass with different compositions. Willemite, rutile and Zn_2TiO_4 were the main crystalline phases in the composite. Electronic conduction was dominant over ionic transfer, suggesting the potential use of these composites as semiconductor materials in electronic devices.

The low-temperature co-fired ceramic (LTCC) technology to prepare multilayer GC substrates has been shown to be the most promising approach for successful microelectronics packaging (Waser, 1992). In LTCC a flexible raw material (green tape) is used as the base. This unsintered film consists of a mixture of glass, ceramic particles and organic solvents. Many tapes are based on borosilicate glass-ceramic composites containing up to 55 vol% of dispersed ceramic particles. The possibility of co-firing several layers simultaneously, consisting of dielectric ceramics with an internal metallic electrode with matched physical and chemical properties between the layers, has the advantage of reducing fabrication variability and costs (Kim and Koh, 2008). Substrate materials with sintering temperature $< 900^\circ\text{C}$ have been developed using rare earth derived borate glass ($\text{La}_2\text{O}_3\text{--B}_2\text{O}_3\text{--TiO}_2$) and $\text{BaO--Nd}_2\text{O}_3\text{--TiO}_2$ (BNT) ceramic additions (Jung *et al.*, 2005). Also, the fabrication of $\text{CaO--B}_2\text{O}_3\text{--SiO}_2$ glass/ CaSiO_3 (CBS/CS) composites via sol-gel process has been introduced (Wang *et al.*, 2011). The variation of density, microstructure and dielectric properties was investigated. It was found that the CS ceramic phase acted as functional filler and it had also an effect on the densification and dielectric properties of the composites. The dielectric properties of the CBS/CS composites obtained with 10% CS (sintered at 850°C) were $\epsilon_r < 5$ and $\tan\delta = 6.4 \times 10^{-4}$ at 1 MHz. Related composites have been developed based on forsterite- $\text{Li}_2\text{O--B}_2\text{O}_3\text{--SiO}_2$ (LBS) for substrates in electronic packaging applications (Sasikala *et al.*, 2008). Forsterite shows low electrical conductivity and dielectric constant, high chemical stability and refractoriness as well as excellent insulation properties, which suggest its use as substrate material in microelectronics. However, forsterite presents a relatively high sintering temperature ($\sim 1500^\circ\text{C}$) which makes it not usable for fabrication of multilayer components. The influence of glass addition on the densification, sintering temperature and dielectric properties of forsterite ceramics has been investigated (Sasikala *et al.*, 2008). Fig. 4(a)

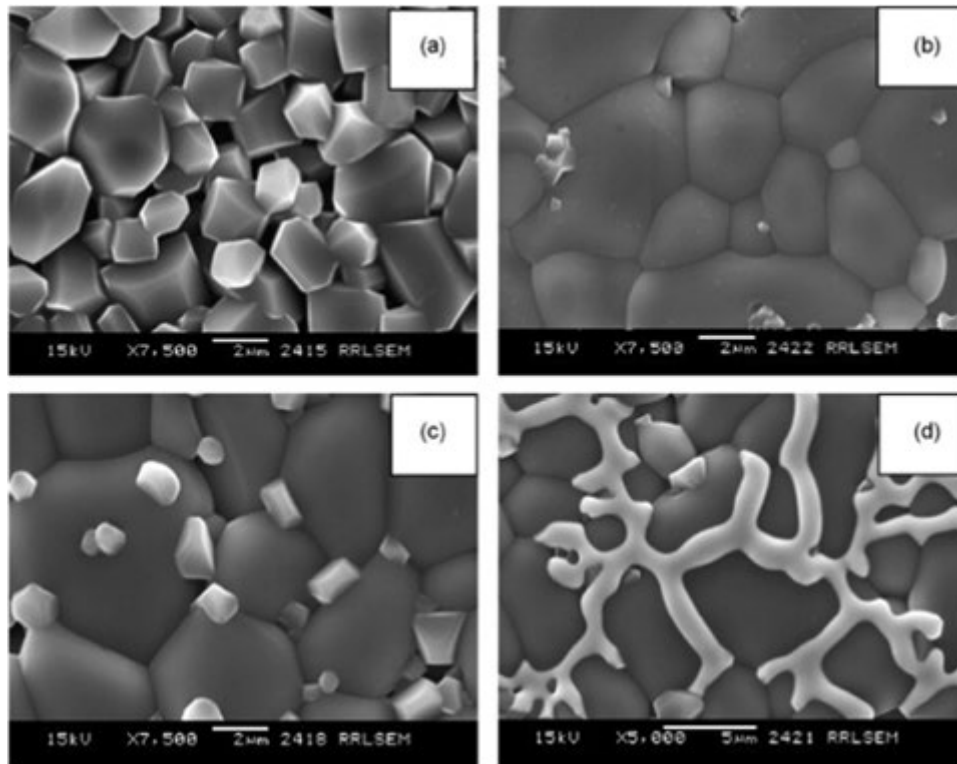


Fig. 4 SEM images of (a) pure Mg_2SiO_4 , (b) $\text{Mg}_2\text{SiO}_4 + 1 \text{ wt\% LBS}$, (c) $\text{Mg}_2\text{SiO}_4 + 5 \text{ wt\% LBS}$, (d) $\text{Mg}_2\text{SiO}_4 + 15 \text{ wt\% LBS}$. Reproduced from Sasikala, T.S., Suma, M.N., Mohanan, P., Pavithran, C., Sebastian, M.T., 2008. Forsterite-based ceramic-glass composites for substrate applications in microwave and millimeter wave communications. *J. Alloy. Compd.* 461, 555–559, with permission of Elsevier B.V.

shows a SEM image of pure forsterite fired at 1500°C, showing a poorly densified microstructure. In Fig. 4(b)-(d), SEM micrographs of forsterite containing 1, 5 and 15 wt% of LBS glass, respectively, are shown. The micrographs indicate a significant degree of densification of the composite samples which is likely due to the beneficial effect of the glass. The microstructures shown in these micrographs suggest a good wettability of the glassy phase leading to a uniform and homogeneous distribution of the crystalline phases during the sintering process. The addition of 15 wt% LBS glass was found to reduce the sintering temperature from 1500°C to about 950°C without markedly affecting the dielectric properties. In addition, the synthesis and characterization of CaO-B₂O₃-SiO₂ (CBS) glass/ceramic composites for LTCC application has been investigated (Chen *et al.*, 2009). In this study, CBS glass/cordierite (Mg₂Al₄Si₅O₁₈) composites were prepared using standard ceramic process. The CTE decreased with the increase in cordierite content, achieving values in the range of $2.2 \times 10^{-6}\text{K}^{-1}$ to $5.2 \times 10^{-6}\text{K}^{-1}$, while the dielectric constant was found to be in the range of 5.2–6.2. Eberstein *et al.* (2009) employed α -Al₂O₃ particles as rigid inclusions in aluminoborosilicate glass to prepare substrates for LTCC applications. The dissolution of alumina in the matrix, sintering kinetics, and crystallization behavior of those GMCs were studied (Müller *et al.*, 2009). Composites of 75 vol% alkali-free 38CaO-4.7Al₂O₃-7.3B₂O₃-50SiO₂ glass (mol %) and 25 vol% commercial alumina powder were prepared. No substantial alumina dissolution in the matrix was found during densification of the composite. The influence of AlN addition on thermal and mechanical properties of cordierite-based glass/ceramic composites has been also investigated (Chen and Liu, 2007). The thermal conductivity of AlN/cordierite-based GCMCs was significantly improved by incorporation of AlN particles. The composite containing 50 vol% AlN exhibited a relatively high thermal conductivity of $6.5 \text{ W m}^{-1}\text{K}^{-1}$. In addition, the mechanical properties of the composites were also improved by incorporation of AlN particles. For example, by addition of 40 vol% AlN, the flexural strength and fracture toughness increased by 81% and 139% respectively, compared to the cordierite-based glass matrix.

The preparation of LZS (Li₂O-ZrO₂-SiO₂) glass-ceramic composites containing Al₂O₃ has been also reported (Arcaro *et al.*, 2017). LZS glass-ceramics exhibit relatively high mechanical strength and hardness as well as high abrasion and wear resistance. However, a limitation for their use as substrates in microelectronic packaging (LTCC technology) is their relatively high CTE ($8.8\text{--}10 \times 10^{-6}\text{K}^{-1}$). Incorporation of alumina nanoparticles to LZS GC matrices was investigated, which led to a significant reduction of the CTE.

Structural Applications

As mentioned above, LAS GCs have been investigated extensively for thermomechanical applications due to their low CTE over a wide temperature range (Xia *et al.*, 2015). Applications of LAS GCs range from microelectronic substrates to precision optics, specifically in components where dimensional stability and precision are required; the typical features provided by low CTE (Xia *et al.*, 2015). On the other hand, LAS GCs exhibit low strength and fracture toughness, typical of brittle GCs, which represents an important disadvantage of LAS GCs for structural applications. To improve the mechanical properties of LAS GCs, carbon fiber reinforced LAS GCMCs with B doping have been fabricated (Xia *et al.*, 2013, 2015). The main goals behind the development of such B-doped GCMCs were the increase of the fracture toughness of the LAS glass-ceramic, the reduction of the viscosity of the LAS matrix and the formation of a graphite layer on the surface of carbon fibers. A remarkable improvement in the mechanical properties was obtained in comparison with the pure LAS matrix composite achieving flexural strength and fracture toughness values of 640 MPa and $19.9 \text{ MPa m}^{1/2}$, respectively. Furthermore, boron doping led to an improvement of the oxidation resistance of the composites at temperatures in the range 600–1000°C.

A BAS glass-ceramic is another structural material that has been considered as suitable matrix for developing GCMCs for high temperature applications. This is based on the high melting temperature (1760°C) of BAS, and its good oxidation resistance and low CTE ($2.29 \times 10^{-6}\text{K}^{-1}$) (Ma *et al.*, 2009). However, BAS glass-ceramics have relatively low flexural strength and fracture toughness ($1.8 \text{ MPa m}^{1/2}$), which limits its use in many load-bearing applications (Ma *et al.*, 2009). Particulate (Ye *et al.*, 2005), whisker (Ye *et al.*, 2003a), platelet (Ye *et al.*, 2003b) and continuous fiber (Bansal, 2005) reinforcements have been investigated to obtain BAS GCMCs with improved mechanical behavior. For example, short silicon carbide and carbon fiber reinforced BAS GCMCs have been obtained by hot-pressing (Ma *et al.*, 2009). Typical microstructures of such composites are shown in Fig. 5, indicating that the fibers are homogeneously dispersed in the BAS matrix in both cases.

Dense BAS and Ba_{0.75}Sr_{0.25}Si₂Al₂O₈ (BSAS) GCMCs reinforced with short carbon fibers (C_{sf}) have been also fabricated by hot pressing (Ye *et al.*, 2008). The carbon fibers showed chemical compatibility with the GC matrices investigated, exhibiting the desired strengthening and toughening effects. By incorporating 30 vol% fibers, increases of 127% and 92% in flexural strength and fracture toughness were achieved compared to the unreinforced BAS GC matrix. The effects of the addition of BN (with doping contents of 10–50 wt%) on the microstructural evolution and mechanical properties of BAS-BN composites fabricated by hot-pressing have been also investigated (Li *et al.*, 2019a). Significant strengthening and toughening effects were confirmed by the incorporation of BN: the flexure strength increased in 123%. BAS-BN composites containing 30 wt% BN showed flexural strength and fracture toughness of $193.5 \pm 6.2 \text{ MPa}$ and $2.57 \pm 0.05 \text{ MPa m}^{1/2}$, respectively. In related research (Aggelis *et al.*, 2013), structural composites based on BMAS GCs reinforced with SiC-Tyranno fibers were prepared by hot-pressing at 1200°C. In this type of composite, a carbon-rich layer usually forms in-situ at the fibers' surface during hot-pressing due to the reaction of SiC with the oxides in the GC matrix. This carbonaceous layer is responsible for the toughening effect of the fibers as it provides a weak fiber/matrix interface leading to significant energy dissipation mechanisms during fracture. These include interfacial debonding, fiber sliding, fiber bridging, and pull-out.

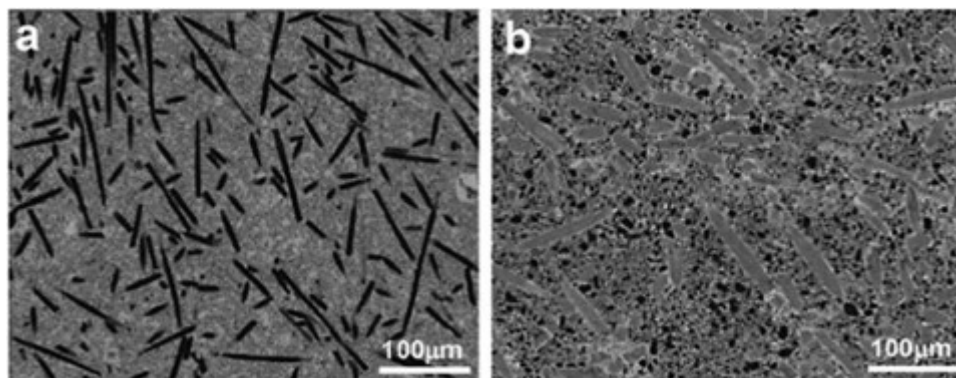


Fig. 5 SEM micrographs of BAS GCMCs with (a) short carbon fiber and (b) short SiC fiber reinforcement. Reproduced from Ma, J., Ye, F., Liu, L., Zhang, H., 2009. Processing and mechanical properties of short fibers/Si₃N₄p reinforced BaO · Al₂O₃ · 2SiO₂ ceramic matrix composites. *Mater. Sci. Eng. A* 520, 158–161, with permission of Elsevier B.V.

A different family of GMCs and GCMCs has been developed more recently exploiting CNTs as the reinforcing phase. For example, MWNT/BAS GCMCs containing 10 vol% MWNTs were successfully fabricated by hot-pressing (Ye *et al.*, 2006) and achieved values of flexural strength and fracture toughness 192% and 143% higher than the matrix, respectively. MWNT pull-out and bridging were identified as the acting toughening mechanisms. In the work of Subhani *et al.* (2013), a comprehensive analysis of published data in the field of CNT-glass/glass-ceramic matrix composites has been published. Indeed numerous studies have reported CNT containing GMCs and GCMCs, including silica (Ning *et al.*, 2003; Xu *et al.*, 2009; Hongbing *et al.*, 2005; Zheng *et al.*, 2008), borosilicate (Thomas *et al.*, 2009), BAS (Ye *et al.*, 2006), aluminoborosilicate (Mukhopadhyay *et al.*, 2011), (Otieno *et al.*, 2010) and vanadium-doped silicate (Giovanardi *et al.*, 2010) matrices. It is found in general that addition of CNTs increases the fracture strength and toughness of the glass or GC matrices and leads to an increase of thermal and electrical conductivity. Even if the improvement in fracture toughness is not as marked as the one achieved by using fiber reinforcement, CNT containing composites show functional properties and cost-effective production, which are advantages that warrant more research in this field. Similarly, GCMCs produced by introducing α -SiC particles and densified by spark plasma sintering also show promising properties (Liu *et al.*, 2010).

Final Remarks

New applications for glass and glass-ceramic matrix composites have emerged and several publications describe the development of different composite systems and fabrication processes. The use of GCMCs in advanced applications like seals in solid oxide fuel cells and biomaterials has been increasingly successful. The period covered in this chapter has also seen an increase in research on novel reinforcement materials for the development of GMCs and GCMCs, in particular carbon nanotubes and graphene or graphene oxide. The literature reviewed has highlighted the efforts addressed to the development of advanced composites in terms of thermo-mechanical robustness and reliability in many different applications, exploiting the advantages of glass and glass-ceramic processing in comparison to polycrystalline ceramics, in particular lower processing temperatures. However a number of challenges remain for the future perspectives and further development of cost-effective and automated processing methods. It is evident that the field will benefit from continuous collaboration among materials scientists, engineers, designers and end-users to design and develop new fillers/reinforcements as well as alternative matrices. It can be anticipated that further efforts will involve dedicated research to improve the reliability of these composites taking into consideration the wide scope for new application fields and the possibility that composite technology offers to combine mechanical robustness and the added functionalities provided by the fillers.

References

- Aggelis, D.G., Dassios, K.G., Kordatos, E.Z., Matikas, T.E., 2013. Damage accumulation in cyclically-loaded glass-ceramic matrix composites monitored by acoustic emission. *Sci. World J.* 2013, 2356–6140.
- Alizadeh, P., Eftekhari Yekta, B., Javadi, T., 2008. Sintering behavior and mechanical properties of the mica-diopside machinable glass-ceramics. *J. Eur. Ceram. Soc.* 28 (8), 1569–1573.
- Amaral, M., Lopes, M.A., Silva, R.F., Santos, J.D., 2002. Densification route and mechanical properties of Si₃N₄-bioglass biocomposites. *Biomaterials* 23, 857–862.
- Amaral, M., Abreu, C.S., Oliveira, F.J., Gomes, J.R., Silva, R.F., 2007. Biotribological performance of NCD coated Si₃N₄-bioglass composites. *Diam. Relat. Mater.* 16 (4–7), 790–795.
- Apel, E., van't Hoen, C., Rheinberger, V., Höland, W., 2007. Influence of ZrO₂ on the crystallization and properties of lithium disilicate glass-ceramics derived from a multi-component system. *J. Eur. Ceram. Soc.* 27 (2–3), 1571–1577.
- Arcaro, S., Moreno, B., Chinarro, E., *et al.*, 2017. Properties of LZS/nanoAl₂O₃ glass-ceramic composites. *J. Alloy. Compd.* 710, 567–574.
- Bansal, N.P., 2005. Strong and tough Hi-nicalon-fiber-reinforced celsian-matrix composites. *J. Am. Ceram. Soc.* 80, 2407–2409.

- Bansal, N.P., Eldridge, J.I., 1998. Hi-Nicalon fiber-reinforced celsian matrix composites: Influence of interface modification. *J. Mater. Res.* 13, 1530–1537.
- Bellucci, D., Sola, A., Gazzari, M., Chiellini, F., Cannillo, V., 2013. A new hydroxyapatite-based biocomposite for bone replacement. *Mater. Sci. Eng. C* 33 (3), 1091–1101.
- Benavente, R., Salvador, M.D., Centeno, A., *et al.*, 2020. Study of microwave heating effect in the behaviour of graphene as second phase in ceramic composites. *Materials* 13 (5), 1119.
- Borrell, A., García-Moreno, O., Torrecillas, R., García-Rocha, V., Fernández, A., 2012. Lithium aluminosilicate reinforced with carbon nanofiber and alumina for controlled-thermal-expansion materials. *Sci. Technol. Adv. Mater.* 13 (1).
- Brochu, M., Gauntt, B.D., Shah, R., Miyake, G., Loehman, R.E., 2006. Comparison between barium and strontium-glass composites for sealing SOFCs. *J. Eur. Ceram. Soc.* 26, 3307–3313.
- Chatzistavrou, X., Tsigkou, O., Amin, H.D., *et al.*, 2012. Sol-gel based fabrication and characterization of new bioactive glass-ceramic composites for dental applications. *J. Eur. Ceram. Soc.* 32 (12), 3051–3061.
- Chen, G.H., Liu, X.Y., 2007. Influence of AlN addition on thermal and mechanical properties of cordierite-based glass/ceramic composites. *J. Mater. Process. Technol.* 190, 77–80.
- Chen, G.H., Tang, L.J., Cheng, J., Jiang, M.H., 2009. Synthesis and characterization of CBS glass/ceramic composites for LTCC application. *J. Alloy. Compd.* 478, 858–862.
- Chen, X.P., Xiang, Z.X., Song, X.F., Yin, L., 2020. Machinability: Zirconia-reinforced lithium silicate glass ceramic versus lithium disilicate glass ceramic. *J. Mech. Behav. Biomed. Mater.* 101, 103435.
- Crovace, M.C., Souza, M.T., Chinaglia, C.R., Peitl, O., Zanotto, E.D., 2016. Biosilicate® – A multipurpose, highly bioactive glass-ceramic. In vitro, in vivo and clinical trials. *J. Noncryst. Solids* 432, 90–110.
- Dassios, K.G., Kordatos, E.Z., Aggelis, D.G., Matikas, T.E., 2013. Nondestructive damage evaluation in ceramic matrix composites for aerospace applications. *Sci. World J.* 2013, 715945.
- De Rose, A.J., Mukerjee, S., Haltiner, Jr., K.J., 2009. US20110269053A1 – Solid Oxide Fuel Cell Having a Glass Composite Seal.
- Demirkiran, H., Hu, Y., Zuin, L., Appathurai, N., Aswath, P.B., 2011. XANES analysis of calcium and sodium phosphates and silicates and hydroxyapatite-Bioglass®45S5 co-sintered bioceramics. *Mater. Sci. Eng. C* 31 (2), 134–143.
- Ducheyen, P., Hench, L.L., 1982. The processing and static mechanical properties of metal fibre reinforced bioglass. *J. Mater. Sci.* 17, 595–606.
- Eberstein, M., Reinsch, S., Müller, R., Deubener, J., Schiller, W.A., 2009. Sintering of glass matrix composites with small rigid inclusions. *J. Eur. Ceram. Soc.* 29 (12), 2469–2479.
- ElanTechnology, 2020. Glass Ceramics Applications & Frit Sealing for Aviation – Elan [WWW Document]. URL <https://www.elantechnology.com/glass/glass-suppliers-industries/glass-ceramics-applications-aviation-industry/> (accessed 24.10.2020).
- Elsaka, S.E., Elnaghy, A.M., 2016. Mechanical properties of zirconia reinforced lithium silicate glass-ceramic. *Dent. Mater.* 32 (7), 908–914.
- Elsayed, H., Carraro, F., Agnoli, S., *et al.*, 2018. Direct ink writing of silica-carbon-calcite composite scaffolds from a silicone resin and fillers. *J. Eur. Ceram. Soc.* 38 (15), 5200–5207.
- Fiocco, L., Elsayed, H., Badocco, D., *et al.*, 2017. Direct ink writing of silica-bonded calcite scaffolds from preceramic polymers and fillers. *Biofabrication* 9 (2), 025012.
- Fiocco, L., Agnoli, S., Pedron, D., *et al.*, 2018. Wollastonite-diopside-carbon composite foams from a silicone resin and inorganic fillers. *Ceram. Int.* 44 (1), 931–937.
- Frajkorová, F., Bodišová, K., Boháč, M., Bartoničková, E., Sedláček, J., 2015. Preparation and characterisation of porous composite biomaterials based on silicon nitride and bioglass. *Ceram. Int.* 41 (8), 9770–9778.
- Fu, S., Hu, H., Chen, J., Zhu, Y., Zhao, S., 2020. Silicone resin derived larnite/C scaffolds via 3D printing for potential tumor therapy and bone regeneration. *Chem. Eng. J.* 382, 122928.
- Galante, R., Figueiredo-Pina, C.G., Serro, A.P., 2019. Additive manufacturing of ceramics for dental applications: A review. *Dent. Mater.* 35 (6), 825–846.
- Gali, S., 2019. Mica glass ceramics for dental restorations. *Mater. Technol.* 34 (1), 2–11.
- Gali, S., Ravikumar, K., Murthy, B.V.S., Basu, B., 2018. Zirconia toughened mica glass ceramics for dental restorations: Wear, thermal, optical and cytocompatibility properties. *Dent. Mater.* 35 (12), 1706–1717.
- García-Moreno, O., Fernández, A., Torrecillas, R., 2010. Conventional sintering of LAS-SiC nanocomposites with very low thermal expansion coefficient. *J. Eur. Ceram. Soc.* 30 (15), 3219–3225.
- García-Moreno, O., Borrell, A., Bittmann, B., Fernández, A., Torrecillas, R., 2011. Alumina reinforced eucryptite ceramics: Very low thermal expansion material with improved mechanical properties. *J. Eur. Ceram. Soc.* 31 (9), 1641–1648.
- Ghaffari, M., Alizadeh, P., Rahimpour, M.R., 2012. Sintering behavior and mechanical properties of mica-diopside glass-ceramic composites reinforced by nano and micro-sized zirconia particles. *J. Non. Cryst. Solids* 358 (23), 3304–3311.
- Giovanardi, R., Montorsi, M., Ori, G., *et al.*, 2010. Microstructural characterisation and electrical properties of multiwalled carbon nanotubes/glass-ceramic nanocomposites. *J. Mater. Chem.* 20, 308–313.
- Gross, S.M., Federmann, D., Rimmel, J., Pap, M., 2011. Reinforced composite sealants for solid oxide fuel cell applications. *J. Power Sources* 196 (17), 7338–7342.
- Ko, H., Lee, H., Lee, J., *et al.*, 2005. US20050147866A1 – Solid Oxide Fuel Cell Sealant Comprising Glass Matrix and Ceramic Fiber and Method of Manufacturing the Same.
- Hench, L.L., Jones, J.R., 2015. Bioactive glasses: Frontiers and challenges. *Front. Bioeng. Biotechnol.* 3, 194.
- Hidayat, N., Istiqomah, Widiyanto, M.Y.H., *et al.*, 2017. Natural Silica Sand/Alumina Ceramic Composites: Promising Candidates for Fuel-Cell Sealants. In: IOP Conference Ser.: Mater. Sci. Eng. 202, 012060.
- Hongbing, Z., Chan, Z., Wenzhe, C., Minquan, W., 2005. Characterization and nonlinear optical property of a multi-walled carbon nanotube/silica xerogel composite. *Chem. Phys. Lett.* 411 (4–6), 373–377.
- Huan, Z., Zhou, J., Duszczek, J., 2010. Magnesium-based composites with improved in vitro surface biocompatibility. *J. Mater. Sci. Mater. Med.* 21, 3163–3369.
- Huan, Z.G., Leeftang, M.A., Zhou, J., Duszczek, J., 2011. ZK30-bioactive glass composites for orthopedic applications: A comparative study on fabrication method and characteristics. *Mater. Sci. Eng. B* 176 (20), 1644–1652.
- Huang, X., Zheng, X., Zhao, G., *et al.*, 2014. Microstructure and mechanical properties of zirconia-toughened lithium disilicate glass-ceramic composites. *Mater. Chem. Phys.* 143 (2), 845–852.
- Huang, Z., Luo, L., Liu, L., *et al.*, 2018. Effect of Al₂O₃ addition on the non-isothermal crystallization kinetics and long-term stability of BCABS sealing glass for IT-SOFCs. *J. Adv. Ceram.* 7, 380–387.
- Jung, B.H., Hwang, S.J., Kim, H.S., 2005. Glass-ceramic for low temperature co-fired dielectric ceramic materials based on La₂O₃-B₂O₃-TiO₂ glass with BNT ceramics. *J. Eur. Ceram. Soc.* 25, 3187–3193.
- Jurczyk, K., Jurczyk, M.U., Niespodziana, K., Jakubowicz, J., Jurczyk, M., 2011. Titanium-10 wt% 45S5 bioglass nanocomposite for biomedical applications. *Mater. Chem. Phys.* 131 (1–2), 540–546.
- Kim, S.H., Koh, J.H., 2008. ZnB₂-doped (Ba, Sr)TiO₃ ceramics for the low-temperature sintering process. *J. Eur. Ceram. Soc.* 28 (15), 2969–2973.
- Kumar, P.H., Singh, V.K., Kumar, P., Yadav, G., Chaturvedi, R.K., 2016. Effect of Al₂O₃ on leucite based bioactive glass ceramic composite for dental veneering. *Ceram. Int.* 42 (2), 3591–3597.
- Le, S., Sun, K., Zhang, N., *et al.*, 2006. Novel compressive seals for solid oxide fuel cells. *J. Power Sources* 161 (2), 901–906.
- Lee, J.C., Kwon, H.C., Kwon, Y.P., Lee, J.H., Park, S., 2007. Porous ceramic fiber glass matrix composites for solid oxide fuel cell seals. *Colloids Surf. A Physicochem. Eng. Asp.* 300 (1–2), 150–153.
- Li, Q., Cai, D., Yang, Z., *et al.*, 2019a. Effects of BN on the microstructural evolution and mechanical properties of BAS-BN composites. *Ceram. Int.* 45, 1627–1633.

- Li, Z., Peng, B., Zhang, T., *et al.*, 2019b. Improving sealing performance of borosilicate glass-ceramics for solid oxide fuel cell applications: Effect of AlN. *J. Eur. Ceram. Soc.* 39 (14), 4194–4201.
- Li, X., Feng, J., Jiang, Y., Lin, H., Feng, J., 2018. Preparation and properties of TaSi₂-MoSi₂-ZrO₂-borosilicate glass coating on porous SiCO ceramic composites for thermal protection. *Ceram. Int.* 44, 19143–19150.
- Li, Z., Khun, N.W., Tang, X.Z., Liu, E., Khor, K.A., 2017. Mechanical, tribological and biological properties of novel 45S5 Bioglass® composites reinforced with in situ reduced graphene oxide. *J. Mech. Behav. Biomed. Mater.* 65, 77–89.
- Liu, L., Ye, F., Zhou, Y., Zhang, Z., 2010. Microstructure compatibility and its effect on the mechanical properties of the α -SiC/ β -Si₃N₄ co-reinforced barium aluminosilicate glass ceramic matrix composites. *Scr. Mater.* 63, 166–169.
- Ma, J., Ye, F., Liu, L., Zhang, H., 2009. Processing and mechanical properties of short fibers/Si₃N₄p reinforced BaO · Al₂O₃ · 2SiO₂ ceramic matrix composites. *Mater. Sci. Eng. A* 520, 158–161.
- Ma, J., Ye, F., Liu, L., Zhang, H., 2010. Processing and microstructure characterization of liquid-phase-sintered, α -SiC matrix composites. *J. Alloy. Compd.* 493 (1–2), L15–L18.
- Makurumje, P., Monteverde, F., Sigalas, I., 2017. Self-generating oxidation protective high-temperature glass-ceramic coatings for Cf/C-SiC-TiC-TaC UHTC matrix composites. *J. Eur. Ceram. Soc.* 37 (10), 3227–3239.
- Montazerian, M., Zanotto, E.D., 2017. Bioactive and inert dental glass-ceramics. *J. Biomed. Mater. Res. - Part A* 105 (2), 619–639.
- Montazerian, M., Alizadeh, P., Eftekhari Yekta, B., 2008a. Pressureless sintering and mechanical properties of mica glass-ceramic/Y-PSZ composite. *J. Eur. Ceram. Soc.* 28 (14), 2687–2692.
- Montazerian, M., Alizadeh, P., Eftekhari Yekta, B., 2008b. Processing and properties of a mica-apatite glass-ceramic reinforced with Y-PSZ particles. *J. Eur. Ceram. Soc.* 28 (14), 2693–2699.
- Morsi, R.M.M., Margha, F.H., Hamzawy, E.M.A., 2019. Preparation and electrical characterization of Zn-titanate/borosilicate glass composites. *Silicon* 11, 1845–1852.
- Mukhopadhyay, A., Otieno, G., Chu, B.T.T., *et al.*, 2011. Thermal and electrical properties of aluminoborosilicate glass-ceramics containing multiwalled carbon nanotubes. *Scr. Mater.* 65 (5), 408–411.
- Müller, R., Meszaros, R., Peplinski, B., *et al.*, 2009. Dissolution of alumina, sintering, and crystallization in glass ceramic composites for LTCC. *J. Am. Ceram. Soc.* 92 (8), 1703–1708.
- Ning, J., Zhang, J., Pan, Y., Guo, J., 2003. Fabrication and mechanical properties of SiO₂ matrix composites reinforced by carbon nanotube. *Mater. Sci. Eng. A* 357 (1–2), 392–396.
- Otieno, G., Koos, A.A., Dillon, F., *et al.*, 2010. Processing and properties of aligned multi-walled carbon nanotube/aluminoborosilicate glass composites made by sol-gel processing. *Carbon* 48 (8), 2212–2217.
- Porwal, H., Grasso, S., Cordero-Arias, L., *et al.*, 2014. Processing and bioactivity of 45S5 Bioglass®-graphene nanoplatelets composites. *J. Mater. Sci. Mater. Med.* 25 (6), 1403–1413.
- Porwal, H., Estili, M., Grünewald, A., *et al.*, 2015. 45S5 Bioglass®-MWCNT composite: Processing and bioactivity. *J. Mater. Sci. Mater. Med.* 26 (6), 199.
- Rampf, M., Höland, W., 2019. Glass-ceramics for dental restoration. In: Pawelec, K.M., Planell, J.A. (Eds.), *Bone Repair Biomaterials: Regeneration and Clinical Applications*. Elsevier, pp. 329–340.
- Ratner, B.D., 2019. Biomaterials: Been there, done that, and evolving into the future. *Annu. Rev. Biomed. Eng.* 21, 171–191.
- Ren, X., Li, H., Fu, Q., Li, K., 2014. Ultra-high temperature ceramic TaB₂-TaC-SiC coating for oxidation protection of SiC-coated carbon/carbon composites. *Ceram. Int.* 40 (7), 9419–9425.
- Rizwan, M., Hamdi, M., Basirun, W.J., 2017. Bioglass® 45S5-based composites for bone tissue engineering and functional applications. *J. Biomed. Mater. Res. A* 105 (11), 3197–3223.
- Bosch, R.H., De Rose, A.J., Fleming, C.D., *et al.*, 2010. EP2028707A3 – Glass Seal With Ceramic Fiber for a Solid Oxide Fuel Cell Stack.
- Sasikala, T.S., Suma, M.N., Mohanan, P., Pavithran, C., Sebastian, M.T., 2008. Forsterite-based ceramic-glass composites for substrate applications in microwave and millimeter wave communications. *J. Alloy. Compd.* 461, 555–559.
- Schepers, E., Ducheyne, P., De Clercq, M., 1989. Interfacial analysis of fiber-reinforced bioactive glass dental root implants. *J. Biomed. Mater. Res.* 23, 735–752.
- Schickel, K., Zurlinden, K., Bergmann, C., *et al.*, 2011. Synthesis of novel tricalcium phosphate-bioactive glass composite and functionalization with rhBMP-2. *J. Mater. Sci. Mater. Med.* 22 (5), 763–771.
- Solntsev, S.S., 2011. High-temperature composite materials and coatings on the basis of glass and ceramics for aerospace technics. *Russ. J. Gen. Chem.* 81, 992–1000.
- Subhani, T., Shaffer, M.S.P., Boccaccini, A.R., 2013. Chapter 7 – Carbon nanotube (CNT) reinforced glass and glass-ceramic matrix composites. In: Banerjee, R., Manna, I. (Eds.), *Ceramic Nanocomposites*. Elsevier Inc, pp. 208–256.
- Bors, S.L., Winchester, S.C., Saltzberg, M.A., Bergna, H.E., 1992. Process for Making Chemically Stabilized Cristobalite. European Patent No. 0482534A2.
- Syed, M.R., Khan, M., Sefat, F., *et al.*, 2019. Chapter 17 – Bioactive glass and glass fiber composite: Biomedical/dental applications. In: Kaur, G. (Ed.), *Biomedical, Therapeutic and Clinical Applications of Bioactive Glasses*. Elsevier, pp. 467–495.
- Taniguchi, S., Kadowaki, M., Yasuo, T., *et al.*, 2000. Improvement of thermal cycle characteristics of a planar-type solid oxide fuel cell by using ceramic fiber as sealing material. *J. Power Sources* 90 (2), 163–169.
- Thomas, B.J.C., Shaffer, M.S.P., Boccaccini, A.R., 2009. Sol-gel route to carbon nanotube borosilicate glass composites. *Compos. Part A Appl. Sci. Manuf.* 40, 837–845.
- Timurkutluk, B., Altan, T., Celik, S., Timurkutluk, C., Palaci, Y., 2019. Glass fiber reinforced sealants for solid oxide fuel cells. *Int. J. Hydrog. Energy* 44 (33), 18308–18318.
- Walker, L.S., Corral, E.L., 2014. Self-generating high-temperature oxidation-resistant glass-ceramic coatings for C-C composites using UHTCs. *J. Am. Ceram. Soc.* 97 (9), 3004–3011.
- Wang, M., Zuo, R., Meng, W., Liu, Y., 2011. Sol-gel derived CaO-B₂O₃-SiO₂ glass/CaSiO₃ ceramic composites: Processing and electrical properties. *J. Mater. Sci. Mater. Electron.* 22, 843–848.
- Wang, Y., Dong, L., Zhang, J., *et al.*, 2017. The application and development of ultra low expansion glass-ceramic in aerospace area. In: Nardelli, C., Xue, S., Yang, H. (Eds.), *AOPC 2017: Space Optics and Earth Imaging and Space Navigation*. SPIE, p. 20.
- Waser, R., 1992. *Ceramic materials for electronics: Processing, properties, and applications*, 2. ed. R. C. Buchanan (Ed.), Marcel Dekker Inc., New York 1991; XII, 532 pp., hardcover, \$ 166.75, ISBN 0-8247-8194-5. *Adv. Mater.* 4 (4).
- Wei, J., Pećanac, G., Malzbender, J., 2015. Mechanical behavior of silver reinforced glass-ceramic sealants for solid oxide fuel cells. *Ceram. Int.* 41 (10), 15122–15127.
- Winkel, A., Meszaros, R., Reinsch, S., *et al.*, 2012. Sintering of 3D-printed glass/HAp composites. *J. Am. Ceram. Soc.* 95, 3387–3393.
- Xia, L., Zhao, G.L., Huang, X.X., *et al.*, 2013. Effect of graphite intercalation compounds in the interfacial zone on the mechanical and thermal properties of unidirectional carbon fiber reinforced spodumene composite. *Acta Mater.* 61, 3522–3532.
- Xia, L., Jin, F., Zhang, T., *et al.*, 2015. Enhanced oxidation resistance of carbon fiber reinforced lithium aluminosilicate composites by boron doping. *Corros. Sci.* 99, 240–248.
- Xie, X., Cerruti, M., 2015. Graphene-bioceramic composites. In: Antoniac, I.V. (Ed.), *Handbook of Bioceramics and Biocomposites*. Springer International Publishing, pp. 431–467.
- Xu, H., Pan, Y., Zhu, Y., Kou, H., Guo, J., 2009. Transparent multi-walled carbon nanotube-silica composite prepared by hot-pressed sintering and its nonlinear optical properties. *J. Alloy. Compd.* 481 (1–2), L4–L7.
- Yang, H., Wu, S., Hu, J., *et al.*, 2011. Influence of nano-ZrO₂ additive on the bending strength and fracture toughness of fluoro-silicic mica glass-ceramics. *Mater. Des.* 32 (3), 1590–1593.

- Ye, F., Yang, J.M., Zhang, L.T., *et al.*, 2001. Fracture behavior of SiC-Whisker-reinforced barium aluminosilicate glass-ceramic matrix composites. *J. Am. Ceram. Soc.* 84, 881–883.
- Ye, F., Chen, S., Iwasa, M., 2003a. Synthesis and properties of barium aluminosilicate glass-ceramic composites reinforced with in situ grown Si_3N_4 whiskers. *Scr. Mater.* 48, 1433–1438.
- Ye, F., Gu, J.C., Zhou, Y., Iwasa, M., 2003b. Synthesis of $\text{BaAl}_2\text{Si}_2\text{O}_8$ glass-ceramic by a sol-gel method and the fabrication of SiCp/ $\text{BaAl}_2\text{Si}_2\text{O}_8$ composites. *J. Eur. Ceram. Soc.* 23 (13), 2203–2209.
- Ye, F., Liu, L., Wang, Y., *et al.*, 2006. Preparation and mechanical properties of carbon nanotube reinforced barium aluminosilicate glass-ceramic composites. *Scr. Mater.* 55 (10), 911–914.
- Ye, F., Liu, L., Huang, L., 2008. Fabrication and mechanical properties of carbon short fiber reinforced barium aluminosilicate glass-ceramic matrix composites. *Compos. Sci. Technol.* 68 (7–8), 1710–1717.
- Ye, F., Liu, L., Zhang, J., Iwasa, M., Su, C.L., 2005. Synthesis of silicon nitride-barium aluminosilicate self-reinforced ceramic composite by a two-step pressureless sintering. *Compos. Sci. Technol.* 65, 2233–2239.
- Zanotto, E.D., 2010. A bright future for glass-ceramics. *Am. Ceram. Soc. Bull.* 89 (8), 19–27.
- Zawrah, M.F., Khattab, R.M., El-Kheshen, A.A., El Fadaly, E., 2017. Sintering and properties of borosilicate glass/Li-Na-K-feldspar composites for electronic applications. *Ceram. Int.* 43 (17), 15068–15073.
- Zhao, Y., Malzbender, J., Gross, S.M., 2011. The effect of room temperature and high temperature exposure on the elastic modulus, hardness and fracture toughness of glass ceramic sealants for solid oxide fuel cells. *J. Eur. Ceram. Soc.* 31 (4), 541–548.
- Zheng, C., Feng, M., Zhen, X., Huang, J., Zhan, H., 2008. Materials investigation of multi-walled carbon nanotubes doped silica gel glass composites. *J. Non. Cryst. Solids.* 354 (12–13), 1327–1330.
- Zhu, T., Zhu, M., Zhu, Y., 2020. Fabrication of forsterite scaffolds with photothermal-induced antibacterial activity by 3D printing and polymer-derived ceramics strategy. *Ceram. Int.* 46 (9), 13607–13614.

High Performance Fibers

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Fiber Development

High performance synthetic fibers often resemble textile fibers in appearance and some are of the same chemical composition; however, they are produced so as to optimize their mechanical properties to achieve enhanced performance (Bunsell, 2009; Hearle, 2001; Chawla, 1998; Moncrieff, 1979).

Such fibers are used in structures for which their flexibility, lightness, and very high mechanical properties, compared to bulk materials, make them indispensable. These fibers have higher strengths and often higher elastic moduli than conventional textile fibers due to the manufacturing processes employed and also, in many cases, due to their molecular or atomic structures. In the case of some high performance fibers, their properties can attain almost the limits of what is physically possible so that very high moduli, even up to that of graphite, can be achieved. Some fibers have been developed to possess great thermal stability for uses at temperatures above the limits at which high performance metals can be used. Although stiff along their lengths fibers are flexible when bent because of their small diameters, which are usually of the order of 10 μm . They are used in applications including high performance tethering ropes, flexible architectural structures, reinforced elastomers, and fiber reinforced composites.

The commercial development of synthetic fibers began in the 1930s with the production of glass fibers in the USA. Glass and glass fibers have approximately the Young's modulus and density of aluminum. Although fibers made from regenerated cellulose, from wood, or other plants, were produced, first in France, toward the end of the nineteenth century and are known as rayon or viscous rayon the first truly synthetic polymeric fibers were produced in 1938. These were polyamide 6.6, developed in the USA and polyamide 6 fibers produced in Germany. These polyamide, or 'nylon' fibers, together with polyester fibers developed in Great Britain in the 1940s are the most important synthetic textile fibers produced. Although of low stiffness, they were the first of a family of organic fibers which have been developed with elastic moduli rivaling and even exceeding that of steel, but with only a fifth or less of the weight. These organic fibers find, however, many industrial applications as in tire reinforcement and anchor lines for off-shore oil platforms. Boron and silicon carbide fibers made by CVD onto a filament of tungsten or carbon were first produced in the early 1960s first in the USA and then in France and Russia. They have the density of glass but twice the Young's modulus of steel. Despite their remarkable properties boron fibers find very limited use because of their high cost. Silicon carbide fibers made by chemical vapor deposition are principally of interest for reinforcing titanium for jet engine applications. Both types of fibers have large diameters of 140 μm which greatly reduces their flexibility and this also limits their use.

Carbon fibers, with a density of a quarter that of steel, were first produced in Great Britain in the middle 1960s. They are made by the pyrolysis of polyacrylonitrile (PAN) precursor fibers and commonly have moduli up to one and half times the modulus of steel but can be up to three times stiffer. An alternative process developed in the 1970s in the USA uses the pitch residue from oil refining or the coking of coal to give fibers with moduli approaching that of graphite. Fine ceramic fibers, for structural applications, started to appear at the end of the 1970s and in the 1980s. One group of these fibers developed in Great Britain and in USA, is based on alumina whereas others developed in Japan are based on silicon carbide. These fibers have Young's moduli ranging from that of steel to twice this value with densities less than half that of steel.

Most fibers have diameters of the order of 10 μm , which can be compared to 70 μm which is the diameter of a human hair. Exceptions however are the boron and SiC fibers made by chemical vapor deposition (CVD) onto cores, which are twice as thick as hair. The fineness of fibers allows even the stiffest of materials to be made in a flexible form as bending stiffness is related to the fourth power of the diameter. However many high modulus fibers are completely elastic, at least at room temperature, and are therefore brittle in tension and in bending. They are most suited to be used as reinforcements in composite materials. The high performance polymer fibers are also used as reinforcements, such as in tires and other composites, but they are not brittle as they deform plastically in compression. They show great toughness which can be exploited in structures such as cables and structures which must resist impacts.

Organic Fibers

Polyamide (PA) or 'nylon' fibers were developed in 1938 by Du Pont in the USA and in Germany by I.G. Farben. These fibers are based upon amide groups ($-\text{C}(\text{O})\text{NH}-$) contained within a chain of carbon atoms making up a backbone of atoms linked by strong covalent bonds (Table 1). However the molecules are linear and can bend and rotate at each bond so that the molecules are not perfectly aligned parallel to the fiber axis, which results in a low Young's modulus. Around 1947 polyethylene terephthalate (PET) or 'polyester' fibers were produced in Great Britain and have become the most widely produced synthetic fibers. Table 1 shows that the polyester molecule contains an aromatic ring which stiffens it compared to the very flexible polyamide structure.

Table 1 Molecular composition of high performance organic fibers

Fiber type	Repeat unit in the macromolecule	Maximum elastic modulus (GPa)	Melting or decomposition temperature °C
Polyamide 6 (Nylon 6)	$\left[\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO} \right]_n$	4	230
Polyamide 6/6 (Nylon 6.6)	$\left[\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO} \right]_n$	5	260
Polyethylene terephthalate (Polyester)	$\left[\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2 \right]_n$	18	260
Polyethylenene naphthalate (PEN)	$\left[\text{O}-\text{C}(=\text{O})-\text{C}_{10}\text{H}_6-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2 \right]_n$	35	275
Vectran	$\left[\text{O}-\text{C}_6\text{H}_4-\text{C}(=\text{O}) \right]_x \left[\text{O}-\text{C}_{10}\text{H}_6-\text{C}(=\text{O}) \right]_y$	80	330
Poly(<i>m</i> -phenylenediamine-isophthalamide) Nomex	$\left[\text{NH}-\text{C}_6\text{H}_3(\text{NH})-\text{CO} \right]_n$	17	400
Poly-paraphenylene/3,4-diphenylether ter- ephthalamide (Technora)	$\left(\text{HN}-\text{C}_6\text{H}_4-\text{NHOC}-\text{C}_6\text{H}_4-\text{CO} \right)_m \left(\text{HN}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_3-\text{NHOC}-\text{C}_6\text{H}_4-\text{CO} \right)_n$	70	500
Poly(<i>p</i> -phenylene terephthalamide) (Kevlar)	$\left[\text{HN}-\text{C}_6\text{H}_4-\text{NH}-\text{CO}-\text{C}_6\text{H}_4-\text{CO} \right]_n$	135	550
Poly(<i>p</i> -phenylene benzobisoxazole) (PBO) (Zylon)	$\left[\text{C}_6\text{H}_4-\text{C}_2\text{N}_2\text{O}_2 \right]_n$	280	650
Poly{2,6-dimidazo [4,5-b:4'.5'-e] pyridinylene-1,4 (2,5-dihydroxy) phenylene} (PIPD) M5	$\left[\text{C}_8\text{H}_4\text{N}_4\text{O}_2 \right]_n$	330	650

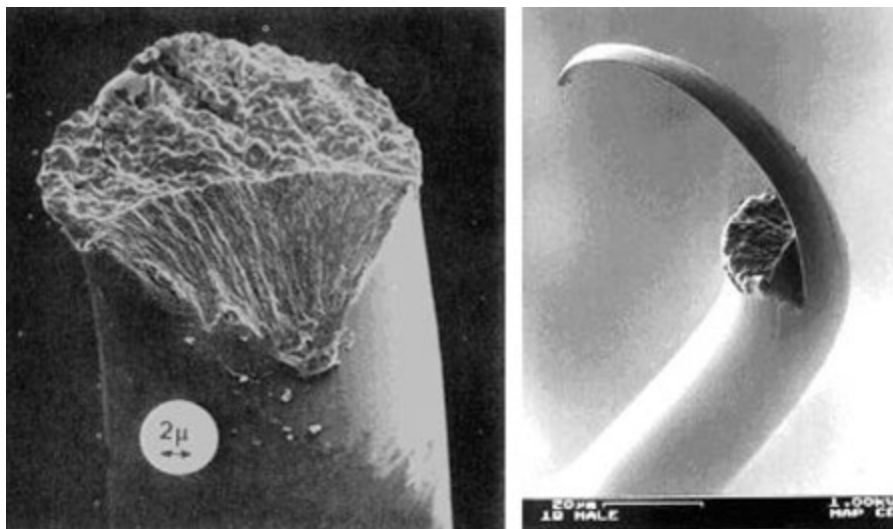


Figure 1 Fracture morphologies: Left, a polyamide 66 fiber broken in tension. Right, a polyamide fiber broken in fatigue.

Both polyamide and polyester fibers melt at around 260 °C. Although both of these latter fibers melt at around the same temperature, it is significant that the polyester fiber, which contains the aromatic rings, shows much higher resistance to discoloration at raised temperatures than does the polyamide fiber. A fiber which is related to PET fibers is the polyethylenenaphthalate (PEN) fiber. [Table 1](#) shows that this latter fiber is based on a molecule which has two aromatic rings which further increases the rigidity of the fiber. The three fibers mentioned above are made by drawing from the melt through a spinneret. The drawing rate determines the final properties. An undrawn fiber will have a strain to failure of some hundreds of a percent and tensile loading will produce not only a very high strain to failure but deformation will involve striction of the filament. Striction is when the diameter of the filament is locally reduced under load and in this region the molecular structure becomes aligned parallel to the fiber axis and the loading direction. Further loading induces an increase in the striction until all the specimen is reduced in cross section and the molecular structure is largely oriented parallel to the fiber axis. Fibers for textile end-uses are drawn during production so as to produce filaments with enhanced molecular orientation, higher strengths, and longitudinal stiffness but with reduced strains to failure, generally of the order of 30%. Striction is not usually seen with this type of fiber. High performance versions of PA and PET fibers, which are destined for industrial applications, are more highly drawn with further reduced strains to failure in the region of 20% for the former and 15% for the latter. PEN fibers are only produced as high performance industrial fibers and have strains to failure of around 6%. The molecular morphology of these fibers consists of microfibrils, with transverse dimensions of around 5 nm, arranged more or less parallel to the fiber axis. Regions within the microfibrils are composed of well ordered arrangements of molecules which are folded as in a concertina. The rest of the structure is made up of less well ordered regions so that the overall molecular structure is semi-crystalline with a crystalline content generally of the order of 40%.

A typical tensile fracture morphology of one of the above thermoplastic fibers is shown in [Figure 1](#) (left). Images of fiber failure morphologies have been cataloged by [Hearle et al. \(2006\)](#). It can be seen that the fracture surface consists of two regions; an initial inclined region corresponding to initiation at the surface and slow crack propagation normal to the fiber axis. The crack opens because of plastic deformation ahead of the crack. Rapid failure finally occurs when the remaining part of the section can no longer support the applied stress. Under particular cyclic conditions the same fiber fails in fatigue and one half of the fatigue break is shown in [Figure 1](#) (Right). The crack has initiated at or near the surface but instead of running normal to the fiber axis it has been deviated to run at a slight angle to the fiber axis, penetrating into the fiber section so that the remaining section finally fails by the tensile process. A particularity of this type of failure is that the minimum load has to be lower than a threshold level so that raising the cyclic loading pattern can stop fatigue failure.

Higher melting points or decomposition temperatures and much higher Young's moduli have been achieved by including more aromatic rings in the molecular main chain and by aligning these very rigid molecules parallel to the fiber ([Table 1](#)). These types of polymers are made by the technology of liquid crystal spinning, as illustrated in [Figure 2](#). Overall, within the melt or solution, the molecular alignment is random however orientation is achieved not by drawing but through the shearing of the solution when the solution passes through the spinneret. Molecular alignment in these fibers occurs because of the very stiff molecules are aligned preferentially parallel to the fiber axis by the shear forces in the spinneret and held together by hydrogen or Van der Waals' bonds. The straighter the molecule the higher the modulus achieved. These liquid crystal polymers do not usually lend themselves to melt spinning and are usually spun from a solution although the Vectran fiber, produced since the 1970s by Hoechst-Celene, is melt spun.

Vectran is a liquid crystal polyester based fiber which, as can be seen from [Table 1](#), has a molecular structure which is not perfectly straight. It is produced by the acetylation polymerization of *p*-hydroxybenzoic acid and 6-hydroxy-2-naphthoic. The good alignment of its molecular structure gives higher rigidity than that found with other polyester fibers but the form of the molecule

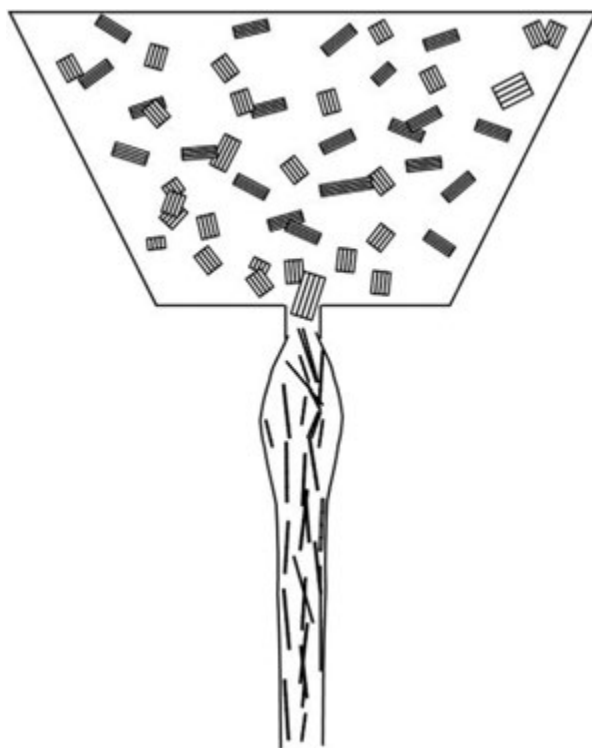


Figure 2 Spinning from a liquid crystal solution.

determines its ultimate rigidity. The fiber is the only melt spun liquid crystal fiber which is available and finds uses in applications such as sail cloth because of its rigidity and resistance in bending.

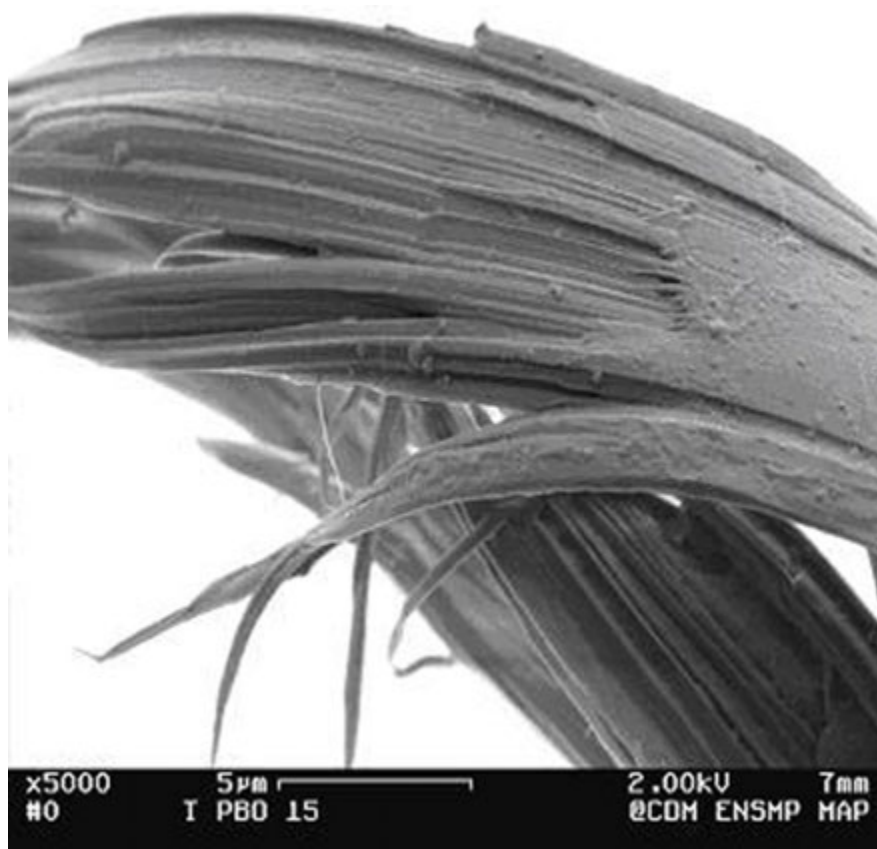
The aramid family of fibers are made up of aromatic polyamides. Nomex was the first fiber of this family, produced in the 1960s by Du Pont. Nomex is a meta-aramid which accounts for an elastic modulus little different from high performance PET but higher temperature resistance. Nomex is widely used for clothing for potentially hazardous conditions where fire is a danger. It is also widely used in paper form as a honey-comb structure in the aeronautical industry. Para-aramids can possess remarkably high Young's moduli, more than 20 times that of conventional polyamide fibers and twice that of glass, as shown in [Table 2](#). This group of fibers, first introduced as the Kevlar fiber from Du Pont, has been available since 1972. These fibers are made from a mesophase or liquid crystal solution of poly (*p*-phenylene terephthalamide (PPTA)) dissolved in concentrated sulfuric acid. If the appropriate concentration is made the solution consists of locally organized PPTA molecules which align with one another. The structure of aramid fibers is very well ordered, however they are highly anisotropic which results in them being weak in all directions except parallel to the fiber axis. A PPTA fiber called kevlar 29, which is used as a reinforcement for specialty tires and also high performance cables has been shown to possess a longitudinal modulus of 80 GPa but a transverse modulus of only 3 GPa ([Wollrett-Blitz et al., 2014](#)). The authors of this chapter obtained their results by a comparison of longitudinal and transverse tests on single fibers ([Wollrett-Blitz et al., 2016](#)). As a consequence of this anisotropy failure of these fibers is nearly always highly fibrillar although local creasing of the fiber can cause a more restricted failure morphology.

In tension Kevlar fibers are five times as strong as steel in air for the same weight. The fibers show little tendency to deform plastically in tension but when they are bent the side in compression undergoes plastic deformation which allows them to accommodate the imposed strain. This results in the fiber being difficult to cut as well as giving great tenacity and resistance to impact loading. Their highly anisotropic behavior means that the fibers are not used in primary loading structures subjected to compressive forces. Aramid fibers, other than Kevlar, which are commercially available are the Twaron fiber developed by Akzo in Holland, now produced by Teijin Twaron, also in Holland and the Technora fiber from Teijin in Japan. Technora is derived from poly-paraphenylene/3,4'-diphenylether terephthalamide, which, as can be seen from [Table 1](#), is not a straight molecule and as a consequence the fiber has an intermediate modulus of around 65 GPa.

In 1998 the Toyobo Company began the commercial production of the Zylon fiber. Its chemical composition is Poly(*p*-phenylene benzobisoxazole (PBO)). The fiber has remarkable properties, in tension, as can be seen from [Table 2](#). It has a Young's modulus which is 40% higher than that of steel with the density of an engineering plastic. Its Young's modulus is twice that of kevlar, since unlike kevlar, the PBO molecule, shown in [Table 1](#), is completely straight thus making the most of the covalent bonds in its structure. PBO fibers however suffer from poor compressive strength as molecular interchain cohesion is assured by Van der Waals' bonds. As can be seen from [Figure 3](#), the fiber fibrillates on failure due to its inherent anisotropy.

Table 2 Comparison of organic fiber properties

Fiber	Diameter (μm)	Specific gravity	Young's modulus E (GPa)	Strength σ (GPa)	Strain to failure ϵ (%)	Specific modulus E/ρ (GPa/g cm^{-3})	Specific strength σ/ρ (GPa/g cm^{-3})
Polyamide 66	30	1.14	<5	1	20	4	0.9
Polyester	20	1.38	15	1	15	10	0.7
Pentex	28	1.4	35	1.1	6	25	0.8
Vectran	20	1.4	65	3.8	3.3	46	2
Nomex	15	1.4	17	0.7	20	12	0.5
Technora	12	1.39	70	3	4.4	50	2.2
Kevlar 49	12	1.45	135	3	4.5	93	2.1
Zylon	12	1.56	280	5.8	2.5	180	3.7
Polyethylene	38	0.96	117	3	3.5	120	3.1

**Figure 3** Detail of the splitting of a Zylon *p*-phenylene benzobisoxazole (PBO) fiber.

Magellan International in collaboration with Du Pont in the US has taken over the development of a fiber, created by the researchers at Akzo in Holland, which at present is called M5. The fiber is said to possess a Young's modulus of 330 GPa or even higher, but, above all, superior compressive properties, such as molecular interchain cohesion, are ensured by hydrogen bonds. The down side of this however may be an increased propensity to absorb water. This fiber has a slightly higher specific gravity of 1.7 compared to other very high modulus organic fibers. Compressive strength is said to be four times higher than that of the PBO fibers and nearly three times higher than kevlar fibers. However the M5 fiber is not yet in general production.

The production of aramid and similar organic fibers involves complex and expensive chemistry however the high performance properties of the fibers is a result of the molecules being aligned parallel to the fiber's axis. Simpler polymers could, if all their molecules were aligned parallel to one another, give materials with the characteristics of high performance materials. Such fibers can be made using a sol-gel in which polyethylene is dissolved in a solvent to make a very dilute solution which is then spun. Such fibers were first produced in Holland by DSM, under the name Dyneema, and then Allied (now Honeywell) in the USA under the name Spectra. The fibers consist of polyethylene molecules which are aligned parallel to the fiber axis with molecular interchain cohesion assured by Van der Waals' forces. They have properties in tension rivaling those of the aramid fibers with a lower specific

Table 3 Compositions (% wt), density, and mechanical properties of various glasses used in glass fiber production

Glass type	<i>E</i>	<i>S</i>	<i>C</i>	<i>D</i>
SiO ₂	54	65	65	74
Al ₂ O ₃	15	25	4	
CaO	18		14	0.2
MgO	4	10	3	0.2
B ₂ O ₃	8		5.5	23
F	0.3			
Fe ₂ O ₃	0.3			
TiO ₂				0.1
Na ₂ O			8	1.2
K ₂ O	0.4		0.5	1.3
Density	2.54	2.49	2.49	2.16
Strength (20 °C) GPa	3.5	4.65	2.8	2.45
Elastic modulus (20 °C) GPa	73.5	86.5	70	52.5
Failure strain (20 °C) %	4.5	5.3	4.0	4.5

gravity (0.97). However their properties in compression are poor. These fibers are limited in temperature to a maximum of 120 °C as they melt around 150 °C and suffer from creep.

Glass Fibers

In 1931 two American firms, which were later to fuse to make the Owens Corning Fiberglas Corporation, developed a commercial method of spinning glass filaments from the melt through spinnerets. The melting point of the most widely used glass is around 1200 °C and the spinnerets are made from platinum. The holes in the spinnerets have diameters of 1 or 2 mm and drawing the filaments produces fibers having diameters usually between 5 and 15 μm. The spinnerets usually contain several hundred holes so that a strand of glass fibers is produced. Several type of glass exist but all are based on silica (SiO₂) which is combined with other elements to create specialty glasses. The compositions and properties of the most common types of glass fibers are shown in Table 3. The most widely used glass for fiber reinforced composites is E-glass. S-glass, which contains a greater amount of alumina, is used to make glass fibers with superior mechanical properties whereas type C has a much reduced alumina content and resists an acid environment. Type D, which has no alumina, but a high content of boron oxide is used for its dielectric properties.

The strength of glass fibers is usually much higher than that of bulk glass as they contain many fewer weakening flaws. However to prevent damage by abrasion they are coated with a protective size which also holds the strand together, acts as a bonding agent with resins and sometimes as an antistatic agent. The structure of glass fibers is amorphous with ionic bonds linking the atomic structure. There appears to be no appreciable residual stresses within the fiber and the structure is isotropic, which means that the Young modulus of glass in fiber form is the same as in bulk form. Glass fibers are cheaper than most other relatively high modulus fibers and do not require very specialized machines or techniques to handle them. Their elastic modulus is however low compared to many other fibers and the specific gravity of glass is relatively high. Glass fibers are most commonly used to reinforce resins which limits their use to less than 300 °C (usually less than 120 °C). Above this range densification of the glass occurs and the fibers become increasingly susceptible to slow crack growth from surface defects. Strength increases with decreasing temperature.

Deposited Fibers

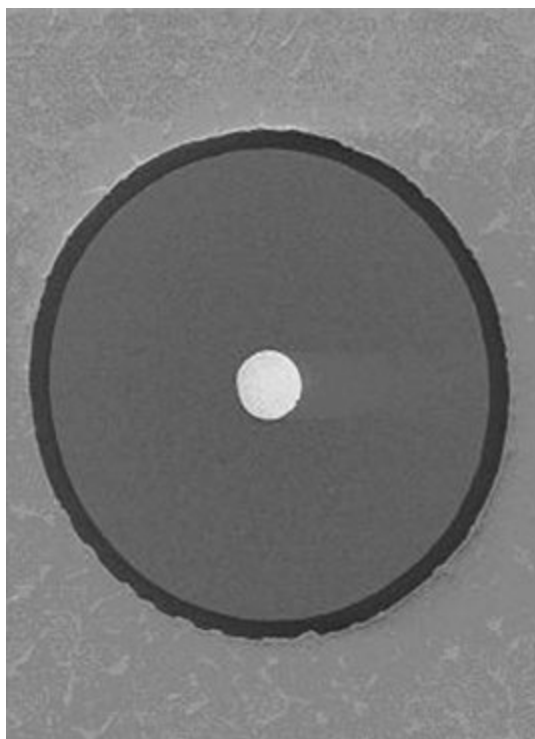
Boron, the fifth element in the Periodic table, is the lightest element with which it is practical to make fibers and they were first produced in the USA at the beginning of the 1960s. Boron fibers are made by chemical vapor deposition in which a mixture of boron trichloride (BCl₃) and hydrogen (H₂) at around 1000 °C passes over a continuous tungsten filament heated by electric current. Boron is deposited on the tungsten filament which has a diameter of 12 μm.

The fibers have Young's moduli exceeding 400 GPa as shown in Table 4 and very high strength both in tension and in compression. This latter quality is enhanced by their large diameter of 140 μm. A cross section of a boron fiber reveals its tungsten core and boron mantle. Boron fibers have proved to be a good reinforcement for light metal alloys particularly when the fiber was protected by a coating of SiC or B₄C however their high cost of production has limited wide use of this type of fiber.

Silicon carbide fibers are also produced by CVD using various chlorosilanes such as CH₃ Si Cl₃ which gives 3HCl and SiC which is deposited onto a tungsten or carbon core. They are of primary interest for the reinforcement of titanium and intermetallic matrices. Fibers with diameters between 100 and 140 μm, are made. The fibers, until recently produced by Textron and now produced by Specialty Materials Inc., are known as SCS-*n*, where *n* is the number of microns of surface coating added onto the diameter to protect it during composite manufacture. SiC fibers have a Young's modulus greater than 400 GPa, as

Table 4 Properties of ceramic fibers produced by chemical vapor deposition

Fiber type	Manufacturer	Trade mark	Composition	Diameter (μm)	Density (g cm^{-3})	Strength (GPa)	Strain to failure (%)	Young's modulus (GPa)
SiC	Specialty materials (formerlyTextron)	SCS-6	SiC on carbon	140	2.7–3.3	3.4–4.0	0.8–1	427
	DERA	Sigma	SiC on tungsten	100	3.4	3.4–4.1	0.8	400–410
B	Specialty materials (formerlyTextron)		Boron on tungsten	100–140	2.57	3–6	1	380–400

**Figure 4** Cross section of a SiC fiber made by chemical vapor deposition (CVD) showing the tungsten core.

shown in [Table 4](#) and can be used to around 1000 °C. [Figure 4](#) shows the cross section of a SiC fiber made by CVD showing the tungsten core.

Carbon Fibers

Carbon is the sixth lightest element and the carbon–carbon covalent bond is the strongest in nature. Many fibers can be converted into carbon fibers, the basic requirement being that the precursor fiber carbonizes rather than melts when heated ([Kaverov et al., 1995](#)). Carbon fibers developed in the USA in the 1950s and early 1960s used fibers regenerated from cellulose. This proved a slow process as the carbon yield from cellulose is only 24% and the atomic structure was poorly organized. Their mechanical properties were not high however such fibers have high thermal conduction properties and are still used in carbon–carbon heat shields and brake pads.

Most carbon fibers though are made by a process developed first in Great Britain and then in Japan in the late 1960s based on the conversion of a modified form of acrylic textile fiber. PAN has a carbon yield of 49% and the properties of carbon fibers made by this route depend on the temperature of pyrolysis. The PAN fibers, held in tension, are first heated to about 250 °C in air which cross links the structure and makes it infusible. Further heating in an inert atmosphere to above 1000 °C eliminates most of the elements other than carbon and around 1500 °C a fully carbon fiber is achieved. At this temperature the strength of carbon fibers reaches a maximum. Above this temperature the basic carbon structural units increase in size which results in a fall in strength whereas the Young's modulus increases continuously with increasing temperature up to around 3000 °C. The structure which results from the pyrolysis of PAN is highly anisotropic, with the basic structural units formed by the carbon atom groups aligned

parallel to the fiber axis. There is complete rotational disorder in the radial direction and the relatively poor stacking of the carbon atoms means that a graphite structure is never achieved. The structure contains pores which account for the density of the fibers being less than that of fully dense carbon. **Table 5** shows some typical properties of carbon fibers, however there exists a considerable range of properties for these fibers. **Figure 5** shows a early PAN based carbon fiber which reveals the general appearance of the precursor fiber. More recently produced carbon fibers are smoother in appearance which helps to increase strength by reducing stress raising irregularities in the surface.

Carbon fibers made from pitch based precursors were developed in the USA in the early 1970s and in Japan in the 1980s. The high carbon yield of pitch which approaches 90% makes it an attractive and cheap source for making carbon fiber precursors. Cost

Table 5 Typical characteristics of carbon fibers

<i>Fiber type</i>	<i>Manufacturer</i>	<i>Trade mark</i>	<i>Diameter (μm)</i>	<i>Density (g cm^{-3})</i>	<i>Strength (GPa)</i>	<i>Strain to failure (%)</i>	<i>Young's modulus (GPa)</i>
Ex PAN							
High strength	Toray	T400H	7	1.80	4.4	1.8	250
High strength	Toray	T1000	5	1.82	7.1	2.4	294
High modulus	Toray	M46J	7	1.84	4.2	1.0	436
High modulus	Toray	M60J	5	1.94	3.9	0.7	588
Ex Pitch							
Oil derived pitch	Nippon graphite fiber	Granoc CN-35	11	2.10	3.6	1.0	350
Oil derived pitch-high modulus	Nippon graphite fiber	Granoc YS-95 A	11	2.16	3.5	0.4	920
Coal tar pitch	Mitsubishi chemicals	Dialead K1352U	10	2.12	3.6	0.58	620
Coal tar pitch	Mitsubishi chemicals	Dialead K13B2U	10	2.16	3.9	0.48	830

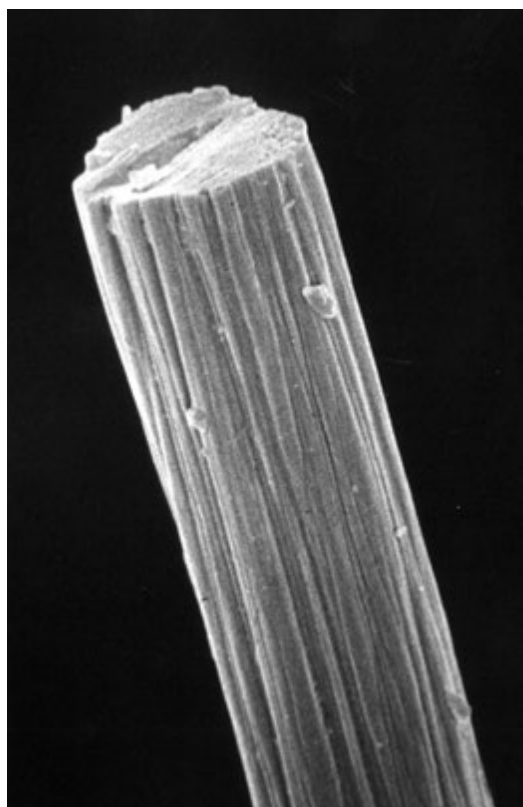


Figure 5 An early polyacrylonitrile (PAN) based carbon fiber.

however is increased by the purification processes by which the pitch is converted into a mesophase or liquid crystal solution which is then spun giving precursor fibers with aligned microstructures. From this point the fabrication route is the same as that for the PAN based fibers. Unlike PAN based fibers, there is no peak in strength at 1500 °C. Pitch based precursors heated to around 2300 °C give fibers with Young's moduli as high as those obtained with PAN based fibers at 2900 °C and heating to these higher temperatures gives even greater stiffness of up to four and a half times that of steel. It is therefore more economical to produce high modulus carbon fibers from pitch than it is from PAN. The properties are due to a less disordered, more graphitic microstructure of the pitch based fibers which however leads to lower compressive strength and increased costs in producing high strength carbon fibers.

In the absence of oxygen carbon fibers are the ideal reinforcement and can be used to above 3000 °C. However the fibers suffer from oxidation from around 400 °C so that they can be used for short exposure times, such in carbon-carbon composite rocket nozzles or heat shields for atmospheric re-entry vehicles, but not for long term applications above this temperature.

Oxide Fibers

Ceramic fibers can be divided into oxide and non-oxide fibers (Bunsell and Berger, 1999). The oxide of aluminum, alumina, is a hard brittle material with excellent refractory properties up to 1600 °C. The atomic structure of this material is assured by a mixture of covalent and ionic bonds. Fibers for structural applications based on forms of alumina were developed first in the UK and in the USA in the 1970s. Alumina exists in a range of phases of which the most stable and crystalline form, to which every other phase is converted around 1200 °C, is alpha alumina which has a Young's modulus of around 400 GPa. Several manufacturers have produced continuous α -alumina fibers as can be seen from Table 6. These fibers are made from slurries consisting of alpha-alumina particles, in an aqueous solution of aluminum salts which is spun and sintered. The control of grain growth and porosity in the production of alpha-alumina fibers is difficult so that the different manufacturing routes adopted have produced fibers with different Young's moduli. The Almax fiber, for example, contains considerable porosity which accounts for its lower modulus than that of Nextel 610.

The difficulties in producing pure alpha-alumina fibers can be overcome by the inclusion of silica in the structure and the development of intermediate alumina phases. The Young's moduli, around 200 GPa, of these fibers are lower compared to that of pure α -alumina and such fibers are produced at a lower cost. This, added to easier handling due to their lower stiffness, makes them attractive for thermal insulation applications, up to at least 1500 °C and as reinforcements for aluminum alloys in the temperature range of 300–350 °C. Alpha-alumina fibers and those of other phases containing silica resist oxidation at high temperature but the high diffusion rates of the elements in their structures above 1000 °C means that they creep and also lose strength around this temperature.

A series of fibers based on a mullite composition consisting of a ratio of 3 mol of alumina to two of silica has been developed by 3M. Mullite has a complex crystallographic structure which is highly resistant to creep at high temperatures. The Nextel 720 fiber from 3M consists of both α -alumina and mullite phases. The microstructure of the fiber is composed of mosaic grains of 0.5 μm with wavy contours, consisting of several slightly mutually misoriented grains and elongated grains. Its Young's modulus is 260 GPa. At high temperatures, above 1000 °C and up to 1500 °C the microstructure of the Nextel 720 fiber leads to a dramatic reduction in creep rate compared to pure alumina fibers but the fiber surface is particularly reactive to alkaline contamination above 1100 °C which leads to the development of grains as the surface and if this occurs, a fall of strength.

Table 6 Properties and compositions of alumina based fibers

Fiber type	Manufacturer	Trade mark	Composition (wt%)	Diameter (μm)	Density (g cm^{-3})	Strength (GPa)	Strain to failure (%)	Young's modulus (GPa)
α -Al ₂ O ₃ fibers	Mitsui mining	Almax	99.9% Al ₂ O ₃	10	3.6	1.02	0.3	344
	3 M	610	99% Al ₂ O ₃ 0.2%–0.3 SiO ₂ 0.4–0.7 Fe ₂ O ₃	10–12	3.75	1.9	0.5	370
Alumina silica fibers	Saffil	Saffil	95% Al ₂ O ₃ 5% SiO ₂	1–5	3.2	2	0.67	300
	Sumitomo	Altex	85% Al ₂ O ₃ 15% SiO ₂	15	3.2	1.8	0.8	210
	3 M	312	62% Al ₂ O ₃ 24% SiO ₂ 14% B ₂ O ₃	10–12 or 8–9	2.7	1.7	1.12	152
	3 M	440	70% Al ₂ O ₃ 28% SiO ₂ 2% B ₂ O ₃	10–12	3.05	2.1	1.11	190
	3 M	720	85% Al ₂ O ₃ 15% SiO ₂	12	3.4	2.1	0.81	260

Table 7 Properties and compositions of silicon based fibers

Fiber type	Manufacturer	Trade mark	Composition (wt %)	Diameter (μm)	Density (g cm^{-3})	Strength (GPa)	Strain to failure (%)	Young's modulus (GPa)
Si-C based	Nippon carbide	Nicalon NLM 202	56.6% Si 31.7% C 11.7% O	14	2.55	2.0	1.05	190
	Ube industries	Tyranno Lox-M	54.0% Si 31.6% C 12.4% O 2.0% Ti	8.5	2.37	2.5	1.4	180
	Nippon carbide	Hi- Nicalon	62.4% Si 37.1% C 0.5% O	14	2.74	2.6	1.0	280
	Nippon carbon	Hi-Nicalon S	SiC + O + C	13	3.0	2.5	0.65	375
SiC	Ube industries	Tyranno SA	SiC + C + O + Al	10	3.0	2.5	0.75	330

SiC Based Fibers

Fibers, based on silicon carbide became available from Japanese producers in the early 1980s. They are made by the pyrolysis of organo-silicon precursor filaments based on polycarbosilane which consists of cycles of six atoms arranged in a similar manner to the diamond structure of β -SiC. The early Nicalon fibers made by Nippon Carbon and the Tyranno fibers from Ube Industries were made by first cross-linking the precursor fibers by heating in air which introduced oxygen into the structure. The Tyranno fibers already contained some oxygen as it was introduced with a small amount of titanium into the precursor to control spinning. The presence of the oxygen resulted in the SiC grains, about 2 nm in size, which were developed during pyrolysis, being surrounded by an amorphous Si-C-O phase and the fibers had Young's moduli of around 200 GPa. This intergranular phase caused the fibers to creep above 1000 °C and its degradation above 1200 °C limited their use. Cross-linking of the precursors by electron irradiation eliminated the need for introducing additional oxygen into the precursors. This process gave rise to the Hi-Nicalon fiber which had no significant oxygen rich amorphous phase, but considerable excess free carbon. The grain size of the Hi-Nicalon fiber is around 10 nm and its Young's modulus is in the range of 265–290 GPa. The fiber is more stable than its predecessors at temperatures above 1000 °C although grain growth occurs. Both Japanese manufacturers have produced a near stoichiometric SiC fiber by extending the above technology and heating the fibers to temperatures of around 1800 °C. The fibers differ in detail which leads to different ultimate properties, as can be seen in [Table 7](#), but all three have grain sizes greater than 50 nm and up to 200 nm. This leads to Young's moduli of up to 400 GPa. These fibers retain their properties in short term tests to around 1400 °C.

Concluding Remarks

A wide range of very different high performance fibers have been developed. Many have low densities making them attractive engineering materials, either embedded in a matrix to form a composite, or by themselves as ropes or other structures. These materials, which are still being improved, are destined to find a wide range of uses some of which would be impossible without the extraordinary properties of high performance fibers.

References

- Bunsell, A.R., 2009. Handbook of Tensile Properties of Textile and Technical Fibres. LLC Boca Raton, FL: Woodhead Publishing Cambridge + CRC Press.
- Bunsell, A.R., Berger, M.-H., 1999. Fine Ceramic Fibers. New York, NY: Marcel Dekker.
- Chawla, K.K., 1998. Fibrous Materials. Cambridge: Cambridge University Press.
- Hearle, J.W.S., 2001. High-Performance Fibres. Cambridge: Woodhead Publishing Ltd.
- Hearle, J.W.S., Lomas, B., Cooke, W.D., 2006. Atlas of Fiber Fracture and Damage to Textiles. LLC Boca Raton, FL: Woodhead Publishing Cambridge + CRC Press, (reprinted 2006).
- Kaverov, A.T., Kazakov, M.E., Varshavsky, V.Ya., 1995. Carbon fibres. In: Kostikov, V.I. (Ed.), Fibre Science and Technology. London: Chapman & Hall, pp. 231–258 (Chapter 2).
- Moncrieff, R.W., 1979. Man-Made Fibers, sixth ed. Guildford: Butterworth.
- Wollrett-Blitz, J., Bunsell, A.R., Halary, J.-L., Joannès, S., Marcellan, A., 2014. Vers de nouvelles applications pour les fibres aramides. L'Actualité Chimique- nov. 2014 N° 390, 1–4.
- Wollrett-Blitz, J., Bunsell, A.R., Joannès, S., Marcellan, A., Bunsell, A.R., 2016. Multi-axial mechanical behavior of aramid fibers and identification of skin/core structure from single fiber transverse compression testing. Journal of Polymer Science Part B: Polymer Physics 54, 374–384.

Spun (Slurry and Sol-Gel) Ceramic Fibers

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Chemical Processing

Chemical or sol-gel processing was first used to produce ceramic oxide fibers in the 1960s (Wainer *et al.*, 1965). A number of chemically derived alumina-silica fibers, notably Saffil (noncontinuous 95% Al_2O_3 -5% SiO_2 fibers) and Nextel™ 312 (continuous aluminum borosilicate fibers), were commercialized in the late 1970s (Stacy, 1988; Birchall *et al.*, 1985; Sowman, 1988). Most applications for these fibers are for thermal insulation, where load-bearing capability is not a major concern. More recently, fibers designed specifically for the reinforcement of composites have been produced, for example, DuPont's Fiber FP and Nextel™ 610 and 720 ceramic oxide fibers.

Oxide Fiber Precursor Chemistry

There are a number of alumina precursors available that are suitable for forming fibers. The aqueous chemistry of aluminum allows for the formation of viscous basic aluminum salt solutions that can be made into fibers by dry spinning. Polymeric aluminoxane precursors have also been used to produce alumina-based fibers. More recently, aluminoxanes that can be melt-spun into fibers have been produced. Details of both types of chemical precursor are given below.

The spinning solution or spin dope must be a high-viscosity ($10\text{--}100\text{ N s m}^{-2}$ (10 000–100 000 cP)) liquid, stable with respect to both crystallization and precipitation of insoluble salts and organic-containing complexes and to rapid increases in viscosity or gelation resulting from the progression of cross-linking of precursor species. Spin dopes prepared using exclusively colloidal sols (e.g., boehmite, AlOOH) are not suitable for forming continuous fibers because they are shear thinning. Colloidal SiO_2 is, however, commonly used as a component in oxide fiber spin dopes. Other SiO_2 precursors such as partially hydrolyzed alkoxides and polysiloxanes have also been used as a method of introducing SiO_2 into fiber compositions. Other inorganic modifiers to oxide fiber compositions can be readily added using soluble salts (e.g., nitrates). Long-chain organic polymers such as polyethylene oxide are commonly added to improve fiber-forming ability and green strength. Using organic polymers as spinning aids, spin dopes can also be prepared using slurries. Slurry-based fibers (e.g., Fiber FP) have high ceramic content relative to organics, so that shrinkage is reduced, leading to simple heat-treatment. Using slurries, a wide variety of compositions can be produced, limited only by the availability of submicrometer powders (French and Cass, 1998). For instance, BaTO_3 , PZT, YAG, and SiC fibers have been produced using a slurry technique. Sol-gel processes have also been used to prepare a variety of fiber compositions not based on alumina, including ZrO_2 , $\text{ZrO}_2\text{--SiO}_2$, TiO_2 , YAG, and Y_2O_3 .

Basic Aluminum Salts

Basic aluminum salts are salts with less than the stoichiometric 3 moles of anion per Al, and have the nominal formula $\text{AlX}_n(\text{OH})_{3-n}$, where X is a ligand such as Cl^- , NO_3^- , or CH_3COOH^- . Basic aluminum salts can be formed using a number of methods, including dissolution of aluminum metal in salt solutions, dissolution of aluminum hydroxides in acid, hydrolysis of alkoxides, and neutralization of acidic salt solutions. The polycationic complexes formed are stabilized against further cross-linking and hydrolysis by complexing ligands (Bertsch, 1989). Basic aluminum salts used for fibermaking contain 0.5–2.0 moles of anion ligand per mole of aluminum. If the amount of ligand is too low, gelation via cross-linking of polynuclear clusters will occur; high amounts of ligand cause difficulties during fiber heat treatment because excessively large amounts of fugitives must be removed during pyrolysis. Large ligands such as lactic acid or acetyl acetonate can be used to produce spinnable precursors but are not desirable, since ceramic yield on firing is lower than smaller ligands such as chlorine. Aluminum chlorohydrates ($\text{AlCl}_x(\text{OH})_y$) are used to prepare a number of commercial fibers, including Fiber FP and PRD-166, Almax™, and Alcen™. Rubilon™ and the Nextel™ series of fibers are produced using aluminum carboxylates.

Polymeric Aluminoxane

Aluminoxanes consist of an Al–O backbone polymer coordinated by chelating ligands such as carboxylates and aceto-acetonates (Glaubitt *et al.*, 1994; Yogo and Iwahara, 1992). Aluminoxanes are synthesized by the addition of the ligand to aluminum alkyls or alkoxides to partially chelate the aluminum, followed by the addition of 0.5–1 moles of water per mole of aluminum to polymerize the aluminoxane. Depending on the ligands used, these precursors can be either melt-spun or dry-spun. Melt-spun

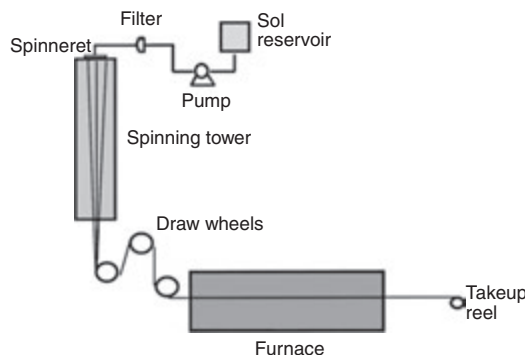


Figure 1 Schematic of sol-gel fiber process.

fibers are cured (to make them infusible) by completing hydrolysis by exposure to humid atmospheres. Sumitomo Altex™ fibers are produced using this technique.

Figure 1 shows a schematic of the sol-gel fiber process. Spin dope is extruded through a spinneret to form small-diameter fibers. The fiber becomes rigid as solvent is evaporated. If the viscosity is too low, the extruded liquid spherodizes into droplets; too high, the fibers become brittle and are easily fractured. After spinning, the green fibers are conveyed into a furnace for heat treatment. Pyrolysis (the conversion of the chemical precursor into a ceramic) typically involves the loss of 50–80% of the initial weight of the green fiber. Volumetric shrinkage can be 80% or higher. Volatile components (including CO, CO₂, H₂O produced by oxidation, plus low molecular weight organics, depending on precursor chemistry) must diffuse out of the fiber during this stage. Thus, pyrolysis must be performed with care to gently decompose the green fiber to the oxide form without forming defects or flaws. Too-rapid evolution of gases can cause pinholes, bubble or void formation, or even bloating, trapping of carbon, phase separation, and cracking. The addition of colloidal or particulate slurries to fiber precursors increases ceramic yield, thereby reducing shrinkage and facilitating pyrolysis.

The goal of heat treatment is to develop a ceramic microstructure with both good strength and good high-temperature properties (i.e., resistance to thermal degradation via grain growth). To achieve high fiber strength at room temperature, a small grain size ($\leq 1.0 \mu\text{m}$) is required. The Griffith equation, $\sigma = K_{Ic} / \sqrt{\pi c}$, indicates that for Al₂O₃ ($K_{Ic} = 3$), a strength of 3 GPa can only be achieved if the flaw size c is $< 1.0 \mu\text{m}$. Thus, not only must defect concentration be kept low by careful fiber processing, but grain size should not exceed this limit. During fiber manufacture, extreme care must be taken in all process stages to prevent the formation of defects and flaws that reduce fiber strength.

Heat Treatment and Fiber Microstructure

Microstructures in alumina-based fibers must be viewed through an understanding of crystalline transformation sequences in alumina, and the effect of silica on microstructure and transformation kinetics. As shown in **Table 1**, all commercial oxide ceramic fibers are based on alumina with varying amounts of silica. The stable phases for alumina-silica fibers with $\leq 28\%$ Al₂O₃ at all temperatures are α -Al₂O₃ and mullite. However, a series of cubic alumina spinels commonly called transition aluminas form in the temperature range 800–1200 °C during heat treatment of alumina and alumina-silica precursors. The first phase to crystallize is either η -Al₂O₃ (cubic) or γ -Al₂O₃ (tetragonal), which form in the range 800–900 °C. In many systems, δ -Al₂O₃ and θ -Al₂O₃ are formed with additional heating in the range 1000–1150 °C. These polymorphs are similar to γ -Al₂O₃ but have a higher degree of ordering on the cation lattice. The transformation to α -Al₂O₃ (a hexagonal crystal structure) occurs above 1200 °C; Mullite (3Al₂O₃ · 2SiO₂) also may crystallize above 1280 °C.

For alumina and alumina-silica fibers, the crystallization of new phases such as mullite and α -Al₂O₃ often result in large grains, causing the fibers to become brittle and weak. A low volumetric nucleation density, which leads to large grain sizes, is typical of both alumina and mullite. For instance, crystallization of α -Al₂O₃ in high-alumina fibers causes the formation of large, porous, spherulitic grains several micrometers in size (McArdle and Messing, 1993). These large grains cause the fibers to become brittle and weak. To avoid this problem, most commercial fibers are stabilized as transition alumina by the addition of SiO₂. The addition of SiO₂ to alumina fibers increases the temperature of the α -Al₂O₃ transformation by as much as several hundred degrees centigrade. This allows the preservation of the submicrometer transition alumina microstructure (and therefore strength and flexibility) for extended periods above 1100 °C. At high silica contents, mullite may crystallize. B₂O₃ is added to some fibers as a grain growth inhibitor; B₂O₃ promotes the formation of a fine-grained mullite structure via 9Al₂O₃ · 2B₂O₃ intermediate phase (Richards *et al.*, 1991). High silica contents will lead to the formation of mullite above 1280 °C, which also can cause weakening of the fibers via grain growth.

Table 1 compares the density, strength, and elastic modulus of commercial ceramic oxide fibers. Commercial fibers can be divided into two classes: (1) those consisting of a mixture of transition alumina and amorphous silica; and (2) fibers containing crystalline α -Al₂O₃. Alumina-silica fibers have density between 2.7 and 3.2 and elastic modulus between 150 and 200 GPa.

Table 1 Composition and properties of commercially available oxide fibers^a

Fiber	Manufacturer	Composition Al_2O_3 - SiO_2	Density	Crystal phase	Tensile strength (GPa)	Elastic modulus (GPa)
Nextel™ 312	3M	62–24 (+ 14% B_2O_3)	2.7	$9Al_2O_3 \cdot 2B_2O_3 + am. SiO_2$	1.7	150
Nextel™ 440	3M	70–28 (+ 2% B_2O_3)	3.05	$\eta-Al_2O_3 + am. SiO_2$	2.0	190
Nextel™ 550	3M	73–27	3.03	$\eta-Al_2O_3 + am. SiO_2$	2.0	193
Nextel™ 610	3M	100–0	3.9	$\alpha-Al_2O_3$	3.0	373
Nextel™ 720	3M	85–15	3.4	$\alpha-Al_2O_3 + mullite$	2.1	260
Altex™	Sumitomo	85–15	3.2	$\gamma-Al_2O_3 + am. SiO_2$	2.0	193
Alcen™	Nitivy	80–20	3.1	$\gamma-Al_2O_3 + am. SiO_2$	1.6	160
Rubilon™	Nichias	68–27 (– 5% B_2O_3)	3.0	$\gamma-Al_2O_3 + am. SiO_2$	1.8	196
Almax™	Mitsui	100–0	3.6	$\alpha-Al_2O_3$	1.8	330
Fiber FP	DuPont ^b	100–0	3.9	$\alpha-Al_2O_3$	1.38	380
PRD-166	DuPont ^b	80 (– 20% ZrO_2)	4.2	$\alpha-Al_2O_3 + t-ZrO_2$	2.3	380

^aComposition data taken from vendor specifications, precursor composition taken from the patent literature.^bNo longer commercially available.

$\alpha-Al_2O_3$ fibers have much higher elastic modulus (380 GPa) as well as higher density (3.6 – 4.2 g cm^{-3}). Within each class, density and elastic modulus is inversely proportional to the alumina content: fibers with high alumina content have high elastic modulus and high density. The density and modulus of $\gamma-Al_2O_3$ is in the range 3.2 – 3.6 g cm^{-3} and 220 GPa respectively; the addition of SiO_2 at 2.2 g cm^{-3} and 70 GPa will reduce both. The addition of B_2O_3 will also reduce density and modulus. The effect of silica content on strength is less clear, since strength is related to flaw size and distribution as well as composition. Most fibers have tensile strength in the range of 1.7–2.1 GPa. An exception is Nextel 610, which has a strength of 3.0 GPa.

Fibers containing crystalline $\alpha-Al_2O_3$ have much higher chemical stability and elastic modulus than fibers containing transition aluminas. They are also not prone to shrinkage at high temperatures caused by crystallization and sintering, and can have higher creep resistance under load at high temperatures. For these reasons, they are used for the reinforcement of metal and ceramic composites; however, achieving fine grain size in $\alpha-Al_2O_3$ fibers is not straightforward. $\alpha-Al_2O_3$ has an intrinsically low volumetric nucleation density, which leads to large grain size and low strength. The addition of seeds or nucleation agents to promote high nucleation density during crystallization is essential if the fine grain sizes required for high strength ($0.5 \mu\text{m}$) are to be achieved. Seeding with submicrometer $\alpha-Al_2O_3$ particles (e.g., Fiber FP) or Fe_2O_3 -based nucleation agents (e.g., Nextel 610) have been used to produce fine-grained, high-density $\alpha-Al_2O_3$.

Ceramic oxide fibers have limited creep resistance at high temperatures compared with SiC fibers; however, progress in fiber processing during the 1990s has enabled the preparation of fibers with significantly improved high-temperature creep properties. Fibers with increased amounts of crystalline phases such as $\alpha-Al_2O_3$ and mullite, and lesser amounts of amorphous phases such as SiO_2 , have reduced deformation at high temperatures. For instance, Nextel 720 fiber, which consists of a mixture of $\alpha-Al_2O_3$ and mullite, has demonstrated considerably greater creep resistance above 1000°C than either alumina-silica or $\alpha-Al_2O_3$ fibers. This has been attributed to the presence of mullite, which is a more creep resistant phase than alumina, plus larger grain size. YAG fibers that exhibit even better creep resistance have been developed at several laboratories. Such YAG fibers have the potential for long-term composite reinforcement at 1200°C and above.

References

- Bertsch, P.M., 1989. Aqueous polynuclear aluminum species. In: Sposito, G. (Ed.), *Environmental Chemistry of Aluminum*. Boca Raton, FL: CRC Press, pp. 88–111.
- Birchall, J.D., Bradbury, J.A.A., Dinwoodie, J., 1985. Alumina fibres: Preparation, properties and applications. In: Watt, W., Perov, B. (Eds.), *Handbook of Composites*, Vol. 1. Amsterdam: Elsevier Science, pp. 115–154.
- French, J.D., Cass, R.B., 1998. Developing innovative ceramic fibers. *Am. Ceram. Soc. Bull.* 77, 61–65.
- Glaubit, W., Sporn, D., Jahn, R., 1994. A new way to spinnable sols derived from modified aluminum alkoxides. *J. Sol-Gel Sci. Technol.* 22, 525–528.
- McArdle, J.L., Messing, G., 1993. Transformation, microstructure development, and densification in $\alpha-Fe_2O_3$ -seeded boehmite-derived alumina. *J. Am. Ceram. Soc.* 76, 214–222.
- Richards, E.A., Goodbrake, C.J., Sowman, H.G., 1991. Reactions and microstructure development in mullite fibers. *J. Am. Ceram. Soc.* 74, 2404–2409.
- Sowman, H.G., 1988. Alumina-boria-silica ceramic fibers from the sol-gel process. In: Klein, L. (Ed.), *Sol-Gel Technology for Thin Films, Fiber Preforms, Electronics and Speciality Shapes*. Park Ridge, NJ: Noyes, pp. 162–183.
- Stacey, M.H., 1988. Developments in continuous alumina-based fibres. *Br. Ceram. Trans.* J 87, 168–172.
- Wainer E., Raynes B.C., Cunningham L. 1965 Liquid polymers, solid articles made therefrom and methods of preparing same. US Pat. No. 3,180,741
- Yogo, T., Iwahara, H., 1992. Synthesis of α -alumina fibre from modified aluminum alkoxide precursor. *J. Mater. Sci.* 27, 1499–1504.

Ceramic Matrix Fiber Composites

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Introduction

Since the 1970s, the aerospace and aviation industry has constantly deepened its research to further improve the qualities of materials in order to extend their application to civil aeronautics. The development of nickel and cobalt-based superalloys are at their limits of use in terms of new environmental requirements, i.e., to obtain high efficiency (fuel economy, lower operating costs) and a reduction in pollution (noise level, emissions). One solution would consist of increasing the temperature of gases in the hot parts of the aircraft engines. The alloys currently used are limited to temperatures close to 1100°C and monolithic ceramics exhibit behavior too brittle for application. Only ceramic matrix composites (CMCs) are potentially able to fill the necessary requirements. Thus, their gradual replacements by composites, have accelerated over the past twenty years (Naslain, 2004). Current CMCs have a much lower densities than metallic materials and can have a much higher temperature capability. The need for high performance materials in industries as diverse as aeronautics, space, automotive, sport, etc., has led to the systematic development of composite materials (Krenkel, 1994; Krupka and Kienzle, 2000; Gadow and Speicher, 2001; Bouillon *et al.*, 2002; Bouillon *et al.*, 2004; Naslain, 2004; Cavalier *et al.*, 2006; Lacombe *et al.*, 2009). In order to be able to integrate this type of composites into the hot parts of the engines, it is necessary to adapt them to withstand the stresses imposed by this environment (high temperature 1400°C, oxidation, corrosion), while guaranteeing properties at least equal to those of superalloys used in terms of thermal conductivity, mechanical resistance, service life, etc. It is for this purpose that various research programs have been set up on new generation CMCs.

Structural composites generally consist of a fibrous reinforcement forming a reinforcement which constitutes the skeleton of the whole, and of a matrix which embeds the fibers. The different CMCs are designated in the form of two headings separated by a forward slash (e.g., C/C, C/SiC, SiC/SiC, oxide/oxide, etc.); the first designating the material of the fiber, the second that of the matrix (Chawla (2012)). These composites are generally said to be “thermostructural”, meaning that they can be used at high temperatures as structural materials. Thus, although monolithic ceramics are relatively hard and brittle, CMCs have the advantage of having non-brittle behavior. Their fields of application are currently mainly aeronautics, space and nuclear. Thus, they are subjected to temperatures ranging from 400°C to more than 2000°C in oxidizing atmospheres (air, reactor combustion gas, etc.) (Christin, 2002; Naslain, 2004; Rosso, 2006; Tang *et al.*, 2007; Padture, 2016).

Initially, this chapter gives a definition of composite materials and focuses on the general behavior of CMCs at room temperature, to show the interest in their development. Then, the general fabrication methods involved in introducing the ceramic matrix into the fibrous reinforcement is explained, in order to provide all the knowledge needed to choose a process and analyze recent developments in manufacturing.

Definition

A so-called composite material results from the association of at least two immiscible materials whose properties complement each other. Its architecture is tailored to achieve on a macroscopic scale, in preferred orientations, an original range of properties that its singular constituents don't possess.

The role of the fibrous reinforcement is to be a strengthening agent, essentially playing a mechanical improvement role. It brings rigidity and mechanical strength and can have preferred orientation. The fibers carry most of the applied load until the composite breaks, so that the breaking of fibers leads to the final failure of composite materials. The fiber constituent has to be protected against any kind of environmental degradation during application to prevent premature failure of composites.

Preforms, formed by the fibers, are densified by a ceramic matrix. The matrix has three main functions: (1) to keep the reinforcement in shape by ensuring the continuity of the material, (2) to ensure the transfer of loads applied to the composite to the fibers and (3) to protect the fibers and the interphase against degradation from the outside environment. In order to limit the residual stresses created during thermal cycling, the matrix must have a thermal expansion coefficient close to that of the reinforcement. The ceramic matrix can consist of a single homogeneous phase or it can include different phases in order to give it specific properties. Thus, there are so-called self-healing matrices which include compounds which, on contact with an oxidizing atmosphere, form glasses which seal the crack networks (Rebillat, 2014). Efficient reinforcement actions by the fibers depend on the interfacial bond strength between the fibers and the matrix in the composite.

Fibrous Reinforcement

Fibers must have a high tensile strength and elastic modulus, combined with good fatigue resistance. They must be thermo-chemically and mechanically compatible with all other constituents so as not to generate parasitic reactions and create networks of cracks by relaxation of high thermal residual stresses. Depending on the type of use, they must also exhibit good resistance to

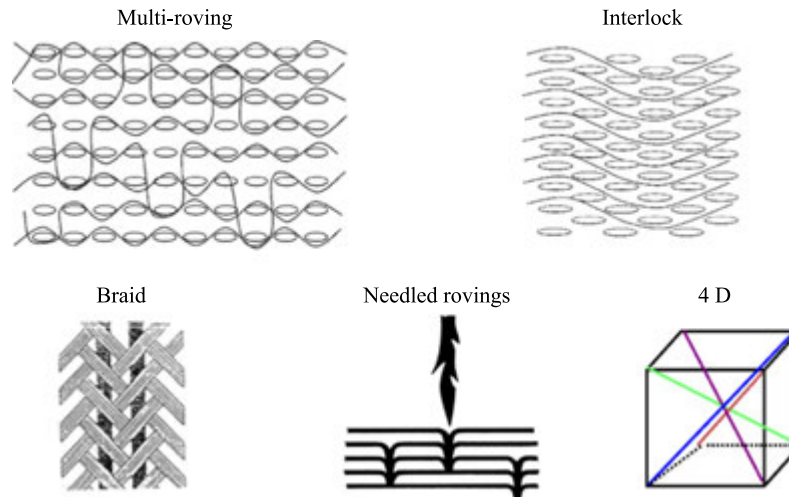


Fig. 1 Various weavings for fibrous reinforcements in composite materials.

oxidation, creep and have low or high thermal conductivity. The fibers can be woven, braided or assembled in the form of semi-finished products (felts, unidirectional sheets, etc.), which constitute a preform of the final part. The fibers used in CMCs typically belong to a family of inorganic mineral fibers (Naslain, 2004; Rosso, 2006). Three types of fibers are generally used: carbon fibers, oxide fibers or carbide fibers (Lee, 1993; Bunsell, 2001).

The choice of fiber reinforcement directions is made with regard to the main loading directions (see Fig. 1). Differences between various weavings, in the way the fibers are laid out, give different strengths and ease of manufacture (Ko, 1989; Ko and Du, 1997). The degree of anisotropy decreases with the number of reinforcement directions. Delaminations between the layers of fabrics are avoided by adapting means of weaving to form three-dimensional weaves (Lee, 1993).

Mechanical Behavior

Properties of Constituents

Ceramic constituents are preferred for their refractoriness and thermal stability, chemical inertness and their low density. They are not considered to be mechanically reliable because of their brittle behavior and sensitivity to impacts. By making ceramic matrix composites, the goal is to introduce a different and more tortuous mode of crack propagation. Despite this while CMCs are composed of brittle constituents, they are assembled so as to form a non-brittle composite capable of being toughened by strain energy absorption, in particular due to weakening of the bond between fiber and matrix (Naslain, 1985, 2004; Bansal, 2005; Chawla, 2012). Because of this additional strain energy absorption mechanism, composites display non-linear elastic behavior and greater resistance to failure, as described below. CMCs are said “reverse”, compared to organic matrix composites, due to a failure deformation of the matrix lower than that of fibers.

Origin of the Non-Linear Behavior of a CMC

Given the high rigidity and low elongation to failure of ceramic matrices, the mechanical properties of a composite are closely related to the nature of the fiber/matrix bond which has chemical origin (interdiffusion and chemical reaction) and/or mechanical origin (thermomechanical shrinking and friction). When the strain in the composite reaches the strain at failure of the matrix, there is some matrix microcracking (Evans and Zok, 1994; Aveston *et al.*, 1971) and a greater load transfer from the matrix to the fibers. The fiber/matrix interface then plays a fundamental role in controlling resistance to failure. Indeed, the threshold interfacial shear stress (between the fiber and the matrix) must not be too strong in order to avoid brittle fracture (behavior close to that of the monolithic matrix) but sufficient to ensure load transfer from the matrix to the fibers (Guillaumat, 1994; Peres, 1988; Evans and Zok, 1994) (see Fig. 2). This is why the presence of a suitable interphase between fiber and matrix was investigated in depth (Aveston *et al.*, 1971; Naslain, 1998). It has long been established that the presence of an interphase of pyrocarbon brings better mechanical properties to a composite thanks to a adapted fiber/matrix bond, playing its role of crack deflector parallel to the fibers (Naslain, 1995) (see Fig. 2(b)).

Too weak a connection does not allow a sufficient load transfer from the matrix to the fibers, whereas too strong a bond leads to brittle rupture (rupture). A suitable bond allows crack deflection along the fibers from mode I loading, perpendicular to fibers, to mode II loading, parallel to fibers (see Fig. 2). This dissipates the energy of crack propagation by the creation of new fiber/matrix surfaces and friction (Guillaumat, 1994; Peres, 1988; Evans and Zok, 1994). The cracks then propagate within the matrix and the fiber bridging process (Marshall *et al.*, 1985). This makes it possible to limit the opening of cracks due to the loading thanks to the closing force exerted by the fibers.

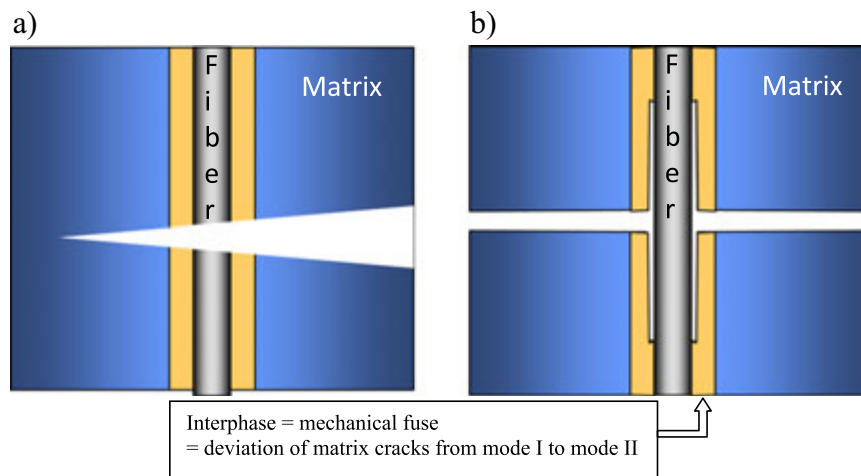


Fig. 2 Damage in a CMC in function of the fiber/matrix bond strength: (a) strong bond and (b) weak bond.

Definition of an Interphase

An interphase is a thin layer that coats the fibers and provides the correct level of bonding between fiber and matrix. Its role is essential and the quality of the mechanical properties of the final composite are very closely linked to it (Kerans and Parthasarathy, 1991; Evans *et al.*, 1991; Rouby and Reynaud, 1993; Evans and Zok, 1994). It is thanks to the interphase in particular that a composite made up of brittle components can exhibit damage limiting behavior. In summary, it performs several essential functions:

- The load transfer between fiber and matrix takes place via the interphase. (Naslain, 1995).
- The interphase acts as a mechanical “fuse”, i.e., it limits the propagation of cracks by deflecting them from mode I to mode II loading, parallel to the fibers.
- The deviation of the crack can be localized within the interphase (cohesive failure) or at the I/F or I/M interface (adhesive failure) (Lamon, 2005).
- The interphase must attenuate local residual stresses of thermal origin that appear during processing at high temperature, linked to the difference in expansion coefficients between fiber and matrix.
- It also has a role in protecting fibers against oxidation.

The interphase must also have good chemical compatibility with the fibers and the matrix. Pyrocarbon is an interphase material that effectively fulfills the mechanical roles described. Its structure in layers parallel to the fiber direction allows for good load transfer as well as efficient crack deflections due to low shear strength (Naslain, 1995) and cohesive fractures (see Fig. 3).

In order for crack deflection to take place effectively in the interphase, the energy of fiber-matrix bond breakage is about four times lower than the breaking energy of a fiber (Budianski *et al.*, 1986). Otherwise, the crack would propagate through the CMC material causing catastrophic brittle fracture. However, the main weak point of pyrocarbon interphases is its high sensitivity to oxidation at temperatures in excess of 400°C. In the presence of oxygen, the oxidation reactions of pyrocarbon are similar to those of carbon (Filipuzzi *et al.*, 1994). Another interphase material, increasingly used for its much better resistance to oxidation is boron nitride (BN) (Morscher, 1997). Despite poorer mechanical strength and less energy-dissipating adhesive breaks, it oxidizes very little at temperatures below 800°C, and upon oxidation forms a healing oxide B_2O_3 , rather than gaseous products alone leading to active oxidation.

Further, the idea of multiplying and extending the crack deflection zones led to development of architected interphases with the superposition of layers of different natures (i.e., sequences) between the fiber and the matrix. Diefendorf and Boisvert (1988) and Boisvert *et al.* (1989) have thus added multilayer carbon/silicon carbide (C/SiC) (liquid deposited between fibers SiC and a SiC matrix) which considerably improved the toughness of SiC/SiC composites. This concept of multilayered interphases went up to the development of sequences at a nanometric scale (Bertrand *et al.*, 2000) (See Fig. 3). Heraud *et al.* (1989) then considered the total sequencing of the matrix within a bidirectional SiC/SiC composite by inserting more compliant materials such as pyrocarbon or boron nitride by chemical vapor infiltration. The formation of a sequenced matrix by interposing one or more weaker layers rigidity leads, according to the authors, to (1) the delay of the initiation of fracture, (2) the increase in fracture energy and (3) the decrease in the sensitivity of the composite to the notch. While mainly found in oxide/oxide composites, a porous material is able to deviate a crack with a branching effect (Fig. 3).

Mechanical Behavior Under Tensile Loading

A ceramic matrix composite subjected to a uniaxial tensile test in the direction of the fibers exhibits three successive damage domains (Naslain, 1985, 2004; Bansal, 2005; Chawla, 2012). These are summarized in Fig. 4. In the first linear elastic domain, the material does not undergo damage, and returns to zero strain when unloaded. The modulus of the composite E_c can be estimated from the modulus of the matrix E_m and that of the fibers E_f by a simple law of mixtures (Eq. 1) (In Fig. 4,

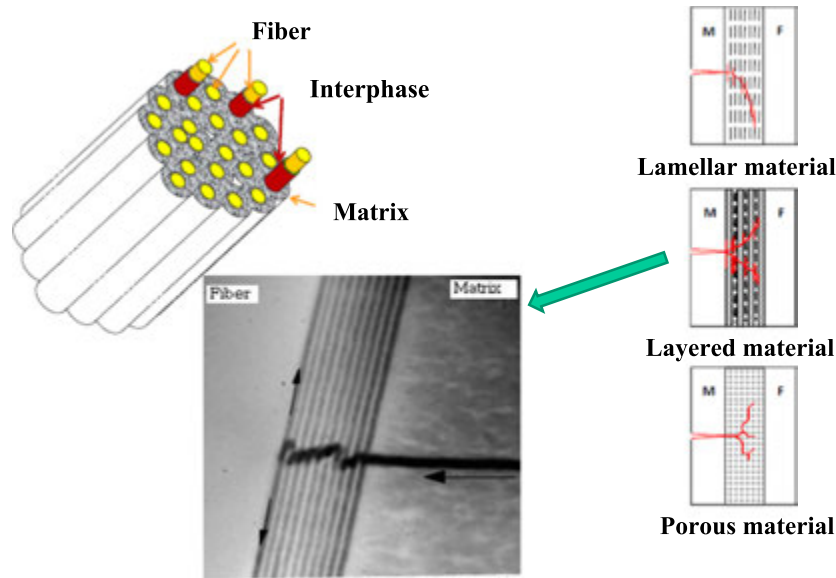


Fig. 3 Deflection of a matrix crack by an interphase. Reproduced from Bertrand, S., Droillard, C., Pailier, R., Bourrat, X., Naslain R., 2000. TEM structure of (PyC/SiC)_n multilayered interphases in SiC/SiC composites. *Journal of the European Ceramic Society* 20 (1), 1–13.

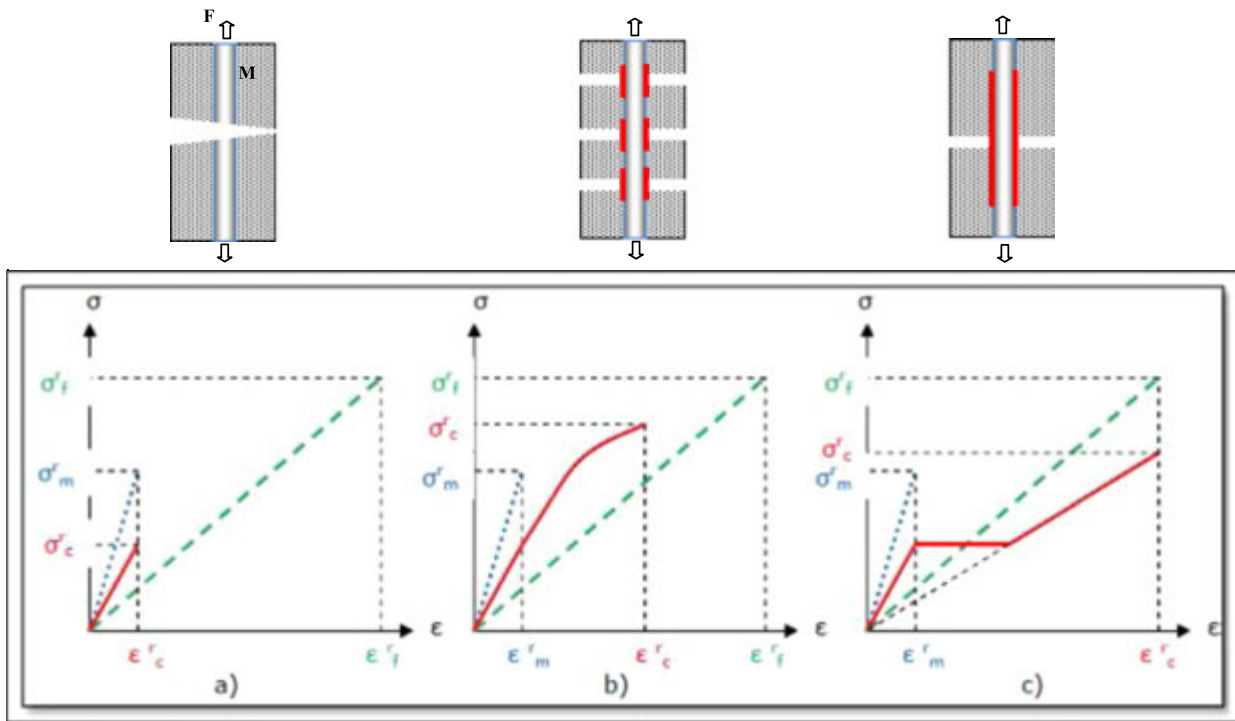


Fig. 4 Relation between the interfacial bond strength and the mechanical behavior of a CMC under tensile loading.

$E_m > E_f$ for the composites), by considering only the fibers in the considered loading direction and without curvature (or negligible curvature):

$$E_c = E_f \cdot V_f + E_m \cdot V_m \quad (1)$$

with:

V_f : filament content or fiber volume (volume fraction)

V_m : matrix content or matrix volume (–volume fraction)

thus $V_m + V_f = 1$

The second domain begins with matrix cracking. These cracks are often created in angular areas where macro-porosities are present in the composite and act as sources of stress concentration. The behavior then becomes non-linear because of the multi-cracking of the matrix. Finally, the last field appears when the state of matrix cracking is saturated. The contribution of the matrix is then negligible and the mechanical behavior is controlled solely by longitudinal fibers: the load being then entirely taken up by the longitudinal fibers. This feature is verified by the very close values between the modulus of the composite and that of the fibers multiplied by the volume fraction of the longitudinal fibers (according to the rule of mixture). The ultimate breakage is thus dictated by the fibers, with a first phase of stable rupture, then a second unstable phase (Lamon, 2001). As the load increases, some fibers (probably because of presence of defects) individually break, resulting in transfer of the load to the surviving fibers. The final break occurs when a critical number of fibers has broken, and the surviving fibers cannot withstand the load increment generated by the breakage of an additional fiber (Lissart and Lamon, 1994).

The extension (range of strains) of these successive steps is directly dependent on the quality of the link between fiber and matrix which consequently, must be perfectly controlled (see Fig. 4). Indeed, if this connection is too weak, fiber/matrix decohesions will be very important: the stress-displacement curve then presents a stress plateau, with complete load transfer on almost all the length of fibers. If the bond is strengthened (but not too strong), on the contrary, the cracks may be deflected on a shorter length along the fiber surface with a highly efficient load transfer. Non extended damaged zones continue into the composite and new matrix cracking can still occur for increasing loading. Multi matrix cracking is then observed and the matrix contributes only partially to support the load up to failure. The decrease in local stiffness along the stress-strain curve becomes regular and the level of failure stress is higher. A well-adapted bond is essential to obtain the desired damageability.

In Fig. 5, stress-strain curves are drawn for each different fiber-matrix bond strength (Droillard *et al.*, 1995; Rebillat, 1996; Naslain, 1998). The changes in slope are not as neat as in Fig. 4 but they can be identified. The level of the elastic limit is very low (around 0.05%) with no evidence (at this scale) of an influence of the interfacial bond strength. For the SiC/SiC composite with a weak interface bond strength, the saturation of matrix cracking occurs at a strain a little lower than 0.4% and further, the fibers sustain almost by themselves the loading up to failure. Thus, the failure stress is close to the product of the volume fraction of fibers and their failure stress. Conversely, for the SiC/SiC composite with an optimized intermediate interface bond strength, no plateau is visible on the stress-strain curve and the matrix participates to the support of a part of the load up to failure. A much higher level of failure stress is then reached.

During a tensile test, unloading/reloading cycles interposed during a tensile test form hysteresis loops which gives access, among other things, to the evolution of the modulus, to residual strains and the energy dissipated during these cycles, as shown in Fig. 6(a). Indeed, the shape of unloading/reloading hysteresis loops for a composite material are uniquely different compared to a metallic material. Opened hysteresis loops show that the phenomenon of energy dissipation is responsible for this behavior, although no damage is generated during such an unloading-reloading loop. This energy dissipation is linked to sliding and friction phenomena at the various friction interfaces of the material, especially between debonded longitudinal fibers and matrix. The dissipated energy due to friction is not the same during unloading and reloading due to a change in the sequence in the steps of fiber sliding (Peres, 1988; Lamon, 2001). Consequently, the cycles are very narrow for small deformations (little dissipated energy) and larger with greater damage to the material. For example, the width of loops is much larger when: (1) the fiber/matrix bond strength is weaker, (2) the lengths of sliding are greater and (3) the matrix crack spacing is greater (see Fig. 6(a)).

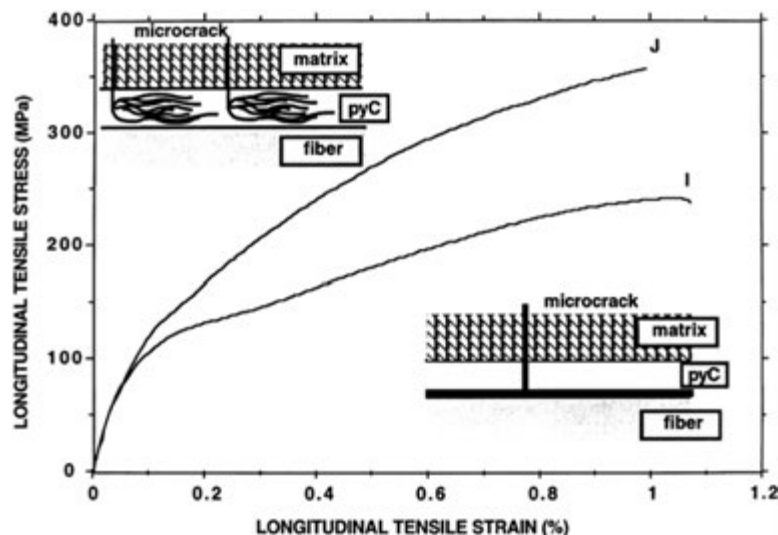


Fig. 5 Stress/strain curves of SiC/SiC composites Tensile curves and crack deflection mechanisms for 2D-Nicalon/PyC/SiC composites with different fiber/matrix bond strength (specimen I with a weak interface and J with a strengthened one). Reproduced from Rebillat, F., 1996. Caractérisation des interfaces et des matériaux d'interphases dans les CMCs. PhD Thesis. University of Bordeaux. Naslain, R., 1998. The design of the fiber-matrix interfacial zone in ceramic matrix composites. Composites Part A 29A, 1145–1155.

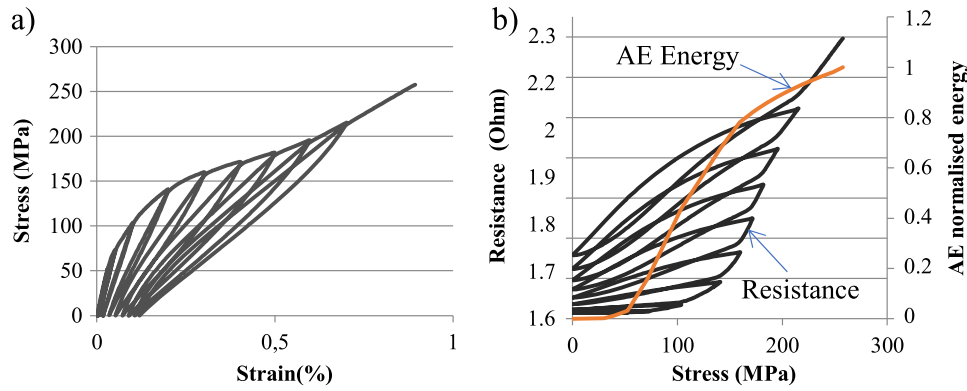


Fig. 6 (a) Stress-strain behavior for a composite with a relatively weak fiber/matrix bond. (b) Electrical resistance and cumulative AE energy during a tensile test with interposed characterization cycles. Reproduced from Simon, C., Herb, V., Rebillat, F., Camus, G., 2017a. Monitoring damage evolution of SiC/(Si-B-C) composites using electrical resistivity: Crack-density based electromechanical modeling. *Acta Materialia* 124, 579–587.

Acoustic emission (AE) has proved to be an interesting technique for quantifying matrix cracking as well as predicting times to rupture (Morscher, 2004; Maillet *et al.*, 2012; Moevus *et al.*, 2008). However, with this technique, it is necessary to monitor the material during all of its service life, because it is sensitive to transitions of states (crack creation for instance), and it cannot evaluate a damage state at zero stress without previous monitoring, which would be useful for maintenance. The recorded acoustic signal in the case of a cumulative count mode (see Fig. 6(b)) shows (1) a signal starting with the first matrix cracking, (2) an increasing cumulative signal related with the progressive damage propagation and (3) a slowing in acoustic emission when the matrix becomes fully cracked.

Many other non-destructive evaluation techniques (NDE), such as acousto-ultrasonic, X-ray or thermography, allow damage detection in various types of materials including CMCs (Bertrand *et al.*, 2017; Jumel *et al.*, 2001). However, most of these techniques (1) often require that the components should be taken out for testing (needing long times), and (2) are more efficient for the detection of out-of-plane flaws (such as delamination) than the detection of typical thin transverse cracks perpendicular to the surface observed in CMCs. Electrical resistance has proved to be a pertinent measure of the damage state for various materials such as carbon fiber-reinforced polymer composites (CFRP) (Schulte and Baron, 1989), particle reinforced polymer composites (Ruschau *et al.*, 1992), and more recently in civil engineering materials (Ranade *et al.*, 2014; Vesely *et al.*, 2015). This technique has the advantage of discrete measurements without damage monitoring, as it provides a physical property of a material at a given time instead of recording transitions of states, as it is the case with AE (see Fig. 6(b)). At room temperature and at high temperature, the measurement of residual resistances (during loading and even at zero stress) is higher than the initial resistance, and increases with the maximum applied stress. This feature has been related to greater damage accumulation, reflected either by the length of the debonded interphase or the density of matrix cracks, depending on which constituent is the best electrical conductor (Smith *et al.*, 2011, 2008; Morscher *et al.*, 2014; Simon *et al.*, 2017a,b). The resistance monitoring can therefore give access to information concerning different damage modes.

Finally, the observation of the failure faces of a composite shows that the fibers don't break on the same plane as the matrix. (see Fig. 7). Fiber pull-out or voids in place of fibers are visible on the failure surfaces. A fiber breaks when locally the failure stress of the fiber is overcome. This critical failure stress is related to the local overloading due to the presence of a defect inside the fiber. It is well known that the defects are randomly distributed and this breaking can only occur along a damage zone. The combination of these factors explains the complex appearance of the failure surface. The average pull-out length becomes respectively an indicator on the fiber/matrix interfacial bond, i.e., weak bonding leads to long pull out lengths while strong bonding leads to shorter pull out lengths. For example, it is shorter when the debonded lengths are lowly extended and respectively, when the fiber/matrix bond is strengthened.

Fiber/Matrix Interfacial Shear Stress

The deviation of a transverse crack by the interphase generates debonding between fiber and matrix over a specific length (see Fig. 8). Thus, in the vicinity of the crack, the matrix is locally unloaded, causing an interfacial slip, governed by the interfacial shear stress τ , as the fiber becomes overloaded (Fig. 8(a)). During unloading and reloading, the fiber elongates in reaction to the stress while the unloaded matrix deforms much less. This generates sliding with associated friction and wear, because of the roughness at the interfaces (see Fig. 8) (Evans *et al.*, 1991; Evans and Zok, 1994).

Load transfer along fiber/matrix interfaces is controlled by the ratio of interfacial shear stress, τ , to fiber radius R . As shown in Eq. 2:

$$\frac{d\sigma_f}{dx} = \frac{2\tau}{R} \quad (2)$$

where σ_f is the stress to which the fiber is locally subjected and x the length along the fiber. In the case of an interface where relative displacements between fiber and matrix are possible, if τ is considered constant (Arnault, 1989), the load - distance profiles are linear along

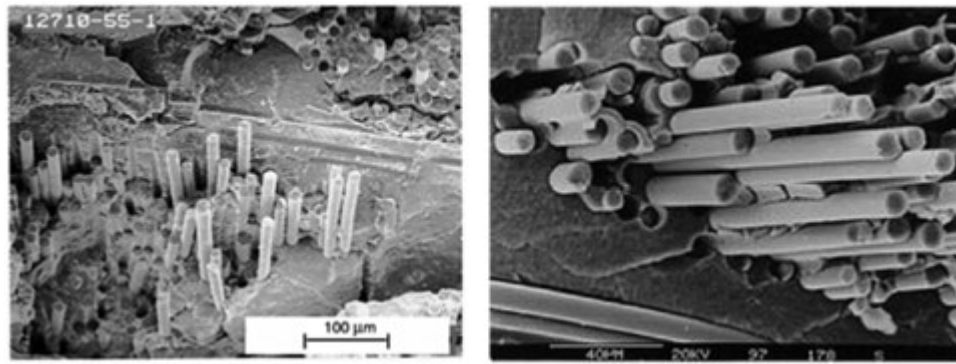


Fig. 7 Failure facies of a C/C composite under tensile loading. Reproduced from Bertran, X., 2013. Comportement en oxydation de matériaux composites C/C dans des applications aéronautiques à faible température. PhD Thesis. University of Bordeaux.

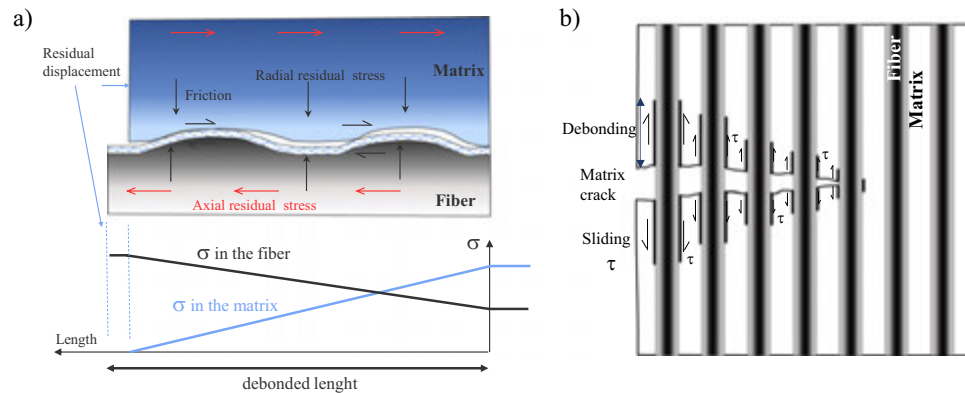


Fig. 8 Representations (a) of the stress-length relationships along a debonded and (b) of a matrix crack in propagation and the mechanisms of energy dissipation involved.

the debonded length (see Fig. 8(a)). With weakening of the interface, the longer is the debonded and overloaded fiber length, and the higher is the probability of finding a defect of critical size.

The interfacial shear stress, τ , also has an important influence on the cracking step. With low τ , the matrix will be unloaded over a longer length (Fig. 8) and any crack creation is prevented on this same length. The result is a more significant distance between the matrix cracks and much larger crack opening, referred to as “residual displacement” in Fig. 8(a). (Rouby and Reynaud, 1993; Curtin, 1991).

It is thus well-known that matrix cracking is a damage mechanism inherent to this type of material. Under oxidizing environments, this feature can be a critical parameter with the formation of crack paths toward fibers and interphase aiding diffusion of oxidizing gaseous species (O_2 , H_2O) and contributing to the dramatic reduction in mechanical properties (Glime and Cawley, 1995; Lamouroux *et al.*, 1999; Christin, 2002; Casas and Martinez-Esnaola, 2003; DiCarlo *et al.*, 2004; Rebillat, 2014). This is why it is preferred that mechanical damage generates numerous thin matrix cracks rather than a few large cracks (see Figs. 4 and 5).

Manufacturing

Choice of Manufacturing Process With Respect to Required Properties

Depending on application, the temperature of use and the life time are generally reciprocally related. For lower temperatures applications around 800°C , such as in aircraft engines, 60,000 h can be required. However, in space propulsion, the material has to last for around 3 min at temperatures above 2000°C (see Fig. 9). In addition, applications may need thermal insulation materials while others require a high thermal conductivity. Whatever the applications, today, most of the industries design their parts such that they operate within the linear elastic domain under thermomechanical loading. Increasing the elastic limit therefore becomes the singular challenge. These properties are strongly linked to the materials properties, such as purity, crystallinity and porosity. Main of these characteristics at the macroscopic scale of the composite are imposed by the choices of constituents but also through the distribution of the matrix inside the fibrous preform (Table 1). The method for manufacturing matrices imposes a major part of the final properties of the matrix and consequently the composite.

The traditional process for developing the matrix is gas infiltration (CVI for Chemical Vapor Infiltration); the phases obtained being pure and crystallized (or at least controlled). However, gas infiltration is a long and expensive process and several other

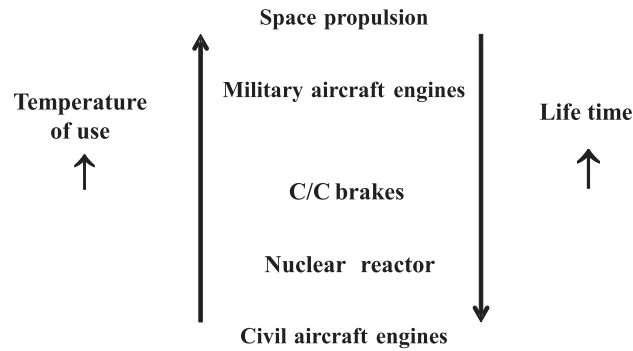


Fig. 9 Schematic of working conditions of various CMCs.

Table 1 Relation between CMC properties and material characteristics (purity, crystallinity, porosity)

Thermal conductivity	↑ Elastic limit	↑ Failure stress	↑ Oxidation resistance	↑ Irradiation resistance	↑ Thermal stability
• Nature and purity of a material • Degree of crystallinity • Porosity	• Low porosity % • Pores with a small size without angular part	• Tailored F/M interface • No degradation of reinforcement	• Nature of materials • Capability of passivation • Purity of phas • Porosity	• Nature of materials • Purity of phases • Degree of cristallinity	• Purity of phases • Crystallization

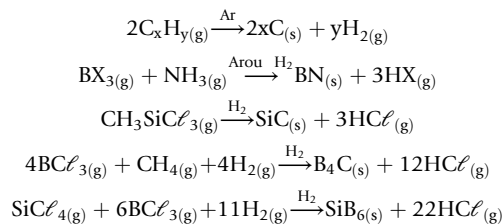
production routes, known as liquid routes (PIP for Polymer Impregnation and Pyrolysis and MI/RMI of silicon for Melt Infiltration/Reactive Melt Infiltration) and slurry routes are possible.

Fabrication by Gasous Route: Chemical Vapor Infiltration (CVI)

CVI gas production processes were developed in the 1960s in the United States and Russia to fabricate ceramic matrix composites. There are different variants: isothermal, pressure gradient, pressure pulsed, pressure gradient temperature, by heating (the Kalamazoo process or film boiling) (Golecki, 1997; Langlais, 2000). We will limit this chapter to the LPCVD (Low Pressure Chemical Vapor Deposition) and I-CVI (Isothermal & Isobar Chemical Vapor Infiltration) processes.

The mechanisms of deposition are similar in both CVD and the CVI processes and consists of depositing a solid on the hot surface of a substrate by reaction/decomposition of gaseous precursors. The basic phenomena comprise: (1) mass transfer in gas phase by diffusion and convection, (2) gas phase homogeneous chemical reactions and (3) surface chemical reactions with deposition (Langlais, 2005) as indicated in Fig. 10.

Various compositions of deposited materials are made possible by changing the nature of the gaseous precursors as given in the examples below:



with $H_y = CH_4, C_3H_6, C_3H_8X = F, Cl, Br$

From a kinetic standpoint, any of the mass transfer or chemical reactions as well as deposition can be rate-controlling. These overall processes are guided by thermodynamics and controlled by chemical kinetics or diffusion. CVD thus involves complex physicochemical processes which bring together homogeneous and heterogeneous transport phenomena and chemical reactions, that are in competition.

The CVI process involves growing a solid deposit within a porous material in order to densify it (Naslain, 2004; Langlais, 2005; Vignoles, 2015). Fig. 11 schematically shows deposit growth within a cylindrical pore. However, the typical assembly of fibers and rovings creates a network of porosity of complex shape with a large pore size distribution from a nano scale up to 500 μm average diameter. This

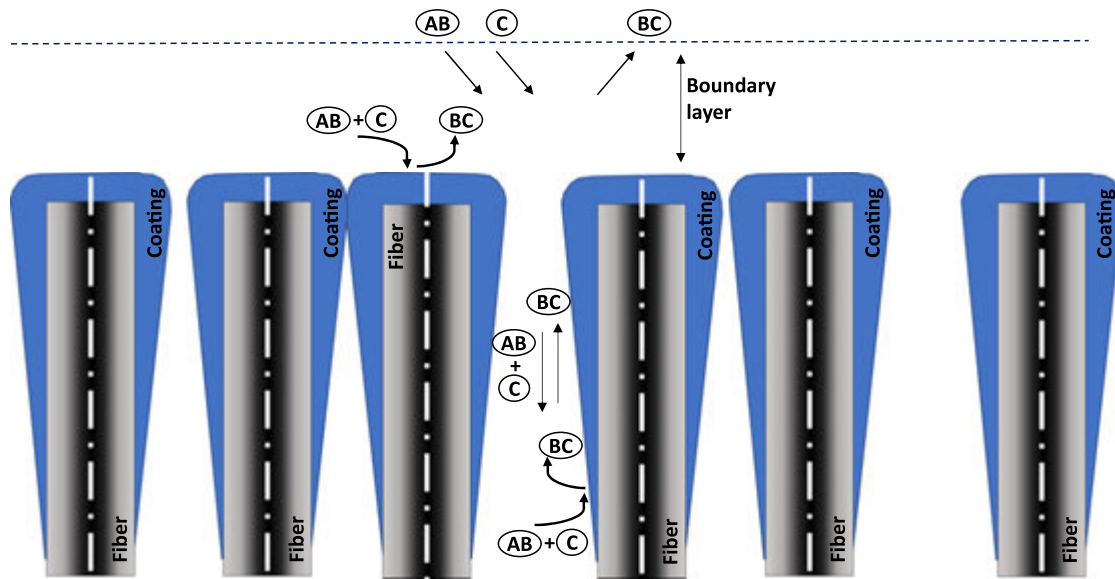


Fig. 10 Schematic view of the different stages of transport and homogeneous and heterogeneous chemistry in CVI.

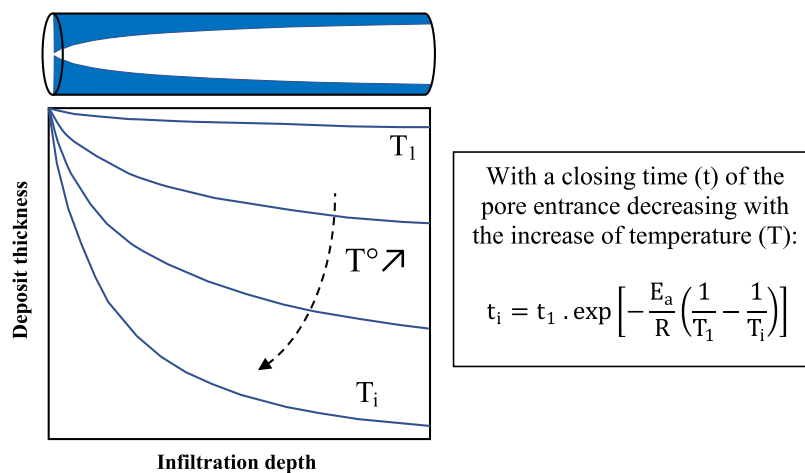


Fig. 11 Schematic of the development of a gradients deposit thickness along a pore in function of the temperature during the CVI process.

becomes the additional difficulty involved with CVI compared to the CVD process. Indeed, the supply of precursors no longer occurs only through the boundary layer but also within the porous medium to bring reactive species deep inside the fibrous preform.

The thin interphase layer constituting the interphase is commonly deposited by this method, prior to infiltration by the matrix material. For longer process times, closure of the pores entrances on the surface generally appears when there is a greater consumption of the gas precursors close to the outside surfaces of the preform, before reactive gas have time to diffuse into the fibrous preform (Fitzer and Gadow, 1986; Fedou *et al.*, 1993) (see Figs. 10 and 11). With the decrease in the opening of the pores following deposition, the resistance to gas transfer into the preform increases. The combination of these phenomena leads to differences in composition between the gas phase in the gaseous environment and within the porous network of the preform. It can even lead to changes in the mechanism of deposition between the outer surface and interior of the preform. Thus, on the surface, the deposition regime is limited by chemical kinetics, while within the preform, it is diffusion which limits the supply of reactive species, leading to a deposition régime limited by mass transfer (Golecki, 1997). All of these phenomena explain the differences of deposited thicknesses between the surface and interior of the preform. So, to get a delayed closing of pore entrances, it is recommended that the processing temperature is decreased in order to reduce the consumption rate at the surface as indicated in Fig. 11, and to lower the working pressure to increase the free diffusion path length inside the preform.

In the complete process, the preform is located within tooling to hold the different layers of fabrics. The whole is then placed in a hot wall reactor at temperatures between 900 and 1100°C and at reduced pressure ($P < 10$ kPa) (Golecki, 1997) (see Fig. 12). During this process, the interphase and matrix deposits are carried out successively using precursors gaseous of different natures.

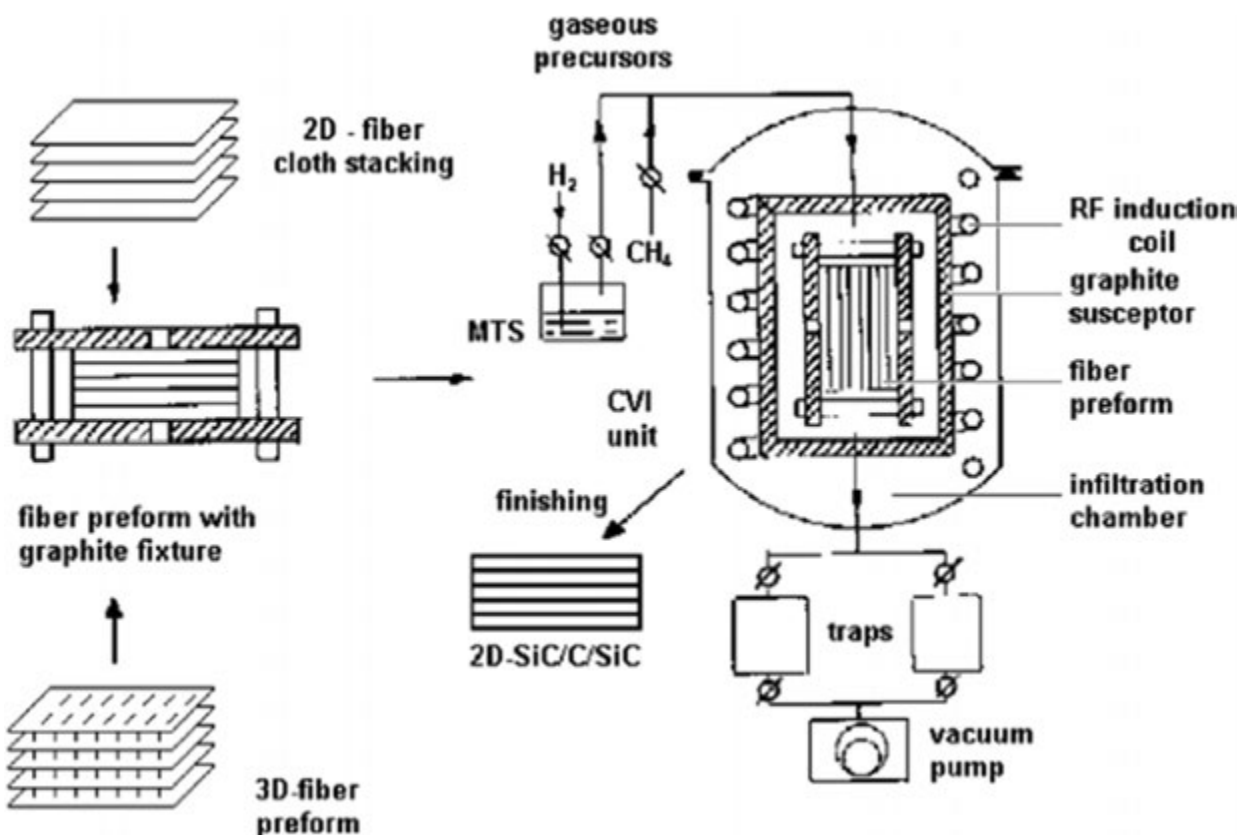


Fig. 12 Schematic view of the different stages for the fabrication of CMC by the CVI process. Reproduced from Naslain, R., 2004. Design, preparation and properties of non-oxide CMCs for application in engines and nuclear reactors: An overview. *Composites Science and Technology* 64, 155–170.

For example, SiC generally has a columnar growth, along the [111] crystallographic direction. The growth of coatings starts from all the developed accessible surfaces (the walls of voids) and stops once the surfaces of coatings meet each other in the narrow spaces. Locally, gas access into voids is prevented across the preforms and large voids remain at the end of the densification step as indicated in Fig. 13. Pores with angular shapes are visible (indicated by arrows). It is from such pores that matrix cracks are generated at low levels of loading.

To delay premature closure of pores, thermal gradients can be introduced into the preform. Forced flow through the preform are may or may not be additionally introduced to enhance the diffusion of gaseous precursor species and/or to reduce reaction rates (Besmann *et al.*, 1991) (see Fig. 14).

To conclude, the main advantages of I-CVI are: (1) limited fiber degradation (low T, P process), (2) high quality matrix deposition with variety of composition and microstructure (crystallinity), (3) near net shaping of composites (self standing preform), high flexibility (different preforms) and limited handling (low man-power cost).

However, the level of residual porosity remains relatively high at 10%–15%. Such a high level of porosity contributes to a lower elastic limit and reduces the thermal conductivity. According to the specifications for deposited materials, these composites should possess enhanced structural, chemical and mechanical stabilities. However, common process times for a densification of a fibrous preform, can require durations as long as a few hundred hours.

Fabrication by a Liquid or Semi-Liquid Route Infiltration

Slurry – Infiltration/hot pressing sintering (SI/HPS) route

The slurry infiltration manufacturing route is a pioneering process used to fabricate glass and glass-ceramic composites which has recently been revisited and adapted for refractory covalent matrices. The goal is to fill all the pores of a fibrous preform with the slurries of the material(s) of the future matrix.

The liquid precursor is a stable suspension (slurry) of fine particles in a solvent with fugitive binders and additives.

The main steps for the whole process are shown in Fig. 15 (Prewo, 1986; Bansal and Setlock, 2001) and can be listed as:

- Tow (or tape, woven, preform) impregnation to get a green prepreg
- Hot pressing for consolidation ($T > 1000^{\circ}\text{C}$)

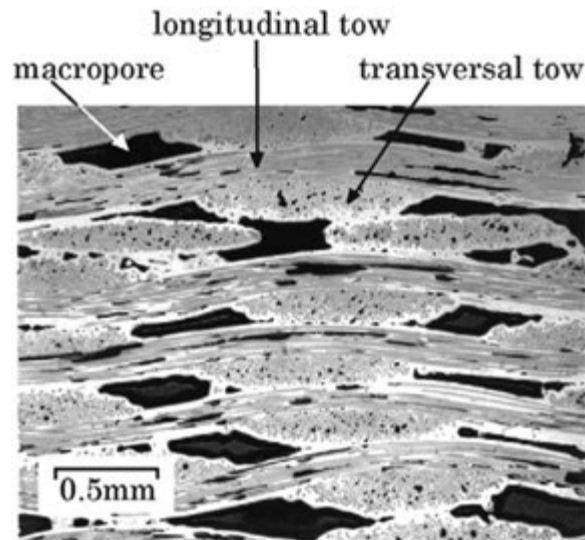


Fig. 13 Observation of a polished cross section of a SiC/SiC composite processed by CVI (SiC fiber – gray, SiC CVI matrix – white, pores – black). Reproduced from Carrere, P., Lamon, J., 2003. Creep behavior of a SiC/Si-B-C composite with a self-healing multilayered matrix. *Journal of the European Ceramic Society* 23, 1105–1114.

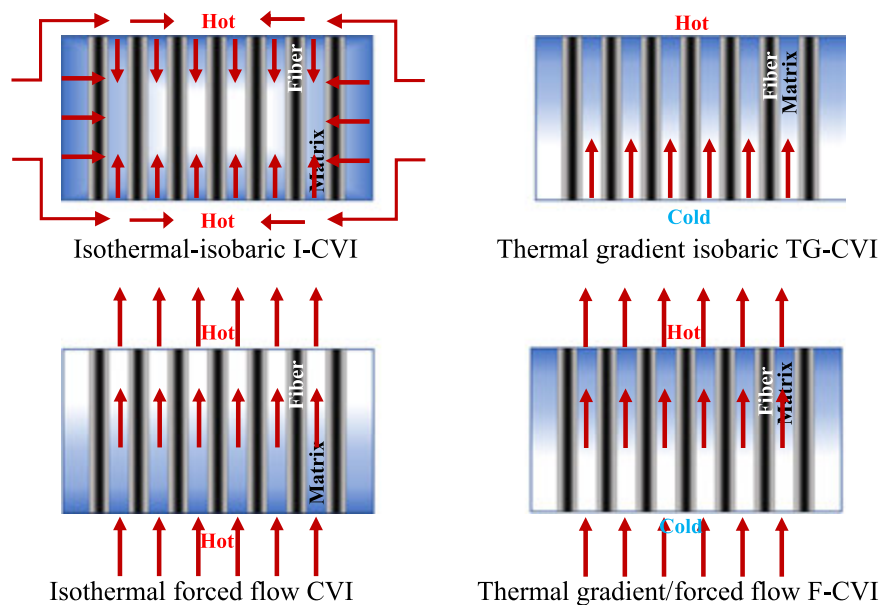


Fig. 14 Enhanced CVI processes (matrix – blue, void – white).

In the slurry, the proportions of powders of different materials can be easily regulated, to obtain a variety of compositions. However, it is necessary to be able to prepare stable suspensions to get homogeneous impregnation and sufficiently high fill rates. Many parameters can be taken into account such as: (1) the nature of the solvent, (2) the pH of the solution, (3) the use or not of a dispersant (often a polymer), (4) the size of the particles (such that they are thin/small enough to move inside fiber bundles) and (5) the final viscosity of the suspension.

Several methods have been considered to introduce the powder into the inside of the fibrous preform:

- Simple impregnation methods which consist of coating each layer of fabric by suspension, before stacking (Prewo, 1986; Bansal and Setlock, 2001);
- Methods of infiltration (Slurry Infiltration) where the suspension is directly deposited on the fabric, possibly aided by vacuum (Levi *et al.*, 1998);
- Injection methods, including RTM (Resin Transfer Molding) processes or Flexible Injection (Scola *et al.*, 2019), which are based on the introduction of the matrix into a mold containing the fibrous reinforcement in order to force the impregnation in to the reinforcement;
- Other more atypical methods such as colloidal processes (Simon, 2005) or VibroIntrusion (Haslam *et al.*, 2000).

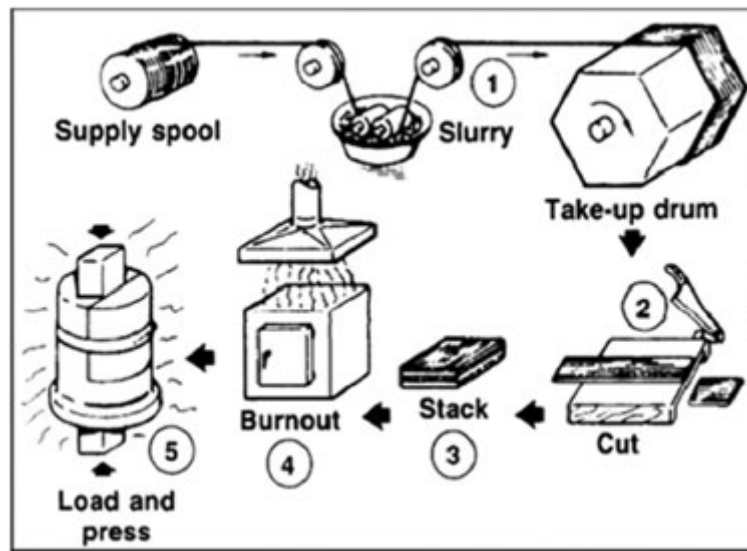


Fig. 15 Vacuum impregnation process of preforms by a slurry. Reproduced from Prewo, K.M., 1986. The development of fiber reinforced glasses and glass ceramics. In: *Tailoring multiphase and composite ceramics*. Materials Science Research, vol. 20, pp. 529–547. New York: Plenum Press. Bansal, N.P., Setlock J.A., 2001. Fabrication of fiber-reinforced celsian matrix composites. *Composites Part A: Applied Science and Manufacturing* 32 (8), 1021–1029.

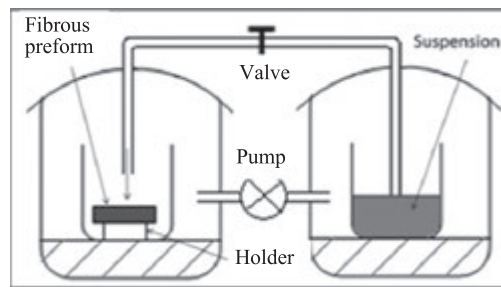


Fig. 16 Vacuum impregnation process of preforms by a slurry.

In addition, vacuum can be applied to the preform to enhance the impregnation step by a slurry or can be used to aspirate submicron powders (ASPs) through the preform.

Vacuum transfer impregnation is a classic method used for the impregnation of porous composites (see Fig. 16). The slurry or slip is allowed to slowly flow down on to a preform, maintained under vacuum. In a pore, during impregnation, the powder is homogeneously distributed in the solvent. After drying, the solvent evaporates and the particles form a layer on the walls of the pores. If the suspension has a low solids loading, large voids appear. This can be avoided with the use of a slip which has a sufficiently high powder loading. The development of such very concentrated slips is thus required for this technique. Vacuum transfer impregnation has the advantage of allowing the impregnation of parts with complex geometries, but the process is long and complex to implement.

Impregnation by the absorption of submicron powders, shown schematically in Fig. 17, is a technique allowing the introduction of powders into a fiber preform by applying pressure to the upper face of the sample, while the lower part is connected to a vacuum chamber. This method forces a powder suspension through the sample. A filter retains particles within the preform while the liquid passes through. Thus, the particles remain trapped within the pores until they are completely filled. The major drawback of this process remains the residual porosity within the powdery medium after impregnation of the powders. The use of a second process to improve densification is usually necessary, but its efficiency depends on the ratio of remaining open porosity.

Depending on the complexity of the geometry and/or the nature of the fiber, pressure and/or a high temperature cannot be used to enhance the sintering. Also, hot pressing is limited, in terms of applied pressure, on a fibrous preform made up of long fibers. This is so processing occurs without breaking fibers and/or introducing a very high level of residual stresses inside the different constituents. Consequently, when a pressureless sintering is only used, the amount of residual porosity can exceed 10% (see Fig. 18) (Prewo *et al.*, 1986; Rahaman and De Jonghe, 1987; Raether, 2013; Ben Ramdane *et al.*, 2017). Since all the matrix is porous with pre-existing processing cracks, the extended thin porous network itself causes deviations in matrix crack paths with a real branching effects

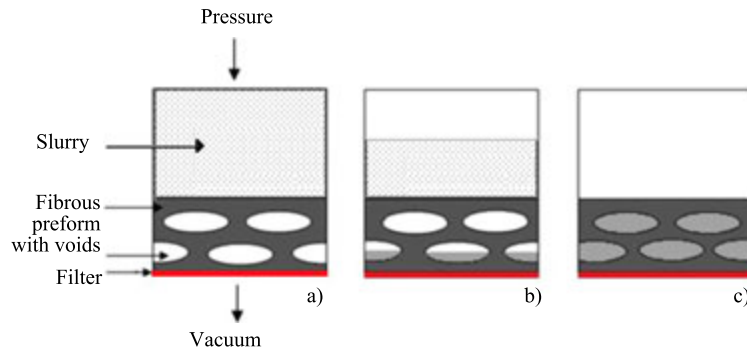


Fig. 17 Schematic diagram of APS: (a) before impregnation, (b) during impregnation, the suspension settling in the pores, (c) after impregnation, the pores are filled with the powder.

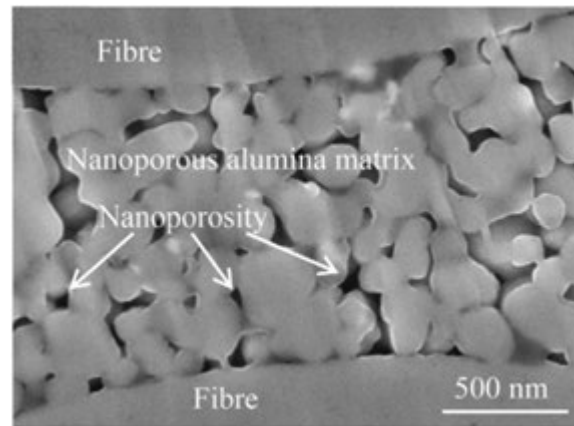


Fig. 18 Cross Section of a Nextel™ 610/alumina weak matrix composite. Reproduced from Ben Ramdane, C., Julian-Jankowiak, A., Valle, R., *et al.*, 2017. Microstructure and mechanical behavior of a Nextel™ 610/alumina weak matrix composite subjected to tensile and compressive loadings. *Journal of the European Ceramic Society* 37 (8), 2919–2932.

and toughening (Zok and Levi, 2001). The contribution of such a matrix to the level of the mechanical resistance of the composite remains modest and the non-linear domain can be reduced, depending on the fibrous architecture (Levi *et al.*, 1998).

To get a dense matrix with a low residual porosity (< 5%), a liquid phase aid is required during HPS (hot pressing sintering). With composites possessing a hermeticity, complex pieces in oxide/oxide composites are manufactured as distributors for exhaust systems (Raether, 2013) and parts in aircraft engines (e.g., Nozzle, Mixer, Center Body, and Engine Core Cowl) as indicated by Gonczy (2015). For non-oxide composites, a well known process is named the Nano-Infiltration Transient Eutectic Phase (NITE) process and involves the infiltration of SiC weaves and rovings by a nano-slurry. The manufacture of dense SiC ceramics is generally achieved by high sintering temperature ($\sim 2000^{\circ}\text{C}$) and/or under pressure ($> 30\text{ MPa}$) using SiC nanometric powder containing additives sintering (carbon, boron, $\text{Al}_2\text{O}_3/\text{SiO}_2$, $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ etc.) (Dong and Katoh, 2002a).

To conclude, the main advantages of the slurry cast process are: (1) a generic process relying on well-known technologies, (2) a residual porosity able to be reduced down to < 5% (hermeticity), (3) a short processing time, (4) near net shaping, and (5) purity and crystallinity. depending of those of the introduced powders.

According to reported specifications, these composites should possess a reduced elastic limit and thermal conductivity values as porosity levels increase. Their thermal stability is also affected by the purity of the constituents and/or the introduction of sintering aids.

Impregnation by an organic precursor of the matrix (PIP)

Polymer impregnation (PI) and pyrolysis (P) is a generic processing technique, which can be used to fabricate CMCs when a fusible (or soluble) polymer precursor of matrix is available. The PIP technique therefore makes it possible to control the composition of the matrix, due particularly to the diversity of organometallic precursors available.

Fig. 19 shows a schematic representation of the PIP process. It consists of: (1) impregnating a polymer precursor into the preform, (2) crosslinking this precursor in situ and (3) pyrolyzing it in order to form a ceramic matrix (Sato *et al.*, 1992; Dong *et al.*, 2002b; Kotani *et al.*, 1999). Numerous PIP cycles must be repeated until the desired densification level is achieved in order to fill the volume shrinkage resulting from the pyrolysis of the precursor (Ziegler *et al.*, 1999; Jones *et al.*, 1999).

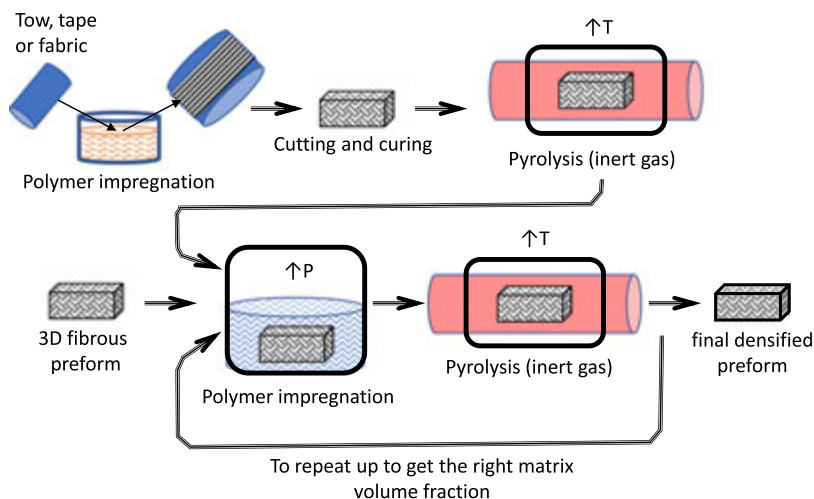


Fig. 19 Schematic of the PIP process.

The pre-ceramic precursors are selected according to their chemical composition, their viscosity, the crosslinking conditions, the ceramic yield, the volume shrinkage during pyrolysis, the microstructure of the matrix obtained or their stability (at temperature, in air and in high humidity) (Greil, 2000; Mutin and Boury, 2001). For example, many polymer precursors possessing a high ceramic yield can be listed as:

phenolic or furanic resin, pitch	carbon
polycarbosilane (PCS)	SiC
perhydropolysilazane (PHPSZ)	Si ₃ N ₄
polyalkylborazine (MAB)	BN
poly-borosilazane (PBSZ-Me)	Si-B-N-C

Different techniques can be used to impregnate the preceramic resin into the preform. The most widely used are: (1) impregnation under reduced pressure, which consists of creating a primary vacuum in an enclosure containing the sample immersed in the resin and (2) the RTM (resin transfer molding) process where the resin is injected under pressure into a preform placed in a mold (Naslain, 2004). A good wetting of the preform by the resin is essential to impregnate a maximum material and make this step efficient.

The cross-linking step (or curing) conditions the progress of the pyrolysis. It allows the formation of bonds between the polymer chains so that mainly methyl groups and heteroatoms (hydrogen, oxygen and nitrogen) are evacuated during pyrolysis. Crosslinking can be carried out thermally, by oxidation in air, by chemical additives, or by irradiation depending on the polymer used.

The pyrolysis step transforms the network obtained by crosslinking into a ceramic. The yield and composition of the final ceramic material depend first on the composition of the precursor, but also largely the crosslinking conditions and pyrolysis. The application of isostatic pressure in an autoclave during pyrolysis can increase the yield of residual condensed phase. It is usually done by conventional heating, but there are also heating processes involving laser pyrolysis, irradiation, or microwave. In general, pyrolysis under an inert atmosphere takes place according to the following steps (Mutin and Boury, 2001):

- (1) degradation, loss of organic compounds (300–600°C);
- (2) mineralization, loss of hydrocarbons and hydrogen (400–1000°C);
- (3) decomposition, loss of CO, SiO, N₂.

However, the composition and crystallinity of the ceramic residue depend on the temperature of pyrolysis, the rate of temperature rise, but also the atmosphere of pyrolysis. For example, the pyrolysis of a polycarbosilane can give a SiC matrix with free carbon under argon, but only SiC under hydrogen (Yajima *et al.*, 1976).

Many dimensional changes occur during polymer-ceramic conversion for bulk component fabrication (Greil and Seibold, 1992; Greil, 1998, 2000) (see Fig. 20). So, the main drawback is the volume shrinkage observed during pyrolysis, with a volume decrease up to more than 50% (Bertran, 2013) (see Fig. 21). The repetition of PIP cycles makes the process long (Ziegler *et al.*, 1999) and expensive, especially since polymer precursors are relatively expensive. This is why this densification technique is still not widely used industrially.

As indicated in Fig. 20, the pre-ceramic resin can be loaded with ceramic, non-reactive powders (C, SiC, Si₃N₄), in order to improve the desired properties of the composite, or else to decrease the volume shrinkage (Kotani *et al.*, 2003; Lee and Kim, 2009; Zhu *et al.*, 2008). Nevertheless, the addition of these charges considerably increases the viscosity of the infiltrant, to the detriment of the impregnation of the preform.

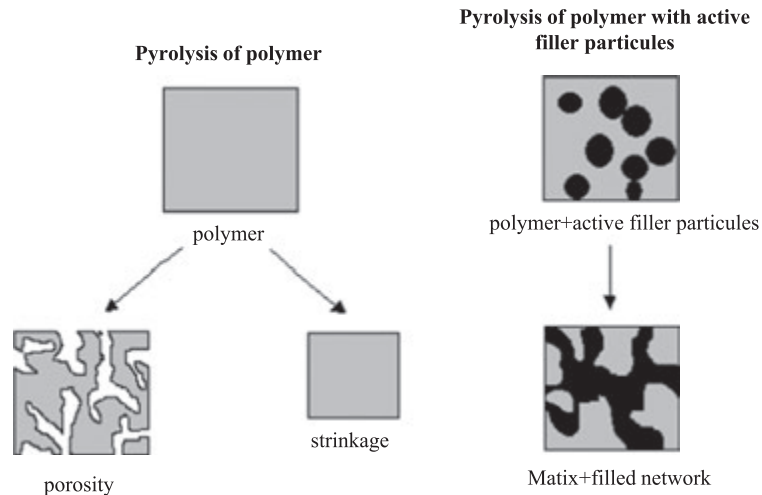


Fig. 20 Volume changes of polymer-ceramic during pyrolysis without and with reactive charge.

To conclude, this process is based on well-known technologies. The PIP-residue is generally amorphous but can be sintered or crystallized with post heat treatments. It is well suited to complex composition and does not require heavy investment. However, the weight loss/shrinkage during pyrolysis may require filler addition and/or multiple PIP sequences. These composites can possess a high residual porosity.

Like the liquid infiltrated CMCs, these composites should possess elastic limits and thermal conductivities which are controlled by porosity levels and their thermal stabilities are related to the impurities present in the polymer precursors.

Hybrid Processing Route or the Use of the MI/RMI Process

Presentation of MI/RMI process and the hybrid route

The previous processes discussed have many drawbacks with a too high a residual porosity level. To get a matrix close to 100% dense, combined processes are generally required which allow complete filling of voids with condensed material as indicated in Fig. 22. To reach such a level of densification, impregnation with a molten material is advised. This material should have a high melting point, allowing to get it (1) in a liquid state for the impregnation at very high temperature, compatible with the thermal-stability of the preform and (2) still in a solid state at high temperature, according to future application temperature requirements. In the case of a metal, the process is named as MI/RMI: Melt infiltration/Reactive melt infiltration. The infiltration temperatures must be higher than the melting temperature of the metal or alloy used, for example: (1) formation of SiC by infiltration of Si, $T_f = 1415^\circ\text{C}$ (Krenkel, 2004), or (2) formation of ZrC by infiltration of Zr, $T_f = 1850^\circ\text{C}$ (Quet, 2007). The melt metal is introduced inside a preform, generally partially filled with by PIP/slurry processing (see Figs. 23 and 24). This infiltration is termed reactive when the metal is consumed by reaction with this filler material to give a more refractory compound (ceramic (for example, carbide, as previously mentioned, by reaction with carbon) or intermetallic).

Historically, the first work on the infiltration of molten silicon dates back to 50 years ago with that of Popper *et al.* on the reactive sintering of SiC (Popper and Davies, 1961). The process was subsequently optimized, then produced industrially by Ford (KT SiC) and the Atomic Energy Authority (REFEL SiC) (Forrest *et al.*, 1972) in Great Britain and Norton Ceramics (NC 435) in the USA. General Electric introduced in early 1970s, the impregnation of ceramics reinforced with carbon fibers (Hillig *et al.*, 1975). The liquid silicon infiltration technology itself has been the subject of numerous patents from General Electric (Brun and Morrison, 1993; Hillig and Morelock, 1980). The liquid silicon impregnation process has been applied to SiC/SiC composites from the beginning of 1990s (Luthra *et al.*, 1993).

Of those routes developed only two have been selected for industrialization (Luthra and Corman, 2001): one path known as “prepreg” and the other “slurry cast” (shown schematically in Fig. 23). The “prepreg” route begins with the deposition of an interphase of doped boron nitride silicon, then a layer of SiC, on Hi-Nicalon or Sylramic fiber bundles or just the deposition of SiC interphase. The bundles are then “dipped” in a slip containing SiC particles, particles of carbon, organic binders and a solvent, then are wound around a mandrel. After drying, the bundles are cut then spread and compressed to form a porous preform. At this stage the preform can be cut according to the desired final geometry. Infiltration by liquid silicon, according to one of the different processes developed by G.E., takes place after an intermediate debinding step at 500°C allowing the decomposition of organic carbon containing products.

The second path known as “slurry cast” differs from the previous one in that the fibers are first woven or braided and then compacted to form a 3D fibrous preform. An interphase identical to the previous one (BN or BN (Si) + SiC) is deposited by CVI. The preform, thus consolidated, is impregnated with the same slip as before then densified by the liquid silicon.

In the case of a liquid silicon infiltration, the conditions used are fairly standard, namely: a temperature below 1450°C , a reduced pressure less than 5×10^2 Pa and an impregnation time of 10–30 min (Brun and Morrison, 1993; Hillig and Morelock,

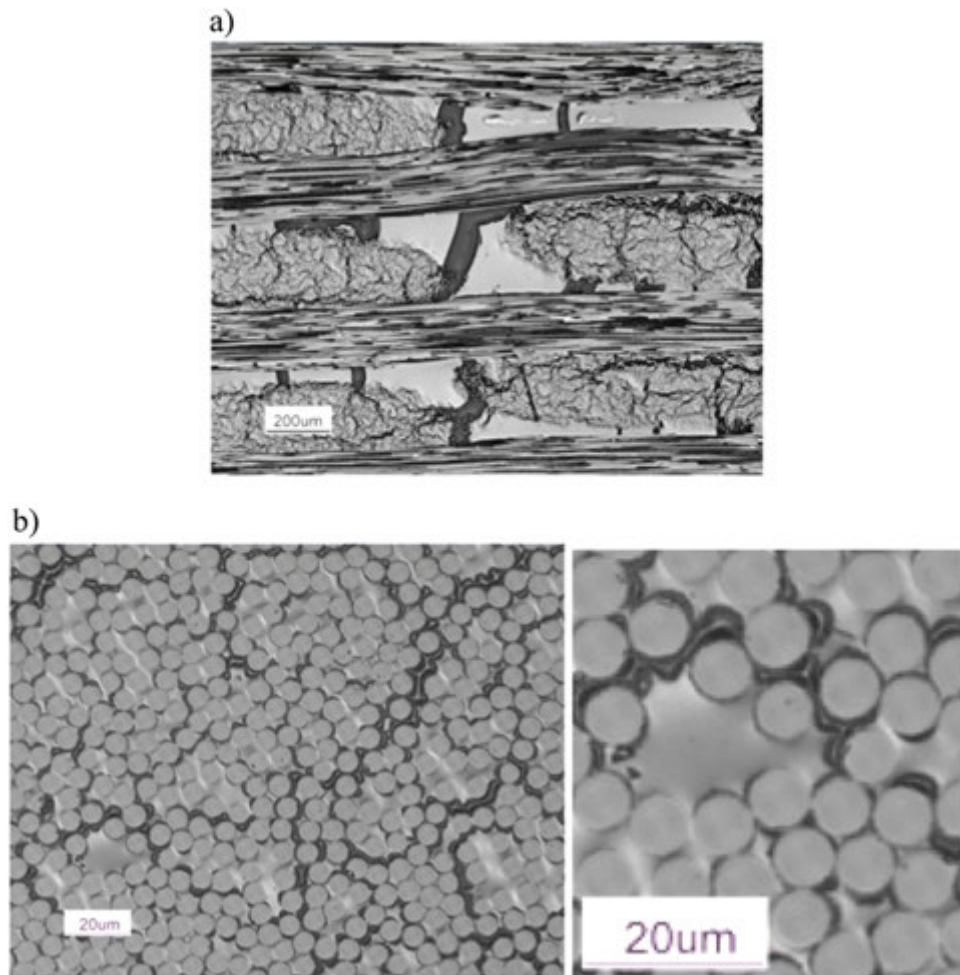


Fig. 21 Electron micrograph of the cross section of a C/C composite after 1 PIP cycles at different magnifications: (a) whole composite and (b) in a bundle. Reproduced from Bertran, X., 2013. Comportement en oxydation de matériaux composites C/C dans des applications aéronautiques à faible température. PhD Thesis. University of Bordeaux.

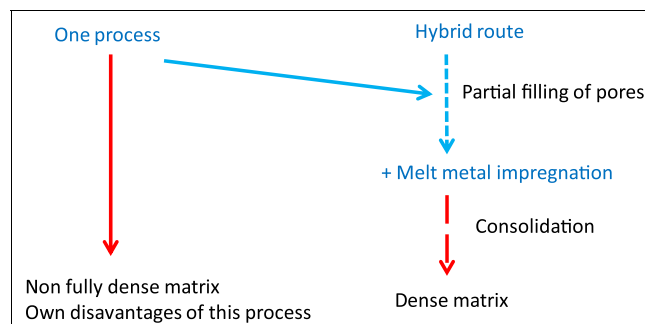


Fig. 22 Combination of processes to get a dense matrix in CMC.

1980). The silicon is brought into contact with the material by means of a nozzle (Luthra and Corman, 2001; Luthra *et al.*, 1993). It can also simply be put on the top of the preform (Luthra *et al.*, 1993) as indicated in Fig. 24. The use of a nozzle reduces the post infiltration machining phase by reducing the excess silicon on the surface of the material.

The essential parameter for the infiltration of a preform is the wetting of the substrate by the molten metal which is then directed inside the preform via the capillary driving forces. Various parameters influence the state of densification and the final composition of the composites produced: the infiltration time, the infiltration temperature, the porosity of the material to be densified, and the size distribution of the pores.

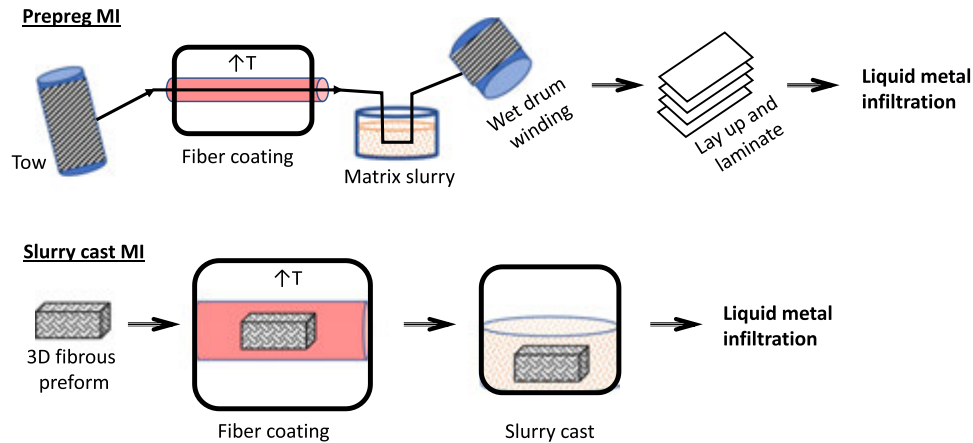


Fig. 23 Impregnation process, prior to the MI step.

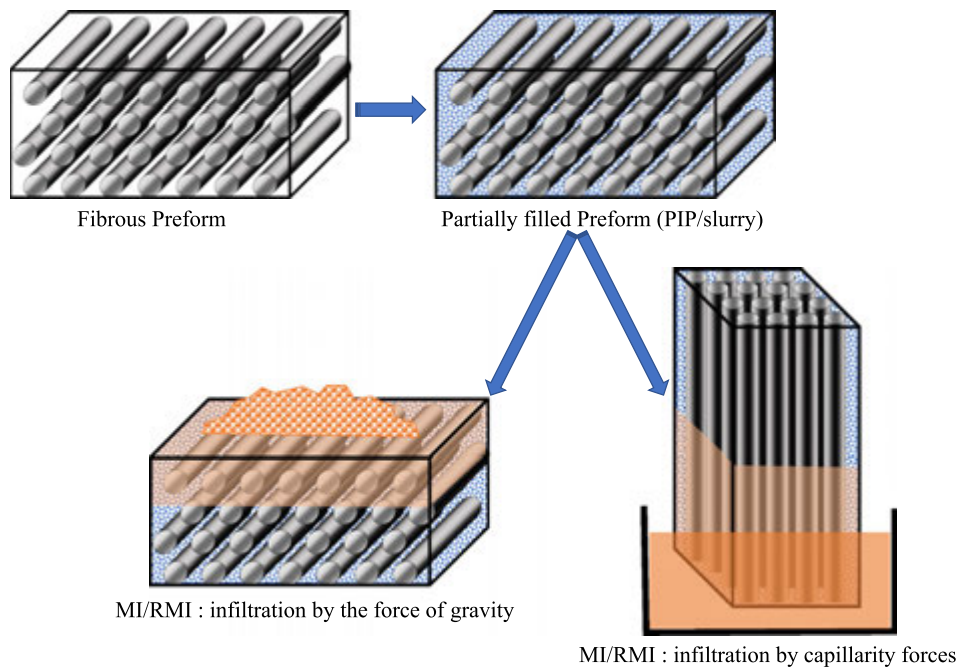


Fig. 24 Schematic of the liquid silicon impregnation process of a fibrous preform, impregnated with a filler material.

To help in the prediction and understanding of the infiltration process, Washburn (see [Mondon, 1996](#)) introduced a mathematical expression allowing the determination of the penetration as a function of time, of a fluid in a porous medium defined by parallel pores and constant section. This simple law is often used to understand the global kinetics of impregnation of a preform. However, the application of this law is limited to short times, to low heights (thus negating the need to account for the forces of gravity) and identical cylindrical pores. Here, the porosity is summarized as an average pore size that is assumed to represent and gather the large distribution of pore distribution in porous structure of fibrous composites.

Specificities of the RMI process with melted silicon

There are many ways possible to develop a porous carbon inside the porosity of the preform (pitch, wood, phenolic resin, aerogels, pyrolysis of an organic binder ([Hucke, 1966](#))).

The wetting of liquid silicon on the carbon is said to be reactive due to a chemical reaction between solid and liquid and the formation of a new phase at the solid/liquid interface. The chemical reaction between carbon and silicon leads to the formation of β -SiC, with an enthalpy of formation (ΔH_{298}°) equal to $-69-73 \text{ kJ mol}^{-1}$ ([Fitzer and Gadov, 1983](#)). This reaction is exothermic and its degree depends on the nature of the carbonaceous substrate ([Sangsuwan et al., 1999](#); [Singh and Behrendt, 1995](#)). Carbon has a solubility in liquid silicon of less than 1 at%, compared to $10^{-2}-10^{-4}$ at% C in solid silicon over a temperature range up to 1800K. The diffusion of carbon in liquid silicon is very fast and depends on temperature ([Pampuch et al., 1986](#)). The material

produced has a microstructure of α - and β -SiC grains forming an interconnected network, in which the remaining volume is occupied by free silicon.

However, the volume of the solid phase occupied by a carbon atom doubles when it is transformed into SiC. Thus, the open porosity of carbon must be large enough to allow the volume increase due to this reaction in presence of silicon. If this is not the case, the access of the molten silicon to the inside of the preform is locally stopped prematurely by the formation of SiC, acting as a cork. This phenomenon is called “choking-off” (Hillig, 1993; Singh and Behrendt, 1994). Fitzer and Gadow (1983) have shown that the infiltration of carbon by silicon requires control of the microstructure and porosity of the initial carbon preform.

Hybrid route applied to SiC/SiC

In this manufacturing process, the fibrous reinforcement is first protected by a specific interphase. The whole is then coated with a SiC matrix, to protect the previous constituents from the diffusion of Si (Nannetti *et al.*, 2001). The material obtained is then impregnated with carbon fillers and/or SiC before being densified with liquid silicon. Generally, the production is done without applying an external pressure, but under vacuum, at a lower temperature than 1500°C (Luthra *et al.*, 1993) (see Fig. 24). The silicon impregnation ends the process and allows the formation of a matrix of SiC, more or less rich in silicon and silicides instead of the initial porosity. The final microstructure, in particular the residual silicon content, will depend on the nature of the constituents of the preform to infiltrate (e.g., grain size, porosity of the preform, non reactive SiC or reactive C, nature of the carbon filler, etc.). Silicon fills all open voids and notably macropores partly filled after impregnation by the filler (see Figs. 25(a) and 26). Many small closed pores inside bundles remain empty of silicon (Fig. 26). The residual porosity is essential linked to the latter voids. For example, if the initial porosity inside the preform is around 40%, it can be reduced to 20% after impregnation of SiC powder and less than 5%, after MI/RMI (Griesser, 2012) (again see Figs. 25(a) and 26).

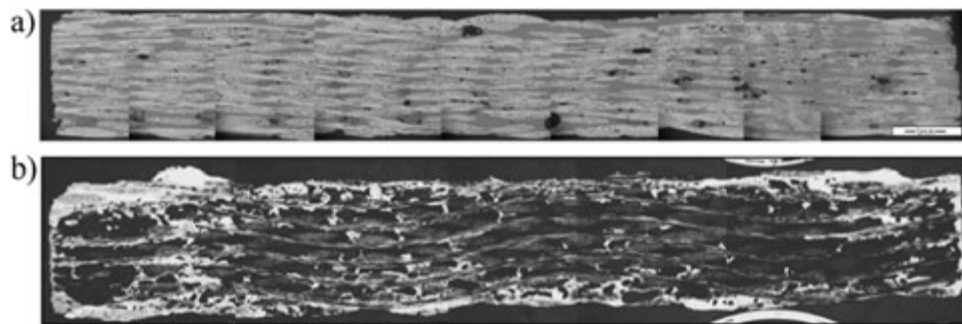


Fig. 25 Liquid silicon impregnation of a SiC perform, impregnated with SiC fillers: (a) optimized impregnation and (b) impregnation prevented by gaseous release (free Si – white, SiC – different shades of gray, pores – black). Reproduced from Griesser, A., 2012. *Réalisation de matériaux composites à conductivité thermique accrue pour l’aéronautique*. PhD Thesis. University of Bordeaux.

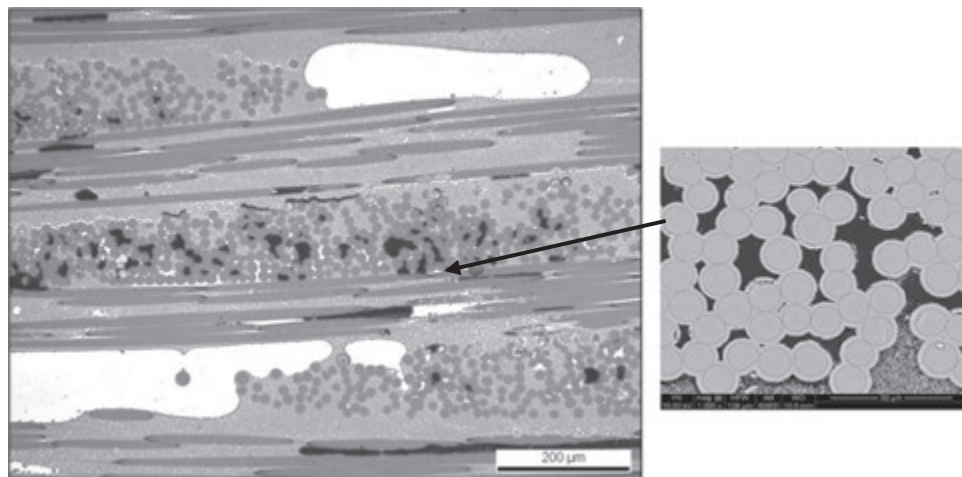


Fig. 26 Detailed observation of a polished cross section on a liquid silicon impregnation of a SiC perform, impregnated with SiC fillers (free Si – white, SiC – different shades of gray, pores – black). Reproduced from Griesser, A., 2012. *Réalisation de matériaux composites à conductivité thermique accrue pour l’aéronautique*. PhD Thesis. University of Bordeaux.

Some authors attribute the presence of excessive porosity to the release of gaseous species within the preform during infiltration by liquid silicon (Morelock, 1986; Zhu and Shobu, 2001; Pan and Baptista, 1998; Griesser, 2012). A typical composite microstructure with such defects is shown in Fig. 25(b). These gaseous species are generated by the reduction of the silica layer present on the surface of the SiC grains, causing resistance to infiltration of the inside of the material, where they remain trapped due to faster infiltration at the outside of the preform. In order to prevent this phenomenon, a slowing of the infiltration is necessary in order to allow the evacuation of the gases produced before full densification of the material. This is possible by providing the silicon indirectly, or by designing a tool allowing the silicon to flow over the preform through a hole (Zhu and Shobu, 2000), either by using a nozzle (porous SiC bar) (Pan and Baptista, 1998), carbon wick (Morelock, 1986).

Furthermore, the presence of free silicon (from 10% to 65%, with reactive or non reactive fillers, or no fillers) within the ceramic composite limits its use to 1400°C and reduces the high temperature mechanical properties especially from 1200 to 1300°C, the extent of this decrease depending on the proportion of silicon (Zhou *et al.*, 1997). In order to allow their use at temperatures above 1400°C and to avoid reduction in mechanical properties at high temperature, the use of silicon alloys has been introduced to reduce the quantity of free silicon. The aim is to allow the precipitation of more refractory silicides to replace residual silicon (Van Rossum and Maex, 1995). Many alloys have been used and the most conclusive results having been obtained with those based on molybdenum (Singh *et al.*, 1991) for application for combustion chamber, and iron for application for brake disc applications (Gadow and Speicher, 2001). However, in order to allow good wetting of the alloy on SiC, an increase in the production temperature of around one hundred degrees above the melting point is sometimes necessary (Pan and Baptista, 1998).

To conclude, this process is faster and less expensive than CVI or PIP, since it allows very quick (less than an hour) and uniform to densification of the (macroscopic) porosities of fiber preforms (Jiang *et al.*, 2015; Tang and Hu, 2017). The need for production temperatures above 1410°C for several minutes requires the use of very stable SiC stoichiometric fibers. The major disadvantage remains the damage caused by the reactions between the molten metal and the C interphase and/or fibers (C or SiC), which can be all the more important as the processing temperature is high. The very reactive silicon with respect to interphase materials (C or BN) requires the prior deposition of a continuous protective layer (generally of SiC). Furthermore, the presence of residual metal after densification can have a negative effect on the mechanical properties at high temperature (in particular when the application temperature approaches the melting point of silicon where is able to flow through opening of cracks and/or react with and destroy with the carbon interphase and fibers by diffusion).

The mechanical characterization carried out on this type of material showed improvements in the linear domain and in the modulus of the composite, as well as better interlaminar properties, compared to a SiC/SiC composite developed by CVI (Corman *et al.*, 2003). Thanks to almost zero porosity composites, a marked increase in their thermal conductivity is also obtained.

Hybrid route applied to C/C

The application of the hybrid route to C/C composites was chosen to overcome their low resistance to oxidation and decrease their manufacturing cost. The first work was conducted within the German Aerospace Center (DLR) in Stuttgart, Germany for applications in the space field. These materials showed very good tribological properties (friction in particular), and their development continued with a view to producing high performance brakes (Krenkel and Fabig, 1995). Today, the goal of research in the area is to eventually use these materials in large amounts for automobile and plane brakes.

However, free silicon is observed within the matrix after silicon infiltration due to the filling of the porosities by the molten metal, (Kochendörfer, 1999; Krenkel, 2001; Schulte-Fischedick *et al.*, 2002; Lenz and Krenkel, 2012). This molten metal can oxidize, and creep when the composite is in use. Its distribution in the C/C composite is related to the matrix crack network developed during the pyrolysis of the carbon resin precursor according to the fiber/matrix strength bond (Kochendörfer, 1999).

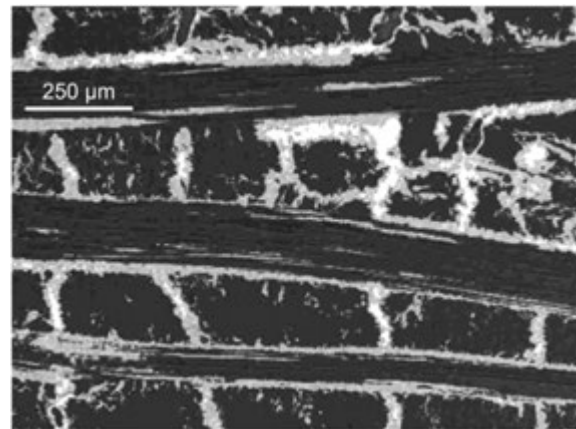


Fig. 27 2D C-C/SiC composite after infiltration of liquid silicon on Cf/C preforms (Si – white, SiC – gray and C/C – black). Reproduced from Schulte-Fischedick, J., Zern, A., Mayer, J., *et al.*, 2002. Thermorphology of silicon carbide in C/C-SiC composites. *Materials Science and Engineering*: A332, 146–152.

After infiltration, formation of a SiC layer around the wires can be observed as well as the presence of carbon (fibers and protective coating) and residual silicon. Some carbon fibers can be partly consumed by reaction with the diffusing silicon along these cracks inside the composite as indicated in Fig. 27.

The RMI process is now used to densified C/C preform with Zr alloys (Tong *et al.*, 2012; Jiang *et al.*, 2014; Tong *et al.*, 2015; Chen *et al.*, 2016) or ZrSi₂ (Pi *et al.*, 2012; Zhang *et al.*, 2014) to get a protective UHTC matrix against oxidation at ultra high temperatures.

Conclusion

The properties typically required of long-fiber Ceramic Matrix Composites are: high mechanical strength, high thermal shock resistance, high stiffness, high toughness, high thermal stability, low density and high corrosion resistance, even at high temperatures.

SiC-matrix composites display a non-linear damageable-elastic behavior when loaded in tension and this is related to different damage phenomena at the scale of the microstructure (matrix microcracking, fiber-matrix debonding) and this damage is responsible for the decrease of stiffness. Failure occurs with some fiber pull-out at a strain depending upon the nature of fibers. Highest failure strengths are achieved when the interfacial bond is intermediate (not too strong) and crack deflection occurs in a diffuse manner in an anisotropic interphase. Such composites are tough and damage tolerant.

CMCs are fabricated by different processing routes depending on the nature of the matrix precursor: gas phase routes (CVI), liquid phase routes (PIP or RMI) and slurry routes, the matrix precursor being a gaseous species, a polymer or a molten element, or a particle suspension (slurry), respectively. The more recent research on a variety of modified processes are generally inspired by the well-known previously existing methods of manufacture. The major goals are still to reduce the cost and to shorten the fabrication time.

The final properties are strongly related to the microstructure of the constituents: purity, crystallinity, grain size, porosity. At the same time, each process allows only some of the required characteristics of microstructure to be realized. The combination of at least two simple methods makes it possible to reduce the disadvantages of each of them.

Thus, CMC, including C/C, composites have already applications in different fields. They are used to fabricate large size hot structures for space-craft and rocket engines for relatively short lifetime parts. Another promising application deals with aerojet engines and land-based gas turbines for cogeneration, where lifetime is of the order of several thousand hours at temperatures of up to 1200°C (if suitably protective environmental barrier coatings are applied). SiC/SiC composites seem to have a bright future in HT-nuclear reactors (fission or fusion) due to their low level of residual radioactivity after irradiation. Finally, C/SiC composites are used in advanced braking systems.

References

- Arnault, V., 1989. Relation entre microstructure et comportement mécanique des composites SiC/SiC: Analyse et rôle de l'interface dans le processus de fissuration matricielle dans les matériaux multi-filamentaires. PhD thesis. Lyon: INSA.
- Aveston, J., Cooper, G., A., Kelly, A., 1971. Single and multiple fracture. In Surrey: IPC Sci. Technol. Press. 4. In: Proceedings of Conference on the Properties of fiber composite of the National Physical Laboratory, pp.15–26.
- Bansal, N.P. (Ed.), 2005. Handbook of Ceramic Composites. Norwell, MA: Kluwer Academic.
- Bansal, N.P., Setlock, J.A., 2001. Fabrication of fiber-reinforced ceramic matrix composites. Composites Part A: Applied Science and Manufacturing 32 (8), 1021–1029.
- Ben Ramdane, C., Julian-Jankowiak, A., Valle, R., *et al.*, 2017. Microstructure and mechanical behaviour of a Nextel™ 610/alumina weak matrix composite subjected to tensile and compressive loadings. Journal of the European Ceramic Society 37 (8), 2919–2932.
- Bertran, X., 2013. Comportement en oxydation de matériaux composites C/C dans des applications aéronautiques à faible température. PhD Thesis. University of Bordeaux.
- Bertrand, R., Caty, O., Mazars, V., *et al.*, 2017. In-situ tensile tests under SEM and X-ray computed micro-tomography aimed at studying a self-healing matrix composite submitted to different thermomechanical cycles. Journal of the European Ceramic Society 37, 3471–3474.
- Bertrand, S., Droillard, C., Paillet, R., Bourrat, X., Naslain, R., 2000. TEM structure of (PyC/SiC)_n multilayered interphases in SiC/SiC composites. Journal of the European Ceramic Society 20 (1), 1–13.
- Besmann, T.M., Sheldon, B.W., Lowden, R.A., Stinton, D.P., 1991. Vapor-phase fabrication and properties of continuous-filament ceramic composites. Science 253 (5024), 1104–1109.
- Boisvert, R.P., Diefendorf, R., Hutter, R., 1989. Interface manipulation in ceramic matrix composites for improved mechanical performance. In: Proceedings of the Fourth Japan-U.S. Conference on Composite Materials, pp. 789–798. Washington, DC.
- Bouillon, E., Lamouroux, F., Baroumes, L., *et al.*, 2002. An improved long life duration CMC for jet aircraft engine applications. In Proceedings of the ASME Turbo Expo 2002: Presented at the 2002 ASME Turbo Expo. New York, NY: American Society of Mechanical Engineers, (ID GT-2002-30625).
- Bouillon, E., Spriet, P., Habarou, G., *et al.*, 2004. Engine test and post engine test characterization of self sealing ceramic matrix composites for nozzle applications in gas turbine engines. In Proceedings of the ASME Turbo Expo 2004: Presented at the 2004 ASME Turbo Expo. New York, NY: American Society of Mechanical Engineers, (ID GT-2004-53976).
- Brun, M.K., Morrison, W.A., 1993. US patent No. 5,205,970 (Method of infiltration forming a silicon carbide body with improved surface finish).
- Budianski, B., Hutchinson, J.W., Evans, A.G., 1986. Matrix fracture in fiber reinforced ceramics. Journal of the Mechanics and Physics of Solids 34, 167–189.
- Bunsell, A.R., 2001. Fibers with high modulus. In: Buschow, J.K.H., Cahn, R.W., Flemings, M.C., *et al.* (Eds.), Encyclopedia of Materials: Science and Technology. Pergamon: Elsevier Science Ltd, pp. 3151–3157.
- Casas, L., Martinez-Esnaola, J.M., 2003. Modelling the effect of oxidation on the creep behavior of fibre-reinforced ceramic matrix composites. Acta Materialia 51, 3745–3757.
- Cavalier, J.C., Berdoyes, I., Bouillon, E., 2006. Composites in aerospace industry. Advanced Science Technology 50, 153–162.
- Chawla, K.K., 2012. Composite Materials Science and Engineering, third ed. New York; Heidelberg; Dordrecht London: Springer-Verlag.
- Chen, X., Dong, S., Kan, Y., *et al.*, 2016. 3D C_f/SiC-ZrC-ZrB₂ composites fabricated via sol-gel process combined with reactive melt infiltration. Journal of the European Ceramic Society 36, 3607–3613.

- Christin, F., 2002. Design, fabrication, and application of thermostructural composites like C/C, C/SiC, and SiC/SiC composites. *Advanced Engineering Materials* 4 (12), 903–912.
- Corman, G.S., Luthra, K.L., Brun, M.K., 2003. Chapter 16 – Silicon melt infiltrated ceramic composites – Processes and properties. In: van Roode, M., Ferber, V., Richerson, D. (Eds.), *Progress in Ceramic Gas Turbine Development*, vol. II, Ceramic Gas Turbine Component Development and Evolution, Fabrication, NDE, Testing and Life Prediction. ASME Press, New York.
- Curtin, W., 1991. Theory of mechanical properties of ceramic matrix composites. *Journal of the American Ceramic Society* 74 (11), 2837–2845.
- DiCarlo, J.A., Yun, H.M., Hurst, J.B., 2004. Fracture mechanisms for SiC fibers and SiC/SiC composites under stress-rupture conditions at high temperatures. *Applied Mathematics and Computation* 152, 473–481.
- Diefendorf, R.J., Boisvert, R.P., 1988. Processing of polymeric precursor, ceramic matrix composites. *MRS Online Proceedings Library Archive* 120, 157–162.
- Dong, S., Katoh, Y., 2002a. Development of SiC/SiC composites by nano-infiltration and transient eutectoid (NITE) process. *Ceramic Engineering & Science Proceedings* 23, 311–318.
- Dong, S.M., Katoh, Y., Kohyama, A., Schwab, S.T., Snead, L.L., 2002b. Microstructural evolution and mechanical performances of SiC/SiC composites by polymer impregnation/microwave pyrolysis (PIMP) process. *Ceramic International* 28 (8), 899–905.
- Dröillard, C., Lamon, J., Bourrat, X., 1995. Strong interface in CMCs, a condition for efficient multilayered interphases. *Ceramic matrix composites-advanced high temperature structural materials: Symposium*. In: Lowden, R.A., Ferber, M.K., Hellmann, J.R., Chawla, K.K., Dipietro, S.G. (Eds.), *Materials Research Society Symposium Proceedings*, vol. 365, pp. 371–76. Boston, MA.
- Evans, A.G., Zok, F.W., 1994. Review: The physics and mechanics of fibre-reinforced brittle matrix composites. *Journal of Materials Science* 29, 3857–3896.
- Evans, A.G., Zok, F.W., Davis, J., 1991. The role of interfaces in fibre-reinforced brittle matrix composites. *Composites Science and Technology* 42, 3–24.
- Fedou, R., Sipp, E., Rebillat, F., Langlais, F., Naslain, R., 1993. A modeling of the isothermal isobaric chemical vapor infiltration (CVI) in a straight cylindrical pore: 3. Application to the CVI of zirconia or yttria. *Journal of Materials Synthesis and Processing* 1 (5), 295–310.
- Filipuzzi, L., Camus, G., Naslain, R., 1994. Oxidation mechanisms and kinetics of 1D-SiC/C/SiC composite Materials: I, An experimental approach. *Journal of the American Ceramic Society* 77, 459–466.
- Fitzer, E., Gadow, R., 1983. Investigations of the reactivity of different carbons with liquid silicon. In: Somiya, S., Kanai, E., Ando, K. (Eds.), *Proceedings of the First International Symposium on Ceramic Components for Engines*. New York: Elsevier Science Publishers, pp. 561–572.
- Fitzer, E., Gadow, R., 1986. Fiber reinforced silicon carbide. *American Ceramic Society Bulletin* 65, 326–335.
- Forrest, C.W., Kennedy, P., Shennan, J.V., 1972. The fabrication and properties of self-bonded silicon carbide. In: Popper, P. (Ed.), *Proceedings of the Fifth Symposium on Special Ceramics at the British Ceramic Research Association*. London: Heywood, pp. 99–123.
- Gadow, R., Speicher, M., 2001. Manufacturing of ceramic matrix composites for automotive applications. *Ceramic Transactions* 128, 25–41.
- Glime, W.H., Cawley, J.D., 1995. Oxidation of carbon fibers and films in ceramic matrix composites: A weak link process. *Carbon* 33 (8), 1053–1060.
- Golecki, I., 1997. Recent advances in rapid vapor-phase densification of high-temperature fiber-matrix composites. In: Singh, J.P. (Eds.), *Proceedings of the 21st Annual Conference on Composites, Advanced Ceramics, Materials, and Structures – B: Ceramic Engineering and Science Proceedings*, vol. 18 (4), pp. 721–730.
- Gonczy, S.T., 2015. Federal Aviation Administration (FAA) airworthiness certification for ceramic matrix composite components in civil aircraft systems. In: *Proceedings of the MATEC Web of Conferences*, vol. 29 (00002), pp. 1–10.
- Greil, P., 1998. Near net shape manufacturing of polymer derived ceramics. *Journal of the European Ceramic Society* 18 (13), 1905–1914.
- Greil, P., 2000. Polymer derived engineering ceramics. *Advanced Engine Materials* 2 (6), 339–348.
- Greil, P., Seibold, M., 1992. Modelling of dimensional changes during polymer/ceramic conversion for bulk component fabrication. *Journal of Materials Science* 27 (4), 1053–1060.
- Griesser, A., 2012. *Réalisation de matériaux composites à conductivité thermique accrue pour l'aéronautique*. PhD Thesis. University of Bordeaux.
- Guillaumat, L., 1994. *Microfissuration des CMCs: Relation avec la microstructure et le comportement mécanique*. PhD Thesis. University of Bordeaux.
- Haslam, J.J., Bertho, K.E., Lange, F.F., 2000. Processing and properties of an all-oxide composite with a porous matrix. *Journal of the European Ceramic Society* 20 (5), 607–618.
- Heraud, L., Naslain, R., Quenisset J.M., 1989. French patent 89 02718 (Procédé de fabrication d'un matériau composite à matrice céramique à ténacité améliorée).
- Hillig, W.B., Mehan, R.L., Morelock, C.R., DeCarlo, V.J., Laskow, W., 1975. Silicon/silicon carbide composites. *American Ceramic Society Bulletin* 54 (12), 1054–1056.
- Hillig W.B., 1993. Melt infiltration – A generic process for making ceramic matrix composites. In: Bansal N.P. (Eds.), *Ceramic Transactions* vol. 38, pp. 3–26.
- Hillig, W.B., Morelock, C.R., 1980. US patent 4.238.433 (Method of making molten silicon infiltration reaction products).
- Hucke, E.E., 1966. US patent 3.235.346 (Composite bodies comprising a continuous framework and an impregnated metallic material and methods of their production).
- Jiang, J., Wang, S., Li, W., Chen, Z., 2015. Fabrication of C/ZrC-SiC composites using Zr-8.8Si alloy by melt infiltration. *Ceramics International* 41, 8488–8493.
- Jiang, J., Wang, S., Li, W., Chen, Z., Zhu, Y., 2014. Preparation of 3D C/ZrC-SiC composites by joint processes of PIP and RMI. *Materials Science and Engineering A* 607, 334–340.
- Jones, R., Szveda, A., Petrak, D., 1999. Polymer derived ceramic matrix composites. *Composites Part A: Applied Science and Manufacturing* 30 (4), 569–575.
- Jumel, J., Lepoutre, F., Enguehard, F., Rochais, D., Cataldi, M., 2001. Microscopic thermal characterization of C/C composites. In: Krenkel, W., Naslain, R., Schneider, H. (Eds.), *High Temperature Ceramic Matrix Composites*. Weinheim: Wiley-VCH Verlag GmbH, pp. 120–126.
- Kerans, R.J., Parthasarathy, T.A., 1991. Theoretical analysis of the fiber pullout and pushout tests. *Journal of the American Ceramic Society* 74 (7), 1585–1596.
- Ko, F., 1989. Preform fiber architecture for ceramic matrix composites. *American Ceramic Society Bulletin* 68 (2), 401–414.
- Ko, F., Du, G., 1997. Chapter 5 – Processing of textile preforms. In: Gutowski, T.G. (Ed.), *Advanced Composites Manufacturing*. New York: John Wiley & Sons, Inc, pp. 157–205.
- Kochendörfer, R., 1999. Low cost processing for C/C-SiC composites by means of liquid silicon infiltration. *Key Engineering Materials* 164–165, 451–456.
- Kotani, M., Kohyama, A., Okamura, K., Inoue, T., 1999. Fabrication of high performance SiC/SiC composite by polymer impregnation and pyrolysis method. *Ceramic Engineering and Science Proceedings* 20 (4), 309–316.
- Kotani, M., Inoue, T., Kohyama, A., Katoh, Y., Okamura, K., 2003. Effect of SiC particle dispersion on microstructure and mechanical properties of polymer derived SiC/SiC composite. *Materials Science and Engineering: A* 357 (1–2), 376–385.
- Krenkel, W., 1994. CMC materials for high performance brakes. In: *Ente per le nuovetecnologie, l'energia e l'ambiente*. (Eds.), *Proceedings of the 27th International Symposium on Automotive Technology and Automation (ISATA)*. Conference on Hybrid and Alternative Fuel Vehicles and Supercars, 863S. Croydon: Automotive Automation Ltd
- Krenkel, W., 2001. Cost effective processing of CMC composites by melt infiltration (LSI-process). *Ceramic Engineering and Science Proceedings* 22, 443–454.
- Krenkel, W., 2004. Carbon fiber reinforced CMC for high-performance structures. *International Journal of Applied Ceramic Technology* 1 (2), 188–200.
- Krenkel, W., Fabig, J., 1995. Tailoring of microstructure in C/C-SiC composites. In: Poursartip, A., Street, K. (Eds.), *Proceedings of the Tenth International Conference on Composite Materials* vol. 4, pp. 601–609. England: Canada V6T 1Z4 and Woodhead Publishing Limited.
- Krupka, M., Kienzie, A., 2000. Fiber reinforced ceramic composites for brake discs. *SAE Technical Paper Series*, 2000-01-2761.
- Lacombe, A., Spriet, P., Allaria, A., Bouillon, E., Habarou, G., 2009. Ceramic Matrix Composites to make breakthroughs in aircraft engine performance. In *Proceedings of 50th AIAA Aerospace Sciences Meeting Including the New Horizons Forum and Aerospace Exposition*. Reston: American Institute of Aeronautics and Astronautics, (119-SDM-75).
- Lamon, J., 2001. A micromechanics-based approach to the mechanical behavior of brittle matrix composites. *Composites Science and Technology* 61, 2259–2272.
- Lamon, J., 2005. Chemical vapor infiltrated SiC/SiC composites (CVI SiC/SiC). In: Bansal N.P. (Eds.), *Handbook of Ceramic Composites*. Boston; Dordrecht; London: Kluwer Academic Publishers, pp. 55–76.

- Lamouroux, F., Bertrand, S., Pailler, R., Naslain, R., Cataldi, M., 1999. Oxidation-resistant carbon-fiber-reinforced ceramic-matrix composites. *Composites Science and Technology* 59, 1073–1085.
- Langlais, F., 2000. Chapter 20 – Chemical vapor infiltration processing of ceramic matrix composites. In: Zweben, A., Kelly, C. (Eds.), *Comprehensive Composite Materials*, vol. 4. Amsterdam; NY: Elsevier, pp. 611–644.
- Langlais, F., 2005. On the chemical steps involved in the chemical vapour infiltration processing of ceramic matrix composites. *Annales de Chimie: Science des Matériaux* 30 (6), 579–592.
- Lee, S.H., Kim, H.D., 2009. Fabrication and physicochemical properties of particulate-reinforced precursor-derived Si-C-N ceramics. *Journal of the Ceramic Society of Japan* 117 (1372), 1339–1344.
- Lee, S.M., 1993. *Handbook of Composite Reinforcements*. New York: John Wiley & Sons Publisher.
- Lenz, F., Krenkel, W., 2012. Carbon fiber reinforced ceramics based on reactive melt infiltration process. *Journal of the Korean Ceramic Society* 49 (4), 287–294.
- Levi, C.G., Yang, J.Y., Dalgleish, B.J., Zok, F.W., Evans, A.G., 1998. Processing and performance of an all-oxide ceramic composite. *Journal of the American Ceramic Society* 81 (8), 2077–2086.
- Lissart, N., Lamon, J., 1994. Damage and failure in ceramic matrix composites: Experimental study and model. *Acta Materialia* 45 (3), 1025–1044.
- Luthra, K.L., Corman, G.S., 2001. Melt infiltration SiC/SiC composites for gas turbine applications. In: Krenkel, W., Naslain, R., Schneider, H. (Eds.), *Proceeding of the 4th High Temperature Ceramic Matrix Composite conference (HTCMC-IV)*. Weinheim: Wiley-VCH, pp. 744–753.
- Luthra, K.L., Singh, R.N., Brun, M.K., 1993. Toughened silcomp composites – Process and preliminary properties. *American Ceramic Society Bulletin* 72 (7), 79–85.
- Maillet, E., Godin, N., R'Mili, M., *et al.*, 2012. Analysis of acoustic emission energy release during static fatigue tests at intermediate temperatures on ceramic matrix composites: Towards rupture time prediction. *Composites Science and Technology* 72, 1001–1007.
- Marshall, D.B., Cox, B.N., Evans, A.G., 1985. The mechanics of matrix cracking in brittle matrix fiber composites. *Acta Metallurgica* 33, 2013–2021.
- Moëvus, M., Rouby, D., Godin, N., *et al.*, 2008. Analysis of damage mechanisms and associated acoustic emission in two SiC/(Si-B-C) composites exhibiting different tensile behaviours. Part I: Damage patterns and acoustic emission activity. *Composites Science and Technology* 68, 1250–1257.
- Mondon, P., 1996. *Etude de structure filamenteuses par mouillage capillaire dynamique*. PhD Thesis. University of Sciences and Technics of Lille.
- Morelock, C.R., 1986. US patent 4.626.516 (Infiltration of Mo-containing material with silicon).
- Morscher, G.N., 1997. Tensile stress rupture of SiC/SiC minicomposites with carbon and boron nitride interphases at elevated temperatures in air. *Journal of the American Ceramic Society* 80, 2029–2042.
- Morscher, G.N., 2004. Stress-dependent matrix cracking in 2D woven SiC-fiber reinforced melt-infiltrated SiC matrix composites. *Composites Science and Technology* 64, 1311–1319.
- Morscher, G.N., Baker, C., Smith, C., 2014. Electrical resistance of SiC fiber reinforced SiC/Si matrix composites at room temperature during tensile testing. *International Journal of Applied Ceramic Technology* 11, 263–272.
- Mutin, P.H., Boury, B., 2001. Chemical processing of ceramics: Pyrolysis of polymeric precursors. In: Meyers, R.A. (Ed.), *Encyclopedia of physical science and technology*, third ed Massachusetts: Elsevier Science Ltd, pp. 621–636.
- Nannetti, C.A., Borello, A., de Pinto, D.A., *et al.*, 2001. C fiber reinforced ceramic matrix composites by a combination of CVI, PIP and RB. In: Krenkel, W., Naslain, R., Schneider (Eds.), *High Temperature Ceramic Matrix Composites*. Weinheim: Wiley-VCH Verlag GmbH, pp. 368–374.
- Naslain, R., 1985. Introduction aux matériaux composites 2. Matrices métalliques et céramiques. In: du, C.N.R.S. (Ed.). Paris: Institut des matériaux composites, DL.
- Naslain, R., 1998. The design of the fibre-matrix interfacial zone in ceramic matrix composites. *Composites Part A* 29A, 1145–1155.
- Naslain, R., 2004. Design, preparation and properties of non-oxide CMCs for application in engines and nuclear reactors: An overview. *Composites Science and Technology* 64, 155–170.
- Naslain, R., 1995. The concept of layered interphases in SiC/SiC. In: Evans, A.G., Naslain, R. (Eds.). *High-Temperature Ceramic-Matrix composites II: Manufacturing and materials development*, Ceramic Transaction vol. 58, pp. 23–39.
- Padture, N.P., 2016. Advanced structural ceramics in aerospace propulsion. *Nature Materials* 15, 804–809.
- Pampuch, R., Walasek, E., Bialoskorski, J., 1986. Reaction mechanism in carbon-liquid silicon systems at elevated temperature. *Ceramics International* 12, 99–106.
- Pan, Y., Baptista, J.L., 1998. The infiltration of cobalt silicides into silicon carbide preforms. *Journal of the European Ceramic Society* 18, 201–207.
- Peres, M., 1988. *Analyse théorique et expérimentale du rôle des paramètres de microstructure sur le comportement des composites à matrice fragile*. PhD Thesis. University of Lyon.
- Pi, H., Fan, S., Wang, Y., 2012. C/SiC-ZrB₂-ZrC composites fabricated by reactive melt infiltration with ZrSi₂ alloy. *Ceramics International* 38, 6541–6548.
- Popper, P., Davies, D.G.S., 1961. The preparation and properties of self-bonded silicon carbide. *Powder Metallurgy* 4 (8), 113–127.
- Prewo, K.M., 1986. The development of fiber reinforced glasses and glass ceramics. In: *Tailoring Multiphase and Composite Ceramics*. Materials Science Research, 20. New York: Plenum Press, pp. 529–547.
- Prewo, K.M., Brennan, J.J., Layden, G.K., 1986. Fiber reinforced glasses and glass-ceramics for high performance applications. *American Ceramic Society Bulletin* 65, 305–322.
- Quet, A., 2007. *Composites de friction à matrice céramique: Relation Composition/structure/comportement tribologique*. PhD Thesis. University of Bordeaux.
- Raether, F., 2013. Ceramic matrix composites – An alternative for challenging construction tasks, materials, technology insights. *Ceramic Applications* 1 (1), 45–49.
- Rahaman, M.N., De Jonghe, L.C., 1987. Creep and densification during sintering of glass powder compacts. *Journal of the American Ceramic Society* 70 (10), 766–774.
- Ranade, R., Zhang, J., Lynch, J.P., Li, V.C., 2014. Influence of micro-cracking on the composite resistivity of engineered cementitious composites. *Cement and Concrete Research* 58, 1–12.
- Rebillat, F., 1996. *Caractérisation des interfaces et des matériaux d'interphases dans les CMCs*. PhD Thesis. University of Bordeaux.
- Rebillat, F., 2014. Advances in self-healing ceramic matrix composites. In: Low, I.M. (Ed.), *Advances in ceramic matrix composites*. Cambridge: Woodhead Publishing, pp. 369–409.
- Rosso, M., 2006. Ceramic and metal matrix composites: Routes and properties. *Journal of Materials Processing Technology* 175 (1–3), 364–375.
- Rouby, D., Reynaud, P., 1993. Fatigue behavior related to interface modification during load cycling in ceramic matrix fibre composites. *Composites Science and Technology* 48, 109–118.
- Ruschau, G.R., Yoshikawa, S., Newnham, R.E., 1992. Resistivities of conductive composites. *Journal of Applied Physics* 72, 953–959.
- Sangsuwan, P., Tewari, S.N., Gatica, J.E., Singh, M., Dickerson, R., 1999. Reactive infiltration of silicon melt through microporous amorphous carbon preforms. *Metallurgical and Materials Transactions B* 30B, 933–944.
- Sato, K., Suzuki, T., Funayama, O., Isoda, T., Itoh, T., 1992. Penetration of carbon fiber reinforced composite by impregnation with perhydropolysilazane followed by pressureless firing. *Ceramic Engineering and Science Proceedings* 13, 614–621.
- Schulte, K., Baron, C., 1989. Load and failure analyses of CFRP laminates by means of electrical resistivity measurements. *Composites Science and Technology* 36, 63–76.
- Schulte-Fischedick, J., Zern, A., Mayer, J., *et al.*, 2002. The morphology of silicon carbide in C/C–SiC composites. *Materials Science and Engineering: A* 332, 146–152.
- Scola, A., Eberling-Fux, N., Turenne, S., Ruiz, E., 2019. New liquid processing of oxide/oxide 3D woven ceramic matrix composites. *Journal of the American Ceramic Society* 102 (6), 3256–3268.
- Simon, C., Rebillat, F., Camus, G., 2017b. Electrical resistivity monitoring of a SiC/(Si-B-C) composite under oxidizing environments. *Acta Materialia* 132, 586–597.
- Simon, C., Herb, V., Rebillat, F., Camus, G., 2017a. Monitoring damage evolution of SiC/(Si-B-C) composites using electrical resistivity: crack-density based electromechanical modeling. *Acta Materialia* 124 (2017), 579–587.

- Simon, R.A., 2005. Progress in processing and performance of porous-matrix oxide/oxide composites. *International Journal of Applied Ceramic Technology* 2 (2), 141–149.
- Singh, M., Behrendt, D.R., 1994. Effect of carbon preform pore volume and infiltrants on the composition of reaction formed silicon carbide materials. *Journal of Materials Synthesis and Processing* 2 (2), 117–123.
- Singh, M., Behrendt, D.R., 1995. Reactive melt infiltration of silicon molybdenum alloys into microporous carbon preforms. *Materials Science and Engineering A* 194, 193–200.
- Singh, M., Pawlik, R., Salem, J.A., Behrendt, D.R., 1991. Mechanical properties of reaction-formed silicon carbide ceramic containing silicon and refractory disilicide phases. In: Bansal, J.P. (Eds.), *Advances in Ceramic Matrix Composites*, Ceramic Transactions vol. 38, pp. 349–359.
- Smith, C.E., Morscher, G.N., Xia, Z., 2008. Monitoring damage accumulation in CMCs using electrical resistivity. *Scripta Materiala* 59, 463–466.
- Smith, C.E., Morscher, G.N., Xia, Z., 2011. Electrical resistance as a nondestructive evaluation technique for SiC/SiC CMC under creep-rupture loading. *International Journal of Applied Ceramic Technology* 8, 298–307.
- Tang, S., Hu, C., 2017. Design, preparation and properties of carbon fiber reinforced ultra-high temperature ceramic composites for aerospace applications: A review. *Journal of Materials Science and Technology* 33, 117–130.
- Tang, S., Deng, J., Wang, S., Liu, W., Yang, K., 2007. Ablation behaviors of ultra-high temperature ceramic composites. *Materials Science and Engineering A* 465, 1–7.
- Tong, Y., Bai, S., Zhang, H., Chen, K., 2012. C/C-SiC composite prepared by Si-10Zr alloyed melt infiltration. *Ceramics International* 38, 3301–3307.
- Tong, Y., Bai, S., Qin, Q.H., Zhang, H., Ye, Y., 2015. Effect of infiltration time on the microstructure and mechanical properties of C/C-SiC composite prepared by Si-Zr10 alloyed melt infiltration. *Ceramics International* 41, 4014–4020.
- Van Rossum, M., Maex, K., 1995. Properties of metal silicides. In: *Emis Data Reviews Series*, 14. London: INSPEC; IEE.
- Vesely, V., Konecny, P., Lehner, P., 2015. Influence of crack propagation on electrical resistivity and ultrasonic characteristics of normal concrete assessed by sequential TPB fracture. *Theoretical and Applied Fracture Mechanics* 80, 2–13.
- Vignoles, G.L., 2015. Chemical vapor deposition/infiltration processes for ceramic composites. In: Boisse, P. (Ed.), *Technology & Engineering*, Chapter 8. Cambridge: Woodhead Publishing, pp. 147–176.
- Yajima, S., Hayashi, J., Omori, M., Okamura, K., 1976. Development of a silicon carbide fibre with high tensile strength. *Nature* 5562 (261), 683–685.
- Zhang, L., Dong, S., Zhou, H., *et al.*, 2014. 3D Cf/ZrC-SiC composites fabricated with ZrC nanoparticles and ZrSi₂ alloy. *Ceramics International* 40, 11795–11801.
- Zhou, H., Webb, J.E., Singh, R.N., 1997. Creep behavior of compositionally varied Si/SiC composites. *Ceramic Engineering and Science Proceedings* 18 (3A), 673–680.
- Zhu, Q., Shobu, K., 2000. SiC-Mo₅Si₃C₁ composites by melt infiltration process. *Journal of Materials Science Letters* 19, 153–155.
- Zhu, Q., Shobu, K., 2001. High temperature mechanical properties of SiCMo₅(Si,Al)₃C composites. *Journal of the American Ceramic Society* 84 (2), 413–419.
- Zhu, Y., Huang, Z., Dong, S., Yuan, M., Jiang, D., 2008. Manufacturing 2D carbon-fiber-reinforced SiC matrix composites by slurry infiltration and PIP process. *Ceramics International* 34 (5), 1201–1205.
- Ziegler, G., Richter, I., Suttor, D., 1999. Fiber-reinforced composites with polymer derived matrix: processing, matrix formation and properties. *Composites Part A: Applied Science and Manufacturing* 30 (4), 411–417.
- Zok, F.W., Levi, C.G., 2001. Mechanical properties of porous-matrix ceramic composites. *Advanced Engineering Materials* 3 (1–2), 15–23.

Ultra-High Temperature Ceramic Matrix Composites

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Introduction

Ultra-high temperature ceramic matrix composites (UHTCMCs) are the next generation of reusable materials for applications above 2000°C in aerospace, military and nuclear fields, where a combination of thermal shock and strong heat fluxes makes the materials choice very narrow. Typical components in UHTCMCs include heat shields and rocket nozzles (Binner *et al.*, 2019; Tang *et al.*, 2007a).

UHTCMCs are constituted of at least two essential elements integrated, e.g., a C or SiC fiber skeleton and an ultra-high temperature ceramic (UHTC) matrix. For extreme temperature applications, the fabric is preferably made of carbon fibers rather than SiC fibers, since carbon fibers have superior strength, modulus, thermal stability and lower cost as compared to SiC fibers (Huang and Young, 1995; Peterlik, 2014). However SiC fibers are preferable for long term applications in oxygen-rich atmospheres at temperatures below 1600°C (Fitzgerald and Shepherd, 2018).

The UHTC matrix can be in turn a composite, e.g., a UHTC phase amongst borides and carbides of the transition metals in groups IV and V combined with SiC or with multiple UHTC phases (e.g., ZrB₂/ZrC) (Kütemeyer *et al.*, 2015).

A composite that performs well does not require coating of the fibrous structure prior to composite processing nor a post-processing environmental external coating. Desired characteristics of these hybrid composites are a weak enough fiber/matrix interface to enable fiber pull-out at fracture, a dense matrix to hinder penetration of corrosive/oxidative gases and liquids and excellent thermo-mechanical properties at temperatures >1500°C, including strength and thermal shock resistance. Moreover, another property required is the capability to be re-used multiple times for short-time employ, exploiting the formation of an in situ external protective coating upon exposure to the service conditions of heat and oxygen (Vinci *et al.*, 2019a,b; Sciti *et al.*, 2018).

The purpose of the following sections is to give a concise overview of the state-of-the-art in the preparation of UHTCMCs classified under sintering or non-sintering routes. Then, the mechanical properties of the different groups of UHTCMCs are presented, together with the best thermo-ablative response materials available to date.

Preparation of UHTCMCs via Non-Sintering Routes

From the perspective of fabricating high performance UHTCMCs, researchers have been developing a spectrum of routes to enrich carbon fiber preforms with UHTC phases. There is a general consensus on the classification of various non-sintering methods: chemical vapor infiltration/deposition (CVI/D), precursor/polymer infiltration and pyrolysis (PIP), and reactive melt infiltration (RMI). All these methods have been readapted from the CMC processing technology to allow the introduction of UHTC phases into the fiber fabric. The UHTC phase concentration can be very different, depending on the process, and it has a remarkable impact on final density and mechanical and erosion resistance properties. It is important to note that a neat separation between various processes appears restrictive because a combination of them is often used.

Precursor/Polymer Infiltration and Pyrolysis (PIP)

Similar to the fabrication of polymer-matrix composites, fiber preforms are infiltrated with low viscous liquid preceramic polymers that will be converted into the ceramic matrix upon pyrolysis. Because of its simplicity, relatively lower processing temperatures and capacity to fabricate components with complex shapes, this technique is very cost effective compared to CVI. Most available preceramic polymers are carbosilane, polysilazane and polyxilosane resulting in SiC, SiCN(O), and SiOC-based composites. As far as we know, metal diboride precursors are not easily available on the market. The MATECH company claims to provide HfC and TaC precursors and therefore some researchers have started an intense investigation on the synthesis of new metal-containing polymers such as HfC/HfN precursors, namely poly(propyl)hafnizane (PPHZ) and poly(ethynyl)hafnizane (PEHZ), (Pope *et al.*, 2007). These can be converted into metal carbides, borides or nitrides by pyrolysis at high temperatures (Colombo *et al.*, 2010; Ionescu *et al.*, 2019; Terauds *et al.*, 2014). Currently, the most feasible way to introduce UHTC phases into these fibrous nets is impregnation of the preforms with a slurry containing the above mentioned preceramic polymers and the UHTC powders, followed by pyrolysis (Servadei *et al.*, 2020). The process is repeated several times to eliminate the residual porosity at most and the maximum processing temperature generally does not exceed 1500°C in order to limit possible fiber damage due to interaction with the reacting fluid (Heidenreich, 2014; Wu *et al.*, 2013). However, the custom-made nature of the metal-containing preceramic polymers often requires processing temperatures up to 1800°C to reach the desired yield. Hu *et al.* verified the detrimental effects of high-temperature on the microstructure and mechanical properties of C/SiC-ZrB₂ composites prepared by PIP, testing them at 1800°C and 2000°C (Hu *et al.*, 2010b).

Advantages of this technique include relatively low temperatures of processing and consequently prevention of fiber damage, fabrication of near-net-shape parts, and possibility of tuning the microstructure of the matrix as required by the temperature of pyrolysis. Despite some drawbacks, such as poorer mechanical properties of the composites compared to those produced by CVI, higher fabrication times and costs of production compared to RMI method (several weeks are needed for the multiple infiltration-pyrolysis cycles), PIP remains one of the most viable techniques for production of heat shields or propulsion parts for space field.

Chemical Vapor Deposition/Infiltration (CVD or CVI)

CVI or CVD are two variants of one largely used ceramic engineering process whereby the material constituting the matrix is deposited or infiltrated into fibrous preform using reactive gases at temperatures above 1000°C. Frequently, CVI/CVD have been widely employed for preparation of C and SiC matrices by methane and silane precursors, but have also been demonstrated to be capable of preparing UHTC composites. In this case, two main routes are possible. The conventional method requires UHTC slurry impregnation followed by CVI – CVD of C to close the porosity (Paul *et al.*, 2014, 2013b; Rubio *et al.*, 2018). Alternatively, MeCl₄, BCl₃H₂ (Me = Ti, Ta, Hf, Zr) in different ratios are used as MeB₂ precursors (Stinton *et al.*, 1988). Beside the requirement of complex and costly equipment, another disadvantage is the very slow deposition rate, leading to a large material energy input and high final costs, as well as the very limited infiltration depth. To overcome this issue, recently new radio frequency (RF) and microwave (MW) heating systems have been developed to decrease the manufacturing time, the main advantage being the deposition of material from inside towards outside, so that the deposition can proceed unhampered until the complete filling of the composite. However, large-size or thick parts are prone to non-uniform deposition and density gradients. In 2004 Sayir (Sayir, 2004) deposited UHTC onto a carbon fiber fabric by a CVI process using gas precursors of HfC, TaC and HfC/TaC. Tang *et al.* fabricated C_f/ZrB₂-SiC composites containing ~4 vol% of ZrB₂ as thin powder layers between fabrics and assessed the pronouncedly improved ablation resistance of the modified carbon composite upon exposure to an oxyacetylene torch flame (Tang *et al.*, 2007c). Likewise, Li *et al.* (2011) fabricated 2D-C_f/ZrB₂-SiC-TaC. The combination of CVI/CVD with PIP has been explored by some researchers for the preparation of UHTCMCs (Tang and Hu, 2017).

Advantages of this technique include relatively low processing temperature ranges, weak fiber/matrix interfaces, matrix microstructure control, and consequently, prevention of fiber damage and better mechanical properties compared to PIP and RMI. Near-net-shape components can be produced by CVI even with complex fiber architectures with 2.5D, 3D orientations. Despite the technological advances (RF and MW heating) CVI remains the process with the highest fabrication times and costs of production.

Reactive Melt Infiltration (RMI)

Reactive melt infiltration (RMI) is a consolidation technique based on the infiltration of molten metal, which reacts in the preform with a porous matrix to form a dense matrix with a higher melting point phase. The preform can be easily modeled into the desired shape before being infiltrated. Infiltration then takes place by capillary action or by applying external pressure and forcing the liquid to flow through the porous preform. Since metals of groups IV and V, e.g., Zr and Hf, have melting points of 1830 and 2130°C respectively, which would compromise the fiber integrity, infiltration of the carbon fiber preform is achieved with alloys which possess notably lower melting points and can be processed at 600°C lower. The same method can be employed also for the sole deposition of refractory boride/carbide coatings on C and SiC fiber preforms (Kütemeyer *et al.*, 2018, 2016; Zhang *et al.*, 2011; Zhu *et al.*, 2012). Zirconium is typically alloyed with lower melting metals such as copper or silver, to give alloys such as Zr₂Cu which significantly lower the operating temperature down to 1100°C or less. Dickerson *et al.* (2004) obtained a ZrC and W matrix via Zr₂Cu infiltration of a porous WC preform. Alternatively, the fiber preform can be infiltrated by other means, e.g., slurry infiltration, with different reactive powders such as B₂O₃ (Kütemeyer *et al.*, 2018), B₄C (Zhang *et al.*, 2011), or elemental boron (Kütemeyer *et al.*, 2016; Vinci *et al.*, 2020a) to give a ceramic matrix made of ZrB₂ and ZrC following reactions (1) and (2):



The liquid copper segregates on the surface of the sample, leaving a ZrC/ZrB₂ matrix with residual Zr₂Cu inside the pores. Other routes involve the use of transition metal-silicide alloys as infiltrating medium (Chen *et al.*, 2018; Maskaly and Chiang, 2008; Ye *et al.*, 2013) exploiting their reactivity towards carbon at reasonable processing temperatures (Phase Equilibria Diagrams Online Database NIST Standard Reference Database 31, 2019) like the example in reaction (3):



Recently, Zeng *et al.* (2017) have proposed the infiltration of C/C with Zr-Ti melt followed by pack cementation to obtain a matrix of Zr_{0.8}Ti_{0.2}C_{0.74}B_{0.26}. The material had a graded structure with a relative density of the matrix variable from 76% to 25%. The RMI method enabled the elimination of almost all porosity. In addition, large near-net shaped UHTCMC pieces can be obtained in a relatively fast process at low temperature. Compared to other infiltration techniques, such as PIP and CVI, RMI has the advantage of being very quick and cost effective. On the other hand, the melts, especially the ones containing transition metals, are very aggressive towards the fiber, and so a protective coating is often required. In addition, the final density of the component might be relatively high, close to that of a UHTC matrix, owing to residual metal alloy trapped in the matrix.

Preparation of UHTCMCs via Sintering Routes

Slurry Infiltration and Sintering (SIS)

Sintering is an essential step for ceramic consolidation, but it is rarely applied to fiber reinforced ceramic matrix composites (CMCs). This is because of (1) the need to apply pressure during sintering limits the component size and (2) the fact that the sintered component can contain degraded fibers and cracks formed due to intense residual stresses arising due to the Coefficient of Thermal Expansion (CTE) mismatch between matrix and fiber, with the fiber typically shrinking less than the matrix. For these reasons CMCs of C/SiC and SiC/SiC, are usually produced by the previously described technologies which are able to consolidate the material at lower temperature with lower matrix shrinkages (Heidenreich, 2014; Nannetti *et al.*, 2004). However, slurry infiltration and sintering (SIS) processes have been rethought for UHTCMC manufacturing. Once optimized the manufacturing procedure, in terms of slurry composition and rheological properties, impregnation methodology, and especially sintering schedule, SIS approach is highly attractive over the other non-sintering routes (Galizia *et al.*, 2018a; Zoli *et al.*, 2018; Zoli and Sciti, 2017). Impregnation of the fiber can occur by filament winding, where the yarn is dipped in a UHTC slurry (Silvestroni *et al.*, 2015b), or by direct immersion of the fabric into the UHTC slurry.

Hot pressing (HP) and spark plasma sintering (SPS) are well known consolidation techniques for bulk ceramics and largely used for UHTCs. The simultaneous application of high heating rates, mechanical pressure and high temperature (plus electrical current for SPS) allow the densification of even poorly sinterable materials, like borides and carbides (Córdoba *et al.*, 2013; Hu *et al.*, 2010a; Jin *et al.*, 2016; Lin *et al.*, 2015; Monteverde, 2007; Todde *et al.*, 2012; Xu *et al.*, 2012). Recently, it has been proved that these techniques can be successfully employed for UHTCMC manufacturing (Hu *et al.*, 2019; Lin *et al.*, 2015; Sciti *et al.*, 2015; Zoli *et al.*, 2020, 2017). However, it is important to mention that the sintering of fiber-reinforced composites, through HP or SPS, requires appropriate setting of the heating cycle in order to obtain a pore and crack-free matrix, preserve the fiber integrity and produce a suitable fiber/matrix interface. These features are in turn dictated by the type of fiber, ceramic matrix composition, fiber/ceramic volumetric ratio and have paramount importance in determining the thermo-mechanical properties of the final composite.

What are generally termed “SiC fibers” are not a pure SiC product, but rather nano-composites made of β -SiC nano-crystallites, turbostratic carbon and an amorphous SiCO phase (Berger, 2012). The presence of these latter two makes the fibers very reactive at high temperature, mainly involving carbon migration outwards and decomposition of the amorphous phase into SiC and SiO₂. Studies on the stability of commercial SiC fibers in UHTC matrices have allowed a thorough understanding of the fiber interaction with borides and carbides as a function of the sintering additive and temperature (Guicciardi *et al.*, 2010; Sciti *et al.*, 2014; Silvestroni *et al.*, 2015a,c, 2016b). SiC fibers reveal a multi-shell morphology upon sintering with an unreacted core, a region of coarsened SiC crystallites and Me-silico-carbides (where Me is the relevant cation of the boride matrix) and an outermost reaction zone of recrystallized SiC platelets, Fig. 1 (Silvestroni and Sciti, 2011). Because of the intrinsic unstable nature of SiC fibers, they behave locally as a sintering aid by reacting with borides and their residual oxides, favoring densification in the closest proximity, Fig. 1(b). Thus, the fiber/matrix interface is typically very strong and no bridging or pull-out during crack propagation can be observed for any matrices or sintering additives (Silvestroni *et al.*, 2010). Mitigation of the SiC fiber consumption can be obtained by use of external coatings, either pyrolytic carbon or Si-B-N-based ones. The application of any type of coatings has however a major weighting in the cost of the final composite.

The same delicate fiber processing has been assessed for all kinds of C fiber, both high strength ones deriving from polyacrylonitrile precursor (PAN-based) and ultra-high modulus deriving from pitch. In the first case, C fibers are obtained upon specific treatments below 2000°C and consist of a turbostratic crystalline structure, which is highly reactive in the sintering environment. In the second case, the fiber manufacturing process includes a heat treatment above 3000°C which results in a high degree of graphitization, which is considered to be more stable during sintering, even at 1900°C (Sciti *et al.*, 2020, 2015; Silvestroni *et al.*, 2016b; Zoli and Sciti, 2017). Nevertheless, in case of overfiring, even pitch-based C fibers may assume a jagged morphology with an important level of fiber degradation, opening and exfoliation, due to reactions with the surrounding ceramic phase, Fig. 2 (Guicciardi *et al.*, 2010; Huang and Young, 1995; Zoli *et al.*, 2017).

UHTCMCs with short fibers

Preliminary explorative studies on the fiber/UHTC interactions at various sintering temperatures and in the presence of different sintering agents started more than 10 years ago, at the Institute of Science and Technology of Ceramics, National Research Council of Italy (ISTEC-CNR) with the support of US AFRL funding. The object of that research activity was the production and characterization of ultra-high temperature ceramics possessing superior fracture toughness, i.e., containing different discontinuous reinforcing phases like SiC platelets, SiC whiskers or SiC/C short fibers. Specific studies coupling thorough microstructural analysis by transmission electron microscopy and mechanical characterization enabled to understand the sintering mechanisms and toughening phenomena occurring in these materials and progressively led to the identification of the critical processing parameters and toughness potential and limits of UHTC matrices reinforced with discontinuous phases (Sciti *et al.*, 2014; Silvestroni *et al.*, 2010).

UHTCMC with short fibers, i.e. starting length < 1 mm, can be readily realized by conventional ceramic technology, including ball milling, shaping and sintering. However, with the increase of the volume fraction of fiber, a homogeneous fiber dispersion is always more challenging to achieve, owing to the steric hindrance of the fibers. To date, up to 60 vol% fibers, with starting length of 300 μ m, can be incorporated in a UHTC slurry (Fig. 3). An increase of fiber amount results in an almost linear decrease of the

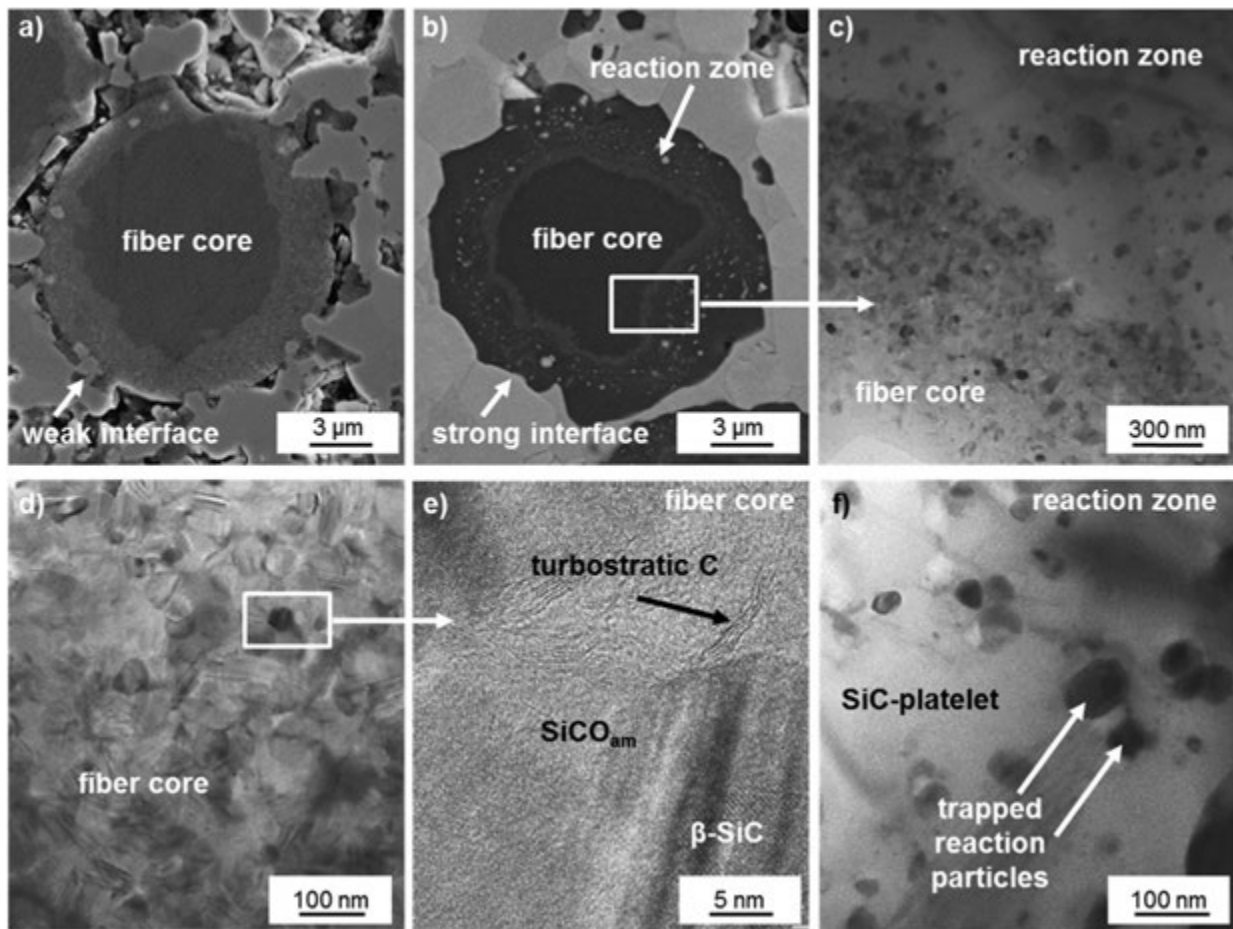


Fig. 1 (a)–(b) Morphology evolution of Hi-Nicalon SiC fiber in a ZrB_2 matrix illustrating the multi layered morphology and formation of different fiber/matrix interfaces after sintering at increasing temperature. (c)–(f) TEM images showing the fiber features with magnified views of (d) the fiber core, (e) the composition of the fiber core and (f) the reaction zone.

final density (down to 84% for content of 50%), since the mass transfer and pore closure mechanisms are strongly obstructed by the fiber network, even under application of high mechanical pressures.

Increased matrix porosity resulting from increased fiber volume fraction has consequences also on the fiber/matrix interface. A more porous matrix will naturally develop weaker interfaces with any type of fiber as compared to a fully dense matrix where the fiber is well anchored in the ceramic phase, **Fig. 1(a)** and **(b)** and **Fig. 2**.

UHTCMCs with continuous fibers

The manufacturing of planar UHTC composites consists of the infiltration of SiC_f or C_f preforms with a UHTC-based slurry followed by their stacking to form a multi-layered green composite with a variety of configurations, e.g., uni-directionally oriented, with fabrics stacked in a $0/90^\circ$ configuration and also with more complex architecture of fiber preform, such as 2D and 2.5D, as shown in **Fig. 4**.

Research performed by [Levine et al. \(2002\)](#) led to a UHTC-based composite reinforced with 35 vol% fiber through filament winding using SiC_f (SCS-9) monofilament, slurry infiltration and hot pressing. However, it is only recently that multifilament SiC_f preforms have been successfully infiltrated by UHTC slurry and sintered. Two routes have been explored: in a first case, ([Silvestroni et al., 2015b](#)) Uni-Directional (UD) tapes of BN coated Hi-Nicalon SiC_f yarns, obtained by infiltration with a solvent-based ZrB_2 - ZrSi_2 slurry using a manual filament winding, were overlapped in a $0/90^\circ$ configuration and sintered by hot pressing at 1450°C . According to a second variation, ([Zoli et al., 2015](#)) UD Tyranno-SA3 SiC_f fabrics were infiltrated by an aqueous ZrB_2 - ZrSi_2 slurry, using a vacuum-bagging technique, stacked and subsequently hot pressed in the temperature range of 1450 – 1600°C . The use of a BN-coating for Hi-Nicalon fibers was effective in hindering fiber degradation during processing. However, regardless of the presence of coating or increased fiber volume fraction, the measured fracture toughness values were similar to monolithic ZrB_2 ceramics owing to an unfavorable $E_{\text{matrix}}/E_{\text{fiber}}$ ratio, which did not allow efficient load transfer from the brittle matrix to the high strength fibers. In addition, it was only when the BN-coating was present that a damage tolerant behavior was observed, whereas in the other cases a brittle fracture prevailed owing to the strong fiber/matrix interface.

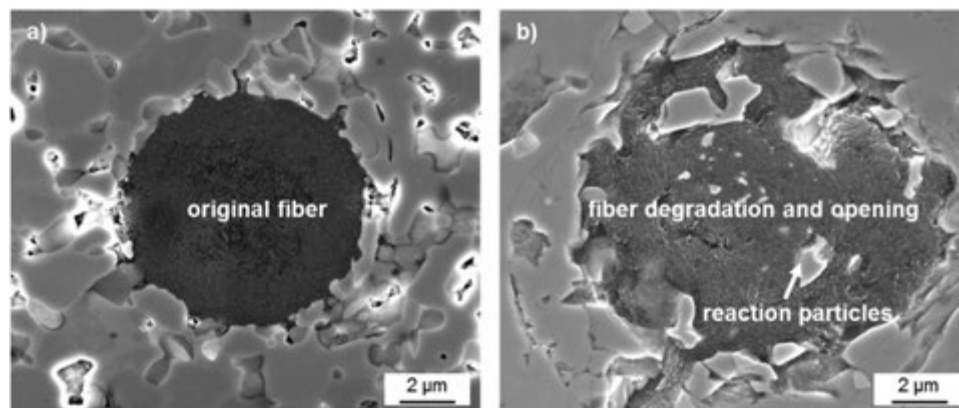


Fig. 2 Effect of increasing sintering temperature on the morphology evolution and interface creation of pitch-derived C fibers immersed in a ZrB_2 matrix and sintered by HP. Examples of reacted (a) and over reacted interfaces (b).

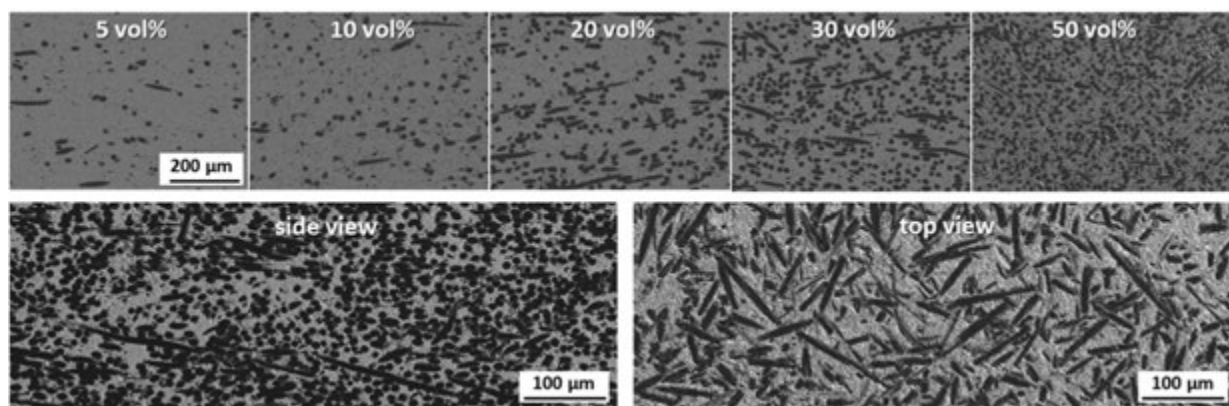


Fig. 3 Examples of microstructure of hot pressed UHTCMC based on ZrB_2 and containing (top) increasing amount of Hi-Nicalon SiC fibers and (bottom) 50 vol% of C fiber viewed from cross section and top surface.

Combinations of carbon fibers and UHTC matrices result in more convenient composites from a flaw tolerance perspective. Also, for this class of composites the choice of fiber type, architecture and fiber/matrix composition ratio are of major importance, as they determine the sintering temperature and hence the fiber/matrix interface, degree of reaction and overall thermo-mechanical performance (Zoli and Sciti, 2017).

One main difference is related to the C_f source. Since PAN-based fibers are more sensitive to reaction with the matrix during sintering at high temperature, a strategy to limit such reaction and the following fiber degradation is the use of nano-sized ZrB_2 powders which allows a notable decrease of sintering temperature from above 1700°C to 1450°C (Zhang *et al.*, 2019). Alternatively, Zhang *et al.* proposed a brushing assisted infiltration followed by vacuum bagging, (Zhang *et al.*, 2019, 2018) and investigated the effect of pyrolytic coating (Zhang *et al.*, 2018) assessing its beneficial effect on the development of suitable fiber/matrix interface.

Generally, C_f are a better solution for strengthening and toughening ultra-high temperature ceramic matrices and for improving their thermal shock resistance, compared to SiC reinforcement (Song *et al.*, 2002; Vinci *et al.*, 2020b; Zoli *et al.*, 2018, 2015; Zoli and Sciti, 2017). On the other hand, C_f -reinforced UHTCs are more sensitive to oxidation than those reinforced with SiC_f (Sciti *et al.*, 2012).

Variations in UHTCMC Manufacture

Functionally Graded Composites

An intense and thorough investigation of UHTCMCs production and performance, either with short or continuous reinforcement and obtained through sintering or non-sintering methods, delineated the potential and limits of this new class of materials. One of

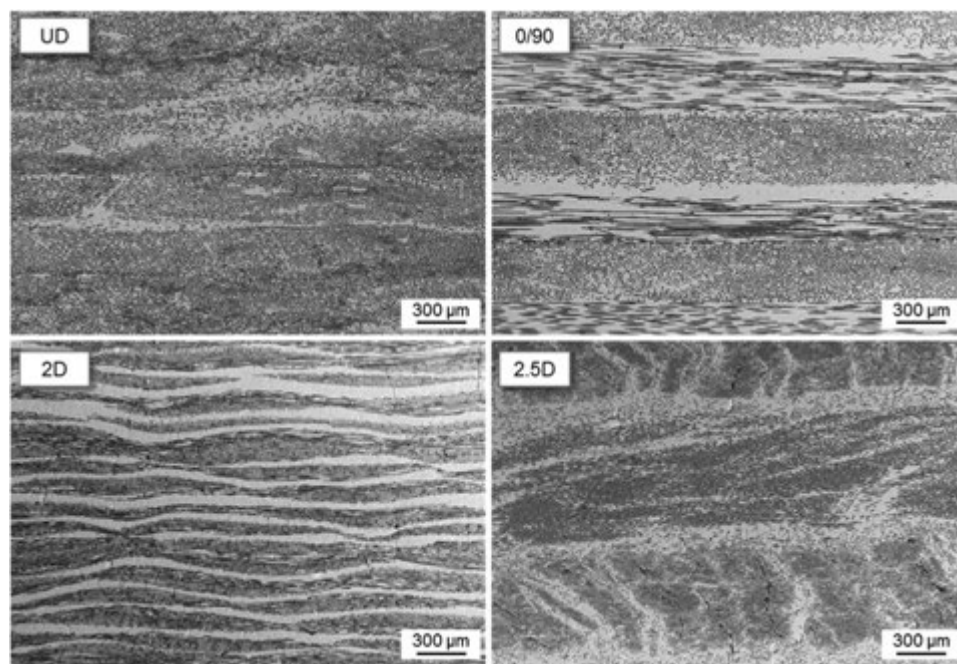


Fig. 4 Examples of UHTCMC composites obtained by SIS using cloths with different architecture of C fibers: unidirectional fabrics stacked in 0/0° configuration (UD), in 0°/90° configuration (0/90), plain clothes stacked with the same orientation (2D) and needle punched preform (2.5D).

the most relevant challenges, in view of the envisaged applications, is most certainly the resistance to highly oxidizing environments.

To benefit both from the ablation resistance properties typical of UHTCs and from a damage tolerant body containing a large fraction of fibers typical of CMCs, one research approach is to design a composite architecture which locally imparts each specific functionality. From what has been discussed above, in order to preserve the toughness in the bulk while improving oxidation performance, an accurate selection of dopants is a fundamental step to impart the desired properties. This can be achieved by modifying the liquid phase during sintering and thus the nature of the oxidation products upon exposure to high temperature environments.

The class of materials known as functional graded material (FGM) was first reported in the 90's for propulsion and airframe structural systems of astronautic flight vehicles to decrease thermal stresses arising during operation (Koizumi, 1993). These engineered materials are characterized by spatially varied microstructures created by a non-uniform distribution of the reinforcement phase with different properties, sizes and shapes, as well as by interchanging the role of reinforcement and matrix materials in a continuous manner. FGMs exhibit a gradual variation of material properties from one surface to the other and thus eliminate local stress concentration generally encountered in laminated multicomponent structures.

This concept has been recently validated in ZrB_2 matrices containing between 0 and 50 vol% of short SiC or C fibers (Silvestroni *et al.*, 2019a,b, 2016a) and with a gradual variation of the type or amount of sintering additive that enabled densification of the UHTC matrix, but limited reaction and degradation of the fibers, Fig. 5(a).

The mechanical properties of the developed FG UHTCMCs outperformed those of the analogous mono-reinforced composites, thanks to the exploitation of favorable residual stresses, achieving fracture toughnesses up to $10 \text{ MPa m}^{0.5}$ at 1500°C . This approach is particularly attractive as it enables a sort of UHTC coating to be obtained on a fiber-rich body in one single sintering step, avoiding problems of CTE mismatch and residual tensional states which could easily lead to spallation. While the processing is indeed that typical of ceramic processing, the obtained FG composites possess avant-garde aspects as compared to traditional CMCs in terms of both performance and cost.

Electrophoretic Deposition (EPD)

EPD has proved to be a facile method to create a thick UHTC coating of $5\text{--}50 \mu\text{m}$ onto C_f preforms (Failla *et al.*, 2019; Galizia *et al.*, 2018a). If EPD is implemented in the conventional SIS process, before the infiltration step, it allows the assembly of C_f into bundles coated with an UHTC coating that could have a different composition with respect to that of the matrix, Fig. 5(b). In this way, the degree of freedom in the design can be increased having the possibility to tailor the matrix composition and texturing. In

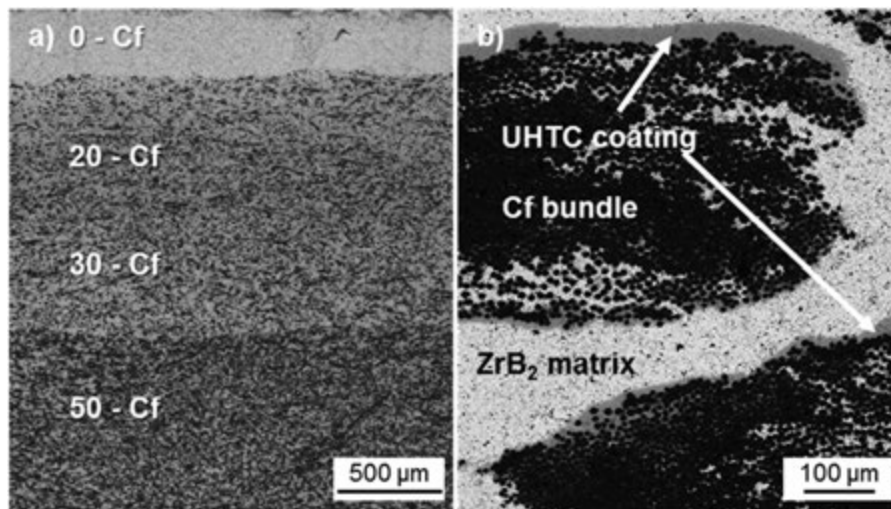


Fig. 5 Examples of UHTCMC obtained by (a) stacking of dry powder mixtures with increasing fiber content forming a FGM, (b) EPD of fiber fabric with a UHTC slurry subsequently infiltrated with a ZrB_2 slurry and sintered.

particular, the texturing in bundles allows to develop weak C/C and C/ ZrB_2 interfaces within the bundles, and this maximizes the overall structural properties (Galizia *et al.*, 2018a).

Mechanical Properties

At present, available mechanical data for UHTCMCs are still poorly reported and high temperature mechanical properties are even more difficult to find. As illustrated above there is plenty of reportage of different microstructural features, such as fiber volume fraction and dispersion, matrix density and composition, which often are not quantified in the published works even if they strongly affect the mechanical response of UHTCMCs. To further complicate a sound comparison of values, the available mechanical properties are measured with different testing approaches and specimen size.

For these reasons, in order to approach a direct comparison of differently processed UHTCMCs, it is preferable to set a test geometry and then compare the shape of load-displacement curves together with the analysis of failures. Fig. 6 shows load-displacement curves for different types of composites obtained by CVI, RMI, PIP and SIS. The experimental materials, still under development, presented here were realized in the framework of the C³HARME project (See “Relevant Websites Section”) and have all been tested using the same conditions and apparatus. Specimens prepared by CVI are reinforced with a 2.5D preform. Specimens prepared by RMI are reinforced with unidirectional (UD) fabrics stacked in a 0/0° configuration, while specimens prepared by PIP are reinforced with unidirectional fabrics stacked in a 0/90° configuration. Specimens manufactured by SIS are reinforced with UD fabrics stacked either in a 0/0° and 0/90° configurations. SEM images inset in Fig. 6 show the fracture surfaces (RMI and SIS) and side view (CVI and PIP) of failed specimens under flexural loading. All curves were obtained with the same test geometry: 4-point bending fixture with a lower span of 20 mm and an upper span of 10 mm; beams of 25 mm × 2.5 mm × 2 mm (length by width by thickness, respectively) and a crosshead speed of 1 mm min⁻¹.

The measured flexural strength of specimens obtained by CVI and containing about 25 vol% fiber with 2.5D architecture was 90 ± 30 MPa. The large scatter was due to the difference in fiber architectures of the specimen after machining. In fact, since bars have smaller dimensions with respect to the representative volumetric elements of fabric preform, tests gave high or low values depending on whether the outer surface under tensile stress had a prevalence of longitudinal (CVI, solid curve) or transverse fiber orientation (CVI, dashed curve), respectively (Galizia *et al.*, 2020). The RMI technique resulted in highly inhomogeneous samples with fiber-rich zones or mostly composed by the UHTC matrix. As a result, large scatter was observed with a maximum flexural strength of 720 MPa, typical of monolithic UHTCs (RMI, solid curve). On the other hand, zones with low fiber content and a dense matrix were typified by large flaws up to 500 μm and extremely low strength (RMI, dashed curve). In any case, catastrophic failure was recorded which suggested limited contribute of the fibers. Partial fiber consumption resulted in only around a 20 vol% fiber fraction after processing, explaining the poor performance. Specimens obtained by PIP and containing about 50 vol% fiber failed under inter-laminar shear. Hence, the actual strength of the composite was underestimated. For this class of composites, talking about inter-laminar shear strength is therefore more appropriate. By increasing the ZrB_2 content, the strength almost doubled, i.e. it increased from 5 MPa (PIP, dashed curve) to 11 MPa (PIP, solid curve).

Unidirectional carbon fiber-reinforced ZrB_2 composites realized by SIS with a FVC of 45 vol% and porosity around 6 vol% failed under a combination of inter-laminar shear and tensile stress. By changing the architecture from unidirectional to a 0/90° configuration the calculated maximum stress decreased from 255 ± 24 MPa (SIS, solid curve) to 150 ± 8 MPa (dashed curve),

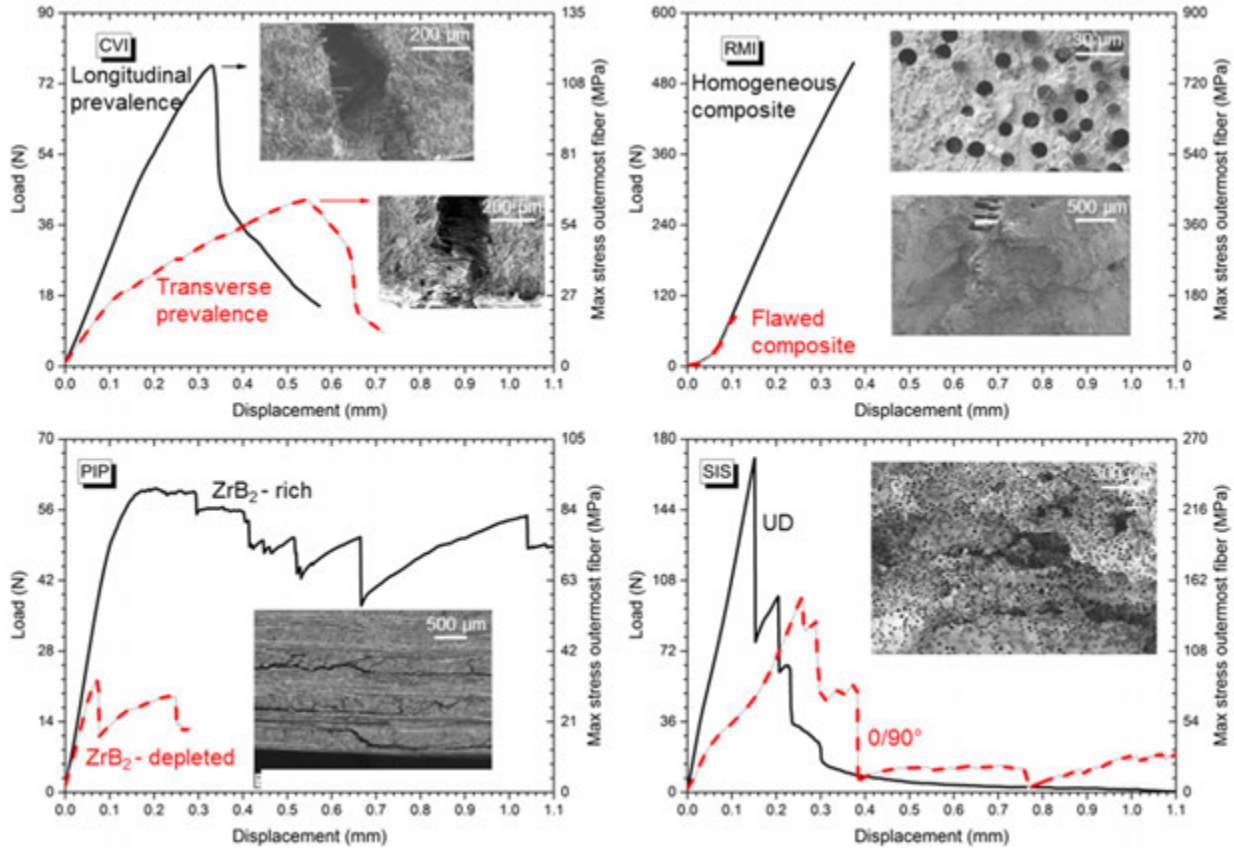


Fig. 6 Typical load-displacement curves of UHTCMCs obtained through different manufacturing routes and fractured at room temperature in a 4-pt bending configuration with representative SEM images inset. Continuous or dashed lines refer to microstructural variation as labeled.

even if in both cases in the outmost surface the fibers were aligned parallel to the tensile stress. In the case of $0/90^\circ$ configuration, the calculated value should be corrected by taking into account the lower elastic modulus of the 90° layers (67 ± 2 GPa) with respect to that of 0° layers (206 ± 2 GPa), as follow:

$$\sigma_f = \frac{MtE_o}{\sum_n I_n E_n} \quad (4)$$

where M , E and I are the bending moment, Young's modulus and centroid moment of inertia of fiber layer in the outmost surface (o) among the n -layers (n), and t is the distance from the neutral axis to the outmost surface. However, Eq. (4) is not yet reliable owing to the failure of the 90° layers when tensile and compressive stresses within these layers exceed 61 ± 13 MPa and 172 ± 16 MPa, respectively. Their failure leads to the decrease of the effective elastic constant of damaged layers, as can be seen from the slope decreasing above 30 N of applied load. Furthermore, since broken 90° layers should offer different elastic constant if subjected to compressive or tensile stresses, the location of the neutral axis is not constant during the test and this should be taken into account in the t parameter. Owing to the difficulties in calculating the non-linear stress variation through the laminate thickness, the most reliable strength test is considered to be tensile testing. Currently, tensile strength data are scarce and limited to room temperature (Rubio *et al.*, 2019) and tensile strength testing is still challenging especially in case of matrix dominated CMCs. Comparison of different materials using the same test geometry enabled to identify the contribution of different microstructural parameters on the mechanical behavior of sintered UHTCMCs (Vinci *et al.*, 2020b).

For high temperature flexural strength and thermal shock, data available are even more limited although, for instance, first tests suggested that the 4-pt room temperature retained flexural strength of sintered UHTCMCs did not suffer the detrimental effects of thermal shock up to 1500°C (tests at higher temperatures are to date not available), and showed a gradual increase of flexural strength with increasing of temperature (Zoli *et al.*, 2018).

The characterization of fracture toughness is also very complicated, due to the lack of an accepted testing standard. Even if it is praxis to provide toughness values, not always the crack-stability criterion is investigated and the tests could not simultaneously

fulfill the plane-strain condition and limited crack tip plasticity (micro-cracking, de-bonding, etc.) (Inoue *et al.*, 2018). Anyway, sintered UHTCMCs seem to point out that interface coating is not a necessary condition to achieve high toughness in reinforced ceramic matrix composites upon manufacturing and processing conditions are carefully designed (Arai *et al.*, 2019).

Thermo-Ablative Performance

In order to validate UHTCMCs for hypersonic applications, the experimental set-up should simulate heat fluxes, gas compositions, surface pressures and flow velocities typical of an atmospheric re-entry. Only few facilities are able to reproduce these conditions. Hypersonic arc-jet wind tunnels are the most commonly employed besides oxyacetylene torch tests (Mungiguerra *et al.*, 2020, 2019, 2018; Paul *et al.*, 2013a; Savino *et al.*, 2018b). Although it is well known that the oxidation behavior of ultra-high-temperature ceramic materials and C-composites is crucial to their use, to date only limited data are available in reduced oxygen partial pressure environments and surface temperatures exceeding 2000°C, which are the most relevant conditions for the application of these materials as leading edges or nozzles.

The literature agrees on a general ablation behavior improvement when a traditional CMC is enriched with UHTC powder with the improvement having a strong dependence on the volume fraction, composition and compaction degree of the UHTC (Li *et al.*, 2013; Silvestroni *et al.*, 2019a,b; Tang *et al.*, 2009, 2007a).

A dedicated study on the effect of the secondary phases on the ablation behavior of ZrB₂ composites reinforced with 40 vol% C short fibers and containing 5 vol% SiC in combination with 5 vol% of silicide of various transition metals (MoSi₂, HfSi₂ or WSi₂) (Silvestroni *et al.*, 2019a,b) demonstrated that all composites successfully withstood extreme conditions in an oxyacetylene torch for 60s, but different responses were observed depending on the matrix composition which primarily impacted on the final density, typically between 83% and 94% of the theoretical value. The temperatures achieved on the surfaces of the samples tested also varied as a function of the residual porosity and ranged from 2080 to 2240°C. HfSi₂ additions offered the best performance and exceeded that of the baseline material that contained only SiC. It is believed that this was due to its ability to promote the elimination of porosity during densification and to the refractory nature of its oxide, HfO₂.

Many approaches have been investigated to implement the functionality of UHTCs into conventional CMCs. One approach is based on the protection of C/C composites with UHTC coatings (Corral and Loehman, 2008; Fu *et al.*, 2016; Haibo *et al.*, 2016; Liu *et al.*, 2013; Sun *et al.*, 2014; Zhou *et al.*, 2010). The main issue typically lies in achieving a good adhesion between the C/C composite and the UHTC phase due to the different chemistry of the materials and the thermal expansion mismatch that can cause the detachment of the coating under severe thermal stresses. (Corral and Loehman, 2008) have successfully achieved a good interface between the CMC and the coating by dip coating the C/C composite, previously heat treated at 1600°C for 4 h to induce graphitization on the surface, in a suspension of ZrB₂/SiC particles dispersed in a phenolic resin. Zhou *et al.* (2010) have obtained a homogeneous and dense coating of ZrB₂/SiC devoid of cracks via vapor silicon infiltration on C/C composites which showed good oxidation resistance up to 1500°C. Another way of implementing these properties is by embedding UHTC particles in the ceramic matrix of C/SiC composites. In this regard, Corral and Tang fabricated C/SiC composites with 4–18 vol% of ZrB₂ inclusions via CVI, and compared it to a C/SiC composite, showing how the former had increased oxidation resistance above 1000°C due to the synergy between B₂O₃ and SiO₂ forming a protective borosilicate scale with higher viscosity (Tang *et al.*, 2007b; Walker and Corral, 2014). Li and Zhang also reported the promising oxidation behavior of C/ZrB₂-SiC composites with high SiC content (Li *et al.*, 2009). In all these cases, the addition of relatively little amounts of UHTC phases significantly improved the oxidation and ablation resistances of CMCs. Therefore, more extensive studies were carried out on fiber reinforced UHTCs, where the UHTC phase was the main constituent, maintaining a non-brittle fracture behavior (Zoli *et al.*, 2018; Zoli and Sciti, 2017). Short-term oxidation tests were carried out on C/ZrB₂-SiC composites in order to evaluate the ability of the UHTC matrix to protect fibers from oxidation (Vinci *et al.*, 2018) and more in depth studies were carried out by TGA in order to assess the oxidation kinetics of carbon fiber reinforced ZrB₂/SiC composites up to 1500°C (Vinci *et al.*, 2017). Based on the promising results obtained

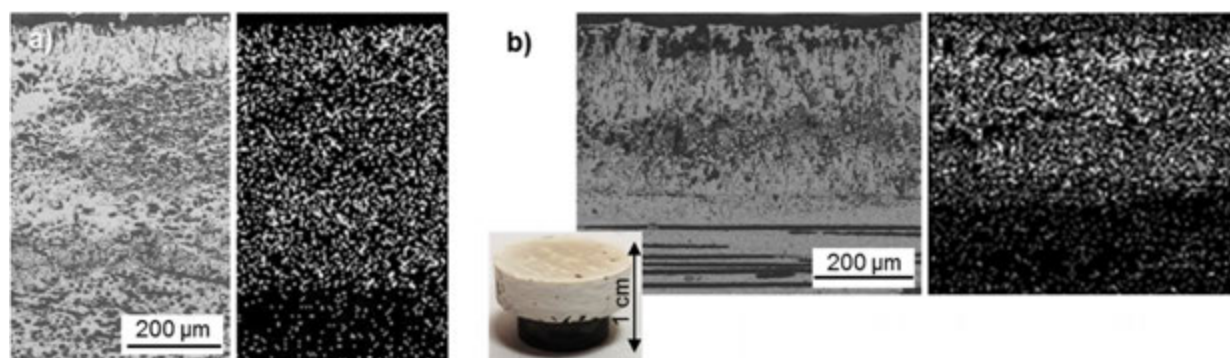


Fig. 7 Cross section SEM images of UHTCMCs containing (a) short or (b) continuous C fibers after exposure to high enthalpy flow above 2500°C with corresponding oxygen diffusion map. The image inset in (b) is an optical picture of the specimen after the test.

from these early studies, experiments moved to testing in relevant conditions. Short and continuous carbon fiber reinforced ZrB_2/SiC composites obtained by SIS were tested in a supersonic arc-jet wind tunnel and analyzed by SEM-EDS. Test specimens were exposed to supersonic plasma flow of simulated air at enthalpies up to 20 MJ kg^{-1} , surface heat fluxes of $1\text{--}5 \text{ MW m}^{-2}$ and stagnation-point pressure of 10 kPa. The maximum temperature measured on the surface of the sample exceeded 2500°C for 400s, the test specimens successfully survived the jet, as they appeared only whitened but still compact. SEM-EDS analysis carried out on the cross-section revealed the formation of a thin compact zirconia layer protecting the underlying pristine material (Mungiguerra *et al.*, 2020, 2019), Fig. 7.

Summary and Future Prospects

Ceramic matrix composites (CMCs) are replacing metals in different application fields thanks to the combination of good mechanical properties even at high temperatures, low deformation and high strength-to-weight ratios (Krenkel and Berndt, 2005). Ultra-high temperature ceramic matrix composites (UHTCMCs) are a new class of CMCs showing near-zero ablation/erosion above 2000°C specifically developed to replace C/C materials in rocket and hypersonic vehicle components such as nozzles, thermal protection system tiles or leading edges (Sciti *et al.*, 2018). The demand to extend the life of those components relates to the need to decrease the cost of space missions. The superior ablation/erosion resistance of components made of monolithic UHTCs has already been demonstrated in the past (Savino *et al.*, 2018a). However, their use in structural applications is limited by their low fracture toughness, low damage and thermal shock resistances. Currently, both non-sintering and sintering manufacturing routes are attracting increasing efforts to properly integrate UHTC matrices with reinforcing elements (Sciti *et al.*, 2018). Well-established non-sintering processes, CVI and PIP, allow the formation of a weak fiber/matrix interface, but the “non-sintered” UHTC matrix could suffer the ablation conditions (Paul *et al.*, 2013b). Owing to the lack of suitable UHTC organic/inorganic precursors in the market, another current strategy aims to enrich C/C or C/SiC with UHTC powders. RMI technology is a time saving technology compared to previous techniques, but fiber/matrix interface and residual metal content are difficult to control (Kütemeyer *et al.*, 2018). Powder slurry infiltration followed by pressure assisted sintering (SIS) is an alternative to non-sintering technologies. Densification of the ultra-refractory matrices through sintering at high temperature is the distinctive feature of this route, but it is also the most critical aspect of the process, because it may lead to embrittlement. SIS is time saving process compared to CVI and PIP and comparable to RMI, moreover it allows the control of fiber volume content and residual porosity through the modification of slurry rheology and sintering parameters, respectively (Sciti *et al.*, 2015; Zoli and Sciti, 2017).

At present, few available mechanical properties of fiber reinforced UHTCs are available, often parameters such as fiber type, volume fraction and dispersion, matrix density and composition are not shown in detail limiting the possibility to compare and correlate properties with microstructure. A race to define new testing standards for the mechanical properties of this subclass of CMCs is in progress. However, a first comparison among the samples realized by different manufacturing processes shows significant differences in mechanical behavior.

More demanding applications will continue to motivate both computational studies and experimental approach research on this field. Moreover, the entry of companies and industrial consortia in the funding sources is expected to accelerate the process toward the achievement of high Technology and Manufacturing Readiness Levels. Therefore, in the near future, efforts of researchers will focus not only on precursors synthesis, manufacturing process, microstructure/property relationships, but will also embrace the issues of real-world applications in extremely hot environments.

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References

- Arai, Y., Inoue, R., Goto, K., Kogo, Y., 2019. Carbon fiber reinforced ultra-high temperature ceramic matrix composites: A review. *Ceram. Int.* 45, 14481–14489.
- Berger, M.-H., 2012. Fine ceramic fibers: From microstructure to high temperature mechanical behavior. In: Bansal, N.P., Singh, J.P., Kriven, W.M., Schneider, H. (Eds.), *Advances in Ceramic Matrix Composites IX*. John Wiley & Sons, Ltd, pp. 1–26.
- Binner, J., Porter, M., Baker, B., *et al.*, 2019. Selection, processing, properties and applications of ultra-high temperature ceramic matrix composites, UHTCMCs – A review. *Int. Mater. Rev.* doi:10.1080/09506608.2019.1652006.
- Chen, X., Ni, D., Kan, Y., *et al.*, 2018. Reaction mechanism and microstructure development of ZrSi_2 melt-infiltrated Cf/SiC-ZrC-ZrB_2 composites: the influence of preform pore structures. *J. Mater.* 4, 266–275. doi:10.1016/j.jmat.2018.05.005.
- Colombo, P., Mera, G., Riedel, R., Soraru, G.D., 2010. Polymer-derived ceramics: 40 years of research and innovation in advanced ceramics. *J. Am. Ceram. Soc.* doi:10.1111/j.1551-2916.2010.03876.x.

- Córdoba, J.M., Chicardi, E., Poyato, R., *et al.*, 2013. Spark plasma sintering of $\text{Ti}_x\text{Ta}_{1-x}\text{C}_{0.5}\text{N}_{0.5}$ -based cermets: Effects of processing conditions on chemistry, microstructure and mechanical properties. *Chem. Eng. J.* 230, 558–566. doi:10.1016/j.cej.2013.06.104.
- Corral, E.L., Loehman, R.E., 2008. Ultra-high-temperature ceramic coatings for oxidation protection of carbon-carbon composites. *J. Am. Ceram. Soc.* 91, 1495–1502. doi:10.1111/j.1551-2916.2008.02331.x.
- Dickerson, M.B., Wurm, P.J., Schorr, J.R., *et al.*, 2004. Near net-shape, ultra-high melting, recession-resistant ZrC/W-based rocket nozzle liners via the displacive compensation of porosity (DCP) method. *J. Mater. Sci.* 39, 6005–6015.
- Failla, S., Galizia, P., Zoli, L., Vinci, A., Sciti, D., 2019. Toughening effect of non-periodic fiber distribution on crack propagation energy of UHTC composites. *J. Alloy. Compd.* 777, 612–618. doi:10.1016/j.jallcom.2018.11.043.
- Fitzgerald, K., Shepherd, D., 2018. Review of SiC/SiC_m corrosion, erosion and erosion-corrosion in high temperature helium relevant to GFR conditions. *J. Nucl. Mater.* 498, 476–494. doi:10.1016/j.jnucmat.2017.09.010.
- Fu, Q.-G., Jing, J.-Y., Tan, B.-Y., *et al.*, 2016. Nanowire-toughened transition layer to improve the oxidation resistance of SiC–MoSi₂–ZrB₂ coating for C/C composites. *Corros. Sci.* 111, 259–266. doi:10.1016/j.corsci.2016.05.013.
- Galizia, P., Failla, S., Zoli, L., Sciti, D., 2018a. Tough salami-inspired Cf/ZrB₂ UHTCMCs produced by electrophoretic deposition. *J. Eur. Ceram. Soc.* 38, 403–409. doi:10.1016/j.jeurceramsoc.2017.09.047.
- Galizia, P., Sciti, D., Saraga, F., Zoli, L., 2020. Off-axis damage tolerance of fiber-reinforced composites for aerospace systems. *J. Eur. Ceram. Soc.* 40, 2691–2698. doi:10.1016/j.jeurceramsoc.2019.12.038.
- Guicciardi, S., Silvestroni, L., Nygren, M., Sciti, D., 2010. Microstructure and toughening mechanisms in spark plasma-sintered ZrB₂ ceramics reinforced by SiC whiskers or SiC-chopped fibers. *J. Am. Ceram. Soc.* 93, 2384–2391. doi:10.1111/j.1551-2916.2010.03730.x.
- Haibo, O., Cuiyan, L., Jianfeng, H., *et al.*, 2016. Self-healing ZrB₂-SiO₂ oxidation resistance coating for SiC coated carbon/carbon composites. *Corros. Sci.* 110, 265–272. doi:10.1016/j.corsci.2016.04.040.
- Heidenreich, B., 2014. C/SiC and C/C-SiC Composites. In: Bansal, N.P., Lamon, J. (Eds.), *Ceramic Matrix Composites: Materials, Modeling and Technology*. Hoboken, NJ: John Wiley, pp. 147–216. doi:10.1002/9781118832998.ch6.
- Hu, C., Sakka, Y., Tanaka, H., *et al.*, 2010a. Microstructure and properties of ZrB₂-SiC composites prepared by spark plasma sintering using TaSi₂ as sintering additive. *J. Eur. Ceram. Soc.* 30, 2625–2631. doi:10.1016/j.jeurceramsoc.2010.05.013.
- Hu, H., Wang, Q., Chen, Z., *et al.*, 2010b. Preparation and characterization of C/SiC–ZrB₂ composites by precursor infiltration and pyrolysis process. *Ceram. Int.* 36, 1011–1016. doi:10.1016/j.ceramint.2009.11.015.
- Hu, P., Cheng, Y., Guo, X., *et al.*, 2019. Architectural engineering inspired method of preparing Cf/ZrC–SiC with graceful mechanical responses. *J. Am. Ceram. Soc.* 102, 70–78. doi:10.1111/jace.16018.
- Huang, Y., Young, R.J., 1995. Effect of fibre microstructure upon the modulus of PAN- and pitch-based carbon fibres. *Carbon* 33, 97–107. doi:10.1016/0008-6223(94)00109-D.
- Inoue, R., Arai, Y., Kubota, Y., Goto, K., Kogo, Y., 2018. Development of short- and continuous carbon fiber-reinforced ZrB₂-SiC-ZrC matrix composites for thermal protection systems. *Ceram. Int.* 44, 15859–15867.
- Ionescu, E., Bernard, S., Lucas, R., *et al.*, 2019. Polymer-derived ultra-high temperature ceramics (UHTCs) and related materials. *Adv. Eng. Mater.* 21, 1900269. doi:10.1002/adem.201900269.
- Jin, H., Meng, S., Xie, W., Xu, C., Niu, J., 2016. ZrB₂-CNTs nanocomposites fabricated by spark plasma sintering. *Materials* 9, 967. doi:10.3390/ma9120967.
- Koizumi, M., 1993. The concept of FGM. In: *Proceedings of the Second International Symposium on Functionally Gradient Materials*.
- Krenkel, W., Berndt, F., 2005. C/C-SiC composites for space applications and advanced friction systems. *Mater. Sci. Eng. A.* 412 (1–2), 177–181. doi:10.1016/j.msea.2005.08.204.
- Kütemeyer, M., Helmreich, T., Rosiwal, S., Koch, D., 2018. Influence of zirconium-based alloys on manufacturing and mechanical properties of ultra high temperature ceramic matrix composites. *Adv. Appl. Ceram.* 117, 62–69. doi:10.1080/17436753.2018.1509810.
- Kütemeyer, M., Schomer, L., Helmreich, T., Rosiwal, S., Koch, D., 2016. Fabrication of ultra high temperature ceramic matrix composites using a reactive melt infiltration process. *J. Eur. Ceram. Soc.* 36, 3647–3655. doi:10.1016/j.jeurceramsoc.2016.04.039.
- Kütemeyer, M., Shandler, D., Koch, D., Friess, M., 2015. Reactive melt infiltration of boron containing fiber reinforced preforms forming a ZrB₂ matrix. In: Mahmoud, M.M., Bhalla, A., Bansal, N.P., *et al.* (Eds.), *Processing and Properties of Advanced Ceramics and Composites VII: Ceramic Transactions 252*. The American Ceramic Society, pp. 169–180.
- Levine, S.R., Opila, E.J., Halbig, M.C., *et al.*, 2002. Evaluation of ultra-high temperature ceramics for aer propulsion use. *J. Eur. Ceram. Soc.* 22 (14–15), 2757–2767. doi:10.1016/S0955-2219(02)00140-1.
- Li, H., Yao, X., Zhang, Y., *et al.*, 2013. Effect of heat flux on ablation behaviour and mechanism of C/C–ZrB₂–SiC composite under oxyacetylene torch flame. *Corros. Sci.* 74, 265–270.
- Li, H., Zhang, L., Cheng, L., Wang, Y., 2009. Ablation resistance of different coating structures for C/ZrB₂–SiC composites under oxyacetylene torch flame. *Int. J. Appl. Ceram. Technol.* 6, 145–150. doi:10.1111/j.1744-7402.2008.02320.x.
- Li, L., Wang, Y., Cheng, L., Zhang, L., 2011. Preparation and properties of 2D C/SiC–ZrB₂–TaC composites. *Ceram. Int.* 37, 891–896. doi:10.1016/j.ceramint.2010.10.033.
- Lin, J., Huang, Y., Zhang, H., Yang, Y., Wu, Y., 2015. Spark plasma sintering of ZrO₂ fiber toughened ZrB₂-based ultra-high temperature ceramics. *Ceram. Int.* 41, 10336–10340. doi:10.1016/j.ceramint.2015.04.148.
- Liu, L., Li, H., Feng, W., *et al.*, 2013. Ablation in different heat fluxes of C/C composites modified by ZrB₂-ZrC and ZrB₂-ZrC-SiC particles. *Corros. Sci.* 74, 159–167. doi:10.1016/j.corsci.2013.04.038.
- Maskaly, G.R., Chiang, Y.-M., 2008. Infiltration processing of transition metal silicide-silicon carbide composites. In: Jessen, T., Ustundag, E. (Eds.), *24th Annual Conference on Composites, Advanced Ceramics, Materials, and Structures: A: Ceramic Engineering and Science Proceedings*. John Wiley & Sons, Ltd, pp. 307–313.
- Monteverde, F., 2007. Ultra-high temperature HfB₂-SiC ceramics consolidated by hot-pressing and spark plasma sintering. *J. Alloy. Compd.* 428, 197–205. doi:10.1016/j.jallcom.2006.01.107.
- Mungiguerra, S., Di Martino, G.D., Cecere, A., *et al.*, 2018. Characterization of carbon-fiber reinforced ultra-high-temperature ceramic matrix composites in arc-jet environment. In: *Proceedings of the 9th International Astronautical Congress*. Bremen, Germany.
- Mungiguerra, S., Di Martino, G.D., Cecere, A., *et al.*, 2019. Arc-jet wind tunnel characterization of ultra-high-temperature ceramic matrix composites. *Corros. Sci.* 149, 18–28. doi:10.1016/j.corsci.2018.12.039.
- Mungiguerra, S., Martino, G.D. Di, Cecere, A., *et al.*, 2020. Ultra-high-temperature testing of sintered ZrB₂-based ceramic composites in atmospheric re-entry environment. *Int. J. Heat Mass Transf.* 156, 119910. doi:10.1016/j.ijheatmasstransfer.2020.119910.
- Nannetti, C.A., Ortona, A., de Pinto, D.A., Riccardi, B., 2004. Manufacturing SiC-fiber-reinforced SiC matrix composites by improved CVI/slurry infiltration/polymer impregnation and pyrolysis. *J. Am. Ceram. Soc.* 87, 1205–1209. doi:10.1111/j.1551-2916.2004.tb20093.x.
- Paul, A., Binner, J.G.P., Vaidyanathan, B., Heaton, A.C.J., Brown, P.M., 2013a. UHTC – Carbon fiber composites: Preparation, oxyacetylene torch testing and characterization. *J. euro* 33, 423–432. doi:10.1016/j.jeurceramsoc.2012.08.018.
- Paul, A., Venugopal, S., Binner, J.G.P., *et al.*, 2013b. UHTC-carbon fibre composites: Preparation, oxyacetylene torch testing and characterisation. *J. Eur. Ceram. Soc.* 33, 423–432. doi:10.1016/j.jeurceramsoc.2012.08.018.
- Paul, A., Binner, J., Vaidyanathan, B., 2014. UHTC composites for hypersonic applications. In: Fahrenholtz, W.G., Wuchina, E.J., Lee, W.E., Zhou, Y. (Eds.), *Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications*. Wiley, pp. 144–166. doi:10.1002/9781118700853.ch7.

- Peterlik, H., 2014. Carbon fibers. In: Bansal, N.P., Lamon, J. (Eds.), *Ceramic Matrix Composites: Materials, Modeling and Technology*. Hoboken, NJ: John Wiley & Sons, Inc., pp. 27–39. doi:10.1002/9781118832998.ch2.
- Phase Equilibria Diagrams Online Database (NIST Standard Reference Database 31), 2019. The American Ceramic Society and the National Institute of Standards and Technology. Figure Number 4443. Available at: www.nist.gov/srd/nist31.cfm.
- Pope, E.J.A., Hepp, J., Kratsch, K.M., 2007. Method for Forming Hafnium Carbide and Hafnium Nitride Ceramics and Preceramic Polymers US 2007/0178038 A1.
- Rubio, V., Ramanujam, P., Binner, J., 2018. Ultra-high temperature ceramic composite. *Adv. Appl. Ceram.* 117, 56–61. doi:10.1080/17436753.2018.1475140.
- Rubio, V., Binner, J., Cousinet, S., *et al.*, 2019. Materials characterisation and mechanical properties of Cf-UHTC powder composites. *J. Eur. Ceram. Soc.* 39, 813–824.
- Savino, R., Criscuolo, L., Di Martino, G.D., Mungiguerra, S., 2018a. Aero-thermo-chemical characterization of ultra-high-temperature ceramics for aerospace applications. *J. Eur. Ceram. Soc.* 38, 2937–2953. doi:10.1016/j.jeurceramsoc.2017.12.043.
- Savino, R., Mungiguerra, S., Di Martino, G.D., 2018b. Testing ultra-high-temperature ceramics for thermal protection and rocket applications. *Adv. Appl. Ceram.* 117, s9–s18.
- Sayir, A., 2004. Carbon fiber reinforced hafnium carbide composite. *J. Mater. Sci.* 39, 5995–6003. doi:10.1023/B:JMSC.0000041696.64055.8c.
- Sciti, D., Savino, R., Silvestroni, L., 2012. Aerothermal behaviour of a SiC fibre-reinforced ZrB₂ sharp component in supersonic regime. *J. Eur. Ceram. Soc.* 32, 1837–1845. doi:10.1016/j.jeurceramsoc.2012.01.019.
- Sciti, D., Guicciardi, S., Silvestroni, L., 2014. Are short Hi-Nicalon SiC fibers a secondary or a toughening phase for ultra-high temperature ceramics? *Mater. Des.* 55, 821–829. doi:10.1016/j.matdes.2013.10.019.
- Sciti, D., Zoli, L., Vinci, A., *et al.*, 2020. Effect of PAN-based and pitch-based carbon fibres on microstructure and properties of continuous Cf/ZrB₂-SiC UHTCMCs. *J. Eur. Ceram. Soc.* 41 (5), doi:10.1016/j.jeurceramsoc.2020.05.032.
- Sciti, D., Natali Murri, A., Medri, V., Zoli, L., 2015. Continuous C fibre composites with a porous ZrB₂ Matrix. *Mater. Des.* 85. doi:10.1016/j.matdes.2015.06.136.
- Sciti, D., Silvestroni, L., Monteverde, F., Vinci, A., Zoli, L., 2018. Introduction to H2020 project C³HARME—next generation ceramic composites for combustion harsh environment and space. *Adv. Appl. Ceram.* 117 (sup 1), 70–75. doi:10.1080/17436753.2018.1509822.
- Servadei, F., Zoli, L., Galizia, P., Vinci, A., Sciti, D., 2020. Development of UHTCMCs via water based ZrB₂ powder slurry infiltration and polymer infiltration and pyrolysis. *J. Eur. Ceram. Soc.* 40, 5076–5084. doi:10.1016/j.jeurceramsoc.2020.05.054.
- Silvestroni, L., Sciti, D., 2011. Oxidation of ZrB₂ ceramics containing SiC as particles, whiskers, or short fibers. *J. Am. Ceram. Soc.* 94, 2796–2799. doi:10.1111/j.1551-2916.2011.04726.x.
- Silvestroni, L., Sciti, D., Melandri, C., Guicciardi, S., 2010. Toughened ZrB₂-based ceramics through SiC whisker or SiC chopped fiber additions. *J. Eur. Ceram. Soc.* 30 (11), 2155–2164. doi:10.1016/j.jeurceramsoc.2009.11.012.
- Silvestroni, L., Capiani, C., Fabbriche, D.D., Melandri, C., 2016a. Novel light and tough ZrB₂-based functionally graded ceramics. *Compos. Part B Eng.* 99, 321–329. doi:10.1016/j.compositesb.2016.06.001.
- Silvestroni, L., Dalle Fabbriche, D., Melandri, C., Sciti, D., 2016b. Relationships between carbon fiber type and interfacial domain in ZrB₂-based ceramics. *J. Eur. Ceram. Soc.* 36, 17–24. doi:10.1016/j.jeurceramsoc.2015.09.026.
- Silvestroni, L., Fabbriche, D.D., Sciti, D., 2015a. Tyranno SA3 fiber–ZrB₂ composites. Part I: Microstructure and densification. *Mater. Des.* 65, 1253–1263. doi:10.1016/j.matdes.2014.08.068.
- Silvestroni, L., Sciti, D., Hilmas, G.E., Fahrenholtz, W.G., Watts, J., 2015b. Effect of a weak fiber interface coating in ZrB₂ reinforced with long SiC fibers. *Mater. Des.* 88, 610–618. doi:10.1016/j.matdes.2015.08.105.
- Silvestroni, L., Sciti, D., Melandri, C., Guicciardi, S., 2015c. Tyranno SA3 fiber–ZrB₂ composites. Part II: Mechanical properties. *Mater. Des.* 65, 1264–1273. doi:10.1016/j.matdes.2014.08.075.
- Silvestroni, L., Melandri, C., Venkatachalam, V., Binner, J., Sciti, D., 2019a. Merging toughness and oxidation resistance in a light ZrB₂ composite. *Mater. Des.* 183, 108078.
- Silvestroni, L., Vinci, A., Failla, S., *et al.*, 2019b. Ablation behaviour of ultra-high temperature ceramic matrix composites: Role of MeSi₂ addition. *J. Eur. Ceram. Soc.* 39, 2771–2781.
- Song, G.M., Li, Q., Wen, G.W., Zhou, Y., 2002. Mechanical properties of short carbon fiber-reinforced TiC composites produced by hot pressing. *Mater. Sci. Eng. A.* 326 (2), 240–248. doi:10.1016/S0921-5093(01)01488-5.
- Stinton, D.P., Besmann, T.M., Lowden, R.A., 1988. Advanced ceramics by chemical vapor deposition techniques. *Am. Ceram. Soc. Bull.* 67 (2), 350–355.
- Sun, C., Li, H., Fu, Q., Zhang, J., 2014. Microstructure and ablation properties of carbon/carbon composites modified by ZrSiO₄. *Corros. Sci.* 79, 100–107. doi:10.1016/j.corsci.2013.10.031.
- Tang, S., Hu, C., 2017. Design, preparation and properties of carbon fiber reinforced ultra-high temperature ceramic composites for aerospace applications: A review. *J. Mater. Sci. Technol.* 33 (2), 117–130. doi:10.1016/j.jmst.2016.08.004.
- Tang, S., Deng, J., Wang, S., Liu, W., 2007a. Fabrication and characterization of an ultra-high-temperature carbon fiber-reinforced ZrB₂-SiC Matrix Composite. *J. Am. Ceram. Soc.* 90, 3320–3322.
- Tang, S., Deng, J., Wang, S., Liu, W., 2007b. Fabrication and characterization of an ultra-high-temperature carbon fiber-reinforced ZrB₂-SiC matrix composite. *J. Am. Ceram. Soc.* 90, 3320–3322. doi:10.1111/j.1551-2916.2007.01876.x.
- Tang, S., Deng, J., Wang, S., Liu, W., Yang, K., 2007c. Ablation behaviors of ultra-high temperature ceramic composites. *Mater. Sci. Eng. A.* doi:10.1016/j.msea.2007.02.040.
- Tang, S., Deng, J., Wang, S., Liu, W., 2009. Comparison of thermal and ablation behaviors of C/SiC composites and C/ZrB₂-SiC composites. *Corros. Sci.* 51, 54–61.
- Terauds, K., Raj, R., Kroll, P., 2014. Ab initio and FTIR studies of HfSiCNO processed from the polymer route. *J. Am. Ceram. Soc.* 97 (3), 742–749. doi:10.1111/jace.12779.
- Todde, S., Licheri, R., Orrù, R., Cao, G., 2012. Spark plasma sintering processing for the evaluation of cryomilled CoNiCrAlY alloys for high temperature applications in oxidizing environment. *Chem. Eng. J.* 200–202, 68–80. doi:10.1016/j.cej.2012.06.009.
- Vinci, A., Zoli, L., Sciti, D., 2018a. Influence of SiC content on the oxidation of carbon fibre reinforced ZrB₂/SiC composites at 1500 and 1650°C in air. *J. Eur. Ceram. Soc.* 38, 3767–3776. doi:10.1016/j.jeurceramsoc.2018.04.064.
- Vinci, A., Zoli, L., Sciti, D., *et al.*, 2019a. Influence of fibre content on the strength of carbon fibre reinforced HfC/SiC composites up to 2100 °C. *J. Eur. Ceram. Soc.* 39 (13), 3594–3603. doi:10.1016/j.jeurceramsoc.2019.04.049.
- Vinci, A., Zoli, L., Sciti, D., *et al.*, 2019b. Mechanical behaviour of carbon fibre reinforced TaC/SiC and ZrC/SiC composites up to 2100°C. *J. Eur. Ceram. Soc.* 39, 780–787. doi:10.1016/j.jeurceramsoc.2018.11.017.
- Vinci, A., Zoli, L., Galizia, P., *et al.*, 2020a. Reactive melt infiltration of carbon fibre reinforced ZrB₂/B composites with Zr₂Cu. *Compos. Part A Appl. Sci. Manuf.* 137, 105973. doi:10.1016/j.compositesa.2020.105973.
- Vinci, A., Zoli, L., Sciti, D., Cesare, M., Guicciardi, S., 2020b. Understanding the mechanical properties of novel UHTCMCs through random forest and regression tree analysis. *Mater. Des.* 145, 97–107. doi:10.1016/j.matdes.2018.02.061.
- Vinci, A., Zoli, L., Landi, E., Sciti, D., 2017. Oxidation behaviour of a continuous carbon fibre reinforced ZrB₂-SiC composite. *Corros. Sci.* 123. doi:10.1016/j.corsci.2017.04.012.
- Walker, L.S., Corral, E.L., 2014. Self-generating high-temperature oxidation-resistant glass-ceramic coatings for C–C composites using UHTCs. *J. Am. Ceram. Soc.* 97, 3004–3011. doi:10.1111/jace.13017.
- Wu, H., Xie, C., Zhang, W., Zhang, J., 2013. Fabrication and properties of 2D C/C–ZrB₂–ZrC–SiC composites by hybrid precursor infiltration and pyrolysis. *Adv. Appl. Ceram.* 112, 366–373.
- Xu, C., Cai, Y., Flodström, K., *et al.*, 2012. Spark plasma sintering of B4C ceramics: The effects of milling medium and TiB₂ addition. *Int. J. Refract. Met. Hard Mater.* 30, 139–144. doi:10.1016/j.jrmhm.2011.07.016.

- Ye, Y., Zhang, H., Tong, Y., Bai, S., 2013. HfC-based coating prepared by reactive melt infiltration on C/C composite substrate. *Ceram. Int.* 39, 5477–5483. doi:10.1016/j.ceramint.2012.12.059.
- Zeng, Y., Wang, D., Xiong, X., *et al.*, 2017. Ablation-resistant carbide $Zr_{0.8}Ti_{0.2}C_{0.74}B_{0.26}$ for oxidizing environments up to 3,000°C. *Nat. Commun.* 8, 15836. doi:10.1038/ncomms15836.
- Zhang, D., Hu, P., Dong, S., *et al.*, 2019. Microstructures and mechanical properties of Cf/ZrB₂-SiC composite fabricated by nano slurry brushing combined with low-temperature hot pressing. *J. Alloy. Compd.* 789, 755–761. doi:10.1016/j.jallcom.2019.03.147.
- Zhang, D., Hu, P., Dong, S., Qu, Q., Zhang, X., 2018. Effect of pyrolytic carbon coating on the microstructure and fracture behavior of the Cf/ZrB₂-SiC composite. *Ceram. Int.* 44 (16), 19612–19618. doi:10.1016/j.ceramint.2018.07.210.
- Zhang, S., Wang, S., Li, W., Zhu, Y., Chen, Z., 2011. Preparation of ZrB₂ based composites by reactive melt infiltration at relative low temperature. *Mater. Lett.* 65 (19–20), 2910–2912. doi:10.1016/j.matlet.2011.06.070.
- Zhou, H., Gao, L., Wang, Z., Dong, S., 2010. ZrB₂-SiC oxidation protective coating on C/C composites prepared by vapor silicon infiltration process. *J. Am. Ceram. Soc.* 93, 915–919. doi:10.1111/j.1551-2916.2009.03481.x.
- Zhu, Y., Wang, S., Li, W., Zhang, S., Chen, Z., 2012. Preparation of carbon fiber-reinforced zirconium carbide matrix composites by reactive melt infiltration at relative low temperature. *Scr. Mater.* 67, 822–825. doi:10.1016/j.scriptamat.2012.07.044.
- Zoli, L., Sciti, D., 2017. Efficacy of a ZrB₂-SiC matrix in protecting C fibres from oxidation in novel UHTCMC materials. *Mater. Des.* 113, 207–213. doi:10.1016/j.matdes.2016.09.104.
- Zoli, L., Vinci, A., Silvestroni, L., *et al.*, 2017. Rapid spark plasma sintering to produce dense UHTCs reinforced with undamaged carbon fibres. *Mater. Des.* 130, 1–7. doi:10.1016/j.matdes.2017.05.029.
- Zoli, L., Vinci, A., Galizia, P., *et al.*, 2020. Is spark plasma sintering suitable for the densification of continuous carbon fibre - UHTCMCs? *J. Eur. Ceram. Soc.* 40 (7), 2597–2603. doi:10.1016/j.jeurceramsoc.2019.12.004.
- Zoli, L., Medri, V., Melandri, C., Sciti, D., 2015. Continuous SiC fibers-ZrB₂ composites. *J. Eur. Ceram. Soc.* 35, 4371–4376.
- Zoli, L., Vinci, A., Galizia, P., Melandri, C., Sciti, D.I., 2018. On the thermal shock resistance and mechanical properties of novel unidirectional UHTCMCs for extreme environments. *Sci. Rep.* 8, 9148. doi:10.1038/s41598-018-27328-x.

Further Reading

- Galizia, P., Zoli, L., Sciti, D., 2018b. Impact of residual stress on thermal damage accumulation, and Young's modulus of fiber-reinforced ultra-high temperature ceramics. *Mater. Des.* 160, 803–809. doi:10.1016/j.matdes.2018.10.019.

Relevant Websites

- <https://c3harme.eu/c3harme>.
<https://www.youtube.com/watch?v=QJpqongYVcs-C3HARME>
 Next Generation Ceramic Composites.
https://en.wikipedia.org/wiki/Ultra_high_temperature_ceramic_matrix_composite
 Ultra high temperature ceramic matrix composite.
<https://www.youtube.com/watch?v=NRVyGoqVCwk-C3HARME>
 Why we do modelling.

Carbon-Matrix Composites

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Composite Materials

A composite material (also known as a composite) is a material with two or more constituents that are artificially put together, so that a certain desired property is exhibited by the composite material, though it is not exhibited adequately by any of the constituents. Composite materials are to be distinguished from alloys. An alloy contains one or more phases, which form naturally, as dictated by the processing temperature, processing pressure and alloy composition.

One of the constituents in a composite is commonly the matrix, which is the constituent that binds the other constituent(s) together. The other constituents serve reinforcing or functional purposes and can be in various morphologies, such as fibers, particles, flakes, etc. The proportion of each constituent is best described by the fraction by volume (i.e., volume fraction) of each constituent. An example of a reinforcing constituent is one having modulus of elasticity considerably greater than that of the matrix, so that the elastic modulus of the composite is enhanced. An example of a functional constituent is one having thermal conductivity considerably higher than that of the matrix, so that the thermal conductivity of the composite is enhanced. For the thermal conductivity enhancement, it is important for the functional constituent to be at a volume fraction that is high enough for there to be a continuous thermal conduction path in the composite.

Composites are commonly classified according to the matrix material. Thus, there are polymer-matrix composites, cement-matrix composites (e.g., concrete), carbon-matrix composites, metal-matrix composites and ceramic-matrix composites. The type of matrix greatly affects the behavior of the composite. For example, the ability of the matrix to withstand high temperatures largely governs the ability of the overall composite to withstand high temperatures. The type of matrix also governs the composite fabrication method, which in turn largely governs the composite cost. Thus, cement-matrix and polymer-matrix composites are inexpensive compared to metal-matrix, carbon-matrix and ceramic-matrix composites.

Introduction to Carbon-Matrix Composites

Carbon-matrix composites refer to composites in which carbon is the matrix (Chung, 2017a). The carbon is solid carbon (essentially 100% carbon), which is to be distinguished from molecules that contain carbon atoms and other atoms.

There are three allotropes of carbon, namely graphite, diamond and fullerene. Graphite consists of sp^2 hybridized carbon atoms, with each carbon layer consisting of hexagonally arranged carbon atoms through a combination of covalent bonding and metallic bonding and the carbon layers in the AB stacking sequence (Fig. 1). Diamond consists of sp^3 hybridized carbon atoms, with each carbon atom being tetrahedrally coordinated through covalent bonding with four other carbon atoms. Fullerene consists of C_{60} molecules, with the carbon atoms in each molecule arranged to form hexagons and pentagons, as needed to form a sphere. The carbon nanotube is a hybrid of graphite and fullerene. Graphene is a single carbon layer, although the definition of graphene has been broadened to include carbon layer stacks consisting of up to 10 carbon layers. Graphene is a member of the graphite family.

Unless noted otherwise, the carbon matrix in carbon-matrix composites is in the graphite family, i.e., it consists of carbon layers, akin to graphite, but the three-dimensional crystal structure of graphite (Fig. 1) is not necessarily exhibited. Compared to the more commonly used polymer matrix, which provides polymer-matrix composites, the carbon matrix is attractive for its high temperature resistance, low coefficient of thermal expansion (CTE), high modulus of elasticity, high strength, high electrical conductivity and high thermal conductivity.

Reinforcement in Carbon-Matrix Composites

The reinforcing constituent in a carbon-matrix composite is most effectively continuous fibers (Chung, 2017b). The continuous fibers are in the form of tows (bundles), with thousands of fibers per tow. The designation 12K, for example, means 12,000 fibers in the tow. The tows are two-dimensionally or one-dimensionally arranged in each ply (i.e., each lamina). An example of a two-dimensional arrangement is one that involves the use of a fabric in the form of woven fibers. An example of a one-dimensional arrangement is one that involves all the fibers oriented in the same direction in the plane of the lamina. A typical composite (known as a laminate) consists of multiple laminae that are held together by the carbon matrix. Because the fibers are in the plane of the laminate, the laminate is much stronger in the plane of the laminate than in the through-thickness direction of the laminate. The interface between adjacent laminae in the laminate is known as the interlaminar interface, which has a substantial thickness (e.g., 10 μm) and is a matrix-rich region.

In order for all the fibers in each tow to contribute effectively to strengthening the composite, the carbon matrix must surround each fiber in each tow. If the carbon matrix surrounds each tow, without adequate filling of the small space between the adjacent

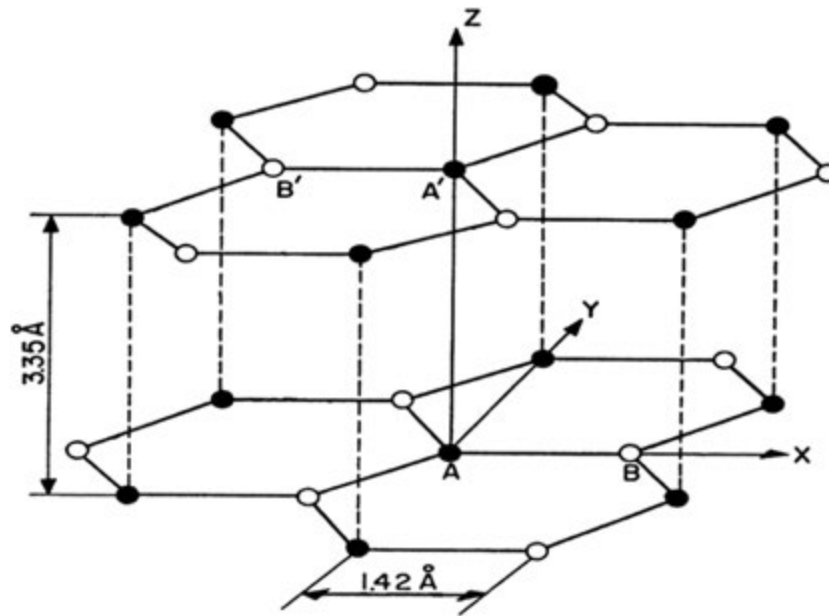


Fig. 1 The crystal structure of graphite.

fibers in a tow, porosity occurs within each tow of the composite and the fibers in the interior of each tow contribute little to strengthening the composite.

The most widely used continuous fiber in carbon-matrix composites is carbon fiber. The carbon fiber carbon-matrix composites (also known as carbon-carbon composites and abbreviated C/C) are the dominant high-temperature lightweight structural material. The continuous fibers can be woven or non-woven. The non-woven form is preferred for high-performance structures, since the fibers are anisotropic (with superior properties in the fiber axis than the transverse direction) and the slight local bending of the fibers in the woven form (Fig. 2) is not desirable for the most effective exploitation of the mechanical properties of the fibers.

In the C/C shown by the optical microscope photograph in Fig. 2, the carbon fibers are biaxially woven and manufactured by SGL Carbon, St. Marys, PA, U.S.A., with the product code SIGRABOND C/C. The carbon fibers are made from polyacrylonitrile (PAN), which is the most widely used polymer that serves as the precursor for carbon fibers. PAN fibers are converted to carbon fibers through a process known as carbonization (also known as pyrolysis).

At the same volume fraction, discontinuous (short) fibers are less effective as a reinforcement than continuous fibers, due to the imperfect bonding between the fibers and the matrix. Thus, at a fixed volume fraction, the strength and elastic modulus increase with increasing fiber length. Particles tend to be even less effective than discontinuous carbon fibers.

Carbon Matrix

The carbon matrix of the composite is in the graphite family. It can have various degrees of crystallinity. A low degree of crystallinity corresponds to turbostratic carbon, which is amorphous carbon with carbon layers that are not well-ordered relative to one another. In particular, in turbostratic carbon, the carbon layers are not perfectly parallel to one another, are not very flat, are limited in area, and are spaced farther apart than the layers in graphite (Fig. 1) (Chung 2019a). The higher is the degree of crystallinity, the more the structure approaches that of graphite. There is a gradation of structures among turbostratic carbons. For both turbostratic carbon and graphite, the in-plane bonding is a mixture of covalent bonding and metallic bonding, whereas the out-of-plane bonding involves van der Waals' forces. As a result, the materials are highly anisotropic, with the elastic modulus, electrical conductivity and thermal conductivity being much higher in the plane of the layers than in the out-of-plane direction.

A high degree of crystallinity of the carbon matrix is beneficial to the oxidation resistance, electrical conductivity, thermal conductivity, and elastic modulus, in addition to reducing the CTE. Because of the additional cost of high-temperature heat treatment that is needed to increase the degree of crystallinity, an increase in cost accompanies an increase in the degree of crystallinity.

The higher the degree of crystallinity, the smaller is the spacing between the carbon layers and the higher is the density. According to the manufacturer, the C/C shown in Fig. 2 exhibits a density of 1.5 g/cm^3 , which is considerably lower than the graphite density of 2.26 g/cm^3 . The low density of the C/C is primarily due to the low density of the carbon matrix.

A carbon fiber is in the graphite family, with the carbon layer (Fig. 1) preferentially oriented along the fiber axis. The degree of preferred orientation of the carbon layers in the carbon matrix tends to be lower than that in carbon fibers. This is partly because the tensile stress applied to the carbon fiber along the fiber axis during the fiber fabrication causes the carbon layers to align preferentially along the fiber axis. It is also because of the large aspect ratio of the fiber. A high degree of preferred orientation is

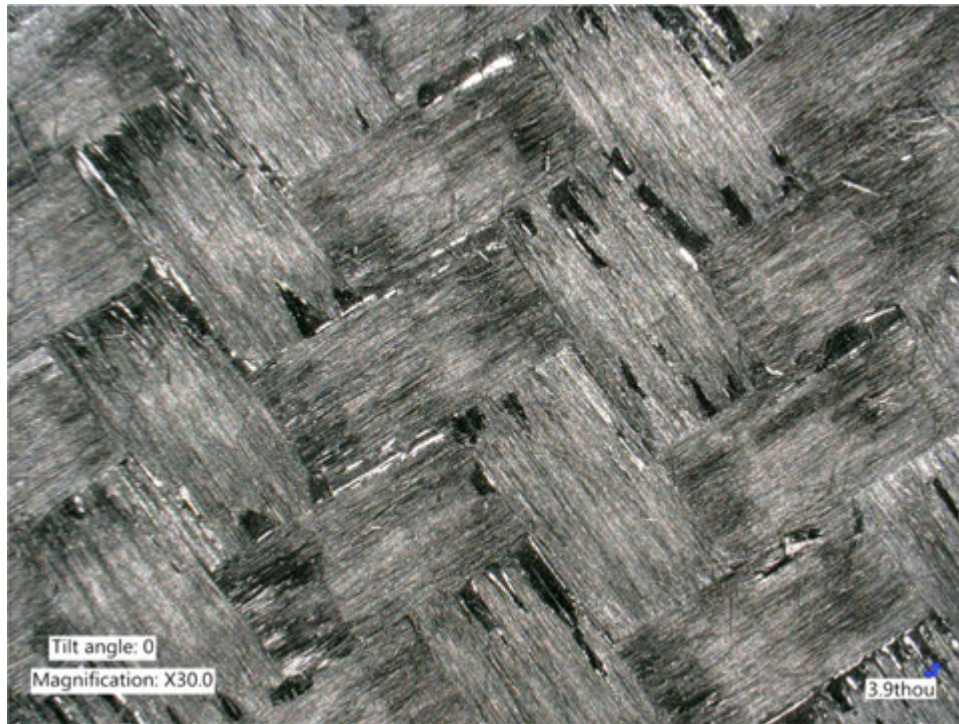


Fig. 2 Optical micrographs of a carbon-carbon composite with woven fibers. The vertical and horizontal scale bars are the same. The short scale bar has length 99 μm (0.0039 in.).

associated with anisotropy in the properties, including the mechanical, electrical and thermal properties. In particular, the thermal conductivity, electrical conductivity and elastic modulus are higher along the fiber axis than the transverse direction.

Fabrication of Carbon-Matrix Composites

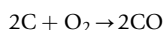
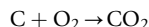
Carbon-matrix composites are commonly made from the corresponding polymer-matrix composites by carbonizing the polymer matrix, which is called the carbon matrix precursor. An example of the carbon matrix precursor is pitch. The carbonization (also known as charring) is conducted at an elevated temperature (e.g., 1000–1500°C) in the absence of oxygen (Chung, 2017a). The char yield of the carbon matrix precursor refers to the yield of the carbon from the precursor through the carbonization process. Prior to the carbonization process, the polymer-matrix composite is commonly subjected to a low-temperature heat treatment (e.g., 200–350°C), which is for the purpose of oxidizing the polymer (changing the molecular structure), so that it does not melt during the heat treatment. This low-temperature heat treatment is known as stabilization (Chung, 2017a). The carbonization process also results in pores, which are detrimental to the mechanical properties. In order to reduce the porosity, the char yield of the carbon matrix precursor should be sufficiently high. In addition, impregnation of the precursor into the pores is conducted by infiltration under pressure, followed by carbonization. Multiple cycles of impregnation followed by carbonization are typically conducted in order to reduce the porosity adequately. This process of porosity reduction is known as densification. To further reduce the porosity, a vapor in the form of a carbonaceous gas (such as methane) is infiltrated into the composite under pressure, and then allowed to decompose under heat to become carbon. This process is known as chemical vapor infiltration (CVI), which is commonly used as the final step of densification, as conducted after the multiple cycles of impregnation and carbonization. In case that a high degree of crystallinity is desired, the carbonization is followed by graphitization, which is conducted at an even higher temperature (e.g., 2000–3000°C). Due to the complexity of the overall process of fabricating carbon-matrix composites, they are expensive compared to the corresponding polymer-matrix composites.

High-Temperature Resistance of Carbon-Matrix Composites

A polymer-matrix composite can withstand temperature up to around 300°C, with the temperature limit depending on the type of polymer. A polymer in the form of a thermoplastic polymer (such as a linear polymer) softens upon heating at the glass transition temperature and melts at the melting temperature, which is above the glass transition temperature. A polymer in the form of a thermoset (such as a network polymer) does not melt, but it decomposes.

In contrast to polymer-matrix composites, a carbon-matrix composite can withstand temperature up to around 2500°C, with the temperature limit increasing with increasing degree of crystallinity (degree of graphitization) of the carbon matrix. In order to obtain a high degree of graphitization, the temperature used to fabricate the carbon-matrix composite needs to be high (e.g., exceeding 2000°C for the purpose of graphitization), with the heating conducted in an inert atmosphere (e.g., argon, with nitrogen being not suitable, due to the reaction of carbon with nitrogen to form cyanide, which is poisonous), thus raising the cost of fabricating the composite. The high temperature resistance is important for numerous applications, such as resistance heating elements, aircraft brakes, re-entry space vehicles, missiles and missile launchers.

In the presence of oxygen (as that in air), carbon is oxidized at temperatures above about 700°C. The oxidation involves the conversion of carbon to vapor, thus causing the carbon to lose mass. The reactions can be the following (Chung, 2019a).



The mass loss means the formation of voids in addition to the reduction in the dimensions of the carbon-matrix composite. Both voids and dimensional reduction decrease the mechanical performance of the composite structure. This limited oxidation resistance greatly limits the high-temperature resistance of carbon-matrix composites, since the presence of at least a low concentration of oxygen commonly occurs in application environments.

In order to enhance the oxidation resistance of carbon-matrix composites, ceramic coatings (such as silicon carbide and silicon dioxide coatings) are often used. Ceramics are more resistant to oxidation than carbon, since they are already in the form of compounds. However, there is a temperature limit even for ceramics. For example, silicon carbide is oxidized and becomes silicon dioxide when the temperature exceeds about 1700°C and oxygen is present. The oxidation of the silicon carbide coating causes pores in the coating, thereby reducing the effectiveness of the coating for protecting the carbon-matrix composite from oxidation. The use of multiple coating layers is often used to provide the combination of coating-composite bonding and oxidation protection. There are approaches other than the use of coatings for enhancing the oxidation resistance of carbon. They include the addition of oxidation inhibitors, glass sealant and other substances to the carbon matrix.

The difference in the coefficient of thermal expansion (CTE) between the ceramic coating and the carbon matrix is another problem. The larger is the CTE mismatch, the greater is the thermal stress that is present upon heating and the greater is the tendency for the coating to debond from the carbon-matrix composite. A method to alleviate the CTE mismatch problem involves the use of a gradation of silicon concentration in the coating, with the silicon concentration being low in the part of the coating proximate to the carbon-matrix composite and relatively high in the part of the coating away from the carbon-matrix composite. In other words, the composition of the coating is not uniform at that of silicon carbide (SiC).

The CTE mismatch between the fiber and carbon matrix is a similar issue that degrades the high-temperature resistance. In addition, in the fabrication of the composite at a high temperature, cooling from the high fabrication temperature tends to cause debonding at the fiber-matrix interface if the CTE mismatch is significant. In order to reduce the CTE mismatch, the use of carbon fiber in conjunction with the carbon matrix is preferred. Thus, C/C is particularly common among carbon-matrix composites for high-temperature structural applications (Bevilacqua *et al.*, 2015; Chen, 2016; Chen *et al.*, 2013; Lu *et al.*, 2019; Nasibulin *et al.*, 2017; Raunija, 2015; Stepashkin *et al.*, 2015). Another reason for the dominance of carbon fibers over ceramic fibers (which also exhibit low CTE) is their combination of wide availability and low cost.

Refractory metals (metals with very high values of the melting point) such as tungsten and molybdenum exhibit low CTE, although the CTE is not as low as that of carbon. However, these refractory metals are heavy (with high values of the density), so that they are not suitable for lightweight structures.

Mechanical Behavior of Carbon-Matrix Composites

Carbon-matrix composites tend to be brittle compared to the corresponding polymer-matrix composites. The brittleness is not attractive for structural applications. Along with the brittleness are low toughness and low impact resistance. In order to circumvent the brittleness issue, the interface between the fiber and carbon matrix is designed so that the bond is not very strong. The interfacial weakness decreases for the strength and modulus of the composite, but it enhances the ductility and toughness. This enhancement is due to the deflection of the cracks as the cracks propagate and meet the fiber-matrix interface. Due to the weakness of the interface, the crack is deflected so that it propagates in the direction of the interface. The deflection causes the overall crack path to be tortuous. The tortuosity causes toughening, due to the energy consumed in crack propagation and the long length of the tortuous path.

According to the manufacturer, the C/C shown in Fig. 2 exhibits flexural strength 150 MPa, flexural modulus (comparable to the tensile modulus) 60 GPa, tensile strength 350 MPa, interlaminar shear strength 8 MPa, in-plane electrical resistivity at room temperature $2.4 \times 10^{-5} \Omega \text{ m}$, ash content 1000 ppm, and maximum application temperature 2000°C in vacuum or inert gas.

Multiscale Carbon-Matrix Composites

Multiscale composites (also known as hierarchical composites) involve constituents in different length scales. For example, a multiscale composite involves microscale continuous fibers, such as carbon fibers (typically of diameter about 7 Å), and nanoscale discontinuous filler, such as carbon nanotubes (typically of diameter less than 0.1 μm), all bound by a carbon matrix, such that the nanoscale filler is distributed in the carbon matrix (Chung, 2019a). Because the interlaminar interface is a matrix-rich region, the nanoscale filler tends to reside mainly in the interlaminar interface region.

The nanoscale filler results in a large area of the interface between the filler and the carbon matrix. Due to the very slight sliding at the interface during vibration (even in the elastic strain regime) and the friction associated with the sliding, the interface results in mechanical energy dissipation and hence enhancement of the vibration damping ability of the composite. This form of viscoelasticity is known as interface-derived viscoelasticity (Chung, 2019b), which is to be distinguished from the more well-known viscoelasticity that is based on bulk viscoelastic deformation (as the viscoelasticity in rubber).

Since the continuous fiber is the primary reinforcement that governs the strength and modulus of the composite, the volume fraction of the continuous fibers should be high (preferably at least 50%), whether the nanoscale discontinuous constituent is present or not. Thus, the volume fraction of the nanoscale constituent must be low. A low volume fraction cannot be achieved if the discontinuous constituent is not in the nanoscale, but, for example, in the microscale.

Another example of a nanoscale constituent is fumed alumina (Wang and Chung, 2016). Fumed alumina is much less expensive than carbon nanotubes. Alumina is a ceramic. Fumed alumina is in the form of porous aggregates of nanoparticles. Due to this morphology, fumed alumina is highly compressible (squishable), so that it can conform to the topography of the surface to which it is compressed. The conformability allows the fumed alumina to conform to the surface topography of the continuous fibers.

Instead of using a nanoscale discontinuous constituent in conjunction with a microscale continuous fiber to achieve a multiscale composite, one may grow a nanoscale constituent (such as carbon nanotubes) on the surface of the microscale continuous fiber (such as carbon fiber). The growth process involves chemical vapor deposition (CVD), using a carbonaceous gas (such as methane) as the carbon precursor. The CVD process is typically assisted by using a catalyst. A problem with this approach is that it is difficult for the carbon matrix to occupy the small space between the adjacent units of the nanoscale constituent (e.g., the small space between the carbon nanotubes grown on the carbon fiber). Another problem with this approach is that the continuous fiber with the grown nanoscale constituent is considerably more difficult to handle than the unmodified continuous fiber. The handleability is needed for the composite fabrication process. Yet another problem is that the thickness of the nanoscale constituent grown on a continuous fiber is substantial, thus causing reduction in the volume fraction of the continuous fiber in the composite. Since the continuous fiber is the primary reinforcement, a reduction in its volume fraction is detrimental to the strength and elastic modulus of the composite, even though the presence of the nanoscale constituent on the surface of the continuous fiber tends to increase the interlaminar shear strength of the composite. Still another problem is the high cost and limited batch volume for the nanoscale constituent growth.

Self-Monitoring

Due to the strategic nature of numerous applications of C/C, it is desirable to monitor (or sense) the stress, strain and damage in these materials. The monitoring of the stress or strain is pertinent to operation control, load monitoring and structural vibration control. The monitoring of the damage is pertinent to structural health monitoring and hazard mitigation. The monitoring can be achieved by measuring the electrical resistance (Wang and Chung, 1997; Xi and Chung, 2019, 2020a,b), the capacitance (Xi and Chung, 2019, 2020a) or the electric field (Xi and Chung, 2020b). The effect of stress/strain on the electrical resistivity (which relates to the resistance) constitutes a piezoresistive effect. The effect of stress/strain on the electric permittivity (which relates to the capacitance) constitutes stress-dependent dielectric behavior. The effect of the stress/strain on the electric field constitutes a piezoelectric effect. All three effects are stronger for C/C than carbon fiber polymer-matrix composite. Since this monitoring does not involve the use of any embedded or attached sensor, it is said to be self-monitoring (also known as structural self-monitoring). In other words, the structural material senses itself.

Self-Powering

Electric power is typically needed for structures. For example, power is needed for the operation of sensors and other devices that are associated with the structure. Self-powering refers to a structure serving as a power source. This is to be distinguished from the embedding of a power source in a structure.

An electret is a permanent (or quasi-permanent) electric dipole. Due to the fact that C/C is an electret and is electrically conductive, it is self-powering (Xi and Chung, 2020b). The electret is due to the interaction of a small fraction of the charge carriers with the atoms. The electret discharges upon short circuiting and charges upon open circuiting. The volumetric power density is much higher for C/C than carbon fiber polymer-matrix composite, due to the higher electrical conductivity of C/C. However, the power density is low, but the energy density is substantial.

Electromagnetic Shielding Effectiveness of Carbon-Matrix Composites

Due to the electrical conductivity of the carbon matrix and the non-conductivity of the typical polymer matrix, carbon-matrix composites tend to be more effective than the corresponding polymer-matrix composites in the electromagnetic interference (EMI) shielding effectiveness (Chung, 2001; Luo and Chung, 1999). EMI shielding is important due to the interference of radio wave and microwave with electronics. The shielding is needed for the electronics as well as the radiation sources. Related to EMI shielding is the shielding of the radiation resulting from the detonation of a nuclear bomb.

Thermal Conductivity of Carbon-Matrix Composites

Due to the thermal conductivity of the carbon matrix and the thermal non-conductivity of the typical polymer matrix, carbon-matrix composites tend to be more thermally conductive than their polymer-matrix composite counterparts. A high thermal conductivity helps to increase the thermal shock resistance. It also facilitates heat dissipation, which is needed for spacecraft, electronic enclosures, heat sinks, etc.

References

- Bevilacqua, M., Babutskyi, A., Chrysanthou, A., 2015. A review of the catalytic oxidation of carbon-carbon composite aircraft brakes. *Carbon* 95, 861–869.
- Chen, W., 2016. Numerical analyses of ablative behavior of C/C composite materials. *Int. J. Heat Mass Transf.* 95, 720–726.
- Chen, Y., Xiao, S., Chen, H., Liu, H., 2013. The effect of catalyzer in the matrix on the structure and performance of carbon/carbon composite. *J. Compos. Mater.* 47 (4), 409–417.
- Chung, D.D.L., 2001. Electromagnetic interference shielding effectiveness of carbon materials. *Carbon* 39 (2), 279–285.
- Chung, D.D.L., 2017a. *Carbon Composites*, second ed. London: Butterworth-Heinemann, [Ch. 7].
- Chung, D.D.L., 2017b. Processing-structure-property relationships of continuous carbon fiber polymer-matrix composites. *Mater. Sci. Eng. R* 113, 1–29.
- Chung, D.D.L., 2019a. *Carbon Materials*. Singapore: World Sci. Pub.
- Chung, D.D.L., 2019b. Interface-derived solid-state viscoelasticity exhibited by nanostructured and microstructured materials containing carbons or ceramics. *Carbon* 144, 567–581.
- Lu, X., Jie, Z., Qian, K., 2019. Densification rate and mechanical properties of carbon/carbon composites with layer-designed preform. *Ceram. Int.* 45 (4), 4167–4175.
- Luo, X., Chung, D.D.L., 1999. Electromagnetic interference shielding using continuous carbon fiber carbon-matrix and polymer-matrix composites. *Compos. Part B* 30 (3), 227–231.
- Nasibulin, A.V., Antipov, E.A., Beilina, N.Y., Dogadin, G.S., Makarov, N.A., 2017. Effect of modifying pitch on carbon-carbon composite material density. *Refract. Ind. Ceram.* 58 (1), 74–77.
- Raunija, T.S.K., 2015. Influence of temperature and time shifts on the densification of randomly oriented carbon/carbon composite. *Def. Sci. J.* 65 (5), 411–417.
- Stepashkin, A.A., Ozherelkov, D.Y., Sazonov, Y.B., Komissarov, A.A., Mozolev, V.V., 2015. Assessment of fracture toughness of a discretely-reinforced carbon-carbon composite material. *Metal Sci. Heat Treat.* 57 (3–4), 229–235.
- Wang, A., Chung, D.D.L., 2016. First report of fumed alumina incorporation in carbon-carbon composite and the consequent improvement of the oxidation resistance and mechanical properties. *Carbon* 101, 281–289.
- Wang, S., Chung, D.D.L., 1997. Self-monitoring of strain and damage by a carbon-carbon composite. *Carbon* 35 (5), 621–630.
- Xi, X., Chung, D.D.L., 2019. Capacitance-based self-sensing of flaws and stress in carbon-carbon composite, with reports of the electric permittivity, piezoelectricity and piezoresistivity. *Carbon* 146, 447–461.
- Xi, X., Chung, D.D.L., 2020a. Corrigendum to Capacitance-based self-sensing of flaws and stress in carbon-carbon composite, with reports of the electric permittivity, piezoelectricity and piezoresistivity. *Carbon* 158, 545.
- Xi, X., Chung, D.D.L., 2020b. Electret-based self-sensing and self-powering in carbon fiber polymer-matrix and carbon-matrix structural composites. *Carbon* 160, 361–389.

Ceramics in Space Applications

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Introduction

The space industry has grown rapidly over recent decades, and this growth is expected to continue. This growth is stimulated in part by the development of low-cost reusable launcher technologies and the increasing use of commercial off-the-shelf (COTS) electronics (MacDonald and Badescu, 2014).

Ceramics are used in a broad range of space applications. These span from high strength high-temperature structural ceramics and Ceramic Matrix Composites (CMCs), ceramics for thermal protection systems, electronics, and wear components. The application areas range from propulsion system hardware for spacecraft, launcher and spacecraft structures, thermal protection systems, and substrates for space optics.

Ceramics have a range of properties such as chemical inertness, high service temperatures, low density, high hardness, and high wear resistance, that make them indispensable for a wide range of space applications. Ceramics can operate at a higher temperature, have reduced density compared to metals, and have higher specific strengths and specific stiffnesses. When metallic alloys in the hot sections of gas turbine engines are replaced by ceramic matrix composites, for example, a weight saving of around one third can be achieved (Misra, 2016). Lower density materials are particularly appealing for the space industry. Relative to advanced polymers and polymer composites, ceramics and ceramic composites are stable at significantly higher temperatures. Operation at higher temperature allows engine efficiencies to be improved, and in some cases enables the use of un-cooled design for components: this can simplify component design and reduce system weight. For structural applications, ceramics also have high specific strength and stiffness, and typically a low thermal expansion coefficient, which can enable designs with minimal thermal strains and give high dimensional stability. The environmental durability of ceramics in the atmosphere is also typically better than for metallic alloys, which can facilitate a longer component design lifetime.

The use of ceramics in space applications has increased steadily in recent decades. This increase is driven in part by a drive for weight reduction, which can lead to an increase in useable payload. Also, two further trends have contributed: the trend towards reusable launchers, and the increasing development of hypersonic spaceplanes and vehicles. Hypersonic vehicles, whether solely intended for atmospheric transit or orbital insertion, are exposed to very high heat fluxes over extended periods. Ceramics, which can operate at far higher temperatures than metals, appear to be an enabling technology for the development of these hypersonic vehicles. Ceramics and CMCs may, therefore, enable the technical feasibility of hypersonic vehicles as a cost-effective route to orbital insertion. Also, the increasing use of ceramics in space applications is driven, or enabled, by improvements in monolithic ceramic and CMC properties, as well as advances and cost reductions in fabrication technology, particularly for CMC reinforcement phases. However, it is still the case that ceramics have a high cost associated with design and fabrication, so a clear advantage must be evident before use is considered.

This chapter provides an overview of the uses of ceramics in their various forms in space applications. This includes a review of the “traditional” uses of ceramics, as well as consideration of emerging trends in ceramic and ceramic matrix composite (CMC) use where new advanced ceramics are replacing other materials such as metallic superalloys. Consideration is given to launchers, as well as satellites and manned spacecraft.

Design Considerations

Current trends within the space industry are toward an increasingly democratized and more commercial approach. Though scientific, navigation and military programs continue to be designed and managed by high-level governmental and intergovernmental agencies, much of the hardware and software development is industry-led. Areas of major change, however, are for smaller missions, now accessible to smaller companies and universities. These missions are often referred to as *New Space* (Sweeting, 2018).

With the miniaturization of both commercial and high-reliability electronics, it has become possible to utilize conventional launchers for *ride-share* missions. Coupled with the development of partially reusable launch vehicles, as well as smaller LEO-oriented launchers, the cost of launch has dramatically reduced in recent years.

It should be noted, however, that the miniaturization trend has not necessarily led to universal reductions in spacecraft mass. Conventional telecommunications spacecraft, such as those developed under the European ARTES framework (“Relevant Website section”), continue to grow in both mass and payload power while constellation-type spacecraft tend to decrease in both. Ceramic materials utilization will vary greatly between the two strategies.

The cost of the launch vehicle is a significant fraction of the launch cost, with propellant accounting for a relatively lesser fraction. Therefore, efforts have been made in the past decade to increase the lifetime of the launch vehicles. Achieving reusability

can necessitate the use of more durable materials in some key areas of launch vehicles, and this may be facilitated by the use of ceramics or ceramic matrix composites.

The use of ceramics in aerospace structural or thermo-structural applications is significantly impacted by their relatively brittle nature. Most ceramics are brittle and exhibit wide distributions of strength from component to component. They are sensitive to surface flaws and defects arising from impurities and variability in processing. This wide distribution of strengths requires the use of statistical processes such as Weibull analysis in the design of ceramic components to assess the likelihood of failure for a given loading condition. Research is ongoing to reduce this variability in the strength of ceramics. The use of reinforcement is effective in increasing the fracture toughness of ceramics. However, the inherently brittle nature of ceramics has undoubtedly limited the utilization of ceramics for applications where catastrophic failure must be avoided.

Much research in ceramics has focused on reducing the wide variability in strength exhibited by ceramics. This involves reducing how sensitive ceramics are to the presence of flaws and is countered by improving the material's fracture toughness. Some ceramics such as Si_3N_4 can be formed with "self-reinforcing microstructure", which results in improved fracture toughness (Pyzik and Beaman, 1993). Although optimizations of microstructure can deliver improvements for some ceramics, an alternative technique is possible; that is to use a reinforcement phase, forming a ceramic matrix composite. The reinforcement may be in the form of, for example, fibers, particles, or whiskers. For achieving the greatest improvement in fracture toughness and avoiding catastrophic failure, continuous fiber reinforcement is effective. Ceramic matrix composites with continuous fiber reinforcement are therefore attractive for highly stressed structural or thermo-structural applications. Although huge advances have been made in these materials, CMCs are not yet a mature material, and use of them in a critical space application entails some risk.

Future advances needed in CMCs include fibers that have good stability at high temperatures, improved environmental barrier coatings to protect from oxidation at high temperatures, and improvements in fiber-matrix inter-phases. Fabrication techniques, particularly for continuous fiber reinforcement are continuously improving. Further improvements in production techniques are needed to further reduce component cost. Technologies for joining mechanisms between ceramics and other materials would also benefit from improvement. In addition to this, improvements are needed in software tools for service life prediction of monolithic ceramic and CMC components (Devi and Rao, 1993).

The Space Environment

The space environment poses unique challenges for materials. Notable features of the space environment include vacuum, electrically neutral and charged particles (or plasma), radiation and micrometeoroids (Meseguer *et al.*, 2012). These effects are typically observed in combination rather than isolation and can cause a range of different issues covered in more detail below.

Vacuum stable materials are those that retain their functional properties in the absence of air and which do not outgas at pressures below 1×10^{-5} mbar. Outgassed matter can condense on cold surfaces and present a significant risk to optical hardware. Ceramics on their own typically present minimal-to-no outgassing risk, but care must be taken with composite materials where organic binders are used.

Ceramics possess greater stability under a Total Ionizing Dose (TID) relative to polymeric materials, owing to their inorganic composition. Ceramics are not immune from radiation effects, however, and care must be taken when ceramic materials are used on external spacecraft surfaces. Where thermo-optical properties are of critical importance, ceramics can be vulnerable to degradation under VUV/UV, low-energy particle irradiation, high temperature and low-energy x-rays.

Application Areas

The most extensive use of ceramics in spacecraft has been in the thermal protection system (TPS). Here, the material requirements are to withstand high temperatures and also the vibration and acoustic loading of re-entry. Ceramics have also been considered for use for structural applications in advanced future spacecraft, including hypersonic space-planes. The material most considered for these applications has been carbon-carbon (C/C) composites. Fiber-reinforced CMCs are also being considered for use and have superior oxidation resistance than C/C composite. In conventional space propulsion systems (liquid and solid propellant thrusters) there are many areas in which ceramics play an essential role. In emerging electric propulsion technologies, ceramics may be useful and they are already used on ion thrusters. Ceramics are also used for thermo-optical coatings, particularly solar reflector coatings. With the advent of 3D printing, the use of 3D printed ceramics for space applications has also been investigated in recent years for both exploration and settlement (Ghidini, 2018).

Ceramics are widely used in the manufacture of electronics. While the manufacture and use of ceramic chip capacitors and resistors are unlikely to change, the use of ceramics in electronic and RF applications is changing. A growing trend within space telecommunications is the move from analog to digital signal processing, meaning that fewer units are needed to operate in the RF domain, and that more of the hardware will make use of polymeric printed circuit boards (PCBs) rather than ceramic-based hybrids. The use of alumina and silicon carbide substrates commonly employed in RF and microwave electronic circuit board and heatsinks are not covered in this review. While some areas of ceramic use are decreasing, other applications are seeing significant growth such as Solid Oxide Fuel Cell (SOFC) and piezoelectric applications. The use of ceramics in SOFCs is advantageous due to their suitable electrical properties, thermal and structural properties and ability to operate at high temperature (Cable *et al.*, 2011; Ramadhani *et al.*, 2017). Piezoelectric ceramic materials (piezoceramics) such as barium titanate, lead zirconate titanate and

lead-free Perovskite ceramics are used as actuators and sensors are not covered here (Maillard *et al.*, 2009; Wu, 2020). Further detail on the use of ceramics in microwave applications is given by Varghese *et al.* (2020).

Thermal Management of Spacecraft

Atmospheric Re-Entry

A variety of thermal management techniques are used for components subject to high heating loads experienced during re-entry. The choice of a suitable TPS technique depends on the average heat load, peak heat load, duration of heat application, required mass of the vehicle, and requirements for re-usability. The duration of heat application has a significant impact on the choice of TPS technique. As well as re-entry in Earth's atmosphere, there is an increased focus on future Lunar and Martian missions. Approaches for TPS combinations for different re-entry requirements associated with Earth and entry for Lunar and Mars missions is given by Rasky *et al.* (2004).

The thermal management strategies may be classified as passive, semi-passive, and active cooling (Meseguer *et al.*, 2012). The passive thermal management strategies refer to the rejection of heat by radiation; semi-passive encompasses heat rejection by use of a phase change in some constituent of the thermal management system (e.g., ablative material or heat pipes), while active thermal management refers to the use of pumped fluid cooling.

Re-entry to the Earth's atmosphere and ultimately landing requires slowing down of a space vehicle from orbital velocity to landing speed. At high Mach numbers, heating effects of a body moving through a fluid become increasingly important. Aerothermodynamic analysis – the analysis of aerodynamic properties at several times the speed of sound—is an extension of aerodynamics to consider thermodynamic effects which become important at high Mach numbers (M). For hypersonic flow the Mach number or M is greater than or equal to 5. For re-entry to the Earth's atmosphere, Mach speeds in excess of $M = 25$ can be experienced. A substantial fraction of the orbital kinetic energy may be converted to heat upon re-entry, requiring the use of a thermal protection system. A summary and review of TPS's is given in more detail by Hurwitz (2010), while some further background and specific examples are discussed in this section.

Design of the thermal protection system for re-entry is a multidisciplinary problem, involving interactions between spacecraft shape, thermal protection material, re-entry flight path, structural mechanics, and flight mechanics (Ley *et al.*, 2009). The peak heat flux to the re-entry vehicle, and also the duration of flight along the re-entry trajectory will affect which cooling strategy is most appropriate. Re-entry trajectories may be classified as either ballistic re-entry trajectories (blunt re-entry capsules like Apollo capsule) and lifting re-entry trajectories (vehicles with lifting body characteristics like such as with a spaceplane like the Space Shuttle). The peak heat flux for a ballistic entry is extremely high, but occurs over a relatively short period of time, while for a lifting re-entry, the peak heat flux is significantly lower but is present for a longer period of time. The fraction of the total heat load absorbed depends on the ratio of skin friction coefficient to the overall drag coefficient of the re-entry vehicle. Blunt re-entry have low ratios of skin friction coefficient to pressure drag coefficient, which minimizes the heat load to the re-entry vehicle (Anderson, 1989; Ley *et al.*, 2009).

Additionally, the chemical composition of the re-entry vehicle's Thermal Protection System (TPS) surface can have a significant effect on the heat load to this same surface. In the bow shock region ahead of the re-entry vehicle, air molecules have a high vibrational energy and may dissociate into atomic oxygen and atomic nitrogen. Depending on the chemical composition of the TPS surface, recombination of dissociated oxygen and nitrogen atoms may occur resulting in the release of dissociation potential energy and thereby increasing the heat load. Surfaces with chemistries conducive to such recombination are termed *catalytic surfaces*, while those not conducive to such recombination are termed *noncatalytic surfaces* (Scott, 1992; Ley *et al.*, 2009). As a result of this, the material used for the TPS of a re-entry vehicle surface is preferably noncatalytic (Hirschel, 2015). Materials that behave in a noncatalytic manner include SiC ceramics and carbon/SiC composite (Ley *et al.*, 2009). SiC can be used to very high temperatures, as it has a sublimation temperature of $\cong 2900\text{K}$.

For space vehicles exposed to moderately high heat fluxes for short periods, a passive thermal insulation strategy may be appropriate and may be achieved using ceramics. The primary function of the TPS is to thermally insulate the structure from the external heat load, while passively cooling through thermal radiation, so that the structure can remain at a lower temperature (Glass, 2008). Radiative heat rejection is aided by the vehicle wall having a high thermal emittance at elevated temperatures. For SiC this is approximately 0.82 at 1000K, increasing to 0.98 at 2000K (Pidan *et al.*, 2005). An alternative strategy is to use the structure of the space vehicle as a heat sink. Rather than applying very thermally insulative materials, incident heat is conducted away from the vehicle surface and into the structure, raising its temperature, while a portion of the incident heat load will be rejected by radiation. This thermal management strategy was used for the X-15 space plane, which used an Inconel structure to allow operation at elevated temperatures (Glass, 2008).

In recent decades there has been strong interest in the development of air-breathing single-stage to orbit (SSTO) spacecraft. For such an SSTO hypersonic vehicle the heat flux during ascent is both high and of long duration (Glass, 2008). These factors have a strong impact on the choice of which thermal management system is most appropriate, and therefore the material choices. The mass of the thermal protection system is also a factor and may become a significant fraction of the total vehicle mass for very high heat flux re-entry vehicles (Ley *et al.*, 2009).

The various thermal management strategies that are used by different space vehicles are shown in Fig. 1 plotted as a function of temperature and exposure period. Re-entry capsules for Earth atmosphere re-entry all use ablative TPS designs as the heat flux is

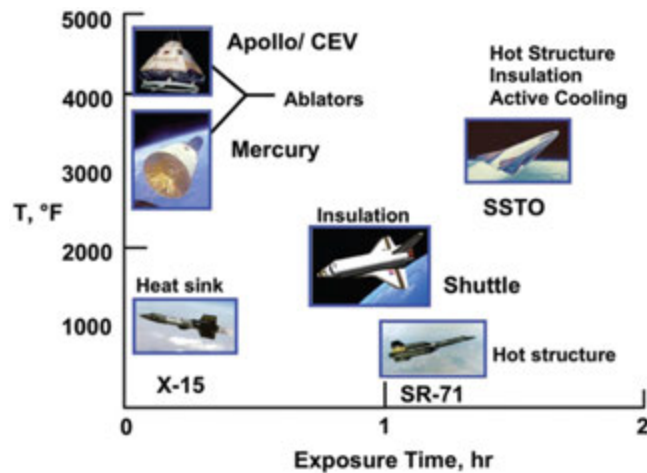


Fig. 1 Various types of thermal management strategy used for different space vehicles plotted as a function of temperature and exposure time. From Glass, D.E., 2008. Ceramic matrix composite (CMC) thermal protection systems (TPS) and hot structures for hypersonic vehicles. Paper presented to Proceedings of the 15th AIAA Space Planes and Hypersonic Systems and Technologies Conference. Available at: <https://ntrs.nasa.gov/citations/20080017096>.

very high, but the exposure period is relatively short (Glass, 2008). For future space vehicles, hot structures may be utilized, or indeed required, for hypersonic vehicles, with the hot structure elements likely made from ceramics. These high temperature capable options are typically driven by a desire to save weight (Hurwitz, 2010).

Thermally insulative thermal protection materials

Several materials-mediated strategies are used for thermal protection of spacecraft and of course, the inherent thermal insulation and temperature stability of ceramics make them ideal for a range of applications whether that be extreme thermal isolation, such as with the Space Shuttle tiles or ablative applications.

The Space Shuttle orbiter is constructed from a traditional aluminum alloy skin-stringer design used for aircraft, and the structure must therefore be maintained at temperatures below 175°C (Glass, 2008). The thermal protection strategy is therefore that of an “insulated spaceplane”. The primary means of maintaining the airframe temperature to its allowable limit is the use of ceramic insulation tiles on the windward surface of the orbiter (Chapline *et al.*, 2010). On the leeward side, where heat fluxes are less extreme, blanket type insulation is used. The re-entry heat fluxes are highest on the nose-cap and wing leading edges, and for these regions reinforced carbon-carbon composite was used (Hurwitz, 2010).

When the Shuttle de-orbits and returns to earth, it enters the Earth’s atmosphere at an altitude of around 122 km and is traveling at around Mach 25. It uses friction with the air to slow down but this has the effect of heating the exterior to several thousand degrees. It is protected using some 24,300 tiles of two types: a black-coated High-Temperature Reusable Surface Insulation tile (HRSI) and a white-coated Low-Temperature Reusable Surface Insulation (LRSI). Both tile types are constructed from a lightweight composite material composed of silica fibers, alumina fibers and borosilicate glass that are fused using microwave processing. The black glass coating of HRSI tiles allows radiation of around 90% of the heat while the bulk of the tile absorbs the rest and they are used on the underside of the craft. The white LRSI tiles are coated with a “whitewash” of silica and alumina compounds and are used on parts of the upper fuselage.

NASA’s Orion crew capsule will similarly use the same insulative material from the Space Shuttle with 970 tiles on its back shell panels to protect the capsule structure during re-entry, as illustrated in Fig. 2. The Orion capsule is designed for re-entry at higher speeds than the Space Shuttle to facilitate re-entry from Mars transit and speeds are expected to be up to 32,000 km/h. Temperatures experienced by the tiles during re-entry are predicted to reach 1700°C. Due to the fragile nature of this material, it is vulnerable to damage from micrometeoroid impact, which could have a deleterious impact on the effectiveness of the TPS. Further detail is given by Harris *et al.* (2018).

The new ESA Intermediate eXperimental Vehicle (IXV) is a demonstrator re-entry craft that has been developed to test atmospheric re-entry approaches and perform in-flight experiments to verify and validate new systems and approaches (Tumino *et al.*, 2016). It combines ablative (Cioeta *et al.*, 2016) and non-ablative approaches (Buffenoir *et al.*, 2016) in the form of P50 cork and Carbon-Silicon Carbide CMCs respectively.

NASA’s Parker Solar Probe (PSP), which will become the closest spacecraft to approach the Sun will approach within 9.9 solar radii at perihelion, where it will experience an incident heat flux of 70 W cm⁻² (Dantzler *et al.*, 2008). The main heat shield of PSP is composed of a sandwich panel of C/C face-sheets that surround a thick layer of thermally insulative carbon foam, illustrated in Fig. 3. The carbon foam layer, which is around 15 cm thick, provides substantial thermal insulation and reduces the heat load to the spacecraft bus to around 0.001% of the incident heat flux from the Sun. C/C was chosen for the face-sheets due to its



Fig. 2 Black colored thermal protection tiles installed on the back shell of NASA's Orion crew capsule during assembly as Kennedy Space Center, Florida, USA. Image from NASA.

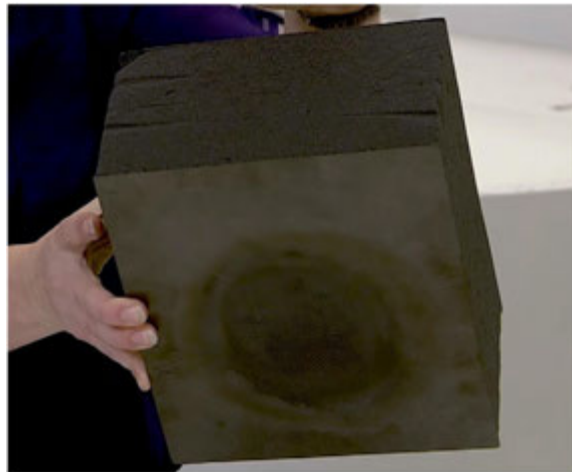


Fig. 3 Section of C/C sandwich panel as used for Parker Space Probe. Image from NASA Goddard.

combination of high specific strength, low outgassing, and ability to operate at the extreme temperatures encountered (Dantzler *et al.*, 2008).

Non-ablative thermal protection materials

Non-ablative thermal protection materials use re-radiation to reject heat back to the atmosphere. These non-ablative thermal protection materials are typically special ceramics, but refractory metals such as rhenium or tungsten may be used in some applications.

Carbon can be used up to very high temperatures in a vacuum (sublimates at very high temperatures). However, carbon would burn during re-entry to the Earth's atmosphere which contains oxygen (Ley *et al.*, 2009). For a re-entry vehicle with the geometric configuration of the Space Shuttle Orbiter, the bow shock has the highest strength, and the temperature increase across the shock is highest, in the nose-cone region (Ley *et al.*, 2009). This is the stagnation point region of the nose. For the Space Shuttle, carbon/carbon composite was used for the nosecone. Applications have also been found for C/C and C/SiC in the Hermes spaceplane, Fig. 4.

Glass (2008) notes that the primary factors/challenges that affect the implementation of CMC materials for hot structures are the environmental durability against dissociated oxygen and nitrogen during re-entry and also the fabrication challenges. Use of ceramics in load bearing structural applications for space have a higher barrier to implementation than non-load bearing applications (Levine and Herbell, 1991). For load-bearing (structural) applications the reliability of the structural component, which is strongly linked to the fracture toughness of the material, becomes of great concern. Reliability may be enhanced by the use of fiber reinforcement to increase fracture toughness; i.e., to form a CMC. Other factors also hinder the implementation of

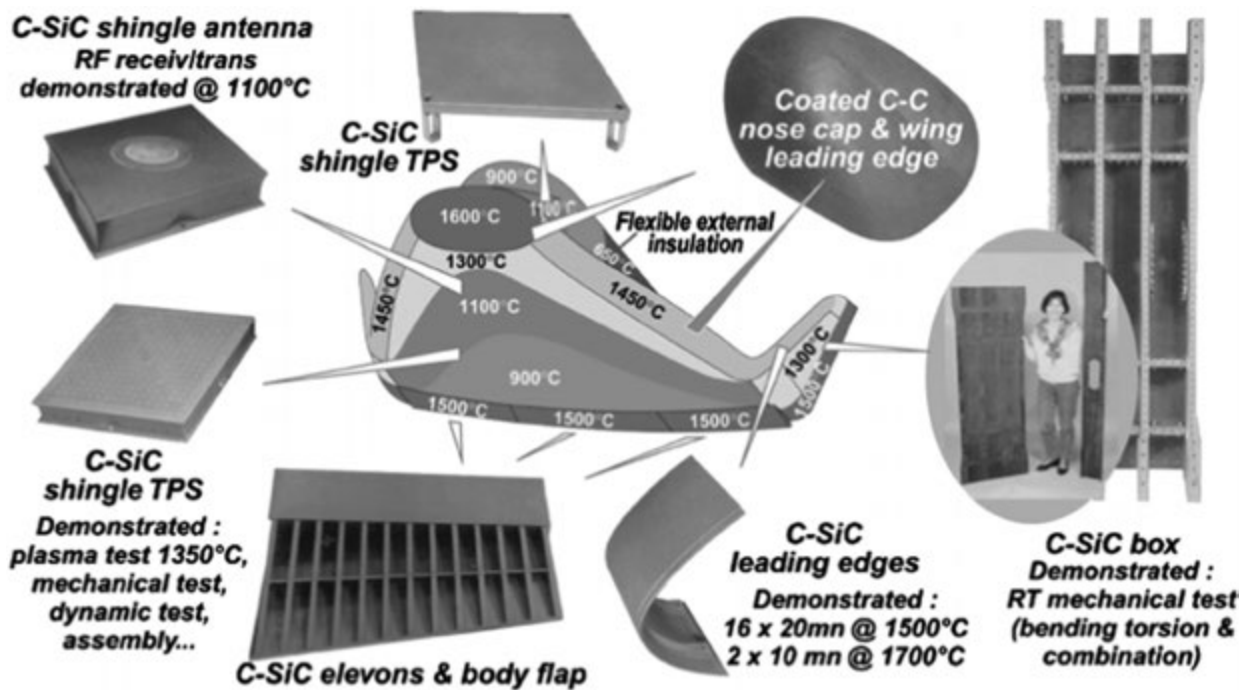


Fig. 4 Overview of materials uses proposed for the thermal protection system of the Hermes spaceplane. From Christin, F.A., 2005. A global approach to fiber nD architectures and self-sealing matrices: From research to production. *International Journal of Applied Ceramic Technology* 2, 97–104.

ceramic or CMCs in load-bearing applications, including challenges in design, development of appropriate design methodologies for these materials, quantitative assessment of reliability and life predictions, joining mechanisms to other hardware, and the high cost of design and fabrication. Advancements in temperature capabilities of fibers are also sought, while toughening mechanisms of matrices, through the use of all-oxide continuous fiber-reinforced CMCs for high temperature structural applications are also under development (Simon, 2005).

Ceramic Thermal Control Coatings for Satellites

The surface of a spacecraft is exposed to widely varying thermal environments over the course of an orbit. Without carefully designed surface thermo-optical properties, such spacecraft would undergo large fluctuations in temperature. In particular, surfaces exposed directly to the Sun's thermal radiation, which is equivalent to approximately 1350 W m^{-2} , would quickly lead to overheating. For satellites, such overheating could lead to failure of electronics, batteries, or other critical hardware, while for crewed spacecraft, over-heating could be hazardous.

In addition to thermal radiation, the surfaces of spacecraft are also exposed to a wide range of non-thermal solar and cosmic radiation. The non-thermal forms of solar radiation include gamma-rays, X-rays, and short wavelength UV radiation in addition to proton and electron fluences, while cosmic radiation includes contributions from gamma-rays, X-rays, and UV radiation. In low earth orbit, spacecraft are also exposed to non-trivial concentrations of atomic oxygen. The outer surfaces of the spacecraft are exposed directly to these various forms of high energy radiation, and these can have damaging effects on thermo-optical coatings. Interaction of charged particles with the thermo-optical coating can also lead to surface charging if the coating is not electrically dissipative or conductive. For this reason, a spacecraft coating needs to serve not only the role of thermal control but also potential control (i.e., electrical potential) (Marco and Remaury, 2004).

The thermal protection system (TPS) of spacecraft typically include a range of different technologies, including multi-layer insulation blankets (MLI), highly reflective optical solar reflector (OSR) panels, and diffusely reflecting or absorbing thermo-optical coatings. Each different technology has its advantages and disadvantages. Ceramic solar reflector coatings are one of the most important solar reflector technologies. These coatings are diffusely reflective, and therefore avoid problems of glint reflections impinging on other parts of the spacecraft. They are lower in mass per unit area than OSRs. In addition, they can be applied conformally to complex geometries, while OSRs are limited to rigid, flat panels (Sun *et al.*, 2018).

Thermal-control coatings passively regulate spacecraft surface temperatures through manipulation of thermo-optical material constants, specifically solar absorptance α_s and infrared emittance ϵ . A simplification of an equation, derived from a combination of the Stefan-Boltzmann law and the first law of thermodynamics (applied to a uniform isotropic sphere), may be used to predict equilibrium surface temperatures of thermal-control surfaces (Doherty *et al.*, 2016). The equilibrium temperature of a spherical body or surface at

normal orientation to some radiation source (T_{sc}) is proportional to the ratio of the normal solar absorptance of the surface (α_s) and the normal emittance of the thermal control surface (ϵ_N) i.e., T_{sc} is proportional to α_s/ϵ_N . The effect of this ratio are summarized in Fig. 5. Lines are shown corresponding to various different values of the α_s/ϵ ratio, along with corresponding equilibrium spacecraft temperatures (T_{sc}) that would occur for a coated isothermal sphere at 1 AU from the Sun (Meseguer *et al.*, 2012).

A number of recent craft will experience extreme thermal and radiative environments. Two spacecraft that will transit very close to the Sun include the European Space Agency's Solar Orbiter (SolO), and the Parker Solar Probe (formerly Solar Probe Plus). The European Space Agency mission, Bepi Colombo, will experience extreme heat and radiation as it makes its journey to Mercury.

Solar reflector (white) coatings are used to minimize the equilibrium temperature of spacecraft surfaces by minimizing absorptivity in the visible and near-infrared range of 0.25–2.5 μm , while maximizing absorption in the middle- to far-infrared spectrum of 3–30 μm (which we refer to as infrared emissivity). This is of greatest importance for radiator panels, which need to reject excess heat from electronics and instrument to space. Any heat absorbed from the space environment must additionally be rejected, which leads to an increase in required radiator mass. These coatings are commonly in the form of a paint, often based on alkali metal-silicates, dimethyl-silicones, or polyurethane binders, with a pigment phase, which is often ZnO (Henninger, 1984). Examples include Z-93P (IITRI, now Alion, USA), AZ-93 (AZ Tech, USA), SG121FD (MAP, France), Nanovation V14 (CeraNovis, Germany), SolarWhite (ENBIO, Ireland).

Completely inorganic coatings such as SolarWhite (Doherty *et al.*, 2016), used on Solar Orbiter, and Nanovation (Holynska *et al.*, 2019), used on Bepi Colombo, are ideally suited to the space environment where degradation of organic bonds can result in an increase in absorptance over time. An alternative treatment to applied surface coatings is the use of Plasma Electrolytic Oxidation (PEO) to grow an oxide layer on a metallic surface (Simchen *et al.*, 2020). However, these treatments, as well as those utilizing polymeric binders with oxide pigments, can be susceptible to moisture and organic pick up during normal assembly activities, as well as storage.

If the absorptance cannot be guaranteed due to mission environmental conditions, a stable, black thermo-optical surface can be preferred. While this comes at a temperature cost, this approach minimizes changes in the thermal management of the craft over its mission life and can simplify the overall system. Flat absorber (black) coatings can be used on the inside or outside of spacecraft, in order to promote radiative heat transfer, and thereby isothermalize the hardware. These typically have an α_s/ϵ_N ratio of 1, as illustrated in Fig. 5. They are used on the outside of spacecraft in some specialized applications, an example being high-temperature MLI to minimize stray light reflections. The Solar Orbiter mission utilizes a black, flat absorber, calcium phosphate ceramic coating, SolarBlack. This extremely thin ($\approx 5 \mu\text{m}$), surface coating has no binder phase to degrade at elevated temperatures, and does not impact the conductivity of the surface at high, or low temperatures (Doherty *et al.*, 2015). SolarWhite and SolarBlack thermal control coatings used on the Solar Orbiter are illustrated in Fig. 6.

The Parker Space Probe (PSP) was launched on 12th August 2018 and will explore the Sun's corona. It will transit closer to the Sun than any previous spacecraft. The Sun-facing heat shield will reach temperatures of around 1400°C at perihelion (Dantzler *et al.*, 2008). The heat-shield of PSP has a solar reflector coating on the Sun-facing surface, which is an aluminum oxide coating approximately 100–125 μm in thickness, which is applied by plasma spray process by Plasma Processes, Inc., (Huntsville, Alabama, USA). This is applied to a C/C composite substrate to reflect a large portion of the incident UV and improve the passive cooling through thermal emittance, illustrated in Fig. 7.

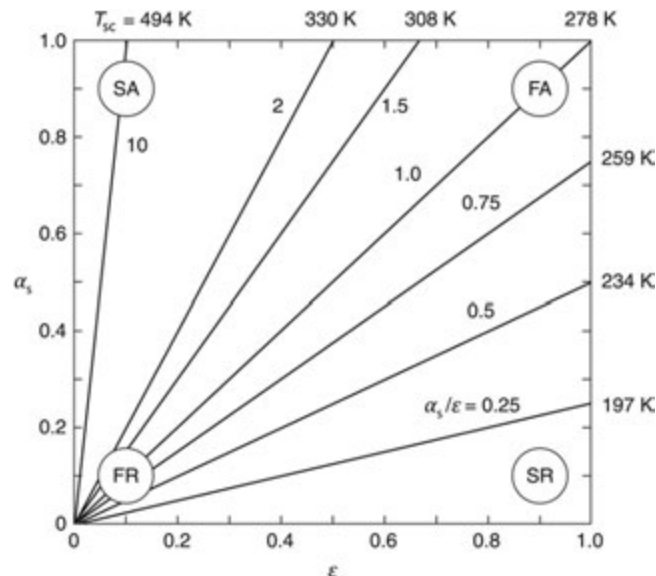


Fig. 5 Solar absorptance (α_s) vs. hemispherical total emittance (ϵ). Regions are denoted as solar absorbers (SA), flat absorbers (FA), solar reflectors (SR), and flat reflectors (FR). Reproduced from Meseguer, J., Pérez-Grande, I., Sanz-Andrés, A., 2012. Spacecraft Thermal Control. Oxford: Woodhead Publishing.



Fig. 6 The ESA Solar Orbiter spacecraft undergoing final inspections at IABG (Germany) before being moved to Cape Canaveral launch site. The SolarWhite coated radiator panels are visible on the underside of the spacecraft; the SolarBlack coated heatshield and High Gain Antenna (HGA) on the upper sides. Image from Airbus Defense and Space, UK. (www.esa.int).

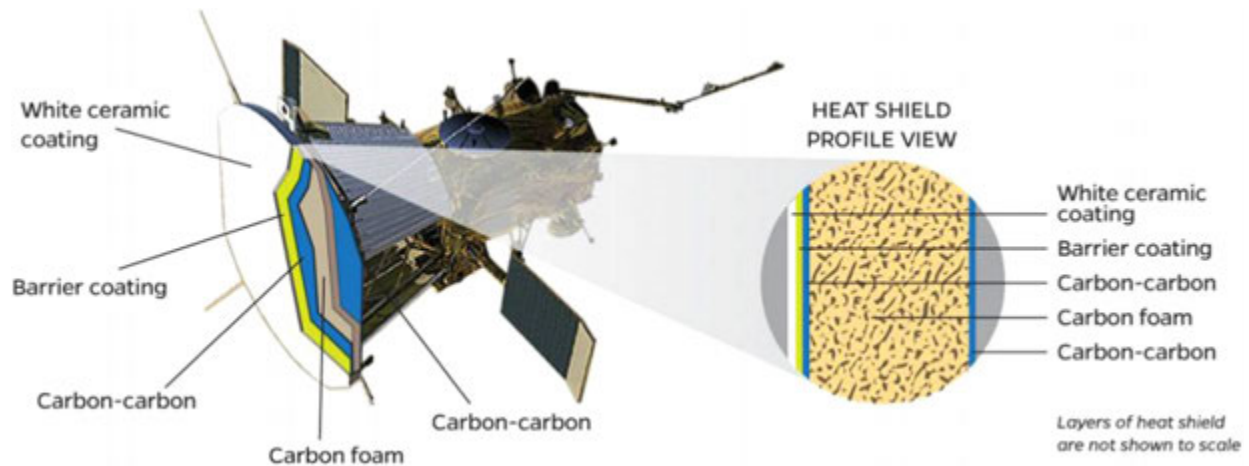


Fig. 7 Schematic illustration of the Parker solar probe heat-shield. Image from Johns Hopkins University.

Space Propulsion Applications

Rocket Engine Components

As with the design of many other components and systems for space applications, a lighter Solid Rocket Motor (SRM) or Liquid Rocket Engine (LRE) allows more payload to be lifted into orbit, which reduces the cost to orbit per unit mass of payload. In LREs, ceramics are considered for thrust chambers, exit cone sections, and a variety of turbopump components including turbine blades, valves, bearings, and other hot-section components.

Solid rocket motor (SRM) nozzles

There are several different parts of a solid rocket motor (SRM). The components involved in generating thrust are the nozzle throat (the narrowest part, where the Mach number becomes 1), and the nozzle exit cone. The nozzle throat has to withstand very high temperatures of $> 3000\text{K}$, very high heat fluxes and thermal gradients. The throat section is also exposed to physical and chemical erosion processes from the hot propellant. This places extreme requirements on the material used for the nozzle throat. The carbonaceous materials graphite and carbon/carbon composites are attractive for this application as they have a significantly lower density ($\rho \cong 2.2 \text{ g cm}^{-3}$) than refractory metals such as niobium ($\rho \cong 8.57 \text{ g cm}^{-3}$) and tungsten ($\rho \cong 19.3 \text{ g cm}^{-3}$). Relative to refractory metals, graphite and carbon/carbon composites additionally have high thermal conductivity. The properties of graphite and carbon/carbon composites therefore make them attractive candidate materials for the throat sections of SRMs. While graphite is a brittle material, carbon/carbon composites have improved tensile properties at elevated temperatures (see Fig. 8) and have become the *de facto* material choice for the throat section of SRM nozzles (Christin, 2008).

Carbon/carbon composites may be constructed based on different geometries of carbon fiber arrangements, either two-dimensional or three-dimensional in nature. Those based on two-dimensional fiber arrangements consist of preforms made from cloth-type fabrics. These are simpler and lower in cost to construct, have a greater tendency for inter-laminar cracking, and are generally limited to thin components. Carbon/carbon composite using two-dimensional preforms are used for example for solid rocket motor cones for some apogee kick motors (Christin, 2008). Three-dimensional reinforced preforms are produced by interweaving, which results in improved delamination resistance and improved isotropy.

For many aerospace applications, high specific strength is required at high temperature. Specific strength is plotted as a function of temperature for several classes of materials in Fig. 9. Ceramics and CMCs have typically lower density than metals, coupled with high strength, which gives them high specific strengths. As shown in Fig. 9, many metals and metallic alloys, including Ti and Inconel, and MMCs have excellent specific strength at room temperature. However, their strength decreases at moderately high temperatures. In contrast, ceramics and CMCs retain their strength to higher temperatures.

Liquid rocket engines (LRE)

Liquid rocket engines (LRE) are comparatively more complex in design than SRMs. They are composed primarily of turbomachinery for pumping of fuel and oxidizer, an injector plate to atomize and mix the propellants, a combustion chamber, and a converging-diverging De Laval nozzle. The combustion chamber and sections of the C-D nozzle from the converging section, nozzle throat, and initial part of the diverging section are the regions of the LRE where the highest heat fluxes occur. The temperatures in these regions may exceed 3300°C in the combustion chamber and $1600\text{--}2700^\circ\text{C}$ in the nozzle section and so are too high for any conventional materials. Therefore, these sections are commonly manufactured as a single unit from a metal such as a copper alloy, with regenerative cooling used to cool these components. The primary material properties required are high thermal conductivity and high strength. The metals used in the combustion chamber and initial section, whether copper or nickel-based superalloys, have a high density (circa $8\text{--}9 \text{ g cm}^{-3}$) and therefore the construction of the whole LRE from these materials would result in a very heavy engine. Therefore, it is desirable to replace metallic components of an LRE, where possible, with high specific strength ceramic components. The primary components considered for replacement by ceramics are the nozzle

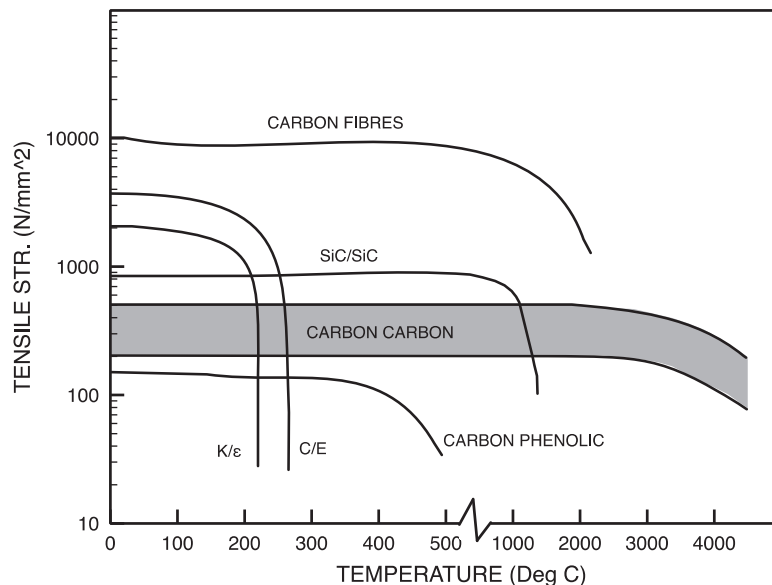


Fig. 8 Tensile strength of some structural composites as a function of temperature. Reproduced from Devi, G., Rao, K.R., 1993. Carbon-carbon composites – An overview. Defence Science Journal 43, 369–383.

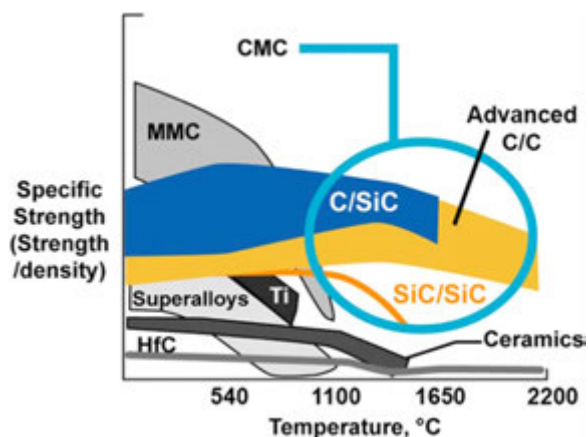


Fig. 9 Specific strength of several material classes as a function of temperature. Adapted from Glass, D.E., 2008. Ceramic matrix composite (CMC) thermal protection systems (TPS) and hot structures for hypersonic vehicles. Paper presented to Proceedings of the 15th AIAA Space Planes and Hypersonic Systems and Technologies Conference. Available at: <https://ntrs.nasa.gov/citations/20080017096>.

extensions, particularly for upper stages, while some investigations of ceramic combustion chambers have also been investigated (Misra, 2016).

A portion of the diverging section of the nozzle, out to an expansion ratio of around 5–8 is typically incorporated into this integrated assembly, and the expanding portion of the nozzle downstream of this is then typically constructed from a different material with use of a different cooling strategy (Ley *et al.*, 2009). This is called a *nozzle extension*. The cooling strategies used for this downstream section of nozzle include regenerative cooling, dump cooling, film cooling, transpiration cooling, and radiative cooling. Metals rather than ceramics have typically been used for the combustion chamber and throat section due to the need to integrate cooling channels for regenerative cooling, and the requirement for thin-walled material of high thermal conductivity to ensure efficient heat transfer from the hot gas to the propellant in the channels, and metals are better suited for this.

Advantages of replacing a metallic nozzle extension with a ceramic one include a reduction in mass (which allows payload mass to be increased), and higher temperature capabilities than metals. In addition, with a ceramic nozzle extension, a simpler cooling strategy may be used which simplifies design and can further reduce mass. Material requirements for use of ceramics in a nozzle extension are quite restrictive. The material must operate at very high temperatures of circa 1700°C, must be chemically resistant, have high thermal shock resistance, have low density, and also be tolerant to damage (Misra, 2016).

Liquid rocket engines have typically utilized either refractory metals or highly thermally conductive metals in combination with some form of propellant cooling. Christin notes that carbon/carbon composites began to be used in some LRE designs from the mid-1990s (Christin, 2008). The primary ceramic materials that are suitable for use in nozzle extensions are C/C composite, SiC/SiC composite, and C/SiC composite (carbon fiber reinforced silicon carbide). SiC/SiC is produced, for example, by Snecma Propulsion Solide, France. SiC/SiC composites may be produced by the chemical vapor infiltration (CVI) method of infiltration of a preform, liquid impregnation and pyrolysis, or a combination of these techniques (Christin, 2008). The CVI infiltration method yields a pure SiC matrix, and results in superior thermal stability than the liquid infiltration method (Christin, 2008). The CVI infiltration method is performed by cracking of methyltrichlorosilane gas to infiltrate a preform at high temperature (Christin, 2008).

SiC/SiC composites exhibit good room temperature strength and are stable up to very high temperatures. SiC/SiC additionally has very good high-temperature strength and specific strength. SiC/SiC has higher fracture toughness than monolithic SiC. These materials have suitable properties for use in the thermal protection systems of re-entry vehicles (Christin, 2008).

One technique for producing SiC/SiC CMCs is the construction of a prepreg, followed by melt infiltration. SiC fibers are first pre-treated with interface layers, which may include boron nitride and silicon carbide (Misra, 2016). The fibers are then formed into a prepreg, held together by a polymer binder incorporating SiC particles. The composite is then heated to high temperature, which decomposes the polymeric binder. Liquid silicon is then infiltrated into the material. This results in a reaction between the silicon and carbon in the prepreg and thereby forms the SiC matrix in situ (Misra, 2016).

A notable example of the use of carbon/carbon composite for a liquid rocket engine is the use for the Pratt & Whitney RL10B-2 liquid rocket engine. This is a cryogenic propellant upper stage LRE. The rocket stage operates at high altitude near-vacuum conditions and therefore requires a high expansion ratio nozzle. A monolithic high expansion ratio nozzle would be very long, which would add to the overall size and mass of the launcher. As a result, the nozzle incorporates a nozzle extension, which allows compact packaging of the LRE inside the launcher, and then extends into position for use (see Fig. 10). The RL10B-2 has been successfully used for the Delta 3 upper stage and the EEC is made from carbon/carbon composite weighing only 92 kg; it is produced by Snecma Propulsion Solide, France (Christin, 2008). This is made from Novoltex[®] C/C composite.

For liquid propellant rocket engines, the thermo-mechanical properties of carbon/ceramic and ceramic/ceramic composites make them well suited for use in exit cones. These materials can be used, for example, in place of metallic cone structure with ablative liner (Christin, 2008). The high allowable use temperature of these materials enables the use of propellant cooling

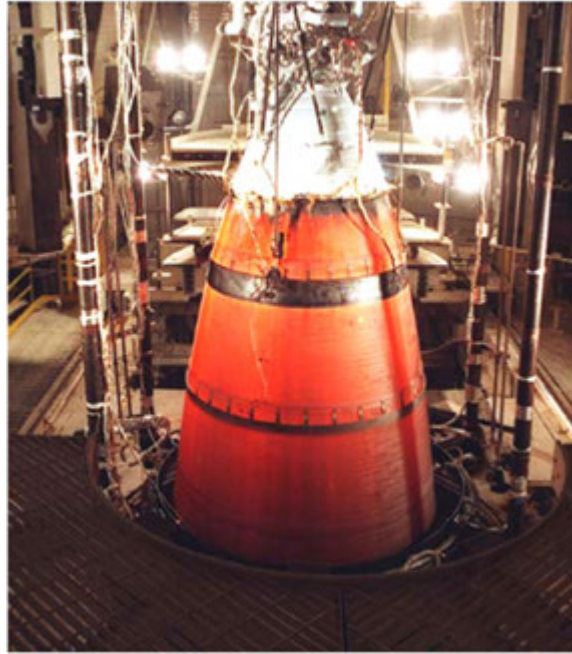


Fig. 10 Pratt & Whitney RL10B-2 liquid rocket engine, incorporating Snecma carbon/carbon nozzle extension. From Christin, F.A., 2008. CMC materials for space and aeronautical applications. In: Krenkel, W. (Ed.), *Ceramic Matrix Composites: Fiber Reinforced Ceramics and Their Applications*. Weinheim: Wiley-VCH Verlag GmbH. pp. 327–351.

techniques in the exit cone (such as film cooling or dump cooling) to be avoided and can thereby result in increased rocket performance and simultaneously decreasing design complexity (Christin, 2008).

Christin (2008) notes that for liquid propellant rocket engines, the nozzle exit cone may be exposed to very hot oxidative combustion gases i.e., this is in contrast to SRMs, where combustion occurs at the propellant grain surface, which on average is more distant from the nozzle. As a result of this, for LREs to use non-cooled high-temperature ceramics, ceramic materials with suitably high oxidation resistance (i.e., superior to that of C/C composite) are required (Christin, 2008). These can include coated C/C composite or other ceramic composites.

Transpiration cooling, mentioned in the previous section for structural applications, for use in LREs involves effusion/injection of one of the propellant components (fuel or oxidizer) through a porous combustion chamber wall into the combustion chamber to achieve cooling in the near-wall region. For this application, sintered metals may be used; however, these can be limited by their maximum operating temperatures and the need to increase the wall thickness to achieve the required structural strength with the porous material (Ley *et al.*, 2009). As an alternative to sintered metals, porous fiber-reinforced CMC may be used as a wall material for transpiration cooling (Ley *et al.*, 2009). CMCs have typically higher maximum operating temperatures than metals, while also having lower density and higher specific strength, which can allow the component mass to be reduced (Ley *et al.*, 2009). In addition, the higher operating temperatures allowed by CMCs would reduce the required flow rate of coolant (Ley *et al.*, 2009).

Misra (2016) notes that one of the systems developed was a hybrid metallic-ceramic design, which incorporated metal tubes into a C/SiC composite structure, with the metal tubes carrying the coolant. In addition, all-ceramic designs have also been developed, and these have the advantage of the potential for lower mass (Misra, 2016). One actively cooled CMC nozzle section demonstrator was developed by Rockwell Scientific Company and tested at NASA Glenn Research Center (Marshall and Cox, 2008). Rather than being constructed from individual tubes that were joined together, this was constructed by weaving the carbon fibers into an integrated tube-wall assembly as a single component. Further flight applications are given by Böhrk (2017). Additionally, there is growing interest in ceramic use in catalyst beds for smaller, monopropellant thrusters, widely used for attitude control thrusters. Hydrazine monopropellant thrusters typically use iridium or cobalt catalyst, which is dispersed onto a bed of porous alumina pellets of diameter 1.5–3 mm (Sutton and Biblarz, 2001) but new additively manufactured alumina structures with feature sizes of 0.15–0.3 mm can be fabricated and have demonstrated equivalence to existing solutions (Essa *et al.*, 2017).

Electric Propulsion

Electric propulsion thrusters use ionizable gases as a means to create accelerated matter and thrust. While electric propulsion thrusters are capable of generating ion speeds far in excess of chemical reactions, the resulting thrust is much lower. These systems are used for attitude control (Ley *et al.*, 2009), as well as being the main propulsion to achieve a high change in velocity, Δv , (e.g., Deep Space 1, Hayabusa, SMART-1, BepiColombo) for interplanetary missions (MacDonald and Badescu, 2014).

The use of ceramic materials in electric propulsion is outlined for two examples below: Ion thruster and the Variable Specific-Impulse Magneto-Plasma (VASIMR) rocket engine. Further details can be found in [Goebel and Katz \(2008\)](#) and the review paper by [Holste et al. \(2020\)](#).

Ion and hall thrusters

Mentioned previously, as the life of a satellite is extended, the use of electric propulsion is subject to the same requirements of reliability, robustness, electromagnetic compatibility (EMC), radiation hardness, non-hazardous interaction with the satellite, and energy efficiency ([Holste et al., 2020](#)). The use of ceramic materials in critical areas of the propulsion systems enables this. Ceramics provide electrical conductivity and erosion stability in the plasma chamber and accelerator grids. Both Ion and Hall thrusters utilize plasma generation to ionize the propellant gas, offering advantages in efficiency and thrust generated respectively ([Goebel and Katz, 2008](#)).

Orbit control thrusters generate low thrust (>0.001 mN) while main propulsion thrusters, such as the T6 Qinetiq thrusters used on Bepi Colombo can generate up to 145 mN each ([Holste et al., 2020](#)). The T6 Qinetiq thruster is a Kaufman-type ion thruster using high density graphite in the accelerating grid ([Luna et al., 2017](#)). The graphite is conductive and stable in the presence of the active species in the plasma plume, minimizing erosion and potential back sputtering of material onto the craft in flight.

Cathode materials – Barium Oxide-Scandate ([Goebel and Katz, 2008](#)) is used in impregnated dispenser cathodes, while lanthanum hexaboride, LaB_6 , is formed as a single component (low work function and high electron emissivity) ([Goebel and Watkins, 2010](#)). While LaB_6 cathodes operate at higher temperatures than the BaO-W dispenser cathodes, it is more robust. As a single material source, there is more of the bulk emitting materials present, and it is able to handle higher current densities. Graphite sheaths can be used with LaB_6 cathodes to provide a low stress support and good electrical contact, while not being susceptible to boron diffusion or formation ([Chu and Goebel, 2012](#)). BN-SiO₂ and BN ([Levchenko et al., 2018](#)) ceramic insulating materials are utilized at the walls and around cathode. BN-SiO₂ and composite materials have been utilized in plasma chambers due to their superior erosion rates, thermal stability and thermal conductivity.

VASIMR

The Variable Specific Impulse Magneto-Plasma rocket is under development by Ad Astra Rocket Company (AARC, Houston, Texas, USA). It is an electric propulsion device composed of three stages: plasma generation using helicon waves, heating of the plasma by single-pass ion cyclotron resonance heating (ICRH), and detachment of the plasma in a magnetic nozzle, as illustrated in [Fig. 11](#). VASIMR produces high and variable specific impulse, which can optimize propellant usage efficiency ([Chang Diaz, 2001](#)). Compared to Hall thrusters, the VX-200 thruster can generate significantly higher thrust (6.7 N) ([de Faoite et al., 2016](#)). The configuration does not use electrodes or grids in contact with the plasma and can those utilize higher plasma temperature ranges. However, this puts a lot of thermal load on the structural and containment sections of the thruster ([Mulcahy et al., 2009](#); [de Faoite et al., 2014](#)). While still under development, the use of ceramics has been identified for areas such as the gas containment tube where the dielectric loss tangent or dissipation factor needs to be as low as possible under high temperature conditions. Comprehensive reviews of temperature dependent mechanical and thermal properties of potential dielectric ceramics that could be used is given in [de Faoite et al. \(2012\)](#) and [\(2013\)](#).

In addition, ceramics are used to make superconductors to create high field strength electromagnets of use for VASIMR and other magneto-plasma thrusters. Ceramic superconductors are used for generating magnetic fields with minimal losses, and for power transfer lines. Different combinations are being investigated with different cooling strategies but two examples are given by [Rey et al. \(2002\)](#) for multi-filamentary tape form containing Bi-2223 ($\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$) and [Patel \(2011\)](#) utilizing MgB_2 as the superconducting ceramic materials.

Windows and Mirrors

Three applications are considered: substrates for space-based telescope mirrors, windows for space vehicles, and cover glass for solar cells for use in spacecraft. These applications are described in turn below.

Glasses and glass-ceramics are used in a variety of space applications. The applications of glasses and glass-ceramics span from readily apparent applications such as windows for space vehicles to more unusual applications. These materials are used as substrates for, e.g., space-based telescope mirrors, missile radomes and cover-glass for solar cells. Glasses and glass-ceramics have a range of optical, electrical, and thermo-structural properties that make them the best-suited materials for numerous space applications.

Windows for Spacecraft

For windows for space vehicles, it is necessary to retain optical transparency. In the space environment, windows are exposed to short-wavelength photons, including UV, vacuum UV, X-rays, and gamma-rays, in addition to high energy particles. Prolonged exposure to these short-wavelength radiations can result in darkening of glass.

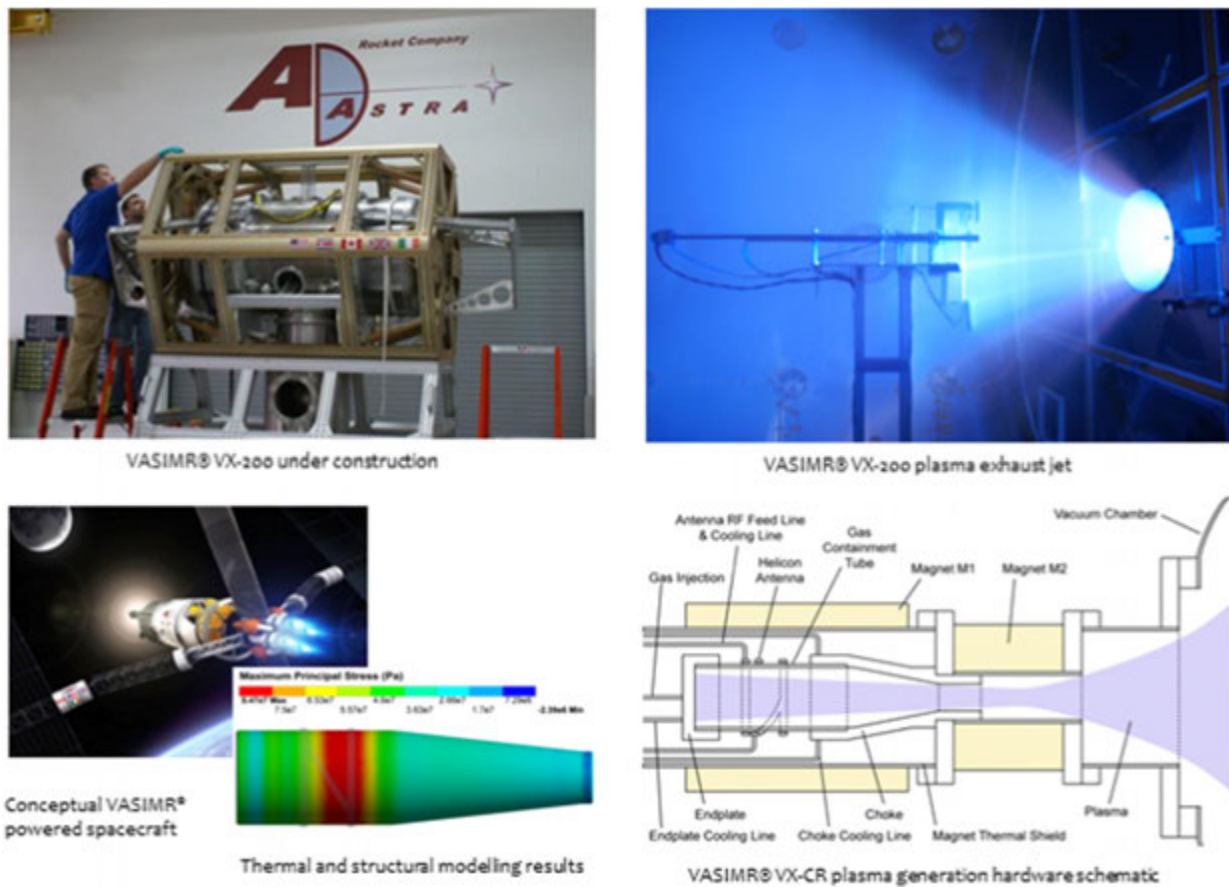


Fig. 11 Upper: VX-200 thruster on alignment rig and test firing (Credit: Ad Astra Rocket Company); Lower: Thermal and structural model results and VASIMR hardware schematic. Reproduced from de Faoite, D., Browne, D.J., Del Valle Gamboa, J.I., Stanton, K.T., 2016. Thermo-structural modelling of a plasma discharge tube for electric propulsion. *Applied Thermal Engineering* 98, 541–552. de Faoite, D., Browne, D.J., Del Valle Gamboa, J.I., Stanton, K.T., 2014. Inverse estimate of heat flux on a plasma discharge tube to steady-state conditions using thermocouple data and a radiation boundary condition. *International Journal of Heat and Mass Transfer* 77, 564–576.



Fig. 12 The Cupola as seen by Steve Bowen during his spacewalk on 3 March 2011 (www.esa.int).

Fused silica has very good resistance to radiation-induced darkening relative to many other glasses. One striking example of a window in Space is in the Cupola section of the International Space Station (see Fig. 12). Similar to the approach used in the Space Shuttle, each window was constructed of three separate panes. These were fused silicate panes consisting of: a debris pane, redundant pressure pane, primary pressure pane: 2.5 and 3.7 cm thick for side and top window pressure panes, respectively (Burt and Christiansen, 2003).

Windows for re-entry spacecraft are subjected to a variety of extreme environmental conditions. These can include high levels of vibration and shock during launch, high aerodynamic and thermal loads during flight at high Mach level, and extreme thermal

loads during atmospheric re-entry, requiring combinations of different materials. For the Space Shuttle orbiter, the windows were composed of three separate panes of glass, the approach later adopted in the ISS Cupola. An inner pane of aluminosilicate glass, similar to that used for the X-15, was used as a pressure pane, to contain the pressure inside the cabin. The outermost pane was not subjected to the cabin pressure, and its role was to withstand the high temperature of over 700°C occurring during re-entry in addition to withstanding thermal shock (Miska, 1991). This outer pane was therefore made from either silica glass or Vycor glass (Corning, USA), due to its high glass transition temperature, excellent thermal shock resistance and low thermal expansion coefficient. A third pane between the inner pressure pane and outer thermal pane serves as a backup in case of failure of either the pressure or thermal pane. This backup pane is also made from silica glass and is significantly thicker than the pressure and thermal panes. Silica glass has good transmittance for UV light, from which the crew of a space vehicle need to be protected. The aluminosilicate glass pane effectively absorbs UV light and is therefore effective in shielding the crew from UV (Miska, 1991).

Mirror Substrates

Substrates for astronomical mirrors are required to have a very high level of dimensional stability. In addition, they must be capable of being polished to an extremely low surface roughness. It is also often required that the substrate be manufacturable in a very large size. For mirror substrates for use in space, the mirror substrate also has the requirement of having low mass. These materials requirements are very demanding and challenging to fulfill. Materials that have been used for in-space mirror substrates include glass and glass-ceramics.

In addition to low thermal expansion glasses and glass-ceramics, some ceramic materials are also attractive as mirror substrates. These include, but are not limited to, SiC, CeSiC[®], as well synthetic cordierite (magnesium iron aluminum silicates). These materials' high thermal conductivities, combined with low thermal expansion coefficients, act to minimize thermal gradients, thermal hysteresis effects, and associated thermal distortion. The principal advantage that ceramics can offer over low-CTE glasses is that manufacturing processes associated with mass reduction can be simplified (Hull *et al.*, 2018; Kamiya and Mizutani, 2018). For example, complex shaped components can be made from CeSiC (see Fig. 13). CeSiC[®] has a very high maximum operating temperature (maximum continuous use temperature of 1400°C). Other benefits of this material include its low density (2.65–2.70 g cm⁻³), and an extremely

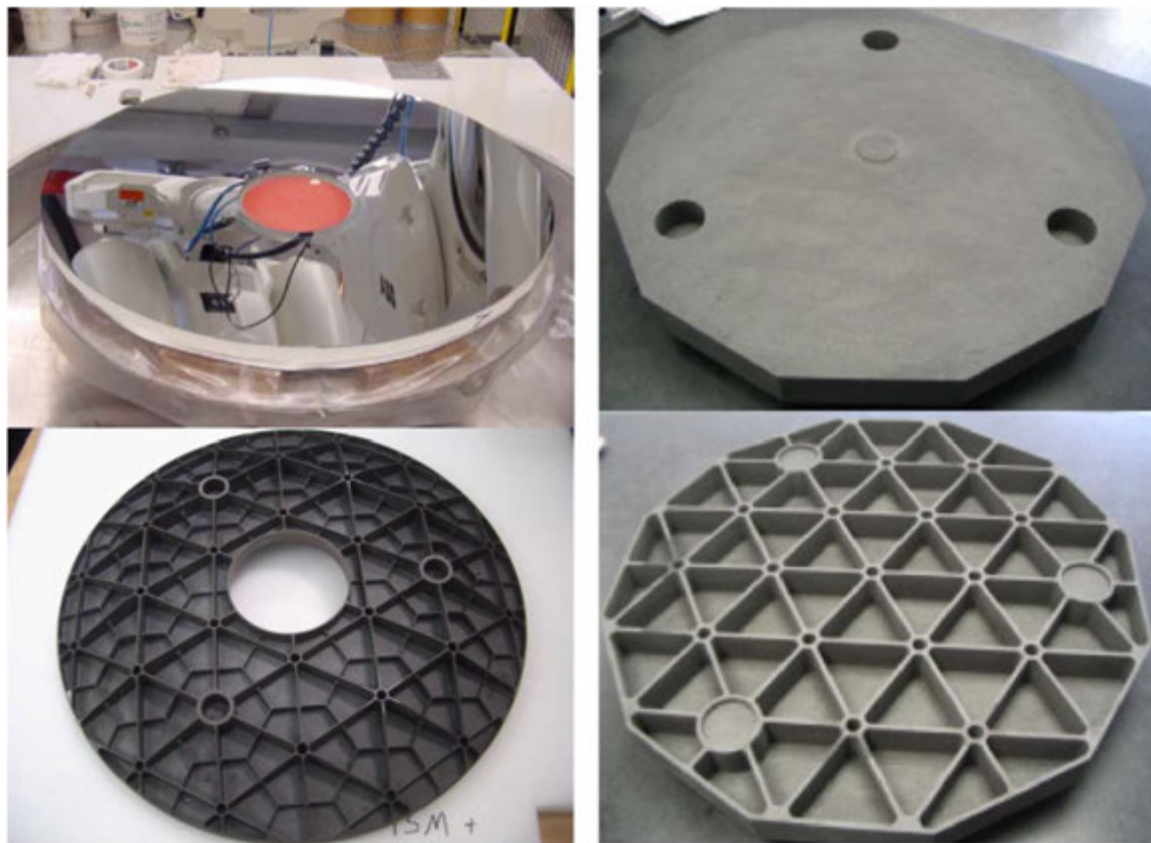


Fig. 13 Left, the front and rear surfaces of the 800 mm diameter lightweight HB-CeSiC mirror. Right, the front and rear surfaces of the lightweight HB-CeSiC optical bench for the mirror, where the three holes are the mounting points for the mirror. Reproduced from Kaneda, H., Naitoh, M., Imai, T., *et al.*, 2010. Cryogenic optical testing of an 800 mm lightweight C/SiC composite mirror mounted on a C/SiC optical bench. *Applied Optics* 49, 3941–3948.

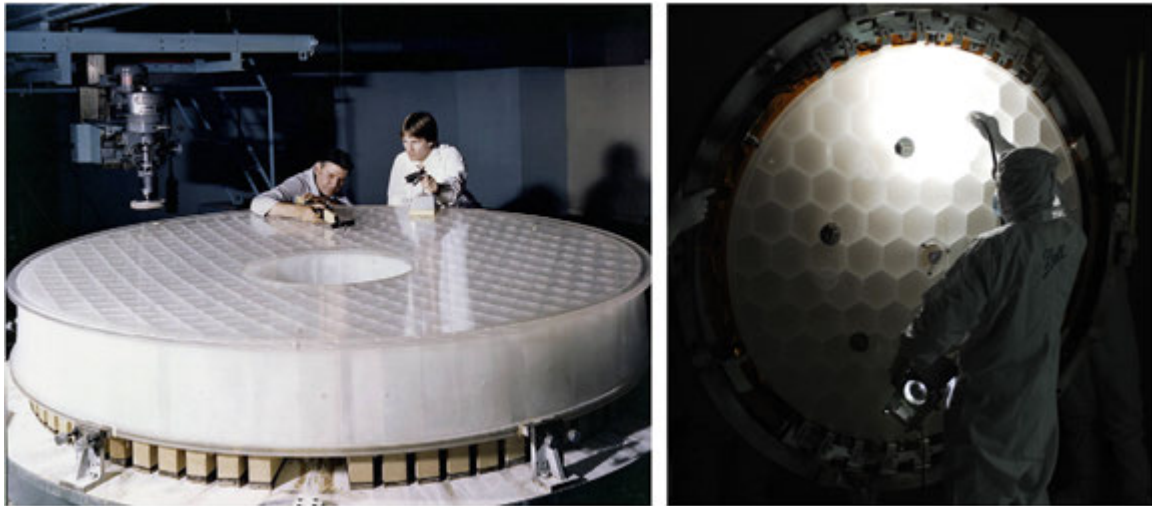


Fig. 14 Left: Inspection of the Hubble Space Telescope primary mirror substrate, made from Corning ULE 7971 (ultra-low expansion) glass. [Image: NASA.] The mirror is 2.4 m in diameter and weighs ≈ 830 kg. This photograph is prior to application of the aluminum and MgF_2 coatings. Right: Honeycomb structure of the Kepler Space Telescope primary mirror substrate made from Corning ULE glass. Image: NASA/Ball Aerospace.

low coefficient of thermal expansion (Kaneda *et al.*, 2010). HB-Cesic[®] is a hybrid carbon fiber-reinforced silicon carbide composite material used for mirror in cryogenic applications (Devilliers *et al.*, 2017).

Corning 7971 is an ultra-low expansion (ULE) glass. It exhibits a near-zero thermal expansion coefficient within the temperature range 5°C to 35°C . The material is a silicate glass containing the addition of 7.5% titania (Miska, 1991). Rather than being produced by melt-quenching, Corning 7971 is produced by chemical vapor deposition (CVD). Use of the CVD process rather than the conventional melt-quenching process allows very high purity to be attained and also allows very accurate control over the composition, although the manufacturing process is slow (Miska, 1991). The thermal expansion coefficient can be directly controlled through the titania concentration (Miska, 1991). To support the glass, a honeycomb structure is typically bonded to the backside, or as an interlayer between two glass pieces. This porous structure minimizes weight. Fusion bonding or frit soda glass can be utilized to adhere the glass to the core, and subsequent annealing undertaken to relief internal stress. The primary mirror of the Hubble Space Telescope (Fig. 14), for example, is made from Corning 7971 ULE glass using this method (Miska, 1991). This mirror is 2.4 m in diameter (and apparently 38 cm thick). The core uses a square-shaped arrangement of support ribs. Top and bottom glass sheets fused to the support structure are approximately 2.5 cm in thickness. Using this construction technique, the mass of the mirror is reduced from ≈ 3600 kg to ≈ 830 kg, or approximately 23% that of an equivalent solid glass mirror of the same dimensions.

In 1968 Schott AG produced a transparent glass-ceramic called Zerodur (ZERODUR[®]). This Lithium aluminosilicate glass-ceramic material has been employed for a number of very large telescope mirror substrates. These glass-ceramics are produced by heat-treatment of glasses of suitable composition, typically containing nucleating agents such as TiO_2 or ZrO_2 . The heat-treatment converts the glass to a glass-ceramic of high crystallinity (see Fig. 15). This glass-ceramic has an extremely low coefficient of thermal expansion, giving good dimensional stability required for telescope applications (Hull *et al.*, 2018). Mass of telescope substrates reduced by 70% using ZERODUR[®] as honeycomb-shaped holes can be milled out from the back, significantly reducing mass for satellites. ZERODUR[®] also used for the extensively in large ground-based telescope applications (Döhning *et al.*, 2009).

Solar Cell Cover Glass

Solar cells are used extensively in almost all satellites. Solar cells need to be protected from the space environment. The factors from which the solar cell must be protected include short wavelength UV radiation (which can damage solar cells), impacts of micrometeorites, and the damaging effects of atomic oxygen (Miska, 1991). As the protection material must be transparent to the wavelength band used for conversion of light to electricity, the cover material is generally a thin glass sheet. The two glass types that have been used for solar cell cover glass are fused silica glass and silicate glass doped with cerium. Ceria-doped borosilicate glass is commonly used with germanium-based solar cells (Beauchamp and Cutts, 2017). Cover glasses can also be coated to offer enhanced properties. Examples include: Anti-reflective coatings (single MgF_2 or multi-layer applied to front side); UV reflective coatings in the <350 nm range to reduce operating temperatures (applied as multi-layer to front side); Static dissipative or 'conductive' coatings (typically Indium Tin Oxide – ITO) but can reduce optical transparency; Infrared coatings to reduce operating temperatures (applied to backside of glass but not commonly used) (Beauchamp and Cutts, 2017).

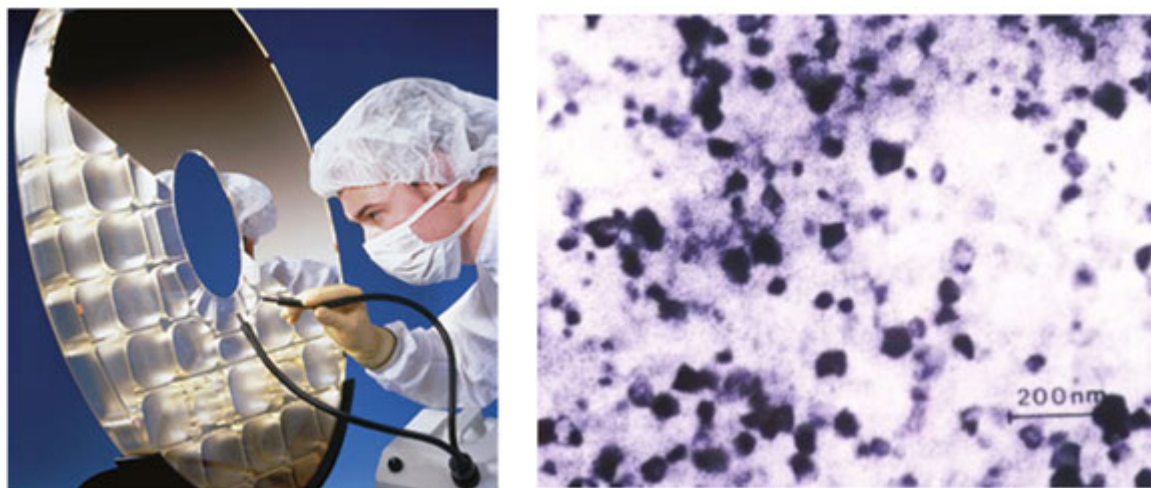


Fig. 15 Schott ZERODUR[®] telescope mirror substrate for the SEVIRI instrument on the MSG-1 satellite (Image from Schott AG); Right: Microstructure of Zerodur[®]. Reproduced from Döhring, T., Jedamzik, R., Westerhoff, T., Hartmann, P., 2009. Four decades of ZERODUR[®] mirror substrates for astronomy. In: Jiang, W., Geyl, R., Cho, M.K., Wu, F. (Eds.), *Proceedings of the 4th International Symposium on Advanced Optical Manufacturing and Testing Technologies: Large Mirrors and Telescopes*, vol. 7281. SPIE. (728103).

Tribological and Wear Applications

As mentioned in previous sections, the space environment poses a number of different problems for different functional elements of a craft. In terms of the moving mechanisms on a craft, the tribological performance of these mechanisms is particularly impacted by the vacuum and temperature fluctuations. As the mission life, scale and complexity has increased, the tribological considerations have had to adapt to keep up, illustrated in **Fig. 16** (Wen and Huang, 2018).

Bearings are used extensively in launchers and satellites, and the applications include bearings in pumps, motors, sliding and rotating hinges and deployment mechanisms, gears, amongst others. A sample of mechanisms and their operating environment is given in **Table 1**. Of note, is the range of speeds used in the different components. Due to the variety of speeds, the use of lubricants may not be possible. This is complicated further in the high vacuum environment of space, as well as temperature variations. Tribological solutions fall into two categories for space mechanisms: fluid (Ley *et al.*, 2009) and solid (Lince, 2020) lubricants.

Fluid lubricated systems are typically chosen for high rpm applications (Wen and Huang, 2018), while solid lubricants are used in low-speed systems. However, under vacuum, issues associated with fluid lubricants include evaporation, creep, outgassing and thermal and atomic oxygen degradation (Sathyan *et al.*, 2010). With lubricated bearing systems (using high molecular weight oils) the viscosity of the lubricant typically varies geometrically with temperature, becoming very viscous at low temperatures and may begin to vaporize/evaporate at higher temperatures. In contrast, lubricant-free or dry lubricant bearing systems may be used over wider temperature ranges. The mechanical loads on systems in space may be lower than those on Earth due to the microgravity conditions. In contrast, turbomachinery used in LREs may be required to operate under very high loads, at high speed, and extreme temperatures.

For solid lubricants, particularly metals, sublimation can be a factor at moderate and high temperatures (Dunn, 2016). Mechanisms such as hinges, gears, bearings and electrical contacts. Lubricants can sublime/outgas (Dunn, 2016). Testing of solid lubricants can be tricky as they are susceptible to moisture pick-up and fail prematurely when tested under atmospheric or partial vacuum conditions. Asperities and contact points will carry the full load without a lubricant and increase the coefficient of friction, wear rates and increase the likelihood of cold welding between metallic pairs. (Bhushan, 2008).

While the density of Si_3N_4 is less than half that of 440C stainless steel, the steel bearings, and TiC-coated steel bearings have a significantly greater thermal conductivity, enabling more efficient heat dissipation. Application of a ceramic coating to the bearing surface has a number of advantages such as chemical inertness and hardness differential. Both of these minimize the potential for cold-welding. Cold welding may occur if a solid solution can be formed between the contacting phases/materials, if the contacting materials have a similar crystal structure, if there is a weak oxide layer present on one or both materials, and/or if there are high contact pressures. High temperature missions like Bepi-Colombo also pose a risk for cold welding due to metal sublimation and cold welding in solar array mechanisms i.e. bearings, slip-rings and cables (Dunn, 2016). TiC-coated bearings were utilized to reduce the risk and minimize contact pressure deformations. Dissimilar pairs are important to minimize adhesive wear, galling and cold-welding (Lince, 2020). The application of ceramic coatings (TiC, TiN, and TiCN) to bearings is a preferred solution in space applications. However, due to the processing temperatures involved during the sputtering process, the bearings have to be rehardened and polished to restore sphericity. Temperatures are not as high for TiN sputtering but this material has a higher coefficient of friction than TiC and is susceptible to changes in coefficient of friction under vacuum (Dunn, 2016). Si_3N_4 bearings can be used to reduce heat generation and have improved heat transfer over TiC/440C bearings. As such, they can operate at high temperatures and speeds. Ceramic bearings are also less reactive and suitable for use with wet or solid lubricants.

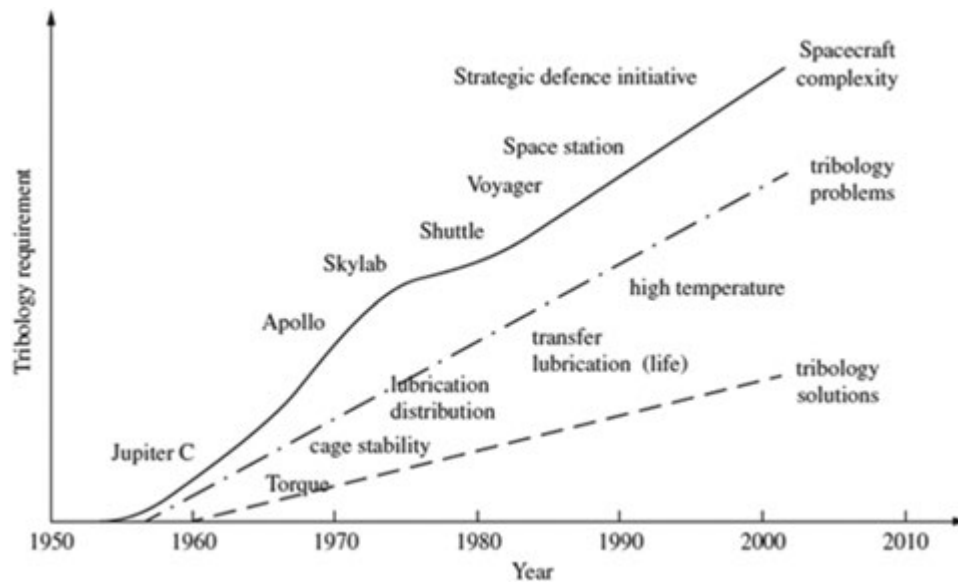


Fig. 16 Growth of tribology advances in space. Reproduced from Kannel, J.W., Dufrane, K.F., 1986. Rolling element bearings in space. In: Proceedings of the 20th Aerospace Mechanisms Symposium, third ed. NASA CP-2423, pp. 121–132. Wen, S., Huang, P., 2018. Principles of Tribology, second ed. Singapore: John Wiley & Sons.

Table 1 Speed ranges and working conditions of some space components

Component	Rotational speed (rpm)	Working conditions
Gyroscope	8000–30,000	High speed, EHL of rolling contact bearing
Torque wheel	3000–10,000	Medium speed
Scanner device	400–1600	Medium and low speed
Tracking antenna	100	Low-speed, boundary lubrication
Reaction wheel	10	Low-speed, boundary lubrication
Filter wheel	< ± 10	Low-speed, boundary lubrication
Sensors	Minor swing	Low-speed, possible lubricating
Sliding ring	Several to 20,000	Large speed range; difficulty in lubricating at low speed

Note: Wen, S., Huang, P., 2018. Principles of Tribology, second ed. Singapore: John Wiley & Sons.

Hybrid bearing systems are combinations of dissimilar materials, such as metal/ceramic and polymer/ceramic. These can be used to minimize wear caused by the adhesive mechanism or cold welding (Ley *et al.*, 2009). Hybrid bearings were used as replacements for all-steel bearings with materials such as silicon nitride (Si_3N_4) or zirconium oxide (ZrO_2). These bearing systems are capable of operating at cryogenic temperatures and the lubricant within the system is the cryogenic liquid H_2 itself (Ley *et al.*, 2009). Switching to a hybrid bearing system increased the life of the turbopumps within the main engine of the Space Shuttle by a factor of 60 (MacDonald and Badescu, 2014).

Additive Manufacture of Ceramics

Additive manufacturing (AM) is a rapidly growing area and its use in space applications for bespoke, one-off pieces, rapid prototyping and ability to produce complex geometries will see it play a more critical role in the space sector over the coming years. AM research typically falls into three categories: metal, polymer and other; the latter, “other”, includes ceramics, cement and regolith (Sacco and Ki-Moon, 2019).

One area of continued development is the ISS where there is on-going research in the field of AM and low gravity production (Matson, 2012). The first polymer printer was installed in 2014, and there are on-going activities focused on the production of ZBLAN fiber optic cables on the ISS. ZBLAN (fluoride glass: $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3\text{-NaF}$) fiber optics produced in zero gravity has the advantage of reducing or removing defects associated with crystallization and phase separation that occur during manufacture in the presence of gravity (Kasap, 2018). Similarly, the reduced effect of gravity is being explored for the production of SiC turbine blades (Misra *et al.*, 2015). However, development activities have to be taken as precursors for part and process validation

(Dordlofva, 2020). Utilizing the polymer filament-style technique, bound powder filaments are being explored for the 3D printing of “green-body” components that are subsequently treated like metal-injection molding components i.e., de-bind to a “brown-body” state and sinter to densify to final finished part. This approach is currently being qualified for SiC, WC and Al_2O_3 thermoplastic filament components.

The range of ceramic materials that have been 3-D printed is increasing, and includes silicon carbide, aluminum oxide, zirconium dioxide, and silicon nitride, as well as composites of these materials. An extensive summary on the range of techniques used to manufacture high-performance ceramics is given by Wang *et al.* (2019). Zhang *et al.* (2020) summarize the use of zirconia and zirconia-based composites in aerospace applications, amongst others. Similar to other AM ceramic materials, minimizing defects and maximizing as-built density are limiting factors if extensive post processing is to be avoided. This requires manufacture at high pre-heat/build plate temperatures (1600°C) and controlled atmospheres (Zhang *et al.*, 2020).

As the technology evolves, crossover into other areas such as electric propulsion is inevitable as complex structures and geometries can be realized. One such area is the area of ion propulsion where the ability to fabricate new, complex geometries for one off applications may drive development as the range of ceramic precursor materials suitable for AM increases. The use of AM is already seeing use in rapid prototyping of metallic components (Guo *et al.*, 2019) for ion thrusters, as well as larger thruster components (Wermuth *et al.*, 2015).

The ability to establish a manned colony of the moon is limited by the infrastructure present to support life (Ghidini, 2018). While there are a number of options, including transporting of fully functional modules to be landed on the moon, the use of regolith to fabricate enclosures presents a natural, less energy intensive alternative. The European Space Agency is investigating how 3-D printing of components using lunar regolith could assist in supporting a base on the Moon. Some small components produced by Lithoz (Lithoz GmbH, Wien, Austria) with high print resolution as part of this study are shown in Fig. 17. Lunar regolith is a mixture of oxides, primarily silicon dioxide and aluminum oxide, in addition to iron oxides (Engelschön *et al.*, 2020). In order to produce 3-D prints, the simulated regolith is ground to a powder and sieved. The powder is then mixed with a UV sensitive binder. Layers of the components are deposited, and then cured by UV light. The completed component is then sintered to densify it. Material development research for this application is ongoing. The advantage of using this regolith material is that it can be 3D printed into the required shapes, and the resulting structure will provide a natural barrier against radiation and temperature fluctuations, Fig. 18 (Cesaretti *et al.*, 2014).

While additive manufacturing is typically associated with the production of finished components, it is also being used to support more traditional manufacturing such as sand and investment casting. AM is used in the fabrication of wax molds for investment casting with a replica of a complex component may be 3-D printed in wax. The wax article is then dipped in ceramic slurry, creating a hard shell around the wax which can then be easily melted out. Molten aluminum can then be cast into the ceramic mold. The lost-wax process is an ancient casting technique, but has been improved on by use of 3-D printing. Similarly, complex cores can be manufactured for the production of complex, hollow, turbine blades (Zhu *et al.*, 2019). The use of AM for the manufacture of large sand casting molds ($4 \times 2 \times 1$ m) has also added a new dimension to the production of large, one-off cast components. Ceramic and binders are used to “print” the negative of the component structure, but with an ability to finely control

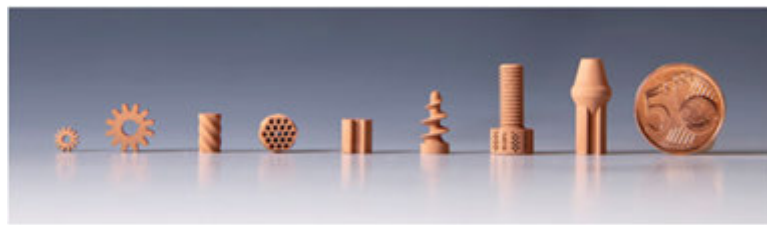


Fig. 17 Components 3-D printed using simulated lunar regolith. Image from ESA (www.esa.int).



Fig. 18 ESA's 3D printed Lunar base concept (www.esa.int).

the position of gates and sprues (Aghaei Meibodi *et al.*, 2019), as well as include active sensors to monitor the effectiveness of the pore (Walker *et al.*, 2018).

Concluding Remarks

With the drive towards weight savings and increased component operating temperatures, ceramic materials are seeing an increased interest and utilization. Ceramic materials offer weight reduction, superior thermo-structural properties, and environmental durability in a wide range of applications.

The development of complex 3-D textile weaving techniques for preforms with multi-axis reinforcement is a key factor in developing Ceramic matrix composites (CMCs) with improved properties. CMCs are enabling reductions in rocket nozzle mass, enabling construction of reusable launch vehicles and reusable space planes. The extent of use of CMCs in space applications is increasing as the focus is shifting for demonstration to validation. CMCs and ceramics foams are key components in thermal protections surfaces on re-entry vehicles, as well as structural components in nozzles.

Advanced ceramics are seeing utilization in electrical propulsion, either as thermally stable, low erosion plasma facing surfaces, cathodes and accelerator grids or dielectric and super-conducting magnetic components.

Ceramics offer high thermal stability, making them the material of choice for re-entry surfaces. They also offer passive cooling solutions through their reflective and radiative properties. Over extended radiation exposure, ceramic solar reflector coatings are more stable under UV and particle radiation than organic matrix coatings.

The increased research in additive manufacturing and the combination of metal-injection molding post process, and ceramic-polymer filaments, promise new applications for ceramic materials. The ability to manufacture complex shapes, with functional cooling channels, already being seen in metals, is of particular interest. Simpler, open pore structures are already being manufactured in ceramic and these will serve to validate the processes for future applications.

References

- Aghaei Meibodi, M., Giesecke, R., Dillenburger, B., 2019. 3D printing sand molds for casting bespoke metal connections. In: Haeusler, M.H., Schnabel, M.A., Fukuda, T. (Eds.), *Intelligent & Informed: Proceedings of the 24th International Conference of the Association for Computer-Aided Architectural Design Research in Asia (CAADRIA)*, vol. 1. Hong Kong: CAADRIA, pp. 133–142.
- Anderson Jr, J.D., 1989. *Introduction to Flight*, third ed. New York: McGraw-Hill.
- Beauchamp, P.M., Cutts, J.A., 2017. *Solar Power Technologies for Future Planetary Science Missions*. NASA/Jet Propulsion Laboratory-Caltech.
- Bhushan, B., 2008. *Nanotribology and Nanomechanics: An Introduction*. Berlin and Heidelberg: Springer.
- Böhrk, H., 2017. Heat flux reduction by transpiration-cooling of CMCs for space applications. In: Bafekrpour, E. (Ed.), *Advanced Composite Materials: Properties and Applications*. Berlin and Boston: De Gruyter.
- Buffenoir, F., Escafre, D., Brault, T., Rival, L., Girard, F., 2016. Dynamical and thermal qualification of the C-SiC nose for the IXV. *Acta Astronautica* 124, 79–84.
- Burt, R.R., Christiansen, E.L., 2003. An enhanced shutter to protect spacecraft windows from meteoroids and orbital debris. *International Journal of Impact Engineering* 29, 139–152.
- Cable, T.L., Setlock, J.A., Farmer, S.C., Eckel, A.J., 2011. Regenerative performance of the NASA symmetrical solid oxide fuel cell design. *International Journal of Applied Ceramic Technology* 8, 1–12.
- Cesaretti, G., Dini, E., De Kestelier, X., Colla, V., Pambaguian, L., 2014. Building components for an outpost on the Lunar soil by means of a novel 3D printing technology. *Acta Astronautica* 93, 430–450.
- Chang Diaz, F.R., 2001. An overview of the VASIMR engine: High power space propulsion with RF plasma generation and heating. *AIP Conference Proceedings* 595, 3–15.
- Chapline, G., Young, J., 2010. Thermal protection systems. In: Lane, H., Chapline, G., Lulla, K. (Eds.), *Wings in Orbit: Scientific and Engineering Legacies of the Space Shuttle 1971–2010*. Houston: NASA, pp. 182–199.
- Christin, F.A., 2008. CMC materials for space and aeronautical applications. In: Krenkel, W. (Ed.), *Ceramic Matrix Composites: Fiber Reinforced Ceramics and Their Applications*. Weinheim: Wiley-VCH Verlag GmbH, pp. 327–351.
- Chu, E., Goebel, D.M., 2012. High-current lanthanum hexaboride hollow cathode for 10-to-50-kW hall thrusters. *IEEE Transactions on Plasma Science* 40, 2133–2144.
- Cioeta, M., Di Vita, G., Signorelli, T., *et al.*, 2016. Design, qualification, manufacturing and integration of IXV ablative thermal protection system. *Acta Astronautica* 124, 90–101.
- Dantzlger, A.A., Strain, R.D., Faulconer, J.W., 2008. *Solar probe + mission engineering study report prepared for NASA's Heliophysics Division*. Available at: <https://solarprobe.gsfc.nasa.gov/SolarProbe+ME.pdf> (accessed December 2020).
- de Faoite, D., Browne, D.J., Stanton, K.T., 2013. Regression analysis of temperature-dependent mechanical and thermal properties of dielectric technical ceramics. *Journal of Materials Science* 48, 451–461.
- de Faoite, D., Browne, D.J., Chang-Díaz, F.R., Stanton, K.T., 2012. A review of the processing, composition, and temperature-dependent mechanical and thermal properties of dielectric technical ceramics. *Journal of Materials Science* 47, 4211–4235.
- de Faoite, D., Browne, D.J., Del Valle Gamboa, J.I., Stanton, K.T., 2014. Inverse estimate of heat flux on a plasma discharge tube to steady-state conditions using thermocouple data and a radiation boundary condition. *International Journal of Heat and Mass Transfer* 77, 564–576.
- de Faoite, D., Browne, D.J., Del Valle Gamboa, J.I., Stanton, K.T., 2016. Thermo-structural modelling of a plasma discharge tube for electric propulsion. *Applied Thermal Engineering* 98, 541–552.
- Devi, G., Rao, K.R., 1993. Carbon-carbon composites – An overview. *Defence Science Journal* 43, 369–383.
- Devilliers, C., Krödel, M.R., Sodnik, Z., Robert, P., 2017. Super-light-weighted HB-Cesic mirror cryogenic test. In: Armandillo, E., Cugny, B., Karafolas, N. (Eds.), *Proceedings of SPIE: International Conference on Space Optics*, vol. 10565. SPIE.105652F.
- Doherty, K.A.J., Carton, J.G., Norman, A., *et al.*, 2015. A thermal control surface for the Solar Orbiter. *Acta Astronautica* 117, 430–439.
- Doherty, K.A.J., Twomey, B., McGlynn, S., *et al.*, 2016. High-temperature solar reflector coating for the Solar Orbiter. *Journal of Spacecraft and Rockets* 53, 1077–1084.
- Döhring, T., Jedamzik, R., Westerhoff, T., Hartmann, P., 2009. Four decades of ZERODUR® mirror substrates for astronomy. In: Jiang, W., Geyl, R., Cho, M.K., Wu, F. (Eds.), *Proceedings of the 4th International Symposium on Advanced Optical Manufacturing and Testing Technologies: Large Mirrors and Telescopes*, vol. 7281. SPIE. (728103).

- Dordlofva, C., 2020. A design for qualification framework for the development of additive manufacturing components – A case study from the space industry. *Aerospace* 7, 25.
- Dunn, B.D., 2016. *Materials and Processes for Spacecraft and High Reliability Applications*. Chichester: Springer.
- Engelschön, V.S., Eriksson, S.R., Cowley, A., *et al.*, 2020. EAC-1A: A novel large-volume lunar regolith simulant. *Scientific Reports* 10, 5473.
- Essa, K., Hassanin, H., Attallah, M.M., *et al.*, 2017. Development and testing of an additively manufactured monolithic catalyst bed for HTP thruster applications. *Applied Catalysts A: General* 542, 125–135.
- Ghidini, T., 2018. Materials for space exploration and settlement. *Nature Materials* 17, 846–850.
- Glass, D.E., 2008. Ceramic matrix composite (CMC) thermal protection systems (TPS) and hot structures for hypersonic vehicles. Paper presented to Proceedings of the 15th AIAA Space Planes and Hypersonic Systems and Technologies Conference. Available at: <https://ntrs.nasa.gov/citations/20080017096>.
- Goebel, D.M., Katz, I., 2008. *Fundamentals of Electric Propulsion: Ion and Hall Thrusters*. NJ: John Wiley & Sons.
- Goebel, D.M., Watkins, R.M., 2010. Compact lanthanum hexaboride hollow cathode. *Review of Scientific Instruments* 81, 083504.
- Guo, N., Xie, K., Sangregorio, M., *et al.*, 2019. 3D printing of ion optics for electric propulsion. *Frontiers in Physics* 145, 00145.
- Harris, R., Stewart, M., Koenig, W., 2018. Thermal protection systems technology transfer from Apollo and Space Shuttle to the Orion Program. In: Proceedings of the AIAA SPACE Forum 2018, Orlando, FL, USA. Available at: <https://ntrs.nasa.gov/citations/20180006812>.
- Henninger, J.H., 1984. Solar absorptance and thermal emittance of some common spacecraft thermal control coatings. NASA, Reference Publication 1121.
- Hirschel, E.H., 2015. *Basics of Aerothermodynamics*, second ed. USA: Springer International Publishing.
- Holste, K., Dietz, P., Scharmann, S., *et al.*, 2020. Ion thrusters for electric propulsion: Scientific issues developing a niche technology into a game changer. *Review of Scientific Instruments* 91, 061101.
- Holynska, M., Butenko, Y., Martins, R., *et al.*, 2019. Studies of white ceramic coatings for ESA's BepiColombo mission to Mercury. *Journal of Spacecraft and Rockets* 56, 1–13.
- Hull, T., Carre, A., Jedamzik, R., 2018. ZERODUR as a dimensionally stable mirror substrate material for spaceborne telescopes. In: Sodnik, Z., Karafolas, N., Cugny, B. (Eds.), *International Conference on Space Optics – ICSSO 2018*, vol. 11180. SPIE, 1118017.
- Hurwitz, F.I., 2010. Thermal protection systems (TPSs). In: Blockley, R., Shyy, W. (Eds.), *Encyclopedia of Aerospace Engineering* 4. United States: John Wiley & Sons Inc. (186).
- Kamiya, T., Mizutani, T., 2018. Development of ultra-lightweight and thermally stable cordierite ceramic mirrors. In: Navarro, R., Geyl, R. (Eds.), *Proceedings of SPIE, Advances in Optical and Mechanical Technologies for Telescopes and Instrumentation III*, vol. 10706. SPIE.
- Kaneda, H., Naitoh, M., Imai, T., *et al.*, 2010. Cryogenic optical testing of an 800 mm lightweight C/SiC composite mirror mounted on a C/SiC optical bench. *Applied Optics* 49, 3941–3948.
- Kasap, H., 2018. Exotic glass fibers for space: The race to manufacture ZBLAN, upward. Available at: https://www.nasa.gov/sites/default/files/atoms/files/upward3_3_book_v4_web.pdf.
- Levchenko, I., Bazaka, K., Ding, Y., *et al.*, 2018. Space micropropulsion systems for Cubesats and small satellites: from proximate targets to furthestmost frontiers. *Applied Physics Reviews* 5, 011104.
- Levine, S.R., Herbell, T.P., 1991. Aerospace applications. In: Schneider, S.J. (Ed.), *Engineered Materials Handbook, Volume 4: Ceramics and Glasses*. OH: ASM International, pp. 1003–1006.
- Ley, W., Wittmann, K., Hallmann, W., 2009. *Handbook of Space Technology*. Munich: John Wiley & Sons.
- Lince, J.R., 2020. Effective application of solid lubricants in spacecraft mechanisms. *Lubricants* 8, 74.
- Luna, J.P., Lewis, R.A., Hutchins, M., 2017. QinetiQ high power electric propulsion system and architectural options for future applications. In: Proceedings of the 35th International Electric Propulsion Conference, Georgia Institute of Technology, USA, Paper IPEC-2017-169.
- Maillard, T., Claeysen, F., LeLetty, R., *et al.*, 2009. Piezo mechatronic based systems in aircraft, space and defense applications. In: Fink, W. (Ed.), *Proceedings of SPIE, Space Exploration Technologies II*, vol. 7331. SPIE, 73310K-1.
- MacDonald, M., Badescu, V., 2014. *The International Handbook of Space Technology*. Berlin: Springer-Verlag.
- Marco, J., Remaury, S., 2004. Evaluation of thermal control coatings degradation in simulated geo-space environment. *High Performance Polymers* 16, 177–196.
- Marshall, D.B., Cox, B.N., 2008. Integral textile ceramic structures. *Annual Review of Materials Research* 38, 425–443.
- Matson, D.M., 2012. Materials science in reduced gravity. *Journal of the Minerals, Metals & Materials Society* 72, 1087–1088.
- Meseguer, J., Pérez-Grande, I., Sanz-Andrés, A., 2012. *Spacecraft Thermal Control*. Oxford: Woodhead Publishing.
- Miska, H.A., 1991. Aerospace and military applications. In: Schneider, S.J. (Ed.), *Engineered Materials Handbook, Volume 4: Ceramics and Glasses*. OH: ASM International, pp. 1016–1020.
- Misra, A.K., 2016. Composite materials for aerospace propulsion related to air and space transportation. In: Njuguna, J. (Ed.), *Lightweight Composite Structures in Transport*. Oxford: Woodhead Publishing, pp. 305–327.
- Misra A.K., Grady J.E., Carter, R., 2015. Additive manufacturing of aerospace propulsion components. Available at: <https://ntrs.nasa.gov/citations/20150023067>.
- Mulcahy, J.M., Browne, D.J., Stanton, K.T., *et al.*, 2009. Heat flux estimation of a plasma rocket helicon source by solution of the inverse heat conduction problem. *International Journal of Heat and Mass Transfer* 52, 2343–2357.
- Patel, M., 2011. *VASIMR Engine Design for a Mission to Mars*. (MSc thesis). San Jose State University.
- Pidan, S., Auweter-Kurtz, M., Herdrich, G., Fertig, M., 2005. Recombination coefficients and spectral emissivity of silicon carbide-based thermal protection materials. *Journal of Thermophysics and Heat Transfer* 19, 566–571.
- Pyzik, A.J., Beaman, D.R., 1993. Microstructure and properties of self-reinforced silicon nitride. *Journal of the American Ceramic Society* 76, 2737–2744.
- Ramadhani, F., Hussain, M.A., Mokhlis, H., Hajimolana, S., 2017. Optimization strategies for solid oxide fuel cell (SOFC) application: A literature survey. *Renewable and Sustainable Energy Reviews* 76, 460–484.
- Rasky D.J., Newfield, M., Zuniga, F., Venkatapathy, E., 2004. Access from space: A new perspective on NASA's space transportation requirements and opportunities. In: Proceedings of the AIAA Space Forum 2004, San Diego, USA, September. doi:10.2514/6.2005-2514.
- Rey, C.M., Hoffman, W.C., Chang-Diaz, F.R., *et al.*, 2002. Design and fabrication of an HTS magnet for the VASIMR experiment. *IEEE Transactions on Applied Superconductivity* 12, 993–996.
- Sacco, E., Ki-Moon, S., 2019. Additive manufacturing for space: Status and promises. *International Journal of Advanced Manufacturing Technology* 105, 4123–4146.
- Sathyan, K., Hsu, H.Y., Lee, S.H., Gopinath, K., 2010. Long-term lubrication of momentum wheels used in spacecrafts – An overview. *Tribology International* 43, 259–267.
- Scott, C.D., 1992. Wall catalytic recombination and boundary conditions in nonequilibrium hypersonic flows – With applications. In: Bertin, J.J., Periaux, J., Ballman, J. (Eds.), *Advances in Hypersonics – Modeling Hypersonic Flows*. Boston: Birkhäuser, pp. 176–250.
- Simchen, F., Sieber, M., Kopp, A., Lampke, T., 2020. Introduction to plasma electrolytic oxidation – An overview of the process and applications. *Coatings* 10, 628.
- Simon, R.A., 2005. Progress in processing and performance of porous-matrix oxide/oxide composites. *International Journal of Applied Ceramic Technology* 2, 141–149.
- Sun, K., Riedel, C.A., Wang, Y., *et al.*, 2018. Metasurface optical solar reflectors using AZO transparent conducting oxides for radiative cooling of spacecraft. *ACS Photonics* 5, 495–501.
- Sutton, G.P., Biblarz, O., 2001. *Rocket Propulsion Elements*, seventh ed. New York: John Wiley & Sons, Inc.
- Sweeting, M.N., 2018. Modern small satellites-changing the economics of space. *Proceedings of the IEEE* 106, 343–361.
- Tumino, G., Mancuso, S., Gallego, J.-M., *et al.*, 2016. The IXV experience, from the mission conception to the flight results. *Acta Astronautica* 124, 2–17.
- Varghese, J., Joseph, N., Jantunen, H., *et al.*, 2020. Microwave materials for defense and aerospace applications. In: Mahajan, Y.R., Johnson, R. (Eds.), *Handbook of Advanced Ceramics and Composites*. USA: Springer.
- Walker, J., Harris, E., Lynagh, C., *et al.*, 2018. 3D printed smart molds for sand casting. *International Journal of Metalcasting* 12, 785–796.

- Wang, J.-C., Dommati, H., Hsieh, S.-J., 2019. Review of additive manufacturing methods for high-performance ceramic materials. *International Journal of Advanced Manufacturing Technology* 103, 2627–2647.
- Wen, S., Huang, P., 2018. *Principles of Tribology*, second ed. Singapore: John Wiley & Sons.
- Wermuth, L., Beyer, S., Sebald, T. *et al.*, 2015. Selective laser melting of noble and refractory alloys for next generation spacecraft thrusters. Paper presented at *Metallic Materials and Processes: Industrial Challenges – MMP 2015*, Deauville, France.
- Wu, J., 2020. Perovskite lead-free piezoelectric ceramics. *Journal of Applied Physics* 127. 190901.
- Zhang, X., Wu, X., Shi, J., 2020. Additive manufacturing of zirconia ceramics: A state-of-the-art review. *Journal of Materials Research and Technology* 9, 9029–9048.
- Zhu, W.-J., Tian, G.-Q., Lu, Y., Miao, K., Li, D.C., 2019. Leaching improvement of ceramic cores for hollow turbine blades based on additive manufacturing. *Advances in Manufacturing* 7, 353–363.

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Porous Ceramics for Energy Applications

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Introduction

Porous ceramics are described as ceramics with high volume fraction of porosities between 20% and 95% and can be classified, according to the pore size, as microporous ceramics with pores less than 2 nm, mesoporous ceramics with pores of 2–50 nm and macroporous ceramics with pores larger than 50 nm (Liu and Chen, 2014). Hierarchically, porous ceramics contain pores of various length scales that are all combined in a single structured porous ceramic. The total porosity, pore size and shape of a porous ceramic can be tailored for the requirements in a targeted application by the geometry, the choice of materials and the manufacturing process (Akhtar *et al.*, 2014a,b). Porous ceramics are materials of industrial importance and are designed and structured in the form of honeycombs, foams, multilayers and membranes. These structured porous materials are widely used in liquid and gas filtration, particle filters and collectors, gas adsorption, hot metal filtration, water purification, dielectric resonators, biomedical implants, bioreactors, catalytic supports, automotive components, fuel cell assemblies, thermal insulations and refractories (Liu and Chen, 2014; Akhtar *et al.*, 2014a,b; Ohji and Fukushima, 2012). These broad applications in different industries are based on, (1) the properties of porous ceramics like high chemical and thermal stability, abrasion and wear resistance, mechanical and functional properties, (2) development of manufacturing approaches to shape ceramic components, and (3) knowledge development on tailoring of composition and microstructures in combination with optimum porous structure, pore sizes and distributions suitable for the targeted applications. Due to the difference in the properties amongst ceramics, oxide ceramics such as silica (Huo *et al.*, 2019), alumina (Ciurans Oset *et al.*, 2018; Hooshmand *et al.*, 2019), zirconia (Huo *et al.*, 2016), mullite (Choo *et al.*, 2019), cordierite (Li *et al.*, 2019), aluminosilicates (Alghamdi *et al.*, 2018; Ojuva *et al.*, 2013), carbide ceramics such as silicon carbide (Kultayeva *et al.*, 2020), nitride ceramics such as silicon nitride (Chun-fang and Bing, 2019) and recently high entropy boride ceramics (Chen *et al.*, 2019a,b) have been processed into porous ceramics for different applications.

In ceramic membranes, catalytic reactors and high temperature fuel cells or electrolyzers (solid oxide cells (SOCs)), the microstructure and pore architecture, such as pore size, pore structure and distribution of active phases/components, play a key role for achieving high performance in separation processes, catalytic processes (Keane, 2003) or to convert fuels into electricity or vice versa. Here we explain the importance of material choice, processing and microstructural design on the performance of advanced porous ceramic structures in three selected energy applications: catalysis, solid-oxide cells and membranes.

Catalysts

Porous ceramics have been directly employed as catalysts, for examples in the form of zeolites (Ennaert *et al.*, 2016), or as catalyst supports for noble metal catalysts, such as cordierite decorated with Pt, Rh catalysts for selective catalytic oxidation (Hung, 2010). Hierarchical porous ceramics in structured form offer the properties required to overcome the shortcoming of conventional catalytic beds and reactors. Porous ceramics used in exhaust treatments contain hierarchically porous structures with pore sizes in the range from 6 nm to 500 μm (Al-Naib, 2018).

Ceramics in catalysis can be used directly as catalyst or as support material for the active catalytic component. Ceramic catalysts are typically oxide ceramics such as transition metal oxides (TMO) (Wang *et al.*, 2018), microporous zeolites (Ennaert *et al.*, 2016) and perovskites (Voorhoeve *et al.*, 1977). The surface chemistry, pore and defect structure of ceramic oxide catalysts have been determined as important parameters for the catalytic performance (Keane, 2003). TMOs are oxides of transition metals (Ti, Ni, V, Cr, Zr etc.) with large variety of chemical composition ranging from mono-oxides to high entropy oxides and crystal structures that are used in different chemical applications, like the oxidation of CO (Chen *et al.*, 2018) and volatile organic compounds (VOCs) (Liu *et al.*, 2016). Zeolites are microporous aluminosilicate ceramics, FAU (Faujasite) and MFI (Mordenite Intervented Framework) type, with tailorable chemistry, crystal structure and porosity making these materials highly efficient for shape selective catalysts with broad applications in biomass conversion and petrochemical industry (Ennaert *et al.*, 2016; Vermeiren and Gilson, 2009). Perovskites are ceramic oxides, typically expressed as ABO_3 compounds, containing two metals A and B. These components have tailorable chemistry and structures depending on the type and size of the metals and are widely used in heterogeneous catalysis, functional layers in solid oxide fuel cells, as multilayer capacitors, piezoelectric transducers and superconductors (Keane, 2003). Porous ceramics are structured to carry catalytic active metals and offer large surface area, efficient mass and heat transfer properties, low pressure drop and appreciable mechanical strength for the enhancement of catalytic performance. The porous ceramic supports are structured in the form of granules, extrudates, honeycombs and laminates. The structured porous ceramics are optimized for their thermal, mechanical, chemical and mass transfer properties for specific catalytic applications (Akhtar *et al.*, 2014a,b).

Metal oxides, including Al_2O_3 , SiO_2 , CeO_2 , SnO_2 , ZrO_2 , are employed as effective catalysts and support materials (Akhtar *et al.*, 2014a,b; Keane, 2003; Alghamdi *et al.*, 2008). For instance, Al_2O_3 is an effective catalyst for double bond isomerization and it is widely used as support material for V_2O_5 for oxidative dehydrogenation of light alkanes (Liu *et al.*, 2016; Wu *et al.*, 2008). The

catalytic properties of metal oxides are dominated by surface and structural defects. Furthermore, metal oxides possess sites suitable for acid-base interactions. Acid-base properties of metal oxides are useful in catalytic oxidation of hydrocarbons, isomerization of olefins, dehydrogenation, and alkylations (Védrine, 2017; Sattler *et al.*, 2014). The redox properties where metal oxides undergo reduction and re-oxidation is well recognized in redox catalysis. Since surface properties and defects in metal oxides play an important role in catalytic reactions, several different processes and methods have been developed to synthesize metal oxide nanoparticles using gas condensation methods, spray pyrolysis, aerosol chemistry, oxidation of metal colloids, precipitation and sol-gel methods with tailored structure and properties (Keane, 2003; Astruc, 2020). The catalytic activity of the TMOs depends on a broad range of surface structures and features, originating from the allocation of metal cations and oxygen anions and structural defects. The crystal structure of TMOs depends on close-pack arrangement of oxygen anions, with metal cations covering interstitial sites. For instance, in mono-oxide, many TMO (TiO and NiO) have rocksalt structure, in which the octahedral sites have cations in an oxygen anion FCC array. The majority of TMOs (MO_2 ; $\text{M} = \text{Ti, Cr, V, Mn, Zr, Pd, etc.}$) have the rutile structure. The rutile structure is produced by filling half of the octahedral sites with cations of the HCP oxygen anion array. In trioxides, few TMOs can reach the +6 oxidation state (Dey *et al.*, 2019). The TMOs are relatively cheap and can be designed and tailored to offer high specific surface area, porosity, active surface sites and have been investigated in mono, mixed and composite catalyst preparation with enhanced performance in CO oxidation, formaldehyde and VOC oxidation (Wang *et al.*, 2018; Liu *et al.*, 2016; Dey *et al.*, 2019). Microporous ceramics, zeolites, are used in catalysis as support for noble metal catalysis in petrochemical industry as well as for shape selective catalysis due to their well defined and tailorable pore sizes and shapes and presence of strong acidic sites (Csicsery, 1984; Gläser and Weitkamp, 2004). Furthermore, microporous ceramics offer the possibilities to be processed into hierarchical structures to tailor the heat and mass transfer kinetics during a catalytic process. Microporous, mesoporous and macroporous ceramics are typically used as supports for catalytically active components. The structures are designed with tailored pores at various length scales to tailor the mass and heat transfer properties to deliver robust supports for catalytic reactions (Akhtar *et al.*, 2014a,b; Ohji and Fukushima, 2012).

Solid Oxide Cells (SOCs)

Solid oxide cells (SOCs) are environmentally friendly and highly efficient electrochemical devices for the conversion of fuels into electricity and vice versa. Solid oxide fuel cells (SOFCs) can convert electricity into fuels whereas solid oxide electrolysis cells (SOECs) can produce fuels from electricity, such as hydrogen. The operating principle of the SOCs and the involved electrochemical reactions in each operation mode are illustrated in Fig. 1. SOCs are multilayered structures containing porous and

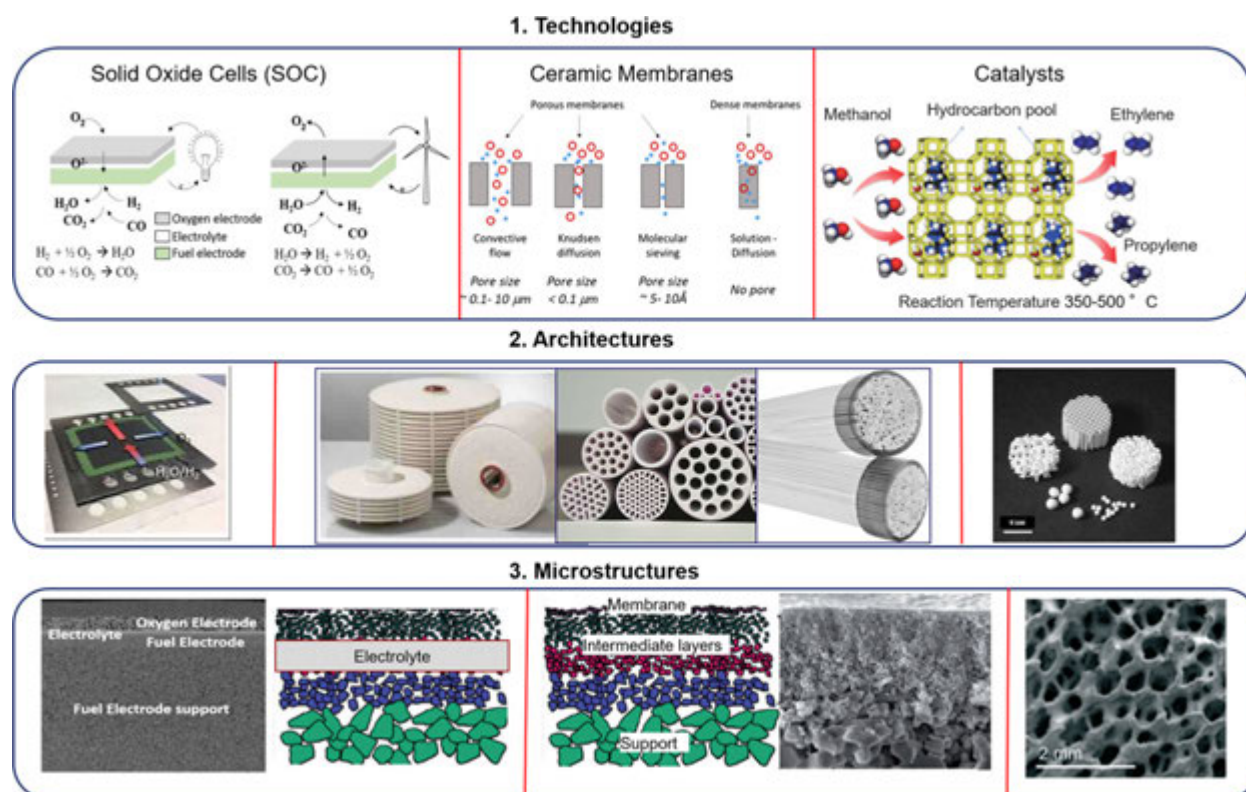


Fig. 1 Illustration of the operation principles of 3 selected examples of applications of porous ceramics in advanced energy technologies. In the top and from left to right: Solid Oxide Cells (SOCs), ceramic membranes and catalysts. Typical architectures and microstructures for the technologies are shown in the middle and bottom rows.

dense layers. The essential components of the SOC are porous fuel electrode, dense electrolyte, porous oxygen electrode and the electrolyte, which separates the fuel electrode from the oxygen electrode. SOCs are typically operated in the temperature range of 600–1000°C. Different designs of the SOCs exist based on the supporting element. If the SOC is supported by the electrolyte, it is known as electrolyte supported SOC. If the SOC has a support layer made up of either fuel electrode material or oxygen electrode material, they are known as fuel electrode supported SOC (Fig. 1) or oxygen electrode supported SOC, respectively. Structurally, both the electrode supports and electrodes are porous in nature to facilitate the gas transport to the reaction interfaces. On the other hand, the electrolyte is a dense layer so that it can separate the gaseous species from fuel electrode and oxygen electrode sides. The pore size, pore size distribution and pore volume in the electrode supports and electrodes play a critical role in the mechanical stability and electrochemical performance of the SOCs, as they control the load bearing material volume, transport properties and reaction surface areas. Thus, the optimization of the microstructure/electrode structure plays a crucial role in developing highly efficient SOCs.

Based on geometry, the SOCs are divided into planar and tubular SOCs. The structural and transport requirements are similar in both planar and tubular configurations. In typical planar electrolyte supported SOCs, the electrolyte layer is much thicker (150–300 μm) compared to fuel electrode and oxygen electrode layers (typically 10–30 μm). In order to reduce the resistance of the electrolyte and improve the performance of the SOCs, architectures with thin electrolytes are developed, leading to electrode supported designs. In typical fuel electrode or oxygen electrode supported SOCs, an additional support layer made of fuel electrode material or oxygen electrode material is included. The support layer thickness is much higher (200–500 μm) compared to fuel electrode layer (10–20 μm), electrolyte layer (10–20 μm) and oxygen electrode layer (20–30 μm). Technologically relevant sizes of the planar SOCs can be in the range of 100 cm^2 to 600 cm^2 with different planar geometries. The tubular SOCs can have dimensions from few μm to mm in diameter and few mm to about 1.5–2 m in length, facilitating faster start-up and large power density depending on the dimensions of the tubes. Depending on the configurations, the fabrication process will be different and the details will be discussed in the Section on “Processing of Porous Ceramics”.

Due to the multilayer architecture of the SOC, consisting of different ceramic and metallic materials with different properties, careful attention must be paid to the appropriate selection of the materials. All components have to show a well matched thermal expansion behavior, chemical compatibility with other layers and chemical stability in the operating atmospheres. The performance of SOCs is not only determined by intrinsic material properties but also depends on the fabrication processes used and the resultant microstructures/porosity. The performance of SOCs can only be improved by using high performance materials in combination with appropriate fabrication methods. In terms of electron/ion transport properties of the porous electrodes, the fuel electrode can be electronic or mixed electronic and ionic conducting material and the oxygen electrode is a mixed electronic and ionic conducting material. A short description of the various fuel and oxygen electrode materials is provided.

Fuel electrode supports and electrodes: The mixture of NiO and Y_2O_3 doped ZrO_2 (YSZ), known as Ni/YSZ cermet, is widely used as the fuel electrode support and fuel electrode in the typical state of the art SOCs (Jiang and Chan, 2004). Ni, formed after reduction of NiO, acts as an electrocatalyst for the oxidation of H_2 and CO and as an electronic conductor, whereas the YSZ acts as a stabilizer for the porous electrode structure and extends the reaction interfaces due to its ionic conductivity. These materials exhibit superior electrochemical performance in general; however, they suffer from redox instability, impurity intolerance and high cost. As alternatives, various materials, such as, Fe-based metals/alloys or electronic conducting ceramics in combination with integrated electrocatalysts have been investigated. The use of Fe-based metals/alloys electrodes are mainly used in the metal supported SOC configuration and comes with a restriction of processing them in protective atmospheres due to their tendency of corrosion. Various perovskite and fluorite structured ceramic materials ($\text{Sr},\text{La})\text{TiO}_3$, $(\text{Sr},\text{Y})\text{TiO}_3$, $(\text{La},\text{Sr})(\text{Cr},\text{Mn})\text{O}_3$, (Tucker, 2010) $(\text{La},\text{Sr})\text{CrO}_3$, $(\text{La},\text{Sr})(\text{Al},\text{Mn})\text{O}_3$, $(\text{La},\text{Sr})(\text{Ti},\text{Mn})\text{O}_3$ (Atkinson *et al.*, 2004) have been investigated as materials for electrodes and electrode contact layers. These materials offer impurity tolerance and redox stability; however, the electrochemical performance is relatively poor due to the lack of sufficient electronic/ionic conductivity and electrocatalytic activity. Wide variety of materials are investigated as fuel electrodes (Sun and Stimming, 2007).

Oxygen electrode supports and electrodes: Perovskite (ABO_3) ceramic compounds (e.g., LaCoO_3 , LaMnO_3 , LaFeO_3 and LaCrO_3) with various A-site and B-site substitutions are widely used as oxygen electrode materials (Sun *et al.*, 2010). The La and Sr from these perovskite ceramics has a tendency to react with the YSZ electrolyte and form high resistance phases like $\text{La}_2\text{Zr}_2\text{O}_7$ and SrZrO_3 . In order to avoid these reactions, to match the thermal expansion behavior with electrolyte and to obtain required transport properties, various A-site and B-site substitutions have been investigated and suitable compositions identified. Furthermore, double perovskites, fluorites and composites of different material classes were also investigated (Kaur and Singh, 2020).

Ceramic Membranes for Liquid and Gas Separation

Porous ceramic membranes are used for separation processes in micro, ultra and nanofiltration that do not allow the use of polymeric membranes including wastewater treatment (Samaei *et al.*, 2018), desalination processes, pervaporation and gas separation (Tsuru, 2008). The exceptional chemical resistance, thermal stability and low fouling tendency make porous ceramic membranes ideal for operation at evaluated temperatures (above 100°C), at relevant application pressures (up to 10 bars and above) and under harsh chemical conditions (Vercauteren *et al.*, 1998). This includes the operation or “in-place cleaning” of ceramic membranes in the entire pH range from 0 to 14 and in organic solvents without the risk for membrane compaction or swelling with chemicals such as ozone, hydrogen peroxide, strong inorganic acids or steam, for example in water treatment of

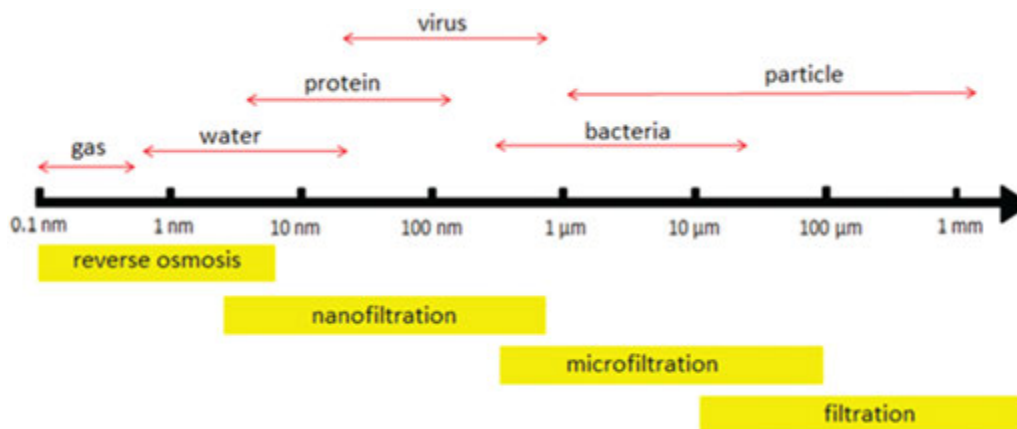


Fig. 2 Type and size of particles and the membrane separation processes to separate them according to their size. From Xu, Q., Zhang, W., 2016. Next-generation graphene-based membranes for gas separation and water purifications. In: Silva, A., Carabineiro, S. (Eds.), *Advances in Carbon Nanostructures*. IntechOpen. doi:10.5772/64396.

highly concentrated organic effluents, such as oil and grease (Madaeni *et al.*, 2013), brackish water, seawater pre-treatment and high temperature desalination (Amin *et al.*, 2016). Disadvantages of ceramic membranes are challenges in handling due to their brittleness and the significantly higher material and fabrication costs compared to polymer membranes.

Fig. 2 summarizes examples of applications for membranes, which can be classified after the pore sizes to achieve the separation task. For more challenging applications, such as nanofiltration, reverse osmosis, pervaporation or gas separation, small pores with very well-defined sizes between 0.1 nm and 10 nm are required. Alternatively, asymmetric dense ceramic membranes are developed for gas separation, based on zeolites (Kosinov *et al.*, 2016), on mixed-conducting materials that transport oxygen ions at high temperatures (Sunarso *et al.*, 2008) or on proton conducting materials (Tao *et al.*, 2015). The driving force for gas transport across the membranes is a chemical potential gradient. The separation or transport mechanism depends on the pore size (and chemistry) of membrane and the size of gas molecules and can include Knudsen diffusion (or activated or surface diffusion), size exclusion (molecular sieving) or solution-dissolution for the dense membranes (van den Berg and Smolders, 1992).

Oxides of alumina, silica, titania and zirconia are the most common ceramic membrane materials for advanced separation processes in wastewater treatment, nanofiltration and gas separation (Tsuru, 2008). According to the requirements of specific applications and operation conditions, membranes are produced in different geometries (see **Fig. 1**), such as plates, tubes or hollow fibers. From these materials, asymmetric membranes can be produced in the form of multi-layer structures based on a macro-porous support and a sequence of different macro, micro and mesoporous layers, depending on the required pore size of the final membrane layer for the separation task (middle, bottom part of **Fig. 1**). Similarly, hierarchically porous multilayer architectures can be used to support dense thin-film ceramic membranes for gas separation, such as zeolite membranes (Caro, 2011), oxygen transport membranes (Ramachandran *et al.*, 2015; Sunarso *et al.*, 2008) or proton conducting membranes (Cai *et al.*, 2009). The fabrication of porous asymmetric membranes includes the basic steps of ceramic processing, mass preparation, shaping and sintering, as outlined in the following section.

Processing of Porous Ceramics

The processing of porous ceramics has been extensively investigated and several methods have been matured for industrial production. The simplest way to process is dry pressing followed by partial sintering to achieve a porous component with around 45% porosity. In the simplest approach, the porosity is mainly controlled by the particle size and shape of the starting ceramic powders. In order to have better control over size and shape of pores and total porosity, several processing approaches have been developed to process ceramics with tailored microstructure required for specific applications. The fabrication of porous ceramics can be classified according to the flow behavior (viscosity) of the ceramic mass, as colloid, plastic or dry forming processes. Typically, the processing of porous ceramics involves mixing of the ceramic component in a solvent (most commonly water) with organic and/or inorganic binder, templating agents (to produce pores) and additional organic additives (e.g., plasticizers, demolding agents). Organic binders are typically added to facilitate the processing of green bodies and offer mechanical integrity and stability to undergo further processing, while inorganic binders can be added in some processes (applications) to bind particles of the ceramic component during the sintering process to impart strength (Akhtar *et al.*, 2014a,b; Ohji and Fukushima, 2012; Hammel *et al.*, 2014). Excess sacrificial binder can also be added to create porosity. Other templating agents are introduced to add additional porosity and pore size to optimize the density and mass and heat transfer properties of the resulting porous ceramic scaffolds. The templates are chosen based on the processing approach, final density of the component, total porosity, shape and size of pores, ease of removal, stress development in the components during removal and environmental impact

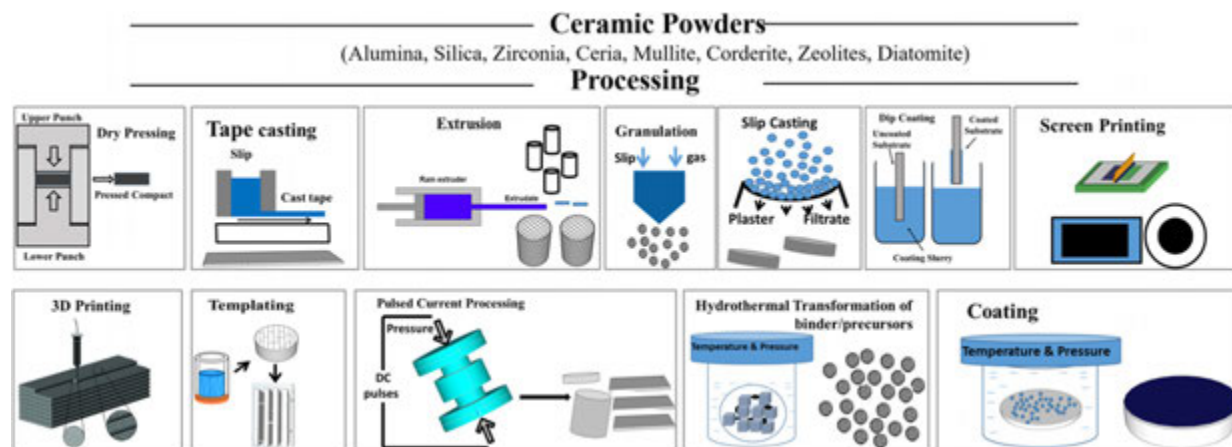


Fig. 3 Overview of different processing methods for shaping of porous ceramics, used in catalysis, solid oxide cells (SOC) and ceramic membranes.

(Keane, 2003; Ciurans Oset *et al.*, 2018; Hooshmand *et al.*, 2019). Once all the components are mixed homogeneously, a shaping operation is performed e.g., molding, granulation, die casting, freeze casting, gel-casting etc., to produce the desired engineering structure. After shaping, a debinding step is carried out to remove organic components and templating agents followed by final consolidation and sintering for mechanical stability. Some commonly used processes for the structuring of macroporous ceramics are foaming, extrusion, slip and tape casting, gel casting, coating, spray drying, and dry pressing. In the case of microporous ceramics such as zeolites, the sintering parameters such as temperature and time are of significance as the higher temperature and time results in destruction of internal porous structure. Therefore, the technology is based on the addition of inorganic binder such as clays and silica to sinter at lower temperatures to preserve micropores (Keane, 2003). Recent work has been focused on the development of binderless approaches for microporous ceramics including (1) conversion of clay binder using hydrothermal process to micro-mesoporous ceramics and (2) consolidation by pulsed current processing by applying pressure and temperature to consolidate by forming mechanically stable bonds by local amorphization. 3D printing has gained significant attention to process 3D structures and has been successfully implemented to design macroscopic ceramic components with hierarchy of pores using traditional and microporous ceramics (Chen *et al.*, 2019a,b; Zocca *et al.*, 2015). A brief description of the most commonly used processing approaches is summarized in the following sections (Fig. 3).

Dry Pressing

Dry pressing of ceramics is a fast-industrial mass production technique based on the axial compaction of loosely granulated ceramic powders with a moisture content below 3% by the force of punches in a die. In uniaxial pressing, usually a top and bottom punch are used. Due to relatively low concentration of organic additives in the powder granulates, the time for removal of organics during the debinding step can be shortened and parts with low tolerances are achieved. For the fabrication of porous ceramics, considerable amounts of sacrificial templates (pore formers) need to be added to create porosity when removed during the heat treatment process. Dry pressing is for example used for isostatic or hot isostatic pressing of porous ceramic filters, catalyst or membrane supports.

Extrusion

Extrusion is a plastic forming process used industrially to shape ceramic components of a fixed, cross-sectional profile by compacting and pushing a ceramic mass with high pressure through a cylindrical barrel and finally through a die. As the plastic mass exits the die it has the desired cross section and can be cut into sections of the desired cross section and length, resulting in honeycombs or rods as catalyst supports or support tubes for SOFC or membranes (Richerson and Lee, 2018; Reed, 1995).

Extrusion has been adopted for processing of hierarchically porous ceramics using traditional and microporous ceramics. The important steps in extrusion are the preparation of ceramic paste containing organic binder and solvent with suitable rheological properties for flowing through a barrel and die system. The extrusion gives great flexibility in designing and tailoring porous ceramic components. Another approach adopted is to extrude the ceramic substrate and deposit a coating of an active catalysts by film growth or by colloidal processing. For catalytic support materials, the extruded substrates can be categorized as low surface area and high surface area substrates. These extruded substrates are used in automotive, chemical processing, oxidation, catalytic combustion and emission control reactors. The commonly used ceramics for extrusion of low surface area substrates are cordierite, mullite, silica and alumina. Zeolites, titania, vanadia, precious and rare-earth metals are supported on these substrates for catalytic application, using film growth, infiltration and washcoat methods (Hung, 2010; Lefevre *et al.*, 2013; Kašpar *et al.*, 2003). High surface area monoliths are extruded using zeolites and high surface area oxides in the form of granules, pellets and extrudates. Similar processing operations are used for high surface area substrates. However, the sintering is performed carefully to keep the

high surface area intact during sintering operation. Furthermore, high surface area monoliths can be catalytically active in case of zeolites and can be decorated with catalysts to enhance the performance. Different types of oxide/carbide materials (Al_2O_3 , SiC, YSZ or MgO), have been specifically developed and extruded into macroporous, mechanically stable and permeable ceramic support tubes for use in advanced multilayer membranes in nanofiltration and gas separation applications (Ramachandran *et al.*, 2014; Buekenhoudt, 2008).

Colloidal Processing

Colloidal processing encompasses a variety of processing methods to shape porous ceramic supports, catalyst structures and electrocatalytic layers for energy applications at industrial scale and include a range of methods such as slip casting, tape casting, freeze casting or dip coating. The colloidal processing can be adjusted to shape ceramics with a targeted type of pore size, pore geometry, tortuosity and surface area. In order to apply the colloidal processing methods for shaping, a suspension of the ceramic component is prepared with controlled and optimized rheological properties with dispersing agent, organic and/or inorganic binders, plasticizers and antifoaming agents. The interparticle forces between the ceramic particles in the suspensions are tailored for optimization of rheological behavior for the process chosen. Colloidal processing techniques are versatile for shaping.

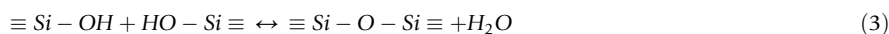
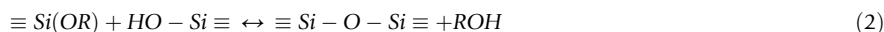
Gel casting has been used widely to process porous alumina, silica, zirconia, coeorderite ceramics and have been extended to zeolites 13X, silicalite-1 (Keane, 2003). Additional templates have been added to impart additional macroporosity and directional channels in porous zeolites (Akhtar *et al.*, 2012a,b; Wang *et al.*, 2016a,b). Structured alumina substrates with controlled porosity, pore size and shape have been demonstrated using expandable polymer microspheres of different sizes using gel casting (Ciurans Oset *et al.*, 2018; Hooshmand *et al.*, 2019).

The tape casting process is a well established ceramic processing technique to produce two dimensional dense and porous layers with a typical thickness between 5 μm and 1 mm (Mistler and Twiname, 2000). Due to this capability of making layers of different thickness and the ability to control the porosity in the layer, this process can be used for the fabrication of different type of layers, for example macro porous support layers (Schmidt *et al.*, 2016) or mesoporous electrocatalytic layers (fuel or air electrodes) or dense layers in planar SOC or membrane reactors (Kaiser *et al.*, 2011). Furthermore, tape casting allows continuous, industrial scalable fabrication of these layers. The key for a defect free layer fabrication is the optimization of the slurry formulation. Tape casting slurries usually consist of ceramic powder, solvent, dispersant, homogenizer, plasticizer and binder. By controlling the amounts of these ingredients, one can design slurry formulations that are suitable to produce layers of different thickness, pore size and pore volume. In addition to this, the casting parameters such as casting height, speed and rate of drying need to be optimized for defect free layer fabrication. The layers can be casted individually and laminated together or can be co-casted together to realize complete multilayer structure in one step. Subsequently, these multilayered assemblies are subjected to organics removal and sintering steps to obtain the final structure.

Screen printing is a well-established mass manufacturing technique to deposit different ceramic materials as thick-film layers (5–100 μm in thickness) on various support materials, for example in glass, electronic and semiconducting industry. Examples include the printing of decals on glasses, coatings in photovoltaics, deposition of electrolytes and electrodes in planar solid oxide cells (SOC) and membranes (Rotureau *et al.*, 2005). In screen printing, a mesh or screen is used to transfer a ceramic ink onto a substrate by a moving squeegee. First the ink is pushed into the open apertures of a mesh and then transferred to a substrate during the reverse stroke of the squeegee while the screen gets in contact with the substrate. A good understanding of the complex relation between the composition of highly loaded inks, their rheology (flow behavior, thixotropy) and the screen-printing parameters during the different printing phases is very important to ensure the fabrication of screen printed layers with accurate dimensions and quality after printing and low dimensional changes during sintering (Phair *et al.*, 2009).

The sol–gel process is a wet chemical technique, in which small metal oxide particles, especially silicon oxide (SiO_2) and titanium oxide (TiO_2), are produced from small precursor molecules (metal alkoxides or salts). The precursor materials undergo a transformation into a colloidal solution (sol) by hydrolysis and condensation reactions with a morphology of the solid phase between an integrated network (or gel) or discrete particles (Brinker and Scherer, 2013).

The three basic steps of hydrolysis and condensation are schematically shown for silicon alkoxides in Eqs. (1–3), according to Brinker (1988)



The process is extensively used and of crucial importance for the fabrication of meso- and microporous layers in ultra-, nanofiltration and gas separation membranes. Furthermore, depending on the speed of hydrolysis and condensation and the used solvent, two routes can be distinguished - the colloidal Sol-Gel route and the polymeric Sol-Gel route. The use of these techniques for the fabrication of very thin porous membrane separation layers with pore sizes down to the angstrom range are discussed in more detail in the section on ceramic membranes for liquid and gas separation.

In dip-coating a liquid film with a thickness between 10 nm and 10 μm is usually deposited on a support by immersion in a Sol-Gel precursor solution or a slurry (Puetz and Aegerter, 2004). After removal of the support with a constant speed, the deposited film is dried through evaporation of the liquid. Finally, a debinding and sintering step is performed (Brinker, 2013). Multiple

coatings with very controlled thickness, porosity and pore size distribution have been applied in porous and dense membranes for liquid and gas separation applications (Ramachandran *et al.*, 2015; Yin *et al.*, 2018). For more details, see Section “Ceramic Membranes for Liquid and Gas Separation”.

Advanced Processing Techniques

Templating

Templating strategies are implemented to create pores at various length scales in porous ceramics ranging from pores of gas molecule sizes, micropores, to large macropores. Templating strategies can be subdivided into soft templating and hard templating. Soft templates used are polymers, surfactants, emulsions, foaming agents and solvents. The soft templating is used to process porous ceramics with mesopores and macropores. A combination of soft templates and solvents can be chosen to produce hierarchical structures containing micro-mesopores and macropores. Hard templating produces porous structures by incorporating solid in the synthesis solution. After templating, the templates are removed by solvent extraction and thermal treatment methods to obtain a negative replica of the template to achieve porous structures. Templating methods have been widely adopted to process porous ceramics of coeenderite, alumina, zirconia, silicon nitride and so on. Zeolites, aluminosilicates, and silicoalumino silicates and meso porous ceramics have also been processed using hard templates and hierarchically porous structures combining different templates (Akhtar *et al.*, 2012a,b, 2014a,b).

Physical vapor deposition (PVD)

PVD methods use the concept of evaporation of a material, which is deposited and condensed onto a substrate. The evaporation sources can be thermal, electric arc, electron beam and laser ablation. Among other things, the energy of the evaporation source, distance between the evaporation source and the type of deposition substrate are the key process parameters that can control the quality of the deposited coatings. More advanced SOC designs, known as μ -SOCs, and ultra-thin separation membranes, where the porous layers are very thin, are areas where these processes are used. Often another supporting element is used in these designs. Often the material to be deposited is in the gaseous or liquid state before coating deposition. PVD methods, particularly laser ablation (Xu *et al.*, 2020), are often used to deposit the thin electrolytes, fuel and oxygen electrodes in advanced SOC designs and ultra-thin nanoporous membrane layers.

Freeze casting

Freeze casting is a processing technique that exploits the anisotropic freezing characteristic of water (or other solvent) to fabricate the porous ceramics. A well dispersed aqueous ceramic slurry is subjected to a controlled temperature gradient to directionally freeze the water. The freezing of water reorganizes the ceramic particles creating templated porous ceramics. The resultant structure is freeze dried to remove the ice crystals and subsequently sintered at appropriate temperature to realize the robust porous ceramic structure. The underlying principles of porous structure formation mechanisms are provided here (Dewille, 2008). The applicability of the process for the SOC designs is discussed in detail (Hedayat *et al.*, 2017). The process is also investigated for the fabrication of ultrafiltration alumina membranes (Liu *et al.*, 2018).

Phase inversion techniques

Phase inversion techniques (immersion precipitation) can produce porous ceramic structures with large, unidirectional pores and is based on an exchange between a solvent (typically N-methyl-2-pyrrolidone, NMP) and a non-solvent/coagulant (typically water) from a slurry. This process is induced when the shaped ceramic body (for example a porous ceramic capillary membrane) is directly introduced into water. The phase inversion then starts by the solvent NMP dissolving from the slurry. A skin layer on the outside of the shaped body is formed. Subsequently, water slowly penetrates the skin layer, enters into the slurry and acts as a nucleation site for exchange of the solvent (NMP) by the non-solvent (water). This exchange process will result in the growth of large pore channels (“finger-like” pores) perpendicular to the skin layer and stops when the solvent and non-solvent diffusion rates have equilibrated. Phase inversion tape casting has been used to develop high performance micro channelled oxygen transport membranes (Cheng *et al.*, 2016).

Novel processing approaches

New processing strategies are emerging for conventional and microporous ceramics. For instance, zeolites are structured using binderless processing to remove the inactive component to reduce inactive component effecting the catalytic performance and structural integrity. The binderless approaches are pulsed current processing of microporous ceramics and conventional ceramic processing followed by hydrothermal treatment to convert inactive components to zeolitic materials (Akhtar *et al.*, 2012a,b, 2014a,b). 3D printing has been gaining attention to structure ceramics with well controlled porous structure and kinetics. 3D printing, commonly termed as additive manufacturing, has been applied to structure monoliths and has potential to replace conventional catalysts and chemical reactors (Chen *et al.*, 2019a,b; Zocca *et al.*, 2015).

Sintering of Porous Ceramics

Sintering is an important final heat treatment step in the fabrication of porous ceramics. The aim is to give the ceramic body sufficient mechanical strength and to achieve a morphological structure with a very well defined grain and pore size by controlling the grain and pore growth in sintering of porous ceramics. The sintering is a process in which the ceramic material tries to reduce the surface energy (Gibbs free energy) by diffusion processes under application of temperature. In the initial sintering stage, at low sintering temperatures T_s well below the melting point of the material T_m ($T_s < 0.5 T_m$), necks are formed between particles by surface diffusion. In the 2nd stage, at sintering temperatures of T_s near the melting point T_m ($T_s \sim 0.5\text{--}0.9 T_m$), grain boundary diffusion starts and leads to grain growth. Larger particles tend to eat the smaller particles because they have a more pronounced curvature and higher surface energy. This process leads to grain growth and formation of larger pores with an overall decrease in total porosity and total surface area. In the final stage of sintering, at temperatures close to the melting point, bulk diffusion leads to full densification of the porous ceramic body by eliminating the last 5%–10% of pores. For the fabrication of porous ceramics, usually heat treatment and temperatures are controlled to limit grain boundary and bulk diffusion phenomena that lead to pore elimination and significant densification.

Structure – Performance Relationship in Porous Ceramics for Energy Devices

Porous Ceramic Catalysts

Structured porous ceramic catalysts are designed with a hierarchy of pores to offer advantages of lower pressure drop, high surface-to-volume ratio, and optimized heat transfer properties and mechanical strength (Akhtar *et al.*, 2014a,b; Lefevre *et al.*, 2014). Catalysts in industrial applications are shaped in the form of granules, extrudates and pellets of different sizes for packing of catalytic beds. The packing of catalytic beds is applicable for (1) metal supported catalysts and (2) zeolite catalysts. However, the traditional shaping and bed packing leads to pressure drop, poor mass transfer kinetics, higher residence time of the reactant and product species, and catalyst deactivation happens at a faster rate. These properties are tailored by controlling the size of the shaped catalyst and controlling the particle size in the shaped entity and porosity distribution to improve performance. Structured catalysts combine Macro-Meso-Micro pores in a structure and typically shaped in form of monoliths, honeycombs, laminates to tailor the mass and heat transfer properties with optimized pressure drop and diffusion while offering mechanically stable structures (Akhtar *et al.*, 2014a,b). This approach has become increasingly important in supported catalysts and zeolite catalyst where structure and properties are optimized with superior catalytic performance and longer lifetime of the active component. The understanding of the structured materials with tailored porosity has been developing and structured packings has been demonstrated in ceramic monoliths with straight channels (Lefevre *et al.*, 2014; Matoh *et al.*, 2019), sheet/gauze metallic packings with catalysts coatings (Rebrov *et al.*, 2001), open cell ceramic foams (Twigg and Richardson, 2007) and 3D printed catalyst support structures with optimizing the architecture of the support combining good mass and heat transfer properties with low pressure drop (Lefevre *et al.*, 2013, 2014).

Catalysts carriers ceramic monoliths

The application of catalytic supports are used in various catalytic applications including petrochemical industry, carbon dioxide conversion, catalytic converters. The porous ceramic scaffolds are decorated with metal nanoparticles. The scaffolds are structured with tailored porosities and properties. Metal nanoparticles are introduced by wash coating, impregnations, precipitation, dip coating, sol-gel and in situ crystallization (Keane, 2003). A key factor in processing the support with the active components is to achieve a strong bond between the catalyst and support to avoid deactivation of catalysts. A classic composition for vehicle exhaust treatment with a washcoat consists of a Al_2O_3 support, a $\text{CeO}_2\text{--ZrO}_2$ mixed oxide, barium/lanthanide oxides as alumina surface area stabilizers and the active metal component Rh, Pt, and Pd (Keane, 2003; Hung, 2010; Kašpar *et al.*, 2003). The geometry of the support is important in determining the catalytic converter performance (Keane, 2003; Lefevre *et al.*, 2013; Kašpar *et al.*, 2003). In some other applications, the shape selectivity of a zeolite is combined with metal catalysts by using the zeolite as support for the metals. For example, hierarchical mesoporous Pd/ZSM-5 zeolite has been used for the selective catalytic hydrogenation of *m*-Cresol to methylcyclohexane, in which the mesoporous ZSM-5 enhances the accessibility for Pd metal and increases the selectivity towards the desired deoxygenated product (Hunns *et al.*, 2016). Similarly Pt/ZSM-5 catalysts with shape selective properties for partial hydrogenation of soybean oil have been reported (Van Aelst *et al.*, 2016).

Zeolite catalysis

Zeolites are aluminosilicates that occur naturally or can be synthesized in the laboratory. Zeolites have made significant contribution in petrochemical and chemical industry as shape and size selective catalyst for hydrocarbon conversion (Csicsery, 1984; Dusselier and Davis, 2018). The performance of zeolites is due to their crystalline framework structures and uniform pore sizes of molecular dimensions and excellent thermal and chemical stability (Akhtar *et al.*, 2014a,b; Keane, 2003; Hedin *et al.*, 2010). Furthermore, a variety of pore sizes exist in zeolites to implement the shape selectivity by carefully choosing a zeolite for catalytic reactions. The size of the zeolite pore window is determined by oxygen in the ring. For instance normal hexane with a kinetic diameter of 5.1 Å can pass through a 10 membered ring zeolite whereas cyclohexane with a kinetic diameter of 6.9 Å would have a

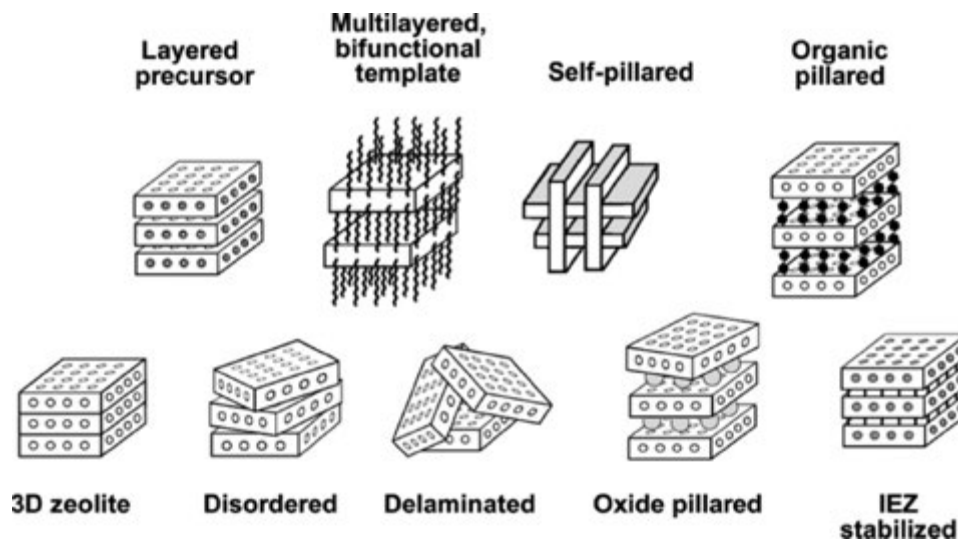


Fig. 4 Layered zeolite materials. Reproduced from Choi, M., Na, K., Kim, J., *et al.*, 2009. Stable single-unit-cell nanosheets of zeolite MFI as active and long-lived catalysts. *Nature* 461, 246–249.

restricted transport through a 10 membered ring zeolite (Jae *et al.*, 2011). The pore sizes are tailorable, defects in zeolites are controllable and methods have been established for structuring of zeolite into macroscopic bodies with hierarchical porosity, which have led to increased performance in many important catalytic reactions, such as cracking, isomerization, alkylation, biomass conversion, methanol to gasoline and olefins and oxidation reactions (Keane, 2003; Vermeiren and Gilson, 2009; Jae *et al.*, 2011; Serrano *et al.*, 2013; Čejka *et al.*, 2016). Zeolite have been designed and synthesized with pore sizes larger than 1 nm with high activity. The large pore zeolites of interest have pores larger than 12 ring zeolites. The hierarchical zeolites are synthesized by modifying the synthesis chemistry and/or by post treatment (Serrano *et al.*, 2013). The breakthrough in zeolite synthesis was made with the synthesis of layered crystals and even monolayer assemblies (Fig. 4). The layered zeolites have potential to replace currently used zeolites in alkylation, dehydration and condensation and less susceptibility to coking and deactivation during catalytic processes (Wang *et al.*, 2016a,b).

Solid Oxide Cell Technology

Structure – Property relationships in SOC

As described in the Section on “Solid Oxide Cells”, together with the material transport properties, the pore size, pore size distribution and pore volume are the key parameters in achieving an efficient performance from the electrodes and electrode support layers. In order to achieve a critical control over the porosity in these layers, several approaches are incorporated into the fabrication methods described in the Section on “Processing of Porous Ceramics”. Some of these approaches are use of poroformers, foaming in the slurries, and adjustment of ceramic power characteristics, partial sintering, reaction sintering and templating. Carefully tailored micro-structure (size, morphology and orientation of grains and pores, etc.) of porous ceramics has led to unique mechanical properties, which cannot be attained even in the dense materials.

Electrode support layers: The electrode support layers should facilitate the transport of the gas molecules to the reaction interfaces at the electrode-electrolyte interfaces, provide the mechanical stability and should possess the required electronic conductivity. Thus, these layers should have large enough pores for the easy gas transport, low enough pore volume to possess required mechanical strength and electronic conductivity, as both these are material volume dependent. Furthermore, the pore size distribution also influences the mechanical strength and conductivity. In addition, these layers should be free of any macro-defects as they severely affect the mechanical stability. Such requirements on the pore characteristics can be realized through the careful optimization of slurry formulations, use of pore formers, adjustment of ceramic powder physical characteristics (such as particle size, surface area) and optimizing the sintering parameters (Pihlatie *et al.*, 2009).

Electrodes: Both the fuel and oxygen electrodes should facilitate the transport of the gas molecules to the reaction interfaces at the electrode-electrolyte interfaces. These electrode structures do not bear any mechanical load and thus the mechanical strength of the layer is not critical. The electronic and ionic transport through the electrodes is a critical parameter in the efficiency of the electrode. Furthermore, the surface area of the electrode, particularly in the mixed electronic and ionic conducting electrodes, decides the reaction surface area and thus, the small pores (high surface area) are preferred. Higher reaction surfaces does result in higher electrochemical performance of the SOCs. Thus, the pores in the electrodes should be of the size that can easily transport the gases, while maintaining high surface area for the highest possible reaction surface area. The pore size, size distribution and pore volume becomes very critical, particularly for the electrodes that requires integration of additional electrocatalytically active materials. For example, the perovskite based fuel electrode materials discussed earlier may not possess sufficient electrocatalytic

activity and thus require integration of other material into these electrodes. Such requirements to enhance the electrochemical performance of the SOCs need the electrodes to have larger pore sizes and higher pore volumes so that these additional catalytic materials can be accommodated inside these pores.

Ceramic Membranes for Liquid and Gas Separation

Performance requirements and characterization of ceramic membranes

Porous ceramic membranes need to fulfill a couple of performance requirements, including mechanical robustness (mechanical strength), high thermal stability, permeability and selectivity. These properties can be determined by static and dynamic methods.

Dynamic methods, include the performance characterization in operation and can be described by few key performance indicators, the productivity (flux, permeability and permeance) and separation ability (including selectivity and separation factors). A detailed description of these parameters can be found elsewhere (Zwolinski *et al.*, 1949; Tan and Rodrigue, 2019).

With *static characterization methods* the microstructure (pore size, pore size distribution, microdefects), surface chemistry and mechanical properties of the membrane can be described. Membrane fabrication is a key step to control these membrane properties that may directly impact the final operational membrane performance. For further details, a couple of different techniques are available for microstructural characterization, including scanning electron microscopy (SEM), atomic force microscopy (AFM) and transmission electron microscopy (TEM) (Tan and Rodrigue, 2019), X-ray computer microtomography (micro-CT), nuclear magnetic resonance (NMR) and small angle neutron scattering methods (SESANS, MSANS) (Tylkowski and Tsibranska, 2015; Anovitz and Cole, 2015).

Relationship between processing, structure and performance of porous membrane layers

For achieving the desired properties of ceramic membranes for high performance in nanofiltration or gas separation, the careful, stepwise fabrication of defect-free hierarchical porous multilayer structures is of crucial importance. As described earlier, the most common membrane architectures consist of a porous support, intermediate layers and separation layers.

The membrane supports are usually prepared from micron sized raw powders by forming them into plates, monoliths, tubes or microtubes by using shaping methods, such as tape casting, slip casting, pressing, extrusion or spinning, and finally sintering them into macroporous bodies. In the case of extruded, tubular supports, wall thicknesses are in the range of millimeters to achieve sufficient mechanical strength with pore sizes usually in the range of several micrometers, supplying sufficient mechanical strength and high permeability (and low pressure drop). Such supports are usually not used directly for high performance separation of small particles in nm size or for gas molecules due to their large pore size and low selectivity and need to be coated with additional layers to gradually reduce the pore size towards the targeted membrane applications (see Fig. 2).

Intermediate and membrane separation layers are usually applied in 3 major steps: (1) the preparation of adequate slurries or sols, (2) the deposition of the layer by dip coating as interlayers or separation layers on the porous support tube and (3) separate thermal treatment of each dried slurry or gel layer. The number of layers that need to be applied on the membrane support, depends on the application requirements for the last layer, which is the membrane separation layer and its pore size determines the separation quality (see Fig. 1).

The permeability of the membrane depends on the porosity, pore tortuosity, pore morphology and thickness of the separation layer(s). Smaller pores and reduced layer thickness are required with increasing demand on the separation size, precision and selectivity from micro to nanofiltration and gas separation, requiring increasing demands on the quality of the coating processes.

In an asymmetric ceramic membrane, usually the first intermediate layer has the function to bridge the (tubular) support structure and the following separation layers with a slurry coating of ceramic particles that are large enough to avoid the penetration of the large pores and particles on the surface of the support and cover them homogeneously. This reduces the risk of the formation of coating defects, such as cracks or pinholes in the separation layers.

The most common way to adapt and process membrane separation layers towards more demanding commercial applications, such as microporous layers for nanofiltration or gas and vapor separation, is the use of carefully chosen sol-gel processes. Alternative coating processes have also been developed for the preparation of membrane layers for special materials and separation tasks, for example chemical vapor deposition (Nomura *et al.*, 2005), hydrothermal synthesis (Jiang *et al.*, 2004), anodic oxidation of alumina (Itoh *et al.*, 1996) and phase separation and leaching (Kukizaki and Nakashima, 2004).

The Sol-Gel method in combination with dip coating is the most common process to form ultrathin meso and microporous layers of ceramic materials with high (compositional) homogeneity, tailored pore size with narrow pore size distribution and stability under pressure and temperature. Depending on the requirements and fineness of the final membrane separation layer, two main routes can be distinguished for the Sol-Gel fabrication of thin film separation layers for ceramic membranes:

In the *colloidal Sol-Gel route*, the hydrolysis and condensation reaction of the precursor material(s) is relatively fast and done in aqueous solution by adjusting the reaction conditions (catalyst, pH, molar ratio of water and speed of addition) to achieve a fully hydrolyzed precursor. The fast condensation reaction results in the formation of particle growth and/or aggregation. For this reason, the control of very small sizes of the particles in the Sol in the nm range or below, which is required for the fabrication of microporous gas separation layers, is challenging.

In the *polymeric Sol-Gel route*, the hydrolysis and condensation of the precursor materials is slower because it is performed in organic solvents, using alkoxide precursors and slowly adding small amounts of water, resulting in partial hydrolysis and the

Table 1 Examples for materials, heat treatment and resulting pore diameter in different type of layers in asymmetric alumina-based membranes

Layer type	Sintering temperature range [°C]	Typical average pore diameter	Typical material
Support	1300–1500	1–10 μm	α -alumina
Slurry layer(s)	700–1300	0.1–1 μm	Boehmite or α -alumina
Sol-Gel layer(s)	600–1000	1 nm to 50 nm	γ -alumina and colloidal SiO_2
Sol-Gel layer	350–600	<2 nm	Polymeric SiO_2

formation of a more gel type network structure. Since the size of the particulates in the gel network is smaller, the polymeric Sol-Gel route, can lead to microporous separation layers, with pore sizes in the range of nanometers and below.

For the sintering of the membrane layers, preferably oxides with relative high melting point (oxides of alumina, silica, titania and zirconia) are chosen to ensure sufficient thermal stability during operation. These layers are then heat treated well below the melting point of the respective oxides to ensure neck formation between the fine particles during the initial phase of sintering. For the second stage of sintering primarily surface diffusion is promoted whereas grain boundary diffusion or bulk diffusion is suppressed to minimize pore growth.

Table 1 summarizes the typical sintering procedure for the different layers in a multi-layer alumina based asymmetric membrane, including materials, ranges of sintering temperatures, and pore diameters for the different layers.

Starting from a macro porous tubular α -alumina support, meso and microporous layers are applied by dip coating of alumina slurries and different alumina and SiO_2 sols and separate sintering. With each layer, the sintering temperature, the particle size, pore size and layer thickness are gradually reduced. During the debinding and sintering, the temperature profile of each layer needs to be adjusted very accurately to avoid the formation of any drying and sintering defects, for example the formation of larger pores, pinholes, cracks or delamination. The exact control of these coating and sintering steps is therefore essential to ensure a defect free microporous membrane layer with exact pore size (distribution) in the nm or Å range to achieve high selectivity and permeability of the membrane for example in nanofiltration or gas separation processes.

Summary and Outlook

Increasing demand for porous ceramics with improved performance in energy applications has already led to the development of new materials, advanced fabrication methods and resulting microstructures. However, new and emerging energy applications put increasing demands on porous ceramics with even better properties and performance based on the critical control of pore size and architecture, mechanical properties and chemical/thermal stability. Here, the tailoring of properties and precise control of the pore size, pore volume and microstructure by careful selection of materials and fabrication methods plays an important role to enable substantially new applications for porous ceramics or to help the breakthrough of new, emerging energy technologies. In energy applications, such progress has been demonstrated in the areas of catalysis, in ceramic membranes or in high temperature ceramic fuel cells and electrolyzers.

References

- Akhtar, F., Andersson, L., Ogunwumi, S., Hedin, N., Bergström, L., 2014a. Structuring adsorbents and catalysts by processing of porous powders. *J. Eur. Ceram. Soc.* 34, 1643–1666. doi:10.1016/j.jeurceramsoc.2014.01.008.
- Akhtar, F., Keshavarzi, N., Shakarova, D., *et al.*, 2014b. Aluminophosphate monoliths with high CO_2 -over- N_2 selectivity and CO_2 capture capacity. *RSC Adv.* 4, 55877–55883.
- Akhtar, F., Andersson, L., Keshavarzi, N., Bergström, L., 2012a. Colloidal processing and CO_2 capture performance of sacrificially templated zeolite monoliths. *Appl. Energy* 97, 289–296. doi:10.1016/j.apenergy.2011.12.064.
- Akhtar, F., Liu, Q., Hedin, N., Bergström, L., 2012b. Strong and binder free structured zeolite sorbents with very high CO_2 -over- N_2 selectivities and high capacities to adsorb CO_2 rapidly. *Energy Environ. Sci.* 5, 7664–7673. doi:10.1039/c2ee21153j.
- Alghamdi, H., Dakhane, A., Alum, A., *et al.*, 2018. Synthesis and characterization of economical, multi-functional porous ceramics based on abundant aluminosilicates. *Mater. Des.* 152, 10–21. doi:10.1016/j.matdes.2018.04.060.
- Alghamdi, K., Hargreaves, J.S.J., Jackson, S.D., 2008. Base catalysis with metal oxides. *Met. Oxide Catal.* 819–843. doi:10.1002/9783527626113.ch21.
- Al-Naib, U.M.B., 2018. Chapter 1 – Introductory chapter: A brief introduction to porous ceramic. In *Recent Advances in Porous Ceramics*. IntechOpen. doi:10.5772/intechopen.74747.
- Anovitz, L.M., Cole, D.R., 2015. Characterization and analysis of porosity and pore structures. *Rev. Miner. Geochem.* 80, 61–164. doi:10.2138/rmg.2015.80.04.
- Astruc, D., 2020. Introduction: Nanoparticles in catalysis. *Chem. Rev.* 120, 461–463. doi:10.1021/acs.chemrev.8b00696.
- Atkinson, A., Barnett, S., Gorte, R.J., *et al.*, 2004. Advanced anodes for high-temperature fuel cells. *Nat. Mater.* 3, 17–27. doi:10.1038/nmat1040.
- Tylkowski, B., Tsihranska, I., 2015. Overview of main techniques used for membrane characterization. *J. Chem. Technol. Metall.* 50 (1), 3–12.
- Brinker, C.J., 2013. Dip coating. In: Schneller, T., Waser, R., Kosec, M., Payne, D. (Eds.), *Chemical Solution Deposition of Functional Oxide Thin Films*. Wien: Springer-Verlag, pp. 233–261. doi:10.1007/978-3-211-99311-8_10.
- Brinker, C.J., Scherer, G.W., 2013. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*. Elsevier Inc. doi:10.1016/C2009-0-22386-5.
- Buekenhoudt, A., 2008. Stability of porous ceramic membranes. *Membr. Sci. Technol.* 13, 1–31. doi:10.1016/S0927-5193(07)13001-1.
- Brinker, C.J., 1988. Hydrolysis and condensation of silicates: Effects on structure. *Journal of Non-Crystalline Solids* 100 (1-3), 31–50.
- Cai, M., Liu, S., Efimov, K., *et al.*, 2009. Preparation and hydrogen permeation of $\text{BaCe}_{0.95}\text{Nd}_{0.05}\text{O}_{3-\delta}$ membranes. *J. Membr. Sci.* 343, 90–96. doi:10.1016/j.memsci.2009.07.011.
- Caro, J., 2011. Are MOF membranes better in gas separation than those made of zeolites? *Curr. Opin. Chem. Eng.* 1, 77–83. doi:10.1016/J.COCE.2011.08.007.
- Čejka, J., Morris, R.E., Serrano, D.P., 2016. Catalysis on zeolites – Catalysis science & technology. *Catal. Sci. Technol.* 6, 2465–2466. doi:10.1039/C6CY90042A.

- Chen, H., Fu, J., Zhang, P., *et al.*, 2018. Entropy-stabilized metal oxide solid solutions as CO oxidation catalysts with high-temperature stability. *J. Mater. Chem. A* 6, 11129–11133. doi:10.1039/C8TA01772G.
- Chen, Z., Li, Z., Li, J., *et al.*, 2019a. 3D printing of ceramics: A review. *J. Eur. Ceram. Soc.* 39, 661–687. doi:10.1016/j.jeurceramsoc.2018.11.013.
- Chen, H., Xiang, H., Dai, F.-Z., Liu, J., Zhou, Y., 2019b. Porous high entropy ($\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{B}_2$): A novel strategy towards making ultrahigh temperature ceramics thermal insulating. *J. Mater. Sci. Technol.* 35, 2404–2408. doi:10.1016/j.jmst.2019.05.059.
- Cheng, S., Huang, H., Ovtar, S., *et al.*, 2016. High-Performance Microchanneled Asymmetric $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95-6}\text{-La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-6}$ -Based Membranes for Oxygen Separation. *ACS Appl. Mater. Interfaces* 8 (7), 4548–4560. Available at: <https://pubs.acs.org/doi/abs/10.1021/acsami.5b10714>.
- Choo, T.F., Salleh, M.A.M., Kok, K.Y., Matori, K.A., 2019. A review on synthesis of multite ceramics from industrial wastes. *Recycling* 4, 1–11. doi:10.3390/recycling4030039.
- Chun-fang, X., Bing, H.A.N., 2019. Preparation of porous silicon nitride ceramics by microwave sintering and its performance evaluation. *J. Mater. Res. Technol.* 8, 5984–5995. doi:10.1016/j.jmrt.2019.09.073.
- Ciurans Oset, M., Nordin, J., Akhtar, F., 2018. Processing of macroporous alumina ceramics using pre-expanded polymer microspheres as sacrificial template. *Ceramics* 1, 329–342.
- Csicsery, S.M., 1984. Shape-selective catalysis in zeolites. *Zeolites* 4, 202–213. doi:10.1016/0144-2449(84)90024-1.
- Deville, S., 2008. Freeze-casting of porous ceramics: A review of current achievements and issues. *Adv. Eng. Mater.* 10, 155–169. doi:10.1002/adem.200700270.
- Dey, S., Dhal, G.C., Mohan, D., Prasad, R., 2019. Advances in transition metal oxide catalysts for carbon monoxide oxidation: A review. *Adv. Compos. Hybrid Mater.* 2, 626–656. doi:10.1007/s42114-019-00126-3.
- Dusselier, M., Davis, M.E., 2018. Small-pore zeolites: Synthesis and catalysis. *Chem. Rev.* 118, 5265–5329. doi:10.1021/acs.chemrev.7b00738.
- Ennaert, T., Van Aelst, J., Dijkmans, J., *et al.*, 2016. Potential and challenges of zeolite chemistry in the catalytic conversion of biomass. *Chem. Soc. Rev.* 45, 584–611. doi:10.1039/C5CS00859J.
- Hammel, E.C., Ighodaro, O.L.R., Okoli, O.I., 2014. Processing and properties of advanced porous ceramics: An application based review. *Ceram. Int.* 40, 15351–15370. doi:10.1016/j.ceramint.2014.06.095.
- Hedayat, N., Panthi, D., Du, Y., 2017. Fabrication of anode-supported microtubular solid oxide fuel cells by sequential dip-coating and reduced sintering steps. *Electrochim. Acta* 258, 694–702. doi:10.1016/j.electacta.2017.11.115.
- Hedin, N., Chen, L., Laaksonen, A., 2010. Sorbents for CO₂ capture from flue gas-aspects from materials and theoretical chemistry. *Nanoscale* 2, 1819–1841.
- Hooshmand, S., Nordin, J., Akhtar, F., 2019. Porous alumina ceramics by gel casting: Effect of type of sacrificial template on the properties. *Int. J. Ceram. Eng. Sci.* 1, 77–84.
- Hung, C.-M., 2010. Characterization and performance of Pt-Pd-Rh cordierite monolith catalyst for selectivity catalytic oxidation of ammonia. *J. Hazard. Mater.* 180, 561–565. doi:10.1016/j.jhazmat.2010.04.070.
- Hunns, J.A., Arroyo, M., Lee, A.F., *et al.*, 2016. Hierarchical mesoporous Pd/ZSM-5 for the selective catalytic hydrodeoxygenation of m-cresol to methylcyclohexane. *Catal. Sci. Technol.* 6, 2560–2564. doi:10.1039/C5CY02072G.
- Huo, W.-L., Zhang, X.-Y., Chen, Y.-G., *et al.*, 2016. Highly porous zirconia ceramic foams with low thermal conductivity from particle-stabilized foams. *J. Am. Ceram. Soc.* 99, 3512–3515. doi:10.1111/jace.14555.
- Huo, W.-L., Zhang, X., Hu, Z., *et al.*, 2019. Silica foams with ultra-large specific surface area structured by hollow mesoporous silica spheres. *J. Eur. Ceram. Soc.* 102, 955–961. doi:10.1111/jace.16115.
- Itoh, N., Kato, K., Tsuji, T., Hongo, M., 1996. Preparation of a tubular anodic aluminum oxide membrane. *J. Membr. Sci.* 117, 189–196. doi:10.1016/0376-7388(96)00063-4.
- Reed, J.S., 1995. *Principles of Ceramics Processing*, second ed. Wiley.
- Jae, J., Tompssett, G.A., Foster, A.J., *et al.*, 2011. Investigation into the shape selectivity of zeolite catalysts for biomass conversion. *J. Catal.* 279, 257–268. doi:10.1016/j.jcat.2011.01.019.
- Jiang, H., Zhang, B., Lin, Y.S., Li, Y., 2004. Synthesis of zeolite membranes. *Chin. Sci. Bull.* 49, 2547–2554. doi:10.1360/03wb0146.
- Jiang, S.P., Chan, S.H., 2004. A review of anode materials development in solid oxide fuel cells. *J. Mater. Sci.* 39, 4405–4439. doi:10.1023/b:jmsc.0000034135.52164.6b.
- Kaiser, A., Foghmoes, S., Chatzichristodoulou, C., *et al.*, 2011. Evaluation of thin film ceria membranes for syngas membrane reactors—Preparation, characterization and testing. *J. Membr. Sci.* 378 (1–2), 51–60. Available at: <https://www.sciencedirect.com/science/article/pii/S037673881000966X>.
- Kašpar, J., Fornasiero, P., Hickey, N., 2003. Automotive catalytic converters: Current status and some perspectives. *Catal. Today* 77, 419–449. doi:10.1016/S0920-5861(02)00384-X.
- Kaur, P., Singh, K., 2020. Review of perovskite-structure related cathode materials for solid oxide fuel cells. *Ceram. Int.* 46, 5521–5535. doi:10.1016/j.ceramint.2019.11.066.
- Kean, M.A., 2003. Ceramics for catalysis. *J. Mater. Sci.* 38, 4661–4675. doi:10.1023/A:1027406515132.
- Kosinov, N., Gascon, J., Kapteijn, F., Hensen, E.J.M., 2016. Recent developments in zeolite membranes for gas separation. *J. Membr. Sci.* 499, 65–79. doi:10.1016/j.memsci.2015.10.049.
- Kukizaki, M., Nakashima, T., 2004. Acid leaching process in the preparation of porous glass membranes from phase-separated glass in the $\text{Na}_2\text{O-CaO-MgO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ system. *Membrane* 29, 301–308. doi:10.5360/membrane.29.301.
- Kultayeva, S., Ha, J.-H., Malik, R., Kim, Y.-W., Kim, K.J., 2020. Effects of porosity on electrical and thermal conductivities of porous SiC ceramics. *J. Eur. Ceram. Soc.* 40, 996–1004. doi:10.1016/j.jeurceramsoc.2019.11.045.
- Lefevre, J., Mullens, S., Meynen, V., Noyen, J. Van, 2014. Structured catalysts for methanol-to-olefins conversion: A review. *Chem. Pap.* 68, 1143–1153. doi:10.2478/s11696-014-0568-0.
- Lefevre, J., Gysen, M., Mullens, S., Meynen, V., Noyen, J.V., 2013. The benefit of design of support architectures for zeolite coated structured catalysts for methanol-to-olefin conversion. *Catal. Today* 216, 18–23. doi:10.1016/j.cattod.2013.05.020.
- Li, H., Li, C., Wu, L., 2019. Porous cordierite ceramics prepared by foam-gelcasting technique: Phase evolution and properties. *J. Alloy. Compd.* 791, 690–699. doi:10.1016/j.jallcom.2019.03.225.
- Liu, P.S., Chen, G.F., 2014. Chapter One – General introduction to porous materials. In: Liu, P.S., Chen, G.F. (Eds.), *Porous Materials: Processing and Applications*. Elsevier, pp. 1–20.
- Liu, Y., Deng, J., Xie, S., Wang, Z., Dai, H., 2016. Catalytic removal of volatile organic compounds using ordered porous transition metal oxide and supported noble metal catalysts. *Chin. J. Catal.* 37, 1193–1205. doi:10.1016/S1872-2067(16)62457-9.
- Liu, Y., Zhu, W., Guan, K., Peng, C., Wu, J., 2018. Freeze-casting of alumina ultra-filtration membranes with good performance for anionic dye separation. *Ceram. Int.* 44, 11901–11904. doi:10.1016/j.ceramint.2018.03.160.
- Madaeni, S.S., Gheshlaghi, A., Rekabdar, F., 2013. Membrane treatment of oily wastewater from refinery processes, Asia-Pacific. *J. Chem. Eng.* 8, 45–53. doi:10.1002/apj.1619.
- Matoh, L., Žener, B., Korošec, R.C., Štangar, U.L., 2019. Chapter 27 – Photocatalytic water treatment. In: Pacheco-Torgal, F., Diamanti, M.V., Nazari, A., *et al.* (Eds.), *Nanotechnology in Eco-efficient Construction: Materials, Processes and Applications*. Woodhead Publishing, pp. 675–702. <https://doi.org/10.1016/B978-0-08-102641-0.00027-X>
- Mistler, R.E., Twinn, E.R., 2000. Tape Casting: Theory and Practice. Wiley. Available at: <https://www.wiley.com/en-us/Tape+Casting%3A+Theory+and+Practice-p-9781574980295>.
- Nomura, M., Ono, K., Gopalakrishnan, S., Sugawara, T., Nakao, S.I., 2005. Preparation of a stable silica membrane by a counter diffusion chemical vapor deposition method. *J. Membr. Sci.* 251, 151–158. doi:10.1016/j.memsci.2004.11.008.
- Ohji, T., Fukushima, M., 2012. Macro-porous ceramics: Processing and properties. *Int. Mater. Rev.* 57, 115–131. doi:10.1179/1743280411Y.0000000006.
- Ojuva, A., Akhtar, F., Tomsia, A.P., Bergström, L., 2013. Laminated adsorbents with very rapid CO₂ uptake by freeze-casting of zeolites. *ACS Appl. Mater. Interfaces* 5, 2669–2676. doi:10.1021/am400122r.

- Phair, J.W., Lundberg, M., Kaiser, A., 2009. Leveling and thixotropic characteristics of concentrated zirconia inks for screen-printing. *Rheol. Acta* 48, 121–133. doi:10.1007/s00397-008-0301-4.
- Pihlatie, M., Kaiser, A., Mogensen, M., 2009. Mechanical properties of NiO/Ni–YSZ composites depending on temperature, porosity and redox cycling. *J. Eur. Ceram. Soc.* 29 (9), 1657–1664. Available at: <https://doi.org/10.1016/j.jeurceramsoc.2008.10.017>.
- Puetz, J., Aegerter, M.A., 2004. Dip coating technique. In: Aegerter, M.A., Mennig, M. (Eds.), *Sol-Gel Technologies for Glass Producers and Users*. US: Springer, pp. 37–48.
- Ramachandran, D.K., Clemens, F., Glasscock, A.J., Søgaard, M., Kaiser, A., 2014. Tailoring the microstructure of porous MgO supports for asymmetric oxygen separation membranes: Optimization of thermoplastic feedstock systems. *Ceram. Int.* 40, 10465–10473. doi:10.1016/j.ceramint.2014.03.017.
- Ramachandran, D.K., Søgaard, M., Clemens, F., Gurauskis, J., Kaiser, A., 2015. Fabrication and performance of a tubular ceria based oxygen transport membrane on a low cost MgO support. *Sep. Purif. Technol.* 147, 422–430. doi:10.1016/j.seppur.2015.02.037.
- Rebrov, E.V., Seijger, G.B.F., Calis, H.P.A., *et al.*, 2001. The preparation of highly ordered single layer ZSM-5 coating on prefabricated stainless steel microchannels. *Appl. Catal. A Gen.* 206, 125–143. doi:10.1016/S0926-860X(00)00594-9.
- Richerson, D.W., Lee, W.E., 2018. *Modern Ceramic Engineering. Properties, Processing, and Use in Design*, fourth ed. New York: CRP Press Taylor & Francis Group. Available at: https://books.google.dk/books?hl=de&lr=&id=fDsPEAAQBAJ&oi=fnd&pg=PP1&dq=richerson+and+lee+and+ceramic&ots=uLKdQcFgv7&sig=jLNPqNqK8ixgv6TpQKwEMcu-Apw&redir_esc=y#v=onepage&q=richerson%20and%20lee%20and%20ceramic&f=false.
- Rotureau, D., Viricelle, J.P., Pijolat, C., Caillol, N., Pijolat, M., 2005. Development of a planar SOFC device using screen-printing technology. *J. Eur. Ceram. Soc.* 25, 2633–2636. doi:10.1016/j.jeurceramsoc.2005.03.115.
- Amin, S.K., Hassan, M., Abdallah, H., 2016. An Overview of Production and Development of Ceramic Membranes Polymeric membranes preparation and applications in water treatment and desalination View project Development of water desalination system View project. Available at: <https://www.researchgate.net/publication/308021080> (accessed 16.11.2020).
- Samaei, S.M., Gato-Trinidad, S., Altaee, A., 2018. The application of pressure-driven ceramic membrane technology for the treatment of industrial wastewaters – A review. *Sep. Purif. Technol.* 200, 198–220. doi:10.1016/j.seppur.2018.02.041.
- Sattler, J.J.H.B., Ruiz-Martinez, J., Santillan-Jimenez, E., Weckhuysen, B.M., 2014. Catalytic dehydrogenation of light alkanes on metals and metal oxides. *Chem. Rev.* 114, 10613–10653. doi:10.1021/cr5002436.
- Schmidt, C.G., Hansen, K.K., Andersen, K.B., *et al.*, 2016. Effect of pore formers on properties of tape cast porous sheets for electrochemical flue gas purification. *J. Eur. Ceram. Soc.* 36 (3), 645–653. Available at: <http://dx.doi.org/10.1016%2Fj.jeurceramsoc.2015.09.030>.
- Serrano, D.P., Escola, J.M., Pizarro, P., 2013. Synthesis strategies in the search for hierarchical zeolites. *Chem. Soc. Rev.* 42, 4004–4035. doi:10.1039/c2cs35330j.
- Sun, C., Stimming, U., 2007. Recent anode advances in solid oxide fuel cells. *J. Power Sources* 171, 247–260. doi:10.1016/j.jpowsour.2007.06.086.
- Sun, C., Hui, R., Roller, J., 2010. Cathode materials for solid oxide fuel cells: A review. *J. Solid State Electrochem.* 14, 1125–1144. doi:10.1007/s10008-009-0932-0.
- Sunarso, J., Baumann, S., Serra, J.M., *et al.*, 2008. Mixed ionic-electronic conducting (MIEC) ceramic-based membranes for oxygen separation. *J. Membr. Sci.* 320, 13–41. doi:10.1016/j.memsci.2008.03.074.
- Tan, X.M., Rodrigue, D., 2019. A review on porous polymeric membrane preparation. Part I: Production techniques with polysulfone and poly (vinylidene fluoride). *Polymers* 11, 1160. doi:10.3390/polym11071160.
- Tao, Z., Yan, L., Qiao, J., *et al.*, 2015. A review of advanced proton-conducting materials for hydrogen separation. *Prog. Mater. Sci.* 74, 1–50. doi:10.1016/j.pmatsci.2015.04.002.
- Tsuru, T., 2008. Nano/subnano-tuning of porous ceramic membranes for molecular separation. In *Journal of Sol-Gel Science and Technology*. Springer. pp. 349–361. doi:10.1007/s10971-008-1712-5.
- Tucker, M.C., 2010. Progress in metal-supported solid oxide fuel cells: A review. *J. Power Sources* 195, 4570–4582. doi:10.1016/j.jpowsour.2010.02.035.
- Twigg, M.V., Richardson, J.T., 2007. Fundamentals and applications of structured ceramic foam catalysts. *Ind. Eng. Chem. Res.* 46, 4166–4177. doi:10.1021/ie061122o.
- Van Aelst, J., Philippaerts, A., Bartholomeeusen, E., *et al.*, 2016. Towards biolubricant compatible vegetable oils by pore mouth hydrogenation with shape-selective Pt/ZSM-5 catalysts. *Catal. Sci. Technol.* 6, 2820–2828. doi:10.1039/C6CY00498A.
- van den Berg, G.B., Smolders, C.A., 1992. Diffusional phenomena in membrane separation processes. *J. Membr. Sci.* 73, 103–118. doi:10.1016/0376-7388(92)80121-Y.
- Védrine, J.C., 2017. Heterogeneous catalysis on metal oxides. *Catalysts* 7, 341. doi:10.3390/catal7110341.
- Vercauteren, S., Keizer, K., Vansant, E.F., Luyten, J., Leysen, R., 1998. Porous ceramic membranes: Preparation, transport properties and applications. *J. Porous Mater.* 5, 241–258. doi:10.1023/a:1009634305315.
- Vermeiren, W., Gilson, J.-P., 2009. Impact of zeolites on the petroleum and petrochemical industry. *Top. Catal.* 52, 1131–1161. doi:10.1007/s11244-009-9271-8.
- Voorhoeve, R.J.H., Johnson, D.W., Remeika, J.P., Gallagher, P.K., 1977. Perovskite oxides: Materials science in catalysis. *Science* 195, 827–833. doi:10.1126/science.195.4281.827.
- Gläser, R., Weitkamp, J., 2004. The application of zeolites in catalysis. In: Baerns, M. (Ed.), *Basic Principles in Applied Catalysis*. Springer, pp. 159–212.
- Wang, Z., Jiao, X., Feng, P., *et al.*, 2016a. Highly porous open cellular TiAl-based intermetallics fabricated by thermal explosion with space holder process. *Intermetallics* 68. doi:10.1016/j.intermet.2015.09.010.
- Wang, Y., Wang, R., Xu, D., *et al.*, 2016b. Synthesis and properties of MFI zeolites with microporous, mesoporous and macroporous hierarchical structures by a gel-casting technique. *New J. Chem.* 40, 4398–4405. doi:10.1039/C5NJ03387J.
- Wang, Y., Li, J., Wei, Z., 2018. Transition-metal-oxide-based catalysts for the oxygen reduction reaction. *J. Mater. Chem. A* 6, 8194–8209. doi:10.1039/C8TA01321G.
- Wu, Z., Kim, H.-S., Stair, P.C., 2008. Resonance raman spectroscopy – Θ -Al₂O₃-supported vanadium oxide catalysts as an illustrative example. In: David Jackson, S., Hargreaves, J.S.J. (Eds.), *Metal Oxide Catalysis*. Wiley, pp. 177–194. doi:10.1002/9783527626113.ch4.
- Xu, M., Yu, J., Song, Y., *et al.*, 2020. Advances in ceramic thin films fabricated by pulsed laser deposition for intermediate – Temperature solid oxide fuel cells. *Energy Fuels* 34, 10568–10582. doi:10.1021/acs.energyfuels.0c02338.
- Yin, X., Guan, K., Gao, P., Peng, C., Wu, J., 2018. A preparation method for the highly permeable ceramic microfiltration membrane – Precursor film firing method. *RSC Adv.* doi:10.1039/c7ra12314k.
- Zocca, A., Colombo, P., Gomes, C.M., Günster, J., 2015. Additive manufacturing of ceramics: Issues, potentialities, and opportunities. *J. Am. Ceram. Soc.* 98, 1983–2001. doi:10.1111/jace.13700.
- Zwolinski, B.J., Eyring, H., Reese, C.E., 1949. Diffusion and membrane permeability. *J. Phys. Colloid Chem.* 53, 1426–1453. doi:10.1021/j150474a012.

Joining of Advanced Ceramics

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Introduction

Joining is generally accepted as one of the key enabling technologies for the implementation of advanced ceramics. It facilitates the use of advanced ceramics by providing a means of manufacturing structures or components which cannot be made (commercially) in one piece, or which can be made less expensively, or with added functionality, via joining.

In the vast majority of applications for advanced ceramics there is a need to effect a joint in some way, i.e., to attach, fix, fasten or adhere one material/component to another. This can be the joining of relatively simple shapes of the same ceramic material to make a more complex geometry – and although there are examples of this, it is relatively rare. More common is the need to join dissimilar materials. Sometimes this can be dissimilar ceramics, but more frequently it involves the joining of a ceramic to either an organic polymer or a metal. There can be numerous reasons for this. Usually, there is a need for different functionalities in an assembly. A simple example would be a ceramic knife for domestic applications. The ceramic is needed as a blade for cutting, whereas the sheath for handling the knife is usually made from a cheaper and more easily formable material, such as a polymer. However, more commonly the ceramic must be joined to a metal. There are many examples of this in industry, i.e., in cutting tools, electrical insulators, and biomedical implants.

It cannot be overstated that if the joint is not suitable for the application for which it is intended, the component is very likely to fail prematurely in service, or even in manufacture.

There is a surprisingly wide array of methods to join ceramics to themselves and to other materials. Note, the term “welding” is avoided. Welding generally refers to joining processes in which both “parent” materials are substantially melted at the *faying surfaces*, i.e., the surfaces to be joined. A substantial heat affected zone (HAZ) is also produced. Such large-scale microstructural and physical disruption rarely occurs when joining ceramics.

Methods for joining ceramics range from mechanical attachment, such as bolting, screw threading and shrink-fitting, where joints are made without the formation of atomic or molecular bonds, to chemical methods, whereby a bond is formed via interatomic level interactions. In turn, chemical methods are usually sub-divided into solid-state and liquid-state methods. However, there are several processes which do not fit neatly into these relatively restrictive definitions and can be considered as hybrid techniques, such as ultrasonic bonding, which is a combination of mechanical and solid-state chemical bonding. For this reason, it may be convenient to consider a spectrum of joining technologies, such as the one shown in Fig. 1.

A number of joining processes are shown in Fig. 1; all are applicable to ceramic–metal combinations and most are applicable to ceramic–ceramic combinations. Fewer are applicable to ceramic–polymer combinations, usually because of the temperature limitations of organic polymers. It is the method of production of the interface between the materials which is considered in Fig. 1. Factors such as design and any differences in the coefficient of thermal expansion (CTE) are not considered. However, such factors are crucial, particularly when designing assemblies/components which must be fit for purpose. Joint design is discussed below.

Mechanical Methods

It is possible to join ceramics via mechanical methods, such as mechanical interlocking, bolts and/or screw threads (Fig. 2). Usually, such designs are only recommended if the final component does not experience arduous service conditions, such as thermal excursions or high shear/torque loading. Machining holes and threads into ceramics is costly, even if most of the work is done in the green (unfired) state. In addition, sharp changes in section and re-entry features, such as those associated with screw threads, should be avoided because they tend to act as stress concentrators. Exceptions to this general philosophy include ceramic knives and scissors (Fig. 2(b)) which frequently have plastic handles attached to a ceramic, most commonly zirconia or alumina, through a combination of mechanical fixing and organic adhesives.

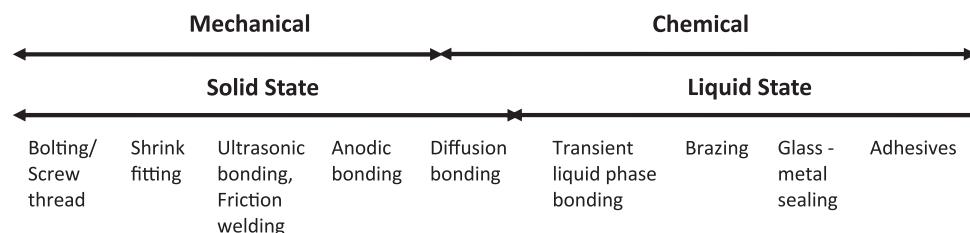


Fig. 1 The joining spectrum.

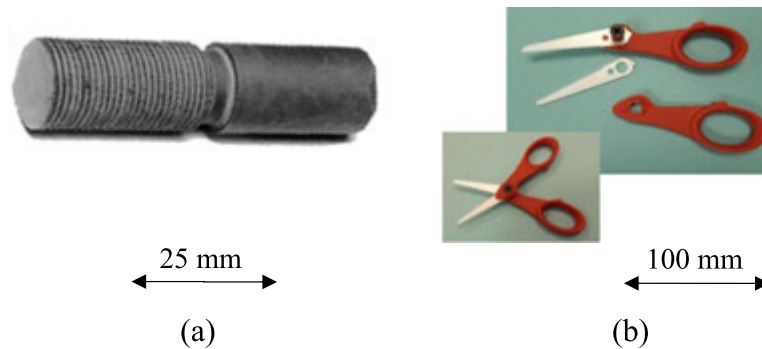


Fig. 2 (a) Silicon nitride rod with a machined-in screw thread and (b) zirconia scissors showing machined-in holes.

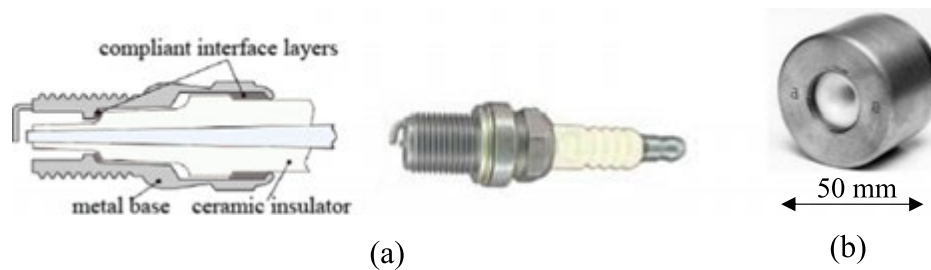


Fig. 3 (a) Automotive spark plug and (b) a wire drawing die with a zirconia insert.

By contrast, automotive spark plugs are manufactured using a mechanical fastening technique which utilizes the difference in CTE between a ceramic and a metal, i.e., shrink fitting. An outer steel casing is heated and placed around the ceramic (alumina) insulator. On cooling, this contracts around the ceramic, so clamping it and placing it in compression. The assembly is shown schematically in **Fig. 3(a)**. Note the presence of compliant interface layers, which in this case are made from aluminum, a low modulus material, in the form of inserts at key points, to absorb stress concentrations induced at sharp corners and changes of section.

Other examples of shrink fitting are found in general engineering as wire drawing dies using zirconia as the insert in a steel housing (**Fig. 3(b)**), and in the biomaterials sector as femoral heads in hip replacements.

Thermomechanical Processes (Hybrid Processes)

There are processes which are best described as thermomechanical, i.e., a hybrid between mechanical and chemical, in that they are produced as a combination of frictional heat and solid phase bonding. These processes are only viable for ceramic-metal combinations, and then only when the metal has a low elastic modulus. Examples include ultrasonic bonding and friction welding.

In ultrasonic bonding, a soft metal, such as aluminum, in the form of a thin foil (typically < 2 mm thick), is joined to a ceramic using an ultrasonic horn. The bond is formed using acoustic waves transmitted via the horn, with typical frequencies between 15–20 kHz and wavelengths of 20–30 μm , along with an applied pressure of 10–30 MPa and bond times of ~ 1 –10 s. During bonding, plastic deformation of the metal, coupled with rupture of surface oxide films, brings atomically clean metal into contact with the ceramic. Mechanical keying then occurs, along with some chemical interactions, to provide a bond. Typical applications are found in Na–S batteries, where Al is joined and sealed to β -alumina.

Friction welding, almost always referred to as a welding technology, although strictly incorrect as no melting of the parent material occurs, is similar to ultrasonic bonding in that a soft metal (again aluminum is the most common) is brought into contact with a ceramic. In this case, the metal, usually in the form of rod typically 1–4 mm in diameter, is rotated and then brought into contact within the ceramic at room temperature. Frictional heat is generated, producing high temperatures at the interface, sufficient to allow plastic deformation of the metal. Rotation then stops within a few seconds and a uniaxial pressure is applied. The metal plastically deforms, and a bond is formed. A flash (collar or upset) is also produced, which beneficially contains many of the surface oxides and inclusions present on the original surface of the metal; this is usually machined away.

Both ultrasonic bonding and friction welding processes are characterized by very sharp interfaces. Joining is postulated to occur via a mechanism in which a combination of local frictional heat and plastic deformation of the metal lead to the creation of a mainly mechanical bond, coupled with a diffusion bond, but only over a distance of a few atomic layers. Although there is little evidence of

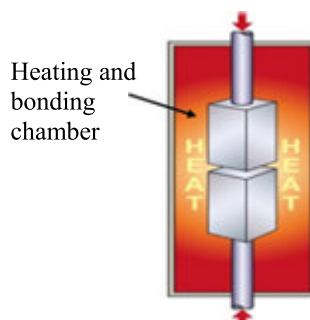


Fig. 4 Generic set-up for uniaxial diffusion bonding.

such diffusion or chemical bonding, bond strengths, even though they are modest, are higher than would be expected from purely “mechanical/friction” adhesion, i.e., “scrubbing” the relatively soft metal around irregularities or into pores in the ceramic surface.

Chemical Methods

There are several chemical methods available for the joining of ceramics. Conventionally, these are described either as solid-phase or liquid-phase, although there are also hybrid techniques. The chemical joining of ceramics, even to similar materials, is “difficult”. This is because of their strong ionic or covalent bonding and the low self-diffusivity of the constituent atoms. This contrasts with the nature of bonding in polymeric and metallic materials.

Therefore, by definition, one of the major considerations in the joining of ceramics to dissimilar materials is how to control the nature of the interface, i.e., the differences in atomic bonding. This consideration, combined with differences in CTE, which can cause excessive strains in a joint line if not designed correctly, are the two main concerns when implementing chemical methods for joining ceramics.

Solid Phase Methods

The hybrid thermomechanical processes discussed above for ceramic–metal combinations both rely on mechanical deformation of the metal, with a modest contribution from diffusion. Conventional solid phase methods for joining ceramics also rely on the same principle of initial mechanical deformation, but combined with a significant contribution from diffusion processes.

Ceramic–ceramic diffusion bonding

Diffusion bonding (DB) is a “solid phase/state” process that induces coalescence of the faying surfaces by the simultaneous application of heat and pressure over a period of time. The process does not involve large macroscopic deformation of the parent materials. Instead, it uses a combination of interdiffusion between the grains of the ceramic(s), together with a softening of any secondary intergranular (glassy) phases. In its optimized form, a diffusion bond between similar ceramics is invisible.

A simplification of the set-up for diffusion bonding is shown in [Fig. 4](#), where two blocks of the same ceramic material are to be uniaxially diffusion bonded.

When uniaxially diffusion bonding two similar ceramics, a “suitable” pressure is applied, generally between 1–20 MPa, at temperatures approximately 0.5–0.8 T_m , where T_m is the melting or softening temperature in K. Diffusion takes too long if the temperature is too low, and if the temperature is too high, there is the possibility of excessive plastic deformation of the whole assembly. Bond duration is dependent on load/pressure and temperature but is typically 30–120 min. The majority of bonds are produced in vacuum; better than 10^{-3} mbar is recommended.

A “suitable” load/pressure is one which allows micro-deformation at the faying surfaces, sufficient to eliminate asperities and bring a larger area of surface together in contact to allow diffusion, but not enough to cause macroscopic buckling or deformation of the whole assembly. The primary process parameters for diffusion bonding are time, temperature and pressure. Other factors such as surface cleanliness (in all chemical bonding processes, faying surfaces should be free from dirt, grease, fingerprints and any other contaminants) and “flatness” are also crucial.

It is important to understand the relationship between roughness and surface flatness, or waviness. For example, the way [Fig. 4](#) is drawn implies that the surfaces to be bonded are smooth, parallel and flat at an optical level, and this is indeed the ideal scenario. However, most machined surfaces have a bimodal distribution of surface roughness. There is the fine-scale surface roughness, frequently described in terms of asperities; this fine-scale surface roughness is usually measured using conventional techniques such as profilometry and represented as R_a . However, there is also the larger-scale roughness associated with undulating or wavy surfaces. These two surface distributions are shown schematically in different physical situations in [Fig. 5](#).

In the situation shown at (a) in [Fig. 5](#), interfacial contact is between two perfectly flat and parallel surfaces; this is the ideal scenario. At (b), the surfaces are parallel, but both contain fine-scale asperities. In principle, this sample should bond successfully,

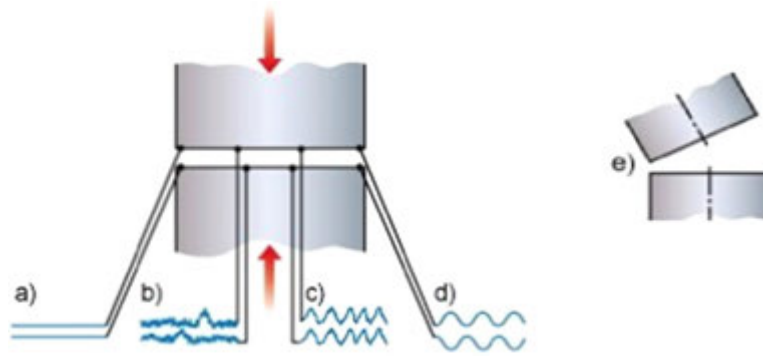


Fig. 5 Examples of surface profiles.

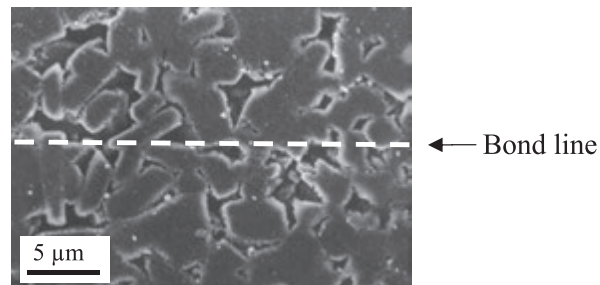


Fig. 6 Alumina–alumina diffusion bond produced using microwave radiation (2.54 GHz) as a heating source.

but there would be a defect in the upper surface: the particularly large depression in the upper surface shown in (b) would be retained after joining. At (c), both surfaces have fine-scale asperities, but both surfaces are too wavy. This bimodal distribution of fine-scale surface roughness and surface waviness is generally unacceptable. Smooth, but wavy, surfaces, such as those shown schematically in (d) will not bond satisfactorily because not enough material would come into contact at the faying surfaces irrespective of the R_a values of the two surfaces. Finally, if as in (e), the surfaces are misaligned, bonding will not occur other than at local contact points.

In practice, the scenario shown schematically in (b) is the most common. Although the scenario in (a) would be ideal, it is seldom economically viable to machine surfaces to this level of flatness. It is commonly accepted that R_a should be less than $0.4\ \mu\text{m}$. A diffusion bond between two 94 wt% Al_2O_3 ceramic rods is shown in **Fig. 6**.

Ceramic–metal diffusion bonding

Ceramics can be bonded to metals using solid phase diffusion bonding. The process parameters are broadly the same as those for ceramic–ceramic bonding, but the mechanism is slightly different because the ceramic has much higher compressive yield stress than the metal. Under these circumstances, the “harder” ceramic surface can force deformation of the asperities of the softer metal during the initial stages of the process. A schematic representation of the process is given in **Fig. 7**.

In (a) in **Fig. 7**, the hard ceramic surface and the comparatively soft metal surface come into contact at asperities of the two surfaces. In (b), the asperities on the metal surface are plastically deformed, so that the ceramic asperities indent (locally) the metal surface. Deformation of the metal continues, as in (c), coupled with diffusional mass transfer, leading to shrinkage of the interfacial voids between the metal and the ceramic. Further diffusional flow within the metal enables a bond to be formed, as in (d), with little or no residual porosity at the joint.

Use of thin interlayers to enhance diffusion bonding

The quality of a diffusion bond can usually be improved by increasing any or all of the primary process parameters, i.e., time, temperature and load/pressure. However, if increasing these parameters is likely to cause irreversible harm to the assembly/component, such as buckling, then the use of interlayers to enhance bonding should be considered. In this context, an interlayer refers to a material whose purpose is to promote solid state diffusion, and hence bonding. Usually, this is a thin layer of metal typically $< 25\ \mu\text{m}$ thick with a low elastic modulus and/or a high atomic diffusivity. (In a different context, the term interlayer can also refer to a material used to overcome CTE mismatches when bonding dissimilar materials. Under these circumstances, the interlayer is usually much thicker, up to several millimeters thick; this is discussed later in Joint Design).

Interlayers to enhance diffusion bonding can be applied as thin coatings $< 10\ \mu\text{m}$ in thickness via electroplating or vapor deposition/sputtering, for example, or they can be pre-placed in the form of foils, usually around $25\ \mu\text{m}$ thick. Chosen

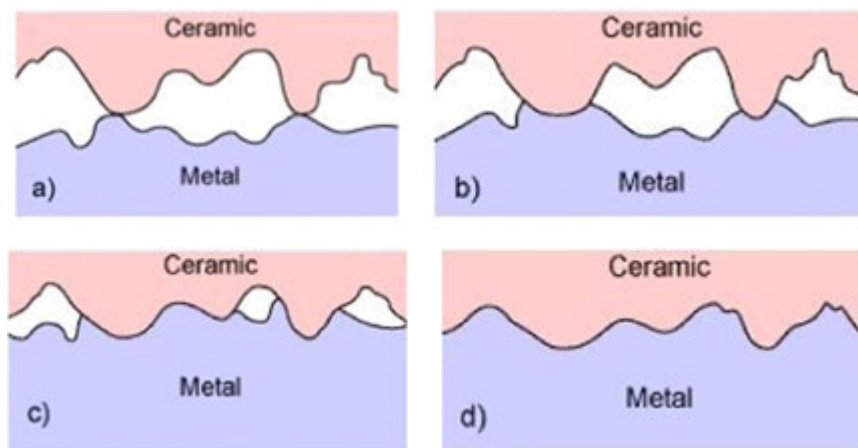


Fig. 7 (a)–(d): Sequence of events during ceramic–metal diffusion bonding.

correctly, interlayers can reduce bonding temperatures, negate excessive surface roughness and alleviate small differences in CTE. However, if a poor choice is made, interlayers can decrease the temperature capability and strength of the bond, and cause issues with corrosion.

Advantages and disadvantages of diffusion bonding

The main advantage of diffusion bonding is that joints can be produced with properties and microstructures very close to those of the parent materials. In addition, diffusion bonding produces no plastic (gross) deformation of the component, so that there is no need for subsequent machining.

The primary disadvantages are the thermal cycle time, even though a number of bonds can be produced simultaneously, and the relative expense of the diffusion bonding equipment, i.e., it is a specialized process.

Hybrid Chemical Processes

Anodic bonding

Anodic bonding has been used to join metals and/or semiconductors to glass with similar CTE, e.g., silicon to Pyrex. Also referred to as field-assisted bonding, electrostatic bonding and Mallory bonding, anodic bonding is similar to diffusion bonding. However, in this process, there is an additional parameter: a d.c. voltage is applied across the materials to be bonded during the process, which induces a strong electrostatic attraction at the interface.

The initial condition of the faying surfaces is critical to the process. Unless the surfaces mate very closely and are very smooth, the bond produced will not be hermetic. The surfaces must have $R_a < 0.05 \mu\text{m}$. The materials to be joined are then heated to a suitable temperature below the softening points of the materials, but high enough for ionic conduction to occur. A typical bonding temperature is about 450°C . A d.c. voltage (1000 V) is applied so that the metal or semiconductor component is at a positive potential relative to the glass, i.e., so that the metal or semiconductor is on the anode side and the glass is on the cathode side of the surfaces to be bonded.

At temperatures between $300\text{--}500^\circ\text{C}$, the cations in the glass, such as sodium ions, are relatively mobile, and on application of a voltage, move away from the interface towards the cathode. This produces a cation-depleted layer at the surface of the glass. The voltage drop across the gap between the silicon and glass causes an electrostatic force which helps to bring the two surfaces together. The force increases as the joint gap decreases, so there is a driving force to bring the two surfaces together. Therefore, where there are points of initial good contact, these will extend outwards, eventually bonding the whole surface. In silicon–Pyrex anodic bonds, oxygen migrating from the Pyrex “reacts” with silicon to form a $\sim 10 \text{ nm}$ thick amorphous silica interfacial reaction layer which constitutes the final bond.

Gas–metal eutectic bonding

A variant of ceramic–metal diffusion bonding occurs when, at the appropriate bonding temperature, the contact between the faying surfaces favors the formation of a liquid phase. This is generally known as gas–metal eutectic bonding.

The best known and most widely used type of gas–metal eutectic bonding is *direct copper bonding*. The process involves heating a copper foil in contact with alumina in a controlled, i.e., slightly oxidizing, gas atmosphere at a temperature of 1070°C . Under these conditions, the surface of the copper oxidizes and forms a eutectic liquid. This can be explained by referring to the phase diagram in Fig. 8. The eutectic liquid reacts with the alumina and, on solidification, a copper aluminate phase is formed at the interface, producing a bond between the copper and the alumina. The process is used extensively in the electronics industry as a means of joining high thermal conductivity copper to alumina substrates.

One variant of this technique is to use pre-oxidized copper; a second variant is to use pre-oxidized aluminum nitride as a high thermal conductivity substrate.

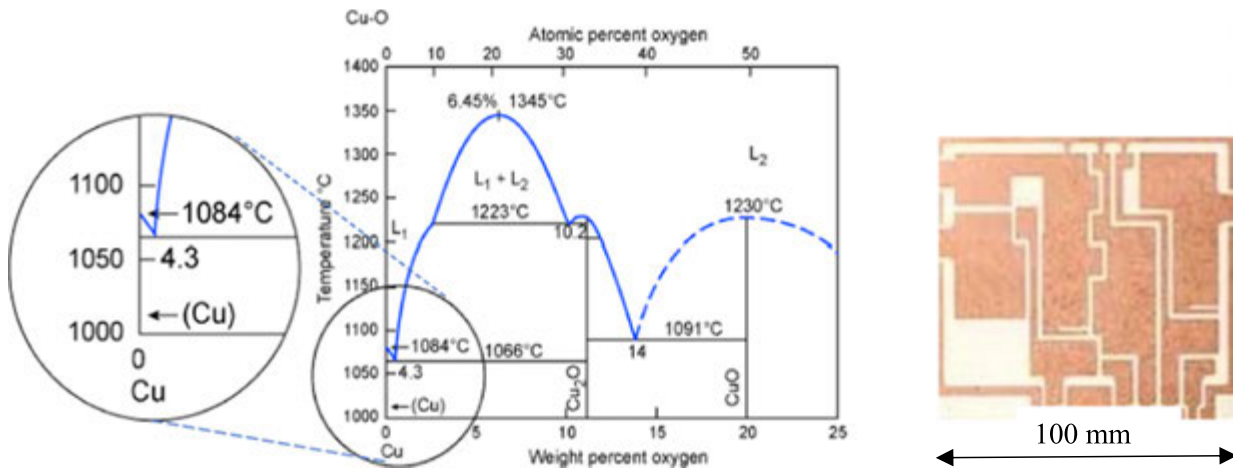


Fig. 8 Cu–O phase diagram and an electronic substrate (alumina–copper) made by direct copper bonding.

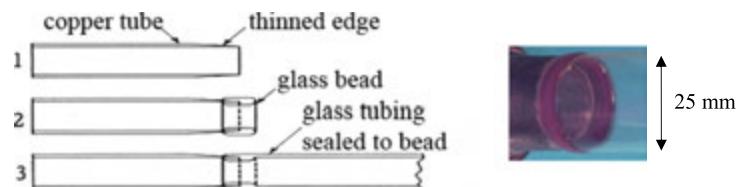


Fig. 9 The Houskeeper process and a typical component.

Glass-to-Metal Bonding and Sealing

Glass-to-metal sealing can be regarded as a liquid phase or fusion technique. The glass is heated to a semi-molten state above its glass transition temperature, T_g , while in contact with the metal. Bonding occurs via wetting and chemical reaction. Glass-to-metal seals are easy to manufacture either in batches or as part of a continuous process. They are relatively inexpensive to produce and can provide highly reliable, hermetic seals with good strength under moderate thermal and mechanical loadings.

The Houskeeper seal is one of the earliest examples of glass-to-metal seals for technical application. Houskeeper seals are used to join glass tubes to copper tubes. A schematic of the design of these seals is shown in Fig. 9 together with an example of a seal. The success of the design is reliant on the metal being relatively ductile; copper is the most common example. Typically, a copper tube is first tapered at the end to be joined. A glass is then brought into contact with the thinned metal and heated to above its softening point. On cooling, as the glass contracts onto the copper, the copper physically yields, absorbing any strains induced in the glass during the process. For this reason, the Houskeeper seal is an example of what is termed a “ductile” glass-to-metal seal.

Glasses can be bonded to metals to form hermetic seals for many other applications. These include electrical feed-through connectors, solid-oxide fuel cells, and biomedical implants. Electrical feed-through connectors are of particular commercial interest; these consist of electrically conducting metal pins enclosed within an electrically insulating glass, which in turn is enclosed in a metal housing. The function of the glass is to provide electrical isolation for the pins, both from other pins and also from the housing, and to protect the system from the external environment, and therefore moisture, for example. A glass-to-metal feed-through assembly is shown in Fig. 10.

There are a wide number of glasses capable of, and in some cases designed for, bonding to metal. Silicate-based glasses and glass-ceramics are commonly used in conjunction with a stainless steel housing and pins. For example, the lithium zinc silicate system has been widely reported as a glass exhibiting good sealing compatibility with stainless steels. An advantage of this system is that the CTE can be tailored, so permitting close match to a range of metals and alloys.

The sealing of glass to various materials, including other glasses, is dependent on the relationship between temperature and viscosity, the differing thermal expansion characteristics of the components to be sealed, the wetting and adhesion characteristics of the molten glass at sealing temperatures, and the chemical durability of the glass during service.

As well as the nature of any chemical bonding, the mechanical integrity of a glass-to-metal seal is dependent on the stress state at the interface(s). Glass-to-metal seals are usually categorized as either matched or compressive. In a matched seal, the CTE of each material is similar. However, in a compression seal, the CTE of the glass is higher than the pin, but lower than the housing. Compression seals are typically stronger than matched seals because the chemical bonding is accompanied by compressive hoop stresses in the glass from the surrounding metal. For matched seals, sealing is predominantly a result of good chemical bonding at the glass-metal interface.

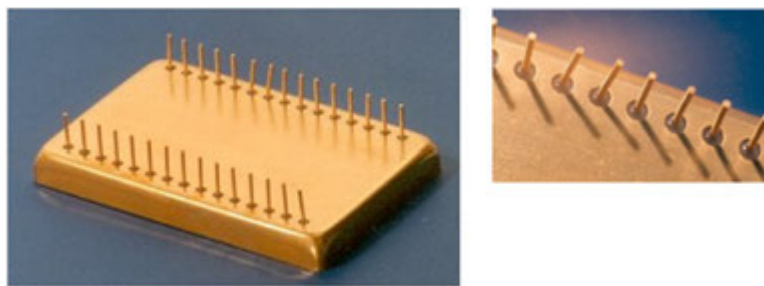


Fig. 10 Glass-to-metal feed-through assembly.

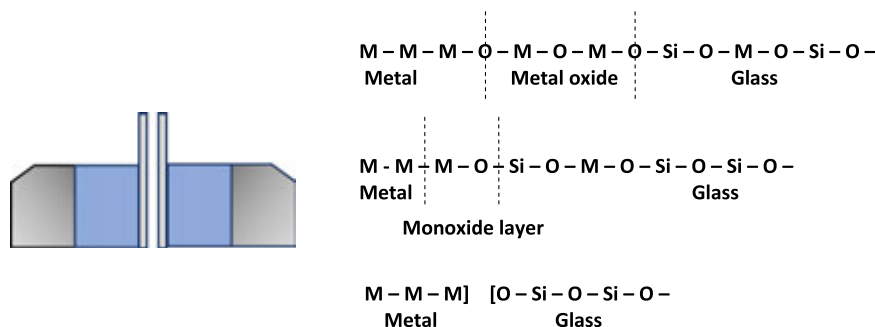


Fig. 11 Schematic of a single pin glass-to-metal seal with idealized bonding models.

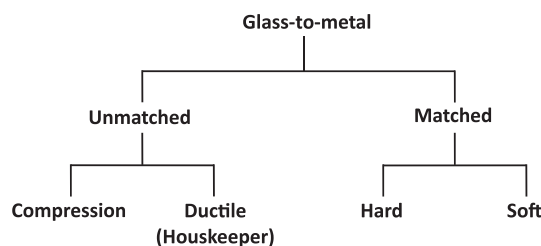


Fig. 12 Types and classification of glass-to-metal seals.

The glass parts are frequently supplied (commercially) as preforms, made by compressing glass powder into the desired shape. The metal pins should be capable of being oxidized so that the oxide layer produced adheres well to the metal. The oxide should also be able to be wet by, and be dissolved by, the glass at elevated temperature to produce a transition reaction layer between the glass and metal with good mechanical strength, as in the schematics in Fig. 11. This transition reaction layer constitutes the bond. It is important to control the thickness of the oxide on the metal. If the layer is too thin, then on dissolution into the glass, the bond with the parent metal will be lost. This will result in a weak bond and a probable loss of hermeticity. If the oxide is too thick, then on completion of the joining cycle, an excessive amount of oxide may remain undissolved, leading to a relatively weak bond.

Seals are generally described and referred to in terms of: the geometry of the metal parts, type of metal or alloy, type of glass, type of joining method, the fabrication technique, or relative thermal expansion of the glass and metal (Fig. 12). The most frequently used classification is based on the last of these; this is then sub-divided based on the type of glass, type of metal, and so on. Matched seals are sub-divided according to the expansion of the glass, and therefore the metal or alloy. Glasses such as borosilicate glasses and vitreous silica with CTEs $< 6 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ are designated hard glasses. Those such as soda-lime-silica glasses with CTEs $> 6 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ are designated soft glasses.

Liquid Phase Methods

The most widely used methods for joining ceramics are based on liquid phase processes whereby a third body (the joining medium or adherend) is placed between the faying surfaces. There are a range of such technologies and media available for these methods, ranging in temperature capability from organic adhesives to metallic solders and brazes, glasses and glass-ceramics and ceramic adhesives.

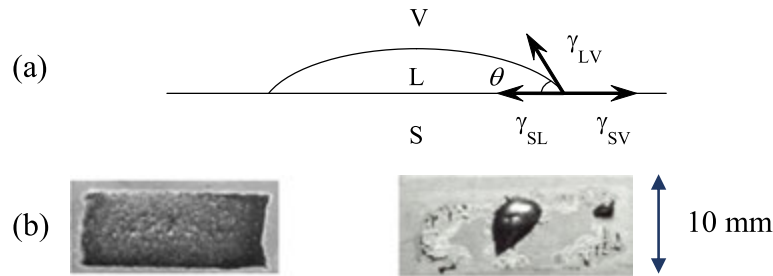


Fig. 13 (a) A spherical cap of liquid, L, in equilibrium, on the surface of a solid, S, above which there is a gaseous region, V, likely to contain the vapor of the liquid, (b) examples of wetting on silicon nitride with Ag–Cu–Ti (left-hand side) and Ag–Cu eutectic (right-hand side).

In nearly all cases the joining medium is placed between the surfaces to be joined and the assembly is heated. This is either to cure the medium, in the case of organic adhesives, and/or melt it, in the case of solders and brazes, to produce the bond. Liquid phase bonding has many practical advantages. Probably the most important of these is the ability of the liquid to be able to flow and fill the joint gap at the faying surfaces completely, even if the individual surfaces are relatively rough and there are relatively large voids in the contact region. Some degree of surface roughness is actually desirable in terms of mechanical keying for strength in shear, particularly for organic adhesives and inorganic “ceramic” adhesives.

In general, liquid phase bonding is quicker than diffusion (solid-state) bonding. However, it should be appreciated that it is common for the joint created in liquid phase bonding to be the weakest link in the assembly. It should also be appreciated that the ability of the liquid to flow over and “wet” the surfaces is critical in enabling bonds of sufficient strength to be formed. Most liquids in contact with a ceramic surface will tend to ball-up. This is rarely advantageous. Therefore, before the various liquid phase methods are described for advanced ceramics, it is relevant to highlight those aspects of wetting behavior of liquids on solids, and particularly ceramics, which are of relevance.

Fundamentals of wetting

As mentioned above, a liquid on the surface of a ceramic will tend to ball up. Therefore, it is necessary to induce the liquid to wet and flow across the surface of the ceramic. A suitable diagram to use to describe wetting of a solid by a liquid is shown in Fig. 13(a). In this diagram, a spherical cap of liquid, L, is in contact with a solid, S, above which there is V, the precise nature of which depends on the ambient environment, but it is usually air, a vacuum or inert gas, which, in reality, is also likely to contain vapor of the liquid. Experiments undertaken to examine wetting of liquids on solids, particularly in the context of liquid metals on ceramics, are termed sessile drop experiments. Examples of results from such sessile drop experiments are shown in Fig. 13(b).

Atoms at a surface of a liquid or solid are deprived of some of their neighbors relative to those in the interior of the liquid or solid, as a consequence of which there is an energy penalty for liquids and solids associated with the creation of a surface in contact with a vacuum, or in contact with another liquid or solid. These energy penalties are known as surface energies, γ , defined as the work that can be obtained from the destruction of unit area of surface, with units of N m^{-1} , i.e., a force per unit length, as shown in Fig. 13(a). The magnitudes of surface energies are determined by the appropriate intermolecular forces; typically, those for metals and ceramics are at least an order of magnitude greater than for organic molecules and polymers.

From Fig. 13(a), treating the surface energies as forces per unit length and resolving horizontally,

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

(Young's equation), where θ is the equilibrium contact angle. For L to wet S, θ should be as low as possible. By convention, $\theta < 90^\circ$ is considered to define a wetting condition, whereas $\theta > 90^\circ$ is considered non-wetting.

Another useful concept is the *work of adhesion*, W_A , which is related to the surface energies according to the Dupré equation. This is the work per unit area which has to be done to separate the liquid from the solid, and is equal to the lowering of the overall free energy per unit area through wetting:

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$

An interface is stable when W_A is positive, i.e., forming the interface lowers the total free energy per unit area of the system. In terms of the contact angle θ , W_A can be written as the Young–Dupré equation:

$$W_A = \gamma_{LV}(1 + \cos \theta)$$

The situation shown in Fig. 13(a) and described by the Young–Dupré equation is an over-simplification for a number of liquid phase methods for joining advanced ceramics because it does not take into account any chemical reactions which might occur between the metal and ceramic. If a reaction takes place, one or more new compounds can form, which may well enhance wetting and adhesion, as in active metal brazing.

Organic adhesives

Adhesives, “glues” or “cements” are non-metallic compounds which are able to spread over a surface to be joined. Therefore, for such joining media when in their liquid form, $\theta < 90^\circ$. It is usual not to have to manipulate the relevant surface energies to achieve wetting. However, prior to joining, the faying surfaces should be cleaned, so that they are free from organic and inorganic contaminants such as dust, moisture or weakly adsorbed organic material.

In general, an organic adhesive is a polymeric material having chemical and physical properties differing from those of the base materials, placed at their faying surfaces, to join the materials together as a result of the attractive forces of this polymeric material.

Polymer-based, organic adhesives represent a relatively straightforward method of joining ceramics to a range of metals, ceramics and other polymeric (plastic) materials. A range of organic adhesives are available, based predominantly on epoxy resins, acrylic adhesives, cyanoacrylate adhesives (“superglues”) and silicones. Such adhesives can be used in applications where the interface (adhesive) service temperature is below $\sim 200^\circ\text{C}$. Above this temperature, unless the adhesive is very well protected, it will char and degrade.

Despite their limitations, organic adhesives offer several advantages. From a commercial perspective they are usually relatively low cost and easy to apply, requiring little or no special equipment or training. From an engineering perspective, an organic adhesive tends to distribute an applied load evenly along the bond-line. The relatively low elastic modulus of organic adhesives enables them to accommodate thermally induced strains. Organic adhesives find use mostly in the traditional ceramics and electronics and photonics sectors, and for other ambient temperature applications such as ceramic knives, in which partially stabilized zirconia blades are joined by organic adhesives to handles made from a variety of materials.

Soldering and brazing

As the temperature requirements of an interface increase, soldering and brazing find widespread use. Typical applications are in machining to bond cutting tools to suitable substrates and in the power electronics industry to join ceramic substrates to copper heat sinks. Soldering and brazing are processes in which a metal or alloy is placed in between the faying surfaces. The metal is frequently in the form of a foil $\sim 50\text{--}100\ \mu\text{m}$ thick. These foils are available commercially, as are equivalent pastes and powders.

The fundamental difference between soldering and brazing is the melting point or liquidus of the material. If the liquidus is below 450°C , the process is termed soldering, while if the liquidus is above 450°C , the process is termed brazing. The bond is assembled and then heated, usually in a vacuum. On heating, the solder or braze melts and a bond is formed. The key is the ability of the solder or braze to wet the ceramic.

Metallization – methods of making a ceramic surface wettable by a liquid metal

Key to the success of liquid phase bonding methods is the ability of the interlayer material to wet and react chemically with the faying surfaces.

There are four basic approaches to induce a liquid metal to wet a ceramic surface. These are:

- (1) The metal hydride process;
- (2) Vapor deposition techniques;
- (3) Sintered metal powder processing (SMPP);
- (4) Active metal brazing (AMB).

In the first of these processes, a paint, typically titanium hydride, together with a powdered solder or copper is deposited onto a ceramic and then heated in an inert atmosphere to produce a metallized coating on the ceramic. In the second of these approaches, a thin layer of metal is deposited onto the ceramic using vapor deposition from a plasma, i.e., by sputtering, rendering it wettable. However, these two techniques are rarely used commercially. By far the most dominant processes are SMPP and AMB.

Sintered metal powder processing (SMPP)

There are various metal powder combinations possible in this method. Here, the principle is to metallize the surface of the ceramic using a metal powder, with or without additives. Once metallized, the ceramic can be bonded to another using a conventional braze free of an active element such as Ag–28 wt% Cu. The dominant process is the Mo–Mn process, known as the moly-manganese process.

There are a number of ways in which the moly-manganese process can be implemented. One method is to begin with a powder slurry consisting of mixed silica glass, molybdenum and manganese to coat the surface of the ceramic. This slurry can be applied by a number of methods such as spraying, brushing or silk screening. The ceramic is then sintered at $1200\text{--}1500^\circ\text{C}$ for about 30 min in a wet hydrogen atmosphere, and then nickel plated and re-sintered at $800\text{--}950^\circ\text{C}$ in a hydrogen atmosphere for 30 min. Typically, the ratio of molybdenum powder to manganese powder is 4:1 by weight. A wet hydrogen atmosphere is one in which $p_{\text{H}_2\text{O}}$ is significant, e.g., a partial pressure of $10^2\text{--}10^3\ \text{Pa}$ or even higher.

The moly-manganese process produces a metallization layer interfaced to an outer layer of molybdenum, together up to $\sim 50\ \mu\text{m}$ thick, adhered to nickel “flash” $\sim 1\text{--}2\ \mu\text{m}$ thick. During the first sintering step, the manganese-containing components of the slurry react with the underlying ceramic to produce glassy phases within the metallization layer which bond both to the underlying ceramic and to the metallic molybdenum within the metallization layer. An example of Mo–Mn metallization is shown in Fig. 14(a); here, the metallization layer and associated nickel flash are together $< 5\ \mu\text{m}$ in thickness.

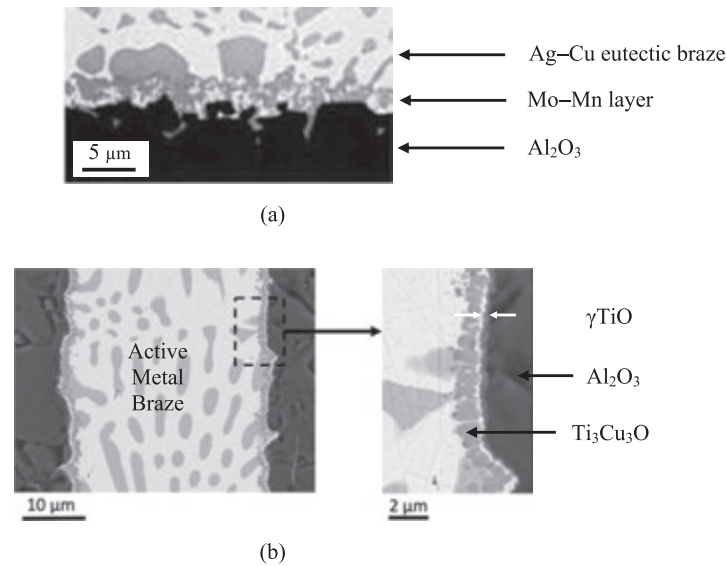


Fig. 14 (a) Mo-Mn metallization interface between Al₂O₃ and Ag-Cu eutectic braze, and (b) interface between an active metal braze and a 99.7 wt% Al₂O₃.

Table 1 Advantages and disadvantages of methods used to render ceramics wettable

	Advantages	Disadvantages
Metal hydride Vapor Deposition	Easy to apply Wide range of materials and compounds can be deposited	Difficult to produce at commercial scale Suitable equipment required
SMPP/Mo-Mn	Very reliable, high strength	Multi-step process Designed for alumina ceramics with secondary glassy phases present
AMB	Easy to use Reliable, with high strength Suitable for oxide and non-oxide ceramics	Braze spread can be difficult to control

Active metal brazing (AMB)

This process is derived from the hydride process. It was recognized that the hydrogen played relatively little part in the actual metallized layer. Instead, it was realised that the titanium component was critical and acted as an “active” element. Subsequent development of this principle has led to the development of a number of active metal brazes where the active metal is ~2–5 wt% of the total braze. Commercially, Ti is the dominant active metal in active metal brazes, but Zr and Hf are also available as active metals.

Until very recently, the moly-manganese process was the dominant liquid phase process for the bonding of engineering ceramics because of its reliability and known provenance. Its disadvantage is that it is a multi-step process requiring specialized equipment which has associated with it time and expense. Hence, over recent years, the use of active metal brazing as a liquid phase brazing process has become increasingly popular. The advantages and disadvantages to each process are summarized in [Table 1](#).

Soldering of ceramics

Soldering of ceramics can be accomplished using low melting point metals and eutectic alloys, modified either by the addition of active elements into the alloy, or by the deposition of a thin film of an active metal on the ceramics together a thin film of solder.

One group of solders are based on Sn-rich Sn-Ag-Ti alloys, which may contain 1.5–4 wt% Ti. These solders make use of the eutectic at Sn–3.5 wt% Ag at 221°C in the Sn-Ag phase diagram. Some solders have been developed for use in air. A key aspect of such technology is that the molten active solder must have its surface disrupted by mechanical means to enable wetting and bonding, because otherwise wetting is prevented by the oxidation of the surface of the solder when soldering in air. Other solders have been formulated and patented based on tin, indium, cadmium and bismuth either by themselves or in combination with tin as the majority components of the solder together with silver, an active metal such as titanium, gallium and a lanthanide such as cerium.

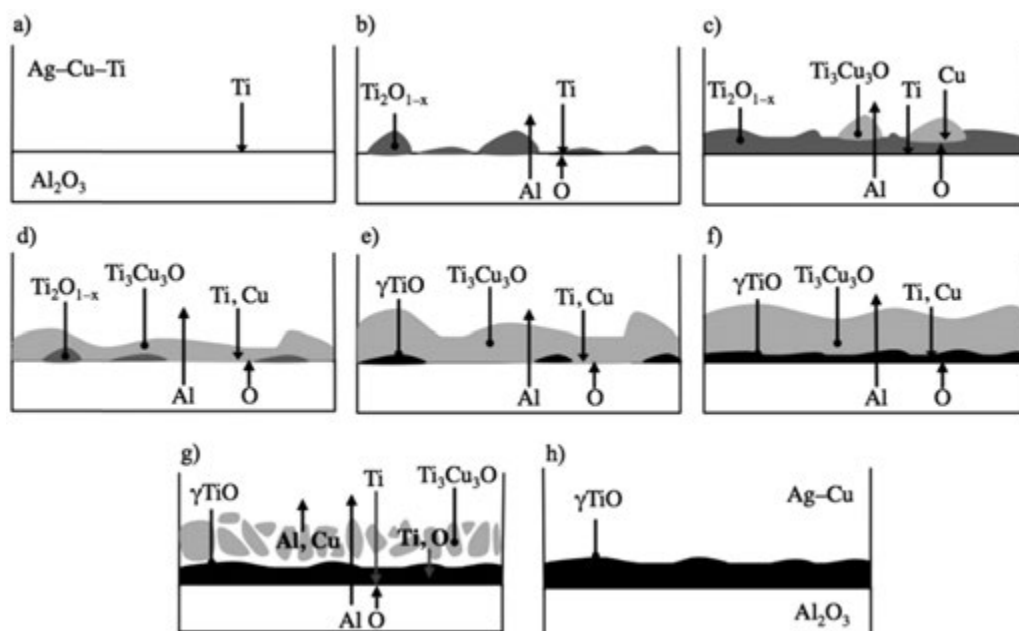


Fig. 15 Evolution of an alumina/Ag-Cu-Ti/alumina joint.

Brazing of ceramics

Brazes are usually referred to in terms of the main element, e.g., Ag-based brazes, Cu-based brazes and Au-based brazes. This leads naturally to a designation in terms of temperature capability. These are brazed in a vacuum atmosphere. To produce the bond the ceramic must either be metallized or an active metal used. Both the Mo-Mn metallization process and AMB are common. Typical microstructures produced are shown in Fig. 14.

The most commonly used active metal brazes are based on Ag-based alloys; these are also the most widely researched family of braze materials. The standard alloy is the Ag-28Cu (wt%) eutectic composition alloy which melts at 780°C. A reactive element such as Ti can be incorporated into the braze to produce the active metal brazes. A schematic of how the various interfacial phases produced during brazing of alumina by Ag-Cu-Ti brazes is shown in Fig. 15. In practice, the choice of time and temperature for optimal brazing of alumina to alumina using a Ag-Cu-Ti active braze is determined by having sufficient chemical reaction that there is a continuous film of both γTiO and $\text{Ti}_3\text{Cu}_3\text{O}$ formed at the Ag-Cu-Ti/alumina interface. A rule of thumb of 30°C above the liquidus temperature for 15–30 min achieves this optimal microstructure, but this can vary according to sample size. When brazing alumina to a metallic alloy such as Kovar®, Fe-29Ni-17Co (wt%), which has a similar CTE to alumina, the conditions for brazing alter because of the affinity of titanium in the braze for iron and nickel in the Kovar – the brazing temperature needs to be closer to the liquidus temperature, e.g., 10°C above, and the brazing time shorter, e.g., 5 min.

Referring to Fig. 15, the microstructural evolution is as follows: (a) Melting of the active metal braze facilitates diffusion of Ti to the surface of the sapphire. (b) $\text{Ti}_2\text{O}_{1-x}$ particles nucleate on sapphire to form a broken layer, with Al diffusing into the active metal braze. (c) $\text{Ti}_3\text{Cu}_3\text{O}$ particles nucleate on a continuous $\text{Ti}_2\text{O}_{1-x}$ layer. (d) Growth of $\text{Ti}_3\text{Cu}_3\text{O}$, primarily parallel to the sapphire surface, into a continuous layer with decomposition of $\text{Ti}_2\text{O}_{1-x}$. (e) Nucleation of γTiO between $\text{Ti}_3\text{Cu}_3\text{O}$ and the sapphire. (f) Formation of a continuous γTiO layer. Holding at the peak temperature for long periods of time results in (g), decomposition of $\text{Ti}_3\text{Cu}_3\text{O}$ and intergranular diffusion of Ti through the $\text{Ti}_3\text{Cu}_3\text{O}$ layer to facilitate rapid growth of γTiO , and finally h) a single thick continuous γTiO layer on the sapphire following complete decomposition of the $\text{Ti}_3\text{Cu}_3\text{O}$.

A variant on AMB uses high-entropy alloys, such as those based on CoFeCrNiCu; work on evaluating such alloys for joining ceramics is still very much at a preliminary stage of research.

Inorganic “ceramic” adhesives

Inorganic adhesives are usually silicate or phosphate-based binders incorporating ceramic particles, most commonly alumina, zirconia and magnesia. Such adhesives are suitable for applications where the components to be joined will only be subjected to very low levels of stress and where hermeticity is not a requirement. Their advantages are that they offer excellent chemical, electrical and high temperature resistance.

The high thermal loading encountered in most ceramic adhesive applications means that the joint design should take into account the mismatch in the CTEs between the inorganic adhesive and the materials to be bonded. Further design considerations should recognize the relatively poor shear strength of these adhesives, and also maximize the length/area of the bond line to distribute the stresses. Inorganic adhesives are solid particles suspended in a liquid matrix, i.e., a paste. A thickness of 200–500 μm is generally recommended in liquid form. After curing under a suitable applied load, this deposited thickness of adhesive should

produce a joint region 20–50 μm in thickness in service. Too thin a layer of adhesive prior to curing will inhibit uniform adhesion across the joint, while too thick a layer will result in cohesive failure within the cured ceramic adhesive. Surfaces to be joined should be etched, abraded or oxidized beforehand to ensure as good a bond as possible is produced.

Testing of Ceramic-Containing Joints

Mechanical testing provides information on the strength of a bond. Conventional tests include tensile testing, bend testing (3-point and 4-point) and shear testing. There are “standards” for testing ceramic–ceramic bonds. The most well-known and used is ASTM F19 “Standard test method for tension and vacuum testing metallized ceramic seals” which is used for testing the hermeticity of brazed joints, testing either the brazing operation or the metallization. The same samples can also be tensile tested. Samples used for this standard are shown in Fig. 16. These samples are relatively easy to produce and readily tested. Care must be taken not to introduce any stress concentration or bending when in the test rig.

An asymmetrical four-point flexure test method is described in ASTM C1469 “Standard Test Method for Shear Strength of Joints of Advanced Ceramics at Ambient Temperature”. The test method is intended for low-intermediate joint strengths. Joints with high strength should not be tested by this test method.

The mechanical testing of ceramic-containing bonds is extremely difficult and data produced must be carefully considered. This is particularly true for ceramic-to-metal combinations where the “strength” can be affected significantly by the mismatch in CTE, and therefore the contribution of residual stresses to the applied loads to failure. Consequently, it is very important to know the bond area and bond geometry when examining and comparing the strengths of ceramic–metal bonds. This is also the reason it is not feasible to create a single standard for the testing of ceramic–metal bonds. Direct comparison of mechanical test data from different studies should only be made when each test has used the same testing techniques and the same sample preparation.

In terms of non-destructive testing (NDT) there are no reliable techniques available because the critical flaw size within the interface is too small for detection. It is possible to model ceramic-containing bonds, at least at the macro scale. Most work considers the levels of strain induced on cooling from a bonding temperature. This gives a good indication of where the highest strains will be located. It also allows an effective method of assessing different joint designs. However, few models consider the effect of new interfacial reaction products.

Joint Design

There are two main obstacles to overcome when joining ceramics, particularly to dissimilar materials such as metals. The first is one of chemical compatibility, which, in general, can be controlled. The discontinuity between the atomic bonding in ceramics and metals can be microstructurally engineered, leading to the creation of a suitable interfacial chemistry.

The second major issue is that of mismatch in CTE. Most ceramics have CTEs between that of silicon carbide, $3 \times 10^{-6} \text{C}^{-1}$, and that of zirconia, $11 \times 10^{-6} \text{C}^{-1}$, whereas most metals have CTEs in the region of $13\text{--}18 \times 10^{-6} \text{C}^{-1}$. It is this CTE mismatch which is probably the single biggest hurdle in ceramic-metal joining, regardless of the process. A brazed joint between disks of silicon nitride and stainless steel is shown in Fig. 17. There is evidence from microstructural evaluation of a strong chemical bond,

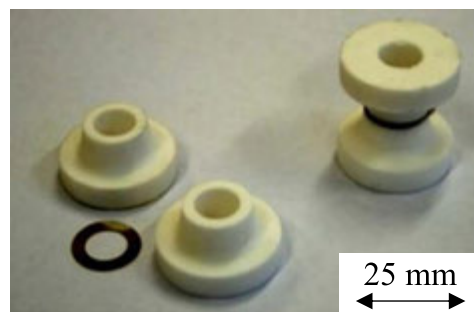


Fig. 16 Test samples used for assessing brazed joints (ASTM F19).

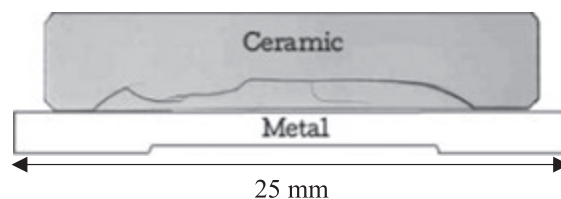


Fig. 17 A brazed joint showing a “dome crack” in silicon nitride (ceramic) due to CTE mismatch.

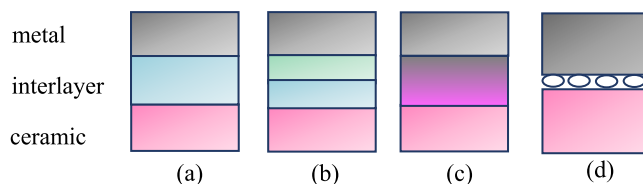


Fig. 18 Various designs for interlayers to overcome CTE mismatch.

so strong that the tensile strains induced in the silicon nitride as a function of cooling from the brazing temperature have caused it to fail. The “dome crack” observed in Fig. 17 is a classic failure due to CTE mismatch.

The problem of CTE mismatch may be overcome by introduction of interlayers (or shims) up to several millimeters thick of material, usually metallic, with appropriate CTEs and elastic modulus, and then bonding via techniques such as diffusion bonding or brazing. Some very simple design concepts for interlayer containing bonds are shown in Fig. 18. Single interlayers are the simplest (Fig. 18(a)), then double interlayers (Fig. 18(b)). The best-known example of a double interlayer was undertaken to produce ceramic turbocharger rotors for the automotive industry. A natural extension of this is an infinite number of very thin interlayers, i.e., a graded structure (Fig. 18(c)). Such functionally graded materials (FGMs), like all interlayers, need to be carefully designed in terms of materials and relative thickness to the bond area. The use of a flexible interlayer has also been investigated; designs include convoluted washers and fibrous mattes (Fig. 18(d)).

Summary

The joining of ceramics, particularly to metals, is a key enabling technology for the industrial implementation of ceramics. There are several ways to control the microstructure to ensure properties at the bond line are fit for purpose, such as strength and hermeticity of the bond. However, regardless of the chemical quality of the bond, poor joint design may result in high levels of residual strain, and properties such as bond strength and reliability may deteriorate.

There are no standards for the production of bonds; for any given component or system, fitness for purpose must be determined by physical experimentation. Finite element modeling can offer some assistance in the design process.

Further Reading

- Ali, M., Knowles, K.M., Mallinson, P.M., Fernie, J.A., 2016. Interfacial reactions between sapphire and Ag–Cu–Ti-based active braze alloys. *Acta Materialia* 103, 859–869.
- ASM International, 1991. *Engineered Materials Handbook: Ceramics and Glasses*. ASM International, Materials Park, Ohio.
- Donald, I.W., 2009. *Glass-to-Metal Seals*. Sheffield: Society of Glass Technology.
- Donald, I.W., Mallinson, P.M., Metcalfe, B.L., Gerrard, L.A., Fernie, J.A., 2011. Recent developments in the preparation, characterization and applications of glass- and glass-ceramic-to-metal seals and coatings. *Journal of Materials Science* 46, 1975–2000.
- Eustathopoulos, N., Nicholas, M.G., Drevet, B., 1999. *Wettability at High Temperatures*. Oxford: Elsevier Science Ltd.
- Fernie, J.A., Drew, R.A.L., Knowles, K.M., 2009. Joining of engineering ceramics. *International Materials Reviews* 54, 283–331.
- Knowles, K.M., van Helvoort, A.T.J., 2006. Anodic bonding. *International Materials Reviews* 51, 273–311.
- Nicholas, M.G., 1998. *Joining Processes*. Dordrecht: Kluwer Academic Publishers.
- Yacobi, B.G., Martin, S., Davis, K., Hudson, A., Hubert, M., 2002. Adhesive bonding in microelectronics and photonics. *Journal of Applied Physics* 91, 6227–6262.

Abrasives

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Introduction

In our day-to-day life, few manufactured products in their production process escape a finishing and/or grinding operation involving abrasive materials. Whatever their origin, abrasive minerals or abrasive tools, their economic weight is huge; more than 10 B€ for the overall abrasives and around 2B€ for the abrasives minerals markets. The other way to assess the importance of such products is the number of patents published regularly; more than 50,000 per decade since the year 2000 (Nadolny, 2014). However, these patents are firstly, mainly related to abrasive tools and secondly, focused on super abrasives – around 10,000 patents per decade these last decades – as well as microcrystalline abrasive materials using sintered abrasive ceramic grains.

For scientists the difficulty will be to evaluate what will be the final performance of their abrasives grains in the numerous end user applications, knowing that such performance is a 50/50 combination between the abrasive grain and the abrasive tool; a common approach in the industrial abrasives community.

Although abrasive minerals are never studied from a detailed academic point of view, for industrial scientists there are big challenges which require scientific knowledge across a broad range of materials science such as crystallography, high temperature chemistry, surface chemistry, tribology, technical and advanced ceramic processing etc. This is what will be seen in the following part of this chapter which is based upon industrial experience of the author.

Minerals for Abrasives

An abrasive mineral is a sharp and hard material used to wear away the surface of softer, less resistant materials. Included within the term are both natural and synthetic substances, ranging from the relatively soft particles to the hardest known material; the diamond.

These natural abrasives like Quartz, Emery, garnet, flint, Zircon, Diamond are marginally used compared to synthetic abrasives produced by electro fused processes or by technical or advanced ceramic processes. Processes must be able to control first of all, crystal size, hardness and toughness, the key parameters to enhance abrasive performance, and also to allow manipulation of crystal and grain shape. Conventional synthetic abrasive grains are far away still based on alumina and silicon carbide which represent 99,9% of the annual World production around 2,500,000 tons (courtesy Imerys Fused Minerals internal source).

Abrasives grains are used in 3 different ways:

- (1) As loose abrasives without any support mainly for polishing applications.
- (2) As bonded abrasives in resin or ceramic wheels for a huge range of applications (Nadolny, 2014).
- (3) As coated abrasives applied by electrostatic process on paper or belt cloth. (see “Relevant Websites section” Abrasives and Finishing for Industrial applications/3M and see Relevant Websites section”).

For industrial applications, all minerals used for abrasive operations are placed above 8 on the Mohs hardness scale which is not satisfactory and not sufficiently accurate to predict what will be the abrasive performance of new synthetic industrial minerals. Producers use a combination of material properties such as Knoop hardness (see Fig. 1) and fracture toughness and associated to specific internal tests which are able to predict what will be the abrasive performance in targeted applications. This is a great challenge indeed, which implies that the mineral producer must have a very good knowledge of his customer application and the abrasive tools producer application as well as the end user application. This knowledge-base is good reason for some producers to be integrated; i.e., they produce minerals for abrasives and abrasive tools like Saint Gobain and 3M for example.

We will see that hardness is not only the necessary property to allow a material to perform as an abrasive. Fracture toughness, K_{1c} , brittleness and crystal structure are the three other characteristics which must be taken into account to evaluate the best candidate for abrasives. If fracture toughness, like hardness can be measured rather easily, brittleness, B , described by the following equation is more difficult to evaluate directly (Medvedovski, 2006).

$$B = \frac{Hv.E}{K_{1c}}$$

with Hv: Vickers Hardness (GPa); E: Young modulus (GPa); K_{1c} : Fracture Toughness ($\text{MPa.m}^{1/2}$)

This formula shows that toughness is a key property in reducing brittleness. As it is impossible to measure Young modulus on single mineral grain, this brittleness formula is replaced by a friability index which is a test commonly used in the abrasive world. The friability index is defined as the weight percentage going through a 250 μm sieve of 10 g of initial abrasive grain size F36, after a ball milling for 5 min with 6 steel balls of 20 mm diameter. Grain F36 (sieves between 350–710 μm , see Table 1) is a size distribution described by the FEPA norm, the European Federation of Abrasive Producers (FEPA, 2006).

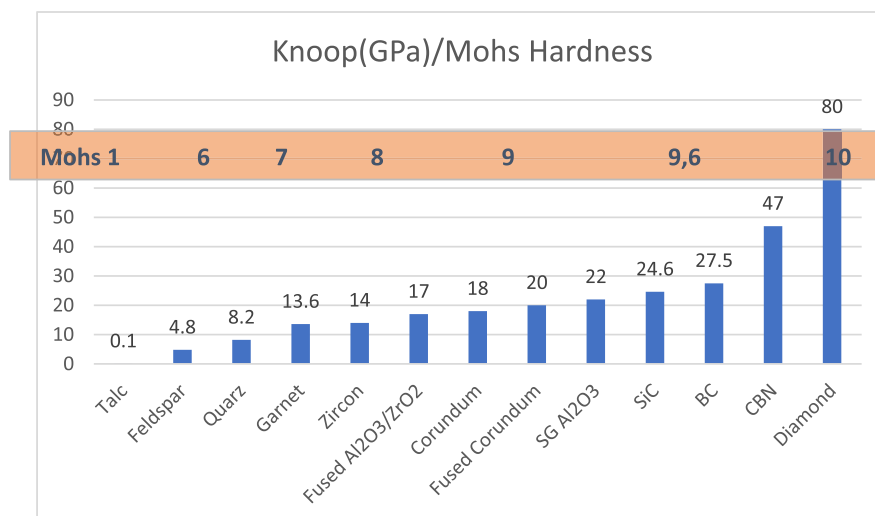


Fig. 1 Knoop/Mohs Hardness data for some natural & synthetic minerals.

Table 1 FEPA grit F36; each grit in the FEPA norm has a size distribution described by the cumulative weight of powder through 5 sieves

	Sieve	Mesh	μm	weight %
F36	1	20	850	0
	2	30	600	< 25
	3	35	500	> 45
	3+4	40	425	> 65
	trough	45	355	< 3

The second test commonly used is a crush test on a single grit sieved between 500 μm and 600 μm and selected to have a blocky shape. This test measures the Compressive Fracture Force (CFF value expressed in Newton) required to break a single grit under an automatic press developed originally by the German company Vollstaedt-Diamant GmbH for quality control of diamonds (Vollstaedt *et al.*, 2003; List *et al.*, 2020). Associated with hardness and toughness, the friability index and the CFF value, which is an average value coming from several hundred crushed single grit, give a very good information about the effect of chemical composition and microstructure. Fig. 2 gives an overview of how these two characteristics relate to physical and chemical properties of materials. Clearly, the sintered materials lead to higher CFF values and a lower friability index.

For abrasive applications, like for ceramics, microstructure is a key parameter. Finer is, better. However, for abrasives the final performance comes from the right balance of hardness/toughness and CFF/friability. Only synthetic minerals can offer such possibilities.

Let's take crystal size as a key to describe the abrasive evolution.

Figs. 3 and 4 show such an evolution to increase abrasive performance. However, it's important to keep in mind that up to now more than 90% of industrial minerals are produced by electro fused processes despite the limit of this process for producing materials with a fine microstructure.

Electro Fused Abrasives

Around 2,000,000 tons/year of alumina (60%) and SiC (40%) are produced using the arc furnace technology known since beginning of twentieth century for the production of ferroalloys and steels. The production of the corundum abrasive family is described Fig. 5.

Raw materials for this process are typically:

- (1) Alumina powder for direct fusion to convert this alumina powder into alumina coarse crystal after cooling and crushing. A low addition of Cr gives either pink or ruby corundum.
- (2) Alumina + Baddeleyite powder to get fused alumina with 25% or 42% ZrO₂ which is the eutectic composition for Al₂O₃/ZrO₂ and has a dendritic microstructure. For these two compositions the cooling step is a key one (Marlin *et al.*, 2011; Fischer *et al.*, 2012) which requires a fast solidification as we will see.

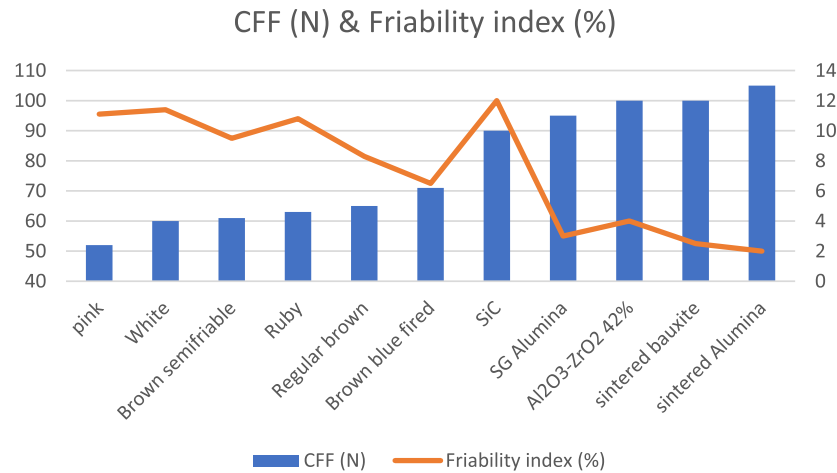


Fig. 2 CFF value and Friability index of main synthetic abrasive minerals.

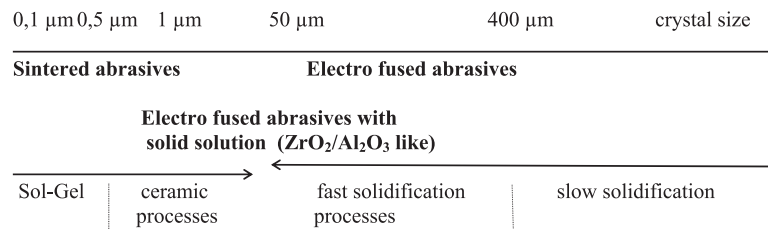


Fig. 3 Process evolution vs. elementary crystal size from electro fused to Sol-Gel processes.

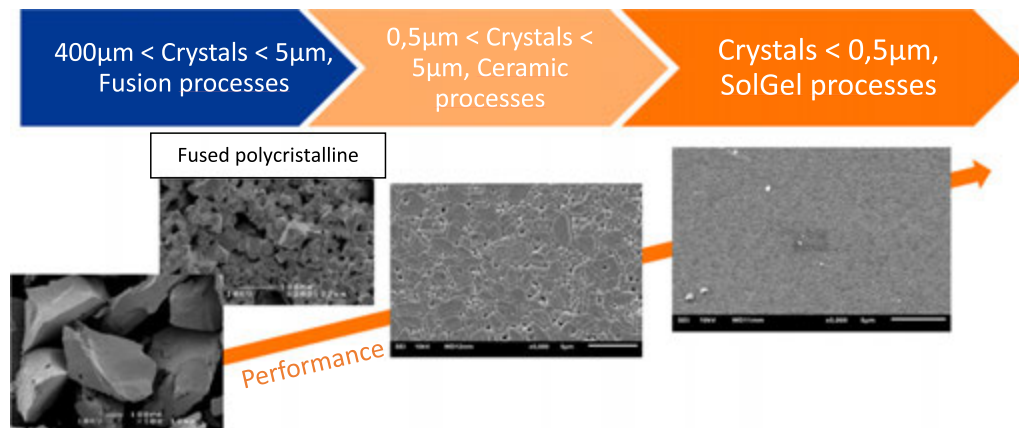


Fig. 4 Crystal sizes obtained from electro fused to sol gel abrasive minerals.

- (3) Bauxite + carbon for a carbo-reduction fusion to produce corundum with different level of Ti. 2%–3% for regular brown and 1%–1.5% for brown semi friable.

These different alumina compositions cover a wide range of abrasive applications.

Table 2 is an overview of the characteristics of such minerals for abrasive applications. All producers supply such types of fused products. (see web sites see “Relevant Websites section”; see “Relevant Websites section”; see “Relevant Websites section”).

They operate with arc furnaces of 2–10 MW power to produce ingots of 10–20 tons following a batch process. In a 4 MW arc furnace 10–12 tons of alumina are melted in 3 h and poured as fast as possible in a crucible to avoid solidification in the casting channel. Regarding the alumina’s refractoriness, the ingot surface solidifies immediately but a full week is required to cool it down totally before the next step. Thus, there is a very low solidification step leading to the abrasive grains after crushing, milling and sizing into FEPA grit sizes. Finally the electro fused abrasive grit can be considered as a single crystal having shapes and densities designed by the process steps mentioned in **Fig. 5**.

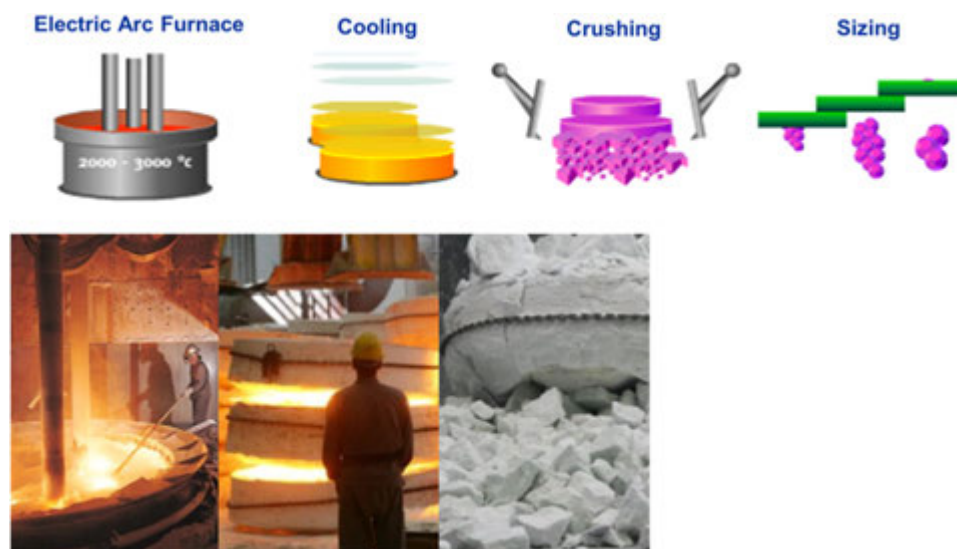


Fig. 5 The fused mineral production process. Cooling, crushing and sizing are the added value steps for the production of abrasive grains (courtesy Imerys fused Minerals).

Table 2 Abrasive fused mineral characteristics (courtesy Imerys Fused Minerals)

Main properties (%)	Corundum						Corundum/Zirconia			SiC
	White	Regular Brown	Brown semifriable	Brown blue fired	Pink	Ruby	Zircon-Mullite	25% ZrO ₂	42% ZrO ₂	Black
Al ₂ O ₃	99.78	96.20	97.88	96.20	99.5	97.80	46.10	75.00	54.50	0.15
Fe ₂ O ₃	0.04	0.15	0.08	0.15	0.05	0.04	0.30	0.30	0.20	0.20
Na ₂ O	0.18				0.18	0.20	0.20			
CaO + MgO		0.30	0.14	0.30			0.10	0.20		
SiO ₂		0.50	0.30	0.50		0.02	18.70	0.46		1.00
TiO ₂		2.85	1.60	2.85			0.10	0.50	2.50	
Cr ₂ O ₃					0.25	2.00				
ZrO ₂							34.30	23.5	41.50	
SiC										98.25
Hardness HK (GPa)	20.5	18.5	18.8	19	19.7	20	15	17	16	25
Friability index	11.4	8.3	9.5	6.5	11.1	10.8	14	3.2	4.3	12
vol weight (g cm ⁻³)	3.96	3.97	3.97	3.97	3.96	3.96	3.66	4.20	4.6	3.15

Two families of fused abrasive minerals require specific cooling equipment able to cool the liquid composition down as fast as possible; these are the alumina/zirconia products and polycrystalline corundum.

The fused alumina composition with 42% (eutectic composition) or 25% zirconia requires that the liquid phase is quenched to get the typical fine dendritic microstructure for such a product (see Fig. 6). The second important characteristic of such products is the ratio between the ZrO₂ high temperature phases cubic + tetragonal to the sum of the three ZrO₂ phases cubic + tetragonal + monoclinic. This ratio called the T factor (measured by X-R-ay diffractometer and the Rietveld method) is linked to the performance of this abrasive mineral. The maintenance of good self sharpening effects during grinding operations giving higher stock removal and longer life time is greater compared to standard fused abrasive minerals. For the eutectic composition the T factor must be above 90%. For the composition with 25% Zirconia the target is the opposite: the T factor being <30% to get a higher toughness and a lower friability index. Many patents claim the effect of additives like TiO₂, Y₂O₃, MgO, CaO can control this T factor (Marlin *et al.*, 2011; Fischer *et al.*, 2012; Gebhardt, 2015).

Only one producer is able to produce a polycrystalline fused corundum (Fig. 4) using a proprietary fast cooling process (Alary and Sachse, 2012). Such grit performs like ceramic grains obtained by sintering processes despite their coarse elementary crystal size, are fine for an electrofused product but still too coarse for a sintered product (Fig. 7).

An other specific product in this family of fused alumina mineral is the so called “blue fired brown corundum” which is a regular or semifriable abrasive. A perfect example of surface modification in the field of abrasive. When you apply a heat treatment under controlled atmosphere and temperature in the range of 1100°C +/- 100°C the brown corundum changes color. To explain this phenomenon we have to come back to the origin of color in natural mineral like sapphire which is the natural blue

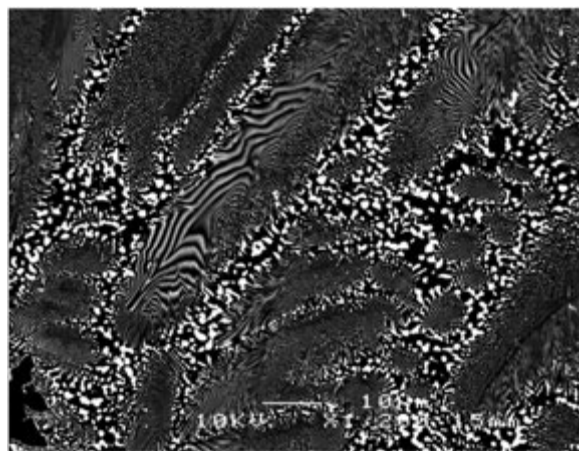


Fig. 6 Fused Alumina 42% Zirconia dendritic microstructure. Alumina crystals in Alumina/Zirconia solid solution. (courtesy Imerys Fused Minerals).

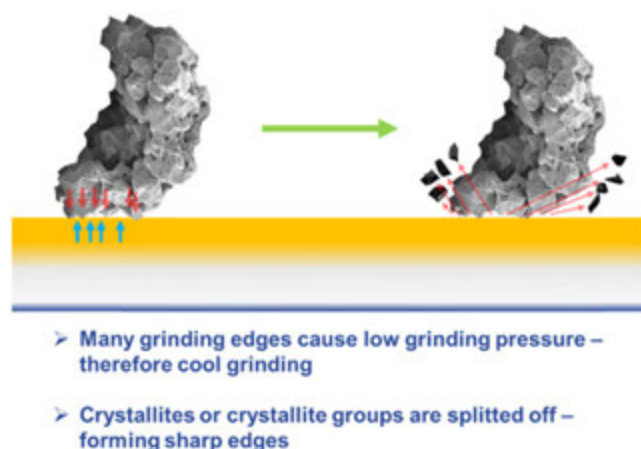
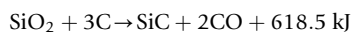


Fig. 7 Polycrystalline fused corundum mineral, a singular product in the electrofused minerals family, working like a sintered ceramic grain. Internal porosity: 15%–20%; CFF: 40N; Friability index:11. Courtesy Imerys Fused Minerals.

corundum having the same impurities, Fe and Ti, substituted in the atomic lattice. (Nassau, 1978, 1987; Moon and Phillips, 1994). During this heat treatment such impurities move to the surface of brown corundum grains which increase the probability of finding Fe^{2+} and Ti^{4+} in adjacent sites in order to realize the electronic exchange described by the oxidation-reduction equilibrium mentioned Fig. 8. The energy (around 2 eV) linked to this electronic transfer is related to the yellow/orange color absorption. Blue is the complementary color of the yellow one. The color change is one thing, but for the abrasive users the interest is that during this heat treatment mechanical and surface properties of the brown fused corundum change. Thus its friability index decreases and toughness and hardness increase leading to an increase in abrasive performance compared to the original brown fused grain.

To conclude this part related to electro fused process, some words about SiC production. Developed by E. Goodrich Acheson end of the nineteenth century the SiC production process is well described by the following web site: see “Relevant Websites section”. A blend of carbon and silica sand react in the electric arc of the two electrodes furnace following the reaction



From this high temperature reaction ($> 2000^\circ\text{C}$) two SiC qualities are produced. In the core area α -SiC the highest grade with coarse grains and in the peripheral area β -SiC is a metallurgical grade with a lower purity $92\% < \text{SiC} < 98\%$. The drawback of this very old process is a huge production of CO and some modifications have been proposed to overcome this problem (Aleonar *et al.*, 2013). The next steps of the production process are similar to those for the production of fused alumina abrasives (Fig. 5).

Depending on the targeted application, the shape of the abrasive grains and not just their size changes the performance of the abrasive tool drastically. For the same equivalent grit sizes an angular grit will have a lower pack density but sharp edges compared to a bulk grit. The first one will be better for cutting the second for grinding or polishing.

Like for fused alumina, all SiC producers for abrasive applications offer their products following the FEPA norm with at least two different loose pack density (LPD) that means different shape from angular to blocky (for SiC minerals see web site: see “Relevant Websites section”).

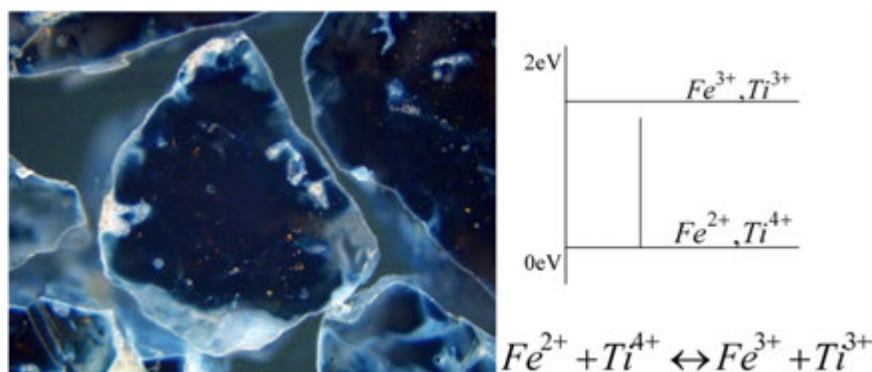


Fig. 8 Electronic transfer at the origin of brown fused alumina blue color blue and grinding performances 25% higher than the original grain!.

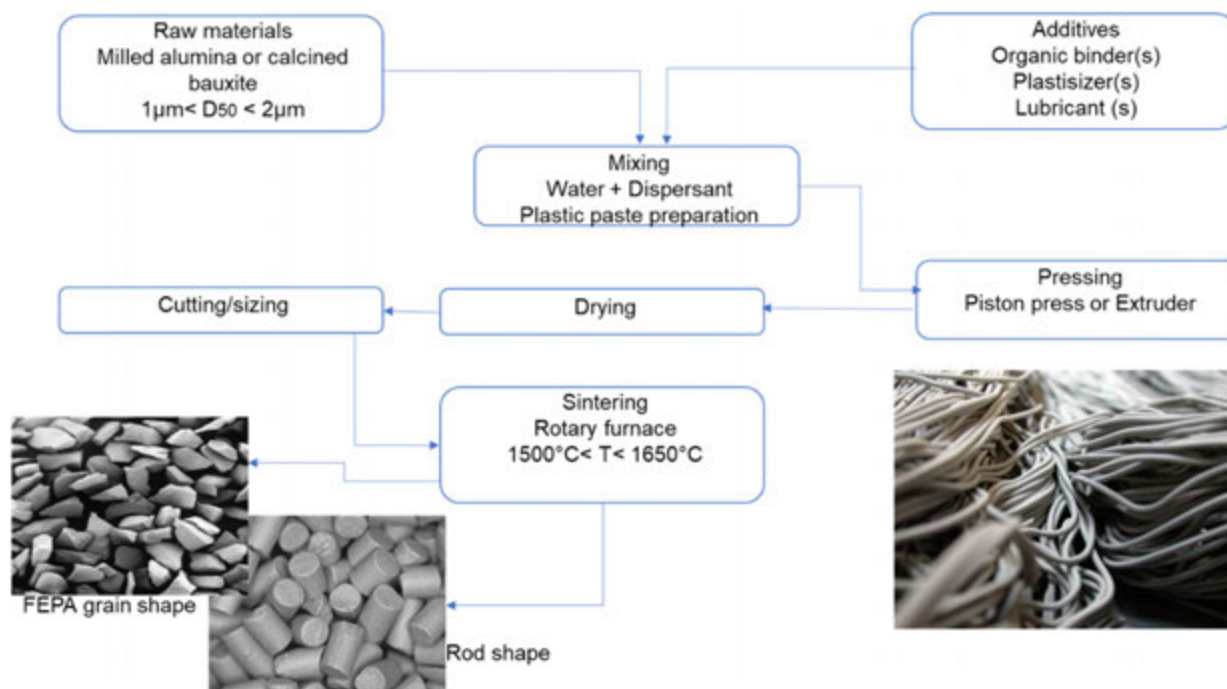


Fig. 9 Sintered abrasives production process following a standard technical ceramic process.

Sintered Abrasives

With fused polycrystalline alumina the limit of the arc furnace technology was reached to produce fine microstructures. To carry on the continuous improvement of manufactured products hard and more wear resistant, a new generation of synthetic abrasive minerals was developed. The sintered abrasives or ceramic grains are produced following processes and scientific approaches used in the field of technical and advanced ceramics.

Elementary crystal sizes of such ceramic grains are 10 to more than 100 times finer than the crystal size of fused polycrystalline abrasives. Their sale price is 10–20 times higher than price of electro fused abrasive but their performances warrant this higher price. With their very fine polycrystalline microstructure these ceramic grains generate new cutting-edges during machining operations. This self-sharpening effect enables enhanced lifetime and surface quality of machined components.

● Extrusion processes

The first generation of such ceramic grains used milled powders of alumina or calcined bauxite as raw materials to produce sintered alumina or bauxite with high density and fine microstructure, but still above a $1\mu m$ grain size. The main producers are Japanese: Showa Denko, Kure Norton and European: Saint Gobain, Alteo, Imerys Fused Minerals (Piquet and Madec, 2006; Tomikawa *et al.*, 2011, 2013). The flow sheet for the process is given in Fig. 9 with some additional photographs illustrating the product before and after sintering.

Table 3 Typical characteristics and rod size of sintered alumina & bauxite abrasive. The green coarser rods are crushed to produce the FEPA grit sizes up to F36 and finer. (courtesy Imerys Fused Minerals)

Main typical properties (%)	Sintered abrasives			
	Alumina	Bauxite	Rod sizes (mm)	
Al ₂ O ₃	99	80	#8	2.14–2.40
Fe ₂ O ₃	0.04	5–8	#10	1.87–2.13
Na ₂ O	0.15	0.1	#12	1.62–1.86
CaO + MgO	0.1	0.30	#14	1.40–1.61
SiO ₂	0.1	6	#16	1.14–1.39
TiO ₂	0.05	4–5	#20	0.90–1.13
density (g/cm ³)	> 3.80	3.65–3.75	#24	0.67–0.89
Hardness <i>HK</i> (GPa)	18–19	16–17	#30	0.4–0.88
Friability index	<2	2		
CFF (N)	90 + / – 5	100 + / – 5		

Table 4 Typical chemical composition of calcined bauxite for abrasive application

Bauxite composition	%
Al ₂ O ₃	80–85
Fe ₂ O ₃	<10
SiO ₂	5 + / – 3
TiO ₂	<5
CaO	<1
K ₂ O + MgO	0.01–0.1

The rod shape is dedicated to a niche application: scarfing grinders for slabs of steel alloys. These rods are available in different diameters (see [Table 3](#)) with a ratio of length to diameter around 2. As shown [Fig. 9](#) these rods are obtained by extrusion of alumina or calcined bauxite ceramic paste through calibrated dies. Such “spaghettis” like extrusions either cut to give little rods or crushed to give regular FEPA grits after drying. They are finally sintered in rotary furnace. If it’s easy to find good technical grade of alumina for ceramic application (P172 SB Alteo, NO713 RF Nabaltec, CT3000SG Almatiss etc.). However, the production of abrasive sintered bauxite requires more attention. Before processing it is important to find the right crude bauxite with a high alumina content, calcine this crude bauxite to transform the alumina hydrate into reactive alumina and finally mill this calcined bauxite to a fine powder. [Table 4](#) gives a typical composition of such a calcined bauxite. After sintering a calcined bauxite abrasive is composed of 3 mains phases; α -alumina, Mullite (3Al₂O₃.2SiO₂) and Tialite (Al₂TiO₅). To perform as abrasive mineral, Mullite and Tialite phases must be limited. They weaken the mechanical properties of the material. To overcome the difficulty of finding good bauxite and to ensure reproducible properties, some producers developed synthetic bauxite by co-milling alumina powders with Ilmenite (Fe₂TiO₅) and Zircon (ZrSiO₄). With low amounts of silica and titanium oxides, such synthetic materials offer very low CFF values and friability index, hardnesses and toughnesses of the best sintered bauxite for this application ([Hirsch and Alary, 2015](#)). After sintering this co-milled composition gives a composite material has the main phases found in Bauxite doped with zirconia particles as re-enforcement.

● Sol-Gel process (the ceramic grains)

Although such high-tech ceramic grains do not represent not more than 15,000 to 20,000 tons per year production, they are at the origin of the most important patents and publications related to their very high performance in the most sophisticated of abrasive applications ([Nadolny, 2014](#); [Huang et al., 2021](#)).

Based on alumina and composites with an alumina matrix, the latest generations of ceramic grains were developed by Saint Gobain and 3M more than 30 years ago. With Sol-Gel ceramic grains we are in the World of Advanced Ceramic, materials having nano size crystal structure.

Applied to abrasive grain the sol-gel chemistry process can be generally described by [Fig. 10](#). Although the actual trend is to give a specific well designed shape geometry to enhance grinding quality and efficiency ([Erickson, 2011](#); [Keipert et al., 2011](#); [Welygan et al., 2012](#); [Monroe, 2013](#); [Yener et al., 2012](#); [Bauer et al., 2012](#)) the shaping step could only be a milling step of the dried gel before sintering.

The first key point being the crystal size reduction the addition of seeds to reduce the α -Al₂O₃ temperature is the rule. Numerous works in the scientific literature ([Kwon and Messing, 2000](#); [McArdle and Messing, 1993](#); [Li et al., 2011](#)) as well as patents (describe the addition of nano particles of α -Al₂O₃, Fe₂O₃, ZrO₂ to reach a sintered density closed to the theoretical one at temperatures more than 100°C below the usual sintering density for technical grade of alumina.

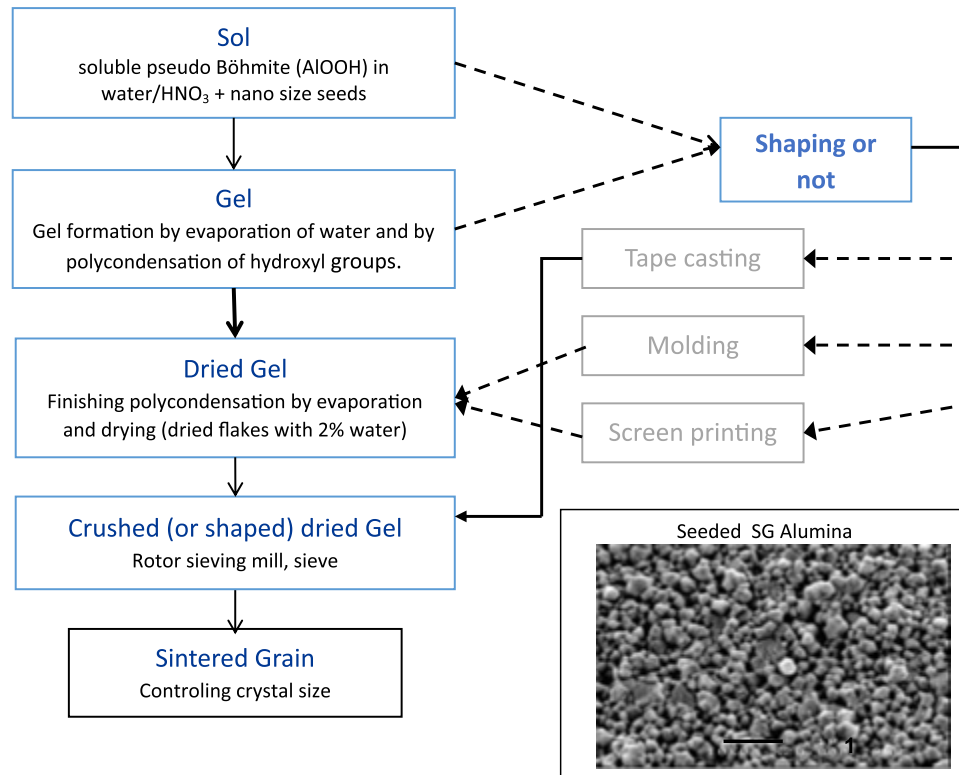


Fig. 10 Outline of the sol – gel process and photomicrograph of powder produced (bar = 1 μm).

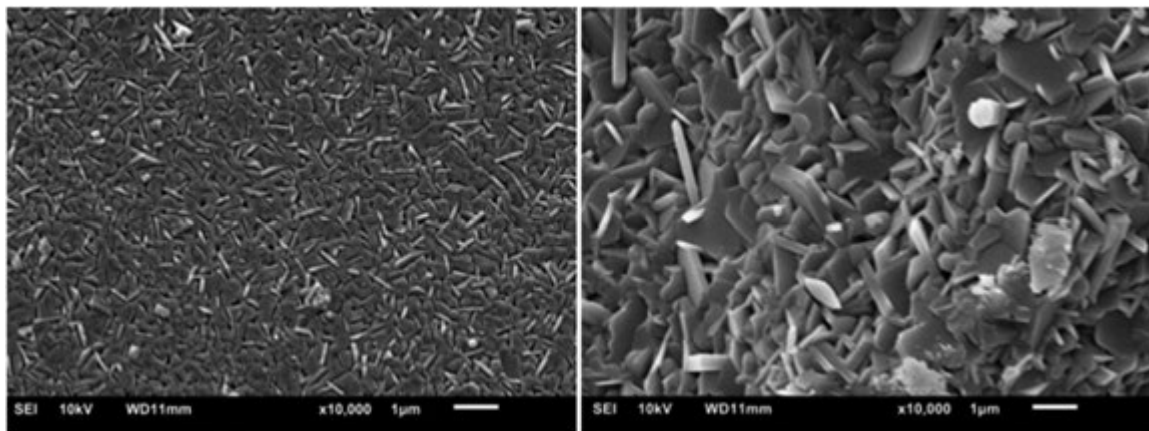
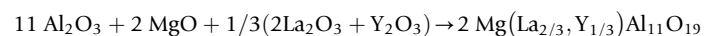


Fig. 11 Alumina/magnetoplumbite sol-gel abrasive composite microstructure. Courtesy Imerys Fused Mineral.

A second key point was contributed by the 3M company which could be considered as the most innovative company in this field. Thanks to an additional step it was proposed to infiltrate the dried gel with lathana, yttria and magnesia salts to create, after sintering, a composite material named Cubitron 321™ (Wood, 2000), which has platelet crystals of magnetoplumbite as reinforcement of the alumina matrix. Such minerals are described by the general formula: $\text{PM}_{12}\text{O}_{19}$ with $\text{P} = \text{Pb}^{2+}$ and $\text{M} = \text{Fe}^{3+}$.

The magnetoplumbite compound found in the 3M product is described by the following chemical reaction and by the typical microstructure Fig. 11.



The fracture toughness of this composite reaches $\approx 4.5 \text{ MPa m}^{1/2}$ compared to $\approx 3 \text{ MPa m}^{1/2}$ for the pure alumina sol-gel abrasive. Hardness of such sol-gel alumina grains reaches between 22 and 24 GPa.

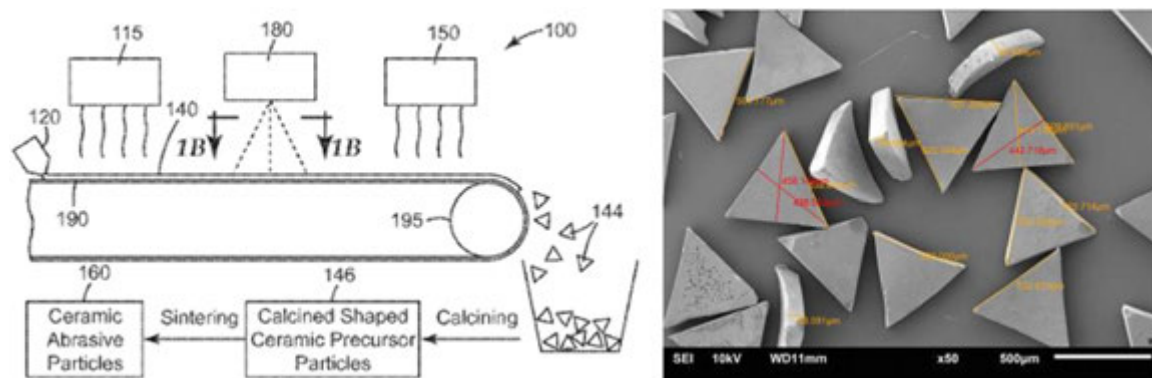


Fig. 12 Laser printing method to produce triangular grain shape. 3M™ patent WO 2012061033 A2.

The last improvement proposed by 3M company (Erickson, 2011; Keipert *et al.*, 2011; Welygan *et al.*, 2012) and followed by some others (Yener *et al.*, 2012; Bauer *et al.*, 2012) was to propose a calibrated shape using different shaping processes such as tape casting, molding, screen printing, laser printing (see Fig. 12).

With a well-designed grain shape, abrasive tools have longer life time, reduce the contact temperature and machining surfaces are cleaner. There are used for precision grinding wheels. Grinding mechanisms are well describe by Nadolny (2014) and Huang *et al.* (2021).

Application Guidance

Having designed the physical properties, grain shape, crystal size and microstructure of the mineral the abrasive producer is able to predict in which type of application the abrasive grain will offer the best performance, taking into account the economic point of view. Sol-gel abrasive grains cost 10 times the price of electro fused one. The qualities of the generic types of abrasives are summarized below.

- (1) BFA (brown fused alumina) – blocky and tough grain for all standard wheels on standard steel.
- (2) WFA (white fused alumina) – weak and friable grain for lab wheels or as blend for improving the cutting ability.
- (3) Semi-friable BFA – weak and tough grain, best price/performance ratio for smaller wheels.
- (4) Pink fused alumina – similar to WFA but longer lifetime.
- (5) Monocrystalline alumina – tough and sharp grain; best lifetime/cutting ability ratio.
- (6) AZ, fused alumina 25% zirconia – higher wear resistance of foundry wheels – mainly used for large diameter wheels in steel plants.
- (7) AZ, fused alumina 40% zirconia – higher wear resistance – due to the specific grain sharpness it matches good to stationary cut-off wheels and even thin wheels.
- (8) Silicon Carbide – hard and sharp grain, standard grain for stone cutting and good for aluminum, titanium.
- (9) Ceramic grain – microcrystalline structured grain with best performance on nearly all materials – self sharpening effect for a higher lifetime.

The final abrasive mineral performances are widely linked to firstly the ability of the abrasive tool manufacturer to make the best composite product. The bond between abrasive grain and his matrix resin or ceramic wheel is key. Thus, it is not in the manufacturers best interest to have a good abrasive grain if it's immediately ripped from the abrasive tool when machining. Secondly, the same product with excellent performance in one application may give the worst performance in the other one. Thus, there is little chance of success without a broad and deep knowledge of the coupling between mineral characteristics and the abrasive application.

Finally, it must be pointed out that there is no bad abrasive mineral, only abrasive minerals badly employed.

References

- Alary, J.A., Sachse, S., 2012. Polycrystalline Al_2O_3 -Bodies Having an Average Crystal Size of Primary Crystals Between 20 μm and 100 μm . Produced by Seeding the Pouring Stream of Liquid Fused Aluminum Oxide. WO 002012041421A1.
- Aleonar, B., Di Piero, S., Schwartz, M., 2013. Process for Producing Silicon Carbide. WO 02013004967A1.
- Bauer, R., Barnes, M., Boussant-Roux, Y. *et al.*, 2012. Method of Forming a Shaped Abrasive Particle. WO 2012 092590 A2.
- Erickson, D., 2011. Shaped Abrasive Particles with Low Roundness Factor. WO 2011005425 A2.
- FEPA, 2006. standard 42-1:2006 & FEPA standard 44-1:2006.
- Fischer, G., Megerle, C., Falz, W., 2012. Method for Producing Zirconia Reinforced Alumina Grains and grains, in Particular Abrasive Grains, Produced by Said Method. WO 002012045302A2.

- Gebhardt, K., 2015. Abrasive Grains Based on Zirconia Alumina. US 9005323 B2.
- Hirsch, A., Alary, J.A., 2015. Sintered Shaped Abrasive Grain on Basis of aluminium oxide comprising Mineralogical Phases Consisting of Mullite, Tialite/Armalcolite, and Baddeleyite/Srilankite, and a Method for Their Production. DE 10 2015 101 701.1.
- Huang, B., Li, C., Zhang, Y., *et al.*, 2021. Advances in fabrication of ceramic corundum abrasives based on sol–gel process. Chinese Journal of Aeronautics. doi:10.1016/j.cja.2020.07.004.
- Keipert, S., Thursber, E., Anderson, T., 2011. Method of Making a Coated Abrasive Article Having Shaped Abrasive Particles and Resulting Product. WO 2011068724 A2.
- Kwon, S., Messing, G.L., 2000. Sintering of mixtures of seeded boehmite and ultrafine α -alumina. Journal of the American Ceramic Society 83, 82–83.
- Li, Z., Li, Z., Zhang, A., *et al.*, 2011. A novel low temperature synthesis technique of sol–gel derived nanocrystalline alumina abrasive. Journal of Sol-Gel Science and Technology 57, 24–30.
- List, E., Frenzel, J., Vollstaedt, H., 2020. A New System for Single Particle Strength Testing of Grinding Powders. <http://vdiamant.de/publikationen.html> (accessed November 2020).
- Marlin, S., Langhor, D., Petigny, S., 2011. Molten Grains of Alumina-Zirconia. WO 002011015995A2.
- McArdle, J.L., Messing, G.L., 1993. Transformation, microstructure development and densification in α -Fe₂O₃ seeded boehmite-derived alumina. Journal of the American Ceramic Society 76, 214–222.
- Medvedovski, E., 2006. Alumina-mullite ceramics for structural applications. Ceramics International 32, 369–375.
- Monroe, L., 2013. Abrasive Particles, Abrasives Articles, and Method of Making and Using the Same. WO 2013188038 A1.
- Moon, A.R., Phillips, M.R., 1994. Defect clustering and color in Fe,Ti: α Al₂O₃. Journal of the American Ceramic Society 77, 356–367.
- Nadolny, K., 2014. State of the art in production, properties and applications of the microcrystalline sintered corundum abrasive grains. International Journal of Advanced Manufacturing Technology 74, 1445–1457.
- Nassau, K., 1978. The origins of color in minerals. American Mineralogist 63, 219–229.
- Nassau, K., 1987. The fifteen causes of color: The physics and chemistry of color. Color Research and Application 12, 4–26.
- Piquet, A.L., Madec, J.M., 2006. Abrasive Grit with High Alumina Content Grain in Particular for Application in Applied and Sintered Abrasives for Example in Scarfing Grinders for Slabs of Steel Alloys. WO 2006018519 A2.
- Tomikawa, S., Miyazawa, H., Iemura, T., 2011. Method for Producing Alumina Sintered Body, Alumina Sintered Body, Abrasive Grain and Grindstone. EP 2636657 A1.
- Tomikawa, S., Miyazawa, H., Iemura, T., 2013. Alumina Sintered Body, Abrasive Grain and Grindstone. EP 2636656 A1.
- Vollstaedt, H., Hess, K.U., List, E., 2003. Single particle characterization of abrasives and superabrasives. In: Proceedings of the Intertech. Vancouver.
- Welygan, D.G., Studiner, C.J., Erickson, D.D. *et al.*, 2012. Laser Method for Making Shaped Ceramic Abrasive Particles, Shaped Abrasive Ceramic Particles and Abrasive Particles. WO 2012061033 A2.
- Wood, W.P., 2000. 3M Cubitron 321 abrasive grain. American Ceramic Society Bulletin 79, 55–56.
- Yener, D., Czerespinski, J., Iyengar, S., Kavanaugh, M., 2012. Abrasive Particles Having Particular Shapes and Method of Forming Such Particles. WO 2012092590 A2.

Relevant Websites

- www.3m.com
3M Science. Applied to Life. 3M United States.
- www.puliteabrasives.com/products
Abrasive.
- www.elfusa.com.br/en
Abrasives.
Elfusa.
- www.nortonabrasives.com
Norton Abrasives North America Homepage.
Norton Abrasives.
- www.washingtonmill.com/products
Products.
Washington Mills.
- www.fiven.com/world-of-silicon-carbide/sic-production-process/
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Wear and Erosion Resistant Ceramic Materials

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Introduction

Thanks to their crystallographic structure and strong interatomic bonds, modern ceramic materials have many excellent properties, such as high hardness, strength, high temperature and chemical stability, high resistance to corrosion and wear. Their weaknesses are low fracture toughness and low resistance to defects and cracks, and the resulting high brittleness and low reliability. To improve their performance in this respect, a lot of research work has been carried out in recent decades. Yet, despite the improvement of fracture toughness and strength of modern ceramic materials, they are still predominantly used in applications which make use of their exceptional hardness and chemical and thermal stability – such as cutting tools, ceramic seals, ball bearings, etc. – i.e., applications without high volume loads but with intense mechanical contact (Kato, 1990). Such applications require high wear resistance and good tribological behavior. Typical and industrially well proven materials include high purity alumina, tetragonal stabilized zirconia, alumina-zirconia-(silica) mixtures, nitride bonded silicon carbide (NBSiC), reaction bonded silicon carbide (RBSiC/SiSiC) (Medvedovski, 2001; Saint-Gobain, 2020 and others).

The resulting tribological performance depends on interplay of many factors. First, the material intrinsic properties, such as hardness, toughness, strength, ductility, and possible work hardening. Second, other (extrinsic) factors are equally important, such as forces applied, relative speed, environmental variables (temperature, atmosphere, humidity, lubrication). And third, the chemical nature of materials in contact, together with lubricants and environment, also play important role, as they determine the tribochemical reactions (Basu and Kalin, 2011).

Friction, especially in unlubricated situations, is a resistance to motion due to the interaction of solid surfaces in contact (Archard, 1953). Low friction is important for some applications, such as bearing, seals, hinges, biomedical joint implants. On the other hand, there are applications where high friction is desirable, like brake pads and tyres. In any case, it is important to have control over the specific friction for a particular application.

Wear is the progressive loss of material due to the tribological interactions at surfaces in contact and relative motion. Such solid body contact might be accompanied also by liquids and gases, thus wear includes various forms such as sliding, rolling, impact, cavitation, erosion. In general, wear is detrimental in many engineering applications, but also in those where it is desirable (grinding, polishing) it is important to have it under control and/or to be able to predict which conditions will have what sort of consequences.

Wear and Erosion Evaluation

In most cases the mechanical wear and erosion performance is observed in combination with a specific counterpart, in accordance with intended applications, or with chemically similar materials. In these types of tests, the sample surfaces are carefully prepared in a defined way, usually ground and polished to a specific surface roughness. According to the standard ISO 20808:2004E (2004) during the wear testing the normal loading forces are set or controlled. Tangential forces are continuously monitored, and from those the coefficient of friction is calculated and recorded. After finishing the test, the worn surfaces (wear tracks) are observed in microscopes, and based on these observations the wear regimes, types, and damage micromechanisms are determined. Typically, also the consequences on the surface (near surface layers) chemical composition are observed. If possible, the material loss due to wear is calculated. The specific wear rate (W) is evaluated as volume loss (V) per distance traveled (L) under an applied normal load (F_p): $W = V/(L F_p)$.

The erosive wear of brittle materials by hard particles bombarding a surface occurs by propagation and interaction of cracks produced by impacting particles. Like abrasion, it can involve both plastic deformation and brittle fracture, and the details depend on both the wearing material and the erodents, as well as on the condition of the impacts, like particle mass, velocity, and impingement angle. Gas blasting methods for evaluation of erosive wear are standardized in the ASTM G76 – 18 (2018) industrial standard.

Tribological behavior is, generally, a complex result of interaction of the material surfaces, which are in contact and in a relative motion. It is a complicated phenomenon which is impossible to exactly predict just from knowledge of other basic mechanical properties. That means, the wear testing for the development of new materials for tribological applications absolutely indispensable (Kato and Adachi, 2002). Wear of materials is usually characterized by its intensity (severity). Generally, it is divided to 'mild', 'severe' and 'ultra severe' regimes (Adachi and Kato, 1997; Kato and Adachi, 2002; Bhushan, 2001). In ceramics is this distinction is very well definable quantitatively. Ceramics are considered mildly worn, i.e., suitable for tribological parts, if their specific wear rate, W , is smaller than $10^{-6} \text{ mm}^3 \text{ m}^{-1} \text{ N}^{-1}$. The interval 10^{-6} – $10^{-5} \text{ mm}^3 \text{ m}^{-1} \text{ N}^{-1}$ is considered transitional, at $W > 10^{-5} \text{ mm}^3 \text{ m}^{-1} \text{ N}^{-1}$ it is 'severe wear', connected to more intense damage mechanisms and usually means insufficient performance for given application. At even higher wear rates ($> 10^{-2} \text{ mm}^3 \text{ m}^{-1} \text{ N}^{-1}$) 'ultra severe wear' is accompanied by thermal shock and massive surface damage (Table 1).

Table 1 General classification of the wear régimes in dry sliding

Wear regime	Wear rate [$\text{mm}^3 \text{m}^{-1} \text{N}^{-1}$]	Wear mechanisms
Mild wear (stress intensity $< K_{IC}$)	$< 10^{-6}$	(Asperity scale failure mode) Abrasion Intergranular cracks Subsurface damage/cracks Grain pullout Tribochemical
Severe wear (stress intensity $> K_{IC}$)	$10^{-5-10-2}$	(Nominal scale failure mode) Fracture mechanics Tensile cracks $\rightarrow$ edge effects 3rd-bodies (linked to grain pullout)
Ultra-severe wear (stress intensity $\gg K_{IC}$)	$> 10^{-2}$	(Nominal scale + few pieces large debris) Thermal shock (nominal scale)

Note: Modified according to Bhushan, B., 1999. Principles and Applications of Tribology. New York: Wiley and Sons.

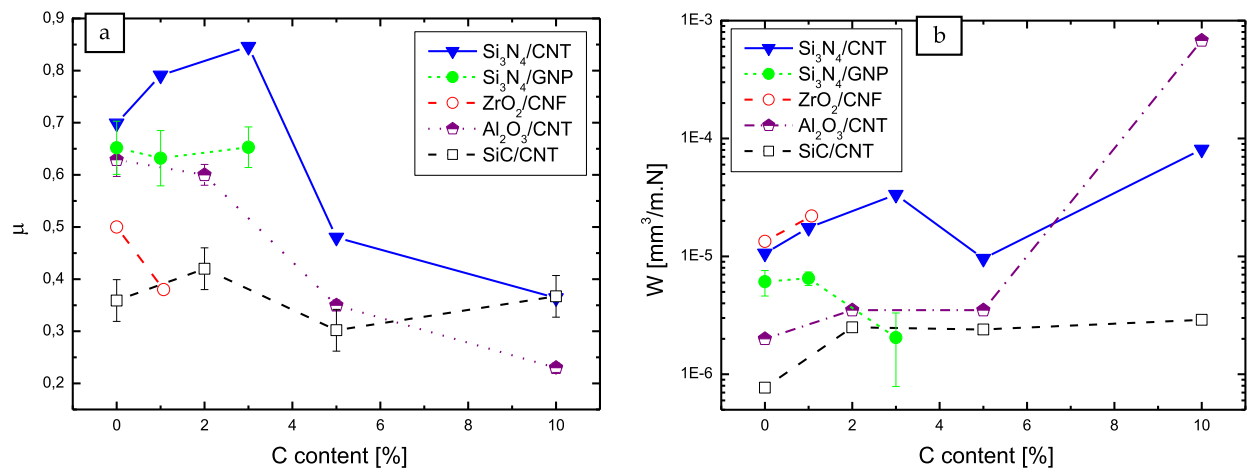


Fig. 1 Dependence of friction coefficient (a) and specific wear rate (b) on the amount of carbon nanophases in the experimental composites with ceramic matrix. According to Hvizdoš, P., Duszová, A., Puchý, V., *et al.*, 2011. Wear behavior of ZrO_2 -CNF and Si_3N_4 -CNT nanocomposites. Key Engineering Materials 465, 495–498. Hvizdoš, P., Puchý, V., Duszová, A., Dusza, J., Balázsi, C., 2012. Tribological and electrical properties of ceramic matrix composites with carbon nanotubes. Ceramics International 38, 5669–5676. Puchý, V., Hvizdoš, P., Dusza, J., *et al.*, 2013. Wear resistance of Al_2O_3 -CNT ceramic nanocomposites at room and high temperatures. Ceramics International 39, 5821–5826. Balko, J., Hvizdoš, P., Dusza, J., Balázsi, C., Gamcová, J., 2014. Wear damage of Si_3N_4 -graphene nanocomposites at room and elevated temperatures. Journal of the European Ceramic Society 34, 3309–3317. Džunda, R., Fides, M., Hnatko, M., *et al.*, 2019. Mechanical, physical properties and tribological behaviour of silicon carbide composites with addition of carbon nanotubes. International Journal of Refractory Metals and Hard Materials 81, 272–280.

Development of Ceramic Materials and Ceramic Matrix Composites for Improved Tribological Performance

In research of the ceramic materials for tribological applications, the material intrinsic properties are optimized in order to meet desired criteria for the specific use. First, control and selection of a suitable basic ceramic material is important. If needed, further tailoring of the material properties for industrial requirements can be achieved by designing specific composite materials – ceramic matrix composites. The benefit of using composites in this area is twofold: (1) possible improvement of fracture toughness and hardness can improve the wear resistance; (2) addition of appropriate secondary phases can lower the friction coefficient thanks to development of self-lubricating effects.

During the last two decades, an interesting development in ceramic matrix composites (based on alumina, zirconia, silicon nitride, silicon carbide, and others) with carbon nanoobjects (nanofibers – CNF, nanotubes – CNT, and graphene nanoplatelets – GNP) have led to promising results in the area of tribological properties (An *et al.*, 2003; Lim *et al.*, 2005; Balázsi *et al.*, 2006; Yamamoto *et al.*, 2008; Hvizdoš *et al.*, 2010b, 2011; Puchý *et al.*, 2013; Maros and Németh, 2017; Belmonte *et al.*, 2013 and others). It was shown that for self-mated tribological pairs the coefficient of friction could be significantly reduced. Fig. 1(a) summarizes the average values of the friction coefficients for alumina, zirconia, silicon nitride, silicon nitride matrix materials with CNT, CNF, or GNP. This reduction, however, was generally accompanied by a lowering of wear resistance (Fig. 1(b)), due to imperfections and defects in the microstructure caused by difficulties with proper distribution and incorporation of CNT/CNF/GNP. In some cases,

however, as seen in Fig. 1(b) for Si_3N_4 -CNT and Si_3N_4 -GNP there are advantageous effects, where abrasion resistance readily improved, most likely due to significantly reduced friction due to phenomenon of solid lubrication. These results will be further commented on for each class of materials.

Oxides I – Alumina Based Ceramics

Alumina (Al_2O_3) is a traditional fine ceramic material. It is one of the least costly and most often used structural ceramics. Its raw materials are cheap and easily obtainable. The most common modification, α - Al_2O_3 , is very strong and stiff. It has very high hardness and wear resistance, excellent dielectric properties from DC up to GHz frequencies, resistance against both strong acids and bases also at elevated temperatures, good thermal conductivity and excellent formability. It is readily available in high purities (99.5% for high temperature applications). Thanks to the excellent combination of properties and attractive price, fine grained high quality Al_2O_3 ceramics have a very wide range of applications. Typical ones are gas laser tubes, abrasion liners, sealing rings, high temperature and high voltage electrical insulators, furnace elements, fiber and wire guides, electronic substrates, ballistic armor, thermometric sensors, biomedical implants, laboratory tubes and sample holders, etc.

Since monolithic material is naturally highly wear resistant, the research effort has been aimed at lowering the coefficient of friction while possibly improving fracture toughness. One of the most interesting proposals was to use the newly developed and promising carbon structures - 1D (filaments, fibers, nanotubes) and/or 2D (graphite/graphene platelets) as composite fillers.

Alumina - CNT composites with a nanotube content of 0–12 wt% were prepared by different techniques by Lim *et al.* (2005) to investigate the influence of the production process on their tribological properties. The best tribological properties were obtained after application of tape casting, followed by lamination and hot pressing. Material loss of the composites was significantly reduced and the coefficient of friction was maintained with CNT additions of up to 12 wt%. CNT agglomeration, so often observed in conventional hot-pressed samples, was significantly suppressed and the CNT distribution was relatively homogeneous. Such efficient distribution of CNTs in the matrix contributed to better compaction of the composites and to better values for both mechanical and tribological properties.

In the work of Puchý *et al.* (2013) a decrease in the coefficient of friction for Al_2O_3 -5 wt% CNT, mainly due to the formation of a tribological film, was found. This behavior is quite stable at temperatures up to 500°C. For materials with the even higher CNT content ($\geq 10\%$), the advantageous low coefficient of friction is only manifested up to temperatures around 300°C, then it rises sharply.

An *et al.* (2003) found a 40% decrease in the coefficient of friction down to 0.3 for the 12 wt% CNT - Al_2O_3 composite. Yamamoto *et al.* (2008) for similar materials achieved a minimum friction with a coefficient of 0.3 for 4 wt% CNT content. According to these works, the rolling motion of the released CNTs, which remain in the area at the interface between the tribological partners, also contributes to the reduction of friction.

Interesting results have recently been obtained in the case of hierarchically grown graphene layers on alumina grains (Hussainova *et al.*, 2016), in which an optimum with a reduced friction coefficient and better abrasion resistance at very low carbon contents, below 1.5 wt% C, was found. Here, even though the amount of carbon filler is very low, its excellent distribution around some of the matrix grains guarantees its good effect. The coefficient of friction decreased from 0.65 to 0.5, while the wear rate decreased by 50%–60% in conditions of mild wear and by 90% in conditions of severe wear.

Oxides II – Zirconia Based Ceramics

Zirconium is found in nature in igneous rocks in the form of zirconia - ZrO_2 , but especially zirconium silicate - zircon (ZrSiO_4). Most of the zirconium materials, are used directly for the production of refractory materials. Zirconia occurs in three polymorphic modifications, monoclinic, tetragonal and cubic (Stevens, 1986). In the monoclinic form it has a density of 6.1 g cm^{-3} . The cubic phase has a face centered structure with a density 6.09 g cm^{-3} . In pure ZrO_2 , the monoclinic phase is stable up to about 1170°C, where it converts to tetragonal. At 2370°C, a cubic phase is formed, stable up to a melting point of 2680°C. The materials used in practice contain various stabilizing additives (various oxides, the most common is yttria) and the stability areas of the individual phases vary considerably.

The conversion of tetragonal to monoclinic modification is associated with a volume increase of about 5%. If the ceramic contains grains of metastable t - ZrO_2 which are capable of martensitic transformation, during crack propagation the tensile stresses at its face cause a $t \rightarrow m$ transformation and energy is absorbed in the transformed zone. This process inhibits crack propagation and improves the mechanical properties of the material (Garvie *et al.*, 1975).

Typical high strength, fracture toughness and chemical stability allow its use in extreme conditions (Garvie *et al.*, 1975). It is chemically resistant to temperatures above the melting point of Al_2O_3 . It has low thermal conductivity (five times lower than Al_2O_3). It resists metal melts and has high abrasion resistance. It is used in oxygen sensors and as a susceptor (heating element) in high-temperature induction furnaces, where it can operate in oxidizing atmospheres at temperatures above 2000°C. It is attractive for nuclear energy, where it is used in inert matrices for the storage of plutonium and nuclear waste. Other applications include cutting tools, seals and pistons in pumps for chemically aggressive and abrasive suspensions, bearings, biomedical implants (e.g., dental prostheses, knee and hip joints) (Garvie *et al.*, 1984), as well as thermal barrier coatings (TBC).

The framework of usability of often used tetragonal zirconia ceramics stabilized by 3% Y_2O_3 (3Y-TZP) has been studied in great depth as part of the effort to use these materials for biomedical implants, materials for teeth and joints (Cales and Chevalier, 1998;

Marro *et al.*, 2009; Hvizdoš *et al.*, 2009, 2010a; Chevalier *et al.*, 2020). 3Y-TZP is prone to low-temperature degradation (LTD), where under certain circumstances in presence of humidity at room and slightly elevated temperatures metastable tetragonal zirconia crystals can spontaneously transform to the monoclinic form, which leads to microcracking and negatively influences its bulk properties. The effect of LTD on the wear resistance was mapped using scratch testing (Hvizdoš *et al.*, 2009), as well as tribological analysis in combination with wide range of loads in speeds (Hvizdoš *et al.*, 2010a). The results of tribological tests were correlated with observations of microstructure and damage régimes, and conditions of 'mild-to-severe' wear transitions for zirconia/zirconia contact were identified (at 10 loads it was at speed approximately $0.1\text{--}0.2\text{ m s}^{-1}$) (Hvizdoš *et al.*, 2010a). It was found that fully tetragonal zirconia is more resistant than the degraded material, and at the same time it was shown that in quite a wide range of conditions only small levels of $t \rightarrow m$ transformation takes place due to mechanical stresses.

In zirconia-CNF composites a strong effect of the filler has been observed (Hvizdoš *et al.*, 2010b), both on the friction coefficient and on the wear rates, (Fig. 1). Microscopic observations of the worn surfaces of ZrO_2 - CNF composite materials reveal pulled-out CNF and indicate the presence of a tribofilm of dispersed graphite and crushed carbon nanofibers. These processes significantly reduce the values of the coefficient of friction, even in the case of a relatively low amount of carbon (1.07 wt%). The lubricating effect induced by the rolling of carbon filaments in the area of contact was not observed (Hvizdoš *et al.*, 2010b). However, the imperfections of the microstructure of the composites also lead to slightly higher specific wear rates which increased by about 50% when compared to the monolithic 3Y-TZP (Fig. 1(b)).

Nitrides – Silicon Nitride Based Ceramics

Silicon nitride (Si_3N_4) is a human-synthesized compound. The bulk material is characterized by a unique set of excellent properties. It has a relatively high strength and fracture toughness, low density (3.2 g cm^{-3}), and, thanks to the SiO_2 surface layer, good resistance to corrosion and oxidation at room and elevated temperatures. Due to the low coefficient of thermal expansion ($3.1\text{--}3.6 \times 10^{-6}\text{ K}^{-1}$ from room temperature up to 1000°C), it also has relatively good thermal shock resistance. The most desirable microstructure, typically used in industrial applications consists of fine $\alpha\text{-Si}_3\text{N}_4$ grains and larger $\beta\text{-Si}_3\text{N}_4$ grains with high aspect ratio. It has high strength and improved fracture toughness (Morrell, 1985). Silicon nitride is a relatively expensive material, but in applications where its excellent properties are combined with its durability and low maintenance, it can also be very economically advantageous as it has excellent resistance to abrasion and erosion. High-quality silicon nitride-based materials have been developed for use in internal combustion engines for valves and cams, where they have proven very successful. Unfortunately, the cost of larger ceramic components has never been reduced enough to be used to make all-ceramic engines or turbochargers. However, high quality components can be manufactured and used in many applications under conditions of high mechanical or thermal stress or abrasion.

In general, the wear behavior of Si_3N_4 -based materials is reported to be controlled by the following mechanisms (Wang and Hsu, 1996; Dong and Jahanmir, 1993; Skopp *et al.*, 1995): (1) mechanically- or thermally-induced microcracking due to fatigue assisted stresses resulting from friction at high normal loads, (2) tribochemical reaction with water vapor at low temperatures and normal loads ($<400^\circ\text{C}$, $<10\text{ N}$) and (3) tribooxidation at temperatures that depend on the composition and nature of the intergranular phases, generally above 500°C (Balko *et al.*, 2014).

As silicon nitride, particularly in self-mated configuration, has relatively high friction (COF over 0.5), various strategies have been applied to lower its value.

When using CNTs as additives, a clear influence of their content on friction and wear was shown by Hvizdoš *et al.* (2011, 2012). For low CNT contents a high friction coefficient was maintained (Fig. 1(a)). It started to decrease only when the CNT fraction reached about 5 wt%. In Si_3N_4 -10% CNT, the COF values decreased to ~ 0.35 . The wear resistance in general decreased but in certain cases some sort of optimum was identified (Si_3N_4 -5% CNT), where the wear rate was the same as for monolithic silicon nitride, but with much lower coefficient of friction (Hvizdoš *et al.*, 2012).

A more efficient improvement seems to be the use of graphene nanoplatelets (Hvizdoš *et al.*, 2013; Llorente *et al.*, 2019; Puchý *et al.*, 2020). As can be seen from Fig. 1(a), even at low proportions (1 and 3 wt% GNP) there was no increase in the coefficient of friction and the wear rate decreased significantly (Fig. 1(b)), mainly due to the improvement of fracture toughness, (Hvizdoš *et al.*, 2013). Llorente *et al.* (2019) showed that at higher contents of GNP, friction can be decreased by 50% at intermediate and high loads. Also, wear resistance was shown to improve in such composites (by up to 63%) in a monotonic way with respect to monolithic silicon nitride. Here, a C-rich tribofilm with oxidized Si_3N_4 particles plays a protective and self-lubricating role (Llorente *et al.*, 2019). When testing Si_3N_4 - GNP composites at elevated temperatures ($300, 500, 700^\circ\text{C}$), the positive effect of GNP gradually disappeared, so that at 700°C the properties of the composites were comparable to the monolithic ceramics, (Balko *et al.*, 2014). On the other hand, it was also shown that even at these temperatures, the GNPs remained structurally and chemically stable and did not decompose within the matrix. It was also found that no transformation of $\beta\text{-Si}_3\text{N}_4$ to $\alpha\text{-Si}_3\text{N}_4$ occurred at any stage of the test, (Balko *et al.*, 2014).

The literature for composites based on silicon nitride generally agree very well (Belmonte *et al.*, 2013; González-Julián *et al.*, 2014) for Si_3N_4 - MWCNT/SWCNT, where the coefficients of friction in the range of stability had values of 0.22–0.24. Generally speaking however, in terms of reductions in friction coefficients, randomly distributed CNTs and GNPs are effective only at relatively high contents, 20% and more (Belmonte *et al.*, 2013; González-Julián *et al.*, 2014; Miranzo *et al.*, 2017).

The wear behavior of composites reinforced by hard nanoparticles has a character different from those reinforced with carbon. Tatarko *et al.* (2010) presented a thorough study of silicon nitride based nanocomposites sintered with a wide range of rare-earth oxides,

which were further doped with SiC nanoparticles and the interesting findings are here reviewed. Introduction of SiC nanoparticles into the silicon nitride matrix improves hardness, strength, resistance to creep, oxidation and corrosion of Si_3N_4 ceramics. [Tatarko et al. \(2010\)](#) further found that the wear resistance increased with decreasing size of rare-earth cations in the Si_3N_4 monoliths as well as the Si_3N_4 -SiC composite materials sintered with different rare-earth oxide sintering additives. The friction coefficient slightly decreased with decreasing ionic radius of RE^{3+} from 0.74 to 0.70 in the case of monoliths and from 0.71 to 0.64 in the case of composites for the materials sintered with La_2O_3 and Lu_2O_3 , respectively. Similarly, the specific wear rate decreased with decreasing ionic radius of RE^{3+} from $3.22 \times 10^{-5} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ to $1.15 \times 10^{-5} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ for the monolithic Si_3N_4 sintered with La_2O_3 and Lu_2O_3 , respectively, and from $1.91 \times 10^{-5} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ to $0.89 \times 10^{-5} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ in the case of composites doped with the same additives. The same study showed that friction coefficient as well as the specific wear rate of composites was always lower compared to the monoliths with the same sintering additives indicating the higher wear resistance of Si_3N_4 -SiC composites.

The bonding strength between Si_3N_4 grains and grain boundary phases increases with decreasing ionic radius of RE^{3+} . Therefore, the highest bonding strength in Si_3N_4 containing Lu_2O_3 as a sintering additive restricts pull-out of the individual silicon nitride grains during the wear experiment. This fact together with its highest hardness and fracture toughness values are the reasons why Si_3N_4 doped by Lu exhibited the best wear resistance among all studied monolithic materials, ([Tatarko et al., 2010](#)).

The addition of SiC nanoparticles to this class of materials led to lower fracture resistance. In spite of that, the composites exhibited higher wear resistance in comparison with that of monolithic Si_3N_4 . This is probably due to their higher hardness whose positive effect was more significant than the influence of the lower fracture toughness, ([Tatarko et al., 2010](#)).

The wear mechanisms and the tribological characteristics were almost analogous for the monolithic Si_3N_4 and the Si_3N_4 -SiC composite materials. The mechanical wear (micro-fracture) and tribochemical reaction were found as the main wear mechanisms for all the studied materials. With increasing wear resistance, the worn surface becomes rather smooth but adherent debris are still present. An addition of SiC into the Si_3N_4 materials results in a higher number of "islands" of coherent debris, which then leads to formation of the protective tribolayer. In addition, the highest amount of coherent debris was observed for the material with the highest wear resistance, i.e., for the composite sintered with Lu_2O_3 , ([Tatarko et al., 2010](#)).

More fractured areas and a higher amount of silicon nitride debris were observed for the specimens having lower wear resistance. Such fractured areas show a mixture of intergranular and transgranular failure modes in the worn surfaces. According to the mechanisms described by [Wang and Hsu \(1996\)](#), [Dong and Jahanmir \(1993\)](#), and [Skopp et al. \(1995\)](#) for wear of silicon nitride-based materials, cracks initiate below the surface and propagate assisted by fatigue effects in a mixed intergranular/transgranular mode leading to microscale delaminations and fragmentation.

The coherent layers formed on the wear surfaces contain large amounts of oxygen, meaning that the layers are composed mainly of the oxidation products of silicon nitride. The formation of oxide may be accelerated by the presence of small particles of silicon nitride formed by fracture under the high contact stresses at the wear interface. These particles have a high specific area, which would increase the amount of reaction products formed compared to a reaction with the bulk of the ceramic.

Unlike the CNT/CNF containing nanocomposites, where the secondary phases not only reduced the coefficient of friction but also lowered the wear resistance, incorporation of SiC nanoparticles left the coefficient of friction unchanged but improved the wear resistance. This suggests that further development has the potential to improve overall tribological performance of ceramic nanocomposites.

Additions of boron nitride particles allows the production of another very interesting class of wear resistant silicon nitride based composites ([Carrapichano et al., 2002](#); [Wei et al., 2006](#); [Kovalčíková et al., 2014](#)). Hexagonal boron nitride (hBN) is attractive for its lubricating effect, high hardness, and when used in an adequate form, e.g., flat platelets, it offers an improvement in fracture toughness. In [Kovalčíková et al. \(2014\)](#) it was found that small quantity of micrometer sized hBN can increase the fracture toughness of the composite by approximately 50% - from 5 up to $7.5 \text{ MPa m}^{1/2}$. Similarly as for CNTs, small amounts of well-integrated hBN platelets do not lubricate and consequently do not lower the COF. However, it was shown that Si_3N_4 with 1 wt% hBN the specific wear rate was lower by 78% compared to the monolithic Si_3N_4 . The main wear mechanism for Si_3N_4 -hBN composites is abrasion with micro-fracture accompanied by tribochemical reaction with surface oxidation.

Carbides I – Silicon Carbide Based Ceramics

Silicon carbide (SiC) is a hard material used in the ceramic industry for many years. Its α -phase, stable to high temperatures, is crystallographically hexagonal and forms when carbon and silicon come into contact at high temperature in a reducing atmosphere. Its high decomposition temperature (2700°C) predetermines it as a material useful for bearings or furnace components. Its very low coefficient of thermal expansion ($4 \times 10^{-6} \text{ K}^{-1}$) without phase transformations guarantees its high temperature stability and thermal shock resistance. Thanks to its high hardness it is used for cutting tools and as a grinding medium. However, due to its brittleness it is very difficult to machine and its mechanical reliability is low. For this reason, SiC based composites with enhanced fracture toughness and formability/machinability are being designed. Again, promising are the carbon phase fillers (CNT, GNP) ([Džunda et al., 2019](#); [Guo et al., 2019](#)), or incorporation of other carbides, e.g., TiN/C with high hardness ([Frajkorová et al., 2012](#); [Fides et al., 2017a](#)).

Silicon carbide-based ceramics generally show lower coefficients of friction than Si_3N_4 materials (see [Table 2](#) and [Fig. 1](#)). SiC-CNT composites exhibit very stable values of the coefficient of friction (0.3–0.4) regardless of amount of CNT, which is probably related to the firm anchoring of CNT in the SiC matrix ([Džunda et al., 2019](#)). As a result, they cannot be released into the contact zone and act as a solid lubricant. Similar behavior is typical in SiC – GNP, where friction even increased slightly with increasing carbon content (except for COF = 0.6 at the higher contents of C – above 5%), probably due to the coarse-grained

Table 2 Typical values of coefficient of friction of unlubricated ceramics at room temperature

Material	Coefficient of friction	references
Al ₂ O ₃	0.3–0.6	Bhushan (1999), Puchý <i>et al.</i> (2013)
ZrO ₂	0.5	Hvizdoš <i>et al.</i> (2011)
Cr ₂ O ₃	0.25	Bhushan (1999)
SiC	0.3–0.35	Bhushan (1999), Džunda <i>et al.</i> (2019)
TiC	0.3	Bhushan (1999)
WC	0.3	Bhushan (1999)
B ₄ C	0.40–0.60	Kovalčíková <i>et al.</i> (2016), Sedlák <i>et al.</i> (2017b)
Si ₃ N ₄	0.25–0.65	Bhushan (1999), Balko <i>et al.</i> (2014), Puchý <i>et al.</i> (2020), Maros and Németh (2017)
TiN	0.25	Bhushan (1999)
BN	0.25	Bhushan (1999)
TiB ₂	0.5–0.6	Puchý <i>et al.</i> (2019), Kovalčíková <i>et al.</i> (2020)
ZrB ₂	0.45–0.55	Medveď <i>et al.</i> (2019), Ivor <i>et al.</i> (2020)
Diamond	0.1	Bhushan (1999)

structure and higher porosity (again for the higher contents). Regarding the wear resistance, it was shown that the good quality distribution and strong CNT bonds grown in-situ on SiC grains led to a very stable abrasion resistance of these materials. Similar behavior was observed for SiC – GNP, especially at low loads. Only at loads around 50 N at high contents (6 wt%) of GNP was the wear rate increased approximately twofold (Hvizdoš *et al.*, 2016).

In the case of SiC – TiN/C composites, at different loads from 5 N to 30 N, they behave very stably, with a slightly increasing coefficients of friction increasing from 0.29 to 0.32–0.39–0.50 (Fides *et al.*, 2017b). These composites also showed very stable wear behavior with low material loss values (about 10^{-6} mm³ m⁻¹ N⁻¹) for all materials up to relatively high loads (Fides *et al.*, 2017b). Their worn tribological surfaces are characterized by abrasion and fracture of the grains, facilitated by an intergranular type of failure, which was also observed in the analysis of mechanical and fracture properties (Fides *et al.*, 2017a). At higher wear loads, microcracks appear, forming mainly at a certain depth (typically around 5–10 μm) under the contact surface (Fides *et al.*, 2017b).

Carbides II – Boron Carbide Materials

Boron carbide (B₄C) is a relatively new industrial material. For the first time it was prepared only in mid-nineteenth century and its exact stoichiometry has been known only since 1934. It has a very high hardness. It is the third hardest known bulk substance after diamond and cubic boron nitride, with a hardness of 34 ± 4 GPa and Young's modulus 360–460 GPa (Sairam *et al.*, 2012). Its melting point is 2450°C and thermal conductivity 30 W m⁻¹ K⁻¹. Electrically, it is a semiconductor, like silicon carbide. Due to its advantageous properties its actual or potential applications include wear resistant components, aerospace materials, lightweight and bullet-proof armors, aerospace components, nuclear absorbers and control rods, etc. (Thévenot, 1990; Sedlák *et al.*, 2017a).

B₄C is a material with low sinterability. To facilitate its densification at lower temperatures and to enhance its mechanical performance (improve strength and fracture toughness), various additives have been tried, mostly boron, alumina, silicon, carbon, TiB₂, SiC, etc. (Kim *et al.*, 2000; Sedlák *et al.*, 2017a). The material can be prepared usually by hot pressing (HP) of very fine grain powders (<2 μm) at high sintering temperatures of 2100–2200°C, heating/cooling rates 10°C. min⁻¹ with typical dwell times of 15–45 min under 30–40 MPa. More recently graphene-based nanostructures attracted interest and are being adopted for use as fillers. In order to preserve their integrity, fast sintering methods are used such as spark plasma sintering (SPS) and flash sintering (FS) (Rehman *et al.*, 2014; Sedlák *et al.*, 2017a,b). To explore the possibilities of using the fast preparation procedures, Sedlák *et al.* (2017a,b) performed a series of experiments and made a comprehensive comparison of B₄C–GNP composites prepared by HP, SPS, and FS, with the total time of sintering being 7.5 h, one hour, and one minute, respectively.

In B₄C–GNP, with GNP contents from 0 up to 6 wt%, prepared by HP and SPS the final densities were about 99% and more, values consistent up to high amounts of GNPs. Flash sintering resulted in densities 91%–95%, when higher amounts of carbon actually led to higher density showing the benefit of densification promoting role of present carbon. Typically, GNPs have preferential directionality because in all methods one axis pressing is used, but the GNP/BN grains bonding is very good, (Kovalčíková *et al.*, 2016; Sedlák *et al.*, 2017a). Hardness is governed by residual porosity and basically independent of the GNP content. In the fully dense materials, the hardness is 20–24 GPa, while in the FS materials it was 15–17 GPa (Sedlák *et al.*, 2017b). The fracture toughness, however, showed clear benefit of the GNP presence. It steadily increased from 3 MPa m^{1/2} for boron carbide up to 4.5 MPa m^{1/2} for the composite with 6 wt% GNP (Kovalčíková *et al.*, 2016). Here, the typical toughening mechanisms by thin platelets were identified. Tribological testing showed that the coefficient of friction is similar both in monolithic B₄C and the composites (0.4–0.6), but the wear rates showed benefit of the improved fracture toughness of GNPs containing composites. The wear was typically severe but W decreased from 1.5×10^{-5} mm³ N⁻¹ m⁻¹ for monolithic B₄C by about 50% for B₄C – 6 wt% GNPs (Sedlák *et al.*, 2017b). As is typical in oxides and nitrides, also in B₄C based materials do tribochemical reactions occur at higher loads and higher temperatures and oxide layers, in the form of SiO₂ islets, are formed on the wear track surface (Sedlák *et al.*, 2017b).

Borides – Titanium-Diboride Based Ceramics

The titanium diboride ceramic is very hard (25 GPa), wear resistant and is a high temperature stable material with high elastic modulus. It is also electrically (resistivity $13 \times 10^{-8} \Omega \text{ m}$) and thermally ($64 \text{ W m}^{-1} \text{ K}^{-1}$) conductive. These properties are useful for a number of applications like cutting tools, wear-resistant parts for demanding conditions, armors, turbine blades, etc. It is, however, poorly sinterable and to achieve a sufficient density, high sintering temperatures and long dwell times have to be used. Such conditions result in grain growth, which causes a decrease of mechanical properties like fracture toughness and strength (Sánchez *et al.*, 2000; Wang *et al.*, 2002). Therefore, much research is aimed at the investigation of titanium diboride composites particularly with metals that could improve sinterability and fracture resistance. With the addition of metallic binders, the fracture toughness of TiB₂-based materials increased from 3 to 5 up to 6–12 MPa m^{1/2} thanks to improved plasticity and crack bridging toughening (Sánchez *et al.*, 2000; Chlup *et al.*, 2015; Fu and Koc, 2018a,b). Because of excellent chemical compatibility, TiB₂-Ti materials are considered very promising also for wear applications. Puchý *et al.* (2019) prepared a series of TiB₂ ceramics and TiB₂-Ti composites by SPS. They show that the high speed of the process prevented the significant grain growth. Moreover, whereas in the monolithic TiB₂ the densification starts at 2100°C, in the Ti containing composites it starts already at approximately 1495°C and relative density above 98% can be achieved. Adding of the metal lowered hardness but increased fracture toughness of the composites. Tribological studies show that for monolithic TiB₂ the friction coefficient is stable (0.5–0.6) for various load values and wear rates increase with increasing load – from 6×10^{-6} up to $17 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ for loads from 1 N up to 10 N. Adding Ti improved the tribological performance, where the best was achieved with the TiB₂ with 20% Ti (Puchý *et al.*, 2019). In this case the friction coefficient decreased with increasing load (from 0.8 down to 0.3) and similarly specific wear rate decreased from 2×10^{-6} down to $0.66 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$. The microscopic observation of the wear tracks showed that in the monolith damage in the form of scales, grooves, scratches and microcracks were dominant. These suggest that adhesion and abrasion by plowing are the main damage mechanisms. The worn surfaces of the composites were flatter, smoother and less scaly. The damage was mostly self-polishing abrasion (Puchý *et al.*, 2019).

Another approach to improve the sinterability but without the softening caused by a metal is the use of SiC, which additionally can increase hardness, fracture toughness and oxidation resistance (Zhao *et al.*, 2014). Kovalčíková *et al.* (2020) also studied the influence of GNP additions to TiB₂-SiC composites on the wear resistance. They found that the presence of SiC (up to 25 wt%) improved the flexural strength from 500 MPa up 601 MPa. Then, addition of GNPs, from 1 to 10 wt% further increased the strength up to 673 MPa. Regarding the tribological properties, additions of SiC did not influence the COF which was 0.50–0.55. Addition of higher amounts of GNP (10 wt%) was necessary to decrease the COF down to 0.47. On the other hand, all GNP containing composites showed higher wear resistance. The specific wear rate of TiB₂-20% SiC was $6 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ while that of TiB₂-20% SiC – GNP was around $10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ for 1–10 wt% GNP at lower loads. The wear mechanism is similar for all TiB₂-SiC and TiB₂-SiC-GNP materials, dominated by abrasion and tribochemical reaction with formation of SiO₂-TiO₂-C based tribofilm (Kovalčíková *et al.*, 2020).

High Entropy Ceramics

In recent years a very promising new class of ceramic materials with unusual crystallographic structures have come to focus (Castle *et al.*, 2018; Dusza *et al.*, 2018). These so-called high entropy carbides (HEC) contain typically four transition metal ions in a carbide superlattice (Castle *et al.*, 2018). Their structure is non-stoichiometric and is slightly distorted over short distances but well-ordered on longer ones with strong ionic bonds (Csanádi *et al.*, 2019). Such crystallography leads to extremely high stiffness. The HECs were synthesized only in small volumes and until now there have not been reports of their tribological properties. However, it has been shown that their mechanical performance (hardness, strength) is far superior (Castle *et al.*, 2018; Csanádi *et al.*, 2019) to the typical ceramics and ceramic based composites and they are expected to possess also excellent wear resistance over a wide range of conditions.

Summary

Advanced dense structural ceramics with high hardness are excellent materials for tribological applications. Their wear resistance is typically very high, and under controlled circumstances, in the mild wear regime, their worn surfaces are smooth, often with a polished appearance, without microcracking. When reduction of dry friction is necessary, adequate composites can be designed. The most popular approaches are introduction of hard nanoparticles that could increase hardness and fracture toughness, and/or new carbon nanoobjects, which are expected to improve fracture toughness and also act as solid lubricants.

As regards the influence of carbon nanotubes, nanofibers, and graphene platelets, tribological analyses have shown a positive influence of their presence in the microstructure. Quite low contents of CNFs (approximately 1 wt%) is enough to decrease the friction coefficients of zirconia/zirconia and zirconia/alumina contacts, from 0.45 down to 0.2, thanks to the creation of a carbon rich tribofilm that works as a solid lubricant. CNTs are less effective and to achieve similar result high amounts are necessary. The coefficient of friction does not change easily in these composites, and in the mild wear regime it remains stable during the tests, only at higher loads and severe wear regime does the friction decrease. The wear resistance then in general decreases but in certain cases some sort of optimum can be found. In the case of GNP, if these are properly distributed in the matrix, the benefit in increasing abrasion resistance due to improved fracture toughness, even at elevated temperatures, has proven to be clear.

In non-oxide ceramics, such as nitrides, carbides, and borides, tribochemical reactions occur at higher loads and higher temperatures and oxide layers tend to form on the worn surfaces, most often in the form of silica islands (Balko *et al.*, 2014; Džunda *et al.*, 2019; Kovalčíková *et al.*, 2020). In composites with CNT and GNP grown in-situ (Hussainova *et al.*, 2016; Džunda *et al.*, 2019), nanotube or platelet agglomeration, so often observed in conventional hot-pressed samples, can be significantly suppressed, and the filler distribution is more homogeneous. Such efficient distribution in the matrix contributes to better compaction of the composites and to higher values of both mechanical and tribological properties.

References

- Adachi, K., Kato, K., 1997. Wear map of ceramics. *Wear* 203–204, 291–301.
- An, J.W., You, D.H., Lim, D.S., 2003. Tribological properties of hot-pressed alumina-CNT composites. *Wear* 255, 677–681.
- Archard, J.F., 1953. Contact and rubbing of flat surfaces. *Journal of Applied Physics* 24, 981–988.
- ASTM G76 – 18, 2018. Standard test method for conducting erosion tests by solid particle impingement using gas jets. West Conshohocken, PA: ASTM International.
- Balázi, C., Fényi, B., Hegman, N., *et al.*, 2006. Development of CNT/Si₃N₄ composites with improved mechanical and electrical properties. *Composites: Part B* 37, 418–424.
- Balko, J., Hvizdoš, P., Dusza, J., Balázi, C., Gamcová, J., 2014. Wear damage of Si₃N₄-graphene nanocomposites at room and elevated temperatures. *Journal of the European Ceramic Society* 34, 3309–3317.
- Basu, B., Kalin, M., 2011. *Tribology of ceramics and composites*. New Jersey: Wiley and Sons.
- Belmonte, M., Ramírez, C., González-Julián, J., *et al.*, 2013. The beneficial effect of graphene nanofillers on the tribological performance of ceramics. *Carbon* 61, 431–435.
- Bhushan, B., 1999. *Principles and Applications of Tribology*. New York: Wiley and Sons.
- Bhushan, B., 2001. *Modern Tribology Handbook*. Boca Raton, Florida 33431: CRC Press LLC.
- Cales, B., Chevalier, J., 1998. Wear behavior of ceramic pairs compared on different testing configurations. In: Jacobs, J., Craig, T. (Eds.), *Alternative Bearing Surfaces in Total Joint Replacement*. West Conshohocken, PA: ASTM International, pp. 186–196.
- Carrapichano, J.M., Gomes, J.R., Silva, R.F., 2002. Tribological behaviour of Si₃N₄-BN materials for dry sliding applications. *Wear* 253, 1070–1076.
- Castle, E., Csanádi, T., Grasso, S., Dusza, J., Reece, M.J., 2018. Processing and properties of high-entropy ultra-high temperature carbides. *Scientific Reports* 8, 8609–8619.
- Chlup, Z., Bača, L., Halasová, M., *et al.*, 2015. Effect of metallic dopants on the microstructure and mechanical properties of TiB₂. *Journal of the European Ceramic Society* 35, 2745–2754.
- Chevalier, J., Liens, A., Reveron, H., *et al.*, 2020. Forty years after the promise of «ceramic steel?»: Zirconia-based composites with a metal-like mechanical behavior. *Journal of the American Ceramic Society* 103, 1482–1513.
- Csanádi, T., Castle, E., Reece, M.J., Dusza, J., 2019. Strength enhancement and slip behaviour of high-entropy carbide grains during micro-compression. *Scientific Reports* 9, 10200.
- Dong, X., Jahanmir, S., 1993. Wear transition diagram for silicon nitride. *Wear* 165, 169–180.
- Dusza, J., Švec, P., Girman, V., *et al.*, 2018. Microstructure of (Hf-Ta-Zr-Nb)C high-entropy carbide at micro and nano/atomic level. *Journal of the European Ceramic Society* 38, 4303–4307.
- Džunda, R., Fides, M., Hnatko, M., *et al.*, 2019. Mechanical, physical properties and tribological behaviour of silicon carbide composites with addition of carbon nanotubes. *International Journal of Refractory Metals and Hard Materials* 81, 272–280.
- Fides, M., Hvizdoš, P., Bystrický, R., *et al.*, 2017a. Microstructure, fracture, electrical properties and machinability of SiC-TiNbC composites. *Journal of the European Ceramic Society* 37, 4315–4322.
- Fides, M., Kovalčíková, A., Hvizdoš, P., *et al.*, 2017b. Mechanical and tribological properties of electrically conductive SiC based cermets. *International Journal of Refractory Metals and Hard Materials* 65, 76–82.
- Frajkorová, F., Hnatko, M., Lenčoš, Z., Šajgalík, P., 2012. Electrically conductive silicon carbide with the addition of TiNbC. *Journal of the European Ceramic Society* 32, 2513–2518.
- Fu, Z., Koc, R., 2018a. Pressureless sintering of TiB₂ with low concentration of Co binder to achieve enhanced mechanical properties. *Materials Science and Engineering: A* 721, 22–27.
- Fu, Z., Koc, R., 2018b. TiNiFeCrCoAl high-entropy alloys as novel metallic binders for TiB₂-TiC based composites. *Materials Science and Engineering: A* 735, 302–309.
- Garvie, R.C., Hannink, R.H., Pascoe, R.T., 1975. Ceramic steel? *Nature* 258, 703–704.
- Garvie, R.C., Urbani, C., Kennedy, D.R., McNeuer, J.C., 1984. Biocompatibility of magnesia-partially stabilized zirconia (Mg-PSZ) ceramics. *Journal of Materials Science* 19, 3224–3228.
- González-Julián, J., Datye, A., Wu, K.-H., Schneider, J., Belmonte, M., 2014. Robust and wear resistant in-situ carbon nanotube/Si₃N₄ nanocomposites with a high loading of nanotubes. *Carbon* 72, 338–347.
- Guo, X., Wang, R., Zheng, P., Lu, Z., Yang, H., 2019. Pressureless sintering of multilayer graphene reinforced silicon carbide ceramics for mechanical seals. *Advances in Applied Ceramics* 118, 409–417.
- Hussainova, I., Baronins, J., Drozdova, M., Antonov, M., 2016. Wear performance of hierarchically structured alumina reinforced by hybrid graphene encapsulated alumina nanofibers. *Wear* 368–369, 287–295.
- Hvizdoš, P., Chintapalli, R., Valle, J., Anglada, M., 2009. Effect of ageing on scratch resistance of 3Y-TZP. *Kovové Materiály - Metallic Materials* 47, 333–339.
- Hvizdoš, P., Mestra, A., Anglada, M., 2010a. Effect of heat treatment on wear damage mechanisms in 3Y-TZP ceramics. *Wear* 269, 26–30.
- Hvizdoš, P., Puchý, V., Duszová, A., Dusza, J., 2010b. Tribological behavior of carbon nanofiber-zirconia composite. *Scripta Materialia* 63, 254–257.
- Hvizdoš, P., Duszová, A., Puchý, V., *et al.*, 2011. Wear behavior of ZrO₂-CNF and Si₃N₄-CNT nanocomposites. *Key Engineering Materials* 465, 495–498.
- Hvizdoš, P., Puchý, V., Duszová, A., Dusza, J., Balázi, C., 2012. Tribological and electrical properties of ceramic matrix composites with carbon nanotubes. *Ceramics International* 38, 5669–5676.
- Hvizdoš, P., Dusza, J., Balázi, C., 2013. Tribological properties of Si₃N₄-graphene nanocomposites. *Journal of the European Ceramic Society* 33, 2359–2364.
- Hvizdoš, P., Fides, M., Kovalčíková, A., *et al.*, 2016. Development of electrically conductive SiC-GPL, SiC-CNT and SiC-TiNbC composites. In: *Proceedings of the Workshop on Graphene/Ceramic Composites: Programme and Abstracts*, p. 50. Cuenca (Spain).
- ISO 20808:2004(E), 2004. Fine ceramics – Determination of friction and wear characteristics of monolithic ceramics by ball-on-disc method.
- Ivor, M., Medved, D., Vojtko, M., *et al.*, 2020. Nanoindentation and tribology of ZrB₂ based luminescent ceramics. *Journal of the European Ceramic Society* 40, 4901–4908.
- Kato, K., 1990. Tribology of ceramics. *Wear* 136, 117–133.
- Kato, K., Adachi, K., 2002. Wear of advanced ceramics. *Wear* 253, 1097–1104.
- Kim, H.-W., Koh, Y.-H., Kim, H.-E., 2000. Densification and mechanical properties of B₄C with Al₂O₃ as a sintering aid. *Journal of the American Ceramic Society* 83, 2863–2865.

- Kovalčíková, A., Balko, J., Balázs, C., Hvizdoš, P., Dusza, J., 2014. Influence of hBN content on mechanical and tribological properties of $\text{Si}_3\text{N}_4/\text{BN}$ ceramic composites. *Journal of the European Ceramic Society* 34, 3319–3328.
- Kovalčíková, A., Sedlák, R., Rutkowski, P., Dusza, J., 2016. Mechanical properties of boron carbide + graphene platelet composites. *Ceramics International* 42, 2094–2098.
- Kovalčíková, A., Tatarko, P., Sedlák, R., *et al.*, 2020. Mechanical and tribological properties of $\text{TiB}_2\text{-SiC}$ and $\text{TiB}_2\text{-SiC-GNPs}$ ceramic composites. *Journal of the European Ceramic Society* 40, 4860–4871.
- Lim, D.S., You, D.H., Choi, H.J., Lim, S.H., Jang, H., 2005. Effect of CNT distribution on tribological behavior of aluminum-CNT composites. *Wear* 259, 539–544.
- Llorente, J., Ramirez, C., Belmonte, M., 2019. High graphene fillers content for improving the tribological performance of silicon nitride-based ceramics. *Wear* 430–431, 183–190.
- Maros, M.B., Németh, A.K., 2017. Wear maps of HIP sintered $\text{Si}_3\text{N}_4/\text{MLG}$ nanocomposites for unlike paired tribosystems under ball-on-disc dry sliding conditions. *Journal of the European Ceramic Society* 37, 4357–4369.
- Marro, F.G., Chintapalli, R., Hvizdoš, P., *et al.*, 2009. Study of near surface changes in yttria-doped tetragonal zirconia after low temperature degradation. *International Journal of Materials Research* 100, 92–96.
- Medved', D., Balko, J., Sedlák, R., *et al.*, 2019. Wear resistance of ZrB_2 based ceramic composites. *International Journal of Refractory Metals and Hard Materials* 81, 214–224.
- Medvedovski, E., 2001. Wear-resistant engineering ceramics. *Wear* 249, 821–828.
- Miranzo, P., Belmonte, M., Osendi, M.I., 2017. From bulk to cellular structures: A review on ceramic/graphene filler composites. *Journal of the European Ceramic Society* 37, 3649–3672.
- Morrell, R., 1985. *Handbook of Properties of Technical and Engineering Ceramics*, Part 1. London: HMSO.
- Puchý, V., Hvizdoš, P., Dusza, J., *et al.*, 2013. Wear resistance of $\text{Al}_2\text{O}_3\text{-CNT}$ ceramic nanocomposites at room and high temperatures. *Ceramics International* 39, 5821–5826.
- Puchý, V., Kováčik, J., Kovalčíková, A., *et al.*, 2019. Mechanical and tribological properties of $\text{TiB}_2\text{-Ti}$ composites prepared by spark plasma sintering. *Kovové Materiály - Metallic Materials* 57, 435–442.
- Puchý, V., Hvizdoš, P., Ivor, M., *et al.*, 2020. Preparation, friction, wear, and fracture of the $\text{Si}_3\text{N}_4\text{-Ag-GNPs}$ composites, prepared by SPS. *Journal of the European Ceramic Society* 40, 4853–4859.
- Rehman, S.S., Ji, W., Khan, S.A., *et al.*, 2014. Microstructure and mechanical properties of B_4C based ceramics with Fe_3Al as sintering aid by spark plasma sintering. *Journal of the European Ceramic Society* 34, 2169–2175.
- Saint-Gobain, 2020. Available at: <https://www.ceramicsrefractories.saint-gobain.com/solutions/wear-resistance> (retrieved 21.10.20).
- Sairam, K., Sonber, J.K., Murthy, T.S.R.C., *et al.*, 2012. Development of $\text{B}_4\text{C-HfB}_2$ composites by reaction hot pressing. *International Journal of Refractory Metals and Hard Materials* 35, 32–40.
- Sánchez, J.M., Azcona, I., Castro, F., 2000. Mechanical properties of titanium diboride based cermets. *Journal of Materials Science* 35, 9–14.
- Sedlák, R., Kovalčíková, A., Múdra, E., *et al.*, 2017a. Boron carbide/graphene platelet ceramics with improved fracture toughness and electrical conductivity. *Journal of the European Ceramic Society* 37, 3773–3780.
- Sedlák, R., Kovalčíková, A., Balko, J., *et al.*, 2017b. Effect of graphene platelets on tribological properties of boron carbide ceramic composites. *International Journal of Refractory Metals and Hard Materials* 65, 57–63.
- Skopp, A., Woydt, M., Habig, H., 1995. Tribological behavior of silicon nitride materials under unlubricated sliding between 22°C and 1000°C. *Wear* 181–183, 571–580.
- Stevens, R., 1986. *Zirconia and Zirconia Ceramics*, second ed. Twickenham: Magnesium Electron Ltd.
- Tatarko, P., Kašiarová, M., Dusza, J., *et al.*, 2010. Wear resistance of hot-pressed $\text{Si}_3\text{N}_4/\text{SiC}$ micro/nano composites sintered with rare-earth oxide additives. *Wear* 269, 867–874.
- Thévenot, F., 1990. Boron carbide – A comprehensive review. *Journal of the European Ceramic Society* 6, 205–225.
- Wang, Y., Hsu, S.M., 1996. Wear and wear transition mechanisms of ceramics. *Wear* 195, 112–122.
- Wang, W., Fu, Z., Wang, H., Yuan, R., 2002. Influence of hot pressing sintering temperature and time on microstructure and mechanical properties of TiB_2 ceramics. *Journal of the European Ceramic Society* 22 (2002), 1045–1049.
- Wei, D., Meng, Q., Jia, D., 2006. Mechanical and tribological properties of hot-pressed h-BN/ Si_3N_4 ceramic composites. *Ceramics International* 32, 549–554.
- Yamamoto, G., Omori, M., Yokomizo, K., Hashida, T., Adachi, K., 2008. Structural characterization and frictional properties of carbon nanotube/alumina composites prepared by precursor method. *Material Science and Engineering B* 148, 265–269.
- Zhao, G., Huang, C., Liu, H., *et al.*, 2014. Microstructure and mechanical properties of $\text{TiB}_2\text{-SiC}$ ceramic composites by reactive hot pressing. *International Journal of Refractory Metals and Hard Materials* 42, 36–41.

Wear and Erosion Resistant Ceramic Coatings

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Introduction

Wear and erosion are the damage phenomena occurring at the contacting surfaces in mutual motion and resulting in gradual removal of part of a material from the contact area. They are closely related to friction, plasticity, fracture and other damage mechanisms occurring in the localized contacts which are subjected to relatively high stresses. Excessive material removal due to abrasion, erosion, corrosion and other mechanisms or their combinations result in a degradation of materials used for the structural components practically in all fields of industry and very often determine the lifetime of the corresponding products. In industry, around half of the wear losses can be attributed to abrasion and almost one tenth to erosion. The annual economic losses due to wear and corrosion in the USA already in early 90s were estimated to exceed 300 billion USD (Cox, 2001). More recent calculations on the global energy losses due to friction, which is closely related to wear, showed that friction has also extremely high economic impact. For example, the energy consumption in heavy-duty road vehicles and buses due to friction in engines, transmissions, tyres, auxiliary equipment, and brakes was estimated to be around 33% of the fuel energy. A reduction in friction may result up to a 2.5 x improvement in fuel economy with corresponding environmental benefits (Holmberg *et al.*, 2014). Analogous calculations in paper mill industry showed that the energy losses are in the range 15%–25% of total energy consumption (Holmberg *et al.*, 2013). Since wear and friction are surface related phenomena, the application of relatively thin low-friction coatings with much higher wear resistance is one of the most effective ways (besides lubrication which is not a subject of the current work) to reduce the wear and friction of the primary materials. This approach brings number of technical and economic benefits, especially due to the possibility to use “cheaper” basic materials which can achieve desired or better performance, extended lifetime and higher reliability due to better properties of the coating. On the other hand, a large number of challenges has to be solved and requirements fulfilled to guarantee the benefits from relatively thin layers subjected to the same or even higher loads than the original uncoated components. The necessary requirements for wear resistant coatings strongly depend on the type of loading regime in the contact area. Holmberg and Matthews (2000) proposed the following modes of tribological contacts: static contact stresses, sliding, surface fatigue, fretting, abrasion, impact and chemical dissolution. Regardless of the contact mode, the universal requirements to all coatings involve sufficiently high hardness and toughness combined with high adhesion, cohesion strength and low friction. The requirements specific for the particular contact mode include coating thickness, load support, proper elasticity, surface finish, etc. However, some variations in properties are possible even within each mode depending on the wear process and loading conditions. In the case of adhesive wear, hardness would be the main parameter whereas in the case of abrasive wear, higher toughness, adhesion and thickness would be required from the coatings, especially at higher loads. The properties necessary for erosion resistance also vary from hardness at low impact angles to hardness, toughness and good adhesion at high angle impact. Obviously, the selection of the coating providing the best wear and erosion resistance in each specific application would be limited not only by the determination of the material system but also by the understanding of the wear and friction mechanisms and their relationships to the coating properties as well its structure and as deposition conditions required for their achievement. Thus, the basics of tribology including dry wear and friction mechanisms, the main properties controlling wear and erosion resistance and the ways of their measurement are described in the first part of this chapter. The second part focuses on the deposition methods of PVD coatings exhibiting mechanical properties desired for wear and erosion resistant coatings by means of formation of nanocomposite structures. The work is intentionally limited to relatively thin PVD coatings. The detail information on the thick wear resistant coatings prepared by various spraying and electro/electroless plating technologies can be found elsewhere (Wolfe *et al.*, 2006; Fauchais *et al.*, 2011; Kuroda *et al.*, 2011).

Introduction to Tribology

Friction, wear, corrosion, erosion and related damage mechanisms as well as lubrication are the subject of tribology – “the science of interacting surfaces in relative motion and practices related there to” (Oberle, 1951; Archard, 1953; Czichos, 1978; Bhushan and Gupta, 1991; Hutchings and Shipway, 2017; Holmberg and Matthews, 2009; Bhushan, 1999; Bhushan, 2000). The word “tribology” originates from Greek “tribos” which means “rubbing” (Archard, 1953). Friction and wear are the consequences of complex interactions and processes involved in the contacts of two mating surfaces. The result of these interactions is determined by the conditions of mechanical loading (sliding, rolling, mixed movement, etc.), properties of each material of the tribocouple (especially hardness, elastic modulus, toughness and their ratios between coating and the substrate), surface conditions in the tribocontact (e.g., roughness) and often also by the environment (and related oxidation resistance, etc.). A brief description of such complex processes in this chapter requires certain simplifications. Therefore, sliding and rolling friction is considered at first as the primary process in which no material removal is involved. Then, wear mechanisms related to the damage resulting from friction forces and resulting in the material removal are described. Erosion is considered to be a specific mode of wear caused by impingement of solid particles, liquid drops or gas bubbles.

Friction

Friction in sliding motion is defined as a tangential resistance to relative motion of contacting bodies (Hutchings and Shipway, 2017; Holmberg and Matthews, 2009). The degree of friction is measured by a dimensionless coefficient of friction (COF), μ , which corresponds to the frictional (tangential) force F_f divided by normal load F_n on the contact (Fig. 1)

$$\mu = F_f / F_n \quad (1)$$

The Eq. (1) is called the first law of friction and means that the friction force is proportional to the loading force. However, friction can be considered also as a mechanism of energy dissipation and in that case, μ can be defined as a ratio of energy loss due to friction, W_f , to total energy in the system, W

$$\mu = W_f / W \quad (2)$$

However, for the development of physical models of friction, the second law of friction is more important. It says that the coefficient of friction does not depend on the contact surface area, A_n (see Fig. 1). The reason is that the contact surface is never absolutely flat, surface undulations and asperities are always present. Thus, the contact surface A_n is only apparent, true contact and load bearing area is limited to the contacts among the asperities. This contact area is several orders of magnitude smaller than A_n (Fig. 2). The macroscopic normal force F_n is applied to these highly localized asperity contacts and the local stresses there are subsequently much higher than the average stress calculated for A_n surface area from normal load F_n . As a result, asperities in the contacts are immediately elastically and even plastically deformed (in the case of brittle material, localized fracture can occur) and the contact area becomes A_r . It is controlled by the lower yield strength of one of the materials in the tribocouple. Since the area A_r is still approximately three orders of magnitude smaller than A_n , there is no direct correlation between friction and A_n .

The third law of friction states that the coefficient of friction does not depend on the sliding speed. However, it is in contrast with the existence of a static coefficient of friction when the friction force for the initiation of sliding at the same normal load is higher than the force during stable sliding at various speeds. The reason is that in static case, A_r can increase (e.g., due to creep) over time.

The friction forces were originally attributed only to the adhesion between asperities and to the shear strength of their connections during sliding (Bowden and Tabor, 1950). However, plastic deformation of the asperities in the contacts and plowing effects resulting from the presence of debris and/or third bodies may also contribute to friction forces and energy dissipation during sliding. Thus, the coefficient of friction consists of:

- adhesion, involving breaking of the adhesive bonds between the asperities;
- plowing, corresponding to the resistance to deformation when a harder counter-surface moves through a softer material;
- deformation (elastic and plastic) and
- other possible components.

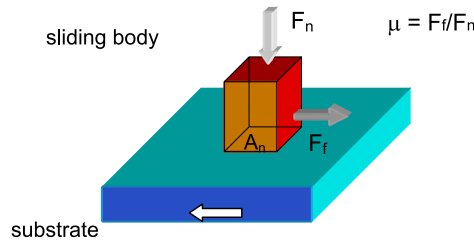


Fig. 1 Schematic of the forces in a sliding tribo-couple subjected to a normal force of F_n and the contact surface, A_n . The friction force F_f is proportional to F_n but the coefficient of friction does not depend on the contact surface A_n .

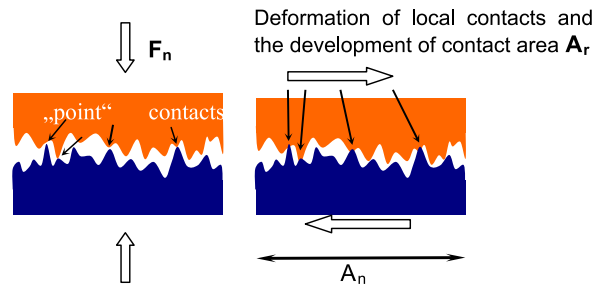


Fig. 2 Schematic of the microscopic contacts between two mating surfaces during normal loading (the scale in vertical direction is unproportionally magnified) – a; the formation of the true contact area A_r among asperities after elastic and plastic deformation during sliding.

The adhesion component or mechanism of friction is proportional to the interfacial shear strength of the contacts between asperities (Bowden and Tabor, 1950; Rabinowicz, 1965) and surface energy of the contacting tribo-couple rather than on the properties of the individual materials. In the real situation, adhesion can be affected by the reactions with the environment and formation of transfer layers. Plowing component appears when one of the materials in the tribo-couple is harder and its asperities penetrate and plow into a softer material. Besides individual asperities, plowing may occur also by the debris originating from previous wear events. Plowing means that the counter-surface is deformed elastically and plastically, both of which result in energy dissipation. Because the elastic part is recoverable, the most of the energy losses have to be related to plastic deformation. The deformation component of the coefficient of friction is determined by the hardness and elastic moduli of the coating, substrate and the counterpart as well as by their shear strength and shear strength of the interface (Heilman and Rigney, 1981). The plowing mechanism is controlled by the resistance to elastic and plastic deformation and the size and geometry of the asperities and/or plowing particles. Additional energy consuming contributions due to elastic hysteresis losses in some viscoelastic surfaces can arise from cyclic deformation and high internal damping. Holmberg *et al.* (2007) suggested that *hysteresis* is an alternative basic mechanism of friction besides adhesion and plowing. A hysteresis mechanism was attributed to the resistance originating from the continuous elastic deformation in the contacts of the moving surfaces whereas plastic (and elastic) deformation was assigned to plowing. However, regardless of the earlier and current classifications, the basic friction mechanisms during sliding remain adhesion, plowing (with plastic deformation) and elastic deformation (hysteresis).

The friction forces occurring during rolling are typically much smaller than during sliding. However, rolling involves also varying amount of sliding, referred to as *slip*. It is a consequence of finite contact area due to elastic deformation of contacting bodies during rolling. Because the radii of the different points in the contact surface are different, unequal tangential displacements leading to interfacial microslips are introduced. Adhesion mechanism in rolling may play only a minor role because of the separation of the contacting surface at the trailing edge occurs in tension rather than in shear. Obviously, the mechanisms resulting from elastic hysteresis and plastic deformation in the rolling contact may also be involved. Further details on rolling mechanisms can be found in (Bhushan and Gupta, 1991).

Wear

In contrast to friction when no material removal occurs, wear is defined as a process of the detachment of material from one or both contacting surfaces moving over another (Bhushan and Gupta, 1991; Hutchings and Shipway, 2017; Holmberg and Matthews, 2009; Bhushan, 2000). Obviously, the main difference is that besides conventional mechanisms considered in friction, fracture processes leading to the detachment of material are involved. Fracture in this case means the loss of cohesion via cracking producing debris released from the surface instead of separation of a body into two or more pieces common in the case of brittle bulk material fractures. The fracture events in the coating/substrate systems during wear may principally occur either at the top surface of the coating, within the coating, along the coating/substrate interface or in the substrate. The rate of the material removal resulting from wear is quantified using universal wear rate parameter K defined as a volume of the material, V , removed from the contact surface under the normal load, F_n , after moving for a distance, l

$$K = K'/H = V/(F_n l), \quad (3)$$

where K' is a constant and H is the hardness of the material. The physical meaning of the wear rate K is the worn volume divided by the mechanical energy introduced into the contact. The energy input corresponds to the load and distance which is equal to the load, velocity and time of the mutual movement. The commonly used dimension of K is ($\times 10^{-6}$) mm^3/Nm .

The wear mechanisms may be classified in several ways depending on the type of relative motion (sliding, rolling, fretting, impact, etc.) and type of wearing contacts (single phase with solid, liquid or gas phase) but the most common approach is based on the dominant wear mechanism. They include adhesive (also called galling or scuffing) wear, abrasive wear, fatigue, chemical (corrosive) wear mechanisms (Fig. 3).

Sometimes, fretting wear, erosive wear by solid particles, fluids or cavitation and electric-arc induced wear are considered as independent mechanisms (Holmberg and Matthews, 2000; Bhushan and Gupta, 1991; Holmberg and Matthews, 2009). However, when the focus is made on the way material removal takes place, the principal wear mechanisms can be reduced to only three cases (Holmberg *et al.*, 2007):

- Adhesion + fracture – it is typical for the tribo-pairs with identical or similar mechanical properties. The debris is formed due to adhesion generated tensile and shear stresses exceeding material strength. The wear rate in this case can be reduced by the reduction of the normal load and/or by using materials with higher strength.
- Abrasion + fracture – it is applicable to the systems with different hardness or when additional hard particles are introduced in the tribo-pair which result in severe plowing. The debris results mainly from excessively high shear stresses (exceeding the strength of the material) and subsequent cracking and detachment when hard particle or asperity moves through softer counterpart. The rate of abrasion can be reduced using harder materials or by load reduction.
- Fatigue + fracture – this mechanisms occur in the materials prone to cyclic fatigue. Crack nucleation, propagation and debris formation result from cyclic loading generating (mainly compressive) stresses exceeding the fatigue limit. This mechanism has usually two phases. In the first phase, surface structure and properties are modified without cracking. It occurs in the second phase when modified material cannot withstand the stresses resulting from damage accumulation during previous cyclic loading.

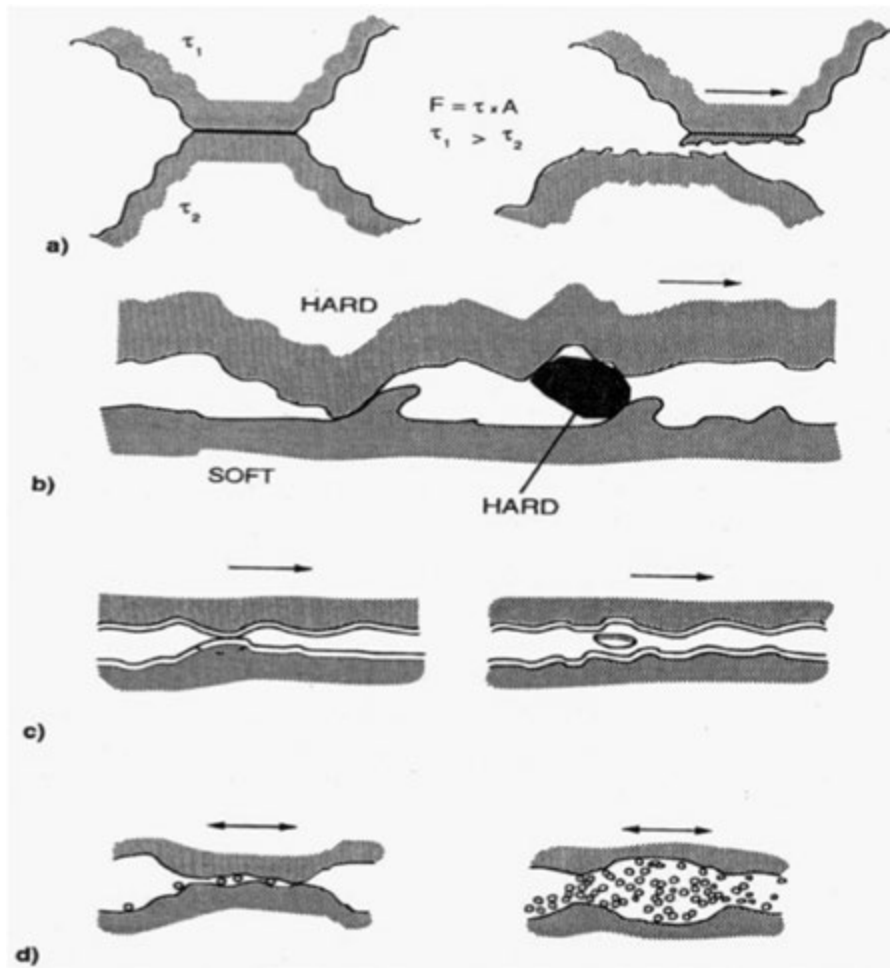


Fig. 3 The main wear mechanism (a) – adhesive, (b) – abrasive, (c) – fatigue, (d) – chemical wear. Reproduced from Holmberg, K., Matthews, A., 2009. *Coatings Tribology: Properties, Techniques and Applications in Surface Engineering*, third ed. Amsterdam: Elsevier Science.

Tribochemical wear, including corrosive wear, is not regarded as an independent mechanism because the corresponding chemical reactions modify the surface composition and properties of the top layer, but the removal of the material occurs via the same three above mentioned mechanisms. Thus, the chemical changes may be considered only as an additional parameter influencing the basic wear mechanisms.

Erosion

Erosion is a wear mode when the removal of the material occurs due to the impact of the solid particles, liquid drops or gas bubbles onto the surface of the material. When hard solid particles carried out by carrier gas or fluid impact the surface of a slightly softer coating with sufficient energy (Fig. 4), a part of the surface material (coating or coating/substrate) is removed analogically to sputtering. Note that the attention in the current work is paid to the erosion by solid particles and the case of erosion by cavities (bubbles) formed in the unstable liquids and imploding against the surface of the solids is not considered. Although the erosion wear by solid particles causes serious concern also in dentistry (Imfeld, 1996) it is highly relevant to energy and engineering industry, e.g., in moving blades, valve shutters and pipe bends etc. in the pipelines for coal transportation and hydrogenation systems, coal and hydraulic turbines, catalytical cracking of oil, heat exchangers, etc. Typical examples of deleterious influence of erosion in engineering represent the wear of blades and vanes in the turbine engines and blades of the helicopters by sand. On the other hand, erosion is successfully exploited in sand blasting, erosive drilling and abrasive deburring (Finnie, 1995).

The erosion by solid particles differs from abrasion by plowing of hard particles by the forces resulting in their movement. In the case of abrasion, the contact pressure depends mainly on the normal load whereas in erosion, the particles are driven by drag of the flow of surrounding medium, gravitational force as well as inter-particle forces and contact forces at the surface (Bhushan and Gupta, 1991; Holmberg and Matthews, 2009).

The erosion rate depends on a number of factors related to both eroding particles and eroded material as well. The main parameters on particle side involve type, number, mass and velocity (energy) of the particles and their angle of incidence. The

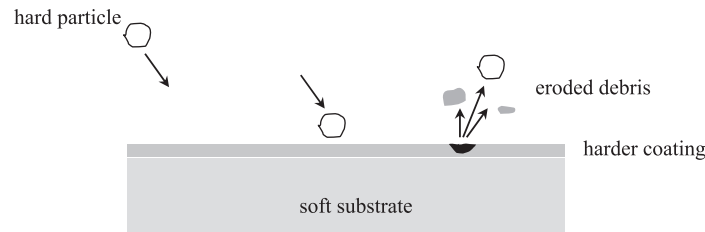


Fig. 4 Schematic of the erosion wear by solid particles.

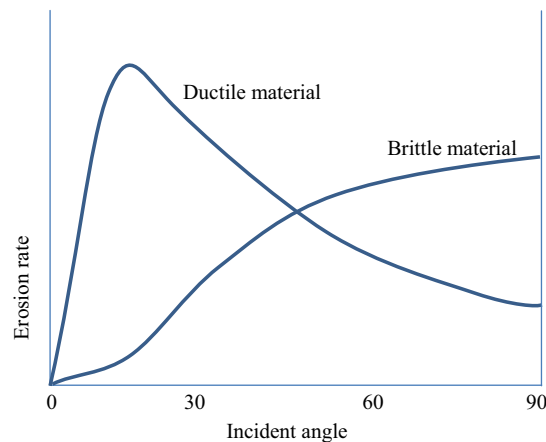


Fig. 5 The schematic comparison of the angular dependencies of erosion rates in ductile and brittle materials.

main properties on the eroded material side are toughness and hardness. In the case of erosion of ductile materials under normal incidence, the maximum erosion ratio, defined as mass eroded material to the mass of particles impacting the surface, is proportional to the density of the particles, square of their velocity and inversely proportional to the hardness of the eroded material. This dependence is similar to that of abrasive wear. The decrease of the angle of incidence from normal increases the erosion rate and the maximum is achieved at around 20° – 30° (Fig. 5). Such behavior can be explained by considering cutting and deformation as two competing mechanisms involved. At small angles of incidence, a cutting mechanism involving plowing and/or fragmentation of the surface is dominant. At normal incidence, deformation mechanisms involving formation of pile-ups (lips) at the edges if the indents, their flattening and gradual removal by subsequent impacts, would dominate. In contrast to ductile materials, brittle materials exhibit the maximum erosion ratio at normal incidence (see Fig. 5). In that case, severe cracking results from the formation of surface ring and conical cracks and/or lateral and median cracks similar to those reported under single indents during hardness tests (Lawn and Swain, 1975). When these cracks interact with the surface, material is released from the surface in the form of chips or lips. At larger angles of incidence, the above mechanisms are suppressed and the erosion rate decreases (Finnie, 1995).

The erosion rate is usually determined from the data obtained from the volumes of the craters produced using rubber wheel abrasion tests at higher loads and/or in micro-abrasion tests at low loads. In the first case, dry sand is continuously supplied into the contact area between a rotating rubber lined wheel pressed against the tested sample under a constant load. This type of testing is normalized in an ASTM standard G-65. In the case of micro-abrasion tests under low loads, liquid slurries of abrasive media (e.g., SiC powder with the particle size in the range of several micrometers) are introduced between the sample and the rotating ball. Such configuration corresponds to the calotester but specialized devices can be used when wider load range is required.

Wear Reduction

The above considerations of classification, models and wear and erosion mechanisms indicate that material removal is a complex process consisting of various deformation and fracture events occurring simultaneously. The ways to reduce wear and erosion depend on the control of the testing conditions as well as of the main properties of the tested coating. As discussed earlier, adhesive wear during dry friction is inversely proportional to the hardness of the coating. Obviously, additional properties involving toughness to reduce fracture and subsequent plowing, stiffness to provide sufficient bearing capability, the counter-part with low tendency to form solution with the coating material, sufficient adhesion, etc. are also important. In the case of abrasive mechanisms, hardness is also the main parameter but a large number of additional parameters and concepts including elastic modulus, ratio of hardness to modulus, strain energy, plastic work etc. have also been considered to find out direct correlations

with the wear resistance (Bhushan and Gupta, 1991; Hutchings and Shipway, 2017; Holmberg and Matthews, 2009; Bhushan, 1999; Kramer, 1983; Leyland and Matthews, 2000, 2004). Because fracture is the critical process in wear, the combination of toughness enhancement (= higher ductility) and higher hardness (= low ductility) is highly desirable but difficult to achieve. For the reduction of erosive wear by solid particles, high resilience of the surface (determined by the ratio of tensile strength and elastic modulus and corresponding to the amount of energy absorbed before deformation or cracking occurs) simultaneously with high hardness and toughness are of principal importance (Bhushan and Gupta, 1991; Kramer, 1983; Leyland and Matthews, 2000, 2004). Again, high hardness and toughness are the primary properties to achieve high wear resistance. On the other hand, the ratio of hardness to elastic modulus, H/E , was found to correlate with wear resistance much better than just hardness (Leyland and Matthews, 2000, 2004). The ratio H/E is also a part of the plasticity index, which is used for the calculation of the limit of elastic behavior in surface contacts (Musil, 2000). Moreover, the yield pressure in a rigid ball on a plate is proportional to the H^3/E^2 ratio (Leyland and Matthews, 2000, 2004) and it is a part of the relationships defining toughness (Lawn and Swain, 1975; Musil, 2012; Musil and Jirout, 2007; Musil, 2012). Thus, the primary requirements for the suppression wear can be reduced to the increase of H/E ratio, because it would result in the reduction of the deformation as well as fracture in the contacts of two moving bodies. $H/E \geq 0.1$ was proposed as a limit for achieving proper combination of hardness and toughness. The ratio can be adjusted by the reduction of elastic modulus rather than by hardness increase via structure modification, especially in the coatings with nanocomposite structures (Leyland and Matthews, 2000; Musil, 2012; Musil and Jirout, 2007; Musil, 2012). At the same time it is clear, that despite H/E ratio is important and very convenient parameter, which can be relatively easily obtained from nanoindentation measurements, it is a simplification relating to material side only. It definitely cannot provide absolute values of wear rates depending on the geometry, loading conditions, real stress distributions, environment, contamination and many other factors.

Structure and Property Control in Hard Coatings

From the viewpoint of mechanical properties, wear and erosion resistant coatings have to exhibit high hardness combined with reasonable elastic modulus and sufficient toughness. To achieve these properties, the requirements to possible candidate materials for coatings can be divided into two levels.

The first level, intrinsic, is given by the nature of the chemical bonds, the electron configuration of the atoms and their mutual interactions. The hard coatings are most often binary, ternary or quaternary ceramic materials based on borides, carbides, nitrides or oxides in combination with transition metals of group IIIB to VIB and optionally containing semi-metals e.g., silicon (Table 1). Usually, the hard coatings are a mixture of metal, ionic or covalent bonds, some of which predominate and determine the properties of the material. For example, the transition metal nitrides have a rather metallic character which is clearly manifested by excellent electrical conductivity, good adhesion and lower hardness compared to ion-bonded coatings. However, they can plastically deform, i.e., they have higher ductility. On the other hand, coatings where the covalent or ionic character prevail (e.g., borides, carbides) are harder, have higher thermal stability and are chemically inert to various aggressive environments. They are however, brittle and almost unable to plastically deform.

The second level is extrinsic, that is, the properties of the hard coatings are controlled by the nature of their structure (amorphous, nanocrystalline, nanocomposite - a combination of nanocrystalline and amorphous phases), grain size, point defects, dislocations, and internal stresses in the crystalline lattice. The extrinsic character can be influenced by changing the deposition parameters during growth of hard coatings. Obviously, the intrinsic properties can be achieved only via selection of proper material system for the coating but the intrinsic properties, including H/E ratio and other properties, can be controlled via structure modification during deposition. Therefore, PVD deposition methods and resulting structure modifications as a way to control the properties required for high wear and erosion resistance of ceramic coatings is discussed elsewhere.

PVD Methods for the Preparation of Hard Coatings

Physical vapor deposition (PVD) methods include a group of deposition techniques where the growth of hard coatings typically occurs in plasma assisted processes in an inert (Ar) or reactive (e.g., Ar + N₂) atmosphere. These are mainly cathodic arc evaporation (ARC) and magnetron sputtering. ARC dominates the industry but in recent years there has been an increase in magnetron sputtering and its progressive modifications (High Power Impulse Magnetron Sputtering – HiPIMS).

ARC technology is based on local evaporation of the target using an electric arc (high currents up to ~150 A, low voltages up to ~80 V). During the deposition, an extremely overheated (15,000°C) cathode spot develops on the target surface which in a short period evaporates the target material, forms a crater and moves to a new surface. The process is accompanied by high ionization of the evaporated atoms (80%) and by the formation of macroparticles that build into the growing films and roughen their surface. During magnetron sputtering, a glow discharge (low currents up to tens of amperes and high voltages of hundreds of volts) is ignited where ionized gas atoms (Ar, N₂, O₂) are accelerated to the target surface and subsequently eject target atoms that are delivered to the substrate and form the coating. The advantage of magnetron sputtering compared to ARC is the reduction of roughness and the absence of macroparticles. In general, both PVD technologies allow for great variability in the chemical and phase composition of the coatings, basically any metal, alloy and ceramic targets can be used and high temperature phases are

Table 1 An overview of PVD ceramic coatings with the prospects for high wear resistance

Coating	Structure	Lattice	Hardness as-deposited (GPa)	References
TiN	Single phase	Cubic	21–36	LeClair (1998)
CrN	Single phase	Cubic	25–26	Knotek <i>et al.</i> (1991)
Cr ₂ N	Single phase	Hexagonal	25–26	Knotek <i>et al.</i> (1991)
NbN	Single phase	Cubic	32–38	Zhitomirsky <i>et al.</i> (1998)
ZrN	Single phase	Cubic	20–30	Qi <i>et al.</i> (2011)
TiC _{0.45} N _{0.55}	Solid solution	Cubic	42	Hultman (2000)
Ti _{0.5} Al _{0.5} N	Solid solution	Cubic	32	Schramm <i>et al.</i> (2017)
Ti _{0.34} Al _{0.66} N	Solid solution	Cubic	36	Mayrhofer <i>et al.</i> (2003)
Cr _{0.5} Al _{0.5} N	Solid solution	Cubic	31	Willmann <i>et al.</i> (2008)
Cr _{0.34} Al _{0.66} N	Solid solution	Cubic	30	Willmann <i>et al.</i> (2008)
Ta _{0.55} Al _{0.45} N	Solid solution	Cubic	29	Mikula <i>et al.</i> (2017)
TiSiN	3D nanocomposite	Cubic/amorphous	30–60	Veprek (2013)
TiB _{2+x}	2D nanocomposite	Hexagonal	34–73	Mikula <i>et al.</i> (2011)
				Mikula <i>et al.</i> (2008)
TiB _{0.80} N _{0.83}	3D nanocomposite	Cubic/hexagonal	37	Mayrhofer <i>et al.</i> (2006)
WC _{1-x}	3D nanocomposite	Hexagonal/amorphous, a-C content up to 7 at%	35–40	El Mrabet <i>et al.</i> (2011)
WC/C	3D nanocomposite	Hexagonal/amorphous, a-C content 7–25 at%	20–23	Makowka <i>et al.</i> (2016)
				Nouvellon <i>et al.</i> (2017)
				Lofaj <i>et al.</i> (2019a,b,c,d)

formed in the coatings at low deposition temperatures or on unheated substrates. By combining different targets, it is possible to create multi-layer systems, superlattices, nanocomposites, etc. After application of the hard film, no further machining of the component surfaces is required.

The main role in the formation of hard coatings by PVD technology is played by two basic processes by which the nature of the structure and the resulting mechanical properties can be controlled: (1) the energy delivered to the growing film and (2) the mixing processes (Musil, 1992).

Energy Delivered to the Growing Film

Deposition of hard coatings by PVD methods is accompanied by low energy ion bombardment with values of ions energy in the range of tens to hundreds of electronvolts (eV), when positively ionized working gas particles or ions formed from target atoms bombard the surface of the coating. Since the ions are very small in size, the transfer of their kinetic energy E_{bi} into the growing film and its heating takes place at the atomic level (so-called “atomic scale heating”). Such a method of heating differs significantly from conventional heating because the kinetic energy of the bombarding ions is transferred to the areas of atomic dimensions and the process is accompanied by extremely rapid cooling ($\sim 10^{14}$ K/s) (Musil, 2006). Kinetic energy E_{bi} has a major influence on the growth of films and their properties. During deposition using ARC or magnetron sputtering, it can be controlled by negative bias applied to substrate U_s , current density on substrate i_s , and deposition rate a_D . Its value is determined according to the following formula (Musil, 2006, 1992):

$$E_{bi} = E_i \gamma_i / \gamma_m = e(U_p - U_s) \gamma_i / \gamma_m e U_s i_s / a_D \quad (4)$$

at a constant substrate temperature T_s , where E_i is the energy of the ions, γ_i is the flow of bombarding ions, γ_m is the flow of sputtered atoms, and U_p is the plasma potential.

During PVD deposition of hard coatings, the kinetic energy E_{bi} , which is defined by the bias U_s , is not the only energy delivered to the growing film. The total energy E_T is the sum of the energies which are determined by other deposition parameters: (a) heating the substrate E_{sh} ; (b) converting the kinetic energy of the bombarding ions E_{bi} and fast neutrals E_{fn} during impact on the surface of the growing film, where $E_p = E_{bi} + E_{fn}$; (c) the heat obtained during the formation of the phases in exothermic chemical reactions E_{ch} ; (d) heating from a sputtered target E_{mt} ; and (e) radiation from plasma E_{rad} . The total E_T energy that is delivered to the growing films can be expressed by the Eq. (5):

$$E_T = E_{sh}(T_s, t_d) + E_p(U_s, i_s, p_T, a_D, t_d) + E_{ch}(t_d + T_{ch}) + E_{mt}(W_d, t_d, d_{S-T}) + E_{rad}(t_d) \quad (5)$$

where T_s is the substrate temperature, t_d is the deposition time, p_T is the total working gas pressure, $W_d = U_d I_d / S$ is the area power density, U_d and I_d are the voltage and current at the cathode, S is the target area, d_{S-T} is the distance target, U_s and i_s are bias and current on substrate and a_D is deposition rate (Musil, 2012).

The combination of the above deposition parameters provides numerous possibilities to influence the structure of the coatings from fibrous and porous through very dense and from columnar to coarse-grained formed by large equiaxial grains.

Mixing Processes

Mixing processes are understood to be the growth of nanocomposite hard coatings by forming ternary, quaternary and multi-element systems. In the deposition of hard coatings, this is accomplished by using compound targets, e.g., CrAl, TiSi, TiB₂ or TaAl, etc. Alternatively, multi-element systems are deposited by co-deposition from compound targets (TiAl target + CrAl target). In this concept, it is not necessary to emphasize substrate bias, such as ion bombardment or substrate heating, although this has some influence on the character of the coating nanostructure. However, in the case of forming nanocomposite structures by mixing processes, chemical bonds, mutual solubility/insolubility of elements, ability of the elements to form solid solutions and inter-metallic phases play more important roles. A very important factor is also the reactive atmosphere e.g., the presence of N₂, O₂, C₂H₂, etc. during deposition, which can significantly affect the growth and structure of hard coatings. The mixing processes can directly influence the formation of the nanocomposite structure in the coatings already during their deposition, that is, the already growing films are formed by the nanocrystalline and/or amorphous phase. The second concept of mixing processes is based on the formation of supersaturated solid solutions which decompose during annealing resulting in nanocomposite coatings.

Low-Energy Ion Bombardment Versus Structure and Mechanical Properties of Hard Coatings

The low-energy ion bombardment of the growing coatings causes atomic “peening” when sputtered atoms that are located on the surface are struck by Ar ions and injected into pores and interstitial spaces in the lattice below the surface of the coatings. The process of incorporation of weakly bonded adsorbed atoms leads to material densification, grain size reduction, and build-up of macrostresses in the coatings (Daniel and Musil, 2013).

Typical hard coatings resistant to wear and erosion are stoichiometric single-phase cubic nitrides of transition metals TiN, CrN, ZrN, TaN, HfN and others prepared by ARC or magnetron sputtering in a reactive atmosphere N₂ and Ar + N₂, respectively. They exhibit a columnar microstructure with elongated grains. Their intrinsic hardness given by the bonds can be influenced by ion bombardment (negative bias) by incorporating point defects into the lattice, increasing density, and reducing grain size. The high density of point and line defects generated during film growth creates obstacles to the movement of dislocations, resulting in strengthening and in an increase in hardness. The values of compression macrostresses are usually in the range of gigapascals (GPa). The hardness of highly stressed TiN deposited at high bias values can reach up to 40 GPa and in the case of CrN up to 35 GPa (LeClair, 1998; Knotek *et al.*, 1991). However, exposure of these hard coatings to temperatures above ~500°C leads to increased diffusivity, annihilation of the defects, atomic rearrangement and recrystallization, causing a reduction in macrostresses and recovery of the structure. As a result, the hardness of the coatings approaches the hardness of bulk TiN (20 GPa) and CrN (14 GPa), respectively. Single-phase hard coatings have found their application particularly in the machining industry. They increase the hardness of the cutting blades and improve the wear resistance of the cutting edges. Due to their lower thermal stability, they are suitable for less demanding cutting processes, turning and milling of carbon steels, some non-ferrous alloys, where the temperature in the tool and workpiece contact does not exceed approximately 500°C. These coatings are also suitable for improving the wear and erosion resistance of forming tools, dies, plastic injection molds and others.

Temperature stability is one of the most important factors for industrial applications. The “tuning” of the above hard coatings by the generation of compression macrostresses by ion bombardment and the loss of hardness at temperatures slightly higher than the deposition temperatures significantly limits their use in high-temperature applications.

Another concept is represented by the superhard TiB_x coatings prepared by nonreactive magnetron sputtering from a stoichiometric TiB₂ target. In this case, Ar low energy ion bombardment affects the chemical composition and character of the nanocomposite structure during growth of the films and the resulting mechanical properties.

Investigated changes of deposition parameters (negative bias U_s expressing kinetic energy E_{bi} according to relation (4) and substrate temperature T_s) (Mayrhofer *et al.*, 2005a; Mikula *et al.*, 2008, 2011), were found to have a significant influence not only on the “design” of the structure and mechanical properties, but also on chemical composition and generation of the internal macrostresses, σ . The TiB_x coatings, in contrast to the TiB₂ target, are overstoichiometric, where the B/Ti concentration ratio decreases monotonically from x = 2.9–2.4 with increasing E_{bi} energy due to the increase in applied negative substrate bias. This can be explained by the different angular distribution of the sputtered B and Ti atoms from the target and by the resputtering of the light boron from the films by Ar ions.

X-ray diffraction analysis (XRD) of TiB_x coatings (Mikula *et al.*, 2011) showed a strong effect of Ar ion bombardment on the structure changes, where the TiB_{2.9} coatings deposited at floating potential (E_{bi} = 8 eV, no applied bias) are characterized by an amorphous or very fine nanocrystalline structure. By applying a bias, the energy of E_{bi} delivered to the growing films was increased > 20 eV supporting the formation of a crystalline hexagonal TiB₂ phase in the coatings. At the same time, a significant preferential orientation of TiB₂ nanocrystallites in the <0001> direction was observed by XRD.

Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) bring a deeper insight into the formation of nanostructures in TiB_x coatings showing that the coatings deposited at very low ion bombardment have randomly oriented nanocrystalline character and the coatings growing at applied negative substrate bias are nanocrystalline and textured (in good agreement with XRD analysis) (Mayrhofer *et al.*, 2005a). In addition, the cross-sectional TEM detail of the textured film revealed a nanocolumnar structure (Fig. 6(a)). Mayrhofer *et al.*, 2005a reported the structure of TiB_x coatings consists of TiB₂ nanocolumns with a diameter of ~20 nm surrounded by an amorphous boron-rich phase (matrix) what is also in good

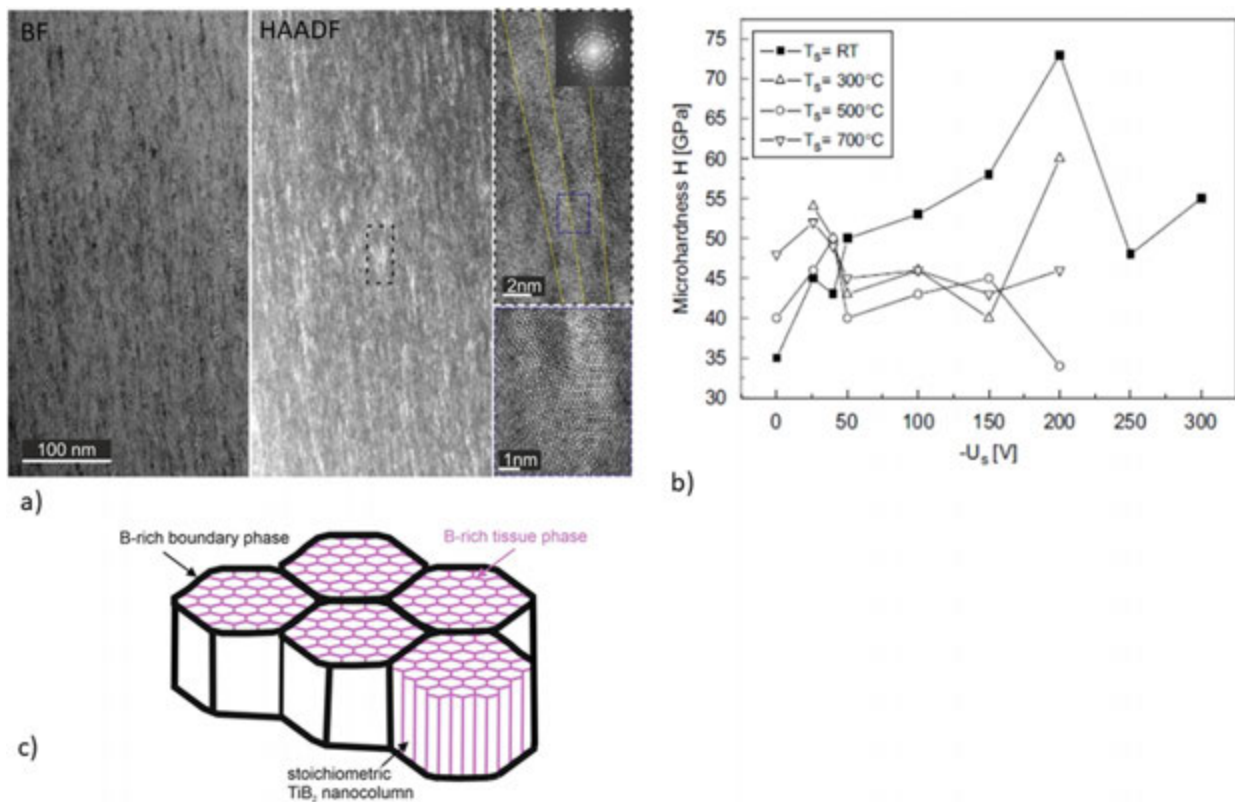


Fig. 6 (a) Cross-section STEM-DF image of as-deposited $\text{TiB}_{3.1}$ coating with corresponding SAED pattern and the inset showing separated subcolumns by yellow lines. In the blue line selected detail are two overlapped individual nanocolumns with a size of a few nanometers; (b) Hardness H of TiB_x coatings as a function of negative substrate bias U_s and substrate temperature T_s ; (c) Schematic representation of the self-organized nanocolumnar structure of $\text{TiB}_{2.4}$ where ~ 20 nm wide columns, encapsulated in excess B and oriented along $\langle 0001 \rangle$, consist of a bundle of ~ 5 nm-diameter TiB_2 subcolumns separated by an ultrathin B-rich tissue phase. Redrawn from (b) Mikula, M., Grančič, B., Buršiková, V., *et al.*, 2008. Mechanical superhard TiB_2 coatings prepared by DC magnetron sputtering. *Vacuum* 82, 278–281. (c) Mayrhofer, P.H., Mitterer, C., Clemens, H., *et al.*, 2005b. Self-organized nanostructures in hard TiB_2 ceramic coatings. *Advanced Engineering Materials* 7, (No. 12).

agreement with overstoichiometric character ($\text{B}/\text{Ti} > 2$) of TiB_x coatings (Fig. 6(c)). Such a self-organized nanocomposite structure is also commonly referred to as a two-dimensional (2D) nanostructure.

The effect of low-energy Ar ion bombardment of growing films was also reflected in mechanical properties. TiB_x coatings that grow during low-energy Ar bombardment have a very high hardness > 34 GPa (Fig. 6(b)) (Mikula *et al.*, 2008). The high hardness is mainly related to the intrinsic nature of the material but also to the extrinsic nanocomposite nature of the structure, because the amorphous boron phase enhances the cohesive strength at the grain boundaries. An increase in the kinetic energy of the incident Ar ions affecting the preferential growth of the (0001) crystalline planes parallel to the substrate, resulted in a further increase in hardness up to ~ 50 GPa.

In addition to nanostructure formation, low-energy bombardment of the growing TiB_x coatings by Ar ions due to the incorporation of defects also generated high compressive internal macrostresses (several GPa). Their increase had a positive effect on increasing hardness up to ~ 73 GPa (Mikula *et al.*, 2008). However, increasing the temperature of the substrate caused annihilation of the defects, relaxation of the structure, and a reduction in internal macrostresses accompanied by a decrease in hardness to the value of ~ 34 GPa (Fig. 6(b)). Despite very high hardness, the use of nanocomposite TiB_x coatings is strongly limited by its low oxidation resistance. At temperatures exceeding 500°C , decomposition occurs and the boron from the matrix reacts with the residual atmosphere containing water vapor to form a volatile boric acid. This leads to structural destruction of the coating. In addition, diboride coatings are brittle in nature and are prone to cracking.

Formation of Nanocomposite Hard Coatings by Mixing Processes

Wear and erosion resistant hard nanocomposite coatings can be grown also by adding additional elements, alloying and using a reactive atmosphere during deposition. The most famous representative of the nanocomposite coatings is a ternary Ti-Si-N system developed by the group of Veprék (Veprék *et al.*, 1995a; Veprék and Reiprich, 1995b; Veprék *et al.*, 2000; Veprék *et al.*, 2005). Transmission electron microscopy (TEM) showed that their structure consists of equiaxial cubic TiN nanocrystallites with a typical size of 3–4 nm and SiN_x interfacial layer, (Fig. 7(a)). The thickness of the amorphous SiN_x interfacial layer should be < 1 nm and it

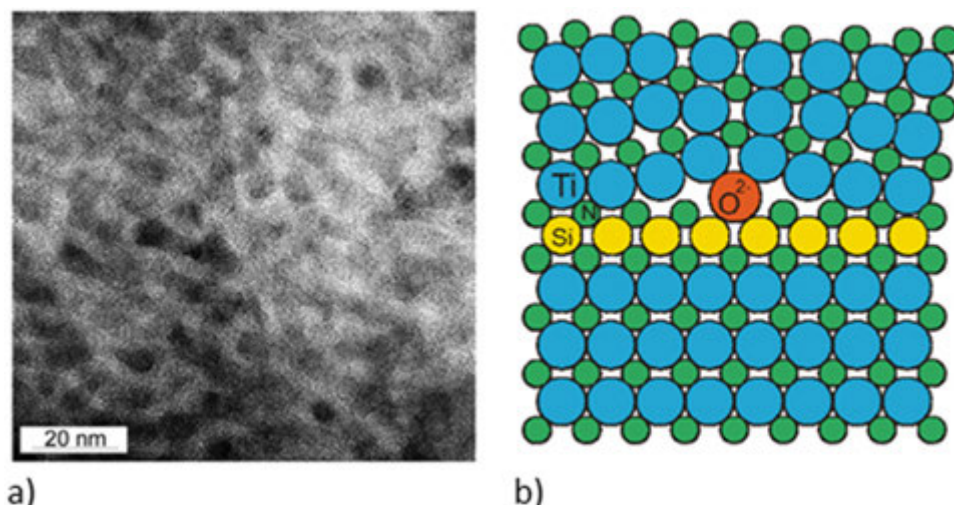


Fig. 7 (a) TEM image of the TiN/SiN_x nanocomposite coating; (b) the oxygen substituting nitrogen in the SiN_x interfacial layer. Reproduced from Veprek, S., 2013. Recent search for new superhard materials: Go nano! Journal of Vacuum Science and Technology A 34, (050822-1–050822-33).

strongly depends on the deposition rate: the higher the speed, the thinner the boundary. The thickness of SiN_x layer determines the hardness: the hardness of ~ 60 GPa was achieved at a thickness of 1 monoatomic layer (it corresponds to ~ 6 at% Si in the coatings). In this case, very strong shear-resistant bonds are formed at the interface between TiN nanocrystallites and SiN_x. When the thickness of the SiN_x layer increased to 2 monoatomic layers (up to 15 at% Si), the cohesive strength decreases, and hardness dropped to about 20 GPa. The nanocomposite structure of Ti-Si-N coatings is temperature stable up to 1000°C.

The most important technological factor determining the nanocomposite structure of Ti-Si-N coatings is the substrate temperature T_s , which must be sufficiently high, at least 550°C and a high deposition rate > 1 nm/s (Veprek, 2013). Under these conditions, decomposition is kinetically controlled by volume diffusion, and the formation of TiN nanocrystallites and amorphous SiN_x interfacial layer occurs faster than Si diffusion into TiN grains. Impurities, especially oxygen, play also very important role in the development of the nanostructure (Fig. 7(b)). Even a very small amount of 0.5–0.8 at% causes a decrease of hardness below 30 GPa, since O₂ atoms incorporated at the interface between TiN nanocrystallites and SiN_x interface layer weaken their bonds. When the amount of oxygen exceeded 0.8 at%, no nanocomposite structure was observed.

Ternary Ti-B-N system represents another very hard nanocomposite coating system. The structure of the TiB_{0.80}N_{0.83} coatings was reported to be composed of 2–3 nanometers cubic TiN and hexagonal TiB₂ nanocrystallites embedded in a disordered, amorphous (Ti) BN_x matrix (Mayrhofer *et al.*, 2006). The hardness of these coatings in the as-deposited state was 37 GPa and increased to 43 GPa after annealing at 800°C due to the densification of the disordered phase. At higher annealing temperatures a coarsening of the nanostructure accompanied by a gradual decrease in hardness to 28 GPa at 1100°C was observed (Veprek *et al.*, 2000). The advantage of Ti-B-N coatings compared to TiB_x is their better thermal stability.

WC/C or W-C:H coatings consisting of tungsten carbide (WC) nanograins embedded in an amorphous (hydrogenated) carbon matrix (a-C:(H)) also represent an interesting concept of nanocomposites formed during growth. They belong to the group of so-called diamond-like carbon (DLC) coatings. W-C:H coatings are usually prepared by ARC or magnetron sputtering from W or WC target in a reactive atmosphere (Ar + acetylene, methane). The addition of hydrogenated carbon from the fragments of the gas precursor resulting from plasma polymerization reactions determines the structural character of the coatings. When the carbon content is 30–40 at%, nanocrystalline W₂C or WC_{1-x} coatings are formed with an a-C content below 7 at% (El Mrabet *et al.*, 2011). They exhibit a high hardness of 35–40 GPa (Abad *et al.*, 2010). An increase in carbon content of up to 65 at% leads to the formation of the nanocomposite WC_{1-x}/a-C coating where the amount of free a-C:H increases to 25 at%. Further addition of carbon to the growing films changes the structure from nanocomposite to fully amorphous and the hardness continues to decrease (El Mrabet *et al.*, 2011; Lofaj *et al.*, 2016; Lofaj *et al.*, 2019a,b,c,d; Makowka *et al.*, 2016; Nouvellon *et al.*, 2017; Voevodin *et al.*, 1999). The character of the structure is also reflected in the tribological properties of the W-C:H coatings. In the case of hard, nanocrystalline WC_{1-x} coatings without a-C:H phase, the self-lubricating ability is low. The coefficient of friction (COF) against a steel ball is above 0.8 and the abrasive wear of the ball dominates. With increasing carbon (and hydrogen) contents and formation of nanocomposite structure, the COF decreases to 0.3–0.6 and adhesive wear becomes the prevalent mechanism. The lowest COFs in the range 0.1–0.2 and the lowest wear rates are achieved in completely amorphous coatings. In this case, the wear mechanisms change from abrasive/adhesive to so-called sliding friction, which is controlled by the formation of a-C:H containing transfer film (Halling, 1983) at the point of contact between the layer and the ball (El Mrabet *et al.*, 2011; Makowka *et al.*, 2016; Nouvellon *et al.*, 2017; Voevodin *et al.*, 1999; Erdemir, 2001; Lofaj *et al.*, 2019a,c). However, the friction versus hardness strongly depends also on the technology of deposition and precursor gas type which affect carbon and hydrogen contents (Lofaj *et al.*, 2019a,b,c,d; Makowka *et al.*, 2016; Nouvellon *et al.*, 2017). The role of hydrogen and its interaction with water vapor in environment has to be

emphasized in this system. It was shown on a-C:H coatings that sufficient hydrogenation can reduce coefficient of friction in dry atmosphere or in high vacuum to <0.01 (superlubricity regime) due to the formation of a transfer layer consisting of hydrogen saturated bonds (Donnet and Grill, 1997; Erdemir, 2000; Erdemir, 2001; Fontaine *et al.*, 2001; Erdemir, 2004; Moura e Silva *et al.*, 2009). Obviously, the case with transfer layer is the exclusion closer to the lubrication mechanisms than to the adhesion, abrasion and deformation mechanisms considered up to now. However, it opens new possibilities to control friction and wear resistance. When returning back to W-C:H coatings, the best combination of hardness, elastic modulus, COF and the lowest wear rates in W-C:H coatings were obtained in the case of HiPPMS and acetylene precursor whereas direct current magnetron sputtering and high target utilization sputtering (HiTUS) with methane produced coatings with slightly lower values (Lofaj *et al.*, 2019a,b,c,d).

W-C:H coatings are successfully used in many engineering applications, e.g., bearings, gearboxes, cutting tools due to high elasticity, chemical inertness and low friction combined with high wear resistance.

Formation of Nanocomposite Hard Coatings by Post-Deposition Annealing

Post-deposition processes, especially annealing, are often used to form nanocomposite structures in hard coatings. This is possible in materials in which, due to the mutual solubility of the input constituents (elements or phases), solid solutions consisting of three or more elements are formed, which usually exist in a wide mutual concentration. Solid solutions are in a thermodynamically unstable state and they decompose into nanocomposite systems due to thermally induced processes often accompanied by a significant increase in hardness.

ARC or magnetron sputtering allow the formation of metastable, supersaturated solid solutions due to the combination of high deposition rates and extremely high cooling rates at the atomic level (10^{14} K/s) (Musil, 2006). This means that during “freezing”, the condensing atoms on the surface of the substrate do not reach the thermodynamically stable state characterized by low formation energy necessary for the formation of a metastable solid solution. For its separation (decomposition) to thermodynamically stable constituents (base phases) a high activation energy is required, and the annealing is one of the ways to supply such energy. The effect can be demonstrated on $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coatings. Under equilibrium conditions, the solubility of AlN in TiN is very low (<2 at% at 1000°C) (Mayrhofer *et al.*, 2014; Schuster and Bauer, 1984) because TiN crystallizes in cubic B1 NaCl lattice, while AlN crystallizes in hexagonal B4 wurtzite lattice. However, during deposition, a supersaturated cubic $\text{Ti}_{1-x}\text{Al}_x\text{N}$ solid solution with an AlN molar fraction up to $x = 0.6\text{--}0.7$ can form (Fella *et al.*, 1988). The temperature stability of this solid solution depends on the proportion of TiN : AlN, but it is sufficiently high. The decomposition occurs at a temperature above 800°C and the resulting structures consisting of nanocrystalline TiN and AlN phases are already thermodynamically stable (Rachbauer *et al.*, 2009; Rachbauer *et al.*, 2011a,b).

The decomposition of the solid solution in a spinodal or precipitation manner changes the mechanical properties of the hard coatings: hardness increases within a certain annealing temperature range and time interval. This phenomenon is called age hardening, and its “size” is determined by the difference in crystal structure and orientation between the decomposing solid solution and the forming new phases.

If the solid solution decomposes in a spinodal manner, rapid demixing of the new phases from the solid solution occurs and a fine-grained nanostructure is formed. The separated phases retain the lattice coherent structure at the early stages of decomposition, e.g., in cubic $\text{Ti}_{1-x}\text{Al}_x\text{N}$, cubic TiN-rich and AlN-rich nanodomains are formed (Mayrhofer *et al.*, 2007, 2003). Their lattice parameters differ slightly from each other (usually up to 5%), causing large microstresses at the interfaces between nanodomains and movement of dislocations is significantly limited. This phenomenon is manifested by resistance to deformation – age hardening. For example, in the case of $\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}$, the onset of decomposition occurs at $\sim 800^\circ\text{C}$ where the hardness increases from ~ 36 GPa to ~ 38.5 GPa (6.5%) (Mayrhofer *et al.*, 2003). Further increase the annealing temperature or time promotes an equilibrium state, i.e., metastable cubic AlN-rich nanodomains are transformed into a stable wurtzite AlN phase incoherent to stable cubic TiN phase. As a result, the microstresses are lost at the interfaces, the structure is relaxed, the movement of the dislocations is not obstructed anymore, and the hardness of the coatings decreases.

A significant hardening effect was also observed in $\text{Ta}_{0.55}\text{Al}_{0.45}\text{N}$ hard coatings, where the hardness increased by 17% from ~ 29.6 GPa to ~ 35.2 GPa during annealing at 1000°C (Mikula *et al.*, 2017). Here, hardening is the result of microstresses at the interfaces between coherent cubic TaN-rich and AlN-rich nanodomains that form during the first stages of spinodal decomposition within the solid solution and prevent further movement of dislocations, see Fig. 8. Subsequent temperature increases to 1200°C led to increased diffusivity, cubic AlN was transformed into stable w-AlN, the structure gradually coarsened, and hardness decreased to ~ 24.6 GPa (Mikula *et al.*, 2017).

Besides the above mentioned ternary systems $\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}$ and $\text{Ta}_{0.55}\text{Al}_{0.45}\text{N}$, hardening associated with solid solution decomposition was reported also in $\text{Cr}_{1-x}\text{Al}_x\text{N}$ (Mayrhofer *et al.*, 2008). In this case, w-AlN precipitates are formed in the cubic CrAlN solid solution (for $x < 0.7$) and c-CrN precipitates in wurtzite CrAlN (for $x > 0.83$), respectively. However, the increase in hardness after annealing at 700°C in $\text{Cr}_{0.32}\text{Al}_{0.68}\text{N}$ was only 2.8% from ~ 30.7 GPa to ~ 31.6 GPa (Willmann *et al.*, 2008).

The thermal stability of the hard coatings defines the temperature, at which the solid solution decomposes, and the formation of nanocomposite structure accompanied by an increase in hardness occurs. Further increase in this temperature and a shift of the beginning of decomposition to obtain coatings for extreme conditions require new approaches. A promising way to achieve higher thermal stability appears to be the formation of quaternary and multi-element systems where hard coatings, in particular $\text{Ti}_{1-x}\text{Al}_x\text{N}$ and $\text{Cr}_{1-x}\text{Al}_x\text{N}$ are alloyed with transition metals from the III-VI group of the Periodic table of the elements (Lind *et al.*, 2011; Forsén *et al.*, 2012, 2013; Rachbauer *et al.*, 2010; Rachbauer *et al.*, 2011b, 2012; Riedl *et al.*, 2013; Chen *et al.*, 2011; Rovere and Mayrhofer, 2008; Rovere *et al.*, 2010). The incorporation of these elements in a substitutional manner replaces Ti and Cr in a

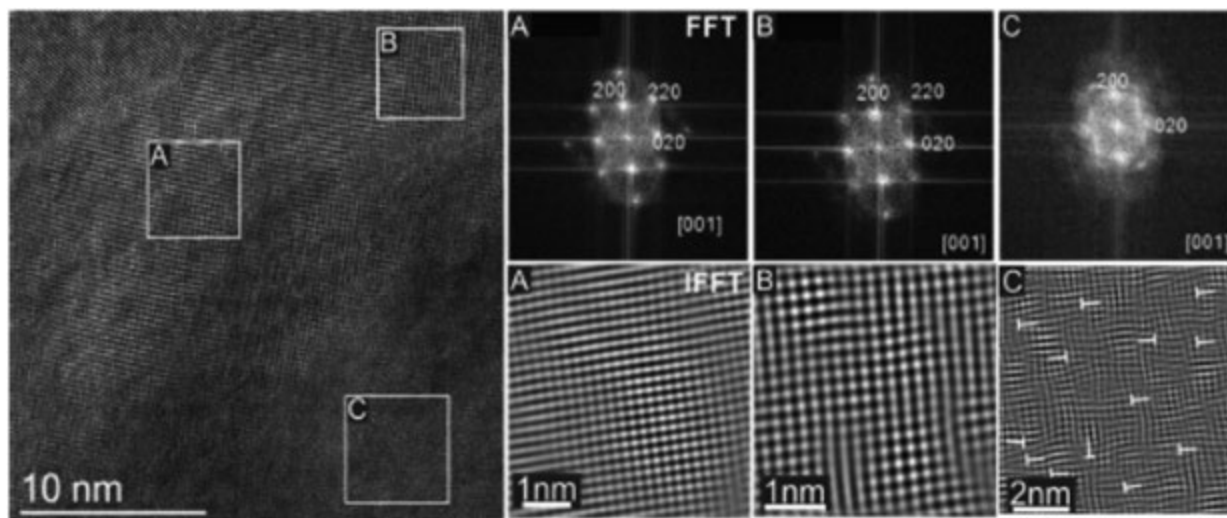


Fig. 8 High resolution TEM image of the $\text{Ta}_{0.55}\text{Al}_{0.45}\text{N}$ coating annealed at 1000°C in vacuum with corresponding Fast Fourier Transformation (FFT) patterns and inverse FFT (IFFT) images for three selected areas A, B, and C. Area A represents region where spinodal decomposition has not yet occurred. FFT pattern shows sharp dots and IFFT image displays lattice fringes without defects. Deformed lattice fringes and several misfit dislocations, which are arranged in low-angle grain boundaries in IFFT of area C shows early stages of spinodal decomposition and formation of coherent nanodomains. Reproduced from Mikula, M., Sangiovanni, D.G., Plašienka, D., *et al.*, 2017. Thermally induced age hardening in tough Ta-Al-N coatings via spinodal decomposition. *Journal of Applied Physics* 121, 155304.

metal sublattices, resulting in a large number of chemical bond variations due to different electron configurations of the individual elements (Mayrhofer *et al.*, 2014).

According to published results describing the quaternary systems $\text{Ti}_{1-x-y}\text{Al}_x\text{TM}_y\text{N}$ (TM = Y, Zr, Hf, Nb and Ta), the AlN concentration interval ($x \sim 0.69$) varies due to the alloying metal when a hard cubic solid solution is formed. While the addition of Y, which is added to improve oxidation resistance, reduces the maximum AlN concentration ($x \sim 0.56$) (Riedl *et al.*, 2013), the alloying by Zr (Chen *et al.*, 2011), Hf (Rachbauer *et al.*, 2012) and Nb (Rachbauer *et al.*, 2011a) does not affect the allowable concentration range of the cubic phase and in case of Ta, the range of x even slightly increases ($x \sim 0.7$) (Rachbauer *et al.*, 2010).

The addition of alloying elements (usually small amounts, $y \leq 0.11$) also affects the phase stability of the cubic solid solution. For instance, the replacement of Ti with pentavalent Nb and Ta increases cohesive energy over a wide AlN concentration range, resulting in the strengthening of bonds between atoms in a cubic solid solution (Mayrhofer *et al.*, 2014).

Strengthening of interatomic bonds is also positively reflected in the thermal stability of quaternary cubic solid solutions. As can be seen in Fig. 9(a)–(c), the alloying of metals from groups III to V slightly decreases the onset temperature of the spinodal decomposition of $\text{Ti}_{1-x-y}\text{Al}_x\text{TM}_y\text{N}$ and the formation of coherent cubic c-AlN-rich and c-Ti (TM)N-rich nanodomains. Unlike $\text{Ti}_{1-x}\text{Al}_x\text{N}$, however, the transformation of c-AlN-rich to w-AlN phase occurs at substantially higher temperatures. Cubic TiTMN phase is stable to high temperatures and, apart from TiYN, does not decompose at temperatures below 1400°C . This is due to the high cohesive forces between atoms, where a much higher temperature is required for phase separation.

Although the structure of $\text{Ti}_{1-x-y}\text{Al}_x\text{TM}_y\text{N}$ solid solutions decomposes spinodally, no significant age hardening during annealing is observed (Fig. 9(d)). An increase of hardness by 2–3 GPa was measured on the Nb and Hf alloyed coatings. In the case of Ta alloying, hardening was not observed, and the addition of Y resulted in a decrease in hardness after annealing.

Another quaternary system is represented by $\text{Ti}_{1-x-y}\text{Al}_x\text{Cr}_y\text{N}$ hard coatings (Forsén *et al.*, 2012) where a metastable cubic TiCrAlN solid solution is formed. The concept of designing these systems is based on a combination of different mechanisms of solid solution decomposition. In the case of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloyed by Cr, the temperature stability increases and a small age hardening ($\sim 3\%$) occurs at 1000°C , which is higher than that of $\text{Ti}_{1-x}\text{Al}_x\text{N}$. Indeed, the presence of chromium in forming coherent cubic nanodomains reduces the stresses caused by some lattice mismatch at their interfaces. In addition, Cr suppresses diffusion processes, so that spinodal demixed coherent nanodomains begin to change to stable and coarse-grained phases more slowly and at higher temperatures. As a result, $\text{Ti}_{0.31}\text{Cr}_{0.17}\text{Al}_{0.52}\text{N}$ maintain a high hardness of 35 GPa at temperatures $> 1100^\circ\text{C}$. $\text{Ti}_{0.33}\text{Al}_{0.67}\text{N}$ at the same temperature had considerably coarser-grains and hardness of only 29 GPa.

In the case of CrAlN alloyed by Ti, the decomposition occurs by two different mechanisms. At the grain boundaries of the solid solution, precipitation of the incoherent w-AlN phase occurs simultaneously with the spinodal decomposition and formation of coherent cubic Ti-enriched TiCr(Al)N and Al-enriched (Ti)CrAlN nanodomains. Spinodal decomposition requires less energy than segregation of Al from solid solution towards grain boundaries and subsequent enrichment of the w-AlN boundary phase. Therefore, a higher temperature is required to separate the Al-enriched cubic (Ti)CrAlN phase. This is also reflected in the thermal stability of the mechanical properties where, unlike the unalloyed $\text{Ti}_{1-x}\text{Al}_x\text{N}$, no significant age hardening is observed, but $\text{Ti}_{0.11}\text{Cr}_{0.28}\text{Al}_{0.61}\text{N}$ and $\text{Ti}_{0.31}\text{Cr}_{0.07}\text{Al}_{0.62}\text{N}$ coatings retain high hardness > 32 GPa up to the temperatures above 1000°C . A decrease in hardness occurs when this temperature is exceeded because (Ti)CrAlN decomposes and the proportion of soft w-AlN in the coatings increases.

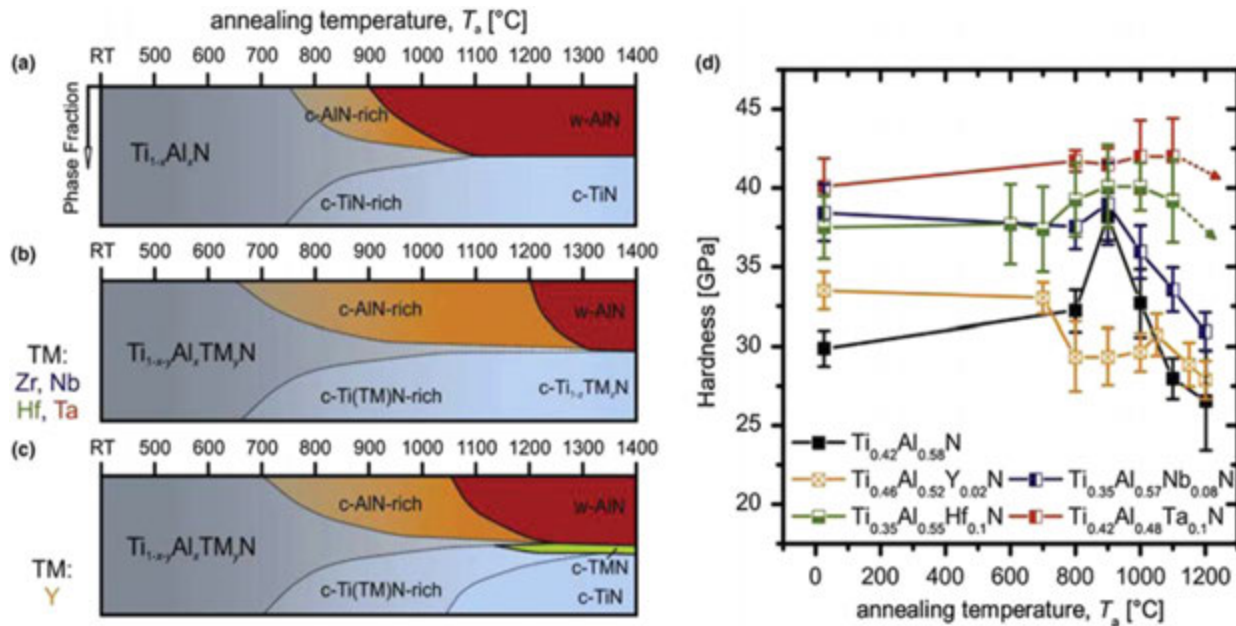


Fig. 9 Schematic of the structural evolution of metastable $\text{c-Ti}_{1-x}\text{Al}_x\text{N}$ as a function of Ta with corresponding phase fractions (a). The formation of c-AlN- and c-TiN-enriched domains during spinodal decomposition is followed by the precipitation of w-AlN and deteriorating mechanical properties (d) in the final dual phase regime. The evolution of quaternary $\text{c-Ti}_{1-x-y}\text{Al}_x\text{TM}_y\text{N}$ alloys is shown for (b) the formation of dual phase structure (w-AlN + c- $\text{Ti}_{1-z}\text{TM}_z\text{N}$) at high temperatures in the case of group IVB and VB TM elements or (c) the formation of three stable phases after decomposition in the case of Y alloyed $\text{Ti}_{1-x}\text{Al}_x\text{N}$. Reproduced from (d) Rachbauer, R., Stergar, E., Massl, S., Moser, M., Mayrhofer, P.H., 2009. Three-dimensional atom probe investigations of Ti-Al-N thin films. *Scripta Materialia* 61, 725–728. Rachbauer, R., Massl, S., Stergar, E., *et al.*, 2011b. Decomposition pathways in age hardening of Ti-Al-N films. *Journal of Applied Physics* 110, 023515. (c) Mayrhofer, P.H., Rachbauer, F., Holec, D., *et al.*, 2014. Protective transition metal nitride coatings. In: Hashmi M.S.J. (Ed.), *Comprehensive materials processing*, vol. 4. Amsterdam: Elsevier, pp. 355–388.

The investigations of $\text{Cr}_{1-x-y}\text{Al}_x\text{TM}_y\text{N}$ quaternary system alloyed with other transition metals up to now are limited to the studies of the influence of yttrium on oxidation behavior (Rovere and Mayrhofer, 2008; Rovere *et al.*, 2010) and on the influence of Ta on the thermal stability of the Cr-Al-Y-Ta-N multicomponent system (Mikula *et al.*, 2016). The solid solution in an unalloyed $\text{Cr}_{0.49}\text{Al}_{0.50}\text{Y}_{0.01}\text{N}$ began to decompose via precipitation mechanism when the temperature exceeded 900 °C. The structure consisted of stable w-AlN and unstable cubic CrN. A further increase in annealing temperature led to a further decomposition of CrN to Cr_2N accompanied by nitrogen loss and then to cubic Cr. In the case of Ta alloyed coatings, the solid solution decomposed at the temperature exceeding ~1000 °C. The positive effect of Ta on the increase of thermal stability of $\text{Cr}_{1-x-y-z}\text{Al}_x\text{Y}_y\text{Ta}_z\text{N}$ can be explained by strengthening of the interatomic bonds (increase of cohesive energy E_c) when the addition of 11 at% Ta to a solid solution increases its decomposition resistance (E_c increases by 4.5%) (Mikula *et al.*, 2016).

The above mentioned ternary and quaternary hard nitride coatings are already used in industry, especially in machining, due to their significantly higher hardness, temperature stability and oxidation resistance compared to single-phase hard coatings. The control of their wear resistance, despite positive prospects resulting from the hardness increase due to structure manipulation, however, requires additional studies of the control of their elastic properties.

Summary

The analysis of the basic requirements to the mechanical properties of material systems for wear and erosion resistant PVD coatings suggests that a proper combination of hardness, elastic modulus and toughness is required to reduce contributions of the main mechanisms involved in friction and wear processes. The possible ways for the control of these properties, especially hardness, in PVD coatings involve, besides selection of the system with high intrinsic hardness, intentional modifications of the composition and structure via alloying by various transition metals and a wide range of decomposition and precipitation processes, respectively.

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References

- Abad, M.D., Muñoz-Márquez, M.A., El Mrabet, S., Justo, A., Sánchez-López, J.C., 2010. Tailored synthesis of nanostructured WC/a-C coatings. *Surface and Coatings Technology* 204, 3490–3500.
- Archard, J.F., 1953. Contact and rubbing of flat surfaces. *Journal of Applied Physics* 24, 981–988.
- Bhushan, B., 1999. *Principles and Application of Tribology*. New York: John Wiley & Sons.
- Bhushan, B., 2000. *Modern Tribology Handbook: Volume One: Principles of Tribology*. New York: CRC Press.
- Bhushan, B., Gupta, B.K., 1991. *Handbook of Tribology Materials, Coatings, and Surface Treatments*. New York: McGraw Hill Inc.
- Bowden, F.P., Tabor, D., 1950. *Friction and Lubrication of Solids*. New York: Oxford University Press.
- Chen, L., Holec, D., Du, Y., Mayrhofer, P.H., 2011. Influence of Zr on structure, mechanical and thermal properties of Ti–Al–N. *Thin Solid Films* 519, 5503–5510.
- Cox, J.W., 2001. Wear and corrosion resistant coatings for non-cutting tool applications. In: Bunshah, F. (Ed.), *Handbook of Hard Coatings Deposition Technologies, Properties and Applications*. New Jersey: Noyes Publications, pp. 411–465.
- Czichos, H., 1978. *Tribology*. Amsterdam: Elsevier.
- Daniel, R., Musil, J., 2013. Novel nanocomposite coatings. In *Advanced and Industrial Applications*. Boca Raton: CRC Press.
- Donnet, C., Grill, A., 1997. Friction control of diamond-like carbon coatings. *Surface and Coatings Technology* 94–95, 456–462.
- El Mrabet, S., Abad, M.D., Sanchez-Lopez, J.C., 2011. Identification of the wear mechanism on WC/C nanostructured coatings. *Surface and Coatings Technology* 206, 1913–1920.
- Erdemir, A., 2001. The role of hydrogen in tribological properties of diamond-like carbon films. *Surface and Coatings Technology* 146–147, 291–297.
- Erdemir, A., 2004. Genesis of superlow friction and wear in diamond like carbon films. *Tribology International* 37, 1005–1012.
- Erdemir, A., Eryilmaz, O.L., Nilufer, I.B., Fenske, G.R., 2000. Synthesis of superlow-friction carbon films from highly hydrogenated methane plasma. *Surface and Coatings Technology* 133–134, 448–454.
- Fauchais, P., Montavon, G., Lima, R.S., Marple, B.R., 2011. Engineering a new class of thermal spray nano-based microstructures from agglomerated nanostructured particles, suspensions and solutions: An invited review. *Journal of Physics D: Applied Physics* 44, 093001.
- Fella, R., Holleck, H., Schultz, H., 1988. Preparation and properties of WC–TiC–TiN gradient coatings. *Surface and Coatings Technology* 36, 257–264.
- Finnie, I., 1995. Some reflections on the past and future of erosion. *Wear* 186–187, 1–10.
- Fontaine, J., Donnet, C., Grill, A., LeMogne, T., 2001. Tribochemistry between hydrogen and diamond-like carbon. *Surface and Coatings Technology* 146–147, 286–291.
- Forsén, R., Johansson, M.P., Odén, M., Ghafoor, N., 2012. Decomposition and phase transformation in TiCrAlN thin coatings. *Journal of Vacuum Science and Technology A* 30, 061506.
- Forsén, R., Johansson, M.P., Odén, M., Ghafoor, N., 2013. Effects of Ti alloying of AlCrN coatings on thermal stability and oxidation resistance. *Thin Solid Films* 534, 392–402.
- Halling, J., 1983. The tribology of surface films. *Thin Solid Films* 108, 103–115.
- Heilman, P., Rigney, D.A., 1981. An energy-based model of friction and its application to coated systems. *Wear* 72, 195–217.
- Holmberg, K., Matthews, A., 2000. Tribological properties of metallic and ceramic coatings. In: Bhushan, B. (Ed.), *Modern Tribology Handbook: Volume One: Principles of Tribology*. New York: CRC Press, pp. 827–870.
- Holmberg, K., Matthews, A., 2009. *Coatings Tribology: Properties, Techniques and Applications in Surface Engineering*, second ed. Amsterdam: Elsevier Science.
- Holmberg, K., Ronkainen, H., Laukkanen, A., Wallin, K., 2007. Friction and wear of coated surfaces – Scales, modeling and simulation of tribomechanisms. *Surface and Coatings Technology* 202, 1034–1049.
- Holmberg, K., Siilasto, R., Laitinen, T., Andersson, P., Jäsberg, A., 2013. Global energy consumption due to friction in paper machines. *Tribology International* 62, 58–77.
- Holmberg, K., Andersson, P., Nylund, N.-O., Mäkelä, K., Erdemir, A., 2014. Global energy consumption due to friction in trucks and buses. *Tribology International* 78, 94–114.
- Hultman, L., 2000. Thermal stability of nitride thin films. *Vacuum* 57, 1–30.
- Hutchings, I.M., Shipway, P., 2017. *Tribology: Friction and Wear of Engineering Materials*, second ed. Oxford: Elsevier.
- Imfeld, T., 1996. Dental erosion. Definition, classification and links. *European Journal of Oral Science* 104, 151–155.
- Knotek, O., Löffler, F., Scholl, H.-J., 1991. Properties of arc-evaporated CrN and (CrAl)N coatings. *Surface and Coatings Technology* 45, 53–58.
- Kramer, B.M., 1983. Requirements for wear resistant coatings. *Thin Solid Films* 108, 117–125.
- Kuroda, S., Watanabe, M., Kim, K., Katanoda, H., 2011. Current status and future prospects of warm spray technology. *Journal of Thermal Spray Technology* 20, 653–676.
- Lawn, B.R., Swain, M.V., 1975. Microfracture beneath point indentation in brittle solids. *Journal of Materials Science* 10, 113–122.
- LeClair, P.R., 1998. *Titanium Nitride Thin Films by the Electron Shower Process*. PhD Thesis. Boston: MIT.
- Leyland, A., Matthews, A., 2000. On the significance of H/E ratio in wear control: A nanocomposite coating approach to optimized tribological behavior. *Wear* 246, 1–11.
- Leyland, A., Matthews, A., 2004. Design criteria for wear-resistant nanostructured and glassy-metal coatings. *Surface and Coatings Technology* 177–178, 317–324.
- Lind, H., Forsén, R., Alling, B., *et al.*, 2011. Improving thermal stability of hard coating films via a concept of multicomponent alloying. *Applied Physics Letters* 99, 091903.
- Lofaj, F., Kvetková, L., Hviščová, P., Gregor, M., Ferdinandy, M., 2016. Reactive processes in the high target utilization sputtering (HiTUS) W-C based coatings. *Journal of the European Ceramic Society* 36, 3029–3040.
- Lofaj, F., Hviščová, P., Zubko, P., Németh, D., Kabátová, M., 2019a. Mechanical and tribological properties of the high target utilization sputtering W-C coatings on different substrates. *International Journal of Refractory Metals and Hard Materials* 80, 305–314.
- Lofaj, F., Kabátová, M., Klich, M., Vaňa, D., Dobrovodský, J., 2019b. The comparison of structure and properties in DC magnetron sputtered and HiPIMS W-C:H coatings with different hydrogen content. *Ceramics International* 45, 9502–9514.
- Lofaj, F., Kabátová, M., Klich, M., Medved', D., Girman, V., 2019c. Tribological behavior of hydrogenated W-C/a-C:H coatings deposited by three different sputtering techniques. *Cerâmica* 65, 58–69.
- Lofaj, F., Kabátová, M., Kvetková, L., Dobrovodský, J., Girman, V., 2019d. Hybrid PVD-PECVD W-C:H coatings prepared by different sputtering techniques: The comparison of deposition processes, composition and properties. *Surface and Coatings Technology* 375, 839–853.
- Makowka, M., Pawlak, W., Konarski, P., Wendler, B., 2016. Hydrogen content influence on tribological properties of nc-WC/a-C:H coatings. *Diamond Related Materials* 67, 16–25.
- Mayrhofer, P.H., Hörling, A., Karlsson, L., *et al.*, 2003. Self-organized nanostructures in the Ti–Al–N system. *Applied Physics Letters* 10, 2049.
- Mayrhofer, P.H., Willmann, H., Reiter, A.E., 2008. Structure and phase evolution of Cr–Al–N coatings during annealing. *Surface and Coatings Technology* 202, 4935–4938.
- Mayrhofer, P.H., Mitterer, Ch., Wen, J.G., Greene, J.E., Petrov, I., 2005a. Self-organized nanocolumnar structure in superhard TiB₂ thin films. *Applied Physics Letters* 86, 131909.
- Mayrhofer, P.H., Mitterer, Ch., Wen, J.G., Petrov, I., Greene, J.E., 2006. Thermally induced self-hardening of nanocrystalline Ti–B–N thin films. *Journal of Applied Physics* 100, 044301.
- Mayrhofer, P.H., Hultman, L., Schneider, J.M., Staron, P., Clemens, H., 2007. Spinodal decomposition of cubic Ti_{1–x}Al_xN: comparison between experiments and modeling. *International Journal of Materials Research* 11, 1054–1059.
- Mayrhofer, P.H., Rachbauer, F., Holec, D., Rovere, F., Schneider, J.M., 2014. Protective transition metal nitride coatings. In: Hashmi, M.S.J. (Ed.), *Comprehensive Materials Processing* 4. Amsterdam: Elsevier, pp. 355–388.

- Mikula, M., Grančič, B., Buršiková, V., *et al.*, 2008. Mechanical superhard TiB₂ coatings prepared by DC magnetron sputtering. *Vacuum* 82, 278–281.
- Mikula, M., Plecenik, T., Vávra, I., *et al.*, 2011. The influence of low-energy ion bombardment on the microstructure development and mechanical properties of TiB_x coatings. *Vacuum* 85, 866–870.
- Mikula, M., Plašienka, D., Roch, T., *et al.*, 2016. Structural evolution of TaN-alloyed Cr–Al–Y–N coatings. *Surface and Coatings Technology* 288, 203–210.
- Mikula, M., Sangiovanni, D.G., Plašienka, D., *et al.*, 2017. Thermally induced age hardening in tough Ta–Al–N coatings via spinodal decomposition. *Journal of Applied Physics* 121, 155304.
- Moura e Silva, C.W., Branco, J.R.T., Cavaleiro, A., 2009. How can H content influence tribological behavior of W-containing DLC coatings. *Solid State Science* 11, 1778–1782.
- Musil, J., 1992. Sputtering systems with enhanced ionization for ion plating of hard wear resistant coatings. In: Takagi, T. (Ed.), *Proceedings of the 1st Meeting on Ion Engineering Society Japan, IESJ-92*. Tokyo: Ionics Publishing Corporation, pp. 295–304.
- Musil, J., 2000. Hard and superhard nanocomposite coatings. *Surface and Coatings Technology* 125, 322–330.
- Musil, J., 2006. Physical and mechanical properties of hard nanocomposite films prepared by reactive magnetron sputtering. In: DeHosson, J.T.M., Cavaleiro, A. (Eds.), *Nanostructured Coatings*. New York: Springer Science Business Media, pp. 407–463.
- Musil, J., 2012. Hard nanocomposite coatings: Thermal stability, oxidation resistance and toughness. *Surface and Coatings Technology* 205, 50–65.
- Musil, J., Jirout, M., 2007. Toughness of hard nanostructured ceramic thin films. *Surface and Coatings Technology* 201, 5148–5152.
- Nouvellon, C., Belchi, R., Libralesso, L., *et al.*, 2017. WC/C:H films synthesized by an hybrid reactive magnetron sputtering/Plasma Enhanced Chemical Vapor Deposition process: An alternative to Cr(VI) based chromium plating. *Thin Solid Films* 630, 79–85.
- Oberle, T.L., 1951. Properties influencing wear of metals. *Journal of Metals* 3, 438–439.
- Qi, Z.B., Sun, P., Zhu, F.P., *et al.*, 2011. The inverse Hall-Petch effect in nanocrystalline ZrN coatings. *Thin Solid Films* 205, 3692–3697.
- Rabinowicz, E., 1965. *Friction and Wear of Materials*. NY: Wiley.
- Rachbauer, R., Holec, D., Lattemann, M., Hultman, L., Mayrhofer, P.H., 2010. Phase stability and decomposition products of Ti–Al–Ta–N thin films. *Applied Physics Letters* 97, 151901.
- Rachbauer, R., Blutmager, A., Holec, D., Mayrhofer, P.H., 2012. Effect of Hf on structure and age hardening of Ti–Al–N thin films. *Surface and Coatings Technology* 206, 2667–2672.
- Rachbauer, R., Stergar, E., Massl, S., Moser, M., Mayrhofer, P.H., 2009. Three-dimensional atom probe investigations of Ti–Al–N thin films. *Scripta Materialia* 61, 725–728.
- Rachbauer, R., Holec, D., Lattemann, M., Hultman, L., Mayrhofer, P.H., 2011a. Electronic origin of structure and mechanical properties in Y and Nb alloyed Ti–Al–N thin films. *International Journal of Materials Research* 102, 735–742.
- Rachbauer, R., Massl, S., Stergar, E., *et al.*, 2011b. Decomposition pathways in age hardening of Ti–Al–N films. *Journal of Applied Physics* 110, 023515.
- Riedl, H., Holec, D., Rachbauer, R., *et al.*, 2013. Phase stability, mechanical properties and thermal stability of Y alloyed Ti–Al–N coatings. *Surface and Coatings Technology* 235, 174–180.
- Rovere, F., Mayrhofer, P.H., 2008. Thermal stability and thermo-mechanical properties of magnetron sputtered Cr–Al–Y–N coatings. *Journal of Vacuum Science and Technology A* 26, 29–36.
- Rovere, F., Music, D., Schneider, J.M., Mayrhofer, P.H., 2010. Experimental and computational study on the effect of yttrium on the phase stability of sputtered Cr–Al–Y–N hard coatings. *Acta Materialia* 58, 2708–2715.
- Schramm, I.C., Pauly, C., Johansson Jöesaar, M.P., *et al.*, 2017. Effects of nitrogen vacancies on phase stability and mechanical properties of arc deposited (Ti_{0.52}Al_{0.48})N_y (y < 1) coatings. *Surface and Coatings Technology* 330, 77–86.
- Schuster, J.C., Bauer, J.J., 1984. The ternary system titanium-aluminium-nitrogen. *Solid State Chemistry* 53, 260.
- Veprek, S., 2013. Recent search for new superhard materials: Go nano!. *Journal of Vacuum Science and Technology A* 34, (050822-1– 050822-33).
- Veprek, S., Reiprich, S., 1995b. A concept for the design of novel superhard coatings. *Thin Solid Films* 268, 64–71.
- Veprek, S., Reiprich, S., Li, S.Z., 1995a. Superhard nanocrystalline composite materials: The TiN/Si₃N₄ system. *Applied Physics Letters* 66, 2640–2642.
- Veprek, S., Veprek-Heijman, M.G.J., Karvankova, P., Prochazka, J., 2005. Different approaches to superhard coatings and nanocomposites. *Thin Solid Films* 476, 1–29.
- Veprek, S., Niederhofer, A., Moto, K., *et al.*, 2000. Composition, nanostructure and origin of the ultrahardness in nc-TiN/a-Si₃N₄/a- and nc-TiSi₂ nanocomposites with H_v = 80 to ≥ 105 GPa. *Surface and Coatings Technology* 133–134, 152–159.
- Voevodin, A.A., O'Neill, J.P., Zabinski, J.S., 1999. Tribological performance and tribochemistry of nanocrystalline WC/amorphous diamond-like carbon composites. *Thin Solid Films* 342, 194–200.
- Willmann, H., Mayrhofer, P.H., Hultman, L., Mitterer, Ch., 2008. Hardness evolution of Al–Cr–N coatings under thermal load. *Journal of Materials Research* 23, 2880–2885.
- Wolfe, D.E., Eden, T.J., Potter, J.K., Jaroh, A.P., 2006. Investigation and characterization of Cr₃C₂-based wear-resistant coatings applied by the cold spray process. *Journal of Thermal Spray Technology* 15, 400–412.
- Zhitomirsky, V.N., Grimbeg, I., Rapoport, L., *et al.*, 1998. Structure and mechanical properties of vacuum arc-deposited NbN coatings. *Thin Solid Films* 326, 134–142.

Oxidation and Corrosion of Non-oxide Ceramics

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Introduction

Nonoxide ceramics include carbides, nitrides, and borides. These materials are thermodynamically unstable in air and rely on the formation of a protective oxide for high-temperature stability. The durability of this protective oxide is thus a critical issue in the application of these materials. The requirements for such a protective oxide are (i) slow growing, (ii) self-healing if damaged, and (iii) resistant to corrosive gases and deposits. The emphasis of this chapter is on silicon carbide (SiC) and silicon nitride (Si₃N₄). These ceramics form a protective layer of silica (SiO₂), which meets most of the above requirements. A limited discussion of other ceramics is also included. Detailed reviews of this field are available (Nickel and Gogotsi, 2000; Opila and Jacobson, 2013).

Oxidation studies are concerned with the kinetics of oxide scale formation and the mechanism of reaction. Oxide scale formation may be followed experimentally by oxide thickness or weight change measurements. Application-oriented studies involve scale growth in actual combustion atmospheres or in a mixture of gases that simulate a combustion atmosphere. The microstructure and composition of the resultant oxide scale are examined with electron-optical methods and x-ray diffraction.

Passive Oxidation of Silica-Forming Ceramics

Oxidation rates of silica formers are controlled by the diffusion rate of oxidant molecules through the SiO₂ scale. The pioneering work on pure Si oxidation (Deal and Grove, 1965) is a useful guide to understanding the oxidation of SiC and Si₃N₄. The oxidant reacts with SiC or Si₃N₄ at the SiO₂/ceramic interface and gaseous products (CO or N₂) escape through the scale. The oxidation kinetics are described by a linear-parabolic rate law:

$$x_o^2 + Ax_o = B(t + \tau) \quad [1]$$

Here x_o is the oxide thickness, t is the time, τ is the time correction for any pre-formed oxide, B is the parabolic rate constant and B/A is the linear rate constant. At short times, eqn [1] reduces to $x_o = \frac{B}{A}(t + \tau)$, indicating that the oxide film growth rate is linear with time. At longer times, eqn [1] reduces to $x_o^2 = Bt$, indicating that oxide film growth rate is parabolic with time. Equation [1] describes SiO₂ growth on Si and SiC; SiO₂ growth on Si₃N₄ generally shows parabolic rates, but is more complex and will be discussed in a later section.

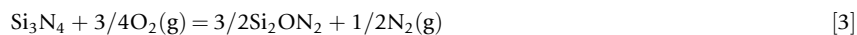
At temperatures below 1200 °C in clean environments the silica scale is amorphous, whereas at higher temperatures or in the presence of impurities cristobalite is found. Analogously to Si, the oxidant is molecular oxygen which permeates through the channels in amorphous silica. Crystallization of the silica scale may lower the oxidation rate of SiC somewhat, but only if the scale is completely transformed to cristobalite (Ogbuji, 1997). More detailed information on oxidation of SiC is available in an extensive review (Presser and Nickel, 2008).

Oxidation of Pure Silica-Forming Materials in Oxygen

SiC oxidizes by the following reaction:



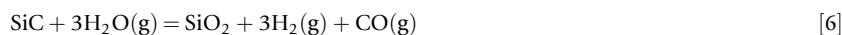
The oxidation rate of Si₃N₄ is about the same as SiC at a temperature of 1500 °C. However, the oxidation rate of Si₃N₄ is slower than that of SiC at lower temperatures. This difference may be related to the formation of an inner scale of silicon oxynitride that is found below the silica scale. The overall oxidation reaction can be written in simplified terms as



Evidence suggests the silicon oxynitride is actually a phase of variable stoichiometry, SiO_xN_y (Ogbuji and Jayne, 1993). The oxidation reaction can then be described as a progressive substitution of oxygen for nitrogen.

Oxidation of Pure Silica-Forming Materials in Other Oxidants

Applications of SiC and Si_3N_4 may involve exposure to other oxidants including CO_2 and water vapor. These oxidation reactions are written for SiC as



Similar reactions can be written for Si_3N_4 . Oxidation rates of SiC in CO_2 are negligible relative to those in dry oxygen. However, oxidation rates of SiC and Si_3N_4 in water vapor are enhanced over those observed in dry oxygen since the solubility of water in silica is much higher than that of oxygen. At high water pressures, bubbles are formed in the silica scale owing to the large amount of gases generated in the oxidation reaction. Significant bubble formation results in non-protective scale formation and rapid material consumption. For conditions with flowing gases, water vapor also reacts with the silica scale to form volatile hydroxide species, as discussed below.

Oxidation of Silica-Forming Materials in Impurity-Containing Environments

Low levels of impurities in the environment are incorporated in the silica scale, which increase the number of broken bonds in the silica structure and allow accelerated transport of oxidant to the ceramic, thus increasing the oxidation rate. When Si_3N_4 is oxidized in impurity-containing environments, oxidation rates are effectively the same as those for SiC. A second effect of impurities is a reduced energy needed for nucleation and crystallization of the silica scale, resulting in cristobalite scale formation at temperatures below 1200 °C.

Sintering additives may be added to SiC and Si_3N_4 to aid in the densification process. These additives also effect the oxidation properties of the materials. First, additives such as Al_2O_3 in SiC may become incorporated in the silica scale, thereby reducing the oxidation resistance of the scale (Singhal and Lange, 1975). Rare-earth oxides in Si_3N_4 change the rate-controlling mechanism for oxidation. In these materials, rare-earth cation diffusion outward to the scale surface controls the oxidation rate (Cubiciotti and Lau, 1978) and results in rare-earth silicate formation on the scale surface. These additives also form grain boundary phases, which may oxidize. Grain boundary compositions that undergo volume expansion under oxidation may lead to catastrophic failure and must be avoided (Patel and Thompson, 1988).

In a heat engine, sulfur in the fuel and sodium, either from a marine environment or fuel impurities, may react to form the highly stable species Na_2SO_4 . Condensed-phase Na_2SO_4 deposits lead to hot corrosion. The dew point for Na_2SO_4 deposition can be calculated from thermodynamic considerations and is a function of pressure and the concentrations of sulfur and sodium. The reactive portion of the Na_2SO_4 is Na_2O , released as follows:



The overpressure of SO_3 in the environment sets an activity of Na_2O . If the activity of Na_2O is sufficiently high (basic molten salt), then SiO_2 will be dissolved as follows:



Rapid diffusion through the liquid leads to more rapid oxidation and consumption of the ceramic. This type of corrosion can also occur in basic coal slags (Ferber *et al.*, 1985). Material consumption occurs as surface attack, which can lead to substantial strength degradation.

Volatilization of Silica-Forming Ceramics

One common degradation route for silica-forming ceramics is volatilization by active oxidation. This is formation of $\text{SiO}(\text{g})$ instead of $\text{SiO}_2(\text{s})$. Since $\text{SiO}(\text{g})$ is volatile, substantial material degradation can occur from active oxidation. Active oxidation occurs in flowing gas streams, at high temperatures, and low oxygen partial pressures. In application, this may be a re-entry environment or heat-treating furnace. Active oxidation occurs in regimes defined by the transition oxygen pressures – from active to passive and from passive to active. Note that these are not the same and may differ by orders of magnitude. As oxidant pressure is gradually increased, an active-to-passive transition occurs. The theory for this transition is based on the condition for a stable SiO_2 scale and was developed for silicon by Wagner (1958) and extended to SiC and Si_3N_4 by Singhal (1976). The passive-to-active transition occurs as oxidant pressure is gradually decreased and the SiO_2 scale decomposes. Models for active/passive transitions have been reviewed recently (Jacobson and Myers, 2011).

Another form of volatilization degradation occurs in steam-containing atmospheres, as referred to earlier.

Here the key reaction is



Although a silica scale grows in a steam environment, simultaneous volatilization leads to more rapid material recession (Opila, 1997). These volatilization rates increase with water vapor partial pressure and gas velocity.

Oxidation of Polymer-Derived Silicon-Based Ceramics

An interesting class of recently developed silicon-based ceramics are formed by decomposition of polymer precursors containing Si, C, N, and/or B to carbides or nitrides (Kroke *et al.*, 2000). Initially these materials appeared to have superior oxidation resistance to SiC and Si₃N₄ produced via conventional methods. However, accounting for volatile species formed during oxidation led to rates similar to other SiO₂ forming materials (Nickel, 1999). Nonetheless, these materials offer great flexibility for composition/property tailoring and are a promising new class of ceramics.

Oxidation of Silicon-Based Composites

The discussion thus far has centered on monolithic ceramics. The major issue with these materials is their low fracture toughness. So far the most promising method to improve fracture toughness is with continuous fibers as reinforcements. An example is SiC fibers in a SiC matrix. These types of composites have a unique set of oxidation/corrosion issues. A fiber coating is required so the fiber does not bond to the matrix. The primary fiber coatings are carbon and boron nitride, which are easily oxidized. Models have been developed for the oxidation of the carbon fiber coatings (Filipuzzi and Naslain, 1993). Boron nitride fiber coatings form a condensed phase oxide which interacts with the growing silica film on the fiber and matrix walls (Jacobson *et al.*, 1999).

Refractory Oxide Coatings on Silica-Forming Ceramics: Environmental Barrier Coatings (EBCs)

One attractive method for ameliorating the corrosion susceptibility of ceramic materials is the use of refractory oxide coatings. This approach combines the desirable mechanical properties of a nonoxide ceramic with the chemical stability of a refractory oxide. The primary requirements for such an oxide coating are (1) acts as a substrate oxidation barrier, (2) thermal stability, minimum susceptibility to phase changes, (3) chemical compatibility with substrate, (4) thermal expansion match to non-oxide substrate, and (5) low reactivity with the environment. Finding an oxide which meets all these requirements is challenging. The low reactivity with the environment suggests a low reactivity oxide or reducing the thermochemical activity of SiO₂ in the coating. This limits corrosion reactions [8] and [9]. Mullite (3Al₂O₃ · 2SiO₂) is a good candidate based on its coefficient of thermal expansion (CTE) match to SiC (Lee *et al.*, 1994) (Requirement 4), however the high activity of SiO₂ in mullite leads to only modest resistance to water vapor induced corrosion. A number of other coating compositions have been studied, which appear to limit water vapor enhanced volatility of SiC based ceramics (Lee, 2014). These include barium strontium aluminosilicates (BSAS) and rare earth silicates. The BSAS composition requires a silicon and mullite layer between the outer coating and substrate, which limits the upper operating temperature. Current development focuses on rare earth silicates, such as Yb₂O₃-SiO₂, which may offer improved behavior. Multilayer coatings with inner layers for a bond coat and CTE match and outer layers for durability (Lee, 2014) are promising developments.

Oxidation of Other Nonoxide Ceramics

Alumina (Al₂O₃)-forming ceramics include AlN and Al₄C₃. Al₂O₃ scales are less susceptible to salt corrosion and water vapor-induced volatilization than SiO₂ scales. There is interest in AlN owing to its high thermal conductivity and its slow oxidation rate in dry oxygen. However, it rapidly oxidizes in water vapor-containing environments due to the formation of micropores in the Al₂O₃ scale.

Boria (B₂O₃)-forming ceramics include BN and B₄C. BN is used as a fiber coating for continuous fiber-reinforced ceramic matrix composites. However, B₂O₃ is a liquid above 450 °C and hence a poor protective oxide. Further, it reacts readily with water vapor forming HBO₂(g), H₃BO₃(g), and H₃B₃O₆(g) which are stable under most conditions.

Oxidation of Ultra-High Temperature Ceramics (UHTCs)

Transition metal (typically Zr, Hf, and Ta) borides, carbides, and nitrides are of interest owing to their hardness and high melting points ($T > 3000$ °C) (Wuchina, 2007). Oxidation rates of these materials are rapid for three reasons. (i) Transition metal oxides generally have high oxygen anion diffusivities. (ii) There is generally a large thermal expansion mismatch between the oxide and

corresponding boride, carbide or nitride. This leads to scale cracking and rapid gas transport paths for oxygen to the underlying material. (iii) Porous oxides may form which also have rapid gas transport paths.

Nevertheless, these compounds, or mixtures of them, form the basis for ultra-high temperature composites, which have generated significant interest for thermal protection systems because of the high melting temperatures of both the base material and their oxides.

ZrB₂, a UHTC that has been studied extensively, oxidizes to form ZrO₂ and B₂O₃. The liquid B₂O₃ serves to limit oxygen transport in the porous ZrO₂, but vaporizes at temperatures above 1400 °C (Parthasarathy *et al.*, 2007). SiC additions to ZrB₂ result in the formation of a surface layer of borosilicate glass which extends the surface protection to higher temperatures (Parthasarathy *et al.*, 2012). However, this borosilicate glass layer is also susceptible to vaporization and loss of liquid by shear forces. Recent attempts to improve the oxidation behavior of ZrB₂ have centered on second phase additions such as Cr- or Ta-containing compounds that result in phase-separated glass layers with lower oxygen transport rates (Talmy *et al.*, 2001) or WC additions that improve the density of the ZrO₂ through transient liquid phase (WO₃) sintering (Zhang *et al.*, 2008).

Carbides and nitrides of Zr, Hf, and Ta have also received considerable attention for ultra-high temperature applications. Oxidation of these materials results in the formation of transition metal oxides and gaseous products CO(g) or N₂(g). Gas generation results in the formation of porous oxides. Porous oxides are undesirable under most conditions, allowing rapid oxidant ingress. However, under severe conditions, porous oxides can be favorable, as they allow egress of product gases without rupturing the oxide scale (Metcalf, 2007). Minimization of product gases can be accomplished by utilizing substoichiometric carbides and nitrides such as ZrC_x or HfN_x with $x < 1$ (Wuchina, 2001).

Summary

This discussion has centered on SiC and Si₃N₄, which form slowly growing SiO₂ scales. This oxide is very stable, but susceptible to basic salt corrosion and volatilization under certain conditions. Variants on SiC and Si₃N₄ include polymer-derived Si based composites and ceramic matrix composites. Each material system has a unique set of oxidation and corrosion issues. Refractory oxide coatings offer the possibility of combining the desirable mechanical properties of silicon-based ceramics with the chemical inertness of an oxide. Other non-oxide ceramics generally form less protective scales in oxidizing environments. Nonetheless transition metal compounds have extremely high melting points and combinations of borides, carbides, and/or nitrides may have acceptable oxidation rates for use in short-term ultra-high temperature applications.

References

- Cubicciotti, D., Lau, K., 1978. Kinetics of oxidation of hot-pressed silicon nitride containing magnesia. *Journal of the American Ceramic Society* 61, 512–517.
- Deal, B.E., Grove, A.S., 1965. General relationship for the thermal oxidation of silicon. *Journal of Applied Physics* 36, 3770–3778.
- Ferber, M.K., Ogle, J., Tenney, V., Hensen, T., 1985. Characterization of corrosion mechanisms occurring in a sintered SiC exposed to basic coal slags. *Journal of the American Ceramic Society* 68, 191–197.
- Filipuzzi, L., Nastain, R., 1993. Oxidation mechanisms and kinetics of 1D-SiC/C/SiC composite materials. *Journal of the American Ceramic Society* 77, 467–480.
- Jacobson, N.S., Morscher, G.N., Bryant, D.R., Tressler, R.E., 1999. High-temperature oxidation of boron nitride: II, boron nitride layers in composites. *Journal of the American Ceramic Society* 82 (1473), 14–82.
- Jacobson, N.S., Myers, D.L., 2011. Active Oxidation of SiC. *Oxidation of Metals* 75, 1–25.
- Kroke, E., Li, Ya-Li, Konetschny, C., Lecombe, E., Fasel, C., Riedel, R., 2000. Silazane derived ceramics and related materials. *Materials Science and Engineering: R: Reports* 26, 97–199.
- Lee, K.N., 2014. Environmental Barrier Coatings (EBCs) for SiC/SiC. In: Bansal, N.P., Lamon, J. (Eds.), *Ceramic Matrix Composites: Materials, Modelling and Technology*. Hoboken, NJ: John Wiley & Sons.
- Lee, K.N., Jacobson, N.S., Miller, R.A., 1994. Refractory oxide coatings on SiC. *MRS Bulletin* 19, 35–38.
- Metcalf, A.G., 2007. Gas evolution during oxidation of refractory borides and carbides at 1500 °C to 2700 °C. *ECS Transactions* 3 (14), 131–142.
- Nickel, K.G., 1999. Corrosion: no problem for precursor-derived covalent ceramics? In: Bill, J., Wakai, F., Aldinger, F. (Eds.), *Precursor-derived Ceramics*. Weinheim, Germany: VCH-Wiley, pp. 188–196.
- Nickel, K.G., Gogotsi, Y.G., 2000. Corrosion of hard materials. In: Riedel, R. (Ed.), *Handbook of Ceramic Hard Materials*. Weinheim, Germany: Wiley-VCH.
- Ogbuji, L.U.J.T., 1997. Effect of oxide devitrification on oxidation kinetics of SiC. *Journal of the American Ceramic Society* 80, 1544–1550.
- Ogbuji, L.U.J.T., Jayne, D.T., 1993. Mechanism of incipient oxidation of bulk chemical vapor deposited Si₃N₄. *Journal of the Electrochemical Society* 140, 759–766.
- Opila, E.J., Hann, R.E., 1997. Paralinear oxidation of CVD SiC in water vapor. *Journal of the American Ceramic Society* 80, 197–205.
- Opila, E.J., Jacobson, N.S., 2013. Oxidation and corrosion of ceramics. In: Reidel, R., Chen, I.-W. (Eds.), *Ceramic Science and Technology: Vol. 4 Applications*. Darmstadt, Germany: Wiley-VCH.
- Parthasarathy, T.A., Rapp, R.A., Opeka, M., Kerans, R.J., 2007. A model for the oxidation of ZrB₂, HfB₂ and TiB₂. *Acta Materialia* 55, 5999–6010.
- Parthasarathy, T.A., Rapp, R.A., Opeka, M., Cinibulk, M.K., 2012. Modeling oxidation kinetics of SiC-containing refractory diborides. *Journal of the American Ceramic Society* 95, 338–349.
- Patel, J.K., Thompson, D.P., 1988. The low-temperature oxidation problem in yttria-densified silicon nitride ceramics. *British Ceramics Transactions* 87, 70–73.
- Presser, V., Nickel, K.G., 2008. Silica on silicon carbide. *Critical Reviews in Solid State Materials Science* 33, 1–99.
- Singhal, S.C., 1976. Thermodynamic analysis of the high temperature stability of silicon nitride and silicon carbide. *Ceramics International* 2, 123–130.
- Singhal, S.C., Lange, F.F., 1975. Effect of alumina content on the oxidation of hot-pressed silicon carbide. *Journal of the American Ceramic Society* 58, 433–435.
- Talmy, I.G., Zaykoski, J.A., Opeka, M.M., Dallek, S., 2001. Oxidation of ZrB₂ ceramics modified with SiC and group IV–VI transition metal diborides. *Electrochemical Society Proceedings* 12, 144–157.
- Wagner, C., 1958. Passivity during the oxidation of silicon at elevated temperatures. *Journal of Applied Physics* 29, 1295–1298.

- Wuchina, E., Opila, E., Opeka, M., Fahrenholtz, W., Talmy, I., 2007. UHTCs: ultra-high temperature ceramic materials for extreme environment applications. *The Electrochemical Society Interface* 16 (4), 30–36.
- Wuchina, E.J., Opeka, M.M., 2001. The oxidation behavior of HfC, HfN, and HfB₂. In: McNallan, M.J., Opila, E.J. (Eds.), *High Temperature Corrosion and Materials Chemistry III: Proceedings of the International Symposium*, The Electrochemical Society, Pennington, NJ, pp. 136 – 143.
- Zhang, S.C., Hilmas, G.E., Fahrenholtz, W.G., 2008. Improved oxidation resistance of zirconium diboride by tungsten carbide additions. *Journal of the American Ceramic Society* 91, 3530–3535.

Overview: Glass and Glass Ceramics

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Glasses are widely used in modern society in traditional areas of architecture, transport, packaging and tableware but also in advanced technologies such as optoelectronics, microelectronics, communications technologies, energy technologies and bio-medical devices. This section is devoted to Glass and Glass Ceramics and their potential for use in these applications.

The first chapter deals with the Glassy State, defining glass as a non-equilibrium, non-crystalline condensed state of matter that exhibits a glass transition. The chapter expands and elaborates on this definition exploring the fundamental concepts of the non-equilibrium state, non-crystalline structure of glasses which is similar to that of their parent supercooled liquids (SCL). In fact the idea that glass combines features of both liquids and solids is discussed as well as its very unique characteristics. Structural features of glasses are introduced including bridging and non-bridging oxygens and the role of network modifiers. Other important concepts such as relaxation phenomena and glass transition are outlined. The role of critical factors that determine glass formation and crystallization processes, such as glass composition, thermal history, diffusion processes, and viscosity is explored as a crucial basis for further research and development of new materials that readily form glasses and have useful applications.

Following this major introduction to the Glassy State, there follow nine chapters concerned with basic glass types. The first of these reviews the alkali- and alkaline-earth-silica binary glass systems which form the base models for more complex glasses and glass-ceramics. In silica, the basic structural unit is a SiO_4 tetrahedron and all corners are joined to adjacent tetrahedra in a continuous 3-D glass network. When alkali or alkaline-earth cations are mixed with silica, formation of non-bridging oxygens occurs which depolymerizes the network and has a profound effect on the properties of the resulting glass or glass-ceramic. The Mixed Alkali Effect is an important topic for discussion along with phase separation. A broad overview of industrial applications is provided where additives enhance the intrinsic glass properties.

Most of the glasses that people experience in their daily lives, articles such as container glass (bottles), flat glass (windows, etc.) and glassware (drinking glasses), are Soda-Lime-Silica (SLS) glasses which are reviewed in the next chapter along with the raw materials used in current SLS production and forming methods. The relevance of viscosity to glass forming are outlined which has enabled automated processes to be developed around the viscosity-temperature behavior of SLS compositions. SLS glasses can also be produced to suitable optical standard for applications such as windscreens, and they have sufficient mechanical characteristics and chemical durability for use in a wide range of applications.

The introduction of Al_2O_3 into silicate glasses usually imparts greater chemical durability, higher viscosity and glass transition temperatures, improves mechanical properties, reduces devitrification tendencies and lowers thermal expansion. The next chapter reviews Aluminosilicate glasses, which are important for various industrial applications. In practice, almost all silicate glasses incorporate alumina either as an impurity or as a larger chemical constituent. Recent experimental and modeling techniques are reviewed which have substantially improved the understanding of the atomic-scale structure, providing a good basis to better control aluminosilicate glass properties.

The next chapter reviews borosilicates glasses which consist of two kinds of network formers, SiO_2 and B_2O_3 , with network modifiers such as alkali and alkaline earth oxides. This is a very important inorganic glass system used in a broad range of applications such as electronics, lighting, cookware, optics, healthcare, pharmaceutical containers, nuclear waste immobilization, and fiber reinforced composites. These applications originate from the unique properties of borosilicate glasses such as low thermal expansion, high mechanical strength and high chemical durability which derive from the unique glass structure. A feature of borosilicate glasses containing alkali ions is their strong tendency to phase separation, which has been taken advantage of to form low thermal expansion products for cookware or high silica (99 wt%) glass for aerospace applications. This chapter reviews both the basic knowledge and current understanding of structure, topology and properties of borosilicate glasses and introduces developments in property prediction realized by both topological models and MD simulations.

The next chapter describes the fundamental material attributes of chalcogenide glasses (ChGs) and glass-ceramics (GCs) for their use in optical applications. It discusses how ChGs composition (glass chemistry) and morphology (homogeneous or phase-separated glass) can be tailored to produce useful components and how microstructural modification associated with the controlled nucleation and growth of nanocrystals within the parent glass leads to glass ceramics with novel functionalities. Various applications are outlined including components for the mid-wave infrared, such as low-cost lenses via precision glass molding, communication fibers, as well as gradient index optics (imaging), low-loss waveguides (signaling), and nonlinear optics (sensing and lighting).

The next two chapters are concerned with Oxynitride Glasses which are formed by the replacement of oxygen atoms by nitrogen in silicate and aluminosilicate glasses in various M-Si-O-N, M-Si-Al-O-N and M-Si-Mg-O-N systems, where M is a modifying cation such as Mg, Ca, Ba, Sc, Y and the rare earth lanthanides. Representation of four and five-component systems are explained and glass forming regions are outlined. Explanations of structural features such as tri-coordinated nitrogen and the existence of SiO_3N and SiO_2N_2 tetrahedra are given and the roles that Al, Mg and other cations play in the structure of oxynitride glasses are discussed. The second of these chapters provides an overview of the effects of glass composition on properties and crystallization of oxynitride glasses. The effect of nitrogen substitution for oxygen in silicate and aluminosilicate glasses is to increase properties such

as glass transition temperature, elastic modulus, viscosity, hardness and slow crack growth resistance as a result of increased cross-linking within the glass network provided by tri-coordinated nitrogen atoms. Progress in understanding how changes in glass composition affect structural parameters and their relationship to properties is discussed. An overview is given on crystallization of oxynitride glasses outlining nucleation and growth of crystal phases to form glass ceramics with significant increases in elastic modulus over the parent glasses.

The next chapter reviews phosphate glasses which are important materials for a variety of technological applications, in optics as laser glasses, in electrochemistry as new electrode/electrolyte materials, as low temperature sealing glasses, in biomedicine as bioglasses, and as hosts for nuclear wastes. While P_2O_5 is a distorted network glass former oxide consisting of PO_4 tetrahedra interconnected through bridging oxygens, it differs from SiO_2 with its SiO_4 units in that one of the oxygens in PO_4 is double bonded to P and therefore nonbridging. The effects of addition of modifier oxides is outlined and this significantly depolymerizes the phosphate structure with subsequent consequences for properties of these glasses. The chemical and physical properties of phosphates glasses are discussed which are closely related to the modification of the composition and structural network by addition of various metal oxides.

The final chapter in the sequence of glass types reviews Halide glasses. Glass formation is common for single halides (Fluorides, Chlorides, Bromides and Iodides). Those that have been developed for optical fibers are mainly based on fluorozirconates with other components. This chapter reviews the various important glass forming systems, in particular fluoride based glasses which have been more extensively studied and developed, particularly as optical fibers, which extends the range of transmission into the mid infrared range.

The next two chapters are complimentary. The first is concerned with annealing and tempering. Annealing is a basic heat treatment step in the production of all glasses to relieve residual tensile stresses which might render it useless in its chosen application. The relationship between glass viscosity and temperature during manufacture is described and the critical viscosity ranges at which stresses form and at which they can be released are detailed. Tempering is another thermal treatment process, used for instance in car windshields, whereby compressive surface stresses are generated to improve the mechanical properties of a glass and cause safe fracture.

The second of these chapters compares Chemical Strengthening and Thermal Strengthening which are two common methods for improving the mechanical properties of silicate glasses. The generation of surface compressive stresses in glasses are reviewed which are able to mitigate the negative impact of surface flaws through the creation of a residual surface compression layer. The crucial parameters affecting chemical strengthening, particularly the kinetics of ion-exchange of alkali ions, are discussed as well as non-conventional methods for ion-exchange strengthening.

In the next chapter, a general overview of glass properties is given with brief descriptions of chemical durability, mechanical, thermal, electrical and optical properties of glass and the effects of glass composition on properties. This is followed by a more in-depth review of optical glass, describing the historical developments and how scientists working with optical instruments identified the need for novel glass types with essentially different dispersion properties. The starting point was the basic electro-dynamics of light and its interaction with matter. At the same time, relevant glass types were under development and thus modern optical glass chemistry was born. The chapter reviews the interplay of the progress of optical design, the arising needs for novel optical materials and the corresponding invention of special optical glasses.

The next two contributions are concerned with glass fibers. In the first of these the focus is on silicate-based glasses because of their great commercial importance as reinforcement fibers for polymer matrix composites. There is also reference to the use of glass fibers in the biomaterials sector as scaffolds in tissue engineering. This is followed by a chapter which examines how the properties of silica (SiO_2) glass make it the medium of choice for optical fiber communications. Topics covered range from the viscosity of silica over its working temperature range that make it suitable for drawing into fiber, to its suitability as a substrate material for trace dopants in modifying its refractive index, to it being the only material that, when doped with the rare earth element erbium, provides optical gain in the same portion of the electromagnetic spectrum as its optimal region of transparency.

The next two chapters cover sol-gel methods for preparing glasses, the first being an introduction to the topic. The second presents a review of the advances in the sol-gel route for preparation of glasses and glass-ceramics, taking into account the physical and chemical aspects governing the process. An overview of the most important developments and applications including sol-gel coatings for optical, as well as protective or photocatalytic, applications. Biomaterials prepared by sol-gel are also highlighted.

The next chapter reviews the field of glass-ceramics (GC). The glass-ceramic process is described involving melting to form a glass followed by a two-stage heat treatment to form crystalline phases by controlled nucleation and crystallization. The advantages over the conventional ceramic forming process are discussed. This is followed by outlines of the major applications of glass-ceramic systems because of their specific combinations of mechanical and functional properties. Applications include: lamp bulb seals, because of GC higher mechanical properties, better temperature resistance, and tailored thermal expansion; hermetic gas sealants for SOFC batteries that must withstand the working temperatures over long times; joining of SiC-based materials, for example in nuclear reactors where GCs provide irradiation stability, chemical inertness, toughness, and high temperature performance; bioactive glass-ceramics, which are easy to synthesize and their mechanical properties are higher than those of glasses; dental restorations; GC insulators, dielectrics for high power capacitors; pyroelectric, piezoelectric and thermoelectric GCs; solid state electrolytes for rechargeable batteries; machinable GCs: GCs for radioactive and hazardous waste encapsulation.

The next contribution is on glass reactive sintering which refers to several technologies, with the common trend of viscous flow sintering of glass combined with physical and chemical reactions. It reviews the distinctive characteristics of glass sintering with reactions having a significant impact on the chemical composition and phase assemblage of the resulting products. The more

conventional technology of sinter-crystallization (sintering with concurrent devitrification of glass powders) is presented in its more recent developments (e.g., additive manufacturing); a survey of more recent technologies concerning extensive glass/oxide additive interaction is also presented. The wide range of combinations of glass powders, oxide additives, reactive binders, etc. opens the way for a new generation of glass-based products in key areas related to health, energy, and environment that are crucial for future well-being.

The use of glasses as hermetic seals is the topic of the next chapter. The joining of glass/metal or glass/ceramic interfaces is a field of research which covers energy-generation systems, electricity, microelectronics and protection against corrosion. An overview is given of the interdisciplinary approach to research and development connecting different areas of knowledge such as the design of glass sealing compositions, melting and processing, adherence and inter-diffusion processes and also the most modern techniques for the study of surfaces and interfacial reactions. Relevant compositions are presented along with the steps of the sealing process as well as conventional and new applications for glass and glass-ceramics as sealing materials.

The final chapter in this section reviews Glasses and Glass-ceramics for Nuclear Waste Immobilization. Oxide glasses – and mainly borosilicates – are the only host used to incorporate high level radioactive waste. Their structural flexibility allows them to accommodate almost all the elements present in waste resulting from spent nuclear fuel reprocessing, and their good self-irradiation resistance and chemical durability associated with their ease of fabrication by melting and casting explain the success of glassy wasteforms today. Descriptions are given of vitrification, and how glass formulation has been adapted to the changes in waste composition. The developments in the precise knowledge of the structure and properties of nuclear glasses are outlined and in particular the way the various elements present in the waste are incorporated into the glassy network and how this can be optimized by modifying the composition of the glass. The long-term behavior is reviewed of nuclear glasses during their geological storage, such as in submerged aqueous media, as well as the impact of internal irradiation on glass structure and properties. While the presence of crystals in nuclear glasses was regarded as undesirable new developments are described to accept partial crystallization for some waste if the containment of the final wasteform remains acceptable, leading to glass composite materials (GCM). Belonging to this family of wasteforms, glass-ceramics that can be obtained by controlled crystallization of glass bearing radio-nuclides are speculated for instance as materials to immobilize actinide-rich waste.

Glasses are important materials that are crucial to human civilization and this section has covered a broad range of subjects related to the most important glass types and other areas of glass science and technology.

The Glassy State

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Introduction

Glasses have been, beyond any doubt, vital materials for the development and well-being of human civilization and are now ubiquitous in our everyday lives. Natural glasses, such as obsidian, are nearly as old as the universe, whereas novel useful glasses are being discovered daily (Zanotto and Mauro, 2017; David Pye, 2016). As summarized in *Welcome to the Glass Age*, by Morse and Evenson (2016), *Glass: the eye of science* by Bolt (2017), and *Glass and Glass-Ceramic Technologies to Transform the World* by Hench (2011), many outstanding innovations can be cited, where glass was the critical material, for instance, optical glass fiber networks that span the globe (Ballato *et al.*, 2017), thin and strong glass sheets for television sets and cell phones (Varshneya and Bihuniak, 2017), high-strength and exceptionally elastic metallic glasses (Li *et al.*, 2019; Shi, 2019), semiconductive chalcogenide glasses (Lin *et al.*, 2018), bioactive glasses for healthcare (Montazerian *et al.*; Montazerian and Zanotto, 2017), and many other incredible applications described in other chapters.

A diverse variety of glass-forming chemistries exist, having a wide range of structural building blocks from which a glassy material is constructed. The detailed nature of these chemical building blocks and how they are connected depend on the particular nature of the chemical bonding in these systems. Here we defend the concept that glass itself is a fascinating state of matter combining aspects of the liquid and solid states. Before elucidating the idea of the glassy state, some basic concepts are defined which will render the modern definition of the glassy state more tangible.

Basic Definitions

Solid

A solid is one of the three traditional, basic states of matter (the others are liquid and gas) where the atomic structure and chemical forces are strong enough to keep that atomic structure and external shape cohesive even when it is not confined in a receptacle. Solids exhibit certain characteristics that distinguish them from liquids and gases. All solids have, for example, the ability to resist some level of forces applied either perpendicular or parallel to their surface, i.e., normal or shear loads, respectively. Such properties depend on the nature of the atoms that form the solid, the way these atoms are arranged and the bonding characteristic between them (see “Relevant Websites section”).

Liquid

Liquid is another principal condensed state of matter; intermediate between a gas and crystalline solid. A liquid will retain its volume, but not its shape when it is poured from one vessel to another. The shape variation might occur in a short or very long time; liquids flow under the force of gravity (or even smaller forces) until their shape conforms to that of the container that they occupy (see “Relevant Websites section”).

Viscous Flow Versus Creep

A characteristic feature of liquids, viscous flow is a cooperative movement of several atomic groups under a positive force field, e.g., gravity. This is quite different from diffusive deformation of solids under stress, such as creeping. While both types of deformation are characterized by rates proportional to the applied stress, they are very distinct on the molecular scale (Hopper and Uhlmann, 1974). The mechanism of creep depends on temperature and applied stress. Dislocation glide or diffusional-flow mechanisms typically dominate creep deformation, and their kinetics is completely distinct from the viscous flow. The most celebrated creep mechanisms are bulk diffusion (Nabarro–Herring creep), grain boundary diffusion (Coble creep), thermally activated and climb-assisted dislocation glide – where the climb is an enabling mechanism, allowing dislocations to move around obstacles. Most of these mechanisms are controlled by vacancy (in single crystals) or grain boundary diffusion (in polycrystals) and are generally triggered after a minimum threshold stress is surpassed, which is composition and temperature dependent. For a detailed description, the reader is invited to study (see “Relevant Websites section”; Poirier, 1985).

Supercooled Liquid (SCL)

SCL is the liquid state that exists between the melting point or liquidus temperature and the glass transition temperature. Supercooled liquids are thermodynamically metastable and tend to crystallize (Zanotto and Mauro, 2017).

Crystal

A crystal is a solid material having a well-ordered atomic structure on a periodic lattice. Crystals can be thermodynamically stable or metastable (they can transform into other crystalline structures under pressure or temperature). Crystalline materials may be composed of a single crystal, or they may be polycrystalline (Zanotto and Mauro, 2017). They can be permanently deformed under an external threshold stress.

Non-Equilibrium Thermodynamic State

The thermodynamic state of a material can be either an equilibrium state or a non-equilibrium state. The values of thermodynamic properties define a thermodynamic equilibrium state. A non-equilibrium state is much more difficult to explain and generally requires the existence of a condition called local thermodynamic equilibrium, which exists when thermodynamic equilibrium occurs locally within a series of small volumes that make up the system. Conversely, a thermodynamic property is any characteristic of a system whose numerical value depends only on the (local) thermodynamic equilibrium state of the system and is independent of how that state was attained (Robert, 2011).

Ergodic State

Ergodicity denotes a system where the time and ensemble averages of properties are equivalent. This implies that the ergodic system explores a sufficient fraction of its configurational phase space to reach this equivalence (Mauro *et al.*, 2010, 2007).

Relaxation

Non-equilibrium materials tend to relax toward the equilibrium condition, even in the absence of any external stress field. Their properties are liable to reach the values of the equilibrium state. This change from a non-equilibrium to an equilibrium state is thus called relaxation (Robert, 2011).

Non-Crystalline Material

A material which lacks the long-range atomic and molecular periodic order of a crystal is called non-crystalline. As first pointed out in the pioneering work of Zachariasen (Zachariasen, 1932) in 1932, the non-crystalline network of oxide glasses is not periodic and symmetrical as in crystals. However, it is not entirely random because the internuclear distances do not fall below a given minimum value.

Amorphous

An amorphous material (AM) has a non-crystalline structure that differs from that of its isochemical liquid, and does not undergo structural relaxation and the glass transition when heated. Please note the distinction between glasses and amorphous solids; the reader is referred to Gupta (1996) for further details. Both glasses and amorphous solids are examples of non-crystalline materials, but glasses exhibit a glass transition, whereas amorphous solids do not. We will show later that glasses relax to the SCL state then crystallize, whereas amorphous materials crystallize without undergoing any relaxation process. Moreover, AM cannot be made from quenching a liquid; amorphous materials are made, e.g., by evaporation-condensation onto a cold substrate or by the destruction of crystalline structures by high energy.

Crystallization

Glasses are unstable against the SCL state. All non-crystalline substances (glasses, SCL or AM) are metastable against their crystalline (solid) counterparts. Hence, they tend to reach thermodynamic equilibrium via crystal nucleation and growth. Crystallization is thus the ultimate fate of all non-crystalline materials (Zanotto and Mauro, 2017).

The Glassy State

A recent definition of glass reads (Zanotto and Mauro, 2017): “Glass is a non-equilibrium, non-crystalline state of matter that appears solid on a short time scale but continuously relaxes towards the liquid state.” This is an intuitive description for the general public. A more detailed definition is “Glass is a non-equilibrium, non-crystalline condensed state of matter that exhibits a glass transition. The structure of glasses is similar to that of their parent supercooled liquids (SCL), and they spontaneously relax toward the SCL state. Their ultimate fate, in the limit of infinite time, is to crystallize.” This definition can also be applied to “non-standard” types of glasses, such as liquid crystals, which are partially crystalline but have a vitreous matrix that exhibits a glass transition (Zanotto and Mauro, 2017).

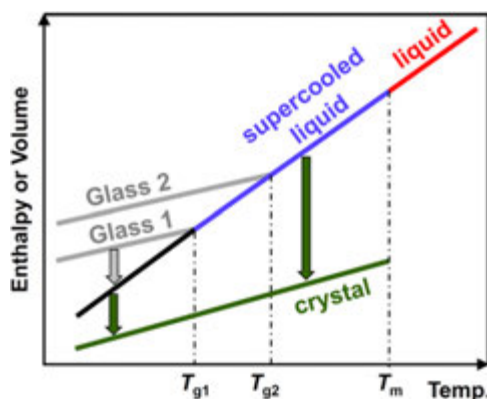


Fig. 1 Schematics of how a first-order thermodynamic property, such as volume or enthalpy, varies with temperature for a glass-forming liquid. Four distinct states are shown: liquid, supercooled liquid, glass, and crystal. T_m = melting point or liquidus temperature, T_g = glass transition temperature. Glass 1: changed from the SCL at a lower cooling rate, and hence, at a lower glass transition temperature (T_{g1}) than glass 2; which became frozen at a higher glass transition temperature (T_{g2}). Most glasses first relax to a SCL state (gray arrow), and then the SCL eventually crystallizes at any temperature below T_m (green arrows). Adapted from: <https://www.youtube.com/watch?v=eYlWiFeKt5o&t=16s>. The glass transition unveiled – A theatrical version.

In this chapter, we dwell on the key concepts of the above definition to dig deeper into the glassy state of matter. To understand its key features, we review here the most well-known diagram in glass science (**Fig. 1**). This figure shows how a first-order thermodynamic property such as molar volume, entropy, or enthalpy varies with temperature for a glass-forming liquid. Through this plot, glass formation is discussed, and the relevant concepts are explained. The different regions in this figure are described as follows (**Zanotto and Mauro, 2017**):

- (1) In equilibrium, the thermodynamically stable liquids only exist above the melting point (T_m) or *liquidus* temperature (T_L). For any given composition, the *liquidus* temperature is the highest temperature of thermodynamic equilibrium between the solid and liquid phases, above which any crystal is unstable and will dissolve in the liquid phase. T_L equals T_m for congruently melting compounds. Therefore, when the temperature is above the T_m of a pure system or T_L for a multi-component system, the liquid is in thermodynamic equilibrium and never crystallizes.
- (2) Supercooled liquids exist between T_m and the glass transition temperature, T_g . They are metastable, i.e., a thermodynamic barrier must be overcome for crystal nucleation to take place, but they eventually crystallize (green arrows) after a certain time.
- (3) If an equilibrium liquid is cooled quickly enough to avoid crystallization, a SCL is obtained. The structure of the liquid rearranges quickly to attain this metastable equilibrium state as the temperature decreases. However, upon continued cooling, as the temperature decreases, the relaxation time of the SCL increases and the system is eventually (temporarily) frozen when the relaxation time exceeds the laboratory observation time. When this happens, the atoms do not have sufficient time to rearrange to the metastable equilibrium state, i.e., the structural reorganization is kinetically arrested. As a result, the enthalpy deviates from the SCL line and follows that of the configurationally frozen system. This freezing of the system occurs continuously and results in a non-equilibrium material known as “glass.” Since the glass transition is a kinetic freezing process, the final enthalpy of glass depends on the cooling rate, which is related to observation time. When the cooling rate is high, the system has less time to relax into a lower energy structure, which leads to greater enthalpy in the final glass. This phenomenon is expressed in **Fig. 1**. This figure shows that glass 2 (e.g., fiberglass) has higher enthalpy or volume than glass 1 (e.g., a monolithic piece of glass having the same composition as the fiber), since the former is cooled faster than the latter. The temperature range between the equilibrium SCL and the frozen liquid (glass) is defined as the “glass transition” range. The temperature at the intercept between the two lines extrapolated from glassy and liquid enthalpies is the characteristic value of the T_g . Due to its higher cooling rate, glass 2 has a higher T_g (T_{g2}), whereas glass 1 has a lower T_g (T_{g1}).

Is Glass a Solid or Liquid?

For many decades, researchers have attempted to define glass as either a liquid or, more typically, as a solid. However, this binary thinking does not do justice to the true complexity of the glassy state, which combines features of both liquids and solids, and also brings along its unique characteristics. Glass appears to be solid on a typical observation time scale: it has mechanical rigidity and elasticity, it can be scratched and fractured, ring and resonate, just as a solid. However, the structures of all glasses are very similar to those of their corresponding SCL, i.e., a liquid property. It should also be noted that glasses also have a property that is unique to the glassy state due to their non-equilibrium and frozen nature; they undergo spontaneous relaxation towards the SCL state. Additionally, unlike regular solids and liquids, the properties of a glass depend not only on its composition and the current temperature and pressure but also on its entire thermal and pressure histories (**Zanotto and Mauro, 2017**). Moreover, it has been

shown that the glassy state itself cannot be expressed as any linear combination of supercooled liquid states (Mauro *et al.*, 2009b; Mauro and Loucks, 2009). The glassy state is, therefore, unique and can be classified as its own (non-equilibrium) state of matter.

The existence of any glass is transient and temporary since it will continuously relax toward the supercooled liquid state and ultimately crystallize (solidify). Given this combination of solid-like and liquid-like properties, glass could be considered as a special hybrid state of matter (the glassy state), where the solid-like properties are evident when probing its mechanical response on a short timescale, but their non-crystalline structures, spontaneous relaxation to the SCL followed by viscous flow, and crystallization behaviors make them more akin to non-equilibrium “frozen” liquids (Zanotto and Mauro, 2017).

Besides the above discussion on the *solid*, *liquid*, and the *non-equilibrium* nature of glass, there are some key features in the definition of glass that should be elaborated upon. These characteristics include relaxation, glass transition, glass structure, and crystallization.

Relaxation

From relatively low to intermediate viscosities ($10^0 < \eta < 10^{11}$ Pa s), most glass-forming melts usually behave as Newtonian liquids, and immediately relax to relieve any applied stress. However, at extremely high viscosities ($\eta > 10^{13}$ Pa s), when the structural relaxation times become longer than the experimental times, these liquids respond to the “rapid” application of a stress as if they were actually elastic materials. It follows that there must be an intermediate range of viscosities where the response of these melts to the application of a stress is intermediate between the behavior of a liquid and that of an elastic solid. Since this behavior has aspects of both viscous and elastic responses, it is known as viscoelasticity or viscoelastic behavior (Shelby, 2005).

The most common basic model for viscoelasticity, known as the Maxwell model, reads (Shelby, 2005):

$$\sigma_t = \sigma_0 \exp\left(-\frac{G(T)}{\eta(T)}\right) \quad (1)$$

where σ_t is the stress at time, t , σ_0 is the stress at time zero, $G(T)$ is the shear modulus, and $\eta(T)$ is the viscosity. The ratio $\eta(T)/G(T)$ has the dimensions of time and is equal to the time required for the stress to decay to $1/e$, or 0.367, of its initial value. This time, which is commonly represented by τ_R , is known as the *average relaxation time*. The stress relaxation time, τ_R , is thus expressed in terms of viscosity and G_∞ ,

$$\tau_R(T) = \frac{\eta(T)}{G_\infty} \quad (2)$$

where G_∞ is the shear modulus measured at infinitely high frequency, which changes little with temperature, whereas both $\tau_R(T)$ and $\eta(T)$ vary dramatically with temperature. The viscosity and stress relaxation time are roughly proportional since the temperature dependence of G_∞ is small. Building on the above definition and considering a typical shear modulus for oxide glasses (in Maxwell’s equation), Angell proposed an operational definition of T_g as the temperature at which the viscosity of the supercooled liquid is equal to 10^{12} Pa s (Angell, 1991).

Replacing $\eta(T)/G(T)$ by τ_R , the expression can be written as:

$$\sigma_t = \sigma_0 \exp\left(-\frac{t}{\tau_R}\right) \quad (3)$$

which describes an exponential relaxation curve. If τ_R is very small, relaxation will occur so rapidly that normal measurements may indicate that the process is instantaneous. If τ_R is very long (e.g., at room temperature for a window glass), the relaxation rate may be so slow that no relaxation is detected in routine measurements. It is reasonably assumed that the infinite frequency shear modulus is essentially temperature independent, the temperature dependence of τ_R can be attributed to the temperature dependence of the viscosity. Assuming a typical room temperature value of G_∞ of $\sim 3 \times 10^{10}$ N m⁻² for oxide glasses, the value of τ_R at a viscosity of 10^{12} Pa s is 33 s, meaning that significant relaxation occurs after ~ 33 s. It follows that relaxation at temperatures in the glass transition range would be expected to occur over times ranging from hours to seconds, as the viscosity decreases with increasing temperature. Since most experimental measurements of T_g involve heating specimens at rates of 3–20 K min⁻¹, we expect that these measurements will indicate relaxation processes occurring on similar timescales ($\sim 1/10$ min = 6 s) and that the T_g values refer to viscosities of the order of 10^{11} to 10^{12} Pa s. This relaxation concept is instrumental in understanding the glass transition phenomenon.

The structural relaxation process can be best appreciated in isothermal experiments, for instance by following refractive index changes of a glass with time at several temperatures below the original T_g as shown schematically in Fig. 2. Such a process has been frequently formulated by the most traditional relaxation equation, often called the KWW (Kohlrausch–William–Watts) function, as follow (Hodge, 1994):

$$\varphi(t, T) = \frac{p(t) - p_\infty(T)}{p_0(T_f) - p_\infty(T)} = \exp\left[-\left(\frac{t}{\tau_k(T)}\right)^{\beta(T)}\right] \quad (4)$$

where φ is the relaxation parameter, p is a property that varies during relaxation (for instance, density, specific heat, or refractive index), p_∞ is the property value for a treatment time long enough for full relaxation, p_0 is the initial value of that property, β is a dimensionless factor, $0 < \beta \leq 1$, and τ_k is the characteristic relaxation time, which can be calculated by the following equation:

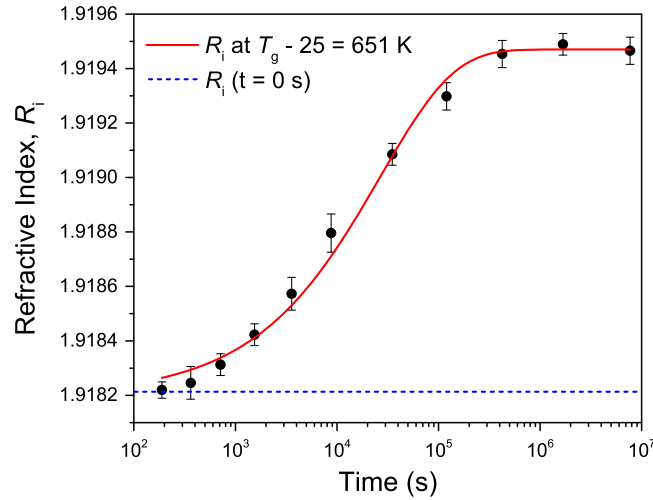


Fig. 2 Time dependence of the refractive index for lead metasilicate glass. Relaxation experiments were performed at 25K below the original glass transition temperature, where the sample was previously treated to equilibrate ($T_g - 25 = 651\text{K}$). The full line is the regression with the KWW equation. The horizontal dotted line shows the refractive index at the initial time. Reproduced from Lancelotti, R.F., Cassar, D.R., Peittl, O., Zanolto, E.D., 2019. Refractive Index Investigation of Structural Relaxation of Oxide Glasses, (in preparation).

$$\tau_k(T) = \frac{\beta(T)\tau_R(T)}{\Gamma\left(\frac{1}{\beta(T)}\right)} \quad (5)$$

where Γ is the gamma function, and τ_R is the average relaxation time, which can be calculated by the Maxwell equation, Eq. (2), using the values of η and G_∞ (10–50 GPa for silicate glasses).

From relaxation experiments, such as that shown in Fig. 2, one can fit Eq. (4) to calculate the values of β and τ_k for a given glass at different temperatures. The KWW equation usually fits quite well the experimental relaxation kinetics carried out not far below the original T_g (say, down to $T_g - 30\text{K}$). However, it does not have any predictive power for the variation of relaxation time with temperature, $\tau(T)$, because β also varies with temperature. The value of β itself is relevant because it gives a measure of the width of the distribution of relaxation times of the numerous “cooperatively rearranging regions” (CRR) that exist in glass formers (Hodge, 1994). The lower the value of β , the wider the relaxation time distribution.

More elaborate empirical models exist, such as the TNM model (Tool–Narayanaswamy–Moynihan) (Hodge, 1994), and the modified recent MAP model (Mauro–Allan–Potuzak) (Mauro *et al.*, 2009a; Guo *et al.*, 2018; Mauro and Mauro, 2018; Wilkinson *et al.*, 2018). The MAP can be used to describe glass relaxation. More details about the implementation of the KWW and MAP equations are provided in Guo *et al.* (2018) and Mauro and Mauro (2018). Moreover, recently a Python-based code was designed by Wilkinson *et al.* to retrieve the evolution of the fictive temperature, viscosity, and relaxation time using the inputs from the temperature path and set of material properties, including the viscosity parameters (Wilkinson *et al.*, 2018).

Fig. 2 shows the structural relaxation kinetics at 25K below the fictive temperature temperatures for lead metasilicate glass (Lancelotti *et al.*, 2019). The refractive index measurements proved to be a very good technique to follow the relaxation during isothermal treatments because the uncertainty of the measurements was only in the fifth decimal place. The KWW equation fitted the experimental data quite well; the full line is a regression obtained using the model. The dotted line represents the initial value of the refractive index for all temperatures. The fitted parameter of the KWW equation, as well as the average relaxation time, calculated by Eq. (2), are shown in Table 1 (Lancelotti *et al.*, 2019).

Glass Transition

Glasses only exist below their respective glass transition temperature, T_g . They are thermodynamically unstable and spontaneously relax toward the supercooled liquid state at any nonzero temperature (gray arrow in Fig. 1). The glass transition takes place at T_g , the temperature where the experimental or observation time, t_{obs} , is similar to the average structural relaxation time of the SCL, τ_R . On the heating path, a glass changes to a SCL at T_g , whereas on the cooling path the SCL temporarily freezes into the glassy state. In isothermal experiments, at any positive temperature, above or below T_g , for sufficiently long times ($t_{\text{obs}} \gg \tau_R$), any SCL or glass relaxes, and then eventually crystallizes to a solid with well-organized atomic structures at short, medium and long range, which is thermodynamically stable below T_m (arrows in Fig. 1; Zanolto and Mauro, 2017).

T_g depends on the cooling rate (observation time). There is a standard value called the standard calorimetric glass transition temperature (T_g), which is measured using a differential scanning calorimetry (DSC) at a heating rate of 10 K min^{-1} . For oxide glasses, this T_g typically corresponds to a viscosity of *ca.* 10^{12} Pa s . Furthermore, T_g varies with composition, thermal history, and mechanical history. Whereas the crystallization of liquid results in an abrupt discontinuity in thermodynamic variables (e.g., volume and enthalpy), the glass transition is not a thermodynamic phase transition. A thermodynamic consequence of this kinetic

Table 1 Adjustable parameters of the KWW equation fitted to the refractive index data and the relaxation time of lead metasilicate glass in Fig. 2. The average relaxation time, τ_R , was also calculated by Eq. (2)

$T(K)$	$\tau_k(s)$	$\beta(T)$	$\tau_R(s)$
651	72,617	0.59	111,718

Note: Lancelotti, R.F., Cassar, D.R., Peitl, O., Zanutto, E.D., 2019. Refractive Index Investigation of Structural Relaxation of Oxide Glasses, (in preparation).

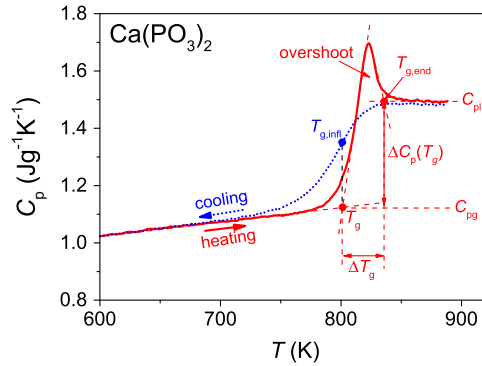


Fig. 3 Temperature dependences of the isobaric heat capacity (C_p) for calcium metaphosphate glass (CaP_2O_6), which were determined using DSC during the heating-cooling cycle (rate: 10 K min^{-1}). The glass-liquid transition during upscan is featured by the C_p jump, $\Delta C_p(T_g)$, whereas the liquid-glass transition is reflected by the C_p drop. The onset temperature of the glass-liquid transition, i.e., the intercept between the extrapolated glass C_p line and the line with the maximum tangent of the C_p rising curve, is defined as the standard glass transition temperature T_g . Reproduced with permission from Yue, Y., 2008. Characteristic temperatures of enthalpy relaxation in glass. *Journal of Non-Crystalline Solids* 354 (12–13), 1112–1118.

transition is that configurational degrees of freedom in the glass are (temporarily) frozen, leading to a sharp loss of second-order thermodynamic properties, such as heat capacity and thermal expansion coefficient (Guo *et al.*, 2018).

This event and key parameters of the calorimetric glass transition are illustrated in Fig. 3, where the changes of the isobaric heat capacity (C_p) with temperature are recorded for a calcium metaphosphate glass during the DSC upscan (heating) and its corresponding liquid during the subsequent downscan (cooling) at the standard rate of 10 K min^{-1} (Zheng *et al.*, 2019; Yue, 2008). The glass transition occurs over a range of temperatures (ΔT_g in Fig. 3), but it is convenient to define a single temperature as an indication of the onset of the glass transition range for a glass. This temperature is termed the standard glass transition temperature (T_g) (Zheng *et al.*, 2019). The standard T_g value is determined as the crossing point temperature of the extrapolated C_{pg} line and the extrapolated line of the rapidly rising C_p line. This T_g value is equal to the temperature ($T_{g, \text{infl}}$) corresponding to the inflection point of the C_p drop line during cooling (see the blue filled circle in Fig. 3). As such, the glass-to-liquid transition during heating is manifested by $\Delta C_p(T_g)$, i.e., the C_p jump from glass C_p at T_g (denoted C_{pg}) to liquid C_p at the ending temperature of glass-to-liquid transition ($T_{g, \text{end}}$) (denoted C_{pl}) (Yue, 2008; Guo *et al.*, 2011). The T_g of different glass systems can vary from below 50K to above 1500K (Zheng *et al.*, 2019).

Ergodicity

The glass transition is intimately connected to the notion of ergodicity. For an ergodic system, the time and ensemble averages of properties are equivalent and implies that the system explores a sufficient fraction of its configurational phase space to reach this equivalence (Mauro *et al.*, 2010, 2007). However, a system that is initially ergodic can become non-ergodic, i.e., if sufficient configurational degrees of freedom are lost. This breakdown of ergodicity can occur either discontinuously or continuously, depending upon the details of the system. Whether or not a system is ergodic is a question of timescale. There are two relevant time scales involved when an experiment is taking place. One is the internal time scale (τ_{int}) on which the dynamics of the system occur, which is essentially a relaxation time over which a system loses “memory” of its preceding states. This internal time scale is related to τ_R . The other is the external time scale (τ_{ext}) on which properties are measured, which defines a measurement window over which the system is observed. The Deborah number (Reiner, 1964) of an experiment is defined as the ratio of internal to external time scales,

$$D = \frac{\tau_{\text{int}}}{\tau_{\text{ext}}} \quad (6)$$

A large Deborah number ($D \gg 1$, $\tau_{int} \gg \tau_{ext}$) indicates that the system visits only a small subset of the available points in phase space during the external (i.e., observation) time scale. Hence, a system with a large Deborah number is non-ergodic. On the contrary, a very small Deborah number ($D \ll 1$, $\tau_{int} \ll \tau_{ext}$) means that the system can explore a greater portion of phase space during the observation time, which leads to an ergodic system. Therefore, both the internal relaxation time of a system and the external observation time determine the ergodicity of the system.

Palmer (1982) introduced the notion of “broken ergodicity,” in which glass can be described as an ensemble of components of the phase space, where each component exhibits internal ergodicity, but transitions between components are not allowed. This breakdown of ergodicity occurs when the Deborah number of the system is near unity, $D \approx 1$. This breakdown is the most fundamental definition of the glass transition, i.e., where the internal relaxation time of a glass-forming system is equal to an external observation time scale ($t_{obs} = \tau_{int}$). The transition between ergodic and nonergodic states, where $D \approx 1$, corresponds to the glass transition. For any realistic system, the loss of ergodicity is a gradual process, i.e., the glass transition involves a continuous breakdown of ergodicity. Thus, the glass transition is fundamentally a process in which a supercooled, ergodic liquid is gradually frozen into a non-equilibrium, non-ergodic glassy state. The glassy state can be observed only when the relaxation time scale of the system becomes much longer than the observation time scale, i.e., the glass transition only takes place when a finite observation time is defined (Varshneya and Mauro, 2019).

In summary, given the above definition, T_g refers to a temperature where the time of observation (of an experiment), t_{obs} , is of the same order as the average structural relaxation time, τ_R , of the supercooled liquid; $t_{obs} \sim \tau_R$. According to Maxwell's relation, $\tau_R = \eta/G_\infty$. For typical oxide glasses in classical laboratory experiments by, e.g., DSC or dilatometer, carried out at $5\text{--}20\text{ K min}^{-1}$, $\eta(T_g) \sim 10^{12}\text{ Pa s}$ and $G_\infty \sim 3 \times 10^{10}\text{ Pa}$, hence, $\tau_R \sim 33\text{ s}$ (Donth, 2001). Additionally, at T_g the τ_R/t_{obs} ratio, the Deborah number, is near unity.

As well as these theoretical concepts, various experimental approaches have been developed to characterize and explain glass transition. As already pointed out, one of the most effective experimental approaches is via DSC studies, which is probably the most sensitive technique to the (small) energy fluctuation during glass transition and relaxation. The glass transition traced by DSC is termed the calorimetric glass transition. T_g can also be measured by thermal expansion or density measurements. The value of T_g for the same glass composition could be slightly different using various measurement methods, even at the same heating rate. It is known that T_g has dynamic characteristic values since it shifts to higher temperatures with an increasing heating rate or cooling rate (Shelby, 2005; Varshneya and Mauro, 2019). To compare the dynamics and physical properties of different glass systems, a standard, unified approach for measuring T_g should be defined. For example, Yue compared the calorimetric glass transition temperature ($T_{g,DSC}$) directly measured by DSC at 10 K min^{-1} with the $T_{g,vis}$ indirectly determined at the viscosity of $\eta = 10^{12}\text{ Pa s}$ (Yue, 2008, 2009), with $T_{g,DSC}$ being defined as the onset temperature of the calorimetric glass transition peak (Fig. 3). As mentioned above, the C_p curve is normally obtained at the standard upscan rate of 10 K min^{-1} (equal to the first downscan rate). He showed that the two sets of T_g values remarkably coincide for oxide glasses (Yue, 2008, 2009). The agreement between $T_{g,vis}$ and $T_{g,DSC}$ can be used for assigning the standard T_g . This allows a direct comparison of the glass transition temperatures among different glassy systems.

Glass Structure

Oxide glasses, such as traditional soda-lime silicate glasses, have network structures composed of SiO_4 tetrahedral building blocks connected by mixed ionic-covalent bonding. Chalcogenide glasses, which contains one or more chalcogens (sulfur, selenium, and tellurium) and exclude oxygen, are built upon two-, three-, and four-coordinated building blocks, which are covalently bonded. Metallic glasses consist mainly of icosahedral units with metallic bonding. Organic polymeric glasses are made through the cross-linking of molecular chains involving van der Waals bonding between chains and covalent intra-molecular bonding. In the recently discovered metal-organic framework glasses, tetrahedral units are connected via coordination bonds. Water can also be quenched into a glassy state and comprises tetrahedral units connected by hydrogen bonds. It is these different types of bonds, resulting from the various electronic structures of the constituent atoms, that lead to different structures, unique state and novel properties of glassy materials (Zheng *et al.*, 2019; Varshneya and Mauro, 2019).

Experimental data and computer simulations of different supercooled liquids and glasses show that their atomic structures below T_g are quite similar to those of their parent supercooled liquid just above T_g (Zanotto and Mauro, 2017; Bykov *et al.*, 2009). Obviously, glasses do not exhibit the ordered crystalline structure as most other ceramic materials but, instead, have a disordered long-range structure with some order at short- and medium-range (3rd–4th neighbors). The most widely used glasses, by far, are oxide glasses, mainly formed from SiO_2 , B_2O_3 , P_2O_5 , As_2O_3 , Sb_2O_3 , GeO_2 , TeO_2 , Al_2O_3 , alkali or alkaline earth oxides, etc. The literature on glass structure is vast because of persistent interest in solid-state chemistry, condensed matter physics, geosciences, and medicine.

Here we aim to highlight a few basic concepts; exemplifying with pure SiO_2 and some of its derivatives. Silicate-based glasses are quite crucial in technology, e.g., optical fibers, electronic screens, architectural materials, and bioactive glasses, but also exist in nature, e.g., obsidian and Libyan Desert glass. Crystalline forms of silica are comprised of a three-dimensionally linked, corner-shared network of SiO_4 tetrahedra (*cf.* Fig. 4(a)). The oxygen links between the Si^{4+} cations ($\dots\text{Si}-\text{O}-\text{Si}\dots$) is called network forming or “bridging” oxygen (BO). When an oxide of another element, typically an alkali or alkaline earth oxide, with +1 or +2 valence, is added to liquid silica, there are too many oxygen anions (O^{2-}) which cannot all bond to two

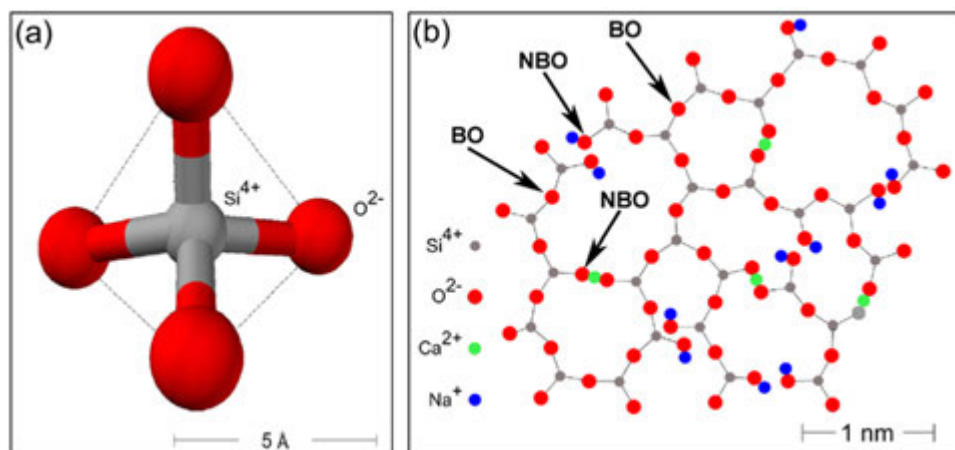


Fig. 4 Sketch of (a) SiO_4 tetrahedra and (b) two-dimensional view of soda-lime silicate glass structure comprised of a corner-shared network of SiO_4 tetrahedra, bridging (BO) and non-bridging oxygens (NBO), connected with Na^+ and Ca^{2+} cations. Adapted from Maraghechi, H., Rajabipour, F., Pantano, C.G., Burgos, W.D., 2016. Effect of calcium on dissolution and precipitation reactions of amorphous silica at high alkalinity. *Cement and Concrete Research* 87, 1–13, with permission from Elsevier.

tetrahedrally coordinated Si^{4+} cations. As a result, some must be connected to only one oxygen of the SiO_4 group. This oxygen is then called “non-bridging” oxygen (NBO). A two-dimensional view of a SiO_2 – CaO – Na_2O glass showing BO and NBO is shown in **Fig. 4(b)** (Stebbins, 2016). In standard models, exactly two NBO are formed from one BO and one extra O^{2-} ion (see Eq. (7) and **Fig. 5(a)**).



Contrary to Si in binary silicate glasses, B in borate glasses has two coordination numbers with oxygen, $^{\text{III}}\text{B}$, and $^{\text{IV}}\text{B}$. In GeO_2 based glasses, $^{\text{IV}}\text{Ge}$, $^{\text{V}}\text{Ge}$, and $^{\text{VI}}\text{Ge}$ are observed in glass structures. In pure B_2O_3 and GeO_2 glasses, only the lowest coordination states $^{\text{III}}\text{B}$ and $^{\text{IV}}\text{Ge}$ exist. As an alkali oxide is added, NBOs are not necessarily formed as in silicates, but to accommodate the added oxide ion, the coordination of the network cation, e.g., $^{\text{IV}}\text{B}$ and $^{\text{V,VI}}\text{Ge}$ increases (cf. **Fig. 5(b)**). As a result, the modifier cations are coordinated by bridging O atoms, which have partial negative charges, e.g., $[\text{III B-O-IV B}]^{-1/4}$ or $[\text{IV Ge-O-V Ge}]^{-1/5}$. When higher amounts of alkali oxide are added, NBOs form and the coordination of network formers decreases again, finally being dominated by the low-coordination numbers (Stebbins, 2016).

The effects of different cations are usually explained by the “cation field strength,” which is the valence divided by the sum of the cation and oxide ion radii (e.g., $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$) (Brown *et al.*, 2019). Multiple modifier cations (M) present in the melt compete for the formation of small coordination shells with short M–NBO distances. The higher field strength cation is expected to win. This phenomenon is also observed in crystals. For example, Ca^{2+} in crystalline diopside has 4 NBO and 4 BO neighbors, while Mg^{2+} has 6 neighbors, all NBO. Modifier cations in the glass will thus interact with both NBO and BO. The interactions in liquids are dynamic, transient, and liable to be important in breaking BO–Si bonds, activating viscous flow. Mixing of different modifier cations will change the configurational entropy, affecting viscosity curve and thermodynamic variables. For example, contrasting to the crystal, randomized distribution of modifiers in glass and liquid contribute largely to the entropy of melting (Brown *et al.*, 2019; Allwardt and Stebbins, 2004). The 3D scheme for the structure of an yttrium aluminosilicate glass (Y_2O_3 – Al_2O_3 – SiO_2) in **Fig. 6** proves how a broad range of possibilities for obtaining a disordered structure disordering is envisaged. This glass is used in *in situ* radiotherapies, irradiating tumors by the radioactive yttrium isotope (^{90}Y). The ^{90}Y cation can have variable coordination numbers in melts and glasses, which varies in complex ways with composition, temperature, and pressure (Christie and Tilocca, 2012). Therefore, elucidation of structure-property relationship is of the utmost importance in many applications.

Crystallization

Glasses are formed when the kinetic demands of thermodynamic equilibrium are not met by manipulating the chemical composition, sample size, or cooling rate of a melt. Following the most common route of glass formation, i.e., quenching from a melt, any SCL can, in principle, be vitrified with a sufficiently high cooling rate (critical cooling rate) that is enough to avert crystallization. It should be stressed once more that when cooling a liquid, vitrification occurs at a temperature T_g , where the structural relaxation time of the SCL becomes equal to or longer than the experimental observation time. Understanding the role of critical factors that determine the vitrification and crystallization processes, such as glass composition, the structure of the SCL, thermal history, and diffusion processes, is a vital step for the study and development of new materials that readily form glasses, or for the successful progress of glass-ceramic science and technology (Montazerian *et al.*, 2015; Davis and Zanotto, 2017).

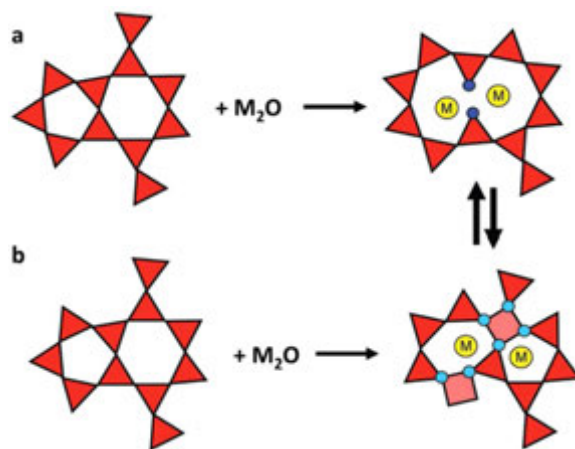


Fig. 5 Schematic illustration of a two-dimensional view of a network liquid such as SiO_2 , B_2O_3 , or GeO_2 before and after addition of a network-modifying oxide (M_2O). Here, SiO_4 tetrahedra are shown as planar triangles that share each of their corners. The reaction shown in (a) mostly happens in silicates where the added oxide forms two NBO (dark blue circles) from a connecting bridging oxygen. The negative charges on the NBOs are neutralized by modifying cations. The structural modification shown in (b) is typically observed in germanates or borates. Here, the addition of oxides increases the coordination number of a network cation, e.g., boron coordination changes from 3 to 4. Instead of forming NBO, oxygen bridges between the higher and lower coordinated network cations (light blue circles). In both cases, the M cations (yellow circles) are dispersed to balance the charges on the O atoms. Reprinted from Stebbins, J.F., Wu, J., Thompson, L.M., 2013. Interactions between network cation coordination and non-bridging oxygen abundance in oxide glasses and melts: Insights from NMR spectroscopy. *Chemical Geology* 346, 34–46, with permission from Elsevier.

Crystal nucleation

Nucleation and crystal growth are the two essential stages of crystallization; nucleation is the homogeneous or induced (catalyzed) formation of nanosized critical crystal clusters (nuclei), which is followed by their spontaneous growth becoming crystals. For glass forming compositions, homogeneous nucleation is typically observed in a temperature range (not far from T_g) well below the temperature of maximum crystal growth rates, whereas heterogeneous nucleation rate versus temperature curves are often close and even overlap with those of crystal growth (Fokin *et al.*, 2006).

Crystallization of glasses (or more correctly, of supercooled liquids) is an exothermic process that can be readily detected by thermal analysis techniques, such as DSC and DTA. In a typical DSC curve of a glass, crystallization is displayed as an exothermic peak after the glass transition, T_g , as depicted in Fig. 7. For stoichiometric compositions, the crystallization temperature (T_c), corresponds to the peak temperature in a DSC trace, whereas the onset crystallization temperature is called T_x . Upon continuous heating, in the end, an endothermic peak is a signature of melting (T_L). For off-stoichiometric compositions, two or more crystallization and melting peaks may appear (Fig. 7; Guo *et al.*, 2018).

Detailed knowledge of the thermodynamics and kinetics of crystal nucleation and growth is crucial, either to avoid devitrification or to control the crystallization process. Glass crystallization-related phenomena, including crystal nucleation, induction periods for nucleation, crystal growth, glass stability against devitrification, and glass forming ability are critical parameters in both academic and industrial studies. These phenomena are usually studied by optical and electron microscopy, X-ray diffraction (XRD), nuclear magnetic resonance (NMR), or DSC tests (Guo *et al.*, 2018; Fokin *et al.*, 2006).

In summary, supercooled liquids are metastable against their crystalline (solid) counterparts, the thermodynamically stable state for $T < T_m$. Hence any SCL will tend to crystallize via crystal nucleation which is then followed by spontaneous growth. Nucleation is a stochastic process, hence, after some average time τ_N (which depends on the material's chemical composition and the temperature), one or more critical crystalline nuclei will form in the SCL. Once the nuclei have reached a critical size, crystal growth spontaneously starts and the material solidifies, transforming into a polycrystalline solid.

In steady-state nucleation conditions, which are typically observed above T_g , the average number of nuclei (N_v) per volume (V) equals $N_v = I_{st} \cdot t$, where $I_{st} (m^{-3} s^{-1})$ is the steady-state nucleation rate at the temperature of study. In this condition, the average nucleation time is $\tau_N = (I_{st} \cdot V)^{-1}$. However, for very deep supercoolings ($T \ll T_g$), where the nucleation induction times, t_{ind} , are significant, t_{ind} must be added to $(I_{st} \cdot V)^{-1}$, hence $\tau_N \leq (I_{st} \cdot V)^{-1} + t_{ind}$ (Fokin *et al.*, 2006; Deubener *et al.*, 2017). τ_N and t_{ind} are shown in Fig. 8, which is an example for a N_v vs. time plot in a fixed temperature (the crystal nucleation and growth temperatures are $T_N = 430^\circ C$ and $T_G = 626^\circ C$, respectively). Hence, to estimate τ_N at very deep supercoolings, one has to extrapolate experimental values of steady-state nucleation rates and obtain nucleation induction times, which are typically measured at and above T_g down to very low temperatures. In any case, the nucleation times are always finite; therefore for infinitely long times, all supercooled liquids should crystallize by nucleation and growth (Fig. 8(b)).

Crystal growth

As soon as the nucleation conditions are attained and some nuclei reach the critical size, crystal growth spontaneously proceeds (there is no thermodynamic barrier for crystal growth). The transport of atoms at the interface between the nucleus and the

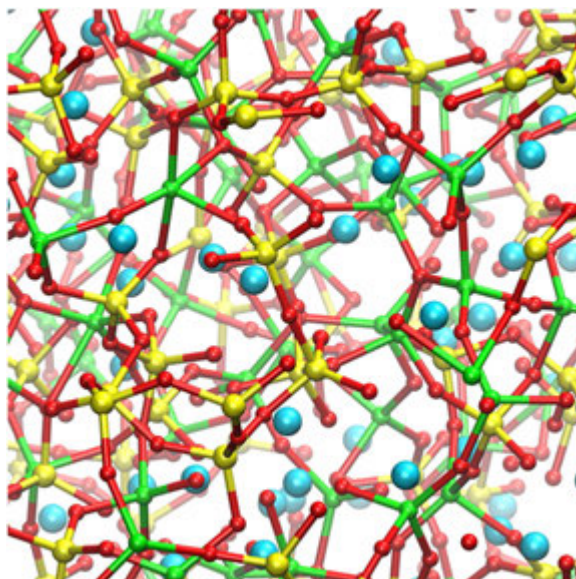


Fig. 6 3D snapshot MD simulations of the structure of a $24.1\text{Y}_2\text{O}_3\text{--}21.4\text{Al}_2\text{O}_3\text{--}54.5\text{SiO}_2$ (mol%) glass. The aluminosilicate network is shown as balls and sticks, with silicon atoms in yellow, aluminum atoms in green, and oxygen atoms in red. The network-modifying yttrium atoms are shown in cyan. The yttrium-doped glasses are used as radioisotope vectors for *in situ* radiotherapies to kill malignant tumors. These glasses containing yttrium isotope (^{90}Y) are made by neutron activation as the last step in the manufacturing process, only a few hours before clinical application. Reprinted with permission from Christie, J.K., Tilocca, A., 2012. Molecular dynamics simulations and structural descriptors of radioisotope glass vectors for *in situ* radiotherapy. *Journal of Physical Chemistry B* 116 (41), 12614–12620. Copyright American Chemical Society 2012.

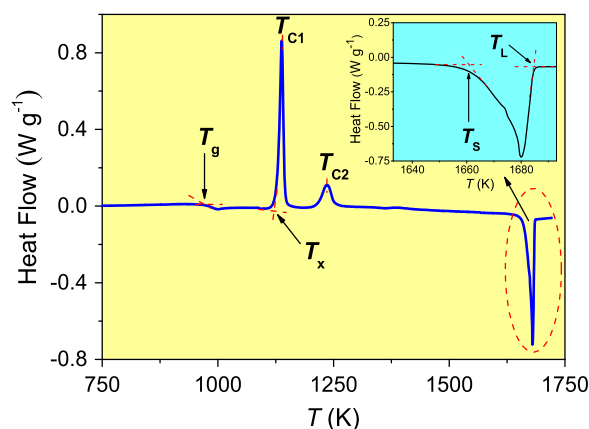


Fig. 7 Typical DSC upscan trace for barium disilicate ($\text{BaO} \cdot 2\text{SiO}_2$) glass showing the glass transition temperature (T_g), the crystallization onset (T_x), the crystallization peak (T_{c1} , T_{c2}), the *Solidus* (T_s) and the *Liquidus* temperatures (T_l). Adapted from Rodrigues, A.M., Cassar, D.R., Fokin, V.M., Zanolto, E.D., 2018. Crystal growth and viscous flow in barium disilicate glass. *Journal of Non-Crystalline Solids* 479, 55–61, with permission from Elsevier.

surrounding SCL matrix is of great importance with regard to kinetic and morphological processes of crystal growth. Three basic models are available to describe crystal growth rates: normal growth, screw dislocation growth, and secondary nucleation or two-dimensional growth (Nascimento *et al.*, 2004, 2011).

During Normal (or Continuous) Growth, the crystal/liquid interface is pictured as rough at an atomic scale. Growth takes place at step sites, which represent a sizable fraction (0.5–1.0) of the interfacial sites. When this fraction does not change appreciably with temperature, the growth rate, $U(T)$, can be expressed as (Nascimento *et al.*, 2004, 2011):

$$U = f \frac{D}{4d_0} \left[1 - \exp\left(-\frac{\Delta G}{k_B T}\right) \right] \quad (8)$$

where f is close to unity, ΔG is the Gibbs free energy, D is the effective diffusion coefficient controlling material transport to the interface, and d_0 is a jump distance (a few Angstrom).

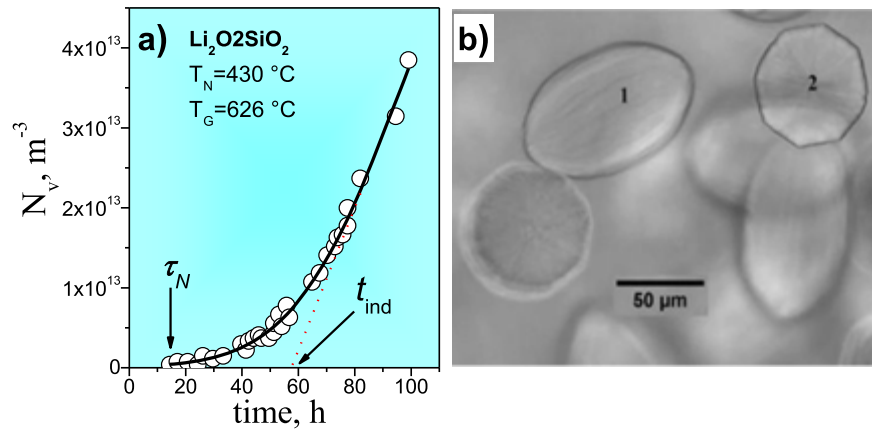


Fig. 8 (a) Typical curve of the number density of crystalline nuclei for lithium disilicate ($\text{Li}_2\text{O} \cdot 2\text{SiO}_2$) glass. (b) Lithium disilicate crystals after nucleation and growth in a LS2 glass. Crystalline ellipsoids can be observed in the plan (1) and front (2) views. Adapted from Fokin, V.M., Kalinina, A.M., Filipovich, V.N., 1981. Nucleation in silicate glasses and effect of preliminary heat treatment on it. *Journal of Crystal Growth* 52 (Part 1), 115–121. Fokin, V.M., Cabral, A.A., Reis, R.M.C.V., Nascimento, M.L.F., Zanotto, E.D., 2010. Critical assessment of DTA-DSC methods for the study of nucleation kinetics in glasses. *Journal of Non-Crystalline Solids* 356 (6–8), 358–367, with permission from Elsevier.

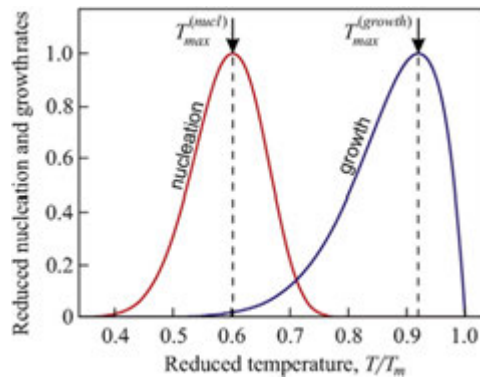


Fig. 9 Typical locations of the maxima of homogeneous nucleation rates, $I(T)$, and growth rates, $U(T)$. Reprinted from Schmelzer, J.W.P., Abyzov, A.S., Fokin, V.M., Schick, C., Zanotto, E.D., 2015. Crystallization of glass-forming liquids: Maxima of nucleation, growth, and overall crystallization rates. *Journal of Non-Crystalline Solids* 429, 24–32, with permission from Elsevier.

In the Screw Dislocation growth model, the interface is assumed to be smooth but imperfect at an atomic scale. Crystal growth takes place at a few step sites provided by screw dislocations that intersect the interface. The growth rate is also given by Eq. (8), where f is the fraction of preferred growth sites (on the dislocation ledges) at the interface. In this case, $f \ll 1$ is given approximately by $f \simeq (T_m - T)/(2\pi T_m)$ (Nascimento *et al.*, 2011).

In the case of Secondary Surface Nucleation or Two-dimensional growth, the interface is smooth and perfect at an atomic scale and thus free of intersecting screw dislocations and growth sites. Growth then takes place by the formation and growth of new two-dimensional nuclei at the interface (Nascimento *et al.*, 2004, 2011).

In both crystal nucleation and growth, the interplay between an increasing driving force for crystallization, ΔG , and decreasing diffusion coefficient (e.g., increase in viscosity) with decreasing temperature results in a maximum of the $I(T)$ and $U(T)$ curves. The maximum growth rate is usually located at higher temperatures than that of the maximum of the (homogeneous) steady-state nucleation rate (Fig. 9; Schmelzer *et al.*, 2015).

Overall crystallization

The overall crystallization of supercooled liquids occurs by a combination of crystal nucleation and growth. The kinetics of such processes is usually described by a theory independently derived between 1937 and 1941 by Johnson & Mehl, Avrami, and Kolmogorov (JMAK theory) (Fokin *et al.*, 2006). In this approach, the evolution of the volume fraction of the crystalline phase is described as a function of time, accounting simultaneously for nucleation and growth. According to this model, the volume fraction of the new phase (in this case a crystal) is given by Eq. (9) (Shelby, 2005; Varshneya and Mauro, 2019; Šesták and Šimon, 2013).

Table 2 Values of the Avrami exponent (n) for several mechanisms of crystallization

<i>Polymorphic change, interface-controlled growth</i>	<i>n</i>	<i>Diffusion-controlled growth</i>	<i>n</i>
Increasing nucleation rate, 3D	> 4	Increasing nucleation rate, 3D	> 2.5
Constant nucleation rate, 3D	4	Constant nucleation rate, 3D	2.5
Decreasing nucleation rate, 3D	3–4	Decreasing nucleation rate, 3D	1.5–2.5
Zero nucleation rate (nucleation site saturation) 3D	3	Constant nucleation rate, 2D	2
Constant nucleation rate, 2D (plate)	3	Zero nucleation rate, 3D	1.5
Zero nucleation rate, 2D (plate)	2	Constant nucleation rate, 1D	1.5
Constant nucleation rate (nucleation site saturation), 1D	2	Zero nucleation rate, 2D	1
Zero nucleation rate, 1D (needle)	1	Zero nucleation rate, 1D	0.5

Note: D: growth dimensionality.

Source: Illeková, E., Šesták, J., 2013. Chapter 13: Crystallization of metallic micro-, nano-, and non-crystalline alloys. In: Šesták, J., Šimon, P. (Eds.), Thermal Analysis of Micro, Nano- and Non-Crystalline Materials: Transformation, Crystallization, Kinetics and Thermodynamics. Netherlands: Springer.

$$\alpha(t) = 1 - \exp \left\{ -g \int_0^t I(T) \left[\int_{t'}^t U(T) dt' \right]^3 dt \right\} \quad (9)$$

where g is a shape factor that depends on the shape of crystals. If the nucleation (I) and growth (U) rates are constant throughout the transformation, and the crystals are spherical, Eq. (9) can be rewritten as:

$$\alpha(t) = 1 - \exp \left[-\frac{gIU^3t^4}{4} \right] \quad (10)$$

When the number of growing crystals, N_0 , does not change with time (typical for fast heterogeneous nucleation on a finite number of active sites, or from quenched-in, athermal nuclei), Eq. (9) transforms to:

$$\alpha(t) = 1 - \exp[-gN_0U^3t^3] \quad (11)$$

Avrami proposed that, in the general case, the following relation should be used:

$$\alpha(t) = 1 - \exp[-Kt^n] \quad (12)$$

where K represents the so-called rate constant, and n is the Avrami coefficient. In typical applications, Eq. (12) is used in the form

$$\ln(-\ln(1 - \alpha)) = \ln K + n \ln t \quad (13)$$

The values of K and n can be estimated by fitting the experimental data of $\alpha(t)$ (crystal volume fraction of isothermally heat-treated glass) to Eq. (13). Thus, the coefficient K includes I and U , or N_0 and U .

In Eq. (13), n is called the Avrami coefficient, and depends on both nucleation and growth mechanisms, as shown in Table 2. The knowledge of that coefficient is very helpful to understand the mechanism of phase transformation at any given temperature (Illeková and Šesták, 2013).

The JMAK theory has been used in numerous studies to analyze experimental data and determine the degree of crystallinity as a function of time in both isothermal and non-isothermal heat treatments of glass systems. Emphasis is usually given to determining the so-called Avrami coefficient $m = n + 1$ obtained from the slopes of experimental $\ln[-\ln(1 - \alpha)^{-1}]$ versus $\ln(t)$ plots. However, there is frequently some uncertainty in such analyses, because different combinations of nucleation and growth laws may lead to the same Avrami coefficient. For this reason, a separate investigation of the growth kinetics may be required to reach definite conclusions. It is important to underline that the JMAK theory, as given by Eqs. (10)–(12), does not apply to non-isothermal processes. These three equations are derived from the assumption of constant nucleation and growth rates, which are not achieved in non-isothermal processes. Therefore, in non-isothermal cases, the general relationships, Eq. (9), must be used to describe overall crystallization (Gutzow and Schmelzer, 1995).

Finally, we should emphasize that the extremely good glass-forming liquids known so far – $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (albite) and B_2O_3 – will also crystallize if they are subjected to sufficient long thermal treatment. This is because their maximum homogeneous nucleation rates are located well below their glass transition temperatures, in a region of very high viscosity, which leads to extremely long nucleation time-lags and low nucleation rates (Zanotto and Cassar, 2017). However, under adequate conditions, they should crystallize.

Summary and Conclusions

It is estimated that more than 10^5 inorganic glasses have already been made (Zanotto and Coutinho, 2004), and billions of others could still be made, however, crystallization (solidification) must be avoided for vitrification. Hence only a small fraction of the possible compositions can be effortlessly vitrified.

Are glasses solids or liquids? We defend that glasses are neither solids nor liquids; instead, they display ambivalent properties: of solids – they ring, resonate, scratch and fracture – and liquids, they have an identical structure as their parent liquids, and also show the unique property of spontaneously relaxing towards the SCL state, even without the influence of any external stress. Moreover, the glassy state itself cannot be expressed as any linear combination of supercooled liquid states.

All glasses are trapped in a frozen, transient state; they will relax toward the supercooled liquid state and ultimately crystallize. The relaxation and crystallization times strongly depend on their chemical composition and on how far below its T_g the glass is being studied. If a glass is being tested only a few degrees below its T_g , relaxation and crystallization take place in a few minutes or hours; whereas, at several hundred degrees below T_g , these processes will only take place in geological time scales. Therefore, in our opinion, the glassy state is a unique non-ergodic, non-equilibrium, non-crystalline state of matter that continuously relaxes and finally crystallizes. The modern definition of glass revised and discussed here can be applied to all types of glasses.

Acknowledgments

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References

- Allwardt, J.R., Stebbins, J.F., 2004. Ca-Mg and K-Mg mixing around non-bridging oxygens in silicate glasses: An investigation using oxygen-17 MAS and 3QMAS NMR. *American Mineralogist* 89, 777–784.
- Angell, C.A., 1991. Relaxation in liquids, polymers and plastic crystals – Strong/fragile patterns and problems. *Journal of Non-Crystalline Solids* 131–133 (Part 1), 13–31.
- Ballato, J., Ebendorff-Heidepriem, H., Zhao, J., Petit, L., Troles, J., 2017. Glass and process development for the next generation of optical fibers: A review. *Fibers* 5 (1), 11.
- Balmer, R.T., 2011. Chapter 2 – Thermodynamic concepts. In: Balmer, R.T. (Ed.), *Modern Engineering Thermodynamics*. Academic Press, pp. 33–56.
- Bolt, M., 2017. Glass: The eye of science. *International Journal of Applied Glass Science* 8 (1), 4–22.
- Brown Jr., G.E., Farges, F., Calas, G., 2019. X-ray scattering and X-ray spectroscopy studies of silicate melts. *Structure, Dynamics, and Properties of Silicate Melts* 32, 317–410.
- Bykov, V.N., Koroleva, O.N., Osipov, A.A., 2009. Structure of silicate melts: Raman spectroscopic data and thermodynamic simulation results. *Geochemistry International* 47 (11), 1067–1074.
- Christie, J.K., Tilotta, A., 2012. Molecular dynamics simulations and structural descriptors of radioisotope glass vectors for in situ radiotherapy. *Journal of Physical Chemistry B* 116 (41), 12614–12620.
- David Pye, L., 2016. Arrival of the glass age affirmed. *International Journal of Applied Glass Science* 7 (4), 407–408.
- Davis, M.J., Zanotto, E.D., 2017. Glass-ceramics and realization of the unobtainable: Property combinations that push the envelope. *MRS Bulletin* 42 (3), 195–199.
- Deubener, J., Montazerian, M., Krüger, S., Peitl, O., Zanotto, E.D., 2017. Heating rate effects in time-dependent homogeneous nucleation in glasses. *Journal of Non-Crystalline Solids* 474, 1–8.
- Donth, E.J., 2001. *The Glass Transition: Relaxation, Dynamics in Liquids and Disordered Materials*. Springer.
- Fokin, V.M., Zanotto, E.D., Yurisyn, N.S., Schmelzer, J.W.P., 2006. Homogeneous crystal nucleation in silicate glasses: A 40 years perspective. *Journal of Non-Crystalline Solids* 352 (26–27), 2681–2714.
- Guo, X., Mauro, J.C., Allan, D.C., Smedskjaer, M.M., 2018. Predictive model for the composition dependence of glassy dynamics. *Journal of the American Ceramic Society* 101 (3), 1169–1179.
- Guo, X., Potuzak, M., Mauro, J.C., *et al.*, 2011. Unified approach for determining the enthalpic fictive temperature of glasses with arbitrary thermal history. *Journal of Non-Crystalline Solids* 357 (16–17), 3230–3236.
- Gupta, P.K., 1996. Non-crystalline solids: Glasses and amorphous solids. *Journal of Non-Crystalline Solids* 195 (1–2), 158–164.
- Gutzow, I.S., Schmelzer, J.W.P., 1995. *The Vitreous State: Thermodynamics, Structure, Rheology, and Crystallization*, second ed. Berlin: Springer.
- Hench, L.L., 2011. Glass and glass-ceramic technologies to transform the world. *International Journal of Applied Glass Science* 2 (3), 162–176.
- Hodge, I.M., 1994. Enthalpy relaxation and recovery in amorphous materials. *Journal of Non-Crystalline Solids* 169 (3), 211–266.
- Hopper, R.W., Uhlmann, D.R., 1974. On diffusive creep and viscous flow. *Materials Science and Engineering* 15 (2–3), 137–144.
- Illeková, E., Šesták, J., 2013. Chapter 13: Crystallization of metallic micro-, nano-, and non-crystalline alloys. In: Šesták, J., Šimon, P. (Eds.), *Thermal Analysis of Micro, Nano- and Non-Crystalline Materials: Transformation, Crystallization, Kinetics and Thermodynamics*. Netherlands: Springer.
- Lancelotti, R.F., Cassar, D.R., Peitl, O., Zanotto, E.D., 2019. Refractive Index Investigation of Structural Relaxation of Oxide Glasses, (in preparation).
- Li, H.X., Lu, Z.C., Wang, S.L., Wu, Y., Lu, Z.P., 2019. Fe-based bulk metallic glasses: Glass formation, fabrication, properties and applications. *Progress in Materials Science* 103, 235–318.
- Lin, C., Rüssel, C., Dai, S., 2018. Chalcogenide glass-ceramics: Functional design and crystallization mechanism. *Progress in Materials Science* 93, 1–44.
- Mauro, J.C., Allan, D.C., Potuzak, M., 2009a. Nonequilibrium viscosity of glass. *Physical Review B – Condensed Matter and Materials Physics* 80 (9), 094204.
- Mauro, J.C., Gupta, P.K., Loucks, R.J., 2007. Continuously broken ergodicity. *Journal of Chemical Physics* 126 (18), 184511.
- Mauro, J.C., Loucks, R.J., Gupta, P.K., 2009b. Fictive temperature and the glassy state. *Journal of the American Ceramic Society* 92 (1), 75–86.
- Mauro, J.C., Loucks, R.J., Sen, S., 2010. Heat capacity, enthalpy fluctuations, and configurational entropy in broken ergodic systems. *Journal of Chemical Physics* 133 (16), 164503.
- Mauro, J.C., Loucks, R.J., 2009. Forbidden glasses and the failure of fictive temperature. *Journal of Non-Crystalline Solids* 355 (10–12), 676–680.
- Mauro, J.C., Mauro, Y.Z., 2018. On the Prony series representation of stretched exponential relaxation. *Physica A: Statistical Mechanics and its Applications* 506, 75–87.
- Montazerian, M., Singh, S.P., Zanotto, E.D., 2015. An analysis of glass-ceramic research and commercialization. *American Ceramic Society Bulletin* 94 (4), 30–35.
- Montazerian, M., Zanotto, E.D., Mauro, J.C., Model-driven design of bioactive glasses: From molecular dynamics through machine learning. *International Materials Reviews*, 2019, doi:10.1080/09506608.2019.1694779.
- Montazerian, M., Zanotto, E.D., 2017. A guided walk through Larry Hench's monumental discoveries. *Journal of Materials Science* 52 (15), 8695–8732.
- Morse, D.L., Evenson, J.W., 2016. Welcome to the glass age. *International Journal of Applied Glass Science* 7 (4), 409–412.
- Nascimento, M.L.F., Ferreira, E.B., Zanotto, E.D., 2004. Kinetics and mechanisms of crystal growth and diffusion in a glass-forming liquid. *Journal of Chemical Physics* 121 (18), 8924–8928.
- Nascimento, M.L.F., Fokin, V.M., Zanotto, E.D., Abzyov, A.S., 2011. Dynamic processes in a silicate liquid from above melting to below the glass transition. *Journal of Chemical Physics* 135 (19), 194703.
- Palmer, R.G., 1982. Broken ergodicity. *Advances in Physics* 31 (6), 669–735.

- Poirier, J.P., 1985. Creep of Crystals: High-Temperature Deformation Processes in Metals, Ceramics and Minerals. Cambridge University Press. p. 260.
- Reiner, M., 1964. The Deborah number. *Physics Today* 17 (1), 62.
- Schmelzer, J.W.P., Abyzov, A.S., Fokin, V.M., Schick, C., Zanolto, E.D., 2015. Crystallization of glass-forming liquids: Maxima of nucleation, growth, and overall crystallization rates. *Journal of Non-Crystalline Solids* 429, 24–32.
- Šesták, J., Šimon, P. (Eds.), 2013. *Thermal Analysis of Micro, Nano- and Non-Crystalline Materials: Transformation, Crystallization, Kinetics and Thermodynamics*. Netherlands: Springer.
- Shelby, J.E., 2005. *Introduction to Glass Science and Technology*. Cambridge: The Royal Society of Chemistry.
- Shi, Y., 2019. Size-dependent mechanical responses of metallic glasses. *International Materials Reviews* 64 (3), 163–180.
- Stebbins, J.F., 2016. Glass structure, melt structure, and dynamics: Some concepts for petrology. *American Mineralogist* 101 (4), 753–768.
- Varshneya, A.K., Bihuniak, P.P., 2017. Cover screens for personal electronic devices: Strengthened glass or sapphire? *American Ceramic Society Bulletin* 96 (5), 20–25.
- Varshneya, A.K., Mauro, J.C., 2019. *Fundamentals of Inorganic Glasses*, third ed. Amsterdam: Elsevier.
- Wilkinson, C.J., Mauro, Y.Z., Mauro, J.C., 2018. RelaxPy: Python code for modeling of glass relaxation behavior. *SoftwareX* 7, 255–258.
- Yue, Y., 2008. Characteristic temperatures of enthalpy relaxation in glass. *Journal of Non-Crystalline Solids* 354 (12–13), 1112–1118.
- Yue, Y., 2009. The iso-structural viscosity, configurational entropy and fragility of oxide liquids. *Journal of Non-Crystalline Solids* 355 (10–12), 737–744.
- Zachariasen, W.H., 1932. The atomic arrangement in glass. *Journal of the American Chemical Society* 54 (10), 3841–3851.
- Zanolto, E.D., Cassar, D.R., 2017. The microscopic origin of the extreme glass-forming ability of Albite and B_2O_3 . *Scientific Reports* 7, 43022.
- Zanolto, E.D., Coutinho, F.A.B., 2004. How many non-crystalline solids can be made from all the elements of the periodic table? *Journal of Non-Crystalline Solids* 347 (1–3), 285–288.
- Zanolto, E.D., Mauro, J.C., 2017. The glassy state of matter: Its definition and ultimate fate. *Journal of Non-Crystalline Solids* 471, 490–495.
- Zheng, Q., Zhang, Y., Montazerian, M., *et al.*, 2019. Understanding glass through differential scanning calorimetry. *Chemical Reviews* 119 (13), 7848–7939.

Relevant Websites

<https://www.britannica.com/science/liquid-state-of-matter>

Britannica
Liquid
Chemistry, Properties, & Facts.

<https://www.britannica.com/science/solid-state-of-matter>

Britannica
Solid
State of matter.

[https://en.wikipedia.org/wiki/Creep_\(deformation\)](https://en.wikipedia.org/wiki/Creep_(deformation))

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Glasses: Alkali and Alkaline-Earth Silicates

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Introduction

When alkali (Li, Na, K, Rb, Cs) and alkaline-earth (Be, Mg, Ca, Sr, Ba) cations are added to pure SiO_2 glass they disrupt the fully continuous network of corner linked SiO_4 tetrahedra. The oxygens shared between the Si atoms, termed bridging oxygens (BO), are broken to form what are termed non-bridging oxygens (NBO). Ideally, for every alkali cation 1 NBO is formed and for every alkaline-earth cation 2 NBOs are formed (cf., [Henderson and Stebbins, 2021](#)). The NBO is attached to one Si atom and charge balanced by the added cation now called a charge compensator. Elements that break BOs to form NBOs in the glass are termed network modifiers whereas elements that tend to generate BOs, like Si and other high field strength cations are termed network formers. The SiO_4 tetrahedra can themselves be classified on the basis of the number of BOs within each tetrahedron. These are termed Q^n species (where n = the number of BOs attached to the Si atom) and depending upon the number of alkali or alkaline-earth cations added to the glass, there can be Q^4 , Q^3 , Q^2 , Q^1 and Q^0 tetrahedra formed (See [Fig. 1](#)). Furthermore, it has recently been found that more than one type of BO may exist in alkali-silicate glasses. The BO can itself be bonded to one or more of the alkali cations (termed MBO) (see [Nesbitt et al., 2015a](#); [Sukenaga et al., 2017](#); [O'Shaughnessy et al., 2017c, 2020](#); [Henderson and Stebbins, 2021](#) and references therein). Such bonds are common in silicate crystal structures such as $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ where the structure is exclusively Q^3 tetrahedra in chains. The Q^3 tetrahedra have 2 MBOs and one regular BO ([Pant and Cruickshank, 1968](#)). Logically, such bonds must be present in glasses because while one Na atom produces 1 NBO and acts as a charge compensator, its coordination number is around 5 ([Gagné and Hawthorne, 2016](#)). Some of these bonds must therefore be to bridging oxygens regardless of whether or not the alkalis are heterogeneously or homogeneously distributed throughout the glass network. Whether or not a bond with the BO forms or the cation simply closely approaches the BO remains a challenging issue. Extensive molecular orbital calculations do show that such bonds are likely and energetically favored ([Gibbs, 1982](#); [Gibbs et al., 1997, 2008](#)). The effects of a modifier cations' influence on BO remains a research area of considerable potential, especially with respect to phase separation and crystallization. Finally, in aluminosilicate glasses another type of oxygen may form: the oxygen tricluster (See [Fig. 1](#)). Oxygen triclusters were first suggested to occur in Al_2O_3 rich glasses by [Lacey \(1963\)](#). It is defined as a group of three network cations, each of which has three or four oxygen first neighbors which share a single oxygen (cf., [Henderson and Stebbins, 2021](#)). They are unlikely to be present in alkali or alkaline-earth silicate glasses.

This chapter starts with discussion of the key historical insights into the glass structure of alkali silicates in contrast to pure silica glass. The chemical reactions occurring when alkali or alkaline-earth cations are introduced into the glass are covered before discussing phase separation, a common phenomenon at low modifier contents. An overview of each of the alkali-silicate binaries is given before discussion of the mixed alkali effect (MAE) when two modifier cations are introduced into the silicate network. Each of the alkaline-earth silica binary glasses are then reviewed. Both alkali and alkaline-earth silicate glasses, and their crystalline counterparts, are used extensively in industrial applications and are often the base glass to which other cations are added to develop numerous applications from window glass, to fiber optics, to biomaterials and more (see below). These applications are briefly discussed.

Silicate Glasses

The structure and physical properties of alkali-containing glasses in general exhibit a dependence upon the type of alkali present in the glass. Different alkali cations have been shown to have a number of effects on changes in activation energy of viscous flow, molar volume and thermal expansion (cf. [Stebbins, 1995](#)), for example. The first diffraction study of an alkali silicate glass was by [Warren and Loring \(1935\)](#), and [Warren and Biscoe \(1938\)](#) on Na-silicate glass. Their diffraction profiles showed a continuous change in appearance with increasing sodium content. They concluded that the structure of sodium silicate glass consisted of tetrahedrally coordinated silicon atoms surrounded by four oxygen atoms, with a bond distance of 1.62 Å. Some of the oxygen atoms are BOs and some NBOs. They did not observe discrete molecules such as SiO_2 , Na_2O , $\text{Na}_2\text{Si}_2\text{O}_5$ or Na_2SiO_3 . The sodium ions are surrounded by six oxygen atoms with an average bond-length of 2.35 Å and arranged in random holes throughout the silicon-oxygen network. It was also observed that as the sodium content increased, the number of non-bridging oxygen atoms increased. In describing the sodium silicate structure, [Warren and Biscoe \(1938\)](#) employed the continuous random network (CRN) model of [Zachariasen \(1932\)](#) to fit the observed data. The random network model accounts for the replacement of a BO with two NBOs upon the addition of each network-modifier oxide, M_2O ($\text{M} = \text{Li, Na, K, Rb, Cs}$). The negative charge of the NBO is balanced by the positively charged alkali cation in order to maintain charge neutrality and it assumes that the alkali atoms are distributed randomly through the network. Subsequent studies by [Greaves et al. \(1981\)](#) and [Greaves \(1985\)](#) suggested that the alkali atoms are heterogeneously distributed in alkali-silicate glasses and the modified random network (MRN) model was

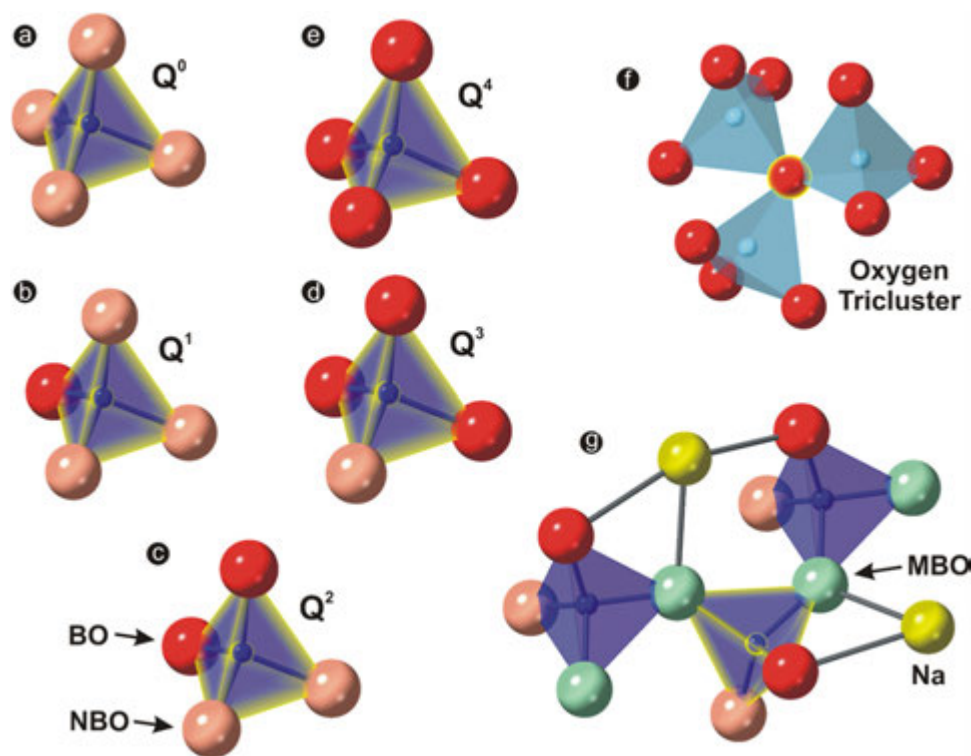


Fig. 1 Various Q^n species: NBO (peach), BO (red), MBO (green) and an oxygen tricluster (red with yellow circle). (a) Q^0 tetrahedron with no BO, (b) Q^1 with 1 BO, (c) Q^2 with 2 BO, (d) Q^3 with 3 BO, (e) Q^4 with 4 BO, (f) Oxygen tricluster (red) being shared with 3 AlO_4 tetrahedra (light blue), (g) partial structure of α - $Na_2Si_2O_5$ showing Q^3 tetrahedra with regular BO (red) and MBO (green) with Na (yellow) attached.

developed. Here the alkali atoms (Na and Ca in his studies) are concentrated around channels that are distributed randomly throughout a more silicate-rich network (see Fig. 2). See Le Losq *et al.* (2019), Greaves (2021) for more current descriptions of this model.

This widely accepted model requires that alkali cations be heterogeneously distributed within a SiO_2 rich network. However, it should be noted that many studies conclude that alkalis are homogeneously distributed throughout the SiO_2 network (e.g., Lee and Stebbins, 2003; 2009; Angeli *et al.*, 2011). Furthermore, the bulk of the experimental work has been on sodium silicate glasses which undergo phase separation. One should keep in mind the question of whether or not the channels are truly representative of the glass structure, or are a result of insipient phase separation or micro segregation due to synthesis and quench conditions (see below for phase separation details).

The way the tetrahedra are linked together constitutes the intermediate-range structure (IRO) or medium-range structure (MRO). Silica glass is primarily composed of rings of between 3- to 7 SiO_4 tetrahedra (cf., Henderson, 2005; Le Losq *et al.*, 2019) with a mean ring size around 6. These rings have in turn been classified as being similar to those found in the crystalline polymorphs of SiO_2 i.e., cristobalite-like, and/or tridymite-like with various proportion of each e.g., 2/3 tridymite, 1/3 cristobalite (Henderson *et al.*, 1984); α -cristobalite/ β -cristobalite (Sonneville *et al.*, 2013). The rings and the extended glass network are composed of SiO_4 tetrahedra (all Q^4) that are fully interconnected through the BOs at the corners of the tetrahedron. The average Si-O bond distance is around 1.61 Å, the O-O distance 2.65 Å, and the first Si-Si distance at around 3.10 Å. The average Si-O-Si angle is around 147°–152° as determined from a number of different techniques (See Henderson and Stebbins, 2021). It is not around 144° as calculated by Mozzi and Warren (1969) (see discussion in Neufeind and Liss, 1996; Henderson, 2005; Eckert, 2018; Henderson and Stebbins, 2021, for an explanation).

The Relationship Between Oxygen and Q^n Speciation

Often the Q^n species distribution in alkali- and alkaline-earth silicate glasses is calculated from their chemical composition (cf., Le Losq *et al.*, 2019) and/or estimated by determining the NBO/T ratio where T = moles of Si (or any tetrahedral network former) and NBO represents the moles of non-bridging oxygen in a glass (Mysen and Richet, 2019). The NBO/T gives an indication of the degree of polymerization. It can be readily calculated for *crystalline materials* but is somewhat misleading for glasses and melts (see below). In addition, it is also widely held that the Q^n species distributions within a glass are given by the disproportion reaction:

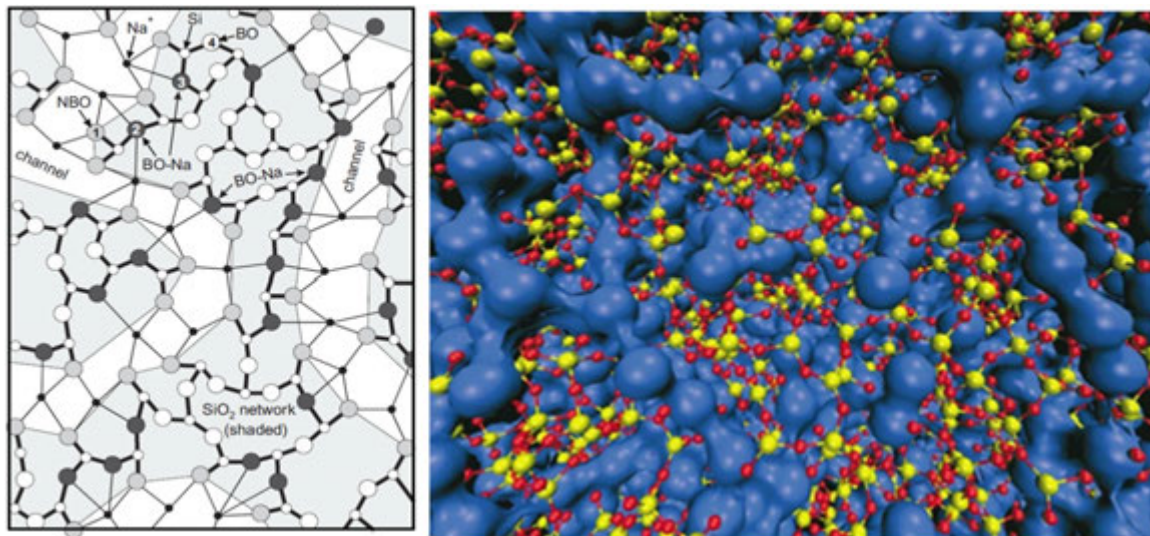


Fig. 2 Examples of a modified random network: (a) showing percolation channels with MBOs present near the channels, atom labeled “1” is an NBO, “2” and “3” are BOs with a Na attached (MBO), “4” is a regular BO shared between two Si atoms; (b) Results of a computer simulation showing “dynamic trajectories” of Na atoms. Red are oxygen atoms and the larger yellow atoms are Si. Reprinted with permission from: (a) Nesbitt, H.W., Henderson, G.S., Bancroft, G.M., Ho, R., 2015a. Experimental evidence for Na coordination to bridging oxygen in Na-silicate glasses: Implications for spectroscopic studies and for the modified random network model. *J. Non-Cryst. Solids* 409, 139–148. copyright 2015. (b) Meyer, A., Horbach, J., Kolb, W., Kargl, F., Schober, H., 2004. Channel formation and intermediate range order in sodium silicate melts and glasses. *Phys. Rev. Lett.* 93, 027801. copyright 2004.



As [Le Losq et al. \(2019\)](#) point out, this reaction is in fact an equilibrium reaction as shown in [Eq. \(2\)](#), which is influenced by a number of factors including the ionic field strength of the cations and fictive temperature of the glass:



The mass balance equation for [Eq. \(2\)](#) is given by:

$$K = [Q^{n-1}][Q^{n+1}]/[Q^n]^2 \quad (3)$$

While this disproportion reaction does generally hold for glasses, there are some caveats. The apparent disproportionation reaction in [Eq. \(1\)](#) yields $[Q^{n-1}] = [Q^{n+1}]$ from stoichiometry; but [Eq. \(3\)](#) shows that $[Q^{n-1}]$ does not have to equal $[Q^{n+1}]$, as long as $[Q^{n-1}][Q^{n+1}] = \text{a constant } (K[Q^n]^2)$. In addition, [Eq. \(2\)](#) ignores polymerization and depolymerization reactions that occur on melting (cf., [Nesbitt et al., 2017c](#); [Henderson and Stebbins, 2021](#)) and secondly, many published glass compositions have not been determined experimentally, but are based on the “as made” nominal compositions which may or may not be accurate, and thirdly, it presumes tetrahedral coordination of the network formers and becomes increasingly inaccurate as T cations take on higher coordinations, especially five- and six-fold configurations.

Crystalline SiO_2 , $\text{Na}_2\text{Si}_2\text{O}_5$, Na_2SiO_3 , $\text{Na}_6\text{Si}_2\text{O}_7$, and Na_4SiO_4 have NBO/T ratios of 0.0, 1.0, 2.0, 3.0, and 4.0, respectively. For binary alkaline-earth crystals such as enstatite (MgSiO_3) and forsterite (Mg_2SiO_4) the NBO/T ratios are 2 and 4, respectively. Such a stoichiometric relationship (1 alkali = 1NBO, 1 alkaline-earth = 2 NBO) does not hold for melts and glasses because polymerization and depolymerization reactions occur on melting of crystals (cf., [Nesbitt et al., 2017b, 2020](#)). Melting of Na_2SiO_3 crystals which only contain Q^2 species produces a melt that contains Q^1 , Q^2 and Q^3 species (with concentration of $Q^3 > Q^1$) (cf., [Richtel et al., 1996](#); [Nesbitt et al., 2017b](#)) as suggested by [Eq. \(1\)](#). However, since Q^3 units have been produced from Q^2 species there has been a polymerization reaction ([Nesbitt et al., 2020](#)) and this is given by:



or more generally as:



Polymerization reactions such as shown in (4) and (5) produce a third oxygen species, free oxygen (FO) or O^{2-} (see [Nesbitt et al., 2011](#); [Moutjoy, 2007](#); [Henderson and Stebbins, 2021](#)). Some alkali or alkaline-earth cations will be bound to O^{2-} (e.g., Na_2O , CaO) rather than to NBOs. The stoichiometric relationship between the NBO and network modifier in the binary glasses does not hold and any calculation of NBO/T will be overestimated, and any nominal Q^n species distribution will be incorrect and becomes increasingly problematic as the silica content decreases. One of the major issues in the literature is that many researchers assume their calculated NBO/T values to be correct and fit their experimental nuclear magnetic resonance (NMR) and Raman data to match their NBO/T values. This leads to a high degree of inaccuracy with regard to Q^n species distributions and large amounts of

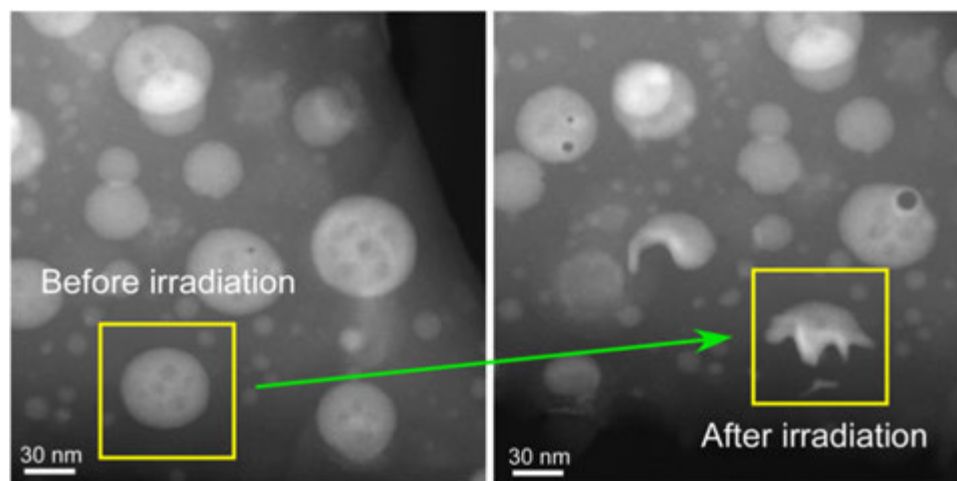


Fig. 3 Phase separation showing the nucleation and growth mechanism in 5BaO-95SiO₂ glass. Light colored Ba-rich spheres form within a Si-rich matrix glass. Righthand HAADF-STEM image shows the effects of irradiation and the mobility of the Ba-rich glass. Reproduced with permission from Gueguen, Y., Houizot, P., Célarié, F., *et al.*, 2017. Structure and viscosity of phase-separated BaO-SiO₂ glasses. *J. Am. Ceram. Soc.* 100 (5), 1982–1993.

contradictory data in the literature. An example of this is the $2Q^2$ peak assignment of Maekawa *et al.* (1991) for their K₂SiO₃ glass. Maekawa *et al.* (1991) fit their NMR data to match a calculated NBO/T value of 2.0 which was substantially different from their experimentally determined values of 2.44 and 1.44 (depending upon whether their four fitted NMR peaks were assigned to Q^0 – Q^3 or Q^1 – Q^4 respectively) (cf., Sawyer *et al.*, 2015). The $2Q^2$ peaks are necessary to get the NBO/T values to match the calculated value of 2.0. A consequence of this assignment is that the literature has many studies using the Maekawa *et al.* (1991) $2Q^2$ peak assignment to justify the presence of $2Q^2$ peaks in other types of fits including Principle Component Analysis (PCA) fits and starting assumptions (cf., Zakaznova-Herzog *et al.*, 2007).

In summary, Q^n species abundances or NBO/T cannot be accurately calculated from bulk melt or glass compositions, contrary to popular belief and practice. For a composition such as Mg₂SiO₄ where the calculated NBO/T is 4.0 the experimentally determined NBO/T value is around ~ 3.2 – 3.6 (cf., Nesbitt *et al.*, 2020). The Q^n distribution must be calculated from experimental Q^n species abundances (see Table 1, footnote 1 of Nesbitt *et al.*, 2020 for the calculation) or by direct measurement of NBO (e.g., Nesbitt *et al.*, 2011).

The presence of FO remains a contentious issue with many people simply refusing to accept its existence despite significant evidence that such a species exists (cf., Nesbitt *et al.*, 2015b; Lee and Kim, 2015). In addition, it is clear that even in these small amounts FO plays a critical role in the melting and crystallization of glasses (Nesbitt *et al.*, 2011, 2017b, 2018, 2020).

While the concept of alkali modifiers, network formers and the MRN has proven useful it has ignored any potential interaction between the modifiers and BOs. The concept of MBOs and their impact on glass properties and behavior has essentially been completely neglected but for a few studies (Kamitsos and Risen, 1984; Bakk *et al.*, 2012; Nesbitt *et al.*, 2015a, 2018; O'Shaughnessy *et al.*, 2017, 2020; Salmon *et al.*, 2019). It remains an area which requires study.

Phase Separation

Phase separation or metastable immiscibility occurs in Li₂O-SiO₂ from 0 to 33.3 mol% Li₂O, in Na₂O-SiO₂ glasses from 0 to 26 mol% Na₂O, CaO-SiO₂ between 1.8 and 21.8 mol% CaO (Tewhey and Hess, 1979), SrO-SiO₂ between ~ 2 and 30 mol% (Greig, 1927), and in BaO-SiO₂ between 0–28 mol% BaO (Levin and Block, 1956; Charles, 1966; Levin, 1967; Haller *et al.*, 1974; Hudon and Baker, 2002a,b; Seward *et al.*, 1984a,b). Rb₂O-SiO₂ and Cs₂O-SiO₂ glasses do not appear to exhibit phase separation. K₂O-SiO₂ glasses also appear to have some immiscibility field but the extent remains somewhat unclear (Charles, 1966; Gupta and Mishra, 1969; Haller *et al.*, 1974; Kawamoto and Tomozawa, 1981) if it occurs at all (Borisova and Ushakov, 1998). Phase separation has not been studied in BeO-SiO₂ glasses. In all cases of immiscibility, if the melt is quenched too slowly the resulting glass appears opalescent due to formation of two glass phases which causes light scattering at their interfaces. Fast quenching can avoid the onset of the immiscible behavior of much of the metastable immiscibility range.

For Li-silicate glasses from 0 to 40.7 mol% Li₂O, lithium disilicate is the stable phase and >40.7 mol% Li₂O, lithium metasilicate is stable (Sycheva and Kostyreva, 2014). In addition, other unidentified metastable Li-silicate phases may also be present (cf., Soares *et al.*, 2003). Non-stoichiometric, Ba-rich phases have also been reported in the BaO-SiO₂ system (e.g., Moulton *et al.*, 2019). Sodium-silicate glasses exhibit similar metastable immiscibility to the Li-silicate glasses. However, the immiscibility range is only up to around 26 mol% Na₂O (near the Na₂Si₃O₇ composition) (Haller *et al.*, 1974). Like the Li-silicate glasses the stable crystalline phases are Na₂Si₂O₅ and Na₂SiO₃.

Hudon and Baker (2002a) investigated miscibility gaps in 41 binary silicate systems. They concluded that phase separation in these systems was due to coulombic repulsion between poorly screened cations. The cations being bonded to BO (MBO), which are strongly polarized towards Si, and by regular NBO. They found that for cations with ionic radii ≥ 87.2 pm, and with coordination numbers (CN) > 5 , the size of their miscibility gaps had a linear dependence on ionic potential. For cations > 26 pm to 87.2 pm (CN between 4 and 5 or above) their miscibility gap does not increase linearly with increase in ionic potential. Cations which have variable crystal field splitting energies (e.g., transition metals) and those with lone pair electrons (e.g., Pb^{2+} , Te^{4+}) also display unique phase separation behavior though these are dealt with elsewhere (Hudon *et al.*, 2004). Phase separation occurs through one of two mechanisms, either nucleation and growth or spinodal decomposition (James, 1975). The former mechanism produces spheres, nuclei, of one liquid that grows within a matrix of a second liquid (Fig. 3) whereas spinodal decomposition produces a diffuse interface between the two liquids. Phase separation and liquid immiscibility are fundamental processes in silicate liquids for both producing large scale differentiation of magmas (Charlier *et al.*, 2011; Charlier, 2015; Hou and Veksler, 2015), and producing kitchenware worldwide (Stookey, 1959).

$\text{Li}_2\text{O-SiO}_2$ Glasses

Lithium silicate glasses behave differently to the other alkali glasses. A similar effect is observed for Be relative to the alkali-earths (see below). These differences appear to be related to the small atomic size and field strength of these cations relative to their other group members. Lithium silicate glasses contain Q^2 , Q^3 and Q^4 species but with significantly more Q^2 and Q^4 compared to the other alkali silicate glasses. In addition, it has a preference for forming Q^2 species at low alkali concentrations relative to the other alkalis with this Q^2 -forming tendency decreasing with increasing cation size and cationic potential (Z/r) of the alkali (cf., Matson *et al.*, 1983; Schramm *et al.*, 1984; Grimmer *et al.*, 1984; Dupree *et al.*, 1986; Maekawa *et al.*, 1991; Hannon *et al.*, 1992; Soltay and Henderson, 2005a,b; O'Shaughnessy *et al.*, 2020, for example).

Xu *et al.* (1989) observed in a series of high Li-silicate glasses (24–33.3 mol% Li_2O) the presence of Q^4 , Q^3 and Q^2 species with the presence of significant Q^2 species. They suggested that the NBO distribution was not random and consistent with the MRN model of silicate glasses. Umesaki *et al.* (1993) also investigated high Li_2O glasses and obtained Q^4 to Q^1 species with the Q^n distribution in agreement with the results of Dupree *et al.* (1990). Umesaki *et al.* (1993) also found lithium atoms to be coordinated by 2–3 oxygen atoms, in accordance with Hannon *et al.* (1992). However, Uhlig and colleagues (Uhlig *et al.*, 1996a,b,c) found that Li is 4-fold coordinated in high Li_2O content glasses. In addition, Kitamura *et al.* (2000) observed that at high pressure (P) the Si-O bond lengthened with increasing P up to 6 GPa, and Buchner *et al.* (2014) noted that distortion of the SiO_4 tetrahedron is the main structural change observed in Li-silicate glasses up to 6 GPa. At 7.7 GPa polyamorphism was observed (Buchner *et al.*, 2014).

Du and Corrales (2006) have performed ab initio molecular dynamics to investigate Li-disilicate glass and melt. Their calculated bond distances and Q^n species distributions are in agreement with experimental studies (cf., Umesaki *et al.* 1993; Xu and Stebbins, 1995). Uchino and Yoko (1999) performed similar simulations on both Li- and Na-silicate glasses. They found that the coordination number of sodium was larger than that of lithium in the glasses. Uchino and Yoko (1999) reported that the coordination environments are influenced by the electronegativities of the alkalis: The Li-O bond overlap is considerably larger than the Na-O bond. This suggests that the Li-NBO bonds have strong covalent interactions and are more likely to interact with NBOs, while sodium is more likely to interact with both BO and NBO atoms.

$\text{Na}_2\text{O-SiO}_2$ Glasses

Misawa *et al.* (1980) reported lengthening of the alkali silicate Si-O bond in comparison to pure vitreous silica; 1.63 and 1.62 Å for the sodium and lithium silicates, respectively. They also noted that the Si-O bond length increases with added alkali. This was later confirmed through other studies (cf. Henderson, 1995). Misawa *et al.* (1980) also reported an observed Si-O bond weakening and the presence of Q^3 tetrahedra as observed by Warren and Bischoe (1938). Greaves *et al.* (1981) and Greaves (1985) data revealed that the structures of sodium silicate glasses remain relatively similar and minor differences in the EXAFS data were attributed to the addition of network modifiers and the distribution of Q^n species. The Na EXAFS spectra showed a higher frequency of oscillations than the Si EXAFS, indicating that the Na-O bond is longer than the Si-O bond and that different bonding interactions are taking place.

In agreement with previous studies, Henderson (1995) reported that sodium silicates were locally structured with tetrahedrally coordinated silicon environments. However, the Si-Si bond distributions decreased with addition of Na_2O , and the contribution from multiple scattering beyond the second coordination sphere increased. This suggested that a degree of intermediate-range ordering was taking place with the addition of sodium. Furthermore, there was an increase in the Si-O bond distance with the addition of sodium, from 1.61 ± 0.02 Å for amorphous silica to 1.66 ± 0.02 Å for 30 mol% Na_2O . This change in bond distance indicated that the network depolymerization effect on the Si-O bond dominated over increased numbers of non-bridging oxygen atoms (Si-NBO bonds are shorter than Si-BO bonds). Above 30 mol% Na_2O the Si-O bond distances decreased owing to the dominating NBO distribution. This relationship suggested that the micro segregation of network modifiers from network formers is significant for sodium concentrations > 30 mol%.

Hoppe *et al.* (1995) noted that their X-ray (XRD) and neutron diffraction (ND) data indicated 2 types of Na sites in their sodium silicate glasses (23.5 and 33 mol% Na_2O) with Na-O distances of 2.25 and 2.55 Å. They concluded that the Na sites were

similar to those found in α -Na₂Si₂O₅ (Na in 5-fold coordination with 4 Na-NBO and 1 Na-BO bonds) and β -Na₂Si₂O₅ (6-fold coordination with 4 Na-NBO and 2 Na-BO bonds). Zotov and Keppler (1998) investigated sodium tetrasilicate glasses around the glass transition ($\cong 773$ K) and concluded there is little change in the short and intermediate-range structure of melt versus glass at this temperature.

The alkali-silicate glasses have been extensively investigated using NMR and Raman spectroscopy (see Henderson and Stebbins, 2021; Le Losq *et al.*, 2019 and references therein). de Jong *et al.* (1981) reported that both lithium and sodium cations tend to have a bimodal distribution throughout the silicate network and form alkali clusters whereas potassium, rubidium and cesium cations exhibited more uniform distributions. They also observed that lithium silicates are more stable with a Q⁴-Q² distribution rather than a Q³-Q³ arrangement. This results in clustering of lithium pairs around the SiO₄ tetrahedra. These conclusions were supported by Matson *et al.* (1983) who investigated $xM_2O \cdot (100 - x)SiO_2$ glasses (M = Li, Na, K, Rb, Cs and $x = 0, 5, 10, 15, 20, 25, 30$) with Raman spectroscopy. Significant changes were observed in the Raman spectra with the addition of small amounts of alkali oxides and high-frequency spectral features were useful in interpreting the distribution of Qⁿ species. No attempt was made to curve fit the spectra. Recently, O'Shaughnessy *et al.* (2020) re-examined the compositions of Matson *et al.* (1983) also using Raman spectroscopy. O'Shaughnessy *et al.* (2020) fit the high frequency Raman envelope characteristic of Qⁿ species. Their approach is novel, and indicates that there are multiple types of Q⁴, Q³ and Q² species present. Unlike previous studies that have fit this envelope, O'Shaughnessy *et al.* (2020) use a consistent approach to band shape and band assignments and they discriminate bands where the alkali is near a BO (MBO) and is not near a BO (NBO). They find that, with increasing alkali-oxide, the proportion of Qⁿ species affected by nearby alkali cations increases. Furthermore, there are 2 Q⁴ bands present in the high frequency envelope which merge at 20 mol% alkali oxide for all binaries.

Molecular dynamics (MD) simulations have been extensively performed on a wide variety of alkali-silicate glasses in order to probe the chemical and physical behavior and properties of alkali-silicate glasses (e.g., Huang and Cormack, 1991, 1992; Smith *et al.*, 1995; Vessal *et al.*, 1996; Du and Cormack, 2004, 2006; Ispas *et al.*, 2001, 2010; Bauchy and Micoulaut, 2011; Jabraoui *et al.*, 2016; Baral *et al.*, 2017, 2019; Zhen *et al.*, 2020).

MD simulations by Huang and Cormack (1991) showed Na and K cations to be positioned around NBOs, forming regions rich in Q³ species and creating extended silica rich regions with alkali rich channels contained within them. This was consistent with the MRN model (Greaves *et al.*, 1981; Greaves, 1985). Huang and Cormack (1991) also proposed that the percentage of Qⁿ species (Q², Q¹ and Q⁰ species) is reflected in the distribution of the alkali and NBO clusters, with Q³ species dominating at the disilicate composition. Their simulations showed that the alkali and NBO distribution is more uniform for potassium silicate glasses than sodium silicate glasses. This suggests that different alkali cations have different behavior in modifying the network structure. Further analysis revealed the NBO per silicon distribution to decrease in order of Li > Na > K.

Smith *et al.* (1995) supported the formation of Q³ and silica rich regions as observed by Huang and Cormack (1991, 1992). Smith *et al.* (1995) also observed the structure of sodium silicate glass to be inhomogeneous with a non-uniform distribution of sodium ions and clustering of sodium around the NBO atoms. With increasing amounts of sodium, the sodium rich and silicate rich regions were observed to extend three-dimensionally. Vedishcheva *et al.* (1995) also found that the cation arrangement within the network is non-uniform, and exists as clusters of negatively charged non-bridging oxygen atoms attracting the positively charged network modifying cations, and vice versa. They also suggested that the tetrahedral Q⁴ species tend to accumulate in silica-rich regions.

Uchino and Yoko (1999) investigated sodium and lithium silicate glasses by ab initio molecular orbital calculations. They reported that in sodium silicate glasses, the Si-O (BO) and the Si-O (NBO) bonds were longer and shorter, respectively, than the corresponding lithium silicate bond-distances.

Furthermore, coordination-numbers for sodium were higher than for lithium in silicate glass. Uchino and Yoko (1999) concluded that Li-O bonds have greater bond-overlap and greater covalent interactions than Na-O bonds and this results from increased covalent interactions in sodium silicate versus lithium silicate glasses. This in turn results in an increase in the tendency for alkali cations to interact with bridging and non-bridging atoms. Uchino and Yoko (1999) concluded that both the size and molecular orbital interactions between alkali cations and the surrounding oxygen atoms determined alkali coordination. Bauchy and Micoulaut (2011) studied the dynamics of Na₂O-3SiO₂ composition glasses and suggested that there were different diffusion regimes with increasing density at fixed temperature. They observed conversion of percolation channels to small pockets once the density increased. The most recent simulations (Ispas *et al.*, 2001, 2010; Jabraoui *et al.*, 2016; Baral *et al.*, 2017, 2019; Zhen *et al.*, 2020) have tended to focus on determining spectroscopic behavior by using classical molecular dynamics (MD) to generate a hypothetical glass structure followed by ab initio MD to determine various spectroscopic responses (i.e., Raman, Infrared (IR), NMR) of the structure.

X-ray photoelectron spectroscopy (XPS) has also been used to investigate sodium and potassium silicate glasses (e.g., Nesbitt *et al.*, 2011, 2015a, 2017c; Sawyer *et al.*, 2015). XPS using an Al K α source (1486 eV photons) has an analysis depth of about 50 angstroms, so it is often used as a surface probe. However, it has been used successfully for bulk analysis of many silicates, and it yields good bulk analyses if precautions are taken. With the Kratos XPS instruments, reproducible O 1 s spectra of pristine fractured glass surfaces can be obtained in a few minutes with excellent resolution of the BO and NBO + O²⁻ peaks (Nesbitt *et al.*, 2011, 2015a,b). The %BO can be obtained easily and precisely from good fits to the spectra; and any surface modification from the x-ray beam can be corrected by plotting the %BO against time, and extrapolating the %BO to $t = 0$. The observed %BO can be compared with that expected theoretically for no O²⁻ (complete conversion of BO to NBO by the Na₂O from the reaction $BO + O^{2-} \rightarrow 2NBO$), and there is excellent agreement between experiment and theory for the low Na glasses (25 and 30 mol%

Na_2O) where the O^{2-} will be much less than 1%. This agreement is excellent evidence that the %BO values from XPS are not only precise, but accurate. For the higher mol% Na_2O glasses (e.g., 45, 50, 55%), the %BO values are larger than that expected for the “complete conversion” values, showing that there is appreciable O^{2-} . For example, for the 50 mol% Na_2O glasses, the mol% O^{2-} is $4\% \pm 2\%$ (Nesbitt *et al.*, 2015b), and this value is in good agreement with the ^{29}Si NMR (Nesbitt *et al.*, 2011, 2015a,b) and the Raman results (Bancroft *et al.*, 2018). The broadened BO peaks also give good evidence for the presence of MBO (Nesbitt *et al.*, 2015a, 2017c).

$\text{K}_2\text{O-SiO}_2$ Glasses

Numerous diffraction (Meneau *et al.*, 2001; Majérus *et al.*, 2004), Raman (Zakaznova-Herzog *et al.*, 2007; Malfait *et al.*, 2007a; O’Shaughnessy *et al.*, 2020), NMR (Sen and Youngman, 2003; Malfait *et al.*, 2007b; Davis *et al.*, 2010; Stebbins and Sen, 2013; Sawyer *et al.*, 2015; Stebbins and Bista, 2019), EXAFS (Kamijo *et al.*, 1996) and XPS (Sawyer *et al.*, 2015) studies have been performed on $\text{K}_2\text{O-SiO}_2$ glasses. The medium-range structure of potassium silicate glasses (5–35 mol% K_2O) was studied by Meneau *et al.* (2001) using wide-angle X-ray scattering (WAXS) and ^{29}Si NMR. They interpreted the first sharp diffraction peak (FSDP) in the WAXS data as being indicative of correlations between voids in the glass network. This was reflected as a decrease in the FSDP line width. The addition of K_2O resulting in increasing voids with more NBOs formed, expansion of the network structure with larger voids relaxing to smaller ones, resulting in a more ordered overall structure. However, for compositions below 20 mol% K_2O , the first sharp diffraction peak was observed to broaden, and this was interpreted as indicating phase separation.

Olivier *et al.* (2001) compared double quantum (DQ) magic angle spinning NMR (MAS NMR) to MD simulations of binary alkali silicate glasses. They concluded that the Q^4 species were connected to other Q^4 and Q^3 species, thus suggesting that the DQ NMR results support the presence of silica-rich regions, in agreement with the NMR data. Sen and Youngman (2003) investigated the Q^n distribution and connectivity of potassium silicate glasses with silica contents ranging from 76.0 to 97.6 mol%. They concluded that Q^3 species along with two different Q^4 species exist in potassium silicate glasses with >83.5 mol% SiO_2 . And, similar to Olivier *et al.* (2001) the different Q^4 species correspond to Q^4 species connected to one or more Q^3 nearest neighbors and Q^4 species with only Q^4 neighbors, denoted by Q^{4-3} and Q^{4-4} , respectively. Sen and Youngman (2003) also proposed that the random distribution of Q^n species leads to the formation of nanoclusters of Q^3 -rich regions in a Q^4 -rich matrix, with percolating Q^3 -rich clusters forming at 7.5 mol% K_2O composition (see earlier comment on the term “clusters”). However, this is in the phase separated compositional region. More recently, Sawyer *et al.* (2012) showed that the amount of free oxygen in $\text{K}_2\text{O-SiO}_2$ glasses appears to be greater than in equivalent composition $\text{Na}_2\text{O-SiO}_2$ glasses. In addition, Nesbitt *et al.* (2017c) have indicated the potential presence of 3 types of BO with 1, 2 and 3 K cations near or bonded to the BO as observed in the K_2SiO_3 crystal structure. In essence, with increasing K_2O the O coordination potentially increases from 2 $\rightarrow$ 5. Such an increase in BO coordination and its influence on physical properties also remains an area that has not been investigated in any detail.

$\text{Rb}_2\text{O-SiO}_2$ and $\text{Cs}_2\text{O-SiO}_2$ Glasses

There are relative few studies of these glasses. Dupree *et al.* (1986) performed a ^{29}Si and ^{133}Cs MAS NMR study of rubidium and cesium alkali silicate glasses. In comparison to sodium and lithium containing silicate glasses from earlier studies (de Jong *et al.*, 1981; Matson *et al.*, 1983; Schramm *et al.*, 1984) they noted that for low concentrations of rubidium and cesium there is little change in the glass structure and a uniform distribution of Q^3 species and associated cations exist. However, they also observed that at high alkali concentrations (>40 mol%) when there is more than one NBO and cation associated with each silicate tetrahedron, then the Q^n species become more variable resulting in the formation of Q^1 , Q^2 and Q^3 species. Bykov *et al.* (2000) investigated rubidium and cesium silicate glasses using Raman spectroscopy. They found Q^n species distributions consistent with the disproportion reaction Eq. (1) above and the results of Maekawa *et al.* (1991). However, they did note that with increasing alkali size the reaction shifted to the left. Malfait *et al.* (2007a) found that there was an increasing proportion of small rings with increasing alkali size. More recently, O’Shaughnessy *et al.* (2017) investigated $\text{Cs}_2\text{O-SiO}_2$ glass (0–35 mol% Cs_2O) at ambient and high T using Raman spectroscopy and noted that below 10 mol% Cs_2O there was little change in Q^3 , Q^4 and Q^2 concentrations but above 15 mol%, Q^3 increases while Q^4 decreased. The Q^2 concentration showed only a slight increase. At high alkali contents there was a splitting of the fitted high frequency Q^n species bands due to the presence of increasing MBO bonds. Jardón-Álvarez *et al.* (2018) measured a series of cesium-silicate glasses using 2D magic angle flipping (MAF) NMR. They interpreted a decrease in the Q^3 shielding anisotropy with increasing Cs content as a lengthening of the NBO bonds from increasing clustering of the Cs around the NBO. In addition a second Q^3 tetrahedron appeared close to a Cs_2O mole fraction of $x = 0.24$ and was attributed to a finite cluster size with shorter Si-NBO bond lengths.

Mixed Alkali Effect

The mixed alkali effect (MAE) occurs when an additional type of alkali or alkaline-earth cation is added to the binary glass. The mix of two different cations affects a variety of physical properties such as diffusion, electrical conductivity amongst others in a non-linear way (Fig. 4). The explanation for the MAE has revolved around dynamic concepts and two concepts in particular, the transport of

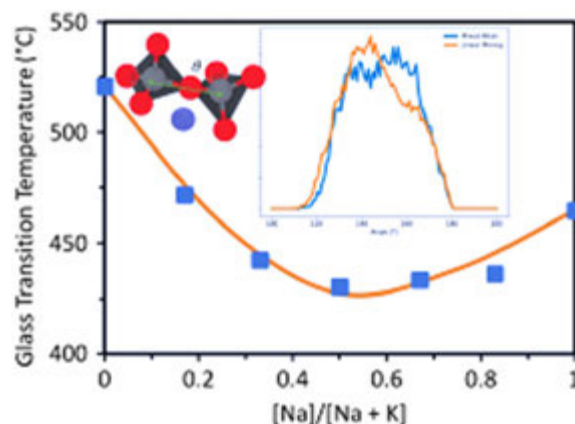


Fig. 4 The non-linear behavior of T_g that occurs when the Na/K ratio is varied in binary alkali-silicate glasses. From Wilkinson, C.J., Potter, A.R., Welch, R.S., *et al.*, 2019. Topological origins of the mixed alkali effect in glass. *J. Phys. Chem. B* 123, 7482–7489.

alkalies through “microdomains” in phase separated glasses or “blocking” of alkali sites as the alkalies migrate in an otherwise homogeneous network (see Henderson, 2005; Wilkinson *et al.*, 2019 and references therein for a summary of the earlier theories).

While the explanation for the MAE remains controversial there does appear to be somewhat of a consensus developing toward a dynamic structure model similar to those of LaCourse (1987), Ingram (1987) and Bunde *et al.* (2004). Currently, the most widely accepted explanation involves cations occupying sites with local structures specific to that cation. Different cations cannot occupy those sites until the vacant site adjusts itself to accommodate the new cation. For example, a vacant Na site has a structural environment suited to the Na^+ cation. When Na^+ moves out of the site the vacant site could accept another Na^+ cation but cannot accept a different cation such as K^+ until the site has adjusted its structural environment to accommodate the much larger K^+ cation. The transport of the different alkalies through the glass will depend on how quickly different sites can adjust to accommodate different cations. Introduction of the new cation also puts additional strain on the glass network due to the different atomic size of the new cation and is well described by a topological modeling approach (Wilkinson *et al.*, 2019). LeLosq *et al.* (2019) have discussed the MAE in aluminosilicate glasses and suggest that while the cation sites are important, the MAE is also related to the degree of heterogeneity of the glasses and the concept of percolation channels.

Albeit less pronounced, the same MAE is found in alkaline-earth silicate glasses where it is called the Mixed Alkaline Earth Effect (MAEE) or more generally the Mixed Modifier Effect (MME). The main reason that MAEE effects are less pronounced than the MAE is that sites must adjust to the 2^+ charge which involves multiple NBO. Very few structural studies have been done on the MAEE in ternary silicate glasses with two AE cations, though the substitution of both Mg by Ca (Calahoo and Zwanziger, 2017; Shan *et al.*, 2017; Zhang *et al.*, 2010), and Mg by Ba (Taniguchi *et al.*, 1997; Lee *et al.*, 2003) has received some attention. When Ba is substituted for Mg in metasilicate glass there is a strong influence on the shielding of the BO and Ba effectively outcompetes Mg for the NBO, leading to significant ordering of the glass (Lee *et al.*, 2003).

The MAEE have been studied in alkali-bearing aluminosilicate glasses in considerable detail (Bäck *et al.*, 2019; Ding *et al.*, 2020; Kjeldsen *et al.*, 2014). The Ding *et al.* (2020) study looked at the inter-play between the Mg for Ca exchange, and three- versus four-fold coordinated B. In fact, ^{14}B is found mainly in end member compositions, rich in either Mg or Ca, whereas ^{13}B and a change in silica connectivity was observed when the concentration of Mg and Ca were roughly equal (Ding *et al.*, 2020). This interplay between the network modifiers and the network formers indicates that, in contrast to pure silicate glasses, the alkaline earth cations may effectively compete for oxygen with weaker network formers (e.g., B, Al). Therefore, the MME may not only be restricted to the modifiers but to chemically complex networks in general. To determine the physical properties of ternary and more complex glasses one should start by consulting Bansal and Doremus (1986) or the SciGlass database (see “Physical Properties section”).

Alkaline-Earth Silicate Glasses

In contrast to the alkali cations, the alkaline-earth (AE) cations have a 2^+ formal charge, a full outer s orbital, and comparable radii. As a result, AE cations bond more readily with multiple oxygens, and therefore are less soluble (Railsback, 2003), and produce more dense silicate glasses and melts (Bottinga and Weill, 1970; Gaskell, 1982). From Be-O to Ba-O the unstrained bond length (r_0) lengthens from 1.38 to 2.29 Å, whereas from Li-O to Cs-O, r_0 changes from 1.46 to 2.42 Å (Brown and Altermatt, 1985; Gagné and Hawthorne, 2016). The interest in the alkaline-earth silicate glasses are three-fold. First, the AE cations, especially Mg and Ca, are ubiquitous in most environments on Earth and from major constituents in seawater, as well as mantle (Railsback, 2003). Second, metallurgical processes often produce refractory glasses, rich in Mg, Ca, Fe, and Si, as a by-product of smelting (e.g., Piatak *et al.*, 2019; Toop and Samis, 1962). Third, AE silicate glasses and glass-ceramics are widely used in industrial applications

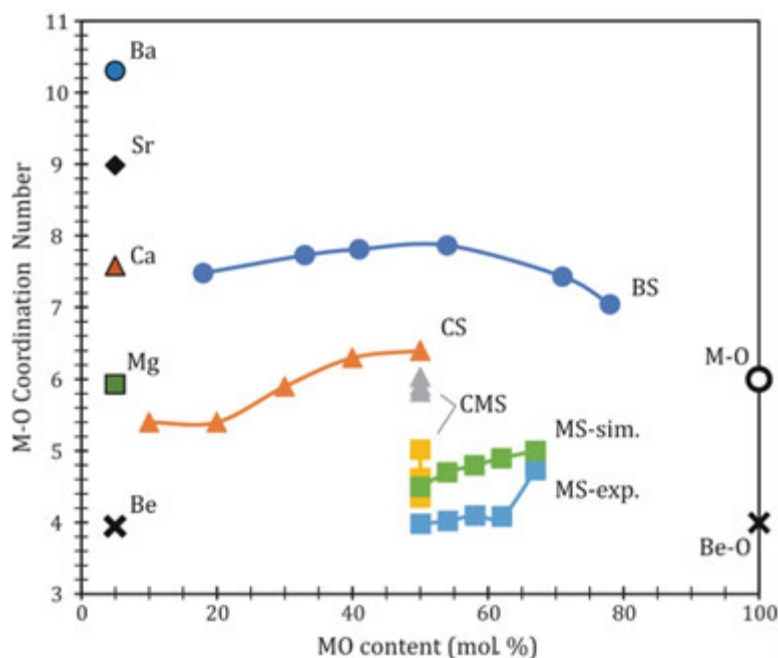


Fig. 5 Representative CN_{MO} for MO-SiO₂ glasses where M is Mg (squares), Ca (triangles), Sr (diamonds), Ba (circles). MgO-SiO₂ data comes from ND data of Wilding *et al.*, MS-exp., and molecular dynamics simulations of Al-Hasni and Mountjoy, MS-sim. CMS refers to CaO-MgO-SiO₂ glass results of Cormier and Cuello. CaO-SiO₂ data (CS) comes from MD simulations of Mead and Mountjoy. BaO-SiO₂ data (BS) comes from personal data of Prof. A. Picinin (UFScar). The grand mean CN_{MO} for oxide-based crystals (Gagné and Hawthorne, 2016) for each of the AE have been plotted at 5% and for the pure MO oxides at 100%. Data of Wilding, M.C., Benmore, C.J., Tangeman, J.A., Sampath, S., 2004b. Evidence of different structures in magnesium silicate liquids: Coordination changes in forsterite- toenstatite-composition glasses. *Chem. Geol.* 213, 281–291. Al-Hasni, B.M., Mountjoy, G., 2014. A molecular dynamics study of the atomic structure of $x(MgO)_{100-x}(SiO_2)$. *J. Non-Cryst. Solids* 400, 33–44. Cormier, L., Cuello, G.J., 2013. Structural investigation of glasses along the MgSiO₃–CaSiO₃ join: Diffraction studies. *Geochim. Cosmochim. Acta* 122, 498–510. Mead, R.N., Mountjoy, G., 2006a. A molecular dynamics study of the atomic structure of $(CaO)_x(SiO_2)_{1-x}$ glasses. *J. Phys. Chem. B* 110, 14273–14278. Mead, R.N., Mountjoy, G., 2006b. A molecular dynamics study of densification mechanisms in calcium silicate glasses CaSi₂O₅ and CaSiO₃ at pressures of 5 and 10 GPa. *J. Chem. Phys.* 125, 154501.

such as in solid-oxide fuel cells (Herrmann *et al.*, 2012; Höland and Beall, 2012), and, when doped with rare earth elements these glasses and glass-ceramics are used in LED and re-writable optical storage devices (e.g., Lin *et al.*, 2019; Wang *et al.*, 2013).

The MgO-SiO₂ System

MgO and SiO₂ are major components in the Earth (Bowen and Andersen, 1914) but are also of interest because magnesium substitutes for ferrous iron in many silicate phases due to their similar charge and radius (Brown and Altermatt, 1985). Structural considerations of AE silicate compositions were initially motivated by a desire to explain phase separation and viscous flow (Bockris *et al.*, 1955; Warren, 1942). Early XRD studies on Mg-metasilicate glasses determined a mean Mg-O bond length of 2.14 Å and a magnesium coordination number (CN_{Mg}) of 4.6. These values showed negligible changes for the molten products of these glasses at 1600–1800°C, where the Mg-O bond lengths increased slightly to 2.16 Å (Waseda and Toguri, 1977). In contrast, the Si-O bond length remained constant, at 1.63 Å up to 1800°C. Although the Mg-O bond length remained similar, the CN_{Mg} increased slightly from 3.7 to 3.9 for glassy 44MgO-56SiO₂ at 1790°C (Waseda and Toguri, 1977). For glassy MgSiO₃, bond lengths (and coordination numbers) for Mg-O and Si-O of 2.08 Å (4.1) and 1.63 Å (4.1), respectively, were found (Yin *et al.*, 1983). Small scale molecular dynamics simulations have confirmed this behavior (Matsui, 1996). However, ultimately the significance of non-integer CN_{Mg} , 4.6, raises questions with respect to the coordination distribution and the role Mg plays in the properties in silicate glasses and melts.

Due to the ambiguity of a fractional CN_{Mg} other structural probes and higher resolution studies have been sought to determine the role of Mg, including Mg *K*-edge X-ray absorption near-edge spectroscopy (XANES), Raman, and ²⁵Mg MAS NMR spectroscopies as well as higher resolution diffraction studies (Cormier and Cuello, 2011; Davis *et al.*, 2011; Kalampounias *et al.*, 2009; Kroeker and Stebbins, 2000; Li *et al.*, 1999; Salmon *et al.*, 2019; Sen and Tangeman, 2008; Shimoda *et al.*, 2008; Shimoda and Okuno, 2006; Taniguchi *et al.*, 1997). The majority of these studies essentially agree that the Mg-O bond length in MgSiO₃ glass is close to ~2 Å, with individual values ranging from 1.99 to 2.08 Å and a coordination number (CN_{Mg}) of ~4.5 (ranging from 4.35 to 4.75 depending on the method and constraints used). Most X-ray-based spectroscopic and diffraction studies interpret the CN_{Mg} to represent a mixture of distorted MgO₄ and MgO₅ polyhedra (Wilding *et al.*, 2004a,b). However, several ²⁹Mg MAS NMR studies suggested that the local Mg environment in MgSiO₃ glass is a distorted octahedron (MgO₆) (Kroeker and Stebbins, 2000; Shimoda

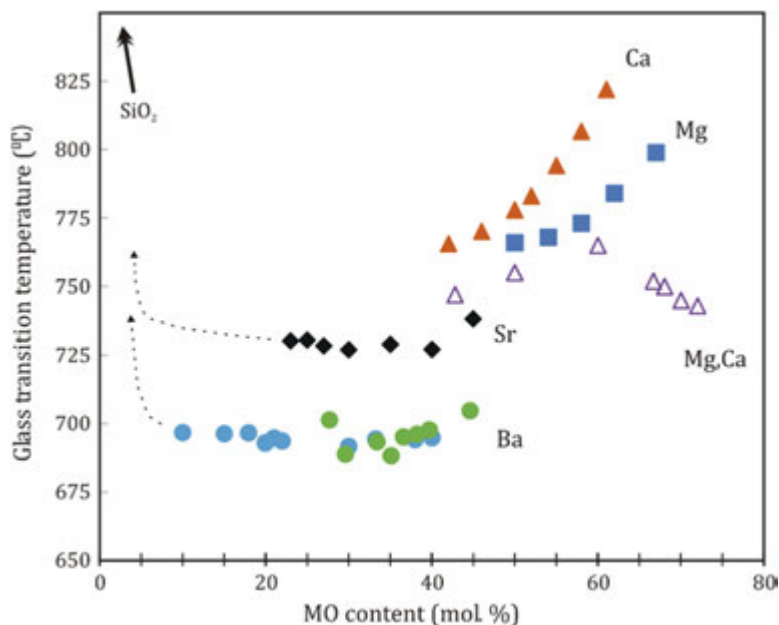


Fig. 6 Glass transition temperature, T_g , as a function of AE composition. T_g data of CaO-SiO_2 glasses (filled triangles) are from Kaseman *et al.*, MgO-SiO_2 glasses (squares) are from Wilding *et al.*, $(\text{Ca,Mg})\text{O-SiO}_2$ glasses (empty triangles) from Nasikas, BaO-SiO_2 data (green circles) from personal data of Dr. L. Silva (UFSCar) and come from calorimetry measurements using a heating rate of 10K/min. The data for SrO-SiO_2 (black diamonds) and BaO-SiO_2 (blue circles) come from dilatometry measurements of Shelby (1979). Dotted lines are inferred trends as pure SiO_2 has a T_g around 1190°C. Errors in T_g are generally $\pm 2\text{--}5^\circ\text{C}$ and errors in composition are generally $\pm 0.5\text{ mol}\%$. From Kaseman, D.C., Retsinas, A., Kalampounias, A.G., Papatheodorou, G.N., Sen, S., 2015. Q-speciation and network structure evolution in invert calcium silicate glasses. *J. Phys. Chem. B* 119, 8440–8445. Wilding, M.C., Benmore, C.J., Tangeman, J.A., Sampath, S., 2004a. Coordination changes in magnesium silicate glasses. *Europhys. Lett.* 67, 212–218. Nasikas, N.K., Edwards, T.G., Sen, S., Papatheodorou, G.N., 2012. Structural characteristics of novel Ca-Mg orthosilicate and suborthosilicate glasses: Results from ^{29}Si and ^{17}O NMR spectroscopy. *J. Phys. Chem. B* 116, 2696–2702.

et al., 2007). If Mg is found in octahedral coordination, it would be the only AE cation that has comparable CN in both crystalline and glassy oxides (Fig. 5). Unlike the other AE cations, the oxygen involved in the Mg polyhedra are mostly NBOs while for the larger cations (e.g., Ca, Ba) bridging oxygens become more important. This is expected to change in more complex compositions (e.g., Lee *et al.*, 2003). The silicon within the MgSiO_3 glass remains in tetrahedral coordination (4.0 ± 0.1) and with only subtle differences reported in the Si-O bond lengths of $1.62 \text{ \AA} \pm 0.01$ (Cormier and Cuello, 2011; Salmon *et al.*, 2019).

The difficulty in determining a mean Mg-O bond length and corresponding CN_{Mg} is due to the overlap and distribution of sites: MgO_4 , MgO_5 , MgO_6 , $\pm\text{MgO}_7$. It is a significant challenge to determine with confidence the CN of any of the alkali or alkaline-earth cations in glasses and melts due to their site distributions. Although clearer in crystalline silicates, this difficulty remains in some situations (e.g., Gagné and Hawthorne, 2016). In early diffraction studies an asymmetric feature in the total structure factors spanning $\sim 1.8\text{--}2.3 \text{ \AA}$ can be modeled using two Mg-O contributions at 1.99 and 2.21 $\text{\AA}$ (Cormier and Cuello, 2011; Wilding *et al.*, 2004a) or a distribution of Mg-O contributions (Cormier and Cuello, 2013). The local environment of Mg in metasilicate glasses has been studied in detail and its behavior at extreme temperatures and pressures has been discussed both experimentally and theoretically (Ghosh *et al.*, 2014; Sakamaki *et al.*, 2014; Salmon *et al.*, 2019; Yi and Lee, 2012). Mg_2SiO_4 glasses and liquids have been studied in detail (Adjaoud *et al.*, 2011; Kohara *et al.*, 2004; De Koker *et al.*, 2008; Sen and Tangeman, 2008; Voronko *et al.*, 2006) as well as invert MgO-SiO_2 glasses where modifier cations are more abundant than silica (Kalampounias *et al.*, 2009; Sen *et al.*, 2009). The CN_{Mg} in glasses may be more rigorously evaluated using simulations. In Mg_2SiO_4 glass, there appears to be roughly 30% MgO_4 , 50% MgO_5 , and 20% MgO_6 (Kohara *et al.*, 2004). The tetrahedral four-fold Mg sites tend to be regular whereas the pentahedral and octahedral sites are rather distorted, as inferred from NMR (Kroeker and Stebbins, 2000). A detailed analysis of Mg in a wide variety of local environments using Mg K-edge XANES may be used as a basis for future studies (Li *et al.*, 1999; Trcera *et al.*, 2009). CN_{Mg} is important as it appears to strongly affect T_g across the $\text{SiO}_2\text{-MgO}$ join, where T_g of invert glasses increases with increasing CN_{Mg} (Wilding *et al.*, 2004a) (Figs. 5 and 6). The results suggest that this is a likely trend for all binary MO-SiO_2 glasses but perhaps not for mixed AE glasses (Fig. 6).

In MgO-SiO_2 glasses, the regions concentrated in Mg are intermixed with the SiO_4 network which is characterized by the network connectivity (Al-Hasni and Mountjoy, 2014; Cormier and Cuello, 2011; Davis *et al.*, 2011; Sen *et al.*, 2009). Ideally, at the orthosilicate composition the connectivity should approach 0, where BO are absent, however, experiments find polymerized Q^n species, $\text{Q} > 0$, which can only exist if O^{2-} is also present in the glass (Sen *et al.*, 2009; Kalampounias *et al.*, 2009; Davis *et al.*, 2011). Simulations indicate the presence of O^{2-} near the metasilicate composition (Al-Hasni and Mountjoy, 2014) whereas experimental evidence from Raman or NMR spectroscopies have suggested O^{2-} is present in suborthosilicate compositions, at

~61% (Kalampounias *et al.*, 2009) and at ~63% (Sen *et al.*, 2009). These results are important for more silica-rich compositions as prior to the last decade structural models of silicate liquids almost ubiquitously assumed that O^{2-} was completely consumed by polymerization reactions and therefore not a significant reactant in these materials (see above).

In comparing the 1D ^{29}Si MAS NMR results to 2D ^{29}Si MAF/MAS NMR studies it is observed that the former systematically overestimate the amount of NBO present. For example, for MgSiO_3 the Q^0 to Q^4 were found to be 1.4%, 19.1%, 53.0%, 25.2%, and 1.4%, respectively, using MAF NMR (Davis *et al.*, 2011) whereas MAS NMR found them to be 0, 25.0, 42.0, 25.7, and 7.3, respectively (Sen *et al.*, 2009). These values are close to a detailed AIM-MD study (Salmon *et al.*, 2019) and contradict several MD studies (Shimoda and Okuno, 2006; Ghosh *et al.*, 2014). Combined, recent NMR, Raman and MD simulations confirm inferences from an early Raman study on a wide range of orthosilicate glasses that O^{2-} is an important oxygen species in silicate melts (Cooney and Sharma, 1990). The relationship between the presence of O^{2-} and the structural, physical and chemical properties of invert glasses remains an area of intensely debated research.

The Ternary MgO-CaO-SiO₂ System

The substitution of Mg by Ca is ubiquitous in AE silicate systems that is important for basic rocks as well as for potential biomedical applications. The diopside composition, $\text{CaMgSi}_2\text{O}_6$, glass has been studied using numerous techniques: ^{25}Mg (George and Stebbins, 1998; Kroeker and Stebbins, 2000; Shimoda *et al.*, 2008), ^{29}Si and ^{17}O NMR (Brandriss and Stebbins, 1988; Nasikas *et al.*, 2012), Ca K-, Mg K-, Si K-, and O K-edge XANES (Binsted *et al.*, 1985; Ildefonse *et al.*, 1995; Li *et al.*, 1999; Moulton *et al.*, 2016b; Trcera *et al.*, 2009), Raman (Franz and Mysen, 1995; Moulton *et al.*, 2016a; Nasikas *et al.*, 2011; Retsinas *et al.*, 2014), X-ray diffraction (XRD) and neutron diffraction (ND) (Cormier and Cuello, 2013; Shimoda *et al.*, 2005; Taniguchi *et al.*, 1997), as well as by theoretical simulations (Sun *et al.*, 2011; Zhang *et al.*, 2010). Finally, Hung *et al.* (2016) provide direct evidence for O^{2-} in near orthosilicate composition (Ca,Mg)-silicate glasses. Other important glasses in this system are found at the compositions of stable mineral phases, åkermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_6$), merwinite ($\text{Ca}_3\text{MgSi}_2\text{O}_8$), and monticellite (CaMgSiO_4), which may serve as entry points into this system.

The CaO-SiO₂ System

The CaO-SiO₂ phase diagram has been re-evaluated by Ottonello *et al.* (2013) whereas the crystal nucleation and growth rates have been studied in detail by Gránásy *et al.* (1998) and Deubener (2005). Early ND, XRD and EXAFS studies focused on the distinctions between the role of Ca and Mg in CaSiO_3 composition glasses (Eckersley *et al.*, 1988; Gaskell *et al.*, 1991; Geere *et al.*, 1983; Mastelaro *et al.*, 2000; Taniguchi *et al.*, 1997; Yin *et al.*, 1986). The EXAFS studies showed an uncanny similarity between the Ca K-edge XANES spectra of $x\text{CaO}-(1-x)\text{SiO}_2$ glasses ($x = 0.32-0.53$) and that of wollastonite (Geere *et al.*, 1983; Gaskell *et al.*, 1991). An ND study refined the local Ca environment to consist of a distribution of Ca-O bond lengths with six near oxygens around 2.24–2.54 Å, and a further oxygen sitting around 2.64 Å, resulting in a total CN_{Ca} of 6.16 ± 0.15 (Eckersley *et al.*, 1988). These results were reinforced by classical molecular dynamics simulation on CaSiO_3 which found a mean Ca-O bond length of 2.48 Å and a CN_{Ca} of 6.3 (Mead and Mountjoy, 2005).

These MD simulations were extended across $x\text{CaO}-(1-x)\text{SiO}_2$ ($x = 0-0.5$) glasses and found that with increasing Ca content there was little change in the Ca-O bond length from 2.37 to 2.42 Å as x changed from 0.1 to 0.5 (Mead and Mountjoy, 2006a). Although the bond length changed by only ~2% the CN_{Ca} increased by 1, from 5.4 to 6.4 across the same interval. The increased CN_{Ca} is due to the additional NBO forming as the CaO content increases. In fact, over the same interval the $\text{CN}_{\text{Ca}}^{\text{BO}}$ decreases from 2.3 to 1.0, whereas $\text{CN}_{\text{Ca}}^{\text{NBO}}$ increases dramatically from 3.1 to 5.4 (Mead and Mountjoy, 2006a,b). These findings of CaSiO_3 glass were supported by a combined ND + RMC study which modeled the distribution of Ca sites between CaO_5 and CaO_7 , and found the a mean CN_{Ca} of 5.83 with $\text{CN}_{\text{Ca}}^{\text{BO}}$ and $\text{CN}_{\text{Ca}}^{\text{NBO}}$ of 0.85 and 4.98, respectively (Cormier and Cuello, 2013). Similarly, ^{43}Ca NMR results found a mean Ca-O bond length of 2.461 and a mean CN_{Ca} of 6.35 (Pedone *et al.*, 2010). Ultimately, in terms of the correlation between CN_{MO} (Fig. 5) and T_g (Fig. 6), these CaO-SiO₂ studies find a comparable trend to MgO-SiO₂ glasses in the invert glass region. These results suggest that regions concentrated in Ca, like regions concentrated in Mg, actually contribute to the network strength of these silicate melts.

All studies on CaO-SiO₂ agree that the SiO₄ connectivity changes gradually across the join (Cormier and Cuello, 2013; Kaseman *et al.*, 2015; Mysen *et al.*, 1982; Neuville, 2006; Pedone *et al.*, 2010; Seo and Tsukihashi, 2004; Tsunawaki *et al.*, 1981; Wu *et al.*, 2004; Zhang *et al.*, 1997). It should be highlighted that, unlike the alkali silicates, NMR studies do not show the systematic trends relating the chemical shielding and quadrupolar parameters to the structural parameters (Pedone *et al.*, 2010). Instead, in order to determine the connectivities in alkaline-earth silicate glasses some constraints or assumptions are required to model the ^{29}Si MAS or MAF NMR spectra. Consequently, earlier ^{29}Si MAS NMR studies using empirical Gaussian fitting were noted to overestimate the Q^2 species by about 15% in CaSiO_3 glass (Charpentier *et al.*, 2013) and only modest correlations between Q^n species and the NMR parameters were found (Pedone *et al.*, 2010). This discrepancy is important because many early Raman studies on connectivity were quantified using empirical corrections based on ^{29}Si MAS NMR results.

CaSiO_3 glass connectivity was studied using ab initio simulations combined with advanced multidimensional NMR methods which found Q^1 - Q^4 of 25.0, 51.7, 18.4 and 5, respectively (Pedone *et al.*, 2010). These results are within error of a 2D ^{29}Si MAS NMR study which found Q^0 - Q^4 of 0.7, 19.3, 54.7, 24.1 and 1.1 (Zhang *et al.*, 1997) and more recent AIM-MD modeling which

found Q^0 - Q^4 of 1, 24, 50, 22, 2, respectively (Salmon *et al.*, 2019). From these models, errors of $\pm 0.5\%$ – 3% depending on the species concentration should be considered an excellent result. Kaseman *et al.* (2015) explored the connectivity of a wide range of CaO-SiO₂ glasses using an empirical Gaussian fitting routine on glasses containing 42%–61% CaO and found CaSiO₃ to have Q^1 - Q^3 of 16.6, 64.0, 19.0 indicating that this model overestimates the amount of Q^2 by $\sim 10\%$. This casts doubt on the absolute values determined across the compositional range but provides a guide to the expected trends. A variety of other studies have investigated the network connectivity of CaO-SiO₂ glasses; however, a comparison of the metasilicate composition alone shows that these studies differ dramatically from the results discussed above (Tsunawaki *et al.*, 1981; Mysen and Frantz, 1993; Franz and Mysen, 1995; Wu *et al.*, 2004; Seo and Tsukihashi, 2004; Mead and Mountjoy, 2005, 2006a).

Network connectivities have been tested by studies which determined the oxygen speciation directly, predominantly from ¹⁷O-based NMR studies (Lee and Stebbins, 2006; Thompson *et al.*, 2012; Kaseman *et al.*, 2015). In general, these studies all indicate that calcium silicate glasses tend to have a mean connectivity within error of their expected values for the reported composition, at least up to 60 mol% CaO (Lee and Stebbins, 2006; Thompson *et al.*, 2012; Kaseman *et al.*, 2015). The ambient condition results above have motivated further studies at gigapascal pressures and high temperatures (Mead and Mountjoy, 2006b; Lee *et al.*, 2014; Neuville *et al.*, 2008; Salmon *et al.*, 2019; Zhang *et al.*, 2010).

Correlations with structure associated with the medium range order have also been investigated in glassy CaSiO₃ (Cormier and Cuello, 2013; Gaskell *et al.*, 1991; Mead and Mountjoy, 2006a,b). In general, as the Ca content increases the number of rings decreases and the proportion of smaller rings decreases (Mead and Mountjoy, 2006a,b). When Mg is substituted for Ca in the metasilicate composition, the smaller Mg cation appears to favor the formation of larger rings (Cormier and Cuello, 2013). Large scale, $> 10,000+$ atoms, glass simulations have further investigated the ring populations (Le Roux and Jund, 2010, 2011) to establish the extent and importance of the medium range structure. We emphasize that chain-like and sheet-like structures, akin to those found in the crystalline phases, have not been found in simulations nor in critical analysis of diffraction features (Mead and Mountjoy, 2005; Cormier and Cuello, 2013) as reported frequently in studies prior to the year 2000. The same was concluded for the BaO-SiO₂ system (Rai and Mountjoy, 2014). In conclusion, alkaline-earth silicate glasses do not contain chain or sheet structures.

Beryllium Silicate Glasses

These glasses have been very rarely studied. This is partially due to the toxicity and carcinogenic nature of BeO. Unlike the other alkaline-earth cations, Be appears to be only found in four-fold coordination and due to its high field strength is considered a network former (Sen and Yu, 2005). The Be-rich melts and the crystalline phase beryl, Be₃Al₂(Si₆O₁₈), have received considerably more attention due to its gem variety, emerald (Riebling and Duke, 1967). Further information can be found on the effects of Be on viscosity (Hess *et al.*, 1996) or on its structural behavior in alkali silicate glasses (Clare *et al.*, 1997; Wójcik *et al.*, 2019).

Strontium Silicate Glasses

Strontium silicate glasses are not common although the effect of Sr on the viscosity for various silicate and aluminosilicate melts are known (Richet and Bottinga, 1986) and the SrO-SiO₂ phase diagram has been re-evaluated (Shukla *et al.*, 2017 and references therein). The properties may be found in: Bansal and Doremus (1986); Iwamoto *et al.* (1984); and Shelby (1979). Sr metasilicate glass has been studied using ND (Cormier *et al.*, 1999) and SrO-2.36SiO₂ glass was investigated by 2D ²⁹Si MAF NMR (Baltisberger *et al.*, 2016); however, neither study came to a conclusion regarding the glass structure. Similar to beryllium, the structure and properties of Sr-bearing aluminosilicate glasses have been more commonly investigated (Novikov *et al.*, 2017; Weigel *et al.*, 2016). The local Sr environment has been investigated in a wide variety of mixed alkali/alkaline-earth aluminoborosilicate nuclear waste glasses using Sr K-edge XANES/EXAFS (McKeown *et al.*, 2003).

The BaO-SiO₂ System

Within this binary the BaSi₂O₅ composition is most studied due to its volume nucleating ability (Fokin *et al.*, 2016; Moulton *et al.*, 2018, 2019; Ramsden and James, 1984; Takahashi *et al.*, 2009a,b; Zanutto and James, 1988) and interesting decoupling behavior just above T_g (Rodrigues *et al.*, 2018). Of the binary alkali or AE-silicate systems, BaO-SiO₂ has the most stable phases at ambient conditions making the structural aspects of this system quite complex. At least nine phases are currently known (Gorelova *et al.*, 2016; Grebenshchikov and Toropov, 1962) and several more are known to contain six-fold silicon at high-pressure (Hazen *et al.*, 1999; Yusa *et al.*, 2007). The phase diagram of the BaO-SiO₂ system has recently been re-evaluated (Oehlschlegel, 1975; Shukla *et al.*, 2018).

An early XRD and ND study on BaSi₂O₅ glass showed sharp peaks associated with the Si-O bonds at 1.60 Å and a broad second peak at 2.76 Å (XRD) or 2.63 Å (ND) which were assigned to the Ba-O and O-O distances, respectively (Hasegawa and Yasui, 1987). Beyond the first coordination sphere, a series of peaks at 3.60, 4.15, and 4.94 Å were interpreted loosely in terms of sheet structures (see comments at the end of the CaO-SiO₂ section) found in sanbornite (Hasegawa and Yasui, 1987). Another study on both crystal and glassy Ba₄Si₆O₁₆ highlighted features in the structure factor of the glass at 1.1 Å⁻¹ and crystal at 1.07 Å⁻¹ indicating some similarity related to the Ba cation distribution (Cormier *et al.*, 1999). Schlenz *et al.* (2002) found an Si-O bond length of 1.62 Å in

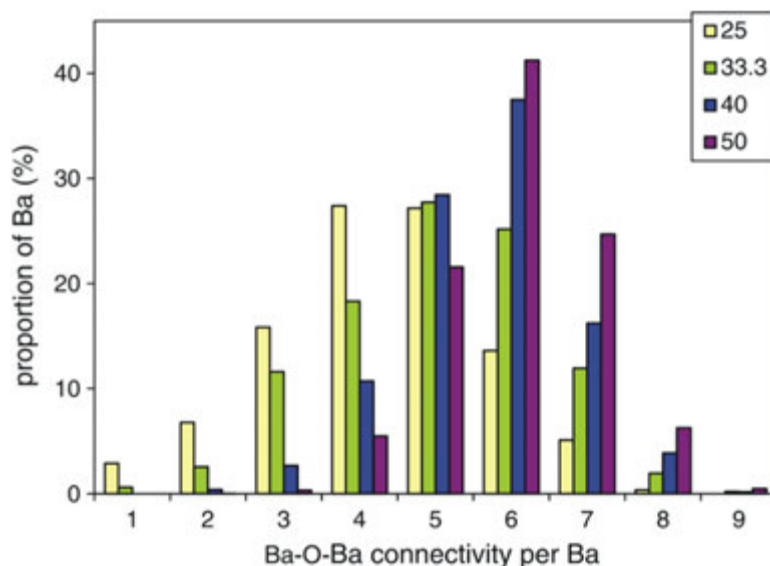


Fig. 7 The Ba-O-Ba connectivity distribution as a function of composition. Reproduced with permission from Rai, M., Mountjoy, G., 2014. Molecular dynamics modelling of the structure of barium silicate glasses BaO-SiO₂. *J. Non-Cryst. Solids* 401, 159–163.

BaSi₂O₅ glass using multiple techniques; however, problems with overlapping features of Ba-O and Si-Si between 2.66 and 2.96 Å precluded clear interpretations. A systematic Si *K*-edge XANES study on crystals and glasses found a monotonic edge shift in the crystalline phases whereas glass of 33.3BaO · 66.6SiO₂ and 37BaO · 63SiO₂ showed a similar response to sanbornite indicating a predominantly Q³-based glass (Bender *et al.*, 2002). These studies have built on a variety of investigations contrasting the crystalline phases against the glasses using Raman (Etchepare, 1970; Franz and Mysen, 1995; Mysen and Frantz, 1993; Takahashi *et al.*, 2009a), ²⁹Si NMR (Schneider *et al.*, 2003) and ¹⁷O NMR (Thompson *et al.*, 2012), Si *K*-edge XANES, XPS (Bender *et al.*, 2002; Schlenz *et al.*, 2002), MD and reverse Monte Carlo (RMC) simulations (Rai and Mountjoy, 2014; Schlenz *et al.*, 2002).

Clarity on the structure of glasses in the BaO-SiO₂ system mainly come from the MD simulations of Rai and Mountjoy (2014) covering the compositions *x*BaO-(1-*x*)SiO₂ (*x* = 0.25, 0.333, 0.4 and 0.5). They found an invariant Si-O bond length of 1.59 Å between 25BaO · 75SiO₂ and 50BaO · 50SiO₂ (Rai and Mountjoy, 2014). A Ba-O bond length of 2.79 Å was found for the nearest neighbor oxygen atoms which is comparable to the 2.76 Å found previously (Hasegawa and Yasui, 1987). The Qⁿ distribution for BaSi₂O₅ of Q¹⁻⁴ was found to be 4.2, 20.4, 43.6, 31.1 (Rai and Mountjoy, 2014), respectively, which is in line with previous MD results which found Q⁰⁻⁴ to be 1, 7, 28.9, 45.2, 17.9 (Schlenz *et al.*, 2002). However, these Qⁿ distributions are considerably broader than experimentally determined Q²⁻⁴ contents found to be 24, 62, and 14, respectively (Schneider *et al.*, 2003). The connectivity of Ba-silicate glasses in the phase separation region at BaO contents of 26.7% and 27.5% found Q³ and Q⁴ proportions of 72.8% and 27.2% and 75.7% and 24.3%, respectively (Baltisberger *et al.*, 2016). These results differ strongly from the MD simulations of the 25 mol% BaO silicate glass which found Q¹⁻⁴ contents of 1.1, 11, 42, and 45.8, respectively (Rai and Mountjoy, 2014), indicating that the former glasses likely suffered phase separation.

The local Ba environment was also investigated by Rai and Mountjoy (2014). The Ba-O distribution shows no absolute minimum between the first and second spheres and therefore, CN_{Ba} was determined using a cutoff of 3.3 Å. CN_{Ba} was found to increase from 6.5 to 6.8 for BaO compositions from 25 to 33 mol% (Rai and Mountjoy, 2014). CN_{Ba} appears to remain constant at 6.8 ± 0.1 up to 50 mol% BaO (Rai and Mountjoy, 2014). This negligible change in CN_{Ba} (Fig. 5) contrasts with CN_{Ca} which showed a monotonic increase, albeit at much higher MO contents (Cormier and Cuello, 2013) and appears to indicate that the large size of the Ba cations imposes a steric limit to its coordination. In fact, for all compositions from 25 to 50 mol% BaO, the Ba-O-Ba connectivity (Fig. 7) was found as continuous channels throughout the network with no indication of phase separation or cluster formation (Rai and Mountjoy, 2014). The role of Ba in the silicate-based glasses remains poorly constrained, especially in relation to MAE effects.

There are many studies of how the AE cations substitute into silicate-based glasses. These studies primarily focus on the MME (Na, K, Ca, Ba – Bäck *et al.*, 2019; Na-Ca-Ba – Lee *et al.*, 2003; Na-Mg – Trcera *et al.*, 2009, 2011a,b; K-Ca-Cs – Zhang *et al.*, 2014) and on substitution of Si for other network formers such as B, Al, Ge, Ti (Ali and Jonson, 2011; Angeli *et al.*, 2012; Majérus *et al.*, 2004; Möncke *et al.*, 2009; Neuville *et al.*, 2008, 2010).

Physical Properties

The common physical properties of binary silicate glasses have a long history that was largely established by the end of the last century. For a concise and cogent overview of essential properties (e.g., density, heat capacity, refractive index, durability,

toughness, strength, etc.) the Handbook of Glass Properties by [Bansal and Doremus \(1986\)](#) is excellent. The seminal works of Bockris, Bottinga, Richet and colleagues should be consulted ([Bockris *et al.*, 1955](#); [Tomlinson *et al.*, 1958](#); [Bottinga and Weill, 1970](#)). For an updated view the reader should consult glass science textbooks: [Shelby \(2005\)](#); [Mauro and Varshneya \(2019\)](#); [Mysen and Richet \(2019\)](#). A list of international databases can be found in the “Relevant Websites section”. Historically, the most important property database has been the SciGlass database which currently consists of 420,000 glass entries, of a wide range of compositions and their properties. The SciGlass database was initiated as the Handbook of Glass Data by [Mazurin *et al.* \(1983\)](#) and is now freely downloadable (see “Relevant Websites section”).

Applications

Silicate-based glasses and glass-ceramics have three main facets that make them advantageous over many other materials: (1) their compositional and corresponding property ranges; (2) their ability to crystallize (e.g., the formation of micro-textured glass-ceramics); (3) the ability to add small amounts of dopants (e.g., 0.5 wt% TiO_2) to the starting composition that may add new properties (e.g., optical, magnetic) in phenomenal fashion. Varying the composition, microtexture and dopants allows manufacturers to adjust the thermal, chemical, mechanical, optical, biological, electrical and magnetic properties to tailor glasses and glass-ceramics for application in essentially every major industry. In many cases there is no material available other than glasses and glass-ceramics, that can be formed and temporarily deformed without forming pores, defects or being permanently damaged.

The discussion below is meant to highlight entry points into the vast literature on applications. For an introduction to binary and more complex silicate-based glasses, glass-ceramics and their applications the reader is referred to the influential work of [Stookey \(1959\)](#) and [Gaskell \(1997\)](#), as well as the volumes by [Lewis \(1989\)](#), [Shelby \(2005\)](#), [Höland and Beall \(2012\)](#), [Mauro and Varshneya \(2019\)](#) or [Goldstein *et al.* \(2020\)](#). The trade-names and compositions of the most important silicate-based commercial glasses can be found in the latter four books.

The important industrial applications can be broadly divided into four categories: materials for building and construction (e.g., cement, tiles, glazes), mechanical applications (e.g., solid oxide fuel cell sealants, armor), medical applications (e.g., implants, dental) and optical-electrical or magnetic devices (e.g., light emitting diode materials, memory devices, lasers). There are few direct applications of simple binary alkali- or alkaline-earth silicate glasses. However, $\text{Li}_2\text{O}-2\text{SiO}_2$ and $\text{BaO}-2\text{SiO}_2$ (see above) have long been important due to the dopants known to enhance their properties. In addition, SiO_2 -rich glasses and the $\text{MgO}-\text{SiO}_2$, $\text{CaO}-\text{SiO}_2$ and $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ systems have been widely used in industry, especially where they have been mixed with Al_2O_3 . This should make obvious the importance of phase separation as it is common in silica-rich glass compositions whereas the MME phenomenon is fundamental in soda-lime-based silicate glasses which constitute the majority of industrial glass production.

The $\text{CaO}-\text{SiO}_2$ system is among the most important industrial systems because of its relevance to cement production where Ca_3SiO_5 and Ca_2SiO_4 and their hydrous and amorphous by-products are crucial components ([Adu-Amankwah *et al.*, 2017](#); [Pioro and Pioro, 2004](#)). Silicate-based mixtures where various combinations of CaO , MgO , Al_2O_3 , B_2O_3 , K_2O , ZnO , Fe_2O_3 , Li_2O , and TiO_2 are found, form the base ingredients of the most common ceramic tiles and glazes used worldwide for over three millennia ([Casasola *et al.*, 2012](#)). The Ca_3SiO_5 and Ca_2SiO_4 phases have been used in dental applications as a standard material for pulp capping due to their antimicrobial attributes and ability to bind with dentine ([Choi *et al.*, 2019](#)). However, more commonly Li_2O -based silicate glasses and glass-ceramics are used due to their favorable translucency (capable of producing a tooth-like appearance), strength, fracture toughness, machinability and chemical durability ([Montazerian and Zanotto, 2017](#)).

Bio-active glasses have a more recent history and are based on mixtures rich in SiO_2 , Na_2O , CaO and P_2O_5 with varying minor components in order to produce durable, chemically and biologically inert glass-ceramics that will bind to bone as implants ([Crovace *et al.*, 2016](#)). These bioglasses have seen intense interest especially in the last decade in medical applications as they can be designed as long lasting or temporary implants that dissolve as the healing process takes place (e.g., [Rahaman *et al.*, 2011](#); [Zheng *et al.*, 2019](#)). In nature, radiolarians draw silica from seawater to form intricate scaffold designs. This means that manipulation of silica-based materials is possible at low temperature. The possibility of low temperature applications has led several groups to pursue these reactions as an alternative synthesis pathway ([Gordon *et al.*, 2009](#)).

Low concentration dopants have at least two crucial effects on glass: (1) to permit volume nucleation, and (2) to promote optical or magnetic properties. Volume nucleation is essential to produce homogeneous crystallization throughout the glass so that properties may be consistent and reliable. An intergrown distribution of acicular crystals is highly desirable to deflect and distribute stresses so that the fracture toughness of glass-ceramics is increased. Combinations of rare-earth element and transition metal dopants in silicate-based glasses have been extensively investigated for use as fiber optic lasers ([Dragic *et al.*, 2018](#)), in optical storage devices ([Lin *et al.*, 2019](#)), in light emitting diode and luminescence materials ([Liu *et al.*, 2018](#)), and as transparent windows, especially for infrared and microwave applications ([Xiao *et al.*, 2020](#)). Finally, ion-exchange glasses and glass-ceramics are produced where a small alkali, such as Li_2O or Na_2O , is substituted for a large one in $\text{M}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ -based glasses ([Beall *et al.*, 2016](#)). Ion-exchange glasses have been used in billions of smartphones in the last decade. When large alkalis are inserted into the glass network, compressive stresses are formed that result in a tougher and stronger glass. More recently, ion exchange glass-ceramics are being pursued as the ion exchange process can induce favorable amorphization and phase changes which open new possible applications beyond that of the original glass ([Beall *et al.*, 2016](#)).

Concluding Remarks

Alkali and alkaline-earth silicate glasses are among the most studied glasses on the earth due to their important chemical and physical properties which make these systems relevant to both volcanology and petrology as well as glass and materials science. At high silica contents, phase separation is an important process that is used to produce low thermal expansion cookware among many other products. More generally, phase separation is a fundamental process that occurs in magmas and results in some of the largest ore deposits on Earth. When mixed together, the mixed alkali effect induces non-linear behavior in the properties that are important for increasing the strength and durability of the glasses. Though much less work has been done on alkaline-earth silicate glasses, they exhibit all of the features found in alkali silicate glasses. The alkali- and alkaline-earth-bearing silicate glasses remain the templates used to understand more complex silicate glasses, to understand the magmatic evolution of Earth and beyond, and to understand the glass-ceramics used every day of our lives.

References

- Adjaoud, O., Steinle-Neumann, G., Jahn, S., 2011. Transport properties of Mg_2SiO_4 liquid at high pressure: Physical state of a magma ocean. *Earth Planet. Sci. Lett.* 312, 463–470. doi:10.1016/j.epsl.2011.10.025.
- Adu-Amankwah, S., Zajac, M., Stabler, C., Lothenbach, B., Black, L., 2017. Influence of limestone on the hydration of ternary slag cements. *Cem. Concr. Res.* 100, 96–109. doi:10.1016/j.cemconres.2017.05.013.
- Al-Hasni, B.M., Mountjoy, G., 2014. A molecular dynamics study of the atomic structure of $x(\text{MgO})_{100-x}(\text{SiO}_2)$. *J. Non-Cryst. Solids* 400, 33–44. doi:10.1016/j.jnoncrsol.2013.11.011.
- Ali, S., Jonson, B., 2011. Compositional effects on the properties of high nitrogen content alkaline-earth silicon oxynitride glasses, $\text{AE} = \text{Mg, Ca, Sr, Ba}$. *J. Eur. Ceram. Soc.* 31, 611–618. doi:10.1016/j.jeurceramsoc.2010.11.005.
- Angeli, F., Villain, O., Schuller, S., Ispas, S., Charpentier, T., 2011. Insight into sodium silicate glass structural organization by multinuclear NMR combined with first-principles calculations. *Geochim. Cosmochim. Acta* 75, 2453–2469.
- Angeli, F., Villain, O., Schuller, S., *et al.*, 2012. Effect of temperature and thermal history on borosilicate glass structure. *Phys. Rev. B Condens. Matter Mater. Phys.* 85, 1–15.
- Bäck, L.G., Ali, S., Karlsson, S., *et al.*, 2019. Mixed alkali/alkaline-earth-silicate glasses: Physical properties and structure by vibrational spectroscopy. *Int. J. Appl. Glass Sci.* 10, 349–362. <https://onlinelibrary.wiley.com/doi/abs/10.1111/ijag.13101>.
- Bakk, I.P., Deme, I., Szieberth, D., Nyulászi, L., 2012. Molecular level investigation of the dynamic structure model in molten and solid alkali glasses. *Struct. Chem.* 23, 1729–1738.
- Baltisberger, J.H., Florian, P., Keeler, E.G., *et al.*, 2016. Modifier cation effects on ^{29}Si nuclear shielding anisotropies in silicate glasses. *J. Magn. Reson.* 268, 95–106. doi:10.1016/j.jmr.2016.05.003.
- Bancroft, G.M., Nesbitt, H.W., Henderson, G.S., *et al.*, 2018. Lorentzian dominated lineshapes and linewidths for Raman symmetric stretch peaks ($800\text{--}1200\text{ cm}^{-1}$) in Q^n ($n=1\text{--}3$) species of alkali silicate glasses/melts. *J. Non. Cryst. Solids* 484, 72–83.
- Bansal, N.P., Doremus, R.H., 1986. *Handbook of Glass Properties*. Toronto: Academic Press Inc, p. 680.
- Baral, K., Li, A., Ching, W.-Y., 2017. Ab initio modeling of structure and properties of single and mixed alkali silicate glasses. *J. Phys. Chem. A* 121, 7697–7708. doi:10.1021/acs.jpca.7b06530.
- Baral, K., Li, A., Ching, W.-Y., 2019. Understanding the atomistic origin of hydration effects in single and mixed bulk alkali-silicate glasses. *J. Am. Ceram. Soc.* 102, 207–221.
- Bauchy, M., Micoulaut, M., 2011. From pockets to channels: Density controlled diffusion in sodium silicates. *Phys. Rev. B* 83, 184118.
- Beall, G.H., Comte, M., Dejneka, M.J., *et al.*, 2016. Ion-exchange in glass-ceramics. *Front. Mater.* 3, 1–11.
- Bender, S., Franke, R., Hartmann, E., *et al.*, 2002. X-ray absorption and photoemission electron spectroscopic investigation of crystalline and amorphous barium silicates. *J. Non-Cryst. Solids* 298, 99–108.
- Binsted, N., Greaves, G.N., Henderson, C.M.B., 1985. An EXAFS study of glassy and crystalline phases of compositions $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite) and $\text{CaMgSi}_2\text{O}_6$ (diopside). *Contrib. Mineral. Petrol.* 89, 103–109.
- Bockris, J.O., Mackenzie, J.D., Kitchener, J.A., 1955. Viscous flow in silica and binary liquid silicates. *Trans. Faraday Soc.* 51, 1734–1748.
- Borisova, N.V., Ushakov, V.M., 1998. High temperature calorimetry of glasses and crystals in the $\text{K}_2\text{O-SiO}_2$ system. *Glass Phys. Chem.* 24, 318–322.
- Bottinga, Y., Weill, D.F., 1970. Densities of liquid silicate systems calculated from partial molar volumes of oxide components. *Am. J. Sci.* 269, 169–182.
- Bowen, N.L., Andersen, O., 1914. The binary system MgO-SiO_2 . *Am. J. Sci.* s4-37, 487–500. Available at: <http://www.ajsonline.org/cgi/doi/10.2475/ajs.s4-37.222.487>.
- Brandriss, M.E., Stebbins, J.F., 1988. Effects of temperature on the structures of silicate liquids: ^{29}Si NMR results. *Geochim. Cosmochim. Acta* 52, 2659–2669. doi:10.1016/0016-7037(88)90034-8.
- Brown, I.D., Altermatt, D., 1985. Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr. Sect. B Struct. Sci.* 41, 244–247. doi:10.1107/2F0108768185002063.
- Buchner, S., Pereira, A.S., Lima, J.C., Balzaretti, N.M., 2014. X-ray study of lithium disilicate glass: High pressure densification and polymorphism. *J. Non-Cryst. Solids* 387, 112–116.
- Bunde, A., Ingram, M.D., Russ, S., 2004. A new interpretation of the dynamic structure model of ion transport in molten and solid glasses. *Phys. Chem. Chem. Phys.* 6, 3663–3668.
- Bykov, K.N., Osipov, A.A., Anfilogov, V.N., 2000. Structural study of rubidium and caesium silicate glasses by Raman spectroscopy. *Phys. Chem. Glasses* 41, 10–11.
- Calahorra, C., Zwanziger, J.W., 2017. The mixed modifier effect in ionic conductivity and mechanical properties for $x\text{MgO}-(50-x)\text{CaO}-50\text{SiO}_2$ glasses. *J. Non-Cryst. Solids* 460, 6–18.
- Casasola, R., Rincón, J.M., Romero, M., 2012. Glass-ceramic glazes for ceramic tiles: A review. *J. Mater. Sci.* 47, 553–582.
- Charles, R.J., 1966. Metastable liquid immiscibility in alkali metal oxide-silica systems. *J. Am. Ceram. Soc.* 49, 55–62.
- Charlier, B., 2015. Stable and metastable silicate liquid immiscibility in ferrobasalts. *Am. Mineral.* 100, 2367–2368.
- Charlier, B., Namur, O., Toplis, M.J., *et al.*, 2011. Large-scale silicate liquid immiscibility during differentiation of tholeiitic basalt to granite and the origin of the Daly gap. *Geology* 39 (10), 907–910.
- Charpentier, T., Menziani, M.C., Pedone, A., 2013. Computational simulations of solid state NMR spectra: A new era in structure determination of oxide glasses. *RSC Adv.* 3, 10550–10578.
- Choi, H.W., Um, S.H., Rhee, S.H., 2019. Synthesis of a $\text{Ca}_3\text{SiO}_5\text{--Ca}_2\text{SiO}_4\text{--Ca}_3\text{Al}_2\text{O}_6$ cement system with rapid setting capacity by spray-pyrolysis coupled with sol-gel method. *J. Biomed. Mater. Res. Part B Appl. Biomater.* 107, 1440–1451.
- Clare, A.G., Wright, A.C., Sinclair, R.N., 1997. A comparison of the structural role of Na^+ network modifying cations in sodium silicate and sodium fluoroberyllate glasses. *J. Non-Cryst. Solids* 213–214, 321–324.

- Cooney, T.F., Sharma, S.K., 1990. Structure of glasses in the systems $\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$, $\text{Mn}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$, $\text{Mg}_2\text{SiO}_4\text{-CaMgSiO}_4$, and $\text{Mn}_2\text{SiO}_4\text{-CaMnSiO}_4$. *J. Non-Cryst. Solids* 122, 10–32.
- Cormier, L., Cuello, G.J., 2011. Mg coordination in a MgSiO_3 glass using neutron diffraction coupled with isotopic substitution. *Phys. Rev. B Condens. Matter Mater. Phys.* 83, 224204. <https://link.aps.org/doi/10.1103/PhysRevB.83.224204>.
- Cormier, L., Cuello, G.J., 2013. Structural investigation of glasses along the $\text{MgSiO}_3\text{-CaSiO}_3$ join: Diffraction studies. *Geochim. Cosmochim. Acta* 122, 498–510.
- Cormier, L., Gaskell, P.H., Creux, S., 1999. Comparison of the low-Q features in diffraction data for silicate glasses and crystals containing Sr or Ba. *J. Non-Cryst. Solids* 248, 84–91.
- Crovace, M.C., Souza, M.T., Chinaglia, C.R., Peiti, O., Zanotto, E.D., 2016. Biosilicate® – A multipurpose, highly bioactive glass-ceramic. In vitro, in vivo and clinical trials. *J. Non-Cryst. Solids* 432, 90–110. doi:10.1016/j.jnoncrysol.2015.03.022.
- Davis, M.C., Sanders, K.J., Grandinetti, P.J., Gaudio, S.J., Sen, S., 2011. Structural investigations of magnesium silicate glasses by ^{29}Si 2D Magic-Angle Flipping NMR. *J. Non-Cryst. Solids* 357, 2787–2795. doi:10.1016/j.jnoncrysol.2011.02.045.
- Davis, M.C., Kaseman, D.C., Parvani, S.M., *et al.*, 2010. $Q^{(n)}$ species determination in $\text{K}_2\text{O-2SiO}_2$ glass by ^{29}Si magic angle flipping NMR. *J. Phys. Chem. A* 114, 5503–5508.
- de Jong, B.H.W.S., Keefer, K.D., Brown Jr, G.E., Taylor, C.M., 1981. X-ray study of lithium disilicate glass: High pressure densification and polymorphism. *Geochim. Cosmochim. Acta* 45, 1291–1308.
- De Koker, N.P., Stixrude, L., Karki, B.B., 2008. Thermodynamics, structure, dynamics and freezing of Mg_2SiO_4 liquid at high pressure. *Geochim. Cosmochim. Acta* 72, 1427–1441.
- Deubener, J., 2005. Structural aspects of volume nucleation in silicate glasses. *J. Non-Cryst. Solids* 351, 1500–1511.
- Ding, Z., Wilkinson, C.J., Zheng, J., *et al.*, 2020. Topological understanding of the mixed alkaline-earth effect in glass. *J. Non-Cryst. Solids* 527, 119696.
- Dragic, P.D., Cavillon, M., Ballato, J., 2018. Materials for optical fiber lasers: A review. *Appl. Phys. Rev.* 5, 041301. doi:10.1063/1.5048410.
- Du, J., Cormack, A.N., 2004. The medium range structure of sodium silicate glasses: A molecular dynamics simulation. *J. Non-Cryst. Solids* 323, 66–79.
- Du, J., Corrales, L.R., 2006. Structure, dynamics and electronic properties of lithium disilicate melt and glass. *J. Chem. Phys.* 125, 114702. doi:10.1063/1.2345060.
- Dupree, R., Holland, D., Williams, D.S., 1986. The structure of binary alkali silicate glasses. *J. Non-Cryst. Solids* 81, 185–200.
- Dupree, R., Holland, D., Mortuza, M.G., 1990. A MAS NMR investigation of lithium silicate-glasses and glass-ceramics. *J. Non-Cryst. Solids* 116, 148–160.
- Eckersley, M.C., Gaskell, P.H., Barnes, A.C., Chieux, P., 1988. Structural ordering in a calcium silicate glass. *Nature* 335, 525–527.
- Eckert, H., 2018. Spying spins on messy materials: 60 years of glass structure elucidation by NMR spectroscopy. *Int. J. Appl. Glass Sci.* 9, 167–187.
- Etchepare, J., 1970. Interprétation des spectres de diffusion Raman de verres de silice binaires. *Spectrochim. Acta Part A mol Spectrosc.* 26, 2147–2154.
- Fokin, V.M., Abyzov, A.S., Zanotto, E.D., *et al.*, 2016. Crystal nucleation in glass-forming liquids: Variation of the size of the “structural units” with temperature. *J. Non-Cryst. Solids* 447, 35–44.
- Franz, J.D., Mysen, B.O., 1995. The Raman spectra and structure of BaO-SiO_2 , SrO-SiO_2 and CaO-SiO_2 melts at 1600°C. *Chem. Geol.* 121, 155–175.
- Gagné, O.C., Hawthorne, F.C., 2016. Bond-length distributions for ions bonded to oxygen: Alkali and alkaline-earth metals. *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.* 72, 602–625.
- Gaskell, D.R., 1982. The densities and structures of silicate melts. In: Saxena, S.K. (Ed.), *Advances in Physical Geochemistry 2*. New York: Springer-Verlag, pp. 153–171.
- Gaskell, P.H., 1997. Structure and properties of glasses – How far do we need to go? *J. Non-Cryst. Solids* 222, 1–12.
- Gaskell, P.H., Eckersley, M.C., Barnes, A.C., Chieux, P., 1991. Medium-range order in the cation distribution of a calcium silicate glass. *Nature* 350, 675–677. doi:10.1038/350675a0.
- Geere, R.G., Gaskell, P.H., Greaves, G.N., Greengrass, J., Binstead, N., 1983. EXAFS and XANES spectra of calcium silicate glasses. In: Bianconi, A., *et al.* (Eds.), *EXAFS and Near-Edge Structure*. Heidelberg: Springer-Verlag, pp. 256–260.
- George, A.M., Stebbins, J.F., 1998. Structure and dynamics of magnesium in silicate melts: A high-temperature ^{25}Mg NMR study. *Am. Mineral.* 83, 1022–1029.
- Ghosh, D.B., Karki, B.B., Stixrude, L., 2014. First-principles molecular dynamics simulations of MgSiO_3 glass: Structure, density, and elasticity at high pressure. *Am. Mineral.* 99, 1304–1314.
- Gibbs, G.V., 1982. Molecules as models for bonding in silicate. *Am. Mineral.* 67, 421–450.
- Gibbs, G.V., Hill, F.C., Boison Jr, M.B., 1997. The SiO bond and electron density distributions. *Phys. Chem. Miner.* 24, 167–1781.
- Gibbs, G.V., Downs, R.T., Cox, D.F., *et al.*, 2008. Bonded interactions and crystal chemistry of minerals: A review. *Z. Kristallogr.* 223, 1–40.
- Goldstein, A., Krell, A., Burshtein, Z., 2020. *Transparent Ceramics*. Hoboken, NJ: John Wiley and Sons, Inc, p. 362.
- Gordon, R., Losic, D., Tiffany, M.A., Nagy, S.S., Sterrenburg, F.A.S., 2009. The glass menagerie: Diatoms for novel applications in nanotechnology. *Trends Biotechnol* 27, 116–127.
- Gorelova, L.A., Bubnova, R.S., Krivovichev, S.V., Krzhizhanovskaya, M.G., Filatov, S.K., 2016. Thermal expansion and structural complexity of Ba silicates with tetrahedrally coordinated Si atoms. *J. Solid State Chem.* 235, 76–84. doi:10.1016/j.jssc.2015.12.012.
- Gránásky, L.G., Wang, T., James, P.F., 1998. Kinetics of wollastonite nucleation in CaO-SiO_2 glass. *J. Chem. Phys.* 108, 7317. doi:10.1063/1.476150.
- Greaves, G.N., 1985. EXAFS and the structure of glass. *J. Non-Cryst. Solids* 71, 203–217.
- Greaves, G.N., 2021. The extended structure of glass. In: Richet, P., (Ed), *Encyclopedia of Glass Science, Technology, History, and Culture*. J Wiley and Sons, Hoboken, NJ.
- Greaves, G.N., Fontaine, A., Lagarde, P., Raoux, D., Gurman, S.J., 1981. Local structure of silicate glasses. *Nature* 293, 611–616.
- Grebenshchikov, R.G., Toropov, N.A., 1962. New data on the barium oxide-silica phase diagram. *Bull. Acad. Sci. USSR Div. Chem. Sci.* 11 (4), 503–509.
- Greig, J.W., 1927. Immiscibility in silicate melts. *Am. J. Sci.* 13 (73), 1–44. doi:10.2475/ajs.s5-13.73.1.
- Grimmer, A.R., Mägi, M., Hahnert, M., *et al.*, 1984. High resolution solid state Si-29 nuclear magnetic resonance spectroscopic studies of binary alkali silicate-glasses. *Phys. Chem. Glasses* 25, 105–109.
- Gueguen, Y., Houizot, P., Célarie, F., *et al.*, 2017. Structure and viscosity of phase-separated BaO-SiO_2 glasses. *J. Am. Ceram. Soc.* 100 (5), 1982–1993.
- Gupta, Y.P., Mishra, U.D., 1969. Electrical conduction and electron microscopy of vitreous solids in the $\text{K}_2\text{O-SiO}_2$ system. *J. Phys. Chem. Solids* 30, 1327–1334.
- Haller, W., Blackburn, D.H., Simmons, J.H., 1974. Miscibility gaps in alkali-silicate binaries-Data and thermodynamic interpretation. *J. Am. Ceram. Soc.* 57, 120–126.
- Hannon, A.C., Vessal, B., Parker, J.M., 1992. The structure of alkali silicate glasses. *J. Non-Cryst. Solids* 150, 97–102.
- Hasegawa, H., Yasui, I., 1987. X-ray and neutron diffraction analyses of barium silicate glass. *J. Non Cryst. Solids* 95–96, 201–208. doi:10.1016/2F50022-3093/2887/2980111-4.
- Hazen, R.M., Yang, H., Finger, L.W., Fursenko, B.A., 1999. Crystal chemistry of high-pressure BaSi_4O_9 in the trigonal (P3) barium tetragermanate structure. *Am. Mineral.* 84, 987–989.
- Henderson, G.S., 1995. A Si *K*-edge EXAFS/XANES study of sodium silicate glasses. *J. Non-Cryst. Solids* 183, 43–50.
- Henderson, G.S., 2005. The structure of silicate melts: A glass perspective. *Can. Mineral.* 43, 1921–1958.
- Henderson, G.S., Stebbins, J.F., 2021. The short-range order (SRO and structure), *Rev. Miner. Geochem* 87.
- Henderson, G.S., Fleet, M.E., Bancroft, G.M., 1984. An X-ray scattering study of vitreous KFeSi_3O_8 and $\text{NaFeSi}_3\text{O}_8$ and reinvestigation of vitreous SiO_2 using quasi-crystalline modelling. *J. Non-Cryst. Solids* 68, 333–349.
- Herrmann, A., Simon, A., Rüssel, C., 2012. Preparation and luminescence properties of Eu^{2+} -doped BaSi_2O_5 glass-ceramics. *J. Lumin.* 132, 215–219.
- Hess, K., Dingwell, D.B., Webb, S.L., 1996. The influence of alkaline-earth oxides (BeO , MgO , CaO , SrO , BaO) on the viscosity of a haplogranitic melt: Systematics of non-Arrhenian behaviour. *Geochim. Cosmochim. Acta* 60 (13), 371–381.
- Höland, W., Beall, G.H., 2012. *Glass Ceramic Technology*, second ed. Hoboken, NJ: The American Ceramic Society, p. 440.

- Hoppe, U., Walter, G., Kranold, R., Stachel, D., Barz, A., 1995. The dependence of structural peculiarities in binary phosphate glasses on their network modifier content. *J. Non-Cryst. Solids* 192&193, 28–31.
- Hou, T., Veksler, I.V., 2015. Experimental confirmation of high-temperature silicate liquid immiscibility in multicomponent ferrobasic systems. *Am. Mineral.* 100, 1304–1307.
- Huang, C., Cormack, A.N., 1991. Structural differences and phase separation in alkali silicate glasses. *J. Chem. Phys.* 95 (5), 3634–3642.
- Huang, C., Cormack, A.N., 1992. Structure and energetics in mixed-alkali-metal silicate glasses from molecular dynamics. *J. Mater. Chem.* 2 (3), 281–287.
- Hudon, P., Baker, D.R., 2002a. The nature of phase separation in binary oxide melts and glasses. I. Silicate systems. *J. Non-Cryst. Solids* 303, 299–345.
- Hudon, P., Baker, D.R., 2002b. The nature of phase separation in binary oxide melts and glasses. II. Selective solution mechanism. *J. Non-Cryst. Solids* 303, 346–353.
- Hudon, P., Jung, I.-H., Baker, D.R., 2004. Effect of pressure on liquid-liquid miscibility gaps: A case study of the systems CaO-SiO₂, MgO-SiO₂ and CaMgSi₂O₆-SiO₂. *J. Geophys. Res.* 109, B03207.
- Hung, I., Gan, Z., Gorkov, P.L., *et al.*, 2016. Detection of “free” oxide ions in low-silica Ca/Mg silicate glasses: Results from ¹⁷O-²⁹Si HETCOR NMR. *J. Non-Cryst. Solids* 445–446, 1–6.
- Ildefonse, P., Calas, G., Flank, A.M., Lagarde, P., 1995. Low Z elements (Mg, Al and Si) K-edge X-ray absorption spectroscopy in minerals and disordered systems. *Nucl. Instrum. Methods Phys. Res. B* 97, 172–175.
- Ingram, M.D., 1987. Ionic-conductivity in glass. *Phys. Chem. Glasses* 28, 215–234.
- Ispas, S., Benoit, M., Jund, P., Jullien, R., 2001. Structural and electronic properties of the sodium tetrasilicate glass Na₂Si₄O₉ from classical and ab initio molecular dynamics simulations. *Phys. Rev. B* 64, 214206.
- Ispas, S., Charpentier, T., Mauri, F., Neuville, D.R., 2010. Structural properties of lithium and sodium tetrasilicate glasses: Molecular dynamics simulations versus NMR experimental and first-principles data. *Solid State Sci.* 12, 183–192.
- Iwamoto, N., Makino, Y., Kasahara, S., 1984. Correlation between refractive basicity and theoretical optical basicity. Part I. Alkaline and alkaline-earth silicate glasses. *J. Non-Cryst. Solids* 68, 379–388.
- Jabraoui, H., Vaills, Y., Hasnaoui, A., Badawi, M., Ouaskit, S., 2016. Effect of sodium oxide modifier on structural and elastic properties of silicate glass. *J. Phys. Chem. B* 120, 13193–13205.
- James, P.F., 1975. Liquid phase separation in glass-forming systems. *J. Mater. Sci.* 10, 1802–1825.
- Jardón-Álvarez, D., Sanders, K.J., Phyto, P., Baltisberger, J.H., Grandanetti, P.J., 2018. Cluster formation of network modifier cations in cesium silicate glasses. *J. Chem. Phys.* 148, 094502.
- Kalampounias, A.G., Nasikas, N.K., Papatheodorou, G.N., 2009. Glass formation and structure in the MgSiO₃–Mg₂SiO₄ pseudobinary system: From degraded networks to ionic like glasses. *J. Chem. Phys.* 131, 114513. doi:10.1063/1.3225431.
- Kamijo, N., Handa, K., Umesaki, N., 1996. Soft X-ray XAFS studies of the local structure of K₂O-SiO₂ glasses. *Mater. Trans. JIM* 37, 927–931.
- Kamitsos, E.I., Risen Jr, W.M., 1984. Vibrational spectra of alkali and mixed alkali pentasilicate glasses. *J. Non-Cryst. Solids* 65, 333–354.
- Kaseman, D.C., Retsinas, A., Kalampounias, A.G., Papatheodorou, G.N., Sen, S., 2015. Q-speciation and network structure evolution in invert calcium silicate glasses. *J. Phys. Chem. B* 119, 8440–8445.
- Kawamoto, Y., Tomozawa, M., 1981. Prediction of immiscibility boundaries of the systems K₂O-SiO₂, K₂O-Li₂O-SiO₂, K₂O-Na₂O-SiO₂, and K₂O-BaO-SiO₂. *J. Am. Ceram. Soc.* 64, 289–292.
- Kitamura, N., Fukumi, K., Mizoguchi, H., *et al.*, 2000. High pressure densification of lithium silicate glasses. *J. Non-Cryst. Solids* 274, 244–248.
- Kjeldsen, J., Smedskjaer, M.M., Mauro, J.C., Yue, Y., 2014. Hardness and incipient plasticity in silicate glasses: Origin of the mixed modifier effect. *Appl. Phys. Lett.* 104, 051913.
- Kohara, S., Suzuya, K., Takeuchi, K., *et al.*, 2004. Glass formation at the limit of insufficient network formers. *Science* 303, 1649–1652.
- Kroeker, S., Stebbins, J.F., 2000. Magnesium coordination environments in glasses and minerals: New insight from high field magnesium-25 MAS NMR. *Am. Mineral.* 85, 1459–1464.
- Lacey, E.D., 1963. Aluminum in glasses and melts. *Phys. Chem. Glasses* 4, 234–238.
- LaCourse, W.C., 1987. A defect model for the mixed alkali effect. *J. Non-Cryst. Solids* 95–96, 905–912.
- Le Losq, C., Cicconi, M.R., Greaves, G.N., Neuville, D.R., 2019. Chapter 13: Silicate glasses. In: Musgraves, J.D., Hu, J., Calvez, L. (Eds.), *Springer Handbook of Glass*. Springer Handbooks, Springer, pp. 441–503.
- Le Roux, S., Jund, P., 2010. Ring statistics analysis of topological networks: New approach and application to amorphous GeS₂ and SiO₂ systems. *Comput. Mater. Sci.* 49, 70–83. doi:10.1016/j.commatsci.2010.04.023.
- Le Roux, S., Jund, P., 2011. Erratum: Ring statistics analysis of topological networks: New approach and application to amorphous GeS₂ and SiO₂ systems [Comput. Mater. Sci. 49 (2010) 70–83]. *Comput. Mater. Sci.* 50, 1217.
- Lee, S.K., Stebbins, J.F., 2003. The distribution of sodium ions in aluminosilicate glasses: A high-field Na-23 MAS and 3Q MAS NMR study. *Geochim. Cosmochim. Acta* 67, 1699–1709.
- Lee, S.K., Stebbins, J.F., 2006. Disorder and the extent of polymerization in calcium silicate and aluminosilicate glasses: O-17 NMR results and quantum chemical molecular orbital calculations. *Geochim. Cosmochim. Acta* 70, 4275–4286.
- Lee, S.K., Stebbins, J.F., 2009. Effects of the degree of polymerization on the structure of sodium silicate and aluminosilicate glasses: An ¹⁷O NMR study. *Geochim. Cosmochim. Acta* 73, 1109–1119.
- Lee, S.K., Kim, E.J., 2015. Probing metal-bridging oxygen and configurational disorder in amorphous lead silicates: Insights from ¹⁷O solid-state nuclear magnetic resonance. *J. Phys. Chem. C* 119, 748–756. doi:10.1021/jp509780f.
- Lee, S.K., Mysen, B., Cody, G., 2003. Chemical order in mixed-cation silicate glasses and melts. *Phys. Rev. B* 68, 1–7. Available at: <http://link.aps.org/doi/10.1103/PhysRevB.68.214206>.
- Lee, S.K., Eng, P.J., Mao, H.K., 2014. Probing of pressure-induced bonding transitions in crystalline and amorphous earth materials: Insights from X-ray Raman scattering at high pressure. *Rev. Mineral. Geochem.* 78, 139–174.
- Levin, E.M., 1967. Structural interpretation of immiscibility in oxide systems: IV. Occurrence, extent, and temperature of the monotectic. *J. Am. Ceram. Soc.* 50, 29–38.
- Levin, E.M., Block, S., 1956. Structural interpretation of immiscibility in oxide systems: I. Analysis and calculation of immiscibility. *J. Am. Ceram. Soc.* 40, 95–106.
- Lewis, M.H., 1989. *Glasses and Glass-Ceramics*. Dordrecht: Springer Netherlands. <http://link.springer.com/10.1007/978-94-009-0817-8>.
- Li, D., Peng, M., Murata, T., 1999. Coordination and local structure of magnesium in silicate minerals and glasses: Mg K-edge XANES study. *Can. Mineral.* 37, 199–206.
- Lin, S., Lin, H., Huang, Q., *et al.*, 2019. A photostimulated BaSi₂O₅: Eu²⁺, Nd³⁺ phosphor-in-glass for erasable-rewritable optical storage medium. *Laser Photon. Rev.* 13, 1900006.
- Liu, X., Zhou, J., Zhou, S., Yue, Y., Qiu, J., 2018. Transparent glass-ceramics functionalized by dispersed crystals. *Prog. Mater. Sci.* 97, 38–96.
- Maekawa, H., Maekawa, T., Kawamura, K., Yokokawa, T., 1991. The structural groups of alkali silicate glasses determined from ²⁹Si MAS NMR. *J. Non-Cryst. Solids* 127, 53–64.
- Majerus, O., Cormier, L., Calas, G., Beuneu, B., 2004. A neutron diffraction study of temperature-induced structural changes in potassium disilicate glass and melt. *Chem. Geol.* 213, 89–102.
- Malfait, W.J., Zakaznova-Herzog, V.P., Halter, W.E., 2007a. Quantitative Raman spectroscopy: High-temperature speciation of potassium silicate melts. *J. Non-Cryst. Solids* 353, 4029–4042.

- Malfait, W.J., Halter, W.E., Morizet, Y., Meier, B.H., Verel, R., 2007b. Structural control on bulk melt properties: Single and double quantum ^{29}Si NMR spectroscopy on alkali silicate glasses. *Geochim. Cosmochim. Acta* 71, 6002–6018.
- Mastelaro, V.R., Zanotto, E.D., Lequeux, N., Cortès, R., 2000. Relationship between short-range order and ease of nucleation in $\text{Na}_2\text{Ca}_2\text{Si}_2\text{O}_9$, CaSiO_3 and PbSiO_3 glasses. *J. Non-Cryst. Solids* 262, 191–199.
- Matson, D.W., Sharma, S.K., Philpotts, J.A., 1983. The structure of high silica alkali-silicate glasses. A Raman spectroscopic investigation. *J. Non-Cryst. Solids* 58, 323–352.
- Matsui, M., 1996. Molecular dynamics simulation of structures, bulk moduli, and volume thermal expansivities of silicate liquids in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$. *Geophys. Res. Lett.* 23, 395–398.
- Mauro, J.C., Varshneya, A.K., 2019. *Fundamentals of Inorganic Glasses*. Elsevier, p. 735.
- Mazurin, O.V., Streltsina, M.V., Shvaiko-Shvaikovskaya, T.P., 1983. *Handbook of Glass Data*. New York: Elsevier, p. 669.
- McKeown, D.A., Kot, W.K., Pegg, I.L., 2003. X-ray absorption studies of the local strontium environments in borosilicate waste glasses. *J. Non-Cryst. Solids* 317, 290–300.
- Mead, R.N., Mountjoy, G., 2005. The structure of CaSiO_3 glass and the modified random network model. *Phys. Chem. Glasses* 46, 311–314.
- Mead, R.N., Mountjoy, G., 2006a. A molecular dynamics study of the atomic structure of $(\text{CaO})_x(\text{SiO}_2)_{1-x}$ glasses. *J. Phys. Chem. B* 110, 14273–14278.
- Mead, R.N., Mountjoy, G., 2006b. A molecular dynamics study of densification mechanisms in calcium silicate glasses CaSi_2O_5 and CaSiO_3 at pressures of 5 and 10 GPa. *J. Chem. Phys.* 125, 154501.
- Meneau, F., Greaves, G.N., Winter, R., Vaills, Y., 2001. WAXS and NMR studies of intermediate and short range order in $\text{K}_2\text{O-SiO}_2$ glasses. *J. Non-Cryst. Solids* 293–295, 693–699.
- Meyer, A., Horbach, J., Kolb, W., Kargl, F., Schober, H., 2004. Channel formation and intermediate range order in sodium silicate melts and glasses. *Phys. Rev. Lett.* 93, 027801.
- Misawa, M., Price, D.L., Suzuki, K., 1980. The short-range structure of alkali disilicate glasses by pulsed neutron total scattering. *J. Non-Cryst. Solids* 37, 85–97.
- Möncke, D., Dussauze, M., Kamitsos, E.I., Varsamis, C.P.E., Ertl, D., 2009. Thermal poling induced structural changes in sodium borosilicate glasses. *Phys. Chem. Glasses Eur. J. Glass Sci. Technol. Part B* 50, 229–235.
- Montazerian, M., Zanotto, E.D., 2017. Bioactive and inert dental glass-ceramics. *J. Biomed. Mater. Res. Part A* 105, 619–639.
- Moulton, B.J.A., Rodrigues, A.M., Pizani, P.S., Sampaio, D.V., Zanotto, E.D., 2018. A Raman investigation of the structural evolution of supercooled liquid barium disilicate during crystallization. *Int. J. Appl. Glass Sci.* 9, 510–517. <http://doi.wiley.com/10.1111/ijag.12356>.
- Moulton, B.J.A., Henderson, G.S., Fukui, H., *et al.*, 2016a. In situ structural changes of amorphous diopside ($\text{CaMgSi}_2\text{O}_6$) up to 20 GPa: A Raman and O K -edge X-ray Raman spectroscopic study. *Geochim. Cosmochim. Acta* 178, 41–61. doi:10.1016/j.gca.2016.01.020.
- Moulton, B.J.A., Henderson, G.S., Sonnevile, C., *et al.*, 2016b. The structure of haplobasaltic glasses investigated using X-ray absorption near edge structure (XANES) spectroscopy at the Si, Al, Mg, and O K -edges and Ca, Si, and Al $L_{2,3}$ -edges. *Chem. Geol.* 420, 213–230. doi:10.1016/j.chemgeo.2015.11.016.
- Moulton, B.J.A., Rodrigues, A.M., Sampaio, D.V., *et al.*, 2019. The origin of the unusual DSC peaks of supercooled barium disilicate liquid. *CrystEngComm* 21, 2768–2778. doi:10.1039/C8CE02054J.
- Mountjoy, G., 2007. The local environment of oxygen in silicate glasses from molecular dynamics. *J. Non-Cryst. Solids* 353, 1849–1853.
- Mozi, R.L., Warren, B.E., 1969. The structure of vitreous silica. *J. Appl. Cryst.* 2, 164–172.
- Mysen, B.O., Frantz, J.D., 1993. Structure and properties of alkali silicate melts at magmatic temperatures. *Eur. J. Mineral.* 5, 393–407.
- Mysen, B.O., Richet, P., 2019. *Silicate Glasses and Melts, Properties and Structure*, second ed. Amsterdam: Elsevier, p. 708.
- Mysen, B.O., Virgo, D., Seifert, F.A., 1982. The structure of silicate melts: Implications for chemical and physical properties of natural magma. *Rev. Geophys.* 20, 353–383.
- Nasikas, N.K., Edwards, T.G., Sen, S., Papatheodorou, G.N., 2012. Structural characteristics of novel Ca-Mg orthosilicate and suborthosilicate glasses: Results from ^{29}Si and ^{17}O NMR spectroscopy. *J. Phys. Chem. B* 116, 2696–2702.
- Nasikas, N.K., Chrissanthopoulos, A., Bouropoulos, N., Sen, S., Papatheodorou, G.N., 2011. Silicate glasses at the ionic limit: Alkaline-earth sub-orthosilicates. *Chem. Mater.* 23, 3692–3697. doi:10.1021/cm2012582.
- Nesbitt, H.W., Bancroft, G.M., Henderson, G.S., 2018. Temperature dependence of Raman shifts and line widths for Q^0 and Q^2 crystals of silicates, phosphates and sulfates. *Am. Mineral.* 103, 72–83.
- Nesbitt, H.W., Bancroft, G.M., Henderson, G.S., 2020. Polymerization during melting of ortho- and meta-silicates: Effects of Q species stability, heats of fusion, and redox state of mid-ocean range basalts (MORBs). *Am. Mineral.* 105, 716–726.
- Nesbitt, H.W., Henderson, G.S., Bancroft, G.M., Ho, R., 2015a. Experimental evidence for Na coordination to bridging oxygen in Na-silicate glasses: Implications for spectroscopic studies and for the modified random network model. *J. Non-Cryst. Solids* 409, 139–148.
- Nesbitt, H.W., Bancroft, G.M., Henderson, G.S., Sawyer, R., Secco, R., 2015b. Direct and indirect evidence for free oxygen (O^{2-}) in MO-silicate glasses. *Am. Mineral.* 100, 2566–2578.
- Nesbitt, H.W., Bancroft, G.M., Henderson, G.S., Richet, P., O'Shaughnessy, C., 2017b. Silicate mineral melting, crystallization and the glass transition: Toward a unified description for silicate phase transitions. *Am. Mineral.* 102, 412–420.
- Nesbitt, H.W., Henderson, G.S., Bancroft, G.M., Sawyer, R., Secco, R.A., 2017c. Bridging oxygen speciation in K-silicate glasses and melts, with implications for spectroscopic studies and glass structure. *Chem. Geol.* 461, 13–22.
- Nesbitt, H.W., Bancroft, G.M., Henderson, G.S., *et al.*, 2011. Bridging, non-bridging and free (O^{2-}) oxygen in $\text{Na}_2\text{O-SiO}_2$ glasses: An X-ray photoelectron spectroscopic (XPS) and nuclear magnetic resonance (NMR) study. *J. Non-Cryst. Solids* 357, 170–180.
- Neufeld, J., Liss, K.D., 1996. Bond angle distribution in amorphous germania and silica. *Ber. Bunsenges. Phys. Chem.* 100, 1341–1349.
- Neuvile, D.R., 2006. Viscosity, structure and mixing in (Ca, Na) silicate melts. *Chem. Geol.* 229, 28–41.
- Neuvile, D.R., Henderson, G.S., Cormier, L., Massiot, D., 2010. The structure of crystals, glasses, and melts along the $\text{CaO-Al}_2\text{O}_3$ join: Results from Raman, Al L - and K -edge X-ray absorption, and ^{27}Al NMR spectroscopy. *Am. Mineral.* 95, 1580–1589.
- Neuvile, D.R., Cormier, L., Montouillout, V., *et al.*, 2008. Structure of Mg- and Mg/Ca aluminosilicate glasses: ^{27}Al NMR and Raman spectroscopy investigations. *Am. Mineral.* 93, 1721–1731.
- Novikov, A.N., Neuvile, D.R., Hennem, L., *et al.*, 2017. Al and Sr environment in tectosilicate glasses and melts: Viscosity, Raman and NMR investigation. *Chem. Geol.* 461, 115–127. doi:10.1016/j.chemgeo.2016.11.023.
- O'Shaughnessy, C., Henderson, G.S., Nesbitt, H.W., Bancroft, G.M., Neuvile, D.R., 2017. The structure of cesium silicate glasses and liquids. *Chem. Geol.* 461, 82–95.
- O'Shaughnessy, C., Henderson, G.S., Nesbitt, H.W., Bancroft, G.M., Neuvile, D.R., 2020. The influence of modifier cations on the Raman stretching modes of Q^0 species in alkali silicate glasses. *J. Am. Ceram. Soc.* 103, 3991–4001.
- Oehlschlegel, G., 1975. Crystallization of glasses in the system $\text{BaO} \cdot 2\text{SiO}_2$ – $2\text{BaO} \cdot 3\text{SiO}_2$. *J. Am. Ceram. Soc.* 58, 148.
- Olivier, L., Yuan, X., Cormack, A.N., Jäger, C., 2001. Combined ^{29}Si double quantum NMR and MD simulation studies of network connectivities of binary $\text{Na}_2\text{O} \cdot \text{SiO}_2$ glasses: New prospects and problems. *J. Non-Cryst. Solids* 293–295, 53–66.
- Otonello, G., Attene, M., Ameglio, D., *et al.*, 2013. Thermodynamic investigation of the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system at high P and T through polymer chemistry and convex-hull techniques. *Chem. Geol.* 346, 81–92. doi:10.1016/j.chemgeo.2012.09.018.
- Pant, A.K., Cruickshank, D.W.J., 1968. The crystal structure of $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$. *Acta Crystallogr. B* 24, 13–19.
- Pedone, A., Charpentier, T., Menziani, M.C., 2010. Multinuclear NMR of CaSiO_3 glass: Simulation from first-principles. *Phys. Chem. Chem. Phys.* 12, 6054–6066.
- Piatak, N.M., Seal, R.R., Hoppe, D.A., Green, C.J., Buszka, P.M., 2019. Geochemical characterization of iron and steel slag and its potential to remove phosphate and neutralize acid. *Minerals* 9, 1–26.

- Piolo, L.S., Piolo, I.L., 2004. Reprocessing of metallurgical slag into materials for the building industry. *Waste Manag.* 24, 371–379.
- Rahaman, M.N., Day, D.E., Sonny Bal, B., *et al.*, 2011. Bioactive glass in tissue engineering. *Acta Biomater.* 7, 2355–2373. doi:10.1016/j.actbio.2011.03.016.
- Rai, M., Mountjoy, G., 2014. Molecular dynamics modelling of the structure of barium silicate glasses BaO-SiO₂. *J. Non-Cryst. Solids* 401, 159–163. doi:10.1016/j.jnoncrysol.2013.12.026.
- Railsback, L.B., 2003. An earth scientist's periodic table of the elements and their ions. *Geology* 31, 737.
- Ramsden, A.H., James, P.F., 1984. The effects of amorphous phase separation on crystal nucleation kinetics in BaO-SiO₂ glasses – Part 1. General survey. *J. Mater. Sci.* 19, 1406–1419. doi:10.1007/BF00563035.
- Retsinas, A., Kalampounias, A.G., Papatheodorou, G.N., 2014. Reaching the ionic limit in the (1-X)[Ca_{0.5}-Mg_{0.5}]O-XSiO₂ pseudo binary glass system with 0.5 < X < 0.27: Glass formation and structure. *J. Non-Cryst. Solids* 383, 38–43. doi:10.1016/j.jnoncrysol.2013.04.008.
- Richet, P., Bottinga, Y., 1986. Thermochemical properties of silicate glasses and liquids: A review. *Rev. Geophys.* 24, 1–25.
- Richet, P., Mysen, B.O., Andrault, D., 1996. Melting and premelting of silicates: Raman spectroscopy and X-ray diffraction of Li₂SiO₃ and Na₂SiO₃. *Phys. Chem. Minerals* 23, 157–172.
- Riebling, E.F., Duke, D.A., 1967. BeO · Al₂O₃ · SiO₂ system: Structural relationships of crystalline, glassy, and molten beryl. *J. Mater. Sci.* 2, 33–39.
- Rodrigues, A.M., Cassar, D.R., Fokin, V.M., Zanotto, E.D., 2018. Crystal growth and viscous flow in barium disilicate glass. *J. Non-Cryst. Solids* 479, 55–61. doi:10.1016/j.jnoncrysol.2017.10.007.
- Sakamaki, T., Kono, Y., Wang, Y., *et al.*, 2014. Contrasting sound velocity and intermediate-range structural order between polymerized and depolymerized silicate glasses under pressure. *Earth Planet Sci. Lett.* 391, 288–295. doi:10.1016/j.epsl.2014.02.008.
- Salmon, P.S., Moody, G.S., Ishii, Y., *et al.*, 2019. Pressure induced structural transformations in amorphous MgSiO₃ and CaSiO₃. *J. Non-Cryst. Solids* 331, 100024.
- Sawyer, R., Nesbitt, H.W., Bancroft, G.M., Thibault, Y., Secco, R.A., 2012. High resolution X-ray photoelectron spectroscopy (XPS) study of K₂O-SiO₂ glasses: Evidence for three types of O and at least 2 types of Si. *J. Non-Cryst. Solids* 358, 290–302.
- Sawyer, R., Nesbitt, H.W., Bancroft, G.M., Thibault, Y., Secco, R.A., 2015. Spectroscopic studies of oxygen speciation in potassium silicate glasses and melts. *Can. J. Chem.* 93, 60–73.
- Schlenz, H., Kirfel, A., Schulmeister, K., *et al.*, 2002. Structure analyses of Ba-silicate glasses. *J. Non-Cryst. Solids* 297, 37–54. doi:10.1016/S0022-3093(01)00922-X.
- Schneider, J., Mastelaro, V.R., Zanotto, E.D., *et al.*, 2003. Qⁿ distribution in stoichiometric silicate glasses: Thermodynamic calculations and ²⁹Si high resolution NMR measurements. *J. Non-Cryst. Solids* 325, 164–178.
- Schramm, C.M., de Jong, B.H.W.S., Parziale, V.E., 1984. 29Si magic angle spinning NMR study on local silicon environments in amorphous and crystalline lithium silicates. *J. Am. Chem. Soc.* 106, 4396–4402.
- Sen, S., Youngman, R.E., 2003. NMR study of Q-speciation and connectivity in K₂O-SiO₂ glasses with high silica content. *J. Non-Cryst. Solids* 331, 100–107.
- Sen, S., Yu, P., 2005. Observation of a stuffed unmodified network in beryllium silicate glasses with multinuclear NMR spectroscopy. *Phys. Rev. B* 72, 132203.
- Sen, S., Tangeman, J., 2008. Evidence for anomalously large degree of polymerization in Mg₂SiO₄ glass and melt. *Am. Mineral.* 93, 946–949. <http://ammin.geoscienceworld.org/cgi/doi/10.2138/am.2008.2921>.
- Sen, S., Maekawa, H., Papatheodorou, G.N., 2009. Short-range structure of invert glasses along the pseudo-binary join MgSiO₃-Mg₂SiO₄: Results from ²⁹Si and ²⁵Mg MAS NMR spectroscopy. *J. Phys. Chem. B* 113, 15243–15248. <http://www.ncbi.nlm.nih.gov/pubmed/19852452>.
- Seo, W.G., Tsukihashi, F., 2004. Molecular dynamics simulation of the thermodynamic and structural properties for the CaO-SiO₂ system. *ISIJ Int.* 44, 1817–1825.
- Seward III, T.P., Uhlmann, D.R., Turnbull, D., 1984a. Phase separation in the system BaO-SiO₂. *J. Am. Ceram. Soc.* 51 (5), 278–285.
- Seward III, T.P., Uhlmann, D.R., Turnbull, D., 1984b. Development of two-phase structure in glasses, with special reference to the system BaO-SiO₂. *J. Am. Ceram. Soc.* 51 (11), 634–643.
- Shan, Z., Li, C., Tao, H., 2017. Mixed alkaline-earth effect on the mechanical and rheological properties of Ca-Mg silicate glasses. *J. Am. Ceram. Soc.* 100, 4570–4580.
- Shelby, J.E., 1979. Effect of morphology on the properties of alkaline earth silicate glasses. *J. Appl. Phys.* 50, 8010–8015.
- Shelby, J.E., 2005. *Introduction to Glass Science and Technology*, second ed. Cambridge: Royal Society of Chemistry (RSC), p. 291.
- Shimoda, K., Okuno, M., 2006. Molecular dynamics study of CaSiO₃-MgSiO₃ glasses under high pressure. *J. Phys. Condens. Matter* 18, 6531–6544. doi:10.1088/0953-8984/18/28/008.
- Shimoda, K., Nemoto, T., Saito, K., 2008. Local structure of magnesium in silicate glasses: A ²⁵Mg 3QMAS NMR Study. *J. Phys. Chem. B* 112, 6747–6752. doi:10.1021/jp711417t.
- Shimoda, K., Miyamoto, H., Kikuchi, M., Kusaba, K., Okuno, M., 2005. Structural evolutions of CaSiO₃ and CaMgSi₂O₆ metasilicate glasses by static compression. *Chem. Geol.* 222, 83–93. doi:10.1016/j.chemgeo.2005.07.003.
- Shimoda, K., Tobu, Y., Hatakeyama, M., Nemoto, T., Saito, K., 2007. Structural investigation of Mg local environments in silicate glasses by ultra-high field ²⁵Mg 3QMAS NMR spectroscopy. *Am. Mineral.* 92, 695–698.
- Shukla, A., Decterov, S.A., Pelton, A.D., 2017. Thermodynamic evaluation and optimization of the SrO-MgO, SrO-SiO₂ and SrO-MgO-SiO₂ systems. *J. Phase Equilib. Diffus.* 38, 615–629. <http://link.springer.com/10.1007/s11669-017-0585-0>.
- Shukla, A., Jung, I.-H., Decterov, S.A., Pelton, A.D., 2018. Thermodynamic evaluation and optimization of the BaO-SiO₂ and BaO-CaO-SiO₂ systems. *Calphad* 61, 140–147.
- Smith, W., Greaves, G.N., Gillan, M.J., 1995. The structure and dynamics of sodium disilicate glass by molecular dynamics simulations. *J. Non Cryst. Solids* 192/193, 267–271.
- Soares Jr, P.C., Zanotto, E.D., Fokin, V.M., Jain, H., 2003. TEM and XRD study of early crystallization of lithium disilicate glasses. *J. Non-Cryst. Solids* 331, 212–227.
- Soltay, L.G., Henderson, G.S., 2005a. The structure of lithium containing silicate and germanate glasses. *Can. Mineral.* 43, 1643–1651.
- Soltay, L.G., Henderson, G.S., 2005b. Structural differences between lithium silicate and lithium germanate glasses by Raman spectroscopy. *Phys. Chem. Glasses* 46, 381–384.
- Sonneville, C., De Ligny, D., Mermet, A., *et al.*, 2013. In situ Brillouin study of sodium aluminosilicate glasses under pressure. *J. Chem. Phys.* 139, 074501. doi:10.1063/1.4818335.
- Stebbins, J.F., 1995. Dynamics and structure of silicate and oxide melts: Nuclear magnetic resonance studies. In: Stebbins, J.F., McMillan, P.F., Dingwell, D.B. (Eds.), *Structure, Dynamics, and Properties of Silicate Melts*. Washington DC: Mineralogical Society of America, pp. 191–246.
- Stebbins, J.F., Sen, S., 2013. Oxide ion speciation in potassium silicate glasses: New limits from ¹⁷O NMR. *J. Non-Cryst. Solids* 368, 17–22.
- Stebbins, J.F., Bista, S., 2019. Pentacoordinated and hexacoordinated silicon cations in a potassium silicate glass: Effects of pressure and temperature. *J. Non-Cryst. Solids* 505, 234–240.
- Stokey, S.D., 1959. Catalyzed crystallization of glass in theory and practice. *Ind. Eng. Chem.* 51, 1957–1960.
- Sukenaga, S., Florian, P., Kanehashi, K., *et al.*, 2017. Oxygen speciation in multicomponent silicate glasses using through bond double resonance NMR spectroscopy. *J. Phys. Chem. Lett.* 8, 2274–2279.
- Sun, N., Stixrude, L., de Koker, N., Karki, B.B., 2011. First principles molecular dynamics simulations of diopside (CaMgSi₂O₆) liquid to high pressure. *Geochim. Cosmochim. Acta* 75, 3792–3802. doi:10.1016/j.gca.2011.04.004.
- Sycheva, G.A., Kostyeva, T.G., 2014. Nucleation and morphology of crystals in simple and complex silicate glasses R'₂O-SiO₂, R'₂O-R''O-SiO₂, (R' = Li, Na, K; R'' = Ca, Mg) synthesized by the Sol-Gel method. *Glass Phys. Chem.* 40, 513–520.
- Takahashi, Y., Masai, H., Fujiwara, T., 2009a. Nucleation tendency and crystallizing phase in silicate glasses: A structural aspect. *Appl. Phys. Lett.* 95, 071904.
- Takahashi, Y., Osada, M., Masai, H., Fujiwara, T., 2009b. Structural heterogeneity and homogeneous nucleation of 1BaO-2SiO₂ glass. *Appl. Phys. Lett.* 94, 211907.

- Taniguchi, T., Okuno, M., Matsumoto, T., 1997. X-ray diffraction and EXAFS studies of silicate glasses containing Mg, Ca and Ba atoms. *J. Non-Cryst. Solids* 211, 56–63. doi:10.1016/S0022-3093(96)00632-1.
- Tewhey, J.D., Hess, P.C., 1979. 2-Phase region in the CaO-SiO₂ system-Experimental data and thermodynamic analysis. *Phys. Chem. Glasses* 20, 41–53.
- Thompson, L.M., McCarty, R.J., Stebbins, J.F., 2012. Estimating accuracy of ¹⁷O NMR measurements in oxide glasses: Constraints and evidence from crystalline and glassy calcium and barium silicates. *J. Non-Cryst. Solids* 358, 2999–3006.
- Tomlinson, J.W., Heynes, M.S.R., Bockris, J.O., 1958. The structure of liquid silicates. Part 2 – Molar volumes and expansivities. *Trans. Faraday Soc.* 54, 1822–1833. doi:10.1039/2Ft9585401822.
- Toop, G.W., Samis, C.S., 1962. Some new ionic concepts of silicate slags. *Can. Metall. Q.* 1, 129–152.
- Trcera, N., Rossano, S., Tarrida, M., 2011b. Structural study of Mg-bearing sodosilicate glasses by Raman spectroscopy. *J. Raman Spectrosc.* 42, 765–772.
- Trcera, N., Rossano, S., Madjer, K., Cabaret, D., 2011a. Contributions of molecular dynamics simulations and ab initio calculations to the interpretation of Mg K-edge experimental XANES in K₂O-MgO-3SiO₂ glass. *J. Phys. Condens. Matter* 23, 255401.
- Trcera, N., Cabaret, D., Rossano, S., *et al.*, 2009. Experimental and theoretical study of the structural environment of magnesium in minerals and silicate glasses using X-ray absorption near-edge structure. *Phys. Chem. Miner.* 26, 241–257.
- Tsunawaki, Y., Iwamoto, N., Hattori, T., Mitsuishi, A., 1981. Analysis of CaO-SiO₂ and CaO-SiO₂-CaF₂ glasses by Raman spectroscopy. *J. Non-Cryst. Solids* 44, 369–378.
- Uchino, T., Yoko, T., 1999. Sodium and lithium environments in single and mixed alkali silicate glasses. An ab initio molecular orbital study. *J. Phys. Chem. B* 103, 1854–1858.
- Uhlig, H., Lamparter, P., Steeb, S., 1996a. Order in Li-Silicate glasses by diffraction methods. *Ber. Bunsenges. Phys. Chem.* 100, 1574–1577.
- Uhlig, H., Hoffman, M.J., Lamparter, H.-P., *et al.*, 1996b. Short-range and medium-range order in lithium silicate glasses. Part I: Diffraction experiments and results. *J. Am. Ceram. Soc.* 79, 2833–2838.
- Uhlig, H., Hoffman, M.J., Lamparter, H.-P., *et al.*, 1996c. Short-range and medium-range order in lithium silicate glasses. Part II: Simulation of the structures by the reverse monte carlo methods. *J. Am. Ceram. Soc.* 79, 2839–2846.
- Umesaki, N., Takahashi, M., Tatsumi, M., Minami, T., 1993. The structure of rapidly quenched glasses in the system Li₂O-SiO₂. *J. Mater. Sci.* 28, 3473–3481.
- Vedishcheva, N.M., Shakhmatkin, B.A., Shultz, M.M., *et al.*, 1995. A thermodynamic, molecular dynamics and neutron diffraction investigation of the distribution of tetrahedral {Si⁽ⁿ⁾} species and the network modifying cation environment in alkali silicate glasses. *J. Non-Cryst. Solids* 192&193, 292–297.
- Vessal, B., Wright, A.C., Hannon, A.C., 1996. Alkali silicate glasses: Interpreting neutron diffraction results using the molecular dynamics simulations technique. *J. Non-Cryst. Solids* 196, 233–238.
- Voronko, Y.K., Sobol, A.A., Shukshin, V.E., 2006. Raman spectra and structure of silicon-oxygen groups in crystalline, liquid, and glassy Mg₂SiO₄. *Inorg. Mater.* 42, 981–988.
- Wang, Z., Guo, S., Li, Q., *et al.*, 2013. Luminescent properties of Ba₂SiO₄: Eu³⁺ for white light emitting diodes. *Phys. B Condens. Matter* 411, 110–113. doi:10.1016/j.physb.2012.11.040.
- Warren, B.E., 1942. The basic principles involved in the glassy state. *J. Appl. Phys.* 13, 602–610.
- Warren, B.E., Loring, A.D., 1935. X-ray diffraction study of the structure of soda-silica glass. *J. Am. Ceram. Soc.* 18 (9), 269–276.
- Warren, B.E., Bischof, J., 1938. Fourier analysis of X-ray patterns of soda-silica glass. *J. Am. Ceram. Soc.* 21, 259–265.
- Waseda, Y., Toguri, J.M., 1977. The structure of molten binary silicate systems CaO-SiO₂ and MgO-SiO₂. *Metall. Trans. B* 8B, 563–568.
- Weigel, C., Le Losq, C., Vialla, R., *et al.*, 2016. Elastic moduli of XAlSiO₄ aluminosilicate glasses: Effects of charge-balancing cations. *J. Non-Cryst. Solids* 447, 267–272. doi:10.1016/j.jnoncrysol.2016.06.023.
- Wilding, M.C., Benmore, C.J., Tangeman, J.A., Sampath, S., 2004a. Coordination changes in magnesium silicate glasses. *Europhys. Lett.* 67, 212–218. doi:10.1209/epl/i2003-10286-8.
- Wilding, M.C., Benmore, C.J., Tangeman, J.A., Sampath, S., 2004b. Evidence of different structures in magnesium silicate liquids: Coordination changes in forsterite- to enstatite-composition glasses. *Chem. Geol.* 213, 281–291.
- Wilkinson, C.J., Potter, A.R., Welch, R.S., *et al.*, 2019. Topological origins of the mixed alkali effect in glass. *J. Phys. Chem. B* 123, 7482–7489.
- Wójcik, N.A., Ali, S., Möncke, D., *et al.*, 2019. The influence of Be addition on the structure and thermal properties of alkali-silicate glasses. *J. Non-Cryst. Solids* 521, 119532. doi:10.1016/j.jnoncrysol.2019.119532.
- Wu, Y.Q., Jiang, G.C., You, J.L., *et al.*, 2004. Theoretical study of the local structure and Raman spectra of CaO-SiO₂ binary melts. *J. Chem. Phys.* 121, 7883–7895.
- Xiao, Z., Yu, S., Li, Y., *et al.*, 2020. Materials development and potential applications of transparent ceramics: A review. *Mater. Sci. Eng. R Rep.* 139, 100518. doi:10.1016/j.mser.2019.100518.
- Xu, X., Li, J., Yao, L., 1989. A study of glass structure in Li₂O-SiO₂, Li₂O-Al₂O₃-SiO₂ and Li-Al-Si-O-N systems. *J. Non-Cryst. Solids* 112, 80–84.
- Xu, Z., Stebbins, J.F., 1995. Li-6 nuclear-magnetic-resonance chemical shifts, coordination number and relaxation in crystalline and glassy silicates. *Solid State Nucl. Magn. Reson.* 5, 103–112.
- Yi, Y.S., Lee, S.K., 2012. Pressure-induced changes in local electronic structures of SiO₂ and MgSiO₃ polymorphs: Insights from ab initio calculations of O K-edge energy-loss near-edge structure spectroscopy. *Am. Mineral.* 97, 897–909.
- Yin, C.D., Okuno, M., Morikawa, H., Marumo, F., 1983. Structure analysis of MgSiO₃ glass. *J. Non-Cryst. Solids* 55, 131–141.
- Yin, C.D., Okuno, M., Morikawa, H., Marumo, F., Yamanaka, T., 1986. Structural analysis of CaSiO₃ glass by X-ray diffraction and Raman spectroscopy. *J. Non-Cryst. Solids* 80, 167–174.
- Yusa, H., Sata, N., Onishi, Y., 2007. Rhombohedral (9R) and hexagonal (6H) perovskites in barium silicates under high pressure. *Am. Mineral.* 92, 648–654.
- Zachariasen, W.H., 1932. The atomic arrangement of glass. *J. Am. Chem. Soc.* 54, 3841–3850.
- Zakaznova-Herzog, V.P., Malfait, W.J., Herzog, F., Halter, W.E., 2007. Quantitative Raman spectroscopy: Principles and application to potassium silicate glasses. *J. Non-Cryst. Solids* 353, 4015–4028.
- Zanotto, E.D., James, P.F., 1988. Experimental test of the general theory of transformation kinetics: Homogeneous nucleation in a BaO·2SiO₂ glass. *J. Non-Cryst. Solids* 104, 70–72. doi:10.1016/2F0022-3093/2888/2990183-4.
- Zhang, F., Tu, Z., Du, X., Zhang, H., Qiu, J., 2014. Femtosecond laser induced migration of alkali ions in calcium silicate glasses. *Mater. Lett.* 137, 92–95.
- Zhang, L., Van Orman, J.A., Lacks, D.J., 2010. Molecular dynamics investigation of MgO-CaO-SiO₂ liquids: Influence of pressure and composition on density and transport properties. *Chem. Geol.* 275, 50–57. doi:10.1016/j.chemgeo.2010.04.012.
- Zhang, P., Grandinetti, P.J., Stebbins, J.F., 1997. Anionic species determination in CaSiO₃ glass using two-dimensional ²⁹Si NMR. *J. Phys. Chem. B* 101, 4004–4008. doi:10.1021/jp9700342.
- Zhen, Z., Ispas, S., Kob, W., 2020. The critical role of the interaction potential and simulation protocol for the structural and mechanical properties of sodosilicate glasses. *J. Non-Cryst. Solids* 532, 119895.
- Zheng, Q., Zhang, Y., Montazerian, M., *et al.*, 2019. Understanding glass through differential scanning calorimetry. *Chem. Rev.* 119, 7848–7939.
- Zotov, N., Keppler, H., 1998. The structure of sodium tetrasilicate glass from neutron diffraction, reverse Monte Carlo simulations and Raman spectroscopy. *Phys. Chem. Miner.* 25, 259–267.

Relevant Websites

<https://github.com/epam/SciGlass>

epam/SciGlass: The database contains a vast set of data on the properties of glass materials.
GitHub.

<http://glassproperties.com/databases/>

Glass Databases.
Glass Properties.

Soda-Lime-Silica Glasses

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Introduction

When the average person uses the term glass they are probably referring to soda-lime-silica (SLS) glass, even if they do not realize that this is the case, as most bulk glass i.e., container glass (bottles; ~45%–50% of the global glass market by weight), flat glass (windows etc.; ~30% of the global glass market by weight), and glassware (drinking glasses) are SLS glasses. The widespread use of SLS glasses is due to the availability of suitable raw materials and automated processes that have been developed around the viscosity-temperature behavior of these compositions. It also reflects the fact that SLS glasses can be produced to suitable optical standard for applications such as windscreens, and have sufficient chemical durability for use in a range of applications.

SLS glasses are readily produced by the melt-quench route wherein a batch of raw materials are heated and react together to form a melt which then forms a glass on cooling. When a glass forming melt such as a soda-lime-silica melt is cooled, rather than undergoing a liquid-solid phase change at, or just below, the temperature, T_m , and crystallizing (T_m being the melting point of the crystals) there is a continuous change from the liquid to a solid through the glass transformation range (see Fig. 1). Hence on cooling an SLS melt first becomes a supercooled liquid then, as it passes through the glass transformation range, it can be viewed as a visco-elastic liquid followed by a visco-elastic solid, before finally becoming a brittle solid. Although the glass transformation (or transition) occurs continuously over a range of temperatures as shown in Fig. 1, for convenience it is often characterized by a single temperature known as the glass transition temperature, T_g , which can be measured using either thermal analysis or dilatometry. For SLS glasses T_g will typically be in the range 530–580°C, although the precise value depends on the specific glass composition and thermal history.

Glasses are therefore not equilibrium phases and eventually on very long timescales all glasses are expected to crystallize (Zanotto and Mauro, 2017). However, for all practical purposes, readily formed glasses such as SLS glasses are stable materials that will remain in the glassy state on at least millennium timescales, as shown by the existence of SLS glasses dating back to ancient Egyptian and Roman times.

Compositions

All glasses have non-crystalline or amorphous atomic structures that are similar to those of the melts from which they are formed. As a result, while they have short range order at the atomic scale they do not exhibit any long range order; the presence of medium range order remains a subject for debate. Hence glasses also do not have fixed chemical compositions (unless they are single component) and for any given glass type a range of chemical compositions is possible. The soda-lime-silica system is no exception and there is a large glass forming region in the soda-lime-silica (SLS) ternary system (see Fig. 2(a)).

Soda-lime-silica ($\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$) glasses are network oxide glasses primarily based on the oxides of sodium, calcium and silica. It is important to note that these oxides are not individually present in the final glass and thus a glass composition

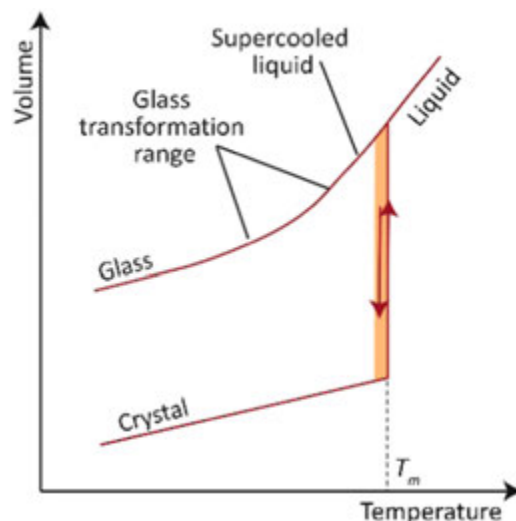


Fig. 1 Volume versus temperature diagram showing the glass transformation as compared to a liquid-solid phase change.

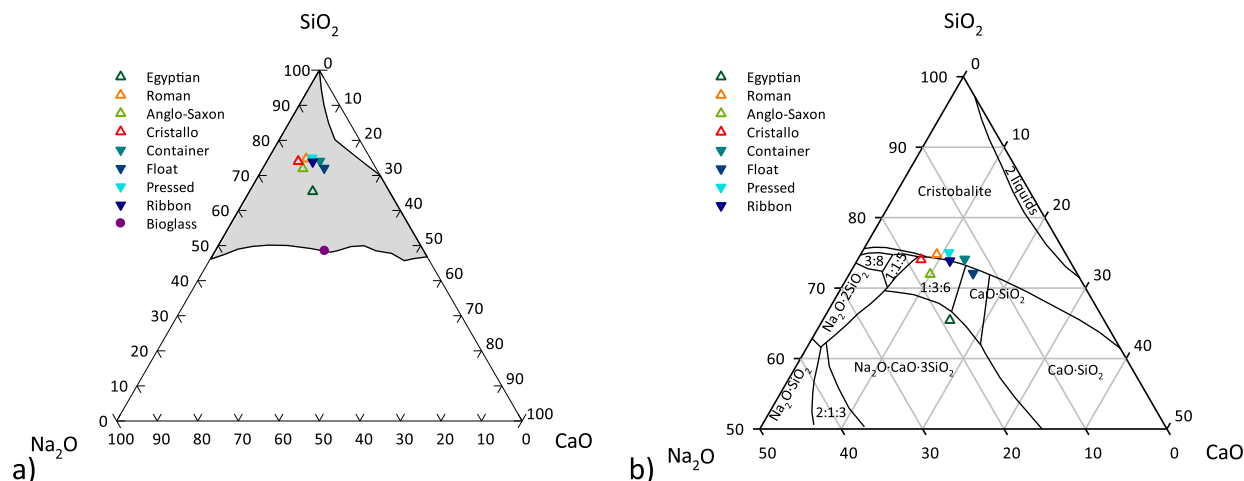


Fig. 2 (a) Na_2O - CaO - SiO_2 ternary diagram (mol%) showing the glass forming region (gray region) and average, reduced, compositions for some ancient/historic (open symbols) and modern SLS glasses (filled symbols); (b) enlargement of the silica rich corner of the Na_2O - CaO - SiO_2 equilibrium phase diagram with the same glass compositions superimposed on it. Compositional reduction based on considering all alkali oxides as Na_2O (corrected for Al_2O_3 charge balance), all alkaline earth oxides as CaO and charge balanced Al_2O_3 as SiO_2 . Based on Bansal, N.P., Doremus, R.H., 1986. Multicomponent commercial glasses. In: Bansal, N.P., Doremus, R.H. (Eds.), *Handbook of Glass Properties*. Orlando: Academic Press. pp. 31–45. Shahid, K.A., Glasser, F.P., 1972. Phase equilibria in glass forming region of the system Na_2O - CaO - MgO - SiO_2 . *Physics and Chemistry of Glasses* 13, 27–42, with additional data from De Raedt, I., Janssens, K., Veeckman, J., *et al.*, 2001. Trace analysis for distinguishing between Venetian and façon-de-Venise glass vessels of the 16th and 17th century. *Journal of Analytical Atomic Spectrometry* 16, 1012–1017. Freestone, I.C., Hughes, M.J., Stapleton, C.P., 2008. The composition and production of Anglo-Saxon glass. In: Evison, V.I., Marzinzik, S. (Eds.), *Catalogue of Anglo-Saxon Glass in the British Museum*. London: The British Museum, pp. 29–46. Lilyquist, C., Brill, R.H., 1993. *Studies in Early Egyptian Glass*. New York: MetPublications. (Metropolitan Museum of Art). Foster, H.E., Jackson, C.M., 2009. The composition of ‘naturally coloured’ late Roman vessel glass from Britain and the implications for models of glass production and supply. *Journal of Archaeological Science* 36, 189–204. Smrček, A., 2010. Compositions of industrial glasses. In: Wallenberger, F.T., Bingham, P.A. (Eds.), *Fiberglass and Glass Technology*. New York: Springer, pp. 229–266.

$x\text{Na}_2\text{O}\cdot y\text{CaO}\cdot z\text{SiO}_2$ is arguably more correctly written as $\text{Na}_{2x}\text{Ca}_y\text{Si}_z\text{O}_{x+y+2z}$, although the compositions are generally reported in oxide terms for convenience. Small amounts of other oxides will also be present in commercial SLS compositions, in most cases due to their effects on processing and/or on the final glass properties. Specifically most commercial SLS glasses will contain at least small amounts of potassia (K_2O), magnesia (MgO) and alumina (Al_2O_3) and thus they could be considered as part of the Na_2O - K_2O - MgO - CaO - Al_2O_3 - SiO_2 glass system. The presence of these other oxides can be expected to result in shifts of the phase boundaries shown in Fig. 2(a) and (b).

Silica (SiO_2) is the network former and is capable of forming a glass on its own. The structure of pure silica glass is a fully connected three dimensional network of corner linked SiO_4 tetrahedra (see Fig. 3(a)), with each Si–O bond having primarily covalent character. However pure silica is difficult to melt on its own as it requires temperatures in excess of 1720°C . In comparison soda-lime-silica glasses that contain the network modifiers soda (Na_2O) and lime (CaO), which depolymerize the network (see Fig. 3(b)), can be produced using less extreme temperatures. In this case the backbone of the glass structure still consists of corner linked SiO_4 tetrahedra, but some of the corner oxygens are now bonded to either a sodium ion or a calcium ion rather than to another silicon. Oxygens that participate in Si–O–Si bonds are known as bridging oxygens (BOs), whereas those that participate in Si–O–Na or Si–O–Ca bonds are known as non-bridging oxygens (NBOs). A single sodium leads to the formation of one NBO and a calcium leads to the formation of two NBOs, with the Na–O and Ca–O bonds both being primarily ionic in character. The depolymerization of the network through the addition of network modifiers significantly reduces the melt viscosity at any given temperature thus enabling SLS glass production at commercially viable temperatures. Although a reduction in melt viscosity at any particular temperature could be achieved just through the addition of soda to silica this results in non-durable “water” glasses, due to the relatively high mobility of sodium ions in the glass structure. Calcium ions occupy similar sites to the sodium ones due to their similar size, impeding the motion of the latter and thus resulting in a sufficiently durable glass that it can be successfully used for the long-term storage of liquids (containers or bottles) as well as exterior windows. A lack of lime arising from improved purification techniques being applied to ashes used as a soda source means that historic Venetian cristallo glasses (see Fig. 2(a) and Table 1) have poor chemical durability, with the result that many examples in museum collections are now suffering from significant degradation.

SLS glass production has a long history with some of the earliest manmade glasses being SLS compositions, with both the ancient Egyptians (~ 1500 BCE) and the Romans producing SLS glass composition. The ancient Egyptian SLS glasses had relatively low silica contents (see Fig. 2(a) and Table 1) compared to subsequent SLS compositions. Since Roman times the molar silica content has varied relatively little although there have been larger variations in the soda and lime contents. In particular, in medieval times in northern Europe where forest plants were as the alkali source, rather than either natron or marine plants

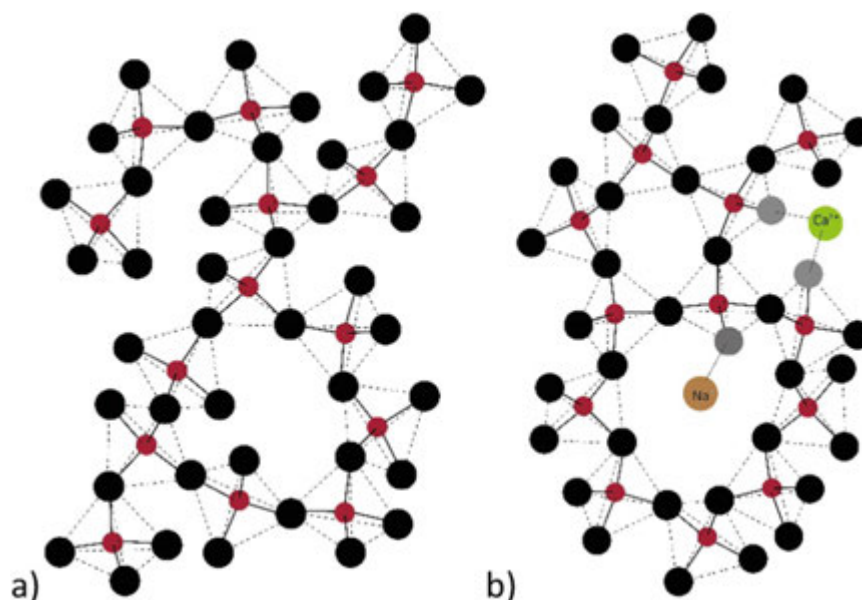


Fig. 3 Schematic diagrams of (a) a pure silica network consisting of corner connected SiO_4 tetrahedra and (b) a soda-lime-silica glass showing one Na^+ ion (pale brown) bonded to a non-bridging oxygen (NBO) and one Ca^{2+} ion (lime green) bonded to 2 NBOs: Si atoms are dark red, bridging oxygens are black, the NBO is gray, solid lines indicate bonds; dashed lines delimit the SiO_4 tetrahedra.

Table 1 Major components of SLS glasses expressed as moles oxide per mole of SiO_2

Oxide	Historic glasses			Modern container glasses			Other modern glasses		
	Egyptian	Roman	Cristallo	White	Green	Amber	Float	Pressed	Ribbon
Na_2O	0.2764	0.2319	0.2290	0.1806	0.1820	0.1868	0.1823	0.1838	0.2102
CaO	0.1448	0.1153	0.0711	0.1436	0.1400	0.1389	0.1283	0.1122	0.0989
Al_2O_3	0.0042	0.0219	0.0071	0.0149	0.0189	0.0167	0.0068	0.0103	0.0164
K_2O	0.0230	0.0069	0.0255	0.0048	0.0066	0.0050	0.0027	0.0184	0.0089
MgO	0.0961	0.0126	0.0348	0.0330	0.0475	0.0412	0.0833	0.0322	0.0584
Fe_2O_3	0.0042	0.0034	0.0013	0.0004	0.0020	0.0014	0.0004	0.0001	—

Note: Based on data from Lilyquist, C., Brill, R.H., 1993. *Studies in Early Egyptian Glass*. New York: MetPublications. (Metropolitan Museum of Art). Foster, H.E., Jackson, C.M., 2009. The composition of 'naturally coloured' late Roman vessel glass from Britain and the implications for models of glass production and supply. *Journal of Archaeological Science* 36, 189–204. Smrček, A., 2010. Compositions of industrial glasses. In: Wallenberger, F.T., Bingham, P.A. (Eds.), *Fiberglass and Glass Technology*. New York: Springer, pp. 229–266.

(barilla), the resultant glass compositions contain large amounts of potassia and have low soda contents and are often therefore considered as potassia-lime-silica glasses rather than soda-lime-silica glasses. In the 19th and 20th centuries there was some limited evolution of composition over time in response to production requirements (Smrček, 2010). However modern compositions tend vary relatively little between manufacturers although there are some differences between container glass and float glass (see Table 2). In particular, the increased use of recycled glass as a batch material in container manufacture is now promoting a tendency towards a common composition.

Typical modern SLS compositions contain ~13–14 mol% Na_2O , ~9–10 mol% CaO and ~72 mol% SiO_2 . The compositions include deliberate additions of alumina to both improve durability and suppress crystallization. The alumina forms AlO_4^- tetrahedra with charge balance being provided by Na^+ ions, which are therefore no longer bonded via an NBO to a silicon. The AlO_4^- tetrahedra form part of the network and thus alumina additions lead to a reduction in NBOs and an increase in network connectivity increasing both viscosity at a given temperature and chemical durability. Magnesia (MgO) is also deliberately added to modern SLS compositions to reduce the liquidus temperature (the temperature at which the last crystal phase would melt on heating) and, like alumina, to suppress the tendency to crystallization, with float (flat) glass having a higher magnesia content than container glass. Some iron will also be present in commercial SLS glasses; the level being dependent on application and allowable cost.

The presence of the additional components in the glass means that the crystalline phase boundaries shown in Fig. 2(b) will be shifted from those shown which are for the three component SLS system. In practice container glass compositions tend to fall in the primary devitrite ($1:3:6$ or $\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$) phase field whereas float glass is close to the silica-devitrite-wollastonite ($\text{CaO} \cdot \text{SiO}_2$) phase boundary, with liquidus temperatures (T_L) typically being in the range of 990–1050°C depending on composition.

Table 2 Compositions of typical high volume commercial SLS glasses (wt%). Container refers to bottles which may be clear, amber or green; float to flat glass; glassware to drinking glasses and A-glass to insulation fibers

Oxide	Container	Float	Glassware	A-glass
Na ₂ O	12–15	12–14	12–14	12–15
CaO	10–12	7–10	7–9	9–11
SiO ₂	70–73	70–74	70–74	71–73
K ₂ O	0–1	0–0.5	0–2.5	0–1.5
MgO	0.5–2	2–4	1–2	1–4
Al ₂ O ₃	1–2	0–1	1–2	0.5–2.5
Fe ₂ O ₃	0–1	0–1	0–0.05	0–0.5
Cr ₂ O ₃	0–0.3	0–0.3	0	0
TiO ₂	0–0.1	0–0.1	0–0.05	0–0.1
B ₂ O ₃	0	0	0	0–0.5
SO ₃	0–0.5	0–0.5	0–0.5	0–0.5

Bioactive glasses, such as 45S5, can also be considered as modified SLS glasses albeit with low silica contents compared to conventional SLS glasses (see Fig. 2(a)) and the addition of a second glass former, P₂O₅. In this case the low silica content combined with high soda and lime contents results in a glass where its solubility in the human body results in beneficial bioactive behavior.

SLS Glass Structure

It is conventional to describe the connectivity of silicate glasses in terms of Q species. The Q species refer to the number of bridging oxygens that participate in Si–O–Si bonds on a given silica tetrahedron. Thus pure silica, which is fully connected, has just Q⁴ tetrahedra. Tetrahedra with one NBO are referred to as Q³, those with two NBOs as Q², three NBOs as Q¹ and isolated tetrahedra with all NBOs as Q⁰. Adding network modifiers, such as Na₂O and CaO will lead to an increase in the number of Qⁿ⁻¹ species at the expense of Qⁿ species. Typical SLS glass compositions contain a mixture of primarily Q³ tetrahedra with some Q⁴ tetrahedra. Although depolymerization largely happens sequentially with Q⁴ units being first converted to Q³ units and only once this is complete are Q³ units converted to Q² units, in practice some Q² tetrahedra are also likely to be present due to disproportionation whereby Q³ ⇌ Q⁴ + Q² also occurs. The amounts of the different Qⁿ species can be measured using nuclear magnetic resonance (NMR).

Although as network modifiers, Na⁺ and Ca²⁺ ions, formally lead to the production of one or two NBOs respectively, in practice these species will be surrounded by both BOs and NBOs from adjacent tetrahedral units with Na having an oxygen coordination of ~6 in alumina free SLS compositions and ~6–8 if alumina is present. Meanwhile Ca has an oxygen coordination of ~4–5 in alumina free compositions (Le Losq *et al.*, 2019). As the amount of alumina in commercial SLS glasses is relatively low all of the alumina can be charge compensated by sodium ions hence such glasses will contain both SiO₄ tetrahedra and a small number of AlO₄ tetrahedra.

Many textbooks still refer to the Zachariasen-Warren continuous random network (CRN) model for glass structure in which the modifiers are essentially randomly distributed. However various lines of evidence indicate that there is, in fact, some clustering of the modifiers through the glass network with the modified random network (MRN) model of Greaves *et al.* (1981) having silica rich regions separated by percolating channels of modifier ions (see Fig. 4). Although Fig. 4 is a schematic of a soda-silica glass only, the improvement in chemical durability seen when lime replaces some of the soda to produce SLS glasses implies that the calcium ions would be located in the same channels as the sodium ions.

Commercial Production of SLS Glasses

Both container and flat glass are made on the large scale with typical container furnaces producing 300 tonnes per day (tpd) of glass. Float furnaces for flat glass are uneconomic below 300 tpd and the largest modern glass plants now can produce 1000 tpd.

Primary raw materials for commercial SLS glass production are a low iron glass making sand (usually > 99 wt% SiO₂), soda ash (Na₂CO₃) which supplies soda (Na₂O), and limestone (CaCO₃) which supplies lime (CaO). Soda ash may be from a mineral source, namely trona Na₃H(CO₃)₂ · 2(H₂O), or is an industrial chemical produced by the Solvay or ammonia-soda process. Industrially produced soda ash is responsible for a significant fraction of the embodied energy of commercial SLS glass and thus there has been increasing interest in mineral sources in recent years. Some soda may also be supplied by sodium sulfate (salt cake) added to aid bubble removal from the melt (fining) and from the alumina sources. The use of sulfate (or sulfide) during manufacture leads to a residual sulfur content in most SLS glasses with contents ranging from ~0.2 wt% SO₃ (equivalent) in colorless glass to ~0.05 wt% SO₃ (equivalent) in amber glass with the S being present in a range of oxidation states (Bingham *et al.*, 2010). As most commercial SLS glasses also contain magnesia (MgO) some lime is also usually supplied by dolomite (xMgCO₃ · (1 – x)CaCO₃; while in the ideal case x = 0.5 in practice it varies with dolomite source). Alumina is supplied by alkali

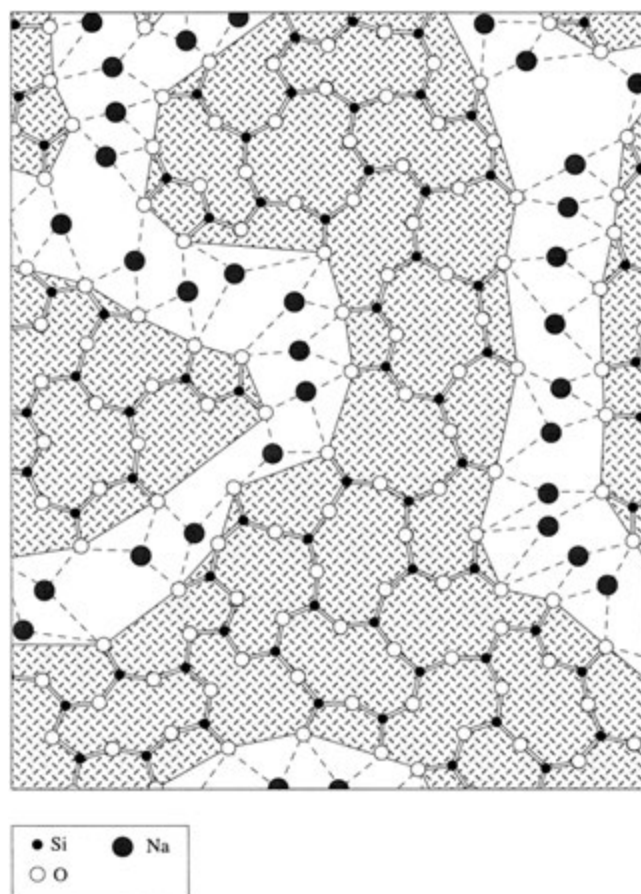


Fig. 4 Schematic 2D diagram of the modified random network model of Greaves *et al.* showing percolating sodium channels separating silica rich regions in a soda-silica glass, with the silica units being represented as trigonal rather than tetrahedral to enable a 2D representation. Based on Greaves, G.N., Fontaine, A., Lagarde, P., Raoux, D., Gurman, S.J., 1981. Local structure of silicate glasses. *Nature* 293, 611–616. Hand, R.J., Seddon, A.B., 1997. An hypothesis on the nature of Griffith's cracks in alkali silicate and silica glasses. *Physics and Chemistry of Glasses* 38, 11–14.

aluminosilicate minerals, such as feldspars or nepheline syenite, which typically also supply some soda, potassia (K_2O) and silica. Any potassia in the final composition is usually a consequence of the alumina source used. Small amounts (typically < 1 wt%) of coloring elements may also be present. Notably iron may be present due to impurities in the raw materials (especially the sand), although it can also be introduced deliberately.

Cullet (recycled glass) will also be used in the glass batch; the use of well controlled in-house cullet from rejected product has long been a feature of commercial glass production, but nowadays significant quantities of cullet come from external sources. In container melting (especially for green glass where impurity levels are less of a concern) over 80% of the glass batch may be cullet but the higher optical requirements in flat glass applications limits the amount of cullet used in float furnaces. Externally sourced cullet can impact the redox conditions in the furnace if it contains relatively large amounts of organic contamination.

While the use of cullet reduces the production energy demand, SLS glass production remains an energy intensive process. It is therefore desirable to develop SLS compositions that can be produced at lower temperatures. This is far from straightforward as a range of often competing factors have to be taken into account. For example, increasing the soda content with respect to the other components would reduce the required melting temperature; however such a change would reduce the chemical durability of the product. The potential for reformulating SLS glass compositions has been reviewed in detail by Bingham (2010) and to be commercially viable any reformulation has to balance a range of production and cost requirements. SLS glass products are commodity items and thus there is a strong downward pressure on costs. Furthermore, the large daily production volumes (300–1000 tpd) mean that companies can be reluctant to implement even small changes.

Compositional changes could also, in principle, be made to alter the properties of the final glass. However, such changes are potentially expensive and could negatively affect processing conditions. Thus, a more common approach is to add value by applying surface coatings using techniques such as chemical and physical vapor deposition (CVD and PVD respectively).

Commercial SLS glass melting furnaces are generally fossil fuel fired using natural gas, oxy-fuel mixtures or oil firing. The burners are positioned above the melt and thus the transfer of heat through the melt by both conduction and radiation is important in the melting process. The use of recuperators or regenerators (larger furnaces) to recover heat from the exhaust gases is essential in maximizing fuel efficiency. As SLS melts are sufficiently conducting, electric boost is used in some glass tanks to provide additional

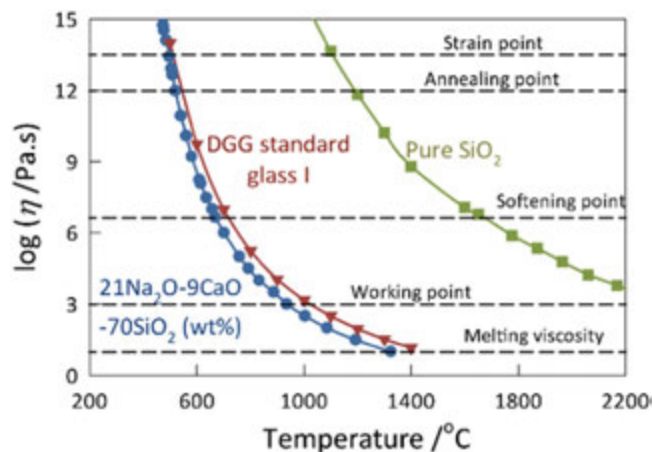


Fig. 5 Viscosity as a function of temperature for pure silica and two SLS compositions (DGG standard glass I and 21Na₂O-9CaO-70SiO₂ (wt%)). Data from Doremus, R.H., 2002. Viscosity of silica. *Journal of Applied Physics* 92, 7619–7629. Note viscosity here is given in Pa s whereas the glass industry commonly uses dPa s.

Joule heating to increase melting rate and pull (glass production) rate. The possibility of utilizing Joule heating means that in principle large scale SLS glass manufacture could be undertaken using all electric melters, and could allow the industry to move away from fossil fuels. However, to be commercially viable for commodity products such as SLS containers and flat glass, this requires a significant reduction in the cost of electricity. To be effective it also requires the electricity supply to be decarbonized.

Viscosity-Temperature Behavior and SLS Glass Production

For network glasses such as SLS glasses melt viscosity is a strong function of temperature (see Fig. 5). This has an impact on glass processing with various viscosity levels being defined based on practical performance.

During glass melting the emphasis is on melting all of the raw materials and homogenizing the resultant melt, together with removal of bubbles from the melt. These processes are generally quicker at high temperatures and lower viscosities, with the melt viscosity typically being ~ 1 Pa s. Even so commercial furnace residence times can be up to 36 h to ensure good quality output. For forming higher viscosities are required and thus glass forming necessarily takes place at lower temperatures than the initial melting stage. The working point (10^3 Pa s) and the softening point ($10^{6.65}$ Pa s) correspond to the highest and lowest temperatures respectively at which a melt can be formed to shape, although this can be further restricted by crystallization. To avoid problems with crystallization the working point (T_W) should be above the liquidus temperature (T_L). For container manufacturing the difference $T_W - T_L$ should be at least 10–20°C. The annealing point (10^{12} Pa s) and the strain point ($10^{13.5}$ Pa s) define the temperature boundaries of the glass transformation range and its importance in annealing; the former temperature is often taken as being the glass transition temperature. For commercial SLS production the melting temperature is typically $\sim 1500^\circ\text{C}$, the forming temperature $\sim 1200^\circ\text{C}$ and the annealing temperature $\sim 550^\circ\text{C}$.

As knowledge of viscosity-temperature (η - T) behavior is essential for good control of commercial glass production a number of equations have been developed to describe this behavior. Of these the Vogel-Fulcher-Tammann (VFT) equation:

$$\log \eta = A + \frac{B}{T - T_0} \quad (1)$$

where A , B and T_0 are constants, is probably best known and is widely used in the glass industry as it provides a good description of the viscosity of glass melts in the temperature range of commercial interest. Lakatos *et al.* (1972, 1976) have published empirical models enabling the parameters A , B and T_0 in the VFT equation to be determined from the composition for a range of glass compositions (see Table 3). More recently Fluegel (2007) has developed a more sophisticated, albeit still empirical, set of calculations for a wide range of glass compositions to determine the parameters in the VFT equation from the composition. This model has been implemented as an Excel spreadsheet downloadable from the web (see “Relevant Website section”), which also produces the viscosity-temperature curve. It should be noted that in the Lakatos fits for the VFT equation, η is measured in dPa s (or Poise, in line with conventional industrial usage) and T in $^\circ\text{C}$, whereas in the Fluegel fits, η is measured in Pa s and T in $^\circ\text{C}$.

While other equations for viscosity-temperature relationships have been developed (see, for example, Mauro *et al.*, 2009) in practice the VFT equation provides a good fit in the range of viscosities of interest to a commercial SLS glass producer.

Commercial forming of SLS glasses is a highly automated process. In the case of bottle production, after melting, refining and conditioning, sausage shaped “gobs” of glass produced from the feeder are formed using an IS (independent section) machine which typically consists of a set of 6–20 sections, each of which is capable of dealing with 1–4 gobs of glass. The glass gob is introduced into a blank mold where the neck and the finish as well as a hollow shape are produced by pressing (wide neck

Table 3 Parameters used to calculate A , B and T_0 in Eq. (1); where $A = \sum_{i=0}^n x_i a_i$, $B = \sum_{i=0}^n x_i b_i$ and $T_0 = \sum_{i=0}^n x_i t_i$ and x_i = weight fraction of oxide/weight fraction of silica

x_i	Limits (wt%)	a_i	b_i	t_i
a_0 (SiO ₂)	59.52–77.02	–1.7130	6237.013	149.4
Li ₂ O/SiO ₂	0.0–3.0	3.18	–11518	–1329
Na ₂ O/SiO ₂	10.41–17.0	1.62	–6601	50
K ₂ O/SiO ₂	0.0–8.7	–0.66	–541	–236
MgO/SiO ₂	0.0–6.0	–5.89	5621	–212
CaO/SiO ₂	4.48–13.0	–0.64	–6063	771
BaO/SiO ₂	0.0–16.54	–0.26	–2103	109
ZnO/SiO ₂	0.0–9.38	–1.60	–376	96
Al ₂ O ₃ /SiO ₂	0.0–8.26	0.87	1521	140
PbO/SiO ₂	0.0–12.22	0.50	–2544	82
B ₂ O ₃ /SiO ₂	0.0–14.37	4.65	–15511	1203
(B ₂ O ₃ /SiO ₂) ²		–0.1627	409.99	–2765

Note: Lakatos, T., 1976. Viscosity-temperature relations in glasses composed of SiO₂-Al₂O₃-Na₂O-K₂O-Li₂O-CaO-MgO-BaO-ZnO-PbO-B₂O₃. *Glasteknisk Tidskrift* 31, 51–54.

containers) or blowing (narrow neck containers). The resultant blank, also known as a parison, is then transferred to a second mold where the final shape is produced by blowing. The molds are made of cast iron and graphite based agents are used to ensure that the glass does not stick to the mold. After forming it is necessary to cool the glass in a controlled fashion through the glass transition region. This minimizes any residual stresses that would otherwise be frozen into the glass, and which could lead to early fracture. Commercially this process involves passing the glass through an annealing furnace, also known as an annealing lehr, in which the glass is reheated to $\sim 550^\circ\text{C}$ (the annealing point) and then is slowly cooled to the strain point (see Fig. 5). Once the glass has cooled to below the strain point it is no longer necessary to slow cool the glass. To aid performance hot and cold end coatings are applied to container glasses prior to entering and after exiting the annealing lehr respectively. The hot end coatings tend to be tin oxide or titania based and enable the lubricious cold end coatings to stick to the glass.

Most modern flat glass is produced by the float process wherein the glass melt is floated out over the surface of a bath of tin kept under a reducing H₂/N₂ atmosphere. The glass does not react with the tin although a small amount does diffuse into the glass surface that is in contact with the tin bath. The thickness of the glass is then determined by the rate at which the glass moves along the tin bath. Once the glass has cooled sufficiently to prevent deformation under its own weight it is lifted from the tin bath and then passes through the annealing lehr. Only after the glass ribbon exits the lehr is it cut into smaller sections. The float process enables the production of large sheets of flat glass with a high quality surface finish and has become the dominant process for flat glass production. Prior to the development of the float process a variety of drawing and polishing processes were utilized (Cable, 1999).

The equilibrium thickness of float glass, t_{gr} is given by considering a surface energy balance

$$\frac{\rho_g g t_g^2}{2} \left(1 - \frac{\rho_g}{\rho_t} \right) = \gamma_{ga} + \gamma_{gt} - \gamma_{ta} \quad (2)$$

where ρ_g and ρ_t are the glass and tin densities (2.5 Mg m^{-3} and 6.5 Mg m^{-3} respectively), γ_{ta} and γ_{gt} are the tin-air and glass-tin surface energies (both $\sim 0.5 \text{ J m}^{-2}$) and γ_{ga} is the glass-air surface energy ($\sim 0.35 \text{ J m}^{-2}$). Substituting these values into Eq. (2) gives an equilibrium thickness of 6.8 mm. Top rolls can be used to produce glass to control the ribbon speed and thus produce glass that is either thinner or thicker than the equilibrium thickness.

The modern ability to produce large volumes of flat glass via the float process has resulted in people forgetting that historically window glass was not very flat due to the limitations of historical “flat” glass production technologies, such as crown glass production. This has resulted in a common myth concerning the flow of old windows, such as those in European cathedrals, over time which simply does not reflect reality. Gulbitten *et al.* (2018) have calculated for a medieval glass composition from Westminster Abbey a maximum flow of $\sim 1 \text{ nm}$ over 10^9 years. The reason that old windows tend to be thicker at the bottom is simply that the glass panes were not uniformly thick in the first place and, when glazing a window, installing the thicker (and thus heavier) section at the bottom is intrinsically more stable.

Optical Properties of SLS Glasses

While SLS glasses are not primarily thought of as optical glasses their optical homogeneity and color are nevertheless important in a number of applications. For example, it is essential that windows, especially in vehicles, exhibit minimal optical distortion. To prevent optical distortion it is necessary that there is a high degree of chemically homogenization and also that there are minimal residual stresses in the glass, as both compositional variation and residual stresses affect the refractive index, which typically is ~ 1.5 for SLS compositions (see, for example, Shahid and Glasser, 1972). Chemical homogenization requires that the different fluids produced when the batch first melts are thoroughly mixed to enable diffusion as, under commercial SLS glass melting conditions, the

Table 4 Colors produced by some transition metal and rare earth ions in SLS glasses

<i>Species</i>	<i>Color</i>
$\text{Cr}^{3+}/\text{Cr}^{6+}$	Green/Yellow
$\text{Mn}^{2+}/\text{Mn}^{3+}$	Colorless/Purple
$\text{Fe}^{2+}/\text{Fe}^{3+}$	Blue green/Yellow
Co^{2+}	Blue
Ni^{2+}	Brown
$\text{Cu}^{+}/\text{Cu}^{2+}$	Colorless/Blue
$\text{Ce}^{3+}/\text{Ce}^{4+}$	Yellow/Colorless
Nd^{3+}	Purple

diffusion distances are only of the order of 0.1 mm. In commercial melting, mixing is achieved primarily through convection arising from temperature gradients along the length of the furnace; the use of electric boost and bubblers can also aid mixing.

Color in SLS Glasses

Color can be produced in SLS glasses by three major mechanisms: solution colors due to the presence of transition metals or rare earth elements, with transition metals giving stronger colors (see [Table 4](#)); absorbing particles that are typically, but not necessarily metallic; and phase separation to produce white or opal glasses.

For solution colors redox control during SLS glass manufacture is critical for achieving both the desired color and good quality glass. Iron is particularly important in the coloring of SLS glasses as it is a common contaminant in the raw materials, as well as small amounts being added as a dopant to produce specific colored and filter glasses. Iron is present in SLS glasses as both Fe^{2+} and Fe^{3+} ions and both ions can occupy tetrahedral and octahedral sites and fully modeling the color produced has to take into account both the redox chemistry and the site occupation ([Volotinen et al., 2008](#)). Fe^{3+} absorbs in the ultraviolet (UV) portion of the spectrum with the absorption band extending into the visible absorbing blue light and thus Fe^{3+} results in the glass having a yellow color. Meanwhile Fe^{2+} absorbs in the infrared (IR) with the absorption band again extending into the visible this time absorbing red light meaning that Fe^{2+} results in the glass appearing blue-green. As Fe^{2+} and Fe^{3+} produce complementary colors, with Fe^{2+} producing the stronger color, decolourisation can be achieved by adjusting the $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratio through the addition of other redox species ([Parker, 2018](#)). Historically this was achieved by additions of As, which was actually added for refining purposes, with Ce being used more recently. An alternative approach, rather than making the melt more oxidizing, is to add Se to provide the complementary color to Fe^{2+} . Depending on the levels of iron present decolourisation may actually produce a glass which although apparently clear is in fact gray when compared visually with a glass that has a lower iron content.

For windows some degree of solar control can be achieved through the presence of iron in the glass, although the use of coatings is an industrially more flexible approach to this. For solar cell applications where very low losses due to absorption are required, the iron levels are reduced to ~ 100 ppm compared to ~ 1000 ppm in conventional float glass.

Amber glasses (see [Fig. 6](#)) involve the $\text{Fe}^{3+}\text{-S}^{2-}$ amber chromophore, which forms during cooling in reduced melts ([Beerken, 2005](#)), and which gives rise to strong absorptions at 295 nm and 425 nm (see [Fig. 6\(a\)](#)). Meanwhile green container glasses are usually colored by chromium (as Cr^{3+}) and iron with melting being carried out under oxidizing conditions – a range of greens can be produced from an emerald green through to an olive green. Lighter greens tend to be produced just using iron. As there is a correlation between the batch redox and the glass color, the batch redox number introduced by [Simpson and Myers \(1978\)](#) can be helpful. If glass melts are strongly colored then this reduces the radiation conductivity through the melt, and as a consequence electric boost may be required in the melting tank.

Absorbing particles are normally nanometric in size i.e., much smaller than the wavelength of light. As a result there is little light scattering but there is strong absorption even at concentrations of < 1000 parts per million (ppm). Examples include Ag which gives a yellow/orange color and Cu which gives a deep red. If the particles approach the wavelength of light in size then light scattering also occurs and this results in different colors in transmission and reflection, with scattering dominating in the latter case; the 4th century CE Roman Lycurgus cup is one of the most famous examples of this type of effect (see, for example, [Barber and Freestone, 1990](#)).

Unlike the other colored glasses mentioned above, white or opal glasses are designed to be opaque. They typically contain 1–5 wt% of precipitated particles that scatter the incident light, with the optimum particle size being about the wavelength of light. In fluoride opals these could be calcium, barium or sodium fluoride.

Photoelasticity and Stress Birefringence

Even though good quality annealed SLS glasses are optically isotropic, in the presence of stress SLS glasses become optically anisotropic and this leads to the production of colored fringes when the glass is observed between crossed polars in a polariscope or a strain viewer. The fringes are related to the principal stresses and two types of fringes can be formed; black isoclinics which give

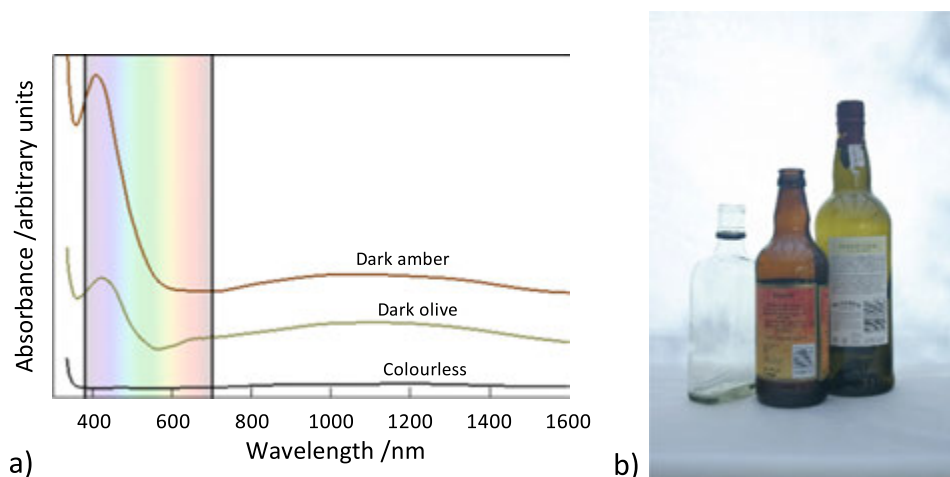


Fig. 6 (a) Absorption spectra for colorless, dark olive and dark amber SLS glasses, based on data in Bingham, P.A., Connelly, A.J., Hand, R.J., *et al.*, 2010. A multi-spectroscopic investigation of sulphur speciation in silicate glasses and slags. *Glass Technology: European Journal of Glass Science and Technology A* 51, 63–80; (b) examples of colorless, amber and olive green container glasses.

information about the orientation of the principal stresses and colored isochromatics that are directly proportional to the difference in principal stresses. Analysis is most straightforward for plane stress situations when it can be shown that:

$$n\lambda = Ct(\sigma_1 - \sigma_2) \quad (3)$$

where n is the fringe order, λ is the wavelength, C is the stress optic coefficient which for SLS glasses is typically ~ 2.6 Brewsters ($1 \text{ Brewster} = 10^{-12} \text{ Pa}^{-1}$) although this does vary with composition (Hemsley, 2015), t is the glass thickness and σ_1 and σ_2 are the principal in-plane stresses. The analysis becomes more complicated for 3-dimensional objects as containers and integrated photoelastic techniques are required (Aben *et al.*, 2014).

Stress birefringence is used in the production environment to determine whether the levels of residual stress in the glass are acceptable and a range of automatic stress meters are available, as well as computer based integrated photoelastic systems. In the case of flat glass production inline photoelastic measurements can be used for ribbon control.

Chemical Durability

Both container and flat glass are required to have sufficient chemical durability to avoid obvious degradation in properties during use, where usage times can be decades or longer. For higher specification applications such as pharmaceutical containers this is measured in standards such as ISO 4802-1:2016 and in fact borosilicate glasses are usually preferred in such applications over SLS glasses due to their higher chemical durability.

The first stage of chemical attack by water involves ion exchange wherein hydronium (H_3O^+) ions exchange with the relatively mobile sodium (Na^+) ions in the glass network. As noted above calcium ions occupy the same type of sites within the glass network as sodium ions, but being doubly charged are less mobile and thus the replacement of soda by lime increases the chemical durability. The fact that in SLS glasses alumina is incorporated into the glass network as AlO_4^- tetrahedra, charge balanced by sodium ions, means that the presence of alumina reduces the mobility of sodium ions enhancing the chemical durability.

If there is limited water on the glass surface then the sodium ions will lead to an increase in the solution pH and eventually this can become sufficiently high that the Si–O–Si bond is subject to attack and congruent dissolution of the glass occurs. If this occurs on the interior surfaces of glass panes in a double glazing unit it can eventually lead to a clouding of the glass surface. Alternatively if the glass is exposed to an exterior environment then the sodium and calcium ions may react with atmospheric components to produce sulfates, carbonates or nitrates on the glass surface. Surface deposits can lead to localized attack and Bange *et al.* (2002) have reported notably different corrosion rates on SLS glass depending on whether the surfaces have been cleaned or not.

For window applications so called “self-cleaning” SLS glass products are available. These glasses have photocatalytic TiO_2 coatings which enable degradation of organic compounds that would otherwise be adsorbed onto the glass surface over time. Such compounds reduce the hydrophilicity of the glass surface and can act as a glue hindering the removal of surface contamination by rain. As a result such “self-cleaning” glasses exhibit a lower degree of surface contamination (soiling) over time (Verità *et al.*, 2007).

Chemical durability of glasses is a complex phenomenon and small compositional changes can have significant effects. For example, the presence of small amounts of tin on the side of float glass that was in contact with the float bath (the tin side) means that the durability of this side is notably better than the “air side” of the same glass as shown by a lower rate change of

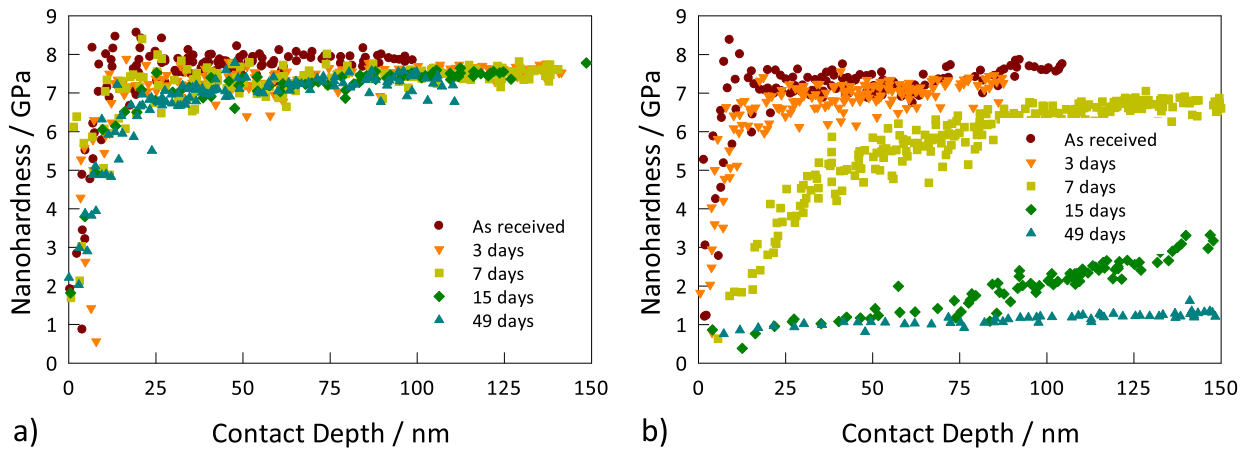


Fig. 7 Nanohardness as function of depth and time of exposure to 95% relative humidity at 40°C of SLS float glass (a) tin side and (b) air side (selected data from Gonzalez Rodriguez, J.A., Hand, R.J., 2013. Evolution of the modulus and hardness of the tin and air sides of float glass as a function of hydration time. *Glass Technology: European Journal of Glass Science and Technology A* 54, 36–41).

Table 5 Typical mechanical properties of soda-lime-silica glasses

Mechanical property	Value
Young's modulus	70–75 GPa
Poisson's ratio	0.22–0.25
Fracture toughness	0.72–0.82 MPa m ^{1/2}
Hardness (Vickers)	5.4–6.6 GPa
Brittleness	6.5–9.0 μm ^{-1/2}
Thermal expansion coefficient	9.0–10.0 × 10 ⁻⁶ K ⁻¹
Stress corrosion <i>n</i> (power law fit)	14–16

the nanohardness with time when exposed to high temperature and relative humidity (see [Fig. 7](#) and [Gonzalez Rodriguez and Hand, 2013](#)).

Mechanical Properties

SLS glasses are hard brittle materials with low values of fracture toughness (see [Table 5](#)) hence they are flaw sensitive. If sufficient load is applied to an SLS glass object to cause fracture, cracking will normally initiate from surface defects introduced via unavoidable mechanical contact during either production and/or use. As a result SLS glasses and glass products do not have a single well-defined fracture strength and the strength of any particular glass object is likely to change with time, with practical strengths typically varying from ~30 MPa to ~100 MPa depending on the age and history of the glass surface. Using:

$$K_{Ic} = C\sigma_f\sqrt{\pi a} \quad (4)$$

where K_{Ic} is fracture toughness, σ_f is failure strength, a is flaw size and C is a constant (~ 1 for simple flaw geometries) indicates that typical surface defects in glass products are of the order of a few 10 s of microns in depth. Statistical methods are commonly required for describing glass strength with the Weibull statistics approach being widely used (see, for example, [Hand and Sangleboeuf, 2018](#)), although it may be equally appropriate to use the normal or log-normal distributions to describe the actual strength data.

Some variation of the mechanical properties of SLS glasses with composition have been reported (see, for example, [Sehgal and Ito \(1999\)](#), [Deriano et al \(2004\)](#), [Kilinc and Hand \(2015\)](#)). Many of the reported variations involve changes in minor components as well as some of the major components with [Sehgal and Ito \(1999\)](#) producing a so-called “less brittle glass” by replacing some of the soda by potassia, some of the lime by magnesia and some of the silica by alumina. Recent work indicates that the less-brittle SLS glass is more correctly described as being crack-resistant as the actual fracture toughness is little changed from that of conventional SLS glasses ([To et al., 2020](#)).

SLS glasses are relatively prone to mechanical failure through thermal shock failure as they have high thermal expansion coefficients (see [Table 5](#)) coupled with low thermal conductivities. Thus although chemical laboratory ware can be made of SLS glass, the lower thermal expansion borosilicate glasses are preferred.

For applications requiring higher strengths SLS glasses may be strengthened by introducing residual surface compressive stresses via thermal or chemical tempering. With flat glass, lamination into a composite structure can also reduce the likelihood of complete catastrophic failure and this approach is widely used in car windscreens and, sometimes in combination with thermal tempering, in architectural applications.

Thermal Tempering

Thermal tempering, which involves rapid cooling from above the glass transition temperature, is most readily applied to simple geometries and thus is most widely used with flat glass although it is used on some glassware as well. For full thermal tempering the maximum surface compressive stress (σ_c) in SLS glasses should exceed 69 MPa and can be up to ~ 100 MPa; the strength of glass components is increased by approximately the value of σ_c (Hand and Sangleboeuf, 2018). If the surface compressive stresses are lower ($24 < \sigma_c < 69$ MPa) then the product may be referred to as heat strengthened. Thin glass (< 3 mm thick) or more complex shapes are more likely to be heat strengthened than fully tempered.

The thermal tempering stress distribution is ideally parabolic and can be modeled by:

$$\sigma = \frac{\sigma_c}{2} \left(1 - \frac{12x^2}{d^2} \right) \quad (5)$$

where d is the thickness of the glass and x is the distance from the centreline. The residual surface compressive stresses decrease with depth and at $x \approx 0.21d$ the residual stresses become tensile and rise to 50% of the maximum surface compressive stress on the centerline. These high interior tensile stresses can cause failure from a defect known as nickel sulfide. In commercial glass production if there is a source of nickel present (sulfur will typically be present from either batch materials or the fuel) small droplets of nickel sulfide can be formed in the melt. These droplets are immiscible with the melt and are difficult to spot. While they do not cause a particular problem in annealed glass, the heat treatment and quenching process used to produce thermally tempered glass can result in them being retained as the metastable high temperature form, α -NiS. Subsequent heating through e.g., solar irradiation can then result in an expansive conversion to the low temperature β -NiS form. If this occurs in a region with high tensile residual stresses, interior microcracking and subsequent spontaneous failure can occur. This problem has arisen in a number of high profile buildings globally. It can be shown that there is a critical NiS inclusion size for this to occur, with larger inclusions being tolerated further from the centreline (Swain, 1981). To avoid this problem manufacturers try to prevent NiS formation in the first place and heat-soak tests are required to identify the problem before the glass is installed.

Chemical Tempering

Chemical tempering involves the replacement of alkali ions in the glass (Na^+ ions in SLS glasses) by larger alkali ions (K^+) through diffusional ion exchange. As chemical tempering is a diffusion based process it is slow and therefore expensive. Hence it is only commercially viable for high end products despite the fact that it can result in a much greater degree of strengthening than is possible with thermal tempering. For SLS glasses a potassium containing salt bath (typically potassium nitrate based) would be used to replace sodium ions by larger potassium ions at a temperature below the glass transition temperature. Much higher surface compressive stresses can be achieved with this technique than is possible with thermal tempering but they are limited to a thin surface layer (the case depth) due to the diffusional nature of the production process. As a result the compensating interior tensile stresses are much lower than is the case with thermally tempered glass. The high surface compressive stresses mean that practical glass strengths can be increased to several hundred MPa for SLS glasses.

Sub-Critical Crack Growth

SLS glasses are susceptible to slow crack growth due to stress corrosion under applied load in the presence of atmospheric water. As shown in Fig. 8(a) the crack velocity, v , is a strong function of the applied stress intensity factor, K_I , given by:

$$K_I = C\sigma\sqrt{\pi a} \quad (6)$$

where σ is the applied stress with the other terms as defined previously (see Eq. (4)). Fig. 8(a) shows that there are 4 distinct regions; namely a threshold ($K_{I_{th}}$) below which stress corrosion does not occur; then a region labeled I during which crack growth is controlled by the reaction between water and the strained Si–O–Si bonds at the crack tip; a plateau region labeled II in which the rate at which water can diffuse to the crack tip becomes important and region III where the transition to fast fracture takes place and the applied stress intensity factor becomes equal to the fracture toughness K_{Ic} . Region I may be fitted using an exponential:

$$v = \frac{da}{dt} = \alpha \exp(K_I), \quad (7)$$

where α is a constant, or a power law function:

$$v = \frac{da}{dt} = AK_I^n, \quad (8)$$

where A and n are both constants. Although the power law description is a purely empirical description it is easier to use when

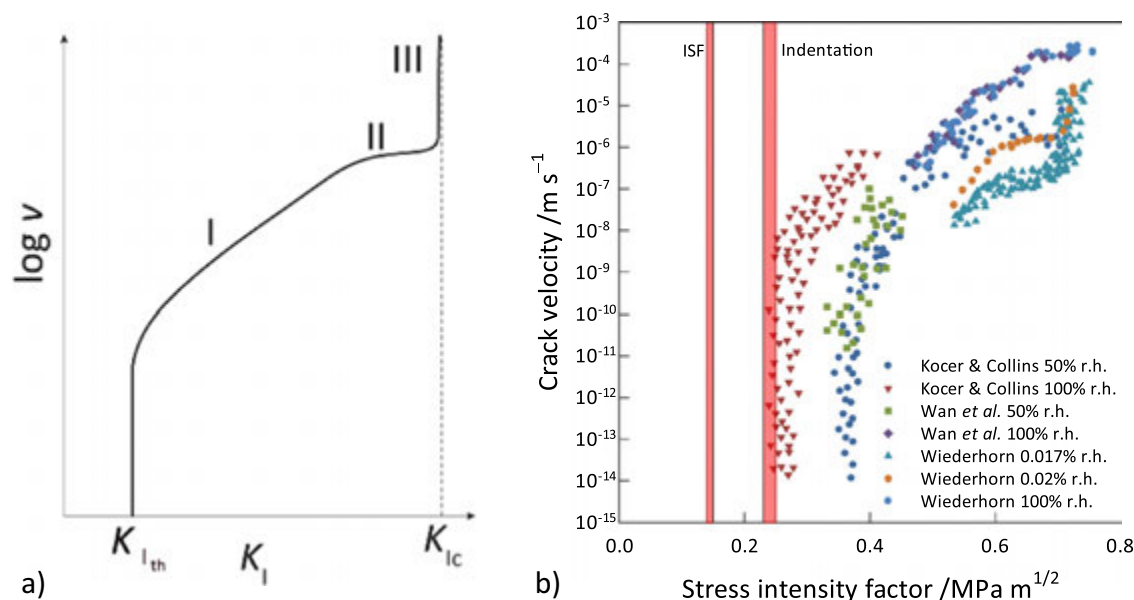


Fig. 8 Crack velocity as a function of applied stress intensity factor. (a) schematic showing threshold $K_{I_{th}}$, regions I, II and III (fast fracture) and (b) SLS data including a particular focus on the threshold region. Figure adapted from Kocer, C., Collins, R.E., 2001. Measurement of very slow crack growth in glass. *Journal of the American Ceramic Society* 84, 2585–2893 using data taken from Sglavo, V.M., Green, D.J., 1996. Threshold stress intensity factor in soda-lime silicate glass by interrupted static fatigue test. *Journal of the European Ceramic Society* 16, 645–651. Sglavo, V.M., Green, D.J., 1999. Indentation determination of fatigue limits in silicate glasses. *Journal of the American Ceramic Society* 82, 1269–1274. Wan, K.-T., Lathabai, S., Lawn, B.R., 1990. Crack velocity functions and thresholds in brittle solids. *Journal of the European Ceramic Society* 6, 259–268. Wiederhorn, S.M., 1967. Influence of water vapour on crack propagation in soda-lime glass. *Journal of the American Ceramic Society* 50, 407–414. ISF refers to the interrupted static fatigue test for threshold measurement and indentation to the indentation test for threshold measurement.

making lifetime predictions. There is disagreement in the literature as to whether there is a clear threshold below which stress corrosion does not occur in SLS glasses with available data indicating a dependence on both relative humidity and test technique (see Fig. 8(b)).

Such sub-critical growth is responsible for the gradual extension of cracks from e.g., impact chips on car windscreens or from edge defects in windows in a frame. In the former case, coatings to repair such damage and prevent sub-critical crack growth are available in the market.

Summary

Soda-lime-silica glasses have been very widely used since ancient times to produce containers, windows and glassware as the raw materials required to produce them are readily available and relatively cheap. By controlling temperature and hence viscosity SLS glasses can be readily formed using highly automated production techniques. Although a wide range of SLS glass compositions can be produced, the relatively narrow range of compositions used commercially represents a good balance between processability and final properties including chemical durability. With suitably pure raw materials very clear glass can be produced, particularly if the iron content can be minimized. Iron plays an important role in the color of container glasses. Color can also be produced through the addition of other dopants, usually in relatively small quantities. As soda-lime-silica glasses have low fracture toughness values the mechanical strength of SLS products is usually controlled by the presence of small surface flaws. In the presence of water such flaws can grow sub-critically due to stress corrosion. The mechanical strength may be improved through the use of residual stresses, introduced via thermal or chemical tempering. Lamination may also be used to provide an additional level of safety if one layer fails.

References

- Aben, H., Errapart, A., Anton, J., 2014. Measuring residual stresses in homogeneous and composite glass materials using photoelastic techniques. In: Shokreih, M.M. (Ed.), *Residual Stresses in Composite Materials*. Cambridge: Woodhead Publishing, pp. 152–172.
- Bange, K., Anderson, O., Rauch, F., *et al.*, 2002. Multi-method characterization of soda-lime glass corrosion. Part 2. Corrosion in humidity. *Glass Science and Technology* 75, 20–33.
- Barber, D.J., Freestone, I.C., 1990. An investigation of the origin of the colour of the Lycurgus Cup by analytical transmission electron microscopy. *Archaeometry* 32, 33–45.
- Beerkens, R., 2005. Sulphate decomposition and sulphur chemistry in glass melting processes. *Glass Technology* 46, 39–46.
- Bingham, P.A., 2010. Design of new energy-friendly compositions. In: Wallenberger, F.T., Bingham, P.A. (Eds.), *Fiberglass and Glass Technology*. New York: Springer, pp. 267–351.

- Bingham, P.A., Connelly, A.J., Hand, R.J., *et al.*, 2010. A multi-spectroscopic investigation of sulphur speciation in silicate glasses and slags. *Glass Technology: European Journal of Glass Science and Technology A* 51, 63–80.
- Cable, M., 1999. Mechanization of glass manufacture. *Journal of the American Ceramic Society* 82, 1093–1112.
- Deriano, S., Rouxel, T., LeFloch, M., Beuneu, B., 2004. Structure and mechanical properties of alkali-alkaline earth-silicate glasses. *Physics and Chemistry of Glasses* 45, 37–44.
- Fluegel, A., 2007. Glass viscosity calculation based on a global statistical modelling approach. *Glass Technology: European Journal of Glass Science and Technology* 48, 13–30.
- Gonzalez Rodriguez, J.A., Hand, R.J., 2013. Evolution of the modulus and hardness of the tin and air sides of float glass as a function of hydration time. *Glass Technology: European Journal of Glass Science and Technology A* 54, 36–41.
- Greaves, G.N., Fontaine, A., Lagarde, P., Raoux, D., Gurman, S.J., 1981. Local structure of silicate glasses. *Nature* 293, 611–616.
- Gulbilen, O., Mauro, J.C., Guo, X., Boratev, O.N., 2018. Viscous flow of medieval cathedral glass. *Journal of the American Ceramic Society* 101, 5–11.
- Hand, R.J., Sangleboeuf, J., 2018. Room temperature mechanical properties of oxide glasses. In: Takada, A., Parker, J., Durán, A., Bange, K. (Eds.), *Teaching Glass Better*. Madrid: International Commission on Glass, pp. 271–286.
- Hemsley, J.A., 2015. *Glass in Engineering Science Vol. 1: Optical Birefringence in Glass*. Sheffield: Society of Glass Technology.
- Kilinc, E., Hand, R.J., 2015. Mechanical properties of soda-lime-silica glasses with varying alkaline earth contents. *Journal of Non-Crystalline Solids* 429, 190–197.
- Lakatos, T., 1976. Viscosity-temperature relations in glasses composed of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-K}_2\text{O-Li}_2\text{O-CaO-MgO-BaO-ZnO-PbO-B}_2\text{O}_3$. *Glasteknisk Tidskrift* 31, 51–54.
- Lakatos, T., Johansson, L., Simmingsköld, B., 1972. Viscosity temperature relations in the glass system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-K}_2\text{O-CaO-MgO}$. *Glass Technology* 13, 88–95.
- Le Losq, C., Cicconi, M.R., Greaves, G.N., Neuville, D.R., 2019. Silicate glasses. In: Musgraves, J.D., Hu, J., Calvez, L. (Eds.), *Springer Handbook of Glass*. Switzerland: Springer Nature, pp. 441–503.
- Mauro, J.C., Yue, Y., Ellison, A.J., Gupta, P.K., Allan, D.C., 2009. Viscosity of glass-forming liquids. *Proceedings of the National Academy of Sciences of the United States of America* 106, 19780–19784.
- Parker, J., 2018. Optical absorption. In: Takada, A., Parker, J., Durán, A., Bange, K. (Eds.), *Teaching Glass Better*. Madrid: International Commission on Glass, pp. 43–56.
- Sehgal, J., Ito, S., 1999. Brittleness of glass. *Journal of Non-Crystalline Solids* 253, 126–132.
- Shahid, K.A., Glasser, F.P., 1972. Phase equilibria in glass forming region of the system $\text{Na}_2\text{O-CaO-MgO-SiO}_2$. *Physics and Chemistry of Glasses* 13, 27–42.
- Simpson, W., Myers, D.D., 1978. The redox number concept and its use by the glass technologist. *Glass Technology* 19, 82–85.
- Smrček, A., 2010. Compositions of industrial glasses. In: Wallenberger, F.T., Bingham, P.A. (Eds.), *Fiberglass and Glass Technology*. New York: Springer, pp. 229–266.
- Swain, M.V., 1981. Nickel sulphide inclusions in glass: An example of microcracking induced by a volumetric expanding phase change. *Journal of Materials Science* 16, 151–158.
- To, T., Jensen, L.R., Smedskjaer, M.M., 2020. On the relation between fracture toughness and crack resistance in oxide glasses. *Journal of Non-Crystalline Solids* 534, 119946.
- Verità, N., Geotti-Bianchini, F., Falcone, R., *et al.*, 2007. Analysis of self-cleaning and float glass: A comparative study of pollution on the glass surfaces under real life conditions. *Glass Technology: European Journal of Glass Science and Technology A* 48, 183–190.
- Volotinen, T.T., Parker, J.M., Bingham, P.A., 2008. Concentrations and site partitioning of Fe^{2+} and Fe^{3+} ions in a soda-lime-silica glass obtained by optical absorbance spectroscopy. *Physics and Chemistry of Glasses: European Journal of Glass Science & Technology B* 49, 258–270.
- Zanotto, E.D., Mauro, J.C., 2017. The glassy state of matter: Its definition and ultimate fate. *Journal of Non-Crystalline Solids* 471, 490–495.

Further Reading

- Bamford, C.R., 1977. *Colour Generation and Control in Glass*. Amsterdam: Sheffield: Society of Glass Technology, (Elsevier Weyl, W.A., 1951; 5th reprint 1999. Coloured glasses).
- Le Bourhis, E., 2014. *Glass: Mechanics and Technology*, second ed. Weinheim: Wiley-VCH.
- Varshneya, A., Mauro, J.C., 2019. *Fundamentals of Inorganic Glasses*, third ed. Amsterdam: Elsevier.

Relevant Website

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Viscosity Calculation.
Glass Properties.

Glasses: Aluminosilicates

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Aluminosilicate glasses are widely used and investigated materials with current and promising technological applications such as high-power laser gain media, flat-panel displays, solid oxide fuel cells, sealing materials, glass-fiber composites and long-term immobilization of wastes, to name a few. They are also abundant in nature and relevant for geological processes as they are chemically close to the natural magmatic compositions of the Earth mantle. Finally at low SiO_2 content, quenched metallurgical slags are mainly composed of aluminosilicate glasses. Introducing Al_2O_3 strongly affects many physico-chemical properties. For instance, it improves fracture strength, increases elastic modulus and chemical resistance or hinders the trend to phase separation. Many properties correlate with the nature of non-framework cations present in the glass and to the flexibility for Al to adopt multiple coordination states. Different aspects of the disorder (network connectivity, Si/Al disorder, short range environment) affect the topological and configurational entropies. Here we address the specificities of the atomic-scale structure in diverse glass models containing alumina with important implications for interpreting and controlling the physico-chemical properties.

Commercial Glasses

Aluminosilicate (AS) glasses, notably at low-alkali content, have high values of tensile strength, resistance to high temperature and excellence resistance to chemical corrosion (Varshneya and Mauro, 2019). They have found widespread commercial application as fibers to reinforce plastics or concrete. E-glass (a low-alkali Ca-Mg aluminoborosilicate glass with 10–15 mol% Al_2O_3) is the most common glass fibers. Nowadays, a major application concerns alkali-free aluminosilicates used as thin glass sheets for liquid crystal flat displays.

With higher amounts of alkalis, aluminosilicate glasses can be used to obtain high surface strength via an ion exchange process. The chemical exchange (typically Na replaced by K) produces a permanent compressive stress in the glass surface that improves resistance to cracks and scratches. This type of glass is exploited in smartphone screens or aircraft windshields and further applications (for instance in automotive) are foreseen. Alkali or alkaline-earth aluminosilicate systems are also the precursor glasses for most glass-ceramics successfully designed for consumer applications.

Al_2O_3 , The Archetypical Intermediate Oxide

Al_2O_3 itself cannot form a glass as it does not satisfy the rules proposed by Zachariasen (1932) for a network former. However, a specificity of Al_2O_3 is to be able to form a glass when it is mixed with some modifying cations (typically alkaline earths or rare-earths). Sun (1947) has classified Al_2O_3 as an intermediate oxide acting as network former or modifier according to the composition. Indeed, Al_2O_3 can be added into the vitreous silicate network by replacing Si^{4+} cations in a tetrahedral environment. In that case, it plays the role of a network former and even small amounts of Al_2O_3 considerably modify the glass properties. Alternatively, Al can enter into high coordinated sites, playing the role of a modifier.

Basic Structural Features

Al in Substitution for Si

Si is a network former occurring as SiO_4 tetrahedra in oxide glasses. In aluminosilicate glasses, Al has a strong preference for tetrahedral coordination and usually substitutes for Si in tetrahedral positions, behaving similarly to a network former. An Al^{3+}O_4 tetrahedron has a charge deficit compared to a Si^{4+}O_4 unit because only three positive charges are brought by Al^{3+} cations. The electrical balance and the stabilization of $(\text{AlO}_4)^-$ tetrahedra are ensured by introducing positive charges brought by alkali (M^+), alkaline earth (M^{2+}) or rare-earth (RE^{3+}) cations. The cations compensating the net negative charge on $(\text{AlO}_4)^-$ units are called charge compensators (or charge-balancing cations), as opposed to a network modifying role when they are associated with non-bridging oxygen atoms (NBOs), participating in this latter case to the loss of network connectivity (depolymerization). A schematic representation of the addition of Al_2O_3 in a silicate glass network is shown in Fig. 1. The introduction of Al_2O_3 results in less NBOs (and thus more bridging oxygen atoms, BOs) and increases network connectivity. As a consequence the network becomes more stiff, the viscosity and the glass transition temperature (T_g) increase.

Since the Al-O bond length (1.76 Å) is longer than for Si-O (1.62 Å) (Cormier et al., 2000b), the AlO_4 tetrahedron is bigger than SiO_4 . The replacement of Si by Al then modifies the network organization and changes the glass physico-chemical properties. Raman spectroscopic investigations of aluminosilicate glasses (Mysen, 1990) revealed that increasing the Al/Si ratio implies a decrease in the force constant due to the weakening of the T-O bonds ($T = \text{Si}$ or Al) when Al substitutes for Si. The structure of aluminosilicate glasses largely depends on the arrangement of SiO_4 and AlO_4 tetrahedra that are forming a skeletal network by corner-sharing through bridging oxygen (BO) atoms.

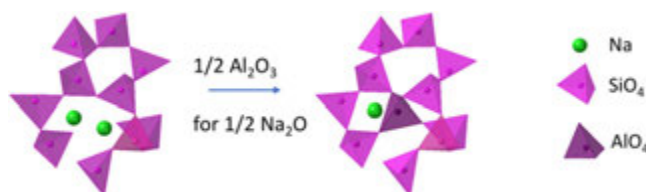


Fig. 1 Schematic representation of replacement of $\frac{1}{2}\text{Na}_2\text{O}$ by $\frac{1}{2}\text{Al}_2\text{O}_3$, resulting in a pair of non-bridging oxygens replaced by one bridging oxygen.

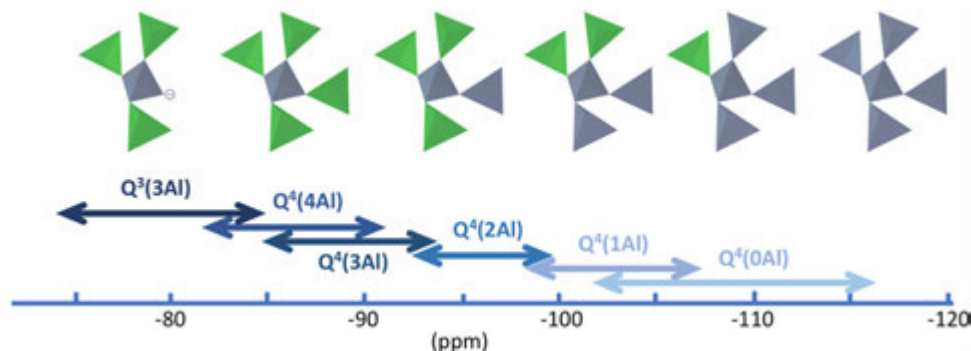


Fig. 2 Changes of the ^{29}Si chemical shifts for the various $Q^n_{\text{Si}}(m\text{Al})$ units in aluminosilicate glasses, as proposed by Engelhardt, G., 1989. Multinuclear solid-state NMR in silicate and zeolite chemistry. Trends in Analytical Chemistry 8, 343–347. doi:10.1016/0165-9936(89)87043-8.

The network connectivity is efficiently probed by Magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. The NMR chemical shift of ^{29}Si is sensitive to the degree of connectivity of the SiO_4 tetrahedra represented by the Q^n notation with n the number of BO on a tetrahedron. The decreasing number of BO displaces the chemical shift to higher values. The Si/Al substitution causes an additional modification of the chemical shift depending on the number m of Al atoms as second neighbors (**Fig. 2**). The moieties for Si and Al are denoted $Q^n_{\text{Si}}(m\text{Al})$ and $Q^n_{\text{Al}}(m\text{Si})$, respectively, indicating m Si–O–Al or Al–O–Si bonds (Edén, 2015). A Q^3_{Si} unit with a negative charge (-2) and one NBO requires a greater number of charge balancing cations in its neighborhood compared to a Q^3_{Si} with a charge (-1). The fully connected Q^4_{Al} species (charge -1) are then favored. Though the different $Q^n_{\text{Si}}(m\text{Al})$ moieties strongly overlap in the ^{29}Si NMR signal, advanced NMR techniques allow the relative amounts of these species to be fully quantified (Hiet *et al.*, 2009).

Another important structural feature is to determine the extent of Si/Al ordering that can be revealed by ^{17}O NMR. This spectroscopy gives access to the various linkages between BO atoms and framework cations, i.e., $^{14}\text{Si-O-}^{14}\text{Si}$, $^{14}\text{Si-O-}^{14,5}\text{Al}$, and $^{14}\text{Al-O-}^{14,5}\text{Al}$. Extensive Si/Al mixing, reflecting chemical order, results in a high fraction of $^{14}\text{Si-O-}^{14}\text{Al}$, whereas a tendency toward disorder leads to high fractions of $^{14}\text{Al-O-}^{14}\text{Al}$ and $^{14}\text{Si-O-}^{14}\text{Si}$ (Lee and Stebbins, 2002).

Al Avoidance Principle

According to the Loewenstein's rule (Loewenstein, 1954), also known as the Al-avoidance principle, there is a strong preference for $^{14}\text{Si-O-}^{14}\text{Al}$ linkages, whereas those of $^{14}\text{Al-O-}^{14}\text{Al}$ are energetically less favorable and avoided due to the local negative charge-accumulation. This rule governs the distribution of framework cations within the network but it seems to suffer many exceptions in alkali/alkaline-earth/rare-earth aluminosilicate glasses (Lee and Stebbins, 1999, 2000a; Lee *et al.*, 2005; Moesgaard *et al.*, 2010; Jaworski *et al.*, 2015). The framework disorder is quantified by the $Q^n_{\text{Si}}(m\text{Al})$ moieties or the oxygen cluster population, T-O-T, that both can be ascertained experimentally using MAS NMR spectroscopy of ^{29}Si and ^{17}O nuclei and confirmed with many molecular dynamics (MD) simulations (Lee and Stebbins, 1999, 2000a, 2002; Lee *et al.*, 2005; Lee and Stebbins, 2006; Moesgaard *et al.*, 2010; Park and Lee, 2012; Jaworski *et al.*, 2015).

To quantify the abundance of Si/Al intermixing, the degree of Al avoidance (Q) was proposed, spanning from complete chemical order ($Q = 1$, complete Al avoidance) to a random distribution of Si and Al ($Q = 0$) (Lee and Stebbins, 1999, 2002). At low Al_2O_3 content, obedience to the Loewenstein's rule is generally valid and implies a non-random mixing of network forming cations (Ando *et al.*, 2018; Ganisetti *et al.*, 2019). However, the proportion of Al–O–Al and Si–O–Al linkages increases with increasing connectivity as more Al_2O_3 is introduced at constant silica content (Lee and Stebbins, 2006, 2009). For instance, chemical ordering ($Q = 0$) is prevalent in Na aluminosilicate compositions except for compositions with $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1$, emphasizing that the Si/Al ordering behavior depends on composition (Na/Si or Si/Al ratios) (Lee and Stebbins, 2000b; Lee *et al.*, 2005; Iftekhar *et al.*, 2009; Lee and Stebbins, 2009; Park and Lee, 2014). Increasing fictive temperatures tend to increase Al–O–Al linkages (Dubinsky, 2006). The size and valence of non-framework cations have also a considerable influence and this effect can be rationalized using the cation field strength, CFS, defined as z/r^2 , with z the cation valence and r the ionic radius

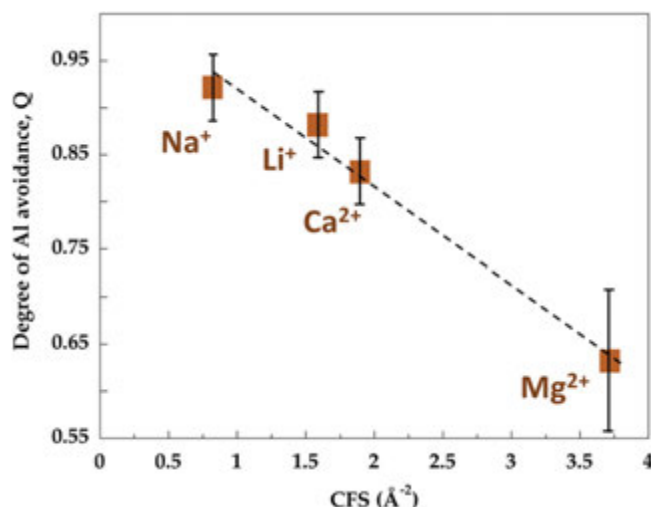


Fig. 3 Effect of cation field strength, CFS, on the degree of Al avoidance, Q . Data from Lee, S.K., Kim, H.-I., Kim, E.J., Mun, K.Y., Ryu, S., 2016. Extent of disorder in magnesium aluminosilicate glasses: Insights from ^{27}Al and ^{17}O NMR. *The Journal of Physical Chemistry C* 120, 737–749. doi:10.1021/acs.jpcc.5b10799.

(Shannon, 1976). Since high CFS favors negative charge concentration, Al atoms tend to be closer and the probability of finding Al-O-Al linkages increases with CFS: RE > Mg > Ca > (Ba, Li) > Na > (K, Rb, Cs) (RE = rare earth) (Stebbins *et al.*, 1999; Lee and Stebbins, 2000a,b; Kelsey *et al.*, 2008; Jaworski *et al.*, 2012; Okhotnikov *et al.*, 2013; Lee *et al.*, 2016). Therefore, RE-aluminosilicate glasses display the highest degree of randomness in their Si/Al distribution (Iftekhar *et al.*, 2009). Breakdown of the Al avoidance is confirmed by several MD simulations (Stein and Spera, 1995; Cormier *et al.*, 2003; Ando *et al.*, 2018; Ganiseti *et al.*, 2019). The effect of CFS on the degree of Al avoidance is shown in Fig. 3 for alkali/alkaline earth cations (Lee *et al.*, 2016). The extent of chemical ordering (Q) manifests a linear decrease with CFS ($Q \approx -0.1 \times \text{CFS} + 1$). It is expected that this simple relationship could not be valid for glasses with higher CFS and/or with RE, with a deviation from the linear trend (Lee *et al.*, 2016).

Aluminosilicate Glass Models

For tectosilicate compositions ($M^{n+}/n\text{Al} = 1$), the fully interconnected network is described by the “Compensated Continuous Random Network” (CCRN) model (Greaves and Ngai, 1995a). The modified random network (MRN) model is used to describe Al_2O_3 -free glasses and imply a micro-segregation of modifiers with the co-existence of two sub-networks: one rich in modifiers and NBOs and another one rich in network formers. For peralkaline(-earth) glasses ($M^{n+}/n\text{Al} > 1$), an intermediate structure between CCRN and MRN prevails. Si^{4+} and Al^{3+} cations are essentially organized in a corner-sharing tetrahedral network with NBOs mainly connected to Si atoms. The M^{n+} cations not used to neutralize the charge-imbalance from $(\text{AlO}_4)^-$ tetrahedra promote the formation of NBOs. Percolating channels similar to those existing in the MRN models have also been proposed in aluminosilicate glasses (Sukenaga *et al.*, 2017; Le Losq *et al.*, 2017). To further consider the distribution of framework units and the violation of the Loewenstein’s rule in aluminosilicate glasses, an extended modified random network (EMRN) model was proposed (Allu *et al.*, 2018; Ganiseti *et al.*, 2019). According to this model, three regions co-exist (Fig. 4): a depolymerized channel region (similar to MRN) and a $\text{SiO}_4/\text{AlO}_4$ network structure region that is separated in “heteronuclear” (mainly Si-O-Al and Al-O-Al) and “homonuclear” (mainly Si-O-Si) regions. M^{n+} cations acting as charge compensator favor the formation of Si-O-Al heteronuclear regions, whereas M^{n+} cations acting as modifiers are associated with several Si-NBO forming depolymerized regions. The Si atoms in excess of Si-O-Al and Si-NBO bonds form SiO_4 -rich “homopolar” regions.

Local environment around Al – Over coordinated Al

Al in tetrahedral coordination is predominantly present in aluminosilicate glasses as in most minerals, zeolites and ceramics. The aluminum environment has been investigated using many experimental techniques: Raman spectroscopy (Brawer and White, 1977; McKeown *et al.*, 1984), X-ray absorption spectroscopy (McKeown *et al.*, 1985; Landron *et al.*, 1992; Wu *et al.*, 1999; Sen, 2000; Neuville *et al.*, 2004b; Moulton *et al.*, 2016) and NMR (McMillan and Kirkpatrick, 1992; Stebbins *et al.*, 2000; Toplis *et al.*, 2000; Neuville *et al.*, 2006).

The phase diagram of a $\text{M}_{2/n}\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system ($n = 1, 2$) can be divided in two domains called peralkaline(-earth) for a ratio $R = M^{n+}/n\text{Al} > 1$ and peraluminous for a ratio $R = M^{n+}/n\text{Al} < 1$. The line $R = 1$ separating these two domains is called the “charge compensation” or “charge balanced” join corresponding to tectosilicate compositions. In the peralkaline(-earth) field ($R > 1$), the concentration of M^{n+} cations allows the full compensation of the charge deficit of each $(\text{AlO}_4)^-$ tetrahedron and Al^{3+} , stabilized in tetrahedral position, behaves as a network former similar to Si^{4+} . M^{n+} cations in excess relative to Al^{3+} play a network modifying role and introduce NBOs into the structure. When R decreases, the number of NBOs decreases and the glass network connectivity increases. In principle, when $R = 1$, no more NBOs should remain in the glass network, all Al^{3+} atoms are

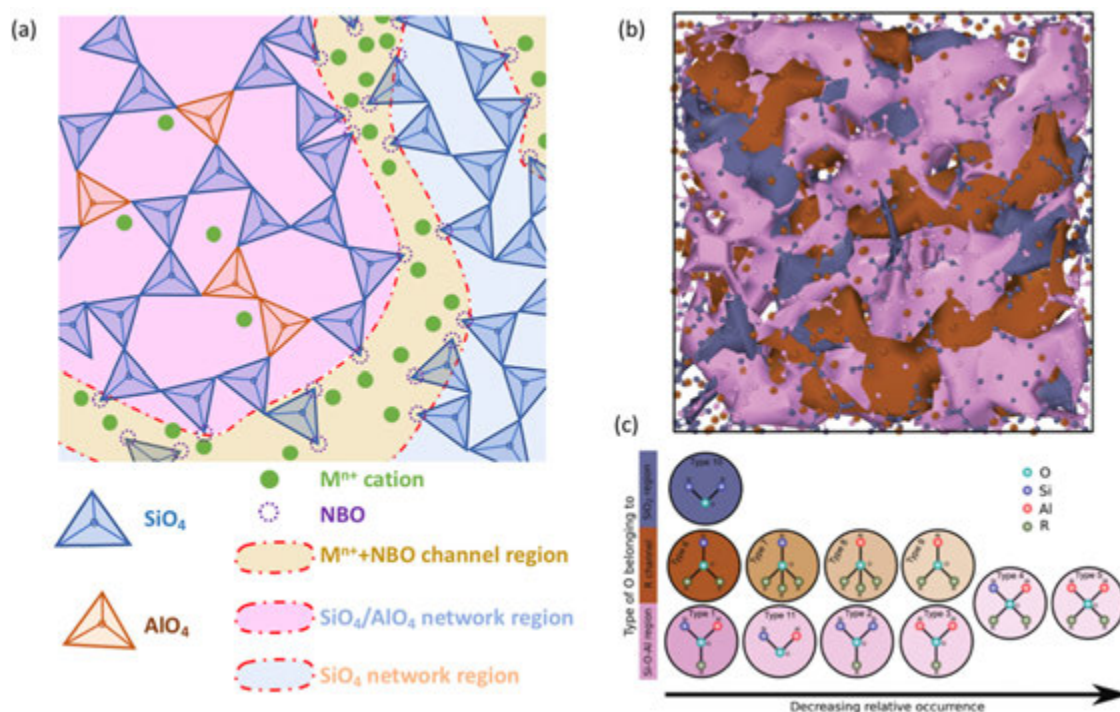


Fig. 4 (a) Schematic 2D representation of the EMRN separating three regions in $M^{n+}O-Al_2O_3-SiO_2$ glasses. (b) MD simulations of a $(Ca,Mg)O-Al_2O_3-SiO_2$ glass showing the SiO_4/AlO_4 network regions (pink), the SiO_4 network region (blue) and the alkaline-earth rich channels (brown). (c) Possible O environments with the background color corresponding to the three regions in (b); the intensity reflects the probability of occurrence of the O type in each region. Reprinted with permission from (a) Allu, A.R., Gaddam, A., Ganiseti, S., *et al.*, 2018. Structure and crystallization of alkaline-earth aluminosilicate glasses: Prevention of the alumina-avoidance principle. *The Journal of Physical Chemistry B* 122, 4737–4747. doi:10.1021/acs.jpcb.8b01811. Ganiseti, S., Gaddam, A., Kumar, R., *et al.*, 2019. Elucidating the formation of Al-NBO bonds, Al-O-Al linkages and clusters in alkaline-earth aluminosilicate glasses based on molecular dynamics simulations. *Physical Chemistry Chemical Physics* 21, 23966–23977. doi:10.1039/C9CP04332B, Copyright (2019) by the Royal Society of Chemistry.

tetrahedrally coordinated and the network is fully connected. In the peraluminous domain ($R < 1$), a deficit in the number of charge compensators does not allow the stabilization of all AlO_4 tetrahedra. Consequently, higher coordinated species (five-fold coordination $[^5]Al$ or six-fold coordination $[^6]Al$) or O triclusters can be present.

However, the emergence of high field NMR in the beginning of 2000s led to a reconsideration of this simple structural picture. The presence of NBOs for glasses along the charge compensation join has been detected by ^{17}O NMR (Stebbins and Xu, 1997). Furthermore, numerous high-resolution solid-state ^{27}Al NMR studies (Toplis *et al.*, 2000; Neuville *et al.*, 2004b; Lee *et al.*, 2004; Neuville *et al.*, 2006, 2007; Allwardt *et al.*, 2007; Neuville *et al.*, 2008; Kelsey *et al.*, 2008; Xue and Kanzaki, 2008; Iftekhar *et al.*, 2012; Jaworski *et al.*, 2012; Park and Lee, 2012, 2014; Le Losq *et al.*, 2014; Novikov *et al.*, 2017) have inarguably revealed that aluminum is present in highly coordinated sites (i.e., five and six-fold coordination, $[^5]Al$ and $[^6]Al$) even in the peralkaline(-earth) domain or along the charge compensation join (Fig. 5). The formation of $[^5]Al$ is clearly favored over that of $[^6]Al$ and both populations of $[^5]Al$ and $[^6]Al$ change with pressure, temperature, composition (Si/Al or M/Al ratios) or with the nature of M^{n+} cations. Aluminum coordination increases under static or dynamic compression, particularly in depolymerized glasses (Sato *et al.*, 1991; Yarger *et al.*, 1995; Lee, 2004; Lee *et al.*, 2004; Allwardt *et al.*, 2005a,b; Kelsey *et al.*, 2009; Lee, 2010; Bista *et al.*, 2015). The effect of temperature has been studied in situ or by varying the quenching rate (Sato *et al.*, 1991; Kanehashi and Stebbins, 2007; Florian *et al.*, 2007; Stebbins *et al.*, 2008; Thompson and Stebbins, 2013; Le Losq *et al.*, 2014). The proportion of $[^5]Al$ tend to increase with increasing temperature (in situ measurement) or fictive temperature (obtained when varying the quenching rate) but the variations are small compared to the effect of pressure. The fraction of $[^5,6]Al$ sites strongly depends on the CFS of non-framework cations with high CFS favoring large population of $[^5,6]Al$ (Fig. 6) (Neuville *et al.*, 2008; Kelsey *et al.*, 2008; Iftekhar *et al.*, 2012; Jaworski *et al.*, 2012). The higher content of $[^5,6]Al$ is also observed for RE-aluminosilicate and Zn-aluminosilicate glasses but these cations seems to follow a different trend (Schaller and Stebbins, 1998; Florian *et al.*, 2007; Iftekhar *et al.*, 2012; Jaworski *et al.*, 2012, 2015; Cormier *et al.*, 2021).

The average cationic potential has been proposed to account for changes in $[^5,6]Al$ fractions with composition (Park and Lee, 2014). The average cationic potential is the ratio of charge (c) to ionic radius (r) normalized by the mole fraction of each non-network cation:

$$\langle c/r \rangle_{ave} = \sum_i x_i \frac{c_i}{r_i}$$

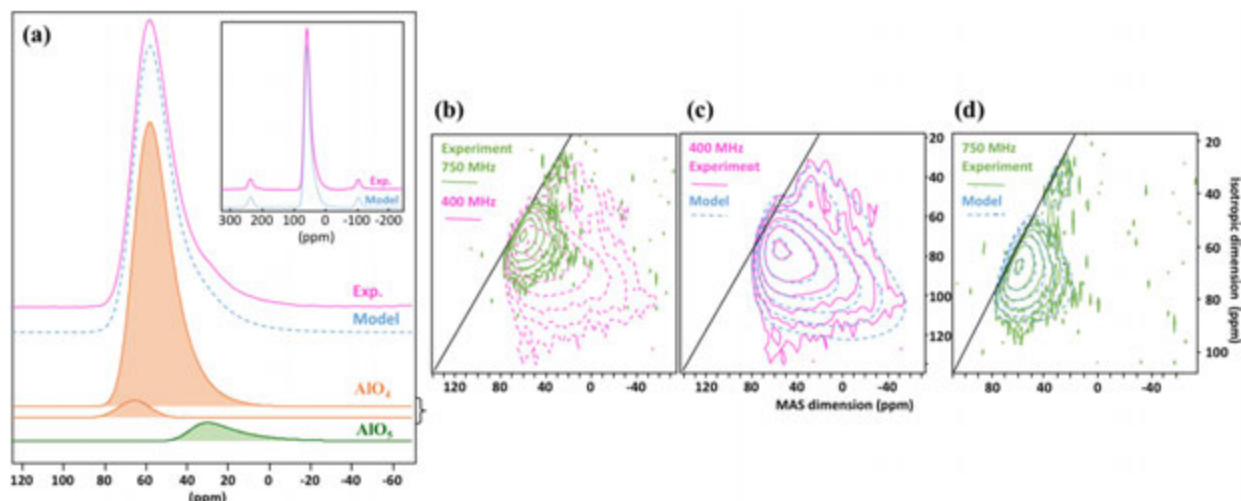


Fig. 5 (a) ^{27}Al ^1D NMR spectrum (750 MHz) of a $\text{CaO-Al}_2\text{O}_3\text{-2SiO}_2$ glass, showing the individual contributions of the $^{[4]}\text{Al}$ and $^{[5]}\text{Al}$ sites, including the spinning sideband of the satellite transition. The inserts show the experimental and simulated spectra (including central transition and first spinning sidebands of the outer transitions). (b) ^{27}Al 3Q MAS NMR spectra for the same glass measured at 400 MHz (9.4T) and 750 MHz (17.6 T). (c) and (d) Comparison between the experimental spectra and the simulated spectra with the same fitting parameters for the two fields. Data from Neuville, D.R., Cormier, L., Massiot, D., 2004b. Al environment in tectosilicate and peraluminous glasses: A ^{27}Al MQ-MAS NMR, Raman, and EXAFS investigation. *Geochimica et Cosmochimica Acta* 68 2004b 5071–5079.

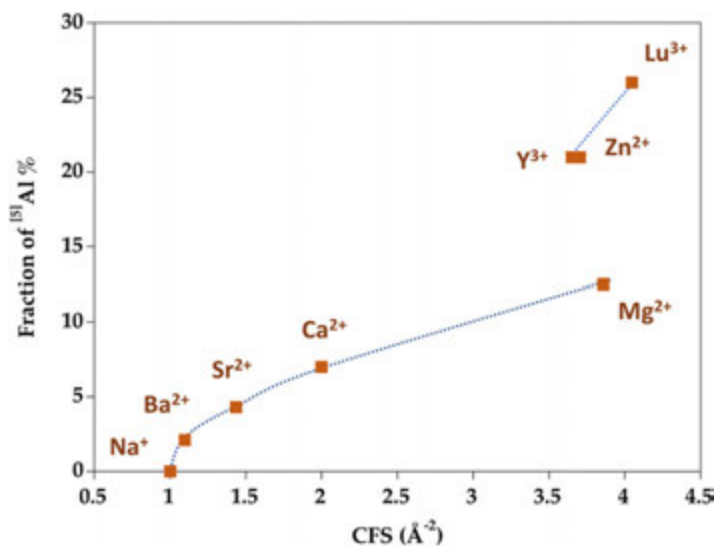


Fig. 6 Changes in the fraction of $^{[5]}\text{Al}$ with CFS for tectosilicate glasses with 50 mol% SiO_2 . Curves are only guide for the eye. Data from Neuville, D.R., Cormier, L., Massiot, D., 2006. Al coordination and speciation in calcium aluminosilicate glasses: Effects of composition determined by ^{27}Al MQ-MAS NMR and Raman spectroscopy. *Chemical Geology* 229, 173–185. Neuville, D.R., Cormier, L., Montouillout, V., *et al.*, 2008. Structure of Mg- and Mg/Ca aluminosilicate glasses: ^{27}Al NMR and Raman spectroscopy investigations. *American Mineralogist* 93, 1721–1731. Iftekhhar, S., Pahari, B., Okhotnikov, K., *et al.*, 2012. Properties and structures of $\text{RE}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ (RE = Y, Lu) glasses probed by molecular dynamics simulations and solid-state NMR: The roles of aluminum and rare-earth ions for dictating the microhardness. *The Journal of Physical Chemistry C* 116, 18394–18406. doi:10.1021/jp302672b. Novikov, A., 2017. Structure and Dynamics of Aluminosilicate Glasses and Melts. (Ph.D. thesis). Orléans:Université d'Orléans. Cormier, L., Delbes, L., Baptiste, B., Montouillout, V., 2021. Vitriification, crystallization behavior and structure of zinc aluminosilicate glasses. *Journal of Non-Crystalline Solids* 555, 120609.

where x_i , c_i and r_i are the mole fraction, the charge and the ionic radius of cation i , respectively. Park and Lee (2014) have summarized (Fig. 7) the population of $^{[5,6]}\text{Al}$ as a function of $\langle c/r \rangle_{\text{ave}}$ in all the ternary or multi-component aluminosilicate glasses studied so far. The population of $^{[5,6]}\text{Al}$ shows an increasing trend when $\langle c/r \rangle_{\text{ave}}$ increases. A threshold is observed at $\langle c/r \rangle_{\text{ave}} = 2$ with a significant increase of the fraction of $^{[5,6]}\text{Al}$ above this value but with considerable dispersion. This is explained because, at a constant $\langle c/r \rangle_{\text{ave}}$, the population of $^{[5,6]}\text{Al}$ strongly depends on both $\text{M}^{n+}\text{O}_{n/2}/\text{Al}_2\text{O}_3$ and Si/Al ratios (Neuville *et al.*, 2006, 2008; Kelsey *et al.*, 2008; Thompson and Stebbins, 2012).

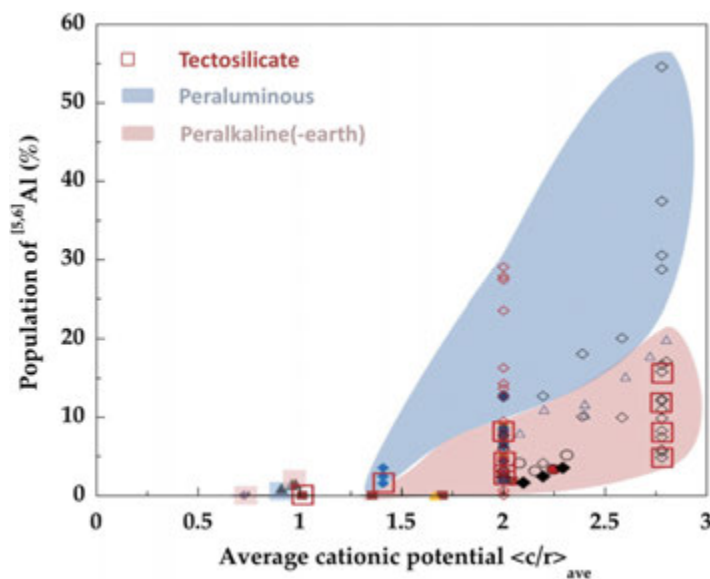


Fig. 7 Change of the fraction of $^{[5]}\text{Al}$ with the average cationic potential for various multicomponent aluminosilicate glasses. Modified from Park, S.Y., Lee, S.K., 2014. High-resolution solid-state NMR study of the effect of composition on network connectivity and structural disorder in multi-component glasses in the diopside and jadeite join: Implications for structure of andesitic melts. *Geochimica et Cosmochimica Acta* 147, 26–42. doi:10.1016/j.gca.2014.10.019. Copyright (2014) by Elsevier.

Each $(\text{AlO}_6)^{3-}$ octahedron is commonly considered as composed of three BOs and three NBOs (Day and Rindone, 1962) and has a network modifying character. Its content is always small compared to $^{[5]}\text{Al}$ because packing requirements for octahedral Al are unfavorable (Lacy, 1963). Conversely, the structural role of $^{[5]}\text{Al}$ as either a network former or a network modifier remains a fundamental debated question (Takahashi *et al.*, 2015). Using MD simulations of Ca-AS glasses, the bond angle distributions of AlO_5 (and SiO_5) units have been analyzed (Wiles *et al.*, 2020), revealing that $^{[5]}\text{Al}$ and $^{[5]}\text{Si}$ environments are consistent with the range of configurations found in a Berry pseudorotation (motion between two trigonal bipyramidal configurations). As $^{[5]}\text{Al}$ sites adopt any environment between the two extreme geometries with a minimal energy cost, the presence of $^{[5]}\text{Al}$ can likely play a governing role in mechanisms of plastic deformation or viscous flow. Similar to $^{[5]}\text{Si}$, $^{[5]}\text{Al}$ could be a transient species, thermally activated, that facilitates the diffusion of NBOs and the exchange of T–O bonds (Stebbins and Farnan, 1992; Farnan and Stebbins, 1994; Neuville *et al.*, 2007). Increasing the fraction of higher coordinated species can help to explain low viscosity at high pressure and reduced viscosities at high temperature (Lee *et al.*, 2004; Allwardt *et al.*, 2007; Wiles *et al.*, 2020). Furthermore, glasses with low hardness tend to have high $^{[5]}\text{Al}$ fractions (Iftikhar *et al.*, 2012; Svensson and Edén, 2013; Lamberson, 2016), suggesting that higher coordinated species could improve mechanical properties.

Oxygen Tricluster

As NBOs have been unexpectedly reported in compositions along the charge balancing joins (Stebbins and Xu, 1997), oxygen triclusters, O_{tri} , were proposed together with highly coordinated Al to maintain the network charge neutrality. By definition, O_{tri} is a special configuration of triply coordinated oxygen, $^{[3]}\text{O}$, only bonded to three tetrahedra (Fig. 8(a) and (b)): one AlO_4 and two SiO_4 or two AlO_4 and one SiO_4 (for this latter case a charge compensator is required in close proximity to maintain charge neutrality). Oxygen atoms coordinated to three, highly charged, tetrahedral cations are in strongly energetic configurations and violate Zachariasen's rules as O atoms are bonded to three network formers. A tricluster configuration can be regarded as an Al^{3+} ion acting as a modifier ion and bonded to NBOs (Fig. 8(c)).

The presence of triclusters results in a more compact packing and, thereby, higher densities are expected (Toplis *et al.*, 1997b). More importantly, triclusters can play a dominant role in transport properties, particularly for self-diffusion of oxygen in melts and viscous flow processes (Toplis *et al.*, 1997b). However, their presence is still debated and their influence on properties not ascertained (Tandia *et al.*, 2011). O_{tri} are mostly supported by MD simulations using classical (Cormier *et al.*, 2003; Barbieri *et al.*, 2004; Tandia *et al.*, 2011; Bouhadja *et al.*, 2014; Agnello *et al.*, 2019) or ab initio approaches (Benoit *et al.*, 2005). Experimentally, they have been detected only in a calcium aluminate glass using advanced NMR methods (Iuga *et al.*, 2005).

The Main Aluminosilicate Systems

Many different glasses can be obtained with aluminum and sometimes an extremely wide range of compositions can be achieved compared to the few crystalline compositions. Richet *et al.* (2006) have reviewed the glass forming regions in several important

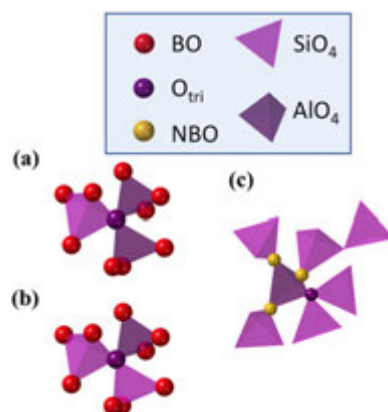


Fig. 8 Common oxygen shared between three tetrahedra: (a) one SiO₄ and two AlO₄ or (b) two SiO₄ and one AlO₄. (c) Al³⁺ in tetrahedral environment, equivalent to (b), with one O tricluster (O_{tri}) and three NBOs in the first coordination shell.

alkali/alkaline earth systems, showing a close connection between glass forming ability (GFA) and viscosity, low liquidus temperature and low configuration heat capacity. The main important families of glasses containing Al₂O₃ are documented in this part, by outlining the current structural knowledge in relation to their important physico-chemical properties.

Aluminate Glasses

Binary aluminate glasses are remarkable materials as they are free of typical glass network forming oxides but contain a high proportion of alkaline-earth or RE oxides. They have excellent mechanical properties (Rosenflanz *et al.*, 2004; Johnson *et al.*, 2005; Rosales-Sosa *et al.*, 2015, 2018), high softening points (Johnson *et al.*, 2005) and some of the highest sound speeds of any glassy systems (Yeganeh-Haeri *et al.*, 1998). Vickers hardness ($H_v = 9.5$ GPa) and elastic modulus ($E = 158$ GPa), reported for a 46Ta₂O₃–54Al₂O₃ glass, are among the highest values among oxide glasses (Rosales-Sosa *et al.*, 2015). Molten aluminates have viscosities that do not follow an Arrhenius behavior and are thus classified as “fragile” (Wallenberger and Brown, 1994; Weber *et al.*, 1998). The fragility of these systems is related to a large configurational entropy as many structural states are available in liquids due to possible change in cationic environment.

Calcium aluminate (CA) glasses are attractive due to a promising infrared (IR) transparency up to $\lambda = 6$ μm (Hafner *et al.*, 1958; Higby *et al.*, 1990; Sung and Kwon, 1999), similar to sapphire. With small SiO₂ doping, they can have ultralow optical losses compared to pure SiO₂ (0.04 dB km^{−1} for a SiO₂-low CA glass compared to 0.16 dB km^{−1} for SiO₂ at 1.55 μm (Lines *et al.*, 1989)). A high elastic modulus of 125 GPa was reached for a ZnO-CA glass-fiber (Wallenberger and Brown, 1994), higher than that of a S-glass (87 GPa) that is the high-strength glass-fiber exploited for reinforcement composites. Such properties make CA glasses of considerable technological value for diverse applications (laser windows, IR domes or windows, IR fiber optics) (Wallenberger and Brown, 1994; Weber *et al.*, 1998; Hwa, 1998). CA glasses are also important as analog systems of metallurgical slags and hydraulic cements (Skibsted *et al.*, 1993; Poe *et al.*, 1994; Douy and Gervais, 2000).

CA glasses can be synthesized using a conventional furnace and quenching rate in a narrow range near the eutectic composition (64CaO–36Al₂O₃, CA36) (Sung and Kwon, 1999). A wider glass formation range (20–80 mol% CaO) can be accessed using containerless methods such as aerodynamic levitation coupled with laser heating (McMillan and Piriou, 1983; Weber *et al.*, 2002; Benmore *et al.*, 2003; Neuville *et al.*, 2010). A technique using solar furnace melting and splat quenching has allowed glasses with fast quenching rates of 10⁶–10⁷ K s^{−1} to be obtained (McMillan and Piriou, 1983; McMillan *et al.*, 1996). The GFA of CA can also be enhanced by addition of various oxides, improving the glass stability and reducing the presence of hydroxyl bonds (Onoda and Brown, 1970; Shelby *et al.*, 1989; Uhlmann *et al.*, 1993; Shelby and Wierzbicki, 1995).

From Al₂O₃-poor glasses to the tectosilicate composition (CaO > 50 mol%), tetrahedrally coordinated Al is the only species detected by high resolution ²⁷Al NMR and Raman spectroscopies, with no change whatever to the quenching rate (McMillan and Piriou, 1983; McMillan *et al.*, 1996; Neuville *et al.*, 2006, 2010). Addition of CaO progressively disrupts the fully-connected network of AlO₄ tetrahedra in CA50 glass (50CaO–50Al₂O₃) and reduces the O coordination (Akola *et al.*, 2013; Edén, 2015). The average oxygen coordination number (CN) around Ca is mainly determined by numerous X-ray and neutron diffraction studies and shows a rather wide range of values from 4 to 5.5 for similar CA compositions between CA30 and CA50 (Morikawa *et al.*, 1983; Hannon and Parker, 2000; Cormier *et al.*, 2000b; Mei *et al.*, 2008a,b; Drewitt *et al.*, 2011; Benmore *et al.*, 2003), probably due to an asymmetric distribution of O neighbors around Ca. MD simulations give a higher average CN of 6, with a wide range of distribution of Ca sites, for various CA glasses (from CA75 to CA25) (Kang *et al.*, 2006; Thomas *et al.*, 2006; Drewitt *et al.*, 2011) but the choice of potentials appears to have a major influence on the estimation of CN for Al and Ca. The role of Ca is not clear but it was proposed that this cation behaves as a network former together with Al (Benmore *et al.*, 2003). Recently, by using a combination of DFT and RMC simulations, the CA36 glass has been described as a topologically disordered cage network with a wide ring size distribution and many large-sized rings (Akola *et al.*, 2013). This structural organization differs from that of CA50

glass and could reflect the high GFA of glasses near the eutectic composition. When $\text{CaO} \leq 50$ mol%, high Al coordinated species $^{[5,6]}\text{Al}$ and O_{tri} begin to appear (McMillan *et al.*, 1996; Iuga *et al.*, 2005; Neuville *et al.*, 2006; Mei *et al.*, 2008a) and these species can also be observed in MD simulations (Drewitt *et al.*, 2011). Using $\{^{17}\text{O}\}\{^{27}\text{Al}\}$ HMQC (heteronuclear multiple quantum correlation) NMR experiments, the formation of $\sim 5\%$ O_{tri} has been evidenced in a CA50 glass (Iuga *et al.*, 2005). Edge or face-sharing AlO_4 units could also be present in Al_2O_3 -rich compositions based on specific Raman bands at $\sim 620\text{ cm}^{-1}$ and 430 cm^{-1} (McMillan and Piriou, 1983).

Structural defects (for instance superoxide O_2^- ion radical or peroxy -O-O- linkages; see Hosono and Abe, 1987) appear to be very specific to CA glasses close to the eutectic and they could explain high photosensitivity to ultraviolet rays (Hosono *et al.*, 1985). Quenching a CA37 melt in strongly reducing conditions has allowed the synthesis of an electride glass, C12A7: e^- (Kim *et al.*, 2011), that contains stabilized solvated electrons trapped in cages of the CA network, which could give a potential glassy electronic conductor. Based on DFT-RMC simulations of CA37 glass, the structural origin of these solvated electrons was proposed to be due to efficient elemental mixing resulting from similar atomic charges for Al and Ca and a network cage structure resulting from considerable fraction of large-sized rings that can host solvated electrons (Akola *et al.*, 2013). However, since the glass transition temperatures of C12A7: e^- glass ($T_g = 973\text{ K}$) radically differs from that of the oxidized glass ($T_g = 1133\text{ K}$) (Kim *et al.*, 2011), fundamentally different structures can be alternatively expected (Edwards, 2011).

Other alkaline-earth glasses obtained using containerless techniques have been investigated: Ba and Ba-Ti aluminates (Skinner *et al.*, 2006, 2012), Ba and Sr aluminates (Alahache, 2011; Licheron *et al.*, 2011), showing glass forming regions in various ranges for Ba (33–37 and 62–75 mol% BaO) and Sr (37–40 and 55–75 mol% SrO). Only glasses with excess of alkaline-earth oxides have been investigated revealing the expected network of corner-sharing AlO_4 tetrahedra.

Rare-earth (RE) aluminates are another class of glasses of high interest due to their luminescence properties, offering potential applications, particularly in the field of white light-emitting diodes. The GFA of these compounds is low and they are mainly prepared using contactless conditions (Weber *et al.*, 1998; Zhang and Navrotsky, 2004; Watanabe *et al.*, 2012). According to Watanabe *et al.* (2012), RE aluminate glasses can be obtained between $0.20 < \text{RE}_2\text{O}_3$ (mol%) < 0.5 and all systems form glasses for 30–32 mol% RE_2O_3 . The glass forming region increases with the RE^{3+} ionic radius and is the widest for the La_2O_3 - Al_2O_3 system (27–50 mol%).

Y_2O_3 - Al_2O_3 (YA) glasses have attracted special interest as a potential glassy laser host (similar to crystalline $\text{Y}_3\text{Al}_5\text{O}_{12}$ garnet, the so-called YAG) and as a system displaying a variety of non-equilibrium phenomena (McMillan *et al.*, 2003; McMillan and Wilding, 2008). Yttrium aluminate glasses were synthesized in the range of 0.2–0.4 mol% Y_2O_3 by aerodynamic levitation or in an iridium wire furnace (Tangeman *et al.*, 2004; Skinner *et al.*, 2008; Nasikas *et al.*, 2011). YA glasses and their melts have been the subject of numerous studies due to the possible existence of polyamorphism in this system (Wilding and McMillan, 2001; Wilding *et al.*, 2002a,b; Wilding and McMillan, 2002; McMillan *et al.*, 2003; Tangeman *et al.*, 2004; Weber *et al.*, 2004; McMillan and Wilding, 2008; Skinner *et al.*, 2008; Greaves *et al.*, 2008; Barnes *et al.*, 2009; Greaves *et al.*, 2009; Nasikas *et al.*, 2011). Aasland and McMillan (1994) have observed the coexistence of two glassy states of identical composition but different structures, densities and thermodynamic properties (Fig. 9). Using differential scanning calorimetry, two glass transition temperatures were determined at $\sim 1135\text{ K}$ and 1300 K and attributed to HDA (high density amorphous) and LDA (low density amorphous) states, respectively (Wilding and McMillan, 2001; Wilding *et al.*, 2002a,b; Nasikas *et al.*, 2011). The two glassy states were mechanically separated to determine their respective densities (3.72 and 3.58 g cm^{-3}), allowing the assignment of the HDA and LDA to the inclusions and the glass matrix, respectively (McMillan and Wilding, 2008). Note that the assignment is surprising since single HDA glass can be formed, suggesting that it is the stable amorphous form, and several studies indicate LDA inclusions in the HDA glass matrix (Florian *et al.*, 2001; Nasikas *et al.*, 2011). The two HDA-LDA states imply a density-driven phase separation that could underline a first-order liquid-liquid phase transition. However the occurrence of this polyamorphism has been strongly debated (Greaves *et al.*, 2008; Barnes *et al.*, 2009; Greaves *et al.*, 2009).

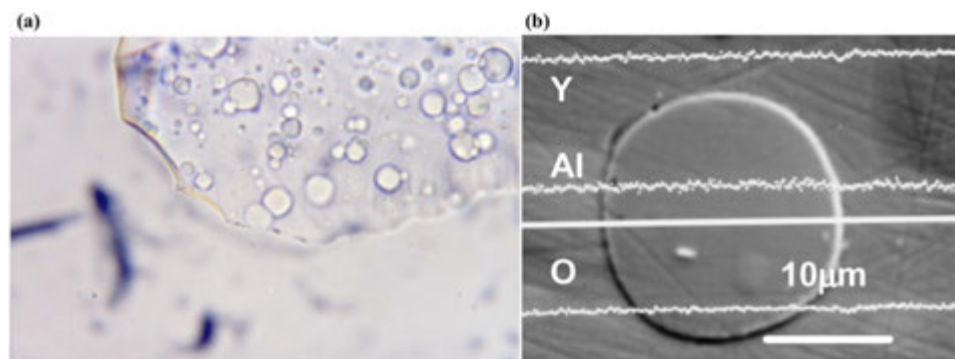


Fig. 9 (a) Photomicrograph of a $23\text{Y}_2\text{O}_3$ - $77\text{Al}_2\text{O}_3$ sample, showing sub-spherical glassy inclusions embedded within a glassy matrix. (b) Electron microprobe analysis for all elements (Y, Al, O) across a single inclusion. The lack of composition change at the inclusion-matrix interface indicates identical chemical compositions. Reprinted from McMillan, P.F., Wilding, M.C., 2008. Direct density determination of low- and high-density glassy polymorphs following a liquid-liquid phase transition in Y_2O_3 - Al_2O_3 supercooled liquids. *Journal of Non-Crystalline Solids* 354, 1015–1025. Copyright (2008) by Elsevier.

Structural studies, using ^{27}Al and ^{89}Y NMR, Raman and diffraction, have been conducted mainly on $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ and $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ glasses among $\text{RE}_2\text{O}_3\text{-Al}_2\text{O}_3$ glasses (Florian *et al.*, 2001; Wilding *et al.*, 2002a,b; Wilding and McMillan, 2002; McMillan *et al.*, 2003; Weber *et al.*, 2004; Tangeman *et al.*, 2004; Nasikas *et al.*, 2011; Watanabe *et al.*, 2020), supported by MD simulations (McMillan *et al.*, 2007; Du and René Corrales, 2007; Cristiglio *et al.*, 2007; Du *et al.*, 2009). Aluminum occurs predominantly in tetrahedral environment but, in La aluminate glasses, the population of $^{[4]}\text{Al}$ slightly increases with Al_2O_3 from 85% for 27 mol% La_2O_3 to 94% for 50 mol% La_2O_3 (Watanabe *et al.*, 2020), while the fraction of $^{[4]}\text{Al}$ is essentially composition independent in YA glasses and has low values between 61% (Watanabe *et al.*, 2020) and 69% (Tangeman *et al.*, 2004). High coordinated Al species are detected in all Y- and La-aluminate glasses with rather large fractions of $^{[5]}\text{Al}$ (24%–28%) and $^{[6]}\text{Al}$ (6%–11%) in YA glasses (Watanabe *et al.*, 2020; Tangeman *et al.*, 2004). ^{27}Al 3Q-MAS reveals the presence of two different $^{[5]}\text{Al}$ environments in a YA glass with 37.5 mol% Y_2O_3 , supporting a phase separation (Florian *et al.*, 2001) but this was not confirmed in further investigations (Tangeman *et al.*, 2004; Nasikas *et al.*, 2011). Diffraction results indicate an average CN of 7 oxygen atoms around La (Weber *et al.*, 2004), as confirmed by MD simulations (Du and René Corrales, 2007). The Y-O distance distribution is asymmetric with distorted six and seven-fold polyhedra ($^{[6]}\text{Y}$ and $^{[7]}\text{Y}$) (Wilding *et al.*, 2002a,b; McMillan *et al.*, 2003; Du *et al.*, 2009). Using ^{89}Y NMR, two distinct sites have been evidenced and interpreted as $^{[8]}\text{Y}$ and possibly $^{[9]}\text{Y}$ (Nasikas *et al.*, 2011). They were associated with different Y environments in the LDA and HDA (Nasikas *et al.*, 2011). An increase in the Y coordination number with increasing Al_2O_3 content emerges based on diffraction and NMR data (Weber *et al.*, 2004; Nasikas *et al.*, 2011). Several conclusions on the polyamorphic transition have been obtained from diffraction results (Fig. 10). Minor changes occur in the local Al environment (Wilding *et al.*, 2002a,b) contrary to the local Y environment that changes from $^{[7]}\text{Y}$ to $^{[8]}\text{Y}$ with the formation of LDA (Weber *et al.*, 2004). This is accompanied by a high-degree of medium range order in glasses with amorphous-amorphous separation, similar to that in La aluminate glasses (Wilding *et al.*, 2002a,b). These changes at medium range distance indicate specific packing among AlO_n and YO_n units as revealed by metal-metal distances (Wilding *et al.*, 2002a,b; McMillan *et al.*, 2003; Weber *et al.*, 2004). These modifications can be ascribed to a shift from corner to edge sharing between polyhedra as the Y coordination increases (Weber *et al.*, 2004). MD simulations confirm that changes in the Y-Y correlations is the main difference between HDA and LDA configurations (McMillan *et al.*, 2003). Furthermore, dynamic density fluctuations have been evidenced in MD simulations (McMillan *et al.*, 2007), confirming experimental indication of unmixing of high and low density liquids at the nanoscale that underlines a liquid-liquid phase transition (Greaves *et al.*, 2008, 2009).

Compared to conventional silicate glasses, RE aluminate glasses have high hardness, high elastic moduli, and high cracking resistance CR, depending on the RE^{3+} ionic radius, r_{RE} . Increasing r_{RE} yields a decrease in packing density, elastic moduli and hardness and an increase in CR (Rosales-Sosa *et al.*, 2018). The proposed mechanism underlying this high CR is the possibility for aluminum to adopt diverse coordination environments. This flexibility is higher than in silicate glasses, for which only SiO_4 tetrahedra are possible, and favors a stress release during plastic deformation. Large r_{RE} (e.g., for La) enhances the flexibility of the glass network compared to small r_{RE} (e.g., for Y). Indeed, Al in tetrahedral environment exists in large fractions in $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$

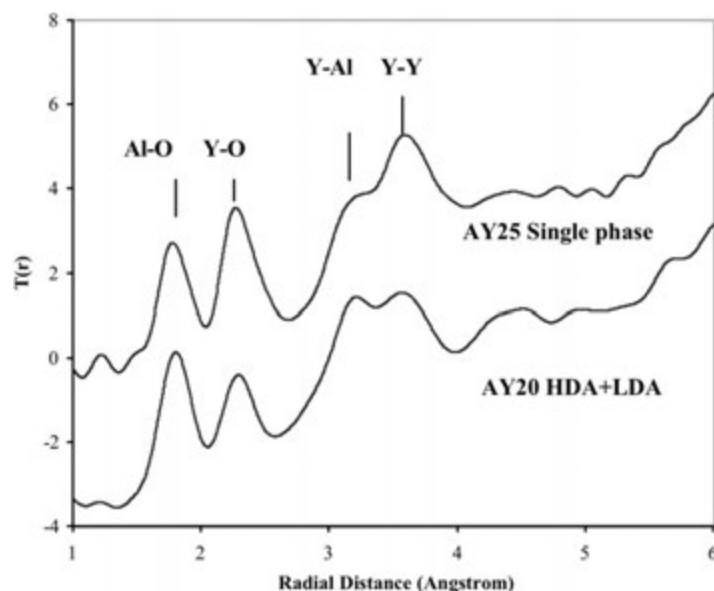


Fig. 10 X-ray total pair-correlation functions for a single-HDA glass (AY25 = $25\text{Y}_2\text{O}_3\text{-}75\text{Al}_2\text{O}_3$) and a two-phase HDA-LDA glass (AY20 = $20\text{Y}_2\text{O}_3\text{-}80\text{Al}_2\text{O}_3$). The Al-O peak remains unchanged on transition from HDA to LDA. Conversely, there is an increase in the Y-O distance and in mid-range order (especially the peak ascribed to Y-Y correlations) in the HDA suggesting higher numbers of corner-shared $\text{AlO}_n\text{-YO}_n$ polyhedra and edge-shared $\text{YO}_n\text{-YO}_n$ polyhedra. Reprinted from Wilding, M.C., Benmore, C.J., McMillan, P.F., 2002a. A neutron diffraction study of yttrium- and lanthanum-aluminate glasses. *Journal of Non-Crystalline Solids* 297, 143–155. Wilding, M.C., McMillan, P.F., Navrotsky, A., 2002b. Thermodynamic and structural aspects of the polyamorphic transition in yttrium and other rare-earth aluminate liquids. *Physica A: Statistical Mechanics and its Applications* 314, 379–390. doi:10.1016/S0378-4371(02)01045-2. Copyright (2002) by Elsevier.

glasses and these $^{[4]}\text{Al}$ are available to increase their oxygen CN under applied stress, whereas $^{[5]}\text{Al}$ and $^{[6]}\text{Al}$ species already exist in significant proportions in $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ glasses so that a local Al change is difficult, associated with a high packing density that reduces densification ability.

Comparing RE^{3+} and M^{2+} aluminate glasses, Watanabe *et al.* (2020) have shown that above a packing density of $\sim 55\%$, the network cannot accommodate only AlO_4 units. The less efficiency of RE^{3+} cations compared to M^{2+} cations for charge compensation of $(\text{AlO}_4)^-$ tetrahedra is related to the high CFS of RE^{3+} cations. RE^{3+} cations attract oxygen atoms more strongly than M^{2+} cations, bringing AlO_4 polyhedra closer to each other and increasing the packing density. Ideally, each RE^{3+} should charge balance three AlO_4 tetrahedra, which is topologically difficult if corner-sharing is maintained.

$\text{Al}_2\text{O}_3\text{-SiO}_2$ Binary Glasses

Replacement of silicon by aluminum has been investigated in the $\text{Al}_2\text{O}_3\text{-SiO}_2$ (AS) binary system. Materials with high alumina content are considered for refractories and small amounts of Al_2O_3 help to homogenize the distribution of RE in optically active devices (Lægsgaard, 2002; Weber *et al.*, 2008). Alumina-rich AS glasses, particularly at the mullite composition, $3\text{Al}_2\text{O}_3\text{-2SiO}_2$, have remarkable high hardness and high indentation cracking resistance with an elastic modulus as high as 134 GPa (Rosales-Sosa *et al.*, 2016). The liquids along the $\text{Al}_2\text{O}_3\text{-SiO}_2$ join cover a wide range of viscosity-temperature behavior, from strong (SiO_2 -rich) to fragile with increasing Al_2O_3 contents (Wilding *et al.*, 2010). There is a wide metastable immiscibility gap in the AS binary, starting above 5 mol% Al_2O_3 and finishing below 60 mol% Al_2O_3 , i.e., near the mullite composition (Macdowell and Beall, 1969; Risbud and Pask, 1977; Risbud, 1982). Though homogeneous glasses are difficult to prepare due to high viscosities for undercooled melts and the tendency to phase separate, they can be prepared using fast-quenching techniques (contactless, flame-spraying, roller-quenching ...) or via a sol-gel route.

The structure of AS glasses was studied from SiO_2 containing Al_2O_3 impurities up to 67 mol% Al_2O_3 , mainly in relation to Al speciation. At very low Al_2O_3 contents, $^{[4]}\text{Al}$ is the most dominant species but distorted $^{[6]}\text{Al}$ and a minor amount of $^{[5]}\text{Al}$ is also present (Poe *et al.*, 1992; Sen and Stebbins, 1995; Sen and Youngman, 2004). The mechanisms of charge compensation for $(\text{AlO}_4)^-$ is still not clear. Oxygen triclusters (Lacy, 1963; Macdowell and Beall, 1969; Schmücker *et al.*, 1997; Schmücker and Schneider, 2002), O vacancies (Lægsgaard, 2002), interstitial Al atoms in the network (Day and Rindone, 1962; Lægsgaard, 2002) or three-coordinated Al ($^{[3]}\text{Al}$) (Brower, 1978, 1979) have been proposed. While the existence of O_{tri} is still debated due to the difficulties to have experimental signatures, computational simulations agree with their formation (Winkler *et al.*, 2004; Tossell and Horbach, 2005). The presence of O_{tri} induces a tightening and densification of the silicate network, increasing the glass stiffness. They have been invoked to favor phase separation and initiate crystallization (Macdowell and Beall, 1969; Schmücker and Schneider, 2002), though structural homogeneity has been suggested at molecular scales (Ando *et al.*, 2018). MD models have shown substantial fractions of $^{[3]}\text{Al}$, for instance $\sim 38\%$ at 5 mol% Al_2O_3 (Poe *et al.*, 1992) but limited experimental evidence for such species exist (Brower, 1978, 1979). Addition of Al_2O_3 results in the rapid disappearance of 3- and 4-membered rings and increases disorder (Okuno *et al.*, 2005; Ando *et al.*, 2018).

At higher Al_2O_3 content (>4 mol%), the three coexisting $^{[4,5,6]}\text{Al}$ species were observed in numerous experimental investigations with somewhat contradictory results (Morikawa *et al.*, 1982; Risbud *et al.*, 1987; Sato *et al.*, 1991; Poe *et al.*, 1992; Sen and Youngman, 2004; Okuno *et al.*, 2005; Weber *et al.*, 2008; Wilding *et al.*, 2010; Ren *et al.*, 2014). A peak at 30 ppm in ^{27}Al NMR spectra, usually assigned to $^{[5]}\text{Al}$, is sometimes attributed to a distorted triclustered $^{[4]}\text{Al}$ configuration (Schmücker and Schneider, 1996, 2002). However, the main observed trend is that $^{[4,5]}\text{Al}$ are the dominant species and $^{[6]}\text{Al}$ persists but in small fractions. A recent ^{27}Al NMR investigation concludes with the absence of significant compositional dependence, even in phase separated glasses, up to 28 mol% Al_2O_3 , and only Si-O- $^{[4,5]}\text{Al}$ and Si-O-Si linkages are detected with no Al-O-Al linkages (Sen and Youngman, 2004). The concentration of $^{[5,6]}\text{Al}$ species increases upon further addition of Al_2O_3 (up to 60 mol% Al_2O_3) (Risbud *et al.*, 1987) and $^{[5]}\text{Al}$ becomes the predominant species (Weber *et al.*, 2008; Hoang, 2007). The exact Al speciation appears to depend on the synthesis conditions and quenching rates (Sato *et al.*, 1991; Poe *et al.*, 1992; Okuno *et al.*, 2005; Ren *et al.*, 2014). For instance, at a slow quench rate, there is no $^{[5]}\text{Al}$ and only the presence of $^{[4]}\text{Al}$ and $^{[6]}\text{Al}$ species is observed (Sato *et al.*, 1991; Poe *et al.*, 1992). MD simulations indicate large fractions of $^{[3]}\text{O}$ (and not O_{tri} as inaccurately stated in the papers) that are bonded to two edge-shared AlO_n polyhedra and an additional corner-shared AlO_4 or SiO_4 tetrahedron (Winkler *et al.*, 2004; Pfeleiderer *et al.*, 2006; Hoang, 2007). From diffraction data, an average low Al-O-T angle of 125° has also been interpreted as edge-shared AlO_n polyhedra in addition to corner-shared units (Weber *et al.*, 2008). Such a configuration indicates a locally dense region and implies Al clustering that could prefigure phase separation. Proximity between all $^{[4,5,6]}\text{Al}$ units has been confirmed by advanced NMR techniques (Ren *et al.*, 2014). As the packing density increases with addition of Al_2O_3 , the elastic moduli and Vickers hardness increase. The improved elastic properties are probably due to the flexibility for Al to adapt its environment to stresses (Rosales-Sosa *et al.*, 2016). MD simulations indicate that indentation results from a shear deformation process at high Al_2O_3 content (Luo *et al.*, 2016). The increasing glass ductility with increasing Al_2O_3 content is caused by a high proportion of high-coordinated Al that prevents the formation of defects acting as weak spots during deformation.

Alkali Aluminosilicate Glasses

Alkali-bearing aluminosilicate glasses have wide applications, such as chemically strengthened cover glasses or precursors for glass-ceramics. $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ (NAS) glasses have attracted attention due to non-monotonic changes in physical properties, such as refractive index, density, viscosity and electrical conductivity (Day and Rindone, 1962; Riebling, 1966; Toplis *et al.*, 1997a,b).

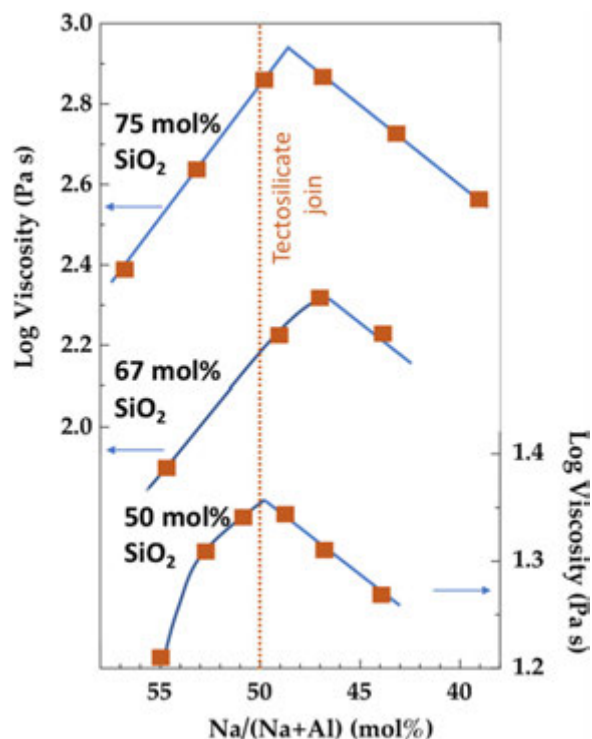


Fig. 11 Experimental viscosities at 1869 K in Na-AS glasses with different SiO₂ contents as a function of Na/(Na + Al). Data from Toplis, M.J., Dingwell, D.B., Lenci, T., 1997b. Peraluminous viscosity maxima in Na₂O-Al₂O₃-SiO₂ liquids: The role of triclusters in tectosilicate melts. *Geochimica et Cosmochimica Acta* 61, 2605–2612.

Viscosity measurements have shown a particularly interesting behavior (Fig. 11) (Riebling, 1966; Toplis *et al.*, 1997a,b): at a constant SiO₂ content, viscosities increase when Al substitutes for Na (ratio $R = \text{Na}/\text{Al} < 1$) with a maximum near $R = 1$ or slightly in the peraluminous region ($R = 1.2$) and then decreases slightly in the peraluminous region ($R > 1$). A similar behavior is also reported for Li₂O-Al₂O₃-SiO₂ (LAS) glasses (Shelby, 1978). In the peralkaline region, the Al environment has been confirmed to be only tetrahedral by ²⁷Al NMR experiments (Lee and Stebbins, 2000b; Allwardt *et al.*, 2005b), consisting of Q⁴ species and conferring a pure network forming role on Al (Gambuzzi *et al.*, 2014). Only ¹⁴Al is also detected in KAS glasses (Thompson and Stebbins, 2011; Le Losq *et al.*, 2017). The extremum in viscosity and its occurrence slightly in the peraluminous region has been strongly debated. This anomaly has not yet been truly understood since it can be attributed to the formation of O_{tri} or Al in high coordination states (Lacy, 1963; Riebling, 1966; Toplis *et al.*, 1997b).

Experiments have failed to evidence the presence of O_{tri} because either this moiety in glasses does not exist or is not present in significant amounts or current experiments are unable to identify it. For instance, the ¹⁷O NMR signature of O_{tri} is predicted to fall in the range of chemical shifts for regular BO (Kubicki and Toplis, 2002). Alternatively, MD simulations usually have significant contents of O_{tri} (typically 1%–10%) (Xiang *et al.*, 2013). The identification of O_{tri} can be an artifact due to fast quenching rates in simulations and, as such, MD models are more representative of a high temperature structure similar to that prevailing in viscosity measurements.

An increase in ¹⁵Al concentration would contribute to a decrease in viscosity (Toplis and Dingwell, 2004) and five-fold coordinated species are considered to be involved in the viscous flow of the network, promoting the exchange of T-O-T links (Farnan and Stebbins, 1994; Stebbins and Farnan, 1992). Their influence is expected to be more important for compositions with very polymerized networks, such as silica or albite, NaAlSi₃O₈, melts.

The presence of ¹⁴Al-O-¹⁴Al linkages is negligible in the peralkaline region but tends to increase for compositions close to $R = 1$ (Lee and Stebbins, 1999, 2009). The values of glass transition temperatures (T_g) steeply increase near $R = 1$, which is explained as changes of the Si speciation from Q³_{Si}(0Al) to Q⁴_{Si}(*m*Al) units based on Raman spectroscopy (Le Losq *et al.*, 2014). In the peraluminous region, the fraction of ¹⁵Al increases and the structure has been considered to be more constrained than for tectosilicate compositions as a result of ring statistics close to a “perfect” six-membered ring distribution (Le Losq *et al.*, 2014). It was concluded that the presence of ¹⁵Al in peraluminous glasses strongly impacts the rheologic and thermodynamic properties.

Li₂O-Al₂O₃-SiO₂ (LAS) glasses have considerable importance as they are the precursors for most of commercialized glass-ceramics. They have also been considered due to the fast Li mobility and the potential development of solid-state electrolytes for ionic batteries (Pechenik *et al.*, 1986, 1988; Greaves and Ngai, 1995a,b; Ross *et al.*, 2015). Similar observations on the conductivity properties were obtained for LAS and NAS (Li and Garofalini, 2004; Zirl and Garofalini, 1990). The initial introduction of Al₂O₃ blocks the alkali channels existing in the MRN model, increasing the activation energy for diffusion (Greaves and Ngai, 1995a). With further addition of Al₂O₃, a large fraction of alkalis changes their structural role, from modifying associated with NBOs, to charge balancing near (AlO₄)[−] units, associated with BOs in

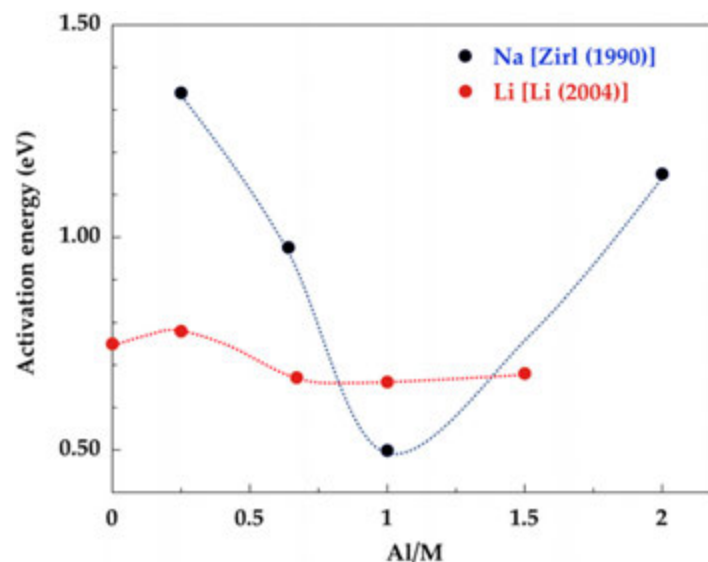


Fig. 12 Variation of the activation energy of alkali diffusion as determined by MD simulations in Na and Li AS glasses as a function of Al/M content ($M = \text{Li}$ or Na). Curves are only guides for the eye. Data from Zirl, D.M., Garofalini, S.H., 1990. Structure of sodium aluminosilicate glasses. *Journal of the American Ceramic Society* 73, 2848–2856, and Li, W., Garofalini, S.H., 2004. Molecular dynamics simulation of lithium diffusion in $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses. *Solid State Ionics* 166, 365–373.

$\text{Si}-\text{BO}-[4]\text{Al}$ bonds. Alkalis become loosely bounded due to large $M^+-\text{BO}$ bond lengths and small $M^+-\text{BO}$ binding energies compared to $M^+-\text{NBO}$ bonds. As a result, the activation energy decreases as $M^+-\text{BO}$ bonds are formed and is the smallest for $M^+/\text{Al} = 1$ (Fig. 12) (Li and Garofalini, 2004; Zirl and Garofalini, 1990). The formation of $[5,6]\text{Al}$ species for $M^+/\text{Al} < 1$ decreases the activation energy, following a reduction of the free volume. Li atoms are found in distorted tetrahedral sites that share edges with TO_4 tetrahedra (Cormier *et al.*, 1998, 2001). Due to Si/Al ordering, AlO_4 units are homogeneously distributed in the network, explaining large inter-alkali distances in AS glasses (Cormier *et al.*, 1998, 2001; Greaves and Ngai, 1995a). The proposed mechanism for alkali diffusion is a hopping process from a $(\text{AlO}_4)^-$ unit to another $(\text{AlO}_4)^-$ unit, provided by a higher free volume than for crystalline counterparts.

Alkaline-Earth Aluminosilicate Glasses

Alkaline-earth aluminosilicate glasses exhibit interesting optical and mechanical properties and form the basis of a plethora of commercial glasses from nuclear, domestic and industrial waste storage, slags, cements, fibers, and industrial glasses.

GFA in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (CAS) system is remarkable since low- SiO_2 glasses can be formed, allowing compositions to be studied along the almost complete $R = \text{CaO}/\text{Al}_2\text{O}_3$ joins. Strong non-linear behavior has been observed for T_g (Higby *et al.*, 1990; Cormier *et al.*, 2005): a minimum at 30–40 mol% SiO_2 along the join $R = \text{Ca}/2\text{Al} = 1$ and at 50–60 mol% SiO_2 along the joins $R = 1.57$ and 3; for these two latter, an additional maximum at 10–20 mol% SiO_2 is also observed. These observations have motivated numerous studies, especially on the connectivity of the tetrahedral aluminosilicate network. A large structure database exists for CAS based on various experimental and modeling techniques (Murdoch *et al.*, 1985; Engelhardt *et al.*, 1985; Merzbacher and White, 1991; Himmel *et al.*, 1991; Stebbins and Xu, 1997; Petkov *et al.*, 2000; Cormier *et al.*, 2000b; Lee and Stebbins, 2000b; Allwardt *et al.*, 2003; Stamboulis *et al.*, 2004; Neuville *et al.*, 2006; Lee and Stebbins, 2006; Neuville *et al.*, 2007; Moesgaard *et al.*, 2010; Thompson and Stebbins, 2011; Tandia *et al.*, 2011; Jakse *et al.*, 2012; Zheng *et al.*, 2012; Thompson and Stebbins, 2012; Bouhadja *et al.*, 2014) to determine the topological disorder, coordination numbers, bond-angle distribution, linkages between polyhedra and fulfillment of the aluminum avoidance principle. From these investigations, a general structural picture emerges that changes with R and SiO_2 content. Near pure SiO_2 , the glass structure is composed of a fully connected network of corner-shared TO_4 tetrahedra and the addition of CaO progressively depolymerizes the network. Al^{3+} cations preferentially replace Si^{4+} cations in tetrahedral positions with Ca^{2+} charge balancing two $(\text{AlO}_4)^-$ tetrahedra. Additionally, Al atoms prefer to occupy fully polymerized Q^4 sites and NBOs are almost entirely associated with Si atoms (Engelhardt *et al.*, 1985; Allwardt *et al.*, 2003). High coordinated Al polyhedra are expected only for insufficient modifier contents. However, a substantial fraction of $[5]\text{Al}$ species and minor amounts of $[6]\text{Al}$ species are present throughout the CAS ternary system, except at high SiO_2 content and for the low silica percalcic region ($\text{SiO}_2 < 16$ mol%) (Fig. 13). The maximum $[5,6]\text{Al}$ fraction is observed near 40 mol% SiO_2 for all joins in the percalcic region with a maximum of 7%–8% $[5]\text{Al}$ (Neuville *et al.*, 2006, 2007). The presence of these high-coordinated species implies higher amounts of NBOs and $[3]\text{O}$ and non-negligible fractions of NBOs are observed along the charge-balanced join (Stebbins and Xu, 1997; Lee and Stebbins, 2006; Stebbins *et al.*, 2008). Ca is acting both as a modifier and as a charge compensator and is localized in distorted sites with 6–7 oxygen neighbors, within interstitial spaces of the tetrahedral network (Cormier *et al.*, 2003; Neuville *et al.*, 2004a; Mongalo *et al.*, 2016). The Al avoidance principle is violated and a quasi-heterogeneous distribution of Al as second neighbors around Si was

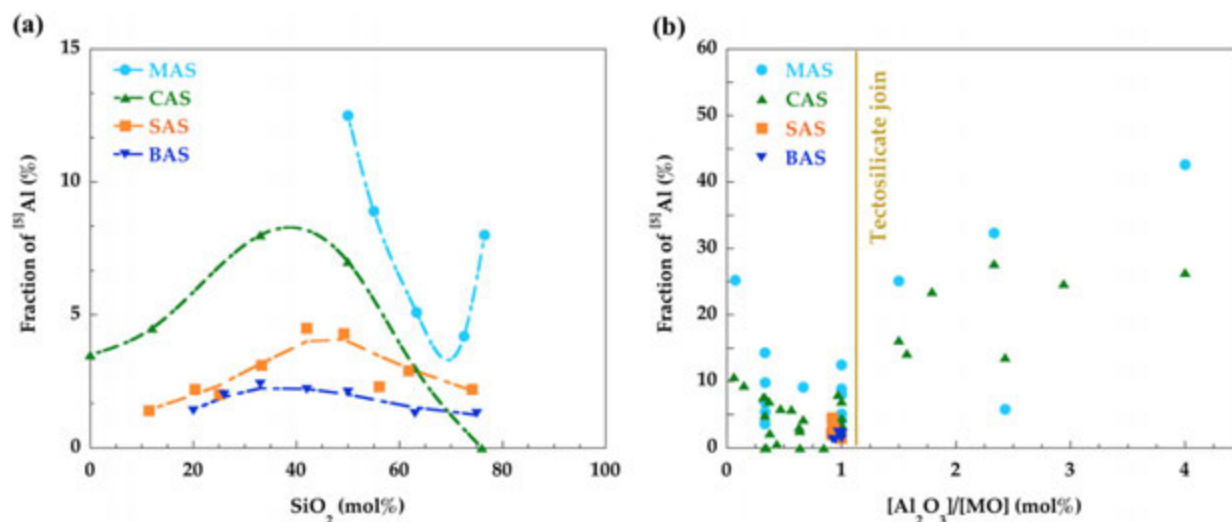


Fig. 13 Comparison of the ^{151}Al fraction in tecto-aluminosilicate glasses containing alkaline-earth cations (MAS: Mg^{2+} ; CAS: Ca^{2+} ; SAS: Sr^{2+} ; BAS: Ba^{2+}) (a) as a function of the SiO_2 content (curves are guides for the eye) or (b) as a function of the ratio $\text{Al}_2\text{O}_3/\text{MO}$. Data from Neuville, D.R., Cormier, L., Massiot, D., 2006. Al coordination and speciation in calcium aluminosilicate glasses: Effects of composition determined by ^{27}Al MQ-MAS NMR and Raman spectroscopy. *Chemical Geology* 229, 173–185. Neuville, D.R., Cormier, L., Montouillout, V., *et al.*, 2008. Structure of Mg- and Mg/Ca aluminosilicate glasses: ^{27}Al NMR and Raman spectroscopy investigations. *American Mineralogist* 93, 1721–1731. Novikov, A.N., Neuville, D.R., Henet, L., *et al.*, 2017. Al and Sr environment in tectosilicate glasses and melts: Viscosity, Raman and NMR investigation. *Chemical Geology* 461, 115–127. doi:10.1016/j.chemgeo.2016.11.023, and Novikov, A., 2017. Structure and Dynamics of Aluminosilicate Glasses and Melts. (Ph.D. thesis). Orléans: Université d'Orléans.

proposed (Moesgaard *et al.*, 2010). This model suggests the existence of depolymerized Si-NBO-Ca regions and highly polymerized regions of alternating SiO_4 -(1/2Ca) AlO_4 units. MD simulations suggest spatial correlation between ^{151}Al and ^{13}O within small 2- and 3-fold membered rings (Benoit *et al.*, 2005; Agnello *et al.*, 2019; Atila *et al.*, 2019). As the SiO_2 content decreases below 40 mol%, Al atoms enter depolymerized Q^3 and Q^2 units and the number of NBOs per SiO_4 tetrahedron decreases (Neuville *et al.*, 2006, 2007; Bouhadja *et al.*, 2014), forming a highly depolymerized network. The lower network connectivity of Al_2O_3 -rich glasses increases the reactivity, which is crucial for developing supplementary cementitious materials (Nie *et al.*, 2020). The presence of NBOs and their distribution on Si and Al units are correlated with the evolution of T_g and the fragility behavior of the corresponding melts. For peraluminous glasses, large proportions of ^{151}Al exceeding 20% are observed but these compositions have been little investigated (Fig. 13(b)) (Neuville *et al.*, 2006, 2007). It has been suggested that non negligible fractions of NBOs are still present within the peraluminous region (Mysen and Toplis, 2007; Thompson and Stebbins, 2011).

The $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ (MAS) system has a reduced GFA but the glass structure follows the general trends observed for CAS (McMillan and Kirkpatrick, 1992; Toplis *et al.*, 2000). The main difference from their CAS counterparts is that higher fractions of $^{15,61}\text{Al}$ species are detected in MAS glasses (Fig. 13) (Neuville *et al.*, 2008). Divalent cations have thus a lower ability to stabilize ^{14}Al than monovalent alkali cations. The average CN for Mg is close to 5 with a distribution between 4-, 5- and 6-fold coordinated sites (Guignard and Cormier, 2008; Mongalo *et al.*, 2016). Therefore, owing to its small size and its localization in interstitial sites of the aluminosilicate network, Mg^{2+} cations perturb the network more severely than Ca^{2+} cations (Navrotsky *et al.*, 1982; Roy and Navrotsky, 1984) and the network distortion can result in the formation of high-coordinated Al. Furthermore, the high CFS for Mg^{2+} favors the stabilization of more concentrated negative charges on NBOs or partially charged BOs involved in $^{14}\text{Al}\text{-O-}^{14}\text{Al}$ linkages. These different influences of Mg^{2+} and Ca^{2+} on the glass structure impact the macroscopic properties (density, Young's modulus, Vickers hardness, coefficient of thermal expansion, liquid fragility) (Smedskjaer *et al.*, 2013).

In mixed Ca-Mg aluminosilicate glasses (CMAS), the fraction of ^{151}Al species increases with MgO content and is less affected by the Si/Al or M^{2+}/Al substitutions (Lee *et al.*, 2005; Neuville *et al.*, 2008; Kelsey *et al.*, 2008; Nie *et al.*, 2020). The network polymerization depends mainly on the content of alkaline-earth ions and to a much lesser extent on the Al/Si and Mg/Ca substitutions (Nie *et al.*, 2020). The degree of Si-Al disorder (presence of $^{14}\text{Al}\text{-O-}^{14}\text{Al}$) increases with the presence of Mg^{2+} cations and increasing Al/Si ratio (Lee *et al.*, 2005; Kelsey *et al.*, 2008). NBOs have more Mg^{2+} cations in their environment than Ca^{2+} cations. These latter cations are thus more associated with Al-O-Si linkages and slightly more available than Mg to charge balance $(\text{AlO}_4)^-$ units (Kelsey *et al.*, 2008). This result is consistent with MD simulations indicating that more Ca ions are acting as charge compensator than Mg (Allu *et al.*, 2018; Ganisetti *et al.*, 2019). The non-random distribution of framework and non-framework cations supports the EMRN model implying an heterogeneous network (Fig. 4).

Mechanical properties have been explored in CAS and MAS glasses (Smedskjaer *et al.*, 2012; Veit and Rüssel, 2016), showing that increasing Al_2O_3 content provokes higher atomic packing density, responsible for higher values of Poisson ratio and that CFS has a high impact on elastic moduli. In CAS and MAS glasses, hardness shows an "anomalous" behavior with a minimum (at ~ 85 mol% SiO_2 for CAS and ~ 70 mol% SiO_2 for MAS) and has higher values for MAS over CAS glasses (Lamberson, 2016). As the hardness correlated with the proportion of $^{151}\text{Al} + ^{161}\text{Al}$ ($R^2 = 0.9\text{--}0.91$), Lamberson (2016) proposed that the presence of

$^{[5,6]}\text{Al}$ prevents the Ca-O bond breaking and reforming, this latter mechanism causing NBO motion and creating shear deformation. Indeed, NBOs are tightly held by $^{[5,6]}\text{Al}$ since edged-shared $^{[5,6]}\text{Al}$ - $^{[4]}\text{T}$ bonds are stronger than $^{[4]}\text{T}$ - $^{[4]}\text{T}$ ones. $^{[5,6]}\text{Al}$ ties up the structure and is beneficial for better crosslinking network fragments. Therefore, $^{[5,6]}\text{Al}$ can prevent or slow down plastic deformation, and consequently hardness is increased. In addition to larger amounts of $^{[5,6]}\text{Al}$ in MAS glasses, Mg-NBO bonds are stronger than Ca-NBO bonds and NBOs have thereby a lower ability to move in a MAS network over a CAS network, such that shear deformation is further inhibited. The different hardness behavior between the two alkaline earth cations is related to both higher proportion of $^{[5,6]}\text{Al}$ and stronger Mg-NBO bonds. The fraction of $^{[5,6]}\text{Al}$ has then a prominent role in controlling mechanical properties (shear deformation and hardness) of tectosilicate glasses with $\text{SiO}_2 < 85$ mol%.

Other alkaline-earth AS glasses have been investigated less though the structure of Sr and Ba AS glasses have been explored (Thompson and Stebbins, 2012; Novikov *et al.*, 2017; Charpentier *et al.*, 2018). The substitution of Si by SrAl_2O_4 favors the formation of small-size rings. A CN for Sr near 6 was determined using an advanced diffraction investigation (Cormier *et al.*, 1999), while a CN of 9 was proposed based on a crude fingerprint XANES approach (Novikov *et al.*, 2017) and MD simulations indicate a broad distribution with maximum at ~ 7 –8 (Charpentier *et al.*, 2018). The proportion of $^{[5]}\text{Al}$ is smaller ($< 5\%$) for Sr^{2+} and Ba^{2+} than for Ca^{2+} and Mg^{2+} (Fig. 13), thus following the trend $\text{Ba} < \text{Sr} < \text{Ca} < \text{Mg}$ that suggests an important size effect for these divalent cations (Thompson and Stebbins, 2012).

Rare-Earth Aluminosilicate Glasses

Glass formation (Makishima *et al.*, 1978, 1982; Hyatt and Day, 1987; Shelby, 1994; Clayden *et al.*, 1999; Iftekhar *et al.*, 2011; Pahari *et al.*, 2012) and the thermodynamic behavior (Zhang and Navrotsky, 2003, 2004) have been investigated in RE-based aluminosilicate glasses (RE-AS). The presence of trivalent RE cations (Sc^{3+} , Y^{3+} and lanthanides) in AS glasses leads to useful physico-chemical and mechanical properties: high refractive index, hardness and elastic modulus, low corrosion. RE-AS glasses are refractory with high T_g values ($T_g > 840^\circ\text{C}$) and high chemical stability (Hyatt and Day, 1987; Shelby and Kohli, 1990; Tanabe *et al.*, 1992; Johnson *et al.*, 2005). Most glass properties depend on the cation mass and CFS with the noticeable exception of Sc-bearing glasses that show anomalously low T_g values, possibly related to Sc clustering (Iftekhar *et al.*, 2011). The density, refractive index, thermal expansion coefficient, microhardness, electrical resistivity all increase with the addition of RE oxides (Makishima *et al.*, 1978; Shelby, 1994; Johnson *et al.*, 2005; Pahari *et al.*, 2012). Decreasing the ionic size increases the elastic moduli and the thermal expansion coefficient (Shelby and Kohli, 1990; Inaba *et al.*, 2000; Tanabe *et al.*, 1992). Owing to high refractive indices, they exhibit excellent optical properties and they can be used in technological applications, such as components in lenses, optical amplifiers, laser hosts, fiber optics. They have also been considered as potential matrices for storage of radioactive wastes (Bardez *et al.*, 2005; Loiseau and Caurant, 2010; Kidari *et al.*, 2012) and explored in radiotherapy for in situ cancer treatment (Christie and Tilocca, 2010a,b). Addition of Al_2O_3 is beneficial to obtain homogeneous glasses with high contents of uniformly dispersed RE^{3+} cations.

RE-AS glasses have pronounced configurational and chemical disorder compared to alkaline or alkaline-earth AS glasses. Whereas tetrahedral coordination is still dominant, large amounts of $^{[5,6]}\text{Al}$ populations prevail throughout the entire range of RE-AS glass forming regions (Jaworski *et al.*, 2015; Schaller and Stebbins, 1998; Florian *et al.*, 2007; Iftekhar *et al.*, 2011; Jaworski *et al.*, 2012; Iftekhar *et al.*, 2012; Pahari *et al.*, 2012; Okhotnikov *et al.*, 2013), with larger amounts compared to mono/divalent cations. The relative amounts of $^{[5,6]}\text{Al}$ grow with decreasing SiO_2 content (Florian *et al.*, 2007; Iftekhar *et al.*, 2012; Jaworski *et al.*, 2012) and increasing CFS (Schaller and Stebbins, 1998; Florian *et al.*, 2007; Iftekhar *et al.*, 2011; Jaworski *et al.*, 2012; Pahari *et al.*, 2012) and depends on the RE/Al ratio:

- (1) When $\text{RE}/\text{Al} < 3$, not enough RE^{3+} cations are present to ensure charge neutralization of $(\text{AlO}_4)^-$ groups and the highest amounts of $^{[5]}\text{Al}$ (35%) and $^{[6]}\text{Al}$ (5%) are observed (Schaller and Stebbins, 1998; Florian *et al.*, 2007; Pahari *et al.*, 2012);
- (2) When $\text{RE}/\text{Al} \geq 3$, $^{[4]}\text{Al}$ is predominant with small fractions of $^{[5,6]}\text{Al}$ and RE cations act as modifiers, depolymerizing the network with the formation of NBOs preferentially localized on SiO_4 tetrahedra (Lin *et al.*, 1996; Schaller and Stebbins, 1998).

The higher coordinated $^{[5,6]}\text{Al}$ species imply a significant cross-linked AS network that is suggested to explain the enhanced Vickers hardness with increasing CFS (Iftekhar *et al.*, 2012; Svensson and Edén, 2013). A pronounced Al/Si atomic disorder (violation of Al avoidance principle) is observed based on NMR results (Iftekhar *et al.*, 2009; Jaworski *et al.*, 2012), as well as MD simulations (Jaworski *et al.*, 2012; Okhotnikov *et al.*, 2013). Even for SiO_2 -rich glasses, in contrast to mono/divalent cations, NBOs directly connected with $^{[6]}\text{Al}$ were experimentally observed using ^{17}O MAS NMR spectroscopy (Jaworski *et al.*, 2015), an observation corroborated by MD simulations (Okhotnikov *et al.*, 2013).

X-ray absorption spectroscopy (XAS) and NMR were used to determine CNs and infer constraints on the cation clustering by leveraging on MD simulations (Ponader and Brown, 1989; Sen and Stebbins, 1995; Du, 2009; Christie and Tilocca, 2010a,b; Jaworski *et al.*, 2012; Iftekhar *et al.*, 2012; Pahari *et al.*, 2012; Okhotnikov *et al.*, 2013). The main factors influencing the local RE environment in glasses have been identified (Ponader and Brown, 1989; Wang *et al.*, 1993; Okhotnikov *et al.*, 2013): as the RE ionic radius increases, the RE-O distances and CNs increase while the sites occupied by RE^{3+} cations become less regular. Lanthanum behaves slightly differently with more regular sites and is considered to be centered in a “cage” formed by the rings of TO_4 tetrahedra. Due to a large ionic radius ratio ($r_{\text{RE}}/r_{\text{O}} > 0.732$) and a strong ionicity of RE-O bonds (Tanabe *et al.*, 1992), CNs for RE^{3+} are larger than for Al^{3+} . Octahedral coordination is the most probable one for the smallest ions (Sc, Lu) and high CNs (7) are observed for large RE cations (La, Y). MD simulations indicate a large distribution of CNs in the range from 4 to 8, with 4-fold and 8-fold coordination being significant only for Sc and La, respectively.

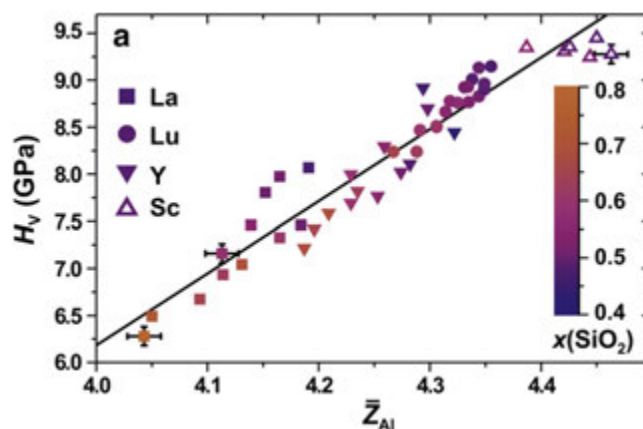


Fig. 14 Vickers hardness, H_V , as a function of the average Al coordination, $\bar{Z}_{Al}$, for various RE aluminosilicate glasses. The solid line is the best-fit ($H_V = -24 + 7.7\bar{Z}_{Al}$; $R^2 = 0.92$) revealing a strong property/structure correlation. Reprinted with permission from Svensson, B., Edén, M., 2013. Structural rationalization of the microhardness trends of rare-earth aluminosilicate glasses: interplay between the RE^{3+} field-strength and the aluminum coordinations. *Journal of Non-Crystalline Solids* 378, 163–167. doi:10.1016/j.jnoncrysol.2013.06.013.

Investigations have established relationships between mechanical properties and structural parameters (Iftekhar *et al.*, 2012; Svensson and Edén, 2013). The CFS or the network connectivity increase with hardness values. However, ideas have emerged that RE ions impact microhardness indirectly through the formation of $^{[5,6]}Al$. Fig. 14 shows an excellent correlation ($R^2 = 0.92$) between Vickers hardness, H_V , and the average Al coordination number for many RE-AS glasses. Therefore, increasing amounts of $^{[5,6]}Al$, originating from the high CFS of RE^{3+} cations, primarily account for the enhanced microhardness. AlO_5 and AlO_6 (and ReO_n) polyhedra are expected to connect different network fragments, yielding a more compact and stiffer network that favors high hardness.

Complex Aluminosilicate Glasses

Chemically complex aluminosilicate glasses are numerous and two aspects have been explored particularly: (1) mixing of different modifiers and (2) mixing of different framework cations (mainly, B^{3+} or P^{5+}).

When more than one type of non-network forming cation is present in AS glasses, the CFS affects their relative distribution between a modifying or charge balancing position. This type of disorder is mirrored in the preference of NBOs and BOs to be bonded to specific cations and in the formation of $^{[5,6]}Al$. Mixing of non-framework cations has been explored in AS glasses with Ca-Mg (Neuvill *et al.*, 2008; Kelsey *et al.*, 2008; Park and Lee, 2012; Smedskjaer *et al.*, 2013; Allu *et al.*, 2018; Ganisetti *et al.*, 2019), Ca-Na (Cormier and Neuvill, 2004; Lee and Sung, 2008; Gambuzzi *et al.*, 2014; Sukenaga *et al.*, 2017), Na-K (Le Losq and Neuvill, 2013; Le Losq *et al.*, 2017), Na-Mg (Park and Lee, 2018), Ca-Mg-Na (Smedskjaer *et al.*, 2013; Kjeldsen *et al.*, 2013; Park and Lee, 2014; Bechgaard *et al.*, 2017). In presence of alkalis and alkaline-earths, NBOs prefer to have proximity towards M^{2+} cations that preferentially play a role of network modifier, whereas BOs are more associated with M^+ cations that act as charge balancing cations in, typically, Si-BO- $^{[4]}Al$ environments. For Ca/Mg mixing, NBOs tend to have a Mg-rich environment, whereas Ca has a greater propensity to be associated with BOs. The non-randomness in the partitioning of non-framework cations around BOs and NBOs is explained by the CFS: higher CFS ($CFS_{M^{2+}} > CFS_{M^+}$ and $CFS_{Mg^{2+}} > CFS_{Ca^{2+}}$) favors proximity of cations to NBOs. However, in a $CaMgSi_2O_6$ - $CaAl_2SiO_6$ join, ^{17}O NMR reveals a Ca-NBO-Si peak, suggesting a preferential bonding of NBOs with Ca and/or a potential unmixing of Ca and Mg (Park and Lee, 2012). If the separation between polymerized regions and channels exists (EMRN model, Fig. 4), Na^+ cations will be preferentially localized in the polymerized Al/Si regions close to $^{[4]}Al$ to ensure charge compensation, while M^{2+} cations will be in channels associated with NBOs in depolymerized Q_{Si}^n species (Gambuzzi *et al.*, 2014; Sukenaga *et al.*, 2017). A major outcome of these studies is an increasing amount of $^{[5]}Al$ with CFS. For instance, the fraction of $^{[5]}Al$ increases from $\sim 5\%$ to $\sim 20\%$ as Ca is substituted by Mg, emphasizing the lower ability of Mg^{2+} to stabilize $^{[4]}Al$ (Neuvill *et al.*, 2008; Kelsey *et al.*, 2008).

The degree of Al/B mixing in boroaluminosilicate or boroaluminate glasses plays an essential role in controlling major physical properties such as chemical durability, phase separation, mechanical strength or crystallization behavior (Du *et al.*, 2000; Du and Stebbins, 2005a,b). The presence of B_2O_3 creates complex competition for M^{n+} cations for charge compensation of $(AlO_4)^-$ or $(BO_4)^-$ tetrahedra (El-Damrawi *et al.*, 1993; Chan *et al.*, 1999; Cormier *et al.*, 2000a; Yamashita *et al.*, 2003; Smedskjaer *et al.*, 2014). M^{n+} cations are firstly consumed to charge stabilize $(AlO_4)^-$ units, limiting the formation of higher Al coordination states. The excess M^{n+} cations are used to convert boron from trigonal (BO_3) to tetrahedral (BO_4) configurations. The proportion of BO_4 units, determined by the ratio $N_4 = BO_4/(BO_4 + BO_3)$, is then lower in boroaluminosilicate glasses compared to borosilicate counterparts. N_4 values increase with decreasing Al_2O_3 content and a maximum value, $N_{4(max)}$, is reached at $R' = ([Na_2O] - [Al_2O_3])/[B_2O_3] = 1$. When $N_4 < N_{4(max)}$ and $M^{n+}/nAl > 1$, NBOs on silicon can also be created but preferential formation of Q_{Si}^3 over BO_4 is observed depending on the M^{n+} cation type (Yamashita *et al.*, 2003). Fig. 15 represents the reactivity of M_nO with

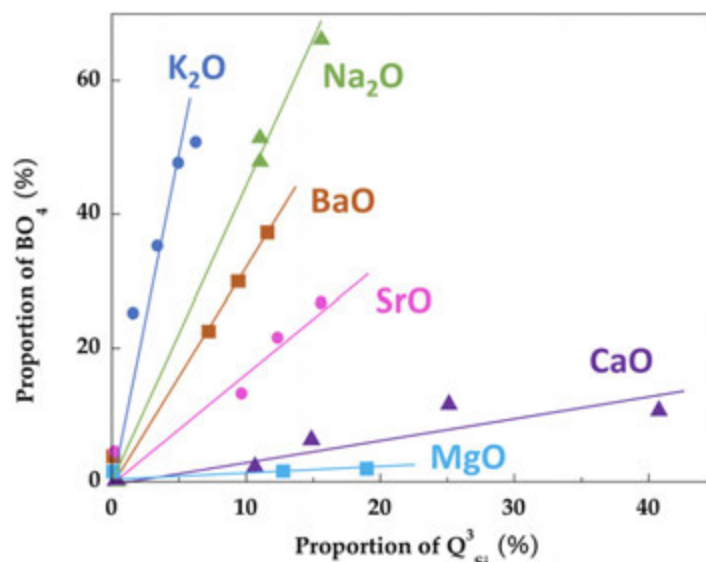


Fig. 15 Relation between the fraction of BO_4 and the fraction of Q_3^{Si} for $0.139 \text{ M}^{\text{n}+}\text{O} - 0.673 \text{ SiO}_2 - (0.188-x) \text{ Al}_2\text{O}_3 - x\text{B}_2\text{O}_3$ ($\text{M}^{\text{n}+} = \text{Na}^+, \text{K}^+, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}$ and Ba^{2+}) glasses. Data from Yamashita, H., Inoue, K., Nakajin, T., Inoue, H., Maekawa, T., 2003. Nuclear magnetic resonance studies of $0.139\text{MO} \cdot 0.673\text{SiO}_2 \cdot (0.188 - x)\text{Al}_2\text{O}_3 \cdot x\text{B}_2\text{O}_3$ ($\text{M} = \text{Mg}, \text{Ca}, \text{Sr}$ and Ba , $\text{M}' = \text{Na}$ and K) glasses. *Journal of Non-Crystalline Solids* 331, 128–136. doi:10.1016/j.jnoncrysol.2003.08.086.

B_2O_3 and SiO_2 , showing that formation of Q_3^{Si} species is favored (and formation of BO_4 is disfavored) in the order $\text{Mg} > \text{Ca} > \text{Sr} > \text{Ba} > \text{Na} > \text{K}$. For compositions with $\text{M}^{\text{n}+}/\text{nAl} < 1$, N_4 values are expected to be equal to zero.

Non-zero population of high-coordinated Al sites are observed in borocaluminosilicate glasses with $\text{Na}/\text{Al} < 1$ (Smedskjaer *et al.*, 2014) or in presence of alkaline-earth cations (Bunker *et al.*, 1991; Baltisberger *et al.*, 1996; Chan *et al.*, 1999; Du and Stebbins, 2005a; Wu and Stebbins, 2009).

Using NMR spectroscopy (Chan *et al.*, 1999; Du and Stebbins, 2005a,b; Angeli *et al.*, 2001), the various structural linkages between AlO_4 , SiO_4 , BO_3 or BO_4 can be identified. $^{[4]}\text{Al}-\text{O}-^{[4]}\text{Al}$, $^{[4]}\text{Al}-\text{O}-^{[4]}\text{B}$ and $^{[4]}\text{B}-\text{O}-^{[4]}\text{B}$ interactions are disfavored (4–4 avoidance) and depend strongly on the composition and the type of cation $\text{M}^{\text{n}+}$. In $\text{B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-(SiO}_2)$ glasses, strong chemical ordering (4–4 avoidance) is respected with K or Na, whereas a trend toward random mixing is observed with Mg or Ca. High Al and/or low $\text{M}^{\text{n}+}$ contents favor obedience to 4–4 avoidance. In addition to lowering N_4 values by the formation of $^{[4]}\text{Al}$, the addition of Al lowers $\text{N}_{4(\text{max})}$ due to the 4–4 avoidance between $^{[4]}\text{B}$ and $^{[4]}\text{Al}$ (Du and Stebbins, 2005a). $\text{N}_{4(\text{max})}$ values are also higher for higher SiO_2 content since Si atoms limit the possibility of $^{[4]}\text{B}-\text{O}-^{[4]}\text{Al}$ linkages and allow a higher fraction of $^{[4]}\text{B}$. In borocaluminosilicate glasses (Chan *et al.*, 1999; Wang and Stebbins, 2004; Du and Stebbins, 2005b), $^{[6]}\text{Al}$ units interact with the dominant BO_3 sites without forming Al enriched regions or Al-O-Al linkages. $^{[4]}\text{Al}-\text{O}-^{[3]}\text{B}$ linkages are more probable than $^{[4]}\text{Al}-\text{O}-^{[4]}\text{B}$ one and they are energetically more stable than $^{[4]}\text{B}-\text{O}-^{[4]}\text{B}$ and $^{[4]}\text{Al}-\text{O}-^{[4]}\text{Al}$ ones. $^{[4]}\text{B}$ interacts preferentially with $^{[5,6]}\text{Al}$ rather than $^{[4]}\text{Al}$, suggesting that $^{[5,6]}\text{Al}$ species are stabilizing $^{[4]}\text{B}$.

References

- Aasland, S., McMillan, P.F., 1994. Density-driven liquid-liquid phase separation in the system $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$. *Nature* 369, 633–636. doi:10.1038/369633a0.
- Agnello, G., Youngman, R., Lamberson, L., *et al.*, 2019. Bulk structures of silica-rich calcium aluminosilicate (CAS) glasses along the molar $\text{CaO}/\text{Al}_2\text{O}_3 = 1$ join via molecular dynamics (MD) simulation. *Journal of Non-Crystalline Solids* 519, 119450. doi:10.1016/j.jnoncrysol.2019.05.026.
- Akola, J., Kohara, S., Ohara, K., *et al.*, 2013. Network topology for the formation of solvated electrons in binary $\text{CaO-Al}_2\text{O}_3$ composition glasses. *Proceedings of the National Academy of Sciences of the United States of America* 110, 10129–10134. doi:10.1073/pnas.1300908110.
- Alahache, S., 2011. Vitrocéramiques transparentes d'aluminates: mécanismes de cristallisation et étude structurale. Orléans: Université d'Orléans.
- Allu, A.R., Gaddam, A., Ganiseti, S., *et al.*, 2018. Structure and crystallization of alkaline-earth aluminosilicate glasses: Prevention of the alumina-avoidance principle. *The Journal of Physical Chemistry B* 122, 4737–4747. doi:10.1021/acs.jpcc.8b01811.
- Allwardt, J.R., Lee, S.K., Stebbins, J.F., 2003. Bonding preferences of non-bridging O atoms: evidence from ^{17}O MAS and 3QMAS NMR on calcium aluminate and low-silica Ca-aluminosilicate glasses. *American Mineralogist* 88, 949–954.
- Allwardt, J.R., Poe, B.T., Stebbins, J.F., 2005a. The effect of fictive temperature on Al coordination in high pressure (10 GPa) sodium aluminosilicate glasses. *American Mineralogist* 90, 1453–1457.
- Allwardt, J.R., Stebbins, J.F., Schmidt, B.C., *et al.*, 2005b. Aluminum coordination and the densification of high-pressure aluminosilicate glasses. *American Mineralogist* 90, 1218–1222.
- Allwardt, J.R., Stebbins, J.F., Terasaki, H., *et al.*, 2007. Effect of structural transition on properties of high-pressure silicate melts: ^{27}Al NMR, glass densities, and melt viscosities. *American Mineralogist* 92, 1093–1104.

- Ando, M.F., Benzine, O., Pan, Z., *et al.*, 2018. Boson peak, heterogeneity and intermediate-range order in binary $\text{SiO}_2\text{-Al}_2\text{O}_3$ glasses. *Scientific Reports* 8, 5394. doi:10.1038/s41598-018-23574-1.
- Angeli, F., Charpentier, T., Gin, S., Petit, J.C., 2001. ^{17}O 3Q-MAS NMR characterization of a sodium aluminoborosilicate glass and its alteration gel. *Chemical Physics Letters* 341, 23–28.
- Atila, A., Ghardi, E.M., Hasnaoui, A., Ouaskit, S., 2019. Alumina effect on the structure and properties of calcium aluminosilicate in the percalcic region: A molecular dynamics investigation. *Journal of Non-Crystalline Solids* 525, 119470. doi:10.1016/j.jnoncrysol.2019.119470.
- Baltisberger, J.H., Xu, Z., Stebbins, J.F., Wang, S.H., Pines, A., 1996. Triple-quantum two-dimensional ^{27}Al magic-angle spinning nuclear magnetic resonance spectroscopic study of aluminosilicate and aluminate crystals and glasses. *Journal of the American Chemical Society* 118, 7209–7214. doi:10.1021/ja9606586.
- Barbieri, L., Corradi, A.B., Lancellotti, I., Leonelli, C., Montorsi, M., 2004. Experimental and computer simulation study of glasses belonging to diopside-anorthite system. *Journal of Non-Crystalline Solids* 345–346, 724–729. doi:10.1016/j.jnoncrysol.2004.08.190.
- Bardez, I., Caurant, D., Loiseau, P., *et al.*, 2005. Structural characterisation of rare earth rich glasses for nuclear waste immobilisation. *Physics and Chemistry of Glasses* 46, 320–329.
- Barnes, A.C., Skinner, L.B., Salmon, P.S., *et al.*, 2009. Liquid-liquid phase transition in supercooled yttria-alumina. *Physical Review Letters* 103, 225702.
- Bechgaard, T.K., Scannell, G., Huang, L., *et al.*, 2017. Structure of MgO/CaO sodium aluminosilicate glasses: Raman spectroscopy study. *Journal of Non-Crystalline Solids* 470, 145–151. doi:10.1016/j.jnoncrysol.2017.05.014.
- Benmore, C.J., Weber, J.K.R., Sampath, S., *et al.*, 2003. A neutron and x-ray diffraction study of calcium aluminate glasses. *Journal of Physics: Condensed Matter* 15, S2413–S2423. doi:10.1088/0953-8984/15/31/316.
- Benoit, M., Profeta, M., Mauri, F., Pickard, C.J., Tuckerman, M.E., 2005. First-principles calculation of the ^{17}O NMR parameters of a calcium aluminosilicate glass. *The Journal of Physical Chemistry B* 109, 6052–6060. doi:10.1021/jp0492570.
- Bista, S., Stebbins, J.F., Hankins, W.B., Sisson, T.W., 2015. Aluminosilicate melts and glasses at 1 to 3 GPa: Temperature and pressure effects on recovered structural and density changes. *American Mineralogist* 100, 2298–2307. doi:10.2138/am-2015-5258.
- Bouhadja, M., Jakse, N., Pasturel, A., 2014. Striking role of non-bridging oxygen on glass transition temperature of calcium aluminosilicate glass-formers. *Journal of Chemical Physics* 140, 234507. doi:10.1063/1.4882283.
- Brawer, S.A., White, W.B., 1977. Raman spectroscopic investigation of the structure of silicate glasses (II). Soda-alkaline earth-alumina ternary and quaternary glasses. *Journal of Non-Crystalline Solids* 23, 261–278.
- Brower, K.L., 1978. Structural and trapping characteristics of a new Al defect in vitreous silica. *Physical Review Letters* 41, 879–881. doi:10.1103/PhysRevLett.41.879.
- Brower, K.L., 1979. Electron paramagnetic resonance of Al E 1' centers in vitreous silica. *Physical Review B* 20, 1799–1811. doi:10.1103/PhysRevB.20.1799.
- Bunker, B.C., Kirkpatrick, R.J., Brow, R.K., Turner, G.L., Nelson, C., 1991. Local structure of alkaline-earth borosilicate crystals and glasses: II, ^{11}B and ^{27}Al MAS NMR spectroscopy of alkaline-earth borosilicate glasses. *Journal of the American Ceramic Society* 74, 1430–1438.
- Chan, J.C.C., Bertmer, M., Eckert, H., 1999. Site connectivities in amorphous materials studied by double-resonance NMR of quadrupolar nuclei: High-resolution $^{11}\text{B} \leftrightarrow ^{27}\text{Al}$ spectroscopy of aluminoborate glasses. *Journal of the American Chemical Society* 121, 5238–5248. doi:10.1021/ja983385i.
- Charpentier, T., Okhotnikov, K., Novikov, A.N., *et al.*, 2018. Structure of strontium aluminosilicate glasses from molecular dynamics simulation, neutron diffraction, and nuclear magnetic resonance studies. *The Journal of Physical Chemistry B* 122, 9567–9583. doi:10.1021/acs.jpcc.8b05721.
- Christie, J.K., Tilotta, A., 2010a. Short-range structure of yttrium alumino-silicate glass for cancer radiotherapy: Car-parrinello molecular dynamics simulations. *Advanced Engineering Materials* 12, B326–B330. doi:10.1002/adem.200980081.
- Christie, J.K., Tilotta, A., 2010b. Aluminosilicate glasses As yttrium vectors for in situ radiotherapy: Understanding composition-durability effects through molecular dynamics simulations. *Chemistry of Materials* 22, 3725–3734. doi:10.1021/cm100847p.
- Clayden, N.J., Esposito, S., Aronne, A., Pernice, P., 1999. Solid state ^{27}Al NMR and FTIR study of lanthanum aluminosilicate glasses. *Journal of Non-Crystalline Solids* 258, 11–19. doi:10.1016/S0022-3093(99)00555-4.
- Cormier, L., Neuville, D.R., 2004. Ca and Na environments in $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2$ glasses: Influence of cation mixing and cation-network interactions. *Chemical Geology* 213, 103–113. doi:10.1016/j.chemgeo.2004.08.049.
- Cormier, L., Calas, G., Creux, S., *et al.*, 1999. Environment around strontium in silicate and aluminosilicate glasses. *Physical Review B* 59, 13517–13520.
- Cormier, L., Ghaleb, D., Delaue, J.M., Calas, G., 2000a. Competition for charge compensation in borosilicate glasses: Wide-angle x-ray scattering and molecular dynamics calculations. *Physical Review B* 61, 14495–14999.
- Cormier, L., Neuville, D.R., Calas, G., 2000b. Structure and properties of low-silica calcium aluminosilicate glasses. *Journal of Non-Crystalline Solids* 274, 110–114. doi:10.1016/S0022-3093(00)00209-X.
- Cormier, L., Neuville, D.R., Calas, G., 2005. Relationship between structure and glass transition temperature in low-silica calcium aluminosilicate glasses: The origin of the anomaly at low silica content: Structure and glass transition temperature relationship. *Journal of the American Ceramic Society* 88, 2292–2299. doi:10.1111/j.1551-2916.2005.00428.x.
- Cormier, L., Delbes, L., Baptiste, B., Montouillout, V., 2021. Vitrification, crystallization behavior and structure of zinc aluminosilicate glasses. *Journal of Non-Crystalline Solids* 555, 120609.
- Cormier, L., Gaskell, P.H., Calas, G., Zhao, J., Soper, A.K., 1998. The environment around Li in the LiAlSiO_4 ionic conductor glass: A neutron scattering and reverse Monte Carlo study. *Physical Review B* 57, R8067–R8070.
- Cormier, L., Galois, L., Delaue, J.M., Ghaleb, D., Calas, G., 2001. Short- and medium-range structural order around cations in glasses: a multidisciplinary approach. *Comptes Rendus de l'Académie des Sciences - Series IV - Physics-Astrophysics* 2, 249–262.
- Cormier, L., Ghaleb, D., Neuville, D.R., Delaue, J.-M., Calas, G., 2003. Chemical dependence of network topology of calcium aluminosilicate glasses: A computer simulation study. *Journal of Non-Crystalline Solids* 332, 255–270. doi:10.1016/j.jnoncrysol.2003.09.012.
- Cristiglio, V., Henet, L., Cuello, G.J., *et al.*, 2007. Ab-initio molecular dynamics simulations of the structure of liquid aluminates. *Journal of Non-Crystalline Solids* 353, 1789–1792. doi:10.1016/j.jnoncrysol.2007.01.075.
- Day, D.E., Rindone, G.E., 1962. Properties of soda aluminosilicate glasses: I, Refractive index, density, molar refractivity, and infrared absorption spectra. *Journal of the American Ceramic Society* 45, 489–496. doi:10.1111/j.1151-2916.1962.tb11040.x.
- Douy, A., Gervais, M., 2000. Crystallization of amorphous precursors in the calcia alumina system: A differential scanning calorimetry study. *Journal of the American Ceramic Society* 83, 70–76. doi:10.1111/j.1151-2916.2000.tb01150.x.
- Drewitt, J.W.E., Jahn, S., Cristiglio, V., *et al.*, 2011. The structure of liquid calcium aluminates as investigated using neutron and high energy x-ray diffraction in combination with molecular dynamics simulation methods. *Journal of Physics: Condensed Matter* 23, 155101.
- Du, J., 2009. Molecular dynamics simulations of the structure and properties of low silica yttrium aluminosilicate glasses. *Journal of the American Ceramic Society* 92, 87–95. doi:10.1111/j.1551-2916.2008.02853.x.
- Du, J., René Corrales, L., 2007. Understanding lanthanum aluminate glass structure by correlating molecular dynamics simulation results with neutron and X-ray scattering data. *Journal of Non-Crystalline Solids* 353, 210–214. doi:10.1016/j.jnoncrysol.2006.06.025.
- Du, J., Benmore, C.J., Corrales, R., Hart, R.T., Weber, J.K.R., 2009. A molecular dynamics simulation interpretation of neutron and x-ray diffraction measurements on single phase $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ glasses. *Journal of Physics: Condensed Matter* 21, 205102. doi:10.1088/0953-8984/21/20/205102.
- Du, L.-S., Stebbins, J.F., 2005a. Network connectivity in aluminoborosilicate glasses: A high-resolution ^{11}B , ^{27}Al and ^{17}O NMR study. *Journal of Non-Crystalline Solids* 351, 3508–3520. doi:10.1016/j.jnoncrysol.2005.08.033.

- Du, L.-S., Stebbins, J.F., 2005b. Site connectivities in sodium aluminoborate glasses: Multinuclear and multiple quantum NMR results. *Solid State Nuclear Magnetic Resonance* 27, 37–49. doi:10.1016/j.ssnmr.2004.08.003.
- Du, W.-F., Kuraoka, K., Akai, T., Yazawa, T., 2000. Study of Al_2O_3 effect on structural change and phase separation in $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass by NMR. *Journal of Materials Science* 35, 4865–4871. doi:10.1023/A:1004853603298.
- Dubinsky, E.V., 2006. Quench rate and temperature effects on framework ordering in aluminosilicate melts. *American Mineralogist* 91, 753–761. doi:10.2138/am.2006.2039.
- Edén, M., 2015. Chapter Four – ^{27}Al NMR studies of aluminosilicate glasses. In *Annual Reports on NMR Spectroscopy*. Elsevier. pp. 237–331. https://doi.org/10.1016/bs.arnmr.2015.04.004.
- Edwards, P.P., 2011. Electrons in cement. *Science* 333, 49–50. doi:10.1126/science.1207837.
- El-Damrawi, G., Müller-Warmuth, W., Doweidar, H., Gohar, I.A., 1993. ^{11}B , ^{29}Si and ^{27}Al nuclear magnetic resonance studies of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ glasses. *Physics and Chemistry of Glasses* 34, 52–57.
- Engelhardt, G., Nofz, M., Forkel, K., *et al.*, 1985. Structural studies of calcium aluminosilicate glasses by high resolution solid state ^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance. *Physics and Chemistry of Glasses* 26, 157–165.
- Farnan, I., Stebbins, J.F., 1994. The nature of the glass transition in a silica-rich oxide melt. *Science* 265, 1206–1208.
- Florian, P., Sadiki, N., Massiot, D., Coutures, J.P., 2007. ^{27}Al NMR study of the structure of lanthanum- and yttrium-based aluminosilicate glasses and melts. *The Journal of Physical Chemistry B* 111, 9747–9757.
- Florian, P., Gervais, M., Douy, A., Massiot, D., Coutures, J.-P., 2001. A multi-nuclear multiple-field nuclear magnetic resonance study of the $\text{Y}_2\text{O}_3-\text{Al}_2\text{O}_3$ phase diagram. *The Journal of Physical Chemistry B* 105, 379–391. doi:10.1021/jp0008851.
- Gambuzzi, E., Pedone, A., Menziani, M.C., *et al.*, 2014. Probing silicon and aluminium chemical environments in silicate and aluminosilicate glasses by solid state NMR spectroscopy and accurate first-principles calculations. *Geochimica et Cosmochimica Acta* 125, 170–185. doi:10.1016/j.gca.2013.10.025.
- Ganisetti, S., Gaddam, A., Kumar, R., *et al.*, 2019. Elucidating the formation of Al-NBO bonds, Al-O-Al linkages and clusters in alkaline-earth aluminosilicate glasses based on molecular dynamics simulations. *Physical Chemistry Chemical Physics* 21, 23966–23977. doi:10.1039/C9CP04332B.
- Greaves, G.N., Ngai, K.L., 1995a. Reconciling ionic-transport properties with atomic structure in oxide glasses. *Physical Review B* 52, 6358–6380. doi:10.1103/PhysRevB.52.6358.
- Greaves, G.N., Ngai, K.L., 1995b. Relating the atomic structure of aluminosilicate glasses to their ionic transport properties. *Journal of Non-Crystalline Solids* 192–193, 405–410. doi:10.1016/0022-3093(95)00382-7.
- Greaves, G.N., Wilding, M.C., Fearn, S., *et al.*, 2008. Detection of first-order liquid/liquid phase transitions in yttrium oxide-aluminum oxide melts. *Science* 322, 566–570.
- Greaves, G.N., Wilding, M.C., Fearn, S., *et al.*, 2009. Liquid-liquid transitions, crystallization and long range fluctuations in supercooled yttrium oxide-aluminum oxide melts. *Journal of Non-Crystalline Solids* 355, 715–721.
- Guignard, M., Cormier, L., 2008. Environments of Mg and Al in $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses: A study coupling neutron and X-ray diffraction and reverse Monte Carlo modeling. *Chemical Geology* 256, 111–118. doi:10.1016/j.chemgeo.2008.06.008.
- Hafner, H.C., Kreidl, N.J., Weidel, R.A., 1958. Optical and physical properties of some calcium aluminate glasses. *Journal of the American Ceramic Society* 41, 315–323. doi:10.1111/j.1151-2916.1958.tb12923.x.
- Hannon, A.C., Parker, J.M., 2000. The structure of aluminate glasses by neutron diffraction. *Journal of Non-Crystalline Solids* 274, 102–109. doi:10.1016/S0022-3093(00)00208-8.
- Hiet, J., Deschamp, M., Pellerin, N., Fayon, F., Massiot, D., 2009. Probing chemical disorder in glasses using silicon-29 NMR spectral editing. *Physical Chemistry Chemical Physics* 11, 6935–6940.
- Higby, P.L., Ginther, R.J., Aggarwal, I.D., Friebele, E.J., 1990. Glass formation and thermal properties of low-silica calcium aluminosilicate glasses. *Journal of Non-Crystalline Solids* 126, 209–215.
- Himmel, B., Weigelt, J., Gerber, T., Nofz, M., 1991. Structure of calcium aluminosilicate glasses: wide-angle X-ray scattering and computer simulation. *Journal of Non-Crystalline Solids* 136, 27–36.
- Hoang, V.V., 2007. Composition dependence of static and dynamic heterogeneities in simulated liquid aluminum silicates. *Physical Review B* 75, 174202. doi:10.1103/PhysRevB.75.174202.
- Hosono, H., Abe, Y., 1987. An oxygen-effervescent aluminate glass. *Journal of the American Ceramic Society* 70, C-38–C-39. doi:10.1111/j.1151-2916.1987.tb04958.x.
- Hosono, H., Yamazaki, K., Abe, Y., 1985. Dopant-free ultraviolet-sensitive calcium aluminate glasses. *Journal of the American Ceramic Society* 68, C-304–C-305. doi:10.1111/j.1151-2916.1985.tb16151.x.
- Hwa, L.-G., 1998. Rayleigh-Brillouin scattering in calcium aluminosilicate glasses. *Journal of Raman Spectroscopy* 29, 269–272.
- Hyatt, M.J., Day, D.E., 1987. Glass properties in the yttria-alumina-silica system. *Journal of the American Ceramic Society* 70, C-283–C-287. doi:10.1111/j.1151-2916.1987.tb04901.x.
- Iftikhar, S., Leonova, E., Edén, M., 2009. Structural characterization of lanthanum aluminosilicate glasses by ^{29}Si solid-state NMR. *Journal of Non-Crystalline Solids* 355, 2165–2174. doi:10.1016/j.jnoncrysol.2009.06.031.
- Iftikhar, S., Pahari, B., Okhotnikov, K., *et al.*, 2012. Properties and structures of $\text{RE}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ ($\text{RE} = \text{Y}, \text{Lu}$) glasses probed by molecular dynamics simulations and solid-state NMR: The roles of aluminum and rare-earth ions for dictating the microhardness. *The Journal of Physical Chemistry C* 116, 18394–18406. doi:10.1021/jp302672b.
- Iftikhar, S., Grins, J., Gunawidjaja, P.N., Edén, M., 2011. Glass formation and structure-property-composition relations of the $\text{RE}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ ($\text{RE} = \text{La}, \text{Y}, \text{Lu}, \text{Sc}$) systems: Rare-earth aluminosilicate glasses. *Journal of the American Ceramic Society* 94, 2429–2435. doi:10.1111/j.1551-2916.2011.04548.x.
- Inaba, S., Todaka, S., Ohta, Y., Morinaga, K., 2000. Equation for estimating the Young's Modulus, shear modulus and vickers hardness of aluminosilicate glasses. *Journal of the Japan Institute of Metals* 64, 177–183. doi:10.2320/jinstmet1952.64.3.177.
- Iuga, D., Morais, C., Gan, Z., *et al.*, 2005. NMR heteronuclear correlation between quadrupolar nuclei in solids. *Journal of the American Chemical Society* 127, 11540–11541. doi:10.1021/ja052452n.
- Jakse, N., Bouhadja, M., Kozaily, J., *et al.*, 2012. Interplay between non-bridging oxygen, triclusters, and fivefold Al coordination in low silica content calcium aluminosilicate melts. *Applied Physics Letters* 101, 201903. doi:10.1063/1.4766920.
- Jaworski, A., Stevansson, B., Edén, M., 2015. Direct ^{17}O NMR experimental evidence for Al-NBO bonds in Si-rich and highly polymerized aluminosilicate glasses. *Physical Chemistry Chemical Physics* 17, 18269–18272. doi:10.1039/C5CP02985F.
- Jaworski, A., Stevansson, B., Pahari, B., Okhotnikov, K., Edén, M., 2012. Local structures and Al/Si ordering in lanthanum aluminosilicate glasses explored by advanced ^{27}Al NMR experiments and molecular dynamics simulations. *Physical Chemistry Chemical Physics* 14, 15866–15878. doi:10.1039/c2cp42858j.
- Johnson, J., Weber, R., Grimsditch, M., 2005. Thermal and mechanical properties of rare earth aluminate and low-silica aluminosilicate optical glasses. *Journal of Non-Crystalline Solids* 351, 650–655. doi:10.1016/j.jnoncrysol.2005.01.065.
- Kanehashi, K., Stebbins, J.F., 2007. In situ high temperature ^{27}Al NMR study of structure and dynamics in a calcium aluminosilicate glass and melt. *Journal of Non-Crystalline Solids* 353, 4001–4010. doi:10.1016/j.jnoncrysol.2007.06.030.
- Kang, E.-T., Lee, S.-J., Hannon, A.C., 2006. Molecular dynamics simulations of calcium aluminate glasses. *Journal of Non-Crystalline Solids* 352, 725–736. doi:10.1016/j.jnoncrysol.2006.02.013.
- Kelsey, K.E., Allwardt, J.R., Stebbins, J.F., 2008. Ca-Mg mixing in aluminosilicate glasses: An investigation using ^{17}O MAS and 3QMAS and ^{27}Al MAS NMR. *Journal of Non-Crystalline Solids* 354, 4644–4653. doi:10.1016/j.jnoncrysol.2008.05.049.

- Kelsey, K.E., Stebbins, J.F., Singer, D.M., *et al.*, 2009. Cation field strength effects on high pressure aluminosilicate glass structure: Multinuclear NMR and La XAFS results. *Geochimica et Cosmochimica Acta* 73, 3914–3933. doi:10.1016/j.gca.2009.03.040.
- Kidari, A., Dussossoy, J.L., Brackx, E., *et al.*, 2012. Lanthanum and neodymium solubility in simplified $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O-Al}_2\text{O}_3\text{-CaO}$ high level waste glass. *Journal of the American Ceramic Society* 95, 2537–2544. doi:10.1111/j.1551-2916.2012.05273.x.
- Kim, S.W., Shimoyama, T., Hosono, H., 2011. Solvated electrons in high-temperature melts and glasses of the room-temperature stable electride $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} \cdot 4\text{e}^-$. *Science* 333, 71–74. doi:10.1126/science.1204394.
- Kjeldsen, J., Smedskjaer, M.M., Mauro, J.C., *et al.*, 2013. Mixed alkaline earth effect in sodium aluminosilicate glasses. *Journal of Non-Crystalline Solids* 369, 61–68. doi:10.1016/j.jnoncrysol.2013.03.015.
- Kubicki, J.D., Toplis, M.J., 2002. Molecular orbital calculations on aluminosilicate tricluster molecules: Implications for the structure of aluminosilicate glasses. *American Mineralogist* 87, 668–678.
- Lacy, E.D., 1963. Aluminium in glasses and in melts. *Physics and Chemistry of Glasses* 4, 234–238.
- Lægsgaard, J., 2002. Theory of Al_2O_3 incorporation in SiO_2 . *Physical Review B* 65, 174104. doi:10.1103/PhysRevB.65.174104.
- Lamberson, L.A., 2016. Influence of Atomic Structure on Plastic Deformation in Tectosilicate Calcium-Aluminosilicate, Magnesium-Aluminosilicate, and Calcium-Galliosilicate Glasses. (Ph.D. thesis). USA: Cornell University.
- Landron, C., Cote, B., Massiot, D., *et al.*, 1992. Aluminium XAS and NMR spectroscopic studies of calcium aluminosilicate glasses. *Physica Status Solidi B* 171, 9–20. doi:10.1002/pssb.2221710102.
- Le Losq, C., Neuville, D.R., 2013. Effect of the Na/K mixing on the structure and the rheology of tectosilicate silica-rich melts. *Chemical Geology* 346, 57–71. doi:10.1016/j.chemgeo.2012.09.009.
- Le Losq, C., Neuville, D.R., Chen, W., *et al.*, 2017. Percolation channels: A universal idea to describe the atomic structure and dynamics of glasses and melts. *Scientific Reports* 7, 16490. doi:10.1038/s41598-017-16741-3.
- Le Losq, C., Neuville, D.R., Florian, P., Henderson, G.S., Massiot, D., 2014. The role of Al^{3+} on rheology and structural changes in sodium silicate and aluminosilicate glasses and melts. *Geochimica et Cosmochimica Acta* 126, 495–517. doi:10.1016/j.gca.2013.11.010.
- Lee, S.K., 2004. Structure of silicate glasses and melts at high pressure: Quantum chemical calculations and solid-state NMR. *The Journal of Physical Chemistry B* 108, 5889–5900.
- Lee, S.K., 2010. Effect of pressure on structure of oxide glasses at high pressure: Insights from solid-state NMR of quadrupolar nuclides. *Solid State Nuclear Magnetic Resonance* 38, 45–57. doi:10.1016/j.ssnmr.2010.10.002.
- Lee, S.K., Stebbins, J.F., 1999. The degree of aluminum avoidance in aluminosilicate glasses. *American Mineralogist* 84, 937–945.
- Lee, S.K., Stebbins, J.F., 2000a. Al–O–Al and Si–O–Si sites in framework aluminosilicate glasses with $\text{Si}/\text{Al} = 1$: Quantification of framework disorder. *Journal of Non-Crystalline Solids* 270, 260–264. doi:10.1016/S0022-3093(00)00089-2.
- Lee, S.K., Stebbins, J.F., 2000b. The structure of aluminosilicate glasses: High-resolution ^{17}O and ^{27}Al MAS and 3QMAS NMR study. *The Journal of Physical Chemistry B* 104, 4091–4100.
- Lee, S.K., Stebbins, J.F., 2002. Extent of intermixing among framework units in silicate glasses and melts. *Geochimica et Cosmochimica Acta* 66, 303–309.
- Lee, S.K., Stebbins, J.F., 2006. Disorder and the extent of polymerization in calcium silicate and aluminosilicate glasses: O–17 NMR results and quantum chemical molecular orbital calculations. *Geochimica et Cosmochimica Acta* 70, 4275–4286.
- Lee, S.K., Sung, S., 2008. The effect of network-modifying cations on the structure and disorder in peralkaline Ca–Na aluminosilicate glasses: O–17 3QMAS NMR study. *Chemical Geology* 256, 326–333. doi:10.1016/j.chemgeo.2008.07.019.
- Lee, S.K., Stebbins, J.F., 2009. Effects of the degree of polymerization on the structure of sodium silicate and aluminosilicate glasses and melts: An ^{17}O NMR study. *Geochimica et Cosmochimica Acta* 73, 1109–1119. doi:10.1016/j.gca.2008.10.040.
- Lee, S.K., Cody, G.D., Mysen, B.O., 2005. Structure and extent of disorder in quaternary (Ca–Mg and Ca–Na) aluminosilicate glasses and melts. *American Mineralogist* 90, 1393–1401.
- Lee, S.K., Cody, G.D., Fey, Y., Mysen, B.O., 2004. Nature of polymerization and properties of silicate melts and glasses at high pressure. *Geochimica et Cosmochimica Acta* 68, 4189–4200.
- Lee, S.K., Kim, H.-I., Kim, E.J., Mun, K.Y., Ryu, S., 2016. Extent of disorder in magnesium aluminosilicate glasses: Insights from ^{27}Al and ^{17}O NMR. *The Journal of Physical Chemistry C* 120, 737–749. doi:10.1021/acs.jpcc.5b10799.
- Li, W., Garofalini, S.H., 2004. Molecular dynamics simulation of lithium diffusion in $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ glasses. *Solid State Ionics* 166, 365–373.
- Licheron, M., Montouillout, V., Millot, F., Neuville, D.R., 2011. Raman and ^{27}Al NMR structure investigations of aluminate glasses: $(1-x)\text{Al}_2\text{O}_3-x\text{MO}$, with $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ and $0.5 < x < 0.75$. *Journal of Non-Crystalline Solids* 357, 2796–2801. doi:10.1016/j.jnoncrysol.2011.03.001.
- Lin, S.-L., Hwang, C.-S., Lee, J.-F., 1996. Characterization of $\text{CeO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ glasses by infrared and x-ray absorption near edge structure spectroscopies. *Journal of Materials Research* 11, 2641–2650. doi:10.1557/JMR.1996.0332.
- Lines, M.E., MacChesney, J.B., Lyons, K.B., *et al.*, 1989. Calcium aluminate glasses as potential ultralow-loss optical materials at 1.5–1.9 μm . *Journal of Non-Crystalline Solids* 107, 251–260. doi:10.1016/0022-3093(89)90470-5.
- Loewenstein, W., 1954. The distribution of aluminum in the tetrahedra of silicates and aluminates. *American Mineralogist* 39, 92–96.
- Loiseau, P., Caurant, D., 2010. Glass-ceramic nuclear waste forms obtained by crystallization of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-ZrO}_2\text{-TiO}_2$ glasses containing lanthanides (Ce, Nd, Eu, Gd, Yb) and actinides (Th): Study of the crystallization from the surface. *Journal of Nuclear Materials* 402, 38–54. doi:10.1016/j.jnucmat.2010.04.021.
- Luo, J., Vargheese, K.D., Tandia, A., Harris, J.T., Mauro, J.C., 2016. Structural origin of intrinsic ductility in binary aluminosilicate glasses. *Journal of Non-Crystalline Solids* 452, 297–306. doi:10.1016/j.jnoncrysol.2016.09.010.
- Maddow, J.F., Beall, G.H., 1969. Immiscibility and crystallization in $\text{Al}_2\text{O}_3\text{-SiO}_2$ glasses. *Journal of the American Ceramic Society* 52, 17–25. doi:10.1111/j.1151-2916.1969.tb12653.x.
- Makishima, A., Tamura, Y., Sakano, T., 1978. Elastic moduli and refractive indices of aluminosilicate glasses containing Y_2O_3 , La_2O_3 , and TiO_2 . *Journal of the American Ceramic Society* 61, 247–249. doi:10.1111/j.1151-2916.1978.tb09291.x.
- Makishima, A., Kobayashi, M., Shimohira, T., Nagata, T., 1982. Formation of aluminosilicate glasses containing rare-earth oxides. *Journal of the American Ceramic Society* 65, C-210–C-211. doi:10.1111/j.1151-2916.1982.tb09954.x.
- McKeown, D.A., Galeener, F.L., Brown Jr., G.E., 1984. Raman studies of Al coordination in silica-rich sodium aluminosilicate glasses and some related minerals. *Journal of Non-Crystalline Solids* 68, 361–378.
- McKeown, D.A., Waychunas, G.A., Brown Jr., G.E., 1985. EXAFS study of the coordination environment of aluminium in a series of silica-rich glasses and selected minerals within the $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ system. *Journal of Non-Crystalline Solids* 74, 349–371.
- McMillan, P.F., Piriou, B., 1983. Raman spectroscopy of calcium aluminate glasses and crystals. *Journal of Non-Crystalline Solids* 55, 221–242.
- McMillan, P.F., Kirkpatrick, R.J., 1992. Al coordination in magnesium aluminosilicate glasses. *American Mineralogist* 77, 898–900.
- McMillan, P.F., Wilding, M.C., 2008. Direct density determination of low- and high-density glassy polymorphs following a liquid-liquid phase transition in $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ supercooled liquids. *Journal of Non-Crystalline Solids* 354, 1015–1025.
- McMillan, P.F., Petuskey, W.T., Coté, B., *et al.*, 1996. A structural investigation of $\text{CaO-Al}_2\text{O}_3$ glasses via ^{27}Al MAS NMR. *Journal of Non-Crystalline Solids* 195, 261–271.
- McMillan, P.F., Wilson, M., Wilding, M.C., 2003. Polyamorphism in aluminate liquids. *Journal of Physics: Condensed Matter* 15, 6105–6121.

- McMillan, P.F., Wilson, M., Wilding, M.C., *et al.*, 2007. Polyamorphism and liquid-liquid phase transitions: Challenges for experiment and theory. *Journal of Physics: Condensed Matter* 19, 415101.
- Mei, Q., Benmore, C.J., Siewenie, J., Weber, J.K.R., Wilding, M., 2008a. Diffraction study of calcium aluminate glasses and melts: I. High energy x-ray and neutron diffraction on glasses around the eutectic composition. *Journal of Physics: Condensed Matter* 20, 245106. doi:10.1088/0953-8984/20/24/245106.
- Mei, Q., Benmore, C.J., Weber, J.K.R., *et al.*, 2008b. Diffraction study of calcium aluminate glasses and melts: II. High energy x-ray diffraction on melts. *Journal of Physics: Condensed Matter* 20, 245107. doi:10.1088/0953-8984/20/24/245107.
- Merzbacher, C.I., White, W.B., 1991. The structure of alkaline earth aluminosilicate glasses as determined by vibrational spectroscopy. *Journal of Non-Crystalline Solids* 130, 18–34.
- Moesgaard, M., Keding, R., Skibsted, J., Yue, Y., 2010. Evidence of intermediate-range order heterogeneity in calcium aluminosilicate glasses. *Chemistry of Materials* 22, 4471–4483. doi:10.1021/cm1011795.
- Mongalo, L., Lopis, A.S., Venter, G.A., 2016. Molecular dynamics simulations of the structural properties and electrical conductivities of CaO-MgO-Al₂O₃-SiO₂ melts. *Journal of Non-Crystalline Solids* 452, 194–202. doi:10.1016/j.jnoncrysol.2016.08.042.
- Morikawa, H., Miwa, S.-I., Miyake, M., Marumo, F., Sata, T., 1982. Structural analysis of SiO₂-Al₂O₃ glasses. *Journal of the American Ceramic Society* 65, 78–81. doi:10.1111/j.1151-2916.1982.tb10361.x.
- Morikawa, H., Marumo, F., Koyama, T., Yamane, M., Oyobe, A., 1983. Structural analysis of 12CaO.7Al₂O₃ glass. *Journal of Non-Crystalline Solids* 56, 355–360. doi:10.1016/0022-3093(83)90493-3.
- Moulton, B.J.A., Henderson, G.S., Sonnevile, C., *et al.*, 2016. The structure of haplobasaltic glasses investigated using X-ray absorption near edge structure (XANES) spectroscopy at the Si, Al, Mg, and O K-edges and Ca, Si, and Al L_{2,3}-edges. *Chemical Geology* 420, 213–230. doi:10.1016/j.chemgeo.2015.11.016.
- Murdoch, J.B., Stebbins, J.F., Carmichael, I.S.E., 1985. High-resolution ²⁹Si NMR study of silicate and aluminosilicate glasses: The effect of network modifying cations. *American Mineralogist* 70, 332–343.
- Mysen, B.O., 1990. Role of Al in depolymerized, peralkaline aluminosilicate melts in the systems Li₂O-Al₂O₃-SiO₂, Na₂O-Al₂O₃-SiO₂, K₂O-Al₂O₃-SiO₂. *American Mineralogist* 75, 120–134.
- Mysen, B.O., Toplis, M.J., 2007. Structural behavior of Al³⁺ in peralkaline, metaluminous, and peraluminous silicate melts and glasses at ambient pressure. *American Mineralogist* 92, 933–946.
- Nasikas, N.K., Sen, S., Papatheodorou, G.N., 2011. Structural nature of polyamorphism in Y₂O₃-Al₂O₃ glasses. *Chemistry of Materials* 23, 2860–2868. doi:10.1021/cm200241c.
- Navrotsky, A., Peraudeau, G., McMillan, P.F., Coutures, J.P., 1982. A thermochemical study of glasses and crystals along the joins silica-calcium aluminate and silica-sodium aluminate. *Geochimica et Cosmochimica Acta* 46, 2039–2047.
- Neuville, D.R., Cormier, L., Flank, A.-M., Briois, V., Massiot, D., 2004a. Al speciation and Ca environment in calcium aluminosilicate glasses and crystals by Al and Ca K-edge X-ray absorption spectroscopy. *Chemical Geology* 213, 153–163.
- Neuville, D.R., Cormier, L., Massiot, D., 2004b. Al environment in tectosilicate and peraluminous glasses: A ²⁷Al MQ-MAS NMR, Raman, and EXAFS investigation. *Geochimica et Cosmochimica Acta* 68, 5071–5079.
- Neuville, D.R., Cormier, L., Massiot, D., 2006. Al coordination and speciation in calcium aluminosilicate glasses: Effects of composition determined by ²⁷Al MQ-MAS NMR and Raman spectroscopy. *Chemical Geology* 229, 173–185.
- Neuville, D.R., Cormier, L., Montouillout, V., *et al.*, 2008. Structure of Mg- and Mg/Ca aluminosilicate glasses: ²⁷Al NMR and Raman spectroscopy investigations. *American Mineralogist* 93, 1721–1731.
- Neuville, D.R., Cormier, L., Montouillout, V., Massiot, D., 2007. Local Al site distribution in aluminosilicate glasses by ²⁷Al MQMAS NMR. *Journal of Non-Crystalline Solids* 353, 180–184. doi:10.1016/j.jnoncrysol.2006.09.035.
- Neuville, D.R., Henderson, G.H., Cormier, L., Massiot, D., 2010. The structure of crystals, glasses, and melts along the CaO-Al₂O₃ join: Results from Raman, Al L- and K-edge X-ray absorption, and ²⁷Al NMR spectroscopy. *American Mineralogist* 95, 1580–1589.
- Nie, S., Thomsen, R.M., Skibsted, J., 2020. Impact of Mg substitution on the structure and pozzolanic reactivity of calcium aluminosilicate (CaO-Al₂O₃-SiO₂) glasses. *Cement and Concrete Research* 138, 106231. doi:10.1016/j.cemconres.2020.106231.
- Novikov, A.N., Neuville, D.R., Hennet, L., *et al.*, 2017. Al and Sr environment in tectosilicate glasses and melts: Viscosity, Raman and NMR investigation. *Chemical Geology* 461, 115–127. doi:10.1016/j.chemgeo.2016.11.023.
- Okhotnikov, K., Svensson, B., Edén, M., 2013. New interatomic potential parameters for molecular dynamics simulations of rare-earth (RE = La, Y, Lu, Sc) aluminosilicate glass structures: Exploration of RE³⁺ field-strength effects. *Physical Chemistry Chemical Physics* 15, 15041–15055. doi:10.1039/c3cp51726h.
- Okuno, M., Zotov, N., Schmücker, M., Schneider, H., 2005. Structure of Al₂O₃-SiO₂ glasses: Combined X-ray diffraction, IR and Raman studies. *Journal of Non-Crystalline Solids* 351, 1032–1038.
- Onoda, G.Y., Brown, S.D., 1970. Low-silica glasses based on calcium aluminates. *Journal of the American Ceramic Society* 53, 311–316. doi:10.1111/j.1151-2916.1970.tb12114.x.
- Pahari, B., Iftikhar, S., Jaworski, A., *et al.*, 2012. Composition-property-structure correlations of scandium aluminosilicate glasses revealed by multinuclear ⁴⁵Sc, ²⁷Al, and ²⁹Si solid-state NMR. *Journal of the American Ceramic Society* 95, 2545–2553. doi:10.1111/j.1551-2916.2012.05288.x.
- Park, S.Y., Lee, S.K., 2012. Structure and disorder in basaltic glasses and melts: insights from high-resolution solid-state NMR study of glasses in diopside-Ca-tschermakite join and diopside-anorthite eutectic composition. *Geochimica et Cosmochimica Acta* 80, 125–142. doi:10.1016/j.gca.2011.12.002.
- Park, S.Y., Lee, S.K., 2014. High-resolution solid-state NMR study of the effect of composition on network connectivity and structural disorder in multi-component glasses in the diopside and jadeite join: Implications for structure of andesitic melts. *Geochimica et Cosmochimica Acta* 147, 26–42. doi:10.1016/j.gca.2014.10.019.
- Park, S.Y., Lee, S.K., 2018. Probing the structure of Fe-free model basaltic glasses: A view from a solid-state ²⁷Al and ¹⁷O NMR study of Na-Mg silicate glasses, Na₂O-MgO-Al₂O₃-SiO₂ glasses, and synthetic Fe-free KLB-1 basaltic glasses. *Geochimica et Cosmochimica Acta* 238, 563–579. doi:10.1016/j.gca.2018.07.032.
- Pechenik, A., Susman, S., Whitmore, D., Ratner, M., 1986. Ionic conductivity in glasses: A Monte-Carlo study of ordered and disordered one-dimensional models. *Solid State Ionics* 18–19, 403–409. doi:10.1016/0167-2738(86)90150-5.
- Pechenik, A., Whitmore, D.H., Susman, S., Ratner, M.A., 1988. Transport in glassy fast-ion conductors. *Journal of Non-Crystalline Solids* 101, 54–64. doi:10.1016/0022-3093(88)90368-7.
- Petkov, V., Billinge, S.J.L., Shastri, S.D., Himmel, B., 2000. Polyhedral units and network connectivity in calcium aluminosilicate glasses from high-energy X-ray diffraction. *Physical Review Letters* 85, 3436–3439.
- Pfleiderer, P., Horbach, J., Binder, K., 2006. Structure and transport properties of amorphous aluminium silicates: Computer simulation studies. *Chemical Geology* 229, 186–197.
- Poe, B.T., McMillan, P.F., Angell, C.A., Sato, R.K., 1992. Al and Si coordination in SiO₂-Al₂O₃ glasses and liquids – A study by NMR and IR spectroscopy and MD simulations. *Chemical Geology* 96, 333–349. doi:10.1016/0009-2541(92)90063-b.
- Poe, B.T., McMillan, P.F., Coté, B., Masiot, D., Coutures, J.P., 1994. Structure and dynamics in calcium aluminate liquids: High-temperature ²⁷Al NMR and Raman spectroscopy. *Journal of the American Ceramic Society* 77, 1832–1838.
- Ponader, C.W., Brown, G.E., 1989. Rare earth elements in silicate systems: I. Effects of composition on the coordination environments of La, Gd, and Yb. *Geochimica et Cosmochimica Acta* 53, 2893–2903. doi:10.1016/0016-7037(89)90166-X.

- Ren, J., Zhang, L., Eckert, H., 2014. Medium-range order in sol-gel prepared $\text{Al}_2\text{O}_3\text{-SiO}_2$ glasses: New results from solid-state NMR. *The Journal of Physical Chemistry C* 118, 4906–4917. doi:10.1021/jp412774h.
- Richet, P., Roskosz, M., Roux, J., 2006. Glass formation in silicates: Insights from composition. *Chemical Geology* 225, 388–401.
- Riebling, E.F., 1966. Structure of sodium aluminosilicate melts containing at least 50 mole % SiO_2 at 1500°C. *Journal of Chemical Physics* 44, 2857–2865. doi:10.1063/1.1727145.
- Risbud, S.H., 1982. STEM and EELS analysis of multiphase microstructures in oxide and non-oxide glasses. *Journal of Non-Crystalline Solids* 49, 241–251. doi:10.1016/0022-3093(82)90122-3.
- Risbud, S.H., Pask, J.A., 1977. Calculated thermodynamic data and metastable immiscibility in the system $\text{SiO}_2\text{-Al}_2\text{O}_3$. *Journal of the American Ceramic Society* 60, 418–424. doi:10.1111/j.1151-2916.1977.tb15525.x.
- Risbud, S.H., Kirkpatrick, R.J., Tagliaiavere, A.P., Montez, B., 1987. Solid-state NMR evidence of 4-, 5, and 6-fold aluminum sites in roller-quenched $\text{SiO}_2\text{-Al}_2\text{O}_3$ glasses. *Journal of the American Ceramic Society* 70, C-10–C-12. doi:10.1111/j.1151-2916.1987.tb04859.x.
- Rosales-Sosa, G.A., Masuno, A., Higo, Y., *et al.*, 2015. High elastic moduli of a $54\text{Al}_2\text{O}_3\text{-}46\text{Ta}_2\text{O}_5$ glass fabricated via containerless processing. *Scientific Reports* 5, 15233. doi:10.1038/srep15233.
- Rosales-Sosa, G.A., Masuno, A., Higo, Y., Inoue, H., 2016. Crack-resistant $\text{Al}_2\text{O}_3\text{-SiO}_2$ glasses. *Scientific Reports* 6, 23620. doi:10.1038/srep23620.
- Rosales-Sosa, G.A., Masuno, A., Higo, Y., Watanabe, Y., Inoue, H., 2018. Effect of rare-earth ion size on elasticity and crack initiation in rare-earth aluminate glasses. *Journal of the American Ceramic Society* 101, 5030–5036. doi:10.1111/jace.15760.
- Rosenflanz, A., Frey, M., Endres, B., *et al.*, 2004. Bulk glasses and ultrahard nanoceramics based on alumina and rare-earth oxides. *Nature* 430, 761–764. doi:10.1038/nature02729.
- Ross, S., Welsch, A.-M., Behrens, H., 2015. Lithium conductivity in glasses of the $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ system. *Physical Chemistry Chemical Physics* 17, 465–474. doi:10.1039/C4CP03609C.
- Roy, B.R., Navrotsky, A., 1984. Thermochemistry of charge-coupled substitutions in silicate glasses: the systems $\text{M1/n} + \text{AlO}_2\text{-SiO}_2$ ($\text{M} = \text{Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Pb}$). *Journal of the American Ceramic Society* 67, 606–610.
- Sato, R.K., McMillan, P.F., Dennison, P., Dupree, R., 1991. High-resolution ^{27}Al and ^{29}Si MAS NMR investigation of $\text{SiO}_2\text{-Al}_2\text{O}_3$ glasses. *The Journal of Physical Chemistry B* 95, 4483–4489.
- Schaller, T., Stebbins, J.F., 1998. The structural role of lanthanum and yttrium in aluminosilicate glasses: A ^{27}Al and ^{17}O MAS NMR study. *The Journal of Physical Chemistry B* 102, 10690–10697. doi:10.1021/jp982387m.
- Schmücker, M., Schneider, H., 1996. A new approach on the coordination of Al in non-crystalline gels and glasses of the system $\text{Al}_2\text{O}_3\text{-SiO}_2$. *Berichte der Bunsengesellschaft für Physikalische Chemie* 100, 1550–1553. doi:10.1002/bbpc.19961000940.
- Schmücker, M., Schneider, H., 2002. New evidence for tetrahedral triclusters in aluminosilicate glasses. *Journal of Non-Crystalline Solids* 311, 211–215. doi:10.1016/S0022-3093(02)01632-0.
- Schmücker, M., MacKenzie, K.J.D., Schneider, H., Meinhold, R., 1997. NMR studies on rapidly solidified $\text{SiO}_2\text{-Al}_2\text{O}_3$ and $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}$ glasses. *Journal of Non-Crystalline Solids* 217, 99–105.
- Sen, S., 2000. Atomic environment of high-field strength Nd and Al cations as dopants and major components in silicate glasses: A Nd LIII-edge and Al K-edge X-ray absorption spectroscopic study. *Journal of Non-Crystalline Solids* 261, 226–236.
- Sen, S., Stebbins, J.F., 1995. Structural role of Nd^{3+} and Al^{3+} cations in SiO_2 glass: A ^{29}Si MAS NMR spin-lattice relaxation, ^{27}Al NMR and EPR study. *Journal of Non-Crystalline Solids* 188, 54–62. doi:10.1016/0022-3093(95)00099-2.
- Sen, S., Youngman, R.E., 2004. High-resolution multinuclear NMR structural study of binary aluminosilicate and other related glasses. *The Journal of Physical Chemistry B* 108, 7557–7564. doi:10.1021/jp031348u.
- Shannon, R.D., 1976. Revised effective ionic radii and systematic studies of interatomic distance in halides and chalcogenides. *Acta Crystallographica A* 32, 751–767.
- Shelby, J.E., 1978. Viscosity and thermal expansion of lithium aluminosilicate glasses. *Journal of Applied Physics* 49, 5885–5891.
- Shelby, J.E., 1994. Rare earths as major components in oxide glasses. *Key Engineering Materials* 94–95, 1–42. doi:10.4028/www.scientific.net/KEM.94-95.1.
- Shelby, J.E., Kohli, J.T., 1990. Rare-earth aluminosilicate glasses. *Journal of the American Ceramic Society* 73, 39–42.
- Shelby, J.E., Wierzbicki, M.M., 1995. Formation and properties of soda lime aluminate glasses. *Physics and Chemistry of Glasses* 36, 17–21.
- Shelby, J.E., Shaw, C.M., Spess, M.S., 1989. Calcium fluoroaluminate glasses. *Journal of Applied Physics* 66, 1149–1154.
- Skibsted, J., Henderson, E., Jakobsen, H.J., 1993. Characterization of calcium aluminate phases in cements by aluminum-27 MAS NMR spectroscopy. *Inorganic Chemistry* 32, 1013–1027. doi:10.1021/ic00058a043.
- Skinner, L.B., Barnes, A.C., Crichton, W., 2006. Novel behaviour and structure of new glasses of the type Ba-Al-O and Ba-Al-Ti-O produced by aerodynamic levitation and laser heating. *Journal of Physics: Condensed Matter* 18, L407–L414. doi:10.1088/0953-8984/18/32/01.
- Skinner, L.B., Barnes, A.C., Salmon, P.S., *et al.*, 2012. Structure and triclustering in Ba-Al-O glass. *Physical Review B* 85, 064201. doi:10.1103/PhysRevB.85.064201.
- Skinner, L.B., Barnes, A.C., Salmon, P.S., Crichton, W.A., 2008. Phase separation, crystallization and polyamorphism in the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ system. *Journal of Physics: Condensed Matter* 20, 205103. doi:10.1088/0953-8984/20/20/205103.
- Smedskjaer, M.M., Youngman, R.E., Mauro, J.C., 2014. Principles of Pyrex® glass chemistry: Structure-property relationships. *Applied Physics A* 116, 491–504. doi:10.1007/s00339-014-8396-1.
- Smedskjaer, M.M., Huang, L., Scannell, G., Mauro, J.C., 2012. Elastic interpretation of the glass transition in aluminosilicate liquids. *Physical Review B* 85, 144203. doi:10.1103/PhysRevB.85.144203.
- Smedskjaer, M.M., Mauro, J.C., Kjeldsen, J., Yue, Y., 2013. Microscopic origins of compositional trends in aluminosilicate glass properties. *Journal of the American Ceramic Society* 96, 1436–1443. doi:10.1111/jace.12298.
- Stamboulis, A., Hill, R.G., Law, R.V., 2004. Characterization of the structure of calcium aluminosilicate and calcium fluoro-aluminosilicate glasses by magic angle spinning nuclear magnetic resonance (MAS NMR). *Journal of Non-Crystalline Solids* 333, 101–107. doi:10.1016/j.jnoncrysol.2003.09.049.
- Stebbins, J.F., Farnan, I., 1992. Effects of high temperature on silicate liquid structure: A multinuclear NMR study. *Science* 255, 586–589. doi:10.1126/science.255.5044.586.
- Stebbins, J.F., Xu, Z., 1997. NMR evidence for excess non-bridging oxygen in an aluminosilicate glass. *Nature* 390, 60–62. doi:10.1038/36312.
- Stebbins, J.F., Lee, S.K., Oglesby, J.V., 1999. Al-O-Al oxygen sites in crystalline aluminates and aluminosilicates glasses: high resolution oxygen-17 NMR results. *American Mineralogist* 84, 983–986.
- Stebbins, J.F., Kroeker, S., Lee, S.K., Kiczinski, T.J., 2000. Quantification of five- and six-coordinated aluminium ions in aluminosilicate and fluoride-containing glasses by high-field, high-resolution ^{27}Al NMR. *Journal of Non-Crystalline Solids* 275, 1–6.
- Stebbins, J.F., Dubinsky, E.V., Kanehashi, K., Kelsey, K.E., 2008. Temperature effects on non-bridging oxygen and aluminum coordination number in calcium aluminosilicate glasses and melts. *Geochimica et Cosmochimica Acta* 72, 910–925. doi:10.1016/j.gca.2007.11.018.
- Stein, D.J., Spera, F.J., 1995. Molecular dynamics simulations of liquids and glasses in the system $\text{NaAlSi}_3\text{O}_8\text{-SiO}_2$: Methodology and melt structures. *American Mineralogist* 80, 417–431.
- Stevenson, B., Edén, M., 2013. Structural rationalization of the microhardness trends of rare-earth aluminosilicate glasses: interplay between the RE^{3+} field-strength and the aluminum coordinations. *Journal of Non-Crystalline Solids* 378, 163–167. doi:10.1016/j.jnoncrysol.2013.06.013.
- Sukenaga, S., Florian, P., Kanehashi, K., *et al.*, 2017. Oxygen speciation in multicomponent silicate glasses using through bond double resonance NMR spectroscopy. *Journal of Physical Chemistry Letters* 8, 2274–2279. doi:10.1021/acs.jpclett.7b00465.

- Sun, K.-H., 1947. Fundamental conditions of glass formation. *Journal of the American Ceramic Society* 30, 277–281. doi:10.1111/j.1151-2916.1947.tb19654.x.
- Sung, Y.-M., Kwon, S.-J., 1999. Glass-forming ability and stability of calcium aluminate optical glasses. *Journal of Materials Science Letters* 18, 1267–1269. doi:10.1023/A:1006680506578.
- Takahashi, S., Neuville, D.R., Takebe, H., 2015. Thermal properties, density and structure of percalcic and peraluminous $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ glasses. *Journal of Non-Crystalline Solids* 411, 5–12. doi:10.1016/j.jnoncrysol.2014.12.019.
- Tanabe, S., Hirao, K., Soga, N., 1992. Elastic properties and molar volume of rare-earth aluminosilicate glasses. *Journal of the American Ceramic Society* 75, 503–506. doi:10.1111/j.1151-2916.1992.tb07833.x.
- Tandia, A., Timofeev, N.T., Mauro, J.C., Vargheese, K.D., 2011. Defect-mediated self-diffusion in calcium aluminosilicate glasses: A molecular modeling study. *Journal of Non-Crystalline Solids* 357, 1780–1786. doi:10.1016/j.jnoncrysol.2010.12.078.
- Tangeman, J.A., Phillips, B.L., Nordine, P.C., Weber, J.K.R., 2004. Thermodynamics and structure of single- and two-phase yttria-alumina glasses. *The Journal of Physical Chemistry B* 108, 10663–10671.
- Thomas, B.W.M., Mead, R.N., Mountjoy, G., 2006. A molecular dynamics study of the atomic structure of $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$ glass with $x = 0.625$ close to the eutectic. *Journal of Physics: Condensed Matter* 18, 4697–4708. doi:10.1088/0953-8984/18/19/021.
- Thompson, L.M., Stebbins, J.F., 2011. Non-bridging oxygen and high-coordinated aluminum in metaluminous and peraluminous calcium and potassium aluminosilicate glasses: High-resolution ^{17}O and ^{27}Al MAS NMR results. *American Mineralogist* 96, 841–853.
- Thompson, L.M., Stebbins, J.F., 2012. Non-stoichiometric non-bridging oxygens and five-coordinated aluminum in alkaline earth aluminosilicate glasses: Effect of modifier cation size. *Journal of Non-Crystalline Solids* 358, 1783–1789. doi:10.1016/j.jnoncrysol.2012.05.022.
- Thompson, L.M., Stebbins, J.F., 2013. Interaction between composition and temperature effects on non-bridging oxygen and high-coordinated aluminum in calcium aluminosilicate glasses. *American Mineralogist* 98, 1980–1987. doi:10.2138/am.2013.4511.
- Toplis, M., Dingwell, D.B., 2004. Shear viscosities of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ liquids: Implications for the structural role of aluminium and the degree of polymerisation of synthetic and natural aluminosilicate melts. *Geochimica et Cosmochimica Acta* 68, 5169–5188.
- Toplis, M.J., Dingwell, D.B., Hess, K.-U., Lenci, T., 1997a. Viscosity, fragility, and configurational entropy of melts along the join $\text{SiO}_2\text{-NaAlSi}_3\text{O}_8$. *American Mineralogist* 82, 979–990.
- Toplis, M.J., Dingwell, D.B., Lenci, T., 1997b. Peraluminous viscosity maxima in $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ liquids: The role of triclusters in tectosilicate melts. *Geochimica et Cosmochimica Acta* 61, 2605–2612.
- Toplis, M.J., Kohn, S.C., Smith, M.E., Poplett, I.J.F., 2000. Fivefold-coordinated aluminium in tectosilicate glasses observed by triple quantum MAS NMR. *American Mineralogist* 85, 1556–1560.
- Tossell, J.A., Horbach, J., 2005. O triclusters revisited: Classical MD and quantum cluster results for glasses of composition $(\text{Al}_2\text{O}_3)_2(\text{SiO}_2)$. *The Journal of Physical Chemistry B* 109, 1794–1797. doi:10.1021/jp0454873.
- Uhlmann, E.V., Weinberg, M.C., Kreidl, N.J., Goktas, A.A., 1993. Glass-forming ability in calcium aluminate-based systems. *Journal of the American Ceramic Society* 76, 449–453.
- Varshneya, A.K., Mauro, J.C., 2019. *Fundamentals of Inorganic Glasses*, third ed. Elsevier.
- Veit, U., Rüssel, C., 2016. Density and Young's Modulus of ternary glasses close to the eutectic composition in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ -system. *Ceramics International* 42, 5810–5822. doi:10.1016/j.ceramint.2015.12.123.
- Wallenberger, F.T., Brown, S.D., 1994. High-modulus glass fibers for new transportation and infrastructure composites and new infrared uses. *Composites Science and Technology* 51, 243–263. doi:10.1016/0266-3538(94)90194-5.
- Wang, J., Brocklesby, W.S., Lincoln, J.R., Townsend, J.E., Payne, D.N., 1993. Local structures of rare-earth ions in glasses: the 'crystal-chemistry' approach. *Journal of Non-Crystalline Solids* 163, 261–267. doi:10.1016/0022-3093(93)91303-K.
- Wang, S., Stebbins, J.F., 2004. Multiple-quantum magic-angle spinning ^{17}O NMR studies of borate, borosilicate, and borocaluminate glasses. *Journal of the American Ceramic Society* 82, 1519–1528. doi:10.1111/j.1151-2916.1999.tb01950.x.
- Watanabe, Y., Masuno, A., Inoue, H., 2012. Glass formation of rare earth aluminates by containerless processing. *Journal of Non-Crystalline Solids* 358, 3563–3566. doi:10.1016/j.jnoncrysol.2012.02.001.
- Watanabe, Y., Masuno, A., Inoue, H., Yanaba, Y., Kato, K., 2020. Influence of modifier cations on the local environment of aluminum in $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ and $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ binary glasses. *Physical Chemistry Chemical Physics* 22, 19592–19599. doi:10.1039/D0CP02778B.
- Weber, J.K.R., Tangeman, J.A., Key, T.S., et al., 2002. Novel synthesis of calcium oxide-aluminum oxide glasses. *Japanese Journal of Applied Physics* 41, 3029–3030. doi:10.1143/jjap.41.3029.
- Weber, J.K.R., Felten, J.J., Cho, B., Nordine, P.C., 1998. Glass fibres of pure and erbium- or neodymium-doped yttria-alumina compositions. *Nature* 393, 769–771. doi:10.1038/31662.
- Weber, R., Benmore, C.J., Siewenie, J., Urquidí, J., Key, T.S., 2004. Structure and bonding in single- and two-phase alumina-based glasses. *Physical Chemistry Chemical Physics* 6, 2480–2483. doi:10.1039/B314957A.
- Weber, R., Sen, S., Youngman, R.E., Hart, R.T., Benmore, C.J., 2008. Structure of high alumina content $\text{Al}_2\text{O}_3\text{-SiO}_2$ composition glasses. *The Journal of Physical Chemistry B* 112, 16726–16733. doi:10.1021/jp807964u.
- Wilding, M.C., McMillan, P.F., 2001. Polyamorphic transitions in yttria-alumina liquids. *Journal of Non-Crystalline Solids* 293–295, 357–365.
- Wilding, M.C., McMillan, P.F., 2002. Liquid polymorphism in yttrium-aluminate liquids. In: Brazhkin, V.V., Buldyrev, S.V., Rzhov, V.N., Stanley, H.E. (Eds.), *New Kinds of Phase Transitions: Transformation in Disordered Substances*. NATO Science Series. Boston: Dordrecht, pp. 57–73.
- Wilding, M.C., Benmore, C.J., McMillan, P.F., 2002a. A neutron diffraction study of yttrium- and lanthanum-aluminate glasses. *Journal of Non-Crystalline Solids* 297, 143–155.
- Wilding, M.C., McMillan, P.F., Navrotsky, A., 2002b. Thermodynamic and structural aspects of the polyamorphic transition in yttrium and other rare-earth aluminate liquids. *Physica A: Statistical Mechanics and its Applications* 314, 379–390. doi:10.1016/S0378-4371(02)01045-2.
- Wilding, M.C., Benmore, C.J., Weber, J.K.R., 2010. High-energy x-ray diffraction from aluminosilicate liquids. *The Journal of Physical Chemistry B* 114, 5742–5746. doi:10.1021/jp907587e.
- Wiles, N.T., Goyal, S., Baker, S.P., 2020. Geometric configuration of five-coordinated Al and Si in tectosilicate calcium aluminosilicate glasses and its effect on plastic flow. *Journal of Non-Crystalline Solids* 543, 120129. doi:10.1016/j.jnoncrysol.2020.120129.
- Winkler, A., Horbach, J., Kob, W., Binder, K., 2004. Structure and diffusion in amorphous aluminum silicate: A molecular dynamics computer simulation. *Journal of Chemical Physics* 120, 384–393. doi:10.1063/1.1630562.
- Wu, J., Stebbins, J.F., 2009. Effects of cation field strength on the structure of aluminoborosilicate glasses: High-resolution ^{11}B , ^{27}Al and ^{23}Na MAS NMR. *Journal of Non-Crystalline Solids* 355, 556–562. doi:10.1016/j.jnoncrysol.2009.01.025.
- Wu, Z., Romano, C., Marcelli, A., et al., 1999. Evidence for Al/Si tetrahedral network in aluminosilicate glasses from Al K-edge x-ray-absorption spectroscopy. *Physical Review B* 60, 9216–9219.
- Xiang, Y., Du, J., Smedskjaer, M.M., Mauro, J.C., 2013. Structure and properties of sodium aluminosilicate glasses from molecular dynamics simulations. *Journal of Chemical Physics* 139, 044507. doi:10.1063/1.4816378.
- Xue, X., Kanzaki, M., 2008. Structure of hydrous aluminosilicate glasses along the diopside-anorthite join: A comprehensive one- and two-dimensional ^1H and ^{27}Al NMR study. *Geochimica et Cosmochimica Acta* 72, 2331–2348. doi:10.1016/j.gca.2008.01.022.

- Yamashita, H., Inoue, K., Nakajin, T., Inoue, H., Maekawa, T., 2003. Nuclear magnetic resonance studies of $0.139MO$ (or M'_2O) $\cdot 0.673SiO_2 \cdot (0.188 - x)Al_2O_3 \cdot xB_2O_3$ ($M = Mg, Ca, Sr$ and Ba , $M' = Na$ and K) glasses. *Journal of Non-Crystalline Solids* 331, 128–136. doi:10.1016/j.jnoncrysol.2003.08.086.
- Yarger, J.L., Smith, K.H., Nieman, R.A., *et al.*, 1995. Al coordination changes in high-pressure aluminosilicate liquids. *Science* 270, 1964–1967.
- Yeganeh-Haeri, A., Ho, C.T., Weber, R., Diefenbacher, J., McMillan, P.F., 1998. Elastic properties of aluminate glasses via Brillouin spectroscopy. *Journal of Non-Crystalline Solids* 241, 200–203. doi:10.1016/S0022-3093(98)00804-7.
- Zachariasen, W.H., 1932. The atomic arrangement in glass. *Journal of the American Ceramic Society* 54, 3841–3851.
- Zhang, Y., Navrotsky, A., 2003. Thermochemistry of glasses in the $Y_2O_3-Al_2O_3-SiO_2$ system. *Journal of the American Ceramic Society* 86, 1727–1732. doi:10.1111/j.1151-2916.2003.tb03547.x.
- Zhang, Y., Navrotsky, A., 2004. Thermochemistry of rare-earth aluminate and aluminosilicate glasses. *Journal of Non-Crystalline Solids* 341, 141–151. doi:10.1016/j.jnoncrysol.2004.04.027.
- Zheng, K., Zhang, Z., Yang, F., Sridhar, S., 2012. Molecular dynamics study of the structural properties of calcium aluminosilicate slags with varying Al_2O_3/SiO_2 ratios. *ISIJ International* 52, 342–349. doi:10.2355/isijinternational.52.342.
- Zirl, D.M., Garofalini, S.H., 1990. Structure of sodium aluminosilicate glasses. *Journal of the American Ceramic Society* 73, 2848–2856.

Borosilicate Glasses

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Introduction

Borosilicate glasses are a family of oxide glasses, which are composed of two kinds of network formers, SiO_2 and B_2O_3 , and network modifiers such as alkali and alkaline oxides. A small amount of intermediate oxides such as Al_2O_3 and other oxides are often included in borosilicate glasses. They are one of the most useful inorganic glass systems, since they are applied in many applications such as health devices, pharmaceutical bottles, nuclear waste immobilization, electronics, lighting devices, cookware, optics, and fiber reinforced composites. These wide applications are attributed to their superior properties, e.g., low thermal expansion coefficient, high electrical resistivity, high optical transparency and low dispersion, and excellent chemical, thermal and mechanical durability. These properties allow borosilicate glass to play a crucial role in wet chemistry laboratories, as beakers, bottles, tubes and reaction vessels are made from this type of glass.

A striking feature of borosilicate glasses is their strong tendency to phase separation, especially when alkali ions are present in the glass. By taking advantage of phase separation, the high silica containing (up to 99 wt%) glass, so called Vycor[®] glass, was invented by Corning in 1939, and has been used in a wide range of applications from laboratory to early spacecraft viewing ports. Vycor[®] features excellent thermal shock resistance due to its low coefficient of thermal expansion (down to $7.5 \times 10^{-7} \text{K}^{-1}$ between 0 and 300°C), and as well as superior optical qualities. In contrast to pure fused silica, it can be easily fabricated in a variety of shapes.

As a modern material, borosilicate glass containing alumina can be drawn into continuous reinforcement fibers for windmill blade materials or discontinuous wool fibers for thermal and acoustic insulation. In recent years, borosilicate glasses have been extensively investigated with respect to their long-term chemical durability in relation to immobilization and disposal of radioactive wastes. In many countries, high-level radioactive waste has been incorporated into alkali borosilicate or phosphate glasses. Vitrification of a mixture of radioactive wastes and borosilicates is an attractive immobilization route owing to the high chemical durability of the vitrified products. It is desirable that the high chemical resistance of borosilicate glass enables the mixture to sustain a corrosive environment for many thousands of years. Typical compositions of borosilicate glasses for various applications can be found in Table 1 and will be described in subsequent sections.

Clearly, the main driving force for the fast development and enhancement of borosilicate glass products must be the requirement of developing a sustainable society and the desire to enhance the understanding of the correlations between the chemical composition, processing conditions, glass structure and properties. In turn, a better understanding of these relationships enable scientists and technologists to predict and tailor the properties of borosilicate glasses and develop new generations of glass products. In particular, the current understanding of borosilicate glass structure is substantially improved as compared to two decades ago, and this is thanks to advanced characterization techniques and computer simulations. This chapter reviews the progress both in revealing the structure of borosilicate glasses, and in predicting the glass properties by using the composition-structure-topology relation. Since there is a vast amount of publications and review articles concerning the structure and properties of borosilicate glasses, we will focus on describing the recent studies on these glass systems. After briefly reviewing some historic aspects of the structure studies, recent advances will be introduced concerning the impact of pressure and fictive temperature on structures of borosilicate glass, as well as the relation between medium-range order structural heterogeneity and thermodynamic properties. Atomistic computer simulation methods such as molecular dynamics that have played an important role in understanding the short and medium range structures and structure-property relationships of borosilicate glasses, as well as the recent developments of interatomic potentials for borosilicate glasses, are then introduced. After that, the recent progress in prediction of physical properties of borosilicate glasses, which have been made by both the rigidity theory and molecular dynamic simulations, will be presented. Finally, the important technological and industrial applications from lab and cook ware, fiber glass, optical and display, to nuclear waste disposal and biomedicine, as well as other potential applications, of borosilicate glasses are summarized.

Structure of Borosilicate Glasses

Characterizations

Short- and medium-range order structure

Like other glass and amorphous materials, borosilicate glasses lack long-range order and their structures are made up of networks consisting of $[\text{SiO}_4]$ and $[\text{BO}_4]$ tetrahedral units and $[\text{BO}_3]$ triangular units. This network features long-range disorder (beyond about 20 Å) and short- (~ 6 Å) and medium range (~ 6 –20 Å) order. The short-range order (SRO) in borosilicate glass means that the O-Si-O bond angle within $[\text{SiO}_4]$ units remains largely unchanged throughout the entire network, and this is the case for both $[\text{BO}_4]$ and $[\text{BO}_3]$ units. SRO also refers to the fact that the geometry of the structural units in the crystalline state can be inherited in

Table 1 Compositions of common borosilicate glasses for various applications

Glass/source	Oxide content, in wt%								Applications
	SiO ₂	B ₂ O ₃	Al ₂ O ₃	Na ₂ O	K ₂ O	CaO	MgO	Others	
Pyrex [®] Corning Code 7740	80.6	13.0	2.3	4.0	–	–	–	0.1 misc. traces	Lab ware, cook ware, others
Duran [®] Schott	81.0	13.0	2.0	(0–4.0)	–	–	–	–	Lab ware, cook ware, others
E-621 Fiberglass Owens Corning	54.5	6.6	14.0	0.8	0.2	22.1	0.6	0.5TiO ₂ 0.2Fe ₂ O ₃ , 0.5F ₂	Fiber glass
C-glass Owens Corning	54.0	10.0	14.0	–	–	17.5	4.5	–	Fiber glass
D-Glass Nippon Electric Glass	70–80	15–21.5	0–2.0	(2.0–5.0)	–	0–2.0	0–1.0	–	Fiber glass
Glass wool Insulation wool	64	4.5	3.5	15.5	1.2	7	3	0.25Fe ₂ O ₃ 0.15SO ₃	Glass wool
Vycor [®] Corning code 7930	96	3	< 1	0.4	–	–	–	< 1ZrO ₂	Porous material
OA-10 Display glass Nippon Elec. Glass	60.0	13.0	15.0	–	–	6.5	–	5.0SrO, 2.0BaO	Glaze, enamel
Glaze/Enamel	39.5	10.8	19.8	10.5	1.5	17.9	–	–	
BK-7 Schott	69.13	10.75	–	10.40	6.29	–	–	6As ₂ O ₃	Optics
AVM Model nuclear waste glass	56.1	25.3	–	18.6	–	–	–	–	Nuclear waste disposal
SON68 French nuclear waste glass	54.9	16.9	5.9	11.9	–	4.0	–	2.4Li ₂ O, 3.0ZnO	Nuclear waste disposal
ISG Model nuclear waste glass	56.2	17.3	6.1	12.2	–	5.0	–	3.3ZrO ₂	Nuclear waste disposal
45S5 Bioactive glass	45	–	–	24.5	–	24.5	–	6P ₂ O ₅	Biomedicine
S53P4 Bioactive glass	53	–	–	23	–	20	–	4P ₂ O ₅	Biomedicine

Note: Data with permission from Hubert, M., Faber, A.J., 2014. On the structural role of boron in borosilicate glasses. *Physics and Chemistry of Glasses: European Journal of Glass Science and Technology Part B* 55, 136–158. Gin, S., Abdelouas, A., Criscenti, L.J., *et al.*, 2013. An international initiative on long-term behavior of high-level nuclear waste glass. *Materials Today* 16, 243–248. Manaktala, H.K., 1992. An assessment of borosilicate glass as a high level waste form. Report no. CNWRA 92-017. Nuclear Regulatory Commission: San Antonio. Lu, X.N., Deng, L., Kuo, P.-H., *et al.*, 2017. Effects of boron oxide substitution on the structure and bioactivity of SrO-containing bioactive glasses. *Journal of Materials Science* 52, 8793–8811.

the glass state upon melt-quenching. Medium-range order (MRO) concerns the arrangement of a group of structural units in an ordered manner, e.g. some multi-member rings have similar structure throughout the network. Physical properties, phase transition behavior, and dynamic and thermodynamic properties of glass are governed by the structural characteristics over different length scales, especially by SRO and MRO domains, as well as different time scales. These properties are not only a function of chemical composition, temperature, and pressure, but also that of the entire thermal and pressure history. As for other classes of materials, the structural and topological characteristics of borosilicate glasses can be probed by means of advanced experimental and computational capabilities. The major challenge is to establish the quantitative connection between glass structure and properties, since often some rules based on established structural theories are not obeyed even for one- or two-component oxide glass systems.

The network structure of oxide glasses has been investigated using a variety of scattering and spectroscopic techniques. The first classical glass structure theory was the random network model proposed by Zachariasen (1932), in which the structural criteria for glass formation were established (Wright and Thorpe, 2013). After 53 years, Greaves (1985) proposed the concept of the modified random network, according to which there are two interconnected disordered regions: the polymerized one consisting of the glass formers and the depolymerized one composed of large concentrations of network modifiers. This concept has been confirmed by both experiments (Almeida *et al.*, 2014; Ojovan, 2016) and Molecular Dynamics modeling (Du and Cormack, 2004).

Recently, advances in instrumentation and new experimental methodologies have greatly enhanced understanding of glass structure at both short-range and intermediate-range length scales. One of the striking breakthroughs is the acquisition of direct experimental evidence for Zachariasen's random network theory (Huang *et al.*, 2012). Nuclear magnetic resonance (NMR) spectroscopy was first applied by Silver and Bray (1958) to determine the boron coordination numbers in borosilicate glasses. Today NMR has become a routine and powerful tool to characterize the SRO and MRO structure, as well as some long-range disorder structural features, of oxide glasses, owing to substantial progress and active development of NMR techniques. Such advances have led to a greatly enhanced understanding of glass structure and property for a wide range of inorganic glass systems. Particularly, for industrially relevant glass compositions containing B_2O_3 , SiO_2 and Al_2O_3 , their nuclear isotopes enable high-resolution NMR studies. The ^{11}B , ^{27}Al and ^{29}Si NMR techniques allow for probing local coordination environments of the network-forming cations. Accurate description of ^{11}B MAS NMR line shapes allows for separating different boron coordination environments, e.g., three-oxygen-coordinated boron (B^{III}) and four-oxygen-coordinated boron (B^{IV}), making it possible to determine the amount of boron involved in borosilicate glasses. It is the NMR method that first detected the most well-known important phenomenon – the *boron oxide anomaly*, in boron-containing glass (Yun and Bray, 1978). The advanced NMR techniques such as ^{11}B magic-angle-spinning (MAS) NMR and multiple quantum MAS NMR can even provide quantitative information on MRO structure, e.g., super-structural units like boroxol rings, and non-ring environments. Such structural information can be used to establish and optimize structural models of many commercial glass compositions. These models are the essential part of the topological constraint modeling procedure to predict physical properties of various glass systems including borosilicate glasses (Smedskjaer *et al.*, 2011).

Besides NMR, Raman spectroscopy is another powerful tool for exploring the SRO and MRO structures, as well as dynamics of boron-containing glasses. In Raman spectroscopy, a glass sample is illuminated with single wavelength (or single frequency) laser light, which can be absorbed, transmitted, reflected, or scattered by the sample. The detailed principle of Raman spectroscopy for characterizing glass structure can be found in literature (Almeida and Santos, 2015; and the references therein). Raman spectroscopy can often be used to identify the presence of terminal anions, like the non-bridging oxygen (NBO) ions in oxide glasses, which are associated with the presence of typical high-frequency peaks in the spectra. It is also crucial to combine theory with experimental Raman spectroscopy data. Glass phase separation, crystallization and other structural changes may also be conveniently followed by Raman spectroscopy.

Borosilicate glasses exhibit the interlinked borate and silicate networks. In Raman spectra of a borosilicate glass, the high frequency band of $>850\text{ cm}^{-1}$ is attributed to silicate networks consisting of tetrahedral silicon (Q^n), whereas intermediate frequency bands ($400\text{--}850\text{ cm}^{-1}$) are associated with MRO structural units, e.g., ordered superstructures such as reedmergnerite $[BSi_3O_8]^{-1}$ and danburite $[B_2Si_2O_8]^{2-}$ (Liu *et al.*, 2016). The bands from 300 to 500 cm^{-1} are characteristic of mixed stretching and bending modes of $Si\text{--}O\text{--}Si$ units, whereas bands in the range of $550\text{--}850\text{ cm}^{-1}$ are caused by ring breathing modes. The bands at 670 , 770 and 808 cm^{-1} are assigned to tetraborate groups, B^{IV} and B^{III} in diborate and boroxol rings, respectively. There are numerous articles dealing with the Raman spectroscopy analysis of borosilicate glasses (Almeida and Santos, 2015; Yadav and Singh, 2015).

Boron anomaly

The structural aspects of borate and borosilicate glass properties are fascinating owing to the boron anomaly. Boron anomaly refers to the phenomenon that a glass property varies non-monotonically with substitution of the network modifier for B_2O_3 in a borate glass system, i.e., a maximum or minimum occurs, depending on the type of property. The best known example is the minimum of the coefficient of thermal expansion (CTE) at a certain concentration of modifier (Uhlmann and Shaw, 1969). The anomaly has been ascribed to the competition between the formation of B^{IV} and the formation of non-bridging oxygens (NBOs). In detail, the initial incorporation of alkali or alkaline earth ions into a borate or borosilicate glass results in a decrease of CTE and an increase in glass transition temperature (T_g). However, after a certain concentration of network modifiers is reached, further addition of modifiers will gradually raise CTE and lower T_g . This behavior can be convincingly explained by the ^{11}B NMR data of a sodium borosilicate glass series, as shown in Fig. 1, where the fraction of the boron cations in BO_4 units (N_4) is plotted against the $[Na_2O]/[B_2O_3]$ ratio for the borosilicate system $Na_2O\text{--}B_2O_3\text{--}SiO_2$ with various $[SiO_2]/[B_2O_3]$ ratio (K values). N_4 increases with $[Na_2O]/[B_2O_3]$ ratio until the maximum value of N_4 is reached, and then it decreases. The increase of N_4 indicates an increased network connectivity, i.e., an increase in bridging oxygen (BO) fraction due to the gradual conversion of B^{III} into B^{IV} . This network tightening process lowers the extent of atomic vibrations upon heating, and thereby lowers CTE. After the maximum value of N_4 is reached, the fraction of BO continuously decreases and hence, the network is less connected. This leads to an increase in the extent of atomic vibration, thereby lowering CTE. The plots in Fig. 1 are separated into five groups, each corresponding to one K value ($[SiO_2]/[B_2O_3]$). As displayed in Fig. 1, the maximum values of N_4 and its corresponding $[Na_2O]/[B_2O_3]$ ratio increase slightly with K and can be determined by finding the intersection of the two lines for each group. In addition, the findings demonstrated in Fig. 1 has also been used to explain the boron anomaly related to other physical properties besides CTE, e.g., glass hardness

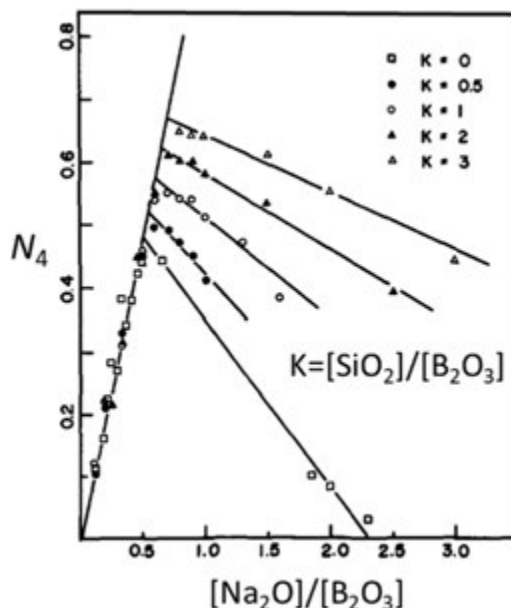


Fig. 1 Fraction (N_4) of the boron cations in BO_4 units versus $[Na_2O]/[B_2O_3]$ ratio for the borosilicate system $Na_2O-B_2O_3-SiO_2$ with various $[SiO_2]/[B_2O_3]$ ratios (K values) based on ^{11}B solid state NMR measurements. Reproduced from Yun, Y.H., Bray, P.J., 1978. Nuclear magnetic resonance studies of the glasses in the system $Na_2O-B_2O_3-SiO_2$. *Journal of Non-Crystalline Solids* 27, 363–380, with permission.

(Smedskjaer *et al.*, 2010). It should be mentioned that the experimental trend shown in **Fig. 1** has been beautifully reproduced by molecular dynamic simulation (see later section on Development of empirical potentials for MD simulations). This is an important step towards deeper insight into the atomic nature of the boron anomaly in borosilicate glasses.

Extensive studies have been conducted to enhance the understanding of the structural origin of the boron anomaly in both borate and borosilicate glasses. ^{11}B NMR was first used by Silver and Bray (1958) to determine boron speciation in pure boron oxide, alkali borate, and borosilicate glasses. Their seminal work built the basis for other scientists to establish the structural models for sodium borosilicate glasses (Yun and Bray, 1978). These structural models are a foundation of the currently derived topological models for predicting glass properties (Smedskjaer *et al.*, 2011). Furthermore, NMR was used to detect the impact of the thermal and mechanical history on boron speciation of borosilicate glasses.

Cooling rate and temperature effect

The fictive temperature (T_f) of a glass is the temperature at which the corresponding liquid structure and properties are frozen in upon cooling (Tool, 1946; Narayanaswamy, 1971; Moynihan *et al.*, 1976). It is a crucial parameter to describe its thermal history and a measure of the average level of its corresponding liquid on the potential energy landscape (Zheng *et al.*, 2019). The determination methods of T_f for any cooling rates are described by Yue *et al.* (2002). The increase of T_f with cooling rate q_c follows the relation (Yue *et al.*, 2004):

$$\log_{10} q_c = 11.35 - \log_{10} \eta(T_f) \quad (1)$$

where $\eta(T_f)$ is the viscosity at T_f of a glass quenched at q_c . The cooling rate (or T_f) has a pronounced impact on the structure and vibrational dynamics of the glass (Angell *et al.*, 2003). Specifically, increasing the cooling rate and T_f was found to enhance the excess density of vibrational states and the boson peak in glass, although its origin is still under debate (Chumakov *et al.*, 2014).

The direct evidence for an increase in NBO content with increasing T_f was achieved by performing NMR measurements on an E-glass composition (a typical borosilicate system) by Kiczinski *et al.* (2005). They found a correlation between T_f and the B^{IV} as shown in **Fig. 2(a)**, confirming the changes in boron coordination with cooling rate. Early on, Sen *et al.* (1998) also discovered the transformation of BO_3 units from boroxyl ring into non-ring configuration in a sodium borate system, and that of BO_4 units into asymmetric BO_3 units in a borosilicate system, with increasing temperature. No temperature-dependent speciation of the silicate units was observed in the borosilicate liquid.

It is seen in **Fig. 2(a)** that two clearly resolved peaks exist at 11 ppm and -1 ppm in the ^{11}B MAS NMR spectra, which were attributed to B^{III} and B^{IV} , respectively. As the quench rate increases, the proportion of B^{IV} decreases from 14% of the total boron in the slow-cooled sample ($T_f = 674^\circ C$), to 9% in the as-drawn fibers ($T_f = 912^\circ C$). When the fast-quenched sample ($q = 10^5 C/s$) was annealed at $43^\circ C$ above T_g and slowly cooled ($1.7 \times 10^{-2} C/s$) to well below T_g , the fraction of B^{IV} increased from 10% to 13%. Moreover, the ^{17}O -enriched E-glass samples had a similar dependence of the boron speciation on the fictive temperature to that of E-glass (**Fig. 2(b)**). As the cooling rate increases from $1.7 \times 10^{-2} C/s$ to $10^3 C/s$, and then to $10^5 C/s$, i.e., T_f increases from $674^\circ C$ to $807^\circ C$, and then to $872^\circ C$, the fraction of the B^{IV} species drops from 16% to 13%, and to 12%, respectively. In addition, raising T_f leads to an increase in the five-coordinated aluminum (Al^{VI}) content in E-glass and this is ascribed to the increase in F-Al bonds. The

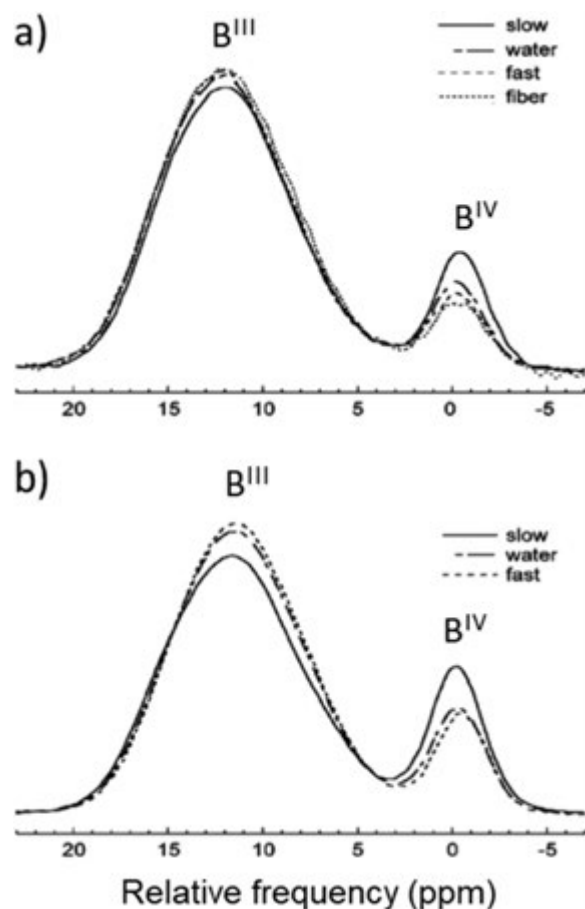


Fig. 2 Impact of the cooling rate on the SRO structure for the E glass system with composition (mol%): $57.3\text{SiO}_2\text{--}6.0\text{B}_2\text{O}_3\text{--}8.7\text{Al}_2\text{O}_3\text{--}24.9\text{CaO--}0.9\text{MgO--}0.8\text{Na}_2\text{O--}0.8\text{F}_2$, and the ^{17}O -enriched sample with a major-element composition similar to that of the above E-glass. The meanings of the labels for the NMR curves are as follows. Slow: slow cooling (rate $q = 1.7 \times 10^{-2}^\circ\text{C/s}$, $T_f = 674^\circ\text{C}$); Water: water quenching ($q = 1 \times 10^3^\circ\text{C/s}$, $T_f = 807^\circ\text{C}$); Fast: fast quenching ($q = 1 \times 10^5^\circ\text{C/s}$, $T_f = 872^\circ\text{C}$); Fiber: fiber quenching ($q = 1 \times 10^6^\circ\text{C/s}$, $T_f = 912^\circ\text{C}$). The standard glass transition temperature (T_g) is 682°C . (a): ^{11}B MAS NMR spectra of E-glass samples. (b) ^{11}B MAS NMR spectra for the ^{17}O enriched sample. Data from Kiczinski, T.J., Du, L.S., Stebbins, J.F., 2005. The effect of fictive temperature on the structure of E-glass: A high resolution, multinuclear NMR study. *Journal of Non-Crystalline Solids* 351, 3571–3578, with permission.

high-temperature melt exhibits considerably higher $\text{B}^{\text{III}}/\text{B}^{\text{IV}}$, $\text{Al}^{\text{V}}/\text{Al}^{\text{IV}}$, and NBO/BO ratios compared to its corresponding glass with the standard T_g (Kiczinski *et al.*, 2005).

Wondraczek *et al.* (2007) systematically investigated the dependence of the SRO and MRO structure and thermodynamic properties on the mechanical history (pressure) and thermal history (cooling rate and T_f). They found that an increase in pressure and a decrease of T_f led to the decrease of the B^{III} species in sodium borosilicate glasses. The sensitivity of the boron speciation to cooling rate was also confirmed by Zheng *et al.* (2012). They found that rapidly cooled borate glasses have lower glass stability against crystallization than slowly cooled ones since the former contain more B^{III} species, leading to easy crystallization.

Pressure effect

The effect of pressure on glass structure has been extensively studied since it is a crucial aspect to be considered in designing and improving glass properties, as well as in understanding the nature of glass. Through these studies, substantial progress has been made in probing the evolution of both SRO and MRO structure in different glass systems during the *in situ* compression and/or in characterizing the structure after *ex situ* compression (Wolf and McMillan, 1995; Lee *et al.*, 2005; McMillan *et al.*, 2007; Yue *et al.*, 2007; Wu *et al.*, 2009; Striepe *et al.*, 2013). The pressure effect on borosilicate glass systems has also attracted attention of scientists as the boron speciation in these glasses is an effective, sensitive probe to reflect the pressure induced structural change (Svenson *et al.*, 2014; Wondraczek *et al.*, 2007).

Fig. 3 shows a typical example for detecting the boron coordination change induced by pressure (Svenson *et al.*, 2014). It exhibits the ^{11}B MAS NMR spectra of both the as-prepared and the 1 GPa compressed borosilicate glass with the composition of $60\text{SiO}_2\text{--}15\text{B}_2\text{O}_3\text{--}15\text{Na}_2\text{O--}10\text{CaO}$ (mol%). The spectra are characterized by a broad peak centered around +15 ppm, attributed to trigonal boron (B^{III}) sites, and a relatively narrow peak centered around 0 ppm, (which is caused by B^{IV}) sites. The fraction of

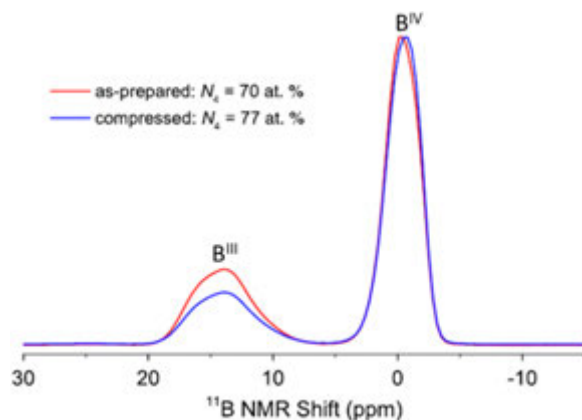


Fig. 3 ^{11}B MAS NMR spectra at 16.4 T of both the as-prepared and the 1 GPa compressed borosilicate glass samples with the composition (mol%) $60\text{SiO}_2\text{--}15\text{B}_2\text{O}_3\text{--}15\text{Na}_2\text{O}\text{--}10\text{CaO}$. The uncertainty of N_4 is ± 2.5 at%. Data with permission from Svenson, M.N., Bechgaard, T.K., Fuglsang, S.D., *et al.*, 2014. Composition-structure-property relations of compressed borosilicate glasses. *Physical Review Applied* 2, 024006.

tetrahedral to total boron numbers (N_4) is determined by conducting the spectral line shape simulation and subsequent peak area integration. It is seen in **Fig. 3** that N_4 increases from 70% to 77% upon isostatic compression at 1 GPa.

Another example is the combined picture concerning the impact of both pressure and fictive temperature on the thermodynamic and structure of a borosilicate glass as shown in **Fig. 4**. By measuring the dependence of pressure and cooling rate on the boron speciation of a borosilicate glass, Wondraczek *et al.* (2007) found that the changes in both the molar volume and the SRO structure were governed by the boron speciation in compression as well as in cooling experiments. They indicated the glasses with a given fraction of B^{IV} and a given molar volume could be achieved either by varying pressure or by changing cooling rate, e.g., by either 400 MPa and $4^\circ\text{C}/\text{min}$ or by 0.1 MPa and $10^{-4}^\circ\text{C}/\text{min}$. As mentioned before, the boron coordination in borosilicate glasses is NMR sensitive to their fictive temperature, as well as to pressure. **Fig. 4** illustrates that the ratio of $\text{B}^{\text{IV}}/\text{B}^{\text{III}}$ in the glass structure increases with decreasing cooling rate (i.e., fictive temperature) and increasing pressure.

Structural heterogeneity and thermodynamic behaviors

To understand the glass transition and thermodynamic properties of glass forming liquids, the structural and dynamic heterogeneities have become one of the key issues to be investigated (Yue, 2004; Matharoo *et al.*, 2006; Moesgaard *et al.*, 2010; Zhang *et al.*, 2013). The structural heterogeneity on intermediate length scale is also a crucial factor for determining glass properties, e.g., optical and photonic properties (Tan *et al.*, 2020), and thermodynamic behavior (Liu *et al.*, 2016; Ando *et al.*, 2018). The MRO structural heterogeneity has an intimate correlation with thermodynamic properties of glass. One of the evidences for this correlation was achieved by studying the impact of boron content on the configurational heat capacity as shown in **Fig. 5** (Liu *et al.*, 2016).

Fig. 5 shows the isobaric heat capacity curves obtained during DSC upscans at $10^\circ\text{C}/\text{min}$ for a borosilicate glass series with the molar compositions $(75-x)\text{SiO}_2 - x\text{B}_2\text{O}_3\text{--}15\text{Na}_2\text{O} - 10\text{CaO}$ with $x = 0, 6, 12, 24, 37.5, 51, 63$, and 75 (Smedskjaer *et al.*, 2011). The inset of the figure demonstrates how to determine standard glass transition temperature (T_g), glass heat capacity (C_{pg}), liquid heat capacity (C_{pl}), and the configurational heat capacity ($C_{p,\text{conf}}$). The difference (ΔC_p) between C_{pl} and C_{pg} is regarded as the approximate configurational heat capacity. The standard T_g is defined as the temperature at the crossing point between the extrapolated straight line of the glass C_p curve and the tangent at the inflection point of the sharp rise in the curve of C_p in the glass transition region. As shown in **Fig. 5**, the C_p curve rises and $C_{p,\text{conf}}$ increases with increasing B_2O_3 content. The T_g value first increases and then decreases with increasing B_2O_3 content.

Both $C_{p,\text{conf}}$ and T_g trends shown in **Fig. 5** are quantitatively represented in **Fig. 6(a)**. The relatively fast increase of $C_{p,\text{conf}}$ with B_2O_3 content in the silica-rich compositions can be attributed to the increase in both B-O-Si network units ($[\text{B}_2\text{Si}_2\text{O}_8]^{2-}$) and 6-membered borate rings with 1 or 2 B^{IV} . In the boron oxide-rich compositions, the $C_{p,\text{conf}}$ remains almost unchanged with B_2O_3 content. This could be ascribed to the balance between the decrease of the fraction of two types of metaborate groups and the increase of the fraction of other borate superstructural units (particularly 6-membered borate rings). T_g exhibits a non-linear trend with increasing B_2O_3 content, i.e., T_g first increases from 830 to 855 K as B_2O_3 initially substitutes SiO_2 , but then monotonically decreases to 777 K. Based on the temperature-constraint theory, this non-linear variation of T_g is mainly caused by the change of the temperature dependent constraints, and the short range order structural evolution of boron (Smedskjaer *et al.*, 2011).

The gradual substitution of B_2O_3 for SiO_2 may lead to the MRO structural change in borosilicate glasses, and this is verified by the Raman spectroscopy results (see inset of **Fig. 6(b)**). The inset of **Fig. 6(b)** shows the full range ($250\text{--}1650\text{ cm}^{-1}$) Raman spectra of the borosilicate glass series. The Raman spectra of borosilicate glasses can generally be divided into three main frequency regions: low-frequency ($300\text{--}550\text{ cm}^{-1}$), medium-frequency ($550\text{--}810\text{ cm}^{-1}$), and high-frequency ($900\text{--}1600\text{ cm}^{-1}$) regions. The assignment of the Raman bands to different vibrational modes has been described in detail by Liu *et al.* (2016).

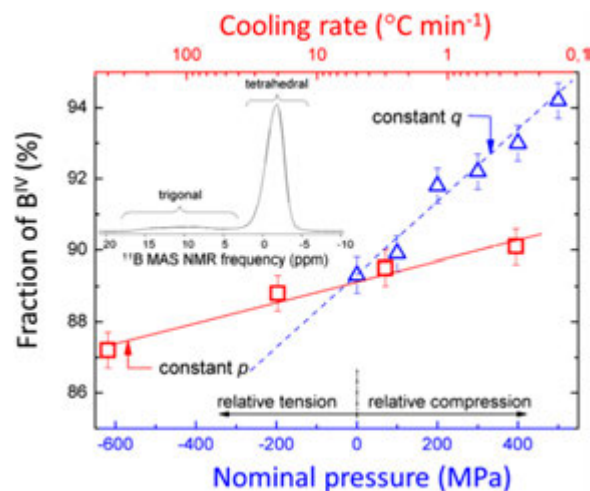


Fig. 4 Fraction of B^{IV} atoms measured by ¹¹B MAS NMR spectroscopy for samples with the molar composition 16Na₂O–10B₂O₃–74SiO₂ as functions of both pressure and cooling rate. The samples were frozen-in at the cooling rate of 4°C/min under elevated pressures (triangle symbols), and frozen-in under ambient pressure but at different cooling rates (square symbols), respectively. On the pressure axis, positive values correspond to compression, and negative values result from extrapolation of the data and correspond to tension relative to the ambient pressure. Inset: NMR spectrum of the sample prepared under the condition of 500 MPa and 4°C/min. Data with permission from Wondraczek, L., Sen, S., Behrens, H., Youngman, R.E., 2007. Structure-energy map of alkali borosilicate glasses: Effects of pressure and temperature. *Physical Review B* 76, 014202.

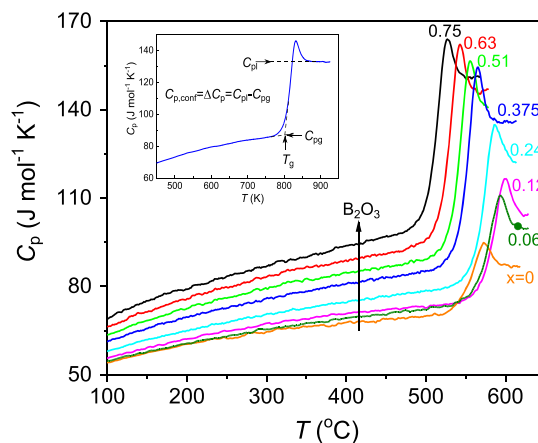


Fig. 5 Isobaric heat capacity (C_p) curves determined by DSC at an upscan rate of 10°C/min subsequent to a downscan at the same rate, for the borosilicate glass series (75- x)SiO₂– x B₂O₃–15Na₂O–10CaO with $x = 0, 6, 12, 24, 37.5, 51, 63$, and 75 mol%, viz., with constant modifier content but varying [B₂O₃]/([SiO₂] + [B₂O₃]) ratio ($=x/75$). Inset: Illustration of determining glass transition temperature (T_g), glass heat capacity ($C_{p,g}$), liquid heat capacity ($C_{p,l}$), the difference between $C_{p,l}$ and $C_{p,g}$, ΔC_p , and the configurational heat capacity ($C_{p,conf}$) by taking the sample with composition with $x = 37.5$ mol%. Data with permission from Smedskjaer J.C., Mauro, M.M., Youngman, R.E., *et al.*, 2011. Topological principles of borosilicate glass chemistry. *Journal of Physical Chemistry B* 115, 12930–12946.

Fig. 6(b) demonstrates an approximately linear relation between $C_{p,conf}$ and the total area of all the Raman bands assigned to MRO structural units, i.e., the algebraic sum of the relative areas of each deconvoluted Raman band. This implies that the increase of $C_{p,conf}$ is linearly correlated with the increased diversity of the MRO structural units. The coordination conversions (i.e., SRO structural changes) have a small contribution to $C_{p,conf}$ in borosilicate glasses, i.e., the changes in the boron coordination account for 25% of the $C_{p,conf}$ (Angeli *et al.*, 2012). This suggests that the diversity of MRO structural units might have a larger contribution to $C_{p,conf}$ in these glasses.

According to the equipartition theorem of energy in statistical thermodynamics, the specific heat is directly linked to the atomic degree of freedom of motions. In borosilicate glasses, a variety of superstructural units containing different numbers of borate rings may involve more conformational states than the SRO structural units. As glass undergoes the glass transition region during heating, MRO structural units are thermally activated. This causes all of the superstructures to break down gradually, i.e., the rings separate from each other, leading to the formation of out-of ring or “loose” [BO_{4/2}][−] and [BO_{3/2}][−] units (Yano *et al.*, 2003). This structural evolution gives rise to the increase of the heat capacity. The change in the content of MRO units has no impact on the

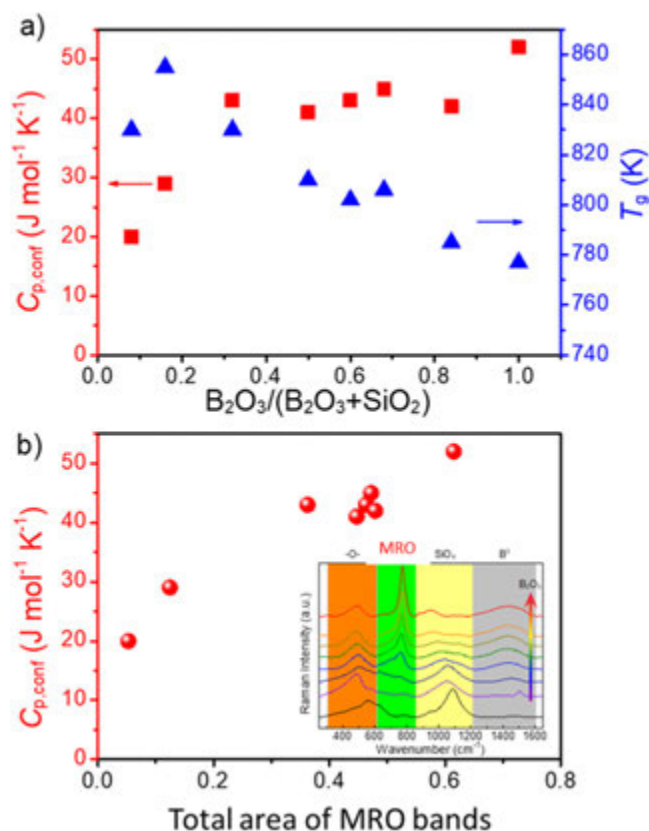


Fig. 6 The connection of the dynamic (T_g) and thermodynamic ($C_{p,conf}$) properties to the degree of the medium-range order (MRO) heterogeneity, which is manifested by the total area of the MRO bands (see Inset), for the borosilicate glass series $(0.75-x)SiO_2-xB_2O_3-0.15Na_2O-0.10CaO$ with $x = 0, 0.06, 0.12, 0.24, 0.375, 0.51, 0.63$, and 0.75 mol. (a) The configurational heat capacity ($C_{p,conf}$) and the glass transition temperature (T_g) as a function of the $[B_2O_3]/([B_2O_3] + [SiO_2]) = x/0.75$. (b) $C_{p,conf}$ as a function of the total integrated area of the Raman band (61–850 cm^{-1}). Inset: The full range (250–1650 cm^{-1}) Raman spectra, which exhibit the vibrational bands associated with bridging oxygen, MRO units, tetrahedral SiO_4 units and the 3-oxygen coordinated boron (B^3), respectively. The total area of the MRO bands is the algebraic sum of the area of each deconvoluted IRO band. Reproduced with permission from Liu, H., Smedskjaer, M.M., Tao, H.Z., *et al.*, 2016. A medium range order structural connection to the configurational heat capacity of borate-silicate mixed glasses. *Physical Chemistry Chemical Physics* 18, 10887–10895.

SRO units (Yano *et al.*, 2003), and thus it is the increased diversity of MRO units that enhances $C_{p,conf}$ and hence the configurational entropy. This makes sense because the configurational entropy is a measure of the diversity of the structural arrangements. In the case of borosilicate glasses, an increase of B_2O_3 causes an extended variety of the superstructural units, and the size of these units is comparable to the length scale of MRO domains.

The topological heterogeneity in compressed sodium borosilicate glasses was explored using the Brillouin and in situ small angle X-ray scattering (SAXS) analyses by Reibstein *et al.* (2011). They extrapolated the SAXS intensity to very low angular regimes, and related it to compressibility. By performing both the Brillouin scattering experiments and the elastic property measurements, they determined the Landau-Placzek ratio, which reflected the amplitude of frozen-in density fluctuations. With increasing fictive pressure, the topological heterogeneity in the glass within both SRO and MRO ranges is significantly lowered. Through both the dynamic heating-cooling and the isothermal heating protocol, it was possible to detect the evolution of density fluctuations upon pressure recovery (Smedskjaer *et al.*, 2014b). The glass structure arrested by the pressure of 470 MPa was completely recovered to that corresponding to 0.1 MPa around the glass transition temperature. Based on the isothermal heating experiments, Reibstein *et al.* (2011) found that the medium- and long-range structure recovery govern macroscopic density relaxation.

Molecular Dynamics Simulations

Background

Molecular dynamics (MD) simulations have been an effective tool in the study of glass and amorphous materials. It is used to generate atomic level glass structures and compute the equilibrium and transport properties of a many-body system where the constituent atoms can be considered as particles which follow the laws of classical mechanics. MD simulations can in many ways complement experimental methods but it also has significant advantages in terms of providing detailed short and medium range structure characteristics in studying glass and amorphous materials. In MD simulations, samples of N number of particles are

taken, then Newton's law of motion for each of the particles is solved to determine its position and velocity in the next time step. Interaction over large number steps are performed until equilibrium is achieved. Based on formulations of statistical mechanics, various thermodynamic properties such as volume, pressure, internal energy, kinetic energy and enthalpy, and related properties such as heat capacity can be calculated (Daan and Smit, 2002). Therefore, in simple words, MD simulation is a technique to obtain various properties of a system by solving Newton's law of motion. Unlike crystalline materials, glass materials do not have long-range order but have short range order similar to related crystals. As a result, in many cases, it is difficult or even impossible to determine the structure of glass using common experimental characterization methods. MD simulations can overcome these barriers and provide valuable insights into the structure and properties of glass. In this section, MD simulations of borosilicate glasses will be summarized.

Development of empirical potentials for MD simulations

The major challenge faced in MD simulations lies in the choice of reliable and transferrable interatomic potentials that is capable to reproduce the glass structure under study (Du, 2015). About four decades ago, MD was first used to analyze silica glasses and since then it has been used to study oxide glasses as well as other amorphous systems. Growing interest in these realms resulted in the development of different types of interatomic potentials to simulate silicate and aluminosilicate systems. However, despite its growing significance in diverse engineering applications, MD simulations of boron-oxides have been a challenge in the glass community due to lack of reliable potentials. Boron (B^{3+}) can take three and four-fold coordination of oxygen, depending on the glass composition and thermal history. Boron anomaly, the non-linear composition dependence of the structure-property of these glasses, originated with the change in boron coordination with composition, which was confirmed by multiple ^{11}B NMR studies (Dell *et al.*, 1983; Wu and Stebbins, 2009). Recent developments on boron related parameters, however, have enabled MD simulations of multicomponent borosilicate glasses. Fig. 7(a) shows the fraction of four-fold coordinated boron (N_4) as a function of R (molar ratio of Na_2O to B_2O_3) and K (molar ratio of SiO_2 to B_2O_3) from MD simulations with potentials developed by Deng and Du (2019). The simulation result is compared with the Dell, Bray and Xiao (DBX) model (Dell *et al.*, 1983) that was based on ^{11}B solid state NMR and shows the quality of the potential to reproduce boron coordination in wide composition ranges.

MD simulations of borosilicate glasses previously used the Born-Mayer-Huggins (BMH) pair-wise potentials with integer charge values. It was able to generate the structure quite reasonably but mechanical properties were not in agreement with experiments (Kieu *et al.*, 2011). Also, to appropriately model such systems required potential sets with variable parameters to properly describe the changing boron environment with glass compositions. Considering this phenomenon, potential sets were developed by various groups of researchers (Takada *et al.*, 1995; Huang and Kieffer, 2003). Kieu *et al.* (2011) proposed a set of empirical potential with compositional dependent charges and A_{B-O} parameter for B-O bond. Later on, Deng and Du (2016) added aluminum parameter to this potential set. Deng and Du (2019) developed a set of empirical potentials with composition dependent A_{B-O} parameter (referred to as Du's potential). These potentials have long range Coulombic interactions and short-range interactions in the Buckingham format:

$$V(r_{ij}) = \frac{Z_i Z_j e^2}{4\pi\epsilon_0 r_{ij}} + A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6 \quad (2)$$

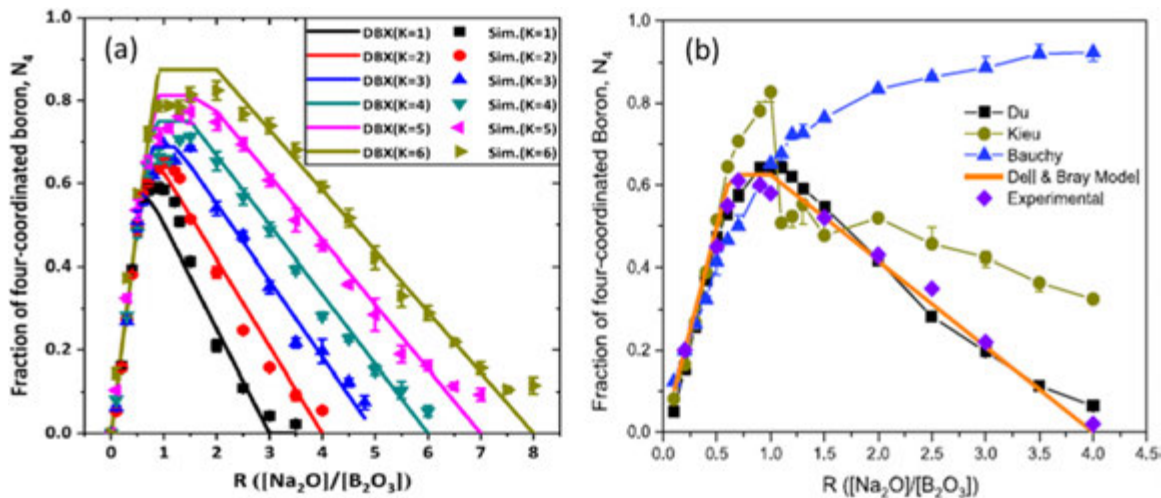


Fig. 7 (a) Fraction of four-coordinated boron, N_4 from the DBX model (solid lines) and simulated structures (dots) as a function of R at different K values; (b) N_4 obtained from Du, Kieu and Bauchy's potentials in Na_2O - B_2O_3 - SiO_2 glasses at $K = 2$. Reproduced from (a) Deng, L., Du, J.C., 2019. Development of boron oxide potentials for computer simulations of multicomponent oxide glasses. *Journal of the American Ceramic Society* 102, 2482–2505. Data with permission from (b) Tuheen, M.I., Deng, L., Du, J.C., 2020. A comparative study of the effectiveness of empirical potentials for molecular dynamics simulations of borosilicate glasses. *Journal of Non-Crystalline Solids* 551, 120413.

Despite similar potential form, the effectiveness of the potential differs significantly. This is shown in Fig. 7(b), where the boron N_4 as a function of R was plotted for three sets of potentials together with those from experiments and the DBX model. The results confirm that the Deng and Du potential (Deng and Du, 2019) has the best agreement with experiments in the whole composition range.

Composition dependent potential parameters are more effective in describing the boron anomaly as observed in the work of Tuheen *et al.* (2020). In this work, Du's (Deng and Du, 2019), Kieu's (Kieu *et al.*, 2011) and Bauchy's potential (Wang *et al.*, 2018) sets were compared. As discussed earlier, Du's potential set has composition dependent A_{B-O} and Kieu's potential has composition dependent A_{B-O} and ion charges. Bauchy's potential set focused on the transferability of the potentials and has all the parameters fixed. As seen in the figure, the potential sets, having composition dependent parameters (Deng and Du, 2019; Kieu *et al.*, 2011), are in better agreement with DBX model as well as experimental values.

Effect of cooling rate and system size on simulated glass structure and properties

Cooling rate used in MD simulations is many orders higher than in the laboratory. Some differences between experiments and simulation results were explained by the difference of cooling rates. MD simulations are performed in relatively small systems containing a few hundreds to tens of thousands of atoms. Therefore, energy exchange is much faster than practical experiment and thus use of high cooling rate is justifiable (Deng and Du, 2018). Again, this melt-quench does not involve heterogenous nucleation at an interface as long as a periodic boundary condition is used. Since the structures of boron-based glasses such as borosilicate and aluminoborosilicate depend on thermal history, glass researchers showed keen interest in the cooling rate effects on these glasses. For example: studies found a decrease in the fraction of four-coordinated boron (N_4) at higher cooling rate (Wu and Stebbins, 2010). In addition, glass annealing temperature can effectively act on the medium range structural units. Increased quenching rate was observed to create more disordered structures. Findings of MD simulations are further influenced by the system size. Deng and Du (2018) performed a systematic study of the effect of system size and cooling rate on the structures and properties of alkali borosilicate glasses. It was observed that both of these parameters can indeed alter the proportion of three- and four-coordinated boron which in turn affects the structure and properties of these glasses. A good agreement was obtained when the glass transition temperature T_g of the simulated glass was extrapolated to the experimental cooling rate. Furthermore, convergence tests are strongly recommended since different structure and property are found to converge at different system size and cooling rate.

Short and medium range structure information

Fig. 8(a) shows the initial configuration of a sodium borosilicate system before melting-quenching towards glass state in MD simulations. Fig. 8(b) displays the structure of the bulk glass generated from MD simulations (Ren *et al.*, 2017). It is clearly seen that the glass possesses network structure made up of SiO_4 tetrahedra, BO_3 triangles, BO_4 tetrahedra and AlO_4 tetrahedra. The glass composition $61.8SiO_2-16B_2O_3-3.8Al_2O_3-18.4Na_2O$ mol% is based on a model nuclear waste glass ISG (see later Section on "Nuclear Waste Disposal"). Glass surface structures are important to understand the surface reactivity and dissolution behaviors. Fig. 8(c) shows the surface structure of the glass from MD simulations. Importantly, it was found that the surface composition (and structural features) are slightly different from the bulk. In particular, there exists an enrichment of sodium on the top of the glass surface and there exist small membered rings that are usually not found in the bulk (Ren *et al.*, 2017).

A reasonable structure of boron-oxide glass generated by MD simulations is able to quantify other structural aspects such as the fraction of bridging and non-bridging oxygens (BO and NBO respectively), Q^n distribution (n is the number of bridging oxygens

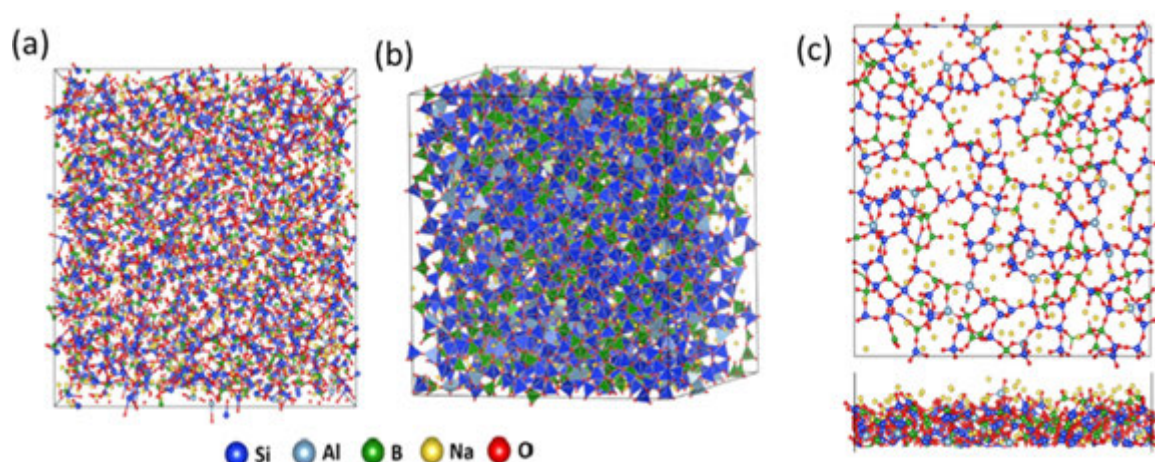


Fig. 8 Bulk and surface structure of sodium aluminoborosilicate glass (composition $61.8SiO_2-16B_2O_3-3.8Al_2O_3-18.4Na_2O$ mol%) from MD simulations. (a) before and (b) after MD simulated melt-quench process, (c) top and side view of relaxed surface. Data with permission from Ren, M.G., Deng, L., Du, J.C., 2017. Bulk, surface structures and properties of sodium borosilicate and borosilicate nuclear waste glasses from molecular dynamics simulations. *Journal of Non-Crystalline Solids* 476, 87–94.

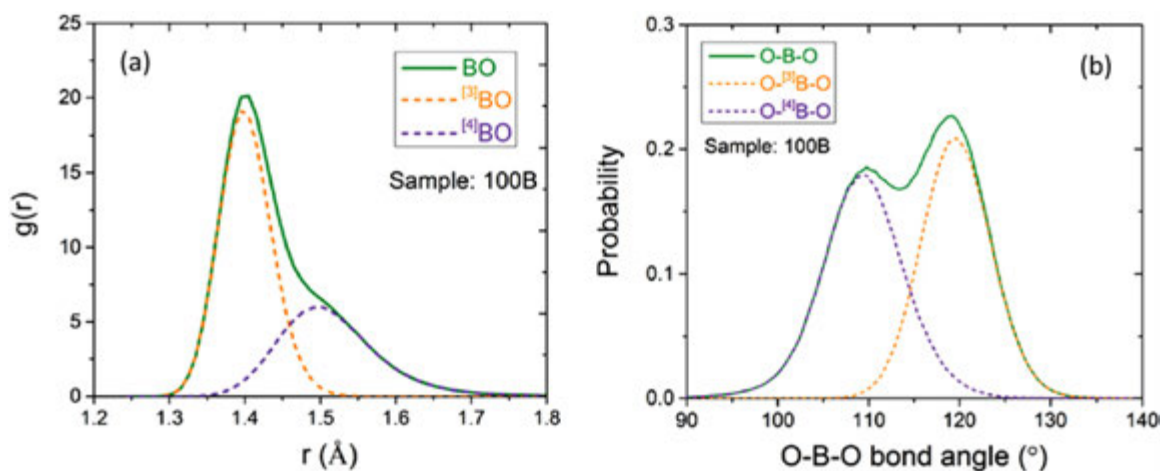


Fig. 9 Deconvoluted (a) B-O partial distribution function and (b) O-B-O bond angle distribution for glass composition of $(56.5-x)\text{SiO}_2-x\text{B}_2\text{O}_3-19.4\text{Na}_2\text{O}-16.5\text{CaO}-5.0\text{SrO}-2.6\text{P}_2\text{O}_5$ ($x = 16.5$). Data with permission from Ren, M.G., Lu, X.N., Deng, L., Kuo, P.-H., Du, J.C., 2018. $\text{B}_2\text{O}_3/\text{SiO}_2$ substitution effect on structure and properties of $\text{Na}_2\text{O}-\text{CaO}-\text{SrO}-\text{P}_2\text{O}_5-\text{SiO}_2$ bioactive glasses from molecular dynamics simulations. *Physical Chemistry Chemical Physics* 20, 14090–14104.

in a tetrahedral unit, $\sim 0-4$). Short-range structural information such as bond distance and bond angle distribution of B-O pairs obtained from MD simulated boron containing glass is shown in Fig. 9(a) and (b) respectively. The deconvoluted partial distribution function of the B-O pair shows two peaks: the peak at ~ 1.4 Å represents three-coordinated boron whereas the peak at ~ 1.5 Å is due to the four-coordinated boron tetrahedra. Similarly, the bond angle distribution of O-B-O shows two peaks. These are at $\sim 109.5^\circ$ and 120° representing the tetrahedral and triangular boron species respectively. The addition of alkali oxide which is a glass modifier, bridging units such as Q^3 break down to generate species with more NBO such as Q^1 and Q^2 . As discussed earlier, in a ternary alkali borosilicate system, addition of sodium first converts three to four-coordinated boron, then the excess of sodium creates NBO around Si and with even further addition, sodium will create NBO for B species and four coordinated boron will revert back to three-coordinated B. Therefore, the number of NBOs associated with Si and B is also composition dependent and requires to be reproduced accordingly. As reported by Deng and Du (2019), potential sets with composition dependent parameters were able to quantify the NBOs which is in good agreement with the DBX model.

NMR spectra from MD simulations

It is possible to calculate NMR spectra based on glass structural models generated from MD simulations. These calculated spectra can be compared with the experimental ones. Fortino *et al.* (2019) assessed a ternary alkali borosilicate system with Du's and Bauchy's potentials (rigid ion model) and shell model based on potential proposed by Stevansson *et al.* (2018). In their work, ^{11}B , ^{29}Si , ^{23}Na NMR spectra were calculated using the Density Functional Theory (DFT) – Gauge Including Projected Augmented Wave (GIPAW) method (Fortino *et al.*, 2019) to compare the effectiveness of these potential sets. The shell based polarizable potential was found to be better describing the second coordination shell of Si. The rigid ion models resulted in good partitioning of three and four coordinated boron.

Other structural aspects: Boroxol rings and larger structural features

Borate and borosilicate glasses consist of different ring structures such as boroxol rings (three membered rings formed by connecting the bridging oxygens of $[\text{BO}_3]$), danburite-like rings (four membered rings connecting 2 Si and 2 B). Presence of smaller rings in the MD simulations can be well affected by the control of system size and cooling rate. Three membered rings formed by boron alone were found to be less common in the MD simulations of sodium borosilicate systems. Rather three membered rings formed by Si alone which is also of higher energy were observed in these structures. The number of smaller rings decreased with the increase of system size (Deng and Du, 2018). Therefore, larger system size results in a consistent number of small rings in simulations. Also, faster cooling rate gives rise to greater number of small rings which are energetically unfavorable. This is again another indication that thermal history of borosilicate glasses affects its structural features and properties.

Prediction of Physical Properties

Prediction by Rigidity Theory

To accelerate the discovery and design of new glass materials, it is critically important for scientists to be able to predict glass properties. In the past decade, substantial progress has been made in developing various approaches for predicting glass properties from glass composition and structure. One of the effective approaches is the rigidity theory (Phillips, 1979; Phillips and Thorpe,

1985; He and Thorpe, 1985). Initially, this theory was proposed based on a fully connected network at 0 K temperature. At $T > 0$, however, a constraint depends on the available thermal energy compared with the energy required to break the constraint. Gupta and Mauro (2009) extended the initial Phillips–Thorpe theory to account for the temperature effect, i.e., the so-called temperature-dependent constraint theory, and thereby they succeeded in predicting both the T_g and liquid fragility of borate systems. This theory treats the atomic structure of glass as a network of rigid constraints, and links the physical properties of glass to the composition, temperature, and pressure dependence of the number of these constraints. Using this theory, for the first time, Smedskjaer *et al.* (2010) accurately predicted the mechanical property of glass – hardness, by establishing a constraint counting model based on the structural data of a borate glass system. The modeled results reflected the boron anomaly effect. The principle of the T -dependent constraint theory is briefly described as follows.

Atoms in a structural network are constrained by their chemical bonds and bond angles. The strength of the constraints depends on the local topology and the charge and size of those atoms. Thus, detailed structural information, e.g., the atomic coordination numbers (CN) of the network formers is required to count the number of constraints per atom (n_c). Both the number of constraints determined by linear bond-stretching ($n_{c,linear} = CN/2$) and that determined by angular bond-bending ($n_{c,angular} = 2CN - 3$) should be summed to obtain the number of constraints (n) for each network-former. According to the temperature-dependent constraint model, a certain critical number of constraints (n_{crit}) must be present for the glass to possess mechanical resistance, i.e., for hardness to become non-zero in three dimensions. When $n < n_{crit}$, the mechanical response is liquid-like. When $n > n_{crit}$, there are enough constraints to make a rigid network a solid-like response. A value of $n = 3$ indicates that a network is rigid in three dimensions, such as the tetrahedral network of silica, which is fully polymerized. A network must be rigid in at least two dimensions to be mechanically resistant. This case corresponds to $n_{crit} = 2.5$ and represents a network that is exactly rigid in two dimensions of the three-dimensional space. The hardness (H_v) of a glass is thus proportional to the number of constraints in excess of $n_{crit} = 2.5$, i.e.,

$$H_v = H_v/dn(n - 2.5) \quad (3)$$

According to the temperature-dependent constraint model, each constraint is associated with an onset temperature, above which the constraints are broken and therefore should not be counted. The onset temperature is a measure of the strength of chemical bonds.

Here, an example for prediction of the hardness is presented in Fig. 10 for the borosilicate glass series with the compositions given in the figure caption (Smedskjaer *et al.*, 2011). Based on the NMR data, the number of the room temperature constraints (n) in this glass series is counted and then the proportionality constant dH_v/dn can be determined by fitting the measured H_v versus n relation to the linear function as shown in the inset of Fig. 7. By inserting n and dH_v/dn into Eq. (3), the hardness of each of the glass series can be calculated as exhibited in Fig. 10. It is seen that there is an excellent agreement between the measured and the calculated H_v values. It should be mentioned that both the two μ constraints per NBO-forming Ca atom and the two μ constraints per NBO-forming Na atom are taken into account when counting the n values. Otherwise, the calculated H_v values would deviate from the measured ones. However, the μ constraints associated with Ca should have a much lower onset temperature than those associated with Na.

Zheng *et al.* (2017) established the most accurate predictive model for silicate glass hardness by adopting the density of angular constraints, i.e., the number of constraints per volume. This model is confirmed to be more accurate than that based on the total number of constraints per atom as shown in Fig. 11. The total constraint density model works as well, since the composition

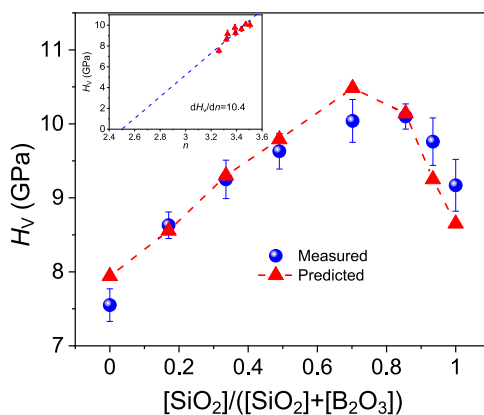


Fig. 10 Comparison between the measured Vickers hardness (H_v) values (Blue spheres) and those (red triangles and dash curve) predicted by the equation $H_v = H_v/dn(n - 2.5)$ for the borosilicate glass series with constant modifier content but varying $[SiO_2]/([SiO_2] + [B_2O_3])$ ratio, viz., $(0.75-x)SiO_2-xB_2O_3-0.15Na_2O-0.10CaO$ with $x = 0, 0.06, 0.12, 0.24, 0.375, 0.51, 0.63$, and 0.75 . Inset: Measured H_v values (red triangles) as a function of the average number of room temperature constraints assuming two μ constraints per rigid NBO-forming Ca atom. The dash line represents the proportionality dH_v/dn (10.4 GPa). Reproduced with permission from Smedskjaer, M.M., Mauro, J.C., Youngman, R.E., *et al.*, 2011. Topological principles of borosilicate glass chemistry. *Journal of Physical Chemistry B* 115, 12930–12946.

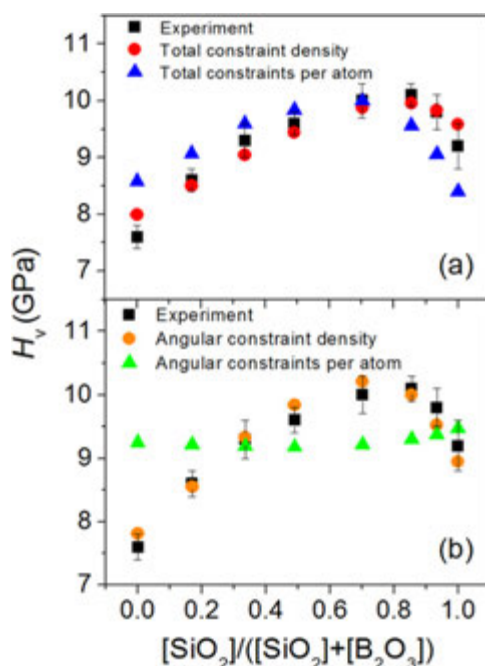


Fig. 11 Composition (i.e., $[\text{SiO}_2]/([\text{SiO}_2] + [\text{B}_2\text{O}_3])$) dependence of the Vickers hardness (H_v) for the series of borosilicate glasses given in Fig. 10. (a) Comparison between the measured H_v values and those predicted using total constraint density and total constraints per atom. (b) Comparison between the measured H_v values and those predicted through angular constraint density and angular constraints per atom, respectively. Data with permission from Zheng, Q.J., Yue, Y.Z., Mauro, J.C., 2017. Density of topological constraints as a metric for predicting glass hardness. *Applied Physics Letters* 111, 011907.

dependence of the total constraints is dominated by the variation in the angular constraints. The total constraint density model has the additional advantage, i.e., it contains only one fitting parameter. Based on the findings of Zheng *et al.* (2017) and combining the approaches of Bauchy *et al.* (2015) and Lamberson (2016), it was concluded that the density of rigid total constraints or rigid angular constraints should be used as a metric for predicting hardness of oxide glasses including borosilicate glasses (Fig. 11).

In Fig. 11(a), the measured hardness values for the borosilicate glasses are compared with those predicted by two constraint models involving total constraint density, and total constraints per atom, respectively. It is seen that the best fit is improved when using the total constraint density rather than the total number of constraints per atom. Fig. 11(b) exhibits that the hardness values predicted using the angular constraint density model also excellently agrees with the experimental ones, while the hardness modeled using angular constraints per atom gives poor agreement. It should be mentioned that the hardness predicted using angular constraint density is slightly better than that using total constraint density.

In addition, to improve the prediction ability and accuracy of the T -dependent constraint models, considerable efforts have been made by glass scientists. The main progress is described as follows. First, the concept of constraint strength was introduced into the topological model, which is a measure of how strongly the modifiers are bound to the surrounding oxygens through columbic forces (Rodrigues and Wondraczek, 2014). Second, the topological model was extended by taking into account that the effective number of intact constraints per modifying cation linearly relates to the charge-to-distance ratio of the modifying cation to oxygen (Hermansen *et al.*, 2014b). Third, the temperature dependent constraint model was modified by considering the structural and topological role of the modifying ion sub-network constituted by alkali ions and their NBO coordination spheres, and thereby, the prediction accuracy of glass dynamic properties is improved (Hermansen *et al.*, 2014a).

Prediction From MD Simulations

Mechanical properties of glasses can be calculated based on the simulated glass structures (Hill, 1952). Bulk, shear and Young's moduli were calculated for borosilicate glass structures obtained from MD simulations and compared with experiments (Deng and Du, 2019; Tuheen *et al.*, 2020). The trend of these moduli followed the experimental values but there was quite an over estimation. When plotted against the sodium content i.e., molar ratio R , the curves of these moduli also represented the boron anomaly – an increasing value followed by a maximum and then decrease. For better prediction of mechanical properties of borosilicate glasses, the potential sets need further improvement. It can be observed from Fig. 12(a), mechanical properties are affected by system size of MD simulations. Moreover, from Fig. 12(b), it can be stated that the system size effect on mechanical properties is less dependent on change in N_4 value compared to the effect of cooling rate.

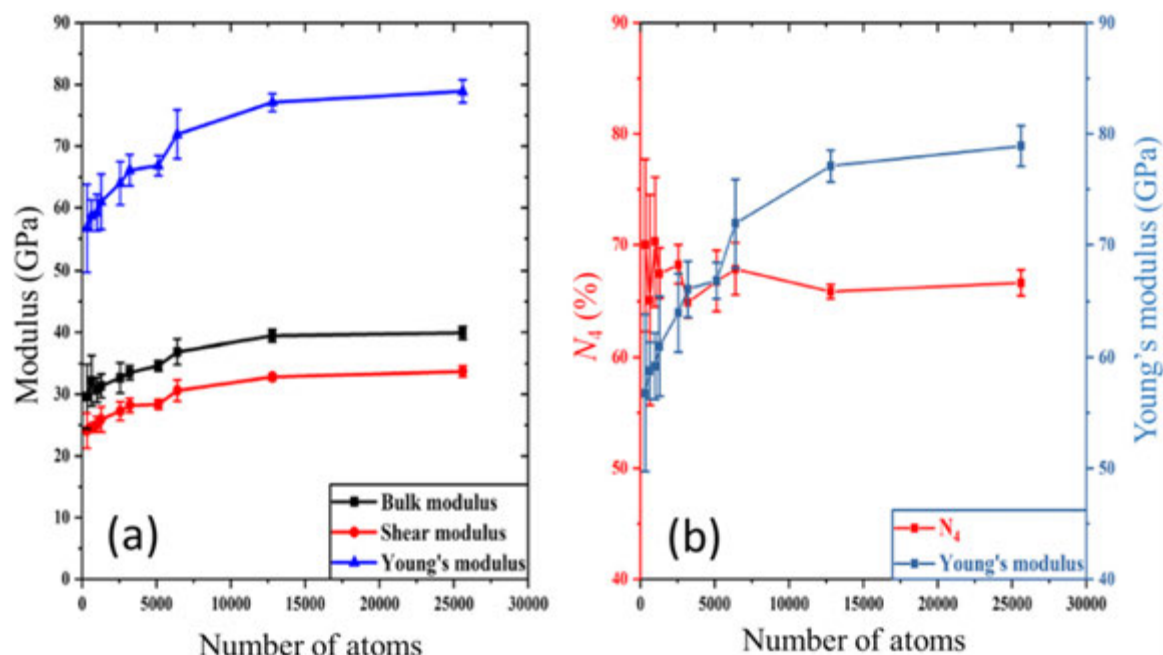


Fig. 12 System size effect on the (a) mechanical properties (b) N_4 and Young's modulus for the glass system $3\text{Na}_2\text{O}-\text{B}_2\text{O}_3-6\text{SiO}_2$. Data with permission from Deng, L., Du, J.C., 2018. Effects of system size and cooling rate on the structure and properties of sodium borosilicate glasses from molecular dynamics simulations. *Journal of Chemical Physics* 148, 024504.

When associated with an isobaric ensemble (NPT, constant number, pressure and temperature), it is possible to capture the final density of borosilicate glasses using MD simulations. Structure generated from MD simulations showed good agreement with the densities obtained from experiments at lower R value (~ 0.7) but deviation occurred at larger values of R (Deng and Du, 2019). Densities obtained for a ternary borosilicate system using Du's, Kieu's and Bauchy's potentials also showed similar results (Tuheen *et al.*, 2020).

Dynamic properties such as ionic diffusion behavior and vibrational density of states (VDOS) of borosilicate glasses can also be analyzed by means of MD simulations. Ren *et al.* (2018) derived the VDOS of a multicomponent boron-oxide system and compared the results with the first principle MD calculation (Pedesseau *et al.*, 2015). As shown in Fig. 13, three-coordinated boron gives rise to a peak around 680 cm^{-1} and the peak for four-coordinated species is located between 1100 and 1500 cm^{-1} .

Ionic diffusion properties in terms of diffusion co-efficient and diffusion energy barrier can be derived from mean square displacement calculations for the MD generated structure of borosilicate glasses. It was found that an increase in the substitution of B_2O_3 for SiO_2 causes a decrease in E_a for the ions in the high temperature range as shown in Fig. 14(a), while the sodium ion diffusion energy barrier at low temperature increases as can be observed in Fig. 14(b), which can be understood by an increase of network connectivity and more close network structures (Ren *et al.*, 2018). The significant decrease in E_a in the high temperature range is in accordance with the experimentally observed fact that adding sufficient amount of boron oxide decreases the melting point and viscosity of borosilicate glasses.

Applications

General Aspects

Borosilicate glass is an important glass type produced widely on the industrial scale and finds many technological applications from lab and kitchen ware, lighting and optics, display, to nuclear waste disposal and biomedicine. The earliest written record of borosilicate glass dates back to 1225 when a Song dynasty Chinese scholar Zhao Ru-Kuo wrote "borax is added so that the glass endures the most severe thermal extremes and will not crack" when describing glass production in Arabia and other places (Smith, 1997). Modern development of borosilicate glasses started from works by Michael Faraday in the UK and Otto Schott and Ernst Abbe in Germany in the 19th century. The research by Schott and Abbe on optical glasses systematically investigated the effects of boron oxide and other glass components on optical properties, which was essentially the beginning of glass science (Smith, 1997). They also found ways to produce borosilicate glasses and developed several thermal shock resistant borosilicate glass brands since 1917. In 1915, scientists at Corning Glass Works patented a low thermal expansion borosilicate glass marketed as Pyrex[®] (Jensen, 2006), which later became a household name due to its wide usage as cookware in kitchens and labware in laboratories.

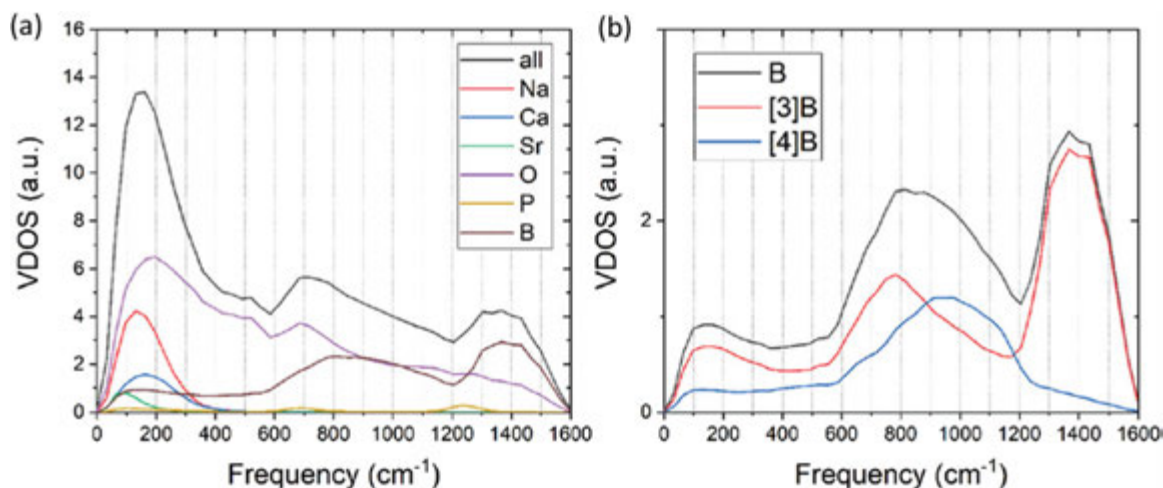


Fig. 13 Total and partial vibrational density of states (VDOS) at 300K for a boron oxide system and partial VDOS for three and four coordinated boron for the glass system with the molar composition: $56.5\text{B}_2\text{O}_3\text{--}19.4\text{Na}_2\text{O--}16.5\text{CaO--}5.0\text{SrO--}2.6\text{P}_2\text{O}_5$. Data with permission from Ren, M.G., Lu, X.N., Deng, L., Kuo, P.-H., Du, J.C., 2018. $\text{B}_2\text{O}_3/\text{SiO}_2$ substitution effect on structure and properties of $\text{Na}_2\text{O--CaO--SrO--P}_2\text{O}_5\text{--SiO}_2$ bioactive glasses from molecular dynamics simulations. *Physical Chemistry Chemical Physics* 20, 14090–14104.

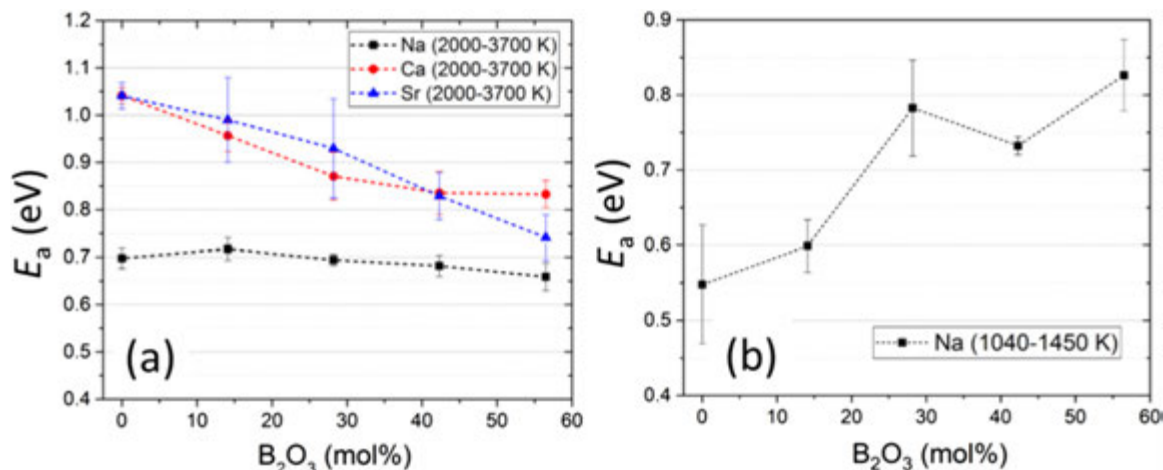


Fig. 14 (a) Modifier cation diffusion energy barrier at high temperature and (b) sodium ion diffusion energy barrier at low temperature as a function of B_2O_3 concentration, for the glass series $(56.5-x)\text{SiO}_2\text{--}x\text{B}_2\text{O}_3\text{--}19.4\text{Na}_2\text{O--}16.5\text{CaO--}5.0\text{SrO--}2.6\text{P}_2\text{O}_5$ ($x=0, 13.1, 28.2, 42.3, 56.5$ in mol%). Data with permission from Ren, M.G., Lu, X.N., Deng, L., Kuo, P.-H., Du, J.C., 2018. $\text{B}_2\text{O}_3/\text{SiO}_2$ substitution effect on structure and properties of $\text{Na}_2\text{O--CaO--SrO--P}_2\text{O}_5\text{--SiO}_2$ bioactive glasses from molecular dynamics simulations. *Physical Chemistry Chemical Physics* 20, 14090–14104.

Addition of boron oxide to silicate glass led to benefits both on glass properties and glass processing, as discovered by the early glass producers (Hubert and Faber, 2014). On the glass property side, it was found that boron oxide can lower the thermal expansion coefficient and increase thermal shock resistance, increase thermal conductivity and mechanical strength, enhance chemical durability and improve optical properties; while on the processing side, it was found that boron oxide can lower melting temperature, lower crystallization tendency, lower viscosity and increase working range of glass, as well as have more efficient dissolution of refractory raw materials. These advantages led to various technological applications of borosilicate glasses that will be discussed in this section. Fig. 15 shows examples of applications of borosilicate glasses from rail road lanterns, cook ware, pharmaceutical bottles, lab ware to display glasses.

Thermal Shock and Chemical Resistant Glass Vessels and Containers

The corrosion and thermal shock resistances of borosilicate glasses originated from their higher chemical inertness and lower thermal expansion coefficient as compared to conventional soda lime silicate glass. These properties make them ideal for glass labwares such as beakers, flasks and retorts that should be colorless and transparent, have high melting point, and resistant to water, acidic and caustic solutions, as well as be able to sustain thermal and mechanical stress. The discovery of borosilicate glass



Fig. 15 Applications of borosilicate glasses. Top left: railroad lantern, top right: kitchen ware, bottom left: pharmaceutical applications, bottom middle: lab ware, bottom right: display glass, center: fiber glass (images are from internet sources: Corning Glass Museum, Pyrex glass history, Corning display glass).

revolutionized the field of glass labware as it provides the ideal combination of the above required properties. Pyrex[®] from Corning and Duran[®] from Schott are among the most well known glass labware brands. Compositions of these and other common borosilicate glasses are listed in [Table 1](#). Both glasses have high silica (> 80 wt%), boron oxide (~ 13 wt%) and a small amount of alumina (~ 2 wt%) and (0–4 wt%) soda. Due to the high silica content, these glasses need to be melted at a higher temperature than the conventional soda lime silica glasses but they possess better thermal and mechanical properties, and higher glass transition and softening temperatures.

Corning's Pyrex is also a commercial success for cookware, especially for use in ovens. Cookware shares some similar requirements to that of labware such as high chemical durability, high thermal shock and mechanical stress resistance. Pyrex has become a synonym for high quality, highly resistant glass cook wares ([Hubert and Faber, 2014](#)). It is worth mentioning that there are current glass products with the Pyrex brand but which no longer have borosilicate composition. These kitchen ware products in the market use tempered soda lime silicate glasses, possibly due to cost considerations ([Smedskjaer et al., 2014a](#)).

Borosilicate glass is also the choice for ampoules and vials for medicine due to their chemical inertness and thermal shock resistance. They are called “neutral glass” due to their high chemical durability and, as a result, cations from the glass will not be leached to degrade the medicine. With the ongoing corona virus pandemic started in early 2020, borosilicate glass vials are in high demand as carriers of the vaccines. In addition to chemical inertness to protect the vaccine from contamination, some vaccines are required to be stored at low temperature (< − 70°C) but used at ambient temperature. Thermal shock resistance of borosilicate glasses is thus an additional advantage.

Glass Fibers and Wools for Insulation and Reinforcement

Borosilicate glass has been used in insulating (glass wool) and textile (long fiber) fiberglass and this is one of the largest technical applications of borates ([Smith, 1997](#)). The E-glass fiber, named after its ability for electrical insulation, as well as high chemical durability and mechanical properties, is among the most well known of the fiber glasses. The base composition of E-glass is calcium boroaluminosilicate with low alkali content (~ 1 wt%) (see [Table 1](#)). While highly resistant to moisture or water corrosion, E-glass fiber has low durability in acidic or caustic conditions. The C-glass fiber was developed to overcome this to be used in highly corrosive conditions. As compared to E-glass, all alkali oxides are removed from the C-glass fiber composition but B₂O₃ concentration is increased and MgO is substituted for some of the CaO. For some applications such as electronics, lower

dielectric constant is preferred. For this purpose, D-glass was developed. D-glass has higher silica (70–80 wt%) and boron oxide (15–20 wt%) concentrations but with lower alumina, alkali and alkali earth oxides. D-glass has poor chemical durability due to high boron oxide concentration. In addition to electrical insulation, E-glass and related fiber glasses also find applications in reinforced plastics or composites for various structural applications. It is worth noting that not all fiber glass is borosilicate based as some are silicate or aluminosilicate based.

Borosilicate glass has also been largely used in the production of glass wool for thermal insulation (Smith, 1997). Development of new borosilicate glass wool compositions and new processing techniques have led to a fiber glass revolution to replace traditional mineral wool as an insulation material. As compared to E-glass or other electrical insulation fiber glass, electrical conductivity is not a critical factor in glass wool for thermal insulation. Consequently, glass wool compositions (Table 1) have high alkali content (10–15 wt%) and typically contain 4–6 wt% boron oxide to lower the liquidus and working temperature to be suitable for the rotary fiberization process which is the preferred industrial process for production of glass wool.

Lighting, Optics and Display

The properties of borosilicate glasses such as low thermal expansion, resistance to high temperature and chemical corrosion, and some unique optical properties make them suitable for optical and lighting applications. In the early days, borosilicate glass was used for shatter resistant railroad lanterns. Modern lighting application also requires glass windows to withstand thermal shock due to different weather conditions. Borosilicate glass, due to its properties mentioned above, has been used in light fixtures such as sealed headlights, lamp covers, halogen bulbs and fluorescent tubes. Other borosilicate glasses, such as BK-7[®] of Schott (composition shown in Table 1) has low refractive index (~ 1.52) for visible light and low dispersion, together with high chemical durability and mechanical strength, are the ideal material for lenses, telescope mirrors, and other optical components.

Another important application of borosilicate glass is liquid crystal display (LCD) that is essentially omnipresent in our everyday life now from watches, smart phones, notepads, laptops, desktop computers to TVs and other large screen displays. Active matrix LCD requires the glass substrate to have thermal mechanical stability, precision geometry control, and perfectly smooth surfaces (Ellison and Cornejo, 2010). Alkali earth borosilicate glass is the basic composition of these display glasses (for example OA-10 glass from Asahi shown in Table 1). These glasses are essentially alkali free to avoid chemical and electronic interaction with the thin film transistor in Active matrix LCD. These glasses are commonly formed by what is known as the fusion technique in which the glass melt flows into a trough and overflows the walls to form a continuous thin ribbon of glass (Ellison and Cornejo, 2010). The formed glass ribbon has two contact free optical quality surfaces. The float technique, using a bath of molten tin, that is commonly used to form normal flat glasses is also used to fabricate LCD glasses but subsequent processing such as polishing of the tin side is required.

Nuclear Waste Disposal

Safe immobilization of nuclear waste is critical to the fuel cycle of nuclear energies. With the development of nuclear power as a clean energy source, more nuclear waste will be produced and need to be safely processed in addition to the defense nuclear wastes. Borosilicate glass is an internationally accepted waste form for nuclear waste disposal and the processing method is known as vitrification. Borosilicate glasses have several technical advantages as compared to other waste forms (Plodinec, 2000; Manaktala, 1992): (1) capability to incorporate a wide range of fission products and actinides; the common waste can have over 30 oxide components, (2) relatively low formation temperature ($< 1200^{\circ}\text{C}$) to be suitable for nuclear waste processing, (3) high waste loading, the ability to incorporate high proportion of waste (up to 40 wt%), (4) waste composition tolerance to accommodate variation of wastes from different sources, (5) resistance to radiation degradation, (6) ability to be produced remotely with simple and reliable process with minimum maintenance, and lastly (7) high resistance to aqueous corrosion and low susceptibility to leaching when in contact with ground water.

In the vitrification process, waste slurry and glass forming compounds known as frits are fed continuously to a melter where the mixture is electrically heated with ceramic electrodes (Manaktala, 1992). The resulting melt is then poured into stainless steel (or other metal) canisters and cooled down to below the glass transition temperature in several hours to days, depending on the canister dimension and cooling environment. The melting temperature of nuclear waste glasses is typical in the range of $1100\text{--}1200^{\circ}\text{C}$, much lower than for industrial glass manufacturing. The low melting temperature is mainly to avoid volatilities of radioactive fission products during the processing. Due to this and other reasons, such as large variations in compositions in waste glasses, the knowledge of industrial glass manufacturing sometimes cannot be directly applied to nuclear waste glass processing. Typical borosilicate glass waste compositions can be found in Table 1. The ternary sodium borosilicate AVM composition is the basic composition of most glass waste forms. SON68 (Table 1) is the French model nuclear waste glass with addition of alumina and calcia. Real waste glass compositions are usually much more complicated with up to 30 or more components.

The International Simple Glass (ISG) is a model nuclear waste glass that was designed to study the corrosion behaviors (Gin et al., 2013). Blocks of 500 g of ISG were prepared and distributed to research groups around the world to study the chemical durability, thermal, mechanical and other properties. As a model nuclear waste glass, the structure of ISG has also been studied by using characterization techniques such as solid state NMR, Raman spectroscopy, high energy X-ray and neutron diffraction (Kaspar et al., 2018; Lu et al., 2019a; Collin et al., 2018). Computer simulations such as molecular dynamics and Monte Carlo are also used

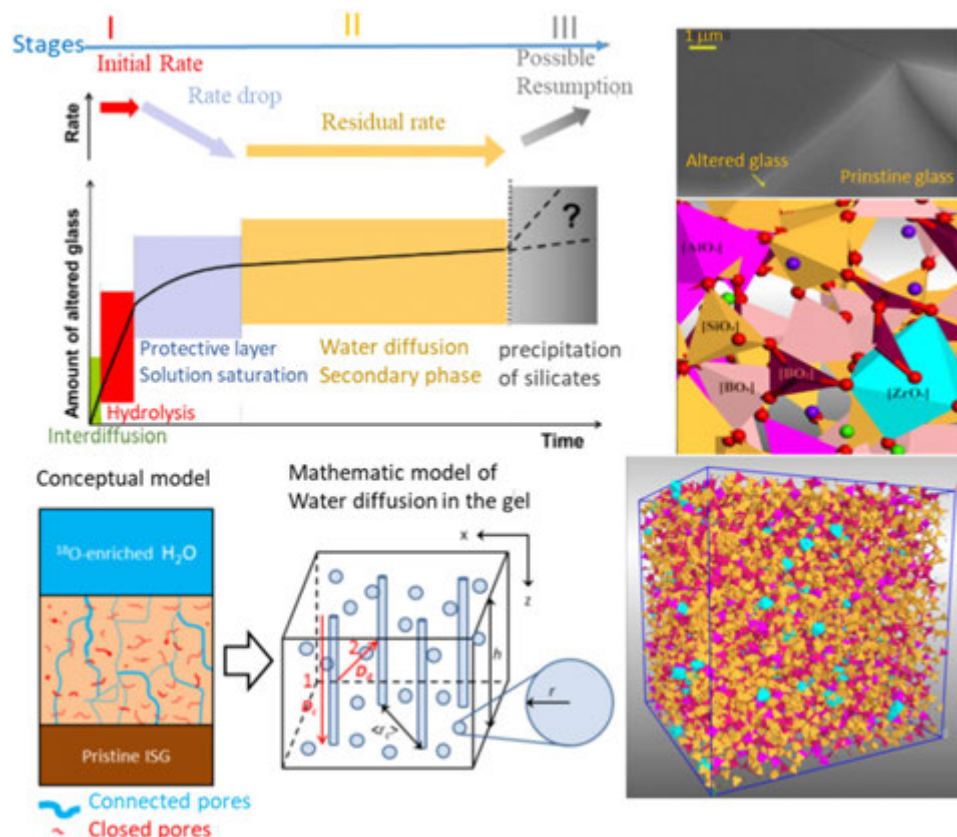


Fig. 16 Stages of corrosion of borosilicate nuclear waste glasses (top left). SEM image of the gel layer formation of a corroded borosilicate nuclear waste glass (top right). Water diffusion models in porous gel layer in borosilicate nuclear glasses (bottom left). Atomistic structure model of International Simple Glass (ISG) (bottom right) and zoomed in picture showing the cation oxygen polyhedra (middle right) from MD simulations. Data from Gin, S., Abdelouas, A., Criscenti, L.J., *et al.*, 2013. An international initiative on long-term behavior of high-level nuclear waste glass. *Materials Today* 16, 243–248. Frankel, G.S., Vienna, J.D., Lian, J., *et al.*, 2018. A comparative review of the aqueous corrosion of glasses, crystalline ceramics, and metals. *npj Materials Degradation* 2, 15. Gin, S., Collin, M., Jollivet, P., *et al.*, 2018. Dynamics of self-reorganization explains passivation of silicate glasses. *Nature Communications* 9, 2169. Collin, M., Fournier, M., Frugier, P., *et al.*, 2018. Structure of international simple glass and properties of passivating layer formed in circumneutral PH conditions. *npj Materials Degradation* 2, 4.

to study the structure and dissolution behaviors (Collin *et al.*, 2018; Lu *et al.*, 2019b; Deng and Du, 2019; Gin *et al.*, 2018; Kerisit and Du, 2019). The atomic structure of ISG glass generated from MD simulations is shown in Fig. 16 (bottom and middle right) and it can be seen that the network structure consists of SiO_4 tetrahedra, AlO_4 tetrahedra and ZrO_6 octahedra, while about 50% boron is four-fold coordinated and the other 50% three-fold coordinated (Collin *et al.*, 2018). Fig. 16 shows stages of nuclear waste glass corrosion, the atomic structure model of ISG from molecular dynamics simulations, and potential water diffusion pathways in the gel layer formed during glass corrosion.

One of the main reasons that borosilicate glass is chosen to immobilize nuclear waste is the high chemical durability in aqueous environment so the glass waste forms can last thousands to hundreds of thousands of years in the geological storage environment. Recent efforts have been devoted to understand the long term chemical durability of borosilicate nuclear waste glasses through intensive research in the US, France, UK, Belgium, Japan and other countries. It was discovered that the corrosion of borosilicate nuclear waste glasses mainly takes place in three stages (Gin *et al.*, 2013): (1) the initial fast dissolution due to ion-exchange of cations in the glass with protons or hydronium ions in the solution and hydrolysis of Si-O-B and Si-O-Si linkages, (2) the steady state corrosion after formation of a gel layer at the interface of the glass and the solution, and (3) a potential resumption of fast corrosion in certain conditions. The corrosion stages of nuclear waste glass are shown in Fig. 16 (top left). While the initial dissolution rate is fast, the residual dissolution rate can be very low and the steady state dissolution can last for thousands or hundreds of thousand years. An important finding from recent intensive studies is that the low residual rate of borosilicate glass dissolution is due to the formation of a silica rich porous gel layer that serves as a passivation layer and significantly slows down the reaction of the remaining glass (Frankel *et al.*, 2018). It was also found that the gel structure is rather dynamic and changes with time (Gin *et al.*, 2018). The reaction characteristics are controlled by the atomic- and micro-structures of the gel layer such as porosity and pore morphology. Solution chemistry such as pH, cation and anion concentration and external conditions such as temperature can also play an important role in nuclear waste glass corrosion. Under certain conditions, such as that due to precipitation of silica rich minerals, the residual dissolution rate can be disrupted and the glass corrosion resumes at a

high rate. Recent findings also suggest that the corrosion of glass can be affected by the corrosion products of metal containers, suggesting complex interactions in near field conditions (Guo *et al.*, 2020). Despite many of these findings, the exact nature of the residual and resumption corrosion are still topics of intensive scientific study.

Biomedical and Other Applications

Borosilicate glass also finds applications in biomedicine. Bioactive glass is a type of inorganic glass that can bond to soft and hard tissues through the formation of a hydroxyl apatite layer (the inorganic mineral component of bone) (Jones, 2015). The dissolution product of bioactive glass was also found to promote gene expression that facilitate tissue growth. As a result, bioactive glass is considered to be a type of third generation bioactive material. Bioactive glasses find applications in bone regeneration, dental and wound healing, and maxillofacial surgeries, commonly used in granular form or as coatings to metal implants, and as scaffolds for tissue engineering. The original bioactive glass as discovered by Larry Hench is silicate based: $\text{Na}_2\text{O}-\text{CaO}-\text{P}_2\text{O}_5-\text{SiO}_2$ (Hench *et al.*, 1971). The compositions of two common bioactive glasses 45S5 and S53P4 are shown in Table 1. These bioactive glasses experience incongruent dissolution while pure borate and phosphate based bioactive glasses, on the other hand, can dissolve congruently and generally dissolve much faster. As silicate based bioactive glass converts to hydroxyl apatite slowly, this leads to residual unconverted glass in vivo. Studies have found that addition of boron oxide can help to regulate the dissolution rate of the silicate based bioactive glasses while maintaining their in vitro and in vivo bioactivity (Lu *et al.*, 2018; Ren *et al.*, 2018; Lu *et al.*, 2017). As a result, partial or full substitution of silica by boron oxide in silicate based bioactive glasses (Table 1) has been studied to find the optimal level of substitution. Borosilicate glass is also used as coatings to load bearing metallic implants to serve as a bioactive interface between the metallic implants and the human body (Oliver *et al.*, 2019; Kuo *et al.*, 2019; Du and Xiang, 2016; Xiang and Du, 2011; Du and Xiang, 2012). Pure borate glasses have also been found to be bioactive and angiogenic. They have been fabricated into glass wool and used for wound dressing for healing of open wounds.

There are also other applications of borosilicate glasses. For example, they have been used in enamels, glazes and frits. Low thermal expansion of borosilicate glasses can have better thermal shock resistance, hence avoiding cracking or crazing of the glaze or enamel (Hubert and Faber, 2014). Another interesting application of borosilicate glass is porous glass based on the phase separation of sodium borosilicate glass in certain compositions. The formed glass is heat treated to form an alkali borate rich phase and a silica rich phase with the alkali borate phase being leached subsequently by using acid solutions, leaving the silica rich porous skeleton. This porous structure can be used for sorption, separation or catalysis support. Alternatively, the porous skeleton can be consolidated to form a high silica glass at a relatively low temperature. One example of such glass is the Vycor[®] glass by Corning, with 97 wt% SiO_2 and 3 wt% B_2O_3 in its final composition (Table 1).

In addition to the wide range of applications discussed above, it is believed that other potential applications will emerge as scientists and engineers discover new properties, behaviors and phenomena of borosilicate glasses that will lead to the next technological fronts as they have done in the past century.

References

- Almeida, R.M., Hickey, R., Jain, H., Pantano, C.G., 2014. Low-energy ion scattering spectroscopy of silicate glass surfaces. *Journal of Non-Crystalline Solids* 385, 124–128.
- Almeida, R.M., Santos, L.F., 2015. Chapter 3 – Vibrational spectroscopy of glasses. In: Affatigato, M. (Ed.), *Modern Glass Characterization*. Wiley.
- Ando, A.F., Benzine, O., Pan, Z.W., *et al.*, 2018. Boson peak, heterogeneity and intermediate-range order in binary $\text{SiO}_2\text{-Al}_2\text{O}_3$ glasses. *Scientific Reports* 8, 5394.
- Angeli, F., Villain, O., Schuller, S., *et al.*, 2012. Effect of temperature and thermal history on borosilicate glass structure. *Physical Review B* 85, 054110.
- Angell, C.A., Yue, Y.Z., Wang, L.M., *et al.*, 2003. Potential energy, relaxation, vibrational dynamics and the boson peak of hyperquenched glasses. *Journal of Physics: Condensed Matter* 15, S1051–S1068.
- Bauchy, M., Qomi, M.J.A., Bichara, C., Ulm, F., Pellenq, R.J.M., 2015. Rigidity transition in materials: Hardness is driven by weak atomic constraints. *Physical Review Letters* 114, 125502.
- Chumakov, A.I., Monaco, G., Fontana, A., *et al.*, 2014. Role of disorder in the thermodynamics and atomic dynamics of glasses. *Physical Review Letters* 112, 025502.
- Collin, M., Fournier, M., Frugier, P., *et al.*, 2018. Structure of international simple glass and properties of passivating layer formed in circumneutral PH conditions. *npj Materials Degradation* 2, 4.
- Daan, F., Smit, B., 2002. Understanding Molecular Simulation: from Algorithms to Applications. In: *Computational Science Series*, second ed., 1. Academic Press.
- Dell, W.J., Bray, P.J., Xiao, S.Z., 1983. ^{11}B NMR studies and structural modeling of $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ glasses of high soda content. *Journal of Non-Crystalline Solids* 58, 1–16.
- Deng, L., Du, J.C., 2016. Development of effective empirical potentials for molecular dynamics simulations of the structures and properties of borosilicate glasses. *Journal of Non-Crystalline Solids* 453, 177–194.
- Deng, L., Du, J.C., 2018. Effects of system size and cooling rate on the structure and properties of sodium borosilicate glasses from molecular dynamics simulations. *Journal of Chemical Physics* 148, 024504.
- Deng, L., Du, J.C., 2019. Development of boron oxide potentials for computer simulations of multicomponent oxide glasses. *Journal of the American Ceramic Society* 102, 2482–2505.
- Du, J.C., Cormack, A.N., 2004. The medium range structure of sodiumsilicate glasses: A molecular dynamics simulation. *Journal of Non-Crystalline Solids* 349, 66–79.
- Du, J.C., Xiang, Y., 2012. Effect of strontium substitution on the structure, ionic diffusion and dynamic properties of 45S5 bioactive glasses. *Journal of Non-Crystalline Solids* 358, 1059–1071.
- Du, J.C., Xiang, Y., 2016. Investigating the structure-diffusion-bioactivity relationship of strontium containing bioactive glasses using molecular dynamics based computer simulations. *Journal of Non-Crystalline Solids* 432, 35–40.
- Du, J.C., 2015. Challenges in molecular dynamics simulations of multicomponent oxide glasses. In: Massobrio, C., Du, J.C., Bernasconi, M., Salmon, P.S. (Eds.), *Molecular Dynamics Simulations of Disordered Materials: From Network Glasses to Phase-Change Memory Alloys*. Springer, pp. 157–180.
- Ellison, A., Cornejo, I.A., 2010. Glass substrates for liquid crystal displays. *International Journal of Applied Glass Science* 1, 87–103.

- Fortino, M., Berselli, A., Stone-Weiss, N., *et al.*, 2019. Assessment of interatomic parameters for the reproduction of borosilicate glass structures via DFT-GIPAW calculations. *Journal of the American Ceramic Society* 102, 7225–7243.
- Frankel, G.S., Vienna, J.D., Lian, J., *et al.*, 2018. A comparative review of the aqueous corrosion of glasses, crystalline ceramics, and metals. *npj Materials Degradation* 2.15.
- Gin, S., Abdelouas, A., Criscenti, L.J., *et al.*, 2013. An international initiative on long-term behavior of high-level nuclear waste glass. *Materials Today* 16, 243–248.
- Gin, S., Collin, M., Jollivet, P., *et al.*, 2018. Dynamics of self-reorganization explains passivation of silicate glasses. *Nature Communications* 9, 2169.
- Greaves, G.N., 1985. EXAFS and the structure of glass. *Journal of Non-Crystalline Solids* 71, 203–217.
- Guo, X.L., Wang, Y.C., Yao, T.K., *et al.*, 2020. Corrosion interactions between stainless steel and lead vanado-iodoapatite nuclear waste form part I. *npj Materials Degradation* 4, 13.
- Gupta, P.K., Mauro, J.C., 2009. Composition dependence of glass transition temperature and fragility. I. A topological model incorporating temperature-dependent constraints. *Journal of Chemical Physics* 130, 094503.
- He, H., Thorpe, M.F., 1985. Elastic properties of glasses. *Physical Review Letters* 54, 2107–2110.
- Hench, L.L., Splinter, R.J., Allen, W.C., Greenlee, T.K., 1971. Bonding mechanisms at the interface of ceramic prosthetic materials. *Journal of Biomedical Materials Research* 5, 117–141.
- Hermansen, C., Mauro, J.C., Yue, Y.Z., 2014a. A model for phosphate glass topology considering the modifying ion sub-network. *Journal of Chemical Physics* 140, 154501.
- Hermansen, C., Rodrigues, B.P., Wondraczek, L., Yue, Y.Z., 2014b. An extended topological model for binary phosphate glasses. *Journal of Chemical Physics* 141, 244502.
- Hill, R., 1952. The elastic behaviour of a crystalline aggregate. *Proceedings of the Physical Society. Section A* 65, 349–354.
- Huang, L.P., Kieffer, J., 2003. Molecular dynamics study of cristobalite silica using a charge transfer three-body potential: phase transformation and structural disorder. *Journal of Chemical Physics* 118, 1487–1498.
- Huang, P.Y., Kurasch, S., Srivastava, A., *et al.*, 2012. Direct imaging of a two-dimensional silica glass on graphene. *Nano Letters* 12, 1081–1086.
- Hubert, M., Faber, A.J., 2014. On the structural role of boron in borosilicate glasses. *Physics and Chemistry of Glasses: European Journal of Glass Science and Technology Part B* 55, 136–158.
- Jensen, W.B., 2006. The origin of Pyrex. *Journal of Chemical Education* 83, 692–693.
- Jones, J.R., 2015. Reprint of: Review of Bioactive Glass: From Hench to Hybrids. *Acta Biomaterialia* 23, S53–S82.
- Kaspar, T.C., Reiser, J.T., Ryan, J.V., Wall, N.A., 2018. Non-destructive characterization of corroded glass surfaces by spectroscopic ellipsometry. *Journal of Non-Crystalline Solids* 481, 260–266.
- Kerisit, S., Du, J.C., 2019. Monte Carlo simulation of borosilicate glass dissolution using molecular dynamics-generated glass structures. *Journal of Non-Crystalline Solids* 522, 119601.
- Kiczinski, T.J., Du, L.S., Stebbins, J.F., 2005. The effect of fictive temperature on the structure of E-glass: A high resolution, multinuclear NMR study. *Journal of Non-Crystalline Solids* 351, 3571–3578.
- Kieu, L.-H., Delaye, J.-M., Cormier, L., Stolz, C., 2011. Development of empirical potentials for sodium borosilicate glass systems. *Journal of Non-Crystalline Solids* 357, 3313–3321.
- Kuo, P.H., Joshi, S.S., Lu, X.N., *et al.*, 2019. Laser coating of bioactive glasses on bioimplant titanium alloys. *International Journal of Applied Glass Science* 10, 307–320.
- Lamberson, L.A., 2016. Influence of Atomic Structure on Plastic Deformation in Tectosilicate Calcium-Aluminosilicate, Magnesium-Aluminosilicate, and Calcium-Galliosilicate. (Ph.D. thesis). Ithaca, NY: Glasses Cornell University.
- Lee, S.K., Eng, P.J., Mao, H.K., *et al.*, 2005. Probing of bonding changes in B_2O_3 glasses at high pressure with inelastic X-ray scattering. *Nature Materials* 4, 851–854.
- Liu, H., Smedskjaer, M.M., Tao, H.Z., *et al.*, 2016. A medium range order structural connection to the configurational heat capacity of borate-silicate mixed glasses. *Physical Chemistry Chemical Physics* 18, 10887–10895.
- Lu, X.N., Deng, L., Kuo, P.-H., *et al.*, 2017. Effects of boron oxide substitution on the structure and bioactivity of SrO-containing bioactive glasses. *Journal of Materials Science* 52, 8793–8811.
- Lu, X.N., Deng, L., Huntley, C., *et al.*, 2018. Mixed network former effect on structure, physical properties, and bioactivity of 45S5 bioactive glasses: An integrated experimental and molecular dynamics simulation study. *Journal of Physical Chemistry B* 122, 2564–2577.
- Lu, X.N., Ren, M.G., Deng, L., Benmore, C.J., Du, J.C., 2019a. Structural features of ISG borosilicate nuclear waste glasses revealed from high-energy X-ray diffraction and molecular dynamics simulations. *Journal of Nuclear Materials* 515, 284–293.
- Lu, X.N., Deng, L., Gin, S., Du, J.C., 2019b. Quantitative structure–property relationship (QSPR) analysis of ZrO_2 -containing soda-lime borosilicate glasses. *Journal of Physical Chemistry C* 123, 1412–1422.
- Manaktala, H.K., 1992. An assessment of borosilicate glass as a high level waste form. Report no. CNWRA 92-017. Nuclear Regulatory Commission: San Antonio.
- Matharoo, G.S., Razul, M.S.G., Poole, P.H., 2006. Structural and dynamical heterogeneity in a glass-forming liquid. *Physical Review E* 74, (050502).
- McMillan, P.F., Wilson, M., Wilding, M.C., *et al.*, 2007. Polymorphism and liquid-liquid phase transitions: Challenges for experiment and theory. *Journal of Physics: Condensed Matter* 19, 415101.
- Moesgaard, M., Keding, R., Skibsted, J., Yue, Y.Z., 2010. Evidence of intermediate-range order heterogeneity in calcium aluminosilicate glasses. *Chemistry of Materials* 22, 4471–4483.
- Moynihan, C.T., Easteal, A.J., DeBolt, M.A., Tucker, J., 1976. Dependence of the fictive temperature of glass on cooling rate. *Journal of the American Ceramic Society* 59, 12–16.
- Narayanaswamy, O.S., 1971. A model of structural relaxation in glass. *Journal of the American Ceramic Society* 54, 491–498.
- Ojovan, M.I., 2016. Mass spectrometric evidencing on modified random network microstructure and medium range order in silicate glasses. *Journal of Non-Crystalline Solids* 434, 71–78.
- Oliver, J.-A.N., Su, Y.C., Lu, X.N., *et al.*, 2019. Bioactive glass coatings on metallic implants for biomedical applications. *Bioactive Materials* 4, 261–270.
- Pedesseau, L., Ispas, S., Kob, W., 2015. First-principles study of a sodium borosilicate glass-former. I. The liquid state. *Physical Review B - Condensed Matter and Materials Physics* 91, 1–18.
- Phillips, J.C., 1979. Topology of covalent non-crystalline solids I: Short-range order in chalcogenide alloys. *Journal of Non-Crystalline Solids* 34, 153–181.
- Phillips, J.C., Thorpe, M.F., 1985. Constraint theory, vector percolation and glass formation. *Solid State Communications* 53, 699–702.
- Plodinec, M.J., 2000. Borosilicate glasses for nuclear waste immobilisation. *Glass Technology* 41, 186–192.
- Reibstein, S., Wondraczek, L., de Ligny, D., *et al.*, 2011. Structural heterogeneity and pressure-relaxation in compressed borosilicate glasses by *in situ* small angle x-ray scattering. *Journal of Chemical Physics* 134, 204502.
- Ren, M.G., Deng, L., Du, J.C., 2017. Bulk, surface structures and properties of sodium borosilicate and boroaluminosilicate nuclear waste glasses from molecular dynamics simulations. *Journal of Non-Crystalline Solids* 476, 87–94.
- Ren, M.G., Lu, X.N., Deng, L., Kuo, P.-H., Du, J.C., 2018. B_2O_3/SiO_2 substitution effect on structure and properties of $Na_2O-CaO-SrO-P_2O_5-SiO_2$ bioactive glasses from molecular dynamics simulations. *Physical Chemistry Chemical Physics* 20, 14090–14104.
- Rodrigues, B.P., Wondraczek, L., 2014. Cationic constraint effects in metaphosphate glasses. *Journal of Chemical Physics* 140, 214501.
- Sen, S., Xu, Z., Stebbins, J.F., 1998. Temperature dependent structural changes in borate, borosilicate and boroaluminate liquids: High-resolution ^{11}B , ^{29}Si and ^{27}Al NMR studies. *Journal of Non-Crystalline Solids* 226, 29–40.
- Silver, A.H., Bray, P.J., 1958. Nuclear magnetic resonance absorption in glass. I. Nuclear quadrupole effects in boron oxide, soda-boric oxide, and borosilicate glasses. *Journal of Chemical Physics* 29, 984.

- Smedskjaer, M.M., Mauro, J.C., Yue, Y.Z., 2010. Prediction of glass hardness using temperature-dependent constraint theory. *Physical Review Letters* 105, 115503.
- Smedskjaer, M.M., Mauro, J.C., Youngman, R.E., *et al.*, 2011. Topological principles of borosilicate glass chemistry. *Journal of Physical Chemistry B* 115, 12930–12946.
- Smedskjaer, M.M., Youngman, R.E., Mauro, J.C., 2014a. Principles of Pyrex[®] glass chemistry: Structure-property relationships. *Applied Physics A: Materials Science and Processing* 116, 491–504.
- Smedskjaer, M.M., Youngman, R.E., Striepe, S., *et al.*, 2014b. Irreversibility of pressure induced boron speciation change in glass. *Scientific Reports* 4, 3770.
- Smith, R.A., 1997. History of the use of B₂O₃ in commercial glass. In: Wright, A.C., Feller, S.A., Hannon, A.C. (Eds.), *Borate Glasses, Crystals & Melts*. Society of Glass Technology, pp. 313–322.
- Stevenson, B., Yu, Y., Edén, M., 2018. Structure-composition trends in multicomponent borosilicate-based glasses deduced from molecular dynamics simulations with improved B-O and P-O force fields. *Physical Chemistry Chemical Physics* 20, 8192–8209.
- Striepe, S., Smedskjaer, M.M., Deubener, J., *et al.*, 2013. Elastic and micromechanical properties of isostatically compressed soda-lime-borate glasses. *Journal of Non-Crystalline Solids* 364, 44–52.
- Svenson, M.N., Bechgaard, T.K., Fuglsang, S.D., *et al.*, 2014. Composition-structure-property relations of compressed borosilicate glasses. *Physical Review Applied* 2, 024006.
- Takada, A., Catlow, C.R.A., Price, G.D., 1995. Computer modelling of B₂O₃. II. Molecular dynamics simulations of vitreous structures. *Journal of Physics: Condensed Matter* 7, 8693.
- Tan, L.L., Huang, L., He, C.C., *et al.*, 2020. Tailoring cluster configurations enables tunable broadband luminescence in glass. *Chemistry of Materials* 32, 8653–8661.
- Tool, A.Q., 1946. Relation between inelastic deformability and thermal expansion of glass in its annealing range. *Journal of the American Ceramic Society* 29, 240–253.
- Tuhen, M.I., Deng, L., Du, J.C., 2020. A comparative study of the effectiveness of empirical potentials for molecular dynamics simulations of borosilicate glasses. *Journal of Non-Crystalline Solids* 551, 120413.
- Uhlmann, D., Shaw, R., 1969. The thermal expansion of alkali borate glasses and the boric oxide anomaly. *Journal of Non-Crystalline Solids* 1, 347–359.
- Wang, M., Krishnan, N.M., Anoop, *et al.*, 2018. A new transferable interatomic potential for molecular dynamics simulations of borosilicate glasses. *J. Non-Cryst. Solids* 498, 294–304.
- Wolf, G.H., McMillan, P.F., 1995. Pressure Effects on Silicate Melt—Structure and Properties. In: Stebbins, J.F., Dingwell, D. and McMillan, P.F. (Eds.), *Structure, Dynamics, and Properties of Silicate Melts*. Walter de Gruyter GmbH, pp. 505–561.
- Wondraczek, L., Sen, S., Behrens, H., Youngman, R.E., 2007. Structure-energy map of alkali borosilicate glasses: Effects of pressure and temperature. *Physical Review B* 76, 014202.
- Wright, A.C., 2010. Borate structures: Crystalline and vitreous. *Physics and Chemistry of Glasses* 51, 1–39.
- Wright, A.C., Thorpe, M.F., 2013. Eighty years of random networks. *Physica Status Solidi* 250, 931–936.
- Wu, J.S., Stebbins, J.F., 2009. Effects of cation field strength on the structure of aluminoborosilicate glasses: High-resolution ¹¹B, ²⁷Al and ²³Na MAS NMR. *Journal of Non-Crystalline Solids* 355, 556–562.
- Wu, J.S., Stebbins, J.F., 2010. Quench rate and temperature effects on boron coordination in aluminoborosilicate melts. *Journal of Non-Crystalline Solids* 356, 2097–2108.
- Wu, J.S., Deubener, J., Stebbins, J.F., *et al.*, 2009. Structural response of a highly viscous aluminoborosilicate melt to isotropic and anisotropic compressions. *Journal of Chemical Physics* 131, 104504.
- Xiang, Y., Du, J.C., 2011. Effect of strontium substitution on the structure of 45S5 bioglasses. *Chemistry of Materials* 23, 2703–2717.
- Yadav, A.K., Singh, P., 2015. A review of the structures of oxide glasses by Raman spectroscopy. *RSC Advances* 5, 67583–67609.
- Yano, T., Kunimine, N., Shibata, S., Yamane, M., 2003. Structural investigation of sodium borate glasses and melts by Raman spectroscopy. III. Relation between the rearrangement of super-structures and the properties of glass. *Journal of Non-Crystalline Solids* 321, 157–168.
- Yue, Y.Z., 2004. Calorimetric studies of the structural heterogeneity of silicate liquids. *Ceramic Transactions* 170, 31–45.
- Yue, Y.Z., Christiansen, J.C., Jensen, S.L., 2002. Determination of the fictive temperature for a hyperquenched glass. *Chemical Physics Letters* 357, 20–24.
- Yue, Y.Z., von der Ohe, R., Jensen, S.L., 2004. Fictive temperature, cooling rate and viscosity of glasses. *Journal of Chemical Physics* 120, 8053–8059.
- Yue, Y.Z., Wondraczek, L., Behrens, H., Deubener, J., 2007. Glass transition in an iso-statically compressed calcium metaphosphate glass. *Journal of Chemical Physics* 126, 144902.
- Yun, Y.H., Bray, P.J., 1978. Nuclear magnetic resonance studies of the glasses in the system Na₂O–B₂O₃–SiO₂. *Journal of Non-Crystalline Solids* 27, 363–380.
- Zachariasen, W.H., 1932. The atomic arrangement in glass. *Journal of the American Chemical Society* 54, 3841–3851.
- Zhang, Y.F., Yang, G., Yue, Y.Z., 2013. Calorimetric signature of structural heterogeneity in a ternary silicate glass. *Journal of the American Chemical Society* 96, 3035–3037.
- Zheng, Q.J., Mauro, J.C., Smedskjaer, M.M., *et al.*, 2012. Glass-forming ability of soda lime borate liquids. *Journal of Non-Crystalline Solids* 358, 658–665.
- Zheng, Q.J., Yue, Y.Z., Mauro, J.C., 2017. Density of topological constraints as a metric for predicting glass hardness. *Applied Physics Letters* 111, 011907.
- Zheng, Q.J., Zhang, Y.F., Montazerian, M., *et al.*, 2019. Understanding glass through differential scanning calorimetry. *Chemical Reviews* 119, 7848–7939.

Relevant Websites

<https://www.cmog.org/article/pyrex>

Corning Museum of Glass.

<https://www.corning.com/worldwide/en/products/display-glass.html>

Display Glass.

<https://www.pyrex.eu/pages/our-history>

OUR HISTORY.

Pyrex[®] website.

Glasses: Chalcogenides

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Introduction

Chalcogenide glasses (ChGs) have received increasing global interest over the past decade due to their suitability for use in infrared (IR) systems (Zhang *et al.*, 2003; Eggleton *et al.*, 2011; Parvanov *et al.*, 2008; Sanghera and Aggarwal, 1999; Zhang *et al.*, 2004). With compositional tuning, their transparency can extend over the full IR spectral range (Zhang *et al.*, 2003; Eggleton *et al.*, 2011; Parvanov *et al.*, 2008; Sanghera and Aggarwal, 1999; Zhang *et al.*, 2004; Buff, 2016; Sissen, 2017; Yadav *et al.*, 2017; Goncalves *et al.*, 2018). Unlike oxide glasses (which have oxygen as a key anionic constituent), ChGs are part of a class of “non-oxide” glasses. This lack of oxygen (O) is important to their use and makes them transparent throughout the IR. Since most metal (M)-O species possess resonance absorption bands in the IR, the removal of oxygen, along with the removal of other potentially absorbing impurities (such as moisture (hydroxide, OH⁻, water, H₂O) and hydrides (M-H)) and any residual particulate from the melting process, is critical in ultimately defining the glass’ resulting transparency. Like halides (glasses based on group VII species), chalcogen (Ch) species (based on group VI elements) combine with other chalcogens or metalloids such as As, Sb, Ge and Ga, to form stable glasses with wide (compositionally-specific) glass forming regions. However, the bonds formed in these glasses are much weaker than M-O bonds and thus ChGs typically are softer, less chemically stable and have lower melting/softening temperatures as compared to oxide glasses. Additionally, due to the bonding present, ChGs can exhibit metastable properties including photosensitivity (radiation-induced structural modification) which varies both with glass composition and the material’s bandgap (defined by the bonds present) and type of exciting radiation (Kolobov and Tominaga, 2012). While these glass attributes may limit the material’s use in some instances, they can also be exploited to extend their use towards the realization of unique optical or physical property functionality (Carlie *et al.*, 2010). There are several excellent reviews on the basic attributes of ChGs for the interested reader that cover these topics (Hilton, 2010; Seddon *et al.*, 2006; Kolobov and Tanaka, 2001; Wang, 2014; Adam and Zhang, 2014; Richardson and Kang, 2020).

While ChGs and related alloys have been extensively studied since the early 1960s, there remains relatively few commercial products based on these glasses. Those that are available were largely developed in the 1960–1970 time frame, for xerographic and other bulk optical applications (Bixby and Ullrich (1956); Texas Instruments (1967)). Hence, these compositions are no longer protected by patents and hence are known by varying product names, manufactured by multiple vendors, such as Amorphous Materials, Umicore, Vitron, and SCHOTT AG. While ChGs were being developed internationally during this time, an excellent review of the history of the effort in the US starting at Texas Instruments and then at Amorphous Materials, including details of early glass development, melting methods, and glass properties, can be found in Hilton (2010). An additional source of data on numerous ChGs developed and/or measured in Russia can be found in Kokorina (1996). While the history of ChGs is rich, the small number (currently 6) of commercially produced compositions is largely due to limited demand of these glasses which until recently, have only been employed in a few *bulk* optical applications (such as in lenses for IR imaging systems). The most common of these has been in IR vision systems (so-called “forward looking IR” or FLIR systems) that allow vision in dark or foggy systems while driving. More recently, use of these glasses in commercial systems such as iPhones has broadened their use and familiarized the public with technology that was previously used solely by the military. Hence, efforts to scale the manufacturability of the glasses to include their forming into suitable, low cost lens elements and systems has led to wide scale academic and industrial work in techniques such as precision glass molding (PGM).

With expanded interest in sensing, security and imaging since 2010, the market for low cost alternatives to expensive crystalline optics such as Ge and Si, has invigorated ChG research efforts worldwide. This common “chicken and egg” conundrum exists for these IR materials, in that, without sufficient chemistry-structure-property data on candidate glasses that can be scaled to commercially-relevant sizes, optical designers cannot put these media into optical design codes that make the scale-up and commercialization of the new compositions economically viable. This blockage, however, has started to ease in recent years, as new data has been published by many groups who have worked to extend lab-scale melts to commercially viable sizes (Gibson *et al.*, 2019). Here, important characteristics required for data sheets include the glass’ transition temperature (T_g), refractive index (n) and its variation with wavelength, ($dn/d\lambda$) or temperature (dn/dT) along with the glass’ viscosity (η) and coefficient of thermal expansion, (CTE). All of these properties are composition specific, challenging to produce with superb repeatability unless made in controlled large scale melting production, and expensive to measure. Additionally, applications may or may not require ultra-high purity for low loss applications at specific wavelengths, and this requirement entails additional processing and cost consideration. Hence, unlike oxide glasses where most of these hurdles have been overcome in the ~100 years that companies have been making those glasses, these challenges still impede production and adoption of new ChG compositions into optical systems. Hence, as optical design teams work to integrate promising candidate materials into new, higher volume optical designs, this will reinforce the need of new glasses and encourage market attractiveness to glass producers.

This chapter discusses glasses and composites based on glasses, multi-phase (glass + crystalline) media where controlled crystallization has been employed to extend their properties towards use as glass ceramics (GCs). For brevity, we confine our discussion to the use of ChGs or GCs to optical applications, with reference to very recent advances in applications where these materials are passive (i.e., examples where the ChG does not contain a rare-earth or transition metal dopant for luminescence purposes). Highlighted are examples of how ChGs can be tuned through composition (glass' chemical constituents), morphology (the glass' homogeneous or phase separated nature), and microstructural modification associated with the controlled nucleation and growth of nanocrystal phases within the parent glass matrix to realize novel functionality (Buff, 2016; Sisken, 2017; Yadav *et al.*, 2017; Richardson, 2018; Li *et al.*, 2014; Yang *et al.*, 2007; Wang *et al.*, 2009; Zhao *et al.*, 2005; Xia *et al.*, 2006; Sisken *et al.*, 2019; Kang *et al.*, 2018a,b; Richardson *et al.*, 2016; Yadav *et al.*, 2019). Briefly discussed is a short summary on the state of the art in exploiting these compositionally defined attributes to enable low cost lenses created via PGM. This chapter discusses key material attributes to ChGs' and ChG-based GCs' for use in the IR. Specifically highlighted are uses in applications for the mid-wave IR (MWIR) spectral region in applications such as low cost lenses via PGM, fibers (communication) and introduces recent progress on new opportunities such as gradient index optics (imaging), low-loss waveguides (signaling), and optical nonlinearity (sensing and lighting).

ChGs: For Bulk Media and Fibers

Processing Characteristics of ChGs

ChGs are amorphous, non-crystalline solids formed largely by the fusion process (often called the melt-quench process) whereby elemental starting materials from group VI and other metalloids are combined and melted in a sealed quartz ampoule prior to homogenization, quenching and annealing. Unlike oxide glasses which can be melted in open crucibles, the high vapor pressures of chalcogen species such as sulfur or selenium, require melting in a sealed container. While melting in a fused silica ampoule may introduce minor oxide impurities to the melt (and for some applications is unacceptable), this trace level of contamination comes with the added benefit of poor wetting. As shown in Fig. 1, this enables melted ChG "rods" to be seamlessly released from their crucible with minimal sticking. Sulfide glasses and glasses containing alkali tend to react more with the crucible and in these melts, ampoules are often coated with carbon to minimize interaction and adhesion (Martin and Boyer, 1990). Such optimization has been shown especially useful in the examination of ChGs for battery applications where doping with Na or Li requires shielding from interaction with the glass crucible ampoule. Such processing considerations are required in the melting of these glasses as their properties can be adversely influenced by such melting environment variables that impact glass properties and crystallization stability.

Crystallization Stability and Compositional Trends

A glass' network structure is defined by its thermal history, i.e., the path that the melt takes from the liquidus melt to form a solid at room temperature. How that glass structure organizes is influenced by the cooling rate used and thus bulk glasses require annealing as their large aspect ratios (interior versus exterior skin) can see vastly different cooling rates that can induce stress and stress birefringence. This volume effect is much less pronounced in the thin diameters of optical fibers where cooling rates are very high. Despite the low thermal conductivities of glass, most fibers do not possess excessive density variation due to forming temperature gradients that degrades their refractive index homogeneity if the preform is compositionally homogeneous. Such thermal history and the distance the glass network is from its "equilibrium state" (for purposes of this discussion, not the state of the equivalent crystal, but that of a well-annealed bulk glass) will impact the resulting glass' properties as well if cooling was sufficient to avoid the nucleation and growth associated with crystallization. Crystallization in all glasses, but especially in fibers, leads to both absorption and scatter loss and thus, needs to be avoided. Various reviews on crystallization behavior in ChGs have been made (Hari *et al.*, 1998), and a subset of topics important to fibers are discussed in more detail here.

Crystallization in glass relies on nucleation and subsequent growth of crystals. Without the formation of stable nuclei, subsequent crystallization cannot occur. Crystallization in glass, in most cases, is undesirable and this is especially true in bulk optical

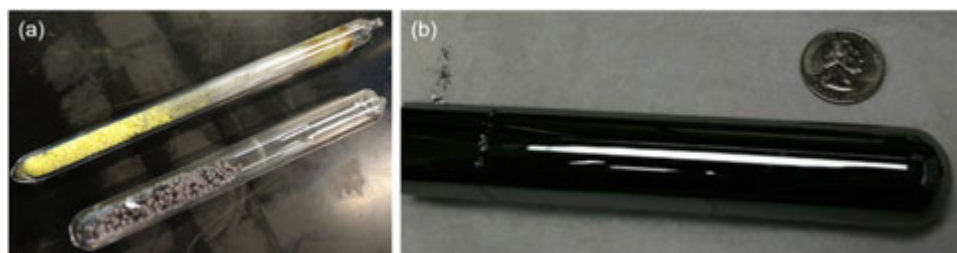


Fig. 1 A batched sulfide (yellow) and selenide (black) ChG prior to melting in a sealed ampoule (a); a 250 g rod of selenide glass after melting (b); shown as a reference for size is a US quarter.

glass and glass fibers where the presence of crystallites can result in scattering loss due to refractive index mismatch. To understand the key conditions of crystallization which must be avoided to ensure low optical loss fibers, one must be familiar with the temperature dependence of both nucleation process in ChGs and the subsequent growth of crystals should stable nuclei form. Stability against crystallization is often inferred by the difference between T_x , the onset of measured crystallization in a glass as indicated by exothermic heat release during thermal analysis measurement (such as differential scanning calorimetry, DSC) and the material's glass transition temperature, T_g . When this temperature difference, ΔT , exceeds $\sim 100^\circ\text{C}$, it is generally considered that a glass can successfully be formed into fibers, avoiding crystallization. Since non-oxide glasses typically have T_g 's much lower than oxide glasses, an estimated ΔT provides an initial insight on how composition, dopant type, and concentration can impact crystallization stability and the probability of being able to fabricate low loss optical fiber. However, a variety of historic references to measurement of critical cooling rates (CCR) of chalcogenide melts as a function of composition (Kokorina, 1996; Mikhailov and Tver'yanovick, 1986) and the role of variation in annealing protocols on refractive index provides insight into the intricacies of such measurements.

It is sometimes difficult to compare compositional dependency of ChG stability across authors, as measurements of ΔT are dependent on measurement heating rate used, which may not always be reported. However, it is useful to see the role compositional variation (rather than configurational variation) plays in glass stability. To illustrate the trend, a common set of glass systems is compared, as shown in Fig. 2 (Adam and Zhang, 2014). Here, two families of $\text{Ge}_{28}(\text{As/Sb})_{12}(\text{S}_x/\text{Se}_{60-x})$ are compared for their stability, ΔT illustrating that stability is largely dominated by chemical rather than configurational effects. In these glasses, only isostructural substitutions have been made to the glass network (as both As and Sb have a CN = 3) and S and Se are both two-coordinated. Hence, the network role of the chemical constituents in these two glass families (comparing As and Sb) are similar, but the magnitude of stability is defined by the type of the lower coordinated species (S or Se) and its quantity. Fibers based on Ge-As-Se-Te glasses have shown some of the lowest losses in ChG fibers investigated and it largely can be attributed to the glass' crystallization stability. As discussed by Shiryaev *et al.* (2004), $\text{Ge}_x\text{As}_{40-x}\text{Se}_{40}\text{Te}_{20}$, where $x = 0-40$, exhibit T_g that ranges from 140 to 320°C depending on Ge content and heating rate. Glasses with less than 35 mol% Ge showed no exothermic features associated with crystallization, indicating impressive high glass stability. Glasses within the ranges of Ge: 6–24 at% and Te: 42–48 at% were shown to have T_g above 200°C with no sign of crystallization during annealing for 20 h at temperatures exceeding T_g by $50-100^\circ\text{C}$ (Tikhomirov *et al.*, 2004).

Nucleation and growth theory can be applied to ChG materials for a variety of fundamental and applied reasons. A summary of these theories and methods to calculate nucleation and growth rates from experimental data (as specifically applied to Tellurite glasses) can be found in Massera (2009). The same protocols have been employed to ChGs as discussed below, to realize optical glass ceramics, where the secondary crystalline phase has a refractive index match to the parent glass to minimize loss. Examples of controlled crystallization in ChGs have been shown to be effective in realizing bulk glass ceramics (to either enhance thermal or mechanical stability (Sharma *et al.*, 2020)), create gradients in refractive index (GRIN) (Richardson, 2018; Siskin, 2017; Kang *et al.*, 2018a,b; Kang *et al.*, 2020a,b) or in commercial products resulting in optical memories based on GeSbTe phase change media (PCM) (Adam and Zhang, 2014; Zhang *et al.*, 2019). Recently, efforts to tailor crystalline phase formation in reversible, low optical loss PCMs for conformal coatings and the formation of permanent optical function realized through optical nanocomposites in bulk and films of ChG have shown that both compositional tuning and the associated understanding of crystal nucleation and growth kinetics can be exploited for new optical applications (Kolobov and Tominaga, 2012; Kolobov and Tanaka, 2001; Richardson and Kang, 2020; Bixby and Ullrich, 1956; Texas Instruments, 1967; Gibson *et al.*, 2019; Richardson, 2018; Kang *et al.*, 2019; Mingareev *et al.*, 2019). Here, tailoring of physical properties through the controlled formation and growth of specific

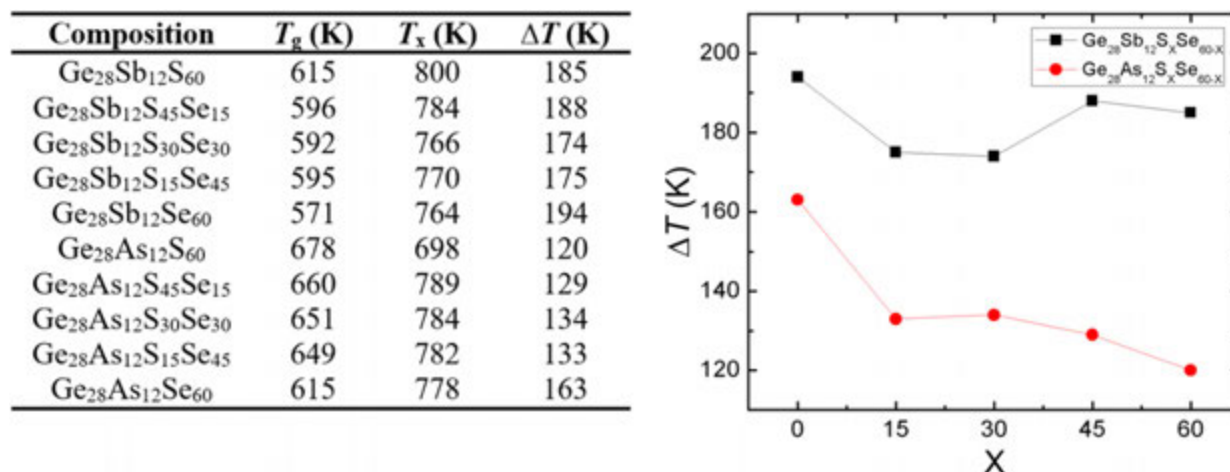


Fig. 2 (Left) glass transition and crystallization temperatures, with corresponding stability windows, for two families of ChGs, (right) ΔT versus S/Se ratio for $\text{Ge}_{28}(\text{As/Sb})_{12}(\text{S}_x/\text{Se}_{60-x})$ plotted based on the tabulated table. Reproduced with permission from Adam, J.L., Zhang, X., 2014. Chalcogenide Glasses: Preparation, Properties and Applications. Woodhead Publishing Limited. Copyright 2014 Elsevier.

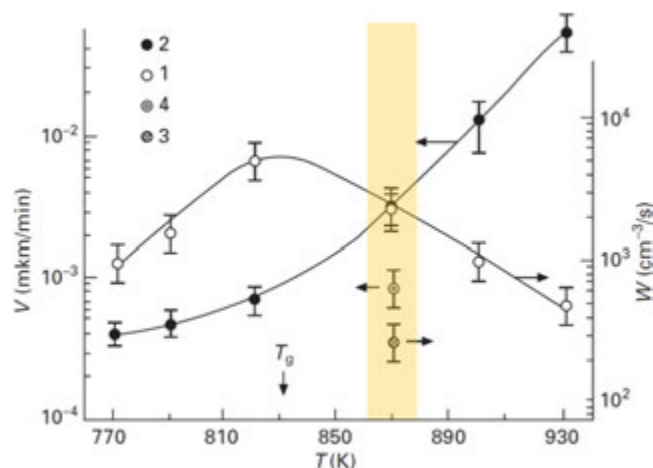


Fig. 3 Temperature dependence of nucleation and growth rates in undoped (data sets 3 & 4) and doped (data sets 1 & 2) $\text{Pr:}(\text{Ga}_2\text{S}_3)_{0.7}(\text{La}_2\text{S}_3)_{0.3}$ glass. The shaded region illustrates the increase (note logarithmic scale) in both nucleation (W) and growth (V) rates with Praseodymium doping level in the glass matrix.

secondary crystalline phases with defined volume fractions can lead to optical function not realized in static glass or crystalline media.

In fibers, crystalline phase formation is largely undesirable and thus, should be avoided. Knowledge of a glass' nucleation and growth rates provides quantitative insight into this process. The formation of rate versus temperature plots for both nucleation and growth (referred to by either I or W to denote nucleation rates and V or U to define growth rates) provides insight not only on the temperatures where crystal nuclei can form, but also at what temperature they grow and at what rate. Clearly, for most optical fiber glass compositions, one desires to operate in temperature regimes where a glass' nucleation rate is very low, and the growth rate for any small concentration of nuclei present approaches zero. This is the target for creating crystallite-free fibers. However, should one want to "selectively" create (or sustain) a nanocrystalline phase within the candidate glass system, knowledge of a glass' I - U curve and its use in defining optimal draw conditions will indicate what extent of crystallite formation and/or growth might occur. The selective use of this strategy for engineering controlled crystallization in tellurite cladding glasses showed that nanocrystal phase formation, known to enhance mechanical properties, was an efficient means to strengthen the outer layer of fibers formed in these typically crystallization-prone glasses (Massera *et al.*, 2010a,b).

Crystallization stability can be influenced not only by network constituents, but also by dopants. The variation in nucleation and growth behavior with doping is especially important when considering compositional selection of rare-earth doped ChGs such as in the development of active media. Since fibers of active, rare earth doped ChGs are one of the leading areas of interest for their use (Richardson and Kang, 2020), we highlight here this effect as example. The impact on both the nucleation and growth behavior of the glass with addition of the rare earth dopant praseodymium is noted in the study by Dianov *et al.* (1997). While illustrated in one ChG composition GaLaS, the impact on both the nucleation and linear growth rate with Pr doping is clear. Fig. 3 shows the variation (data set 1 and 2) in nucleation (W) and growth (V) for $\text{Pr:}(\text{Ga}_2\text{S}_3)_{0.7}(\text{La}_2\text{S}_3)_{0.3}$ glass as a function of temperature (K) as compared to the undoped material (data set 3 and 4). At the common temperature of 870K (highlighted with gray shading), comparing the rates for nucleation and growth, one observes that as compared to the undoped glass, the doped glass exhibits an almost 10-fold increase in nucleation rate, along with a concurrent increase in growth rate (approximated to $\sim 200 \times$). These data suggest that the dopant's presence in the glass network increases the likelihood that stable nuclei will form and once formed, will grow at a faster rate. This infers that measurement of nucleation and growth rates on actual compositions is needed to inform the expected crystallization stability of the material upon fiberization.

Viscosity (η) and Temperature (T) Dependence

A glass' viscosity (η , in units of Pa s) and temperature (T) dependence is a material-specific attribute, defined by the bonding in the glass matrix and to first order, the glass' average bond strength. For ChGs, this attribute is especially important in applications such as precision glass molding (PGM) and in the drawing of optical fibers. Defining the suitable fiber draw conditions (draw temperature and draw rate) is a fairly straight forward process when a glass' viscosity- temperature (η - T) behavior is known. Since core and cladding glasses should have similar T_g and CTE behavior to ensure compatibility during drawing, it is assumed that the η - T response of these two glasses, while differing slightly in index, will be close in both their thermal position (lateral shift) and curve steepness. These attributes of a η - T curve and its shape are important as they determine whether the glass has a short (steep) slope or long (less steep) range of processing temperatures. This short/long nomenclature is often used to highlight the ease (long) or difficulty (short) by which a glass can be fiberized as these terms define the temperature required for both flow and sometimes avoidance of crystallization. A similar η - T behavior between core and clad glass allows fiber drawing with minimal interface defects

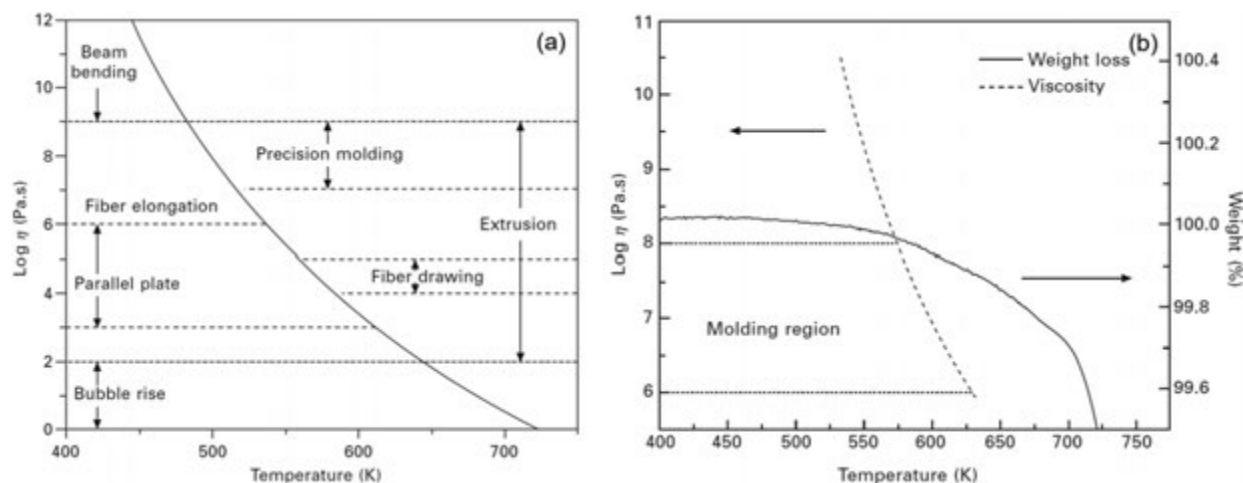


Fig. 4 (a) An overview of the viscosity regions for a ChG, showing the ranges for measurements [left] and hot-forming applications [right], (b) a comparison of the viscosity and volatilization curves for $\text{Ge}_{10}\text{As}_{40}\text{Se}_{50}$ glass showing evidence of out-gassing in the molding region. Reproduced with permission from Adam, J.L., Zhang, X., 2014. Chalcogenide Glasses: Preparation, Properties and Applications. Woodhead Publishing Limited. Copyright 2014 Elsevier.

(bubbles, trapped gas, or micro-delamination). Such defects would compromise (increase) the measured loss of the fiber. The literature contains multiple examples of such data for some ChG compositions, but as it is a time-consuming and instrumentation-specific measurement to make. Hence, such data are often not reported for more exotic or exploratory glasses as considerable measurement and specific sample fabrication are required and exploratory melts are frequently small in volume and not homogeneous.

Measurements of thermal properties including glass viscosity behavior as a function of composition is well studied. A detailed discussion of experimental methods and typical thermal behavior in ChGs is reviewed in Adam and Zhang (2014). Fig. 4(a) highlights the key thermal signature regimes for viscosity illustrating the measurement methods (left side of Fig. 4(a)) and the typical glass processing windows for typical glass manufacturing protocols (right side of Fig. 4(a)). Of relevance to the topic of ChGs for fibers are the temperature range for extrusion (10^2 – 10^9 Pa s) such as that for forming extruded rods or cane and that for fiber drawing (10^4 – 10^5 Pa s). These ranges will vary with composition and may vary with individual fiber drawing apparatus, but are generally accepted as a guide to predicting variation in formation behavior with composition. Fig. 4(b) overlays a η - T curve for a GeAsSe glass with a thermogravimetric spectrum that defines the weight loss of that glass with temperature. Shown in the figure is evidence that the onset of volatilization of glass constituents occurs near the low temperature range of precision glass molding. As compared to the data shown in Fig. 4(a), this temperature range is below the temperature range where fiberization for this glass takes place (at $\eta \sim 10^4$ – 10^5 Pa s), thus suggesting that compositional variation during drawing could occur without strict temperature control. Such compositional variation (volatilization) could lead to accompanying refractive index variations if special care is not taken to control temperature excursions for ChGs.

Fig. 5 illustrates how a characteristic viscosity-temperature curve varies with composition for a simple binary As–Se glass (Musgraves *et al.*, 2011). This plot is illustrative of the correlation between glass fluidity and network structure. Several key points are important to highlight when evaluating viscosity in ChG glasses by multiple experimental (such as by beam bending viscosity (BBV) – shown as the lower temperature data points and parallel plate viscometry (PPV) – shown as the upper temperature data points). Not shown are points defined by the fiber elongation method which requires fibers to be formed and measured using a specialized set up to yield data through the region ($\sim 10^{7.6}$ Pa s). Firstly, while there are varying discussions on the best means to “fit” experimental data (Mauro *et al.*, 2016), most literature data employ the Vogel-Fulcher-Tammann (VFT) method. The steepness of the viscosity curve is indicative of the working range available to draw, but the lateral position (in temperature) provides a gauge of the variation in energy needed to sever the structural units present to initiate flow. Glasses to the left in the series have much lower three-coordinated As present and thus a higher Se content which in this binary system, forms rings and chains of Se. Se–Se bonds have a lower bond energy than As–Se bonds and thus, these higher Se content glasses see an onset of flow at lower temperatures. The similarity in the shape of the series of curves is testament to the structural role of the primary bonds, found in the $\text{AsSe}_{3/2}$ pyramidal units that make up the “building blocks” in this glass and the Se_n chains that interconnect the pyramids. $\text{As}_{40}\text{Se}_{60}$, the stoichiometric glass contains only interconnected pyramidal units and no homopolar Se–Se bonds.

These data are especially important when considering the formation of low cost optics such as lenses prepared by a precision glass molding (PGM) technique. Often simply referred to as “molding”, the primary objective is that the glass be sufficiently stable to crystallization (have a high ΔT) to not devitrify upon the reheating cycle that accompanies the molding process. Secondly, it is desirable that a suitably short (and thus cost-effective) molding cycle be created whereby glass can be loaded into a molding machine, rapidly heated to a suitable molding temperature (as defined by its viscosity such as shown in Figs. 4(a) and 5), be fluid enough at that temperature to form a desired shape under an applied load, then be cooled such that the load can be

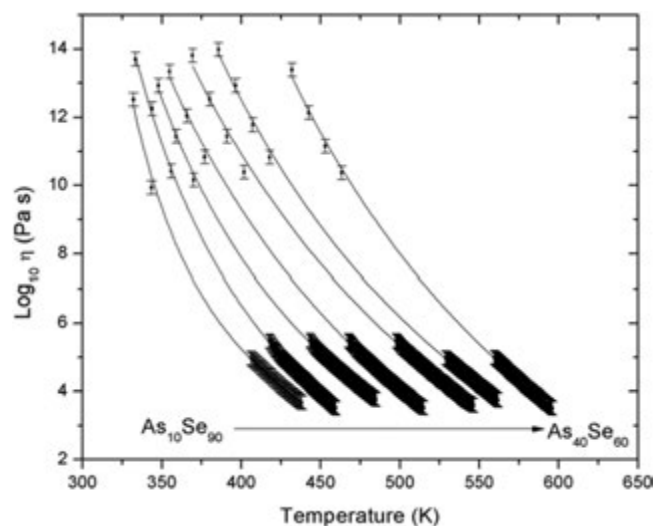


Fig. 5 Viscosity curves for the $\text{As}_x\text{Se}_{100-x}$ glass family from $x = 10$ (left-most) to $x = 40$ (right-most) obtained through beam bending and parallel plate viscometry. Reproduced with permission from Musgraves, J.D., Wachtel, P., Novak, S., Wilkinson, J., Richardson, K., 2011. Composition dependence of the viscosity and other physical properties in the arsenic selenide glass system. *J. Appl. Phys.* 110, 063503. Copyright 2011 AIP.

released and the cooled lens can be ejected from the machine. While simple in principal, the process is complex as there are various levels of property changes imparted to the glass by this “new” thermal history. Not only does the glass network structure change, but so too does its density, refractive index and, depending on composition, other aspects such as relaxation phenomena. Here, a glass’ network undergoes time dependent changes with temperature. Since ChGs have T_g which in some cases are as low as $\sim 100\text{--}200^\circ\text{C}$ above room temperature, there exists enough thermal driving force at room temperature, to cause time dependent variations in properties with time at room temperature. This is important in systems that must perform over a range of temperatures where the change in an optical system’s focus, needs to remain stable. This effect has been studied in a variety of publications, which have been summarized for a variety of ChGs in Koontz (2014). Hence, while interesting and more widely applied for a wide variety of ChGs being employed in low cost IR imaging systems, molded IR optics still require optimization for specific commercial applications where their thermal and physical properties play a guiding role.

Novel Optical Function and Gradient Properties

The above discussions highlight properties of ChGs which like other oxide and halide glasses, are important for their use as glasses or glass ceramics and how these properties often impact their manufacturability. Discussed in subsequent sections is how one can exploit some of the common misconceptions of ChGs towards generating unique function. Often, ChGs are seen as “limited” in their use due to their bonding and the impact of this on function. As discussed by Carlie *et al.* (2010), this “perceived” set of limitations (low T_g , weak (er) bonds, low chemical durability, poor thermal stability) can be used towards deliberate modification of any physical properties. Below, we focus on such knowledge to optimized aspects of optical function in ChGs.

GRIN via Spatially Controlled Nucleation and Growth

To control and manipulate light propagation in bulk imaging systems, multiple optical components are selected and combined to realize the desired optical function, across a defined spectral window. Here, individual IR optical components comprised of varying optical materials (glasses, crystals, and semiconductors) are often fabricated into complex, non-planar geometries exploiting their unique optical properties (Zhang *et al.*, 2003; Cha *et al.*, 2012; Hisakuni and Tanaka, 1995; Ramachandran *et al.*, 1997; Beadie *et al.*, 1998; Saitoh and Tanaka, 2003; Sanchez *et al.*, 2011; Kumaresan *et al.*, 2013). Legacy optical design and fabrication strategies often require costly multi-step manufacturing processes which limit system design flexibility, and this can lead to an increase in the size, weight, and power consumption (SWaP) potentially impacting both the performance and/or cost of the resulting imaging system (Zhang *et al.*, 2003; Cha *et al.*, 2012; Hisakuni and Tanaka, 1995; Ramachandran *et al.*, 1997; Beadie *et al.*, 1998; Saitoh and Tanaka, 2003; Sanchez *et al.*, 2011; Kumaresan *et al.*, 2013; Booth, 2014). These issues can be significant in bulk IR systems where high density crystalline materials are widely used, as these optical materials possess monochromatic/chromatic aberrations and/or limitations in performance at elevated temperatures (Moore, 1980; Li, 1980). Next-generation imaging systems will require materials with enhanced multi-spectral or broadband optical functionality, thus further challenging the aim to reduce the number of components in an optical system and resulting platform footprint. Reducing SWaP in optical

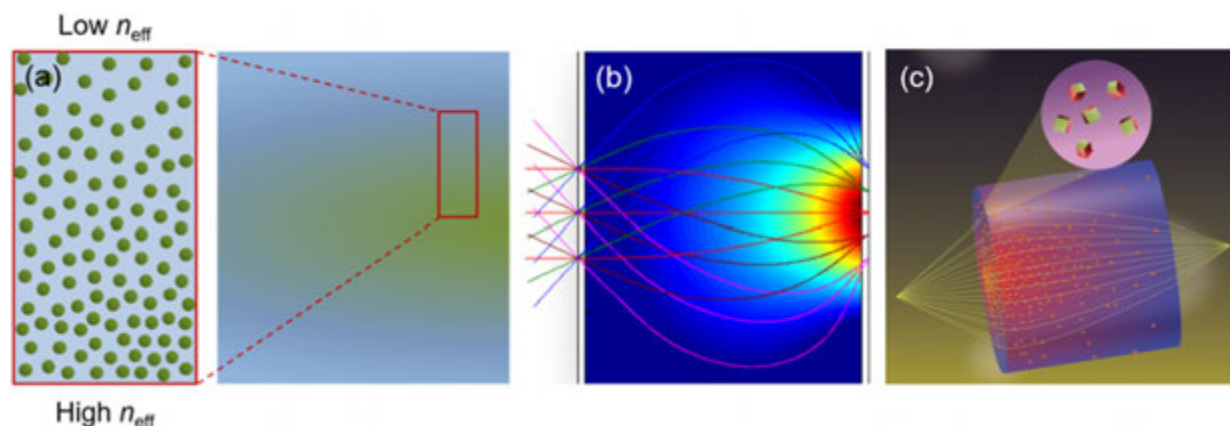


Fig. 6 (a) a GRIN medium where the density of high-index nanocrystals (green) are spatially varied within a low-index matrix (blue), (b) ray tracing through a resulting flat lens, and (c) a 3-D view of the flat lens where high-index nanocrystals' distribution, a GRIN profile, and ray tracing are shown. Reproduced with permission from (c) Kang, M., Sisken, L., Lonergan, C., *et al.*, 2020b. Monolithic chalcogenide optical nanocomposites enable infrared system innovation: Gradient Refractive Index (GRIN) optics. *Adv. Opt. Mater.* 8, 2000150. Copyright 2020 Wiley.

systems through the creation and use of IR nanocomposite materials possessing GRIN profiles provides a viable solution to this challenge (Moore, 1980). Here the optical composite, in the form of a bulk component or planar waveguide, can yield a uniquely tailorable solution exploiting tunable optical function created by combining the desirable attributes of effective media. A key strategy to create GRIN profiles within a single medium involves spatial control of a high refractive index phase in a medium. Conversion of a base glass to a glass-ceramic where the spatial variation in the volume fraction of high index nanocrystallites in a low index base glass can be tailored results in a transparent GRIN effective medium, as illustrated in Fig. 6(a)–(c) (Richardson, 2018; Richardson *et al.*, 2016; Kang *et al.*, 2020a,b). This technique provides a novel method to both miniaturize and enhance current IR components over that realized solely on homogeneous, single phase spherical or aspherical lenses thereby enabling a flat lens with a low chromatic aberration and a substantially reduced SWaP.

Bulk GRIN Materials

Recently, it has been reported that GeSe₂–As₂Se₃–PbSe (GAP–Se) ChGs with PbSe content of ~10–45 mol% in their bulk form are spontaneously separated into Pb-rich and Pb-deficient amorphous phases upon standard melt-quench protocol, as shown in Fig. 7(a) and (b) (Goncalves *et al.*, 2018). The energetically-favorable route to phase separation consistently seen in this material system has gained interest from optical designers and glass scientists since the Pb-rich amorphous phases, once thermally treated, can be exclusively converted into nanocrystallites with an index greater than that of the surrounding matrix. This matrix remains amorphous, as evidenced by bright and dark field (BF and DF) transmission electron microscope (TEM) images in Fig. 7(c) (Kang *et al.*, 2020a,b; Francois-Saint-Cyr *et al.*, 2019). Specifically, a DF TEM image collected from a base glass with PbSe content of 20 mol% shows sub-wavelength, amorphous secondary phases within an amorphous matrix, as indicated by the bright, circular phases in a dark matrix. The contrast between the secondary phases and the matrix in the DF TEM image suggests that the atomic percentage of heavy constituents in the secondary phases is greater than that in the matrix while the entire nanocomposite remains amorphous. A heat treatment of the base glass with PbSe content of 20 mol% selectively crystallizes the Pb-rich secondary phases, thereby generating high-refractive index nanocrystallites, as indicated by asymmetric shapes of the secondary phases in the DF TEM image. The crystalline fringes existing exclusively within the dark, secondary phases in the high-resolution BF TEM image coherently indicate the emergence of Pb-containing nanocrystals. An increase in the content of PbSe to 40 mol% and a subsequent heat treatment of the composition in the immiscibility zone induces inverse microstructures of the pre- and post-annealed GAP–Se glass with 20 mol% of PbSe. This indicates that the effective index of nanocomposites increases upon heat treatment, while maintaining their transparency as an effective medium. Since the number density and the crystallinity of the high-refractive index, Pb-rich phases can be controlled by knowledge of the nucleation and growth rates of these phases, and thus a prescribed thermal treatment protocol, a combination of the material chemistry and the process leads to our demonstration of a promising method to create a GRIN within a single component. This has been experimentally validated through the use of a gradient heat (growth step) treatment to create a varying number density of Pb-rich phases where the extent of their crystallinity, size, and volume fraction within a glass matrix enables one to spatially tune the effective index of the nanocomposite, as shown in Fig. 7(d) (Kang *et al.*, 2020a,b).

Planar GRIN Materials

The GAP–Se material system with lower dimensions has been promising due to its versatility of integration into multi-component structures such as conformal coating as well as its ability to form high refractive index phases. During a thermal evaporation process which has been widely used to deposit ChG films, source materials are condensed on a room temperature or cold substrate. As the

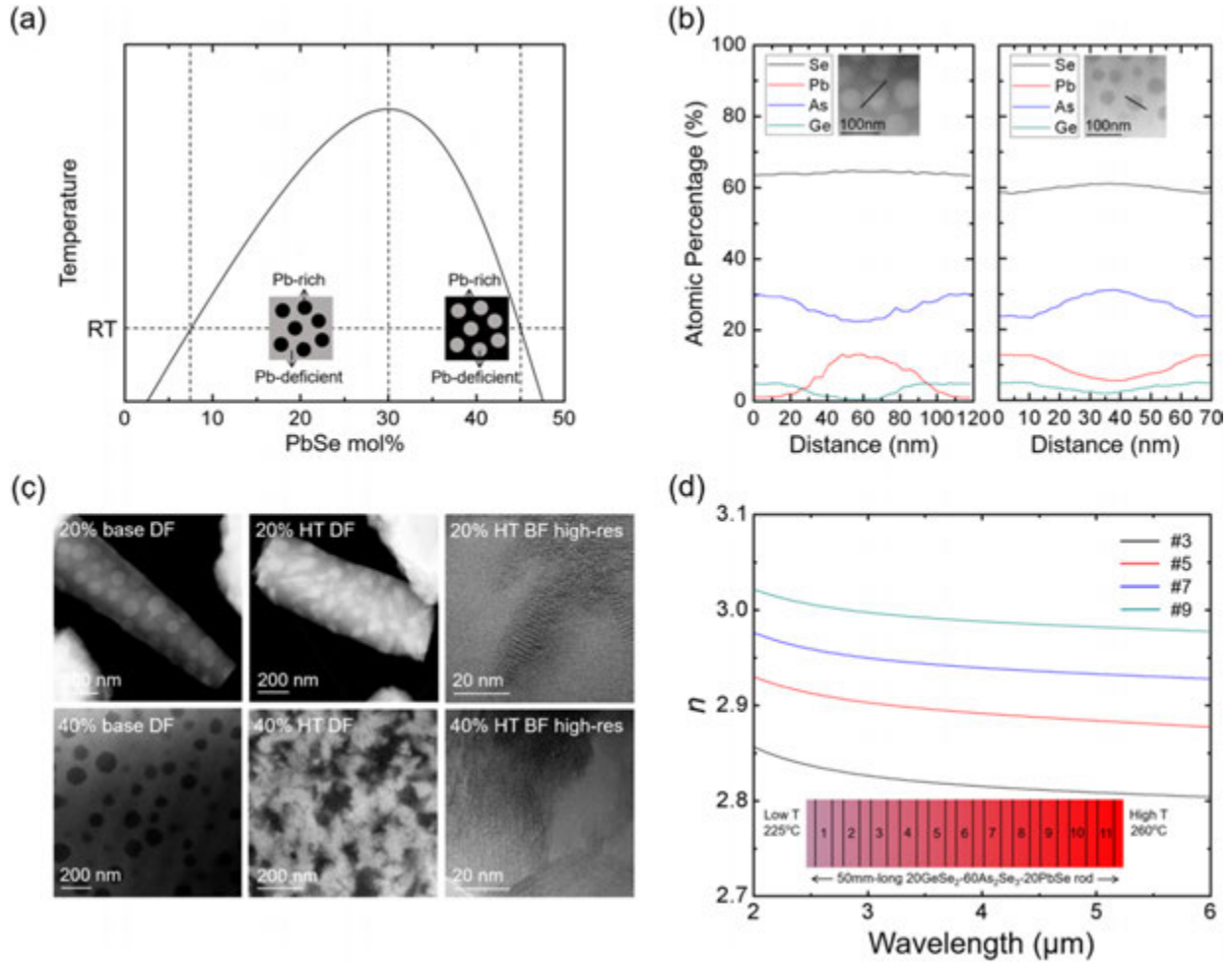


Fig. 7 (a) phase separation of bulk GAP-Se glasses upon standard melt-quench protocol, (b) element segregation across co-existing two phases, (c) microstructures of base glasses and glass-ceramics, (d) GRIN formation in a single bulk glass component. Reproduced with permission from (a) and (b) Gonçalves, C., Kang, M., Sohn, B.-U., *et al.*, 2018. New candidate multicomponent chalcogenide glasses for supercontinuum generation. *Appl. Sci* 8, 2082. Copyright 2018 MDPI. (c) and (d) Kang, M., Siskin, L., Lonergan, C., *et al.*, 2020b. Monolithic chalcogenide optical nanocomposites enable infrared system innovation: Gradient Refractive Index (GRIN) optics. *Adv. Opt. Mater.* 8, 2000150. Copyright 2020 Wiley.

thermal history in the deposition is energetic, the structure of deposited films remains far from equilibrium and do not typically undergo phase separation upon their deposition; i.e., it remains amorphous with a high concentration of molecular clusters with strained bonds, thereby lowering the activation energy required to transform them to a more stable configuration (Kang *et al.*, 2018a,b, 2019; Mingareev *et al.*, 2019; Mingareev *et al.*, 2020). Therefore, the as-deposited films are energetically metastable and sensitive to external stimulation such as laser exposure and thermal treatment. It has been reported that laser exposure with a wavelength near the optical bandgap energy of the film induces the otherwise homogeneous amorphous structure to be transformed into Pb-rich amorphous phases within a Pb-deficient amorphous matrix (Kang *et al.*, 2018a,b, 2019; Mingareev *et al.*, 2019, 2020). Since the laser exposure-induced Pb-rich amorphous phase is energetically unstable, post heat treatment leads to the conversion of the amorphous phase into Pb-rich nanocrystals with a refractive index far greater than that of the Pb-deficient matrix which still remains amorphous, as shown in Fig. 8(a) (Kang *et al.*, 2018a,b). It has been shown that laser exposure can be locally controlled and the laser fluence (power density $\times$ time) dictates the number density of Pb-rich amorphous phases which subsequently become high refractive index nanocrystals upon heat treatment, as illustrated in Fig. 8(b) (Kang *et al.*, 2018a,b). The effective refractive index (n_{eff}) of the resulting GC nanocomposite films increases with the volume fraction of the high refractive index nanocrystals. The nanocomposite film's n_{eff} can be approximated by the following equation (Kang *et al.*, 2020a,b):

$$n_{\text{eff}} \approx V_{\text{matrix}} \times n_{\text{matrix}} + \sum_{i=1}^N (V_{i,\text{secondary phase}} \times n_{i,\text{secondary phase}})$$

where n and V correspond to the refractive index and the volume fraction of the nanocomposite's phases, respectively. Fig. 8(c) shows that the novel photo-thermal process has been utilized to induce spatially-controlled crystallization within GAP-Se films, thereby realizing a GRIN component such as a diffraction grating structure (Kang *et al.*, 2018a,b).

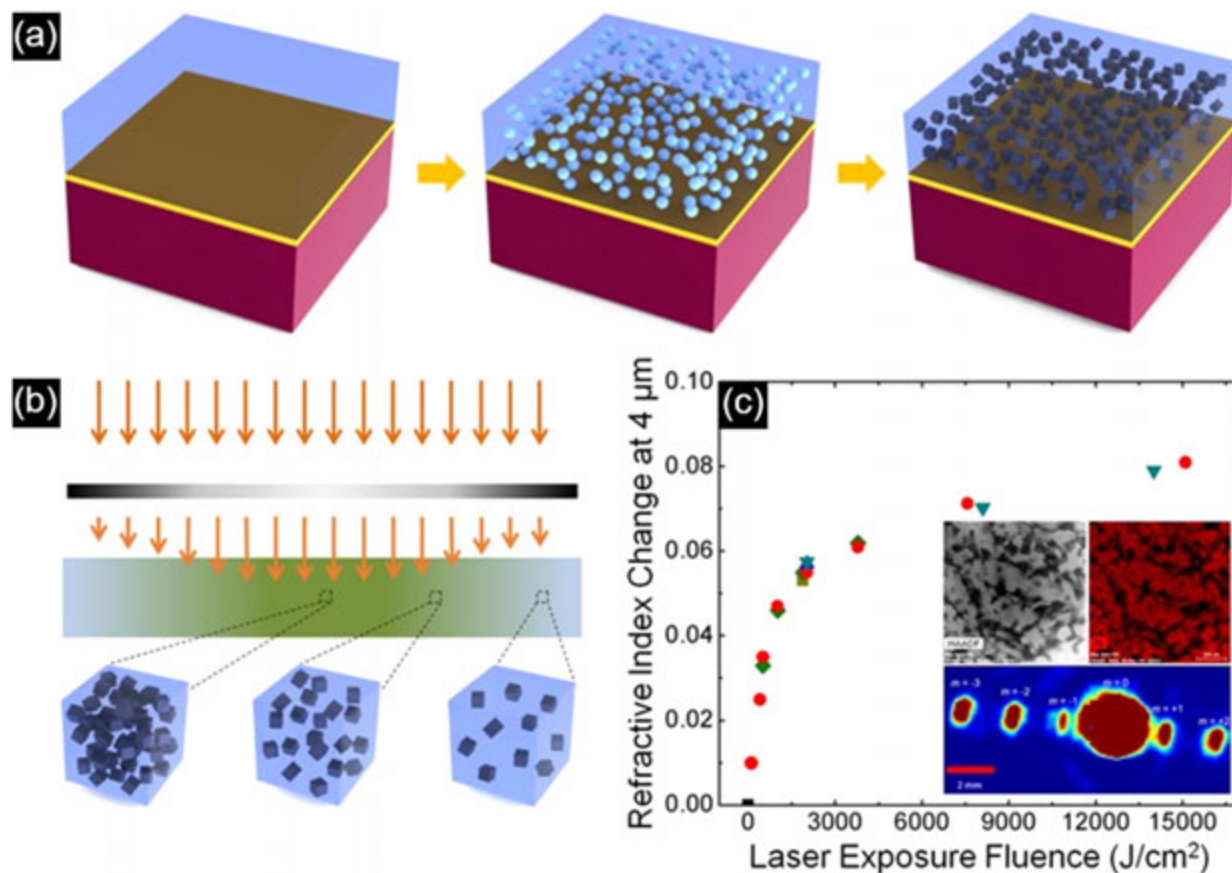


Fig. 8 (a) Film deposition and photo-thermal process leading to the formation of high index nanocrystals within a low index glass matrix, (b) Spatially-controlled laser exposure enabling a GRIN profile, and (c) Utilization of a process-structure-property relationship towards a diffractive GRIN structure. Reproduced with permission from Kang, M., Swisher, A.M., Pogrebnyanov, A.V., *et al.*, 2018b. Ultra-low dispersion multicomponent thin film chalcogenide glass for broadband gradient index optics. *Adv. Mater.* 30, 1803628. Copyright 2018 Wiley.

Low-Loss Waveguides

Reduction in the ChG material's dimension lends unique nature and planar system design opportunities to the device system. Due to their excellent light confinement, large refractive index, and broadband optical transparency, ChGs such as As_2S_3 and Ge-Sb-S have been actively utilized as optical waveguides, resonators, and interface layers in multi-material micro-phonic systems (Serna *et al.*, 2018; Du *et al.*, 2016; Hu *et al.*, 2007; Xia *et al.*, 2010). Furthermore, their exceptionally high nonlinearity and low multiphoton absorption are ideal for all optical signal processing, allowing ChG-based waveguides to be a core building block of integrated optical circuits (Musgraves *et al.*, 2011). Meanwhile, the most important functionality of waveguides is signal transport with minimum optical loss which has been shown to be as low as a few tenths of dB/cm in some ChG films. One of major sources for the loss is due to optical scattering which can occur from fabrication defects such as sidewall roughness, or where waveguides bend. This phenomenon is presented in a recent work where a series of As_2S_3 waveguides with different bend radii were tested to quantify the optical loss at the bending point, as shown in Fig. 9(a)–(c) (Xia *et al.*, 2010). Here, the bend waveguide simulation clearly indicates that the optical loss increases exponentially with decreasing bend radius (i.e., increasing curvature of the waveguide). To mitigate this issue, the addition of a GRIN structure to a bending point of a waveguide has been proposed, as shown in Fig. 9(d)–(f) where electric (E_z) and magnetic (H_z) field components of a wave propagating along a silica-based waveguide are observed to maintain their intensities and be confined within the waveguide (Cao *et al.*, 2017).

Optical Nonlinearity

Nonlinear Optical Property Measurements in ChG

The optical nonlinearity of a material significantly depends on the intensity of incident light which in turn is determined by a spacing between a laser beam source and a target material. The z-scan technique utilizes the phenomenon where a target sample is moved along the z-axis to vary incident beam intensity and extract its nonlinear optical parameters, as illustrated in

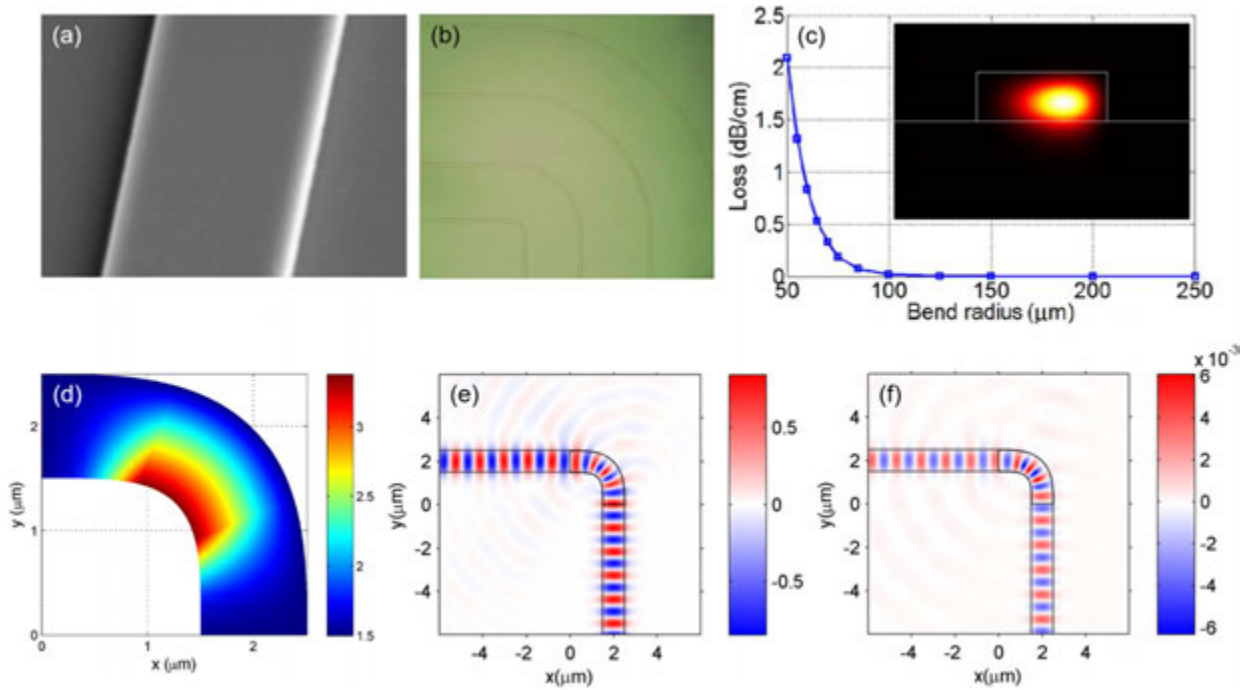


Fig. 9 (a) a SEM image of As_2S_3 waveguides on LiNbO_3 substrates, (b) an optical image of the waveguides with different bend radii, (c) optical loss based on bend waveguide simulations, (d) a GRIN structure in silica-based bend waveguides, (e) E_z of the waveguide in TE_0 mode, and (f) H_z of the waveguide in TE_0 mode. Reproduced with permission from (a)–(c) Xia, X., Chen, Q., Tsay, C., Arnold, C.B., Madsen, C.K., 2010. Low-loss chalcogenide waveguides on lithium niobate for the mid-infrared. *Opt. Lett.* 35, 3228. Copyright 2010 OSA. (d)–(f) reproduced with permission from Cao, Y., Mittra, R., Liu, Z., Zheng, J., 2017. Sharp bend in two-dimensional optical waveguide based on gradient refractive index structure. *Appl. Opt.* 56, 5336. Copyright 2017 OSA.

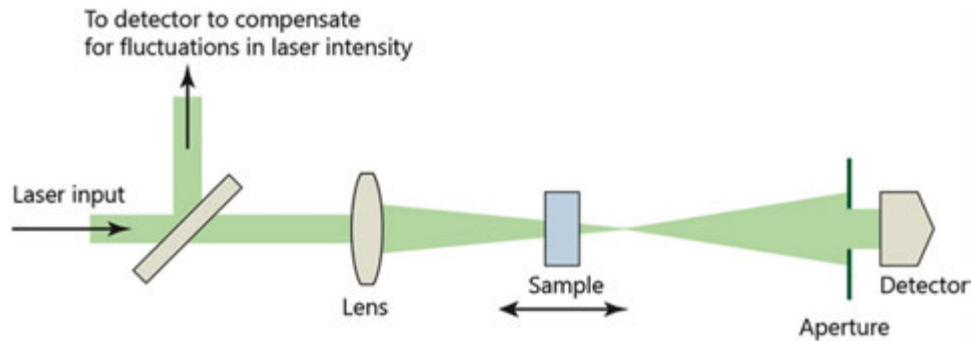


Fig. 10 A schematic of z-scan measurement configuration.

Fig. 10 (Sheik-Bahae *et al.*, 1989, 1991). Specifically, the z-scan technique is used to measure the nonlinear refractive index (n_2) and the nonlinear absorption coefficient (α) to measure both real and imaginary components of the optical nonlinearity. For n_2 , a closed-aperture configuration is used. The sample is placed in the focal plane of the lens, and then moved along the (axial) z axis direction, defined by the Rayleigh length. Since the target material reacts like a weak z-dependent lens in this configuration, the far-field aperture makes it possible to detect small distortions in the original beam. The focusing power of this weak nonlinear lens depends on n_2 , and therefore it is possible to extract its value by analyzing the z-dependent data acquired by the detector. For α , an open-aperture configuration is used. Specifically, the far-field aperture is removed and the whole signal is measured by the detector. In the whole signal, the small distortions in the original beam are insignificant and the z-dependent signal variation becomes dominant due to the nonlinear multi-photon absorption.

Z-scan is the most common method that has been used to measure n_2 and α for optical materials across a broad spectral window, though new techniques, such as D-scan (Serna *et al.*, 2019, 2018), have been developed for materials in other forms (i.e., planar thin films). Extension of these methods to the spectral window of use relies on an appropriate experimental set up (source/detector) and measurement away from the wavelength of resonance (typically defined as $h\nu/2$, where $h\nu$ is the optical bandgap

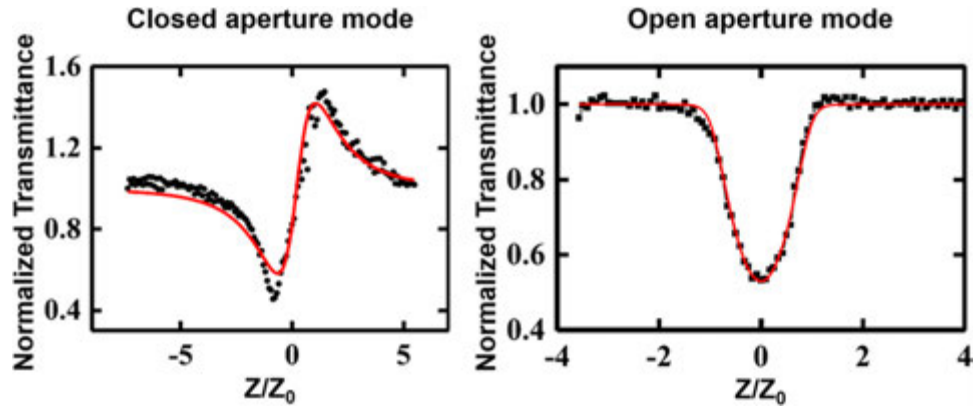


Fig. 11 Closed- and open-modes 4.6 μm z-scan profiles of $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$ bulk glasses. Reproduced with permission from Sohn, B.-U., Kang, M., Choi, J., *et al.*, 2019. Observation of very high order multi-photon absorption in GeSbS chalcogenide glass. *APL Photon.* 4, 036102. Copyright 2019 AIP.

energy of the media under test). **Fig. 11** shows representative closed- and open-modes z-scan profiles collected from $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$ bulk glasses (Sohn *et al.*, 2019). Each set of data includes two types of z-scan measurements including closed and open modes. The z-scan data in the closed mode are fitted with the following equation (Sohn *et al.*, 2017; Wang *et al.*, 2017; Bristow *et al.*, 2007; Kato *et al.*, 1995; Gholami *et al.*, 2011):

$$T_{CA} = 1 + \frac{4\Delta\varphi_0\left(\frac{z}{z_0}\right)}{\left[1 + \left(\frac{z}{z_0}\right)^2\right]\left[9 + \left(\frac{z}{z_0}\right)^2\right]}$$

where T_{CA} , $\Delta\varphi_0$, z , and z_0 are normalized transmittance in a closed-aperture mode, nonlinear refraction-induced phase change of the laser beam, sample location, and Rayleigh length, respectively. Values of $\Delta\varphi_0$ extracted from a fitted curve are then inserted in the following equation to extract values of nonlinear refractive indices:

$$n_2 = \frac{\Delta\varphi_0\lambda}{2\pi I_{00}L_{\text{eff}}}$$

where λ , I_{00} , and L_{eff} are laser wavelength, peak intensity, and effective path length for multiphoton absorption, respectively. The z-scan data in the open mode are fitted with the following equation (Sohn *et al.*, 2017; Wang *et al.*, 2017; Bristow *et al.*, 2007; Kato *et al.*, 1995; Gholami *et al.*, 2011):

$$T_{OA(nPA)} = \frac{1}{\left\{1 + (n-1)\alpha_n L_{\text{eff}} \left[\frac{I_{00}}{1 + \left(\frac{z}{z_0}\right)^2} \right]^{n-1} \right\}^{\frac{1}{n-1}}}}$$

where $T_{OA(nPA)}$, n , α_n correspond to normalized transmittance in an open-aperture mode, integer, and multiphoton absorption coefficient, respectively.

MWIR and LWIR Supercontinuum Generation in ChGs

Here, recent progress on Ge-Sb-S and Ge-Te-AgI based ChGs is introduced as model component behaviors to illustrate compositional variation on optical performance and other variation when formed into fiber. Among ChGs with wide transparency window and large refractive index facilitating mode confinement and bandgap engineering for photonic devices, Ge-based glasses with heavy metal oxide create smaller multiphoton spectra for laser and fiber optic applications (Fuxi, 1992). This phenomenon has necessitated the investigation of Ge-based ternary system's compositional dependence on its optical properties. $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$ has been demonstrated as one of the promising waveguide materials due to its radiation resistance and lower environmental toxicity as compared to As-based ChGs as well as its broadband optical transparency far into the MWIR spectral region and large optical nonlinearities (Vahalova *et al.*, 2000; Petit *et al.*, 2006; Asami *et al.*, 1997). A recent study utilizes $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$ waveguides to demonstrate supercontinuum (SC) generation (Choi *et al.*, 2016). **Fig. 12(a)** shows a schematic of $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$ ridge waveguide fabricated on a SiO_2 substrate where the films were deposited into a patterned substrate using thermal evaporation and tapers at input and output ports in the waveguide to facilitate fiber-waveguide coupling (Choi *et al.*, 2016). To see the evolution of SC generation as a function of input laser peak power (P_{peak}), a femtosecond fiber laser was guided into the $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$ waveguide. The resulting spectrum broadens from 130 to 320–510–840 nm at -30 dB level as P_{peak} increases from 120 to 220–280–340 W, respectively, as shown in **Fig. 12(b)** (Choi *et al.*, 2016). The remarkably large spectral broadening of 900 nm shows that GeSbS waveguides with a relatively large nonlinear parameter and negligible nonlinear losses could be a promising platform for

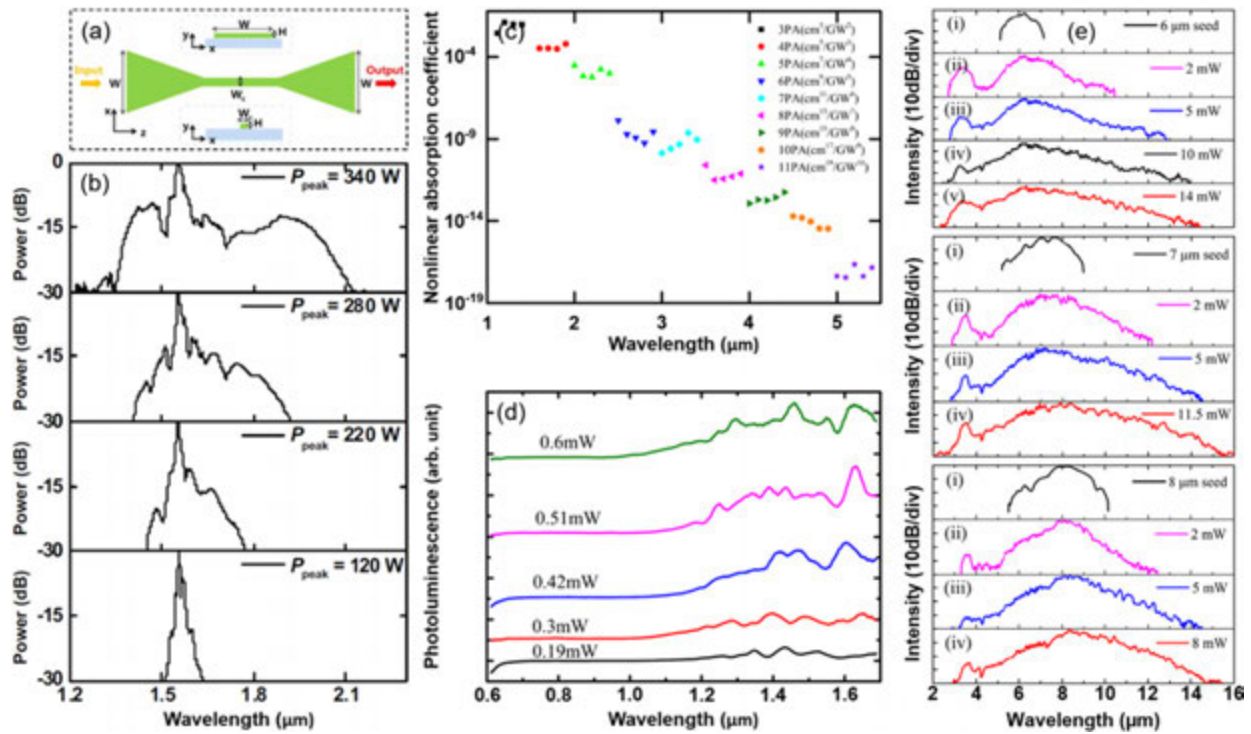


Fig. 12 (a) Schematic of Ge₂₃Sb₇S₇₀ waveguide (sky color: SiO₂ substrate, light green color: Ge₂₃Sb₇S₇₀ film), (b) output SC spectrum in Ge₂₃Sb₇S₇₀ waveguide as a function of input peak power, (c) multiphoton absorption coefficients of Ge₂₃Sb₇S₇₀ bulk glasses in the range 1.1–5.5 μm, (d) photoluminescence of Ge₂₃Sb₇S₇₀ bulk glasses induced by four-photon absorption. (e) experimental SC spectra pumped at 6, 7, and 8 μm in a step-index fiber consisting of (Ge₁₀Te₄₃)₉₀-(AgI)₁₀ core with two claddings including (Ge₁₀Te₄₀)₉₀-(AgI)₁₀ and Ge₁₀Sb₁₀Se₈₀. Reproduced with permission from (a) and (b) Choi, J., Han, Z., Sohn, B., *et al.*, 2016. Nonlinear characterization of GeSbS chalcogenide glass waveguides. *Sci. Rep.* 6, 39234. Copyright 2016 Springer Nature. (c) and (d) reproduced with permission from Sohn, B.-U., Kang, M., Choi, J., *et al.*, 2019. Observation of very high order multi-photon absorption in GeSbS chalcogenide glass. *APL Photon.* 4, 036102. Copyright 2019 AIP. (e) reproduced with permission from Zhao, Z., Wu, B., Wang, X., *et al.*, 2017. Mid-infrared supercontinuum covering 2.0–16 μm in a low-loss telluride single-mode fiber. *Laser Photon. Rev.* 11, 1700005. Copyright 2017 Wiley.

nonlinear optics applications at telecommunication wavelengths. Meanwhile, despite the implications from the nonlinear figure of merit, it is not always the case that the real part of the nonlinear susceptibility is the only factor worth maximizing for optical applications. The imaginary part of the nonlinear susceptibility is likewise important in that it can be utilized for photodetection, nonlinearly generated light sources, and band-structure identification (Sohn *et al.*, 2019; Zhao *et al.*, 2017). In this context, multiphoton absorption behavior and resulting photoluminescence (PL) of Ge₂₃Sb₇S₇₀ bulk glasses have been recently studied as shown in Fig. 12(c) and (d). Fig. 12(c) shows up to eleven-photon absorptions which is by far the highest order multiphoton absorption experimentally recorded to date (Sohn *et al.*, 2019). Such understanding of inter-band gap energy transition levels is crucial in applications such as SC or high harmonic generation where high pump intensities are required, since sub-bandgap excitation wavelength is much preferred to avoid any radiation-induced structural modification. Fig. 12(d) shows the PL signal observed between 1.1 and 1.68 μm, with its intensity increasing with the incident pump power (Sohn *et al.*, 2019). The slope obtained between the PL signal and input intensity was extracted to be 3.9, which is very close to the integer 4, implying that the PL is associated with four-photon absorption. The results pave the way towards new photonic device design leveraging very high order multiphoton absorption effects and multiphoton-excited PL. Meanwhile, the replacement of a light element for a heavier one typically enhances the optical nonlinearity of the materials (Wang, 2014) and broadens their optical transparency window (Wilhelm *et al.*, 2007). Especially, telluride glasses have been reported to possess the highest optical nonlinearity and broadest transmission window (Wilhelm *et al.*, 2007). Also, Se–Se induced multiphoton absorption, known to limit the broadening of SC spectra of telluride glasses, has been overcome by several candidate systems such as Ge–Te–I (Wilhelm *et al.*, 2007), Ge–Ga–Te (Danto *et al.*, 2006), and Ge–Te–AgI (Wang *et al.*, 2012; Conseil *et al.*, 2012) without containing Se. For iodine-containing tellurides, the high atomic weight of iodine allows the glass matrix's low phonon character to be maintained, thereby retaining the far-IR transparency. Furthermore, the nonlinearity of tellurides has been known to be further improved by doping with Cu or Ag (Ogusu and Shinkawa, 2009) and, based upon aforementioned findings, the Ge–Te–AgI glass system has been promising for fiber drawing and SC generation in the MWIR. Fig. 12(e) shows SC spectra excited by different pump wavelengths at 6, 7, and 8 μm in a (Ge₁₀Te₄₃)₉₀-(AgI)₁₀ fiber (Zhao *et al.*, 2017). At each pumping wavelength, the SC spectrum broadens as the pump power increases. The SC spectra are extended to 14.5, 16, and 15.4 μm under maximum pump power at different pump wavelengths of 6,

Table 1 Experimental MWIR SC generation in the ChG fiber (more than 12 μm)

Fiber	Fiber length (cm)	ZDW (μm)	Pump wavelength (μm)	SC bandwidth (μm)
As-Se	8.5	5.83	6.3	1.4–13.3 (30 dB)
As-Se	3	5.5	9.8	2–15.1 (–)
Ge-Sb-Se	20	5.5	6	1.8–14 (–)
Ge-As-Se-Te	23	10.5	4.5	1.5–14 (30 dB)
Ge-Te-AgI	14	10.5	7	2–16 (40 dB)

Note: Reproduced with permission from Zhao, Z., Wu, B., Wang, X., *et al.*, 2017. Mid-infrared supercontinuum covering 2.0–16 mm in a low-loss telluride single-mode fiber. *Laser Photon. Rev.* 11, 1700005. Copyright 2017 Wiley.

7, and 8 μm , respectively. **Table 1** tabulates the experimental SC data generated in a variety of ChG fibers where Te-based fibers have a broader transparent window than other ChG fibers, making them suitable for SC generation in the MWIR (Zhao *et al.*, 2017).

Summary

The key material attributes of chalcogenide glass and glass ceramic materials aimed at enabling their use in a variety of IR applications is presented. The ability to control and utilize the glass' composition, microstructure (where a glass ceramic is formed), and the material's resulting optical properties in bulk, film, fiber, and waveguide forms is reviewed. Also discussed are lingering issues that remain as challenges to the community in translating these glasses into these forms, including relevant microstructural and optical metrology methods which have been used to assess them. The effort and progress made by the glass science and engineering community as well as the optical design and fabrication "users" of the glasses has advanced considerably since the turn of the century. These efforts will likely continue as researchers and manufacturers evaluate and develop strategies to further optimize properties suitable for higher volume applications. Such work will enable chalcogenide glasses for use in a diverse range of applications and highlight the promising future of these novel materials in next generation optical systems and beyond.

References

- Adam, J.L., Zhang, X., 2014. Chalcogenide Glasses: Preparation, Properties and Applications. Woodhead Publishing Limited.
- Asami, T., Matsuishi, K., Onari, S., Arai, T., 1997. Low frequency Raman scattering spectra of $(\text{GeS}_2)_{1-x}(\text{Sb}_2\text{S}_3)_x$ amorphous semiconductors. *J. Non-Cryst. Solids* 211, 89.
- Beadie, G., Rabinovich, W.S., Sanghera, J., Aggarwal, I., 1998. Fabrication of microlenses in bulk chalcogenide glass. *Opt. Commun.* 152, 215.
- Bixby W.E., Ullrich O.A., 1956. Method for the production of a photographic plate, U.S. Patent 2,753,278.
- Booth, M.J., 2014. Adaptive optical microscopy: The ongoing quest for a perfect image. *Light Sci. Appl.* 3, e165.
- Bristow, A., Rotenberg, N., van Driel, H., 2007. Two-photon absorption and Kerr coefficients of silicon for 850–2200 nm. *Appl. Phys. Lett.* 90, 191104.
- Buff, A.K., 2016. A Study of Crystallization Behavior in Phase Separated Chalcogenide Glasses. Master Thesis. University of Central Florida.
- Cao, Y., Mittra, R., Liu, Z., Zheng, J., 2017. Sharp bend in two-dimensional optical waveguide based on gradient refractive index structure. *Appl. Opt.* 56, 5336.
- Carlie, N., Musgraves, J.D., Zdyrko, B., *et al.*, 2010. Integrated chalcogenide waveguide resonators for mid-IR sensing: leveraging material properties to meet fabrication challenges. *Opt. Express* 18, 26728.
- Cha, D.H., Kim, H., Hwang, Y., Jeong, J.C., Kim, J., 2012. Fabrication of molded chalcogenide-glass lens for thermal imaging applications. *Appl. Opt.* 51, 5649.
- Choi, J., Han, Z., Sohn, B., *et al.*, 2016. Nonlinear characterization of GeSbS chalcogenide glass waveguides. *Sci. Rep.* 6, 39234.
- Conseil, C., Bastien, J.C., Boussard-Pledel, C., *et al.*, 2012. Te-based chalcogenide glasses for far-infrared optical fiber. *Opt. Mater. Express* 2, 1470.
- Danto, S., Houzot, P., Boussard-Pledel, C., *et al.*, 2006. A family of far-infrared-transmitting glasses in the Ga-Ge-Te system for space applications. *Adv. Funct. Mater.* 16, 1847.
- Dianov, E.M., Shiryayev, V.S., Izyneev, A.A., Plotnichenko, G.E., Charbanov, M.F., 1997. Crystallization kinetics of praseodymium-doped $(\text{Ga}_2\text{S}_3)_{0.7}(\text{La}_2\text{S}_3)_{0.3}$ glass. *Inorg. Mater.* 33, 975.
- Du, Q., Huang, Y., Li, J., *et al.*, 2016. Low-loss photonic device in Ge-Sb-S chalcogenide glass. *Opt. Lett.* 41, 3090.
- Eggleton, B.J., Luther-Davies, B., Richardson, K.A., 2011. Chalcogenide photonics. *Nat. Photon.* 5, 141.
- Francois-Saint-Cyr, H., Kang, M., Martin, I., *et al.*, 2019. Three-dimensional microstructural characterization of novel chalcogenide nanocomposites for gradient refractive index applications. *Microsc. Microanal.* 25, 2500.
- Fuxi, G., 1992. Structure, properties and applications of chalcogenide glasses: A review. *J. Non-Cryst. Solids* 140, 184.
- Gholami, F., Zlatanovic, S., Simic, A., *et al.*, 2011. Third-order nonlinearity in silicon beyond 2350 nm. *Appl. Phys. Lett.* 99, 081102.
- Gibson, D., Bayya, S., Nguyen, V., *et al.*, 2019. Multispectral IR optics and GRIN. In: *Proceedings of the SPIE*, vol. 10998, 10998-12.
- Goncalves, C., Kang, M., Sohn, B.-U., *et al.*, 2018. New candidate multicomponent chalcogenide glasses for supercontinuum generation. *Appl. Sci.* 8, 2082.
- Hari, P., Taylor, P.C., King, W.A., LaCourse, W.C., 1998. Metastable, drawing-induced crystallization in As_2Se_3 fibers. *J. Non-Cryst. Solids* 227, 789.
- Hilton, A.R., 2010. Chalcogenide Glasses for Infrared Optics. McGraw Hill.
- Hisakuni, H., Tanaka, K., 1995. Optical fabrication of microlenses in chalcogenide glasses. *Opt. Lett.* 20, 958.
- Hu, J., Tarasov, V., Agarwal, A., *et al.*, 2007. Fabrication and testing of planar chalcogenide waveguide integrated microfluidic sensor. *Opt. Express* 15, 2307.
- Kang, M., Siskin, L., Cook, J., *et al.*, 2018a. Refractive index patterning of infrared glass ceramics through laser-induced vitrification. *Opt. Mater. Express* 8, 2722.
- Kang, M., Swisher, A.M., Pogrebnyanov, A.V., *et al.*, 2018b. Ultra-low dispersion multicomponent thin film chalcogenide glass for broadband gradient index optics. *Adv. Mater.* 30, 1803628.
- Kang, M., Malendevych, T., Yin, G., *et al.*, 2019. Scalable laser-written Ge-As-Pb-Se chalcogenide glass-ceramic films and the realization of infrared gradient refractive index elements. In: *Proceedings of the SPIE*, vol. 10998, 109980E-1.

- Kang, M., Francois-Saint-Cyr, H., Martin, I., *et al.*, 2020a. Unveiling true three-dimensional microstructural evolution in novel chalcogenide nanocomposites as a route to infrared gradient refractive index functionality. *Microsc. Microanal.* 26 (S2), 1–3.
- Kang, M., Siskin, L., Loneragan, C., *et al.*, 2020b. Monolithic chalcogenide optical nanocomposites enable infrared system innovation: Gradient Refractive Index (GRIN) optics. *Adv. Opt. Mater.* 8, 2000150.
- Kato, T., Suetsugu, Y., Takagi, M., Sasaoka, E., Nishimura, M., 1995. Measurements of the nonlinear refractive index in optical fiber by the cross-phase-modulation method with depolarized pump light. *Opt. Lett.* 20, 988.
- Kokorina, V.F., 1996. *Glasses for Infrared Optics*. CRC Press.
- Kolobov, A.V., Tanaka, K., 2001. Photoinduced phenomena in amorphous chalcogenides: from phenomenology to nanoscale. In: Nalwa, H.S. (Ed.), *Handbook of Advanced Electronic and Photonic Materials and Devices*. Academic Press.
- Kolobov, A.V., Tominaga, J., 2012. *Chalcogenides: Metastability and Phase Change Phenomena*. Springer.
- Koontz, E., 2014. Characterization of Structural Relaxation in Inorganic Glasses Using Length Dilatometry. PhD Dissertation. Clemson University.
- Kumaresan, Y., Rammohan, A., Dwivedi, P.K., Sharma, A., 2013. Large area ir microlens arrays of chalcogenide glass photoresists by grayscale maskless lithography. *ACS Appl. Mater. Interfaces* 5, 7094.
- Li, H.H., 1980. Refractive index of silicon and germanium and its wavelength and temperature derivatives. *J. Phys. Chem. Ref. Data* 9, 561.
- Li, L., Lin, H., Qiao, S., *et al.*, 2014. Integrated flexible chalcogenide glass photonic devices. *Nat. Photon.* 8, 643.
- Martin, S.W., Bloyer, D.R., 2010. Preparation of high-purity vitreous B_2S_3 . *J. Am. Ceram. Soc.* 73, 3481.
- Massera, J., 2009. Nucleation and Growth of Tellurite-Based Glasses Suitable for Mid-infrared Applications. PhD Dissertation. Clemson University.
- Massera, J., Haldeman, A., Milanese, D., *et al.*, 2010a. Processing and characterization of a core-clad tellurite glass preforms and fibers fabricated by rotational casting. *J. Opt. Mater.* 32, 582.
- Massera, J., Remond, J., Musgraves, J.D., *et al.*, 2010b. Nucleation and growth behavior of glasses in the TeO_2 - Bi_2O_3 - ZnO glass system. *J. Non-Cryst. Solids* 356, 2947.
- Mauro, J.C., Tandia, A., Vargheese, K.D., Mauro, Y.Z., Smedskjaer, M.M., 2016. Accelerating the design of functional glasses through modeling. *Chem. Mater.* 28, 4267.
- Mikhailov, M.D., Tveryanovick, A.S., 1986. Critical cooling rates of chalcogenide glass-forming melts. *Fizika I Khimiya Stekla* 12, 274.
- Mingareev, I., Kang, M., Malendevych, T., *et al.*, 2019. Laser-induced modification of local refractive index in infrared glass-ceramic films. In: *Proceedings of the SPIE*, vol. 10906, 109060X.
- Mingareev, I., Kang, M., Truman, M., *et al.*, 2020. Spatial tailoring of the refractive index in infrared glass-ceramic films enabled by direct laser writing. *Opt. Laser Technol.* 126, 106058.
- Moore, D.T., 1980. Gradient-index optics: A review. *Appl. Opt.* 19, 1035.
- Musgraves, J.D., Wachtel, P., Novak, S., Wilkinson, J., Richardson, K., 2011. Composition dependence of the viscosity and other physical properties in the arsenic selenide glass system. *J. Appl. Phys.* 110, 063503.
- Ogusu, K., Shinkawa, K., 2009. Optical nonlinearities in As_2Se_3 chalcogenide glasses doped with Cu and Ag for pulse durations on the order of nanoseconds. *Opt. Express* 17, 8165.
- Parvanov, S., Vassilev, V., Tomova, K., 2008. Optical properties of new chalcogenide glasses from the $GeSe_2$ - Sb_2Se_3 - $PbSe$ system. *Mater. Lett.* 62, 2021.
- Petit, L., Carlie, N., Richardson, K.C., *et al.*, 2006. Correlation between physical, optical and structural properties of sulfide glasses in the system Ge - Sb - S . *Mater. Chem. Phys.* 97, 64.
- Ramachandran, S., Pepper, J.C., Brady, D.J., Bishop, S.G., 1997. Micro-optical lenslets by photo-expansion in chalcogenide glasses. *J. Lightwave Technol.* 15, 1371.
- Richardson, K., Kang, M., 2020. Chalcogenide materials for mid-wave infrared fiber. In: Jackson, S., Vallee, R., Bernier, M. (Eds.), *Mid-Infrared Fibre Photonics*. Elsevier.
- Richardson, K., Buff, A., Smith, C., *et al.*, 2016. Engineering novel infrared glass ceramics for advanced optical solutions. In: *Proceedings of the SPIE*, vol. 9822, 982205.
- Richardson, K., Kang, M., Siskin, L., *et al.*, 2018. Advances in infrared GRIN: A review of novel materials towards components and devices. In: *Proceedings of the SPIE*, vol. 10627, 106270A.
- Saitoh, A., Tanaka, K., 2003. Self-developing aspherical chalcogenide-glass microlenses for semiconductor lasers. *Appl. Phys. Lett.* 84, 1725.
- Sanchez, E.A., Waldmann, M., Arnold, C.B., 2011. Chalcogenide glass microlenses by inkjet printing. *Appl. Opt.* 50, 1974.
- Sanghera, J.S., Aggarwal, I.D., 1999. Active and passive chalcogenide glass optical fibers for IR applications: A review. *J. Non-Cryst. Solids* 256, 6.
- Seddon, A.B., Pan, W.J., Furniss, D., *et al.*, 2006. Fine embossing of chalcogenide glasses – A new fabrication route for photonic integrated circuits. *J. Non-Cryst. Solids* 352, 2515.
- Serna, S., Lin, H., Alonso-Ramos, C., *et al.*, 2018. Nonlinear optical properties of integrated $GeSbS$ chalcogenide waveguides. *Photon. Res.* 6, B37.
- Serna, S., Lin, H., Alonso-Ramos, C., *et al.*, 2019. Engineering third order optical nonlinearities in hybrid chalcogenides-on-silicon platform. *Opt. Lett.* 44, 5009.
- Sharma, R., Welch, R., Kang, M., *et al.*, 2020. Impact of morphology and microstructure on the mechanical properties of Ge - As - Pb - Se glass ceramics. *Appl. Sci.* 10, 2836.
- Sheik-Bahae, M., Said, A.A., van Stryland, E.W., 1989. Sensitive measurement of optical nonlinearities using a single beam. *Opt. Lett.* 14, 955.
- Sheik-Bahae, M., Hutchings, D.C., Hagan, D.J., van Stryland, E.W., 1991. Dispersion of bound electron nonlinear refraction in solids. *IEEE J. Quantum Electron.* 27, 1296.
- Shiryaev, V.S., Adam, J.-L., Zhang, X.H., 2004. Calorimetric study of characteristic temperatures and crystallization behaviour in Ge - As - Se - Te glass system. *J. Phys. Chem. Solids* 65, 1737.
- Siskin, L., 2017. Laser-Induced Crystallization Mechanisms in Chalcogenide Glass Materials for Advanced Optical Functionality. PhD Dissertation. University of Central Florida.
- Siskin, L., Kang, M., Veras, J.M., *et al.*, 2019. Infrared glass ceramics with multi-dispersion and gradient refractive index attributes. *Adv. Funct. Mater.* 29, 1902217.
- Sohn, B.-U., Kang, M., Choi, J., *et al.*, 2019. Observation of very high order multi-photon absorption in $GeSbS$ chalcogenide glass. *APL Photon.* 4, 036102.
- Sohn, B.-U., Monmeyran, C., Kimerling, L.C., Agarwal, A.M., Tan, D.T.H., 2017. Kerr nonlinearity and multi-photon absorption in germanium at mid-infrared wavelengths. *Appl. Phys. Lett.* 111, 091902.
- Texas Instruments, 1967. Multi-component chalcogenide glass compositions, US3338728A (Ge - P - Te), US3343972A (Ge - Te - As) and US3360649A (Ge - Sb - S).
- Tikhomirov, V.K., Furniss, D., Seddon, A.B., *et al.*, 2004. Glass formation in the Te -enriched part of the quaternary Ge - As - Se - Te system and its implication for mid-infrared optical fibres. *Infrared Phys. Technol.* 45, 115.
- Vahalova, R., Tichy, L., Vlcek, M., Ticha, H., 2000. Far infrared spectra and bonding arrangement in some Ge - Sb - S glasses. *Phys. Status Solidi A* 181, 199.
- Wang, H., Zhang, X., Yang, G., *et al.*, 2009. Micro-crystallization of the infrared transmitting chalcogenide glass in $GeSe_2$ - As_2Se_3 - $PbSe$ system. *Ceram. Int.* 35, 83.
- Wang, R., 2014. *Amorphous Chalcogenides: Advances and Applications*. Pan Stanford Publishing.
- Wang, T., Venkatram, N., Gosciniaik, J., *et al.*, 2017. Multi-photon absorption and third-order nonlinearity in silicon at mid-infrared wavelengths. *Opt. Express* 21, 32192.
- Wang, X., Nie, Q., Wang, G., *et al.*, 2012. Investigation of Ge - Te - AgI chalcogenide glass for far-infrared application. *Spectrochim. Acta. A: Mol. Biomol. Spectrosc.* 86, 586.
- Wilhelm, A.A., Boussard-Pledel, C., Coulombier, Q., *et al.*, 2007. Development of far-infrared-transmitting Te based glasses suitable for carbon dioxide detection and space optics. *Adv. Mater.* 19, 3796.
- Xia, F., Zhang, X., Ren, J., *et al.*, 2006. Glass formation and crystallization behavior of a novel $GeSe_2$ - Sb_2S_3 - PbS chalcogenide glass system. *J. Am. Ceram. Soc.* 89, 2154.
- Xia, X., Chen, Q., Tsay, C., Arnold, C.B., Madsen, C.K., 2010. Low-loss chalcogenide waveguides on lithium niobate for the mid-infrared. *Opt. Lett.* 35, 3228.
- Yadav, A., Kang, M., Smith, C., *et al.*, 2017. Influence of phase separation on structure-property relationships in the $(GeSe_2-3As_2Se_3)_{1-x}PbSe_x$ glass system. *Phys. Chem. Glasses* 58, 115.
- Yadav, A., Buff, A., Kang, M., *et al.*, 2019. Melt property variation in $GeSe_2$ - As_2Se_3 - $PbSe$ glass ceramics for infrared gradient refractive index (GRIN) applications. *Int. J. Appl. Glass Sci.* 10, 27.
- Yang, G., Zhang, X., Ren, J., *et al.*, 2007. Glass formation and properties of chalcogenide in a $GeSe_2$ - As_2Se_3 - $PbSe$ system. *J. Am. Ceram. Soc.* 90, 1500.

- Zhang, X.H., Guimond, Y., Bellec, Y., 2003. Production of complex chalcogenide glass optics by molding for thermal imaging. *J. Non-Cryst. Solids* 326, 519.
- Zhang, X.H., Ma, H., Lucas, J., 2004. Evaluation of glass fibers from the Ga-Ge-Sb-Se system for infrared applications. *Opt. Mater.* 25, 85.
- Zhang, Y., Chou, J.B., Li, J., *et al.*, 2019. Broadband transparent optical phase change materials for high-performance nonvolatile photonics. *Nat. Commun.* 10, 4279.
- Zhao, D., Xia, F., Chen, G., *et al.*, 2005. Formation and properties of chalcogenide glasses in the $\text{GeSe}_2\text{-As}_2\text{Se}_3\text{-CdSe}$ system. *J. Am. Ceram. Soc.* 88, 3143.
- Zhao, Z., Wu, B., Wang, X., *et al.*, 2017. Mid-infrared supercontinuum covering 2.0–16 μm in a low-loss telluride single-mode fiber. *Laser Photon. Rev.* 11, 1700005.

Glasses: Oxynitride Glass Formation and Structure

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Introduction

In modern industrial sectors, such as microelectronics, optoelectronics, communications technologies and biomedical devices, research continues to find useful lighter, stiffer materials, including glasses, with superior mechanical properties such as higher elastic moduli, hardness, strength and fracture toughness. The replacement of some of the oxygen atoms by nitrogen in oxide glasses (principally silicates, aluminosilicates and phosphates) leads to definite improvements in these properties and changes in thermal and other properties as a result of extra cross-linking of the glass network when nitrogen substitutes for oxygen.

The preparation, structure and properties of these oxynitride glasses have been extensively studied and some success has been achieved in understanding how changes in glass composition affect structural parameters and their relationship to properties. A number of reviews of oxynitride glasses have been published (Hampshire, 1993; Leng-Ward and Lewis, 1989; Sakka, 1995; Hampshire, 2003, 2008; Pomeroy and Hampshire, 2008; Becher *et al.*, 2011).

Early Research on Nitrogen Solubility in Commercial Glasses

Seeds or small bubbles caused by gaseous inclusions are always problematic in glass manufacture, particularly for optical glasses. It was shown (Todd, 1956; Neerman and Bryan, 1959) that often these defects consisted mainly of nitrogen. Mulfinger and Meyer (1963) and Mulfinger (1966) reported on the first investigations of physical and chemical solubilities of gaseous nitrogen in soda-lime-silica glasses and how this related to inclusions encountered in glass manufacture. The physical solubility of nitrogen in these glasses was found to be extremely low after bubbling nitrogen gas through the glass melt at 1400°C for 16 h.

By melting the glass in a gas furnace under reducing conditions, 10 times more nitrogen is dissolved than with the physical solubility. In strongly reducing atmospheres considerably more nitrogen is chemically dissolved (between 100 and 10⁴ times that of the physical solubility). If ammonia gas is bubbled through the glass melt at 1400°C for 5 h the chemical solubility of nitrogen in the glass reaches 0.33 wt.%, a value more than 10⁵ times higher than that for physical solubility. Mulfinger (1966) proposed that nitrogen substitutes for oxygen in the SiO₄ tetrahedra within the silicate network when conditions are reducing. This substitution leads to a higher than average coordination of non-metal atoms as in:

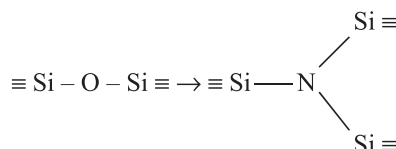


Fig. 1 shows a simple representation of a nitrogen atom bonded to three SiO₄ tetrahedra in a silicate glass. This results in increased crosslinking and, hence, a more rigid glass network.

Elmer and Nordberg (1967) introduced ten times as much nitrogen (3 wt.%) into a porous borosilicate glass, used as high-energy lamp envelopes, by heating in ammonia. Significant changes in properties of the glass were observed: increases in indentation hardness and electrical resistivity, and a decrease in thermal expansion coefficient. In this case, the changes observed in the physical properties of the glass resulted from the incorporation of nitrogen into the glass structure as hypothesized by Mulfinger (1966). A higher annealing temperature was required for these nitrogen-containing glasses. Normally for the borosilicate glass, devitrification could be induced electrolytically as a result of concentration of alkali ions at the cathode caused by their migration under the influence of the electric field. However, it was reported that the nitrogen-containing glasses did not crystallize as easily, thought to be due to increased viscosity, because of the presence of (=NH) and (=N-) groups.

Harding and Ryder (1970) introduced small concentrations of nitrogen into a commercial container glass batch using silicon nitride and reported increased softening temperature, viscosity and resistance to devitrification.

Davies and Meherali (1971) measured the equilibrium solubility of nitrogen in aluminosilicate melts (<38 mol.% SiO₂) similar in composition to many blast furnace slags. They found that severe reducing conditions had to be imposed in order to dissolve significant amounts of nitrogen into these melts and concluded that the solubility of nitrogen was chemical rather than physical increasing with increasing basicity, indicating that bridging rather than non-bridging oxygen atoms in the aluminosilicate glass structure were involved in the exchange reaction.

Dancy and Janssen (1976) compared physical and chemical methods of incorporating nitrogen into CaO-SiO₂-Al₂O₃ metallurgical slag melts under reducing conditions. In the presence of graphite, the solubility of nitrogen increases as a function of

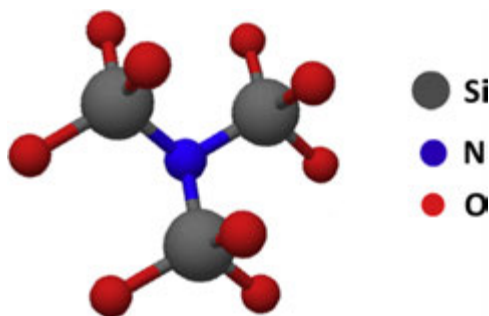


Fig. 1 Representative structure showing a tri-coordinated nitrogen atom bonded to three SiO_4 tetrahedra in an oxynitride glass.

the CaO content and inversely with the SiO_2 content. The solubility is between 0.25 and 2.5 wt.% N after 24 h at 1550°C and varies with temperature, whereas, when Si_3N_4 was added to the melt (under N_2), nitrogen incorporation was very rapid and reached significantly higher levels (4 wt.%). It was suggested that most silicate melts are not significantly reducing enough to dissolve N_2 to any great extent and that it was necessary to dissolve nitrogen from nitride compounds such as silicon nitride.

Substitution of Nitrogen Into Silicates and Aluminosilicates

In all silicates, the fundamental structural unit consists of a central Si atom surrounded by 4 oxygen atoms at the corners of a tetrahedron – SiO_4 – carrying 4 negative charges. The tetrahedra share oxygen corners to form rings, chains, 2-dimensional sheets or 3-D networks. The AlO_4 tetrahedron with 5 negative charges is approximately the same size as SiO_4 and so it can replace the SiO_4 tetrahedron without structural change provided that electrical neutrality is maintained by the presence of other cations (e.g., Na, Ca, Mg, etc).

Wild *et al.* (1968) reported on crystal structure determination of α and β silicon nitrides in which the local atomic arrangement is a tetrahedral array of N atoms around a central Si atom, similar to the SiO_4 tetrahedron within silicates. A surprising result was that in α - Si_3N_4 about 1 in 30 N atoms are replaced by O atoms with compensating cation vacancies. They argued that it should be possible to replace much more N by O, which could be done by simultaneously replacing Si^{4+} by Al^{3+} to maintain the charge balance and had predicted that there was “a good possibility of developing a completely new range of nitride and oxynitride materials – vitreous as well as crystalline – based on the Si-Al-O-N system.” This led to the discovery that up to 65% Al_2O_3 could be reacted with silicon nitride to form an expanded β - Si_3N_4 solid solution – β' -SiALON (Jack and Wilson, 1972) and the proposal that nitrogen could be easily incorporated into the network of silicate and aluminosilicate glasses (Jack, 1976).

During this period, major interest was shown in silicon nitride and how it could be sintered to full density. One problem is that its self-diffusivity is quite low and atomic species only become sufficiently mobile for densification at temperatures where the decomposition of silicon nitride commences ($\sim 1850^\circ\text{C}$). Initial investigations (Lumby and Coe, 1970) involved hot-pressing α - Si_3N_4 with MgO at temperatures up to 1750°C which resulted in materials with much higher strengths than previously found. Wild *et al.* (1972) investigated the role of MgO in hot-pressing showing that it reacts with the surface silica always present on Si_3N_4 particles and at temperatures above 1400°C it forms a liquid into which some nitrogen is incorporated and this cools to give a magnesium silicon oxynitride glass as shown by subsequent divitrification to form enstatite (MgSiO_3) and silicon oxynitride ($\text{Si}_2\text{N}_2\text{O}$). As hot-pressing is restricted to simple shapes, this is a serious disadvantage for more complicated components. It was subsequently found that a combination of Y_2O_3 and Al_2O_3 additives (Tsuge and Nishida, 1978) provided the necessary conditions for pressureless liquid phase sintering (Hampshire and Jack, 1981) with the formation of an intergranular Y-Si-Al-O-N glass phase on cooling.

As progress was made in understanding the nature of silicon nitride ceramics (Riley, 2000; Lange, 2006; Hampshire, 2009), how additive chemistry controlled microstructure and how microstructure affected properties (Becher *et al.*, 1998; Sun *et al.*, 1998), there was a growing impetus to understand the nature of these intergranular oxynitride glass phases. This resulted in a number of investigations, as outlined below, of oxynitride glass formation, structure, properties and crystallization in various M-Si-O-N, M-Si-Al-O-N and M-Si-Mg-O-N systems, where M is a modifying cation such as Mg, Ca, Ba, Sc, Y and the rare earth lanthanides.

Preparation of Si-Based Oxynitride Glasses

Oxynitride glasses have conventionally been synthesized by mixing the appropriate powders – silica, alumina, the modifying oxide(s) plus silicon nitride or aluminum nitride – in isopropyl alcohol in a ball mill, followed by evaporation of the alcohol. Compacts of the mixtures (up to 100 g) are melted in boron nitride lined graphite crucibles under 0.1 MPa nitrogen pressure at temperatures in the range 1650 – 1750°C for 1 h, after which the crucible is quickly removed from the furnace and poured into a preheated graphite mold at ~ 850 – 900°C . The glass is annealed close to its glass transition temperature (T_g) for one hour to

remove stresses and then slowly cooled (Hampshire *et al.*, 1994; Hampshire, 2008). Glasses that have been prepared by this route have been studied most extensively.

The upper limit for firing temperatures is determined by thermal decomposition of Si_3N_4 , whereas the lower limit is set by the temperature for complete melting of the particular composition. Oxynitride melts have higher viscosities than their oxide equivalents at these temperatures (Hampshire *et al.*, 1985). The temperature must thus be high enough to give the melt a fluidity that ensures good homogenization, but low enough to avoid decomposition reactions.

The main difficulties encountered in the preparation of oxynitride glasses are the fairly high melting temperatures, the requirement for a low oxygen partial pressure during melting, to avoid oxidation of glass forming components, and also the limited number of nitride compounds to be used as the source of nitrogen. All investigators found that viscosity increases with N content (Hampshire and Pomeroy, 2004). There are also a limited number of non-reactive crucible materials with oxides reacting too easily with oxynitride melt compositions and platinum or molybdenum also reacting under reducing conditions. Hence the use of BN or BN-coated graphite crucibles.

Oxynitride glasses can also be prepared by melting mixtures of a pure metal or the metal hydride with silica and silicon nitride under a N_2 atmosphere which has enabled the preparation of oxynitride glasses with significantly higher concentrations of nitrogen up to 18–20 at.% (Hakeem *et al.*, 2005; Sharafat *et al.*, 2008, 2009).

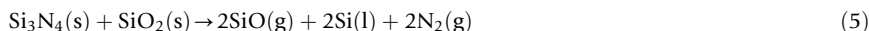
Oxynitride glasses have also been prepared at lower temperatures by using sol-gel techniques (Brinker and Haaland, 1983; Brow and Pantano, 1984a) in which oxide gels are converted to oxynitride gels by treatment with flowing anhydrous ammonia at temperatures in the range 700–1100°C. Brinker and Haaland (1983) synthesized dense, colorless and homogeneous glasses in the Na-Al-Ba-Si-O-N system.

Elemental losses have been reported to occur, to a varying degree, during the preparation of oxynitride glasses above $\sim 1550^\circ\text{C}$. Loehman (1985) compared the relative oxidation or reduction tendencies of possible reactions occurring in oxynitride melts using standard Gibbs energies (ΔG°) plotted as functions of temperature on an Ellingham diagram. The positions of the ΔG° versus T plots for the following oxidation reactions (1) and (2) allow the stabilities of melts containing Si_3N_4 or AlN and various oxides to be determined:



Modifier (M) oxides such as MgO , CaO , Al_2O_3 , Y_2O_3 and Li_2O have ΔG° values which are more negative than ΔG° for oxidation of Si_3N_4 or AlN and thus are stable in M-Si-Al-O-N melts under reducing conditions whereas oxides such as Na_2O , K_2O , B_2O_3 and P_2O_5 have ΔG° values which are more positive and thus they are reduced and the nitrides are oxidized. Jankowski and Risbud (1983) prepared compositions in the Si-Ca-Al-B-O-N system but were only able to form glasses when the B_2O_3 content of the batch was less than ~ 3 wt.%, otherwise weight losses were high causing bubbles. Coon *et al.* (1983) reported substantial losses of B_2O_3 and Na_2O on melting N-containing borosilicate glasses.

Frischat and Schrimpf (1980) reported that only about 80% of the initial amount of N was incorporated into a Na_2O -CaO- SiO_2 glass when N was added as Si_3N_4 . Bachar *et al.* (2012) reported similar results for incorporation of N from Si_3N_4 into Na_2O -CaO- SiO_2 bioactive glass compositions. Many reports of significant weight losses during melting are concerned mainly with M-Si-O-N glasses (without Al) where M is an alkali metal such as Na or K. During melting under reducing conditions, silica dissociates to form divalent Si as $\text{SiO}(\text{g})$ or liquid Si (which forms colloidal precipitates in the glass on cooling) according to (Sharafat *et al.*, 2015):



The partial pressure of SiO, the gaseous product from these reactions, at temperatures of $\sim 1700^\circ\text{C}$ is high enough to account for the losses observed. In reactions (3) and (5), elemental Si is formed in the melt and loss of SiO occurs along with N_2 in reactions (4) and (6). This loss along with loss of a small amount of the modifier also occurs when preparing nitrogen rich glasses in AE-Si-O-N (AE = Mg, Ca, Sr, Ba) systems (Sharafat *et al.*, 2008, 2009). The losses were found to increase with higher concentrations of nitrogen in the starting mixture and also with increasing temperature. Glasses containing Al in various M-Si-Al-O-N systems tend to exhibit much lower weight losses.

One consequence of the formation of the elemental Si in oxynitride glasses is the dark color and lack of transparency. Messier and Deguire (1984) ascribed the dark color in Y-Si-Al-O-N glasses to the presence of Si-rich metallic precipitates caused by thermal decomposition during processing. They found that glasses, prepared using AlN as the nitrogen source, were much more transparent than those prepared using Si_3N_4 . Korgul and Thompson (1993) showed that lack of transparency was associated with dark precipitates in Mg-Si-Al-O-N and Y-Si-Al-O-N glasses and analysis confirmed that they contained Si and FeSi_2 , formed by reaction of Fe impurities, present in the initial powders, with Si_3N_4 . However, glasses prepared using AlN as the nitrogen source did not exhibit better transparency.

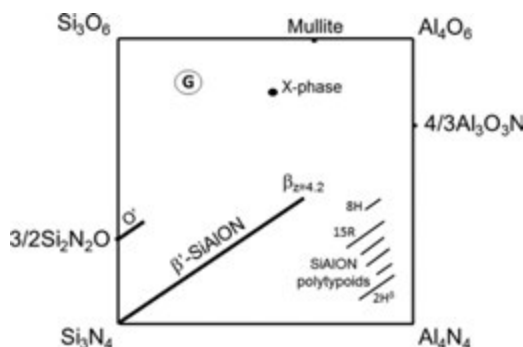


Fig. 2 The four-component Si-Al-O-N system showing the solid phases which exist: β' -SiAlON and its range of solid solution, O', X-phase, sialon polytypoids and a small area of glass (G).

Glass Formation in Oxynitride Systems and Their Representation

Jack (1977) explored glass formation in the MgO-SiO₂-AlN and Y₂O₃-SiO₂-AlN ternary systems and reported up to 10 at.% N for Mg-Si-Al-O-N glasses and 12 at.%N for Y-Si-Al-O-N glasses. Loehman (1979) also investigated the Y₂O₃-SiO₂-AlN ternary system. Glasses were prepared with up to 7 at.% N. Pastuszak and Verdier (1983) determined the glass formation in different M_xO_y-SiO₂-AlN ternary systems where M = Mg, Ca, Ba, Mn, Nd. Messier and Gleisner (1988) explored the glass forming region in the Li₂O-SiO₂-AlN ternary and reported up to 9 at.% N in one composition. Rocherulle *et al.* (1989a) investigated the Gd₂O₃-SiO₂-AlN and Nd₂O₃-SiO₂-AlN ternary systems in which small regions of glass formation were found with nitrogen contents of 2 wt.%. Rocherulle *et al.* (1989b) determined the extent of oxynitride glass regions within Li-Si-Al-O-N and Li-Si-O-N systems. Murakami *et al.* (1995) investigated the Yb₂O₃-AlN-SiO₂ ternary system and reported glass formation in the range 30–50 mol.% AlN, 30–50 mol.% Yb₂O₃ and 50–70 mol.% SiO₂ after melting at 1550°C.

The problem with a simple ternary representation is that it is insufficient to cover all possible compositions. As oxynitride glasses in various M-Si-Al-O-N systems are synthesized from five components: SiO₂, Al₂O₃, Si₃N₄, AlN, and the modifying oxide (s), an alternative approach is based on reciprocal salt systems (Findlay, 1927; Zernicke, 1955) which consist of two or three cations and two anions. The compositions are expressed in equivalent percent (eq.%) of cations and anions instead of atomic, molar or weight percentages (Jack, 1976; Gauckler *et al.*, 1978). One equivalent of any element always reacts with one equivalent of any other element or species.

The four-component Si-Al-O-N system (see Jack, 1991) is a square plane which has, as components, the oxides and nitrides of silicon and aluminum as shown in Fig. 2. In this system, it is convenient to let the bottom left hand corner of the square represent one mole of Si₃N₄ with 12 +ve and 12 -ve valencies. The other corners of the square represent Al₄N₄, Al₄O₆ and Si₃O₆. In going from left to right, 3Si⁴⁺ is gradually replaced by 4Al³⁺ and from bottom to top 4N³⁻ is replaced by 6O²⁻. Fig. 2 shows the solid phases which are known to exist in this system but not the compatibility and phase relationships. The main phase of interest is the β' -SiAlON solid solution (Jack and Wilson, 1972; Jack, 1976) with a range of compositions: β' -Si_{6-z}Al_zO_zN_{8-z} where $z = 0$ is Si₃N₄ and the limit of solid solution is approximately $\beta'_{z=4.2}$. Silicon oxynitride, Si₂N₂O also has a limited range of solid solution (marked O'). The liquid region at 1700°C in the SiO₂-rich corner is quite extensive (Jack, 1991) but there is only a very limited glass forming region (marked G) and very rapid quenching is required (Roebuck, 1978; see also Leng-Ward and Lewis, 1989). Other phases in this system are X-phase and sialon polytypoids (8H, 15R, 12H, 21R, 27R and 2H⁶) with structures based on that of wurtzite-type AlN (Thompson *et al.*, 1983).

Any point in the square represents a combination of 12 positive and 12 negative valence units. The cations and anions are thus treated separately. The concentrations can be expressed as equivalent percentages (eq.%) of either cations or anions as follows:

$$\text{equivalent percentage (eq.\%) Si} = (4[\text{Si}] \times 100) / (4[\text{Si}] + 3[\text{Al}]) \quad (7)$$

where [Si] and [Al] are, respectively, the atomic concentrations of Si and Al in any composition and 4 and 3 are their respective normal valencies.

$$\text{equivalent \% (eq.\%) Al} = 100 - \text{eq.\% Si} \quad (8)$$

For the anions:

$$\text{equivalent \% (eq.\%) of nitrogen} = (3[\text{N}] \times 100) / (2[\text{O}] + 3[\text{N}]) \quad (9)$$

where [O] and [N] are, respectively, the atomic concentrations of oxygen and nitrogen within any composition and 3 and 2 are their respective valencies.

$$\text{equivalent \% (eq.\%) oxygen} = 100 - \text{eq.\% N} \quad (10)$$

The introduction of a further cation gives a five-component system represented by Jänecke's triangular prism (Jänecke, 1907) shown in Fig. 3 for the Y₄O₆-Y₄N₄-Si₃N₄-Si₃O₆-Al₄N₄-Al₄O₆ (Y-Si-Al-O-N) system (see Hampshire, 2008). Any vertical plane within the prism has a constant N:O ratio.

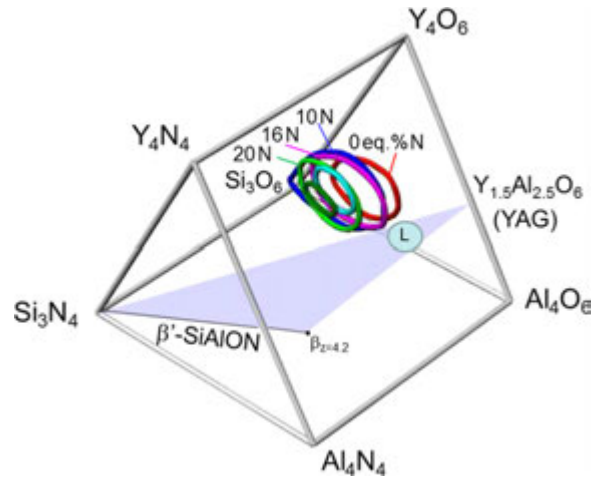


Fig. 3 The Y-Si-Al-O-N system using Jänecke's prism representation showing the complete glass forming region and the $\text{Si}_6\text{N}_8-\beta'_{z=4.2}-\text{Y}_{1.5}\text{Al}_{2.5}\text{O}_6$ (YAG) plane on which is an area of liquid formation (L) at 1550°C. Based on data from: (a) Drew, R.A.L., Hampshire, S., Jack, K.H., 1981. Nitrogen Glasses. Proceedings of the British Ceramic Society 31, 119–132. (b) Redington, W., Redington, M., Hampshire, S., Serantoni, M., 2003. Properties of some high Al content glasses in various lanthanide–Si–Al–O–N systems. Journal of Non-Crystalline Solids 316, 74–81.

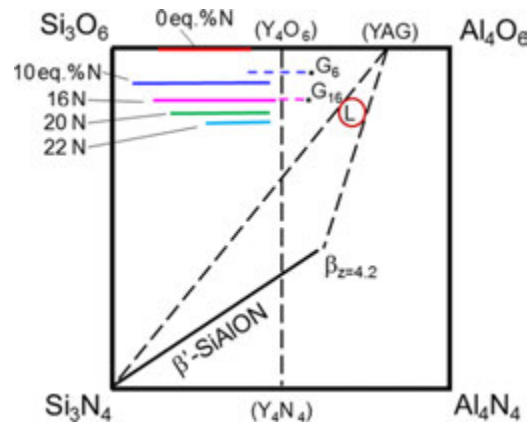


Fig. 4 Plan view of Y-Si-Al-O-N Jänecke prism showing projections of the glass forming regions at 0, 10, 16, 20 and 22 eq.% N and the $\text{Si}_6\text{N}_8-\beta'_{z=4.2}-\text{YAG}$ plane with area of liquid (L). Also shown is higher Al glass formation at 6 eq.% N (G_6) and 16 eq.% N (G_{16}). After: (a) Drew, R.A.L., Hampshire, S., Jack, K.H., 1981. Nitrogen Glasses. Proceedings of the British Ceramic Society 31, 119–132. (b) Redington, W., Redington, M., Hampshire, S. and Serantoni, M., 2003. Properties of some high Al content glasses in various lanthanide–Si–Al–O–N systems. Journal of Non-Crystalline Solids 316, 74–81.

With a modifying cation M (in this case Y) with valency v_M :

$$\text{equivalent \% (eq.\%) of M} = (v_M[M] \times 100) / (4[\text{Si}] + 3[\text{Al}] + v_M[M]) \quad (11)$$

The complete glass forming region for the Y-Si-Al-O-N system based on data of Drew *et al.* (1981) is outlined in the Jänecke prism of Fig. 3 using a computer-based drawing system developed by Redington-Keely *et al.* (2000). AutoCAD® combined with AutoLISP® allows data from multiple sources to be integrated. The colored rings represent the glass forming regions on vertical planes of 0, 10, 16, 20, 22 and 26 eq.% N (Redington *et al.*, 2003). The limit of the $\text{Y}_2\text{O}_3\text{--SiO}_2\text{--Al}_2\text{O}_3$ glass region (0 eq.% N) is shown on the oxide face of the prism and this expands initially with a larger glass forming region at 10 eq.% N. The glass forming region then diminishes becoming smaller as nitrogen content increases until the solubility limit for nitrogen is reached, in this case at ~28–30 eq.% N. The $\text{Si}_6\text{N}_8-\beta'_{z=4.2}-\text{Y}_{1.5}\text{Al}_{2.5}\text{O}_6$ (YAG) plane is also shown on which can be seen an area of liquid formation (marked L) at 1550°C indicated by Hohnke and Tien (1983).

A plan view can be seen in Fig. 4 which shows projections of the glass forming regions on the vertical planes at 0, 10, 16, 20 and 22 eq.% N (after Drew *et al.*, 1981). Also shown is the $\text{Si}_6\text{N}_8-\beta'_{z=4.2}-\text{YAG}$ plane and the area of liquid (L). Based on this, Redington *et al.* (2003) investigated higher Al content compositions and found that glass formation extended along the dashed lines up to compositions containing 56 eq.% Al at 6 eq.% N (marked G_6) and up to 54 eq.% Al at 16 eq.% N (marked G_{16}). The

Table 1 Effect of N on lowest eutectic temperatures ($^{\circ}\text{C}$) in binary silicate ($\text{M}_x\text{O}_y\text{-SiO}_2$) systems

<i>M</i>	<i>M_xO_y-SiO₂</i>	<i>M-Si-O-N</i>
Mg	1540	1390
Ca	1485	1440
Y	1640	1500
Al	1595	1470
Ce	1560	1470

Note: Data from: Hampshire, S., Jack, K.H., 1981. The kinetics of densification and phase transformation in nitrogen ceramics. *Proceedings of the British Ceramic Society* 31, 37-49; Hampshire, S., Drew, R.A.L. and Jack, K.H., 1985. Oxynitride Glasses. *Physics and Chemistry of Glasses* 26, 182-186.

higher Al and N content glasses (54 eq.% Al at 16 eq.% N) were also reported for the Sm-Si-Al-O-N system while high Al (56 eq.%) glasses were reported at lower N (6 eq.%) for Y-, La-, Nd-, Sm- and Dy-Si-Al-O-N systems.

Hampshire *et al.* (1985) explored the complete glass forming region within the Mg-Si-Al-O-N Jänecke prism and glasses are formed with up to 25 eq.% N. They also show quite extensive glass formation within the Ca-Si-Al-O-N system on a vertical section equivalent to 20 eq.% N. Nd-Si-Al-O-N glasses were also prepared with similar compositions to establish comparative properties.

Loehman (1980) presented his previous results of oxynitride glass formation on the $\text{Y}_2\text{O}_3\text{-SiO}_2\text{-AlN}$ ternary plane within the $\text{Y}_4\text{O}_6\text{-Y}_4\text{N}_4\text{-Si}_3\text{N}_4\text{-Si}_3\text{O}_6\text{-Al}_4\text{N}_4\text{-Al}_4\text{O}_6$ Jänecke prism. The glass forming region within the Mg-Si-Al-O-N Jänecke prism with up to 10 at.% N was also illustrated. Loehman also showed a projection on the ternary $\text{MgO-SiO}_2\text{-Al}_2\text{O}_3$ phase diagram of the results for glass compositions containing 10 wt.% Si_3N_4 . The glass-forming region roughly corresponded to the region within the oxide ternary that is liquid at 1600°C . Compositions with high Si or low Al contents were generally phase separated or contained bubbles ("frothy") including a limited range of phase separated Mg-Si-O-N glasses. Phase separated Ca-Si-O-N glasses were prepared containing 10 wt.% Si_3N_4 and addition of ~ 5 wt.% Al_2O_3 suppresses the phase separation giving homogeneous glasses. Other glasses were prepared in the La-Si-Al-O-N and Li-Si-Al-O-N systems but no details reported (Loehman, 1980).

Jankowski and Risbud (1983) prepared compositions in the Si-Ca-Al-O-N system and glasses with nitrogen contents up to 11 at.% were formed. Tu *et al.* (1995) found a more extensive glass forming region in the Sm-Si-Al-O-N system with up to 40 eq.% N. Zhang *et al.* (1996) indicated an extensive glass forming region in the Nd-Si-Al-O-N and La-Si-Al-O-N systems.

In M-Si-O-N systems, much smaller glass-forming regions are observed which confirms the ability of Al_2O_3 to extend the range of glass formation in both silicate and oxynitride systems. The miscibility gap in various silicate binary systems extends into the equivalent M-Si-O-N system with resulting phase separation in some glasses as in the following systems: Mg-Si-O-N (Jack, 1977; Loehman, 1980; Drew *et al.*, 1981; Shaw *et al.*, 1984); Mg-Sc-Si-O-N (Tredway and Loehman, 1985); Li-Si-O-N (Wusirika and Chyung, 1980; Rocherulle *et al.*, 1989b); Ca-Si-O-N (Loehman, 1980; Hampshire *et al.*, 1985); Ce-Si-O-N (Ohashi and Hampshire, 1991); Y-Si-O-N (Ohashi *et al.*, 1995).

More homogeneous glasses with much higher nitrogen contents are possible by using a pure metal or metal hydride rather than the oxide as in the following systems: Sr-Si-O-N – Sr metal (Sharafat *et al.*, 2009) - glasses containing up to 36 eq.% Sr and 45 eq.% N; Ca-Si-O-N (Sharafat *et al.*, 2008) using CaH_2 - glasses with up to 36 eq.% Ca and 42 eq.% N; Ba-Si-O-N (Sharafat and Jonson, 2011) using BaH_2 - glasses with up to 36 eq.% Ba and 42 eq.% N.

All of these investigations of oxynitride glass formation showed that the compositional ranges which formed homogeneous glasses were more extensive than the corresponding oxide system. This can be explained by considering the melting range for the glasses. A study of the initial liquid formation temperature for mixtures of silicon nitride and metal oxides (M_xO_y) showed that the lowest solidus temperatures in the corresponding $\text{M}_x\text{O}_y\text{-SiO}_2$ system are lowered by the addition of nitrogen (Hampshire and Jack, 1981; Hampshire *et al.*, 1985) as shown in Table 1. As nitrogen increases the viscosity of the liquid, this, together with a larger melting range, increases the tendency for glass formation and suppresses crystallization.

Effect of Fluorine on Oxynitride Glass Formation

Fluorine in silicate and aluminosilicate glasses acts as a powerful network disrupter which substitutes for bridging oxygen ions (Hill *et al.*, 1999) and lowers melting temperatures. Hanifi *et al.* (2009) investigated the effects of fluorine on the extent of the original glass forming region (Hampshire *et al.*, 1985) on the $6\text{Ca}^{2+} - 3\text{Si}^{4+} - 4\text{Al}^{3+}$ ternary vertical plane in the Ca-Si-Al-O-N Jänecke prism at 20 eq.% N by substituting 5 eq.% F for oxygen. After melting compositions at 1650°C , they found that glass formation extends to more Ca-rich compositions (40–49 eq.% Ca) when F is present.

The melting endotherm temperatures were measured by differential thermal analysis (DTA) for the Ca-Si-Al-O-N-F glasses, which were found to be in the range $1150\text{--}1300^{\circ}\text{C}$. Hanifi *et al.* (2011) compared these with liquidus temperatures reported for corresponding cation ratio compositions in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ ternary system (Levin *et al.*, 1964). It was found that the addition of both nitrogen and fluorine reduces the liquidus temperatures of all compositions investigated.

At low Al contents (6 eq.%), melting temperatures decrease from $1400\text{--}1430^{\circ}\text{C}$ to $1240\text{--}1270^{\circ}\text{C}$. As Ca content increases (up to 49 eq.% Ca), liquidus temperatures are too high for melting to occur at 1650°C in the oxide system but melting temperatures for the Ca-Si-Al-O-N-F glasses are in the range of $1165\text{--}1225^{\circ}\text{C}$, around 800°C lower. In the Ca-Si-Al-O-N system, compositions in

this region are not fully melted even at 1700°C and contain solid crystalline phases (Hampshire *et al.*, 1985). For the SiO₂-rich and Al₂O₃-rich compositions within the Ca-Si-Al-O-N-F glass forming region, liquidus temperatures are 100–250°C lower than their oxide equivalents. At Al contents of 30–35 eq.%, liquidus temperatures decrease from 1430–1530°C to 1265–1270°C. The melting temperature for a composition of (in eq.%): 35Ca:50Si:15Al:75O:20N:5F is reduced from 1600°C to 1240°C.

At 5 eq.% F substitution for oxygen, the solubility limit for N is ~25 eq.%. When 1 eq.% F is substituted for oxygen, the maximum nitrogen content substantially increases to 40 eq.% N at the composition (in eq.%) 28Ca:57Si:15Al:59O:40N:1F. It was concluded that fluorine affects the dissolution of nitrogen into the melt by significantly lowering the liquidus temperature. A glass with composition (in eq.%) 28Ca:57 Si:15Al:75O:20N:5F was successfully melted at 1400°C and cast into bars. It is clear that the role of fluorine is to reduce the melting range which enhances glass formation.

Oxynitride Glass Structure

The properties of glasses are a function of their structural features (Rouxel, 2007) involving short-range order, i.e., coordination number (CN), interatomic bonding, etc., and also meso-scale structures such as sheets, chains, rings, etc., made up of SiO₄ tetrahedra which are shared in three dimensions in such a way that there is a distribution of different Si-O-Si bond angles. Each oxygen corner forms a bond – a bridge – between two SiO₄ tetrahedra in the glass network and these are known as Bridging Oxygens (BO's). The number of bridging oxygens, n , per Si tetrahedron is denoted as Q^n .

Alkali metals, alkaline earths and rare earths that have a preference for ionic bonding and have higher CN's than Si serve as network modifiers (Stanworth, 1948) and they occupy interstitial sites in the network, reducing the unoccupied free volume in the structure and creating Non-Bridging Oxygens (NBO's). To maintain charge neutrality each NBO is associated with the positive charge of a nearby alkali ion. With a divalent modifier M such as Mg, Ca or Sr, every M^{2+} ion must have two neighboring NBO's and is much more tightly bonded to the silicate network, providing stronger network linkages and hence improved chemical durability and lower ionic conductivity, due to lower ion mobility through the network (Shelby, 1985).

Al^{3+} is an intermediate ion in that it can act as a glass former when combined with Si^{4+} ions. Al is generally in octahedral coordination in crystalline materials but its CN can be as low as 4 in glasses where $[AlO_4]^{5-}$ structural units replace $[SiO_4]^{4-}$ units and replacing NBO's with cross-linking Al-O-Si bonds requires charge balance of the $[AlO_4]^{5-}$ by the modifying cations. The modifier becomes a "network dwelling" ion in an interstitial site within the network. Increase in cross-linking occurs until the ratio $[Al]:1/x[M^{x+}]$ is exceeded and results in the formation of more NBO's. The Al^{3+} effectively becomes a network modifying ion in 6-fold coordination (Day and Rindone, 1962).

In much of the early literature cited above on oxynitride glass formation, many authors also presented results showing progressive changes in physical or thermal properties with increasing nitrogen content and speculated that these changes were a result of extra cross-linking as tri-coordinated nitrogen replaced di-coordinated oxygen in the glass network as first suggested by Mulfinger (1966). Structural factors that can cause changes in properties include variations in BO's versus NBO's, Si-O-N coordination, the coordination of Al and other cations with oxygen, average bond lengths, etc. Structural features of oxynitride glasses have been assessed using Fourier Transform Infrared (FTIR) and Raman spectroscopy, Nuclear Magnetic Resonance (NMR) and X-ray Photoelectron Spectroscopy (XPS).

FTIR Spectroscopy

A number of authors have reported IR absorption spectra for different oxynitride glasses: SiO₂-Si₃N₄ films (Chu *et al.*, 1968); Na₂O-SiO₂-Si₃N₄ (Brow and Pantano, 1984b); Na₂O-CaO-SiO₂-Si₃N₄ (Frischat and Schrimpf, 1983; Brow and Pantano, 1984b); Y-Si-Al-O-N (Loehman, 1979); Li-K-Si-Al-O-N (Luping *et al.*, 1983); M-Si-Al-O-N where M = Mg, Ca, Ba, Li (Videau *et al.*, 1997). The shape and position of the main absorption peak centered around 1045 cm⁻¹ in the SiO₂ and silicate spectra attributed to asymmetrical stretching vibration modes of Si-O-Si bonds shifts to lower wave numbers with increasing nitrogen content, and the merging of Si-O and Si-N bands widens the spectra. This is clear evidence for the substitution of oxygen by nitrogen in the silicate network.

Videau *et al.* (1997) analyzed IR spectra of M-Si-Al-O-N glasses, where M = Mg, Ca, Ba, Li with composition: $M_{0.37}Si_{0.53}Al_{0.1}O_{1.58-3x}/2N_x$ with x varying from 0 to 1. The IR spectra for the Mg-containing glasses is shown in Fig. 5. Increase of the nitrogen content leads to the broadening of the band in the 800–1000 cm⁻¹ absorption range with, simultaneously, an occurrence of two maxima at around 1050 and 1000 cm⁻¹ for Mg₂ to Mg₄ (increasing N). An increase of the intensity and a shift towards the lower frequencies of the absorption band is attributed to Si-O⁻ (Mg²⁺) bond vibrations for Mg₁. As N is introduced, formation of Si-N bonds involves the weakening of neighboring Si-O-(Si, Al) bonds with the appearance of: Si-N around 1050 cm⁻¹; N-Si-O...(Si) between 970 and 1000 cm⁻¹; Si-N vibrations around 950 cm⁻¹, in (N₃Si)-O-(SiN₃) molecular entities with Si-N-Si vibration modes between 850 and 950 cm⁻¹ (corresponding vibrations become overlapped with those of the Si-O⁻ (Mg²⁺) non-bridging bond).

In the 650–800 cm⁻¹ absorption range, the characteristic band at 730 cm⁻¹ for the AlO₄ tetrahedra was identified in the aluminosilicates (Mg₁ x = 0) but the characteristic band for (Al_{IV}-O) disappeared when N was introduced and evidence for the

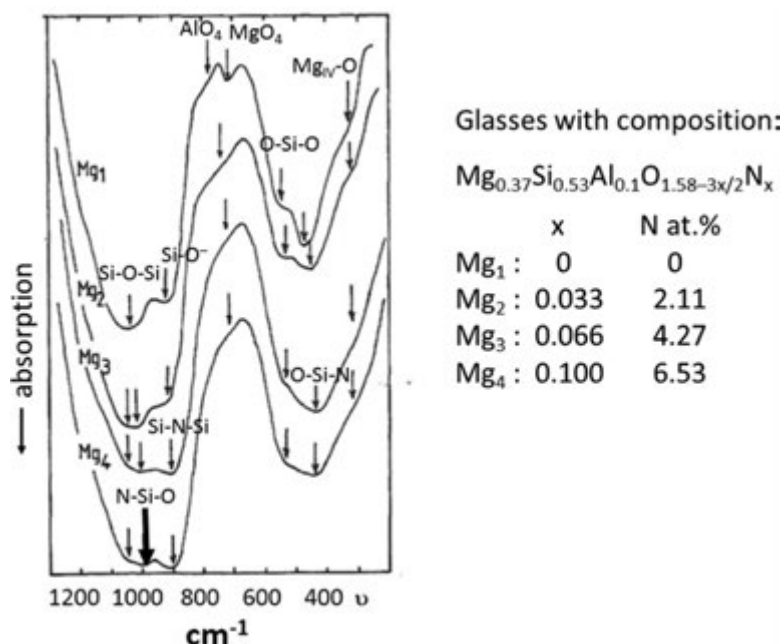


Fig. 5 The IR spectra for glasses with compositions $\text{Mg}_{0.37}\text{Si}_{0.53}\text{Al}_{0.1}\text{O}_{1.58-3x/2}\text{N}_x$ with x varying from 0 (Mg₁) to 1 (Mg₄). After Videau, J.J., Etourneau, J., Rocherulle, J., Verdier, P., Laurent, Y., 1997. Structural approach of sialon glasses: M-Al-Si-O-N. *Journal of the European Ceramic Society* 17, 1955–1961.

presence of MgO_4 tetrahedra is shown. In Mg-Si-Al-O-N glasses, Al takes on octahedral coordination with oxygen (AlO_6) and Mg becomes a network former as more nitrogen is incorporated (Hampshire *et al.*, 1985; Videau *et al.*, 1997).

X-ray Photoelectron Spectroscopy

The XPS binding energies of an element are related to the fractional atomic charge about that element. Thus, the position of the elemental binding energy will depend on the electronegativities of neighboring elements. Elements with similar chemical environments will have similar electron binding energies.

Brow and Pantano (1984b) showed that in Na-Ca-Si-O-N glasses the primary N 1s binding energies are similar to those for crystalline Si_3N_4 , providing direct evidence for the presence of tri-coordinated nitrogen in the glass structure (see Fig. 1). It was assumed that low-energy components of the N 1s photoelectron spectra may have resulted from the presence of non-bridging nitrogen groups such as (a) $\equiv \text{Si} - \text{N}^- - \text{Si} \equiv$ and (b) $\equiv \text{Si} - \text{N}^{2-}$ shown in Fig. 6. The local charge on the non-bridging nitrogen ions is balanced by the presence of interstitial metal ions in close proximity.

Schneider *et al.* (1997) analyzed Ca-Mg-Si-Al-O-N glasses containing up to 10 at.% N by XPS. In glasses with more than 5 at.% N there was evidence for additional bondings which related to the existence of “non-cross-linked” nitrogen forming less than three covalent bonds to the network as in (a) and (b) above (Fig. 6). This means that N may bond with either a modifying cation or be left with a dangling bond. While the strength of the Si-O bond ($U_{\text{Si-O}} = 800$ kJ/mol) is seen to be stronger than for the Si-N bond ($U_{\text{Si-N}} = 437$ kJ/mol), that is Si-O has a greater stretching force constant, calculations show that the Si-N bond is more resistant to bending (Rouxel, 2007), which combined with the increased coordination with Si would increase the rigidity of the network. Bonding is much more covalent for Si-N than for Si-O so that bending is more difficult for Si-N-Si than for Si-O-Si linkages, contributing to the greater rigidity.

Solid State Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR)

More details of the structural aspects of oxynitride glasses were determined from solid state MAS NMR. High-resolution solid-state ^{29}Si MAS NMR spectra from inorganic materials were first obtained in 1980 and early work on oxynitride glasses using this analysis technique was carried out by Aujla *et al.* (1986). The ^{29}Si spectrum from an oxide glass of composition $\text{Y}_{1.03}\text{Si}_{1.27}\text{Al}_{1.27}\text{O}_6$ consists of one broad peak with chemical shift centered at -83 ppm but it was not possible to resolve different degrees of polymerization of this SiO_4 peak into Q^2 , Q^3 , Q^4 . When 15 eq.% N was substituted for oxygen to form a glass of composition $\text{Y}_{1.03}\text{Si}_{1.27}\text{Al}_{1.27}\text{O}_{5.1}\text{N}_{0.6}$ the spectrum was resolved into three contributing peaks centered at -83 , -71 and -60 ppm which are characteristic of SiO_4 , SiO_3N and SiO_2N_2 tetrahedral units.

Bachar *et al.* (2016) compared the ^{29}Si MAS NMR spectra of bioactive glasses with compositions (mol.%): $(55-3x)\text{SiO}_2-13.5\text{CaO}-31.5\text{Na}_2\text{O}-x\text{Si}_3\text{N}_4$ where $x = 0-4$ ($x = 4$ corresponds to 3.3 at.% N). Deconvolution analysis was carried out to

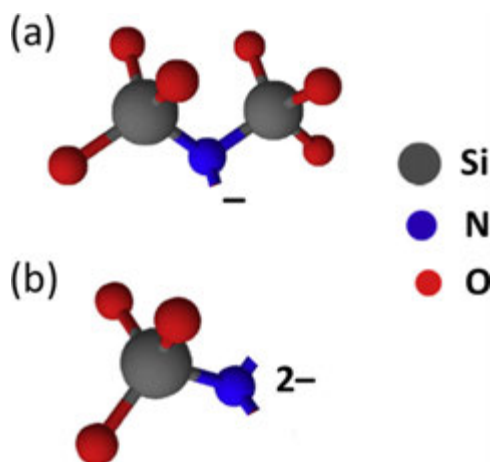


Fig. 6 Representative structures showing N-SiO₄ bonding in silicate glasses: (a) the N atom acts as a bridge between 2 SiO₄ tetrahedra, (b) Non-bridging N atoms may also be present - O₃Si-N²⁻. Charge balance is from interstitial metal cations in close proximity.

determine the contributions of different Qⁿ modes. In the spectrum of the glass without nitrogen (**Fig. 7(a)**), the main contributions in the signal are located around -78.1 and -85.3 ppm, attributed respectively to Q² (37%) and Q³ (63%) units. When nitrogen is substituted for oxygen, more Si environments appear with two new bands at around -70 and -59 ppm, attributed to SiO₃N and SiO₂N₂ units, respectively, similar to the spectra reported by Aujla *et al.* (1986). **Fig. 7(b)** shows that addition of the maximum nitrogen (3.3 at.%) results in more SiO₃N tetrahedra, fewer Q³ units and the appearance of Q⁴ units and SiO₂N₂ tetrahedra.

Glasses with composition Y_{1.03}Si_{1.27}Al_{1.27}O_{6-3x/2}N_x where x is 0.8 and 1.2 to give 20 and 28 eq.% N, respectively, were analyzed using NMR by Kruppa *et al.* (1991). The ¹⁵N spectrum of the glass indicates that there are [NSi₃] or possibly [NSi₂Al] units in the structure and also [-NSi₂] units (~20%). Further evidence that nitrogen atoms may bond to only two (or even one) Si atom was provided by Sakka (1995) who studied Na-Si-O-N and Y-Si-Al-O-N glasses by ²⁹Si, ²⁷Al and ¹⁵N MAS NMR. The average CN for N in the Na-Si-O-N glass is 2.42 which allows a simple calculation to conclude that 58% of N atoms are bonded to two Si atoms and only 42% to three Si atoms (Jin *et al.*, 1993; Sakka, 1995). Unuma *et al.* (1992) by means of MD calculations obtained CN = 2.3. In the Y-Si-Al-O-N glass, the average CN for N is 2.86 which suggests that 86% of the N atoms are 3-fold coordinated and 14% are 2-fold coordinated. The local charge on the nitrogen ions with CN < 3 is balanced by the presence of interstitial modifying cations in their local environment.

Sakka (1995) also suggested that in oxynitride glasses containing Al, Si-N bonding is preferred to Al-N bonding. Thus, as all nitrogens are preferentially bonded to silicon, it is possible to estimate the average number of nitrogens bonded to each silicon, i.e., x in each SiO_(4-x)N_x tetrahedron within the glass network. **Fig. 8** shows the variation in the average number of nitrogens per tetrahedron as a function of nitrogen content for a range of glass compositions given in **Table 2**, calculated using the formula $x = 3(x_N/x_{Si})$, where x_i represents atomic fraction of i (N or Si). It is seen that for most glasses the average number of nitrogens bonded to silicon does not exceed 1 until a nitrogen content of 15 eq.% is reached. For the B-phase glass with a higher Al:Si ratio, more than one nitrogen is bonded to silicon if the nitrogen content exceeds about 10 eq.% N.

Lofaj *et al.* (2004a) studied the effects of rare earth (RE) elements and nitrogen on the structure of RE-Si-Mg-O-N glasses (RE = Sc, Y, La, Nd, Sm, Gd, Yb and Lu) with different nitrogen contents. NMR showed that nitrogen modifies the glass structure depending on the RE by increasing the content of SiO₃N units (Qⁿ ⇒ Qⁿ⁺¹) at the expense of Q² units and this appears to be more effective in Lu-containing glasses than those with La. Despite that, the effects of rare-earth modifiers and nitrogen as a network former are independent and additive and a synergy effect was not observed.

Raman Spectroscopy

Rouxel *et al.* (1990) used Raman spectroscopy to analyze SiYAlON glasses and obtained two broad peaks, the main one at ~950 cm⁻¹ which shifted to higher wave number with increasing N content. This was assigned to a vibrational mode involving perturbed SiO₄ tetrahedral units with Si-O-Al or Si-O-Y linkages.

Dolecekic *et al.* (2007) carried out Raman spectroscopic analyses on Er-Si-Al-O-N glasses with N contents of 0, 5, 8, 15 and 22 eq.% and constant cation ratios of Er:Si:Al = 3.45:3:2. Careful deconvolution of the Raman spectra showed that Al³⁺ is in 4-fold coordination with oxygen. Also the proportion of Q³ silicate species decreases as nitrogen content increases and there is a corresponding increase in the proportion of Q⁴ (oxynitride) species, implying that a transformation occurs of the type:



shown schematically in **Fig. 9** with the extra crosslinking between individual tetrahedra.

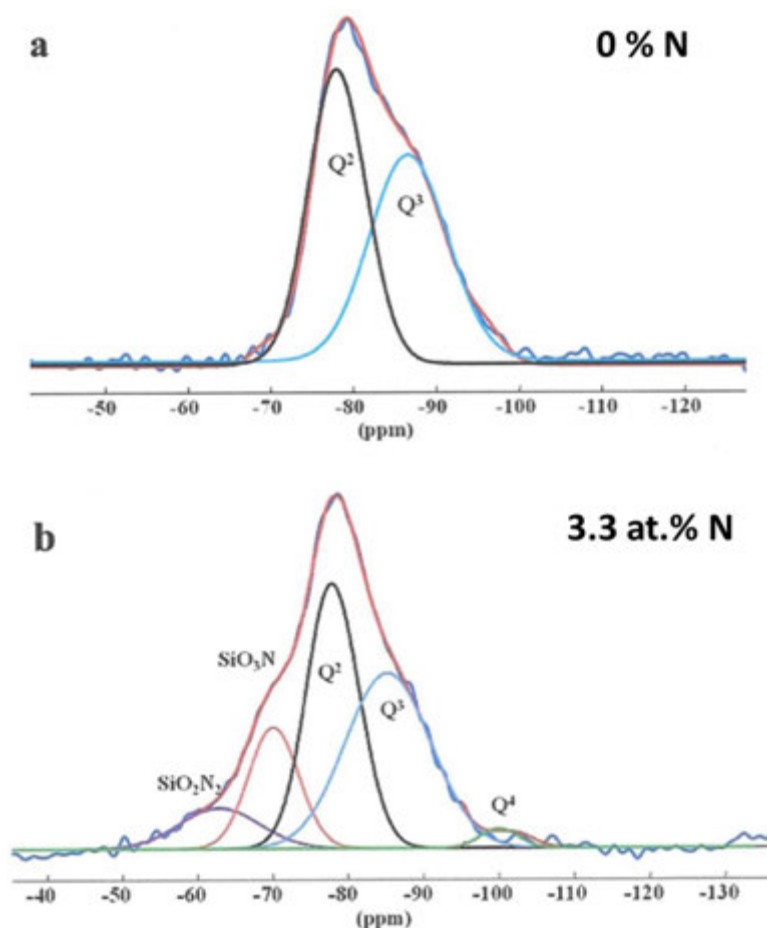


Fig. 7 ^{29}Si MAS NMR spectra of glasses with compositions (mol.%): $(55-3x)\text{SiO}_2-13.5\text{CaO}-31.5\text{Na}_2\text{O}-x\text{Si}_3\text{N}_4$ (a) $x = 0$, (b) $x = 4$, corresponds to 3.3 at.% N showing deconvolution analysis to determine the contributions of different Q^n modes. After Bachar, A., Mercier, C., Tricoteaux, A., *et al.*, 2016. Bioactive oxynitride glasses: Synthesis, structure and properties. *Journal of the European Ceramic Society* 36, 2869–2881.

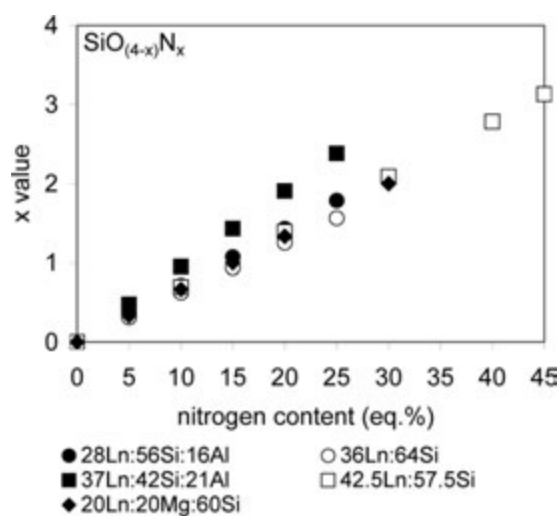
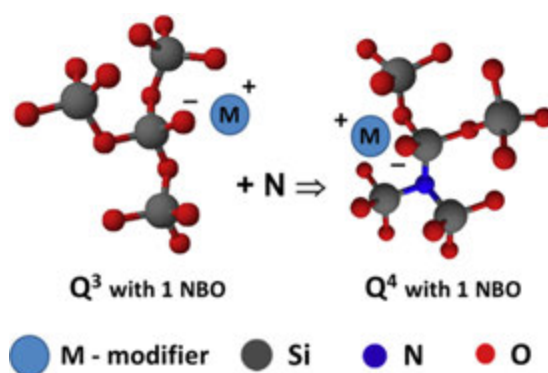


Fig. 8 Average number of nitrogen atoms bonded to silicon as a function of nitrogen content for glasses with different cation ratios (compositions expressed in eq.%). Ln represents a lanthanide (La, Nd, Sm, Gd, Yb, Er, Lu) or Y. After Pomeroy M.J., Hampshire, S., 2008. SiAlON Glasses: Effects of nitrogen on structure and properties. *Journal of the Ceramic Society of Japan* 116, 755–761.

Table 2 Glass compositions (in equivalent percentages – eq.%) of well characterized glasses

Given glass name/type	Modifiers		Concentration (eq.%)					Reference
	M1	M2	M1	M2	Si	Al	N	
Standard composition M-SiAlON	Mg, Ca, Y, lanthanides		28		56	16	0 – 22	Hampshire <i>et al.</i> (1985)
Mixed modifier standard composition M1-M2-SiAlON	Mg, La or Nd	Y or Er	0 – 28	28 – 0	56	16	17	Pomeroy <i>et al.</i> (2003)
Standard composition Y-, Ln-SiON B-phase	Lanthanides, Y Y, Er, Yb		36 37		64 42	0 21	0 – 20 0 – 22	Ohashi <i>et al.</i> (1995) Menke <i>et al.</i> (2000), Doleckecic <i>et al.</i> (2007)
Wollastonite	La, Nd		42.5		57.5	16	0 – 45	Zhang <i>et al.</i> (1996)
Rare Earth RE-MgSiON	RE = Sc, Y, La, Nd, Sm, Gd, Yb, Lu	Mg	20	20	60	0	0 – 30	Lofaj <i>et al.</i> (2004a,b)
Mixed Ca-M2 SiAlON	Ca	Er, Nd, Y	20 – 10	0 – 10	50	30	0 – 20	García-Bellés <i>et al.</i> (2013), Clausell <i>et al.</i> (2018)

**Fig. 9** Representative structures showing that with N addition, Q³ SiO₄ unit transforms to a Q⁴ unit. SiO₃N units with nominal – 5 charge require extra local positive charge for charge compensation. This allows modifier ions such as Y³⁺ to be accommodated as “network dwelling” cations within the network without creating non-bridging oxygens (NBOs).

The [SiO₃N]^{5–} group requires the presence of an extra positive charge locally to balance the extra negative charge from the N anion and therefore the situation is somewhat similar to that for an [AlO₄]^{5–} tetrahedron within the network, which also requires an extra positive charge to make it isoelectronic with the SiO₄ tetrahedron. However, extra Si cations are introduced into the system by Si₃N₄ and, because each N is coordinated to 3 silicon atoms, therefore, oxynitride glasses containing SiO₃N groups can accommodate more modifiers in charge compensating “network dwelling” sites than the equivalent oxide glasses without creating NBO's as shown in Fig. 9.

Al Bonding and Coordination in M-Si-Al-O-N Glasses (M – Modifier)

In M-Si-Al-O-N glasses, Al, as well as Si, can be in 4-fold coordination with oxygen (and potentially with N) and thus, be a network former (Lemercier *et al.*, 1996; McMillan *et al.*, 1998). However, the Al-O network bond would be somewhat weaker (and less covalent) than the Si-O bond. On the other hand, while Si-N bonding is prevalent in SiAlON glasses, most studies indicate that Al-N bonding does not occur in many oxynitride glasses (Unuma *et al.*, 1992; Sakka, 1995; McMillan *et al.*, 1998). Typically, the Al coordination with oxygen can be 4, 5 or 6 in oxide and non-oxide glasses. For example, Schneider *et al.* (1997) indicated that in their Si-Al-O-N glasses well over half of the Al was coordinated with four oxygens, ~ one third being five-fold coordinated with the rest in six-fold coordination and that the average Al-O coordination increased as either the Al or N content of the glass increased. Lemercier *et al.* (1996) also noted that the Al coordination with oxygen shifted from 4 to 5 and 6-fold as the Al:Si ratio increased in Y-Si-Al-O-N glasses with fixed Y and N contents which was confirmed by ²⁷Al MAS NMR findings. More Al-O-Si linkages would form displacing Si-O-Si units with little change in NBOs or the degree of cross-linking of the network. On the other hand, increased 5- and 6-fold coordination of Al was observed when the Al:Y ratio decreased in glasses with fixed Si and N contents, and the number of NBOs was suggested to increase due to a decrease in Si-O-Al linkages (Rouxel *et al.*, 1990, 2005).

Even though many glasses studied have sufficient modifier cations to charge balance aluminum in four-fold coordination, the fact that Al exists in 5- and 6-fold coordination confirms its intermediate character. Sakka (1995) indicates that about 56% aluminum is in 4-fold coordination in a glass with cation composition: 21Y:48Si:31Al (eq.%) where Y:Al ratio is 0.68 and the

remaining Al is in 5-fold coordination. Rouxel *et al.* (2005) reported that 75%–85% of Al in glasses in the Ca-, Mg-, Ca-Mg-, Ca-Y-, Mg-Y- and Mg-Ca-Y- Si-Al-O-N systems is in 4-fold coordination and the remaining Al in 5-fold coordination but in these glasses M:Al ratio varied from 2.2 to 2.6.

Using ^{29}Si and ^{27}Al MAS NMR, Leonova *et al.* (2008) explored the structures of La-Si-(Al)-O-(N) glasses prepared using the lanthanide metal with a wide range of cation/anion compositions (up to 60 eq.% N). As N content increases SiO_3N tetrahedra dominate in glasses containing <20% N but SiO_2N_2 units are found in glasses with >35% N in La-Si-Al-O-N glasses and requiring >50% N in samples devoid of Al. Al is predominantly present in tetrahedral coordination as AlO_4 units in aluminosilicate glasses and in La-Si-Al-O-N glasses with <20% N. Al in 5-fold coordination amounts to ~10% of the total and < 5% of Al is in octahedral coordination. Whereas there are clear preferences for forming Si–N bonds, Al–N bonding occurs in glasses containing at least 35% N. This corroborates the findings of Deckwerth *et al.* (2001) who detected AlO_3N and AlO_2N_2 tetrahedra by ^{27}Al MAS NMR spectroscopy in contrast to an earlier report by the same authors (Schneider *et al.*, 1997) based on XPS where they found no evidence of Al–N bonding. Thus, in the high N content La-Si-Al-O-N glasses prepared by Leonova *et al.* (2008) SiO_2N_2 and AlO_3N tetrahedra are dominating and interlinked mainly through Si–N–Si and Si–O–Al bridges.

The Role of Modifier (M) Cations

Field strength calculations (Rouxel, 2007) are often used to consider bond strengths within glasses. These are based on Coulombic interactions between a cation and an anion and provide some general insights into the relative strengths of various M–O (or N) bonds. The relationship most frequently used is the cationic field strength:

$$\text{CFS} = z_c / (r_c)^2 \quad (13)$$

where z_c is the ionic charge and r_c the ionic radius of the cation. Generally, network formers have higher CFS values, modifiers have low values and intermediates have intermediate values.

The difference in charge between $[\text{AlO}_4]^{5-}$ and $[\text{SiO}_4]^{4-}$ tetrahedra in the network requires that additional cations are present locally for charge balance (e.g., Mg^{2+} , Ca^{2+} , Y^{3+} , Ln^{3+}). Although the Y–O bond is weaker than the oxygen bond with either Si or Al, its coordination with multiple oxygens and the associated high cationic field strength indicates that Y can improve the strength of the glass network (Becher *et al.*, 2011). In oxynitride glasses, as shown earlier (Hampshire *et al.*, 1985; Videau *et al.*, 1997), the addition of Mg can cause Al to take on more 6-fold coordination with oxygen and go into four-fold coordination with oxygen itself and thus become a network former as nitrogen is incorporated in the glass. In this case, the Si–N bonding introduces extra bridging bonds and cross linkages of Mg–O–Si network chains while Al^{3+} serves for charge compensation. In mixed cation Ca–Mg–Si–Al–O–N glasses Mg has a higher CFS than calcium, which means that the replacement of Ca by Mg increases the rigidity and the stiffness of the vitreous network (Rouxel *et al.*, 2005). In oxynitride glasses, the partial occurrence of Mg in tetrahedral positions, which is enhanced by the presence of nitrogen, leads to an increase of the CFS of Mg atoms so that network compactness is higher than in the corresponding oxide glass. Therefore, effects directly related to the tightening of the network, such as property changes, are expected to increase.

On the other hand, substitution of Ca for Y in Ca–Y–Si–Al–O–N glasses does not appear to alter AlO_4 coordination and so a highly cross-linked network forms (Si–O–Al and Si–N–Si linkages), with randomly distributed Ca^{2+} in network interstitials (Videau *et al.*, 1997; Rouxel *et al.*, 2005).

Rare earth (RE) aluminosilicate glasses contain high field strength trivalent RE^{3+} cations. Based on the ionic radii given by Shannon (1976) and assuming 6-fold coordination of RE^{3+} , field strengths fall in the intermediate range from $2.94 \text{ \AA}^{-2}$ for Ce^{3+} to $4.05 \text{ \AA}^{-2}$ for Lu^{3+} , reflecting the higher cation–oxygen bond energies. Field strength for La^{3+} is $2.82 \text{ \AA}^{-2}$, similar to that for Ce^{3+} , and CFS for Y^{3+} is $3.70 \text{ \AA}^{-2}$. In Y glasses with increasing Y:Si ratio, the ^{29}Si NMR peak shifts upwards, indicating a smaller shielding of the Si nucleus because of the substitution of Y for Al, which may be related to the conversion of BO's to NBO's (Uhlig *et al.*, 1998). At the same time, peaks become narrower, suggesting an ordering of the network. ^{27}Al MAS NMR analysis by Schaller and Stebbins (1998) shows that one major effect of Y^{3+} is to promote the conversion of AlO_4 groups to higher-coordinate species (5 or 6). La acts as a network modifier in La–Si–Al–O–N glasses in that it depolymerizes the Si tetrahedral network with $\text{Q}^n \Rightarrow \text{Q}^{n-1}$ conversions (Leonova *et al.*, 2008). A slight deshielding of the $^{27}\text{Al}_{\text{IV}}$ signals with increasing La^{3+} content is observed which may indicate some depolymerization also of the AlO_4 tetrahedra.

The large ionic radii of the rare earths (RE) and the more ionic character (~70%, based on electronegativity calculations) of the RE–O bond result in higher coordinations with oxygen. i.e., $\text{CN} \geq 6$ (Menke *et al.*, 2000). This also depends on the $r_{\text{RE}}:r_{\text{O}}$ ionic radii ratio where Er and larger REs having 7–9-fold coordination and smaller REs having 6-fold coordination. In oxide and oxynitride glasses with cation compositions of 55Si:20RE:25Al and 45Si:30RE:25Al there is a greater number of Si tetrahedron bridges (i.e., an increased population of higher Q^n values) as the ratio of Si to RE increases. This trend indicates that Si–O–Si bridges are promoted at the expense of Si–NBO–RE linkages when Si replaces RE, resulting in an overall increase in network connectivity. In both the oxide and oxynitride series, the number of Si tetrahedron bridges increases as the size of the RE cation decreases (as CFS of RE increases), thus promoting greater network connectivity.

It can be concluded that, generally, the glass network in oxynitride glasses comprises $\text{SiO}_{(4-x)}\text{N}_x$ tetrahedra, with average x values controlled by N:Si ratios, which are bridged either by Si–O–(Si,Al) linkages or tri-coordinate N–Tetrahedra linkages, and also AlO_4 tetrahedra which are mainly bridged by bi-coordinate O–Tetrahedra linkages.

These structural changes with N substitution for oxygen have significant effects on glass properties which will be reviewed elsewhere.

References

- Aujla, R.S., Leng-Ward, G., Lewis, M.H., *et al.*, 1986. An NMR study of silicon coordination in Y-Si-Al-O-N glasses. *Philosophical Magazine B* 54, L51–L56.
- Bachar, A., Mercier, C., Tricoteaux, A., *et al.*, 2016. Bioactive oxynitride glasses: Synthesis, structure and properties. *Journal of the European Ceramic Society* 36, 2869–2881.
- Bachar, A., Mercier, C., Tricoteaux, A., *et al.*, 2012. Effects of addition of nitrogen on bioglass properties and structure. *Journal of Non-Crystalline Solids* 358, 693–701.
- Becher, P., Hampshire, S., Pomeroy, M.J., *et al.*, 2011. An overview of the structure and properties of silicon-based oxynitride glasses. *International Journal of Applied Glass Science* 2, 63–83.
- Becher, P.F., Sun, E.Y., Plucknett, K.P., *et al.*, 1998. Microstructural design of silicon nitride with improved fracture toughness: I. Effects of grain size and shape. *Journal of the American Ceramic Society* 81, 2821–2830.
- Brinker, C.J., Haaland, D.M., 1983. Oxynitride glass-formation from gels. *Journal of the American Ceramic Society* 66, 758–765.
- Brow, R.K., Pantano, C.G., 1984a. Incorporation of nitrogen in silica-gel thin-films. *American Ceramic Society Bull* 63, 1109. [1109].
- Brow, R.K., Pantano, C.G., 1984b. Nitrogen coordination in oxynitride glasses. *Journal of the American Ceramic Society* 67, C72–C74.
- Chu, T.L., Szidon, J.R., Lee, C.H., 1968. Films of silicon nitride-silicon dioxide mixtures. *Journal of the Electrochemical Society* 115, 318–322.
- Clausell, C., Barba, A., Jarque, J.C., *et al.*, 2018. Compositional effects on cross-link density of Ca-(Mg)-(Y)-Si-Al-oxyfluoronitride glasses. *Journal of the American Ceramic Society* 101, 189–200.
- Coon, D.N., Rapp, J.G., Bradt, R.C., Pantano, C.G., 1983. Mechanical properties of silicon-oxynitride glasses. *Journal of Non-Crystalline Solids* 56, 161–166.
- Dancy, E.A., Janssen, D., 1976. Dissolution of nitrogen in metallurgical slags. *Canadian Metallurgical Quarterly* 15, 103–110.
- Davies, M.W., Meherali, S.G., 1971. Equilibrium solubility of nitrogen in aluminosilicate melts. *Metallurgical Transactions* 2, 2729–2733.
- Day, D.E., Rindone, G.E., 1962. Properties of soda aluminosilicate glasses: I. Refractive index, density, molar refractivity, and infrared absorption spectra. *Journal of the American Ceramic Society* 45, 489–496.
- Dolecekic, E., Pomeroy, M.J., Hampshire, S., 2007. Structural characterisation of Er-SiAlON glasses by Raman spectroscopy. *Journal of the European Ceramic Society* 27, 893–898.
- Drew, R.A.L., Hampshire, S., Jack, K.H., 1981. Nitrogen glasses. *Proceedings of the British Ceramic Society* 31, 119–132.
- Elmer, T.H., Nordberg, M.E., 1967. Effect of nitriding on electrolysis and devitrification of high-silica glasses. *Journal of the American Ceramic Society* 50, 275–279.
- Findlay, A., 1927. *The Phase Rule and Its Applications*, sixth ed. London: Longmans Green.
- Frischat, G.H., Schrimpf, C., 1980. Preparation of nitrogen-containing Na₂O-CaO-SiO₂ glasses. *Journal of the American Ceramic Society* 63, 714–715.
- Frischat, G.H., Schrimpf, C., 1983. Property-composition relations of N₂-containing Na₂O-CaO-SiO₂ glasses. *Journal of Non-Crystalline Solids* 56, 153–160.
- García-Bellés, A.R., Monzó, M., Barba, A., *et al.*, 2013. Factors controlling properties of Ca-Mg, Ca-Er, Ca-Nd or Ca-Y-modified Aluminosilicate Glasses Containing Nitrogen and Fluorine. *Journal of the American Ceramic Society* 96, 2839–2845.
- Gaukler, L.J., Lukas, H.L., Henig, E.-Th., Petzow, G., 1978. Representation of phase equilibria in systems with a double exchange reaction. *Calphad* 2, 349–356.
- Hakeem, A.S., Dauce, R., Leonova, E., *et al.*, 2005. Silicate glasses with unprecedented high nitrogen and electropositive metal contents obtained by using metals as precursors. *Advanced Materials* 17, 2214–2216.
- Hampshire, S., 1993. Oxynitride glasses and glass ceramics. In: Chen, I.W., Becher, P.F., Mitomo, M., Petzow, G., Yen, T.-S. (Eds.), *Silicon Nitride Ceramics – Scientific and Technological Advances*, Materials Research Society Symposium Proceedings 287. Pittsburgh, USA: MRS, pp. 93–104.
- Hampshire, S., 2003. Oxynitride glasses, their properties and crystallisation – A review. *Journal of Non-Crystalline Solids* 316, 64–73.
- Hampshire, S., 2008. Oxynitride glasses. *Journal of the European Ceramic Society* 28, 1475–1483.
- Hampshire, S., 2009. Silicon nitride ceramics. *Materials Science Forum* 606, 27–41.
- Hampshire, S., Drew, R.A.L., Jack, K.H., 1985. Oxynitride glasses. *Physics and Chemistry of Glasses* 26, 182–186.
- Hampshire, S., Jack, K.H., 1981. The kinetics of densification and phase transformation in nitrogen ceramics. *Proceedings of the British Ceramic Society* 31, 37–49.
- Hampshire, S., Nestor, E., Flynn, R., *et al.*, 1994. Yttrium oxynitride glasses: Properties and potential for crystallisation to glass-ceramics. *Journal of the European Ceramic Society* 14, 261–273.
- Hampshire, S., Pomeroy, M.J., 2004. Effect of composition on viscosities of rare earth oxynitride glasses. *Journal of Non-Crystalline Solids* 344, 1–7.
- Hanifi, A.R., Genson, A., Pomeroy, M.J., Hampshire, S., 2009. Oxyfluoronitride glasses with high elastic modulus and low glass transition temperatures. *Journal of the American Ceramic Society* 92, 1141–1144.
- Hanifi, A.R., Pomeroy, M.J., Hampshire, S., 2011. Novel glass formation in the Ca-Si-Al-O-N-F system. *Journal of the American Ceramic Society* 94, 455–461.
- Harding, F.L., Ryder, R.J., 1970. Effects of silicon nitride addition to a container glass batch. *Glass Technology* 11, 54–58.
- Hill, R., Wood, D., Thomas, M., 1999. Trimethylsilylation analysis of the silicate structure of fluoro-alumino-silicate glasses and the structure role of fluorine. *Journal of Materials Science* 34, 1767–1774.
- Jack, K.H., 1976. Review: Sialons and related nitrogen ceramics. *Journal of Materials Science* 11, 1135–1158.
- Jack, K.H., 1991. Sialons. In: Brook, R.J. (Ed.), *Concise Encyclopedia of Advanced Ceramic Materials*. Elsevier, pp. 411–416.
- Jack, K.H., 1977. Sialon glasses. In: Riley, F.L. (Ed.), *Nitrogen Ceramics*. Leyden: Noordhoff, pp. 257–262.
- Jack, K.H., Wilson, W.I., 1972. Ceramics based on the Si-Al-O-N and related systems. *Nature Physical Science* 238, 28–29.
- Jänecke, E., 1907. Über eine Darstellungsform der van't Hoff'schen Untersuchungen über ozeanische Salzablagerungen III. *Zeitschrift für Anorganische und Allgemeine Chemie* 53, 319–326.
- Jankowski, P.E., Risbud, S.H., 1983. Formation and characterization of oxynitride glasses in the Si-Ca-Al-O-N and Si-Ca-Al, B-O-N systems. *Journal of Materials Science* 18, 2087–2094.
- Jin, J., Yoko, T., Miyaji, F., *et al.*, 1993. Neutron diffraction study on the structure of NaSiON oxynitride glass. *Journal of the American Ceramic Society* 76, 630–634.
- Korgul, P., Thompson, D.P., 1993. The transparency of oxynitride glasses. *Journal of Materials Science* 28, 506–512.
- Kruppa, D., Dupree, R., Lewis, M.H., 1991. ¹⁵N MAS NMR in the YSiAlON system. *Materials Letters* 11, 195–198.
- Lange, F.F., 2006. The sophistication of ceramic science through silicon nitride studies. *Journal of the Ceramic Society of Japan* 114, 873–879.
- Lemerrier, H., Rouxel, T., Fargeot, D., Besson, J.-L., Piriou, B., 1996. Yttrium SiAlON glasses: Structure and mechanical properties-elasticity and viscosity. *Journal of Non-Crystalline Solids* 201, 128–145.
- Leng-Ward, G., Lewis, M.H., 1989. Oxynitride glasses and their glass-ceramic derivatives. In: Lewis, M.H. (Ed.), *Glasses and Glass Ceramics*. London: Chapman and Hall, pp. 106–155.
- Leonova, E., Hakeem, A.S., Jansson, K., *et al.*, 2008. Nitrogen-rich La-Si-Al-O-N oxynitride glass structures probed by solid state NMR. *Journal of Non-Crystalline Solids* 354, 49–60.
- Levin, E.M., Robbins, C.R., McMurdie, H.F., 1964. *Phase Diagrams for Ceramists*. 220. Columbus, USA: American Ceramic Society.

- Loehman, R.E., 1979. Preparation and properties of yttrium-silicon-aluminum oxynitride glasses. *Journal of the American Ceramic Society* 62, 491–494.
- Loehman, R.E., 1980. Oxynitride Glasses. *Journal of Non-Crystalline Solids* 42, 433–446.
- Loehman, R.E., 1985. Oxynitride Glasses. *Treatise on Materials Science & Technology* 26, 119–149.
- Lofaj, F., Deriano, S., LeFloch, M., Rouxel, T., Hoffmann, M.J., 2004a. Structure and rheological properties of the RE-Si-Mg-O-N (RE = Sc, Y, La, Nd, Sm, Gd, Yb and Lu) glasses. *Journal of Non-Crystalline Solids* 344, 8–16.
- Lofaj, F., Satet, R., Hoffmann, M.J., de Arellano López, A.R., 2004b. Thermal expansion and glass transition temperature of the rare-earth doped oxynitride glasses. *Journal of the European Ceramic Society* 24, 3377–3385.
- Lumby, R.J., Coe, R.F., 1970. The influence of some process variables on the mechanical properties of hot-pressed silicon nitride. *Proceedings of the British Ceramic Society* 15, 91–101.
- McMillan, P.F., Sato, R.K., Poe, B.T., 1998. Structural characterization of Si-Al-O-N glasses. *Journal of Non-Crystalline Solids* 224, 267–276.
- Menke, Y., Peltier-Baron, V., Hampshire, S., 2000. Effect of rare-earth cations on properties of SiAlON glasses. *Journal of Non-Crystalline Solids* 276, 145–150.
- Messier, D.R., Deguire, E.J., Hira, K., Kanzaki, S., 1995. Thermal decomposition in the system Si-Y-Al-O-N. *Journal of the American Ceramic Society* 67, 602–605.
- Messier, D.R., Gleisner, R.P., 1988. Preparation and characterisation of Li-Si-Al-O-N glasses. *Journal of the American Ceramic Society* 71, 422–425.
- Mulfinger, H.-O., 1966. Physical and chemical solubility of nitrogen in glass melts. *Journal of the American Ceramic Society* 49, 462–467.
- Mulfinger, H.-O., Meyer, H., 1963. Physical and chemical solubility of nitrogen in glass melts. *Glastechnische Berichte* 36, 481–483.
- Murakami, Y., Akiyama, K., Yamamoto, H., 1995. Phase relation and formation of Sialons and oxynitride glasses in the $\text{Si}_3\text{N}_4\text{-Yb}_2\text{O}_3\text{-AlN-SiO}_2$ system. *Journal of the Ceramic Society of Japan* 103, 772–776.
- Neerman, J.C., Bryan, F.R., 1959. Sampling and analysis of bubbles in glass by mass spectrometry. *Analytical Chemistry* 31, 532–535.
- Ohashi, M., Hampshire, S., 1991. Formation of Ce-Si-O-N glasses. *Journal of the American Ceramic Society* 74, 2018–2020.
- Ohashi, M., Nakamura, K., Hira, K., Kanzaki, S., 1995. Formation and properties of Ln-Si-O-N glasses. *Journal of the American Ceramic Society* 78, 71–76.
- Pastuszak, R., Verdier, P., 1983. M-Si-Al-O-N glasses (M = Mg, Ca, Ba, Mn, Nd), existence range and comparative study of some properties. *Journal of Non-Crystalline Solids* 56, 141–146.
- Pomeroy, M.J., Mulcahy, C., Hampshire, S., 2003. Independent effects of nitrogen substitution for oxygen and magnesium substitution by yttrium on the properties of Mg-Y-Si-Al-O-N glasses. *Journal of the Ceramic Society of Japan* 86 (3), 458–464.
- Pomeroy, M.J., Hampshire, S., 2008. SiAlON glasses: Effects of nitrogen on structure and properties. *Journal of the Ceramic Society of Japan* 116, 755–761.
- Redington-Keely, W., Redington, M., Hampshire, S., 2000. Liquid formation in the Y-Si-Al-O-N system. *Materials Science Forum* 325–326, 237–242.
- Redington, W., Redington, M., Hampshire, S., Serantoni, M., 2003. Properties of some high Al content glasses in various lanthanide-Si-Al-O-N systems. *Journal of Non-Crystalline Solids* 316, 74–81.
- Riley, F.L., 2000. Silicon nitride and related materials. *Journal of American Ceramic Society* 83, 245–265.
- Rocherulle, J., Guyader, J., Verdier, P., Laurent, Y., 1989b. Li-Si-Al-O-N and Li-Si-O-N oxynitride glasses study and characterization. *Journal of Materials Science* 24, 4525–4530.
- Rocherulle, J., Verdier, P., Laurent, Y., 1989a. Preparation and properties of gadolinium oxide and oxynitride glasses. *Materials Science and Engineering B* 2, 265–268.
- Roebuck, P.H.A., 1978. The silicon-aluminium-oxygen-nitrogen system. PhD thesis. UK: University of Newcastle upon Tyne.
- Rouxel, T., 2007. Elastic properties and short-to medium-range order in glasses. *Journal of American Ceramic Society* 90, 3019–3039.
- Rouxel, T., Besson, J.L., Rzepka, E., Goursat, P., 1990. Raman spectra of SiYAlON glasses and ceramics. *Journal of Non-Crystalline Solids* 122, 298–302.
- Rouxel, T., Dély, N., Sangleboeuf, J.C., *et al.*, 2005. Structure–property correlations in Y–Ca–Mg–Sialon glasses: Physical and mechanical properties. *Journal of the American Ceramic Society* 88, 889–896.
- Sakka, S., 1995. Structure, properties and applications of oxynitride glasses. *Journal of Non-Crystalline Solids* 181, 215–224.
- Schaller, T., Stebbins, J.F., 1998. The structural role of lanthanum and yttrium in aluminosilicate glasses: A ^{27}Al and ^{17}O MAS NMR study. *Journal of Physical Chemistry B* 102, 10690–10697.
- Schneider, M., Gasparov, V.A., Richter, W., Deckworth, M., Rüssel, C., 1997. XPS studies on oxynitride glasses in the system Si-Al-O-N. *Journal of Non-Crystalline Solids* 215, 201–207.
- Shannon, R.D., 1976. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica A* 32, 751–767 <http://abulafia.mt.ic.ac.uk/shannon/>
- Sharafat, A., Forslund, B., Grins, J., Esmaeilzadeh, S., 2009. Formation and properties of nitrogen-rich strontium silicon oxynitride glasses. *Journal of Materials Science* 44, 664–670.
- Sharafat, A., Grins, J., Esmaeilzadeh, S., 2008. Glass-forming region in the Ca-Si-O-N system using CaH_2 as Ca source. *Journal of the European Ceramic Society* 28, 2659–2664.
- Sharafat, A., Jonson, B., 2011. Glasses in the Ba-Si-O-N System. *Journal of the American Ceramic Society* 94, 2912–2917.
- Sharafat, A., Jonson, B., Pomeroy, M.J., Hampshire, S., 2015. Issues associated with the development of transparent oxynitride glasses. *Ceramics International* 41, 3345–3354.
- Shaw, T.M., Thomas, G., Loehman, R.E., 1984. Formation and Microstructure of Mg-Si-O-N Glasses. *Journal of the American Ceramic Society* 67, 643–647.
- Shelby, J.E., 1985. Formation and properties of calcium aluminosilicate glasses. *Journal of the American Ceramic Society* 68 (3), 155–158.
- Stanworth, J.E., 1948. On the structure of glass. *Journal of the Society of Glass Technology* 32, 154–172.
- Sun, E.Y., Becher, P.F., Plucknett, K.P., *et al.*, 1998. Microstructural design of silicon nitride with improved fracture toughness: II. Effects of yttria and alumina additives. *Journal of the American Ceramic Society* 81, 2831–2840.
- Thompson, D.P., Korgul, P., Hendry, A., 1983. The structural characterisation of sialon polytypoids. In: Riley, F.L. (Ed.), *Progress in Nitrogen Ceramics* 65. Dordrecht: Martinus Nijhoff (Springer), pp. 61–74. [NATO ASI Series (Series E: Applied Sciences)].
- Todd, B.J., 1956. Mass spectrometer analysis of gases in blisters in glass. *Journal of the Society of Glass Technology* 40, 32–38T.
- Tredway, W.K., Loehman, R.E., 1985. Scandium-containing oxynitride glasses. *Journal of the American Ceramic Society* 68, C131–C133.
- Tsuge, A., Nishida, K., 1978. High-strength hot-pressed Si_3N_4 with concurrent Y_2O_3 and Al_2O_3 additions. *American Ceramic Society Bulletin* 57, 424–431.
- Tu, H.Y., Sun, W.Y., Wang, P.L., Yan, D.S., 1995. Glass-forming region in the Sm-Si-Al-O-N system. *Journal of Materials Science Letters* 14, 1118–1122.
- Uhlig, H., Hoffmann, M.J., Lamparter, P., Steeb, S., 1998. Atomic structure of rare earth Si-Al-O-N glasses. *Zeitschrift für Naturforschung – Physical Sciences* 53a, 259–264.
- Unuma, H., Maekawa, H., Kiyono, H., *et al.*, 1992. ^{29}Si MAS NMR of Na-Si-O-N oxynitride glasses. *Journal of the Ceramic Society of Japan* 100, 1272–1276.
- Videau, J.J., Etourneau, J., Rocherulle, J., Verdier, P., Laurent, Y., 1997. Structural approach of sialon glasses: M-Al-Si-O-N. *Journal of the European Ceramic Society* 17, 1955–1961.
- Wild, S., Grieveon, P., Jack, K.H., 1968. The crystal chemistry of phases in the Si-N-O and related systems. Progress Report No.1, UK Ministry of Defence, Contract No. N/CP.61/9411/67/4B/MP387.
- Wild, S., Grieveon, P., Jack, K.H., 1972. The crystal structures of alpha and beta silicon and germanium nitrides. In: Popper, P. (Ed.), *Special Ceramics 5*. Stoke-on-Trent: The British Ceramic Research Association, pp. 385–395.
- Wusirika, R.R., Chyung, C.K., 1980. Oxynitride Glasses and Glass-ceramics. *Journal of Non-Crystalline Solids* 38–39, 39–44.
- Zernicke, J., 1955. *Chemical Phase Theory*. Deventer, The Netherlands: Kluwer.
- Zhang, E., Liddell, K., Thompson, D.P., 1996. Glass forming regions and thermal expansion of some Ln-Si-Al-O-N glasses (Ln = La, Nd). *British Ceramic Transaction* 95, 169–172.

Glasses: Oxynitride Glass Properties and Crystallization

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Introduction

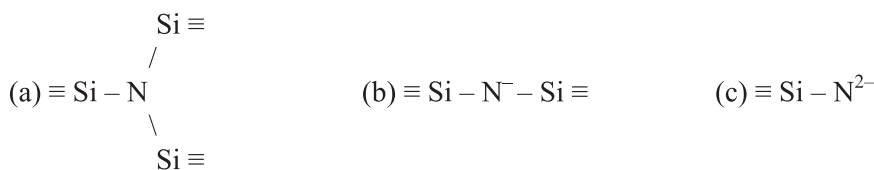
In modern industrial sectors, such as microelectronics, optoelectronics, communications technologies and biomedical devices, research continues to find useful lighter, stiffer materials, including glasses, with superior mechanical properties such as higher elastic moduli, hardness, strength and fracture toughness. The replacement of some of the oxygen atoms by nitrogen in oxide glasses (principally silicates, aluminosilicates and phosphates) leads to definite improvements in these properties and changes in thermal and other properties as a result of extra cross-linking of the glass network when nitrogen substitutes for oxygen.

The preparation, structure and properties of these oxynitride glasses have been extensively studied and some success has been achieved in understanding how changes in glass composition affect structural parameters and their relationship to properties. A number of reviews of oxynitride glasses have been published (Hampshire, 1993; Leng-Ward and Lewis, 1989; Sakka, 1995; Hampshire, 2003, 2008; Pomeroy and Hampshire, 2008a; Becher *et al.*, 2011; see also Hampshire, 2021, this volume).

Initial Studies of Effects of Nitrogen on Properties of Oxynitride Glasses

In the earliest reports of oxynitride glasses (Mulfinger, 1966), it was shown that small concentrations of nitrogen increased the softening temperature, viscosity and crystallization resistance of soda-lime-silica glasses. Elmer and Nordberg (1967) observed significant increases in indentation hardness and electrical resistivity, and a decrease in thermal expansion coefficient when nitrogen was incorporated into a borosilicate glass. A higher annealing temperature was required for these N-containing glasses.

Coon *et al.* (1983) studied the effect of nitrogen on Na-Si-O-N, Na-Ca-Si-O-N and Na-B-Si-O-N glasses and found that Young's modulus (*E*), microhardness and fracture toughness increased with increasing N content. Schrimpf and Frischat (1983) studied Young's modulus (*E*) and viscosity in N₂-containing Na₂O-CaO-SiO₂ glasses, both properties increasing with N content. They calculated Young's modulus for the glass based on mole fractions of component oxides along with considerations of the different ways in which N could be bonded with SiO₄ tetrahedra:



By comparing experimental data and calculated values of *E*, it was concluded that the most prevalent linkages were tri-coordinated N as in (a) above.

Jack (1977) suggested that as little as 1 at% N could increase the softening temperature, viscosity and devitrification resistance of M-Si-Al-O-N glasses (*M* = Mg, Y). Loehman (1979, 1980) prepared M-Si-Al-O-N (*M* = Ca, Mg, La, Y) glasses and proposed that nitrogen content could be correlated with properties. Glass transition temperature (*T_g*), microhardness and fracture toughness were seen to increase while thermal expansion coefficient decreased with increasing amounts of nitrogen added to these aluminosilicate glasses. However, the nitrogen was added as silicon nitride and therefore increases in N content in these glasses would also have resulted in increases in Si:(*M* + Al) ratio and, therefore, the changes in properties would have been influenced by the cation concentrations and were not due only to increases in N content.

Systematic investigations by Drew *et al.* (1981) measured the properties of glasses with fixed M:Si:Al cation ratios and, thus, they were able to show, unambiguously, how changes in N:O ratio affected properties. For glasses in the Ca-, Mg-, Nd- and Y- Si-Al-O-N systems with fixed cation composition of (eq%) 28M: 56Si:16Al, incorporation of nitrogen results in increases in glass transition temperature (*T_g*), shown in Fig. 1, and also microhardness, viscosity, resistance to devitrification, refractive index, dielectric constant and a.c. conductivity (see Hampshire *et al.*, 1985).

Sakka *et al.* (1983) reported increases in glass transition temperature (*T_g*), softening temperature (*T_s*) and microhardness (*H_v*) for Ca-Si-Al-O-N glasses where the mole ratios of the original oxides were kept constant: 36CaO:24Al₂O₃:40SiO₂ and up to 5.5 wt% N was introduced by addition of Si₃N₄ or AlN. They also showed that Young's modulus (*E*) of a Y-Si-Al-O-N glass increased with N content. It was suggested that, in view of increases in density with nitrogen, increases in *H* and *E* were due to compaction of the glass network. Homeny and McGarry (1984) reported increases in density, hardness, Young's modulus and fracture toughness with increasing nitrogen content for a series of Mg-Si-Al-O-N glasses with fixed Mg:Si:Al ratio and up to 4.6 wt% N.

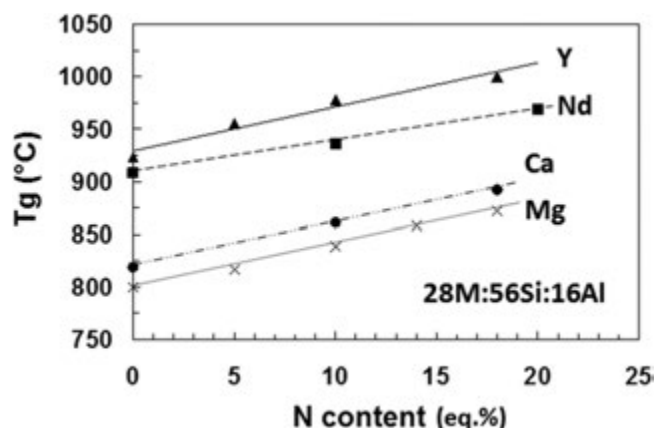


Fig. 1 Effect of N (eq%) on glass transition temperature (T_g) for glasses with fixed cation ratio of 28Y:56Si:16Al. After Hampshire, S., 2008. Oxynitride glasses. *Journal of the European Ceramic Society* 28, 1475–1483.

In a more extensive study of the Y–Si–Al–O–N system (Hampshire *et al.*, 1994), it was confirmed that glass transition temperature (T_g), viscosity, microhardness and elastic moduli all increase systematically while coefficient of thermal expansion (CTE) decreases with increasing N:O ratio for different series of glasses. The same trends were also confirmed by Sun *et al.* (1996) and more extensive data is given by Becher *et al.* (2011). As an example, Fig. 2 shows that values of Young's modulus increase by up to 25%–30% as ~17–20 eq% N is substituted for oxygen at fixed cation ratios (Hampshire *et al.*, 1994; Sun *et al.*, 1996).

It was considered that these effects were due to changes within the glass structure as 2-coordinated bridging oxygen atoms are replaced by 3-coordinated nitrogen atoms which leads to increased cross-linking of the network (Mulfinger, 1966; Hampshire *et al.*, 1985; Hampshire, 2008; see also Hampshire, 2021, this volume).

Structural Considerations in Relation to Properties

Properties are often correlated with a structural parameter, the glass compactness (C_g) which is calculated according to the expression:

$$C_g = (\sum x_i V_i \cdot N) \rho / \sum x_i M_i \quad (1)$$

where x_i is the ionic fraction of ion i , V_i the spherical volume of ion i , and M_i is its ionic mass; N is Avogadro's number and ρ is the glass density. The value for V_i can be calculated using the ionic radii given by Shannon (1969), although this may depend upon their local coordination within the glass. Glass compactness, also known as the atomic packing density, represents the minimum theoretical volume occupied by the ions in the glass divided by the overall effective volume or molar volume (MV) of the glass.

$$MV = \sum x_i M_i / \rho \quad (2)$$

Free volume (FV) is equal to molar volume less the volume occupied by ions. C_g has proven to provide predictions of the major trends in glass properties (Rouxel, 2007). In terms of the increases observed in oxynitride glass properties with increasing nitrogen, N to modifier bonding is more covalent and leads to higher glass compactness (Pomeroy and Hampshire, 2008a; Becher *et al.*, 2011) and rigidification (Richet *et al.*, 2010) of the glass structure.

Field strength calculations (Rouxel, 2007) are often used to consider bond strengths within glasses. These are based on Coulombic interactions between a cation and an anion and provide some general insights into the relative strengths of various M–O (or M–N) bonds. The relationship most frequently used is the cationic field strength:

$$CFS = z_c / (r_c)^2 \quad (3)$$

where z_c is the ionic charge and r_c the ionic radius of the cation. Generally, network formers have higher CFS values, modifiers have low values and intermediates have intermediate values (see also discussion in Hampshire, 2021, this volume).

The strength of the Si–O bond ($U_{\text{Si-O}} = 452$ kJ/mol) is apparently stronger than for the Si–N bond ($U_{\text{Si-N}} = 355$ kJ/mol), which means that Si–O has a greater stretching force constant; however, calculations show that the Si–N bond is more resistant to bending (Rouxel, 2007), which combined with the increased coordination with Si would increase the rigidity of the network. Bonding is much more covalent for Si–N than for Si–O and the bending resistance of the N–Si≡ unit is almost ten times higher than that of the O–Si= unit (De Graaf *et al.*, 2004) so enhancing network rigidity. As a result, bending is more difficult for Si–N–Si than for Si–O–Si linkages, contributing to greater stiffness and increases in elastic modulus (Becher *et al.*, 2011).

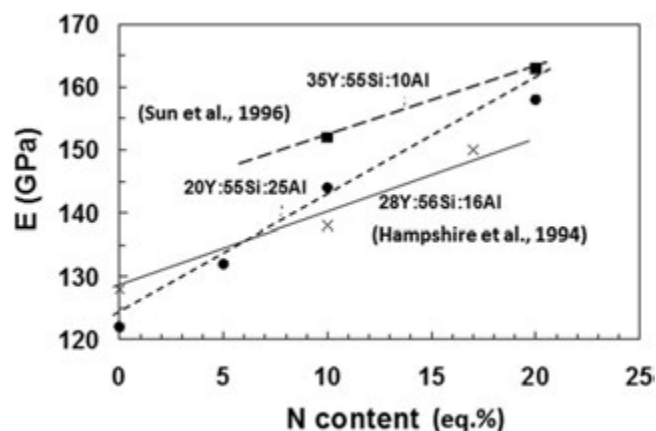


Fig. 2 Effect of N (eq%) on Young's modulus (E) for glasses with fixed Y:Si:Al ratios. Data from Hampshire, S., Nestor, E., Flynn, R., *et al.*, 1994. Yttrium oxynitride glasses: Properties and potential for crystallization to glass-ceramics. *Journal of the European Ceramic Society* 14, 261–273. Sun, E.Y., Becher, P.F., Hwang, S.-L., *et al.*, 1996. Properties of silicon-aluminum-yttrium oxynitride glasses. *Journal of Non-Crystalline Solids* 208, 162–169.

Effect of Nitrogen on Hardness and Young's Modulus

Property data for oxynitride glasses (Sun *et al.*, 1996; Lofaj *et al.*, 2003; Pomeroy *et al.*, 2003; Rouxel *et al.*, 2005; Dölekçekiç *et al.*, 2007) have been analyzed (Pomeroy and Hampshire, 2008a) and most reports show good linear relationships between glass property values and nitrogen content with correlation coefficients generally of the order of 0.99. For microhardness, the gradients lie in the range 0.07–0.13 GPa eq% N^{-1} as shown in Table 1. Generally then, the substitution of 20 eq% N for oxygen in these glasses would be expected to increase the hardness of the glass by 1.4–2.6 GPa. The increased rigidity and degree of network compaction with nitrogen content of oxynitride glasses is often cited for the increase in hardness with nitrogen content (Hampshire *et al.*, 1984; Lofaj *et al.*, 2003; Pomeroy *et al.*, 2003; De Graaf *et al.*, 2004; Rouxel *et al.*, 2005; Daucé *et al.*, 2008; Pomeroy and Hampshire, 2008a; Paraschiv *et al.*, 2015).

Based on data of oxynitride glass hardness for a wide range of glass compositions in the literature, Paraschiv *et al.* (2015) investigated whether the change in hardness due to partial replacement of oxygen by nitrogen in an oxide glass can be quantitatively predicted using only basic topological information about the glassy network. They also presented new hardness data for a series of alkaline earth aluminosilicate glasses containing nitrogen. A model was derived, based on the topological constraint theory (Mauro, 2011), to account for the effect of N for O substitution on glass hardness. Analysis of the wide range of experimental data confirmed that glass hardness increases approximately linearly with the nitrogen content, suggesting its independence of the base oxide cation composition. By deriving the topological bond constraint model of glass hardness and comparing it to the experimental data, it was inferred that this increase in hardness can be quantitatively predicted by a simple enumeration of the additional room temperature bond-stretching and bond-bending constraints arising from the N for O substitution (Paraschiv *et al.*, 2015). The conclusion was that the topological model may thus be useful for designing new oxynitride glass compositions with targeted hardness values.

As shown in Table 2, for elastic modulus, E, gradients of the plots of E v. N content are in the range 0.85–1.8 GPa eq% N^{-1} with the majority of gradients in the range 1.1–1.4 GPa eq% N^{-1} . It is worth noting that the maximum gradient of 1.8 GPa eq% N^{-1} was obtained from data acquired using nanoindentation rather than the ultrasonic pulse echo method by which the other data were measured. Generally then, the substitution of 20 eq% N for oxygen in these glasses would be expected to increase Young's modulus by 22–28 GPa.

Effect of Nitrogen on Thermal Properties

Changes in Viscosity with Nitrogen Content

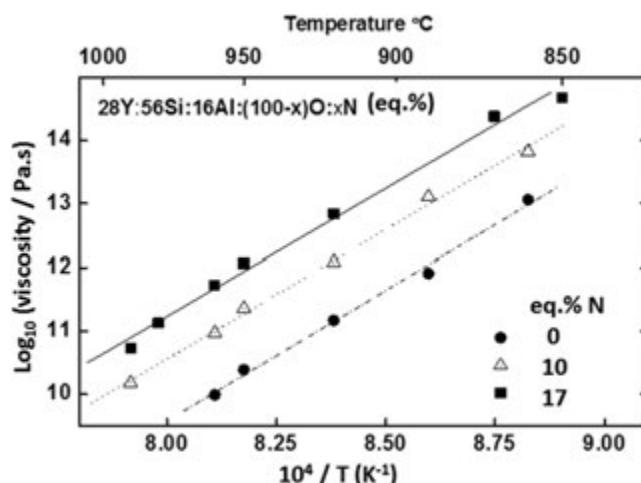
Rouxel *et al.* (1992) and Hampshire *et al.* (1994) observed that viscosity increases by almost 3 orders of magnitude simply by replacing 17 eq% oxygen by nitrogen in a series of glasses with composition (eq%): 28Y:56Si:16Al:(100 - x)O: xN (x = 0, 10, 17). Fig. 3 shows the viscosity-reciprocal temperature relationships for these glasses derived from 3-point creep tests on the glasses. The presence of nitrogen leads to a significant decrease in creep strain. The transient creep is reduced and a steady-state stage is reached much more quickly (Rouxel *et al.*, 1992). The creep rate dependence on stress during stationary creep was measured from incremental stress steps at a constant temperature of 900°C for the glass containing 10 eq% N. The stress exponent, n, was found to be equal to 1.01, which suggests a linear viscoelastic behavior. Similar trends have been reported for other oxynitride glasses containing different modifying cations and with different cation ratios (Becher and Ferber, 2004).

Table 1 Linear correlation data for variation of microhardness H_v with nitrogen content for various oxynitride glasses (H_v measured by indentation using Vickers method)

Glass compositions	Cation ratios (in eq%)	N content range eq% N	Load (kg)	Plot H_v v. N gradient ($\text{GPa eq\% N}^{-1}$)	R^2	References
28Y: 56Si: 16Al		0–17	0.3	0.100	0.95	Hampshire <i>et al.</i> (1994)
20Y: 55Si: 25Al		0–20	nanoind.	0.134	0.94	Sun <i>et al.</i> (1996)
20La: 60Si: 20Mg		0–20	0.5	0.075	0.97	Lofaj <i>et al.</i> (2003)
37Er: 42Si: 21Al		0–15	0.1	0.060	0.99	Dölekçekiç <i>et al.</i> (2007)
37Y: 42Si: 21Al		0–15	0.1	0.070	0.98	Dölekçekiç <i>et al.</i> (2004)
20Ca: 50Si: 30Al		0–15	0.3	0.080	0.98	García-Bellés <i>et al.</i> (2013)
Varying La and Si		0–25	1.0	0.110	–	Hakeem <i>et al.</i> (2007)

Table 2 Linear correlation data for variation of Young's modulus E with nitrogen content for various oxynitride glasses (E measured using ultrasonic pulse echo method)

Glass compositions	Cation ratios (in eq%)	N content range eq% N	Plot E v. N gradient ($\text{GPa eq\% N}^{-1}$)	R^2	References
28Y: 56Si: 16Al		0–17	1.45	0.99	Hampshire <i>et al.</i> (1994)
28Mg: 56Si: 16Al		0–15	1.34	0.99	Pomeroy <i>et al.</i> (2003)
14Mg: 14Y: 56Si: 16Al		0–15	1.32	0.99	Pomeroy <i>et al.</i> (2003)
28Y: 56Si: 16Al		0–15	1.54	0.99	Pomeroy <i>et al.</i> (2003)
37Er: 42Si: 21Al		0–15	0.85	0.91	Dölekçekiç <i>et al.</i> (2007)
37Y: 42Si: 21Al		0–15	1.1	0.99	Dölekçekiç <i>et al.</i> (2004)
20Ca: 50Si: 30Al		0–15	0.88	0.99	García-Bellés <i>et al.</i> (2013)
20Y: 55Si: 25Al		0–20	1.80	0.99	Sun <i>et al.</i> (1996) ^a

^a E measured by nanoindentation technique.**Fig. 3** Viscosity-reciprocal temperature relationships for glasses with composition (eq%): 28Y:56Si:16Al:(100 – x)O:xN ($x = 0, 10, 17$). Data from Hampshire, S., Nestor, E., Flynn, R., *et al.*, 1994. Yttrium oxynitride glasses: Properties and potential for crystallization to glass-ceramics. *Journal of the European Ceramic Society* 14, 261–273.

Variation of T_g with N Content

As with other properties, linear correlations are also observed between nitrogen substitution levels and glass transition temperature as was shown in Fig. 1 with good correlation coefficients. Pomeroy and Hampshire (2008a) analyzed gradients and standard error values obtained from linear regression analysis of data of T_g v. nitrogen content from various reports in the literature (Hampshire *et al.*, 1984; Sun *et al.*, 1996; Pomeroy *et al.*, 2003; Lofaj *et al.*, 2004b; Rouxel *et al.*, 2005; Dölekçekiç *et al.*, 2007). Regression coefficients were close to 0.99 for fourteen sets of data analyzed with standard error values in the range 1.3–7.8°C, indicating excellent linear correspondence between glass transition temperature and nitrogen substitution level. Gradients fall between 2.6 and 4.1°C eq% N^{-1} with most values falling close to 3°C eq% N^{-1} . Accordingly, a general rule can be established that the effect of nitrogen in oxynitride glasses is to increase glass transition temperature by about 3°C for each equivalent percentage nitrogen substituted for oxygen. For a 20 eq% N substitution level, therefore, increases of about 60°C are expected. Littleton softening temperatures (Lofaj *et al.*, 2004b) and

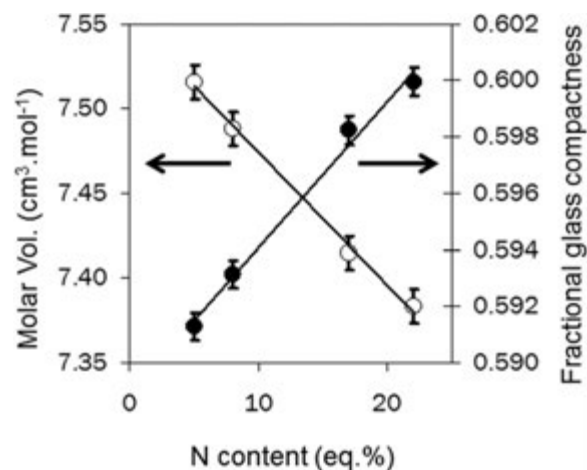


Fig. 4 Effect of nitrogen content on molar volume and fractional glass compactness for a series of glasses with cation composition (eq%): 37Y:42Si:21Al. Data from Dölekçekiç, E., Pomeroy M.J., Hampshire, S., 2004. The effect of preparation route and nitrogen content on Y-SiAlON glasses. Key Engineering Materials 264–268, 1927–1930.

dilatometric softening temperatures, $T_{s,dil}$. (Pomeroy *et al.*, 2003; Dölekçekiç *et al.*, 2004, 2007) also increase linearly with nitrogen content. In general, slopes of plots of $T_{s,dil}$ v. N content are similar to those for T_g v. N, i.e., in the range $2.3\text{--}3.8^\circ\text{C eq\% N}^{-1}$.

Effect of Nitrogen Content on Glass Molar Volume and Fractional Glass Compactness

A number of studies (Pomeroy *et al.*, 2003; Dölekçekiç *et al.*, 2004; Lofaj *et al.*, 2004b) have shown good linear correlations between molar volume and N content and between fractional glass compactness and N content of oxynitride glasses. Fig. 4 shows a plot of molar volume and fractional glass compactness as a function of nitrogen content for a glass with cation composition: 37Y:42Si:21Al (eq%). There are clearly linear correlations. The changes in compactness (atomic packing) indicate that the replacement of oxygen by nitrogen induces a contraction of the glass structure, which is linked to the increased coordination of nitrogen compared to oxygen. Fig. 5 shows data for this glass which exemplifies the linear dependence of Young's modulus, E , on fractional glass compactness and also shows that there is linear correspondence between microhardness, H_v , and glass compactness. Rouxel (2007) has conclusively shown that, for a wide variety of different types of glasses, Young's modulus is controlled by the compactness of the glass structure. Thus, the linear trend shown in Fig. 5 between Young's modulus and fractional glass compactness is wholly expected. Other data for Ca- and Ca-Y-Si-Al-O-N glasses confirm linear relationships between Young's modulus (and hardness) and fractional glass compactness.

Structural Implications of Nitrogen Content – Property Relationships

Based upon the data presented, it is clear that linear relationships arise between the nitrogen content of oxynitride glasses and elastic modulus, hardness, glass transition temperature, dilatometric or Littleton softening temperature, $\log(\text{viscosity})$, molar volume and fractional glass compactness. In addition, the gradients of the linear relationships are similar for a wide range of different oxynitride glass compositions and modifier types. The linearity of the relationships can be explained by the fact that each eq% nitrogen substitution introduces the same number of additional crosslinks into the glass network. Accordingly, the extent of network crosslinking will increase linearly with eq% N. This will have the result of contracting the glass network thus increasing glass compactness and decreasing molar volume in a linear manner. For glass transition temperature (T_g) and the softening temperatures, increased levels of crosslinking will increase resistance to the vibration of atoms (T_g) or the relative movement of glass structural units (softening). Thus, values of T_g and the softening temperatures should also increase linearly as oxygen is sequentially replaced by nitrogen. The same arguments can be made for viscosity since increased crosslinking will increase the resistance to the shear of structural units over one another. Whilst good linear correlations exist between elastic modulus or microhardness and nitrogen content, Rouxel (2007) shows that they are an indirect result of increases in fractional glass compactness and decreases in molar volume. Accordingly, fractional glass compactness and molar volume data are essential to a full understanding of how properties vary with glass composition.

Subcritical Crack Growth (SCG) Resistance of Oxynitride Glasses

The subcritical crack growth (SCG) resistance in water of Y-Si-Al-O-N glasses and their oxide equivalents have been reported using different loading configurations (Coon, 1998; De Graaf *et al.*, 2006a) but with the same relationship between crack velocity,

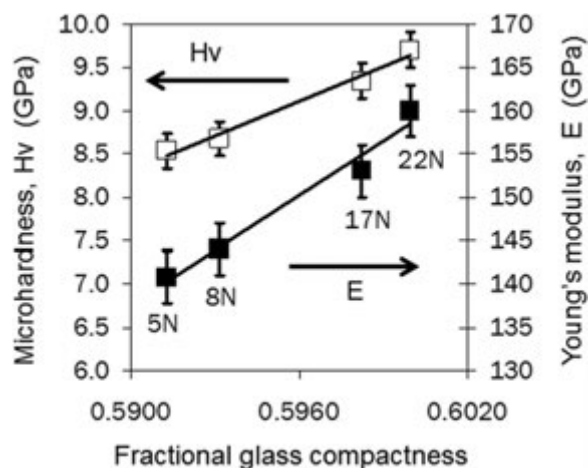


Fig. 5 Effect of fractional glass compactness on microhardness and Young's modulus for a series of glasses with cation composition (eq%): 37Y:42Si:21Al. 5N, 8N, 17N, 22N refer to nitrogen contents (in eq%). Data from Dölekçekiç, E., Pomeroy M.J., Hampshire, S., 2004. The effect of preparation route and nitrogen content on Y-SiAlON glasses. *Key Engineering Materials* 264–268, 1927–1930.

v , and the applied stress intensity, K_I :

$$V = A(K_I)^n \quad (4)$$

where A is a constant and n is the power-law exponent. De Graaf *et al.* (2006a) found that n for a Y-Si-Al-O-N glass containing ~7 at% N was significantly higher ($n = 63$) than for a yttrium aluminosilicate glass ($n = 21$), while Coon (1998) reported, for a Y-Si-Al-O-N glass containing 18 at% N, subcritical crack velocities in the range 5×10^{-7} – 6×10^{-5} m/s, obtained for stress intensities ranging from 0.675 to 0.686 MPa $m^{0.5}$, respectively, and an even higher value of n ($= 142$).

Variations in Optical Properties with Nitrogen Content

Optical properties of oxynitride glasses have been studied. The refractive index of all oxynitride glasses was found to increase with increasing nitrogen content (Drew *et al.*, 1981; Coon *et al.*, 1989) due to its high ionic polarisability. Near IR transmission of a Ca-Si-Al-O-N glass significantly increases, and the absorption at 2.7 μm observed for the oxide glass disappears when 18 eq% nitrogen substitutes for oxygen, whereas UV transmission was found to be impaired, the absorption edge shifting to longer wavelengths (Drew *et al.*, 1981; Hampshire *et al.*, 1985).

Effects of Cation Composition on Properties of Oxynitride Glasses

Y-Si-Al-O-N Glasses

The effect of varying Si:Al and Y:Al ratios on properties of glasses with constant O:N ratio were investigated by: Hampshire *et al.* (1994); Sun *et al.* (1996); Hampshire and Pomeroy (2004); Becher *et al.* (2011). As Si:Al ratio increases, T_g and viscosity increase while elastic moduli, hardness and thermal expansion coefficient decrease. With increasing Al:Y ratio, elastic moduli and thermal expansion coefficient decrease while the T_g and viscosity decrease to a minimum at 16 eq% Al and then increase with further increase in Al content.

With a fixed N content of 17 eq% and fixed Si content of 56 eq%, as Y:Al ratio decreases, there is a reduction in viscosity of greater than 1 order of magnitude as Al content increases from 4 eq% to 16 eq% Al and then, with further increase in Al to 22 eq%, viscosity increases again. Overall, these effects can be assumed to be related to changes in the density of the glass network and the numbers of non-bridging oxygens as Al changes from 4-fold coordination with oxygen to 5- or 6-fold. At higher Al:Y ratios, when 4 co-ordinated Al is prevalent, enhancement of the cross-linking of the glass network occurs, caused by the formation of more Al-O-Si linkages as Raman spectroscopy analyses indicated (Rouxel *et al.*, 1990). It appears that changes in the Al:Si ratio do not affect the degree of cross linking of the network significantly but simply lead to the replacement of Si-O-Si bridges by Al-O-Si linkages.

Rare Earth (RE) Oxynitride Glasses

Properties of various RE-Si-Al-O-N glasses have been investigated by a number of authors (Murakami and Yamamoto, 1994; Ohashi *et al.*, 1995; Ramesh *et al.*, 1997; Menke *et al.*, 2000a,b; Becher *et al.*, 2002, 2011; Pomeroy *et al.*, 2005). As the atomic number of the lanthanide ion increases, the rare earth ion size decreases and glass transition temperature (T_g), softening temperature (T_s), Young's modulus and hardness increase linearly with increases in cation field strength, CFS (where $CFS = v/r^2$,

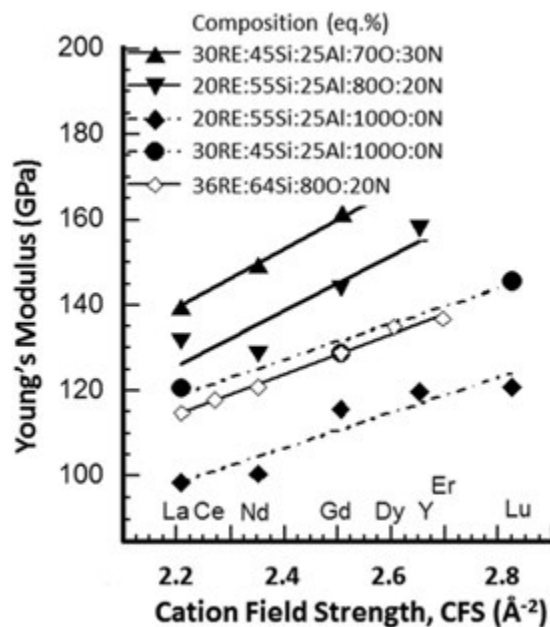


Fig. 6 Changes in Young's modulus of RE-Si-Al-O-N glasses as a function of cation field strength and nitrogen contents. Young's modulus increases with increase in N content and with decrease in RE cation radius. Data from Ohashi, M., Nakamura, K., Hirao, K., Kanzaki, S., Hampshire, S., 1995. Formation and properties of Ln-Si-O-N glasses. *Journal of the American Ceramic Society* 78, 71–76. Becher, P.F., Waters, S.B., Westmoreland, C.G., Riester, L., 2002. Influence of composition on the properties of SiREAL oxynitride glasses: RE = La, Nd, Gd, Y, or Lu. *Journal of the American Ceramic Society* 85, 897–902. Becher, P., Hampshire, S., Pomeroy, M.J., *et al.*, 2011. An overview of the structure and properties of silicon-based oxynitride glasses. *International Journal of Applied Glass Science* 2, 63–83.

v = valency, r = ionic radius). **Fig. 6** shows linear changes in Young's modulus as a function of RE cation field strength for glasses with different fixed cation ratios and fixed O:N ratios (data on RE-Si-Al-O-N compositions from [Becher *et al.*, 2002](#); data on RE-Si-O-N compositions from [Ohashi *et al.*, 1995](#); calculation of CFS from ionic radius assuming 6-fold coordination of RE with O). As the rare earth cation field strength increases (decreasing ionic radius), the Young's modulus increases linearly.

However, differences were noted for Eu and other rare earths which did not always fall on the $E v$ CFS linear plot ([Menke *et al.*, 2000a,b](#)). Eu^{3+} is known to reduce to Eu^{2+} in aluminosilicate glasses. [De Graaf *et al.* \(2003\)](#) have also shown that both Sm and Yb can undergo a reduction from the trivalent state in oxides to the divalent state in oxynitride glasses, the degree of conversion depending on melting time. Emission spectra of Sm-containing glasses show the presence of both Sm^{3+} as well as Sm^{2+} , which is also reflected in the data for Young's modulus and density. In the reflection spectra of Yb-containing glasses, a broad absorption band for Yb^{2+} indicates a similar reduction, while a second absorption band suggests the presence of some remnant Yb^{3+} . The other properties of these glasses also confirm a mixed Yb oxidation state. These effects are attributed to the reducing power of chemically incorporated nitrogen in the glass matrix, as clearly demonstrated for Eu-Si-Al-O-N glasses ([Menke *et al.*, 2000b](#)). With a change from Eu^{3+} to Eu^{2+} , the luminescence characteristics change ([De Graaf *et al.*, 2003, 2006b](#)) to give an extended range of emission up to longer wavelengths (500–650 nm) which is ascribed to a combination of energy transfer between the different sites and change of the Eu^{2+} site distribution.

Many studies show that the temperature-dependent viscosity shifts to higher temperatures as the rare earth ion size decreases. **Fig. 7** demonstrates the effects of different rare earth cations (RE = Ce, Sm, Eu, Er and also Y) on viscosity – reciprocal temperature relationships for RE-Si-Al-O-N glasses with fixed cation ratio of 28RE:56Si:16Al ([Hampshire and Pomeroy, 2004](#); [Hampshire, 2008](#)). At any temperature (for example, in the range 825–930°C), viscosity decreases by ~ 3 orders of magnitude in the order: $\text{Er} \geq \text{Y} > \text{Sm} > \text{Ce} > \text{Eu}$. As indicated above, Eu is in the +2 state which is a much larger ion than Eu^{3+} . Viscosity, as with other properties, increases almost linearly with increase in cation field strength of the RE ion.

As shown previously, Al content has a significant effect on viscosity. [Becher and Ferber \(2004\)](#) reported viscosity results for alumina-free La-Si-O-N glasses and showed that the viscosity-temperature plots are shifted by approximately +50°C on the temperature scale compared with La-Si-Al-O-N glasses, which represents more than one order of magnitude increase in viscosity at a fixed temperature. Thus, reducing the alumina content of these oxynitride glasses results in more refractory glasses with higher viscosities. Overall, a change of almost 6 orders of magnitude in viscosity can be achieved by increasing N and modifying the overall RE:Si:Al cation ratio and the type of rare earth ion.

The RE ions strongly affect the molar volume of the glass, with the smaller ions exerting stronger bonding (i.e., higher CFS) on the $(\text{Si,Al})(\text{O,N})_4$ tetrahedra and forming a more compact network. Overall, the trends in properties suggest that there is a tightening of the glass network by (1) extra cross-linking as a result of increasing nitrogen content, and (2) a decrease of the rare earth cation radius.

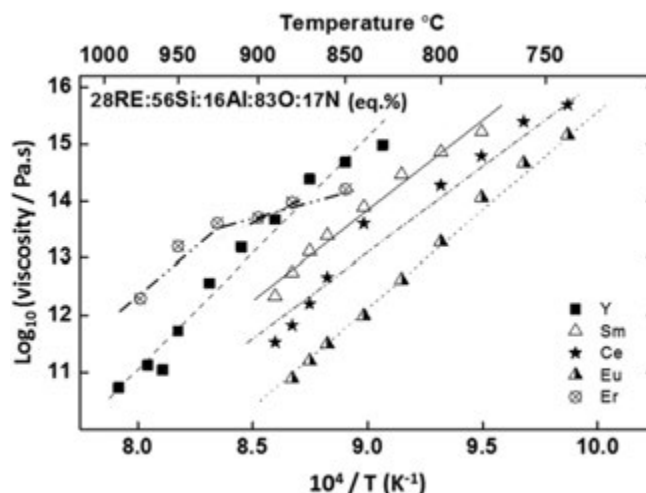


Fig. 7 Viscosity-reciprocal temperature relationships for a series of glasses with cation ratio (in eq%): 28RE:56Si:16Al (RE = Y, Sm, Ce, Eu, Er) and fixed N content of 17 eq%. After Hampshire, S., 2008. Oxynitride Glasses. *Journal of the European Ceramic Society* 28, 1475–1483.

RE-Si-Mg-O-N glasses

Studies of properties and structure of RE-Si-Mg-O-N glasses (RE = Sc, Y, La, Nd, Sm, Gd, Yb and Lu) have also been undertaken (Lofaj *et al.*, 2004a,b) and show similar trends to those found for RE-Si-Al-O-N glasses. Hardness, elastic modulus, viscosity, thermal expansion coefficient, glass transition temperature and softening temperature increase linearly with increasing cation field strength, CFS, as found for RE-Si-Al-O-N glasses.

In these glasses, nitrogen modifies the glass structure by increasing the content of SiO_3N tetrahedra with extra bridging corners at the expense of SiO_4 units sharing only 2 corners, as found also in Er-Si-Al-O-N glasses (Dölekçekiç *et al.*, 2007). In the RE-Si-Mg-O-N glasses, this depends on the rare earth cation; Lu was found to be more effective in formation of SiO_3N units than La (Lofaj *et al.*, 2004a). Replacing La by Lu results in approximately one order of magnitude increase in viscosity.

Effect of Fluorine on Properties of Oxynitride Glasses

One of the major disadvantages to the use of oxynitride glasses for high stiffness/high hardness applications is the fact that melting at temperatures of the order of 1650–1700°C are required to achieve sufficiently low viscosities for glass pouring. Increased glass viscosities also mean that glass forming or drawing processes must be carried out at higher temperatures than are normal for conventional glasses. However, fluorine can be successfully substituted for oxygen at the same time as nitrogen (Hanifi *et al.*, 2009, 2012; García-Bellés *et al.*, 2013). The network terminating effect of fluorine induces significant reductions in glass melting temperatures, T_g and dilatometric softening temperatures. Interestingly, elastic modulus and hardness are virtually unaffected by fluorine substitution.

The effects of nitrogen and fluorine substitution on properties of a Ca-Si-Al-O-N-F glass are independent and additive rather than synergistic. As a result of these independent and additive effects, nitrogen substitution levels affect glass properties in oxyfluoronitride glasses to similar extents as are observed in oxynitride glasses. Young's modulus and microhardness values for these glasses are controlled by changes in fractional glass compactness which in turn is controlled by the free volume of the glass structure which is dependent on the structural changes resulting from compositionally induced variations of crosslink density.

Fluorine substitution for oxygen in Ca-Si-Al-O-N glasses yields significant decreases in glass transition temperature and glass melting temperature as well as increasing nitrogen solubility to levels much higher than that previously reported for F-free oxynitride glasses. The important effect that N results in increased elastic modulus is not diminished by the addition of fluorine. Thus, it is possible to produce novel oxyfluoronitride glasses with a high elastic modulus but melting and working can be carried out at more conventional glass processing temperatures.

Crystallization of Oxynitride Glasses to Form Glass-Ceramics

As with other silicate glasses, oxynitride glasses may be heat treated at the appropriate temperatures to crystallize as glass-ceramics (Hampshire *et al.*, 1985; Leng-Ward and Lewis, 1989; Besson *et al.*, 1993; Ramesh *et al.*, 1996, 1998; Liddell and Thompson, 1997; Gonon *et al.*, 2000; Menke *et al.*, 2005, 2007). The conventional process to produce a glass-ceramic involves two steps: a lower temperature heat treatment of glasses to induce nucleation, generally just above the glass transition temperature, followed by

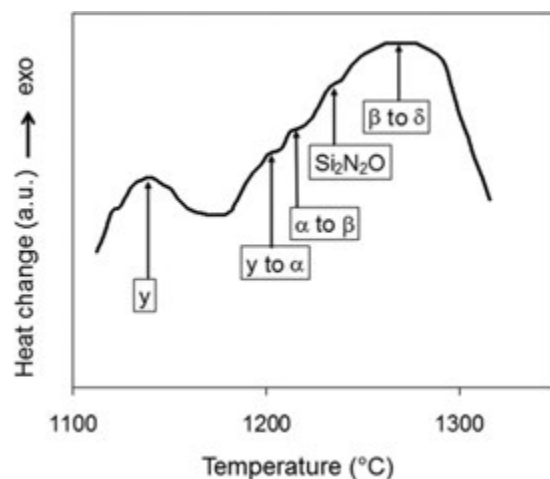


Fig. 8 DTA curve showing crystallization events at different temperatures in glass with composition (eq%): 28Y:56Si:16Al:83O:17N. Crystal phases formed include different $\text{Y}_2\text{Si}_2\text{O}_7$ polymorphs and $\text{Si}_2\text{N}_2\text{O}$. After Hampshire, S., Pomeroy, M.J., 2012. Grain boundary glasses in silicon nitride: A review of chemistry, properties and crystallisation. *Journal of the European Ceramic Society* 32, 1925–1932.

heating to a second higher temperature, the so-called crystallization temperature, to allow growth of the pre-formed nuclei. The crystalline phases formed depend on both the composition of the parent glass and the heat-treatment process. The glass-ceramic transformations in a glass of composition (in eq%) 28Y:56Si:16Al:83O:17N have been studied (Ramesh *et al.*, 1998) using both classical and differential thermal analysis techniques and these two methods were found to be in close agreement. Optimum nucleation and crystallization temperatures were determined in relation to the glass transition temperature. The major crystalline phases present are mixtures of different forms of yttrium disilicate and silicon oxynitride.

The devitrification of this Y–Si–Al–O–N glass is highly complex due to the fact that all 5 polymorphs of yttrium disilicate can form under varying conditions of heat treatment and also silicon oxynitride as shown in Fig. 8. The optimum nucleation conditions correspond to those which offer the best heterogeneous nucleation condition for the γ - to α - plus β - yttrium disilicate phase transformation. The devitrification processes in Y–Si–Al–O–N glasses can be simplified by partially substituting Y with a rare earth ion such that the average ionic radius of the mixed modifier system is compatible with a single disilicate polymorph (Pomeroy and Hampshire, 2008b; Hampshire and Pomeroy, 2012).

Other crystalline phases which have received some attention include B-phase ($\text{Y}_2\text{SiAlO}_5\text{N}$) (Gonon *et al.*, 2000), Iw-phase ($\text{Y}_2\text{Si}_3\text{Al}(\text{O},\text{N})^{10}$) (i.e., ~ 10 eq% N) and wollastonite (YSiO_2N) which are formed on heat treatment at temperatures below 1200°C of a glass of composition (in eq%) 35Y:45Si:20Al:77O:23N. At higher temperatures heat treatment results in formation of α -yttrium di-silicate ($\text{Y}_2\text{Si}_2\text{O}_7$), apatite ($\text{Y}_2\text{Si}_3\text{O}_{12}\text{N}$) and YAG ($\text{Y}_3\text{Al}_2\text{O}_{12}$) (Hampshire *et al.*, 1994). At relatively low heat treatment temperatures of ~ 950 – 1100°C , the nucleation and growth of N-wollastonite (YSiO_2N) and the intermediate phases B and Iw are kinetically favored over that of the more stable equilibrium phases YAG and $\text{Si}_2\text{N}_2\text{O}$. B-phase has the pseudo α -wollastonite structure. Normally, it might be expected that this structure would consist of layers of Y^{3+} and rings of $(\text{Si},\text{Al})(\text{O},\text{N})_4$ tetrahedra but it was shown that the formation of these rings is suppressed by the incorporation of nitrogen (Gonon *et al.*, 2000).

Further studies, by analytical transmission electron microscopy, including electron spectroscopic imaging, have shown that B-phase forms after crystallization heat treatment at 1050 and 1150°C of Er- and Y/Yb- Si–Al–O–N glasses (Menke *et al.*, 2005, 2007). The crystals take up a wide range of composition; the erbium cation percentage varies around that of the expected B-phase composition ($\text{Er}_2\text{SiAlO}_5\text{N}$), but aluminum content is slightly lower and silicon content higher than this. In addition, Er content is strongly anti-correlated with Si content. A comparison of B-phase compositions after crystallization of equivalent glasses formed with either yttrium, erbium or ytterbium shows that the B-phase solid solution range depends on the particular cation radius. As a consequence of this, the degree of crystallization and the composition of the residual glass will, for equivalent glasses, also depend on the cation radius. In addition to crystal growth, the crystallization heat treatment results in a phase separation of the residual glass whereby smaller Si- and N-rich amorphous features form. These features are effectively pinning the boundaries of growing crystals.

The properties of the glass-ceramics are significantly higher than those of the parent glasses with, for example, values of elastic modulus greater than 200 GPa.

Potential Applications for Oxynitride Glasses

So far, oxynitride glasses have not found any real application. Their potential applications include use as passive coatings on electronic substrates, high-speed hard disk drive substrates. Bachar *et al.* (2016) have studied bioactive glasses containing nitrogen and there may be possibilities of developing bioglasses with improved strength and elastic modulus. Luo *et al.* (2013) investigated

transparent oxynitride glasses with a view to improved ballistic resistance for transparent armor materials. The work of De Graaf *et al.* (2003) shows potential for oxynitride glasses as host materials for LED phosphors. One area of oxynitride glass research that has not been covered here is phosphorus oxynitride glasses based on Li-P-O-N and related systems. These materials may have potential for use in solid-state lithium batteries.

Summary

Oxynitride glass formation occurs in a number of M-Si-O-N, M-Si-Al-O-N and M-Si-Mg-O-N systems. As nitrogen content increases, properties such as glass transition temperature, elastic modulus, viscosity, hardness and slow crack growth resistance increase as a result of increased cross-linking of nitrogen within the glass network. Most reports show good linear relationships between glass property values and nitrogen content with correlation coefficients generally of the order of 0.99. The linearity of the relationships can be explained by the fact that each eq% nitrogen substitution introduces the same number of additional crosslinks into the glass network with the consequent increases in rigidity and degree of network compaction (decrease in molar volume). There is a clear linear dependence of Young's modulus, and also microhardness, on fractional glass compactness.

For a constant cation composition, viscosity increases by more than 2 orders of magnitude as ~ 17 eq% oxygen is replaced by nitrogen. For rare earth oxynitride glasses with constant nitrogen content, viscosity, Young's modulus and Tg and other properties increase linearly with increasing cation field strength (decreasing ionic radius).

Many studies on crystallization of oxynitride glasses have been carried out which have identified suitable two stage heat treatments for nucleation and growth of crystal phases, including different yttrium disilicate phases and B-phase (M_2SiAlO_5N ; M=Y, Er, Y+Yb), to form glass ceramics with significant increases in strength and elastic modulus over the parent glasses.

Addition of fluorine extends glass formation in oxynitride systems and allows dissolution of higher levels of nitrogen into glasses. Fluorine lowers glass transition temperature but does not have any effect on elastic modulus or microhardness.

References

- Bachar, A., Mercier, C., Tricoteaux, A., *et al.*, 2016. Bioactive oxynitride glasses: Synthesis, structure and properties. *Journal of the European Ceramic Society* 36, 2869–2881.
- Becher, P., Hampshire, S., Pomeroy, M.J., *et al.*, 2011. An overview of the structure and properties of silicon-based oxynitride glasses. *International Journal of Applied Glass Science* 2, 63–83.
- Becher, P.F., Ferber, M.K., 2004. Temperature-dependent viscosity of SiREAL-based glasses as a function of N:O and RE:Al ratios (RE = La, Gd, Y, and Lu). *Journal of the American Ceramic Society* 87 (7), 1274–1279.
- Becher, P.F., Waters, S.B., Westmoreland, C.G., Riester, L., 2002. Influence of composition on the properties of SiREAL oxynitride glasses: RE = La, Nd, Gd, Y, or Lu. *Journal of the American Ceramic Society* 85, 897–902.
- Besson, J.-L., Billières, D., Rouxel, T., *et al.*, 1993. Crystallization and properties of a Si-Y-Al-O-N glass ceramic. *Journal of the American Ceramic Society* 76 (8), 2103–2105.
- Coon, D.N., 1998. Subcritical crack growth in a Y-Si-Al-O-N glass. *Journal of Non-Crystalline Solids* 226 (3), 281–286.
- Coon, D.N., Doyle, T.E., Weidner, J.R., 1989. The refractive indexes of Y-Si-Al-O-N glasses. *Journal of Non-Crystalline Solids* 108, 180–186.
- Coon, D.N., Rapp, J.G., Bradt, R.C., Pantano, C.G., 1983. Mechanical properties of silicon-oxynitride glasses. *Journal of Non-Crystalline Solids* 56, 161–166.
- Dauç, R., Keding, R., Sangleboeuf, J.-C., 2008. On the relations between ISE and structure in some RE(Mg)SiAlO(N) glasses. *Journal of Materials Science* 43, 7239–7246.
- De Graaf, D., Hintzen, H.T., de With, G., 2006a. Subcritical crack growth and power law exponent of Y-Si-Al-O(N) glasses in aqueous environment. *Journal of Materials Science* 41 (18), 6031–6034.
- De Graaf, D., Hintzen, H.T., Hampshire, S., de With, G., 2003. Long wavelength Eu^{2+} emission in Eu-doped Y-Si-Al-O-N Glasses. *Journal of the European Ceramic Society* 23, 1093–1097.
- De Graaf, D., Braciszewicz, M., Hintzen, H.T., Sopicka-Lizer, M., de With, G., 2004. The influence of the composition on (the load-dependence of) the microhardness of Y-Si-Al-O-N glasses as measured by Vickers indentation. *Journal of Materials Science* 39, 2145–2149.
- De Graaf, D., Le Rol, S., Hintzen, H.T., Le Gendre, L., de With, G., 2006b. Mixed oxidation states of Yb and Sm in Si-Al-O-N glasses. *Journal of the European Ceramic Society* 26 (13), 2497–2501.
- Dölekçekiç, E., Pomeroy, M.J., Hampshire, S., 2004. The effect of preparation route and nitrogen content on Y-SiAlON glasses. *Key Engineering Materials* 264–268, 1927–1930.
- Dölekçekiç, E., Pomeroy, M.J., Hampshire, S., 2007. Structural characterisation of Er-SiAlON glasses by Raman spectroscopy. *Journal of the European Ceramic Society* 27, 893–898.
- Drew, R.A.L., Hampshire, S., Jack, K.H., 1981. Nitrogen glasses. *Proceedings of the British Ceramic Society* 31, 119–132.
- Elmer, T.H., Nordberg, M.E., 1967. Effect of nitriding on electrolysis and devitrification of high-silica glasses. *Journal of the American Ceramic Society* 50, 275–279.
- García-Bellés, A.R., Monzó, M., Barba, A., *et al.*, 2013. Properties of Ca-(Y)-Si-Al-O-N-F glasses: Independent and additive effects of fluorine and nitrogen. *Journal of the American Ceramic Society* 96 (4), 1131–1137.
- Gonon, M.F., Descamps, J.C., Cambier, F., Thompson, D.P., 2000. Determination and refinement of the crystal structure of M_2SiAlO_5N "B-phase" (M = Y, Er, Yb). *Ceramics International* 26 (1), 105–111.
- Hakeem, A.S., Grins, J., Esmaeilzadeh, S., 2007. La-Si-O-N glasses Part II: Vickers hardness and refractive index. *Journal of the European Ceramic Society* 27, 4773–4777.
- Hampshire, S., 1993. Oxynitride glasses and glass ceramics. In: Chen, I.W., Becher, P.F., Mitomo, M., Petzow, G., Yen, T.-S. (Eds.), *Silicon Nitride Ceramics – Scientific and Technological Advances*, Materials Research Society Symposium Proceedings 287. Pittsburgh: MRS, pp. 93–104.
- Hampshire, S., 2003. Oxynitride glasses, their properties and crystallisation – A review. *Journal of Non-Crystalline Solids* 316, 64–73.
- Hampshire, S., 2008. Oxynitride glasses. *Journal of the European Ceramic Society* 28, 1475–1483.
- Hampshire, S., 2021. Glasses: Oxynitride glass formation and structure. In: Pomeroy, M.J. (Ed.), *Encyclopedia of Materials: Technical Ceramics and Glasses*. Elsevier. (This volume).
- Hampshire, S., Pomeroy, M.J., 2004. Effect of composition on viscosities of rare earth oxynitride glasses. *Journal of Non-Crystalline Solids* 344, 1–7.
- Hampshire, S., Pomeroy, M.J., 2012. Grain boundary glasses in silicon nitride: A review of chemistry, properties and crystallisation. *Journal of the European Ceramic Society* 32, 1925–1932.

- Hampshire, S., Drew, R.A.L., Jack, K.H., 1984. Viscosities, glass transition temperatures, and microhardness of Y-Si-Al-O-N glasses. *Journal of the American Ceramic Society* 67 (3), C46–C47.
- Hampshire, S., Drew, R.A.L., Jack, K.H., 1985. Oxynitride glasses. *Physics and Chemistry of Glasses* 26, 182–186.
- Hampshire, S., Nestor, E., Flynn, R., *et al.*, 1994. Yttrium oxynitride glasses: Properties and potential for crystallisation to glass-ceramics. *Journal of the European Ceramic Society* 14, 261–273.
- Hanifi, A.R., Genson, A., Pomeroy, M.J., Hampshire, S., 2009. Oxyfluoronitride glasses with high elastic modulus and low glass transition temperatures. *Journal of the American Ceramic Society* 92, 1141–1144.
- Hanifi, A.R., Genson, A., Pomeroy, M.J., Hampshire, S., 2012. Independent but additive effects of fluorine and nitrogen substitution on properties of a calcium aluminosilicate glass. *Journal of the American Ceramic Society* 95, 600–606.
- Homeny, J., McGarry, D.L., 1984. Preparation and mechanical properties of Mg-Al-Si-O-N glasses. *Journal of the American Ceramic Society* 67 (11), C225–C227.
- Jack, K.H., 1977. Sialon glasses. In: Riley, F.L. (Ed.), *Nitrogen Ceramics*. Leyden: Noordhoff, pp. 257–262.
- Leng-Ward, G., Lewis, M.H., 1989. Oxynitride glasses and their glass-ceramic derivatives. In: Lewis, M.H. (Ed.), *Glasses and Glass Ceramics*. London: Chapman and Hall, pp. 106–155.
- Liddell, K., Thompson, D.P., 1997. Heat treatment of wollastonite type Y-Si-Al-O-N glasses. *Journal of Materials Science* 32 (4), 887–892.
- Loehman, R.E., 1979. Preparation and properties of yttrium-silicon-aluminum oxynitride glasses. *Journal of the American Ceramic Society* 62, 491–494.
- Loehman, R.E., 1980. Oxynitride glasses. *Journal of Non-Crystalline Solids* 42, 433–466.
- Lofaj, F., Satet, R., Hoffmann, M.J., de Arellano López, A.R., 2004b. Thermal expansion and glass transition temperature of the rare-earth doped oxynitride glasses. *Journal of the European Ceramic Society* 24, 3377–3385.
- Lofaj, F., Deriano, S., LeFloch, M., Rouxel, T., Hoffmann, M.J., 2004a. Structure and rheological properties of the RE-Si-Mg-O-N (RE = Sc, Y, La, Nd, Sm, Gd, Yb and Lu) glasses. *Journal of Non-Crystalline Solids* 344, 8–16.
- Lofaj, F., Hvizdoš, P., Dorázková, F., *et al.*, 2003. Indentation moduli and microhardness of RE-Si-Mg-O-N glasses (RE=Sc, Y, La, Sm, Yb and Lu) with different nitrogen content. *Materials Science and Engineering A357*, 181–187.
- Luo, Z., Qu, G., Zhang, Y., Cui, L., Lu, A., 2013. Transparent oxynitride glasses: Synthesis, microstructure, optical transmittance and ballistic resistance. *Journal of Non-Crystalline Solids* 378, 45–49.
- Mauro, J.C., 2011. Topological constraint theory of glass. *American Ceramic Society Bulletin* 90, 31–37.
- Menke, Y., Peltier-Baron, V., Hampshire, S., 2000a. Effect of rare-earth cations on properties of SiAlON glasses. *Journal of Non-Crystalline Solids* 276, 145–150.
- Menke, Y., Falk, L.K.L., Hampshire, S., 2005. The crystallisation of Er-Si-Al-O-N B-phase glass-ceramics. *Journal of Materials Science* 40 (24), 6499–6512.
- Menke, Y., Hampshire, S., Falk, L.K.L., 2007. Effect of composition on crystallization of Y/Yb-Si-Al-O-N B-phase glasses. *Journal of the American Ceramic Society* 90, 1566–1573.
- Menke, Y., Baron, V., Lemerrier, H., Hampshire, S., 2000b. Influence of the atmosphere on the oxidation state of the Eu-ion in a SiAlO(N) glass and glass-ceramic. *Materials Science Forum* 325–326, 277–282.
- Mulfinger, H.-O., 1966. Physical and chemical solubility of nitrogen in glass melts. *Journal of the American Ceramic Society* 49, 462–467.
- Murakami, Y., Yamamoto, H., 1994. Properties of oxynitride glasses in the Ln-Si-Al-O-N systems (Ln = rare-earth). *Journal of the Ceramic Society of Japan* 102, 231–236.
- Ohashi, M., Nakamura, K., Hirao, K., Kanzaki, S., Hampshire, S., 1995. Formation and properties of Ln-Si-O-N glasses. *Journal of the American Ceramic Society* 78, 71–76.
- Paraschiw, G.L., Gomez, S., Mauro, J.C., *et al.*, 2015. Hardness of oxynitride glasses: Topological origin. *Journal of Physical Chemistry B* 119, 4109–4115.
- Pomeroy, M.J., Hampshire, S., 2008a. SiAlON glasses: Effects of nitrogen on structure and properties. *Journal of the Ceramic Society of Japan* 116, 755–761.
- Pomeroy, M.J., Hampshire, S., 2008b. Controlled crystallisation of a Y-Si-Al-O-N glass typical of grain boundary glasses formed in silicon nitride-based ceramics. *Journal of the Ceramic Society of Japan* 116, 722–728.
- Pomeroy, M.J., Mulcahy, C., Hampshire, S., 2003. Independent effects of nitrogen substitution for oxygen and magnesium substitution by yttrium on the properties of Mg-Y-Si-Al-O-N glasses. *Journal of the American Ceramic Society* 86 (3), 458–464.
- Pomeroy, M.J., Nestor, E., Ramesh, R., Hampshire, S., 2005. Properties and crystallisation of rare earth SiAlON glasses containing mixed trivalent modifiers. *Journal of the American Ceramic Society* 88 (4), 875–881.
- Ramesh, R., Nestor, E., Pomeroy, M.J., Hampshire, S., 1997. Formation of Ln-Si-Al-O-N glasses and their properties. *Journal of the European Ceramic Society* 17, 1933–1939.
- Ramesh, R., Nestor, E., Pomeroy, M.J., Hampshire, S., 1998. Classical and DTA studies of the glass-ceramic transformation in a YSiAlON glass. *Journal of the American Ceramic Society* 81 (5), 1285–1297.
- Ramesh, R., Nestor, E., Pomeroy, M.J., *et al.*, 1996. Potential of NdSiAlON glasses for crystallisation to glass-ceramics. *Journal of Non-Crystalline Solids* 196, 320–325.
- Richet, N.F., Rouxel, T., Kawaji, H., Nicolas, J.-M., 2010. Boson peak, elastic properties, and rigidification induced by the substitution of nitrogen for oxygen in oxynitride glasses. *Journal of the American Ceramic Society* 93 (10), 3214–3222.
- Rouxel, T., 2007. Elastic properties and short-to medium-range order in glasses. *Journal of American Ceramic Society* 90, 3019–3039.
- Rouxel, T., Huger, M., Besson, J.-L., 1992. Rheological properties of Y-Si-Al-O-N glasses – Elastic moduli, viscosity and creep. *Journal of Materials Science* 27, 279–284.
- Rouxel, T., Besson, J.-L., Rzepka, E., Goursat, P., 1990. Raman spectra of SiYAlON glasses and ceramics. *Journal of Non-Crystalline Solids* 122, 298–302.
- Rouxel, T., Dély, N., Sangleboeuf, J.C., *et al.*, 2005. Structure–property correlations in Y–Ca–Mg–sialon glasses: Physical and mechanical properties. *Journal of the American Ceramic Society* 88, 889–896.
- Sakka, S., 1995. Structure, properties and applications of oxynitride glasses. *Journal of Non-Crystalline Solids* 181, 215–224.
- Sakka, S., Kamiya, K., Yoko, T., 1983. Preparation and properties of Ca-Al-Si-O-N oxynitride glasses. *Journal of Non-Crystalline Solids* 56, 147–155.
- Schrimpf, C., Frischat, G.H., 1983. Property-composition relations of N₂-containing Na₂O-CaO-SiO₂ glasses. *Journal of Non-Crystalline Solids* 56, 153–160.
- Shannon, R.D., 1969. Effective ionic radii in oxides and fluorides. *Acta Crystallographica B25*, 751–756.
- Sun, E.Y., Becher, P.F., Hwang, S.-L., *et al.*, 1996. Properties of silicon-aluminum-yttrium oxynitride glasses. *Journal of Non-Crystalline Solids* 208, 162–169.

Glasses: Phosphates

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Phosphate Glasses and Their Use

A study of phosphate glasses was initiated more than 100 years ago by the investigations of Otto Schott *et al.* on the optical properties of alkaline earth phosphate glasses (Kreidl and Weyl, 1941). However, the troubles related to the melting of phosphate glasses and poor chemical durability of these early prepared glasses delayed temporarily their further investigation. In the early 1960s, a noticeable interest in their application as laser hosts reestablished phosphate glass research. One of the advantages of the phosphate glasses is the possibility to dissolve a large amount of rare-earth elements. They also have large rare-earth stimulated emission cross-sections and low nonlinear refractive indices which makes them good material for high power laser radiation (Weber, 1990; Campbell and Suratwala, 2000).

Due to their unique properties such as low melting temperatures and a very high coefficient of thermal expansion compared with silicate-based glasses, the phosphate glasses were thus proven to be good candidates for a variety of specialty applications (Shelby, 2005). In particular, the low glass transition temperature of phosphate glasses, usually in the range 300–400°C, can drop even lower in some specific cases. Furthermore, a thermal expansion coefficient greater than $20 \times 10^{-6} \text{K}^{-1}$ makes phosphate glasses applicable for sealing of low-temperature components, e.g., tin- and zinc-bearing phosphates (Morena, 2000). Along with low processing temperature, <400°C, the most important requirements for the sealing glass formulations are high chemical durability and high electrical resistivity. Therefore, in the permanent search for new sealing glasses, the phosphate-based formulations containing oxynitrides satisfactorily fulfill these conditions, exhibiting an enormous enhancement in the chemical durability (Rajaram and Day, 1988).

Also, the addition of one or more oxides such as Al_2O_3 , CaO , and Fe_2O_3 (Legeros and Lee, 2004) improves significantly the chemical durability. For example, the binary iron phosphate glasses are best known for their exceptional chemical durability and high solubility of various nuclear waste compounds which sets the direction of their application as a host material for vitrification of nuclear wastes (Day *et al.*, 1998; Mesko *et al.*, 1998; Fang *et al.*, 2001). In addition, many studies of phosphate-based glasses are related to electrical conductivity investigations. Lithium phosphate glasses have gained recent interest due to their potential applications as amorphous electrolytes in solid-state batteries (Moreau *et al.*, 2009; Ducdot and Souquet, 2001; Ishiyama *et al.*, 2014; Ravaine, 1980). The liquid lithium electrolytes consist of lithium salts and organic polymer liquids. In contrast, the inorganic solid electrolytes such as phosphate glass-based lithium electrolytes show numerous advantages over the organic liquid solvents (Ducdot and Souquet, 2001). In parallel, accelerating interest in lithium phosphate glass-ceramics made it possible to interpret trends in ionic conductivity and its dependence on the microstructure. A large body of the work on the structural and electrical properties of lithium phosphate compositions, which includes phosphates with NASICON-type (superionic conductors) structures, reveals a structural versatility and wide range of compositions (Fu, 1997; Kotobuki and Koishi, 2013; Patil *et al.*, 2013; Nikolić *et al.*, 2013; He *et al.*, 2014; Nuernberg and Rodrigues, 2017; Nuernberg *et al.*, 2017, 2018; Xiao *et al.*, 2019; Narváez-Semanate and Rodrigues, 2010). The base chemical formula of these compounds can be written as $\text{LiM}_2(\text{PO}_4)_3$, where M is a tetravalent cation such as Ge, Ti, Zr, Sn. Among the aforementioned tetravalent cations, Ti in the $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) system leads to the basic NASICON compound with the highest lithium conductivity and lowest activation energy (Takada, 2013; Cao *et al.*, 2014).

Phosphate glasses containing transition metal oxides (TMO) such as Fe_2O_3 , V_2O_5 , WO_3 and MoO_3 , have been widely investigated in the last few years due to their semiconducting nature that opened another field of applications: in electrochemical, electronic, and optoelectronic devices. It is well known that in these glasses electronic conduction occurs by electron transfer between transition metal ions in different valence states following the small polaron hopping mechanism (Ishiyama *et al.*, 2014; Austin and Mott, 1969; Mackenzie and Nasu, 1985; Murawski *et al.*, 1979; Moguš-Milanković *et al.*, 1999; Nikolić *et al.*, 2018; Pavić *et al.*, 2018a,b). Moreover, phosphate glasses containing alkali and silver oxides in combination with transition metal oxides represent the mixed ion-polaron conductive glasses (Nikolić *et al.*, 2018; Pavić *et al.*, 2018b). In these glass systems, two types of charge carriers, ions and polarons participate in the conduction process making these glasses prospective mixed conductors in solid-state batteries as cathode/anode materials (Nakata *et al.*, 2016). Also, mixed ion-polaron phosphate glass-ceramics have become a subject of numerous studies since many functional glass-ceramics improve mechanical, electrical, magnetic, and optical properties as a result of the controlled glass crystallization (Garbarczyk *et al.*, 2004, 2007, 2009, 2015; Pietrzak *et al.*, 2009, 2011, 2013, 2016a,b; Pavić *et al.*, 2014, 2018a, 2019, 2020; Moguš-Milanković *et al.*, 2012, 2015; Chen *et al.*, 2018).

Phosphate-based glasses and glass-ceramics are the most prominent materials in the repair and regeneration of damaged soft and hard tissues (Jones and Clare, 2012; Ren *et al.*, 2013). The main reason why phosphate glasses are of interest for use as biomaterials is their ability to dissolve completely in aqueous solutions into safe non-toxic dissolution products (biocompatibility). A characteristic of bioactive glasses and glass-ceramics is the formation of a biologically active apatite layer which provides the bonding with bone (Knowles, 2003; Ahmed *et al.*, 2004b). It is worth noting that the bioactivity of glasses mainly depends on the compositions of bioactive materials which can be controlled by the surface modifications, implying various forms of bioactive glass, such as beads or fibers (Hossain *et al.*, 2014). They have also attracted much interest in bone tissue engineering (Rahaman *et al.*, 2011) as well as soft tissue regeneration (Shah *et al.*, 2005) and drug delivery applications (Moioli *et al.*, 2007).

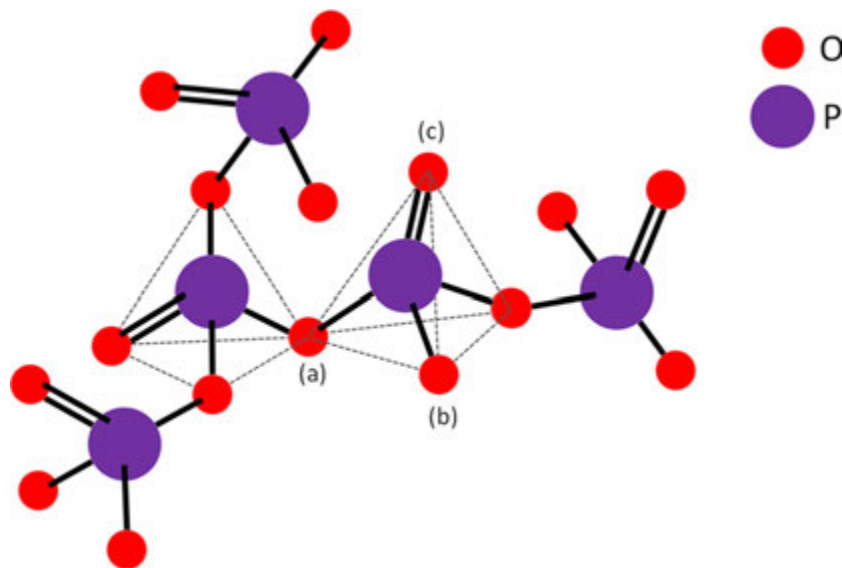


Fig. 1 A three-dimensional network of PO_4 tetrahedra with (a) bridging, (b) non-bridging oxygens and (c) double-bonded oxygens to form the network of vitreous P_2O_5 .

Various properties of phosphate glasses that make them a candidate for numerous applications in many fields are closely related to their atomic structure. In the next section, a brief review is given of the main structural features of phosphate glasses with a special emphasis on the bonding arrangements in the glass structures.

Basic Structure of Phosphate Glasses

The electronic configuration of phosphorus (P) is $3s^2 3p^3$ that forms four sp^3 hybrid orbitals and the fifth electron in d orbital assists in the formation of π -bonding molecular orbitals with 2p oxygen electrons (Cruickshank, 1961; Mitchell, 1969). Consequently, in glasses and crystalline phosphates, the phosphorus creates P-tetrahedra that are connected through the covalent bridging oxygens and form various phosphate anions. Thus, when bonded to oxygens, phosphorus forms several oxide structures but the crucial one is P_4O_{10} (phosphorus pentoxide) where the three P-tetrahedra are bonded through P-O-P oxygens and the fourth is double-bonded to oxygen, $\text{P}=\text{O}$. Fig. 1 shows a three-dimensional network of PO_4 tetrahedra with bridging oxygens (a), non-bridging oxygens (b) and double-bonded oxygen (c). Phosphorus (P) having tetrahedral coordination is classified as a network former element and Zachariasen (1932) identified a vitreous P_2O_5 as a typical distorted network glass former oxide.

The phosphate glass network is constructed of PO_4 units interconnected through bridging oxygens, where at least one of the oxygens is nonbridging (Zachariasen, 1932). The structure of phosphate glasses is usually described by Q^n terminology (Liebau, 1981) where the “ n ” represents the number of bridging oxygens per P-tetrahedron as displayed in Fig. 2. Thus, the Q^3 tetrahedra represent a cross-linked network as in vitreous P_2O_5 , Q^2 corresponds to the polymer-like metaphosphate chains whereas Q^1 is related to the pyrophosphate (dimer) units and Q^0 is associated with isolated orthophosphate anions. Therefore, the structure of phosphate glasses is constituted by various arrangements of phosphate units that depend on the modifier type and concentration. In fact, the modifier oxide addition to the phosphate network causes a break up of P-O-P bonds (depolymerization of the phosphate network) and forms negatively charged P-O⁻ bonds which are compensated with the modifier cations by forming covalent bonds. Moreover, Hoppe (1996) developed a set of rules for network changes upon the addition of modifying atoms to describe the disruption of P-O-P bonding units as a function of P_2O_5 content.

The structure of phosphate glasses depends also on O/P ratio which determines the number of bonds formed through bridging oxygens as depicted in Fig. 2(b). Thilo (1959) classified phosphate compositions into ultraphosphates, ($\text{O}/\text{P} < 3$); polyphosphates ($\text{O}/\text{P} > 3$) and metaphosphates with $\text{O}/\text{P} = 3$. In that sense, Van Wazer (1958) established a description of the local arrangement of phosphate glass polyhedra which depends on the ratio between polymerization/depolymerization degree of phosphate and modifier units. Therefore, the short-range order of phosphate structure is related to the close coordination environment of an ion whereas the medium-range order is defined as linkages of phosphate polyhedra that form larger structures.

In order to clarify the structure of phosphate glasses, there have been two excellent publications (Abe, 1983; Martin, 1991a) and perhaps the most complete and cited review entitled: “Review: the structure of simple phosphate glasses” by Brow (2000) where the most important factors that affect the phosphate glass structure and experimental techniques used are described in detail. Also, a Handbook of Glasses recently published, represents a comprehensive overview of the diverse field of glass science, with an article dedicated to the phosphate glass families providing basic information on their specific applications (Musgraves et al., 2019).

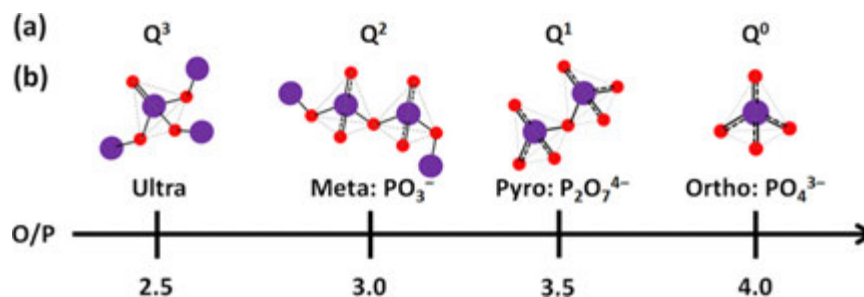


Fig. 2 (a) Phosphate tetrahedra are described by Q^n nomenclature in phosphate glasses. (b) Structural units in phosphate glass network, and (c) O/P ratio for different Q^n structure.

Vitreous P₂O₅ (v-P₂O₅)

Studies of the vitreous P₂O₅ structure analyzed by new structural probes such as solid-state nuclear magnetic resonance (NMR) spectroscopy, X-ray absorption spectroscopy (XAS); and neutron diffraction analyses have been reported (Galeener and Mikkelsen, 1979; Meyer, 1997; Hoppe *et al.*, 1998; Suzuya *et al.*, 1998; Hudgens and Martin, 1993). Since v-P₂O₅ is highly hygroscopic and volatile the preparation of anhydrous glass demands a specific handling procedure, usually in a dry-box (Hudgens and Martin, 1993). Without going into the details of the results of the local structure of v-P₂O₅ from each of these structural probes, it should be pointed out that the basic constituent of P₂O₅ glass is the Q³ tetrahedron having three bridging oxygen bonds to neighboring tetrahedra (*p*-BO) and one short bond to a terminal oxygen (*p*-TO). These tetrahedra are interconnected forming a three-dimensional phosphate network.

Binary and Ultraphosphate Glasses

The introduction of a modifier oxide to v-P₂O₅ creates the non-bridging oxygens, P-NBO, generating depolymerization of the phosphate network where the terminal oxygens are linked to modifier cations and the Q³ tetrahedra are transformed into Q² units. Further addition of modifier oxide significantly depolymerizes the phosphate structure, converting Q² to isolated Q¹ units. Therefore, depolymerization of the phosphate network with the addition of the modifier oxide (R₂O) can be described by the reaction: $2Q^n + R_2O = 2Q^{(n-1)}$ and the glass composition is determined as $(xR_2O)(1-x)P_2O_5$. Depending on R₂O content (x) it is possible to distinguish different types of phosphate glasses. For example, compositions in the range $0 \leq x < 0.5$ represents ultraphosphates which contain some Q² and mainly Q³ phosphate units which are responsible for a high reactivity in water. Metaphosphate network, $x = 0.5$, consists of Q² units and is described as long polyphosphate chains or rings where more modifier ions are bonded to the non-bridging oxygens. In polyphosphate glasses, $x > 0.5$, phosphate chains are shorter and in pyrophosphates, the network is dominated by Q¹ dimer phosphate units with a stoichiometry of $x = 0.67$.

Glass formation of binary phosphate systems containing alkali (R₂O) or alkaline earth (RO) oxides is in the range $x = 0.55$ – 0.65 for the conventional melting process forming glass networks based on Q² units. On the other hand, phosphate glasses with low coordination metal (CN < 6) oxides such as ZnO, PbO, SnO or Fe₂O₃ prepared by a melt quenching process create a structure that mostly consists of pyrophosphate, Q¹, units and molecular segments in which non-bridging oxygens are linked to the smaller valence cations, forming, for example, P–O–Fe²⁺ bonds. Usually, in these glass systems, a small amount of metaphosphate (PO₃)⁻ and orthophosphate (PO₄)³⁻ units co-exist with pyrophosphates units (Fang *et al.*, 2001).

In order to provide a qualitative description of the phosphate glass structure, the most used techniques are Raman and FTIR spectroscopies. Both spectroscopies exhibit characteristic vibrational modes of the different phosphorus units which depend on the depolymerization degree of the phosphate network. Changes in the Raman and FTIR spectra reveal a transition of phosphate structure between the cross-linked network of ultraphosphates and polymer-like long phosphate chains of metaphosphates as a function of type and content of modifier atoms, i.e., variation of the glass composition (Brow, 2000; Musgraves *et al.*, 2019).

New spectroscopic techniques such as ³¹P magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy allow quantification of various phosphorous units in the network and determination of the structural environment of phosphorous atoms depending on the degree of polymerization. The chemical shift of the ³¹P nuclei is sensitive to the type of modifier cations that are bonded to nonbridging oxygens which define the bond strength between them. Two-dimensional (2D) ³¹P NMR spectra are employed for detecting the connectivity between phosphorus units through dipolar correlation techniques, such as double quantum (DQ) MAS NMR. In this technique the dipolar interactions between ³¹P nuclei are related to the homo- and heteronuclear (³¹P in combination with other nuclei such as ²⁷Al, ¹¹B, ⁷³Ge, ⁷Li, ²³Na) correlations and hence in 2D plots the proximity between different, for example, Q² and Q¹ sites can be detected. Furthermore, many advanced 2D multiple quantum or pulse sequences NMR techniques can provide additional information on the network bonding connectivity such as INADEQUATE, REDOR, DQ-DRENAR, HECTOR, etc., which are described by Brow (2000) and Musgraves *et al.* (2019). There are also several new probes used in studying the phosphate glass structure such as X-ray absorption spectroscopy (XAS) X-ray photoelectron (XPS)

spectroscopy, and neutron diffraction techniques which provide essential information on bonding arrangements in the phosphate network. Moreover, computational modeling based on *ab initio* (Uchino and Ogata, 1995) and molecular dynamics (MD) (Alder and Wainwright, 1959; Cormack and Cao, 1996) gives rise to knowledge of molecular orbitals interpretation that can explain the influence of the modifying cations on phosphate network changes.

Phosphate Glasses in Biomedicine

Phosphate-based glasses belong to a class of materials with a wide application in diverse fields of biomaterials engineering; from hard and soft tissue repair and regeneration (Knowles, 2003; Kiani *et al.*, 2012; Sharmin and Rudd, 2017; Combes and Rey, 2010) to drug delivery (Baino *et al.*, 2016; Lapa *et al.*, 2020) and dental materials (Combes and Rey, 2010). The versatile nature of phosphate glasses in biomedical applications is based on the fact that they dissolve harmlessly in the body over a timescale that can vary from a few hours to several months depending on their composition (Knowles, 2003; Kiani *et al.*, 2012). Since phosphate-based glasses can incorporate various chemical elements in broad percentages, and can readily be prepared in various geometric forms (disks, microtubes, microspheres, fibers), their solubility can be easily tuned by precise variations in composition and morphology enabling a controlled interaction of the glass and the tissue, and delivery of therapeutically useful substances to the specific target sites at a controlled rate.

A revolutionary step in the medical application of glasses was the discovery of the first bioactive glass by Larry Hench and co-workers in the early 1970s (Hench *et al.*, 1971). They showed that silicate-based glass of composition $45\text{SiO}_2\text{-}24.5\text{Na}_2\text{O-}24.5\text{CaO-}6\text{P}_2\text{O}_5$ (in wt%), known as 45S5 bioglass, provokes positive reactions of tissue resulting in the formation of a biologically active hydroxycarbonate apatite (HCA) layer which provides the bonding interface with the tissues (Hench *et al.*, 1971; Hench, 1998). Therefore, bioactivity can be defined as a capacity of a material to react with physiological fluids and form tenacious bonds to hard and soft tissues through cellular activity (Hench, 1998; Day and Boccaccini, 2005). Over the years, bioactive properties were found in other silicate-based, but also in phosphate-based and borate-based glasses (Islam *et al.*, 2017).

Bioactive phosphate glasses are mainly based on the ternary $\text{Na}_2\text{O-CaO-P}_2\text{O}_5$ system (Knowles, 2003; Islam *et al.*, 2017; Ahmed *et al.*, 2004a,b) which contains elements present in the human body with important biological roles (P, Ca, Na = 1, 1.5 and 0.2 wt%, respectively) (Lapa *et al.*, 2020). However, other modifying oxides such as TiO_2 , SrO, CuO, ZnO, Ag_2O , MgO, and Fe_2O_3 can be added to phosphate glasses to induce specific property, functional, or biological response (Islam *et al.*, 2017). The addition of metal oxides generally increases chemical durability, decreases the tendency for crystallization, and improves the mechanical properties of phosphate glasses, but simultaneously, metal ions can also have an active role in a biological response. For instance, silver and copper ions are known to exhibit antibacterial properties (Knowles, 2003; Lapa *et al.*, 2020), iron ions improve cell attachment (Lapa *et al.*, 2020) whereas calcium, magnesium and strontium ions improve bone mineralization, osteoblast proliferation, and differentiation (Lapa *et al.*, 2020). Altogether, the combination of these properties offers a vast range of possibilities for the development of bioactive phosphate-based glasses for specific biomedical applications such as bone regeneration and bone-ligament regeneration, wound healing, muscle cell delivery systems, and nerve tissue regeneration (Lapa *et al.*, 2020).

Besides the above-mentioned metal ions, many other therapeutic substances have been used or proposed for use with phosphate-based bioactive glasses. These include fluorine which helps prevent dental caries (Knowles, 2003), chemotherapy drug cisplatin (Pickup *et al.*, 2012) and radionuclei for radiotherapy (Sene *et al.*, 2008). For such diverse biomedical applications, the most important requirement is the possibility to prepare glass in various geometrical forms and over a wide range of sizes. Indeed, bioactive phosphate-based glasses have been fabricated in different forms, from disks, microspheres (Ahmed *et al.*, 2019; Hossain *et al.*, 2015; Gupta *et al.*, 2018) to fibers (Sharmin and Rudd, 2017; Lapa *et al.*, 2020) and microtubes (Abou Neel *et al.*, 2007). The phosphate-based glass fibers can be used for cell transportation and device expansion, as a nerve conduit, and as a scaffold for muscle regeneration since they provide tissue-like fibrous constructs that can guide the cell growth (Deshmukh *et al.*, 2020). Also, phosphate glass fibers readily form microtubes and hence can be integrated with various polymers to help nutrient diffusion and ingrowth of vascularization when employed as scaffolds for hard and soft tissue regeneration (Deshmukh *et al.*, 2020). On the other hand, microspheres provide a stable surface for proliferation and cell attachment preventing tissue damage and hemorrhage which make them applicable in radiotherapy (Ahmed *et al.*, 2019; Hossain *et al.*, 2015; Gupta *et al.*, 2018; Deshmukh *et al.*, 2020). The synthesis of bioactive phosphate-based glasses in different forms involves special preparation techniques. The classical melt-quenching produces phosphate-based glass in a bulk form whereas microspheres are commonly manufactured via dropping crushed glass particles down a vertical tube furnace, pouring molten glass onto stainless steel plates to create droplets, sol-gel method and spray drying of sols, and flame spheroidization processes (Gupta *et al.*, 2018). The fabrication of continuous glass fibers has more commonly been achieved via melt drawing but they have also been produced from preformed rods (Ahmed *et al.*, 2019).

Electrical and Optical Properties of Phosphate Glasses

Electrically conducting phosphate glasses have attracted much attention over the last decades due to their potential use either as the electrolyte, electrode material, or other specific components in various modern devices from solid-state batteries and fuel cells, to smart windows and chemical sensors (Dudot and Souquet, 2001; Minami *et al.*, 2006; Cao *et al.*, 2014; Xiao *et al.*, 2019; Grady *et al.*, 2020). In particular, phosphate glasses offer extreme compositional and preparation variability which enables tuning of the

types and mechanisms of the electrical conduction. That is, the type of conduction – ionic, electronic, or mixed polaronic-ionic – depends primarily on the composition whereas the mobility of charge carriers (ions and/or electrons) depends on their interaction with the glass network and local structural setting.

From the point of view of optical and optoelectronic applications, phosphate-based glasses are in high demand since they have been demonstrated to be promising contenders to silicate-based glasses. Thanks to a very open and disordered matrix structure (Seneschal *et al.*, 2005) a high level of rare earth-ions can be incorporated into the phosphate network, hence serving as an excellent host matrix for lasers, fibers, and optical lenses (Yamanaka *et al.*, 1981; Weber, 1990; Ehrt and Seeber, 1991; Hutchinson and Allik, 1992; Jiang *et al.*, 2000). Furthermore, phosphate glasses show the ability to be melted with fluorides for the production of fluoride phosphate/fluorophosphate glasses with excellent optical properties (Möncke and Eckert, 2019) whereas Ag-doped phosphate glass is a well-known radiophotoluminescence (RPL) dosimeter (Piesch and Burgkhardt, 1994; Miyamoto *et al.*, 2011; Kodaira *et al.*, 2018; Sholom and McKeever, 2020). The next sections cover the basics of electrical conduction mechanisms with an overview of important compositional-structural effects on electrical transport and a brief description of the opto(electronic) applications of phosphate glasses.

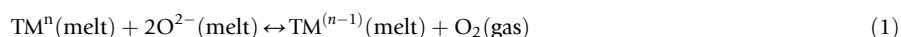
Ionic and Electronic (Polaronic) Conductivity in Phosphate-Based Glasses

Phosphate glasses containing alkali, alkaline-earth oxides or silver oxides are ionically conducting materials. In these glasses, ionic transport arises from the movement of modifier cations through the glass network (Martin, 1991b; Dyre *et al.*, 2009). Therefore, the ionic conductivity depends on the concentration and the mobility of mobile cations, whereas the mobility itself is influenced by their attractive interactions with the “immobile” glass network, and also by the mutual repulsion interactions between mobile ions themselves.

Depending on the composition, the ionic conductivity of phosphate-based glasses spans many orders of magnitude reaching values comparable to that of liquid electrolytes. For instance, silver phosphate glasses doped with silver halides or silver chalcogenides (Minami, 1987; Rousselot *et al.*, 1995; Bhattacharya and Ghosh, 2004; Bhattacharya *et al.*, 2006; Das *et al.*, 2005; Ren and Eckert, 2013) exhibit extremely high mobility of silver ions and are classified as fast ionic conductors with applications as solid electrolytes in optical switches and memory devices. The fast transport of silver ions in these glasses results from the highly depolymerized phosphate structure lacking typical network connectivity through which silver ions easily diffuse.

Another good example of the role of the glass structure on the dynamics of mobile ions is the phenomenon called the Mixed Glass-Former Effect (MGFE) (Zielniok *et al.*, 2007; Agarwal *et al.*, 2004; Muñoz *et al.*, 2009; Kumar and Rao, 2004; Prasad *et al.*, 1990). The mixed glass-former effect is evidenced in a nonlinear change in ionic conductivity when one glass former is gradually substituted by the second one while the alkali concentration is kept constant. The magnitude of the conductivity increase differs for different glass systems indicating that the origin of this phenomenon is related to the variations in structural arrangements of the network units. This has opened a new research field directed towards the development of lithium ion-based phosphate glass systems suitable for application as electrolytes for lithium batteries (Duclot and Souquet, 2001; Ritchie, 2004). For instance, several reports (Magistris *et al.*, 1985; Muñoz *et al.*, 2009; Raguene *et al.*, 2011; Storek *et al.*, 2012; Larink *et al.*, 2012) have shown that the mobility of Li^+ ions is significantly enhanced when B_2O_3 is gradually substituted by P_2O_5 . Interesting results have been observed on mixed matrix glasses of the type $\text{Li}_2\text{O}-\text{P}_2\text{O}_5-\text{GeO}_2$ and $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5-\text{GeO}_2$ containing a fixed amount of Li_2O along with two and three glass-formers, respectively (Sklepić *et al.*, 2017; Moguš-Milanković *et al.*, 2013, 2016; Mošner *et al.*, 2013). Similarly as with B_2O_3 , the addition of GeO_2 has a direct impact on the changes of conductivity through the formation of mixed structural units which serve as compensating sites for lithium ions. Furthermore, it was also reported that the mixing of P_2O_5 and B_2O_3 as glass-forming oxides exhibits a similar effect on Na^+ ion transport due to the formation of bridging B-O-P bonds which enhances easier sodium ion hopping as a result of smaller binding energy for ions (Christensen *et al.*, 2013). This result is promising since it promotes sodium-conducting mixed former systems based on P_2O_5 as an attractive candidate for the new-generation of energy-storage devices containing sodium instead of lithium ions, being almost equally effective in batteries but significantly cheaper.

On the other hand, phosphate glasses containing transition metal oxides (TMOs) such as V_2O_5 , WO_3 , MoO_3 , Fe_2O_3 , are amorphous semiconductors and exhibit electronic conduction via “small polaron hopping” mechanism (Mott, 1968; Mott, 1969; Austin and Mott, 1969; Murawski *et al.*, 1979; Šantić and Moguš-Milanković, 2012). In these glasses, the TM ions are present in different oxidation states and the conduction takes place by thermally activated small polaron hopping from the TM ion of lower to TM ion of higher oxidation state. Therefore, polaronic transport depends on the total amount of TMO as well as on the relative fraction of TM ions in different oxidation states (Moguš-Milanković and Day, 1993; Moguš-Milanković *et al.*, 2004, 2005a,b, 2012; Šantić and Moguš-Milanković, 2012; Nikolić *et al.*, 2018). While the amount of TMO is a matter of choice of the glass stoichiometry and can vary widely in phosphate glass, the fraction of TM ions in different oxidation states is determined by the equilibrium between TM redox couples in the melt:



The above redox reaction depends upon several factors such as melting temperature, time, atmosphere, types of raw materials, and the presence of other substances in the batch (Moguš-Milanković and Day, 1993; Ray *et al.*, 1999; Fang *et al.*, 2001). By varying these factors, the fraction of TM ions in the glass changes which directly influences the polaronic conductivity. Interestingly,

however, polaronic conductivity in phosphate glasses containing Fe_2O_3 and MoO_3 depends strongly on the fraction of TM ions in different oxidation states, whereas for phosphate glasses with V_2O_5 and WO_3 polaronic conductivity is more influenced by the features of the glass structure, in particular clustering of transition metal units which facilitates the transport of polarons. The application of polaronic phosphate glasses includes the development of electrode materials and is directed towards designing more complex mixed polaron-ion conductive glasses.

Mixed Polaron-Ion Phosphate Glasses

Interest in investigating mixed conductive phosphate glasses is the fact that TMOs along with alkali oxides as modifiers can form glasses with P_2O_5 glass-former in a wide compositional range. Based on this, these glasses have the potential to exhibit tuneable polaronic and ionic conductivity which makes them especially attractive for application as cathodes in solid-state batteries since both electronic and ionic conductivities are equally important in cathode processes (Huang *et al.*, 2001; Wang and Hong, 2007; Ma *et al.*, 2007; Riess, 1997).

The type and content of each component, the transition metal and alkali (or silver) oxide, in phosphate glasses determine the conduction mechanisms which enables controllable contributions of polaronic and ionic conductivity and gradual transition from predominantly polaronic to predominantly ionic transport with a fine variation in the glass composition. However, the presence of two types of charge carriers can have a negative impact on overall conductivity due to their mutual interactions resulting in the formation of neutral entities that do not participate in electrical transport. This effect, called the *Ion-Polaron Effect* (Bazan *et al.*, 1996) was first discovered in $\text{Li}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$ glasses where the authors showed that the substitution of WO_3 by Li_2O results in a deep minimum in electrical conductivity which can be attributed to a strong coupling of lithium ions and polarons. While ionic and polaronic conduction in phosphate glasses separately have been well detailed, their dependence or independence in the mixed systems seems to be in strong correlation with glass composition of the system under study (Montani and Frechero, 2003, 2006; di Prátula *et al.*, 2015; Garbarczyk *et al.*, 2000, 2003; Salman *et al.*, 2016; Jozwiak and Garbarczyk, 2005; Pavić *et al.*, 2018b; Nikolić *et al.*, 2018). Furthermore, studies on $\text{Na}_2\text{O}-\text{MoO}_3-\text{P}_2\text{O}_5$ (Bih *et al.*, 2001) and $\text{Li}_2\text{O}-\text{MoO}_3-\text{P}_2\text{O}_5$ (Bih *et al.*, 2000, 2008) glasses demonstrated that the conductivity mechanism is predominately polaronic in the alkali oxide poor region and mixed ionic-polaronic conductivity in the alkali oxide rich region. Special attention was paid to the determination of various factors that might influence complex ion-polaron transport, for example, the number density of ions versus polarons, their mobility as well as specific structural features of the glass network. The contribution of ionic conductivity was found to be very low in these glasses suggesting hindered mobility of alkali ions. Similarly, small mobility of alkali ions was identified in $\text{Na}_2\text{O}/\text{K}_2\text{O}/\text{Cs}_2\text{O}-\text{WO}_3-\text{P}_2\text{O}_5$ glasses (Barczyński, 2008) where DC conductivity was found to drastically decrease as up to 20 mol% alkali oxide is added at the expense of P_2O_5 . Such a conductivity trend was explained by the exclusion of a fraction of tungsten ions from the polaron hopping process when the alkali oxide is present in phosphate glass. Additionally, Šantić and Moguš-Milanković (2012) presented a detailed review on multicomponent glass systems based on iron phosphate glasses (IPG). By altering composition and preparation conditions, the electrical conductivity of glasses based on the $\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5$ system may vary over many orders of magnitude from 10^{-5} to 10^{-12} ($\Omega \text{ cm}$)⁻¹. A significant amount of alkali oxide (Na_2O) influences the conductivity mechanism in these glasses which changes from polaronic to ionic. An interesting observation is made regarding the contribution of silver cations in the mixed transport which is significantly higher if compared to the other monovalent cations. The high mobility of Ag^+ ions in phosphate-based glasses originates from their weak interactions with the phosphate glass network which make them loosely bound and easy to diffuse (Garbarczyk *et al.*, 2000, 2003; Bhattacharya *et al.*, 2006; Pavić *et al.*, 2018b).

Rare-Earth Ion Host Matrices

The start of solid-state lasers in the 1960s indicated a new era of phosphate glass research. Ever since then, phosphate-based glasses have been intensively investigated as rare-earth ion host matrices in laser systems, fibers, and optical lenses (Yamanaka *et al.*, 1981; Weber, 1990; Ehrt and Seeber, 1991; Hutchinson and Allik, 1992; Jiang *et al.*, 2000). Incorporation of rare-earth ions into the phosphate glass matrix is possible thanks to the very open and disordered phosphate matrix structure (Seneschal *et al.*, 2005). The laser-active rare-earth ions, like erbium, ytterbium, and neodymium, can be incorporated as dopants in a phosphate glass matrix in high concentrations without clustering (Hwang *et al.*, 2000). Among them, ytterbium is one of the most commonly used for the fabrication of phosphate glass for optoelectronic applications (Hutchinson and Allik, 1992; Pugliese *et al.*, 2016; Zervas and Codemard, 2014). Overall, the high solubility of rare-earth ions in the phosphate glass matrix, good chemical stability, and high optical damage threshold make phosphate glasses almost an ideal material for optical fibers.

In the field of optical lenses, phosphate glasses have found their application where the use of their low T_g helps in reducing the temperature and time of processing. On the other hand, their lower softening temperatures (500–800°C) present an advantage, but also a disadvantage since phosphate glass can suffer from thermal degradation under high-power operation. However, in comparison to silicate glasses, certain phosphate compositions have large rare-earth stimulated emission cross-sections and low thermo-optical coefficients which are desirable properties for high power laser applications (Weber, 1990).

Fluoride Phosphate/Fluorophosphate (FP) Glasses

Another important advantage of phosphate glasses is their ability to be melted with fluorides for the production of fluoride phosphate/fluorophosphate (FP) glasses for optical applications. Here, it is important to note that phosphate glasses with a glass network containing anions with phosphorus-fluorine bonds, such as the $(\text{PO}_3\text{F})^{2-}$ species, are called “fluorophosphate” glasses whereas those characterized with separate phosphate and fluoride anions in the glass network are known as “fluoride phosphate glasses” (Möncke and Eckert, 2019). The high fluorine-containing phosphate glasses are excellent for optical glasses with positive anomalous dispersion (Weber *et al.*, 1976; Ehrt, 2015, 2018; Möncke and Eckert, 2019). Moreover, FP glasses are good hosts for luminescent rare-earth ions, as they combine the optical properties of fluoride glasses with the higher mechanical and thermal stability of phosphate glasses (Galleani *et al.*, 2017).

Phosphate Dosimeters

Apart from their high ionic conductivity and related applicative importance, phosphate glasses doped with silver ions have found their application in dosimetry since they are RPL (radiophotoluminescence) dosimeters for the dose range from tens of μGy up to several hundreds of Gy (Piesch and Burghardt, 1994; Miyamoto *et al.*, 2011; Kodaira *et al.*, 2018; Sholom and McKeever, 2020). In particular, it was showed that dose-response curves of Ag^{2+} EPR signals and optical absorption of Ag-doped phosphate glass demonstrate a non-linear, monotonic increase with dose up to several hundreds of kGy which enables proper and precise calibration, thus qualifying these materials for the dosimetry for high-dose applications (Sholom and McKeever, 2020).

Phosphate Glasses for Immobilization of Nuclear Wastes

The development of a host for the immobilization of nuclear waste is focused on various vitreous waste forms including borosilicate, high silica, and phosphate glasses. High waste loading in a borosilicate melt is considered in most countries, except in Russia where aluminophosphate glasses have been approved since the late 1980s. Parameters affecting the waste glass performance, such as chemical durability, waste forms solubility, thermal and mechanical stability must be optimized relative to processing considerations such as melt temperature, waste solubility, melt corrosion, and volatility of hazardous species.

In the past, iron phosphate glasses have received considerable interest for use in vitrifying nuclear waste due to their exceptionally high chemical durability (DR). The value for DR at about $10^{-9} \text{ g cm}^{-2} \text{ day}^{-1}$, determined from the weight loss of bulk samples immersed in deionized water at 90°C , is obtained for $40\text{Fe}_2\text{O}_3\text{-}60\text{P}_2\text{O}_5$ mol% glass composition with O/P ratio close to 3.5. This implies that the pyrophosphate structure where the replacement of the easily hydrolyzed P–O–P bonds by the more chemically resistant P–O–Fe bonds is responsible for such good chemical durability. Such a dissolution rate is up to 100 times lower than that of window glass (Mesko *et al.*, 1998; Fang *et al.*, 2001; Yu *et al.*, 1997).

Other advantages for using phosphate glasses in vitrifying nuclear wastes are the low melting temperatures at about $\sim 1000^\circ\text{C}$ and high loading of wastes rich in Cs, Mo, U, and Cr which are poorly soluble in borosilicate glass (Day *et al.*, 1998). Also, iron phosphate glasses are particularly well suited for vitrifying wastes that contain appreciable amounts of sulfates, halides, and actinides. These components have a high solubility in iron phosphate melts, which diminish the obligatory pre-treatment of the wastes, in which the quantity of these components should be reduced to the level required for nuclear waste processes. Also, the retention of volatile species in an iron phosphate waste form is typically high, especially in those iron phosphate compositions that can be processed at lower temperatures. Thus, based on the research of iron phosphate glass waste form compositions it can be concluded that iron phosphate glass is a viable alternative for vitrifying many types of nuclear wastes.

References

- Abe, Y. (Ed.), 1983. Topics in Phosphorus Chemistry, eleventh ed. New York: Wiley.
- Abou Neel, E.A., Young, A.M., Nazhat, S.N., Knowles, J.C., 2007. A facile synthesis route to prepare microtubes from phosphate glass fibres. *Advanced Materials* 19, 2856–2862.
- Agarwal, A., Seth, V.P., Gahlot, P.S., *et al.*, 2004. Study of electron paramagnetic resonance, optical transmission and dc conductivity of vanadyl doped $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3\text{-Li}_2\text{O}$ glasses. *Journal of Alloys and Compounds* 377, 225–231.
- Ahmed, I., Ren, H., Booth, J., 2019. Developing unique geometries of phosphate-based glasses and their prospective biomedical applications. *Johnson Matthey Technology Review* 63, 34–42.
- Ahmed, I., Lewis, M., Olsen, I., Knowles, J.C., 2004a. Phosphate glasses for tissue engineering: Part 1. Processing and characterisation of a ternary-based $\text{P}_2\text{O}_5\text{-CaO-Na}_2\text{O}$ glass system. *Biomaterials* 25, 491–499.
- Ahmed, I., Lewis, M., Olsen, I., Knowles, J.C., 2004b. Phosphate glasses for tissue engineering: Part 2. Processing and characterization of a ternary-based $\text{P}_2\text{O}_5\text{-CaO-Na}_2\text{O}$ glass fibre system. *Biomaterials* 25, 501–507.
- Alder, B.J., Wainwright, T.E., 1959. Studies in molecular dynamics. I. General method. *Journal of Chemical Physics* 31, 459–466.
- Austin, I.G., Mott, N.F., 1969. Polarons in crystalline and non-crystalline materials. *Advances in Physics* 18, 41–102.
- Baino, F., Novajra, G., Miguez-Pacheco, V., Boccaccini, A.R., Vitale-Brovarone, C., 2016. Bioactive glasses: Special applications outside the skeletal system. *Journal of Non-Crystalline Solids* 432, 15–30.
- Barczyński, R.J., 2008. Mixed conductivity in tungstenite–phosphate glasses containing alkali metal ions. *Journal of Non-Crystalline Solids* 354, 4275–4277.

- Bazan, J.C., Duffy, J.A., Ingram, M.D., Mallace, M.R., 1996. Conductivity anomalies in tungstate-phosphate glasses: Evidence for an ion-polaron interaction? *Solid State Ionics* 86, 497–501.
- Bhattacharya, S., Ghosh, A., 2004. Conductivity spectra in fast ion conducting glasses: Mobile ions contributing to transport process. *Physical Review B* 70, 172203.
- Bhattacharya, S., Dutta, D., Ghosh, A., 2006. Dynamics of Ag^+ ions in Ag_2S -doped superionic AgPO_3 glasses. *Physical Review B* 73, 104201.
- Bih, L., El Omari, M., Réau, J.M., *et al.*, 2000. Electronic and ionic conductivity of glasses inside the $\text{Li}_2\text{O}-\text{MoO}_3-\text{P}_2\text{O}_5$ system. *Solid State Ionics* 132, 71–85.
- Bih, L., El Omari, M., Reau, J.M., *et al.*, 2001. Electrical properties of glasses in the $\text{Na}_2\text{O}-\text{MoO}_3-\text{P}_2\text{O}_5$ system. *Materials Letters* 50, 308–317.
- Bih, L., Abbas, L., Nadiri, A., Khemakhem, H., Elouadi, B., 2008. Investigations of molybdenum redox phenomenon in $\text{Li}_2\text{O}-\text{MoO}_3-\text{P}_2\text{O}_5$ phosphate glasses. *Journal of Molecular Structure* 872, 1–9.
- Brow, R.K., 2000. The structure of simple phosphate glasses. *Journal of Non-Crystalline Solids* 263, 1–28.
- Campbell, J.H., Suratwala, T.I., 2000. Nd-doped phosphate glasses for high-energy/high-peak-power lasers. *Journal of Non-Crystalline Solids* 263, 318–341.
- Cao, C., Li, Z.B., Wang, X.L., Zhao, X.B., Han, W.Q., 2014. Recent advances in inorganic solid electrolytes for lithium batteries. *Frontiers in Energy Research* 2.25.
- Chen, Y., Chen, G.H., Liu, X.Y., Yang, T., 2018. Enhanced up-conversion luminescence and optical thermometry characteristics of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped transparent phosphate glass-ceramics. *Journal of Luminescence* 195, 314–320.
- Christensen, R., Olson, G., Martin, S.W., 2013. Ionic conductivity of mixed glass former $0.35\text{Na}_2\text{O} + 0.65(x\text{B}_2\text{O}_3 + (1-x)\text{P}_2\text{O}_5)$ glasses. *The Journal of Physical Chemistry B* 117, 16577–16586.
- Combes, C., Rey, C., 2010. Amorphous calcium phosphates: Synthesis, properties and uses in biomaterials. *Acta Biomaterialia* 6, 3362–3378.
- Cormack, A.N., Cao, Y., 1996. Molecular dynamics simulation of silicate glasses. *Molecular Engineering* 6, 183–227.
- Cruikshank, D.W.J., 1961. 1077. The rôle of 3 d-orbitals in π -bonds between (a) silicon, phosphorus, sulphur, or chlorine and (b) oxygen or nitrogen. *Journal of the Chemical Society (Resumed)*, 5486–5504.
- Das, S.S., Gupta, C.P., Srivastava, V., 2005. Ion transport studies in zinc/cadmium halide doped silver phosphate glasses. *Ionics* 11, 423–430.
- Day, D.E., Wu, Z., Ray, C.S., Hrma, P., 1998. Chemically durable iron phosphate glass wasteforms. *Journal of Non-Crystalline Solids* 241, 1–12.
- Day, R.M., Boccaccini, A.R., 2005. Effect of particulate bioactive glasses on human macrophages and monocytes in vitro. *Journal of Biomedical Materials Research Part A* 73, 73–79.
- Deshmukh, K., Kovářik, T., Křenek, T., *et al.*, 2020. Recent advances and future perspectives of sol–gel derived porous bioactive glasses: A review. *RSC Advances* 10, 33782–33835.
- di Prátula, P.E., TERNY, S., Cardillo, E.C., Frechero, M.A., 2015. The influence of transition metal oxides type M^+/M^{++} on the vanadium–tellurite glasses electrical behavior. *Solid State Sciences* 49, 83–89.
- Duclot, M., Souquet, J.L., 2001. Glassy materials for lithium batteries: Electrochemical properties and devices performances. *Journal of Power Sources* 97, 610–615.
- Dyre, J.C., Maass, P., Roling, B., Sidebottom, D.L., 2009. Fundamental questions relating to ion conduction in disordered solids. *Reports on Progress in Physics* 72, 046501.
- Ehrt, D., 2015. Phosphate and fluoride phosphate optical glasses – Properties, structure and applications. *Physics and Chemistry of Glasses-European Journal of Glass Science and Technology Part B* 56, 217–234.
- Ehrt, D., 2018. Deep-UV materials. *Advanced Optical Technologies* 7, 225–242.
- Ehrt, D., Seeber, W., 1991. Glass for high performance optics and laser technology. *Journal of Non-Crystalline Solids* 129, 19–30.
- Fang, X., Ray, C.S., Mogoš-Milanković, A., Day, D.E., 2001. Iron redox equilibrium, structure and properties of iron phosphate glasses. *Journal of Non-Crystalline Solids* 283, 162–172.
- Fu, J., 1997. Fast Li^+ Ion Conduction in $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{SiO}_2-\text{P}_2\text{O}_5$ Glass-Ceramics. *Journal of the American Ceramic Society* 80, 1901–1903.
- Galeener, F.L., Mikkelsen Jr, J.C., 1979. The Raman spectra and structure of pure vitreous P_2O_5 . *Solid State Communications* 30, 505–510.
- Galleani, G., Ledemi, Y., de Lima Filho, E.S., *et al.*, 2017. UV-transmitting step-index fluorophosphate glass fiber fabricated by the crucible technique. *Optical Materials* 64, 524–532.
- Garbarczyk, J.E., Machowski, P., Wasiucionek, M., *et al.*, 2000. Studies of silver–vanadate–phosphate glasses by Raman, EPR and impedance spectroscopy methods. *Solid State Ionics* 136, 1077–1083.
- Garbarczyk, J.E., Pietrzak, T.K., Wasiucionek, M., *et al.*, 2015. High electronic conductivity in nanostructured materials based on lithium-iron-vanadate-phosphate glasses. *Solid State Ionics* 272, 53–59.
- Garbarczyk, J.E., Machowski, P., Wasiucionek, M., Jakubowski, W., 2003. Electrical properties of $\text{AgI}-\text{Ag}_2\text{O}-\text{V}_2\text{O}_5-\text{P}_2\text{O}_5$ glasses. *Solid State Ionics* 157, 269–273.
- Garbarczyk, J.E., Jozwiak, P., Wasiucionek, M., Nowinski, J.L., 2004. Enhancement of electrical conductivity in lithium vanadate glasses by nanocrystallization. *Solid State Ionics* 175, 691–694.
- Garbarczyk, J.E., Jozwiak, P., Wasiucionek, M., Nowinski, J.L., 2007. Nanocrystallization as a method of improvement of electrical properties and thermal stability of V_2O_5 -rich glasses. *Journal of Power Sources* 173, 743–747.
- Garbarczyk, J.E., Wasiucionek, M., Jozwiak, P., Nowinski, J.L., Julien, C.M., 2009. Novel nanomaterials based on electronic and mixed conductive glasses. *Solid State Ionics* 180, 531–536.
- Grady, Z.A., Wilkinson, C.J., Randall, C.A., Mauro, J.C., 2020. Emerging role of non-crystalline electrolytes in solid-state battery research. *Frontiers in Energy Research* 8.218.
- Gupta, D., Hossain, K.M.Z., Ahmed, I., Sottile, V., Grant, D.M., 2018. Flame-spheroidized phosphate-based glass particles with improved characteristics for applications in mesenchymal stem cell culture therapy and tissue engineering. *ACS Applied Materials & Interfaces* 10, 25972–25982.
- He, K., Zu, C., Wang, Y., *et al.*, 2014. Stability of lithium ion conductor NASICON structure glass ceramic in acid and alkaline aqueous solution. *Solid State Ionics* 254, 78–81.
- Hench, L.L., 1998. Bioceramics. *Journal of the American Ceramic Society* 74, 1487–1510.
- Hench, L.L., Splinter, R.J., Allen, W.C., Greenlee, T.K., 1971. Bonding mechanisms at the interface of ceramic prosthetic materials. *Journal of Biomedical Materials Research* 5, 117–141.
- Hoppe, U., 1996. A structural model for phosphate glasses. *Journal of Non-Crystalline Solids* 195, 138–147.
- Hoppe, U., Walter, G., Barz, A., Stachel, D., Hannon, A.C., 1998. The PO bond lengths in vitreous probed by neutron diffraction with high real-space resolution. *Journal of Physics: Condensed Matter* 10, 261.
- Hossain, K.M.Z., Patel, U., Ahmed, I., 2015. Development of microspheres for biomedical applications: A review. *Progress in Biomaterials* 4, 1–19.
- Hossain, K.M.Z., Hasan, M.S., Felfel, R., Ahmed, I., 2014. Development of phosphate-based glass fibers for biomedical applications. In: Ahmed, I. (Ed.), *Hot Topics in Biomaterials*. Future Science Ltd, pp. 104–115.
- Huang, H., Yin, S.C., Nazar, L.S., 2001. Approaching theoretical capacity of LiFePO_4 at room temperature at high rates. *Electrochemical and Solid State Letters* 4, 170.
- Hudgens, J.J., Martin, S.W., 1993. Glass transition and infrared spectra of low-alkali, anhydrous lithium phosphate glasses. *Journal of the American Ceramic Society* 76, 1691–1696.
- Hutchinson, J.A., Allik, T.H., 1992. Diode array-pumped Er, Yb: Phosphate glass laser. *Applied Physics Letters* 60, 1424–1426.
- Hwang, B.C., Jiang, S., Luo, T., *et al.*, 2000. Cooperative upconversion and energy transfer of new high Er^{3+} - and Yb^{3+} - Er^{3+} -doped phosphate glasses. *The Journal of the Optical Society of America B* 17, 833–839.
- Ishiyama, T., Suzuki, S., Nishii, J., *et al.*, 2014. Proton conducting tungsten phosphate glass and its application in intermediate temperature fuel cells. *Solid State Ionics* 262, 856–859.

- Islam, M.T., Felfel, R.M., Abou Neel, E.A., *et al.*, 2017. Bioactive calcium phosphate-based glasses and ceramics and their biomedical applications: A review. *Journal of Tissue Engineering* 8, 1–16.
- Jiang, S., Luo, T., Hwang, B.C., *et al.*, 2000. Er^{3+} -doped phosphate glasses for fiber amplifiers with high gain per unit length. *Journal of Non-Crystalline Solids* 263, 364–368.
- Jones, J., Clare, A., 2012. *Bio-Glasses: An Introduction*. John Wiley & Sons.
- Jozwiak, P., Garbacz, J.E., 2005. Mixed electronic–ionic conductivity in the glasses of the $\text{Li}_2\text{O}-\text{V}_2\text{O}_5-\text{P}_2\text{O}_5$ system. *Solid State Ionics* 176, 2163–2166.
- Kiani, A., Lakhkar, N.J., Salih, V., *et al.*, 2012. Titanium-containing bioactive phosphate glasses. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 370, 1352–1375.
- Knowles, J.C., 2003. Phosphate based glasses for biomedical applications. *Journal of Materials Chemistry* 13, 2395–2401.
- Kodaira, S., Yanagida, Y., Koguchi, Y., *et al.*, 2018. Note: Complementary approach for radiation dosimetry with Ag^+ -activated phosphate glass. *Review of Scientific Instruments* 89, 116106.
- Kotobuki, M., Koishi, M., 2013. Preparation of $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$ solid electrolyte via a sol–gel route using various Al sources. *Ceramics International* 39, 4645–4649.
- Kreidl, N.J., Weyl, W.A., 1941. Phosphates in ceramic ware: IV, Phosphate glasses. *Journal of the American Ceramic Society* 24, 372–378.
- Kumar, S., Rao, K.J., 2004. Lithium ion transport in germanophosphate glasses. *Solid State Ionics* 170, 191–199.
- Lapa, A., Cresswell, M., Jackson, P., Boccaccini, A.R., 2020. Phosphate glass fibres with therapeutic ions release capability – A review. *Advances in Applied Ceramics* 119, 1–14.
- Larink, D., Eckert, H., Reichert, M., Martin, S.W., 2012. Mixed network former effect in ion-conducting alkali borophosphate glasses: Structure/property correlations in the system $(\text{M}_2\text{O})_{1/3}((\text{B}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x})_{2/3}$ ($\text{M} = \text{Li}, \text{K}, \text{Cs}$). *The Journal of Physical Chemistry C* 116, 26162–26176.
- Legeros, R.Z., Lee, Y.K., 2004. Synthesis of amorphous calcium phosphates for hard tissue repair using conventional melting technique. *Journal of Materials Science* 39, 5577–5579.
- Liebau, F. (Ed.), 1981. *Structure and Bonding in Crystals II*. London: Academic Press.
- Ma, J., Wang, C., Wroblewski, S., 2007. Kinetic characteristics of mixed conductive electrodes for lithium ion batteries. *Journal of Power Sources* 164, 849–856.
- Mackenzie, J.D., Nasu, H., 1985. The electrical conductivity of transition metal oxide-based glasses. In: Adler, D., Fritzsche, H., Ovshinsky, S.R. (Eds.), *Physics of Disordered Materials*, first ed. Boston, MA: Springer, pp. 469–482.
- Magistris, A., Chiodelli, G., Villa, M., 1985. Lithium borophosphate vitreous electrolytes. *Journal of Power Sources* 14, 87–91.
- Martin, S.W., 1991a. Review of the structures of phosphate glasses. *European Journal of Solid State and Inorganic Chemistry* 28, 163–205.
- Martin, S.W., 1991b. Ionic conduction in phosphate glasses. *Journal of the American Ceramic Society* 74, 1767–1784.
- Mesko, M.G., Day, D.E., Bunker, B.C., 1998. Immobilization of high-level radioactive sludges in iron phosphate glass. In: Shulz, W.W., Lombardo, N.J. (Eds.), *Science and Technology for Disposal of Radioactive Tank Wastes*, first ed. Boston, MA: Springer, pp. 379–392.
- Meyer, K., 1997. Characterization of the structure of binary zinc ultraphosphate glasses by infrared and Raman spectroscopy. *Journal of Non-Crystalline Solids* 209, 227–239.
- Minami, T., 1987. Recent progress in superionic conducting glasses. *Journal of Non-Crystalline Solids* 95, 107–118.
- Minami, T., Hayashi, A., Tatsumisago, M., 2006. Recent progress of glass and glass-ceramics as solid electrolytes for lithium secondary batteries. *Solid State Ionics* 177, 2715–2720.
- Mitchell, K.A.R., 1969. Use of outer d orbitals in bonding. *Chemical Reviews* 69, 157–178.
- Miyamoto, Y., Takei, Y., Nanto, H., *et al.*, 2011. Radiophotoluminescence from silver-doped phosphate glass. *Radiation Measurements* 46, 1480–1483.
- Moguš-Milanković, A., Day, D.E., 1993. Thermally stimulated polarization and dc conduction in iron phosphate glasses. *Journal of Non-Crystalline Solids* 162, 275–286.
- Moguš-Milanković, A., Day, D.E., Šantić, B., 1999. DC conductivity and polarisation in iron phosphate glasses. *Physics and Chemistry of Glasses* 40, 69–74.
- Moguš-Milanković, A., Sklepić, K., Skoko, Ž., *et al.*, 2012. Influence of nanocrystallization on the electronic conductivity of zinc iron phosphate glass. *Journal of the American Ceramic Society* 95, 303–311.
- Moguš-Milanković, A., Sklepić, K., Blažanović, H., *et al.*, 2013. Influence of germanium oxide addition on the electrical properties of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ glasses. *Journal of Power Sources* 242, 91–98.
- Moguš-Milanković, A., Šantić, A., Ličina, V., Day, D.E., 2005a. Dielectric behavior and impedance spectroscopy of bismuth iron phosphate glasses. *Journal of Non-Crystalline Solids* 351, 3235–3245.
- Moguš-Milanković, A., Šantić, A., Pavić, L., Sklepić, K., 2015. Iron phosphate glass-ceramics. *Croatia Chemica Acta* 88, 553–560.
- Moguš-Milanković, A., Šantić, A., Reis, S.T., Furić, K., Day, D.E., 2004. Mixed ion–polaron transport in $\text{Na}_2\text{O}-\text{PbO}-\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5$ glasses. *Journal of Non-Crystalline Solids* 342, 97–109.
- Moguš-Milanković, A., Šantić, A., Reis, S.T., Furić, K., Day, D.E., 2005b. Studies of lead–iron phosphate glasses by Raman, Mössbauer and impedance spectroscopy. *Journal of Non-Crystalline Solids* 351, 3246–3258.
- Moguš-Milanković, A., Sklepić, K., Mošner, P., Koudelka, L., Kalenda, P., 2016. Lithium-ion mobility in quaternary boro–germano–phosphate glasses. *The Journal of Physical Chemistry B* 120, 3978–3987.
- Moioli, E.K., Clark, P.A., Xin, X., Lal, S., Mao, J.J., 2007. Matrices and scaffolds for drug delivery in dental, oral and craniofacial tissue engineering. *Advanced Drug Delivery Reviews* 59, 308–324.
- Möncke, D., Eckert, H., 2019. Review on the structural analysis of fluoride-phosphate and fluoro-phosphate glasses. *Journal of Non-Crystalline Solids: X* 3, 100026.
- Montani, R.A., Frechero, M.A., 2003. The conductive behavior of silver vanadium-molybdenum tellurite glasses. *Solid State Ionics* 158, 327–332.
- Montani, R.A., Frechero, M.A., 2006. Mixed ion–polaron transport in lithium vanadium-molybdenum tellurite glasses. *Solid State Sciences* 177, 2911–2915.
- Moreau, F., Durán, A., Muñoz, F., 2009. Structure and properties of high Li_2O -containing aluminophosphate glasses. *Journal of the European Ceramic Society* 29, 1895–1902.
- Morena, R., 2000. Phosphate glasses as alternatives to Pb-based sealing frits. *Journal of Non-Crystalline Solids* 263, 382–387.
- Mošner, P., Vorokhta, M., Koudelka, L., *et al.*, 2013. Effect of germanium oxide on the structure and properties of lithium borophosphate glasses. *Journal of Non-Crystalline Solids* 375, 1–6.
- Mott, N.F., 1968. Conduction in glasses containing transition metal ions. *Journal of Non-Crystalline Solids* 1, 1–17.
- Mott, N.F., 1969. Conduction in non-crystalline materials: III. Localized states in a pseudogap and near extremities of conduction and valence bands. *Philosophical Magazine* 19, 835–852.
- Muñoz, F., Montagne, L., Pascual, L., Duran, A., 2009. Composition and structure dependence of the properties of lithium borophosphate glasses showing boron anomaly. *Journal of Non-Crystalline Solids* 355, 2571–2577.
- Murawski, L., Chung, C.H., Mackenzie, J.D., 1979. Electrical properties of semiconducting oxide glasses. *Journal of Non-Crystalline Solids* 32, 91–104.
- Musgraves, J., Hu, J., Calvez, L., 2019. *Springer Handbook of Glass*, first ed. Springer.
- Nakata, S., Togashi, T., Honma, T., Komatsu, T., 2016. Cathode properties of sodium iron phosphate glass for sodium ion batteries. *Journal of Non-Crystalline Solids* 450, 109–115.
- Narváez-Semanate, J.L., Rodrigues, A.C.M., 2010. Microstructure and ionic conductivity of $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ NASICON glass-ceramics. *Solid State Ionics* 181, 1197–1204.
- Nikolić, J., Pavić, L., Šantić, A., *et al.*, 2018. Novel insights into electrical transport mechanism in ionic-polaronic glasses. *Journal of the American Ceramic Society* 101, 1221–1235.
- Nikolić, J.D., Smiljanjić, S.V., Matijašević, S.D., *et al.*, 2013. Preparation of glass-ceramic in $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{GeO}_2-\text{P}_2\text{O}_5$ system. *Processing and Application of Ceramics* 7, 147–151.

- Nuernberg, R.B., Rodrigues, A.C.M., 2017. A new NASICON lithium ion-conducting glass-ceramic of the $\text{Li}_{1+x}\text{Cr}_x(\text{Ge}_y\text{Ti}_{1-y})_{2-x}(\text{PO}_4)_3$ system. *Solid State Ionics* 301, 1–9.
- Nuernberg, R.B., Pradel, A., Rodrigues, A.C., 2017. A systematic study of glass stability, crystal structure and electrical properties of lithium ion-conducting glass-ceramics of the $\text{Li}_{1+x}\text{Cr}_x(\text{Ge}_y\text{Ti}_{1-y})_{2-x}(\text{PO}_4)_3$ system. *Journal of Power Sources* 371, 167–177.
- Nuernberg, R.B., Rodrigues, A.C., Ribes, M., Pradel, A., 2018. Electrochemical properties of NASICON-structured glass-ceramics of the $\text{Li}_{1+x}\text{Cr}_x(\text{Ge}_y\text{Ti}_{1-y})_{2-x}(\text{PO}_4)_3$ system. *Electrochimica Acta* 283, 1835–1844.
- Patil, V., Patil, A., Yoon, S.J., Choi, J.W., 2013. Structural and electrical properties of NASICON type solid electrolyte nanoscaled glass-ceramic powder by mechanical milling for thin film batteries. *Journal of Nanoscience and Nanotechnology* 13, 3665–3668.
- Pavić, L., Šantić, A., Nikolić, J., *et al.*, 2018b. Nature of mixed electrical transport in Ag_2O – ZnO – P_2O_5 glasses containing WO_3 and MoO_3 . *Electrochimica Acta* 276, 434–445.
- Pavić, L., Sklepić, K., Skoko, Ž., *et al.*, 2019. Ionic conductivity of lithium germanium phosphate glass-ceramics. *The Journal of Physical Chemistry C* 123, 23312–23322.
- Pavić, L., Nikolić, J., Grača, M.P., *et al.*, 2020. Effect of controlled crystallization on polaronic transport in phosphate-based glass-ceramics. *International Journal of Applied Glass Science* 11, 97–111.
- Pavić, L., Graca, M.P., Skoko, Ž., Moguš-Milanković, A., Valente, M.A., 2014. Magnetic properties of iron phosphate glass and glass-ceramics. *Journal of the American Ceramic Society* 97, 2517–2524.
- Pavić, L., Skoko, Ž., Gajović, A., Su, D., Moguš-Milanković, A., 2018a. Electrical transport in iron phosphate glass-ceramics. *Journal of Non-Crystalline Solids* 502, 44–53.
- Pickup, D.M., Newport, R.J., Knowles, J.C., 2012. Sol–gel phosphate-based glass for drug delivery applications. *Journal of Biomaterials Applications* 26, 613–622.
- Piesch, E., Burghardt, B., 1994. Photoluminescence dosimetry: The alternative in personnel monitoring. *Radioprotection* 29, 39–67.
- Pietrzak, T.K., Garbacz, J.E., Gorzkowska, I., *et al.*, 2009. Correlation between electrical properties and microstructure of nanocrystallized V_2O_5 – P_2O_5 glasses. *Journal of Power Sources* 194, 73–80.
- Pietrzak, T.K., Garbacz, J.E., Wasiucionek, M., *et al.*, 2011. Electrical properties vs. microstructure of nanocrystallized V_2O_5 – P_2O_5 glasses – An extended temperature range study. *Solid State Ionics* 192, 210–214.
- Pietrzak, T.K., Wasiucionek, M., Nowiński, J.L., Garbacz, J.E., 2013. Isothermal nanocrystallization of vanadate–phosphate glasses. *Solid State Ionics* 251, 78–82.
- Pietrzak, T.K., Jerzy, E., Wasiucionek, M., Nowiński, J.L., 2016a. Nanocrystallisation in vanadate phosphate and lithium iron vanadate phosphate glasses. *Physics and Chemistry of Glasses-European Journal of Glass Science and Technology Part B* 57, 113–124.
- Pietrzak, T.K., Wasiucionek, M., Michalski, P.P., Kaleta, A., Garbacz, J.E., 2016b. Highly conductive cathode materials for Li-ion batteries prepared by thermal nanocrystallization of selected oxide glasses. *Materials Science and Engineering: B* 213, 140–147.
- Prasad, P.S.S., Rani, A.D., Radhakrishna, S., 1990. Mixed glass former effect in AgI – Ag_2O – V_2O_5 – P_2O_5 quaternary amorphous solid electrolytes. *Materials Chemistry and Physics* 25 (5), 487–499.
- Pugliese, D., Boetti, N.G., Lousteau, J., *et al.*, 2016. Concentration quenching in an Er-doped phosphate glass for compact optical lasers and amplifiers. *Journal of Alloys and Compounds* 657, 678–683.
- Raguenet, B., Tricot, G., Silly, G., Ribes, M., Pradel, A., 2011. Revisiting the 'mixed glass former effect' in ultra-fast quenched borophosphate glasses by advanced 1D/2D solid state NMR. *Journal of Materials Chemistry* 21, 17693–17704.
- Rahaman, M.N., Day, D.E., Bal, B.S., *et al.*, 2011. Bioactive glass in tissue engineering. *Acta Biomaterialia* 7, 2355–2373.
- Rajaram, M., Day, D.E., 1988. Preparation and properties of oxynitride glasses made from $27\text{R}_2\text{O}$ 20BaO $\cdot 3\text{Al}_2\text{O}_3 \cdot 50\text{P}_2\text{O}_5$ glass. *Journal of Non-Crystalline Solids* 102, 173–180.
- Ravaine, D., 1980. Glasses as solid electrolytes. *Journal of Non-Crystalline Solids* 38, 353–358.
- Ray, C.S., Fang, X., Karabulut, M., Marasinghe, G.K., Day, D.E., 1999. Effect of melting temperature and time on iron valence and crystallization of iron phosphate glasses. *Journal of Non-Crystalline Solids* 249, 1–16.
- Ren, J., Eckert, H., 2013. Anion distribution in superionic Ag_3PO_4 – AgI glasses revealed by dipolar solid-state NMR. *The Journal of Physical Chemistry C* 117, 24746–24751.
- Ren, M., Cai, S., Zhang, W., *et al.*, 2013. Preparation and chemical stability of CaO – P_2O_5 – Na_2O – B_2O_3 porous glass ceramics. *Journal of Non-Crystalline Solids* 380, 78–85.
- Riess, I., 1997. Chapter 7 – Electrochemistry of mixed ionic–electronic conductors. In: Gellings, P.J., Bouwmeester, H.J.M. (Eds.), *The CRC Handbook Of Solid State Electrochemistry*, first ed. Boca Raton: CRC Press.
- Ritchie, A.G., 2004. Recent developments and likely advances in lithium rechargeable batteries. *Journal of Power Sources* 136, 285–289.
- Rousselot, C., Malugani, J.P., Mercier, R., *et al.*, 1995. The origins of neutron scattering prepeaks and conductivity enhancement in AgI containing glasses. *Solid State Ionics* 78, 211–221.
- Salman, F., Khalil, R., Hazaa, H., 2016. Impedance measurements of some silver ferro-phosphate glasses. *Advanced Materials Letter* 7, 593–598.
- Šantić, A., Moguš-Milanković, A., 2012. Charge carrier dynamics in materials with disordered structures: A case study of iron phosphate glasses. *Croatia Chemica Acta* 85, 245–254.
- Sene, F.F., Martinelli, J.R., Okuno, E., 2008. Synthesis and characterization of phosphate glass microspheres for radiotherapy applications. *Journal of Non-Crystalline Solids* 354, 4887–4893.
- Seneschal, K., Smektala, F., Bureau, B., *et al.*, 2005. Properties and structure of high erbium doped phosphate glass for short optical fibers amplifiers. *Materials Research Bulletin* 40, 1433–1442.
- Shah, R., Sinanan, A.C.M., Knowles, J.C., Hunt, N.P., Lewis, M.P., 2005. Craniofacial muscle engineering using a 3-dimensional phosphate glass fibre construct. *Biomaterials* 26, 1497–1505.
- Sharmin, N., Rudd, C.D., 2017. Structure, thermal properties, dissolution behaviour and biomedical applications of phosphate glasses and fibres: A review. *Journal of Materials Science* 52, 8733–8760.
- Shelby, J.E., 2005. *Introduction to Glass Science and Technology*, second ed. Cambridge: The Royal Society of Chemistry.
- Sholom, S., McKeever, S.W., 2020. High-dose dosimetry with Ag-doped phosphate glass: Applicability test with different techniques. *Radiation Measurements* 132, 106263.
- Sklepić, K., Banhatti, R.D., Tricot, G., *et al.*, 2017. Insights from local network structures and localized diffusion on the ease of lithium ion transport in two mixed glass-former systems. *The Journal of Physical Chemistry C* 121, 17641–17657.
- Storek, M., Böhmer, R., Martin, S.W., Larink, D., Eckert, H., 2012. NMR and conductivity studies of the mixed glass former effect in lithium borophosphate glasses. *The Journal of Chemical Physics* 137, 124507.
- Suzuya, K., Price, D.L., Loong, C.K., Martin, S.W., 1998. Structure of vitreous P_2O_5 and alkali phosphate glasses. *Journal of Non-Crystalline Solids* 232, 650–657.
- Takada, K., 2013. Progress and prospective of solid-state lithium batteries. *Acta Materialia* 61, 759–770.
- Thilo, E., 1959. Die kondensierten Phosphate. *Naturwissenschaften* 46, 367–373.
- Uchino, T., Ogata, Y., 1995. Ab initio molecular orbital calculations on the electronic structure of phosphate glasses. Sodium phosphate glasses. *Journal of Non-Crystalline Solids* 181, 175–188.
- Van Wazer, J.R., 1958. *Phosphorus and its Compounds*. 1. New York: Interscience Publishers.
- Wang, C., Hong, J., 2007. Ionic/electronic conducting characteristics of LiFePO_4 cathode materials: The determining factors for high rate performance. *Electrochemical and Solid State Letters* 10, A65–A69.
- Weber, M.J., 1990. Science and technology of laser glass. *Journal of Non-Crystalline Solids* 123, 208–222.
- Weber, M.J., Layne, C.B., Saroyan, R.A., Milam, D., 1976. Low-index fluoride glasses for high-power Nd lasers. *OptCo* 18, 171–172.
- Xiao, W., Wang, J., Fan, L., Zhang, J., Li, X., 2019. Recent advances in $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ solid-state electrolyte for safe lithium batteries. *Energy Storage Materials* 19, 379–400.

- Yamanaka, C., Kato, Y., Izawa, Y., *et al.*, 1981. Nd-doped phosphate glass laser systems for laser-fusion research. *IEEE Journal of Quantum Electronics* 17, 1639–1649.
- Yu, X., Day, D.E., Long, G.J., Brow, R.K., 1997. Properties and structure of sodium-iron phosphate glasses. *Journal of Non-Crystalline Solids* 215, 21–31.
- Zachariasen, W.H., 1932. The atomic arrangement in glass. *Journal of the American Chemical Society* 54, 3841–3851.
- Zervas, M.N., Codemard, C.A., 2014. High power fiber lasers: A review. *IEEE Journal of Selected Topics in Quantum Electronics* 20, 219–241.
- Zielniok, D., Cramer, C., Eckert, H., 2007. Structure/property correlations in ion-conducting mixed-network former glasses: Solid-state NMR studies of the system $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{P}_2\text{O}_5$. *Chemistry of Materials* 19, 3162–3170.

Halide Glasses

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Introduction

Glass as an Outstanding Material

Glass is a major material that takes an important part in our modern societies. It is more recent than metals – only a few thousand years – and takes advantage of its visible transparency, low cost and ability to be shaped in complex forms and huge sizes. Most common glass is referred to as soda lime silica glass, associating silica with the oxides of calcium and sodium.

While it has been extensively studied and developed, some scientific questions are still waiting for a satisfactory answer. Glass may be considered as a frozen liquid and thus it appears as a non-crystalline solid. The vitreous state is a particular state of matter that is intermediate between a crystal and a liquid.

At first glance, glass formation may appear as exceptional and restricted to a few chemical systems. Following numerous investigations and developments it appears now that glass formation is rather general, even though many materials cannot be obtained in the vitreous state. The occurrence of halide glasses – fluorides, chlorides, bromides, iodides – confirms this view. This chapter intends to describe the various glasses that belong to this group.

A Quick Historical Survey

Glasses based on beryllium fluoride BeF_2 were reported by Goldschmidt (1926) in the early part of the 20th century. A few years later multicomponent fluoroberyllate glasses were synthesized and characterized (Heyne, 1933). A major contribution was made by Sun (1949a) during the 1940s at Kodak Eastman laboratories. He also patented the first glasses based on aluminum fluoride. In addition he confirmed vitreous zinc chloride ZnCl_2 and reported vitreous silver halides AgCl , AgBr and AgI . Later vitreous zinc bromide was synthesized (Duffy and Ingram, 1983; Hu *et al.*, 1983). In the case of Be and Zn, the structural unit was found to be a tetrahedron: BeF_4 (Warren and Hill, 1934) and ZnCl_4 , which emphasizes the similarity with vitreous silica. The pioneering work of Winter (1955, 1957) must also be emphasized – various vitreous halides were reported: AlF_3 , SnCl_2 , PbBr_2 , PbI_2 .

The serendipitous discovery of the first fluorozirconate glasses in 1974 (Poulain *et al.*, 1975) was the starting point for very numerous studies on Heavy Metal Fluoride Glasses (HMFG) (Baldwin *et al.*, 1981; Comyns, 1989; Poulain, 1983; Aggarwal and Lu, 1991; France *et al.*, 1990; Katsuyama and Matsumura, 1989; Poulain, 2004, 2010). These investigations were stimulated by the prospects for ultralow optical losses that could lead to long haul, repeaterless fiber optic links (Shibata *et al.*, 1981; Gannon, 1980; France *et al.*, 1989). It appeared very attractive for submarine telecommunications and also for some defense projects. However, despite significant advances, this topic was largely abandoned after 1990. After major telecom labs discontinued the work, some small companies continued to manufacture fluoride glass optical fibers for infrared transmission. Since then, thousands of glass compositions have been identified and make the basis for further developments.

This chapter presents a review of halide glasses, either monohalides or polyhalides. It does not describe oxyhalide and chalcogenide glasses that are important groups and have been largely investigated.

The main features of halide glasses are often expressed by comparison to silica and borosilicate glasses. They may be summarized as follows:

- Low characteristic temperatures: melting, softening.
- Extended optical range, especially in the mid-infrared spectrum
- Limited mechanical properties: they appear as soft glasses
- Sensitivity to water: most chloride glasses are hygroscopic.
- Devitrification tendency.

Some of these properties open new fields of applications while others appear as limitations and raise technical problems.

Glass Compositions

Monocomponent Glasses

Several halides can exist in the vitreous form. They sometimes require fast quenching rates, and are obtained only as thin samples. This is not the case for BeF_2 and ZnCl_2 which can be cast as bulk samples. Sun (1946) reported silver halide glasses: AgCl , AgBr , AgI . Morey (1939) mentioned vitreous PbCl_2 , while Winter (1955, 1957) synthesized glass from AlF_3 , SnCl_2 , PbBr_2 and PbI_2 . ZnBr_2 glass was described later by Duffy and Ingram (1983) and Hu *et al.* (1983). It should be noted that these glasses could have

Table 1 Fluoroberyllate glass compositions (mol%)

BeF_2	AlF_3	MgF_2	CaF_2	SrF_2	BaF_2	PbF_2	LaF_3	LiF	KF
40	20	20				20			
20	30	5				45			
47	24		8.6				7.5	12.9	
33.5	22.9	21.1			22.5				
53								21	26
48	5	10	7.5						29.5
54.1	4.3	14	11.2	7	5		4.4		

been obtained under special conditions. The purity and the structure of the starting materials influence glass formation, and also the overall processing.

Monohalide Glasses

Fluoride glasses

Fluoroberyllates

Pure beryllium fluoride exists in the glassy form. It has been associated with other fluorides to improve glass quality and to adjust the physical and chemical properties. Various examples may be found in several review papers (Jahn, 1961; Rawson, 1967; Baldwin *et al.*, 1981).

Binary glasses have been reported in the BeF_2 -MF (M = Li, Na, K, Rb, Cs) and BeF_2 -M'F₂ (M' = Mg, Ca, Sr) systems. Alkali glasses are more stable than the alkaline earth glasses that require fast quenching to avoid crystallization. The extended work of K. H. Sun emphasizes the good compatibility of aluminum fluoride with BeF_2 to enhance glass formation. Typical glass compositions are shown in Table 1.

The main interest for fluoroberyllate glasses results from their low refractive index (close to 1.3), and non-linear refractive index (Weber *et al.*, 1978; Videau *et al.*, 1979). This feature is particularly attractive for the very high power lasers developed for nuclear fusion (Weber, 1980). This was probably the reason for the numerous works implemented in Russia in the late 1960s. Researchers at ATT Bell Labs have investigated the index dispersion of some fluoroberyllate glasses from which large NA (Numerical Aperture) fibers could be drawn.

The practical development of BeF_2 -based glasses was blocked by the toxicity of beryllium compounds. While toxicity rather affects beryllium oxide, no risk could be taken with fluoride. Another concern was hygroscopicity. Vitreous BeF_2 is hygroscopic, but multicomponent fluoroberyllates can withstand ambient atmosphere for many years (Sun, 1979). As a result, the interest of fluoroberyllate glasses is confined to fundamental research networks, or worse, in science museums!

Fluorozirconates

The first fluoride glasses based on zirconium tetrafluoride were discovered by Michel Poulain in March 1974, while trying to synthesize new crystalline complex fluorides (Poulain *et al.*, 1975). This initiated a range of studies on "Heavy Metal Fluoride Glasses". The limits for glass formation were determined first in the ZrF_4 - BaF_2 -NaF ternary system as shown in Fig. 1. It was a host for neodymium fluoride NdF_3 acting as an active element for emission at 1048 nm.

Further research confirmed the occurrence of glasses in numerous ternary systems such as ZrF_4 - BaF_2 -ThF₄ (Poulain *et al.*, 1977) and ZrF_4 - BaF_2 -NdF₃ (Lucas *et al.*, 1978) as shown in Fig. 2 as well as ZrF_4 - BaF_2 -LaF₃ (Lecoq and Poulain, 1979) (see Fig. 3), ZrF_4 - BaF_2 -UF₄ (Aliaga *et al.*, 1978), ZrF_4 - BaF_2 -CaF₂, ZrF_4 - BaF_2 -YF₃ and ZrF_4 - BaF_2 -GdF₃ (Mitachi, 1982). Two technical elements brought large advances in glass synthesis. The first one was the ammonium fluoride processing that allows preparation from oxides in open crucibles (Poulain and Lucas, 1978). This process leads to faster synthesis, larger samples at lower cost. It was only later that the authors realized that this process was already used by K.H. Sun 30 years earlier (Sun, 1949b). The second element was the discovery of the stabilizing effect of aluminum fluoride: a small addition of AlF_3 (<5 mol%) to a fluorozirconate glass melt was sufficient to reduce significantly the critical cooling rate required for obtaining crystal-free clear samples (Lecoq and Poulain, 1980a). Then quaternary glasses were reported in the ZrF_4 - BaF_2 - AlF_3 -MF_n (M = Li, Na, Ca, La, Y, Nd, Th) systems (Lecoq and Poulain 1980a,b). Lower cooling rate means larger bulk samples, and indeed, multikilogram glass windows could be cast. Incorporation of CsF was also studied (Kawamoto and Nohara, 1985). Ternary glasses were also investigated in the ZrF_4 -BiF₃-LiF or -NaF systems and glass formation areas are shown in Fig. 4.

The close similarity between zirconium and hafnium is well known to solid state chemists, and so it was expected to achieve glass formation in fluorohafnate systems. This was confirmed in the early stages of research. The glass forming area in the HfF_4 - BaF_2 -LaF₃ ternary system is shown in Fig. 5.

A large R & D effort was devoted to HMFG in the 1980s, mainly for their potential ultra low optical losses in the mid infrared range. Theoretical calculations lead to a minimum value of transmission losses ranging from 10^{-2} to 10^{-3} dB/km, depending on glass composition (Shibata *et al.*, 1981; Gannon, 1980; France *et al.*, 1989). Numerous laboratories and research centers were involved in this field: NRL and ATT in the USA, NTT, KDD, Hoya and Furukawa in Japan, BT in England, Siemens in Germany,

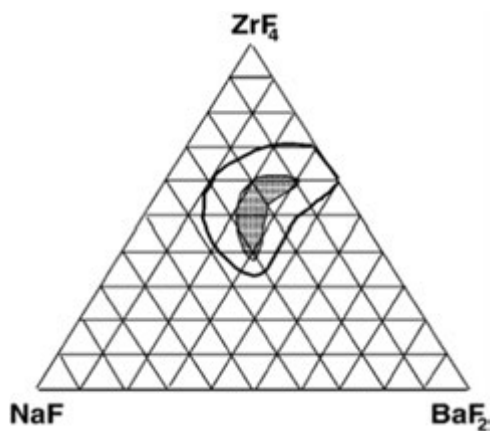


Fig. 1 First fluorozirconate glass discovered in the ZrF_4 - BaF_2 - NaF ternary system. Reproduced from Poulain, M.A., Poulain, M.J., Lucas, J., 1975. Verres Fluores Au Tetrafluorure De Zirconium Propriétés Optiques d'un Verre Dope Au Nd^{3+} . Materials Research Bulletin 10 (4), 243–246. [https://doi.org/10.1016/0025-5408\(75\)90106-3](https://doi.org/10.1016/0025-5408(75)90106-3).

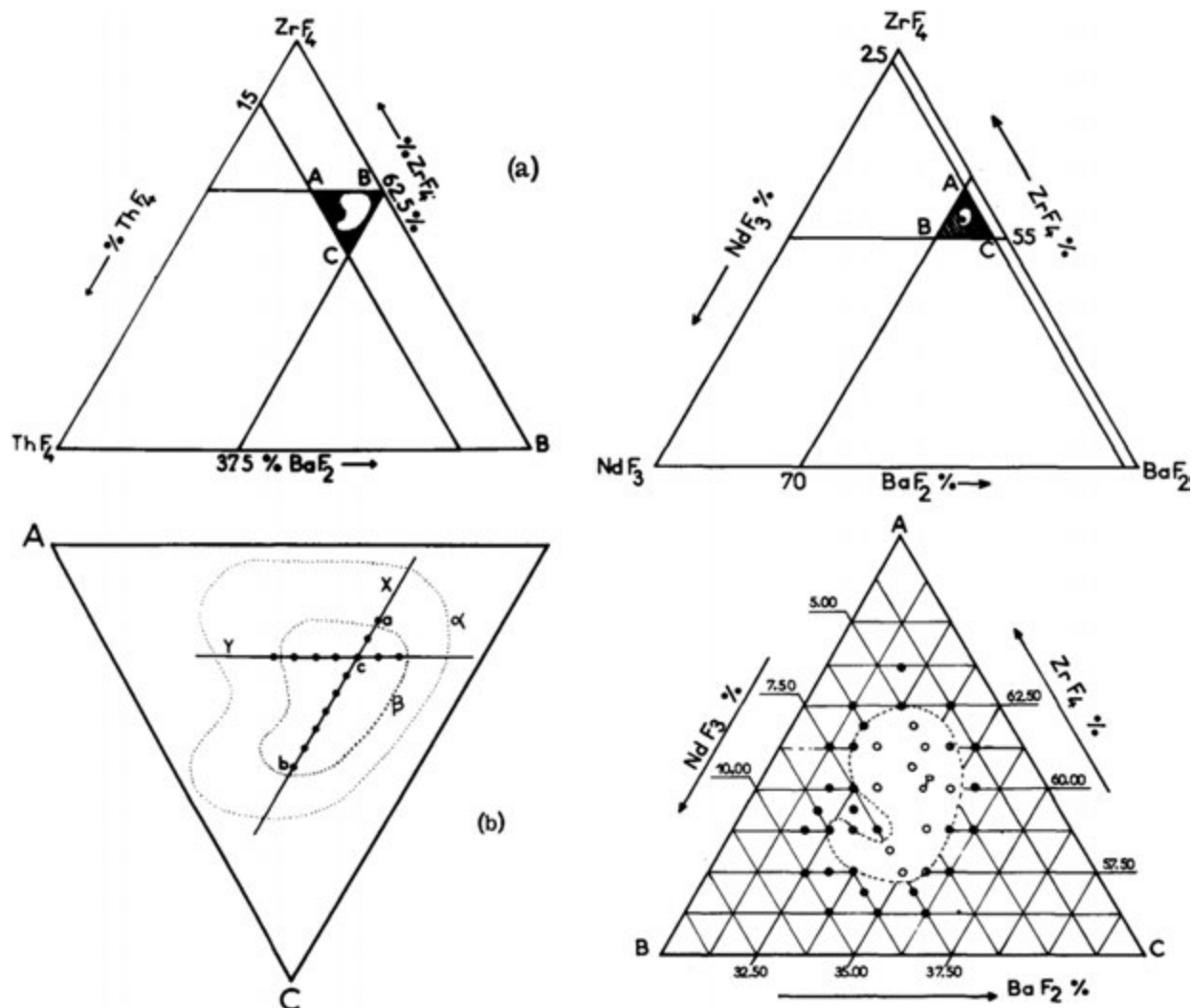


Fig. 2 Glass forming areas in the ZrF_4 - BaF_2 - ThF_4 and ZrF_4 - BaF_2 - NdF_3 ternary systems. Reproduced from Poulain, M., Lucas, J., 1978. Une nouvelle classe de matériaux, les verres fluorés au tétrafluorure de zirconium. Verres et Réfractaires 32 (4), 505–513.

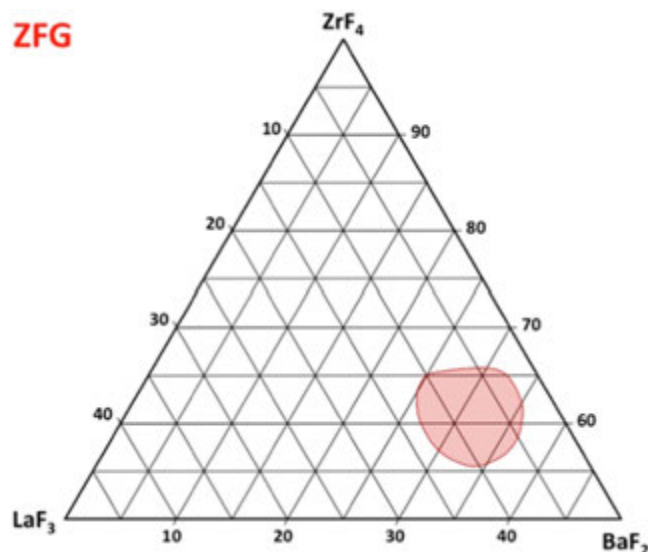


Fig. 3 Glass forming area in the $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3$ ternary system. Reproduced from Lecoq, A., Poulain, M., 1979. Lanthanum fluorozirconate glasses. *Journal of Non-Crystalline Solids* 34 (1), 101–110. [https://doi.org/10.1016/0022-3093\(79\)90009-7](https://doi.org/10.1016/0022-3093(79)90009-7).

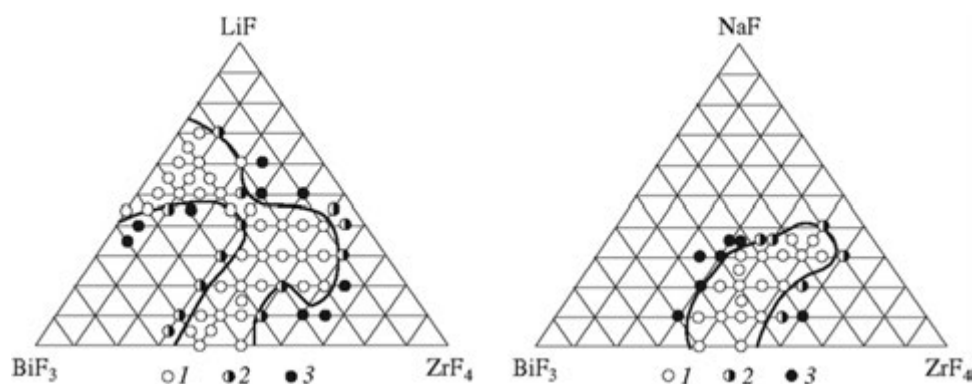


Fig. 4 Vitreous areas in the $\text{ZrF}_4\text{-BiF}_3\text{-LiF}$ and $\text{ZrF}_4\text{-BiF}_3\text{-NaF}$ ternary systems. Reproduced from Merkulov, E.B., Logoveev, N.A., Goncharuk, V.K., Yaroshenko, R.M., 2007. Glass formation in the $\text{ZrF}_4\text{-BiF}_3\text{-MeF}$ (Me=Li, Na, K) fluoride systems. *Glass Physics and Chemistry* 33, 106–108.

Alcatel and France Telecom in France, CSELT in Italy, Telecom Australia and Telebras in the southern hemisphere. In addition, subsequent funding from US Air Force and various state agencies worldwide allowed numerous academic laboratories to conduct fundamental and applied studies on HMFG, leading to a better understanding of the material properties and processing optimization. Specific symposia were organized and collections of the corresponding papers were published (Lucas and Moynihan, 1985; Drexhage *et al.*, 1987; Almeida, 1987; Yamane and Moynihan, 1988; Frischat and Moynihan, 1991; MacFarlane, 1991; Poignant *et al.*, 1993; Gan and MacFarlane, 1995; Bartholomew *et al.*, 1996). To date, the total number of scientific papers, patents and contributions largely exceeds 10,000. Publications on this subject, which provide a global view of the state of art of fluoride glasses include several books (Comyns, 1989; Aggarwal and Lu, 1991; France *et al.*, 1990), book chapters (Drexhage, 1985; Videau and Portier, 1985; Katsuyama and Matsumura, 1989; Sanghera *et al.*, 1998; Poulain, 2004, 2010) and review papers (Baldwin *et al.*, 1981; Poulain, 1983; Lucas, 1989).

The chemical composition of glasses can vary continuously within limits that are defined by the stability versus devitrification. This makes a significant difference with crystalline materials for which composition is ruled by stoichiometry, resulting in fixed physical properties: thermal, optical, mechanical... This provides an advantage for adjusting optimum characteristics of optical fibers, such as numerical aperture, optical transmission, chemical durability, thermal stability and strength. Addition of 4 mol% AlF_3 to $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3$ (ZBLA) and $\text{ZrF}_4\text{-BaF}_2\text{-NaF}$ (ZBNA) glasses increased their stability (see Fig. 6). Glass formation in the $\text{ZrF}_4\text{-BaF}_2\text{-YF}_3\text{-AlF}_3$ quaternary system is shown in Fig. 7. The combination of the ZBLA and ZBNA glasses leads to the ZBLAN ($\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3\text{-NaF}$) glass which, in practice, most fluorozirconate glass components are made from and that have low critical cooling rates. Standard glass compositions based on ZrF_4 are given in Table 2.

Since fluoride glass components and optical fibers are commercially available (Le Verre Fluore, 2020; Fiberlabs, Inc., 2020; Thorlabs, 2020), scientific papers rather focus on physical properties and photonic applications, as described in the next section.

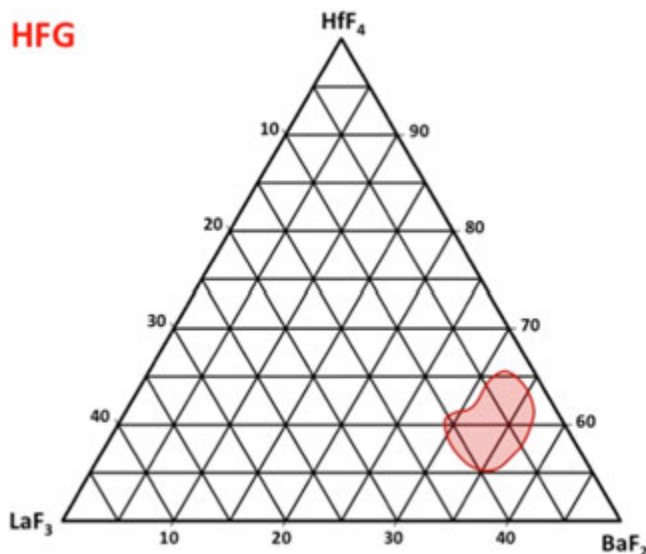


Fig. 5 Glass forming area in the HfF_4 - BaF_2 - LaF_3 ternary system. Reproduced from Drexhage, M.G., Moynihan, C.T., Saleh, M., 1980. Infrared transmitting glasses based on hafnium fluoride. *Materials Research Bulletin* 15, 213–219.

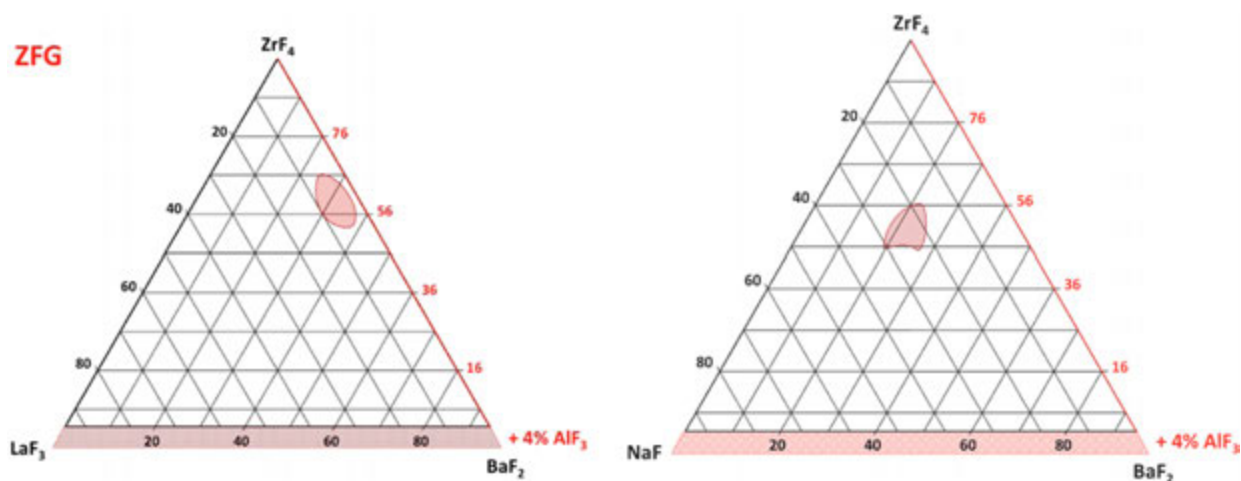


Fig. 6 Glass forming systems for the ZBLA and ZBNA glasses. By comparison with the ZrF_4 - BaF_2 - LaF_3 and ZrF_4 - BaF_2 - NaF systems, incorporation of 4 mol% AlF_3 increases glass stability. The combination of these two glasses leads to the ZBLAN glass. Reproduced from Lecoq, A., Poulain, M., 1980a. Etude Du Rôle Stabilisateur de l'aluminium Dans Les Verres Au Tétrafluorure de Zirconium. *Verres Réfractaires* 34 (3), 333–342.

Fluoroaluminates

The first mention of fluoroaluminate glass may be found in a 1946 patent by K. H. Sun (Sun and Callear, 1949), largely known for his contributions to fluoroberylate glasses. He reported glass formation in the AlF_3 - PbF_2 - MgF_2 - SrF_2 system. However this did not attract much attention. The development of fluorozirconates provoked a growing interest for these glasses. A few years later, more systematic studies were performed. Glasses were prepared by quenching compositions in the AlF_3 - CaF_2 , AlF_3 - BaF_2 , AlF_3 - PbF_2 binary systems. Later, some more stable compositions were identified. They belong to the AlF_3 - BaF_2 - CaF_2 (Kanamori *et al.*, 1981), AlF_3 - BaF_2 - YF_3 - CaF_2 (Kanamori *et al.*, 1981) and AlF_3 - BaF_2 - YF_3 - ThF_4 (Poulain *et al.*, 1981a) systems (Fig. 8).

Samples more than 6 mm thick could be prepared in these quaternary systems, and rods could be drawn into fibers. Numerous other fluoroaluminate glasses have been synthesized in multicomponent systems including zinc, alkali, magnesium and rare earths (Poulain *et al.*, 1982b). A small amount of zirconium fluoride increases glass stability (Izumitani *et al.*, 1987). Commercial fluoroaluminate glass fibers are available (Fiberlabs, Inc., 2020; Le Verre Fluore, 2020). By comparison to fluorozirconates they offer a better chemical durability and a less extended transmission range in the mid IR. Fluoroaluminate glass compositions are reported in Table 3.

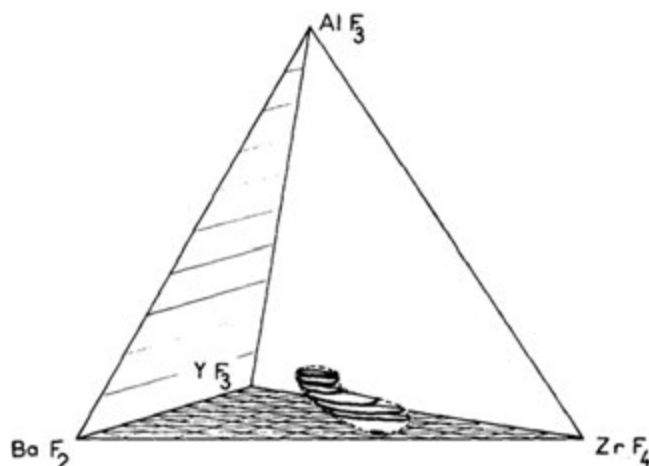


Fig. 7 Glass formation in the $\text{ZrF}_4\text{-BaF}_2\text{-YF}_3\text{-AlF}_3$ quaternary system. Reproduced from Lecoq, A., Poulain, M., 1980b. Fluoride glasses in the $\text{ZrF}_4\text{-BaF}_2\text{-YF}_3\text{-AlF}_3$ quaternary system. *Journal of Non-Crystalline Solids* 41 (2), 209–217. [https://doi.org/10.1016/0022-3093\(80\)90166-0](https://doi.org/10.1016/0022-3093(80)90166-0).

Table 2 Fluorozirconate glass compositions (mol%)

Glass	ZrF_4	HfF_4	BaF_2	LaF_3	AlF_3	NaF	LiF	PbF_2
ZB	60		40					
ZBL	60		34	6				
ZBLA	57		34	5	3			
HBLA		57	36	3	4			
ZBGA	60.5		31.7	3.8 (Gd)	4			
ZBYA	45		36	11 (Y)	8			
ZBNA	52		24		4	20		
ZBLAN	53		20	4	3	20		
ZBLALi	53		20	4	3		20	
ZBLANP	48		17	4	3	20		8
ZBLALiP	48		17	4	3		20	8

Fluoroindates

Not surprisingly, the discovery of the first fluoroindate glasses arose in laboratories specialized in solid state fluorides. The glass forming ability of InF_3 was reported almost simultaneously by Michel Poulain in March 1980 (Poulain *et al.*, 1981b), and a few days later by a team of researchers from Le Mans University (Miranday *et al.*, 1982). It was a few years before more systematic studies were implemented, in Le Mans, Bordeaux (Videau *et al.*, 1986) and Rennes universities (Poulain and Poulain, 1988; Messaddeq and Poulain, 1991; Poulain *et al.*, 1992a,b; Messaddeq *et al.*, 1993), and also in Japan (Nishii *et al.*, 1989). Fedorov *et al.* (2000) made an extended review of these glasses. It appears that the glass forming systems based on InF_3 are more numerous than those based on ZrF_4 . This is exemplified by the occurrence of several binary glasses associating InF_3 and various other fluorides: SrF_2 , BaF_2 , PbF_2 . However, to date, the thermal stability of the best fluoroindates is still lower than observed in optimized fluorozeirconates.

Systematic investigations were implemented with GaF_3 (Soufiane and Poulain, 1993) that exhibits a large chemical similarity with InF_3 . Numerous binary, ternary and multicomponent vitreous systems have been reported (Poulain, 2010). Gallium may replace indium in most fluoroindate glass compositions, and reversely InF_3 may substitute for GaF_3 in fluorogallate glasses. Such substitutions are likely to increase glass stability. In practice, fluorogallate glasses are not considered as a group distinct from fluoroindates.

Most standard fluoroindate glass compositions derive from the IZBS glass (mol%): 40 InF_3 , 20 ZnF_2 , 20 BaF_2 , 20 SrF_2 (Messaddeq and Poulain, 1991) with some variations, substitutions and additions (see Fig. 9). Typical vitreous systems based on IZBS with other fluorides are shown in Fig. 10, while various compositions are given in Table 4.

The synthesis of fluoroindate glasses appears more critical than that of fluorozeirconates mainly because devitrification is more difficult to control. In addition fining must take into account the oxidation-reduction processes that result from the two-oxidation states of indium (+3 and +1). The ammonium bifluoride processing may be used for glass synthesis, but the complete fluorination of the oxides requires time and temperature adjustments.

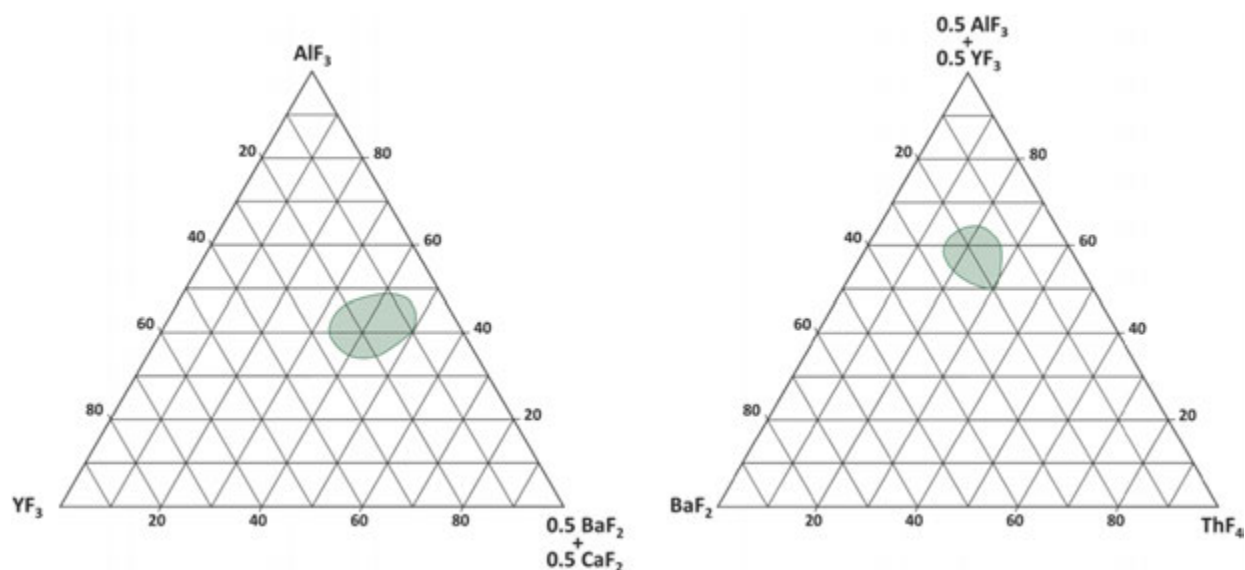


Fig. 8 Vitreous areas in fluoroaluminate systems. Reproduced from Poulain, M., 1983. Halide glasses. *Journal of Non-Crystalline Solids, Preparation, Properties, and Structure of Special Glasses*, 56 (1), 1–14. [https://doi.org/10.1016/0022-3093\(83\)90439-8](https://doi.org/10.1016/0022-3093(83)90439-8).

Table 3 Fluoroaluminate glass compositions (mol%)

Glass	AlF_3	YF_3	BaF_2	SrF_2	CaF_2	ZnF_2	MgF_2	ThF_4	ZrF_4	NaF
YABC	40	20	20	20						
BATY	28.7	28.7	20					22.6		
ZnBTA	20		20			40		20		
AFG3H	30.2	8.3	10.6	13.2	20.2		3.5		10.2	3.8
ABZYzn	20	20	30			10			20	
AZBZnYC	20	10	20		10	20			20	

Other fluoride compositions

The glass forming ability of various fluorides in multicomponent systems has been largely investigated and some compositions are given in **Table 5**. However most of them did not lead to practical developments for different reasons: devitrification tendency, cost, radioactivity, optical absorption.

A first group consists of glasses based on 3d transition metals: VF_3 , MnF_2 , FeF_3 , CoF_2 , NiF_2 , CuF_2 and ZnF_2 (Miranday *et al.*, 1981; Jacoboni *et al.*, 1983). They have been discovered and characterized in terms of structure and magnetic, electrical and luminescence properties at Le Mans university (Jacoboni, 1987).

By analogy with zirconium and hafnium tetrafluoride, it was expected that other tetrafluorides could also form glasses in multicomponent systems. Indeed various glasses may be obtained with ThF_4 and UF_4 . Others include UF_4 - BaF_2 - MF_2 - $M'F_3$ ($M = Mn, Cu, Zn$; $M' = V, Fe, Ga, In$), ThF_4 - BaF_2 - LnF_3 , (Lucas *et al.*, 1981) ThF_4 - BaF_2 - LiF (Poulain and Poulain, 1983). The ThF_4 - BaF_2 -(Yb,Y) F_3 - ZnF_2 systems have been largely investigated (Bouaggad *et al.*, 1987) as shown in **Fig. 11**. Note that a glass was also obtained in the TiF_4 - BaF_2 - NaF system as an analog to the first fluorozirconate glass.

Scandium fluoride ScF_3 forms glasses in the ScF_3 - BaF_2 - YF_3 system with possible incorporation of alkali fluoride (Poulain *et al.*, 1982a). Glasses based on VF_3 have also been reported.

Some divalent fluorides show a limited glass forming ability. This is the case for zinc fluoride that forms binary ZnF_2 - SrF_2 glasses (Messaddeq and Poulain, 1991) and ternary ZnF_2 - BaF_2 - LnF_3 ($Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb$) glasses (Fonteneau *et al.*, 1980). The limits of glass formation in each of these ternary systems are shown in **Fig. 12**. Multicomponent glasses have been studied in the ZnF_2 - BaF_2 - SrF_2 - YF_3 system (Jia *et al.*, 2018). Binary MnF_2 - BaF_2 glasses (Djouama *et al.*, 2007) and ternary ZnF_2 - CdF_2 - BaF_2 glasses have been observed (Matecki *et al.*, 1982) shown in **Fig. 13**. All these examples show that glass formation in fluoride systems is far from being an exception. There is little doubt that numerous new glasses could be observed in other multicomponent systems. The number of possibilities is still larger if several halides are associated.

Chloride glasses

There are specific features of chloride glasses in comparison with fluorides. First, characteristic temperatures (glass transition, softening and melting) are lower and come closer to room temperature. Most chlorides are hygroscopic and this makes synthesis

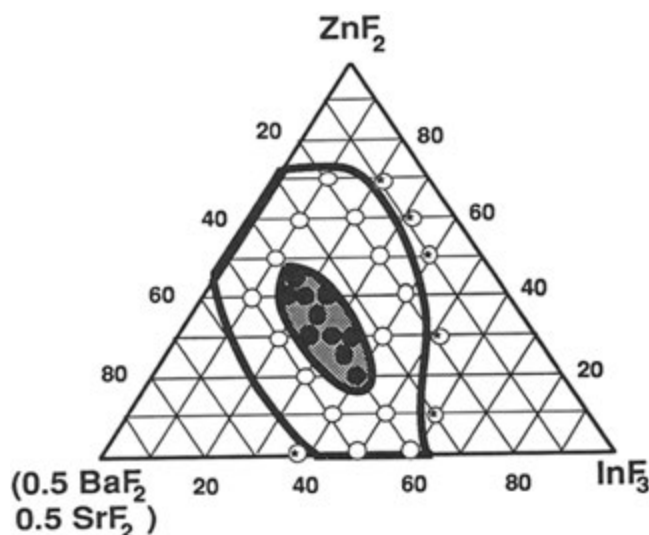


Fig. 9 Glass formation in the $\text{InF}_3\text{-ZnF}_2\text{-BaF}_2\text{-SrF}_2$ system (IZBS glass). Reproduced from Messaddeq, Y., Poulain, M.J., 1991. Stabilizing effect of indium in divalent fluoride glasses. *Materials Science Forum* 67–68, 161–168.

and characterization more difficult. This low chemical durability also limits possible applications. Some chloride glass compositions are given in [Table 6](#).

Glasses based on ZnCl_2

Vitreous zinc chloride ZnCl_2 is probably the best-known chloride glass. [Maier \(1925\)](#) was first to report it and studied its structure and some physical properties. Zinc chloride may be associated with alkali halides, but it appears that multicomponent glasses based on ZnCl_2 are rarely more stable against devitrification than ZnCl_2 itself. Glass synthesis requires special equipment to avoid moisture contamination. As shown in [Fig. 14](#) several vitreous systems have been investigated, for example $\text{ZnCl}_2\text{-KCl-MCl}_2$ where $M = \text{Mg, Ca, Sr, Ba}$.

Glasses based on CdCl_2

Cadmium is in the same column of the periodic table of elements as Zinc. It may be noted that glass progenitors often belong to the same column and this is an empirical criterion for glass formation. There are numerous examples: Si and Ge for oxides, Zr, Hf and Th for fluorides. Indeed cadmium chloride glasses have been reported ([Poulain et al., 1983](#)) in the $\text{CdCl}_2\text{-BaCl}_2\text{-MCl}$ ($M = \text{Na, K}$) system. These glass compositions, shown in [Fig. 15](#), are obtained by quenching as thin samples.

Glasses based on BiCl_3

Stable glasses have been described by [Angell and Ziegler \(1981\)](#) in the $\text{BiCl}_3\text{-KCl}$ binary system and also in the $\text{BiCl}_3\text{-KCl-NaCl}$ ternary system ([Ziegler and Angell, 1982](#)).

Glasses based on PbCl_2

Several authors have reported vitreous PbCl_2 ([Morey, 1939; Winter, 1955](#)). Multicomponent glasses have also been described including the $\text{PbCl}_2\text{-AgCl-CsCl}$ ternary system. It should be noted also that for $\text{CuCl-PbCl}_2\text{-RbCl}$ glasses the main glass progenitor seems to be CuCl ([Angell et al., 1985](#)).

Glasses based on ThCl_4

Chinese researchers have reported various chloride glasses based on thorium. As shown in [Fig. 16](#), several ternary systems have been investigated, for example $\text{ThCl}_4\text{-PbCl}_2\text{-CuCl}$, $\text{ThCl}_4\text{-PbCl}_2\text{-AgCl}$ and $\text{ThCl}_4\text{-PbCl}_2\text{-NaCl}$, $\text{ThCl}_4\text{-KCl-NaCl}$ ([Gan et al., 1985; Dai et al., 1988](#)).

TeX glasses

Glasses are formed in the Te-Cl system. The general formula is $\text{Te}_{(1-x)}\text{Cl}_x$ ($0.32 < x < 0.62$) ([Zhang et al., 1987](#)). While stoichiometry applies in halide glasses, it is no more the case in chalcogenide glasses in which Se-Se or Te-Te bonds will modify continuously the anion to cation ratio. In this respect the TeX glasses ($X = \text{halide or chalcogen}$) should rather be considered as chalcogenide glasses.

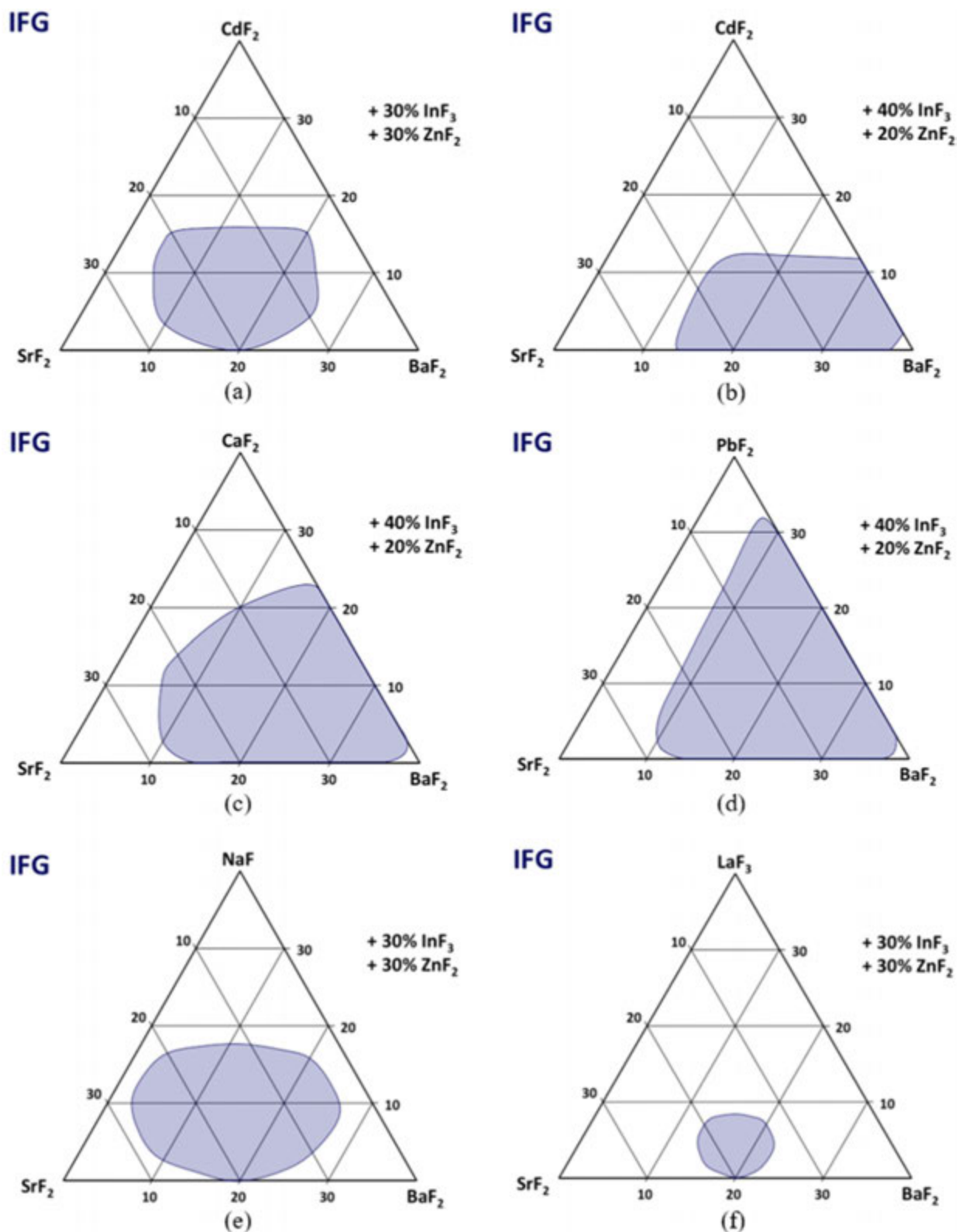


Fig. 10 Fluoroindate glass forming systems based on the IZBS glass. Reproduced from Messaddeq, Y., Delben, A., Boscolo, M., *et al.*, 1993. New fluoroindate glass compositions. *Journal of Non-Crystalline Solids* 161, 210–212. [https://doi.org/10.1016/0022-3093\(93\)90701-X](https://doi.org/10.1016/0022-3093(93)90701-X).

Table 4 Fluoroindate glass compositions (mol%)

Glass	InF_3	GaF_3	BaF_2	SrF_2	CaF_2	ZnF_2	PbF_2	YF_3	ThF_4	CdF_2	NaF
IYB	50		10					40			
IZBS	40		20	20		20					
IZBSC	40		15	20	5	20					
IZSBN	30		15	20		30					5
BiZnYbT	30		30			20		10 (Yb)	10		
PIB	50		20				20				
PGZn		40				17	43				
PZG		25				25	50				
PIGCZ	15	20				15	30			20	

Table 5 Miscellaneous multi-component fluoride glass compositions (mol%)

Glass	ScF_3	YF_3	FeF_3	BaF_2	SrF_2	CaF_2	ZnF_2	CdF_2	ThF_4	PbF_2	NaF	LiF
ZnSr					40		60					
ZnBT				20			40		20			
CdZnB				40			20	40				
SYB	40	40		20								
TLi									30			70
TBLi				10					30			60
ZnBTYb		28.3 (Yb)		15			28.3		28.3			
FPN			45							25	30	
ABZYZn	20	20		30			10			20		

Bromide glasses

The chemical behavior of bromides is close to that of chlorides. Not surprisingly glass formation is observed with the same cations as in chloride glasses. Some bromide glass compositions are given in [Table 7](#).

Glasses based on ZnBr_2

Vitreous zinc bromide has been reported by [Duffy and Ingram \(1974, 1983\)](#) and was studied later by [Hu et al. \(1983\)](#). Incorporation of alkali bromides leads to binary and multicomponent bromide glasses. Several binary and ternary glasses have been reported: $\text{ZnBr}_2\text{-KBr}$; $\text{ZnBr}_2\text{-TlBr}$ ([Fuding, 1985](#)); $\text{ZnBr}_2\text{-CaBr}_2\text{-KBr}$ ([Kadono et al., 1988](#)); $\text{ZnBr}_2\text{-PbBr}_2\text{-MBr}$ ($\text{M}=\text{K}, \text{Rb}, \text{Cs-Tl}$) ([Nasu et al., 1985](#)); $\text{ZnBr}_2\text{-RbBr}$, $\text{ZnBr}_2\text{-RbBr}$, $\text{ZnBr}_2\text{-TlBr-GaBr}_3$ ([Nasu et al., 1985](#)). A typical vitreous diagram ($\text{ZnBr}_2\text{-PbBr}_2\text{-TlBr}$) is shown in [Fig. 17](#).

Glasses based on BiBr_3

Bromide glasses have been synthesized by [Angell and Ziegler \(1981\)](#) in the $\text{BiBr}_3\text{-KBr}$ binary system and compared with BiCl_3 -based glasses ([Ziegler and Angell, 1982](#)).

Glasses based on PbBr_2

Various bromide glasses have been synthesized with lead bromide as the major glass former. The $\text{PbBr}_2\text{-AgBr-CsBr}$ ternary system has been investigated. Other systems based on PbBr_2 as outlined above have also been reported, namely $\text{ZnBr}_2\text{-PbBr}_2\text{-MBr}$ ($\text{M}=\text{K}, \text{Rb}, \text{Cs-Tl}$) ([Nasu et al., 1985](#)) see [Fig. 17](#). Even though they include ZnBr_2 , lead bromide should be considered as the main glass progenitor.

Glasses based on CdBr_2

Ternary glasses have been reported in the $\text{CdBr}_2\text{-PbBr}_2\text{-TlBr}$ system ([Fuding, 1985](#)).

Glasses based on GaBr_3

While there is no report of glasses based on GaCl_3 , bromide glasses have been synthesized in the $\text{GaBr}_3\text{-NaBr}$ and $\text{GaBr}_3\text{-TlBr}$ binary systems ([Nasu et al., 1985](#)). More stable glasses are likely to exist in multicomponent combinations.

TeBr_x glasses

The Te-Br association also leads to glasses ([Zhang et al., 1987](#)). The vitreous domain is expressed by the general formula $\text{Te}_{(1-x)}\text{Br}_x$ ($0.3 < x < 0.5$). It is similar to the Te-Cl system.

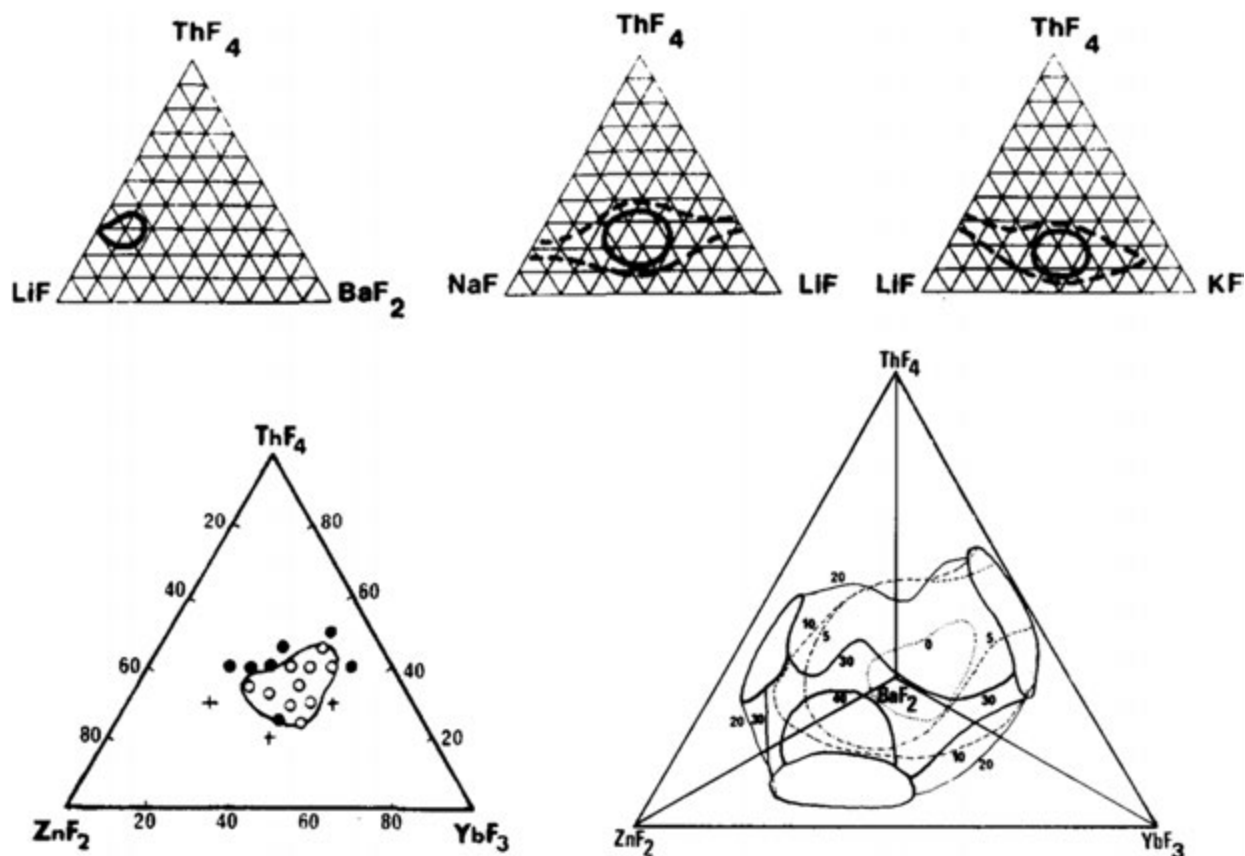


Fig. 11 ThF₄-based fluoride glass systems. Reproduced from Poulain, M.A., Poulain, M.J., 1983. ThF₄ and LiF based glasses. *Journal of Non-Crystalline Solids, Preparation, Properties, and Structure of Special Glasses*, 56 (1), 57–61. [https://doi.org/10.1016/0022-3093\(83\)90446-5](https://doi.org/10.1016/0022-3093(83)90446-5). Fonteneau, G., Slim, H., Lucas, J., 1982. Stabilization of heavy metals fluoride glasses. *Journal of Non-Crystalline Solids* 50, 61–69.

Iodide Glasses

Some Iodide glass compositions are given in [Table 8](#).

Glasses based on ZnI₂

It does not seem that zinc iodide exists in the vitreous form. However binary glasses ZnI₂-KI and ZnI₂-TlI have been reported ([Nasu et al., 1985](#)).

Glasses based on CdI₂

Iodide glasses based on cadmium have been investigated in the CdI₂-KI-CsI and CdI₂-PbI₂-CsI ternary systems ([Byron and Gannon, 1983](#)).

Glasses based on PbI₂

[Cheng and Jin \(1995\)](#) reported a vitreous PbI₂, confirming the early report of [Winter \(1955\)](#). He also studied binary glasses xPbI₂-(1-x)AgI with 0.35 < x < 1 ([Cheng and Jin, 1995](#)). Multicomponent lead iodide glasses were not investigated but a large number of ternary glasses are likely to exist.

Other Iodides

There are common features between heavy halides, and this is largely observed in halide glasses. Then one could expect that iodide glasses could be found in chemical systems based on thorium, tellurium, bismuth and possibly gallium. Research in this field has been limited by experimental factors: hygroscopicity and low characteristic temperatures. More importantly, there were no real prospects for application for such materials.

Polyhalide glasses

Insofar as glasses are formed with all halides, it appeared logical to investigate chemical systems where different halides were combined. The aim of such research was to increase glass stability versus devitrification and to modify some physical properties, especially refractive index. There are two possible ways: either the incorporation of halides in standard glasses or new glass forming

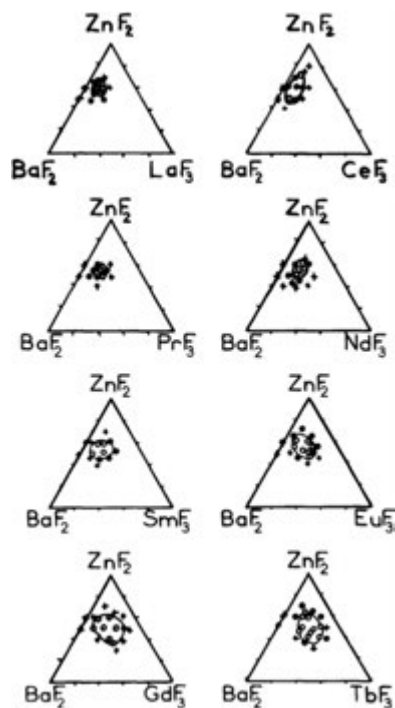


Fig. 12 Zinc fluoride-based glass forming systems $\text{ZnF}_2\text{-BaF}_2\text{-LnF}_3$ ($\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Eu, Gd, Tb}$). Reproduced from Fonteneau, G., Slim, H., Lahaie, F. and Lucas, J., 1980. Nouveaux Verres Fluores Transmetteurs Dans l'infrarouge Dans Les Systemes $\text{LnF}_3\text{-BaF}_2\text{-ZnF}_2$. Materials Research Bulletin 15 (10), 1425–1432.

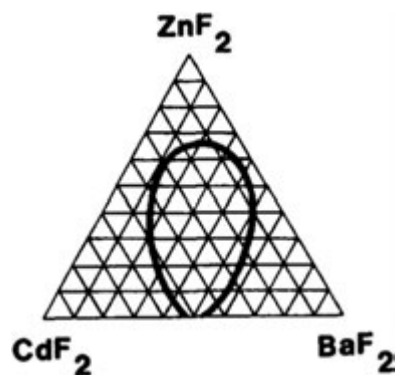


Fig. 13 Glass formation area in the $\text{ZnF}_2\text{-CdF}_2\text{-BaF}_2$ system. Reproduced from Matecki, M., Poulain, M., Poulain, M., 1982. Verres aux halogenures de cadmium, I.- Verres fluores. Materials Research Bulletin 17 (10), 1275–1281. [https://doi.org/10.1016/0025-5408\(82\)90162-3](https://doi.org/10.1016/0025-5408(82)90162-3).

Table 6 Chloride glass compositions (mol%)

Acronym	ZnCl_2	CdCl_2	PbCl_2	BiCl_3	ThCl_4	BaCl_2	NaCl	KCl	CuCl	CsCl
ZKB	60					20		20		
ZKP	60		20					20		
ZKB	60		20			20				
BiK				55				45		
BiKCs				77				11		12
CdBK		50				40		10		
CdBK					40		30	30		
CdPK		45	45					10		
TPK			30		35			30		
TPC			40		30				30	

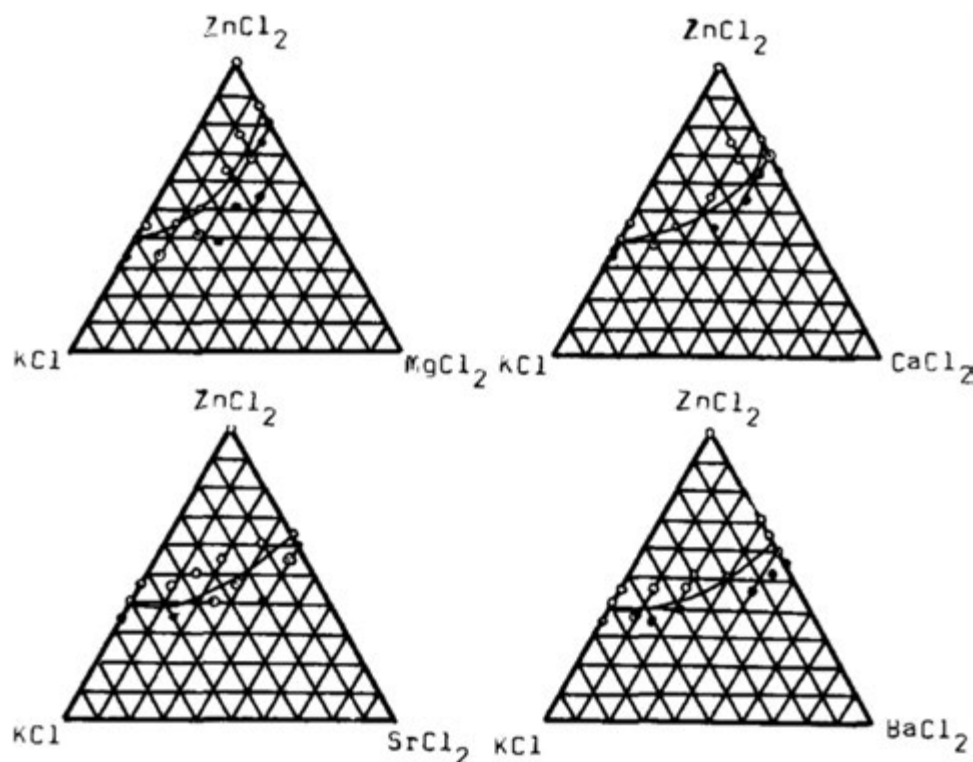


Fig. 14 Chloride glasses based on ZnCl_2 -KCl- MCl_2 systems where $\text{M}=\text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$.

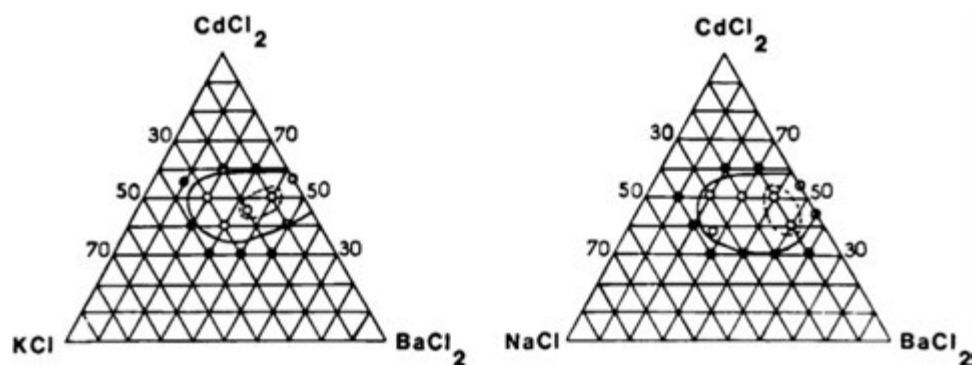


Fig. 15 Cadmium chloride glasses in CdCl_2 - BaCl_2 -MCl systems ($\text{M}=\text{Na}, \text{K}$). Reproduced from Poulain, M.A., Matecki, M., Mouric, J.-L., Poulain, M.J., 1983. Cadmium halide glasses. II. – Chloride glasses. *Materials Research Bulletin* 18 (5), 631–636. [https://doi.org/10.1016/0025-5408\(83\)90222-2](https://doi.org/10.1016/0025-5408(83)90222-2).

systems. The first approach corresponds to the incorporation of halides in fluorozirconate and fluoroaluminate glasses. The second one is exemplified by numerous fluorochloride glasses in chemical systems based on cadmium.

Fluorohalide Glasses

Incorporation of halides in fluorozirconates

Alkali chlorides MCl ($\text{M}=\text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) have been combined with ZrF_4 - BaF_2 binary glasses. The corresponding ternary systems appear in **Fig. 18**. **Fig. 19** shows the existence of ZrF_4 - BaFCl and ZrF_4 - SrFCl binary glasses extending across the ternary system (Elyamani and Poulain, 1987). More complex glasses (Inoue and MacFarlane, 1987; Parker *et al.*, 1987; Tatsumisago *et al.*, 1988; Elyamani *et al.*, 1991) have also been reported. Some fluorochloride glass compositions are given in **Table 9**. The incorporation of bromides is difficult in open crucibles as atmospheric oxygen reacts with glass melt, releasing gaseous bromine. Fluorozirconate glasses containing lead iodide were investigated as materials for the storage of radioactive iodine (Poulain, 1981a,b).

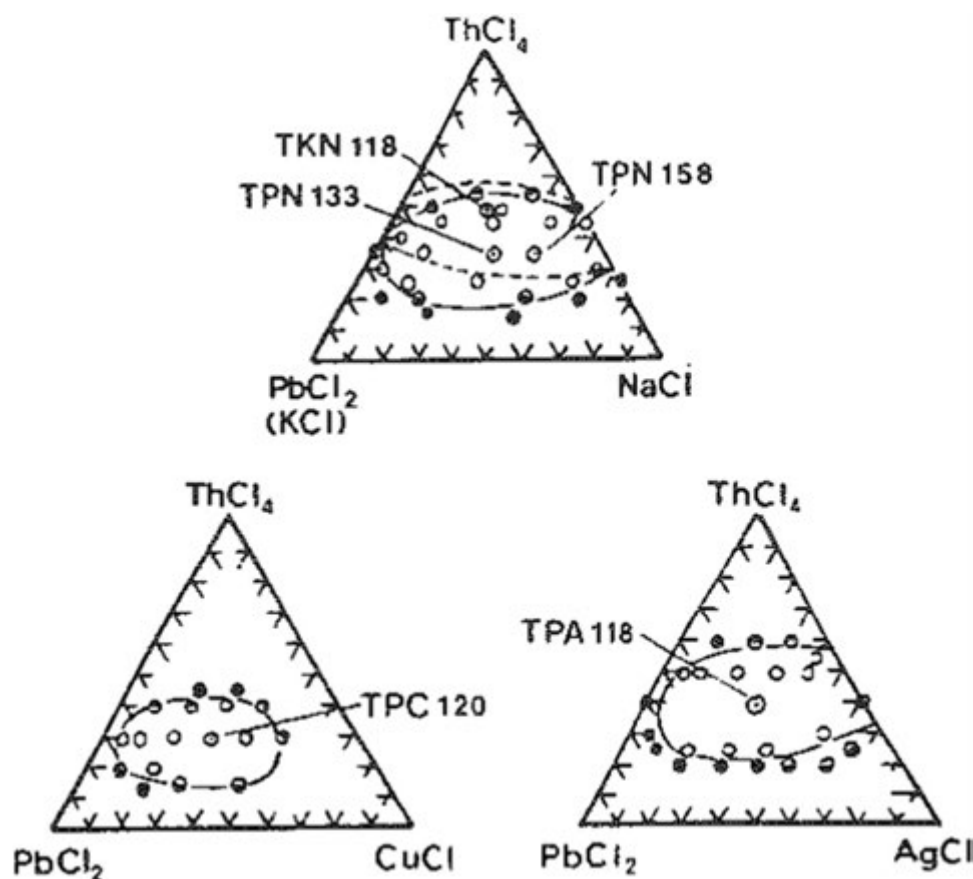


Fig. 16 Thorium chloride based ternary glass systems. Reproduced from Gan, F., Dai, Y., Hu, H., 1985. Preparation, properties and structure of chloride glasses in systems of $\text{ThCl}_4\text{-PbCl}_2\text{-RCl}$ ($\text{R}=\text{Na, Cu or Ag}$). Materials Science Forum 5, 113–120. <https://doi.org/10.4028/www.scientific.net/MSF.5-6.121>.

Table 7 Bromide glass compositions (mol%)

Acronym	ZnBr_2	CdBr_2	PbBr_2	BiBr_3	BaBr_2	KBr	TlBr
ZKB	50				15	35	
ZKP	50		10			40	
ZKCdB	45	5			10	40	
ZKT	60					20	20
BiK				60		40	
CdBK		50			40	10	
CdPK		45	45			10	

Fluorochloride glasses

Cadmium fluorochloride glasses in systems such as $\text{CdCl}_2\text{-BaF}_2\text{-CdF}_2$, $\text{CdCl}_2\text{-BaF}_2\text{-NaF}$ etc... have been largely studied for their extended infrared transmission (Matecki *et al.*, 1983; Mouric *et al.*, 1985; Matecki *et al.*, 1987; Jha and Parker, 1991; Matecki and Poulain, 1992; Aitken *et al.*, 1993). Among numerous ternary systems of particular note are $\text{CdCl}_2\text{-BaF}_2\text{-CdF}_2$, $\text{CdCl}_2\text{-BaF}_2\text{-NaF}$ etc... These are shown in Fig. 20. Some fluorochloride glass compositions based on CdF_2 are given in Table 10. These glasses may be cast as thick samples (> 4 mm) and they are less sensitive to water than chloride glasses.

Manganese fluorochlorides are obtained in some ternary systems containing barium and sodium chlorides: $\text{MnF}_2\text{-BaCl}_2\text{-NaF}$; $\text{MnF}_2\text{-BaCl}_2\text{-NaCl}$; $\text{MnF}_2\text{-BaCl}_2\text{-ZnF}_2$; $\text{MnF}_2\text{-BaCl}_2\text{-MnCl}_2$ (Dai *et al.*, 1991).

Halides in other fluoride glasses

Chlorides may also be combined with fluoroaluminate glasses (Miura *et al.*, 1988, 1991) and also in fluoroindate glasses (Akella *et al.*, 1997).

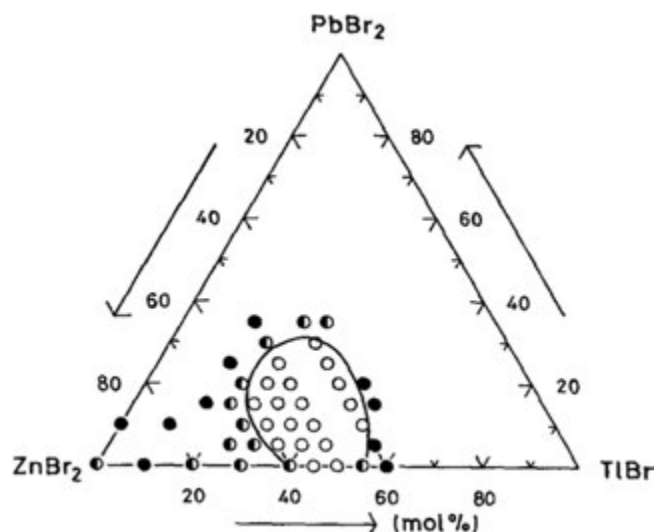


Fig. 17 Bromide glasses in the ZnBr_2 - PbBr_2 - TlBr ternary system. Reproduced from Nogami, M., Sawanobori, N., Makihara, M., Hayakawa, J., 1985. Preparation of glasses in the ZnBr_2 - PbBr_2 - TlBr system. *Journal of Materials Science Letters* 4, 271–272.

Table 8 Iodide glass compositions

Acronym	ZnI_2	CdI_2	PbI_2	KI	TlI	CsI	AgI
ZK	55			45			
ZKP	50		10	40			
ZKCdB	45	5		40			
ZKT	60			20	20		
CdKCs		48		26		26	
CdCsTI		48			26	26	
PA			60				40

Heavy halide glasses

Glasses based on Zn

Incorporation of bromides in zinc chloride has a stabilizing effect versus devitrification. This is exemplified by the following systems: ZnCl_2 - KBr - PbBr_2 , ZnCl_2 - ZnBr_2 - KX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), ZnCl_2 - KI - KBr . Similarly, the glass forming ability of zinc bromide is enhanced by other halides. Various glasses have been reported in binary and ternary systems: ZnBr_2 - TlBr - TlI ; ZnBr_2 - KCl ; ZnBr_2 - KI ; ZnBr_2 - TlCl ; ZnBr_2 - TlI .

Glasses based on Cd

Polyhalide glasses are observed in multicomponent systems based on cadmium. Among others significant systems are the CdX_2 - PbX_2 - KI ternary or the 30CdBr_2 - 43.5PbCl_2 - 26.5TlI glass (Fuding, 1985; Tatsumisago *et al.*, 1988).

Glasses based on Bi

The glass forming ability of bismuth halides increases in mixed halide combinations. Examples include the following systems: BiCl_3 - KBr , BiBr_3 - KI , BiBr_3 - TlBr - PbCl_2 .

Glasses based on Pb

Several studies were implemented on glasses based on lead chloride, bromide and iodide, firstly because of their stability against water: the solubility of lead halide is low, and as the glasses are usually prepared from aqueous solutions, then it may be expected that resulting glasses are not hygroscopic. The second reason lies in the existence of vitreous forms of PbBr_2 and PbI_2 . According to the “confusion principle”, multicomponent glasses should be more stable and withstand slower cooling rates.

The following vitreous systems have been identified: PbBr_2 - AgBr - CuCl - CsBr (Nasu *et al.*, 1985); PbBr_2 - CdBr_2 - TlI (Fuding, 1985), CdX_2 - PbX_2 - KI (Petrová *et al.*, 1989), PbCl_2 - CuCl - RbCl ; PbCl_2 - PbI_2 - CdCl_2 (Angell *et al.*, 1985), PbI_2 - PbBr_2 - KCl / KBr ; PbBr_2 - PbI_2 - CuCl or CuBr - KBr (Zhang *et al.*, 1992) ; PbI_2 - AgI - KCl / KBr (Cheng and Jin, 1995).

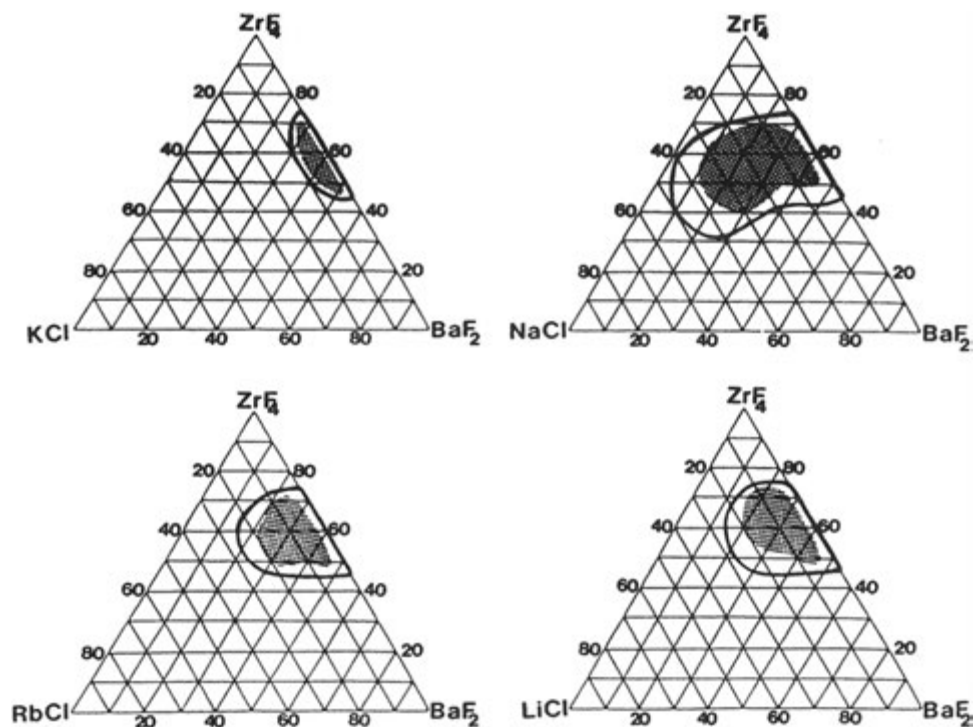


Fig. 18 Combinations of ZrF_4 - BaF_2 binary glasses with alkali chlorides MCl ($\text{M}=\text{Na}, \text{K}, \text{Rb}, \text{Li}$). Reproduced from Poulain, M., Elyamani, A., 1987. Chlorofluorozirconate glasses. *Materials Science Forum* 19–20, 73–86.

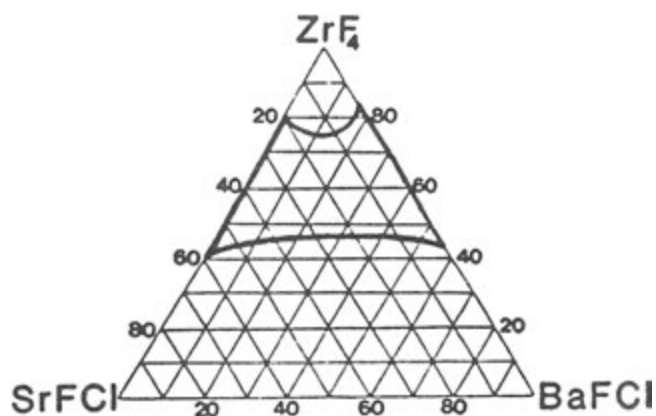


Fig. 19 Vitreous chlorofluorozirconates of strontium and barium. Reproduced from Poulain, M., Elyamani, A., 1988. Barium and strontium chlorofluorozirconate glasses. *Materials Science Forum* 32–33, 143–148.

Table 9 Fluorochloride glass compositions (mol%)

ZrF_4	BaF_2	BaFCl	LaF_3	AlF_3	NaF	ThF_4	LiCl	NaCl	KCl	RbCl
75		25								
60	30						10			
60	30							10		
60	30								10	
60	30									10
51.5	20.5		5.3	3.2	14.5			5		
50	30		3			5		12		

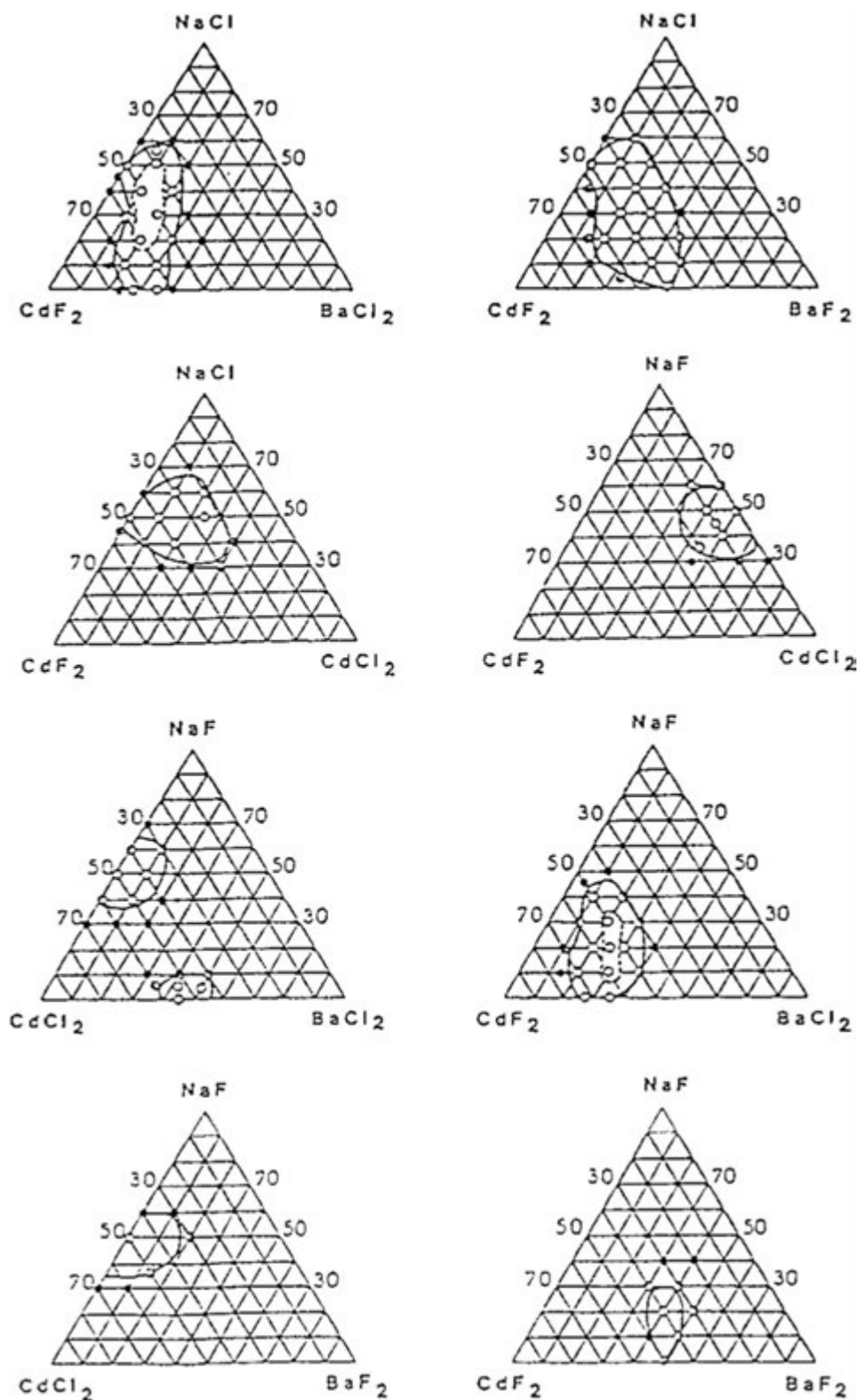


Fig. 20 Cadmium mixed halide glasses with barium and alkali cations. Reproduced from Mouric, J.L., Matecki, M., Poulain, M., Poulain, M., 1985. Progress in cadmium halide glasses. *Materials Science Forum* 5, 135–144. <https://doi.org/10.4028/www.scientific.net/MSF.5-6.135>.

Table 10 Glass compositions based on CdF₂ (mol%)

Glass	CdF ₂	CdCl ₂	BaF ₂	BaCl ₂	PbCl ₂	NaCl	KCl	NaF	KF
CBX1	40	30	30						
CBX2	65	2		33					
CBN1	42	11	11			36			
CBN2	53			11		36			
CBNX2	49	4		11		36			
CBNX3	33	17	34					13	3
CKX	15	45					40		40
CPN	40				10	50			

Miscellaneous

Angell *et al.* (1985) reported glasses based on silver halides and investigated their ionic conductivity. Typical glass compositions belong to the binary AgX-CsX (X=Cl,Br,I) (Lichkova *et al.*, 1988), for example 69AgX-31CsX (X = 0.45I + 0.55Br). Note that Nishii *et al.* (1985) obtained 10 mm thick samples for the 59AgX-39CsX-2PbX₂ (X = 0.38I + 0.62Br) (Angell *et al.*, 1985).59AgX-39CsX-2PbX₂.

Physical Properties

Composition-Property Relationships

There are strong correlations between chemical composition and physical properties. Halides – fluorine, chlorine, bromine, iodine – exhibit a high electronegativity, fluorine being the most electronegative element of the periodic table. The ionic character of the chemical bonding decreases from fluorides to iodides while the ionic radius increases from 135 nm for F[−] to 220 nm for I[−], resulting in lower bond strength. This directly influences thermal properties, namely glass transition and melting temperatures, and thermal expansion. In the same way, microhardness and fracture toughness decrease from fluorides to heavier halides.

Refractive index is ruled by the polarisability of the elements and the chemical bonds. In a general way the lowest refractive indices are expected in fluorides, while the larger ones should be observed in heavy halides, bromides and iodides. Non linear optical properties are usually correlated to refractive index and will follow the same trend.

Transparency appears as the most evident optical property. It is limited in the UV range by electronic transitions and in the infrared by lattice vibrations. Consequently fluorides will be more transparent in the UV spectrum, while iodides are expected to shift their IR absorption edge towards long wavelengths.

Optical Properties

UV Transmission

Fluoride glasses are transparent ranging from the UV spectrum to the mid-infrared. However the position of the absorption edges depends on the chemical composition which relates to the electronic band gap. The optimum situation is the association of fluorine anions and light cations. Glasses based on beryllium fluoride have the most extended UV transmission, to below 160 nm. Vitreous BeF₂ should be transparent at still smaller wavelengths on condition that it is extremely pure: traces of transition metals, hydroxyls and anionic oxygen have a drastic influence on UV absorption.

AlF₃-based glasses are good candidates for UV transmission. Unfortunately few data are available in this field. A first limitation relates to the difficulty in synthesizing ultra pure glasses with low content of transition metals. By comparison, the vapor phase processes used for silica make it easier. A second limitation arises from the heavy cations entering the glass composition: Ba, Sr, La, Y and even Ca and Na will reduce light transmission at short wavelengths. This limitation is difficult to overcome as stable fluoroaluminate glasses are obtained only in multicomponent systems. While BeF₂ incorporation would be beneficial in this respect, ZrF₄ is preferred in practice.

The UV edge of fluoro-zirconate glasses is shifted to longer wavelengths by comparison to fluoroberyllates and fluoroaluminates. However the development of optical fibers has led to very pure materials. Current ZBLAN windows are transparent beyond 210 nm. Further studies are needed to assess if it is the intrinsic limit.

Infrared transmission

The frequency corresponding to the maximum absorption in the infrared spectrum depends on bond strength and reduced mass of the M-F pair. It may be expressed by the following relation:

$$\nu = (1/2\pi)(k/\mu)^{1/2} \quad (1)$$

where k is strength constant, and μ is the reduced mass. Bond strength decreases as the ionic radius of the anion increases. Under these conditions, the position of the fundamental absorption peak is shifted to lower frequency when moving from fluorine to chlorine, bromine and iodine.

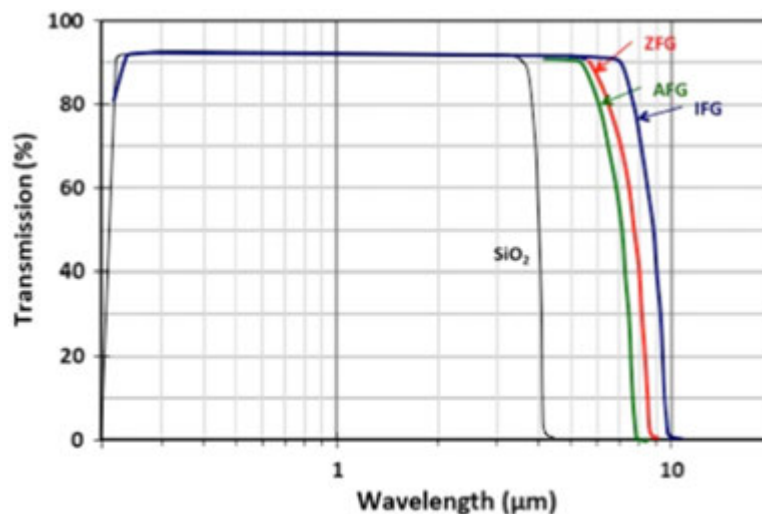


Fig. 21 Optical transmission range of standard fluoride glasses: fluoroaluminates (AFG), fluorozirconates (ZFG) and fluoroindates (IFG), compared with SiO_2 . Sample thickness: 3 mm. Reproduced from Poulain, M., 1984. *Les Verres Halogénés*. L'Actualité Chimique. 37–44.

In practice the position of the IR absorption edge is ruled by a multiphonon process and the corresponding frequency is several times larger than for the fundamental peak. It also depends on sample thickness. ZBLAN glass provides a significant example: IR edge is $6.5 \mu\text{m}$ for a 2 mm thick window (50% transmission) and $4.2 \mu\text{m}$ for an optical fiber (1 dB/m). By comparison fundamental absorption is observed around $18 \mu\text{m}$.

Simple rules may be used to assess the relative transmission of glasses. IR cut-off increases with ionic radius of both cation and anion. Also it is larger when cation charge is small. As a result it increases according to the following sequences:

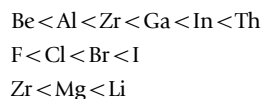


Fig. 21 compares the spectral transmission of 3 mm thick samples of fluoride glasses: the IR edge for fluorozirconate glasses is shifted to smaller wavelength for fluoroaluminates and to larger wavelength for fluoroindates. The same behavior is observed for fluoride glass fibers. Heavy halide glasses –chlorides, bromides, iodides– transmit further in the IR spectrum. While this feature appears attractive, they are not used in practice because of physical limitations: hygroscopicity, low softening temperature, poor mechanical properties.

The potential for ultralow optical losses

Optical transmission of materials is limited by electronic transitions (Urbach tail) for short wavelength, and multiphonon absorption at long wavelength, in the IR spectrum. A third loss mechanism: Rayleigh scattering, takes place between these two edges. The global loss curve for a ZBLAN optical fiber exhibits a typical V shape that is illustrated in **Fig. 22**. The maximum transparency is observed at the bottom of this V curve. In the case of silica, theoretical losses are below 0.2 dB/km. This minimum depends on the material. It may be lower if the IR absorption edge is shifted toward long wavelength (Cozmuta *et al.*, 2020). This is the case for halide glasses, especially zinc chloride, as reported by Van Uiter (1979). Heavy Metal Fluoride Glasses (HMFG) also appear to be potential materials for ultralow optical losses. The theoretical minimum attenuation value of ZBLAN ranges between 10^{-2} and 10^{-3} dB/km at $\sim 3 \mu\text{m}$. Fluoroindates and cadmium fluorochloride glasses should exhibit still lower attenuation in the 3–4 μm range.

However the attenuation of the real optical glass fibers is larger than expected by theory. **Fig. 23** shows optical transmission (optical losses expressed in dB/km.) of commercial fluoride glass fibers based on AlF_3 , ZrF_4 and InF_3 . Attenuation is close to 1 dB/km for ZBLAN fibers. Limitations arise from the absorption induced by traces of impurities (Cr, Fe, Co, Ni, Cu) and by extrinsic scattering occurring from nucleation and interface defects. It has been emphasized that drawing fibers in microgravity could inhibit nucleation and improve ZBLAN fiber performance.

Refractive indices

The polarisability of the fluorine anion is very low, and consequently the refractive index of fluoride glasses is smaller than that of oxide glasses. Vitreous BeF_2 has the smallest refractive index of all glasses: 1.29. In multicomponent fluoride glasses that contain heavy cations (Sr, Ba, Y, La...) it is larger, and ranges from 1.4 in light fluoroaluminates to 1.5 in fluorozirconates and fluoroindates. Even when heavier cations, e.g., Pb or Bi, are incorporated, refractive index does not exceed 1.6. Gan (1995) gives a very good review of fluoride glass optical properties.

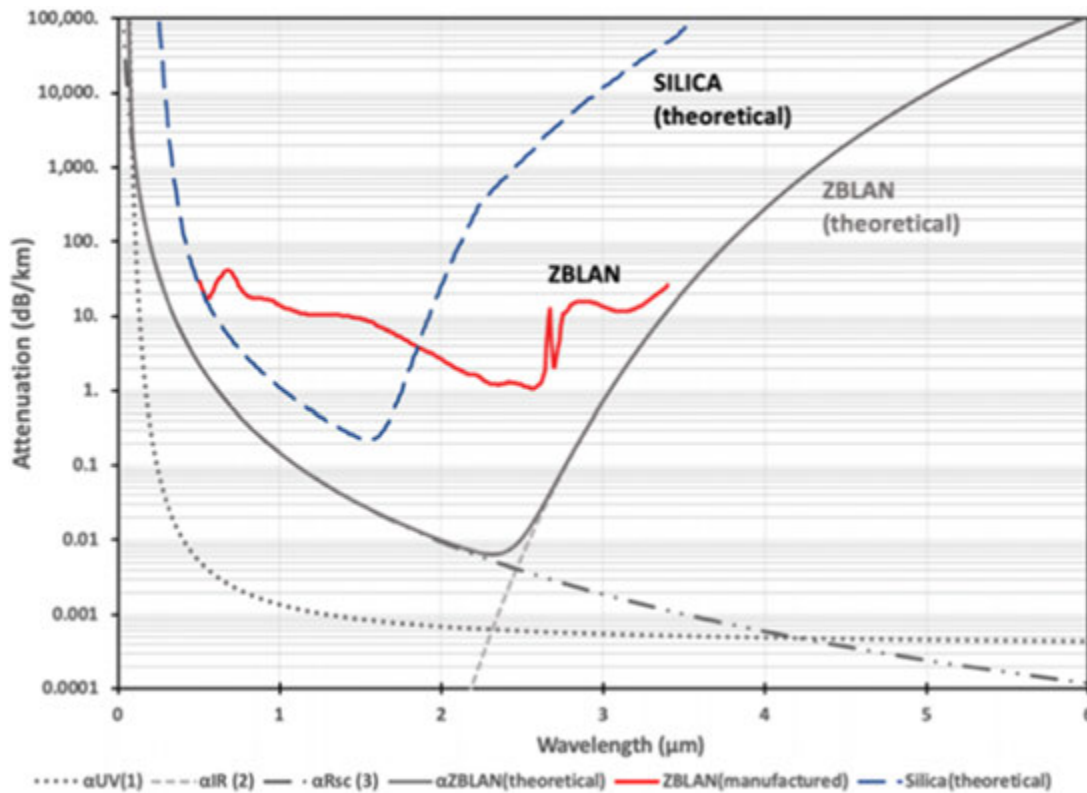


Fig. 22 Theoretical loss spectra (attenuation, dB/km) for a typical ZBLAN optical fiber (solid gray line) as function of wavelength (μm). The major components to the attenuation, UV (dotted line), IR (dashed gray line) and Rayleigh scattering (dash-dotted gray line) are shown. For reference, the theoretical loss spectra for silica optical fiber (dashed blue line) and that of industry best manufactured ZBLAN (solid red line) are also included. Reproduced from Cozmuta, I., Cozic, S., Poulain, M., Poulain, S., Martini, J.R.L., 2020. Breaking the silica ceiling, ZBLAN-based opportunities for photonics applications. In: Optical Components and Materials XVII, 11276:112760R. Waikoloa: International Society for Optics and Photonics. <https://doi.org/10.1117/12.2542350>.

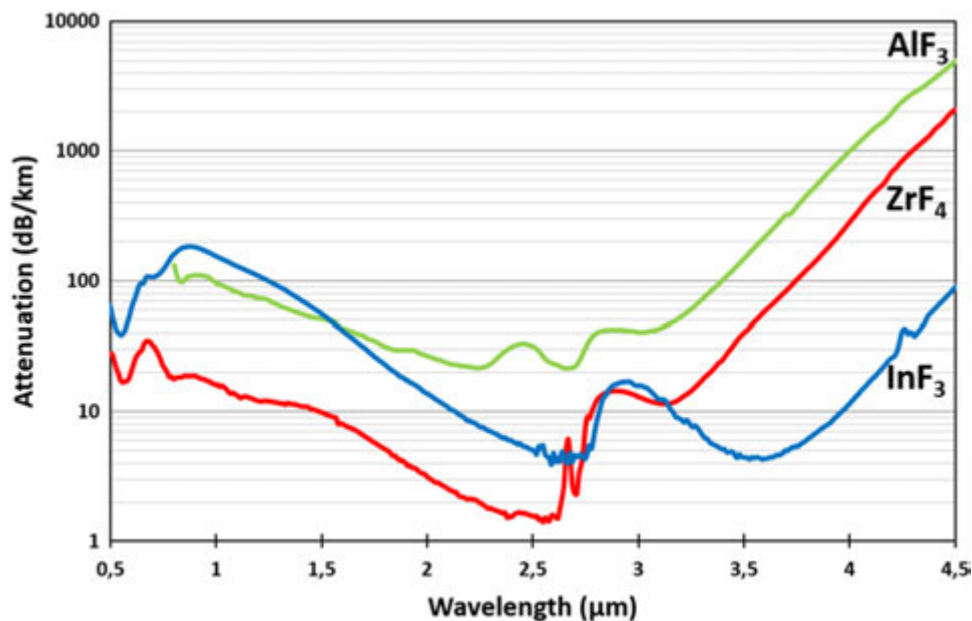


Fig. 23 Optical transmission of commercial fluoride glass fibers. Optical losses expressed in dB/km. Glasses based on AlF_3 , ZrF_4 and InF_3 . Reproduced from Le Verre Fluore, 2020. Fluoride glass components. Available at: www.Leverrefluore.Com.

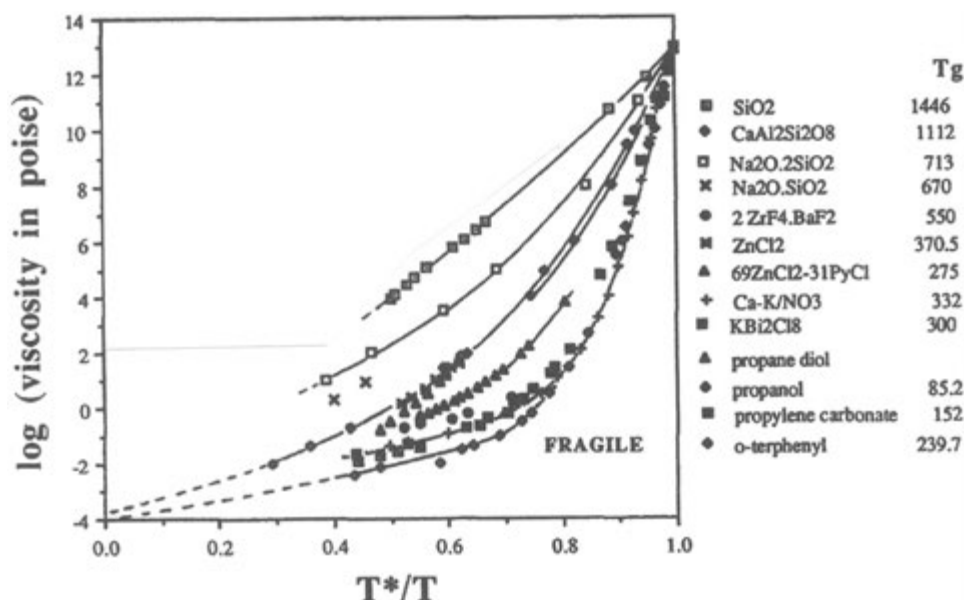


Fig. 24 Viscosity/Temperature diagram exemplifying the Strong $\rightarrow$ Fragile behavior in glass forming liquids. T^* is the temperature at which viscosity reaches 10^{12} Pa s. Reproduced from Angell, C.A., 1991. Relaxation in liquids, polymers and plastic crystals – Strong/fragile patterns and problems. *Journal of Non-Crystalline Solids* 131–133 (June), 13–31. [https://doi.org/10.1016/0022-3093\(91\)90266-9](https://doi.org/10.1016/0022-3093(91)90266-9). (Proceedings of the International Discussion Meeting on Relaxations in Complex Systems).

It is possible to calculate the value of the refractive index from its molar composition. The method was introduced by Sun (1947) and revised by Baldwin *et al.* (1981). It is currently used for adjusting the composition of core and cladding glasses for ZBLAN and fluorindate glass fibers.

As expected, refractive index increases in heavier halide glasses. Average n value is 1.5 for fluoride glasses while it reaches 1.6 for cadmium fluorochlorides. Few data are available for even heavier halide glasses. Measurements are made difficult by their hygroscopic character.

Thermal Properties

Characteristic temperatures

Glass scientists and engineers use several characteristic temperatures.

- Glass transition temperature T_g that corresponds to the solid/liquid transition.
- Softening temperature for which glass is deformed under its own weight.
- Temperature of crystallization onset, T_x .
- Crystallization temperature T_c , for which crystallization rate is a maximum.
- Melting temperature T_m which corresponds to the beginning of the melting process (first exothermic peak).
- Liquidus temperature T_l for which molten glass does not contain any crystal.

Thermal analysis (DTA and DSC) is an effective way to measure T_g , T_x , T_c and T_m . Because it concerns kinetic processes, their values depend on heating rate (or cooling rate) during the analysis. The usual value is 10 K/min.

Characteristic temperatures depend on glass composition. They are higher for fluorides and lower for chloride, bromide and iodide glasses. T_g ranges from 250 to 300°C for most fluoride glasses while is close to 50°C for BiCl₃ and BiBr₃ based glasses. Alkali ions (Li^+ , Na^+ , K^+) decrease T_g while fluoride glasses free of sodium and barium exhibit much larger T_g .

Crystallization temperatures T_x and T_c are observed somewhere between T_g and T_m . The difference $T_x - T_g$ reflects glass stability versus devitrification. Melting temperature of glasses is measured on reheating. As crystallization occurs first, thermal analysis records the melting temperature of the different crystalline phases resulting from the devitrification process. In multicomponent glasses several exothermic peaks are observed, and melting temperature cannot be determined unambiguously.

A reverse situation arises for liquidus temperature: T_l is unique, but it may be difficult to measure by thermal analysis. The empirical “two third” rule applies to most halide glasses. It is expressed by the following relation:

$$T_g/T_l = 2/3 \quad (2)$$

where temperatures are in Kelvin. This relation was first described by Kauzmann (1948) and has been observed in glass forming systems many times (Winter, 1955; Sakka and Mackenzie, 1971; Bruce, 1987).

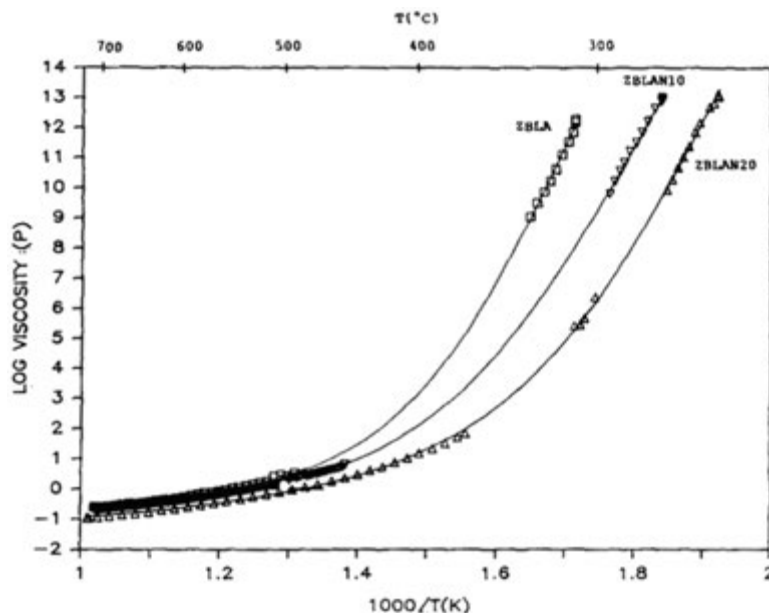


Fig. 25 Viscosity as a function of temperature for fluorozirconate glasses with different sodium concentrations (0, 10 and 20 mol%). Reproduced from Hasz, W.C., Crichton, S.N., Moynihan, C.T., 1988. Viscosity temperature dependence of ZrF_4 -based melts. *Materials Science Forum* 32–33, 589–594.

Thermal expansion coefficient

The coefficient of thermal expansion CTE of halide glasses is larger than that of oxides. This higher coefficient is consistent with the differences in chemical bonding and formal ionic charges. For typical heavy metal fluoride glasses it ranges from 140 to $220 \times 10^{-7} \text{ K}^{-1}$. These values are larger than those for soda lime silica and other oxide glasses ($\sim 90 \times 10^{-7} \text{ K}^{-1}$). The CTE of BeF_2 that is isostructural with SiO_2 is $68 \times 10^{-7} \text{ K}^{-1}$. In chloride and bromide glasses CTE is larger and ranges from 250 to $400 \times 10^{-7} \text{ K}^{-1}$.

Note that there is an empirical relationship between thermal expansion and glass transition which was expressed by Van Uiter (1979):

$$\alpha \cdot T_g^2 = C_t \quad (3)$$

where T_g is expressed in Kelvin. According to Bruce (1987), the constant $C_t = 5.8$ for a set of fluoride glasses. Accordingly, elements that decrease T_g also increase CTE which is the case for alkali cations, barium and lead.

Heat capacity C_p

Heat capacity measurements have been reported only for fluorozirconate glasses. While the isostatic heat capacity C_p is expressed in $\text{J g}^{-1} \text{ K}^{-1}$, it is more convenient to consider the data on a per mole of atoms basis, that is: $C_p = C_p \cdot M$, where M is the average atomic weight of the glass. By so doing, it can be seen that the C_p values for ZBLA glass approach the Dulong-Petit limit of $3R$ ($24.9 \text{ J mol}^{-1} \text{ K}^{-1}$ for the vibrational heat capacity of solids). Similar results are observed for other fluorozirconate and fluorohafnate glasses (Bruce, 1987). The difference between heat capacity of solid glass below T_g and molten glass above T_g is also approximately constant ($14 \text{ J mol}^{-1} \text{ K}^{-1}$) (Bruce, 1987).

Viscosity

Several authors have investigated the viscosity of fluoride glasses. The behavior of vitreous BeF_2 can be compared to that of vitreous silica: on a logarithmic scale, the plot of viscosity vs reciprocal temperature T^{-1} is linear. In fact both BeF_2 and silica are exceptions. For most glasses the viscosity/temperature change deviates from the Arrhenius behavior. While industrial glasses follow the Talmann-Vogel-Fulcher law, the viscosity of fluoride glasses is still more non linear. They belong to the group of “fragile glasses” as introduced by Angel (1991) and exemplified by Fig. 24. A typical viscosity/temperature curve for fluorozirconate glasses with different sodium concentrations is reproduced in Fig. 25. Viscosity is very low around the liquidus temperature, less than 1 poise, and decreases sharply above glass transition. Devitrification makes viscosity measurements difficult for $\eta < 10^4$ poise.

Electrical Properties

In halide glasses electrons are engaged in chemical bonds, either ionic or partly covalent. Their mobility is very low and consequently they appear as insulating materials. However some ionic species may induce a significant ionic conductivity. This has been

extensively studied in fluoride glasses (Ravaine, 1985; Kavun *et al.*, 2018). Conduction is ensured by fluorine anions (Leroy *et al.*, 1978). It is different from the mechanism observed in oxide glasses in which alkali cations are mobile. No conduction has been observed with Na^+ ions (Reau *et al.*, 1990), while both F^- and Li^+ ions take part in electrical conduction in the $\text{ZrF}_4\text{-BaF}_2\text{-ThF}_4\text{-LiF}$ glasses (Reau *et al.*, 1985) and $\text{ZrF}_4\text{-BaF}_2\text{-LiF}$ glasses (Kawamoto *et al.*, 1990). The largest ionic conductivity has been reported in a fluoroindate glass.

In heavier halide glasses, the conduction process should be different: the mobility of chloride and bromide anions is very small, while alkali cations – Li^+ , Na^+ – could ensure some ionic conductivity. Studies require dry glove boxes because of hygroscopicity.

Devitrification

Glass formation

Several authors have tried to relate glass forming ability and chemical composition, on the basis of a disordered network or disordered packing. As glasses have been reported in covalent, ionic and metallic materials, it clearly does not depend on the nature of the chemical bonding.

Glass formation remains largely empirical. The so-called “confusion principle” has often been used as a guideline to find glass compositions more stable against devitrification. This principle states that glass stability increases with the number of glass components: a quaternary glass should be more stable than a ternary glass which is also more stable than a binary glass. A good example is observed in fluoride glasses: devitrification tendency decreases according to the sequence:

$$\text{ZB} < \text{ZBL} < \text{ZBLA} < \text{ZBLAN}$$

$\text{Z} = \text{ZrF}_4$; $\text{B} = \text{BaF}_2$; $\text{L} = \text{LaF}_3$; $\text{A} = \text{AlF}_3$; $\text{N} = \text{NaF}$

In oxide glasses, soda lime silica glass is much more stable than pure silica.

Kinetic studies

Numerous papers relate to the devitrification of HMFG, especially fluorozirconates (Poulain, 1992). Most of them use thermal analysis at temperatures higher than T_g to quantify the relative amount of crystalline phase. They are based on the Johnson-Mehl-Avrami-Kolmogorov (JMAK) relation (Avrami, 1938; Kolmogorov, 1939; Johnson and Mehl, 1939):

$$x = 1 - \exp(-kt)^n \quad (4)$$

Where x is the crystalline fraction, t is time, k is a constant that depends on nucleation and crystal growth and n is the Avrami exponent. This exponent can take different values depending on nucleation and growth mechanisms. This relation applies to an isothermal process. It is assumed that the constant k changes with temperature according to:

$$k = k_0 \exp(-E/RT) \quad (5)$$

Three kinetic parameters derive from the JMAK relation: n , E and k_0 . The physical meaning of activation energy E and frequency constant k_0 is not clear.

In a general way, the chemical composition of the crystalline phases resulting from devitrification is different from that of the parent glass. Apart from fluoride glasses, devitrification has also been studied in cadmium fluorochloride glasses.

Chemical Durability

Solubility in water

Chemical durability appears a major concern for halide glass development. Numerous studies have been implemented on fluorozirconate glasses (Simmons and Simmons, 1991). The critical reagent is water. Most papers are concerned with the behavior in aqueous solutions. When a piece of glass is immersed in water, it undergoes a slow chemical attack. As a result the surface is damaged and the pH of the solution drops (it becomes acidic). The rate of attack depends on pH and it increases rapidly as pH decreases: it is a catastrophic process! However the rate of attack is very low at pH 8. Bulk glass is stable in buffered solution at this pH (Simmons, 1987). In practice, it is essential to avoid liquid water staying on the glass surface. Simmons and Simmons (1991) have given an excellent review of the behavior of fluoride glasses in aqueous solutions in which it is noted that the rate of attack is slow. This allows the use of water for polishing fluoride bulk glasses and preforms.

Fluoroaluminate glasses are less corroded by water than ZBLAN glass (Poulain *et al.*, 1981a; Izumitani *et al.*, 1987). Fluoroindates are comparable with fluorozirconates. The sensitivity to water is larger in heavy halide glasses. Glasses based on ZnCl_2 , ZnBr_2 , BiCl_3 and BiBr_3 are soluble in water. In a general way, there is some correlation between the behavior of crystalline compounds and that of the glass they produce. Thus it is advantageous to incorporate significant amounts of insoluble halides. In this respect glasses based on lead and silver halides exhibit larger resistance to attack by water.

Atmospheric stability

Stability in ambient atmosphere is also controlled by water. Relative humidity is currently close to 50%. Deliquescent glasses such as vitreous ZnCl_2 attract water molecules resulting eventually in a liquid phase. Other sodium-rich glasses adsorb water molecules in wet atmosphere and form a hydrated layer.

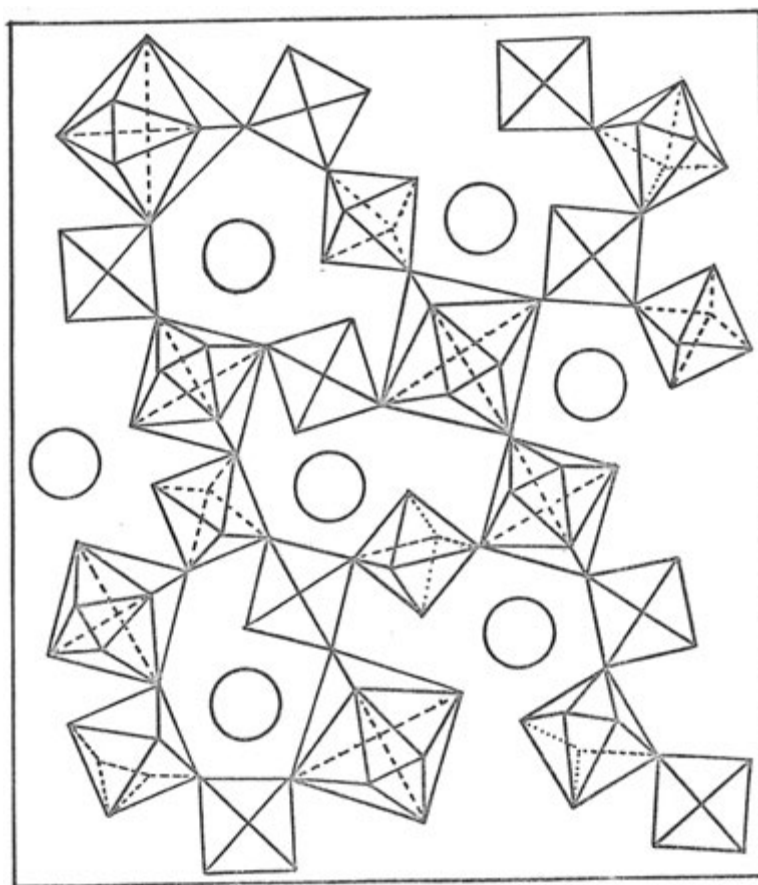


Fig. 26 First structural model of fluorozirconate glass. Circles are for Barium ions. Polyhedra represent AlF_6 , ZrF_6 , ZrF_7 , ZrF_8 and LnF_8 groups. After Chanthanasinh, M., 1976. Synthèse de nouveaux verres fluorés à base de tétrafluorure de zirconium. Caractérisation et études spectroscopiques. Thèse de 3ème Cycle, Rennes, Rennes 1.

Fluoroaluminate and fluorozirconate glasses are stable in a normal atmosphere at room temperature for years, under the condition that water condensation is prevented. When temperature increases, a slow interaction occurs between the glass surface and water molecules which produces gaseous HF while OH^- ions are formed and diffuse through the glass surface. Water molecules are also activated under laser beam at $2.94\ \mu\text{m}$. The process has been studied for laser power transmission by ZBLAN glass fibers. Depending on laser power and pulse duration, fiber surface may be damaged.

Strong fluorinating reagents (F_2 , ClF_3) do not alter fluoride glass surfaces. Gaseous oxygen does not react with fluoride glasses, even above T_g . Reactive atmospheres have been used for glass processing. The purpose was to oxidize the reduced species in the glass melt. Reagents include CCl_4 (Robinson, 1985), SF_6 , NF_3 (Nakai *et al.*, 1986). In practice, dry air makes it simpler.

Structure

In contrast to crystalline phases, vitreous structure have long range disorder and there is no periodicity in the atomic arrangement. However, short range order is similar in crystals and in glass. Thus, in the first coordination shell, both interatomic distances and coordination numbers (CNs) are more or less the same in glass and in crystals. Differences are likely to occur in the second coordination shell, especially in multicomponent glasses. Structural information may be provided by various techniques such as XRD, neutron diffraction, XSAFS, XANES, and computer simulations.

Local Order

There is little doubt about local order in halide glasses, at least as far as glass formers are concerned. BeF_2 -based glasses are considered to be isostructural with silica glasses, with BeF_4 tetrahedra as the structural unit. In heavy metal fluoride glasses, the main coordination polyhedra are octahedra (AlF_6 , GaF_6 , InF_6 , ZnF_6 , LiF_6) or square antiprism and dodecahedra ZrF_8 , HfF_8 , ThF_8 .

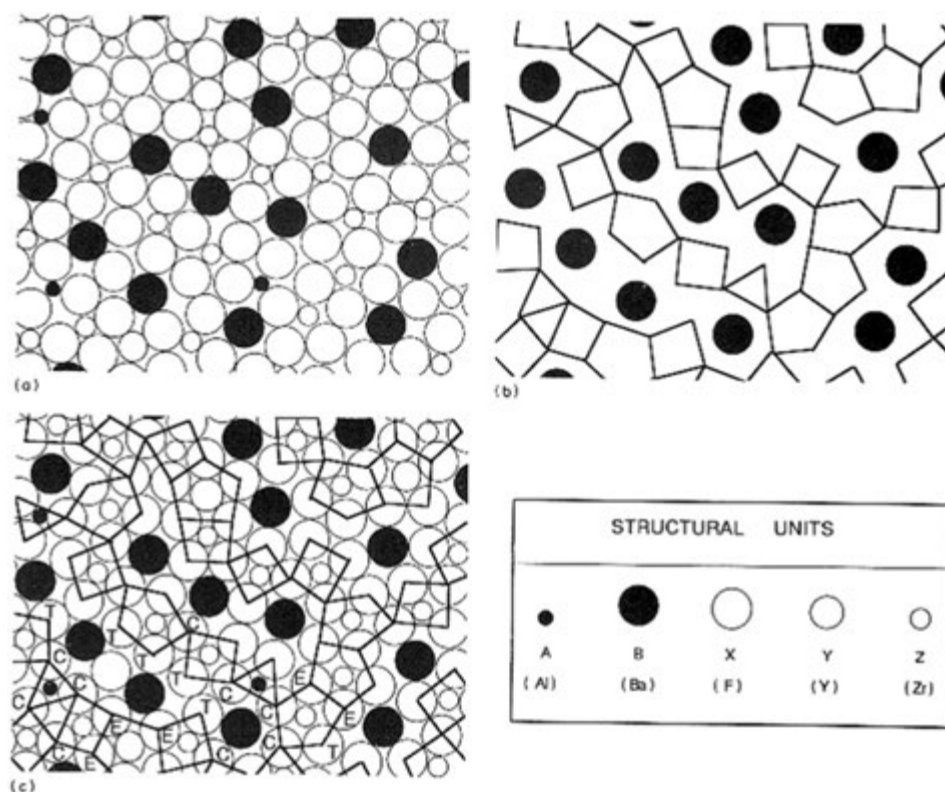


Fig. 27 Bidimensional schematic of a fluorozirconate glass according to the random packing and the network models. After Poulain, M., 1989. Glass systems and structures. In: Comyns, A.E. (Ed.), *Fluoride Glasses*. Chichester, NY: John Wiley and Sons, pp. 11–48. (Critical Reports on Applied Chemistry 27).

In fact, solid state chemistry reports that coordination is largely ruled by the r/R ratio, in which r is the ionic radius of the cation and R the ionic radius of the anion. Large cations such as alkali and alkaline earth elements present in glass compositions are often reported as modifiers. Taking this r/R ratio into account, it should be expected that in fluorides the cations are surrounded by a rather large number of anions: from 8 to 10. This has been confirmed by structural studies (Coupé *et al.*, 1983; Simmons *et al.*, 1991).

In chloride glasses coordination number is 4 for Zn in ZnCl_2 and 6 for cadmium in fluorochloride glasses. In crystalline BiCl_3 , bismuth forms a pyramidal group with three near neighboring chlorine atoms at 0.25 nm and interactions with other chlorine at 0.32 nm. It may also be described as a pseudo tetrahedron $\text{BiCl}_3(\text{lp})$ in which lp represents the lone pair of $6s^2$ electrons attached to the trivalent bismuth. One may assume that the local environment is similar in bismuth halide glasses.

The Network Model

Glass structure is classically described on the basis of the Random network model. This concept was introduced by Zachariasen (1932), who deduced that vitrifying oxides should form small coordination polyhedra, triangles and tetrahedra. This model could also be applied to fluoroberyllate glasses. Heavy metal fluoride glasses are an exception to this approach, insofar as the CNs of Zr, Hf and Th are rather close to 8.

However it is possible to construct a network on the basis of square antiprisms and bipyramids sharing corners and edges. In this model larger cations such as Na^+ , Ba^{2+} are inserted in the voids of this network. A first example was given by Chanthanasinh (1976) shown in Fig. 26. It is consistent with further models of Kawamoto (1985) and Lucas (1989). In the structure of vitreous ZnCl_2 , Zn is tetrahedrally coordinated by chlorine atoms. At first glance it may appear similar to the structure of silica glass. However, it appears to be a random close packing of chlorine anions with zinc cations in tetrahedral holes (Desa *et al.*, 1982).

Disordered Packing and Lacunar Model

An alternative description of glass structure is a random packing of the most voluminous ions in which cations are inserted in sites existing in this structure. As large cations can take part in this packing, the only acceptable insertion sites are surrounded by anions (Poulain, 1981a,b). Fig. 27 shows a bidimensional schematic of the structure of a ZBLA glass, with the alternative network model (Poulain, 1989).

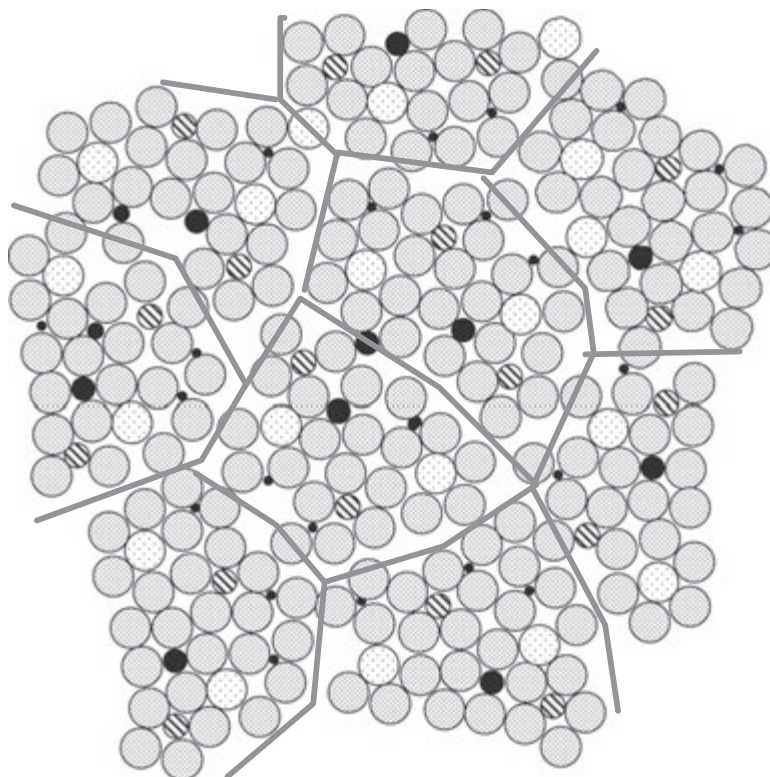


Fig. 28 2D representation of the structure of ZBLAN glass according to the lacunar model of the vitreous state. After Poulain, M., 1996. Vacancy model of glass. In: Proceedings of the 10th ISNOG symposium, B:10–15. Corning, NY.

The random packing description must be completed assuming that vacancies exist in this packing, creating packing faults (Poulain, 1996). These vacancies are simply missing ions and their distribution is bidimensional. As shown in Fig. 28, this leads to a cluster model. This model applies to halide glasses and also to metallic glasses. These two models – random network and lacunar – are complementary: the first one outlines the chemical bonding, while the second one puts the emphasis on volume and vacancy mobility; it also gives a physical meaning to glass transition.

Applications and Prospects

Optical transmission is the primary field for potential applications. Indeed it was investigated many years ago for fluoroberyllate glasses. The development of optical fibers has opened up further possibilities, and the reduced phonon energy of halide glasses offers prospects for new lasers. Nevertheless applications face practical problems as halide glasses are less robust than oxides and many are sensitive to water. As hygroscopicity is much higher with chlorides, bromides and iodides, most developments have focused on fluorides.

UV Optical Components

As pointed out above, fluoroberyllate glasses should be ideal for UV transmitting lenses and windows. Unfortunately the toxicity of Be and the purity requirements caused major problems that could not be overcome in view of the limited market size of such components. However, AlF_3 -based glasses are other candidates that have not been seriously investigated. They compete with ultrapure silica and fluoride single crystals (LiF). However, fluoride glasses are less sensitive than pure silica glass to photo-darkening (Jiang *et al.*, 2015).

Broadband Transmission Optical Fibers

Fluoride glass fibers are transparent over a very wide spectral range, from UV to mid infrared. At short wavelengths, extrinsic absorption may arise from transition metal impurities, especially Cr, Fe, Ni and Cu. Ideally, their concentrations in fluoride glasses should be in the ppb range (Ohishi *et al.*, 1983; France, 1990). Typical attenuation curves for the Visible and the IR spectrum are displayed in Fig. 23. Such fibers are used for remote spectroscopy and IR instrumentation.

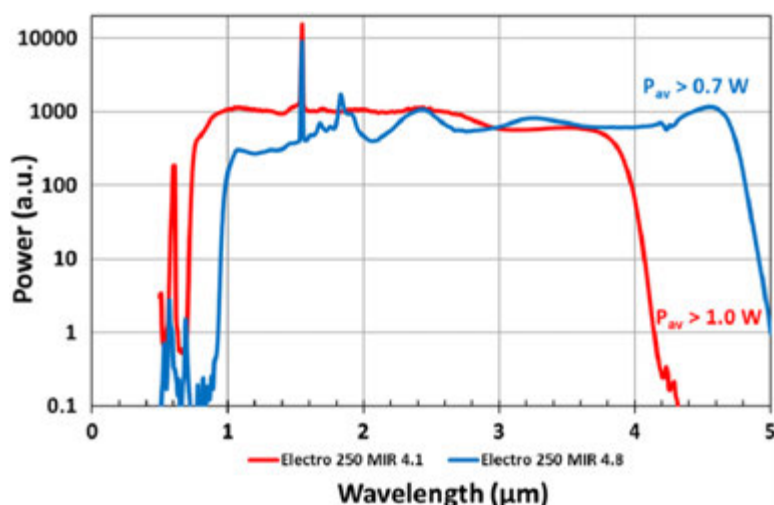


Fig. 29 Supercontinuum emission obtained by pumping at 1550 nm in a ZBLAN glass fiber (red) and in a fluoroindate glass fiber (blue). Reproduced from Le Verre Fluore, 2020. Fluoride glass components. Available at: www.Leverrefluore.Com.

An important use of fluoride glass fibers concerns astronomy: several telescopes may be coupled in the K band (around 2.6 μm) through fiber links. Various astronomy projects have been successfully conducted using single mode ZBLAN fibers: FLUOR (Perrin *et al.*, 1995), OHANA (SPIE, 2002), GRAVITY (Blind *et al.*, 2015), SPIROU (Micheau *et al.*, 2012), SPIP.

Laser power transmission is also a promising field for fluoride glasses, especially at wavelengths larger than 2000 nm: fluoride fibers are more transparent than silica beyond 2100 nm. Coupling laser to fibers allows much more flexibility in practical use, especially for medical applications. This is the case for the Er:YAG laser at 2.94 μm . At this wavelength internal transmission exceeds 98% over 2 m. ZBLAN glass fibers withstand pulses in excess of 1 J.

Fiber Lasers

A fiber laser requires a pumping source, usually a laser diode, and a rare earth doped optical fiber. The advantages of this configuration are the following:

- long interaction length (by comparison to crystal lasers);
- high power density in fiber core;
- single mode laser beam (if the fiber is single mode);
- all solid state structure.

The laser cavity can be made using mirrors or preferentially Bragg Gratings inscribed in the fiber.

Numerous lasers have been constructed using rare earth doped fluoride fibers. The low phonon energy of the fluoride glass matrix influences the spectroscopic properties of the rare earth ions: the number of nearly purely radiative transitions increases significantly, and therefore so does the number of new wavelengths in a fiber laser form, both towards the blue and UV, and towards the mid IR (Allain *et al.*, 1989; Allen and Esterowitz, 1989; Carter *et al.*, 1992; Jackson, 2006; Pollnau and Jackson, 2008; Zhu and Peyghambarian, 2010; Hudson, 2014; Fortin *et al.*, 2015; Tyazhev *et al.*, 2020). Another advantage is clearly a higher solubility of rare-earth fluorides in the fluoride glass host, which results in higher rare-earth concentrations and therefore shorter fiber lasers.

The availability of IR pumping sources made possible visible emission by up-conversion. This was largely investigated in the 1990s and led to various blue, green and red experimental fiber lasers. Nowadays blue GaN laser diodes appear to be a more convenient choice to develop powerful visible lasers. Mid infrared lasers based on fluoride glass fibers are under development at 2.3 and 4.3 μm . Fiber lasers operating around 2.8 μm are already commercial, both as CW 10 W, and femtosecond lasers.

Optical amplification

Fiber-optic communication is mainly conducted in the wavelength region where optical fibers have small transmission losses. This low-loss wavelength region ranges from 1260 to 1625 nm, and is divided into five wavelength bands referred to as the O-, E-, S-, C- and L-bands. Current networks are designed for the 1.55 μm window (C band). However increasing data flow requires that other bands should be used: O-band (1260–1360 nm), E-band (1360–1460 nm), S-band (1460–1530 nm) and L-band (1565–1625 nm).

Telecommunication networks require special components for WDM (wavelength division multiplexing) and optical amplifiers for signal transmission and distribution. In the C-band Erbium-Doped Fiber Amplifiers (EDFA) are universally used. But silica fibers cannot be used for the other bands because their phonon energy is too large. Praseodymium doped fluoride fibers have been

studied for amplification in the E-band (Durteste *et al.*, 1991; Ohishi *et al.*, 1991; Yamada *et al.*, 1997) while thulium-doped fibers have been developed for optical amplification in the S-band (Luthi *et al.*, 2005).

Supercontinuum Sources

Supercontinuum generation has emerged as a specific field. It is formed when a collection of non-linear processes act together upon a pump beam in order to cause the large spectral broadening of the original pump beam. While materials exhibiting large non linearity would be favored, paradoxically, commercial devices use silica and fluoride glasses in which non linearity is very small. This is compensated by longer interaction length which is easily achieved in optical fibers. The two main requirements are low optical losses and high peak power in the pulsed pump laser.

Supercontinuum sources based on fluoride glasses were first reported by Xia *et al.* (2006, 2007) and this led to further investigations (Qin *et al.*, 2009; Théberge *et al.*, 2013; Kubat *et al.*, 2013; Swiderski, 2014; Fischbach *et al.*, 2015; Gauthier *et al.*, 2016; Michalska *et al.*, 2017). Their emission spectrum ranges from 0.7 to 4.1 and 4.8 μm , as can be seen in Fig. 29 which shows pumping at 1550 nm in ZBLAN and fluoroindate glass fibers. Their output power depends on pump power which may reach 30 W for experimental set-ups.

Supercontinuum sources may be considered as “white light” sources operating in the IR spectrum. They are finding applications in a diverse range of fields, including optical coherence tomography (OCT), fluorescence lifetime imaging, frequency combs, contactless chemical analysis, gas sensing and many others.

Other Applications

Because chlorides and bromides are hygroscopic, practical interest has focused on fluoride glasses. Bulk components have limited applications, and are used mainly for research purposes. Rare earth doped slabs and rods are used for fluorescent references and as active media for laser emission.

Undoped glass may be used for windows and lenses. For current applications, single crystals -CaF₂ or BaF₂- are preferred. However glasses offer the possibility of fine adjustment of refractive index. In addition, casting techniques allow large size and complex shapes. For example, a window 50 cm in diameter was made by Owens Corning for the NRL.

Cerium doped fluorohafnate glasses were studied as scintillating materials for the LHC (Large Hadron Collider) at CERN (Auffray *et al.*, 1996). However crystalline materials were preferred.

Summary

Glass formation is common in halide systems. Single halides exist in the vitreous state, for example BeF₂, ZnCl₂, ZnBr₂ and PbI₂. Other halides may vitrify by fast quenching, while more numerous halides act as glass progenitors in multicomponent systems:

- Fluorides: AlF₃, ZrF₄, HfF₄, GaF₃, InF₃, ScF₃, VF₃, CrF₃, FeF₃, ThF₄, UF₄, MnF₂, ZnF₂,
- Chlorides: CdCl₂, ThCl₄, BiCl₃, PbCl₂,
- Bromides: CdBr₂, BiBr₃, PbBr₂,
- Iodides: ZnI₂, CdI₂, PbI₂.

A number of polyhalide glasses have been investigated: fluorohalides and mixed heavy halides. Because of environmental problems, research on glasses based on beryllium and thorium was ended.

Fluoride glasses have been more extensively studied and developed. In a first step the prospect for long haul and low optical losses attracted significant interest and funding. Later, optical fibers appeared to be complementary to silica fibers for infrared transmission and fiber lasers.

In spite of their potential for infrared technologies, heavy halide glasses have been less developed, mainly because of their hygroscopicity. New encapsulation techniques could open promising perspectives.

References

- Aggarwal, I.D., Lu, G. (Eds.), 1991. Fluoride Glass Fiber Optics. Academic Press.
- Aitken, B.G., Annunziata, F.A., Bartholomew, R.F., *et al.*, 1993. Rare earth-doped, stabilized cadmium halide glasses. United States US5240885A, filed September 21, 1992, and issued August 31, 1993. Available at: <https://patents.google.com/patent/US5240885A/en>.
- Akella, A., Downing, E.A., Hesselink, L., 1997. New fluoroindate glass compositions. Journal of Non-Crystalline Solids 213–214, 1–5. [https://doi.org/10.1016/S0022-3093\(97\)00038-0](https://doi.org/10.1016/S0022-3093(97)00038-0).
- Aliaga, N., Fonteneau, G., Lucas, J., 1978. Verres à base de tétrafluorure d'uranium. Annales de Chimie Science des Matériaux 3, 51.
- Allain, J.Y., Monerie, M., Poignant, H., 1989. Erbium-doped fluorozirconate single-mode fibre lasing at 2.71 μm . Electronics Letters 25 (1), 28–29. <https://doi.org/10.1049/el:19890020>.
- Allen, R., Esterowitz, L., 1989. CW diode pumped 2.3 μm fiber laser. Applied Physics Letters 55 (8), 721–722.
- Almeida, R.M., 1987. Halide Glasses for Infrared Fiber Optics. NATO ASI Series. Martinus Nijhoff Publishers.

- Angell, C.A., 1991. Relaxation in liquids, polymers and plastic crystals — strong/fragile patterns and problems. *Journal of Non-Crystalline Solids* 131–133, 13–31. doi:10.1016/0022-3093(91)90266-9. (Proceedings of the International Discussion Meeting on Relaxations in Complex Systems).
- Angell, C.A., Ziegler, D.C., 1981. Inorganic chloride and mixed halide glasses with low maximum phonon energy. *Materials Research Bulletin* 16, 279–283.
- Angell, C.A., Liu, C.L., Sundar, H.G.K., 1985. Far IR transmitting halide glasses. *Materials Science Forum* 5, 189–192. https://doi.org/10.4028/www.scientific.net/MSF.5-6.189.
- Auffray, E., Moine, B., Nikl, M., *et al.*, 1996. Cerium doped heavy metal fluoride glasses, a possible alternative for electromagnetic calorimetry. *Nuclear Instruments and Methods in Physics Research A* 380, 524–536.
- Avrami, M., 1938. Kinetics of phase change, I general theory. *The Journal of Chemical Physics* 7 (12), 1103–1112.
- Baldwin, C.M., Almeida, R.M., Mackenzie, J.D., 1981. Halide glasses. *Journal of Non-Crystalline Solids* 43 (3), 309–344. https://doi.org/10.1016/0022-3093(81)90101-0.
- Bartholomew, R.F., Bruce, A., Clare, A.G., Tick, P.A. (Eds.), 1996. *Non Oxide Glasses* 10. *Journal of Non Crystalline Solids*, vols. 213–214. North Holland Publishing; Elsevier Science.
- Blind, N., Eisenhauer, F., Gillessen, S., *et al.* 2015. GRAVITY, The VLTI 4-beam combiner for narrow-angle astrometry and interferometric imaging. *ArXiv:1503.07303 [Astro-Ph]*, March. Available at: <http://arxiv.org/abs/1503.07303>.
- Bouagga, A., Fonteneau, G., Lucas, J., 1987. New zirconium free multicomponent fluoride glasses. *Materials Research Bulletin* 22 (5), 685–689. https://doi.org/10.1016/0025-5408(87)90118-8.
- Bruce, A.J., 1987. The thermal properties of fluoride glass. In: Almeida, R.M. (Ed.), *Halide Glasses for Infrared Fiber Optics*. NATO ASI Series. Dordrecht: Springer Netherlands, pp. 149–162. Available at: https://doi.org/10.1007/978-94-009-3561-7_9.
- Byron, K.C., Gannon, J.R., 1983. CdI₂ glasses. *Glass Technology* 24, 146.
- Carter, J.N., Smart, R.G., Tropper, A.C., Hanna, D.C., 1992. Thulium-doped fluorozirconate fibre lasers. *Journal of Non-Crystalline Solids* 140, 10–15. https://doi.org/10.1016/S0022-3093(05)80732-X.
- Chanthanasinh, M., 1976. Synthèse de nouveaux verres fluorés à base de tétrafluorure de zirconium. Caractérisation et études spectroscopiques. Thèse de 3ème Cycle, Rennes, Rennes 1.
- Cheng, J., Jin, Z., 1995. New lead-halide-based glass-forming systems. *Journal of Non-Crystalline Solids* 184, 213–217. https://doi.org/10.1016/0022-3093(94)00614-8 (Non-oxide glasses).
- Comyns, A.E., 1989. Fluoride glasses. In: *Critical Reports on Applied Chemistry*, 27. Chichester: John Wiley & Sons.
- Coupé, R., Louër, D., Lucas, J., Léonard, A.J., 1983. X-ray scattering studies of glasses in the system ZrF₄-BaF₂. *Journal of the American Ceramic Society* 66 (7), 523–529. https://doi.org/10.1111/j.1151-2916.1983.tb10595.x.
- Cozmuta, I., Cozic, S., Poulain, M., Poulain, S., Martini, J.R.L., 2020. Breaking the silica ceiling, ZBLAN-based opportunities for photonics applications. In *Optical Components and Materials XVII*, 11276:112760R. Waikoloa: International Society for Optics and Photonics. https://doi.org/10.1117/12.2542350.
- Dai, G.J., Zhang, C.S., Huang, S.T., 1991. Progress in divalent mixed-halide glasses. *Materials Science Forum* 67–68, 125–128. https://doi.org/10.4028/www.scientific.net/MSF.67-68.125.
- Dai, Y., Hu, H., Gan, F.X., 1988. Investigation on water dissolution of ThCl₄ based glass using dynamic ion selective electrode method. *Materials Science Forum* 32–33, 273–278. https://doi.org/10.4028/www.scientific.net/MSF.32-33.273.
- Desa, J.A.E., Adrian, C., Wright, A.C., Wong, J., Sinclair, R.N., 1982. A neutron diffraction study of the structure of vitreous zinc chloride. *Journal of Non Crystalline Solids* 51, 57–86.
- Djouama, T., Boutarfaia, A., Poulain, M., 2007. Fluoride glasses based on the ZrF₄ – BaF₂ – MnF₂ system. *Optoelectronics and Advanced Materials* 1 (3), 122–128.
- Drexhage, M.G., 1985. Chapter 4 – Heavy-metal fluoride glasses. In: Tomozawa, M., Doremus, R.H. (Eds.), *Treatise on Materials Science & Technology*. Glass IV 26. Elsevier, pp. 151–243. https://doi.org/10.1016/B978-0-12-341826-5.50009-0.
- Drexhage, M.G., Moynihan, C.T., Robinson, M. (Eds.), 1987. *Halide Glasses*. *Materials Science Forum*, vol. 19–20. Switzerland; Germany; UK; USA: Trans Tech Publications. (2 vols).
- Duffy, J.A., Ingram, M.D., 1974. Lewis acid-base interactions in inorganic oxyacids, molten salts and glasses – III, Co-ordination studies of thallium, lead and bismuth in sulfate/chloride/bromide glass systems. *Journal of Inorganic and Nuclear Chemistry* 36 (1), 43–47. https://doi.org/10.1016/0022-1902(74)80655-X.
- Duffy, J.A., Ingram, M.D., 1983. Zinc bromide glass. *Journal of Non-Crystalline Solids* 58 (1), 143–144. https://doi.org/10.1016/0022-3093(83)90109-6.
- Durteste, Y., Monerie, M., Allain, J.Y., Poignant, H., 1991. Amplification and lasing at 1.3 μm in praseodymium-doped fluorozirconate fibres. *Electronic Letters* 27, 626–628.
- Elyamani, A., Poulain, M.J., 1987. Chlorofluorozirconate glasses. *Materials Science Forum* 19–20, 73–86.
- Elyamani, A., Matecki, M., Poulain, M.J., 1991. Nucleation and crystallization in a RbCl containing fluorozirconate glass. *Materials Science Forum* 67–68, 211–218.
- Fedorov, P.P., Zakalyukin, R.M., Ignat'eva, L.N., Bouznik, V.M., 2000. Fluoroindate glasses. *Russian Chemical Reviews* 69 (8), 705–716. https://doi.org/10.1070/RC2000v069n08ABEH000582.
- Fiberlabs, Inc., 2020. Fiberlabs, fluoride glass fibers. Available at: www.fiberlabs.com.
- Fischbach, S., Gorbach, A.V., Di Nuzzo, D., Da Como, E., 2015. Near infrared ultrafast pump-probe spectroscopy with ZrF₄-BaF₂-LaF₃-AlF₃-NaF Fiber Supercontinuum. *Applied Physics Letters* 107 (2), 021103. https://doi.org/10.1063/1.4926915.
- Fonteneau, G., Slim, H., Lahaie, F., Lucas, J., 1980. Nouveaux Verres Fluores Transmetteurs Dans l'infrarouge Dans Les Systemes LnF₃-BaF₂-ZnF₂. *Materials Research Bulletin* 15 (10), 1425–1432. https://doi.org/10.1016/0025-5408(80)90097-5.
- Fortin, V., Bernier, M., Bah, S.T., Vallée, R., 2015. 30 W fluoride glass all-fiber laser at 2.94 μm. *Optics Letters* 40 (12), 2882–2885. https://doi.org/10.1364/OL.40.002882.
- France, P.W., 1990. Extrinsic absorption. In: *Fluoride Glass Optical Fibres*, pp. 131–85. Glasgow; London: Blackie.
- France, P.W., Drexhage, M.G., Parker, J.M., *et al.*, 1990. *Fluoride Glass Optical Fibres*. Glasgow; London: Blackie.
- France, P.W., Carter, S.F., Day, C.R., Moore, M.W., 1989. Optical properties and applications. In: Comyns, A.E. (Ed.), *Fluoride Glasses*, *Critical Reports on Applied Chemistry*, vol. 27. Chichester, NY: John Wiley and Sons, pp. 87–122.
- Frischat, G.H., Moynihan, C.T. (Eds.), 1991. *Halide Glasses VI*. *Materials Science Forum* vols. 67–68. Switzerland; Germany; UK; USA: Trans Tech Publications.
- Fuding, M., 1985. Glass-forming tendency of some halide glasses. *Materials Science Forum* 5, 95–104. https://doi.org/10.4028/www.scientific.net/MSF.5-6.95.
- Gan, F., 1995. Optical properties of fluoride glasses: A review. *Journal of Non-Crystalline Solids* 184, 9–20. https://doi.org/10.1016/0022-3093(94)00592-3 (Non-oxide glasses).
- Gan, F., MacFarlane, D.R. (Eds.), 1995. *Non Oxide Glasses* 9. *Journal of Non-Crystalline Solids*, vol. 184.
- Gan, F., Dai, Y., Hu, H., 1985. Preparation, properties and structure of chloride glasses in systems of ThCl₄-PbCl₂-RCl (R=Na, Cu or Ag). *Materials Science Forum* 5, 113–120. https://doi.org/10.4028/www.scientific.net/MSF.5-6.121.
- Gannon, J.R., 1980. Optical fibre materials for operating wavelengths longer than 2 μm. *Journal of Non-Crystalline Solids* 42, 698–699.
- Gauthier, J.-C., Fortin, V., Carrée, J.-Y., *et al.*, 2016. Mid-IR supercontinuum from 2.4 to 5.4 μm in a low-loss fluoroindate fiber. *Optics Letters* 41 (8), 1756–1759. https://doi.org/10.1364/OL.41.001756.
- Goldschmidt, W.M., 1926. Geochemische Verteilungsgeetze. *Skrifter Norske Vid. Akad. (Oslo)* 8, 127.
- Heyne, G., 1933. Fluoroberylate glasses. *Angewandte Chemie* 46, 473–477.
- Hu, H., Fuding, M., Mackenzie, J.D., 1983. New halide glasses – Bromide glasses based on ZnBr₂ I. Vitreous zinc bromide. *Journal of Non-Crystalline Solids* 55 (1), 169–172. https://doi.org/10.1016/0022-3093(83)90018-2.
- Hudson, D.D., 2014. Invited paper, short pulse generation in mid-IR fiber lasers. *Optical Fiber Technology, Short Pulse Fiber Lasers* 20 (6), 631–641. https://doi.org/10.1016/j.yofte.2014.08.003.

- Inoue, S., MacFarlane, D.R., 1987. Glass forming tendency of $\text{ZrF}_4\text{-BaF}_2$ systems containing chlorides. *Materials Science Forum* 19–20, 27–32.
- Izumitani, T., Yamashita, T., Tokida, M., Miura, K., Tajima, H., 1987. Physical, chemical properties and crystallization tendency of the new fluoroaluminate glasses. In: Almeida, M.R. (Eds.), *Halide Glasses for Infrared Fiberoptics*. NATO ASI Series. Dordrecht, Springer Netherlands, pp. 187–197. Available at: https://doi.org/10.1007/978-94-009-3561-7_12.
- Jackson, S.D., 2006. Midinfrared holmium fiber lasers. *IEEE Journal of Quantum Electronics* 42 (2), 187–191. <https://doi.org/10.1109/JQE.2005.861824>.
- Jacoboni, C., 1987. Transition metal fluoride glasses (TMFG), synthesis, properties, structure. In: Almeida, R.M. (Eds.), *Halide Glasses for Infrared Fiberoptics*. NATO ASI Series. Dordrecht: Springer Netherlands, pp. 341–355.
- Jacoboni, C., Le Bail, A., De Pape, R., 1983. Fluoride glasses of 3d transition metals. *Glass Technology* 24 (3), 164–167.
- Jahn, W., 1961. Fluoroberyllate glasses. *Glastechnische Berichte* 34, 107.
- Jha, A., Parker, J.M., 1991. Preparation of infrared transmitting CdF_2 based mixed halide glasses. *Physics and Chemistry of Glasses* 32 (1), 1–12.
- Jia, S., Li, C., Zhao, Z., *et al.*, 2018. Er^{3+} -doped $\text{ZnF}_2\text{-BaF}_2\text{-SrF}_2\text{-YF}_3$ fluoride glasses for 2.7 μm laser applications. *Materials Letters* 227 (September), 97–99. <https://doi.org/10.1016/j.matlet.2018.05.062>.
- Jiang, X., Joly, N.Y., Finger, M.A., *et al.*, 2015. Deep-ultraviolet to mid-infrared supercontinuum generated in solid-core ZBLAN photonic crystal fibre. *Nature Photonics* 9 (2), 133–139. <https://doi.org/10.1038/nphoton.2014.320>.
- Johnson, W.A., Mehl, R.F., 1939. Reaction kinetics in processes of nucleation and growth. *Transactions of the American Institute of Mining, Metallurgical, and Petroleum Engineers* 135, 416–442.
- Kadono, K., Nakamichi, H., Tanaka, H., 1988. Raman spectra of ZnBr_2 -based glasses. *Materials Science Forum* 32–33, 433–436. <https://doi.org/10.4028/www.scientific.net/MSF.32-33.433>.
- Kanamori, T., Oikawa, K., Shibata, S., Manabe, T., 1981. $\text{BaF}_2\text{-CaF}_2\text{-YF}_3\text{-AlF}_3$ glass systems for infrared transmission. *Japanese Journal of Applied Physics* 20 (5), L326–L328. [https://doi.org/10.1016/0022-3093\(83\)90431-3](https://doi.org/10.1016/0022-3093(83)90431-3).
- Katsuyama, T., Matsumura, H., 1989. Glass fibers for infrared transmission. In *Infrared Optical Fibers*. Adam Hilger; IOP publishing.
- Kauzmann, W., 1948. The nature of the glassy state and the behavior of liquids at low temperatures. *Chemical Reviews* 43 (2), 219–256. <https://doi.org/10.1021/cr60135a002>.
- Kavun, V.Y., Slobodyuk, A.B., Merkulov, E.B., Polyantsev, M.M., Goncharuk, V.K., 2018. Synthesis and ion mobility in glasses of $\text{ZrF}_4\text{-BiF}_3\text{-Rb}(\text{Cs})\text{F}$ fluoride systems. *Russian Journal of Inorganic Chemistry* 63 (2), 149–156. <https://doi.org/10.1134/S0036023618020080>.
- Kawamoto, Y., 1985. Progress in structural study of ZrF_4 -based glasses. *Materials Science Forum* 6, 417–426. <https://doi.org/10.4028/www.scientific.net/MSF.5-6.417>.
- Kawamoto, Y., Nohara, I., 1985. Ionic conductivity of $\text{ZrF}_4\text{-BaF}_2\text{-CsF}$ glasses. *Materials Science Forum* 5–6, 767. <https://doi.org/10.4028/www.scientific.net/MSF.5-6.767>.
- Kawamoto, Y., Kanno, R., Ichimura, C., 1990. Ionic conduction in $\text{XMF} \cdot (95 - x)\text{ZrF}_4 \cdot 5\text{LaF}_3$ (M, alkali metals) glasses II. Ionic Conduction in $\text{XMF} \cdot (95 - x)\text{ZrF}_4 \cdot 5\text{LaF}_3$ (M, Li, Na, K, Rb or Cs) glasses. *Journal of Non-Crystalline Solids* 124 (2), 271–274. [https://doi.org/10.1016/0022-3093\(90\)90273-0](https://doi.org/10.1016/0022-3093(90)90273-0).
- Kolmogorov, A.N., 1939. On statistical theory of crystallization of metals. *Bull. Acad.Sci. URSS (Sci. Mat. Nat.)* vol. 3, pp. 355–359.
- Kubat, I., Agger, C.S., Moselund, P.M., Bang, O., 2013. Mid-infrared supercontinuum generation to 4.5 μm in uniform and tapered ZBLAN step-index fibers by direct pumping at 1064 or 1550 nm. *Journal of the Optical Society of America B* 30 (10), 2743–2757. <https://doi.org/10.1364/JOSAB.30.002743>.
- Le Verre Fluore. 2020. Fluoride glass components. Available at: www.Leverrefluore.Com.
- Lecoq, A., Poulain, M., 1979. Lanthanum fluorozirconate glasses. *Journal of Non-Crystalline Solids* 34 (1), 101–110. [https://doi.org/10.1016/0022-3093\(79\)90009-7](https://doi.org/10.1016/0022-3093(79)90009-7).
- Lecoq, A., Poulain, M., 1980a. Etude Du Rôle Stabilisateur de l'aluminium Dans Les Verres Au Tétrafluorure de Zirconium. *Verres Réfractaires* 34 (3), 333–342.
- Lecoq, A., Poulain, M., 1980b. Fluoride glasses in the $\text{ZrF}_4\text{-BaF}_2\text{-YF}_3\text{-AlF}_3$ quaternary system. *Journal of Non-Crystalline Solids* 41 (2), 209–217. [https://doi.org/10.1016/0022-3093\(80\)90166-0](https://doi.org/10.1016/0022-3093(80)90166-0).
- Leroy, D., Lucas, J., Poulain, M., Ravaine, D., 1978. Etude de la conduction ionique de verres a base de ZrF_4 . *Materials Research Bulletin* 13 (11), 1125–1133. [https://doi.org/10.1016/0025-5408\(78\)90199-X](https://doi.org/10.1016/0025-5408(78)90199-X).
- Lichkova, N.V., Despotuli, A.L., Zagorodnev, V.N., Minenkova, N.A., 1991. Superionic glasses based on silver and caesium monohalides. *Materials Science Forum* 67–68, 601–606. [doi:10.4028/www.scientific.net/MSF.67-68.601](https://doi.org/10.4028/www.scientific.net/MSF.67-68.601).
- Lucas, J., 1989. Fluoride glasses. *Journal of Materials Science* 24 (1), 1–13. <https://doi.org/10.1007/BF00660926>.
- Lucas, J., Moynihan, C.T. (Eds.), 1985. *Halide Glasses I & II*. Materials Science Forum vols. 5–6. Switzerland; Germany; UK; USA: Trans Tech Publications. (2 vols).
- Lucas, J., Chanthanasinh, M., Poulain, M.J., *et al.*, 1978. Preparation and optical properties of neodymium fluorozirconate glasses. *Journal of Non-Crystalline Solids* 27 (2), 273–283. [https://doi.org/10.1016/0022-3093\(78\)90130-8](https://doi.org/10.1016/0022-3093(78)90130-8).
- Lucas, J., Slim, H., Fonteneau, G., 1981. New fluoride glasses based on 4f and 5f elements. *Journal of Non-Crystalline Solids* 44, 31–35.
- Luthi, S.R., Silva, M.B.C., Bastos-Filho, C.J.A., Martins-Filho, J.F., Gomes, A.S.L., 2005. TDFA/Raman hybrid amplifiers covering the entire S-band pumped by a single laser. *IEEE Photonics Technology Letters* 17 (10), 2050–2052. <https://doi.org/10.1109/LPT.2005.856373>.
- MacFarlane, D.R. (Eds.), 1991. *Halide Glasses 7*. Journal of Non-Crystalline Solids, vol. 140. North Holland Publishing; Elsevier Science.
- Maier, C.G., 1925. ZnCl_2 glass. U.S. Bureau of Mines. Tech. paper no. 360.
- Matecki, M., Poulain, M., 1992. Composition adjustments in cadmium fluorochloride glasses. *Journal of Non-Crystalline Solids* 140 (January), 82–86. [https://doi.org/10.1016/S0022-3093\(05\)80746-X](https://doi.org/10.1016/S0022-3093(05)80746-X) (Proceedings of the Seventh International Symposium on halide glasses).
- Matecki, M., Poulain, M., Poulain, M., 1982. Verres aux halogénures de cadmium, I.- Verres fluores. *Materials Research Bulletin* 17 (10), 1275–1281. [https://doi.org/10.1016/0025-5408\(82\)90162-3](https://doi.org/10.1016/0025-5408(82)90162-3).
- Matecki, M., Poulain, M., Poulain, M., 1987. Alkali cadmium halide glasses. *Materials Science Forum* 19–20, 47–54. <https://doi.org/10.4028/www.scientific.net/MSF.19-20.47>.
- Matecki, M., Poulain, M., Poulain, M., 1983. Cadmium halide glasses. In: Day, D.E., Frischat, G.H. (Eds.), *Preparation, Properties, and Structure of Special Glasses*, Journal of Non-Crystalline Solids 56 (1–3), 81–86. Available at: [https://doi.org/10.1016/0022-3093\(83\)90450-7](https://doi.org/10.1016/0022-3093(83)90450-7).
- Messaddeq, Y., Poulain, M.J., 1991. Stabilizing effect of indium in divalent fluoride glasses. *Materials Science Forum* 67–68, 161–168.
- Messaddeq, Y., Delben, A., Boscolo, M., *et al.*, 1993. New fluorindate glass compositions. *Journal of Non-Crystalline Solids* 161, 210–212. [https://doi.org/10.1016/0022-3093\(93\)90701-X](https://doi.org/10.1016/0022-3093(93)90701-X).
- Michalska, M., Hlubina, P., Swiderski, J., 2017. Mid-infrared supercontinuum generation to 4.7 μm in a ZBLAN fiber pumped by an optical parametric generator. *IEEE Photonics Journal* 9 (2), 1–7. <https://doi.org/10.1109/JPHOT.2017.2690340>.
- Micheau, Y., Bouchy, F., Pepe, F., *et al.*, 2012. SPIRou @ CFHT, fiber links and pupil slicer. In: *Ground-Based and Airborne Instrumentation for Astronomy IV*, vol. 8446 (September), 84462R. Available at: <https://doi.org/10.1117/12.926084>.
- Miranday, J.-P., Jacoboni, C., De Pape, R., 1981. New transition metal fluoride glasses. *Journal of Non Crystalline Solids* 43, 393–401.
- Miranday, J.-P., Jacoboni, C., De Pape R., 1982. Glasses containing fluorine, their preparation and their application. US4328318 (A), issued May 4, 1982. Available at: https://worldwide.espacenet.com/publicationDetails/biblio?FT=D&date=19820504&DB=&locale=en_EP&CC=US&NR=4328318A&KC=A&ND=4.
- Mitachi, S., 1982. Fluoride glasses in the $\text{BaF}_2\text{-GdF}_3\text{-ZrF}_4$ system for optical fibres transmitting in the mid-infrared. *Physics and Chemistry of Glasses* 23 (6), 190–195.
- Miura, K., Masuda, I., Itoh, K., *et al.*, 1991. Fluorozircono-aluminate glass fiber. *Material Science Forum* 67–68, 335–340.
- Miura, K., Masuda, I., Tokida, M., Yamashita, T., 1988. Chlorine doped fluorozircono-aluminate glass. *Materials Science Forum* 32–33, 367–372. <https://doi.org/10.4028/www.scientific.net/MSF.32-33.367>.
- Morey, G.W., 1939. *Properties of Glass*. vol. 77. American Chemical Society. (Monograph Series, American Chemical Society).
- Mouric, J.L., Matecki, M., Poulain, M., Poulain, M., 1985. Progress in cadmium halide glasses. *Materials Science Forum* 5, 135–144. <https://doi.org/10.4028/www.scientific.net/MSF.5-6.135>.

- Nakai, T., Mimura, Y., Tokiwa, H., Shinbori, O., 1986. Dehydration of fluoride glasses by NF₃ processing. *Journal of Lightwave Technology* 4 (1), 87–89. <https://doi.org/10.1109/JLT.1986.1074631>.
- Nasu, H., Yamato, D.P., Heo, J., Mackenzie, J.D., 1985. Preparation and properties of non-fluoride halide glasses. *Materials Science Forum* 5, 121–126. <https://doi.org/10.4028/www.scientific.net/MSF.5-6.121>.
- Nishii, J., Kaite, Y., Yamagishi, T., 1985. New halide glass of the AgCX-CsX (X=I, Br) system. *Journal of Non-Crystalline Solids* 74, 411–415.
- Nishii, J., Kaite, Y., Yamagishi, T., 1989. Preparation and properties of ZnF₂-InF₃-GaF₃-PbF₂-LaF₃ Glasses. *Physics and Chemistry of Glasses* 30 (2), 55–58.
- Ohishi, Y., Kanamori, T., Kitagawa, T., *et al.*, 1991. Pr³⁺-doped fluoride fiber amplifier operating at 1.31 μm. *Optics Letters* 16 (22), 1747–1749. <https://doi.org/10.1364/OL.16.001747>.
- Ohishi, Y., Mitachi, S., Kanamori, T., Manabe, T., 1983. Optical absorption of 3d transition metals and rare earth elements in zirconium fluoride glasses. *Physics and Chemistry of Glasses* 24 (5), 135–140.
- Parker, J.M., Clare, A.G., Seddon, A.B., Morris, J., Pitt, N., 1987. Chlorine doped ZBLAN glasses. *Materials Science Forum* 19–20, 475–482.
- Perrin, G.S., Coude du Foresto, V., Ridgway, S.T., Mariotti, J.-M., Benson, J.A., 1995. Fibered recombination unit for the infrared-optical telescope array. In: *Fiber Optics in Astronomical Applications*, 2476. International Society for Optics and Photonics. pp. 120–129. <https://doi.org/10.1117/12.211845>.
- Petrová, B., Frumar, M., Stránská, E., Hložánek, I., 1989. New halide glasses of the CdX₂-PbX₂-Kl (X=Cl, Br) systems. *Journal of Materials Science* 24 (12), 4555–4556. <https://doi.org/10.1007/BF00544544>.
- Poignant, H., Ronarch, D., Griscom, D.L. (Eds.), 1993. Halide Glasses 8. *Journal of Non Crystalline Solids*, vol. 161. Elsevier Science; North Holland Publishing. (1 vols.).
- Pollnau, M., Stuart, J., 2008. Advances in mid-infrared fiber lasers. In: *NATO Security through Science Series C, Environmental Security*, pp. 315–346. Available at: https://doi.org/10.1007/978-1-4020-6463-0_9.
- Poulain, M., 1981a. Glass formation in ionic systems. *Nature* 293 (5830), 279–280.
- Poulain, M., 1981b. Incorporation de l'iode Dans Les Verres à Bas Point de Fusion. *European Applied Research Reports – Nuclear Science and Technology Section 3* (5), 1005–1096.
- Poulain, M., 1983. Halide glasses. *Journal of Non-Crystalline Solids* 56 (1), 1–14. [https://doi.org/10.1016/0022-3093\(83\)90439-8](https://doi.org/10.1016/0022-3093(83)90439-8) (Preparation, Properties, and Structure of Special Glasses).
- Poulain, M., 1989. Glass systems and structures. In: Comyns, A.E. (Ed.), *Fluoride Glasses*. Chichester, NY: John Wiley and Sons, pp. 11–48. (Critical Reports on Applied Chemistry 27).
- Poulain, M., 1992. Overview of crystallization in fluoride glasses. *Journal of Non-Crystalline Solids* 140 (January), 1–9. [https://doi.org/10.1016/S0022-3093\(05\)80731-8](https://doi.org/10.1016/S0022-3093(05)80731-8) (Proceedings of the Seventh International Symposium on halide glasses).
- Poulain, M., 2004. Properties and applications of fluoride glasses. In *Non Crystalline Materials for Optoelectronics*. Bucharest: INOE, pp. 335–361. (M. Popescu).
- Poulain, M., 2010. Fluoride glasses, properties, technology and applications. In: Murugan, G.S. (Ed.), *Photonic Glasses and Glass-Ceramics*. Research Signpost, pp. 1–28. <https://eprints.soton.ac.uk/341194/>.
- Poulain, M., Lucas, J., 1978. Une nouvelle classe de matériaux, les verres fluorés au tétrafluorure de zirconium. *Verres et Réfractaires* 32 (4), 505–513.
- Poulain, M., Chanthanasinh, M., Lucas, J., 1977. Nouveaux Verres Fluores. *Materials Research Bulletin* 12 (2), 151–156. [https://doi.org/10.1016/0025-5408\(77\)90157-X](https://doi.org/10.1016/0025-5408(77)90157-X).
- Poulain, M., Soufiane, A., Messaddeq, Y., Aegerter, M., 1992b. Fluoride glasses, synthesis and properties. *Brazilian Journal of Physics* 22 (3), 205–216.
- Poulain, M.A., Poulain, M.J., 1983. ThF₄ and LiF based glasses. *Journal of Non-Crystalline Solids, Preparation, Properties, and Structure of Special Glasses* 56 (1), 57–61. [https://doi.org/10.1016/0022-3093\(83\)90446-5](https://doi.org/10.1016/0022-3093(83)90446-5).
- Poulain, M.A., Poulain, M.J., Lucas, J., 1975. Verres Fluores Au Tetrafluorure De Zirconium Propriétés Optiques d'un Verre Dope Au Nd³⁺. *Materials Research Bulletin* 10 (4), 243–246. [https://doi.org/10.1016/0025-5408\(75\)90106-3](https://doi.org/10.1016/0025-5408(75)90106-3).
- Poulain, M.A., Poulain, M.J., Matecki, M., 1981a. Verres Fluores a Large Bande de Transmission Optique et a Haute Resistance Chimique. *Materials Research Bulletin* 16 (5), 555–564. [https://doi.org/10.1016/0025-5408\(81\)90121-5](https://doi.org/10.1016/0025-5408(81)90121-5).
- Poulain, M.A., Poulain, M.J., Matecki, M., 1982a. Verres Au Fluorure de Scandium. *Materials Research Bulletin* 17 (5), 661–669. [https://doi.org/10.1016/0025-5408\(82\)90050-2](https://doi.org/10.1016/0025-5408(82)90050-2).
- Poulain, M.A., Poulain, M.J., Matecki, M., 1982b. Rare earths in fluoride glasses: The LnF₃-AlF₃-ThF₄-BaF₂ systems and related glasses. *Journal of Non-Crystalline Solids* 51 (2), 201–215. [https://doi.org/10.1016/0022-3093\(82\)90006-0](https://doi.org/10.1016/0022-3093(82)90006-0).
- Poulain, M.A., Matecki, M., Mouric, J.-L., Poulain, M.J., 1983. Cadmium halide glasses. II. – Chloride glasses. *Materials Research Bulletin* 18 (5), 631–636. [https://doi.org/10.1016/0025-5408\(83\)90222-2](https://doi.org/10.1016/0025-5408(83)90222-2).
- Poulain, M.J., Poulain, M.A., 1988. Trivalent fluoride glasses. *Materials Science Forum* 32–33, 137–142.
- Poulain, M.J., Poulain, M.A., Messaddeq, Y., Soufiane, A., 1992a. Fluoroindate glasses. In: Bruce, A., Hiremath, B. (Eds.), *Solid-State Optical Materials*, Ceramic Transactions 28. Westerville, OH: American Ceramic Society, pp. 381–392.
- Poulain, M., 1996. Vacancy model of glass. In: *Proceedings, B:10–15*. Corning, NY.
- Poulain, M.J., Poulain, M.A., Maze, G., 1981b. Nouveaux verres fluorés. *European Union EP0036373A1*, filed March 17, 1981, and issued September 23, 1981. Available at: <https://patents.google.com/patent/EP0036373A1/fr?inventor=Marcel+Poulain&sort=new&page=1>.
- Qin, G., Yan, X., Kito, C., *et al.*, 2009. Ultrabroadband supercontinuum generation from ultraviolet to 6.28 μm in a fluoride fiber. *Applied Physics Letters* 95 (16), 161103. <https://doi.org/10.1063/1.3254214>.
- Ravaine, D., 1985. Ionic transport properties in glasses. *Journal of Non-Crystalline Solids* 73 (1), 287–303. [https://doi.org/10.1016/0022-3093\(85\)90355-2](https://doi.org/10.1016/0022-3093(85)90355-2) (Glass Science and Technology Problems and Prospects for 2004).
- Rawson, H., 1967. Inorganic glass-forming systems. In: *Non-Metallic Solids*, 2. Academic Press.
- Reau, J.M., Kahnt, H., Poulain, M., 1990. Ionic transport studies in mixed alkali-fluorine conductor glasses of composition ZrF₄·BaF₂·LaF₃·AF (A = Li, Na) and ZrF₄·BaF₂·ThF₄·LiF. *Journal of Non-Crystalline Solids* 119 (3), 347–350. [https://doi.org/10.1016/0022-3093\(90\)90308-9](https://doi.org/10.1016/0022-3093(90)90308-9).
- Reau, J.M., Senegas, J., Aomi, H., Hagenmuller, P., Poulain, M., 1985. Alkali fluoride containing fluorozirconate glasses, electrical properties and NMR investigation. *Journal of Solid State Chemistry* 60 (2), 159–164. [https://doi.org/10.1016/0022-4596\(85\)90107-0](https://doi.org/10.1016/0022-4596(85)90107-0).
- Robinson, M., 1985. Preparation and purification of fluoride glass starting materials. *Materials Science Forum* 5, 19–34. <https://doi.org/10.4028/www.scientific.net/MSF.5-6.19>.
- Sakka, S., Mackenzie, J.D., 1971. Relation between apparent glass transition temperature and liquidus temperature for inorganic glasses. *Journal of Non-Crystalline Solids* 6, 145–162.
- Sanghera, J., Busse, L.E., Aggarwal, I.D., Rapp, C., 1998. Fluoride glass-based fibers. In: *Infrared Fiber Optics*. Boca Raton; Boston; London: CRC Press.
- Shibata, S., Horiguchi, M., Jingui, K., *et al.*, 1981. Prediction of loss minima in infra-red optical fibres. *Electronics Letters* 17 (21), 775–777. <https://doi.org/10.1049/el:19810544>.
- Simmons, C.J., 1987. Chemical durability of fluoride glasses: III. The effect of solution pH. *Journal of the American Ceramic Society* 70, 654–661.
- Simmons, C.J., Simmons, J.H., 1991. Chemical durability of fluoride glasses. In: Aggarwal, I.D., Lu, G. (Eds.), *Fluoride Glass Fiber Optics*. Boston, MA: Academic Press, pp. 275–305.
- Simmons, J.H., Simmons, C.J., Ochoa, R., 1991. Fluoride glass structure. In: Aggarwal, I.D., Lu, G. (Eds.), *Fluoride Glass Fiber Optics*. Boston, MA: Academic Press, pp. 37–84.
- Soufiane, A., Poulain, M., 1993. New fluorogallate glasses. *Journal of Non-Crystalline Solids* 161, 206–209. (Proceedings of the Eight International Symposium on Halide Glasses). [https://doi.org/10.1016/0022-3093\(93\)90700-8](https://doi.org/10.1016/0022-3093(93)90700-8).
- SPIE, 2002. Interferometry for Optical Astronomy II. In: *Proceeding Society of Photo-Optical Instrumentation Engineers*, vol. 4838. Waikoloa: SPIE.

- Sun, K.H., 1946. Glass forming substances. *Glass Industry* 27 (11), 555.
- Sun, K.H., 1947. Calculation of the refractive index of a glass as a direct function of its composition. *Journal of the American Ceramic Society* 30 (9), 282–287.
- Sun, K.H., 1979. Fluoride glasses. *Glass Technology* 20 (1), 36–40.
- Sun, K.H., 1949a. Fluoride Glass. US 2,466,507, issued 04 1949. Available at: <https://pdfpiw.uspto.gov/piw?Docid=US2466509&idkey=NONE&homeurl=http%3A%252F%252Fpatft.uspto.gov%252Fnetahtml%252FPTO%252Fpatimg.htm>.
- Sun, K.H., 1949b. Fluoride Glass. US 2,466,508, issued 04 1949. Available at: <https://pdfpiw.uspto.gov/piw?Docid=US2466509&idkey=NONE&homeurl=http%3A%252F%252Fpatft.uspto.gov%252Fnetahtml%252FPTO%252Fpatimg.htm>.
- Sun, K.H., Callear, T.E., 1949. Fluoride Glass. US 2,466,506, issued 04 1949. Available at: <https://pdfpiw.uspto.gov/piw?Docid=US2466509&idkey=NONE&homeurl=http%3A%252F%252Fpatft.uspto.gov%252Fnetahtml%252FPTO%252Fpatimg.htm>.
- Swiderski, J., 2014. High-power mid-infrared supercontinuum sources, current status and future perspectives. *Progress in Quantum Electronics* 38 (5), 189–235. <https://doi.org/10.1016/j.pquantelec.2014.10.002>.
- Tatsumisago, M., Akamatsu, Y., Minami, T., 1988. Effects of cation-mixing and anion-mixing in halide glasses on ionic conductivity. *Materials Science Forum* 32–33, 617–622. <https://doi.org/10.4028/www.scientific.net/MSF.32-33.155>.
- Théberge, F., Daigle, J.-F., Vincent, D., *et al.*, 2013. Mid-infrared supercontinuum generation in fluorindate fiber. *Optics Letters* 38 (22), 4683–4685. <https://doi.org/10.1364/OL.38.004683>.
- Thorlabs, 2020. Fluoride glass fibers. Available at: www.thorlabs.com.
- Tyazhev, A., Starecki, F., Cozic, S., *et al.*, 2020. Watt-level efficient 2.3 μm thulium fluoride fiber laser. *Optics Letters* 45 (20), 5788–5791. <https://doi.org/10.1364/OL.403450>.
- Van Uitert, L.G., 1979. Relation between melting point, glass transition temperature and thermal expansion for inorganic crystals and glasses. *Journal of Applied Physics* 50 (12), 8052–8061.
- Videau, J.J., Dance, J.M., Portier, J., Dubois, B., 1986. Study of glasses based on InF_3 . *Revue de Chimie Minérale* 23, 789–795.
- Videau, J.-J., Portier, J., 1985. Fluoride glasses. In: *Inorganic Solid Fluorides*, pp. 309–329. Materials Science Series. New York: London: Academic Press.
- Videau, J.-J., Fava, J., Fouassier, C., Hagenmuller, P., 1979. Elaboration et Propriétés Optiques de Nouveaux Verres Fluores Actives Au Neodyme. *Materials Research Bulletin* 14 (4), 499–506. [https://doi.org/10.1016/0025-5408\(79\)90192-2](https://doi.org/10.1016/0025-5408(79)90192-2).
- Warren, B.E., Hill, C.F., 1934. Structural study of BeF_2 glass. *Zeitschrift für Kristallographie* 89, 481–486.
- Weber, M.J., 1980. Glass for neodymium fusion lasers. *Journal of Non-Crystalline Solids* 42 (1), 189–196. [https://doi.org/10.1016/0022-3093\(80\)90021-6](https://doi.org/10.1016/0022-3093(80)90021-6).
- Weber, M.J., Milam, D., Smith, W.L., 1978. Nonlinear refractive index of glasses and crystals. *Optical Engineering* 17 (5), 175463. <https://doi.org/10.1117/12.7972266>.
- Winter, A., 1955. Les formateurs de verres et le tableau périodique des éléments. *Verres et Réfractaires* 9 (3), 147.
- Winter, A., 1957. Glass formation. *Journal of the American Ceramic Society* 40 (2), 54–58. <https://doi.org/10.1111/j.1151-2916.1957.tb12574.x>.
- Xia, C., Kumar, M., Kulkarni, O.P., *et al.*, 2006. Mid-infrared supercontinuum generation to 4.5 μm in ZBLAN fluoride fibers by nanosecond diode pumping. *Optics Letters* 31 (17), 2553–2555. <https://doi.org/10.1364/OL.31.002553>.
- Xia, C., Kumar, M., Cheng, M.-Y., *et al.*, 2007. Power scalable mid-infrared supercontinuum generation in ZBLAN fluoride fibers with up to 1.3 watts time-averaged power. *Optics Express* 15 (3), 865–871.
- Yamada, M., Kanamori, T., Ohishi, Y., *et al.*, 1997. Pr^{3+} -doped fluoride fiber amplifier module pumped by a fiber coupled master oscillator/power amplifier laser diode. *IEEE Photonics Technology Letters* 9 (3), 321–323. <https://doi.org/10.1109/68.556060>.
- Yamane, M., Moynihan, C.T. (Eds.), 1988. Halide glasses V. *Materials Science Forum*, vols. 32–33. Switzerland; Germany; UK; USA: Trans Tech Publications.
- Zachariasen, W.H., 1932. The atomic arrangement in glass. *Journal of the American Chemical Society* 54, 3840.
- Zhang, K., Liu, J., Zhao, X., Li, H., 1992. Heavy halide glasses based on lead bromide and lead iodide. *Journal of Non-Crystalline Solids* 140, 225–228. [https://doi.org/10.1016/S0022-3093\(05\)80771-9](https://doi.org/10.1016/S0022-3093(05)80771-9) (Proceedings of the Seventh International Symposium on halide glasses).
- Zhang, X., Lucas, J., Fonteneau, G., 1987. A new glass family based on tellurium chalcogenides. *Materials Science Forum* 19–20, 67–72. <https://doi.org/10.4028/www.scientific.net/MSF.19-20.67>.
- Zhu, X., Peyghambarian, N., 2010. High-power ZBLAN glass fiber lasers: Review and prospect. *Advances in Optoelectronics* 2010, 1–23. (Article ID 501956). <https://doi.org/10.1155/2010/501956>.
- Ziegler, D.C., Angell, C.A., 1982. High refractive index, low Abbe number halide glasses. *Applied Optics* 21 (12), 2096–2098. https://doi.org/10.1364/AO.21.2096_1.

Glass: Annealing and Tempering

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Introduction

Glass is a ubiquitous material in our everyday lives. Most glass products that surround us are produced via a melting process, starting from a mix of raw materials (batch) that is heated up to produce a molten liquid, homogenized, then rapidly cooled down and shaped into the desired form (Hubert, 2019). The rapid cool-down process generally experienced during the forming step can generate stresses in the material, which are detrimental to its mechanical performance. Manufacturers thus need to carry out specific steps to minimize the stresses in their products before releasing them on the market. Stresses in glass can be relieved via a controlled thermal treatment, called annealing. Annealing is therefore an integral part of the glass manufacturing process and is performed on most products found on the market.

On the other hand, under some specific controlled conditions, the formation of thermal stresses in the material can be used to an advantage to strengthen the glass article, using the so-called thermal tempering process.

For both annealing and tempering processes, control of the thermal history of a glass is thus critical. This chapter describes the key principles governing the annealing and tempering processes. To understand these principles, it is important to understand the evolution of glass and its structure as function of temperature. First, the relationship between glass viscosity and temperature will be described. Stresses, and the critical viscosity ranges at which they form and at which they can be released (annealed) will be detailed. Finally, the strategies by which glass manufacturers can take advantage of a controlled formation of stresses in glass products (tempering) will be described.

Viscosity Versus Temperature in Glass

Viscosity (η) is defined as the resistance of a material to deformation at a given rate. While it is expressed in Pa.s in the S.I. system, the preferred unit used in the glass-making world is the Poise (1 Pa.s = 10 poises, or 1 poise = 0.1 Pa.s).

The viscosity of a glass depends on its composition, and thus the temperatures at which the different process steps take place depend on the type of glass produced. Therefore, characteristic temperatures are better defined by a corresponding viscosity for each glass. The typical characteristic temperatures in the glass-making process and their corresponding viscosities are described in Table 1. Viscosity curves for different types of glasses, highlighting the impact of glass composition on its characteristic temperatures, are presented in Fig. 1.

The forming processes used to produce different types of glass articles – e.g., pressing or molding for bottles, drawing for fibers, etc., – are typically operated at different viscosities, upon cooling from the molten glass. During these processes, glass articles experience a rapid cooling rate, i.e., a rapid viscosity increase, spanning several orders of magnitude, while it goes from a liquid state at relatively low viscosities (~ 100 poises) at the melting temperature, to a solid state at lower temperatures. The transition between the liquid-like and solid-like behavior occurs at the so-called “glass transition” temperature.

At low viscosities (in the “liquid like state”), the glass structure can rearrange itself and relax constraints. At higher viscosities (lower temperatures, in the “solid like state”), the degrees of freedom to relax constraints reduce considerably, and it becomes impossible to release constraints. With the rapid changes in temperature and viscosity experienced by a glass article during the forming process, the glass is subject to thermal gradients and goes rapidly from low viscosities to higher viscosities, leading to the formation of thermal stresses. To relieve these stresses, the glass thus needs to be brought back to a temperature (= a viscosity) at which the glass structure has enough degrees of freedom to re-arrange itself and relax the constraints created. This process, called annealing, is typically carried out around the annealing point of the glass.

Stresses in Glass

In general, stresses in a material are detrimental to its mechanical properties (Guin, 2019). Glass makers thus need to reduce as much as possible the stresses in their products before putting them on the market. Stresses can arise from different sources and may be permanent or temporary.

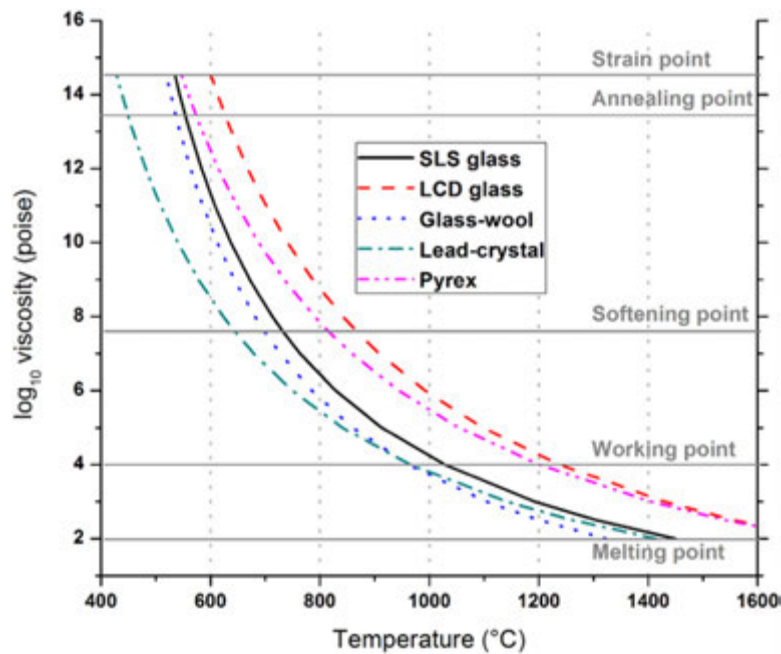
The stresses generated in a glass are dependent on several factors, following the equation:

$$\sigma = \frac{E}{1 - \mu} \cdot \frac{\rho \cdot C_p}{\lambda} \cdot h \cdot d^2 \cdot b \quad (1)$$

Where σ is the stress generated in the product (in Pa), E is the Young's modulus of the glass (in Pa), α is its thermal expansion coefficient (in K^{-1}), μ its Poisson's ratio (dimensionless), ρ is the density of the glass (in $Kg\ m^{-3}$), C_p its specific heat (in $J\ Kg^{-1}\ K^{-1}$),

Table 1 Characteristic temperatures and corresponding viscosities in the glass-making process

Characteristic temperature	Corresponding viscosity	Definition
Melting point	10^1 Pa.s 10^2 Poise	In glass-making, temperature at which the viscosity is considered good for obtaining a well-fined melt with good homogeneity within the melting tank This does not correspond to a physical melting point as for crystals
Working point	10^3 Pa.s 10^4 Poise	Temperature/viscosity around which forming of articles typically occur. Often, the “working range” would be expressed, corresponding to a viscosity range of 10^2 to 10^6 Pa.s (10^3 to 10^7 Poise)
Softening point (Littleton point)	$10^{6.65}$ Pa.s $10^{7.65}$ Poise	Temperature at which the glass deforms under its own weight at a rate of 1 mm/min Defined by ASTM C338
Glass transition	$10^{-12-12.6}$ Pa.s $10^{-13-13.6}$ Poise	Temperature (or range of temperatures) where the glass transitions between a liquid-like material to a solid-like material
Annealing point	$10^{12.4}$ Pa.s $10^{13.4}$ Poise	Temperature at which the stresses generated during forming can be released by viscous relaxation within about 15 min
Strain point	$10^{13.5}$ Pa.s $10^{14.5}$ Poise	Temperature at which the stresses generated during cooling/forming can be released within about 15 h. Below this temperature, relieving the internal stresses is practically impossible

**Fig. 1** Viscosity curves for different glass families and characteristic temperatures commonly used in the glass-making industry (SLS = Soda-Lime-Silicate glass; LCD = Liquid Crystal Display glass).

λ is its thermal conductivity (in $\text{W m}^{-1} \text{K}^{-1}$), h is the cooling rate applied to the article (in K s^{-1}), d is the dimension/thickness of the article (in m), and b is a dimensionless shape factor (differs for flat glass versus tubes versus bottles/containers).

This equation clearly highlights that the generation of stresses in a glass is dependent both on the nature of the glass itself (its intrinsic properties) and on the process used (size/shape of the article and cooling rate applied). Therefore, for a similar thermal history (cooling rate):

- (1) For a given glass composition, the stresses generated may be different between articles of different shape/size.
- (2) For an article of a given size/shape, the stresses generated may be different if the composition of the glass is changed, i.e., if the intrinsic properties of the glass are different.

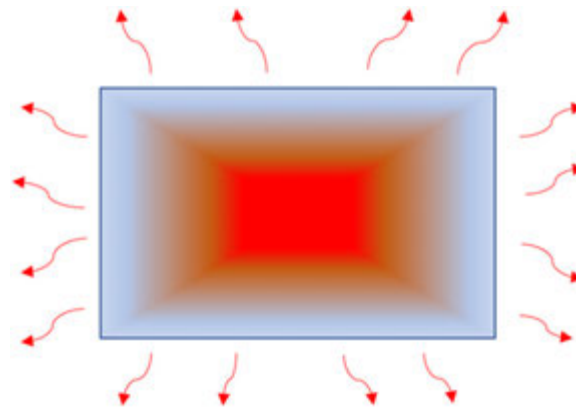


Fig. 2 Example of thermal gradient created upon cooling in a piece of glass.

These are very important considerations to keep in mind on the production of glass and annealing or tempering processes. These need to be adjusted to the type of glass produced, the type of article produced, and to the thermal history experienced by this article.

Thermal Stresses

During the forming process, glass typically experiences rapid cooling rates, during which it will contract. These cooling rates are often non uniform throughout the article, leading to the generation of thermal gradients in the product, and thus different parts of the product will contract at different rates, as illustrated in [Fig. 2](#), leading to different rates of expansion/contraction at different locations in the piece of glass. In general, the surface will cool down faster than the center of the material.

The thermal gradients thus formed lead to the formation of thermal stresses. As indicated in [Table 1](#), thermal stresses can be relieved at temperatures around the annealing point, and below the strain point, stresses in the material are virtually “frozen in” and cannot be relieved. The stresses created by a rapid, non-uniform cooling from above the annealing point to below the strain point of the glass are thus permanent stresses. These permanent stresses will remain in the product unless relieved using a controlled annealing process.

While permanent stresses cannot be formed below the strain point, temporary stresses can still be generated during the cooling of the glass from below that temperature. Despite their temporary nature, these stresses can lead to thermal shock and breakage of the glass if they exceed the maximum stress the glass can withstand.

Non-Thermal Stresses

Not all the sources of stresses in a glass are related to its thermal history. Defects such as inclusions (e.g., non-molten batch particles, crystals formed by devitrification of the melt, pieces of refractory from the melting tank, foreign particles from the forming process, etc.) typically have different thermal expansions than the glass matrix. Upon cooling, these defects will create some permanent stresses in the material. Inhomogeneities in the glass compositions, or cords, are another possible source of permanent stresses.

Contrary to thermal stresses, the stresses arising from defects or chemical inhomogeneities cannot be relieved by annealing.

Annealing Process

Basic Principles

The goal of the annealing process is to relieve the permanent stresses generated during the forming process of a glass article. As indicated in [Table 1](#), thermal stresses can be relieved at the so-called annealing point, and glass producers will carry out a controlled heat treatment, the annealing, in order to improve the mechanical performance of their product.

In the annealing process, the glass is first (re)heated up to a temperature slightly above its annealing point. The article needs to be kept at this temperature long enough to reach thermal equilibrium throughout the entire article. From the point where thermal equilibrium is achieved in the product and the stresses are relieved by visco-elastic relaxation, the key is to cool the article slow enough, down to below its strain point to avoid re-creating permanent thermal stresses. The cool-down process between the annealing and the strain point should thus be gradual, slow and uniform. Once the temperature in the article is below the strain point, the cooling rate can be increased, as from that point only temporary stresses can be generated. However, this cooling rate should not be too high in order to avoid breakage due to thermal shock.

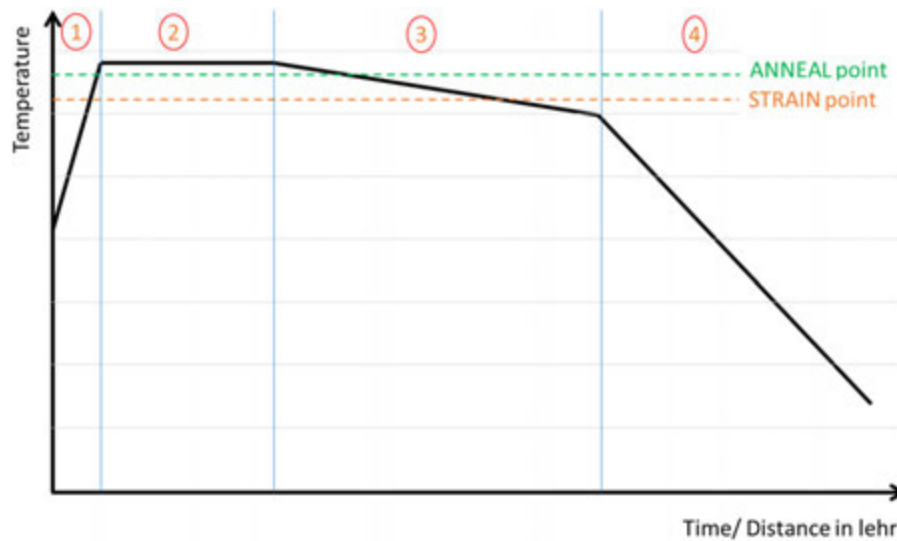


Fig. 3 Typical temperature profile in an annealing lehr.

Annealing Lehrs

In most industrial glass production, the annealing step is performed in continuous annealing lehrs. The glass articles coming from the forming process are conveyed through the lehr, in which the temperature profile is designed following the principles described above. Annealing is usually followed by further post-processing and inspection steps. Glass producers must ensure that their lehr has a good thermal uniformity (e.g., left to right, top to bottom) to avoid creating thermal gradients throughout their product.

As indicated in Eq. (1), the stresses generated in a glass depend not only on its properties, but also on the shape of the article being manufactured, and annealing curves need to be designed specifically for each glass and product. Thicker products, or thicker parts in an article of variable thickness (for instance, the bottom and the mouth of a bottle are usually thicker than the main body) typically require longer times to reach thermal equilibrium, and this needs to be taken into account in order not to create stresses in these areas.

A typical annealing profile for a glass product is shown in Fig. 3, highlighting four main steps:

- (1) Rapid re-heating of the product: to bring it to a temperature slightly above the anneal point of the glass.
- (2) Dwell for thermal equilibration: critical to reach a homogeneous temperature throughout the entire article before cooling down.
- (3) Slow cool down: between the anneal point and the strain point. The cooling down needs to be uniform throughout the product during this step. Thicker articles (or thicker parts within an article) typically require slower cooling rates to avoid creating excessive thermal gradients.
- (4) Faster cool down: below the strain point, only temporary stresses can be created, and higher cooling rates can be applied. This faster cooling rate is usually applied for economic reasons, to shorten the overall time required for the annealing process (and thus shorten production times) in industrial production.

Glasses produced at the lab scale, or articles produced by glass artists are typically annealed in static furnaces (or *kilns*). The pieces of glass are introduced into a furnace that has been previously heated up to the annealing temperature. After closing the kiln, the heating is switched off, allowing for a slow cooling of the article down to room temperature. Care should be taken to not open the kiln too early in order to avoid the creation of stresses or thermal shocks in the product.

It should be noted that, during the annealing process, the glass article should not be heated up to a temperature too high above its annealing point, as reaching too low a viscosity could lead to a deformation of the product by viscous sagging.

Impact of Annealing on Glass Properties

As mentioned previously, the glass undergoes structural changes as it cools down from a liquid-like material to a solid-like material. Contrary to crystals, where the transition from liquid to solid is sharp and occurs at a very precise temperature (the melting point of the crystal), this transition is gradual in glass and occurs over a range of temperature around the glass transition temperature (Doremus, 1994). Due to this gradual transition, the cooling rate experienced by the glass can impact its structure. In other words, depending on the cooling rate applied, the glass structure may have more or less time to re-arrange before reaching a viscosity at which the structure is “frozen in” (i.e., below the strain point).

The thermal history of a glass (and cooling rate) will impact its properties, such as density (Narayanaswamy, 1971). The density of a given glass will increase with lower cooling rates. Optical properties, such as refractive index, are dependent on the density of

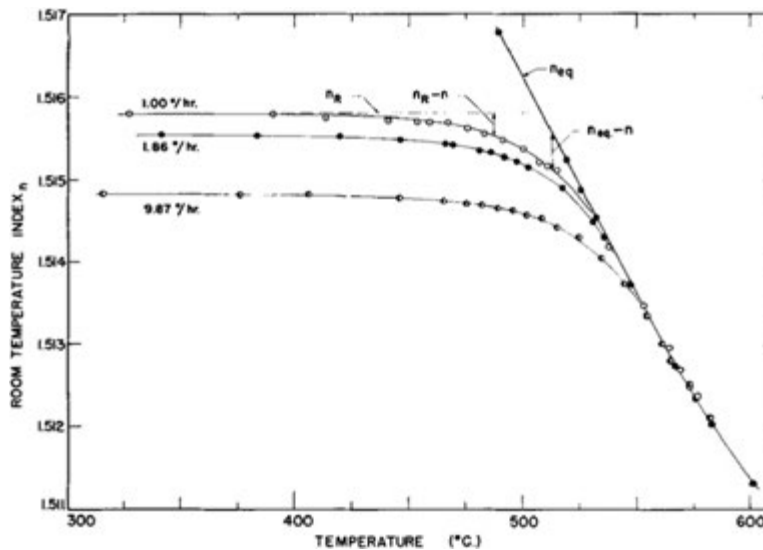


Fig. 4 Variation of the refractive index during cooling at constant rates. Reproduced from Lillie, H., Ritland, H., 1954. Fine annealing of optical glasses. *Journal of the American Ceramic Society* 37 (10), 466–473, with permission John Wiley and Sons

the glass, and are thus impacted by the thermal history of the glass. **Fig. 4** shows an example of the evolution of the refractive index of a glass as function of the cooling rate applied. With increased cooling rate, the glass at room temperature shows a lower refractive index (correlated to a lower density). While such a change in refractive index may not be an issue for many common everyday glass products (such as bottles or glassware), small variations of refractive index may be critical for optical applications (lenses, telescope mirrors), where very high optical homogeneity is required to avoid image distortions or chromatic aberrations. The annealing process is therefore all the more critical for optical glasses.

On the other hand, this dependence of the refractive index on the thermal history of the glass can be taken advantage of, as the refractive index of a product can be fine-tuned by tuning the annealing process applied to the glass. This strategy is used by optical glass manufacturers (Schott, 2019). It should be noted that the thermal history of the glass can also have an impact on some post-processing steps, such as ion-exchange (Zhang and Guo, 2020).

Quantification of the Stresses

Polarimeters (or polariscopes) can be used to measure the angle of rotation caused by passing polarized light (mono-directional) through an optically active material. Differences in the optical properties of this material will induce a difference in the rotation of this polarized light, which can be observed and quantified.

Perfect glasses are isotropic materials, meaning their properties (thermal, optical, etc.) are the same in all directions. However, the presence of stresses can lead to local deformations in the structure and thus to local changes in properties, notably in its refractive index, causing so-called birefringence. In other words, stresses present in the glass will have an impact on the way light travels through it, and this impact is proportional to the magnitude of the stress in the material.

Polariscopes can thus be used to observe and quantify stresses in glass articles (McKenzie and Hand, 1999). An example of glass products with high stresses and low stresses, observed using a polarimeter, is shown in **Fig. 5**.

Glass producers typically use this type of device as part of their standard inspection/quality control process (Redner, 1995). These are placed after the annealing lehrs and allow operators to identify and reject products with excessive internal stress.

Stresses in glass articles can be due to improper/insufficient annealing. Using polarimetry to evaluate stresses is thus particularly important when sending a new product through an annealing lehr to ensure it is properly set to minimize stresses. However, as mentioned previously, stresses can also be due to the presence of defects or chemical inhomogeneities in the products. These types of stresses cannot be relieved by annealing. When stresses are observed in the product, it is thus also important to carry out additional analyses (such as microscopic observations) to understand the root cause for the stresses and carry out proper troubleshooting.

Taking Advantage of Thermal Stresses

The goal of annealing is to reduce stresses in a glass article. As described previously, rapid cooling of a glass during its forming can lead to the formation of stresses, with uneven levels of stresses throughout articles. This inhomogeneity of the stress distribution within the article is one of the main sources of a reduction in mechanical properties, and the reason for a need for the annealing process.

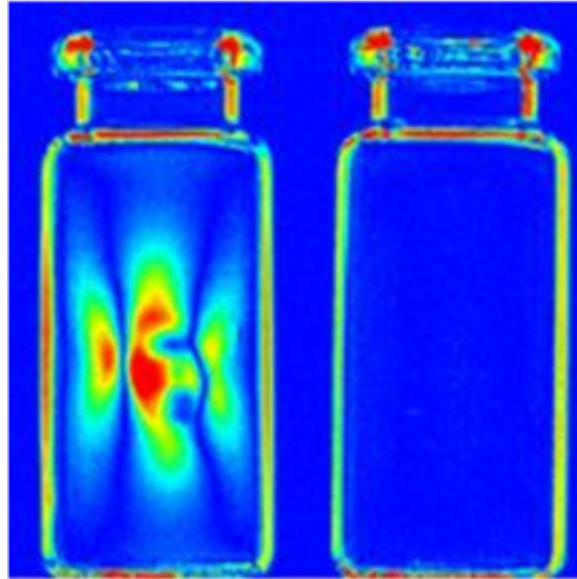


Fig. 5 Observation of stresses by birefringence in glass jars. The jar on the left shows stresses at its center, while the jar on the right shows much lower stresses. Picture courtesy of ilis GmbH and Körber Pharma Inspection.

The strength of glass is primarily controlled by the existence of flaws on the surface due to processing and handling. These flaws will grow when placed under tension and can lead to the eventual failure of the glass article. Fortunately, it has been discovered that flaws which are under a compressive stress will not propagate, a concept which forms the basis for all known strengthening techniques for glass. Creating a compression layer at the surface of a glass product can be beneficial to its mechanical performance, provided this can be done in a homogeneous way. Such compression layer can be achieved via a controlled thermal treatment of the glass and the controlled formation of stresses, via the so-called tempering process. In the case of tempering, the formation of stresses is thus an advantage for the product.

Thermal Tempering

In thermal tempering, a glass product is heated to near but below the softening temperature and then rapidly quenched (Gardon, 1980). As a result, the glass will possess a lower surface temperature than the interior during cooling, as illustrated in Fig. 6. The temperature difference is maintained by sustained cooling until the surface of the glass cools to room temperature. As the center of the glass cools more slowly to room temperature it contracts to a smaller specific volume while the high specific volume of the surface layer remains unchanged. The difference in specific volume is in majority due to differences in the thermal expansion of the glass upon cooling, while to a lesser extent due to a difference in fictive temperature (the temperature at which the liquidus structure has become frozen in) between the surface and the bulk (Narayanaswamy, 1978).

Rapid quenching is required to maintain the necessary temperature differential through the thickness of the glass sheet which becomes increasingly difficult as the thickness of the glass sheet is reduced. The required quenching rates can be achieved through various means, including quenching the glass article directly into liquids such as water, oil, or molten salts, and solid contact quenching such as with metal or graphite plates. The most commonly used process for commercial products is convective quenching using enormous volumes of forced air. Due to the limitations of hot glass sheet conveyance and convective cooling, thermal tempering of commercial products has traditionally been limited to glasses of approximately 3 mm and thicker, although recent innovations in thin glass conveyance, have enabled some tempering of thinner glasses down to 2 mm.

The tempering process leads to a surface compressive layer that gives the glass improved strength over annealed glass. To a first approximation, the stress distribution in thermally tempered glass can be represented by a simple parabola, with the magnitude of the surface compressive stress approximately equal to twice the center tension (Barsom, 1968), as illustrated in Fig. 7. The magnitude of the residual stress is highly dependent on various factors including the thermal expansion curve of the glass – where glasses with higher CTE (coefficient of thermal expansion) produce higher stresses, the temperature from which the glass is quenched from – higher temperature producing higher stresses, and the quenching rate – faster quenching resulting in higher stresses.

Thermally tempered glass, sometimes called safety glass, is often applied in situations where a safe fracture behavior is required to prevent injury in the case of failure, being used to strengthen automobile side and rear windows, as well as household objects such as shower doors, coffee tables, etc. Thermally tempered glass also exhibits improved resistance to thermal shock and has found use in recent years in cookware, replacing the more expensive borosilicate glasses used in traditional products. It is desirable that when thermally tempered glass breaks, unlike annealed glass, it shatters into rock-salt like pieces which do not have sharp

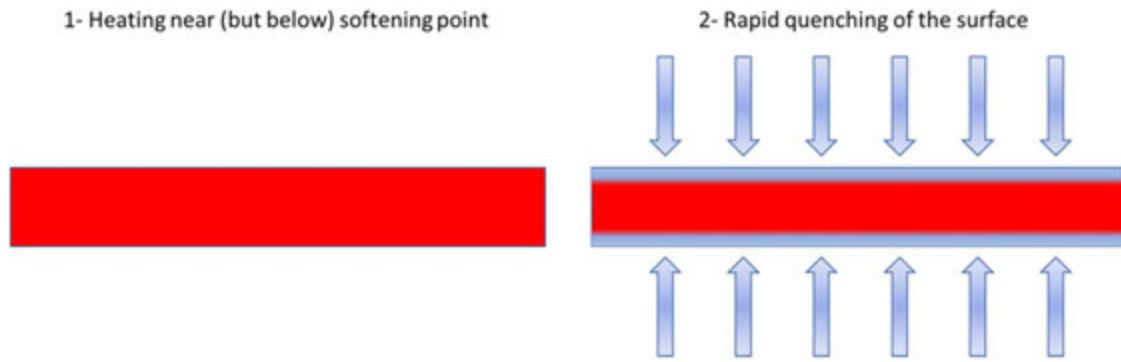


Fig. 6 Schematic illustration of the rapid quenching of the surface during thermal tempering.

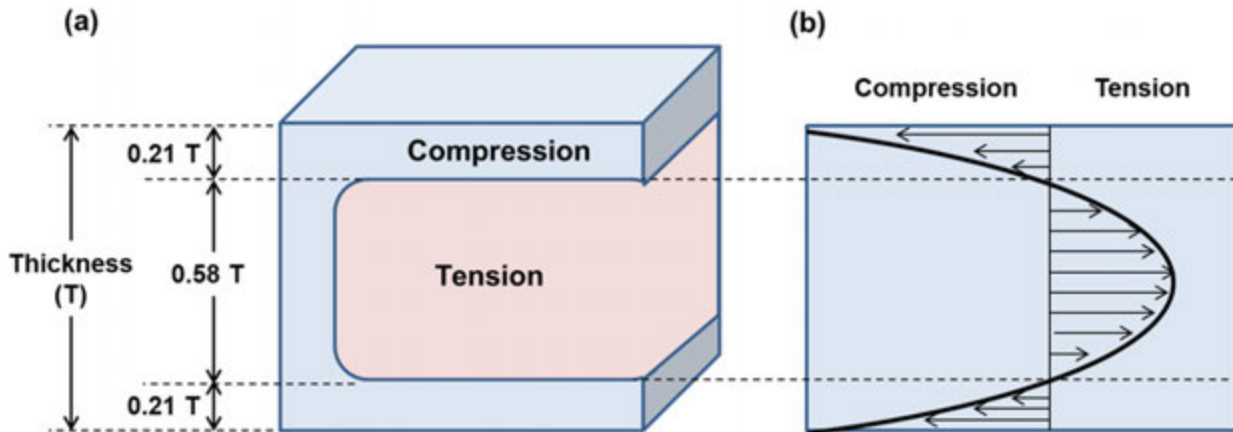


Fig. 7 (a) typical through-thickness stress profile in a tempered glass plate. (b) stress profile within the glass plate.

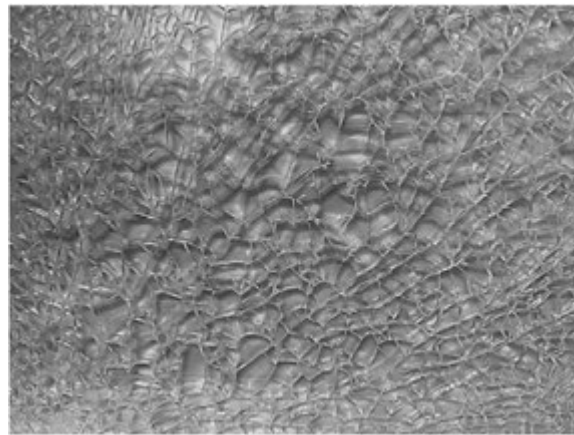


Fig. 8 A typical fracture pattern for a glass article achieving full temper.

edges or needle-like shapes (see [Fig. 8](#)). For this reason, it is required that all necessary cutting, grinding, etching, or finishing is done before the tempering process is performed.

The desired fracture behavior of tempered glass is sometimes referred to as “dicing” and occurs when the glass has achieved “full temper” ([Gardon, 1980](#)). The “dicing” threshold of tempered glass is an arbitrarily defined fracture behavior which can be considered safe to the end user in the event of glass failure. Standards exist worldwide such as ASTM C1048 and ANSI Z97.1 in the United States, EN12150-1 in Europe, GOST 5727-88 in Russia, JIS R 3206 in Japan, and GB 15763.2 in China. The standards are nearly identical across countries in that a fractured piece of tempered soda-lime glass is required to form at least 30–40 fragments



Fig. 9 The thermally tempered rear window of an automobile as photographed through a polarizing lens showing clear difference in stress due to the impingement of air jets during the initial quench. Picture adapted from Tal, E.J., 2020. Tempered Glass. Retrieved from Wikicommons: <https://commons.wikimedia.org/w/index.php?Curid=41083207>.

in an area of 50 mm $\times$ 50 mm (1.6 fragments per cm²) for thick glasses > 3 mm, with current Japanese standards requiring at least 60 fragments in the case of thinner glass (Timoshenko and Goodier, 1951; Gulati, 1997).

Therefore, the applicability to refer to a glass article as “tempered” does not solely depend on the stresses produced in the tempering process but is more dependent on the way the glass breaks. Glass articles processed in this manner which possess a residual compressive surface stress, but which do not fracture in the safe manner, are simply referred to as “heat-strengthened”.

It should be noted that strengthening by rapid quenching of the surfaces is the principle behind the famously strong Prince Rupert’s drops, obtained by pouring drops of molten glass in water, creating a strong compressive layer at their surface. These thermally tempered Prince Rupert’s drops can resist hammer blows, but when damaged, explode in very tiny particles; see also (Smarter Everyday, 2013).

Commercial Tempering Processes

In commercial tempered glass manufacturing lines, all necessary cutting, grinding, etching, or finishing is first done on the precursor glass articles – as such sharp contacts after tempering can result in breakage. The prepared glass articles are then fed onto ceramic rollers by continuous feeding or in a batch process in the loading zone. The rollers convey the glass articles into the tempering oven, which is held at a temperature near, but below, the softening temperature of the glass composition being tempered.

For typical soda-lime silicate glasses which are used in most tempered glass applications the oven would be in the range of 600–650°C. Once inside of the oven, the glass is held for a specified time until a uniform temperature is achieved throughout the glass thickness. In more sophisticated tempering lines, the rollers will periodically reverse directions to keep the glass moving at all times and prevent permanent sagging between the rollers. In some innovative new tempering lines, the hot glass is conveyed using an air bed instead of discrete rollers, which enables the glass to be heated to a higher temperature and safely conveyed to the quench – a technology which enables tempered glasses down to 2 mm (Vehmas *et al.*, 2015).

Once the glass reaches a uniform temperature, the glass is conveyed rapidly out of the opposite end of the furnace from which it entered. Upon exiting the furnace, the glass passes between an array of nozzles which momentarily blast high-pressure air onto the glass and rapidly cool the surfaces.

In fact, an observant driver will notice when wearing polarized sunglasses that they may be able to pick out the nozzle pattern used in thermal tempering when looking at the rear window of passing automobiles – an example of which is shown in Fig. 9. After the initial blast, the air pressure is then reduced, and the glass is oscillated under the nozzles to allow it to cool for safe handling, before being subsequently removed from the unloading zone. The finished glass articles are inspected for defects and occasionally taped and broken to confirm that they have achieved “full temper”.

It should be emphasized that the thermal tempering process is based on the controlled formation of stresses in a uniform manner throughout a glass article. This is very complex to achieve in product with a non-uniform thickness profile, such as traditional bottles, and is therefore mainly limited to glass products with uniform thickness profiles (windows, windshields, glass plates, etc.).

As mentioned previously, due to limitations in convection cooling rates and thermal gradients that can be achieved in thin glass articles, thermal tempering is typically limited to articles of thickness 3 mm and above. For thinner articles, e.g., cell phone screens, for which the thickness is typically below 1 mm, strengthening via creation of stress profiles can be obtained using chemical strengthening, or ion-exchange (not discussed here).

Summary

Stresses in glass articles have a strong impact on their mechanical performance. The forming process used during the manufacturing of these articles usually lead to the formation of stresses, non-uniformly distributed, weakening the product. These thermal stresses can be relieved from the glass by performing a controlled thermal treatment called annealing. In the annealing process, the product is heated up at a temperature slightly above its annealing point, and after thermal uniformity is reached, a slow cool down is carried out. Annealing allows one to minimize thermal stresses in the product, but will not reduce stresses arising from defects, inclusions or chemical inhomogeneities. The amount of residual stresses in a product is monitored using polariscopes. Stress measurement is an integral part of the quality control process for a large array of the glass products surrounding us in our everyday lives (windows, bottles, tableware, etc.).

While the thermal stresses formed during the forming process are undesirable, in certain conditions, a controlled formation of stresses via an additional thermal treatment can actually lead to an improvement in the mechanical performance of a product. Thermal tempering is the controlled formation of compressive stresses at the surface of glass products via a rapid quenching process after re-heating the glass close to its softening point. Due to practical limitation in cooling rates achievable, tempering is typically limited to products uniform in thickness, and thicker than 3 mm. Despite these limitations, tempered glass is a very common product on the market. When breaking, tempered glass articles shatter in a characteristic pattern with very small fragments, familiar to most who have witnessed windshields or other “safety glass” breaking event.

In both annealing and tempering processes, the intrinsic properties of the glass (based on its composition), its thermal history, and the size and shape of the glass article are critical parameters that all need to be considered by the glass producers.

References

- Barsom, J., 1968. Fracture of tempered glass. *Journal of the American Ceramic Society* 51 (2), 75–78.
- Doremus, R., 1994. *Glass Science*, second ed. New York: Wiley.
- Gardon, R., 1980. Thermal tempering of glass. In: Uhlmann, D., Kreidl, N. (Eds.), *Glass: Science and Technology Vol.5 - Elasticity and Strength in Glass*. New York: Academic Press, pp. 146–216.
- Guin, J.-P.G., 2019. Mechanical properties of glass. In: Musgraves, D., Hu, J., Calvez, L. (Eds.), *Springer Handbook on Glass*. Cham: Springer International Publishing, pp. 227–271.
- Gulati, S., 1997. Frangibility of tempered soda-lime glass sheet. *Glass Performance Days*. 13–15.
- Hubert, M., 2019. Industrial glass processing and fabrication. In: Musgraves, D., Hu, J., Calvez, L. (Eds.), *Springer Handbook of Glass*. Cham: Springer International Publishing, pp. 1193–1229.
- McKenzie, H., Hand, R., 1999. *Basic Optical Stress Measurement in Glass*. Sheffield: Society of Glass Technology.
- Narayanaswamy, O., 1971. A model of structural relaxation in glass. *Journal of the American Ceramic Society* 54 (10), 491–498.
- Narayanaswamy, O., 1978. Stress and structural relaxation in tempering glass. *Journal of the American Ceramic Society* 61 (3–4), 146–152.
- Redner, A., 1995. Measuring stress in glass production: A key quality control operation. *Glass Production Technology International*. 180–183.
- Schott, A.G., 2019. TIE-27: Stress in Optical Glass. Mainz, Germany.
- Smarter Everyday, 2013. Mystery of Prince Rupert's Drop at 130,000 fps - Smarter Every Day 86. Retrieved from Youtube: <https://www.youtube.com/watch?v=xe-f4gokRBs>.
- Timoshenko, S., Goodier, J., 1951. *Theory of Elasticity*, second ed. New York: McGraw-Hill Book Co.
- Vehmas, J., Kylvaja, H., Rantala, M., 2015. US Patent No. US9617181B2 - Method of Heating a Glass Sheet for Tempering.
- Zhang, L., Guo, X., 2020. Thermal history and its implications: A case study for ion exchange. *Journal of the American Ceramic Society* 103 (7), 3971–3977.

Glass: Chemical and Thermal Strengthening

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Introduction

Glass is a key material of various applications, from windows to packaging containers to screens for electronic devices. Nevertheless, its employment is limited by its brittle nature; not only are oxide glasses characterized by poor mechanical strength but also they are not reliable due to the wide distribution of strength values. Surface flaws decrease the glass strength dramatically in spite of the theoretical strength being of the order of several gigapascals. **Fig. 1** shows the glass strength as a function of the surface crack size; a 1 μm surface defect decreases the strength from the gigapascal range to megapascals (Bradt, 2011; Bradt and Tressler, 2013). The development of stronger glasses could enable the production of lighter products and is, therefore, a key to the extension of glass utilization in new applications. Therefore, several techniques have been developed to improve glass strength: techniques such as etching, polishing and coating are used to increase glass strength by removing or inhibiting surface flaws, while thermal and chemical strengthening improve glass strength by reducing the negative impact of surface flaws by the creation of a residual surface compression layer as originally proposed in the 17th century through the “magical” Prince Rupert’s drop (Wondraczek *et al.*, 2011; Mauro, 2014; Varshneya, 2018).

Thermal tempering and chemical strengthening are the most effective methods for improving the mechanical resistance of glass (Karlsson *et al.*, 2010; Varshneya, 1994, 2018). Both techniques rely, basically, on the production of a compressive layer in the glass surface that shields the surface cracks and prevents their propagation; hence, the intensity of the surface compression and the thickness of the surface compression layer are crucial parameters. Thermal tempering has been abundantly used to reinforce glass used in automotive and architectural applications, furniture and kitchenware. Chemical strengthening has attracted much attention since the introduction of electronic devices with displays covered by a thin glass layer and the subject has renewed interest in recent times as demonstrated by several recent scientific publications (Varshneya, 2006, 2010a,b, 2018).

In the present chapter, the two strengthening methods, chemical strengthening and thermal tempering, are compared. The generation of surface compression and the kinetics of the processes are reviewed. Moreover, some non-conventional innovative methods for ion-exchange strengthening are mentioned.

Thermal Tempering

Thermal tempering is the most common technique for improving the mechanical strength of flat or almost-flat soda-lime silicate or borosilicate glass bodies. It is based on the generation of a surface compressive stress by a very rapid cooling of the glass body from a temperature well above the strain point (Shelby, 2005; Wondraczek *et al.*, 2011; Varshneya and Mauro, 2019; Sheth *et al.*, 2019).

The process consists of two fundamental stages: initially, the glass component is heated in a first chamber at the specified “tempering temperature”; then, it is quickly moved into a second chamber where is subjected to a very rapid cooling under the effect of compressed air forcedly blown on its surface. Here, since the surface cools down faster than the interior of the glass, a

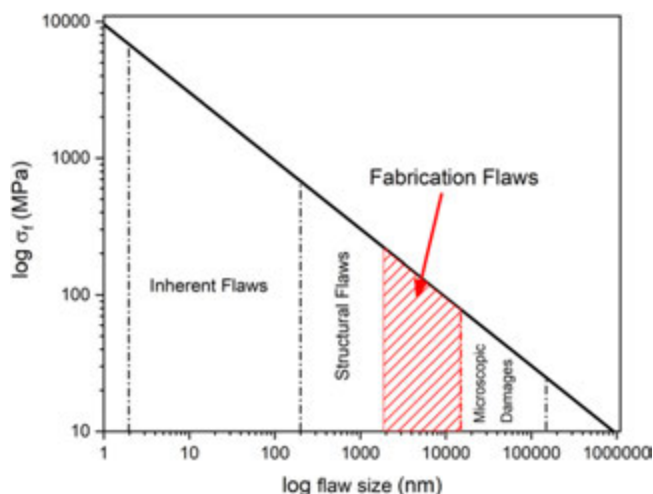


Fig. 1 Tensile strength versus surface flaw size in soda lime silica glass. Reproduced from Bradt, R.C., 2011. The fractography and crack patterns of broken glass. *Journal of Failure Analysis and Prevention* 11, 79–96. Bradt, R.C., Tressler, R.E., 2013. *Fractography of Glass*. New York: Springer.

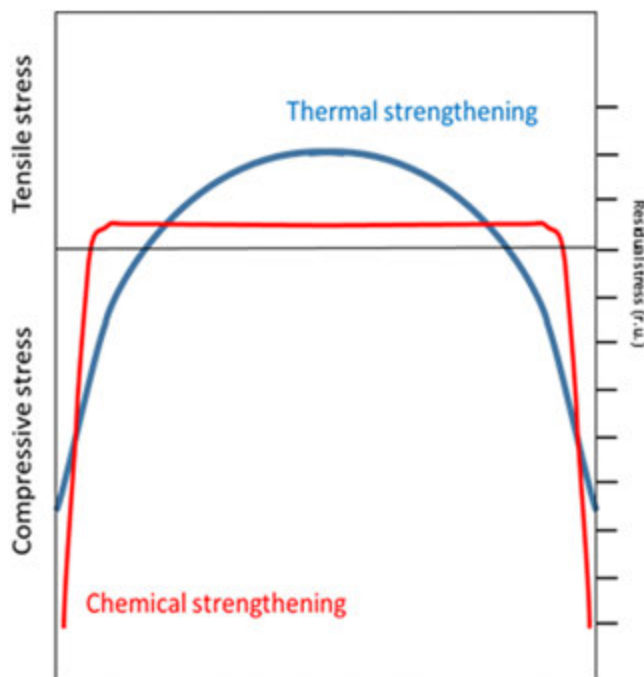


Fig. 2 Residual stress distribution in glass subjected to chemical strengthening and thermal strengthening.

temperature gradient is created with the glass still being above the strain point, i.e., without the formation of significant stresses due to viscoelastic relaxation. However, as the surface reaches room temperature, the core is still warm, although being in a “solid-elastic” regime, and final cooling down to room temperature places it into tension while the surface goes into compression. The generated compressive stress, embracing about one fifth of the thickness of the glass on both surfaces, reinforces the area around surface flaws and improves the glass strength (Shelby, 2005; Karlsson *et al.*, 2010). A parabolic shape characterizes the stress profiles produced by thermal strengthening, resembling the temperature gradient created upon cooling (Shelby, 2005; Gardon, 1980; Varshneya, 1994). A typical residual stress profile produced by thermal tempering is shown in Fig. 2 (and compared to that generated by chemical strengthening) where it is clear that the core of the material is subjected to significant residual tensile stress.

Depending on the glass thickness and especially on the processing conditions (fundamentally, tempering temperature and cooling speed), the intensity of the residual stress (surface compression and corresponding core tension) can be varied. According to ASTM C1048-18 standard, if the surface compression is larger than 67 MPa the glass is defined as fully tempered or toughened; when the surface compression is between 24 and 52 MPa the glass is classified as heat strengthened (ASTM C1048 – 18, 2018). Correspondingly, with reference to the EN 12150 European norm, the characteristic bending strength is 120 MPa or 70 MPa for toughened and heat strengthened glass, respectively. In the former, due to the very intense tension in the core, when fracture occurs, the very large amount of strain energy can be dissipated by the formation of many surfaces and the glass shatters. The resulting small fragments are harmless (compared with big sharp glass fragments produced in annealed or heat strengthened glass) and toughened glass is therefore classified as safety glass (Veer *et al.*, 2009).

The deep surface compression produced by thermal tempering reinforces the area around large surface cracks. Nevertheless, there is a physical limit for the thickness of a glass to be thermally tempered, commonly around 2 mm; thinner glass cannot be strengthened to a significant extent due to the small temperature gradient which can be generated upon quenching. Moreover, thermal tempering is difficult to be applied to specimens with complex shape since the cooling effect generated by compressed air cannot be uniform on both surfaces for components which are essentially different from plate glass. Optical distortions represent an additional critical issue for thermally strengthened glass; they are generated because of the maintenance of the component at temperatures higher than the strain point before final quenching.

One final unusual aspect is the possibility for thermally toughened glasses to break spontaneously. Such phenomena can occur because of the presence of NiS inclusions in the glass core retained in a metastable state because of the very high cooling rates. If the transformation to the stable phase occurs, volume increases and this generates defects in the region under tensile stress which can lead to shattering (Kasper, 2019).

Chemical Strengthening

Chemical strengthening, also known as ion-exchange strengthening, is usually carried out by replacing smaller alkali ions in the glass, e.g., Li^+ and Na^+ , with larger alkali ions, e.g., K^+ , at a temperature below the glass transition temperature (Evers, 1969;

Varshneya, 2010a,b; Karlsson *et al.*, 2010; Mazzoldi *et al.*, 2013). Stuffing larger ions into the smaller alkali sites produces a compressive layer near the glass surface that reinforces the area around surface flaws and improves the mechanical strength of the glass. Although the compressive layer is smaller than the one produced by thermal strengthening, the surface compressive stress is larger (Fig. 2). Since the alkali ions are substituted during ion-exchange, chemical strengthening is usually applied to improve the strength of glasses containing significant amounts of alkali ions (Talimian and Sglavo, 2017a; Saunders and Kubichan, 1969; Gy, 2008; Varshneya, 2010a; Varshneya and Kreski, 2012). However, there are few reports claiming that this concept can be extended to replacing alkali-earth ions and improving the strength of alkali-free glasses (Mauro *et al.*, 2016).

Typical chemical strengthening techniques are based on the exchange of alkali ions. Larger ions, usually potassium, penetrate the glass surface and take the place of smaller alkalis, i.e., lithium or sodium. The “stuffing effect” accounts for the creation of compressive stresses which depend on the concentration of the invading ions. The process is typically carried out by placing the glass components in a molten salt bath (usually, KNO_3) for several hours at a temperature below the T_g . The thickness of the compressive layer, called case depth, depends on the depth of the ion-exchange layer which, in turn, depends on the inter-diffusion of alkalis.

Kinetics of the Chemical Reaction Between Salt and Glass

The following chemical reaction describes the chemical reaction between the glass surface and molten salt:



Garfinkel (1968) reported that the cation concentration at the glass surface, A_{glass}^+ , increases gradually with the concentration of ions in the salt, A_{salt}^+ , according to a sigmoid function; however, in practice, it is assumed that the equilibrium is established immediately after the immersion of glass in the molten salt. Araujo *et al.* explained the final concentration of alkali ions at the glass surface on a thermodynamic basis: the equilibrium between the glass surface and the salt bath is established when the difference of chemical potential of alkali ions in salt and glass is the same according to (Araujo, 2004; Araujo *et al.*, 2003; Araujo, 1993):

$$\mu_A^{\text{glass}} - \mu_A^{\text{bath}} = \mu_B^{\text{glass}} - \mu_B^{\text{bath}} \quad (2)$$

where μ_i^j is the chemical potential of elements of alkali cations in glass or salt and it is given by:

$$\mu_i^j = \frac{\partial(-kT \ln Q)}{\partial N_i} \quad (3)$$

where N_i is the number of ions, k is the Boltzmann constant and Q the partition function:

$$Q = q_A^{N_A} q_B^{N_B} \sum_{N_{AB}} \Omega(N_A, N_B, E(N_{AB})) \exp\left(\frac{-E(N_{AB})}{kT}\right) \quad (4)$$

where q_i is the partition function of the phase of interest (glass or salt) when it contains only ions of i . The mixing energy of different ions must also be considered when several ions are present. The summation part of Eq. (4) represents all possible values of interaction energy. Ω is the number of states of a particular interaction that can be estimated in simple systems; the detailed calculations can be found in previous work (Araujo, 2004; Fu and Mauro, 2013). By using the molar concentration of elements X_i and considering the bond strength changes in the salt and glass, the equilibrium constant, K_{eq} , is given by:

$$K_{\text{eq}} = \left(\frac{X_A^{\text{glass}} X_B^{\text{bath}}}{X_B^{\text{glass}} X_A^{\text{bath}}} \right) F(\text{bath}) F(\text{glass}) = \frac{q_A^{\text{glass}} q_B^{\text{bath}}}{q_B^{\text{glass}} q_A^{\text{bath}}} \quad (5)$$

where F is the Helmholtz free energy, which is a function of the interactions of atoms and ions in the salt bath and glass. In a system where the temperature and salt composition are not changing, the degree of freedom becomes zero. Therefore, there is a unique glass surface composition that, in turn, determines the chemical driving force for the diffusion of cations into the glass. It should be noted that the difference in chemical potentials is also affected by various parameters such as the polarization of ions in the salt (Garfinkel, 1968; Nordberg *et al.*, 1964).

The exchange of ions between the glass surface and interior parts occurs by the interdiffusion. Potassium ions diffuse inward, and glass alkalis, i.e., sodium ions, diffuse outward. During the ion-exchange process, the electric charge and mass remain balanced and, hence, the flux of ions is the first requirement of the process. Therefore, the total ions flux gradient should be zero to satisfy the charge neutrality:

$$\nabla \cdot J_A + \nabla \cdot J_B = 0 \quad (6)$$

Jost (1960) employed the flux gradient balance and described the mutual-diffusivity as a function of the number of ions in a small volume, N , and the diffusivity of every individual ion. The mutual diffusivity for a binary exchange can be written as:

$$\tilde{D} = \frac{D_A D_B}{N_A D_A + N_B D_B} \quad (7)$$

where D_A and D_B are the self-diffusion coefficients. The mutual-diffusivity is a function of the mobile ions ratio involved in ion-exchange. Therefore, mutual diffusivity is a function of distance from the surface (Araujo, 2004; Araujo *et al.*, 2003), and the diffusion equation can be written as

$$\frac{\partial C}{\partial x} = \frac{D_K}{1 - \alpha C} \left[\frac{\partial^2 C}{\partial x^2} + \frac{\alpha}{1 - \alpha C} \left(\frac{\partial C}{\partial x} \right)^2 \right] \quad (8)$$

where α depends on the ratio between the diffusion coefficient of ions, $\alpha = 1 - (D_K/D_{Na})$. Varshneya and Milberg (1974) have reported on the variable inter-diffusion coefficient in potassium-sodium ion-exchanged borosilicate glasses and the variation of the diffusion coefficient is related to the mixed alkali effect in silicate glass reported by Doremus (1974) and by Lacharme (1970). Ingram *et al.* (2000, 2005) have reported that a series of structural modifications account for the coefficient variations. Such variations have been usually reported for long ion-exchange treatments or particular glass compositions.

The produced concentration profiles using chemical strengthening can be fitted well by using a complementary error function where the diffusivity is considered constant (Varshneya, 2010a):

$$\frac{C(x, t) - C_i}{C_s - C_i} = \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right) \quad (9)$$

where C_s is the concentration of potassium at the surface of ion-exchanged glass, C_i the potassium concentration of the as-received glass and t is the time. The inter-diffusion coefficient, D , depends on temperature following the Arrhenius' law:

$$D = D_0 \exp \left(\frac{-Q}{RT} \right) \quad (10)$$

where Q is the activation energy and R the perfect gas constant. The activation energy of ion-exchange can be measured by performing a series of ion-exchanges at various temperatures; the interdiffusion coefficient can be measured by fitting the produced concentration profiles using Eq. (9), and the activation energy can be determined using Eq. (10). Table 1 summarizes the interdiffusion coefficient of alkali ions in soda lime silica and alkali-silicate glasses. The activation energy of the alkali ions interdiffusion in silicate glasses is generally between 120 and 160 kJ mol⁻¹.

Fig. 3 shows the potassium concentrations profile in an alkali-borosilicate glass subjected to ion-exchange in pure potassium nitrate salt at 450 and 465°C; the profiles were fitted using Eq. (9) (Talimian and Sglavo, 2017b), assuming the diffusion coefficient to be composition independent. However, as pointed out above, in some conditions (e.g., for high temperature or long duration processes), Eq. (9) overestimates the depth of the ion-exchanged layer (as in the sample subjected to ion-exchange at 465°C). Therefore, more complex models should be used to fit the concentration profiles and estimate the diffusion coefficients:

Table 1 Typical interdiffusion coefficient, D , of alkali silicate and soda-lime silica glass at the ion exchange temperature

Diffusing ions	D (cm ² s ⁻¹)	
	20R ₂ O.80SiO ₂ (at 400°C)	Soda-lime-silica glass (at 530°C)
K ⁺	4.0×10^{-10}	1.2×10^{-11} (at 450°C)
Rb ⁺	4.5×10^{-10}	1.2×10^{-11}
Cs ⁺	1.1×10^{-11}	5.4×10^{-12}

Note: Schneider, S.J., 1991. Engineered Materials Handbook: Vol. 4. Ceramics and Glasses. CRC Press. (ASM International Handbook Committee). Karlsson, S., Jonson, B., Wondraczek, L., 2012. Copper, silver, rubidium and caesium ion exchange in soda lime silica float glass by direct deposition and in line melting of salt pastes. Glass Technology - European Journal of Glass Science and Technology A 53, 1–7.

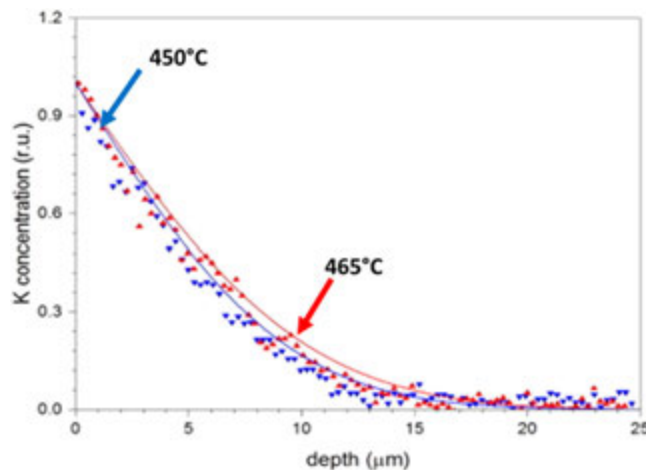


Fig. 3 Potassium concentration vs. depth in sodium borosilicate glass subjected to Na/K ion-exchange for 4 h at 450°C and 465°C. Reproduced from Talimian, A., Sglavo, V.M., 2017b. Ion-exchange strengthening of borosilicate glass: Influence of salt impurities and treatment temperature. Journal of Non-Crystalline Solids 456, 12–21.

one possibility is to use the Boltzmann-Matano method based on microprobe chemical analysis as well as employing complex models available for inter-diffusion (Lupascu *et al.*, 1996).

Stress Generation by Ion-Exchange

Ion-exchange produces a layer in the glass surface whose molar volume is larger than the substrate due to the stuffed alkali ions; this results in the generation of surface compression. The build-up of compressive stress is assumed to be similar to the thermal stress in metals subjected to nitridation (Varshneya *et al.*, 2015; Varshneya, 2010a,b, 2006). Therefore, by using the thermo-elasticity analogy, the stress-strain relationship for an element located in the ion exchange layer (Fig. 4) where all alkali ions are replaced with the larger invading ions can be written as:

$$\begin{aligned}\varepsilon_{xx} &= \left(\frac{1}{E}\right) [\sigma_{xx} - \nu(\sigma_{yy} + \sigma_{zz})] + BC \\ \varepsilon_{yy} &= \left(\frac{1}{E}\right) [\sigma_{yy} - \nu(\sigma_{xx} + \sigma_{zz})] + BC \\ \varepsilon_{zz} &= \left(\frac{1}{E}\right) [\sigma_{zz} - \nu(\sigma_{yy} + \sigma_{xx})] + BC \\ \varepsilon_{xy} &= \frac{\sigma_{xy}}{G}; \varepsilon_{yz} = \frac{\sigma_{yz}}{G}; \varepsilon_{xz} = \frac{\sigma_{xz}}{G}\end{aligned}\quad (11)$$

where C is the concentration of invading ions (i.e., potassium), while E , G and ν are the Young's modulus, shear modulus and Poisson's ratio, respectively. B is the linear strain of glass per unit concentration change of alkali oxide, otherwise defined as linear network dilation coefficient (LNDC):

$$B = \frac{1}{3\Delta C} \frac{\Delta V}{V_0} \quad (12)$$

In a semi-infinite plate which is ion-exchanged in the x -direction, the plate is allowed to expand freely in such direction; therefore, the generated stress along the x -axis, σ_{xx} , is zero. The bulk glass constrains the surface layers; therefore, there is no strain in the y or z -axes, $\varepsilon_{yy} = \varepsilon_{zz} = 0$. By applying these boundary conditions to Eq. (11), the generated stress can be estimated as:

$$\sigma_{yy} = \sigma_{zz} = -\frac{BEC}{1-\nu} \quad (13)$$

The following equation was adopted to describe the generation of surface compression in glasses subjected to ion exchange as a function of the invading ions concentration, C , (Cooper and Krohn, 1969; Garfinkel and King, 1970):

$$[\sigma_{yy}]_x = [\sigma_{zz}]_x = -\frac{BEC}{1-\nu} + \left(\frac{BE}{\delta(1-\nu)}\right) \int_0^\delta C(x)dx \quad (14)$$

where δ is the thickness of the glass. The second term represents the balancing tension generated because of the compatibility of the exchanged layer to the uninfluenced bulk glass. It is clear that stress relaxation at high temperature is not considered in

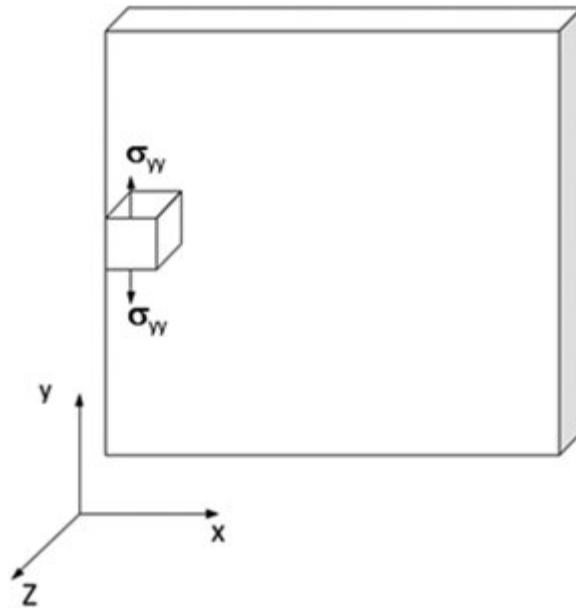


Fig. 4 Schematic unit of a semi-infinite glass sheet subjected to ion exchange along x -axis. Only the generated stress in one direction is shown.

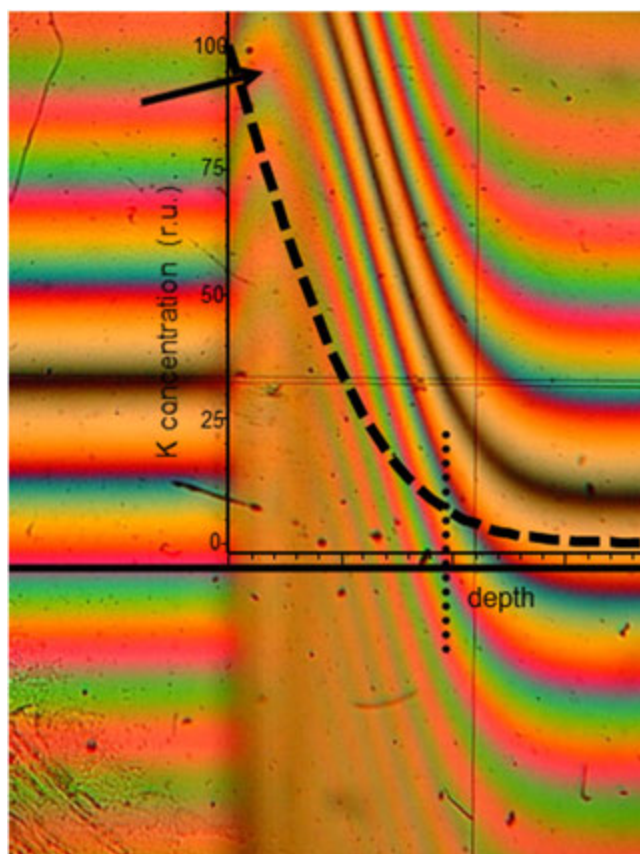


Fig. 5 Polariscope side view of chemically strengthened glass and the corresponding potassium concentration profile; the arrow shows the maximum compressive stress location. Reproduced from Gy, R., 2008. Ion exchange for glass strengthening. *Materials Science and Engineering: B* 149, 159–165.

Eq. (14). Cooper and Krohn (1969) have investigated such stress relaxation and the compressive stress produced by ion exchange after time t was estimated as:

$$\sigma_{yy}(x, t) = \frac{-BE}{1-\nu} \left(\frac{1}{\delta} \int_0^{t_1} R(t_1 - t) \left(\frac{\partial}{\partial t} \int_0^\delta C(x) dx \right) dt \right) \quad (15)$$

where R and t_1 are the normalized relaxation function and the ion exchange time, respectively. The first perception of the compression profile is that the compressive profile follows the concentration profile produced by ion exchange (Shen and Green, 2004a,b). Eq. (15) predicts that the maximum compression is produced at the glass surface. Fig. 5 shows the cross-section of a silicate glass subjected to chemical strengthening observed by polarized light, the typical potassium concentration profile being overlapped. The maximum compressive stress is located below the surface (Gy, 2008). The ion-exchanged layer is composed of a series of glass layers with slightly different composition, thus being characterized by different relaxation behavior which can be affected also by some salt bath impurities like water (Sane and Cooper, 1987; Lezzi *et al.*, 2014; Lezzi and Tomozawa, 2015; Seaman *et al.*, 2014; Tomozawa *et al.*, 2001).

Generally, the estimated surface compression is significantly larger than the measured and this is accounted for by the dilation glass network (Tandia *et al.*, 2012; Kreski *et al.*, 2012).

By assuming that the ion-exchanged glass has a molar volume similar to the compositionally equivalent as-melt glass, CEAM, LNDC is given by:

$$B = \left(\frac{1}{3C_0} \right) \ln \left(\frac{V_{CEAM}}{V_{Raw}} \right) \cong \frac{V_{CEAM} - V_{Raw}}{3V_{Raw}C_0} \quad (16)$$

where C_0 is the mole fraction of alkali glass in the exchanged layer and V_{Raw} the molar volume of the raw glass. The volume change is divided by three in order to obtain the linear dilation (Varshneya *et al.*, 2015). The estimated LNDC is usually about three to five times larger than the values measured from the stress profiles, this phenomenon being known as “dilation anomaly” (Varshneya *et al.*, 2015; Varshneya, 1975). Plastic deformation can occur upon stuffing larger ions into the glass and it is probably responsible for the observed differences (Varshneya, 2010b). Several efforts have been made to improve the understanding of network dilation

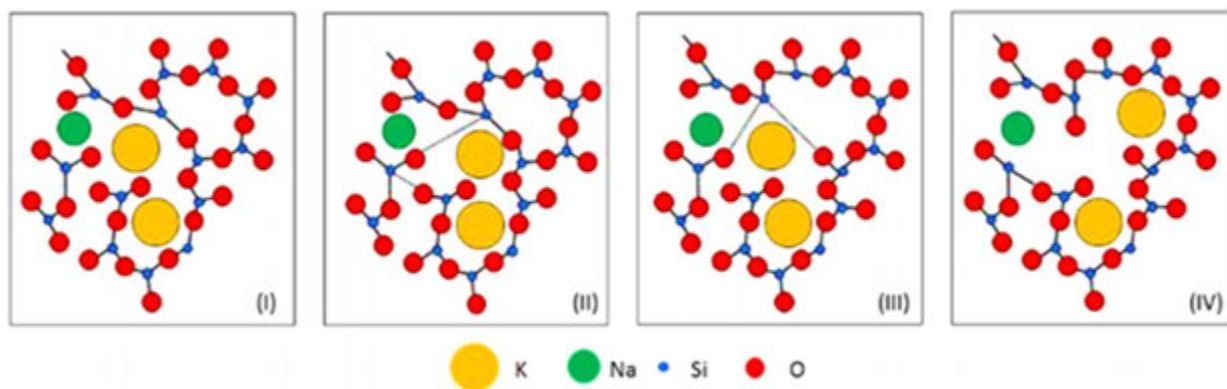


Fig. 6 Schematic illustration of structural modification of glass by breaking and reforming of bridging oxygen atoms during ion exchange. The bridging oxygen of a Q^4 group is stretched, weakened, broken and recombined with a Q^2 to accommodate a larger potassium cation. Reproduced from Ingram, M.D., Davidson, J.E., Coats, A.M., Kamitsos, E.I., Kapoutsis, J.A., 2000. Origins of anomalous mixed-alkali effects in ion-exchanged glasses. *Glass Science and Technology* 73, 89–104. Varshneya, A.K., Olson, G.A., Kreski, P.K., Gupta, P.K., 2015. Buildup and relaxation of stress in chemically strengthened glass. *Journal of Non-Crystalline Solids* 427, 91–97.

anomaly. Although the source of the dilation anomaly is controversial (Varshneya, 2010a), the glass relaxation, both structural and stress, are known to be responsible for such anomaly.

Temperature provides the required activation energy for stress relaxation; therefore, ion-exchange carried out for long times may result in the loss of the compressive stress (Varshneya *et al.*, 2015; Gutzow *et al.*, 2011; Shen *et al.*, 2003; Seaman *et al.*, 2014; Sane and Cooper, 1987). Therefore, stress relaxation is considered to be the main reason for the difference between the compressive stress profiles and potassium ion concentration profiles in samples (Tyagi and Varshneya, 1998; Varshneya *et al.*, 2015; Shen *et al.*, 2003). Several efforts have been made in order to formulate the correlation of residual stress and potassium concentration profiles. (Macrelli, 2018; Macrelli *et al.*, 2019, 2020). Nevertheless, even when stress relaxation due to viscous flow is considered in chemically strengthened glass (Varshneya, 2010a; Green, 2008), the surface compression is always significantly smaller than the estimates (Varshneya, 2016; Varshneya *et al.*, 2015). Varshneya (2016) has proposed a model to explain the reason for the limited residual stress. The model predicts that a series of structural changes occur in glass to host larger ions; this results in the production of smaller surface compression (Varshneya, 2016; Varshneya *et al.*, 2015; Ingram *et al.*, 2005). Cation-induced relaxation of the network, CIRON, has been proposed to describe the stress loss by short-range structural evolutions (Ingram *et al.*, 2005; Sglavo *et al.*, 2014). In such a model, the diffusion of cations into the glass occurs by breaking the bridging oxygens corresponding to Q^2 and Q^4 species and the formation of new Q^3 species. Fig. 6 shows a schematic illustration of structural modification in the diffusion pathway of potassium ions in a silicate glass (Ingram *et al.*, 2005, 2000). The glass layer with the new structure has a smaller volume; consequently, the resulting compression is smaller.

Although the ion-exchanged glass is more stable after the mentioned structural relaxation processes, its structure and, therefore, the volume is different from the glass with similar chemical composition produced by melting (Varshneya *et al.*, 2015; Varshneya, 2016). Therefore, the stress-free ion-exchanged glass is also called “forbidden glass” due to the different structure from the as-melted glass (Mauro and Loucks, 2009). It is worth mentioning that the structural evolution and stress relaxation of glass during ion exchange and chemical strengthening are open questions and need to be answered.

After the initial structural relaxation, the glass undergoes long-range structural relaxations that produce a glass structure similar to that which is obtained in a glass synthesized by melting the same chemical composition; these processes may last several years at low temperatures (Potuzak *et al.*, 2011; Lu *et al.*, 1999; Gutzow *et al.*, 2011). Although the stress loss includes various processes from very fast, picoseconds, to very slow, decades, the relaxation processes occurring in an intermediate time are of interest for chemical strengthening. Thus, viscous flow of glass has been considered responsible for stress relaxation, which is represented by mechanical models which essentially consist of Burger elements, a Maxwell and a Voigt-Kelvin element in series, attached to a rigid support (Varshneya, 2016; Tyagi and Varshneya, 1998; Sane and Cooper, 1987; Shen *et al.*, 2003).

Another approach to analyze the relaxation behavior is the stretched exponential model, proposed empirically by Kohlrausch (1847); it fits well the stress relaxation behavior of disordered and quenched molecular systems (Potuzak *et al.*, 2011; Lu *et al.*, 1999; Phillips, 1996). The property subject to relaxation, which is the surface stress, is a function of time:

$$\sigma_t^R = \sigma_0^R e^{-(t/\tau)^\gamma} \quad (17)$$

where σ_t^R and σ_0^R are the residual stress and the zero-time residual stress, respectively, t is time, τ the relaxation time, and γ the exponent factor which accounts for the non-Maxwellian behavior of the glass (Varshneya *et al.*, 2015). This function can also be used for structural relaxations in the frequency domain (Lu *et al.*, 1999; Phillips, 1996).

Eq. (17) has only two free parameters: the relaxation time and the stretching exponent, where $0 < \gamma \leq 1$. Low values of γ correspond to more complex relaxation mechanisms (Phillips, 1996; Gutzow *et al.*, 2011). Two particular values for γ are expected for inhomogeneous glassy systems: $\gamma = 0.6$ for short-range transitions such as stress relaxations and $\gamma = 0.43$ for long-range

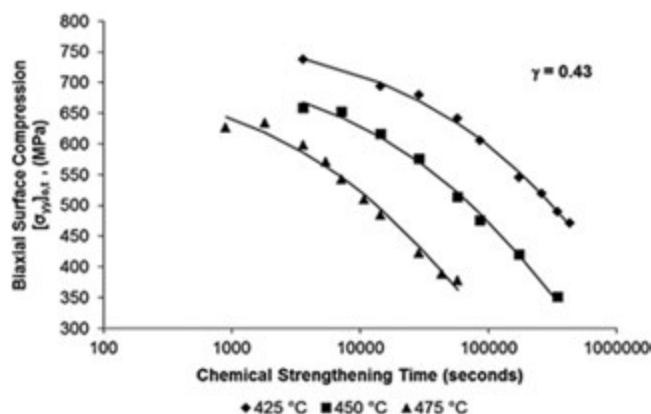


Fig. 7 Surface compression in ion-exchanged soda lime silica glass as a function of chemical strengthening time; ion-exchange was performed at 425, 450 and 475°C. The experimental data are fitted with Eq. (17). Reproduced from Varshneya, A.K., Olson, G.A., Kreski, P.K., Gupta, P.K., 2015. Buildup and relaxation of stress in chemically strengthened glass. *Journal of Non-Crystalline Solids* 427, 91–97.

structural relaxations (Potuzak *et al.*, 2011). These numbers are known as “magic” values of glass relaxations; these numbers were deduced from the axiomatic diffusion trap model and had been validated using commercial glass specimens (Potuzak *et al.*, 2011; Phillips, 1996). Fig. 7 shows the residual compressive stress in soda-lime silica glass as a function of chemical tempering time and temperature; the experimental data is fitted using Eq. (17) with $\gamma = 0.43$.

Typically, the relaxation time lies between 10^5 and 10^7 s for the temperatures at which ion exchange is carried out. Moreover, the relaxation temperature is well fitted by the Vogel-Fulcher expression (Gutzow *et al.*, 2011; Varshneya, 2006; Doremus, 1994):

$$\tau(T) = \tau_0 e^{-Q \frac{T - T_0}{T_0}} \quad (18)$$

where T is the relaxation temperature, and T_0 and Q being Vogel-Fulcher parameters which are obtained by fitting the experimental data with Eq. (18).

For successful chemical strengthening, strong compressive stress with enough depth is a must to reinforce the surface around flaws and, consequently, increase the mechanical strength. Because of the diffusional nature of the process, producing the desired exchanged layer requires the glass to be subjected to elevated temperatures for several hours. Therefore, finding the critical parameters and their influences are the very first requirements of chemical strengthening of glass.

Chemical Tempering Methods

Four fundamental approaches can be used to perform chemical strengthening. In the most typical method glass is immersed in molten salt containing the invading alkali ions, i.e., Na^+ and K^+ ; alternatively, a mixed salts layer which partially melts at the ion exchange temperature can be applied on the glass surface; some processes can be carried out by using vapor-phase exchange; finally, electric field-assisted methods can be used (Karlsson *et al.*, 2010; Gy, 2008; Varshneya and Kreski, 2012; Varshneya, 2010a, 2018). Less common methods such as plasma, pressure or microwave-assisted methods have been advanced in the past which are not discussed here.

Chemical Tempering Using Molten Salt

The use of a molten salt is the most common industrial method for performing chemical strengthening. Glass components are placed for several hours in a steel vessel containing the molten salt. In most common practices silicate glasses containing enough alkalis, lithium or sodium, are immersed in molten potassium nitrate at a temperature below the glass strain point. Although there are several parameters influencing the ion-exchange process and, in turn, the efficiency of chemical strengthening, the basic factors that require to be optimized are:

- (1) temperature and time;
- (2) glass composition;
- (3) salt bath composition.

Glass composition

The chemical composition of the host glass has a major influence on the mobility of ions, generation of compression and stress relaxation. Since alkali ions are exchanged, the glass must contain a significant amount of alkalis such as lithium or sodium; therefore, alkali containing glasses are generally strengthened by chemical tempering. Aluminosilicate glasses show the highest

strength increase due to high alkali diffusivity and low-stress relaxation (Varshneya and Milberg, 1974; Morris *et al.*, 2004; Yoshida *et al.*, 2004; Varshneya and Spinelli, 2009; Xinwei and Rüdiger, 2011; Jiang *et al.*, 2013; Aaldenberg *et al.*, 2016). Although soda-lime silica glasses contain a larger amount of sodium than aluminosilicate glasses, the generated compressive stress is smaller due to the more rapid stress relaxation of soda-lime silica glass (Tool, 1948; Shen *et al.*, 2003; Shen and Green, 2004a,b; Doremus, 1974; Varshneya *et al.*, 2015). Alkali-borosilicate glass shows typically a moderate increase in the strength because of the limited concentration of alkali ions (Talimian and Sglavo, 2017a,b; Varshneya and Milberg, 1974).

Several efforts have been made to improve the efficiency of chemical strengthening by optimizing the glass composition. Deeper ion-exchanged layers can be produced in glasses containing two alkali oxides, i.e., sodium and potassium; however, this accelerates the stress relaxation. The strength of aluminosilicate glasses can be improved by increasing Al_2O_3 concentration until it reaches the same concentration as the alkali oxides. While increasing the amount of aluminum oxide has a small influence on the strengthening of soda lime silica glass, the concentrations of magnesium oxide and calcium oxide are important to improve the concentration of exchange ions. (Karlsson *et al.*, 2010; Gross, 2019; Tandia *et al.*, 2019) The addition of some oxides such as P_2O_5 and ZnO is claimed to be beneficial for chemical tempering; conversely, both lead and boron are known to have a negative influence. Effects of chemical composition on the glass properties are complex, particularly when several components are present. Hence, machine learning models have been applied in glass design; this can enable the development of new glass compositions with desired properties such as high diffusivity of alkali ions and high resistance to stress relaxation. (Tandia *et al.*, 2019; Onbaşı *et al.*, 2020).

Temperature and time

Inter-diffusion of alkali ions in the glass is the fundamental process for chemical tempering; therefore, time and temperature are two basic factors affecting the depth and the composition of the ion-exchanged layer. An appropriate temperature provides the required activation energy for the inter-diffusion of alkali ions and, therefore, the depth of the ion-exchanged layer can be tailored by performing ion-exchange at various temperatures. Fig. 8 shows potassium concentration profiles produced in soda-lime silica glass by performing ion exchange at 420, 460 and 490°C for 72 h.

Although deep ion-exchanged layers can be obtained at higher temperatures, processes carried out close to the strain point result in the relaxation of the generated surface compression (Shen *et al.*, 2003). Fig. 9 shows relaxation of compressive stress of 100 MPa in a soda-lime glass subjected to various temperatures. The surface compression reduces very rapidly (in a few minutes) at temperatures higher than 500°C that makes chemical strengthening essentially impractical.

The activation energy for inter-diffusion of alkali ions is of the order of 120–160 kJ mol^{-1} , while the activation energy of stress relaxation by viscous flow is in the range 300–600 kJ mol^{-1} (Varshneya and Mauro, 2019). Therefore, generally, performing ion-exchange at lower temperatures produces larger surface compression.

Salt bath composition and impurities

The composition of the salt bath has an important effect on the ion-exchange and the final properties of chemically strengthened glass. The salt composition affects the glass surface composition and, consequently, modifies the final properties of the glass. In fact, as the chemical potential of ions depends on their concentration in the salt bath, one would expect that any variation of molten salt bath composition should change the ion-exchange process. Fu and Mauro (2013) reported on the dependence of the mutual diffusion coefficient on glass and salt and showed that the contamination of potassium nitrate with limited amounts of sodium could be beneficial to the inter-diffusion process. Hassani and Sglavo (2019) have studied the effect of potassium nitrate systematically contaminated with sodium on the chemical strengthening of soda lime silica glass. Fig. 10 shows the surface compression produced by chemical strengthening in salt baths containing different amounts of sodium contamination. Interestingly, only relatively large amounts of sodium (in excess to 1 wt%) show an impact on surface compressions, the case depth appearing to be independent of sodium contamination.

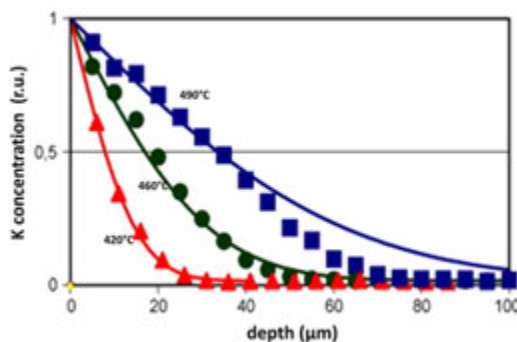


Fig. 8 Potassium concentration profiles in samples subjected to Na/K ion-exchange for 72 h at 420, 460 and 490°C. The solid line represents the data fitted using Eq. (9). Reproduced from Gy, R., 2008. Ion exchange for glass strengthening. Materials Science and Engineering: B 149, 159–165.

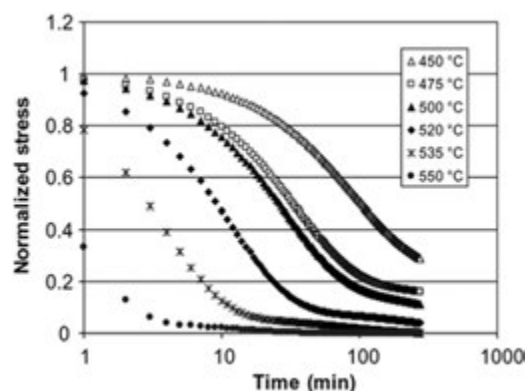


Fig. 9 Normalized residual stress vs. time in soda-lime silica glass at various temperatures. Reproduced from Shen, J., Green, D.J., Tressler, R.E., Shelleman, D.L., 2003. Stress relaxation of a soda lime silicate glass below the glass transition temperature. *Journal of Non-Crystalline Solids* 324, 277–288.

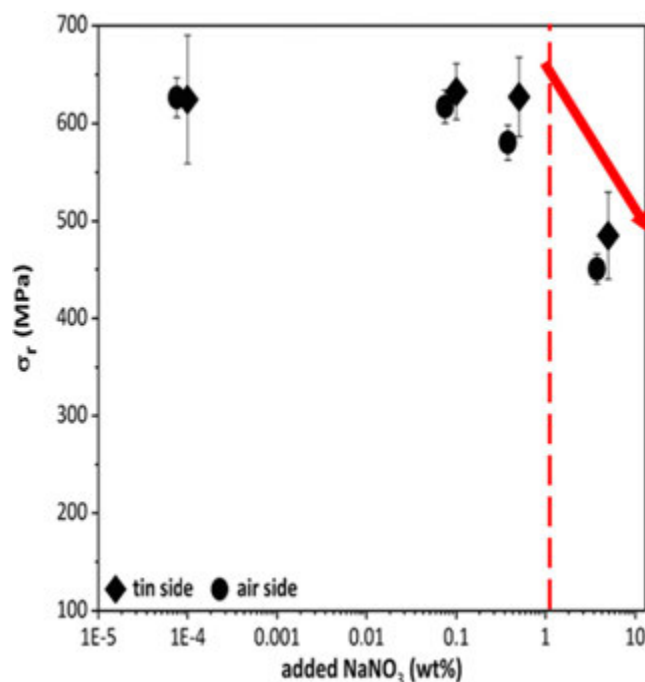


Fig. 10 Surface compressive stress vs. the concentration of sodium impurity in potassium nitrate; the samples were subjected to ion exchange at 450°C for 4 h. Reproduced from Hassani, H., Sglavo, V.M., 2019. Effect of Na contamination on the chemical strengthening of soda-lime silicate float glass by ion-exchange in molten potassium nitrate. *Journal of Non-Crystalline Solids* 515, 143–148.

Conversely, alkaline earth cations, such as calcium or magnesium, have a detrimental impact on the chemical strengthening of glasses. Potassium nitrate salt bath contaminated by limited amounts of calcium or magnesium are considered “non-functional” since the resulting surface compression in the glass is much smaller than that produced using pure potassium nitrate (Kolitsch *et al.*, 1981; Sglavo, 2019; Sglavo *et al.*, 2017). Fig. 11 shows the impact of a few ppm of calcium on the surface compression of soda-lime silica glass subjected to ion-exchange at 450°C for 4 h. Calcium ions can block $\text{Na}^+ \text{-K}^+$ ion-exchange by taking the alkali site on the glass surface.

Water is another source of salt contamination in chemical strengthening; it can diffuse into the glass surface and affect the stress relaxation (Seaman *et al.*, 2014; Tomozawa *et al.*, 2001).

The increase of impurity concentration and contamination of salt may result in the deactivation of the salt bath after several ion-exchange processes; hence, a new salt bath should be used to obtain the desired properties. However, using pure salts has an economic drawback as well as environmental concerns about the disposal of the contaminated salt. Therefore, several solutions, such as using mixtures of old salts and pure potassium nitrate or the addition of some chemical, such as Si(OH)_4 , have been proposed.

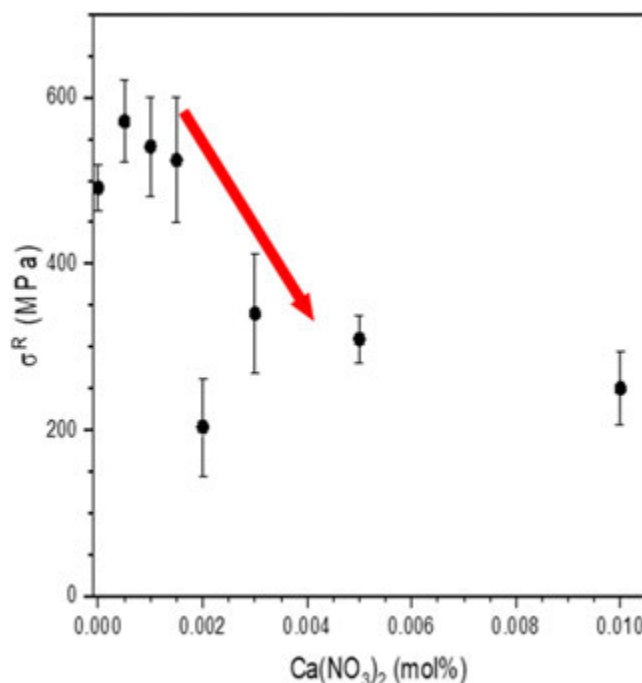


Fig. 11 Surface compressive stress vs. calcium contamination of potassium nitrate; soda lime silica glass was subjected to ion exchange at 450°C for 4 h. Reproduced from Sglavo, V.M., Talimian, A., Ocsko, N., 2017. Influence of salt bath calcium contamination on soda lime silicate glass chemical strengthening. *Journal of Non-Crystalline Solids* 458, 121–128.

Molten Salt-Free Chemical Strengthening

There is an interest in performing chemical strengthening without using molten salt due to the economic and environmental concerns about the use of large amounts of nitrate salts. Therefore, alternative methods, where salt-containing pastes, salt-spray and vapor deposition are employed, have been advanced (Sil'vestrovich *et al.*, 1990, 1984; Karlsson *et al.*, 2015, 2012; Sundberg *et al.*, 2019).

In one case, the glass surface is covered by a mixture of salts, typically potassium nitrate and potassium chloride, starting from a concentrated water suspension (salt-spray or salt paste techniques). The high viscosity of the salt mixture (where a residual solid is present) compared to pure potassium nitrate enables ion-exchange to be performed at a higher temperature than the conventional chemical strengthening using molten salt. Although non-conventional ion-exchange processes such as Na⁺-Rb⁺ or Na⁺-Cs⁺ can be produced by using the salt paste technique, the generation of surface compression is questionable because of fast stress relaxation at high temperatures (Karlsson *et al.*, 2012). Moreover, it is noteworthy that the depth of ion exchange layer (DOL) is considerably smaller than the average size of flaws on the glass surface (ca. 5 μm).

Vapor deposition is another molten salt-free technique for performing chemical strengthening. Here, a layer is deposited from a potassium- (or other elements) containing aerosol on the glass surface, and afterwards, ion-exchange is carried out by heat treatment at temperature below the glass strain point. High residual compressive stress can be achieved due to the relatively low ion exchange temperature; moreover, the vapor deposition and ion-exchange steps can be merged together in order to reduce the production cost (Karlsson *et al.*, 2015).

Electric field-assisted ion-exchange

Most research on chemical strengthening focuses on promoting the interdiffusion of alkali ions and the ability of the glass to be ion-exchange by optimizing the glass composition; however, there are some methods where the diffusion of alkali ions can be accelerated by the assistance of an external factor, such as ultrasonic waves, microwave radiation or electric fields. (Abou-El-Leil and Cooper, 1978; Kai and Jong, 2013; Talimian *et al.*, 2017, 2020; Shaisha and Cooper, 1981).

During electric-field assisted ion exchange (EF-IE), alkali ions are pushed in the direction of the applied E-field; it introduces a new driving force to the ion exchange process. Therefore, the produced ion exchange layer depends on both the applied electric field and the diffusion of ions. Fig. 12 shows potassium concentration profiles produced in soda-lime silica glass tubes by using electric field-assisted ion-exchange at 400°C. The concentration profiles resemble a step function, and a deep ion-exchanged layer with a DOL similar to conventional ion-exchange methods can be produced when a strong enough E-field is applied.

Fig. 13 shows Vickers indentations on the surface of SLS glass subjected to conventional Na⁺-K⁺ ion exchange and electric field-assisted ion exchange. There are no visible cracks surrounding the imprint in samples subjected to EF-IE, thus indicating that

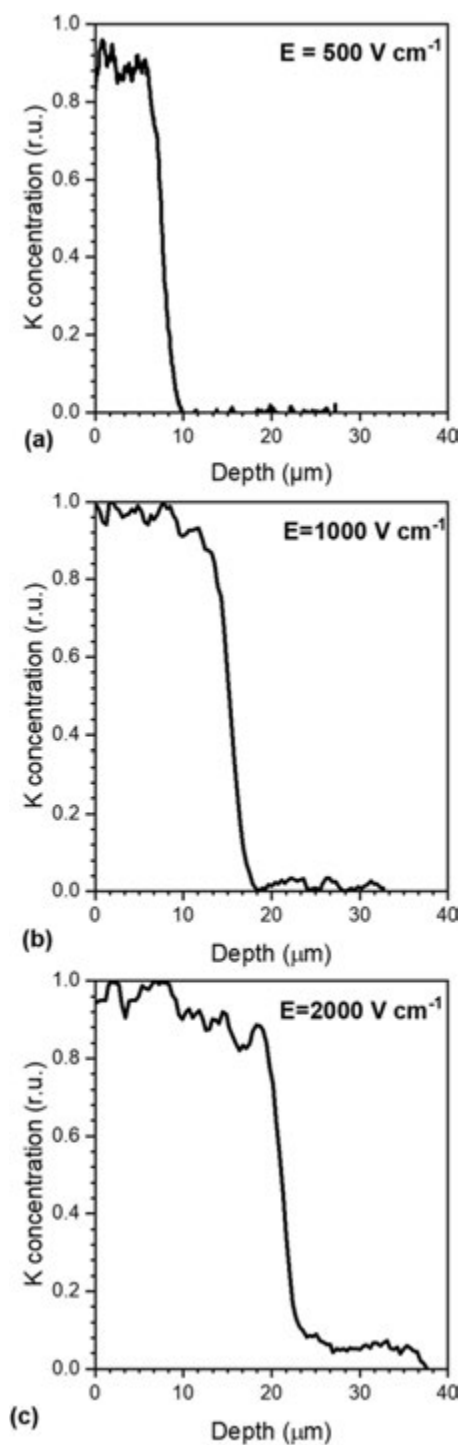


Fig. 12 Potassium concentration profiles as a function of applied E-field. The concentration profiles were produced in soda lime silica glass using EF-IE. Reproduced from Talimian, A., Scardi, P., Sglavo, V.M., 2020. Sodium-caesium electric field assisted ion exchange in a mixed-alkali (Na, K) lime silicate glass. *Journal of Non-Crystalline Solids* 550, 120390.

EF-IE produces large compressive stress. The short duration of EF-IE and lower temperature in comparison to the conventional method suppresses stress relaxation and, therefore, larger surface compression is produced.

Moreover, EF-IE enables the replacement of small alkali ions in the glass, such as sodium, with significantly larger cations like cesium. Although the generated compressive stress by $\text{Na}^+ - \text{Cs}^+$ ion exchange is intuitively expected to be significantly larger than $\text{Na}^+ - \text{K}^+$, experimental results indicate that the residual stress is significantly smaller; the structural modifications of glass during ion-exchange account for the limited stress generation (Talimian *et al.*, 2017, 2020; Ingram *et al.*, 2000, 2005).

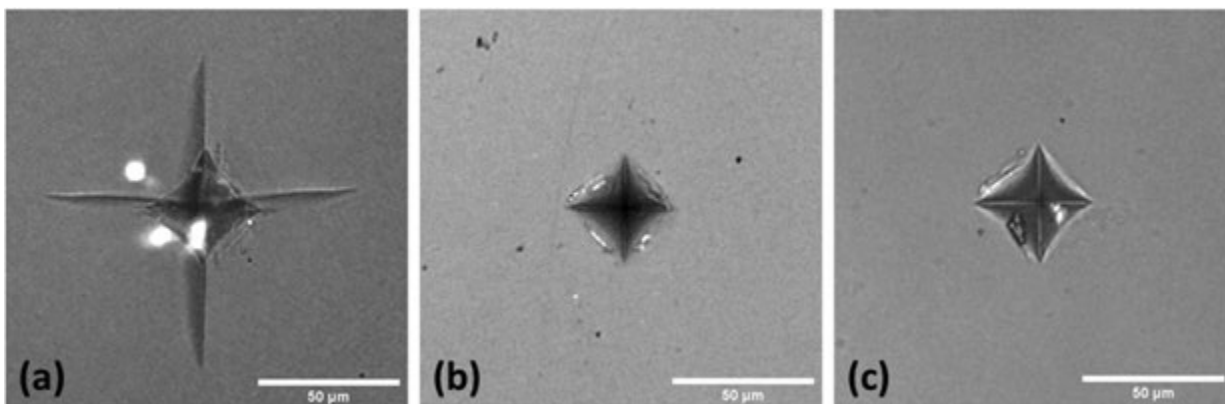


Fig. 13 Vickers indentation ($P = 500$ gf and $t: 15$ s) on soda lime silica glass: (a) as-received glass, (b) $\text{Na}^+ - \text{K}^+$ ion-exchanged at 400°C for 5 min, (c) $\text{Na}^+ - \text{Cs}^+$ ion exchanged using EF-IE ($E = 2000 \text{ V cm}^{-1}$, $t = 5$ min). Reproduced from Talimian, A., Scardi, P., Sglavo, V.M., 2020. Sodium-caesium electric field assisted ion exchange in a mixed-alkali (Na, K) lime silicate glass. *Journal of Non-Crystalline Solids* 550, 120390.

In order to perform successful ion exchange, the glass article should act as an insulator between the different poles of the electric field and this raises technical issues concerning insulation at high temperatures. In addition, non-uniform exchange of ions on the glass surface may result in inhomogeneous residual stress, which results in strength degradation. Hence, electric field-assisted ion exchange strengthening of glass has remained less practical so far.

Engineered stress profiles

The strengthening of glass by producing Engineered Stress Profiles, ESP, is a relatively recent method for improving the mechanical properties of glass (Glass *et al.*, 2000; Green, 2003; Abrams, 2004; Green, 2008). ESP glasses have a residual stress profile which increases from the surface (where it is almost zero) until it reaches a maximum at a definite depth; thus the apparent fracture toughness increases with the crack depth (Sglavo *et al.*, 2004a). Because of this, surface cracks can grow in a stable way before final failure thus making the strength independent of the surface flaw size (Glass *et al.*, 2000; Abrams *et al.*, 2003; Abrams, 2004; Sglavo *et al.*, 2007). Furthermore, multiple surface cracks appear before failure, which act as an initial warning (Abrams, 2004; Green, 2008; Sglavo *et al.*, 2004b).

ESP can be produced in glass by a double ion-exchange process. A deep ion-exchanged layer is produced by a long normal chemical strengthening process. Then, a second step is carried out by a short inverse ion-exchange, such as immersing the ion-exchanged glass in a molten salt comprising of $\text{KNO}_3/\text{NaNO}_3$ for a few minutes (Sglavo and Green, 2004; Green, 2003).

Summary

Thermal tempering and chemical strengthening are two common methods for improving the mechanical properties of glass. Both techniques are based on the production of a residual surface compression which shields surface defects and cracks; therefore, the intensity of surface compression and its depth are of crucial importance for successful strengthening.

In spite of the efforts made to study the generation of compressive stress and influential parameters in chemical strengthening, the understanding is still rudimentary. The effect of temperature and time on strengthening has been extensively studied, but the effects of other factors such as glass composition and salt impurities still require further investigation. Alternative ion-exchange methods, such as electric field-assisted or molten salt-free approaches, require further study in order to improve the strengthening efficiency.

References

- Aaldenberg, E.M., Lezzi, P.J., Seaman, J.H., Blanchet, T.A., Tomozawa, M., 2016. Ion-exchanged lithium aluminosilicate glass: Strength and dynamic fatigue. *Journal of the American Ceramic Society* 99, 2645–2654.
- Abou-El-Leil, M., Cooper, A.R., 1978. Fracture of soda-lime glass tubes by field-assisted ion exchange. *Journal of the American Ceramic Society* 61, 131–136.
- Abrams, M.B., 2004. Crack Propagation and Fracture in Engineered Stress Profile Glass. Doctor's Thesis in Materials Science and Engineering. The Pennsylvania State University.
- Abrams, M.B., Green, D.J., Glass, S.J., 2003. Fracture behavior of engineered stress profile soda lime silicate glass. *Journal of Non-Crystalline Solids* 321, 10–19.
- Araujo, R., 1993. Interdiffusion in a one-dimensional interacting system. *Journal of Non-Crystalline Solids* 152, 70–74.
- Araujo, R., 2004. Thermodynamics of ion exchange. *Journal of Non-Crystalline Solids* 349, 230–233.
- Araujo, R.J., Likitvanichkul, S., Thibault, Y., Allan, D.C., 2003. Ion exchange equilibria between glass and molten salts. *Journal of Non-Crystalline Solids* 318, 262–267.
- Bradt, R.C., 2011. The fractography and crack patterns of broken glass. *Journal of Failure Analysis and Prevention* 11, 79–96.
- Bradt, R.C., Tressler, R.E., 2013. *Fractography of Glass*. New York: Springer.
- ASTM C1048 – 18, 2018. Standard Specification for Heat-Strengthened and Fully Tempered Flat Glass. West Conshohocken, PA: ASTM International.
- Cooper, A.R., Krohn, D.A., 1969. Strengthening of glass fibers: 11, Ion exchange *. *Journal of the American Ceramic Society* 52, 665–669.

- Doremus, R.H., 1974. Mixed-alkali effect and interdiffusion of Na and K ions in glass. *Journal of the American Ceramic Society* 57, 478–480.
- Doremus, R.H., 1994. *Glass Science*. Hoboken: John Wiley & Sons.
- Evers, M., 1969. Method And Apparatus For Strengthening Glass By Ion Exchange. US Patent 3,486,995.
- Fu, A.I., Mauro, J.C., 2013. Mutual diffusivity, network dilation, and salt bath poisoning effects in ion-exchanged glass. *Journal of Non-Crystalline Solids* 363, 199–204.
- Gardon, R., 1980. Chapter 5 – Thermal tempering of glass. In: Uhlmann, D.R., Kreidl, N.J. (Eds.), *Glass Science and Technology. Elasticity and Strength in Glasses*, vol. 5. Elsevier, pp. 145–216.
- Garfinkel, H.M., 1968. Ion-exchange equilibria between glass and molten salts. *The Journal of Physical Chemistry* 72, 4175–4181.
- Garfinkel, H.M., King, C.B., 1970. Ion concentration and stress in a chemically tempered glass. *Journal of the American Ceramic Society* 53, 686–691.
- Glass, S.J., Abrams, M., Matalucci, R.V., 2000. New Glass Technologies for Enhanced Architectural Surety®: engineered Stress Profiles (ESP) in Soda-Lime-Silica Glass. Sandia National Labs Report. Springfield, VA: National Technical Information Service, US Department of Commerce.
- Green, D.J., 2003. Critical parameters in the processing of engineered stress profile glasses. *Journal of Non-Crystalline Solids* 316, 35–41.
- Green, D.J., 2008. Recent developments in chemically strengthened glasses. In: Kriven, W.M. (Ed.), 64th Conference on Glass Problems: Ceramic Engineering and Science Proceedings. John Wiley & Sons, Inc, pp. 253–266.
- Gross, T.M., 2019. Chemical strengthening of glass. In: Musgraves, J.D., Hu, J., Calvez, L. (Eds.), *Springer Handbook of Glass*. Switzerland: Springer International Publishing.
- Gutzow, I.S., Mazurin, O.V., Schmelzer, J.W.P., et al., 2011. *Glasses and the Glass Transition*. Hoboken, NJ: Wiley-VCH.
- Gy, R., 2008. Ion exchange for glass strengthening. *Materials Science and Engineering: B* 149, 159–165.
- Hassani, H., Sglavo, V.M., 2019. Effect of Na contamination on the chemical strengthening of soda-lime silicate float glass by ion-exchange in molten potassium nitrate. *Journal of Non-Crystalline Solids* 515, 143–148.
- Ingram, M.D., Wu, M.H., Coats, A., et al., 2005. Evidence from infrared spectroscopy of structural relaxation during field assisted and chemically driven ion exchange in soda lime silica glasses. *Physics and Chemistry of Glasses* 46, 84–89.
- Ingram, M.D., Davidson, J.E., Coats, A.M., Kamitsos, E.I., Kapoutsis, J.A., 2000. Origins of anomalous mixed-alkali effects in ion-exchanged glasses. *Glass Science and Technology* 73, 89–104.
- Jiang, L., Guo, X., Li, X., et al., 2013. Different K^+ – Na^+ inter-diffusion kinetics between the air side and tin side of an ion-exchanged float aluminosilicate glass. *Applied Surface Science* 265, 889–894.
- Jost, W., 1960. *Diffusion in Solids, Liquids, Gases*. Academic Press.
- Kai, X., Jong, H., 2013. Electric field-assisted Ag^+ migration for PbS quantum dot formation in glasses. *Journal of Non-Crystalline Solids* 377, 254–256.
- Karlsson, S., Jonson, B., Stalhandske, C., 2010. The technology of chemical glass strengthening – A review. *Glass Technology - European Journal Of Glass Science and Technology A* 51, 41–54.
- Karlsson, S., Jonson, B., Wondraczek, L., 2012. Copper, silver, rubidium and caesium ion exchange in soda lime silica float glass by direct deposition and in line melting of salt pastes. *Glass Technology - European Journal of Glass Science and Technology A* 53, 1–7.
- Karlsson, S., Ali, S., Limbach, R., Strand, M., Wondraczek, L., 2015. Alkali salt vapour deposition and in-line ion exchange on flat glass surfaces. *Glass Technology - European Journal of Glass Science and Technology A* 56, 203–213.
- Kasper, A., 2019. Spontaneous cracking of thermally toughened safety glass. Part one: Properties of nickel sulphide inclusions. *Glass Structures & Engineering* 4, 279–313.
- Kohlrusch, R., 1847. Nachtrag über die elastische Nachwirkung beim Cocon-und Glasfaden, und die hygroskopische Eigenschaft des Ersteren. *Annalen der Physik* 12, 393–425.
- Kolitsch, A., Richter, E., Hinz, W., 1981. The influence of small cationic contaminations upon alkaline self diffusion between molten salt and glass. *Silikattechnik* 32, 311–312.
- Kreski, P.K., Varshneya, A.K., Cormack, A.N., 2012. Investigation of ion-exchange ‘stuffed’ glass structures by molecular dynamics simulation. *Journal of Non-Crystalline Solids* 358, 3539–3545.
- Lacharme, J.P., 1970. Measurement of diffusion coefficients of sodium and potassium in mixed glasses. *Comptes Rendus des Seances de l’Academie des Sciences Serie C: Sciences Chimiques* 270, 1350–1353.
- Lezzi, P.J., Tomozawa, M., 2015. An overview of the strengthening of glass fibers by surface stress relaxation. *International Journal of Applied Glass Science* 6, 34–44.
- Lezzi, P.J., Seaman, J.H., Tomozawa, M., 2014. Strengthening of E-glass fibers by surface stress relaxation. *Journal of Non-Crystalline Solids* 402, 116–127.
- Lu, X., Arruda, E.M., Schultz, W.W., 1999. The effect of processing parameters on glass fiber birefringence development and relaxation. *Journal of Non-Newtonian Fluid Mechanics* 86, 89–104.
- Lupascu, A., Kevorkian, A., Boudet, T., et al., 1996. Modeling ion exchange in glass with concentration-dependent diffusion coefficients and mobilities. *Optical Engineering* 35, 1603–1610.
- Macrelli, G., 2018. Chemically strengthened glass by ion exchange: Strength evaluation. *International Journal of Applied Glass Science* 9, 156–166.
- Macrelli, G., Varshneya, A.K., Mauro, J.C., 2019. Simulation of glass network evolution during chemical strengthening: Resolution of the subsurface compression maximum anomaly. *Journal of Non-Crystalline Solids* 522, 119457.
- Macrelli, G., Özben, N., Kayaalp, A.C., Çelikbilek Ersundu, M., Sökmen, İ., 2020. Stress in ion exchanged soda-lime silicate and sodium aluminosilicate glasses: Experimental and theoretical comparison. *International Journal of Applied Glass Science* 11, 730–742.
- Mauro, J.C., 2014. Grand challenges in glass science. *Frontiers in Materials* 1, 20.
- Mauro, J.C., Loucks, R.J., 2009. Forbidden glasses and the failure of fictive temperature. *Journal of Non-Crystalline Solids* 355, 676–680.
- Mauro, J.C., Truesdale, C.M., Adib, K., Whittier, A.M., Martin, A.W., 2016. Chemical strengthening of alkali-free glass via pressure vessel ion exchange. *International Journal of Applied Glass Science* 7, 446–451.
- Mazzoldi, P., Carturan, S., Quaranta, A., Sada, C., Sglavo, V.M., 2013. Ion exchange process: History, evolution and applications. *Rivista Del Nuovo Cimento* 36, 397–460.
- Morris, D.J., Myers, S.B., Cook, R.F., 2004. Indentation crack initiation in ion-exchanged aluminosilicate glass. *Journal of Materials Science* 39, 2399–2410.
- Nordberg, M.E., Mochel, E.L., Garfinkel, H.M., Olcott, J.S., 1964. Strengthening by ion exchange. *Journal of the American Ceramic Society* 47, 215–219.
- Onbaşlı, M.C., Tandia, A., Mauro, J.C., 2020. Mechanical and compositional design of high-strength corning gorilla® glass. In: Andreoni, W., Yip, S. (Eds.), *Handbook Of Materials Modeling: Applications: Current and Emerging Materials*. Cham: Springer International Publishing.
- Phillips, J.C., 1996. Stretched exponential relaxation in molecular and electronic glasses. *Reports on Progress in Physics* 59, 1133.
- Potuzak, M., Welch, R.C., Mauro, J.C., 2011. Topological origin of stretched exponential relaxation in glass. *The Journal of Chemical Physics* 135, 214502.
- Sane, A.Y., Cooper, A.R., 1987. Stress buildup and relaxation during ion-exchange strengthening of glass. *Journal of the American Ceramic Society* 70, 86–89.
- Saunders, A.E., Kubichan, R.E., 1969. Strengthening Glass by Multiple Alkali Ion Exchange. US Patent 3,433,611.
- Seaman, J.H., Lezzi, P.J., Blanchet, T.A., Tomozawa, M., 2014. Degradation of ion-exchange strengthened glasses due to surface stress relaxation. *Journal of Non-Crystalline Solids* 403, 113–123.
- Sglavo, V.M., Green, D.J., 2004. Flaw-insensitive ion-exchanged glass: II, Production and mechanical performance. *Journal of the American Ceramic Society* 84, 1832–1838.
- Sglavo, V.M., Larentis, L., Green, D.J., 2004a. Flaw-insensitive ion-exchanged glass: I, Theoretical Aspects. *Journal of the American Ceramic Society* 84, 1827–1831.
- Sglavo, V.M., Prezzi, A., Zandonella, T., 2004b. Engineered stress-profile silicate glass: High strength material insensitive to surface defects and fatigue. *Advanced Engineering Materials* 6, 344–349.
- Sglavo, V.M., Prezzi, A., Green, D.J., 2007. In situ observation of crack propagation in ESP (Engineered Stress Profile) Glass. *Engineering Fracture Mechanics* 74, 1383–1398.
- Sglavo, V.M., Talimian, A., Ocsko, N., 2017. Influence of salt bath calcium contamination on soda lime silicate glass chemical strengthening. *Journal of Non-Crystalline Solids* 458, 121–128.

- Sglavo, V.M., Quaranta, A., Allodi, V., Mariotto, G., 2014. Analysis of the surface structure of soda lime silicate glass after chemical strengthening in different KNO_3 salt baths. *Journal of Non-Crystalline Solids* 401, 105–109.
- Sglavo, V., 2019. Chapter 16 – Chemical strengthening of silicate glasses: Dangerous and beneficial impurities. In: Sundaram, S. (Ed.), *Proceedings of the 79th Conference on Glass Problems*, Ceramic Transactions, Vol. 267. American Ceramic Society – Wiley.
- Shaisha, E.E., Cooper, A.R., 1981. Ion-exchange of soda-lime glass with univalent cations. *Journal of the American Ceramic Society* 64, 278–283.
- Shelby, J.E., 2005. *Introduction to Glass Science and Technology*. London: Royal Society of Chemistry.
- Shen, J., Green, D.J., 2004a. Prediction of stress profiles in ion exchanged glasses. *Journal of Non-Crystalline Solids* 344, 79–87.
- Shen, J.W., Green, D.J., 2004b. Effect of the K/Na ratio in mixed-alkali lime silicate glasses on the rheological and physical properties. *Journal of Non-Crystalline Solids* 344, 66–72.
- Shen, J., Green, D.J., Tressler, R.E., Shelleman, D.L., 2003. Stress relaxation of a soda lime silicate glass below the glass transition temperature. *Journal of Non-Crystalline Solids* 324, 277–288.
- Sheth, N., Howzen, A., Campbell, A., *et al.*, 2019. Effects of tempering and heat strengthening on hardness, indentation fracture resistance, and wear of soda lime float glass. *International Journal of Applied Glass Science* 10, 431–440.
- Sil'vestrovich, S.I., Samkova, L.G., Raikhel, A.M., 1990. Ion-exchange hardening of glass with a solid-phase reagent. *Glass and Ceramics* 47, 75–76.
- Sil'vestrovich, S.I., Samkova, L.G., Kazakov, V.D., Korshunova, L.F., 1984. Strengthening industrial glasses by ion exchange with solid-phase reagents. *Glass and Ceramics* 41, 471–474.
- Sundberg, P., Grund Bäck, L., Orman, R., Booth, J., Karlsson, S., 2019. Simultaneous chemical vapor deposition and thermal strengthening of glass. *Thin Solid Films* 669, 487–493.
- Talimian, A., Sglavo, V.M., 2017a. Can annealing improve the chemical strengthening of thin borosilicate glass? *Journal of Non-Crystalline Solids* 465, 1–7.
- Talimian, A., Sglavo, V.M., 2017b. Ion-exchange strengthening of borosilicate glass: Influence of salt impurities and treatment temperature. *Journal of Non-Crystalline Solids* 456, 12–21.
- Talimian, A., Mariotto, G., Sglavo, V.M., 2017. Electric field-assisted ion exchange strengthening of borosilicate and soda lime silicate glass. *International Journal of Applied Glass Science* 8, 1–10.
- Talimian, A., Scardi, P., Sglavo, V.M., 2020. Sodium-caesium electric field assisted ion exchange in a mixed-alkali (Na, K) lime silicate glass. *Journal of Non-Crystalline Solids* 550, 120390.
- Tandia, A., Vargheese, K.D., Mauro, J.C., 2012. Elasticity of ion stuffing in chemically strengthened glass. *Journal of Non-Crystalline Solids* 358, 1569–1574.
- Tandia, A., Onbasli, M.C., Mauro, J.C., 2019. Machine learning for glass modeling. In: Musgraves, J.D., Hu, J., Calvez, L. (Eds.), *Springer Handbook of Glass*. Springer International Publishing.
- Tomozawa, M., Kim, D.-L., Agarwal, A., Davis, K.M., 2001. Water diffusion and surface structural relaxation of silica glasses. *Journal of Non-Crystalline Solids* 288, 73–80.
- Tool, A.Q., 1948. Effect of heat-treatment on the density and constitution of high-silica glasses of the borosilicate type*. *Journal of the American Ceramic Society* 31, 177–186.
- Tyagi, V., Varshneya, A., 1998. Measurement of progressive stress buildup during ion exchange in alkali aluminosilicate glass. *Journal of Non-Crystalline Solids* 238, 186–192.
- Varshneya, A., 1975. Influence of strain energy on kinetics of ion exchange in glass. *Journal of the American Ceramic Society* 58, 106–109.
- Varshneya, A.K., 1994. Chapter 18 – Strength and toughness. In *Fundamentals of Inorganic Glasses*. San Diego: Academic Press.
- Varshneya, A.K., 2006. *Fundamentals of Inorganic Glasses*, second ed. Sheffield: Society of Glass Technology.
- Varshneya, A.K., 2010a. Chemical strengthening of glass: Lessons learned and yet to be learned. *International Journal of Applied Glass Science* 1, 131–142.
- Varshneya, A.K., 2010b. The physics of chemical strengthening of glass: Room for a New View. *Journal of Non-Crystalline Solids* 356, 2289–2294.
- Varshneya, A.K., 2016. Mechanical model to simulate buildup and relaxation of stress during glass chemical strengthening. *Journal of Non-Crystalline Solids* 433, 28–30.
- Varshneya, A.K., 2018. Stronger glass products: Lessons learned and yet to be learned. *International Journal of Applied Glass Science* 9, 140–155.
- Varshneya, A.K., Milberg, M.E., 1974. Ion exchange in sodium borosilicate glasses. *Journal of the American Ceramic Society* 57, 165–169.
- Varshneya, A.K., Spinelli, I.M., 2009. High-strength, large-case-depth chemically strengthened lithium aluminosilicate glass. *American Ceramic Society Bulletin* 88, 27–33.
- Varshneya, A.K., Kreski, P.K., 2012. The chemistry of chemical strengthening of glass. In: Varshneya, A.K., Schaeffer, H.A., Richardson, K.A., Wightman, M., David Pye, L. (Eds.), *Processing, Properties, and Applications of Glass and Optical Materials: Ceramic Transactions* 231. The American Ceramic Society, pp. 107–114.
- Varshneya, A.K., Mauro, J.C., 2019. Chapter 18 – Strength and Toughness. In: Varshneya, A.K., Mauro, J.C. (Eds.), *Fundamentals of Inorganic Glasses*, third ed. Elsevier.
- Varshneya, A.K., Olson, G.A., Kreski, P.K., Gupta, P.K., 2015. Buildup and relaxation of stress in chemically strengthened glass. *Journal of Non-Crystalline Solids* 427, 91–97.
- Veer, F.A., Louter, P.C., Bos, F.P., 2009. The strength of annealed, heat-strengthened and fully tempered float glass. *Fatigue and Fracture of Engineering Materials and Structures* 32, 18–25.
- Wondraczek, L., Mauro, J.C., Eckert, J., *et al.*, 2011. Towards ultrastrong glasses. *Advanced Materials* 23, 4578–4586.
- Xinwei, W., Rüdiger, D., 2011. Sodium tracer diffusion in a sodium aluminosilicate glass. *Journal of Non-Crystalline Solids* 357.
- Yoshida, S., Hidaka, A., Matsuoka, J., 2004. Crack initiation behavior of sodium aluminosilicate glasses. *Journal of Non-Crystalline Solids* 344, 37–43.

Properties of Glass Materials

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Definition of Glass

In everyday language the term glass designates a transparent substance, possessing the properties of hardness, rigidity, and brittleness, and, apart from transparency, these are the typical properties one normally associates with a solid. Glass also possesses a number of properties which are characteristic of the liquid state, and classification of glass as a liquid of very high viscosity rather than a solid would be in accordance with modern views (McMillan, 1979). Unlike crystals, glass does not have a sharp melting point, but like crystalline solids, glasses show elasticity (Paul, 1990).

Due to the complexity of the structure of glass, it is not altogether surprising that an exact, all-encompassing definition for glass remains elusive, and instead a number of definitions have been suggested over the years. A more generally accepted definition is that offered by ASTM (C162) which states “a glass is an inorganic product of fusion which has cooled to a rigid condition without crystallization.” However, the ASTM definition limits the definition of glass to inorganic constituents, which fails to explain organic and molecular glasses that now represent a rapidly growing area of study (Varshneya and Mauro, 2010; Doremus, 1994). Newly developed solution based sol–gel synthesis of oxide materials occurs at much lower temperature than traditional solid-state fusion processes and also allows powderless non-fusion processing of glasses. X-ray and electronic diffraction studies have shown that glass lacks long-range periodic atomic arrangement, and every type of glass exhibits time-dependent glass transformation behavior (Paul, 1990; Shelby and Lopes, 2005). Pointing this out, Varshneya and Mauro (2010) suggest a scientific definition of glass as “a solid having a non-crystalline structure, which continuously converts to a liquid upon heating.” Zarzycki (1991) favors a more simplified definition: “a glass is a non-crystalline solid exhibiting the phenomenon of glass transition.” Thereby this definition also conveniently separates non-crystalline materials into the categories of glass and amorphous materials.

The Glass Transition

Glass is usually formed on solidification from the melting stage. The cooling is so rapid that crystallization does not have the time to occur. With a further decrease in temperature, viscosity continues to increase, resulting in a progressive freezing of the liquid to its final solidification. The relationship between crystal, liquid, and glass can be explained by means of specific volume as a function of temperature (see Figure 1).

On cooling from an elevated temperature (T_s), at the point of solidification (or freezing), two phenomena may occur. There is either a discontinuous change in volume at the melting point if the liquid crystallizes, or crystallization is avoided and liquid passes to a supercooled state (between T_s and T_g) and the volume of the liquid decreases steadily until there is a decrease in the expansion coefficient at a range in temperature called the glass transformation range. Below this temperature range the glass structure does not relax and the expansion coefficient is usually same as that for the crystalline solid. The intersection between the curve of the glassy state and that for the supercooled liquid is known as the glass transition temperature, T_g (Kingery and Uhlmann *et al.*, 1976). This T_g varies with cooling rate (see Figure 1) and thus it is more accurate to call it a transformation range rather than a fixed point (Lancry and Régnier *et al.*, 2012). The glass transition temperature increases with increasing cooling rate. The specific volume of the formed glass follows this same trend, increasing with increased cooling rate. With a slower cooling rate the time available for the structure to relax increases and the supercooled liquid persists to a lower temperature resulting in a higher-density glass.

Structure of Glass

A number of models exist to describe the structure of glass, including a random network model, a crystallite model, as well as other structural models. Random network theory, which is originally based on the ideas of Zachariasen, is the most common model used for explaining glass structure. Here only the random network model is briefly discussed and readers are referred to the following literature for details of other models (Zarzycki, 1991; Kingery *et al.*, 1976; Uhlmann and Kreidl, 1983; Doremus, 1994).

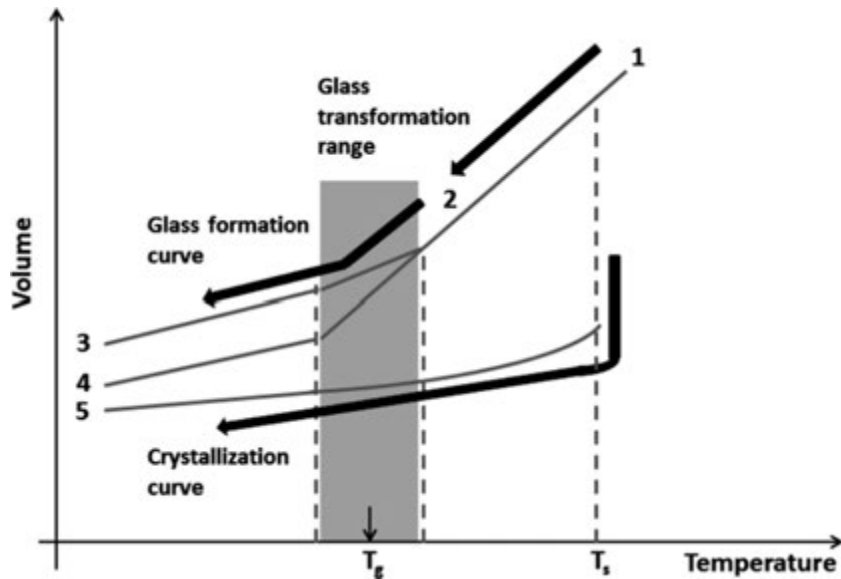


Figure 1 Schematic specific volume–temperature relationships for crystallization and glass formation. 1: liquid, 2: supercooled liquid, 3: glass on fast cooling, 4: glass on slow cooling, 5: crystal; T_s : melting temperature, T_g : glass transition temperature.

Random Network Model

The random network model depicts glass as a three-dimensional network, lacking symmetry and periodicity, in which no unit of the structure is repeated at regular intervals. For oxide glass, these networks are composed of oxygen polyhedra. Assuming that a glass should have an energy content similar to that of the corresponding crystal, Zachariasen (1932) suggested four rules for the formation of an oxide glass:

- i. An oxygen atom should be linked to not more than two glass forming atoms.
- ii. The coordination number of glass-forming atoms is low, 4 or less.
- iii. Oxygen polyhedra share corners, not edges or faces.
- iv. For 3-D networks, at least three corners of each polyhedron should be shared.

The bonding force responsible for the formation of the network structure in crystalline silica (SiO_2) forms similar networks in glass (see Figure 2(a)) and is considered as network formers. Alkali silicates form glass easily and when alkali oxides such as Na_2O are added to silica glass, the sodium ions become part of the structure and occupy random positions distributed throughout the structure to provide charge neutrality (see Figure 2(b)).

These alkali oxides (e.g., Na_2O , K_2O , Li_2O , CaO , MgO , and PbO) provide additional oxygen ions that modify the network structure. For this reason, they are known as network modifiers. With an increase in the amount of modifiers, the ratio of oxygen to silicon also increases and breaks up the three-dimensional network with the formation of singly-bonded oxygens that do not participate in the network, thus reducing the length of the chain. The principal effect of these modifiers is a reduction in melting temperature and working temperature by decreasing the viscosity. An excess of modifiers can make melting sufficiently simple and mobile that crystallization occurs in preference during the formation of glass. Cations of higher valency and lower coordination number than the alkalis and alkali earth metals may act as both network formers and modifiers and are referred to as intermediates; for example, ZrO_2 , TiO_2 , Al_2O_3 , ZnO .

Amorphous Phase Separation

The phenomenon of amorphous phase separation (APS) in glasses has, for decades now, been an important topic in glass research. It has been the subject of many investigations and there is an entire area of glass science devoted to this phenomenon in different glass-forming systems.

A homogeneous single phase separates into two or more phases of different compositions, if the free energy of the system with two or more distinct phases is lower than that of the system with one single homogeneous phase (Paul, 1990). Phase separation that occurs above the glasses melting point (the liquidus line) is known as stable immiscibility, whereas phase separation at temperatures below the liquidus is known as metastable immiscibility. There are two routes to the formation of discrete phases by metastable phase separation; these are either by spinodal decomposition or by nucleation and growth process. The route taken depends on the free energy of the mixing of the system. Figure 3 shows an immiscibility diagram for the binary sodium silicate system when heat treated in different regions of the phase diagram. The dark phase in the figure represents a sodium rich

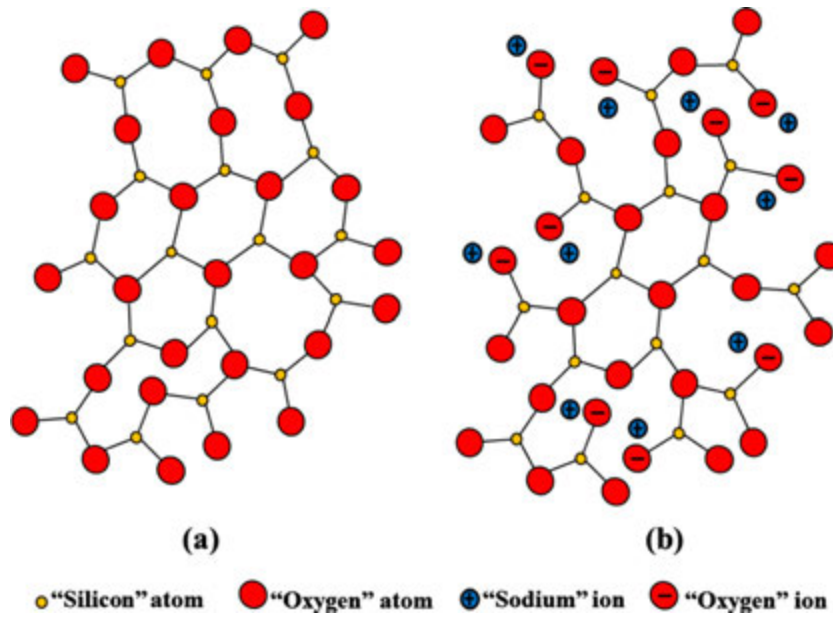


Figure 2 Schematic two-dimensional glass structures: (a) amorphous SiO_2 network; (b) SiO_2 network modified through addition of Na_2O .

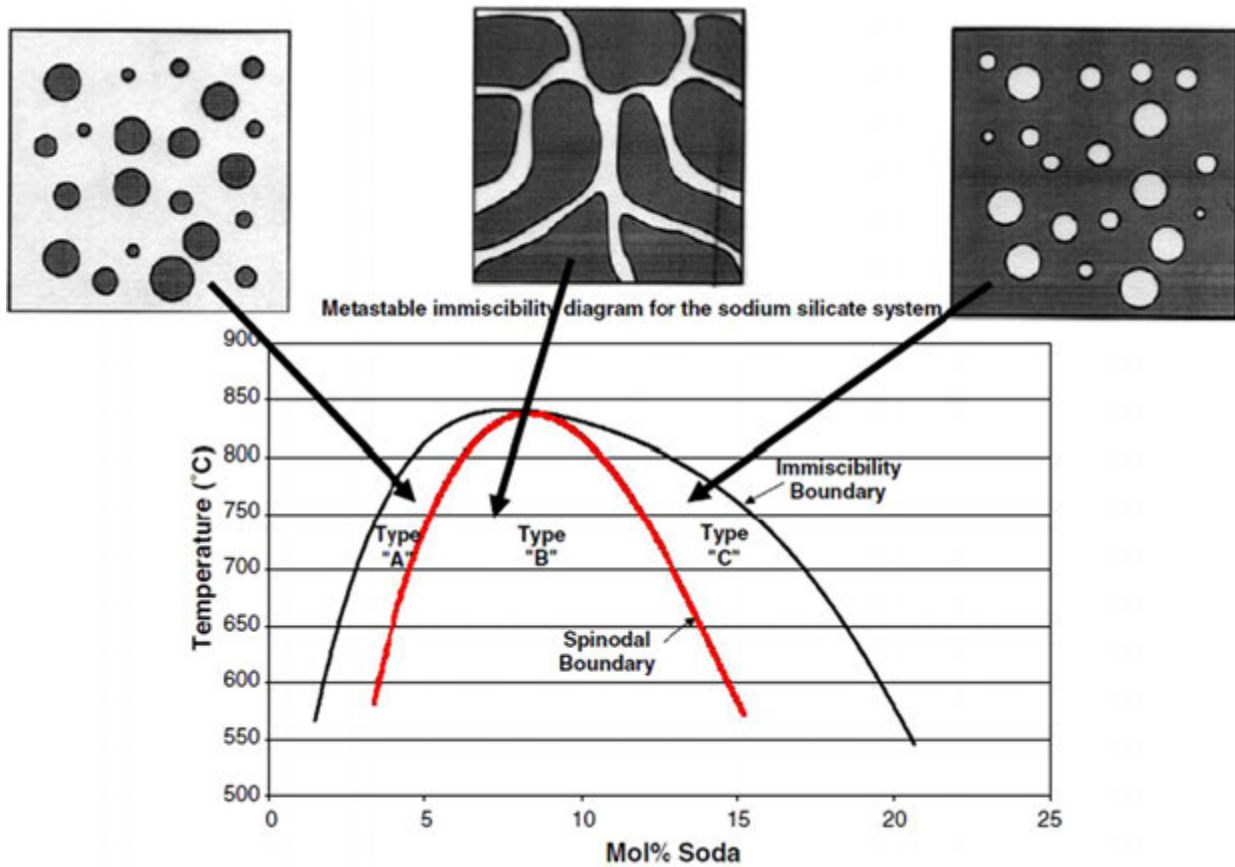


Figure 3 Metastable immiscibility diagram for the sodium silicate system showing typical morphologies (Wheaton and Clare, 2007).

composition and light phase denotes a silica rich composition. Phase separation in type A and type C (see [Figure 3](#)) are in a binodal region and undergo APS by nucleation and growth process, whereas type B is within the spinodal region and undergoes APS by spinodal decomposition.

Spinodal Decomposition

Because phase separation into the binodal and spinodal regions are achieved by means of different thermodynamic processes, the morphology of the separated phases in each region are distinctly different. Phase separation in the spinodal region refers to a continuous type of phase transformation in which the change begins as small fluctuations in composition, and the compositional differences grow with time resulting in two continuous interpenetrating phases. Since these changes occur spontaneously and as apparently no energy barrier is present to hinder the separation, the region is considered unstable. The system will lower its free energy by continuously changing the composition of two phases until the equilibrium is reached. At this equilibrium, the free energy is in the lowest state and compositions remain constant. Afterwards the phase-separated regions will grow in size through diffusion. The boundary between phases is initially diffuse but sharpens with time. The phases formed in the spinodal region show a high degree of connectivity ([Wheaton and Clare, 2007](#)).

Nucleation and Growth

In the binodal region, a large change in composition must occur to lower the free energy of the system, and thus form nuclei. This region is referred as the metastable region, as the system is unstable to small fluctuations in composition but becomes stable at larger changes in composition. Once nucleated, the new phase will grow in size through diffusion. During the growth stage, the composition of the nucleated phase is unchanged with time, for a constant temperature. The phase separation resulting from nucleation and growth is characterized by spherical droplets, with low connectivity, of random size and distribution with a sharp boundary existing between the two phases. [Figure 4](#) shows etched surfaces of sodium borosilicate glass where the structures are formed by (a) nucleation and growth and (b) spinodal decomposition.

Chemical Durability of Glasses

Chemical durability is a property of a material that is measured by its ability to resist the corrosive action of water, aqueous solution of acids, alkalis and salts. The chemical durability of glasses is superior to most metals and polymers. However, non-silicate glasses are susceptible to dissolution in aqueous solution, especially with low pH solutions. Almost all kind of glasses readily dissolve in hydrofluoric acid (HF) which attacks the network bonds. The glasses, which possess excellent chemical durability, are also attacked significantly if exposed to very high or low pH, – particularly at elevated temperatures.

Chemical Reaction Mechanism

Chemical stability and the resistance of a glass to any chemical attack depend on factors like the solution type, exposure time and temperature, and condition of the glass surface. There are several processes involved during chemical attack by an aqueous solution on glass. However, every chemical attack involves dissociation of water into H^+ or OH^- ions. Ion exchange occurs if the glass contains alkali or other highly mobile ions, where the solution attacks the network bonds to keep the concentration ratio of the components in glass and solution identical. This ion exchange process between highly mobile ions from glass and protonic species from the liquid solution is known as *congruent dissolution* and requires the presence of a liquid or water vapor. Most of the commercial glasses are silicate based glasses that contain alkali ions, and thus their dissolution process usually occurs by congruent

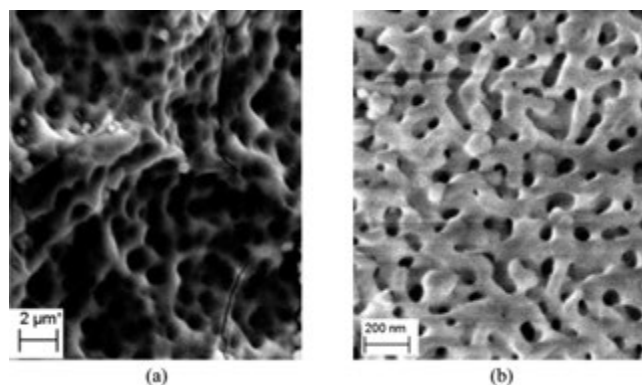


Figure 4 Sodium borosilicate glass showing (a) a droplet microstructure and (b) a connective structure ([Hasanuzzaman et al., 2013, 2014](#)).

dissolution. The reaction products form a layer on the glass surface and influence the further dissolution rate. On the contrary, non-aqueous solutions (i.e., organic) do not react with glass.

At extreme pH (< 1 or > 9), silicate based glasses dissolve at a higher rate where the ion exchange process and leached thin silica gel layer is no longer the determining factor for the dissolution. The chemical attack occurs directly on the Si–O bonds at these extreme pH conditions. For phase separated alkali borosilicate glasses, where two interconnecting phases: a silica-rich phase, and an alkali-rich borate phase formed up on heat-treatment. Leaching is then used on the heat-treated glass to selectively remove alkali borate phase which has very low durability even in weak acids, while silica phase is resistant to this weak acids. A post-leach alkali wash step is needed to remove trapped silica gel and leave behind a silica-rich porous skeleton. The heat-treatment step and leaching conditions can be adjusted to achieve the desired pore size, pore volume, and surface area. Zircon or zirconia can be used to improve the durability of a porous glass (Kiefer, 1989; Marques, 2008; Kiefer, 1989; Okubu *et al.*, 1987; Paul, 1990; Hasanuzzaman *et al.*, 2014).

Crystallization Effect on Chemical Durability

The chemical durability of glasses can be influenced by crystallization if the crystalline phase has properties different to those of the base glass. During crystallization, the mobile ions (i.e., Na^+ or Li^+) of the glass moved in to very durable crystals. In general, the durability of crystalline glass-ceramic is superior to that of amorphous glass. The durability depends on the nature of the crystalline phases formed, the nature of the glassy matrix, and the overall microstructure of the resulting glass-ceramic.

Mechanical and Thermal Properties

Eventhough most glasses possess high hardness values compared to other materials, their brittle nature makes them vulnerable to many engineering applications. Plenty of work has been done to improve the fracture toughness of glass. A number of mechanical and thermal properties of glasses are discussed below which are determining factors for using glass in specific engineering applications.

Viscosity

Viscosity is an important property of glass. Most processing techniques require the viscosity to be in a certain range (10^3 – 10^7 dPa s) at a certain temperature. This is known as the *working point*. At temperature when viscosity of glass reaches $10^{7.6}$ dPa s is defined as the *softening point*. At this point glass, deforms rapidly and is used for glassblowing or sintering. In the glass transformation range (see Figure 1), most glasses show viscosity in the range of 10^{12} – $10^{13.5}$ dPa s, and the upper limit 10^{13} dPa s is called the *annealing point*. Annealing is very important for relaxation of stresses generated during hot forming of glasses (Krause, 2005). At 30–40 °C below the annealing point, where the viscosity is $10^{14.5}$ dPa s, the relaxation of stress requires more time (> 3 h) compare to the annealing point (< 1 h). This is known as the *strain point*. The optimum stress relaxation temperature to use should be chosen according to the application and the requirements of dimensional accuracy.

Below the glass transformation temperature (T_g), the viscosity of glass increases many orders of magnitude and the structure becomes frozen-in (quasi-solid). The rate of cooling influences the density of the glass and also the formation of crystals. In sodium silicate glasses, the most common glass system, increasing the alkali content breaks up the three-dimensional network with the formation of singly-bonded oxygens that do not participate in the network, thus reducing the length of the chain. The principal effect of increased alkali content is to reduce the melting temperature by decreasing the viscosity, which would indicate a lower T_g . However, variations are observed for glass compositions containing B_2O_3 , which is known as the *boric oxide anomaly*. Increasing alkali content in sodium borate glass compositions converts BO_3 triangles to BO_4 tetrahedra, thereby increasing the network connectivity. Therefore, the glass transition temperature increases. Non-bridging oxygen (NBO) sites do not become apparent until the alkali content is increased to approximately 30 mol% (Vogel *et al.*, 1985). In other studies with borosilicate glass, it was mentioned that NBO's are not generated in glasses with a $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ ratio < 0.5 (Saiki *et al.*, 2010; Chen *et al.*, 2004). Replacement of alkali oxide (Na_2O) by alkaline earth oxide (CaO), while maintaining a constant silica concentration, strengthens the network by replacement of the low field strength sodium ion by the higher field strength divalent alkaline earth ions and thus increases the T_g (Shelby and Lopes, 2005).

Strength

The high theoretical structural strength of glasses (ranges from 1 to 100 GPa), which depends on glass composition, is an attractive property. However, this high strength of glasses cannot be utilized in practical applications due to presence of flaws/defects on its surface which reduce the actual fracture strength by many orders of magnitude. These flaws, in the form of tiny chips or cracks, act as stress concentrators. At the tips of these flaws, stress concentration may be introduced by a load which exceeds the theoretical strength and cause fracture/breakage of the glass. Contact with other hard objects often cause flaws on glass surface. Chemical attacks and thermal stresses introduced during rapid cooling may also generate flaws on glass surface. Annealing can also be a

reason for the reduction of strength as it may introduce small crystals to the glass surface. The thermal expansion mismatch between the matrix glass and these crystals during cooling lead to flaws. In general, it is very challenging to keep glass surfaces free from flaw formation during production process or during annealing. Lubrication or coatings are often applied to the fresh glass surfaces to help prevent the formation of flaws. Reducing the flaw length below the Griffith critical crack length for crack growth, by etching or polishing is another way to improve the glass strength.

Strengthening of glass

As discussed earlier the strength of glasses can be improved by preventing or removing the flaws from the surface which causes the reduction of glass strength. The other way is to prevent the crack growth. Tensile stress concentrates on crack tip while mechanical load is applied to glass and crack propagation occurs when it overcomes the residual compressive stress. Compressive strength of glass which is very high can be exploited for strengthening. Internal stresses can be introduced to the glass by thermal tempering (quenching of softened glass) or ion exchange. By air-quenching glass, compressive stresses can be formed on the surface while the interior is held in tension. In this way, the strength of glass can be increased typically 4–6 times. Such glass is commonly used in bus stops and automobile applications and it has the added advantage that the glass crumbles when broken, as opposed to forming dangerous shards. Ion-exchange or ‘chemical toughening’ works by replacing sodium ions, for example, with potassium ions (which are 30% larger), by immersion of the glass into a bath of molten potassium nitrate. Chemical toughening can be applied to glass objects of complex shapes. Oftentimes, polymeric materials (polycarbonates) are used in combination with glass to form layered composite materials with enhanced properties, as is the case with bullet-proof glass, for example.

Thermal Expansion Behavior

The length and volume of a glass usually increases with increasing temperature. The thermal expansion curve measured by dilatometry gives three important properties – the thermal expansion coefficient (α), glass transformation temperature (T_g), and dilatometric softening temperature (T_d). Coefficient of thermal expansion is a measure of the rate of expansion with temperature. For glasses, the measured expansion coefficient is one directional and measured value is *linear thermal expansion coefficient* (α_l). The linear thermal expansion coefficient value of commercial glasses is measured over a specified temperature range and most cases from 0 to 300 °C, 20 to 300 °C, or 25 to 300 °C (Shelby and Lopes, 2005). Figure 5 shows the linear thermal expansion curve of a bulk sample of an alkali borosilicate glass (Hasanuzzaman *et al.*, 2013). The glass expands until 305 °C, above which the glass contracts suddenly up to about 425 °C, before expanding again. The contraction above 305 °C is believed due to bending of bonds which absorbs the lattice expansion by changing position of atoms. The filling of interstices inhibits further contraction and causes expansion again. Shelby and Lopes (2005) and Kingery *et al.* (1976) revealed a dramatic distinction in thermal expansion behavior between quenched glasses and glasses which had been annealed prior to dilatometric thermal behavior characterization. Quenched glasses showed very prominent contraction–expansion characteristics (see Figure 5). For annealed glasses the expansion–contraction was minimal and to a large extent ‘washed out’ as a result of annealing the glass above T_g . The sudden expansion in the temperature range 430 to 520 °C is referred to as the transformation range and indicates the onset of viscoelastic behavior, where bond breaking is predominant. The onset temperature of the transformation range at 430 °C is attributed to T_g . The temperature of maximum expansion is identified at 550 °C and can be referred to as the dilatometric softening temperature (T_d). A sharp contraction occurs at about 560 °C after the dilatometric softening temperature which corresponds to viscous flow of the sample under stresses imposed by the dilatometric push rod. The linear thermal expansion coefficient of a glass is an essential property for thermally induced stress formation. This property (linear thermal expansion coefficient) is utilized in tempering processes for generating compressive surface layers in order to prevent flaw propagation, hence increasing strength.

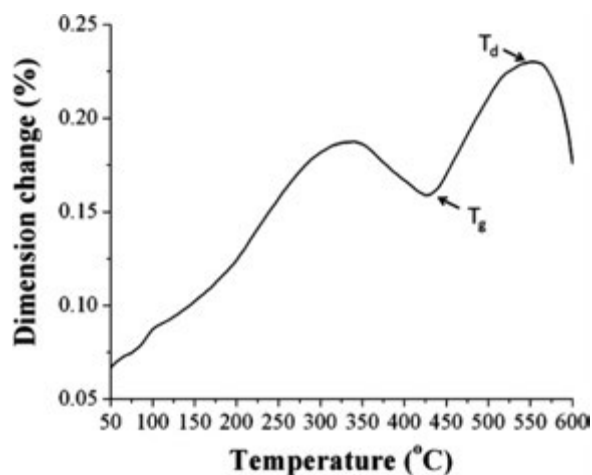


Figure 5 Linear thermal expansion curve of alkali borosilicate glass obtained at 10 °C min⁻¹ (Hasanuzzaman *et al.*, 2013).

Electrical Properties

Glasses are well known for their excellent insulating properties. Most oxide glasses are ionic conductor, but very poor electrical conductor due to low numbers of free monovalent ions. Due to its high insulating properties, glasses are used in the area of electrical and electronics engineering for the production of seals, high-voltage insulators, microelectronic packaging, high-vacuum tubes, lamps, etc.

Resistivity

Electrical conductivity in glasses depends on mobility of ions – especially alkali ions. Therefore, the conductivity of the alkali silicate glasses increases with the increasing alkali oxide content. However, for the glasses containing two or more alkali oxides, the *mixed-alkali effect* occurs where the conductivity decreases. Addition of alkaline earth oxide to any alkali containing glass also decreases the electrical conductivity. The immobile divalent alkali earth ions block and occupy the interstitial sites and thus reduce the mobility of the alkali ions in a glass. The conductivity of a glass also very much depend on temperature. At room temperature, the mobility of ions is so small that volume resistivity almost always lies beyond the range of measurement. The ionic mobility increases with increasing temperature and as a result resistivity also decreases. Crystallization also influences the conductivity. If the formed crystal removes alkali ions from the residual glass, the conductivity usually decreases. However, conductivity of the glass-ceramic increases if the crystal phase is free of alkali ions.

Dielectric Properties

The dielectric constant (ϵ_r) of a glass can be described as the relative increase of capacitances by introducing polarizable dielectric into a condenser which is previously separated in vacuum. The dielectric constant of technical glasses usually lies between 4.5 and 8 which is within the range of other electrically insulating material (Krause, 2005). The dielectric constant of glasses primarily depends on the electronic and ionic polarization and increases with temperature. However it decreases very slowly over a wide range of frequency. Content of heavy metals in glass, such as lead and barium containing glasses, gives high values of dielectric constant. If a dielectric material is situated in an alternative electromagnetic field, where reversing the polarities and shifting the dipoles occurs, an inherent dissipation of electromagnetic energy causes heating and the loss quantifies as dielectric loss. The small phase shift (δ) of practical performance to ideal loss free performance is parameterized as *loss tangent* ($\tan \delta$). Dielectric loss commonly depends on relaxation and becomes high around the relaxation or resonance frequencies of the polarization. Dielectric loss in the glasses correlates with its content, frequency, and temperature.

Optical Properties

The optical properties of glasses are of utmost importance and can be subdivided into three categories – refraction, absorption, and transmission of light. Glass is among only few other solids that transmit light in the visible region of the spectrum. Therefore, the development of optical glasses with appropriate refractive index and dispersion characteristics plays an important role in modern scientific evolution, especially in nano-science, medical science, astronomy, and biology.

Refraction of Light

The *refractive index* (n_i) of a material is defined as the ratio of velocity of light in a vacuum to that in a defined material. The refractive index of a glass is not a constant, but depends on the wavelength of the incident light, known as *dispersion*. Dispersion, a decisive factor for optical applications, explains the entire refractive index curve with the wave length of the light over the desired range. Dispersion causes the separation of white or compound light into its constituent colors in prisms, and chromatic aberration in optical lenses. Mean dispersion is the difference between the refractive indices of hydrogen, $n_F - n_C$ ($\lambda_F = 486.1$ nm, $\lambda_C = 656.3$ nm), measured at the F and C emission lines (Shelby and Lopes, 2005; Krause, 2005). For technical glasses, this dispersion value lies between 0.007 and 0.013 (Krause, 2005).

The refractive indices of technical glasses are usually designated as n_D at the yellow emission line of sodium (589.3 nm) or n_d for at yellow emission line of helium (587.6 nm). Due to very close proximity of these wavelengths, there is very little variance of the refractive indices and they generally lie within the range 1.47–1.57. Only exception is for lead based glasses where PbO content is >35% ($n_d = 1.7$) (Krause, 2005; Newton and Davison, 1989).

Effect of composition of glasses on refractive index

Increasing electron density or polarizability also increases the refractive index of a glass. Glasses containing low atomic number ions, which have low electron density and low polarizabilities, also have low refractive indices. Non-bridging oxygens are more polarizable than bridging oxygens. As a result, formation of non-bridging oxygens in a glass system due the compositional change increases the refractive index of that glass and vice versa. For commonly used alkali silicate glasses, refractive indices increases with

increasing alkali oxide concentration. Density and refractive index are directly correlated, such that increasing the density of glass also increases its refractive index.

Absorption

Ultraviolet (UV) light with wavelength (100–400 nm) cannot transmit through glass even if it is transparent. The electrons attached to molecules in typical glasses can absorb radiation at UV wavelengths which are beyond their ultraviolet edge. Conversion of a glass network from bridging state to non-bridging state shifts the ultraviolet edge to lower frequencies and toward the visible region of the spectrum. A very intense absorption band can be achieved in glasses by adding small concentration of impurities (i.e., iron) which result in a very intense absorption band due to transfer of electron from cations to neighboring anions. This absorption band is called *charge transfer band*. Absorption of light in the visible region of spectrum is known as color. Coloring of glass can be created by a number of mechanisms, like (1) addition of either 3d transition metal ions or 4f rare earth (lanthanide) ions, (2) formation or precipitation of colloidal particles, (3) presence of charge transfer bands in the visible region of spectrum, (4) light scattering due to phase separation or other optical defects.

Common Glass Systems

The primary glass formers in commercial oxide glasses are silica (SiO_2), boron oxide (B_2O_3), and phosphorus pentoxide (P_2O_5), all of which readily form single component glasses (Shelby and Lopes, 2005). Of these, other than silica, only boron oxide has some commercial importance and only when mixed with silica. Silica is the most important glass former and silicate glasses represent more than 95% of industrial glass production (Zarzycki, 1991). Silica-based glass is technically important for its excellent chemical resistance (except HF and alkali) and small expansion coefficient which makes it a very good candidate for thermal shock resistance (Zarzycki, 1991). Glass can be classified in different groups according to their intended usage or by their chemical composition. The following sections describe the most common types of glass according to their chemical composition.

Soda-Lime Glass or Commercial Glass

Soda-lime glass is the most common commercial glass. It is comparatively inexpensive and amenable to recycling. A typical composition of this glass is 70–75 wt% SiO_2 , 12–16 wt% of Na_2O , and 10–15 wt% CaO (Bauccio, 1994; Pfaender, 1996). A small percentage of other reagents can be added for specific properties and application requirements. The principal addition in this type of glass, other than silica (SiO_2), is sodium oxide or soda (Na_2O). Even though sodium oxide contains oxygen atoms, it is held together by ionic rather than covalent bonds. The sodium atoms in the mixture donate electrons to the oxygen atom, producing a mixture of negatively charged oxygen ions and positively charged sodium ions. The oxygen atom with an extra electron binds to one silicon atom and does not form a bridge between pairs of silicon atoms. Therefore, the melting temperature of the mixture is considerably reduced (Bloomfield, 2001). Relatively high amount of alkali content in the glass also causes an increase of the thermal expansion coefficient by about 20 times (Pfaender, 1996). Since sodium ions are so soluble in aqueous solution, calcium oxide (CaO) is added to the mixture to improve its insolubility. Soda-lime glass is produced on a large scale and used for bottles, drinking glasses, and windows. Its light transmission properties, as well as low melting temperature, make it suitable for use as window glass. Its smooth and non-reactive surface makes it excellent as containers for food and drinks. Nowadays recycled glass, also known as cullet, is used to make green glass, which helps to save energy and reduce emissions.

Lead Glass

Lead glass is similar to soda-lime glass where lime is replaced by a larger part of lead oxide (PbO). Lead glass typically contains 55–65 wt% SiO_2 , 18–38 wt% of PbO , and 13–15 wt% Na_2O or K_2O (Bauccio, 1994; Pfaender, 1996). Lead glass is usually used for decorative glassware. It is also included in special optical glasses for their high refractive index. The networks in lead glass are more complete than those in soda-lime glass and thus they are stronger and have less internal friction (Bloomfield, 2001). Lead oxide also makes the glass dense, hard, and X-ray absorbing, and therefore suitable for use in radiation shielding.

Aluminosilicate Glass

Aluminosilicate glasses are usually prepared from a ternary system with a typical composition 52–58 wt% SiO_2 , 15–25 wt% of Al_2O_3 , and 4–18 wt% CaO (Bauccio, 1994). With low thermal expansion and high softening temperature, this glass can tolerate high temperature better than soda-lime glass and is used in thermometers, combustion tubes, cookware, halogen lamps, furnaces, and fiberglass insulation.

Borosilicate Glass

Borosilicate glass contains substantial amounts of silica (SiO_2) and boron oxide ($\text{B}_2\text{O}_3 > 8\%$) as glass network formers, and are typically composed of 70–80 wt% SiO_2 , 7–13 wt% of B_2O_3 , 4–8 wt% Na_2O or K_2O , and 2–8 wt% of Al_2O_3 (Bauccio, 1994; Pfaender, 1996). Glass containing 7–13 wt% of B_2O_3 is known as low-borate borosilicate glass, and is mainly used to produce chemical apparatus, lamps, and tube envelopes. Glasses containing 15–25% B_2O_3 , is known as high-borate borosilicate glass. High-borate borosilicate glass is also known as leachable alkali-borosilicate glass with an optimum composition of 62.7 wt% SiO_2 , 26.9 wt% of B_2O_3 , 6.6 wt% Na_2O , and 3.5 wt% of Al_2O_3 (Elmer, 1992). This glass can be further processed to produce Controlled Pore Glass (CPG) which is widely used as a stationary media in chromatography, or alternatively, the pores can be closed up to yield a clear impervious glass known as Vycor 96% silica glass, commonly used in cookware. The increase of B_2O_3 content, coupled with a very fine-scale secondary phase separation within the silica phase increases the chemical resistance, and in this aspect high-borate borosilicate glass differs greatly from low-borate.

Effect of Composition on Glass Properties

The major compounds in borosilicate glass are silicon dioxide and boron trioxide. Alkali metal oxides and alkali earth metal oxides are added up to a certain level in order to optimize the properties. Some other oxides, for example, Al_2O_3 , TiO_2 , ZrO_2 , are added to achieve specific properties depending on end-user requirements. In some cases coloring and refining components are also added.

Silicon Dioxide (SiO_2)

Silicon dioxide is the glass former in borosilicate glass composition. Higher levels of silica increases the melting temperature as well as the working point, and reduces the coefficient of thermal expansion. With lower levels of silica the resistance to acids deteriorates (Peuchert *et al.*, 2004).

Boron trioxide (B_2O_3)

Boron trioxide reduces melting and working temperatures and improves hydrolytic stability when used below 13% by weight in the composition (Reben and Li, 2011). Higher boron trioxide contents have an adverse effect on acid resistance and increases highly volatile alkali metal borates. On the other hand, lower borate contents increase the melting point of the glass by creating secure bonds with alkali metal ions. This helps to reduce the susceptibility to crystallization (Peuchert *et al.*, 2004). Borate also play a major role in reducing the dielectric constant of glass (Reben and Li, 2011).

Alkali Metal Oxides

Sodium oxide (Na_2O) is widely used as a flux, especially in borosilicate glass composition, along with other alkali metal oxides like potassium dioxide (K_2O), lithium dioxide (Li_2O), and lead oxide (PbO). Alkali metal oxide reduces the working temperature and plays an important role in setting the thermal expansion. If the alkali metal oxides content is above a certain limit, glasses exhibit a high coefficient of thermal expansion (Marques, 2008). A higher level of alkali oxide also causes an adverse effect on hydrolytic stability (Peuchert *et al.*, 2004). Peuchert *et al.* (2004) also discussed the role of alkali metal oxides on crystallization and suggested using at least two alkali metal oxides, even in small amounts, in order to have a positive effect on resisting unwanted crystallization. They also reported that beyond 1000 °C, potassium borates evaporate more easily than sodium borates, while lithium borates are, by comparison, more stable in terms of evaporating when the glass is heated (Shelby and Lopes, 2005). Li^+ forms strong bonds with the glass network and increases the acid resistance of the glass (Marques, 2008). The use of PbO , which is an excellent flux, is becoming limited these days due to concerns regarding lead toxicity.

Alkali Earth Metal Oxides

Calcium oxide (CaO) is most commonly used as a property modifier component in glass composition. Small amounts of magnesium oxide (MgO), zinc oxide (ZnO), strontium oxide (SrO), and barium oxide (BaO) are also added separately based on application requirements. Calcium oxide can help greatly to accelerate the phase separation of borosilicate glasses (Eguchi *et al.*, 1988; Kokubu *et al.*, 1987; Yazawa *et al.*, 1994). It also has a stabilizing effect on acid resistance (Watzke *et al.*, 1998). It has been found that limiting CaO to small amounts reduces the evaporation of highly volatile sodium and potassium borate compounds during hot forming (Peuchert *et al.*, 2004). If the amount of CaO exceeds certain limit, devitrification is likely to take place. Moreover, heat resistance and alkali resistance also deteriorate with high contents of CaO (Kokubu *et al.*, 1987). Eguchi *et al.* (1988) has proposed using ZnO to promote ZrO_2 retention in the SiO_2 rich phase at a time of phase separation, thereby maximizing ZrO_2 content in the porous silica-rich skeleton for enhanced alkali-durability.

Other Property Modifying Oxides

Zirconium dioxide (ZrO_2), aluminum trioxide (Al_2O_3), and titanium dioxide (TiO_2) are other commonly used property-modifying oxides. It has been shown that ZrO_2 greatly improves the alkali resistance of borosilicate glass without the glass suffering in terms of the hydrolytic stability and resistance to acids (Kiefer, 1989; Marques, 2008; Kiefer, 1989; Kokubu *et al.*, 1987; Paul, 1990). However, higher ZrO_2 contents increase the working point as well as the risk of flaws forming in the glass. With excessively high ZrO_2 contents, crystallization is likely to occur (Eguchi *et al.*, 1988). Although small amounts of ZrO_2 suppress devitrification, they reduce the growth rate of phase separation due to an increase of glass viscosity (Kukizaki, 2010). There is also a risk of passing un-melted ZrO_2 into the product (Peuchert *et al.*, 2004). Kord *et al.* (2009) claim that addition of ZrO_2 (6 mol%) almost doubled the bending strength. Alumina, most commonly used as a modifying oxide (Eguchi *et al.*, 1988), has mixed effect on the property of the borosilicate glass. It increases insolubility as well as resistance to devitrification of the borosilicate glass, while inhibiting phase separation (Marques, 2008; Rose *et al.*, 2011; Doremus, 1994). Fluidity of the glass decreases with the addition of Al_2O_3 in these glass compositions (Marques, 2008). Alumina also acts as a balancing component to allow relatively high levels of CaO in the borosilicate system. Alumina also acts to prevent cracks during leaching (porous glass production) and improve moldability by minimizing the viscosity change relative to the change in temperature (Kokubu *et al.*, 1987). Titania is used in small quantities for special applications where UV absorption is required (Peuchert *et al.*, 2004; Shorrocks and Yale, 1993). It is also believed that the presence of TiO_2 suppresses crystallization (Mojumdar, 2004).

Refining Component

Borosilicate glasses can be refined with small amounts ($\leq 1\%$ by weight) of conventional refining agents, such as chlorides, for example, NaCl, and sulphates, Na_2SO_4 or BaSO_4 , fluorides, and bromides. Amongst other refining agents CeO_2 , As_2O_3 , Sb_2O_3 , and CaF are noteworthy (Yazawa *et al.*, 1999; Peuchert *et al.*, 2004). These refining components are also used to remove undesirable color tinges.

Coloring Components

Fe_2O_3 , Cr_2O_3 , and CoO are the most commonly used coloring components in glasses. Oxides of other transition elements (copper, manganese, nickel, vanadium, titanium) and rare earths (mainly neodymium and praseodymium) are also used to obtain different colored glasses, usually $< 3 \text{ wt}\%$ (Pfaender, 1996).

References

- Bauccio, M.L. (Ed.), 1994. *Engineered Materials Reference Book*, second ed. USA: ASM International.
- Bloomfield, L., 2001. *How Things Work: The Physics of Everyday Life*, second ed. New York: Wiley.
- Chen, D., Miyoshi, H., Masui, H., Akai, T., Yazawa, T., 2004. NMR study of structural changes of alkali borosilicate glasses with heat treatment. *Journal of Non-Crystalline Solids* 345–346, 104–107.
- Doremus, R.H., 1994. *Glass Science*, second ed. New York, NY: John Wiley & Sons.
- Eguchi, K., Tanaka, H., Yamaguro, T., Yazawa, T., 1988. Chemically durable porous glass and process for the manufacture thereof. US Patent: 4,778,777.
- Elmer, T.H., 1992. Porous and Reconstructed Glasses. *Engineered Materials Handbook* 4, 427–432.
- Hasanuzzaman, M., Rafferty, A., Olabi, A.G., 2014. Effects of zircon on porous structure and alkali durability of borosilicate glasses. *Ceramics International* 40, 581–590.
- Hasanuzzaman, M., Sajja, M., Rafferty, A., Olabi, A.G., 2013. Thermal behaviour of zircon/zirconia-added chemically durable borosilicate porous glass. *Thermochimica Acta* 555, 81–88.
- Kiefer, W., 1989. Borosilicate glass. US Patent: 4,870,034.
- Kingery, W.D., Uhlmann, D.R., Bowen, H.K., 1976. *Introduction to Ceramics*, second ed. New York: Wiley.
- Kokubu, Y., Chiba, J., Saita, K., 1987. Porous glass, process for its production and glass material used for the production. US Patent: 4,665,039.
- Kord, M., Marghussian, V.K., Eftekhari-Yekta, B., Bahrami, A., 2009. Effect of ZrO_2 addition on crystallization behaviour, porosity and chemical–mechanical properties of a $\text{CaO-TiO}_2\text{-P}_2\text{O}_5$ microporous glass ceramic. *Materials Research Bulletin* 44 (8), 1670–1675.
- Krause, D., 2005. Glasses. In: Martienssen, W., Warlimont, H. (Eds.), *Springer Handbook of Condensed Matter and Materials Data*. Berlin Heidelberg: Springer, pp. 523–572.
- Kukizaki, M., 2010. Large-scale production of alkali-resistant Shirasu porous glass (SPG) membranes: Influence of ZrO_2 addition on crystallization and phase separation in $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ glasses; and alkali durability and pore morphology of the membranes. *Journal of Membrane Science* 360 (1–2), 426–435.
- Lancry, M., Régnier, E., Poumellec, B., 2012. Fictive temperature in silica-based glasses and its application to optical fiber manufacturing. *Progress in Materials Science* 57 (1), 63–94.
- Marques, P., 2008. Borosilicate glass compositions and uses thereof. US Patent: 7,341,966.
- McMillan, P.W., 1979. *Glass-Ceramics*. London: Academic Press.
- Mojumdar, S.C., 2004. The Microstructure and optical transmittance thermal analysis of sodium borosilicate bio-glasses. *Journal of Thermal Analysis and Calorimetry* 78 (1), 145–152.
- Newton, R.G., Davison, S., 1989. *Conservation of glass*, for series: Butterworths series in conservation and museology. Butterworths.
- Paul, A., 1990. *Chemistry of Glasses*, second ed. London; New York: Chapman and Hall.
- Peuchert, U., Kunert, C., Bartsch, R., 2004. Borosilicate glass with high chemical resistance and use thereof. US Patent: 6,794,323.
- Pfaender, H.G., 1996. *Schott Guide to Glass*. London: Chapman & Hall.
- Reben, M., Li, H., 2011. Thermal stability and crystallization kinetics of $\text{MgO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ glasses. *International Journal of Applied Glass Science* 2 (2), 96–107.
- Rose, P.B., Woodward, D.I., Ojovan, M.I., Hyatt, N.C., Lee, W.E., 2011. Crystallisation of a simulated borosilicate high-level waste glass produced on a full-scale vitrification line. *Journal of Non-Crystalline Solids* 357 (15), 2989–3001.
- Saiki, K., Sakida, S., Benino, Y., Nanba, T., 2010. Phase separation of borosilicate glass containing sulfur. *Journal of the Ceramic Society of Japan* 118 (7), 603–607.

- Shelby, J.E., Lopes, M. (Eds.), 2005. *Introduction to Glass Science and Technology*. Cambridge: The Royal Society of Chemistry.
- Shorrock, P., Yale, B., 1993. Borosilicate glass composition. US Patent: 5,219,801.
- Uhlmann, D.R., Kreidl, N.J., 1983. *Glass-forming Systems*. New York: Academic Press.
- Varshneya, A.K., Mauro, J.C., 2010. Comment on Misconceived ASTM Definition of "Glass" by A.C. Wright. *Eur. J. Glass Sci. Technol. A* 51 (1), 28–30.
- Vogel, W., Kreidl, N.J., Lense, E., 1985. *Chemistry of Glass*. Columbus, Ohio: American Ceramic Society.
- Watzke, E., Kampfer, A., Brix, P., Ott, F., 1998. Borosilicate glass of high chemical resistance and low viscosity which contains zirconium oxide and lithium oxide. US Patent: 5,736,476.
- Wheaton, B.R., Clare, A.G., 2007. Evaluation of phase separation in glasses with the use of atomic force microscopy. *Journal of Non-Crystalline Solids* 353 (52–54), 4767–4778.
- Yazawa, T., Kuraoka, K., Du, W., 1999. Effect of Cooling Rate on Pore Distribution in Quenched Sodium Borosilicate Glasses. *The Journal of Physical Chemistry B* 103 (45), 9841–9845.
- Yazawa, T., Tanaka, H., Eguchi, K., Yokoyama, S., 1994. Novel alkali-resistant porous glass prepared from a mother glass based on the $\text{SiO}_2\text{--B}_2\text{O}_3\text{--RO--ZrO}_2$ (R=Mg, Ca, Sr, Ba and Zn) system. *Journal of Materials Science* 29 (13), 3433–3440.
- Zachariasen, W.H., 1932. The atomic arrangement in glass. *Journal of the American Chemical Society* 54 (10), 3841–3851.
- Zarzycki, J., 1991. *Glasses and the Vitreous State*. Cambridge; New York: Cambridge University Press.

Further Reading

C162, C162, 1945. *Compilation of ASTM Standard Definitions*. The American Society for Testing Materials, Philadelphia PA.

Optical Glass: Challenges From Optical Design

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Introduction

Current technological trends such as augmented reality, automotive assistance systems, laser technology and three-dimensional printing would not be possible without modern photonics (Petzold, 2018). Such systems have been made possible through a revolution in the field of optics over the last 50 years and – simultaneously – of the materials used within.

Optical design started to trigger the development of novel optical materials about 400 years ago, with the invention of the first microscopes and telescopes in the 17th century (Hartmann, 2014). However, even by the end of the 19th century the manufacturing methods for such optical instruments were still unsatisfying. This was the starting point for Carl Zeiss who ran a manufactory of optical instruments at Jena University to team up with optics expert Ernst Abbe to design high quality microscopes. They identified the need for novel glass types with – compared to what was common at that time – essentially different dispersion properties.

At the same time the glass chemist Otto Schott was making experimental glass melts which he sent to Abbe and which were found to meet exactly the need defined by Abbe and Zeiss (Petzold, 2018; Hartmann, 2014; Hartmann *et al.*, 2010). Thus modern optical glass chemistry was born (Bach and Neuroth, 1998).

The outline of optical glasses given here follows the red thread provided by the interplay of progressing optical design, arising needs for novel optical materials and the corresponding invention of special optical glasses. The starting point is the basic electrodynamics of light and its interaction with matter.

Basic Electrodynamics

Electromagnetic Waves and Their Interaction With Matter

The basic physics of electrodynamics (Jackson, 1999), including the interaction with matter, is described by Maxwell's equations:

$$\begin{aligned}\nabla \cdot \mathbf{D} &= \rho \\ \nabla \cdot \mathbf{B} &= 0 \\ \nabla \times \mathbf{E} &= -\dot{\mathbf{B}} \\ \nabla \times \mathbf{H} &= \mathbf{j} + \dot{\mathbf{D}}\end{aligned}\quad (1)$$

$\mathbf{E}$ and $\mathbf{H}$ denote the electric and the magnetic field. $\mathbf{B}$ is the magnetic flux density, $\mathbf{D}$ is the dielectric displacement. In (1) and throughout this text, bold letters symbolize vector quantities. The dot denotes the time derivative. ρ and $\mathbf{j}$ stand for charge and current density, respectively. Material equations are needed to close Maxwell's equations:

$$\begin{aligned}\mathbf{D} &= \varepsilon \cdot \varepsilon_0 \cdot \mathbf{E} = (1 + \chi_E) \cdot \varepsilon_0 \cdot \mathbf{E} \\ \mathbf{B} &= \mu \cdot \mu_0 \cdot \mathbf{H} = (1 + \chi_M) \cdot \mu_0 \cdot \mathbf{H}\end{aligned}\quad (2)$$

ε_0 is the vacuum permittivity (in SI units) and amounts to $\varepsilon_0 = 8.854 \times 10^{-12}$ As/(Vm). ε is the relative permittivity and is a material property. χ_E is called electric susceptibility. μ_0 is the vacuum permeability and amounts to $\mu_0 = 4\pi \times 10^{-7}$ Vs/(Am). μ is the relative permeability and is a material property. χ_M is called magnetic susceptibility. For conventional optical materials one finds $\chi_E > 0$, $\chi_M = 0$. In general ε and μ are second rank tensor quantities. In homogeneous isotrop media, like glasses, they can be replaced by a scalar quantity, which we do in the following.

The complete optical properties for any spatial combination of matter are included in the solution of Eqs. (1) and (2) and by using appropriate boundary conditions. In the absence of mobile charges and currents, the solutions of Eqs. (1) and (2) are undamped electromagnetic waves.

Wave Propagation in Vacuum

In infinite vacuum, Eqs. (1) and (2) can be solved (Jackson, 1999) using the following boundary conditions and material equations:

$$\varepsilon = 1, \mu = 1, \rho(\mathbf{r}) = 0, \mathbf{j}(\mathbf{r}) = 0 \quad (3)$$

with $\mathbf{r} = (x, y, z)$ being the vector representing the position in space. After applying a few vector operations, a wave equation for the electric field $\mathbf{E}$ in vacuum is obtained:

$$\Delta \mathbf{E} - \varepsilon_0 \mu_0 \ddot{\mathbf{E}} \quad (4)$$

Once Eq. (4) has been solved, the magnetic field can be calculated from Maxwell's equations.

Any solution of Eq. (4) can be represented by an integral over a set of fundamental solutions, for instance, polarized planar waves:

$$E = \iiint_{\mathbf{k}} \left(v_1(\mathbf{k}) \mathbf{e}_1(\mathbf{k}) e^{i(\mathbf{k}\mathbf{r} - \omega t)} + v_2(\mathbf{k}) \mathbf{e}_2(\mathbf{k}) e^{i(\mathbf{k}\mathbf{r} - \omega t)} \right) \quad (5)$$

$\mathbf{k}$ is the wave vector which indicates the direction in which each individual plane wave $v_{1,2}(\mathbf{k}) \mathbf{e}_{1,2}(\mathbf{k}) e^{i(\mathbf{k}\mathbf{r} - \omega t)}$ propagates. ω is the corresponding angular frequency. From inserting Eq. (5) in Eq. (4) it follows that ω must fulfill the condition $\omega = c \cdot k$ with c given by:

$$c^2 = \frac{\omega^2}{k^2} = \frac{1}{\varepsilon_0 \mu_0} \quad (6)$$

c is the vacuum velocity of electromagnetic waves, in particular of light. k^2 denotes the scalar product $\mathbf{k} \cdot \mathbf{k}$.

The corresponding wavelength λ follows from $\lambda = 2\pi/k$ with $\mathbf{k} = |\mathbf{k}| \cdot \mathbf{e}_1(\mathbf{k})$ and $\mathbf{e}_2(\mathbf{k})$ are unit vectors which are orthogonal to $\mathbf{k}$ and to each other (electromagnetic waves are transversal waves). $v_1(\mathbf{k})$ and $v_2(\mathbf{k})$ are the corresponding amplitudes the magnitude of which is determined by the boundary conditions.

Wave Propagation in an Ideal Transparent Refracting Medium

In the case when all geometric dimensions are much larger than the wavelength of the light, the propagation of these electromagnetic waves can be described as light rays. A ray is propagating in the direction of the corresponding $\mathbf{k}$ vector. As demonstrated by Fig. 1 for a lens shaped material in vacuum, this ray will change its direction at the interface between vacuum (or air) and a solid material such as glass, i.e., it will be refracted (Petzold, 2018). The size of this effect is given by Snell's law (Perret-Optic, 2005):

$$\frac{\sin(\alpha + \gamma)}{\sin(\gamma)} = n \quad (7)$$

n is a material constant, the so-called refractive index.

Within the formalism of electrodynamics, this effect is described by applying the value $\varepsilon = n^2$ for the relative permittivity in the glass. With this, the corresponding boundary conditions at the interface will lead to the direction change of $\mathbf{k}$ observed. For the wave function in the glass, $\varepsilon = n^2$ means:

$$E = \iiint_{\mathbf{k}} \left(v_1(\mathbf{k}) \mathbf{e}_1(\mathbf{k}) e^{i(n\mathbf{k}\mathbf{r} - \omega t)} + v_2(\mathbf{k}) \mathbf{e}_2(\mathbf{k}) e^{i(n\mathbf{k}\mathbf{r} - \omega t)} \right) \quad (8)$$

So the velocity of light in the glass is c/n rather than just c .

As Fig. 1 (redrawn from Perret-optics, 2005) also demonstrates, n is not a constant but dependent on the wavelength or frequency: $n = n(\lambda_0) = n(\omega)$. Note that λ_0 denotes the vacuum wavelength. In the glass, λ is given by $\lambda = \lambda_0/n$ which is consistent with the relationship between wavelength and angular frequency in a material with refractive index n , i.e., $\lambda \cdot \omega/2\pi = c/n$.

In most cases and if it is not stated otherwise, n refers to the vacuum wavelength of the "d" absorption line at 587.49 nm which is caused by Helium and which has first been observed in the solar spectrum. This can be indicated by writing " n_d " (Bach and Neuroth, 1998).

The dispersion of the different wavelengths after refraction is definitely a challenge both for optical design and optical material development. For perfect optical imaging, it should be zero.

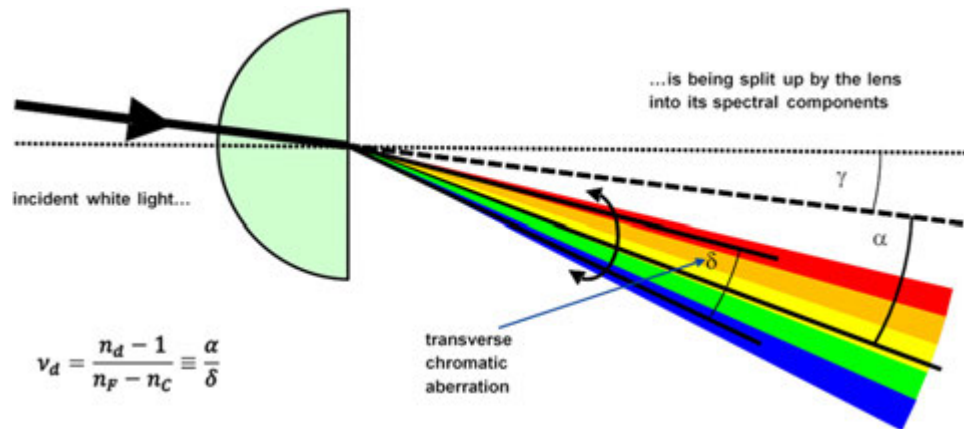


Fig. 1 Significance of Refractive index and Abbe number. Modified and redrawn from Perret-Optic, 2005. Available at: www.perret-optic.ch/optometrie/correction_optique/matiere_optique_qualite_%20physique/matiere_optique_qualite_phys_gb.htm. (downloaded on 02/09/2005).

With respect to the importance of this issue, Ernst Abbe ([Bach and Neuroth, 1998](#)) introduced a dimensionless number to characterize the dispersion of an optical material. Its significance is also demonstrated in [Fig. 1](#). It is equal to α/δ , i.e., the proportion of the refraction angle α of a wavelength in the center of the visible spectrum (587.49 nm, see above) and the angle δ indicating the difference of the refraction angles of the blue and the red fringe of the visible spectrum. “blue” is represented by the Hydrogen F absorption line (486.12 nm), “red” is represented by the Hydrogen CF line (656.27 nm).

The following consideration leads to a relationship between α/δ and the refractive indices at the three wavelengths 486.12 nm, 587.49 nm, and 656.27 nm. With $\sin(\varphi) = \varphi$ for any small angle φ one obtains $1 + \alpha = n_d$. Applying this relationship on the red and the blue ray as well, one finally obtains Abbe's classical definition:

$$v_d = \frac{n_d - 1}{n_F - n_C} \equiv \frac{\alpha}{\delta} \quad (9a)$$

In the new definition, “green” is represented by the Mercury e line (546.074 nm), “blue” is represented by the Cadmium F' line (479.99 nm), “red” is represented by the Cadmium C' line (643.8469 nm).

$$v_e = \frac{n_e - 1}{n_{F'} - n_{C'}} \quad (9b)$$

The new definition had become necessary because the classical definition of the Abbe number refers to the three colors red, yellow, and blue whereas today's color generation usually starts at red, green, and blue (RGB) as basic color set.

Wave Propagation in a Weakly Absorbing Medium

Weak absorbance can be taken into account by the planar wave formalism if one introduces a complex refractive index ([Jackson, 1999](#)).

With

$$n^* = n + i \cdot n_i \quad (10)$$

and

$$\kappa := 2 \cdot i \cdot n_i \cdot k \quad (11)$$

one obtains for any plane wave $E_{k,\omega}$ with wave vector $\mathbf{k}$ and angular frequency ω :

$$E_{k,\omega} = v_{1,2}(\mathbf{k}) e_{1,2}(\mathbf{k}) e^{i(n\mathbf{k}\cdot\mathbf{r} - \omega t) - \frac{\kappa\cdot\mathbf{r}}{2}} \quad (12)$$

This means that the plane wave is attenuated in the direction of its propagation. The intensity E^2 exponentially decreases with $\kappa \cdot \mathbf{r}$ so that $|\kappa| = 2 \cdot i \cdot n_i \cdot 2\pi/\lambda$ is equal to the absorption coefficient.

Close to the absorption edge in the UV spectral range, materials, in most cases, show strong absorptions, optical materials become non-transparent and leave the assumption of being weakly absorbing media (see [Fig. 9](#)).

Optical Glass: Challenges From Optical Design

The Abbe Diagram

A good starting point for understanding the systematics of optical glass is the Abbe Diagram where optical glasses are sorted according to their refractive indices and Abbe numbers. This order system reflects the necessities of optical design which in return have triggered the developments of optical glasses in the last centuries.

[Fig. 2](#) shows the Abbe Diagram according to both its classical and the new definition ([schott.com, 2019](#)).

The acronyms of the various glass types are listed in [Table 1](#):

In the following section, the significance of the glasses in the different parts of the Abbe diagram are explained. It will also be explained why the upper left of the Abbe diagram is empty (and will always be).

Challenge From Conventional Lens Making: High n to Suppress Spherical Aberration

To understand the necessities from optical design, one has to consider the technologies for manufacturing optical components as they had dominated until the late 20th century.

Lens making, in particular grinding and polishing, can easily be carried out by a set-up of rotating devices ([Hartmann, 2014](#)), see [Fig. 3](#) (redrawn from [Schwertz, 2008](#)). The polishing or grinding device oscillates around the center of curvature of the lens element to be polished. Both the polishing device and the lens support rotate around their axes. The sketch shows the polishing of a convex lens element. There is, however, also an equivalent setup for concave lens elements.

The disadvantage of such a machine is that it can only produce spherical spheres. Spherical surfaces, however, cause spherical aberration, see [Fig. 4](#).

Spherical aberration is an issue that primarily affects rays far off the optical axis. To assess the effect for a lens element such as the one in [Fig. 4](#) and to find a way to suppress it, it is necessary to start with Snell's law:

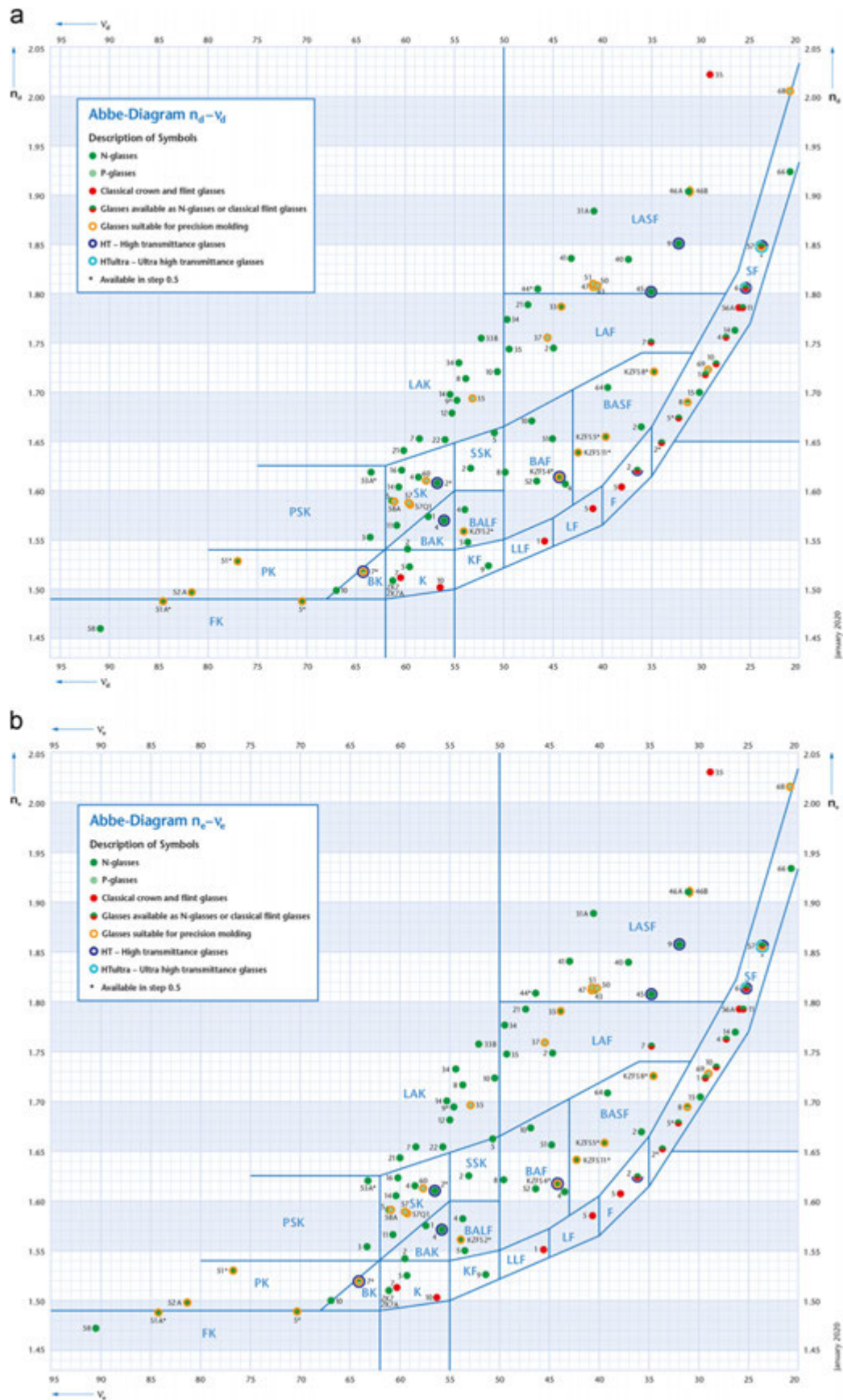
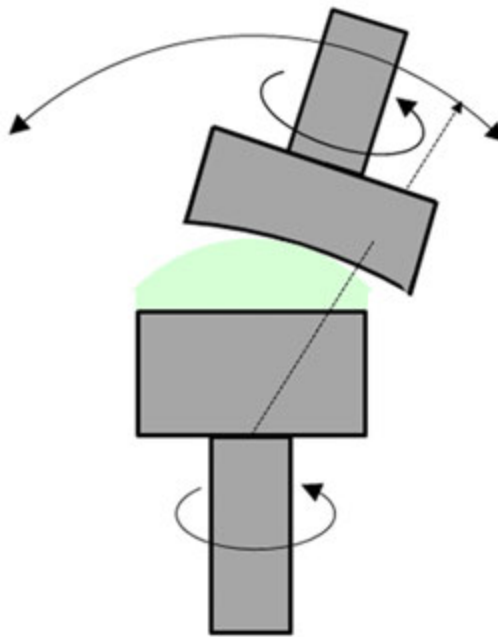


Fig. 2 Abbe diagram (a) According to classical definition; (b) According to the new definition. Reproduced from Schott.com, 2019. (a) Available at: https://www.schott.com/d/advanced_optics/a6ff96d2-72ae-46ea-bd33-73acb318f4f6/1.9/schott-abbe-diagram-nd-vd-jan-2018-de.pdf. Downloaded 02.03.2021. (b) https://www.schott.com/d/advanced_optics/352d8a40-86d7-41e5-b478-dd2450fb14ce/1.10/schott-abbe-diagram-ne-ve-jan-2018-de.pdf. Downloaded 02.03.2021.

Table 1 Significance of the acronyms for glass types

FK	Fluorite crown
PK	Phosphate crown
PSK	Dense phosphate crown
BK	Borosilicate crown
BAK	Barium crown
SK	Dense crown
K	Crown
LAK	Lanthanum crown
SSK	Very dense crown
BALF	Barium light flint
KF	Crown/flint
LASF	Lanthanum dense flint
LAF	Lanthanum flint
BAF	Barium flint
BASF	Barium dense flint
LF	Light flint
LLF	Very light flint
F	Flint
SF	Dense flint
ZK	Zinc crown
KZSF	Special short flint

**Fig. 3** Conventional lens making. Redrawn from Schwartz, K., 2008. An Introduction to the Optics Manufacturing Process. University of Arizona, College of Optical Sciences. (OPTI 521 report).

$$n \cdot \sin(\alpha) = \sin(\beta) = \sin(\alpha + \gamma) \quad (13)$$

and the following geometrical relationship between the radius of curvature R of the spherical surface of the lens element, the distance h between the incoming ray and the optical axis, the angles α , γ and the focal length f , i.e., the position where the ray under consideration crosses the optical axis:

$$R \cdot \sin(\alpha) = h = (R - R \cdot \cos(\alpha) + f) \cdot \tan(\gamma) \quad (14)$$

For small values of h and α , one may apply 1st order Taylor which gives $\sin(\alpha) \approx \alpha$, $\sin(\alpha + \gamma) \approx \alpha + \gamma$, $\cos(\alpha) \approx 1$, $\tan(\gamma) \approx \gamma$. With this, Snell' law becomes $n \cdot \alpha = \alpha + \gamma$, the geometrical relationship becomes $R \cdot \alpha = f \cdot \gamma$. This means for f :

$$f = \frac{R}{n - 1} \quad (15)$$

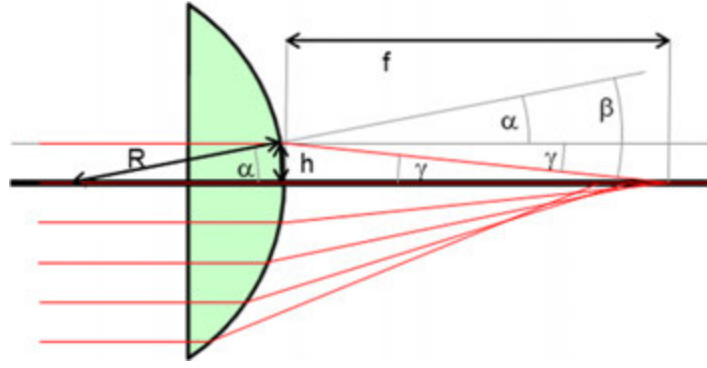


Fig. 4 Spherical aberration.

So for small values of h and α , the focal length is independent of h , i.e., there is no longitudinal spherical aberration.

For bigger values of h and α , a 2nd order Taylor approximation has to be applied which means $\cos(\alpha) \approx 1 - \alpha^2/2$ in particular. This means for f :

$$f = \frac{R}{n-1} - R \cdot \frac{\alpha^2}{2} = \frac{R}{n-1} - \frac{h^2}{2R} \quad (16)$$

So for bigger values of h and α , the focal length depends on h via $h^2/(2R)$, i.e., there is longitudinal spherical aberration. To minimize $h^2/(2R)$, R must be as large as possible. To prevent a change of the focal length of the rays close to the optical axis, this increase of R has to be compensated by a corresponding increase of n .

This fact has directed optical glass development over more than 200 years! One major drive to develop glasses with high refractive indices has been the need to suppress spherical aberration.

How to Make Glasses With High Refractive Index n

Through the Clausius-Mosotti equation (Kittel, 2018) for the wavelength range of visible light (Lorentz-Lorenz equation), the refractive index – a macroscopic quantity – in said wavelength range can be related to the atomic polarizability – a microscopic quantity:

$$\frac{n^2 - 1}{n^2 + 2} \equiv \frac{\chi_E}{\chi_E + 3} = \frac{\rho}{M} \frac{1}{3\epsilon_0} \sum_j N_j \alpha_j \quad (17)$$

ρ is the density, M the molar mass of the glass, N_j the number of atoms of the j -th type of element/mole, and α_j is the corresponding electronic polarizability. It characterizes the linear electronic response of an atom to an imposed electric field. By said electric field, an electric dipole μ is induced which size is described as follows:

$$\mu = \alpha \cdot E_{\text{local}} \quad (18)$$

Note that Eq. (18) refers to the local electric field whereas (2) refers to the global electric field. The difference between both of these is explained in the textbooks such as (Jackson, 1975) where the derivation of Eq. (17) is given. It is this difference between local and global electric field which is responsible for the rather complicated expressions in Eq. (17).

Considering Eq. (17), one finds that dense packing and high electronic polarizabilities of the atoms involved are necessary to obtain high refractive indices.

A rough analysis gives a hint of how high electronic polarizabilities can be achieved (Hartmann et al., 2010). Considering a spherical atom or ion with a homogeneous electronic charge density, the dipole μ induced by the local electric field E_{local} is:

$$\mu = ze \cdot d_E = 4\pi\epsilon_0 \cdot R^3 \cdot E_{\text{local}} \quad (19)$$

z is the number of electrons and e is the elementary charge. See Fig. 5 (redrawn from Föll, 2019) for the significance of d_E . Eq. (19) is derived by the following consideration:

The force exerted on the nucleus by E_{local} is given by the product of its charge $+ze$ and E_{local} . The balancing force from the electron cloud is given by Coulomb's law. Note that for the latter, only the part of the electronic charge at radii $r < |d_E|$ counts (a sphere charged on the outside has no field in the inside, and therefore no force), i.e., $-ze \cdot |d_E|^3/R^3$. One obtains Eq. (20) from which Eq. (19) follows by fraction reduction:

$$\frac{(ze) \cdot \left(-ze \cdot \frac{|d_E|^3}{R^3} \right) d_E}{4\pi\epsilon_0 \cdot |d_E|^2} + ze \cdot E_{\text{local}} = 0 \quad (20)$$

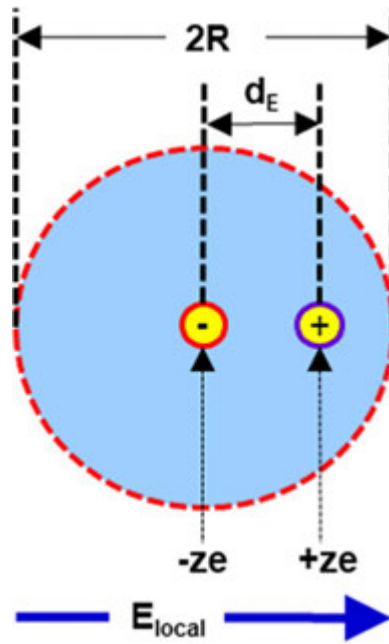


Fig. 5 Atom Size and Polarizability. Redrawn from Föll, H., 2019. Electronic Materials. University of Kiel. Available at: www.tf.uni-kiel.de/matwis/amat/elmat_en/kap_3/backbone/r3_2_2.html. (Downloaded 17.06.2019).

Comparing Eqs. (18) and (19) the polarizability per atom follows as:

$$\alpha = 4\pi\epsilon_0 \cdot R^3 \quad (21)$$

Although the assumption of spherical atoms or ions is not always justified, the general tendency is true that the electronic polarizability scales with the size of the atoms or ions. So large atoms are required.

For oxide glasses most of the electronic polarizability comes from the oxygen anion, which is larger than most cations, as found in the periodic system. In order to obtain very high refractive indices oxygen is usually combined with cations, which have the same size or are even larger than the oxygen anion. Such cations are found in the lower left corner of the periodic system, see Fig. 6, which provides the effective ion radii (Shannon and Prewitt, 1969; Bach and Neuroth, 1998) for all cations that are important for glass making, the bandgaps of the corresponding oxides (Portier *et al.*, 2001; Gillen and Robertson, 2013; Ma *et al.*, 2017; Islam *et al.*, 2012; Quah and Cheong, 2015; Ziletti *et al.*, 2015; Robertson, 2004; Hsu *et al.*, 2013; Guo *et al.*, 2018; Abul-Hail *et al.*, 2012; Mansoob Khan *et al.*, 2014) and Dietzel's field strength for all cations commonly used in glassmaking (Dietzel, 1942).

Note that cation radii depend on charge and coordination number; for the periodic table, the charges and coordination numbers of the cations in the most stable/common simple oxides have been selected. The ionic radius of the oxygen ion is 1.4 Å in six-fold coordination. It does not depend strongly on the coordination number, however, so that 1.4 Å may be taken as a universal value.

Therefore, the large ions pave the path for the development of higher refractive index glasses which enable the correction of spherical aberration, i.e., by moving to higher values along the vertical axis of the Abbe diagram (Shannon and Prewitt, 1969; Jackson, 1999; Portier *et al.*, 2001; Schwartz, 2008; Islam *et al.*, 2012; Gillen and Robertson, 2013; Ma *et al.*, 2017; Kittel, 2018; Föll, 2019).

The second essential task of optical imaging is to suppress chromatic aberration. In contrast to spherical aberration, it is not caused by shortcomings of the manufacturing process but by the dispersion, i.e., the frequency dependence, of the electronic polarizability, which is an essential feature of the latter.

Challenge From an Intrinsic Material Property: Dispersion

The electronic polarizability describes the material response to an electric field imposed from outside. In optics, this field is oscillating at high frequencies (10^{14} – 10^{15} Hz). By nature, optical glasses are transparent in this frequency range. Note that transparency of a solid material, which has been known to mankind for several thousand years, can only be understood by taking into account the quantum mechanics concept of electronic bands (see Figs. 9 and 10). There is a high frequency absorption edge, however, which does not only limit transmission in the UV but also gives rise to the observed dispersion, i.e., the frequency or wavelength dependence of the electronic polarizability.

The essential features can be illustrated considering a mechanical analog, the spring pendulum, Fig. 7.

With the angular frequency ω of the exciting force $f = f_0 \cdot \cos(\omega t)$ approaching the angular eigenfrequency ω_0 from below, one observes a super-linearly increasing response $x = x_0 \cdot \cos(\omega t)$, i.e., an increase of the dispersion.

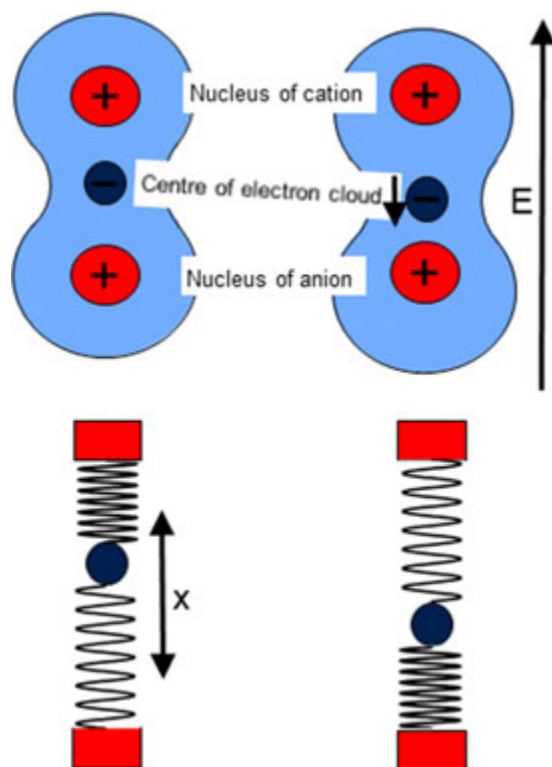


Fig. 7 Mechanical Analog of a two-cation molecule.

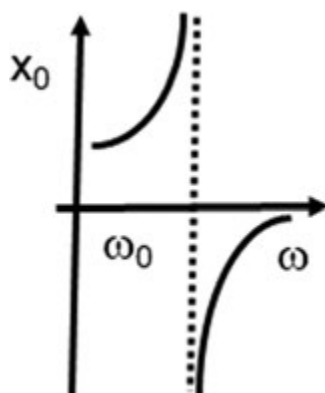


Fig. 8 Frequency dependence of the response to an external force or electric field.

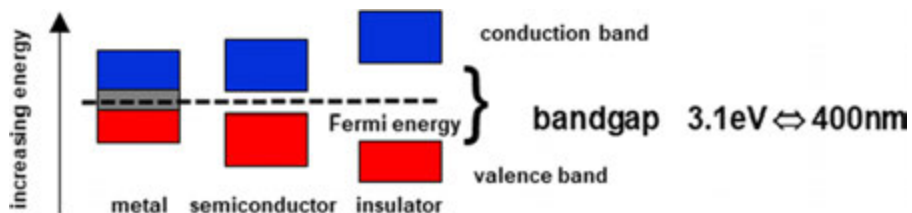


Fig. 9 Lower limit for the bandgap of oxides entering an optical glass. Redrawn from Energyeducation.ca, 2019. Available at: https://energyeducation.ca/encyclopedia/Band_gap. (Downloaded on 17.06.2019).

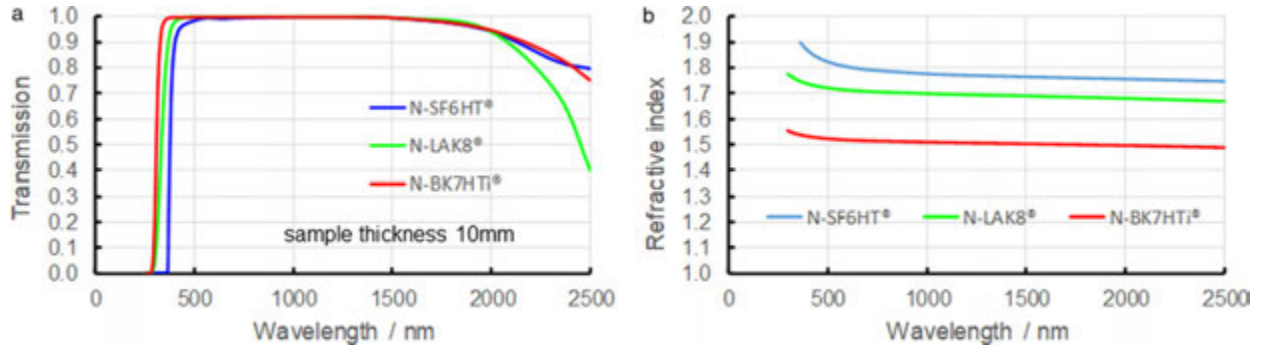


Fig. 10 Comparison of (a) Transmission and (b) Refractive Index variation dependent upon Wavelength.

How to Make Glasses With Low Dispersion

As has been said, the material selection for low-dispersion glasses should be such that oxides with small bandgaps should be avoided, in particular oxides with a bandgap smaller than 3.1 eV, which corresponds to an absorption edge at the low wavelength borderline of the visible window, i.e., 400 nm, see again Fig. 6.

Comparing the requirements resulting from the demand for high indices and low dispersion, some antagonism between these two goals exists. The cations belonging to the oxides with high bandgaps are in the upper right corner of the periodic system, not in the lower left one where the cations particularly suited for a high refractive index are found. Considering Fig. 6, however, there are some oxides which meet both requirements – among them BaO, a classical component of high index, low dispersion glasses.

Unfortunately, the stated antagonism is not a unique feature of optical glasses but the consequence of a universal law, the so-called Kramers-Kronig relations (Kittel, 2018) which state that within linear response theory, there is an interrelation between the real part and the imaginary part for any susceptibility, in particular for the electric susceptibility, independent from the material (glass or polymer or ...):

$$\varepsilon(\omega) = 1 + \chi = 1 + \chi_r(\omega) + i\chi_i(\omega) \quad (23)$$

$$\chi_r(\omega) = \frac{2}{\pi} \cdot P \int_0^{\infty} \frac{\omega' \cdot \chi_i(\omega')}{\omega'^2 - \omega^2} \cdot d\omega' \quad (24)$$

P: Cauchy's principal value of the integral.

With $\varepsilon = n^2 = (n + i \cdot n_i)^2 = n^2 + 2 \cdot i \cdot n \cdot n_i = n^2 + n \cdot |k| \cdot \lambda / 2\pi$, $\kappa = |k|$, one gets:

$$n^2(\omega) = 1 + \frac{2c}{\pi} \cdot P \int_0^{\infty} \frac{n(\omega') \kappa(\omega')}{\omega'^2 - \omega^2} \cdot d\omega' \quad (25)$$

The message conveyed by Eq. (25) is that in any material there is no high refractive index without an absorbance issue (consider the numerator of Eq. (25); there has to be a non-zero k in the vicinity of ω on the frequency scale) and a dispersion issue (consider the denominator of Eq. (25)).

This is what makes optical material development a challenge. It also explains why the upper left corner of the Abbe diagram is empty and will be forever.

In addition to this general finding, the Kramers-Kronig rules have a practical application.

A crude but very practical simplification of Eq. (25) is the Sellmeier series. It approximates the complete dispersion of a transparent material by three sharp absorption lines; two lines in the UV part of the electromagnetic spectrum and one in the infrared part with coefficients B_i , C_i . Note that the coefficients B_i are unitless and the coefficients C_i are usually given in μm^2 and λ is given in μm . The coefficients have to be provided for each glass (and will be available in any comprehensive optical glass catalog):

$$n(\lambda) = \left(1 + \frac{B_1}{1 - \frac{C_1}{\lambda^2}} + \frac{B_2}{1 - \frac{C_2}{\lambda^2}} + \frac{B_3}{1 - \frac{C_3}{\lambda^2}} \right)^{\frac{1}{2}} \quad (26)$$

Challenge From Glass Making

With what has been said so far, glasses only consisting of components such as BaO would be perfectly suited as optical materials. Such compositions, however, do not fit to the rules of glassmaking. A glass forming composition must have a certain amount (rule of thumb: > 50 mol%) of glass formers, i.e., oxides with strong covalent bonds. One may identify suitable oxides

by considering field strength (see Dietzel, 1942) of the corresponding cations, see again Fig. 6. For oxides, Dietzel's field strength F is defined as:

$$F = \frac{z_c}{(r_c + r_o)^2} \quad (27)$$

z_c is the charge of the cation, r_c is the radius of the cation, and r_o is the radius of an oxygen ion.

The higher the latter, the more suited the corresponding oxides are for glassmaking. This is why silicon dioxide, germanium dioxide, boron trioxide and phosphorus pentoxide are called (glass) network formers whereas other oxides are classed as network modifiers or intermediates, depending on the field strength (Dietzel, 1942).

For optical glasses, usually one or more of these network formers is combined with, e.g., barium oxide BaO (see above). With respect to the combination of a high-enough bandgap material, a not-so-small cation radius, and also not-so-small value of Dietzel's cation field strength, one other prominent network modifier oxide to be combined with network formers is lanthanum oxide La_2O_3 .

With respect to the inclusion of barium oxide and lanthanum oxide within the compositions of optical glasses, a number of optical glass types bear their names, see Table 1. However, numerous other network modifier oxides are used in optical glasses, e.g., to optimize the packing density which is another criterion for high polarizability, see the Clausius-Mosotti Eq. (17) above.

To a certain extent, intermediate oxides such as niobium pentoxide, bismuth oxide or tellurium dioxide may substitute for network formers. This gives rise to niobium phosphate, bismuth, and tellurite glasses.

Transmission

The interdependence between refractive index, dispersion, and absorption suggests that, beside the optical position in the Abbe diagram, transmission is the third critical property of optical glass.

The intrinsic property involved is called pure transmission. It gives the exponential attenuation $e^{-\kappa \cdot d}$ of the electromagnetic radiation in a sample and can be determined from its transmission by correction for the reflection losses at both sides.

The transmission T of an absorbing plate of thickness d is given by Soler (1997):

$$T = \frac{(1 - \rho)^2 e^{-\kappa \cdot d}}{1 - \rho^2 e^{-2 \cdot \kappa \cdot d}} \quad (28)$$

ρ is the reflection at the surface. For perpendicularly incident light, ρ is given by:

$$\rho = \frac{(1 - n)^2}{(1 + n)^2} \quad (29)$$

With (28) and (29), the pure transmission can be calculated from measured transmission data, see Fig. 9.

Oxides used for optical glassmaking are selected with respect to their transparency in the visible range, which always means the near infrared also. There is, however, a low wavelength boundary of the transmission window. This UV absorption edge may come close to the visible range by design if a high dispersion or low Abbe number is required by the application, see Fig. 9 and below.

Roughly speaking, the UV absorption edge marks the bandgap of the glass, which in return is determined by the bandgaps of the oxides involved. Analyzing the glass structure one finds that the position of the UV absorption edge depends on the quotient of the number of bridging oxygens and the number of network former cations. The larger this quotient, the further this edge is in the UV.

The quotient will be a maximum in a glass consisting of network formers only. In vitreous silica (glass made from high-bandgap SiO_2), for instance, this quotient is "2" since all oxygen atoms are building a bridge from one silicon atom to another. If one adds modifiers like low-bandgap Na_2O , some of these bridges are destroyed. In $\text{Na}_2\text{O-SiO}_2$ glass, the said quotient is "1". Simultaneously to adding Na_2O to SiO_2 glass, the UV edge will move to longer wavelengths.

As it is clear from the above, moving the UV edge to longer wavelengths will increase the refractive index (usually wanted) and the dispersion (usually unwanted, but there are exceptions). However, this is not the only possible reason for an absorption edge close to the visible range. UV blocking may be another motive. This can be achieved by TiO_2 or CeO_2 doping (see the bandgaps of these oxides in Fig. 6). This doping will also protect the glass from damage caused by UV (solarization).

Optical Glass Families

With what has been said so far, it is expected that glass families suited for high index and/or low dispersion should be combinations of borates, silicates and heavy ion oxides (Bach and Neuroth, 1998). Indeed, this is the case, see Fig. 11 (Bach and Neuroth, 1998).

Remarkably, the two cations which have been identified as particularly attractive for optical glasses above by theoretical considerations, i.e., Barium and Lanthanum, really play a prominent role. Barium- and Lanthanum containing glasses like N-LAK8 with low dispersion and high index can be found in the top center of the Abbe diagram.

In the bottom center, there are glasses like Schott N-BK7® with low dispersion and moderate refractive index for regular optics. In the bottom left, there are ultralow dispersion phosphate glasses for high-end optics. No glasses can be found in the top left because of the Kramers-Kronig relations.

The special role of high dispersion glasses like N-SF6 situated in the top right position of the Abbe diagram is discussed below.

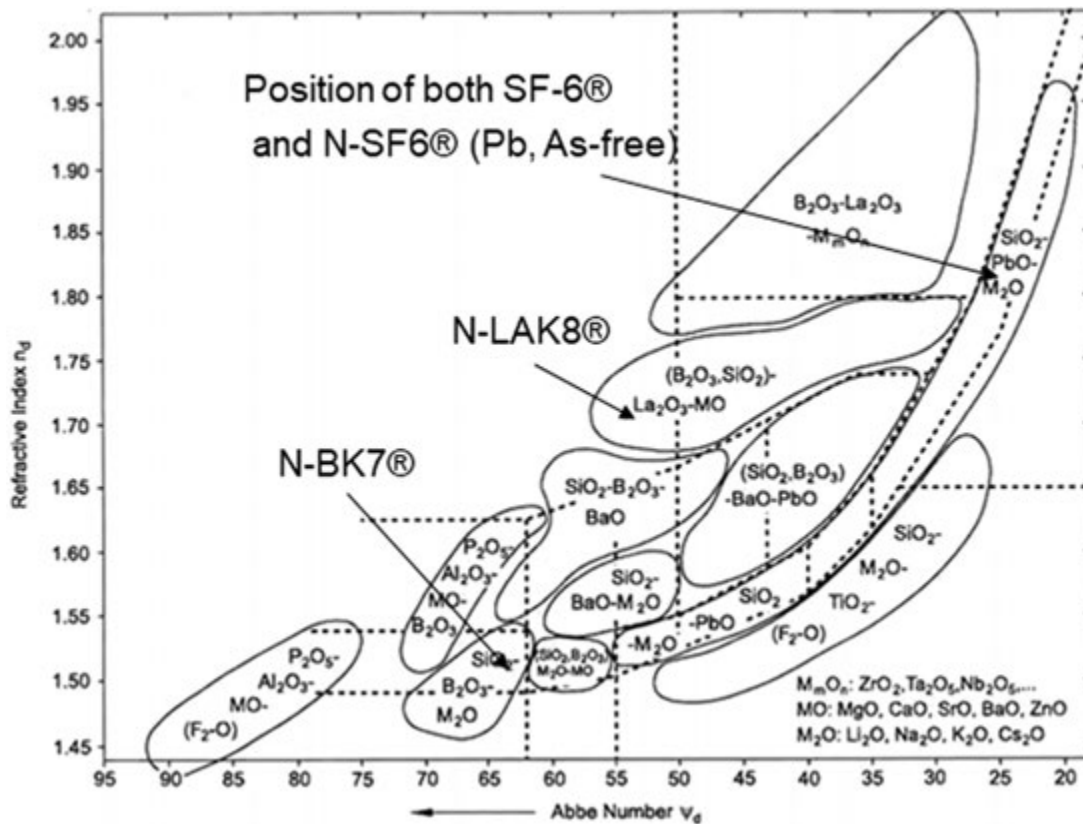


Fig. 11 Families of optical glasses (see Bach, H., Neuroth, N. (Eds.), 1998. *The Properties of Optical Glass*, Schott Series on Glass and Glass Ceramics, second ed. Berlin, Heidelberg, New York: Springer).

Note that in most formerly lead oxide-containing glasses, PbO has now been substituted. For some of them, for instance SF6, both the classical and the arsenic- and lead-free N-type glass are available.

Meeting the Above Challenges by Glass Selection and Multi-Lens-Element Optical Design

With a glass like N-LAK8, a single lens element combining low spherical and chromatic aberration can be manufactured (Fig. 12(a); note that the primary color issue is intentionally exaggerated). For most applications, however, this is not enough: it is desirable to make certain aberrations to be almost or exactly zero.

These tasks can only be fulfilled with a multiple lens element set-up. Splitting up the refractive power of an optical system among various lens elements significantly reduces spherical aberration; combining lens positive and negative elements with very much different Abbe numbers enables color correction.

Primary Axial Color Correction by a Two Element Lens System: Achromatic Lens

A two-lens element system where the “red focus” and the “blue focus” are at the same point is called achromatic lens, see Fig. 12(b). Such a complete suppression of primary axial color is possible by combining a positive element with a high Abbe-number and a negative element with a low Abbe-number (Fischer *et al.*, 2008).

To find a suitable combination of refractive indices and Abbe numbers, some calculations are necessary. The starting points are the lens maker’s equation and the additivity rule for the inverse focal lengths of thin lens elements:

$$\frac{1}{f} = (n - 1) \cdot \left(\frac{1}{R_1} - \frac{1}{R_2} \right) \quad (27)$$

$$\frac{1}{f} = \frac{1}{f_1} + \frac{1}{f_2} \quad (28)$$

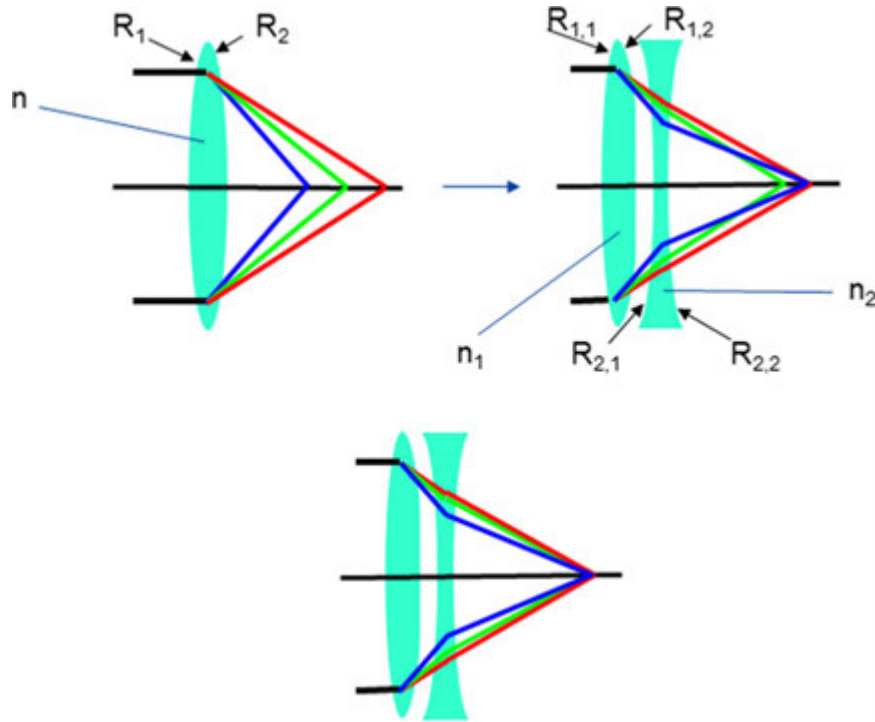


Fig. 12 (a) Primary color correction. Single lens element: Note that R_1 has a positive value (Convex to the left) whereas R_2 has a negative one (Convex to the right); (b) Achromat: Primary Axial Color Correction, Residual Secondary Axial Color; (c) Semi-Apochromat Correction.

With this, then for the blue and the red focal length of the two-lens-element system:

$$\frac{1}{f_{blue}} = \frac{1}{f_{1,blue}} + \frac{1}{f_{2,blue}} = (n_{1,blue} - 1) \cdot \left(\frac{1}{R_{1,1}} - \frac{1}{R_{1,2}} \right) + (n_{2,blue} - 1) \cdot \left(\frac{1}{R_{2,1}} - \frac{1}{R_{2,2}} \right) \quad (29)$$

$$\frac{1}{f_{red}} = \frac{1}{f_{1,red}} + \frac{1}{f_{2,red}} = (n_{1,red} - 1) \cdot \left(\frac{1}{R_{1,1}} - \frac{1}{R_{1,2}} \right) + (n_{2,red} - 1) \cdot \left(\frac{1}{R_{2,1}} - \frac{1}{R_{2,2}} \right) \quad (30)$$

If both the blue and the red focal length are to be the same, the following equation must hold:

$$0 = (n_{1,blue} - n_{1,red}) \cdot \left(\frac{1}{R_{1,1}} - \frac{1}{R_{1,2}} \right) + (n_{2,blue} - n_{2,red}) \cdot \left(\frac{1}{R_{2,1}} - \frac{1}{R_{2,2}} \right) \quad (31)$$

As both $1/R_{1,1}$ and $-1/R_{1,2}$ are positive, $(n_{1,blue} - n_{1,red})$ should be small in order not to create too high a value of the positive first term and thus make the later compensation by the negative second term less easy.

$R_{2,1}$ and $-R_{2,2}$ are both negative so that compensation of the first term is possible. At this point, it has to be decided which factor of the second term, either $(n_{2,blue} - n_{2,red})$ or $(R_{2,1} - R_{2,2})$ should bear the load of compensation. A big value of $(R_{2,1} - R_{2,2})$ means a negative lens element with small radii of curvature which causes spherical aberration and is neither easy to manufacture nor to handle. So preferably, $(n_{2,blue} - n_{2,red})$ is increased.

Thus finally it is necessary to combine, e.g., a positive lens element of N-LAK8 with a negative lens element of a glass with a small Abbe number, namely N-SF6, for primary axial color correction, see Fig. 2.

To give numbers: with N-LAK8: $n_{blue}(479.99 \text{ nm}) = 1.722974$, $n_{red}(643.84) = 1.709615$, $n_{green}(546.07 \text{ nm}) = 1.716160$ and N-SF6: $n_{blue}(479.99 \text{ nm}) = 1.829796$, $n_{red}(643.84 \text{ nm}) = 1.7974931$, $n_{green}(546.07 \text{ nm}) = 1.812659$ as well as with $R_{1,1} = -R_{1,2} = 7.5966 \text{ cm}$ and $R_{2,1} = -R_{2,2} = -18.3702 \text{ cm}$, one obtains $f = 10 \text{ cm}$ for blue and red, and $f = 9.9928 \text{ cm}$ for green.

Secondary Axial Color Correction by Selecting Glasses With Anomalous Partial Dispersion

For a two lens element system, where not only the “red focus” and the “blue focus”, but also the “green focus” are at the same point (secondary axial color correction), glasses are required with a special so-called partial dispersion. *With a grain of salt*, this quantity corresponds to the second derivative of the refractive index with respect to the wavelength – in a similar way as the Abbe number corresponds to the first derivative. Calculating the optical performance of a two lens element system with primary color correction it can be shown that this system will also display secondary color correction if both lens elements – which have different Abbe numbers – have the same relative partial dispersion, i.e., the same quotient of partial dispersion and principal dispersion, see Fig. 13(a). Note that besides the already mentioned spectral lines, the blue mercury g line (435.8 nm) is referred to here as well.

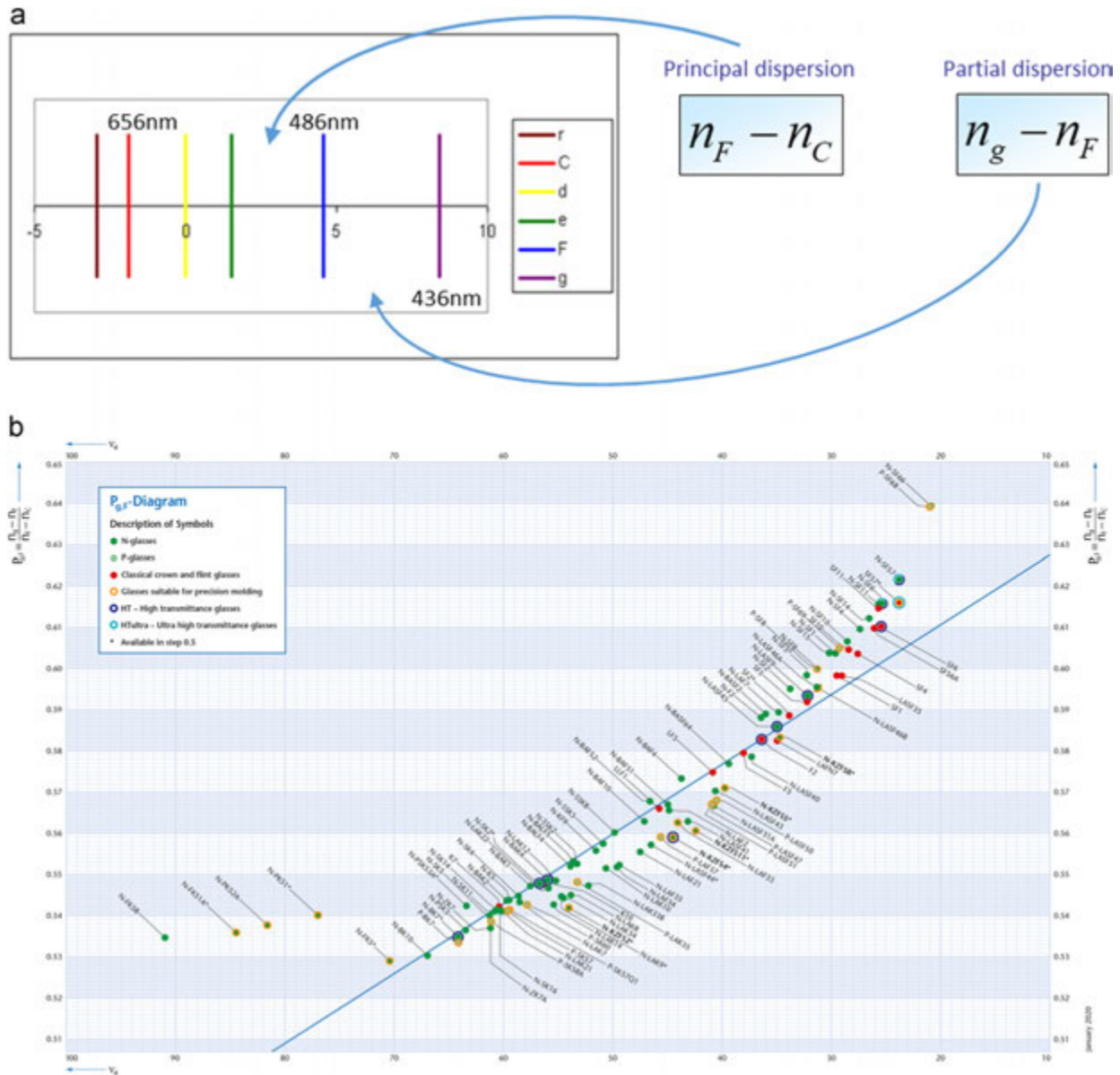


Fig. 13 (a) Significance of partial dispersion and (b) Diagram of partial dispersion for glasses. Reproduced from Schott.com, 2019. Available at: https://www.schott.com/d/advanced_optics/436c7f72-e980-44c2-b14b-0c5c952cca7f/1.8/schott-ebbe-diagramm-pgf-februar-2016-de.pdf. Downloaded 02.03.2021.

The most common definition of relative partial dispersion refers to the wavelengths is:

$$P_{g,F} = \frac{n_g - n_F}{n_F - n_C} \quad (32)$$

Combinations with the different Abbe number but the same partial dispersions are not easy to find because, in general, there is a proportionality between partial dispersion and Abbe number. There are, however, exceptions from that rule – the so-called glasses with anomalous partial dispersion – so that combinations may be found of glasses with different Abbe numbers but the same relative partial dispersion, see Fig. 13(b) (schott.com, 2019).

Two lens element systems with full primary and secondary axial color correction are called Semi-apochromatic lens, see Fig. 12(c). A suitable combination is a positive lens element of, e.g., N-SSK8 (on-line in partial dispersion map, $n_d = 50$, $P_{g,F} = 0.56$) with a negative lens element of N-KZFS11 (off-line, $n_d = 42.4$, $P_{g,F} = 0.5605$), see Fig. 2.

To give numbers: with N-SSK8: $n_{\text{blue}}(479.99 \text{ nm}) = 1.627128$, $n_{\text{red}}(643.84) = 1.614598$, $n_{\text{green}}(546.07 \text{ nm}) = 1.620676$ and N-KZFS11: $n_{\text{blue}}(479.99 \text{ nm}) = 1.649150$, $n_{\text{red}}(643.84 \text{ nm}) = 1.633952$, $n_{\text{green}}(546.07 \text{ nm}) = 1.641325$ as well as with $R_{1,1} = -R_{1,2} = 1.8389 \text{ cm}$ and $R_{2,1} = -R_{2,2} = -2.2305 \text{ cm}$, one obtains $f = 10 \text{ cm}$ for blue and red and green.

Note that the glasses selected are at completely different positions in the Abbe diagram than the above pair N-LAK8 and N-SF6.

New Materials and Technologies

Magnetorheological Finishing

For centuries, there have been only high refractive indices and splitting of refractive power among several lens elements as counter-measures against spherical aberration. This has changed with modern manufacturing technologies, e.g., magnetorheological finishing, see Fig. 14. This technology allows spherical aberration to be suppressed by giving any glass the aspherical shape required for optimal imaging (Fischer *et al.*, 2008).

Magnetorheological finishing (Schwartz, 2008) is illustrated in Fig. 15. The rotating lens touches the magnetorheological fluid, which covers a rotating wheel. In addition, the lens holder swings back and forth. This would lead to a spherical polish if the abrasive power of the fluid were constant over time. However, the viscosity of the fluid and thus the abrasive power can be adjusted by a magnetic field. By computer control of the magnetic field, aspherical polishing is achieved. Together with corresponding CNC etc., very precise aspheric lenses can be made from any glass.

Precision Molding

A low cost alternative to magnetorheological finishing is precision molding, see Fig. 16. In contrast to magnetorheological finishing, however, this technology requires special glasses (Fig. 17 (schott.com, 2019)) which can be molded at not-too-high temperatures (so-called low T_G -glasses; T_G : glass transition temperature).

Optoceramics

The development of translucent ceramics for technical applications started in the 1950s (Coble, 1959, 1961). Those high tech ceramics were made possible through the initial development of “powder metallurgy” transferred into the ceramic world (Schneider, 1991). Thus, translucent polycrystalline alumina has enabled the construction of high pressure sodium and ceramic metal halide lamps (Wei, 2007; Rea *et al.*, 2009). Through availability of starting powders with increased purity and finer particle size it was finally possible to achieve highly transparent ceramics for the use of laser oscillation in the 1990s (Ikesue *et al.*, 1995). In order to achieve this, the researchers had to decrease significantly all possible scatter sources, such as grain boundary phases, residual pores and secondary phases, which cause significant losses that prohibit laser oscillation in the translucent ceramic laser gain medium (Ikesue and Aung, 2008). Thus, using cubic materials, birefringent light scatter due to different refractive indices in the different crystal axes is avoided. The grain boundaries are engineered in such way that no light scatter occurs; and pores are reduced to the ppm level, leading to transparent ceramics with optical qualities comparable to single crystals of similar compositions (e.g., (Lu *et al.*, 2000; Lee *et al.*, 2006; Prasad *et al.*, 2007; Huhle *et al.*, 2007; Ivanov *et al.*, 2007)).

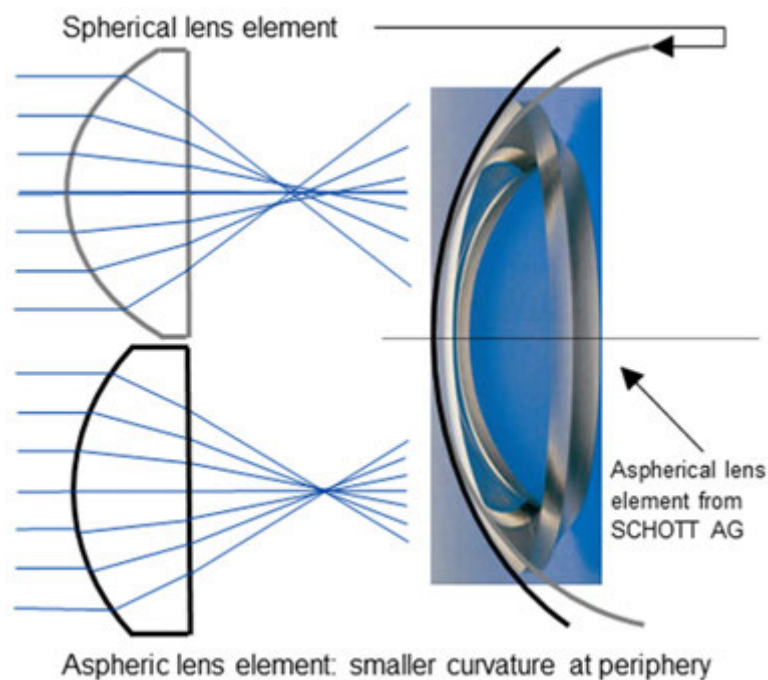


Fig. 14 Spheric and aspheric lenses.

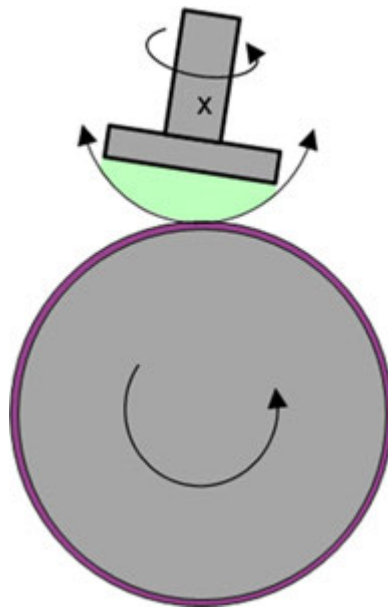


Fig. 15 Magnetorheological finishing.

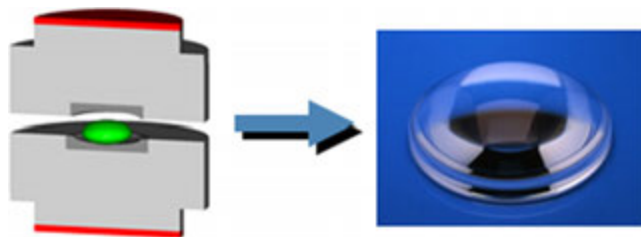


Fig. 16 Precision molding.

Within the development of imaging optics the main target is a sufficient optical quality while maintaining compact and preferably light construction of the optical system, i.e., the total number of imaging lenses must be kept as low as possible. With the current available glass melting and molding techniques, only such glass types can be produced with high quality that are located in an Abbe diagram, in which the refractive index is plotted against the Abbe number, in a certain range (**Fig. 2(a)**) (Menke, 2011). Crystalline materials and polymers show different optical positions within the Abbe diagram; thus, with transparent polycrystalline ceramics extraordinary property areas that glass currently cannot reach (Yoshida *et al.*, 2006; Kvatchadze *et al.*, 2006) are principally possible. This offers the possibility for color correction, reduced birefringence and thus smaller lenses within an optical system.

YAG ceramics are available in high optical quality both as single crystals as well as ceramic materials; however, the optical position of YAG is not unique, lying just above the magical line (**Table 2**) (Menke, 2011). They are mainly used within HID lamps.

Transparent spinel ceramics MgAl_2O_4 have been developed within different laboratories, but their optical properties are also not far from the “magical line” (**Table 2**). However, as the transmittance window for spinel ceramics ranges from ~ 150 nm to $6\text{ }\mu\text{m}$ and its mechanical properties are outstanding, they are a useful material class for application as e.g., last lens element for steppers and defense windows.

As the spinel crystal phase allows the incorporation of different ions, it is possible to tune their optical properties, especially their dispersion characteristics (**Table 2**) (Menke *et al.*, 2014), not needing to account for glass forming regions.

Transparent yttrium stabilized cubic ZrO_2 (YSZ) ceramics were first demonstrated by Tosoh Corp. (Tsukuma, 1986; Tsukuma *et al.*, 1988). Because of the presence of TiO_2 as a sintering aid, birefringence can occur in these sintered ceramics, so special post-processing procedures have to be performed, to reduce stresses (Peuchert *et al.*, 2009). The optical position of YSZ is quite unique with a high refractive index $n_d \sim 2.1\text{--}2.2$ and a $v_d \sim 30\text{--}39$ (**Table 2**), depending upon its composition (Menke *et al.*, 2009a).

Translucent and transparent perovskite ceramics of the type $(\text{Ba}\{(\text{Sn}_u\text{Zr}_{1-u})_x\text{Mg}_y\text{Ta}_z\})_v\text{O}_w$; $(\text{Ba}\{(\text{Sn}_u\text{Zr}_{1-u})_x\text{Zn}_t\text{Mg}_{1-t}\}_y\text{Nb}_z)_v\text{O}_w$ have been shown to exhibit high refractive index and Abbe number, which are useful as optical parts for optical devices, such as lenses, prisms or optical path control plates (Kintaka, 2007; Murata.com, 2021).

Another multicomponent class of cubic ceramics are those within the so-called pyrochlore structure (Menke and Peuchert, 2008; Menke and Ikese, 2009; Menke *et al.*, 2009b) showing special optical positions, especially in their dispersion (**Table 2**), and

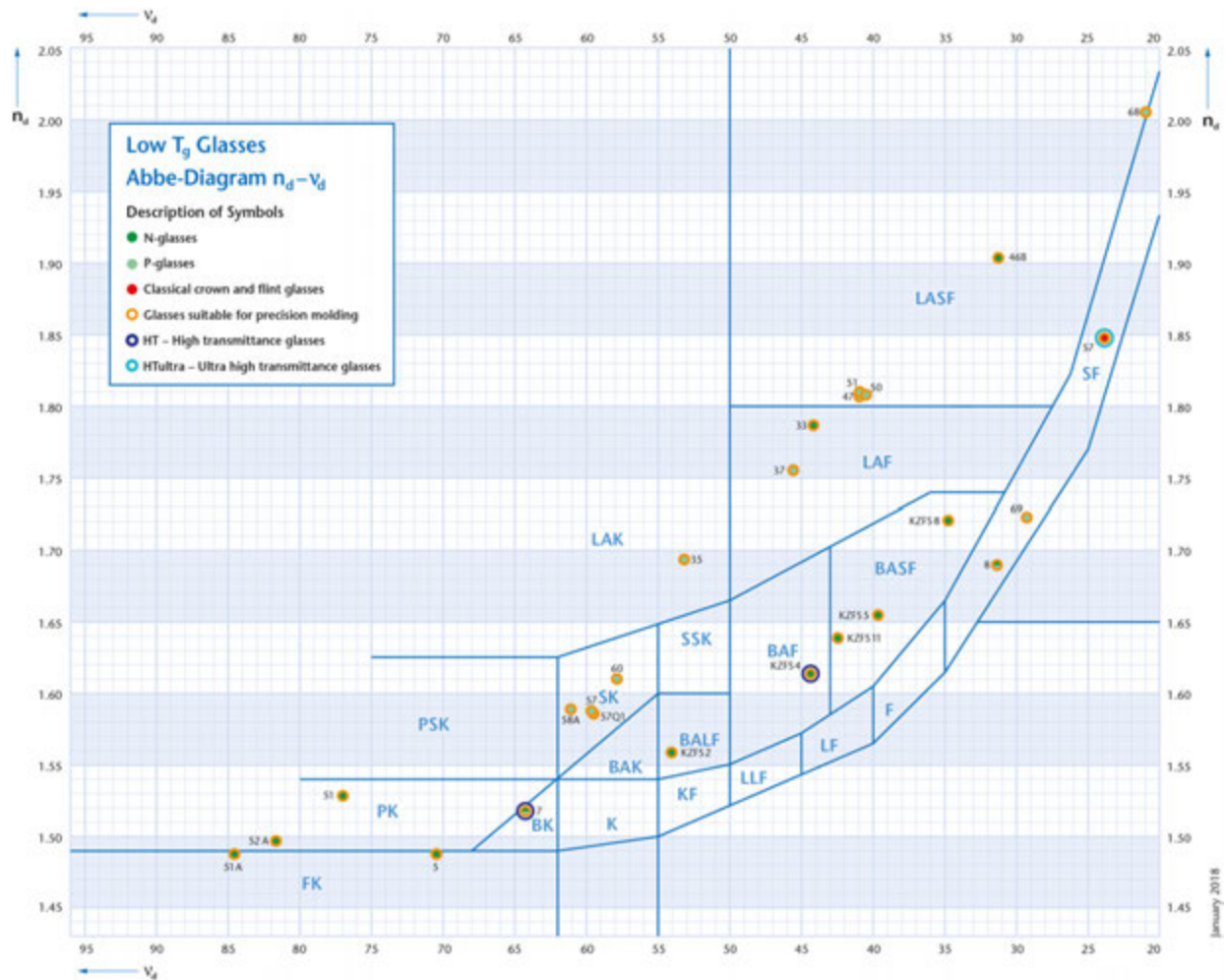


Fig. 17 Low Tg glasses. Reproduced from Schott.com, 2019. Available at: https://www.schott.com/d/advanced_optics/316ba9d5-cd3e-46bb-937c-6bca8b06aefc/1.12/schott-abb-diagram-low-tg-jan-2018-de.pdf. Downloaded 02.03.2021.

Table 2 Optical data of different transparent ceramics

	<i>Mg-Spinel based</i>	<i>YAG based</i>	<i>Spinel Variation</i>	<i>Y₂O₃ based</i>	<i>Pyrochlore based</i>	<i>Perovskite based</i>	<i>ZrO₂ based</i>
n_d	1.72	1.83	1.85	1.91	2.04	2.05	2.16
v_d	62	52	55	36	40	30	34

useful for specialized optical applications in conjunction with PK and FK glasses; thus this is useful for application in gauss-type lens optical systems (e.g., for single-lens reflex cameras), for aberration correction.

References

- Abul-Hail, R.C.H., Hussein, H.F., Al-Fregi, A.A., 2012. The effect of gamma-Irradiation on the absorption spectra and optical energy gap of selenium dioxide thin films. *Science Journal of Physics* 2012, 4.
- Bach, H., Neuroth, N. (Eds.), 1998. *The Properties of Optical Glass*, Schott Series on Glass and Glass Ceramics, second ed. Berlin, Heidelberg, New York: Springer.
- Coble, R.L., 1959. Preparation of transparent ceramic Al_2O_3 . *American Ceramic Society Bulletin* 38, (507).
- Coble, R.L., 1961. Sintering crystalline solids II. Experimental test of diffusion models in powder compacts. *Journal of Applied Physics* 32, 793–799.
- Dietzel, A., 1942. Die Kationenfeldstärken und ihre Beziehungen zu Entglasungsvorgängen, zur Verbindungsbildung und zu den Schmelzpunkten von Silikaten. *Zeitschrift für Elektrochemie* 48, 9–23.
- Energyeducation.ca, 2019. Available at: https://energyeducation.ca/encyclopedia/Band_gap. (downloaded on 17.06.2019).
- Fischer, R.E., Tadic-Galeb, B., Yoder, P.R., 2008. *Optical System Design*, second ed. SPIE Press, McGraw-Hill.
- Föll, H., 2019. *Electronic Materials*. University of Kiel. Available at: www.tf.uni-kiel.de/matwis/amat/elmat_en/kap_3/backbone/r3_2_2.html. (downloaded 17.06.2019).

- Gillen, R., Robertson, J., 2013. Electronic structure of lanthanide oxide high K gate oxides. *Microelectronic Engineering* 109, 72–74.
- Guo, S., Zhu, Z., Hu, X., *et al.*, 2018. Ultrathin tellurium dioxide: Emerging direct bandgap semiconductor with high-mobility transport anisotropy. *Nanoscale* 10, 8397–8403.
- Hartmann, P., 2014. Optical Glass. Bellingham, WA: SPIE.
- Hartmann, P., Jedamzik, R., Reichel, S., Schreder, B., 2010. Optical glass and glass ceramic historical aspects and recent developments: A Schott view. *Applied Optics* 49 (16), D157–D176.
- Hsu, H.-H., Chang, C.-Y., Cheng, C.-H., *et al.*, 2013. Fully room-temperature IGZO thin film transistors adopting stacked gate dielectrics on flexible polycarbonate substrate. *Solid-State Electronics* 89, 194–197.
- Hulie, J.C., Gentilman, R., Stefanik, T.S., 2007. Domestically produced ceramic YAG laser gain material for high power SSLs. *Laser Source Technology for Defense and Security III* 6552, 65520B.
- Ikesue, A., Aung, Y.L., 2008. Ceramic laser materials. *Nature Photonics* 2, 721–727.
- Ikesue, A., Kinoshita, T., Kamata, K., Yoshida, K., 1995. Fabrication and optical properties of high-performance polycrystalline Nd:YAG ceramics for solid-state lasers. *Journal of the American Ceramic Society* 78, 1033–1040.
- Islam, M.M., Bredow, T., Heitjans, P., 2012. The ionic conductivity in lithium-boron oxide materials and its relation to structural, electronic and defect properties: Insights from theory. *Journal of Physics: Condensed Matter* 24, 203201.
- Ivanov, M.G., Kopilov, Y.L., Osipov, V.V., Solomonov, V.I., Chrustov, V.R., 2007. Proceedings of the 3rd Laser Ceramic Symposium, O-S-3. Paris, France.
- Jackson, J.D., 1975. *Classical Electrodynamics*, second ed. New York: John Wiley and Sons Inc, (Chapter 4).
- Jackson, J.D., 1999. *Classical Electrodynamics*, 1999. Hoboken: John Wiley & Sons.
- Kintaka, Y., 2007. Patent WO07049434 Translucent ceramic, method for manufacturing the same, optical component, and optical apparatus (Murata Manufacturing).
- Kittel, C., 2018. *Kittel's Introduction to Solid State Physics*, ninth ed. Hoboken: John Wiley & Sons.
- Kvatchadze, V., Kalabegishvili, T., Vylet, V., *et al.*, 2006. Ceramic MgO: LiF: Promising material for selective detector. *Radiation Effects and Defects in Solids* 161 (5), 305–311.
- Lee, S.H., Kochawattana, S., Messing, G.L., Dumm, J., 2006. Solid-state reactive sintering of transparent polycrystalline Nd: Yag ceramics. *Journal of the American Ceramic Society* 89, 1945–1950.
- Lu, J., Song, J., Prabhu, M., *et al.*, 2000. High-power Nd:Y₃Al₅O₁₂ ceramic laser. *Japanese Journal of Applied Physics* 39, L1048–L1050.
- Ma, X., Zhang, Y., Dong, Y., Jia, R., 2017. First-principles calculations of electronic and optical properties of aluminum-doped β -Ga₂O₃ with intrinsic defects. *Results in Physics* 7, 1582–1589.
- Mansoor Khan, M., Ansari, S.A., Pradhan, D., *et al.*, 2014. Defect-induced band gap narrowed CeO₂ nanostructures for visible light activities. *Industrial & Engineering Chemistry Research* 53 (23), 9754–9763.
- Menke, Y., 2011. Chapter 5.9. – Transparent ceramics. In: Träger, F. (Ed.), *Handbook of Lasers and Optics*, second ed. Dordrecht: Springer, pp. 332–343.
- Menke, Y., Blaum, P., Peuchert, U., Okano, Y., 2014. Spinel Optoceramics, US Patent: 8679996 (Schott).
- Menke, Y., Ikesue, A., 2009. Method of Producing Transparent Ceramics. Patent EP20090156993.
- Menke, Y., Ikesue, A., Peuchert, U., 2009a. Ceramic Material, Useful to Prepare Optical Element Such as Lenses and Prisms, Comprises Zirconium, Hafnium and Fluorine, where Ceramic Material is Stabilized by Stabilizer, e.g., Oxides of Yttrium, Scandium, Magnesium and Calcium. Patent DE102009030951.
- Menke, Y., Ikesue, A., Peuchert, U., 2009b. Passive Optoceramics with Cubic Crystal Structure, Process for Manufacturing the Same and their Uses. Patent EP20090157002.
- Menke, Y., Peuchert, U., 2008. Optoceramics, Optical Elements Manufactured Thereof and their Use As Well As Imaging Optics. Patent EP20080155823.
- Murata.com, 2021. Research and Development of Transparent Ceramics for Optical Applications. Murata Manufacturing Co., Ltd. Available at: [https://corporate.murata.com/en-eu/about/newsroom/techmag/metamorphosis18/paper/01_\(01.02.2021\)](https://corporate.murata.com/en-eu/about/newsroom/techmag/metamorphosis18/paper/01_(01.02.2021)).
- Perret-Optic, 2005. Available at: www.perret-optic.ch/optometrie/correction_optique/matiere_optique_qualite_%20physique/matiere_optique_qualite_phys_gb.htm. (downloaded on 02/09/2005).
- Petzold, U., 2018. Chapter 5 – Optical glass: A high tech base material as key enabler for photonics. In: Sglavo, V.M. (Ed.), *Advances in Glass Science and Technology*. IntechOpen. doi:10.5772/intechopen.73925.
- Peuchert, U., Okano, Y., Menke, Y., Reichel, S., Ikesue, A., 2009. Transparent ceramics for application as optical lenses. *Journal of the European Ceramic Society* 29, 283–291.
- Portier, J., Campet, G., Kwon, C.W., Etourneau, J., Subramanian, M.A., 2001. Relationships between optical band gap and thermodynamic properties of binary oxides. *International Journal of Inorganic Materials* 3, 1091–1094.
- Prasad, N.S., Edwards, C., Trivedi, S.B., Kutcher, S., Wang, C.-C., *et al.*, 2007. Recent progress in the development of neodymium-doped ceramic yttria. *IEEE Journal of Selected Topics in Quantum Electronics* 13, 831–837.
- Quah, H.J., Cheong, K.Y., 2015. Effects of annealing time on the electrical properties of the Y₂O₃ gate on silicon. *Journal of Experimental Nanoscience* 10 (1), 19–28.
- Rea, M.S., Bullough, J.D., Akashi, Y., 2009. Several views of metal halide and high-pressure sodium lighting for outdoor applications. *Lighting Research and Technology* 41 (4), 297–320.
- Robertson, J., 2004. High dielectric constant oxides. *European Physical Journal Applied Physics* 28, 265–291.
- Schneider, S.J., 1991. ASM international handbook committee. In *Engineered Materials Handbook: vol. 4. Ceramics and Glasses*. CRC Press.
- Schott.com, 2019. Available at: https://www.schott.com/d/advanced_optics/a6ff96d2-72ae-46ea-bd33-73acb318f4f6/1.9/schott-abbe-diagram-nd-vd-jan-2018-de.pdf; https://www.schott.com/d/advanced_optics/352d8a40-86d7-41e5-b478-dd2450fb14ce/1.10/schott-abbe-diagram-ne-ve-jan-2018-de.pdf; https://www.schott.com/d/advanced_optics/436c7f72-e980-44c2-b14b-0c5c952cca7f/1.8/schott-abbe-diagramm-pgf-februar-2016-de.pdf; https://www.schott.com/d/advanced_optics/316ba9d5-cd3e-46bb-937c-6bca8b06aefc/1.12/schott-abbe-diagram-low-tg-jan-2018-de.pdf. (downloaded 06/17/2019).
- Schwartz, K., 2008. An Introduction to the Optics Manufacturing Process. University of Arizona, College of Optical Sciences. (OPTI 521 report).
- Shannon, R.D., Prewitt, C.T., 1969. Effective ionic radii in oxides and fluorides. *Acta Crystallographica B25*, 925–946.
- Soler, F.J.P., 1997. Multiple reflections in an approximately parallel plate. *Optics Communications* 139, 165–169.
- Tsukuma, K., 1986. Transparent titania-yttria-zirconia ceramics. *Journal of Materials Science Letters* 5, 1143–1144.
- Tsukuma, K., Takahata, T., Tsukidate, T., 1988. Transparent ZrO₂-Y₂O₃-TiO₂ ceramics. In: Somiya, S., Yamamoto, N., Yanagida, H. (Eds.), *Advances in Ceramics*, vol. 24. Science and Technology of Zirconia. Westerville, OH: American Ceramic Society, p. 287.
- Wei, G.C., 2007. Structural and optical ceramics: Yesterday, today, and tomorrow. *Key Engineering Materials* 336–338, 905–910.
- Yoshida, K., Yabe, T., Uchida, S., Ikesue, A., Kamimura, T., 2006. New trends on solid-state lasers. *AIP Conference Proceedings* 830, 14–20.
- Ziletti, A., Carvalho, A., Trevisanutto, P.E., *et al.*, 2015. Phosphorene oxides: Bandgap engineering of phosphorene by oxidation. *Physical Review B* 91, 085407.

Glass Fibers

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Fabrication

The characteristic ability of glasses to be drawn stems from their viscoelastic nature, or in other words the fact that their deformation under stress is a strong function of time and deformation rate. Glassy materials, above the glass transition temperature, T_g , show Newtonian viscosity, i.e., the stress is linearly proportional to the strain rate. This property is exploited in the drawing of glass fibers. We can write, in terms of normal stresses and strains:

$$\sigma = \eta \dot{\epsilon} \quad [1]$$

where σ is the stress, η is the viscosity, and $\dot{\epsilon}$ is the strain rate. The deformation proceeds at a constant volume, i.e., an increase in length is accompanied by a decrease in the cross-sectional area. If an incremental increase in length is dl , and the corresponding decrease in cross-section is $-dA$, then:

$$\frac{dl}{l} = d\epsilon = -\frac{dA}{A}$$

where l and A are the instantaneous values of length and cross-sectional area, respectively. We introduce the strain rate by dividing throughout by incremental time, dt . Thus:

$$\dot{\epsilon} = \frac{d\epsilon}{dt} = -\frac{dA}{A} \frac{1}{dt} = -\frac{dA}{dt} \frac{1}{A} = -\frac{\dot{A}}{A} \quad [2]$$

If F is the applied load, then from eqns [1] and [2] we can write:

$$F = \eta \dot{\epsilon} A = -\eta \dot{A} \quad [3]$$

Equation [3] states that the rate at which the fiber becomes thinner is proportional to the applied force *not the applied stress*. This means that thinner and thicker regions suffer cross-sectional reduction at an equal rate; hence, there is no tendency for preferential thinning of the drawn glass where the stress is locally raised by a local decrease in fiber cross-sectional area. Thinning of drawn viscous fibers is, thus, uniform and stable. This is different from tensile thinning of most materials, which becomes interrupted by rupture after a certain strain due to a preferential local thinning instability, known as necking.

The stability of glass fibers against localization of deformation, and hence against necking, is further reinforced by the fact that for a given load, as the viscosity increases the strain rate decreases. This has indeed very important implications in fiber drawing. In order to understand these implications we need to examine the temperature dependence of viscosity. This temperature dependence is given by:

$$\eta = A \exp(Q/RT)$$

where Q is the molar activation energy, A is a pre-exponential constant, and R is the universal gas constant. This equation indicates that the viscosity varies inversely in an exponential manner with the temperature. As thinner regions of the fiber cool more rapidly, the viscosity of such regions increases resulting in a decrease in the rate at which the thin region gets thinner. This allows the thicker regions to catch up and increases further the resistance of the drawn fiber material against necking.

Glass Fibers for Reinforcement of Polymers

A schematic representation of the conventional fabrication procedure for glass fibers is shown in Figure 1. The raw materials are heated in a hopper and the molten glass is fed into electrically heated platinum or platinum–rhodium bushings having multiple holes. Typically, each bushing contains 200 holes at its base. A constant head of molten glass is kept in the tank. The molten glass flows by gravity through these holes forming fine continuous filaments which are gathered together and passed around a fast-rotating collet, followed by drawing at a speed of 1–2 km min^{−1}. Glass flows out of a platinum bushing at a rate given by:

$$q = \frac{kh r^4}{\nu l}$$

where r is the radius, l is the length, ν is the kinematic viscosity (i.e., dynamic viscosity, η , divided by density, ρ), and h is the hydrostatic pressure generated by the head of glass in the bushing. The fibers exiting the bushing are cooled, subjected to a surface

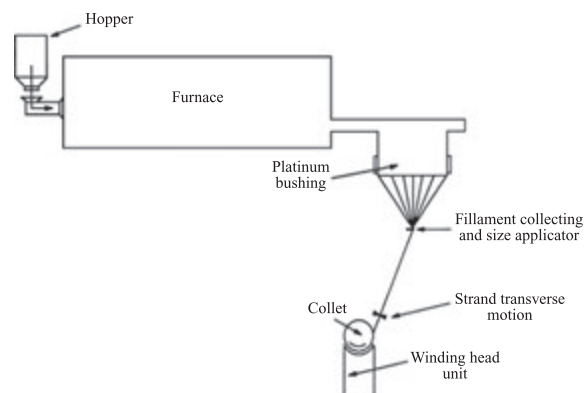


Figure 1 Schematic of the conventional fabrication procedure for glass fibers.

treatment (using an organic size such as a starch oil), and given a stretching treatment by the take-up spool. A size, consisting of an aqueous polymer emulsion, is applied before winding on a drum.

Typically, the glass fibers have a diameter between 5 and 20 μm . The final glass fiber diameter is a function of the bushing orifice diameter, viscosity (itself a function of composition and temperature), and the head of glass in the hopper. The viscosity is generally around 100Pas for good fiberization. During the glass fiber stretching treatment by the take-up spool, the take-up speed is 50–60 ms^{-1} , which is slightly higher than the drawing speed, and thus the as-wound glass fiber suffers a stretch.

Glass filaments are easily damaged by the introduction of surface defects. The sizing treatment provides for ease of handling, protects against surface damage, and binds the filaments into a strand. In almost any fiber drawing process from a melt, the melt viscosity is by far the most important process control parameter. If a single glass filament breaks, the glass will drip across other filaments and cause a breakdown of the whole drawing process. Filament breakage can occur because of undissolved particles in the glass, abrasion, devitrification, or any instability due to changes in viscosity/winding speed (Proctor, 1971).

An important characteristic of glass fiber is its extreme flexibility, which of course stems from its fine diameter and low modulus. Textile processes of weaving, knitting, etc. can be used with fine, flexible glass fibers to produce fabrics, tapes, sleeves, and ropes. E-glass fiber has a diameter between 3 and 20 μm and is commonly used for insulation purposes as well as for reinforcement of polymers. Frequently, glass fibers are chopped to obtain short, staple fibers.

Sol–Gel Processing of Glass Fibers

The conventional processing of glass fibers, as described above, involves direct melting of raw materials, followed by drawing of the molten glass through electrically heated platinum bushings. A major problem with any direct melting process is that the temperatures involved are very high. Quite frequently, the melt viscosity at reasonable temperatures is too high to allow proper homogenization. At times the oxides show large differences in volatility and direct melting results in large losses of some of the constituents. All these problems have led to processing of ceramics and glasses via a chemical route. This allows a high degree of homogeneity on a molecular scale and consequently high-purity glasses or ceramics can be obtained. In particular, the sol–gel technique of making glass fibers has become important.

Essentially the sol–gel route for making any glass or ceramic involves the formation of the appropriate glass or ceramic structure by chemical polymerization of suitable compounds in the liquid state (sol) at low temperatures. A sol is a colloidal suspension in which the individual particles are so small that no sedimentation occurs. The particle size in a sol generally varies between 1 and 100 nm. A gel is a suspension in which the liquid medium is viscous enough to behave more or less like a solid.

The precursor material for glass fibers in the form of a gel is obtained from the sol. The unwanted residues (water, organic compounds, etc.) are removed from the gel by heating at temperatures much lower than those used in direct melting processes, and the desired glass or ceramic is obtained in an appropriate form (powder, film, fiber, etc.). As the solvent liquid is lost, the sol viscosity increases until it becomes rigid, i.e., it gels. A well-controlled rate of drying is required because of the large shrinkage that accompanies the drying process.

Fiber drawing is carried out in the course of sol-to-gel conversion. The gelled fibers are then heated to produce glass fibers. There are some very general but important points to be considered in sol and gel spinning. Spinning of dilute solutions into gels results in a minimum of polymer chain entanglement. Gelled fibers are then highly porous and elastic, and should be stretched by drawing while in a temperature gradient. This removes the solvent and decreases the porosity. The viscosity of sols and gels can also be a function of time at constant temperature; for example, when a tetraethoxysilane $[\text{Si}(\text{OC}_2\text{H}_5)_4]$ –water–hydrochloric acid–alcohol solution of appropriate composition is held at near room temperature, hydrolysis and polycondensation occur and the solution viscosity increases. Fibers can be drawn at a viscosity of about 10Pas, which occurs during the course of sol-to-gel transition. It should be pointed out that for an alkoxide solution to be spinnable (Sakka, 1982) the solution must have linear polymers and an appropriate ratio of $[\text{H}_2\text{O}]/[\text{Si}(\text{OC}_2\text{H}_5)_4]$, called the r -ratio. An r -ratio < 2 gives a spinnable solution.

Table 1 Chemical composition of some common glass fibers

Compound	E-glass	C-glass	S-glass	Cemfil
SiO ₂	55.2	65.0	65.0	71.0
Al ₂ O ₃	8.0	4.0	25.0	1.0
CaO	18.7	14.0		
MgO	4.6	3.0	10.0	
Na ₂ O	0.3	8.5	0.3	Na ₂ O + K ₂ O = 11
K ₂ O	0.2			
Li ₂ O	7.3	5.0		< 1.0

Table 2 Typical properties of some glass fibers

Glass fiber type	Density (g cm ⁻³)	Tensile strength (GPa)	Young's modulus (GPa)
E-glass	2.54	1.7–3.5	69–72
S-glass	2.48	2.0–4.5	85
C-glass	2.48	1.7–2.8	70
Cemfil	2.70		80

Chemical Composition

Silica-based glass fiber has been around for a long time. Common glass fiber is readily available commercially in a variety of different chemical compositions. Most glass fibers are silica-based ($\sim 50\text{--}60\%$ SiO₂) and contain a host of other oxides of calcium, boron, sodium, aluminum, iron, etc. They are commonly used for reinforcement of thermosetting and thermoplastic polymers. **Table 1** gives the compositions of some commonly used glass fibers in composites. The designation E stands for electrical as E-glass is a good electrical insulator besides having good strength and a reasonable Young's modulus; C stands for corrosion as C-glass has a better resistance to chemical corrosion; S stands for high silica content and S-glass is able to withstand higher temperatures than others. Most continuous glass fiber produced is of the E-glass type.

Structure

Silica-based glass is a generic term representing an interesting and versatile class of materials. Glasses of various compositions can be obtained and they show very different properties. Structurally, however, all silica-based glasses have the same basic building block: a tetrahedron made up of four oxygen ions bonded covalently to a silicon ion at the center. The composition of a single tetrahedron is thus SiO₄. Each oxygen ion is, however, shared by *two* tetrahedrons, giving the bulk composition of SiO₂. It is this basic building block that is repeated in three dimensions in silica and silica-based materials. Different repeat patterns result in different structures for the same composition. The addition of other oxides of metals such as sodium, calcium, aluminum, magnesium, etc., to silica serves to alter the network structure and the bonding, and consequently the properties, mainly a reduction in viscosity which makes for easy processing. The presence of crystalline regions is undesirable in a glass because such regions act as stress raisers. Glass fibers are quite isotropic; Young's modulus and thermal expansion coefficient are the same along the fiber axis and perpendicular to it. This, of course, is a result of the amorphous, three-dimensional network structure of glass, i. e., there is no preferential alignment of any structural units such as polymer chains along the fiber axis.

Properties

Compared with most other inorganic fibers, silica-based glasses generally have a comparatively low density. The strength can be quite high, but the elastic modulus is not very high. Thus, while the strength-to-weight ratio of glass fibers is quite attractive in comparison with other inorganic fibers, their modulus-to-weight ratio is only moderate. Typical properties of different glass fibers are summarized in **Table 2**.

Although resistance to fire and many chemicals are very attractive features of glass, moisture can decrease the strength of glass fiber. In particular, the adsorption of moisture by freshly made glass fiber results in a drastic decrease in its strength. Glass fibers are also susceptible to what is called static fatigue, i. e., they cannot withstand loads for long periods of time. This is due to the phenomenon of stress corrosion induced by the ambient moisture.

Common glass fiber such as E-glass becomes severely corroded in an alkaline atmosphere such as in cement or concrete. Some special alkali-resistant glass fibers have therefore been developed. The properties of one such fiber, called Cemfil, are given in Table 2.

Fracture

Many brittle, amorphous materials such as thermosetting polymers and silica-based inorganic glasses show some tell-tale markings on their fracture surfaces (Mecholsky *et al.*, 1977; Chandan *et al.*, 1994). Typically, the fracture surface of a glass fiber shows four distinct regions. These regions surrounding the origin point of fracture are: a smooth mirror region, a mist region of small radial ridges, a hackle region consisting of large ridges, and finally a region of extensive crack branching. It turns out that the product of strength, σ , and the square root of the distance of each of these regions from the origin of fracture is a constant. One can write:

$$\sigma R_i^{0.5} = A_i$$

where R_i are the radii of the mirror-mist, mist-hackle, or crack-branching boundaries. These radii can be related to the initial flaw depth, a , or the half-width, b , through the fracture mechanics analysis:

$$\frac{c}{R_i} = \frac{K_{Ic} Y^2}{2A_i^2}$$

where $c = (ab)^{0.5}$, Y is a geometrical constant, and K_{Ic} is the critical stress intensity factor or fracture toughness.

Applications

Glass fiber is available in a variety of shapes and forms. Some of the important ones include continuous fiber and roving, staple fiber, and chopped strand mat. Staple fibers are strands of individual filaments 200–400 mm long and are excellent for providing bulkiness for filling, filtration, etc. Chopped strand glass fibers consist of fibers chopped to various lengths, 3–50 mm, mainly for the purpose of mixing with a resin for making composites. Glass fiber MTCG-S consist of randomly dispersed chopped fibers or continuous fiber strands, held together with a resin.

Glass fibers find applications in a vast array of markets.

Automotive Market

The automobile industry is one of the largest users of glass fiber. Polymer matrix composites containing glass fibers are used to make external body panels, bumper beams, pultruded body panels and air ducts, engine components, etc. Parts made of glass-fiber-reinforced polymers are much lighter than metallic ones, making the automobile more fuel efficient.

Aerospace Market

Glass-fiber-reinforced composites are used to make aircraft parts such as wings, helicopter rotor blades, engine ducts, etc. Glass fiber has a relatively low elastic modulus. Hence, it is more common to use glass-fiber-reinforced polymer composites in the interior of an airplane rather than in primary structural parts. The radar transparency characteristic of glass has given it some key uses in the radar-evading stealth technologies.

Marine Market

Sailing boats and hulls and decks of commercial fishing boats and military mine-hunters are frequently made of glass-fiber-reinforced polymers. Glass-fiber-reinforced polyester is commonly used in making boats of all sizes.

Civil Construction

This is another large market where glass fiber is widely used. Typical applications include the use of glass fibers in polymeric resins for paneling, bathtubs and shower stalls, doors, windows, etc. Glass fibers are also used as reinforcement in a variety of household items such as paper, tapes, lampshades, etc. Some special alkali-resistant glass fibers have been developed for reinforcement of cement and concrete. Commonly, steel bars are used for such purposes. Cement, however, is very alkaline. An ordinary glass fiber such as E-glass will be severely corroded in an alkaline atmosphere, hence the need for special, alkali-resistant glass fibers (Majumdar, 1970; Hannant, 1978). The bonding between glass fiber and cement is mainly mechanical and has its origin in the shrinkage that occurs when the cement is set.

Sporting Goods

Not surprisingly, the sporting goods industry was one of the first to make use of glass-fiber-reinforced composites. Examples include bicycle frames, tennis rackets, golf-club shafts, cricket bats, skis, etc. Braided fibers in a resin matrix give high torsional stiffness to skis.

Electrical/Electronic Market

Glass fibers are used extensively in printed circuit boards, industrial circuit breakers, conduits for power cables, etc.

Biomaterial Applications

Glass fibers based on binary calcium phosphate glasses (Ahmed *et al.*, 2008) or $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$ glasses (Haaparanta *et al.*, 2015) have been used for scaffolds used in tissue engineering. The glasses enhance bone formation within highly porous scaffolds generated by randomly interwoven glass fibers.

Conclusions

Glass fibers are a very versatile class of materials. They are used extensively as a reinforcement fiber for polymeric resins such as epoxy and unsaturated polyester. The stiffness of glass fiber is lower than that of other reinforcement fibers, but it possesses the distinct advantage of combining a very high strength with low density and, most of all, a very reasonable cost. Glass fiber will continue to be used as a major reinforcement fiber well into the future. The composition, structure and property information given in this paper has been augmented by Jones and Huff (2009).

References

- Ahmed, I., Parsons, A.J., Palmer, G., *et al.*, 2008. Weight loss, ion release and initial mechanical properties of a binary calcium phosphate glass fibre/PCL composite. *Acta Biomaterialia* 4 (5), 307–1314.
- Chandan, H.C., Parker, R.D., Kalish, D., Bradt, R.C., Tressler, R.E., 1994. *Fractography of Glass*. New York: Plenum, 143.
- Haaparanta, A.-M., Uppstu, P., Hannula, M., *et al.*, 2015. Improved dimensional stability with bioactive glass fibre skeleton in poly(lactide-co-glycolide) porous scaffolds for tissue engineering. *Materials Science and Engineering: C* 56, 457–466.
- Hannant, D.J., 1978. *Fibre Cements and Fibre Concretes*. New York: Wiley.
- Jones, F.R., Huff, N.T., 2009. Structure and properties of glass fibres. In: Bunsell, A.R. (Ed.), *Handbook of Tensile Properties of Textile and Technical Fibres*. Oxford: Woodhead Publishing, pp. 529–573.
- Majumdar, A.J., 1970. Glass fibre-reinforced cement and gypsum products. *Proceedings of the Royal Society of London* A319, 69.
- Mecholsky, J.J., Freiman, S.W., Morey, S.N., 1977. Fractographic analysis of optical fibres. *American Ceramic Society Bulletin* 56, 1016.
- Proctor, B.A., 1971. Fibre-reinforced composite materials. *Composites* 2, 85.
- Sakka, S., 1982. *Treatise on Materials Science & Technology*, 22. New York: Academic Press, 129.

Glass: Optical Fibers – Manufacture and Properties

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Introduction

An optical fiber is a highly flexible cylindrical structure composed of a highly transparent dielectric material designed to transport energy at wavelengths – from the visible to the infrared portion of the electromagnetic spectrum – from one end of the fiber to the other using a mechanism of total internal reflection.

When one considers that the energy of a photon in the visible/near infrared region of the electromagnetic spectrum is of the order of one electron volt and that, for elements in the lower periods of the periodic table, the energy gap between a full valence shell and an empty conduction shell is typically many electron volts, one can appreciate that valence electrons for such elements cannot be excited into the higher energy levels by the absorption of such low energy photons. As all stoichiometric compounds are filled just to the top of the valence band there is no mechanism for light to be absorbed in such compounds which consequently must be transparent. Stoichiometric materials composed of low atomic number elements are therefore the candidate materials for the fabrication of optical fibers.

Compounds such as molecular oxygen (O_2) and molecular nitrogen (N_2), silica (SiO_2), perspex (PMMA), polycarbonate, soda (Na_2O), lime (CaO), boric oxide (B_2O_3), phosphorous oxide (P_2O_5), etc., are all transparent to visible and near infrared light. The air of free-space has long been a medium for line-of-sight optical communications. Indeed all of the solid materials in the above list have been involved in the history of guided optical fiber communications when in their non-crystalline glassy form, either as individual pure substances or when mixed together in suitable combinations (Cherin, 1983). Pure silica glass, first proposed by Kao and Hockham (1966), has emerged as the main substrate material for long and short distance optical fiber communications. However polymer, sodium borosilicate, and soda lime silicate glass fibers have found minor roles in short distance fiber optics.

Light guidance in optical fibers is obtained through two mechanisms of total internal reflection (Hecht, 2005): conventional and resonant. Conventional total internal reflection occurs when light, already inside a core medium, is reflected back into the core from the interface with a surrounding less dense medium called the cladding. Sometimes the core is a uniform glass rod and the cladding is the surrounding air, as in the fibers of flexible endoscopes (Hopkins and Kapany, 1954), but more typically the core consists of the same material as the cladding but now doped with trace elements of an additional compound that slightly raises its density, and thereby its refractive index, so that the reflection can take place safely deep within the overall structure as indicated in Fig. 1.

The atomic size in the transparent medium is four orders of magnitude smaller than the wavelength of the guided light and so the transparent medium can be treated as a continuum in its interaction with this light. The “optical size” of the wave guiding core is a combination of its physical dimension and its refractive index difference with the cladding ($n_1 - n_2$), where n_1 is the refractive index of the core and n_2 is that of the cladding. This size is embodied in a parameter called the normalized frequency V , where $V = (2\pi a/\lambda) \sqrt{(n_1^2 - n_2^2)}$, where a is the core radius and λ is the wavelength. For large V -values the guiding mechanisms can be typically understood and calculated in terms of Fresnel’s laws of reflection as indicated in Fig. 1(b). However, when the V -value is small Maxwell’s equations need to be deployed for a more rigorous analysis (Gloge, 1971).

One of the earliest proposed single mode fibers was a single-material structure with an air-guiding core of pure silica suspended with minimal silica supports at the center of a hollow silica tube (Kaiser *et al.*, 1973) schematically indicated in Fig. 2(a). While unsuccessful at that time, the technological advances in the intervening years have made such air-guiding structures commercially feasible. Outwardly resembling conventional fibers, single-material micro-structured fibers consist of a cylindrical glass body with voids in the cross-section of the cladding region forming a pattern of holes running along the length of the fiber. These air-filled holes have the effect of reducing the cladding’s average refractive-index relative to that of the core so that selective doping of the core is no longer required to elevate its relative refractive index. The effective refractive index difference between the pure silica core and the holey cladding can now provide guidance by the conventional total internal reflection mechanism. These fibers are generally known as holey fibers (Monro *et al.*, 2000) schematically represented in Fig. 2(b).

In recent decades, while the basic transparent media have remained the same, a different guiding mechanism for confining the light in the core region has emerged. If, in a holey fiber, the pattern of holes is arranged in a regular spatial pattern of constant pitch, Λ , and where the pitch is not much different from the wavelength of the propagating light, then a resonant reflectivity can be achieved. Just as atoms in a crystal structure reflect X-rays of a wavelength similar to the atomic spacing, corresponding to the Bragg condition, so can optical fibers with a regular spatial pattern of features incorporated into its cross-section reflect light back into a core region that itself corresponds to a “defect” in the regular pattern. The core region can be either void or solid so either air-guidance or glass-guidance can be achieved in such fibers. Fibers with this second guiding mechanism are referred to as photonic band-gap fibers or photonic crystal fibers (Birks *et al.*, 1997) and are schematically represented in Fig. 2(c).

In all optical fibers, the transparency is due to the electronic band-gap, and the guidance is due either to the conventional refractive index difference or to a photonic band-gap.

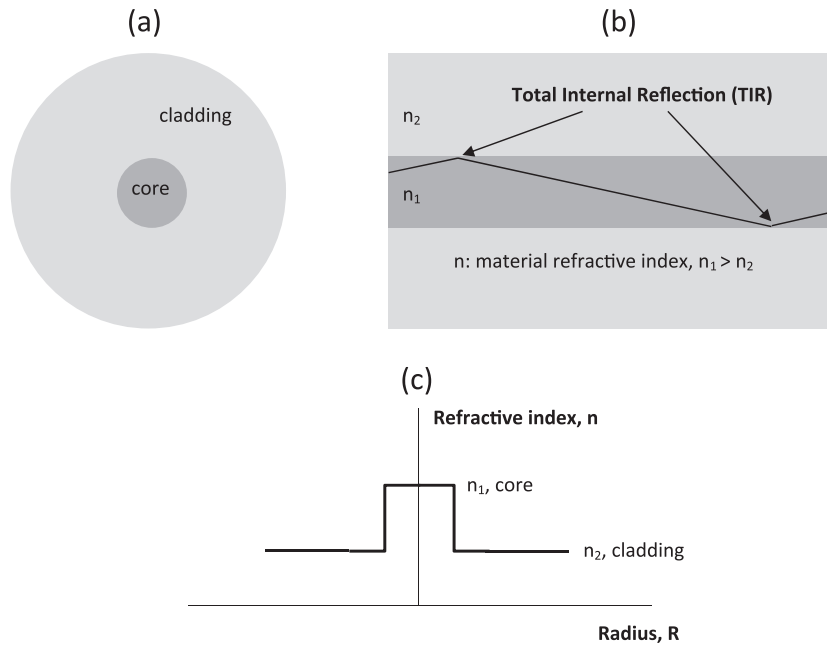


Fig. 1 Optical fiber guidance. (a) Fiber cross-section, (b) Fiber longitudinal-section, (c) Refractive index profile.

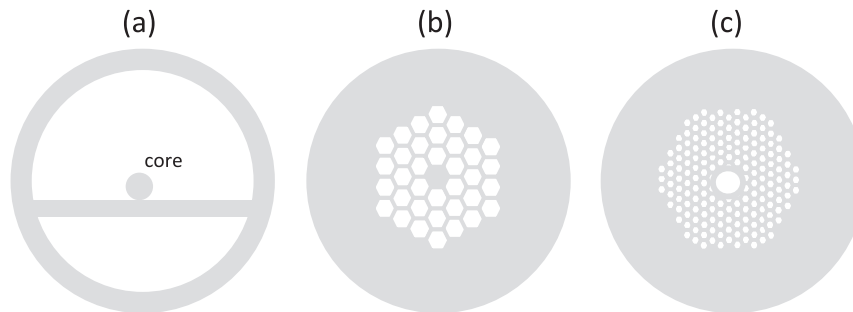


Fig. 2 Single material micro-structured fibers. (a) Suspended core fiber, (b) Holey fiber, (c) Photonic crystal fiber.

Silica Fibers

A concentration of 1 mol% of germania (GeO_2) raises the refractive index of silica by approximately 0.1% (Mitschke, 2016). The standard telecommunications fiber typically has a germania-doped silica core surrounded by a lower index cladding of pure silica, each with a circular cross-section. The cladding diameter for this standard fiber is 125 μm . This is the basic structure that will form the backbone of this review. Fibers made from other materials and made for other purposes will be mentioned as required. Optical fibers can be conveniently divided into two subclasses called single-mode (with comparatively small cores) and multi-mode (with comparatively large cores). The demarcation between the two depends on the “optical size” of the core relative to the operating wavelength. As mentioned above the core’s “optical size” is a function of the core’s diameter, the refractive index difference between the core and the cladding, and also takes account of the spatial distribution or ‘profile’ of that refractive index.

Single-mode fibers have core diameters of between 4 and 10 μm with values of relative refractive index difference Δ of about 0.1%, while multimode fibers have core diameters of between 50 and 100 μm with Δ values of about 1%. Within the core, the refractive index distribution can be uniform (step-index), or it can be gradual (graded-index), as indicated in Fig. 3. Indeed, for reasons that will become clear, in standard optical telecommunications jargon the “step index” is synonymous with the single-mode fiber, and the “graded index” is synonymous with the multi-mode fiber. The cladding index is typically uniform, in each case however for wave-guidance, it is necessary that the core index be greater than the cladding index for at least some region of its cross-section. For the majority of applications, most of the light energy propagates in the core and only a small fraction of it travels in the cladding. Any outer protective jacket is optically isolated from the core, so we can usually ignore its effects in theoretical calculations in which an unbounded cladding is assumed. For the purposes of this review the properties of the protective jacket will not be considered in any great detail.

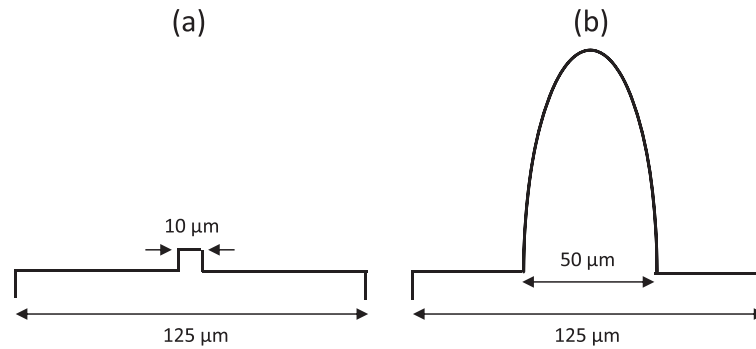


Fig. 3 Refractive index profile of standard telecommunications fibers. (a) Step-index (Single-mode), (b) Graded-index (Multi-mode).

Light Propagation

Optical fibers are typically weakly-guiding (Gloge, 1971); this term takes for granted that the refractive index difference between the core and the cladding is less than 1%. The circular step index core is canonical and calculations on it can be expressed in analytic form. The circular step index single-mode fiber is particularly tractable and, indeed, single mode cores with other refractive index profiles can fortuitously be expressed in an “equivalent-step” form (Millar, 1981).

Geometrical optics can give a reasonable insight into how light is guided in these weakly guiding fibers. With reference to Fig. 4, the critical angle, θ_c , for rays of light in the core region of refractive index n_1 incident on the boundary of the lower index cladding n_2 , above which light is totally internally reflected back into the core is given by $\sin \theta_c = n_2/n_1$. Since n_1 and n_2 are nearly equal, θ_c must be very close to 90° . Remembering that the angle of incidence is measured with respect to the normal to the boundary, this means that only those rays of light that are almost parallel to the boundary are totally internally reflected.

A mode can loosely be identified with the family of rays all propagating at the same angle. The number of modes that can propagate in the step-index fiber is related to the optical size of the core or its V-value, as mentioned above. Only one mode propagates on the step-index fiber for V-values of less than 2.405; this is the fundamental mode and it propagates at all frequencies (Snyder and Love, 1981). The fundamental mode has the shape of a Gaussian or Normal distribution, with the maximum in the center of the core and the evanescent tails of the distribution extending into the cladding. Single-mode fibers are those designed to propagate only the fundamental mode and are usually designed to operate as close to the V-value of 2.405 as possible where the fraction of modal power propagating in the core is about 80% with the remaining 20% propagating in the cladding. At smaller V-values the modal shape is more spread out and the mode is less tightly confined to the core.

The exact radial distribution of the electric field of each mode is found from the solutions of Maxwell’s equations. For the circular step-index fiber the modal field solutions are oscillatory in the core and are given by the Bessel functions, while the evanescent cladding fields are given by the modified Bessel functions. The modal eigenvalues, or propagation constants, are obtained by numerically matching the fields and their derivative at the core/cladding boundary. Unlike the fundamental mode, each other mode has a cut-off frequency below which it is no longer guided, so the number 2.405 is actually the cut-off V-value of the second mode. As the frequency increases above the cut-off point of a mode, that mode becomes more tightly confined into the core and therefore is more strongly guided (Snyder and Love, 1981).

Multimode fibers typically have V-values above 50 and can have over one thousand modes propagating and so modal analysis can prove very cumbersome. However since their ‘optical size’ is large, it is found that the simpler geometrical, or ray optics, as described above, are appropriate.

Transmission Bandwidth

The bandwidth of a fiber is determined by the combined influence of its structural parameters, its materials properties, and on the chromatic and intermodal dispersion of the propagating signal.

Multimode Fibers: The bandwidth of multimode fibers is basically determined by the intermodal dispersion as the different group velocities of the different modes causes the temporal spreading of an input pulse of light as it propagates along the fiber. It thereby limits the rate at which sharp input pulses can be injected into the fiber and be successfully detected as separate pulses at the output end. However the effective optical path of each mode can be made the same by suitably grading the refractive index of the core so that the maximum index lies along the fiber axis and the index falls to zero at the core/cladding boundary. In such a case the low order modes – with their angles almost parallel to the axis – travel the shortest paths but in the dense medium, while modes at higher angles to the axis travel longer paths but now in a less dense medium. The group velocities of the different modes can thereby be equalized. The optimum refractive index profile is found to be close to the parabolic shape, as in Fig. 3(b), although the slightest distortion of the profile can radically degrade the performance (Cherin, 1983). Multimode fibers have still some relevance in short-haul applications but have been superseded in long-haul networks by single mode fibers.

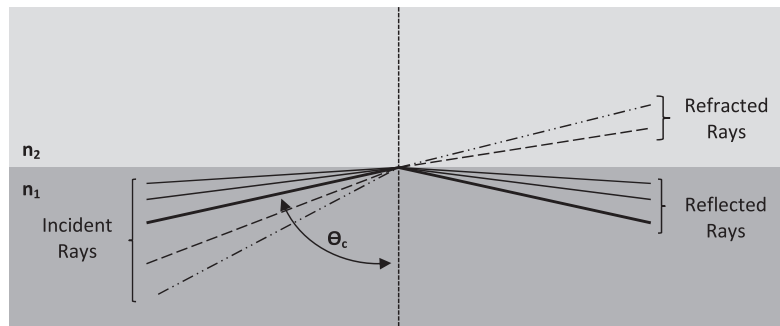


Fig. 4 Geometrical optics description of total internal reflection.

Single Mode Fibers: Chromatic dispersion is the dominant bandwidth limiting effect on single mode fibers and is caused by propagation-delay differences among different spectral components of the signal; it includes material dispersion and waveguide dispersion (Marcuse, 1979) which is associated with the guidance effects of the fiber structure. Material dispersion arises because the refractive index of the material is different for different wavelengths, and waveguide dispersion arises because modal confinement also varies with wavelength. Profile dispersion arises because the core materials and cladding material may have different variations with wavelength, but this additional dispersion tends to be small compared with the other two dispersion effects (Gambling *et al.*, 1979).

Fortunately, dispersion from different effects can compensate each other in their overall contribution to chromatic dispersion in single-mode fibers. By balancing the (negative) material dispersion against the (positive) waveguide dispersion, it is possible to locate a wavelength for which there is zero chromatic dispersion in these fibers. Thus, while in bulk germania-doped silica for which the material dispersion is zero near the wavelength of 1300 nm (Payne and Gambling, 1975), by a suitable choice of core diameter and relative refractive index difference, the wavelength of minimum chromatic dispersion can be positioned in the 1500–1600 nm region where the transmission loss is lowest. Fibers that achieve this effect are referred to as dispersion-shifted fibers and can have a sophisticated double cladding structure, so-called doubly-clad or W-fibers (Monerie, 1982), as indicated in Fig. 5(a). The more sophisticated core/cladding structures of multiply-clad fibers (Cohen *et al.*, 1979), see Fig. 5(b), can achieve almost perfect cancellation of material dispersion by the waveguide dispersion over an extended spectral range and are referred to as dispersion-flattened fibers (Okamoto *et al.*, 1979).

Strictly the fundamental mode of a perfectly circular fiber is a superposition of the two identical mode shapes corresponding to two orthogonal polarizations each propagating with the same propagation constant which can generally be treated as one entity. However birefringence effects, arising when each polarization of the fundamental mode has a different propagation constant, due to core-ellipticity or strain-induced anisotropy, may limit the bandwidth at wavelengths where the more dominant chromatic dispersion is a minimum. Such restrictions on bandwidth in single-mode fibers can be removed if only one of the polarization states of the fundamental mode is allowed to propagate. Truly single-mode propagation may be achieved in high-birefringent fibers of which there are three main types: the elliptical core (Shibata *et al.*, 1983), the bow-tie (Birch *et al.*, 1982), and the PANDA (Sasaki *et al.*, 1986) fibers, illustrated schematically in Fig. 6(a), (b), and (c), respectively. However such fibers have not found widespread use in optical communications networks.

Micro-structured fibers: While it is not anticipated that micro-structured fibers will replace conventional fibers in long-haul applications they do display interesting dispersion behavior. Holey fibers with a large effective refractive index difference (i.e. with a large holey area) can have its waveguide dispersion dominate the material dispersion and so shift the zero dispersion wavelength to wavelengths shorter than 1300 nm, which is impossible in conventional germania doped silica fibers (Monro *et al.*, 2000).

Another recent innovation has been the multi-core fibers which have already been demonstrated with up to 31 single-mode cores assembled, in much the same manner as the above micro-structured fibers, in a cladding with the conventional diameter of 125 μm . These fibers are proposed as a new space division multiplex (SDM) technology for next generation communications (Hayashi and Nakanishi, 2018).

Loss and Gain Mechanisms in Optical Fibers

Transmission loss is one of the most important properties of an optical fiber as it determines, to a large extent, the separation between the repeaters required to regenerate the transmitted signals in long-haul links. In a repeater the optical signal is converted into an electronic form in which it can be conveniently amplified and then reconverted back into an optical signal to continue its journey. These opto-electronic repeaters are expensive so the cost of any system is significantly affected by fiber losses which determine the number of such repeaters required in an optical communications link.

The different loss mechanisms are due to material effects such as absorption and scattering, and bending effects due to jacketing and installation. However, the expensive opto-electronic conversion stage can be eliminated from optical communications links by inserting an optical fiber amplifier into the link in which the signal remains in its optical form throughout. Light amplification can be achieved in the standard germania-doped silica core by exploiting its slight inherent non-linearity through stimulated

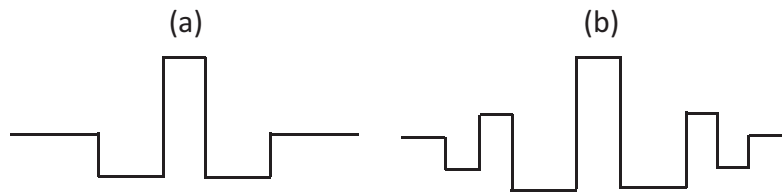


Fig. 5 Multiply-clad dispersion control fibers. (a) Dispersion shifting depressed-clad, (b) Dispersion flattening quadruple-clad.

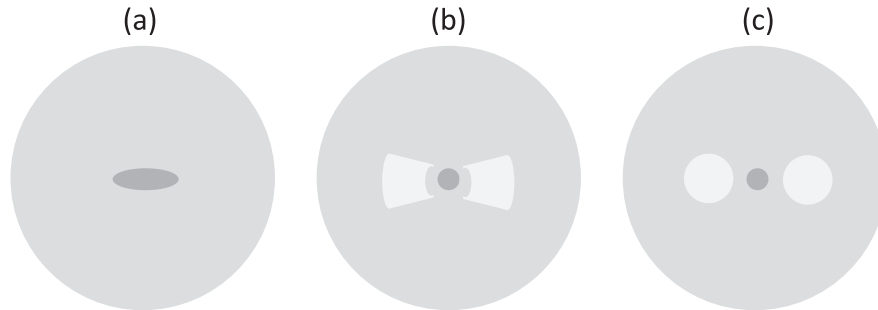


Fig. 6 Polarization-maintaining fibers. (a) Elliptical core, (b) Bow-tie, (c) Panda.

Raman scattering (Stolen *et al.*, 1984). Alternatively by doping the core region with an element from one of the higher periods of the periodic table, typically one of the rare-earth elements, for which the energy gap between the valence and conduction levels is of the order of one electron volt, thereby matching the energy of the propagating photons, it is possible to achieve light amplification or gain of the transmitted signal by stimulated emission of radiation in a single pass through this special fiber (Koester and Snitzer, 1964).

Materials effects

Absorption: There are two main resonance absorptions (i.e., regions of anomalous dispersion) in silica that bound the region-of-transparency relevant to optical communications; one is related to the electronic transition between the valence band and the conduction band, and the other is due to molecular vibrations in the tetragonal structure of SiO_4 units in the silica glass network. The electronic transition occurs in the UV region with a tail that extends into the visible. The bonds in the tetrahedral building blocks are characterized by various types of vibrational modes whose resonance wavelengths and their harmonics are distributed throughout the IR region. At the wavelengths of interest in optical communications the absorption losses due to the electronic transition are negligible in the range from 1300 nm to 1600 nm whereas the absorption due to the molecular vibration prohibits transmission in silica beyond wavelengths of about 1675 nm. The global loss minimum in silica is about 0.2 dBkm^{-1} which occurs at 1550 nm (Miya *et al.*, 1979).

There can be additional absorption losses from impurities such as Si-OH species (with peaks at 950, 1250 and 1390 nm) and transition metal ions. All of these additional losses have virtually been eliminated from the modern manufacture processes of silica optical fibers. However their traces remain in the terminology; wavelengths less than 950 nm are referred to as the first-window, wavelengths less than 1390 nm are the second-window, and wavelengths centered on 1550 nm are the third-window. The complete region of transparency of silica is now available for optical communications. The range of wavelengths from 1260 to 1360 nm is now referred to as the O-band (O for original), the range from 1360 to 1460 nm is the E-band (E for extended), the 1460–1530 nm range is the S-band (S for short wavelength), the range from 1530 to 1565 nm is the C-band (C for conventional) and is also referred to as the Er-window, the range from 1565 to 1625 nm is the L-band (L for long wavelength), and finally the range from 1625 to 1675 nm is the U-band (U for ultra-long wavelength). There is no letter designating the earliest wavelengths centered at 870 nm where the losses are too great for modern optical communications.

Scattering: In addition to the inherent absorption loss due to the two resonances that frame the relevant region-of-transparency in silica, there is the loss due to Rayleigh scattering (Stacey, 1956). Rayleigh scattering in amorphous glass arises from the inherent random nature of the thermodynamic fluctuations in its density or refractive-index and it cannot be eliminated. Rayleigh scattering loss scales with the negative fourth power of the wavelength (λ^{-4}), so it becomes rapidly smaller for longer wavelengths. Routine measured losses in mass-produced silica fibers range from about 1.0 dBkm^{-1} at the 1000 nm wavelength to about 0.2 dBkm^{-1} at the 1550 nm wavelength.

Proposals to use heavier molecules than silica such as the fluorides (France *et al.*, 1987) and the chalcogenides (Sanghera and Aggarwal, 1997) in order to shift the infrared tail to longer wavelengths and thereby exploit the ultra-low Rayleigh scattering in this region have not succeeded in displacing silica as the material of choice for fiber optics. The mechanical properties of fibers made from these materials cannot seem to compete with those of silica either.

Bending losses

Micro bend effects result from the statistical micro-deviations of the fiber from a straight line which arise in manufacturing processes such as coating and cabling. Microbends of the order of 100 nm to 1 μ m tend to be significant contributors to loss (Gardner, 1975).

Macro bends, with the bend radii of the order of centimeters, are due to unavoidable bends in the installed cables. One can loosely understand the loss effect in ray-optics terms. On entering the bent section of the fiber the angle of incidence of the ray at the core/cladding boundary on the outer side of the bend reduces, and if the new angle of incidence is less than the critical angle then the ray is refracted into the cladding and power is lost, or leaked, from the guided mode.

Amplifier fibers

Raman fiber amplifiers (RFAs) exploit stimulated Raman scattering due to the slight non-linearity of the standard transmission fiber, or alternatively requires a short length of highly non-linear fiber to serve as the amplifier.

Rare-earth doped optical fiber amplifiers rely on stimulated emission provided by the downward electron transitions in the rare-earth ions doping the core and sometimes the regions of the cladding adjacent to the core. The ions are excited, or pumped, with a lower wavelength (higher frequency hence higher energy) source than the signal wavelength. Of all the possible rare-earth elements, only erbium (Er^{3+}) operates at suitable telecommunications wavelengths when silica is its host glass (Mears *et al.*, 1987). Erbium doped fiber amplifiers (EDFAs) offer a broad transition at the wavelength of 1550 nm which fortuitously corresponds to the wavelength of least transmission loss (C-band) on silica fibers.

Fiber Fabrication

In this section the material requirements and fabrication techniques leading to the production of low-loss and high-bandwidth optical fibers are described.

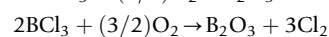
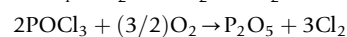
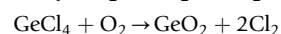
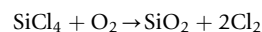
The material systems must be capable of providing a core with a slightly higher refractive-index than that of the cladding in a stable insensitive structure that is capable of being drawn into a fiber. The core and cladding materials must therefore have similar viscosities and coefficients of thermal expansion. The material must be low-loss in the regions of the wavelength spectrum where semiconductor diodes are available. To obtain high transmission bandwidth, the refractive-index distribution in the core must be capable of being profiled. These material requirements limit the field of candidate materials to glasses and plastics. In turn, many plastics are excluded from consideration because the presence of hydrogen in their structures give rise to very high losses and their molecular size leads to very high scattering losses. For this reason emphasis is mainly confined to inorganic glasses.

Modern optical communications had its inception with the research paper from the Standard Telecommunications Laboratories (UK) (Kao and Hockham, 1966) which argued that the strong optical attenuation in glass was not an intrinsic property of the glass but was due to impurities in its chemical composition. It further suggested that silica was the most suitable candidate glass for optical fiber as its region-of-transparency matched the wavelength available from the recently invented semiconductor laser diode. Indeed it had been the demonstration of the ruby laser (Maiman, 1960) providing a coherent optical carrier wave that had prompted the investigation of the possibility of high bandwidth optical communications in the first place. Optical wavelengths had the promise of orders-of-magnitude more information bandwidth than the micro-wave radiation then being concurrently developed for satellite communications during the space-race.

Concentrating here on the high-silica fibers, emphasis will be placed on the two-step process of first producing the high purity preform and then drawing the preform into a fiber. The preform is a large scale rod of glass containing the core and cladding materials incorporated during a deposition process to obtain the required spatial distribution of dopant material for the required fiber refractive index profile. The rod could be up to 1 m long with a diameter of between 10 to 50 mm. The step of scaling down the preform to yield the fiber is referred to as fiber drawing. In this step the rod is softened by heating and then stretched out by pulling in a fiber-drawing machine. Both steps will now be described in more detail.

Preform Fabrication

There are several alternative ways of making the preform that are proprietary to different manufacturers and that all rely on vapor phase processes. These techniques use pure silica as a substrate material and then add trace amounts of dopant to it in order to change its refractive index and allow a waveguide to be formed. In a typical vapor phase reaction, high purity chloride precursors such as SiCl_4 , GeCl_4 , POCl_3 , BCl_3 , purified by distillation, undergo a high-temperature oxidation process or hydrolysis to form oxides of silicon and the dopant elements. For oxidation the completed chemical reactions are as follows (Partus and Saifi, 1980):



Gaseous chlorine evaporates, and solid silicon dioxide condenses as an amorphous substance on cool surfaces and can form the fused silica glass at suitable temperatures. Dopant materials such as GeO_2 and P_2O_5 raise the refractive index of silica, whereas B_2O_3 reduces it.

The different preform fabrication techniques are classified as to whether the glass material deposition is an inside or outside process. For the outside process, the glass material is deposited directly onto a target surface called a bait rod, while in the inside process glass deposition occurs on the inside of a fused silica tube.

Outside vapor deposition (OVD) or the soot process was developed by Corning Glass Works (Keck and Schultz, 1973). Glass is deposited in thin layers on the outside of a massive cylindrical bait rod of aluminum oxide. The precursor chemicals are fed into a burner flame so that sub-microscopic glass particles are generated and condense on the surface of the bait rod. Meanwhile the bait rod is rotated and translated so that a uniform layer is formed. The cycle is repeated so that many such layers are deposited and during the deposition the concentrations of dopant for each layer are adjusted so that the resultant structure already contains the dopant profile as required for the desired refractive index profile of the finished fiber. Each deposited layer is porous (soot) so the assembly is then heated to allow evaporation of the trapped gasses including any humidity that may have entered from the hydrocarbon flame. Further heating sinters the glass layer so that porosity is removed. Once the glass is compact, the bait rod can be extracted and the preform tube collapsed into a solid rod.

Developed at Bell Laboratories, the most common inside process is modified chemical vapor deposition (MCVD) (MacChesney *et al.*, 1974). As in the OVD case, the idea is to form glassy layers of differently doped silica on the inside surface of a silica tube which will later become the outer part of the cladding. Gaseous vapors of the precursor chemicals are passed through the bore of the tube along and around which a burner is passed. In the heated zone porous glass is thereby deposited in thin layers onto the inner surface of the tube. Here no residual gas or water vapor can be trapped because the precursor chemicals do not come into contact with the flame. The porous glass is then sintered and the hollow tube is collapsed into a solid rod. In this case the starting tube needs to be of very high purity and uniformity. There can be burn-off of dopants from the innermost layer during the collapse phase leading to a dip in the profile of the eventual refractive index. Fortunately such a dip has very little effect on the shape of the propagating mode (Hussey and Pask, 1982).

Plasma chemical vapor deposition (PCVD) developed by the Phillips Research Laboratories (Geittner *et al.*, 1976) is a variant of MCVD where the gas burner is replaced with a microwave generator which generates a plasma inside the tube. The plasma is constant enough that rotation of the tube is not required and sintering is not required as the layers of glass are deposited free of pores. Very precise control of the refractive index profile is achievable with this process in which it is not uncommon to deposit 2000 layers. The central dip in the refractive index also occurs here during the final collapse stage.

Vapor phase axial deposition (VAD) was developed in Japan (Sudo *et al.*, 1978) and is quite different from the ones described earlier in that the glass is deposited at the end of a seed rod and the structure is allowed to grow by extending the length of the rod. The cross-sectional refractive index profile is obtained through an elaborate geometry of burner flames and positions of nozzles that bring in the precursor chemicals. Constant turning provides the required rotational symmetry. The deposition is initially porous so the soot is sintered by pulling the entire rod through a suitably heated zone and yields the preform that requires no further collapse.

Preforms for the microstructured fibers can start with a solid rod into which holes may be drilled to achieve the desired cross-sectional pattern. More commonly the preform is assembled by stacking a number of same-material glass tubes together to form a bundle. One can replace individual tubes with solid rods or with tubes of thicker walls to achieve the desired cross-sectional pattern. The central tube can either be replaced with a rod or left void if solid-core guidance or air-guidance, respectively, is desired. The stack is then fused together and may in turn be inserted into a solid thick-walled tube, again of the same material, before being drawn into the eventual fiber. Recently the technology of 3D printing has been applied to the production of microstructured preforms and has the feature that the individual holes produced need not necessarily be circular (Chu *et al.*, 2019). The opportunities that such flexibility provides have yet to be explored.

Each of the above processes yields a preform which is a short fat scaled-up model of the desired fiber cross-section. A 1 m long preform of 25 mm diameter will yield 40 km of standard 125 μm diameter fiber.

Fiber Drawing

The drawing process must yield a fiber whose diameter is precisely controlled. In addition the fiber's strength must be preserved by applying a protective coating which shields the newly drawn fiber from mechanical abrasion and adverse atmospheric effects; it also helps minimize micro bending loss. A drive mechanism feeds the preform into a heated region where it necks down to form a fiber which is pulled from the hot-zone in which the preform is brought to its working temperature, defined as corresponding to a viscosity of approximately 10^4 poise, which is in the range of 1700°C to 2000°C for silica. The important requirement that the constituent glasses in the fiber cross-section have similar viscosities and thermal expansion coefficients is automatically satisfied in weakly guiding fibers and in single-material fibers. The diameter of the fiber is measured at a point shortly after it is formed and this measured value is fed into an elaborate closed loop control system. Within the controller the measured fiber diameter is compared with a desired value thereby generating a signal to adjust the drawing speed such that the fiber diameter reaches the desired value. Modern production processes are capable of producing 125 μm diameter fibers to within an accuracy of 0.1 μm . After the diameter is measured the protective coating is applied to the fiber by way of an extruder. The protective coating may

consist of two layers: an inner soft and pliable layer, and an outer hard layer resistant to abrasion. Epoxides and polyimides or acrylates and silicones are used. The coating material is then cured and the fiber may be subject to further mechanical testing before it reaches the drawing mechanism where it is wound onto a spool.

References

- Birch, R.D., Payne, D.N., Varnham, M.P., 1982. Fabrication of polarization maintaining fibers by gas phase etching. *Electronics Letters* 18, 1036–1037.
- Birks, T.A., Knight, J.C., St. Russell, J.C., 1997. Endlessly single-mode photonic crystal fiber. *Optics Letters* 22, 961–963.
- Cherin, A.H., 1983. *An Introduction to Optical Fibers*. New York: McGraw Hill.
- Chu, Y., Fu, X., Luo, Y., *et al.*, 2019. Silica optical fiber drawn from 3D printed preforms. *Optics Letters* 44 (21), 5358–5361.
- Cohen, L.G., Lin, C., French, W.G., 1979. Tailoring zero chromatic dispersion into the 1.5–1.6 μm low-loss spectral region of single-mode fibres. *Electronics Letters* 15, 334–335.
- France, P.W., Carter, S.F., Moore, M.W., Day, C.R., 1987. Progress in fluoride fibers for optical communications. *British Telecom Technology Journal* 28–44.
- Gambling, W.A., Matsumura, H., Ragdale, C.M., 1979. Mode dispersion, material dispersion, and profile dispersion in graded index single mode fibers. *IEE Journal on Microwaves, Optics and Acoustics* 3, 239–246.
- Gardner, W.B., 1975. Microbending loss in coated and uncoated optical fibers. In: *Proceedings of the Topical Meeting on Optical Fiber Transmission*. Optical Society of America. Paper WA3-1.
- Geitner, P., Kuppers, D., Lydtin, H., 1976. Low-loss optical fiber prepared by plasma-activated chemical vapour deposition (PCVD). *Applied Physics Letters* 28 (11), 645–646.
- Gloge, D., 1971. Weakly guiding fibers. *Applied Optics* 10, 2252–2258.
- Hayashi, T., Nakanishi, T., 2018. Multi-core optical fibers for the next generation communications. *SEI Technical Review* 86, 23–28.
- Hecht, E., 2005. *Optics*, fourth ed. New York: Addison Wesley.
- Hopkins, H.H., Kapany, N.S., 1954. A flexible fibrescope, using static scanning. *Nature* 173, 39–41.
- Hussey, C.D., Pask, C., 1982. Theory of the profile moments description of single mode fibers. *IEE Proceedings H - Microwaves, Optics and Antennas* 129 (3), 123–154.
- Kaiser, P., Marcatili, E.A.J., Miller, S.E., 1973. A new optical fiber. *Bell Labs Technical Journal* 52, 265–269.
- Kao, K.C., Hockham, G.A., 1966. Dielectric-fibre surface waveguides for optical frequencies. *Proceedings of the Institution of Electrical Engineers* 113, 1151–1158.
- Keck, D.B., Schultz, P.C., 1973. Method of Producing Optical Waveguide Fibers. US Pat. 3 711 262
- Koester, C.J., Snitzer, E., 1964. Amplification in a fiber laser. *Applied Optics* 3 (10), 1182–1186.
- MacChesney, J.B., O'Connor, P.B., Presby, H.M., 1974. A new technique for preparation of low-loss and graded-index optical fibers. *Proceedings of the IEEE* 62, 1280–1281.
- Maiman, T.H., 1960. Stimulated optical radiation in ruby. *Nature* 187, 493.
- Marcuse, D., 1979. Interdependence of waveguide and material dispersions. *Applied Optics* 18, 2930–2932.
- Mears, R.J., Reeky, L., Poole, S.B., Payne, D.N., 1987. Low-noise erbium-doper fiber amplifier operating at 1.54 μm . *Electronics Letters* 23, 1026–1028.
- Millar, C.A., 1981. Direct method of determining equivalent-step-index profiles for monomode fibers. *Electronics Letters* 17, 458–460.
- Mitschke, F., 2016. *Fiber Optics: Physics and Technology*, second ed. Berlin Heidelberg: Springer Verlag.
- Miya, T., Terunuma, Y., Hosaka, T., Miyashita, T., 1979. Ultimate low-loss single-mode fiber at 1.55 μm . *Electronics Letters* 15, 106–108.
- Monerie, M., 1982. Propagation in doubly-clad singlemode fibers. *IEEE Journal of Quantum Electronics* 18, 535–542.
- Monro, T.M., Bennett, P.J., Broderick, N.G.R., Richardson, D.J., 2000. Holey fibers with random cladding distribution. *Optics Letters* 25, 206–208.
- Okamoto, K., Eda-iro, T., Kawana, A., Miya, T., 1979. Dispersion minimization in single mode fibers over a wide spectral range. *Electronics Letters* 15, 729–731.
- Partus, F.P., Saifi, M.A., 1980. Lightguide Preform Manufacture. *Western Electric Engineer* 24 (1), 39–47. (winter Issue).
- Payne, D.N., Gambling, W.A., 1975. Zero material dispersion in optical fibers. *Electronics Letters* 11, 176–178.
- Sanghera, J.S., Aggarwal, I.D., 1997. Development of chalcogenide glass fiber optics at NRL. *Journal of Non-Crystalline Solids* 213/214, 63–67.
- Sasaki, Y., Hosaka, T., Horiguchi, M., Noda, J., 1986. Design and fabrication of low-loss and low crosstalk polarization-maintaining optical fibers. *IEEE Journal of Lightwave Technology* 4 (3), 1097–1102.
- Shibata, N., Okamoto, K., Suzuki, K., Ishida, Y., 1983. Polarization properties of elliptical-core fibers and stress-induced birefringent fibers. *Journal of the Optical Society of America A* 73 (12), 1792–1798.
- Snyder, A.W., Love, J.D., 1981. *Optical Waveguide Theory*, first ed. London: Chapman and Hall.
- Stacey, K.A., 1956. *Light Scattering in Physical Chemistry*. New York: Academic Press.
- Stolen, R.H., Lee, C., Jain, R.K., 1984. Development of the stimulated Raman spectrum in single mode silica fibers. *Journal of the Optical Society of America B* 1, 652–657.
- Sudo, S., Kawachi, M., Eda-iro, T., Izawa, T., 1978. Low OH-content optical fiber fabricated by the vapour-phase axial-deposition method. *Electronics Letters* 14, 534–535.

Glasses: Sol-Gel Methods: An Introduction

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Introduction

The physical and chemical properties of conventional glasses have been analyzed for a long time and their applications are well known (Scholze, 1991; Zarzycki, 1991). Glasses are generally used in the field of optical materials and containers but also as fibers for reinforcement and some peculiar applications such as nuclear wastes storage. Usual glasses (window glass and other silicates) are generally done by a multiple steps process including, the melting of the different oxides at a high temperature followed by an refining and finally quenching. The last step causes the freezing of the amorphous structure of the melt. It is followed by an annealing treatment which relaxes the thermal strain. In the last decades a new kind of glasses has been extensively studied in literature. These amorphous materials are no more prepared using the classical melting and refining processes but by the sol-gel method.

In the early 1980s (Gottardi, 1982) it was demonstrated that the 'sol-gel process' could be a way to synthesize materials as different as ceramics, glasses or composites. Since then, three books (Klein, 1988; Brinker and Scherer, 1990; Sakka, 2005) have shown the possibilities of these techniques to allow the synthesis of materials in the form of bulk products, films, or fibers. The sol-gel synthesis was reported as early as the nineteenth century by Ebelmen (1845), who reported the formation, by slow hydrolysis of silicic esters, of a transparent solid which showed no evidence of crystallization. In the 1930s sol-gel dip coating was mentioned for the first time in the patent literature (Geffecken and Berger, 1939). Perhaps the reason for so few investigations in the past into the use of sol-gel methods in glass technology is that traditional ideas about glass formation have always involved high temperature. As already mentioned, the classical procedure for making glasses includes a step at elevated temperature which ensures that the raw materials have reacted and dissolved and the liquid structure is then preserved by super cooling of the melt. In the sol-gel route this high temperature step is eliminated, the homogenization is achieved in the solution at room temperature and cross-linking and preservation of the liquid structure is accomplished by the gelling step. Further heat treatments only serve to remove organic species, hydroxyls and porosity.

What is the sol-gel process and why is it so attractive for materials scientists? A precise definition of the sol-gel route is difficult because it corresponds to a variety of techniques and processes in which one of the steps uses material in the form of a gel. Thus, instead of giving a definition, it is more relevant for what follows to understand what is meant by a gel. A gel will be defined as a 'two-phase medium composed of a solid and a fluid, obtained by an isotropic and progressive aggregation from a solution.' Obviously, this definition is restrictive but it has the advantage of describing exactly the kind of material of interest in this chapter. The sol-gel process has several flexibilities and unique features that are of significant importance in preparing ultrapure homogeneous glasses:

- The high purity of the starting compounds can be preserved during the process. The use of synthetic organometallic chemical compounds guarantees high purity. Because of the expected high purity of gel derived glasses, an obvious interest of the sol-gel route is the possibility of producing optical glass components (mirrors, lenses or preforms for optical fibers).
- For multicomponent systems, rapid homogenization of the different chemical species can be achieved at a molecular level by chemical reactions in the low-viscosity starting solution.
- In the case of compositions leading to glass, the gel is amorphous and can be transformed into a glass over a low-temperature range, without melting or refining. The sintering treatment is carried out at temperatures one-third to one-half lower than those required for melting of the glass-forming components, practically in the vicinity of the glass transition temperature. This lower processing temperature reduces the risks of contamination and losses of volatile components (e.g., B_2O_3 , P_2O_5).
- The morphology of the product, film, fiber or bulk material, can be controlled by the adjustment of the viscosity at room temperature. The use of liquids allows the ready fabrication of thin films and fibers.

The purpose of this chapter is to explain through an example (the conversion of an aerogel into a glass) the different steps of the synthesis and transformation of gels as precursors for glass preparation. A great many technical and commercial products contain the glass-former silica. For this reason we will describe the preparation of a silica glass, the preparation of other glasses follows similar lines. In the last part of this paper we will give an example of the synthesis of porous glasses for the confinement of nuclear wastes.

Principle of the Sol-Gel Glass Route

The challenge of the sol-gel glass process is to obtain a solid material that is dense, inorganic, and amorphous from a room-temperature liquid (not a melt) which is generally a homogeneous mixture of organic compounds. Several transformations of the liquid compounds are necessary, as shown schematically below:

Solution

Gelation

- Destabilisation of a colloidal sol
- Hydrolysis and polycondensation $\text{Si}(\text{OR})_4$

↓

Wet Gel

Drying

- Classical drying (xerogel)
- Supercritical drying (aerogel)

↓

Dry gel

Densification

- Hot pressing
- Sintering

↓

Glass

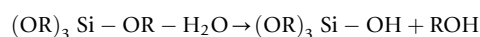
The first step is the formation of a gel from the solution. There are two classical ways of obtaining silica-based gels: the destabilization of silica sols or the hydrolysis and polycondensation reactions of an organometallic compound of silicon (Section 3). Both methods lead to non-crystalline materials containing substantial amounts of water and organic species which can be eliminated by suitable drying treatments. The drying process can be carried out at ambient temperature but during this drying stage considerable shrinkage occurs converting the wet and soft gel into a dried and harder porous solid (xerogel). The drying procedure is crucial and must be performed extremely slowly because it induces capillary phenomena which can destroy the gel network and lead to the breaking up of the solid network.

To avoid these problems supercritical drying is required, as described in Section 4. After supercritical drying, the gel (which is called an aerogel) is a solid material, amorphous, but extremely porous (80–99% porosity) (Aegerter, 2011). The last step of the transformation is a densification heat treatment necessary to convert the dried gels into solid glasses devoid of porosity (sintering) (Section 5). Gels which are originally non-crystalline may crystallize during the heat treatment. The successful formation of a glass is the result of a competition between phenomena which lead to densification and those which promote crystallization (Section 6). In Section 7, we propose the use of these porous materials as host matrices for the synthesis of multi-phase materials (doped glass, glass-ceramics, composites, etc.).

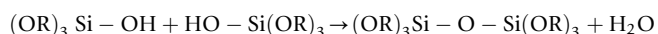
Gel Synthesis

There are two methods for the preparation of gels which can be used for making glasses. The first one is the destabilization of a colloidal sol (Iler, 1979). This method is based on the preparation of stable sols in a liquid medium using non-crystalline particles of colloidal sizes. The destabilization occurs by a modification of the pH or an increase of temperature which favors the collision between colloidal particles. The second method involves the hydrolysis and polycondensation reactions of an organometallic compound $\text{Si}(\text{OR})_4$ which is dissolved in alcohol in the presence of a limited amount of water ions (Brinker and Scherer, 1990). This method is more suited for obtaining a pure glass, owing to the higher purity of the organometallic compounds compared to colloidal sols which contains traces of alkali.

The hydrolysis reaction replaces the alkoxide groups OR with hydroxyl groups OH:



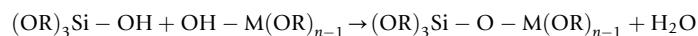
By condensation reactions, two silanol groups give rise to siloxane bonds Si–O–Si:



In reality, the reactions are simultaneous and incomplete. A part of the organic groups are still present after gelation and the polycondensation leads to the reticulation of chains containing unreacted silanol groups. Finally, the chemical composition of the gel is not SiO_2 but $\text{SiO}_x(\text{OR})_y(\text{OH})_z$. In a certain sense the OR groups play the role of non-bridging oxygen in alkali-containing glasses. Therefore, such organic components can also be characterized as network modifiers. The most common alkoxides used in the literature are tetraethoxysilane, $\text{Si}(\text{OC}_2\text{H}_5)_4$, and tetramethoxysilane, $\text{Si}(\text{OCH}_3)_4$.

In the case of multicomponent glasses, we can replace the silicon atom by other network formers known in glass science. The net reaction is customary represented by





where M is a network-forming cation (M=B, P, Ti, Al, Zr). Some glass components (elements of groups 1 and 2) do not form suitable alkoxides. Water-soluble salts such as acetates and nitrates can be used for these constituents (James, 1988; Brinker and Scherer, 1990; Sakka, 2005).

Drying Process

After gelation, the gel is a two-phase medium containing the solid network and the liquid (alcohol–water). During classical drying (evaporation of the liquid) capillary forces collapse the skeletal gel structure, giving rise to a hard glassy product (xerogel) with a significant shrinkage. Moreover, drying induces the formation of cracks and the breaking up of the material. Various alternatives to slow drying are methods involving a favorable compromise between the capillary forces and the mechanical resistance of the gel network: strengthening the gel by reinforcement, reducing the surface tension, enlarging the pores, etc. (Toki, 1988; Brinker and Scherer, 1990).

However the most efficient method is the supercritical drying. The goal of supercritical drying (SCD) is to eliminate these capillary forces which occur when the vapor/liquid surface is in contact with the solid part of the gel. The magnitude of these stresses is dependent on the interfacial energy γ of the liquid. It is possible to suppress γ if the pressure and the temperature pass over the critical point of the liquid. In this pressure and temperature domain, gas and liquid are no longer distinguishable and the γ value becomes zero. According to the temperature and pressure required, the experiments are performed in an autoclave. Supercritical fluid drying was initially developed by Kistler (1932). For the material obtained, he proposed the term ‘aerogel’ to indicate that air now replaces the liquid previously filling the fine texture of the solid network. After supercritical drying, the silica gel is a dry material, very porous (80–99%), and brittle compared to silica glass. The mechanical strength and elastic moduli are a factor of 10^3 – 10^4 (depending on the porosity) lower than those of silica glass (Woignier *et al.*, 2011a). IR and Raman spectroscopies show that the dried gels contain hydroxyls and organic species either as adsorbed or structural groups. The scattering techniques: Small Angle Neutron or X-rays Scattering (SANS, SANS), gives information on the structure and degree of compaction in the clusters forming the gel network. The aerogel network can be described as an assembly of clusters (~ 50 nm). The clusters can be fractal (fractal dimension $D_f \sim 2$), built by the aggregation of small particles (~ 1 – 2 nm) (Marlière *et al.*, 2001). The porosity is totally open and covers the range of meso- and macroporosity (Anes *et al.*, 2014; Reichenauer *et al.*, 2001).

Although the gel network is rather different from that of silica glass, Raman, IR, and NMR spectroscopies, which characterize the molecular structure, reveal vibrational bands and peaks identical to those observed in vitreous silica. The next step in the process converts this porous and somewhat organic material to dense silica avoiding crystallization.

Aerogel–Glass Transformation

As previously mentioned, gels are made of amorphous silica, like in glass, but the main differences are the huge porosity and the high content of hydroxyl and organic groups of the gels. Thermal treatments should eliminate the undesirable chemical species and the pores. Thermograms obtained by differential thermal analysis (DTA), thermogravimetry and dilatometry show three temperature ranges related to aerogel evolution. The DTA endothermic bands within the range 25–200 °C are attributed to vaporization of water and alcohol. Exotherms in the temperature range 250–500 °C are attributed to the oxidation of the organic species. Dilatometric data show that the conversion to dense glass by sintering begins in the temperature range (500–1000 °C) and the densification increases rapidly around 1000 °C (Woignier *et al.*, 2000), a temperature much lower than the melting temperature of silica quartz (1610 °C).

IR spectroscopy is a useful tool to follow the structural and chemical changes during the gel to-glass conversion. The transmission spectrum at room temperature exhibits several absorption peaks related to adsorbed water, silanol and organic groups. The evolution of the spectra can be directly related to the thermal analysis; the peaks attributed to molecular water and to organics can be removed at relatively low temperature. After heat treatment at 1100 °C, the spectrum is identical to that of a conventional silica glass with a high OH content (~ 5000 ppm). The modification of the mechanical properties is not related to the temperature range but rather to the densification state. At low temperature, before the sintering temperature range, the mechanical properties are not strongly affected by the heat treatment. However, the elastic Young's modulus and the mechanical strength increase by a factor of 10^3 – 10^4 with densification and become identical to those of silica glass.

In the same way, when densification proceeds, SANS data reveal the structure evolution of the gels (Woignier *et al.*, 1999). The cluster size decreases, the particles grow and D_f tends toward a value of 3. These transformations indicate a rearrangement of the clusters toward a higher degree of compaction. The sintering proceeds by a viscous flow mechanism (Scherer, 1977).

Characterization of Gel-Sintered Glass and Comparison with Conventional Glass

The gel-sintered glass obtained after a controlled heat treatment above 1000 °C is dense, transparent, and exhibits physical properties identical to those of melt-quenched silica. Transmission measurements in the UV and IR spectral ranges indicate the absence of transition metal impurities and confirm the good optical quality of the gel-sintered glass. The most important difference

is the high OH content which can promote foaming and crystallization at temperatures higher than 1200 °C. If necessary, a dehydration heat treatment (halogenation) can be used in order to eliminate completely the OH content (Phalippou *et al.*, 1984).

It has been supposed in the literature that glasses produced from gels can differ from conventionally melt-quenched glasses. Previous work (Konijnendijk *et al.*, 1973; Mukherjee, 1988) on the preparation of alkali borosilicate glasses by the melting of gel (not sintering) shows that the homogeneity of glasses produced from gels is achieved in a much shorter melting time than in the conventional process. However, experimental results on the structural relaxation in gel-sintered glasses (Scherer and Brinker, 1986) lead to the conclusion that no significant differences exist after the gel has been sintered near T_g . A SAXS study on the kinetics of phase separation in gel-derived and melt-quenched soda-silica glass demonstrated that OH accelerates the growth of the new phase appearing in the parent matrix (Neilson *et al.*, 1986). Additionally, for similar OH contents there is no striking difference between the phase separation behavior of the gel and ordinary glass. Brillouin and low-frequency Raman scattering (Terki *et al.*, 1996; Caponi *et al.*, 2004) have shown small differences between sintered silica aerogel and vitreous glass. These differences in the sound velocity, the hypersonic attenuation, and the frequency of the so called 'boson peak' (characteristic of the medium range order) can also be attributed to the higher OH content. Finally, despite structural differences before sintering, the structure and properties of gels heat treated above T_g become indistinguishable from those of conventional glasses obtained by quenching the melt, if the gel and the glass are identical in composition (including OH content). Another question is whether gel-derived glasses exhibit the same crystallization behavior as ordinary glasses (Mackenzie, 1988). In contrast to the expected advantage of the sol-gel route (its ability to produce glasses having compositions which normally crystallize when quenching the melt), it has been shown that gels of glass-forming systems tend to nucleate and crystallize at much lower temperatures than conventional glasses. This behavior has been attributed to the high OH content and higher surface area, which could lead to enhanced rates of crystal nucleation (Zanotto, 1992). Glass formation by the gel route requires heating the gel at a slow rate followed by holding the gel at a temperature in the vicinity of T_g . This is a risky path to follow because the nucleation region has to be crossed (Uhlmann *et al.*, 1988). It is worth noting that the compression process that speeds up the densification sometimes avoids extensive crystallization of the amorphous gel (Zarzycki, 1997).

Porous Glasses

New kinds of glasses have been studied and synthesized for specific application: the porous glasses. General agreement is that porous glasses exhibit physical behavior similar to that of dense glasses, more or less affected by the porosity. Porous glasses can originate from different processes. The first way was from conventional melting and quenching process which is modified to produce bubbles in the melt or pores in the dense structure. The bubbles are obtained for example, by the decomposition of carbonates during the melting. An example of application of the foamed glasses is as biomaterials for bone prosthesis (Gough *et al.*, 2004). Another example of porous glass obtained from the classical way is the microphase separated and leached 'Vycor' glass. An acidic corrosion treatment dissolves the 'weak' (borate) phase and creates a continuous porosity in the silicate phase. By controlling the composition and the heat treatment it is possible to adjust the pore size (Elmer, 1992).

Xerogels and aerogels previously described can be considered as porous glasses although the very different way used to attain the 'glassy' state. The potential applications of these very porous materials are for catalysis, insulator, acoustic transducers, energy storage devices (Aegerter, 2011). Another possible interest of these porous materials is as a host matrix for the synthesis of multi-phase materials. The large pore volume is used as a sponge to incorporate chemical species with the objective to get a two phases material. However, the counterpart of this porosity is the poor mechanical properties and the consequence is that very porous materials crack during filling because of capillary forces.

It is generally admitted that inclusion of particles or fibers in the material could improve the mechanical properties. In previous works it has been shown that it is possible to adjust the apparent density, the mechanical properties and the permeability by the addition of silica powder in the monomer solution, just before gelation (Toki *et al.*, 1988; Reynes *et al.*, 2001). The mechanical performance increases by a factor 5, the mean pore diameter and the permeability increase too and this composite aerogel is able to resist the capillary stresses during the pore filling by a liquid.

The different kinds of gel-derived porous glasses (xerogels, aerogels and composite aerogels) have been used as host matrix for very different applications. Guest molecules are deposited on the surface of the skeleton when the liquid is further evaporated. The tailoring of the mean pore size and of the pore size distribution is needed to facilitate a homogeneous dispersion of doping molecules within the texture. Graded porous volume with graded pore size could be obtained (Gui *et al.*, 2011). The control of the chemical species diffusion inside the porosity has been done to synthesize gels and glasses showing graded properties such as gradient refractive index (Yamane and Inami, 1992). Soaking by solutions of rare-earth ions has been also successfully applied to synthesize doped silica glasses interesting for their Faraday effect. These glasses contain Er, Mn and Dy with different Verdet constant (Bouaziz *et al.*, 1986). For these optical applications the very pure optical quality of the silica network issued from the sol-gel route is one of the important parameters.

The impregnation of gel derived porous glasses has also been proposed for the containment of nuclear wastes (Woignier *et al.*, 2000; Deptula *et al.*, 2011). In this case, the important key is the very high chemical durability of the silica matrix which traps the nuclear wastes and protects them against water corrosion (Woignier *et al.*, 2011). After the soaking treatment, the host matrix is dried, then sintered. The resulting material is a composite constituted by nuclear wastes crystals embedded into a silica matrix. The initial dissolution rate of such a composite in water is 10^2 times lower than that of the nuclear classical glasses (Reynes *et al.*, 2001).

Conclusions

In summary, the material resulting from the sol-gel route is a precursor of glass but it is also a material with a polymerizable structure, a high OH content, a high surface area and a high pore volume. Compared with a glass of the same oxide composition, the dried gels have higher structural energies. Surface area, silanol groups, and additional free volume (because of a lower cross-link density) contribute to this high free energy and during the thermal conversion to glass the gel changes to become more highly connected while reducing its surface area and free volume (James, 1988).

Gel-derived silica glass exhibits physical properties identical to those of conventional silica glass. The advantage of the sol-gel route is the low heat treatment temperatures and the high level of purity of the sintered material. The process has been extended to bulk multicomponent glasses (borosilicate, phosphosilicate, lanthanide-doped glasses, etc.). For optical applications, gradient index (GRIN) optical elements (Yamane and Inami, 1992) and optical lenses without the need for polishing have been synthesized. New glass matrices for the containment of nuclear wastes have been generated by the sol-gel route (Reynes *et al.*, 2001; Deptuła *et al.*, 2011). In the field of coatings on glass, the application of thin coatings by the sol-gel route is competitive with sputtering, as it is simple and less costly (Dislich, 1984). Major products are sun-shielding layers, non-reflective coatings, scratch-resistant surfaces, and films with a low dielectric permittivity.

Keeping in mind that producing glasses is only one end product of this process, new types of material are being developed. The intermediate stages of the process give the potential for generating new families of materials, for example by combining polymer synthesis with sol-gel techniques (Schmidt and Wolter, 1990; Sakka, 2005; Aegerter, 2011). These combinations produce hybrid networks (organic/inorganic) where the organic constituents are not eliminated by heat treatment and participate to the network connectivity. Another family of new materials results from the biphasic character of the gel; the porous texture of the gel can be used as a host matrix (Woignier *et al.*, 2005). The porosity allows the impregnation of the gel with a liquid species. The possibility of adjusting the pore volume and the diversity of potential liquids (monomers, electrolytes, salts in solution, gelifying solutions, etc.) extend the possibilities of the sol-gel glass process to a large range of products, from doped silica glass to composite and container materials.

Besides the technological interest, the sol-gel route also presents various fundamental, interesting problems. Gels have been used to test experimentally models of aggregation (monomer-cluster, cluster-cluster) and the associated structures calculated by numerical simulation. Aerogels are ideal materials in the sense that the evolution of physical properties in relation to the structure can be experimentally studied over the whole range of porosity from 0 to 99%. Moreover, the small size of the pores can lead to specific behavior of molecules in confined media (Fehr *et al.*, 2003).

References

- Aegerter, M., Leventis, N., Koebel, M., 2011. *Aerogels Handbook*. New York: Springer.
- Anez, L., Calas-Etienne, S., Primera, J., Woignier, T., 2014. Gas and liquid permeability in nano composites gels: Comparison of Knudsen and Klinkenberg correction factors. *Microporous Mesoporous Mater.* 200, 79–85.
- Bouaziz, J., Bourret, D., Sempere, R., 1986. Diffusion phenomena in partially densified silica gels and doped silica glasses elaboration. *J. Non-Cryst. Solids* 82, 225–231.
- Brinker, J.F., Scherer, G.W., 1990. *Sol-Gel Science*. New York: Academic Press.
- Caponi, S., Fontana, A., Mattarelli, A., Montagna, M., Terki, F., Woignier, T., 2004. Influence of thermal treatment in high and low frequency dynamics of silica porous systems. *J. Non-Cryst. Solids* 61, 345–346.
- Deptuła, A., Miłkowska, M., Łada, W., Olczak, T., *et al.*, 2011. Sol-gel processing of silica nuclear waste glasses. *N. J. Glass Ceram.* 1, 105–111.
- Dislich, H., 1984. New glasses. *J. Non-Cryst. Solids* 73, 599–612.
- Ebelmen, M., 1845. Sur une production artificielle de silice diaphane. *C. R. Acad. Sci.* 21, 502–507.
- Elmer, T.H., 1992. Porous and Reconstructed Glasses in *Engineered Materials Handbook*, Vol. 4, Ceramic and Glasses. Materials Park, Ohio: ASM International, 427–432.
- Fehr, C., Dieudonné, P., Primera, J., Woignier, T., 2003. Solid state polymorphism of liquid crystals in confined geometries. *Eur. Phys. J. E Soft Matter* 12 (1), 13–16.
- Geffecken, W., Berger, E., 1939. Dtsch. Reichspatent 736 411. Jenaer Glaswerk Schott gen. Jena.
- Gottardi, V., 1982. Proceeding of the first international workshop on gels. *J. Non-Cryst. Solids* 43.
- Gough, J.E., Jones, J.R., Hench, L.L., 2004. Nodule formation and mineralisation of human primary osteoblasts cultured on a porous bioactive glass scaffold. *Biomaterials* 25, 2039–2046.
- Gui, J.-Y., Zhou, B., Zhong, Y.-H., Du, A., Shen, J., 2011. Fabrication of gradient density SiO₂ aerogel. *J. Sol-Gel Sci. Technol.* 58, 385–393.
- Iler, R.K., 1979. *The Chemistry of Silica*. NY: Wiley Interscience.
- James, P.F., 1988. The gel to glass transition: Chemical and microstructural evolution. *J. Non-Cryst. Solids* 100, 93–114.
- Kistler, S.S., 1932. Coherent expanded aerogel. *J. Phys. Chem.* 36, 52–64.
- Klein, L.C., 1988. *Sol Gel Technology for Thin Films, Fibers, Preforms, Electronics and Specially Shapes*. Park Ridge, NJ: Noyes.
- Konijnendijk, W.L., Van Duuren, M., Groenendijk, H., 1973. Preparation of homogeneous borosilicate glasses by wet chemical processing. *Verres Refract* 27 (1), 11–13.
- Mackenzie, J.D., 1988. Applications of the sol-gel process. *J. Non-Cryst. Solids* 100, 162–169.
- Marlière, C., Woignier, T., Dieudonné, P., Primera, J., Lamy, M., Phalippou, J., 2001. Two fractal structures in aerogel. *J. Non-Cryst. Solids* 285 (1–3), 175–180.
- Mukherjee, S.P., 1988. Ultrastructure glasses from sol-gel processes. In *Sol Gel Technology for Thin Films, Fibers, Preforms, Electronics and Specially Shapes*. Park Ridge, NJ: Noyes, 247–257.
- Neilson, G.F., Weinberg, M.C., Smith, G.L., 1986. Effect of OH content on phase separation behaviour of soda-silica glasses. *J. Non-Cryst. Solids* 82, 137–142.
- Phalippou, J., Woignier, T., Zarzycki, J., 1984. Behaviour of monolithic silica aerogels at temperatures above 1000 °C. In: Hench, L.L., Ulrich, D.R. (Eds.), *Ultrastructure Processing of Ceramics, Glasses and Composites*. New York: Wiley Interscience, pp. 70–87.
- Reichenauer, G., Scherer, G.W., 2001. Effects upon nitrogen adsorption analysis in aerogels. *J. Colloid Interface Sci.* 236, 385–386.
- Reynes, J., Woignier, T., Phalippou, J., 2001. Permeability measurement in composite aerogels: Application to nuclear waste storage. *J. Non-Cryst. Solids* 285, 323–327.
- Sakka, S., 2005. *Handbook of Sol-Gel Science and Technology*. New York: Kluwer Academic Press.

- Scherer, G.W., 1977. Sintering of low-density glasses: I, theory. *J. Am. Ceram. Soc.* 60 (5–6), 236–239.
- Scherer, G.W., Brinker, C.J., 1986. Structural relaxation in gel-derived glasses. *J. Non-Cryst. Solids* 82, 191–197.
- Schmidt, H., Wolter, H., 1990. Organically modified ceramics and their applications. *J. Non-Cryst. Solids* 121, 428–435.
- Scholz, H., 1991. *Glass: Nature, Structure, and Properties*. New York: Springer-Verlag.
- Terki, F., Levellut, C., Boissier, M., Pelous, J., 1996. Low-frequency dynamics and medium range order in vitreous silica. *Phys. Rev. B* 53 (5), 2411–2418.
- Toki, M., Miyashita, S., Takeuchi, T., Kanabe, S., Kochi, A., 1988. A large-size silica glass produced by a new sol–gel process. *J. Non-Cryst. Solids* 100 (1–3), 479–482.
- Uhlmann, D.R., Weinberg, M.C., Teowee, G., 1988. Crystallization of gel-derived glasses. *J. Non-Cryst. Solids* 100, 154–161.
- Wignier, T., Beurroies, I., Sempere, R., Phalippou, J., 1999. Plastic densification in silica aerogel. *Eur. Phys. J. Appl. Phys.* 6, 267–271.
- Wignier, T., Reynes, J., Phalippou, J., Dussossoy, J.L., 2000. Nuclear waste storage in gel-derived materials. *J. Sol–Gel Sci. Technol.* 19, 833–837.
- Wignier, T., Primera, J., Lamy, M., Fehr, C., Anglaret, E., 2005. The use of gels as host matrices for chemical species. Different ways to control the permeability and the mechanical properties. *J. Non-Cryst. Solids* 350, 298–306.
- Wignier, T., Calas, S., Alaoui, A., Primera, J., 2011a. Mechanical properties of nano composites aerogels. *J. Sol–Gel Sci. Technol.* 58, 385–393.
- Wignier, T., Calas, S., Reynes, J., 2011b. From Nano composites aerogels to glass ceramics. *Solid State Phenomena* 172–173, 791–796.
- Yamane, M., Inami, M., 1992. Variable refractive index by sol–gel process. *J. Non-Cryst. Solids* 147–148, 606–613.
- Zanotto, E.D., 1992. The formation of unusual glasses. *J. Non-Cryst. Solids* 147–148, 820–823.
- Zarzycki, J., 1991. *Glasses and the Vitreous State*, Cambridge Solid State Science Series. Cambridge: Cambridge University Press.
- Zarzycki, J., 1997. Past and present of the sol gel science. *J. Sol–Gel Sci. Technol.* 8, 17–22.

Further Reading

- Vollet, D.R., Donnati, D.A., Ibanez Ruiz, A., De Castro, W.C., 2003. Structural evolution of aerogels prepared from TEOS sono-catalysis upon heat treatment up to 1100 °C. *J. Non-Cryst. Solids* 332, 73–79.

Glasses and Glass-Ceramics Prepared by Sol–Gel

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Introduction

For thousands of years, glass and ceramic materials have been produced using conventional melting and sintering processes that involve high temperature. Diverse alternative routes have been proposed, most of them focused on the reduction of the melting and sintering temperature (Dimitriev *et al.*, 2008). Between them, the “Sol–gel chemistry” constitutes a new and flexible non-traditional method for processing ceramic and glass materials at low temperatures since it is a wet-chemical technique. The possibility offered by Sol–gel technology to produce an extensive range of nano-/micro-structures combined with the good control of the properties makes it one powerful technique to fabricate materials (Owens *et al.*, 2016).

The first approach related to Sol–gel method appeared in the mid-nineteenth century (1846), when Ebelmen, a French chemist, observed how silicic esters hydrolyze slowly in the presence of humidity giving hydrated silica (Ebelmen, 1846; Schneller *et al.*, 2013). However, the term “sol–gel” was first proposed by Graham in 1864 and almost 100 years later appeared in the first patent for Sol–gel dealing with the synthesis of SiO₂ and TiO₂ materials for optical applications (Bahuguna *et al.*, 2016). These compositions were re-formulated by Schroeder (1969) and further used in the fabrication of thin films on glass substrates by Sol–gel at industrial scale. In the same year, Mazdiyasn *et al.* (1969) prepared high-purity barium titanate powders.

In addition to the benefit of the low processing temperatures, Sol–gel process shows advantages as high homogeneity, molecular control of the composition and a wide variety of compositions with many different properties.

The importance of “Sol–gel process” became apparent in 1981, in the first “International Workshop on Glasses and Glass Ceramics from Gels” organized by Prof. Vittorio Gottardi and held in Padova, Italy. In this conference, the Sol–gel community, around 30 attendants mainly from glass research centers from Europe, opened the field to the industrial and academic world.

The first stage of the Sol–gel process is the preparation of a stable solution (sol), followed by a gelation and solvent evaporation resulting in the formation of a “gel”, densification and crystallization being the final stages. Even though there are several processing routes, two are the better established in the literature: the colloidal route and the polymeric route, represented in Fig. 1. These routes have a common point the “gelification stage”, although the beginning is essentially different. In the colloidal route, the method starts from a colloidal suspension of small particles in a continuous liquid medium, where the gravitational forces are negligible. In the case of the polymeric route, the “sol” is obtained by controlled hydrolysis and condensation of metal-organic precursors (e.g., metal alkoxides or alkylalkoxides). In both cases, to incorporate a destabilizer or a catalyst increases the viscosity and transforms sol into gel, obtaining a continuous network that encloses the liquid phase. At this point, the gel maintains its shape. Drying and aging steps follow for removing the liquid phase (solvent).

The first materials prepared by Sol–gel were pure inorganic materials. However, in the eighties, Schmidt (1984) at the Fraunhofer Institute began to introduce organic groups in the inorganic networks, which had a big impact in the Sol–gel synthesis. The possibility to create novel materials allowed the expansion of the Sol–gel method to other areas. Livage (1997) explained the impact of synthesizing inorganic–organic hybrid materials that provide unique properties by combining the stability of the inorganic part with the flexibility and functionality of the organic part. This idea was linked to the concept of “chemie douce” referring to the processes of soft inorganic chemistry for creating tailored hybrid organic-inorganic materials. The versatility of blending inorganic with organic phases, gave rise to outlining different structures from ordered dispersions of inorganic bricks in hybrid matrix to highly controlled nano segregation of organic polymers within inorganic matrix (Sanchez *et al.*, 2001). The structure and the properties depend on the nature of the inorganic and organic molecules as well as the synergy between them. Sanchez *et al.* (2003) classified these Sol–gel materials in four types depending on the degree of organization including from ordinary hybrid networks from organically modified metal alkoxides to the synthesis or mesostructured hybrid networks that combine nano-building blocks and self-assembly approaches (Sanchez *et al.*, 2010).

Yanagisawa *et al.* (1990) and Kresge *et al.* (1992), Mobil and Japanese scientists turned the screw in this field thanks to the creation of the first mesoporous hybrid silicate, bringing the opportunity to create novel systems combining the pore size, shape and symmetry control with a tailored surface with amazing properties, in most cases, referred to optics.

The physical-chemical variables involved in the process are crucial to determine the final structure, morphology, and chemical composition of the products. The ability to design and control the different stages of the Sol–gel process allows new materials with enhanced and tailored properties to be prepared. The technique is compatible with many conventional material processing methods (e.g., casting, dip coating, spin coating, doctor blading, and spray coating), allowing the processing of sol–gel-derived materials in a variety of structural shapes, such as nanoparticles, supported thin films and coatings with controlled thicknesses, patterned surfaces, membranes, and monoliths. The potentiality and possibilities of designing original structures and compositions is reflected in the high impact in high-tech industries and optical fields of applications (Green *et al.*, 2003; Soler-Illia and Innocenzi, 2006; Fan *et al.*, 2008; Soller-Illia *et al.*, 2011) (Fig. 2).

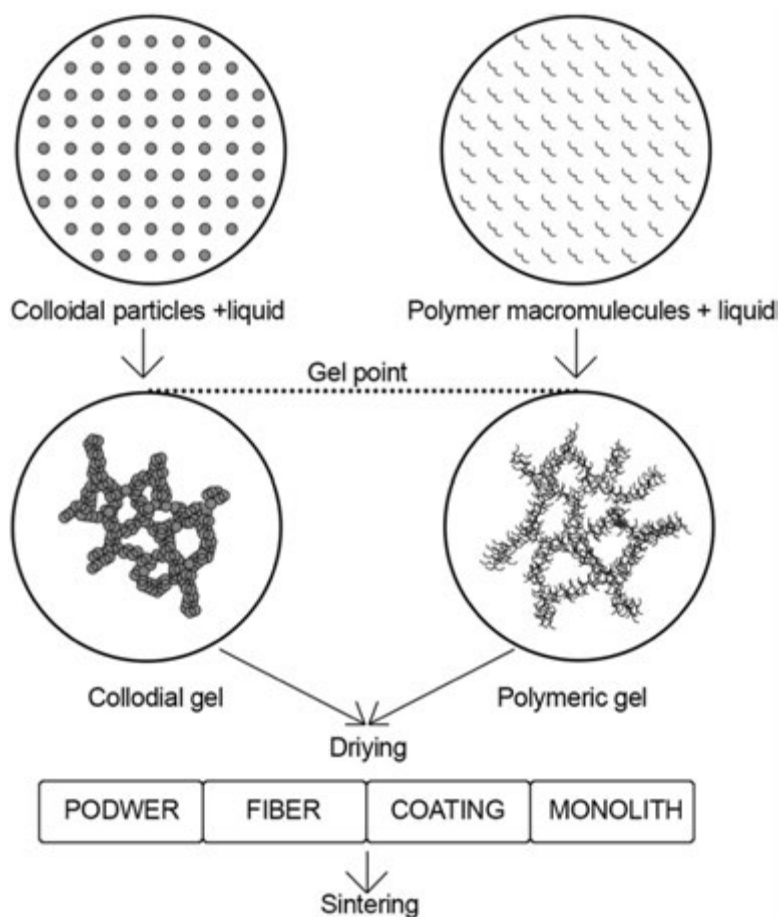


Fig. 1 Colloidal and polymeric sol-gel routes.

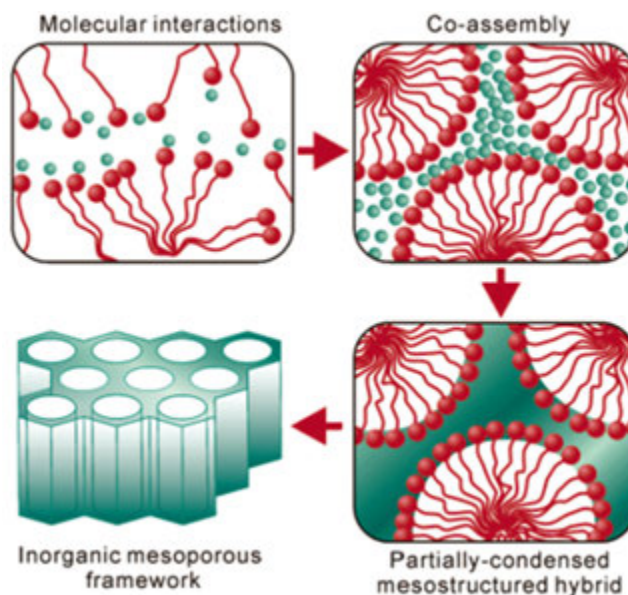


Fig. 2 Critical aspects of sol-gel chemistry mesostructure assembly. Reproduced from Boettcher, S.W., Fan, J., Tsung, C.-K., *et al.*, 2007. Harnessing the sol-gel process for the assembly of non-silicate mesostructured oxide materials. *Accounts of Chemical Research* 40 (9), 784–792.

In this review, we present an insight on the advances in Sol-gel route, considering the physical and chemical aspects implicated in the process as well as an overview of the most important developments and applications. The better developed and used polymeric route is described in deeper detail.

Physical-Chemical Basis of the Process

Several papers appeared between 1846 and 1927 explaining the formation of hydrolyzed derivatives of silica. King and Threlfall (1928) deposited the first patent for partial hydrolyzed alkoxysilanes, describing the preparation of a solution of silica using a reaction between an ester of silicic acid and water. It was mentioned that the proportion of water must not exceed that required to convert the ester into an alcohol.

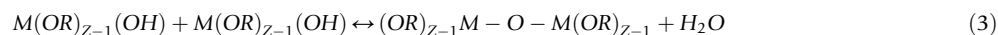
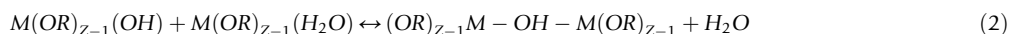
Although the discovery and the first developments on the formation of gel focused on silica as main element, a huge variety of metals can be used instead or mixed with silica. Ray (1934) from Carbon Chemical Corporation patented the hydrolysis and condensation processes for a generic metal that can be other than silicon. After specific studies and observations of Roy and Osborn (1954) the use of metal-organic precursors expanded a lot including a long list of metallic elements that can be prepared by Sol-gel.

Nowadays, many papers describe in detail the hydrolysis of alkoxides, especially metal alkoxides, using Eq. (1), in which M is a metal (Si, Al, In, Ti, Zr, Sn, Pb, Cr, Ta, etc.) and R an alkyl group. This reaction is followed and combined with the condensation (Eqs. (2) and (3)).

Hydrolysis:



Condensation can follow two routes, and usually both occur:



Metal-organic compounds are typically the most used precursors, especially tetra alkoxysilanes and tetra-methoxy-silanes. If the reactivity of the precursor is high, the reactions will occur so quickly to become difficult to control. The reactivity relates to the number of sites able to form Si-O-Si bonds. In case of alkoxides, this can be controlled by the modification of the group R: If the non-hydrolysable radicals increase, then the functionality decreases. Following this, alkoxides have a hydrolysis slower than alkyl-alkoxides.

Villegas Broncano and Fernandez Navarro (1987) reviewed the polycondensation reactions from monomeric units of the same specie as well as copolymerization of a mixture of different monomers. In this last case, it is important to control carefully the kinetics as they have different behavior.

With hydrolysis and condensation reactions, it is possible to create highly branched structures; when complete condensation takes place, compact oxides are produced. The structural differences depend on the basic equations (Eqs. (1) and (2)). Conditions such as the pH, catalyst and H₂O/alkoxide ratio affect the final structure. Chang and Ring (1992) explained the control of the reactions of hydrolysis and condensation deeply studying the aggregation of the species throughout the transition from the sol to the gel state.

Sakka and Kamiya (1982) described the relation between the hydrolysis of TEOS and the amount of HCl incorporated in the reaction. In the same decade, different publications confirmed that hydrolysis becomes more rapid by employing either basic or acid catalysts. The most used catalysts are mineral acids or ammonia but others, such as KOH, KF, HF are also known. Pope and Mackenzie (1986) studied the effect of a variety of catalysts on the hydrolysis and condensation of TEOS (Tetraethyl orthosilicate) and their relationship with the time needed for gelation, as shown in Fig. 3.

Chang and Ring (1992) exposed the relationship of reactions shown in Eqs. (1) and (2) with pH. In acid conditions, the hydrolysis is slower, the condensation rate increasing the aggregation of high-branched clusters forming a network. Under basic conditions a much-accelerated nucleophilic attack is involved. Larger structures have tendency to interact with smaller ones, exchanging OH⁻ and releasing OR groups. The size of the polymer formed is higher than those formed in acidic conditions and they show higher density.

The gel point is defined as the moment at which the variation of the viscoelastic function with the vibration is at a minimum. The characteristics of the bonds define the final structure of the gels. Flory (1974) described the gel behavior where modulus of elasticity depends on the interlinking density of the network. Flory indicates that gelification is strongly dependent on the bonds, a main issue to control the network evolution through scale time. Once the polymeric network grows, the amount of clusters decreases and, so, the sol is not able to flow, becoming a viscous gel supporting a static load without floating. Rabinovich (1985) described the factors provoking the acceleration of the gelation point, in particular, the temperature, the increasing of the water ratio, a higher concentration of alkoxides and the increment of pH.

The obtained gel contains a high free energy because of its large surface area, high amount of chemically bound water and the final high volume. Orgaz-Orgaz (1988) studied the densification steps of the gel, which is an irreversible process in which the decrease in free energy proceeds along with a decrease in surface area, a reduction in pore size and volume.

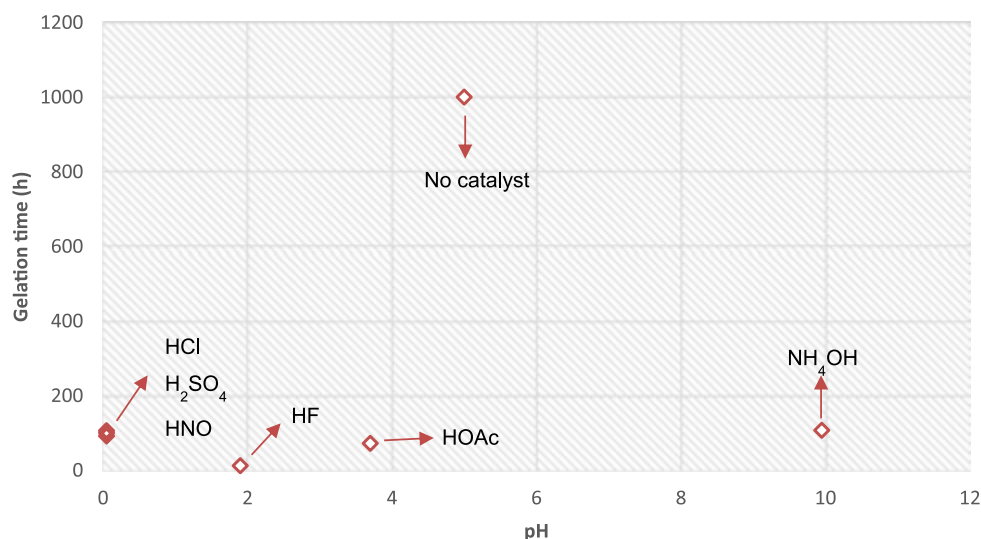


Fig. 3 Effects of catalyst on pH and gel times for TEOS hydrolyzed with 4 equivalents of water. The catalyst concentration is 0.05 mol: TEOS. Modified from Pope, E., Mackenzie, J., 1986. Sol-gel processing of silica. II. The role of the catalyst. *Journal of Non-Crystalline Solids* (87), 185–198.

Once the gel point is reached, the structures corresponding to fast gelation times are opened and porous, due to the lack of possibility to link further rearrangement. Vega and Scherer (1989) demonstrated by NMR that mobile and immobile polymers exist in the sol at the gelation point. At this moment, chemical reactions are still occurring and are crucial to define the properties as they affect the drying and sintering.

The following step to gelation point is aging. Polymerization is a main reaction involved in this step, increasing the connectivity by condensation reactions caused by the availability of hydrolyzed remaining groups. pH and temperature at which the gel is achieved govern the time necessary to complete the aging that goes from a few days to several months. Drying occurs after the aging with the transition from wet gel to a dry one by physical water and solvents desorption.

Scherer (1992) described the drying of gels in two consequent steps. The first one, called “Constant Rate Period” (CRP), is characterized by a constant evaporation rate, where part of the liquid evaporates by capillary force. The wet gel shrinks continuously under compression, and the remaining liquid fills the pores. This initial period is critical for the control of the gel cracking because of the capillary tensions generated in the remaining liquid. It is possible to control cracking by adjusting the evaporation rate, the results being inversely proportional to the pore size: the higher the pore size the more reduced is the cracking. In the second step a small evaporation of the liquid still in the gel occurs, being the crucial phase in which cracking could appear. Preventive measures must be taken to avoid it, like lowering drying velocities from the beginning or by using hypercritical-drying condition (Bisson *et al.*, 2003).

A final homogeneous and dense glass or glass-ceramic results after a consolidation period that includes the thermal treatment of the gel. Numerous researchers explained that the gel densification and its properties depend on the sequential gelation, aging and drying parameters under which it was prepared.

Although Sol-gel steps are apparently sequential, in the case of coatings formation a competition is present between evaporation and condensation reactions. Brinker *et al.* (1992) explained how capillary forces influence the system promoting compaction during the evaporation and generating a resistance to it during condensation. They also described the effect of different balances between evaporation and condensation rates on the structure of the formed coating. In addition to the reaction rates and duration of each stage, other parameters need to be controlled to achieve a desired coating, and the method of deposition used strongly determines the final structure and is closely related to the specific applications.

Another important Sol-gel process relates to the preparation of monodispersed silica nanoparticles of controllable and uniform size, reported by Stöber and Fink (1968). It remains as the most used wet synthetic route to obtain silica nanoparticles. The synthesis takes place when a molecular precursor (typically tetraethylorthosilicate) reacts with water in an alcoholic medium in presence of ammonia as catalyst. Esquena *et al.* (1997) prepared silica particles with sizes above 1 μm by Sol-gel process. In this case, the reaction takes place in the aqueous medium in an acidic emulsion media using HCl. During the first minutes of reaction, the solution turns to a turbid suspension as evidence of the particle formation.

Li and Zhao (2013) proposed that during the Stöber process, a rapid burst of nuclei occurs, and the uniform particles grow without additional nucleation because of the attachment of constituent solutes in a kinetically controlled ambient. Following this idea, the Stöber process extended to obtain titanium nanoparticles, was more difficult to control due to its high reactivity. The preparation of core-shell nanoparticles combining SiO₂ or TiO₂ as shell and different compounds as core have gained interest in recent years (Kobayashi *et al.*, 2005; Yang *et al.*, 2013; Bai *et al.*, 2016).

Applications

The extensive possibilities of compositions able to be prepared by sol-gel, the inorganic, hybrid or organic precursors used in the different synthesis routes, and the multiples shapes of final products, from thick coatings to thin films, powders, monoliths or aerogels with amazing properties, allows this synthesis method to be applied in a variety of fields. The often-used materials, as metals, glasses, ceramics, or plastics, cover a traditional application, but these pure materials do not fulfill the requirements of many new innovative requirements or the design of multifunctional materials. The outbreak of hybrid synthesis by Sol-gel in the past decades made an enormous progress and lead to new materials with enhanced properties and cost-effective prices in many cases.

The objective of this section is to give a look and summarize the most important applications in the field of glasses and glass-ceramics, from biomaterials to optics, photo-catalysis or protective coatings. The goal is to describe the huge possibilities of this synthesis route and their applications and possibilities in the field of material science and technology.

The preparation of coatings is the most developed field of application of Sol-gel process. Large substrates with different shapes can be coated by cost-effective processes. Coatings are prepared from a single inorganic precursor, as well as by the combination of organic and inorganic materials. Single and multi-component oxide coatings are produced as monolayers or structures of films to provide different functionalization to glass and other substrates.

Deposition Methods for Sol-Gel Coating

Brinker and Scherer (1990) described the parameters implicated in the deposition process and highlighted that the rate of evaporation and condensation process determines the pore volume, pore size and surface area of the final films. A brief description of the most important methods used to prepare coatings is presented considering the factors involved in each method and the variety of applications.

Dip Coating Deposition

The dip-coating process involves the controlled vertical withdrawal of the substrate from the liquid at a specific velocity U_0 as shown in Fig. 4(a) (Brinker *et al.*, 1991). Scriven (1988) described the five stages of this coating process: immersion, followed by the start-up, deposition and drainage as simultaneous stages; evaporation as a final step occurs throughout the whole process.

During the immersion, while the substrate pulls the fluid going deep into the sol, two flow sol dynamic layers are generated (Streamline point "S", Fig. 4(b)). As shown in Fig. 4(b), the outer layer (O), returns into the bath while the inner one (I) takes the substrate direction (Brinker and Hurd, 1994). The final thickness of the coatings strongly relates with the dynamics of these two layers and the position of S point (Scriven, 1988; Brinker *et al.*, 1991).

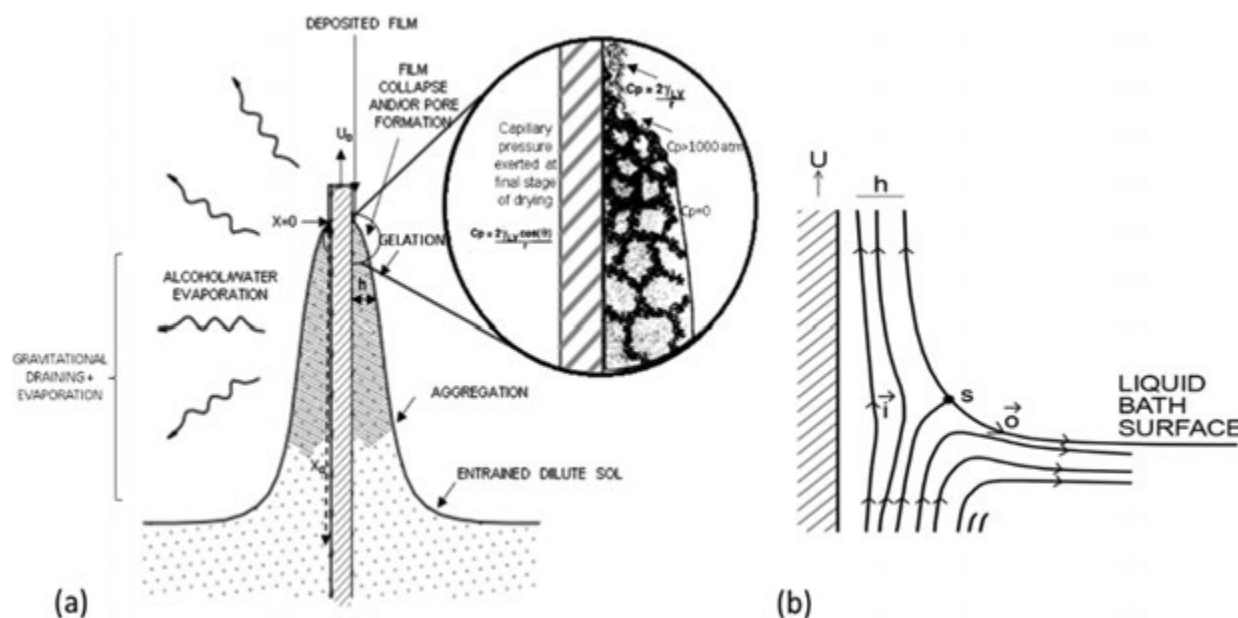


Fig. 4 (a) Schematic of the dip coating process with sequential stages during the development of the structure. (b) Sol flow patterns during dip coating. Modified from Brinker, C.J., Sehgal, R., Hietalab, S.L., *et al.*, 1994. Sol-gel strategies for controlled porosity inorganic materials. *Journal of Membrane Science* (94), 84–102.

Fig. 4(a) shows the parabolic shape provoked by the non-constant evaporation rate in the proximity of the drying line. The pore size is controlled by the structure, composition, rates of condensation and evaporation and the capillary pressure, which, as can be observed in Fig. 4(a), takes a different value in each part of the parabolic shape (Brinker *et al.*, 1994).

Strawbridge and James (1986) described for the first time the different parameters that affect the final thickness. The equations were further modified to include new parameters that allow the most realistic behavior to be described. Brinker and Scherer (1990) advanced that the thickness variation depends on three important parameters, shown in Eq. (4), while the viscosity and density are constant. The relationship simplifies when considering that the lower the withdrawal rate, the thinner is the film, mainly due to an overlap between the deposition and drying stages (Thomas, 1994).

$$\text{thickness} \propto \frac{(\text{viscosity})(\text{withdrawal rate})^{1/2}}{(\text{density})} \quad (4)$$

Guglielmi and Zenezini (1990) proposed a new equation (Eq. (5)) that includes the measurable parameters of the sol, and fits well the evolution of film thickness in inorganic sols.

$$t_p = 10^{-3} \left(\frac{C_p}{\rho_p} \right) I \left(\frac{\eta U}{\rho g} \right)^{\frac{1}{2}} \quad (5)$$

Where t_p is the thickness of the heat-treated coating, C_p is the concentration of the solution expressed in grams of silica per litre, ρ_p is the density of the heat-treated coating expressed in $\text{gr} \cdot \text{cm}^{-3}$, η is the viscosity of the liquid, U is the withdrawal rate, ρ is the viscosity of the liquid and g is the gravitational acceleration.

During the evaporation step, the density of the coatings and the surface tension are constantly changing; this dynamic situation influences the drying profile which is also related to the ambient conditions as well as the specific characteristics of the sol and the substrate.

Brinker *et al.* (1994) described in detail how polymer or particle size, structure, reactivity, relative rates of reactions, liquid surface tension and the dipping withdrawals affect the final microstructure and thickness of the coating.

Spin Coating Deposition

Spin coating process is the simplest method to produce uniform thin films on flat substrates with thicknesses from nanometers to micrometers, (Sahu *et al.*, 2009). Bornside *et al.* (1987) described the spin process consisting of four stages: deposition, spin up, spin off and evaporation of the solvents. Like the dip-coatings process, the evaporation overlaps with the other stages. The deposition begins when the sol falls on a rotating substrate, which is accelerated up to the final speed. Secondly, a centrifugal force governs the spin up stage by letting the liquid flow radially and allowing the fluid to reach a uniform thickness. During the spin off stage, the excess of liquid on the surface flows to the perimeter. The evaporation of the solvent proceeds throughout all the steps governing the last stage, mainly when the vapor is overhead and saturated with volatile components. The rate of evaporation is a function of the partial pressure of the solvents and the amount of volatile components. The forced convection of the vapor above creates a mass transfer coefficient that is also uniform, generating a constant rate of evaporation.

Spin coating has an evident advantage due to the higher layer uniformity in comparison with others deposition techniques (Strawbridge and James, 1986). Ideally, the thickness is inversely proportional to the square root of the rotation speed (Thomas, 1994). Although, it is overly sensitive to the spin speed, the viscosity of coating solution, and roughness of the substrate.

However, the dip-coating and spin-coating processes present important limitations, the most important related with the maximum thickness obtained (Castro *et al.*, 2004). To solve this aspect, and other limitations, many efforts were developed to produce Sol-gel coatings with other techniques, such as EPD deposition.

Electrophoretic Deposition

Since dip-coating and spin-coating techniques focus on flat substrates and thin thicknesses, electrophoresis deposition was proposed as good alternative method to Sol-gel coating (Sheffer *et al.*, 2003; Castro *et al.*, 2004).

Clark *et al.* (1988) defined the electrophoresis as the movement of charged particles in a fluid (suspension) due to the application of an external electric field. According to Van der Biest and Vandeperre (1999), electrophoretic deposition is a combination of two processes, electrophoresis, and deposition. The electrophoresis involves the motion of charged particles in a stable suspension under an electric field, while the deposition is the result of the impact of these particles against the electrode of opposite sign. The rate of migration depends on many factors including size and shape of particles, physical and chemical characteristics of the support medium, the strength of the electromotive force and the ionic strength of the buffer. The power supply also plays an important role and a constant voltage or constant current can be used, although constant current is preferred with longer electrophoresis times.

On the other hand, the deposited mass is a function of different parameters such as particle concentration, electrophoretic mobility, area of the substrate, applied field and deposition time.

Spray Coating

In many cases, spray coating is chosen because of its suitability to cover surfaces without limits of geometry or dimensions, and the simplicity of the equipment needed. [Chen et al. \(1999\)](#) defined the process as the atomization/spraying of a suspension of droplets of the order of tens to hundreds of micrometers, followed by a drying process to produce a continuous surface of solid particles. To generate droplets, the liquid can be atomized by rotary disks, two-fluid nozzles or ultrasonic nebulizers, depending on the droplet size required. Larger particles arrive first to the substrate surface, creating a coating with different particle sizes, and porosity.

Different physicochemical parameters such as pH, viscosity or temperature affect the structure of the coating.

Applications of Sol-Gel Coatings

Optical and Photonics Applications

Inorganic and organic-inorganic hybrid Sol-gel coatings showed important optical applications due to their emissions, luminescence, optical nonlinearity and sensing properties, which modify the reflectance, transmission or absorption of the substrate. Moreover, Sol-gel process allows the incorporation of optically active particles or molecules into the Sol-gel matrix, and the possibility to dope them.

For many years, different oxides as Sol-gel layers for photovoltaic cells, especially TiO_2 with SiO_2 in different configurations, proved successful, improving the solar cells efficiency ([Pettit et al., 1985](#); [Lee et al., 2003](#); [Faustini et al., 2010](#)). Other oxides such as ZnO are also developed for similar applications. The review of [Znaidi \(2010\)](#) deeply describes the preparation and characterization of ZnO Sol-gel coatings.

Light emitting diodes reached unique results for highly condensed films. [Shi et al. \(2015\)](#) studied the photo-activation of hybrid Sol-gel coatings for its use as diodes and, [Yilmaz et al. \(2015\)](#) described the preparation of *n*-ZnO films on p-Si substrates diodes by dip-coating. Many papers report the use of white light emitting diodes ([Kim et al., 2009](#); [Keskenler et al., 2013](#); [Fu et al., 2013](#); [Nayak et al., 2009](#)). Although Schottky-prepared diodes combining different precursors and layers showing many advances, there still exists the need for the development of novel phosphor materials to increase down-conversion efficiencies ([Gouveia-Neto et al., 2012](#); [Righini et al., 2019](#)).

Particular attention was paid to the preparation of oxyfluoride glass-ceramics (OxGCs) for photonic applications after the pioneering work of [Wang and Ohwaki \(1993\)](#) ([de Pablos Martín et al., 2002](#)).

The Sol-gel route appears as a promising alternative to prepare OxGC films and bulk materials avoiding the limitation of melt-quenching (MQ) such as the loss of fluoride content. OxGCs are polycrystalline materials containing active lanthanide-fluoride nano-crystals (NCs) that crystallize in a glass matrix. The doping of nanocrystal with rare earth allows the optical properties to be improved ([Gorni et al., 2018a,b](#); [Zhou et al., 2018](#)). The incorporation of active nano-crystalline phases into a silica glass matrix combines the low phonon energies of fluoride nanocrystals ($250\text{--}450\text{ cm}^{-1}$) with the excellent thermal, mechanical, and chemical stability of oxide glass matrices. The low phonon energy can reduce the non-radiative de-excitation probability of the luminescent RE ions by the multi-phonon relaxation ([Gorni et al., 2018a,b](#)). [Gorni et al. \(2017a,b\)](#) prepared crack-free $80\text{SiO}_2\text{--}20\text{LaF}_3$ coatings doped with $3\%\text{Nd}^{3+}$ and Er^{3+} , confirming the incorporation of the dopants in the NC and including up to 18% wt of LaF_3 , the highest crystalline fraction ever reported ([Gorni et al., 2019](#)), [Fig. 5](#).

In particular, doped $\text{SiO}_2\text{--LaF}_3$ materials are interesting for optical and photonic applications such as photovoltaic devices where the efficiency of solar cells could be improved by modifying and widening the solar spectrum range able to be used, and as dielectric ceramics used in resonators, for planar integrated photonic applications, etc. Lanthanide-doped GdF_3 is considered a promising host because Gd^{3+} ions can act as a sensitizer for other Ln^{3+} ions and enhance the luminescence processes ([Chen et al., 2008](#)). On the other hand, $\text{SiO}_2\text{--NaGdF}_4$ or $\text{SiO}_2\text{--GdF}_3$ matrix may be suitable for infrared and tunable phosphors, sensing, solar cells, plasma display panels, biomedical imaging, and others ([Yin et al., 2012](#)). YF_3 -based sol-gel nano-glass-ceramics are good candidates for photovoltaic applications such as efficient phosphors due to the wide band gap (4.10 eV) and the fact that Y^{3+} sites can be substituted by some trivalent RE ions. The preparation of these materials as coatings is gaining more and more interest because new and novelty applications are possible, such as displays or smart windows.

Protective Coatings

The use of Sol-gel coatings is a good alternative to improve the resistance to corrosion or abrasion of metal substrates reducing the contact between substrate and aggressive medium.

[Durán et al. \(2018\)](#) classified Sol-gel protective coatings in three groups:

- Inorganic and organic-inorganic hybrid coatings with low content of organic groups with sintering temperature between 400°C and 500°C .
- Organic-Inorganic hybrid coatings with high organic content cured under 200°C .
- Inorganic and hybrid coatings with corrosion inhibitors.

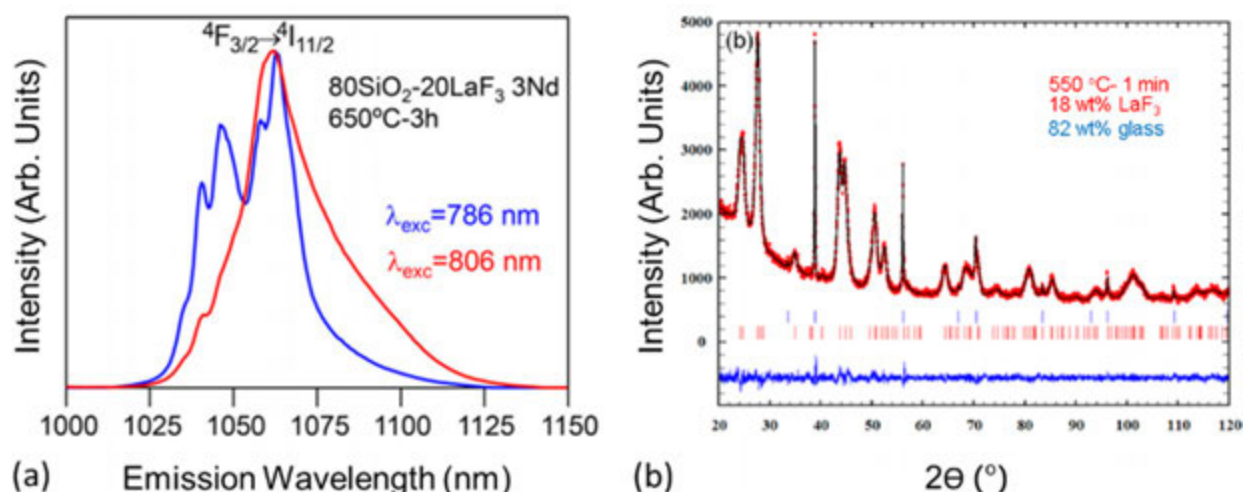


Fig. 5 (a) Normalized emission spectra of Nd^{3+} in the 80SiO_2 - 20LaF_3 Sol-gel supported layer treated at 650°C for 3 h doped with 3% Nd^{3+} obtained by exciting at 786 nm (blue line) and 806 nm (red line). Data correspond to 9K. (b) Quantitative Rietveld refinement of the LaF_3 crystalline fraction with NaF as internal standard for 80SiO_2 - 20LaF_3 0.5Er^{3+} bulk GC treated at 550°C for 1 min. Reproduced from Gorni, G., Balda, R., Fernández, J., *et al.*, 2017a. Oxyfluorideglass-ceramic fibers doped with Nd^{3+} structural and optical characterization. CrystEngComm – Royal Society of Chemistry (19), 6620–6629. Gorni, G., Balda, R., Fernández, J., *et al.*, 2017b. 80SiO_2 - 20LaF_3 oxyfluoride glassceramic coatings doped with Nd^{3+} for optical applications. International Journal of Applied Glass Science, 1–10. Gorni, G., Velázquez, J.J., Mosa, J., *et al.*, 2019. Transparentsol-gel oxyfluoride glass-ceramics with high crystalline fraction and study of RE incorporation. Nanomaterials (9), 1–16.

Inorganic coatings provide good corrosion protection against oxidation and nitridation in anhydrous media of stainless steels (Shane and Mecartney, 1990; Atik and Aegerter, 1992; de Sanctis *et al.*, 1995; de Damborenea *et al.*, 1995; Voevodin *et al.*, 2001). SiO_2 and SiO_2 - ZrO_2 Sol-gel coatings are the most studied compositions, but others were also considered such as ZrO_2 , B_2O_3 , SiO_2 - B_2O_3 , SiO_2 - ZrO_2 , SiO_2 - TiO_2 , ZrO_2 - Y_2O_3 , ZrO_2 - CeO_2 . Inorganic coatings of SiO_2 constitute an efficient protection of surface mirrors for solar collectors (Morales and Durán, 1997). However, the sensitivity to corrosion in electrolytic media is high due to the presence of micro-cracks or defects in the pure inorganic coatings. The incorporation of low amounts of organic groups allows reductions in the penetration of the electrolyte compared to pure inorganic films, offering better electrochemical behavior as well as increased ductility and thickness (Gallardo *et al.*, 2003). These hybrid coatings are demonstrated to be also suitable for biological applications when bioactive powders are incorporated, inducing the formation of hydroxyapatite when in contact with physiological solutions (Gallardo *et al.*, 2001; Garcia and Durán, 2006).

Inorganic-organic hybrid coatings with high organic contents are appropriate for protecting light alloys such as aluminum, magnesium, or their alloys, widely used in automotive, aeronautic and aerospace industries. Conde *et al.* (2002) demonstrated that corrosion resistance of aluminum alloys improves when polymeric sols are prepared with the addition of colloidal suspension. This type of coating is quite interesting because it combines the properties of organic compounds (flexibility, high density, (Rosero-Navarro *et al.*, 2009a,b) and compatibility with the paint system) with those of inorganic components (scratch resistance, durability, etc.).

The most recent trend in corrosion protection is the incorporation of inhibitors in hybrid Sol-gel coatings, the third group. Protective coatings with inhibitors permit repair of damages without external intervention, the so-called *self-healing effect*. Two different types of coatings are considered: (1) conversion coatings obtained from rare earths and inorganic coatings of pure inhibitors produced by Sol-gel (Fahrenholz *et al.*, 2002; Conde *et al.*, 2008; Rosero-Navarro *et al.*, 2011); (2) coatings obtained by incorporation of inhibitors to hybrid coatings (Rosero-Navarro *et al.*, 2009a,b; Carvalho *et al.*, 2014). These films can be furthered coated with epoxy paints for use in the aircraft industry (Durán *et al.*, 2018).

In other approaches, a number of organic compounds such as triazole and thiazole derivatives, 8-hydroxyquinoline and phosphonate-containing compounds or nano-reservoirs or nano-containers are also investigated as alternative corrosion inhibitors, associated with their good compatibility with hybrid coatings (Borisova and Schukin, 2013; Chen and Fu, 2012). However, it is difficult to control the release of the inhibitor to ensure a continued delivery to corrosion sites.

Last approaches focus on the combination of protective layers to arrive to an effective long-lasting corrosion protection (Castro *et al.*, 2020). Fig. 6 provides a schematic of the protective structure consisting of a first anodizing layer cover with a pure glass-like CeO_2 inhibiting layer finally protected with a thick hybrid SiO_2 layer.

Porous Coatings for Sensors, Biosensors and Photo-Catalysis

It is possible to control the porosity (pore volume and pore size) of inorganic coatings obtained by Sol-gel by adjusting the rate of condensation and evaporation and using structure-directing agents (surfactants) (Brinker *et al.*, 1994). These porous materials

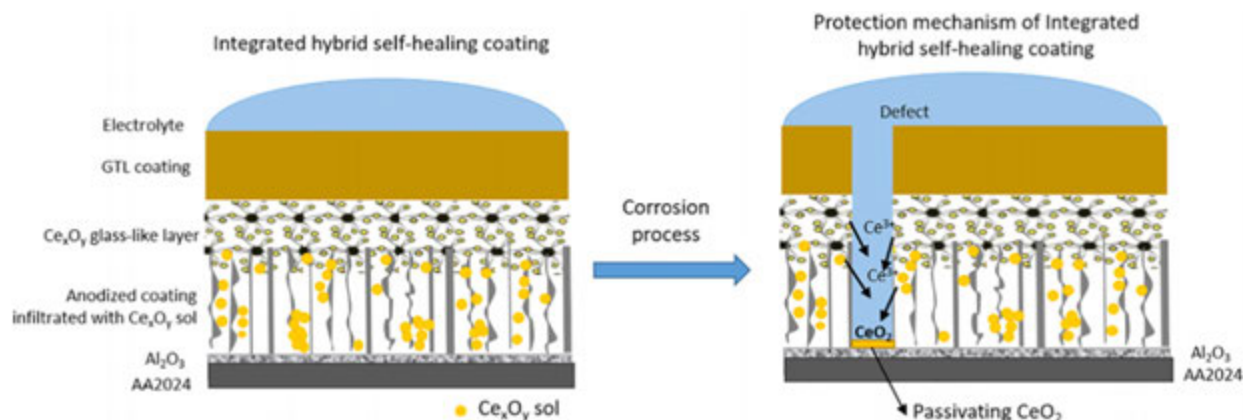


Fig. 6 Schematic illustration of the combined system and protective mechanism of A3-Ce-GTL integrated system. Reproduced from Castro, Y., Ozmen, E., Durán, A., 2020. Integrated self-healing coating system for outstanding corrosion protection of AA2024. *Surface & Coatings Technology* 387 (125521).

Photocatalytic degradation of methyl orange (MO) $c=3\text{mg/L}$, UV-irradiation, 50 cm^2

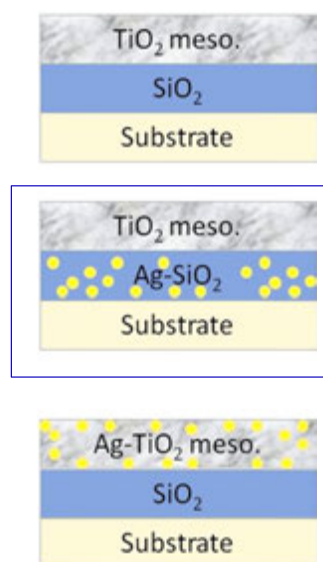
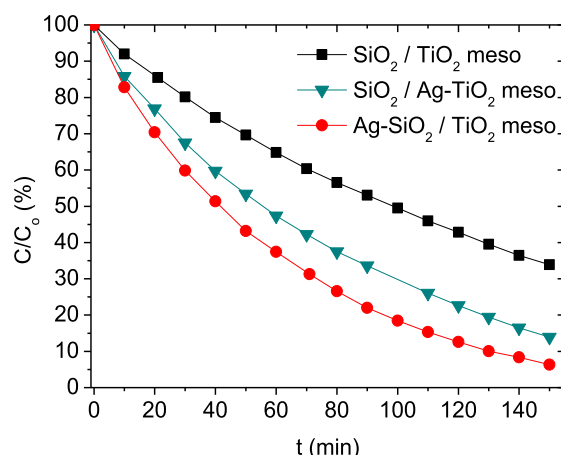


Fig. 7 Photocatalytic degradation of MO by different $\text{SiO}_2/\text{TiO}_2$ nanostructured coating systems doped with silver nanoparticles (Ag NPs). Modified from Roldán, M.V., Castro, Y., Pellegrini, N., Durán, A., 2015. Enhanced photocatalytic activity of mesoporous $\text{SiO}_2/\text{TiO}_2$ sol-gel coating doped with Ag nanoparticles. *Journal of Sol-Gel Science and Technology* 76, 180–194.

present high surface area and intrinsic porosity, showing unique structures. Due to their special characteristics, they find many applications as sensors, biosensors and photocatalysts.

Photo-catalytic activity of mesoporous TiO_2 coatings attracted high attention. Fujisjima *et al.* (2008) intensely studied the photocatalytic behavior of TiO_2 coatings, concluding that their super-hydrophilicity constitutes a great advantage for this application (Sharma *et al.*, 2006). The Dionysiou group (Antoniou and Dionysiou, 2007; Quici *et al.*, 2010) is a key reference in this field. On the other hand, Arconada *et al.* (2011, 2010, 2009) described the photocatalytic activity of multilayer mesoporous TiO_2 films in aqueous solution (methyl orange) and in gas phase (trichloroethylene, hydrogen sulfide and methyl ethyl ketone). The control of crystallinity and the structural and textural properties of the semiconductor, such as the specific surface area, porosity, volume and distribution of the pore size are crucial to improve the photocatalytic behavior. In general, the addition of surfactants increases the thickness of the coatings generating catalysts with high meso-porosity and specific surface area, suggesting a higher contact surface between pollutant and semiconductor, and higher photocatalytic activity (Castro and Durán, 2015).

Other important application of mesoporous TiO_2 coatings involves the combination of biocidal activities with self-cleaning properties. Roldán *et al.* (2015) described the preparation of different systems consisting of a layer of SiO_2 followed by a mesoporous or dense layer, doped with silver nanoparticles (Ag NPs) (Fig. 7). The authors reported the preparation of dense and mesoporous $\text{SiO}_2/\text{TiO}_2$ coatings doped with Ag nanoparticles and found very high and synergic photocatalytic and bactericidal

activities. The best photocatalytic activity appears when Ag nanoparticles situate in the SiO_2 layer, whereas the best bactericidal property is reached when the Ag nanoparticles are in the TiO_2 layer.

Although TiO_2 is the most widely used semiconductor for photocatalytic applications, other oxides, such as SiO_2 , Al_2O_3 , ZnO or their combinations are also utilized (Pal and Sharon, 2002). A high porosity and specific surface area is necessary to promote an extensive contact between the organic compounds and the semiconductor surface (Haas-Santo *et al.*, 2001).

Sol-gel coatings also have an extensive field of applications as optical sensors to determine pH, ionic species or solvents as well as gas sensors and biosensors (Jerónimo *et al.*, 2007). The films change their optical behavior as response to environmental changes (Jeon *et al.*, 2013). pH sensitive dyes can be immobilized in Sol-gel films to be used as indicators. Absorption, fluorescence, and luminescence are used for detection. Depending on the indicator and Sol-gel precursors used the response time changes from less than 1 s to more than 4.5 min (Nguyen *et al.*, 1999; Ertekin *et al.*, 2003). Lifetime and stability can also vary from hours to months (Lobnik *et al.*, 2001; Wang *et al.*, 2003). Sensitive systems for gas detection based on Sol-gel coatings were also widely developed as the nano porosity of the Sol-gel matrix is used as a path for gas molecules where functional particles can be embedded and films show a reversible change in optical transmittance when exposed to certain gases, providing detection limits of 10 ppm (Martucci *et al.*, 2003). Based on the immobilization of reagent of colored complexes, thin films for ionic species detection are extensively used with detection limits above 1 ppm (Wallington *et al.*, 1997).

The availability of transparent coatings with a wide variety of matrices, along with the possibility to entrap biomolecular dopants, opened the door to the development of biosensors from Sol-gel coatings (Jerónimo *et al.*, 2007). The immobilized biomolecules maintain their biological functions and structures inside the Sol-gel matrix. Blyth *et al.* (1995) developed the first biosensor by Sol-gel for nitrogen monoxide and carbon monoxide detection, revealing that thin films are more efficient for bio-detection than monoliths. Enzymes like oxidoreductases and glucose oxidases remains active within the Sol-gel matrix and different sensing systems are still being developed (Ramanathan *et al.*, 1997).

Biomaterials Made by Sol-Gel

Sol-gel materials have been extensively studied for biomedicine and biomedical applications, including the design of materials in bio-sensing and bio-production (Avnir *et al.*, 2006). Nowadays, Sol-gel biomaterials are used in bio-encapsulation and drug release applications and as innovative bioactive materials. The behavior of a specific biomolecule in the inorganic, organic or hybrid nanocomposite material environment, determines the possibilities of these biomolecules to keep their native properties (Jin and Brennan, 2002).

Enzyme-based biosensors are an important field under development. Fukushima *et al.* (1988) and Jin and Brennan (2002) reported the immobilization of cells and enzymes using Sol-gel, demonstrating the good efficiency. Different compositions and hybrid organic-inorganic sol gel materials are reported for reducing the denaturalization of the enzymes during the aging of the inorganic network (Ellerby *et al.*, 1992; Gill and Ballesteros, 2000; Livage *et al.*, 2001).

Tan *et al.* (2005) stated for the first time a hybrid composite made with chitosan/silica, one of the most studied composites nowadays (Zhou *et al.*, 2015; Spirk *et al.*, 2013; Budnyak *et al.*, 2014). Hybrid chitosan and silica are suitable for cholesterol oxidase, amylase, urease, catalase and invertase. Similar hybrid systems are used for cell encapsulations. Sol-gel is a rapid process for immobilizing cells into a stable biomatrix; (Alvarez *et al.*, 2007) demonstrated the high activity and longevity of cells entrapped in silica matrix.

On the other hand, porous Sol-gel materials with cationic amino groups that interact with alginate are demonstrated to be suitable for proliferation and insulin secretion both in vivo and in vitro. Sakai *et al.* (2001) designed a Sol-gel synthesis route for preparing microcapsules with double layer of alginate used in bio-artificial pancreas. These organic-inorganic microcapsules derived from Sol-gel are thus suitable for use in the field of bio-artificial organs.

Sol-gel process is also applied in the biomedical field as implants and sensors where a molecular control of hydroxyapatite incorporation is required, together with the biological behavior of proteins and cells (Hench, 1997). These materials do not provoke rejection by the human body and over time, they are partially reabsorbed and replaced by natural bone.

Bioactive Sol-gel materials shaped as coatings, monoliths or powders are used to obtain an efficient bond to bone by chemical reactions occurring at the interface of the bone tissue that improve the nucleation of the hydroxyapatite. These bioactive Sol-gel materials promote hydroxyapatite multilayer formation on the bone tissue, both in vivo and in vitro. Pereira and Hench (1996) described the mechanism of hydroxyapatite formation on different gel silica substrates. Sepulveda *et al.* (2001) made a full comparison between bioactive glasses made by melt quenching and by Sol-gel, obtaining remarkable differences in the surface area. The biocompatibility of the implant is determined not only by the availability of growth of the apatite, but also by the capacity to absorb proteins (Lobel and Hench, 1996).

There is a clinical need for materials to stimulate the repair of bone by kindling the body's own healing mechanisms. Bone can heal itself if the defect is small, but needs assistance if the defect is over a critical size. Temporary templates (scaffolds) act as guides and stimulus for vascularised bone growth. Inherently brittle materials cannot be used in applications that experience cyclic loads, the current bioactive materials needing toughness and plasticity. The obvious way to improve toughness is to make a composite material, using a bioactive ceramic or glass as the inorganic phase within a biodegradable polymer as the organic matrix. The degradation can be made more congruent by careful polymer selection and manipulation or by developing specialized types of nanocomposites. Jones and Valliant (2011) and Martin *et al.* (2012) tried to understand how each property of the glass and hybrid

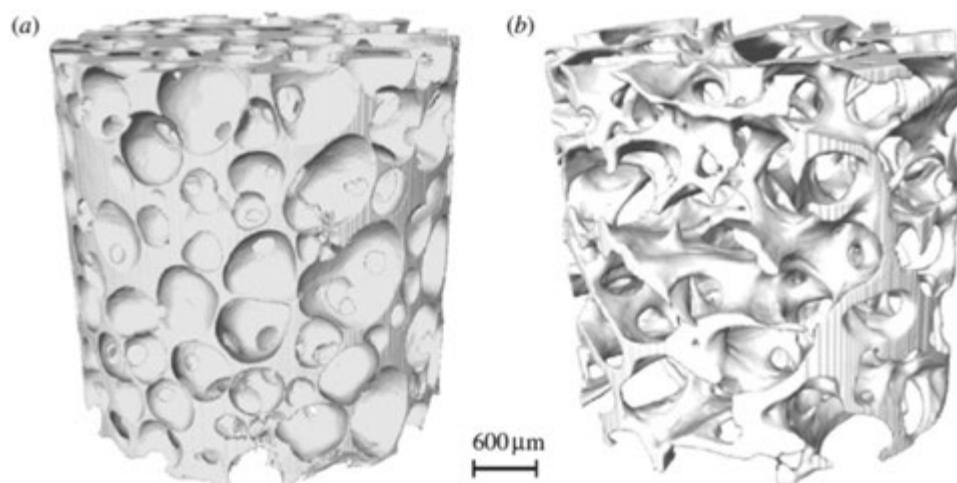


Fig. 8 X-ray microtomography images of (a) bioactive glass foam scaffold and (b) trabecular bone. Reproduced from Martin, R.A., Yue, S., Hanna, J.V., *et al.*, 2012. Characterizing the hierarchical structures of bioactive sol-gel silicate glass and hybridscaffolds for bone regeneration. *Philosophical Transactions of the Royal Society A* 370 (1663), 1422–1443.

scaffolds affects cellular response to optimize the materials and ensure long-term success and clinical products. They focused on the characterization of the hierarchical structures of Sol-gel glasses and hybrids, from atomic-scale amorphous networks, through the covalent bonding between components in hybrids and nanoporosity, to quantifying open macroporous networks of the scaffolds. Nondestructive in situ monitoring of degradation and bioactivity mechanisms of the materials are also included (Fig. 8).

Boccaccini and Zheng (2017) reviewed silicate-based bioactive glass nanoparticles (BGN) with unique properties in biomedical applications. Sol-gel synthesis of BGN is drawing widespread attention, because the convenience and versatility it offers to tune the properties of BGN. Considering the importance of the BGN morphology and composition to their biomedical applications, strategies to control the size, shape, pore structure and composition of BGN are relevant. BGN are particularly interesting biomaterials for bone related applications, but they also have potential for other biomedical applications, e.g., in soft tissue regeneration/repair.

Other Applications

Sol-gel process permits (Boccaccini and Zheng, 2017) preparation of a wide range of outstanding products; some of them gave rise to special fields of research inside the Sol-gel community.

Aerogels have unique properties due to the possibility of controlling the shape and size of pores at low processing temperatures. The extremely low density of these materials explains their amazing thermal and acoustic insulation properties. Aerogels are used as composites (Shajesh *et al.*, 2009; Moner-Girona *et al.*, 2002), absorbents (Rao *et al.*, 2007) and sensors, and have a huge variety of possible science and technology applications (Gurav *et al.*, 2010).

Brinker and Scherer (1985) reported the fabrication of fibers as a new field of applications of Sol-gel materials. Fibers prepared by Sol-gel can be used for reinforcement, superconducting, electrolytic or optical applications, as well as for improving chemical durability (Russel-Flores *et al.*, 1993; Sakka, 1990).

Different Sol-gel routes continue to be active for preparing Fe_2O_3 -C fibers for anodes in Li-ion batteries (Changbin *et al.*, 2018) and PES-TiO₂ hollow fiber hybrid membranes were recently reported by Lu *et al.* (2017). Sol-gel xerogels are applied as sensors and fuel cells taking advantage of the elevated controlled porosity (Grattan *et al.*, 1991; Li *et al.*, 2011).

In the field of optical applications, bulk gels and monoliths are essential parts of fiber optics, lenses, glasses with graded refractive index, etc. (Grant and Glass, 1997).

References

- Alvarez, G.S., Desimone, M.F., Diaz, L.E., 2007. Immobilization of bacteria in silica matrices using citric acid in the sol-gel process. *Applied Microbiology and Biotechnology* 73 (5), 1059–1064.
- Antoniou, M.G., Dionysiou, D.D., 2007. Application of immobilized titanium dioxide photocatalysts for the degradation of creatinine and phenol, model organic contaminants found in NASA's spacecrafts wastewater streams. *Catalysis Today* 124, 215–223.
- Arconada, N., Castro, Y., Durán, A., 2010. Photocatalytic properties in aqueous solution of porous TiO₂-anatase films prepared by sol-gel process. *Applied Catalysis A: General* 385, 101–107.
- Arconada, N., Castro, Y., Duran, A., Hequet, V., 2011. Photocatalytic oxidation of methyl ethyl ketones over sol-gel mesoporous and meso-structured TiO₂ films obtained by EISA method. *Applied Catalysis B: Environmental* 107, 52–58.

- Arconada, N., Durán, A., Suárez, S., *et al.*, 2009. Synthesis and photocatalytic properties of dense and porous TiO₂-anatase thin films prepared by sol-gel. *Applied Catalysis B: Environmental* 86, 1–7.
- Atik, M., Aegerter, M.A., 1992. Corrosion resistant sol-gel ZrO₂ coatings on stainless steel. *Journal of Non-Crystalline Solids* 147–148, 813–819.
- Avnir, D., Coradin, T., Lev, O., Livage, J., 2006. Recent bio-applications of sol-gel materials. *Journal of Materials Chemistry* 16, 1013–1030.
- Bahuguna, G., Mishra, N.K., Chaudhary, P., *et al.*, 2016. Thin film coating through sol-gel technique. *Research Journal of Chemical Sciences* 6 (7), 65–72.
- Bai, A.B., Song, H., He, G., *et al.*, 2016. Facile synthesis of core-shell structured ZrO₂@SiO₂ via a modified Stöber method. *Ceramics International* 42 (6), 7583–7592.
- Bisson, A., Rigacci, A., Lecomte, D., *et al.*, 2003. Drying of silica gels to obtain aerogels: Phenomenology and basic techniques. *Drying Technology* 21 (4), 593–628.
- Blyth, D.J., Aylott, J.W., Richardson, D.J., Russell, D.A., 1995. Sol-gel encapsulation of Metalloproteins for the development of optical biosensors for nitrogen monoxide and carbon monoxide detection. *Analyst* 120, 2725–2730.
- Boccaccini, A.R., Zheng, K., 2017. Sol-gel processing of bioactive glass nanoparticles: A review. *Advances in Colloid and Interface Science* 249, 363–373.
- Borisova, D.M.H., Schukin, D.G., 2013. Influence of embedded nanocontainers on the efficiency of active anticorrosive coatings for aluminum alloys part II: Influence of nanocontainer position. *Applied Materials & Interfaces* 5, 80–87.
- Bornside, D.E., Macosko, C.W., Scriven, L.E., 1987. Modeling of spin coating. *Journal of Imaging Technology* 13 (4), 122–130.
- Brinker, J.C., Scherer, G.W., 1990. Film formation. In *Sol-Gel Science*. Oxford: Elsevier, pp. 787–836.
- Brinker, C.J., Frye, G.C., Hurd, A.J., Ashley, C.S., 1991. Fundamentals of sol-gel dip coating. *Thin Solid Films* 201, 97–108.
- Brinker, C.J., Hurd, A., 1994. Fundamentals of sol-gel dip-coating. *Journal de Physique III, EDP Science* 4 (7), 1231–1242.
- Brinker, C.J., Hurd, A.J., Schunk, P.R., *et al.*, 1992. Review of sol-gel thin film formation. *Journal of Non-Crystalline Solids* 147, 424–436.
- Brinker, C.J., Scherer, G.W., 1985. Sol-gel-glass: I. Gelation and gel structure. *Journal of Non-Crystalline Solids* 70, 301–322.
- Brinker, C.J., Sehgal, R., Hietalab, S.L., *et al.*, 1994. Sol-gel strategies for controlled porosity inorganic materials. *Journal of Membrane Science* 94, 84–102.
- Budnyak, T.M., Tertykh, V.A., Yanovska, E.S., 2014. Chitosan immobilized on saponite surface in extraction of V(V), Mo(VI) and Cr (VI) oxoanions. *Chemistry, Physics and Technology of Surface*. 445–453.
- Carvalho, J.B., Silva, R.S., Cesarino, I., *et al.*, 2014. Influence of the annealing temperature and metal salt precursor on the structural characteristics and anti corrosion barrier effect of CeO₂ sol-gel protective coatings of carbon steel. *Ceramics International* 40, 13437–13446.
- Castro, Y., Durán, A., 2015. Sol-gel TiO₂ materials and coatings for photocatalytic and multifunctional applications. In: Levy, D., Zayat, M. (Eds.), *The Sol-Gel Handbook*. Wiley-VCH, pp. 911–928.
- Castro, Y., Ferrari, B., Durán, A., Moreno, R., 2004. Effect of rheology and processing parameters on the EPD coatings of basic sol-gel particulate sol. *Journal of Materials Science* 39, 845–849.
- Castro, Y., Ozmen, E., Durán, A., 2020. Integrated self-healing coating system for outstanding corrosion protection of AA2024. *Surface & Coatings Technology* 387 (125521).
- Changbin, S., Sihao, C., Zhen, L., 2018. Controllable synthesis of Fe₂O₃-carbon fiber composites via a facile sol-gel route as anode materials for lithium ion batteries. *Applied Surface Science* 427, 476–484.
- Chang, S.Y., Ring, T.A., 1992. Map of gel times for three phase region tetraethoxysilane, ethanol and water. *Journal of Non-Crystalline Solids* 147/148, 56–61.
- Chen, C.H., Emond, M.H.J., Kelder, E.M., *et al.*, 1999. Electrostatic sol-spray deposition of nanostructured ceramic thin films. *Journal of Aerosol Science* 30 (7), 959–967.
- Chen, D., Wang, Y., Yu, Y., Huang, P., 2008. Structure and optical spectroscopy of eu-doped glass ceramics containing GdF₃ nanocrystals. *Journal of Physical Chemistry* 112, 18943–18947.
- Chen, T., Fu, J., 2012. An intelligent anticorrosion coating based on pH-responsive supramolecular nanocontainers. *Nanotechnology* 23 (50).
- Clark, D.E., Dalzell, W.J., Folz, D.C., 1988. Electrophoretic alumina sol-gel coatings on metallic substrates. *Ceramic Engineering and Science Proceedings* 9, 1111–1118.
- Conde, A., Arenas, M.A., de Frutos, A., de Damborenea, J., 2008. Effective corrosion protection of 8090 alloy by cerium conversion coatings. *Electrochimica Acta* 53 (26), 7760–7768.
- Conde, A., Durán, A., de Damborenea, J., 2002. Protección contra la corrosión de aleaciones de aluminio mediante recubrimientos sol-gel. *Boletín de la Sociedad Española de Cerámica y Vidrio* 41 (3), 319–323.
- de Damborenea, J., Pellegrini, N., Durán, A., 1995. Electrochemical behaviour of SiO₂ sol-gel coatings on stainless steel. *Journal of Sol-Gel Science and Technology* 4, 239–244.
- de Sanctis, O., Gómez, L., Pellegrini, N., Durán, A., 1995. Behaviour in hot ammonia atmosphere of SiO₂-coated stainless steels produced by sol-gel procedure. *Surface and Coatings Technology* 70 (2–3), 251–255.
- Dimitriev, Y., Ivanova, Y., Iordanova, R., 2008. History of sol-gel science and technology. *Journal of the University of Chemical Technology and Metallurgy* 43 (2), 181–192.
- Durán, A., Castro, Y., Conde, A., Damborenea, J.J., 2018. Sol-gel protective coatings. In *Handbook of Sol-Gel Science and Technology*. Springer International Publishing, pp. 2369–2433.
- Ebelmen, M., 1846. Sur les combinaisons des acides borique et silicique avec les ethers. *Annales de Chimie et de Physique* 25, 129–166.
- Ellerby, L.M., Nishida, C.R., Nishida, F., *et al.*, 1992. Encapsulation of proteins in transparent porous silicate glasses prepared by the sol-gel method. *Science* 255 (5048), 1113–1115.
- Ertekin, K., Alp, S., Yenigul, B., *et al.*, 2003. Photophysical and photochemical characteristics of an azlactone dye in sol-gel matrix; a new fluorescent pH indicator. *Dyes and Pigments* 56, 125–133.
- Esquena, J., Pons, R., Azemar, N., *et al.*, 1997. Preparation of monodisperse silica particles in emulsion media. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 123–124, 575–586.
- Fahrenholz, W.G., O'Keefe, M.J., Zhou, H., Grant, J.T., 2002. Characterization of cerium-based conversion coatings for corrosion protection of aluminum alloys. *Surface and Coatings Technology* 155 (2–3), 208–213.
- Fan, J., Boettcher, S.W., Tsung, K.-C., *et al.*, 2008. Field-directed and confined molecular assembly of mesostructured materials: Basic principles and new opportunities. *Chemistry of Materials* 20, 909–921.
- Faustini, M., Nicole, L., Boissière, C., *et al.*, 2010. Hydrophobic, antireflective, self cleaning and antifogging sol-gel coatings: An example of multifunctional nanostructured materials for photovoltaic cells. *Chemistry of Materials* 22, 4406–4413.
- Flory, P.J., 1974. Introductory lecture. *Faraday Discussions of the Chemical Society* 57, 7–18.
- Fujisjima, A., Zhang, X., Tryk, D.A., 2008. TiO₂ photocatalysis and related surface phenomena. *Surface Science Reports* 63, 515–582.
- Fukushima, Y., Okamura, K., Imai, K., 1988. A new immobilization technique of whole cells and enzymes with colloidal silica alginate. *Biotechnology and Bioengineering* 32 (5), 584–594.
- Fu, Q., Chen, J., Shi, C., Ma, D., 2013. Room-temperature sol-gel derived molybdenum oxide thin films for efficient and stable solution-processed organic light emitting diodes. *Journal American Chemical Society* 135 (13), 6024–6029.
- Gallardo, J., Durán, A., García, C.C., *et al.*, 2003. Effect of sintering temperature on the corrosion and wear behaviour of protective SiO₂-based sol gel coating. *Journal of Sol-Gel Science and Technology* 27 (2), 175–183.
- Gallardo, J., Galliano, P., Durán, A., 2001. Bioactive and protective sol-gel coatings on metals for orthopaedic prostheses. *Journal of Sol-Gel Science and Technology* 21, 6574.
- García, C.C., Durán, A., 2006. Bioactive coatings deposited on titanium alloys. *Journal of Non-Crystalline Solids* 352 (32–35), 3488–3495.
- Gill, I., Ballesteros, A., 2000. Bioencapsulation within synthetic polymers (Part 1): Sol-gel encapsulated biologicals. *Trends in Biotechnology* 18, 282–297.
- Gorni, G., Balda, R., Fernández, J., *et al.*, 2017a. Oxyfluoride glass-ceramic fibers doped with Nd³⁺ structural and optical characterization. *CrystEngComm – Royal Society of Chemistry* 19, 6620–6629.

- Gorni, G., Balda, R., Fernández, J., *et al.*, 2017b. 80SiO₂-20LaF₃ oxyfluoride glass ceramic coatings doped with Nd³⁺ for optical applications. *International Journal of Applied Glass Science*. 1–10.
- Gorni, G., Balda, R., Fernández, J., *et al.*, 2018a. Effect of the heat treatment on the spectroscopic properties of Er³⁺-Yb³⁺ doped transparent oxyfluoride nano-glass-ceramics. *Journal of Luminescence* 193, 51–60.
- Gorni, G., Velázquez, J.J., Mosa, J., *et al.*, 2018b. Transparent glass-ceramic produced by sol-gel: A suitable alternative for photonic materials. *Materials* 11 (212), 1–30.
- Gorni, G., Velázquez, J.J., Mosa, J., *et al.*, 2019. Transparent sol-gel oxyfluoride glass-ceramics with high crystalline fraction and study of RE incorporation. *Nanomaterials* 9, 1–16.
- Gouveia-Neto, A., da Silva, A., Bueno, L.A., da Costa, E.B., 2012. Luminescent features of sol-gel derived rare earth multi-doped oxyfluoride nano-structured phosphors for white LED application. *Journal of Luminescence* 132, 299–304.
- Grant, S., Glass, R.S., 1997. A sol-gel based fiber optic sensor for local blood pH measurements. *Sensors and Actuators B* 45, 35–42.
- Grattan, K.T., Badini, G.E., Palmer, A.W., 1991. Use of sol-gel techniques for fibre-optic sensor applications. *Sensors and Actuators A*. 25–27, 483–487.
- Green, D.L., Lin, J.S., Lam, Y.-F., *et al.*, 2003. Size, volume fraction, and nucleation of Stober silica nanoparticles. *Journal of Colloid and Interface Science* 266, 346–358.
- Guglielmi, M., Zenezini, S., 1990. The thickness of sol-gel silica coatings obtained by dipping. *Journal of Non-Crystalline Solids* 121 (1–3), 303–309.
- Gurav, J.L., Jung, I.-K., Park, H.-H., *et al.*, 2010. Review article: Silica aerogel: Synthesis and applications. *Journal of Nanomaterials* 2010, 1–12.
- Haas-Santo, K., Fichtner, M., Schubert, K., 2001. Preparation of microstructure compatible porous supports by sol-gel synthesis for catalyst coatings. *Applied Catalysis A: General* 220, 79–92.
- Hench, L.L., 1997. *Sol-Gel Materials for Bioceramic Applications*. London: Department of Materials, Imperial College of Science Technology and Medicine.
- Jeon, D., Yoo, W.J., Seo, J.K., *et al.*, 2013. Fiber-optic pH sensor based on sol-gel film immobilized with neutral red. *Optical Review* 20 (2), 209–213.
- Jerónimo, P.C., Araújo, A.N., Conceição, M., Montenegro, B., 2007. Optical sensors and biosensors based on sol-gel films. *Talanta* 72, 13–27.
- Jin, W., Brennan, J.D., 2002. Properties and applications of proteins encapsulated within sol-gel derived materials. *Analytica Chimica Acta* 461 (1), 1–36.
- Jones, J.R., Valliant, E.M., 2011. Softening bioactive glass for bone regeneration: Sol gel hybrid materials. *Soft Matter* 7 (11), 2083–2095.
- Keskenler, E.F., Tomakin, M., Dogan, S., *et al.*, 2013. Growth and characterization of Ag/n-ZnO/p-Si/Al heterojunction diode by sol-gel spin technique. *Journal of Alloys and Compounds* 550, 129–132.
- Kim, K., Song, Y.W., Leem, J., *et al.*, 2009. Preparation and analysis of schottky diodes with Au and sol-gel-processed ZnO thin films. *Journal of the Korean Physical Society* 55 (1), 140–143.
- King, G., Threlfall, R., 1928. Material for Forming Coatings, for the use as Impregnating Agents or for Like Purposes. United States, Patent No. 1.809.755.
- Kobayashi, Y., Katakami, H., Mine, E., *et al.*, 2005. Silica coating of silver nanoparticles using a modified Stöber method. *Journal of Colloid and Interface Science* 283 (2), 392–396.
- Kresge, C.T., Leonowicz, M.E., Roth, W.J., *et al.*, 1992. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature* 359, 710–712.
- Lee, S.-C., Lee, J.-H., Oh, T.-S., Kim, Y.-H., Lee, J.H., 2003. Fabrication of tin oxide film by sol-gel method for photovoltaic solar cell system. *Solar Energy Materials & Solar Cells* 74 (3–4), 481–487.
- Li, H., Jin, D., Yu, Q., Tu, H., 2011. Optical humidity sensing proton-conducting sol-gel glass monolith. *Journal of Power Sources* 196, 3836–3840.
- Livage, J., 1997. Sol-gel processes. *Current Opinion in Solid State and Materials Science* 2 (2), 132–138.
- Livage, J., Coradin, T., Roux, C., 2001. Encapsulation of biomolecules in silica gels. *Journal of Physics Condensed Matter* 13 (33), 673–691.
- Li, W., Zhao, D., 2013. Extension of the Stöber method to construct mesoporous SiO₂ and TiO₂ shells for uniform multifunctional core-shell structures. *Advanced Materials* 25, 142–149.
- Lobel, K.D., Hench, L.L., 1996. In-vitro protein interaction with a bioactive gel-glass. *Journal of Sol-Gel Science and Technology*. 69–76.
- Lobnik, A., Majcen, N., Niederreiter, K., Uray, G., 2001. Optical pH sensor based on the absorption of antenna generated europium luminescence by bromothymolblue in a sol-gel membrane. *Sensors and Actuators B* 74, 200–206.
- Lu, S.-H., Liu, M., Xu, Z.-L., 2017. A novel PES-TiO₂ hollow fiber hybrid membrane prepared via sol-gel process assisted reverse thermally induced phase separation (RTIPS) method. *Journal of Membrane Science* 528, 303–315.
- Martin, R.A., Yue, S., Hanna, J.V., *et al.*, 2012. Characterizing the hierarchical structures of bioactive sol-gel silicate glass and hybrid scaffolds for bone regeneration. *Philosophical Transactions of the Royal Society A* 370 (1963), 1422–1443.
- Martucci, A., Sartori, S., Muffato, A., *et al.*, 2003. Sol-gel synthesis of -Na₂O.xAl₂O₃ films. *Journal of the American Ceramic Society* 86 (11), 1965–1968.
- Mazdiyasi, K.S., Dolloff, R.T., Smith, J.S., 1969. Preparation of high-purity submicron barium titanate powders. *The American Ceramic Society* 52 (10), 523–526.
- Moner-Girona, M., Martínez, E., Esteve, J., *et al.*, 2002. Micromechanical properties of carbon-silica aerogel composites. *Applied Physics A* 74, 119–122.
- Morales, A., Durán, A., 1997. Sol-Gel protection of front surface silver and aluminium mirrors. *Journal of Sol-Gel Science and Technology* 8, 451–457.
- Nayak, P.K., Yang, J., Kim, J., *et al.*, 2009. Spin-coated Ga-doped ZnO transparent conducting thin films for organic light-emitting diodes. *Journal of Physics D: Applied Physics* 42, 1–6.
- Nguyen, T., McNamara, K.P., Rosenzweig, Z., 1999. Optochemical sensing by immobilizing fluorophore-encapsulating. *Analytica Chimica* 400, 45–54.
- Orgaz-Argaz, F., 1988. Gel to glass conversion: Densification kinetics and controlling mechanisms. *Journal of Non-Crystalline Solids* 100, 115–141.
- Owens, G.J., Singh, R.K., Foroutan, F., *et al.*, 2016. Sol-gel based materials for biomedical applications. *Progress in Materials Science* 77, 1–79.
- de Pablos Martín, A., Durán, A., Pascual, M.J., 2002. Nanocrystallisation in oxyfluoride systems: Mechanisms of crystallisation and photonic properties. *International Materials Reviews* 57 (3), 165–186.
- Pal, B., Sharon, M., 2002. Enhanced photocatalytic activity of highly porous ZnO thin films prepared by sol-gel process. *Materials Chemistry and Physics* 76 (1), 82–87.
- Pereira, M.M., Hench, L.L., 1996. Mechanisms of hydroxyapatite formation on porous gel-silica substrates. *Journal of Sol-Gel Science and Technology* 7, 59–68.
- Pettit, R.B., Brinker, C.J., Ashley, C.S., 1985. Sol-gel double layer antireflection coatings for silicon solar cells. *Solar Cells* 15 (3), 267–278.
- Pope, E., Mackenzie, J., 1986. Sol-gel processing of silica. II. The role of the catalyst. *Journal of Non-Crystalline Solids* 87, 185–198.
- Quici, N., Litter, M., Vera, M., *et al.*, 2010. Effect of key parameters on the photocatalytic oxidation of toluene at low concentrations in air under 254 + 185 nm UV irradiation. *Applied Catalysis B: Environmental* 95, 312–319.
- Rabinovich, E.M., 1985. Review: Preparation of glass by sintering. *Journal of Materials Science* 20, 4259–4297.
- Ramanathan, K., Kamalasanan, M.N., Malhotra, B.D., *et al.*, 1997. Immobilization and characterization of lactate dehydrogenase on TEOS derived sol-gel films. *Journal of Sol-Gel Science and Technology* 10, 309–316.
- Rao, V.A., Hegde, N.D., Hirashima, H., 2007. Absorption and desorption of organic liquids in elastic superhydrophobic silica aerogels. *Journal of Colloid and Interface Science* 305, 124–132.
- Ray, A.B., 1934. Method of Depositing Silica on Material. United States, Patent No. 2.027.931.
- Righini, G.C., Enrichi, E., Zur, L., Ferrari, M., 2019. Rare Earth doped glasses and light managing in solar cells. *Journal of Physics* 1221, 1–5.
- Roldán, M.V., Castro, Y., Pellegri, N., Durán, A., 2015. Enhanced photocatalytic activity of mesoporous SiO₂/TiO₂ sol-gel coating doped with Ag nanoparticles. *Journal of Sol-Gel Science and Technology* 76, 180–194.
- Rosero-Navarro, N.C., Curioni, M., Castro, Y., 2011. Glass-like CexOy sol-gel coatings for corrosion protection of aluminium and magnesium alloys. *Surface & Coatings Technology* 206 (2–3), 257–264.
- Rosero-Navarro, N.C., Pellice, S., Castro, Y., 2009a. Improved corrosion resistance of AA2024 alloys through hybrid organic-inorganic sol-gel coatings produced from sols with controlled polymerization. *Surface & Coatings Technology* 203 (13), 1897–1903.

- Rosero-Navarro, N.C., Figiel, P., Jedrzejewski, R., *et al.*, 2009b. Influence of cerium concentration on the structure and properties of silica-methacrylate sol-gel coatings. *Journal of Sol-Gel Technology* 54, 301–311.
- Roy, R., Osborn, E.F., 1954. The system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. *American Mineralogist* 39, 853–885.
- Russel-Flores, R.S., Harris, B., Cooke, R.G., *et al.*, 1993. Application of sol-gel processing techniques for the manufacture of fiber-reinforced ceramics. *Journal of the American Ceramic Society* 76 (10), 2635–2643.
- Sahu, N., Parija, B., Panigrahi, S., 2009. Fundamental understanding and modeling of spin coating process: A review. *Indian Journal of Physics* 83 (4), 493–502.
- Sakai, S., Ono, T., Iijima, H., Kawakami, K., 2001. Synthesis and transport characterization of alginate/aminopropyl silicate/alginate microcapsule: Application to bioartificial pancreas. *Biomaterials*. 2827–2834.
- Sakka, S., 1990. Sol-gel processing of insulating electroconducting and superconducting fibers. *Physical and Chemical Properties of Shaped Materials: (e) Fibers* 121, 417–423.
- Sakka, S., Kamiya, K., 1982. The sol-gel transition in the hydrolysis of metal alkoxides in relation to the formation of glass fibers and films. *Journal of Non-Crystalline Solids* 48 (1), 31–46.
- Sanchez, C., Rozes, L., Ribot, F., *et al.*, 2010. "Chimie douce": A land of opportunities for the designed construction of functional inorganic and hybrid organic-inorganic nanomaterials. *Compte Rendus Chimie* 13, 3–39.
- Sanchez, C., de A.A. Soler-Illia, G.J., Ribot, F., *et al.*, 2001. Designed hybrid organic-inorganic nanocomposites from functional nanobuilding blocks. *Chemistry of Materials* 13 (10), 3061–3083.
- Sanchez, C., de A.A. Soler-Illia, G.J., Ribot, F., Grosso, D., 2003. Designing of functional nano-structured materials through the use of controlled hybrid organic-inorganic interfaces. *Compte Rendus Chimie: Nanomaterials and Their Physical Properties* 6, 1131–1151.
- Scherer, W.G., 1992. Recent progress in drying of gels. *Journal of Non-Crystalline Solids* 147, 363–374.
- Schmidt, H., 1984. Organically modified silicates by the sol-gel process. In: *MRS Proceedings*, vol. 32, p. 327. Fraunhofer.
- Schneller, T., Waser, R., Kosec, M., Payne, D. (Eds.), 2013. *Chemical Solution Deposition of Functional Oxide Thin Films*. Springer.
- Schroeder, H., 1969. Oxide layers deposited from organic solutions. *Physics of Thin Films* 5, 87–141.
- Scriven, L.E., 1988. Physics and applications of dip coating and spin coating. *Materials Research Society Proceedings* 121, 717–729.
- Sepulveda, P., Jones, J.R., Hench, L.L., 2001. Characterization of Melt Derived 45S5 and sol-gel-derived 58S Bioactive Glasses. *Journal of Biomedical Materials Research* 58 (6), 734–740.
- Shajesh, P., Smitha, S., Aravind, P.R., Warriar, K.G.K., 2009. Effect of 3-glycidoxipropyltrimethoxysilane precursor on the properties of ambient pressure dried silica aerogels. *Journal of Sol-Gel Science and Technology* 50, 353–358.
- Shane, M., Mecartney, M.L., 1990. Sol-gel synthesis of zirconia barrier coatings. *Journal of Materials Science* 25, 1537–1544.
- Sharma, S.D., Singh, D., Saini, K.K., *et al.*, 2006. Sol-Gel-derived super-hydrophilic nickel doped TiO_2 film as active photo-catalyst. *Applied Catalysis A: General* 314, 40–46.
- Sheffer, M., Groysman, A., Mandlet, D., 2003. Electrodeposition of sol-gel films on Al for corrosion protection. *Corrosion Science* 45, 2893–2904.
- Shi, S., Allonas, X., Crouté-Barghorn, C., Chemtob, A., 2015. Activation of the sol-gel process by visible light-emitting diodes (LEDs) for the synthesis of inorganic films. *New Journal of Chemistry* 39, 5686–5693.
- Soler-Illia, G.J., Innocenzi, P., 2006. Mesoporous hybrid thin films: The physics and chemistry beneath. *Chemistry-A European Journal* 12, 4478–4794.
- Soller-Illia, G.J., Angelomé, P.C., Fuentes, M.C., *et al.*, 2011. Mesoporous hybrid and nanocomposite thin films. A sol-gel toolbox to create nanoconfined systems with localized chemical properties. *Journal of Sol-Gel Science and Technology* 57, 299–312.
- Spirk, S., Findenig, G., Doliska, A., *et al.*, 2013. Chitosan-silane sol-gel hybrid thin films with controllable layer thickness and morphology. *Carbohydrate Polymers*. 285–290.
- Stöber, W., Fink, A., 1968. Controlled growth of monodisperse silica spheres in the micron size range. *Journal of Colloid and Interface Science* 26, 62–69.
- Strawbridge, I., James, P.F., 1986. The factors affecting the thickness of sol-gel derived silica coatings prepared by dipping. *Journal of Non-Crystalline Solids* 86, 381–393.
- Tan, X., Tian, Y., Cai, P., 2005. Glucose biosensor based on glucose oxidase immobilized in sol-gel chitosan/silica hybrid composite film on Prussian blue modified glass carbon electrode. *Analytical and Bioanalytical Chemistry* 381, 500–507.
- Thomas, I.M., 1994. Optical coating fabrication. In: Klein, L.C. (Ed.), *Sol-Gel Optics Processing and Applications*. Livermore, California: Kluwer Academic Publishers, pp. 141–168.
- Van der Biest, O.O., Vandepierre, L.J., 1999. Electrophoretic deposition of materials. *Annual Review of Materials Science* 29, 327–352.
- Vega, A.J., Scherer, G.W., 1989. Study of structural evolution of silica gel using ^1H and ^{29}Si NMR. *Journal of Non-Crystalline Solids* 111, 153–166.
- Villegas Broncano, M.A., Fernandez Navarro, J.M., 1987. Preparacion de vidrios de silicatos alcalinos por el método sol-gel. *Boletín Sociedad Española de Cerámica y Vidrio* 26 (2), 99–108.
- Voevodin, N.N., Grebasch, N.T., Soto, W.S., *et al.*, 2001. An organically modified zirconate film as a corrosion-resistant treatment for aluminium 2004-T3. *Progress in Organic Coatings* 41, 287–293.
- Wallington, S.-A., Labayen, T., Poppe, A., *et al.*, 1997. Sol-gel entrapped materials for optical sensing of solvents and metal ions. *Sensors and Actuators B* 38–39, 48–52.
- Wang, E., Chow, K.-F., Kwan, K., *et al.*, 2003. Fast and long term optical sensors for pH based on sol-gel. *Analytica Chimica Acta* 495, 45–50.
- Wang, Y., Ohwaki, J., 1993. New transparent vitroceraamics codoped with Er^{3+} and Yb^{3+} for efficient frequency upconversion. *Applied Physics Letters* 63, 3268–3270.
- Yanagisawa, T., Shimizu, T., Kuroda, K., Kato, C., 1990. The preparation of Alkyltrimethylammonium-Kanemite complexes and their conversion to microporous materials. *Bulletin of the Chemical Society of Japan* 63 (4), 988–992.
- Yang, T., Liu, J., Zheng, Y., *et al.*, 2013. Facile fabrication of core-shell-structured Ag@carbon and mesoporous yolk-shell-structured Ag@carbon@silica by an extended Stöber method. *Chemistry-A European Journal* 19, 6942–6945.
- Yilmaz, M., Caldiran, Z., Deniz, A.R., *et al.*, 2015. Preparation and characterization of sol-gel derived n-ZnO thin film for Schottky application. *Applied Physics A Materials Science & Processing* 119, 547–552.
- Yin, W., Zhao, L., Zhou, L., *et al.*, 2012. Enhanced red emission from $\text{GdF}_3\text{:Yb}^{3+}$, Er^{3+} upconversion nanocrystals by Li^+ doping and their application for bioimaging. *Chemistry-A European Journal* 18, 9239–9245.
- Zhou, H.Y., Jiang, L.J., Cao, P.P., *et al.*, 2015. Glycerophosphate-based chitosan thermosensitive hydrogels and their biomedical applications. *Carbohydrate Polymers* 117, 524–536.
- Zhou, J., Leão Jr., J.L., Liu, Z., *et al.*, 2018. Impact of lanthanide nanomaterials on photonic devices and smart application. *Small* 14, 1–29.
- Znaldi, L., 2010. Sol-gel deposited ZnO thin films: A review. *Materials Science and Engineering B* 174, 18–30.

Glass-Ceramics and Their Applications

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Introduction

Although glass crystallization has been known for a long time, the use of this phenomenon in a systematic, controlled way for the development of glass-ceramics for industrial applications only began in the 1960s. The glass-ceramics developed over the last 60 years have various useful properties: thermal resistance, transparency, mechanical resistance, bioactivity. The objectives of this chapter are first to give general information about the glass-ceramic process and its advantages over the conventional ceramic process, and then to present applications of some glass-ceramics systems according to their main properties. Note that a given glass-ceramic system often combines multiple attributes, making it useful for various applications. Examples of compositions or trademarks are given where they are significant in their field of application, but it should be noted that many other glass-ceramics exist or are under development.

Glass-ceramics are polycrystalline materials resulting from the controlled crystallization of a glass precursor, also called parent glass. As shown in Fig. 1, the first step of the process is the melting and the shaping of the glass. This step can be achieved by conventional glassmaking techniques such as rolling, pressing or casting, but also by using alternative routes such as sol-gel, CVD (Chemical Vapor Deposition). One or several crystalline phases are subsequently obtained by controlled nucleation and crystallization during the crystallization heat-treatment. Fig. 2 shows the microstructure of the final material which is usually predominantly crystalline, although it may contain a significant volume fraction of residual glass.

The properties of the final glass-ceramic are mainly governed by the properties of the crystalline phases, their volume fractions and their microstructures. However, the amount of residual glass and its properties also play an important role, for example through its influence on the interconnectivity of the crystalline phase. Taking this into account, numerous glass-ceramics exhibit very good mechanical/thermomechanical properties in combination with functional properties (electrical, optical, biological ...).

Among the numerous advantages of the glass-ceramic process over the ceramic powder route, the following can be highlighted:

- (1) Glass-ceramics are generally highly homogeneous and pore free;
- (2) Crystallites can exhibit various morphologies and sizes, allowing for instance nanostructured materials;
- (3) According to the crystallization mechanism, the crystals can be randomly or preferentially orientated in the glass-ceramic and respectively lead to isotropic or anisotropic properties;
- (4) Metastable phases can be produced;
- (5) Glassmaking techniques allow various shapes and large size parts;
- (6) Large size transparent or translucent parts can be produced;
- (7) Tight geometric and dimensional tolerances can be achieved as crystallization usually leads to very low volume variations.

The overwhelming majority of glass-ceramics are made up of oxide compounds produced from silicate parent glasses although phosphate or mixed silicate/phosphate glass-ceramics are also encountered, for example in electrical and biomedical applications. Some systems such as $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (LAS) with β -eucryptite (LiAlSiO_4) or β -spodumene ($\text{LiAlSi}_2\text{O}_6$) crystals and $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (MAS) with cordierite ($\text{Al}_4\text{Mg}_2\text{Si}_5\text{O}_{18}$) crystals are widely used, mainly for their superior thermomechanical properties.

Microstructure and Synthesis

Most of the applications of the glass-ceramics require homogeneous and isotropic microstructures. Growth of crystals is schematized in Fig. 3(a), and must take place on nuclei well dispersed in the whole volume of the parent glass. In some rarer cases, the targeted properties can only be obtained through a highly preferential orientation of the crystals. This can be achieved by promoting a surface nucleation, and subsequently the propagation of a crystallization front from the surface into the bulk as shown in Fig. 3(b).

Although occurring for some glass compositions, resulting in formation of $\text{Li}_2\text{Si}_2\text{O}_5$, BaSi_2O_5 or $\text{Si}_2\text{P}_2\text{O}_7$ crystals, spontaneous bulk (volume) homogeneous nucleation is rare and surface nucleation at lower energy sites is the rule. However, heterogeneous bulk nucleation can be induced by adding nucleation agents, either oxides such as TiO_2 (rutile or anatase), ZrO_2 , ZrTiO_4 and Cr_2O_3 or noble metals such as Au or Ag, in the parent glass composition. These compounds produce a phase separation in the parent glass that initiates the nucleation.

Theory of nucleation and crystallization in glass-ceramics has been widely investigated (James, 1989; Müller *et al.*, 2000). However, application of models to practical cases is rather complex. Basically, the nucleation rate I is a function of the temperature T that goes through a maximum at temperature T_n usually around a hundred degrees above the glass transition temperature T_g of the parent glass. Once nuclei are formed in the glass, crystallization results from the epitaxial growth of the crystalline phase. Growth rate J is related to the transfer equilibrium of new atoms at the surface of the crystal. Growth rate also goes through a

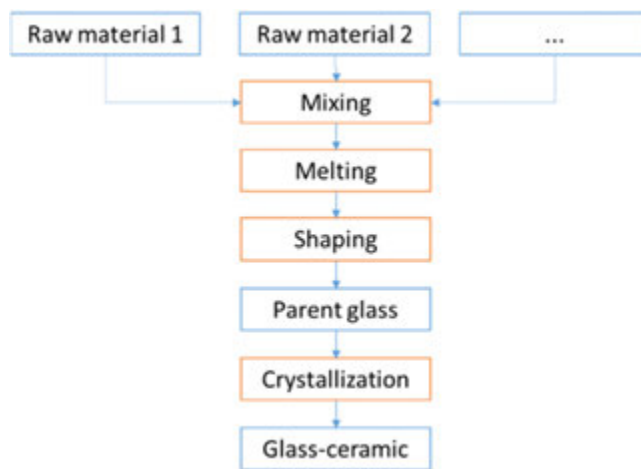


Fig. 1 Process flowsheet usually followed to manufacture glass-ceramics.

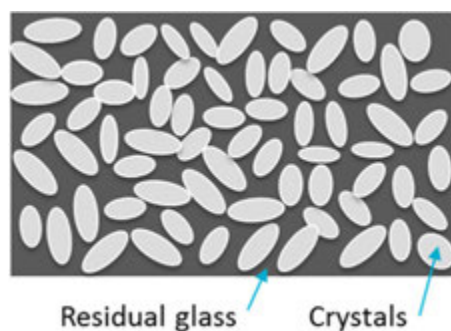


Fig. 2 Schematic representation of the microstructure of a glass-ceramic.

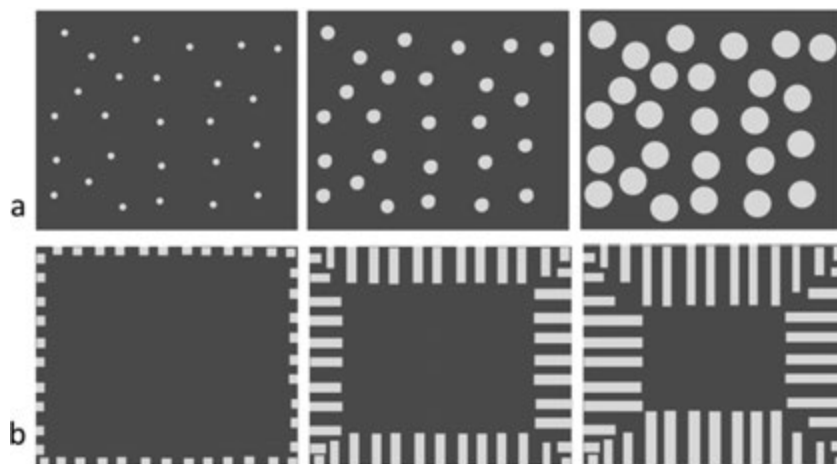


Fig. 3 Schematic representation of nucleation and crystal growth. Volume (a) and surface (b) mechanisms.

maximum at a temperature T_c higher than T_n . **Fig. 4** exhibits the nucleation and growth rates over temperature. The temperature dependent characteristics of the parent glass that strongly influence the nucleation and growth rates of the crystals are the viscosity η and the surface tension σ . A lower viscosity η increases the atomic diffusion from the parent glass to the crystals, while the reaction rate between the atoms and the crystal surface is governed by the surface tension σ .

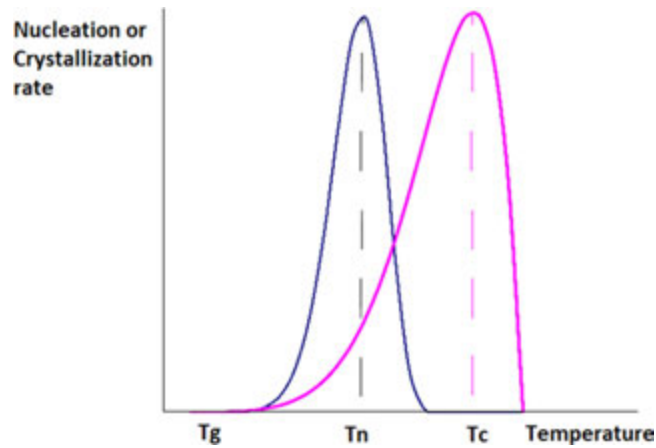


Fig. 4 Schematic illustration of the variation of nucleation rate and growth rate with temperature.

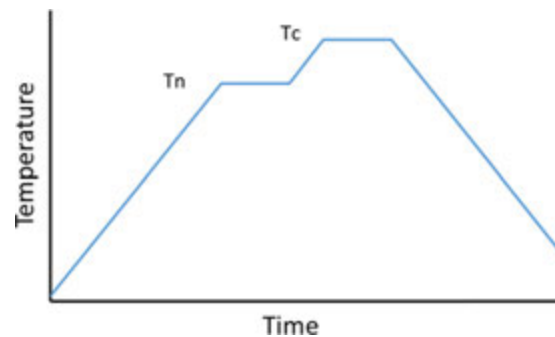


Fig. 5 Schematic illustration of the temperature profile of a 2-stage crystallization heat-treatment.

Key Points of the Process

The crystalline phases formed during the crystallization treatment, their volume fractions, and their microstructure are dependent on the parent glass composition and the heat treatment conditions. Consequently, the requirements to process a glass-ceramic are that the elements of the targeted crystalline phases must be compatible with a low enough melting temperature of the glass and that it does not crystallize in the temperature range required for the shaping step. Subsequently, if the difference between T_n and T_c is high enough, a control of the microstructure through nucleation and growth is possible by a two-stage heat treatment as illustrated in [Fig. 5](#).

In most cases, the density of the crystals formed is higher than that of the parent glass. Conversely, the density of the residual glass is usually lower. As a result, the difference in density between the parent glass and the final glass-ceramic, and consequently the dimensional variations during crystallization, are weak. It should be noted that as crystallization is operated at a temperature significantly higher than T_g , the internal stresses that may result from these volume changes are rapidly relaxed. However, a low viscosity as a result of a high temperature can lead to geometric distortion. Consequently, the viscosity of the parent glass at the crystallization temperature must be kept between 10^9 and 10^{11} Pa s to allow stress relaxation but prevent sagging. Distortions can also result from temperature gradients leading to a non-homogeneous crystallization. As crystallization is an exothermal reaction, this problem is exacerbated for large size parts of low thermal conductivity. It is also important to emphasize that, due to the difference of thermal expansion between the different phases composing the glass-ceramic, internal stresses are created when cooling below T_g (i.e., in the elastic domain) after the crystallization treatment. Even if in some cases these stresses may lead to the reinforcement of the material, they may also affect the performance, as for example the thermal fatigue resistance.

For some applications requiring specific geometries, such as dielectric multilayer substrates for instance, shaping cannot be realized by glassmaking techniques at the initial stage of the parent glass. This is also the case for glass compositions showing a risk of uncontrolled crystallization during cooling. In those cases, the ceramic powder process, from a parent glass powder (i.e., pressing, casting..., and subsequent sintering), is used. Note that by this processing route, the glass powder is sometimes mixed with ceramic powders to form a “composite” material.

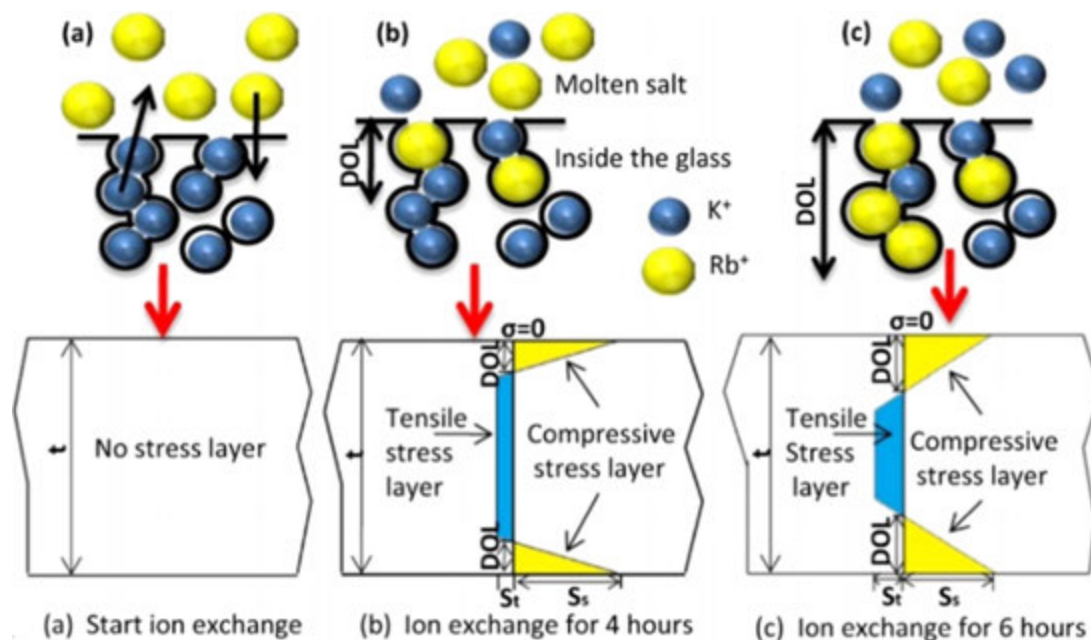


Fig. 6 Mechanism of chemical strengthening by ion exchange in RbNO_3 salt. Reproduced from Shan, Z., Liu, J., Liu, M., *et al.*, 2018. Surface strengthening of lithium disilicate glass-ceramic by ion-exchange using Rb, Cs nitrates. *Ceramics International* 44, 12466–12471.

Applications of Glass-Ceramics Exploiting Thermomechanical Properties

The good thermomechanical properties and the low cost of glass-ceramics make them very useful for a large range of applications. Missile nose cones, called radomes, were the very first application of glass-ceramics, before kitchenware (Suzdal'tsev *et al.*, 2010). Pyroceram® (Corning) was used for its thermal shock resistance and erosion resistance, years before it arrived on kitchen shelves. In the context of the Cold War, the USSR developed some glass-ceramics such as AS-418 and AS-370. Note that glass-ceramics are sometimes referred to as "sitalls" in papers from former Soviet Union countries.

Thermal-Shock Resistance

Some glass-ceramics systems are characterized by low thermal expansion coefficients that, associated with a rather good mechanical strength, provide a high resistance to thermal shock. This property combined with good transparency, is the origin of the commercial success of glass-ceramics in the field of inexpensive kitchen utensils and cookware (Bach and Krause, 2005). The first commercial product was called Pyroceram® 9608 (Corning), with a thermal expansion of $0.7 \times 10^{-6} \text{K}^{-1}$, and that mainly contained β -spodumene solid solutions ($\text{LiAlSi}_2\text{O}_6 - \text{SiO}_2$) with rutile (TiO_2) as minor phase (added as nucleating agent). Since then, other materials containing β -spodumene have been developed such as Cer-Vit™ (Owens-Illinois), Hercuvit™ (PPG), or Neoceram™ N-11 (Nippon Electric Glass). All these materials are white. Glass-ceramics containing β -quartz solid solutions are suitable for transparent products. Several compositions of this type of glass-ceramic have been developed, such as Vision® (Corning), Ceran® (Schott), Neoceram™ N-0 (Nippon Electric Glass), or Kerablack® (Eurokera). These materials are still used in everyday life, especially in cooktops.

High Mechanical Properties

High strength and high toughness glass-ceramics are obtained by crystallization of a glass that leads to particular microstructures made of interlocking crystals. This is the case with crystallization of enstatite (MgSiO_3), potassium fluorrichterite ($\text{KNaCaMg}_5\text{Si}_8\text{O}_{22}\text{F}_2$), and fluorcanasite ($\text{K}_2\text{Na}_4\text{Ca}_5\text{Si}_{12}\text{O}_{30}\text{F}_4$) that leads to high flexural strength ($> 200 \text{ MPa}$) and high fracture toughness ($> 3 \text{ MPa m}^{1/2}$) (Beall, 1991; Mirsaneeh *et al.*, 2006). Lithium disilicate and miserite glass-ceramics are also very strong (Pinckney *et al.*, 1999). All of these glass-ceramics are extensively used for medical applications.

High strength glass-ceramics were also developed by using the ion exchange technique (Beall *et al.*, 2016). This method consists in the exchange of alkali ions (of the residual glass or crystal phase) by larger ones by soaking the material in a bath of molten salt. As shown in Fig. 6, it results in a compressive stress layer at the surface and a stress profile over depth, which increases the strength. The $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system in Li_2SO_4 bath (Mg^{2+} exchanged by 2Li^+) was experimented first and led to an increase of the fracture strength of around 300 MPa (Beall *et al.*, 1967). The $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Li}_2\text{O}$ system is also used by exchanging Li^+ ions for

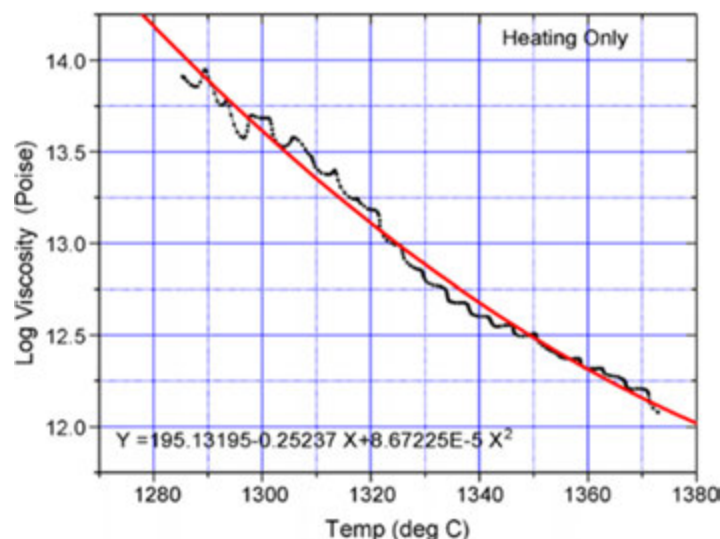


Fig. 7 Beam-bending viscosity vs. temperature of a Sr-feldspar glass-ceramic. Reproduced from Beall, G.H., 2009. Refractory glass-ceramics based on alkaline earth aluminosilicates. *Journal of the European Ceramic Society* 29, 1211–1219.

Na^+ or K^+ (Takeuchi *et al.*, 1997). This strengthening process is still under investigation for more complex systems (Beall *et al.*, 2016; Fischer *et al.*, 2008; Ponsot *et al.*, 2014).

Some high strength and high toughness glass-ceramics are developed for armor applications such as bulletproof vests and vehicle protection. Transparent materials such as Transarm® (Alstom) and Resistan® (Schott) are also developed for armored windows. Due to the military use of these material, compositions are usually not disclosed, but many systems are used such as $\text{Li}_2\text{O}-\text{SiO}_2$, $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$, $\text{Li}_2\text{O}-\text{ZnO}-\text{SiO}_2$ and more (Benítez *et al.*, 2017).

The crystallization of a layer at the surface of a glass is investigated as an alternative to heat or chemical strengthening of a glass. The surface then shows a lower expansion coefficient than the glass, so the surface layer is under compressive stress after cooling. Glass-ceramics from the $\text{SiO}_2-\text{Al}_2\text{O}_3-\text{Li}_2\text{O}$ system were successfully surface reinforced by surface crystallizing β -eucryptite and β -spodumene (Priller *et al.*, 1996). The $\text{SiO}_2-\text{Al}_2\text{O}_3-\text{ZnO}$ system is also of interest (Bocker *et al.*, 2017). Other more complex systems are under investigation (Teixeira *et al.*, 2019).

Very High Temperature Use

Applications of glass-ceramics are usually limited to temperatures below 1000°C due to the decrease of their mechanical properties as a result of the decrease of the residual glass viscosity, or because of thermal decomposition, or both. This deterioration is unavoidable, but a glass-ceramic containing strontium and barium feldspar crystals of the celsian type showed no deformation up to 1450°C as shown in Fig. 7 (Beall, 2009). Its linear thermal expansion is about $4 \times 10^{-6}\text{K}^{-1}$ and its parent glass melts at 1650°C . Mullite glass-ceramics containing a high level of excess silica can be used at 1550°C without deformation but the parent glass melting point reaches 1750°C .

Specific Uses

Glass-ceramics with a near zero coefficient of thermal expansion are used for very specific applications. Zerodur® (Corning) is extensively used in telescope mirrors thanks to its very high homogeneity regarding its thermal expansion and its very low level of bubbles (Döhning *et al.*, 2008; Jedamzik *et al.*, 2006). It was characterized for use as mirror blanks in extremely large telescopes with diameter superior to 30 m (Döhning *et al.*, 2006). Fig. 8 shows the Zerodur mirror developed for the Extremely Large Telescope. Astrosital® (LZOS - Lytkarino Optical Glass Plant) is also used for telescope mirrors. Glass-ceramics with specific thermal expansion are used in reflectors and gyroscopes (Covino and Bennett, 1986).

Glass-Ceramics for Bonding and Sealing

Glass-Ceramic-to-Metal Bonding

Glass-to-metal bonds are extensively used in many applications such as lamp bulb seals, but it has limits. Glass-ceramics are more suitable for this purpose because of their higher mechanical properties, better temperature resistance, and tunable thermal



Fig. 8 Secondary mirror for the extremely large telescope made of Zerodur® (Credit to Schott).

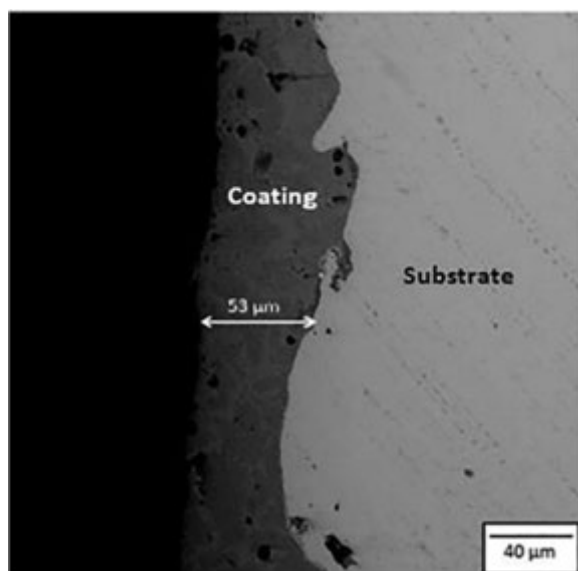


Fig. 9 Cross-section view of glass-ceramic coated Ti6Al4V alloy. Reproduced from Sanyal, S., Shukla, M., Dandapat, N., Ghosh, S., 2018. In vitro evaluation of bioactive glass ceramic coating for application on Ti6Al4V based biomedical implants. *Journal of Non-Crystalline Solids* 500, 22–29.

expansion. To realize such seals, the glass is applied as a slurry and crystallized in an environment that prevents the metal from oxidizing. The glass-ceramics can be used as coatings or as seals between multiple metallic parts.

Fe-based alloys have a wide range of thermal expansion coefficients from 3 to $18 \times 10^{-6} \text{K}^{-1}$ depending on their composition. For mild steel, pre-oxidation leads to the formation of non-stoichiometric FeO that induces a diffusion of Fe^{2+} . This diffusion creates a thermal expansion gradient at the interface which would be beneficial if it were not accompanied by a stress gradient. Atmosphere and processing must therefore be well controlled to form Fe_2O_3 rather than FeO. Glass-ceramics from the $\text{Li}_2\text{O}-\text{ZnO}-\text{SiO}_2$ (LZS) and $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (LAS) are effective sealants for many Fe-based alloys. Precipitated phases such as iron phosphide and chromium silicide tend to form at the interface, but the addition of CuO in the glass suppresses this problem and a clean oxide interface can be formed (Donald *et al.*, 2011).

Titanium and Ti-based alloys are mainly used in the aerospace industry or in orthopedic implants. The thermal expansion coefficient of the most widely used alloy for industrial application Ti6Al4V is $9.4 \times 10^{-6} \text{K}^{-1}$, and pure Ti thermal expansion is $9.2 \times 10^{-6} \text{K}^{-1}$ (Staff *et al.*, 2016). Lithium silicate glass-ceramics are often used to coat Ti dental implants because it is therefore possible to obtain tunable esthetic properties, similar to those of a tooth. They are also used on ceramic dental restorations. For Ti6Al4V alloys, glass-ceramic coatings from the $\text{SiO}_2-\text{CaO}-\text{Na}_2\text{O}-\text{MgO}-\text{P}_2\text{O}_5-\text{K}_2\text{O}$ and $\text{SiO}_2-\text{Al}_2\text{O}_3-\text{CaO}-\text{P}_2\text{O}_5-\text{CaF}_2$ systems were successfully used (Verné *et al.*, 2004; Sanyal *et al.*, 2018). Fig. 9 shows an example of glass-ceramic coating on Ti6Al4V.

Ni-based superalloys are mostly used in high temperature parts of turbine engines because of their good thermomechanical properties and high corrosion resistance. Depending on their composition, they exhibit thermal expansion coefficients from 12 to

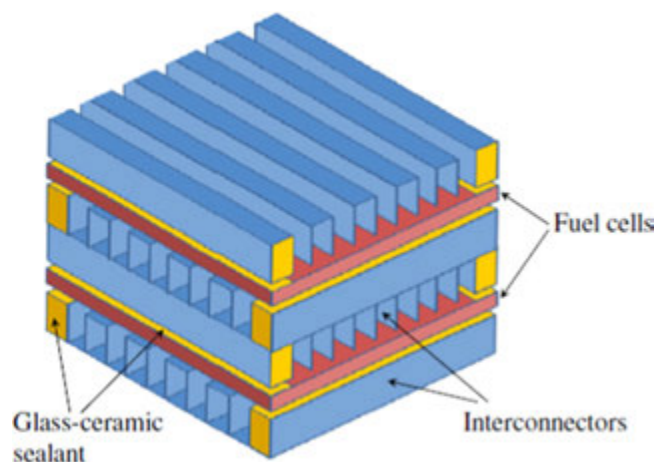


Fig. 10 Example of sealing configuration in planar SOFCs. Reproduced from Tulyaganov, D.U., Reddy, A.A., Kharton, V.V., Ferreira, J.M.F., 2013. Aluminosilicate-based sealants for SOFCs and other electrochemical applications – A brief review. *Journal of Power Sources* 242, 486–502.

$16 \times 10^{-6} \text{K}^{-1}$ (Donald *et al.*, 2011). Lithium silicate glass-ceramic with an addition of 2% ZnO was used to seal Inconel 600, Haynes 230, and Hastelloy C-276. However, the interfaces degrade at 800°C , except for Inconel 600 which deteriorates between 800°C and 900°C (Bengisu *et al.*, 2004). Glass-ceramics from the $\text{ZnO-Al}_2\text{O}_3\text{-SiO}_2$ system can operate up to 1000°C but may be porous, so a mix with BaO-MgO-SiO_2 glass is required to create a fully protective coating (Datta and Das, 2005). BaO-MgO-SiO_2 based glass-ceramics were also used alone as a bonding layer between a Nimonic alloy AE 435 substrate and a 8 wt% Ytria Stabilized Zirconia top coat (Ghosh, 2014).

Sealants in Solid Oxide Fuel Cells

Solid oxide fuel cells (SOFC) are devices producing electricity directly from the oxidation of a fuel. A solid electrolyte (e.g., yttrium-doped zirconia YSZ) is used to carry the oxygen ions from the cathode to the anode. SOFC operate at high temperatures, i.e., from 650 to 1000°C , to allow the electrolyte to reach a sufficiently high ionic conductivity. One advantage of a high working temperature is that expensive catalysts are avoided and consequently the device is not vulnerable to carbon monoxide catalyst poisoning. However, SOFC batteries are composed of multiple interconnected cells joined by hermetic gas sealants that must withstand the working temperatures for long times. Fig. 10 shows the schematic of a planar SOFC.

The material used as SOFC seals must show the following features: chemical stability in oxidizing and reducing atmospheres, chemical compatibility, electrical insulation, high bond strength, hermeticity, long service life when exposed to high temperature and thermal cycles, and a coefficient of thermal expansion from 10 to $12 \times 10^{-6} \text{K}^{-1}$. Glass-ceramics are the most commonly used materials as sealants for SOFC batteries. These glass-ceramics belong to different systems, but their service life in the aggressive environment of the battery remains a problem for long-term operation.

Phosphate glass-ceramics showed volatilization and reaction with the nickel-zirconia cermet anode at operating temperature, along with a decomposition in a humidified fuel atmosphere (Lessing, 2007). Many barium aluminosilicate glass-ceramics react with the interconnect leading to delamination (Tulyaganov *et al.*, 2013). A high boron content forms volatile compounds with water vapor, degrading the seal. However, many of the developed glass-ceramics are boro-silicate based because boron decreases the viscosity, but the boron content is often lowered to reduce the degradation problems. Different boro-silicate based systems were explored over the years such as $\text{MgO-BaO-B}_2\text{O}_3\text{-SiO}_2$ (Rodríguez-López *et al.*, 2016), $\text{MgO-BaO-B}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$, $\text{MgO-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$, $\text{BaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$, $\text{SrO-La}_2\text{O}_3\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$, $\text{BaO-MgO-SrO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$, or $\text{BaO-MgO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ (Lessing, 2007; Ley *et al.*, 1996). Boron-free glass-ceramics were also developed to prevent degradation and therefore create more durable sealants. These later belong to different systems such as $\text{CaO-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ with addition of MgO , La_2O_3 or ZnO (Smeacetto *et al.*, 2010), $\text{Na}_2\text{O-SiO}_2$ with addition of Fe_2O_3 (Lin *et al.*, 2018b), $\text{SrO-La}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ (Jin and Lu, 2010), or $(\text{CaO,MgO,ZnO})\text{-Al}_2\text{O}_3\text{-BaO-SiO}_2$ (Lara *et al.*, 2004). Researches on other battery compounds aim at reducing the operating temperature of SOFCs, which would allow the use of glass-ceramics without any degradation.

Joining for SiC-Based Materials

SiC and SiC-based materials are considered for different high temperature applications, especially in jet engines, reentry vehicles, and fusion and fission reactors thanks to its irradiation stability, chemical inertness, toughness, and high temperature performance. However, complex or large SiC-based parts cannot be manufactured easily, so joining them is mandatory for a larger scale use. Joining of SiC composite parts is difficult because the joint needs to be resistant to fluxes of high energy neutrons and to high

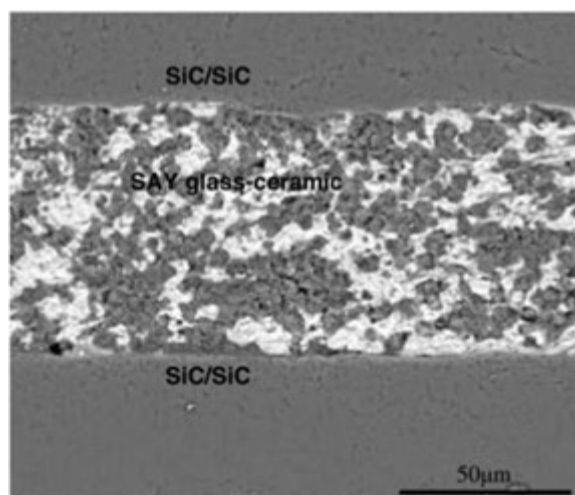


Fig. 11 Micrograph of the cross-section of a SiC/SiC joined SAY glass-ceramic. Reproduced from Ferraris, M., Salvo, M., Casalegno, V., *et al.*, 2008. Joining of machined SiC/SiC composites for thermonuclear fusion reactors. *Journal of Nuclear Materials* 375, 410–415.

temperature gradients. It is possible to produce glass-ceramics with the required properties, and their pressureless joining process makes them advantageous. **Fig. 11** shows an example of glass-ceramic joint between two SiC/SiC composites.

The most explored systems are $\text{CaO-Al}_2\text{O}_3$ (CA) and $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ (SAY). CA glass-ceramics show a high temperature stability with a softening point around 1300°C . SiC/SiC joined with CA were mechanically tested, and a shear strength of 104 ± 25 MPa was measured through torsion tests (Salvo *et al.*, 2013). The microstructure and damaging of CA glass-ceramics were observed after Si-ion irradiation (Casalegno *et al.*, 2018). SiC/SiC joined with a SAY glass-ceramic exhibits a bending strength of 120 MPa at room temperature. Irradiation tests were carried out, and the joint was maintained after irradiations of 16.3×10^{24} n m^{-2} at 600°C and $31\text{--}32 \times 10^{24}$ n m^{-2} at 820°C . Bending tests before and after irradiation proved that the mechanical properties of the joint were not affected (Ferraris *et al.*, 2012). Glass-ceramics containing rare-earth aluminosilicates were also developed using $\text{RE}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ (RE: Nd, Dy, Ho, Y, Yb, or Sc) systems. These were used to join two SiC rods through laser-assisted heating, and 4-point bending strength and He leak-rate tests were realized at room temperature after thermal treatments. Glass-ceramic containing Nd exhibited a high bending strength of 149 MPa, followed by Ho (136 MPa), Y (132 MPa), and Dy (126 MPa). Helium leak rates of about 10^{-10} mbar L s^{-1} are obtained for different thermal treatments depending on the composition, so the joints are gas tight ($< 10^{-8}$) (Herrmann *et al.*, 2017).

Some materials are very promising for SiC and SiC-based materials joining to form complex assemblies, but there is a lack of complete high temperature characterization regarding the mechanical properties, leak rates, and irradiation resistance.

Application of Glass-Ceramics in the Field of Healthcare

Most of the glass-ceramics are biocompatible materials able to be implanted in a living body without poisoning it or being rejected. Some even show bioactive or bioresorbable properties. This means that they integrate a biological process, for instance by forming a biologically active layer on its surface that allows creating bonds with the tissues (El-Meliagy and Van Noort, 2011). These properties allow glass-ceramics to be used for implants.

Bioactive Glass-Ceramics for Implant and Bone Tissue Regeneration

Usual bioactive materials are ceramics (e.g., hydroxyapatite) and glasses (e.g., 45S5 Bioglass®). However, bioceramics are quite complex and expensive to produce and bioactive glasses exhibit low mechanical strength and toughness. Dense bioactive glass-ceramics are easy to synthesize through glassmaking techniques and their mechanical properties are higher than those of glasses. The bioactive glass-ceramics used, or under development, are mainly composed of SiO_2 , P_2O_5 , CaO and MgO with addition of CaF_2 , Na_2O or K_2O (Vitale-Brovarone *et al.*, 2008; Mahato *et al.*, 2017; Kokubo, 1991).

Porous glass-ceramics with complex shapes can also be obtained by powder sintering of a porous green body shaped by techniques such as polymer foam replication, solution combustion, freeze casting or 3D printing (Gerhardt and Boccaccini, 2010). **Fig. 12** shows the porous structure of a glass-ceramic derived from 45S5 Bioglass®.

Some glass-ceramics are currently used for clinical applications. Ceravital® (Ernst Leitz, Wetzlar) was developed in 1973 and was the first glass-ceramic for clinical use. It contains apatite and its composition evolved over time, but its low mechanical properties make it useful only for low load-bearing parts, such as replacement of the ossicular chain in the middle ear. Cerabone® (Nippon Electric Glass) is made of apatite-wollastonite with a very fine microstructure that induces high mechanical

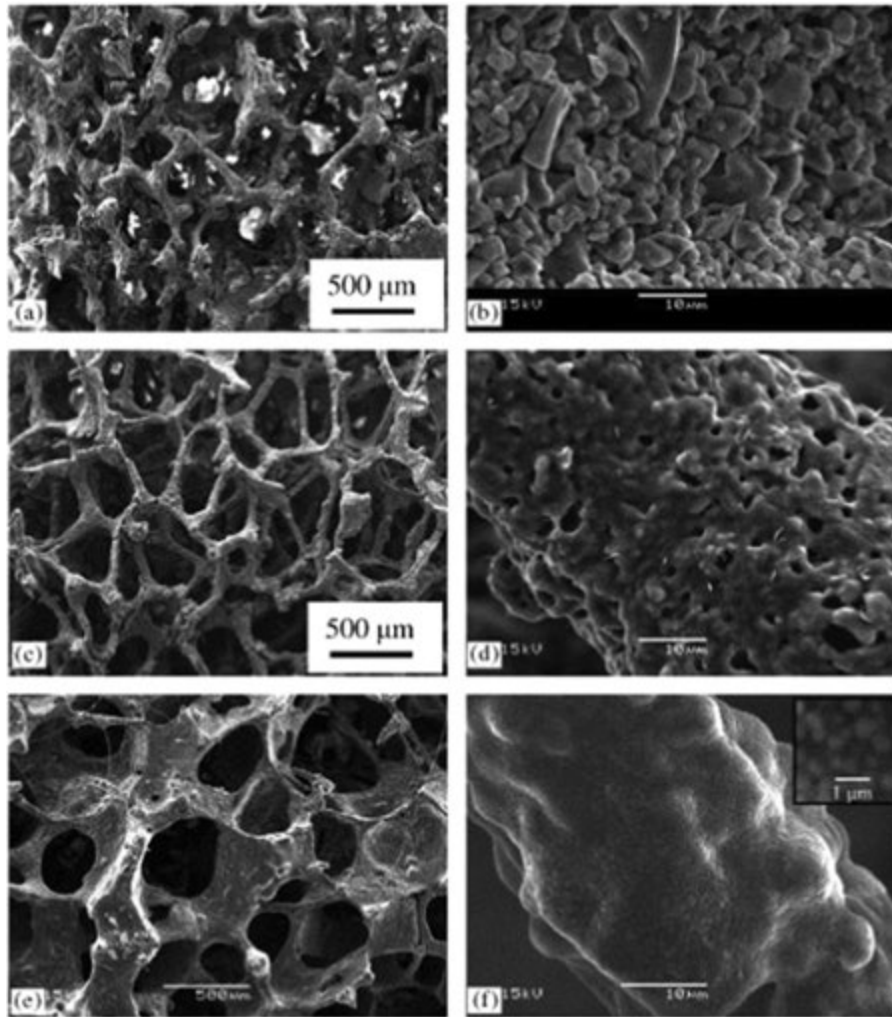


Fig. 12 Pore structure and microstructure of 45S5 Bioglass®-derived foams sintered at (a)–(b) 900°C for 5 h; (c)–(d) 950°C for 2 h; and (e)–(f) 1000°C for 1 h. Reproduced from Chen, Q.Z., Thompson, I.D., Boccaccini, A.R., 2006. 45S5 Bioglass®-derived glass-ceramic scaffolds for bone tissue engineering. *Biomaterials* 27, 2414–2425.

properties and strong bond with bones, leading to its use in reconstructing iliac crests, vertebrae, intervertebral disks, and as filling powder for bone defects (De Aza *et al.*, 2007). Ilmaplant-L1® is an apatite-wollastonite glass-ceramic exclusively used for maxillofacial implants. Bioverit I® and Bioverit II® are glass-ceramics containing apatite and fluorophlogopite mica which are used in orthopedic surgery (e.g., ligament fixation of the knee, tibial plateau, replacement of vertebrae and osteotomy) or head and neck surgery (e.g., rhinoplasty, maintenance of orbit, and reconstruction of skull base, auditory canal, and frontal sinus) (Höland and Vogel, 2013).

Research on the synthesis of new bioactive glass-ceramics coupled with the development of new forming techniques is still abundant to this day. The objectives are to improve the bioactivity, mechanical properties, and formability of glass-ceramics in order to use them for the rapid regeneration of any bone in the human body.

Hyperthermia Treatments of Cancerous Tumors

The amount of blood vessels in tumors is lower than in healthy tissues, so a high temperature (around 43°C) can destroy cancer cells without harming the surrounding tissues, or at least make them more sensitive to other treatments such as chemotherapy or radiotherapy (Abdel-Hameed *et al.*, 2009). Glass-ceramics containing ferrimagnetic particles (usually magnetite Fe_3O_4), which can be heated by induction, are of potential interest for the development of these hyperthermia treatments. Numerous types and compositions of glass-ceramics have been investigated and applied with reference to the treatment of different types of cancer cells. In addition, some of these glass-ceramics are bioactive. In the case of tumorous bone tissue, they can bond to the tissues and increase the recovery after destroying the tumor. As listed in recent reviews (Miola *et al.*, 2018; Lin *et al.*, 2018a), many systems



Fig. 13 Lithium disilicate molar crown milled by CAD/CAM technique. Reproduced from Sadid-Zadeh, R., Kastavochristou, A., Squires, T., Simon, M., 2019. Accuracy of marginal fit and axial wall contour for lithium disilicate crowns fabricated using three digital workflows. *Journal of Prosthetic Dentistry* 123, 121–127.

were explored to improve the magnetic and bioactive properties, such as $\text{Fe}_2\text{O}_3\text{--CaO--SiO}_2\text{--B}_2\text{O}_3\text{--P}_2\text{O}_5$ (Kokubo, 1991), $\text{SiO}_2\text{--Na}_2\text{O--CaO--P}_2\text{O}_5\text{--FeO--Fe}_2\text{O}_3$ (Bretcanu *et al.*, 2006), and $\text{CaO--SiO}_2\text{--P}_2\text{O}_5\text{--Na}_2\text{O--Fe}_2\text{O}_3$ (Singh *et al.*, 2008). In vivo studies remain to be conducted to confirm the potential of use of these materials.

Dental Restoration

Materials used for dental restoration are not implanted, but are bonded to existing teeth. They require high mechanical properties to be as resistant as a natural tooth, good durability in the oral environment and esthetic properties (Denry and Holloway, 2010). Multiple glass-ceramic compositions were synthesized and are now commonly used for inlays, onlays, crowns, and bridges. Glass-ceramic veneers also exist to modify the aspect of the restoration in order to obtain the same color (hue, chroma and value), fluorescence, opalescence, and opacity as the patient's teeth. Veneers can be applied on glass-ceramic or metallic restoration parts (Pini *et al.*, 2012).

The major crystalline phases of the mostly used glass-ceramics for dental restoration are fluoromica (e.g., DICOR®, Corning/Dentsply), leucite (e.g., IPS Empress®, Ivoclar Vivadent), leucite-apatite (e.g., IPS d. SIGN®, Ivoclar Vivadent), lithium disilicate (e.g., IPS e.max® CAD, Ivoclar Vivadent), and sanidine (Vitablocks® Mark II, Vita Zahnfabrik) (Shenoy and Shenoy, 2010; Pröbster *et al.*, 1997; Montazerian and Zanotto, 2017). Specific fluorapatite glass-ceramic veneers exist for lithium disilicate restoration such as IPS e.max® Ceram. Glass-ceramics crystallized from the $\text{Li}_2\text{O--P}_2\text{O}_5\text{--ZrO}_2\text{--SiO}_2$ are used to cover ZrO_2 root posts before applying a glass-ceramic crown (e.g., IPS Empress Cosmo®, Ivoclar Vivadent) (Montazerian and Zanotto, 2017).

Even though glass-ceramics are very useful for dental restoration, only lithium disilicate has a high enough fracture resistance to be used in posterior teeth restoration as in Fig. 13. Other crystalline phases are also under investigation, such as fluorrichterite $\text{KNaCaMg}_5\text{Si}_8\text{O}_{22}\text{F}_2$, fluorcanasite $\text{K}_2\text{Na}_4\text{Ca}_5\text{Si}_{12}\text{O}_{30}\text{F}_4$, and apatite-mullite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2\text{--}3\text{Al}_2\text{O}_3\text{--}2\text{SiO}_2$ (Pollington, 2011). Diopside glass-ceramics are also investigated for ZrO_2 veneering.

Electrical Applications of Glass-Ceramics

Insulators

Withstanding high voltages is an essential requirement for insulators in the field of electrical engineering and solid-state electronics. In addition, a good thermal conductivity, a low thermal expansion, and a thermal stability of the electrical properties is required as significant heating can be produced in high performance electric devices. Dielectric breakdown is related to defects acting as sources of local electrical stress concentration. In conventional ceramic dielectrics, porosity, crystallographic defects, impurities, grain boundaries or interfaces with secondary phases seriously affect their performances. Low porosity and low grain size improve the breakdown resistance. On that point, the advantage of glasses is their high homogeneity and the absence of pores. Thus, their electrical breakdown strength can be an order of magnitude higher than that of the conventional ceramic dielectrics. However, most of the glasses exhibit high dielectric losses. In this regard, glass ceramics from the $\text{MgO--Al}_2\text{O}_3\text{--SiO}_2$ or $\text{ZnO--Al}_2\text{O}_3\text{--SiO}_2$ system exhibit superior performances. Note that recently, low dielectric constant and low dielectric loss micro-nanostructured glass-ceramics, containing albite feldspars ($\text{NaAlSi}_3\text{O}_8$) with very low residual glass volume fractions ($< 6 \text{ vol}\%$), have been obtained by powder fast sintering methods (Fuentes *et al.*, 2018, 2019).

Glass-Ceramics Dielectrics for High Power Capacitors

The development of high energy storage density capacitors (HESDCs) requires materials able to withstand very high electric fields. Indeed, energy density w (J cm^{-3}) increases linearly with the dielectric constant ϵ_r and quadratically with the electrical field E :

$$\omega = \frac{\epsilon_0 \epsilon_r E^2}{2}$$

As previously mentioned, the advantage of glass over ceramics is the higher electrical strength. The drawback is their low dielectric constant. Crystallization of suitable phases in the glass can improve the dielectric constant (Letz *et al.*, 2014). This is for example the case in the $\text{Na}_2\text{O} - \text{PbO} - \text{Nb}_2\text{O}_5 - \text{SiO}_2$ glass system with the crystallization of NaNbO_3 preferentially to $\text{Pb}_2\text{Nb}_2\text{O}_7$ (Jun *et al.*, 2008). Precipitation of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) ferroelectric crystals is also widely investigated (Xiao *et al.*, 2016; Wang *et al.*, 2014). Commercial products such as Schott Poweramic™ are titanate-based glass-ceramics. However, when using the conventional crystallization process, the volume fraction of residual glass is often high and limits the final dielectric constant. Furthermore, due to their strong difference in dielectric constant, the interfaces between the residual glass and the crystals accumulate charges which leads to interfacial polarization (Pan *et al.*, 2006).

Pyroelectric/Piezoelectric Glass-Ceramics

Piezoelectricity results of the lack of a center of symmetry in the material. This excludes glasses and ceramics based on crystalline phases owning a symmetry center. Piezoelectric polycrystalline ceramics are usually ferroelectrics. For these materials, the random orientation of the crystals leads to a center of symmetry that can be broken by alignment of the crystal ferroelectric domains by applying an external electric field. This is not possible with non-ferroelectric phases that require either single crystals or textured polycrystals.

Piezoelectric glass-ceramics based on ferroelectric or non-ferroelectric phases have been investigated for a long time (Halliyal *et al.*, 1989; Davis *et al.*, 2008). Among the main ferroelectric phases crystallized are the perovskites BaTiO_3 , PbTiO_3 , LiNbO_3 , NaNbO_3 , widely encountered in ceramic materials (Wu and Zhu, 1986; Fernandes Graça and Almeida Valente, 2017). Contrary to ferroelectrics, the non-ferroelectric phases are less known and used. This is mainly due to their lower piezoelectric performances and the need to induce a significant preferential orientation of the crystals during the process. The piezoelectric charge coefficient d_{33} of ferroelectrics can reach several hundred pC/N, while non-ferroelectrics usually have a d_{33} around 10 pC/N. However, non-ferroelectric piezoelectrics are good candidates for applications at high temperature as they do not suffer from aging due to slow depoling over time and do not have a Curie temperature. Highly textured lead-free glass-ceramics based on the non-ferroelectric Sr-fresnoite $\text{Sr}_2\text{TiSi}_2\text{O}_8$ crystals can be obtained through surface crystallization (Halliyal *et al.*, 1985; Renoirt *et al.*, 2019).

Thermoelectric Glass-Ceramics

Thermoelectric (TE) materials show Seebeck and Peltier effects and consequently are able to directly convert heat into electrical power and reciprocally. Efficiency of a thermoelectric material is related to its figure of merit ZT given by:

$$ZT = \frac{S^2 T}{\rho \kappa}$$

With S the Seebeck coefficient, T the temperature, κ the thermal conductivity and ρ the electrical resistivity. A good thermoelectric material requires the maximization of the power factor S^2/ρ and the minimization of thermal conductivity κ . Moreover, the conversion efficiency increases with temperature. Conventional thermoelectric materials like Bi_2Te_3 or PbTe are environmentally harmful and use rare elements. In addition, their high-temperature stability is low.

Potential interest of thermoelectric glass-ceramics is based on the fact that the residual glass can hinder the thermal conductivity. However, residual glass volume fraction must be sufficiently low to allow 3D interconnectivity of the TE crystals. In addition, the crystallization process offers the possibility to synthesize nanostructured materials which can also be positive for the material properties. Various systems have been investigated such as the Sr-Ti-Nb-Si-B-O system with $\text{Sr}(\text{Ti,Nb})\text{O}_3$ crystals (Lingner *et al.*, 2013), Te-As-Se-Cu system with $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ (BST) crystals (Cui *et al.*, 2015), or Bi-Sr-Co-O system with $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_x$ crystals (Lingner *et al.*, 2015). Note that to achieve low residual glass fraction and then increase the electric conductivity, glass-ceramics can be prepared by spark plasma sintering (SPS) of a mix of glass powder and high TE phases.

Solid State Electrolytes for Rechargeable Batteries

Glasses and glass-ceramics are good candidates to develop low-cost rechargeable batteries based on safe solid electrolytes (Minami *et al.*, 2006). Glasses are good ionic conductors at high temperature due to the mobility of modifier cations. Conductivity of the cations is a function of the electronic configuration of the ions in the outermost orbital, and the ionic radius. The most favorable ions are Li^+ . Moreover, conductivity in sulfide glasses is higher than in oxide glasses. However, room temperature conductivity of these glasses remains too low to compete with organic electrolyte solutions used today in commercial Li-ion batteries.

Numerous works have highlighted an enhancement of Li^+ conductivity by controlled crystallization of the parent glass in a large range of systems such as $\text{Li}_2\text{S-P}_2\text{S}_5$ (Mizuno *et al.*, 2005; Xu *et al.*, 2016), $\text{Li}_2\text{S-P}_2\text{S}_5\text{-Me}$ ($\text{Me} = \text{SiS}_2, \text{GeS}_2, \text{SnS}_2, \text{Sb}_2\text{S}_3, \text{La}_2\text{S}_3, \dots$) (Liu *et al.*, 2014), $\text{Li}_3\text{BO}_3\text{-Li}_2\text{SO}_4$ (Tatsumisago *et al.*, 2017), or $\text{Li}_2\text{S-P}_2\text{S}_5\text{-X}$ ($\text{X} = \text{LiI}, \text{LiCl}, \text{LiBr}$) (Choi *et al.*, 2018). Room temperature ionic conductivity of the glass-ceramic $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ reaches $1.2 \cdot 10^{-2} \text{ S cm}^{-1}$, which is very close to that of liquid electrolytes (Kamaya *et al.*, 2011).



Fig. 14 Crack deflection by mica crystals in Macor[®] glass-ceramic. Reproduced from Grossman, D.G., 1978. Machining a machinable glass-ceramic. *Vacuum* 28, 55–61.

The use of sodium ions instead of lithium ions presents the advantage of lower cost and better availability of sodium sources. Sulfide glass-ceramics of the $\text{Na}_2\text{S}-\text{P}_2\text{S}_5$ system showing a sodium-ion conductivity of $2 \cdot 10^{-4} \text{ S cm}^{-1}$ at room temperature was achieved by stabilization of cubic Na_3PS_4 crystals with superionic conductivity (Hayashi *et al.*, 2012). As in the case of Li^+ solid electrolytes, a large range of glass compositions are under investigation, as for example $\text{Na}_2\text{S}-\text{P}_2\text{S}_5-\text{GeS}_2$ (Tanibata *et al.*, 2018). However, the conductivities are still two orders of magnitude lower than those of conventional liquid-electrolyte systems.

Note that most of the work published on this topic highlights the strong influence of the processing route on the structure and properties: melt-quenching, high-energy ball milling, solution synthesis method.

Machinable Glass-Ceramics

For some technical applications, it is necessary to obtain a precise shape. Generally, the easiest way to get the desired shape is to create it when the material is in the form of a glass, then to crystallize it into a glass-ceramic. However, if the desired shape is too complex, it may not be possible to obtain it in a glass form. Machinable glass-ceramics have therefore been developed to produce parts with specific and complex architectures. These glass-ceramics can be divided into two main families: mechanically machinable and chemically machinable. Note that some of them are also machinable using a laser.

Mechanical Machining

These glass-ceramics have specific mechanical properties that allow them to be precisely machined using ordinary and inexpensive cutting tools, without cracks or internal stress. As shown in Fig. 14, these glass-ceramics contain mica crystals which induce a house of cards microstructure which creates numerous interfaces acting as barriers for crack propagation. The damage induced by the machining is then confined to the residual glass and allows a tolerance of about $10 \mu\text{m}$. CAD/CAM techniques are mostly used, especially for dental applications (Thompson *et al.*, 1996; Gali, 2018).

MACOR[®] (Corning) contains fluorophlogopite mica crystals $\text{K}_{1-x}\text{Mg}_3\text{Al}_{1-x}\text{Si}_{3+x}\text{O}_{10}\text{F}_2$ and is a very versatile material that has been, and still is, a great commercial success. It is used in medical equipment, aerospace (e.g., retaining rings on doors, windows and hinges of space shuttles), electronic (e.g., high voltage insulators), lasers (e.g., spacers and reflectors), high vacuum (e.g., insulators), welding nozzles, and in the nuclear sector. Photoveel[®] (Sumikin Photon) is used in the electrical industry for its electrical and heat insulation properties. Vitronit[®] (Vitron Spezialwerkstoffe) shows high temperature resistance and electrical insulation capabilities. It is used in many fields such as welding technology and electrical engineering (Höland and Beall, 2012).

DICOR[®] (Corning/Dentsply) contains tetrasilic fluoromica crystals $\text{K}_{1-x}\text{Mg}_{2.5+x/2}\text{Si}_4\text{O}_{10}\text{F}_2$ and is used for dental restoration. It has an appearance and mechanical properties very similar to those of natural human teeth, and ceria is added to induce fluorescence (Li *et al.*, 2014). DICOR[®] is machinable through CAD/CAM. This technique can also be applied for Vitablocs[®] Marks II (Vita Zahnfabrik), IPS Empress[®] CAD (Ivoclar Vivadent) and IPS e.max[®] CAD (Ivoclar Vivadent).

Chemical Machining

Chemically machinable glass-ceramics are made by crystallizing a lithium silicate glass containing small amounts of photosensitizers such as silver and cerium oxide. Thanks to these additions, the glass becomes photosensitive (Borrelli, 2016). After forming the glass, localized UV irradiation is carried out on the areas to be removed as shown in Fig. 15. Note that other irradiation

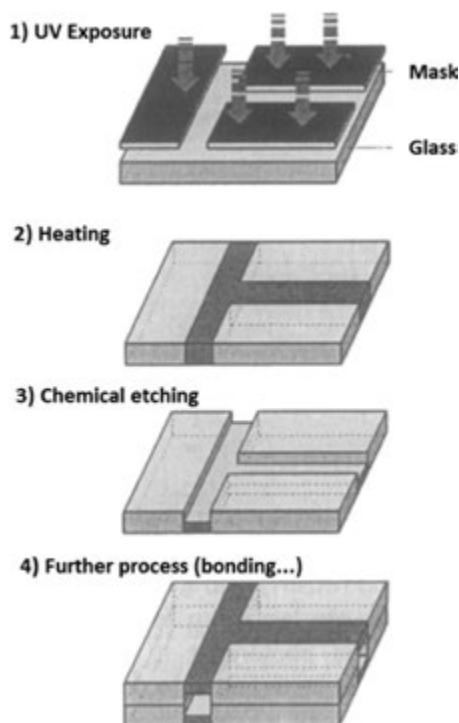


Fig. 15 Etching process of photosensitive glass-ceramic. Reproduced from Dietrich, T.R., Ehrfeld, W., Lacher, M., Krämer, M., Speit, B., 1996. Fabrication technologies for microsystems utilizing photoetchable glass. *Microelectronic Engineering* 30, 497–504.

sources are explored such as X-rays (Imanieh *et al.*, 2008). After crystallization, the previously irradiated areas are chemically unstable due to the formation of Li_2SiO_3 . An etching (usually with HF) eliminates these areas, and a second crystallization creates chemically resistant $\text{Li}_2\text{Si}_2\text{O}_5$ crystals.

These materials are used to manufacture high-precision (μm) components. Fotoceram® (Corning Glass) contains Ce^{3+} as photosensitive ion and Ag^+ as nucleating agent. It is used for many applications including magnetic recording head pads, inkjet printer plates and fluidic devices. Foturan® (Schott) is widely used in microfluidics (e.g., printheads, lab-on-a-chip components), semiconductors (e.g., CMOS and memory modules), sensors, RF-MEMS (e.g., substrates, capacitors, and filters), and telecoms (e.g., optical waveguides). Foturan II® (Schott) allows a finer microstructure thanks to a better homogeneity of the photosensitive particles in the glass. APEX® Glass (3D Glass Solutions) is interesting for wafer-level packaging, RF packages (e.g., inductors and antennas), optoelectronics, and microcavities (Höland and Beall, 2012).

Laser Machining

A lesser known technique is the laser machining of glass-ceramics. It is used for radomes because their mechanical machining and polishing are quite long and expensive steps. Moreover, laser machining does not require the piece to be cooled down. This technique was also used to create blind holes in glass-ceramics used for cooktops (e.g., Ceran Suprema®, Schott) in order to place the temperature sensor as close as possible to the outer surface of the cooktop (Sola *et al.*, 2010). This laser machining does not modify the composition of the heat affected zone but decreases its mechanical properties. The laser machining of bioactive glass-ceramics is also under investigation for medical applications. To date, this shaping technique is rarely used but may be of interest in the implant and dentistry fields.

Glass-Ceramics From Wastes

Given the expansion of industrial activities, the amount of waste produced is constantly increasing. It is therefore necessary to recycle or isolate them. Creating glass-ceramics incorporating these wastes is interesting because the presence of crystals and a glassy phase allow some variations in the waste compositions, as opposed to typical ceramics which are very composition dependent. Two families of wastes must be distinguished: radioactive wastes and hazardous but non-radioactive wastes.

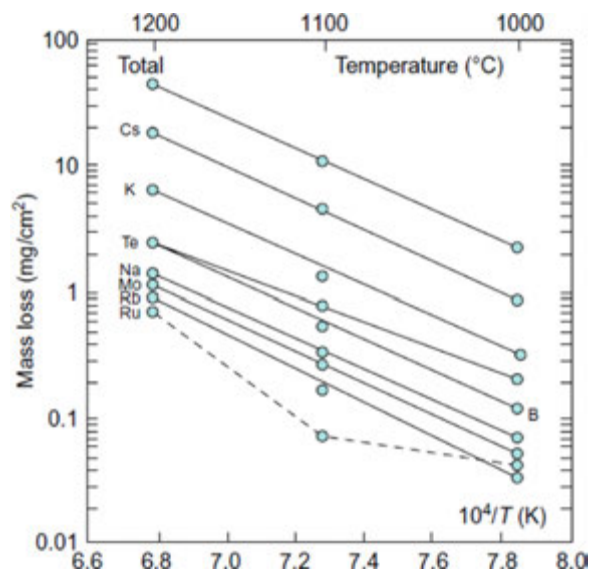


Fig. 16 Volatilization of waste radionuclides with temperature. Reproduced from Ojovan, M.I., Lee, W.E., 2014. *An Introduction to Nuclear Waste Immobilization*, second ed. London: Elsevier.

Radioactive Product Confinement

Radioactive wastes result from the reprocessing of spent nuclear fuels following their use in nuclear reactors and to a lesser extent, from medical and technical use of radioelements. Reprocessing (recovery of uranium and plutonium) releases fission products with a much shorter half-life than uranium, but which remains in the order of several hundred thousand years. They are called high-level wastes (HLW). They must therefore be isolated from the biosphere by incorporating them into durable matrices. Generally, borosilicate glasses are used for this application, but glass-ceramics can also be used and have better properties, especially mechanical properties (Ojovan and Lee, 2014). An important parameter is durability, i.e. the period during which it is possible to contain the radioactive elements without dangerous radiation escaping from the material.

Some of these glass-ceramics are obtained by the conventional processing route (i.e. melting and two step heat treatments for crystallization). This is the case for the following glass-ceramic compounds. The first system studied, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-BaO}$, contains celsian $\text{BaAl}_2\text{Si}_2\text{O}_8$ as main phase along with pyrochlore $\text{RE}_2\text{Ti}_2\text{O}_7$, scheelite BaMoO_4 , pollucite $\text{CsAlSi}_2\text{O}_6$ and molybdenum-nosean $\text{Na}_8\text{Al}_6\text{MoO}_4(\text{SiO}_4)_6$. The $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-BaO}$ system, mainly containing fresnoite $\text{Ba}_2\text{TiSi}_2\text{O}_8$ as well as pyrochlore, scheelite and priderite $\text{BaFe}_2\text{TiO}_6\text{O}_{16}$, was also studied. However, these two systems did not have a higher durability than the glasses used at the time, even though their mechanical properties were higher. The $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-CaO-TiO}_2\text{-SiO}_2$ system led to sphene CaTiSiO_5 glass-ceramics with no or almost no minor phases. Their mechanical properties and durability are high, and losses from volatile species (e.g., Cs, Mo, Na) are lower than those obtained when using borosilicate glasses. Fig. 16 shows the volatilization of main elements during glass melting that can be reduced using certain compounds (e.g., B_2O_3 or TiO_2 for Ce). The $\text{CaO-Al}_2\text{O}_3\text{-TiO}_2\text{-ZrO}_2\text{-SiO}_2$ system leads to crystallization of zirconolite $\text{CaZrTi}_2\text{O}_7$ along with some secondary phases such as pseudobrookite Fe_2TiO_5 , augite $(\text{Ca, Mg, Fe})\text{Si}_2\text{O}_6$ and cheykinite $\text{Ce}_4\text{Fe}_2\text{Ti}_3\text{SiO}_4\text{O}_{22}$. Glass-ceramics obtained from natural basalt were also used for waste immobilization, leading to the formation of many different crystalline phases due to the complex composition of basaltic rocks. These basaltic glass-ceramics can also be produced by crystallization immediately after casting the glass, a process described below that leads to other crystalline phases (Caurant et al., 2009; Donald, 2009).

Another way to synthesize a glass-ceramic is to crystallize it immediately after the melting step without returning to room temperature. This process leads to a lower manufacturing cost as glass-ceramics usually crystallize above 800°C . However, not all glass-ceramics can crystallize this way, as the maximum nucleation and crystallization rates must necessarily overlap (McCloy and Goel, 2017). Materials described hereafter are produced this way. Glass-ceramics based on diopside $\text{CaMgSi}_2\text{O}_6$, also containing powellite CaMoO_4 and perovskite CaTiO_3 , were produced and up to 30 wt% of waste can be incorporated. Their durability is higher than previously mentioned materials, so diopside glass-ceramics were the first candidates for immobilization of HLW. Some other crystalline phases can be obtained through this process using different compositions, such as apatite and powellite (Caurant et al., 2009; Donald, 2009).

Despite all the compositions developed, these glass-ceramics have not yet been implemented on a large scale because borosilicate glass is still preferred as its synthesis is well understood.

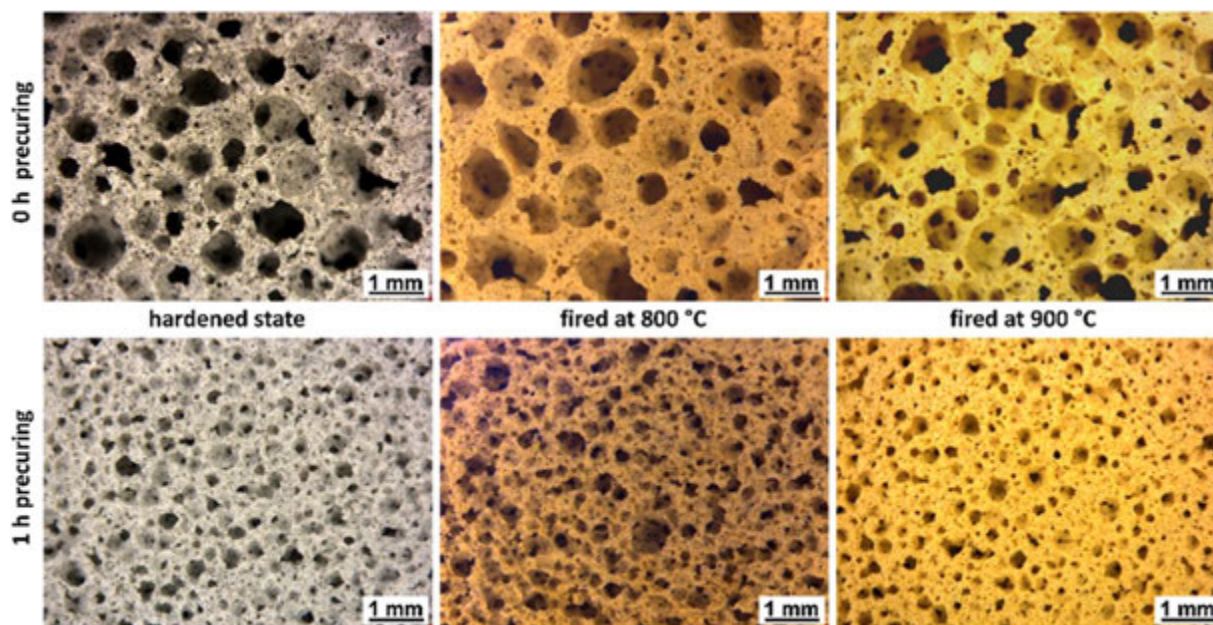


Fig. 17 Microstructural morphology of the VBA foams in the hardened state and after firing treatments (actual colors). Reproduced from Rincón Romero, A., Salvo, M., Bernardo, E., 2018. Up-cycling of vitrified bottom ash from MSWI into glass-ceramic foams by means of “inorganic gel casting” and sinter-crystallization. *Construction and Building Materials* 192, 133–140.

Toxic Wastes Disposal and Recovery

Toxic wastes include slags, ashes, dusts, sludges, incinerated wastes, and other hazardous but non-radioactive products released by various industries. The aim is to incorporate heavy (e.g., Pd, Cd, Hg) and toxic (e.g., As, Sb) metals into durable and if possible functional glass-ceramic matrices (Colombo *et al.*, 2003).

The synthesis of glass-ceramics incorporating slag from metallurgical processes has been extensively studied. At the end of the 1960s, Slagceram (GB) and Slagsital (USSR) were developed from these wastes for applications in the building industry. Many studies have been carried out using different waste compositions, nucleating agents and synthesis processes, leading to many different crystal phases (e.g., melilite, augite, lithium disilicate, diopside and wollastonite) (Rawlings *et al.*, 2006). In the late 1980s, Silceram glass-ceramics were developed and their properties allow their potential use in applications requiring resistance to thermal shock, erosion, impact and abrasion. Glass-ceramic floor tiles were also produced with 30 wt% slags (Dana and Das, 2003).

Coal fly ash is a waste produced when coal is burned to produce energy. Only a small part is used for cement production, so the glass-ceramic production is interesting for its reuse. Addition of CaCO_3 and TiO_2 lead to a glass-ceramic that can be used as a refractory material although its crystallization is long and happens at 1000°C (Cumpston *et al.*, 1992). A very esthetic material with good mechanical properties that looks like dark marble and malachite were proposed for building applications such as benches, walls or floor tiles (Leroy *et al.*, 2001). Glass-ceramics from the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--Li}_2\text{O}$ system were used to incorporate coal bottom ash. It may be used in cooktops, photolithographic processes and substrates for telescopes thanks to its low expansion coefficient. Foams for thermal insulation applications were also developed from coal fly ash and waste glass (Zhu *et al.*, 2016).

Municipal solid wastes are partly recycled, but some of them have to be incinerated, creating energy but also new wastes. Fly ash is recovered by air pollution control systems and contains mainly SiO_2 , CaO and Al_2O_3 . The presence of heavy metals (e.g., As, Hg, Pb, Sb, Sn) and organic pollutants makes isolation necessary (Kalogirou *et al.*, 2010). As glass-ceramics formed from these residues tend to crystallize from the surface, the sinter-crystallization process is mainly used. The main crystalline phases in materials synthesized from these wastes usually are diopside, wollastonite, ferrobustamite ($\text{CaO}_{1-x}\text{FeO}_x\text{SiO}_2$), gehlenite or augite. Glass-ceramics from municipal wastes were developed as promising materials for thermal energy storage for concentrating solar power (Py *et al.*, 2017).

Many other glass-ceramics have been synthesized from other wastes: copper and phosphorus slags, gasification process slags, electric arc furnace dust, cement dust, ore refining waste, fluorescent glass waste, sewage sludge, anodizing waste, hydrometallurgy waste, clay refining waste, and so on. Some foamed glass-ceramics that may be of interest for thermal insulation were also developed as shown in Fig. 17 (Wu *et al.*, 2005; Ding *et al.*, 2015; Xi *et al.*, 2018; Liu *et al.*, 2018).



Fig. 18 Neopariés exterior walls in Getty Center, Los Angeles.

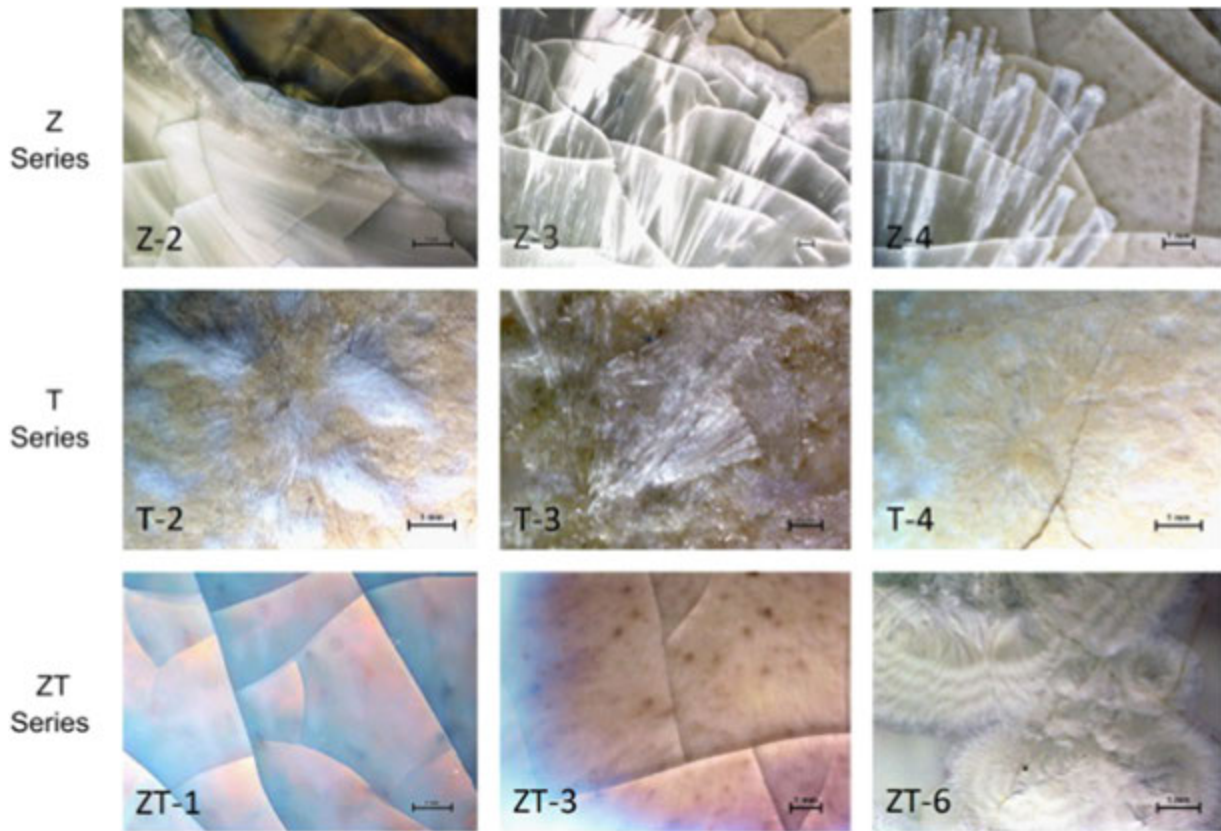


Fig. 19 Glazes crystallized from the $\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system with addition of ZnO (Z series), TiO_2 (T series) and both (ZT series). Reproduced from Pekkan, K., 2015. The thermal and microstructural behavior of a $\text{R}_2\text{O}-\text{RO}-(\text{ZnO})-\text{Al}_2\text{O}_3-(\text{TiO}_2)-\text{SiO}_2$ based macro-crystalline raw glaze system. *Ceramics International* 41, 7881–7889.

Esthetic Materials

Some of the glass-ceramics listed in the previous section on waste recycling have sufficient mechanical properties associated with a good esthetic appearance which allow their use as building materials. Their use has been quite limited so far, which is certainly due to the apprehensiveness of using materials synthesized from hazardous waste, despite their immobilization.

There are also commercial glass-ceramics that combine good mechanical properties with good esthetics. Neopariés® (Nippon Electric Glass) is the most commonly used material, especially for large interior and exterior walls (see Fig. 18). It can be produced

as flat or curved plates, and its color can be easily changed (Marangoni *et al.*, 2017). It contains wollastonite crystals, as well as Cryston® (Asahi Glass) which is used as cladding material. Transparent glass-ceramics containing β -quartz crystals such as Éclair® (Eurokera) and Firelite® (Nippon Electric Glass) are not only used for decoration but also in fire-resistant windows.

A glaze is the application of a glass to the surface of a ceramic object or tile to increase its resistance to the environment or to improve its esthetic properties. This technique has existed since 1000 BCE, so many colors and shades have been developed over time by adding different additives to the glass and by changing the annealing temperatures. However, since the 1990s, higher abrasion resistance, hardness, and chemical resistance have been required. Glass-ceramic glazes (also called crystalline glazes) were then developed to meet these requirements. The crystalline phases most often found in glass-ceramic glazes are zircon (ZrSiO_4), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), wollastonite (CaSiO_3), celsian ($\text{BaAl}_2\text{Si}_2\text{O}_8$), leucite (KAlSi_2O_6), cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) and mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$). High concentrations of TiO_2 and Fe_2O_3 lead to the crystallization of rutile and hematite respectively as they precipitate during cooling of the glass. Small variations of composition can lead to very different visual effects as shown in Fig. 19. Some glass-ceramic glazes also show specific properties, such as photocatalytic activity for self-purification of their environment, aventurine effect caused by macroscopic crystals giving a sparkling effect to the glaze, or metallic aspect without using toxic and heavy compounds (Casasola *et al.*, 2012).

References

- Abdel-Hameed, S.A.M., Hessien, M.M., Azooz, M.A., 2009. Preparation and characterization of some ferromagnetic glass-ceramics contains high quantity of magnetite. *Ceramics International* 35, 1539–1544.
- Bach, H., Krause, D., 2005. *Low Thermal Expansion Glass Ceramics*, second ed. Springer.
- Beall, G.H., 1991. Chain silicate glass-ceramics. *Journal of Non-Crystalline Solids* 129, 163–173.
- Beall, G.H., 2009. Refractory glass-ceramics based on alkaline earth aluminosilicates. *Journal of the European Ceramic Society* 29, 1211–1219.
- Beall, G.H., Karstetter, B.R., Rittler, H.L., 1967. Crystallization and chemical strengthening of stuffed β -quartz glass-ceramics. *Journal of the American Ceramic Society* 50, 181–190.
- Beall, G.H., Comte, M., Dejnek, M.J., *et al.*, 2016. Ion-exchange in glass-ceramics. *Frontiers in Materials* 3, 1–11.
- Bengisu, M., Brow, R.K., White, J.E., 2004. Interfacial reactions between lithium silicate glass-ceramics and Ni-based superalloys and the effect of heat treatment at elevated temperatures. *Journal of Materials Science* 39, 605–618.
- Benitez, T., Gómez, S., Novaes de Oliveira, A., Travitzky, N., Hotza, D., 2017. Transparent ceramic and glass-ceramic materials for armor applications. *Ceramics International* 43.
- Bocker, C., Funke, C., Rüssel, C., 2017. Strengthening of a zinc silicate glass by surface crystallization. *Materials Letters* 207, 41–43.
- Borrelli, N.F., 2016. *Photosensitive Glass and Glass-Ceramics*. Taylor & Francis.
- Bretcanu, O., Verné, E., Cöbisson, M., Tiberto, P., Allia, P., 2006. Temperature effect on the magnetic properties of the coprecipitation derived ferrimagnetic glass-ceramics. *Journal of Magnetism and Magnetic Materials* 300, 412–417.
- Casalegno, V., Kondo, S., Hinoki, T., *et al.*, 2018. $\text{CaO-Al}_2\text{O}_3$ glass-ceramic as a joining material for SiC based components: A microstructural study of the effect of Si-ion irradiation. *Journal of Nuclear Materials* 501, 172–180.
- Casasola, R., Rincón, J.M., Romero, M., 2012. Glass-ceramic glazes for ceramic tiles: A review. *Journal of Materials Science* 47, 553–582.
- Caurant, D., Loiseau, P., Majerus, O., Aubin Chevaldonne, V., Bardez, I., 2009. *Glasses, Glass-Ceramics and Ceramics for Immobilization of Highly Radioactive Nuclear Wastes*. Nova Publishers.
- Choi, S.-J., Lee, S.-H., Ha, Y.-C., *et al.*, 2018. Synthesis and electrochemical characterization of a glass-ceramic $\text{Li}_7\text{P}_2\text{S}_8\text{I}$ solid electrolyte for all-solid-state Li-ion batteries. *Journal of The Electrochemical Society* 165 (5), A957–A962.
- Colombo, P., Brusatin, G., Bernardo, E., Scarinci, G., 2003. Inertization and reuse of waste materials by vitrification and fabrication of glass-based products. *Current Opinion in Solid State and Materials Science* 7, 225–239.
- Covino, J., Bennett, J.M., 1986. *Laser-Gyro Materials Studies*. Naval Weapons Center, China Lake.
- Cui, S., Boussard-Plédel, C., Calvez, L., *et al.*, 2015. Comprehensive study of tellurium based glass ceramics for thermoelectric application. *Advances in Applied Ceramics* 114 (1), 42–47.
- Cumpston, B., Shadman, F., Risbud, S., 1992. Utilization of coal-ash minerals for technological ceramics. *Journal of Materials Science* 27, 1781–1784.
- Dana, K., Das, S.K., 2003. High strength ceramic floor tile compositions containing Indian metallurgical slags. *Journal of Materials Science Letters* 22, 387–389.
- Datta, S., Das, S., 2005. A new high temperature resistant glass-ceramic coating for gas turbine engine components. *Bulletin of Materials Science* 28, 689–696.
- Davis, M.J., Vullo, P., Mitra, I., *et al.*, 2008. Ferroelectric and nonferroelectric (polar) piezoelectric glass-ceramics. *Journal of American Ceramic Society* 91 (9), 2878–2885.
- De Aza, P.N., De Aza, A.H., Pena, P., De Aza, S., 2007. Bioactive glasses and glass-ceramics. *Boletín de la Sociedad Española de Cerámica y Vidrio* 46, 45–55.
- Denry, I., Holloway, J.A., 2010. Ceramics for dental applications: A review. *Materials* 3, 351–368.
- Ding, L., Ning, W., Wang, Q., Shi, D., Luo, L., 2015. Preparation and characterization of glass-ceramic foams from blast furnace slag and waste glass. *Materials Letters* 141, 327–329.
- Döhring, T., Hartmann, P., Jedamzik, R., Thomas, A., Lentz, F.-T., 2006. Properties of Zerodur mirror blanks for extremely large telescopes. In: *Proceedings of the 2nd International Symposium on Advanced Optical Manufacturing and Testing Technologies: Large Mirrors and Telescopes*. Xian, China.
- Donald, I.W., 2009. Immobilization of radioactive materials as a glass-ceramic wasteform. In: Donald, I.W. (Ed.), *Waste Immobilization in Glass and Ceramic Based Hosts: Radioactive, Toxic and Hazardous Wastes*. Wiley.
- Donald, I.W., Mallinson, P.M., Metcalfe, B.L., Gerrard, L.A., Fernie, J.A., 2011. Recent developments in the preparation, characterization and applications of glass- and glass-ceramic-to-metal seals and coatings. *Journal of Materials Science* 46, 1975–2000.
- El-Meliegy, E., Van Noort, R., 2011. *Glasses and Glass Ceramics for Medical Applications*. Sheffield, UK: Springer.
- Fernandes Graça, M.P., Almeida Valente, M., 2017. Ferroelectric glass-ceramics. *Materials Research Society Bulletin* 42 (3), 213–219.
- Ferraris, M., Casalegno, V., Rizzo, S., *et al.*, 2012. Effects of neutron irradiation on glass ceramics as pressure-less joining materials for SiC based components for nuclear applications. *Journal of Nuclear Materials* 429, 166–172.
- Fischer, H., De Souza, R.A., Wätjen, A.M., *et al.*, 2008. Chemical strengthening of a dental lithium disilicate glass-ceramic material. *Journal of Biomedical Materials Research - Part A* 87, 582–587.
- Fuertes, V., Cabrera, M.J., Soares, J., *et al.*, 2018. Hierarchical micro-nanostructured albite-based glass-ceramic for high dielectric strength insulators. *Journal of the European Ceramic Society* 38, 2759–2766.
- Fuertes, V., Cabrera, M.J., Soares, J., *et al.*, 2019. Microstructural study of dielectric breakdown in glass-ceramics insulators. *Journal of the European Ceramic Society* 39, 376–383.

- Gali, S., 2018. Mica glass ceramics for dental restorations. *Materials Technology* 34, 2–11.
- Gerhardt, L.-C., Boccaccini, A.R., 2010. Bioactive glass and glass-ceramic scaffolds for bone tissue engineering. *Materials* 3, 3867–3910.
- Ghosh, S., 2014. Microstructure and mechanical properties of a glass-ceramic bond coated TBC system. *Procedia Materials Science* 6, 425–429.
- Halliyal, A., Bhalla, A.S., Cross, L.E., Newnham, R.E., 1985. Dielectric, piezoelectric and pyroelectric properties of $\text{Sr}_2\text{TiSi}_2\text{O}_8$ polar glass-ceramic: A new polar material. *Journal of Materials Science* 20, 3745–3749.
- Halliyal, A., Bhalla, A.S., Newnham, R.E., Cross, L.E., 1989. Glass–ceramics for piezoelectric and pyroelectric devices. In: Lewis, M.H. (Ed.), *Glasses and Glass-Ceramics*, first ed London: Chapman & Hall, pp. 273–315.
- Hayashi, A., Noi, K., Sakuda, A., Tatsumisago, M., 2012. Superionic glass-ceramic electrolytes for room-temperature rechargeable sodium batteries. *Nature Communication* 3, 856–861.
- Herrmann, M., Ahmad, S., Lippmann, W., Seifert, H.J., Hurtado, A., 2017. Rare earth (RE: Nd, Dy, Ho, Y, Yb, and Sc) aluminosilicates for joining silicon carbide components. *International Journal of Applied Ceramic Technology* 14, 675–691.
- Höland, W., Beall, G.H., 2012. *Glass-Ceramic Technology*, second ed. Wiley.
- Höland, W., Vogel, W., 2013. Machinable and phosphate glass-ceramics. In: Hench, L.L. (Ed.), *An Introduction to Bioceramics*. Imperial College Press, pp. 215–228.
- Imanieh, M.H., Eftekhari Yekta, B., Marghussian, V., Aghaei, A., 2008. Effect of X-ray irradiation on solarization and crystallization of photosensitive glasses containing Ce, Sb, Sn and Ag. *Journal of Non-Crystalline Solids* 354, 3752–3755.
- James, P.F., 1989. Volume nucleation in silicate glasses. In: Lewis, M.H. (Ed.), *Glasses and Glass-Ceramics*, 1st ed London: Chapman & Hall, pp. 59–105.
- Jedamzik, R., Müller, R., Hartmann, P., 2006. Homogeneity of the linear thermal expansion coefficient of ZERODUR® measured with improved accuracy. *Optomechanical Technologies for Astronomy*.
- Jin, T., Lu, K., 2010. Thermal stability of a new solid oxide fuel/electrolyzer cell seal glass. *Journal of Power Sources* 195, 195–203.
- Jun, L., Jun, D., Qun, T., Changhui, M., 2008. Lead sodium niobate glass-ceramic dielectrics and internal electrode structure for high energy storage density capacitors. *IEEE Transactions on Electron Devices* 55, 3549–3554.
- Kalogirou, E., Themelis, N., Samaras, P., Karagiannidis, A., Kontogianni, S., 2010. Fly ash characteristics from waste-to-energy facilities and processes for ash stabilization. In: *Proceedings of the ISWA World Congress 2010*. Hamburg, Germany.
- Kamaya, N., Homma, K., Yamakawa, Y., *et al.*, 2011. A lithium superionic conductor. *Nature Materials* 10, 682–686.
- Kokubo, T., 1991. Bioactive glass ceramics: Properties and applications. *Biomaterials* 12, 155–163.
- Lara, C., Pascual, M.J., Prado, M.O., Durán, A., 2004. Sintering of glasses in the system $\text{RO-Al}_2\text{O}_3\text{-BaO-SiO}_2$ ($\text{R} = \text{Ca, Mg, Zn}$) studied by hot-stage microscopy. *Solid State Ionics* 170, 201–208.
- Leroy, C., Ferro, M.C., Monteiro, R.C.C., Fernandes, M.H.V., 2001. Production of glass-ceramics from coal ashes. *Journal of the European Ceramic Society* 21, 195–202.
- Lessing, P.A., 2007. A review of sealing technologies applicable to solid oxide electrolysis cells. *Journal of Materials Science* 42, 3465–3476.
- Letz, M., Besinger, J., Hovhannisyann, M., *et al.*, 2014. Glass ceramics as dielectrics for high power capacitors. In: *Proceedings of the International Power Modulator and High Voltage Conference*. pp.1 4. IEEE: Santa Fe, USA .
- Ley, K.L., Krumpelt, M., Kumar, R., Meiser, J.H., Bloom, I., 1996. Glass-ceramic sealants for solid oxide fuel cells: Part I. Physical properties. *Journal of Materials Research* 11, 1489–1493.
- Li, R.W.K., Chow, T.W., Matinlinna, J.P., 2014. Ceramic dental biomaterials and CAD/CAM technology: State of the art. *Journal of Prosthodontic Research* 58, 208–216.
- Lin, D., Tan, S., Lin, F., *et al.*, 2018b. Improving the sealing performance of glass-ceramics for SOFCs applications by a unique “composite” approach: A study on $\text{Na}_2\text{O-SiO}_2$ glass-ceramic system. *Journal of the European Ceramic Society* 38, 4488–4494.
- Lin, Y., Mauro, J.C., Kaur, G., 2018a. Bioactive glasses for cancer therapy. In: Gurbinder, K. (Ed.), *Biomedical, Therapeutic and Clinical Applications of Bioactive Glasses*, first ed. Elsevier, pp. 273–312.
- Lingner, J., Letz, M., Jakob, G., 2013. SrTiO_3 glass-ceramics as oxide thermoelectrics. *Journal of Materials Science* 48, 2812–2816.
- Lingner, J., Funahashi, R., Combe, E., Letz, M., Jakob, G., 2015. Thermoelectric sintered glass-ceramics with a $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_x$ phase. *Applied Physic A* 120 (1), 59–66.
- Liu, T., Lin, C., Liu, J., *et al.*, 2018. Phase evolution, pore morphology and microstructure of glass ceramic foams derived from tailings wastes. *Ceramics International* 44, 14393–14400.
- Liu, Z.Q., Tang, Y.F., Lu, X.J., Ren, G.H., Huang, F.Q., 2014. Enhanced ionic conductivity of sulfide-based solid electrolyte by incorporating lanthanum sulfide. *Ceramics International* 40, 15497–15501.
- Mahato, A., Kundu, B., Mukherjee, P., Nandi, S.K., 2017. Applications of different bioactive glass and glass-ceramic materials for osteoconductivity and osteoinductivity. *Transactions of the Indian Ceramic Society* 76, 149–158.
- Marangoni, M., Nait-Ali, B., Smith, D.S., *et al.*, 2017. White sintered glass-ceramic tiles with improved thermal insulation properties for building applications. *Journal of the European Ceramic Society* 37, 1117–1125.
- McCloy, J.S., Goel, A., 2017. Glass-ceramics for nuclear-waste immobilization. *MRS Bulletin* 42, 233–240.
- Minami, T., Hayashi, A., Tatsumisago, M., 2006. Recent progress of glass and glass-ceramics as solid electrolytes for lithium secondary batteries. *Solid State Ionics* 177, 2715–2720.
- Miola, M., Pakzad, Y., Banijamali, S., *et al.*, 2018. Glass-ceramics for cancer treatment: So close, or yet so far? *Acta Biomaterialia* 83, 55–70.
- Mirsaneh, M., Reaney, I.M., James, P.F., Hatton, P.V., 2006. Effect of CaF_2 and CaO substituted for MgO on the phase evolution and mechanical properties of K-fluorrichterite glass ceramics. *Journal of the American Ceramic Society* 89, 587–595.
- Mizuno, F., Hayashi, A., Tadanaga, K., Tatsumisago, M., 2005. New, highly ion-conductive crystals precipitated from $\text{Li}_2\text{S-P}_2\text{S}_5$ glasses. *Advanced Materials* 17, 918–921.
- Montazerian, M., Zanolto, E.D., 2017. Bioactive and inert dental glass-ceramics. *Journal of Biomedical Materials Research - Part A* 105, 619–639.
- Müller, R., Zanolto, E.D., Fokin, V.M., 2000. Surface crystallization of silicate glasses: Nucleation sites and kinetics. *Journal of Non-Crystalline Solids* 274, 208–231.
- Ojovan, M.I., Lee, W.E., 2014. *An Introduction to Nuclear Waste Immobilization*, second ed. London: Elsevier.
- Pan, M.J., Gorzkowski, E.P., Bender, B.A., Wu, C.C., 2006. The effect of interfacial polarization on the energy density of ferroelectric glass-ceramics. In: *Proceedings of the 15th International Symposium on the Applications of Ferroelectrics*. pp. 25–28. IEEE: Sunset Beach, NC, USA.
- Pinckney, L., Beall, G.H., Andrus, R., 1999. Strong sintered miserite glass-ceramics. *Journal of the American Ceramic Society* 82, 2523–2528.
- Pini, N.P., Aguiar, F.H.B., Leite Lima, D.A.N., *et al.*, 2012. Advances in dental veneers: Materials, applications, and techniques. *Clinical, Cosmetic and Investigational Dentistry* 4, 9–16.
- Pollington, S., 2011. Novel glass-ceramics for dental restorations. *Journal of Contemporary Dental Practice* 12, 60–67.
- Ponsot, I., Dal Mas, G., Bernardo, E., Dal Maschio, R., Sglavo, V.M., 2014. Double strengthening by ion exchange of sintered nepheline glass-ceramics: A new simplified method. *Journal of Ceramic Processing Research* 15, 411–417.
- Priller, S., Frischat, G.H., Pye, L.D., 1996. Strengthening of glass through surface crystallization of β -spodumeness. *Journal of Non-Crystalline Solids* 196, 144–149.
- Pröbster, L., Geis-Gerstorf, J., Kirchner, E., Kanjantra, P., 1997. In vitro evaluation of a glass-ceramic restorative material. *Journal of Oral Rehabilitation* 24, 636–645.
- Py, X., Sadiki, N., Olives, R., Goetz, V., Falcoz, Q., 2017. Thermal energy storage for CSP (Concentrating Solar Power). *EPJ Web of Conference* 148.
- Rawlings, R.D., Wu, J.P., Boccaccini, A.R., 2006. Glass-ceramics: their production from wastes – A Review. *Journal of Materials Science* 41, 733–761.
- Renoit, M.-S., Maury, N., Dupla, F., Gonon, M., 2019. Structure and properties of piezoelectric strontium fresnoite glass-ceramics belonging to the Sr-Ti-Si-Al-K-O system. *Ceramics* 2, 86–97.

- Rodríguez-López, S., Haanappel, V.A.C., Durán, A., *et al.*, 2016. Glass-ceramic seals in the system MgO-BaO-B₂O₃-SiO₂ operating under simulated SOFC conditions. *International Journal of Hydrogen Energy* 41, 15335–15345.
- Salvo, M., Casalegno, V., Rizzo, S., *et al.*, 2013. Glasses and glass-ceramics as brazing materials for high-temperature applications. In: Sekulić, D.P. (Ed.), *Advances in Brazing: Science, Technology and Applications*, first ed Woodhead Publishing Limited, pp. 525–544.
- Sanyal, S., Shukla, M., Dandapat, N., Ghosh, S., 2018. In vitro evaluation of bioactive glass ceramic coating for application on Ti6Al4V based biomedical implants. *Journal of Non-Crystalline Solids* 500, 22–29.
- Shenoy, A., Shenoy, N., 2010. Dental ceramics: An update. *Journal of Conservative Dentistry* 13, 195–203.
- Singh, R.K., Kothiyal, G.P., Srinivasan, A., 2008. Magnetic and structural properties of CaO-SiO₂-P₂O₅-Na₂O-Fe₂O₃ glass ceramics. *Journal of Magnetism and Magnetic Materials* 320, 1352–1356.
- Smeacetto, F., Salvo, M., D'Hérin Bytner, F.D., Leone, P., Ferraris, M., 2010. New glass and glass-ceramic sealants for planar solid oxide fuel cells. *Journal of the European Ceramic Society* 30, 933–940.
- Sola, D., Peña, J.I., Buñuel, M.A., 2010. Glass ceramic laser machining for cooktop appliances. *Advanced Materials Research* 83–86, 777–784.
- Staff, M.T., Fernie, J.A., Mallinson, P.M., Whiting, M.J., Yeomans, J.A., 2016. Fabrication of a glass-ceramic-to-metal seal between Ti-6Al-4V and a strontium boroaluminate glass. *International Journal of Applied Ceramic Technology* 13, 956–965.
- Suzdal'tsev, E.I., Kharitonov, D.V., Anashkina, A.A., 2010. Analysis of existing radioparent refractory materials, composites and technology for creating high-speed rocket radomes. Part 3. Manufacturing technology for glass ceramic radomes, problems and future improvement. *Refractories and Industrial Ceramics* 51, 289–294.
- Takeuchi, Y., Mitachi, S., Nagase, R., 1997. High-strength glass-ceramic ferrule for SC-type single-mode optical fiber connector. *IEEE Photonics Technology Letters* 9, 1502–1504.
- Tanibata, N., Noi, K., Hayashi, A., Tatsumisago, M., 2018. Preparation and characterization of Na₃PS₄-Na₄GeS₄ glass and glass-ceramic electrolytes. *Solid State Ionics* 320, 193–198.
- Tatsumisago, M., Takano, R., Nose, M., *et al.*, 2017. Electrical and mechanical properties of glass and glass-ceramic electrolytes in the system Li₃BO₃-Li₂SO₄. *Journal of the Ceramic Society of Japan* 125 (6), 433–437.
- Teixeira, A.H.B., Venturelli, H.H., Montedo, O.R.K., Oliveira, A.P.N., 2019. Strengthened surface crystallized 19.6Li₂O · 11.0ZrO₂ · 69.4SiO₂ and 20.0Li₂O · 6.7ZrO₂ · 68.9SiO₂ · 4.4Al₂O₃ glass-ceramics. *Materials Science and Engineering: A* 751, 62–69.
- Thompson, J.Y., Bayne, S.C., Heymann, H.O., 1996. Mechanical properties of a new mica-based machinable glass ceramic for CAD/CAM restorations. *Journal of Prosthetic Dentistry* 76, 619–623.
- Tulyaganov, D.U., Reddy, A.A., Khariton, V.V., Ferreira, J.M.F., 2013. Aluminosilicate-based sealants for SOFCs and other electrochemical applications – A brief review. *Journal of Power Sources* 242, 486–502.
- Verné, E., Fernández Vallés, C., Vitale-Brovarene, C., Spriano, S., Moisescu, C., 2004. Double-layer glass-ceramic coatings on Ti6Al4V for dental implants. *Journal of the European Ceramic Society* 24, 2699–2705.
- Vitale-Brovarene, C., Verné, E., Robiglio, L., *et al.*, 2008. Biocompatible glass-ceramic materials for bone substitution. *Journal of Materials Science: Materials in Medicine* 19, 471–478.
- Wang, J.W., Tang, L.J., Shen, B., Zhai, J.W., 2014. Property optimization of BST-based composite glass ceramics for energy-storage applications. *Ceramics International* 40 (1), 2261–2266.
- Wu, J.P., Boccaccini, A.R., Lee, P.D., Kershaw, M.J., Rawlings, R.D., 2005. Glass ceramic foams from coal ash and waste glass: production and characterisation. *Advances in Applied Ceramics* 105, 32–39.
- Wu, M., Zhu, P., 1986. Piezoelectricity, pyroelectricity and ferroelectricity in glass-ceramics based on PbTiO₃. *Journal of Non-Crystalline Solids* 84, 344–351.
- Xi, C., Zheng, F., Xu, J., *et al.*, 2018. Preparation of glass-ceramic foams using extracted titanium tailing and glass waste as raw materials. *Construction and Building Materials* 190, 896–909.
- Xiao, S., Xiu, S., Zhang, W., *et al.*, 2016. Effects of Ba_xSr_{1-x}TiO₃ ceramics additives on structure and energy storage properties of Ba_{0.4}Sr_{0.6}TiO₃-BaO-B₂O₃-Al₂O₃-SiO₂ glass-ceramic. *Journal of Alloys and Compounds* 675, 15–21.
- Xu, R.C., Xia, X.H., Yao, Z.J., *et al.*, 2016. Preparation of Li₇P₃S₁₁ glass-ceramic electrolyte by dissolution-evaporation method for all-solid-state lithium ion batteries. *Electrochimica Acta* 219, 235–240.
- Zhu, M., Ji, R., Li, Z., *et al.*, 2016. Preparation of glass ceramic foams for thermal insulation applications from coal fly ash and waste glass. *Construction and Building Materials* 112, 398–405.

Glass Reactive Sintering

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Introduction

Compared to crystalline ceramics, glasses feature a distinctive advantage in the possibility of sintering at just moderately high temperatures (Mackenzie and Shuttleworth, 1949; Prado *et al.*, 2001; Olevsky *et al.*, 2006; Wadsworth *et al.*, 2016). In fact, glass powders may coalesce and form a ‘pyroplastic’ mass once put above the so-called dilatometric softening point, in turn placed slightly above the transition temperature, T_g (Rawson, 1980). At this specific temperature, the thermal expansion of a piece of softened glass is exactly counterbalanced by its contraction – due to viscous flow –, under axial compression, induced by the same dilatometric equipment (in a typical push rod dilatometer, pieces are placed in heated chamber and they are pressed by means of a ceramic connecting rod, which transfers the expansion to a strain gauge; Sighinolfi, 2010; Tian *et al.*, 2013).

It is evident that the dilatometric softening point – corresponding to a viscosity of $10^{11.5}$ Pa s (Rawson, 1980) – actually represents a minimum temperature for glass sintering, that could be adopted in hot pressing operations (Bernardo *et al.*, 2006), where the viscous flow is enhanced by much more intense mechanical load, compared to that operated by a dilatometer. An optimum temperature for pressure-less glass sintering could be estimated as 50–100°C above the dilatometric softening temperature (Ray and Tiwari, 2001), still well below “Littleton” softening point, corresponding to gross viscous flow, for a viscosity of approximately $10^{6.6}$ Pa s (Rawson, 1980). In other words, powder compacts, once fired at the optimum temperature, turn into a nearly pore-free body, with a homogeneous shrinkage. The final component may exhibit an excellent retention of the geometry of the “green” body, except for the size reduction, in case of good initial particle packing and simple shape (for complex three-dimensional features, such as internal voids, cantilevers, overhangs, glass sintering is not actually “pressureless”, since gravity is no longer negligible; Andreev and Zakharov, 2012, 2014). Even very simple shapes are lost in case of “overfiring”, i.e., sintering at excessively high temperatures; glasses with an abrupt reduction of viscosity with increasing temperature (“short” glasses, e.g., featuring a short temperature interval between viscosity values of 10^4 and 10^8 dPa s, as reported by Karamanov *et al.*, 2002), are obviously more delicate.

Contactless optical dilatometers offer a simple way to assess the sintering of ceramic powder compacts, with increasing temperature, according to any firing schedule, without any applied pressure (dimensional changes are detected by means of light beams, detected by high resolution image sensors; Paganelli, 2002; Sighinolfi, 2010); applied to glasses, optical dilatometry provides evidence of the optimum sintering temperature, with shape retention (Karamanov *et al.*, 2013). Interestingly, being contactless, i.e., not interfering with the sintering process, the apparatus gives an excellent representation of some reactions occurring upon viscous flow sintering, e.g., those leading to more or less significant expansion of samples, by gas release, such as “bloating” of traditional ceramics or “foaming” of cellular glasses (Gualtieri, 2007; Teixeira *et al.*, 2017).

The reactions occurring upon glass sintering must be defined carefully. The present paper aims at providing the most important and most recent findings concerning viscous flow sintering of glass accompanied by *reactions with a significant impact on the chemistry and on the phase assemblage* of the resulting glass-based product. The distinction is not trivial, especially in cellular glasses.

Glass foams probably represent the most appreciable evidence of the advantages of glass sintering, at moderate temperatures (850–1000°C), compared to glass melting (>1400°C). In fact, the first procedures for the manufacturing of foams (dating back to nearly one century ago), relying on gas bubbling in molten glass, were successfully replaced by glass sintering with concurrent gas evolution from selected additives (foaming agents), thus offering a fundamental up-cycling option for waste glasses (Scarinci *et al.*, 2005). When operating with fully thermally degradable additives, such as carbon (carbon black, graphite) or organic compounds, the pyroplastic mass of softened glass is expanded by formation of carbon monoxide and/or carbon dioxide, ideally with no impact on glass chemistry. However, the commercial production of glass foams actually involves intensive chemical interaction between glass and foaming agents, since the oxygen used for CO/CO₂ generation does not simply derive from an oxidative atmosphere, but also from the reduction of manganic and ferric oxides dissolved in a specifically formulated glass (in turn mixed with waste glass), for the sake of homogeneity (Scarinci *et al.*, 2005).

In many other cases the foaming agent is not completely degraded, so that residues are incorporated in the pyroplastic mass (e.g., SiO₂ from the oxidation of SiC, CaO from the decomposition of CaCO₃), and they may promote some crystallization (e.g., formation of wollastonite, CaSiO₃, from CaO/glass interaction; Scarinci *et al.*, 2005). To summarize, glass foams, in most cases, are properly products of a glass reactive sintering process; they may be excluded just considering the low *quantity* of interactions, in turn due to the limited amount of additives (typically well below <5 wt%).

Glass-Ceramics From Sinter-Crystallization: What Reaction?

A strict definition of glass-ceramics corresponds to the availability of a homogenous glass, in the form of powders or bulk pieces, in a first step. In a second step, when put above T_g , glass turns into a metastable super-cooled liquid, that may transform in a (at least) partially crystallized solid, by relatively long holding times at temperatures at which nucleation and crystal growth are maximized, before final cooling. The second step is often termed as “ceramization” (Höland and Beall, 2012; Pannhorst, 1997). According to this definition, the so-called ‘petrurgic process’ (applied since the 1970s, e.g., in the so-called “Silceram” ceramics, deriving from molten metallurgical slags; Rawlings *et al.*, 2006), should not be treated as a glass-ceramic manufacturing process, since it consists of the controlled cooling of a silicate melt, typically (but not exclusively) with a long intermediate temperature holding stage, at which crystals nucleate and grow. The process evidently resembles the crystallization of natural rocks (Francis *et al.*, 2002), but it keeps, from glass-ceramics, the idea of fine tuning of microstructures by engineering of heat treatment conditions, particularly the cooling rate (from 1 to 10°C/min).

With the sinter-crystallization process, the transformation of glass into a partially crystallized material, i.e., a *physical* reaction, overlaps with viscous flow sintering. Compared to the processing of bulk glass pieces, sinter-crystallization offers advantages in terms of quality and reduction of overall cost. In fact, any defect in a bulk piece of glass (e.g., gas bubbles from vitrification reactions) remains in the glass-ceramic body, after ceramization, so that high quality, pore-free glass-ceramic articles (like cooking tops, radomes, magnetic disc substrates etc.; Höland and Beall, 2012) are obtained only after high quality glass processing. A long and expensive refining step is required for bulk pieces; powdered glass, on the contrary, is assumed to be pore free. A second occasion of cost saving comes from the simplified ceramization, mostly occurring by a single step treatment at the sintering temperature. A high degree of crystallization may be achieved in very short times, since the surface of glass powders is a preferred site for nucleation, even in the absence of nucleating agents (Müller *et al.*, 2000; Prado and Zanotto, 2002; Francis *et al.*, 2004; Hernández-Crespo *et al.*, 2006). In selected cases (“fast sinter-crystallization”), the holding time may not exceed 30 min, at the end of a very fast heating step (a “direct heating”), e.g., the insertion of glass powder compacts in the furnace directly at the sintering temperature, is also possible, as shown by Bernardo (2008).

Main Fields of Application

In general, there are three fundamental application fields for sinter-crystallization, such as:

- (1) Materials for (bone) tissue engineering.
- (2) Ceramic-metal and ceramic-ceramic joining.
- (3) Waste-derived construction materials.

The following sub-sections will be dedicated to the key aspects of the applications.

Sintered glass-ceramics in biomedical applications

The use of glass-ceramics in bone tissue applications dates back to 1970s. At that time, the huge bioactivity potential of bioglasses, namely Hench’s 45S5 bioglass (nowadays a sort of “golden standard” for bioceramics) had been already disclosed (Piotrowski *et al.*, 1975; Hench, 1977, 2006). An improvement of mechanical properties (i.e., strength, toughness, hardness), generally determined by the transformation of glasses into glass-ceramics, coupled with the bioactivity of silicate and phosphate crystal phases, motivated the research on glass-ceramics, including those from surface crystallization of powdered glass (Gerhardt and Boccaccini, 2010; Montazerian and Zanotto, 2016). The improvement of mechanical properties, compared to parent glasses, is not important just in the perspective of load-bearing implants, but also in terms of easy machinability and workability, particularly appreciated in dental applications (Albakry *et al.*, 2004; Höland *et al.*, 2007; Höland and Rheinberger, 2008).

Kokubo’s apatite-wollastonite and Biosilicate® glass-ceramics are fundamental examples of sinter-crystallized “bio-glass-ceramics”. The first is significant for the attempt to produce a glass-ceramic with a crystal phase (apatite) presenting obvious similarities with the mineral fraction of bone (oxyfluoro-apatite in the glass-ceramic, hydroxyl-apatite in natural bone) and acting as Ca^{2+} reservoir for new bone (Kokubo *et al.*, 1982; Hench and Kokubo, 1998). The second is interesting in highlighting the potential of slight compositional changes, in tuning the crystallization/bioactivity balance, in glasses deriving from 45S5 (Filho *et al.*, 1996; Peitl *et al.*, 2001; Crovace *et al.*, 2016; Pinto *et al.*, 2018).

A quite well recognized drawback of 45S5 concerns the processing. When subjected to viscous flow sintering, it easily undergoes crystallization, with degradation of the bioactivity. Li *et al.* (1992), as an example, showed that the in vitro formation rate of a hydroxycarbonate apatite layer (HCA) on the surface of a 45S5 bioactive glass decreased with increasing crystallization degree. This observation was the starting point for a revision of formulations, in turn leading to “bioglasses resisting crystallization” upon sintering (Souza *et al.*, 2017; Bellucci and Cannillo, 2018; Bellucci *et al.*, 2018), including bioglass 13–93 (Kolan, *et al.*, 2011; Liu *et al.*, 2013; Motealleh *et al.*, 2019), from one hand, and to “bioglasses with enhanced bioactivity after crystallization”, on the other. The second class actually refers to more recent observations, according to which HCA formation could be delayed, but not entirely inhibited, by reducing the amount of residual glassy phase (Moura *et al.*, 2007; Zanotto, 2010). A number of in vitro, in vivo and clinical studies have shown that the osteoconductivity, osteoinductivity, biocompatibility, and antibacterial

properties, exhibited by nearly fully crystallized Biosilicate® glass-ceramics, are comparable to those of amorphous 45S5 (Crovace *et al.*, 2016; Pinto *et al.*, 2018).

45S5 practically turns into Biosilicate® after minor corrections of the proportions between Na₂O, CaO, SiO₂ and P₂O₅ (23.75 wt% Na₂O, 23.75% CaO, 48.5% SiO₂ and 4% P₂O₅ for Biosilicate®, against 24.5 wt% Na₂O, 24.5% CaO, 45% SiO₂ and 6.0% P₂O₅ for 45S5) (Hench, 2006; Granito *et al.*, 2009). Like in Kokubo's glass-ceramics, the crystallization yields a silicate and a phosphate phase (Na₂CaSi₂O₆ and NaCaPO₄); depending on the heat treatment conditions, however, the phosphate phase may be formed (2P variant) or not (1P variant) (Crovace *et al.*, 2016; Pinto *et al.*, 2018).

Several research groups are currently active in the “engineering of crystal phases” of bioactive glass-ceramics. Highly soluble calcium silicates, as an example, may be replaced by calcium-magnesium silicates such as diopside (CaMgSi₂O₆) and akermanite (Ca₂MgSi₂O₇), which dissolve less rapidly in the human body, but exhibit higher strength (Juraski *et al.*, 2017). CEL2 glass-ceramics (belonging to the SiO₂-P₂O₅-CaO-MgO-K₂O-Na₂O system; Vitale-Brovarone *et al.*, 2009) and alkali-free glass-ceramics (based on CaO-MgO-SiO₂-P₂O₅-CaF₂ system; Goel *et al.*, 2011) provide excellent examples.

Some crystal phases exhibit an intrinsic flexibility in hosting several ions, in turn allowing a fine tuning of biological response: Zreiqat and coworkers, as an example, introduced glass-ceramics based on hardystonite - Ca₂ZnSi₂O₇ (Roohani-Esfahani *et al.*, 2013, 2016; Li *et al.*, 2019) -, belonging to the same mineral group (“melilites”) of the previously mentioned akermanite. The crystal structure, comprising of Ca²⁺ ions sandwiched between Zn(Si₂O₇)⁴⁻ sheets, leads to many solid solutions, by replacement of Ca²⁺ (e.g., with Sr²⁺), as well as by modifications in the sheets (e.g., with Mg²⁺ instead of Zn²⁺) (Kaminskii *et al.*, 1986; Giuli *et al.*, 2000; Chihara *et al.*, 2007; Joseph and Sebastian, 2010; Wu *et al.*, 2014; Warren, 2015). Most of hardystonite bioceramics actually derive from the sintering of crystalline powders previously prepared the sol-gel method (Wu *et al.*, 2005, 2008; Wu and Chang, 2013); hardystonite-yielding glasses are typically obtained by deviation from the stoichiometry of the silicate, resulting in the precipitation of a secondary, biologically inert, crystalline phase, such as gahnite (ZnAl₂O₄), according to the presence of Al₂O₃ (Roohani-Esfahani *et al.*, 2013).

Most glass-ceramic systems are exploited for the manufacturing of highly porous scaffolds, according to different fabrication techniques, including replica of sacrificial PU sponges (Baino and Vitale-Brovarone, 2012; Roohani-Esfahani and Zreiqat, 2012; Desimone *et al.*, 2013; Baino and Vitale-Brovarone, 2014), direct foaming of glass suspensions (undergoing progressive gelation, owing to organic or inorganic binders) (Sepulveda and Binner, 1999; Conzenbach *et al.*, 2007) and, more recently, additive manufacturing technologies, such as direct ink writing or “robocasting” (Eqtesadi *et al.*, 2014; Ben-Arfa *et al.*, 2019), powder-based 3D printing and stereolithography, starting from fine powders and sacrificial organic binders (Thavorniyutikarn *et al.*, 2017; Schmidt *et al.*, 2018; Elsayed *et al.*, 2018a, 2019a).

The delicate balance of viscous flow and crystallization acts as further tuning parameter. On the one hand, the viscous flow may determine the filling of voids, left in the struts of open-celled foams from the replica technique, left by the burn-out of the polymer template at the early stages of sintering; dense struts obviously favor the mechanical properties (Vitale-Brovarone *et al.*, 2009). On the other hand, crystallization is useful in “freezing” the viscous flow, so that macro-pores from “primary shaping” (i.e., printing, foaming) are not substantially altered (except for some shrinkage) and they may be accompanied by a multitude of micron-sized pores, from incomplete densification, favouring cell attachment and infiltration of body fluids (Elsayed *et al.*, 2017a).

Fig. 1(a) provides an example of highly porous scaffold (Kelvin cell architecture) from digital light processing of a glass corresponding to the stoichiometry of a Sr-Mg containing hardystonite solid solution (Ca_{1.4}Sr_{0.6}Zn_{0.7}Mg_{0.3}Si₂O₇): the high crystallization tendency of stoichiometric glass (upon firing at 100°C) effectively leads to micro-porous struts (Fig. 1(b)).

Glass-ceramic joints

One of the most interesting applications of sintered glass-ceramics is represented by the use as sealants for the fabrication of solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs), for clean energy production. Sandwiched between the metallic

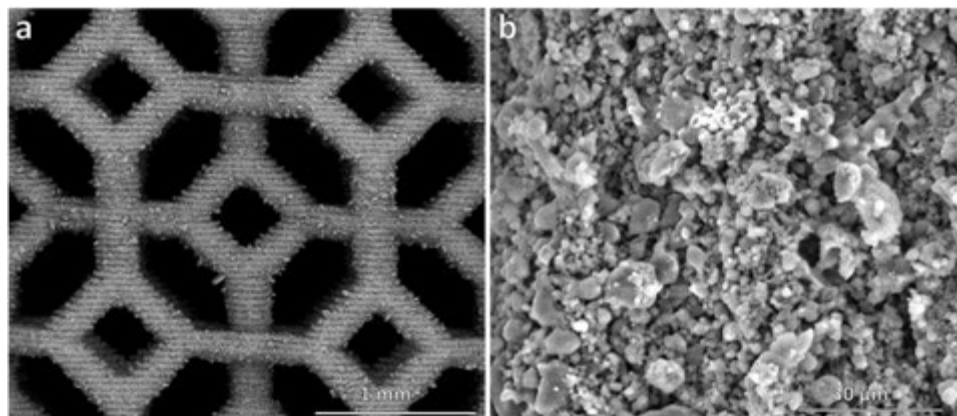


Fig. 1 Low magnification (a) and high magnification (b) details of a glass-ceramic scaffold from digital light processing of a glass based on a Sr-Mg hardystonite solid solution.

interconnect (classically comprising a ferritic stainless steel), and the ceramic electrolyte (typically yttria stabilized zirconia), glass powder densify and from a semi-crystalline continuous joint, by sinter-crystallization (Mahato *et al.*, 2015).

A distinctive character of SOFCs/SOECs is that the thermal treatment used for the manufacturing is not a final step, since the obtained products are employed at high temperatures, typically from 650 to 800°C, under oxidizing and reducing environments. Mechanical degradation, as well as volatilization and diffusion of the components, must be carefully prevented, in order to preserve gas-tightness and high electrical resistivity ($> 10^3 \Omega \text{ m}$), according to Rodríguez-López *et al.*, 2016.

The crystallization during sintering is interesting for achieving strong joints, but it is conditioned by several constraints. In fact, the coefficient of thermal expansion (CTE) of glass-ceramic joint must be quite close to that of adjoining parts, to minimize thermal stresses, upon cyclic operation (Rodríguez-López *et al.*, 2017; Javed *et al.*, 2018). The developed phases should remain stable upon time, to prevent variations in CTE and degradation of the self-healing effect, consisting of the relaxation of stresses operated by the softening of quite abundant residual glass phase. Alkali-containing formulations are undoubtedly interesting for achieving joints with high CTE (above $9 \cdot 10^{-6} \text{ K}^{-1}$), but they are also delicate in terms of excessive electrical conductivity (Chou *et al.*, 2011). Interestingly, the previously mentioned Ca-Mg silicates (namely diopside) are included among the crystal phases in glass-ceramic sealants (Sabato *et al.*, 2019); glass-ceramics from alkali-free formulations, based on Ba and Sr silicates (exhibiting high CTE values), were also proposed (Kaur *et al.*, 2012).

The characteristic ability of softened glass to adhere on oxide and/or oxidized surfaces is at the basis of the development of glass-ceramic joints in other fields, including sodium-based batteries (Song *et al.*, 2011; Smeacetto *et al.*, 2017) and, above all, numerous ceramics, such as SiC, Al_2O_3 and yttria-stabilized zirconia (Smeacetto *et al.*, 2009; Reddy *et al.*, 2013; Zhu *et al.*, 2013; Herrmann *et al.*, 2014; Döhler *et al.*, 2017; Sun *et al.*, 2019; Akram *et al.*, 2019).

Sintered glass-ceramics for building applications

Sinter-crystallization is appreciable also for the special optical properties of some products, which can be used as cladding in the building industry, as a valuable alternative to natural stones, such as marble and granite (Höland and Beall, 2012), starting from the well-known Neoparies[®], produced and marketed by Nippon Electric Glass Co. Ltd since 1970s.

Glass-making and subsequent “ceramization” are obviously expensive, but the manufacturing of glass-ceramics does not compromise natural landscapes (as in the case of quarrying, Pelekasi *et al.*, 2012), with the fundamental advantages of far superior mechanical properties and durability of the products. $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ glasses, even in the absence of conventional volume nucleation agents (such as TiO_2 and ZrO_2), are converted into wollastonite glass-ceramics by sintering of coarse glass granules (1–7 mm) at 950–1000°C (Höland and Beall, 2012). A surface-induced nucleation determines the formation of wollastonite crystals at the boundaries of former glass granules (reshaped and glued by viscous flow), successively growing towards the center (upon heating at 1100°C), in the form of many thin needles. The distinctive marble-like appearance derives from differential light scattering occurring at highly crystallized boundaries and less crystallized cores of former glass granules (Höland and Beall, 2012).

The concept of Neoparies[®] has been a reference for many “waste-derived glasses” (Gutzow *et al.*, 1998). With the specific term we do not refer to glasses which are not usable, fully or partially, in the manufacturing of the original articles (“waste glasses”, mentioned before), but we denote glasses deriving from the dissolution of several inorganic residues (slags, ashes, mining tailings, etc.) in a homogeneous melt, cooled down avoiding crystallization (Rincón Romero *et al.*, 2016). When properly formulated, these glasses offer a complete stabilization of hazardous pollutants, such as heavy metals (Colombo *et al.*, 2003); in some cases, waste stabilization does not depend on the embedding of hazardous ions in the glass structure, but on the thermal destruction (e.g., dismantling of the characteristic, and highly hazardous, fibrous structure of asbestos-containing waste) (Rincón Romero *et al.*, 2016). The high costs of plants and the energy consumption, in waste vitrification, have been compensated, besides by avoided disposal costs, by the extra revenue from glass-ceramic building materials, since the early 1960s, i.e., soon after the discovery of the very first glass-ceramics, by Stookey, in 1953 (Höland and Beall, 2012; Rincón Romero *et al.*, 2016). The manufacturing of glass-ceramics is actually the most established valorization way for inorganic waste, as supported by an extremely vast literature (Colombo *et al.*, 2003; Rawlings *et al.*, 2006; Chinnam *et al.*, 2013; Rincón Romero *et al.*, 2016), and by extensive industrial production, under trade names such as “Slagsittals”, “Slagceram” and the previously cited “Silceram” (Rawlings *et al.*, 2006; Höland and Beall, 2012).

In the specific field of waste-derived glass-ceramics, sinter-crystallization provides valid solutions for usual drawbacks, such as the control of defects and the visual appearance. As previously mentioned, high quality glass-ceramics from bulk crystallization need high quality glass preforms, obtained by means of extensive refining of the glass melt. This operation may be difficult with waste-derived glasses, where heavy metals determine a dark coloration and a consequently poor radiative thermal conduction. Extensive refining, in addition, brings risks of corrosion of refractories in glass tanks and evaporation of some hazardous volatile components (e.g., PbO). The pleasant marble-like appearance of Neoparies[®] is reproduced in waste-derived materials, even at a finer scale, starting from powders $< 100 \mu\text{m}$, leading to nearly pore-free tiles, after uniaxial pressing and firing, needing limited machining (Rincón Romero *et al.*, 2016).

Highly porous construction materials, for thermal and acoustic insulation, deserve a specific discussion. As mentioned in the introduction, glass foams are substantial examples of glass sintering; more precisely, they mostly derive from the coupling of viscous flow and gas evolution, from decomposition or oxidation reaction of selected additives, mixed with glass powders. A significant expansion occurs if the additive is activated at a temperature at which the glass viscosity is a specific range $10^{3.3}\text{--}10^6 \text{ Pa s}$ (Petersen *et al.*, 2017); high viscosities hinder the expansion, whereas low viscosities determine the coarsening and the collapse of the cellular structure (Scarinci *et al.*, 2005). The sudden increase of viscosity operated by crystallization complicate the obtainment

of glass-ceramic foam by direct sintering (Hasheminia *et al.*, 2012); high strength semi-crystalline foams were reported from mixtures of glasses not prone to crystallization (e.g., soda-lime glass) and glasses undergoing crystallization (Bernardo *et al.*, 2010a; Chen *et al.*, 2019), according to a more extensive reactive sintering (discussed in a following section).

The direct foaming of glass aqueous suspensions, mentioned for the production of bioactive glass-ceramic scaffolds, provides a valid alternative, in handling glasses undergoing crystallization without additives. Foamed structures are formed at low temperature, according to intensive mechanical stirring (with the help of surfactants) of suspensions subjected to progressive hardening, before consolidation by sinter-crystallization. Recent investigations have highlighted the hardening of glass suspensions by weak alkali activation, i.e., by formation of surface gels, in turn formed by partial dissolution of glass powders. Highly porous glass-ceramics may reach excellent strength-to-density ratios (strength exceeding 6 MPa, with open porosity of ~80 vol%; Rincon Romero *et al.*, 2018).

Sinter-Crystallization Aided by Chemical Reactions

The sinter-crystallization of waste-derived glasses derives from a quite complicate interaction between viscous flow and crystallization, activated by surfaces but also by specific components, such as iron oxides, acting as nucleating agents. Iron oxides actually configure a condition of “sintering-reaction-crystallization”, since a *chemical* interaction overlaps with viscous flow and crystallization. In fact, magnetite (Fe_3O_4 , or $\text{FeO} \cdot \text{Fe}_2\text{O}_3$), i.e., iron oxide with iron ions in mixed oxidation state ($\text{Fe}^{2+}/\text{Fe}^{3+}$), is a powerful nucleating agent, but its formation from waste-derived glasses depends on vitrification conditions (chemistry of the system controlled *a priori*) and/or sintering conditions, i.e., chemical interaction with the firing atmosphere (chemistry of the system controlled *a posteriori*). On the one hand Karamanov *et al.* (2000) observed that the addition of C (1.5%–2%) to the glass batch promoted the separation of magnetite and enhanced the crystallization, upon sintering. On the other hand, Liu *et al.* (2015) found that iron oxidation, causing an increase of viscosity, reduced the crystal growth of silicates; this fact could be prevented by applying sintering in inert (N_2) or reactive (CO) atmosphere. Bernardo *et al.* (2009a), starting from a glass with a low $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, observed that magnetite was promoted by oxidation, in turn more pronounced for fine ($<40\ \mu\text{m}$) than for coarse glass powders ($<80\ \mu\text{m}$).

The concept of glass sintering with concurrent chemical interaction between softened glass and atmosphere has been exploited beyond waste-derived glasses. Chenu *et al.* (2012, 2016), as an example, presented glass reactive sintering as a tool for the synthesis of NZP glass-ceramics. NZP phases consist a class of fast ion conductors, named after the most representative member, $\text{NaZr}_2(\text{PO}_4)_3$. A number of solid solutions is feasible, according to the many possibilities of ionic substitutions; however, NZP monoliths are hardly achievable by means of solid state sintering, at temperatures exceeding 1000°C . When operating with a sodium phosphate glass, including SnO and WO_3 , NZP phase containing tungsten (IV) and tin (IV), could be achieved by the sintering of powders, at a temperature not exceeding 750°C . In air or oxygen atmosphere, glass particles undergo sintering with concurrent oxidation reaction, in turn triggering the crystallization of the desired NZP phase.

Glass-Ceramics From Extensive Reactive Sintering

In the previous paragraph we discussed cases of limited chemical interactions occurring upon sintering. The sintering of a glass with additives gives excellent opportunities for mixing at a quasi-molecular level; in other words, additives bring oxides that are dissolved in the pyroplastic mass determined by viscous flow sintering, with dramatic effects on phase evolution. In general, additives consist of secondary glasses or reactive oxides, in the form of powders or precursors; in latter case, very recent investigations focused on reactive binders, e.g., additives contributing to both shaping of glass powders and chemistry of the final ceramic, considering the not negligible ceramic residue left upon heat treatment.

Sintered Glass-Ceramics From Mixtures of Glasses

As stated above, sinter-crystallization corresponds to a delicate balance between viscous flow and crystallization. It has been widely shown that a good densification, with remarkable crystallization, may be achieved, from fine glass powders ($<40\ \mu\text{m}$) (Bernardo *et al.*, 2009a), by a single step firing treatment just at the crystallization temperature (inferred from an exothermic peak in the DTA plot), once placed suitably above the dilatometric softening point. With limited gaps between the two temperatures, the sudden enhancement of glass viscosity operated by crystal precipitation complicates the sintering; improvements in the densification may be obtained by forcing the viscous flow, i.e., increasing the firing temperature and/or the heating rate (Bernardo *et al.*, 2009b). An interesting alternative is represented by the mixing of waste-derived glass with waste glass, e.g., material from dismantled containers. A new glass-ceramic, from the simultaneous sintering of two glasses, may be manufactured without correcting the formulation of the waste-derived glass, from industrial plasma vitrification of municipal solid waste incinerator fly ash (Bernardo *et al.*, 2010b).

Soda-lime or pharmaceutical boro-alumino-silicate container glass are poorly sensitive to crystallization, so that they could be introduced, mixed with waste-derived glass, to offer extra softened material, keeping its flowing ability in any stage above T_g , upon firing (unlike softened waste-derived glass, undergoing crystallization). Their role as “sintering aid” for waste-derived glasses,

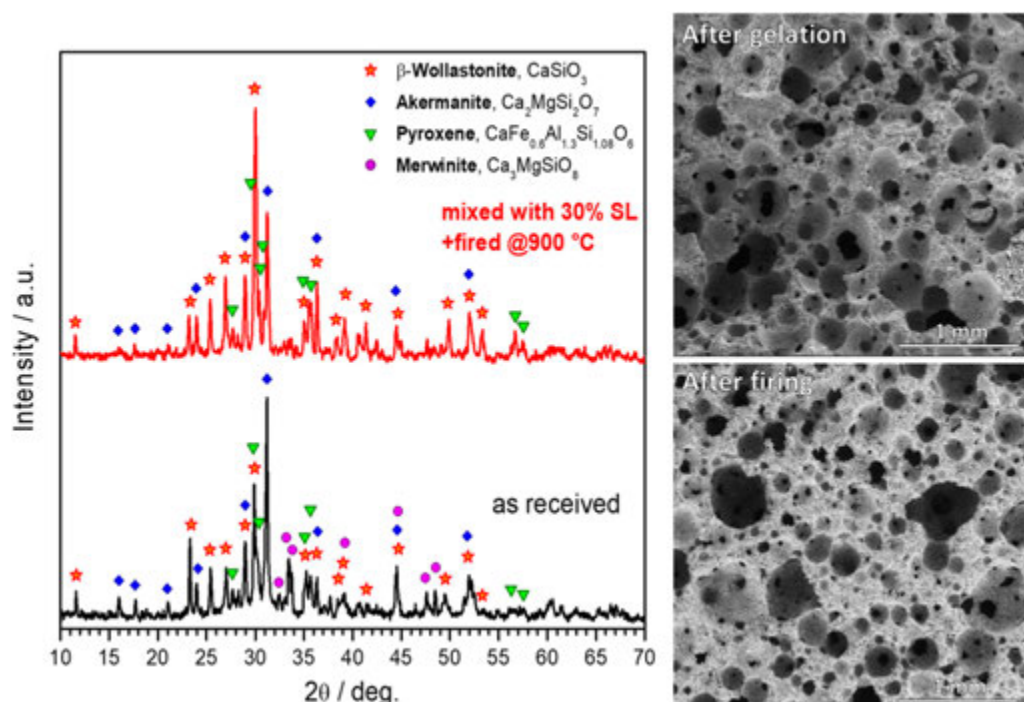


Fig. 2 Obtainment of a highly porous glass-ceramic from a semi-crystallized residue mixed with soda-lime glass.

however, does not simply correspond to the dilution of the material which is more sensitive to crystallization (useful, as previously mentioned, for the manufacturing of semi-crystalline foams). In other words, the softened extra glass does not simply fill the voids left by inadequate sintering of waste-derived glass, but it causes a complex chemical interaction. The phase assemblage is reshaped, as an effect of the ionic interdiffusion at the interface between different glasses: silica-poor crystal phases, such as melilite solid solutions (e.g., gehlenite, $\text{Ca}_2\text{Al}_2\text{SiO}_7$), are replaced by silicates (wollastonite and pyroxene solid solutions) and silica-rich aluminosilicates (e.g., anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$) (Bernardo *et al.*, 2010b).

Since the reshaping of the phase assemblage has consequences on the chemical formulation of the residual glass phase, the addition of a secondary glass may improve the stabilization of pollutants included in waste-derived glasses (Monich *et al.*, 2018). Finally, if we consider the obtainment of porous glass-ceramics from mechanical stirring (“frothing”) of alkali activated suspensions of glass powders, the secondary glass may improve the gelation. Fig. 2(a) shows the microstructure of a foam from a partially crystallized glass-based residue from plasma vitrification of asbestos-containing waste (Europlasma Inertam, Bordeaux, France), combined with soda-lime glass (30 wt%) (Authors’ unpublished results). The addition of soda-lime glass allowed the gelation of a suspension with low alkalinity (1 M NaOH). Fig. 2(b) shows the above-mentioned reshaping of phase assemblage upon sintering at 900°C: akermanite and pyroxene, dominant in the as-received residue, were partially dissolved, with enhanced precipitation of wollastonite.

Direct Sintering of Waste-Derived Glass-Ceramics

Waste glasses (less properly termed “recycled glass”) have a fundamental role in the management of inorganic waste, well beyond their use as sintering aids. In fact, the ultimate strategy for energy and cost savings, in waste vitrification, quite paradoxically consists of avoiding the same process (Rincón Romero *et al.*, 2016). Especially operating with waste with limited hazardousness, the inclusion of pollutants in a chemically stable glass matrix may be performed just letting the waste dissolve, at least partially, in the pyroplastic mass offered by common glasses. This constitutes the basis for the so-called glass-ceramics from “direct sintering” (Rawlings *et al.*, 2006; Valderrama *et al.*, 2019).

The effectiveness of chemical interaction is essential, since it denotes the transition from glass matrix composites, in which oxides remain *physically* dispersed in a glass matrix (e.g., in the case of Al_2O_3 plate-like monocystals, the brittleness of the matrix is reduced owing to crack deflection at glass/reinforcement interfaces; Boccaccini and Trusty, 1996; Boccaccini and Winkler, 2002) and glass-ceramics. Glass-ceramics from direct sintering, although there is no stage in which the starting raw materials are mixed and converted into a homogeneous glass, are generally accepted as a variant of sintered glass-ceramics, owing to the generally observed phase evolution (Rawlings *et al.*, 2006; Rincón Romero *et al.*, 2016; Valderrama *et al.*, 2019). Waste glasses, besides promoting the densification by viscous flow sintering, react with oxides from inorganic waste, leading to silicate and aluminosilicate crystals similar to those developed by glass devitrification.

Direct sintering finds analogies in the processing of traditional porcelain ceramics. In porcelain and in porcelain stoneware some components (feldspar minerals) melt and form a liquid phase (at 1100–1200°C), incorporating residues from the others (quartz and clay minerals). Silica from the transformation of clays and from quartz is dissolved in the liquid provided by feldspars, cooling into a glass phase, in turn hosting mullite crystals, from the same transformation of clays, and un-reacted quartz crystals (Sánchez *et al.*, 2010). In directly-sintered glass-ceramics, waste glasses offer the fluxing action of feldspars at much lower temperature (1000°C) and host crystals, from thermal transformations of inorganic waste (e.g., decomposition of fayalite, Fe_2SiO_4 , in slag from copper metallurgy, as shown by Ponsot *et al.*, 2014) as well as from glass/waste interactions and also from glass/clay interactions (when clay minerals are added as binders in glass/waste mixtures, as reported by Bernardo *et al.*, 2009c).

Low temperature treatments, instead of vitrification, may be useful to stabilize selected pollutants. As an example, F-containing waste (Ponsot *et al.*, 2013), once included in directly sintered glass-ceramics, do not undergo decomposition reactions that would lead to evolution of fluorine. In general, however, directly sintered glass-ceramics evidently lack homogeneity, so that some pollutants may selectively accumulate in regions not completely dissolved in the liquid phase provided by the glass component. In addition, the residual porosity (in the order of 30%–35%) and the water absorption could be far above those of real sinter-crystallized glass-ceramics, natural stones and even traditional ceramics (Rincón Romero *et al.*, 2016; it should be noted that a water absorption above 2% corresponds to products with limited frost resistance, not adequate for many architectonic applications, as reported by Kumar *et al.*, 2001).

Layered glass-ceramics offer an interesting solution for the drawbacks of direct sintering. A single-step treatment causes the simultaneous direct sintering of a base body, formed by a glass/waste mixture, and sinter-crystallization of a glaze; the glaze may derive by itself from glass powders obtained by the vitrification of the same starting glass/waste mixture, added with some additives (e.g., zircon, to achieve a light coloration) (Binhussain *et al.*, 2014; Cetin *et al.*, 2015). The poor properties of the base body are no longer significant, since mechanical strength, color and stabilization of pollutants depend on the much denser glazed side (that to be exposed to the environment), showing negligible water absorption. Strength, color and shrinkage of the glaze can be tuned according to the amount and nature of additives. Vitrification of waste becomes more sustainable, since it is applied only to a limited amount of starting materials, to be exploited for the glaze; the single firing reduces the costs of the deposition of a glaze on a previously sintered base body.

The direct sintering of waste glass/inorganic waste is the reference also for a number of glass-ceramic foams. Inorganic waste partially replace glass powders, to be expanded by the action of foaming additives (such as SiC); reacting with the softened glass, during foaming, they yield a substantial crystallization, in turn enhancing the mechanical properties (Fernandes *et al.*, 2009; Zhu *et al.*, 2016; Zhang *et al.*, 2016; Wang *et al.*, 2018; Xi *et al.*, 2018). Interestingly, some glass-ceramic foams without expensive foaming additives. As an example, iron oxide provided by iron-rich minerals, such as basalt scoria (unemployed volcanic mineral, as shown by Marangoni *et al.*, 2014) and metallurgical slags (e.g., slag from the refining of precious metals, as shown by Ponsot and Bernardo, 2013), contributes both to foaming, by oxygen release, (passing from ferric oxide to ferrous oxide) and to crystallization, by formation of iron-containing silicates.

Direct Sintering of Glass-Ceramics With Engineered Crystal Phases

Besides waste, oxides can be considered pure, or in much simpler mixtures. The reaction between oxides and glasses may be easily controlled, e.g., by controlling the particle size and the processing temperature. Oxides can be considered pure, or in much simpler mixtures (compared to many waste streams). The reaction between oxides and glasses may be easily controlled, e.g., by controlling the particle size and the processing temperature. As an example, Müller *et al.* (2009) showed that no substantial alumina dissolution can be observed, from composites of 75 vol% alkali-free calcium-alumino-borosilicate glass and 25 vol% dispersed alumina particles, sintered, starting from fine powders (5 μm), below 900°C. Above this temperature, wollastonite, due to the crystallization of the glass matrix, declines, whereas calcium alumino-silicate (anorthite) is favored, as a consequence of the dissolution of the secondary oxide phase.

Lee *et al.* (2010) showed the substantial mineralogical equivalence between glass-ceramics from sinter-crystallization of a (relatively B- and Al-rich) alumino-boro-silicate glass and reactive sintering of a (relatively B- and Al-poor) commercial borosilicate glass (Corning 7070) powders added with aluminum borate hydrate ($2\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$). In both cases, the crystal phases consisted of $\text{Al}_4\text{B}_2\text{O}_9$ or $\text{Al}_{18}\text{B}_4\text{O}_{33}$ whiskers, known to greatly enhance the fracture toughness of the glass matrix, by crack deflection. The toughening effect of whiskers, in samples derived from commercial boro-silicate glass, was compromised by the abundant residual porosity; however, the phase evolution testified the occurrence of reaction (the simple dehydration of aluminum borate hydrate would lead simply to $\text{Al}_4\text{B}_2\text{O}_9$).

Glass-oxide interactions give an excellent opportunity even for the manufacturing marble-like glass-ceramics, avoiding the expensive processing of Neoparies[®] and enabling the up-cycling of a specified glass, namely clear LCD glass. The glass can be used in both fine and coarse fractions (<90 μm , >600 μm) (Authors' unpublished results), mixed with $\text{Mg}(\text{OH})_2$ and reactive alumina ($\gamma\text{-Al}_2\text{O}_3$), in form of micro-sized powders (<10 μm) as shown by the scheme in Fig. 3(a). Pressed and fired at 1000–1100°C, the mixture easily yields cordierite-based glass-ceramics, without any melting step. The specific phase ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, i.e., $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) derives from the chemical reaction between fine LCD glass and the low cost additives, yielding extra MgO and Al_2O_3 ; coarse LCD glass particles simply “dilute” the crystal phases (see the diffraction patterns in Fig. 3(b)). In particular, the newly developed crystals (besides cordierite, spinel, enstatite and another Mg alumino-silicate phase) are formed mainly from fine

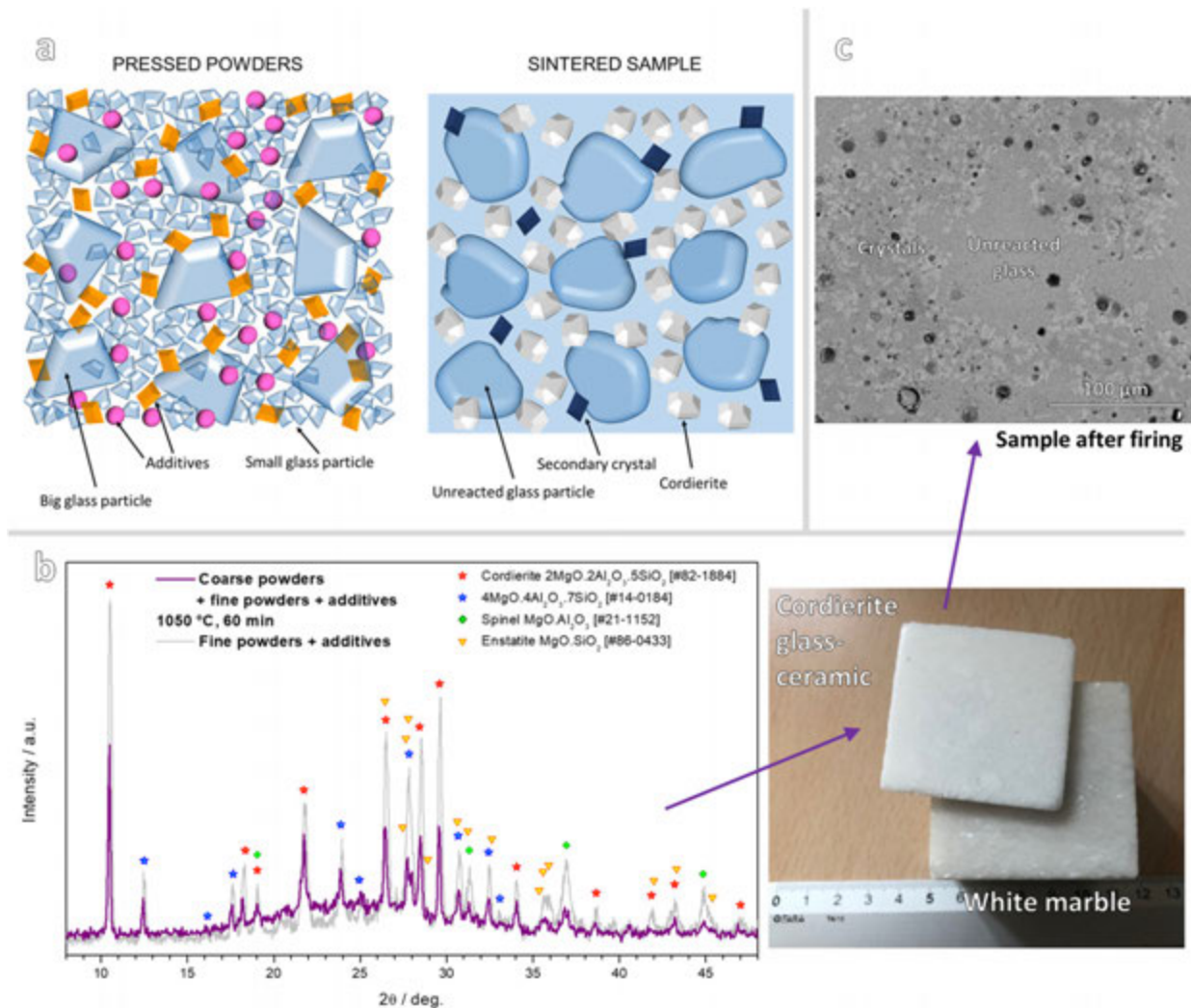
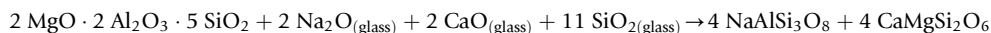
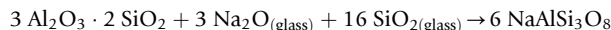
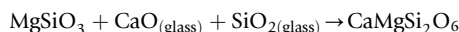


Fig. 3 Obtainment of a cordierite glass-ceramic from glass reactive sintering with selected additives: (a) concept; (b) diffraction patterns and esthetic appearance (compared to that of white marble); (c) detail of amorphous zone surrounded by crystals.

glass powders and concentrate around “islands” of un-reacted glass (Fig. 3(c)). Like in Neoparies[®], the marble-like appearance derives from the different crystallization degree of boundaries (crystals and small unreacted glass areas) and cores (residue of coarse powders, unreacted). The crystallization of cordierite is promising for the high infrared emissivity of the specific phase, to reduce overheating under exposition to sunlight (Xiaofang *et al.*, 2002).

Neoparies[®] inspire also directly-sintered wollastonite glass-ceramics (fired at 850–1000°C), obtained from common soda-lime window glass (< 150 μm) mixed with varying amounts (up to 25 wt%) of powdered “crystallization promoter”, in turn corresponding to the direct sintering (at 1100°C) of kaolin clay, CaCO_3 , BaO and ZnO (Zhang and Liu, 2013). Wollastonite crystallizes by reaction between glass and gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$), from the crystallization promoter. The inclusion of promoter determines a quite delicate trade-off between densification (an increase of solid inclusions, in softened soda-lime glass, obviously complicates the viscous flow) and reaction (wollastonite increases with increasing content Ca-rich promoter), that may be adjusted operating on firing time and temperature. In optimized conditions (2 h at 850°C, 25% promoter), directly-sintered glass-ceramics exhibit an excellent bending strength (exceeding 100 MPa) combined with very limited open porosity (water absorption far below 0.5%). Similar glass-ceramics may be obtained with window glass mixed with pure gehlenite (Si and Ding, 2018).

Albite ($\text{NaAlSi}_3\text{O}_8$) and diopside ($\text{CaMgSi}_2\text{O}_6$) represent further examples of newly formed crystal phases from ‘extensive reactive sintering’ of common soda-lime glass and crystallization promoters, in the form of mullite/enstatite/quartz or enstatite/cordierite mixtures, in turn deriving from the calcination of kaolin and talc (Zhang *et al.*, 2011). CaO, Na₂O and SiO₂ from soda-lime are reactants for the transformation of enstatite (MgSiO_3), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and cordierite into diopside, albite and diopside/albite mixtures, respectively, as follows:



The reaction paths may change according to the chemistry of the glass; a relatively Mg-rich glass may determine the decomposition of mullite, used as crystallization promoter, into silica, in turn “absorbed” in the formation of diopside, and corundum ($\alpha\text{-Al}_2\text{O}_3$), as separate phase (Si *et al.*, 2016).

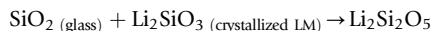
Diopside-based glass-ceramics are interesting as basis for further reaction. Feng *et al.* (2015) showed that a glass frit, “normally” leading to sintered $\text{CaMgSi}_2\text{O}_6$ glass-ceramics (Feng *et al.*, 2012), may interact with MgTiO_3 powders (up to 14 wt%) and form a diopside glass-ceramic with Mg_2SiO_4 and CaTiO_3 as additional phases (owing to a $\text{Ca}^{2+}/\text{Mg}^{2+}$ exchange between silicates and titanates), upon sintering at 950°C. The phase assemblage can be tuned according to the amount of MgTiO_3 ; in optimized conditions, the resulting glass-ceramics exhibit a very low dielectric constant combined with high quality factor and nearly zero temperature coefficient of resonant frequency (very low dielectric dissipation), useful for application as substrates in telecommunication and satellite broadcasting industry (for frequencies in the microwave range).

The previously mentioned albite deserves a particular attention. It belongs to the vast family of feldspars, known to feature distinctive “framework” crystal structures (“tecto-silicates”), deriving from those of crystalline silica polymorphs (Höland and Beall, 2012). SiO_4 tetrahedra are replaced by AlO_4 units, with the charge deficiency (Al^{3+} instead of Si^{4+}) compensated by the presence of alkali and alkaline earth ions in the spaces between tetrahedra (empty, in the case of silica), so that feldspars are also known as “stuffed derivatives of silica”. The so-called “feldspathoid” minerals are similar, except for a higher degree of silica substitution (higher Al/Si ratio). While alkaline earth feldspars (e.g., anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$) and some feldspathoids (e.g., nepheline, $\text{NaAlSi}_3\text{O}_8$, kalsilite, KAlSi_3O_8 , leucite, KAlSi_2O_6) are key constituents in certain glass-ceramics (Höland and Beall, 2012), alkaline feldspars are less common. Pure minerals exhibit an excellent glass-forming ability but the resulting glasses do not crystallize in practical periods of time (Höland and Beall, 2012).

The sinter-crystallization of fine glass powders (multi-component waste-derived glasses or more stoichiometric glasses) has been proven as a fundamental tool for achieving glass-ceramics with such “unusual” crystal phases, owing to the above-mentioned stimulation of crystallization operated by surfaces (Bernardo *et al.*, 2008). Reactive sintering provides a valid alternative, also starting from exceptionally stable glasses, such as lead-containing glasses from dismantled cathode ray tubes. Lu *et al.* (2018) obtained glass-ceramics featuring orthoclase (potassium-sodium feldspar, $(\text{K},\text{Na})\text{AlSi}_3\text{O}_8$; major crystalline phase in an amount of 42–44 wt%) and lead feldspar ($\text{PbAl}_2\text{Si}_2\text{O}_8$) by sintering, at 1000–1100°C, “funnel” glass (lead-containing glass constituting the part of CRTs hidden inside the old TV sets, as described by Ling and Poon, 2014) combined directly with kaolinite or with a mullite/cristaballite mixture (from calcined kaolinite). The obtained phase assemblage provided a successful immobilization of lead ions (in both lead feldspar and residual glass phase).

Fluorine is a fundamental component in glasses converted into many useful glass-ceramics (Höland and Beall, 2012), i.e., in fluorosilicates and in silico-phosphates, including Kokubo’s wollastonite-fluoroapatite glass-ceramics (Hench and Kokubo, 1998). It is not surprising that oxide additives could be replaced by fluorides, in direct sintering approaches to glass-ceramics, starting from waste glasses. Cuspidine ($\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$) as well as fluoramphibole crystals (complex fluoro-silicates crystallizing in form of interlocking needles with huge aspect ratio, leading to high fracture toughness; Höland and Beall, 2012) are easily achieved by sintering soda-lime glass with fluorides (LiF , NaF , MgF_2 , CaF_2 , BaF_2) and/or fluormica (e.g., natural mineral close to the stoichiometry of fluorphlogopite, $\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$), at a temperature of 800–1000°C (Zhang *et al.*, 2006; Zhang and Gao, 2007; Si *et al.*, 2012, 2018). Complex structures, such as those of the fluoramphiboles fluorrichterite ($\text{Na}_2\text{CaMg}_5\text{Si}_8\text{O}_{22}\text{F}_2$) and fluorwinchite ($(\text{Na},\text{K})\text{CaMg}_5\text{Si}_8\text{O}_{22}\text{F}_2$), form by interdiffusion between softened glass and additive (Na^+ and Ca^{2+} from glass to fluormica, K^+ , Mg^{2+} and F from fluormica to glass) (Zhang *et al.*, 2006). It should be noted that mica minerals may have hydroxyls instead of F (e.g., phlogopite is described by the general formula $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{F},\text{OH})_2$), so that glass/mica composites lead to reactions also leading to F -free phases, such as diopside (Faeghi-Nia, 2011).

Reactive sintering implies a “microstructural design”, not only in terms of chemical formulation and mineralogy, but also in terms of “morphology”. Those based on lithium disilicate ($\text{Li}_2\text{Si}_2\text{O}_5$) were the first glass-ceramics developed by Stookey; although “older” than any glass-ceramic system, they are still quite attractive, especially in restorative dentistry, because of their high strength and their translucency, comparable to that of natural teeth (Höland and Beall, 2012). The controlled crystallization of a suitable glass (“LD” glass) yields a multitude of tiny crystals, even below 1 μm (Zhao *et al.*, 2014). Some crack deflection at glass/crystal interface is observed (the fracture toughness may exceed 3 $\text{MPa m}^{0.5}$; Höland and Beall, 2012), but at a lower level, compared to the cases of ceramics with highly elongated interconnected crystals (such as Si_3N_4 and SiAlON ceramics or the previously mentioned fluoramphibole glass-ceramics). Zhao *et al.* (2014) succeeded in developing glass-ceramics with highly elongated $\text{Li}_2\text{Si}_2\text{O}_5$ crystals by reactive sintering under pressure (at 820–890°C) of silica glass and lithium metasilicate (Li_2SiO_3), previously obtained from the crystallization (at 490°C) of a stoichiometric glass (50 mol% Li_2O , 50% SiO_2 ; “LM” glass), according to:



Ideally, the reaction reproduces what typically found, on a finer scale, in conventional lithium disilicate glass-ceramics, i.e., the formation of the desired phase after the precipitation of lithium metasilicate precursor (Höland and Beall, 2012). In practice, the

reaction is conducted with some silica excess (resulting in some residual glass phase) and in the presence of some LD glass powders: large grains, from the reaction, may coexist with small ones from the crystallization of LD (Zhao *et al.*, 2014). The optimization of the microstructure, according to the relative amounts of components and the sintering conditions is the object of current research (Zhao, *et al.*, 2019).

Glass-Ceramics From the Interaction Between Glass and Reactive Binders

The quality of the previously mentioned glass-ceramic sealants for SOFC/SOEC is strongly conditioned by the debinding step. Usual manufacturing implies manual deposition or screen-printing of fine glass powders mixed with organic binders, e.g., PVB (Sabato *et al.*, 2016), dispersed in a solvent. The burn-out of organic matter must be completed at the early stages of heat treatment, to avoid the development of cracks and pores, like in any other ceramic systems (Cima *et al.*, 1989; Evans *et al.*, 1991; Chartier *et al.*, 1995; Enneti *et al.*, 2012). In the case of SOFC/SOEC, however, the debinding involves sandwich structures, with glass powders laying between a metal substrate and a ceramic electrolyte. The sandwich is mechanically consistent before debinding and after sintering (with concurrent crystallization); nothing can be said in the intermediate stage, with glass powders slightly bound just by mutual attrition. There is a substantial risk of misalignment of the pieces to be sealed.

Recent investigations have highlighted the potential of alternative binders, consisting of silicone resins, i.e. materials belonging to the vast class of “preceramic polymers”, for the distinctive ability to leave an abundant ceramic residue, when subjected to heat treatments above 500°C (Colombo *et al.*, 2010; Bernardo *et al.*, 2014). If treated in air, silicones transform into highly reactive amorphous silica, that may dissolve in the pyroplastic mass determined by the viscous flow of a glass filler. This opportunity was first shown by Ohl *et al.* (2011), who developed translucent glass scaffolds starting from a silicone resin filled with Duran® glass powders.

The use of a silica-yielding binder involves a revision of the formulations, since the chemistry of the glass filler evidently changes, especially operating with silicones with high ceramic yield (the amount of silica may exceed 80% of the weight of the silicone polymer, as reported by Colombo *et al.*, 2010). The revision may be applied to the overall formulation, operating with extra fillers, or to the chemistry of the glass. Ohl *et al.* (2011) compensated the extra silica left from the silicone by adding Na₂O and B₂O₃, by means of a secondary filler (borax), so that the overall chemical formulation of Duran glass could be preserved. In other cases, the “polymer-derived” silica was exploited to form extra crystal phases, reacting with selected fillers, beside those formed by crystallization of the starting glass, e.g., normally yielding a wollastonite-apatite glass-ceramic (Elsayed *et al.*, 2015; Zocca *et al.*, 2015). The overall chemistry changes, but the approach is undoubtedly flexible.

The revision of the formulation of the starting glass offers a simplification, in the sense that the final product is determined just by chemical interaction of silicone binder and glass, with no other additive. Starting from a reference glass-ceramic system (sinter-crystallized, from powder bound by conventional fugitive binders, as reported by Elsayed *et al.*, 2018b), the parent glass is replaced by a “silica-defective variant”, for which the batch comprises a reduced amount of silica-yielding raw materials. Once finely powdered, the silica-defective glass is embedded in a silicone binder, degrading into reactive silica upon heating; the mixing of softened silica-defective glass and silica residue of the binder yields a mixture with the same overall oxide formulation of the reference glass. For a proper formulation (i.e., amount of SiO₂ “removed” from the reference glass, to form the silica-defective variant, and “recovered” by means of the binder), the mixture undergoes crystallization, leading to a glass-ceramic with a nearly identical phase assemblage than the original glass-ceramic, and with limited residual porosity as illustrated by the scheme in Fig. 4. The approach has been just applied to SOFC/SOEC sealants and scaffolds from direct ink writing of silicone-glass pastes (Elsayed *et al.*, 2019b); the effectiveness of mixing should be assessed for many other glass-ceramic systems, but a large potential is envisaged even for other applications, e.g., glass-ceramic coatings (Parchovianský *et al.*, 2016).

The investigations on scaffolds for bone tissue engineering actually highlighted a specific advantage of silicones as reactive binders (Elsayed *et al.*, 2019a). A reference glass CaO-Na₂O-B₂O₃-SiO₂ system (Fernandes *et al.*, 2016) was used to form reticulated scaffolds, by direct ink writing of glass powder and fugitive binder, which exhibited a substantial viscous collapse upon ceramization. The viscous flow could be limited by forcing the crystallization, by rapid heating, but this could modify the phase assemblage as well. On the contrary, powders of a silica-defective variant underwent softening, but remained supported by the stiff “silica skeleton” from the silicone; the desired phase assemblage was achieved without substantial viscous collapse of the reticulated scaffolds. The supporting role of reactive silicone binders in glass-ceramic components processed by means of additive manufacturing technologies finds analogies in other ceramic systems, e.g., in TiO₂ porous structures from powder-bed 3D printing of titania powders bound by Ti-based organometallic compounds (Grant *et al.*, 2018).

Besides in the chemistry, silicones are attractive also for “basic” operations, in powder-based 3D printing. As shown by Zocca *et al.* (2015), silicone powders may be just “physically” mixed with glass powders and transformed into a “glue” for the same glass powders, by a simple solvent jet. In other words, solvent droplets “activate” the binder, by partial dissolution; this avoids any risk of injectors clogging or inhomogeneous deposition, by progressive evaporation of solvent, when depositing solvent-binder mixtures.

The use of silicone reactive binders actually brings also advantages in the introduction of extra phases. More precisely, silicone/glass mixtures offer a simple opportunity for the development of composites involving silicates combined with a carbon phase, which represent a very promising class of biomaterials (Thamaraiselvi and Rajeswari, 2004). Besides mechanical properties, the

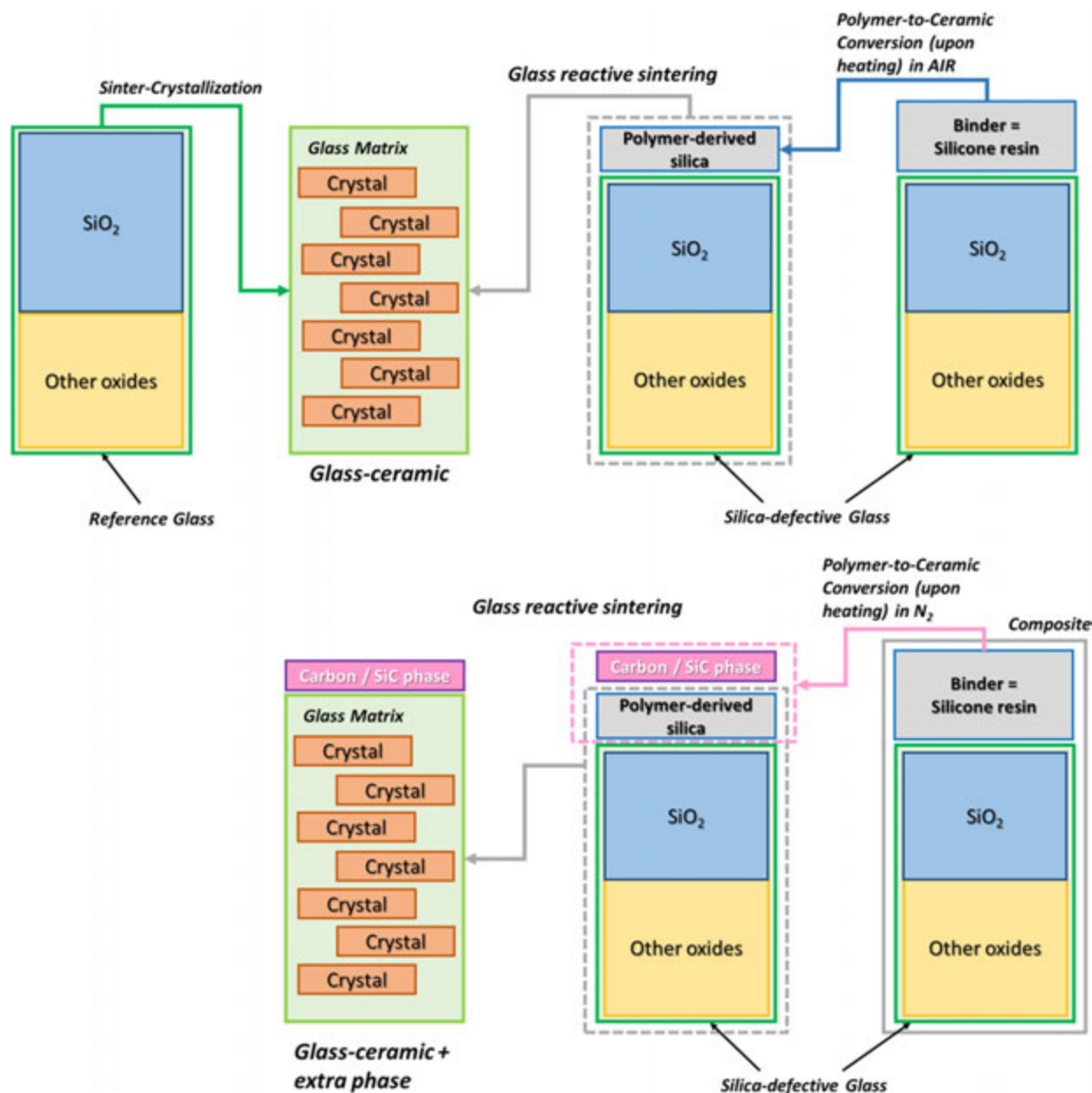


Fig. 4 Schemes for the obtainment of glass-ceramics and glass-ceramic matrix composites from “silica-defective glasses” and reactive silicone binders.

carbon phase can improve the functionalities, e.g., by enabling photothermal effect (in turn exploited for ablation therapy of cancer cells, as shown by [Chen et al. \(2015\)](#)). If the firing is not performed in oxidative atmosphere, silicones yield a silicon oxycarbide (SiOC) ceramic residue, which can be roughly described as a silica rich phase (featuring some Si–C bonds, besides Si–O) mixed with carbon nanosheets, at least below 1200°C (phase separation with formation of SiC crystals is known to occur at higher temperatures, as reported by [Colombo et al., 2010](#)). The silica-rich phase may be used to react with a silica-defective glass, whereas the carbon phase could stay inert, as shown by [Fig. 4](#) (bottom part).

[Fig. 5](#) shows a scaffold (Authors’ unpublished results) from direct ink writing of a silica-defective glass (based on a glass yielding wollastonite-diopside glass-ceramics ([Fiocco et al., 2015a](#)), with SiO_2 reduced by 15 wt%), fired at 900°C in flowing N_2 . The glass was mixed with MK polymer (90 wt% of the silica to be recovered, Wacker Chemie, Germany) and fumed silica (10 wt% of the silica to be recovered); the mixture was designed in order to exploit just the silica-rich phase of SiOC. [Fig. 5](#) provides also an interesting comparison of the diffraction patterns of composites with those of mixtures, calculated in order to be fired in air, with all MK transformed into silica (mixtures with glass A, with 7.5% SiO_2 recovered from silicone and fumed silica, and with glass B, with 15% SiO_2 recovered from silicone and fumed silica). It can be clearly seen that the patterns do not substantially differ from

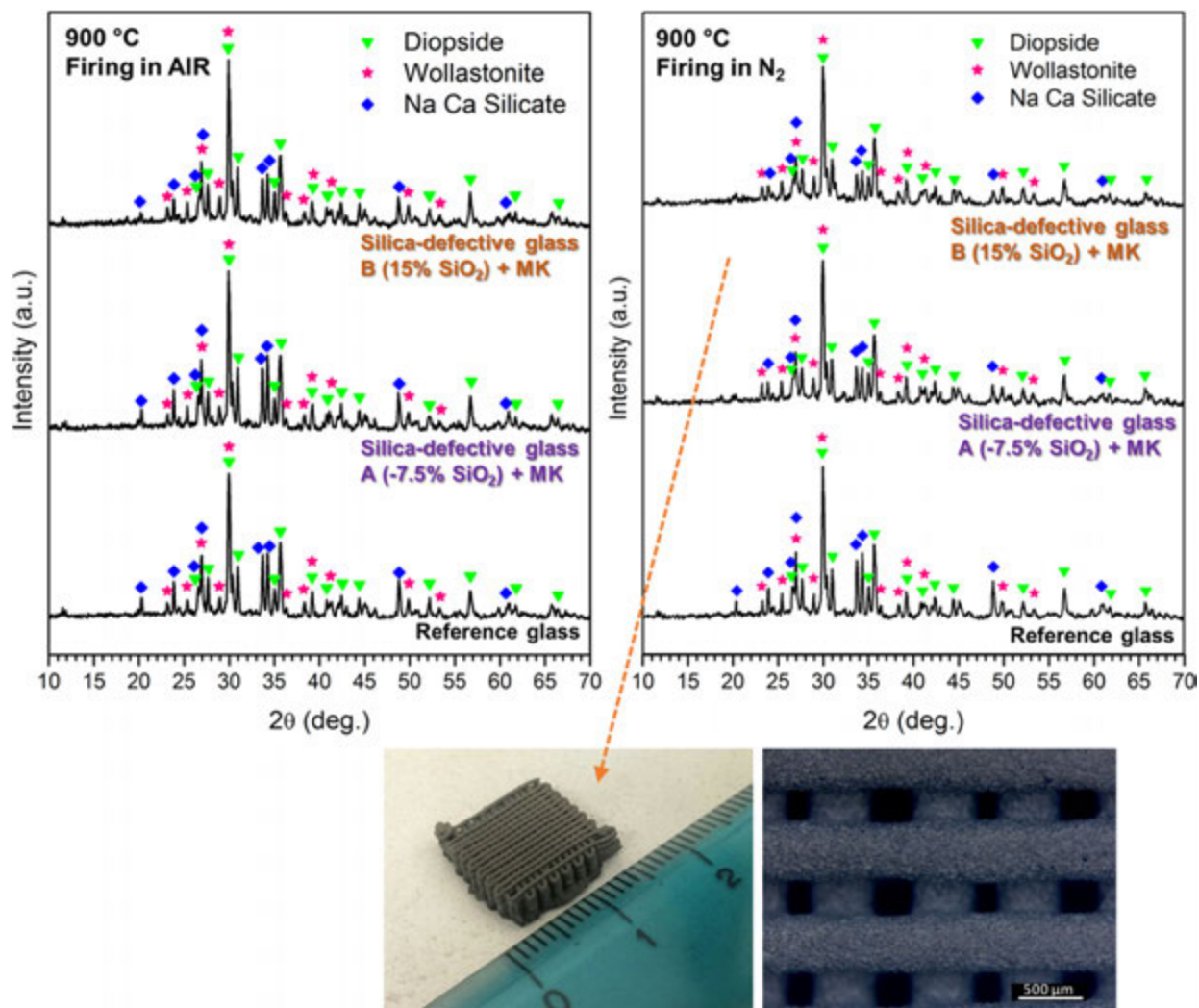


Fig. 5 Obtainment of glass-ceramic scaffolds from silicone polymer and “silica-defective” glasses, in both air and nitrogen.

each other or from that of a glass-ceramic from the reference glass. An exception is given by the intensity of crystal peaks, known to be proportional to the amounts of crystal phases: the intensity of peaks of silicate phases in the composite was downscaled, with a good matching with the expected “dilution” operated by the extra (amorphous) carbon phase.

Polymer-Derived Glass-Ceramics

The previously mentioned investigations all actually configure examples of a “high glass approach”. Glass powders, however, may be used even in low amounts (‘low glass approach’), to support silicone-derived glass-ceramics (Fiocco *et al.*, 2015a). In fact, an ultimate example of glass-ceramics by direct sintering may be represented by silicones interacting with oxide fillers (carbonates, sulfates, hydroxides or directly oxides), in the form of both micro- and nano-sized powders. The quasi-molecular mixing between silica from the polymers and other oxides generally favors the obtainment of highly phase pure silicate ceramics, at low temperatures. These ceramics may be seen as a subgroup of the so-called “polymer-derived ceramics” (ceramics from the transformation of preceramic polymers, Colombo *et al.*, 2010), mixed with “passive” (not reacting with the ceramic residue of the preceramic polymer) or “active” (reacting with the residue and/or with firing atmosphere) fillers, as proposed by Greil (1995), (1998), but they have specific features.

The distinctive, partially covalent chemical bonding of silicates complicates the ionic interdiffusion, especially in the case of quite complex structures, such as mixed silicates, e.g., Ca-Mg, Ca-Zn silicates (Bernardo *et al.*, 2014). The desired phases (i.e. those predicted according to the molar balance between silica and other oxides) are easily developed once secondary fillers (Na-phosphate, Na- and Ca-borates) do not contribute to (or only to) the crystal phases but yield some liquid phase upon firing. The ceramic residue of silicones is amorphous and highly defective (Bernardo *et al.*, 2014) but, as mentioned before, “solid”

(silicates are formed well below the transition temperature of silica glass); the extra liquid dissolves the other components and enables a faster ionic interdiffusion, and finally forms a boro- or phospho-silicate glass, in low amounts (Fiocco *et al.*, 2015a,b).

Borates and phosphates are actually “multifunctional” fillers, since they may:

- (1) Bring components for the synthesis of the desired phase (like the other fillers);
- (2) Release water vapor (when used in their hydrated form), at relatively low temperature, i.e., in silicones still in their polymeric state (enabling a significant foaming);
- (3) Bring components for the formation of a liquid phase, later transforming into a glass, also by partial dissolution of the other components.

Polymer-derived ceramics may turn into “polymer-derived glass-ceramics”. Pre-ceramic polymers are confirmed in their role of transferring polymer forming technologies (injection, extrusion, foaming, etc.) to the domain of ceramics.

In the last systems, glass powders may be used as extra fillers. If featuring the same stoichiometry of the silicone-filler mixture, they lead to glass-ceramics with nearly identical phase assemblage, independently from their content. In the most interesting cases the amount of glass is limited (not exceeding 30 wt%), and it is intended to correct a fundamental issue of “polymer-derived glass-ceramics”, represented by the formation of cracks, in turn due to gas release (from ceramic transformation of silicones), still in progress at the moment of the formation of (rigid) crystals. An increased amount of borates or phosphates would lead to enhanced viscous phase, enabling some stress relaxation, with risks of significant deviation from the stoichiometry of the reference silicates; operating with glass, the viscous phase is enhanced as well, but the crystallization of the same glass keeps the crystallization degree substantially unchanged (Fiocco *et al.*, 2015b).

Also in the case of “polymer-derived glass-ceramics” one fundamental application concerns additive manufacturing of bio-ceramic scaffolds, namely by direct ink writing of silicone-based pastes, including glass powders or not. Recent experiences showed the manufacturing of Biosilicate[®] glass-ceramic scaffolds just from oxide fillers (comprising phosphates) (Elsayed *et al.*, 2019c); on the contrary, stronger wollastonite-diopside scaffolds were achieved by using a paste comprising a glass with the same overall formulation of the silicone-filler mixture (SiO₂: 51.7 wt%; CaO: 32.1%; MgO: 11.5%; Na₂O: 2.2%; P₂O₅: 2.5%) (Elsayed *et al.*, 2017b).

Glass Reaction Sintering as a New Route to Glass-Making

Preparing a glass by sintering rather than melting allows the reduction of technological temperatures and the formation of complex shapes by the methods of ceramic technology. The practical melting temperature of a glass is significantly higher than the thermodynamic melting point (the liquidus temperature) of a crystal mixture of the same composition, because high viscosity at the liquidus temperature slows the dissolution of particles and arrests glass refining. Sintering of pulverized glass or glass microbeads provides a possible alternative for glasses with particularly high processing temperatures (e.g., alumina-based glasses) (Wang *et al.*, 2001; Rozenflanz *et al.*, 2004).

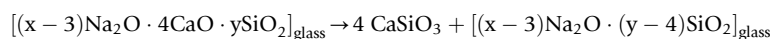
Sintering may lead to glass and glass-ceramic bulk samples even without any preliminary preparation of glass particles. Reaction sintering under isostatic pressure (RSIP) offers interesting opportunities: the formation of small amounts of a low viscosity liquid intermediate phase, by direct reaction between some reactants (e.g., Na₂O and SiO₂), triggers the dissolution of the other components, enabling the obtainment of near net-shape glass bodies at much lower temperatures than melting. This is particularly important when the corrosion of melter components and the volatility of glass constituents are of concern, like in the stabilization of refractory-rich high level radioactive waste (Lutze *et al.*, 1998; Gong *et al.*, 1999, 2000). The possible separation of ZrO₂ particles is interpreted as a result of super-saturation of the glass phase rather than incomplete dissolution (Gong and Lutze, 2002).

Besides radioactive waste, the approach can be extended to the manufacturing porous bioactive ceramics (with pores 100–200 μm and ≤5 μm in diameter) (Gong *et al.*, 2001), in pellets pressed at 7 MPa and simultaneously heated at 950°C (at least 250°C below the temperature that required by glass melting). Amorphous silica, P₂O₅, Ca(OH)₂ and Na₂C₂O₄ (sodium oxalate) lead to completely amorphous pieces, while the addition of hydroxyapatite yields a rhenanite (β-NaCaPO₄)/wollastonite glass-ceramic, according to specific reaction path:

- (1) Formation of rhenanite (with water vapor release, leading to pores) by reaction between apatite and sodium silicate phase, accompanied by diffusion of calcium in sodium silicate phase:



- (2) Crystallization of wollastonite from calcium-enriched sodium silicate phase:



Like in the case of the above-mentioned polymer-derived glass-ceramics, there is potential for a real design of the crystal phases.

Concluding Remarks

Glass reactive sintering may be seen as a vast domain of technologies, relying on extensive reactions between glass particles and (possibly) selected additives. The control of reactions is not significant just for the microstructural development, including the formation of “unusual” phases (e.g., feldspar phases, free carbon) but also for the overall processing, including the most recent trends, such as additive manufacturing. The huge number of combinations between glass powders, oxide additives, reactive binders etc. opens the way for a new generation of glass-based products, in key areas of industrial development (health, energy, environment), to be disclosed in the near future.

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References

- Akram, M.Y., Casalegno, V., Ferraris, M., *et al.*, 2019. Joining and mechanical testing of oxide/oxide (Nextel™610/alumina-zirconia) ceramic composites. *Journal of the European Ceramic Society* 39, 2510–2517.
- Albakry, M., Guazzato, M., Swain, M.V., 2004. Influence of hot pressing on the microstructure and fracture toughness of two pressable dental glass–ceramics. *Journal of Biomedical Materials Research – Part B Applied Biomaterials* 71, 99–107.
- Andreev, D.V., Zakharov, A.I., 2012. Study of the rheology of sintered glass ceramic materials by torsion of thin-walled tubes. *Refractories and Industrial Ceramics* 53, 31–39.
- Andreev, D.V., Zakharov, A.I., 2014. Comprehensive method of studying and predicting the deformation of ceramic products during sintering. *Refractories and Industrial Ceramics* 54, 366–375.
- Baino, F., Vitale-Brovarone, C., 2012. New trends in bone tissue engineering scaffolds: hierarchically porous glass and glass-ceramic structures. In: Rimondini, L., Bianchi, C.L., Verné, E. (Eds.), *Surface Tailoring of Inorganic Materials for Biomedical Applications*. UAE: Bentham Science Publishers, pp. 376–391.
- Baino, F., Vitale-Brovarone, C., 2014. Bioactive glass and glass-ceramic foam scaffolds for bone tissue restoration. In: Netti, P. (Ed.), *Biomedical Foams for Tissue Engineering Applications*, first ed. Cambridge, UK: Woodhead Publishing, pp. 213–248.
- Bellucci, D., Cannillo, V., 2018. A novel bioactive glass containing strontium and magnesium with ultra-high crystallization temperature. *Materials Letters* 213, 67–70.
- Bellucci, D., Cannillo, V., Anesi, A., *et al.*, 2018. Bone regeneration by novel bioactive glasses containing strontium and/or magnesium: A preliminary in-vivo study. *Materials* 11, 2223.
- Ben-Arfa, B.A.E., Neto, A.S., Palamá, I.E., *et al.*, 2019. Robocasting of ceramic glass scaffolds: Sol–gel glass, new horizons. *Journal of the European Ceramic Society* 39 (4), 1625–1634.
- Bernardo, E., 2008. Fast Sinter-crystallization of a glass from waste materials. *Journal of Non-Crystalline Solids* 354, 3486–3490.
- Bernardo, E., Stoll, E., Boccaccini, A.R., 2006. Novel basalt fibre reinforced glass matrix composites. *Journal of Materials Science* 41, 1207–1211.
- Bernardo, E., Doyle, J., Hampshire, S., 2008. Sintered feldspar glass–ceramics and glass–ceramic matrix composites. *Ceramics International* 34, 2037–2042.
- Bernardo, E., Esposito, L., Rambaldi, E., *et al.*, 2009a. Sintered esseneite-wollastonite-plagioclase glass-ceramics from vitrified waste. *Journal of the European Ceramic Society* 29, 2921–2927.
- Bernardo, E., Scarinci, G., Edme, E., Michon, U., Planty, N., 2009b. Fast-sintered gehlenite glass-ceramics from plasma-vitrified municipal solid waste incinerator fly ashes. *Journal of the American Ceramic Society* 92, 528–530.
- Bernardo, E., Esposito, L., Rambaldi, E., Tucci, A., 2009c. ‘Glass based stoneware’ as a promising route for the recycling of waste glasses. *Advances in Applied Ceramics* 108, 2–8.
- Bernardo, E., Scarinci, G., Bertuzzi, P., Ercole, P., Ramon, L., 2010a. Recycling of waste glasses into partially crystallized glass foams. *Journal of Porous Materials* 17, 359–365.
- Bernardo, E., Bonomo, E., Dattoli, A., 2010b. Optimisation of sintered glass–ceramics from an industrial waste glass. *Ceramics International* 36, 1675–1680.
- Bernardo, E., Fiocco, L., Parciannello, G., Storti, E., Colombo, P., 2014. Advanced ceramics from preceramic polymers modified at the nano-scale: A review. *Materials* 7, 1927–1956.
- Binhussain, M.A., Marangoni, M., Bernardo, E., Colombo, P., 2014. Sintered and glazed glass-ceramics from natural and waste raw materials. *Ceramics International* 40, 3543–3551.
- Boccaccini, A.R., Trusty, P.A., 1996. Toughening and strengthening of glass by Al_2O_3 platelets. *Journal of Materials Science Letters* 15, 60–63.
- Boccaccini, A.R., Winkler, V., 2002. Fracture surface roughness and toughness of Al_2O_3 -platelet reinforced glass matrix composites. *Composites – Part A: Applied Science and Manufacturing* 33, 125–131.
- Cetin, S., Marangoni, M., Bernardo, E., 2015. Lightweight glass-ceramic tiles from the sintering of mining tailings. *Ceramics International* 41, 5294–5300.
- Chartier, T., Ferrato, M., Baumard, J.-F., 1995. Influence of the debinding method on the mechanical properties of plastic formed ceramics. *Journal of the European Ceramic Society* 15, 899–903.
- Chen, Y.-C., Chiu, W.-T., Chen, J.-C., *et al.*, 2015. The photothermal effect of silica–carbon hollow sphere–concanavalin A on liver cancer cells. *Journal of Materials Chemistry B* 3, 2447–2454.
- Chen, Z., Wang, H., Ji, R., *et al.*, 2019. Reuse of mineral wool waste and recycled glass in ceramic foams. *Ceramics International* 45, 15057–15064.
- Chenu, S., Lebullenger, R., Bénard-Rocherullé, P., *et al.*, 2012. Glass reactive sintering as an alternative route for the synthesis of NZP glass–ceramics. *Journal of Materials Science* 47, 486–492.
- Chenu, S., Bénard-Rocherullé, P., Lebullenger, R., Rocherullé, J., 2016. Characterisation of a new NZP material prepared from reactive sintering of a phosphate based glass. *Physics and Chemistry of Glasses: European Journal of Glass Science and Technology Part B* 57, 206–212.
- Chihara, H., Koike, C., Tsuchiyama, A., 2007. Compositional dependence of infrared absorption spectra of crystalline silicates – III. Melilite solid solution. *Astronomy and Astrophysics* 464, 229–234.

- Chinnam, R.K., Francis, A.A., Will, J., Bernardo, E., Boccaccini, A.R., 2013. Review. Functional glasses and glass-ceramics derived from iron rich waste and combination of industrial residues. *Journal of Non-Crystalline Solids* 365, 63–74.
- Chou, Y.-S., Thomsen, E.C., Williams, R.T., *et al.*, 2011. Compliant alkali silicate sealing glass for solid oxide fuel cell applications: Thermal cycle stability and chemical compatibility. *Journal of Power Sources* 196, 2709–2716.
- Cima, M.J., Lewis, J.A., Devoe, A.D., 1989. Binder distribution in ceramic greenware during thermolysis. *Journal of the American Ceramic Society* 72, 1192–1199.
- Colombo, P., Brusatin, G., Bernardo, E., Scarinci, G., 2003. Inertization and reuse of waste materials by vitrification and fabrication of glass-based products. *Current Opinion in Solid State and Materials Science* 7, 225–239.
- Colombo, P., Mera, G., Riedel, R., Soraru, G.D., 2010. Polymer-Derived-Ceramics: 40 years of research and innovation in advanced ceramics. *Journal of the American Ceramic Society* 93, 1805–1837.
- Crovace, M.C., Souza, M.T., Chinaglia, C.R., Peitl, O., Zanotto, E.D., 2016. Biosilicate® – A multipurpose, highly bioactive glass-ceramic. In vitro, in vivo and clinical trials. *Journal of Non-Crystalline Solids* 432, 90–110.
- Desimone, D., Li, W., Roether, J.A., *et al.*, 2013. Biosilicate-gelatin bone scaffolds by the foam replica technique: Development and characterization. *Science and Technology of Advanced Materials* 14, 045008.
- Döhler, F., Zschechel, T., Kasch, S., Schmidt, T., Rüssel, C., 2017. A glass in the CaO/MgO/Al₂O₃/SiO₂ system for the rapid laser sealing of alumina. *Ceramics International* 43, 4302–4308.
- Elsayed, H., Zocca, A., Bernardo, E., *et al.*, 2015. Development of bioactive silicate-based glass-ceramics from preceramic polymer and fillers. *Journal of the European Ceramic Society* 35, 731–739.
- Elsayed, H., Rincón Romero, A., Ferroni, L., *et al.*, 2017a. Bioactive glass-ceramic scaffolds from novel 'Inorganic gel casting' and sinter-crystallization. *Materials* 10, 171.
- Elsayed, H., Colombo, P., Bernardo, E., 2017b. Direct ink writing of wollastonite-diopside glass-ceramic scaffolds from a silicone resin and engineered fillers. *Journal of the European Ceramic Society* 37, 4187–4195.
- Elsayed, H., Zocca, A., Schmidt, J., *et al.*, 2018a. Bioactive glass-ceramic scaffolds by additive manufacturing and sinter-crystallization of fine glass powders. *Journal of Materials Research* 33, 1960–1971.
- Elsayed, H., Javed, H., Sabato, A.G., Smeacetto, F., Bernardo, E., 2018b. Novel glass-ceramic SOFC sealants from glass powders and a reactive silicone binder. *Journal of the European Ceramic Society* 38, 4245–4251.
- Elsayed, H., Schmidt, J., Bernardo, E., Colombo, P., 2019a. Comparative analysis of wollastonite-diopside glass-ceramic structures fabricated via stereo-lithography. *Advanced Engineering Materials* 21, 1801160.
- Elsayed, H., Picicco, M., Dasan, A., *et al.*, 2019b. Glass powders and reactive silicone binder: Interactions and application to additive manufacturing of bioactive glass-ceramic scaffolds. *Ceramics International* 45, 13740–13746.
- Elsayed, H., Rebesan, P., Crovace, *et al.*, 2019c. Biosilicate® scaffolds produced by 3D-printing and direct foaming using preceramic polymers. *Journal of the American Ceramic Society* 102, 1010–1020.
- Enneti, R.K., Park, S.J., German, R.M., Atre, S.V., 2012. Review: Thermal debinding process in particulate materials processing. *Materials and Manufacturing Processes* 27, 103–118.
- Eqtasadi, S., Motealleh, A., Miranda, P., *et al.*, 2014. Robocasting of 45S5 bioactive glass scaffolds for bone tissue engineering. *Journal of the European Ceramic Society* 34, 107–118.
- Evans, J.R.G., Edirisinghe, M.J., Wright, J.K., Crank, J., 1991. On the removal of organic vehicle from moulded ceramic bodies. *Proceedings of the Royal Society A* 432, 321–340.
- Faeghi-Nia, A., 2011. Crystallization and sintering behavior of phlogopite–soda lime composite. *Journal of Non-Crystalline Solids* 357, 3385–3391.
- Feng, K.-C., Chou, C.-C., Tsao, C.-Y., *et al.*, 2015. A novel phase-controlling-sintering route for improvement of diopside-based microwave dielectric materials. *Ceramics International* 41, S526–S529.
- Feng, K.-C., Chou, C.-C., Chu, L.-W., Chen, H., 2012. Zirconia nucleating agent on microstructural and electrical properties of a CaMgSi₂O₆ diopside glass–ceramic for microwave dielectrics. *Materials Research Bulletin* 47, 2851–2855.
- Fernandes, H.R., Tulyaganov, D.U., Ferreira, J.M.F., 2009. Production and characterisation of glass ceramic foams from recycled raw materials. *Advances in Applied Ceramics* 109, 9–13.
- Fernandes, J.S., Gentile, P., Moorehead, R., *et al.*, 2016. Design and properties of novel substituted borosilicate bioactive glasses and their glass-ceramic derivatives. *Crystal Growth and Design* 16, 3731–3740.
- Filho, O.P., Latorre, G.P., Hench, L.L., 1996. Effect of crystallization on apatite-layer formation of bioactive glass 45S5. *Journal of Biomedical Materials Research* 30, 509–514.
- Fiocco, L., Elsayed, H., Dagano, J.M.K.F., Soares, V.O., Bernardo, E., 2015a. Silicone resins mixed with active oxide fillers and Ca–Mg silicate glass as alternative/integrative precursors for wollastonite-diopside glass-ceramics foams. *Journal of Non-Crystalline Solids* 416, 44–49.
- Fiocco, L., Elsayed, H., Ferroni, L., *et al.*, 2015b. Bioactive wollastonite-diopside foams from preceramic polymers and reactive oxide fillers. *Materials* 8, 2480–2494.
- Francis, A.A., Rawlings, R.D., Boccaccini, A.R., 2002. Glass-ceramics from mixtures of coal ash and soda-lime glass by the peturgic method. *Journal of Materials Science Letters* 21, 975–980.
- Francis, A.A., Rawlings, R.D., Sweeney, R., Boccaccini, A.R., 2004. Crystallization kinetic of glass particles prepared from a mixture of coal ash and soda-lime cullet glass. *Journal of Non-Crystalline Solids* 333, 187–193.
- Gerhardt, L., Boccaccini, A.R., 2010. Bioactive glass and glass ceramic scaffolds for bone tissue engineering. *Materials* 3, 3867–3910.
- Giuli, G., Bindi, L., Bonazzi, P., 2000. Rietveld refinement of okayamalite, Ca₂SiB₂O₇: Structural evidence for the B/Si ordered distribution. *American Mineralogist* 85, 1512–1515.
- Goel, A., Rajagopal, R.R., Ferreira, J.M.F., 2011. Influence of strontium on structure, sintering and biodegradation behaviour of CaO–MgO–SrO–SiO₂–P₂O₅–CaF₂ glasses. *Acta Biomaterialia* 7, 4071–4080.
- Gong, W., Lutze, W., 2002. Electron microscopy study of reaction sintered HLW glass. *MRS Proceedings* 757, II.5, 2.
- Gong, W., Lutze, W., Ewing, R.C., 2000. Reaction sintered glass: A durable matrix for spinel-forming nuclear waste compositions. *Journal of Nuclear Materials* 278, 73–84.
- Gong, W., Abdelouas, A., Lutze, W., 2001. Porous bioactive glass and glass-ceramics made by reaction sintering under pressure. *Journal of Biomedical Materials Research* 54, 320–327.
- Gong, W., Lutze, W., Abdelouas, A., Ewing, R.C., 1999. Vitrification of radioactive waste by sintering under pressure. *Journal of Nuclear Materials* 265, 12–21.
- Gonzenbach, U.T., Studart, A.R., Steinlin, D., Tervoort, E., Gauckler, L.J., 2007. Processing of particle-stabilized wet foams into porous ceramics. *Journal of the American Ceramic Society* 90, 3407–3414.
- Granito, R.N., Ribeiro, D.A., Rennó, A.C.M., *et al.*, 2009. Effects of biosilicate and bioglass 45S5 on tibial bone consolidation on rats: A biomechanical and a histological study. *Journal of Materials Science: Materials in Medicine* 20, 2521–2526.
- Grant, L.O., Alameen, M.B., Carazzone, J.R., Higgs, C.F., Cordero, Z.C., 2018. Mitigating distortion during sintering of binder jet printed ceramics. In: *Proceedings of the 29th Annual International Solid Freeform Fabrication Symposium – An Additive Manufacturing Conference*, pp. 135–142. Austin, TX, USA.
- Greil, P., 1995. Active-filler-controlled pyrolysis of preceramic polymers. *Journal of the American Ceramic Society* 78, 835–848.
- Greil, P., 1998. Near net shape manufacturing of polymer derived ceramics. *Journal of the European Ceramic Society* 18, 1905–1914.
- Gualtieri, A.F., 2007. Thermal behavior of the raw materials forming porcelain stoneware mixtures by combined optical and in situ X-ray dilatometry. *Journal of the American Ceramic Society* 90, 1222–1231.

- Gutzow, I., Pascova, R., Karamanov, A., Schmelzer, J., 1998. The kinetics of surface induced sinter-crystallization and the formation of glass-ceramic materials. *Journal of Materials Science* 33, 5265–5273.
- Hasheminia, S., Nemati, A., Eftekhari Yekta, B., Alizadeh, P., 2012. Preparation and characterisation of diopside-based glass-ceramic foams. *Ceramics International* 38, 2005–2010.
- Hench, L.L., 1977. Analysis of bioglass fixation of hip prostheses. *Journal of Biomedical Materials Research* 11, 267–282.
- Hench, L.L., 2006. The story of Bioglass[®]. *Journal of Materials Science: Materials in Medicine* 17, 967–978.
- Hench, L.L., Kokubo, T., 1998. Properties of bioactive glasses and glass-ceramics. In: Black, J., Hastings, G. (Eds.), *Handbook of Biomaterial Properties*. London: Chapman & Hall, pp. 355–563.
- Hernández-Crespo, Ma.S., Romero, M., Rincón, J.Ma., 2006. Nucleation and crystal growth of glasses produced by a generic plasma arc-process. *Journal of the European Ceramic Society* 26, 1679–1685.
- Herrmann, M., Lippmann, W., Hurtado, A., 2014. Y₂O₃-Al₂O₃-SiO₂-based glass-ceramic fillers for the laser-supported joining of SiC. *Journal of the European Ceramic Society* 34, 1935–1948.
- Höland, W., Rheinberger, V., 2008. Dental glass-ceramics. In: Kokubo, T. (Ed.), *Bioceramics and Their Clinical Applications*. Woodhead Publishing Series in Biomaterials, pp. 548–568.
- Höland, W., Beall, G.H., 2012. *Glass-Ceramic Technology*. New Jersey: John Wiley & Sons.
- Höland, W., Rheinberger, V., Apel, E., van't Hoen, C., 2007. Principles and phenomena of bioengineering with glass-ceramics for dental restoration. *Journal of the European Ceramic Society* 27, 1521–1526.
- Javed, H., Sabato, A.G., Herbrig, K., *et al.*, 2018. Design and characterization of novel glass-ceramic sealants for solid oxide electrolysis cell (SOEC) applications. *International Journal of Applied Ceramic Technology* 15, 999–1010.
- Joseph, T., Sebastian, M.T., 2010. Microwave Dielectric Properties of (Sr_{1-x}A_x)₂(Zn_{1-x}B_x)Si₂O₇ Ceramics (A = Ca, Ba and B = Co, Mg, Mn, Ni). *Journal of the American Ceramic Society* 93, 147–154.
- Juraski, A.D.C., Rodas, A.C.D., Elsayed, H., *et al.*, 2017. The in vitro bioactivity, degradation, and cytotoxicity of polymer-derived wollastonite-diopside glass-ceramics. *Materials* 10, 425.
- Kaminskii, A.A., Belokoneva, E.L., Mill, B.V., Sarkisov, S.E., Kurbanov, K., 1986. Crystal structure, absorption, luminescence properties, and stimulated emission of Ga gehlenite (Ca_{2-x}Nd_xGd_{2-x}Si_{1-x}O₇). *Physica Status Solidi (a)* 97, 279–290.
- Karamanov, A., Piscicella, P., Cantalini, C., Pelino, M., 2000. Influence of Fe³⁺/Fe²⁺ ratio on the crystallization of iron-rich glasses made with industrial waste. *Journal of the American Ceramic Society* 83, 3153–3157.
- Karamanov, A., Dzhantov, B., Paganelli, M., Sighinolfi, D., 2013. Glass transition temperature and activation energy of sintering by optical dilatometry. *Thermochimica Acta* 553, 1–7.
- Karamanov, A., Di Gioacchino, R., Piscicella, P., Pelino, M., Hreglich, A., 2002. Viscosity of iron rich glasses obtained from industrial wastes. *Glass Technology* 43, 34–38.
- Kaur, G., Pandey, O.P., Singh, K., 2012. Interfacial study between high temperature SiO₂-B₂O₃-AO-La₂O₃ (A = Sr, Ba) glass seals and Crofer 22APU for solid oxide fuel cell applications. *International Journal of Hydrogen Energy* 37, 6862–6874.
- Kokubo, T., Shigematsu, M., Nagashima, Y., *et al.*, 1982. Apatite- and wollastonite-containing glass-ceramics for prosthetic application. *Bulletin of the Institute for Chemical Research, Kyoto University* 60, 260–268.
- Kolan, K.C.R., Leu, M.C., Hilmas, G.E., Brown, R.F., Velez, M., 2011. Fabrication of 13-93 bioactive glass scaffolds for bone tissue engineering using indirect selective laser sintering. *Biofabrication* 3, 025004.
- Kumar, S., Singh, K.K., Ramachandrarao, P., 2001. Effects of fly ash additions on the mechanical and other properties of porcelainised stoneware tiles. *Journal of Materials Science* 36, 5917–5922.
- Lee, H.K., Zerbetto, S., Colombo, P., Pantano, C.G., 2010. Glass-ceramics and composites containing aluminum borate whiskers. *Ceramics International* 36, 1589–1596.
- Li, J.J., Dunstan, C.R., Entezari, A., *et al.*, 2019. Novel bone substitute with high bioactivity, strength, and porosity for repairing large and load-bearing bone defects. *Advanced Healthcare Materials* 8, 1801298.
- Li, P., Yang, Q., Zhang, F., Kokubo, T., 1992. The effect of residual glassy phase in a bioactive glass-ceramic on the formation of its surface apatite layer in vitro. *Journal of Materials Science: Materials in Medicine* 3, 452–456.
- Ling, T.-C., Poon, C.-S., 2014. Use of recycled CRT funnel glass as fine aggregate in dry-mixed concrete paving blocks. *Journal Cleaner Production* 68, 209–215.
- Liu, X., Rahaman, M.N., Hilmas, G.E., Bal, B.S., 2013. Mechanical properties of bioactive glass (13-93) scaffolds fabricated by robotic deposition for structural bone repair. *Acta Biomaterialia* 9, 7025–7034.
- Liu, Z., Zong, Y., Li, H., 2015. Preparation and characterization of glass – Ceramic under various sintering atmospheres. *Materials Letters* 159, 122–125.
- Lu, X., Yang, J., Ning, X.-A., Shih, K., Wang, F., 2018. Crystallization pathways in glass-ceramics by sintering cathode ray tube (CRT) glass with kaolin-based precursors. *Journal of the European Ceramic Society* 38, 5184–5191.
- Lutze, W., Gong, W., Abdelouas, A., Ewing, R.C., 1998. Vitrification of high-level radioactive waste by sintering under pressure. *MRS Proceedings* 506.223.
- Mackenzie, J., Shuttleworth, R., 1949. A phenomenological theory of sintering. *Proceedings of the Physical Society. Section B* 62, 833–852.
- Mahato, N., Banerjee, A., Gupta, A., Omar, S., Balani, K., 2015. Progress in material selection for solid oxide fuel cell technology: A review. *Progress in Materials Science* 72, 141–337.
- Marangoni, M., Secco, M., Parisatto, M., *et al.*, 2014. Cellular glass-ceramics from a self foaming mixture of glass and basalt scoria. *Journal of Non-Crystalline Solids* 403, 38–46.
- Monich, P.R., Romero, A.R., Höllen, D., Bernardo, E., 2018. Porous glass-ceramics from alkali activation and sinter-crystallization of mixtures of waste glass and residues from plasma processing of municipal solid waste. *Journal of Cleaner Production* 188, 871–878.
- Montazerian, M., Zanotto, E.D., 2016. History and trends of bioactive glass-ceramics. *Journal of Biomedical Materials Research Part A* 104, 1231–1249.
- Motealleh, A., Eftejadi, S., Perera, F.H., *et al.*, 2019. Reinforcing 13–93 bioglass scaffolds fabricated by robocasting and pressureless spark plasma sintering with graphene oxide. *Journal of the Mechanical Behavior of Biomedical Materials* 97, 108–116.
- Moura, J., Teixeira, L.N., Ravagnani, C., *et al.*, 2007. In vitro osteogenesis on a highly bioactive glass-ceramic (Biosilicate[®]). *Journal of Biomedical Materials Research - Part A* 82A, 545–557.
- Müller, R., Zanotto, E.D., Fokin, V.M., 2000. Surface crystallization of silicate glasses: Nucleation sites and kinetics. *Journal of Non-Crystalline Solids* 274, 208–231.
- Müller, R., Meszaros, R., Peplinski, B., *et al.*, 2009. Dissolution of alumina, sintering, and crystallization in glass ceramic composites for LTCC. *Journal of the American Ceramic Society* 92, 1703–1708.
- Ohi, C., Kappa, M., Wilker, V., Bhattacharjee, S., *et al.*, 2011. Novel open-cellular glass foams for optical applications. *Journal of the American Ceramic Society* 94, 436–441.
- Olevsky, E.A., Tikare, V., Garino, T., 2006. Multi-scale study of sintering: A review. *Journal of the American Ceramic Society* 89, 1914–1922.
- Paganelli, M., 2002. Using the optical dilatometer: To determine sintering behavior. *American Ceramic Society Bulletin* 81, 25–30.
- Pannhorst, W., 1997. Glass ceramics: State-of-the-art. *Journal of Non-Crystalline Solids* 219, 198–204.
- Parchovianský, M., Barroso, G., Petrikova, I., *et al.*, 2016. Polymer derived glass ceramic layers for corrosion protection of metals, ceramic for energy conversion, storage, and distribution systems. *Ceramic Transactions* 256, 187–200.
- Peiti, O., Zanotto, E.D., Hench, L.L., 2001. Highly bioactive P₂O₅-Na₂O-CaO-SiO₂ glass-ceramics. *Journal of Non-Crystalline Solids* 292, 115–126.

- Pelekasi, T., Menegaki, M., Damigos, D., 2012. Externalities, NIMBY syndrome and marble quarrying activity. *Journal of Environmental Planning and Management* 55, 1192–1205.
- Petersen, R.R., König, J., Yue, Y., 2017. The viscosity window of the silicate glass foam production. *Journal of Non-Crystalline Solids* 456, 49–54.
- Pinto, K.N.Z., Tim, C.R., Crovace, M.C., *et al.*, 2018. Scaffolds of bioactive glass-ceramic (Biosilicate[®]) and bone healing: A biological evaluation in an experimental model of tibial bone defect in rats. *Bio-Medical Materials and Engineering* 29, 665–683.
- Piotrowski, G., Hench, L.L., Allen, W.C., Miller, G.J., 1975. Mechanical studies of the bone bioglass interfacial bond. *Journal of Biomedical Materials Research* 9, 47–61.
- Ponsot, I., Bernardo, E., 2013. Self glazed glass ceramic foams from metallurgical slag and recycled glass. *Journal of Cleaner Production* 59, 245–250.
- Ponsot, I., Falcone, R., Bernardo, E., 2013. Stabilization of fluorine-containing industrial waste by production of sintered glass-ceramics. *Ceramics International* 39, 6907–6915.
- Ponsot, I., Pontikes, Y., Baldi, G., *et al.*, 2014. Magnetic glass ceramics by sintering of borosilicate glass and inorganic waste. *Materials* 7, 5565–5580.
- Prado, M.O., Zanutto, E.D., 2002. Glass sintering with concurrent crystallization. *Comptes Rendus Chimie* 5, 773–786.
- Prado, M.O., Zanutto, E.D., Müller, R., 2001. Model for sintering polydispersed glass particles. *Journal of Non-Crystalline Solids* 279, 169–178.
- Rawlings, R.D., Wu, J.P., Boccaccini, A.R., 2006. Glass-ceramics: Their production from wastes-A Review. *Journal of Materials Science* 41, 733–761.
- Rawson, H., 1980. *Properties and Applications of Glass*. Amsterdam: Elsevier.
- Ray, A., Tiwari, A.N., 2001. Compaction and sintering behaviour of glass-alumina composites. *Materials Chemistry and Physics* 67, 220–225.
- Reddy, A.A., Goel, A., Tulyaganov, D.U., *et al.*, 2013. Study of calcium-magnesium-aluminum-silicate (CMAS) glass and glass-ceramic sealant for solid oxide fuel cells. *Journal of Power Sources* 231, 203–212.
- Rincon Romero, A., Salvo, M., Bernardo, E., 2018. Up-cycling of vitrified bottom ash from MSWI into glass-ceramic foams by means of 'Inorganic gel casting' and sinter-crystallization. *Construction and Building Materials* 192, 133–140.
- Rincón Romero, A., Marangoni, M., Cetin, S., Bernardo, E., 2016. Recycling of inorganic waste in monolithic and cellular glass-based materials for structural and functional applications. *Journal of Chemical Technology and Biotechnology* 91, 1946–1961.
- Rodríguez-López, S., Haanappel, V.A.C., Durán, A., *et al.*, 2016. Glass–ceramic seals in the system MgO–BaO–B₂O₃–SiO₂ operating under simulated SOFC conditions. *International Journal of Hydrogen Energy* 41, 15335–15345.
- Rodríguez-López, S., Wei, J., Laurenti, K.C., *et al.*, 2017. Mechanical properties of solid oxide fuel cell glass-ceramic sealants in the system BaO/SrO–MgO–B₂O₃–SiO₂. *Journal of the European Ceramic Society* 37, 3579–3594.
- Roohani-Esfahani, S.I., Zreiqat, H., 2012. Ceramic scaffolds, current issues and future trends. In: Ramalingam, M., *et al.* (Eds.), *Integrated Biomaterials in Tissue Engineering*. USA: Wiley, pp. 25–46.
- Roohani-Esfahani, S.-I., Newman, P., Zreiqat, H., 2016. Design and fabrication of 3D printed scaffolds with a mechanical strength comparable to cortical bone to repair large bone defects. *Scientific Reports* 6, 19468.
- Roohani-Esfahani, S.-I., Chen, Y., Shi, J., Zreiqat, H., 2013. Fabrication and characterization of a new, strong and bioactive ceramic scaffold for bone regeneration. *Materials Letters* 107, 378–381.
- Rozenflanz, A., Frey, M., Endres, B., *et al.*, 2004. Bulk glasses and ultrahard nanoceramics based on alumina and rare-earth oxides. *Nature* 430, 761–764.
- Sabato, A.G., Cempura, G., Montinaro, D., *et al.*, 2016. Glass-ceramic sealant for solid oxide fuel cells application: Characterization and performance in dual atmosphere. *Journal of Power Sources* 328, 262–270.
- Sabato, A.G., Rost, A., Schilm, J., *et al.*, 2019. Effect of electric load and dual atmosphere on the properties of an alkali containing diopside-based glass sealant for solid oxide cells. *Journal of Power Sources* 415, 15–24.
- Sánchez, E., García-Ten, J., Sanz, V., Moreno, A., 2010. Porcelain tile: Almost 30 years of steady scientific-technological evolution. *Ceramics International* 36, 831–845.
- Scarinci, G., Brusatin, G., Bernardo, E., 2005. Chapter 2.7 – Glass foams. In: Scheffler, M., Colombo, P. (Eds.), *Glass Foams, in Cellular Ceramics: Structure, Manufacturing, Properties and Applications*. Weinheim: Wiley–VCH Verlag GmbH.
- Schmidt, J., Elsayed, H., Bernardo, E., Colombo, P., 2018. Digital light processing of wollastonite-diopside glass-ceramic complex structures. *Journal of the European Ceramic Society* 38, 4580–4584.
- Sepulveda, P., Binner, J.G.P., 1999. Processing of cellular ceramics by foaming and in situ polymerisation of organic monomers. *Journal of the European Ceramic Society* 19, 2059–2066.
- Si, W., Ding, C., 2018. An investigation on crystallization property, thermodynamics and kinetics of wollastonite glass ceramics. *Journal of Central South University* 25, 1888–1894.
- Si, W., Wang, Z., Zhang, W., Pan, W., 2016. Preparation of glass-ceramics by reactive crystallization with waste glass and mullite. *Key Engineering Materials* 697, 561–564.
- Si, W., Ding, C., Wang, R., Pan, W., 2018. Effect of fluoride on the reactive crystallization of fluoramphibole glass-ceramics. *Xiyu Jinshu Cailiao Yu Gongcheng/Rare Metal Materials and Engineering* 47, 259–263.
- Si, W., Ding, C., Zhang, W., Wang, X., Gao, H., 2012. Effect of CaF₂ on properties of glass-ceramics prepared by reactive crystallization of soda-lime glass. *Kuei Suan Jen Hsueh Pao/Journal of the Chinese Ceramic Society* 40, 1703–1707.
- Sighinolfi, D., 2010. Thermal expansion investigation on glasses used in ceramic industry. *Ceramic Forum International* 87, E33–E36.
- Smeacetto, F., Radaelli, M., Salvo, M., *et al.*, 2017. Glass-ceramic joining material for sodium-based battery. *Ceramics International* 43, 832933.
- Smeacetto, F., Chrysanthou, A., Salvo, M., Zhang, Z., Ferraris, M., 2009. Performance and testing of glass-ceramic sealant used to join anode-supported-electrolyte to Crofer22APU in planar solid oxide fuel cells. *Journal of Power Sources* 190, 402–407.
- Song, S., Wen, Z., Liu, Y., Wu, X., Lin, J., 2011. Bi-doped borosilicate glass as sealant for sodium sulfur battery. *Journal of Non-Crystalline Solids* 357, 3074–3079.
- Souza, M.T., Rennó, A.C.M., Peiti, O., Zanutto, E.D., 2017. New highly bioactive crystallization-resistant glass for tissue engineering applications. *Translational Materials Research* 4, 014002.
- Sun, L., Liu, C., Fang, J., Zhang, J., Lu, C., 2019. Crystallization behavior and thermal properties of B₂O₃-containing MgO–Al₂O₃–SiO₂–Li₂O glass-ceramic and its wettability on Si₃N₄ ceramic. *Journal of the European Ceramic Society* 39, 1532–1539.
- Teixeira, L.B., Fernandes, V.K., Maia, B.G.O., Arcaro, S., de Oliveira, A.P.N., 2017. Vitrocrystalline foams produced from glass and oyster shell wastes. *Ceramics International* 43, 6730–6737.
- Thamaraiselvi, T.V., Rajeswari, S., 2004. Biological evaluation of bioceramic materials – A review. *Trends in Biomaterials and Artificial Organs* 18, 9–17.
- Thavorniyutikarn, B., Tesavibul, P., Sitthiseripratip, K., *et al.*, 2017. Porous 45S5 Bioglass[®]-based scaffolds using stereolithography: Effect of partial pre-sintering on structural and mechanical properties of scaffolds. *Materials Science and Engineering C* 75, 1281.
- Tian, Y.L., Cui, Z., Yuan, C.M., *et al.*, 2013. Study on dependability and repeatability of measurement method of mean linear thermal expansion coefficients of glasses. *Advanced Materials Research* 694–697, 1271–1275.
- Valderrama, D.M.A., Cuaspad, J.A.G., Roether, J.A., Boccaccini, A.R., 2019. Development and characterization of glass-ceramics from combinations of slag, fly ash, and glass cullet without adding nucleating agents. *Materials* 12, 2032.
- Vitale-Brovarone, C., Bairo, F., Verné, E., 2009. High strength bioactive glass-ceramic scaffolds for bone regeneration. *Journal of Materials Science: Materials in Medicine* 20, 643–653.
- Wadsworth, F.B., Vasseur, J., Llewellyn, E.W., *et al.*, 2016. Sintering of viscous droplets under surface tension. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* 472, 20150780.
- Wang, H., Chen, Z., Ji, R., Liu, L., Wang, X., 2018. Integrated utilization of high alumina fly ash for synthesis of foam glass ceramic. *Ceramics International* 44, 13681–13688.
- Wang, L., Mei, L., He, G., Li, J., Xu, L., 2001. Preparation of Ce: YAG glass-ceramics with low SiO₂. *Journal of the American Ceramic Society* 94, 3800–3803.

- Warren, B., 2015. XV. The Structure of Melilite $(\text{Ca,Na})_2(\text{Mg,Al})_1(\text{Si,Al})_2\text{O}_7$. *Zeitschrift für Kristallographie - Crystalline Materials* 74, 131–138.
- Wu, C., Chang, J., 2013. A review of bioactive silicate ceramics. *Biomedical Materials* 8, 032001.
- Wu, C., Chang, J., Zhai, W., 2005. A novel hardystonite bioceramic: Preparation and characteristics. *Ceramics International* 31, 27–31.
- Wu, C., Ramaswamy, Y., Chang, J., *et al.*, 2008. The effect of Zn contents on phase composition, chemical stability and cellular bioactivity in Zn–Ca–Si system ceramics. *Journal of Biomedical Materials Research - Part B Applied Biomaterials* 87, 346–353.
- Wu, C., Chen, Z., Yi, D., Chang, J., Xiao, Y., 2014. Multidirectional effects of Sr-, Mg-, and Si-containing bioceramic coatings with high bonding strength on inflammation, osteoclastogenesis, and osteogenesis. *ACS Applied Materials and Interfaces* 26, 4264–4276.
- Xi, C., Zheng, F., Xu, J., *et al.*, 2018. Preparation of glass-ceramic foams using extracted titanium tailing and glass waste as raw materials. *Construction and Building Materials* 190, 896–909.
- Xiaofang, L., Feng, Z., Huajun, S., *et al.*, 2002. Effects of synthesis method on microstructure and infrared radiant characteristics of cordierite. *Journal of Ceramics*. (Online publication).
- Zanotto, E.D., 2010. A bright future for glass-ceramics. *American Ceramic Society Bulletin* 89, 19–27.
- Zhang, Q., He, F., Shu, H., *et al.*, 2016. Preparation of high strength glass ceramic foams from waste cathode ray tube and germanium tailings. *Construction and Building Materials* 111, 105–110.
- Zhang, W., Gao, H., 2007. Effect of fluormica addition on reactive crystallization in machinable fluoramphibole glass-ceramics. *Kuei Suan Jen Hsueh Pao/ Journal of the Chinese Ceramic Society* 35, 1396–1400.
- Zhang, W., Liu, H., 2013. A low cost route for fabrication of wollastonite glass-ceramics directly using soda-lime waste glass by reactive crystallization-sintering. *Ceramics International* 39, 1943–1949.
- Zhang, W.-y., Gao, H., Li, B.-y., Jiao, Q.-b., *et al.*, 2006. A novel route for fabrication of machinable fluoramphibole glass-ceramics. *Scripta Materialia* 55, 275–278.
- Zhang, W.Y., Gao, H., Xu, Y., 2011. Sintering and reactive crystal growth of diopside–albite glass-ceramics from waste glass. *Journal of the European Ceramic Society* 31, 1669–1675.
- Zhao, T., Li, A.-J., Qin, Y., *et al.*, 2019. Influence of SiO_2 contents on the microstructure and mechanical properties of lithium disilicate glass-ceramics by reaction sintering. *Journal of Non-Crystalline Solids* 512, 148–154.
- Zhao, T., Qin, Y., Zhang, P., Wang, B., Yang, J.-F., 2014. High-performance, reaction sintered lithium disilicate glass-ceramics. *Ceramics International* 40, 12449–12457.
- Zhu, M., Ji, R., Li, Z., *et al.*, 2016. Preparation of glass ceramic foams for thermal insulation applications from coal fly ash and waste glass. *Construction and Building Materials* 112, 398–405.
- Zhu, W., Chen, J., Jiang, C., Hao, C., Zhang, J., 2013. Joining of porous alumina with a $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ glass-ceramic. *Journal of the American Ceramic Society* 96, 1738–1744.
- Zocca, A., Elsayed, H., Bernardo, E., *et al.*, 2015. 3D-printed silicate porous bioceramics using a non-sacrificial preceramic polymer binder. *Biofabrication* 7, 025008.

Glasses and Glass-Ceramics as Sealing Materials

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Introduction

Sealing glasses have traditionally been used for the sealing of lamps and vacuum tubes by means of a slow and expensive process which required sealing temperatures close to 1400°C. The beginning of the development of sealing glasses started with research carried out by Owens Illinois and Corning Glass Works. The objective was the preparation of glasses with good flow properties at temperatures around 500°C and with a thermal expansion coefficient sufficiently low to be applied in sealing the front plate of TV tubes. Glasses in the system ZnO-PbO-B₂O₃ were developed for this purpose (Sinhdeo and Shukla, 1984).

At the end of the 1950's, a research group from Fairchild Semiconductor Company considered that the sealing glasses developed by the television industry could also be used to join the alumina plates employed to encapsulate the silicon integrated circuits and protect them from environmental humidity. Nevertheless, the thermal expansion coefficient of the glasses in the system ZnO-PbO-B₂O₃ ($7\text{--}12 \times 10^{-6}\text{K}^{-1}$) is too high to adjust to an alumina-based ceramic ($\sim 6.5 \times 10^{-6}\text{K}^{-1}$) and to the metallic conductors embedded through the glass ($4\text{--}4.7 \times 10^{-6}\text{K}^{-1}$). The modifications introduced in the glass composition in order to decrease the thermal expansion coefficient would invariably lead to an increase in the softening temperature. The solution to the problem consisted of uniformly dispersing a ceramic phase of very low thermal expansion coefficient; these composite materials provided a sufficiently wide thermal expansion coefficient interval able to cover the needs of the microelectronics industry throughout the 1960s.

The increasing complexity of the silicon integrated systems demanded new sealing glasses with sealing temperatures as low as (<450°C) which led to the development of glasses with high thermal expansion coefficients and very low softening temperatures and also to the study of glass-ceramics for sealing (Forbes, 1967; Ray *et al.*, 1973a,b, 1976; Tindyal and Ott, 1978). These latter materials combine the good thermal properties of the glasses with a high mechanical and chemical resistance.

In parallel to the advances in the preparation of new glass compositions for sealing, much effort has been dedicated to the development of new sealing procedures and with the purpose of understanding the reaction mechanisms taking place at the glass/ceramic and glass/metal interfaces. The extensive literature on these topics, more than 3500 citations (source: Scopus), is indicative of the complexity and technological and scientific importance of sealing glasses and glass-ceramics.

Requirements for Sealing Glasses

The glass properties must be precisely adjusted to certain values in order to be used as a hermetic seal in a particular system. The specifications that the glass must fulfill in order to be effective as a sealing material depend on the nature of the materials to be sealed, the complexity of the system, the different functionalities that the seal must perform and the system working conditions (Sinhdeo and Shukla, 1984). In many of the applications, the glass sealant will not only carry out the sealing function but also perform other functions such as electrical insulator, environmental protection, chemical and mechanical protection, diffusional barrier, etc.

Flow Temperature and Viscosity

The glass fluidity required to perform the seal depends on the adjustment between the parts to be sealed, the application of the sealing glass and the sealing time. Using polished surfaces and under pressure, sealants with viscosities as high as 10^{10} dPa s or even higher may be employed. Nevertheless, when there is a poor adjustment between components, considerable fluidity is necessary; the viscosity must be as low as 10^4 dPa s or even lower. In any case, the sealing must be carried out at a temperature below the melting temperature or the degradation temperature of the materials to be sealed. Normally, the melting temperature of the materials to be sealed is sufficiently high and the limitations come from the maximum temperature at which the whole system can be exposed without suffering damage. This is the case for electronic systems where the complexity and sensitivity of the integrated circuits impose sealing temperatures even lower than 200°C. This requirement considerably limits the possible suitable compositions.

When a glass-ceramic is applied, there is an increase of viscosity due to the crystallization process with the corresponding adjustment of properties and a final rigid material at high temperature can be obtained, desirable for the most refractory sealing applications. Fig. 1 shows the viscosity-temperature curves for some sealing glasses for solid oxide fuel cells (SOFC) with typical sealing and operation temperatures between 800 and 950°C (Rodríguez-López *et al.*, 2020). After crystallization these glasses become rigid seals with final viscosities at the operation temperature around 10^{12} dPa s which make them mechanically stable.

Together with direct glass viscosity measurements using a high temperature viscometer, hot-stage microscopy is a very useful tool to investigate the sintering and flow of glass powders, providing information about the relevant viscosity points, wettability and adherence on different substrates (Pascual *et al.*, 2005; Lara *et al.*, 2004).

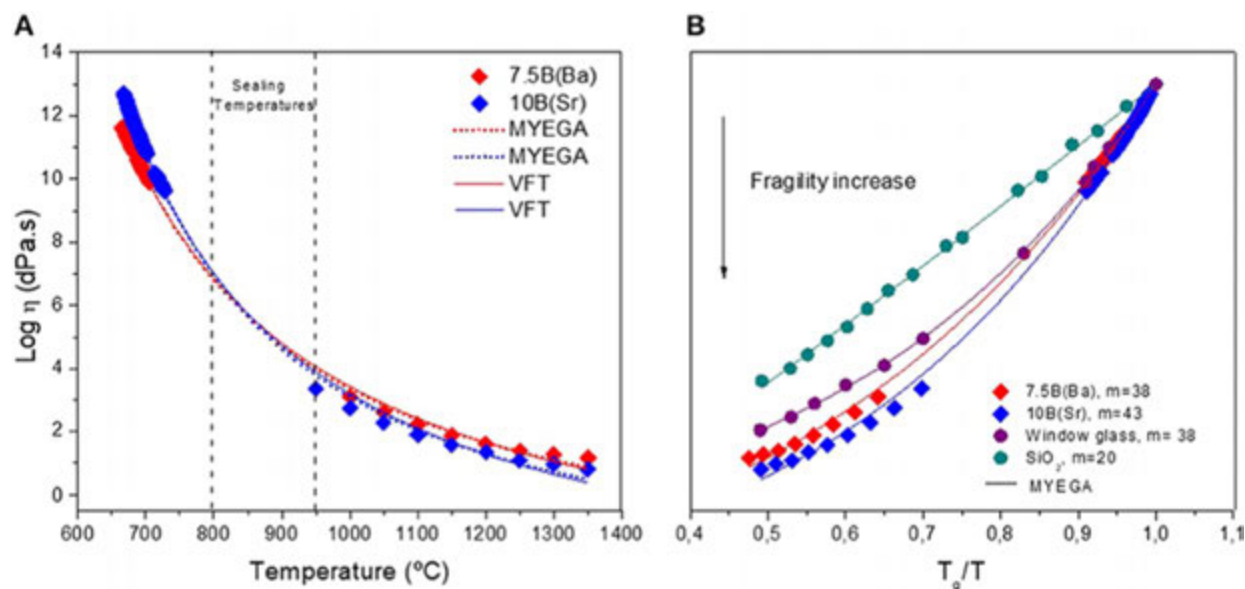


Fig. 1 (A) Viscosity-temperature curves for the sealing glasses 7.5B(Ba) and 10B(Sr) for SOFC. Fit of the experimental points: VFT equation (continuous lines) and MYEGA equation (dotted lines). (B) Viscosity curves vs. T_g/T for the glasses 7.5B(Ba), 10B(Sr), window glass and silica, the continuous lines show the fit with MYEGA equation. After Rodríguez-López, S., Malzbender, J., Justo, V.M., *et al.*, 2020. Thermo-mechanical stability and gas-tightness of glass-ceramics joints for SOFC in the system MgO-BaO/SrO-B₂O₃-SiO₂. *Frontiers in Materials* 7. doi:10.3389/fmats.2020.00019.

Thermal Expansion Coefficient

The thermal expansion coefficient (α) must be adjusted to one of the materials to be sealed from room temperature up to the glass transformation temperature. The differences in thermal expansion between the glass and the materials to be sealed can generate mechanical stresses provoking fracture of the glass or the loss of adherence between the glass and the system materials (Varshneya and Mauro, 2019; Dai *et al.*, 2017). The fit of α will, therefore, influence the mechanical stability of the system, especially in those cases in which it is going to be under thermal cycles of heating and cooling during its useful life (Rodríguez-López *et al.*, 2017). As a reference, stresses generated due to thermal expansion coefficient differences equal to or lower than $0.5 \times 10^{-6} \text{K}^{-1}$ are considered tolerable. In some cases, a suitable design of the seal geometry can determine that the generated mechanical stresses are compressive, reinforcing the mechanical properties of the system.

The α of glass materials with fixed composition, structure and microstructure is time independent. When the material constituting the seal is a glass-ceramic, it is necessary to consider the dimensional as well as thermal expansion coefficient changes that will occur during the glass devitrification process, specially taking into account that, in most cases, the sealing, nucleation and crystal growth take place during a unique and continuous process. Fig. 2 shows an example of a good fit of the thermal expansion between glass-ceramics and steels, FeCrAlloy and Crofer22APU. The glass-ceramics were obtained from different thermal treatments of the glass Mg1.5–55. The crystallization process ensures a better fit of the α due to the crystallization of phases with the desired α (Lara, 2006).

Adherence

The establishment of a hermetic seal implies the formation of an interface between the glass material and a ceramic or metallic material. The joining at the interface can take place as a consequence of van der Waals forces or by means of the formation of chemical bonding through different mechanisms that comprise interdiffusion, oxidation and phase transformations.

The thermomechanical stability of the interface requires the establishment of a chemical equilibrium. The glass/metal and ceramic/metal interfaces are not normally compatible from the point of view of the redox reactions, and the reactions taking place imply metal oxidation and the reduction of a cation for the glass or ceramic material. In industrial processes, the necessary oxide layer for the equilibrium at the interface is generated by means of the pre-oxidation of the metallic materials (Shen *et al.*, 2019; Fakouri Hasanabadi *et al.*, 2020).

Chemical Durability

In many applications, the sealing glass performs a protection function against attack from ambient humidity or very corrosive atmospheres. The technical problem in many cases is to make the sealing temperature low enough to carry out the sealing without

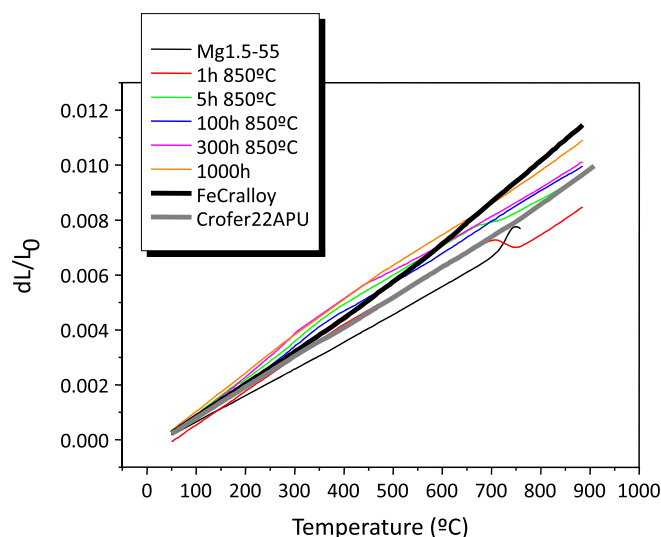


Fig. 2 Dilatometric curve of Mg1.5-55 glass and corresponding glass-ceramics obtained after treatment at 850°C during different times (from 1 h to 1000 h) and the dilatometric curve for steels FeCrAlloy and Crofer22APU. After Lara, C., 2006. Sellos vitrocerámicos del sistema RO-BaO-SiO₂ R=Mg, Zn para pilas de combustible de óxido sólido SOFC. Ph.D. thesis. Universidad Autónoma de Madrid (UAM).

damaging the system, and with a high chemical resistance. In conventional glasses, these properties vary in opposing senses with the composition.

New applications demand sealing glasses with, for example, a high resistance against attack from molten salts or dual atmospheres (reducing/oxidizing) at a high temperature, high enough to achieve gas-tightness and avoid diffusion problems that limit the development of certain energy-generation systems (Pascual *et al.*, 2003; Rodríguez-López *et al.*, 2016b).

Electrical Resistance

Glass is often going to be the insulating material between two metallic conductors. In addition, to the previously mentioned specifications, it is necessary to add a high electrical resistance that ensures suitable electrical insulation between conductors (Rodríguez-López *et al.*, 2016b). In many cases, alkaline-free glasses are prepared which have a high electrical resistance, albeit at the expense of increasing the glass softening temperature.

Control of Emission Gases

The sealing glasses must not generate, either during the sealing process or operation, reaction products which could damage the system to be sealed. The emission of traces of water vapor can particularly affect systems sensitive to humidity, such as integrated systems.

The outlined specifications constitute those that the sealing material must generally fulfill. The importance of any of them will depend on the specific application. Due to the high number of specifications, often required simultaneously, the formulation of sealing glasses and their treatment have become a field of research and development of high technological impact.

Compositions of Glasses for Sealing

Sealing and enameling glasses are classified according to some of their characteristics such as composition, thermal expansion coefficient, dilatometric softening temperature or the specific application in which they are used (Donald, 1993a; James, 1995; Takamori, 1979). On the other hand, the final seals can be classified in different categories according to different criteria. As a consequence, the seals can be classified as a function of geometry, type of metal or alloy used for the metallic parts, preparation method, adherence mechanism or nature and intensity of the residual mechanical stress of the seal.

Frequently, the sealing glasses are classified into two wide categories according to the α value. Hard glasses are those with α lower than $5 \times 10^{-6} \text{K}^{-1}$ and for soft glasses, α is higher than $8 \times 10^{-6} \text{K}^{-1}$. In general, the glasses with high α have relatively low transformation and softening temperatures and are often referred to as sealing glasses. On the contrary, low α glasses have high transformation and softening temperatures.

Table 1 Compositions of silicate and borosilicate glasses for sealing (mol%)

SILICATE GLASSES												T_s ($^{\circ}\text{C}$)	$\alpha \cdot 10^6 \text{K}^{-1}$
Li_2O	Na_2O	K_2O	MgO	BaO	ZnO	B_2O_3	Al_2O_3	SiO_2	PbO	Other constituents			
–	15.1	5	–	10.1	5	12.2	–	44.9	–	7.2CaF ₂ + NiO + CoO	435	14.4	
12.9	–	19.5	4.9	–	–	–	6.1	53	–	CaO	480	14.1	
40.1	–	–	–	–	–	–	7.5	52.4	–	–	500	11.9	
35.2	–	–	–	–	–	–	7.5	57.3	–	–	500	10.9	
–	–	–	–	–	–	–	–	59.9	40.1	–	–	7.4	
21.1	–	–	–	–	–	–	8.9	56.0	–	Cu ₂ O + Fe ₂ O ₃	840	2.3	
BOROSILICATE GLASSES													
25.3	–	–	5.8	–	–	63.4	1.7	3.9	–	–	515	8.3	
–	–	–	–	–	–	26.6	–	30.8	42.6	–	–	8	
14.4	–	–	4.6	–	–	70.7	–	10.3	–	–	500	7.6	
4.4	5.4	1.4	1.6	–	–	63.8	1.3	22.1	–	–	465	6.1	
1.7	2.8	1.6	–	1.3	–	14.1	4.7	72.9	–	KCl	460	5.4	
–	–	–	–	–	41.1	24.0	–	18.1	6.4	10.4CuO	571	5	
–	–	–	–	–	60.1	25.8	–	12.3	0.7	SnO ₂	–	4.5	
–	–	–	–	–	56.3	23.1	–	17.4	–	P ₂ O ₅	700	4.2	

Due to the relationship of the nature of the oxide glass formers and the final properties, it is scientifically very appropriate to classify the sealing glasses according to the glass forming system they belong to. In this case, two large groups can again be distinguished, namely glass and glass-ceramic materials.

Glass Materials for Sealing

Silicate and borosilicate glasses

Many glass compositions for sealing are based on silicate and borosilicate systems (Kreidl, 1983). The most common systems include alkaline silicates and borosilicates, lead silicates, zinc and lead silicates, lead borosilicates and zinc borosilicates (Table 1). Lithium oxide is a constituent in many compositions, particularly mixed alkali compositions. Alumina is a constituent of almost all compositions due to its stabilizing effect.

The α and softening temperatures of these glasses cover a wide range of values, between 2.3 and $15 \times 10^{-6} \text{K}^{-1}$, and between 400 and 850°C , respectively. Table 1 lists some typical compositions and thermal properties of the corresponding glasses (Pascual *et al.*, 1997).

Borate glasses

Many of the glass-forming systems include boron oxide as a main constituent, together with alumina, lead and zinc oxides.

Most of these glasses possess softening temperatures lower than 500°C , and are the basis of the low temperature sealing glasses with wide application in microelectronics (Donald, 1993a). Their range of α , $(5 - 15) \times 10^{-6} \text{K}^{-1}$, makes them compatible with materials such as alumina, metallic alloys and steels. The addition of metallic halides provides glasses with very low softening temperatures, high α and low viscosity. However, lead oxide or lead fluoride is avoided in sealing-glass compositions due to their toxic character. The chemical durability of the borate glasses, although higher than that of phosphate glasses, is lower than that of silicate and borosilicate glasses.

Phosphate glasses

Phosphate glasses for sealing contain phosphorus proportions around 50 mol% due to the higher stability of this type of composition against hydrolytic attack (Ray *et al.*, 1973a,b, 1976; Tindiyala and Ott, 1978; Kobayashi, 1987; Chambers *et al.*, 1989; Abe and Hosono, 1989; Peng and Day, 1991a,b). As a consequence of the particular structure of these glasses, the attack by water occurs through a mechanism of hydrolysis of the phosphate chains and congruent glass dissolution (Martin, 1991; Bunker *et al.*, 1984; Rajaram and Day, 1988). The low resistance against hydrolytic attack has limited the commercial application of many of these glasses and has hindered taking advantage of their good thermal and optical properties. The phosphate glasses exhibit high α together with very low softening and melting temperatures, both very relevant properties from the point of view of low temperature sealing.

Resistance to hydrolytic attack may be improved by adding alkaline-earth oxides or high polarizability metals, capable of creating chelates with non-bridging oxygens of the phosphate chains, and thereby increasing their interconnection (Ray *et al.*, 1973a,b, 1976; Tindiyala and Ott, 1978). Incorporation of alumina, even in small amounts, considerably improves the chemical resistance of the phosphate glasses due to the capability of aluminum for establishing bridging oxygens between different phosphate chains. Unfortunately, the improvement in the hydrolytic resistance of the phosphate glasses produced by the addition

Table 2 Some commercial sealing glasses

Manufacturer and code	Type of glass	Application	T_s (°C)	Operating T (°C)	$\alpha \cdot 10^6 K^{-1}$
Corning 1990	Alkaline phosphate	Seal for iron	500	512	$\alpha_{0-300} = 12.4$
Schott 8095	Alkaline lead silicate	Seal for copper	630	982	$\alpha_{20-300} = 9.1$
Schott 8512	Glass containing FeO	Seal for 52Ni/Fe alloy	660	975	$\alpha_{20-300} = 9.1$
Schott 8418	Alkaline alkaline-earth silicate	Seal for alloy 51Ni/1Cr/Fe	708	1.035	$\alpha_{20-300} = 9.0$
Schott 8531	Lead silicate	Seal for copper/Semiconductor encapsulation	585	822	$\alpha_{20-300} = 9.0$
GB Glass GS85	Alkaline alkaline-earth borosilicate	Graduated seals	710	–	$\alpha_{50-400} = 8.3$
Schott 8454	Alkaline alkaline-earth silicate	Seal for alloy 28Ni/23Co/Fe and alumina ceramics	745	1.050	$\alpha_{20-300} = 6.4$
Corning 7056	Borosilicate	Seal for Kovar	718	1.058	$\alpha_{0-300} = 5.2$
Schott 8250	High boron contain glass	Seal for Mo and alloy 28Ni/18Co/Fe	715	1.060	$\alpha_{20-300} = 5.0$
Corning 7052	Borosilicate	Seal for Kovar, Mo or W	712	1.128	$\alpha_{0-300} = 4.6$
Corning 7720	Borosilicate	Seal for W	755	1.146	$\alpha_{0-300} = 3.6$
Schott 8435	Borosilicate	Seal for Kovar or Mo and Al_2O_3	550	800–900	$\alpha = 5.8$

of stabilizing oxides provokes a parallel increase in the softening temperature and a decrease in α . Some of the compositions of phosphate sealing glasses can be found in refs. (Brow *et al.*, 1998; Brow, 2000; Morena, 2000).

An alternative method to improve the hydrolytic resistance without substantially altering the thermal properties is nitridation in an anhydrous NH_3 atmosphere. Nitrogen incorporation up to proportions of 15 wt% produce an increment of the hydrolytic resistance of up to three orders of magnitude without notably diminishing the α value (Pascual and Durán, 1996a,b). Compositions of nitrided phosphate glasses belong to the alkaline metaphosphate, alkaline-earth metaphosphate, and alkaline-alkaline earth phosphate and lead alkaline phosphate systems. Nitrogen incorporation in the phosphate glasses provides sealing glasses with a wide range of thermal expansion coefficients and very low sealing temperatures. The hydrolytic resistance of these glasses with maximum nitrogen content is of the same order of magnitude as those of commercial soda-lime glasses.

Recently, the addition of a certain proportion of silicon nitride has been proposed to tailor the structural, chemical and thermal properties of phosphate sealing glasses (Jiang *et al.*, 2018).

Glasses based on other oxide glass formers

A certain number of sealing glass compositions are based on less common oxide formers, in particular, Sb_2O_3 , As_2O_3 and V_2O_5 (Zhang *et al.*, 2014). Some of the compositions containing Sb_2O_3 present high α , $\alpha > 20 \times 10^{-6} K^{-1}$, together with a very low softening temperature, $< 300^\circ C$.

Devitrifying Sealing Glasses

The glasses described in the previous sections remain in the glassy state during and after sealing. Nevertheless, sealing glasses which totally or partially crystallize during the sealing process have been developed (Lee *et al.*, 1990; Volf, 1984). These glasses, firstly described by Claypoole (1959), are called devitrifying sealing glasses. They were originally based on zinc and lead borate systems of high thermal expansion coefficient or on zinc borosilicate systems of lower thermal expansion coefficient (McMillan, 1979). The crystallizing sealing glasses are normally used as glass powder mixed with an agglomerant; crystallization takes place during sealing through a mechanism of superficial nucleation.

In Table 2, some commercial glasses based on some of the previously mentioned systems are listed. There is a great variety of commercial glasses developed for sealing numerous metals, alloys and semiconductors, including silicon, tungsten, molybdenum, platinum and low expansion nickel-iron alloys containing 42%, 46% and 52% of Ni, stainless steels and iron.

Glass-ceramic materials for sealing

Glass-ceramic materials, defined as ceramic polycrystalline materials, prepared by controlled crystallization were developed for the first time by Corning Glass Works in the 1950's (Strand, 1986; Grossman, 1982; Beall and Duke, 1983; Smith, 1989; Donald and Cahn, 1993b; Deubener *et al.*, 2018). Nowadays, glass-ceramic materials are becoming more relevant in the field of glass/metal sealing. These materials are processed and formed in the same way as glass followed by a controlled crystallization process through a thermal treatment. The crystallinity of the sealing glass-ceramics can exceed 90%, while the size of the crystals is not normally greater than $1 \mu m$. The crystalline phases present, their proportion and microstructure depend on the glass composition, the thermal treatment and the presence or absence of nucleating agents and their nature.

The principles for the design and fabrication of glass-ceramic sealants are very similar to the fabrication of glass/metal seals. Nevertheless, the properties can be varied in a wide range of values through careful control of the crystallization process.

In conventional glasses, crystallization initiates at the surface and progresses towards the interior of the material giving rise to microstructures with large anisotropic crystals. These materials are in general mechanically weak because the big crystals act as

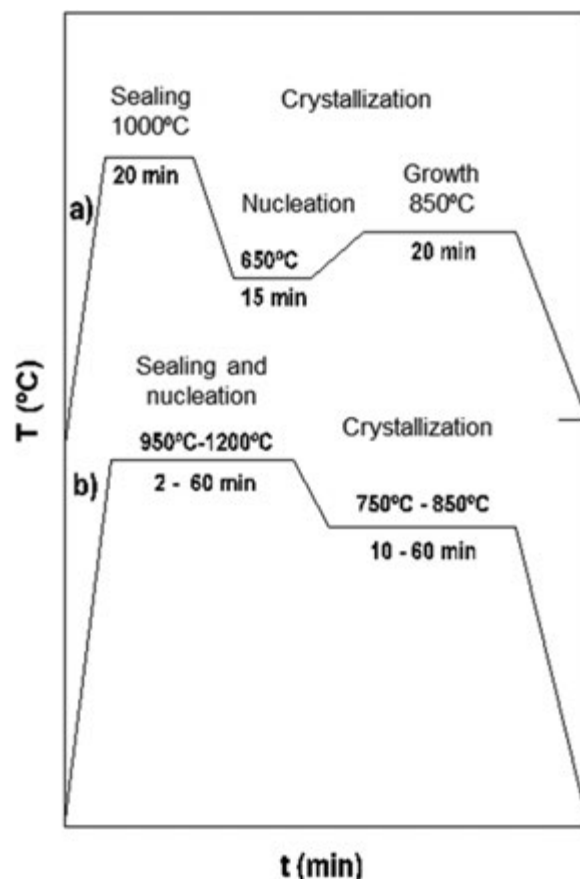


Fig. 3 Thermal cycle scheme for the fabrication of a seal with glass-ceramic S. (a) with Inconel 718 and Hastelloy C276, (b) with stainless Steel 430 type. After Pascual, M.J., Pascual, L., Durán, A., 1997. Vidrios y vitrocerámicos para soldadura: usos tradicionales y nuevas áreas de aplicación. Boletín de la Sociedad Española de Cerámica y Vidrio 36 (4), 383–398.

stress concentration centers. The control of the crystallization process through the introduction in the composition of suitable proportions of nucleating agents and a careful thermal treatment can, on the other hand, lead to the formation of isotropic microstructures composed of small randomly oriented crystals, linked by a residual glassy phase.

A glass-ceramic material is normally prepared employing a two-step thermal treatment (Fig. 3). During the nucleation step, a great number of small heterogeneities or crystallization nuclei are formed in the glass bulk from which crystals are developed in a second thermal treatment step at a higher temperature than for nucleation.

In practice, high nucleation rates are achieved by adding suitable nucleating agents to the batch. The most employed nucleating agents include elemental metals, oxides, metallic halides and sulfides (McMillan *et al.*, 1966a; Grossman, 1982). The mechanism according to which a nucleating agent acts has not clearly been determined for all glass-ceramic systems. Nevertheless, some mechanisms have been proposed (McMillan *et al.*, 1966a) which imply the precipitation of small crystals of a compound formed by the reaction between the nucleating agent and the glass constituents.

In a first approximation, the thermal expansion coefficient of a glass-ceramic material is an additive function of the thermal expansion of the different phases present and may be represented by the following relationship (Hammeter and Loehman, 1987):

$$\alpha_{\text{glass-ceramic}} = \frac{\left(\frac{\alpha_1 K_1 W_1}{\rho_1} + \frac{\alpha_2 K_2 W_2}{\rho_2} + \dots \right)}{\left(\frac{K_1 W_1}{\rho_1} + \frac{K_2 W_2}{\rho_2} + \dots \right)} \quad (1)$$

where α_i is the thermal expansion coefficient of the different phases in the glass-ceramic, K_i is their elastic modulus, W_i the corresponding weight fractions and ρ_i , their densities. The ability of the glass-ceramic materials to adapt their thermal-expansion characteristics is, hence, a direct consequence of the capability to control the nature and proportion of the crystalline phases present in the final glass-ceramic material.

As is the case for glasses, glass-ceramic materials useful for sealing applications can be classified according to composition, more specifically to the glass forming system.

In addition to devitrifying glasses, glass-ceramics can be obtained from the sintering and crystallization of powders following specific and controlled thermal treatment in order to achieve a final material with the desired microstructure and properties. In this case, all parameters related to the precursor glass powders, such as particle size and shape factor, must also be controlled.

Silicate glass-ceramics

The compositions of silicate glass-ceramics for sealing are mainly based on alkaline silicates, alkaline-earth silicates, zinc silicate, cadmium silicate and lead silicates.

The $\text{Li}_2\text{O}-\text{SiO}_2$ system, with small additions (< 5 wt%) of sodium, potassium, boron, aluminum or zinc, constitute the base of the alkaline silicate glass-ceramics. The addition of P_2O_5 or F^- as nucleating agents induces the crystallization of lithium metasilicate and disilicate together with silica phases or β -spodumene. Depending on the proportions and the nature of the phases present, the resulting glass-ceramics exhibit moderate to high thermal expansions ($\alpha = 8\text{--}19 \times 10^{-6}\text{K}^{-1}$) (McMillan *et al.*, 1966b; West and Glasser, 1970).

Glass-ceramic materials from the $\text{Li}_2\text{O}-\text{ZnO}-\text{SiO}_2$ system were prepared for the first time by McMillan and Partridge (1963). Later studies on this system were undertaken by Chen and McMillan (1985a,b) and Donald *et al.* (1989, 1992). These materials can contain from 30 up to 59 wt% zinc oxide. Normally, P_2O_5 is used as nucleant but the influence of a great number of transition metal oxides on the crystallization, microstructure and thermal expansion characteristics have also been explored. The investigated oxides include TiO_2 , ZrO_2 , HfO_2 , V_2O_5 , Nb_2O_5 , Ta_2O_5 , Cr_2O_3 , MoO_3 , WO_3 , NiO and CuO (Chen and McMillan, 1985b; Donald *et al.*, 1992). The nucleant efficiency considering the activation energy for crystallization is directly related with the field intensity of the metallic cation and it is particularly important for molybdenum, wolframium and vanadium. Applying a standard thermal treatment, the thermal expansion coefficient (α) can vary in the range $(11\text{--}16) \times 10^{-6}\text{K}^{-1}$, depending on the added nucleant species.

The number of papers on glass-ceramics of the $\text{MgO}-\text{ZnO}-\text{SiO}_2$ system is very limited (Metcalf and Donald, 1991). It is well known that the glass forming ability of this system is favored by the incorporation of small additions of Al_2O_3 , together with TiO_2 as nucleating agent. The glass-ceramic materials contain variable proportions of enstatite solid solution, willemite and cristobalite, and their thermal expansion coefficients are in the range $(3.5\text{--}10.2) \times 10^{-6}\text{K}^{-1}$, depending on the crystallization temperature employed.

Glass-ceramics of the $\text{Li}_2\text{O}-\text{PbO}-\text{SiO}_2$ system contain small amounts of Al_2O_3 . The main crystalline phases are lithium and cadmium silicates. Other types of glass-ceramic materials are included in the $\text{PbO}-\text{SiO}_2$ system, which incorporate P_2O_5 and TiO_2 in order to obtain a wide range of thermal expansion coefficients. As mentioned previously, the tendency now is to totally avoid PbO due to its toxicity.

Aluminosilicate glass-ceramics

The aluminosilicate glass-ceramic materials for sealing are mainly based in the systems $\text{Li}_2\text{O}-\text{MO}-\text{Al}_2\text{O}_3-\text{SiO}_2$, $\text{M} = \text{Mg}, \text{Ca}$ or Ba , $\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ and $\text{Li}_2\text{O}-\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$, employing TiO_2 , ZrO_2 , or a mixture of both, as nucleating agent.

In the $\text{Li}_2\text{O}-\text{MO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ systems, $\text{M} = \text{Mg}, \text{Ca}$ or Ba , the main developed crystalline phases include, together with silica, solid solutions of β -spodumene, β -eucryptite, β -quartz, cordierite, enstatite, wollastonite, sphene and celsian. Depending on the crystalline phases present, thermal expansion coefficients can range from zero to even negative values to $9 \times 10^{-6}\text{K}^{-1}$ (McMillan and Partridge, 1972).

The preparation of glass-ceramics in the $\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system, free of alkalines, was developed by Corning Glass Works, employing TiO_2 as nucleating agent. The prepared glass-ceramics presented relatively low thermal expansion coefficients and contain gahnite and rutile as main crystalline phases. Later works in this system were carried out by McMillan and Partridge (1972), Partridge *et al.* (1989a,b) and Vargin and Miklyukov (1968), using TiO_2 as nucleant, and Strand *et al.* (1976) and Holleran and Martin (1987) employing ZrO_2 . Depending on the glass composition and the adopted thermal treatment, it is possible to obtain materials with an α between 3 and $15 \times 10^{-6}\text{K}^{-1}$. The materials with higher thermal expansions contain a significant proportion of cristobalite.

Glass-ceramic materials of zinc aluminosilicate containing lithium as the alkaline oxide have also been prepared. Omar *et al.* (1991) prepared glass-ceramics in the system $\text{Li}_2\text{O}-\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ that contain 13 wt% of Li_2O and up to 28 wt% ZnO . The addition of TiO_2 and ZrO_2 as nucleating agents promotes the crystallization of phases: $\beta_{11}-\text{Li}_2\text{ZnSiO}_4$, $\gamma_0-\text{LiZnSiO}_4$, β -spodumene and β -eucryptite; the corresponding thermal expansion coefficients are in the range $(3.6\text{--}10.0) \times 10^{-6}\text{K}^{-1}$.

Boroaluminosilicate glass-ceramic materials

Zinc boroaluminosilicate glass-ceramics are derived from the corresponding zinc aluminosilicate systems by partial substitution of boron oxide, favoring the crystallization of zinc aluminate, zinc borate and quartz.

Phosphate glass-ceramic materials

Many of the papers on glass-ceramic materials in this system are dedicated to the preparation of biomaterials based on calcium phosphate for their application as implants.

The attention focused on this system as a potential base for the preparation of sealing materials has been limited. Particularly interesting are the works from Wilder *et al.* (1982) on the crystallization behavior of a number of phosphate systems including

$\text{Na}_2\text{O-CaO-P}_2\text{O}_5$, $\text{Na}_2\text{O-BaO-P}_2\text{O}_5$, $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ and $\text{Li}_2\text{O-BaO-P}_2\text{O}_3$ employing TiO_2 , ZrO_2 , Y_2O_3 , La_2O_3 , Ta_2O_5 , WO_3 and platinum as nucleating agents. The thermal expansion coefficients obtained for these systems are in the range $(16.2\text{--}22.5) \times 10^{-6}\text{K}^{-1}$.

Wang and James (1990) demonstrated that TiO_2 together with Al_2O_3 can be used to promote crystallization in calcium phosphate glasses. The glass-ceramics possess thermal expansion coefficients in the range $(8.6\text{--}14.1) \times 10^{-6}\text{K}^{-1}$.

Additionally, Langlet *et al.* (1992) studied the crystallization behavior of aluminum phosphate glasses and demonstrated that Li_2O , NaPO_3 and AlF_3 can favor crystallization.

A compilation of relevant glass-ceramic compositions for sealing and the important characteristics to be taken into account for a successful seal was published by Donald *et al.* (2011). Additionally, composite materials formed from the mixture of glass or glass-ceramic compositions with ceramic or metallic fillers in order to improve or enhance the sealing material properties is another important field of research.

Glasses or Glass-Ceramics for Sealing - Relative Advantages

The selection of a glass or a glass-ceramic material as a seal depends on the properties that the final application requires and on the thermal characteristics of the system to be sealed.

As well as glasses, glass-ceramics can be easily applied and formed at high temperature while they are in a glassy state. During this first step of the process, the interfacial reactions: glass/metal or glass/ceramic take place, which ensure adherence between the materials to be sealed.

One of the notable advantages of glass-ceramics compared with the corresponding glasses is the possibility to obtain a wide range of thermal expansion coefficients and, in some cases, nonlinear expansion characteristics by means of the control of composition, addition of nucleating agents and the crystallization thermal treatment. As a consequence, the possibility of a better fit between thermal expansion coefficients can be widened with the subsequent improvement of the mechanical stability of the system.

Glass-ceramic materials possess a mechanical resistance often comparable with the corresponding ceramic materials. For those applications in which the mechanical resistance is the major relevant property, glass-ceramic materials have advantages over glasses due to the latter's well-known fragility. In addition, glass-ceramics are more refractory than glasses and in many cases possess higher chemical resistance.

On the other hand, glasses have advantages over glass-ceramics in providing high thermal expansion coefficients and also very low softening temperatures. Relative to processing, sealing with a glass can be carried out in a single step with corresponding savings of time and money while the crystallization step in a glass-ceramic can be slow and complicated and requires more complex technologies.

The Sealing Process

In the sealing process, a series of steps can be considered, each of which determines the final result and the quality of the seal (Mizuhara and Oyama, 1991; Tomsia and Pask, 1991; Moorhead and Kim, 1991; Beauchamp and Burchett, 1991; Sugamuna, 1991; Price, 1984; Dalton, 1956; Kohl, 1967).

Cleaning of the Components

Before the application of the seal, it is essential that the surfaces of the components to be sealed are free of any residual dust, organic matter or grease that can generate gas products during the sealing process. The presence of any dirt can promote the appearance of bubbles or other defects at the same time as reducing adherence between the glass and the material to be sealed. Moreover, glass requires a previous cleaning treatment to eliminate the foreign elements adhered to its surface, especially water vapor. Often, the glass is immersed in an aqueous hydrofluoric acid solution before use.

The cleaning of the components can include different methods from utilization of solvents to vacuum cleaning (Mizuhara and Oyama, 1991; Price, 1984; Dalton, 1956; Kohl, 1967).

Previous Treatments

It is usual, although not always essential, to pre-oxidize the metallic parts before sealing. The pre-oxidation of the metallic elements ensures the further formation by diffusion at the glass-metal interface necessary to achieve gas-tightness of the seal. The mechanical resistance of the interface depends on both the thickness of the oxide layer and its composition.

Application of Glass

An essential step for the achievement of a good seal is application of the glass on the materials to be sealed. The objective of this process is to obtain a thin and uniform layer of glass that, on thermal treatment, provides a seal with a uniform thickness and without defects.

Different techniques have been tested for applying the glass. Depending on the method, it is possible to start using melted glass, glass powder or a preform.

Preform

The use of a preform is quite common with sealing glass-ceramic materials and especially when an intermediate glass is applied to ensure adherence and a good fit of thermal expansion coefficients (Mizuhara and Oyama, 1991). The preform is located between the materials to be sealed and is fixed to them during the thermal treatment by means of, for example, a graphite mold.

Glass injection

The melted glass is injected, under pressure, between the components to be sealed that are held in place with the help of a mold. The simultaneous application of vacuum at the opposite end of the mold improves the glass fluidity, facilitating the elimination of the trapped gases and ensuring perfect fit of the glass and the surfaces to be sealed. Moreover, it is a fast process and easy to automate.

Use of agglomerants

One of the most employed procedures starts from the milled glass, mixed with an agglomerant such as amilacetate or nitro-cellulose. The mixture, in the form of a paste or cement, is easily applied on the surfaces to be sealed employing diverse techniques. It is a simple process that allows the glass thickness to be easily controlled but has the inconvenience of the high proportion of solvents and organic matter that are introduced. The technique requires a careful further thermal treatment to eliminate the rest of the agglomerant material employed.

Sedimentation

Pliskin and Conrad (1964) used a sedimentation technique designed to obtain a uniform layer of glass powder on a substrate. The uniformity of the glass layer depends of the dielectric constant of the employed media. In low dielectric constant media, the glass particles tend to agglomerate in the suspension and deposit forming a rough surface. In high-dielectric constant media, the deposited layer is rather uniform on its surface but tends to be thicker towards the substrate borders. Pliskin and Conrad improved the technique using both media of high and low dielectric constant in double layers depositing a flat and uniform glass onto the substrate. The glass layer deposited on the substrate is heated up to temperatures slightly higher than the glass softening point to form a film. By means of this technique, thicknesses of 1.50 μm can be obtained with a difference in thickness between the different layers of $\pm 0.03 \mu\text{m}$ and an average variation through the same layer of 0.06 μm .

Immersion

The technique of immersion, described in Dalton (1956) first patents, is a useful procedure to seal metallic components of different dimensions. The materials to be sealed are immersed in the glass melt and once extracted they preserve a thin glass film that seals by compression.

A modification of this procedure is the use of a preheated iron tip to extract the glass by immersion in the melt. The tip is heated to a temperature higher than the softening temperature so the sealing glass flows from the tip onto the part to be sealed.

Pulverization

Sealing by pulverization of the preheated pieces to be sealed, with sealing glass powder, has been described by Dalton (1956). A uniform glaze is firstly obtained on the surfaces that finally seal during thermal treatment under mechanical load. Better results are obtained when starting from preheated powder at 200–300°C.

Tape process

The sealing technique by tape, also suggested by Dalton (1956) has been used in areas such as the metallization of ceramic parts in ceramic-metal seals or in the sealing of optical cells or lasers. Although the sealing glasses for tape processing have been commercially available for long time, the literature on its utilization is scarce. Additionally, this technique presents the inconvenience of its high cost.

Thermal Treatment

Once the glass has been applied on the materials to be sealed, the whole system undergoes a heating process under load; normally a reducing or neutral atmosphere is preferable (Tomsia and Pask, 1991).

The first step of thermal treatment requires slow heating, especially if the applied glass has been mixed with an agglomerant in order to eliminate the organic matter and traces of the employed solvents. After stabilization at a low temperature, the glass is subjected to a temperature suitable for optimum glass flow and wettability and, at the same time, the excess of glass is eliminated and only a thin glass layer between the components is retained. In glasses of certain composition, their devitrification can be induced by means of a suitable thermal treatment. Finally, the joint is slowly cooled down to room temperature to avoid the appearance of mechanical stresses.

When the material constituting the seal is a glass-ceramic, the thermal process will include heating up to a temperature high enough for the glass to flow followed by a nucleation process at lower temperature, and finally a crystallization process at more elevated temperature.

Most of the mentioned methods use the approach of conventional sealing in a furnace. Laser welding is an alternative sealing technology that will not be discussed here but detailed information and references can be found in [Pablos-Martín et al. \(2020\)](#).

Adherence of the Seal - Bonding Theories

The nature of the bonding between a glass and a metal has been the subject of considerable controversy and the relevant factors have gradually emerged. A certain number of theoretical approximations tend to elucidate the main factors determining the adherence between a metallic or ceramic substrate and a glass and the conditions that must be given to achieve a good chemical bonding at the interface.

Thermodynamic Approach

From the practical point of view, the first condition to obtain a seal or glass-metal coating is that the glass wets the metal surface and, as a consequence, spreads on it.

When a liquid comes into contact with a solid, a new interface is created, and the liquid may or may not spread on it. According to thermodynamics, the liquid will spread only if the energy resulting from the new solid-liquid interface is smaller than the corresponding solid-vapor interface. The greater this difference in energy, the greater is the extension of the contact surface between the liquid and the solid. The driving force of the wetting process is then related to the difference in energy between the solid-vapor and solid-liquid interfaces. Nevertheless, since the configuration with the lowest superficial energy is a sphere, there is an additional force that resists spreading of the liquid on the solid surface. This behavior is often studied as a function of the contact angle between the drop of liquid and the solid ([Donald and Cahn, 1993b](#); [Beauchamp and Burchett, 1991](#)) ([Fig. 4](#)). The drop shape is a function of three energy terms, as described by Young's classical equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (2)$$

where γ_{sv} , γ_{sl} and γ_{lv} are the interfacial energies of the solid-vapor, solid-liquid and liquid-vapor interfaces, respectively.

A liquid will wet a solid ($\theta < 90^\circ$) when the energy of the system diminishes as a consequence of the formation of the solid-liquid interface. The greater the degree of wetting, the smaller the angle θ will be. Of course, no liquid will exhibit the maximum contact angle of 180° , even in the case that the liquid does not wet the solid due to the distorting influence of gravity on the liquid droplet.

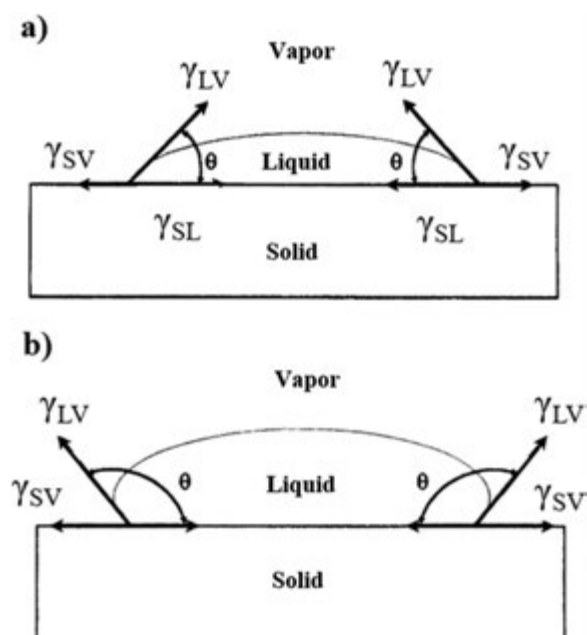


Fig. 4 Sessile drop configurations for the situations of: a) liquid wetting a solid, and b) liquid not wetting a solid. After Pascual, M.J., Pascual, L., Durán, A., 1997. Vidrios y vitrocerámicos para soldadura: usos tradicionales y nuevas áreas de aplicación. Boletín de la Sociedad Española de Cerámica y Vidrio 36 (4), 383–398.

The concept of work of adhesion, W_A , was introduced by Dupré (1869): the work of adhesion is equal to the decrease of free energy produced as a consequence of the creation of a new interface. The relationship between the work and the superficial energies can be expressed by the equation:

$$W_A = \gamma_{sv} + \gamma_{LV} - \gamma_{sL} \quad (3)$$

An interface will be stable if W_A is positive, when the formation of the interface lowers the free energy of the system. Introducing the contact angle, the relevant equation is:

$$W_A = \gamma_{sv}(1 + \cos\theta) \quad (4)$$

It is possible to experimentally obtain quantitative values of the bond strength and the behavior of different glass/metal systems.

Although the thermodynamic approximation must be carefully treated, it can be used as a first approximation in order to know if there are favorable conditions in a given system.

One of the first conclusions that can be extracted is that if the liquid has a lower surface energy than the solid substrate, the system can diminish its energy by means of the extension of the liquid phase on the solid surface, so the liquid wets the solid. However, this conclusion may be incorrect since it can suggest, for example, a change in the solid surface diminishing both its energy and wettability (Beauchamp and Burchett, 1991; Loehman, 1989).

The simple thermodynamic approximation does not assume reaction between liquid and solid. If there is a chemical reaction at the interface that generates a new product, the associated drop in free energy can promote adhesion (King, 1933). The introduction of the new terms leads to the equation

$$W_A = \gamma_{LV}(1 + \cos\theta) + \gamma_{Ri} - C\Delta G^\circ \quad (5)$$

where γ_{Ri} is the interfacial energy between the solid and the reacting interfacial layer, ΔG° is the Gibbs free energy for the new interfacial compound formation and C is a constant.

A spontaneous reaction is characterized by a negative value for ΔG° that increases W_A and diminishes θ . In order to know the most probable reactions under bonding conditions, ΔG° can be calculated from the available thermodynamic data. The reactions with more negative ΔG° values will be thermodynamically more favored, although the derived data must again be treated with precaution when a given reaction may not be kinetically favored.

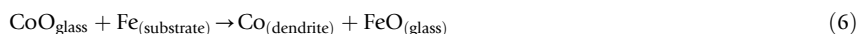
Mechanical Bonding

In principle, the adherence between an enamel and a metallic substrate was believed to have its origin in mechanical type phenomena. These theories have a wide acceptance due to the fact that the interface between a metal and a porcelain enamel often appears rough, even with an initially flat substrate. It was thought that the bonding between the rough substrate and the glass was a consequence of a purely mechanical effect, and two theories appeared that try to explain the mechanisms through which this roughness could be generated.

Dendrite theory

This theory is based on the observation of metallic dendrites that appear in the interfacial region after sealing a glass to a metal (King, 1933; Healy and Andrews, 1951; Khachatryan *et al.*, 2019). These metallic dendrites are suggested to be responsible for the adherence, acting as cleavage points between the metallic substrate and the glass.

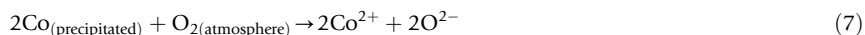
The dendrites could form as a consequence of the reaction between a metallic oxide present in the glass with a metallic element in the substrate. For example, when a glass containing CoO is used for sealing an iron substrate, the following reaction can take place:



The dendrites of metallic cobalt would, thus, be responsible for the adherence between the glass and iron substrate.

Electrolytic theory

The electrolytic theory proposes that the roughness of the metallic substrate is produced during the glass application, due to the electrolytic type or galvanic corrosions (Staley, 1934; Richmond *et al.*, 1953; Moore *et al.*, 1954). For example, the bonding between a glass containing CoO with an iron substrate in air results from the precipitation of the metallic cobalt as proposed by the dendrite theory. Nevertheless, it was thought that those precipitates formed by contact between the glass and iron substrate constituted the basis of the localized electrolytic or galvanic cells. The net effect was the dissolution of iron into the glass and the formation of a pitted surface on which the glass could flow between the voids. The process could take place as follows:



Nevertheless, the presence of more reducible oxides that should originate in a rougher substrate does not lead to stronger bonding.

Mutual Solubility and Formation of Intermediate Compounds

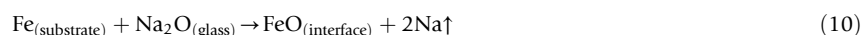
Other mechanisms for stabilizing bonding between a metallic substrate and a glass is by means of the formation of a chemical compound or a transition interface. The oxide layer on the metal generally formed by pre-oxidation can be dissolved in the glass, forming an intermediate layer progressively richer in the metallic oxide. Alternatively, the bonding could be obtained through the formation of an intermediate compound that joins the glass to the metallic or oxide surface. This theory is very much related with thermodynamic and chemical approximations, and it is possible to predict the formation of a compound.

Chemical bond

From a chemical or molecular point of view, the bond can have a transition zone in which the metallic bond of the substrate is gradually substituted by an ionic-covalent bond of the glass.

King (1933) proposed the formation of a strong chemical bond at the glass/metal interface in conditions in which the glass is saturated with an oxide of the metallic substrate. When the oxide of the metal is dissolved into the glass up to saturation, the metallic ions remain at the surface promoting the metal-metal bond through the interface. At elevated temperatures, when the metallic ions in the glass and the atoms of the metallic substrate are relatively mobile, a continuous exchange at the glass-metal interface will take place, establishing a dynamic equilibrium that could remain if the glass is not saturated with the oxide. At low temperatures, when the mobility of the atoms and ions is lower, an electronic exchange at the interface may exist, and ions and atoms can alternate in properties depending on the concentration of electrons or the degree of ionization. The atoms and ions of intermediate character can constitute the transition between the metallic and ionic-covalent states, assuming that the saturated state of the interface is maintained. The solubility of the metallic oxide and, in turn, the bond strength can be modified changing the glass composition. For example, when sealing iron and glass, the solubility of FeO into the glass increases with increasing proportion of forming oxides, such as silica or boron oxide, and diminishes with the incorporation of modifier oxides.

When the metallic substrate does not present an oxide layer or the pre-oxidized layer dissolves without reaching saturation, certain redox reactions between the metal and the glass must take place to achieve or maintain the proper conditions for establishing a chemical bond. The reaction between a glass and a metallic substrate free of oxide would occur in this case through a two-step mechanism. At first, a redox reaction takes place that leads to the formation of an oxide layer on the metal at the interface. Second, the dissolution of this oxide into the glass takes place. The saturation at the interface can be achieved even in the absence of an oxide layer formed by pre-oxidation. Nevertheless, if the reactions between a glass and a metal are not thermodynamically favorable (if the value of ΔG° for oxide formation is positive), the reaction will not proceed spontaneously under normal conditions. In this case, the reaction can only progress if the conditions of the sealing process are modified. As an example, for sealing an iron substrate without oxide layer with a sodium silicate, the following reaction was proposed (Tomsia and Pask, 1990; Pask and Tomsia, 1981; Pask, 1987a,b; Kramer and Massey, 1984; Partridge, 1990):



The global free energy for this reaction can be written as follows

$$\Delta G = \Delta G^0 + RT \ln \frac{[a_{\text{FeO}(\text{interface})} \cdot x a_{\text{Na}}^2]}{[a_{\text{Fe}} \cdot x a_{\text{Na}_2\text{O}(\text{glass})}]} \quad (11)$$

where a is the chemical activity of each component.

Under normal conditions, the chemical activities are equal to one, and $\Delta G = \Delta G^\circ$. If ΔG° is positive, the reaction will proceed spontaneously. Nevertheless, it can also proceed if the value of the activity quotient is less than one. This situation can happen if, by means of control of the process parameters, a low sodium partial pressure, a low activity for FeO and a high activity for Na_2O can be guaranteed.

From the point of view of the formation of a chemical bond, it is necessary to highlight the role of so-called adherence promoters. These are oxides of easily reducible metals which are able to react with the metallic substrate ensuring the maintenance of saturation conditions, e.g., cobalt or nickel oxides when sealing on iron substrates. If, during the sealing process, the complete dissolution of the oxide layer coming from the pre-oxidation of the substrate into the glass takes place, the metal iron will come in contact with the glass, reducing the adherence promoter oxide, forming more of the substrate oxide and enhancing adherence. In this way, the interfacial saturation with the substrate in the oxidized state is ensured during sealing. Donald *et al.* (2008) describe this process in more detail.

Applications

Conventional applications

Glass/metal and glass-ceramic/metal seals have found a wide range of applications in electronics and engineering. Glass is a quasi-ideal material for this type of application due to its ability to form hermetic and mechanically strong joints with metals and to be impermeable versus gases, a good electrical insulator, reasonably refractory and a low-cost material.

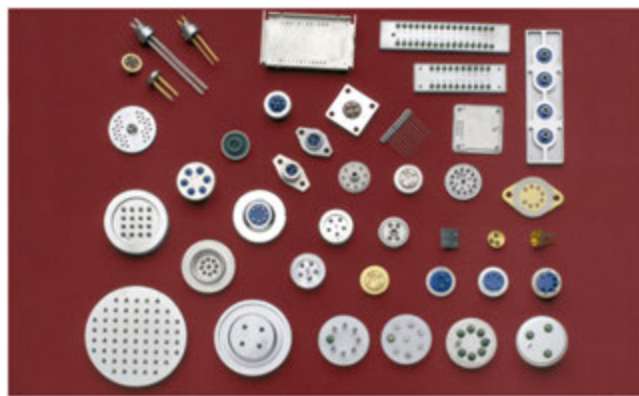


Fig. 5 Example of sealed metal pieces. Courtesy of Vactron S.A, <https://www.vac-tron.es/en/multi-lead-feedthrough.html>). The glass sealants are used for the fabrication of filaments, pyrotechnics, sensors, micro-sensors, etc.

Traditionally, the field of application of sealing glasses has extended to the fabrication of incandescent and vapor lamps, vacuum tubes, radar magnetrons and microwave connectors, TV tubes, switches, high pressure sodium lamps, magnetic recording heads and high-voltage supplies. In a wide sense, the field also includes porcelain enameling and coatings for high-temperature or mechanical protection.

In composite structures, such as lamps and electron tubes, glass is used because it transmits light, can easily form useful shapes, provides electrical insulation, and is chemically inert versus corrosive and oxidizing environments. The glass and the metal can also be joined with organic adhesives or metallization and soldering techniques, although they are less frequently used.

Glass-ceramic/metal seals are a more modern technology used for more complex applications. [McMillan et al. \(1966a,c\)](#) were the first to show that glass-ceramics could be employed to produce seals exhibiting superior properties compared with glass/metal seals. Some of the applications of the glass-ceramic/metal seals include tube covers for laser and refractory vacuum tubes, vacuum switches, high-temperature insulation and high pressure pyrotechnic actuators ([Nash et al., 1983](#); [Tummala, 1991](#)).

In the field of image reproduction, the development of devitrifiable glasses for sealing made the fabrication of color TV tubes possible. In planar visualization systems, such as the visualization panels for gas discharge, the sealing glass has a protective role in addition to a sealant, maintaining a narrow and precise spacing between the flat glass sheets that constitute the screen.

The complexity and sensitivity of silicon microelectronic systems has notably increased in parallel with the demand for new sealing glasses for sealing at low temperature. Glasses of the $\text{PbO-ZnO-B}_2\text{O}_3$ system, with a high lead content and softening temperature below 300°C have permitted alumina pieces used for the encapsulation of these systems to be sealed. The glass acts as a sealant between two alumina plates. Other glass systems have been explored for this application such as borates and phosphates, as well as composite materials. Additionally, glass-ceramic materials have been identified as possible candidates for the encapsulation of advanced systems in substitution of alumina. A wide review of the applications of substrates and glass-ceramic coatings on metals applicable in microelectronics in substitution of alumina has been published by [Partridge et al. \(1989a,b\)](#). Glass-ceramics of the systems $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ (LAS), $\text{ZnO-Al}_2\text{O}_3\text{-SiO}_2$ (ZAS) and $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ (MAS), prepared by bulk nucleation or powder sintering, are compatible with thin and thick layer microelectronics and can be used in a great variety of applications. The metallic substrates covered with a glass-ceramic offer the advantage of good thermal dissipation, which is necessary when the packing density of the circuit components is high. Glass-ceramics of cordierite combined with copper are currently used by IBM due to the low dielectric constant of cordierite and the good fit with the thermal expansion coefficient of silicon ([Fig. 5](#)).

New applications

The reliable joining of Ceramic Matrix Composites (CMCs) using glasses and glass-ceramics is a key technology for their use in applications characterized by harsh environmental conditions, such as energy production, aeronautics, aerospace, etc. where large and complex geometries are involved and it is a work in continuous development ([Ferraris et al., 2020a](#)).

On the other hand, new compositions have been developed for the preparation of stable glass-metal seals with titanium and titanium alloys for use in components such as the heads of batteries. Some compositions have been patented, for example compositions containing CaO , Al_2O_3 , B_2O_3 , SrO and BaO ([Brow and Watkins, 1992](#)). Research involving Ti-6Al-4V has also been reported ([Staff et al., 2016](#)).

Nevertheless, the most recent application for sealing glasses still under development is related with power generation systems: gas separation membranes ([Lundin et al., 2017](#)), lithium and sodium batteries ([Brow and Watkins, 1991](#); [Smeacetto et al., 2017](#); [Manthina et al., 2019](#)), molten carbonate fuel cells (MCFC) ([Williams et al., 1993](#); [Izaki et al., 1993](#); [Ohtsuti et al., 1993](#); [Ota, 1997](#); [Mugikura et al., 1998](#); [Terada et al., 1999](#); [Pascual, 2000](#)) and solid oxide fuel cells (SOFC) ([Fergus, 2005](#); [Mahapatra and Lu, 2010](#); [Blum et al., 2011](#); [Haanappel et al., 2005](#); [Buchkremer and Conradt, 2010](#); [Cela Greven, 2015](#); [Yana et al., 2019](#); [Rodríguez-López, 2016a](#)). In particular, the field of sealing glasses for SOFC has led to about 600 papers (source Scopus) and numerous patents in the literature. Especially relevant are the pioneering works of Rolla, PNNL, RWTH-Aachen and FZ-Jülich.

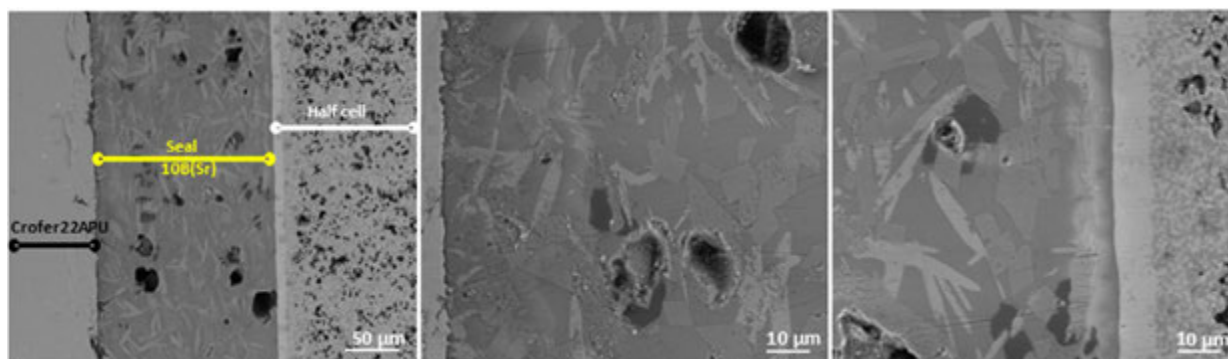


Fig. 6 Union Crofer22APU-glass-ceramic-8YSZ of composition 10B(Sr) sealed at 850°C for 10 h. (A) General view. (B) Steel-sealant interface. (C) Sealant-8YSZ interface. After de Pablos-Martín, A., Rodríguez-López, S., Pascual, M.J., 2020. Processing technologies for sealing glasses and glass-ceramics. *International Journal of Applied Glass Science* 11 (3), 552–568.

In most of these applications, the glass must work at high temperature in a very corrosive environment and undergo thermal cycling. **Fig. 6** shows a typical joint Crofer22APU-glass-ceramic-8YSZ present in a SOFC. The glass-ceramic shows a good densification and good bonding with both steel and YSZ. Most current research on sealing materials deals with improvement of their thermomechanical behavior and self-healing ability and there is still ample margin to investigate and optimize compositions, processing and properties (Ferraris *et al.*, 2020b).

References

- Abe, Y., Hosono, H., 1989. Phosphate glasses and glass-ceramics. In: Kanazawa, T. (Ed.), *Inorganic Phosphate Materials*. Amsterdam: Elsevier Science, pp. 247–281.
- Beall, G.H., Duke, D.A., 1983. Glass-ceramic technology. In: Uhlman, D.R., Kreidl, N.J. (Eds.), *Glass: Science and Technology* vol. 1. Glass-Forming Systems. New York: Academic Press, pp. 403–445.
- Beauchamp, E.K., Burchett, S.N., 1991. Techniques of seal design. In *Engineered Materials Handbook*, vol. 4 Ceramics and Glasses. Novelt, OH: ASTM International, pp. 532–541.
- Blum, L., Groß, S.M., Malzbender, J., *et al.*, 2011. Investigation of solid oxide fuel cell sealing behavior under stack relevant conditions at Forschungszentrum Jülich. *Journal of Power Sources* 196, 7175–7181.
- Brow, R., 2000. Review: The structure of simple phosphate glasses. *Journal of Non-Crystalline Solids* 263–264 (1), 1–28. doi:10.1016/S0022-30939900620-1.
- Brow, R.K., Alam, T.M., Tallant, D.R., James Kirkpatrick, R., 1998. Spectroscopic studies on the structures of phosphate sealing glasses. *MRS Bulletin* 23 (11), 63–67. doi:10.1557/S088376940003102X.
- Brow, R.K., Watkins, R.D., 1991. High Expansion, Lithium Corrosion Resistant Sealing Glasses. U.S. Patent Number: 5 021 307, Jun.4.
- Brow, R.K., Watkins, R.D., 1992. Sealing Glasses for Titanium and Titanium Alloys. U.S. Patent Number: 5 104 738, Apr.14.
- Buchkremer, H.P., Conradt, R., 2010. Durable sealing concepts with glass sealants or compression seals. *Advances in electrocatalysis, materials, diagnostics and durability materials for high temperature fuel cells materials durability*. In: Vielstich, W. (Ed.), *Handbook of Fuel Cells*. John Wiley and Sons, Ltd.
- Bunker, B.C., Arnold, G.W., Wilder, J.A., 1984. Phosphate glass dissolution in aqueous solutions. *Journal of Non-Crystalline Solids* 64, 291–316.
- Cela Greven, B., 2015. Glass Ceramic Sealant Reinforcement for High Temperature Applications. Ph.D. thesis. RWTH Aachen.
- Chambers, R.S., Gerstle, F.P., Monroe, S.L., 1989. Viscoelastic effects in a phosphate glass-metal seal. *Journal of the American Ceramic Society* 72 (6), 929–932.
- Chen, Z.X., McMillan, P.W., 1985a. Crystallization behavior of a high-zinc-content $\text{Li}_2\text{O}-\text{ZnO}-\text{SiO}_2$ glass-ceramic. *Journal of the American Ceramic Society* 68 (4), 220–224.
- Chen, Z.X., McMillan, P.W., 1985b. Microstructure and properties of $\text{MgO}-\text{ZnO}_2-\text{SiO}_2$ alkali-free glass-ceramics. *Journal of Materials Science* 20, 3428–3438.
- Claypoole, S.A. 1959. Composite Article and Method (devitrified solder glass). US Patent 2889952.
- Dai, S., Elisberg, B., Calderone, J., Lyon, N., 2017. Sealing glass-ceramics with near-linear thermal strain, part III: Stress modeling of strain and strain rate matched glass-ceramic to metal seals. *Journal of American Ceramic Society* 100, 3652–3661. doi:10.1111/jace.14821.
- Dalton, R.H., 1956. Solder glass sealing. *Journal of the American Ceramic Society* 39 (3), 109–112.
- de Pablos-Martín, A., Rodríguez-López, S., Pascual, M.J., 2020. Processing technologies for sealing glasses and glass-ceramics. *International Journal of Applied Glass Science* 11 (3), 552–568.
- Deubener, J., Allix, M., Davis, M., *et al.*, 2018. Updated definition of glass-ceramics. *Journal of Non-Crystalline Solids* 501 (1), 3–10. doi:10.1016/j.jnoncrysol.2018.01.033.
- Donald, I.W., 1993a. Preparation, properties and chemistry of glass and glass-ceramic-to-metal-seals and coatings. *Journal of Materials Science* 28, 2841–2886.
- Donald, I.W., 1993b. Glass ceramics – An update. In: Cahn, R.W. (Ed.), *Encyclopedia of Materials Science and Technology*. Oxford: Pergamon Press, pp. 1689–1695. (3rd Supplement).
- Donald, I.W., Metcalfe, B.L., Morris, A.E.P., 1992. Influence of transition additions on the crystallization kinetics, microstructures and thermal expansion characteristics of a lithium zinc silicate glass. *Journal of Materials Science* 27, 2979–2999.
- Donald, I.W., Metcalfe, B.L., Gerrard, L.A., 2008. Interfacial reactions in glass-ceramic-to-metal seals. *Journal of the American Ceramic Society* 91 (3), 715–720. doi:10.1111/j.1551-2916.2007.02024.x.
- Donald, I.W., Metcalfe, B.L., Wood, D.J., Copley, J.R., 1989. The preparation and properties of some lithium zinc silicate glass-ceramics. *Journal of Materials Science* 24, 3892–3903.
- Donald, I.W., Mallinson, P.M., Metcalfe, B.L., Gerrard, L.A., Fernie, J.A., 2011. Recent developments in the preparation, characterization and applications of glass- and glass-ceramic-to-metal seals and coatings. *Journal of Materials Science* 46, 1975–2000. doi:10.1007/s10853-010-5095-y.
- Dupré, A., 1869. In *Theorie Mechanique de la Chaleur*. Paris: Gauthier-Villars, Imprimeur-Librairie.

- Fakouri Hasanabadi, M., Malzbender, J., Groß-Barsnick, S.M., *et al.*, 2020. Finite element optimization of sample geometry for measuring the torsional shear strength of glass/metal joints. *Ceramics International* 46, 4857–4863. doi:10.1016/j.ceramint.2019.10.221.
- Fergus, J.W., 2005. Sealants for solid oxide fuel cells. *Journal of Power Sources* 147, 46–57.
- Ferraris, M., Casalegno, V., Smeacetto, F., Salvo, M., 2020a. Glass as a joining material for ceramic matrix composites: 25 years of research at Politecnico di Torino. *International Journal of Applied Glass Science* 11, 569–576. doi:10.1111/ijag.15032.
- Ferraris, M., Pierre, S., De la, Sabato, A.G., *et al.*, 2020b. Torsional shear strength behavior of advanced glass-ceramic sealants for SOFC/SOEC applications. *Journal of the European Ceramic Society* 40 (12), 4067–4075. doi:10.1016/j.jeurceramsoc.2020.04.034.
- Forbes, D.W.A., 1967. Solder glass seals in semi-conductor packaging. *Glass Technology* 8 (2), 32–42.
- Grossman, D.G., 1982. Glass-ceramic applications. In: Simmons, J.H., Uhlman, D.R., Beall, G.H. (Eds.), *Advances in Ceramics 4, Nucleation and Crystallization in Glasses*. Columbus, OH: Amer. Ceram. Soc., pp. 249–260.
- Haanappel, V.A.C., Shemet, V., Gross, S.M., *et al.*, 2005. Behaviour of various glass–ceramic sealants with ferritic steels under simulated SOFC stack conditions. *Journal of Power Sources* 150, 86–100. doi:10.1016/j.jpowsour.2005.02.015.
- Hammeter, W.F., Loehman, R.E., 1987. Crystallization kinetics of a complex lithium silicate glass-ceramic. *Journal of the American Ceramic Society* 70 (8), 577–582.
- Healy, J.H., Andrews, A.I., 1951. The cobalt-reduction theory for the adherence of sheet-iron ground coats. *Journal of the American Ceramic Society* 34 (7), 207–214.
- Holleran, L.M., Martin, W., 1987. Glass-Ceramics Suitable for Dielectric Substrates. US Patent 4714687-A.
- Izaki, Y., Mugikura, Y., Koda, E., *et al.*, 1993. The basic performance of large scale MCFC. In: Shores, D., Uchida, I., Maru, H., Selman, J.R. (Eds.), *Proceedings of the Third International Symposium on Carbonate Fuel Cell Technology. High Temperature Materials and Battery Divisions.*, vol. 93-3. Pennington: The Electrochemical Society, Inc., pp. 119–130.
- James, P.F., 1995. Glass-ceramics: New compositions and uses. *Journal of Non-Crystalline Solids* 181, 1–15.
- Jiang, X., Li, Z., Zhuang, H., *et al.*, 2018. Stable phosphate-based glass for low-temperature sealing applications: Effect of Si₃N₄ dopant. *Ceramics International* 44, 20227–20231.
- Khachatryan, H., Baek, S., Leeb, S., *et al.*, 2019. Metal to glass sealing using glass powder: Ion induced crystallization of glass. *Materials Chemistry and Physics* 226, 331–337.
- King, R.M., 1933. Mechanics of Enamel Adherence, VIII. *Journal of the American Ceramic Society* 16, 232–238.
- Kobayashi, K., 1987. DTA and TMA compositional dependencies in ZnO-SiO₂-B₂O₃-P₂O₅ and PbO-SiO₂-B₂O₃-GeO₂ glass systems. *Bulletin of the American Ceramic Society* 66 (4), 685–687.
- Kohl, W.H., 1967. *Handbook of Materials and Techniques for Vacuum Devices*. New York: Reinhold Publishing.
- Kramer, D.P., Massey, R.T., 1984. Vacuum injection molding of glass-metal electrical components. In: Mangels, J.A. (Ed.), *Forming of Ceramics. Advances in Ceramics 9*. Columbus, OH: American Ceramic Society, pp. 265–273.
- Kreidl, N.J., 1983. Glass forming systems. In: Uhlmann, D.R., Kreidl, N.J. (Eds.), *Glass: Science and Technology 1*. New York: Academic Press, pp. 105–299.
- Langlet, M., Saltzberger, M., Shannon, R.D., 1992. Aluminum metaphosphate glass-ceramics. *Journal of Materials Science* 27, 972–982.
- Lara, C., 2006. Sellos vitrocerámicos del sistema RO-BaO-SiO₂ R=Mg, Zn para pilas de combustible de óxido sólido SOFC. Ph.D. thesis. Universidad Autónoma de Madrid (UAM).
- Lara, C., Pascual, M.J., Durán, A., 2004. Glass-forming ability, sinterability and thermal properties in the systems RO-BaO-SiO₂ R = Mg, Zn. *Journal of Non-Crystalline Solids* 348, 149–155.
- Lee, J.S., Perng, J.C., Huang, C.W., 1990. Devitrification and physical properties of PbO-ZnO-B₂O₃ low-temperature solder glasses. *Glass Technology* 31.77
- Loehman, R.E., 1989. Interfacial reactions in ceramic-metal systems. *Bulletin of the American Ceramic Society* 68 (4), 891–896.
- Lundin, S.B., Law, J.O., Patki, N.S., Wolden, C.A., Way, J.D., 2017. Glass frit sealing method for macroscopic defects in Pd-based composite membranes with application in catalytic membrane reactors. *Separation and Purification Technology* 172, 68–75.
- Mahapatra, M.K., Lu, K., 2010. Seal glass for solid oxide fuel cells. *Journal of Power Sources* 195, 7129–7139.
- Manthina, V., Song, G., Singh, P., Mahapatra, M.K., 2019. Silica-free sealing glass for sodium-beta alumina battery. *International Journal of Applied Ceramic Technology* 16, 887–895. doi:10.1111/ijac.13093.
- Martin, S.W., 1991. Review of the structure of phosphate glasses. *European Journal of Solid State and Inorganic Chemistry* 28, 163–205.
- McMillan, P.W., 1979. *Glass Ceramics*, second ed. Amsterdam: Elsevier, pp. 245–266.
- McMillan, P.W., Partridge, G., 1972. The dielectric properties of certain ZnO-Al₂O₃-SiO₂ glassceramics. *Journal of Materials Science* 7 (8), 847–855.
- McMillan, P.W., Hodgson, B.P., Partridge, G., 1966a. Sealing glass-ceramics to metals. Part 1. Selection of materials and direct sealing methods. *Glass Technology* 71 (4), 21–127.
- McMillan, P.W., Philips, S.V., Partridge, G., 1966b. Structure and properties of lithium silicate glass-ceramic. *Journal of Materials Science* 1 (3), 269–279.
- McMillan, P.W., Partridge, G., Hodgson, B.P., Heap, H.R., 1966c. Sealing glass-ceramics to metals. Part 2. Sealing by intermediate bonds. *Glass Technology* 7, 128–133.
- McMillan, P.W., Partridge, G., 1963. Improvements in or Relating to Glass-Ceramics and Their Production, UK Patent 943 599.
- Metcalfe, B.L., Donald, I.W., 1991. The production of some glass and glass-ceramic matrix composites. *Silicates Industriels* 5–6, 99–102.
- Mizuhara, H., Oyama, T., 1991. Ceramic/metal seal. In *Engineered Materials Handbook*, vol. 4 *Ceramics and Glasses*. Novelty, OH: ASTM International, pp. 502–510.
- Moore, D.G., Pitts, J.W., Richmond, J.C., Harrison, W.N., 1954. Galvanic corrosion theory for adherence of porcelain enamel ground coats to steel. *Journal of the American Ceramic Society* 37 (1), 1–6.
- Moorhead, A.J., Kim, H., 1991. Joining oxide ceramics. In *Engineered Materials Handbook*, vol. 4 *Ceramics and Glasses*. Novelty, OH: ASTM International, pp. 511–522.
- Morena, R., 2000. Phosphate glass as alternatives to Pb-based sealing frits. *Journal of Non-Crystalline Solids* 263, 382–387. doi:10.1016/S0022-30939900678-X.
- Mugikura, Y., Yoshida, F., Izaki, Y., *et al.*, 1998. Performance and life of 10-kW molten carbonate fuel cell stack using Li/K and Li/Na carbonates as electrolyte. *Journal of Power Sources* 75 (1), 108–115.
- Nash, T.R., Pashby, E.M., Collet, R.L., 1983. Experience in the use of glassceramics for high voltage vacuum tube envelopes. *Glass Technology* 24 (6), 298–301.
- Ohtsutir, F., Seki, T., Takeuchi, S., Kasumori, A., 1993. Development of indirect internal reforming molten carbonate fuel cell. In: Shores, D., Uchida, I., Maru, H., Selman, J.R. (Eds.), *Proceedings of the Third International Symposium on Carbonate Fuel Cell Technology. High Temperature Materials and Battery Divisions*, vol. 93-3. Pennington: The Electrochemical Society, Inc., pp. 48–62.
- Omar, A.A., El-Shennani, A.W.A., El-Ghannam, A.R., 1991. Thermal expansion of Li₂O-ZnO-Al₂O₃-SiO₂ glasses and corresponding glass-ceramics. *Journal of Materials Science* 26, 6049–6056.
- Ota, K., 1997. Materials durabilities for MCFC. In: *Proc.-Electrochemical Soc., Carbonate Fuel Cell Techonology*, vol. 97-4. Pennington: The Electrochemical Society, pp. 238–259.
- Partridge, G., Elyard, C.A., Budd, M.I., 1989a. Glass-ceramics in substrate applications. In: Lewis, M.H. (Ed.), *Glasses and Glass-Ceramics*. London: Chapman and Hall, pp. 226–271.
- Partridge, G., Elyard, C.A., Keatman, H.D., 1989b. Glass-ceramic materials for use in substrate and packaging applications. *Glass Technology* 30, 215–222.
- Partridge, G.R., 1990. Part 2: Joining glass-ceramics to metals. In: Nicholas, M.G. (Ed.), *Joining of Ceramics*. London: Chapman and Hall, pp. 31–354. (Institute of Ceramics).
- Pascual, L., Durán, A., 1996a. Nitridation of glasses in the system R₂O-MO-P₂O₅. *Materials Research Bulletin* 31 (1), 77–95.
- Pascual, L., Durán, A., 1996b. Nitridation of mixed alkali phosphate glasses. *Physics and Chemistry of Glasses* 37 (4), 143–148.
- Pascual, M.J., 2000. Materiales vítreos para el sellado de pilas de combustible de carbonatos fundidos MCFC. Ph.D. thesis. Universidad Autónoma de Madrid (UAM).

- Pascual, M.J., Pascual, L., Durán, A., 1997. Vidrios y vitrocerámicos para soldadura: usos tradicionales y nuevas áreas de aplicación. *Boletín de la Sociedad Española de Cerámica y Vidrio* 36 (4), 383–398.
- Pascual, M.J., Durán, A., Prado, M.O., 2005. A new method for determining fixed viscosity points of glasses. *Physics and Chemistry of Glasses* 46 (5), 512–520. doi:10.1111/j.1551-2916.2005.00322.x.
- Pascual, M.J., Durán, A., Valle, F.J., Berjoin, R., Pascual, L., 2003. Corrosion of borosilicate sealing glasses for molten carbonate fuel cells. *Journal of the American Ceramic Society* 86 (11), 1918–1926. doi:10.1111/j.1151-2916.2003.tb03582.x.
- Pask, J.A., 1987a. From technology to the science of glass/metal and ceramic/metal sealing. *Bulletin of the American Ceramic Society* 66, 1587–1592.
- Pask, J.A., 1987b. Chemical bonding at glass-to-metal interfaces. In: Moddeman, W.E., Merten, C.W., Kramer, D.P. (Eds.), *Technology of Glass, Ceramic and Glass-Ceramic-to-Metal Sealing*, MD-vol. 4. New York: American Society of Mechanical Engineers, pp. 1–7.
- Pask, J.A., Tomsia, A.P., 1981. Wetting, spreading and reactions at liquid/solid interfaces. In: Pask, J.A., Evans, A. (Eds.), *Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems* (Mat. Sci. Res. vol. 14). New York: Plenum Press, pp. 411–419.
- Peng, Y.B., Day, D.E., 1991a. High thermal expansion phosphate glasses, I. *Glass Technology* 32 (5), 166–173.
- Peng, Y.B., Day, D.E., 1991b. High thermal-expansion phosphate glasses, II. *Glass Technology* 32 (6), 200–205.
- Pliskin, W.A., Conrad, E.E., 1964. A simple method for measuring the thickness and refractive index of transparent layers without altering them. *Journal de Physique* 25, 17–20. doi:10.1051/jphys:01964002501-201700.
- Price, J.W., 1984. The Kovar to glass seal. *British Society of Scientific Glass Blowers Journal* 22, 34–40.
- Rajaram, M., Day, D.E., 1988. Preparation and properties of oxynitride glasses made from $27\text{R}_2\text{O} \cdot 20\text{BaO} \cdot 3\text{Al}_2\text{O}_3 \cdot 52\text{SiO}_2$. *Journal of Non-Crystalline Solids* 102, 173–180.
- Ray, N.H., Plaisted, R.J., Robinson, W.D., 1976. Oxide glasses of very low softening point, IV. Preparation and properties of ultraphosphate glasses containing B_2O_3 . *Glass Technology* 17 (2), 66–71.
- Ray, N.H., Lewis, C.J., Laycock, J.N.C., Robinson, W.D., 1973a. Oxide glasses of very low softening point. Part 1. Preparation and properties of some lead phosphate glasses. *Glass Technology* 14 (2), 50–55.
- Ray, N.H., Lewis, C.J., Laycock, J.N.C., Robinson, W.D., 1973b. Oxide glasses of very low softening point. Part 2. Preparation and properties of some zinc phosphate glasses. *Glass Technology* 14 (2), 55–59.
- Richmond, J.C., Moore, D.G., Kirpatrick, H.B., Harrison, W.N., 1953. Relation between roughness of interface and adherence of porcelain enamel to steel. *Journal of the American Ceramic Society* 36, 410–416.
- Rodríguez-López, S., 2016a. Propiedades termo-mecánicas de sellos vitrocerámicos del sistema $\text{RO-MgO-B}_2\text{O}_3\text{-SiO}_2$ $\text{R}=\text{Ba}, \text{Sr}$ para SOFC. Ph.D. thesis. Universidad Autónoma de Madrid (UAM).
- Rodríguez-López, S., Haanappel, V.A.C., Durán, A., *et al.*, 2016b. Glass-ceramics in the system $\text{MgO-BaO-B}_2\text{O}_3\text{-SiO}_2$ under simulated SOFC conditions. *International Journal of Hydrogen Energy* 41, 15335–15345. doi:10.1016/j.ijhydene.2016.07.051.
- Rodríguez-López, S., Wei, J., Laurenti, K.C., *et al.*, 2017. Mechanical properties of solid oxide fuel cell glass-ceramic sealants in the system $\text{BaO/SrO-MgO-B}_2\text{O}_3\text{-SiO}_2$. *Journal of the European Ceramic Society* 37, 3579–3594. doi:10.1016/j.jeurceramsoc.2017.03.054.
- Rodríguez-López, S., Malzbender, J., Justo, V.M., *et al.*, 2020. Thermo-mechanical stability and gas-tightness of glass-ceramics joints for SOFC in the system $\text{MgO-BaO/SrO-B}_2\text{O}_3\text{-SiO}_2$. *Frontiers in Materials* 7. doi:10.3389/fmats.2020.00019.
- Shen, Z., Zhang, Y., Chen, Y., Song, X., Zhang, T., 2019. Effect of pre-oxidization condition on glass-to-metal sealing. *Journal of Non-Crystalline Solids* 521, 119488.
- Sinhdeo, N.N., Shukla, R.K., 1984. Solder glass processing. In: Uhlmann, D.R., Kreidl, N.J. (Eds.), *Glass: Science and Technology*, vol. 2. Boston: Academic Press Inc, pp. 169–207.
- Smeacetto, F., Radaelli, M., Salvo, M., *et al.*, 2017. Glass-ceramic joining material for sodium based battery. *Ceramic International* 43, 8329–8333.
- Smith, G.P., 1989. Some recent advances in glasses and glass-ceramics. *Materials and Design* 10 (2), 54–63.
- Staff, M.T., Fernie, J.A., Mallinson, P.M., Whiting, M.J., Yeomans, J.A., 2016. Fabrication of a glass-ceramic-to-metal seal between Ti–6Al–4V and a strontium boroaluminate glass. *International Journal of Applied Ceramic Technology* 13 (5), 956–965. doi:10.1111/ijac.12535.
- Staley, H.F., 1934. Electrolytic reactions in vitreous enamels and their relation to the adherence of enamels to steel. *Journal of the American Ceramic Society* 13, 163–1687.
- Strand, Z., 1986. Glass-ceramics materials. In *Glass Science and Technology*. Amsterdam: Elsevier, pp. 230–235.
- Strand, Z., Spirkova, B., Dusil, J., 1976. Nucleation and crystallization in the zinc oxide-alumina-silica(zicon) system. *Journal Ceramics-Silikáty* 20, 225.
- Sugamuna, K., 1991. Joining non-oxide ceramics. In *Engineered Materials Handbook*, vol. 4 Ceramics and Glasses. Novaty, OH, USA: ASTM International, pp. 523–531.
- Takamori, T., 1979. Chapter 5 – Solder glasses. In: Tomozawa, M., Doremus, R.H. (Eds.), *Glass II - Treatise on Materials Science and Engineering* 17. New York: Academic Press Inc, pp. 173–255.
- Terada, S., Suemitsu, T., Sato, M., Ito, V., 1999. Corrosion and protection of materials in molten carbonate fuel cells. *Materia* 38 (3), 216–219.
- Tindyal, M.A., Ott, W.R., 1978. Lithium-zinc-phosphate glasses. *Ceramic Bulletin* 57 (4), 432–437.
- Tomsia, A.P., Pask, J.A., 1990. In: Nicholas, M.G. (Ed.), *Joining in Ceramics*. London: Chapman and Hall, pp. 7–30. [Institute of Ceramics].
- Tomsia, P., Pask, J.A., 1991. Glass/metal and glass-ceramic/metal seals. In *Engineered Materials Handbook*, vol. 4 Ceramics and Glasses. Novaty, OH: ASTM International, pp. 493–501.
- Tummala, R.R., 1991. Ceramic and glass-ceramic packaging in the 1990s. *Journal of the American Ceramic Society* 74, 895–908.
- Vargin, V.V., Miklyukov, E.M., 1968. *Zhurnal Prikladnoy Khimii* 11, 194.
- Varshneya, A.K., Mauro, J.C., 2019. Chapter 10 – Thermal expansion of glass. In: *Fundamentals of Inorganic Glasses*, third ed. Elsevier, pp. 253–271.
- Volf, M.B., 1984. Chemical approach to glass. In: *Glass Science and Technology*, 7. Amsterdam: Elsevier, pp. 325–330.
- Wang, T., James, P.F., 1990. In: Holland, D. (Ed.), *IOP Proceedings of the 2nd International Conference on New Materials and their Applications*. Institute of Physics Conference Series no. 111. Bristol: University of Warwick, pp. 401–410.
- West, A.R., Glasser, F.P., 1970. Crystallization of lithium zinc silicate glasses. 1. Phase equilibria in the system $\text{Li}_4\text{SiO}_4 - \text{Zn}_2\text{SiO}_4$. *Journal of Materials Science* 5 (4), 676–688.
- Wilder, J.A., Healey, J.T., Bunker, B.C., 1982. In: Simmons, J.H. (Ed.), *Advances in Ceramics* 4. Columbus, OH: American Ceramic Society, pp. 313–326.
- Williams, M.C., Parsons, E.L., George, T.J., 1993. Status of molten carbonate fuel cell Technology Development. In: Shores, D., Uchida, I., Maru, H., Selman, J.R. (Eds.), *Proceedings of the Third International Symposium on Carbonate Fuel Cell Technology*. High Temperature Materials and Battery Divisions 93–3. Pennington: The Electrochemical Soc., Inc., pp. 1–10.
- Yana, J., Wua, Y., Lina, D., *et al.*, 2019. Structural transformation-induced surface strengthening of borosilicate sealing glass for solid oxide fuel cells. *Ceramics International* 45, 15629–15635.
- Zhang, X.Y., He, W.Q., Li, C., *et al.*, 2014. Crystallization stability of Sb_2O_3 -doped vanadium phosphate sealing glass analyzed by XPS. *Advanced Materials Research* 1030–1032, 43–47. doi:10.4028/www.scientific.net/amr.1030-1032.43.

Glasses and Glass-Ceramics for Nuclear Waste Immobilization

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Introduction

As in all other industries and human activities, the nuclear industry generates waste during energy production (electricity) or weapons fabrication. However, in the case of nuclear industry some of these wastes are highly radioactive and must be isolated durably from the biosphere in highly durable matrices for several thousands of years or more in order to limit their potential impact on the environment (Jantzen *et al.*, 2011; Vernaz *et al.*, 2012; Pegg, 2015). This is different from the case of certain types of non-nuclear hazardous industrial or domestic waste that can be recycled to make useful materials (glasses, glass-ceramics) that severely limit the rate of release of toxic elements (heavy metals) in the environment (Colombo *et al.*, 2003; Donald, 2007, 2016).

In commercial nuclear power reactors, the burn up of ^{235}U enriched UO_2 fuel under thermal neutrons produces energy due to the fission of uranium nuclei and generates a wide spectrum of fission products (Table 1), and actinides by neutron capture (plutonium and other actinides).

Several countries such as the US, Canada and Sweden decided not to reprocess their spent nuclear fuel leaving it in interim storage while waiting for possible disposal (open fuel cycle), whereas for several decades other countries such as France, Russia, the UK and Japan reprocessed their spent nuclear fuel to recover remaining uranium and plutonium to prepare new nuclear fuel (MOX fuel, mixed oxide fuel consisting of Pu mixed with natural uranium, reprocessed uranium, or depleted uranium) and also to reduce the radiotoxicity of the ultimate waste containing the fission products and minor actinides (closed fuel cycle) (Wilson, 1996; Rodríguez-Penalonga and Moratilla Soria, 2017). Indeed, spent nuclear fuel may still contain about 96 wt% of reusable material (U + Pu) to produce energy. The ultimate high level radioactive waste (HLW) recovered after the reprocessing of spent nuclear fuel coming from energy production (commercial waste) and also that coming from plutonium weapons fabrication referred to as defense waste (Metcalf and Donald, 2013) are today conditioned by dissolution at the atomic scale in highly durable glassy or partially crystallized matrices (Ojovan and Lee, 2007; Caurant *et al.*, 2009; Jantzen, 2011; Vernaz *et al.*, 2012; Donald, 2016; Jantzen and Ojovan, 2019). In these wasteforms, the glassy and crystalline phases play the role of solvent for almost all the species – radioactive or not – initially present in the waste (Fig. 1). Several other nuclear waste generally less radioactive (low or intermediate radioactive level waste) than the reprocessing waste originating for instance from nuclear installations dismantling or other sources could also be immobilized in glassy matrices (Sobolev *et al.*, 2005; Cantrel *et al.*, 2015; Girolid *et al.*, 2018; Achigar *et al.*, 2021).

In this chapter, after considering the nature and composition of HLW, and the specifications of an efficient wasteform to incorporate these wastes, the focus will be on the vitrification processes performed by melting the mixture of a glass frit with waste, and on the way several problematic elements present in the waste such as cesium, technetium, molybdenum, zirconium, lanthanides and actinides can be incorporated into the structure of glasses (such radioactive wasteforms are generally called nuclear glasses or nuclear waste glasses). The effect of glass composition changes on the incorporation of some of these elements (solubilization, demixing in the melt, crystallization) will also be considered by focusing on alkali-lime aluminoborosilicate type wasteforms that represent the main type of nuclear glasses used worldwide for HLW containment. The case of waste incorporation in glass-ceramics that can be envisaged to immobilize non-separated HLW or separated long-lived radionuclides will also be developed. After an interim storage period, all these conditioned wastes will have to be kept by geological disposal in a deep underground repository following a multiple barrier containment approach (Ewing *et al.*, 2016; Grambow, 2016; Laverov *et al.*, 2016) where the glassy or partially crystallized wasteforms will constitute the first containment barrier. The long-term behavior against water alteration and self-irradiation of nuclear glasses will also be addressed.

Nature of Highly Radioactive Waste and Need for Their Immobilization

HLW generally contain high amounts of α , β and γ radionuclides which are particularly harmful to the living world, even if radioactivity also exists in nature (^{235}U , ^{238}U , ^{232}Th , ^{40}K). They are produced in nuclear reactors, the aim of which is to produce electricity or plutonium for military purposes. In both cases, nuclear fuel is subjected to a neutron flux leading to the production of energy (and then electricity for power reactors) and the formation of fission products (FP, Table 1) and minor actinides (MA: Np, Am, Cm) generated by neutron capture mainly by ^{238}U (as for Pu formation) that constitute very dangerous (highly radioactive and toxic) non-reusable ultimate wastes. These wastes represent only around 4 wt% (comprising mainly FP and 0.1 wt% MA) of the spent fuel for power reactors.

In the context of nuclear weapons, spent fuel is reprocessed by dissolution in acid solutions to recover plutonium (Metcalf and Donald, 2013). Civilian spent fuel can be reprocessed in the same way (Purex process), in order to recover the uranium and plutonium remaining in the spent fuel (about 96 wt%) to prepare new nuclear fuel (Wilson, 1996; Bonin, 2008; Nuclear Energy Agency, 2018). In both cases, the remaining ultimate HLW that are present as concentrated aqueous nitric solutions are stored during long periods in metallic tanks to enable a significant decrease of their radioactivity and thermal power before conditioning.

Table 1 Main families of fission products occurring in spent nuclear fuel before reprocessing. The values given in this table correspond to that of a UO_2 spent fuel enriched with 3.5% ^{235}U (burn-up 33 GWday t^{-1} in a pressurized water reactor, 3 years after discharge) given in kg by ton of U before burning. It can be remarked that rare earths (Y + lanthanides) constitute the most abundant family of fission products in wt%. More than 300 radionuclides (β , γ emitters) are produced during fuel burn-up but more than 60% of them will have disappeared several times after spent fuel discharge. Nearly 40 elements of the Mendeleyev classification from Ge to Dy are generated during fission reactions

Chemical family	Weight (kg/U)
Rare gases (Kr, Xe)	5.6
Alkalis (Cs, Rb)	3
Alkaline-earths (Sr, Ba)	2.4
Rare earths (Y, lanthanides)	10.2
Transition metals (Mo, Zr, Tc)	7.7
Chalcogens (Se, Te)	0.5
Halogens (I, Br)	0.2
Noble metals (Ru, Rh, Pd)	3.9
Others (Ag, Cd, Sn, Sb...)	0.1

Note: Boullis, B., Devezeaux de Lavergne, J.-G., 2006. The treatment of spent fuel: A well-controlled sector. Clefs CEA 53, 19–25. (in French).

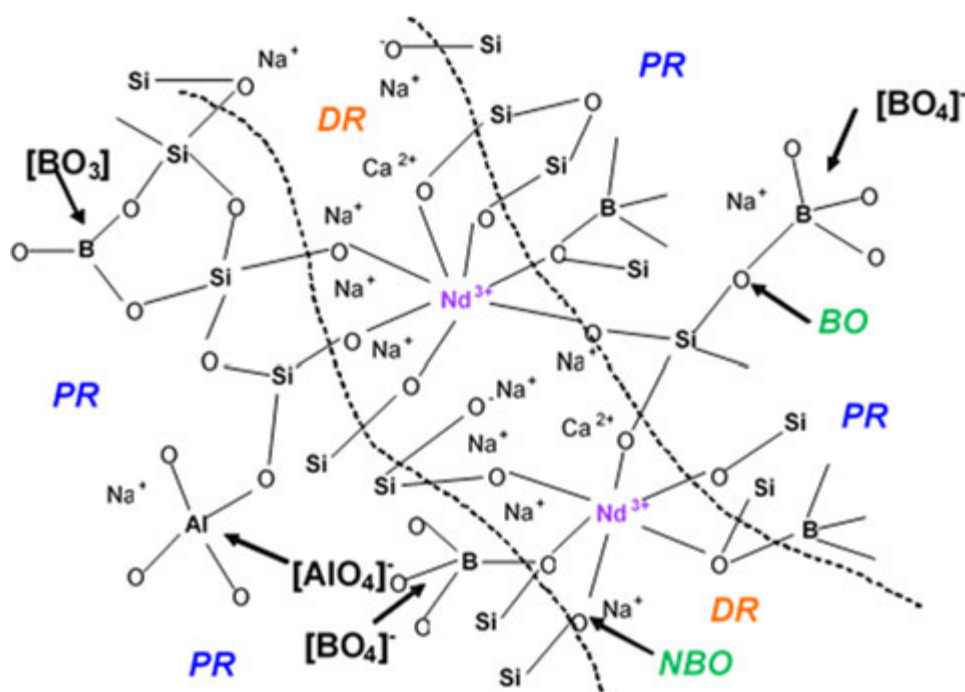


Fig. 1 Structural scheme showing the way fission products such as neodymium (one of the most abundant lanthanides present in HLW, Fig. 3) may enter into the structure of a peralkaline borosilicate nuclear glass. Nd^{3+} ions may be located in the depolymerized regions (DR) of the glass structure that are rich in non-bridging oxygen atoms (NBOs) and alkali + alkaline-earth cations (here Na^+ and Ca^{2+}). In these regions, NdO_n polyhedra can be locally charge compensated by alkali + alkaline-earth cations. Polymerized regions (PR) rich in bridging oxygen atoms (BOs) are also shown.

Depending on the type of nuclear reactor, fuel and cladding nature, on the fuel composition and burn-up, and on the particularities of the extraction processes, the composition of HLW may strongly vary between countries and within the same country over time. For instance, the concentrations of FP are relatively low in the HLW solutions, originating from the reprocessing of defense spent fuels or civilian spent fuels using natural uranium (0.7% ^{235}U), because of their low burn-up in comparison with the HLW solutions originating from pressurized water reactors (PWR) using ^{235}U -enriched fuel (Donald *et al.*, 1997; Donald, 2016), because the amount of FP increases proportionally with the burn-up of the fuel. As they contain long-lived α and β radionuclides for which half-lives can reach thousands to millions of years (MA, ^{135}Cs , ^{99}Tc , ^{93}Zr ...), HLW must be isolated from the biosphere from thousands to hundreds of thousands of years, at least until their radiotoxicity level drops back to the radiotoxicity level of the initial uranium ore (Fig. 2).

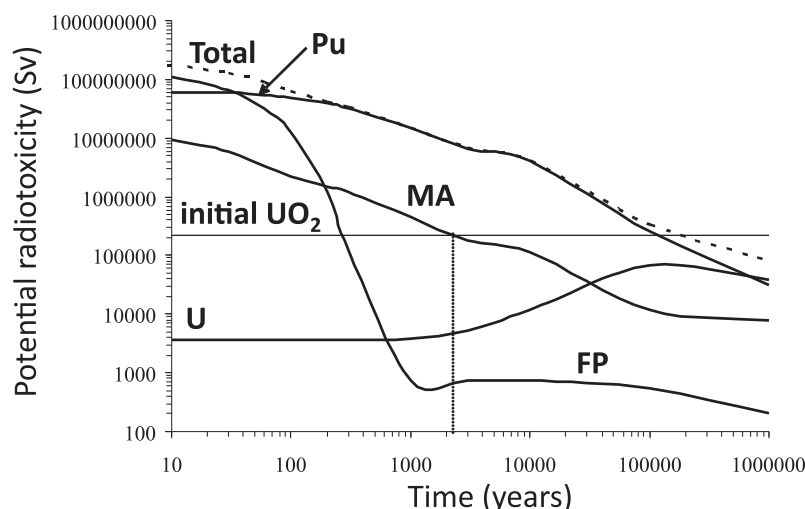


Fig. 2 Changes with time of the potential radiotoxicity (expressed in Sv/ton of initial uranium metal) of a UO_2 enriched spent fuel with 3.5% of ^{235}U from a power reactor (burn-up 33 GWd t^{-1} and 3 years after discharge) showing the contribution of plutonium, uranium, minor actinides (MA) and fission products (FP). The level of radiotoxicity of the initial natural uranium ore (UO_2) taking into account ^{235}U enrichment is indicated for comparison (horizontal line). The vertical dotted line indicates the time needed for MA to reach a radiotoxicity level close to that of the initial ^{235}U -enriched fuel. It clearly appears that after plutonium extraction from the waste (reprocessing), the most problematic long-term radionuclides are MA. After reprocessing (Pu and U extraction), the main contribution to the potential radiotoxicity will be due (during 2–3 centuries) to the short-lived β -emitters such as ^{137}Cs and ^{90}Sr (FP) and then to the long-lived α -emitters such as ^{241}Am , ^{243}Am and ^{244}Cm (MA). Modified from Bardez, I., 2004. Study of the Structural Characteristics and Properties of Glasses Rich in Rare Earths Intended for the Immobilization of Fission Products and Long-lived Elements. (Ph.D. thesis). University Pierre and Marie Curie Paris. (in French). Available at: <https://pastel.archives-ouvertes.fr/pastel-00001075>.

Immobilization of Highly Radioactive Nuclear Waste

HLW solutions originating from spent nuclear fuel reprocessing contain FP, MA and also additional non-radioactive but relatively abundant elements coming from the Purex process (P, Na) and from the corrosion of the tanks (Fe, Ni, Cr) in which are kept HLW solutions (Fig. 3). Because of the risks of diffusion and dispersion of these wastes in the biosphere and also to facilitate their transport and storage, they must be conditioned in solid and highly durable matrices before deep underground disposal. Nowadays, all the elements present in HLW solutions are immobilized together in the same matrix, but numerous studies have been carried out in order to selectively extract from these solutions the most active and long-lived α or β radionuclides such as MA and Cs (^{135}Cs half-life of 2.3 million years) using enhanced reprocessing processes with appropriate extracting molecules (Madic *et al.*, 2002; Bonin, 2008) and then to find specific very durable wasteforms for these separated radionuclides (Caurant *et al.*, 2009). For instance, many works have been carried out on highly durable ceramic (zirconates, phosphates, titanates) and also on glass-ceramic matrices for the specific immobilization of MA (Guy *et al.*, 2002; Caurant *et al.*, 2009). Similar types of studies have also been conducted on ceramics, glasses and glass-ceramics for the immobilization of plutonium-rich waste (Muller and Weber, 2001; Zhang *et al.*, 2017). The possibility to immobilize long-lived ^{129}I (half-life of 15.7 million years) in glassy and ceramic matrices has also been investigated, iodine being recovered separately during spent fuel dissolution in nitric solutions (Lemesle *et al.*, 2014; Riley *et al.*, 2016; Yang *et al.*, 2017).

Because of its low chemical durability, its high thermal power (due to the high concentration of thermal radionuclides) and its high specific area, the solid calcine that can be obtained after water evaporation and calcination of HLW solutions is not itself an efficient wasteform without the addition of other elements (such as Si, B, Al, alkalis and alkaline-earths for borosilicate glassy wasteforms). It can only be considered as an intermediate product that must be immobilized by dissolution or dispersion (by partial or total encapsulation) in a more durable solid matrix. When looking for an efficient wasteform for HLW containment, several important points must be considered concerning both the properties of the final matrix and the difficulties that can be encountered for its synthesis in radioactive environment (Caurant *et al.*, 2009; Jantzen and Ojovan, 2019). For instance, concerning the properties of the matrix:

- (1) The matrix must incorporate almost all the elements (radioactive or not) of the wastes with a sufficiently high loading to limit the volume of the wasteform (high incorporation capacity) while taking into account the heating generated by radionuclides disintegration - such as ^{137}Cs , ^{90}Sr , ^{241}Am and ^{244}Cm - that could affect matrix structure and microstructure and could be problematic for storage and disposal (increase of the minimum distance between canisters).
- (2) The matrix must exhibit very good long-term behavior concerning both its resistance against alteration by water (liquid and vapor) and its resistance against self-irradiation. Even if structural evolution occurs specially under the effect of α -decays, the chemical durability and the capacity of the matrix to retain radionuclides must remain acceptable.

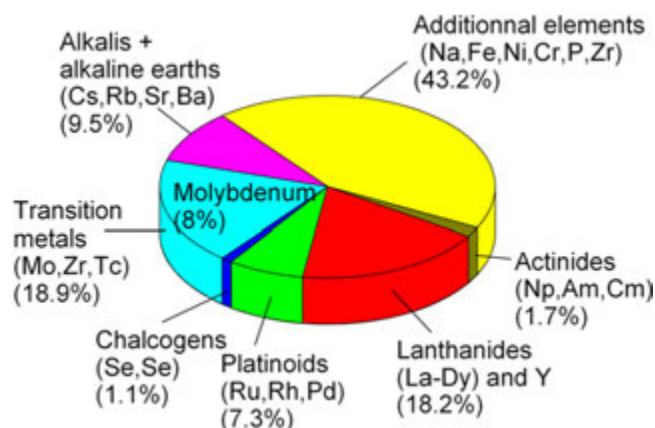


Fig. 3 Relative abundance (in wt% of oxides) of the different families of elements present in HLW solutions originating from the reprocessing of an UO_2 enriched (3.5% ^{235}U) spent fuel (see details in the legend of Table 1).

Concerning the synthesis of the wasteform:

- (1) The process to incorporate the wastes into the matrix must be as simple as possible and the number of steps must be small in order to avoid the production of high amounts of secondary radioactive wastes and to reduce the cost of immobilization.
- (2) The temperature of synthesis must not be too high to limit the risks of evaporation and to take into account furnaces and canisters limitation.

To meet these requirements, numerous kinds of glasses, glass-ceramics and crystalline (single phase or multiphase) matrices have been envisaged (Hench *et al.*, 1986; Donald *et al.*, 1997; Donald, 2007; Lee *et al.*, 2006; Caurant *et al.*, 2009; Jantzen and Ojovan, 2019). Nevertheless, because of their ease of synthesis (melting + casting), their high loading capacity related to their structural flexibility and lack of stoichiometry facilitating waste incorporation, their very good self-irradiation resistance and good chemical durability, glassy matrices still represent today the main type of matrix implemented on an industrial scale since 1978 to immobilize HLW (Vernaz *et al.*, 2012; Ojovan and Lee, 2010; Gin *et al.*, 2017b). In glassy wasteforms the majority of the elements coming from HLW may adapt, more easily than in crystalline phases, their local environment according to their size, their ionic charge and the amount of non-bridging oxygen atoms (NBOs) and charge compensators available in glass composition (see Fig. 1 for Nd^{3+} ions incorporation in a borosilicate glass). Nevertheless, many studies have been performed to develop matrices consisting of a glassy phase and one or more durable crystalline phases able to incorporate wastes in their structure and a current tendency is to accept partial crystallization in glassy matrices to reach higher waste loading, if it is not detrimental to the containment properties of the wasteform (Caurant *et al.*, 2007b; Crum *et al.*, 2012) (Fig. 4).

In comparison with glassy wasteforms, due to their lower structural flexibility associated with long range order and their more complex preparation (grinding + pressing + sintering steps), single phase ceramic matrices are not well adapted to incorporate the wide spectrum of elements with different sizes and charges present in HLW solutions (Fig. 3). They are more adapted for the containment of specific radionuclides (MA, Pu, Cs) (Aubin-Chevaldonnet *et al.*, 2007; Wang and Liang, 2012; Orlova and Ojovan, 2019). Indeed, the composition and the structure of such matrices must be selected according to the crystallographic sites available to immobilize the elements from the waste. Nevertheless, even if their synthesis appears more complex than that of glasses, multi-phase ceramics such as the Synroc ceramics containing different highly durable crystalline phases each adapted to immobilize different groups of the elements present in HLW or in actinide-rich waste have been envisaged (Gregg and Vance, 2016).

Vitrification of Highly Radioactive Nuclear Waste

Nowadays, HLW recovered from civilian and defense spent fuel reprocessing are incorporated by dissolution into the structure of borosilicate or aluminophosphate glasses melted in ceramic or metallic melters at temperatures not exceeding 1100–1150°C and cast in metallic containers to obtain large glass blocks (~400 kg) before interim storage, using continuous melting processes industrialized over more than 40 years (Vernaz *et al.*, 2012). Because of the lack of sufficient glass formers, fluxing agents and charge compensators in HLW compositions (Fig. 3), it is necessary during melting to add to the waste a high proportion (~70–80 wt%) of a glass frit (supplied by a glassmaker) to provide the glass former (SiO_2 , B_2O_3 , P_2O_5), intermediate (Al_2O_3) and modifier (Na_2O , Li_2O , CaO) oxides necessary to form the glassy network (Fig. 1) and to enable the dissolution in this structure of the elements coming from the waste (Fig. 5).

Using a pre-prepared glass frit to mix with the waste rather than a mixture of raw materials (oxides, carbonates...) as classically done in the commercial glass industry enables a large amount of melt able to dissolve the waste to be obtained more rapidly during heating. Moreover, this also avoids the generation in a radioactive environment of gases such as CO_2 coming from the raw

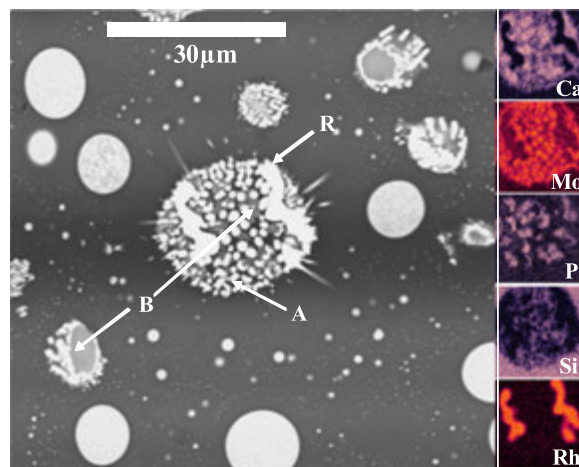


Fig. 4 Back-scattered SEM image and EDX cartography of a partially crystallized borosilicate glass developed for the immobilization of Mo- and P-rich HLW waste. The EDX cartography shows the distribution of the elements in the large crystallized droplet located in the center of the image. A: white phase containing Ca and Mo (CaMoO_4); B: gray phase containing P and Ca (NaCaPO_4); R: white phase containing rhodium. Reproduced from Caurant, D., Majerus, O., Fadel, E., *et al.*, 2007b. Effect of molybdenum on the structure and on the crystallization of $\text{SiO}_2\text{-Na}_2\text{O-CaO-B}_2\text{O}_3$ glasses. *J. Am. Ceram. Soc.* 90, 774–783, with permission from John Wiley and Sons.



Fig. 5 Example of a borosilicate glass frit (right), calcined inactive waste (left) and inactive nuclear borosilicate glass (top) that can be synthesized at lab-scale to test glass frit formulation. Because of the high amounts of elements present in the waste that absorb in the visible domain (transition metals, lanthanides), the glass has a black color.

materials. The choice of the composition of the glass frit results from a compromise between its incorporation capacity and its reactivity with the waste during melting which limits the waste loading ($\sim 18\text{--}35\text{ wt\%}$), the properties of the melt (viscosity) and its low liquid-liquid phase separation and crystallization tendency during cooling in the canister (the cooling rate is close to $1^\circ\text{C}/\text{min}$ in the bulk of glass blocks), and the properties of the final wasteform (long-term behavior) as explained above. For instance, the crystallization of poorly durable phases likely to incorporate radionuclides or of SiO_2 and Al_2O_3 -rich phases such as nepheline ($\text{NaAlSi}_3\text{O}_8$) that removes glass forming elements from the glass matrix and would induce a decrease of its chemical durability is usually avoided (Kim *et al.*, 1995). Another issue related to crystallization could be the formation of cracks in the glass that can be due to the difference of thermal expansion coefficient between the crystals and the glass or to the incorporation of actinides in large size crystals (Chouard *et al.*, 2019). The melt viscosity must be around 10 Pa s both to enable a good melt homogenization (waste dissolution rate) and fining, to limit the evaporation of volatile elements and to enable melt casting in canisters. As classical soda-lime silica melts exhibit a viscosity close to 10^3 Pa s at 1100°C they are not suitable for waste vitrification in comparison with the borosilicate and aluminophosphate melts used in nuclear waste vitrification plants which are much less viscous. As waste composition variations may occur during industrial nuclear production, it is also necessary that the glass frit formula must be flexible enough to maintain acceptable wasteform properties (Vernaz *et al.*, 2012). To reach a final glass frit formulation, numerous laboratory scale and pilot unit tests using simulated inactive waste, followed by tests with radioactive waste in a hot laboratory are required (Jantzen, 2011; Vernaz *et al.*, 2012). In simulated inactive waste the radioactive elements (^{137}Cs , ^{90}Sr ...) can be replaced by stable natural isotopes (^{133}Cs , ^{88}Sr ...) whenever possible or using inactive surrogates exhibiting close chemical properties, for example, lanthanides to substitute actinides and rhenium to substitute technetium.

The first tentative use of glass as nuclear wasteform was investigated in Canada in the 1950s (Lutze, 1988), but the first industrial plant to produce borosilicate nuclear glasses only started in 1978 in France, using a metallic melter (Sombret, 1993).

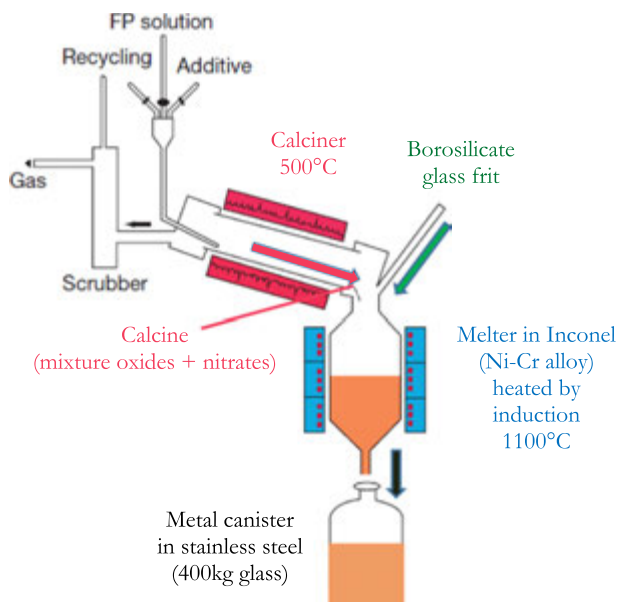


Fig. 6 Scheme of the metallic melter used in France at the La Hague plant to immobilize commercial HLW in borosilicate glasses (glass production capacity $\sim 25 \text{ kg h}^{-1}$). In this two-step vitrification process, liquid waste solutions are firstly evaporated and calcined in a rotating furnace (in red). Melt stirring in the furnace enables the presence of significant amounts of insoluble noble metals by limiting the sedimentation risks. Modified from Vernaz, E., Gin, S., Veyer, C., 2012. Waste glass. In: Konings, R.J.M. (Ed.), *Comprehensive Nuclear Materials*, vol. 5. pp. 451–483. with permission from Elsevier.

Since this date, several industrial vitrification plants have been developed over the world to immobilize civilian or defense HLW using either ceramic or metallic melters (Ojovan and Lee, 2005; Jantzen *et al.*, 2011; Pegg, 2015; Donald, 2016). Metallic melters used in France and in the UK are made of refractory metallic Ni-Cr-rich alloys in which the melt is heated indirectly by induction from the furnace wall and HLW solutions are calcined before injection simultaneously with a glass frit into the furnace (Fig. 6) (Sombret, 1993; Harisson, 2014), while ceramic melters used for instance in the US, Russia, Japan and China are made of refractory ceramic blocks in which the melt is heated directly by the Joule effect by means of submerged electrodes whereas HLW can be injected as slurry directly into the furnace (Jantzen, 2011). A more recent alternative melting technique referred to as cold crucible induction process enabling the melt to be directly heated by induction is employed in particular in France and in Russia (Sobolev *et al.*, 2005; Vernaz *et al.*, 2012; Stefanovsky *et al.*, 2010).

Usually, in all cases, the melt must be as homogeneous as possible in the furnace in order to limit the problems that could be induced by the settling of particles (clogging, short-circuits) and to reduce the presence of heterogeneities in the glass. However, melt stirring allows melts to be processed with significant amounts of insoluble particles such as noble metals. The glass frit composition and waste loading are usually chosen to avoid, as much as possible, important crystallization and liquid-liquid phase separation during melting and cooling in canisters. Nevertheless, whatever the glass frit composition, the noble metals coming from HLW (Table 1) are almost insoluble in the melt (solubility $\sim 100 \text{ ppm}$) and are present as micrometric crystalline heterogeneities in glasses (RuO_2 , Pd, Rh, Pd-Te alloy) (Fig. 4). They represent only a very small fraction in the glass ($< 1 \text{ vol\%}$), but their presence in the melt increases its viscosity and affects its electrical conductivity (Pflieger *et al.*, 2009), and during cooling they may act as nucleation sites for heterogeneous crystallization (Pacaud *et al.*, 1991; Orlhac *et al.*, 1999; Chouard *et al.*, 2015). Classically, at laboratory scale or full-scale, tests are carried out on inactive compositions to evaluate the melt crystallization and phase separation tendency by studying the nature and the amounts of crystals or separated phases formed either after casting (to check melt homogeneity) or after isothermal treatments between the melting temperature and the glass transition temperature (T_g), or after controlled cooling from the melt (Orlhac *et al.*, 1999; Rose *et al.*, 2011; Chouard *et al.*, 2016) (Fig. 7).

In order to avoid any risk of crystallization during the interim storage and geological disposal, the glass temperature in canisters (due to radioactivity) must always remain lower than T_g , where atomic diffusion is very weak. This limits waste loading or involves adapting glass composition to increase T_g . For instance, for the French R7T7 borosilicate nuclear glass with $T_g \sim 510^\circ\text{C}$, the equilibrium temperature reached in glass bulk one day after melt casting in canisters is about 400°C (i.e., about 100°C below T_g) and then very slowly decreases (Fig. 8). The experimental crystallization studies and long-term simulations performed on this glass confirmed that the main crystalline phases (CaMoO_4 , ZnCr_2O_4 , CeO_2) that may form could only grow at the beginning of melt cooling above T_g (Fig. 8). For instance, it was estimated by simulation that the time required to reach the total crystallization of CeO_2 and ZnCr_2O_4 phases in this glass (without considering the presence of platinoid heterogeneities) would be respectively 10^{28} and 57.10^3 years at 690°C (i.e., well above T_g) (Orlhac, 1999).

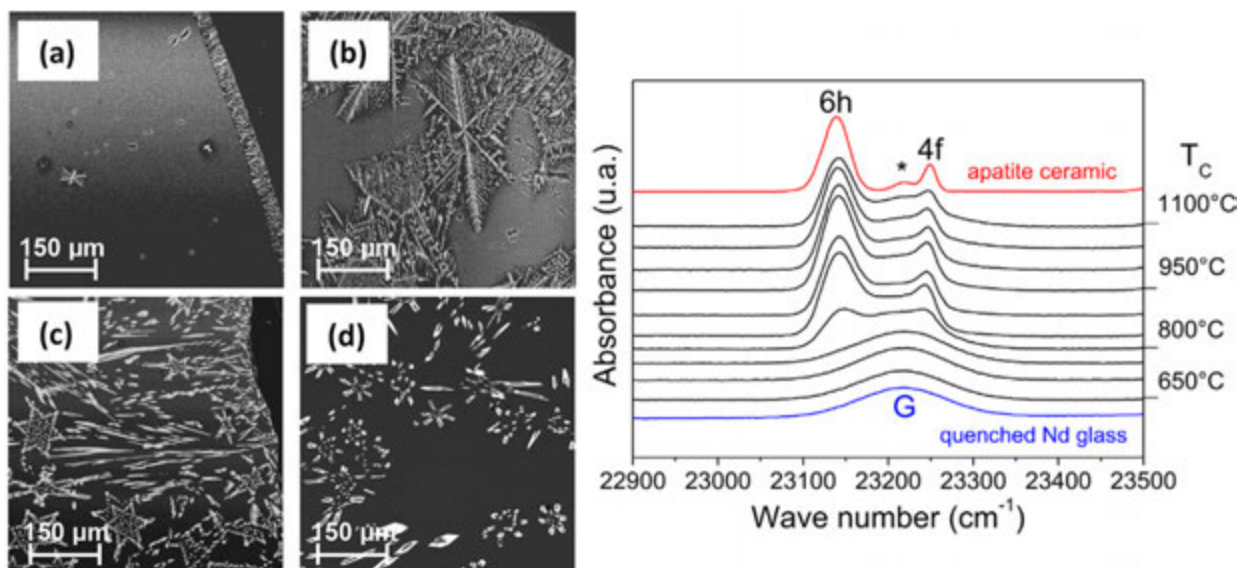


Fig. 7 (left) Back-scattered electrons SEM images showing surface and bulk crystallization of $\text{Ca}_2\text{Nd}_8(\text{SiO}_4)_6\text{O}_2$ (apatite) crystals in a Nd_2O_3 -rich inactive nuclear borosilicate glass heat treated 6 h at T_c : (a) 750°C, (b) 800°C, (c) 950°C, (d) 1050°C. (right) Evolution of the Nd^{3+} optical absorption spectrum with the heat treatment temperature T_c showing the progressive incorporation of Nd^{3+} from the glass to the 6h and 4f sites of apatite crystals. Reproduced from Chouard, N., Caurant D., Majérus O., *et al.*, 2016. Thermal stability of $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-CaO}$ glasses with high Nd_2O_3 and MoO_3 concentrations. *J. Alloy. Compd.* 671, 84–99, with permission from Elsevier.

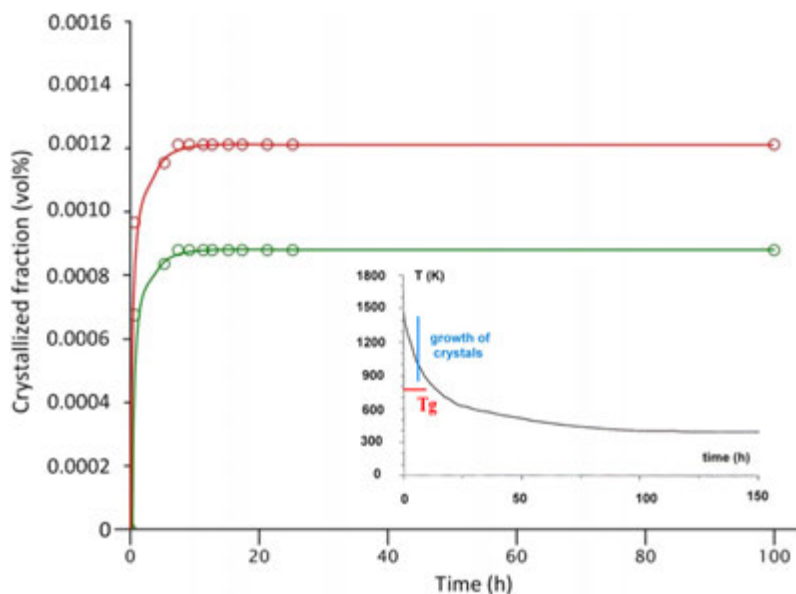


Fig. 8 Model of the changes of the crystallized fraction (in vol%) of ZnCr_2O_4 (red) and CeO_2 (green) formed during cooling in the bulk of the R7T7 glass as a function of the time after melt casting in canister, following the bulk thermal change shown in the inset (natural cooling of a 400 kg cylindrical glass block). The crystallized fractions were calculated from the nucleation and crystal growth rates of the two phases versus temperature. It appears that a very weak crystallization is only expected at the beginning of melt cooling. Based on Orhac, X., 1999. Study of the Thermal Stability of Nuclear Glass. Long-Term Evolution Modeling (Ph.D. thesis). France: University of Montpellier II. (In French) Available at: http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/31/058/31058405.pdf.

Nuclear Glasses Structure and Waste Incorporation

Even if numerous works have been performed on various kinds of glass compositions, such as iron phosphate and lead iron phosphates (Sales and Boatner, 1986; Jantzen, 2011; Bohre *et al.*, 2017), and lanthanide borosilicates (Meaker *et al.*, 1996;

Table 2 Average composition of the French R7T7 nuclear borosilicate glass produced to immobilize HLW originating from the reprocessing of ^{235}U enriched UO_2 spent nuclear fuel with a waste loading of about 17 wt%. Fines suspension correspond to metallic particles present in HLW solutions generated during the fuel shearing operation. The inactive version of this glass, used for laboratory experiments, is referred to as SON68 glass

Oxide	wt%
SiO_2	45.6
B_2O_3	14.1
Na_2O	9.9
Al_2O_3	4.7
CaO	4.0
Fe_2O_3	1.1
$\text{NiO} + \text{Cr}_2\text{O}_3$	0.2
Li_2O	2.0
ZnO	2.5
P_2O_5	0.2
(FP + Zr) oxides + fines suspension	16.4
actinide oxides	0.6

Note: Vernaz, E., Gin, S., Veyer, C., 2012. Waste glass. In: Konings, R.J.M. (Ed.), *Comprehensive Nuclear Materials*, vol. 5. Elsevier Science, pp. 451–483.

Jantzen, 2011) to immobilize HLW, borosilicate glasses remain with aluminophosphate glasses (belonging to the P_2O_5 - Al_2O_3 - Na_2O system) the only kinds of glassy wasteforms produced industrially for HLW immobilization. However, because of their inferior chemical durability in aqueous environment and thermal stability, and the fact that their melts are more corrosive than borosilicate melts, aluminophosphate glasses are less used than borosilicate glasses (Bohre *et al.*, 2017). Nevertheless, aluminophosphate glasses can incorporate more easily in their structure higher amounts of molybdenum, actinides, lanthanides, sulfates and halides and thus appear more adapted than borosilicate glasses to incorporate for instance Russian waste with high content of Al, Mo and sulfates (Laverov *et al.*, 2016).

To illustrate the chemical complexity of nuclear glasses used to immobilize HLW, the composition of the French R7T7 borosilicate nuclear glass is given in Table 2 and Fig. 9 where SiO_2 , B_2O_3 , Al_2O_3 , Na_2O , Li_2O , CaO and ZnO come from the glass frit and the other compounds from HLW solutions (Fig. 3). In order to study at laboratory scale the structure, the thermal stability and the long-term behavior (chemical durability and self-irradiation effects) of such very complex borosilicate glasses, researchers preferentially used simplified and inactive compositions, such as the International Simple Glass (ISG) as reference glass which is a 6-oxide glass (SiO_2 , B_2O_3 , Al_2O_3 , Na_2O , CaO , ZrO_2) considered as a good analog of the R7T7 glass (Kaspar *et al.*, 2019).

In such borosilicate nuclear glass compositions, the amount of SiO_2 (< 50 wt%) is significantly lower than in commercial soda-lime silicate glasses such as flat glass (> 70 wt%) and the presence of significant amounts of alkali oxides and B_2O_3 (close to 30 wt% in the R7T7 glass) enable them to be melted and cast at relatively low temperature (1100–1150°C) in comparison with soda-lime silicate glasses (~1400–1500°C) because of the well-known fluxing and fluidizing effect of B_2O_3 and alkali oxides. Moreover, to limit the risks of matrix demixing during melt cooling, the relative proportions of SiO_2 , B_2O_3 and alkali oxides are chosen outside the phase separation region in the ternary SiO_2 - B_2O_3 -(Na_2O , Li_2O) phase diagrams (Jantzen, 1986). Nevertheless, in order to maintain a good chemical durability against water alteration the proportion of B_2O_3 + alkali oxides must not be too high. As in borosilicate nuclear glasses there is generally an excess of alkali and alkaline-earth oxides compared to Al_2O_3 (such glasses are called peralkaline glasses), the glassy network is constituted of interconnected SiO_4 , BO_4^- , BO_3 and AlO_4^- units with alkali and alkaline-earth cations charge compensating the BO_4^- and AlO_4^- units (Fig. 10), AlO_4^- units being preferentially charge compensated by alkali cations (Caurant *et al.*, 2008). The excess of alkali and alkaline-earth oxides of the glass frit forms NBOs on SiO_4 tetrahedra which enables the majority of the wide spectrum of fission products and actinides that are present as cationic M^{n+} species in the waste to be incorporated, forming more or less strong M–O–Si bonds (see the Nd–O–Si bonds in Fig. 1). These alkali and alkaline-earth cations are not dispersed homogeneously in the glass structure but tend to form percolation channels in NBO-rich regions (depolymerized regions in Fig. 1) (Le Losq *et al.*, 2017) in which can be incorporated M^{n+} cations.

In comparison with cationic species, anionic species such as halide (F^- , Cl^- , I^-) and sulfur (S^{2-}) that may be present in several kinds of HLW are hardly soluble in borosilicate glasses because of the difficulty to connect them efficiently to the borosilicate network and their high tendency to volatilize during melting (Gin *et al.*, 2017b). The facility to dissolve M^{n+} cations in a borosilicate glass structure depends on both their size and charge. Generally, the higher their cationic field strength F_s , the higher their tendency to impose their local environment with strong M–O bonds with the oxygen anions available in the glass structure and the lower their solubility due to an increasing phase separation or crystallization tendency (the field strength of a cation in an oxide can be defined as $F_s = Z/d^2$ where Z is the cation charge and d is the mean cation-oxygen distance). When M^{n+} cations are linked to the borosilicate network, they form MO_n polyhedra with BOs or/and NBOs and their preference to connect to NBOs increases with F_s . For instance, lanthanide Ln^{3+} cations are preferentially connected to NBOs whereas alkali cations have both

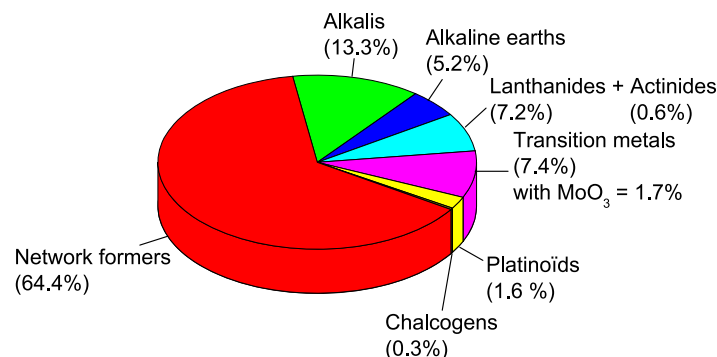


Fig. 9 Relative abundance (wt%) of the different families of elements present in the R7T7 nuclear glass composition.

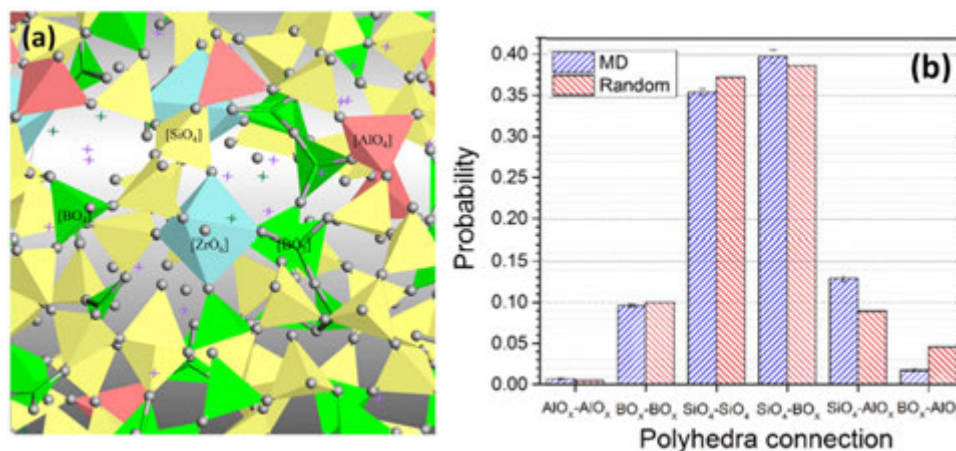


Fig. 10 (a) Snapshot of a 6-oxides borosilicate glass structure with composition close to that of the ISG glass from molecular dynamics simulations showing the interconnection between SiO_4 (yellow), BO_3 and BO_4 (green), AlO_4 (pink) and ZrO_6 (blue) polyhedra. The purple and green crosses represent respectively sodium and calcium cations. (b) Occurrence probability of different connections between SiO_4 , BO_x ($x = 3$ or 4) and AlO_x ($x = 4$ (98%) and $x = 3$ or 5 (2%)) polyhedra in a 4-oxides borosilicate glass ($\text{SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}$) derived from the ISG glass by converting CaO to Na_2O and ZrO_2 to SiO_2 under the same mole percentage. Molecular dynamics simulation results (blue) are compared to theoretical values by assuming a random distribution of network former atoms (red): the similarity of the results shows that the network former atoms tend to be randomly distributed. Reproduced from Lu, X., Deng, L., Kerisit, S., Du, J., 2018. Structural role of ZrO_2 and its impact on properties of borosilicate nuclear waste glasses. NPJ Mater. Degrad. 2, 19, with permission from Springer Nature. Ren, M., Deng, L., Du, J., 2017. Bulk, surface structures and properties of sodium borosilicate and borosilicate nuclear waste glasses from molecular dynamics simulations. J. Non Cryst. Solids 476, 87–94, with permission from Elsevier.

NBOs and BOs in their coordination sphere (Du and Cormack, 2005). The lowest F_s cations such as alkalis and alkaline-earths insure local charge compensation around MO_n polyhedra and complete the bond valence of the oxygen atoms engaged in M–O–Si bonds (see the example of NdO_n polyhedra charge compensated by Na^+ and Ca^{2+} cations in Fig. 1); these cations are thus essential to facilitate the dissolution of M^{n+} cations in the glassy network (formation of NBOs + charge compensation of MO_n polyhedra), and they strongly contribute to its structural flexibility. Nevertheless, peraluminous borosilicate glass compositions defined by an excess of Al^{3+} cations in comparison with the amount of alkali and alkaline-earth cations have also been envisaged as potential wasteforms with enhanced physical and chemical properties in comparison with peralkaline borosilicate glasses because of the possibility of high F_s elements present in HLW such as lanthanides to act as charge compensators of AlO_4^- units (Gasnier *et al.*, 2014; Piovesan *et al.*, 2018).

Let us now consider successively the incorporation in the structure of nuclear borosilicate glasses of several families of elements present in HLW.

Incorporation of Alkalis and Alkaline-Earths

The alkali and alkaline-earth cations that may be present in HLW (Cs^+ , Rb^+ , Mg^{2+} , Ba^{2+} , Sr^{2+}) play the same role of modifier or charge compensator as the alkali and alkaline-earth cations brought by the glass frit, and so they are thus generally easily dissolved in the glass structure. Nevertheless, depending on waste composition, they may partly separate and crystallize with anionic entities poorly soluble in the melt and in the glass such as orthophosphate (PO_4^{3-}) and molybdate (MoO_4^{2-})

polyanions (Fig. 4), also coming from the waste but that are not connected to the borosilicate network (obviously the alkali and alkaline-earth cations Na^+ , Li^+ and Ca^{2+} brought by the glass frit may also separate with these anionic entities). Such separation can be a problem if for instance the long-lived ^{137}Cs isotope crystallizes in poorly durable phases such as alkali molybdates because Cs^+ has a high mobility in the geological environment. Nevertheless, the crystallization of such alkali-rich phases may also lead to an increase of the overall wasteform durability if they do not percolate through the surrounding glass (see below, the case of molybdenum) (Nicoleau *et al.*, 2015).

Incorporation of Transition Metals

Numerous transition metals are present in HLW, originating either from nuclear fuel fission (Tc, Mo, Zr...), from reprocessing equipment (Fe, Ni, Cr) or from metallic cladding (Zr). Some of these metals can be particularly problematic during the vitrification process or for the long-term properties of the wasteforms because they can be highly volatile, such as Tc (for which all isotopes are radioactive) or may exhibit low solubility in the melt and during cooling because of their high tendency to phase separate (Mo) and/or to crystallize (Cr) which limits the waste loading, if wasteforms without crystals are to be obtained.

The case of technetium

As Tc^{7+} is very volatile during melting (it is present as very mobile TcO_4^- anions not connected to the borosilicate network), it is important to try to increase its retention by operating under more reducing conditions in order to promote Tc^{4+} that is less volatile, probably because it is present as less mobile TcO_6 octahedral units connected to the borosilicate network (Muller *et al.*, 2014). About 0.4 wt% TcO_2 is present in the R7T7 glass. In laboratory scale experiments, rhenium that belongs to the same column of the periodic table as Tc, is frequently used as a non-radioactive surrogate for Tc (Goel *et al.*, 2013).

The case of chromium

Chromium is poorly soluble in borosilicate melts and the R7T7 glass contains about 0.5 wt% Cr_2O_3 . It is non-radioactive and only comes from the reprocessing and vitrification process (tank and metallic melter corrosion). It is mainly present as Cr^{3+} (mixed with Cr^{6+} whose proportion depends on the redox melting conditions) in borosilicate glasses with a strong stabilization in an octahedral CrO_6 environment. This may explain the high crystallization tendency of Cr_2O_3 or spinel phases such as ZnCr_2O_4 in the presence of spinel-forming components such as ZnO (Fig. 8) which may lead to deleterious effects on melter performance (Hrma *et al.*, 2006).

The case of zirconium

Zirconium is both a fission product (with about 20% ^{93}Zr , a long-lived isotope with half-life of 1.5 million years) and an additional element coming from the fuel metallic cladding (zircalloy). It can also be present in the glass frit added to the waste to improve glass durability. The R7T7 glass contains about 2.7 wt% ZrO_2 . Zirconium only occurs as Zr^{4+} in borosilicate glasses and is preferentially located in octahedral ZrO_6 sites connected to the silicate network by strong Zr-O-Si bonds, but Zr-O-B may also exist (Galoisy *et al.*, 1999; Lu *et al.*, 2018) (Fig. 10). Alkali and alkaline-earth cations insure local electroneutrality and complete the bond valences of oxygen atoms surrounding zirconium that thus acts as a reticulating agent because it induces a decrease of the proportion of NBOs. As a consequence, the addition of ZrO_2 to the glass leads to a significant increase of T_g . Moreover, ZrO_6 units would be preferentially charge compensated rather than the BO_4 units (Angeli *et al.*, 2008). Consequently, in spite of its high F_s , Zr^{4+} is usually rather well incorporated in the network of nuclear borosilicate glasses if there are enough charge compensators available. Nevertheless, the crystallization of Zr-rich phases such as ZrO_2 and ZrSiO_4 can occur for particular borosilicate glass compositions, but these phases are well-known for their high chemical durability (Chen *et al.*, 2020). Moreover, it has been shown that ZrO_2 addition to borosilicate glasses induces a decrease of the initial dissolution rate in water but leads to a greater degree of alteration for longer times (Caillateau *et al.*, 2008) which can be explained by the local strengthening of the glass network in the Zr neighborhood due to the strong Zr-O-Si bonds. Finally all zirconium remains in the alteration layer on the glass surface (Angeli *et al.*, 2008).

The case of molybdenum

Molybdenum is a rather abundant stable fission product present in HLW solutions (Fig. 3) that mainly occurs as Mo^{6+} in nuclear borosilicate glasses prepared in oxidizing conditions. Due to its high F_s , Mo^{6+} occurs as isolated and mobile molybdate (MoO_4^{2-}) tetrahedral entities in the depolymerized regions of the structure rich in alkali and alkaline-earth cations (Fig. 11). Indeed, Mo-O-Si bonds between Mo and the glassy network cannot exist according to bond valence considerations because in such a situation the oxygen atom connecting Mo and Si would be overbonded (Calas *et al.*, 2003).

Similarly to other highly charged (+5, +6, +7) elements present as isolated oxoanionic species in borosilicate glasses (PO_4^{3-} , CrO_4^{2-} , TcO_4^-), Mo is thus poorly soluble in the structure of borosilicate glasses (solubility $\sim 1\text{--}3$ mol% MoO_3) and has a high tendency to phase separate during melting and cooling, and then to crystallize as alkali and alkaline-earth molybdates (Fig. 12). For instance, during the vitrification process, the presence of important amounts of molybdenum in the waste can lead to the formation of a Mo-rich phase called "yellow phase" that separates from the glass melt during vitrification and is undesirable

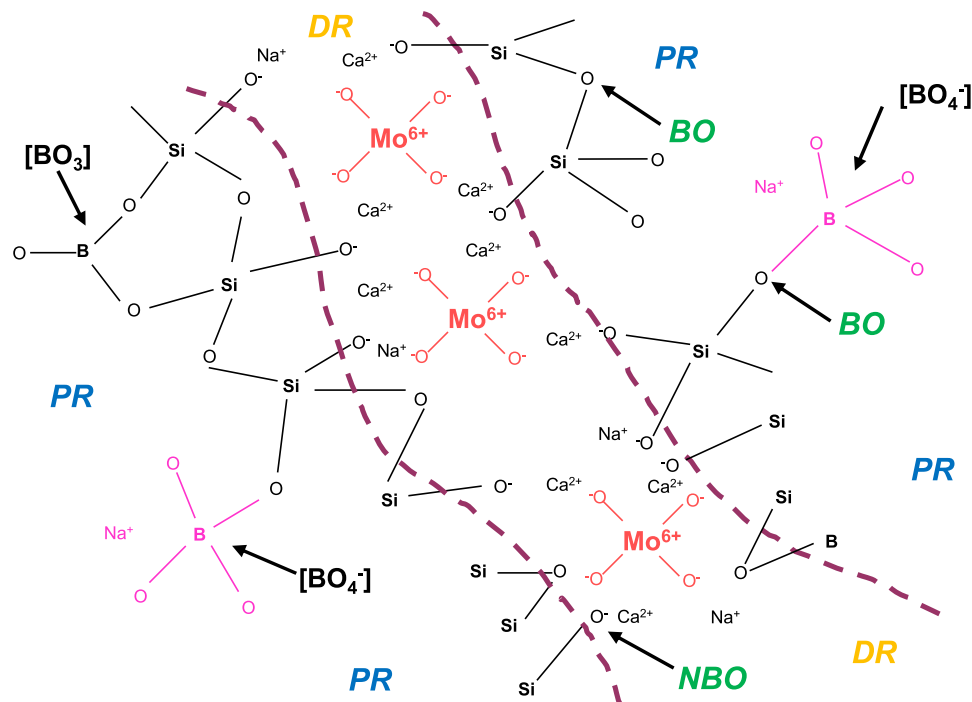


Fig. 11 Structural scheme showing the way molybdenum may enter in borosilicate nuclear glasses as isolated MoO_4^{2-} entities located in the depolymerized regions (DR) of the glassy network rich in non-bridging oxygen atoms (NBOs) and alkali + alkaline-earth cations (here Na^+ and Ca^{2+}). Polymerized regions (PR) rich in bridging oxygen atoms (BOs) are also shown.

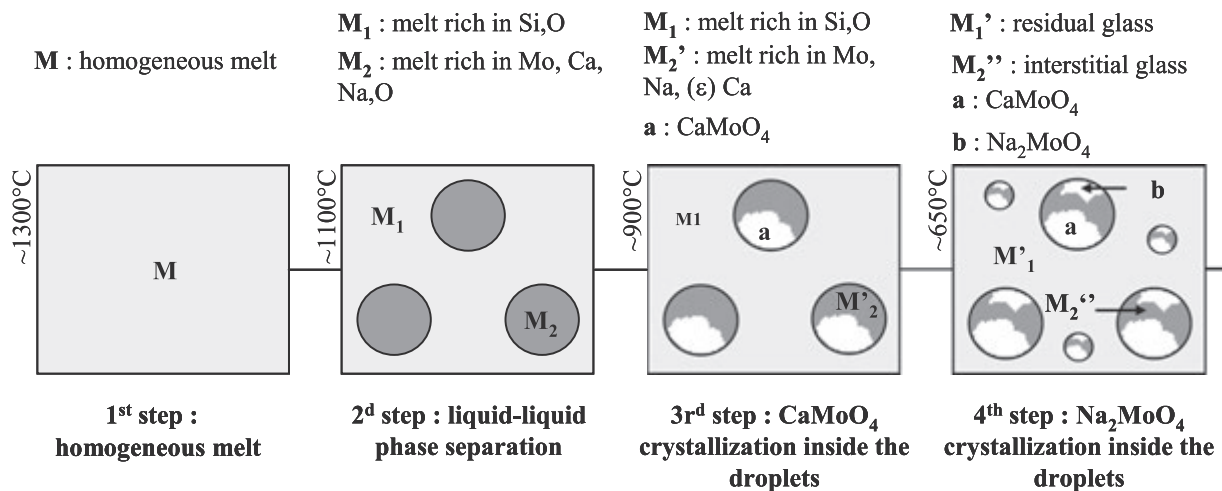


Fig. 12 Schematic showing the microstructural changes during melt cooling of a Mo-rich soda-lime borosilicate glass showing 4 steps: (1) homogeneous melt M during melting ($T > 1100^\circ\text{C}$), (2) liquid-liquid phase separation ($M_1 + M_2$) during cooling forming droplets M_2 , (3) CaMoO_4 crystallization ($T \leq 900^\circ\text{C}$) and (4) Na_2MoO_4 crystallization ($T \leq 650^\circ\text{C}$) in the droplets M_2 . Based on Magnin, M., 2009. Study of Phase Separation and Crystallization Phenomena in Soda-lime Borosilicate Glass Enriched in MoO_3 . (Ph.D. thesis). Paris: University Pierre and Marie Curie. Available at: https://inis.iaea.org/collection/NCLCollectionStore/_Public/42/039/42039802.pdf.

both for melter operations and wasteform properties which limits waste loading (McKeown *et al.*, 2017). The situation is different for phosphate glasses where Mo^{6+} can be connected to the phosphate network through $\text{Mo}-\text{O}-\text{P}$ bonds with a high fraction of MoO_6 entities, which explains the higher MoO_3 solubility in this kind of glass (Santagneli *et al.*, 2007). For instance, up to 83 mol % MoO_3 can be dissolved in pure P_2O_5 glass (Bridge and Patel, 1986).

As alkaline-earth molybdates such as CaMoO_4 (powellite) are much less soluble in water than alkali molybdates, that may also incorporate radioactive Cs, if crystallization cannot be avoided – as in Mo-rich waste (Fig. 4) – it is strongly preferable to orientate

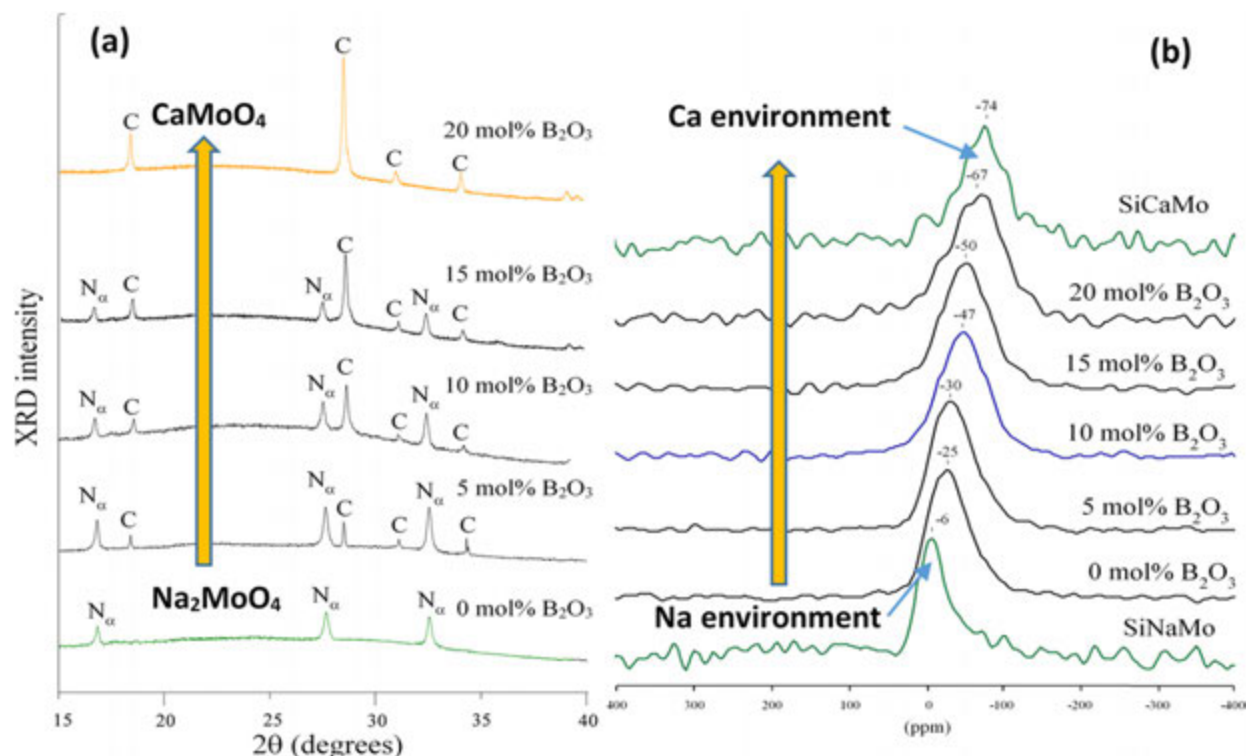


Fig. 13 (a) Changes in XRD patterns with B₂O₃ content of slowly cooled soda-lime borosilicate glasses containing about 2.5 mol% MoO₃ showing the increasing CaMoO₄ (C) crystallization tendency at the expense of Na₂MoO₄ (N_α) when the B₂O₃ content increases. (b) Changes with B₂O₃ content of ⁹⁵Mo MAS NMR spectra of quenched soda-lime borosilicate glasses containing about 2.5 mol% MoO₃ compared with spectra of reference glasses of the SiO₂-CaO-MoO₃ (SiCaMo) and SiO₂-Na₂O-MoO₃ (SiNaMo) systems showing the progressive Ca-enrichment in the environment of MoO₄²⁻ entities when the B₂O₃ content increases. Modified from Magnin, M., Schuller, S., Mercier, C., *et al.*, 2011. Modification of molybdenum structural environment in borosilicate glasses with increasing content of boron and calcium oxide by ⁹⁵Mo MAS NMR. *J. Am. Ceram. Soc.* 94, 4274–4282, permission from John Wiley and Sons.

crystallization towards alkaline-earth molybdates. This can be performed for instance by increasing the B₂O₃ content in Mo-rich borosilicate glasses. As BO₄⁻ units are preferentially charge compensated by alkalis, their presence in the glassy network (Fig. 1) induces an increase of the proportion of alkaline-earth cations in the region surrounding MoO₄⁻ entities which promotes the crystallization of alkaline-earth molybdates at the expense of alkali molybdates (Caurant *et al.*, 2007b; Magnin *et al.*, 2011) (Figs. 12 and 13).

The presence in HLW or the addition to the melt of certain elements such as lanthanides and vanadium can help the incorporation of molybdenum in borosilicate melts and glasses. For instance, it has been shown that the progressive addition of Nd₂O₃ to a Mo-rich borosilicate glass enables molybdate crystallization to be suppressed during melt cooling (Chouard *et al.*, 2011). This beneficial effect of lanthanides on molybdenum solubility has also been found for other lanthanides of various sizes (La, Ce, Sm, Er, Yb) (Patil *et al.*, 2018). Two alternative structural models have been proposed to explain this effect of lanthanides, all considering that Ln³⁺ and MoO₄²⁻ ions are located in the same regions of the glass structure (Chouard *et al.*, 2011; Brehault *et al.*, 2018). As lanthanides are already present in significant concentration in HLW (Fig. 3), their presence may participate in molybdenum stabilization in nuclear borosilicate glasses. It has also been reported that the addition of vanadium as V₂O₅ in Mo-rich borosilicate glasses would help to stabilize MoO₄²⁻ and to avoid yellow phase formation; the presence of VO₄³⁻ tetrahedral units sharing alkali cations with MoO₄²⁻ would be responsible for this effect (McKeown *et al.*, 2017). Recent studies also indicate that the addition of P₂O₅ to Mo-rich borosilicate glasses would help MoO₃ dissolution in the melt, probably by forming phosphorus-rich regions able to incorporate molybdenum (Prakash *et al.*, 2019; Krishnamurthy *et al.*, 2020). Magnesium aluminosilicate glass compositions have also been reported to incorporate more molybdenum than borosilicate glasses (Tan *et al.*, 2015). It is interesting to note that in spite of their low durability, the separation or/and crystallization of alkali molybdates in borosilicate glasses does not necessarily imply a decrease of the chemical durability in water of the overall wastefrom. For example, the separation of isolated (i.e., non-percolating) sodium molybdate particles in a borosilicate glass may lead to an increase of the surrounding glass durability (due to Na₂O depletion and decrease of the proportion of NBOs) which controls the alteration of the poorly durable sodium molybdate particles dispersed in the glass (Fig. 14) (Nicoleau *et al.*, 2015).

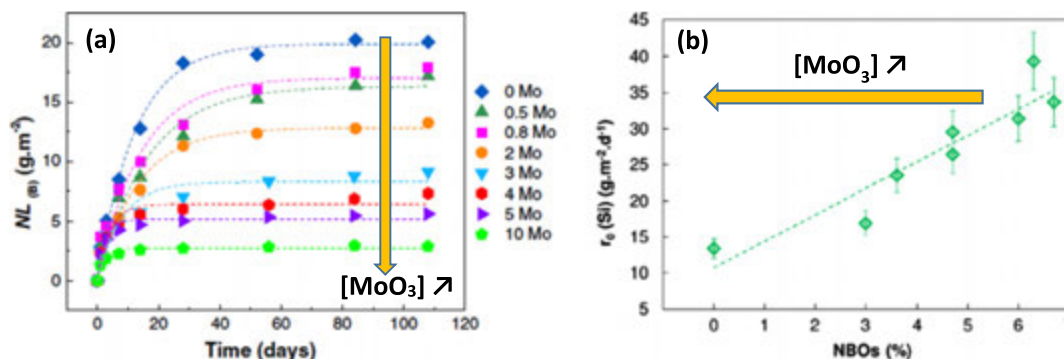


Fig. 14 (a) Evolution with time of the normalized mass loss for boron during alteration at 90°C in water of a sodium borosilicate glass with increasing MoO₃ contents (0–10 mol%) showing an important decrease of the amount of glass altered. Above 1.4 mol% MoO₃ glasses were heterogeneous (phase separation + Na₂MoO₄ crystallization). (b) Evolution of the initial dissolution rate r_0 for Si for the same glass series as a function of the percentage of NBOs (that decreases with MoO₃ content). A clear correlation is observed between the decrease of r_0 of the glassy phase (where Si is located) and the drop in the number of NBOs (increase of the polymerization of the glassy network). Modified from Nicoleau, E., Schuller, S., Angeli, F., *et al.*, 2015. Phase separation and crystallization effects on the structure and durability of molybdenum borosilicate glass. *J. Non Cryst. Solids* 427, 120–133, p. 130 permission from Elsevier.

Incorporation of Lanthanides and Actinides

Lanthanides (Ln) with yttrium represent one of the most abundant family of FP in HLW (**Fig. 3**) where the four largest Ln (La, Ce, Pr, Nd) represent more than 90 wt% of all Ln. Only a small fraction of lanthanides is radioactive (the longest-lived Ln isotope is ¹⁵¹Sm with half-life of 93 years and low concentration) and all Ln are poorly soluble in water. Due to their 4fⁿ electronic configuration with deep 4f level, lanthanides mainly occur at oxidation state +III, except Ce that frequently exists as Ce³⁺ and Ce⁴⁺ depending on redox conditions. In comparison, the amount of actinides (An) in HLW is much smaller than that of lanthanides (**Fig. 3**) but they are all radioactive (α -radionuclides). They mainly consist of minor actinides (Np, Am, Cm) and small amounts of U and Pu. Because of their 5fⁿ electronic configuration, U, Np and Pu may occur at higher oxidation state than +III, but as the energy and the spatial extension of the 5f orbital drops rapidly with increasing actinides atomic number, heavier actinides (Am, Cm) behave more as lanthanides and only exist as Am³⁺ and Cm³⁺ in glasses (Eller *et al.*, 1985). This is the reason why Ln³⁺ (such as Nd³⁺) with close ionic radius to Am³⁺ and Cm³⁺ are frequently used as Am and Cm non-radioactive surrogates in laboratory experiments on nuclear glasses. It has also been shown that in borosilicate glasses Nd³⁺ and Am³⁺ behave similarly during crystallization (Bardez-Giboire *et al.*, 2017).

The case of lanthanides

Despite their high F_s Ln³⁺ cations are usually well dissolved in nuclear borosilicate glasses. Nevertheless, for high waste loading the crystallization of Ln-rich phases may be observed during melt cooling such as Ca₂Ln₈(SiO₄)₆O₂ (apatite) (**Fig. 7**), and Ln borates and borosilicates depending on glass composition (Quintas *et al.*, 2008; Chen *et al.*, 2020). Moreover, the size of Ln³⁺ cations may strongly impact the nature of RE-rich crystals and glass crystallization tendency (Loiseau *et al.*, 2004; Quintas *et al.*, 2008; Kidari *et al.*, 2012; Chen *et al.*, 2020). Even if a phase like Ca₂Ln₈(SiO₄)₆O₂ exhibits a good chemical durability, it tends to become amorphous and swell under self-irradiation due to the α -decay of MA that can partly substitute for Ln in crystal structures (Weber, 1983). This could then induce local strains and cracks in the surrounding glass (Weber *et al.*, 1979) depending on crystal size which would be problematic for the long-term behavior of wasteforms; this requires control of their crystallization and particularly their size or to avoid Ln-rich phase formation, modifying for instance glass composition to improve Ln³⁺ solubility (Chouard *et al.*, 2019). Moreover, it has been reported that the crystallization of Ca₂Ln₈(SiO₄)₆O₂ in borosilicate glasses tends to make them less durable against water alteration because of the changes of both the composition (CaO and Ln₂O₃ depletion), the structure and the durability of the surrounding glass in comparison with a homogeneous glass (Nicoleau *et al.*, 2016). Nevertheless, glass-ceramics containing Ca₂Ln₈(SiO₄)₆O₂ or NaLn₉(SiO₄)₆O₂ crystals have been proposed as wasteform for actinides immobilization because of the capacity of apatite crystals to incorporate trivalent actinides in their structure (Caurant *et al.*, 2006; Zhao *et al.*, 2001).

Ln₂O₃ is very weakly soluble in pure silica glass (strong phase separation tendency) due to the high F_s of Ln³⁺ ions that do not succeed to satisfy their environment because of the insufficient quantity of NBOs, and thus rapidly tend to form clusters. The addition of alkali and alkaline-earth oxides enables its solubility to significantly increase both by creating numerous NBOs and by bringing alkali and alkaline-earth cations that may ensure local charge compensation in the region surrounding LnO_n polyhedra as shown in **Fig. 1**. When added to silicate or borosilicate glasses, Ln₂O₃ usually act as modifier oxide forming NBOs (**Fig. 15**) and Ln³⁺ are linked to NBOs forming strong Ln–O–Si bonds which explains the rise of T_g with Ln₂O₃ content (Schaller *et al.*, 1999; Kidari *et al.*, 2012; Gaddam *et al.*, 2019). Moreover, the impact of La₂O₃ content on the alteration kinetics of borosilicate glasses shows that lanthanum improves their chemical durability in water and La³⁺ ions (as other Ln) are almost integrally retained in the alteration layer on the glass surface (Molières *et al.*, 2013; Ménard *et al.*, 1998).

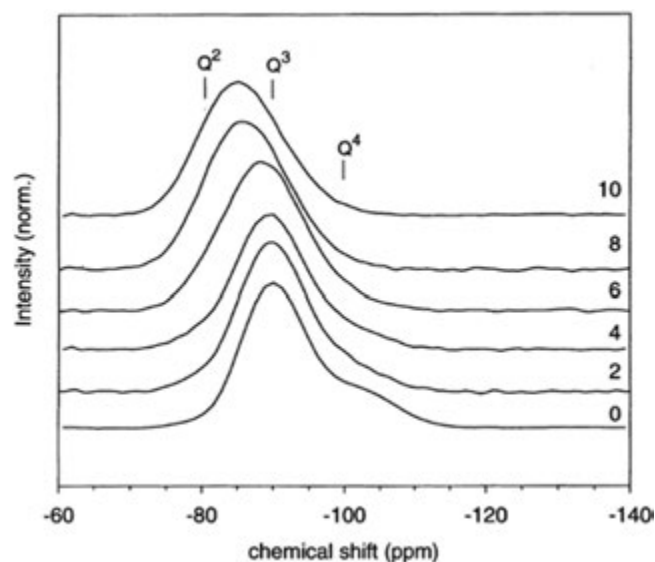


Fig. 15 Changes in ^{29}Si MAS NMR spectra when increasing amounts of La_2O_3 (0–10 mol%) are added to $75\text{SiO}_2\text{-}25\text{Na}_2\text{O}$ glass showing evidence of the depolymerization of the silicate network and the modifier role of La_2O_3 (Q^n represents SiO_4 tetrahedral units with n BOs). Reproduced from Schaller, T., Stebbins, J.F., Wilding, M.C., 1999. Cation clustering and formation of free oxide ions in sodium and potassium lanthanum silicate glasses: Nuclear magnetic resonance and Raman spectroscopic findings. *J. Non Cryst. Solids* 243, 146–157, with permission from Elsevier.

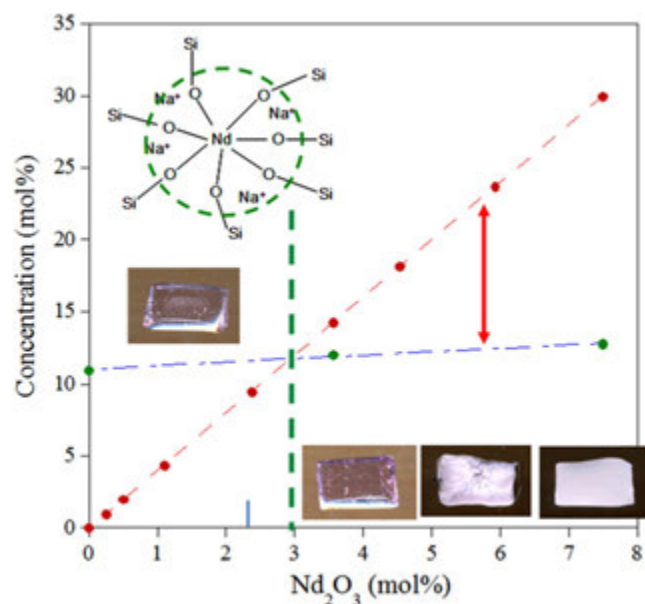


Fig. 16 Evolution with the Nd_2O_3 content in a borosilicate glass ($64\text{SiO}_2\text{-}9.3\text{B}_2\text{O}_3\text{-}3.2\text{Al}_2\text{O}_3\text{-}15\text{Na}_2\text{O}\text{-}6.5\text{CaO}\text{-}2\text{ZrO}_2$ mol%): (in red) of the amount of $\text{Na}_2\text{O} + \text{CaO}$ needed to compensate the negative charge excess of NdO_7 polyhedra (see Fig. 1) in the glass structure (4 moles ($\text{Na}_2\text{O} + \text{CaO}$) for 1 mole Nd_2O_3); (in green) of the amount of $\text{Na}_2\text{O} + \text{CaO}$ available both to charge compensate NdO_7 polyhedra and to supply NBOs for their formation, taking into account the amount of charge compensators used for the compensation of AlO_4^- and BO_4^- units deduced from NMR results. Above about 3 mol% Nd_2O_3 (vertical dotted green line) there is not enough NBOs and charge compensators available to enable the incorporation of Nd^{3+} as isolated NdO_7 entities which thus rapidly tend to agglomerate and to separate or crystallize as $\text{Ca}_2\text{Nd}_8(\text{SiO}_4)_6\text{O}_2$ phase (apatite) when the charge compensators deficiency increases (red arrow). The pictures of slowly cooled samples (6°C min^{-1}) from the melt with increasing Nd_2O_3 content show their strong crystallization tendency when the amount of $\text{Na}_2\text{O} + \text{CaO}$ becomes insufficient.

To be stabilized and uniformly dispersed in a glass structure, Ln^{3+} needs to satisfy easily its environment finding enough alkali or alkaline-earth cations and NBOs (Angeli et al., 2013). When adding increasing amounts of Ln_2O_3 to glass, Ln^{3+} remains soluble in the glass network as long as there are enough charge compensators, but beyond this concentration limit the separation or crystallization of a Ln-rich phase can be observed (Fig. 16).

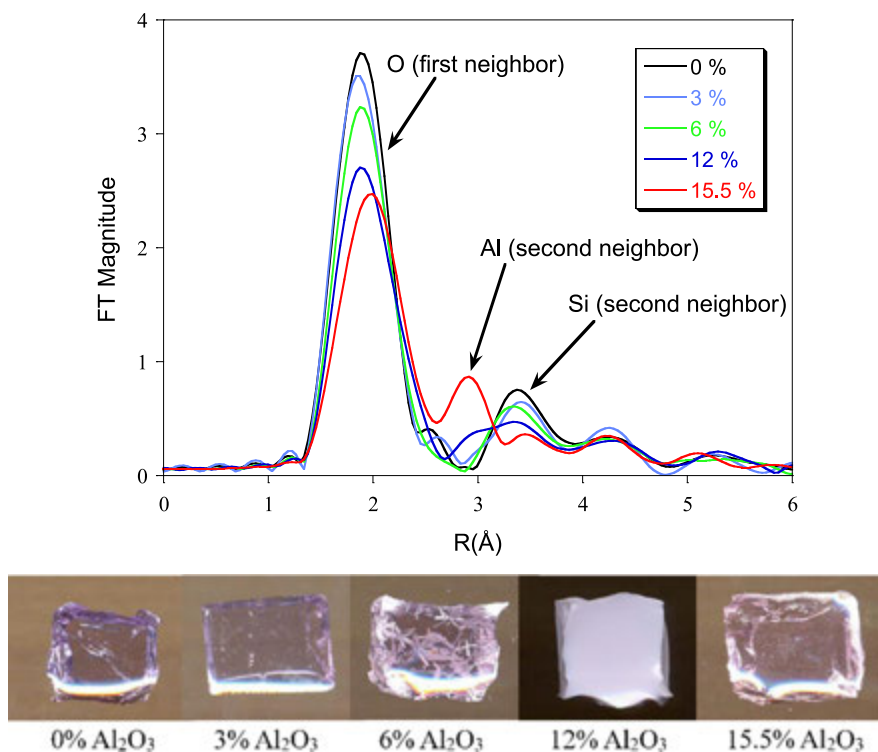


Fig. 17 Changes in the Fourier transforms of the Nd L_{III} -edge EXAFS spectra of neodymium in a borosilicate glass (61.8SiO₂-9B₂O₃-16.5Na₂O-7.2CaO-2ZrO₂-3.5Nd₂O₃ mol.%) to which increasing amounts of Al₂O₃ (0–15.5 mol%) were progressively substituted for Na₂O + CaO, keeping all other concentrations constant. All compositions were peralkaline except that with 15.5 mol% Al₂O₃ was peraluminous and for which there is evidence for the presence of Al as second neighbor of Nd (Nd³⁺ acts as charge compensator of AlO₄[−] units inducing a decrease of the second neighbor distance). The images given at the bottom of the curves show the changes in the aspect of the glasses after cooling from the melt at 6°C min^{−1}. No crystals were observed with 0 and 3 mol% Al₂O₃, but crystals (Ca₂Nd₆(SiO₄)₆O₂) and phase separation (100 nm Nd-rich droplets) were detected respectively with 6 and 12 mol% Al₂O₃ because of the decreasing amount of Na₂O + CaO available to enable dissolution of Nd³⁺ ions. However, when the glass became peraluminous (15.5 mol% Al₂O₃), Nd³⁺ ions were again dispersed in the glass structure. Based on Bardez, I., 2004. Study of the Structural Characteristics and Properties of Glasses Rich in Rare Earths Intended for the Immobilization of Fission Products and Long-lived Elements. (Ph.D. thesis). Paris: University Pierre and Marie Curie. (in French). Available at: <https://pastel.archives-ouvertes.fr/pastel-00001075>.

Al₂O₃ content also has an important effect on the stabilization of Ln³⁺ in borosilicate glasses. For instance, the addition of increasing amounts of Al₂O₃ to a peralkaline borosilicate glass progressively destabilizes Ln³⁺ because aluminum (mainly present as AlO₄[−] units) is charge compensated in priority compared to LnO_n polyhedra which induces a progressive depletion of charge compensators available for lanthanides, and the separation or crystallization tendency of Ln-rich phases increases. However, when the composition becomes peraluminous (i.e., when there is not enough alkali and alkaline-earth cations to compensate all AlO₄[−] units), the solubility of Ln₂O₃ begins to increase because an increasing number of Nd³⁺ act as charge compensators for the excess AlO₄[−] units (Fig. 17), increasing their dispersion and thus their solubility in the glass structure. Such peraluminous borosilicate glasses have been envisaged to immobilize waste with high Ln₂O₃ contents because of their ability to incorporate higher quantities of Ln₂O₃ than peralkaline glasses and they exhibit higher chemical durability (Gasnier *et al.*, 2014; Piovesan *et al.*, 2018).

The case of actinides

While the chemical properties and the behavior of Am and Cm in borosilicate glasses appear close to that of trivalent lanthanides such as Nd (oxidation state +III, similar size, deep 4f and 5f levels) that can be used as Am or Cm surrogates, this is not the case for lighter actinides U, Np and Pu. Indeed, these three actinides may exist in different oxidation states (U⁴⁺, U⁵⁺, U⁶⁺, Np³⁺, Np⁴⁺, Np⁵⁺, Pu³⁺, Pu⁴⁺) depending on the conditions of glass preparation (temperature and redox). Plutonium mainly occurs as Pu⁴⁺ ions in nuclear glasses prepared under neutral or oxidizing conditions and it is only under strongly reducing conditions that almost all Pu⁴⁺ ions can be reduced to Pu³⁺ ions (Cachia *et al.*, 2006; Deschanel *et al.*, 2007). Neptunium exists as Np³⁺ only in glasses melted under strongly reducing conditions and mainly as Np⁴⁺ + Np⁵⁺ in glasses melted under more oxidizing conditions, whereas uranium is present as U⁴⁺ in glasses melted under reducing conditions and as both U⁵⁺ and U⁶⁺ if glasses are melted in oxidizing conditions (Gin *et al.*, 2017b). Because of their lower F_o, trivalent actinides (Pu³⁺, Am³⁺, Cm³⁺) are generally more soluble in glasses than actinides with higher oxidation states. This is true for plutonium whose solubility of Pu³⁺ is significantly higher than that of Pu⁴⁺. For instance, Pu solubility can be increased from 2.5 (melting in air without reducing agent)

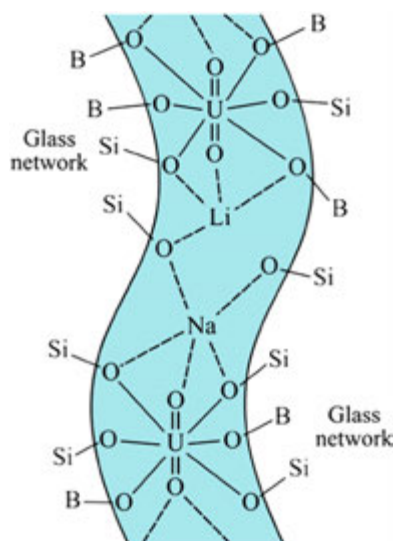


Fig. 18 Structural scheme showing the way UO_2^{2+} (uranyl) entities could be incorporated in the depolymerized regions of a borosilicate glass. Reproduced from Connelly, A.J., Hyatt, N.C., Travis, K.P., *et al.*, 2013. The effect of uranium oxide additions on the structure of alkali borosilicate glasses. *J. Non Cryst. Solids* 378, 282–289, with permission from Elsevier.

to more than 4 wt% PuO_2 (melting in Ar with reducing agent) in a borosilicate glass (Cachia *et al.*, 2006). However, in the case of the highest uranium and neptunium oxidation states (U^{6+} , Np^{5+}) the situation is different because these elements would occur respectively as highly covalent linear uranyl (UO_2^{2+}) and neptunyl (NpO_2^{2+}) entities (Gin *et al.*, 2017b). These entities would be more soluble than the lower oxidation states of U and Np because of their easy dissolution in the depolymerized regions of the borosilicate glass structure where they would be connected to the NBOs of the network and charge compensated by modifier cations as has been proposed for uranyl entities (Fig. 18) (Connelly *et al.*, 2013). Structural studies performed on Pu^{3+} and Cm^{3+} in borosilicate glasses showed that these species are well dispersed in the glass structure and are respectively located in 8- and 7-fold coordinated sites (Deschanel *et al.*, 2007). Concerning the immobilization of Pu-rich waste in glassy wasteforms, it has been shown that lanthanide borosilicate glasses containing more than 40 wt% Ln_2O_3 (La_2O_3 , Nd_2O_3 , Gd_2O_3) were able to incorporate up to about 10 wt% PuO_2 whereas borosilicate glasses may dissolve only up to about 2 wt% and are less durable (Shiryaev *et al.*, 2009). As lanthanides, due to their very low solubility in water, Am, Cm and Pu are almost totally retained in the alteration layer on the glass surface, while the retention of Np and U in this layer may be lower depending on their oxidation state in the aqueous medium (Gin *et al.*, 2017b; Ménard *et al.*, 1998).

Long-Term Behavior of Nuclear Glasses

As it is usually considered that HLW must be isolated from the biosphere at least until their radiotoxicity level will drop back to the radiotoxicity level of the initial uranium ore used to prepare the fuel (Fig. 2), glassy wasteforms must keep their containment properties for a very long time, at least several tens of thousands of years. For this, they must exhibit very good long-term behavior concerning both their resistance against the self-irradiation induced by the decay of the radionuclides incorporated into their structure and their resistance against alteration by water (liquid or vapor) that may be in contact with the glass during geological disposal.

Self-Irradiation Resistance of Nuclear Glasses

The presence of high quantities of α and β radioactive elements (FP + MA) in nuclear glasses will induce numerous atomic displacements during their storage and disposal (Table 3). Indeed, during the α -decay of actinides, the α -recoil nuclei (with 80–120 keV energy) lose their energy in elastic collisions with the nuclei of their neighborhood and the α -particles produced (helium nuclei with 4–5 MeV energy) deposit their energy mainly by ionization processes but also by elastic collisions at the end of their paths. For each α -decay about 2400 atomic displacements are induced in the glass structure by the emitted α -particle and the recoil of the new nucleus. For β -particles (electrons) and γ -radiation, the energy transfer is dominated by ionization and electronic excitation processes and the effects on glass structure are expected to be much weaker because of the very low number of atomic displacements. Nevertheless, due to the short half-life of abundant FP such ^{137}Cs and ^{90}Sr , β -decays are the main source of radioactivity and heat generation in the first 500 years, while after this period MA become the main source (Fig. 2).

Table 3 Characteristics of α , β and γ radiations in nuclear glasses due to fission products and minor actinides

Irradiation	Number of events after 10^4 years	Range	Number of atomic displacements per event
α -decay	10^9		
α -particle		$\sim 20 \mu\text{m}$	~ 400
recoil nuclei		30 nm	~ 2000
β -decay	$7 \cdot 10^{19}$	$\sim 1 \text{ mm}$	~ 1
γ	$2 \cdot 10^{19}$	$\sim 2 \text{ cm}$	$\ll 1$

Note: Gin, S., Jollivet, P., Tribet, M., Peugeot, S., Schuller, S., 2017b. Radionuclides containment in nuclear glasses: An overview. *Radiochim. Acta* 105, 927–959.

While in ceramics the accumulation of atomic displacements frequently leads to amorphization (destruction of the long-range order) and swelling (increase of the volume) (Weber *et al.*, 1998), the effect of self-irradiation on the structure and properties is expected to be weaker for nuclear glasses that are already amorphous. In order to evaluate the impact of irradiation damage on the structure and the physical and containment properties of nuclear glasses during storage and disposal, different kinds of accelerated tests are performed (Weber, 2014). For example, in order to simulate the effect of α -decays on glasses, samples can be prepared by incorporating short-lived actinides such as ^{238}Pu or ^{244}Cm (with half-lives of respectively 87 and 18 years) or external irradiation experiments with charged particles (heavy ions, α -particles) can be performed on inactive samples (Weber *et al.*, 1997). Molecular dynamics is also used to simulate the displacement cascades generated in borosilicate glasses by heavy nuclear projectiles which is very helpful to understand the structural effects of α -decays (Peugeot *et al.*, 2014). The effects of γ -irradiation can be simulated using radioactive external sources and β -irradiation can be simulated by external irradiation with electrons (Van de Graaff accelerator). Internal and external irradiation experiments simulating α -decays showed that for borosilicate glasses with compositions close to that of the R7T7 nuclear glass, the density only slightly decreases ($< 1\%$) (Fig. 19) and an improvement of mechanical properties is observed ($\sim 30\%$ hardness reduction and increased resistance to cracking) (Peugeot *et al.*, 2006, 2014).

The behavior in glass structure of helium atoms formed after α -decays and capture of 2 electrons by each α -particle and the consequences of their possible accumulation in the glass structure remain to be clearly evaluated. However, the amount of helium generated in nuclear glasses used for commercial HLW immobilization would be only around 0.1–1 at% after 10^6 years and the formation of bubbles of significant size ($> 10 \text{ nm}$) has not been observed at room temperature (Gin *et al.*, 2017b; Peugeot *et al.*, 2014). Studies have also been performed to evaluate the impact of α -decays on the chemical durability of glasses. Leaching tests have been carried out in water on externally irradiated or short-lived actinides-doped borosilicate glasses. Whereas studies performed on self-irradiated and externally irradiated borosilicate nuclear glasses previously concluded that α -activity has no significant impact on the glass alteration rate by water (Peugeot *et al.*, 2007), more recent works show non-negligible impact of radiation damage on their alteration rate (Tribet *et al.*, 2020), which may affect to some extent the containment properties during disposal over the very long-term. Moreover, the alteration rate in water tends to increase if irradiated glasses are previously altered by water in vapor phase, which is expected to occur for a long time during disposal before alteration with liquid water (Bates *et al.*, 1984; Majerus *et al.*, 2020).

The impact of transmutation of radioactive elements present in nuclear glasses is also important to consider. The transmutation of FP such as ^{137}Cs and ^{90}Sr are accompanied by important valence and ionic radius changes ($\text{Cs}^+ \rightarrow \text{Ba}^{2+}$ and $\text{Sr}^{2+} \rightarrow \text{Y}^{3+} \rightarrow \text{Zr}^{4+}$) that can be easily accommodated in the flexible structure of nuclear glasses that contain high amounts of NBOs and charge compensators. For MA, as decay products are also actinides, they are expected to be incorporated similarly in glass structure (Gin *et al.*, 2017b).

The effect of self-irradiation on the structure of the glassy network of borosilicate glasses has been examined by structural characterizations on irradiated samples. Concerning β -decays, external irradiation of borosilicate glasses by electrons showed the formation of paramagnetic defects (as evidenced by EPR, Electron Paramagnetic Resonance), changes in the polymerization of the glassy network and the formation of dissolved molecular oxygen (Malchukova *et al.*, 2009). However, the presence of transition metals such as chromium and iron may significantly diminish the amount of defects and the structural changes induced under β -irradiation. This effect can be attributed to the capacity of transition metals to change their state charge by electron trapping leading to stable valence states, but this would not suppress the defects produced by hole trapping (electron holes being generated in glasses during electron irradiation) (Malchukova *et al.*, 2009). Concerning α -decays, NMR investigations of ^{244}Cm doped ISG glass showed only small modifications of the local structure: a slight variation of the environment of AlO_4^- units and a weak decrease ($\sim 7\%$) of the proportion of BO_4^- units were observed (Fig. 20). The decrease of the proportion of BO_4^- units under α self-irradiation was explained by local melting plus rapid quenching effects in the glass structure due to α -recoils and α -particles (Charpentier *et al.*, 2016), similar to the well-known effect of the quenching rate on the $\text{BO}_4^- \leftrightarrow \text{BO}_3$ equilibrium in borosilicate glasses (Angeli *et al.*, 2018). Moreover, during their displacement in the glass structure, the energy loss of α -particles would partly repair the regions damaged by α -recoils as shown by sequential and simultaneous ion irradiations (Mir *et al.*, 2015). These structural modifications and the formation of other point defects and changes in ring size distribution under α -irradiation that have also been reported may explain why irradiated borosilicate glasses are more reactive with water than pristine glasses (Tribet *et al.*, 2020).

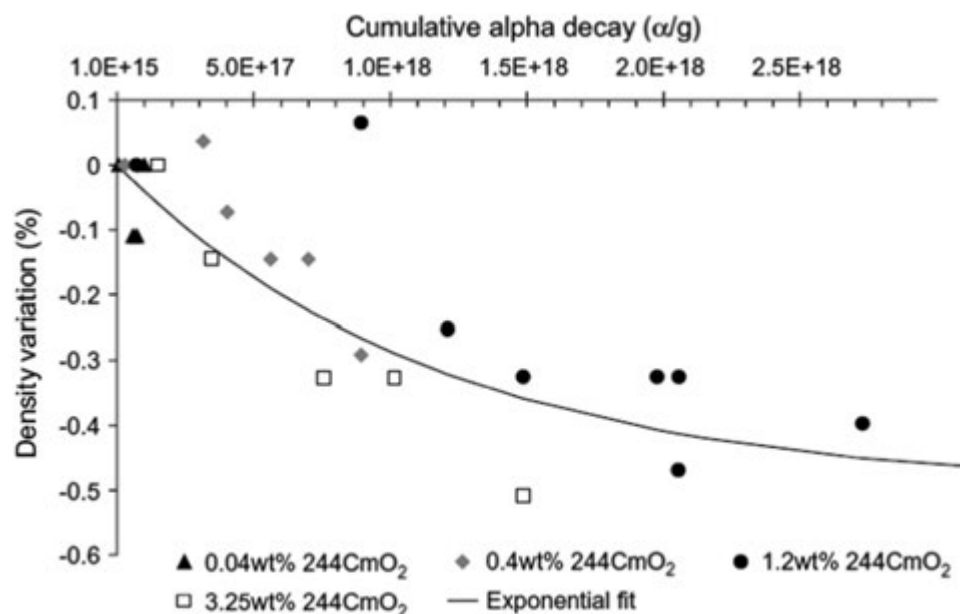


Fig. 19 Evolution versus the α -decay cumulative dose of the density of a borosilicate glass doped with ^{244}Cm . A cumulative dose of about $3 \cdot 10^{18} \alpha/\text{g}$ corresponds to several thousand years of storage of active nuclear borosilicate glasses. Reproduced from Peugeot, S., Cachia, J.-N., Jégou, C., *et al.*, 2006. Irradiation stability of R7T7-type borosilicate glass. *J. Nucl. Mater.* 354, 1–13, p. 7. with permission from Elsevier.

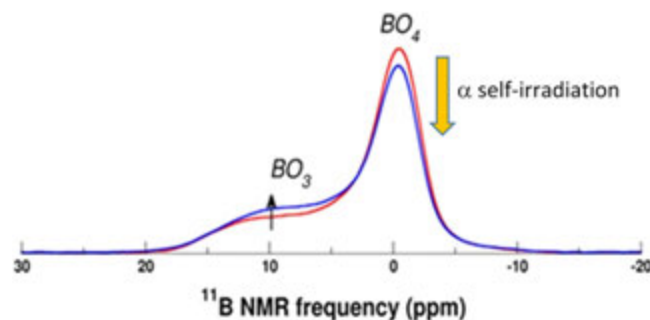


Fig. 20 Comparison between the ^{11}B MAS NMR spectra (9.4 T) of a damaged (in blue) and annealed (in red) ^{244}Cm doped (0.13 mol% Cm_2O_3) borosilicate ISG glass. The damaged glass has accumulated an α -decays dose of $4.4 \times 10^{18} \alpha \text{ g}^{-1}$ equivalent to 10^4 years of disposal and the annealed glass has accumulated an α -decays dose of $7 \times 10^{16} \alpha \text{ g}^{-1}$. Modified from Charpentier, T., Martel, L., Mir, A.H., *et al.*, 2016. Self-healing capacity of nuclear glass observed by NMR spectroscopy. *Sci. Rep.* 6, 25499. Authorized by Springer Nature.

Resistance of Nuclear Glasses Against Alteration in Aqueous Environment

As any material, glasses chemically react with their environment and degrade over a long period of time. As oxide materials, the main “corroding” agent of glasses is water, either in the vapor or in the liquid state. This chemical degradation is an issue to all glasses and glass applications, such as natural glasses, commercial glasses and glasses of the cultural heritage. In the case of nuclear waste glasses, the central question is that of the kinetics: at which rate will the glass degrade into the alteration products and release the radioactive nuclei? It is considered that once the glass has degraded, the radiotoxic elements are released from this first barrier, and then their containment relies on the other barriers (Vernaz *et al.*, 2012). The degradation by water, or aqueous alteration, is the only process leading to the breakdown of the containment properties, as the other evolving processes such as crystallization may occur over a considerably longer period of time (Fig. 8).

Water reacts with glass by (1) hydration and ionic exchange, and (2) hydrolysis (Grambow and Müller, 2001; Conradt, 2008). Glass hydration and ionic exchange do not modify the glass structure; they produce a “hydrated glass” bearing molecular water and Si-OH (silanol) groups in place of the Si-OM groups where M are cations exchangeable with H^+ , such as alkali and alkaline-earth ions:



Hydrolysis is the nucleophilic, or acid-base reaction of water with the M-O bonds that breaks these bonds and produces solvated M species (M is any element bound to oxygen). The multi-step hydrolysis of the M-O bonds that form the glass network (M = Si, Al, B...) leads to the destabilization and dissolution of the glass material:



Every hydrolysis reaction has an equilibrium constant $K_{\text{eq},M}(T)$ that controls the amount of element M to be dissolved at a given temperature T and at equilibrium. Every hydrolysis reaction also has a kinetic rate $R_{M,T}(t)$ that is the initial rate $R_{M,T,0}$ weighted by the affinity factor:

$$K_{\text{eq},M}(T) = \exp\left(-\frac{\Delta G_M^0(T)}{RT}\right) \quad (3)$$

$$R_{M,T}(t) = R_{M,T,0} \left(1 - \frac{Q_M(t)}{K_{\text{eq}}(T)}\right) \quad (4)$$

Where $Q_M(t)$ is the reaction product of the hydrolysis of M at time t and $R_{M,T,0}$ is the initial rate.

In multicomponent glasses such as nuclear glasses, all components have different solubilities, all varying differently with the pH. The dissolution is then generally non-congruent, producing an alteration layer at the interface between the pristine glass and the solution, which contains the most insoluble components. For instance, alkalis and boron pass into solution, while Zr, Al (charge-compensated by Ca) (Angeli *et al.*, 2001), Fe, La, Mg, Ca generally stay completely or partially in the silicate alteration gel (depending on the pH) (Molières *et al.*, 2013). Moreover, the material dissolution is irreversible because the reverse reactions cannot back-produce the starting glass. Because of its low solubility and structural role as main network former, the dissolution rate of the glass is considered to be limited by the dissolution rate of SiO_2 . The affinity term controlling the kinetics is then the equilibrium with SiO_2 as amorphous silica (or as cristobalite in some geochemical models).

An important experimental approach is to measure the glass dissolution kinetics in static conditions (representative of the deep disposal condition) in various conditions of T, S/V (S surface of exposed glass, V volume of the solution), pH and solution composition. The solution is sampled at regular intervals and analysed by ICP-OES. From the measured concentrations $C_i(t)$, the normalized leached fractions in every element i are calculated by:

$$\text{NL}_i(t) = \frac{C_i(t) \times V}{x_i \times m \times \Sigma} \quad (5)$$

Where V is the volume of the solution, x_i is the mass fraction of element i in the glass composition, m is the mass of glass powder engaged in the experiment and Σ is the specific surface of the glass powder (in $\text{m}^2 \text{g}^{-1}$). Then, $\text{NL}_i(t)$ is in $\text{g m}^{-2} \text{d}^{-1}$ and represents the amount of dissolved glass considering the amount of element i that has passed into solution. Because B is very rarely found in the alteration layer, it is considered as a good tracer of the dissolution and is used to calculate the glass leached fraction and follows the glass dissolution kinetics (Fig. 14). Following numerous experimental studies (Caillateau *et al.*, 2008; Gin *et al.*, 2012), the glass dissolution rate in static conditions is divided into three successive regimes: the initial rate, a transition regime, and the residual rate regime (Fig. 21). The initial rate is the dissolution rate in very dilute conditions when no diffusion barrier slows down the kinetics. It is a property of the glass that strongly depends on its composition, on the temperature and on the pH of the solution (Frugier *et al.*, 2008). Secondary influencing parameters are the glass structure (Angeli *et al.*, 2018; Mascaraque *et al.*, 2017) and the chemistry of the solution such as its ionic strength (Icenhower and Dove, 2000) and the presence of complexing species (Tournié *et al.*, 2013). The transition regime corresponds to the progressive decrease of the dissolution rate by several orders of magnitude, which has two origins: the saturation of the solution with silica (affinity term Q/K_{eq} approaching 1) and the formation of an alteration layer or sub-layer with diffusion barrier properties (passivating layer). This alteration layer ends up in turn transforming into more stable products. At some time, an almost stationary regime establishes, when the diffusion rate of the reactive species through the passivating layer equals the rate of transformation of this layer into other, less passivating, products. This residual rate regime corresponds to the slow dissolution and transformation of the glass into a hydrated, porous silicate gel modified with other insoluble products (such as Zr and some amount of Al, La, Ca...). It can last a very long time, but it is also possible that at some moment, by exceeding some solubility product and/or induction time, a more insoluble and non-passivating Si-bearing product precipitates, which may take control of the kinetics and resume the dissolution of the glass by destroying the passivating layer (Fig. 21). This resumption regime has been observed in specific conditions of high pH and/or temperature, caused by the formation of zeolite phases (Fournier *et al.*, 2014).

The most extensive studies have been undertaken on the SON68 glass (inactive version of the R7T7 French nuclear glass). In a closed system composed of (initially) pure water at 50°C , the assessed residual rate of the SON68 glass is about $5.10^{-5} \text{ g m}^{-2} \text{d}^{-1}$, that is about 7 nm/year (Frugier *et al.*, 2008). This temperature of 50°C is considered representative of the actual temperature of the surface of the glass canisters over a very long time. The surface microstructure of a SON68 glass altered for 25 years in slowly flowing water equilibrated with granite, sand and (Ni,Cr) corrosion products, at 90°C and 100 bars, is depicted in Fig. 22 (Gin *et al.*, 2011). The alteration layer is composed of a hydrated glass, a porous gel and crystalline phyllosilicate phases in the outer part of the gel and on the surface. The dense layer that bears the passivating properties is located at the interface between the pristine glass and the hydrated glass, its diffusion coefficient is about $10^{-21} \text{ m}^2 \text{s}^{-1}$ characterizing a dense, solid phase.

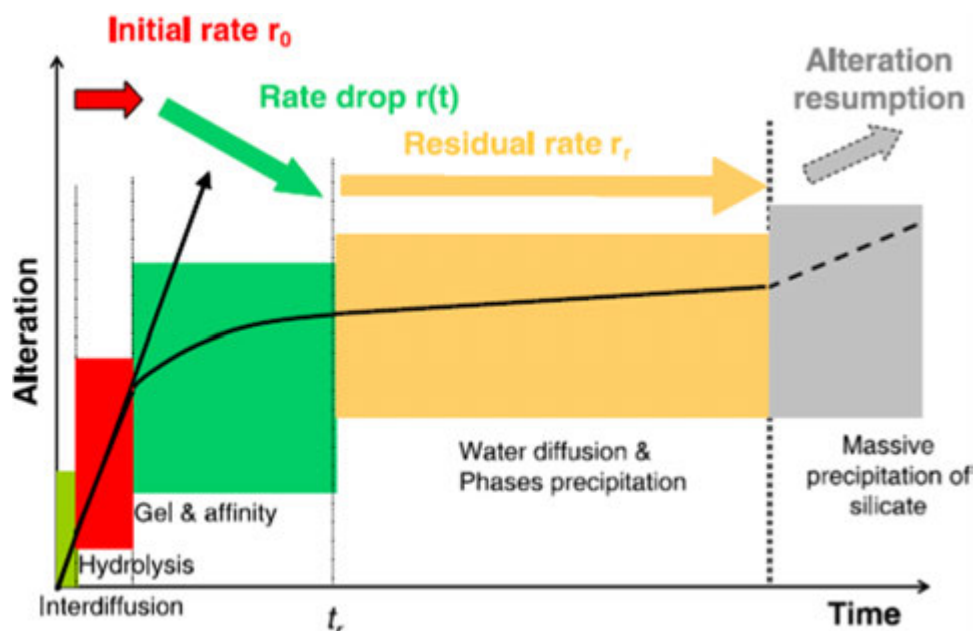


Fig. 21 The three successive regimes of the dissolution rate in water of a nuclear borosilicate glass in static conditions: the initial rate, the transition regime, and the residual rate regime. The duration of these different regimes depends on both glass composition and alteration conditions. In specific conditions, a resumption regime can be observed for long times, due to silicate phases precipitation that may affect the passivating power of the alteration layer. Reproduced from Gin, S., Beaudoux, X., Angéli, F., Jégou, C., Godon, N., 2012. Effect of composition on the short-term and long-term dissolution rates of ten borosilicate glasses of increasing complexity from 3 to 30 oxides. *J. Non Cryst. Solids* 358, 2559–2570, p. 2665, with permission from Elsevier.

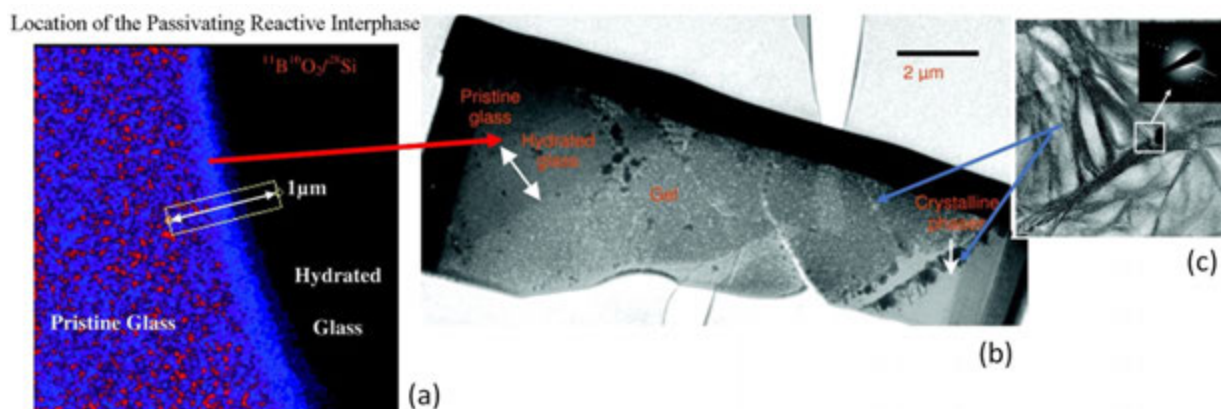


Fig. 22 Microstructure of the alteration layer of the SON68 inactive French nuclear borosilicate glass altered for 25 years at 90°C and 100 bars in a confined granitic medium. (a) NanoSIMS analysis of the interface between the pristine glass and the hydrated glass showing a 200 nm thick dense layer. The diffusion coefficient of boron through this layer is of the order $10^{-21} \text{ m}^2 \text{ s}^{-1}$ (b) TEM bright-field image of a FIB cross-section of the altered glass surface, showing the pristine glass and the alteration layer divided into a hydrated glass, a porous silicate gel and a top layer of phyllosilicates (phyllosilicates are also found in the porous gel). (c) TEM bright-field image of the phyllosilicates with an electron diffraction pattern of a crystallized grain. Reproduced from Gin, S., Guittouneau, C., Godon, N., *et al.*, 2011. Nuclear glass durability: New insight into alteration layer properties. *J. Phys. Chem. C* 115, 18696–18706. Authorized by The American Chemical Society.

Because of the nonlinear time and temperature dependency of the various reaction rates, and because of the coupling of these rates with transport processes through an evolving layer, there is no general theory to predict the kinetics of the dissolution, nor the nature, stability, and properties of the alteration layer. Predictions on the long-term can only be made based on geochemical models using parameters (equilibrium constants, kinetic parameters, diffusion coefficients) determined experimentally on a given glass-environmental system (Frugier *et al.*, 2008; Verney-Carron *et al.*, 2010). Archeological glasses or natural glasses altered for very long times in specific, stable conditions are used to validate the prediction capacities of these models (Verney-Carron *et al.*, 2008; Parruzot *et al.*, 2015).

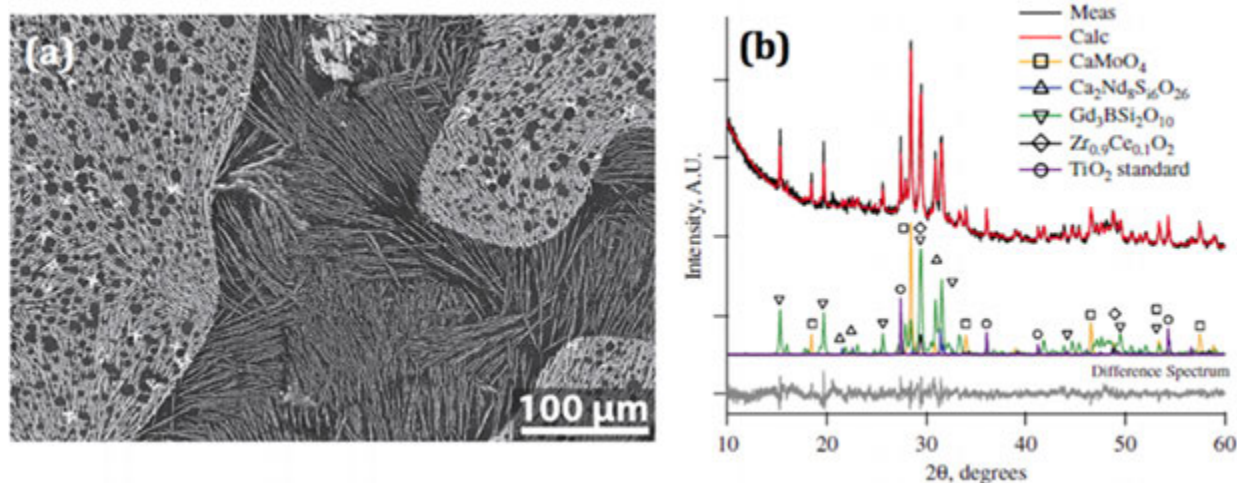


Fig. 23 Multi-phase crystallization occurring during the cooling of an aluminoborosilicate melt containing 42 wt% simulated nuclear waste. (a) SEM image (back-scattered electrons) putting in evidence a large scale phase separation in the liquid followed by crystallization in the two phases. (b) X-ray diffraction pattern of the glass-ceramic presented in (a) with identification of the crystalline phases. Reproduced from Crum, J.V., Turo, L., Riley, B., Tang, M., Kossoy, A., 2012. Multi-phase glass-ceramics as a waste form for combined fission products: Alkalies, alkaline earths, lanthanides, and transition metals. *J. Am. Ceram. Soc.* 95, 1297–1303 p. 5, with permission from John Wiley and Sons.

New mechanisms of glass dissolution and transformation at the interface between the pristine glass and the gel layer have been proposed, following dissolution mechanisms observed for silicate minerals (the coupled interface dissolution-precipitation model, CIDP) (Hellmann *et al.*, 2015). The development of analytical techniques with high spatial resolution, such as atomic probe tomography (APT) and advanced TEM techniques, as well as the use of isotopic tracers have allowed progress in the understanding of the chemical and microstructural changes of the alteration layer and of its diffusion properties (Gin *et al.*, 2017a). Particular attention has been drawn to the effect of environmental parameters such as the presence of iron corrosion products coming from the steel canister, or the composition of the groundwater (De Echave *et al.*, 2018). For instance, concerning the SON68 borosilicate glass, the presence of Fe²⁺ ions in the anoxic water (Michelin *et al.*, 2013), or the presence of Mg²⁺ ions (as in the groundwater of the Callovo-Oxfordian site envisaged for the disposal of the French nuclear glass) (Grambow, 2016) cause the precipitation of Fe-silicate or Mg-smectite phases (Thien *et al.*, 2012), which limit the dissolution rate drop by hindering the formation of a dense passivating layer.

In the scenario of the long-term evolution of the French disposal site established by ANDRA (Grambow, 2016), the nuclear glass will be first exposed to water in the vapor state, for a long period of time of several thousands of years, because of the hydrogen pressure produced by the anoxic corrosion of the steel canisters (Narayanasamy *et al.*, 2019). The alteration of the glass in a vapor state is specific and cannot be confused with the glass alteration in liquid water at high S/V. Water in vapor state or in the film adsorbed onto the glass surface has not the same dynamics and solvation properties as water in “bulk” liquid state. Moreover, the elements dissolved from the glass are not diluted in a liquid phase, so that the precipitation of secondary phases is rapid, modifying the glass surface chemistry (Majérus *et al.*, 2020). Further research is necessary to improve the understanding of the glass alteration in these specific conditions.

Glass-Ceramic Wasteforms

For a long time, the presence of crystals in nuclear glasses was regarded as undesirable because of the modification they may induce on the composition and durability against water of the surrounding glass and on the melting process, but now there is a general trend to accept partial crystallization for some waste if the containment of the final wasteform remains acceptable (Jantzen and Ojovan, 2019). Many studies have been performed to develop nuclear wasteforms consisting of a glassy phase and one or more crystalline phases able to incorporate non-separated HLW or separated long-life wastes in their structure (Donald, 2016; Caurant, 2017; McCloy and Goel, 2017). In the general case, such matrices made of crystals dispersed in a more or less abundant glassy phase are called glass composite materials (GCM) (Lee *et al.*, 2006). This is the case for instance of high waste loading wasteforms within which uncontrolled melt crystallization may occur during natural cooling of the melt (Figs. 4 and 23).

Glass-ceramics wasteforms correspond to a particular type of GCM containing small and numerous crystals homogeneously dispersed in a glassy phase that are obtained after controlled heat treatment of a glass containing the waste (nucleation + growth stages) (Fig. 24(a)) or controlled cooling of a melt, in order to produce a matrix with desired microstructure and crystalline phases in a durable residual glass. These crystalline phases are generally chosen according to their durability and their capacity to incorporate particular categories of elements present in the waste, such as long-lived radionuclides. Similar kind of matrices made of a durable glassy phase and homogeneously dispersed crystals of desired nature and size can also be obtained by sintering a

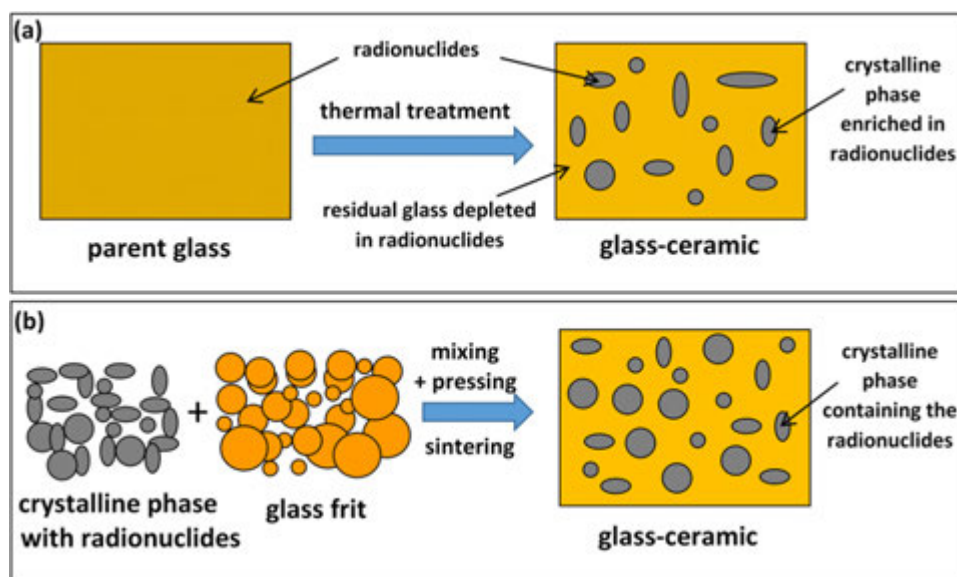


Fig. 24 Principle of the specific immobilization of long-life radionuclides in a glass-ceramic wasteform prepared by (a) crystallization (nucleation + growth) of a glass (referred to as parent glass) containing the radionuclides or (b) sintering a mixture of powders made of a glass frit and crystals in which are already incorporated the radionuclides.

mixture made of a glass powder and a crystalline phase already containing a particular category of elements present in HLW (encapsulation) (Fig. 24(b)).

The motivations for the studies on glass-ceramics for waste containment are varied:

- (1) Improvement of mechanical properties, thermal stability and chemical durability in comparison with glassy waste forms.
- (2) Research of more efficient and highly durable matrices than glasses to contain specifically separated long-life radionuclides in a highly durable crystalline phase (acting as first containment barrier) itself dispersed in a durable residual glass that can be considered as the second barrier against wasteform dissolution by water (Fig. 24(a)). In the case where the wastes to immobilize are not completely pure (for example actinide-rich waste with some fission products or other elements), the presence of the residual glass can be efficient to immobilize impurities.

Historically, in the 1970s, the first glass-ceramics which have been considered to contain nuclear wastes were prepared by heat treatment of glasses and the initial motivation was only to improve the mechanical and thermal properties of borosilicate glassy wasteforms (Donald *et al.*, 1997). The first complete work conducted on glass-ceramic matrices for containment of non-separated wastes was carried out in the 1980s on glass-ceramics containing CaTiSiO_5 (titanite) crystals dispersed within an aluminosilicate glassy matrix synthesized by nucleation and growth heat treatment of a glass containing TiO_2 (titanite is a mineral phase known for its capacity to incorporate actinides in its structure and to exhibit good chemical durability) (Hayward, 1988). More recently, several works have been performed on glass-ceramics containing zirconolite ($\text{CaZrTi}_2\text{O}_7$) crystals for the containment of separated MA that can be specifically isolated from HLW solutions by enhanced separation processes (Loiseau *et al.*, 2004; Caurant *et al.*, 2006). In this case, the aim was to obtain, after thermal treatment (nucleation + growth, Fig. 25) of a calcium aluminosilicate glass of suitable composition containing ZrO_2 , TiO_2 and MA surrogates (Ln), a wasteform acting as a double containment barrier for MA, with the objective of accommodating as much MA as possible in the zirconolite crystals (high partition coefficient) (Figs. 24(a) and 26). In the ideal case, the parent glass composition should be chosen such that the nucleation rate of the crystalline phase in the bulk is very high (to promote internal crystallization rather than crystallization from the surface) and that the partition coefficient of radionuclides between the crystalline phase and residual glass is high. In the case of the zirconolite-based glass-ceramics, the amount of crystalline phase and the partition coefficient of Ln between zirconolite crystals and the residual glass could be controlled by modification of the parent glass composition, for instance of the Al_2O_3 content (Fig. 26). Nevertheless, in spite of several composition changes performed for this system, a significant amount of Ln always remains in the residual glass and therefore does not benefit from a double containment barrier (Loiseau *et al.*, 2003; Caurant *et al.*, 2007a).

One alternative way to increase the partitioning ratio of the waste between the glass and the crystals is to prepare a wasteform not by crystallization of a glass already containing the waste as in glass-ceramics (Fig. 24(a)), but by encapsulating a highly durable crystalline phase containing the waste (prepared independently in a first stage) in a durable glass by sintering a mixture of two powders with adapted particle sizes (Fig. 24(b)). For instance, actinide wasteforms prepared by encapsulating highly durable pyrochlore ($\text{Gd}_2\text{Zr}_2\text{O}_7$, $\text{La}_2\text{Zr}_2\text{O}_7$) particles in a borosilicate or lead silicate glass have been proposed (Fig. 27) (Pace *et al.*, 2005; Boccacini *et al.*, 2007).

In all cases, the choice of the crystalline phase in which the radionuclides are expected to be incorporated is generally based on results from literature: knowledge of natural and highly durable crystalline phases (natural analogs) having incorporated natural

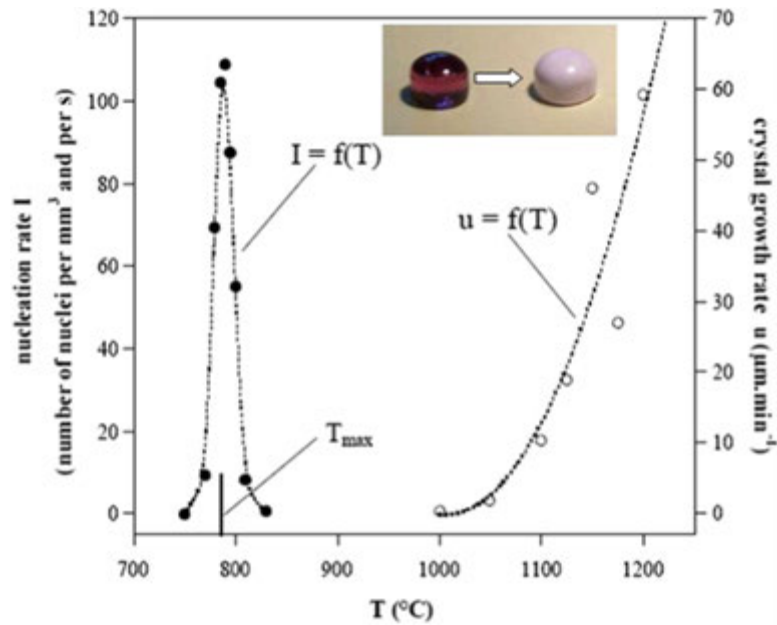


Fig. 25 Nucleation ($I = f(T)$) and crystal growth rate ($u = f(T)$) curves of zirconolite ($\text{CaZrTi}_2\text{O}_7$) crystals in the bulk of a calcium aluminosilicate glass containing ZrO_2 and TiO_2 and leading to zirconolite-based glass-ceramics (Fig. 24). I and u curves are well separated which limits crystallization during melt cooling and allows to control the preparation of glass-ceramics using a two-step thermal treatment (the picture given at the top of the figure shows the transformation of a Nd-doped glass into a glass-ceramic).

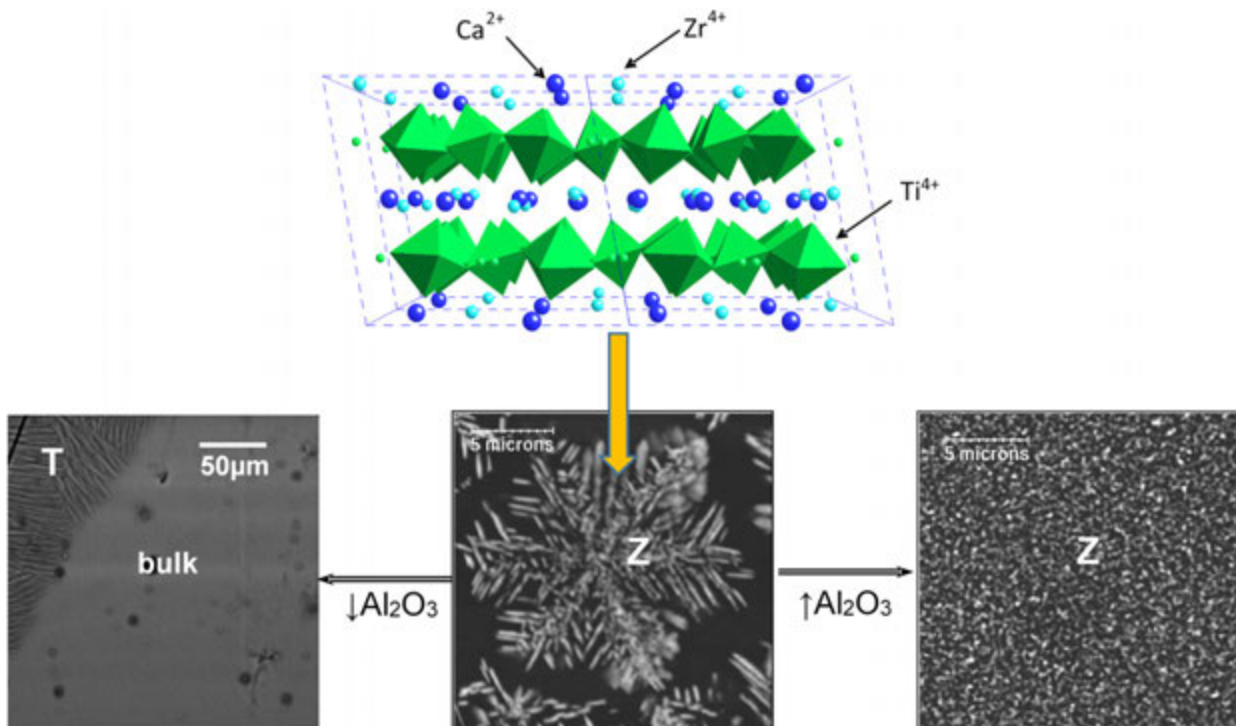


Fig. 26 Changes of the density of zirconolite crystals (Z) formed in the bulk of a glass-ceramic as a function of the variation of Al_2O_3 content (± 2.7 mol%) in a calcium aluminosilicate parent glass containing ZrO_2 and TiO_2 (T : titanite crystals (CaTiSiO_5) growing from glass surface). Glass-ceramics were prepared by a double heat treatment: nucleation at 810°C (2 h) and growth at 1050°C (2 h). Changes in the Al_2O_3 content in the parent glass strongly affect the zirconolite crystallization rate which can be explained by a competition between Al^{3+} , Ti^{4+} and Zr^{4+} for charge compensators in favor of Al^{3+} that destabilizes Ti^{4+} and Zr^{4+} and promotes zirconolite ($\text{CaZrTi}_2\text{O}_7$) crystallization. The zirconolite structure is shown at the top of the figure (MA^{3+} and Ln^{3+} can substitute for Ca^{2+} and Zr^{4+} with adapted compensation charge schemes). Modified from Caurant, D., Loiseau, P., Bardez, I., Gervais, C., 2007a. Effect of Al_2O_3 concentration on zirconolite ($\text{Ca}(\text{Zr,Hf})\text{Ti}_2\text{O}_7$) crystallization in $(\text{TiO}_2, \text{ZrO}_2, \text{HfO}_2)$ -rich SiO_2 - Al_2O_3 - CaO - Na_2O glasses. J. Mater. Sci. 42, 8558–8570. Permission from Springer Nature.

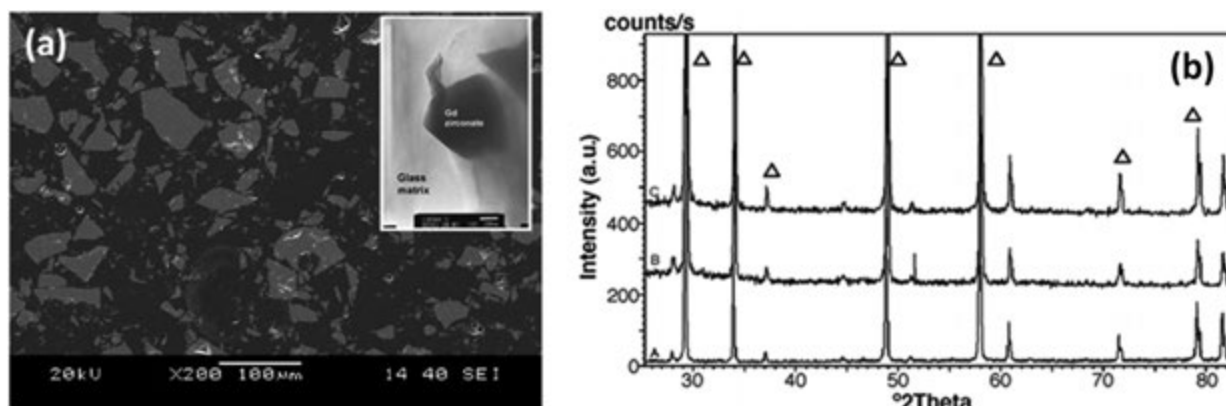


Fig. 27 (a) SEM image of a $\text{Gd}_2\text{Zr}_2\text{O}_7$ pyrochlore-based borosilicate GCM wasteform obtained by encapsulation by sintering under pressure (5 MPa) at 620°C (2 h) a mixture made of $\text{Gd}_2\text{Zr}_2\text{O}_7$ and borosilicate glass powders. The TEM image given at the top right of the SEM image shows the absence of reaction between pyrochlore crystals and the glassy matrix during sintering. (b) XRD patterns of the $\text{Gd}_2\text{Zr}_2\text{O}_7$ powder (bottom) and of the glass + $\text{Gd}_2\text{Zr}_2\text{O}_7$ (30 vol%) mixture sintered at 650°C in atmosphere (middle) or under pressure (top) showing only the pyrochlore XRD lines. Reproduced from Boccaccini, A.R., Berthier, T., Seglem, S., 2007. Encapsulated gadolinium zirconate pyrochlore particles in soda borosilicate glass as novel radioactive waste form. *Ceram. Int.* 33, 1231–1235, p. 1233, with permission from Elsevier.

radionuclides (U, Th), studies on single-phase ceramics able to incorporate radionuclides and exhibiting very good long-term containment properties as demonstrated by leaching and irradiation tests.

In comparison with nuclear glasses, such GCM prepared either by the classical glass-ceramic technology (melting of a glass + crystallization thermal treatment) or by encapsulation (grinding + sintering) remain more complicated to synthesize than nuclear glasses, because of additional steps that can be difficult to achieve in a radioactive environment. Nevertheless, studies continue around the world on these types of matrices consisting of a highly durable crystalline phase able to incorporate actinide-rich waste dispersed in a glass (Liao *et al.*, 2017; Kong *et al.*, 2018). Moreover, the concept of double containment barrier in glass-ceramic wasteforms is also envisaged to increase the efficiency of the immobilization of non-radioactive hazardous wastes in comparison with homogeneous glassy wasteforms (Caurant *et al.*, 2017). This is the case for instance for chromium-rich industrial waste for which the possibility to prepare spinel-based glass-ceramics with a high partitioning ratio of chromium in the spinel ($\text{MgCr}_x\text{Al}_{2-x}\text{O}_4$) crystals has been demonstrated (Liao *et al.*, 2016).

Summary

About 70 years after the first studies on nuclear waste vitrification and more than 40 years after the start of industrial vitrification, oxide glasses – and mainly borosilicates – always remain the only host used to incorporate high level radioactive waste (HLW) from commercial and defense sources despite the many works that have been carried out on ceramic matrices. Their great structural flexibility, allowing them to accommodate almost all the elements present in the waste resulting from spent nuclear fuel reprocessing, their good self-irradiation resistance and chemical durability associated with their ease of fabrication by melting and casting explain the success of glassy wasteforms still today. Vitrification is now used in many countries around the world with constant improvements and the development of new types of melters.

Since the start of vitrification, a large number of works have been carried out to adapt glass formulation to the changes in waste composition, with an increasingly precise knowledge of the structure and properties of nuclear glasses, and in particular of the way the various elements present in the waste are incorporated into the glassy network and how this incorporation can be optimized by adapting the composition of the glass. Very extensive studies are still in progress in order to understand and to model the long-term behavior of nuclear glasses during their geological storage (alteration mechanisms in submerged aqueous medium or in the presence of water vapor, impact of internal irradiation on glass structure and properties). For a long time, the presence of crystals in nuclear glasses was regarded as undesirable because of the modification they may induce on their properties and on their impact on the melting process, but now there is a general trend to accept partial crystallization for some waste if the containment of the final wasteform remains acceptable, leading to glass composite materials (GCM). Belonging to this family of wasteforms, glass-ceramics that can be obtained by controlled crystallization of a glass bearing radionuclides can be envisaged for instance to immobilize actinide-rich waste.

The building of new nuclear power stations around the world with possible spent fuel reprocessing will lead in the future to an increasing need for waste vitrification. Moreover, the emergence of new radioactive wastes of various compositions coming for instance from the decommissioning and dismantling of old nuclear facilities and, in the more distant future, of new types of waste coming from new generations of nuclear power reactors requiring reprocessing of the spent fuel will still require many studies on new nuclear glass compositions for their immobilization.

References

- Achigar, S., Caurant, D., Régnier, E., Majérous, O., 2021. Dismantling nuclear waste rich in P_2O_5 , MoO_3 and ZrO_2 : How do these oxides incorporate in aluminoborosilicate glasses? *J. Nucl. Mater.* 544, 152731.
- Angeli, F., Boscarino, D., Gin, S., *et al.*, 2001. Influence of calcium on sodium aluminosilicate glass leaching behaviour. *Phys. Chem. Glasses* 42, 279–286.
- Angeli, F., Charpentier, T., Molières, E., *et al.*, 2013. Influence of lanthanum on borosilicate glass structure: A multinuclear MAS and MQMAS NMR investigation. *J. Non Cryst. Solids* 376, 189–198.
- Angeli, F., Charpentier, T., Jollivet, P., *et al.*, 2018. Effect of thermally induced structural disorder on the chemical durability of international simple glass. *NPJ Mater. Degrad.* 2, 31.
- Angeli, F., Charpentier, T., Gaillard, M., Jollivet, P., 2008. Influence of zirconium on the structure of pristine and leached soda-lime borosilicate glasses: Towards a quantitative approach by ^{17}O MQMAS NMR. *J. Non Cryst. Solids* 354, 3713–3722.
- Aubin-Chevaldonnet, V., Caurant, D., Dannoux, A., *et al.*, 2007. Preparation and characterization of $(Ba,Cs)(M,Ti)_8O_{16}$ ($M = Al^{3+}, Fe^{3+}, Ga^{3+}, Cr^{3+}, Sc^{3+}, Mg^{2+}$) hollandite ceramics developed for radioactive cesium immobilization. *J. Nucl. Mater.* 366, 137–160.
- Bardez-Giboire, I., Kidari, A., Magnin, M., *et al.*, 2017. Americium and trivalent lanthanides incorporation in high-level waste glass-ceramics. *J. Nucl. Mater.* 492, 231–238.
- Bates, J.K., Seitz, M.G., Steinler, M.J., 1984. The relevance of vapor phase hydration aging to nuclear waste isolation. *Nucl. Chem. Waste Manag.* 5, 63–73.
- Boccaccini, A.R., Berthier, T., Seglem, S., 2007. Encapsulated gadolinium zirconate pyrochlore particles in soda borosilicate glass as novel radioactive waste form. *Ceram. Int.* 33, 1231–1235. p. 1233.
- Bohre, A., Avasthi, K., Petkov, V.I., 2017. Vitreous and crystalline phosphate high level waste matrices: Present status and future challenges. *J. Ind. Eng. Chem.* 50, 1–14.
- Nuclear Energy Agency, 2018. State-of-the-art report on the progress of nuclear fuel cycle chemistry. In *Nuclear Science*. Paris: OECD/NEA Publishing, https://www.oecd-neo.org/jcms/pl_14970/state-of-the-art-report-on-the-progress-of-nuclear-fuel-cycle-chemistry
- Bonin, B., 2008. Treatment and recycling of spent nuclear fuel. Actinide partitioning -application to waste management. In: Bonin, B., Bouquin, B., Dozol, M., Lecomte, M., Forestier, A. (Eds.), *Commissariat à l'Energie Atomique. Gif-sur-Yvette: A Nuclear Energy Division Monograph*. <https://www.cea.fr/english/Pages/resources/nuclear-energy-monographs/treatment-recycling-spent-nuclear-fuel.aspx>.
- Brehault, A., Patil, D., Kamat, H., *et al.*, 2018. Compositional dependence of solubility/retention of molybdenum oxides in aluminoborosilicate-based model nuclear waste glasses. *Phys. Chem. B* 122, 1714–1729.
- Bridge, B., Patel, N.D., 1986. The elastic constants and structure of the vitreous system Mo-P-O. *J. Mater. Sci.* 21, 1187–1205.
- Cachia, J.-N., Deschanel, X., Den Auwer, C., *et al.*, 2006. Enhancing cerium and plutonium solubility by reduction in borosilicate glass. *J. Nucl. Mater.* 352, 182–189.
- Cailloteau, C., Angeli, F., Devreux, F., *et al.*, 2008. Insight into silicate-glass corrosion mechanisms. *Nat. Mater.* 7, 978–983.
- Calas, G., Legrand, M., Galois, L., Ghaleb, D., 2003. Structural role of molybdenum in nuclear glasses: An EXAFS study. *J. Nucl. Mater.* 322, 15–20.
- Cantrel, E., Courtadon, A., Blanchard S., Girod C., 2015. Management of HL deposits for the D&D of UP1 reprocessing plant – Retrieval and treatment scenarios. In: *Proceedings of the WM 2015 Conference*, March 15–19, 2015, Phoenix, Arizona, USA. Available at: <http://archive.wmsym.org/2015/papers/15295.pdf>.
- Caurant, D., 2017. Glass-ceramics for waste immobilization. In: Neuville, D., Cormier, L., Caurant, D., Montagne, L. (Eds.), *From Glass to Crystal. Nucleation, Growth and Phase Separation: From Research to Applications*. Les Ulis: EDP Sciences, pp. 491–526.
- Caurant, D., Majérous, O., Loiseau, P., *et al.*, 2006. Crystallization of neodymium-rich phases in silicate glasses developed for nuclear waste immobilization. *J. Nucl. Mater.* 354, 143–162.
- Caurant, D., Loiseau, P., Bardez, I., Gervais, C., 2007a. Effect of Al_2O_3 concentration on zirconolite $(Ca(Zr,Hf)Ti_2O_7)$ crystallization in (TiO_2,ZrO_2,HfO_2) -rich $SiO_2-Al_2O_3-CaO-Na_2O$ glasses. *J. Mater. Sci.* 42, 8558–8570.
- Caurant, D., Majérous, O., Fadel, E., *et al.*, 2007b. Effect of molybdenum on the structure and on the crystallization of $SiO_2-Na_2O-CaO-B_2O_3$ glasses. *J. Am. Ceram. Soc.* 90, 774–783.
- Caurant, D., Loiseau, P., Majérous, O., *et al.*, 2009. *Glasses, Glass-ceramics and Ceramics for Immobilization of Highly Radioactive Nuclear Wastes*. Hauppauge, NY: Nova Science Publishers.
- Caurant, D., Quintas, A., Majérous, O., Charpentier, T., Bardez, I., 2008. Structural role and distribution of alkali and alkaline-earth cations in rare earth-rich aluminoborosilicate glasses. *Adv. Mater. Res.* 39–40, 19–24.
- Charpentier, T., Martel, L., Mir, A.H., *et al.*, 2016. Self-healing capacity of nuclear glass observed by NMR spectroscopy. *Sci. Rep.* 6, 25499.
- Chen, H., Marcial, J., Ahmadzadeh, M., Patil, D., McCloy, J., 2020. Partitioning of rare earths in multiphase nuclear waste glass-ceramics. *Int. J. Appl. Glass Sci.* 11, 660–675.
- Chouard, N., Caurant, D., Majérous, O., *et al.*, 2011. Effect of neodymium oxide on the solubility of MoO_3 in an aluminoborosilicate glass. *J. Non Cryst. Solids* 357, 2752–2762.
- Chouard, N., Caurant, D., Majérous, O., *et al.*, 2015. Effect of MoO_3 , Nd_2O_3 , and RuO_2 on the crystallization of soda-lime aluminoborosilicate glasses. *J. Mater. Sci.* 50, 219–241.
- Chouard, N., Caurant, D., Majérous, O., *et al.*, 2016. Thermal stability of $SiO_2-B_2O_3-Al_2O_3-Na_2O-CaO$ glasses with high Nd_2O_3 and MoO_3 concentrations. *J. Alloy. Compd.* 671, 84–99.
- Chouard, N., Caurant, D., Majérous, O., *et al.*, 2019. External irradiation with heavy ions of neodymium silicate apatite ceramics and glass-ceramics. *J. Nucl. Mater.* 516, 11–29.
- Colombo, P., Brusatin, G., Bernardo, E., Scarinci, G., 2003. Inertization and reuse of waste materials by vitrification and fabrication of glass-based products. *Curr. Opin. Solid State Mater. Sci.* 7, 225–239.
- Connelly, A.J., Hyatt, N.C., Travis, K.P., *et al.*, 2013. The effect of uranium oxide additions on the structure of alkali borosilicate glasses. *J. Non Cryst. Solids* 378, 282–289.
- Conrad, R., 2008. Chemical durability of oxide glasses in aqueous solutions: A review. *J. Am. Ceram. Soc.* 91, 728–735.
- Crum, J.V., Turo, L., Riley, B., Tang, M., Kosoy, A., 2012. Multi-phase glass-ceramics as a waste form for combined fission products: Alkalies, alkaline earths, lanthanides, and transition metals. *J. Am. Ceram. Soc.* 95, 1297–1303. p. 5.
- De Echave, T., Tribet, M., Jollivet, P., *et al.*, 2018. Effect of clayey groundwater on the dissolution rate of SON68 simulated nuclear waste glass at 70°C. *J. Nucl. Mater.* 503, 279–289.
- Deschanel, X., Peugeot, S., Cachia, J.N., Charpentier, T., 2007. Plutonium solubility and self-irradiation effects in borosilicate glass. *Prog. Nucl. Energy* 49, 623–634.
- Donald, I.W., 2007. Immobilisation of radioactive and non-radioactive wastes in glass-based systems: An overview. *Eur. J. Glass Sci. Technol. A* 48, 155–163.
- Donald, I.W., 2016. Vitrification of radioactive and hazardous wastes. In: *The Science and Technology of Inorganic Glasses and Glass-Ceramics: From the Past to the Present to the Future*. Sheffield: Society of Glass Technology, pp. 261–300.
- Donald, I.W., Metcalfe, B.L., Taylor, R.N.J., 1997. The immobilization of high level radioactive wastes using ceramics and glasses. *J. Mater. Sci.* 32, 5851–5887.
- Du, J., Cormack, A.N., 2005. The structure of erbium doped sodium silicate glasses. *J. Non Cryst. Solids* 351, 2263–2276.
- Eller, P.G., Jarvinen, J.D., Purson, J.D., *et al.*, 1985. Actinide valences in borosilicate glass. *Radiochim. Acta* 39, 17–22.
- Ewing, R.C., Whittleston, R.A., Yardley, B.W.D., 2016. Geological disposal of nuclear waste: A primer. *Elements* 12, 233–237.
- Fournier, M., Gin, S., Frugier, P., 2014. Resumption of nuclear glass alteration: State of the art. *J. Nucl. Mater.* 448, 348–363.
- Frugier, P., Gin, S., Minet, Y., *et al.*, 2008. SON68 nuclear glass dissolution kinetics: Current state of knowledge and basis of the new GRAAL model. *J. Nucl. Mater.* 380, 8–21.

- Gaddam, A., Fernandes, H.R., Tulyaganov, D.U., Ferreira, J.M.F., 2019. The structural role of lanthanum oxide in silicate glasses. *J. Non Cryst. Solids* 505, 18–27.
- Galoisy, L., Pélégri, E., Arrio, M.-A., *et al.*, 1999. Evidence for 6-coordinated zirconium in inactive nuclear waste glasses. *J. Am. Ceram. Soc.* 82, 2219–2224.
- Gasnier, E., Bardez-Giboire, I., Montouillout, V., *et al.*, 2014. Homogeneity of peraluminous $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-CaO-Nd}_2\text{O}_3$ glasses: Effect of neodymium content. *J. Non Cryst. Solids* 405, 55–62.
- Gin, S., Guittonneau, C., Godon, N., *et al.*, 2011. Nuclear glass durability: New insight into alteration layer properties. *J. Phys. Chem. C* 115, 18696–18706.
- Gin, S., Jolivet, P., Barba Rossa, G., *et al.*, 2017a. Atom-probe tomography, TEM and ToF-SIMS study of borosilicate glass alteration rim: A multiscale approach to investigating rate-limiting mechanisms. *Geochim. Cosmochim. Acta* 202, 57–76.
- Gin, S., Jolivet, P., Tribet, M., Peugeot, S., Schuller, S., 2017b. Radionuclides containment in nuclear glasses: An overview. *Radiochim. Acta* 105, 927–959.
- Gin, S., Beaudoux, X., Angéli, F., Jégou, C., Godon, N., 2012. Effect of composition on the short-term and long-term dissolution rates of ten borosilicate glasses of increasing complexity from 3 to 30 oxides. *J. Non Cryst. Solids* 358, 2559–2570, p. 2665.
- Girold, C., Francois, S., Petit, L., *et al.*, 2018. French innovative processes in the field of thermal treatment for decommissioning and legacy waste. In *Proceedings of the 44th Annual Waste Management Conference (WM2018)*. Phoenix: Waste Management Symposia, Inc, pp. 3074–3087. <https://hal-cea.archives-ouvertes.fr/cea-02339255>.
- Goel, A., McCloy, J.S., Windisch, C.F., *et al.*, 2013. Structure of rhenium-containing sodium borosilicate glass. *Int. J. Appl. Glass Sci.* 4, 42–52.
- Grambow, B., 2016. Geological disposal of radioactive waste in clay. *Elements* 12, 239–245.
- Grambow, B., Müller, R., 2001. First-order dissolution rate law and the role of surface layers in glass performance assessment. *J. Nucl. Mater.* 298, 112–124.
- Gregg, D.J., Vance, S., 2016. Synroc tailored waste forms for actinide immobilization. *Radiochim. Acta* 105, 907–925.
- Guy, C., Audubert, F., Lartigue, J.-E., *et al.*, 2002. New conditionings for separated long-lived radionuclides. *C. R. Phys.* 3, 827–837.
- Harisson, M.T., 2014. Vitrification of high level waste in the UK. *Procedia Mater. Sci.* 7, 10–15.
- Hayward, P.J., 1988. The use of glass ceramics for immobilising high level wastes from nuclear fuel recycling. *Glass Technol. Eur. J. Glass Sci. Technol. A* 29, 122–136.
- Hellmann, R., Cotte, S., Cadet, E., *et al.*, 2015. Nanometre-scale evidence for interfacial dissolution–reprecipitation control of silicate glass corrosion. *Nat. Mater.* 14, 307–311.
- Hench, L.L., Clark, D.E., Harker, A.B., 1986. Nuclear waste solids. *J. Mater. Sci.* 21, 1457–1478.
- Hrma, P., Vienna, J.D., Wilson, B.K., Plaisted, T.J., Heald, S.M., 2006. Chromium phase behavior in a multi-component borosilicate glass melt. *J. Non Cryst. Solids* 352, 2114–2122.
- Icenhower, J.P., Dove, P.M., 2000. The dissolution kinetics of amorphous silica into sodium chloride solutions: Effects of temperature and ionic strength. *Geochim. Cosmochim. Acta* 64, 4193–4203.
- Jantzen, C.M., 1986. Systems approach to nuclear waste glass development. *J. Non Cryst. Solids* 84, 215–225.
- Jantzen, C.M., 2011. Development of glass matrices for high level radioactive wastes. In: Ojovan, M.I. (Ed.), *Handbook of Advanced Radioactive Waste Conditioning Technologies*. Cambridge: Woodhead Publishing Ltd, pp. 230–292.
- Jantzen, C.M., Ojovan, M.I., 2019. On selection of matrix (wasteform) material for higher activity nuclear waste immobilization (Review). *Russ. J. Inorg. Chem.* 64, 1611–1624.
- Jantzen, C.M., Brown, K.G., Pickett, J.B., 2011. Durable glass for thousands of years. *Int. J. Appl. Glass Sci.* 1, 38–62.
- Kaspar, T.C., Ryan, J.V., Pantano, C.G., *et al.*, 2019. Physical and optical properties of the international simple glass. *NPJ Mater. Degrad.* 3.15.
- Kidari, A., Dussossoy, J.-L., Brackx, E., *et al.*, 2012. Lanthanum and neodymium solubility in simplified $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O-Al}_2\text{O}_3\text{-CaO}$ high level waste glass. *J. Am. Ceram. Soc.* 95, 2537–2544.
- Kim, D.S., Peeler, D.K., Hrma, P., 1995. Effect of crystallisation on the chemical durability of simulated nuclear waste glasses. *Ceram. Bull.* 61, 177–185.
- Kong, L., Wei, T., Zhang, Y., Karatchevseva, I., 2018. Phase evolution and microstructure analysis of $\text{CaZrTi}_2\text{O}_7$ zirconolite in glass. *Ceram. Int.* 44, 6285–6292.
- Krishnamurthy, A., Nguyen, T., Fayek, M., Shabaga, B., Kroeker, S., 2020. Network structure and dissolution properties of phosphate-doped borosilicate glasses. *J. Phys. Chem. C* 124, 21184–21196.
- Laverov, N.P., Yuditsev, S.V., Kochkin, B.T., Malkovsky, V.I., 2016. The Russian strategy of using crystalline rock as a repository for nuclear waste. *Elements* 12, 253–256.
- Le Losq, G., Neuville, D.R., Chen, W., *et al.*, 2017. Percolation channels: A universal idea to describe the atomic structure and dynamics of glasses and melts. *Sci. Rep.* 7.16490.
- Lee, W.E., Ojovan, M.I., Stennett, M.C., Hyatt, N.C., 2006. Immobilisation of radioactive waste in glasses, glass composite materials and ceramics. *Adv. Appl. Ceram.* 105, 3–12.
- Lemesle, T., Méar, F.O., Campayo, L., *et al.*, 2014. Immobilization of radioactive iodine in silver aluminophosphate glasses. *J. Hazard. Mater.* 264, 117–126.
- Liao, C., Tang, Y., Liu, C., Shih, K., Li, F., 2016. Double-barrier mechanism for chromium immobilization: A quantitative study of crystallization and leachability. *J. Hazard. Mater.* 311, 246–253.
- Liao, C.-Z., Liu, C., Su, M., Shih, K., 2017. Quantification of the partitioning ratio of minor actinide surrogates between zirconolite and glass in glass-ceramic for nuclear waste disposal. *Inorg. Chem.* 56, 9913–9921.
- Loiseau, P., Caurant, D., Majerus, O., Baffier, N., 2003. Crystallization study of $(\text{TiO}_2\text{ZrO}_2)$ -rich $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ glasses. *J. Mater. Sci.* 38, 843–852.
- Loiseau, P., Caurant, D., Baffier, N., Mazerolles, L., Fillet, C., 2004. Glass-ceramic nuclear waste forms obtained from $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-ZrO}_2\text{-TiO}_2$ glasses containing lanthanides (Ce, Nd, Eu, Gd, Yb) and actinides (Th): Study of internal crystallization. *J. Nucl. Mater.* 335, 14–32.
- Lu, X., Deng, L., Kerisit, S., Du, J., 2018. Structural role of ZrO_2 and its impact on properties of borosilicate nuclear waste glasses. *NPJ Mater. Degrad.* 2.19.
- Lutze, W., 1988. Silicate glasses. In: Lutze, W., Ewing, R.C. (Eds.), *Radioactive Waste Forms for the Future*. Elsevier Science Publishers B. V., pp. 1–159.
- Madic, C., Leconte, M., Baron, P., Boullis, B., 2002. Separation of long-lived radionuclides from high active nuclear waste. *C. R. Phys.* 3, 797–811.
- Magnin, M., Schuller, S., Mercier, C., *et al.*, 2011. Modification of molybdenum structural environment in borosilicate glasses with increasing content of boron and calcium oxide by ^{95}Mo MAS NMR. *J. Am. Ceram. Soc.* 94, 4274–4282.
- Majerus, O., Lehuédé, P., Biron, I., *et al.*, 2020. Glass alteration in atmospheric conditions: Crossing perspectives from cultural heritage, glass industry, and nuclear waste management. *NPJ Mater. Degrad.* 4, 27.
- Malchukova, E., Boizot, B., Petite, G., Ghaleb, D., 2009. Irradiation effects in oxide glasses doped with transition and rare-earth elements. *Eur. Phys. J. Appl. Phys.* 45, 10701.
- Mascaraque, N., Bauchy, M., Smedskjaer, M.M., 2017. Correlating the network topology of oxide glasses with their chemical durability. *J. Phys. Chem. B* 121, 1139–1147.
- McCloy, J.S., Goel, A., 2017. Glass-ceramics for nuclear-waste immobilization. *MRS Bull.* 42, 233–240.
- McKeown, D.A., Gan, H., Pegg, I.L., 2017. X-ray absorption and Raman spectroscopy studies of molybdenum environments in borosilicate waste glasses. *J. Nucl. Mater.* 488, 143–149.
- Meaker, T.F., Peeler, D.K., Marra, J.C., Pareizs, J.M., Ramsey, W.G., 1996. Actinide solubility in lanthanide borosilicate glass for possible immobilization and disposition. In: *MRS Proc.*, 465. Scientific Basis for Nuclear Waste Management. pp. 1281–1286.
- Ménard, O., Advocat, T., Ambrosi, J.P., Michard, A., 1998. Behaviour of actinides (Th, U, Np and Pu) and rare earths (La, Ce and Nd) during aqueous leaching of a nuclear glass under geological disposal conditions. *Appl. Geochem.* 13, 105–126.
- Metcalfe, B.L., Donald, I.W., 2013. Management of radioactive waste (RAW) from nuclear weapons programmes. In: Lee, W.E., Ojovan, M.I., Jantzen, C.M. (Eds.), *Radioactive Waste Management and Contaminated Site Clean-up. Processes, Technologies and International Experience*. Sawston: Woodhead Publishing, pp. 775–800.
- Michelin, A., Burger, E., Rebiscoul, D., *et al.*, 2015. Silicate glass alteration enhanced by iron: Origin and long-term implications. *Environ. Sci. Technol.* 47, 750–756.
- Mir, A.H., Peugeot, S., Toulemonde, M., *et al.*, 2015. Defect recovery and damage reduction in borosilicate glasses under double ion beam irradiation. *EPL* 112, 36002.
- Molières, E., Angeli, F., Jolivet, P., *et al.*, 2013. Chemical durability of lanthanum-enriched borosilicate glass. *Int. J. Appl. Glass Sci.* 4, 383–394.
- Muller, I., Weber, W.J., 2001. Plutonium in crystalline ceramics and glasses. *MRS Bull.* 26, 698–706.
- Muller, I.S., McKeown, D.A., Pegg, I.L., 2014. Structural behavior of Tc and I ions in nuclear waste glass. *Procedia Mater. Sci.* 7, 53–59.

- Narayanan, S., Jollivet, P., Godon, N., *et al.*, 2019. Influence of composition of nuclear waste glasses on vapor phase hydration. *J. Nucl. Mater.* 525, 53–71.
- Nicoleau, E., Schuller, S., Angeli, F., *et al.*, 2015. Phase separation and crystallization effects on the structure and durability of molybdenum borosilicate glass. *J. Non Cryst. Solids* 427, 120–133, p. 130.
- Nicoleau, E., Angeli, F., Schuller, S., *et al.*, 2016. Rare-earth silicate crystallization in borosilicate glasses: Effect on structural and chemical durability properties. *J. Non Cryst. Solids* 438, 37–48.
- Ojovan, M.I., Lee, W.E., 2005. *An Introduction to Nuclear Waste Immobilisation*. Oxford: Elsevier.
- Ojovan, M.I., Lee, W.E., 2007. *New Developments in Glassy Nuclear Wasteforms*. Hauppauge, NY: Nova Science Publishers.
- Ojovan, M.I., Lee, W.E., 2010. Glassy wasteforms for nuclear waste immobilization. *Metall. Mater. Trans. A* 42, 837–851.
- Orlhac, X., 1999. *Study of the Thermal Stability of Nuclear Glass. Long-term Evolution Modeling* (Ph.D. thesis). France: University of Montpellier II, (In French). http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/31/058/31058405.pdf.
- Orlhac, X., Fillet, C., Phalippou, J., 1999. Study of crystallization mechanisms in the French nuclear waste glass. *Mater. Res. Soc. Symp. Proc.* 556, 263–270.
- Orlova, A.I., Ojovan, M.I., 2019. Ceramic mineral waste-forms for nuclear waste immobilization. *Materials* 12, 2638.
- Pacaud, F., Fillet, C., Jacquet-Francillon, N., 1991. Effect of platinoids on French LWR reference glass properties. *Mater. Res. Soc. Symp. Proc.* 257, 161–167.
- Pace, S., Cannillo, V., Wu, J., *et al.*, 2005. Processing glass-pyrophyllite composites for nuclear waste encapsulation. *J. Nucl. Mater.* 341, 12–18.
- Parruzot, B., Jollivet, P., Rébiscoul, D., Gin, S., 2015. Long-term alteration of basaltic glass: Mechanisms and rates. *Geochim. Cosmochim. Acta* 154, 28–48.
- Patil, D.S., Konale, M., Gabel, M., *et al.*, 2018. Impact of rare earth ion size on the phase evolution of MoO₃-containing aluminoborosilicate glass-ceramics. *J. Nucl. Mater.* 510, 539–550.
- Pegg, I.L., 2015. Turning nuclear waste into glass. *Phys. Today* 68, 33–39.
- Peuget, S., Cachia, J.-N., Jégou, C., *et al.*, 2006. Irradiation stability of R777-type borosilicate glass. *J. Nucl. Mater.* 354, 1–13, p. 7.
- Peuget, S., Broudic, V., Jégou, C., *et al.*, 2007. Effect of alpha irradiation on the leaching behaviour of nuclear glass. *J. Nucl. Mater.* 362, 474–479.
- Peuget, S., Delaye, J.-M., Jégou, C., 2014. Specific outcomes of the research on the radiation stability of the French nuclear glass towards alpha decay accumulation. *J. Nucl. Mater.* 444, 76–91.
- Pflieder, R., Malki, M., Guari, Y., Larionova, J., Grandjean, A., 2009. Electrical conductivity of RuO₂-borosilicate glasses: Effect of the synthesis route. *J. Am. Ceram. Soc.* 92, 1560–1566.
- Piovesan, V., Bardez-Giboire, I., Fournier, M., *et al.*, 2018. Chemical durability of peraluminous glasses for nuclear waste conditioning. *NPJ Mater. Degrad.* 2, 7.
- Prakash, A.D., Singh, M., Mishra, R.K., *et al.*, 2019. Studies on modified borosilicate glass for enhancement of solubility of molybdenum. *J. Non Cryst. Solids* 510, 172–178.
- Quintas, A., Caurant, D., Majérus, O., Dussossoy, J.-L., Charpentier, T., 2008. Effect of changing the rare earth cation type on the structure and crystallisation behaviour of an aluminoborosilicate glass. *Phys. Chem. Glasses* 49, 192–197.
- Riley, B.J., Vienna, J.D., Strachan, D.M., McCloy, J.S., Jerden, J.L., 2016. Materials and processes for the effective capture and immobilization of radioiodine: A review. *J. Nucl. Mater.* 470, 307–326.
- Rodríguez-Penalonga, L., Moratilla Soria, B.Y., 2017. A review of the nuclear fuel cycle strategies and the spent nuclear fuel management technologies. *Energies* 10, 1235.
- Rose, P.B., Woodward, D.I., Ojovan, M.I., Hyatt, N.C., Lee, W.E., 2011. Crystallisation of a simulated borosilicate high-level waste glass produced on a full-scale vitrification line. *J. Non Cryst. Solids* 357, 2989–3001.
- Sales, B.C., Boatner, L.A., 1986. Lead-iron phosphate glass. In: Lutze, W., Ewing, R.C. (Eds.), *Radioactive Waste Forms for the Future*. Elsevier Science Publishers B. V, pp. 193–231.
- Santagneli, S.H., de Araujo, C.C., Strojek, W., *et al.*, 2007. Structural studies of NaPO₃-MoO₃ glasses by solid-state nuclear magnetic resonance and Raman spectroscopy. *J. Phys. Chem. B* 111, 10109–10117.
- Schaller, T., Stebbins, J.F., Wilding, M.C., 1999. Cation clustering and formation of free oxide ions in sodium and potassium lanthanum silicate glasses: Nuclear magnetic resonance and Raman spectroscopic findings. *J. Non Cryst. Solids* 243, 146–157.
- Shiryaev, A.A., Zubabichus, Y.V., Stefanovsky, S.V., Ptashkin, A.G., Marra, J.C., 2009. XAFS of Pu and Hf L_{III} edge in lanthanide-borosilicate glass. *Mater. Res. Soc. Symp. Proc.* 1193, 259–265.
- Sobolev, I.A., Dimitriev, S.A., Lifanov, F.A., *et al.*, 2005. Vitrification processes for low, intermediate radioactive and mixed wastes. *Glass Technol.* 46, 28–35.
- Sombret, C.G., 1993. The vitrification of high-level wastes in France: From the lab to industrial plants. BNS/OECD-NEA Symposium on the safety of the nuclear fuel cycle Brussels: June 3–4, 1993. Available at: https://inis.iaea.org/collection/NCLCollectionStore/_Public/25/047/25047841.pdf.
- Stefanovsky, S.V., Lebedev, V.P., Ptashkin, A.G., Dmitriev, S.A., Marra, J.C., 2010. Cold crucible inductive melting technology - Application to vitrification and ceramization of high level and actinide wastes. *Adv. Sci. Technol.* 73, 183–193.
- Tan, S., Ojovan, M.I., Hyatt, N.C., Hand, R.J., 2015. MoO₃ incorporation in magnesium aluminosilicate glasses. *J. Nucl. Mater.* 458, 335–342.
- Thien, B.M.J., Godon, N., Ballesterio, A., Gin, S., Ayrat, A., 2012. The dual effect of Mg on the long-term alteration rate of AVM nuclear waste glasses. *J. Nucl. Mater.* 427, 297–310.
- Tournié, A., Majérus, O., Lefèvre, G., *et al.*, 2013. Impact of boron complexation by Tris buffer on the initial dissolution rate of borosilicate glasses. *J. Colloid Interface Sci.* 400, 161–167.
- Tribet, M., Mir, A.H., Gillet, C., *et al.*, 2020. New insights about the importance of the alteration layer/glass interface. *J. Phys. Chem. C* 124, 10032–10044.
- Vernaz, E., Gin, S., Veyer, C., 2012. Waste glass. In: Konings, R.J.M. (Ed.), *Comprehensive Nuclear Materials* 5. Elsevier Science, pp. 451–483.
- Verney-Carron, A., Gin, S., Libourel, G., 2008. A fractured roman glass block altered for 1800 years in seawater: Analogy with nuclear waste glass in a deep geological repository. *Geochim. Cosmochim. Acta* 72, 5372–5385.
- Verney-Carron, A., Gin, S., Frugier, P., Libourel, G., 2010. Long-term modeling of alteration-transport coupling: Application to a fractured Roman glass. *Geochim. Cosmochim. Acta* 74, 2291–2315.
- Wang, L., Liang, T., 2012. Ceramics for high level radioactive waste solidification. *J. Adv. Ceram.* 1, 194–203.
- Weber, W.J., 1983. Radiation-induced swelling and amorphization in Ca₂Nd₆(SiO₄)₆O₂. *Radiat. Eff.* 77, 295–308.
- Weber, W.J., 2014. Radiation and thermal ageing of nuclear waste glass. *Proc. Mater. Sci.* 7, 237–246.
- Weber, W.J., Ewing, R.C., Angell, C.A., *et al.*, 1997. Radiation effects in glasses used for immobilization of high-level waste and plutonium disposition. *J. Mater. Res.* 12, 1948–1978.
- Weber, W.J., Ewing, R.C., Catlow, C.R.A., *et al.*, 1998. Radiation effects in crystalline ceramics for the immobilization of high-level nuclear waste and plutonium. *J. Mater. Res.* 13, 1434–1484.
- Weber, W.J., Turcotte, R.-P., Bunnell, L.R., Roberts, F.P., Westsik, J.H., 1979. Radiation effects in vitreous and devitrified simulated waste glass. In: Chikalla, T.D., Mendel, J.E. (Eds.), *Ceramics in Nuclear Waste Management*, National Information Service. VA: Springfield, pp. 294–299.
- Wilson, P.D., 1996. *The Nuclear Fuel Cycle. From Ore to Waste*. Oxford: Oxford University Press.
- Yang, J.H., Park, H.-S., Cho, Y.-Z., 2017. Al₂O₃-containing silver phosphate glasses as hosting matrices for radioactive iodine. *J. Nucl. Sci. Technol.* 54, 1330–1337.
- Zhang, Y., Gregg, D.J., Kong, L., Jovanovich, M., Triani, G., 2017. Zirconolite glass-ceramics for plutonium immobilization: The effects of processing redox conditions on charge compensation and durability. *J. Nucl. Mater.* 490, 238–241.
- Zhao, D., Li, L., Davis, L.L., Weber, W.J., Ewing, R.C., 2001. Gadolinium borosilicate glass-bonded Gd-silicate apatite: A glass-ceramic nuclear waste form for actinides. *Mater. Res. Soc. Symp. Proc.* 663, 199–206.

Further Reading

Donald, I.W., 2010. Waste immobilization in glass and ceramic based hosts. In *Radioactive, Toxic and Hazardous Wastes*. Chichester: Wiley.

Ojovan, M.I., 2011. *Handbook of Advanced Radioactive Waste Conditioning Technologies*. Cambridge: Woodhead Publishing Limited.

Ojovan, M.I., Lee, W.E., Kalmykov, S.N., 2019. *An Introduction to Nuclear Waste Immobilisation*, third ed. Oxford: Elsevier.

Relevant Websites

<https://www.nuclear-power.net/nuclear-power-plant/nuclear-fuel/nuclear-fuel-cycle/open-fuel-cycle-vs-closed-fuel-cycle/>

About the nuclear fuel cycle.

Open Fuel Cycle vs Closed Fuel Cycle - Nuclear-power.net.

<https://international.andra.fr/solutions-long-lived-waste/cigeo>

Cigeo.

Andra international.

<https://www.youtube.com/watch?v=YaJ8SU40Cz4>

Hanford Vitrification Plant.

YouTube.

<https://www.world-nuclear.org/information-library/nuclear-fuel-cycle/introduction/nuclear-fuel-cycle-overview.aspx>

Nuclear Fuel Cycle Overview - World Nuclear Association.

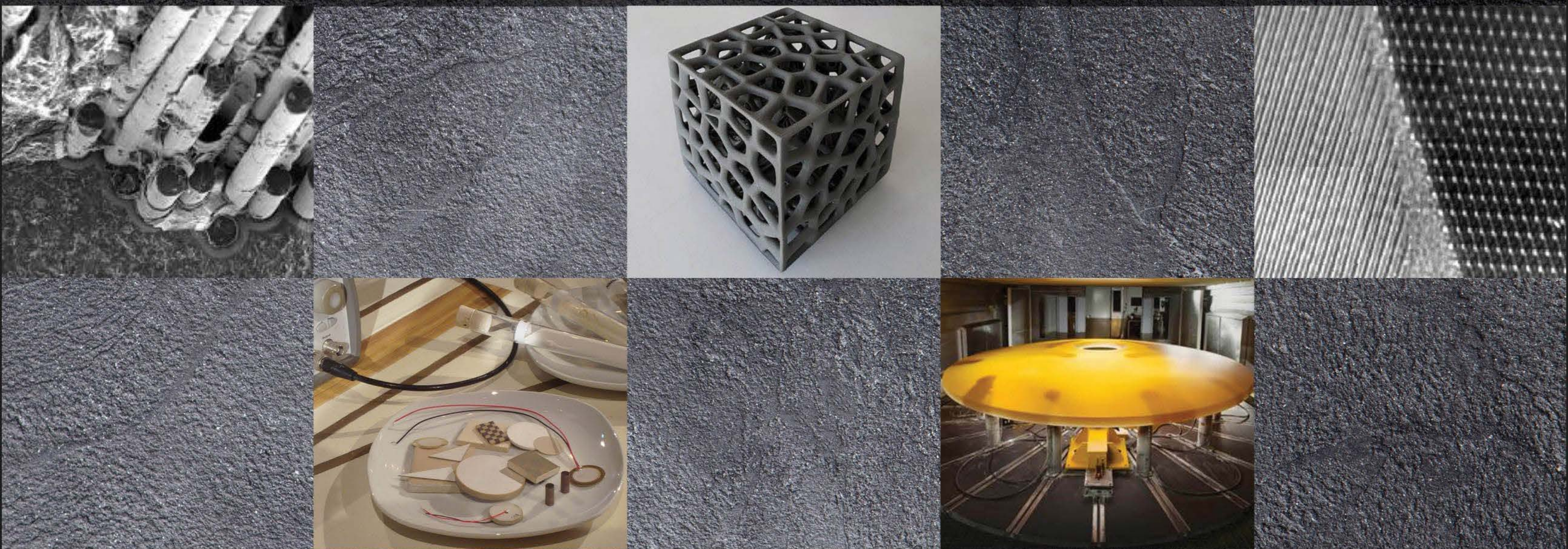
<https://www.youtube.com/watch?v=VOUJSIKly8g>

Recycling used nuclear fuel - Orano la Hague.

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Volume 3



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CONTENT OF VOLUME 3

List of Contributors for Volume 3	ix
Content of All Volumes	xv

VOLUME 3

Overview: Electroceramics and Ceramics and Glasses in Energy Generation and Storage <i>Carmen Galassi</i>	1
Photovoltaics: Advanced Inorganic Materials <i>Abdelilah Slaoui and Reuben T Collins</i>	5
Ion Conducting Materials: Superionic Conductors and Solid-State Ionics <i>Junichi Kawamura</i>	17
Development, Structure, and Mechanical Properties of Sulfide Solid Electrolytes <i>Koji Ohara, Atsushi Sakuda, and Akitoshi Hayashi</i>	38
Solid Oxide Fuel Cells <i>Alessandra Sanson and Angela Gondolini</i>	49
Laser Processing of Energy Storage Materials <i>Heungsoo Kim and Alberto Piqué</i>	59
Aluminum, Gallium, and Indium Nitrides <i>Qilin Hua, Bei Ma, and Weiguo Hu</i>	74
Novel Nitride Phosphors <i>M Bettinelli</i>	84
Phosphors: VUV Excitation <i>Jean-Claude Krupa and AZMS Rahman</i>	89
Silicon Carbide Electronic Devices <i>PG Neudeck and GK Sujan</i>	93
Scintillator Crystals <i>D Klimm</i>	103
Ceramics for Laser Technologies <i>Jan Hostaša</i>	110
Ceramic Sensors for Industrial Applications <i>David Degler, Frank Allmendinger, and Nicolae Barsan</i>	125
Pyroelectric Crystals, Ceramics, and Thin Films for IR Sensors <i>Roger W Whatmore</i>	139
Superconducting Materials <i>Peter Majewski</i>	151
Superconductors: Borocarbides <i>Günter Fuchs, Karl-Hartmut Müller, and Vladimir N Narozhnyi</i>	162
The RABiTS Approach for Second Generation (2G) High Temperature Superconductors <i>Martin W Rupich</i>	174

Ferrite Ceramics at Microwave Frequencies: Applications and Characterization <i>Jean-Luc Mattei, Alexis Chevalier, and Vincent Laur</i>	183
Ferrite Magnets: Properties and Applications <i>Jean-Marie Le Breton</i>	206
Ferrites <i>PJ van der Zaag</i>	217
Multiferroic Composites <i>Xianfeng Liang, Huaihao Chen, Cheng Tu, Zhaoqiang Chu, Cunzheng Dong, Yifan He, Yuyi Wei, Yuan Gao, Hwaider Lin, and Nian X Sun</i>	225
Zinc-Oxide-Based Electronics and Photonics <i>David J Rogers, Ferechteh H Teherani, Eric V Sandana, and Philippe Bove</i>	241
Varistor Electrical Properties: Microstructural Effects <i>Zumret Topcagic and Thomas E Tsovilis</i>	254
Latest Trend of ZnO Multilayer Ceramic Varistors <i>Eiichi Koga, Yoshiko Higashi, and Michio Matsuoka</i>	272
Dielectric, Ferroelectric, Antiferroelectric, Relaxor, Piezoelectric Ceramics: Definitions and Main Applications <i>Floriana Craciun</i>	281
Electroceramics: Modeling of Sintering, Microstructure Evolution and Functional Properties <i>Constantin Hutanu, Vlad Alexandru Lukacs, and Liliana Mitoseriu</i>	295
BaTiO ₃ -Based Ceramics: Fundamentals, Properties and Applications <i>Vincenzo Buscaglia, Maria Teresa Buscaglia, and Giovanna Canu</i>	311
The PZT System <i>Florian Jean and Christian Courtois</i>	345
Lead-Free Piezoelectric Ceramics <i>Barbara Malič, Mojca Otoničar, Kristian Radan, and Jurij Koruza</i>	358
Electrostrictive Ceramics and Their Applications <i>Simone Santucci and Vincenzo Esposito</i>	369
Low-Loss Ceramics in Mobile Communications <i>K Wakino, H Tamura, and GK Sujan</i>	375
Small-Scale Energy Harvesting Devices for Smart Electronics <i>Sumanta Kumar Karan, Rammohan Sriramdas, Min-Gyu Kang, Yongke Yan, and Shashank Priya</i>	391
Multilayer Ceramic Actuators <i>K Uchino</i>	426
Multilayer Glass–Ceramic/Ceramic Composite Substrates <i>Jobin Varghese, Nina Joseph, and Heli Jantunen</i>	437
Functional Ceramics through Novel Chemical Approaches <i>K Kato, Y Torii, and G Majumdar</i>	452
Overview: Bioceramics and Bioreactive Glasses <i>Anne Leriche and Francis Cambier</i>	458
Bone as a Material: Lessons From Nature <i>Laura M O'Sullivan and Laoise M McNamara</i>	459
Overview of Substitutes for Bone Replacement: Natural and Synthetic Products <i>Nicolas Somers and Marie Lasgorceix</i>	473

New Trends in Ceramics for Orthopedics <i>Laurent Gremillard and Jérôme Chevalier</i>	493
New Trends in Ceramics for Dentistry <i>Paola Palmero</i>	501
Oxide Ceramics for Biomedical Applications <i>Corrado Piconi and Anna Tampieri</i>	511
Non-Oxide Ceramics as Biomaterials <i>Stuart Hampshire</i>	526
Carbon in Biomedical Engineering <i>Jill S Kawalec</i>	533
Yttria-Stabilized Zirconia as a Biomaterial: From Orthopedic Towards Dental Applications <i>Helen Reveron and Jérôme Chevalier</i>	540
ZTA Ceramics for Biomedical Applications <i>Frank Kern, Paola Palmero, and Wolfgang Burger</i>	553
Phosphates <i>David Grossin</i>	567
Apatitic and Tricalcic Calcium Phosphate-Based Bioceramics: Overview and Perspectives <i>Christophe Drouet and Christèle Combes</i>	575
Calcium Phosphates in Biomedical Engineering <i>Maria Canillas, Antonio H de Aza, and Miguel A Rodríguez</i>	595
Bioceramics in Regenerative Medicine <i>Simone Sprio, Anna Tampieri, Massimiliano Dapporto, Michele Iafisco, and Monica Montesi</i>	601
Bioactive Glasses and Glass-Ceramics <i>Francesco Baino</i>	614
Calcium Phosphate Cements <i>Aoife Culliton and Eamonn De Barra</i>	624
Bone Regeneration With Ceramics Scaffold <i>Vida Strasser and Maja Dutour Sikirić</i>	646
Advanced Processes for the Design of Customized Ceramic Medical Devices <i>Eric Champion and Patricia Pascaud-Mathieu</i>	662
Bioactive and Biodegradable Polymer-Based Composites <i>Lukas Gritsch and Aldo R Boccaccini</i>	674
Surface Treatment of Bioceramics <i>Nicolas Somers and Marie Lasgorceix</i>	701
Chemical Functionalization of Calcium Phosphate Bioceramic Surfaces <i>Chantal Damia, Amandine Magnaudeix, and Betty Laverdet</i>	716
Thermally Sprayed Materials for Biomedical Applications <i>Andreas Killinger and Rainer Gadow</i>	732
Design of Tissue Engineering Scaffold by Means of Mathematical Modeling <i>Stefan Scheiner</i>	750
Unconventional, Nature-Inspired Approaches to Develop Bioceramics for Regenerative Medicine <i>Anna Tampieri, Simone Sprio, Monica Sandri, Elisabetta Campodoni, Andrea Ruffini, Laura Mengozzi, and Silvia Panseri</i>	758
Assessment of Mechanical Properties of Bioceramics <i>Gilbert Fantozzi</i>	772

Mechanical Properties of Dental Ceramics <i>Fei Zhang and Jozef Vleugels</i>	784
Biological Assessment of Bioceramics: In Vitro and In Vivo Tests <i>Maria H Fernandes and Pedro de Sousa Gomes</i>	798
Zirconia Ceramics: Clinical and Biological Aspects in Dentistry <i>Andraž Kocjan, Tadej Mirt, Ralf-Joachim Kohal, Zhijian Shen, and Peter Jevnikar</i>	817
Subject Index	832

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CONTENT OF ALL VOLUMES

List of Contributors for Volume	ix
Editor Biographies	xxiii
Preface	xxv

VOLUME 1

Overview: Manufacture of Ceramics and Microstructural Developments in Ceramics <i>Francis Cambier and Anne Leriche</i>	1
Synthesis of Oxide and Non-Oxide Advanced Ceramics <i>Prashant N Kumta</i>	2
Synthesis of Ceramic Powders by Wet Chemical Routes <i>Paola Palmero</i>	27
Self-Propagating High-Temperature Synthesis <i>Jerzy Lis</i>	40
Hydrothermal Synthesis <i>Ender Suvaci and Emel Özel</i>	59
Ultrasonic Sprayed Aerosol for Ultrafine Ceramic Powder Synthesis <i>Sylvie Foucaud and Yann Leconte</i>	69
Calcination and Phase Transformations <i>Gary L Messing</i>	83
Preceramic Polymers as Precursors of Advanced Ceramics: The Polymer-Derived Ceramics (PDCs) Route <i>Yuji Iwamoto, Günter Motz, Emanuel Ionescu, and Samuel Bernard</i>	93
Organic Additives in Ceramic Processing <i>Anne Aimable and Thierry Chartier</i>	103
Powder Mixing and Grinding Processes for Ceramics <i>David Houivet and Jérôme Bernard</i>	112
Powder Granulation and Compaction <i>Michele Dondi</i>	136
Colloid Casting Processes: Slip Casting, Centrifugal Casting, and Gel Casting <i>Nur S Yüzbaşı and Thomas Graule</i>	146
Processing of Ceramics by Direct Coagulation Casting <i>Margarida Almeida and Joaquim M Vieira</i>	154
Extrusion <i>Stuart Blackburn and Marcin Szymiczek</i>	162
Ceramic Injection Molding <i>Moritz v Witzleben and Tassilo Moritz</i>	179

Tape Casting and Lamination <i>Eric R Twiname</i>	189
Freeze Casting <i>Dominique Hautcoeur</i>	195
Additive Manufacturing <i>Andrea Zocca, Giorgia Franchin, Paolo Colombo, and Jens Günster</i>	203
Green Machining of Ceramics <i>Fabrice Petit</i>	222
Screen Printing <i>Danjela Kuscser</i>	227
Sintering of Ceramics: An Overview <i>Anne Leriche, Francis Cambier, and Stuart Hampshire</i>	233
Solid-State Sintering <i>John E Blendell and Wolfgang Rheinheimer</i>	249
Liquid Phase Sintering: Fundamentals <i>Suk-Joong L Kang</i>	258
Viscous Sintering <i>George W Scherer</i>	265
Hot Pressing and Hot Isostatic Pressing <i>Mathias Herrmann and Jan Räthel</i>	270
Reaction Sintering <i>Carmen Baudín</i>	278
Flash Sintering and Other Rapid Sintering Techniques <i>David Salamon</i>	286
Spark Plasma Sintering <i>Umberto Anselmi-Tamburini</i>	294
Cold Sintering and Hydrothermal Sintering <i>Graziella Goglio, Arnaud Ndayishimiye, Catherine Elissalde, and Clive A Randall</i>	311
Microwave Sintering of Ceramics <i>Jean-Marc Chaix</i>	327
Porous Ceramics Processing <i>Manabu Fukushima, Akihiro Shimamura, Paolo Colombo, Hideki Hyuga, Tatsuki Ohji, and Yu-ichi Yoshizawa</i>	342
Porous Ceramics Including Fibrous Insulation, Structure and Properties of <i>M Fukushima, T Ohji, P Colombo, and Y-I Yoshizawa</i>	346
Control of the Microstructure in Ceramics <i>Anne Leriche, Stuart Hampshire, and Francis Cambier</i>	349
Templated Grain Growth of Textured Ceramics <i>Gary L Messing</i>	367
Functionally Graded Ceramics <i>Omer Van der Biest and Achim Neubrand</i>	374
Transparent Ceramics: Materials, Processing, Properties and Applications <i>Marc Rubat du Merac</i>	399
Geopolymers and Geopolymer-Derived Composites <i>Waltraud M Kriven</i>	424

Overview: Characterization and Modelling of Ceramics and Glasses <i>Michael Pomeroy and Stuart Hampshire</i>	439
Ceramic Genomics: Total Bond Order Density <i>Wai-Yim Ching</i>	441
Predictive Modeling of Ceramic Materials <i>Sarah Guerin, Syed AM Tofail, and Damien Thompson</i>	475
Molecular Dynamics Simulations of Glass Structure <i>Mattias Edén</i>	481
Computation of Phase Diagrams for Ceramics <i>Sara Serena, Angel Caballero, Antonio H de Aza, and Maria A Sainz</i>	498
Characterization of Ceramic Powders <i>Martin J Murtagh and Navin Venugopal</i>	517
Amorphous Materials: Vibrational Spectroscopy <i>PF McMillan</i>	530
MAS NMR Analysis of Ceramics and Glasses <i>Yajie Gao</i>	536
X-Ray Powder Diffraction <i>Scott T Mixture</i>	549
Case Studies in the X-ray Diffraction of Ceramics <i>Maurice Gonon</i>	560
Introduction to Transmission Electron Microscopy; The Basics <i>Ann-Katrin Fetzner, Maximilian Trapp, Stefan Lauterbach, and Hans-Joachim Kleebe</i>	578
High Resolution Analytical Electron Microscopy of Ceramics and Glasses <i>Jennifer Cookman, Michele Conroy, and Ursel Bangert</i>	600
Introduction to Three Dimensional Electron Crystallography <i>Andrew Stewart and Ute Kolb</i>	618
Preparation of Ceramic, Glass-Ceramic and Glasses for Microstructural Examination <i>Michael J Pomeroy</i>	634
Scanning Electron Microscopy for Ceramics and Glasses <i>Michael J Pomeroy</i>	651
Fractography: Brittle Materials <i>John J Mecholsky, Jr.</i>	662
Thermal Analysis Techniques for Technical Ceramics and Glasses <i>Michael J Pomeroy</i>	676
High-Temperature Characterization of Glasses and Melts <i>Sohei Sukenaga and Hiroyuki Shibata</i>	689
Overview: Mechanical and Physical Properties and Property Testing of Ceramics and Glasses <i>Anne Leriche and Francis Cambier</i>	704
Elastic and Inelastic Behavior of Ceramics <i>Daniele Mari and Robert Schaller</i>	705
Indentation of Ceramics <i>Emilio Jiménez-Piqué</i>	718
Contact Damage Resistance and Tribological Behavior of Ceramic/Carbon Nanostructure Composites <i>Manuel Belmonte</i>	733

Methods of Determination of Young's Modulus and Tensile, Flexural and Compressive Strength <i>Sylvain Meille</i>	745
Fracture Toughness Measurement <i>Tanja Lube</i>	762
R-Curve Behavior of Ceramics <i>Marc J Anglada</i>	775
Subcritical Crack Growth: Basic Relations and Experimental Evaluation <i>Malika Saâdaoui</i>	797
Subcritical Crack Growth: Modeling of the v-K Curve in Different Environments <i>Raul Bermejo</i>	811
Ceramics: Transformation Toughening <i>DB Marshall and RHJ Hannink</i>	818
Mixed-Mode Fracture and Microstructural Aspects of Crack Propagation <i>Delia Gutiérrez-Campos and Yuk Ming X Hung-Hung</i>	823
R-Ratio and Microstructure Effects <i>Delia Gutiérrez-Campos, Eliana Pinto-González, and Elvira Saab-Llatas</i>	841
Thermal Properties of Ceramic Materials <i>David S Smith and Benoît Naït-Ali</i>	855
Thermal Shock Behavior of Ceramics: Fundamentals and Thermal Shock Resistance Parameters <i>Carmen Baudín</i>	867
Thermal Shock and Thermal Fatigue Behavior of Ceramics: Microstructural Effects <i>Gilbert Fantozzi and Malika Saâdaoui</i>	879
Creep Behavior of Ceramics <i>Gilbert Fantozzi and Arturo Dominguez-Rodriguez</i>	891
Nonoxide Ceramics, Creep and Creep Rupture of: Silicon Nitrides and Silicon Carbides <i>SM Wiederhorn</i>	908
Dislocations in Ceramic Materials <i>Jacques Rabier</i>	911
Corrosion of Ceramics in Aqueous Environments <i>Mathias Herrmann</i>	921
Corrosion and Degradation of Glass <i>Dagmar Galusková and Dušan Galusek</i>	932

VOLUME 2

Overview: Oxide Ceramics and Non-oxide Ceramics <i>Stuart Hampshire and Michael Pomeroy</i>	1
Structural and Thermostructural Ceramics <i>Jon Binner and Tammana SRC Murthy</i>	3
Alumina, Structure and Properties <i>Carmen Baudín</i>	25
Low Thermal Expansion Ceramic and Glass-Ceramic Materials <i>Pascal Pilate and Florimond Delobel</i>	47

Mullite: Structure and Properties <i>Gi��le L Lecomte-Nana and Aghiles Hammas</i>	59
Aluminum Titanate, Structure and Properties <i>Salvador Bueno and Carmen Baud��n</i>	76
Zirconia Ceramics, Structure and Properties <i>Anne Leriche, Francis Cambier, and Helen Reveron</i>	93
Si ₃ N ₄ -Ceramics: An Introduction <i>MJ Hoffmann</i>	105
Si ₃ N ₄ Ceramics, Structure and Properties <i>Monika Tatarkov��, Peter Tatarko, and Pavol ��ajgal��k</i>	109
SiALONs and the Representation of Phase Relationships <i>Stuart Hampshire</i>	119
Si-Al-O-N Ceramics, Structure and Properties <i>Ali ��elik and Servet Turan</i>	128
Aluminum Nitride and ALON Ceramics, Structure and Properties of <i>JW McCauley</i>	144
SiC Ceramics, Structure, Processing and Properties <i>Young-Wook Kim and Rohit Malik</i>	150
High Thermal Conductivity Ceramics <i>Mikito Kitayama</i>	165
MAX Phases, Structure, Processing, and Properties <i>Nick Goossens, Bensu Tunca, Thomas Lapauw, Konstantina Lambrinou, and Jozef Vleugels</i>	182
ZrB ₂ , HfB ₂ , OsB ₂ and IrB ₂ Boride Ceramics: Processing, Structure, and Properties <i>Nina Orlovskaya, Holden Hyer, Yongho Sohn, Mykola Lugovy, Gurdial Blugan, Thomas Graule, Jakob Kuebler, Sergey Yarmolenko, Jagannathan Sankar, and Michael J Reece</i>	200
Directionally-Solidified Eutectic Oxide Ceramics <i>VM Orera^{��} and J Llorca</i>	216
Overview: High-Performance Ceramics and Ceramic Composites <i>Michael Pomeroy</i>	225
Ceramic Matrix Composites With Roughly Equiaxed Reinforcements: Microstructure and Mechanical Behavior <i>Gilbert Fantozzi and J��r��me Chevalier</i>	227
Nanoscale Ceramic Composites <i>GS Thompson and MP Harmer</i>	240
Ceramic Matrix Graphene and Carbon Nanotube Composites <i>Katalin Bal��zsi, M��nika Furk��, and Csaba Bal��zsi</i>	243
Short Fiber Ceramic Matrix Composites (SF-CMCs) <i>Walter Krenkel, Stefan Flauder, and Georg Puchas</i>	260
Glass and Glass-Ceramic Matrix Composites for Advanced Applications: Part I: Properties and Manufacturing Technologies <i>Dino Boccaccini, Maria Cannio, Enrico Bernardo, and Aldo R Boccaccini</i>	277
Glass and Glass-Ceramic Matrix Composites for Advanced Applications: Part II: Applications <i>Dino Boccaccini, Maria Cannio, Enrico Bernardo, and Aldo R Boccaccini</i>	288

^{  }Deceased.

High Performance Fibers <i>AR Bunsell</i>	304
Spun (Slurry and Sol–Gel) Ceramic Fibers <i>DM Wilson</i>	314
Ceramic Matrix Fiber Composites <i>Francis Rebillat</i>	317
Ultra-High Temperature Ceramic Matrix Composites <i>Luca Zoli, Diletta Sciti, Antonio Vinci, Pietro Galizia, Frédéric Monteverde, Simone Failla, and Laura Silvestroni</i>	340
Carbon-Matrix Composites <i>Deborah DL Chung</i>	353
Ceramics in Space Applications <i>Barry Twomey, Daithi de Faoite, Kevin AJ Doherty, and Kenneth T Stanton</i>	359
Porous Ceramics for Energy Applications <i>Andreas Kaiser, Bhaskar R Sudireddy, and Farid Akhtar</i>	380
Joining of Advanced Ceramics <i>John A Fernie and Kevin M Knowles</i>	393
Abrasives <i>Jean-André Alary</i>	406
Wear and Erosion Resistant Ceramic Materials <i>Pavol Hvizdoš</i>	416
Wear and Erosion Resistant Ceramic Coatings <i>František Lofaj and Marián Mikula</i>	425
Oxidation and Corrosion of Non-oxide Ceramics <i>NS Jacobson and EJ Opila</i>	440
Overview: Glass and Glass Ceramics <i>Stuart Hampshire</i>	445
The Glassy State <i>Maziar Montazerian and Edgar D Zanutto</i>	448
Glasses: Alkali and Alkaline-Earth Silicates <i>Benjamin JA Moulton and Grant S Henderson</i>	462
Soda-Lime-Silica Glasses <i>Russell J Hand</i>	483
Glasses: Aluminosilicates <i>Laurent Cormier</i>	496
Borosilicate Glasses <i>Yuanzheng Yue, Manzila I Tuheen, and Jincheng Du</i>	519
Glasses: Chalcogenides <i>Myungkoo Kang and Kathleen A Richardson</i>	540
Glasses: Oxynitride Glass Formation and Structure <i>Stuart Hampshire</i>	555
Glasses: Oxynitride Glass Properties and Crystallization <i>Stuart Hampshire</i>	569
Glasses: Phosphates <i>Andrea Moguš-Milanković, Ana Šantić, and Luka Pavić</i>	580

Halide Glasses <i>Marcel Poulain</i>	591
Glass: Annealing and Tempering <i>Mathieu Hubert and Peter J Lezzi</i>	623
Glass: Chemical and Thermal Strengthening <i>Ali Talimian and Vincenzo M Sglavo</i>	632
Properties of Glass Materials <i>M Hasanuzzaman, A Rafferty, M Sajjia, and A-G Olabi</i>	647
Optical Glass: Challenges From Optical Design <i>Ulrich Fotheringham, Martin Letz, Uwe Petzold, Simone Ritter, and Yvonne Menke-Berg</i>	658
Glass Fibers <i>KK Chawla</i>	676
Glass: Optical Fibers – Manufacture and Properties <i>Conleth D Hussey</i>	681
Glasses: Sol–Gel Methods: An Introduction <i>T Woignier and J Phalippou</i>	689
Glasses and Glass-Ceramics Prepared by Sol–Gel <i>María E Cruz, Yolanda Castro, and Alicia Durán</i>	695
Glass-Ceramics and Their Applications <i>Maurice Gonon and Florian Dupla</i>	709
Glass Reactive Sintering <i>Acacio Rincon Romero, Hamada Elsayed, Jozef Kraxner, and Enrico Bernardo</i>	728
Glasses and Glass-Ceramics as Sealing Materials <i>María J Pascual</i>	746
Glasses and Glass-Ceramics for Nuclear Waste Immobilization <i>Daniel Caurant and Odile Majérus</i>	762

VOLUME 3

Overview: Electroceramics and Ceramics and Glasses in Energy Generation and Storage <i>Carmen Galassi</i>	1
Photovoltaics: Advanced Inorganic Materials <i>Abdelilah Slaoui and Reuben T Collins</i>	5
Ion Conducting Materials: Superionic Conductors and Solid-State Ionics <i>Junichi Kawamura</i>	17
Development, Structure, and Mechanical Properties of Sulfide Solid Electrolytes <i>Koji Ohara, Atsushi Sakuda, and Akitoshi Hayashi</i>	38
Solid Oxide Fuel Cells <i>Alessandra Sanson and Angela Gondolini</i>	49
Laser Processing of Energy Storage Materials <i>Heungsoo Kim and Alberto Piqué</i>	59
Aluminum, Gallium, and Indium Nitrides <i>Qilin Hua, Bei Ma, and Weiguo Hu</i>	74
Novel Nitride Phosphors <i>M Bettinelli</i>	84

Phosphors: VUV Excitation <i>Jean-Claude Krupa and AZMS Rahman</i>	89
Silicon Carbide Electronic Devices <i>PG Neudeck and GK Sujan</i>	93
Scintillator Crystals <i>D Klimm</i>	103
Ceramics for Laser Technologies <i>Jan Hostaša</i>	110
Ceramic Sensors for Industrial Applications <i>David Degler, Frank Allmendinger, and Nicolae Barsan</i>	125
Pyroelectric Crystals, Ceramics, and Thin Films for IR Sensors <i>Roger W Whatmore</i>	139
Superconducting Materials <i>Peter Majewski</i>	151
Superconductors: Borocarbides <i>Günter Fuchs, Karl-Hartmut Müller, and Vladimir N Narozhnyi</i>	162
The RABiTS Approach for Second Generation (2G) High Temperature Superconductors <i>Martin W Rupich</i>	174
Ferrite Ceramics at Microwave Frequencies: Applications and Characterization <i>Jean-Luc Mattei, Alexis Chevalier, and Vincent Laur</i>	183
Ferrite Magnets: Properties and Applications <i>Jean-Marie Le Breton</i>	206
Ferrites <i>PJ van der Zaag</i>	217
Multiferroic Composites <i>Xianfeng Liang, Huaihao Chen, Cheng Tu, Zhaoqiang Chu, Cunzheng Dong, Yifan He, Yuyi Wei, Yuan Gao, Hwaider Lin, and Nian X Sun</i>	225
Zinc-Oxide-Based Electronics and Photonics <i>David J Rogers, Ferechteh H Teherani, Eric V Sandana, and Philippe Bove</i>	241
Varistor Electrical Properties: Microstructural Effects <i>Zumret Topcagic and Thomas E Tsovilis</i>	254
Latest Trend of ZnO Multilayer Ceramic Varistors <i>Eiichi Koga, Yoshiko Higashi, and Michio Matsuoka</i>	272
Dielectric, Ferroelectric, Antiferroelectric, Relaxor, Piezoelectric Ceramics: Definitions and Main Applications <i>Floriana Craciun</i>	281
Electroceramics: Modeling of Sintering, Microstructure Evolution and Functional Properties <i>Constantin Hutanu, Vlad Alexandru Lukacs, and Liliana Mitoseriu</i>	295
BaTiO ₃ -Based Ceramics: Fundamentals, Properties and Applications <i>Vincenzo Buscaglia, Maria Teresa Buscaglia, and Giovanna Canu</i>	311
The PZT System <i>Florian Jean and Christian Courtois</i>	345
Lead-Free Piezoelectric Ceramics <i>Barbara Malič, Mojca Otoničar, Kristian Radan, and Jurij Koruza</i>	358

Electrostrictive Ceramics and Their Applications <i>Simone Santucci and Vincenzo Esposito</i>	369
Low-Loss Ceramics in Mobile Communications <i>K Wakino, H Tamura, and GK Sujan</i>	375
Small-Scale Energy Harvesting Devices for Smart Electronics <i>Sumanta Kumar Karan, Rammohan Sriramdas, Min-Gyu Kang, Yongke Yan, and Shashank Priya</i>	391
Multilayer Ceramic Actuators <i>K Uchino</i>	426
Multilayer Glass–Ceramic/Ceramic Composite Substrates <i>Jobin Varghese, Nina Joseph, and Heli Jantunen</i>	437
Functional Ceramics through Novel Chemical Approaches <i>K Kato, Y Torii, and G Majumdar</i>	452
Overview: Bioceramics and Bioreactive Glasses <i>Anne Leriche and Francis Cambier</i>	458
Bone as a Material: Lessons From Nature <i>Laura M O'Sullivan and Laoise M McNamara</i>	459
Overview of Substitutes for Bone Replacement: Natural and Synthetic Products <i>Nicolas Somers and Marie Lasgorceix</i>	473
New Trends in Ceramics for Orthopedics <i>Laurent Gremillard and Jérôme Chevalier</i>	493
New Trends in Ceramics for Dentistry <i>Paola Palmero</i>	501
Oxide Ceramics for Biomedical Applications <i>Corrado Piconi and Anna Tampieri</i>	511
Non-Oxide Ceramics as Biomaterials <i>Stuart Hampshire</i>	526
Carbon in Biomedical Engineering <i>Jill S Kawalec</i>	533
Yttria-Stabilized Zirconia as a Biomaterial: From Orthopedic Towards Dental Applications <i>Helen Reveron and Jérôme Chevalier</i>	540
ZTA Ceramics for Biomedical Applications <i>Frank Kern, Paola Palmero, and Wolfgang Burger</i>	553
Phosphates <i>David Grossin</i>	567
Apatitic and Tricalcic Calcium Phosphate-Based Bioceramics: Overview and Perspectives <i>Christophe Drouet and Christèle Combes</i>	575
Calcium Phosphates in Biomedical Engineering <i>Maria Canillas, Antonio H de Aza, and Miguel A Rodríguez</i>	595
Bioceramics in Regenerative Medicine <i>Simone Sprio, Anna Tampieri, Massimiliano Dapporto, Michele Iafisco, and Monica Montesi</i>	601
Bioactive Glasses and Glass-Ceramics <i>Francesco Baino</i>	614
Calcium Phosphate Cements <i>Aoife Culliton and Eamonn De Barra</i>	624

Bone Regeneration With Ceramics Scaffold <i>Vida Strasser and Maja Dutour Sikirić</i>	646
Advanced Processes for the Design of Customized Ceramic Medical Devices <i>Eric Champion and Patricia Pascaud-Mathieu</i>	662
Bioactive and Biodegradable Polymer-Based Composites <i>Lukas Gritsch and Aldo R Boccaccini</i>	674
Surface Treatment of Bioceramics <i>Nicolas Somers and Marie Lasgorceix</i>	701
Chemical Functionalization of Calcium Phosphate Bioceramic Surfaces <i>Chantal Damia, Amandine Magnaudeix, and Betty Laverdet</i>	716
Thermally Sprayed Materials for Biomedical Applications <i>Andreas Killinger and Rainer Gadow</i>	732
Design of Tissue Engineering Scaffold by Means of Mathematical Modeling <i>Stefan Scheiner</i>	750
Unconventional, Nature-Inspired Approaches to Develop Bioceramics for Regenerative Medicine <i>Anna Tampieri, Simone Sprio, Monica Sandri, Elisabetta Campodoni, Andrea Ruffini, Laura Mengozzi, and Silvia Panseri</i>	758
Assessment of Mechanical Properties of Bioceramics <i>Gilbert Fantozzi</i>	772
Mechanical Properties of Dental Ceramics <i>Fei Zhang and Jozef Vleugels</i>	784
Biological Assessment of Bioceramics: In Vitro and In Vivo Tests <i>Maria H Fernandes and Pedro de Sousa Gomes</i>	798
Zirconia Ceramics: Clinical and Biological Aspects in Dentistry <i>Andraž Kocjan, Tadej Mirt, Ralf-Joachim Kohal, Zhijian Shen, and Peter Jevnikar</i>	817
Subject Index	832

Overview: Electroceramics and Ceramics and Glasses in Energy Generation and Storage

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Over the last two decades Electroceramics and Ceramics and Glasses in Energy Generation and Storage, perhaps the most economically important member of engineered ceramics, have become one of the most important research areas in materials science both through improvements in basic knowledge and their significant growing technological impact.

Electroceramics include advanced ceramic materials that are used in a wide variety of electrical, optical and magnetic applications.

Technology and device applications drive research in this growing field that includes ionically conducting, semiconducting, superconducting, magnetic and dielectric ceramics, used in domains as diverse as energy conversion and storage, consumer electronics and communication, medicine and health care, transportation, industrial production, power engineering.

The Section “Electroceramics and Ceramics and Glasses in Energy Generation and Storage” covers all the main topics related, from basics of the material science to the processing technologies and several applications. The chapters are grouped following the main focus, and the reader will be helped by the keywords as many of them cover different aspects like material properties, characterizations and applications.

The First Five Chapters are Related to Energy Conversion and Storage

Photovoltaics

Advanced Inorganic Materials: the commercial first PV modules are based on single-crystal and multicrystalline silicon wafers, the second generation is based on inorganic semiconductor thin films; the next generation is driven by concepts aimed at ultra-high efficiency and/or ultra-low cost regimes and involving nanotechnologies, multiple junctions, and bandgap engineering.

Ion Conducting Materials

Superionic Conductors and Solid-State Ionics: review of solid electrolytes which show purely ionic conduction and mixed conductors which show both ionic and electronic conduction and their applications in sensors, high power batteries, electrolysis of gaseous molecules and gas separation.

Development, Structure, and Mechanical Properties of Sulfide Solid Electrolytes: the sulfide solid electrolytes with a high lithium ion conductivity and their mechanical properties are addressed.

Solid Oxide Fuel Cells

The chapter describes the types of SOFCs, technological trends in the recent years and the progress in material's development and processing (electrolytes, anode substrates and anodes, cathode, interconnect, protective and contact coatings, sealings).

Laser Processing of Energy Storage Materials

The laser-based processing techniques for the fabrication of energy storage devices including three laser-based processing techniques (LIFT, PLD and LSM) for the fabrication of energy storage devices are reviewed.

Six Chapters Survey Materials for Electronics and Optoelectronics

Aluminum, Gallium, and Indium Nitrides

Outlook of fundamental properties of Aluminum, Gallium, and Indium Nitrides and insight into the potential applications of GaN-based electronic/optoelectronic.

[☆]Now research fellow at Politecnico di Milano, Department of Mechanical Engineering.

Novel Nitride Phosphors

Nitride and oxynitride families have proved to be excellent hosts for the development of efficient phosphors for white pcLEDs, emitting all over the visible range; development of the perfect phosphors for LEDs, and nitride and oxynitride materials will play an important role for future applications.

Phosphors

VUV Excitation: as far as vacuum ultraviolet (VUV) optical excitations are concerned, the most suitable materials are the large band gap inorganic lattices activated by rare earth ions. These phosphors are mainly sintered oxo (phosphates, borates, aluminates, etc.), oxofluoride or fluoride compounds.

Silicon Carbide Electronic Devices

Silicon Carbide is useful for realizing short-wavelength blue and UV optoelectronics; SiC RF devices are applied in high-frequency solid-state high-power amplification; silicon-on-insulator circuits can perform complex digital and analog signal-level functions up to 300°C.

Scintillator Crystals

NaI and other low melting point halide crystals are often used as scintillator crystals. They are suitable for easy working conditions (T, p, energy of radiation). Issues to maintain high optical quality are discussed.

Ceramics for Laser Technologies

The ceramics for laser technologies are single-phase polycrystalline materials, doped with transition metals or lanthanides. They are transparent in the wavelength range of the absorption and emission range and they must have the thermal and mechanical properties to withstand the laser operation.

Two Chapters are Specifically Dedicated to Ceramics for Sensors

Ceramic Sensors for Industrial Applications

Different gas sensors types (pellistor-type gas sensors, gas sensors based on solid ionic conductors and chemoresistive gas sensors based on semiconducting metal oxides) based on ceramic materials and their working principles are presented.

Pyroelectric Crystals, Ceramics, and Thin Films for IR Sensors

IR Sensors for detection of radiation in the infrared radiation (IR) bands of 3–5 mm and especially 8–14 mm are introduced. Pyroelectric detectors have found a huge range of applications in products ranging from fire alarms to intruder detectors, in instrumentation such as gas analysis, and in thermal imaging.

Three Chapters Deal With Superconducting Materials

Superconducting Materials

Survey of the different types of superconducting materials, including an introduction to superconductivity and its important fundamental parameters. The review also introduces the major superconducting materials which currently represent the basis for superconducting devices and which may be important candidates for future application. Fundamental materials aspects of these materials and how they affect their superconducting properties are presented as well.

Superconductors

Borocarbides: rare-earth nickel borocarbides are magnetic superconductors showing both, coexistence and competition of superconductivity and magnetic order. The interplay between superconductivity and magnetism is discussed for $\text{HoNi}_2\text{B}_2\text{C}$.

The RABiTS Approach for Second Generation (2G) High Temperature Superconductors: overview of the Rolling Assisted Bi-axially Textured Substrate (RABiTS™) process for fabricating long length high temperature superconducting (HTS) wire based on the $(\text{RE})\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ materials ((RE)BCO) where RE is a rare earth. The RABiTS process is one of three template technologies developed for the roll-to-roll manufacturing of long length.

Four Chapters Introduce the Ceramic Magnetic Materials

Ferrite Ceramics at Microwave Frequencies: Applications and Characterization

Ferrite ceramics with their magnetic properties and low loss are applied as passive microwave components operating over a wide range of frequencies. The basics and main properties are surveyed with specific reference to the application at Microwave Frequencies.

Ferrite Magnets

Properties and Applications: permanent magnets materials are magnetic materials that can keep their magnetization once they are submitted to a magnetic field. They are denoted as hard magnetic materials and their magnetization remains stable at the temperature of use.

Ferrites: soft ferrites with cubic, spinel lattice structure have found widespread use in electronic applications as inductor or transformer cores; their applications and new developments in thin films.

Multiferroic Composites: these extremely interesting materials with coupled ferromagnetic and ferroelectric orders with huge potential for technological applications. Their multifunctional properties of multiferroic composites facilitate the development of novel electronic devices for various sensing, transduction, and antenna applications. Their characterization, modeling and applications (sensor, inductor, filters, antennas), are surveyed.

Three Chapters are Focused on Zinc Oxide

Zinc-Oxide-Based Electronics and Photonics

Overview of the existing and emerging ZnO electronics/photonics applications (Varistors, Optical Filtering, Transparent Conductors, solar cell technologies, Transparent/Flexible Electronics, Light Emitters, Sensors).

Varistor Electrical Properties: Microstructural effects

Even though ZnO varistors have been extensively investigated the last four decades, the research on this topic is still noticeably dynamic and active. This work correlates some aspects of the varistor technology and their microstructural effects on the macroscopic electrical properties. Emphasis is given to academic and industrial research results.

Latest Trend of ZnO Multilayer Ceramic Varistors

Multilayer ceramic varistors (MLCVs) are usually employed as protection devices from overvoltages; new varistor material composition is introduced but also MLCVS with a discharge cavity between internal electrodes.

Nine Chapters are Focused on Dielectric/Ferroelectric/Piezoelectric/Electrostrictive Ceramic Materials

Dielectric, Ferroelectric, Antiferroelectric, Relaxor, Piezoelectric Ceramics

Definitions and Main Applications: the properties of dielectric crystalline media for different structures are defined and the main types of dielectric ceramics interesting for applications are presented. In the second section, basic concepts related to dielectrics, piezoelectric, ferroelectric, antiferroelectric, and relaxor ceramics are introduced.

Electroceramics

Modeling of Sintering, Microstructure Evolution and Functional Properties: a few examples of theoretical and modeling approaches regarding the description of ferroelectric polycrystalline ceramics, in particular ferroelectrics, are presented: models for describing the sintering process and microstructure evolution, including the description of the role of defects, interfaces, grain boundaries and size effects on the electrical properties.

BaTiO₃-Based Ceramics

Fundamentals, Properties and Applications: survey of 70 years of continuous investigation BaTiO₃, the first ferroelectric and piezoelectric ceramic developed for commercial applications. It is still widely used, especially as a high permittivity dielectric in multilayer ceramic capacitors (MLCCs) and as a semiconducting material in thermistors with positive temperature coefficient of

resistivity (PTCR). Barium titanate still attracts great attention as a model ferroelectric system and key component of materials for applications in capacitors, lead-free piezoelectric devices, ceramics and composites for energy storage.

The PZT System

lead zirconate titanate (PZT) constitute the best family of piezoelectric and ferroelectric materials suitable for integration into devices such as piezoelectric actuators, sensors and transducers. Crystal structure, synthesis route, piezoelectric properties and their modification by acceptor or donor doping or valence compensation and correlations between microstructure and performance relations are addressed.

Lead-Free Piezoelectric Ceramics: three main groups of lead-free perovskite piezoelectrics, KNN-, NBT-, and BT-based, their structure, phase relations, properties, synthesis and processing are focussed, linked to applications. Environmental and health concerns are discussed.

Electrostrictive Ceramics and Their Applications: in-depth analysis of the physics of electrostriction, types of electrostrictive materials, comparison with piezoelectrics and applications Survey of the behind the properties and applications (mainly micro-electromechanical systems).

Low-Loss Ceramics in Mobile Communications: the importance of low-loss ceramics in high-frequency applications is growing with their use for mobile communications, intelligent transportation systems (ITSs), wireless local area networks (LANs), bluetooth systems, etc. Their application in dielectric resonators, multilayer substrates, multichip modules (MCMs), and dielectric antennas and ceramic capacitors is surveyed.

Small-scale Energy Harvesting Devices for Smart Electronics: energy harvesting from ambient mechanical vibrations and stray magnetic fields is described with emphasis on fundamentals governing the material selection and implementation. Small-scale energy harvesting devices are explored with relevance towards wireless sensors and biomedical applications.

Multilayer Ceramic Actuators

Development history on the improvement of reliability and durability in multilayer actuators, and various applications, with a particular emphasis on recent three researchers: Pb-free piezoelectric materials, base metal (Cu) internal electrode, and diesel injection valve application.

Two Chapters are Focused on Technologies That are Relevant for Several Materials and Applications

Multilayer Glass–Ceramic/Ceramic Composite Substrates: Review of the processing of multilayer glass–ceramic/composite substrates prepared by HTCC, LTCC, ULTCC. Survey of UHTCs and cold sintering/room temperature fabrication/upside-down composite fabrication and of the production of substrates and packages by combining functional layers and passive electronic components in one multilayer co-sinterable module.

Functional Ceramics Through Novel Chemical Approaches

Chemical modification and processing of different thin films are presented. KTN thin films prepared by the chemical solution deposition method and UV-processing used for the patterning of the films are focused. The epitaxy and optical transmittance of KTN films from the EGME-modified precursor combined with UV treatment is discussed.

Photovoltaics: Advanced Inorganic Materials

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Photovoltaic Market

By 2050 world energy consumption is predicted to grow from the present 13–30 TW yr. To meet this huge demand, the global energy sector will be facing two main pressing issues, declining fossil reserves and climate change due to man-made greenhouse gas emissions. To reduce carbon emissions, nuclear power for electricity supply is a potentially important source. The fraction of world needs which can be supplied by nuclear will depend upon considerations such as the size of nuclear fuel reserves, the efficiency of old or even new generations of nuclear reactors when using lower grade uranium ores, and, more importantly, finding satisfactory solutions for nuclear waste disposal or storage. Fig. 1 plots the present world-wide energy consumption of oil, coal and natural gas and compared to nuclear, hydro and renewable energy technologies. The last convert the energy from different natural sources such as sun, tides, wind and others, into its usable forms such as electricity. Fig. 1 shows nuclear flattening out in and probably for the near future. On the other hand, the global renewable energy consumption increases significantly and its market is anticipated to grow rapidly during the forecast period owing to increased emissions of greenhouse gases (GHGs), particularly CO₂ due to utilization of fossil fuels for generation of energy. In addition, limited presence of fossil fuel on the earth as well its volatile prices fuels the renewable energy market. However, generation of energy from renewable sources requires huge investment. The global renewable energy market was valued at \$928.0 Billion in 2017, and is expected to reach \$1512.3 Billion by 2025, registering a growth rate of 6.1% from 2018 to 2025.

While all renewable energy sources need to be considered in meeting the energy challenge, solar energy, which includes biofuels, solar thermal energy, and photovoltaics (PVs), may arguably be the only renewable source capable of supplying a significant fraction of energy at predicted future levels. This is primarily because of the enormous energy resource represented by the sun which continuously floods the earth with 125,000 TW of power. This sector has only just begun to reveal its enormous potential for growth. Furthermore, the drop in solar photovoltaics (PVs) system prices allowed the investments to be used for installing 131 GW of PV panels in 2019, bringing the cumulative PV installation to 635 GW and thus capable of producing more than 585 TWh (terawatt hours). Yet, this represents only 2.2% of electricity share worldwide, but 3.9% in Europe.

Photovoltaics: Advanced Inorganic Materials

Based on IRENA report in June 2020, newly installed renewable power capacity increasingly costs less than the cheapest power generation options based on fossil fuels. Thus, more than half of the renewable capacity added in 2019 achieved lower electricity costs than new coal. New solar and wind projects are undercutting the cheapest of existing coal-fired plants. Indeed, solar and wind power costs have continued to fall, complementing the more mature bioenergy, geothermal and hydropower technologies. Fig. 2 shows that photovoltaic (PV) manufacturing was growing at approximately 30% per year since year 2000 and this rate is slightly decreasing due to economic crisis and industry consolidation (Fig. 2). It is worth reminding that the important growth has been the result of government policies (subsidies or feed-in tariff), mainly in Japan and in Germany. PV production was further stimulated by the goals for PVs set in, for instance, the EU White and Green Paper of 12% of the total energy and 22% of electricity generated by all renewable energies and 3 GWp in Europe for PVs in 2010. More recently, the EU seeks to have a 20% share of its gross final energy consumption from renewable sources by 2020. As a matter of fact, the growth in electricity from PV has been dramatic, rising from just 7.4 TWh in 2008 to 115.0 TWh in 2018. Similarly, the Solar America Initiative in the United States calls for investments to make PV power competitive with other forms of renewable energy and a growing number of states have mandated renewable energy standards. Overall, cumulative PV installation worldwide reached 635 GW in 2019 while it was 140 GW in 2013. The most rapid growth in annual production over the last 5 years has been observed in Asia, where China, Taiwan and Malaysia together now account for more than 80% of worldwide production (Fig. 2). The impressive progress is also due to the substantial technology improvements in materials quality, devices processing, fabrication and design, and also in characterizations. All these together led to better device performance and reliability, and lowered the systems costs. Electricity costs from utility-scale solar PV fell 13% year-on-year, reaching nearly seven cents (USD 0.068) per kilowatt-hour (kWh) in 2019.

Since 1980, most of the total PV modules shipments are based on single-crystal and multicrystalline silicon wafers (Fig. 3). This is typically referred to as the first generation of PVs. Fulfilling the projected demand for crystalline silicon based cells and modules will require innovative research and development to increase the efficiency and reduce the cost. Major activities directed toward such goals will be addressed below. Projections based on historical cost reduction trends has suggested that the price for conventional silicon solar cells will drop over years to a competitive level with fossil fuel. This is now the case in several parts of the world. The second PV generation based on inorganic semiconductor thin films has the potential for much lower costs and will also be addressed here. Finally, third generation PV concepts aimed at ultra-high efficiency and/or ultra-low cost regimes and involving nanotechnologies, multiple junctions, and bandgap engineering will be considered. These approaches are already on the laboratory research bench and in some instances (e.g., multijunction approaches) nearing market production. Prior to describing these materials and related technologies for PV conversion, a brief discussion of solar cell operation and key figures of merit will be presented.

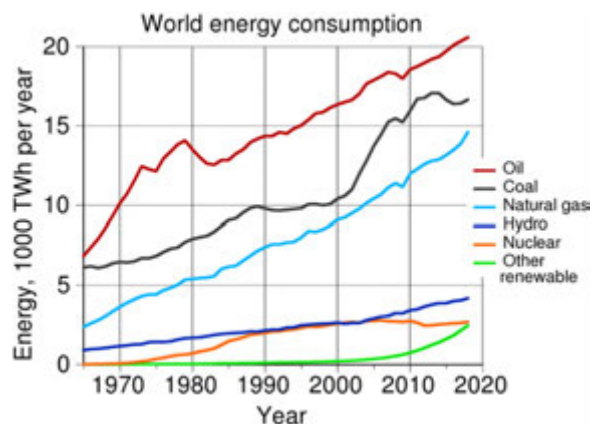


Fig. 1 World energy consumption; data source: IAE, EurObserv'ER, JRC, EWEA and GWA. Reference Module in Materials Science and Materials Engineering. doi:10.1016/B978-0-12-803581-8.02728-4.

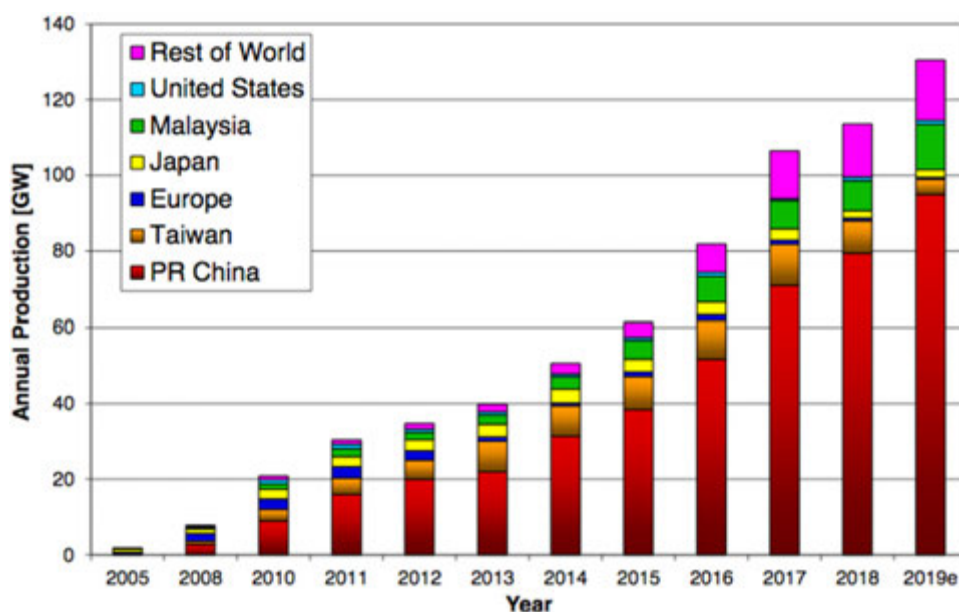


Fig. 2 World PV cell/module production from 2005 to 2019 (estimate). Data source: Photon International 2019, PV News- 2019 and JRC-PV-2019.

PV Devices

A solar cell is a semiconductor device that converts photons from the sun into electricity. Fig. 4 shows the generic structure and operation of a single junction inorganic solar cell. At the heart of the cell is the light absorbing semiconductor material which converts photons into carriers (electrons and holes) via the PV effect. The different PV materials discussed in this chapter are identified by the composition and properties of the absorbing material (Slaoui and Reuben, 2007). After carrier generation, the electrons and holes separate and are collected at the contacts. There are two main modes for charge carrier separation: drift of carriers, driven by the built-in electrostatic field of a p–n junction, and diffusion of carriers from zones of high to low carrier concentration following an electrochemical potential gradient. When drift is important, the structure of the cell can be used to compensate for poor diffusion. When diffusion is used, then improvement in material quality becomes more of the focus. Drift is typical of thin film inorganic cells which are normally p–n junction devices which relatively high defect densities, while diffusion is more important for high efficiency single-crystal cells and is the driving transport mechanism for dye or organic solar cells. These later approaches have significant potential for low cost energy production but will not be discussed here. An in-depth review of organic PV technologies was recently published by Cao and Xue (Cao and Xue, 2014).

The properties of the contacts and window layers are also critical to device performance. At least one contact needs to be both electrically conducting and transparent to photons in the spectral range where the absorber creates carriers. Transparent conductive oxides are the material of choice for this purpose. It is also important to point out that the simple structure and the division into

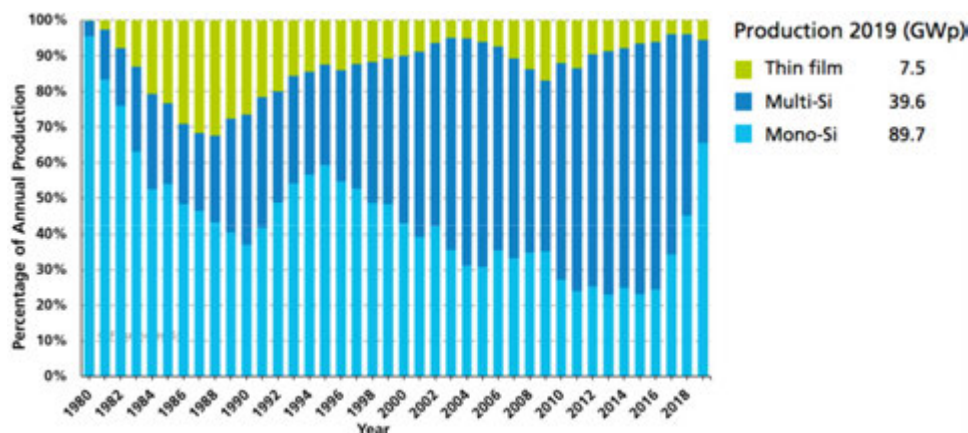


Fig. 3 Distribution of cell production by technology in 2019. Data source: From 2000 to 2009: Navigant; from 2010: IHS Markit. Graph: PSE Project GmbH 2020.

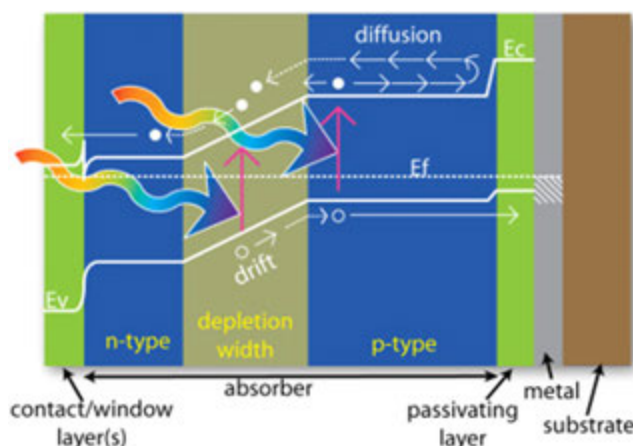


Fig. 4 Schematic of the structure and of carrier generation and separation in a p-n junction solar cell. E_v is the valence band energy, E_f is the Fermi level, and E_c is the conduction band energy (with courtesy of Sarah Kurtz).

well-defined layers with specific functions shown in [Fig. 4](#) is not adequate to describe many solar cells. In a number of designs light enters through the substrate, and contacts can be quite complicated, fabricated from several layers and with significant inter-diffusion at metallurgical junctions.

Figures of Merit

Here we discuss some of the basic metrics for characterizing PV devices which are typically quoted by the industry and appear in the rest of this chapter. [Fig. 5](#) shows a typical current voltage (J-V) characteristic for a solar cell in the dark and under illumination. Power is generated when the cell operates in the fourth quadrant of the graph where voltage is positive and current is negative. The fill factor is the power produced at the maximum power point on the illuminated J-V curve divided by the product of the open circuit voltage (V_{oc}) and short circuit current (J_{sc}). We can think of it as a measure of how rectangular the JV characteristic is in the fourth quadrant. Another useful measure, quantum efficiency (QE), is the ratio of the number of charge carriers collected by the solar cell to the number of photons at a given illuminating energy. Ideally it is a step function at the bandgap of the absorber. In real devices, however, this is never the case and there is also a roll off at higher energies.

The most fundamental measure of performance is, of course, the energy conversion efficiency – the portion of energy in the form of sunlight that can be converted via photovoltaics into electricity by the solar cell to electrical energy. Two decades ago, Shockley and Queisser (S-Q) ([Shockley and Queisser, 1961](#)) used a detailed balance approach to estimate the thermodynamic efficiency limit for solar cells with a single absorbing material (a single junction design as shown in [Fig. 4](#)). Their approach balanced the radiative transfer between the sun, modeled as a black body at 6000K, and the solar cell assumed to be a 300K black body which absorbs photons with energy above an energy threshold (the band gap). They varied the band gap of the absorber and

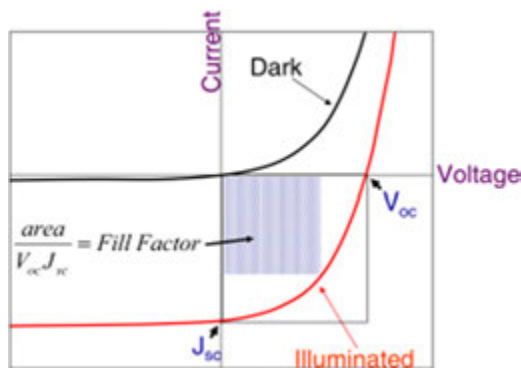


Fig. 5 Current voltage (J–V) characteristics of a solar cell with and without illumination. The open circuit voltage (V_{oc}), short circuit current (J_{sc}), and fill factor are identified on the figure. Reproduced by permission of the MRS Bulletin.

the solid angle from which the solar cell can collect the sun radiation (concentration). As the band gap of the absorber increases, the open circuit voltage increases, but, because only photons with energy above the bandgap are converted into carriers, short circuit current decreases. This leads to a maximum in efficiency as a function of band gap. For unconcentrated solar irradiance, a maximum efficiency limit of $\sim 31\%$ at a gap near 1.3 eV was found. For full solar concentration (46,300 suns) maximum efficiency was $\sim 41\%$ for a 1.1 eV material. One limiting factor for higher efficiencies is that the excess kinetic energy of hot photogenerated carriers created by the absorption of supra-bandgap photons is lost as heat through phonon emission, and the other limiting factor is that photons less than the bandgap are not absorbed. Designs which attempt to increase cell efficiencies above the S–Q single junction limit by addressing one or both of these loss mechanisms are often termed third generation approaches in literature. Several are discussed below.

PV Materials

Crystalline Silicon

As stated above, most of the nowadays shipped PV modules are single-crystal, or multicrystalline based cells. Thus most efforts at the laboratory and industry scales went to the improvement of silicon based solar cells efficiency implementing innovative and low cost processes. Research and development in this area learned from silicon integrated circuits technologies and developed structures that maximizes the electron-hole generation and reduces surface and bulk recombinations. Thus, cells have reached laboratory performances converting nearly one-fourth of the incident photons into electrical power – reaching about 92% of its reported “theoretical limit”. To go further, more complicated designs and structures are sought. Among the advanced structures that allow cells reaching efficiencies over 22% on multicrystalline silicon and 24% on monocrystalline silicon (**Fig. 6**), there are single-sided and doubled-sided buried contacts (SSBC and DSBC), the metal/insulator/n-type/p-type (MINP), bifacial cells (BFC), the rear contact solar cells (RCC) and the heterojunction structure (HIT). The highest efficiency cells combine advanced structures such as RCC at the back and HIT at the front which allows to reach 26.7%. Detailed routes can be found in the recent proceedings of PV conferences.

Another important research activity dealing with silicon based cells is how to close the differences between the less perfect materials, namely multicrystalline silicon, and the single-crystal cell. The roles of defects and impurities – and their interactions and impacts on solar cell performance – remain important. Thus R&D still concerns understanding the nature of the defects resulting from the growth and processing and materials treatments to minimize the carrier losses at unwanted active sites ([Beaucarne and Slaoui, 2006](#)). These have included processes involving hydrogen, lithium, aluminum, arsenic, and phosphorus for front and back surfaces. The development of plasma and other nitriding processes by the semiconductor electronics industry has led to improvements in single and multicrystalline. Additionally, the economics of using less material has led the industry to investigate the production and use of thinner wafers, going from standard 300 μm thick wafers down to 100 μm . This however presents considerable difficulties in handling and processing because of mechanical fragility for these very thin wafers thickness and extremes in temperature cycling and thermal stresses they must endure during processing.

Among original thinned “wafer” technologies that have been investigated, there are Sliver® cells. The former one is composed of silicon strips that are produced by micro-machining narrow 100 μm deep grooves into a-Si wafer. These bifacial cells have had efficiencies up to about 18%, with prototype minimodules (560 cm^2 area) above 12% efficiency. The cells are being considered for transparent and concentrating modules, in addition conventional module use, but the reproducibility is a critical issue. A great effort was also deployed these last years to explore new technology without wire-sawing ([Slaoui et al., 2002](#)). Thus, several kerfless wafering techniques have been proposed: epitaxial Si lift-off, stress-induced spalling, and smart-cut. Using an epitaxial Si lift-off technique, a thin wafer is epitaxially grown on a porous seed Si wafer by atmospheric chemical deposition (APCVD) and exfoliated from the parent seed wafer. Epitaxial growth of high quality Si wafers, comparable to high performance CZ wafers, was

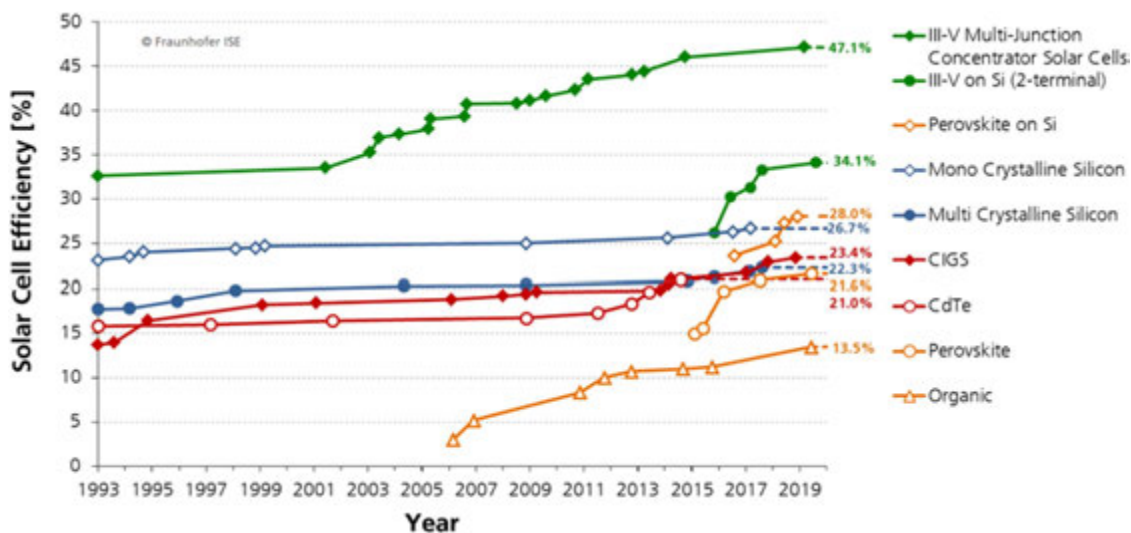


Fig. 6 Evolution of Solar Cell Efficiency since 1993 for different photovoltaic materials. Data: Green, M.A., Dunlop, E.D., Hohl-Ebinger, J., *et al.*, 2019. Solar cell efficiency tables (version 55). Progress in PV: Research and Applications. Graph: PSE Projects GmbH 2020.

demonstrated, and high efficiency above 21% based on a 35 μm thickness Si wafer was achieved. The stress-induced technique or SLIM-cut employs a stress induced layer on the Si wafer, and the stress is activated by thermal expansion mismatch between the stress layer and the Si wafer for spalling of thin wafers. Recently, a novel method of electrodeposit-assisted stripping (EAS) has been developed where a thin stress layer is electro-deposited at room temperature, and the lattice mismatch between the stress layer and the wafer induces a large stress field, which causes the lift-off of a thin Si wafer without high temperature annealing. Another kerfless wafering technique based on a smart cut technique invented in 1990s was attempted to fabricate thin wafers of tens of micrometer thickness for Si solar cells using a MeV proton implanter. The implanted protons are penetrated into a certain depth of the donor wafers depending on the proton acceleration energy. The implanted wafers are subsequently annealed to be exfoliated by hydrogen micro-bubble formation and crack propagation. The proton induced exfoliation technique is a relatively simple and clean vacuum process compared with the epitaxial Si lift-off method.

Thin Films

Thin-film PVs are attempting since several years to enter the world commercial markets (Fig. 3). Although their market share is still very small, the interest is driven in part by capacity problems with crystalline Si. The arguments favoring thin-film PV are based on low materials utilization, large-scale manufacturing advantages, and better energy economy for production and product recovery. Thin film technologies also enable other new and desirable properties for specialized applications (flexible modules, semi-transparent modules, etc.). In addition, research results with these systems have been very impressive with laboratory device efficiencies for some systems over 20%. Despite the very positive potential of these technologies, there is a strong need for intensive basic research to better understand fundamental properties of these materials and devices, especially of interfaces, low cost, high performance transparent conducting oxide (TCO) materials, new multijunction designs, alternative module concepts, and of methods for increasing device and module efficiencies. This section begins with a discussion of polycrystalline and amorphous silicon as well as the chalcogenide thin film cell technologies followed by TCO materials.

From amorphous to polycrystalline silicon films

Amorphous silicon (a-Si:H) is a very attractive material for large area thin film electronics, namely as thin film transistor for flat panel displays, as color sensors, or as absorbing layer for solar cells. The main advantages of this material is the low deposition temperature that offers the use of glass and flexible substrates, the potential of tuning the energy bandgap (1.7–1.9 eV), the facility of doping by adding dopant gases during film growth, and finally the possibility of stacking layers without severe constraints. Several physical or chemical deposition techniques are used to produce hydrogenated amorphous silicon such as magnetron evaporation, plasma enhanced CVD, and more recently very high frequency CVD. The main drawbacks when using such disordered material for solar cells are its low charge carrier mobility and diffusion length due to bond angle and bond length distortion, in addition to the strong sensitivity of the silicon-hydrogen bonds to the solar radiation. Consequently while higher open circuit voltages can be achieved on a-Si:H based solar cells, the photocurrent is limited by insufficient absorption of the solar spectrum and by high carriers recombination. Despite these limitations, single- and multijunction solar cells and large area modules based on a-Si:H and related alloys, e.g., a-Si_{1-x}Gex:H are now established on the market. The use of stacked multijunction cells (a-Si:H/a-Si:H/a-SiGe:H) led to high QE records. The a-SiGe:H layer is employed as a bottom cell because alloying the silicon with germanium conducts to narrower optical gap and therefore to broader optical absorption. To increase the

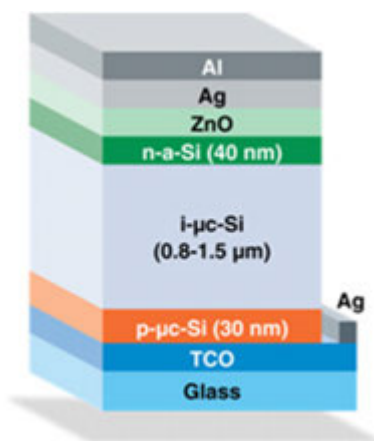


Fig. 7 A schematic structure of an amorphous (a-Si)/microcrystalline silicon ($\mu\text{c-Si:H}$) hybrid solar cell structure (with courtesy of E. Fortunato *et al.*).

efficiency further and reduce light-induced degradation of the cells, a combination of amorphous and microcrystalline silicon ($\mu\text{c-Si:H}$) is used nowadays (Fig. 7). The $\mu\text{c-Si:H}$ layer consists of an amorphous tissue with coherent regions of crystalline grains having sizes from nanometer scale to micrometer scale. The $\mu\text{c-Si:H}$ can be prepared at low temperatures by the same techniques as amorphous silicon and has absorption spectra similar to crystalline silicon. Furthermore, these materials contain several percent of hydrogen, thus remaining grain boundaries activity is neutralized.

As for the solar cells, by using a single junction cell with a homogenous microstructure, a stabilized efficiency of $\eta = 10\%$ on texture-etched ZnO:Al has been obtained. Reported stabilized efficiencies for a-Si/ $\mu\text{c-Si}$ tandem cells are approaching 12.5%. The highest confirmed efficiency for tandem submodules (Kaneka Co.) based on a-Si/ $\mu\text{c-Si}$ is 11.4%. For triple-bandgap a-Si/a-SiGe/ $\mu\text{c-Si:H}$ cells, a world record initial efficiency of 15% for thin film silicon PV technology has been obtained, using optical enhancement techniques, such as textured back reflectors and in some cases also intermediate selectively reflecting layers. Apart from the triple-bandgap a-Si/a-SiGe/ $\mu\text{c-Si:H}$ approach, the a-Si/ $\mu\text{c-Si}/\mu\text{c-Si}$ is also under investigation. United Solar Ovonic reported a stabilized efficiency of 13.3% for a-Si/ $\mu\text{c-Si}/\mu\text{c-Si}$ triple junction structures. There are still windows for further improvements by better controlling the interfaces and reducing defects in the layers.

As a natural extension of the trend toward higher crystallinity of the active layer, there is some effort in developing thin-film polycrystalline silicon. Such thin crystalline silicon films grown on various foreign substrates is formed by a variety of different methods that can be distinguished by the principle of the deposition process: chemical vapor deposition including the conventional high temperature CVD (APCVD, LPCVD), CVD on liquid layers (CVDOLL), plasma enhanced CVD (PECVD), the ion assisted deposition (IAD), the liquid phase epitaxy (LPE), and the solid phase crystallization of amorphous silicon (SPC), the aluminum induced crystallization (AIC), the laser induced crystallization (LIC). Except the LIC process, most of these methods result on polycrystalline silicon materials with fine grains ($< 10 \mu\text{m}$) and show relatively short minority carrier lifetimes compared to multi- or monocrystalline silicon material. Minority carrier diffusion lengths are usually in the range of only a few μm , smaller or comparable to the film thicknesses. The analysis of minority carrier properties of poly-Si films is intrinsically complicated by its inhomogeneous nature that results from the broad grain size distribution and potential fluctuations within individual grain boundaries. As a consequence, the open circuit voltage of such poly-Si thin film cell is quite small ($< 570 \text{ mV}$). The efforts toward reducing the barrier height and thus charge carrier recombination include the doping of the absorber layer, lowering the trap density at the grain boundary by strong hydrogenation and increasing the grain size.

An interesting approach towards a higher conversion efficiency is the HTJ that combines an absorbing large grains polysilicon layer formed by the AIC process, thickened by an absorbing Si film grown by CVD, and adding on top an emitter made of doped a-Si:H thin film. Such combination resulted so far in an efficiency approaching 10%. In order to be successful, thin-film polysilicon devices need to improve further and reach more than 16% module efficiency on superstrate configuration, with a process that is industrially applicable.

Thin-film CdTe, copper indium selenide, its alloys and related chalcopyrites

Polycrystalline thin film solar cells utilizing the II–VI semiconductor cadmium telluride and alloys of the I–III–VI materials, copper indium diselenide (CuInSe_2) and copper gallium diselenide (CuGaSe_2), are rapidly entering the marketplace. These materials have a number of interesting properties which make them attractive candidates for thin film PV technologies. Both CdTe and the Cu(InGa)Se_2 (CIGS) alloys are direct band gap compound semiconductors with energy gaps in the 1.1–1.6 eV range which are nearly ideal for single junction solar cell efficiency (Fig. 8). They have high optical absorption coefficients ($> 10^5 \text{ cm}^{-1}$) allowing for thin absorber layers. They are also more tolerant of defects than, for example, silicon and III–V compound semiconductors like GaAs. In spite of the high density of grain boundaries in the films, laboratory solar cells with record efficiencies of 21% (CdTe) and 23.4% (CIGS) have been reached (Fig. 6). There is even evidence that grain boundaries are beneficial, assisting carrier collection.

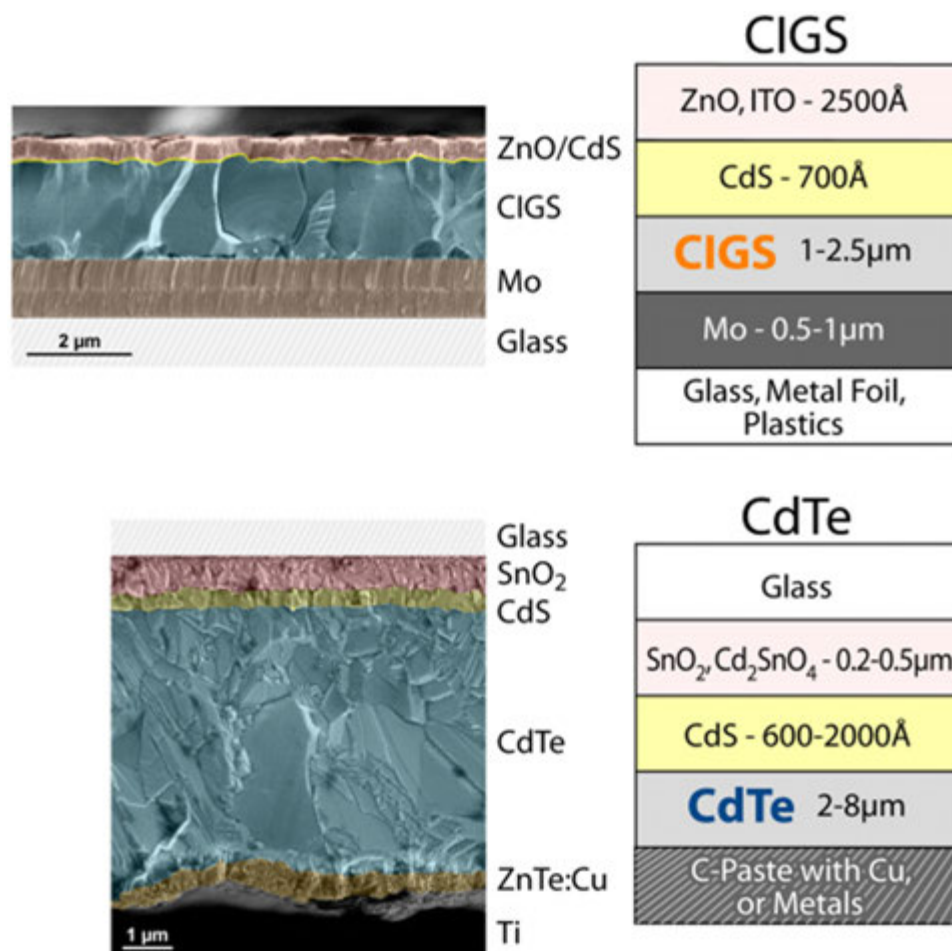


Fig. 8 CIGS (top) and CdTe (bottom) PV structures seen in cross-section using SEM (left side of panel) and viewed schematically (right side of panel) (with courtesy of E. Fortunato *et al.*).

Doping in these materials arises, in fact, from native defect formation during deposition and processing rather than introduction of substitutional impurities. This also means controlled doping and conductivity is one of the challenges in optimizing cells.

They also have similar cell structures. The junction itself is typically a heterointerface between n-type CdS and the p-type CIGS or CdTe absorber layer. Light enters through the CdS side of the device and current is carried away by a TCO film which is in contact with the CdS. Since CdS has a bandgap of 2.4 eV, it absorbs in the blue, however, photons absorbed in it produce little to no photocurrent. For this reason, both CdTe and CIGS cell processing seek to make the CdS layer as thin as possible while still remaining free of pinholes which create shorts between the TCO and absorber layers lowering V_{oc} and cell performance. This is especially problematic for CdTe cells where S diffusion into the CdTe during post growth anneals further decreases the CdS layer thickness. The inclusion of thin buffer layers between the TCO and CdS, such as a highly resistive transparent oxide, is found to improve efficiency. The exact role of the buffer layer, whether it simply introduces resistance into shorts or changes the interfacial energetics, is not well understood and optimizing this interface is an important area for materials innovation.

There are also some significant differences in the physical properties and processing of cells from CdTe and CIGS. The highest efficiency CdTe cells operate in a superstrate configuration with light entering through the glass on which the cell is grown. The record efficiency laboratory devices are prepared by high temperature absorber growth (near 600°C). Nearly all preparation schemes follow the CdTe growth with an anneal near 400°C in an atmosphere of CdCl₂ and oxygen that promotes grain regrowth, improves the CdTe carrier lifetime, diffuses the junction region, increases p-type conductivity in CdTe, and forms oxides. Back contacts to CdTe often involve Cu incorporation (e.g., Cu doped graphite paste or Cu doped ZnTe). The Cu diffuses rapidly through the device and may be a stability issue. An optimized back contact for CdTe devices, and better understanding of back contact/CdTe interfacial energetics, is a critical need.

In contrast, CIGS thin film cells are grown in a substrate configuration with the TCO contact as the last, rather than first, layer deposited. The highest efficiency CIGS cells are grown by physical vapor deposition and the grain microstructure is defined by a complex evolution from Cu rich to In and Ga rich phases during growth. Reproducing this growth path with other more manufacturable deposition options is a major challenge. In optimized devices, the Ga alloy composition is graded by 5% across

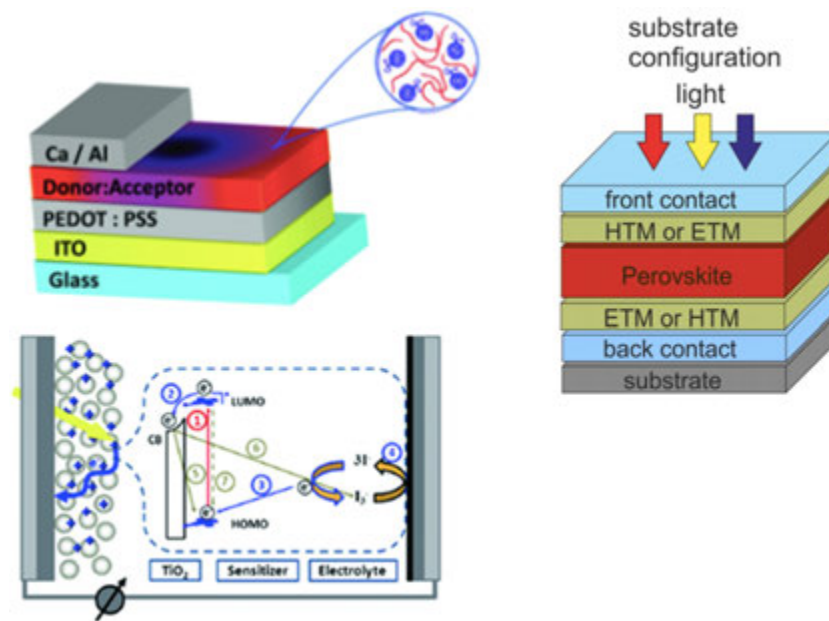


Fig. 9 An Organic solar cell structure (left); a Dye Sensitized Solar Cell structure (Middle); a Perovskite Solar Cell (right).

the absorber layer. Incorporation of Na ions, which occurs naturally as an aspect of growth on soda lime glass substrates, is also important to optimize the CIGS device efficiency. Although there is not a definitive explanation for the beneficial effects of Na, Na is believed to reduce the resistivity of the film. Typical absorber deposition temperatures are over 500°C for CIGS and a post-deposition anneal in a Se atmosphere is recommended. Decreasing deposition and post growth anneal thermal budgets for both CdTe and Cu(InGa)Se₂ are important cost reduction goals. The typical CIGS back contact is a molybdenum film. Device film adhesion issues are often traceable to issues with the molybdenum film. Cu(InGa)Se₂ devices where S is substituted for Se are also being explored allowing broader tunability of electronic properties and structural properties.

While reasonable stability under operation has been demonstrated for CdTe and CIGS solar cells, the performance of both can degrade in the presence of moisture. For this reason, they are encapsulated between glass sheets to seal the front and back surfaces of the modules, with polymer compounds sealing the edges and bonding the laminate together. Alternative polymer encapsulation schemes are also explored for CIGS devices. Finally, we note that issues of scarce elements (e.g., In) and toxicity (e.g., Cd) are frequently discussed in the context of both technologies. Whether or not either a truly significant issue depends at least in part upon feasibility, cost, and implementation of recycling and element recovery at end of product life. For example, First Solar, Inc., one of the rapidly growing CdTe panel manufacturers, includes panel recycling as part of product lifecycle management.

From organic to hybrid structures

In addition to crystalline-Si (c-Si) solar and inorganic thin film cells and modules, other thin film photovoltaic technologies – including organic solar cells (OSCs), dye-sensitized solar cells (DSSCs), and perovskite solar cells (PeSCs) – have gained attention for their many attractive properties, including low-cost, light weight, low fabrication temperatures, mechanical flexibility, and short energy payback times. In terms of their power conversion efficiencies (PCEs), they also exhibit respectable performance; the certificated PCEs of OSCs, DSSCs, and PeSCs have reached 13.5%, 14.3%, and 21.6%, respectively (Fig. 6).

Fig. 9(a) displays a typical device structure of an organic photovoltaic device (Chen *et al.*, 2014). The organic blend layer is sandwiched between two electrodes. The photoactive layer of the most common model device consists of poly(3-hexylthiophene) (P3HT) as the electron donor and phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) as the electron acceptor. Such materials are used because they possess different electron affinities and offset energy structures. The donors and acceptors are intermixed directly to maximize the interfacial area and this arrangement is often referred to as a “bulk heterojunction” (BHJ). After the absorption of photons by the organic semiconductors, excitons are generated. Because the binding energy of the excitons in organic semiconductors is usually high, they can be separated and turned into free charge carriers effectively after they have diffused to the donor-acceptor junctions. In such BHJ device, the high interfacial area leads to a high density of free charge carriers, due to efficient exciton dissociation at the donor-acceptor junctions. Finally, the photon generated holes and electrons are transported through the organic donor and acceptor semiconductors, respectively, to the corresponding electrodes, eventually resulting in a photocurrent. Present investigations concern the control of the morphology through various methods, such as thermal annealing, solvent annealing, and the use of processing cosolvents has been proposed for improving the device performances. Further, the development of low-bandgap (LBG) conjugated polymer donors, which allow them harvest photons with long wavelength from solar irradiations, also significantly improves the efficiency of OPVs. More recently, the efficiency of the OPVs prepared with

nonfullerene electron acceptors have reached a value of over 13%, thereby opening up new opportunities for even higher efficiencies approaching 18%.

As for the Dye Sensitized Solar Cell (DSSC) devices, Fig. 9(b) illustrates its working principle. This hybrid structure consists of a mesoporous TiO_2 working electrode (anode), a Pt counterelectrode (CE; cathode), and an electrolyte (e.g., an iodine-based redox mediator). When the device is illuminated, the sensitizer (dye) is photoexcited. The excited electrons in the LUMO are injected into the conduction band (CB) of TiO_2 , generating the oxidation state of the sensitizer (S^+). Meanwhile, the injected electrons on the CB of TiO_2 are transported to the transparent conducting substrate and then to the counter-electrode through the external electric circuit. The oxidized sensitizers are reduced by the redox couple I^-/I_3^- , thereby regenerating the ground state of the sensitizer (S). Simultaneously, the I^- ions are oxidized to I_3^- complexes and diffuse to the CE. Subsequently, the complexes are reduced to I^- ions at the CE, thereby completing the current circuit. There are also several competitive phenomena, which result in current loss, including recombination of the injected electrons with the HOMO of the dyes and/or with the I^-/I_3^- couple. Relaxation of the sensitizers to the ground states through a nonradiative decay process is another common loss path. Recent improvements in efficiencies of DSSC have been achieved by designing new dyes, such as zinc porphyrin dyes (YD2-o-C8). A recorded efficiency value of 14.30% was reported for a device prepared with metal-free organic co-sensitizers and with Co(II/III) -based redox electrolyte.

A strong alternative to the DSSC is the organic/inorganic hybrid perovskite structure. Fig. 9(c) displays a schematic of a typical perovskite solar cell. The perovskite absorbing material has the formula ABX_3 , where A, B, and X are ionic units. For organic/inorganic hybrid perovskites, A, B, and X are a large organic cation, a smaller metal cation (e.g., Pb^{2+} , Sn^{2+} , or Ge^{2+}), and a halide anion (I, Cl, or Br), respectively. Meanwhile, A and B are usually monovalent and divalent cations to fulfill charge neutrality. For instance, in the representative perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$, the A- and B-site cations are CH_3NH_3^+ and Pb^{2+} , respectively. At present, most high-performance perovskite solar cells (PeSCs) adopt an all-solid-state device configuration; For instance, the perovskite material is embedded between a mesoporous TiO_2 layer, which is permeated by the perovskite, and a high-work-function hole-transporting layer (HTL) – for example the spiro-MeOTAD. The TiO_2 layer is usually first deposited on a glass substrate precoated with a transparent conducting oxide (TCO). A high-work-function metal (e.g., gold) is deposited on the HTM. The working principle involves the perovskite layer absorbing the incident light, thereby exciting electrons and holes. These charges are extracted and transported by the TiO_2 layer and HTM, respectively, leading to a photocurrent. The continuous improvements in efficiencies of PeSCs involve many key factors, including the optimization of device structures, deposition conditions, composite manipulation and stability aspects. At the date of writing this document, a certified PCE of 25.2% has been reported, very close to that of the single crystalline solar cell record of 26.7%.

Transparent contact oxides based contacts chalcopyrites

TCOs become essential for many important components of PV devices ranging from crystalline Si heterojunction cells (HIT) to organic PV polymer solar cells (Figs. 6 and 9). They are used as electrode elements, structural templates, or diffusion barriers. They are essential to tune the open circuit device voltage by choosing the right work function. The suitable characteristics of the TCO materials include high optical transmissivity across a wide spectrum and low resistivity. Additionally, TCOs for terrestrial PV applications must use low cost materials and some may require device-technology specific properties.

The first TCO, namely CdO , was reported already in early 1990s and was both optically transparent and electrically conducting. Since then, three oxides have emerged as commercially important transparent conductors: (1) indium oxide, (2) tin oxide, and (3) zinc oxide. The properties and crystal chemistry of the transparent conducting indium oxide family of materials are very well documented nowadays since it is the highest performance, best understood material in the TCO class. By volume, however, the most deposited TCO today is SnO_2 which is used in IR-efficient architectural window applications. ZnO is also primarily currently used in window coatings but recent processing-related performance improvements and low cost makes it an attractive replacement for high-cost in-based TCOs.

Another possible choice of replacement of ITO electrode especially for large area high-efficiency cells is the use of optically transparent nanopatterned metal films. Indeed, it was recently discovered that metal films patterned with arrays of nanoscale holes transmit light with efficiencies much higher than expected from purely geometric considerations. The benefits are low sheet-resistance, withstanding larger deformations associated with substrate bending and substantial cost savings.

Multijunction Tandem Cells

The multijunction cell approach is most mature and most successful third generation technique for improving performance over a single junction cell. Here solar cells are stacked in order of their bandgap, with solar radiation entering the largest band gap cell first. Light is automatically filtered as it passes through the stack, with each cell absorbing a narrow energy range of above band gap photons thereby minimizing hot carrier losses. Below band gap photons are transmitted. Those with energies above the smallest band gap in the stack have a high probability of being absorbed minimizing below band gap losses. The result is a multi-junction solar cell with an ideal efficiency determined by the number of cells in series. The theoretical efficiency limit is 86.8% for an infinite number of band gap energies at very high concentration levels. If bandgaps are appropriately selected so that each cell in the stack generates nearly the same current, the cells can be interconnected in series making monolithic integration possible.

The most simple and common multijunction structure is the two junction thin film that utilizes a hydrogenated amorphous silicon (a-Si:H) upper junction (see discussion above) with a bandgap near 1.7 eV and second lower junction of microcrystalline silicon (μ c-Si:H) with a bandgap near 1.1 eV. This combination is almost ideal for a two-cell stack and boosts amorphous silicon stabilized cell efficiency from 9.5% for a single junction to better than 11% for the stack, under the one-sun air mass 1.5 (AM1.5G) spectrum condition. Triple junction designs which incorporate an additional amorphous layer, such as a: SiGe alloy, are beginning to enter manufacturing with stabilized efficiencies in excess of 13%. While this design represents a materials science tour de force, it is difficult to realize the full benefit of multiple junctions when the solar cells are made from polycrystalline or amorphous materials with lower crystal perfection.

Maximizing device efficiency requires long minority carrier lifetimes and, hence, high materials quality. Crystalline group IV (Si and Ge) and III–V compound semiconductors (GaAs, InP, and the numerous III–V alloys) are the best candidates for multi-junction cells. The III–V materials, in particular, are ideal for fabricating such MTJ solar cells for two reasons: they can be grown with excellent material quality using techniques such as molecular beam epitaxy and organometallic chemical vapor deposition and their band gaps span a wide spectral range (typically between 0.4 and 2.4 eV), mostly with direct bandgaps, implying high absorption coefficients. When fabricating these alloys, there are a number of possible ways to mix the endpoint compounds, even within a single-crystal layer, to tailor the optical or electrical properties. In general, lattice-matched materials are the easiest to manufacture with high quality. The lattice-matched nature of the $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}/\text{Ga}_{0.99}\text{In}_{0.01}\text{As}/\text{Ge}$ cell is one of the reasons for its strong success. There has been success, however, with lattice mismatched structures, which increases the range of materials/band gap combinations which can be considered in optimizing a cell design. Perhaps the most exciting aspect of III–V multi-junction cell development is the broad range of phase space yet to explore in optimizing cell designs. It is known, for example, that the currents in the triple junction $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}/\text{Ga}_{0.99}\text{In}_{0.01}\text{As}/\text{Ge}$ device are not optimally matched, and insertion of an additional junction with a 1.0 eV band gap directly above the Ge junction would improve efficiency. A GaInAsN alloy which has the desired band gap and is lattice matched has been studied extensively for this application but, so far, cannot be integrated with the required materials quality.

Modern preparation techniques such as wafer bonding to mitigate the effects of lattice mismatch has been also explored. World record for a monolithic triple-junction solar cell manufactured by wafer bonding has been increased to 34.1% and an efficiency record of 24.3% achieved for a solar cell with the III-V semiconductor layers deposited directly on the silicon. In this structure, the different layers absorb light from different spectral ranges: gallium indium phosphide (GaInP) in the 300–660 nm range (visible light), aluminum gallium arsenide (AlGaAs) in the 600–840 nm range (near infrared light) and silicon in the 800–1200 nm range (long-wavelength light). Recent research utilized GaInP/GaAs//GaInAsP/GaInAs as four junction solar cell (4JSC) and demonstrated a very high efficiency of 46% thanks also to the wafer bonding. The development of solar cells with more than four junctions is still in its very beginning. Nevertheless, the highest efficiency ever achieved up to end of 2019 has been obtained with a AlGaInP/AlGaAs/GaAs/GaInAs/GaInAs/GaInAs six junction solar cell.

The efficiencies already achieved with crystalline multijunction cells are truly astounding, and it seems likely that values near 50% are not that far off. These cells, however, were originally developed for space applications where power to weight ratio is the key figure of merit and they are too costly for flat plate terrestrial power production. Integration of the cells with lower cost solar concentrator designs, however, has the potential for enabling cost competitive systems. While concentrator designs are not being covered here, their development and improvement is equally (or perhaps more) important than improvements in cell efficiency to continuous cost reductions in PV systems based on high efficiency multijunction cells.

Emerging Materials and Cells Concepts

To overcome the S–Q efficiency limit mentioned above, there are preliminary reports and experiments on advanced exciting cell concepts which include several nanotechnology and hot-electron approaches such as the quantum dot (QD) cell and relatives using quantum rods and quantum pods. There are several approaches based on semiconductor QDs that could lead to ultra-high efficiencies through enhanced photocurrent. Among them:

Multiple exciton generation (MEG)

The formation of multiple excitons from a single absorbed photon occurs when the energy of the photon absorbed is greater than the semiconductor bandgap (Klimov *et al.*, 2007). Such process is well known in bulk semiconductors and is termed impact ionization (I.I.); it is the inverse of the Auger process whereby two electron-hole pairs recombine to produce a single highly energetic electron-hole pair. However, the probability that such phenomenon happens in bulk semiconductor is very low because the excess energy simply dissipates away as heat before it can cause other electron-hole pairs to form. But in semiconductor QDs, the rate of energy dissipation is significantly reduced, and the charge carriers are confined within a small volume, thereby increasing their interactions enhancing the probability for multiple excitons (MEG) to form (see Fig. 10). Theoretical considerations have reported a thermodynamic limit of about 45%. Quite recently very efficient MEG has been reported for PbSe, PbS, and PbTe QDs. Up to three excitons/photon have been measured in 2.9 nm diameter PbSe QDs when the energy of the photon absorbed is four times that of the bandgap, and up to seven excitons/photon have been reported for excitation at eight times the bandgap. More importantly, MEG has been reported for silicon QDs that might open larger opportunities for applications of such phenomenon in solar cells. These observations of MEG have effectively occurred in isolated QDs. The enhanced photocurrent

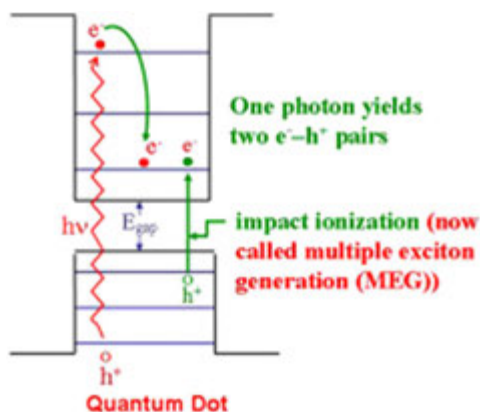


Fig. 10 Enhanced electron-hole pair (exciton) multiplication in QDs that could lead to enhanced solar photon conversion efficiency in QD solar cells. Reproduced by permission of the MRS Bulletin.

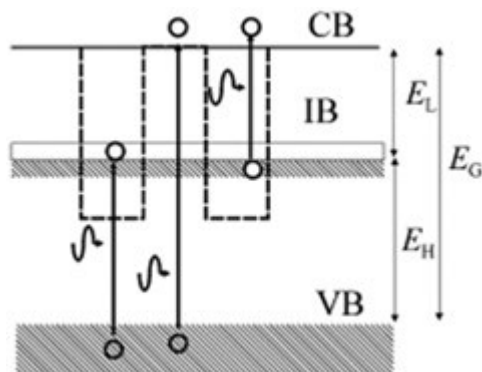


Fig. 11 Structure of an intermediate band material also showing the possible optical transitions (with courtesy of A. Marti).

possible with MEG has not been observed, to date, in a solar cell structure. The issue is one of finding a device design which incorporates QDs or wires and can directly collect the carriers generated within the nanostructure. Several configurations have been proposed including imbedding the QDs in polymers, imbedding them in other semiconductors, applying dots in place of the dye in a dye-sensitized solar cell design, and formation of QD solids from an assembled array of dots. Developing device designs that exhibit and ultimately take advantage of MEG to increase cell efficiency is presently an extremely active area of research.

Intermediate band approach

In this approach, QDs of binary or ternary semiconductors are used to create an intermediate band (IB) that allows the harvesting of a much larger portion of the available solar spectrum. Because of the IB, below bandgap energy photons can contribute to the cell photocurrent by pumping electrons from the valence band (VB) to the IB and from the IB to the CB (Fig. 11). But most importantly, since the IB is isolated from the CB and the VB by a zero density of states, "carrier relaxation" between bands becomes difficult and the carrier statistics in each band is described by its own quasi-Fermi level. The energy states of the QDs forming the intermediate bandgap can be controlled by the size of the dot. It can be shown that, under this assumption, the voltage supplied by the cell, given by the electron and hole quasi-Fermi level split, is still limited by the high bandgap E_G and not by any of the lower bandgaps (E_L or E_H). The study of the limiting PV conversion efficiency of the IB approach reveals a limiting efficiency of 47% at one sun (63% at full solar concentration) for this concept as compared to 43% for a two-gap tandem solar cell at one sun (55% for full solar concentration).

Several groups have been investigating QD-IB structures, but no devices using this approach have yet been validated. Among them prototype cells consists of 10 layers of InAs/GaAs QDs sandwiched by p and n GaAs emitters and grown by molecular beam epitaxy MBE in the Stranski-Krastanov growth mode. Such structures still suffer from poor absorption in the QDs and low open circuit voltage due to structural defects induced during the growth.

Another approach considers the use of Nitrogen in III-V or Oxygen in ZnMnTe to form an IB. For the latest, it is reported that the location and the width of the IB is determined by the O content. Calculations based on the detailed model predict maximum

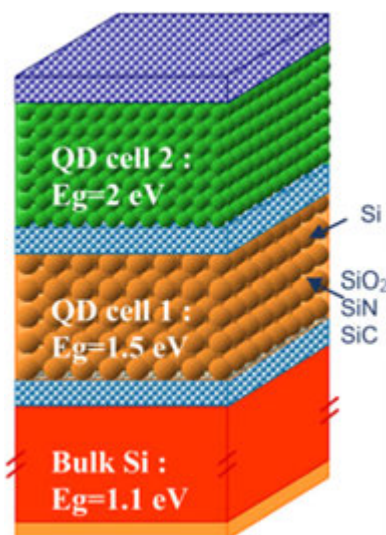


Fig. 12 Schematic view of a two-cell “all silicon” tandem cell using silicon quantum dots embedded in SiO_2 , or SiN or SiC matrix (with the courtesy of G. Conibeer, UNSW).

efficiency of more than 55% in alloys with 2% of O. Additional investigations look to epitaxial techniques to grow ZnOxSe_{1-x} materials.

All-silicon tandem cells approach

As mentioned above the tandem cell concept is well established as a way of improving solar cell performance. Obviously there is a strong interest in implementing tandem cells based entirely on silicon thanks to the advantages of the QDs. Indeed, the first advantage of the QDs is their tunable bandgap. It means that the wavelength at which they will absorb or emit radiation can be adjusted: the larger the size, the longer the wavelength of light absorbed, and the greater the output voltage. On the other hand, a lower bandgap results in the capture of more photons including those in the red end of the solar spectrum, resulting in a higher output current but a lower output voltage. Thus, the highest solar-electric energy conversion can be theoretically achieved by using a superlattice based on a mixture of QDs of different sizes for harvesting the maximum proportion of the incident light effectively. Ideally such superlattices can then be used as the higher bandgap cells in a tandem stack. When applied to silicon (Fig. 12), the efficiency limit is found to reach 42.5% and 47.5% for two-cell and three-cell “all-silicon” stacks, compared to 29% for a single silicon cell considering only radiative and Auger recombination.

To successfully implement the all-silicon tandem concept, the following features need to be demonstrated: control of dot size and therefore bandgap, enhanced optical strength, adequate transport, P–I–N junctions (high V_{oc}), doping, work function control, and interconnected cells. Thanks to the development of nanotechnologies, control of QD size, and density in oxide, nitride, and carbide matrices has been demonstrated as witnessed by high-resolution TEM observations and photoluminescence measurements. However, obtaining the required charge transport properties in such systems are still under investigations in many research institutes, and might need some years of studies.

References

- Beaucarne, G., Slaoui, A., 2006. Polycrystalline silicon solar cells. In: Poortmans, J., Arkhipov, V. (Eds.), *Thin Film Solar Cells: Fabrication, Characterization and Application*. John Wiley & Sons Ltd., pp. 97–132.
- Gao, W., Xue, J., 2014. Recent progress in organic photovoltaics: Device architecture and optical design. *Energy & Environmental Science* 7, 2123–2144.
- Chen, F.C., Chou, C.H., Chuang, M.K., 2014. Chapter 6 – High-performance bulk-heterojunction polymer solar cells. In: Lin, Z., Wang, J. (Eds.), *Low-Cost Nanomaterials*. London: Springer-Verlag.
- Klimov, V.I., Ivanov, S.A., Nanda, J., 2007. Single-exciton optical gain in semiconductor nanocrystals. *Nature* 447, 441–446.
- Shockley, W., Queisser, H.J., 1961. Detailed balance limit of efficiency of p–n junction solar cells. *Journal of Applied Physics* 32, 510–519.
- Slaoui, A., Reuben, R.T., 2007. Advanced inorganic materials for photovoltaics. *Material Research Society Bulletin* 32, 211–215.
- Slaoui, A., Poortmans, J., Caymax, M., 2002. High temperature deposition and epitaxy of Si and SiGe. In: Bergmann, R. (Ed.), *Growth, Characterization and Electronic Application of Amorphous and Crystalline Si Thin Films*. Transworld Research Network, pp. 147–181. (Research Signpost 37/661).

Ion Conducting Materials: Superionic Conductors and Solid-State Ionics

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Electrical conduction of solid is mostly by electrons or holes as in the case of metals and semiconductors. However, some special types of solids show ionic conduction, the conductivity values of which are often as high as those of aqueous electrolyte solutions. Although, the ionic conduction in solids was already known by Michael Faraday in 19th century (Funke, 2013), it is noticed very useful for applications after 1970: for example, for gas sensors, lithium ion batteries, fuel cells etc. They have been called *solid electrolytes* or *superionic conductors* now; the latter is used especially for those have unusually high ionic conductivity. Faraday found silver ion conduction in Ag_2S , which has also electron conduction together. These materials are now called *Mixed Ionic-Electronic Conductors (MIEC)*, which are inevitable for electrode materials of battery and fuel cell. Growing research on ionic transport in solids and its application after 1970, a technical term of *solid-state ionics* has been established, which refers to the science and technology of ions in motion in solids. International journals of "Solid State Ionics" and "Ionics" have been published, where new materials, applications and fundamental studies have been reported.

Classification of Solids With Ionic Conduction

Ionic conduction in solid was first observed in inorganic crystals like $\alpha\text{-AgI}$, PbF_2 etc., it is now recognized in many varieties of material. Morphologies of ion conducting solids can be classified into crystalline, amorphous (or glassy), and organic polymer materials. Nano-, micro-composite materials are also studied recent years. The ionic species of conduction (mobile ions) also spread from Ag^+ , Cu^+ , F^- to include Li^+ , Na^+ , H^+ , O^{2-} etc.; even Mg^{2+} or higher valence cations are also reported mobile in some solids.

Typical ion conducting solids are listed in Tables 1 and 2 with their conductivity and mobile ions. The temperature dependence of conductivity for representative solid electrolytes is shown in Fig. 1.

Fast mobile ions in solids are limited to some monovalent cations like Ag^+ , Cu^+ , Li^+ , Na^+ , and H^+ , which have rather small ion radius comparing to the surrounding anions. Higher valent cations despite their small ion size are so strongly bound to the surrounding anions that it is difficult to move easily in solids. In spite of this, some challenges have been reported on Mg^{2+} , Ce^{2+} , Sc^{3+} conductors as shown in Table 1.

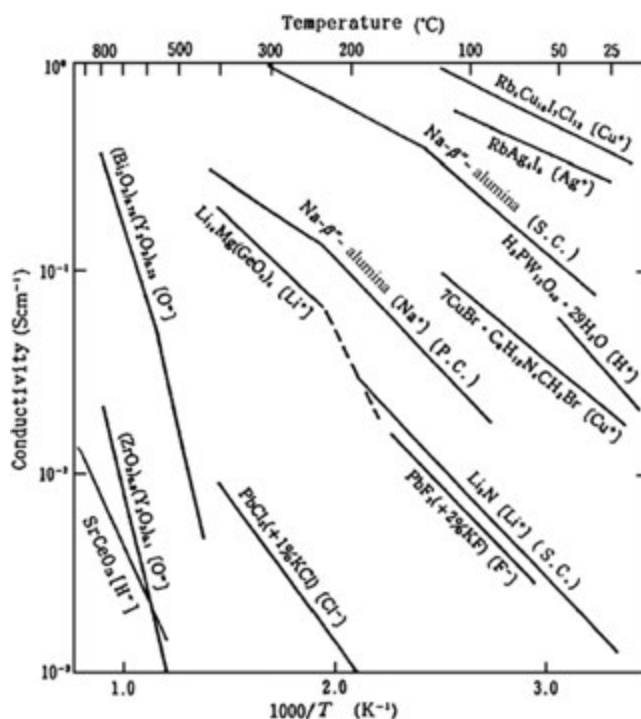
Table 1 Typical ion conducting solids (crystalline solids)

Mobile ion	Composition	Conductivity (S cm^{-1})	Note
Ag^+	RbAg_4I_5	2.7×10^{-1} (25°C)	
	$\text{Ag}_6\text{I}_4\text{WO}_4$	4.7×10^{-2} (25°C)	
Cu^+	$7\text{CuBr} \cdot \text{C}_6\text{H}_{12}\text{N}_4\text{CH}_2\text{Br}$	2.1×10^{-2} (20°C)	
	$\text{RbCu}_4\text{Cl}_3\text{I}_2$	3.4×10^{-1} (25°C)	
H^+	$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$	2.0×10^{-1} (25°C)	
	CsHSO_4	8×10^{-3} (160°C)	Superprotonic
	$\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$	2×10^{-2} (1000°C)	
Li^+	Li_3N	3×10^{-3} (25°C)	
	$\text{La}_{0.25}\text{Li}_{0.18}\text{TiO}_3$	1×10^{-3} (25°C)	LLT
	$\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$	1.3×10^{-1} (300°C)	LISICON
	$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$	1.2×10^{-3} (25°C)	Thio-LISICON
	$\text{Li}_2(\text{BH}_4)(\text{NH}_2)$	2×10^{-4} (25°C)	Hydride
Na^+	$\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$	2×10^{-1} (300°C)	β -Alumina
	$\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$	3×10^{-1} (300)	NASICON
K^+	$\text{K}_2\text{O} \cdot 5.2\text{Fe}_2\text{O}_3 \cdot 0.8\text{ZnO}$	1.8×10^{-2} (300)	
Mg^{2+}	$\text{MgZr}_4(\text{PO}_4)_6$	3×10^{-3} (800)	
Sc^{3+}	$\text{Sc}_2(\text{WO}_4)_3$	2×10^{-5} (600°C)	
F^-	PbF_2 (+ 2%KF)	2×10^{-2} (200°C)	
	$\text{Bi}_{0.9}\text{K}_{0.1}\text{F}_{2.8}$	7×10^{-4} (25°C)	
Cl^-	PbCl_2 (+ 3% KCl)	3×10^{-3} (300°C)	
	SnCl_2	2×10^{-2} (200°C)	
O^{2-}	$(\text{ZrO}_2)_{0.9}(\text{Y}_2\text{O}_3)_{0.1}$	2.0×10^{-2} (800°C)	
	$(\text{Bi}_2\text{O}_3)_{0.75}(\text{Y}_2\text{O}_3)_{0.25}$	8×10^{-2} (600°C)	
	$\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.115}\text{Co}_{0.085}\text{O}_3$	6×10^{-2} (600°C)	

Table 2 Typical ion conducting solids (glass, glass ceramics, polymer, composite)

Mobile ion	Composition	Conductivity ($S\text{ cm}^{-1}$)	Note
Ag^+	$60\text{AgI} \cdot 40\text{Ag}_2\text{MoO}_4$	2×10^{-2} (25°C)	Glass
	$\text{AgI} \cdot \text{Al}_2\text{O}_3\text{PVA}$ etc.	$10^{-3} \sim 10^{-2}$ (25°C)	Nano-particle
Cu^+	$50\text{CuI} \cdot 50\text{CuPO}_3$	1.5×10^{-3} (25°C)	Glass
Li^+	$37\text{Li}_2\text{S} \cdot 18\text{P}_2\text{S}_5 \cdot 45\text{LiI}$	10^{-3} (25°C)	Glass
	$50\text{LiI} \cdot 50\text{Al}_2\text{O}_3$	3×10^{-4} (25°C)	Mesoporous composite
	$\text{PEO} \cdot \text{LiClO}_4$	1×10^{-5} (25°C)	Polymer
	$\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{TiO}_2 \cdot \text{P}_2\text{O}_5$	1.3×10^{-3} (25°C)	Glass ceramics
H^+	$\text{ZrO}_2 \cdot 3(\text{PO}_{2.5}) + x\text{H}_2\text{O}$	1×10^{-2} (25°C)	Sol-gel glass
F^-	$(\text{InF}_3)_{0.35}(\text{SnF}_2)_{0.2}(\text{PbF}_2)_{0.35}$	8×10^{-4} (150°C)	Glass

Abbreviation: PEO, polyethylene oxide.

**Fig. 1** Conductivity of ion conducting solids. S.C. single crystals, P.C. poly crystal.

As anions are, in general, larger in size than cations, their mobility is lower than that of cations. However, comparatively small size anions such as F^- and O^{2-} are mobile in some solids. In particular, F^- ions in Bi–Pb–In–Sn compounds or glasses are very mobile even near the room temperature. O^{2-} conductors are mostly used at high temperatures above 500°C for sensors or fuel cells. In particular a series of stabilized zirconia is a stable good O^{2-} conductor and is very important for practical uses.

Mechanism of Ionic Conduction in Solids

Fundamental Migration Mechanism of Ions in Solid

There are many types of conduction mechanisms depending on the crystal or non-crystal structure of the solid electrolytes. In a broad way, they are classified into two categories; Type A: sub-lattice liquid type, Type B: point-defect type.

(a) Type A: Sub-lattice liquid type

Most surprising ionic conductors are in this category, whose conductivity is more than 10^{-3} to 10 S cm^{-1} , which is the same order of liquid electrolytes or molten salts. So-called “superionic conductors” are in this category. A typical example is the high temperature phase of silver iodide ($\alpha\text{-AgI}$) which is stable above 147°C to the melting temperature 550°C . The ionic conductivity of $\alpha\text{-AgI}$ is 10 S cm^{-1} at 500°C , which is *higher* than its liquid state. The entropy change ΔS_t of the $\beta\text{-}\alpha$ transition at 147°C is

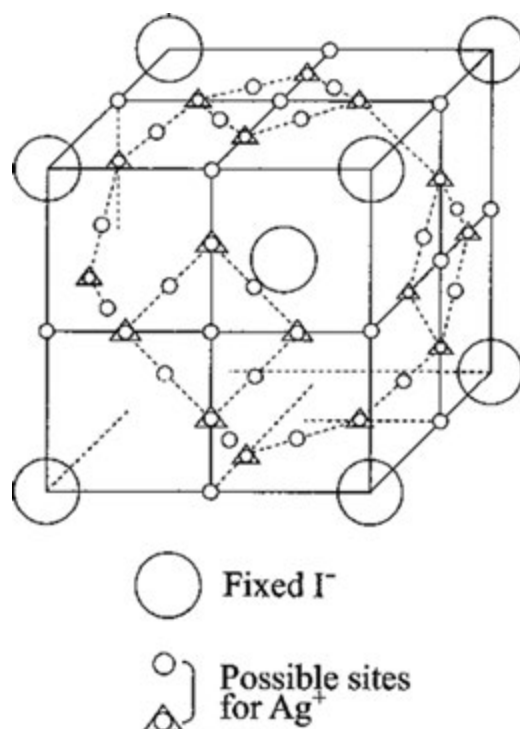


Fig. 2 Stock model of α -AgI structure.

$14.5 \text{ JK}^{-1} \text{ mol}^{-1}$ which is larger than the value $\Delta S_f 11.3 \text{ JK}^{-1} \text{ mol}^{-1}$ at the melting temperature of 550°C ; this means a half of the component ions (Ag^+) is fused at β - α transition and the remaining half (I^-) melts at normal melting point. This is similar to the case of liquid crystal or plastic crystals, which is categorized to a “meso-phase” in between solid and liquid.

Actually, detailed structure analysis of the type A crystals confirmed this concept. In case of the α -AgI, the iodide ions construct a fixed bcc. sublattice, where the silver ions are distributing and migrating randomly among them. A simple picture is shown in **Fig. 2**, where the two I^- locate at the center and the corners of bcc lattice, while the two Ag^+ are distributing in 42 sites in a unit cell. Moreover, detailed analysis of neutron scattering revealed the silver ions are traveling among these positions very fast like in liquid. Thus, the type A ionic conductor can be regarded as a meso-phase between liquid and solid. Similar sublattice liquid state is observed in fluoride structured F^- conductor PbF_2 , whose conductivity is also 1 S cm^{-1} at 900K as shown in **Fig. 3**. It is regarded as a superionic phase like α -AgI, although the transition to the superionic state is a continuous second order type (Faraday transition), which is different from first order transition of β to α -AgI (Catlow, 1989).

α -AgI or PbF_2 is an example of three dimensional (3D) ionic conductor, where the mobile ions can move any directions through the 3D conduction channels. 2D and 1D ionic conductors are also known. A typical example is sodium ion conduction in Na β -alumina ($\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$), which has a layered structure as shown in **Fig. 4**. The crystal framework is formed by spinel block layers composed of aluminum and oxygen. Na^+ ions (large gray circles) are distributing in a plane between the two spinel layers which are supported by the pillars of oxygen (double circles).

The array of Na^+ ions in the plane is ideally ortho-triangle, however the midpoint between oxygen-pillars (called *mid-oxygen site*; small circles in **Fig. 5**) are also energetically available. Therefore, Na^+ ions can easily move from their normal sites to the mid-oxygen sites and vice versa, which give rise to the liquid-like high Na^+ ion conduction. In comparison to the above mentioned AgI or PbF_2 which have 1st or 2nd order phase transitions to low temperature insulator phases, Na β -alumina shows no clear phase transition even below 10K , whose conductivity decreases linearly in Arrhenius plot; so that some authors (Boyce and Huberman, 1979) categorize AgI as type I, PbF_2 to type II and Na β -alumina to type III.

One dimensional or quasi-1D ionic conduction is often found in tunnel structured compounds. An example is a ramsdellite-type Li_2TiO_3 , in which Li^+ ions migrate through a tunnel surrounded by octahedra and tetrahedra of TiO_n . Some hollandite-type crystals as $\text{K}_{2x}\text{Mg}_x\text{Ti}_{8-x}\text{O}_{16}$ has also one dimensional tunnels surrounded by TiO_n . The potassium ions K^+ are distributing and moving freely in the tunnels, which give rise to the very high conductivity of 10 S cm^{-1} at microwave frequency. However, the conductivity at low frequency or dc region becomes very low probably due to some blocking impurities or defects in the tunnels.

When the tunnels of different directions are connected with each other, the macroscopic ionic conduction becomes 3D. The Na superionic conductor (NASICON) family represented as $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ($x < 2$) is a typical example (see Section on Sodium Ion Conductors).

It is necessary to mention briefly the structure and conduction mechanism of amorphous ionic conductors such as AgI- Ag_2MoO_4 glass or solid polymer electrolytes as PEO- LiClO_4 shown in **Table 2** (Junichi Kawamura *et al.*, 2006). Although these

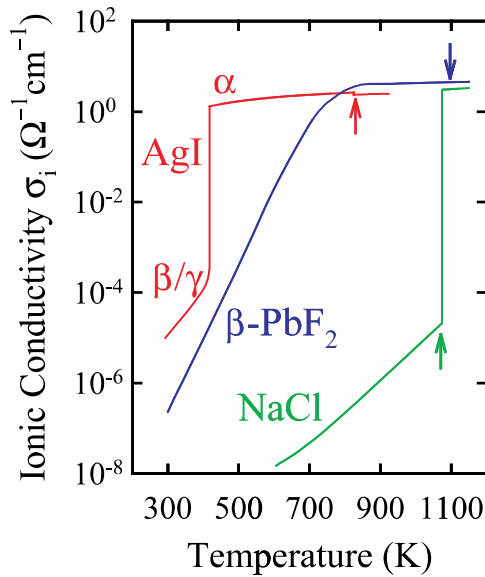


Fig. 3 Ionic conductivity of AgI, PbF₂ and NaCl, from Hull, 2004.

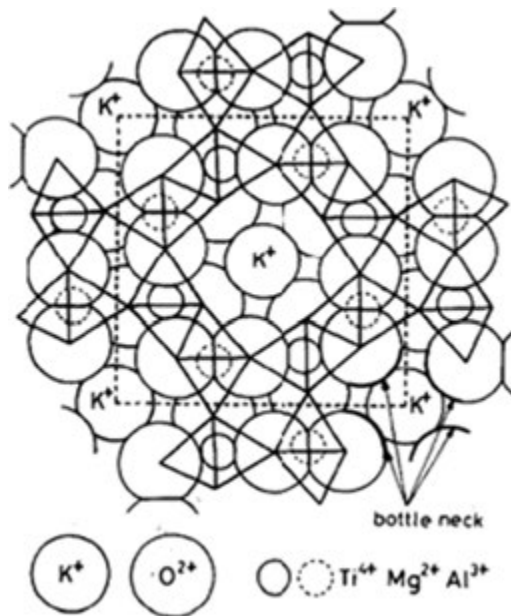


Fig. 4 Structure of Hollandite type one dimensional K⁺ conductor (Yoshikado *et al.*, 1982).

materials have no long-range order like crystals, they have some short (~ 1 nm) and intermediate (~ 10 nm) range orders. In case of AgI-Ag₂MoO₄ glass, the glass is locally composed of AgI₄ and MoO₄ units connected randomly. The silver ions are mainly moving through the AgI rich regions like in the α -AgI, which link to form random conduction channels. In lower temperatures, some silver ions are trapped by the oxide ions resulting to the decrease in conductivity. No thermodynamic phase transition is seen, but the glass transitions are observed between the melt and the superionic glass as well as between the superionic glass and insulator glass. In case of the polymer electrolyte as PEO-LiClO₄, the lithium ion is trapped in a cage made of coordinating four oxygens in polyethyleneoxide network, whose micro Brownian motion allows the lithium ion to migrate from one cage to the other like transferring an apple through many baskets by bucket brigade manner.

(b) Type B: Point-defect type

Any ionic crystal has in principle some extent of ionic conductivity due to the intrinsic lattice defects in the crystal. Typical examples are so called Frenkel and Schottky defects created by the thermal energy at a temperature. Frenkel defect is a pair of

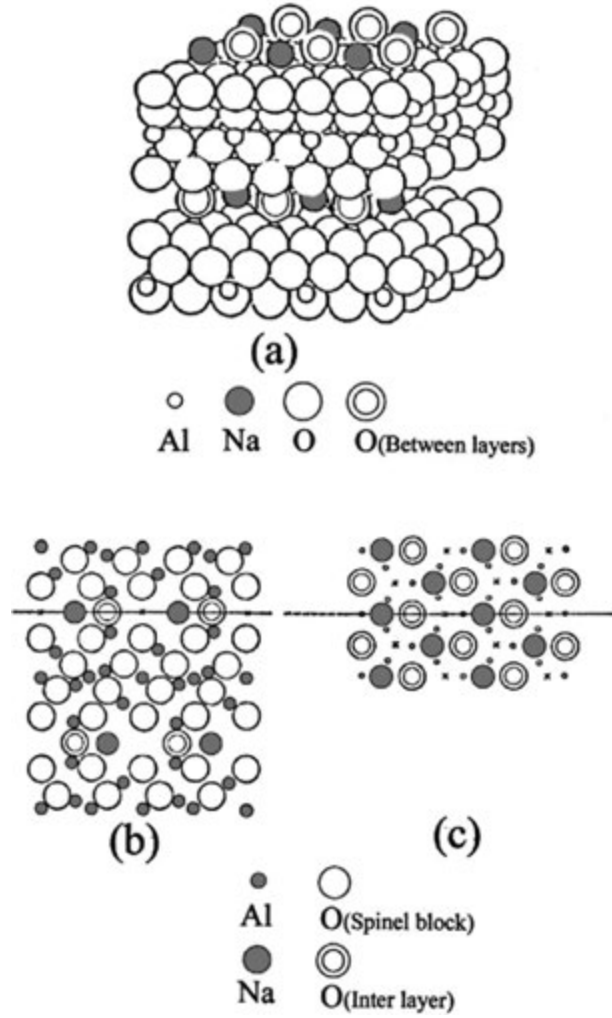


Fig. 5 Layer structure of β alumina. (a) Outward appearance, (b) cross-sectional plane perpendicular to layer, (c) arrangement of Na^+ between layers.

interstitial cation M_i and cation vacancy V'_M , whereas the Shottky defect is a pair of cation vacancy V'_M and anion vacancy V'_x as shown in Fig. 6.

Number density of the defects n can be expressed by defect equilibrium; for example, in case of Frenkel defects as,

$$n(T) = \sqrt{NN'} \exp\left(\frac{-G_F}{2kT}\right) \quad (1)$$

where N and N' are the number of normal sites and interstitial sites respectively. ΔG_F is the formation free energy of a Frenkel defect pair, k is the Boltzmann constant, T is the absolute temperature. Thus, the intrinsic defect density is determined by the defect formation free energy ΔG_F . On the other hand, extrinsic defects can be artificially created by heterovalent doping, for example, the doping of MgCl_2 to NaCl creates sodium vacancy V'_{Na} . The concentration of the extrinsic defects can be calculated by defect equilibrium theory (Kroger, 1964).

Once some defects are created in a crystal, they can migrate rather easily in the solid. There are fundamentally three ways of ionic transport by lattice defects; (1) vacancy mechanism, (2) interstitial mechanism, and (3) interstitialcy mechanism which are illustrated schematically in Fig. 7.

Small cations can migrate by both interstitial and vacancy mechanisms, although the large anions diffuse mostly by anion vacancy process. A typical example is the oxide-ionic conduction in stabilized zirconias such as $(\text{ZrO}_2)_{0.9}(\text{Y}_2\text{O}_3)_{0.1}$ (see Section on Oxide Ion Conductors), where an O^{2-} ion hops from its normal site to an adjacent anion vacancy V_{O} leaving a new vacancy behind. Another example is the fluoride-ionic conduction in fluorite-type solid solutions composed of $\text{Ca}_{1-x}\text{Na}_x\text{F}_{2-x}$ ($x \leq 0.05$), in which a monovalent sodium replaces a divalent calcium in CaF_2 to create a fluoride ion vacancy. In these materials, the vacant sites of movable ions are rather limited, for example, in the above described stabilized zirconia the number of oxide-ion vacancies is only 5% of normal anion sites. Thus, the ionic conductivity of the defect type solid is not so high as that of type 1 superionic conductors.

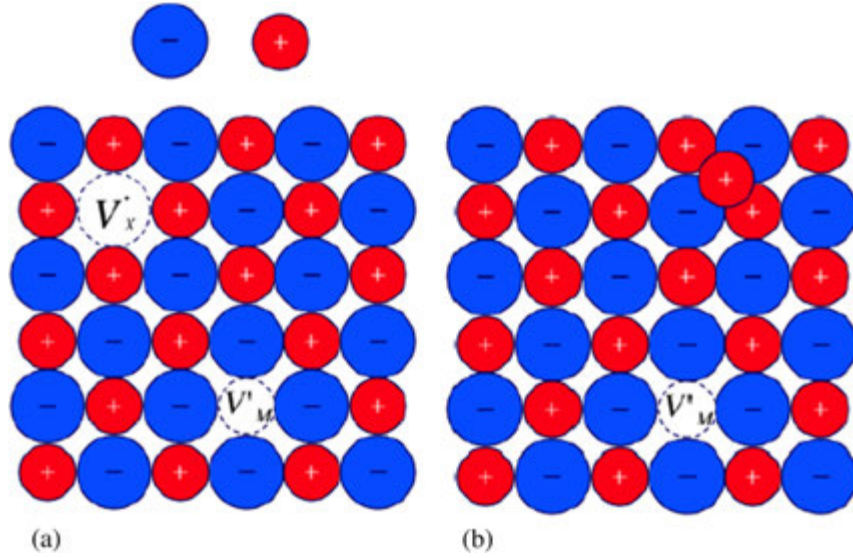


Fig. 6 Schematic model of (a) Schottky defect and (b) Frenkel defect.

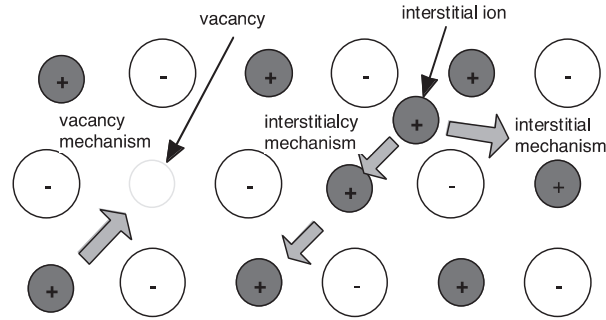


Fig. 7 Typical ion transport mechanisms in point defect type ionic conductor; (1) vacancy mechanism, (2) interstitial mechanism and (3) interstitialcy mechanism.

Theory of Ionic Conduction in Solids

When the carrier density n is known, the ionic conductivity σ can be estimated by the following Nernst formula as,

$$\sigma = zen\mu \quad (2)$$

where μ is the mobility of the mobile ions; z and e represent their ionic valence and elementary charge, respectively. In case of Type A superionic conductors, the carrier density n is equal to the total mobile ions; for example, all Ag^+ in $\alpha\text{-AgI}$. In the case of Type B defect type solid, n is the number of the mobile defects expressed like Eq. (1). For vacancy mechanism, the charge carriers are regarded as vacancies instead of mobile ions themselves, thus the n should be the number of the vacancies.

The mobility μ in Eq. (2) is related to the diffusion coefficient D of the mobile ion by,

$$\mu = zeD/kT \quad (3)$$

Thus the ionic conductivity σ is expressed as the following Nernst–Einstein equation:

$$\sigma = (ze)^2 nD/kT \quad (4)$$

The diffusion coefficient of an ion in solid is well described by “jump model”; a mobile ion located in a bottom of a potential well with thermal vibration ν_0 attempt frequency overcomes a potential barrier ΔG_m in order to move to another site as shown in Fig. 7. Then the transition rate $\nu(T)$ is expressed as,

$$\nu(T) = \nu_0 \exp\left(\frac{-\Delta G_m}{kT}\right) \quad (5)$$

Table 3 Diffusion coefficients D_σ and D_{Tr} for several solid electrolytes

Material	Mobile ion	Temperature ($^{\circ}\text{C}$)	D_σ ($\text{cm}^2 \text{s}^{-1}$)	D_{Tr} ($\text{cm}^2 \text{s}^{-1}$)
$(\text{ZrO}_2)_{0.85}(\text{CaO})_{0.15}$	O^{2-}	1000	4.2×10^{-8}	4.2×10^{-8}
$\alpha\text{-AgI}$	Ag^+	200	2.53×10^{-5}	1.76×10^{-5}
$\alpha\text{-RbAg}_4\text{I}_5$	Ag^+	25	3.68×10^{-5}	1.75×10^{-5}
Sodium β -alumina	Na^+	25	6.8×10^{-7}	4.0×10^{-7}
Potassium β -alumina	K^+	25	3.17×10^{-9}	9.6×10^{-10}
Silver β -alumina	Ag^+	25	3.1×10^{-7}	1.7×10^{-7}
$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$	H^+	27	4.5×10^{-6}	

Abbreviations: D_{comp} , component diffusion coefficient; D_{Tr} , tracer diffusion coefficient.

and the diffusion coefficient D is expressed as,

$$D = \frac{1}{6} v a^2 \quad (6)$$

where a is the jump distance shown in Fig. 7.

Thus, the ionic conductivity is expressed as,

$$\sigma(T) = \frac{(z_i e)^2 a^2 v_0}{kT} n_i \exp\left(\frac{-\Delta G_m}{kT}\right) \quad (7)$$

In case of Type A superionic conductors, since the n_i is almost independent of temperature the slope of $\log \sigma T$ vs. $1/T$, which is usually called *activation energy* gives the estimation of the barrier height.

On the other hand, in case of Type B defect type ionic conductors, the n_i strongly depends on the temperature as given in Eq. (1) for intrinsic Frenkel defect case. In this case the ionic conductivity is expressed as,

$$\sigma(T) = \frac{(z_i e)^2 a^2 v_0}{kT} \sqrt{N N'} \exp\left(\frac{-\Delta G_m + \Delta G_F/2}{kT}\right) \quad (8)$$

So, the apparent activation energy gives the sum of the defect formation and migration energies. The estimation of these energy values is a key subject of the solid state ionics, which are tabulated in some literatures (Kroger, 1964). One can say, the Type A superionic conductor is a limit of Type B with negligible value of ΔG_F .

It is worthwhile to compare the diffusion coefficient D_σ from conductivity experiment with the values from other experiments such as a tracer diffusion coefficient D_{Tr} by radio isotope experiment, or pulse-field gradient NMR technique D_{NMR} etc. An example is given in Table 3, where the value estimated from the conductivity by Eq. (4) is expressed by D_σ . Fairly good agreement is seen between D_{comp} and D_{Tr} , however small difference is also seen. The ratio of them is called Haven ratio HR or correlation factor f , which is an index of many-body effect and/or backward correlations of mobile ions.

The diffusion phenomenon that changes the chemical composition of the solid is called *chemical diffusion* and its coefficient is named the *chemical diffusion coefficient* (D_{chem}). In mixed conductors (see Section on Mixed Ionic-Electronic Conductors) such as $\text{Ag}_{2+\delta}\text{S}$ the diffusion of Ag^+ from the outside is accompanied by the diffusion of excess electrons changing the composition of the solid. The D_{chem} value of $\text{Ag}_{2+\delta}\text{S}$ at 200°C is evaluated to $0.1\text{--}0.3 \text{ cm}^2 \text{s}^{-1}$ and that of $\text{Ag}_{2+\delta}\text{S}$ is $0.5\text{--}1.5 \text{ cm}^2 \text{s}^{-1}$ depending on the composition. The chemical diffusion coefficient is now very useful to analyze electrode reactions in lithium ion batteries, SOFC etc.

Typical Examples of Ionic Conductor

Silver and Copper Ion Conductors

As is already explained above, the best-known example is $\alpha\text{-AgI}$, which has a sublattice melting superionic conductor state above 147°C ; below this temperature, it transforms into a β (wurtzite) or γ (zincblend) phase of poor conductivity as shown in Fig. 2. Many attempts have been made to stabilize the high conductivity $\alpha\text{-AgI}$ phase down to the lower temperatures, for example, by substituting other cations M for silver or substituting other anions X for iodide ions. Table 4 shows some room temperature-type silver ion conductors thus synthesized. Of these, RbAg_4I_5 has the highest conductivity of $2.7 \times 10^{-1} \text{ S cm}^{-1}$ at room temperature.

Similar to $\alpha\text{-AgI}$, the high temperature crystal form of CuI is an average structure with high Cu^+ conductivity. Similar attempts were made to stabilize the superionic phase to room temperature. Copper ion conductors thus synthesized are listed in Table 1.

Among these, $\text{Rb}_4\text{Cu}_{16}\text{Cl}_{13}\text{I}_7$ exhibits the highest conductivity, $4.7 \times 10^{-1} \text{ S cm}^{-1}$ at room temperature; this value is the highest one not only among the Cu^+ -conductors but also among all kind of solid electrolytes ever known.

Some other attempts have been made to stabilize the high temperature superionic phase to room temperature; (1) by glass formation with other oxides etc., (2) confined nano-size structures. For the glass formation, for example, the melt of AgI and some

Table 4 Typical sodium ion conductors

Mobile ion	Composition	Conductivity (25°C) ($S\text{ cm}^{-1}$)	Note
Na^+	$\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$	2×10^{-1} (300°C)	Na β -Alumina
	$\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$	3×10^{-1} (300°C)	NASICON
	$\text{Na}_2\text{O}-\text{R}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$	2×10^{-2} (300°C)	Narpsio (R=rare earth)
	Na_3PS_4	2×10^{-4} (25°C)	
	$\text{Na}_2\text{B}_{10}\text{H}_{10}$	10^{-2} (110°C)	Hydride

oxides as Ag_2MoO_4 are quenched to room temperature, whose ionic conductivity is about 10^{-3} S cm^{-1} . The confined nano-size crystals are made by various techniques such as mechanical milling, sol-gel synthesis, or after annealing of glassy materials etc., whose ionic conductivity is around $10^{-4} \sim 10^{-3}\text{ S cm}^{-1}$, as shown in [Table 2](#).

Sodium Ion Conductors

A well-known sodium ion conducting solid is so called Na β -alumina, the chemical composition of which is typically expressed as $\text{Na}_2\text{O}_{11}\text{Al}_2\text{O}_3$. The crystal has a layer structure and the incorporated sodium ions can migrate along the layer as shown in [Fig. 5](#). β'' -alumina which is represented as $\text{Na}_2\text{O} \cdot 4 \sim 6\text{ Al}_2\text{O}_3 \cdot x\text{MO}_n$ also have a layer structure and the sodium ion conductivity of these materials is higher than that of Na β -alumina. Other cations such as Ag^+ , K^+ , Li^+ , Sr^{2+} , Ba^{2+} and Eu^{2+} can be fully substituted for sodium ions in Na β -alumina and the resultant ceramics show electrical conduction due to the migration of those ions. Na β'' -alumina is used as a solid electrolyte for sodium-sulfur batteries (NaS batteries) for large-scale energy storage systems (see Section on Application Examples). Another typical sodium ion conductor is a series of NASICON, the chemical composition of which is represented as $\text{Na}_{1+x}\text{Zr}_x\text{Si}_{3-x}\text{O}_{12}$ ($x < 2$). In this type of oxide, sodium ions are surrounded by a 3D network of SiO_4 tetrahedra and ZrO_6 or PO_6 octahedra which share corners, and the sodium ions are mobile through the channel of the network structure. Glass ceramics called Narpsio of $\text{Na}_2\text{O}-\text{R}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$ (R=rare earth), which consist of a skeleton structure of $12(\text{SiO}_4)^{4-}$ tetrahedra-membered rings exhibit high Na^+ conductivity up to 10^{-1} S cm^{-1} at 300°C and has good biocompatibility. Hollandite type 1D conductor $\text{Na}_x\text{Ti}_{2-x}\text{Ga}_{4+x}\text{O}_{11}$ has very high Na^+ conductivity only at high frequency (see Section on Fundamental Migration Mechanisms of Ions in Solid). Most of work have been done on oxide materials, however some new types of sodium ion conductors are developed; for example, as a sulfide of a cubic Na_3PS_4 is found to show $2 \times 10^{-4}\text{ S cm}^{-1}$ at 25°C and is used for an all solid state sodium battery ([Hayashi et al., 2012](#)). A very new group of ionic conductors based on boron hydrides as $\text{Na}_2\text{B}_{10}\text{H}_{10}$ is discovered to show 10^{-2} S cm^{-1} at 110°C, which has a unique icosahedral dodecahydro-closo-dodecaborate ($\text{B}_{12}\text{H}_{11}^{2-}$) anions ([Udovic et al., 2014](#); [Table 4](#)).

Lithium Ion Conductors

Recent advancement of lithium ion batteries strongly demands lithium ion conductors both for active materials for electrodes and electrolytes. As for the solid electrolytes, lithium ion conductivity of 10^{-3} S cm^{-1} is now achieved by sulfide based materials; for example, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ shows $1.2 \times 10^{-3}\text{ S cm}^{-1}$ at 25°C ([Fig. 8](#); [Kamaya et al., 2011](#)), and some glassy or partially crystalline glasses have the same order ([Fig. 8](#)). Lithium nitride Li_3N has also 10^{-3} S cm^{-1} at room temperature. Unfortunately, however these materials are unstable under open air.

Since oxide materials are known rather stable under open atmosphere, many efforts have been devoted to find new materials with high lithium ion conductivity. The conductivity of $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ (named LISICON) is about $1 \times 10^{-2}\text{ S cm}^{-1}$ at 200°C and that of $\alpha\text{-Li}_2\text{SO}_4$ is extremely high ($\sim 1\text{ S cm}^{-1}$) above 573°C. Li β -alumina prepared by ion-exchange from Na β alumina shows 10^{-3} S cm^{-1} at 25°C. $\text{La}_{0.51}\text{Li}_{0.34}\text{TiO}_{2.94}$, which is a perovskite-type oxide based on $\text{La}_{2/3}\text{TiO}_3$ has high conductivity at room temperature. Glass ceramics composed of $\text{Li}_{1.55}\text{Ti}_{1.75}\text{Al}_{0.25}\text{Si}_{0.3}\text{P}_{2.7}\text{O}_{12}$ with a NASICON-type crystalline phase has $1.2 \times 10^{-3}\text{ S cm}^{-1}$ at 25°C, which is called “OHARA glass” and is commercially available. Although those oxides are stable in open air, they are reduced by a contact with lithium metal, which hampers the application to lithium battery. Some Garnet-type structured compounds as $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$, $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$ and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) are found stable to the contact to lithium metal and has a reasonable conductivity of 10^{-4} S cm^{-1} at room temperature, which can be used for all-solid state lithium batteries ([Venkataraman Thangadurai et al., 2004](#)). For the application to thin film batteries, rather low conductivity glasses such as Li_3PO_4 ($\sim 10^{-6}\text{ S cm}^{-1}$ at 25°C) or its oxynitride called LIPON can be used for the electrolyte; they are stable to both lithium metal anode as well as high voltage cathodes.

An interesting new class of lithium ion conductors have been developed in hydride series starting from LiBH_4 . LiBH_4 has a lithium ion conductivity of 10^{-2} S cm^{-1} above 117°C, and its derivative of $\text{Li}_4(\text{BH}_4)(\text{NH}_2)_3$ shows $2 \times 10^{-4}\text{ S cm}^{-1}$ at room temperature ([Motoaki Matsuo et al., 2009](#)). These hydrides are stable to lithium metal, although they react with oxide cathodes.

In relation to the lithium ion battery, a great advance has been achieved in organic or organic-inorganic hybrid ion conductors, where polymer, gel, ionic liquid and plastic solids are included. In particular, organic polymers or gel electrolytes are used as the electrolyte for lithium ion batteries. The details of the organic-inorganic hybrid ion conductors are out of this colloumn; some of them are listed in [Tables 2](#) and [5](#) ([MacFarlane and Forsyth, 2001](#); [Junichi Kawamura et al., 2006, 2007](#)). The highest conductivity of

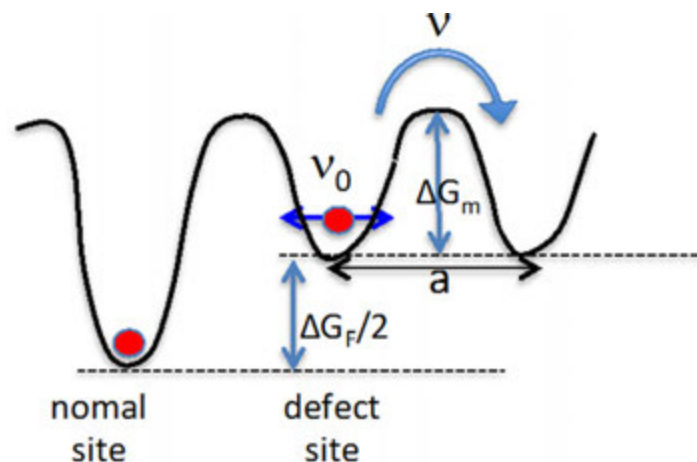


Fig. 8 Jump model of ion migration in solids.

Table 5 Typical lithium ion conductors

Mobile ion	Composition	Conductivity (25°C) ($S\text{ cm}^{-1}$)	Note
Li^+	Li_3N	3×10^{-3}	
	$\text{La}_{0.25}\text{Li}_{0.18}\text{TiO}_3$	1×10^{-3}	LLT
	$\text{Li}_{2+2x}\text{Zn}_{1-x}(\text{GeO}_4)_4$	2×10^{-6}	LISICON
	$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$	1.2×10^{-3}	Thio-LISICON
	$\text{Li}_2(\text{BH}_4)(\text{NH}_2)$	2×10^{-4}	Hydride
	$\text{Li}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$	10^{-3}	Li- β -Alumina
	$\text{Li}_{1.55}\text{Ti}_{1.75}\text{Al}_{0.25}\text{Si}_{0.3}\text{P}_{2.7}\text{O}_{12}$	1.2×10^{-3}	OHARA glass
	$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$	10^{-4}	LLZ
	$\text{Li}_3\text{PO}_3.9\text{N}_{0.17}$	2×10^{-6}	LIPON
	$\text{Li}_{3-2x}(\text{In}_{1-x}\text{M}_x)_2(\text{PO}_4)_3$	10^{-5}	
	$37\text{Li}_2\text{S} \cdot 18\text{P}_2\text{S}_5 \cdot 45\text{LiI}$	10^{-3}	Glass
	$50\text{LiI} \cdot 50\text{Al}_2\text{O}_3$	3×10^{-4}	Mesoporous composite
	$\text{PEO} \cdot \text{LiClO}_4$	10^{-5}	Polymer

the polymer electrolytes is around 10^{-4} S cm^{-1} at room temperature although the transference number of the lithium is less than 0.5 and the counter anion is much higher.

Proton (or Hydride Ion) Conductors

A good proton-conducting solid would be a promising material for future hydrogen energy systems. They will be of use as a solid electrolyte for fuel cells, hydrogen production, hydrogen separation, hydrogen sensors, and membrane reactors. Various kinds of proton conducting solids have been synthesized. They are roughly classified into six categories as represented in Table 6 with typical compounds belonging to each category. Hydrated heteropoly acids such as $\text{H}_3\text{Mo}_{12}\text{PO}_{40} \cdot 29\text{H}_2\text{O}$ and $\text{H}_3\text{W}_{12}\text{PO}_{40} \cdot 29\text{H}_2\text{O}$ show very high protonic conductivity at room temperature. However, they are unstable at elevated temperatures even below 100°C to loose the water molecules to decrease in their conductivity. The conductivity of CsHSO_4 , which is an anhydrous compound, increases at 144°C due to transformation of its crystal structure. Some related materials as $\text{M}_3\text{H}(\text{XO}_4)_2$ ($\text{M}=\text{Rb}, \text{Cs}, \text{NH}_4$; $\text{X}=\text{S}, \text{Se}$) or phosphates have been known to show high proton conductivity up to 10^{-2} S cm^{-1} at around 200°C "superprotonic" state. A typical structure of the superprotonic state is shown in Fig. 9 for CsH_2PO_4 , where the PO_4 is rotating very fast to promote the proton jump between the two oxygens.

The charge carriers in H_3O^+ β'' -alumina and NH_3^+ β'' -alumina are considered to be partly protons and partly hydronium or NH_4^+ must be replaced for Na^+ by ion exchange of conventional $\text{Na-}\beta''$ alumina. It is known that the mobility of protons in H_xWO_3 and H_xMoO_3 is very high. But the conductivity itself cannot be measured since electronic conduction in these oxides is much higher than that of protons.

Organic polymers based on polyethyleneoxide or polyvinylalcohol with inorganic acid shows proton conduction, the conductivities of which are the order of $1 \times 10^{-4}\text{ S cm}^{-1}$ at room temperature.

Table 6 Typical solid proton conductors

Category and material	Conductivity ($S\text{ cm}^{-1}$)	Note
<i>Hydrate compounds</i>		
$\text{H}_3\text{Mo}_{12}\text{PO}_{40} \cdot 29\text{H}_2\text{O}$	2×10^{-1} (25°C)	Room temperature type. Unstable at dry atmosphere
$\text{H}_3\text{W}_{12}\text{PO}_{40} \cdot 29\text{H}_2\text{O}$	2×10^{-1} (25°C)	
$\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$	4×10^{-3} (20°C)	
$\text{HClO}_4 \cdot \text{H}_2\text{O}$	3×10^{-4} (27°C)	
$\text{Sb}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$	3×10^{-4} (25°C)	
<i>Anhydrous compounds</i>		
$\text{C}_6\text{H}_{12}\text{N}_2(\text{H}_2\text{SO}_4)_{1.5}$	2×10^{-4} (200°C)	Stable below 200°C
$\text{Li}(\text{N}_2\text{H}_5)\text{SO}_4$	1×10^{-4} (160°C)	
CsHSO_4	2.7×10^{-3} (147°C)	
KOH	2×10^{-3} (350°C)	mp. 406°C
<i>β-alumina type oxides</i>		
$\text{H}_3\text{O}^+ \cdot \beta\text{-Al}_2\text{O}_3$	1×10^{-4} (25°C)	Prepared by ion exchange method
$\text{NH}_4 \cdot \text{H}_3\text{O}^+ \cdot \beta''\text{-Al}_2\text{O}_3$	1×10^{-4} (25°C)	
$\text{NH}_4^+ \cdot \beta/\beta''\text{-Ga}_2\text{O}_3$	1×10^{-2} (200°C)	
<i>H-insertion compounds</i>		
H_xWO_3		W-bronze structure. High electronic conduction. With protons in motion
H_xMoO_3		
<i>Oxides with lattice defects</i>		
$(\text{ThO}_2)_{0.85}(\text{Y}_2\text{O}_3)_{0.15}$	6×10^{-3} (1200°C)	Perovskite-type structure Protonic conduction under H-containing atmosphere
$\text{La}_{0.96}\text{Ca}_{0.04}\text{YO}_{3-\alpha}$	5×10^{-4} (1000°C)	
$\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$	1×10^{-2} (900°C)	
$\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_{3-\alpha}$	2×10^{-2} (800°C)	
<i>Organic polymers-inorganic acids</i>		
$\text{PEO-H}_2\text{SO}_4$	2×10^{-4} (25°C)	Polyethylene oxide
$\text{PVA-H}_3\text{PO}_4$	$1 \times 10^{-5} \sim 1 \times 10^{-3}$ (25°C)	

Development of proton conducting ceramics which are stable over a wide range of temperature has been desired because they are very useful materials for electrochemical energy conversion and sensors (see Section on Application Examples). Some doped perovskite-type oxide solid solutions based on SrCeO_3 and BaCeO_3 are known to exhibit appreciable protonic conduction under a hydrogen-containing atmosphere at elevated temperatures. $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ and $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ belong to this class of proton conductors. These ceramics exhibit only p type electronic conduction in the atmosphere free from water vapor or hydrogen. However, when water vapor or hydrogen is introduced into the atmosphere at high temperature, electronic conductivity decreases and protonic conduction occurs rapidly. When the SrCeO_3 based ceramics are exposed to hydrogen gas at high temperature, they become almost pure protonic conductors, the conductivity of which is about $1 \times 10^{-2} S\text{ cm}^{-1}$ at 900°C (somewhat lower than that of YSZ shown in Fig. 1). Since zirconate-based ceramic $\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-\delta}$ exhibits proton conduction and their mechanical strength as well as chemical stability is better than those of cerates, they are used as a solid electrolyte for hydrogen sensors (see Section on Application Examples) although its conductivity is rather low.

It is necessary to add some recent reports on hydride ion conductors. The existence and possible transport of hydride ion (H^-) in some oxides are reported in $12\text{CaO}-7\text{Al}_2\text{O}_3$ (Hayashi *et al.*, 2002), $\text{BaTiO}_{2.4}\text{H}_{0.6}$ (Yoji Kobayashi *et al.*, 2012), La_2LiHO_3 etc. (Kobayashi *et al.*, 2016; $\sigma = 10^{-6} S\text{ cm}^{-1}$ at 500K), in which the observed ionic conductivity is reported not due to the proton (H^+) conduction but by hydride ion (H^-). The size of the H^- ion is about 1.2 Å, which is suitable for ionic conduction. Although some critical discussions are still going (Norby *et al.*, 2004), these materials might open a new frontier of ionics field (Table 7).

Other Cation Conductors

Some other cations are conducting in solids, although their conductivity is rather low; for example, potassium ions K^+ can move in the tunnel-structured oxide $\text{K}_2\text{O}_{5.2}\text{Fe}_2\text{O}_{30.8}\text{ZnO}$. Divalent cation conductors $\text{M}^{(\text{II})}\text{Zr}_4(\text{PO}_4)_6$ are known, where $\text{M}^{(\text{II})}$ is Mg^{2+} , Zn^{2+} , Mn^{2+} etc.; for example, $\text{MgZr}_4(\text{PO}_4)_6$ has the Mg^{2+} ion conductivity of $3.4 \times 10^{-3} S\text{ cm}^{-1}$ at 800°C (Nomura *et al.*, 1992). As was shown in the previous sections, β - and β'' -alumina are capable to allow many kinds of cations to migrate in its conduction planes; for example, Ba^{2+} , Cd^{2+} , Sr^{2+} , Eu^{2+} , most of which are prepared by exchanging Na^+ ions with those ions. Trivalent cations of Sc^{3+} and Al^{3+} were reported mobile in $\text{Sc}(\text{WO}_4)_3$ and $\text{Al}(\text{WO}_4)_3$ respectively, although their conductivities are rather low $10^{-5} S\text{ cm}^{-1}$ at 600°C (see Table 1).

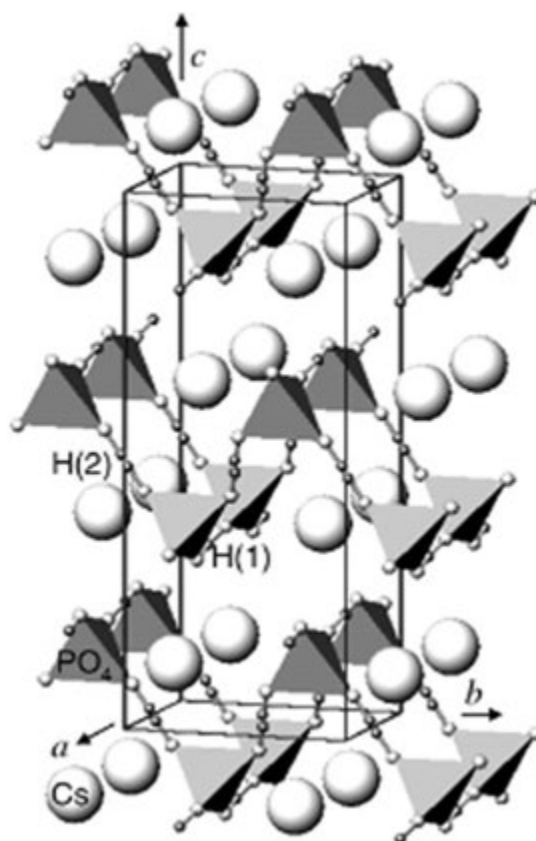


Fig. 9 Structure model of CsH_2PO_4 (from Haile *et al.*, 2007).

Table 7 Typical solid proton and hydride ion conductors

Material	Conductivity (S cm^{-1})	Note
$\text{H}_3\text{Mo}_{12}\text{PO}_{40} \cdot 29\text{H}_2\text{O}$	2×10^{-1} (25°C)	Unstable at dry atmosphere
$\text{H}_3\text{W}_{12}\text{PO}_{40} \cdot 29\text{H}_2\text{O}$	2×10^{-1} (25°C)	Unstable above 100°C
$\text{H}_2\text{UO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$	4×10^{-3} (20°C)	
$\text{Sb}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$	3×10^{-2} (25°C)	
$\text{C}_6\text{H}_{12}\text{N}_2(\text{H}_2\text{SO}_4)_{1.5}$	2×10^{-4} (200°C)	Stable below 200°C
$\text{Li}(\text{N}_2\text{H}_5)\text{SO}_4$	1×10^{-4} (160°C)	
CsHSO_4	2.7×10^{-3} (147°C) I	
KOH	2×10^{-3} (350°C)	
$\text{H}_3\text{O}^+ - \beta\text{-Al}_2\text{O}_3$	1×10^{-4} (25°C)	Prepared by ion exchange method
$\text{NH}_4^+ - \beta\text{-}\beta''\text{-Ga}_2\text{O}_3$	1×10^{-2} (200°C)	
H_xWO_3		Mixed conductor
H_xMoO_3		
$(\text{ThO}_2)_{0.85}(\text{Y}_2\text{O}_3)_{0.15}$	6×10^{-3} (1200°C)	Perovskite-type structure
$\text{La}_{0.96}\text{Ca}_{0.04}\text{YO}_{3-x}$	5×10^{-4} (1000°C)	Protonic conduction under H-containing atmosphere
$\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-x}$	1×10^{-2} (900°C)	
$\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_{3-x}$	2×10^{-2} (800°C)	
$\text{PEO-H}_2\text{SO}_4$	2×10^{-4} (25°C)	Polyethylene oxide
$\text{PVA-H}_3\text{PO}_4$	$1 \times 10^{-5} \sim 10^{-3}$ (25°C)	Polyvinyl alcohol
La_2LiHO_3	1×10^{-6} (237°C)	Hydride ion conductor?

Fluoride and Chloride Ion Conductors

As a fluoride anion is monovalent and the smallest in its size among different kinds of anions, it is expected to be mobile in solids. Fluorite (CaF_2) is a typical fluorite-type structure of f.c.c. and the array of anions is somewhat coarse. As already shown in Fig. 1, the fluoride ion conductivity of PbF_2 is $3 \times 10^{-6} \text{ S cm}^{-1}$ at 600K and increases up to $10^{-4} \text{ S cm}^{-1}$ at 800°C , where some (5 ~ 10%)

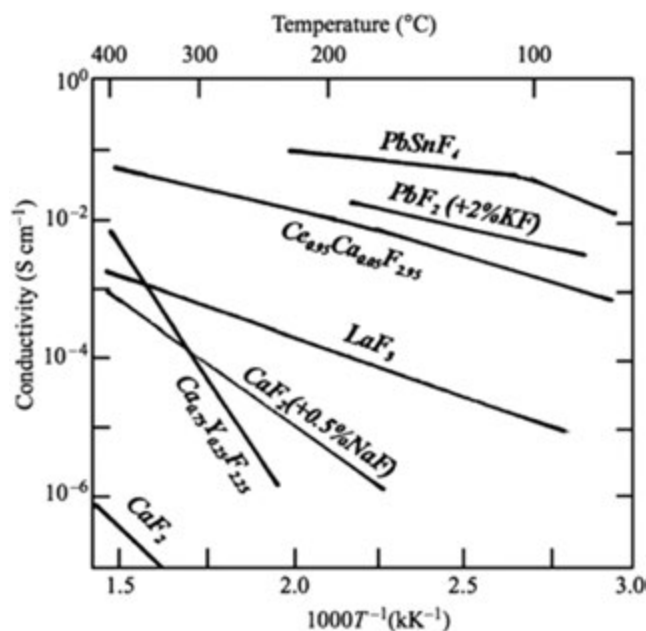


Fig. 10 Conductivity of fluoride ion conductors.

Table 8 Typical fluoride ion conductors

Material	Conductivity ($S\text{ cm}^{-1}$)	Note
$\text{Ca}_{0.894}\text{U}_{0.091}\text{Ce}_{0.005}\text{F}_{2.187}$	8×10^{-3} (150°C)	Fluoride
$\text{Pb}_{0.45}\text{Bi}_{0.25}\text{F}_{2.25}$	6×10^{-3} (150°C)	
PbSnF_4	8×10^{-2} (150°C)	
$\text{Ce}_{0.95}\text{Ca}_{0.05}\text{F}_{2.95}$	6×10^{-3} (150°C)	Tysonite
$(\text{ZrF}_4)_{0.50}(\text{BaF}_2)_{0.35}(\text{CsF})_{0.15}$	3×10^{-6} (150°C)	Glass
$(\text{InF}_3)_{0.35}(\text{SnF}_2)_{0.30}(\text{PbF}_2)_{0.35}$	8×10^{-4} (150°C)	

fluoride anions distribute in interstitial sites and generate fluoride ion vacancies which cause the high fluoride ion conductivity at high temperature.

A doping of lower valent cations for calcium sites creates anion vacancies, which allows fluoride anions to migrate in the crystal. The solid solution $(\text{CaF}_2)_{0.95}(\text{NaF})_{0.05}$ is an example. In fact, there are many kinds of fluoride ion conductors. They are roughly classified into three categories, ie, fluorite-type, PbCl_2 -type, and tysonite-type. Among the fluoride ion conductors, PbSnF_4 , whose crystal structure is a fluorite-related type, shows the highest conductivity as shown in Fig. 10. Since the tysonite-type LaF_3 is chemically stable with moderate conductivity, it is used as a selective electrode for fluoride ion sensors. Some fluoride glasses as $(\text{InF}_3)_{0.35}(\text{SnF}_2)_{0.4}(\text{PbF}_2)_{0.35}$ has also high conductivity around 10^{-3} S cm^{-1} at 150°C. Typical fluoride conductors are listed in Table 8.

As chloride ions are larger in size than fluoride ions, oxide ions and most of cations of the metallic elements, it is difficult for them to migrate easily in solids. However, some chloride ion conductors are known although their conductivity is low; for example, $(\text{PbCl}_2)_{0.97}(\text{KCl})_{0.33}$ shows $3 \times 10^{-3}\text{ S cm}^{-1}$ at 300°C. Doped SnCl_2 shows also high chloride conductivity but is chemically unstable in the atmosphere. It has been reported that the perovskite-type chloride CsPbCl_3 exhibits chloride ion conduction of $1 \times 10^{-3}\text{ S cm}^{-1}$ at 500°C.

Oxide Ion Conductors

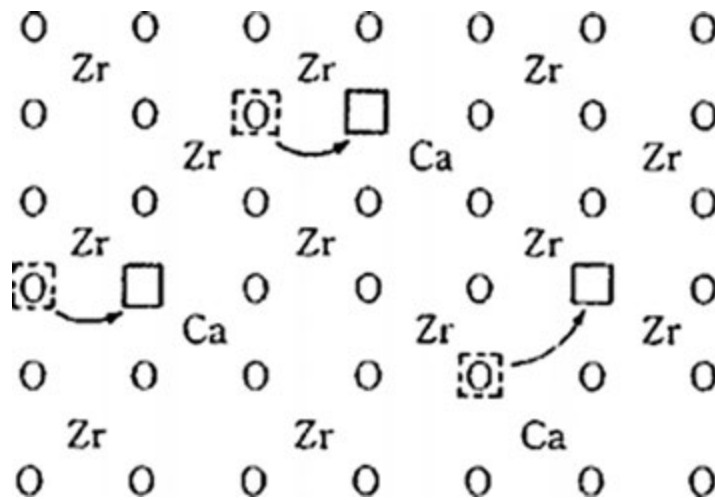
Similar to the fluoride ion conductors, rather small size oxide anion O^{2-} is often mobile in some solid oxides at elevated temperatures. Many kinds of oxide-ion conductors are known and are classified into several types (Tables 9 and 10). A series of defect fluorite-type oxides which have an appreciable amount of oxide ion vacancy is the most familiar. The host oxides are tetravalent oxides MO_2 or trivalent oxides (sesqui-oxides) M_2O_3 ; typical example of the former is stabilized zirconia, in which trivalent or divalent cations are partially substituted for tetravalent zirconium in ZrO_2 . Thus, oxide ion vacancies are formed as a

Table 9 Classification of oxide-ion conductors

Crystal type	Host oxide	Example
Fluoride-type		
MO ₂ -based	ZrO ₂ CeO ₂ ThO ₂	(ZrO ₂) _{0.92} (Y ₂ O ₃) _{0.08} (ZrO ₂) _{0.8} (Sm ₂ O ₃) _{0.2} (ThO) _{0.9} (CaO) _{0.1}
MO _{1.5} -based	Bi ₂ O ₃	(Bi ₂ O ₃) _{0.85} (Nb ₂ O ₅) _{0.15}
Perovskite-type		
Single perovskite	CaTiO ₃ LaGaO ₃	CaTi _{0.7} Al _{0.3} O _{3-α} La _{0.8} Sr _{0.2} Ga _{0.8} Mg _{0.2} O _{3-α}
Perovskite-related	Ba ₂ In ₂ O ₅	Ba ₂ In _{1.75} Ce _{0.25} O _{5.125}
Scheelite-type	PbWO ₄	Pb _{0.8} La _{0.2} WO _{4.1}

Table 10 Classification of oxide-ion conductors

Crystal type	Host oxide	Example
Fluorite	ZrO ₂ CeO ₂ ThO ₂ Bi ₂ O ₃	(ZrO ₂) _{0.92} (Y ₂ O ₃) _{0.08} (ZrO ₂) _{0.8} (Sm ₂ O ₃) _{0.2} (ThO) _{0.9} (CaO) _{0.1} (Bi ₂ O ₃) _{0.85} (Nb ₂ O ₅) _{0.15}
Single perovskite	CaTiO ₃ LaGaO ₃ BaTiO ₃	CaTi _{0.7} Al _{0.3} O _{3-α} La _{0.8} Sr _{0.2} Ga _{0.8} Mg _{0.2} O _{3-α} Na _{0.5} Bi _{0.5} TiO ₃
Perovskite-related	Ba ₂ In ₂ O ₅	Ba ₂ In _{1.75} Ce _{0.25} O _{5.125}
Scheelite-type	PbWO ₄	Pb _{0.8} La _{0.2} WO _{4.1}


Fig. 11 Mechanism of oxide ion conduction in stabilized zirconia.

result of charge compensation as shown in Fig. 11. At elevated temperatures of several hundred degree Celsius, oxide ions can easily move with the help of the vacancies and give rise to the high oxide ion conductivity. A representative ceramic is yttria-stabilized zirconia (YSZ), the typical composition of which is (ZrO₂)_{0.92}(Y₂O₃)_{0.08} (8Y). This ceramic is very popular and widely used in many fields because the conductivity is fairly good and cheap in cost. Magnesium-doped zirconia is often used because of its good resistance to thermal shock and calcium-doped zirconia because of low cost, although the conductivity is not as high as that of YSZ.

Ceria-based solid solutions composed of (CeO₂)_{1- x} (M₂O₃) _{x} are also oxide ion conductors of this class and the conductivity is, in general, higher than that of zirconias, although they are not so strong against a reducing atmosphere at high temperature as

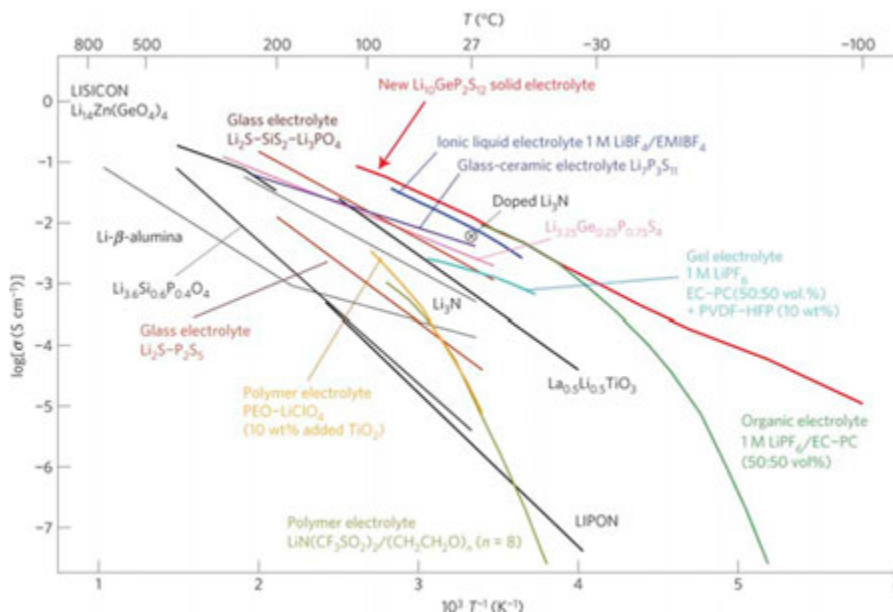


Fig. 12 Temperature dependence of conductivity of lithium ion (Kamaya *et al.*, 2011).

zirconia. The solid solutions based on thorium such as $(\text{ThO}_2)_{0.9}(\text{CaO})_{0.1}$ are oxide ion conductors although they are accompanied by hole conduction under an oxidizing atmosphere.

The conductivity of pure $\alpha\text{-Bi}_2\text{O}_3$ (below 730°C) is low and electronic. However, it is transformed above 730°C to $\delta\text{-Bi}_2\text{O}_3$ which belongs to the defect fluorite-type structure and this phase exhibits very high oxide ion conductivity as shown in Fig. 12. This high conductivity phase can be stabilized by substituting tri-, penta-, or hexavalent cations partially for bismuth; for example, $(\text{Bi}_2\text{O}_3)_{0.73}(\text{Y}_2\text{O}_3)_{0.27}$, $(\text{Bi}_2\text{O}_3)_{0.85}(\text{Nb}_2\text{O}_5)_{0.15}$, and $(\text{Bi}_2\text{O}_3)_{0.75}(\text{WO}_3)_{0.25}$, which exhibit high conductivity at around 500°C . However, they are not available for practical use since they are easily reduced under a reducing atmosphere at elevated temperatures. $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$.

Another category of oxide ion conductors is a series of *perovskite-type oxides* which have oxide ion vacancies in their lattice. The oxide ion vacancies are created by partial substitution of lower valent cations for host cations. One example is $\text{CaTi}_{0.7}\text{Al}_{0.3}\text{O}_{2.85}$ in which the tetravalent titanium in CaTiO_3 is partially replaced by trivalent aluminum to create oxygen vacancies, whose conductivity is as high as that of calcia-stabilized zirconia although it contains some electronic conduction under an oxidizing atmosphere at high temperature. Among the perovskite-type oxides, the LaGaO_3 -based oxides such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.115}\text{Co}_{0.085}\text{O}_3$ have very high oxide ion conductivity at around 600°C where next generation SOFC is expected to operate. The high-temperature phase (above 950°C) of brownmillerite $\text{Ba}_2\text{In}_2\text{O}_5$ is also a typical example, in which one sixth of the oxygen in the normal perovskite structure is deficient. This high conductivity phase can be stabilized by substituting cerium or zirconium partially for indium. Scheelite-type oxides such as PbWO_4 have been reported to exhibit oxide ion conduction with moderate conductivity.

Mixed Ionic-Electronic Conductors

The charge carrier in a solid electrolyte is typically one kind of ions of which the solid is composed. Stabilized zirconia, Na β -alumina and RbAg_4I_5 under normal condition are regarded as pure ionic conductors of oxide ions, sodium ions, and silver ions, respectively. However, some solids show both ionic and electronic conduction and sometimes the electronic conductivity σ_e is much higher than the ionic conductivity σ_i although the ionic conductivity itself is markedly high. These solids are called *mixed ionic-electronic conductors* (MIEC) or simply *mixed conductors*. The mixed conduction is often attributed to a nonstoichiometry of the compound especially in case of ionic crystals as oxides, sulfides and halides, where not only ionic defects but also electronic defects such as excess electrons e^- or holes h^+ can be generated by the nonstoichiometry. However, it is worth noted that even in a metallic solid like LiIn alloy, the lithium (ion) is fast diffusing, which can be categorized in MIEC also.

Silver chalcogenides such as $\text{Ag}_{1+\delta}\text{S}$ and $\text{Ag}_{1+\delta}\text{Se}$ seem outwardly to be n type electronic conductors. However, Ag^+ ion conductivity of these solids at elevated temperatures ($> 200^\circ\text{C}$) is in the order of 1 S cm^{-1} which is comparable to that of $\alpha\text{-AgI}$ at the same temperature range. The electronic conductivity is a few orders of magnitudes higher than the ionic one depending on the composition. Cu_2S is another example of a chalcogenide mixed conductor. This material shows Cu^+ ion conduction as well as p type electronic (hole) conduction.

Some insertion compounds can be put into this category; for example, Li_xCoO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$, Li_xTiS_2 , etc., are known as the cathode materials for lithium ion batteries, which have both electronic (hole) and lithium ionic conductivities. Also, in the anode

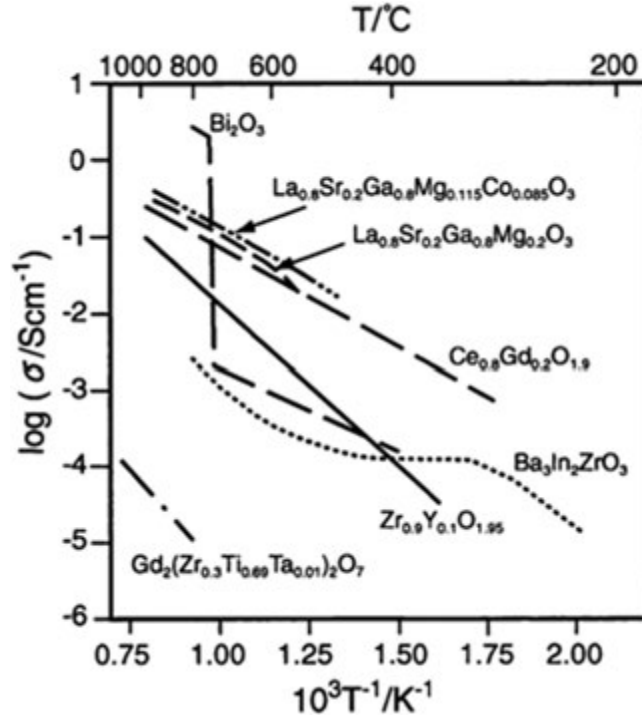


Fig. 13 Conductivity of typical oxide ion conductors (Sasaki, 2013).

(negative electrode) materials as Li_xC and alloys as Li_xIn , Li_xSn , Li_xSi , Li_xAl , Li_xMg , etc., are thought of electronic and lithium ion conductors. Another interesting example is $\beta\text{-Mg}_3\text{Bi}_2$, which has large diffusivity of Mg since the sublattice of small Mg is melting among the fixed Bi sublattice like $\alpha\text{-AgI}$ (Barnes *et al.*, 1994). H_xWO_3 which is used for electrochromic devices has large hydrogen mobility as well as high electronic conductivity.

Most important application of the ion-electron mixed conductors is the Solid Oxide Fuel Cells (SOFC), which works in very high temperature up to 800 to 1000°C where no metallic electrode is stable. Thus, the electronic conduction of oxide ceramics are used for the electrode materials, which have also the conductivity of oxide ions (Fig. 12). As was shown above, some oxide ion conductors have electronic (hole) conductivity under reduced or oxidative atmosphere, which is a drawback for the electrolyte but is useful for the electrodes.

Ceria-based oxide ion conductors as $(\text{CeO}_2)_{0.8}(\text{Sm}_2\text{O}_3)_{0.2}$ and $(\text{CeO}_2)_{0.8}(\text{Gd}_2\text{O}_3)_{0.2}$ become partially electronic conductors under a reducing atmosphere at high temperatures, where the ceria electrolytes are partially reduced and nonstoichiometric oxygen defects are formed with excess electrons which contribute to the electronic conduction. In general, the electronic conductivity of an oxide electrolyte at elevated temperatures is influenced by partial oxygen pressure ($p\text{O}_2$) surrounding them. The n type electronic conductivity σ_n increases with decreasing $p\text{O}_2$, whereas p type electronic conductivity σ_p increases with increase in $p\text{O}_2$. It is known that the relations between σ_n or σ_p and $p\text{O}_2$ are given by

$$\sigma_n = \sigma_n^0 \exp p\text{O}_2^{-1/n} \quad (9)$$

and

$$\sigma_p = \sigma_p^0 \exp p\text{O}_2^{1/n} \quad (10)$$

where n is a natural number, and σ_n^0 and σ_p^0 are constants which are independent of the partial pressure of oxygen. It is accepted that the ionic conductivity σ_i itself is rarely dependent on $p\text{O}_2$ for many oxide electrolytes. Accordingly, the total conductivity σ is expressed as,

$$\sigma = \sigma_i + \sigma_n^0 \exp p\text{O}_2^{-1/n} + \sigma_p^0 \exp p\text{O}_2^{1/n} \quad (11)$$

The relation between the logarithm of conductivity and logarithm of $p\text{O}_2$ is illustrated in Fig. 13. The hatched regions indicate the mixed conduction domains, and between them there exists an ionic conduction domain where the electronic conductivity is negligibly small. The outer sides of the mixed conduction domains are electronic conduction regions.

Some perovskite-type oxides containing transition elements exhibit mixed conduction at elevated temperatures. Doped-lanthanum cobaltites are mixed conductors in which oxide ions and holes are the charge carriers. The electronic conductivity is a few orders of magnitudes higher than that of the oxide ionic, although the ionic conductivity itself is sufficiently high ($> 1 \times 10^{-1} \text{ S cm}^{-1}$). High temperature-type protonic conductors based on, for example, SrCeO_3 and BaCeO_3 are a kind of mixed conductor under humidified air at high temperature. In this case, the charge carriers are both protons and electron holes.

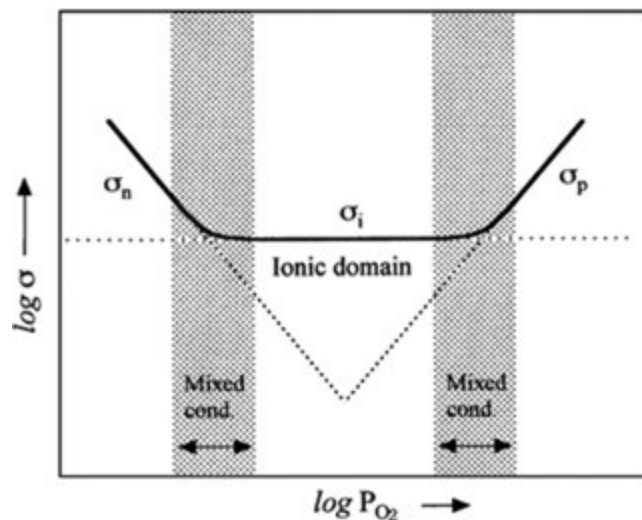


Fig. 14 Dependence of conductivity on oxygen partial pressure in the case of mixed conducting oxides.

Applications of Ion Conducting Solids

Benefits of Ion Conducting Solids for Applications

Ion conducting solids, ie, solid-state ionics materials are classified as solid electrolytes and mixed conductors, both of which have peculiar functions applicable in the field of advanced technologies. A solid electrolyte is a functional material in which mobile ions play an important role. In general, solid electrolytes have the following benefits:

- (i) They have both an electrical and a chemical function.
- (ii) They can serve both as ionic and structural materials.

With regards to point (ii) a solid electrolyte has a dual function, ie, it acts both as a structural material and as an ion conductor. In this sense, solid electrolytes are convenient compared to ion conducting liquids which need a container. With regard to (i) these materials conduct electricity while they simultaneously give rise to some chemical reactions at the surface of the electrolyte. Inversely, when different chemical reactions take place at both sides of the solid electrolyte surfaces, an electromotive force (EMF) is generated across the electrolyte.

Three Fundamental Functions Applicable to Devices

Ion conducting solid has the following three essential functions applicable to many electrochemical devices, ie, appearance of electromotive force, preferential permeation of a specific ion, and formation of large space charge.

An EMF is caused when a difference in concentration (or activity) of a specified chemical component is generated between the two sides of an ion conducting solid diaphragm. **Fig. 14** illustrates this phenomenon for the case of an oxide ion conductor. In this oxygen concentration cell the EMF, E , is given by

$$E = \frac{RT}{4F} \ln \frac{pO_2(1)}{pO_2(2)} \quad (12)$$

where $pO_2(1)$ and $pO_2(2)$ are the oxygen partial pressures in electrode compartment (1) and (2), respectively. This EMF phenomenon can be applied to chemical sensors and power cells (**Fig. 15**).

Fig. 16 shows a schematic illustration of the preferential permeation of oxygen in the case of an oxide ion conductor as an example. This function is based on a property that only one kind of ion can move in a solid electrolyte. Using this function, one can extract a specified element from a mixture or a molecule. This can be applied to the electrolysis of molecules and separation of specified gas from gas mixture. Formation of large space charge is caused by uneven distribution of mobile ions after an electric field was applied.

Application Examples

There are many possible applications of ion conducting solids. First group is chemical sensors; for example, oxygen gas sensors for automobile engine control or steel making, NO_x sensors and cleaner for exorsts gas controle, CO_2 sensors. Second group is

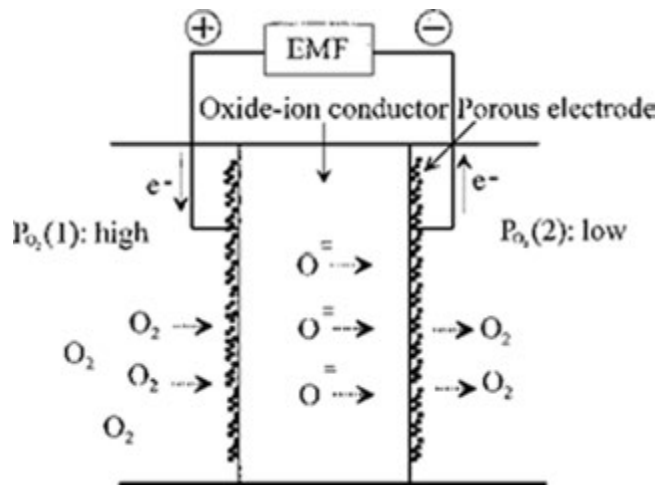


Fig. 15 EMF of oxygen concentration cell.

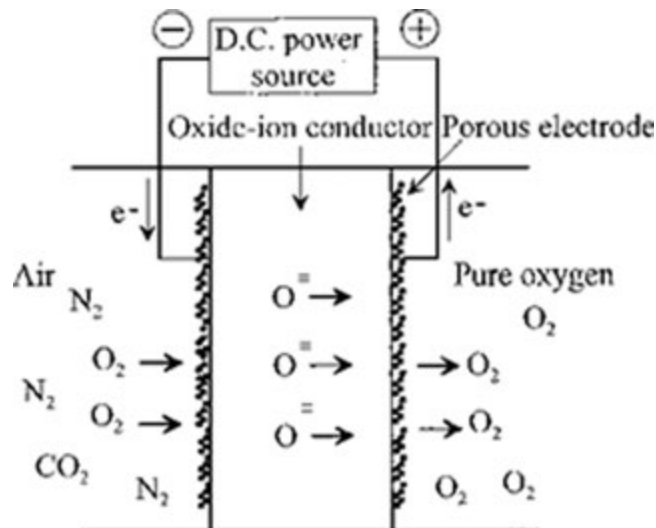


Fig. 16 Oxygen purification by oxide ion conductor.

electrochemical energy sources such as lithium ion battery, NaS battery and various fuel cells. Third kind is for ion transfer membrane for gas purification, electrochemical reactors. Fourth kind is for electronic devices as electrochromic display, or atom-switch etc. Some of them are depicted below.

(a) Sensors

The appearance of an EMF across a solid electrolyte is based on the principle of an electrochemical cell or battery. The batteries for practical use are classified into "signal" cell and "power" cell. The signal cell is used as a sensor for measuring the concentration of a specified material. For example, with regards to oxygen, if $p_{O_2}(1)$ in Eq. (12) is known and is constant, the partial pressure of oxygen in compartment (2) can be determined from the EMF of the cell and this functions as an oxygen sensor. Oxygen sensors using stabilized zirconia as an oxide ion conductor are now widely used for the analysis of exhaust gases from engines, industrial furnaces, respiration, etc. This sensor works at temperatures higher than 400°C . At lower temperatures the electrode polarization and ohmic resistance are too large to give an exact EMF of the cell. They are also used to probe the oxygen activity in molten iron in the steel making process. Besides the oxygen sensors, a fluoride ion sensor using fluoride ion-conducting solid LaF_3 and a sodium sensor using $\text{Na } \beta\text{-alumina}$ are in practical use. A hydrogen sensor for molten aluminum in industrial casting processes has been developed using the proton conducting ceramic of $\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-x}$. SO_x and NO_x sensors using sodium ion conductor or oxide ion conductors with sulfates or nitrates as auxiliary materials are developed.

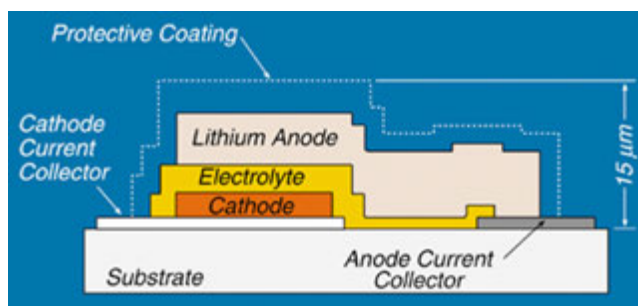


Fig. 17 Concept of all-solid-state thin-film lithium battery (Bates *et al.*, 2000).

(b) Lithium ion batteries

After the invention of rechargeable Lithium Ion Batteries (LIB) in 1980, they have been used in mobile phone, PC, tablet, etc., for IT devices and now for plug-in-hybrid (PHV) and electric vehicles (EV). For this purpose, the lithium ion transport in solids, liquid, polymer and gels has been widely investigated. A conventional lithium ion battery consists of lithium transition metal oxide (eg, LiCoO_2 , LiMn_2O_4 , LiFePO_4 , etc.) for cathode, lithium carbon (Li_xC) or lithium alloys (Li_xSn , Li_xSi , etc.) for anode, and organic liquid electrolyte ($\text{EC} + \text{DMC} + \text{LiPF}_6$, etc.). Those cathode and anode materials are considered as ion-electron mixed conductors as shown in the section on Mixed Ionic-Electronic Conductors, although whose ionic conductivity is much smaller than the electronic one.

If the liquid electrolyte of the LIB is replaced by a solid electrolyte, an all-solid state lithium battery can be constructed, which has a big merit on safety and long life stability. For this purpose, sulfide based solid electrolytes such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ and similar glasses are developed as the first candidate since its conductivity is as high as conventional liquid electrolytes. However, it is rather unstable against the contact to lithium metal and water. Oxide based solid electrolytes such as LIPON, LLZ etc., are the other candidates, which are stable to lithium metal although the conductivity is lower than the sulfides. In order to reduce the resistance of the solid electrolyte, thin film technology is developed to construct all-solid-state thin-film batteries (TFB), in which the electrolyte thickness is $1\text{ }\mu\text{m}$ or less and the total thickness is less than $100\text{ }\mu\text{m}$ (see Fig. 17). In spite of the small capacity of the TFB it is now recognized very suitable for micro wearable or implant devices as well as energy harvesting applications.

(c) NaS battery

Because of the larger natural abundance of sodium than lithium, many studies are under going to construct large scale sodium batteries for mega watt (MW) class. The principle of the sodium battery is similar to that of lithium, however the higher reactivity of sodium hampered the development. Only so called NaS battery is commercially available at present. The working principle of a NaS battery is shown in Fig. 18. A single cell is made of a $\text{Na}\beta''$ -alumina ceramic tube containing liquid sodium metal and surrounded by molten sulfur. The cell is sealed in a stainless steel tube working as a current collector. The cell is working above 300°C to keep the sodium and sulfur in molten state. Single cell voltage is 1.8 V and the capacity of 1220 Wh, which is assembled to 384 cells of 400 kWh. Farther assembling them to construct large scale energy storage system up to 50 MW is developed by NGK Insulators, LTD, Japan, which is now widely used for back-up system and load leveling of wind and solar energies.

(d) Solid oxide fuel cell (SOFC)

The principle of the SOFC is shown in Fig. 19, where the hydrogen gas reacts with oxide ions in solid electrolyte (eg, YSZ) to produce water and electricity. This type of power generator is, in principle, very high in efficiency, clean in exhaust gas, and silent to run. Siemens-Westinghouse Co. have developed 100 kW-scale SOFC. IX and Tokyo Gas have sold s SOFC of max. 700 W for home stationary use, which is equipped with reforming system of natural gas to hydrogen and cogeneration system to use the exhost heat for hot water supply.

(e) Electrolysis of gaseous molecules

If a fuel cell is operated inversely, hydrogen is obtained from steam; for example, polymer electrolyte type PEM electrolyzer and solid oxide electrolyzer cell (SOEC) are known. This method is a promising way to produce hydrogen effectively in large scale, and will be a powerful tool for the future age of hydrogen economy, however the efficiency and cost are still the neck for practical use. Steam electrolysis is also possible using proton conducting ceramics. In this case pure hydrogen free from water vapor is obtained.

(f) Gas separation

By using oxide ion conductors or proton conductors, pure oxygen or hydrogen gas can be obtained in a one-step operation as shown in Fig. 16. Electrochemical oxygen pumps made of stabilized zirconia are on the market. This device can pump up or add oxygen gas preferentially from or to a gas mixture and is utilized in many laboratories. A hydrogen pump which uses proton-conducting ceramics is in development.

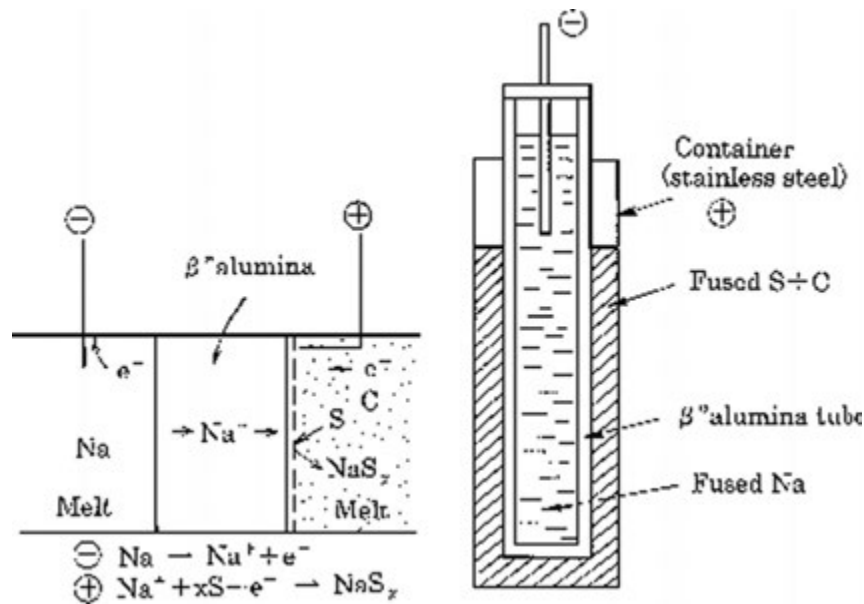


Fig. 18 Concept and structure of NaS battery.

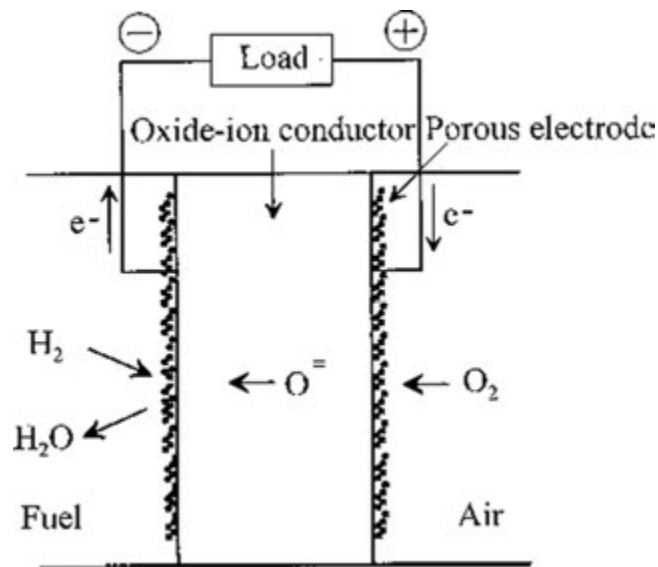


Fig. 19 Concept of solid oxide fuel cell (SOFC).

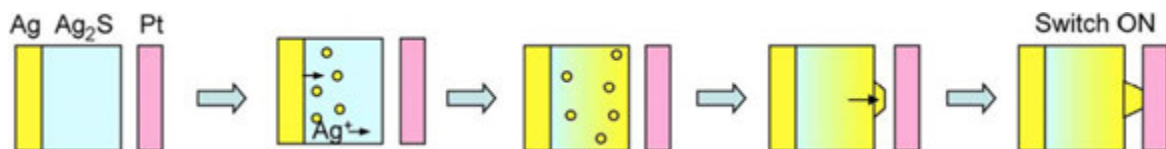


Fig. 20 Principle of atomic switch (Aono and Hasegawa, 2010).

(g) Atomic switch or nano-ionics circuits

Electrochemical deposition of metals from solid electrolyte is common phenomena in solid state ionics, however whose nano-scale control is now open the door to new electric circuit technology called "Atomic Switch" (Aono and Hasegawa, 2010), "Nanoionics switch" (Wase and Aono, 2007). The principle is shown in Fig. 20, where Ag metal wire works as a source of silver ions and Pt metal is

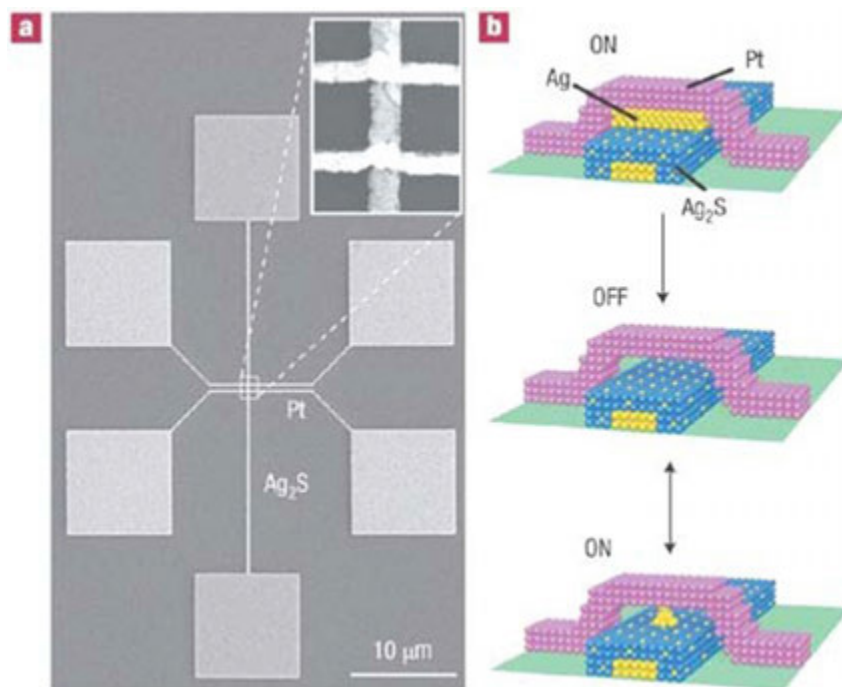


Fig. 21 An example of nano-ionics switch architecture (Wase and Aono, 2007).

the collector of deposited silver metal filament. Ag_2S is an ionic-electronic mixed conductor which works as a transfer channel of silver ions and also electronic current conductor when the switch is on. When the top Ag electrode is positively biased and Pt is negative, a potential difference appears on the gap between the Pt and Ag_2S , which generates the accumulation of silver ions in the Ag_2S and finally the oversaturated silver metals start to form a small needle at the bottom of the Ag_2S . The needle finally contacts to the Pt electrode and the both electrodes are short circuited. When the potential bias is reversed, the precipitated silver needle between the Ag_2S and Pt is absorbed into the Ag_2S and the circuit is now open. Starting from this principle, many circuit designs are now proposed. A prototype device design is shown in Fig. 21. These phenomena are reversible in nano-scale and is used for a memory device, switching device, synaptic switch etc. For this purpose, not only the Ag_2S but many ionic conductors and mixed conductors have been tested now.

References

- Aono, M., Hasegawa, T., 2010. The atomic switch. One of the ultimate switches could be an atomic switch, where two terminals in a metal–oxide–metal structure are connected or disconnected by a metal atomic bridge or wire-like filament. *Proc. IEEE* 98, 2228–2236.
- Barnes, A.C., Guo, C., Howells, W.S., 1994. Fast-ion conduction and the structure of $\beta\text{-Mg}_3\text{Bi}_2$. *Journal of Physics – Condensed Matter* 6, 467–471.
- Bates, J.B., Dudney, N.J., Neudecker, B., Ueda, A., Evans, C.D., 2000. Thin-film lithium and lithium-ion batteries. *Solid State Ionics* 135, 33–45.
- Boyce, J.B., Huberman, B.A., 1979. Superionic conductors: Transitions, structures, dynamics. *Physics Reports* 51, 189–265.
- Catlow, C.R.A., 1989. Superionic fluorites. In: Laskar, A.L., Chandra, S. (Eds.), *Superionic Solids and Solid Electrolytes*. Boston: Academic Press, pp. 339–379.
- Funke, K., 2013. Solid state ionics: From Michael Faraday to green energy – The European dimension. *Science and Technology of Advanced Materials* 14, 043502. 50 pp.
- Haile, S.M., Chisholm, C.R., Sasaki, K., Boysen, D.A., Uda, T., 2007. Solid acid proton conductors: From laboratory curiosities to fuel cell electrolytes. *Faraday Discussions* 134, 17–39.
- Hayashi, A., Noi, K., Sakuda, A., Tatsumisago, M., 2012. Superionic glass-ceramic electrolytes for room-temperature rechargeable sodium batteries. *Nature Communications* 3, Article number: 856.
- Hayashi, K., Matsuishi, S., Kamiya, T., Hirano, M., Hosono, H., 2002. Light-induced conversion of an insulating refractory oxide into a persistent electronic conductor. *Nature* 419, 462–465.
- Hull, S., 2004. Superionics: Crystal structures and conduction processes. *Reports on Progress in Physics* 67, 1233–1314.
- Kamaya, N., Homma, K., Yamakawa, Y., *et al.*, 2011. A lithium superionic conductor. *Nature Materials* 10, 682–686.
- Kawamura, J., Asayama, R., Kuwata, N., Kamishima, O., 2006. Ionic transport in glass and polymer: Hierarchical structure and dynamics. In: Sakuma, T., Takahashi, H. (Eds.), *Physics of Solid State Ionics*. India: Research Signpost, pp. 193–246.
- Kawamura, J., Kuwata, N., Asayama, R., 2007. Ionic motion in organic inorganic hybrid materials. In: Seichiro Ikehata (Ed.), *Protonics in Plastic Materials*. Kerala, India: Transworld Research Network, pp. 1–26.
- Kobayashi, G., Hinuma, Y., Matsuoka, S., *et al.*, 2016. Pure H^- conduction in oxyhydrides. *Science* 351, 1314–1317.
- Kobayashi, Y., *et al.*, 2012. An oxyhydride of BaTiO_3 exhibiting hydride exchange and electronic conductivity. *Nature Materials* 11, 507–511.
- Kroger, F.A., 1964. *The Chemistry of Imperfect Crystals*. Amsterdam: North-Holland.
- MacFarlane, D.R., Forsyth, M., 2001. Plastic crystal electrolyte new perspectives on solid state ionics. *Advanced Materials* 13, 957–966.
- Matsuo, M., Remhof, A., Martelli, P., *et al.*, 2009. Complex hydrides with $(\text{BH}_4)^-$ and $(\text{NH}_2)^-$ anions as new lithium fast-ion conductors. *Journal of American Chemical Society* 131, 16389–16391.

- Nomura, K., Ikeda, S., Ito, K., Einaga, H., 1992. Framework structure, phase transition, and transport properties in $\text{MII}Zr_4(\text{PO}_4)_6$ compounds (MII = Mg, Ca, Sr, Ba, Mn, Co, Ni, Zn, Cd, and Pb). *Bulletin of the Chemical Society of Japan* 65, 3221–3227.
- Norby, T., Widerøe, M., Glöckner, R., Larring, Y., 2004. Hydrogen in oxides. *Dalton Transactions*. 3012–3018.
- Sasaki, K., Eguchi, K., 2013. Oxide ion conductors. In *Design, Synthesis and Application of Ionic Conducting Materials*. Tokyo: TIC Pub., (in Japanese).
- Thangadurai, V., Kaack, H., Weppner, W.J.F., 2004. Novel fast lithium ion conduction in garnet-type $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ (M = Nb, Ta). *Journal of the American Ceramic Society* 86, 437–440.
- Udovic, T.J., Matsuo, M., Tang, W.S., *et al.*, 2014. Exceptional superionic conductivity in disordered sodium decahydro-closo-decaborate. *Advanced Materials* 26, 7622–7626.
- Wase, R., Aono, M., 2007. Nanoionics-based resistive switching memories. *Nature Materials* 6, 833–840.
- Yoshikado, S., Ohachi, T., Taniguchi, I., *et al.*, 1982. AC ionic conductivity of Hollandite type compounds from 100 Hz to 37.0 GHz. *Solid State Ionics* 7, 335–344.

Further Reading

- Bruce, P.C., 1995. *Solid State Electrochemistry*. Cambridge: Cambridge University Press.
- Chandra, S., 1981. *Superionic Solids*. New York: North-Holland.
- Colomban, P., 1992. *Proton Conductors*. Cambridge: Cambridge University Press.
- Gellings, P.J., 1996. *The CRC Handbook of Solid State Electrochemistry*. Gellings-Bouwmeester: CRC Press.
- Gschneidner, K.A., Eyring, L., 2000. *Handbook on the Physics and Chemistry of Rare Earth*. Amsterdam: Elsevier.
- Iwahara, H., Esaka, T., Uchida, H., Maeda, N., 1981. Proton conduction in sintered oxides and its application to steam electrolysis for hydrogen production. *Solid State Ionics* B 3/4, 359–363.
- Kudo, T., Fueki, K., 1990. *Solid State Ionics*. Tokyo: Kodansha VCH.
- Kudo, T., Kawamura, J., 2005. Fast ionic conductors. In: Sorrell, C.C., Sugihara, S., Nowotny, J. (Eds.), *Materials for Energy Conversion Devices*. Woodhead Publishing in Materials. Cambridge: Woodhead Publishing Ltd., pp. 174–211.
- Laskar, A.L., Chandra, S., 1989. *Superionic Solids and Solid Electrolytes: Recent Trends*. San Diego, CA: Academic Press.
- Minh, N.Q., Takahashi, T., 1995. *Science and Technology of Ceramic Fuel Cells*. Amsterdam: Elsevier.

Development, Structure, and Mechanical Properties of Sulfide Solid Electrolytes

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Introduction

Since their commercialization in the 1990s, lithium-ion secondary batteries (LIBs) have been widely used in mobile phones, personal computers, automobiles, and aircraft as high-voltage and high-energy-density batteries, thus contributing to our daily lives. Recently, the research and development of all-solid-state batteries have been accelerating to further improve the safety and performance of LIBs. For all-solid-state batteries, the risk of liquid leakage and ignition can be suppressed by replacing the conventionally used organic electrolyte with a flame-retardant inorganic solid electrolyte, increasing their safety and reliability. All-solid-state batteries are mainly classified into two types: thin-film and bulk types. The thin film type is fabricated by laminating electrode active materials, then solid electrolytes are formed by sputtering or vapor deposition, while the bulk type is fabricated by laminating layers of different powders. The bulk type is suitable for large batteries because the capacity can be increased by increasing the amount of the electrode active material powder.

In a bulk type, a mixture of electrode active material, solid electrolyte, and conductive additive powders are used as a composite electrode. To realize a uniform electrode reaction in the electrode layer, it is key to form a path for the continuous conduction of sufficient ions or/and electrons to the active material. For this reason, research and development on bulk-type all-solid-state batteries have focused on the following two points:

- (1) Finding a solid electrolyte with a high ionic conductivity.
- (2) How to build an excellent solid–solid interface between electrode active materials and solid electrolytes.

This chapter first introduces the development of sulfide solid electrolytes with a high lithium ion conductivity. After that, the structures of typical sulfide glasses under several conditions are described. Finally, results obtaining by the authors for the mechanical properties of sulfide solid electrolytes that are advantageous for forming a solid–solid interface are given.

Crystalline Solid Electrolytes

Typical sulfide solid electrolytes that have been developed so far are summarized in [Table 1](#). Sulfide solid electrolytes are mainly classified into three types: crystal, glassy, and glass ceramic. A series of sulfide crystals called thio-LISICON was developed in the 2000s, and $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ of the Li_4GeS_4 – Li_3PS_4 series was reported to have a high lithium ionic conductivity of $2.2 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature ([Kanno and Murayama, 2001](#)). These sulfide crystals have low ionic conductivities of $10^{-7} \text{ S cm}^{-1}$ or less for simple compositions such as Li_4GeS_4 and Li_4SiS_4 , but the substitution of Ge^{4+} or Si^{4+} to Al^{3+} or P^{5+} increases the lithium ionic conductivity. In 2010, the sulfide crystal $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) with a very high ionic conductivity on the order of $10^{-2} \text{ S cm}^{-1}$ was found ([Bron et al., 2013](#); [Kamaya et al., 2011](#)). Then, the sulfide crystal $\text{Li}_{9.54}\text{SiP}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ with the highest ever reported ionic conductivity of $2.5 \times 10^{-2} \text{ S cm}^{-1}$ was discovered in 2016 ([Kato et al., 2016](#)). An all-solid-state battery using this crystal as a solid electrolyte has an extremely high charge and discharge of 1500C at 100°C. On the other hand, Ge- and Si-containing systems have problems with the stability of highly reducible negative electrodes such as lithium metal. As systems that do not contain Ge or Si, $\text{Li}_{9.6}\text{P}_3\text{S}_{12}$ ([Bron et al., 2013](#)) of the LGPS type and $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) ([Boulinau et al., 2012](#)) of the argyrodite type were discovered, which have high ionic conductivities of $10^{-3} \text{ S cm}^{-1}$. These sulfide crystals are usually produced by a solid-phase synthesis in which raw powders are mixed and then heated at a high temperature of 400–700°C. Yubuchi et al. reported that an argyrodite-type sulfide crystal can be synthesized in a liquid phase in a mixed solvent of THF and ethanol ([Yubuchi et al., 2019](#)). Since the argyrodite crystals are dissolved in the solvent, argyrodite solid electrolytes can be deposited so as to cover the electrode active material particles, and a wide contact interface can be formed between the electrode active material and the solid electrolyte.

Glassy and Glass-ceramic Solid Electrolytes

Prior to the development of the above-mentioned crystalline sulfide solid electrolytes, Li_2S – P_2S_5 – LiI ([Mercier et al., 1981](#)) and Li_2S – B_2S_3 – LiI ([Wada et al., 1983](#)) glassy electrolytes exhibiting a conductivity of about $10^{-3} \text{ S cm}^{-1}$ were reported in the 1980s. A melt-quench method is generally used to synthesize amorphous materials such as glasses. The authors and others prepared that oxy-sulfide glasses with various lithium ortho-oxo acids of the form Li_xMO_y ($\text{Li}_x\text{MO}_y = \text{Li}_4\text{SiO}_4, \text{Li}_3\text{PO}_4$) added to the Li_2S – SiS_2 system by the melting method ([Aotani et al., 1994](#); [Minami et al., 2006](#)). In both glasses, a high ionic conductivity of $10^{-3} \text{ S cm}^{-1}$ was exhibited when a small amount (5 mol%) of lithium ortho-oxo acid was added. On the other hand, a mechanochemical

Table 1 Chemical composition of some sulfide solid electrolytes and their conductivities at room temperature

Composition	Conductivity at RT ($S\text{ cm}^{-1}$)	Classification	Reference
$\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$	2.2×10^{-2}	Crystal	Kanno and Murayama (2001)
$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$	1.2×10^{-2}	Crystal	Kamaya <i>et al.</i> (2011)
$\text{Li}_{10}\text{SnP}_2\text{S}_{12}$	4×10^{-3}	Crystal	Bron <i>et al.</i> (2013)
$\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$	2.5×10^{-2}	Crystal	Kato <i>et al.</i> (2016)
$\text{Li}_{10.35}[\text{Sn}_{0.27}\text{Si}_{1.08}]\text{P}_{1.65}\text{S}_{12}$	1.1×10^{-2}	Crystal	Sun <i>et al.</i> (2017)
$\text{Li}_{9.6}\text{P}_3\text{S}_{12}$	1.2×10^{-3}	Crystal	Kato <i>et al.</i> (2016)
$\text{Li}_6\text{PS}_5\text{Cl}$	1.3×10^{-3}	Crystal	Boulineau <i>et al.</i> (2012)
$70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$	1.6×10^{-4}	Glass	Zhang and Kennedy (1990)
$30\text{Li}_2\text{S} \cdot 26\text{B}_2\text{S}_3 \cdot 44\text{LiI}$	1.7×10^{-3}	Glass	Wada <i>et al.</i> (1983)
$50\text{Li}_2\text{S} \cdot 17\text{P}_2\text{S}_5 \cdot 33\text{LiBH}_4$	1.6×10^{-3}	Glass	Yamauchi <i>et al.</i> (2013)
$63\text{Li}_2\text{S} \cdot 36\text{SiS}_2 \cdot 1\text{Li}_3\text{PO}_4$	1.5×10^{-3}	Glass	Aotani <i>et al.</i> (1994)
$70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5 (\text{Li}_7\text{P}_3\text{S}_{11})$	1.7×10^{-2}	Glass-ceramic	Seino <i>et al.</i> (2014)
$80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$	1.3×10^{-3}	Glass-ceramic	Mizuno <i>et al.</i> (2006)
$63\text{Li}_2\text{S} \cdot 27\text{P}_2\text{S}_5 \cdot 10\text{LiBr}$	8.4×10^{-3}	Glass-ceramic	Ujiie <i>et al.</i> (2014)
$60\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5 \cdot 10\text{Li}_3\text{N}$	1.4×10^{-3}	Glass-ceramic	Fukushima <i>et al.</i> (2017)

method has been developed for forming an amorphous material (Hayashi *et al.*, 2001; Hayashi *et al.*, 2016), in which high-speed planetary ball mills are used to mechanically crush and grind raw materials to induce a chemical reaction. This method enables the production of glass at ordinary temperatures and ordinary pressure. Since the composite is a fine powder, it can be easily used for bulk-type all-solid-state batteries. Furthermore, although the Li_2S content of the glass obtained by the melt quenching method was only up to 70 mol%, the Li_2S content in the Li_2S – P_2S_5 system was increased to 75 mol% by using the mechanochemical method (Hayashi *et al.*, 2001). Moreover, it was found that a glass ceramic with a Li_2S content of 80 mol% was precipitated by heat-treating the glass above the crystallization temperature, which is similar to the LGPS-type phase and has a high ionic conductivity of 10^{-3} S cm^{-1} (Mizuno *et al.*, 2006). A glass-ceramic phase having a Li_2S content of 70 mol% obtained by heating and crystallizing a glass exhibited a high ionic conductivity of 10^{-2} S cm^{-1} (Seino *et al.*, 2014). Furthermore, it has been found that a sulfide glass having a Li_2S content of 75 mol% exhibits a high ionic conductivity if it is heated at a high temperature before crystallization (Shiotani *et al.*, 2017).

Structure for Li_2S – P_2S_5 Glassy System (Ohara *et al.*, 2016)

The lithium ionic conductivity of $67\text{Li}_2\text{S} \cdot 33\text{P}_2\text{S}_5$ ($67\text{Li}_2\text{S}$), $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$ ($70\text{Li}_2\text{S}$), and $75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ ($75\text{Li}_2\text{S}$) glasses are 5.6×10^{-5} , 1.4×10^{-4} , and $3.0 \times 10^{-4}\text{ S cm}^{-1}$, respectively. The bulk structure and the environment of the Li^+ ions were studied by structural analysis combining X-ray and neutron diffraction with the aid of density functional theory (DFT)/reverse Monte Carlo (RMC) simulation and Raman spectroscopy to reveal the relationship between structural properties and lithium ionic conductivity.

To quantitatively evaluate the fraction of PS_x polyhedral anions, the Raman spectra of $67\text{Li}_2\text{S}$, $70\text{Li}_2\text{S}$, and $75\text{Li}_2\text{S}$ glasses were obtained, as shown in Fig. 1(a). Bands in the frequency range of 330 – 480 cm^{-1} are sensitive to the S–P–S bond angle. On the basis of previous studies (Mizuno *et al.*, 2005; Tachez *et al.*, 1984), we assigned the three bands at approximately 425 , 410 , and 390 cm^{-1} to the stretching vibration of the $\text{P}_2\text{S}_6^{3-}$ (ortho-thiophosphate) ion, $\text{P}_2\text{S}_7^{4-}$ (pyro-thiophosphate) ion, and $\text{P}_2\text{S}_6^{4-}$ (an ethane like structure with a P–P bond) ion, respectively. Since the scattering coefficient in Raman spectroscopy is affected by the PS_x polyhedral anion (Iwamoto *et al.*, 1987; Umesaki *et al.*, 1993), the ratios of the $\text{P}_2\text{S}_6^{3-}$, $\text{P}_2\text{S}_7^{4-}$, and $\text{P}_2\text{S}_6^{4-}$ ions were estimated by a Lorentzian function, shown as dotted lines in Fig. 1(b), and are summarized as open circles, open triangles, and open squares in Fig. 1(c), respectively. It is clear that the ratio of $\text{P}_2\text{S}_6^{3-}$ ions increases with the Li_2S content, while the ratios of $\text{P}_2\text{S}_7^{4-}$ and $\text{P}_2\text{S}_6^{4-}$ ions decrease. This tendency is in good agreement with that observed in previous studies (Hayashi *et al.*, 2010a,b; Mizuno *et al.*, 2005). Furthermore, the band corresponding to the stretching vibration of the P–P bond also disappears at approximately 530 cm^{-1} for the $75\text{Li}_2\text{S}$ glass, as shown in the inset of Fig. 1(a). Since the band at 547 cm^{-1} for polycrystalline $\text{Li}_4\text{P}_2\text{S}_6$ is characterized by the stretching vibration of the P–P bonds (Mercier *et al.*, 1982), the bands observed at 530 cm^{-1} in the glasses are related to the P–P stretching vibration. The disappearance of this band is consistent with the decrease in the ratio of $\text{P}_2\text{S}_6^{4-}$ ions. Intriguingly, it was found that $\text{P}_2\text{S}_6^{4-}$ ions exist in these glasses with ratios of approximately 33.0%, 18.3%, and 4.4% in $67\text{Li}_2\text{S}$, $70\text{Li}_2\text{S}$, and $75\text{Li}_2\text{S}$, respectively, whereas they should not be contained in the stoichiometric compositions ($0\text{PS}_4:100\text{P}_2\text{S}_7$ in $67\text{Li}_2\text{S}$, $50\text{PS}_4:50\text{P}_2\text{S}_7$ in $70\text{Li}_2\text{S}$, and $100\text{PS}_4:0\text{P}_2\text{S}_7$ in $75\text{Li}_2\text{S}$). This means that there is a sulfur deficiency in these glasses. The sulfur deficiency is consistent with the result of an inductively coupled plasma analysis. Hayashi *et al.* (2010b) found by NMR measurement that a small number of $\text{P}_2\text{S}_6^{4-}$ ions are formed in the glass ceramic $70\text{Li}_2\text{S} \cdot 28\text{P}_2\text{S}_5 \cdot 2\text{P}_2\text{S}_3$, and the degradation of conductivity is expected to be caused by the formation of $\text{P}_2\text{S}_6^{4-}$ ions.

To extract quantitative information on the atomic arrangements in the glassy materials from the diffraction data, the total correlation functions $4\pi r\rho_0 g(r)$, where ρ_0 is the average atom number density and $g(r)$ is the pair distribution function, were

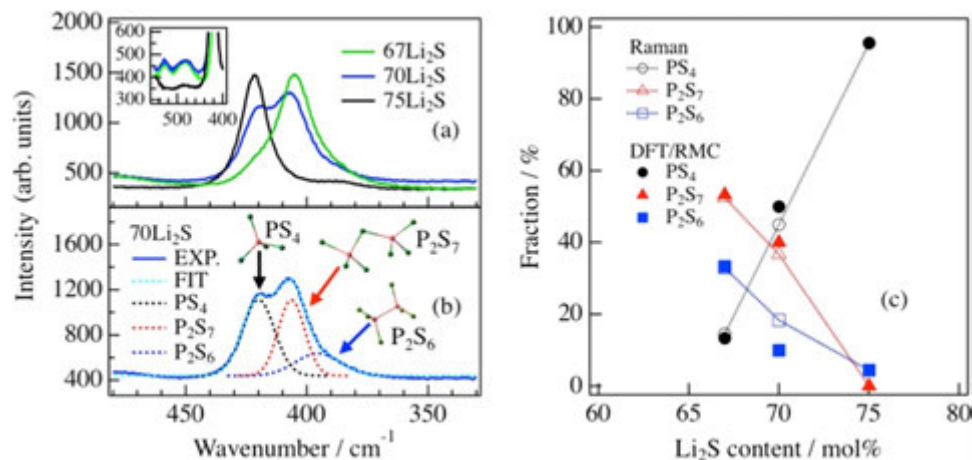


Fig. 1 (a) Raman spectra in the range of 330–480 cm⁻¹ for Li₂S–P₂S₅ glasses. Black, blue, and green lines represent 75Li₂S, 70Li₂S, and 67Li₂S glasses, respectively. The spectra in the range of 400–560 cm⁻¹ are enlarged in the inset for clarity. (b) Spectral decomposition of Raman spectrum for 70Li₂S glass. Blue line, experimental data; dotted lines, fitting results for all PS polyhedra (light-blue), and PS₄ (black), P₂S₇ (red), and P₂S₆ (blue) anions. (c) PS_x polyhedral fractions for Li₂S–P₂S₅ glasses derived from Raman spectra (open marks) and DFT/RMC model (filled marks).

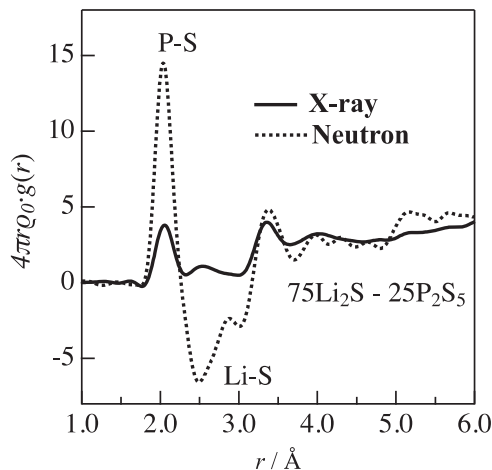


Fig. 2 Total correlation functions $4\pi r \rho_0 g(r)$ for 75Li₂S glasses derived from X-ray (solid line) and neutron (dotted line) diffraction results.

calculated for each glass by Fourier transformation of the X-ray and neutron diffraction data (Keen, 2001). Fig. 2 shows $4\pi r \rho_0 g(r)$ for 75Li₂S glass. From the negative coherent scattering length of neutrons for ⁷Li (hereafter the superscript is omitted), it is possible to identify the P–S and Li–S correlation lengths. The first peak at approximately 2.0 Å in both sets of diffraction data is related to the P–S correlation associated with the PS₄ tetrahedral anions, while the second negative peak at approximately 2.5 Å is related to the Li–S correlation length. Both lengths are similar for all compositions and hence do not provide any specific information to help identify the structural features.

To uncover the relationship between the glassy structure and the high ionic conductivity for these glasses, the authors modeled the atomic structure of the Li₂S–P₂S₅ glasses by DFT/RMC simulation using X-ray and neutron diffraction data, fixing the ratios of the PS₄³⁻, P₂S₇⁴⁻, and P₂S₆⁴⁻ ions on the basis of Raman spectroscopy measurements to reproduce the plausible glassy structures. The DFT/RMC model is consistent with the experimental data.

To obtain information on the partial correlation in real space, the partial pair distribution functions (PDFs), $g_{ij}(r)$, for the Li₂S–P₂S₅ glasses were calculated from the DFT/RMC model. $g_{ij}(r)$ for P–S correlation, $g_{P-S}(r)$, has a peak at approximately $r = 2.0$ Å and a shoulder on the high- r side. This bond length is consistent with that of a bridging sulfur (BS) in a P–S–P bond. $g_{Li-S}(r)$ also has a peak at approximately $r = 2.5$ Å, which is consistent with the experimental results for the PDF. Furthermore, $g_{P-P}(r)$ has two peaks at $r = 2.2$ Å and $r = 3.5$ Å, corresponding to the bond length of the P₂S₆⁴⁻ ion and the correlation length of the P₂S₇⁴⁻ ion, respectively. All the $g_{ij}(r)$ peaks except for that of Li–Li are well defined and sharp because the combination of X-ray diffraction, neutron diffraction, and DFT calculation provides us with a sufficient number of factors for each correlation. Note that the difference between the three glasses is very small, suggesting that their atomic correlations are very similar.

Table 2 N_{i-j} : Partial coordination number of j atoms around i atoms

Samples	67Li ₂ S glass	70Li ₂ S glass	75Li ₂ S glass
N_{P-Li}	2.04	2.20	3.23
N_{P-P}	0.36	0.13	0.09
N_{P-S}	3.64	3.87	3.92
N_{Li-Li}	0.55	0.66	0.79
N_{Li-P}	0.98	0.94	1.11
N_{Li-S}	4.74	4.57	4.58
N_{S-Li}	2.93	2.96	3.41
N_{S-P}	1.09	1.07	1.00
N_{S-S}	0.40	0.28	0.21

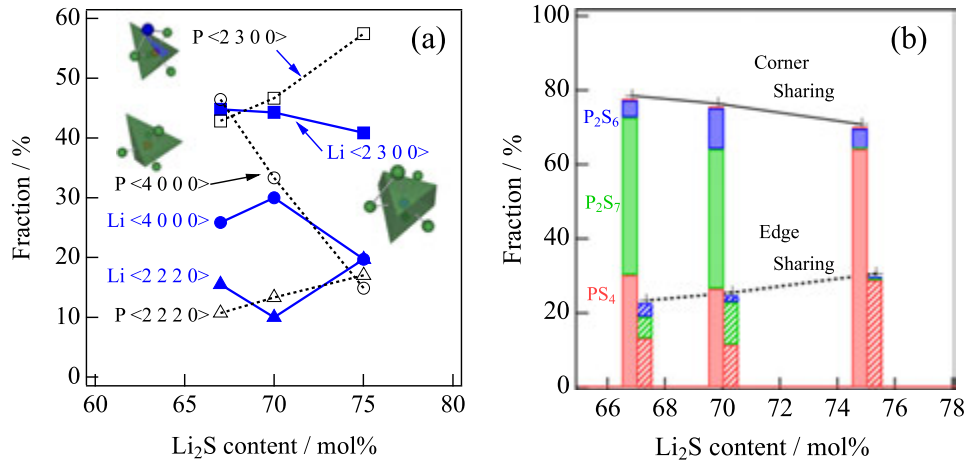


Fig. 3 (a) Comparison between P-centered (open marks with dotted line) and Li-centered Voronoi polyhedra (filled marks with solid line) for Li₂S–P₂S₅ glasses derived from DFT/RMC model. (b) Polyhedral connection statistics for Li₂S–P₂S₅ glasses calculated using DFT/RMC model. All connections are between PS_x and LiS_y polyhedra. Red, green, and blue represent PS₄^{3–}, P₂S₇^{4–}, and P₂S₆^{4–} ions, respectively. Filled and hatched bars represent corner and edge sharing, respectively.

To understand the short-range correlation in detail, the coordination numbers in the Li₂S–P₂S₅ glasses calculated up to 3.2 Å are summarized in Table 2. The coordination number of S around P, N_{P-S} , increases with increasing Li₂S content owing to the disappearance of the P₂S₆^{4–} ions. N_{P-Li} also increases, while N_{Li-P} and N_{Li-S} remain almost constant in the three compositions.

To obtain the coordination environment of the Li⁺ ions in detail, Voronoi polyhedron statistics were calculated by Voronoi tessellation analysis (Borodin, 1999; Finney, 1970), in which the coordination is assigned by a Voronoi index $\langle n_3, n_4, n_5, n_6 \rangle$, where n_i denotes the number of i -edged faces and $\sum_i n_i$ is the total coordination number. The results for Li-centered Voronoi polyhedra calculated up to 3.2 Å are shown in Fig. 3(a), together with results for P-centered polyhedra. This length of 3.2 Å corresponds to the first coordination length of the Li–S correlation determined by the DFT/RMC model. Therefore, the calculation of P-centered Voronoi polyhedra includes information about the coordination environment beyond the first coordination length of P–S correlation. The P-centered Voronoi polyhedra up to the first coordination environment have no composition dependence. It is clear that the fractions of $\langle 2\ 3\ 0\ 0 \rangle$ and $\langle 2\ 2\ 2\ 0 \rangle$ P-centered Voronoi polyhedra beyond the first coordination environment are greater than that of $\langle 4\ 0\ 0\ 0 \rangle$ Voronoi polyhedra in the Li₂S–P₂S₅ glasses, as shown by black dotted lines in Fig. 3(a), which is consistent with the coordination number for P–Li correlation, N_{P-Li} . This increase in the fraction of higher-index Voronoi polyhedra occurs with increasing Li₂S content, which indicates that the number of Li⁺ ions around the PS_x polyhedral anion increases. On the other hand, the results for the Li-centered Voronoi polyhedral, shown in Fig. 3(a) as blue solid lines, have no dependence on the Li₂S content, which is also consistent with the coordination number for Li–P correlation, N_{Li-P} . Although the distribution of Li⁺ ions has not been characterized, it has been found that the simple Voronoi polyhedra for Li-centered polyhedra are dominant in the DFT/RMC model owing to the consideration of the electron state for Li⁺ ions in the DFT calculation. It is suggested that the free volume around PS_x polyhedral anions allows the distribution of Li⁺ ions at a higher Li₂S content.

The extent of polyhedral connection between PS_x and LiS_x polyhedra in the Li₂S–P₂S₅ glasses through corner, edge, and face sharing is calculated as shown in Fig. 3(b). The results are classified on the basis of PS_x polyhedral anions. The filled and hatched bars indicate corner sharing and edge sharing, respectively. The fraction of edge sharing increases relative to that of corner sharing with increasing Li₂S content, which is related to the bond angle distribution of the S–Li–S triplet. This means that an increase in the

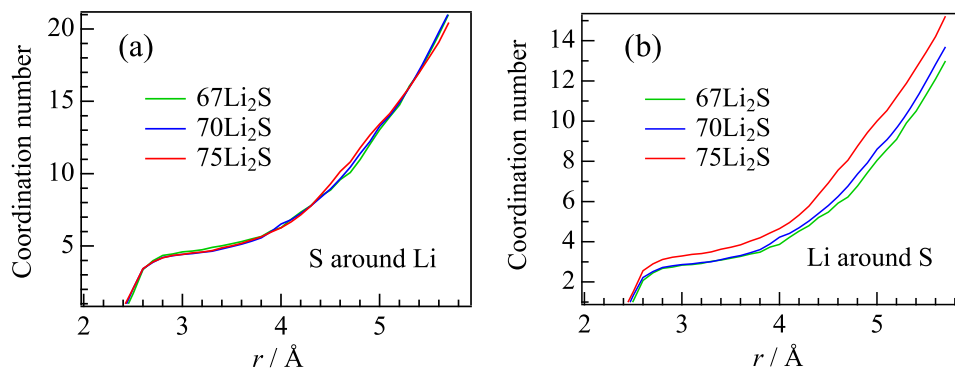


Fig. 4 Relationship between the bond length and the coordination number for the Li-S (a) and S-Li (b) correlations derived using the DFT/RMC model.

Li₂S content does not affect the local coordination environment of Li⁺ ions, and the free volume around the PS_x polyhedral anion decreases. On the other hand, the fraction of each PS_x polyhedral anion in the 67Li₂S and 70Li₂S glasses is almost the same, although we expected a distinct difference between the compositions. This result shows the distribution of Li⁺ ions in each PS_x polyhedral anion.

To evaluate the free volume, we calculated the bond length relative to the coordination number of the S around Li, $N_{\text{Li-S}}$, and Li around S, $N_{\text{S-Li}}$, as shown in Fig. 4(a) and (b). The maximum bond length of 5.7 Å was determined from the Li-S-P bond length (3.2 Å + 2.5 Å), corresponding to the length calculated from polyhedral connection statistics. As can be seen in Fig. 4(b), $N_{\text{Li-S}}$ in this system has no composition dependence, which is consistent with the Li-centered Voronoi polyhedra. On the other hand, $N_{\text{S-Li}}$ in 75Li₂S was found to be larger than that of the other glasses as shown in Fig. 4(b), which suggests that the free volume around S ions is smallest in 75Li₂S. Intriguingly, $N_{\text{S-Li}}$ is larger for 70Li₂S than for 67Li₂S at 3.8 Å and over. Thus, as the Li₂S content increases in this system, the free volume around the Li ion does not change, while that around S decreases. The DFT/RMC structure is consistent with both the diffraction data and the Raman data (Fig. 5(a)), and we compared the electronic structure in terms of each PS_x polyhedral anion for the 70Li₂S glass. Fig. 5(b) and (c) show the partial density of states (*p*-DOS) of the 70Li₂S glass for the S 3*p*-orbital and P 3*p*-orbital, respectively. It is apparent that the orbitals form a hybrid orbital between the phosphorus and sulfur; the highest occupied molecular orbital (HOMO) is located at -4.0 to -0.5 eV and the lowest unoccupied molecular orbital (LUMO) is located at 1.5–5.0 eV. The positive charge of the P ion is large owing to the hybrid orbital. However, the *p*-DOS plots of the P ion reveal that the *p*-DOS for the P₂S₇ anion differs from those for the PS₄ and P₂S₆ anions (Fig. 5(c)). A shallow level appears near the bottom of the LUMO at approximately 2.0 eV in the P₂S₇ anion, which corresponds to a covalent bond between the P ion and the BS ion in the P₂S₇ anion. This electron transfer is expected to weaken the positive charge of the P ions, which attract Li⁺ ions to the P₂S₇ anions more strongly than the other PS_x polyhedral anions. Furthermore, the attracted Li⁺ ions tend to remain around the P₂S₇ anions, which may suppress the lithium ionic conduction in solid electrolytes. On the other hand, the P₂S₆ anion has almost the same electronic structure as the PS₄ anion and does not suppress the lithium ion conduction compared with the P₂S₇ anion, although we expected strong suppression of the Li ion conduction as shown by Hayashi *et al.* (2010a,b). It is well known that the diffusion of cations is accelerated by the polarization of anions (Alcaraz *et al.*, 2007; Trullàs *et al.*, 2003; Wilson and Madden, 1993). Also, the Li⁺ ion distribution is clearly affected by the polarization of anions (Tahara *et al.*, 2015), which means that the edge sharing between PS_x and LiS_y polyhedra is related to the lithium ionic conduction. Actually, the lithium ionic conductivity of 75 Li₂S without P₂S₇ anions is higher than that of the other glasses. Furthermore, Li₂S-SiS₂ glasses with added LiI exhibiting large polarization have a high ionic conductivity (Kennedy, 1986).

Structural Change of 75Li₂S·25P₂S₅ Glass During Annealing (Shiotani *et al.*, 2017)

The ionic conductivity of 75Li₂S·25P₂S₅ (75Li₂S) sulfide glass, which consists of glassy and crystalline phases, is improved by optimizing the conditions of the heat treatment, i.e., annealing. Fig. 6(a) shows the reduced PDF $G(r) = 4\pi r \rho_0 (g(r) - 1)$, where ρ_0 is the average atom number density and $g(r)$ is the pair distribution function obtained from the X-ray diffraction data, for each annealing treatment. On the basis of the previous section, the first peak at around 2.0 Å is related to the P-S correlation associated with the PS₄ tetrahedral anions and has no dependence on the annealing treatment. This means that the PS₄ tetrahedral anions remain in the structure during the crystallization. On the other hand, the relative intensities of the second and third peaks at around 3.3 and 4.1 Å, respectively, which are related to the S-S correlations as shown in Fig. 6(b), change between the glassy and crystalline phases. The second peak decreases upon crystallization, whereas the third peak increases. The peak at around 7.0 Å is related to the P-P correlation, as shown in Fig. 6(c), and increases upon crystallization, which indicates the formation of ordered PS₄ tetrahedral anions.

Even though the ionic conductivity increases during the optimized annealing, the differential PDF analysis indicates that the glassy structure undergoes no structural change in the sulfide glass-ceramic electrolyte at a crystallinity of 33.1% after annealing at

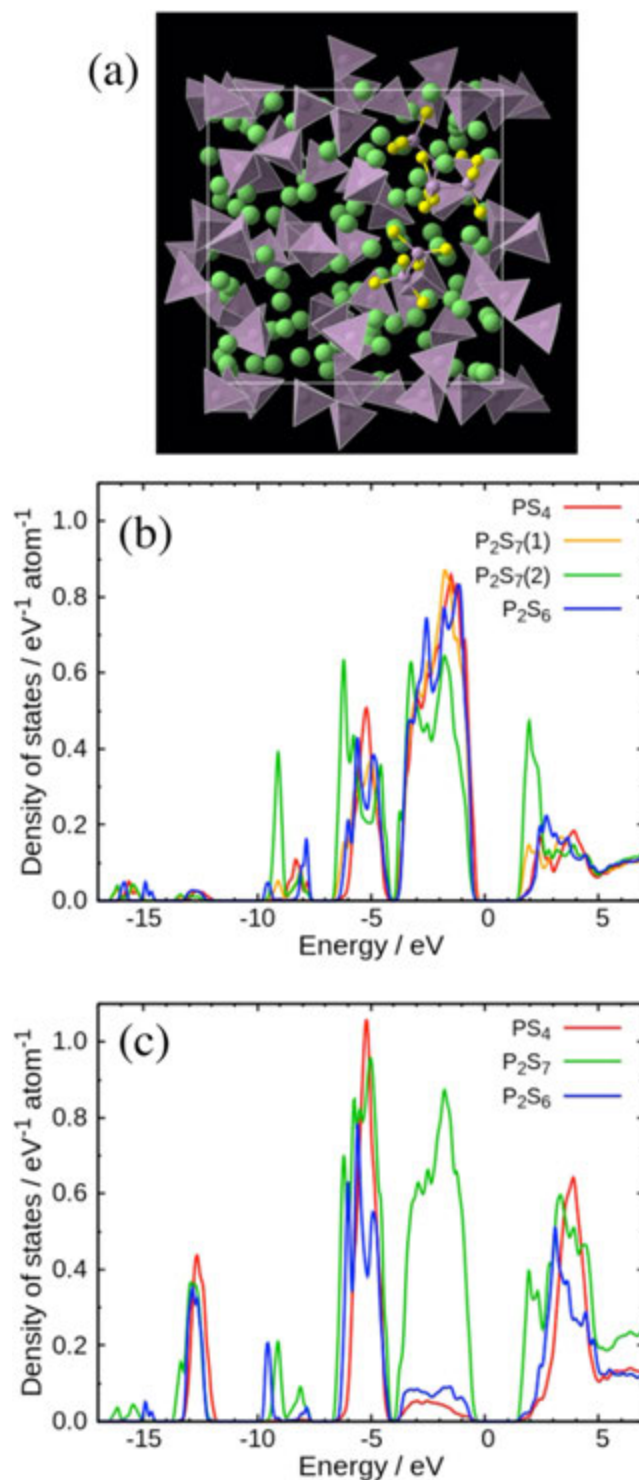


Fig. 5 (a) DFT/RMC model of 70Li₂S glass. Green, Li; purple, P and PS polyhedral anions; yellow, S. Polyhedral partial DOS for (b) S *p*-orbital and (c) P *p*-orbital of 70Li₂S glass.

200°C. We observed the formation of a nanocrystalline phase before the crystallization from the X-ray and electron diffraction patterns, which means that Bragg peaks were deformed. Thus, the ionic conductivity in the mixture of glassy and crystalline phases is improved by the coexistence of the nanocrystalline phase. Fig. 7 summarizes the crystallinity under each annealing condition. As can be seen, the ionic conductivity decreased after crystallization. It is well known that glasses have long-range density fluctuations in their structures (Wright, 2005; Fischer, 1993). Such fluctuations may be related to the improvement of ionic conductivity by the

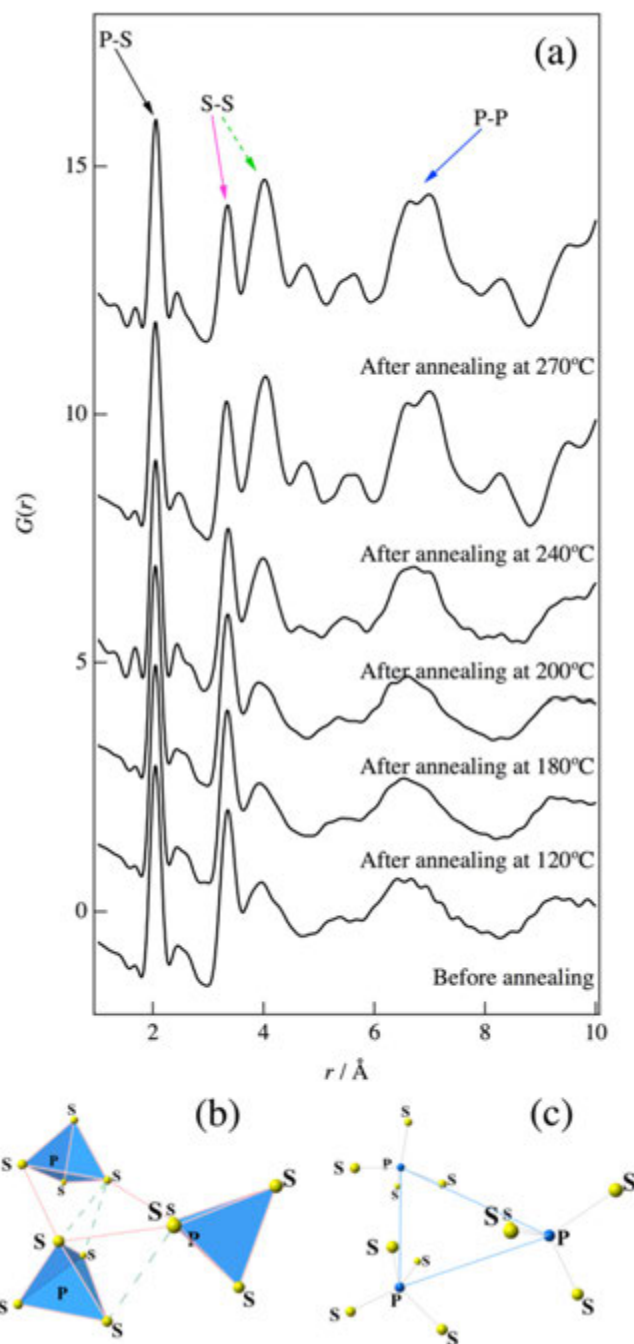


Fig. 6 Reduced pair distribution functions, $G(r)$, obtained from a Fourier transformation of $S(Q)$ and atomic configurations for the $75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ glasses: (a) $G(r)$ before annealing and after annealing at 120, 180, 200, 240, and 270°C. (b) Typical atomic configuration of S-S correlations. The correlations at around 3.3 and 4.1 Å are connected by pink and green lines, respectively. The PS_4 tetrahedral anions are highlighted in blue. (c) Typical atomic configuration of P-P correlations. The correlations around 7.0 Å are connected by blue lines.

structural relaxation caused by the annealing treatment. However, the d-PDF indicated that the glassy structure shows no structural change in the sulfide glass-ceramic electrolytes. On the other hand, Schirmeisen *et al.* suggested that the fast ionic conduction of mobile ions in nanostructured LiAlSiO_4 glass ceramics is caused by the local movement of ions at the interfaces between the glassy phase and embedded crystallites. The existence of an electrical relaxation process with a very low activation energy, which is absent in pure LiAlSiO_4 glass, has been demonstrated by time-domain electrostatic force spectroscopy (Schirmeisen, 2007). Actually, we observed the formation of a nanocrystalline phase in the diffraction pattern after the annealing, which means that the Bragg peaks were deformed. Moreover, the nanocrystalline phase was verified by TEM and electron diffraction. Fig. 8(a) and (b) show bright-field (BF) images of sulfide glassy electrolytes before annealing and after annealing at 180°C, respectively. The electron diffraction

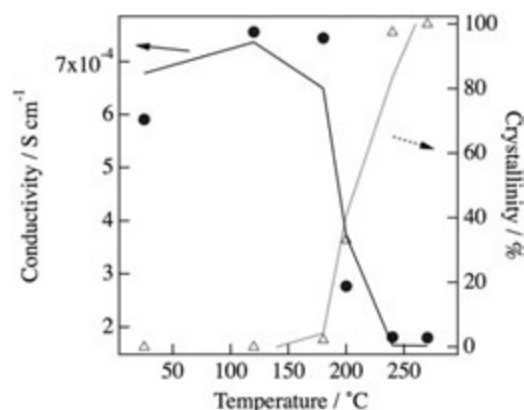


Fig. 7 Crystallinity obtained from d-PDF under each annealing condition and the lithium ionic conductivity.

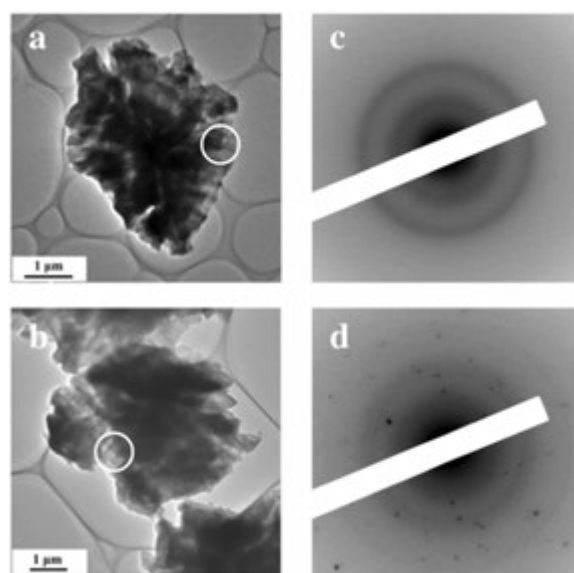


Fig. 8 TEM images and selected area electron diffraction patterns of the 75Li₂S·25P₂S₅ sulfide glass ceramic. (a,b) Bright-field images before annealing and after annealing at 180°C. (c,d) Selected area electron diffraction patterns obtained from the bright-field images.

patterns obtained from the BF images are shown in **Fig. 8(c)** and **(d)**. Spots can be seen in the electron diffraction after annealing that did not exist before annealing according to this preliminary analysis, as also reported by Tsukasaki *et al.* (2017). Thus, we suggest that the existence of such nanocrystalline phases, which are a minority component in the glass ceramic, will lead to greater ionic conduction than that of a pure sulfide glass.

Young's Moduli of the Sulfide Glasses (Kato *et al.*, 2018a,b)

Li₂S–P₂S₅ glasses have low Young's moduli (18–25 GPa) and excellent formability, allowing them to be highly densified by room-temperature pressure sintering (Sakuda *et al.*, 2013). These mechanical properties of the sulfide electrolytes contribute to the formation of a good contact at the solid-solid interfaces between the solid electrolytes and electrode active materials, leading to the excellent electrochemical performances of all-solid-state batteries. We summarize the Young's moduli of sulfide glasses using mean atomic volumes (Soga *et al.*, 1976) because the ion packing densities of the glasses can be easily estimated by calculating the mean atomic volumes from their densities. Young's moduli and the calculated mean atomic volumes of the Li₂S–P₂S₅ glasses are shown in **Fig. 9**. Young's modulus increases with decreasing mean atomic volume. The decrease in the mean atomic volume in the Li₂S–P₂S₅ glasses is associated with structural changes. The main anions in these glasses change from PS₃^{3–} (meta-thiophosphate) to P₂S₇^{4–} (pyro-thiophosphate) and PS₄^{3–} (ortho-thiophosphate) with increasing Li₂S content, suggesting that the anions change from a chain to an isolated structure by breaking the bridging structure of the P–S–P bonds as mentioned in the previous section (Ohara *et al.*, 2016). It is considered that mean atomic volume decreases (and ion packing density increases) with the increasing

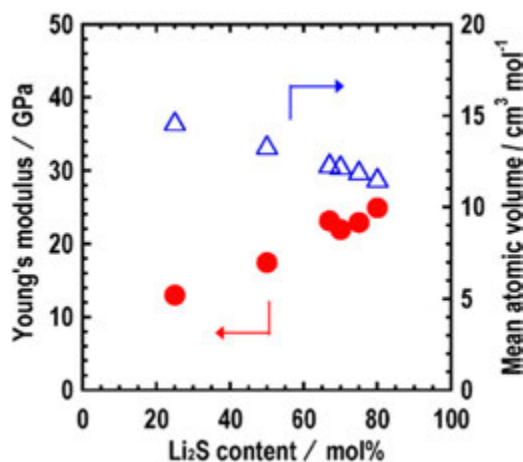


Fig. 9 Young's moduli and mean atomic volumes of $\text{Li}_2\text{S-P}_2\text{S}_5$ glasses.

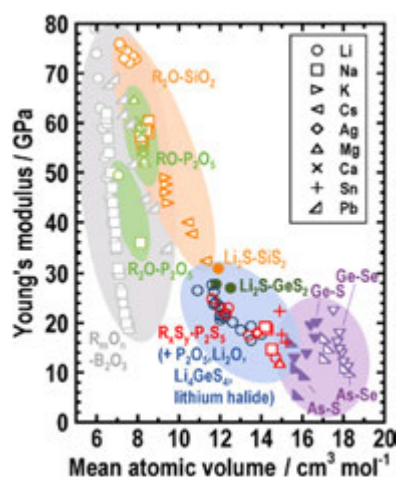


Fig. 10 Relationship between mean atomic volume and Young's modulus for $\text{Li}_2\text{S-P}_2\text{S}_5$ sulfide glasses (blue area) and other silicate (orange area), phosphate (green area), borate (gray area), and chalcogenide (purple area) glasses.

isolation of the anions in their glasses, which is a possible reason for the increase in Young's modulus. **Fig. 10** shows Young's moduli of sulfide glasses (Kato *et al.*, 2018a; Sakuda *et al.*, 2013), along with those of oxide glasses (Ashizuka and Sakai, 1983; Ashizuka *et al.*, 1983; Takahashi and Osaka, 1983) and other chalcogenide glasses (Guin *et al.*, 2002; Mel'nichenko *et al.*, 2002, 2009). In general, there is a good correlation between Young's modulus and mean atomic volume. As can be seen in this figure, oxide glasses have higher Young's moduli and smaller mean atomic volumes, while chalcogenide glasses have lower Young's moduli and larger mean atomic volumes. The sulfide glasses are in the intermediate region between the oxide glasses and other chalcogenide glasses. The Young's moduli of sulfide glasses are smaller than those of garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ and perovskite-type $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$, known as oxide solid electrolytes (100–200 GPa) (Matsui *et al.*, 2014; Ohara *et al.*, 2010; Wolfenstine *et al.*, 2018). Note that one of the factors causing the deterioration of the all-solid-state batteries is the volume change caused by charging and discharging of the electrode active material. If a solid electrolyte at the interface with an electrode active material is too hard, the volume expansion of the electrode active material cannot be tolerated, and either the electrode active material or the solid electrolyte is destroyed at the interface. Furthermore, the interface between the electrode and the solid electrolyte may be lost when the electrode active material shrinks. To maintain adhesion at the interface between the electrode and the solid electrolyte during such a volume change in the electrode active material, the solid electrolyte needs to have a certain "softness". The Young's modulus of a sulfide electrolyte is smaller than that of an oxide electrolyte. The mechanical properties of the sulfide electrolytes contribute to the formation of good contacts at the solid-solid interfaces between the solid electrolytes and electrode active materials during charging and discharging. Kato *et al.* evaluated the discharge capacity of all-solid-state batteries using two electrolytes with similar ionic conductivities and different Young's moduli ($75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ glass: $2.4 \times 10^{-4} \text{ S cm}^{-1}$, 23 GPa, and $70(\text{Li}_2\text{S-P}_2\text{S}_5) - 30\text{LiI}$ glass: $2.2 \times 10^{-4} \text{ S cm}^{-1}$, 17 GPa) (Kato *et al.*, 2018a,b). Si was used as an electrode material in this evaluation. It was found that $70(\text{Li}_2\text{S-P}_2\text{S}_5) - 30\text{LiI}$ glass with a small Young's modulus maintains a higher capacity after several cycles of charging and discharging (**Fig. 11**). Thus, the Young's

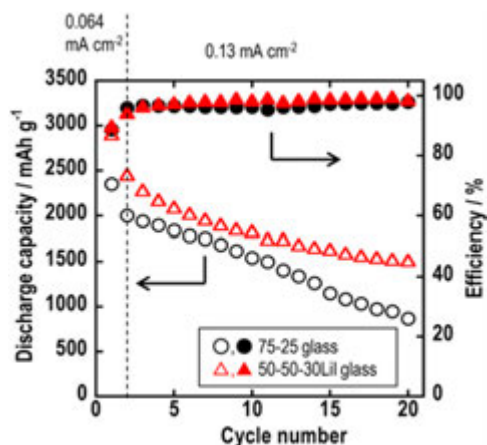


Fig. 11 Cycle performance of all-solid-state cells using Si composite electrodes containing 75Li₂S–25P₂S₅ (75–25) and 70(Li₂S–P₂S₅)–30LiI (50–50–30LiI) glass electrolytes.

modulus of the solid electrolyte is one of important factors to be considered when constructing an all-solid-state battery with high performance.

Concluding Remarks

This chapter introduced the development of sulfide solid electrolytes with a high lithium ion conductivity and the structural features of typical sulfide glasses. In addition, the mechanical properties of sulfide solid electrolytes were described. Through recent research and development, many solid electrolytes having an ionic conductivity of 10^{-3} S cm⁻¹ or more have been found, and some solid electrolytes with ionic conductivity on the order of 10^{-2} S cm⁻¹ have also been discovered. On the other hand, to obtain satisfactory performance with these solid electrolytes, it is important to construct a suitable interface between the electrode active material and the solid electrolyte in an all-solid-state battery and to maintain the interface during long-term charge-discharge cycles. Attention must also be paid to the mechanical properties, which are closely related to the interface phenomena, and thus the Young's moduli of sulfide solid electrolytes are focused on. From the knowledge obtained so far, the further development of solid electrolytes is expected, and we hope the commercial realization of all-solid-state batteries that will enrich to our daily lives.

Acknowledgments

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References

- Alcaraz, O., Bitrián, V., Trullàs, J., 2007. Molecular dynamics study of polarizable point dipole models for molten sodium iodide. *The Journal of Chemical Physics* 127, 154508.
- Aotani, N., Iwamoto, K., Takada, K., Kondo, S., 1994. Synthesis and electrochemical properties of lithium ion conductive glass, Li₃PO₄–Li₂S–SiS₂. *Solid State Ionics* 68, 35–39.
- Ashizuka, M., Sakai, T., 1983. *Journal of the Ceramic Society of Japan* 91, 176–182.
- Ashizuka, M., Sakai, T., Iwata, A., 1983. *Journal of the Ceramic Society of Japan* 91, 86–94.
- Borodin, V.A., 1999. *Philosophical Magazine A* 79, 1887–1907.
- Boulineau, S., Courty, M., Tarascon, J.-M., Viallet, V., 2012. Mechanochemical synthesis of Li-argyrodite Li₆PS₄X (X=Cl, Br, I) as sulfur-based solid electrolytes for all solid state batteries application. *Solid State Ionics* 221, 1–5.
- Bron, P., Johansson, S., Zick, K., *et al.*, 2013. Li₁₀SnP₂S₁₂: An affordable lithium superionic conductor. *Journal of the American Chemical Society* 135, 15694–15697.
- Finney, J.L., 1970. *Proceedings of the Royal Society of London, Series A* 319, 479–493.
- Fischer, E.W., 1993. Light scattering and dielectric studies on glass forming liquids. *Physica A: Statistical Mechanics and its Applications* 201, 183–206.
- Fukushima, A., Hayashi, A., Yamamura, H., Tatsumisago, M., 2017. Mechanochemical synthesis of high lithium ion conducting solid electrolytes in a Li₂S–P₂S₅–Li₃N system. *Solid State Ionics* 304, 85–89.
- Guin, J.-P., Rouxel, T., Keryvin, V., *et al.*, 2002. Indentation creep of Ge–Se chalcogenide glasses below T_g: elastic recovery and non-Newtonian flow. *Journal of Non-Crystalline Solids* 298, 260–269.
- Hayashi, A., Hama, S., Morimoto, H., Tatsumisago, M., Minami, T., 2001. Preparation of Li₂S–P₂S₅ amorphous solid electrolytes by mechanical milling. *Journal of the American Ceramic Society* 84, 477–479. [2020/03/07].
- Hayashi, A., Minami, K., Tatsumisago, M., 2010a. Development of sulfide glass-ceramic electrolytes for all-solid-state lithium rechargeable batteries. *Journal of Solid State Electrochemistry* 14, 1761–1767.

- Hayashi, A., Minami, K., Ujije, S., Tatsumisago, M., 2010b. Preparation and ionic conductivity of $\text{Li}_7\text{P}_3\text{S}_{11-x}$ glass-ceramic electrolytes. *Journal of Non-Crystalline Solids* 356, 2670–2673.
- Hayashi, A., Sakuda, A., Tatsumisago, M., 2016. Development of sulfide solid electrolytes and interface formation processes for bulk-type all-solid-state Li and Na batteries. *Frontiers in Energy Research* 4.[2016-July-15].
- Iwamoto, N., Umesaki, N., Takahashi, M., *et al.*, 1987. Molecular dynamics simulation of Li_4SiO_4 melt and glass. *Journal of Non-Crystalline Solids* 95–96, 233–240.
- Kamaya, N., Homma, K., Yamakawa, Y., *et al.*, 2011. A lithium superionic conductor. *Nature Materials* 10, 682–686.
- Kanno, R., Murayama, M., 2001. Lithium ionic conductor thio-LISICON: The $\text{Li}_2\text{S}-\text{GeS}_2-\text{P}_2\text{S}_5$ system. *Journal of The Electrochemical Society* 148, A742–A746.
- Kato, Y., Hori, S., Saito, T., *et al.*, 2016. High-power all-solid-state batteries using sulfide superionic conductors. *Nature Energy* 1, 16030.
- Kato, A., Nose, M., Yamamoto, M., *et al.*, 2018a. Mechanical properties of sulfide glasses in all-solid-state batteries. *Journal of the Ceramic Society of Japan* 126, 719–727.
- Kato, A., Yamamoto, M., Sakuda, A., Hayashi, A., Tatsumisago, M., 2018b. Mechanical properties of $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glasses with lithium halides and application in all-solid-state batteries. *ACS Applied Energy Materials* 1, 1002–1007.
- Keen, D., 2001. A comparison of various commonly used correlation functions for describing total scattering. *Journal of Applied Crystallography* 34, 172–177.
- Kennedy, J.H., 1986. A highly conductive Li^+ -glass system: $(1-x)(0.4\text{SiS}_2-0.6\text{Li}_2\text{S})-x\text{LiI}$. *Journal of the Electrochemical Society* 133, 2437.
- Matsui, M., Takahashi, K., Sakamoto, K., *et al.*, 2014. Phase stability of a garnet-type lithium ion conductor $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. *Dalton Transactions*. 43, 1019–1024.
- Mel'nichenko, T.D., Fedeleš, V.I., Mel'nichenko, T.N., *et al.*, 2009. On the approximate estimation of the surface tension of chalcogenide glass melts. *Glass Physics and Chemistry* 35, 32–42.
- Mel'nichenko, T.N., Fedeleš, V.I., Yurkin, I.M., Mel'nichenko, T.D., 2002. Application of the free volume concept to glasses in the Ge–As–S system. *Glass Physics and Chemistry* 28, 25–32.
- Mercier, R., Malugani, J.P., Fahys, B., Douglande, J., Robert, G., 1982. Synthèse, structure cristalline et analyse vibrationnelle de l'hexathiohypodiphosphate de lithium $\text{Li}_4\text{P}_2\text{S}_6$. *Journal of Solid State Chemistry* 43, 151–162.
- Mercier, R., Malugani, J.-P., Fahys, B., Robert, G., 1981. Superionic conduction in $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ -LiI glasses. *Solid State Ionics* 5, 663–666.
- Minami, T., Hayashi, A., Tatsumisago, M., 2006. Recent progress of glass and glass-ceramics as solid electrolytes for lithium secondary batteries. *Solid State Ionics* 177, 2715–2720.
- Mizuno, F., Hayashi, A., Tadanaga, K., Tatsumisago, M., 2005. New, highly ion-conductive crystals precipitated from $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ Glasses. *Advanced Materials*. 17, 918–921.
- Mizuno, F., Hayashi, A., Tadanaga, K., Tatsumisago, M., 2006. High lithium ion conducting glass-ceramics in the system $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$. *Solid State Ionics* 177, 2721–2725.
- Ohara, K., Kawakita, Y., Pusztai, L., *et al.*, 2010. Structural disorder in lanthanum titanate: The basis of superionic conduction. *Journal of Physics: Condensed Matter* 22, 404203.
- Ohara, K., Mitsui, A., Mori, M., *et al.*, 2016. Structural and electronic features of binary $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glasses. *Scientific Reports* 6, 21302.
- Sakuda, A., Hayashi, A., Tatsumisago, M., 2013. Sulfide solid electrolyte with favorable mechanical property for all-solid-state lithium battery. *Scientific Reports* 3, 2261.
- Schirmeisen, A., Taskiran, A., Fuchs, H., *et al.*, 2007. Fast Interfacial Ionic Conduction in Nanostructured Glass Ceramics. *Physical Review Letters* 98, 225901.
- Seino, Y., Ota, T., Takada, K., Hayashi, A., Tatsumisago, M., 2014. A sulphide lithium super ion conductor is superior to liquid ion conductors for use in rechargeable batteries. *Energy & Environmental Science* 7, 627–631.
- Shiotani, S., Ohara, K., Tsukasaki, H., Mori, S., Kanno, R., 2017. Pair distribution function analysis of sulfide glassy electrolytes for all-solid-state batteries: Understanding the improvement of ionic conductivity under annealing condition. *Scientific Reports* 7, 6972.
- Soga, N., Yamanaka, H., Hisamoto, C., Kunugi, M., 1976. Elastic properties and structure of alkaline-earth silicate glasses. *Journal of Non-Crystalline Solids* 22, 67–76.
- Sun, Y., Suzuki, K., Hori, S., Hirayama, M., Kanno, R., 2017. Superionic conductors: $\text{Li}_{10+x}[\text{Sn}_y\text{Si}_{1-y}]_1+\delta\text{P}_{2-\delta}\text{S}_{12}$ with a $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ -type structure in the $\text{Li}_3\text{PS}_4\text{-Li}_4\text{SnS}_4\text{-Li}_4\text{SiS}_4$ quasi-ternary system. *Chemistry of Materials* 29, 5858–5864.
- Tachez, M., Malugani, J.-P., Mercier, R., Robert, G., 1984. Ionic conductivity of and phase transition in lithium thiophosphate Li_3PS_4 . *Solid State Ionics* 14, 181–185.
- Tahara, S., Kawakita, Y., Shimakura, H., *et al.*, 2015. Intermediate-range chemical ordering of cations in molten RbCl-AgCl . *The Journal of Chemical Physics* 143, 044509.
- Takahashi, K., Osaka, A., 1983. *Journal of the Ceramic Society of Japan* 91, 116–120.
- Trullàs, J., Alcaraz, O., González, L.E., Silbert, M., 2003. Structure and dynamics of molten AgCl . The inclusion of induced polarization. *The Journal of Physical Chemistry B* 107, 282–290.
- Tsukasaki, H., Mori, S., Morimoto, H., Hayashi, A., Tatsumisago, M., 2017. Direct observation of a non-crystalline state of $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ solid electrolytes. *Scientific Reports* 7, 4142.
- Ujije, S., Hayashi, A., Tatsumisago, M., 2014. Preparation and electrochemical characterization of $(100-x)(0.7\text{Li}_2\text{S}-0.3\text{P}_2\text{S}_5)-x\text{LiBr}$ glass-ceramic electrolytes. *Materials for Renewable and Sustainable Energy* 3, 18.
- Umesaki, N., Takahashi, M., Tatsumisago, M., Minami, T., 1993. Structure of rapidly quenched glasses in the system $\text{Li}_2\text{O-SiO}_2$. *Journal of Materials Science* 28, 3473–3481.
- Wada, H., Menetrier, M., Levasseur, A., Hagenmuller, P., 1983. Preparation and ionic conductivity of new $\text{B}_2\text{S}_3\text{-Li}_2\text{S-LiI}$ glasses. *Materials Research Bulletin* 18, 189–193.
- Wilson, M., Madden, P.A., 1993. Polarization effects in ionic systems from first principles. *Journal of Physics: Condensed Matter* 5, 2687–2706.
- Wolfenstine, J., Allen, J.L., Sakamoto, J., Siegel, D.J., Choe, H., 2018. Mechanical behavior of Li-ion-conducting crystalline oxide-based solid electrolytes: a brief review. *Ionics*. 24, 1271–1276.
- Wright, A.C., Hulme, R.A., Sinclair, R.N., 2005. A small angle neutron scattering study of long range density fluctuations in vitreous silica. *Physics and Chemistry of Glasses* 46, 59–66.
- Yamauchi, A., Sakuda, A., Hayashi, A., Tatsumisago, M., 2013. Preparation and ionic conductivities of $(100-x)(0.75\text{Li}_2\text{S}-0.25\text{P}_2\text{S}_5)-x\text{LiBH}_4$ glass electrolytes. *Journal of Power Sources* 244, 707–710.
- Yubuchi, S., Uematsu, M., Hotehama, C., *et al.*, 2019. An argyrodite sulfide-based superionic conductor synthesized by a liquid-phase technique with tetrahydrofuran and ethanol. *Journal of Materials Chemistry A* 7, 558–566.
- Zhang, Z., Kennedy, J.H., 1990. Synthesis and characterization of the $\text{B}_2\text{S}_3\text{-Li}_2\text{S}$, the $\text{P}_2\text{S}_5\text{-Li}_2\text{S}$ and the $\text{B}_2\text{S}_3\text{-P}_2\text{S}_5\text{-Li}_2\text{S}$ glass systems. *Solid State Ionics* 38, 217–224.

Solid Oxide Fuel Cells

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Introduction

The first description of the so-called 'gaseous voltaic battery' or 'wet cell battery' belongs to Sir William Grove: "I will...mention one [experiment] which goes a step further than any hitherto recorded; and affords, I think, an important illustration of the combination of gases by platinum (Grove, 1839, 1842). Simultaneously, Shönbein suggested the explanation of this polarization phenomenon as a consequence of a series of galvanic experiments concluding "...that the current in question is caused by the combination of hydrogen with oxygen... and not by contact" (Schonbein, 1839) (referring to a controversially discussed 'contact theory' widely used in the early nineteenth century for the explanation of electrical phenomena). In comparison to batteries with liquid electrolytes, which were also developed during this period (Daniell element), the main disadvantage of the fuel cell was considered the need of continuous gas supply. Batteries became therefore the more convenient, practical, and compact choice of small-scale power supply until today.

It was necessary to wait almost one century for Baur and Preis to construct the first solid oxide fuel cells (SOFCs), i.e., galvanic cells using a solid oxygen ion conductor as electrolyte (Baur and Preis, 1937). In this attempt they investigated various porcelains, clays, and zirconia-based materials as solid electrolytes. A tubular stack test consisting of eight zirconia tubes filled with coke (as fuel and anode) and a kind of powder bath of magnetite used as cathode was finally able to deliver a power of 0.045 W (i.e., 0.18 W l⁻¹ or about 120 μA cm⁻²).

Apart from zirconia, the materials selection of these first SOFCs refers to a "fuel element" (Baur and Treadwell, 1916), which is known today as molten carbonate fuel cell. Regarding the applicability of their fuel cells, Baur and Preis concluded that their modified zirconia materials would fulfill all technical requirements but were hindered by their high price.

SOFCs are nowadays one of the most promising devices for stationary clean energy production, due to their minimal Green House Gas (GHG) emissions, fuel flexibility (from hydrogen to hydrocarbons and biogas), high efficiency and power density.

SOFCs Working Principle

The SOFC core is constituted by a dense solid electrolyte sandwiched between two porous electrodes (anode and cathode) as presented in Fig. 1. SOFCs can be divided in anionic and protonic on the basis of the ion that migrates through the electrolyte membrane. In anionic-SOFC the electrolyte is an oxygen ion transport material, while in protonic-SOFC is a proton conductor. As reported in Fig. 1, the different ion involved in electrolyte conduction governs the side at which the water is collected even if the oxidation and reduction sides remains the same; the reduction of oxygen to produce O²⁻ takes place at the cathode while the H₂ oxidation to form H⁺ species at the anode. The electrons produced by the reactions finally flow through the external circuit that connect the electrodes and allows the collection of the current.

While, in recent years protonic SOFCs technology has reached significant advancement in terms of performance and reliability (Singh et al., 2019), up to now, only anionic SOFC have found commercial applications.

Independent in shape and size, state-of-the-art SOFCs typically contain 8 mol% yttria-stabilized zirconia (8YSZ, Y_{0.15}Zr_{0.85}O_{1.93}) as electrolyte, a perovskite-based cathode (strontium-substituted modifications of lanthanum manganite like La_{1-x-y}Sr_xMnO₃ with 0.15 < x < 0.4 and 0 < y < 0.05) and a composite of 8YSZ and metallic nickel as anode.

Description of the Various Types of SOFCs

Solid oxide fuel cells can be mainly grouped into tubular and planar designs. Both types can consist of one or several single cells per stacking unit, i.e., on a single tube or in a single multilayer. Depending on the application, tubular SOFCs have dimensions from needle-like to lengths of about 1.5–2 m for rapid start-up times and large gross power, respectively. On the other hand, the planar is the most common SOFC design thanks to its higher performance. This architecture can lead to two different stacks containing metallic or ceramic interconnect material as well as with cells with thick (electrolyte-supported, 1st generation cells) or thin (electrode-supported, 2nd generation cells) membranes with thicknesses usually of 150–250 μm and 5–20 μm, respectively (Tietz, 2003; Blum et al., 2005). The size of technologically relevant planar cells varies from 10 × 10 cm² to 25 × 25 cm² or corresponding areas in round or rectangular shape.

The today general tendency of reducing the operating temperature from about 1000°C to 500–800°C favors cell designs with thin electrolytes, lower ohmic resistance and, therefore, higher power density, passing from the 1st to the 2nd generation of cells (as schematized in Fig. 2). For this reason, many developers have considered electrode-supported cells the best choice for realizing SOFCs operating at reduced temperature (Tietz, 2003; Blum et al., 2005).

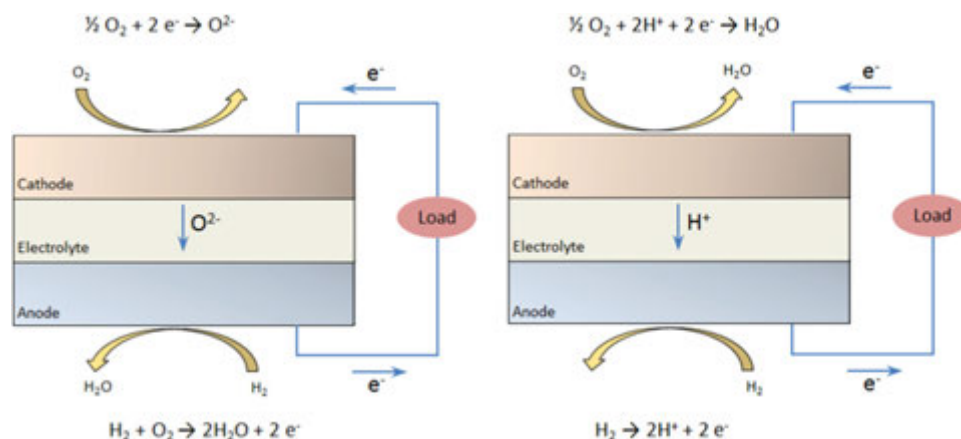


Fig. 1 Schematic representation of the anionic (on the left) and protonic (on the right) SOFC working principle.

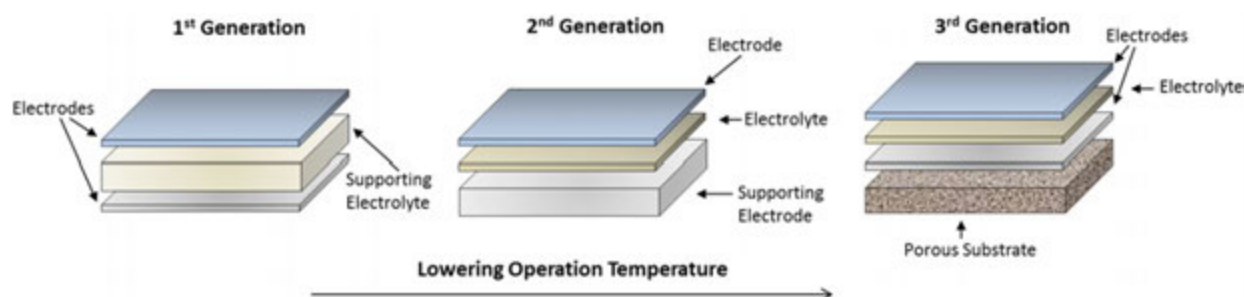


Fig. 2 Schematic illustration of the SOFC generations architectures.

The term 'electrode-supported' has been initially introduced to explicitly indicate that in such fuel cells the mechanical stability is transferred from the thick, dense electrolyte layer to an even thicker, porous electrode (0.5–1.5 μm). The second generation of cells could be supported on the anode or cathode side. Although the cathode-supported configuration showed better structural stability and lower-cost cathode material (Gondolini *et al.*, 2012; Su *et al.*, 2015) the anode-supported one is preferred for the easier manufacturing. During recent years, more interest is devoted to the 3rd generation SOFCs (Fig. 2) in which the mechanical strength is given by the electrode side, though not necessarily by the electrode substrate. In all these cases, the substrate is always porous to allow gas transport to and from the anode. The materials used for such substrates are metals or alloys, or even refractory ceramics. In the case of insulating substrates, they only deliver the fuel gas to the anode and the current path has to be established along the substrate surface instead of passing perpendicular to the substrate surface as in electrically conductive substrates. In the case of metallic substrates the thermomechanical compatibility is one of the main issue to be faced, because they often have higher thermal expansion coefficients than the other cell components. Ferritic stainless steel is one of the most considered materials thanks to a coefficient of expansion similar to the ones of the cell ceramic materials (YSZ, GDC, electrolyte, or anode functional layer). Furthermore, its lower cost in comparison to either YSZ or GDC, cathodic and anodic materials leads to an overall reduction of the cost of the device. However, metal-supported cells (MS-SOFC) suffer of strong cation interdiffusion between the different components during manufacturing and severe corrosion at high operating temperature ($\geq 800^\circ\text{C}$). For this architecture, colloidal and wet-colloidal methods are then used to produce and sinter thin films of electrolyte on the anode substrate and therefore lower the cell manufacturing and reach operating temperatures compatible with stainless steel (Krishnan, 2017; Tucker, 2010). On the porous substrate, the cell components are deposited in the sequence anode–electrolyte–cathode. Normally the coatings are realized by screen printing, slurry coating, wet powder spraying, or atmospheric plasma spraying. Even if the substrate is made of the anode material, Ni/8YSZ, it has been found beneficial for the electrochemical performance to apply an additional anode layer called "functional anode" having a finer microstructure and therefore a better electrocatalytic conversion capability of the fuel gas. The layers typically have thicknesses of 5–20 μm for the functional anode, 10–20 μm for the electrolyte, and 50–80 μm for the cathode (Fig. 3). Also, the cathode is nowadays composed of two layers: an electrochemically fine-grained composite of the electrolyte material and the electrocatalyst (lanthanum manganite) and a coarse current collection layer supplying air and electrons to the composite layer.

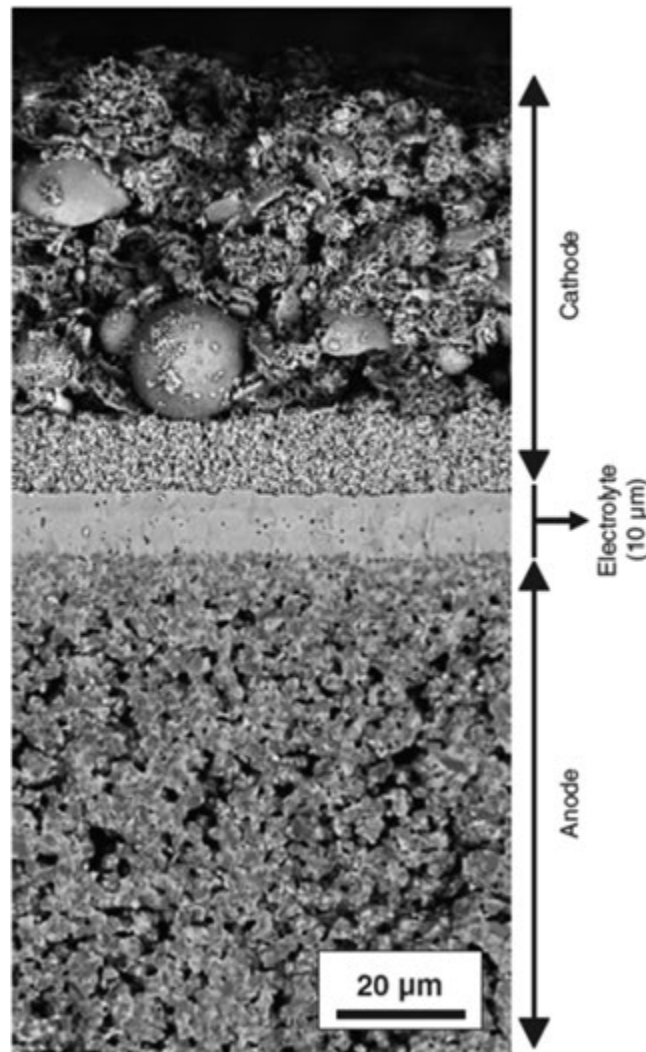


Fig. 3 Microstructure of an anode-supported SOFC with a 10 μm thick solid electrolyte. In this magnification, the anode would end up in a thickness of about 100 μm (?). Courtesy of Forschungszentrum Jülich.

The Technological Trends During the Recent Years

Three main areas of research are addressed for making SOFC technology competitive with other electricity generators: (1) Reduce the costs of materials, components, cells, and stacks, e.g., by applying low-cost technical-grade raw materials, by reducing the manufacturing costs (e.g., reduction of sintering temperatures, reduction of sintering steps, application of conventional ceramic, or metallurgical processing methods, simplification of production processes, including the use of additive manufacturing techniques), by decreasing the thickness of components, especially the anode substrate, by the integration of cheaper metal supports and interconnect materials. (2) Decrease the operating temperature to obtain higher performance, power density, and efficiency. Simultaneously, this implies lower degradation processes and costs (due to a smaller number of cells required for a certain gross power). The higher performance gives more flexibility in operation and that is why the switch from electrolyte-to anode-supported designs has taken place. Performance has been further increased by using new cathode materials, lowering the electrolyte thickness and optimizing their microstructures. (3) Decrease the degradation processes and increase durability and reliability (in operation and in component fabrication). Different studies have revealed that these goals are more easily achieved in small-scale applications (1–5 kW) than with larger systems (100–1000 kW). Several degradation phenomena have been addressed like chromium poisoning of the cathode, contact resistances at the interfaces (especially at the interconnect) the long-term stability of electrolytes, anodes, and cathodes, and the influence of fuel gases and contaminants (coking, sulfur poisoning). The development of alternatives anodes with respect to NiO-based material and cathodes with respect to the Cr and Co-based ones moves the SOFC development in this direction addressing several issues of cell degradation such as Ni coalescence and agglomeration, carbon and sulfur tolerance, robustness during the redox cycling and cation interdiffusion. In the same direction, the development of different

Table 1 Ionic conductivity (σ_i) of different oxygen ion conductors (in S cm^{-1})

Material	σ_i at 800°C	σ_i at 600°C
$\text{Zr}_{0.85}\text{Y}_{0.15}\text{O}_{1.93}$	5.0×10^{-2}	6.2×10^{-3}
$\text{Zr}_{0.80}\text{Sc}_{0.10}\text{Al}_{0.02}\text{O}_{1.90}$	1.2×10^{-1}	1.1×10^{-2}
$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$	6.5×10^{-2}	1.3×10^{-2}
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.90}\text{Mg}_{0.1}\text{O}_{3-x}$	1.1×10^{-1}	1.6×10^{-2}
$\text{La}_{10}\text{Si}_6\text{O}_{27}$	1.7×10^{-2}	8.2×10^{-2}

Table 2 Ionic conductivity of CeO_2 doped with Y, Sm, and Gd

Composition	Dopant	Ionic conductivity		
		500°C	600°C	700°C
$\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$	Gd^{3+}	0.0095	0.0253	0.054
$\text{Ce}_{0.887}\text{Y}_{0.113}\text{O}_{1.9435}$	Y^{3+}	0.0087	0.0344	0.1015
$\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{1.95}$	Sm^{3+}	0.0033	0.0090	0.0200

Note: Wang, F., Lyu, Y., Chu, D., *et al.*, 2019. The electrolyte materials for SOFCs of low-intermediate temperature: Review. *J. Mater. Sci. Technol.* 35, 1551–1562. Steele, B.C.H., 2000. Appraisal of $\text{Ce}_{1-y}\text{Gd}_y\text{O}_{2-y/2}$ electrolytes for IT-SOFC operation at 500°C. *Solid State Ion.* 129, 95–110. Ralph, J.M., 1998. A Study of Doped Ceria Electrolytes. PhD Study. University of London. Wang, D.Y., Park, D.S., Griffith, J., Nowick, A.S., 1981. Oxygen-ion conductivity and defect interactions in yttria-doped ceria. *Solid State Ion.* 2, 95–105. Shemilt, J.E., Williams, H.M., 1999. Effects of composition and processing method on the low temperature conductivity of samaria-doped ceria electrolytes. *J. Mater. Sci. Lett.* 18, 1735–1737.

buffering and protective layers able to prevent cation diffusion between the different elements of the cell. Metal support technology would increase mechanical ruggedness, redox tolerance and rapid thermal cyclability while recently additive manufacturing techniques have opened new ways to customize and potentially reduce the cost, of the single cell.

Progress in Materials Development and Processing

Electrolytes

As mentioned before, SOFCs use a solid oxide ion conductor as electrolyte material. This material must have sufficient ionic conductivity for O^{2-} or H^+ ions at operating temperature. To lower the operating temperatures, thin electrolyte films on porous electrode substrates are now preferred. The four main material systems for oxygen conductive electrolyte are partially cation substituted ZrO_2 , CeO_2 , and LaGaO_3 as well as apatites. The ionic conductivities of these solid electrolytes are listed in **Table 1**.

Apart from the apatite $\text{La}_{10}\text{Si}_6\text{O}_{27}$, the other solid electrolytes have ionic conductivity about 2 times higher than that of 8YSZ at 800°C and lower temperatures. Therefore, the improvement can be significant for electrolyte-supported cells but is negligible for electrode-supported cells. Assuming an electrolyte thickness of 10 μm and ionic conductivity of 0.05 S cm^{-1} and 0.12 S cm^{-1} for 8YSZ and ScSZ, respectively, at 800°C (**Table 1**), this leads to an ohmic loss over the electrolyte layer of about 20 m Ω and 8 m Ω , respectively. These values are much smaller than the overpotentials at the cathode which are in the range of 100–400 m Ω . Only the apatite, an ion conductor with excess oxygen ions on interstitial sites instead of oxygen vacancies (as in the other materials), has a different temperature dependence and smaller activation energy of the ionic conductivity. Therefore, the value at 800°C is rather low, but the material surpasses the conductivity of 8YSZ at 600°C and outperforms also the other materials at and below 500°C (**Nakayama and Sakamoto, 1998**). During exposure at 1000°C it was found in several studies that 8YSZ samples showed a higher decrease of conductivity than samples with a higher Y_2O_3 content. The best conductivity values after annealing were reached by samples with 10 mol% Y_2O_3 . The aging of zirconia stabilized with 7.8 mol% Sc_2O_3 directly correlated with the decrease in conductivity and temperature. Similar investigations with Sc_2O_3 contents between 8 mol% and 12 mol% showed only slight degradation effects after aging at 1000°C (up to 6000 h). Samples with 11 mol% Sc_2O_3 remained nearly unchanged with respect to conductivity. Up to the present, however, the lower price and larger availability of yttria lead to its dominant use as a stabilizer in contrast to scandia.

Below 800°C the conductivity of CeO_2 -based compounds is several times higher than the traditional 8YSZ electrolyte. For this reason, this material is one of the best candidates for the production of SOFC working at intermediate temperature (600–800°C). However, Ce^{4+} in the CeO_2 structure is partially reduced to Ce^{3+} at high temperature or in reducing atmosphere with a consequent lowering of the ionic conductivity, increasing of electronic conductivity and lattice expansion that lead to the decrease of the open circuit voltage and of the mechanical properties of the complete cell. To improve the reliability of this material two main approaches are generally used. The first one is improving the material stability in reducing environment by co-doping rare earth elements, a practice that leads to an increase of ionic conductivity. Y, Gd, and Sm show the lowest size mismatch, exhibiting the highest conductivity as summarized in **Table 2**.

On the other hand, an electronic barrier layer (such as 8YSZ film) can be added between GDC and anode to improve the stability of the entire cell (Wang *et al.*, 2019). However high process temperatures lead to a GDC and YSZ interaction/interdiffusion during the sintering process at 1200°C reducing the cell performance; in this case low temperature heating treatments and processes are preferentially used for SOFC development. Cerium oxides-based compounds are generally applied for the development of the technology at intermediate temperature, (between 600 and 800°C) and for low temperature SOFC (350–600°C) mixed with alkali carbonates (Na, Li, K, and mixtures of them). Among several formulations, sodium carbonate-SDC composites (Na_2CO_3 -SDC) is one of the most promising composite due to its superior conductivity and to the high melting point of Na_2CO_3 , which prevents the liquid phase formation in the operative range (below 600°C) (Khan *et al.*, 2018).

Pure lanthanum gallate is a poor ionic conductor. When replacing La^{3+} or Ga^{3+} ions by Sr^{2+} or Mg^{2+} ions, high ionic conduction is obtained (Ishihara *et al.*, 1994). Time-dependent measurements on $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ (Huang *et al.*, 1998) have shown that the conductivity at 700°C in air is nearly unchanged, amounting to 0.073 S cm^{-1} over a period of 200 h. LSGM presents very good chemical stability in oxidizing and reducing atmosphere and shows ionic conductivity in a wide range of oxygen partial pressures. However, it reacts with NiO of the anode to form lanthanum–nickel oxide. This leads to a deterioration of the ionic conduction and the anode function. This reaction can be suppressed applying a diffusion barrier layer of $(\text{Ce,Sm})\text{O}_{2-x}$. On the other hand, the preparation of thin film LSGM dense electrolyte is more difficult in respect to CeO_2 -based and YSZ materials; for this reason the development of mature thin film deposition technology is now considered to push the development of LSGM electrolytes (Wang *et al.*, 2019).

In terms of protonic conductors, the most considered materials are the solid solutions obtained coupling two barium-based perovskites: BaCeO_3 and BaZrO_3 (Hossain *et al.*, 2018). The former is more conductive but is severely unstable in CO_2 atmosphere, while the latter is stable but is definitely more refractive and less conductive. The solid solution between the two, eventually doped with Y^{3+} , gives rise to a reasonably stable material with good conductive properties.

Anode Substrates and Anodes

The most commonly applied anode material is a nickel/YSZ cermet produced starting from a mixture of nickel oxide and YSZ powder. In the final structure of the electrode, the nickel oxide is then commonly reduced to nickel during the start-up phase of the cell or stack by the prevailing fuel atmosphere. The nickel serves as a catalyst for the oxidation reaction of the hydrogen and is finely dispersed around the YSZ particles. The function of the zirconia skeleton is to stabilize the porous electrode structure, to create an extended reaction zone by increasing the number of three-phase boundaries, and also to adapt the thermal expansion coefficient between the nickel and the other cell components.

The demands for an anode substrate with good electrical conductivity, good gas permeability, and fine-grained homogeneous microstructure can be obtained by the powders currently used and were studied in detail for Ni/8YSZ anode substrates. Since the anode substrate accounts for more than 90% of the material expenditure of the ceramic parts, this component is the most promising candidate for saving material. Therefore, low-cost nickel oxides of technical powder quality were considered (Tietz *et al.*, 2000) to replace the NiO used hitherto which satisfies very high demands on quality.

The introduction of an additional anode functional layer (see Fig. 1), allowed to divide the two tasks of the Ni/8YSZ anode substrate, i.e., the mechanical stability and the electrocatalytic conversion of the fuel. In this way it was possible to separately improve the material properties of the anode functional layer and the anode substrate. Therefore new cermets based on Ni/ Al_2O_3 or Ni/ TiO_2 were synthesized (Meschke *et al.*, 2001) to match the thermal expansion coefficient of the 8YSZ avoiding the thermoelastic bending during cell fabrication (Steinbrech *et al.*, 1997) and to reduce the costs of the substrate. However, during cell fabrication, a severe interaction with the anode layer was observed due to liquid-phase sintering, which led to a detrimental decrease of electrochemical performance. The cermet obtained mixing Ni with the electrolyte powder is therefore still the most common material used as anode in SOFC.

Apart from cermets, other materials have been considered as anode substrate, i.e., able to support the mechanical strength of the cell, among them metals (ferritic steels) or ceramics with n-type conductivity are the most studied. These alternatives offer solutions for the highly demanded reoxidation stability of the anode cermets, because they do not undergo a strong volume expansion during reoxidation. In particular, metal supported SOFCs (MS-SOFCs) have attracted considerable research interest for cost reduction, improved mechanical robustness and thermal shock resistance which make this technology attractive also for mobile applications. Many materials have been investigated for use as metal supports for SOFC and are typically either nickel or iron based. The coefficient of thermal expansion (CTE) of the metals has to be matched to that of the electrolyte to enable rapid thermal cycling and to increase cell durability. Table 3 lists some candidate materials to be used as metal support with their respective CTE.

Ni have been used by several research groups as support material. However, its low redox cycling tolerance, high susceptibility to coking and sulfur species, high cost and poor CTE matching with the electrolyte, restricted its application. The addition of Fe to Ni (in particular with weight ratio close to 1:1) allows to lower cost, improves the CTE but does not bring to any improvement in terms of stability in oxidant environment (Krishnan, 2017). Ni–Al porous substrates were also used for the production of MS-SOFC. Even the CTE with the electrolyte are different the degradation in the layers interface has not been observed over 100 h of operation in dry hydrogen (Solovyev *et al.*, 2015). On the other hand, ferritic stainless steels, have received significant interest due to their low cost, thermal compatibility with YSZ and CGO and better stability than Ni-based supports. Moreover, these alloys

Table 3 Candidate metal supports for MS-SOFC with CTE. The CTE of electrolytes (YSZ, CGO-LSGM) are in the order of 10–12 ppm K⁻¹

Metal	CTE (ppm K ⁻¹)
NiCrAlY, NiCrAl	15–16
Ni–Al	15
Ni	16.5
Ni–Fe (1:1)	13.7
300-Series stainless steel	18–20
400-Series stainless steel	10–12

Note: Tucker, M.C., 2010. Progress in metal-supported solid oxide fuel cells: A review. *J. Power Sour.* 195, 4570–45826. Krishnan, V.V., 2017. Recent developments in metal-supported solid oxide fuel cells *WIREs. Energy Environ.* 6, 246. doi:10.1002/wene.246. Gondolini, A., Mercadelli, E., Sangiorgi, A., Sanson, A., 2017. Integration of Ni-GDC layer on a NiCrAl metal foam for SOFC application. *J. Eur. Ceram. Soc.* 37, 1023–1030.

produce a thin, continuous, conductive chromia scale that is beneficial for the longevity of the cell. However, to improve the durability of these systems and avoid severe corrosion, ferritic steels have to be coated increasing the complexity of the overall cell manufacturing. In addition ferritic steel-supported SOFCs have to be produced using protection atmosphere during thermal cycles to hinder severe corrosion in air and Fe and Cr diffusion in the electrodic layer, that may lead to losing the n-type electronic conductivity of highly conductive ceramics (Marina *et al.*, 2002). To avoid that, NiCrAlY and NiCrAl supports have been considered for the production of MS-SOFC. The presence of Al in the foam produces, in fact a continuous Al₂O₃ scale at the surface of the metal that improve its oxidation resistance and make possible to thermally treat the layers at low temperature (up to 1050°C) in oxidant environment (Gondolini *et al.*, 2017). The cell produced showed decent stability after 54 redox cycles even if a partial delamination of anode substrate-anode functional layer occurs due to the volume variation between nickel and nickel oxide (Costa *et al.*, 2018).

Besides mechanical damage during reoxidation, anode cermets suffer also from sulfur poisoning or coking from the fuel gas, if the methane contains contaminants or insufficient amounts of water for internal reforming, respectively. Although efficient and compact desulfurizers are available and a controlled system operation can solve these problems, there is a continuous search for ceramic anode materials overcoming these drawbacks. In most cases, perovskite materials have been investigated for this purpose (Atkinson *et al.*, 2004) such as (Sr,La)TiO₃, (Sr,Y)TiO₃, (La,Sr)(Cr,Mn)O₃, (La,Sr)CrO₃, (La,Sr)MnO₃, (La,Sr)FeO₃, (Sr,Mg)MoO₆, (Sr,Fe)MoO₆, etc.

SrTiO₃-based compounds have attracted attention due to their good conductivity, dimensional stability and higher tolerance and resistance towards sulfur poisoning and carbon depositions. Tuning the substitution and stoichiometry levels on A- and B-sites of SrTiO₃-based perovskite (La, Nb, Y, and Ce) allows to achieve good catalytic activity for hydrogen oxidation, electrical conductivity and chemical stability in respect to the other perovskite-based materials at 700–850°C. The electrical conductivity of Y-SrTiO₃(YST) materials changes with the concentration of strontium in their structure, however the addition of small amount of Ni or ceria impregnation is necessary to improve its hydrogen catalytic activity (Shu *et al.*, 2019). Lanthanum-doped SrTiO₃ (LST) has shown good electronic conductivity and chemical/thermal stability in wide ranges of temperature, oxygen partial pressure and in presence of H₂S. However, this material shows lower electrochemical performance than Ni-based anode under humidified hydrogen. For this reason, LST is combined with other oxide ion conductors (CeO₂-based compounds and YSZ) and doped with different elements that precipitates in form of nanoparticles (Ni, Co, Fe, Pd, Ru, etc.) under strong reducing condition to improve its electrochemical and catalytic performances (Shu *et al.*, 2019; Gondolini *et al.*, 2018).

LaSrCrO₃-based materials (LSCr) are applied as SOFC anode materials especially when doped with cations with lower coordination number (Mn, Co, Fe, etc.) that enhanced LSC catalytic activity. LSCr doped with manganese is one of the most used perovskite thanks to its high temperature stability, good resistance to carbon deposit and redox stability (Tao and Irvine, 2003). Doping with Iron (LSCrF) on the other hand, gives a composition with excellent activity in the oxidation of H₂S and CH₄, however it exhibits poor electrical conductivity in respect to La-SrTiO₃-based compositions (Shu *et al.*, 2019). Also, nichelates (such as La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.44}Ni_{0.66}O_{3–d}) and molibdates (such as Gd₂Ti_{1.4}Mo_{0.7}O_{7–d}, Sr₂MgMoO_{6–d}) have recently showed very promising properties as anodes (Sreedhar, 2019).

As pure ceramics, however, the cell performance has always been lower than for the conventional Ni/8YSZ anode, because these anodes either do not have sufficient electronic or ionic conductivity or are not catalytically active. To improve the performance small additions of catalysts, element doping and the incorporation of ceramic composites is often considered. Further research and development are anyway necessary to achieve properties comparable with the ones shown by conventional anodes.

Cathode

Perovskite materials of the ABO₃ type are generally used as the cathode material mixed with an electrolytic phase to increase the triple phase boundary (TPB) and therefore the cell efficiency. A frequently used cathode material is lanthanum manganite (LaMnO₃, LSM) with substitutions of strontium or calcium at the A-site (Minh, 1993). Both A- and B-site substitutions have been

investigated extensively, so that these ceramics can be selected according to the demands made on their properties such as thermal expansion coefficient, electronic or ionic conductivity, and chemical interaction with the electrolyte. LSM is still the most popular cathode material in SOFC application, due to the thermomechanical compatibility with YSZ. LSM however, chemically interacts with YSZ at temperature higher than 1300°C, for this motivation a CeO₂-based coating is generally deposited between the electrolyte and cathode materials. The composite between LSM and YSZ is, up to now, the best combination of stability, performance and simply manufacturing (Sreedhar *et al.*, 2019). Lanthanum or strontium cobaltites have attracted much attention because of their high mixed ionic–electronic conduction. Indeed, (La,Sr)CoO₃ shows a higher cathodic performance than (La,Sr)MnO₃, but the cobaltite possesses a very different thermal expansion in comparison to YSZ (Tietz, 1999) and it reacts easily with this electrolyte at high temperatures ($\geq 1000^\circ\text{C}$), forming highly resistive La₂Zr₂O₇ or SrZrO₃ compounds. These unfavorable solid-state reactions can be avoided, when a ceria-based diffusion barrier layer is applied (Chen *et al.*, 1995). As a compromise between thermal expansion mismatch and electrochemical performance, the composition La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O₃ (LSFC) has been established as an alternative to (La,Sr)MnO₃ cathodes for reduced operating temperatures since the mid-1990s (Chen *et al.*, 1995; Sahibzada *et al.*, 1997). The advantage of such mixed ionic–electronic conducting cathodes relies on their increased reactive catalytic surface area over the whole perovskite grains. Therefore, the charge transfer of adsorbed oxygen atoms takes place directly on the perovskite surface. The increase in oxygen ion conductivity and hence in mixed conductivity is generally correlated with an increasing thermal expansion (Ullmann *et al.*, 2000). Therefore, an improvement of the transport properties is always linked to an increasing mismatch in thermal expansion related to the other cell components. In recent years, many studies have been devoted to the improvement of the electrochemical activity and microstructure stability of LSCF-based electrode materials to develop highly active and durable oxygen electrodes for intermediate and low temperature SOFCs. For doing so, different strategies including, nano-architecture, surface decoration, interface manipulation or design were considered. This led to the increase of electrocatalytic activities, reduction of the activation energy-area specific resistance, reduction in the surface segregation and chemical reactivity promoting microstructural stability and resistance towards contaminants such as chromium, sulfur, and boron under SOFC operation conditions (Jiang, 2019).

A rough classification of cathode materials regarding their electrocatalytic activity follows the order: LaCoO₃ > LaMnO₃ > LaFeO₃ > LaCrO₃. The electrocatalytic activity also varies with alkaline-earth concentration in the perovskite. Generally, cobalt-based compositions present higher conductivity with respect to the cobalt-free ones; on the other hand, CTE mismatch between cathode and electrolyte is disadvantageous for long time operation. For this reason, additional studies on cobalt-free perovskite materials are necessary to design higher performance cathode compositions (Hashim *et al.*, 2019).

Interconnect

The interconnect in SOFC stacks is the component that electrically connects the single cells and in planar systems additionally separates the gas compartments from each other and it is therefore subjected at the same time to highly reducing and oxidizing atmospheres. Interconnects must satisfy many different criteria: good electrical conductivity, gas tightness (to prevent O₂ and H₂ mixing), chemical compatibility with the adjacent components of the fuel cell, high corrosion resistance to the reaction gases, matched thermal expansion ($10\text{--}13 \times 10^{-6}\text{K}^{-1}$) and last, but not least, reasonable costs. In order to meet these requirements, two classes of materials have been developed for interconnects, namely ceramic and metallic materials (Anderson and Tietz, 2003). Whereas ceramic interconnects played a dominant role in the early SOFC developments, metallic interconnects are nowadays the most used materials due to the general trend toward lower operating temperatures (Bianco *et al.*, 2019).

Practically all ceramic interconnects which have been developed are based on LaCrO₃ for its strong chemical stability and excellent electric conductivity at temperature around 1000°C in fuel gas atmosphere. However, at lower temperatures lanthanum chromites exhibit oxygen deficiency as a consequence of their p-type semi conductive behavior with consequent reduction of electrical conductivity. In addition, lanthanum chromites show undesirable swelling in reducing atmospheres caused by the reduction of Cr⁴⁺ ions to Cr³⁺ and the formation of oxygen vacancies leading to strong internal stresses and possible cracking during operation.

Apart from these physical handicaps, the materials costs as well as the fabrication and processing costs due to the low sinterability are the most critical issues for ceramic interconnects.

Hence, while the advantages of metallic interconnects are obvious (high electrical conductivity, good ability for processing, and lower cost) they are strongly affected by corrosion and increasing resistance during operation, chromium evaporation, low high-temperature strength.

The long-term stability of the metallic interconnect is essentially governed by its corrosion characteristics. The materials used for interconnects are alloys forming chromium or alumina oxide (Bianco *et al.*, 2019). The former is preferred because it ensures sufficiently high conductivity of the thin oxide scales. Meanwhile several ferritic steels have been developed especially for SOFC application containing only very small amounts of aluminum and silicon to avoid the formation of highly resistive oxide scales and low amounts of manganese for the formation of (Cr,Mn)₃O₄ spinels as the outer corrosion scale (Quadackers *et al.*, 2003; Mehran *et al.*, 2019). Fe–Cr Alloy are at the moment the most considered materials for interconnects. In order to have suitable thermomechanical properties, however, the alloy is commonly modified with the dispersion of oxide particles of reactive elements such as Nb, Y, La, Ce, and Zr (Seo *et al.*, 2008). These oxides contribute to improve the scale adhesion to the substrate considerably reducing their growth and the outward Cr transport (Pint and Wright, 2005).

The main focus in interconnect development is still the improvement of the corrosion behavior, but also the reduction of contact resistance of the corrosion scales or in combination with coatings and the reduction of chromium evaporation to avoid a detrimental poisoning of the cathode with chromium species (Hilpert *et al.*, 1996). All these phenomena contribute mainly to the observed degradation of stack voltage during operation, but it is not yet clarified to what extent (Fontana *et al.*, 2012; Mehran *et al.*, 2019).

Protective and Contact Coatings

Many attempts have been made to reduce the damaging effect of chromium vapors on the cathode side by suitable protective layers. Other than being dense to prevent outward diffusion of chromium and inward diffusion of oxygen ions, the protective coating materials should possess high electrical conductivity ($ASR < 0.1 \Omega \text{ cm}^2$) and TEC not more than 10% different from the one of the interconnector, to ensure durability (Mah *et al.*, 2017).

Mainly two classes of compounds have been examined for this purpose: Perovskites and Spinel Oxide. Their function as diffusion barriers against volatile Cr species strongly depends on the quality of the layers (gas tightness, crack density).

As already mentioned, perovskites exhibit p-type electronic conduction and are stable in low oxygen partial pressure. The first perovskite to be developed was plasma-sprayed coatings of lanthanum chromite. These coatings are characterized by high contact resistances and high fabrication costs in comparison to ceramic methods using slurries or pastes. However, the reactivity of lanthanum chromite with metals, either with Cr- or Fe-based alloys, is low and the metal/ceramic interface is very stable under operating conditions. More recently ferrite-based composition such as LSCF have been considered as protective layer, but LSC still represent the most suitable material with ASR of $0.0028 \Omega \text{ cm}^2$ after 1600 h of operation at intermediate temperature (Tan *et al.*, 2019).

Spinel oxide of general formula AB_2O_4 are the most successful materials able to suppress chromium evaporation. The cubic spinel structure comprises divalent, trivalent or quadrivalent A and B ions in octahedral and tetrahedral sites respectively. The ratio between A and B cation governs the electrical conductivity and TEC of these materials. The highest conductivity up to now has been shown by $Cu_{1.3}Mn_{1.7}O_4$ even if the most studied compounds considered the Mn–Co System.

Chemical interactions between coatings and interconnect material increase when the alkaline earth content in the ceramic is increased. Often perovskite materials have been brought in contact with Cr-based alloys or steels and the formation of chromates (e.g., $CaCrO_4$ or $SrCrO_4$) was observed (Larring and Norby, 2000), leading to progressive decomposition of the perovskite material and a brittle interface. To reduce this effect, the application of cobalt oxide or cobalt manganese spinel between perovskite and alloy (Larring and Norby, 2000; Zahid *et al.*, 2004) as well as metals such as Nickel (Demeneva *et al.*, 2019) as being considered, showing a stable contact resistance with time.

Coating the ferritic steel Crofer22APU by wet powder spraying with a porous Co_3O_4 layer or a metallic Co layer leads to the formation of a new dense Cr-free reactive layer under the SOFC operating conditions (Zahid *et al.*, 2004). As a reaction product of Mn from the oxide scale of the steel and the Co_3O_4 layer, this dense layer may act as a barrier against vapor-phase transport of volatile Cr species. Contact materials are electrically conductive ceramics to improve the contact between interconnect and electrode. Whereas for the anode side metallic nickel is used (as mesh, foam, or paste), on the cathode side often ceramic cathode-like compositions are used, which possess conductivities in the range of $50\text{--}500 \text{ S cm}^{-1}$. Because there are no electrochemical requirements to be obeyed for the contact materials, they can vary significantly from the electrode materials and be optimized with regard to other physical and chemical properties than the electrodes. Apart from the electrical conductivity, the most important properties are the thermal expansion and the sintering behavior at assembling temperatures in the range of $800\text{--}1100^\circ\text{C}$. Because the contact layer thickness may vary between $30 \mu\text{m}$ and $200 \mu\text{m}$ and ceramic materials heat-treated below 1000°C are usually very porous, the specific conductivity of the material should be high. This is in fact the case for lanthanum cobaltites having specific conductivities up to 1700 S cm^{-1} . On the contrary, the thermal expansion of these cobaltites has a strong mismatch with the other cell components. For electrically conductive ceramics, therefore, a compromise between acceptable conductivity and tolerable mismatch in thermal expansion has to be made as for the cathode materials.

Regarding the deposition techniques, the choice depends on the materials to be deposited and the morphology of the surface considered. The most common are magnetron sputtering, screen printing, sol–gel dip coating and electrodeposition (Mah *et al.*, 2017).

Sealings

In planar SOFCs, gastight seals must be realized along the edges of each cell, along the outer edges of the stacking layers, and the gas manifold to separate the two gas compartments and to insulate the stacking layers from each other. There are different approaches that have been developed for sealing SOFCs: brazing, compressive seals, glass, glass ceramics, and glass composites (Smeacetto *et al.*, 2013). Irrespective to the material, the sealant must satisfy several different requirements: zero (or at least very low) gas permeability; good adhesion to the elements of the cell and interconnect; chemical, thermal and mechanical stability during manufacturing and operation; CTE compatible with the other elements; High electrical resistivity ($> 10^5 \Omega \text{ cm}$); minimum volatilization, elements diffusion, and reactivity with the operation gases; characteristics temperatures (softening, maximum shrinkage, etc.) compatible with the operation ones; superior thermal shock resistance; good sinterability, easy processing, and absence of defects; self-healing ability and obviously low cost (Tulyaganov *et al.*, 2013). Glass or glass ceramics are well known for joining of metals, especially the joining of steels (Donald, 1993) and are considered in great details as they can meet, in principle,

most of the requirements of an ideal sealant. Glass-ceramics in particular, are considered the most suitable candidates as their composition flexibility can be used to match the requirements of different materials. Many of these products are commercially available, but most of the sealing products are produced for low-temperature joining and room-temperature applications. However, no commercial product fulfills the requirement of a thermal expansion coefficient in the range of $10\text{--}13 \times 10^{-6}\text{K}^{-1}$ up to high temperatures. Therefore, many SOFC developers started their own sealing development. Most studies have been carried out on barium calcium aluminosilicate (BCAS) and barium calcium magnesium aluminosilicate (BCMAS). The comparison of BAS, CAS, and MAS glasses using B_2O_3 as a fluxing agent and TiO_2 , ZrO_2 , NiO , and Cr_2O_3 as a nucleating agent showed that the barium glass tended to react with chromium steel more than the other glasses, showed a faster crystallization, and an appropriate thermal expansion (Lahl *et al.*, 2000, 2002; Tulyaganov *et al.*, 2013). These materials can however interact forming BaCrO_4 in the presence of oxygen. For these reasons, different other compositions have been considered, such as the ones belonging to the $\text{Na}_2\text{O}\text{--}\text{SiO}_2$ system or diopside (Lin *et al.*, 2018) or $(\text{CaMgSi}_2\text{O}_6)$ – alkali one (Sabato *et al.*, 2019). Compatibility studies between steels and glasses clearly showed that the sealing material alone does not lead to a good joining. It is more important to adopt the interconnect/sealant couple. Under oxidizing conditions, the formed oxide scales of ferritic steels (chromium oxide scale at the inner interface to the steel followed by a scale of manganese chromium spinel at the outer interface toward the glass) are partially dissolved by the glass. This leads, on the one hand, to a good adhesion and sticking between sealant and steel, on the other hand, however, to a destabilization of the steel at the three-phase boundary glass/metal/air. Thus, good sticking and stability against corrosion may become conflicting objectives. As already mentioned, besides glass-ceramics, compressive seals and brazing systems have also been investigated (Fergus, 2005). In the case of compressive seals, metallic gaskets and mica-based materials (vermiculite, phlogopite) were tested. All seals are not hermetically gastight and require high mechanical loads for reaching low leakage rates. The latter greatly affects the mechanical stability of the cell: other than an higher mechanical resistance the high load requires an extremely flat cell therefore decreasing the level of warpage tolerated. To date, no stack has been successfully operated with such sealing systems. Also, the brazing has not yet reached a reliably applied status, but the use of $\text{Ag}\text{--}\text{CuO}\text{--}\text{Ti}$ brazes in combination with an insulating layer seems to offer technologically interesting alternatives to the glass-ceramic sealants (Weil *et al.*, 2005).

Remaining Issues/Technological Hurdles to Be Solved

During the recent decade, much progress has been made to bring SOFC systems to application and market. The selection of the material plays a crucial role to determine the performance and the reliability of the SOFC technology and needs to be further improved. Good advancements in this respect have been obtained through the development of more efficient and cheaper SOFC, lowering the operating temperature, widen the range of application and increase the durability. The production of thin film structures improves the overall cell performance and electrolyte conductivity leading to systems working at temperature below 600°C supported by metal interconnects (MS-SOFC). The use of metal supports with different material compositions, trace element doping and the deposition of protecting layers by means of advanced manufacturing techniques, pushed the MS-technology towards commercialization. MS-SOFCs have a great potential to be applied as vehicle Auxiliary Power Units (APUs), particularly in the $600\text{--}650^\circ\text{C}$ operation temperature (Krishnan, 2017) that is, up to now, the great balance between production costs and performances. Even if the technology is in the verge of final commercialization, there is still need of material development especially in terms of sealants and reducing the use of rare earth materials. Finally, much more work is needed to push the development of protonic SOFC in terms of cell, interconnector and sealing materials toward more practical applications.

References

- Anderson, H.U., Tietz, F., 2003. Interconnects. In: Singhal, S.C., Kendall, K. (Eds.), *High-Temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications*. New York: Elsevier Advanced Technology, pp. 173–195. (ISBN 1-85617-387-9).
- Atkinson, A., Barnett, S., Gorte, R.J., *et al.*, 2004. Advanced anodes for high-temperature fuel cells. *Nat. Mater.* 3, 17–27.
- Baur, E., Preis, H., 1937. Über Brennstoffzellen-Ketten mit Festleitern. *Z. Elektrochem.* 43, 727–732.
- Baur, E., Treadwell, W.E., 1916. Brennstoffelement. German Patent 325783.
- Bianco, M., Ouweltjes, J.P., Van herle, J., 2019. Degradation analysis of commercial interconnect materials for solid oxide fuel cells in stacks operated up to 18000 hours. *Int. J. Hydrog. Energy* 44 (5929), 31406–31422.
- Blum, L., Meulenberg, W.A., Nabielek, H., Steinberger-Wilckens, R., 2005. Worldwide SOFC technology overview and benchmark. *Int. J. Appl. Ceram. Tech.* 2, 482–492.
- Costa, R., Han, F., Szabo, P., *et al.*, 2018. Performances and limitations of metal supported cells with strontium titanate based fuel electrode. *Fuel Cells* 18, 251–259.
- Chen, C.C., Nasrallah, M.M., Anderson, H.U., Alim, M.A., 1995. Impedance response of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ based electrochemical cells. *J. Electrochem. Soc.* 142, 491–496.
- Demeneva, N.V., Kononenko, O.V., Matveev, D.V., Kharton, V.V., Bredikhin, S.I., 2019. Composition-gradient protective coatings for solid oxide fuel cells interconnectors. *Mater. Lett.* 240, 201–204.
- Donald, I.W., 1993. Preparation, properties and chemistry of glass and glass-ceramic-to-metal seals and coatings. *J. Mater. Sci.* 28, 2841–2886.
- Fergus, J.W., 2005. Sealants for solid oxide fuel cells. *J. Power Sour.* 147, 46–57.
- Fontana, S., Chevalier, S., Caboche, G., 2012. Metallic interconnects for solid oxide fuel cell: Performance of reactive element oxide coating during 10, 20 and 30 months exposure. *Oxid. Metals* 78, 307–328.
- Gondolini, A., Mercadelli, E., Sangiorgi, A., Sanson, A., 2017. Integration of Ni-GDC layer on a NiCrAl metal foam for SOFC application. *J. Eur. Ceram. Soc.* 37, 1023–1030.
- Gondolini, A., Mercadelli, E., Constantin, G., *et al.*, 2018. On the manufacturing of low temperature activated $\text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_{3-\delta}\text{--Ce}_{1-x}\text{Gd}_x\text{O}_{2-\delta}$ anodes for solid oxide fuel cell. *J. Eur. Ceram. Soc.* 38, 153–161.

- Gondolini, A., Mercadelli, E., Pinasco, P., *et al.*, 2012. Alternative production route for supporting $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ - $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (LSM-GDC) Int. J. Hydrog. Energy 37 (10), 8572–8581.
- Grove, W.R., 1839. On voltaic series and the combination of gases by platinum. Phil. Mag. Ser. 3 (14), 127–130.
- Grove, W.R., 1842. On a gaseous voltaic battery. Phil. Mag. Ser. 3 (21), 417–420.
- Hashim, S.S., Liang, F., Zhou, W., Surnarso, J., 2019. Cobalt-free perovskite cathodes for solid oxide fuel cells. ChemElectroChem 6, 3549–3569.
- Hilpert, K., Das, D., Miller, M., Peck, D.H., Wei, R., 1996. Chromium vapor species over solid oxide fuel cell interconnect materials and their potential for degradation processes. J. Electrochem. Soc. 143, 3642–3647.
- Hossain, S., Abdalla, A.M., Radenahmad, N., Zakaria, A.K.M., Azad, A.K., 2018. Highly dense and hemically stable proton conducting electrolyte sintered at 1200°C. Int. J. Hydrog. Energy 43 (211), 894–907.
- Huang, K., Tichy, R.S., Goodenough, J.B., 1998. Superior perovskite oxide-ion conductor; strontium- and magnesium-doped LaGaO_3 : I, phase relationships and electrical properties. J. Am. Ceram. Soc. 81, 2565–2575.
- Ishihara, T., Matsuda, H., Takita, J., 1994. Doped LaGaO_3 perovskite type oxide as a new oxide ionic conductor. J. Am. Chem. Soc. 116, 3801–3803.
- Jiang, S.P., 2019. Development of lanthanum strontium cobalt ferrite perovskite electrodes of solid oxide fuel cells – A review. Int. J. Hydrog. Energy 44, 7448–7493.
- Khan, M.A., Xu, C., Song, Z., *et al.*, 2018. Synthesize and characterization of ceria based nano-composite materials for low temperature solid oxide fuel cell. Int. J. Hydrog. Energy 43, 6310–6317.
- Krishnan, V.V., 2017. Recent developments in metal-supported solid oxide fuel cells. WIREs Energy Environ. 6, 246. doi:10.1002/wene.246.
- Lahl, N., Bahadur, D., Singh, K., Singheiser, L., Hilpert, K., 2002. Chemical interaction between aluminosilicate base sealants and the components on the anode side of solid oxide fuel cells. J. Electrochem. Soc. 149, A607–A614.
- Lahl, N., Singh, K., Singheiser, L., Hilpert, K., Bahadur, D., 2000. Crystallisation kinetics in $\text{AO-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$ glasses (A=Ba, Ca, Mg). J. Mater. Sci. 35, 3089–3096.
- Larring, Y., Norby, T., 2000. Spinel and perovskite functional layers between Plansee metallic interconnect (Cr-5 wt% Fe-1wt% Y_2O_3) and ceramic ($\text{La}_{0.85}\text{Sr}_{0.15}\text{O}_{1.91}\text{MnO}_3$) cathode materials for solid oxide fuel cells. J. Electrochem. Soc. 147, 3251–3256.
- Lin, C.K., Lin, T.W., Wu, S.H., Shiu, W.H., Lee, R.Y., 2018. Creep rupture of the joint between a glass-ceramic sealant and lanthanum strontium manganite-coated ferritic stainless steel interconnect for solid oxide fuel cells. J. Eur. Ceram. Soc. 38, 2417–2429.
- Mah, J.C.W., Muchtar, A., Somalu, M.R., Ghazali, M.J., 2017. Metallic Interconnects for solid oxide fuel cells: A review of protective coatings and deposition techniques. Int. J. Hydrog. Energy 42, 9219–9229.
- Marina, O.A., Canfield, N.L., Stevenson, J.W., 2002. Thermal, electrical and electrocatalytic properties of lanthanum-doped strontium titanate. Solid State Ionics 149, 21–28.
- Mehran, M., Kim, T.-H., Khan, M.Z., *et al.*, 2019. Highly durable nano-oxide dispersed ferritic stainless steel interconnects for intermediate temperature solid oxide fuel cells. J. Power Sour. 439, 227109.
- Meschke, F., Dias, F.J., Tietz, F., 2001. Porous Ni/TiO_2 substrates for planar solid oxide fuel cell applications. J. Mater. Sci. 36, 5719–5728.
- Minh, N.Q., 1993. Ceramic fuel cells. J. Am. Ceram. Soc. 76, 563–588.
- Nakayama, S., Sakamoto, M., 1998. Electrical properties of new type high oxide ionic conductor $\text{RE}_{10}\text{Si}_6\text{O}_{27}$ (RE=La, Pr, Nd, Sm, Gd, Dy). J. Eur. Ceram. Soc. 18, 1413–1418.
- Pint, B.A., Wright, I.G., 2005. Oxidation behavior of ODS Fe-Cr alloys oxid. Metals 63, 193–213.
- Quadackers, W.J., Piron-Abellan, J., Shemet, V., Singheiser, L., 2003. Metallic interconnectors for solid oxide fuel cells – A review. Mater. High Temp. 20, 115–127.
- Sabato, A.G., Rost, A., Schilm, J., Kusnezoff, M., Smeacetto, F., 2019. Effect of electric load and dual atmosphere on the properties of an alkali containing diopside-based glass sealant for solid oxide cells. J. Power. Sour. 4151, 15–24.
- Sahibzada, M., Steele, B.C.H., Zheng, K., Rudkin, R.A., Metcalfe, I.S., 1997. Development of solid oxide fuel cells based on a $\text{Ce}(\text{Gd})\text{O}_{2-x}$ electrolyte film for intermediate temperature operation. Catal. Today 38, 459–466.
- Schonbein, C.F., 1839. On the voltaic polarization of certain solids and fluid substances. Phil. Mag. Ser. 3 (14), 43–45.
- Seo, H.S., Jin, G., Jun, J.H., Kim, D.-H.H., Kim, K.Y., 2008. Effect of reactive elements on oxidation behaviour of Fe-22Cr-0.5Mn ferritic stainless steel for a solid oxide fuel cell interconnect. J. Power Sour. 178, 1–8.
- Shu, L., Sunarso, J., Hashim, S.S., *et al.*, 2019. Advanced perovskite anodes for solid oxide fuel cells: A review. Int. J. Hydrog. Energy 44, 31275–31304.
- Singh, K., Kannan, R., Thangadurai, V., 2019. Perspective of perovskite-type oxides for proton conducting solid oxide fuel cells. Solid State Ion. 339, 114951.
- Smeacetto, F., Salvo, M., Santarelli, M., *et al.*, 2013. Int. J. Hydrog. Energy 38, 588–596.
- Solovoyev, A.A., Rabotkin, S.V., Shipilova, A.V., *et al.*, 2015. Solid oxide fuel cell with Ni-Al support. Int. J. Hydrog. Energy 40, 14077–14084.
- Sreedhar, I., Agarwal, B., Goyal, P., Singh, S.A., 2019. Recent advances in material and performance aspects of solid oxide fuel cells. J. Electroanal. Chem. 848, 113315–113351.
- Steinbrech, R.W., Caron, A., BlaG, G., Dias, F.J., 1997. Influence of sintering characteristics on component curvature of electrolyte-coated anode substrates. In: Stimming, U., Singhal, S.C., Tagawa, H., Lehnert, W. (Eds.), Solid Oxide Fuel Cells (SOFC-V). Pennington, NJ: The Electrochemical Society, pp. 727–736.
- Su, S., Gao, X., Zhang, Q., Kong, W., Chen, D., 2015. Anode-versus cathode-supported solid oxide fuel cell: Effect of cell design on the stack performance. Int. J. Electrochem. Sci. 10, 2487–2503.
- Tan, K.H., Rahman, H.A., Taib, H., 2019. Coating layer and influence of transition metal for ferritic steel interconnector solid oxide fuel cell: A review. Int. J. Hydrog. Energy 44, 30591–30605.
- Tao, S.W., Irvine, J.T.S., 2003. A redox-stable efficient anode for solid oxide fuel cells. Nat. Mater. 2, 320–323.
- Tietz, F., 1999. Peculiarities in the thermal expansion behavior of ceramic fuel cell materials. In: Vincenzini, P. (Ed.), Proceedings of the 9th CIMTEC-World Ceramic Congress and Forum on New Materials. Innovative Materials in Advanced Energy Technologies, Vol. 24, pp. 61–70. Faenza, Italy: Techna Publishers S.r.l.
- Tietz, F., 2003. Materials selection for solid oxide fuel cells. Mater. Sci. Forum 426–432, 4465–4470.
- Tietz, F., Dias, F.J., Simwonis, D., Stover, D., 2000. Evaluation of commercial nickel oxide powders for components in solid oxide fuel cells. J. Eur. Ceram. Soc. 20, 1023–1034.
- Tucker, M.C., 2010. Progress in metal-supported solid oxide fuel cells: A review. J. Power Sour. 195, 4570–4582.
- Tulyaganov, D.U., Reddy, A.A., Kharton, V.V., Ferreira, J.M.F., 2013. Aluminosilicate-based sealants for SOFCs and other electrochemical applications – A brief Review. J. Power Sour. 242, 486–502.
- Ullmann, H., Trofimenko, N., Tietz, F., Stover, D., Ahmad-Khanlou, A., 2000. Correlation between thermal expansion and oxide ion transport in mixed conducting perovskite-type oxides for SOFC cathodes. Solid State Ion. 138, 79–90.
- Wang, F., Lyu, Y., Chu, D., *et al.*, 2019. The electrolyte materials for SOFCs of low-intermediate temperature: Review. J. Mater. Sci. Technol. 35, 1551–1562.
- Weil, K.S., Coyle, C.A., Darsell, J.T., Xia, G.G., Hardy, J.S., 2005. Effects of thermal cycling and thermal aging on the hermeticity and strength of silver-copper oxide air-brazed seals. J. Power Sour. 152, 97–104.
- Zahid, M., Tietz, F., Sebold, D., Buchkremer, H.P., 2004. Reactive coatings against chromium evaporation in solid oxide fuel cells. In: Mogensen, M. (Ed.), Proceedings of the 6th European SOFC Forum. European Fuel Cell Forum, Lucerne, Vol. 2, pp. 820–827. Oberrohrdorf, Switzerland.

Laser Processing of Energy Storage Materials

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Introduction

The past decade has brought a growing interest in energy storage and renewable energy sources such as rechargeable batteries and solar cells to meet the increasing energy demands of a wide-range of devices, in particular smaller scale electronic devices, such as portable personal electronics and micro-electromechanical systems (MEMS). To accommodate this demand, it is essential to develop small-scale energy storage systems. Many techniques have been applied to manufacture small-scale energy storage systems, such as thin-film, stretchable and three-dimensional (3D) batteries (Sun *et al.*, 2013; Mazor *et al.*, 2012; Wang *et al.*, 2011; Bates *et al.*, 2000). Among many techniques utilized to date, laser-based process techniques, such as laser-induced forward transfer (LIFT), pulsed laser deposition (PLD) and laser surface modification (LSM), have been proposed as practical approaches to integrate various types of micropower sources, such as thin-film microbatteries, ultracapacitors, and solar cells for small scale electronic devices.

Lasers are a versatile tool that delivers energy at selected locations with a laser beam size of several microns, thus allowing microscale processing of materials. One of the key advantages in lasers is their direct-writing capability that can eliminate expensive photolithographic patterning processes in many device fabrications, thus lowering the manufacturing cost (Arnold *et al.*, 2007; Hon *et al.*, 2008; Piqué and Chrisey, 2001; Roy, 2007; Serra and Piqué, 2019). Furthermore, since photons can be absorbed near the surface region, laser light is an ideal tool for surface modification without damaging the substrate underneath, thus allowing the use of plastic substrates for flexible devices. Recently, three-dimensional (3D) electrodes have been proposed to enhance the power density in microbatteries while the high energy density of these systems is maintained (Ferrari *et al.*, 2015; Jeyaseelan and Rohan, 2009; Oudenhoven *et al.*, 2011). Laser processing techniques can be utilized to manufacture these 3D electrodes for Li-ion microbatteries (Ferrari *et al.*, 2015). In addition, laser processing techniques can also be utilized to embed the battery components into the device package, which can reduce the device size and weight (Sutto *et al.*, 2006). Therefore, the future of laser processing techniques for manufacturing micropower sources looks very promising. This chapter will provide a brief review of LIFT techniques used for fabricating ultracapacitors and thick-film microbatteries, PLD techniques used for fabricating thin-film microbatteries, and LSM processes used for 3D electrode microbatteries. Lastly, we will discuss challenges and future of laser processing techniques to develop advanced energy storage systems.

Laser-Induced Forward Transfer Techniques

Laser induced forward transfer (LIFT) is an additive direct write technique that allows high-resolution printing of complex materials from a donor film to a receiver substrate using a pulsed laser beam. Fig. 1 shows a schematic illustration of the basic components of the LIFT system. A pulsed laser beam is used to induce the printing of material from a donor film onto a receiver substrate. The donor film is prepared on a laser-transparent quartz wafer by applying the material to be transferred. The receiver substrate is placed on the x-y stage, facing the donor film separated by a distance of 50–1000 μm . Laser beam is focused on the backside of the donor film by a microscope objective. Upon absorbing the incident laser pulse above the threshold energy, material is ejected from the donor film and transferred toward the receiver substrate. The laser fluences of 10–100 mJ cm^{-2} are typically used for LIFT of battery materials. In comparison with other printing techniques, LIFT processes can be performed at ambient conditions without using clean-room environments or vacuum.

One important feature of the LIFT process for battery materials is that the printed materials typically show porous structures. These porous structures are an essential feature for batteries due to an increased contact area for the electrolyte permeating the active electrode materials, leading to improved charge transfer and accordingly an enhancement in utilization of the electrode materials. Another important feature of the LIFT printing in comparison to inkjet printing is the former's suitability to print high viscosity nanoinks due to its nozzle-free nature (Piqué *et al.*, 2008; Duocastella *et al.*, 2012). Despite its simplicity, inkjet printing is limited to printing only low viscous inks to avoid clogging of the dispensing nozzles (Calvert, 2001). Thus, LIFT printing of high viscosity pastes enables a wide range of applications such as 3D interconnects, metamaterials, free-standing structures, and circuit repairs (Auyeung *et al.*, 2009; Auyeung *et al.*, 2011; Kim *et al.*, 2010, 2013; Mathews *et al.*, 2013; Piqué *et al.*, 2008, 2013; Wang *et al.*, 2010a). In this section, we will discuss the LIFT printing of active electrodes in energy storage systems, such as batteries and capacitors.

Laser Printing of Thick Film Electrodes

Lasers have been used to print thick-film electrodes for alkaline and Li-ion microbatteries (Kim *et al.*, 2007, 2012, 2014; Ollinger *et al.*, 2006a,b; Piqué *et al.*, 2004; Wartena *et al.*, 2004). Compared to sputter-deposited thin-film electrodes, laser-printed thick-film electrodes produce much higher capacities per electrode area. This enhanced cell performance is related to the previously mentioned porous structures of the laser printed electrodes because this porosity allows improved Li-ion diffusion across the

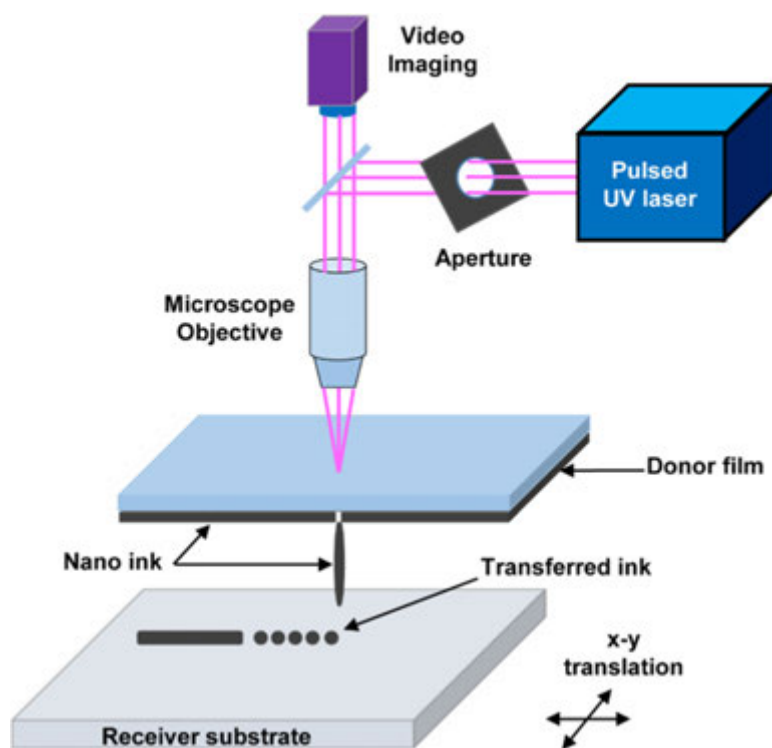


Fig. 1 A schematic illustration of the laser-induced forward transfer (LIFT) setup.

electrodes without a significant internal resistance loss. Kim *et al.* (2007) used a ns-laser ($\lambda = 355$ nm) to print both thick-film electrodes (LiCoO_2 cathode and carbon anode) for Li-ion microbatteries and studied their electrochemical properties. In this work, the laser-printed electrodes were separated by a laser-cut porous membrane that was soaked with a gel polymer electrolyte to build mm-size solid-state packaged Li-ion microbatteries. Fig. 2(a) and (b) shows a cross-sectional schematic diagram and an SEM image of a typical Li-ion microbattery printed by LIFT.

It is important to produce thicker electrodes for achieving high charge/discharge capacity in Li-ion microbatteries. One important feature of LIFT is that the thickness of the printed films can be easily controlled by changing the number of printing passes. As seen in Fig. 2(c), the thickness and mass of the LiCoO_2 cathodes can be linearly increased with the number of LIFT printing passes. Accordingly, the charge/discharge capacity can also be increased with the cathode film thickness (up to $115\ \mu\text{m}$ thick). (See Fig. 2(d)). In this case, a porous structure with high surface areas allows better ionic and electronic transport through the thick electrodes ($\sim 115\ \mu\text{m}$) with small internal cell resistance. In addition, these thick film microbatteries also exhibit a fast discharge rate, which is important for high-power density device applications. The cell with a $68\ \mu\text{m}$ thick LiCoO_2 cathode provides a maximum density of $38\ \text{mW cm}^{-2}$ at a discharge rate of $10\ \text{mA cm}^{-2}$. It is useful to compare the battery performances (discharge capacities per active electrode area) of LIFT-printed thick-film electrodes with those made by sputter-deposited thin-films. Typical sputter-deposited thin-film electrodes (thickness = $2.5\ \mu\text{m}$, active area = $1\ \text{cm}^2$) produce a discharge capacity of $160\ \mu\text{Ah cm}^2$ at a discharge rate of $100\ \mu\text{A cm}^2$ (Bates *et al.*, 2000) while the LIFT-printed thick-film electrodes (thickness = $115\ \mu\text{m}$, active area = $0.49\ \text{cm}^2$) produce a discharge capacity of $\sim 2600\ \mu\text{Ah cm}^2$ at the same discharge rate. Although the volumetric capacity is three times smaller than that of the sputter-deposited electrodes, the laser-printed thick film microbatteries can deliver orders of magnitude higher discharge capacity per active electrode area. Thus, the laser-printed thick film microbatteries might be suitable for small portable electronics where limited space is available for the power source.

Compared to lithium-ion batteries, lithium-sulphur batteries can deliver a much higher theoretical discharge capacity ($1675\ \text{mAh g}^{-1}$), which is an order of magnitude higher than that of olivine LiFePO_4 electrode ($170\ \text{mAh g}^{-1}$). Rosenberg and Hintennach (2013) fabricated lithium-sulphur based electrodes by LIFT using a XeCl excimer laser ($\lambda = 308$ nm). In this design, electrodes were prepared by three printing steps: First, a carbon binder mixture was printed on the substrate, then the sulphur was printed onto the carbon layer, and finally a thin carbon layer was printed to fully cover the sulphur materials within carbon matrix. The thickness of all three layers was $\sim 60\ \mu\text{m}$. The cells based on these laser-printed electrodes were cycled galvanostatically between 1.0 and 3.0 V versus Li/Li^+ and exhibited a remarkably high discharge capacity as high as $\sim 1200\ \text{mAh g}^{-1}$ at the 1 C current rate and a 79% capacity retention after 400 cycles.

Laser Printing of Solid State Electrolytes

Typical Li-ion battery systems consist of a lithiated metal oxide cathode, a lithium metal (or carbon/graphite) anode, and a lithium ion conducting membrane soaked with a liquid electrolyte. A liquid electrolyte is commonly utilized in commercial Li-ion

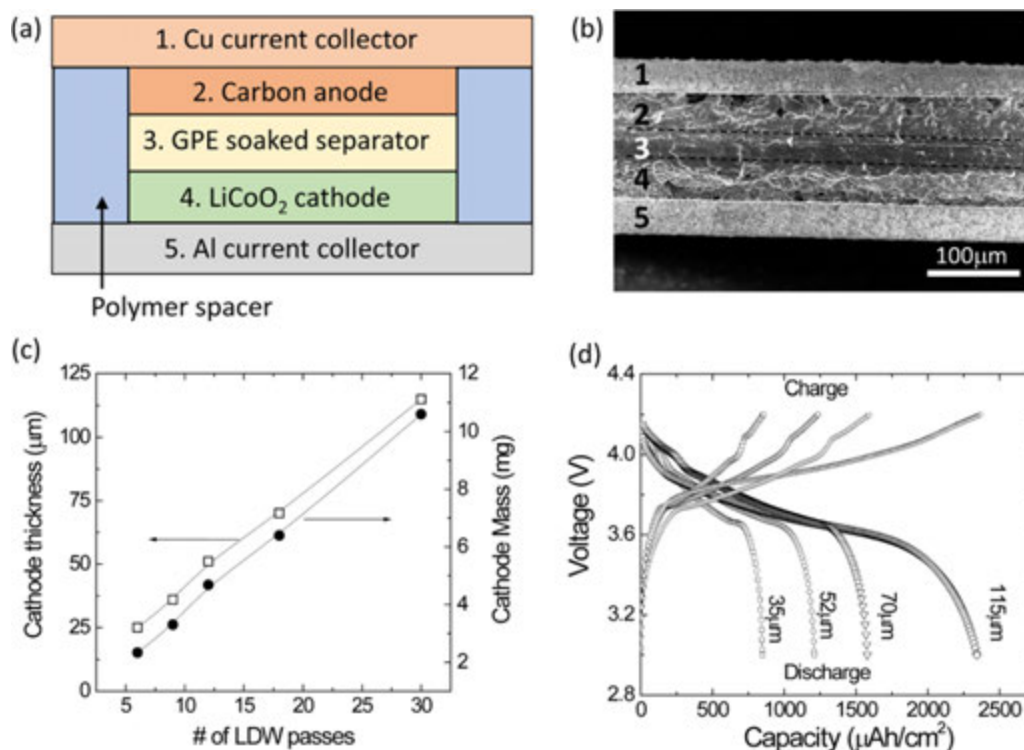


Fig. 2 (a) Cross sectional schematic diagram (not to scale) of a typical Li-ion microbattery. (b) Cross sectional SEM micrograph of a packaged thick-film Li-ion microbattery. (c) LiCoO₂ Cathode thickness vs. Cathode mass as a function of the number of LIFT passes. (d) Voltage vs. capacity per unit area for a Li ion microbatteries with different thicknesses of LiCoO₂ Cathodes. Reprinted Kim, H., Auyeung, R.C.Y., Piqué, A., 2007. Laser-printed thick-film electrodes for solid-state rechargeable Li-ion microbatteries. *J. Power Sources* 165, 413–419. Copyright (2007), with permission from Elsevier.

batteries due to its high ionic conductivity. Recently, there is a strong interest in developing all-solid state battery, which utilizes a solid-state electrolyte since the use of liquid electrolyte may cause safety and leakage issues. LIFT process was used to print a solid-state electrolyte membrane for Li-ion microbatteries (Ollinger *et al.*, 2006a,b). This solid state electrolyte membrane offers some important advantages in comparison to a liquid electrolyte. It provides a proper strength and flexibility of the co-polymer matrix, while exhibiting the proper electrochemical behaviour for ionic liquids with an ionic conductivity of 1–3 mS cm⁻¹. Thus, the laser-printed solid electrolyte membrane can serve as both the separator and the electrolyte. Fig. 3(a) shows the optical image of laser-printed solid-state membrane on a glass substrate. This membrane was dried at 75°C for 1 h creating a continuous flexible pinhole free membrane. As shown in Fig. 3(b), it is flexible enough to be lifted from the glass substrate using tweezers without breaking the membrane. Fig. 3(c) shows the charge/discharge cycles of a Li-ion microbattery prepared with the 20 μm thick laser-printed solid-state membrane, the Li-metal anode and the 30 μm thick LiCoO₂ cathode. This battery was charged/discharged at 40 μA cm⁻² and exhibited a discharge capacity of 495 μAh cm⁻² with a coulomb efficiency of 98% after the 4th cycle. However, the coulomb efficiency of this battery decreased below 50% after 100 cycles. Thus, more investigations are necessary to further improve the battery performance for “all laser-printed batteries” based on the solid-state electrolyte membrane.

Laser Printing of Ultracapacitors

Ultracapacitors, also known as supercapacitors, are electrochemical energy storage and power generation devices that show electrochemical properties similar to both batteries and capacitors. Similar to batteries, ultracapacitors can store a large amount of energy during charging state and similar to capacitors, they can discharge very high power density in a very short time. Hydrous ruthenium oxide has been proposed as an excellent electrode for ultracapacitors because rapid insertion and release of electrons and protons can occur in this material due to its high specific surface area (Sarangapani *et al.*, 1996). One of the advantages in LIFT is that it can print complex ink composed of the electrode material and relevant electrolyte. Arnold *et al.* (2002) fabricated a planar type of hydrous ruthenium oxide ultracapacitors by printing a composite ink composed of ruthenium oxide and electrolyte. As shown in Fig. 4(a) and (b), ultracapacitors were printed on 1 cm² gold-coated quartz substrate using LIFT technique and then they were laser micromachined into four electrically isolated cells. The charge/discharge curves for these ultracapacitors are shown in Fig. 4(c). The ultracapacitors delivered the linear charge/discharge behaviour at constant current rates, suggesting ideal capacitor behaviour. These ultracapacitors connected in series and parallel combination can be discharged at high current rate (> 50 mA) for delivering the proper additive values (see Fig. 4(d)) (Arnold *et al.*, 2003).

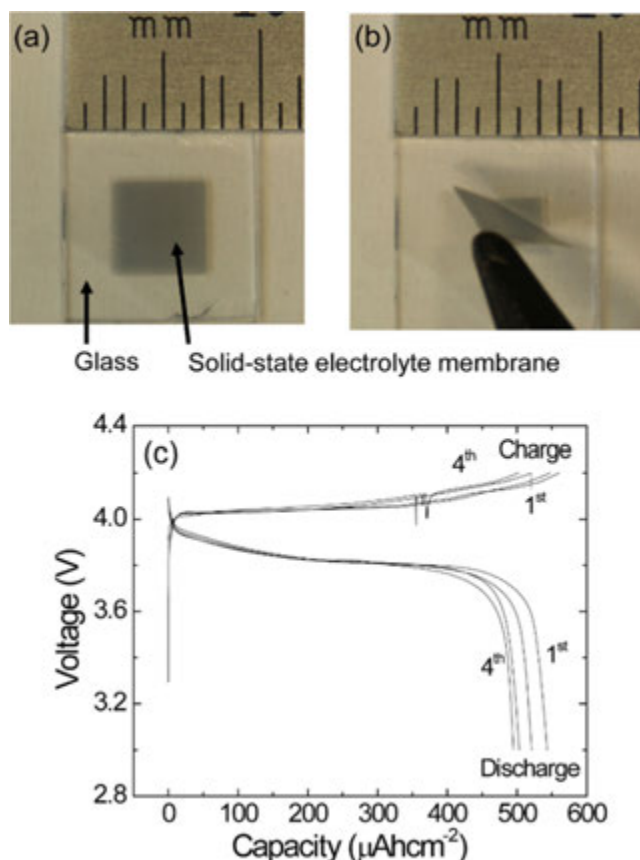


Fig. 3 Optical images of (a) the laser-printed solid-state membrane on a glass substrate and (b) membrane partially lifted off of glass substrate by tweezers. (c) Charge-discharge performance of a packaged Li microbattery (LiCoO₂/solid electrolyte membrane/Li) cycled between 4.2 and 3 V at current density of 40 μA/cm². The battery was tested in air at 25°C. The active electrode area is 1 cm². Reprinted from Ollinger, M., Kim, H., Sutto, T.E., Piqué, A., 2006a. Laser direct-write of polymer nanocomposite. *Appl. Sur. Sci* 252, 8212–8216. Copyright (2006), with permission from Elsevier.

In summary, LIFT is a powerful technique for printing thick films for microbatteries and ultracapacitors. Thick-film electrodes (cathodes and anodes) with high discharge capacities were fabricated by LIFT printing for microbatteries. LIFT process was also used for printing solid state electrolyte membranes with an ionic conductivity of 1–3 mS cm⁻¹.

Pulsed Laser Deposition Techniques

Pulsed laser deposition (PLD) is a physical vapor deposition (PVD) technique that allows high quality thin film deposition of materials in a vacuum chamber using a high power pulsed laser beam. Fig. 5 shows a schematic illustration of the basic components of the PLD system. A high power pulsed laser beam is focused inside a vacuum chamber onto the target which is typically rotated to avert its fast deterioration and maintain its surface under approximately constant conditions. Upon laser irradiation, the target material is vaporized and creates a plasma plume that expands from the target to the substrate, producing a thin film on the substrate. The target-substrate distance can be adjusted between 4 and 10 cm. Key parameters that can affect the film properties are laser fluence, substrate temperature and oxygen partial pressure. Furthermore, the use of lattice matched substrates with the film is also important to grow epitaxial thin films with preferred orientations.

PLD process for thin film growth has some important advantages over other PVD processes: (1) PLD process can occur at dynamic range of chamber pressures from ultrahigh vacuum (UHV) to very high pressures (up to beyond 1 Torr) and in any kind of background gas, such as oxygen or argon. (2) It can grow multilayer thin films using a multi-target carousel system since the laser beam can be alternatively focused over two or more targets. This capability is well suited for manufacturing complex stacks, such as layered battery structures. (3) It allows a congruent transfer of the composition between the target and the film. This is attributed to the extremely high heating rates on the target surface due to its strong interaction with the laser irradiation. When the laser fluence is increased above the ablation threshold where the absorbed laser energy becomes higher than that needed for evaporation, the flux of vaporized species is not dependent on the vapor pressures of the target constituents. This nonequilibrium process leads to the congruent evaporation of the

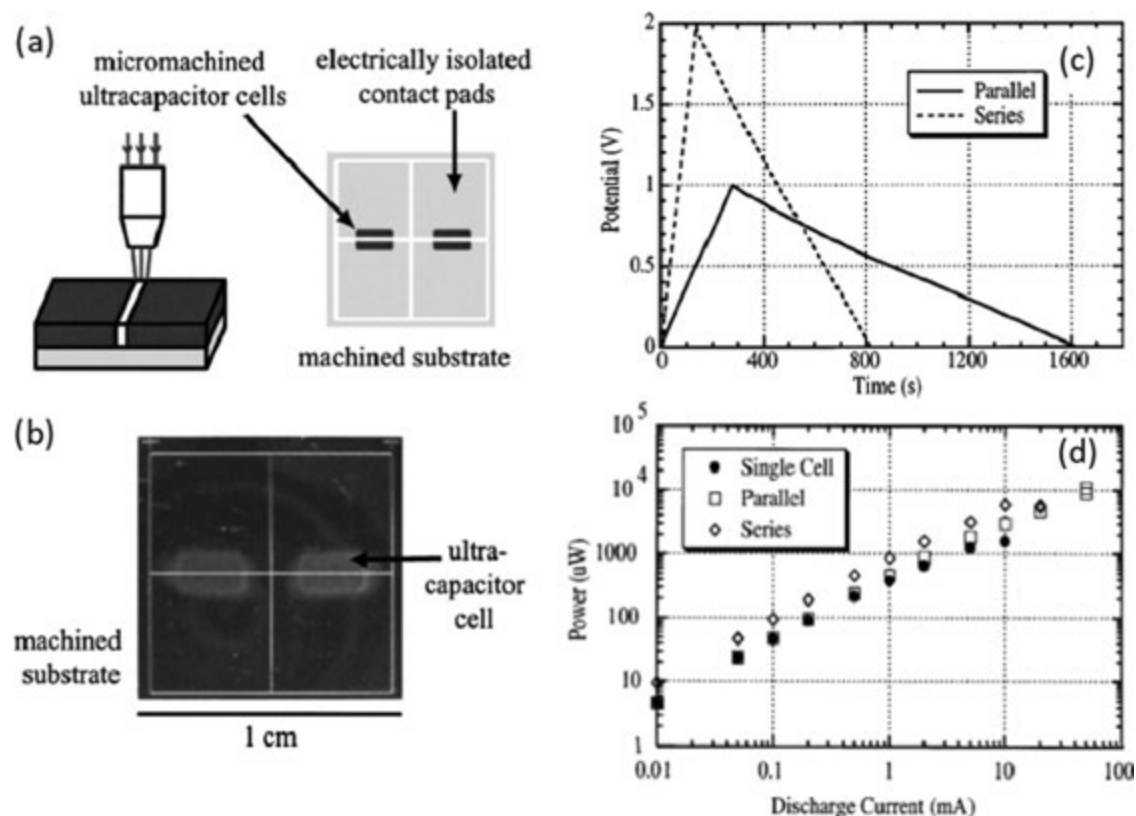


Fig. 4 (a) Micromachining to produce a planar $\text{RuO}_2\cdot 0.5\text{H}_2\text{O}$ micro-ultracapacitor. (b) Picture laser machined planar micro-ultracapacitors on gold-coated quartz substrate. (c) Plot showing the charging/discharging behaviour of hydrous ruthenium oxide ultracapacitor printed by LIFT. Cell is charged at $50\text{ }\mu\text{A}$ and discharged at $10\text{ }\mu\text{A}$. Starting lines are indicative of ideal capacitor behaviour. Total electrode mass is $100\text{ }\mu\text{g}$ with a footprint of 2 mm^2 . (d) Power as a function of discharge current for a single ultracapacitor cell as well as parallel and series combinations. The power is calculated over $0\text{--}1\text{ V}$ for the single cell and parallel combination, and $0\text{--}2\text{ V}$ for the series combination. Reproduced with the permission from Arnold, C.B., Wartena, R.C., Swider-Lyons, K.E., Piqué, A., 2003. Direct-write planar micro-ultracapacitors by laser engineering. *J. Electrochem. Soc.* 150, A571–A575. Copyright (2003), The Electrochemical Society.

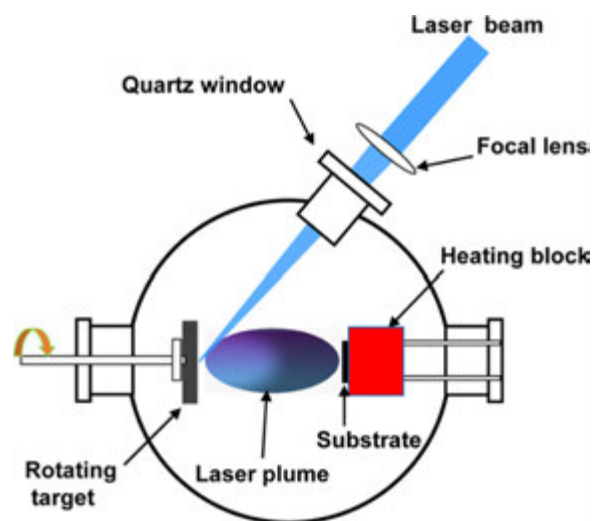


Fig. 5 Schematic of the basic components of a pulsed laser deposition (PLD) system.

target material. It is very difficult to achieve this stoichiometric transfer between target and substrate from other PVD processes such as sputtering or e-beam. The electrochemical properties of pulsed-laser deposited thin film electrodes (cathodes, anodes and solid electrolytes) for lithium ion microbatteries will be discussed in this section.

Table 1 Kinetic energy of species and heat-treatment for LiCoO₂ thin-films grown by PLD and sputtering techniques

Method of preparation	Kinetic energy (eV)	Crystallization temperature	Heat-treatment	References
PLD	10–100	300–600°C	In-situ heating No post-annealing	(Julien <i>et al.</i> , 2001; Xia <i>et al.</i> , 2006)
Sputtering	5–10	700–800°C	In-situ heating Post-annealing	(Bates <i>et al.</i> , 2000; Kim, 2004)

PLD of Cathode Thin Films

Recently, thin film Li-ion microbatteries have received increasing interests due to their potential applications as micropower sources for small scale devices such as micro-sensors and implantable medical sensors. PLD technique has been used to fabricate various cathode thin films for Li-ion microbatteries, including LiCoO₂, LiNiO₂, LiNi_{0.8}Co_{0.2}O₂, LiMn₂O₄, Li(NiMnCo)O₂ and LiFePO₄. In Li-ion microbatteries, an ideal thin-film cathode is a well-crystallized, layered structure of lithiated oxides. Thus, a post deposition annealing process at relatively high temperatures is commonly used to achieve good film crystallinity. However, this high temperature annealing step often creates microcracks in the lithiated films that cause a shorting problem in thin-film microbatteries. Furthermore, this high temperature annealing also damages the current collecting layers and substrate underneath the cathode films. One of advantages in PLD grown thin films is that the film can be crystallized at relatively low temperatures compared to those grown by other PVD techniques. This is because the kinetic energy (10–100 eV) of the ejected species in the laser-induced plasma plume is much higher than those from other PVD techniques, such as sputtering (5–10 eV) and evaporation (<1 eV) (Eason, 2006; Chrisey and Hubler, 1994). As shown in Table 1, LiCoO₂ cathode thin films fabricated by sputtering require a post deposition annealing (700–800°C) (Bates *et al.*, 2000; Kim, 2004) to achieve better crystallized films, while the same cathode thin films grown by PLD can be crystallized at temperatures (300–600°C) without any postdeposition annealing. Kuwata *et al.* (2006) reported that PLD-grown LiCoO₂ thin films become well-crystallized structures with a high density and smooth surface morphology without sign of cracks, thus essential for high performance in thin film batteries. Julien *et al.* also fabricated the well-crystallized LiCoO₂ thin films with a single layered structure at 300°C.

The crystallographic orientation is also important parameter to affect the electrochemical activity of the cathode thin films. In general, highly oriented thin films can easily be formed by PLD process due to a layer-by-layer growth mode of the PLD films (Chrisey and Hubler, 1994). Xia and Lu (2007) fabricated LiCoO₂ cathode thin films by PLD and the results showed that the (003) preferred orientation leads to reduced Li-ion diffusivity while the (101) and (104) orientations tend to increase the Li-ion diffusivity. The substrates also play an important role to determine the microstructure of the cathode thin films. For example, LiNi_{0.5}Mn_{0.5}O₂ cathode thin films were grown by PLD technique on two different substrates (Au and stainless-steel) and the results showed that the films grown on stainless-steel formed along a spinel structure due to a severe interdiffusion between the film and the substrate during high temperature deposition process, while the films grown on Au substrate showed a layered structure. The battery based on LiNi_{0.5}Mn_{0.5}O₂ cathode thin film on the Au substrate exhibited a reversible capacity of ~150 mAh g⁻¹, which is four times higher than that of the stainless-steel substrate (40 mAh g⁻¹) (Xia *et al.*, 2008).

Even though the film stoichiometry is normally close to the target stoichiometry in PLD, it is not necessarily true in the case that the targets consist of volatile light elements such as lithium (Simmen *et al.*, 2008). If a target contains lithium, this light element can be easily scattered by background gas molecules in the laser-induced plasma plume or be ejected by energetic species arriving at the film surface during PLD process. Thus, the lithium content in the deposited film tends to be lower than the target. This lower lithium content in the film will cause structural changes and impurity formation and eventually degrade the battery performance. Simmen *et al.* (2008) fabricated LiMn₂O₄ cathode thin films with a desired lithium content by PLD using a Li-excess composite target and achieved a discharge capacity of ~42 μAh cm⁻² μm⁻¹. LiCoO₂ cathode thin films were also fabricated by PLD using a target containing 15% excess Li₂O content with a reasonably good discharge capacity (50–60 μAh cm⁻² μm⁻¹) (Xia and Lu, 2007).

Vanadium oxide thin films have been used as cathode material of Li-ion batteries due to its large theoretical specific capacity (V₂O₅, 147 mAh g⁻¹) (Mauger and Julien, 2018). One advantage of vanadium oxide is that crystalline V₂O₅ films can be grown by PLD at a relatively low temperatures as low as 200°C. Madhuri *et al.* (2002) reported that highly c-axis orientated crystalline V₂O₅ cathode thin films were successfully synthesized on ITO-coated glass substrate by PLD at relatively low temperatures as low as 200°C. Recently, amorphous vanadium oxides (a-VO_x) thin films are becoming a popular cathode material for Li-ion-ion batteries because a-VO_x can offer shorter diffusion paths and thus can deliver high discharge capacity in comparison to crystalline VO_x counterparts. PLD has been successfully utilized for manufacturing a-VO_x thin films on stainless steel substrates from V₂O₅ target in the oxygen partial pressures of 0–30 Pa (Petnikota *et al.*, 2018). The cells based on these V₂O₅ cathode thin films exhibited a reversible specific capacity as high as 300 mAh g⁻¹ at the C/10 current rate and a 90% capacity retention after 100 cycles. Table 2 shows the electrochemical properties of various cathode thin films fabricated by PLD.

PLD of Anode Thin Films

Amorphous silicon (a-Si) thin films have been widely studied as a potential anode for Li-ion batteries due to its large theoretical capacity (Li₂₂Si₅, 4200 mAh g⁻¹). Although there is a huge volume expansion (>300%) during lithiation, Xia and Lu (2007)

Table 2 Electrochemical properties of thin-film cathodes fabricated by PLD

Material	Substrate	Capacity	References
LiCoO ₂	SiO ₂ /Si	64 $\mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$	(Kuwata <i>et al.</i> , 2006)
LiCoO ₂	Pt/Cr/SiO ₂	69 $\mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$	(Matsuda <i>et al.</i> , 2018)
LiCo _{0.5} Al _{0.5} O ₂	SnO ₂ -glass	30 mAh g^{-1}	(Perkins <i>et al.</i> , 1999)
LiNi _{0.8} Co _{0.2} O ₂	Ni	60 $\mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$	(Wang <i>et al.</i> , 2001)
LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂	Si, Ni	98 $\mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$	(Ramana <i>et al.</i> , 2007)
LiFePO ₄ -C	Pt/Si	20 $\mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$	(Lu <i>et al.</i> , 2008)
Li _{1.13} Mn ₂ O _{3.73}	stainless steel	42 $\mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$	(Simmen <i>et al.</i> , 2008)
LiNi _{0.5} Mn _{0.5} O ₂	Au	150 mAh g^{-1}	(Xia <i>et al.</i> , 2008)
LiNi _{0.5} Mn _{0.5} O ₂	stainless steel	40 mAh g^{-1}	(Xia <i>et al.</i> , 2008)
Li _{1.2} Mn _{0.54} Ni _{0.13} Co _{0.13} O ₂	Au	70 $\mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$	(Yan <i>et al.</i> , 2013)
a-VO _x	stainless steel	300 mAh g^{-1}	(Petnikota <i>et al.</i> , 2018)

successfully deposited a-Si thin films on stainless-steel substrates at room temperature by PLD for thin film microbatteries. The cells based on the a-Si thin films (120 nm thick) exhibited a stable discharge capacity of $\sim 50 \mu\text{Ah cm}^{-2}$ between 0.1 and 1.5 V at a current density of $100 \mu\text{A cm}^{-2}$ for 50 charge/discharge cycles with a small capacity fade rate (0.2% per cycle). Thus, the a-Si thin film anode can effectively minimize the volume expansion during lithiation process and result in an improved capacity retention compared to the crystallized silicon (c-Si).

Recently, there have been many efforts on developing Si-based composite anodes by combining the Si with carbon-based components such as single-wall carbon-nanotube (SWCNT) and multilayer graphene (MLG). (Biserni *et al.*, 2015; Chou *et al.*, 2010; Radhakrishnan *et al.*, 2013). For example, Chou *et al.* fabricated Si-SWCNT composite anodes by depositing Si film onto SWCNT paper at room temperature by PLD. The cell based on the a-Si/SWCNT composite anode exhibited a specific capacity of 163 mAh g^{-1} at a current rate of 25 mA g^{-1} , which is more than 60% improvement of the pristine CNT paper (Chou *et al.*, 2010). Radhakrishnan *et al.* (2013) fabricated Si-MLG composite anodes for Li-ion batteries by depositing ultra-thin Si layers onto a MLG-coated Ni foam substrate using PLD. The MLG layer grown by CVD serves as a conducting platform, thus helping to avoid contact losses from volume expansion during lithiation processes of the Si anode, while the Ni foam serves as a current collector as well as provides a larger surface area in comparison to thin metal foils. Electrochemical test results on the Si-MLG composite anodes showed a stable specific capacity of 2400 mAh g^{-1} during the cycling test, whereas the cells based on the pure Si anodes exhibited a fast fading capacity after 1st cycle due to the volume expansion. Biserni *et al.* (2015) fabricated Si-C composite anodes by depositing $1 \mu\text{m}$ -thick porous a-Si layer on copper foils at room temperature by PLD, followed by CVD of carbon layers. In this design, the porous nanostructure of Si film accommodates the volume expansion, while the disordered carbon layer promotes the formation of a stable solid electrolyte interface (SEI) layer and protects the Si from direct contact with the electrolyte. Electrochemical test on these Si-C composite anodes showed a specific capacity of $\sim 75 \mu\text{Ah cm}^{-2}$ after 1000 cycles at a current rate of $540 \mu\text{A cm}^{-2}$. Moreover, the capacity of this composite anode can be improved to $\sim 175 \mu\text{Ah cm}^{-2}$ by thickening the Si thickness to $2.5 \mu\text{m}$.

Due to a relatively small volume change ($<0.2\%$) during charge/discharge cycles, spinel lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) has been considered as a good anode material for Li-ion batteries. This anode exhibits a theoretical specific capacity of 175 mAh g^{-1} and a large voltage plateau at 1.55 V during charge/discharge profiles. One drawback of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is a poor electrical conductivity, which limits their application. Deng *et al.* (2009) fabricated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode thin films on Pt/Ti/SiO₂/Si substrates at room temperature by PLD using a KrF excimer laser (248 nm). Annealing the as-deposited films at temperatures of $600\text{--}800^\circ\text{C}$ improved the charge/discharge capacity. Fig. 6 shows the charge discharge curves for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode films at a current rate of $20 \mu\text{A cm}^{-2}$ between 1 and 2 V. These anode thin films exhibited a charge-discharge plateau at $\sim 1.55 \text{ V}$ (Fig. 6(a)) and a discharge capacity of 149 mAh g^{-1} after 30 cycles (Fig. 6(b)). Amorphous LiNiVO_4 anode thin films were also grown by PLD using a Li-excess target ($\text{Li}_{1.2}\text{NiVO}_4$) for thin film microbatteries (Tang *et al.*, 2006). The cells based on these anode thin films showed a reasonably good battery performance with a discharge capacity of $410 \mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$ after 50 cycles. Table 3 lists the electrochemical properties of various cathode thin films fabricated by PLD technique.

PLD of Solid Electrolyte Films

In order to develop all solid-state thin-film batteries, thin films of solid-state electrolytes with high ionic conductivity and low electronic conductivity are required. PLD technique has been successfully employed to fulfil these requirements in growing thin films of various solid-state electrolytes, such as lithium phosphorous oxynitride (LIPON) (Zhao *et al.*, 2002), $\text{Li}_{2.2}\text{V}_{0.54}\text{Si}_{0.46}\text{O}_{3.4}$ (LVSO) (Kuwata *et al.*, 2004; Zhao and Qin, 2003), $\text{Li}_4\text{SiO}_4\text{--Li}_3\text{PO}_4$ (Sakuda *et al.*, 2010), $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ (thio-LISICON) (Ohta *et al.*, 2005), $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ (LLTO) (Ahn and Yoon, 2005), and $80\text{Li}_2\text{S--}20\text{P}_2\text{O}_5$ films (Sakurai *et al.*, 2011). Zhao *et al.* (2002) fabricated LIPON thin films on three different substrates (Si-wafer, Au/Si, and Al/glass) by PLD in an N_2 gas atmosphere using a Li_3PO_4 target. The ionic conductivity of $1.6 \times 10^{-6} \text{ S cm}^{-1}$ was observed from the LIPON thin films deposited under the optimum PLD conditions (200 mTorr of N_2 gas and a laser fluence of 15 J cm^{-2}). Kuwata *et al.* (2004) fabricated $\text{Li}_{2.2}\text{V}_{0.54}\text{Si}_{0.46}\text{O}_{3.4}$ (LVSO)

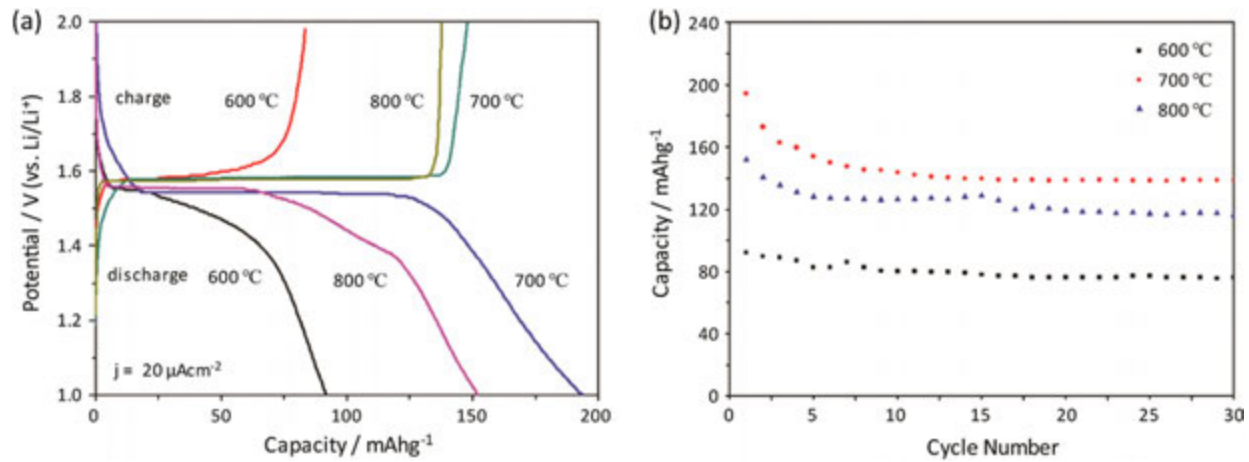


Fig. 6 (a) Charge/ discharge curves and (b) Discharge capacity vs. cycle number of $\text{Li}_4\text{Ti}_4\text{O}_{12}$ anode thin films annealed at various temperatures (600–800 °C) at a current rate of $20 \mu\text{A cm}^{-2}$ between 1.0 and 2.0 V. Reprinted from Deng, J.Q., Lu, Z.G., Belharouak, I., Amine, K., Chung, C.Y., 2009. Preparation and electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film electrodes by pulsed laser deposition. *J. Power Sources* 193, 816–821. Copyright (2009), with permission from Elsevier.

Table 3 Electrochemical properties of thin-film anodes fabricated by PLD. SS represents stainless steel

Material	Substrate	Voltage (Current rate)	Capacity	References
a-Si	SS	0.0005–1.5 V (100 $\mu\text{A cm}^{-2}$)	64 $\mu\text{Ah cm}^{-2}$	(Park <i>et al.</i> , 2006)
a-Si	Si, SS	0.01–1.5 V (100 $\mu\text{A cm}^{-2}$)	50 $\mu\text{Ah cm}^{-2}$	(Xia <i>et al.</i> , 2007)
Si-SWCNT	SWCNT	0.01–2 V (25 mA g^{-1})	163 mAh g^{-1}	(Chou <i>et al.</i> , 2010)
Si-graphene	Ni	0.05–1 V (C/5 rate)	2400 mAh g^{-1}	(Radhakrishnan <i>et al.</i> , 2013)
Si-C	Cu	0.05–1.5 V (540 $\mu\text{A cm}^{-2}$)	75 $\mu\text{Ah cm}^{-2}$	(Biserni <i>et al.</i> , 2015)
$\text{Li}_4\text{Ti}_5\text{O}_{12}$	Pt/Ti/SiO ₂ /Si	1.0–2.0 V (10 $\mu\text{A cm}^{-2}$)	157 $\mu\text{Ah g}^{-1}$	(Deng <i>et al.</i> , 2009)
LiNiVO_4	Si, SS	0.1–3.0 V (100 $\mu\text{A cm}^{-2}$)	410 $\mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$	(Tang <i>et al.</i> , 2006)

solid electrolyte thin films by depositing the films on quartz substrates by PLD and the LVSO films showed an ionic conductivity of $2.5 \times 10^{-7} \text{ S cm}^{-1}$. Ahn *et al.* fabricated $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ (LLTO) thin film electrolytes by PLD at 400–600 °C. The 360 nm-thick LLTO thin films showed an amorphous phase with an ionic conductivity of $2.0 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. The LLTO/ LiCoO_2 /Pt cells exhibited 63% capacity retention after 300 cycles (Ahn and Yoon, 2005). Table 4 lists electrical properties of various solid-electrolyte thin-films fabricated by PLD. The ionic conductivity of PLD-grown solid electrolyte thin films was observed in a range from 10^{-4} to $10^{-7} \text{ S cm}^{-1}$, while the electrical conductivity exhibited very low (10^{-7} – $10^{-14} \text{ S cm}^{-1}$). Thus, these PLD-grown solid electrolyte thin films are very promising for manufacturing solid state thin film microbatteries.

Recently, all solid state thin film microbatteries have attracted much attention due to their excellent potential for improving their safety and reliability compared to conventional lithium batteries containing flammable organic liquid electrolytes. PLD was successfully utilized to grow individual layers sequentially. Kuwata *et al.* (2004) fabricated all solid state thin film microbatteries, consisting of LiCoO_2 cathode, LVSO solid electrolyte, and amorphous SnO anode, by a sequential PLD process. These thin film microbatteries exhibited an initial capacity of $9.5 \mu\text{Ah cm}^{-2}$ and 45% capacity retention after 100 cycles at a current rate of $44 \mu\text{A cm}^{-2}$ between 0.01 and 3 V. Matsuda *et al.* (2018) also fabricated all solid-state microbatteries using an amorphous Li_3PO_4 solid electrolyte film by a sequential PLD process. Fig. 7(a) shows a cross sectional SEM image of a $\text{Li}/\text{Li}_3\text{PO}_4/\text{LiCoO}_2/\text{Pt}$ thin film microbattery, indicating a columnar-like LiCoO_2 cathode. As shown in Fig. 7(b), this microbattery exhibited excellent battery performances: discharge capacity of $97 \mu\text{Ah cm}^{-2}$ (or $44 \mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$), which is 64% of the theoretical volumetric capacity of LiCoO_2 ($69 \mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$).

Table 4 Electrochemical properties of electrolyte thin-films prepared by PLD

Material	Substrate	ionic conductivity (S/cm)	References
LiPON	Si, Au/Si, Au/glass	1.6×10^{-6}	(Zhao <i>et al.</i> , 2002)
$\text{Li}_{2.2}\text{V}_{0.54}\text{Si}_{0.46}\text{O}_{3.4}$ (LVSO)	quartz	2.5×10^{-7}	(Kuwata <i>et al.</i> , 2004)
$\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ (LLTO)	Pt	2.0×10^{-5}	(Ahn and Yoon, 2005)
$\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ (thio-LISCON)	Quartz	1.7×10^{-4}	(Ohta <i>et al.</i> , 2005)
$80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5$	Si	2.8×10^{-4}	(Sakurai <i>et al.</i> , 2011)
$\text{Li}_4\text{SiO}_4\text{-Li}_3\text{PO}_4$	Quartz	1.6×10^{-6}	(Sakuda <i>et al.</i> , 2010)

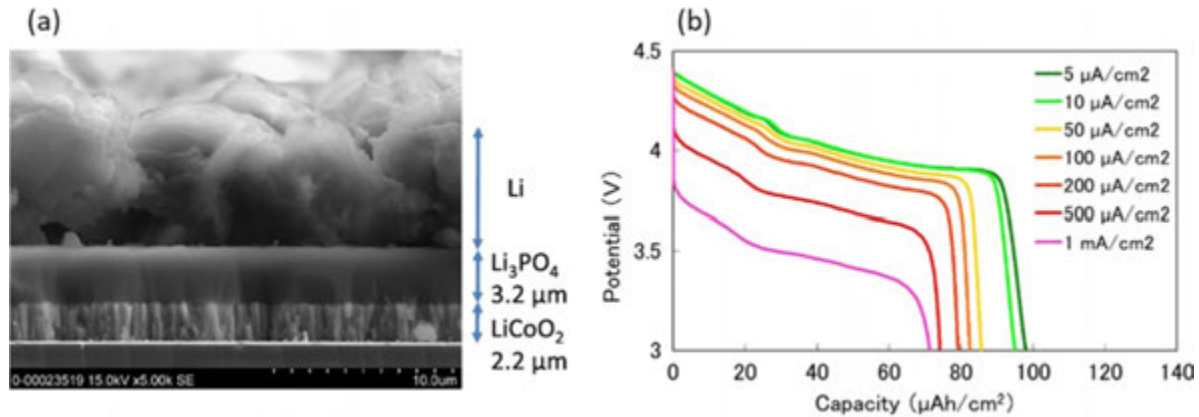


Fig. 7 (a) Cross-sectional SEM image of Li/Li₃PO₄/LiCoO₂ thin-film batteries fabricated by sequential PLD process. (b) Discharge profiles of Li/Li₃PO₄/LiCoO₂ thin-film batteries at different current rates from 1 $\mu\text{A cm}^{-2}$ to 1 mA cm^{-2} in 3.0–4.4 V potential range. Reprinted from Matsuda, Y., Kuwata, N., Kawamura, J., 2018. Thin-film lithium batteries with 0.3–30 nm thick LiCoO₂ films fabricated by high-rate pulsed laser deposition. *Solid State Ion.* 320, 38–44. Copyright (2018), with permission from Elsevier.

In summary, PLD has been considered as an ideal technique for growing thin films of cathodes, anodes and solid electrolytes for thin film microbatteries. Well-crystallized and textured cathode thin films were fabricated by PLD due to their relatively low crystallization temperatures and good adhesion properties. PLD has been successfully utilized for growing anode materials such as amorphous silicon, silicon-based composite and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes. PLD-grown solid electrolyte thin films have been proved to exhibit good ionic conductivity (10^{-4} – 10^{-7} S cm^{-1}) and low electrical conductivity (10^{-7} – 10^{-14} S cm^{-1}). Lastly, a sequential PLD growth was used in the fabrication of all solid-state thin film microbatteries exhibiting reasonably good battery performance. In addition, due to increasing demand for flexible devices, manufacturing thin film microbatteries on flexible substrates such as polyimide (Kapton) would be highly desirable. On this matter, the use of PLD technique might be possible to grow active materials at low temperatures ($< 300^\circ\text{C}$) since films grown by PLD are usually crystallized at relatively low temperatures compared to other PVD techniques such as sputtering and e-beam.

Laser Surface Modification (LSM)

Lasers are widely used to modify the surface properties of renewable energy materials to improve their performance in photo-voltaic devices and power sources. Laser surface modification (LSM) has been applied extensively in the fabrication of solar cells. Recently, LSM for batteries has also been shown to improve the battery performance. This section reviews three LSM processes for Li-ion batteries: laser structuring, laser annealing and laser drying.

Laser Structuring for 3D Electrodes

Recently, the development of three-dimensional (3D) electrodes was proposed to enhance the discharge capacities while maintaining high power density of lithium microbatteries (Jeyaseelan and Rohan, 2009; Long *et al.*, 2004; Notten *et al.*, 2007; Oudenhoven *et al.*, 2011). However, increasing both energy density and power density simultaneously is very challenging issue due to the increased internal resistance. Lasers were successfully employed to texture various thin-film and thick-film electrodes to form 3D structures with improved Li-ion diffusion kinetics (Kim *et al.*, 2012; Kohler *et al.*, 2011, 2013; Pröll *et al.*, 2011, 2014). There are two different types of laser structuring processes: one is “self-organized structuring” process and the other is “direct

structuring” process. In general, the self-organized structuring process can be applied for thin film and thick film electrodes that have small electrode footprint areas such as microbatteries, while the direct structuring process can be applied for large area electrodes such as pouch cells (Pfleging, 2018).

The self-organized structuring process was applied for structuring LiCoO₂ cathode thick films ($\sim 30\ \mu\text{m}$ thick) using a KrF excimer laser ($\lambda = 248\ \text{nm}$) (Kim *et al.*, 2012). By adjusting laser fluences and number of laser pulses, self-organized conical microstructures were created on the film surface (see Fig. 8(b)). In this case, the structuring process can be explained by selective material ablation and consequent re-deposition of material. As shown in Fig. 8(c), the cell based on this laser-structured LiCoO₂ cathode thin film exhibited a discharge capacity of $\sim 70\ \text{mAh g}^{-1}$ after 100 cycles, which is two times higher than that of the unstructured thin film ($36\ \text{mAh g}^{-1}$). In this case, the enhanced discharge capacity is attributed to the improved Li-ion diffusion rate through 3D microstructures of the cathode. Although uniform surface texture can be achieved by an excimer laser ablation, the processing speed is very slow so that it can be used for small electrode area such as microbatteries.

For large area laser structuring processes, high power femtosecond (fs) lasers with high repetition rates were utilized to directly ablate the electrode materials to form 3D micro-grids (Park *et al.*, 2019; Pröll *et al.*, 2014; Smyrek *et al.*, 2016). The use of fs-laser pulses can minimize the damage to the cathode material near the ablated region resulting in uniformly distributed micro-grid structures, while minimizing the amount of material loss ($< 15\%$) during the process. For example, 3D micro-grid structures of LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ (NMC) cathodes with various film thicknesses (100–210 μm) were fabricated by a fs-laser ablation (Park *et al.*, 2019). Fig. 9 shows a schematic illustration of the laser structuring system. Fig. 10(a) shows SEM image of 3D micro grid structures of the laser-structured NMC thick film electrode (210 μm). As shown in Fig. 10(b), the groove was

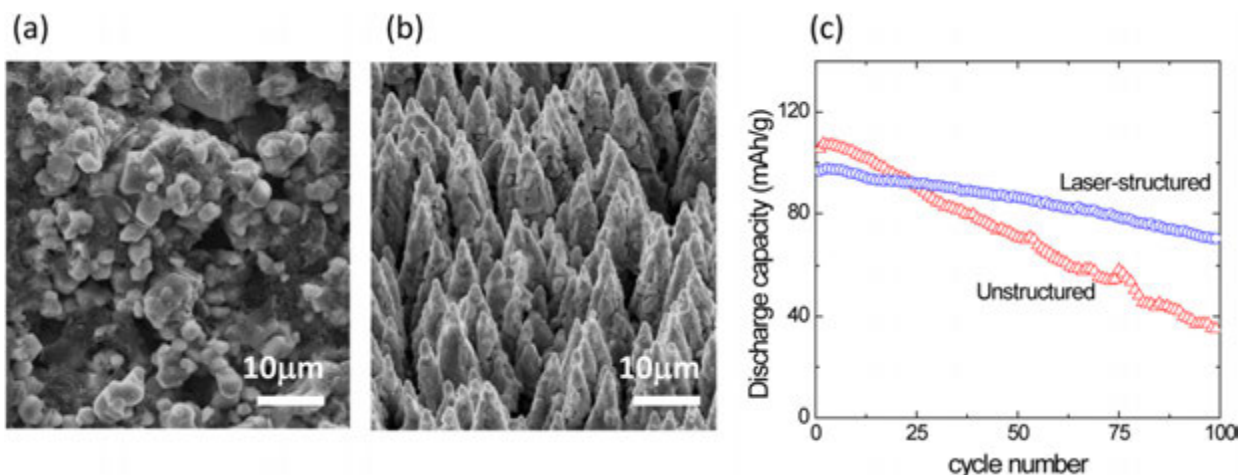


Fig. 8 SEM images of (a) unstructured and (b) laser structured LiCoO₂ cathode thin-film. (c) Discharge profiles of Li/LiCoO₂ thin-film batteries at C/5 current rate between 3.0 and 4.2 V. Reproduced from Kim, H., Proell, J., Kohler, R., Pfleging, W., Piqué, A., 2012. Laser-printed and processed LiCoO₂ cathode thick films for Li-ion microbatteries. *J. Laser Micro/Nanoeng.* 7, 320–325. Copyright (2012), with permission from Japan Laser Processing Society.

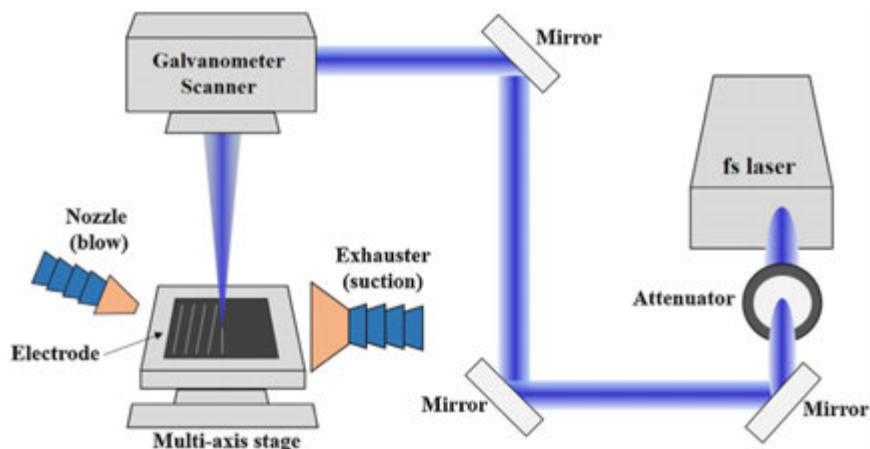


Fig. 9 Schematic of laser structuring process using a fs-laser system. Reprinted from Park, J., Hyeon, S., Jeing, S., Kim, H.-J., 2019. Performance enhancement of Li-ion battery by laser structuring of thick electrode with low porosity. *J. Ind. Eng. Chem.* 70, 178–185. Copyright (2019), with permission from Elsevier.

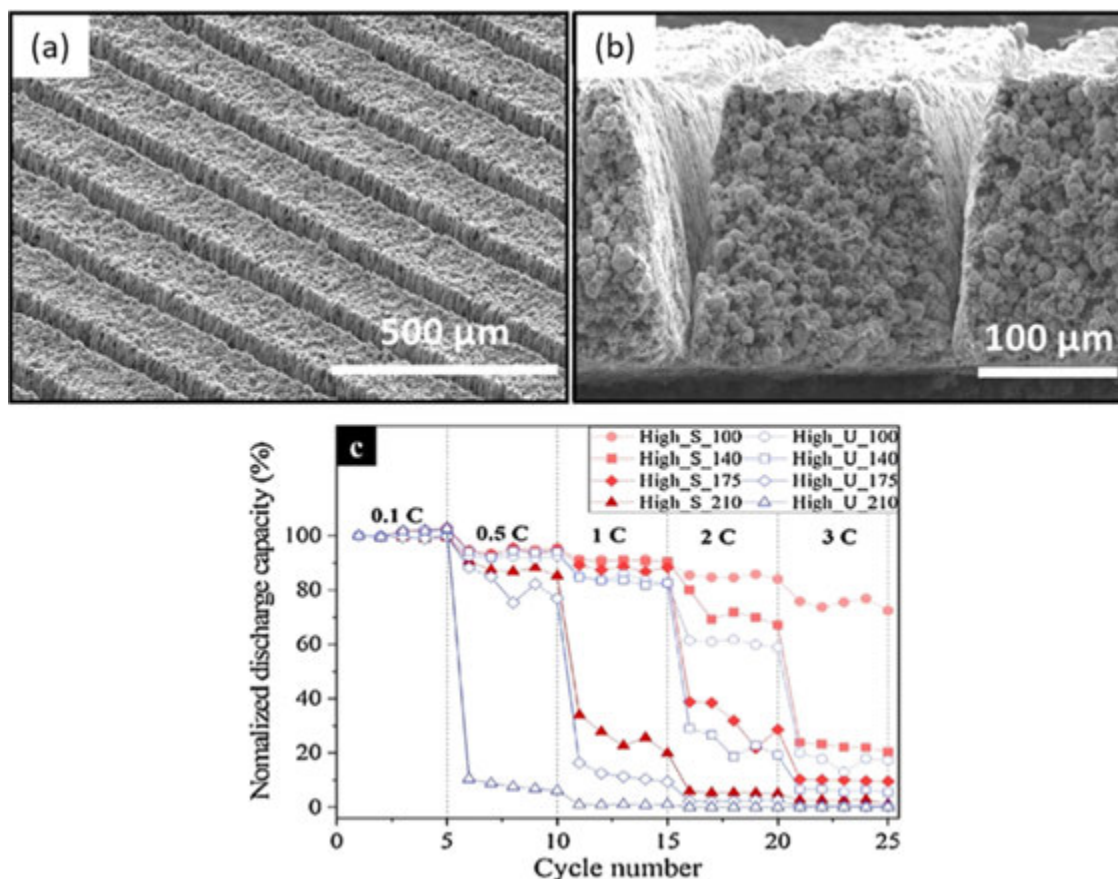


Fig. 10 (a) Top view and (b) cross-sectional SEM images of laser structured $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ (NMC) cathode thick films (210 μm thick). (c) Normalized discharge capacity of Li/NMC batteries at different current rates from 1 to 3C between 3.0 and 4.2 V. “High_S_100” represents a structured electrode with a thickness of 100 μm and high porosity. “High_U_100” represents an *unstructured* electrode with a thickness of 100 μm and high porosity. Reprinted from Park, J., Hyeon, S., Jeing, S., Kim, H.-J., 2019. Performance enhancement of Li-ion battery by laser structuring of thick electrode with low porosity. *J. Ind. Eng. Chem.* 70, 178–185. Copyright (2019), with permission from Elsevier.

formed over entire thickness of the electrode and no evidence of melting or re-solidification was observed, indicating little thermal effect during the laser structuring. Fig. 10(c) shows the normalized discharge capacity of the cells based on the unstructured and structured NMC thick films with various electrode thicknesses (100–210 μm) at different current rates (0.1–3 C). As the current rate increases, the discharge capacity of the unstructured electrode dropped quickly, while the laser-structured electrodes always showed higher capacity retentions than the unstructured electrodes. For example, the laser-structured NMC electrode (100 μm) showed 70% capacity retention at 3 C rate, which is one order of magnitude higher than the unstructured NMC electrode ($\sim 5\%$). These results suggest that laser-structured 3D electrodes are suitable for fast charging/discharging devices at a higher current rate.

Laser Annealing of Thin Film Electrodes

In general, annealing processes can improve the microstructures of the thin film electrodes and accordingly, increase the electrochemical performance of the electrodes. On the other hand, rapid thermal annealing can also form some cracks on the surface due to volume expansion and shrinkages. Laser annealing processes have been applied for improving the crystalline phases of thin-film electrodes such as LiCoO_2 and LiMn_2O_4 cathodes (Kohler *et al.*, 2011; Pröll *et al.*, 2014). Pröll *et al.* (2012) demonstrated that sputter-deposited Li–Mn–O thin films were annealed by a high power diode laser ($\lambda = 940 \text{ nm}$) to form a spinel like phase. The grain size of the as-deposited film was $< 10 \text{ nm}$ while the laser annealed film at 600°C for 2000 s showed the lateral grain sizes of $\sim 500 \text{ nm}$ (See Fig. 11(a) and (b)). As shown in Fig. 11(c), a spinel-like Li–Mn–O phase can be obtained under the optimized laser annealing conditions ($T = 680^\circ\text{C}$ for 100 s), showing the typical bands of Mn–O compounds at 629 cm^{-1} (A_{1g} species). Similar Raman spectra could be observed for slightly lower annealing temperature of $T = 600^\circ\text{C}$ with a longer annealing time ($t = 2000 \text{ s}$) (Fig. 11(c)). Cyclic voltammetry (CV) scans showed two redox peaks for spinel thin films, indicating that the annealed films were well crystallized and intercalation processes were reversible (Fig. 11(d)).

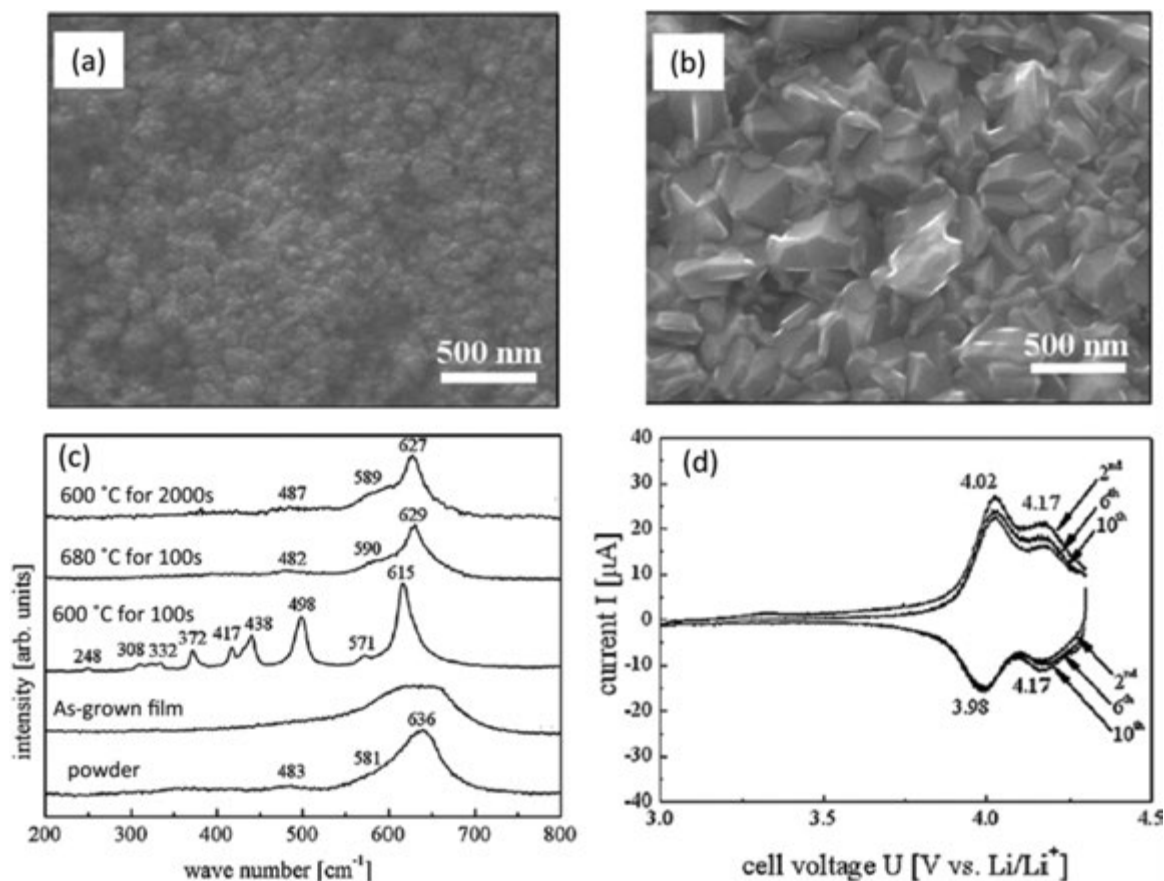


Fig. 11 SEM images of Li-Mn-O films: (a) as-deposited and (b) laser annealed for $t = 2000$ s at $T = 600$ °C. Laser annealing processes were performed under ambient air. (c) Raman spectra of Li-Mn-O thin films with various annealing temperatures and times. Raman spectra of the spinel LiMn_2O_4 reference and of the as-grown film are added for comparison. (d) Cyclic voltammogram of Li-Mn-O film laser annealed for $t = 2000$ s at $T = 600$ °C. Reprinted from Pröll, J., Kohler, R., Mangang, A., *et al.*, 2012. Diode laser heat treatment of lithium manganese oxide films. *Appl. Surf. Sci.* 258 (12), 5146–5152. Copyright (2012), with permission from Elsevier.

Laser Drying of Thick Film Electrodes

One important step in battery manufacturing processes is a drying process for wet thick film electrodes. Typically, thick film electrodes (cathodes and anodes) are prepared from the slurry that consists of active material powders, conductive graphite, binders, solvents and some organic additives. Once the slurry is applied on the current collector by tape casting, this wet electrode must be dried with hot air or thermal radiation in order to improve the film adhesion (Günther *et al.*, 2016). It was reported that rapid drying using infrared radiation can cause a separation of active particles and binders, thus affecting adhesion of electrode on the current collector. Vedder *et al.* (2016) developed a laser-based drying process of water-based battery electrodes (LiFePO_4 cathodes and graphite anodes) using a fibre laser ($\lambda = 1070$ nm). By laser drying of these electrodes, coin cell capacity of 355 mAh g^{-1} can be achieved. In comparison to conventional oven drying process, this laser drying process could save the energy consumption by 50%. The laser drying speed of $50 \text{ cm}^2 \text{ s}^{-1}$ was achieved so far while further improvement might be possible using high power lasers. However, since the fast drying of electrodes with high power lasers may cause crack formation, careful optimization of process conditions will be required for upscaling of the laser based drying process technique.

In summary, LSM processes have been used as a useful tool for structuring thin film and thick film electrodes to form 3D electrodes for high-power and high-energy lithium-ion batteries. Well-crystallized cathode thin films were produced by the laser annealing process. In addition, the electrolyte wetting process is also important step in battery manufacturing since the process takes few hours to couple of days to achieve complete electrolyte impregnation. It was reported that laser structuring of the electrodes accelerated the wetting process by at least one order of magnitude, thereby reducing the manufacturing cost (Habedank *et al.*, 2019).

Challenging Issues and Outlook

Although laser-based processing techniques have been widely used in energy storage systems, there are some challenging issues in these techniques. The first challenging issue is developing reliable packaging processes for batteries. It is necessary that all active

components be sealed using the minimum weight and volume possible. For instance, many microelectronic devices may not allow the use of coin cells as their power sources due to their larger volume size yet limited capacity. In these cases, it might be possible to design microbatteries to be embedded on a chip. Since lasers can also be used to micromachine the chip surface to fabricate the pockets for embedded microbatteries and then directly print the battery components onto the devices via LIFT, laser processes are likely to play an important role in advanced microelectronic devices in the near future.

Second, for the integration of microbatteries into the other microdevices on a chip, high quality solid-state electrolytes must be developed. Although LIFT and PLD processes were used for manufacturing solid state electrolytes, the ionic conductivity of these electrolytes is much lower compared to liquid electrolytes, resulting in lower battery performance. Thus, improved solid state electrolytes must be developed in the near future.

Finally, the thickness of PLD grown electrodes must be increased in order to achieve larger discharge capacities in thin film microbatteries. In general, typical thickness of PLD-grown thin film electrodes is less than 3 μm because the cell resistance increases with the electrode thickness. This limited thickness issue can be solved by co-depositing conductive carbon and/or other active electrode materials. For this purpose, PLD processes can be used to deposit these composite electrodes by alternatively ablating carbon and electrode targets. These carbon-containing composite electrodes will be helpful to increase the electrode thickness beyond 3 μm and thus, achieve large discharge capacity with a minimum cell resistance loss.

Summary

Three laser-based processing techniques (LIFT, PLD and LSM) for the fabrication of energy storage devices have been reviewed. First, the LIFT technique has been demonstrated to print thick film electrodes and solid-state electrolyte membranes for Li-ion microbatteries and ruthenium oxide/electrolyte composite materials for planar ultracapacitors. The microbatteries fabricated with LIFT-printed thick film electrodes exhibited a high discharge capacity ($\sim 2600 \text{ mAh cm}^{-2}$), which is an order of magnitude higher than those of the sputter-deposited thin film electrodes. The LIFT process was also proposed to sequentially print all battery components (cathode, solid-state electrolyte and anode) to prepare all solid-state Li-ion microbatteries, which can be integrated into other microdevices on a chip. Secondly, the PLD technique was demonstrated as a practical tool to deposit numerous cathodes, anodes, and solid-state electrolytes for thin film microbatteries. Since PLD films can be crystallized at relatively low temperatures, well-crystallized, highly textured electrodes can be produced by PLD at lower temperatures compared to the sputter-deposited thin film electrodes. Moreover, the PLD technique was also successfully utilized to fabricate all solid-state thin film microbatteries by depositing all components sequentially. Thirdly, the LSM process was successfully applied to produce 3D architectures on various thin-film and thick-film electrodes for Li-ion microbatteries with improved battery performance including increased capacity retention and fast discharge rate.

In general, these laser-based processes can be utilized to integrate energy storage systems into other microdevices on a chip at various stages of the device fabrication steps. For instance, PLD can be used at the beginning of the device fabrication step since the deposited films may need to be patterned for devices, while LIFT printing can be applied at any stage of the device fabrication steps due to its direct-write additive capability. Hence, LIFT printing of a microbattery for a certain device might occur even after the device has already been fabricated. Lastly, the LSM process can be applied at any point of the device fabrication steps as well as it can be applied to selected locations on a device across a wide range of scales. Therefore, these laser-based processing techniques offer great potential for the manufacture of next generation embedded energy storage devices.

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References

- Ahn, J.K., Yoon, S.G., 2005. Characteristics of amorphous lithium lanthanum titanate electrolyte thin films grown by PLD for use in rechargeable lithium microbatteries. *Electrochem. Solid-State Lett.* 8, A75–A78.
- Arnold, C.B., Serra, P., Piqué, A., 2007. Laser direct-write techniques for printing of complex materials. *MRS Bull.* 32, 23–31.
- Arnold, C.B., Wartena, R.C., Swider-Lyons, K.E., Piqué, A., 2003. Direct-write planar microultracapacitors by laser engineering. *J. Electrochem. Soc.* 150, A571–A575.
- Arnold, C.B., Wartena, R.C., Pratap, B., Swider-Lyons, K.E., Piqué, A., 2002. Direct writing of planar ultracapacitors by laser forward transfer processing. *Proc. SPIE* 4637, 353–360.
- Auyeung, R.C.Y., Kim, H., Birnbaum, A.J., *et al.*, 2009. Laser decal transfer of freestanding microcantilevers and microbridges. *Appl. Phys. A* 97, 513–519.
- Auyeung, R.C.Y., Kim, H., Charipar, N., *et al.*, 2011. Laser forward transfer based on a spatial light modulator. *Appl. Phys. A* 102, 21–26.
- Bates, J., Dudney, N.J., Neudecker, B., Ueda, A., Evans, C.D., 2000. Preferred orientation of polycrystalline LiCoO_2 films. *J. Electrochem. Soc.* 147, 59–70.
- Biserni, E., Xie, M., Brescia, R., *et al.*, 2015. Silicon algae with carbon topping as thin-film anodes for lithium-ion microbatteries by two-step facile method. *J. Power Sources* 274, 252–259.
- Calvert, P., 2001. Inkjet printing for materials and devices. *Chem. Mater.* 13, 3299–3305.
- Chou, S.L., Zhao, Y., Wang, J.Z., *et al.*, 2010. Silicon/single-walled carbon nanotube composite paper as a flexible anode material for lithium ion batteries. *J. Phys. Chem. C* 114, 15862–15867.

- Chrisey, D.B., Hubler, G.K., 1994. Pulsed Laser Deposition of Thin Films. New York: Wiley.
- Deng, J.Q., Lu, Z.G., Belharouak, I., Amine, K., Chung, C.Y., 2009. Preparation and electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film electrodes by pulsed laser deposition. *J. Power Sources* 193, 816–821.
- Duocastella, M., Kim, H., Serra, P., Piqué, A., 2012. Optimization of laser printing of nanoparticles suspensions for microelectronic applications. *Appl. Phys. A* 106, 471–478.
- Eason, R., 2006. Pulsed Laser Deposition of Thin Films, second ed. New York: Wiley.
- Ferrari, S., Loveridge, M., Beatti, S.D., *et al.*, 2015. Latest advances in the manufacturing of 3D rechargeable lithium microbatteries. *J. Power Sources* 286, 25–46.
- Günther, T., Billot, N., Schuster, J., *et al.*, 2016. The manufacturing of electrodes: Key process of the future success of lithium-ion batteries. *Adv. Mater. Res* 1140, 304–311.
- Habedank, H.B., Günter, F.J., Billot, N., *et al.*, 2019. Rapid electrolyte wetting of lithium-ion batteries containing laser structured electrodes: In situ visualization by neutron radiography. *Int. J. Adv. Manuf. Technol.* 102, 2769–2778.
- Hon, K.K.B., Li, L., Hutchings, I.M., 2008. Direct writing technology – Advances and developments. *CIRP Ann. Manuf. Technol.* 57, 601–620.
- Jeyaseelan, A.V., Rohan, J.F., 2009. Fabrication of three-dimensional substrates for Li microbatteries on Si. *Appl. Surf. Sci.* 256, S61–S64.
- Julien, C., Camacho-Lopez, M.A., Escobar-Alarcon, L., Haro-Poniatowski, E., 2001. Fabrication of LiCoO_2 thin-film cathodes for rechargeable lithium microbatteries. *Mat. Chem. Phys.* 68, 210–216.
- Kim, H., Auyeung, R.C.Y., Piqué, A., 2007. Laser-printed thick-film electrodes for solid-state rechargeable Li-ion microbatteries. *J. Power Sources* 165, 413–419.
- Kim, H., Melinger, J.S., Khachatrian, A., *et al.*, 2010. Fabrication of terahertz metamaterials by laser printing. *Opt. Lett.* 35, 4039–4041.
- Kim, H., Sutto, T.E., Piqué, A., 2014. Laser materials processing for micropower source applications: A review. *J. Photon. Energy* 4, 040992.
- Kim, H., Proell, J., Kohler, R., Pflöging, W., Piqué, A., 2012. Laser-printed and processed LiCoO_2 cathode thick films for Li-ion microbatteries. *J. Laser Micro/Nanoeng.* 7, 320–325.
- Kim, H., Piqué, A., Charipar, K.M., Auyeung, R.C.Y., Duocastella, M., 2013. Laser printing of conformal and multi-level 3D interconnects. *Appl. Phys. A* 113, 5–8.
- Kim, W.S., 2004. Characteristics of LiCoO_2 thin film cathodes according to the annealing ambient for the post-annealing process. *J. Power Sources* 134, 103–109.
- Kohler, R., Besser, H., Hagen, M., *et al.*, 2011. Laser micro-structuring of magnetron-sputtered SnO_x thin films as anode material for lithium ion batteries. *Microsyst. Technol.* 17, 225–232.
- Kohler, R., Proell, J., Bruns, M., *et al.*, 2013. Conical surface structures on model thin-film electrodes and tape-cast electrode materials for lithium-ion batteries. *Appl. Phys. A* 112, 77–85.
- Kuwata, N., Kumar, R., Toribami, K., *et al.*, 2006. Thin film lithium ion batteries prepared only by pulsed laser deposition. *Solid State Ion.* 177, 2827–2832.
- Kuwata, N., Kawamura, J., Toribami, K., Hattori, T., Sata, N., 2004. Thin-film lithium-ion battery with amorphous solid electrolyte fabricated by pulsed laser deposition. *Electrochem. Commun.* 6, 417–421.
- Long, J.W., Dunn, B., Rolison, D.R., White, H.S., 2004. Three-dimensional battery architectures. *Chem. Rev.* 104 (10), 4463–4492.
- Lu, Z.G., Lo, M.F., Chung, C.Y., 2008. Pulsed laser deposition and electrochemical characterization of $\text{LiFePO}_4\text{-C}$ composite thin films. *J. Phys. Chem.* 112, 7069–7078.
- Madhuri, K.V., Rao, K.S., Naidu, B.S., Hussain, O.M., Pinto, R., 2002. Characterization of laser-ablated V_2O_5 thin films. *J. Mater. Sci. Mater. Electron.* 13, 425–432.
- Mathews, S.A., Auyeung, R.C.Y., Kim, H., Charipar, N.A., Piqué, A., 2013. High-speed video study of laser-induced forward transfer of silver nano-suspensions. *J. Appl. Phys.* 114, 1–9. (064910).
- Matsuda, Y., Kuwata, N., Kawamura, J., 2018. Thin-film lithium batteries with 0.3–30 μm thick LiCoO_2 films fabricated by high-rate pulsed laser deposition. *Solid State Ion.* 320, 38–44.
- Mauger, A., Julien, C.M., 2018. V_2O_5 thin films for energy storage and conversion. *AIMS Mater. Sci.* 5, 349–401.
- Mazor, H., Golodnitsky, D., Bustein, L., Gladkikh, A., Peled, E., 2012. Electrophoretic deposition of lithium iron phosphate cathode for thin-film 3D-microbatteries. *J. Power Sources* 198, 264–272.
- Notten, P.H.L., Roozeboom, F., Niessen, R.A.H., Baggetto, L., 2007. 3-D integrated all-solid-state rechargeable batteries. *Adv. Mater.* 19 (24), 4564–4567.
- Ohta, N., Takada, K., Osada, M., *et al.*, 2005. Solid electrolyte, thio-LISICON thin film prepared by pulsed laser deposition. *J. Power Sources* 146, 707–710.
- Ollinger, M., Kim, H., Sutto, T.E., Piqué, A., 2006a. Laser direct-write of polymer nanocomposite. *Appl. Sur. Sci.* 252, 8212–8216.
- Ollinger, M., Kim, H., Sutto, T.E., Martin, F., Piqué, A., 2006b. Laser printing of nanocomposite solid-state electrolyte membranes for Li micro-batteries. *J. Laser Micro/Nanoeng.* 1, 102–105.
- Oudenhoven, J.F.M., Baggetto, L., Notten, P.H.L., 2011. All-solid-state lithium-ion microbatteries: A review of various three-dimensional concepts. *Adv. Energy Mater.* 1, 10–33.
- Park, J., Hyeon, S., Jeing, S., Kim, H.-J., 2019. Performance enhancement of Li-ion battery by laser structuring of thick electrode with low porosity. *J. Ind. Eng. Chem.* 70, 178–185.
- Park, M.S., Wang, G.X., Liu, H.K., Dou, S.X., 2006. Electrochemical properties of Si thin film prepared by pulsed laser deposition for lithium ion micro-batteries. *Electrochim. Acta* 51, 5246–5249.
- Perkins, J.D., Bahn, C.S., Parilla, *et al.*, 1999. LiCoO_2 and $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ thin film cathodes grown by pulsed laser ablation. *J. Power Sources* 81–82, 675–679.
- Petrikota, S., Chua, R., Zhou, Y., Edison, E., Srinivasan, M., 2018. Amorphous vanadium oxide thin films as stable performing cathodes of lithium and sodium-ion batteries. *Nanoscale Res. Lett.* 13, 363.
- Pflöging, W., 2018. A review of laser electrode processing for development and manufacturing of lithium-ion batteries. *Nanophotonics* 7 (3), 549–573.
- Piqué, A., Chrisey, D.B., 2001. Direct-Write Technologies for Rapid Prototyping Applications. San Diego, CA: Academic Press.
- Piqué, A., Kim, H., Auyeung, R.C.Y., Smith, A., 2013. Laser forward transfer of functional materials for digital fabrication of microelectronics. *J. Imaging Sci. Technol.* 57, 040101.
- Piqué, A., Arnold, C.B., Kim, H., Ollinger, M., Sutto, T.E., 2004. Rapid prototyping of micropower sources by laser direct-write. *Appl. Phys. A* 79, 783–786.
- Piqué, A., Auyeung, R.C.Y., Kim, H., Metkus, K.M., Mathews, S.A., 2008. Digital microfabrication by laser decal transfer. *J. Laser Micro/Nanoeng.* 3, 163–169.
- Pröll, J., Kohler, R., Torge, M., *et al.*, 2011. Laser microstructuring and annealing processes for lithium manganese oxide cathodes. *Appl. Surf. Sci.* 257, 9968–9976.
- Pröll, J., Kohler, R., Mangang, A., *et al.*, 2012. Diode laser heat treatment of lithium manganese oxide films. *Appl. Surf. Sci.* 258 (12), 5146–5152.
- Pröll, J., Kim, H., Piqué, A., Seifert, H.J., Pflöging, W., 2014. Laser-printing and femtosecond-laser structuring of LiMn_2O_4 composite cathodes for Li-ion microbatteries. *J. Power Sources* 255, 116–124.
- Radhakrishnan, G., Adams, P.M., Foran, B., Quinzio, M.V., Brodie, M.J., 2013. Pulsed laser deposited Si on multilayer graphene as anode material for lithium ion batteries. *APL Mater.* 1, 1–6. (062103).
- Ramana, C.V., Zaghib, K., Julien, C.M., 2007. Pulsed-laser deposited $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ thin films for application in microbatteries. *Appl. Phys. Lett.* 90, 021916.
- Rosenberg, S., Hintennach, A., 2013. Laser printed lithium sulphur micro electrodes for Li/S batteries. *Russ. J. Electrochem.* 50, 327–335.
- Roy, S., 2007. Fabrication of micro- and nano-structured materials using mask-less processes. *J. Phys. D: Appl. Phys.* 40, R413.
- Sakuda, A., Hayashi, A., Hama, S., Tatsumisago, M., 2010. Preparation of highly lithium-ion conductive $80\text{Li}_2\text{S}-20\text{P}_2\text{O}_5$ thin-film electrolytes using pulsed laser deposition. *J. Am. Ceram. Soc.* 93, 765–768.
- Sakurai, Y., Sakuda, A., Hayashi, A., Tatsumisago, M., 2011. Preparation of amorphous $\text{Li}_4\text{SO}_4\text{-Li}_3\text{PO}_4$ thin films by pulsed laser deposition for all-solid-state lithium secondary batteries. *Solid State Ion.* 182, 59–63.
- Sarangapani, S., Tilak, B., Chen, C., 1996. Materials for electrochemical capacitors. *J. Electrochem. Soc.* 143, 3791–3799.
- Serra, P., Piqué, A., 2019. Laser-induced forward transfer: Fundamentals and applications. *Adv. Mater. Technol.* 4, 1800099.
- Simmen, F., Lippert, T., Novák, P., *et al.*, 2008. The influence of lithium excess in the target on the properties and compositions of $\text{Li}_{1+x}\text{Mn}_2\text{O}_{4.5}$. *Appl. Phys. A* 93, 711–716.

- Smyrek, P., Pröll, J., Seifert, H.J., Pflöging, W., 2016. Laser-induced breakdown spectroscopy of laser-structured $\text{Li}(\text{NiMnCo})\text{O}_2$ electrodes for lithium-ion batteries. *J. Electrochem. Soc.* 163 (2), A19–A26.
- Sun, K., Wei, T.-S., Ahn, B.Y., *et al.*, 2013. 3D printing of interdigitated Li-ion microbattery architectures. *Adv. Mater.* 25, 4539–4543.
- Sutto, T.E., Ollinger, M., Kim, H., Arnold, C.B., Piqué, A., 2006. Laser transferable polymer-ionic liquid separator/electrolytes for solid-state rechargeable lithium-ion microbatteries. *Electrochem. Solid-State Lett.* 9, A69–A71.
- Tang, S.B., Xia, H., Lai, M.O., Lu, L., 2006. Amorphous LiNiVO_4 thin-film anode for microbatteries grown by pulsed laser deposition. *J. Power Sources* 159, 685–689.
- Vedder, C., Hawelka, D., Wolter, M., *et al.*, 2016. Laser-based drying of battery electrode layers. In: *Proceedings of the 35th International Congress on Applications of Lasers & Electro-Optics (ICALEO) N501*, pp. 501–506.
- Wang, C., Zheng, W., Yue, Z., Too, C.O., Wallace, G.G., 2011. Buckled, stretchable polypyrrole electrodes for battery applications. *Adv. Mater.* 23, 3580–3584.
- Wang, G.X., Lindsay, M.J., Ionescu, M., *et al.*, 2001. Physical and electrochemical characterization of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ thin-film electrodes deposited by laser ablation. *J. Power Sources* 97–98, 298–302.
- Wang, J., Auyeung, R.C.Y., Kim, H., Charipar, N.A., Piqué, A., 2010a. Three-dimensional printing of interconnects by laser direct-write of silver nanopastes. *Adv. Mater.* 22, 4462–4466.
- Wartena, R.C., Curtright, A.E., Arnold, C.B., Piqué, A., Swider-Lyons, K.E., 2004. Li-ion microbatteries generated by a laser direct-write method. *J. Power Sources* 126, 193–202.
- Xia, H., Lu, L., 2007. Texture effect on the electrochemical properties of LiCoO_2 thin films prepared by PLD. *Electrochim. Acta* 52, 7014–7021.
- Xia, H., Lu, L., Ceder, G., 2006. Substrate effect on the microstructure and electrochemical properties of LiCoO_2 thin films grown by PLD. *J. Alloy. Compd.* 417, 304–310.
- Xia, H., Tang, S., Lu, L., 2007. Properties of amorphous Si thin film anodes prepared by pulsed laser deposition. *Mater. Res. Bull.* 42, 1301–1309.
- Xia, H., Lu, L., Meng, Y.S., 2008. Growth of layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin films by pulsed laser deposition for application in microbatteries. *Appl. Phys. Lett.* 92, 011912.
- Yan, B., Liu, J., Song, B., Xiao, P., Lu, L., 2013. Li-rich thin film cathode prepared by pulsed laser deposition. *Sci. Rep.* 3, 1–5. (3332).
- Zhao, S., Qin, Q., 2003. Li-V-Si-O thin film electrolyte for all-solid-state Li-ion battery. *J. Power Sources* 122, 174–180.
- Zhao, S., Fu, Z., Qin, Q., 2002. A solid-state electrolyte lithium phosphorus oxynitride film prepared by pulsed laser deposition. *Thin Solid Films* 415, 108.

Aluminum, Gallium, and Indium Nitrides

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Introduction

Electroceramics, III-nitride semiconductors, including aluminum nitride (AlN), gallium nitride (GaN), and indium nitride (InN), are highly promising building blocks for solid-state optoelectronics and high-power electronics (Strite and Morkoç, 1992). In general, the III-nitrides have wurtzite crystal structure at ambient conditions, and the direct bandgap changes from 6.2 eV of AlN, 3.4 eV of GaN, to 0.7 eV of InN. Their ternary alloys such as aluminum gallium nitride (AlGaIn) and indium gallium nitride (InGaIn) provide the possibility of tuning the bandgaps continuously spanning from the deep ultraviolet (UV) into the whole visible spectrum. Till now, the III-nitrides are showing large amount of commercialized optoelectronics devices, including light-emitting diodes (LEDs) (Nakamura *et al.*, 1993; Funato *et al.*, 2006; Iso *et al.*, 2007), laser diodes (LDs) (Nakamura *et al.*, 1998a,b), UV photodetectors (Pernot *et al.*, 2000; Chen *et al.*, 1997; Muñoz *et al.*, 1997), and solar cells (Neufeld *et al.*, 2008; Jani *et al.*, 2007; Jiang *et al.*, 2017), which are widely applied in energy harvesting and saving.

AlN, GaN and InN are typically crystallized as a thermodynamically stable phase - wurtzite (space group is $P6_3mc$ (C_{6v}^4)), a metastable zinc-blende structure (space group is $F43m$ (T_d^2)), and a rock-salt structure at high-pressure phase transition (Strite and Morkoç, 1992; Morkoç, 2001). Moreover, III-nitrides have a large dielectric breakdown field and excellent electron transport properties (*e.g.*, the high mobility and large saturated drift velocity) that are very suitable for high-power, high-frequency electronic applications. And the main focus is AlGaIn/GaN based high-electron-mobility transistor (HEMTs) (Mishra *et al.*, 2002; Liu *et al.*, 2017; Yong *et al.*, 2005; Palacios *et al.*, 2005; Hu *et al.*, 2009). Due to the unique characteristics such as high-temperature stability and low sensitivity in radiation, it makes III-nitrides be very potential materials in harsh environments, *e.g.*, high temperature, radiation condition.

When compared to other wide bandgap semiconductors, III-nitrides exhibit an essential feature for the formation of heterostructures, such as quantum wells, quantum dots, and superlattices. The III-nitride heterostructures can be fabricated through major crystal growth techniques, including the metal-organic chemical vapor deposition (MOCVD) (Hu *et al.*, 2007c,b), hydride vapor-phase epitaxy (HVPE) (Hu *et al.*, 2010; Xu *et al.*, 2015; Ito *et al.*, 1990), and molecular beam epitaxy (MBE) (Jain *et al.*, 2000; Moustakas *et al.*, 2001; Yoshida *et al.*, 1982). However, the lattice mismatch in the heterojunctions of III-nitrides in general seriously hinders the growth of high-quality nitrides. And the shortage of lattice-matched and thermal-compatible substrate is the main difficulty for the wide development of III-nitrides (Strite and Morkoç, 1992; Moustakas *et al.*, 2001). Sapphire and silicon carbide (SiC) are the most promising substrates, and Si substrate is also in the accelerating development with low-cost and compatible epitaxial process. Since wurtzite III-nitrides are non-central-symmetric structures, they and their heterostructures exhibit the large spontaneous and piezoelectric polarization effects along the *c*-axis. Upon applying strains on the heterostructures, performances of III-nitride based devices will be significantly affected due to the large piezoelectric polarization response. That is, the piezoelectric potential (piezo-potential) is generated at the interface with the induced strain, which may act as a virtual gate to modulate the charge transport characteristics across metal-semiconductor interfaces or *p-n* junctions (also called as the piezotronic effect) (Wu and Wang, 2016; Du *et al.*, 2018a; Hu *et al.*, 2018; Pan *et al.*, 2019). Some typical GaN-based optoelectronic/electronic devices are outlined with enhanced performances under external strain. This chapter makes an outlook of fundamental properties of AlN, GaN, and InN, and provides significant insight into the potential applications of GaN-based electronic/optoelectronic devices by introducing strain effects. The key parameters of wurtzite AlN, GaN and InN are summarized in Table 1.

Aluminum Nitride

AlN possesses excellent physical properties including high melting point of $>2000^\circ\text{C}$, large thermal conductivity of $285\text{ W m}^{-1}\text{ K}^{-1}$ (Slack *et al.*, 1987), high hardness of $\sim 12\text{ GPa}$ on the plane (0001), and good capability of high-temperature and chemical resistance. AlN has a dynamically stable wurtzite phase with lattice constants ($a = 3.112\text{ \AA}$ and $c = 4.982\text{ \AA}$) (Yu, 2001), and a wide bandgap of 6.2 eV at room temperature. So, it can act as an insulating ceramic in electronic devices and exhibit the potential in optoelectronic applications at the UV spectrum. More impressively, AlN alloyed with GaN to form the ternary alloy - AlGaIn allows to extend the spectral response range from the UV to blue region, which is very suitable for optoelectronic devices (Pernot *et al.*, 2000), and is attracting the majority of interests.

Owing to the reactivity of Al with oxygen in the AlN lattice, high purity source materials and an oxygen-free environment are required to grow pure AlN. As reported, the commercial AlN typically contains extremely few oxygen (about $1 \pm 1.5\text{ at\%}$). High-quality

Table 1 Parameters of wurtzite structured AlN, GaN and InN. ("New Semiconductor Materials. Characteristics and Properties" www.ioffe.ru/SVA/NSM/Semicond/)

Parameters	AlN	GaN	InN
Bandgap (eV)	6.2	3.4	0.7
Density (g cm ⁻³)	3.255	6.15	6.81
Lattice constant (Å)	a=3.112 c=4.982	a=3.189 c=5.186	a=3.533 c=5.693
Coefficient of thermal expansion (K ⁻¹)	$\frac{\Delta a}{a}=4.15 \times 10^{-6}$ $\frac{\Delta c}{c}=5.27 \times 10^{-6}$	$\frac{\Delta a}{a}=5.59 \times 10^{-6}$ $\frac{\Delta c}{c}=3.17 \times 10^{-6}$	$\frac{\Delta a}{a}=3.8 \times 10^{-6}$ $\frac{\Delta c}{c}=2.9 \times 10^{-6}$
Thermal conductivity κ (W m ⁻¹ K ⁻¹)	285	130	45
Refraction index	2.1–2.2	2.29	2.9
Dielectric constants	$\epsilon_0=8.5 \pm 0.2$ $\epsilon_\infty=4.68\text{--}4.84$	$\epsilon_0=8.9$ $\epsilon_\infty=5.35$	$\epsilon_0=15.3$ $\epsilon_\infty=8.4$
Phonon modes (cm ⁻¹)	TO=667 E ₂ =665 LO=910	A ₁ (TO)=533 E ₁ (TO)= 559 E ₂ =144, 569 A ₁ (LO)=710 E ₁ (LO)=741	TO=478 LO=694
Melting point (°C)	3000	2500	1100
Bulk modulus (GPa @ 300K)	210	210 ± 10	140
Electron mobility (cm ² V ⁻¹ s ⁻¹)	300	1000	3200
Effective electron mass	0.4m ₀	0.2m ₀	0.11m ₀
Electron concentration (cm ⁻³)	< 10 ¹⁶	~ 10 ¹⁷	> 10 ¹⁹
Breakdown field (V cm ⁻¹)	1.2–1.8 × 10 ⁶	5 × 10 ⁶	–
Piezoelectric constants (C cm ⁻²)	$e_{33}=1.46$ $e_{31}=-0.60$	$e_{33}=0.73$ $e_{31}=-0.49$	$e_{33}=0.97$ $e_{31}=-0.57$
Spontaneous polarization charge P_0 (C cm ⁻²)	– 0.081	– 0.029	– 0.032

AlN is well fabricated on both silicon and sapphire substrates by employing the MBE and MOCVD growth techniques. The high-quality pure AlN crystal shows insulating electrical characteristics due to the low intrinsic carrier concentration, defect, and impurity. The undoped AlN has an electrical resistance of $10^{11} \sim 10^{13} \Omega \text{ cm}$, while the doped AlN has a decrease resistance of $10^5 \sim 10^6 \Omega \text{ cm}$. Its breakdown is found at an electrical field of $1.2\text{--}1.8 \times 10^6 \text{ V cm}^{-1}$. And the electron mobility is estimated at $300 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. AlN also exhibits n-type and p-type conduction with refined doping growth.

The room temperature bandgap of AlN is typically characterized by the optical absorption spectra. Oxygen impurity in AlN could have an influence on the optical parameters, *e.g.*, bandgap, refraction index, and dielectric constant. The refractive index of AlN ranges from 2.1 to 2.2. The static and high-frequency dielectric constants are 8.5 and 4.6, respectively. Moreover, the phonon structure of AlN has also been investigated, and the longitudinal optical (LO), transverse optical (TO), and E₂ modes are at 910 cm^{-1} , 667 cm^{-1} and 665 cm^{-1} , respectively. (Brafman *et al.*, 1968).

Due to the piezoelectric properties, AlN is very suitable for mechanical signal sensing, mechanical energy harvesting and converting applications, such as surface acoustic wave sensors (SAWs), thin-film bulk acoustic resonator (FBAR), and micro-machined ultrasound transducers. In addition, AlN based deep UV LED (at 210 nm) (Taniyasu *et al.*, 2006) was reported for the optoelectronic applications.

Gallium Nitride

GaN has been most intensively studied in III-nitride materials, which is the typical representative of third-generation semiconductors (Strite and Morkoç, 1992; Bougrov *et al.*, 2001). GaN has a wurtzite crystal structure, and its wide bandgap of 3.4 eV allows practical applications in optoelectronic, high-power and high-frequency devices. There are three main challenges for the research on GaN: shortage of suitable substrate, large background carrier concentration, and process difficulty. Generally, undoped GaN is found to be n-type, which may be induced by nitrogen vacancies. High-quality GaN exhibits electron concentrations of $4 \times 10^{16} \text{ cm}^{-3}$ on various substrates at room temperature. Obtaining p-type GaN has permitted us to fabricate/use a large number of *p-n* junction based optoelectronic and electronic devices, *e.g.*, LEDs.

Due to the stabilities in high temperature, caustic chemicals, and ionizing radiation, GaN-based devices are of great importance used in harsh environments including high-temperature, caustic and radiation conditions. GaN is insoluble or unreactive with most solutions at room temperature, including DI water, acids, and alkali. So, conventional wet etching techniques are not very effective for GaN processing. Instead, the dry etching techniques, *e.g.*, reactive ion etching, provide the possibility for rapid etching

of GaN. The wurtzite structured GaN has lattice constants ($a = 3.189 \text{ \AA}$ and $c = 5.186 \text{ \AA}$). Additionally, the GaN lattice constant shows some variations which may be induced by growth condition, impurity concentration, and film stoichiometry.

GaN can be grown on the substrate of sapphire or SiC, despite the mismatch of lattice constants. The n-type and p-type GaN are achieved by doping with Si (or O) and Mg, respectively. However, introducing Si and Mg atoms would influence on the growth of GaN crystals, and making the thin film brittle, as a result of tensile stresses. Moreover, the coefficient of thermal expansion would be observed to be $\Delta a/a = 5.59 \times 10^{-6} \text{ K}^{-1}$ and $\Delta c/c = 3.17 \times 10^{-6} \text{ K}^{-1}$ over a temperature range of 300–700K (Maruska and Tietjen, 1969). And the thermal conductivity is $130 \text{ W m}^{-1} \text{ K}^{-1}$. The phonon modes of GaN can be identified by Raman spectrum. The $A_1(\text{TO})$ and $E_1(\text{TO})$ modes are at 533 and 559 cm^{-1} , respectively, while the E_2 modes are at 144 and 569 cm^{-1} . And the $A_1(\text{LO})$ and $E_1(\text{LO})$ modes are at 710 and 741 cm^{-1} , respectively (Strite and Morkoç, 1992). Moreover, the refraction index of GaN is 2.29 (Bougrov *et al.*, 2001), and the static and frequency dielectric constants are 8.9 and 5.35 , respectively. (Bougrov *et al.*, 2001).

GaN has excellent electrical properties for high-power, high-speed, and high-frequency electronic applications. It can withstand a large electrical breakdown field of $1.2\text{--}1.8 \times 10^6 \text{ V cm}^{-1}$. The high field electron velocity of GaN is obtained at $1.9 \times 10^7 \text{ cm s}^{-1}$. The high electron mobility of GaN is $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and furthermore, the highest mobility is obtained in the AlGaIn/GaN heterojunctions, which is enhanced by the presence of the 2-dimensional electron gas (2°) at the heterointerface. Due to the unique properties, GaN is increasingly developing into commercialized products in blue LEDs, UV LDs, HEMTs, microwave power amplifiers, and THz devices.

Indium Nitride

InN has a small bandgap of $\sim 0.7 \text{ eV}$ at room temperature and shows very potential applications in LEDs, solar cells and high-speed electronics. InN alloyed with GaN to form the ternary alloy - GaInN LEDs, whose bandgap is tuned ranging from the IR (0.7 eV) to the UV (3.4 eV). However, there are some challenges or difficulties in InN, such as p-type doping InN, and the growth of ternary alloys with GaN or AlN with a large amount of In. Suffering from the poor thermal stability, InN cannot be grown at high-temperature conditions as the conventional AlN or GaN growth techniques. InN would fast dissolve at a temperature of $> 500^\circ\text{C}$. Similarly, InN also lacks a reasonable substrate, but it has large electron concentration ($> 10^{18} \text{ cm}^{-3}$), which is due to large densities of nitrogen vacancies. The electron mobility of InN can be as high as $3000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. In addition, InN is a wurtzite crystal with lattice parameters ($a = 3.533 \text{ \AA}$ and $c = 5.693 \text{ \AA}$). Through the reflection and transmission measurements, the effective electron mass and the refraction index of InN are estimated as $m_e = 0.11m_0$ and $n = 2.9$, respectively. And the TO and LO phonon modes are at 478 and 694 cm^{-1} , respectively. (Osamura *et al.*, 1975).

Their Alloys – AlGaIn and InGaIn

Many works have focused on the properties of III-nitride alloys, because the alloys based semiconductor devices exhibit excellent characteristics with the optimization of heterostructures. Similar to GaAs alloyed with AlAs and InAs, GaN alloys with AlN and InN can be used in practical applications of high-performance solid-state optoelectronics and high-power electronics. The bandgap and lattice constant of the alloys are tuned with the composition of AlN, GaN, and InN, as shown in Fig. 1.

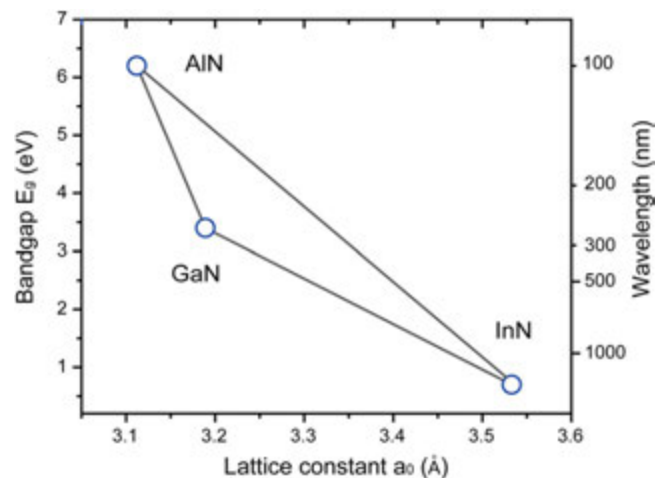


Fig. 1 Bandgap and lattice constant for AlN, GaN, and InN.

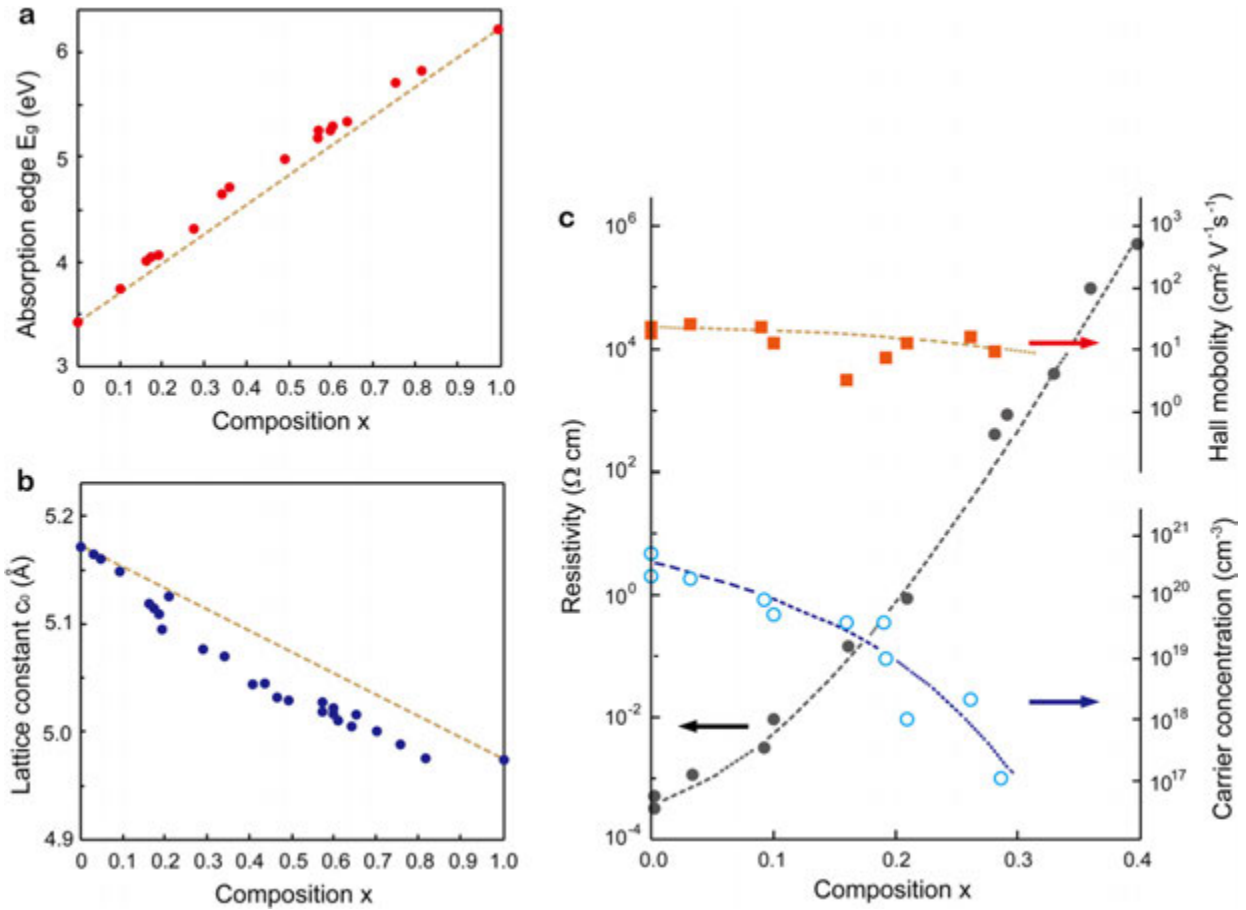


Fig. 2 Al compositional dependence of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ on (a) bandgap, (b) lattice constant, (c) resistivity, carrier concentration, and electron mobility at room temperature. Data from Yoshida, S., Misawa, S., Gonda, S., 1982. Properties of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ films prepared by reactive molecular beam epitaxy. *Journal of Applied Physics* 53, 6844–6848.

Aluminum Gallium Nitride

AlGa_N has attracted more attention in III-nitride alloys due to the unique characteristics of AlGa_N/Ga_N heterojunctions (Strite and Morkoç, 1992; Morkoç, 2001). AlGa_N/Ga_N has a large lattice mismatch, and V-shaped cracks would form when AlGa_N was grown on Ga_N (Ito *et al.*, 1990). To date, the high-quality AlGa_N layers are commonly grown on the substrate of sapphire or (111) Si, almost always with additional Ga_N layers. As the alloy together formed with Ga_N and Al_N, $\text{Al}_x\text{Ga}_{1-x}\text{N}$ shows the tunable bandgap ranging from 3.4 eV ($x = 0$) to 6.2 eV ($x = 1$), which is essential to fabricate LEDs in the blue and deep UV regions. As measured by the Al and Ga X-ray radiation, the Al mole fraction of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ can be tailored up to $x = 0.45$.

With the increasing of Al mole fraction, n-type conductivity, carrier concentration, mobility and lattice constant all show monotonous decreasing trends, as shown in Fig. 2. The resistivity has an obvious increase by ten orders of magnitude, which ranges from 10^{-4} to $10^6 \Omega \text{ cm}$, and the carrier concentration has a reduction from 2×10^{20} to 10^{17} cm^{-3} , when the Al mole fraction increases from $x = 0$ to $x = 0.4$. In addition, $\text{Al}_x\text{Ga}_{1-x}\text{N}$ has a good thermal stability up to 900°C , when $x = 0.5$. The refraction index (400–500 nm) is ~ 2.42 as $x = 0.2$. Moreover, the increase of the phonon frequencies with the Al mole fraction is smaller than expected from a linear extrapolation for the TO and E_2 modes while it is slightly larger for the $E_1(\text{LO})$ mode. Together with Ga_N, AlGa_N has been developed into commercial products in the blue and UV LEDs, blue LDs, UV detectors, and HEMTs.

Indium Gallium Nitride

Also as a tunable bandgap alloy, InGa_N has a direct bandgap span from the infrared (0.7 eV for In_N) to the ultraviolet (3.4 eV for Ga_N). By changing the amount of In, the properties of $\text{In}_x\text{Ga}_{1-x}\text{N}$ can be obviously tuned, as shown in Fig. 3. The ratio of In/Ga is in general between 0.02/0.98 and 0.3/0.7. The lattice constant and bandgap of $\text{In}_x\text{Ga}_{1-x}\text{N}$ show linear relations with the In mole fraction (Nagatomo *et al.*, 1989; Osamura *et al.*, 1972). The In is active at high temperature, and may occur the re-evaporation of In during the growth. As reported, a phase separation is found in the $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy with low In mole fraction

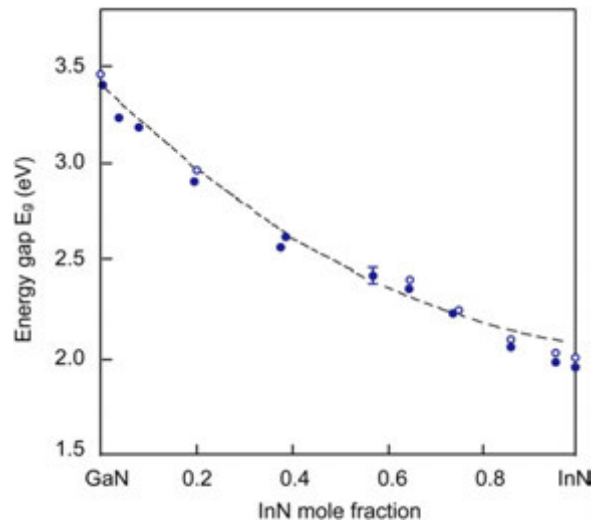


Fig. 3 InN compositional dependence of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ on bandgap at room temperature. Data from Osamura, K., Nakajima, K., Murakami, Y., *et al.*, 1972. Fundamental absorption edge in GaN, InN and their alloys. Solid State Communications 11, 617–621.

through a high-temperature annealing processing (700°C, Ar) (Osamura *et al.*, 1975). The high-quality single crystal $\text{In}_{0.22}\text{Ga}_{0.78}\text{N}$ can be achieved at the high-temperature (800°C) CVD growth (Yoshimoto *et al.*, 1991).

Devices and Applications

Due to the unique characteristics (*e.g.*, tunable direct bandgap, high electron mobility, high saturation velocity, high absorption coefficient, and high thermal stability and conductivity), AlN, GaN, InN and their alloys have paved the way into the high-performance optoelectronic and electronic devices, and the related commercial applications. Specifically, InGaN/GaN-based LEDs and AlGaN/GaN-based HEMTs are two key devices widely studied for the research and applications of III-nitrides. Furthermore, III-nitrides (*e.g.*, GaN) exhibit spontaneous and piezoelectric polarization due to the non-central-symmetric wurtzite structure. The strong polarity of the covalent bond between Ga and N atoms causes the spontaneous polarization. The separation of the dipole centers in the GaN crystal induces large piezoelectric polarization upon strain along the *c*-axis. Different from the Si and GaAs semiconductors, polarization is a vital effect on the III-nitrides, which greatly affects device performances. Indeed, it is of great importance to investigate the polarization effect on the III-nitride devices. Additionally, piezoelectric polarization potential (piezo-potential) induced by external strain can effectively control carrier transport characteristics at the interface, which is also called piezotronic effect (Pan *et al.*, 2019; Hu *et al.*, 2018).

Piezotronic Effect

The wurtzite structured AlN, GaN and InN semiconductors both possess piezoelectric and semiconductor properties, and have large piezoelectric constants (see Table 1). Upon an external strain, the piezo-potential is produced at the heterointerface along the *c*-axis, and has an influence on the carrier transport characteristics, which is the basis of the piezotronic effect (Wu and Wang, 2016; Du *et al.*, 2018a; Hu *et al.*, 2018; Pan *et al.*, 2019).

Polarization is related to the polarity of the crystal. Under a normal compressive stress, the *c*-plane GaN nanowire exhibits the tunable Schottky barrier behavior with the piezoelectric polarization, but the *m*-plane GaN nanowire does not show that (Zhao *et al.*, 2015). The piezoelectric polarization intensity is dependent on the strain of the crystal. When there is no strain but spontaneous polarization in the III-nitride heterojunction, the spontaneous polarization is along the [0001] direction, the negative polarization charge will be distributed on the Ga-plane, and the positive polarization charge will be distributed on the N-plane. When it is subjected to the biaxial tensile stress, the piezoelectric polarization along the *c*-axis is aligned with the spontaneous polarization; when it is subjected to the biaxial compressive stress, the piezoelectric polarization along the *c*-axis is opposite to the spontaneous polarization. The displaced charge centers of the Ga cations and N anions under strain cause the generation of the electric dipole moment in the crystal, and thus piezo-potential is formed in the macroscopic straining orientation. The piezo-potential intensity of the III-nitride heterojunctions can reach the order of 1 MV cm^{-1} , and the polarization charge density can reach $1 \times 10^{12} \text{ cm}^{-2}$, which can significantly tune the band structure of the heterojunction, thus affecting the carriers transport behavior.

Upon strains on the crystal, spontaneous and piezoelectric polarizations are simultaneously demonstrated. Net polarization (P_{NP}) in crystal volume unit is the sum of spontaneous (P_{SP}) and piezoelectric polarization (P_{PE}):

$$P_{NP} = P_{SP} + P_{PE}$$

For a given material, the piezoelectric property can be evaluated through the polarization vector P and the strain tensor S_{jk} :

$$P_i = e_{ijk} S_{jk}$$

where e_{ijk} is a third-rank tensor of piezoelectric coefficients.

The relationship between electricity and elasticity through the piezoelectric effect can be given as:

$$\sigma = c_E S - e^T E$$

$$D = e S + \kappa E$$

where D is the electric polarization, σ is the stress tensor, c_E is the elastic tensor, and κ is the dielectric tensor.

For an III-nitride layer on a biaxial strain, the effective piezoelectric polarization is:

$$P_z^{\text{piezo}} = [e_{31} - (C_{31}/C_{31}) \cdot e_{33}] \cdot \varepsilon_{\perp}$$

where C_{31} and C_{33} are elastic constants, and $\varepsilon_{\perp}$ is the in-plane strain. For coherently strained $\text{Al}_x\text{Ga}_{1-x}\text{N}$ on a relaxed GaN layer, the strain ε is expected to be proportional to x . It is tensile and given by

$$\varepsilon_{\perp} = 2x(a_{\text{GaN}} - a_{\text{AlGa}})/a_{\text{AlGa}}$$

The magnitude of the strain reduces to 0.0495x for the case of the c -plane lattice constants of 3.112 Å and 3.189 Å for AlN and GaN, respectively. Here x is in the range of 0–1 and indicates the AlN mole fraction in the alloy. The piezoelectric polarization is $P_z^{\text{piezo}} = -4.26x \times 10^{-2} \text{ C cm}^{-2}$ or $2.66x \times 10^{13} \text{ e cm}^{-2}$ and points along the [000-1] direction. The corresponding difference in spontaneous polarization between $\text{Al}_x\text{Ga}_{1-x}\text{N}$ and GaN is also expected to be proportional to x and is given by $\Delta P^{\text{piezo}} = -4.26x \times 10^{-2} \text{ C cm}^{-2}$ or $3.25x \times 10^{13} \text{ e cm}^{-2}$. The two polarization effects have the same sign for Ga-polarity and tensile strain in the alloy, and point in the [000-1] direction (Morkoç *et al.*, 1999). In the layer of $\text{In}_x\text{Ga}_{1-x}\text{N}$, the differential spontaneous polarization between $\text{In}_x\text{Ga}_{1-x}\text{N}$ and GaN is much smaller, $\Delta P^{\text{pon}} = -0.003x$, corresponding to $1.88x \times 10^{12} \text{ e cm}^{-2}$. Furthermore, the $\text{In}_x\text{Ga}_{1-x}\text{N}$ layer on GaN would be under compressive strain. The amplitude of the in-plane strain is $\varepsilon_{\perp} = -0.195x$ if 3.533 Å and 3.189 Å are used for c -plane lattice constants for InN and GaN. Here x is in the range of 0–1 and indicates the InN mole fraction, and $\Delta P^{\text{piezo}} = +0.176x$ or $1.1x \times 10^{14} \text{ e cm}^{-2}$. For an InN mole fraction of 0.15, $P_z^{\text{piezo}} = 1.65 \times 10^{13} \text{ e cm}^{-2}$. In this case, the piezoelectric polarization dominates and is opposite in direction but even larger in absolute magnitude (Morkoç, 2001; Morkoç *et al.*, 1999). For the AlGa case, the sign of piezoelectric polarization is such as to produce a potential energy for electrons sloping down from the Ga-plane to the N-plane. In a structure with Ga polarity, the potential will slope down from the AlGa surface toward the AlGa/GaN heterointerface. This potential gradient will help to drive free electrons to the heterointerface forming a 2°. In the presence of an ohmic metal contact on the AlGa surface, electrons will flow from the contact toward the 2° below that layer (Morkoç, 2001; Morkoç *et al.*, 1999).

AlGa/GaN HEMTs

Due to the excellent performances in high-power, high-speed and high-frequency, AlGa/GaN HEMTs have great application prospects, such as radio-frequency, power amplifiers, broadband communication, radar, power inverter, and sensors. Fig. 4(a) shows the schematic illustration of the AlGa/GaN HEMT.

GaN has many advantages including higher breakdown voltages and higher operational temperature. Large lattice mismatch between AlN and GaN induces a strain in the AlGa layer, producing a piezoelectric field. Together with the large conduction band offset and the spontaneous polarization result in high electron sheet charge density.

Various device optimization techniques are developed: (1) the use of the field-plate, T-shaped or Y-shaped gate electrodes; (2) the insertion of AlN barrier between the GaN and AlGa layers that increases the conduction band offset and the 2DEG density and decreases the alloy disorder scattering, leading to the increase of mobility; and (3) the introduction of the double-heterojunction structure that enhances the 2DEG transport properties, *e.g.*, the InGa layer under the channel brings negative polarization charges at the heterointerface, result in improving the carrier confinement in the channel. In general, AlGa/GaN HEMTs exhibit the depletion-mode (D-mode) behavior. However, the enhancement-mode (E-mode) is getting progress. Several approaches are presented for the E-mode technology by the usages of very thin AlGa layers, fluoride-based plasma treatment, the recess gate structure, and the InGa cap layers.

Another way to optimize the device performance is by adopting the piezotronic effect to control the carrier transport in the AlGa/GaN HEMT. The existence of 2DEG at the AlGa/GaN heterointerface is the basic to control carriers transport behavior for achieving special performances, which is related to the spontaneous and piezoelectric polarization of the strained AlGa and GaN layers. Without an external strain, positive/negative polarization charges turn up at the bottom/top surface of the AlGa layer due to intrinsic polarization. Electrons are driven by the electric fields to the triangle-shaped potential well at the AlGa/GaN heterointerface, forming the 2DEG. Under a tensile strain, piezoelectric charges are newly generated at the top surface of the GaN layer, causing that the potential well and the net positive polarization charges become shallower and decrease at the AlGa/GaN heterointerface, as shown in Fig. 4(b) and (c). Thus, fewer electrons are confined in the potential well and current becomes smaller with the increase of tensile strain. Similarly, the compressive strain is also investigated in HEMT, demonstrating that it will increase the current due to more electrons in the potential well. Moreover, the heterojunction electron gas and electric transport properties

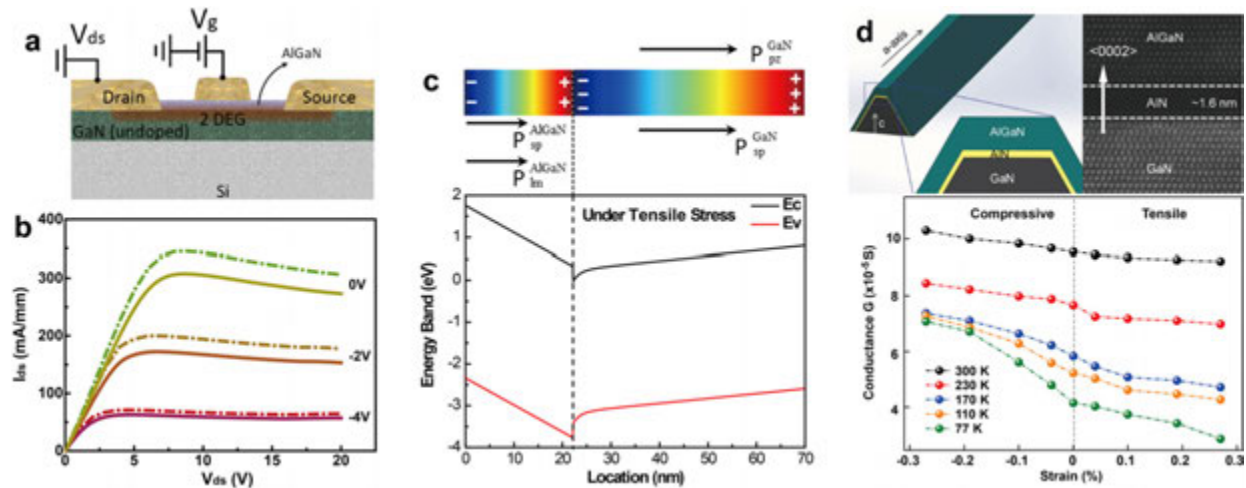


Fig. 4 Piezotronic effect on the AlGaIn/GaN HEMTs. (a) A typical schematic of HEMT. (b) Output ($I_{ds} - V_{ds}$) characteristics of the strained HEMT (the dashed and solid lines represent the strain-free and tensile strain conditions, respectively). (c) Schematic energy band diagrams of the AlGaIn/GaN heterojunction under tensile strain condition. (d) The performance of the AlGaIn/AlN/GaN heterostructure microwires under strain at various temperature. Reproduced with permissions from Liu, T., Jiang, C., Huang, X., *et al.*, 2017. Electrical transportation and piezotronic-effect modulation in AlGaIn/GaN MOS HEMTs and unpassivated HEMTs. *Nano Energy* 39, 53–59. Wang, X., Yu, R., Jiang, C., *et al.*, 2016. Piezotronic effect modulated heterojunction electron gas in AlGaIn/AlN/GaN heterostructure microwire. *Advanced Materials* 28, 7234–7242.

of AlGaIn/AlN/GaN microwires at low temperatures are easily tuned by piezotronic effect, as shown in Fig. 4(d). The conductance shows more remarkable change at low temperature under strains, due to the suppressed screening against piezoelectric polarization. Therefore, piezotronic effect is an innovative way to optimize the performance of HEMT and will provide some inspiration for designing novel human-machine interfaces (Zhang *et al.*, 2020).

InGaIn/GaN LEDs

Due to the high brightness, tunable/wide emission wavelength, and high reliability, III-nitride LEDs (*e.g.*, InGaIn/GaN MQW) are being extensively developed into energy-efficient solid-state light sources aim to replace the incandescent and gas discharge lamps (Iso *et al.*, 2007; Nakamura *et al.*, 1993). The white-light LEDs is essential to achieving $> 200 \text{ lm W}^{-1}$ in market-ready systems by 2025 (Morgan Pattison *et al.*, 2018). The high-performance LEDs demonstrate some ubiquitous applications in the field of white light illumination, full-color displays, visible light communication (VLC), and medical micro-imaging vehicles. Moreover, the newly developed LEDs with micro-pixelated design (*i.e.*, micro-LEDs) enables monolithic integration of multiple devices, and is an ideal platform for single-chip full-color emissive microdisplays, promising to challenge the conventional LEDs and OLED technologies.

Together with the piezoelectric polarization, the optical excitation of the wurtzite structured III-nitride semiconductors can be tuned with the use of strain, leading to the piezo-phototronic effect (Wu and Wang, 2016; Du *et al.*, 2018a; Pan *et al.*, 2019). It is an emerging field of band structure engineering through interfacing tuning with the coupling of semiconductor properties, piezoelectric polarization, and optical excitation. Under the strain-induced piezoelectric polarization charges (piezo-charges) as a virtual “gate”, the band structure can be effectively modulated to achieve tunable optoelectronic performances, including light emission enhancement (Yang *et al.*, 2011), solar cell efficiency (Sun *et al.*, 2019), dual-channel VLC (Du *et al.*, 2016), and pressure sensing/imaging (Pan *et al.*, 2013).

Ongoing research is dedicated to improving device performances, *e.g.*, the structure for more efficient light generation/extracting. In addition, the piezo-phototronic effect is also used to enhance the performances of InGaIn/GaN LEDs. Thermal issue is inevitable for LEDs that takes near 80% of the input power and thus causes temperature increase, leading to the degradations in lifetime and light-output, or risking catastrophic failure (Du *et al.*, 2018b; Christensen and Graham, 2009; Hu *et al.*, 2007a). Additionally, the integrated EL intensity at 364K is only 67.8% of that at 300K (Du *et al.*, 2018b). And hence, it is very important to deal with thermal issues in high power LEDs. Impressively, an effective way to relieve the thermal issue is the use of the piezo-phototronic effect, which can enhance the EL intensity at the high temperature with strains. The micro-stripe arrayed blue InGaIn/GaN MQW LED is shown in Fig. 5(a). Due to the lattice mismatch of the InGaIn/GaN heterointerface, in-plane compressive strain in the InGaIn layers causes the energy band tilted and gradually misaligns the wave functions of electron and hole. Upon an external strain, piezo-potential is generated and opposite to that induced by internal strain, partly counteracting the piezoelectric charges in the vicinity of the interface, which makes the energy band more flatten and the wave functions of electron and hole more overlapped. Consequently, the electron/hole recombination rate increases, and so does the emission efficiency of micro-LED. The EL intensity increases with the increase of external strain (Fig. 5(b)). When the temperature increases from 300K to 380K with no external strain, the EL intensity gets a continuous decrease, probably due to the increase of nonradiative recombination

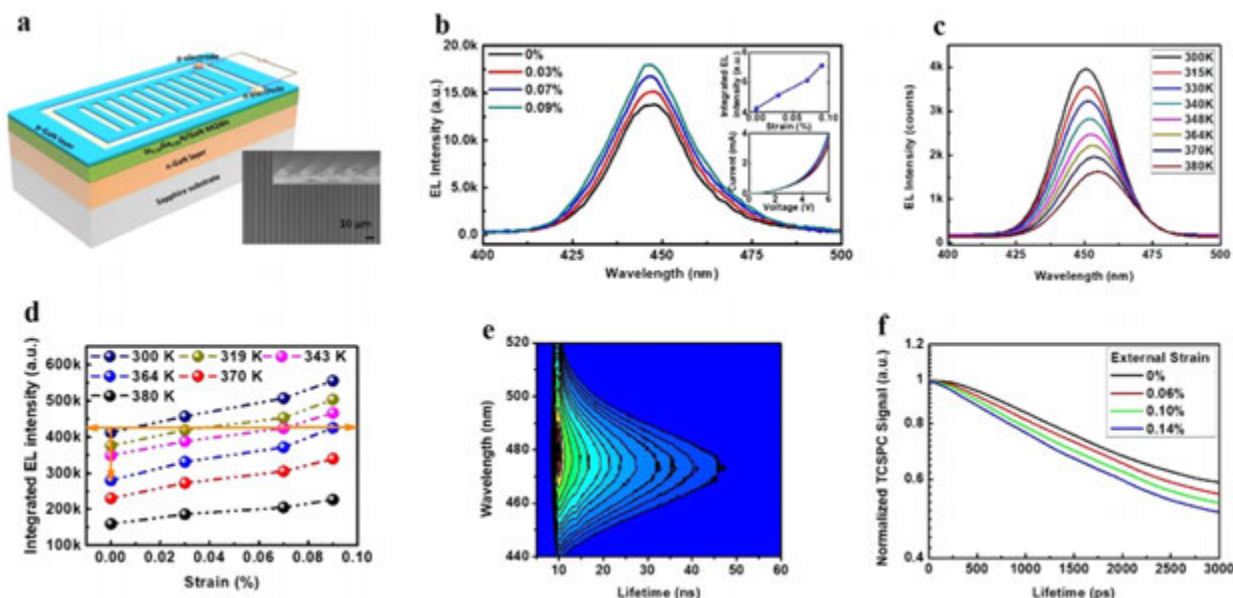


Fig. 5 Piezo-phototronic effect on the InGaN/GaN LEDs. (a-d) Blue InGaN/GaN MQW LED. (a) Schematic illustration of the LED. (b) EL spectra under different strains with a 5 mA injection current. The insets show the dependence of integrated EL intensities on strain and the I-V characteristics under various strains. (c) EL spectra under different temperatures. (d) The integrated EL intensity *versus* strain under different temperatures. (e-f) VLC with green InGaN/GaN SQW LED. (e) Contour plot of time-resolution PL spectra. (f) Time-resolution PL with various strains. Reproduced from Du, C., Jing, L., Jiang, C., *et al.*, 2018b. An effective approach to alleviating the thermal effect in microstripe array-LEDs via the piezo-phototronic effect. *Materials Horizons* 5, 116–122. Du, C., Huang, X., Jiang, C., *et al.*, 2016. Tuning carrier lifetime in InGaN/GaN LEDs via strain compensation for high-speed visible light communication. *Scientific Reports* 6, 37132.

behavior including defects, Auger recombination and dislocations, and the decrease of the spontaneous emission rate as well. A 4.6 nm red-shift is also observed in emission wavelength, induced by the shrinkage of the energy band (Fig. 5(c)). These worse conditions caused by the thermal issue do harm to the lighting. Obviously, the integrated EL intensity is monotonously enhanced when the external strain increases with temperatures (Fig. 5(d)) (Du *et al.*, 2018b). In addition, the piezo-phototronic effect has potential applications in high-speed optoelectronic devices, such as ultra-fast display or VLC. With the strain modulation, the green InGaN/GaN SQW LED exhibits an increase of the PL intensity and a 55% reduction of the carrier lifetime with strains (Fig. 5(e) and (f)), which dramatically increase the single-chip VLC modulation width to 117 MHz (Du *et al.*, 2016).

Conclusion and Outlook

AlN, GaN, InN and their alloys exhibit outstanding structural, electrical and optical properties, *e.g.*, high electron mobility, high saturation velocity, direct and tunable bandgap, large dielectric breakdown field, high absorption coefficient, and high thermal stability and conductivity, which are very promising semiconductors for industrial applications of optoelectronics and electronics in harsh environments. The III-nitrides have thermodynamically stable wurtzite crystal phase at ambient conditions, and the direct bandgap ranges from 6.2 eV of AlN, 3.4 eV of GaN, to 0.7 eV of InN. Their ternary alloys such as AlGaIn and InGaIn provide the possibility of tuning the bandgaps continuously span from the deep UV into the whole visible spectrum.

Lack of lattice-matched substrates, insufficient control of impurity levels, defects and dislocations, difficult growth of high-quality p-type doping layers, and process difficulty for layer pattern are still challenges for the ongoing research and development on the III-nitrides. Sapphire, SiC and Si are presented to be suitable substrates for III-nitrides growth. High-quality AlN, GaN, InN and their alloys can be grown by the use of the MBE and MOCVD techniques. But it is still needed to develop the high-quality III-nitride layers and heterostructures for future high-power, high-performance electronic and optoelectronic applications.

Due to the non-central-symmetric wurtzite structures, III-nitrides simultaneously demonstrate spontaneous and piezoelectric polarization. The electrical or optical properties of III-nitrides can be effectively tuned/controlled by external strains, which lead to the large piezoelectric polarization response. And hence, the piezotronic (or piezo-phototronic) effect is employed, by strain-induced piezoelectric charges at the heterointerface, to modulate the charge generation, combination, and transport characteristics. The typical devices, *i.e.*, AlGaIn/GaN HEMTs and InGaIn/GaN QW LEDs are demonstrated, and show the enhanced performances under the effect of external strains, which represents an effective approach for device optimization.

This chapter makes an outlook of fundamental properties of AlN, GaN, and InN, and provides significant insight into the potential applications of GaN-based electronic/optoelectronic devices by introducing strain effects. However, a large amount of

work should be done for further investigations on approaching the level of understanding of technologically important materials as the first-/second-generation semiconductors (e.g., Si and GaAs).

References

- Bougrov, V., Levinstein, M.E., Rumyantsev, S.L., Zubrilov, A., 2001. Gallium nitride (GaN). In: Levinstein, M.E., Rumyantsev, S.L., Shur, M.S. (Eds.), *Properties of Advanced Semiconductor Materials: GaN, AlN, InN, BN, SiC, SiGe*. New York: John Wiley & Sons, Inc.
- Brafman, O., Lengyel, G., Mitra, S.S., *et al.*, 1968. Raman spectra of Al_xN , cubic BN and BP. *Solid State Communications* 6, 523–526.
- Chen, Q., Yang, J.W., Osinsky, A., *et al.*, 1997. Schottky barrier detectors on GaN for visible-blind ultraviolet detection. *Applied Physics Letters* 70, 2277–2279.
- Christensen, A., Graham, S., 2009. Thermal effects in packaging high power light emitting diode arrays. *Applied Thermal Engineering* 29, 364–371.
- Du, C., Huang, X., Jiang, C., *et al.*, 2016. Tuning carrier lifetime in InGaN/GaN LEDs via strain compensation for high-speed visible light communication. *Scientific Reports* 6, 37132.
- Du, C., Hu, W., Wang, Z.L., 2018a. Recent progress on piezotronic and piezo-phototronic effects in III-group nitride devices and applications. *Advanced Engineering Materials* 20, 1700760.
- Du, C., Jing, L., Jiang, C., *et al.*, 2018b. An effective approach to alleviating the thermal effect in microstripe array-LEDs via the piezo-phototronic effect. *Materials Horizons* 5, 116–122.
- Funato, M., Ueda, M., Kawakami, Y., *et al.*, 2006. Blue, green, and amber InGaN/GaN light-emitting diodes on semipolar {11-22} GaN bulk substrates. *Japanese Journal of Applied Physics* 45, L659–L662.
- Hu, J., Yang, L., Whan Shin, M., 2007a. Mechanism and thermal effect of delamination in light-emitting diode packages. *Microelectronics Journal* 38, 157–163.
- Hu, W.-G., Liu, X.-L., Zhang, P.-F., *et al.*, 2007b. A comparison between AlN films grown by MOCVD using dimethylethylamine and trimethylaluminum as the aluminum precursors. *Chinese Physics Letters* 24, 516–519.
- Hu, W.G., Liu, X.L., Jiao, C.M., *et al.*, 2007c. Using different carrier gases to control AlN film stress and the effect on morphology, structural properties and optical properties. *Journal of Physics D: Applied Physics* 40, 7462–7466.
- Hu, W., Ma, B., Li, D., *et al.*, 2009. Mobility enhancement of 2DEG in MOVPE-grown AlGaIn/GaN HEMT structure using vicinal (0 0 0 1) sapphire. *Superlattices and Microstructures* 46, 812–816.
- Hu, W., Ma, B., Li, D., *et al.*, 2010. Effects of the AlN interlayer on the distribution and mobility of two-dimensional electron gas in AlGaIn/GaN heterojunctions. *Japanese Journal of Applied Physics* 49, 035701.
- Hu, W., Kalantar-Zadeh, K., Gupta, K., Liu, C.-P., 2018. Piezotronic materials and large-scale piezotronics array devices. *MRS Bulletin* 43, 936–940.
- Iso, K., Yamada, H., Hirasawa, H., *et al.*, 2007. High brightness blue InGaN/GaN light emitting diode on nonpolar-plane bulk GaN substrate. *Japanese Journal of Applied Physics* 46, L960–L962.
- Ito, K., Hiramatsu, K., Amano, H., Akasaki, I., 1990. Preparation of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ /GaN heterostructure by MOVPE. *Journal of Crystal Growth* 104, 533–538.
- Jain, S.C., Willander, M., Narayan, J., Overstraeten, R.V., 2000. III-nitrides: Growth, characterization, and properties. *Journal of Applied Physics* 87, 965–1006.
- Jani, O., Ferguson, I., Honsberg, C., Kurtz, S., 2007. Design and characterization of GaN/InGaN solar cells. *Applied Physics Letters* 91, 132117.
- Jiang, C., Jing, L., Huang, X., *et al.*, 2017. Enhanced solar cell conversion efficiency of InGaN/GaN multiple quantum wells by piezo-phototronic effect. *ACS Nano* 11, 9405–9412.
- Liu, T., Jiang, C., Huang, X., *et al.*, 2017. Electrical transportation and piezotronic-effect modulation in AlGaIn/GaN MOS HEMTs and unpassivated HEMTs. *Nano Energy* 39, 53–59.
- Maruska, H.P., Tietjen, J.J., 1969. The preparation and properties of vapor-deposited single-crystal-line GaN. *Applied Physics Letters* 15, 327–329.
- Mishra, U.K., Parikh, P., Yi-Feng, W., 2002. AlGaIn/GaN HEMTs—an overview of device operation and applications. *Proceedings of the IEEE* 90, 1022–1031.
- Morgan Pattison, P., Hansen, M., Tsao, J.Y., 2018. LED lighting efficacy: Status and directions. *Comptes Rendus Physique* 19, 134–145.
- Morkoç, H., 2001. Aluminum, gallium, and indium nitrides. In: Buschow, K.H.J., Cahn, R.W., Flemings, M.C., Ilshner, B., Kramer, E.J., Mahajan, S., Veyssière, P. (Eds.), *Encyclopedia of Materials: Science and Technology*. Oxford: Elsevier.
- Morkoç, H., Cingolani, R., Gil, B., 1999. Polarization effects in nitride semiconductor device structures and performance of modulation doped field effect transistors. *Solid-State Electronics* 43, 1909–1927.
- Moustakas, T.D., Iliopoulos, E., Sampath, A.V., *et al.*, 2001. Growth and device applications of III-nitrides by MBE. *Journal of Crystal Growth* 227–228, 13–20.
- Muñoz, E., Monroy, E., Garrijo, J.A., *et al.*, 1997. Photoconductor gain mechanisms in GaN ultraviolet detectors. *Applied Physics Letters* 71, 870–872.
- Nagatomo, T., Kuboyama, T., Minamino, H., Omoto, O., 1989. Properties of $\text{Ga}_{1-x}\text{In}_x\text{N}$ Films Prepared by MOVPE. *Japanese Journal of Applied Physics* 28, L1334–L1336.
- Nakamura, S., Senoh, M., Mukai, T., 1993. High-power InGaN/GaN double-heterostructure violet light emitting diodes. *Applied Physics Letters* 62, 2390–2392.
- Nakamura, S., Senoh, M., Nagahama, S.-i., *et al.*, 1998a. Continuous-wave operation of InGaN/GaN/AlGaIn-based laser diodes grown on GaN substrates. *Applied Physics Letters* 72, 2014–2016.
- Nakamura, S., Senoh, M., Nagahama, S.-i., *et al.*, 1998b. InGaN/GaN/AlGaIn-based laser diodes grown on GaN substrates with a fundamental transverse mode. *Japanese Journal of Applied Physics* 37, L1020–L1022.
- Neufeld, C.J., Toledo, N.G., Cruz, S.C., *et al.*, 2008. High quantum efficiency InGaN/GaN solar cells with 2.95 eV band gap. *Applied Physics Letters* 93, 143502.
- Osamura, K., Nakajima, K., Murakami, Y., *et al.*, 1972. Fundamental absorption edge in GaN, InN and their alloys. *Solid State Communications* 11, 617–621.
- Osamura, K., Naka, S., Murakami, Y., 1975. Preparation and optical properties of $\text{Ga}_{1-x}\text{In}_x\text{N}$ thin films. *Journal of Applied Physics* 46, 3432–3437.
- Palacios, T., Chakraborty, A., Rajan, S., *et al.*, 2005. High-power AlGaIn/GaN HEMTs for Ka-band applications. *IEEE Electron Device Letters* 26, 781–783.
- Pan, C., Dong, L., Zhu, G., *et al.*, 2013. High-resolution electroluminescent imaging of pressure distribution using a piezoelectric nanowire LED array. *Nature Photonics* 7, 752.
- Pan, C., Zhai, J., Wang, Z.L., 2019. Piezotronics and piezo-phototronics of third generation semiconductor nanowires. *Chemical Reviews* 119, 9303–9359.
- Pernot, C., Hirano, A., Iwaya, M., *et al.*, 2000. Solar-blind UV photodetectors based on GaN/AlGaIn p-i-n photodiodes. *Japanese Journal of Applied Physics* 39, L387–L389.
- Slack, G.A., Tanzili, R.A., Pohl, R.O., Vandersande, J.W., 1987. The intrinsic thermal conductivity of AlN. *Journal of Physics and Chemistry of Solids* 48, 641–647.
- Strite, S., Morkoç, H., 1992. GaN, AlN, and InN: A review. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena* 10, 1237–1266.
- Sun, J., Hua, Q., Zhou, R., *et al.*, 2019. Piezo-phototronic effect enhanced efficient flexible perovskite solar cells. *ACS Nano* 13, 4507–4513.
- Taniyasu, Y., Kasu, M., Makimoto, T., 2006. An aluminium nitride light-emitting diode with a wavelength of 210 nanometres. *Nature* 441, 325–328.
- Wu, W., Wang, Z.L., 2016. Piezotronics and piezo-phototronics for adaptive electronics and optoelectronics. *Nature Reviews Materials* 1, 16031.
- Xu, K., Wang, J.-F., Ren, G.-Q., 2015. Progress in bulk GaN growth. *Chinese Physics B* 24, 066105.
- Yang, Q., Wang, W., Xu, S., Wang, Z.L., 2011. Enhancing light emission of ZnO microwire-based diodes by piezo-phototronic effect. *Nano Letters* 11, 4012–4017.
- Yong, C., Yugang, Z., Chen, K.J., Lau, K.M., 2005. High-performance enhancement-mode AlGaIn/GaN HEMTs using fluoride-based plasma treatment. *IEEE Electron Device Letters* 26, 435–437.
- Yoshida, S., Misawa, S., Gonda, S., 1982. Properties of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ films prepared by reactive molecular beam epitaxy. *Journal of Applied Physics* 53, 6844–6848.

- Yoshimoto, N., Matsuoka, T., Sasaki, T., Katsui, A., 1991. Photoluminescence of InGaN films grown at high temperature by metalorganic vapor phase epitaxy. *Applied Physics Letters* 59, 2251–2253.
- Yu, G., 2001. Aluminum nitride (AlN). In: Levinshtein, M.E., Rumyantsev, S.L., Shur, M.S. (Eds.), *Properties of Advanced Semiconductor Materials: GaN, AlN, InN, BN, SiC, SiGe*. New York: John Wiley & Sons, Inc.
- Zhang, S., Ma, B., Zhou, X., *et al.*, 2020. Strain-controlled power devices as inspired by human reflex. *Nature Communications* 11, 326.
- Zhao, Z., Pu, X., Han, C., *et al.*, 2015. Piezotronic effect in polarity-controlled GaN nanowires. *ACS Nano* 9, 8578–8583.

Novel Nitride Phosphors

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Ce- and Tb-Doped Rare-Earth Silicon Oxynitrides

Long-wavelength $\text{Ce}^{3+} 5d \rightarrow 4f$ band emission was observed in Y–Si–O–N materials (van Krevel *et al.*, 1998); its exact position depends on the nephelauxetic effect, crystal field splitting of the $5d$ -level and Stokes shift. The crystal field splitting decreases when more N^{3-} versus O^{2-} is coordinated to Ce^{3+} , which is ascribed to the higher formal charge of nitrogen versus oxygen (van Krevel *et al.*, 1998). The Stokes shift becomes smaller in the series $\text{Y}_5(\text{SiO}_4)_3\text{N} > \text{Y}_4\text{Si}_2\text{O}_7\text{N}_2 > \text{YSiO}_2\text{N} > \text{Y}_2\text{Si}_3\text{O}_3\text{N}_4$, related to an increasing rigidity due to more extended cross-linking between SiX_4 ($\text{X} = \text{O}, \text{N}$) tetrahedra in this direction (respectively: single SiX_4 units, Si_2X_7 dimers, Si_3X_9 rings, and $(\text{Si}_3\text{X}_7)_n$ layers).

The highest emission wavelength was observed for $\text{Y}_2\text{Si}_3\text{O}_3\text{N}_4\text{:Ce}$ (≈ 504 nm), whose position can only be negligibly influenced by replacement of $(\text{SiN})^+$ by $(\text{AlO})^+$ resulting in $\text{Y}_2\text{Si}_{3-x}\text{Al}_x\text{O}_{3-x}\text{N}_{4-x}\text{:Ce}$ compounds (van Krevel *et al.*, 2000). Despite a high solid solubility up to $x = 0.6$ which significantly modifies the chemical composition of the host lattice, evidently the local coordination around the Ce^{3+} ion remains almost the same. This effect was ascribed to the larger ionic size of Ce^{3+} as compared to Y^{3+} resulting in preferential coordination of the dopant ion with oxygen as compared to nitrogen (van Krevel *et al.*, 2000).

Other examples of Ce^{3+} -doped rare-earth silicon oxynitride phosphors are $\text{La}_5\text{Si}_3\text{O}_{12}\text{N}$, $\text{La}_4\text{SiO}_7\text{N}_2$, LaSiO_2N , and $\text{La}_3\text{Si}_8\text{O}_4\text{N}_{11}$ (Dierre *et al.*, 2007). All these materials emit blue light upon UV excitation; the strongest emission was observed for the $\text{La}_3\text{Si}_8\text{O}_4\text{N}_{11}$ host, which showed also the highest doping level (20 at%) at which concentration quenching occurred.

In a similar way the position of the $5d$ excitation band of Tb^{3+} incorporated in these host lattices can be shifted (van Krevel, 2000). For $\text{Y}_4\text{Si}_2\text{O}_7\text{N}_2\text{:}10\%\text{Tb}$ the excitation maximum at 255–265 nm is overlapping with the absorption edge of the host lattice, resulting in both a high absorption (90%) and quantum efficiency (85%) for 254 nm excitation (van Krevel, 2000). In this way the necessity of sensitization of the Tb emission in commercial phosphors by co-doping with Ce (Blasse and Grabmaier, 1994) can be avoided.

Rare-Earth-Doped Sialon Materials

α -Sialon (for α -Si–AlON) materials originate from α - Si_3N_4 in which Si has been replaced by Al, N has been replaced by O, and for charge compensation a metal M is added, resulting in the general composition $\text{M}_{m/\text{val}}\text{Si}_{12-(m+n)}\text{Al}_{(m+n)}\text{O}_n\text{N}_{16-n}$ ($\text{M} = \text{Li}, \text{Ca}, \text{rare earth}$). These materials are well known because of their high durability under chemical, thermal, and mechanical attack. Based on the criterion of bond directness, these matrices are considered to be promising for rare-earth activation (Grekov and Chernovets, 1998).

Doping the α -Sialon matrix with Tb^{3+} gives the characteristic green $^5\text{D}_4 \rightarrow ^7\text{F}_5$ emission ~ 545 nm (Xie *et al.*, 2002; van Krevel *et al.*, 2002), but with low quantum efficiency for 254 nm excitation (van Krevel *et al.*, 2002). This is probably due to overlap of the $5d$ Tb^{3+} excitation band with the α -Sialon host-lattice conduction band resulting in radiationless transitions by photo-ionization processes (van Krevel *et al.*, 2002).

Pr^{3+} -doped α -Sialon shows red luminescence due to $4f \rightarrow 4f$ transitions from the $^3\text{P}_0$ and $^1\text{D}_2$ emitting levels (Xie *et al.*, 2002). The emission band of Ce^{3+} in the α -Sialon matrix is at quite a high wavelength (≈ 495 nm) (Grekov *et al.*, 1999), 515–540 nm (van Krevel *et al.*, 2002). The exact position of the $5d \rightarrow 4f$ emission band depends on the excitation wavelength, indicating that some variation exists in local Ce coordination (van Krevel *et al.*, 2002).

For Eu^{2+} doping a similar $5d \rightarrow 4f$ band emission was observed in the range 550–590 nm (Xie *et al.*, 2002; van Krevel *et al.*, 2002). The emission peak shifts to a longer wavelength with increasing amounts of europium (Xie *et al.*, 2002). Despite systematic changes in chemical composition of the host lattice (i.e., m and n), the emission is not strongly influenced. This indicates that the Eu^{2+} ion dominates its local coordination, induced by the difference in size and the available space in the interstitial site (van Krevel *et al.*, 2002). The Eu-doped α -Sialon samples are yellow-green colored (Xie *et al.*, 2002; van Krevel *et al.*, 2002), and therefore can be efficiently excited by visible radiation in the range 400–450 nm.

Recently, long wavelength band emission was also reported for rare-earth ions in Sialon glasses (up to 500 nm for Ce^{3+} (de Graaf *et al.*, 2003a), and as long as 640 nm for Eu^{2+} (de Graaf *et al.*, 2003b)).

Pr^{3+} -doped β -Sialon of composition $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}\text{:Pr}_x$ ($z = 0\text{--}2.0$, $x = 0.016$) showed red luminescence in the range 600–650 nm upon excitation with 460 nm blue light, indicating that the phosphor can be excited by blue LEDs (Liu *et al.*, 2011). The luminescence spectra showed that the integrated red emission from 600 to 650 nm increased with temperature between 298 and 473 K. This unexpected phenomenon is proposed to be the result of the coupling of the $^1\text{D}_2$ and $^3\text{P}_0$ excited states of the $4f^2$ configuration.

The luminescence of Eu^{2+} in two oxonitridoaluminosilicates (Sialons), namely $\text{SrSi}_5\text{AlO}_2\text{N}_7$ and $\text{SrSiAl}_2\text{O}_3\text{N}_2$, was investigated (Xie *et al.*, 2005). The samples were synthesized by high temperature sintering under N_2 atmosphere. A single broad band in the blue-green region was observed upon UV excitation for both $\text{SrSi}_5\text{AlO}_2\text{N}_7\text{:Eu}^{2+}$ and $\text{SrSiAl}_2\text{O}_3\text{N}_2\text{:Eu}^{2+}$ at room temperature.

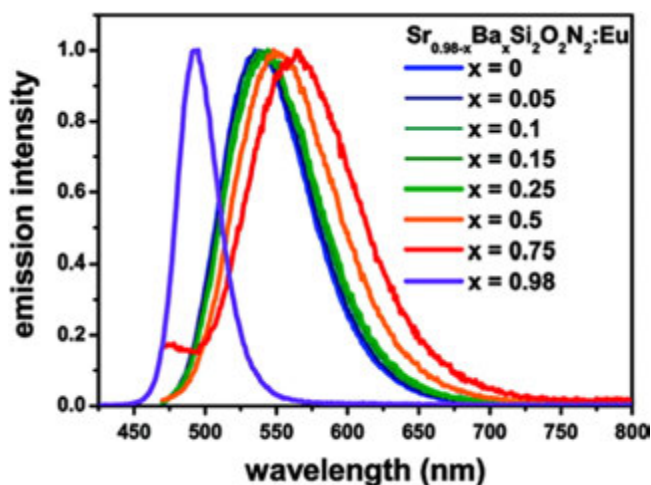


Fig. 1 Normalized emission spectra for $\text{Sr}_{0.98-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:2\%\text{Eu}$ ($x = 0 - 0.98$) at RT ($\lambda_{\text{ex}} = 450$ nm). Reprinted with permission from Bachmann, V., Ronda, C., Oeckler, O., Schnick, W., Meijerink, A., 2009. Color point tuning for $(\text{Sr,Ca,Ba})\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ for white light LEDs. Chemistry of Materials 21, 316–325, Copyright 2009, American Chemical Society.

The short-wavelength emission were attributed to the weak crystal-field strength as a result of long distances between the dopant ion and the ligand anions. The effect of the Eu^{2+} concentration on the emission intensity was discussed and the CIE chromaticity coordinates of both samples were presented.

An important step forward on a related composition was made recently through a cooperation between the University of Innsbruck and OSRAM GmbH (Hoerder *et al.*, 2019). The phosphor $\text{Sr}[\text{Li}_2\text{Al}_2\text{O}_2\text{N}_2]:\text{Eu}^{2+}$ was developed, which is an almost ideal material for pcLEDs, in terms of optimal spectral position for a red phosphor, exceptionally small spectral full width at half maximum and excellent thermal stability.

Eu-Doped Alkaline-Earth Silicon Nitrides and Oxynitrides

Deep-red band emission was discovered by van Krevel (2000) for Eu^{2+} incorporated in alkaline-earth silicon nitrides, such as $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$; $\lambda_{\text{em}} = 620\text{--}640$ nm) and $\text{BaSi}_7\text{N}_{10}:\text{Eu}$ ($\lambda_{\text{em}} \approx 660$ nm). Emission above 600 nm is very uncommon for Eu^{2+} (Blasse and Grabmaier, 1994), and this is a consequence of the large nephelauxetic effect and large crystal field splitting caused by nitrogen. Due to a concomitant shift of the $4f \rightarrow 5d$ absorption band into the visible region, these compounds are strongly orange-red colored. Moreover, these materials are capable of efficiently converting the absorbed 400–450 nm radiation into red light. Because of the high application potential for light emitting diode (LED) lighting when combined with UV-blue emitting LEDs, in 1999 a patent was filed on such materials (Hintzen *et al.*, 2001). In the meantime, also the thermoluminescence behavior of $\text{Ba}_2\text{Si}_5\text{N}_8:\text{Eu}$ was reported by Höpfe *et al.* (2000).

For Eu doped in host lattices with a higher M/Si ratio (i.e., lower degree of cross-linking between SiN_4 tetrahedra), the emission is at lower wavelengths, i.e., blue-green emission at ~ 515 nm for $\text{MgSiN}_2:\text{Eu}$ (Gaido *et al.*, 1974) and red emission at ~ 620 nm for $\text{CaSiN}_2:\text{Eu}$ (Lee *et al.*, 1997). For MgSiN_2 also the luminescence of the rare-earth ions Sm and Yb was studied (Dubrovskii *et al.*, 1981). While generally excitation takes place with electromagnetic radiation, for $\text{MgSiN}_2:\text{Eu}$ also data have been published for cathode-ray excitation (Bondar *et al.*, 2001) and for $\text{CaSiN}_2:\text{Eu}$ also electroluminescence was reported (Lee *et al.*, 1997).

Large amount of oxygen results in silicon-oxynitrides, in which deep red Eu^{2+} emission at 650 nm was reported for $\text{LaEu-Si}_2\text{N}_3\text{O}_2$, while green band emission at 549 nm was found for $\text{La}_{0.9}\text{Eu}_{0.1}\text{Si}_3\text{N}_{5-x}\text{O}_x$ (Uheda *et al.*, 2000). The amount of oxygen can be further increased by replacement of $(\text{SiN})^+ \rightarrow (\text{AlO})^+$ and/or $(\text{LaN})^\circ \rightarrow (\text{MO})^\circ$ ($\text{M} = \text{alkaline earth}$), resulting in, for example, $\text{SrSiAl}_2\text{O}_3\text{N}_2$ for which blue-green Eu^{2+} emission and blue Ce^{3+} emission were reported at about 487 nm and 466 nm, respectively (Fiedler *et al.*, 2002).

The color tuning of the efficient LED phosphor $\text{Sr}_{1-x-y-z}\text{Ca}_x\text{Ba}_y\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}_z^{2+}$ ($0 \leq x, y \leq 1$; $0.005 \leq z \leq 0.16$) was investigated (Bachmann *et al.*, 2009). Tuning of the emission color was achieved by changing the Eu^{2+} concentration or by substitution of the host lattice cation Sr^{2+} by Ca^{2+} or Ba^{2+} (Fig. 1). Luminescence data show that the quenching temperature decreases with substitution of Sr by Ca, whilst for Ba substitution the quenching temperature remains high. Color tuning by partial substitution of Sr^{2+} by Ba^{2+} is the best way to optimize the color point of the phosphor while retaining high quantum yield and high quenching temperature.

The $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ nitride phosphor was prepared by the carbothermal reduction and nitridation method and characterized by X-ray diffraction (Piao *et al.*, 2006). Two absorption bands were observed with maxima at about 330 and 420 nm, so that the phosphor can be effectively excited by InGaN LEDs. The emission peak position of $(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Si}_5\text{N}_8$ materials was observed to shift

from 618 to 690 nm with increasing dopant ion concentration. The redshift behavior of the emission band was discussed making reference to the configuration coordinate model. Related results were simultaneously obtained in a separate study on the broader system of Eu^{2+} -doped $\text{M}_2\text{Si}_5\text{N}_8$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) (Li *et al.*, 2006). The materials with $\text{M} = \text{Ca}, \text{Sr}$ showed typical broad band emission in the orange to red spectral range, depending on M and the Eu^{2+} concentration. $\text{Ba}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ showed emission maxima shifting from 580 to 680 nm with increasing Eu^{2+} content. The long-wavelength excitation and emission was attributed to the effect of covalency and a strong crystal-field on the $5d \rightarrow 4f$ band of Eu^{2+} in the nitride coordination sphere. The conversion efficiency increases moving from Ca to Ba and Sr upon excitation at 465 nm. In particular, $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$, with a high quantum efficiency (75%–80%) and a minimal thermal quenching at 150°C, was found to be a valuable red-emitting phosphor for white-LED applications. The influence of the replacement of Sr by Ca on the structural and luminescence properties of Eu^{2+} -doped $\text{Sr}_2\text{Si}_5\text{N}_8$ was studied in detail from the crystallographic and spectroscopic point of view (Li *et al.*, 2008). The maximum of the emission band of the dopant can be shifted by partial introduction of Ca in $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$, resulting in red emission moving from 620 to 643 nm.

The orange-red emitting phosphors based on $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ ($\text{M} = \text{Sr}, \text{Ba}$) have shown to have the potential to be widely utilized in white LEDs due to their enhancement of the color rendering index, giving rise to warm white light emission. For this reason, the thermal degradation in air was investigated for a series of $\text{M}_{2-x}\text{Si}_5\text{N}_8:\text{Eu}_x$ ($\text{M} = \text{Sr}, \text{Ba}$) phosphors prepared by solid-state reaction. (Yeh *et al.*, 2012). Degradation was only observed in $\text{Sr}_{2-x}\text{Si}_5\text{N}_8:\text{Eu}_x$ with $x = 0.10$, but it did not occur in $\text{Sr}_{2-x}\text{Si}_5\text{N}_8:\text{Eu}_x$ with $x = 0.02$ and the Ba analog with $x = 0.10$. The thermal degradation in $\text{Sr}_{2-x}\text{Si}_5\text{N}_8:\text{Eu}_x$ with $x = 0.10$ is attributed to the formation of an amorphous layer on the surface of the phosphor grains during the heat treatment in oxidizing atmosphere, accompanied by the oxidation of Eu^{2+} ions to Eu^{3+} .

The Eu^{2+} -doped phosphors $\text{Ca}_{1-x}\text{Eu}_x\text{AlSiN}_3$ ($x = 0\text{--}0.2$) were prepared by self-propagating high-temperature synthesis (Piao *et al.*, 2007). A strong absorption band at 460 nm was observed in the excitation spectra, which is suitable for the blue light emitted by InGaN/GaN LEDs. The optimized sample $\text{Ca}_{0.98}\text{Eu}_{0.02}\text{AlSiN}_3$ gave rise to red emission peaking at 649 nm. The CIE coordinates (0.647, 0.347) with high color saturation indicated that this is a promising candidate as a red emitting phosphor for InGaN/GaN-based white LEDs for general illumination or displays.

The new phosphor $\text{SrAlSi}_4\text{N}_7:\text{Eu}^{2+}$ was synthesized at high temperature in a radio-frequency furnace (Hecht *et al.*, 2009). The crystal structure of the host compound $\text{SrAlSi}_4\text{N}_7$ was determined using X-ray diffraction data. The Eu^{2+} -doped compound shows a typical broadband emission in the orange-red spectral region ($\lambda_{\text{max}} \approx 632$ nm for 2% Eu doping level, 450 nm excitation). The luminescence behavior makes the phosphor an attractive candidate material as red component in warm white light LEDs with high color rendering index.

The compounds $\text{M}[\text{Mg}_3\text{SiN}_4]$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Eu}$) were prepared by solid-state reaction (Schmiechen *et al.*, 2014). They are isotypic and crystallize in the tetragonal space group $I4_1/a$, as shown by single-crystal X-ray diffraction. $\text{Sr}[\text{Mg}_3\text{SiN}_4]:\text{Eu}^{2+}$ is characterized by red luminescence ($\lambda_{\text{max}} = 615$ nm) with one of the narrowest red emission reported in the literature so far for Eu^{2+} -phosphors (~ 43 nm). On the basis of this outstanding narrow red emission, $\text{Sr}[\text{Mg}_3\text{SiN}_4]:\text{Eu}^{2+}$ may point the way to a next generation of red phosphor materials for application in illumination-grade white pc-LEDs.

Eu-Doped Aluminum-Oxynitrides With β -Alumina and Other Structures

The previously mentioned replacement $(\text{SiN})^+ \rightarrow (\text{AlO})^+$ can be used in the reversed direction for the design of oxynitrides starting from aluminates. Another way to obtain oxynitrides from M-aluminates is to replace (M^{n+}O) by $(\text{M}^{(n+1)+}\text{N})$. Examples are given by $\text{LaAl}_{12}\text{O}_{18}\text{N}$ with the magnetoplumbite structure (Wang *et al.*, 1988) (derived from $\text{SrAl}_{12}\text{O}_{19}$ by replacement of $(\text{SrO})^\circ$ by $(\text{LaN})^\circ$) and $\text{BaAl}_{11}\text{O}_{16}\text{N}$ with the β -alumina structure (Jansen *et al.*, 1997) (derived from $\text{NaAl}_{11}\text{O}_{17}$ by replacement of $(\text{NaO})^+$ by $(\text{BaN})^+$). Doping this last host lattice with Eu^{2+} gives a blue-emitting phosphor enabling combination of a higher color rendering index with a high lumen output of a tricolor lamp (Jansen *et al.*, 1999) as compared to the commercial $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ blue-emitting phosphor (which host lattice can be derived from $\text{NaAl}_{11}\text{O}_{17}$ by replacement of $(\text{NaAl})^{4+}$ by $(\text{BaMg})^{4+}$). Moreover, the presence of N^{3-} ions prevents the conversion of Eu^{2+} into Eu^{3+} , which is reported to be the main cause for the degradation of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ (Oshio *et al.*, 1998).

A number of additional new oxynitride and nitride phosphors have been recently developed by the $(\text{SiN})^+ \rightarrow (\text{AlO})^+$ or other replacements, also starting from basic structures different from the one of β -alumina (Yin *et al.*, 2014; Xia *et al.*, 2016; Cui *et al.*, 2017; Fang *et al.*, 2019). In many cases, these replacements (also referred to as chemical unit co-substitutions (Hoel *et al.*, 2010)) have led to improvements in the phosphor performance, such as better thermal stability of the emission intensity. In general, chemical unit co-substitution has become an emerging and valuable design strategy for the evolution of novel phosphors from existing ones.

Outlook

Since 1996, numerous materials belonging to the nitride and oxynitride families have proved to be excellent hosts for the development of efficient phosphors for white pcLEDs, emitting all over the visible range. In particular, phosphors emitting in the blue, green and red regions have been developed, employing various dopant rare earth ions, such as Ce^{3+} , Eu^{2+} , Tb^{3+} and Pr^{3+} , and using both allowed $5d \rightarrow 4f$ and forbidden $4f \rightarrow 4f$ transitions. However, the most important application of these doped materials is

in the field of Eu^{2+} -doped phosphors emitting in the red through $5d \rightarrow 4f$ transitions, usefully exploiting the strong crystal field splitting of the $5d$ orbitals and large covalency induced by the nitride ion N^{3-} , compared to simple oxide hosts. As an example, the recently developed $\text{Sr}[\text{Li}_2\text{Al}_2\text{O}_2\text{N}_2]:\text{Eu}^{2+}$ phosphor (Hoerder *et al.*, 2019) is an almost ideal material for pcLEDs. However, in the last years, competing red phosphors have been proposed and applied, especially fluoride host materials containing the $3d^3$ ion Mn^{4+} in octahedral coordination. In this hosts, the dopant ion is able to emit sharp bands in the useful red region around 632 nm in fluoride hosts, due to the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition (Zhou *et al.*, 2018), upon excitation in the violet or blue regions. Moreover, halogen-based nanocrystalline lead perovskite materials have become additional candidates for the production of the red component in warm white light pcLEDs. A very significant review of the chemical and optical properties of the three prominent classes of red emitting materials $[\text{A}_2\text{MF}_6:\text{Mn}^{4+}]$ ($\text{A} = \text{K}, \text{Na}, \text{and Cs}$; $\text{M} = \text{Si}, \text{Ge}, \text{Zr}, \text{Sn}, \text{and Ti}$) and $\text{XSiF}_6:\text{Mn}^{4+}$ ($\text{X} = \text{Ba or Zn}$), the nitridoaluminate phosphor ($\text{Sr}[\text{LiAl}_3\text{N}_4]:\text{Eu}^{2+}$), and nanocrystals of cesium lead iodide perovskite (CsPbI_3) has been published a few years ago (Lin *et al.*, 2016). The race is still on for the development of the perfect phosphors for LEDs, and nitride and oxynitride materials will certainly play a very important role.

References

- Bachmann, V., Ronda, C., Oeckler, O., Schnick, W., Meijerink, A., 2009. Color point tuning for $(\text{Sr,Ca,Ba})\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ for white light LEDs. *Chemistry of Materials* 21, 316–325.
- Blasse, G., Grabmaier, B.C., 1994. *Luminescent Materials*. Berlin: Springer.
- Bondar, V., Axelrud, L., Davydov, V., Felner, T., 2001. Synthesis, structure and luminescence of $\text{A}_2\text{B}_4\text{C}_5$ nitrides. *Materials Research Society Symposium Proceedings* 639.
- Cui, D., Song, Z., Xia, Z., Liu, Q., 2017. Luminescence tuning, thermal quenching, and electronic structure of narrow-band red-emitting nitride phosphors. *Inorganic Chemistry* 56, 11837–11844.
- de Graaf, D., Hintzen, H.T., de With, G., 2003a. The influence of the composition on the luminescence of $\text{Ce(III)-Ln-Si-Al-O-N}$ glasses ($\text{Ln} = \text{Sc}, \text{Y}, \text{La}, \text{Gd}$). *Journal of Luminescence* 104, 131–136.
- de Graaf, D., Hintzen, H.T., Hampshire, S., de With, G., 2003b. Long wavelength Eu^{2+} emission in Eu -doped Y-Si-Al-O-N glasses. *Journal of the European Ceramic Society* 23, 1093–1097.
- Dierre, B., Xie, R.-J., Hirotsaki, N., Sekiguchi, T., 2007. Blue emission of Ce^{3+} in lanthanide siliconoxynitride phosphors. *Journal of Materials Research* 22, 1933–1941.
- Dubrovskii, G.P., Zykov, A.M., Chernovets, B.V., 1981. Luminescence of rare-earth activated MgSiN_2 . *Izvestiya Akademii Nauk SSSR Inorganic Materials* 17, 1421–1425.
- Fang, M.-H., Mahlik, S., Lazarowska, A., *et al.*, 2019. Structural evolution and effect of the neighbouring cation on the photoluminescence of $\text{Sr}(\text{LiAl}_3)_{1-x}(\text{SiMg}_3)_x\text{N}_4:\text{Eu}^{2+}$ Phosphors. *Angewandte Chemie - International Edition* 58, 7767–7772.
- Fiedler, T., Jermann, F., Ellens, A., Zachau, M., 2002. Novel nitride-based phosphors for LED applications. In: *Proceedings of the 1st ECS Meeting*, Philadelphia, PA, USA, abstract 1191.
- Gaido, G.K., Dubrovskii, G.P., Zykov, A.M., 1974. Photoluminescence of MgSiN_2 activated by europium. *Izvestiya Akademii Nauk SSSR Inorganic Materials* 10, 564–566.
- Grekov, F.F., Chernovets, B.V., 1998. Criteria for selection of matrices for luminophors activated with lanthanides. *Russian Journal of Applied Chemistry* 71, 194–197.
- Grekov, F.F., Feopyentov, A.V., Chernovets, B.V., Chernysheva, T.E., 1999. Effect of a complex of coactivators on photo-luminescence in silicon nitride. *Russian Journal of Applied Chemistry* 72, 931–936.
- Hecht, C., Stadler, F., Schmidt, P.J., *et al.*, 2009. $\text{SrAlSi}_4\text{N}_7:\text{Eu}^{2+}$ - A nitridoalumosilicate phosphor for warm white light (pc)LEDs with edge-sharing tetrahedra. *Chemistry of Materials* 21, 1595–1601.
- Hintzen, H.T., van Krevel, J.W.H., Botty, G.F.M., 2001. Red-Emitting Luminescent Materials European Patent Application no. EP 1104799 A1.
- Hoel, C.A., Gallardo Amores, J.M., Morán, E., *et al.*, 2010. High-pressure synthesis and local structure of corundum-type $\text{In}_{2-2x}\text{Zn}_x\text{Sn}_x\text{O}_3$ ($x \leq 0.7$). *Journal of the American Chemical Society* 132, 16479–16487.
- Hoerder, G.J., Seibald, M., Baumann, D., *et al.*, 2019. $\text{Sr}[\text{Li}_2\text{Al}_2\text{O}_2\text{N}_2]:\text{Eu}^{2+}$ - A high-performance red phosphor to brighten the future. *Nature Communications* 10, 1824.
- Höppe, H.A., Lutz, H., Morys, P., Schnick, W., Seilmeier, A., 2000. Luminescence in Eu^{2+} -doped $\text{Ba}_2\text{Si}_5\text{N}_8$: Fluorescence, thermoluminescence, and upconversion. *Journal of Physics and Chemistry of Solids* 61, 2001–2006.
- Jansen, S.R., Hintzen, H.T., Metselaar, R., 1997. Phase relations in the $\text{BaO-Al}_2\text{O}_3\text{-AlN}$ system: Materials with the β -alumina structure. *Journal of Solid State Chemistry* 129, 66–73.
- Jansen, S.R., Migchels, J., Hintzen, H.T., Metselaar, R., 1999. Eu -doped barium aluminium oxynitride with the β -alumina-type structure as a new blue-emitting phosphor. *Journal of the Electrochemical Society* 146, 800–806.
- Lee, S.S., Lim, S., Sun, S.S., Wager, J.F., 1997. Photoluminescence and electroluminescence characteristics of $\text{CaSiN}_2:\text{Eu}$ phosphor. In: Hariz, A. (ed.), In: *Proceedings of the Smart Materials, Structures, and Integrated Systems*, vol. 3241, pp. 75–83. Adelaide: SPIE.
- Li, Y.Q., van Steen, J.E.J., van Krevel, J.W.H., *et al.*, 2006. Luminescence properties of red-emitting $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) LED conversion phosphors. *Journal of Alloys and Compounds* 417, 273–279.
- Li, Y.Q., de With, G., Hintzen, H.T., 2008. The effect of replacement of Sr by Ca on the structural and luminescence properties of the red-emitting $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ LED conversion phosphor. *Journal of Solid State Chemistry* 181, 515–524.
- Lin, C.C., Meijerink, A., Liu, R.-S., 2016. Critical red components for next-generation white LEDs. *Journal of Physical Chemistry Letters* 7, 495–503.
- Liu, T.-C., Cheng, B.-M., Hu, S.-F., Liu, R.-S., 2011. Highly stable red oxynitride $\beta\text{-SiAlON}:\text{Pr}^{3+}$ phosphor for light-emitting diodes. *Chemistry of Materials* 23, 3698–3705.
- Oshio, S., Matsuoka, T., Tanaka, S., Kobayashi, H., 1998. Mechanism of luminescence decrease in $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor by oxidation. *Journal of the Electrochemical Society* 145, 3903–3907.
- Piao, X., Machida, K.-I., Horikawa, T., *et al.*, 2007. Preparation of $\text{CaAlSiN}_3:\text{Eu}^{2+}$ phosphors by the self-propagating high-temperature synthesis and their luminescent properties. In: *Chemistry of Materials*, 19. pp. 4592–4599.
- Piao, X., Horikawa, T., Hanzawa, H., Machida, K.-I., 2006. Characterization and luminescence properties of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphor for white light-emitting-diode illumination. *Applied Physics Letters* 88. (art. no. 161908).
- Schmiechen, S., Schneider, H., Wagatha, P., *et al.*, 2014. Toward new phosphors for application in illumination-grade white pc-LEDs: the nitridomagnesiumsilicates $\text{Ca}[\text{Mg}_3\text{SiN}_4]:\text{Ce}^{3+}$, $\text{Sr}[\text{Mg}_3\text{SiN}_4]:\text{Eu}^{2+}$, and $\text{Eu}[\text{Mg}_3\text{SiN}_4]$. In: *Chemistry of Materials*, 26. pp. 2712–2719.
- Uehda, K., Takizawa, H., Endo, T., *et al.*, 2000. Synthesis and luminescent property of Eu^{3+} -doped LaSi_3N_5 phosphor. *Journal of Luminescence* 87–89, 967–969.
- van Krevel, J.W.H., 2000. On New Rare-Earth Doped M-Si-Al-O-N Materials: Luminescence Properties and Oxidation Resistance (Ph.D. thesis). Eindhoven University of Technology.
- van Krevel, J.W.H., Hintzen, H.T., Metselaar, R., 2000. On the Ce^{3+} luminescence in the melilite type oxynitride compound $\text{Y}_2\text{Si}_3\text{-xAl}_x\text{O}_3\text{-xN}_{4-x}$. *Materials Research Bulletin* 35, 747–754.

- van Krevel, J.W.H., Hintzen, H.T., Metselaar, R., Meijerink, A., 1998. Long-wavelength Ce^{3+} emission in Y–Si–O–N materials. *Journal of Alloys and Compounds* 268, 272–277.
- van Krevel, J.W.H., van Ruiten, J.W.T., Hintzen, H.T., Metselaar, R., Mandal, H., 2002. Luminescence properties of terbium-, cerium-, or europium-doped α -Sialon materials. *Journal of Solid State Chemistry* 165, 19–24.
- Wang, X.H., Lejus, A.M., Vivien, D., Collongues, R., 1988. Synthesis and characterization of lanthanide aluminum oxynitrides with magnetoplumbite-like structure. *Materials Research Bulletin* 23, 43–49.
- Xia, Z., Miao, S., Molokeev, M.S., Chen, M., Liu, Q., 2016. Structure and luminescence properties of Eu^{2+} doped $\text{Lu}_x\text{Sr}_{2-x}\text{SiN}_x\text{O}_{4-x}$ phosphors evolved from chemical unit co-substitution. *Journal of Materials Chemistry C* 4, 1336–1344.
- Xie, R.-J., Mitomo, M., Uheda, K., Xu, F.F., Akimune, Y., 2002. Preparation and luminescence spectra of calcium- and rare-earth ($\text{R} = \text{Eu}$, Tb, and Pr)-co-doped α -Sialon ceramics. *Journal of the American Ceramic Society* 85, 1229–1234.
- Xie, R.-J., Hirosaki, N., Yamamoto, Y., *et al.*, 2005. Fluorescence of Eu^{2+} in strontium oxonitridoaluminosilicates (SiAlONS). *Journal of the Ceramic Society of Japan* 113, 462–465.
- Yeh, C.-W., Chen, W.-T., Liu, R.-S., *et al.*, 2012. Origin of thermal degradation of $\text{Sr}_{2-x}\text{Si}_5\text{N}_8\text{:Eu}_x$ phosphors in air for light-emitting diodes. *Journal of the American Chemical Society* 134, 14108–14117.
- Yin, L.-J., Chen, G.-Z., Wang, C., *et al.*, 2014. Tunable luminescence of $\text{CeAl}_{11}\text{O}_{18}$ based phosphors by replacement of $(\text{AlO})^+$ by $(\text{SiN})^+$ and co-doping with Eu. *ECS Journal of Solid State Science and Technology* 3, R131–R138.
- Zhou, Q., Dolgov, L., Srivastava, A.M., *et al.*, 2018. Mn^{2+} and Mn^{4+} red phosphors: Synthesis, luminescence and applications in WLEDs. A review. *Journal of Materials Chemistry C* 6, 2652–2671.

Further Reading

- Chen, W.-T., Sheu, H.-S., Liu, R.-S., Attfield, J.P., 2012. Cation-size-mismatch tuning of photoluminescence in oxynitride phosphors. *Journal of the American Chemical Society* 134, 8022–8025.
- George, N.C., Denault, K.A., Seshadri, R., 2013. Phosphors for solid-state white lighting. *Annual Review of Materials Research* 43, 481–501.
- Lin, Y.-C., Karlsson, M., Bettinelli, M., 2016. Inorganic phosphor materials for lighting. *Topics in Current Chemistry* 374, [art. no. 21].
- Wang, L., Xie, R.-J., Suehiro, T., Takeda, T., Hirosaki, N., 2018. Down-conversion nitride materials for solid state lighting: Recent advances and perspectives. *Chemical Reviews* 118, 1951–2009.
- Xia, Z., Liu, Q., 2016. Progress in discovery and structural design of color conversion phosphors for LEDs. *Progress in Materials Science* 84, 59–117.
- Xia, Z., Xu, Z., Chen, M., Liu, Q., 2016. Recent developments in the new inorganic solid-state LED phosphors. *Dalton Transactions* 45, 11214–11232.
- Xie, R.-J., Hirosaki, N., 2007. Silicon-based oxynitride and nitride phosphors for white LEDs-A review. *Science and Technology of Advanced Materials* 8, 588–600.
- Xie, R.-J., Hirosaki, N., Li, Y., Takeda, T., 2010. Rare-earth activated nitride phosphors: Synthesis, luminescence and applications. *Materials* 3, 3777–3793.
- Xie, R.-J., Hintzen, H.T., 2013. Optical properties of (oxy)nitride materials: A review. *Journal of the American Ceramic Society* 96, 665–687.
- Ye, S., Xiao, F., Pan, Y.X., Ma, Y.Y., Zhang, Q.Y., 2010. Phosphors in phosphor-converted white light-emitting diodes: Recent advances in materials, techniques and properties. *Materials Science and Engineering R: Reports* 71 (1), 1–34.

Phosphors: VUV Excitation

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Introduction

The luminescent materials known as phosphors convert energy into electromagnetic radiation, usually in the visible energy range. As far as vacuum ultraviolet (VUV) optical excitations are concerned, the most suitable materials are the large band gap inorganic lattices activated by rare earth ions. These phosphors are mainly sintered oxo (phosphates, borates, aluminates, etc.), oxofluoride, or fluoride compounds. VUV optical excitations in these systems, ranging between soft X-rays and conventional UV, result either in a direct excitation of the luminescence center or an excitation of the host lattice, which will transfer part of the energy to the emitting levels of the activator.

The development of industrial applications in lighting and flat color display screens based on a xenon plasma discharge, which generates VUV radiation within an energy range of approximately 8.5 to 7 eV (145 and 180 nm), has induced a revival of interest in VUV-excited phosphors and in VUV spectroscopy using synchrotron radiation facilities. Both applications need very efficient and stable phosphors under ionizing conditions. In addition, mercury-free fluorescent lamps require, phosphors with a quantum yield higher than 1 (quantum cutters) in order to approach the energy efficiency of mercury excitation. There are some drawbacks in commercially available phosphors to be used in Hg-free lamps, which include low efficiency, easy degradation under VUV excitation, imperfect color coordinates, etc. Therefore, new phosphors that can efficiently convert VUV light into blue, green and red lights would be of great interest to the field. Besides applications in lighting and flat color display, VUV phosphors are also very suitable for scintillators. VUV scintillator has wide range of applications in medical imaging, nuclear physics, security scanning and astronomy. Some applications require very fast scintillation response which triggered the search for new materials in this area.

Excitations in the Rare Earth Center

Direct optical excitations of rare earth ions in the solid state occur via transitions between quasi-atomic states resulting from degeneracy removal of $^{2S+1}L_J$ free-ion levels by a spherical crystal field perturbation. In the $4f^n$ ground state configuration, transitions between crystal field levels are forbidden by the parity conservation rule and only small admixtures of wave functions of opposite parity into the $4f^n$ wave functions can induce f–f electric dipole transitions. Therefore, the 4f–4f intra-configuration transitions are forced electric dipole transitions, and consequently will appear in absorption and emission spectra as weak (the intensity is directly related to the degree of mixing) and very sharp bands. These two characteristics are in contrast to a strong absorption spread over a broad energy domain as required for efficient phosphors but, in compensation, the forced transitions between crystal field levels within the open f-shell give rise to relatively spectrally pure luminescence, the duration of which is convenient for phosphor applications in display devices. Therefore, rare earth ions are appropriate activators for such applications.

Trivalent rare earth compounds can also provide strong absorptions when energetic photons induce electron promotions from the $4f^n$ ground state toward d-states belonging to the first excited configuration, $4f^{n-1}5d$. Electric dipole transitions which occur between two configurations of opposite parity are Laporte allowed at first order. In general, they give rise to very intense absorption bands and, due to the greater radial extension of the d-orbitals, these bands are widely vibronic in character and very sensitive to crystal field interaction. The magnitude of the crystal field splitting of the fivefold orbitally degenerated 5d levels, and their coupling with the remaining $4f^{n-1}$ states, are therefore important factors to consider in phosphor modeling.

In rare earth phosphors, when UV or VUV radiations populate optically a 5d-state, radiative and/or nonradiative channels are available for energy relaxation in the solid state. Energy transfer to the emitting 4f-level occurs through lattice phonon relaxation and intra-system energy crossing when the energies match. The efficiency of the latter process depends upon the magnitude of the square overlap integrals between absorption and emission. Following the well-known configuration coordinate model, coordinate displacement between the equilibrium positions of the ground and 5d excited states, called the Franck–Condon shift, can be adjusted in phosphor design by choosing suitable host anionic groupings in order to fix the emission frequency or to increase the phosphor efficiency.

It is worthwhile considering that the variation of the energy of the lowest 4f–5d level versus the number of f-electrons in the shell follows the variation of $3+/4+$ redox potential along the lanthanide series. It is related to the ability of the trivalent rare earth ion to lose one electron and consequently to the stabilization energy of the $4+$ state.

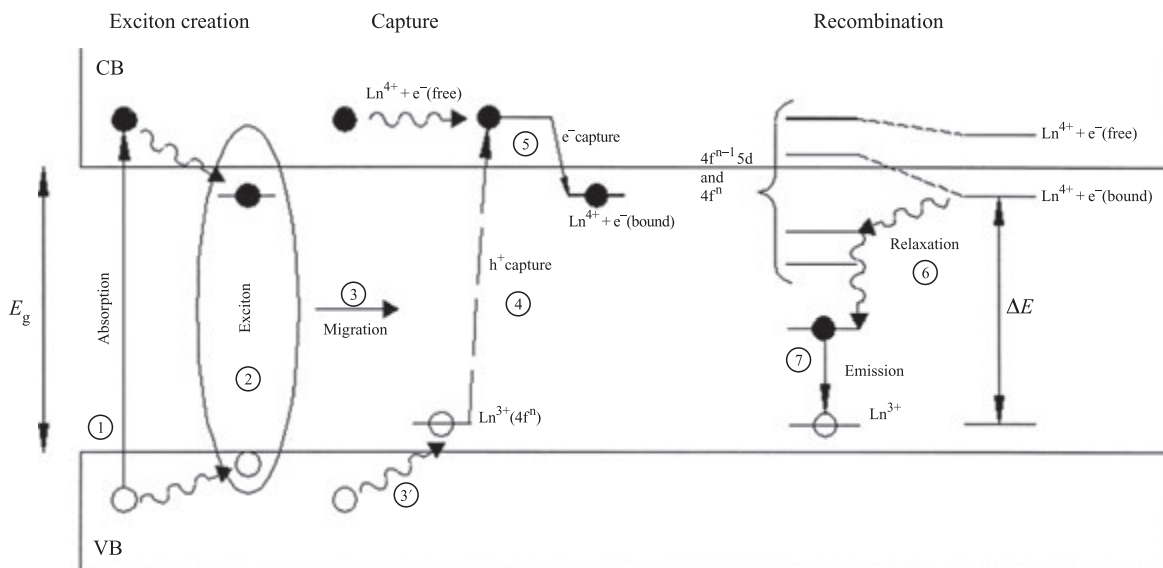


Fig. 1 Energy scheme of exciton and free charge carriers recombination on rare earth impurity involving the autoionization states.

Absorption Involving the Doping Ion and Conduction Band States

In large band gap materials, the energy levels of the impurity center are sparsely distributed between the valence and conduction bands. This is especially true for trivalent rare earth ions with discrete quasiatomic states displayed within the large forbidden band gap of insulators (Fig. 1). In the combined host + rare earth impurity system, the VUV absorption can promote one electron from the ground state of the rare earth ion to excited 5d-states that overlap energetically the conduction band of the host. In the case of a strong coupling between these 5d-states and the continuum of the solid, the electron can be completely delocalized in the conduction band and the autoionization process of the rare earth ion occurs, giving rise to the $(\text{Ln}^{3+} + h^+) + e^-$ (free) state. The capture of the free-electron interpreted in the frame of the model of the exciton trapped on the impurity center as $(\text{Ln}^{3+} + h^+) + e^-$ (bounded) state, results in energy emission that corresponds to the excess of the exciton recombination energy. Part of this energy can be transferred to the 4f emitting level through, for example, dipole–dipole interaction in the case of allowed transitions or higher order multipole interactions for the quasi-forbidden ones.

The propensity of the rare earth ion to give up one electron should be regarded as its hole acceptor capability. It means that these ions embedded in a solid will develop a more or less intense short range potential for hole attraction depending upon the stabilization energy of the $4+$ state. This is the case for Ce^{3+} and Tb^{3+} with one more f-electron than, respectively, the empty and half shell.

Absorption Involving the Doping Ion and Valence Band States

In the VUV energy range, a charge transfer (CT) from the immediate rare earth ion neighbors to the impurity ion states can occur via electron delocalization from states having essentially a ligand character (2p in oxides and fluorides) and forming the valence band to states localized on the rare earth ion. This interaction results in $(\text{Ln}^{3+} + e^-) + h^+$ (free) state formation.

The electron transfer probability, for a given ligand, should be connected to the electron affinity of the rare earth ion, which depends on the degree of filling of the open f-shell. The electron affinity follows the $2 + 1/3 +$ redox potential variation along the lanthanide series according to the stabilization energy variation of the $2+$ state. It is easy to understand that Eu^{3+} with a $4f^6$ configuration will easily gain one electron in order to reach the $4f^7$ more stabilized configuration of the half-series. The same conclusion stands for Yb^{3+} with a $4f^{13}$ configuration.

In addition to the electron affinity of the metallic ion, the energy of the CT process depends strongly on the electronegativity of the ligand. Fluorides, for example, place this transition at the highest energy, much higher than oxides and sulfides and even higher than the 4f–5d transitions. For this reason and thanks to its high electron-affinity, the CT band of Eu^{3+} (Yb^{3+}), embedded in fluoride compounds, can be recorded easily.

The last consideration on the CT band energy position rests on the ligand–metal ion distance. Long distances accounting for ionic bondings provide high energy CT whereas more covalent bondings result in lower energy CT. For the same ligand, the CT energy depends on the coordination number, which determines the ligand–metal ion distance.

The recombination of the free hole with the electron bounded on the rare earth center provides energy that can be transferred to the rare earth radiative level.

When electron acceptors such as Sm^{3+} , Eu^{3+} , Tm^{3+} with a relatively high electron affinity are embedded in solids, they develop a short range potential to attract electrons. They are hole donors and the resulting excited CT state ($\text{Ln}^{2+} + \text{h}^+$) is generally well coupled to the lattice vibrations. Consequently, in the configuration coordinate model, the associated Franck–Condon shift of the CT state is larger than for d-states and of opposite sign. The CT state will relax via the common pathways: resonant or phonon assisted energy transfer, radiative and nonradiative relaxation, following the theoretical developments of Förster and Dexter whenever there is an overlap between emission and absorption.

Host-Sensitized Luminescence

When the energy of the incoming photons becomes higher than the fundamental absorption of the host, which corresponds to the excitonic absorption threshold, the luminescence excitation mechanisms are different. Compared to the direct absorption in the luminescence center, the fundamental or intrinsic absorption is two or three orders stronger in magnitude, and consequently, the quasi totality of the incoming VUV photons are absorbed by the lattice if we neglect the reflectivity. Excitation by a photon with energy greater than the band gap, E_g , results in the creation of a hot hole in the valence band and of a hot electron in the conduction band. Electrons and holes thermalize with a characteristic time of the order of 10^{-12} s and the energy lost for phonons during this step is of the order of 0.5 to $2 E_g$ per electron. Two main excitation mechanisms induced by thermalized electronic excitations are then possible: either radiative or nonradiative energy transfer from excitons or sequential hole and electron captures involving a charge transfer on the impurity center. The same impurity ion can undergo different mechanisms depending upon the electronic structure of the host crystal, the space distribution of secondary electronic excitations and the presence of additional electron and hole traps.

In the VUV phosphor applications, in order to obtain acceptable energy efficiencies, phosphors with quantum yield greater than 1 are highly desirable. Such a process can take place in so-called photon multiplication, in which the VUV photon absorbed by the host lattice can induce two or more visible photons of activator luminescence. This process is based on the effect of electronic excitations (EE) multiplication when the kinetic energy of the fast photoelectron or hole is enough for the creation of one or more other secondary electronic excitations as a result of inelastic scattering on valence or activator electrons. Before transferring their excitation energy to the luminescent centers, EEs also go through thermalization processes such as electron–electron inelastic scattering, electron–phonon interaction and energy migration through the lattice. The number of secondary EEs is determined by the ratio between the photon energy and the average energy necessary to create an EE: $E_{EE} = 1.5\text{--}3 E_g$. For insulators with a wide band gap and a narrow valence band, as is the case in fluorides, the multiplication threshold is close to $2 E_g$. In turn, in oxides where the width of the valence band (E_v) is of the order of the band gap, the multiplication threshold turns out to be $(2 E_g + E_v)$. The total phosphor efficiency depends on the efficiency of the secondary electronic excitation transfer mechanism from the crystalline host to the luminescence center and on the efficiency of the radiative relaxation in this center.

In addition to the materials and device development, understanding the luminescence mechanism is very important. To understand the underlined luminescence mechanism in rare-earth doped VUV phosphors, it is required to clarify the energy levels within the band gap of phosphor. While there may not be any energy level present in the pure host materials, doping with rare-earth elements give new or additional energy levels. Fig. 2 shows the photoluminescence (PL) and PL excitation (PLE) spectra of

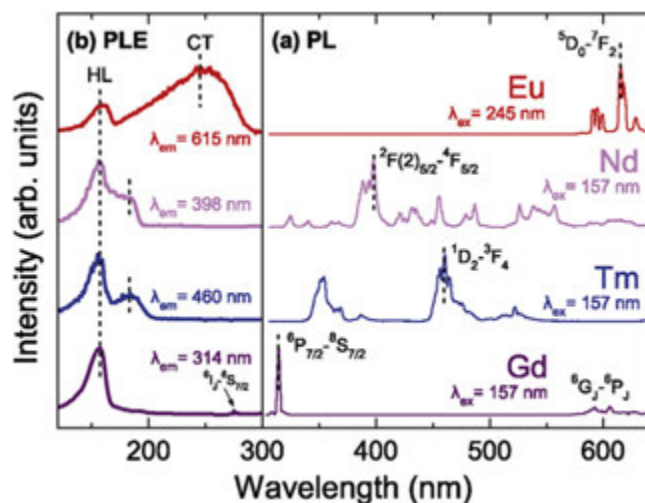


Fig. 2 PL (a) and PLE (b) spectra of Ln^{3+} doped YAlO_3 . λ_{ex} and λ_{em} show excitation wavelength for PL and monitored emission wavelength for PLE, respectively. Marks of dashed lines indicate typical emission and excitation peaks. CT and HL peaks in PLE spectra were attributed to charge transfer transition and host lattice excitation, respectively. Reprinted from Shimizu, Y., Ueda, K., Inaguma, Y., 2017. Photoluminescence excitation spectra of lanthanide doped YAlO_3 in vacuum ultraviolet region. *Optical Materials* 66, 327–331, with permission from Elsevier.

Ln^{3+} (Nd, Eu, Gd, Tm) doped YAlO_3 samples to investigate the emission and excitation related energy level within the band gap of the host lattice. PL spectra shown in Fig. 2(a) were measured under the VUV photoexcitation at 157 nm. These are typically sharp peaks originated from 4f–4f transitions of Ln^{3+} ions. PLE spectra were obtained by monitoring luminescence at 314, 398, 460 and 615 nm in Gd^{3+} -, Nd^{3+} -, Tm^{3+} - and Eu^{3+} -doped samples, respectively. PLE peak at 157 nm (7.9 eV) was observed in all samples regardless of doping element. This peak is due to host lattice (HL) excitation as the band gap energy of host lattice is close to 8 eV. Broad shape peaks in the PLE spectra are assigned to CT peaks. The peak at 277 nm is due to 4f–4f transition.

In phosphor efficiency, there is an additional factor that should be taken into account, in the fundamental absorption region where the absorption coefficient is very high. In this region, the influence of the surface defects inducing surface losses is of prime importance in the luminescence quenching.

Conclusion

VUV phosphor still remains as one of the active research area in solid state luminescent materials due to its robustness and applications into the electronics and medical physics. Besides various applications, VUV phosphors are very good to study luminescence mechanism of rare earth ions in the ultraviolet region. Understanding luminescence mechanism will be helpful to design new phosphors in the emerging area of medical sciences and electronics.

Further Reading

- Bernard, J.E., Berry, D.E., Williams, F., 1983. Introduction to energy transfer and relevant solid-state concepts. In: Di Bartolo, B. (Ed.), *Energy Transfer Processes in Condensed Matter*, vol. 114. New York, NY: Plenum Press, pp. 1–101. NATO ASI Series B: Physics.
- Blasse, G., 1991. Materials science of the luminescence of inorganic solids. In: Di Bartolo, B. (Ed.), *Luminescence of Inorganic Solids*. New York, NY: Plenum, pp. 457–494.
- Blasse, G., Grabmaier, B.C., 1994. *Luminescent Materials*. Berlin: Springer.
- Chen, S., Wang, Y., Zhang, J., *et al.*, 2014. Luminescent properties of novel $\text{K}_3\text{R}(\text{PO}_4)_2\text{:Tb}^{3+}$ (R=Y and Gd) phosphors for displays and lightings. *Journal of Luminescence* 150, 46–49.
- Gérard, I., Krupa, J.C., Simoni, E., Martin, P., 1994. Investigation of charge transfer $\text{O}^{2-}\text{--Ln}^{3+}$ and $\text{F}^-\text{--Ln}^{3+}$ in $\text{LaF}_3\text{:}(\text{Ln}^{3+}, \text{O}^{2-})$ and $\text{YF}_3\text{:}(\text{Ln}^{3+}, \text{O}^{2-})$ systems. *Journal of Alloys and Compounds* 207, 120–127.
- He, J., Zhang, S., Zhou, J., *et al.*, 2015. Luminescence properties of an orange-red phosphor $\text{GdAl}_3(\text{BO}_3)_4\text{:Sm}^{3+}$ under VUV excitation and energy transfer from Gd^{3+} to Sm^{3+} . *Optical Materials* 39, 81–85.
- Hüfner, S., 1978. *Optical Spectra of Transparent Rare Earth Compounds*. New York, NY: Academic Press.
- Jørgensen, C.K., 1962. *Orbitals in Atoms and Molecules*. New York, NY: Academic Press.
- Jørgensen, C.K., 1971. *Modern Aspects of Ligand-Field Theory*. Amsterdam: North-Holland.
- Kaiheriman, M., Sidike, A., Maimaitinasier, A., Rehman, A., 2015. Photoluminescence properties of Tb^{3+} -doped sodalite under VUV–UV light excitation. *Journal of Luminescence* 157, 411–415.
- Krupa, J.C., Queffelec, M., 1997. UV and VUV optical excitations in wide band gap materials doped with rare earth ions: 4f–5d transitions. *Journal of Alloys Compounds* 250, 287–292.
- Pejchal, J., Fukuda, K., Babin, V., *et al.*, 2016. Luminescence mechanism in doubly Gd, Nd-codoped fluoride crystals for VUV scintillators. *Journal of Luminescence* 169, 682–689.
- Shaht, S.K.K., Swart, H.C., Ntwaeaborwa, O.M., 2014. Investigation of luminescent properties of $\text{Ca}_{0.3}\text{Sr}_{0.7}\text{Al}_2\text{O}_4\text{:Tb}^{3+}, \text{Eu}^{3+}$ excited using different excitation sources. *Journal of Electron Spectroscopy and Related Phenomena* 197, 72–79.
- Shimizu, Y., Ueda, K., Inaguma, Y., 2017. Photoluminescence excitation spectra of lanthanide doped YAlO_3 in vacuum ultraviolet region. *Optical Materials* 66, 327–331.
- Song, K.S., Williams, R.T., 1993. *Self-Trapped Excitons: Series in Solid-State Sciences*. vol. 105. Berlin: Springer.
- Struck, C.W., Fonger, W.H., 1991. *Understanding Luminescence Spectra and Efficiency Using Wp and Related Functions (Inorganic Chemistry Concepts)*. vol. 13. Berlin: Springer.
- Yen, W.M., Shionoya, S., Yamamoto, H., 2007. *Fundamentals of Phosphors*. New York, NY: CRC Press Taylor & Francis.

Silicon Carbide Electronic Devices

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Introduction

The status of emerging silicon carbide (SiC) wide-bandgap semiconductor electronics technology is briefly surveyed. SiC-based electronic devices and circuits are being developed for use in high-temperature, high-power, and/or high-radiation conditions under which conventional semiconductors cannot function (Buttay *et al.*, 2011). Projected performance benefits of SiC electronics are briefly illustrated for several applications. However, most of these operational benefits of SiC have yet to be realized in actual systems, primarily owing to the fact that the growth techniques of SiC crystals are relatively immature and device fabrication technologies are not yet sufficiently developed to the degree required for widespread, reliable commercial use. Key crystal growth and device fabrication issues that limit the performance and capability of high-temperature and/or high-power SiC electronics are identified. The electrical and material quality differences between emerging SiC and mature silicon electronics technology are highlighted.

Properties of SiC

Silicon carbide occurs in many different crystal structures, called polytypes. A comprehensive introduction to SiC crystallography and polytypism can be found in Powell *et al.* (1993). Despite the fact that all SiC polytypes chemically consist of 50% carbon atoms covalently bonded with 50% silicon atoms, each SiC polytype has its own distinct set of electronic properties. While there are over 100 known polytypes of SiC, only a few are commonly grown in a reproducible form acceptable for use as semiconductors. The most common polytypes of SiC being developed for electronics are 3C-SiC, 4H-SiC, and 6H-SiC (Pizzagalli, 2014). 3C-SiC, also referred to as β -SiC, is the only form of SiC with a cubic crystal structure. The noncubic polytypes of SiC are sometimes ambiguously referred to as α -SiC. 4H-SiC and 6H-SiC are only two of many possible SiC polytypes with a hexagonal crystal structure. Similarly, 15R-SiC is the most common of many possible SiC polytypes with a rhombohedral crystal structure.

Because some important electrical device properties are nonisotropic with respect to crystal orientation, lattice site, and surface polarity, further understanding of SiC crystal structure and terminology is necessary. As discussed more thoroughly in Powell *et al.* (1993), different polytypes of SiC are actually composed of different stacking sequences of Si–C bilayers (also called Si–C double layers), where each single Si–C bilayer can simplistically be viewed as a planar sheet of silicon atoms coupled with a planar sheet of carbon atoms. The plane formed by a bilayer sheet of silicon and carbon atoms is known as the basal plane, while the crystallographic c -axis direction, also known as the stacking direction or the [0001] direction, is defined normal to Si–C bilayer plane. Fig. 1 depicts schematically the stacking sequence of the 6H-SiC polytype, which requires six Si–C bilayers to define the unit cell repeat distance along the c -axis [0001] direction. The [1 $\bar{1}$ 00] direction depicted in Fig. 1 is often referred to as the a -axis direction. The silicon atoms labeled 'h' or 'k' in Fig. 1 denote Si–C double layers that reside in 'quasi-hexagonal' or 'quasi-cubic' environments with respect to their immediately neighboring above and below bilayers. SiC is a polar semiconductor across the c -axis, in that one surface normal to the c -axis is terminated with silicon atoms while the opposite normal c -axis surface is terminated with carbon atoms. As shown in Fig. 1, these surfaces are referred to as the 'silicon face' and 'carbon face,' respectively.

Owing to the differing arrangement of silicon and carbon atoms within the SiC crystal lattice, each SiC polytype exhibits unique electrical and optical properties. Some of the more important semiconductor electrical properties of the 3C, 4H, and 6H silicon carbide polytypes at room temperature are given in Table 1. More detailed electrical properties can be found in Choyke *et al.* (1997) and Pensl *et al.* (1998) and references therein. Even within a given polytype, some important electrical properties are nonisotropic, in that they are strong functions of crystallographic direction of current flow and applied electric field (e.g., electron mobility for 6H-SiC). Dopants in SiC can incorporate into energetically nonequivalent quasi-hexagonal (h) C-sites or Si-sites, or quasi-cubic (k) C-sites or Si-sites (only Si-sites are labeled h or k in Fig. 1). While all dopant ionization energies associated with various dopant incorporation sites should normally be considered for utmost accuracy, Table 1 lists only the shallowest ionization energies of each impurity.

For comparison, Table 1 also includes comparable properties of silicon and GaAs. Because silicon is the semiconductor employed in most commercial solid-state electronics, it is the yardstick by which other semiconductor materials must be evaluated against. To varying degrees the major SiC polytypes exhibit advantages and disadvantages in basic material properties compared to silicon. The most beneficial superior material properties of SiC over silicon listed in Table 1 are its wide bandgap energy, exceptionally high breakdown electric field, high thermal conductivity, and high carrier saturation velocity. The electrical device performance benefits that each of these properties enable are discussed in the next section, as are system-level benefits enabled by improved SiC devices.

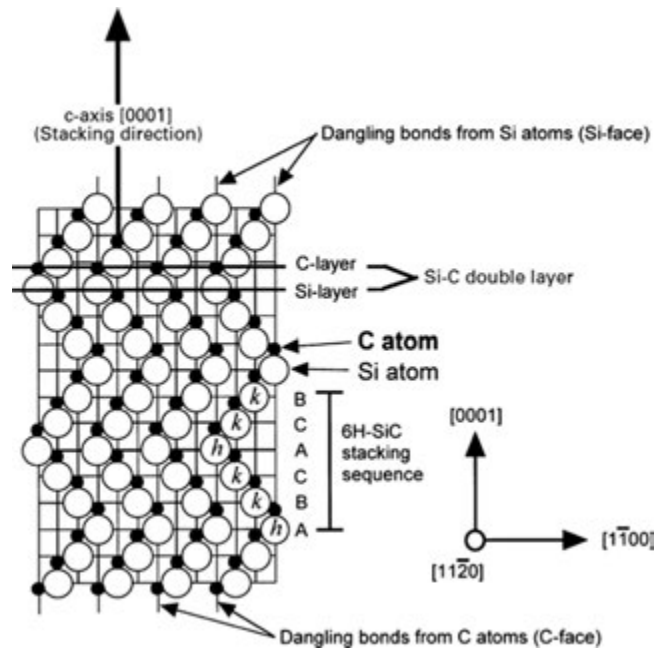


Fig. 1 Schematic cross-section ((1120) plane) of the 6H-SiC polytype. Reproduced by permission of IOP Publishing from Semiconductor Interfaces, Microstructures, and Devices: Properties and Applications, 1993, pp. 257–93.

Table 1 Comparison of properties of selected SiC polytypes with silicon and GaAs ($T=300$ K)

Property	Silicon	GaAs	4H-SiC	6H-SiC	3C-SiC
Bandgap (eV)	1.1	1.42	3.2	3.0	2.3
Relative dielectric constant	11.9	13.1	9.7	9.7	9.7
Breakdown field at $N_D=10^{17} \text{ cm}^{-3}$ (MV cm^{-1})	0.6	0.6	$\parallel$ c-axis: 3.0	$\parallel$ c-axis: 3.2, $\perp$ c-axis: >1	>1.5
Thermal conductivity ($\text{W cm}^{-1} \text{ K}^{-1}$)	1.5	0.5	3–5	3–5	3–5
Intrinsic carrier concentration (cm^{-3})	10^{10}	1.8×10^6	$\sim 10^{-7}$	$\sim 10^{-5}$	~ 10
Electron mobility at $N_D=10^{16} \text{ cm}^{-3}$ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	1200	6500	$\parallel$ c-axis: 800, $\perp$ c-axis: 800	$\parallel$ c-axis: 60, $\perp$ c-axis: 400	750
Hole mobility at $N_A=10^{16} \text{ cm}^{-3}$ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	420	320	115	90	40
Saturated electron velocity (10^7 cm s^{-1})	1.0	1.2	2	2	2.5
Donor dopants and shallowest ionization energy (meV)	P: 45, As: 54	Si: 5.8	N: 45, P: 80	N: 85, P: 80	N: 50
Acceptor dopants and shallowest ionization energy (meV)	B: 45	Be, Mg, C: 28	Al: 200, B: 300	Al: 200, B: 300	Al: 270
Commercial wafer diameter as of 1999 (cm)	30	15	5	5	None

Sources: Sze (1981), Harris (1995), Choyke *et al.* (1997), Pensl *et al.* (1998), and references therein.

Electronics Benefits of SiC

The wide bandgap energy and low intrinsic carrier concentration of SiC allow it to maintain semiconductor behavior at much higher temperatures than silicon, which in turn permits SiC semiconductor device functionality at these much higher temperatures. Semiconductor electronic devices function in the temperature range where intrinsic carrier concentrations are negligible so that conductivity is controlled by intentionally introduced dopant impurities. Furthermore, the intrinsic carrier concentration, n_i , is a fundamental prefactor to well-known equations governing undesired junction reverse-bias leakage currents. As temperature increases, intrinsic carriers increase exponentially so that undesired leakage currents grow unacceptably large, and eventually at still higher temperatures, the semiconductor device operation is overcome by uncontrolled conductivity as intrinsic carriers exceed intentional device dopings. Depending on specific device design, the intrinsic carrier concentration of silicon generally confines silicon device operation to junction temperatures less than 300°C . The much smaller intrinsic carrier concentration of SiC theoretically permits device operation at junction temperatures exceeding 800°C , and 600°C SiC device operation has been experimentally demonstrated for a few prototype SiC devices.

The high breakdown field and high thermal conductivity of SiC coupled with high operational junction temperatures theoretically permit extremely high power densities and efficiencies to be realized. The high breakdown field of SiC relative to silicon

enables the blocking voltage region of a power device to be roughly 10 times thinner and 10 times more heavily doped, permitting roughly a 100-fold decrease in the blocking region resistance. For device topology reasons discussed in [Bhatnagar and Baliga \(1993\)](#) and [Chow et al. \(1998\)](#), the high breakdown field and wide energy bandgap of SiC also enable much faster power switching than is possible in comparably volt-amp rated silicon power-switching devices. Therefore, SiC-based power converters can operate at higher switching frequencies with much greater efficiency (i.e., less switching energy loss). Higher switching frequency in power converters is highly desirable because it permits use of smaller capacitors, inductors, and transformers, which in turn can reduce overall system size and weight.

While the smaller on-resistance and faster switching of SiC help minimize energy loss and heat generation, the higher thermal conductivity enables more efficient removal of waste heat energy from the active device. Because heat energy radiation efficiency increases greatly with increasing temperature difference between the device and the cooling ambient, the ability of SiC to operate at high junction temperatures permits much more efficient cooling to take place, so that heatsinks and other device-cooling hardware (i.e., fan cooling, liquid cooling, air conditioning, etc.) typically needed to keep high-power devices from overheating can be made much smaller or even eliminated.

While the preceding discussion has focused on high-power switching for power conversion, many of the same arguments can be applied to devices used to generate and amplify radio-frequency (RF) signals used in radar and communications applications. In particular, the high breakdown voltage and high thermal conductivity coupled with high carrier saturation velocity allow SiC microwave devices to handle much higher power densities than their silicon or GaAs RF counterparts, despite the disadvantage in low-field carrier mobility of SiC ([Table 1; Weitzel and Moore, 1998](#)). The high power density reduces the number of devices required to generate large total RF powers needed for fixed-base high-power RF transmission applications, thus minimizing RF matching difficulties and cooling requirements to reduce the overall system size and cost. SiC RF transistors are not well suited for low-power products, such as handheld cell telephone units.

Uncooled operation of high-temperature and/or high-power SiC electronics would enable revolutionary improvements in aerospace systems. Replacement of hydraulic controls and auxiliary power units with distributed 'smart' electromechanical controls and sensors capable of harsh-ambient operation will lead to substantial jet-aircraft weight savings, reduced maintenance, reduced pollution, higher fuel efficiency, and increased operational reliability. SiC high-power solid-state switches will also afford large efficiency gains in electric power management and control. Performance gains from SiC electronics could enable the public power grid to meet the increased consumer electricity demand without building additional generation plants, and improve power quality and operational reliability through 'smart' power management. More efficient electric motor drives, enabled by improved SiC power devices, will benefit industrial production systems as well as transportation systems such as diesel-electric railroad locomotives, electric mass-transit systems, nuclear-powered ships, and electric automobiles and buses.

Hostile environment SiC semiconductor devices and ICs offer little advantage if they cannot be reliably packaged and connected to form a complete system capable of operating in such environments. With proper materials selection, modifications of existing IC packaging technologies appear feasible for nonpowerSiC circuit packaging up to 300 °C. Prototype electronic packages that can withstand over 1000 h of heat soaking without electrical bias at 500 °C have been demonstrated ([Salmon et al., 1998](#)). Harsh environment passive components, such as inductors, capacitors, and transformers, must also be developed for operation in demanding conditions before the full system-level benefits of SiC electronics can be successfully realized.

SiC Crystal Growth

At the start of the semiconductor electronics era, SiC was considered an early transistor material candidate along with germanium and silicon. However, reproducible wafers of reasonable consistency, size, quality, and availability at acceptable cost are a prerequisite for commercial mass production of semiconductor electronics. Because SiC sublimates instead of melting at reasonably attainable pressures, SiC cannot be grown by conventional seeded melt-growth techniques such as those employed in the manufacture silicon wafers. This prevented the realization of SiC crystals suitable for mass production of electronics until the late 1980s. Prior to 1980 experimental SiC electronic devices were mostly confined to small (typically $\sim 1 \text{ cm}^2$), irregularly shaped SiC crystal platelets grown as a by-product of the Acheson process for manufacturing industrial abrasives ([Acheson, 1892](#)) or by the Lely process ([Lely, 1955](#)).

There have also been numerous efforts, some of which are still ongoing, to grow heteroepitaxial single-crystal 3C-SiC layers on top of large-area wafer substrate materials such as silicon or sapphire. These efforts have always resulted in SiC layers with high densities of structural defects. While some limited semiconductor electronic devices and circuits have been implemented in 3C-SiC grown on silicon, the performance benefits of these electronics are severely limited to the point where almost none of the operational benefits of SiC over silicon have been realized.

[Tairov and Tsvetkov \(1978\)](#) established the basic principles of a modified seeded sublimation growth process for 6H-SiC. This process, also referred to as the modified Lely process, was a breakthrough for SiC in that it offered the first possibility of reproducibly growing acceptably large single crystals of SiC that could be cut and polished into mass-produced SiC wafers. The growth process is based on heating polycrystalline SiC source material to $\sim 2400 \text{ °C}$ under conditions where it sublimates into the vapor phase and subsequently condenses onto a cooler SiC seed crystal. This produces a somewhat cylindrical boule of single-crystal SiC that grows taller at a rate of a few millimeters per hour. The preferred orientation of the growth in the sublimation process is such that vertical growth of a taller cylindrical boule proceeds along the [0001] crystallographic *c*-axis direction (i.e.,

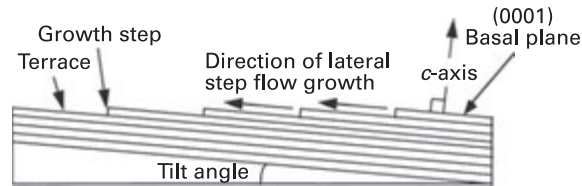


Fig. 2 Cross-sectional schematic representation of 'off-axis' polished SiC surface used for homoepitaxial growth. When growth conditions are properly controlled and there is a sufficiently short distance between steps, silicon and carbon adatoms impinging onto the growth surface find their way to steps where they bond and are incorporated into the crystal. Thus, ordered lateral 'step flow' growth takes place, which enables the polytype stacking sequence of the substrate to be exactly mirrored in the growing epilayer (reproduced (with modifications) by permission of IOP Publishing from 'Semiconductor Interfaces, Microstructures, and Devices: Properties and Applications,' 1993, pp. 257–93).

vertical direction in Fig. 1). Circular '*c*-axis' wafers with surfaces that lie normal (perpendicular) to the *c*-axis can then be sliced from the roughly cylindrical boule. Other growth orientations (such as along the *a*-axis) are also being investigated, but are not nearly as available and well developed as *c*-axis-grown wafer material.

After further development of the sublimation growth process, mass-produced sublimation-grown wafers (6H-SiC polytype, 2.5 cm diameter) became commercially available in 1989. The vast majority of SiC semiconductor electronics development has taken place since then. Other companies have subsequently entered the SiC wafer market, and sublimation-grown wafers of the 4H-SiC polytype have also been widely commercialized. *n*-Type, *p*-type, and semi-insulating SiC wafers of 2.5 to 5 cm in diameter are commercially available, and prototype wafers as large as 10 cm in diameter have been grown in the laboratory.

Wafer size, cost, and quality are all very critical to the manufacturability and process yield of mass-produced semiconductor microelectronics. Compared to commonplace silicon and GaAs wafer standards, 4H- and 6H-SiC wafers are small, expensive, and generally of inferior quality. However, such disparities are expected considering that silicon and GaAs wafers have undergone decades of commercial process refinement, and that SiC is an extraordinarily hard material making it very difficult to properly saw and polish.

Most SiC electronic devices are not fabricated directly in sublimation-grown wafers, but are instead fabricated in much higher quality epitaxial SiC layers that are grown on top of the sublimation-grown wafer. Therefore, the controlled growth of high-quality epilayers directly impacts on the realization of SiC electronic devices and circuits. An interesting variety of SiC epitaxial growth methods, ranging from liquid-phase epitaxy, molecular beam epitaxy, and chemical vapor deposition (CVD), have been investigated (Choyke *et al.*, 1997; Pensl *et al.*, 1998). The CVD growth technique is generally accepted as the most promising method for attaining epilayer reproducibility, quality, and throughputs required for mass production.

In the simplest terms, variations of SiC CVD are carried out by heating SiC substrates in a chamber with flowing silicon- and carbon-containing gases that decompose and deposit silicon and carbon onto the wafer allowing an epilayer to grow in a well-ordered single-crystal fashion under well-controlled conditions. Conventional SiC CVD epitaxial growth processes are carried out at substrate growth temperatures between 1400 and 1600 °C at pressures from 0.1 to 1 atm resulting in growth rates of the order of micrometers per hour (Powell and Larkin, 1997). Higher temperature (up to 2000 °C) SiC CVD growth processes are also being pioneered to obtain higher SiC epilayer growth rates of the order of hundreds of micrometers per hour (Kordina *et al.*, 1997).

Homoepitaxial growth, whereby the polytype of the SiC epilayer matches that of the SiC substrate, is accomplished by step-controlled epitaxy (Kimoto *et al.*, 1997). Step-controlled epitaxy is based on growing epilayers on an SiC wafer polished at an angle (called the 'tilt angle' or 'off-axis angle') of typically 3–8° off the (0001) basal plane, resulting in a surface with atomic steps and flat terraces between steps as depicted schematically in Fig. 2. When growth conditions are properly controlled and there is a sufficiently short distance between steps, silicon and carbon adatoms impinging onto the growth surface find their way to steps where they bond and are incorporated into the crystal. Thus, ordered lateral 'step flow' growth takes place which enables the polytypic stacking sequence of the substrate to be exactly mirrored in the growing epilayer. When growth conditions are not properly controlled or when steps are too far apart (as can occur with SiC substrate surfaces that are polished to within less than 1° of the basal plane), growth adatoms can nucleate and bond in the middle of terraces instead of at the steps, which leads to growth of poor-quality 3C-SiC (Kimoto *et al.*, 1997; Powell and Larkin, 1997). It is impractical to intentionally vary the polytype of SiC epilayers, so that heterojunction device structures have not been demonstrated using single-crystal SiC–SiC heterojunctions.

It is important to note that most as-grown SiC epilayers contain varying densities of undesirable defects and surface morphological features which affect SiC device processing and performance to varying degrees (Neudeck, 2000). Micropipes and closed-core screw dislocations originating in *c*-axis substrates propagate through subsequently grown epilayers. Nonideal epilayer surface features commonly observed include 'triangular inclusions,' 'growth pits,' and macrosteps formed by coalescence of multiple SiC growth steps (i.e., 'step bunching') during epitaxy. Pregrowth wafer polishing as well as growth initiation procedures have been shown to have a strong impact on the formation of undesirable epitaxial growth features (Powell and Larkin, 1997). Continued reduction of these defects will clearly help pave the way for increasingly capable SiC devices, especially devices for very high-power applications.

In situ doping during CVD epitaxial growth is primarily accomplished through the introduction of nitrogen (usually N₂) for *n*-type and aluminum (usually trimethyl- or triethylaluminum) for *p*-type epilayers. Some alternative dopants such as phosphorous, boron, and vanadium have also been investigated for *n*-type, *p*-type, and semi-insulating epilayers, respectively. While reasonable variation in epilayer doping can be achieved by strictly varying the flow of dopant gases, the site competition doping method

(Larkin, 1997) has enabled a much broader range of SiC doping to be accomplished. In addition, site competition epitaxy has also made moderate epilayer dopings more reliable and repeatable. Commercial epilayer thickness and doping tolerances are specified at 25 and 50%, respectively, while doping uniformities of 7% and thickness uniformities of 4% over 30 mm wafers have been reported in developmental research (Burk and Rowland, 1997).

SiC Device Fabrication

In order to minimize the development and production costs of SiC electronics, it is essential that SiC device fabrication takes advantage of existing silicon and GaAs wafer processing infrastructure as much as possible. Most of the steps necessary to fabricate SiC electronics starting from SiC wafers can be accomplished using somewhat modified commercial silicon electronics processes and fabrication tools. While 4H-SiC and 6H-SiC device processing methods are discussed in this section, these processes are generally applicable to other polytypes of SiC, except for the case of 3C-SiC grown on silicon where all processing temperatures need to be kept below the melting temperature of silicon ($\sim 1400^\circ\text{C}$).

Patterned Doping by Ion Implantation

The fact that diffusion coefficients of most dopants in SiC are negligibly small below $\sim 1800^\circ\text{C}$ is excellent for maintaining device junction stability, because dopants do not undesirably diffuse as the device is operated for long times at high temperatures. Unfortunately, however, this characteristic also precludes the use of conventional dopant diffusion, a highly useful technique widely employed in silicon microelectronics manufacturing, for patterned doping of SiC. Therefore, laterally patterned doping of SiC is almost exclusively carried out by ion implantation. This somewhat restricts the depth that most dopants can be implanted to less than $1\text{ }\mu\text{m}$ using conventional dopants and implantation equipment. Compared to silicon processes, SiC ion implantation requires a much higher thermal budget to achieve acceptable dopant implant electrical activation.

Summaries of ion implantation processes for various dopants can be found in (Pensl *et al.*, 1998). Most of these processes are based on carrying out implantation at elevated temperatures ($\sim 500\text{--}800^\circ\text{C}$) using a patterned high-temperature masking material. The elevated temperature during implantation promotes some lattice self-healing during the implant, so that damage and segregation of displaced silicon and carbon atoms does not become excessive, especially in high-dose implants often employed for ohmic contact formation. Co-implantation of carbon with *p*-type dopants has been shown to improve the electrical conductivity of high-dose *p*-type layers (Zhao *et al.*, 1997).

Following ion implantation, the patterning mask is generally stripped prior to carrying out a very high-temperature ($\sim 1200\text{--}1800^\circ\text{C}$) anneal, the purpose of which is to achieve maximum electrical activation of dopant ions. At higher implant anneal temperatures, the SiC surface morphology can seriously degrade as damage-assisted sublimation etching of the SiC surface begins to take place (Capano *et al.*, 1998). Because sublimation etching is driven primarily by loss of silicon from the crystal surface, annealing in silicon overpressures can be used to prevent surface degradation during high-temperature anneals. Such overpressure is often achieved by close proximity solid sources, such as using an enclosed SiC crucible with SiC lid and/or SiC powder near the wafer, or by annealing in a silane-containing atmosphere.

Contacts

All useful semiconductor electronics require conductive signal paths in and out of each device as well as conductive interconnects to carry signals between devices on the same chip and to external circuit elements that reside off-chip. While SiC itself is theoretically capable of high-performance operation under extreme conditions, such functionality is useless without contacts and interconnects that are also capable of operation under the same conditions to enable complete circuit functionality. The durability and reliability of metal-semiconductor contacts and interconnects are one of the main factors limiting the operational high-temperature limits of SiC electronics. Most reported SiC metallizations appear sufficient for long-term device operation at temperatures up to 300°C . Depending on the device structure and application, SiC Schottky diode reverse leakage currents generally become excessive at temperatures greater than 400°C . SiC ohmic and Schottky contacts to meet the demanding requirements needed for harsher environment operation (i.e., temperatures $>400^\circ\text{C}$, high current densities, and/or oxidizing environments) are a challenging topic of ongoing research activity.

Specific overviews of SiC metal-semiconductor contact technology can be found in Porter and Davis (1995), Crofton *et al.* (1997), and Saxena and Steckl (1998). There are both similarities and a few differences between SiC contacts and contacts to conventional narrow-bandgap semiconductors (e.g., silicon, GaAs). The same basic physics and current transport mechanisms that are present in narrow-bandgap contacts, such as surface states, Fermi pinning, thermionic emission, and tunneling, also apply to SiC contacts. A natural consequence of the wider bandgap of SiC is higher effective Schottky barrier heights. Analogous to narrow-bandgap contact physics, the microstructural and chemical state of the SiC-metal interface is crucial to contact electrical properties. Therefore, premetal deposition surface preparation, metal deposition process, choice of metal, and postdeposition annealing can all greatly affect the resulting performance of metal-SiC contacts. Because the chemical nature of the starting SiC surface is strongly dependent on surface polarity, it is not uncommon to obtain significantly different results when the same contact process is

applied to the silicon face surface as opposed to the carbon face surface. While Schottky contact barrier height does somewhat depend on metal–semiconductor work-function difference, the dependence is weak enough to suggest that surface state charge also plays a significant role in determining the effective barrier height of SiC Schottky junctions. Undesired nonuniformities in SiC surface properties owing to crystal defects and surface structure variations are widely suspected as the cause of uneven current flow and higher-than-expected leakage current barrier heights extracted by C – V methods typical in experimental SiC Schottky diodes. Thus, barrier heights extracted by C – V methods typically are higher than those extracted by I – V measurements.

While SiC specific ohmic contact resistances at room temperature are generally higher than in contacts to narrow-bandgap semiconductors, they are nevertheless sufficiently low for most envisioned SiC applications. Lower specific contact resistances are usually obtained to n -type 4H- and 6H-SiC ($\sim 10^{-4}$ – $10^{-6} \Omega \text{ cm}^2$) than to p -type 4H- and 6H-SiC ($\sim 10^{-3}$ – $10^{-5} \Omega \text{ cm}^2$). Consistent with narrow-bandgap ohmic contact technology, it is easier to make low-resistance ohmic contacts to heavily doped SiC. Regardless of doping, it is common practice with SiC to thermally anneal ohmic contacts to obtain the minimum possible contact resistance. Most SiC ohmic contact anneals are performed at temperatures around 900–1000 °C in nonoxidizing environments. Depending on the contact metallization employed, this anneal generally causes limited interfacial reactions (usually metal carbide or metal silicide formation) that broaden and/or roughen the metal–semiconductor interface.

Patterned Etching

At room temperature, no known wet chemical etches single-crystal SiC. Therefore, most patterned etching of SiC for electronic devices and circuits is accomplished using dry-etching techniques. Yih *et al.* (1997) give an excellent summary of dry SiC etching results. The most commonly employed process involves reactive ion etching (RIE) of SiC in fluorinated plasmas. Sacrificial etch masks (often metals) are deposited and photolithographically patterned to protect desired areas from being etched. The SiC RIE process can be implemented using standard silicon RIE hardware, and typical 4H- and 6H-SiC RIE rates are of the order of hundreds of angstroms per minute. Well-optimized SiC RIE processes are typically highly anisotropic with little undercutting of the etch mask, leaving smooth surfaces. One of the keys to achieving smooth surfaces is preventing ‘micromasking’ where masking material is slightly etched and randomly redeposited onto the sample, effectively masking very small areas on the sample that were intended for uniform etching. This can result in ‘grass’-like etch residue features being formed in the unmasked regions, which is undesirable in most cases. In special cases, RIE under conditions promoting micromasking is useful in greatly roughening the SiC surface to reduce the contact resistance of subsequently deposited ohmic metallizations.

While RIE rates are sufficient for many electronic applications, much higher SiC etch rates are necessary to delineate features of the order of tens to hundreds of micrometers deep that are needed to realize advanced sensors, microelectromechanical systems (MEMS), and some very high-voltage power device structures. High-density plasma dry-etching techniques, such as electron cyclotron resonance (ECR) and inductively coupled plasma (ICP), have been developed to meet the need for deep etching of SiC. Residue-free patterned etch rates exceeding 1000 Å min^{-1} have been demonstrated (Yih *et al.*, 1997).

Patterned etching of SiC at very high etch rates has also been demonstrated using photoassisted and dark electrochemical wet etching (Shor *et al.*, 1997). By choosing proper etching conditions, this technique has demonstrated a very useful dopant-selective etch-stop capability. However, there are major incompatibilities of the electrochemical process that make it undesirable for VLSI mass production, including extensive pre-etching and postetching sample preparation, etch isotropy and mask undercutting, and somewhat nonuniform etching across the sample.

Metal–Oxide–Semiconductor Technology

The vast majority of semiconductor integrated circuit chips in use rely on silicon metal–oxide–semiconductor field effect transistors (MOSFETs), whose electronic advantages and operational device physics are summarized in other elsewhere in this work. Given the extreme usefulness and success of MOSFET-based electronics in silicon, it is naturally desirable to implement high-performance inversion channel MOSFETs in SiC. Like silicon, SiC forms a thermal SiO_2 oxide when it is heated to high temperatures in an oxygen environment. While this enables SiC MOS technology to somewhat follow the highly successful path of silicon MOS electronics, there are nevertheless important differences in insulator quality and device processing that prevent SiC MOSFETs from realizing their full potential. While the following discussion attempts to quickly highlight key issues facing SiC MOSFET development, more detailed insights can be found in Afanasev *et al.* (1997), Brown *et al.* (1997), Cooper (1997), and Ouisse (1997). In highlighting the difficulties facing SiC MOSFET development, it is important to keep in mind that early silicon MOSFETs faced similar developmental challenges that took many years of dedicated research to overcome successfully.

From a purely electrical point of view, there are two prime operational deficiencies of SiC oxides and MOSFETs compared to silicon MOSFETs. First, effective inversion channel mobilities in most SiC MOSFETs are much lower (typically well under $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for inversion electrons) than one would expect based on silicon inversion channel MOSFET carrier mobilities. This seriously reduces the transistor gain and current-carrying capability of SiC MOSFETs, so that they are not nearly as advantageous as theoretically predicted. Second, SiC oxides have not proved to be as reliable as well-developed silicon oxides, in that SiC MOSFETs are more prone to threshold voltage shifts, gate leakage, and oxide failures than comparably biased silicon MOSFETs. The excellent works by Cooper (1997) and Brown *et al.* (1997) discuss noteworthy differences between the basic electrical properties of n -type vs. p -type SiC MOS devices.

SiC MOSFET oxide electrical performance deficiencies appear to be mostly attributable to differences between silicon and SiC thermal oxide quality and interface structure that cause the SiC oxide to exhibit undesirably higher levels of interface state densities ($\sim 10^{11}$ – 10^{12} eV $^{-1}$ cm $^{-2}$), fixed oxide charges ($\sim 10^{11}$ – 10^{12} cm $^{-2}$), charge trapping, carrier oxide tunneling, and roughness-related scattering of inversion channel carriers. SiC surfaces are well known to be much rougher than silicon surfaces, owing to off-angle polishing needed to support SiChomoepitaxy as well as step-bunching that can occur during SiC homoepilayer growth. The wide bandgap of SiC reduces the potential barrier impeding tunneling of carriers into SiC thermal oxides, so that perfectly grown oxides on atomically smooth SiC are not be as reliable as silicon thermal oxides (Agarwal *et al.*, 1997). Therefore, it is highly probable that alternative gate insulators will have to be developed for optimized implementation of inversion channel SiC FETs for the most demanding high-power and/or high-temperature electronic applications.

Prototyping and Production of SiC Electronic Devices

This section briefly summarizes a variety of experimentally realized SiC electronic devices broken down by major application areas. The operational performance of experimental SiC devices is compared to that predicted theoretically as well as the capabilities of existing silicon and GaAs devices. SiC process and materials technology issues limiting the capabilities of various SiC device topologies are highlighted as key issues to be addressed in further SiC technology development.

Optoelectronics and Sensors

The wide bandgap of SiC is useful for realizing short-wavelength blue and UV optoelectronics. 6 H-SiC-based blue p–n junction light emitting diodes (LEDs) were the first SiC-based devices to reach high-volume commercial sales. These epitaxially grown, dry-etch, mesa-isolated p–n junction diodes were the first mass-produced LEDs to cover the blue (~ 250 – 280 nm peak wavelength) portion of the visible spectrum. Because the bandgap of SiC is indirect (i.e., the conduction minimum and valence band maximum do not coincide in crystal momentum space), luminescent recombination in the LEDs is governed by inherently inefficient indirect transitions mediated by impurities and phonons. Therefore, the efficiency of SiC blue LEDs is limited to well below 1%. While commercially successful from 1989 to 1995, SiC-based blue LEDs have been totally replaced by the emergence of much brighter, more efficient direct-bandgap GaN blue LEDs.

SiC has proved to be much more efficient at absorbing short-wavelength light, which has enabled the realization of SiC UV-sensitive photodiodes that serve as excellent flame sensors in turbine-engine combustion monitoring and control (Brown *et al.*, 1998). The wide bandgap of 6H-SiC is useful for realizing low photodiode dark currents, as well as sensors that are blind to undesired near-IR wavelengths produced by heat and solar radiation. Commercial SiC-based UV flame sensors, again based on epitaxially grown, dry-etch, mesa-isolated 6H-SiC p–n junction diodes, have successfully reduced harmful pollution emissions from gas-fired ground-based turbines used in electrical power generation systems.

The high-temperature capabilities of SiC allow the production of catalytic metal–SiC and metal–insulator–SiC (MIS) prototype gas sensor structures with great promise for combustion engine emission monitoring applications (Lloyd Spetz *et al.*, 1997; Hunter *et al.*, 1998). High-temperature operation of these structures, not possible with silicon, enables rapid detection of changes in hydrogen and hydrocarbon content to sensitivities of parts per million in very small sensors that could easily be placed unobtrusively anywhere in an engine. Once they have been more fully developed, these sensors could assist in active combustion control to reduce harmful pollution emissions from automobile and aircraft engines. While generally beyond the scope of this chapter, SiC is also likely to play a significant role in emerging MEMS applications (Mehregany *et al.*, 1998).

RF Electronics

The main use of SiC RF devices appears to be in high-frequency solid-state high-power amplification at frequencies from around 600 MHz (UHF band) to perhaps around 10 GHz (X band). As discussed by Weitzel and Moore (1998), the high breakdown voltage and high thermal conductivity coupled with high carrier saturation velocity allow SiC RF transistors to handle much higher power densities than their silicon or GaAs RF counterparts, despite the disadvantage of SiC in low-field carrier mobility (Table 1). The higher breakdown field of SiC permits higher drain breakdown voltage, allowing RF operation at higher drain biases, which leads to higher SiC MESFET output power densities. The higher thermal conductivity of SiC is also crucial in minimizing channel self-heating so that phonon scattering does not seriously degrade channel carrier velocity and current. Similar RF output power arguments can be made for SiC-based static induction transistors (SITs). While 4H-SiC MESFETs for high-power RF applications are now commercially available, increasingly beneficial SiC RF transistors should continue to evolve as SiC crystal quality and device processing technology continue to improve.

In addition to high-power RF transistors, SiC mixer diodes show excellent promise for reducing undesired intermodulation interference in RF receivers (Fazi and Neudeck, 1998). More than 20 dB dynamic range improvement has been demonstrated using nonoptimized SiC Schottky diode mixers. Such dynamic range improvement could prove particularly beneficial to RF systems where numerous receivers and high-power transmitters are closely located, such as on a commercial passenger aircraft or military surface ship.

High-Temperature Devices and ICs

Commercially available silicon-on-insulator circuits can perform complex digital and analog signal-level functions up to 300 °C when high-power output is not required. Thus, aside from ICs where it is advantageous to combine signal-level functions with high-power or unique SiC sensors/MEMS onto a single chip, more expensive SiC circuits solely performing low-power signal-level functions appear largely unjustifiable for low-radiation applications at temperatures below 250–300 °C. In high-power systems, junction self-heating and high electrothermal stress mean silicon devices cannot function above 100–200 °C. Thus, the transition to SiC is necessary at lower temperatures in high-power applications.

Achieving long-term operational reliability is the primary ongoing challenge of realizing 300–600 °C SiC devices and circuits. IC device technologies covered in other chapters in this work that have been used to successfully implement circuits in silicon and GaAs are to varying degrees candidates for use as a basis for SiC integrated circuits at $T > 300$ °C. High-temperature gate-insulator reliability, discussed in the section on SiC device fabrication, is needed for the successful realization of MOSFET-based integrated circuits. Gate-to-channel Schottky diode leakage limits the peak operating temperature of SiC MESFET circuits to around 400 °C. Prototype bipolar SiC transistors exhibit poor gains, but improvements in SiC crystal growth and surface passivation could greatly improve SiC BJT gains to make SiC bipolar devices a more viable technology (Wang *et al.*, 1996). As discussed previously, a common obstacle to all technologies is reliable long-term operation of contacts, interconnects, passivation, and packaging at $T > 300$ °C. Robust circuit designs that accommodate large changes in device operating parameters with temperature will be necessary for circuits to function successfully over the very wide temperature ranges (as large as 650 °C spread) enabled by SiC. Device behaviors that have traditionally been unimportant to design and simulation of silicon-based device and circuits, such as freezeout of incompletely ionized dopant atoms, must now be included for proper design and simulation of SiC devices and circuits. Because of carrier freezeout effects, it may prove difficult to realize SiC-based ICs operational at temperatures much lower than -55 °C.

Because signal-level circuits are operated at relatively low electric fields well below the electrical failure voltage of most micropipes, micropipes affect signal-level circuit process yields to a much lesser degree than they affect high-field power device yields. Small-scale prototype logic and analog amplifier SiC-based ICs have been demonstrated using SiC variations of common device topologies (Harris *et al.*, 1994; Xie *et al.*, 1994; Diogu *et al.*, 1996; Brown *et al.*, 1997; Ryu *et al.*, 1998). These prototypes are not commercially viable, largely owing to their high cost, unproven reliability, and limited temperature range that is mostly covered by silicon-on-insulator circuitry. However, increasingly capable and economical SiC integrated circuits will continue to evolve as SiC crystal growth and device fabrication technology continue to improve. Nonidealities in SiC epilayers, such as variations in epilayer doping and thickness, surface morphological defects, and slow charge trapping/detrapping phenomena causing unwanted device I – V drift, limit the yield, size, and manufacturability of SiC high-temperature ICs (Brown *et al.*, 1997).

High-power Switching

While SiC devices offer large potential benefits to high-power systems, solid-state devices in these systems are also the most susceptible to deficiencies in SiC material quality and process variations. This is primarily because these devices operate at high electric fields and high current densities that place the greatest electrical stresses on the semiconductor and surrounding device materials. Prototype SiC devices have demonstrated excellent area-normalized performance often well beyond (more than 10 times) the theoretical power density of silicon power electronics. However, the presence of crystal defects such as micropipes has prevented scale-up of small-area prototypes to large areas that can reliably deliver high total operating currents in large-scale power systems. Since the early 1990s SiC micropipe densities have dropped from hundreds to several tens per square centimeter of wafer area, resulting in corresponding improvements in peak SiC device operating currents from less than 1 A to several tens of amps. However, further defect reductions of at least an additional order of magnitude will be necessary before commercially viable power device yields at these current ratings can be expected.

In addition to micropipes, the density of nonhollow core (elementary) screw dislocation defects in SiC wafers and epilayers has been measured to be of the order of several thousand per square centimeter of wafer area. While these defects are not nearly as detrimental to device performance as micropipes, experiments have shown that they degrade the local material properties such as breakdown field and minority carrier lifetime (Neudeck, 2000). While localized breakdown is well known to degrade silicon device reliability in high-power switching applications, the exact impact on SiC high-power switching devices remains to be quantified. The electrical significance of other dislocation defects, if any, also remains to be ascertained.

For SiC power devices to function successfully at high voltages, peripheral breakdown owing to edge-related electric field crowding must be avoided through careful device design and proper choice of insulating/passivating dielectric materials. The peak voltage of most prototype high-voltage SiC devices has been limited by edge-related breakdown (often destructive), especially in SiC devices capable of blocking multiple kilovolts. In addition, most testing of multikilovolt SiC devices has required the device to be immersed in specialized high-dielectric fluids or gas atmospheres to minimize damaging electrical arcing and surface flashover at device peripheries. A variety of edge termination methods, many of which were originally pioneered in silicon high-voltage devices, have been applied to prototype SiC power devices with varying degrees of success. The higher voltages and higher local electric fields of SiC power devices will place larger stresses on packaging and on-wafer insulating materials, so it is unclear whether traditional materials used to insulate/passivate silicon high-voltage devices will prove sufficient for reliable use in SiC high-voltage devices, especially if those devices are to be operated at high temperatures.

The high-power diode rectifier is a critical building block of power conversion circuits. The most important SiC diode rectifier device design tradeoffs roughly parallel well-known silicon rectifier tradeoffs, except for the fact that numbers for current densities, voltages, power densities, and switching speeds are typically much higher in SiC. The high breakdown field of SiC and wide energy bandgap permit operation of SiC metal–semiconductor Schottky diodes at much higher voltages (i.e., kilovolts) and current densities than is practical with silicon-based Schottky diodes. For blocking voltages up to around 3 kV, unipolar SiC Schottky rectifiers appear to offer lower turn-on voltages ($\sim 1\text{--}2$ vs. ~ 3 V) and faster switching speeds (owing to no appreciable minority carrier injection/charge storage) than SiC p–n junctions (Chow *et al.*, 1998). In rectifiers that block over ~ 3 kV, bipolar minority carrier charge injection (i.e., conductivity modulation) should enable SiCp–n diodes to carry higher current densities than unipolar Schottky diodes whose drift regions conduct solely using dopant-atom majority carriers. Hybrid Schottky/p–n rectifier structures first developed in silicon that combine p–n junction reverse blocking with low Schottky forward turn-on should prove extremely useful to realizing application-optimized SiC rectifiers (Dahlquist *et al.*, 1998; Held *et al.*, 1998). As with silicon bipolar devices, reproducible localized control of minority carrier lifetime will be important in optimizing switching speed vs. ON-state current density performance. SiC minority carrier lifetimes of the order of several microseconds have been measured in high-quality epilayers (Kordina *et al.*, 1996), and lifetime reduction via intentional impurity incorporation and introduction of radiation-induced structural defects appears feasible.

Three terminal power switches that use small drive signals to control large voltages and currents are also critical building blocks of high-power conversion circuits. As summarized by Chow *et al.* (1998), a variety of prototype three-terminal SiC power switches have been demonstrated. For the most part SiC solid-state switches are based on well-known silicon device topologies, like the thyristor, vertical and lateral channel MOSFETs, IGBTs, etc., that try to maximize power density via vertical current flow using the substrate as one of the device terminals. Because these switches all contain high-field junctions responsible for blocking current flow in the off state, their maximum operating currents are primarily restricted by the material quality deficiencies discussed previously.

Silicon power MOSFETs and IGBTs are extremely popular in power circuits largely because their MOS gate drives are well insulated and require little drive signal power, and the devices are ‘normally off’ in that there is no current flow when the gate is unbiased at 0 V. However, as discussed previously, the performance and reliability of SiC power device structures with inversion channel MOS field-effect gates (i.e., MOSFETs, IGBTs, etc.) are limited by poor inversion channel mobilities and questionable oxide reliability at high temperatures. Thus, SiC device structures that do not rely on high-quality gate oxides, such as the thyristor, appear favorable for more immediate realization, despite some nontrivial drawbacks in operational circuit design and switching speed.

Some nontraditional power switch topologies have been proposed to somewhat alleviate SiC oxide and material quality deficiencies while maintaining normally off insulated gate operation. Lateral and vertical doped-channel power SiC MOSFETs and JFETs that can be completely depleted by built-in potentials at zero gate bias so that they are ‘normally off’ have been demonstrated. With the assistance of lateral surface electric field tailoring techniques, Baliga (1996) has suggested that lateral-conduction SiC power devices could deliver better power densities than traditional vertical SiC power device structures. Baliga also proposed advantageous high-voltage switching by pairing a high-voltage SiC MESFET or JFET with a lower voltage silicon power MOSFET.

Further Information

Many of the chapters on Semiconducting Devices in this work contain useful background on a variety of basic semiconductor device structures, the SiC versions of which are described here. In addition to the works referred to in this chapter, the readers are advised to see the following review paper (Buttay *et al.*, 2011) on SiC power electronic devices.

References

- Acheson, A.G., 1892. British Patent 17911 (the method has been described in Knippenberg, W.F., 1963. Growth phenomena in silicon carbide. Philips Research Reports 18, 161–274. Edited by the Research Laboratory of N.V., Eindhoven, Netherlands: Philips Gloeilampenfabriken).
- Afanasev, V.V., Bassler, M., Pensl, G., Schulz, M., 1997. Intrinsic SiC/SiO₂ interface states. Phys. Status Solidi (a) 162, 321–338.
- Agarwal, A.K., Seshadri, S., Rowland, L.B., 1997. Temperature dependence of Fowler–Nordheim current in 6H- and 4H-SiC MOS capacitors. IEEE Electr Device L. 18, 592–594.
- Baliga, B.J., 1996. Prospects for development of SiC power devices. In: Nakashima, S., Matsunami, H., Yoshida, S., Harima, H. (Eds.), Silicon Carbide and Related Materials 1995. Bristol, UK: IOP Publishing, pp. 1–6.
- Bhatnagar, M., Baliga, B.J., 1993. Comparison of 6H-SiC, 3C-SiC, and Si for power devices. IEEE T. Electron. Dev. 40, 645–655.
- Brown, D.M., Downey, E., Ghezzi, M., *et al.*, 1997. Silicon carbide MOSFET integrated circuit technology. Phys. Status Solidi (a) 162, 459–479.
- Brown, D.M., Downey, E., Kretschmer, J., *et al.*, 1998. SiC flame sensors for gas turbine controlsystems. Solid-State Electron 42, 755–760.
- Burk Jr., A.A., Rowland, L.B., 1997. Homoepitaxial VPE growth of SiC active layers. Phys. Status Solidi (b) 202, 263–280.
- Buttay, C., Planson, D., Allard, B., *et al.*, 2011. State of the art of high temperature power electronics. Mater Sci Eng: B 176, 283–288.
- Capano, M.A., Ryu, S., Melloch, M.R., Cooper Jr., J.A., Buss, M.R., 1998. Dopant activation and surface morphology of ion implanted 4H- and 6H-silicon carbide. J. Electron. Mater. 27, 370–376.
- Chow, T.P., Ramungul, N., Ghezzi, M., 1998. Wide bandgap semiconductor power devices. In: Pearton, S.J., Shul, R.J., Wolfgang, E., Ren, F., Tenconi, S. (Eds.), Power Semiconductor Materials and Devices, vol. 483. Warrendale, PA: Materials Research Society, pp. 89–102.
- Choyke, W.J., Matsunami, H., Pensl, G., 1997. Silicon Carbide – A Review of Fundamental Questions and Applications to Current Device Technology. Berlin: Wiley-VCH.

- Cooper Jr., J.A., 1997. Advances in SiC MOS technology. *Phys. Status Solidi (a)* 162, 305–320.
- Crofton, J., Porter, L.M., Williams, J.R., 1997. The physics of ohmic contacts to SiC. *Phys. Status Solidi (b)* 202, 581–604.
- Dahlquist, F., Zetterling, C.M., Ostling, M., Rottner, K., 1998. Junction barrier Schottky diodes in 4H-SiC and 6H-SiC. In: Pensl, G., Morkoc, H., Monemar, B., Janzen, E. (Eds.), *Silicon Carbide, III-Nitrides, and Related Materials*. Materials Science Forum 264–8. Switzerland: Trans Tech, pp. 1061–1064.
- Diogu, K.K., Harris, G.L., Henry, H.S., *et al.*, 1996. Implementation of a 83MHz high temperature *b*-SiC MESFET operational amplifier. In *Trans. 3rd Int. High Temperature Electronics Conf.* Albuquerque, NM: Sandia National Laboratories, pp. 160–161.
- Fazi, C., Neudeck, P., 1998. Use of wide-bandgap semiconductors to improve intermodulation distortion in electronic systems. In: Pensl, G., Morkoc, H., Monemar, B., Janzen, E. (Eds.), *Silicon Carbide, III-Nitrides, and Related Materials*. Materials Science Forum 264–8. Switzerland: Trans Tech, pp. 913–915.
- Harris, G.L., 1995. *Properties of SiC*. London: Institute of Electrical Engineers.
- Harris, G.L., Wongchotigul, K., Henry, H., *et al.*, 1994. Beta SiCSchottky diode FET invertersgrown on silicon. In: Spencer, M.G., Devaty, R.P., Edmond, J.A., *et al.* (Eds.), *Proc. 5th Int. Conf Silicon Carbide and Related Materials*. Bristol, UK: IOP Publishing, pp. 715–717.
- Held, R., Kaminski, N., Niemann, E., 1998. SiC merged p-n/Schottky rectifiers for high voltage applications. In: Pensl, G., Morkoc, H., Monemar, B., Janzen, E. (Eds.), *Silicon Carbide, III-Nitrides, and Related Materials*. Materials Science Forum 264–8. Switzerland: Trans Tech, pp. 1057–1060.
- Hunter, G.W., Neudeck, P.G., Chen, L.Y., *et al.*, 1998. SiC-based Schottky diode gas sensors. In: Pensl, G., Morkoc, H., Monemar, B., Janzen, E. (Eds.), *Silicon Carbide, III-Nitrides, and Related Materials*. Materials Science Forum 264–8. Switzerland: Trans Tech, pp. 1093–1096.
- Kimoto, T., Itoh, A., Matsunami, H., 1997. Step-controlled epitaxial growth of high-quality SiC layers. *Phys. Status Solidi (b)* 202, 247–262.
- Kordina, O., Bergman, J.P., Hallin, C., Janzen, E., 1996. The minority carrier lifetime of n-type 4H- and 6H-SiC epitaxial layers. *Appl. Phys. Lett.* 69, 679–681.
- Kordina, O., Hallin, C., Henry, A., *et al.*, 1997. Growth of SiC by “hot-wall” CVD and HTCVD. *Phys. Status Solidi (b)* 202, 321–334.
- Larkin, D.J., 1997. SiC dopant incorporation control using site competition CVD. *Phys. Status Solidi (b)* 202, 305–320.
- Lely, S., 1955. Darstellung von einkristallen von siliciumcarbid und beherrschung von art und menge der eingebautenverunreinigungen. *Ber. Deut. Keram. Ges.* 32, 229–236.
- Lloyd Spetz, A., Baranzahi, A., Tobias, P., Lundstrom, I., 1997. High temperature sensors based on metal-insulator-silicon carbide devices. *Phys. Status Solidi (a)* 162, 493–511.
- Mehregany, M., Zorman, C., Narayanan, N., Wu, C.H., 1998. Silicon carbide MEMS for harsh environments. *Proc. IEEE* 14, 1594–1610.
- Neudeck, P.G., 2000. Electrical impact of SiC structural crystal defects on high electric field devices. In: Devaty, R.P., Rohrer, G.S. (Eds.), *Silicon Carbide and Related Materials 1999*. Materials Science Forum 264–8. Switzerland: Trans Tech, pp. 1161–1166.
- Ouisse, T., 1997. Electron transport at the SiC/SiO₂ interface. *Phys. Status Solidi (a)* 162, 339–368.
- Pensl, G., Morkoc, H., Monemar, B., Janzen, E., 1998. *Silicon Carbide, III-Nitrides, and Related Materials*. Materials Science Forum 26408. Switzerland: Trans Tech.
- Pizzagalli, L., 2014. Stability and mobility of screw dislocations in 4H, 2H and 3C silicon carbide. *Acta Mater.* 78, 236–244.
- Porter, L.M., Davis, R.F., 1995. A critical review of ohmic and rectifying contacts for silicon carbide. *Mater. Sci. Eng B34*, 83–105.
- Powell, J.A., Larkin, D.J., 1997. Process-induced morphological defects in epitaxial CVD silicon carbide. *Phys. Status Solidi (b)* 202, 529–548.
- Powell, J.A., Pirouz, P., Choyke, W.J., 1993. Growth and characterization of silicon carbide polytypes for electronic applications. In: Feng, Z.C. (Ed.), *Semiconductor Interfaces, Microstructures, and Devices: Properties and Applications*. Bristol, UK: IOP Publishing, pp. 257–293.
- Ryu, S.H., Kornegay, K.T., Cooper Jr., J.A., Melloch, M.R., 1998. Digital CMOS ICs in 6H-SiC operating on a 5V power supply. *IEEE Trans. Electron Devices* 45, 45–53.
- Salmon, J.S., Johnson, R.W., Palmer, M., 1998. Thick film hybrid packaging techniques for 500°C operation. In *Trans. 4th Int. High Temperature Electronics Conf.* Piscataway, NJ: IEEE, pp. 103–108.
- Saxena, V., Steckl, A.J., 1998. Building blocks for SiC devices: Ohmic contacts, Schottky contacts, and p-n junctions. In: Park, Y.S. (Ed.), *Semiconductors and Semimetals*, vol. 52. New York: Academic Press, pp. 77–160.
- Shor, J.S., Kurtz, A.D., Grimberg, I., Weiss, B.Z., Osgood, R.M., 1997. Dopant-selective etch stops in 6H and 3C SiC. *J. Appl. Phys.* 81, 1546–1551.
- Sze, S.M., 1981. *Physics of Semiconductor Devices*, second ed. New York: Wiley-Interscience.
- Tairov, Y.M., Tsvetkov, V.F., 1978. Investigation of growth processes of ingots of silicon carbide single crystals. *J. Cryst. Growth* 43, 209–212.
- Wang, Y., Xie, W., Cooper Jr., J.A., Melloch, M.R., Palmour, J.W., 1996. Mechanisms limiting current gain in SiC bipolar junction transistors. In: Nakashima, S., Matsunami, H., Yoshida, S., Harima, H. (Eds.), *Silicon Carbide and Related Materials 1995*. Bristol, UK: IOP Publishing, pp. 809–812.
- Weitzel, C.E., Moore, K.E., 1998. Silicon carbide and gallium nitride RF power devices. In: Pearton, S.J., Shul, R.J., Wolfgang, E., Ren, F., Tenconi, S. (Eds.), *Power Semiconductor Materials and Devices*, vol. 483. Warrendale, PA: Materials Research Society, pp. 111–120.
- Xie, W., Cooper Jr., J.A., Melloch, M.R., 1994. Monolithic NMOS digital integrated circuits in 6H-SiC. *IEEE Electron Device Lett.* 15, 455–457.
- Yih, P.H., Saxena, V., Steckl, A.J., 1997. A review of SiC reactive ion etching in fluorinated plasmas. *Phys. Status Solidi (b)* 202, 605–642.
- Zhao, J.H., Tone, K., Weiner, S.R., *et al.*, 1997. Evaluation of ohmic contacts to p-type 6H-SiC created by C and Al coimplantation. *IEEE Electr. Device L.* 18, 375–377.

Scintillator Crystals

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Physical Effect and Construction of Devices

Scintillators perform the transformation of high energy radiation into visible light. Most contemporary scintillator crystals (SCs) are either halides or oxides; an overview is given in [Table 1](#). Desirable properties for SCs are high transformation efficiency, stability under the working conditions and high optical transparency. These requirements are best met by crystals with low point defect density.

High energy radiation such as α -, β -, γ -, X-rays, protons, or neutrons can interact with matter and exchange energy (inelastic interaction). The main type of interaction depends on the energy E_0 of the radiation. The photoelectric effect prevails for $E_g < E_0 < 300$ keV (E_g =energy gap), whereas Compton scattering can usually be observed at higher $E_0 > 300$ keV. Moreover, the direct transformation of energy into matter (electron–positron pair formation) becomes possible for $E_0 > 1.022$ MeV. Different scintillating amorphous materials (glasses, plastics) and crystals perform the conversion of high energy radiation into visible light with wavelength around 400 nm ($E_1 \approx 3$ eV).

The conversion proceeds in multiple steps by the repeated interaction with the scintillator material ([Fig. 1](#)), where the energy of photons is reduced by multiple interaction from E_0 to E_1 . The examination of the visible light is often possible by the naked eye; photo multiplier tubes (PMT) or photodiodes are alternative light detectors. The number of photo-electrons (ph-e⁻) N that can be registered by the light detector grows with increasing E_0 . The theoretical upper limit $N = E_0/E_1 \approx 3 \times 10^5$ for $E_0 = 1$ MeV cannot be reached as a part of the incoming energy is wasted in nonradiative processes. The light yield for the highly effective scintillator crystal CsI(Tl) is $N \approx (5...6) \times 10^4$ ph-e⁻ MeV⁻¹ (cf. [Table 2](#)). Some ‘modern’ materials such as BaBrI ([Bouret-Courchesne et al., 2010](#)) are not daltonide compounds with fixed stoichiometry, but solid solutions (in this case between BaI₂ and BaBr₂). Especially compounds of the heavier halogens bromine and iodine, such as SrI₂, are often very hygroscopic or sensitive against oxygen and crystal growth as well as subsequent handling require special care ([Guguschev et al., 2014](#)).

One crucial property of the scintillator is the absorption coefficient α . It allows to describe the loss of intensity $I(E_0) = I_0 \exp[-\alpha z]$ of the incoming radiation of energy E_0 within the material depth z . At the absorption edge ($E > E_g$) the absorption reaches values of typically $\alpha = (10^5...10^6)$ cm⁻¹. For energies far above E_g the coefficient was found to drop according to the empirical relation $\alpha \sim Z_{\text{eff}}^4/E_0^3$ ($Z_{\text{eff}} = Z - \sigma_n$ is the average effective atom number, $\sigma_n \ll Z$ is the shielding due to electrons). Materials that contain atoms with high Z numbers are especially suitable for scintillator applications. Information on the spectral composition of the incident radiation can be obtained from the time dependent spectra of the emitted light (decay time of light intensity τ_d).

Particles with energy of about 100 keV can give rise to X-ray transitions, if elements with high atomic number are present within the material. The lifetime of excited states is usually short ($\tau \approx 10^{-15}$ s) and results, due to the Heisenberg relation $\Delta E \cdot \tau \geq \hbar$, in natural line widths of $\Delta E \approx 1$ eV. Desirable properties are:

Table 1 Scintillator crystals

Full name	Chemical formula	Abbreviation
Cesium iodide (Tl doped)	CsI(Tl)	–
Cesium fluoride	CsF	–
Sodium iodide (Tl doped)	NaI(Tl)	–
Calcium fluoride (Eu doped)	CaF ₂ (Eu)	–
Barium chloride	BaCl ₂	(ceramic)
Barium fluoride	BaF ₂	–
Strontium iodide	SrI ₂	–
Lanthanum bromide	LaBr ₃ (Ce, Ba)	–
Bismuth germanate	Bi ₄ Ge ₃ O ₁₂	BGO
Bismuth silicate	Bi ₄ Si ₃ O ₁₂	BSO
Lead tungstate	PbWO ₄	PWO
Cadmium tungstate	CdWO ₄	CWO
Yttrium aluminate (Ce doped)	YAlO ₃ (Ce)	YAP(Ce) = YALO(Ce)
Lutetium aluminate (Ce doped)	LuAlO ₃ (Ce)	LuAP(Ce)
Gadolinium orthosilicate (Ce doped)	Gd ₂ SiO ₅ (Ce)	GSO(Ce)
Lutetium orthosilicate (Ce doped)	Lu ₂ SiO ₅ (Ce)	LSO(Ce)
lutetium yttrium orthosilicate	Lu _{≈0.6} Y _{≈1.4} SiO ₅ (Ce)	LYSO(Ce, Ca)
Zinc sulfide	ZnS	–
Cadmium telluride	CdTe	–

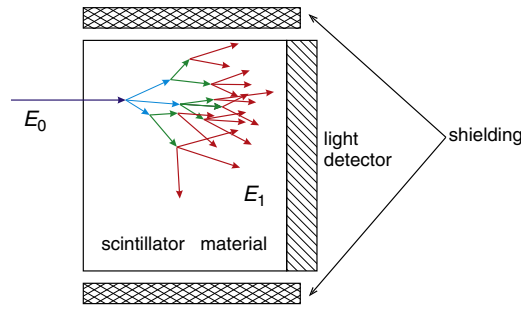


Fig. 1 Principle of a scintillator detector. Usually photo multiplier tubes (PMT) or photodiodes are used as light detector.

Table 2 Melting temperature, density, effective Z number, emission maximum, photoelectron yield and decay time for some halide scintillator crystals

	T_m ($^{\circ}\text{C}$)	ρ (g cm^{-3})	Z_{eff}	$\lambda_{\text{em}}^{\text{max}}$ (nm)	yield ($\text{ph-e}^{-}/\text{MeV}$)	τ_d (ns)
CsI(Tl)	621	4.51	54	550	52 000...56 000	3500/600
NaI(Tl)	651	3.67	50	415	38 000	230
$\text{CaF}_2(\text{Eu})$	1418	3.18	17	435	19 000	940
BaF_2	1354	4.88	53	310	10 000	630/0.8
CsF	682	4.63	53	390	2000	5
$\text{BaBr}(\text{Eu})$	>710	5.2		413	$81\,000 \pm 3000$	297/482

- Emission maximum close to 400 nm to match the maximum sensitivity of PMTs.
- Refractive index close to 1.5 to obtain maximum optical coupling to the PMT input window that is usually made of glass.
- Short τ_d to obtain good temporal resolution.
- High absorption for the incident radiation.
- High conversion rate from E_0 to E_1 with low nonradiative background.
- Low absorption for the generated light.
- Stability under harsh working conditions (hard radiation, high T , mechanical shocks).

In low Z materials as plastics or some glasses, the Compton effect dominates over a broad range ($20 \text{ keV} \lesssim E_0 \lesssim 10 \text{ MeV}$) and no single peaks can be observed in the spectrum. Accordingly, low Z scintillators are used if no energy information of the incidenting radiation is needed. In the following, only crystalline scintillator materials will be considered.

Growth of SCs

The growth of crystals with applications in high energy radiation will not be discussed here in detail, but the main scintillators are listed below for sake of completeness:

- (a) ZnS. For SC applications the material is often doped with Ag. The typical photoelectron yield is ca. 25% of NaI(Tl) for γ radiation. The material is often used as polycrystalline powder for screens. Single crystals can be obtained by gas phase transport. Growth from the melt is difficult, as ZnS melts only under high pressure at $T_m^{\text{ZnS}} \simeq 1800^{\circ}\text{C}$. Depending on the crystallization conditions, ZnS crystallizes either in the hexagonal wurtzite or in the cubic zincblende structure. As the difference between both structures consists only in a different stacking of Zn-S planes, poly-types are rather frequent.
- (b) ZnSe, CdTe. Gas phase transport, Vertical Bridgman (VBr), or traveling heater method (THM) crystals of both chalcogenides and of solid solutions (Cd, Zn)Te with high resistivity are used as detectors for high energy radiation (security screening, astrophysical research).

The application of different SCs is often restricted by the available crystal size. The requirements for a crystal to be used as scintillator include a size of typically at least $1 \times 1 \times 1 \text{ cm}^3$ and a sufficiently high absorption $\alpha(E_0) \gtrsim 0.1 \text{ cm}^{-1}$. Such requirements can be met by nearly all substances mentioned here. On the other hand, imaging techniques such as positron emission tomography (PET), computer tomography (CT), X-ray telescopes or luggage scanning need either arrays of up to 10 000 SCs or larger crystals of up to ca. 50 cm diameter.

Table 3 Melting temperature, density, effective Z number, emission maximum, photoelectron yield and decay time for some oxide scintillator crystals

	T_m (°C)	ρ (g cm ⁻³)	Z_{eff}	λ_{em}^{max} (nm)	yield (ph-e ⁻ /MeV)	τ_d (ns)
Bi ₄ Ge ₃ O ₁₂	1050	7.13	75	480	8 000...10 000	300/60
PbWO ₄	1120	8.28	73	420	11...14	30/2
CdWO ₄	1325	7.9	65	470	12 000...15 000	14 000
YAlO ₃ (Ce)	1875	5.55	36	350	18 000	27
LuAlO ₃ (Ce)	1910	8.34	65	350	14 000	18
Gd ₂ SiO ₅ (Ce)	1950	6.71	59	430	12 500	60
Lu ₂ SiO ₅ (Ce)	2150	7.41	66	420	25 000	40

SCs are used for the registration of hard radiation. This hard radiation can lead to the formation of structural defects in the crystal and therefore to damage of the detector. Usually point defects (vacancies, interstitials) are produced, if the kinetic energy that is transferred from the incident particle or photon to one atom of the crystal exceeds the binding energy of this atom. Crystal structures with 'heavy' atoms have not only the advantage of high α but also of the high inertia of these high Z atoms. Generally, the lattice energy and therefore the activation energy for the formation of structural defects is positively correlated with the melting point. Therefore the most stable (with respect to radiation hardness) SCs are found among the oxides with extremely high T_m mentioned in [Table 3](#).

Chemical purity (absence of contaminants besides intended doping) of the SCs is very important for radiation hardness, as the local inhomogeneity around extrinsic point defects formed by foreign atoms usually lowers the activation energy for the formation of more extended defects as vacancy clusters. On the other hand; extended defects such as dislocations or even grain boundaries do often not prevent effective scintillation. For example, BGO scintillates as single crystal, as thin film, and even as ceramic material. The absence of extended defects is important, if scintillation light from large crystal volumes has to be collected within a light detector. Otherwise intrinsic light loss by scattering would reduce the yield of the SC.

SCs are usually grown from the melt by the VBr or Czochralski (Cz) methods. For data sheets and general reading about radiation measurements the reader is reminded to the homepage of 'Saint-Gobain Crystal Scintillation Products' [Saint-Gobain \(2015\)](#). Recommended review articles on SCs are by [Ishii and Kobayashi \(1992\)](#), [Melcher et al. \(1991\)](#), and more recently by [Yoshikawa et al. \(2013\)](#).

Halides

Halide crystals for scintillators and other optical applications are usually grown by VBr, but the growth by Cz was reported too. [Gugushev et al. \(2014\)](#) reported the application of floating dies, for example, of graphite for halide crystal pulling, which help to stabilize the shape of the growing crystal. For large SCs with volumes of ≥ 1000 cm³ extreme purity is especially important for obtaining high transparency in the optical region. Otherwise, the scintillation light would not reach the SC surface. As VBr works usually with smaller T gradients G_T than Cz, the former method provides large halide crystals with reduced thermal stresses. Graphite is chemically inert to halide melts and is usually applied for crucibles and constructive parts.

An interesting method for the pulling of large alkali halide crystals (diameter ≤ 450 mm, mass ≤ 300 kg, pulling rate ca. 6 mm h⁻¹) was reported by [Zaslavsky \(1999\)](#). In this method, a conical platinum crucible is connected to a feeder containing the molten starting material. The melt is supplied to the conical crucible using an inert gas pressure. As the melt height in the crucible is set to exceed only slightly the actual diameter of the growing crystal, the free surface of the melt is very small, leading to negligible evaporation losses of the activator thallium.

Halides are, typically in the order $I^- < Br^- < Cl^- < F^-$, sensitive against hydrolysis with traces of moisture that can be present in the starting materials or in the growth atmosphere. At $p_{total} = 1$ bar and $T = 690$ °C (69 K above $T_m^{(CsI)}$ or 8 K above $T_m^{(CsF)}$, respectively), the chemical reactions



where (X=I, F) have the following equilibrium constants:

$$K^{(CsX)} = \frac{[CsOH][HX_{(gas)}]}{[CsX][H_2O_{(gas)}]} \quad [2]$$

$K^{(CsI)} = 2.4 \times 10^{-10}$ and $K^{(CsF)} = 1.1 \times 10^{-5}$. Graphite is an advantageous crucible material for halides, as the chemical reaction



helps to remove water from the system and thus to avoid hydrolysis (1). If carbon is heated under wet Ar (1 ppm H₂O) up to the T_m of CsI, NaI, or CsF (600 °C range), then $p_{H_2O} \gg 10^{-6}$ bar drops from 10^{-6} bar to a few 10^{-12} bar. Upon heating to the melting point of CaF₂ (1418 °C) $p_{H_2O} \gg 10^{-15}$ bar, thus drastically reducing the fluoride hydrolysis.

The earth alkali fluorides CaF₂ and BaF₂ exhibit considerably higher melting points as compared to the alkali halides. Melting can lead therefore to the transformation of hydroxides into oxides. As the solubility of the oxides in the fluoride crystals is small, scattering centers (precipitates) that decrease the optical transparency may form. Moreover, the highly reductive conditions within the graphite crucibles can lead to the reduction $Me^{2+} \rightarrow Me^+ \rightarrow Me$ and to the formation of color centers. In the following the main properties of halides are outlined:

NaI(Tl), CsI(Tl) NaI(Tl) is the most common SC due to its high visible light yield; the crystals convert about 12% of the γ -ray energy into $E_1 = 3$ eV photons. Cesium iodide and sodium iodide (undoped and more often doped with Tl) are grown up to 50 cm in diameter by VBr. Both substances are at least slightly hygroscopic. The emission maximum at 550 nm is not well matched to the maximum sensitivity of PMTs but rather to the sensitivity of photodiodes.

CsF is an effective SC with short τ_d ; but unfortunately very hygroscopic.

BaF₂, CaF₂(Eu) Both cubic crystals are usually grown under vacuum (to reduce $p_{H_2O} \gg 10^{-6}$ bar) by VBr from graphite crucibles. BaF₂ is the fastest known scintillator. Its scintillation exhibits two decay constants that may be used to obtain spectral resolution of the incident radiation, as the ratio between both components depends on the ionizing ability of the incident radiation. CaF₂ is a slow SC. Its low $Z_{eff}^{CaF_2} = 17$ (as compared to $Z_{eff}^{BaF_2} = 53$) makes calcium fluoride an ideal material for the detection of β -particles.

Oxides

Oxides in the oxidation state m are always in equilibrium with some finite oxygen partial pressure $p_{O_2}^{eq}$. If p_{O_2} the ambient is $> p_{O_2}^{eq}$, through the reaction



the higher valent $MeO_{(m+1)/2}$ can be formed. As $p_{O_2}^{eq}$ rises with T , higher p_{O_2} have to be maintained for very high melting oxides. Ellingham diagrams represent the stability ranges for the oxides with different valencies that are nearly linear in the $T - RT \ln p_{O_2}$ plane. For more details the reader is referred to [Pelton \(1991\)](#) and [Klimm et al. \(2009\)](#). **Fig. 2** gives an overview on the $p_{O_2}^{eq}(T)$ for different pure oxides and provides an estimation about the stability range of mixed oxide melts. An annealing treatment under defined p_{O_2} adjust the valency of some metal ions (e.g., Pb^{2+} in the case of PWO) to the desired level.

Many metals that can be formed if oxides are heated above the stability range for the corresponding p_{O_2} (Pb, Cd, Bi, Ga) can alloy with Pt and other noble metals. The T_m of such alloys are usually much lower than $T_m^{(Pt)}$. Adequate $p_{O_2} > p_{O_2}^{eq}(T)$ have to be applied in such cases.

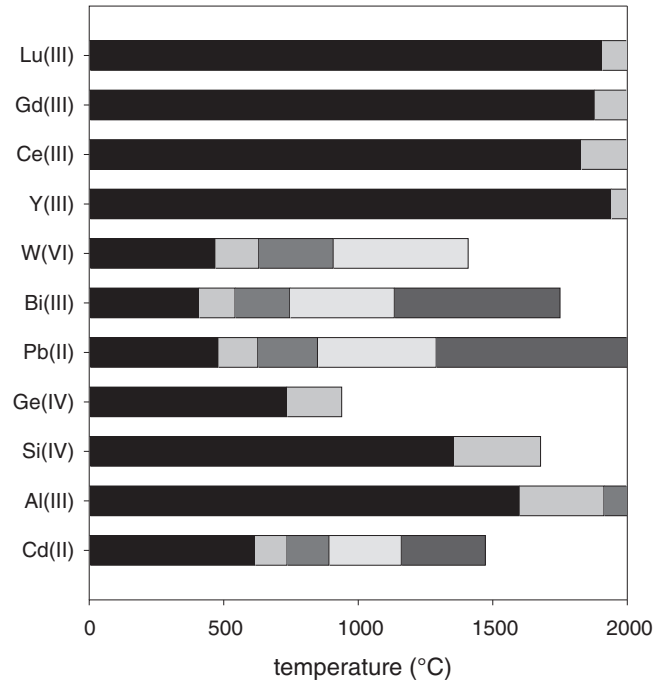


Fig. 2 Stability regions of different metal oxides. The subsequent bars mark (from the left to the right) the stability ranges for (a) $p_{O_2} < 10^{-20}$ bar, (b) 10^{-20} bar $\leq p_{O_2} \leq 10^{-15}$ bar, (c) 10^{-15} bar $\leq p_{O_2} \leq 10^{-10}$ bar, (d) 10^{-10} bar $\leq p_{O_2} \leq 10^{-5}$ bar, (e) 10^{-5} bar $< p_{O_2} \leq 1$ bar on the T axis.

The growth of oxides with medium $T_m \lesssim 1500^\circ\text{C}$ is usually performed in conventional Cz setups using resistive or rf heating. Platinum or Pt alloys are the conventional materials for crucibles, seed holders, and other constructive parts that are in contact to the melt, as Pt is almost stable against metal oxide melts if heated under air with $p_{\text{O}_2} \cong 0.2$ bar. Bismuth germanate ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$), bismuth silicate ($\text{Bi}_4\text{Si}_3\text{O}_{12}$, not treated here in detail) and the tungstate SCs from the upper part of Table 3 can be grown by this method. More problems arise upon the growth of oxide crystals with $T_m \gtrsim 1500^\circ\text{C}$ where Pt cannot be used. Iridium can substitute Pt in this higher T range; but Ir has some drawbacks compared to Pt in addition to substantial higher production costs: (1) Below $T \simeq 1200^\circ\text{C}$ Ir should only be heated in oxygen-free atmosphere ($p_{\text{O}_2} \lesssim 10^{-5}$ bar), as the formation of volatile IrO_2 destroys the metal. Even above 1200°C only $p_{\text{O}_2} \leq 10$ mbar should be used. (2) Brittleness and porosity of Ir parts are, depending on the production technology, usually considerably higher than those of Pt.

Some high melting oxides from the bottom part of Table 3 can be grown under almost oxygen-free atmosphere ($p_{\text{O}_2} \lesssim 10^{-15}$ bar) by Cz from molybdenum or tungsten crucibles. Both metals are more noble than the RE metals or Al, respectively, and less expensive than Ir. Petrosyan *et al.* (1998) reported the VBr growth of lutetium orthoaluminate (LuAP) within Mo tubes under Ar/ H_2 atmosphere ($T_m^{(\text{LuAlO}_3)} = 1900^\circ\text{C}$).

The highest-melting SCs are RE aluminates or RE silicates. The stability ranges for the RE(III) oxides (Fig. 2) are widely extended to very low p_{O_2} . Therefore, the application of fairly reductive atmospheres without reduction of the oxide to the RE metal is possible. Y_2O_3 behaves here very similar to the true rare earth metal oxides Lu_2O_3 , Gd_2O_3 , Ce_2O_3 . It should be mentioned, that even nominally ‘inert’ atmospheres as Ar are not really inert. A 5N noble gas contains 10^{-5} bar impurities that might be either oxidative (O_2) or reductive (e.g., H_2 , CO , CH_4). Accordingly, the behavior of the melt within such ‘inert’ atmospheres can be highly unpredictable. Alumina is for $p_{\text{O}_2} \geq 10^{-14}$ bar stable up to the melting points of all SCs from Table 3.

Ce_2O_3 is nearly as stable as the other RE(III) oxides under reductive atmosphere; but behaves differently under oxidizing atmosphere. Then oxidation $\text{Ce}_2\text{O}_3 \rightleftharpoons \text{CeO}_{1.72} \rightleftharpoons \text{CeO}_{1.82} \rightleftharpoons \text{CeO}_2$ takes place. At $T = 1600^\circ\text{C}$ the oxygen content at which the intermediate cerium oxides with mixed valency are stable is in the 10^{-10} bar $\lesssim p_{\text{O}_2} \lesssim 10^{-5}$ bar range and shifts upwards with T . The yellow color of some Ce doped SCs is due to the partial oxidation $\text{Ce(III)} \rightleftharpoons \text{Ce(IV)}$ and can often be bleached by annealing the crystals in suitable atmosphere.

Usually RE aluminates and silicates are grown by Cz with inductive heating. Coupling the rf heating energy directly to the crucible wall allows to obtain temperatures of up to $T_m \simeq 2200^\circ\text{C}$. Careful adjustment of the temperature gradients to values of typically $G_T \lesssim 30 \text{ K cm}^{-1}$ near the liquid/solid interface of the growing crystal and within the crystal has however to be performed. Both afterheaters and thermal insulation can reduce the high G_T that are typical for rf heated Cz growth, and avoid thermal cracking and overheating of the melt. If the heat insulation of the crucible wall is insufficient, the melt in the vicinity of the walls is strongly overheated and intensely evaporates, which can result in the change of the melt stoichiometry (cadmium tungstate, lead tungstate), in the formation of metastable phases (bismuth silicate), or in fracture of the crucible (lutetium orthosilicate, gadolinium orthosilicate, lutetium aluminum perovskite). Reiche *et al.* (1985) showed that bottom heaters can suppress the crystallization on the crucible bottom. A typical setup for the growth of high T_m oxides is shown in Fig. 3. Felt, grains, and ceramic parts are either made of alumina or, for the highest T_m , zirconia. However, the application of zirconia ceramics has to be performed with caution, as the electric conductivity of ZrO_2 rises drastically for $T \gtrsim 1000^\circ\text{C}$. Dangerous discharges can often be avoided by separating the induction coil from the zirconia ceramic with a fused silica tube.

The growth of oxides with high melting point is expensive for a number of reasons:

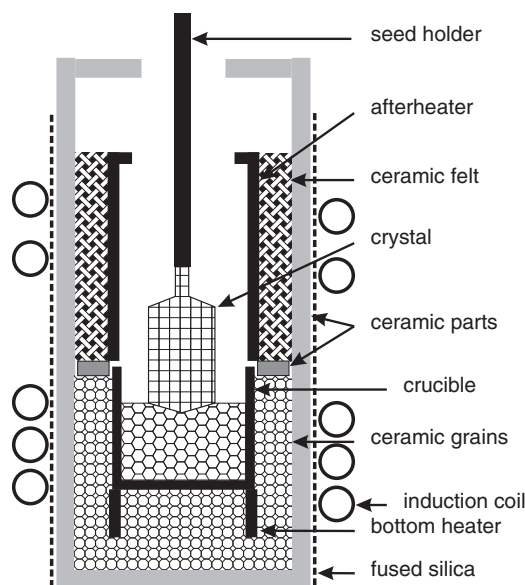


Fig. 3 Cz-growth setup for oxides with $T_m \gtrsim 1500^\circ\text{C}$.

- (a) The energy consumption is high.
- (b) The experimental setups (Fig. 3) are complicated and Ir (instead of Pt) has to be used.
- (c) Crucible erosion increases considerably with T .
- (d) Many RE oxides and even SiO_2 with high purity ($\geq 4\text{ N}$) are expensive.

For these reasons the mass production of such crystals (except YAG that is also used for laser applications) is restricted. Low melting point SCs, such as NaI or BGO, are nowadays the ‘working horses’ for most applications. Nevertheless, the superior properties of some modern SCs as Lu_2SiO_5 , Gd_2SiO_5 , or Y_2SiO_5 in terms of radiation hardness and thermal stability, allow to expect a growing demand for these new materials, particularly if large dimensions are not necessary.

PWO The growth of $\gtrsim 300\text{ mm}$ long boules by the Cz method employing resistive or rf heating has been reported by different authors. Quantum yield and radiation hardness depend considerably on the growth atmosphere and are found to degrade if the crystal deviates from the exact stoichiometry. Namely, point defects such as Pb^{3+} , O^- , and F centers are responsible for the slow scintillation decay component and for the afterglow. Furthermore, the tetragonal crystals exhibit a cleavage plane (001) that can cause fractures during growth or processing of the boules. The yellow color of some crystals is usually not due to impurities of the starting material but connected with excess oxygen during growth and subsequent annealing. This leads to an absorption band peaked at 430 nm.

CWO Remarkable results (crystal diameter 55 mm, length 250 mm) were reported from Kharkov, Ukraine by Bondar *et al.* (1997); but the material can be prepared in thin films as well, for the detection of α - and β -particles. Negative effects related to non-stoichiometry and impurities occur like in the case of PWO. Possible impurities are ^{232}Th and ^{226}Ra . These are especially crucial for scintillator applications and can lead to background activities of typically $10\text{ }\mu\text{Bq kg}^{-1}$.

CdWO_4 and ZnWO_4 are the only pseudo-binary compounds formed by the systems CdO (or ZnO)– WO_3 . In both cases these pseudo-binary compounds are considerably more stable against thermal decomposition and/or evaporation at elevated T than the simple metal oxides.

BGO This material can be used for scintillator applications as single crystal, as thin film and as ceramic product. Usually boules of up to 15 cm diameter are grown by Cz, but growth by VBr was reported too. The scintillation efficiency of BGO depends strongly ($\simeq 1\%\text{K}^{-1}$) on temperature.

The abbreviation BGO is used for both bismuth germanates $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ and $\text{Bi}_{12}\text{GeO}_{20}$; only the former is used as SC. The growth is usually performed from Pt crucibles, but unfortunately Pt is partially solved by the melt and can form metallic inclusions within the crystal. Low thermal gradients must be used in order to avoid overheating and the loss of Bi_2O_3 by evaporation.

YAP(Ce) (=YALO), LuAP(Ce) All three binary yttrium aluminates with different stoichiometry ratio have $T_m > 1800^\circ\text{C}$. Both garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$, YAG) and perovskite are important for laser as well as for scintillator applications. Petrosyan *et al.* (1998) described growth and properties of LuAlO_3 (LuAP).

LSO(Ce), GSO(Ce), LYSO(Ce) These RE orthosilicates crystallize monoclinic. GSO shows high anisotropy of the thermal expansion and of the elastic constants. Careful adjustment of the thermal gradients and growth along the b axis were reported to reduce cleavage problems in Cz crystals. Boule dimensions can reach a diameter of 80 mm and a length of 280 mm. Crystal color as well as surface quality depend on the oxygen content in the growth atmosphere (usually N_2). $\text{Y}_2\text{SiO}_5(\text{Ce})$ can also be grown from stoichiometric melts by Cz, but some other RE orthosilicates as Ce_2SiO_5 and La_2SiO_5 were reported to melt incongruently.

These crystals combine high efficiency, short decay time, and excellent radiation hardness with high thermal stability of the scintillation properties. They SCs have mainly been established in the last decade and can be regarded as good potential materials. Unfortunately, the extremely high $T_m^{(\text{Lu}_2\text{SiO}_5)} \simeq 2150^\circ\text{C}$, that is close to the breakdown of Ir crucibles, and the high price of Lu_2O_3 restrict the availability of single crystals.

Summary

NaI(Tl) and other low melting point halide crystals are often used as SCs. They are suitable for ‘easy’ working conditions (T , p , energy of radiation). Boule diameters up to 50 cm can be obtained. Hydrolysis of the halides must be avoided to obtain high optical quality. $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ or different tungstates represent alternatives. The main defects that are introduced during oxide crystal growth are connected with the maintenance of the desired valency level. RE silicates and aluminates exhibit extremely good SC properties, but due to their high T_m the growth of crystals is difficult and expensive.

References

- Bondar, V.G., Burachas, S.F., Katrunov, K.A., Martynov, V.P., Ryzhikov, V.D., 1997. Effects of structure microdefects on scintillation and photostimulated properties of CdWO_4 crystals. SPIE Proc 3359 (1997), 530–533.
- Bourret-Courchesne, E.D., Bizari, G., Hanrahan, S.M., *et al.*, 2010. $\text{BaBr}_2\text{:Eu}^{2+}$, a new bright scintillator. Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip 613, 9597.

- Gugushev, C., Calvert, G., Podowitz, S., *et al.*, 2014. The application of floating dies for high speed growth of CsI single crystals by edge-defined film-fed growth (EFG). *J. Cryst. Growth* 404, 231–240.
- Ishii, M., Kobayashi, M., 1992. Single crystals for radiation detectors. *Cryst. Growth Charact. Mater.* 23, 245–311.
- Klimm, D., Ganschow, S., Schulz, D., *et al.*, 2009. Growth of Oxide Compounds under Dynamic Atmosphere Composition. *J. Cryst. Growth* 311, 534–536.
- Melcher, C.L., Schweitzer, J.S., Manente, R.A., Peterson, C.A., 1991. Application of single crystals in oil well logging. *J. Cryst. Growth* 109, 37–42.
- Pelton, A.D., 1991. In: Cahn, R.W., Haasen, P., Kramer, E.J. (Eds.), *Materials Science and Technology*, vol. 5. Weinheim: VCH, p. 1991.
- Petrosyan, A.G., Shirinyan, G.O., Pedrini, C., *et al.*, 1998. Bridgman Growth and Characterization of $\text{LuAlO}_3\text{-Ce}^{3+}$ Scintillator Crystals. *Cryst. Res. Technol.* 33, 241–248.
- Reiche, P., Hermeneit, B., Schultze, D.A., 1985. Modified Heater System for RF-Czochralski Equipments. *Cryst. Res. Technol.* 20, 845–849.
- Saint-Gobain Cristaux, Nemours CEDEX, 2015. France, Available at: <http://crystals.saint-gobain.com/ScintillationMaterials.aspx> (accessed 05.08.15).
- Yoshikawa, A., Chani, V., Nikl, M., 2013. Czochralski growth and properties of scintillating crystals. *Acta Phys. Pol. A* 124, 250–264.
- Zaslavsky, B.G., 1999. Automated pulling of large-diameter alkali halide scintillation single crystals from the melt. *J. Crystal Growth* 200, 476–482.

Ceramics for Laser Technologies

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Introduction

Solid-state lasers have been studied since the discovery of laser in the 1960s (Maiman, 1960), and have since found a vast range of applications from materials production industry to medicine, analytical methods, metrology or defense, with single crystals as the active medium. After the discovery of synthetic yttrium aluminum garnet (YAG, $\text{Y}_3\text{Al}_5\text{O}_{12}$) as a nearly ideal laser host and the successful laser tests of Nd:YAG at room temperature by Geusic *et al.* (1964), YAG with rare earth doping became the material of choice thanks to the narrow emission linewidth and reasonably long fluorescence lifetime. Until now YAG single crystals are still the most commonly used solid-state laser host. Although there have been successful laser tests with polycrystalline gain media already in the early years of the “laser era”: Dy:CaF₂ (Hatch *et al.*, 1964) laser under cryogenic conditions, and later in the 1970s Nd:Y₂O₃-ThO₂ (Greskovich and Chernoch, 1973), the tests remained at the laboratory level, since these materials could not compete with the optical quality of single crystals. Another important group of laser host materials are glasses. Since the focus of this chapter is on ceramic materials, neither glass nor single crystal laser materials will be discussed here, except for comparison.

Ceramic laser gain media are single-phase polycrystalline materials, mainly with cubic crystalline structure, doped with active laser ions, the transition metals or lanthanides. All laser gain media have the stringent requirement of transparency in the wavelength range of the absorption and emission range, they need to allow the incorporation of the active ion in their crystal structure, and they must have the thermal and mechanical properties to withstand the laser operation. Moreover, compared to transparent ceramic materials for other applications (phosphors, light converters, protective windows), the optical quality of laser gain media must be very high, and microstructure as pore-free as possible.

While there has been interest in the production of polycrystalline laser gain media, and of transparent ceramics in general, the optical quality of ceramics was not high enough to allow laser emission for practical use.

The first understanding of the possibility to reach transparency in ceramics probably arose from Coble's work on translucent alumina. The use of a pure powder, sintering additive and a specific controlled sintering atmosphere showed the direction that later led to the production of transparent ceramics. In 1984, de With and van Dijk (1984) and in 1990 the group of Sekita together with Yanagitani from the Konoshiba Chemical Company (Sekita *et al.*, 1990) reported on the production of translucent and transparent YAG ceramics, respectively, but the optical quality was still not sufficient for laser emission. Finally, Ikesue *et al.* (1995) presented Nd:YAG laser ceramics produced by reactive sintering of oxides under vacuum with the use of a sintering aid, and later on, 1.46 kW of output power was reported with the use of a ceramic Nd:YAG laser rod prepared from precipitated YAG powder (Lu *et al.*, 2002).

The research of transparent ceramics for laser applications has made a leap ahead in the past decades in the understanding of the conditions and processes leading to materials of high optical quality, and in the preparation and testing of new materials. Although in mass production transparent ceramics still do not replace single crystals, they already find practical applications, especially where they overperform single crystals.

The ceramic production process provides a series of advantages over the traditional single crystal melt-growth techniques:

- *Production conditions*

Production wise, while in the Czochralski crystal growth method the material has to be melted and the growth times can reach tens of days depending on the crystal size, ceramic sintering occurs at temperatures often few hundreds of °C below the melting temperature, and last from hours to tens of hours, depending on the production method.

- *Dopant concentration*

Avoiding the presence of melt, the segregation of ions in ceramics is significantly limited, allowing higher concentrations of dopant ions in the host: while the maximum concentration of Nd in Czochralski-grown YAG single crystals is 2%–2.5% (The notation used for the concentration of dopants in garnets describes the amount of doping ions which substituted the ions in the crystal lattice of the host. In the case of 1% Nd:YAG this means that one 1% of Y³⁺ ions were substituted by Nd³⁺ ions, and the chemical formula is Nd_{0.03}Y_{2.97}Al₅O₁₂), Nd:YAG ceramics were produced with Nd doping as high as 8% (Dubinskii *et al.*, 2005).

- *Shaping flexibility*

Perhaps the most important advantage of transparent ceramics is the high flexibility of the production process, particularly in terms of near-net-shaping and of the spatial control of the distribution of the doping ions. The production of single crystal components is expensive also because it requires cutting and machining from the as-grown boule to the final shape. Moreover, there are growth-induced inhomogeneities (core and facets related to the orientation of the crystal seed, variation in composition along the growth direction, segregation of doping ion), which further limit the final-part to grown-crystal volume ratio, i.e., there is a significant amount of scrap material from the production of single crystal components.

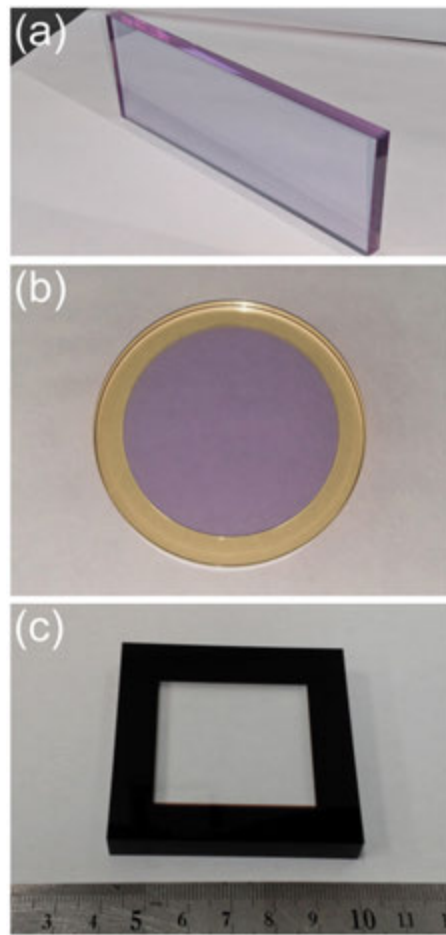


Fig. 1 Laser ceramics produced by Konoshima Chemical Corp.; Nd:YAG slab $160 \times 60 \times 8 \text{ mm}^3$ (a), Nd:YAG with Sm:YAG edge cladding, 100 mm in diameter with Sm:YAG thickness of 10 mm and 10 mm thick (b) and Yb:YAG with Cr:YAG edge cladding (c). Courtesy Konoshima Chemical supported by Baikowski Japan.

- *Spatial control of composition*

In the case of components with non-uniform dopant distribution, some geometries may be produced also from single crystals by bonding. This process, however, requires expensive high-precision polishing, and is used for planar bonded interfaces. Ceramic processing offers a number of shaping methods that allow the production of such structures in the green state, i.e., during the shaping of powders or after a light pre-sintering, providing then a composite structure with well controlled distribution of the dopant(s) without the need of additional post processing.

- *Size*

Ceramic technology also allows the production of larger components (at least in two directions) than single crystals, e.g., the large-aperture amplifiers for high-power laser research facilities, which often have an edge cladding with a different dopant (see Section Applications, beyond the state of the art.), as illustrated in Fig. 1.

On the other hand, laser-quality transparent ceramics are difficult to obtain and even a slight variation in the production process parameters can deteriorate the final performance. The main challenge in the preparation of transparent ceramics for lasers is the elimination of porosity and second phases, which has to be dealt with at every step of the fabrication process. Up to now, the reproducibility of the production of transparent ceramics is one of the factors limiting their commercial use.

Optical Transparency

Transparency of a material depends mainly on its composition and microstructure. The former is an important issue for the primary choice of the material itself. In the particular case of laser host materials, they have to be transparent in the range of wavelengths of interest (absorption, emission) in order to allow laser oscillation, i.e., the crystal host should not interfere with the

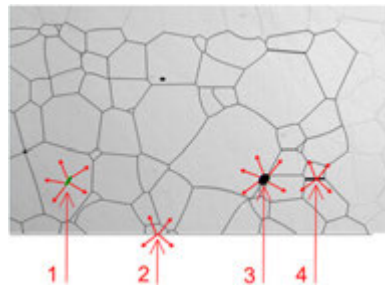


Fig. 2 Illustration of the scattering of light in optically isotropic transparent ceramics: scattering by secondary phases (1), surface roughness (2), porosity (3) and on a grain boundary (4).

passing radiation. This depends on the structure of the electron energy bands of the material; for the range from UV or visible to NIR, transparent materials are mostly oxides, halides and chalcogenides.

Theoretical transmittance of a material (when absorption is neglected) may be calculated from its refractive index, as described by Eq. (1), which considers transmission losses only due to Fresnel reflection on the two faces of the material at normal incidence. Messing's group proposed to reserve the term *transparent* for ceramics with in-line transmittance at least 95% of the theoretical value, to distinguish truly transparent ceramics from translucent ones (Kochawattana *et al.*, 2008).

$$T_{th} = \frac{2n}{n^2 + 1} \quad (1)$$

As already mentioned above, the transparency of ceramic materials is strongly affected by the microstructure, in particular by inhomogeneities acting as scattering centers.

Transparent ceramics are polycrystalline materials composed of usually randomly oriented grains in the size range from tens of nm to tens-hundreds of μm . In the case of optically anisotropic materials, viz. materials with a non-cubic crystalline structure where the refractive index varies with the orientation of the crystal, different orientation of the single grains can cause losses in direct transparency due to birefringence. Although it is possible to produce transparent ceramics with a non-cubic crystal structure, it is very difficult to achieve the optical quality suitable for laser applications. Approaches to solve this issue are discussed later.

In optically isotropic ceramics, where the issue of birefringence is not present for the wavelengths of interest (Burnett *et al.*, 2001) the scattering centers are mostly pores and second phases. Light scattering occurs on heterogeneities of the optical medium; the most typical scattering sources in a transparent ceramic material are illustrated in Fig. 2.

The presence of second phases may in most cases be prevented by a careful control of composition, use of highly pure materials and by avoiding contamination during the production process. A single-phase material is required for laser-quality transparent ceramics, since any additional phase in the system with a different refractive index will scatter light. It has to be said that, unlike single crystals technology, ceramic processing requires also a favorable powder morphology in order to obtain defect-free materials. The combination of high purity, desired particle size distribution and spherical shape is a difficulty faced by many producers and researchers in the field of transparent ceramics; often the solution lies in in-house precipitation of powders (Sanghera *et al.*, 2011a). Second phases may be also present in the form of nanometric crystallites at grain boundaries, which may appear at slow cooling rates after sintering and cause both scattering losses and decrease in laser efficiency (Ikesue *et al.*, 2006).

The presence of porosity, on the other hand, is inherent to ceramic materials, which are made by the sintering of powders. However, whereas conventional ceramics with 99.9% of the theoretical density would already be considered fully dense materials, in the case of transparent ceramics, 0.1% porosity can reduce the in-line transmittance even to zero. The effect of pores on scattering is usually higher than that of secondary phases, because the difference between refractive index of the material and the pore is larger. For practical purposes, it does not make a difference whether the pore is void or contains air or other gas introduced during the material fabrication process, as these have a significantly lower refractive index than solids, usually very close to unity.

The intensity of scattering depends on the wavelength of the incident light and on the size of the scattering center: when the two are close, the scattering intensity increases. In the visible-to-NIR range, the effect of micrometer-sized pores and defects is much higher compared to that of finer porosity. In laser ceramics the requirement of a microstructure free of scattering centers is even more stringent as scattering of light leads directly to losses in laser efficiency (defined as the ratio between the input, mostly the incident pump power or the pump power absorbed by the gain medium, and the output power of the laser), and the suggested upper limit of porosity for laser ceramics is 150 ppm (Ikesue and Yoshida, 1999).

There is an extensive amount of literature dealing with the transmittance of ceramics and the effect of microstructure (Apetz and van Bruggen, 2003; Ikesue *et al.*, 2005; Ikesue and Yoshida, 1999; Krell *et al.*, 2009a, 2014; Pabst and Hostaša, 2013; Pecharrmán *et al.*, 2009), and with the evaluation of porosity in these highly dense materials, which, unlike most ceramics, allow also the use of optical techniques (Boulesteix *et al.*, 2010; Krell *et al.*, 2014; Stuer *et al.*, 2012).

As far as the approaches to produce transparent ceramics from optically anisotropic materials are concerned, there are two main directions: reduction of grain size, or the orientation of grains.

The first possibility has been more widely studied, as it can be applied to generally any material, and most attention has been paid to transparent Al_2O_3 as a counterpart to monocrystalline sapphire. Krell *et al.* (2009b), Pecharrmán *et al.* (2009) and later

Stuer *et al.* (2012), managed to produce translucent-to-transparent alumina with submicrometric and nanometric grains. Still, the transmittances do not reach the theoretical values in the visible and NIR range, and although the obtained results are promising in the area of protective windows, the transparency is not high enough for laser materials.

It is the second option that has proved useful for the fabrication of laser gain media. The principle lies in the creation of a texture by orienting the crystalline grains in the same direction with the use of a strong magnetic field during the shaping step. This approach has been proposed by the Taira group (Akiyama *et al.*, 2011) for the production of a ceramic laser material from hexagonal (and thus optically anisotropic) neodymium-doped fluorapatite, $\text{Nd}^{3+}:\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. In the cited work the authors apply a strong magnetic field (1.4 T) during colloidal forming step to create an oriented microstructure making use of the magnetic anisotropy of Nd^{3+} ions and densify the material by means of hot isostatic pressing. The obtained polycrystalline ceramics allowed laser operation.

The optical properties and laser performance of gain media are also affected by the presence of oxygen crystal defects like oxygen vacancies, or impurities. These latter may be present in the starting powders, introduced to the material during the production process, but also added intentionally as sintering aids, as discussed in Section Sintering aids.

Thermal Properties

After optical characteristics, thermal, thermos-optical and thermo-mechanical properties are the most important in solid-state lasers. Thermal conductivity of the active medium determines the cooling geometry of the whole laser device, because especially in high-power lasers a significant amount of heat is generated during the laser oscillations. The presence of large temperature gradients can lead to the creation of stresses in the material, surface deformation and variation in optical properties, deformation of the laser beam profile, decrease in laser efficiency, and in the worst case can lead to the fracturing of the laser medium (Cousins, 1992). For laser applications it is thus important that the material has a high thermal conductivity and low thermal expansion coefficient.

One advantage of ceramic materials is their relatively high thermal conductivity with respect to that of glasses: the thermal conductivity of glasses is usually around $1 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature, while that of ceramics can reach values about one order of magnitude higher depending on the composition and the presence of doping ions, comparable to that of single crystals. Moreover, ceramic materials have a higher shock resistance compared to their single crystalline counterparts.

Ideal transparent ceramics do not contain second phases and contain only a small amount of pores, which would decrease their thermal conductivity (although compared to the effect on optical properties, the change in thermal conductivity would be very small). For the same composition, the only difference between a ceramic and a single crystal is the polycrystalline microstructure of the former, viz. the presence of grain boundaries. Indeed, thanks to the crystalline structure and a nearly defect-free microstructure, the thermal conductivity of polycrystalline ceramics at room and at elevated temperature is identical to that of single crystals with the same composition. Grain boundaries become important at low temperatures, when the phonon mean free path approaches the same order of magnitude (Pabst and Hostaša, 2011) and phonons are scattered. A significant difference in thermal conductivity between single- and polycrystalline YAG was observed at cryogenic temperatures (Yagi *et al.*, 2007). A maximum of the thermal conductivity was observed at temperatures between 25K and 40K, with the peak value of about $800 \text{ W m}^{-1} \text{ K}^{-1}$ measured for the single crystal and $100 \text{ W m}^{-1} \text{ K}^{-1}$ for the ceramics, and there was a decreasing trend of thermal conductivity with decreasing grain size. The effect of grain size has been addressed in Bisson *et al.* (2007) and Klemens, (1993). As described by Klemens (1993), at high frequencies the strongest scattering is due to point defects, while at low frequencies it is the case of extended defects: boundaries. Another important source of phonon scattering are lattice defects represented by the dopant ions. At low temperatures, the effect of dopant and grain boundaries may be comparable (Sarhou *et al.*, 2017), but the influence of doping ions remains significant also at elevated temperatures (Hostaša *et al.*, 2019). The problem has been elaborated by Sato *et al.* (2009), and by Gaumé *et al.* (2003), who proposed a model for the prediction of the thermal conductivity of doped crystals. It can be said that while the possibility to incorporate the doping ions in the crystal lattice of the host strongly depends on the ionic radii of the substituting and substituted ions, the difference of their atomic mass is what affects the thermal conductivity. An example is the Yb doping in YAG and LuAG. While the size of Yb^{3+} , Y^{3+} and Lu^{3+} ions is comparable, the atomic mass of Y (89 g mol^{-1}) is about a half of that of the two lanthanides (173 g mol^{-1} and 175 g mol^{-1} for Yb and Lu, respectively). When 5% of Y or Lu is substituted by Yb, the thermal conductivity of YAG at room temperature drops by more than 30%, while that of LuAG remains nearly unchanged (Beil *et al.*, 2010; Hostaša *et al.*, 2019).

Thermal conductivity of the most common crystalline laser host materials at room temperature is shown in Table 1, together with other important properties. Correct selection of materials, taking into account their thermal properties, can help avoid the deterioration of laser beam quality and the decrease in the efficiency and output power deriving from thermal effects (Sanghera *et al.*, 2011a). A possibility to mitigate these effects, provided by the ceramic processing, is the production of materials with engineered doping distribution (Esposito *et al.*, 2014).

Processing Technologies

Transparent ceramics may be prepared by a wide range of methods offered by the ceramic technology. However, the production of laser-quality transparent ceramics requires a precise control of every step of the process in order to avoid the formation of defects.

Table 1 Laser host materials and their properties at room temperature; the presented data were measured either on ceramics or single crystals, as the difference is usually very small and not all are available for ceramic materials; an intermediate value or a data range is presented in the case of multiple values of a comparable relevance for a given material and property

Material	Thermal conductivity at room temperature ($W m^{-1} K^{-1}$)	Transparency range (μm) ^a	Thermal expansion coefficient ($\times 10^{-6} K^{-1}$)	Thermo-optic coefficient dn/dt ($\times 10^{-6} K^{-1}$)	Density ($g cm^{-3}$)	Melting temperature ($^{\circ}C$)
YAG	10.7	0.23–6.4	6.1	7.8–8.4	4.56	1940
LuAG	8	0.23–6.3	6.1	4.9–8.3	6.67	2060
Sc ₂ O ₃	16.5	0.23–6.7	6.4	8.12	3.86	2430
Lu ₂ O ₃	11.4	0.23–7.7	6.1	7.1	9.42	2444
Y ₂ O ₃	13.0	0.25–9.6	6.3	6.08	5.04	2430
CaF ₂	10	0.13–12	19.2	–12.7	3.18	1420
MgAl ₂ O ₄	19–24	0.19–6.0	5.9	9–14	3.58	2135

^aThe transparency range is approximate, with the IR transmittance cutoff corresponding to values from 0% to 50% of transmittance, depending on the source of data.

Note: Data from (Beil *et al.*, 2010; Brown *et al.*, 2016; Furuse *et al.*, 2014; Goldstein and Krell, 2016; Harris *et al.*, 2013; Hostaša *et al.*, 2019; Kong *et al.*, 2015; Le Garrec *et al.*, 2013; Nigara, 1968; Rubat du Merac *et al.*, 2013; Sanghera *et al.*, 2012; Sarthou *et al.*, 2017; Slack, 1962; Wang *et al.*, 2013).

The purity and morphology requirements of the starting powders are pivotal. Often, nanometric and sub-micrometric powders provide the best results, as long as they are only loosely agglomerated. The shaping process needs to provide a uniform green body without variations in density or composition, and free from voids, bubbles or other inhomogeneities. The creation of large defects or cracks could also arise from the thermal removal of water, organic additives or other compounds, sometimes added during the shaping step, from which gas is released or which evaporate with the increase of temperature. The full densification is then obtained by sintering, often under vacuum or pure gas atmosphere, by the application of external pressure, or by a combination of these methods.

The aim of this section is to illustrate the most commonly used approaches and possibilities and to point out the important issues and parameters that are encountered in the production of transparent ceramics for laser applications.

Powders

The availability of fine, highly pure powders has been increasing in the past decades, giving more possibilities also for the production of transparent ceramics from commercially available starting materials. Nevertheless, the requirements of transparent ceramics for laser applications are very high, and especially in the research area, laboratory-synthesized powders are often preferred (Sanghera *et al.*, 2011a).

Most of the production processes involve the use of submicrometric or nanometric powders because of their high specific surface area and the high reactivity, possibly composed of spherical particles, which can be readily packed into dense structures. The decrease of particle size also leads to the increase of surface curvature, supporting thus further densification (Cannon and Carter, 1989; Fang and Wang, 2010).

However, the right shape and size of the particles is not enough. Agglomeration, and above all the presence of hard agglomerates in the powders during the shaping process can introduce inhomogeneities and voids in the microstructure, which cannot be removed at later stages of the production process (Sanghera *et al.*, 2011b). Of course, both the particle size and presence of hard agglomerates may be controlled by a milling step, yet considering the possible contamination from milling media and container.

Two different approaches can be followed for the production of transparent ceramics, as already mentioned in Section “Optical Transparency” for the case of YAG:

- sintering of synthesized powders with the desired composition (Lu *et al.*, 2001; Sanghera *et al.*, 2011a),
- solid-state reaction sintering of a mixture of the constituent oxide powders (Bonnet *et al.*, 2018; Ikesue *et al.*, 1995; Lee *et al.*, 2006).

The synthesis of powders provides a better control over the powder characteristics and very high chemical homogeneity, whereas the solid-state reaction offers a major flexibility for the preparation of new batches and an easier scaling up. Synthesized powders are more suitable for certain shaping methods, e.g., casting, and for fast sintering processes like SPS, where the process speed would be limited by the no need for a solid-state reaction to occur.

There are numerous methods used for the synthesis of powders, among which the most important ones are precipitation ((Kim *et al.*, 2015; Li *et al.*, 2000), used also by the Konoshima company (Yagi *et al.*, 2007)) and thermal decomposition (e.g., flame spray pyrolysis (Jones *et al.*, 2018)).

A crucial step in the case of precipitation is the thermal treatment – calcination of powders, during which the precursor crystallizes. The choice of the proper calcination temperature is very important, since too low temperatures would not lead to the

formation of the desired phase, which could cause problems during sintering, while too high temperature would lead to the coarsening of the particles, formation of necks and even hard agglomerates, which would be difficult to disintegrate.

The reactive sintering is attractive especially in research, where the process flexibility and possibility to prepare batches of arbitrary size is much appreciated especially in the case of garnet ceramics, a lot of effort has been made to understand the reaction mechanisms and the roles of sintering aids and dopants (Boulesteix *et al.*, 2009; Hostaša *et al.*, 2012; Stevenson *et al.*, 2011b). For YAG, the reactive sintering model has been described by Ikesue *et al.* (2013) and Kupp *et al.* (2014), discussing also the effect of the particle size of Y_2O_3 and Al_2O_3 . The respective chemical reactions are shown below, in Section YAG. The preparation process is less complex than precipitation of YAG powders; however, the importance of the characteristics of starting powders is crucial.

As a general rule, there is a difference in the microstructure between the ceramics produced from the synthesized powders and those obtained by solid-state reaction sintering: although it is strongly dependent on the sintering process, the typical grain size of solid-state sintered materials may be about one order of magnitude larger (e.g., in YAG tens of microns compared to few microns in ceramics produced from a precipitated powder).

Under all processing conditions it is critical to maintain the correct stoichiometry of the powder, mainly to avoid the formation of second phases (e.g., in YAG).

Shaping

The most common shaping methods in transparent ceramics production are dry pressing, slip casting and tape casting. Pressing has been used for its simplicity, and provides good results for simple geometries. Slip casting has proved particularly useful for the production of highly uniform green bodies and unconventional shapes. The advantage of tape casting lies in the ease of the preparation of planar materials with structured dopant distribution. Recently, good results were obtained also with the use of gel casting of Nd:YAG (Jing *et al.*, 2018), a method more commonly used for the shaping of transparent spinel, and extrusion was used to produce polycrystalline YAG fibers with diameter below 30 μm (Kim *et al.*, 2017). Finally, a fully transparent YAG ceramics with co-axial Nd^{3+} distribution was prepared by additive manufacturing process (Jones *et al.*, 2018).

Dry pressing, granulation

The powder is compacted by the application of pressure; uniaxial in a die, isostatic with the application of pressure through a liquid, or a combination of both. The use of cold isostatic pressing has proved very useful for the increasing of the density of the pressed compact before sintering, providing a better packing of the powder particles and leading to increased transparency.

To obtain uniform green body by pressing it is important that the powders flow well and do not contain hard agglomerates. Unfortunately, that is often not the case for fine particles, which tend to be voluminous and are difficult to press. An efficient way to increase the flowability of a powder, and consequently the packing density of a dry-pressed green body, is the granulation of powders before pressing.

Granulation of powders for transparent ceramics is usually performed by spray drying or freeze drying of suspensions: suspension droplets are fixed either by the evaporation or freezing and subsequent sublimation of the dispersing phase. When pressed, the granulated powders can be rearranged more easily to remove voids and provide a more uniform compact. Ikesue *et al.* illustrated the effect of the change in one parameter of the spray drying process on the final porosity of transparent YAG ceramics (Ikesue and Yoshida, 1999).

The role of granulation is even more important in the case of powder mixtures, where the desired composition is maintained within the granules, preventing particles with different size or density from separation and maintaining homogeneity.

Slip casting

Slip casting is another traditional ceramic shaping method. To obtain transparent ceramics, the slurry has to be free of bubbles and agglomerates, and should have a high solid loading; Appiagyei *et al.* (2008) found that the best results were obtained with well-dispersed Newtonian suspensions. Slip casting has been successfully employed by the Konoshima company with the use of precipitated YAG powders (Yagi *et al.*, 2007), while the group of Boulesteix used slip casting to produce transparent garnet ceramics by reaction sintering (Bonnet *et al.*, 2015).

While usually gypsum molds are used for slip casting, the contamination risks in transparent ceramics technology require porous materials that do not release any impurities in the green body, and thus sometimes the material of choice is porous alumina (Ivanov *et al.*, 2016).

A variation of the slip casting method, pressure casting, or pressure-assisted slip casting also provided good results (Kopylov *et al.*, 2009), and an illustration of pressure-cast Nd:YAG ceramics made via reactive sintering by the group of Boulesteix is shown in Fig. 3.

Tape casting

Tape casting is a method born for the production of thin ceramic sheets. A suspension is prepared with a high content of organic binder and dispersant, which is cast in the form of a thin foil (tape) of a typical thickness about 100 μm (Messing *et al.*, 2009), that is elastic due to the high content of organic additives and can be easily manipulated. To obtain a bulk piece, the tape sheets can be stacked and compressed together at slightly elevated temperature (usually not above 100°C), when the organic binders soften

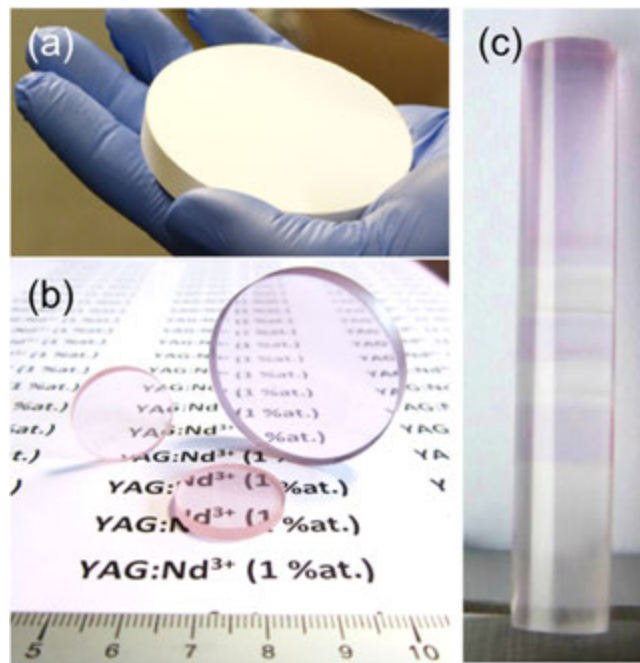


Fig. 3 Nd:YAG ceramic components produced by pressure casting at 3 MPa of an aqueous suspension of $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Nd}_2\text{O}_3$ powder mixture; (a) pressure-cast green body, (b) sintered disks, (c) a rod composed of layers of Nd:YAG and layers of dopant-free YAG. Courtesy Dr. Boulesteix, Univ. Limoges, joint laboratory IRCER/CILAS.

(Mistler and Twinaime, 2000). Due to the high content of organic additives, a particular attention has to be paid during the debinding (burnout) heat treatment, which is a necessary step before sintering, so that all the organics are removed, but no damage is caused to the green body from the released gases.

Tape casting is particularly useful for the production of bulk layered, planar-shaped ceramics, because it provides a high-precision control over dopant distribution in the sintered component and low concentration of defects. Although diffusion between the layers cannot be avoided during the sintering, the thickness of the dopant diffusion gradient profile is in the range of 100 μm (Hostaša *et al.*, 2016; Kupp *et al.*, 2010), depending on the sintering process.

The possibilities of tape casting of transparent YAG laser ceramics have been extensively studied in the past decade (Hostaša *et al.*, 2017; Kupp *et al.*, 2010; Tang *et al.*, 2012). This technique is very well suited for the production of planar laser waveguides (Ge *et al.*, 2014; Jiang *et al.*, 2019; Ma *et al.*, 2016), where the guiding structure is made by a thin layer (tens to hundreds of μm thickness) of a doped laser gain medium confined between two parts with a different refractive index, often the dopant-free host material, which has very similar thermomechanical behavior as the gain medium.

Densification Methods

Although high densities can be achieved by conventional sintering in air under atmospheric pressure, this method does not provide a sufficient driving force for the full closure of pores necessary to produce transparent ceramics. Therefore, high-performance sintering methods need to be applied, often accompanied by the addition of a sintering aid. The most common methods are vacuum sintering, sintering in a gas atmosphere (e.g., hydrogen, oxygen) and pressure assisted sintering, viz. hot pressing (HP), hot isostatic pressing (HIP) and spark plasma sintering (SPS, also called Electric current assisted sintering, ECAS). A concise review on the densification methods of transparent ceramics was presented by Wang *et al.* (2013).

Vacuum sintering

Vacuum sintering has been successfully used for the production of different kinds of laser ceramics, including YAG, Y_2O_3 , Sc_2O_3 , Lu_2O_3 (Ikessue *et al.*, 1995; Wang *et al.*, 2013). The application of vacuum before and during sintering helps with the removal of pores by both degassing, reducing the amount of gas in the material from the very beginning, and by providing an additional force that helps the densification. The closing of pores under vacuum is beneficial to the densification process, owing to a lower amount of gas that has to diffuse from the pore, and by facilitating the evaporation – condensation process inside pores. As a result, the risk of pore entrapment inside grains is also lower. Vacuum sintering is further useful by providing a clean atmosphere, especially in the case of vacuum furnaces with refractory metal (W or Mo) hot zone shielding and heating elements.

The sintering temperatures are usually few hundred of °C below the melting temperature and sintering times usually range from hours to tens of hours. Often, small amounts of sintering aids are used to decrease the sintering temperature, promote pore closure and control grain growth.

The high vacuum acts as a reducing atmosphere, removing oxygen from the crystal structure of oxides. The as-sintered materials then often have to be annealed in air or oxygen atmosphere. In Yb-doped laser ceramics, where the presence of Yb^{3+} only is required, the annealing serves both to eliminate oxygen vacancies and to oxidize Yb^{2+} ions.

Vacuum-sintered ceramics usually have large grains (tens of μm), which limit their thermo-mechanical performance.

Two-step sintering was proposed to limit grain size by separating the grain growth from the densification process. The material is heated to a higher temperature and quickly cooled down to a slightly lower soaking temperature (the difference is usually about 100–200°C), high enough to promote grain boundary diffusion, but not grain growth, and the soaking time ranges from hours to tens of hours. The resulting microstructure is fine-grained with pores mostly at grain boundaries. Such microstructure is also well-fit for a post-HIP treatment, which eliminates the remaining porosity. This approach was successfully used to obtain transparent Sc_2O_3 and Lu_2O_3 ceramics (Serivalsatit and Ballato, 2010; Serivalsatit *et al.*, 2013).

Pressure-assisted sintering

As was listed above, the main three pressure-assisted sintering techniques applied for the production of transparent ceramics are HP, HIP and SPS.

Hot pressing uses a uniaxial application of pressure on a compact placed in a heated die to enhance densification through the rearrangement and deformation of particles. The use of hot pressing only can lead to transparent ceramics, but to achieve laser-quality materials, it is coupled with a post-HIP treatment (Sanghera *et al.*, 2011a).

Spark plasma sintering is similar to hot pressing, viz. the powder or pre-formed piece is placed in a die and is uniaxially pressed while heated. The difference is in the application of electric current in SPS, which passes through the die and the sample and heats by the Joule effect. During the SPS of transparent ceramics, electrically isolating materials, the heating occurs mainly from the die. SPS can be used to sinter nanometric powders without or only with a reduced amount of sintering aids, and compared to other methods, it is very fast (the whole treatment including the cooling is a matter of tens of minutes up to hours), providing high densification and fine-grained microstructure with very small pores, also thanks to the relatively lower temperatures. SPS has been successfully applied in the sintering of sesquioxides, providing good results without the necessity of a post-HIP treatment (An *et al.*, 2014; Boulesteix *et al.*, 2014). A comprehensive summary on the application of SPS for the production of transparent ceramics is provided in Nečina and Pabst (2018).

In the case of hot pressing (HP) and spark plasma sintering (SPS) the forming can take place directly inside the furnace in the mold where the sample is pressed during the firing (Boulesteix *et al.*, 2014). This approach may easily lead to the introduction of impurities (mainly carbon) and does not necessarily provide a uniform compact (also due to the powder characteristics, cf. Section “Sesquioxides”), and therefore the shaping inside the SPS die is not advised for the fabrication of laser ceramics.

Hot isostatic pressing, unlike HP or SPS, uses mostly gas to apply pressure on the sintered ceramics placed in a heated chamber, and thus presents no limitation to the number or shape of the objects except for the dimension of the chamber. HIP is often applied to increase the density of samples that have been previously sintered up to the so-called closed porosity density (95%–99% of the theoretical density). The ideal microstructure of materials to undergo post-HIP treatment is composed of small grains with pores localized at grain boundaries. As was noted above, such microstructures may be achieved by the use of two-step sintering, or by HP or SPS.

Pressure-assisted sintering methods, in particular SPS and HIP, usually produce microstructures with smaller grain size, e.g., compared to vacuum sintering. This is achieved thanks to the lower sintering temperatures and shorter times allowed by the application of pressure.

Other sintering approaches

Pressureless sintering in air usually doesn't provide sufficiently dense ceramics, and with the exception of CaF_2 , discussed later in Section CaF_2 , it has to be followed by a HIP treatment (Wang *et al.*, 2016). The use of oxygen or hydrogen atmosphere gave good results in the sintering of Y_2O_3 (Zhang *et al.*, 2009) or LuAG (Zhou *et al.*, 2017). Oxygen atmosphere is also useful in pre-sintering calcination or post-sintering annealing treatments.

Hot forming is an unusual method – from the point of view of ceramic technology – used for the preparation of fluoride ceramics, where bulk singles are exposed to high pressure at elevated temperature (as in HP) and, basically, the single crystal is deformed to such extent that its structure breaks and turns to polycrystalline (Akchurin *et al.*, 2013). The idea behind hot forming is to eliminate optical inhomogeneities present in the single crystals. Although the obtained materials are pore-free, they are not fully isotropic due to the uniaxial application of pressure, and the whole process including the growth of the crystal is long and demanding.

Sintering aids

The use of sintering additives appeared to be a necessity for the production of high-quality transparent ceramics. The most commonly used are SiO_2 (sometimes added in the form of an organic precursor, TEOS), MgO , CaO , ZrO_2 ; in the case of HP and SPS processes, it is mostly LiF . Sintering aids promote densification and control grain growth, but they also introduce impurities, which may negatively affect the laser performance, as was shown for silicon (Gaumé *et al.*, 2012). The decrease of the amount of

sintering aids in YAG while maintaining the optical quality has been successfully pursued by the Messing group (Lee *et al.*, 2009; Stevenson *et al.*, 2011a), and recently Ikesue and Aung presented the synthesis of Yb:YAG ceramics by vacuum sintering followed by HIP without any sintering aid (Ikesue and Aung, 2017), which is a significant accomplishment. The production of laser sesquioxide ceramics without sintering aids by a combination of sintering under vacuum or in air followed by HIP has also been reported (Toci *et al.*, 2020; Wang *et al.*, 2016), as well as by SPS (Boulesteix *et al.*, 2014).

Materials

A major part of this section presents materials for ceramic laser gain media and details on their production and performance, and part is dedicated to other transparent ceramics used in lasers. An overview of material properties of the discussed laser hosts is presented in Table 1.

The most commonly used ceramic laser hosts are oxides, mainly rare earth garnets and cubic sesquioxides, and fluorides, in particular CaF_2 . The active luminescent ions are lanthanides and transition metals, which enter the crystal lattice of the host by substitution. The selection of a suitable host–dopant combination thus depends on the capacity of the host to accommodate the active ion in the crystal lattice. The advantage of rare-earth garnets and sesquioxides is the similar size of Y^{3+} , Sc^{3+} and the lanthanide ions. The most commonly used dopants are Nd^{3+} and Yb^{3+} for emission around 1 μm , Er^{3+} for emission around 1.5–1.6 μm and 3 μm , and Tm^{3+} and Ho^{3+} with emission in the 2 μm region. Nd^{3+} doping has been of strongest interest for decades; however, with the availability of efficient laser diodes, the use of Yb^{3+} is on the rise, in particular for high-power lasers (Paul David *et al.*, 2018).

For more information about the crystalline structure of laser hosts, dopants and spectroscopic characterization, the kind reader is suggested to look into the following publications: (Ikesue *et al.*, 2013; Koechner, 2006).

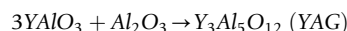
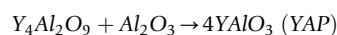
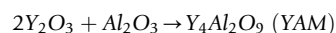
Garnets

Thanks to their optical, thermal and mechanical properties, synthetic rare-earth garnet single crystals with rare-earth doping have been the material of choice for solid-state lasers, and thanks to the success in obtaining YAG laser ceramics in the 1990s (Ikesue *et al.*, 1995; Lu *et al.*, 2000), the polycrystalline garnets have been considered a promising alternative to single crystals, and have been studied significantly up to now. These materials have the chemical formula $\text{A}_3\text{B}_2\text{C}_3\text{O}_{12}$ and a cubic structure (group Ia3d), where rare earth dopants occupy the dodecahedral A site.

YAG

YAG is most important transparent ceramic material for laser applications. A significant amount of research effort has been dedicated to the preparation and study of first Nd:YAG, and later Yb:YAG transparent ceramics for laser applications in the last two decades, bringing many interesting and important results.

As described in Section “Sintering aids”, YAG ceramics are produced either by the sintering of YAG powders, or by a reactive sintering of the single constituent oxide powders. In the latter case, the reactions occur at temperatures above 1000°C with two intermediate phases – monoclinic $\text{Y}_4\text{Al}_2\text{O}_9$, denoted YAM, and a perovskite YAlO_3 phase referred to as YAP, which has two polymorphs: orthorhombic and hexagonal. The latter is sometimes also referred to as YAH. The formation of the phases is described by the following equations:



The YAG phase is a nearly linear compound, and the deviations of stoichiometry may cause the presence of either Al_2O_3 or YAP phase in the sintered material.

As a general rule, the microstructure of YAG ceramics produced by the reactive sintering of the constituent oxide powders is coarser compared to that made from fine synthesized YAG powders. The exact grain size then depends on the sintering conditions. Transparent YAG ceramics are mostly sintered under vacuum at 1700–1800°C, usually with the use of silica as a sintering aid, both in the case of YAG powders and reactive sintering (Ikesue *et al.*, 1995; Sekita *et al.*, 1990). The use of CaO and MgO, or a combination of the two or with SiO_2 has also proved useful. MgO is particularly useful for the control of grain size (Yang *et al.*, 2012). The typical doping ions in YAG for lasers are Nd^{3+} , Yb^{3+} and Er^{3+} .

Materials of optical quality comparable to single crystals have already been produced, and thanks to the shaping techniques of ceramics, the performance and possibilities of single crystal technology have already been surpassed, e.g., by the large-aperture slabs produced by the Konoshima company (see Fig. 1). Nevertheless, so far the commercialization of transparent YAG ceramics has still been limited.

At laboratory scale, Nd:YAG gain media in the shape of a 120 × 50 × 3 mm slab (Chen *et al.*, 2014) or disk 80 mm in diameter and 6 mm thick (Ikesue *et al.*, 2006) produced by dry pressing and vacuum sintering, or Er:YAG rod 3 mm in diameter and 62 mm long with structured doping prepared by tape casting (Ter-Gabrielyan *et al.*, 2010) were reported.

Nd:YAG ceramics may be prepared with much higher Nd concentrations compared to single crystals, which allowed to obtain increased laser efficiencies (Dubinskii *et al.*, 2005; Ikesue *et al.*, 1996). High dopant concentration has also been successfully applied for Yb:YAG, reaching 10%–20% in the thin-disk or microchip lasers (Dong *et al.*, 2007). The interest in Yb:YAG arises from the possibility to construct compact lasers with the use of laser diodes. Conversely, the use of a mixed co-doping Nd,Cr in YAG allows solar-pumping of the laser through the absorption of Cr^{3+} and the energy transfer from Cr^{3+} to Nd^{3+} ions (Suzuki *et al.*, 2019).

LuAG

LuAG, $\text{Lu}_3\text{Al}_5\text{O}_{12}$, is a very interesting alternative to YAG thanks to its good thermal properties, viz. for the very low effect of rare-earth doping on its thermal conductivity (see Section “Processing Technologies”) and the availability to easily accommodate lanthanides. A lower influence of the thermo-optical effects (thermal lens) was reported for Yb:LuAG compared to Yb-doped YAG, Sc_2O_3 and Lu_2O_3 (Pirri *et al.*, 2014). Thanks to its similarity to YAG, also in-situ production of YAG-LuAG composite structures is possible, e.g., for waveguides (see Section Tape casting).

Like YAG, LuAG is mostly sintered under vacuum, often by reactive sintering of oxide powders (Xu *et al.*, 2012). Recently, the production of 0.8% Nd:LuAG slabs $58 \times 40 \times 5.5$ mm and $52 \times 39 \times 7.5$ mm by solid-state sintering under vacuum followed by HIP was reported (Liu *et al.*, 2019).

Other garnets

Other rare-earth-doped synthetic garnets have also been tested as laser gain media ($\text{Gd}_3\text{Ga}_5\text{O}_{12}$, GGG;), and there has been an interest in the use of mixed garnets (e.g., YSAG, $\text{Y}_3\text{Sc}_x\text{Al}_{5-x}\text{O}_{12}$) for the possibility to tune the absorption and emission bands and enhance the emission by the variation of the crystalline structure of the host (Feng *et al.*, 2005). Flashlamp-pumped Cr,Nd:GSGG ($\text{Gd}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$) is another promising laser material (Koechner, 2006).

Sesquioxides

Sesquioxides have the chemical formula M_2O_3 , where M is a metal, usually Y, Sc, Lu, or La, offering an easy substitution sites for lanthanide lasing ions. These materials have a cubic structure (group Ia3), high melting temperatures (above 2400°C) and are often difficult to grow as single crystals. There is a particular interest in sesquioxide laser gain media given their thermal conductivity; both pure Sc_2O_3 and Y_2O_3 have high thermal conductivity; however, due to the low mass of Y and Sc compared to lanthanides it drops with the addition of the dopant, especially in the case of Yb doping, which requires higher concentrations. Conversely, Lu_2O_3 , as in the case of LuAG, maintains its conductivity with increasing doping. Moreover, the laser emission efficiency can be significantly improved at cryogenic temperatures.

Y_2O_3 has already long been proposed as a promising laser gain medium, however its production in sufficiently high quality and dimensions was not so immediate. There is a strong limitation to the possible growth of Y_2O_3 single crystals due to its high melting temperature and to a phase transformation taking place at around 2325°C. Pure Y_2O_3 has a relatively high thermal conductivity, although decreasing significantly with the introduction of lanthanide doping ions, and a wide transparency range.

First successful attempts to produce transparent polycrystalline Y_2O_3 used a significant amount of additives (ThO_2 , or later La_2O_3 , (Greskovich and Chernoch, 1973; Ivanov *et al.*, 2016)). Recently, high-quality 5% Yb: Y_2O_3 ceramics have been prepared by vacuum sintering of precipitated nanoparticles (1700°C for 2 h) followed by HIP (1775°C for 4 h at 198 MPa), with the use of a small amount of ZrO_2 , reaching 10.6% slope efficiency (Wang *et al.*, 2017). Laser-grade 2% Yb: Y_2O_3 ceramics were prepared by Sanghera *et al.* (2011a) by hot pressing of precipitated powders with a small amount of LiF, and a slope efficiency reaching 45% was obtained both in continuous wave and pulsed mode. Slope efficiency of 48% was reported for cryogenically cooled 0.5% Er: Y_2O_3 ($20.7 \times 2 \times 5$ mm), but no details on the material production were provided (Ter-Gabrielyan *et al.*, 2008).

Sc_2O_3 is very similar to yttrium oxide in terms of material properties, and it is a candidate material for diode-pumped lasers. Transparent Sc_2O_3 ceramics have been prepared mostly from nanopowders, by vacuum sintering (Dai *et al.*, 2018; Lu *et al.*, 2003) or by combination the of vacuum sintering and HIP (Serivalsatit and Ballato, 2010; Toci *et al.*, 2020).

Lu_2O_3 has a slightly lower thermal conductivity compared to the two previously mentioned oxides; however, as noted above, it does not decrease with the addition of dopant. This makes Lu_2O_3 interesting for high dopant concentrations, useful mostly for Yb. While most of the works report on the production by vacuum sintering of nanometric powders, pressure-assisted methods have also provided very good results. Sanghera *et al.* (2011b) reported on the production of Yb: Lu_2O_3 by hot pressing (followed by HIP). The produced materials reached a laser slope efficiency of 74% and 16 W output power. More recently, the production of Nd: Lu_2O_3 via SPS has been reported both with (An *et al.*, 2014) and without the use of a sintering aid (Boulesteix *et al.*, 2014).

As in the case of mixed garnets, it is possible to tune the spectroscopic properties by mixing the sesquioxide composition thanks to their miscibility. Moreover, while the addition of La_2O_3 to Y_2O_3 is sometimes in the literature addressed as the use of a sintering aid, the quantity involved (e.g., at 10%) suggests that the final material is a mixed sesquioxide, which is easier to sinter compared to pure yttria. Laser efficiency of 17.5% was reported for 8% Yb($\text{La}_x\text{Y}_{1-x}$) $_2\text{O}_3$ ceramics prepared by vacuum sintering of nanopowders (Ivanov *et al.*, 2015) at only 1650°C for 20 h.

CaF₂

Among fluorides, the main material of choice for lasers is CaF₂ doped with rare earth ions, in particular with ytterbium. Yb:CaF₂ has been proposed, together with Yb:YAG, as one of the possible gain media for the ambitious European project HiPER – High Power laser Energy Research focused on laser-driven inertial fusion, albeit more likely in the form of a single crystal (Chanteloup *et al.*, 2010).

As mentioned above in Section “Other sintering approaches”, one approach used for the production of transparent CaF₂ ceramics is hot forming, hot pressing of single crystals, a relatively time-consuming process. The production of transparent CaF₂ by the more classical ceramic approaches have not provided impressive results until the recent work of Mortier's group, using pressureless sintering of Yb:CaF₂ nanopowders prepared by a soft chemistry process (Gredin and Mortier, 2016, Sarthou *et al.*, 2016).

MgAl₂O₄

MgAl₂O₄ spinel is a material of choice mainly for transparent windows and domes for aggressive environments thanks to its very good mechanical properties and resistance. It is produced from widely available and relatively inexpensive materials, MgO and Al₂O₃, and is already produced in large dimensions, mainly by hot pressing or by pressureless sintering in air followed by HIP. Attempts have been made to employ spinel with Cr, Mn, Ti, or Ni doping as a laser gain medium (single crystals grown by the micro-pulling-down (Jouini *et al.*, 2007a,b)), however its main use in laser technology is elsewhere. When doped with Co²⁺, spinel can be used as a saturable absorber for passive Q-switching in the wavelength range around 1.5 μm. Sanghera *et al.* also prepared highly transparent spinel for laser exit window aperture (Sanghera *et al.*, 2011a).

Non-Gain-Media Ceramics for Lasers

Apart from laser gain media, transparent ceramics are promising candidates also for other laser components, in particular absorbers and magneto-optical materials.

Absorbers

Absorbing ceramic components in lasers can be divided in two categories:

- absorbing cladding to suppress undesired amplified spontaneous emission (ASE),
- saturable absorbers.

Absorbing cladding may be realized by different approaches (principally a light absorbing, liquid or solid with a refractive index matching the laser gain medium) and it serves to absorb amplified spontaneous emission (ASE) and internal reflections of parasitic oscillations, which would limit the laser performance. It is particularly important in high-energy lasers, where the losses would create also problems with thermal management and laser beam profile. The solution for bulk laser gain media (slabs, disks) offered by the ceramic technology is production of composite structures, where the host material is doped with lasing ion (Yb³⁺, Nd³⁺) in the core and with absorbing doping (Cr⁴⁺ or Sm³⁺) in the cladding, sintered in one piece without the need of further bonding or depositions (Paul David *et al.*, 2018).

Saturable absorbers are absorbing optical components whose transmittance increases when the light intensity reaches a threshold. The main use of saturable absorbers is in passive Q-switching, a method for the generation of short pulses, often of high energy and with high repetition rate, by the change in the level of losses in the laser resonator. The materials of choice are often Cr⁴⁺:YAG for the 1 μm region, V³⁺:YAG for 1.3 μm and Co²⁺:MgAl₂O₄ for the 1.5 μm region. As in the case of absorbing cladding, ceramic technology allows the production of passively Q-switched laser in one piece, e.g., Nd:YAG/Cr:YAG (Taira, 2011; Tsunekane *et al.*, 2010).

Magneto-optical materials

Another type of transparent ceramic materials of recent interest are magneto-optical materials, that is Faraday rotators characterized by a high Verdet constant, changing the polarization of the light beam passing through the material by the application of a magnetic field. These materials have been produced mainly as single crystals of terbium gallium garnet (TGG, Tb₃Ga₅O₁₂), with the limitation of size to 30–40 mm. Another promising material, terbium aluminum garnet (TAG, Tb₃Al₅O₁₂), is difficult to produce as a single crystal due to incongruent melting. This clearly leaves a lot of space for the development of ceramic solutions, especially for the production of large-aperture components. First TGG transparent ceramics are already commercially available, with Verdet constant equivalent to that of a single crystal, and other materials, e.g., (Tb_{0.6}Y_{0.4})₃Al₅O₁₂ (Aung and Ikesue, 2017; Wan *et al.*, 2019) or ceramic yttrium iron garnet, YIG (Ikesue and Aung, 2018) are under investigation with promising results.

Applications, Beyond the State of the Art

Probably the main advantage of transparent ceramic technology lies in the shaping possibilities, in particular to produce composite or gradient structures without the need of post-processing and bonding. This was illustrated by a number of examples above, viz. composite ceramics for Q-switched lasers, cladding or waveguides. Planar waveguide lasers use the difference in refractive index between the thin layer of the laser medium and the two adjacent parts of the sandwich-like structure. The difference in refractive index may be caused simply by the laser doping ion (Jiang *et al.*, 2019) or by the use of another host, as in the case of YAG-Yb:LuAG-YAG structure (Ma *et al.*, 2016).

The shaping methods offer approaches for the shaping of materials with different geometries (slab, disk, thin disk, fiber) and dimensions. Recent advancements show that while for certain applications it is necessary to produce large gain media, miniaturization is also very interesting. The production of thin disk microchip lasers (composite thin disk with waveguides), where the gain medium is only hundreds of micrometers thick, has been proposed by Taira (2007). Eventually, the microchip lasers using ceramic YAG components were successfully tested in spark plugs for car industry (Tsunekane *et al.*, 2010), and a more recent work presented an elaborate Q-switched laser Nd:YAG/Sm:YAG microchip coupled with a Cr^{4+} :YAG part (Kong *et al.*, 2015).

Bonding still has its place, for the combination of materials with significantly different properties or production processes, e.g., with the recent possibilities of room temperature bonding (Kausas *et al.*, 2017) it would be possible to get the best both of ceramic and single crystal technology. The coupling of ceramics with single crystals has already been successfully used in 2005 (Yagi *et al.*, 2005). Bonding solutions are also useful when a minimum thickness of the interdiffusion is required. While in the case of composite structures prepared by pressing or tape casting the interdiffusion layer may be even 200 μm thick (Hostaša *et al.*, 2016), recently, Ikesue *et al.* (2018) presented a bonding method providing composites with a very clear defect-free interface. The same group also presented an approach for the growth of single crystals from transparent ceramics, which would provide materials without grain boundaries and without the optical defects typical for melt-grown single crystals (Ikesue *et al.*, 2013).

The application potential of laser ceramics is significant, covering the whole field currently using the single crystalline counterparts and beyond, and providing the advantage of a more economical use of strategic materials such as rare earth oxides. Yet, their real use is still strongly limited, partly because of low competition and relatively high prices. With a higher availability of ceramic laser gain media, there should be no obstacles in their use e.g., in diode-pumped lasers both for pulsed and continuous wave operation. Meanwhile, the ongoing research in the field of transparent ceramics keeps presenting novel materials and technological solutions and increasing quality.

Currently, there is a lot of interest in very-high-power lasers in the fields of defense and experimental physics, where large-aperture gain media are required. In terms of laser output, the Lawrence Livermore National Labs (LLNL) reported the first achievement of 67 kW and 100 kW continuous wave was achieved by a number of producers of direct energy weapons, using diode arrays and multiple large Nd:YAG or Yb:YAG slabs produced by the Konoshiba company (Sanghera *et al.*, 2013). While LLNL laser uses Nd:YAG slabs, Yb:YAG gain media have been installed in a number of high-power laser facilities, viz. GENBU in Japan; DiPOLE in the UK; HILASE in the Czech Republic, or Lucia laser chain at LULI, France (Paul David *et al.*, 2018).

References

- Akchurin, M.S., Basiev, T.T., Demidenko, A.A., *et al.*, 2013. CaF_2 :Yb laser ceramics. *Opt. Mater.* 35, 444–450.
- Akiyama, J., Sato, Y., Taira, T., 2011. Laser demonstration of diode-pumped Nd^{3+} -doped fluorapatite anisotropic ceramics. *Appl. Phys. Express* 4, 022703.
- An, L., Ito, A., Zhang, J., Tang, D., Goto, T., 2014. Highly transparent Nd^{3+} : Lu_2O_3 produced by spark plasma sintering and its laser oscillation. *Opt. Mater. Express* 4, 1420–1426.
- Apetz, R., van Bruggen, M.P.B., 2003. Transparent alumina: A light-scattering model. *J. Am. Ceram. Soc.* 86, 480–486.
- Appigayei, K.A., Messing, G.L., Dumm, J.Q., 2008. Aqueous slip casting of transparent yttrium aluminum garnet (YAG) ceramics. *Ceram. Int.* 34, 1309–1313.
- Aung, Y.L., Ikesue, A., 2017. Development of optical grade $(\text{Tb}_x\text{Y}_{1-x})_3\text{Al}_5\text{O}_{12}$ ceramics as Faraday rotator material. *J. Am. Ceram. Soc.* 100, 4081–4087.
- Beil, K., Friedrich-Thornton, S.T., Tellkamp, F., *et al.*, 2010. Thermal and laser properties of Yb:LuAG for kW thin disk lasers. *Opt. Express* 18, 20712–20722.
- Bisson, J.F., Yagi, H., Yanagitani, T., *et al.*, 2007. Influence of the grain boundaries on the heat transfer in laser ceramics. *Opt. Rev.* 14, 1–13.
- Bonnet, L., Boulesteix, R., Maître, A., *et al.*, 2015. Manufacturing issues and optical properties of rare-earth (Y, Lu, Sc, Nd) aluminate garnets composite transparent ceramics. *Opt. Mater.* 50 (part A), 2–10.
- Bonnet, L., Boulesteix, R., Maître, A., *et al.*, 2018. Influence of (Nd + Y)/Al ratio on sintering behavior and optical features of $\text{Y}_{3-x}\text{Nd}_x\text{Al}_5\text{O}_{12}$ ceramics for laser applications. *Opt. Mater.* 77, 264–272.
- Boulesteix, R., Maître, A., Baumard, J.F., Rabinovitch, Y., 2010. Quantitative characterization of pores in transparent ceramics by coupling electron microscopy and confocal laser scanning microscopy. *Mater. Lett.* 64, 1854–1857.
- Boulesteix, R., Maître, A., Baumard, J.F., Sallé, C., Rabinovitch, Y., 2009. Mechanism of the liquid-phase sintering for Nd:YAG ceramics. *Opt. Mater.* 31, 711–715.
- Boulesteix, R., Epherre, R., Noyau, S., *et al.*, 2014. Highly transparent Nd:Lu $_2\text{O}_3$ ceramics obtained by coupling slip-casting and spark plasma sintering. *Scr. Mater.* 75, 54–57.
- Brown, D., Tornegård, S., Kolis, J., 2016. Cryogenic nanosecond and picosecond high average and peak power (HAPP) pump lasers for ultrafast applications. *High Power Laser Sci. Eng.* 4, (e15).
- Burnett, J.H., Levine, Z.H., Shirley, E.L., 2001. Intrinsic birefringence in calcium fluoride and barium fluoride. *Phys. Rev. B.* 64, 241102.
- Cannon, R.M., Carter, W.C., 1989. Interplay of sintering microstructures, driving forces, and mass transport mechanisms. *J. Am. Ceram. Soc.* 72, 1550–1555.
- Chanteloup, J.C., Albach, D., Lucianetti, A., *et al.*, 2010. Multi kJ level laser concepts for HiPER facility. *J. Phys. Conf. Ser.* 244, 012010.
- Chen, J., Li, J., Xu, J., *et al.*, 2014. 4350 W quasi-continuous-wave operation of a diode face-pumped ceramic Nd:YAG slab laser. *Opt. Laser Technol.* 63, 50–53.
- Cousins, A.K., 1992. Temperature and thermal stress scaling in finite-length end-pumped lasers rods. *IEEE J. Quantum Electron.* 28, 1057–1069.
- Dai, Z., Liu, Q., Toci, G., *et al.*, 2018. Fabrication and laser oscillation of Yb:Sc $_2\text{O}_3$ transparent ceramics from co-precipitated nano-powders. *J. Eur. Ceram. Soc.* 38, 1632–1638.

- de With, G., van Dijk, H.J.A., 1984. Translucent $\text{Y}_3\text{Al}_5\text{O}_{12}$ ceramics. *Mater. Res. Bull.* 19, 1669–1674.
- Dong, J., Shirakawa, A., Ueda, K., *et al.*, 2007. Laser-diode pumped heavy-doped Yb:YAG ceramic lasers. *Opt. Letters* 32, 1890–1892.
- Dubinskii, M., Goff, J.R., Merkle, L.D., Castillo, V.K., Quarles, G.J., 2005. Q-switched laser operation of 8% ceramic Nd:YAG. In *Conference on Lasers and Electro-Optics/Quantum Electronics and Laser Science and Photonic Applications Systems Technologies*. Paper CTuQ3. Washington D.C.: Optical Society of America.
- Esposito, L., Hostaša, J., Piancastelli, A., *et al.*, 2014. Multilayered YAG-Yb:YAG ceramics: Manufacture and laser performance. *J. Mater. Chem. C* 2, 10138–10148.
- Fang, Z.Z., Wang, H., 2010. Sintering of ultrafine and nanosized particles. In: Fang, Z.Z. (Ed.), *Sintering of Advanced Materials*. Cambridge: Woodhead Publishing Ltd, pp. 434–473.
- Feng, T., Shi, J., Chen, J., Jiang, D., 2005. Synthesis and greatly enhanced fluorescence emission of transparent Nd-doped $\text{Y}_3\text{Sc}_x\text{Al}_{5-x}\text{O}_{12}$ ceramics. *J. Mater. Res.* 20, 2322–2327.
- Furuse, H., Yasuhara, R., Hiraga, K., 2014. Thermo-optic properties of ceramic YAG at high temperatures. *Opt. Mater. Express* 4, 1794–1799.
- Gaumé, R., He, Y., Markosyan, A., Byer, R.L., 2012. Effect of Si-induced defects on 1 μm absorption losses in laser-grade YAG ceramics. *J. Appl. Phys.* 111, 093104.
- Gaumé, R., Viana, B., Vivien, D., Roger, J.P., Fournier, D., 2003. A simple model for the prediction of thermal conductivity in pure and doped insulating crystals. *Appl. Phys. Lett.* 83, 1355–1357.
- Ge, L., Li, J., Zhou, Z., *et al.*, 2014. Fabrication of composite YAG/Nd:YAG/YAG transparent ceramics for planar waveguide laser. *Opt. Mater. Express* 4, 1042–1049.
- Geusic, J.E., Marcos, H.M., Van Uitert, L.G., 1964. Laser oscillations in Nd-doped yttrium aluminum, yttrium gallium and gadolinium garnets. *Appl. Phys. Lett.* 4, 182–184.
- Goldstein, A., Krell, A., 2016. Transparent ceramics at 50: Progress made and further prospects. *J. Am. Ceram. Soc.* 99, 3173–3197.
- Gredin, P., Mortier, M., 2016. Optical properties of fluoride transparent ceramics. In: Tressaud, A., Poeppelmeier, K. (Eds.), *Progress in Fluorine Science Series: Photonic and Electronic Properties of Fluoride Materials*. Amsterdam: Elsevier, pp. 65–87.
- Greskovich, C., Chernoch, J.P., 1973. Polycrystalline ceramic lasers. *J. Appl. Phys.* 44, 4599–4606.
- Hatch, S.E., Parsons, W.F., Weagley, R.J., 1964. Hot-pressed polycrystalline $\text{CaF}_2:\text{Dy}^{2+}$ laser. *Appl. Phys. Lett.* 5, 153–154.
- Harris, D., Johnson, L., Seaver, R., *et al.*, 2013. Optical and thermal properties of spinel with revised (increased) absorption at 4 to 5 mm wavelengths and comparison with sapphire. *Opt. Eng.* 52, 087113.
- Hostaša, J., Esposito, L., Piancastelli, A., 2012. Influence of Yb and Si content on the sintering and phase changes of Yb: YAG laser ceramics. *J. Eur. Ceram. Soc.* 32, 2949–2956.
- Hostaša, J., Nečina, V., Uhlířová, T., Biasini, V., 2019. Effect of rare earth ions doping on the thermal properties of YAG transparent ceramics. *J. Eur. Ceram. Soc.* 39, 53–58.
- Hostaša, J., Biasini, V., Piancastelli, A., Vannini, M., Toci, G., 2016. Layered Yb:YAG ceramics produced by two different methods: Processing, characterization, and comparison. *Opt. Eng.* 55, 087104.
- Hostaša, J., Piancastelli, A., Toci, G., Vannini, M., Biasini, V., 2017. Transparent layered YAG ceramics with structured Yb doping produced via tape casting. *Opt. Mater.* 65, 21–27.
- Ikesue, A., Yoshida, K., 1999. Influence of pore volume on laser performance of Nd:YAG ceramics. *J. Mater. Sci.* 34, 1189–1195.
- Ikesue, A., Aung, Y.L., 2017. Synthesis of Yb:YAG ceramics without sintering additives and their performance. *J. Am. Ceram. Soc.* 100, 26–30.
- Ikesue, A., Aung, Y.L., 2018. Development of optical grade polycrystalline YIG ceramics for faraday rotator. *J. Am. Ceram. Soc.* 101, 5120–5126.
- Ikesue, A., Kamata, K., Yoshida, K., 1996. Effects of neodymium concentration on optical characteristics of polycrystalline Nd:YAG laser materials. *J. Am. Ceram. Soc.* 79, 1921–1926.
- Ikesue, A., Aung, Y.L., Lupei, V., 2013. *Ceramic Lasers*. Cambridge: Cambridge University Press.
- Ikesue, A., Kinoshita, T., Kamata, K., Yoshida, K., 1995. Fabrication and optical properties of high-performance polycrystalline Nd:YAG ceramics for solid-state lasers. *J. Am. Ceram. Soc.* 78, 1033–1040.
- Ikesue, A., Yoshida, K., Yamamoto, T., Yamaga, I., 2005. Optical scattering centers in polycrystalline Nd:YAG laser. *J. Am. Ceram. Soc.* 80, 1517–1522.
- Ikesue, A., Aung, Y.L., Kamimura, T., Honda, S., Iwamoto, Y., 2018. Composite laser ceramics by advanced bonding technology. *Materials* 11, 271.
- Ikesue, A., Aung, Y.L., Taira, T., *et al.*, 2006. Progress in ceramic lasers. *Annu. Rev. Mater. Res.* 36, 397–429.
- Ivanov, M., Kopylov, Y., Kravchenko, V., *et al.*, 2015. Optical, luminescent and laser properties of highly transparent ytterbium doped yttrium lanthanum oxide ceramics. *Opt. Mater.* 50 (Part A), 15–20.
- Ivanov, M., Kalinina, E., Kopylov, Y., *et al.*, 2016. Highly transparent Yb-doped $(\text{La}_x\text{Y}_{1-x})_2\text{O}_3$ ceramics prepared through colloidal methods of nanoparticles compaction. *J. Eur. Ceram. Soc.* 36, 4251–4259.
- Jiang, N., Zhao, Y., Zhu, Z., *et al.*, 2019. Fabrication and laser performance of planar waveguide LuAG/Yb:LuAG/LuAG ceramics. *Opt. Mater.* 89, 149–156.
- Jing, W., Li, F., Yu, S., *et al.*, 2018. High efficiency synthesis of Nd:YAG powder by a spray co-precipitation method for transparent ceramics. *J. Eur. Ceram. Soc.* 38, 2454–2461.
- Jones, I.K., Seeley, Z.M., Cherepy, N.J., Duoss, E.B., Payne, S.A., 2018. Direct ink write fabrication of transparent ceramic gain media. *Opt. Mater.* 75, 19–25.
- Jouini, A., Yoshikawa, A., Brenier, A., Fukuda, T., Boulon, G., 2007a. Optical properties of transition metal ion-doped MgAl_2O_4 spinel for laser application. *Phys. Status Solidi* 4, 1380–1383.
- Jouini, A., Yoshikawa, A., Guyot, Y., *et al.*, 2007b. Potential candidate for new tunable solid-state laser between 1 and 2 μm : Ni^{2+} -doped MgAl_2O_4 spinel grown by the micro-pulling-down method. *Opt. Mater.* 30, 47–49.
- Kausas, A., Zheng, L., Taira, T., 2017. Structured laser gain-medium by new bonding for power micro-laser. In: Clarkson W.A., Shori R.K., (Eds.), *Proceedings of the SPIE 10082, Solid State Lasers XXVI: Technology and Devices*. 100820Z.
- Kim, H.J., Hay, R.S., McDaniel, S.A., *et al.*, 2017. Lasing of surface-polished polycrystalline Ho:YAG (yttrium aluminum garnet) fiber. *Opt. Express* 25, 6725–6731.
- Kim, W., Villalobos, G., Baker, C., *et al.*, 2015. Overview of transparent optical ceramics for high-energy lasers at NRL. *Appl. Opt.* 54, F210–F221.
- Klemens, P.G., 1993. Heat conduction in solids by phonons. *Thermochim. Acta* 218, 247–255.
- Kochawattana, S., Stevenson, A., Lee, S.H., *et al.*, 2008. Sintering and grain growth in SiO_2 doped Nd:YAG. *J. Eur. Ceram. Soc.* 28, 1527–1534.
- Koehnner, W., 2006. *Springer Series in Optical Sciences: Laser Principles in Solid-State Laser Engineering*. Berlin: Springer.
- Kong, W., Tsunekane, M., Taira, T., 2015. Diode edge-pumped passively Q-switched microchip laser. *Opt. Eng.* 54, 090501.
- Kopylov, Y.L., Kravchenko, V.B., Bagayev, S.N., *et al.*, 2009. Development of $\text{Nd}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ laser ceramics by high-pressure colloidal slip-casting (HPCSC) method. *Opt. Mater.* 31, 707–710.
- Krell, A., Hutzler, T., Klimke, J., 2009a. Transmission physics and consequences for materials selection, manufacturing, and applications. *J. Eur. Ceram. Soc.* 29, 207–221.
- Krell, A., Klimke, J., Hutzler, T., 2009b. Advanced spinel and sub- μm Al_2O_3 for transparent armour applications. *J. Eur. Ceram. Soc.* 29, 275–281.
- Krell, A., Hutzler, T., Klimke, J., 2014. Defect strategies for an improved optical quality of transparent ceramics. *Opt. Mater.* 38, 61–74.
- Kupp, E.R., Messing, G.L., Anderson, J.M., *et al.*, 2010. Co-casting and optical characteristics of transparent segmented composite Er:YAG laser ceramics. *J. Mater. Res.* 25, 476–483.
- Kupp, E.R., Kochawattana, S., Lee, S.H., Misture, S., Messing, G.L., 2014. Particle size effects on yttrium aluminum garnet (YAG) phase formation by solid-state reaction. *J. Mater. Res.* 29, 2303–2311.
- Le Garrec, B., Cardinali, V., Bourdet, G., 2013. Thermo-optical measurements of ytterbium doped ceramics (Sc_2O_3 , Y_2O_3 , Lu_2O_3 , YAG) and crystals (YAG, CaF_2) at cryogenic temperatures. In: *Proceedings of the SPIE Volume 87800. High-Power, High-Energy, and High-Intensity Laser Technology, and Research Using Extreme Light: Entering New Frontiers with Petawatt-Class Lasers*. 87800E.
- Lee, S.H., Kupp, E.R., Stevenson, A.J., *et al.*, 2009. Hot isostatic pressing of transparent Nd:YAG ceramics. *J. Am. Ceram. Soc.* 92, 1456–1463.

- Lee, S.H., Kochawattana, S., Messing, G.L., *et al.*, 2006. Solid-state reactive sintering of transparent polycrystalline Nd:YAG ceramics. *J. Am. Ceram. Soc.* 89, 1945–1950.
- Li, J.G., Ikegami, T., Lee, J.H., Mori, T., Yajima, Y., 2000. Co-precipitation synthesis and sintering of yttrium aluminum garnet (YAG) powders: The effect of precipitant. *J. Eur. Ceram. Soc.* 20, 2395–2405.
- Liu, T., Feng, T., Sui, Z., *et al.*, 2019. 50 mm-aperture Nd:LuAG ceramic nanosecond laser amplifier producing 10 J at 10 Hz. *Opt. Express* 27, 15595–15603.
- Lu, J., Song, J., Prabhu, M., *et al.*, 2000. High-power Nd:Y₃Al₅O₁₂ ceramic laser. *Jpn. J. Appl. Phys.* 39, L1048–L1050.
- Lu, J., Prabhu, M., Ueda, K., *et al.*, 2001. Potential of ceramic YAG lasers. *Laser Phys.* 11, 1053–1057.
- Lu, J., Bisson, J.F., Takaichi, K., *et al.*, 2003. Yb³⁺:Sc₂O₃ ceramic laser. *Appl. Phys. Lett.* 83, 1101–1103.
- Lu, J., Ueda, K.I., Yagi, H., *et al.*, 2002. Neodymium doped yttrium aluminum garnet (Y₃Al₅O₁₂) nanocrystalline ceramics – A new generation of solid state laser and optical materials. *J. Alloys Compd.* 341, 220–225.
- Ma, C., Zhu, J., Liu, K., *et al.*, 2016. Longitudinally diode-pumped planar waveguide YAG/Yb:LuAG/YAG ceramic laser at 1030.7 nm. *Opt. Lett.* 41, 3317–3319.
- Maiman, T.H., 1960. Stimulated optical radiation in Ruby. *Nature* 187, 493–494.
- Messing, G.L., Kupp, E.R., Lee, S.H., Juwondo, G.Y., Stevenson, A.J., 2009. Method for manufacture of transparent ceramics. US Pat. US20090108507.
- Mistler, R.E., Twinn, E.R., 2000. Tape Casting: Theory and Practice. Wiley-American Ceramic Society.
- Nigara, Y., 1968. Measurement of the optical constants of yttrium oxide. *Jpn. J. Appl. Phys.* 7, 404–408.
- Nečina, V., Pabst, W., 2018. Electric current assisted sintering of ceramics – Steps and pitfalls on the way to transparency. In: Olson, H. (Ed.), *Polycrystalline Materials: Synthesis, Performance and Applications*. New York: Nova Science Publishers, Inc., pp. 99–177.
- Pabst, W., Hostaša, J., 2011. Thermal conductivity of ceramics: From monolithic to multiphase, from dense to porous, from micro to nano. In: Wythers, M.C. (Ed.), *Advances in Materials Science Research*, vol. 7. New York: Nova Science Publishers, pp. 1–112.
- Pabst, W., Hostaša, J., 2013. A closed-form expression approximating the mie solution for the real-in-line transmission of ceramics with spherical inclusions or pores. *Ceram. Silik.* 57, 151–161.
- Paul David, S., Jambunathan, V., Lucianetti, A., Mocek, T., 2018. Overview of ytterbium based transparent ceramics for diode pumped high energy solid-state lasers. *High Power Laser Sci.* 6, e62.
- Pecharrormán, C., Mata-Osoro, G., Díaz, L.A., Torrecillas, R., Moya, J.S., 2009. On the transparency of nanostructured alumina: Rayleigh-Gans model for anisotropic spheres. *Opt. Express* 17, 6899–6912.
- Pirri, A., Toci, G., Ciofini, M., *et al.*, 2014. Thermal lens measurements in Yb-doped YAG, LuAG, Lu₂O₃, Sc₂O₃ ceramic lasers. *J. Phys. Conf. Ser.* 497, 012013.
- Rubat du Merac, M., Kleebe, H., Müller, M., Reimanis, I., 2013. Fifty years of research and development coming to fruition; unraveling the complex interactions during processing of transparent magnesium aluminate (MgAl₂O₄) spinel. *J. Am. Ceram. Soc.* 96, 3341–3365.
- Sanghera, J., Bayya, S., Villalobos, G., *et al.*, 2011a. Transparent ceramics for high-energy laser systems. *Opt. Mater.* 33, 511–518.
- Sanghera, J., Kim, W., Baker, C., *et al.*, 2011b. Laser oscillation in hot pressed 10% Yb³⁺:Lu₂O₃ ceramic. *Opt. Mater.* 33, 670–674.
- Sanghera, J., Kim, W., Villalobos, G., *et al.*, 2012. Ceramic laser materials. *Materials* 5, 258–277.
- Sanghera, J., Kim, W., Villalobos, G., *et al.*, 2013. Ceramic laser materials: Past and present. *Opt. Mater.* 35, 693–699.
- Sarthou, J., Aballéa, P., Patriarche, G., *et al.*, 2016. Wet-route synthesis and characterization of Yb:CaF₂ optical ceramics. *J. Am. Ceram. Soc.* 99, 1992–2000.
- Sarthou, J., Duquesne, J.Y., Becerra, L., Gredin, P., Mortier, M., 2017. Thermal conductivity measurements of Yb:CaF₂ transparent ceramics using the 3 ω method. *J. Appl. Phys.* 121, 245108.
- Sato, Y., Akiyama, J., Taira, T., 2009. Effects of rare-earth doping on thermal conductivity in Y₃Al₅O₁₂ crystals. *Opt. Mater.* 31, 720–724.
- Sekita, M., Haneda, H., Yanagitani, T., Shirasaki, S., 1990. Induced emission cross section of Nd:Y₃Al₅O₁₂ ceramics. *J. Appl. Phys.* 67, 453–458.
- Serivalsatit, K., Ballato, J., 2010. Submicrometer grain-sized transparent erbium-doped scandia ceramics. *J. Am. Ceram. Soc.* 93, 3657–3662.
- Serivalsatit, K., Wasanapiarnpong, T., Kucera, C., Ballato, J., 2013. Synthesis of Er-doped Lu₂O₃ nanoparticles and transparent ceramics. *Opt. Mater.* 35, 1426–1430.
- Slack, G.E., 1962. Thermal Conductivity of MgO, Al₂O₃, MgAl₂O₄, and Fe₃O₄ Crystals from 31 to 3001K. *Phys. Rev.* 126, 427–441.
- Stevenson, A.J., Kupp, E.R., Messing, G.L., 2011a. Low temperature, transient liquid phase sintering of B₂O₃-SiO₂-doped Nd:YAG transparent ceramics. *J. Mater. Res.* 26, 1151–1158.
- Stevenson, A.J., Li, X., Martinez, M.A., *et al.*, 2011b. Effect of SiO₂ on densification and microstructure development in Nd:YAG transparent ceramics. *J. Am. Ceram. Soc.* 94, 1380–1387.
- Stuer, M., Bowen, P., Cantoni, M., Pecharrormán, C., Zhao, Z., 2012. Nanopore characterization and optical modeling of transparent polycrystalline alumina. *Adv. Funct. Mater.* 22, 2303–2309.
- Suzuki, Y., Ito, H., Kato, T., *et al.*, 2019. Continuous oscillation of a compact solar-pumped Cr, Nd-doped YAG ceramic rod laser for more than 6.5 h tracking the sun. *Sol. Energy* 177, 440–447.
- Taira, T., 2007. Ceramic YAG lasers. *C.R. Phys.* 8, 138–152.
- Taira, T., 2011. Domain-controlled laser ceramics toward Giant Micro-photonics [Invited]. *Opt. Mater. Express* 1, 1040–1050.
- Tang, F., Cao, Y., Huang, J., *et al.*, 2012. Multilayer YAG/Re:YAG/YAG laser ceramic prepared by tape casting and vacuum sintering method. *J. Eur. Ceram. Soc.* 32, 3995–4002.
- Ter-Gabrielyan, N., Merkle, L.D., Newburgh, G.A., Dubinskii, M., 2008. Cryogenically-cooled laser based on resonantly-pumped Er³⁺:Y₂O₃ ceramic. In: *Proceedings of the Conference on Lasers and Electro-Optics and Conference on Quantum Electronics and Laser Science*. Washington D.C.: Optical Society of America.
- Ter-Gabrielyan, N., Merkle, L.D., Kupp, E.R., Messing, G.L., Dubinskii, M., 2010. Efficient resonantly pumped tape cast composite ceramic Er:YAG laser at 1645 nm. *Opt. Lett.* 35, 922–924.
- Toci, G., Hostaša, J., Patrizi, B., *et al.*, 2020. Fabrication and laser performances of Yb:Sc₂O₃ transparent ceramics from different combination of vacuum sintering and hot isostatic pressing conditions. *J. Eur. Ceram. Soc.* 40 (3), 881–886.
- Tsunekane, M., Inohara, T., Ando, A., *et al.*, 2010. High peak power, passively Q-switched microlaser for ignition of engines. *IEEE J. Quantum Electron.* 46, 277–284.
- Wan, Z., Wang, Y., Zhang, J., *et al.*, 2019. Effect of (Tb + Y)/Al ratio on microstructure evolution and densification process of (Tb_{0.6}Y_{0.4})₂Al₅O₁₂ transparent ceramics. *Materials* 12, 300.
- Wang, J., Ma, J., Zhang, J., *et al.*, 2017. Yb:Y₂O₃ transparent ceramics processed with hot isostatic pressing. *Opt. Mater.* 71, 117–120.
- Wang, S.F., Zhang, J., Luo, D.W., *et al.*, 2013. Transparent ceramics: Processing, materials and applications. *Prog. Solid State Chem.* 41, 20–54.
- Wang, Z., Zhang, L., Yang, H., *et al.*, 2016. High optical quality Y₂O₃ transparent ceramics with fine grain size fabricated by low temperature air pre-sintering and post-HIP treatment. *Ceram. Int.* 42, 4238–4245.
- Xu, C.W., Luo, D.W., Zhang, J., *et al.*, 2012. Diode pumped highly efficient Yb:Lu₃Al₅O₁₂ ceramic laser. *Laser Phys. Lett.* 9, 30.
- Yagi, H., Yanagitani, T., Numazawa, T., Ueda, K., 2007. The physical properties of transparent Y₃Al₅O₁₂. Elastic modulus at high temperature and thermal conductivity at low temperature. *Ceram. Int.* 33, 711–714.
- Yagi, H., Takaichi, K., Ueda, K., *et al.*, 2005. The physical properties of composite YAG ceramics. *Laser Phys.* 15, 1338–1344.
- Yang, H., Qin, X., Zhang, J., *et al.*, 2012. The effect of MgO and SiO₂ codoping on the properties of Nd:YAG transparent ceramic. *Opt. Mater.* 34, 940–943.
- Zhang, J., An, L., Liu, M., Shimai, S., Wang, S., 2009. Sintering of Yb³⁺:Y₂O₃ transparent ceramics in hydrogen atmosphere. *J. Eur. Ceram. Soc.* 29, 305–309.
- Zhou, D., Shi, Y., Xie, J., *et al.*, 2017. Laser grade Yb:LuAG transparent ceramic prepared by nanocrystalline pressure-less sintering in reducing H₂. *Opt. Mater. Express* 7, 1274–1280.

Further Reading

- Goldstein, A., Krell, A., 2016. Transparent ceramics at 50: Progress made and further prospects. *J. Am. Ceram. Soc.* 99, 3173–3197.
- Grishin, M. (Ed.), 2010. *Advances in Solid-State Lasers: Development and Applications*. Vukovar: Intech.
- Ikesue, A., Aung, Y.L., Taira, T., *et al.*, 2006. Progress in ceramic lasers. *Annu. Rev. Mater. Res.* 36, 397–429.
- Ikesue, A., Aung, Y.L., Lupei, V., 2013. *Ceramic Lasers*. Cambridge: Cambridge University Press.
- Koechner, W., 2006. *Springer Series in Optical Sciences: Laser Principles in Solid-State Laser Engineering*. Berlin: Springer.
- Kong, L., Huang, Y., Que, W., *et al.*, 2015. *Transparent Ceramics*. Cham: Springer International Publishing.
- Krell, A., Hutzler, T., Klimke, J., 2014. Defect strategies for an improved optical quality of transparent ceramics. *Opt. Mater.* 38, 61–74.
- Li, J., Pan, Y., Zeng, Y., *et al.*, 2013. The history, development, and future prospects for laser ceramics: A review. *Int. J. Refract. Met. Hard Mater.* 39, 44–52.
- Messing, G.L., Stevenson, A.J., 2008. Toward pore-free ceramics. *Science* 322, 383–384.
- Wang, S.F., Zhang, J., Luo, D.W., *et al.*, 2013. Transparent ceramics: Processing, materials and applications. *Prog. Solid State Chem.* 41, 20–54.
- Xiao, Z., Yu, S., Li, Y., *et al.*, 2020. Materials development and potential applications of transparent ceramics: A review. *Mater. Sci. Eng. R Rep.* 139, 100518.
- Yang, H., Zhang, J., Luo, D., *et al.*, 2013. Novel transparent ceramics for solid-state lasers. *High Power Laser Sci. Eng.* 1, 138–147.

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Ceramic Sensors for Industrial Applications

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Introduction

Gas sensors based on oxide materials are an established technology in safety applications, i.e., the detection of toxic or flammable gases, as well as environmental monitoring or process control. Their small size, cost-efficient production and low power consumption are advantages compared to analytical instrumentation, which on the one hand has often a higher accuracy and large application range, but on the other hand is rather large and expensive. With the fast-growing need for monitoring process or environmental parameters, the demand for suitable sensors is increasing. Today, sensors are a key technology in a world with an ever-increasing interconnectivity and, thus, essential for the internet of things or Industry 4.0. Gas sensors possess the outstanding capability to provide chemical information from an omnipresent media, the gas phase. The variety of sensor types and oxide materials offer suitable sensor solutions for various applications and sensor capable to operate in various conditions, ranging from ambient air over exhaust systems to industrial ovens at several hundred degrees. The following sections introduce different gas sensors types based on ceramic materials and describe their working principles.

Definitions of Gas Sensors and Characteristic Properties

Gas sensors are chemical sensors, i.e. devices that transform chemical information, which is the concentration of one or several analyte gases, into an analytically useful signal. The sensor consists of a receptor part and a transducer part, which are the two basic functional units of any chemical sensor. The receptor unit transforms the chemical information into a form of energy, which is transformed into a useful analytical signal by the transducer unit subsequently. Ceramic materials are commonly used as receptor unit for gas sensors and in most cases combined with an electrical or electrochemical transducer unit (Hulanicki *et al.*, 1991).

Depending on the transducer unit, the sensor readout is typically based on resistance/conductance, voltage or current measurement (Hulanicki *et al.*, 1991). This raw signal or readout is in many cases used to calculate a sensor signal, which indicates the change with respect to a reference condition. There is no universal way to calculate the sensor signal S from a sensor readout R and one should choose the most suitable way to calculate the sensor signal.

$$S_{diff.} = R_0 - R_{gas} \quad (1a)$$

$$S_{diff.} = R_{gas} - R_0 \quad (1b)$$

$$S_{ratio} = \frac{R_0}{R_{gas}} \quad (2a)$$

$$S_{ratio} = \frac{R_{gas}}{R_0} \quad (2b)$$

One common way of calculating a sensor signal is calculating the difference (equations 1) of the readout in the reference condition (R_0) and the one during gas exposure (R_{gas}). The difference is calculated in a manner to obtain a signal, which has a positive value, e.g. if the readout decreases with increasing analyte concentration, the readout during exposure is subtracted from the readout in the reference condition (Eq. 1(a)). Another common way the calculate sensor signals is calculating the ratio of the readouts (Eq. 2), the obtained ratio is usually calculated in a manner to obtain values larger than 1. Whether the signal is calculated by difference or ratio, strongly depends on the response behavior of the sensor; a set of examples is shown Fig. 1.

The response of the electrochemical gas sensor (Fig. 1(a)) is linear and within the same order of magnitude as the readout in the reference condition, while the chemoresistive sensors (Fig. 1(b)) show a non-linear response and the readout in reference conditions and under analyte exposure differ by several orders of magnitude. When comparing the sensor signals calculated by difference of the electrochemical cells and a chemoresistive gas sensor (Fig. 1(c)), one obtains a suitable calibration curve with distinguishable signals for the electrochemical cells. And the difference in the readout in reference conditions (U_0) is compensated by calculating the signals, showing that both sensors show a very similar behavior. This is different for the chemoresistive gas sensor, which shows no distinguishable signals for different analyte concentrations, i.e., signals obtained by calculating a difference are not suitable for these gas sensors. But when calculating the sensor signals for the chemoresistive sensors as ratios (Fig. 1(d)), one obtains a suitable calibration curve, which displays the different response behavior of the two sensors in this example. A comparison of the numerical values of the sensors signals calculated as difference or ratio (Fig. 1(c) and (d)) shows that the values strongly vary depending on how the signals are calculated and, thus, the mere value of a sensor signal is not a universal measure to compare sensors. In addition to the sensor signals there are other important properties, which are commonly used to describe the performance of gas sensors, namely the sensitivity, selectivity and stability.

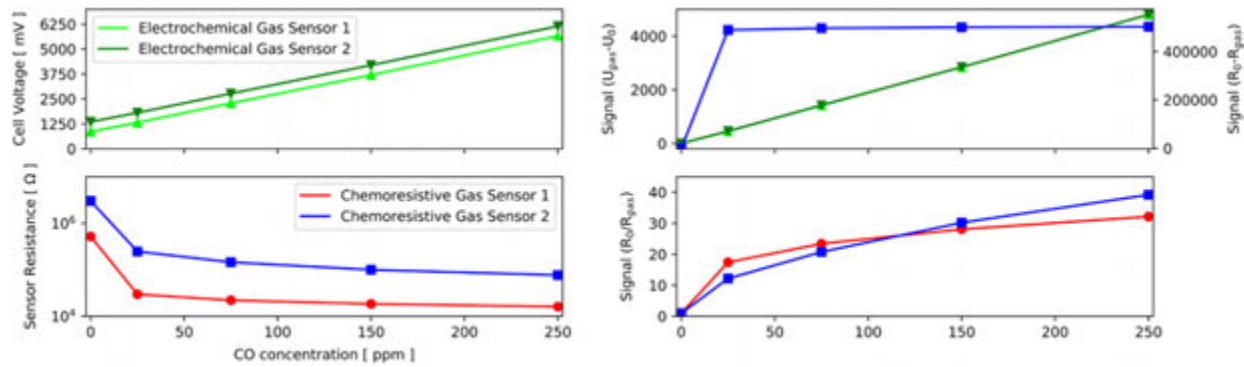


Fig. 1 Examples comparing sensor readout and sensor signals for different types of gas sensors. The readout of electrochemical (a) and chemoresistive (b) gas sensors is used to calculate the sensor signals as difference (c) and ratio (d). For the electrochemical cells the signals are calculated from the measured potentials (U_0 and U_{gas}) according to the Eq. 1(b), for the chemoresistive gas sensors from the measured resistances (R_0 and R_{gas}) according to Eqs. 1(a) or 2(a), respectively. For the sake of clarity, not all signals are shown.

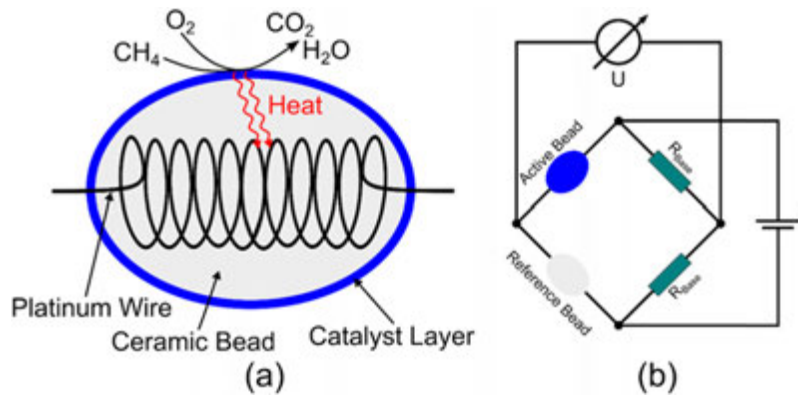


Fig. 2 Cross-section of a ceramic bead (a) and schematic measurement circuit (b) of a pellistor.

The sensitivity of a sensor expresses the change in the readout or signal per concentration unit of the analyte, i.e., the slope of the calibration curve (Gründler, 2007). The sensitivity should neither be confused with the sensor signal nor the detection limit. It is given by

$$b = \frac{dS}{dc} \quad (3)$$

where b is the sensitivity, S the sensor signal and c the concentration of the analyte. For linear calibration curves, the sensitivity is constant, while for non-linear calibration curves, e.g. showing a power law relation, the sensitivity depends on the concentration range. In the latter case, the sensor typically shows concentration ranges with higher and lower sensitivity (Danzer, 2007). Directly comparing the sensitivity of different sensors is rather ambitious and a more solid basis for such a comparison is given by the analytical sensitivity, which includes the accuracy (standard deviation) of the measurement as well.

The selectivity of a sensor describes its ability to respond to a group of certain analytes from a larger set of analytes. If the sensor is able to respond to one single analyte in a set of analytes, the sensor is referred to as specific (Gründler, 2007).

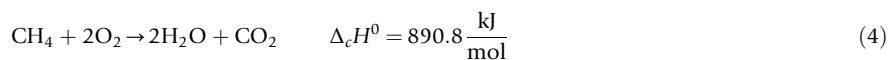
The stability of a sensor is its ability to maintain its performance for a certain period of time. Stability is measured by different indicators, such as drift of baseline and sensors signal, as well as retaining its sensitivity, selectivity or response/recovery time (Gründler, 2007; Bochenkov and Sergeev, 2010).

Catalytic Combustion Gas Sensors

A widely applied type ceramic sensor for combustible gases is the pellet resistor or short pellistor. Pellistors are thermometric gas sensors, which transform the heat of a combustion reaction into a measurable electronic readout. Typical applications are detection and monitoring of flammable gases and vapors in air (Gründler, 2007; Bársony *et al.*, 2009).

The active sensing element of a pellistor is a coil of Pt wire, which is embedded in a ceramic bead (e.g., Al_2O_3) and coated with a catalyst layer consisting of noble metals like Pt, Pd or Rh (Fig. 2(a)). The bead is heated to operation temperatures above $450^\circ C$

by passing current through the Pt coil. The gas reception takes place by combusting the analyte, e.g., hydrocarbons such as methane (Eq. (4)), on the catalyst in the presence of atmospheric oxygen.



The heat of combustion ($\Delta_c H^0$) causes a temperature increase of the bead and the embedded Pt wire. Due to the temperature dependence of the specific resistance of Pt, the resistance of Pt wire varies according to Eq. (5).

$$\rho_T = \rho_{T_0} \cdot (1 + 0.0039(T - T_0)) \quad (5)$$

where ρ_T denotes the specific resistance of Pt at the temperature T and ρ_{T_0} the known specific resistance at a reference temperature T_0 . Due to this relation the temperature change caused by the combustion of the analyte is translated into an electronic signal. The bead's temperature is not only changed by catalytic reactions and additional factors, such as fluctuations in gas flow, ambient temperature or heat conductivity of the surrounding atmosphere, as well, cause temperature changes. In order to compensate this effect, an additional bead without a catalytic coating is used as a reference. Both beads are kept in the same environment and, thus, changes in the ambient conditions will affect both. While the catalytic combustion of the analyte, i.e., gas sensing, will only take place on the active bead (Chou, 2000; Gründler, 2007; Bársony *et al.*, 2009).

For the electrical measurement, the active and the reference bead are placed in Wheatstone bridge (Fig. 2(b)). The asymmetric resistance change in the two beads, caused by a catalytic combustion reaction, results in an imbalance in the Wheatstone bridge. The imbalance is measured as a voltage change, which is proportional to the concentration and nature of the combustible gas. For most analytes, pellistors show an almost linear response within a range of 0%–100% of the lower explosion limit. Taking methane as example, a typical pellistor shows a linear increase of the voltage up to 5% of methane, which corresponds to the lower explosion limit. Between the lower explosion limit and the stoichiometric mixture (~ 9% methane in air), the voltage first levels before it steeply increases close to the stoichiometric mixture, where the voltage reaches a maximum. Above the stoichiometric mixture, the voltage decreases. Thus, in oxygen lean conditions, the sensing properties of a pellistor are compromised and the measured signal indicates an analyte concentration, which is lower than the actual one (Chou, 2000; Bársony *et al.*, 2009).

Pellistors are sensitive to a large variety of flammable gases and vapors. On the one hand, this implies a strong cross-interference, i.e., poor selectivity, if several flammable compounds are present. On the other hand, one single sensor is suitable for different analytes or applications. Usually pellistors are calibrated to a certain gas like methane or n-pentane. Correction factors are used to calibrate a pellistor for other analyte gases. Depending on the analyte these factors are larger or smaller than 1. Another source of cross-interference is the concentration of atmospheric oxygen. Pellistors are designed to operate in a range of oxygen excess to the stoichiometric mixture of the analyte gas and oxygen.

Gas Sensors Based on Ion Conducting Metal Oxides

Gas sensors based on ion conducting metal oxides are typically electrochemical sensors, in which the ion conducting metal oxides act as solid electrolyte. Furthermore, metal oxides are used as active electrode materials, e.g., for mixed-potential gas sensors. In all cases, the spontaneous or electrically stimulated analyte-electrode interaction is translated into an analytically useful signal, either by a potentiometric, amperometric or coulometric approach (Hulanicki *et al.*, 1991; Pasierb and Rekas, 2009). Metal oxides used as solid electrolytes have a sufficient thermodynamic stability in the operation conditions, e.g., they do not show degeneration due to redox reactions, and the ionic conductivity should be larger than electronic conductivity ($\sigma_{\text{ion}} \gg \sigma_{\text{electronic}}$). The electronic conductivity depends on the temperature as well as on the oxygen partial pressure and, thus, for a given metal oxide, the ionic conductivity is dominant within a certain regime (electrolytic domain). The mobile ion species in the solid electrolyte is either directly converted from the analyte gas or an equilibrium involving the analyte gas, or formed using an auxiliary phase, which interacts with the analyte gas and is itself an ion conductor (Pasierb and Rekas, 2009; Guth and Wiemhöfer, 2019).

Yttria-stabilized zirconia (YSZ) is a classic example for a solid electrolyte, as it presents a large band gap of 5.1 eV, which limits the electronic conductivity, and is a good oxygen ion conductor at high temperatures (600–1500°C). An electrochemical cell based on an YSZ electrolyte and two porous Pt electrodes (see Fig. 3) can be used as an oxygen concentration cell:



Given that the oxygen partial pressures in both half-cells are different ($p'_{\text{O}_2} > p''_{\text{O}_2}$) and there is no exchange of molecular oxygen through the electrolyte (gas tight metal oxide), the oxygen partial pressure tends to equilibrate. If the outer circuit of the electrochemical cell (6) is closed, the partial pressures are able to equilibrate by the following reactions taking place at the three-phase-boundary (YSZ-Pt-gas phase). In the half-cell with the higher partial pressure (p'_{O_2}), molecular oxygen reacts with oxygen vacancies in YSZ involving electrons provided by the Pt electrode forming lattice oxygen:



In the half-cell with the lower oxygen partial pressure, the opposite reaction occurs and lattice oxygen is converted into molecular oxygen:

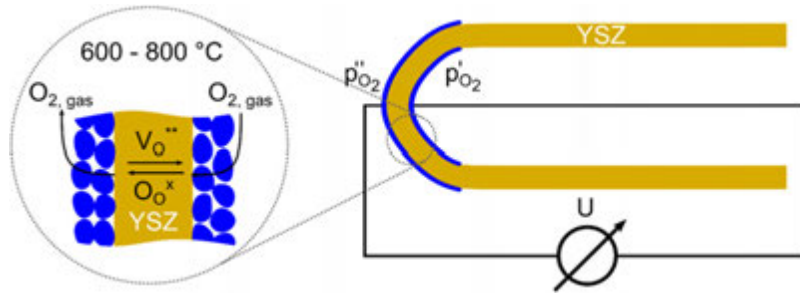


Fig. 3 Schematic setup of a potentiometric oxygen sensor based on a solid state electrolyte (brown), with two porous measurement electrodes (blue) based on the same material. The right side shows the general setup; the left side a magnification of the assembly of the electrode and electrolyte.

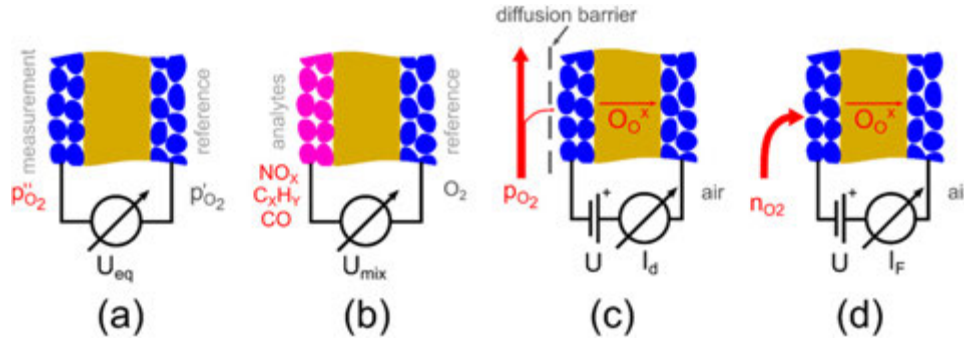


Fig. 4 Schematic setups of different types of solid state electrolyte gas sensors: Potentiometric gas sensor with a Nernstian behavior (a), mixed-potential gas sensor (b), amperometric gas sensor with a diffusion barrier (c) and coloumetric gas sensor (d). Adapted from Guth, U., 2008. Gas sensors. In: Bard, A.J., Inzelt, G., Scholz, F. (Eds.), *Electrochemical Dictionary*, first ed. Heidelberg: Springer-Verlag Berlin Heidelberg, pp. 293–297. doi:10.1007/978-3-340-74598-3.



The overall reaction of (7) and (8) is the transport of oxygen from the half-cell with the higher oxygen partial pressure to the half-cell with the lower oxygen partial pressure:



In case of a closed circuit, the exchange of oxygen results in a current flow in the outer circuit. In case of an open circuit, the different partial pressures result in a potential difference between the two electrodes. Thus, the readout is either the measured current or potential (Moos *et al.*, 2009; Guth and Wiemhöfer, 2019). Oxygen ion conductors represent one of the most common class of ceramics used for ion conductor gas sensors, but there are other materials, in which other ions such as H^+ , Li^+ or Na^+ are the mobile ion species (Pasierb and Rekas, 2009).

The potentiometric readout of a pair of electrodes, which shows a Nernstian behavior (Fig. 4(a)), is determined by the different chemical potentials of the analytes, i.e., typically partial pressures, in the two half-cells and described by the Nernst equation:

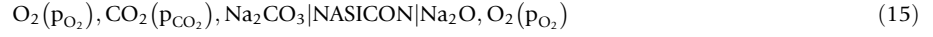
$$E_{\text{eq}} = \frac{RT}{zF} \cdot \ln\left(\frac{p_{\text{gas}}^{\prime\prime}}{p_{\text{gas}}^{\prime}}\right) \quad (10)$$

where E_{eq} is the electro motoric force (EMF) in equilibrium, R the universal gas constant, z the number of transferred electrons, F the Faraday constant and $p_{\text{gas}}^{\prime}$ and $p_{\text{gas}}^{\prime\prime}$ the partial pressures of the analyte gas. Eq. (10) is not only valid for gas mixtures and is as well applicable to molten materials, like liquid metals or molten glasses (Pasierb and Rekas, 2009; Guth and Wiemhöfer, 2019). In simple setups, the reference is a gas mixture with a known analyte concentration, e.g. air as an oxygen reference. An alternative is the use of solid references, e.g., Ni-NiO-mixtures, which are suitable oxygen references (Moos *et al.*, 2009; Guth and Wiemhöfer, 2019).

Oxygen ion conductors like YSZ are not limited to the detection of oxygen and are suitable to detect gases, which are in equilibrium with the oxygen ions in the solid electrolyte, or gases, which are in equilibrium with oxygen (Guth and Wiemhöfer, 2019). For the first case, examples are H_2O or CO_2 , which are in equilibrium with oxygen by Eqs. (11) and (12), respectively. For the latter case examples are water gas mixtures (13) or NO (14).



Furthermore, the measured analyte can differ from the mobile ion species in the solid electrolyte if an auxiliary phase is used on the measurement electrode. An example for an auxiliary phase are CO_2 sensors based on Na^+ ion conductor, e.g., $\text{Na}-\beta''\text{-Al}_2\text{O}_3$ or Na-super-ionic-conductors (NASICON), which use Na_2CO_3 as an auxiliary phase to interact with the analyte gas CO_2 :



For a constant oxygen partial pressure and a constant activity of Na^+ at the reference electrode, which can be achieved by using Na^+ -containing oxides or Na. Such a setup results in a Nernstian behavior and the potential is proportional to the CO_2 partial pressure:

$$E_{\text{eq}} = E^0 + \frac{RT}{2F} \ln(\text{p}_{\text{CO}_2}) \quad (16)$$

where E^0 is the EMF of the cell in standard conditions (Pasierb and Rekas, 2009).

Potentiometric solid electrolyte gas sensors are not limited to electrodes showing a Nernstian behavior, i.e., a potential determined by thermodynamic equilibrium conditions. By using two different, well-selected electrodes (Fig. 4(b)), one obtains a so-called mixed-potential or non-Nernstian setup, operating based on non-equilibrium kinetic principles, i.e., the rate of electrode reactions. A typical mixed-potential setup consists of an oxygen electrode as a reference electrode and a working electrode with a low response to oxygen but a high response to certain analyte gases (H_2 , CO, hydrocarbons or NO_x). The electrodes are arranged either in a gas-symmetric setup, i.e., both exposed to the same gas mixture, or in a non-symmetric setup, in which the reference electrode is exposed to an external reference gas mixture, e.g., air (Moos *et al.*, 2009; Guth and Wiemhöfer, 2019).

Considering for example a carbon monoxide sensitive working electrode and a reference electrode in air, the following electrode reactions are possible for the working (17) and the reference (18) electrode:



In sum, both half-cell reactions correspond to the oxidation of CO to CO_2 (19). The kinetics of both electrode reactions depend on the electrode materials used. The mixed potential is the potential at which both reactions (17 and 18) proceed with the same reaction rate and, thus, the mixed potential depends on the selected electrode material. For example, if reaction (17) is more favored than reaction (18), the oxygen reduction becomes the rate limiting step and non-Nernstian behavior is observed (Miura *et al.*, 1998). A key factor in designing mixed-potential gas sensor is the selection of suitable electrode materials for the working electrode, which determines the sensitivity and selectivity, e.g., by its catalytic properties. Non-Nernstian behavior can be achieved by using metallic working electrodes (e.g., Ni, Ag or Au) or oxides, ranging from binary oxides (e.g. CeO_2 , Nb_2O_5 or SnO_2) over ternary (e.g., EuNbO_4 or LaCrO_3) to mixed oxides ($\text{LaCr}_{0.8-x}\text{Ga}_x\text{O}_{3-\delta}$ or $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Ga}_y\text{O}_{3-\delta}$) used as working electrode. However, the selection of electrode materials is largely based on an empirical process rather than knowledge-based selection derived from understanding of the fundamental processes in details (Guth and Wiemhöfer, 2019).

For mixed-potential gas sensors, the quantitative relation of the EMF and the analyte gas concentration is given by the theory by N. Miura, which is based on the Butler-Volmer equation. According to Miura's theory, there is a logarithmic relation between the measured mixed potential and the analyte concentration equation (Miura *et al.*, 1998):

$$E_{\text{mix}} \propto \ln(\varphi_{\text{analyte}}) \quad (20)$$

The behavior of different potentiometric solid electrolyte gas sensors during the exposure to propane in a low oxygen background is shown in Fig. 5. Thermodynamically controlled electrodes with a catalytically active material are characterized by a lambda-leap (Fig. 5, blue line); at the reactive electrode surface, the non-equilibrated gas mixture is fully combusted to H_2O and CO_2 . Thus, in oxygen rich mixtures a low potential is measured, which drastically increases around the stoichiometric mixture. Using catalytically inactive electrode materials, e.g., LaCrO_3 , it is possible to selectively measure the free oxygen concentration in the gas mixture, i.e., the voltage is independent of combustible gases in the gas mixture (Fig. 5, gray line). According to Eq. (20), kinetically controlled (non-Nernstian) electrodes show logarithmic dependence on the concentration of the combustible gas (Fig. 5, red line).

An amperometric readout (Fig. 4(c)) of gas sensor based on ionic conductors is achieved by operation voltages, at which the electrode reaction is solely limited by the gas transport. Typically the rate of gas transport is limited by using a small hole or porous ceramic as a diffusion barrier. The measured current, I_{lim} , depends on fixed parameters, such as the dimensions of the diffusion barrier, the diffusion constant, D_{gas} , and the mole fraction, x_{gas} , of the analyte gas:

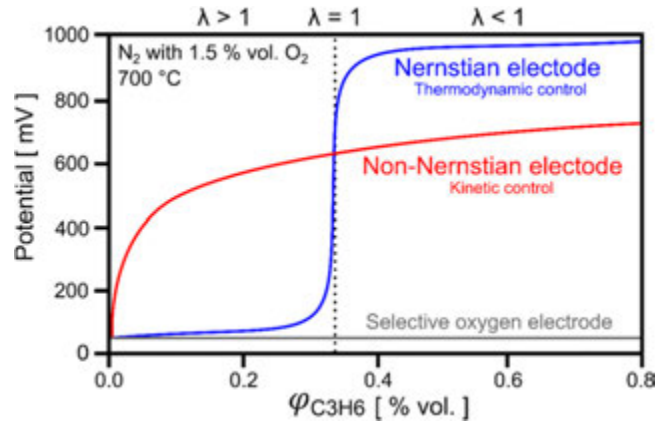


Fig. 5 Cell voltages of a pair of Nernstian electrodes (blue) and a mixed potential gas sensor (red) as a function of the propene concentration in an oxygen background of 1.5% vol. Adapted from Guth, U., Zosel, J., 2004. Electrochemical solid electrolyte gas sensors -Hydrocarbon and NO_x analysis in exhaust gases. *Ionics* 10 (5–6), 366–377. doi:10.1007/BF02377996.

$$I_{lim} = -\frac{zFD_{gas}Ap}{RTL} \ln(1 - x_{gas}) \quad (21)$$

For a small hole, the dimensions of the diffusion barrier are the area, A , and the length, L . For low analyte gas concentrations ($x_{gas} \ll 1$), Eq. (21) simplifies to:

$$I_{lim} = \left(-\frac{zFD_{gas}Ap}{RTL} \right) x_{gas} = const \cdot x_{gas} \propto p_{gas} \quad (22)$$

Thus, for low analyte gas concentrations, there is a linear relation between the analyte gas and the measured current. Amperometric ion conductor gas sensors are used as wideband lambda probes in internal combustion engine cars and allow the simultaneous detection of O₂, NO_x and hydrocarbons (Guth and Wiemhöfer, 2019).

Another measurement principle based on a current readout is the coulometric operation (Fig. 4(d)), which is based on Faraday's law:

$$n = \frac{Q}{zF} = \frac{I_F t}{zF} \quad (23)$$

where n is the amount of the analyte gas, Q is the charge, I_F the current and t the time. Strictly following Faraday's law, the current is directly proportional to the amount of the analyte gas reacting and passing through the solid electrolyte. Gas measurements can be either done by titration or in a gas flow. If the measurement is done by titration, the amount of the analyte gas is obtained by integration over time:

$$n = \frac{Q}{zF} = \frac{1}{zF} \int_{t_1}^{t_2} (I - I_{Base}) dt \quad (24)$$

where I_{Base} is the current in the absence of any analyte gas in the mixture. In a continuous gas flow, the sensors consist of a pump cell and a potentiometric cell and the measured current depends on the analyte gas concentration, the molar volume of the analyte and flow rate of the gas:

$$x_{gas} = \frac{I - I_r}{zF} \frac{V_m}{dV/dt} \quad (25)$$

where x_{gas} is molar fraction of the analyte gas, I_r is the residual current due to the electronic contribution to the conduction, V_m is the molar volume of the analyte gas and dV/dt is the flow rate.

Coulometric gas sensors based on ionic conductors can be used to detect a large variety of reducing (H₂, hydrocarbons) or oxidizing gases (oxygen) and have the advantage that there is no need for calibration of the sensor, since they strictly follow Faraday's law (Guth and Wiemhöfer, 2019).

Gas Sensors Based on Semiconducting Metal Oxides

Chemoresistive gas sensors based on semiconducting metal oxides (SMOX) represent one of the most versatile category of gas sensors. Their small size, relatively low power consumption and cost-efficient production, along with their high sensitivity, long lifetime and various methods to modify their selectivity, are the basis for their widespread success. At elevated and high temperatures SMOX show distinct changes of their conductivity due to changes in the surrounding atmosphere. Their sensing

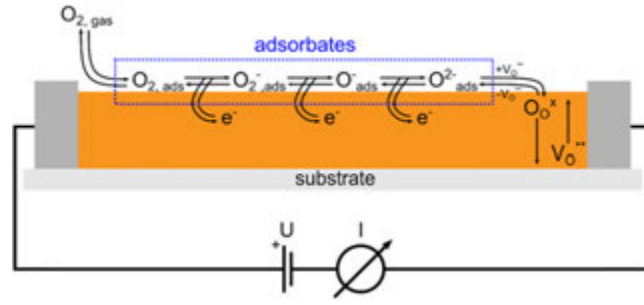


Fig. 6 Possible reaction path of the oxygen exchange reaction of a bulk-active SMOX used as chemoresistive oxygen sensor. Adsorbed species are labeled with the suffix ads and their charge is indicated by minus. Bulk species are represented using the Kröger-Vink notation.

mechanisms and gas sensing performances strongly depend on the nature of the material, its microstructure and the operation conditions (Kim *et al.*, 2013; Neri, 2015).

There are two major types of chemoresistive SMOX. In the first case, the SMOX comes to equilibrium throughout the whole solid, i.e., surface and bulk of the material. This is typically achieved by sufficiently high operation temperatures ($> 700^\circ\text{C}$). These bulk-active gas sensors show a dependence of conductivity on the oxygen partial pressure. In the second case, the bulk of the SMOX does not come to equilibrium with the surrounding atmosphere. This situation is typically found for SMOX operated at temperatures below 400°C . The conductivity of surface-active SMOX depends on charged species adsorbed on the surface. The equilibrium between the adsorbed charged species and the gas phase is influenced by various reactive gases, even at trace levels, and, thus, makes surface-active SMOX highly sensitive to various analyte gases (Kim *et al.*, 2013).

Bulk-Active SMOX

At high temperatures ($> 700^\circ\text{C}$), an exchange reaction of oxygen in the gas phase and the SMOX lattice takes place. This reaction includes the adsorption of atmospheric oxygen, its ionization and dissociation, as well as the diffusion of oxygen/oxygen vacancies within the SMOX. However, the actual sequence of these steps is often indistinguishable and various pathways may be possible (Maier, 1993; Kim *et al.*, 2013). An example for the oxygen exchange reaction is given in Fig. 6. Typical examples of SMOX showing such an oxygen exchange at high temperatures are SrTiO_3 , TiO_2 or SnO_2 (Choi and Tuller, 1988; Maier and Göpel, 1988; Nowotny *et al.*, 2008).

The overall reaction of the oxygen exchange is summarized as follows, using the Kröger-Vink notation of point defects:



where $V_{\text{O}}^{\cdot\cdot}$ are double ionized oxygen vacancies, e' are electrons and $\text{O}_{\text{O}}^{\times}$ are oxygen ions in an oxygen lattice site with no charge difference to ideal lattice structure. For sake of simplicity, the involved metal ion species are neglected. For n-type SMOX, electrons are taken from the conduction band. If the concentration of electrons in the conduction band gets smaller, i.e., the Fermi energy is close to the valence band, the electron neutrality of the reaction is preserved by extracting electrons from the valence band, creating holes (h') in the valence band. In this case, the exchange reaction of oxygen is:



Due to the equilibrium between electrons and holes both reactions (26 and 27) are linked and can be formally described by one of the reactions. However, both reactions occur at the same time and their contribution to the oxygen exchange reaction depends on the oxygen partial pressure. In an oxide the concentration of oxygen vacancies is by far smaller than the concentration of lattice oxygen ($V_{\text{O}}^{\cdot\cdot} \ll \text{O}_{\text{O}}^{\times}$) and the concentration of lattice oxygen is considered to be constant. Thus, the concentration of oxygen vacancies and electrons is proportional to the oxygen partial pressure:

$$[e']^{-4} \cdot [V_{\text{O}}^{\cdot\cdot}]^{-2} \propto p_{\text{O}_2} \quad (28)$$

Neglecting the ionic contribution to the conductivity of the SMOXs, the conductivity (σ) depends on the concentration and mobility (μ) of electrons and holes:

$$\sigma = e(\mu_{e'} \cdot [e'] + \mu_{h'} \cdot [h']) \quad (29)$$

where e is the elementary charge. Depending on the majority charge carrier a SMOX will show n-type ($[e'] \gg [h']$) or p-type ($[e'] \ll [h']$) behavior.

The conductivity of a bulk-active SMOX as a function of the oxygen partial pressure is generally described by the following equation:

$$\sigma \propto [e'] \propto \exp\left(-\frac{E_A}{kT}\right) \cdot (p_{\text{O}_2})^{\frac{1}{m}} \quad (30)$$

where E_A is the activation energy of the defect formation during the oxygen exchange reaction and $\frac{1}{m}$ an exponent, which depends

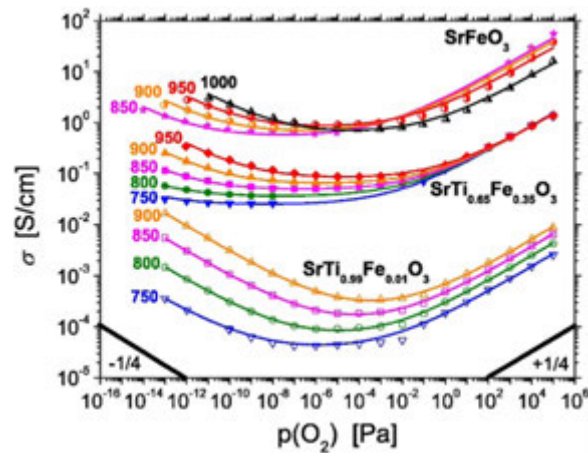


Fig. 7 Conductivity of different bulk-active SMOX as a function of the oxygen partial pressure at different operation temperatures. With increasing oxygen partial pressure, the conductivity changes from n-type ($m = -1/4$) to p-type ($m = +1/4$) behavior. Reprinted from Kim, I.D., Rothschild, A., Tuller, H.L., 2013. Advances and new directions in gas-sensing devices. *Acta Materialia* 61 (3), 974–1000. doi:10.1016/j.actamat.2012.10.041.

on the chemistry taking place at a certain oxygen partial pressure. Depending on the oxygen partial pressure, different values for m are found. For low oxygen partial pressure, the electrons are the majority charge carrier and their concentration is larger than the acceptor impurity concentration, which can be neglected and m equals -6 . In intermediate oxygen concentrations, the concentration of electrons is much smaller than the acceptor impurity concentration. The oxygen vacancy concentration is approximately equal to the constant concentration of acceptor impurities. As long as electrons are the majority charge carrier, i.e., as long as the reaction described in Eq. (26) dominates, m equals -4 . With the proceeding incorporation of atmospheric oxygen the concentration of electrons in the conduction band decreases until formation of holes (27) dominates the oxygen exchange. In this situation the conductance is dominated by holes ($[e'] \ll [h]$), i.e., the SMOX transitions from an n-type to a p-type semiconductor and m equals $+4$. The transition from n-type to p-type conduction and the change in the relation between conductance and oxygen partial pressure is observed for various materials (see Fig. 7).

At high oxygen concentrations, the holes are still the dominant charge carrier and their concentration is determined by the constant concentration of acceptor impurities and, thus, the conductance is independent of the oxygen partial pressure (Choi and Tuller, 1988; Nowotny *et al.*, 2008).

As shown in Eq. (30) and Fig. 7, the conductance not only depends on the oxygen partial pressure but is influenced by the operation temperature as well. Thus, using bulk-active SMOX as oxygen sensors, requires an accurate and stable temperature control to avoid an interfering effect of temperature offsets or fluctuations. Another, yet more exceptional, approach achieves a temperature independence by tailoring the material in fashion that two opposite effects balance each other. Such an example is $\text{SrTi}_{0.65}\text{Fe}_{0.35}\text{O}_3$, which is shown in Fig. 7 (Kim *et al.*, 2013).

Oxygen sensing with bulk-active SMOX is based on the exchange reaction of atmospheric oxygen and lattice oxygen of the SMOX, which traps or releases electrons from the solid and, thus, alters the charge carrier concentration of the whole material. The oxygen exchange reaction and the subsequently changed charge carrier concentration are the reception process. The transduction, i.e., translating the change in the charge carrier concentration into an electrical signal, is implemented by a resistance measurement.

Assigning a SMOX as such to the bulk-active or surface-active type is rather ambiguous; depending on the operation temperature, the same SMOX can be either a bulk-active or surface-active gas sensing material. For example, SnO_2 is the most widely used SMOX for surface-active gas sensors, but operated at sufficiently high operation temperatures ($\sim 600^\circ\text{C}$), the material's bulk equilibrates with atmospheric oxygen and the conductance is proportional to the oxygen partial pressure (Maier and Göpel, 1988; Ihokura and Watson, 1994).

Surface-Active SMOX

For bulk-active SMOX, the interaction with the gas phase, namely atmospheric oxygen, affects the whole volume of the material. For surface-active SOMX, which are operated at intermediate temperatures ($100\text{--}400^\circ\text{C}$), the interaction with the gas phase only affects the surface region of the material, while the bulk remains unaffected by the atmosphere. The oxygen exchange reaction (Fig. 6) will only change adsorbed species and the composition of the surface. The sequence and major species of the oxygen exchange at intermediate temperatures were discussed by various authors and still remain under discussion (Barsan and Weimar, 2001; Gurlo, 2006; Kim *et al.*, 2013). For key n-type SMOX, namely SnO_2 , WO_3 and In_2O_3 , the current model describes the interaction with atmospheric oxygen as the formation and cancelation of oxygen vacancies at the surface of the material (Degler *et al.*, 2019). Using a modified Kröger-Vink notation (+ and $-$ to indicate the charge with respect to the lattice position) to avoid confusion with the bulk oxygen exchange, the oxygen exchange at intermediate temperatures can be described as follows:



where V_{O}^{++} is a surface oxygen vacancy, O_{O} surface oxygen and k_{ads} or k_{des} the rate constants of the adsorption or desorption of oxygen, respectively. The process described in Eq. (31) is referred to as ionosorption, since the adsorption involves a charge transfer between the adsorbed species and the solid. The concentration of ionosorbed oxygen depends on the oxygen partial pressure, the number of adsorption sites, i.e., oxygen vacancies, and electrons available at the surface. The total number of ionosorbed species is limited to a fraction of a monolayer (10^{-5} to 10^{-3}) by the so-called Weisz limitation (Weisz, 1953). Furthermore, the concentration of ionosorbed oxygen is influenced by the partial pressure of oxygen, the number of electrons available at the surface and the presence of other reactive gases, first and foremost reducing gases, which are oxidized by surface oxygen. A simple example is the oxidation of CO by the ionosorbed oxygen:



The oxidation reaction of other reducing gases or vapors, e.g., alcohols or other volatile organic compounds, may result in a more complex surface chemistry, including partial oxidation products. Oxidizing gases, such as NO_2 , have as well an impact on the surface composition of SMOX and the total number of ionosorbed species. Interfering compounds, especially water vapor, have a large impact on the surface chemistry of SMOX, competing for the same sites or reaction partners and inhibiting surface reactions. The nature of all surface reactions is determined by various parameters; the SMOX itself and the operation temperature have a large impact on the reactions with reducing or oxidizing gases as well as the influence of interfering compounds (Sänze and Hess, 2014; Degler *et al.*, 2015).

According to the Eqs. (31) and (32), the surface concentration of ionosorbed oxygen, or vice-versa oxygen vacancies, is determined by the composition of the surrounding atmosphere, namely the concentrations of oxygen and reducing gases. Only the surface of the material is changed by these reactions and, thus, the oxygen vacancies concentration at the surface and in the bulk of the material varies and results in the formation of space charge layers. If the oxygen vacancy concentration at the surface is lower than the one in the bulk ($[V_{\text{O}}^{++}]_{\text{surf}} < [V_{\text{O}}^{++}]_{\text{bulk}}$) an electron depletion layer is formed at the surface, which is described by an upwards band bending ($eV_s > 0$). While if the oxygen vacancy concentration at the surface is higher than the one in the bulk ($[V_{\text{O}}^{++}]_{\text{surf}} > [V_{\text{O}}^{++}]_{\text{bulk}}$) an electron accumulation layer is formed, which corresponds to a downwards band bending ($eV_s < 0$). If both vacancy concentrations are equal ($[V_{\text{O}}^{++}]_{\text{surf}} \approx [V_{\text{O}}^{++}]_{\text{bulk}}$), there is no band bending caused by the reactions with the atmosphere. In the absence of an initial band bending, e.g., due to additional donor or acceptor states, this situation is referred to as flat band situation (Degler *et al.*, 2019).

The surface band bending affects the electron concentration at the surface. If all donors are fully ionized (Schottky approximation), the surface concentration of electrons in a depletion layer is described by the following Boltzmann distribution:

$$n_s = n_b \cdot \exp\left(-\frac{eV_s}{k_B T}\right) \quad (33)$$

where n_s and n_b are the surface or bulk concentration of electrons, respectively, e is the elementary charge of an electron, V_s is the surface band bending, k_B is the Boltzmann constant and T the absolute temperature (Barsan and Weimar, 2001).

A typical surface-active SMOX gas sensor is based on a porous layer of SMOX grains, which are connected, but show no sintering necks. In this case, the resistance of the full layer R is determined by the resistance of the grain-grain-boundary, which depends on the surface concentration of electrons n_s , which, according to Eq. (33), exponentially depends on the surface band bending V_s :

$$R \propto n_s \propto \exp\left(\frac{eV_s}{k_B T}\right) \quad (34)$$

Surface-active SMOX gas sensors typically show strong responses, i.e. resistance changes of one or more orders of magnitude, to changes in the atmosphere and the sensor signals are calculated as a ratio (Eq. 2). In case of an n-type SMOX exposed to a reducing gas (Eq. 2(a)) and using Eq. (34), one obtains the following relation for the sensor signal:

$$S = \frac{R_0}{R_{\text{gas}}} \propto \frac{\exp\left(\frac{eV_{s,0}}{k_B T}\right)}{\exp\left(\frac{eV_{s,\text{gas}}}{k_B T}\right)} = \exp\left(\frac{e\Delta V_s}{k_B T}\right) \quad (35)$$

where R_0 is the resistance in the reference condition and R_{gas} the resistance under gas exposure. As shown in Eq. (35), the sensor signal is proportional to changes in the surface band bending, caused by the space charge layer created by the difference in the oxygen vacancy concentration or other ionosorbed species, which is determined by the surface chemistry (Eqs. (31) and (32)).

The Eqs. (33) to (35) describe the situation for an electron depletion layer. In case of an electron accumulation layer, a different relation is valid (Barsan *et al.*, 2010):

$$S = \frac{R_0}{R_{\text{gas}}} \propto \frac{\exp\left(\frac{eV_{s,0}}{2k_B T}\right)}{\exp\left(\frac{eV_{s,\text{gas}}}{2k_B T}\right)} \propto \exp\left(\frac{e\Delta V_s}{2k_B T}\right) \quad (36)$$

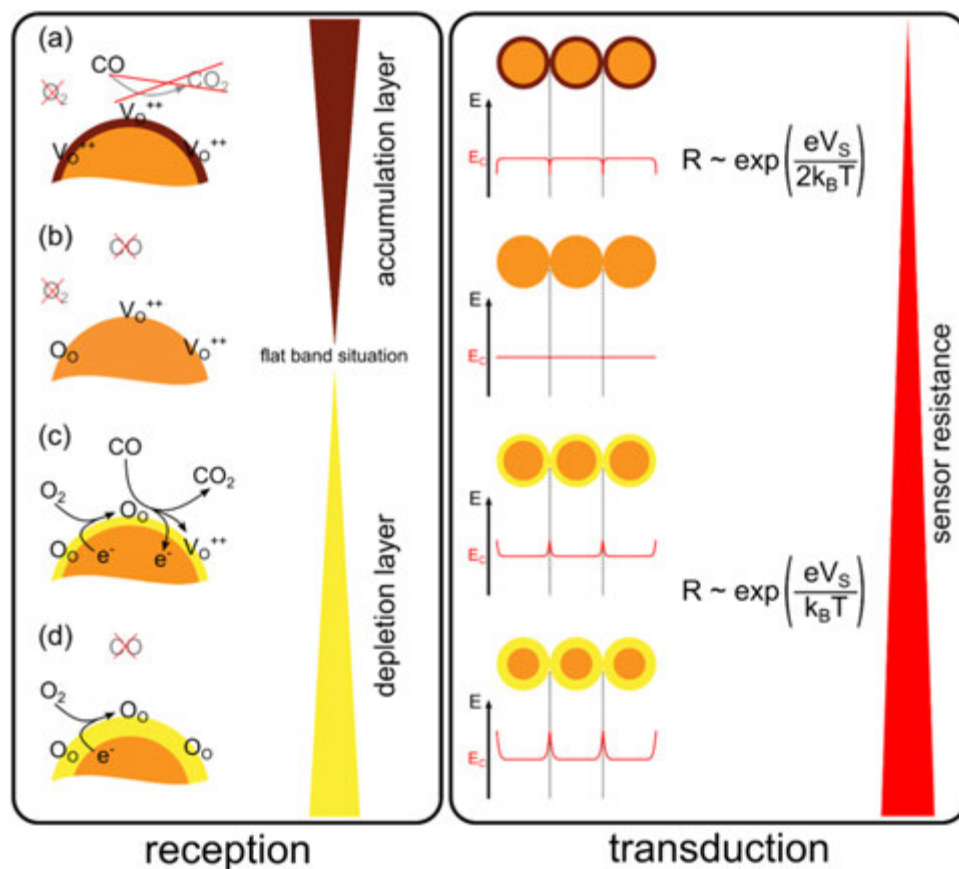


Fig. 8 Working principle of surface-active n-type SMOX showing the gas reception (left) and transduction (right) in four important conditions: Formation of an accumulation layer in oxygen-lean conditions (a), flat band situation (b) and depletion layer in the presence (c) and absence (d) of an analyte gas in an oxygen excess. The unaffected bulk region is shown in orange, the depletion layer in yellow and the accumulation layer in brown. Reprinted from Degler, D., Weimar, U., Barsan, N., 2019. Current understanding of the fundamental mechanisms of doped and loaded semiconducting metal oxide-based gas sensing materials. *ACS Sensors*. doi:10.1021/acssensors.9b00975.

Accumulation layer controlled conduction is typically found for p-type SMOX in ambient conditions, i.e., high oxygen backgrounds (Barsan *et al.*, 2010; Kim and Lee, 2014). For n-type SMOX, accumulation layers occur when the SMOXs are exposed to reducing gases in low oxygen backgrounds or when being exposed to high concentrations of reducing gases in humid atmospheres (Barsan *et al.*, 2011; Barsan *et al.*, 2015). The gas sensing mechanism for pristine n-type SMOX is summarized in Fig. 8.

The gas sensing mechanism (Fig. 8) of pristine surface-active SMOX involves a series of surface reactions, which involve the formation or cancelation of surface oxygen vacancies or the formation of other charged surface species and results in the formation of a space charge layer, which determines the surface concentration of electrons. The interaction of oxygen and analyte gases and how these reactions influence the surface concentration of electrons largely depends on the chemical and electrical properties of a specific SMOX and can be further influenced by doping or loading with additives. Similar to bulk-active SMOX, chemical reaction and the subsequent changes in the charge carrier concentration represent the reception mechanism, but with one important difference that only the surface of the material is affected. The transduction is implemented by a resistance measurement typically. Since only the surface of the material is affected, the conduction through the sensing layer, i.e., the transduction, is strongly influenced by the microstructure of the material.

Introducing additives, typically other main or transition group elements, into SMOX materials is widely used to improve the gas sensing properties of surface-active SMOX. Additives form different structures, ranging from doping the SMOX, i.e., incorporating single foreign atoms/ions in the SMOX lattice, to loadings, i.e., separate metallic or oxide phases attached to SMOX surface. Dopants and loadings largely influence the chemical and electrical properties of the SMOX, and the resulting sensitization effect of an additive has a chemical and electrical contribution, rather than solely altering the chemical or electrical properties (Degler *et al.*, 2019).

One of the goals of additives is the improvement of the catalytic activity of the typically poorly reactive SMOX. However, solely an increased reactivity does not necessarily result in an increased sensor effect. First, the catalytically enhanced reaction must affect the charge carrier concentration of the SMOX to contribute the gas reception. Second, this change must be reversible and sufficiently strong. The latter point marks a major difference between a good chemoresistive gas sensor and an efficient catalyst. A

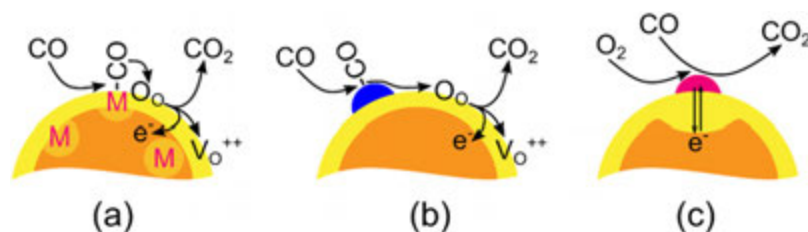


Fig. 9 Proposed sensitization mechanisms of additives in surface-active SMOX materials used as chemoresistive gas sensors. Dopants (a) change the electronic properties of the SMOX, indicated by the lighter color around the additives, and affect the surface chemistry by creating new surface sites. Loadings either change the gas sensing mechanism by a spillover mechanism (b), which increases the surface reactivity, or a Fermi-level control mechanism (c), which is based on the electronic coupling of the SMOX and additive.

sensor requires a temporary change of the material's properties, which are result in the sensor signal, while an efficient catalyst requires a swift recovery of the initial, reactive state, in order to obtain a high turnover rate. Thus, SMOX-based gas sensors and catalysts typically have opposed requirements to the chemical reaction taking place (Müller *et al.*, 2018; Degler *et al.*, 2019).

To understand the effect of additives of SMOX different models were developed, which largely depend on the structure of the introduced additive. Dopants (Fig. 9(a)) could have an electrical or chemical effect as well as both. Taking a foreign cation replacing a lattice cation as example, this could result in the formation of additional donor or acceptor states, depending on the relative charge of the foreign ion with respect to the original lattice ion. The electrical effect will be strongly influenced by the distribution of the foreign ions in the SMOX. The distribution involves the concentration as well as the oxidation state of dopants and determines whether dopants cause a shift of the Fermi level in the whole material or an intrinsic band bending at the surface. Dopants at the surface of the SMOX material may offer new reaction sites with different properties than the ones on the original SMOX and, thus, alter the reactivity (Degler *et al.*, 2019).

Loadings are present as metallic or oxide clusters at the SMOX surface (Fig. 9(b) and (c)), depending on the material preparation as well as the operation condition of the gas sensor. One typical sensitization mechanism of loadings is the spillover of one of the species involved in the surface chemistry (Fig. 9(b)), which results in an increased reactivity of the surface, i.e., is supposed to enhance the gas reception. Spillover sensitization is typically assigned to metallic loadings, which are not electronically coupled with the supporting SMOX, and involve either the spillover of the analyte, usually a reducing gas, or molecular oxygen. The spillover of a reducing gas involves the adsorption on the loading, possibly an activation or partial reaction of the reducing gas, and the transfer to the SMOX surface, where the reducing gas reacts with oxygen from the SMOX surface. The spillover of oxygen has a more ambivalent effect on the gas reception: on the one hand, the increased oxygen coverage on the SMOX surface offers more reaction sites for reducing gases, increasing the probability of a successful interaction, i.e., gas reception. On the other hand, the increased adsorption of oxygen favors the cancelation of oxygen vacancies, i.e., compensates the gas reception.

The other major sensitization mechanism of loadings is the so-called Fermi-level control mechanism (Fig. 9(c)), which has a chemical and an electrical contribution to the sensitization effect. The electronic contribution implies different work functions of the SMOX and loading, which result in an alignment of the two Fermi levels. Consequently, the Fermi level of the SMOX is pinned by the loading and in the vicinity of the loading the space charge layer is determined by the electronic coupling with the loading. The magnitude of the space charge layer changes if the work function of the loading changes, e.g., due to changes in its composition, which can be caused by surface reactions. The chemical contribution is related to the shift of the reaction with the analyte gas from the SMOX to the loading. This shift is caused by the generally higher reactivity of various loadings, such as oxides of Rh, Pd, Ag or Pt, and a deactivation of the SMOX near the loading. The deactivation originates from the typically high band bending induced by the electronic coupling, which limits the surface concentration available for oxygen ionosorption (Eq. (31)), therefore decreasing the number of reactive oxygen available to oxidize the analyte gas (Eq. (32)). In case of the Fermi-level control mechanism, the electrical and chemical effects of the loading result in a control of the space charge layer in the SMOX by the composition of the loading, which changes when reacting with analyte gases. Since the gas reception is controlled by the loading, it is possible to strongly change the selectivity of a gas sensing material (see Fig. 10). The spatial limitation of the electronic coupling results in a strong dependency of the sensitization effect on the concentration, size and distribution of the loading (Degler *et al.*, 2019).

Introducing additives in SMOX is a powerful tool to influence the gas sensing properties by changing the gas reception. There are further parameters having an impact on the gas sensing properties of surface-active SMOX. The morphologies and micro-structure of the sensing material have a strong impact on the conduction in the sensing layer, i.e., the transduction, and therefore on the gas sensing properties.

The morphology of the sensing layer determines the accessibility of gases into the sensing layer. In a compact sensing layer or for a single crystalline SMOX (Fig. 11(a)), gases are not able to access the volume of the sensing material and only will interact with the outermost region of the gas sensing layer. Thus, the inner volume is not affected by the gas phase. For an n-type SMOX, the omission of oxygen ionosorption from the gas phase prevents the formation of a depletion layer and consequently the resistance in the volume will be lower. Two parallel resistors represent this situation in the equivalent circuit shown in Fig. 11. One is

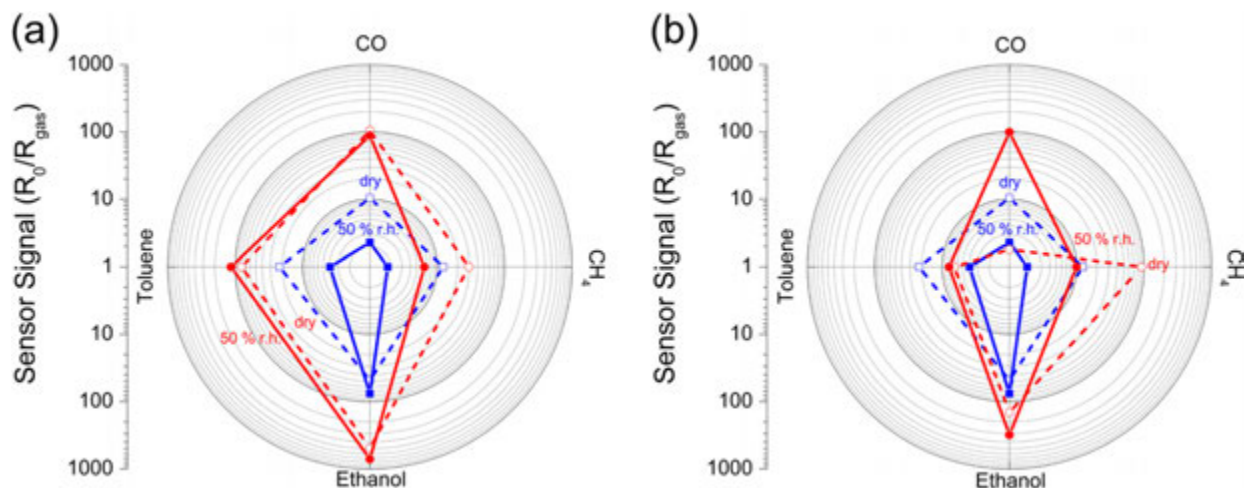


Fig. 10 Effect of different loadings on SnO₂-based gas sensing materials. Metallic Au-loadings (a) sensitize the material by an oxygen-spillover, increasing the general reactivity and having minor impact on the selectivity towards the different analyte gases. PdO-loadings (b) sensitize the material by a Fermi-level control mechanism, having a stronger impact on the selectivity since the gas response is controlled by the PdO loading. The sensor response of the pristine SnO₂ is shown in blue as comparison for the loaded materials (red). Measurements in dry air are plotted with dashed lines and empty symbols, measurements in humid air (50%RH) are plotted with straight lines and filled symbols. Reprinted from Tofighi, G., *et al.*, 2019. Microfluidically synthesized Au, Pd and AuPd nanoparticles supported on SnO₂ for gas sensing applications. *Sensors & Actuators: B Chemical* 292, 48–56.

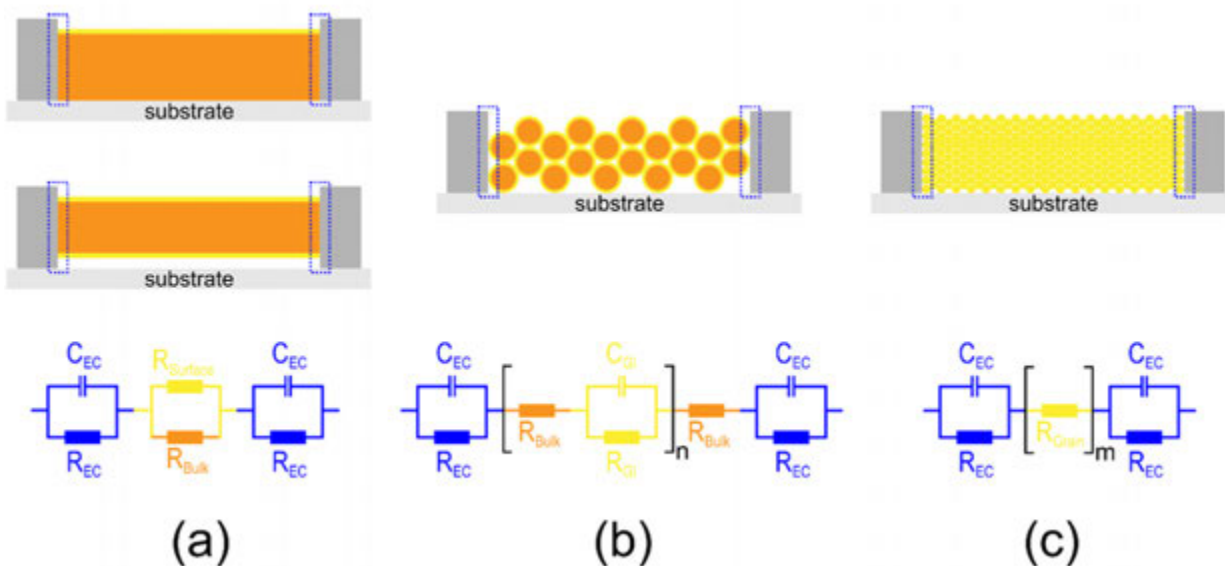


Fig. 11 Schematic representation of the charge transport in different surface-active SMOX layers: Compact layer (a, top), single crystal nanowire (a, middle) and the corresponding equivalent circuit for these two layer morphologies (a, bottom); The conduction paths is represented by a series the two electrode contacts (blue), which are determined by the work function difference of the two materials, and two parallel resistors representing the conductivity of the surface (yellow) and bulk (orange). Porous layer of SMOX grains with a radius larger than the Debye length (b, top) and the corresponding equivalent circuit (b, bottom); the conduction paths are represented by a series of the two electrode contacts and a repetition of a resistor, which represents the bulk of a SMOX grain, and the grain – grain interface (GI), which is represented by a parallel resistor and capacitor. Porous layer of SMOX grains with a radius smaller than the Debye length (c, top) and the corresponding equivalent circuit (c, bottom); the conduction paths are represented by the two electrode contacts and a series of resistors representing each fully depleted grain. Reprinted from Degler, D., Weimar, U., Barsan, N., 2019. Current understanding of the fundamental mechanisms of doped and loaded semiconducting metal oxide-based gas sensing materials. *ACS Sensors*. doi:10.1021/acssensors.9b00975.

representing the surface resistance, which is sensitive to changes in the gas phase, and one the bulk resistance, which is not affected by the gas phase, but mainly contributes to the conduction. For compact layers or single crystals, only a small fraction of the SMOX material contributes to the gas sensing effect and the changes in the less conductive surface region result only in a minute change in the overall resistance. In contrast, in porous layers (Fig. 11(b) and (c)), the gases access the whole volume of the sensing layer and

evenly influence the SMOX material. However, the consumption of the analyte gas can result in a concentration gradient within the sensing layer and gradually decrease the sensing effect in the volume of the gas sensing layer (Barsan and Weimar, 2001).

For porous layers, the size and interface of the SMOX grains additionally influence the transduction. The size of a SMOX grain does not only consider the geometrical size, i.e., grain diameter d , but rather considers the ratio of the grain diameter and the size of the depletion layer, or Debye length λ_D . Grains are large if the diameter is larger than twice the Debye length ($d > 2\lambda_D$), while grains are small if the diameter is smaller than twice the Debye length ($d < 2\lambda_D$). In case of large grains, the current will preferentially pass through the bulk of the grain, but at each grain-grain-boundary, the electrons have to pass the depletion layer. The situation at the grain-grain-boundary resamples a back-to-back Schottky barrier, which determines the conduction. The corresponding equivalent circuit for an n-type SMOX with an electron depletion layer (Fig. 11(b), bottom) comprises of a series of a resistor with a parallel capacitor, which represents the grain-interface, with a serial resistor, which represents the bulk of a grain. In case of small grains, the SMOX grains are fully depleted and the charge transport is limited by the surface concentration of electrons. The corresponding equivalent circuit is represented by a series of resistors (Fig. 11(c), bottom), each one representing one SMOX grain (Barsan and Weimar, 2001). Discussions focusing on p-type SMOX are given elsewhere (Barsan *et al.*, 2010; Kim and Lee, 2014).

Surface-active SMOX typically display a power-law relation between the analyte concentration and the obtained sensor signal. Thus, surface-active SMOX are often highly sensitive to trace amounts of analytes, but have a low sensitivity for high analyte concentrations. Pristine, as well as most of the doped and loaded, SMOX react with a large variety of analyte gases and one sensor is often suitable for detection of various gases. This lack of selectivity is one of the major drawbacks of surface-active SMOX. In order to overcome these disadvantages, several strategies are possible, including using filters, modulating the operation temperature of the sensor or building sensor arrays, which consist of several sensor elements showing an orthogonal response pattern. A related drawback is the strong interference of water vapor, which is present in most ambient environments. Chemoresistive gas sensors based on SMOX have a high life expectancy of 10 years or more. However, their stability and reliability suffer from operation in oxygen lean conditions, or the exposure to compounds poisoning the gas sensors, such as silicon oil. Despite the several drawbacks, surface-active SMOX are suitable for various applications ranging from the detection of harmful over substances process monitoring to applications in health and comfort.

Conclusion

Gas sensors based on ceramic materials include a large variety of different sensor principles. Ceramic gas sensors cover a large range of applications, but for certain environments, some materials or sensor principles are favorable or some even not suitable. Thus, all the presented types of gas sensors are currently found in applications, e.g., the detection of flammable gases by pellistors or chemoresistive sensors (surface active-SMOX) or controlling the exhaust catalysts in internal combustion engine cars using potentiometric or amperometric sensors based on solid-state ion conductors. With the increasing importance of smart and connected systems, gas sensors will gain importance as they can provide chemical information from the surrounding environment, i.e., directly from or via the gas phase. The emerging of Industry 4.0 and the Internet of Things pose new requirements on the sensors' sensitivity, selectivity and stability as well as their suitability for certain applications, e.g. miniaturized systems for small sizes and low power consumption, or highly robust sensor which operate in harsh environments. All these requirements are demanding tasks for the development of sensor technology on various levels, including new materials, new approaches to design and manufacture sensor devices, develop sensor systems and analyze the data obtained by sensors. Compiling with these tasks requires a profound understanding of the fundamental processes of ceramic gas sensors to find knowledge-based and target-oriented solutions. Thus, the development of ceramic gas sensors should always comprise the development of new materials, devices or systems, as well as investigating and understanding their fundamental principles.

References

- Barsan, N., *et al.*, 2010. Modeling of sensing and transduction for p-type semiconducting metal oxide based gas sensors. *Journal of Electroceramics* 25 (1), 11–19. doi:10.1007/s10832-009-9583-x.
- Barsan, N., Weimar, U., 2001. Conduction model of metal oxide gas sensors. *Journal of Electroceramics* 7 (3), 143–167. doi:10.1023/A:1014405811371.
- Barsan, N., Hübner, M., Weimar, U., 2011. Conduction mechanisms in SnO₂ based polycrystalline thick film gas sensors exposed to CO and H₂ in different oxygen backgrounds. *Sensors and Actuators B: Chemical* 157 (2), 510–517. doi:10.1016/j.snb.2011.05.011.
- Barsan, N., Reibold, J., Weimar, U., 2015. Conduction mechanism switch for SnO₂ based sensors during operation in application relevant conditions; implications for modeling of sensing. *Sensors and Actuators B: Chemical* 207, 455–459. doi:10.1016/j.snb.2014.10.016.
- Bársony, I., Dücső, C., Fürjes, P., 2009. Thermometric gas sensing. In: Comini, E., Faglia, G., Sberveglieri, G. (Eds.), *Solid State Gas Sensing*, first ed. New York: Springer Science+Business Media, LLC, pp. 237–260. doi:10.1007/978-0-387-09665-0.
- Bochenkov, V.E., Sergeev, G.B., 2010. Sensitivity, selectivity, and stability of gas-sensitive metal-oxide nanostructures. In: Umar, A., Hahn, Y.-B. (Eds.), *Metal Oxide Nanostructures and Their Applications*, first ed. American Scientific Publishers, pp. 31–52.
- Choi, G.M., Tuller, H.L., 1988. Defect structure and electrical properties of single-crystal Ba_{0.03}Sr_{0.97}TiO₃. *J. Am. Ceram. Soc.* 714, 201–205.
- Chou, J., 2000. Catalytic combustible gas sensors. In: Chou, J. (Ed.), *Hazardous Gas Monitors: A Practical Guide to Selection, Operation and Applications*, first ed. New York: McGraw-Hill Book Company, pp. 37–45.
- Danzer, K., 2007. *Analytical Chemistry – Theoretical and Metrological Fundamentals*, first ed. Springer-Verlag Berlin Heidelberg. doi:10.1007/b103950.

- Degler, D., *et al.*, 2015. Identifying the active oxygen species in SnO₂ based gas sensing materials: An operando IR spectroscopy study. *The Journal of Physical Chemistry C* 119 (21), 11792–11799. doi:10.1021/acs.jpcc.5b04082.
- Degler, D., Weimar, U., Barsan, N., 2019. Current understanding of the fundamental mechanisms of doped and loaded semiconducting metal oxide-based gas sensing materials. *ACS Sensors* 4 (9), 2228–2249. doi:10.1021/acssensors.9b00975.
- Gründler, P., 2007. *Chemical Sensors – An Introduction for Scientists and Engineers*. Berlin/Heidelberg/New York: Springer-Verlag Berlin Heidelberg, doi:10.1007/978-3-540-45743-5.
- Giurlo, A., 2006. Interplay between O₂ and SnO₂: Oxygen ionosorption and spectroscopic evidence for adsorbed oxygen. *ChemPhysChem* 7 (10), 2041–2052. doi:10.1002/cphc.200600292.
- Guth, U., 2008. Gas sensors. In: Bard, A. J., Inzelt, G., Scholz, F. (Eds.), *Electrochemical Dictionary*, first ed. Heidelberg: Springer-Verlag Berlin Heidelberg, pp. 293–297. doi:10.1007/978-3-340-74598-3.
- Guth, U., Zosel, J., 2004. Electrochemical solid electrolyte gas sensors -Hydrocarbon and NO_x analysis in exhaust gases. *Ionics* 10 (5–6), 366–377. doi:10.1007/BF02377996.
- Guth, U., Wiemhöfer, H.-D., 2019. Gas sensors based on oxygen ion conducting metal oxides. In: Barsan, N., Schierbaum, K.-D. (Eds.), *Gas Sensors Based on Conducting Oxides*, first ed. Amsterdam: Elsevier, pp. 13–60.
- Hulanicki, A., Glab, S., Ingman, F., 1991. Chemical sensors: Definitions and classification. *Pure and Applied Chemistry* 63 (9), 1247–1250. doi:10.1351/pac199163091247.
- Ihokura, K., Watson, J., 1994. *The Stannic Oxide Gas Sensor: Principles and Applications*. CRS Press, Inc. first ed.
- Kim, H.-J., Lee, J.-H., 2014. Highly sensitive and selective gas sensors using p-type oxide semiconductors: Overview. *Sensors and Actuators B: Chemical* 192, 607–627. doi:10.1016/j.snb.2013.11.005.
- Kim, I.D., Rothschild, A., Tuller, H.L., 2013. Advances and new directions in gas-sensing devices. *Acta Materialia* 61 (3), 974–1000. doi:10.1016/j.actamat.2012.10.041.
- Maier, J., 1993. Defektchemie: Zusammensetzung, Transport und Reaktionen im festen Zustand - Teil I: Thermodynamik. *Angewandte Chemie* 105 (3), 333–482.
- Maier, J., Göpel, W., 1988. Investigations of the bulk defect chemistry of polycrystalline Tin(IV) oxide. *Journal of Solid State Chemistry* 72 (2), 293–302. doi:10.1016/0022-4596(88)90032-1.
- Miura, N., *et al.*, 1998. Highly selective CO sensor using stabilized zirconia and a couple of oxide electrodes. *Sensors and Actuators, B: Chemical* 47 (1–3), 84–91. doi:10.1016/S0925-4005(98)00053-7.
- Moos, R., *et al.*, 2009. Solid state gas sensor research in Germany – A status report. *Sensors* 9 (6), 4323–4365. doi:10.3390/s90604323.
- Müller, S.A., *et al.*, 2018. Exploiting synergies in catalysis and gas sensing using noble metal-loaded oxide composites. *ChemCatChem* 10 (5), 864–880. doi:10.1002/cctc.201701545.
- Neri, G., 2015. First fifty years of chemoresistive gas sensors. *Chemosensors* 3 (1), 1–20. doi:10.3390/chemosensors3010001.
- Nowotny, M.K., *et al.*, 2008. Defect chemistry of titanium dioxide. Application of defect engineering in processing of TiO₂-based photocatalysts. *Journal of Physical Chemistry C* 112 (14), 5275–5300. doi:10.1021/jp077275m.
- Pasler, P., Rekas, M., 2009. Solid-state potentiometric gas sensors-current status and future trends. *Journal of Solid State Electrochemistry* 13 (1), 3–25. doi:10.1007/s10008-008-0556-9.
- Sänze, S., Hess, C., 2014. Ethanol gas sensing by indium oxide: An operando spectroscopic Raman-FTIR study. *The Journal of Physical Chemistry C* 118, 25603–25613. doi:10.1021/jp509068s.
- Tofighi, G., *et al.*, 2019. Microfluidically synthesized Au, Pd and AuPd nanoparticles supported on SnO₂ for gas sensing applications. *Sensors & Actuators: B. Chemical* 292, 48–56.
- Weisz, P.B., 1953. Effects of electronic charge transfer between adsorbate and solid on chemisorption and catalysis. *The Journal of Chemical Physics* 21 (9), 1531–1538. doi:10.1063/1.1699292.

Pyroelectric Crystals, Ceramics, and Thin Films for IR Sensors

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Introduction

The pyroelectric effect is the change in electrical dipole moment occurring in a polar dielectric due to a change in its temperature. As a consequence of this effect, a detectable current can be made to flow in an external circuit connected to a piece of polar dielectric, allowing the temperature change to be sensed. This effect has been known for many years (Lang, 1999), and since about 1960 it has been extensively studied for the detection of radiation in the two “atmospheric window” infrared radiation (IR) bands of 3–5 μm and especially 8–14 μm . The ambient-temperature operation of pyroelectric detectors gives them a number of important advantages over the cryogenically cooled photon detectors such as mercury cadmium telluride or indium antimonide. Pyroelectric detectors have found a huge range of applications in products ranging from fire alarms to intruder detectors, in instrumentation such as gas analysis, and in thermal imaging. Detectors have been demonstrated that work from the visible through the IR to submillimeter and millimeter wavelengths. They have also been used at radiation modulation frequencies from a few hertz to many gigahertz.

The pyroelectric coefficient is a vector $\bar{p}$, equal to the rate of change of the spontaneous polarization $\bar{P}_S$ with temperature (T):

$$\Delta \bar{P}_S = \bar{p} \Delta T \quad (1)$$

Fig. 1 shows a schematic diagram of a pyroelectric IR detector. It consists of a thin piece of pyroelectric material (the “element”), which has conducting electrodes (usually on its major surfaces) such that there is a component p of $\bar{p}$ perpendicular to the electrodes. These have area A . The pyroelectric charges generated by a change in element temperature can be detected as a current, i_p , flowing in an external circuit such that:

$$i_p = Ap \{dT/dt\} \quad (2)$$

dT/dt is the rate of change of the element’s temperature with time. Thus pyroelectric devices are coupled to the changes of any input energy flux that generate a change in element temperature. Typically, an IR detector will be constructed as shown schematically in Fig. 1, with a high-input impedance amplifier (usually a MOSFET) connected to the element. The largest pyroelectric effects are generally observed in the class of polar dielectric materials known as ferroelectrics (Lines and Glass, 1977). A major advantage of these is that they can be used in polycrystalline form, because they can be electrically poled. This produces a net spontaneous polarization and thus a net pyroelectric effect.

The pyroelectric effect and devices using them have been extensively reviewed previously (see, e.g., Putley, 1970; Whatmore, 1986). Hence, this chapter will briefly review the ways in which the physics of pyroelectric radiation detector operation affects the choice of materials to use in them, discuss the range of such materials, with specific reference to ferroelectric crystals, ceramics, and thin films, and their uses in one of the most exciting recent applications of the devices to emerge into practical applications in the last 10 years, namely uncooled thermal imaging.

Pyroelectric IR Detectors and Materials Figures-of-Merit

The analysis of a pyroelectric detector, shown schematically in Fig. 1, requires consideration of both the thermal and electrical circuits. Radiation with power $W(t)$ sinusoidally modulated at a frequency ω so that $W(t) = W_0 e^{i\omega t}$ is incident on the surface of the element (area A and thickness d), which has emissivity η . The element has a thermal capacity H and a thermal conductance to the

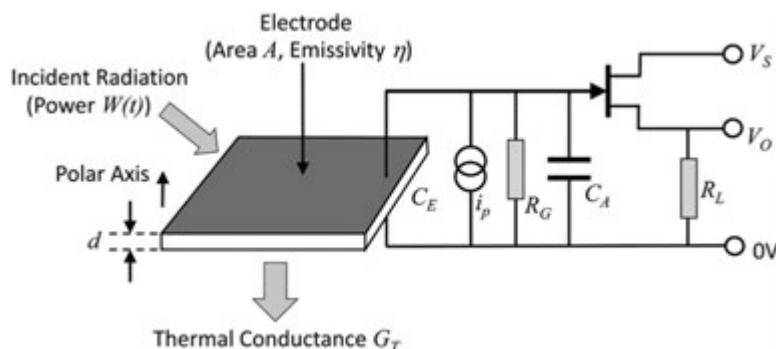


Fig. 1 Schematic diagram of a pyroelectric detector element.

surroundings G_T giving a thermal time constant $\tau_T = H/G_T$. A high-input impedance field effect transistor (FET) used as a source follower amplifier amplifies the electrical signal produced. R_G is the gate resistor, giving an electrical time constant $\tau_E = R_G(C_E + C_A)$ where C_E is the capacitance of the element and C_A the capacitance of the amplifier.

The τ_T and τ_E are the fundamental factors that determine the frequency response of the detector. It can be shown that the pyroelectric current, i_p , generated per watt of input power (the current responsivity R_i) is:

$$\frac{i_p}{W_o} = R_i = \frac{\eta p A \omega}{G_T \sqrt{(1 + \omega^2 \tau_T^2)}} \quad (3)$$

The voltage responsivity of the detector shown in Fig. 1 is simply derived from i_p and the electrical admittance (Y) presented to it. The pyroelectric voltage (V_p) generated on the gate of the FET (and therefore the output voltage V_o for a unity amplifier gain) is given by i_p/Y and the voltage responsivity is R_V where:

$$R_V = \frac{i_p}{Y W_o} = \frac{R_G \eta p A \omega}{G_T \sqrt{(1 + \omega^2 \tau_T^2)} \sqrt{(1 + \omega^2 \tau_E^2)}} \quad (4)$$

The responsivity is maximized by minimizing the element's thermal capacity (i.e., making it thin) and by minimizing G_T (i.e., thermally isolating it from its surroundings).

If the element capacitance C_E is large compared with C_A then R_V reduces to:

$$R_V = \frac{\eta p}{c' \epsilon \epsilon_o A \omega} \quad (5)$$

where c' is the volume-specific heat, ϵ_o is the permittivity of free space, and ϵ is the relative permittivity of the pyroelectric material. For such a detector, the response is proportional to F_V :

$$F_V = \frac{p}{c' \epsilon \epsilon_o} \quad (6)$$

Eq. (6) only contains parameters describing properties of the pyroelectric material, and is therefore a figure-of-merit (FOM), which can be used to compare different materials for their potential voltage responsivities. If $C_A \gg C_E$ the voltage response is proportional to:

$$F_i = \frac{p}{c'} \quad (7)$$

Eq. (7) gives another material FOM. Therefore the choice of the appropriate material will depend both on the amplifier to be used (e.g., JFET have higher input capacitances than MOSFET) and on the size of the detector element. Small area detector elements tend to favor high dielectric constant materials and vice versa to produce a good match between C_A and C_E . If there are a number of elements or detector points defined on a single plate of material, lateral thermal diffusion in the plate will tend to "smear-out" high spatial frequency information. In this case, it would be appropriate to introduce the thermal diffusivity (κ) in the denominator of these FOM, so that lower diffusivity materials will be favored. However, the introduction of technologies (e.g., "reticulation") to physically disconnect adjacent elements would eliminate this need.

It is evidently insufficient to consider only the response of a detector when analyzing its usefulness for a particular application. It is generally necessary to analyze both intrinsic and extrinsic noise signals and compare them with the response. Johnson noise generated by the dielectric loss of the detector material is usually the most important source of electrical noise in the important frequency ranges from 1 to 100 Hz, if the amplifier noise sources are minimized. The total electrical conductance g (consisting of the parallel conductances of gate bias resistor R_G and the AC conductance of the detector element g_D) gives rise to the Johnson noise. It can be shown that for frequencies much less than ω_G , where $\omega_G = (R_G C_E \tan \delta)^{-1}$ ΔV_J is given by:

$$\Delta V_J = \sqrt{\frac{4kTR_G}{1 + \omega^2 \tau_E^2}} \quad (8)$$

(where k is Boltzmann's constant). This leads to an ω^{-1} dependence at frequencies $\omega \gg \tau_E^{-1}$. For frequencies greater than τ_E^{-1} and ω_G the Johnson noise generated by the AC conductance of the detector element frequently dominates in pyroelectric detectors so that the specific detectivity of the detector (D^*) is given by:

$$D^* = R_V \frac{\sqrt{A}}{\Delta V_J} = \frac{\eta d}{\sqrt{4kT}} \times \frac{p}{c' \sqrt{\epsilon \epsilon_o \tan \delta}} \times \frac{1}{\sqrt{\omega}} \quad (9)$$

Thus to maximize D^* in the region where Johnson noise dominates, it is desirable to maximize:

$$F_D = \frac{p}{c' \sqrt{\epsilon \epsilon_o \tan \delta}} \quad (10)$$

which forms the third FOM for pyroelectric materials. (This is frequently expressed in units of $\mu\text{Pa}^{-1/2}$.)

Pyroelectric Material Selection

As noted in the introduction, all polar dielectric materials show the pyroelectric effect, which implies that there is potentially a huge range of materials to choose from for devices. The material FOMs F_V , F_i , and F_D derived in the previous section serve as a useful guide for selecting a particular material for a given application. If the detector element and amplifier have well-matched capacitances and the amplifier noise has been minimized, then the device noise will be dominated by the Johnson noise generated by the dielectric loss in the element. In this case, maximizing F_D will maximize the detectivity. If one of the other noise sources is dominant or if the capacitance of the element dominates the input capacitance of the amplifier, then maximizing F_V will maximize the detectivity. On the other hand, if the capacitance of the element is small in comparison with that of the input capacitance of the amplifier, and the noise sources other than that due to the dielectric loss of the element are dominant, then maximizing F_i will maximize the detectivity.

In certain types of devices, the physical design of the detector element is constrained by the application and/or fabrication technologies, which can have an effect on the selection of materials. For example, in solid-state thermal imaging arrays, it is necessary to put a certain number of detector elements into an area that is at the focus of a lens (typically made of germanium), which will image the scene at the wavelength of interest. This means attaching a plate of the pyroelectric material to a silicon chip, which carries an array of MOSFET amplifiers and switches designed to read out the pyroelectric signals. The size of such electronic chips is limited (typically to 1 or 2 cm across), which in turn limits the maximum area of the detector elements. (A typical example would be an array of 80 μm square elements on a 100 μm pitch in a 100 $\times$ 100 imaging array.) In a well-matched detector, we would like the element capacitance to be of the same order as the amplifier input capacitance, which will typically be about 1 pF. It is thus important, if performance is to be optimized, to select a material that possesses a dielectric constant that will give a good capacitance match for a given element thickness, d . The thickness is determined by two considerations, one theoretical and one practical. Intuitively, it might be thought best to minimize the element thickness (and therefore its thermal capacity H) to maximize the temperature change for a given energy input. However, it is necessary to consider the balance between H and the thermal conductance G_T at the required operating frequency of the device. For practical reasons, it may not be possible to reduce G_T below a certain value. A practical value for a particular design of array might be perhaps 10–20 $\mu\text{W K}^{-1}$. If the device is to operate at ca 50 Hz, then a thermal time constant of 20 ms for the device would be appropriate. It is then simple to show that for our example of an 80 μm square element with a volume-specific heat of 2.5 $\text{MJ m}^{-3}\text{K}^{-1}$, the element thickness must be around 25 μm . Hence, for a C_E of 1 pF, the permittivity of the material should be around 440. A smaller element (say 40 $\times$ 40 μm) will require a material with an even higher permittivity (ca. 1000), unless the thermal conductance can be lowered by an improvement in the thermal isolation technology. Thus choosing a material with a higher F_D for this application may not necessarily give better performance than another material with a lower F_D if its permittivity is much lower than this value. The second consideration determining element thickness is technological. Many of the best pyroelectric materials are oxides, which are brittle and have a tendency to break during handling when in very thin sections. Hence, if a bulk ceramic material is used, then the minimum attainable thickness (say 15–20 μm) may push the selection of a material toward one with a higher dielectric constant. On the other hand, technologies are now emerging (see below) by which thin films of ferroelectric materials can be deposited directly onto active silicon chips while maintaining good thermal isolation. In such cases, the thickness of the detector element can be very thin indeed ($< 1 \mu\text{m}$) and it may be more advantageous to choose a material with a moderate dielectric constant.

This simple example serves to show that, while the FOM listed above can be useful in guiding one in the right general direction for selecting a material, it is essential to consider the full details of any device's operation and manufacturing technology in choosing the most appropriate material to use.

A further consideration in the selection of materials is the frequency dependence of the dielectric properties. The vast majority of pyroelectric devices operate at very low frequencies (usually < 100 Hz, frequently < 10 Hz). Most of the so-called "low-frequency" dielectric properties reported in the literature have been measured at 1 kHz or above. For many materials, the loss tangent rises rapidly as the frequency decreases in the range 100–0.1 Hz. This means that pyroelectric FOM based on dielectric data measured in the range of 1 kHz may be of use in cross-comparing values of F_V but are of questionable utility in comparing values of F_D as the low-frequency dependences of the dielectric losses of the different materials may differ.

It was noted in the introduction that ferroelectrics show the largest pyroelectric coefficients by virtue of the changes in their spontaneous polarizations with temperature as the temperature increases toward the Curie temperature, T_C . This leads to a maximum in the pyroelectric coefficient at T_C . The dielectric constant in a proper ferroelectric also increases and peaks at T_C . It is possible to show from Devonshire theory (Lines and Glass, 1977) that in a proper ferroelectric in the absence of an electric bias field the ratio $p/\sqrt{\epsilon}$, and hence the detectivity at constant $\tan\delta$, are constant below T_C , meaning that the devices require little-or-no thermal stabilization to maintain a stable performance.

The major compromise as the temperature approaches T_C is an increase in dielectric loss due to an increased facility of domain wall movement, which tends to reduce F_D , and a tendency to depole the ferroelectric, giving a general loss in activity (especially for ceramics). This means that most ferroelectrics are operated well below their T_C . However, if an electric bias field is applied to the ferroelectric, the polarization and the pyroelectric effect will be stabilized in the region of and above T_C . It is also observed that the dielectric constant tends to reduce, as does the dielectric loss as the domain walls are effectively "swept out" of the material by the field. The consequence of this is that very large pyroelectric coefficients in conjunction with large dielectric constants and low dielectric losses can be measured in the region of T_C . This is the principle of the "dielectric bolometer" by which the pyroelectric coefficient is given by:

$$p = \left(\frac{dD}{dT} \right)_E \quad (11)$$

The following discussion separates pyroelectric materials into two groups: “intrinsic” pyroelectrics, which are operated well below T_C ; dielectric bolometer materials, which are operated close to T_C ; but with an electrical bias applied and ferroelectric thin films.

Bulk Pyroelectric Materials

Intrinsic Pyroelectrics

The reviews by [Whatmore \(1986\)](#) and [Kulwicki et al. \(1992\)](#) have considered in detail the properties of many of the “intrinsic” bulk (as opposed to thin film) pyroelectric materials. There are many different types of pyroelectrics, including single crystals, polymers, and ceramics. The triglycine sulphate (TGS) family was one of the earliest materials to be used for single-element detectors. Many modifications to this compound have been developed, including the deuterated isomorph deuterated triglycine sulphate (DTGS) in which deuteration is used to raise T_C ; the replacement of some of the glycine groups by alanine, which serves to stabilize P_S above T_C ; and the replacement of the sulphate groups by, for example, fluoroberyllic acid deuterated triglycine fluoroberyllate (DTGFB). The room-temperature properties of TGS and DTGS are listed in [Table 1](#).

The materials are water-soluble and can be grown as large single crystals from aqueous solution. They possess relatively low dielectric constants and exhibit very high F_V values, which means that they are still used in high-performance single-element detectors, such as for spectroscopic analysis. Outside this area, their water solubility and low Curie temperatures means that their use is confined to the pyroelectric vidicon (see, e.g., [Putley et al., 1972](#)). Here, their low thermal diffusivities are advantageous. Lithium tantalate is an example of an oxide single crystal that is widely used in commercial single-element detectors because of its relatively good pyroelectric properties – especially F_V (see [Table 1](#)), high T_C , good chemical stability, ready commercial availability, and ease of handling. Its properties are not particularly favorable for use in thermal imaging arrays because of its low permittivity. The thermal diffusivities perpendicular to the polar axis are quite high, which can lead to issues of thermal crosstalk between adjacent elements of detector arrays at low modulation frequencies, if the array element size is small. Many other oxide single crystal materials have been studied for their use in pyroelectric applications. The tungsten bronze family has been of considerable interest, as the pyroelectric coefficients obtained are high. $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ was of particular interest with a pyroelectric coefficient more than three times that of LiTaO_3 and double that of DTGS, with high permittivities, making them potentially of interest for arrays of small detectors. However, the crystals are hard to grow in large sizes, are not readily available commercially, and have relatively low Curie temperatures, so the user must be careful not to accidentally depole the devices using them by allowing them to get too hot. New ferroelectric crystals based on the solid solutions.

$x\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3-(1-x)\text{PbTiO}_3$ (PMNT) have been extensively studied over the last few years because of their excellent piezoelectric properties and potential applications in medical ultrasound and sonar systems ([Park and Shrout, 1997](#)). The pyroelectric properties of some of these have been studied. [Table 1](#) shows the properties of a crystal with $x = 0.74$ (PMNT(74/26)) and an example of a ternary solid solution crystal containing lead indium niobate (PIMNT(21/49/30)). These crystals are rhombohedral at room temperature and exhibit a transition to a ferroelectric, tetragonal phase before they become paraelectric (and depole completely). This transition means that crystals need to be repoled if the R–T transition temperature (T_{R-T}) is exceeded, which is inconvenient. The crystals containing lead indium niobate have significantly higher values of T_{R-T} and thus may be more useful. Nevertheless, the pyroelectric coefficients of these materials are very high, and the values of F_D some of the highest in non-TGS oxide-based systems, being comparable with LiTaO_3 . They also have the advantage of being materials that are commercially available, being grown for the piezoelectric application.

The ferroelectric polymers polyvinylidene fluoride (PVDF) and the vinylidene fluoride–trifluoroethylene (P(VDF/TrFE)) copolymers exhibit ferroelectric behavior and interesting pyroelectric effects. PVDF is commercially available as poled and electroded polymer sheets of varying thicknesses. PVDF needs to be mechanically stretched before poling to develop its ferroelectric properties. The P(VDF/TrFE) copolymers, however, can be cast from the melt or methyl ethyl ketone solution directly into the ferroelectric phase. They are thus particularly interesting for pyroelectric applications in which a film of pyroelectric is deposited directly onto a silicon substrate for making arrays. The properties of PVDF and a P(70VDF/30TrFE) polymer are illustrated in [Table 1](#). These properties are typical of those that can be achieved in this system. These are characterized by low pyroelectric coefficients and low dielectric constants coupled with moderate dielectric losses. As a consequence, the F_V values are similar to those of LiTaO_3 , but the F_D values are much lower. The low dielectric constants of these materials make them relatively unfavorable for large arrays of very small ($<100\ \mu\text{m}$ square) detectors for the thermal imaging applications, although thin-film detectors with areas around this value have been made on micromachined silicon ([Setiadi et al., 1996](#); [Kohler et al., 1998](#)).

Many ceramic ferroelectrics has been explored for their possible applications in pyroelectric devices and a large proportion of these are based upon the lead zirconate–lead titanate ($\{1-x\}\text{PbZrO}_3-x\text{PbTiO}_3$ –PZT) perovskite solid solution series. The compositions of greatest interest are located either close to the lead zirconate end of the phase diagram or close to lead titanate. The dielectric constants and losses of these compositions are lower than the corresponding values close to those at the morphotropic phase boundary at $x = 0.47$, which are commonly used for piezoelectric device applications. Pyroelectric properties typical of these types of materials (referred to as Mod PZ and Mod PT, respectively) are listed in [Table 1](#). The materials are characterized by

Table 1 The electrical and thermal properties of several pyroelectric materials

Material name	Material type	p $\mu \text{ cm}^{-2} \text{ K}^{-1}$	Dielectric properties		Meas't freq. Hz	Volume specific heat (c') $\text{MJ m}^{-3} \text{ K}^{-1}$	Curie temp. $^{\circ}\text{C}$	F_i $10^{-12} \text{ m V}^{-1}$	F_v $\text{m}^2 \text{ C}^{-1}$	F_D $\mu \text{ Pa}^{1/2}$	Thermal diffusivity ^a $\mu \text{ m}^2 \text{ s}^{-1}$	References
			ϵ	$\tan\delta$ (%)								
TGS	Crystal	325	41	2.0	1000	2.25	49.5	144	0.398	54	0.33	(Felix <i>et al.</i> , 1978)
DTGS	Crystal	335	32	1.4	1000	2.25	60.1	149	0.530	75	0.30	(Felix <i>et al.</i> , 1978)
LiTaO ₃	Crystal	182	43	0.031	200	3.13	620	58	0.153	168	1.3(C) ^b ; 2.3(S) ^b	(Glass, 1968; Stokowski, 1976; Byer and Roundy, 1972; Nakamura <i>et al.</i> , 2010; Schossig <i>et al.</i> , 2014)
Sr _{0.5} Ba _{0.5} Nb ₂ O ₆	Crystal	600	400	0.3	1000	2.34	121.0	256	0.072	79	0.67	(Maciolek and Liu, 1973; Choy <i>et al.</i> , 1992)
PMNT(74/26)	Crystal	1530	643	0.3	100	2.56	90 (R-T) ^c	597	0.105	144	0.44	(Tang <i>et al.</i> , 2005)
PIMNT (21/49/30)	Crystal	754	529	0.1	50	2.50	125 (R-T) ^c	302	0.064	142	0.44	(Liu <i>et al.</i> , 2011)
PVDF	Polymer	30	11	2	1000	2.3	NA	13	0.134	9	NA	(Sussner <i>et al.</i> , 1978; DasGupta, 1991)
P(VDF75-TrFE25)	Polymer	46	10	1.7	100	2.27	90.0	20	0.241	17	0.08	(Iguchi <i>et al.</i> , 2007; Neumann <i>et al.</i> , 1991; Vonmunch <i>et al.</i> , 1993)
Mod PZ	Ceramic	410	290 350	0.3 0.9	1000 90	2.67	230.0	154	0.050	55 28	0.46	(Whatmore and Ainger, 1983; Whatmore <i>et al.</i> , 1993; Lang, 1989)
Mod PT	Ceramic	350	220	1.0 3.0	1000 33	3.15	> 250	111	0.057	25 15	1.21	(Shirane and Hoshino, 1951; Bhide <i>et al.</i> , 1968; Remeika and Glass, 1970; Whatmore, 1986)

^aThermal diffusivities quoted are measured perpendicular to the polar axis in single crystals.^bC = Congruently melting composition; S = Stoichiometric composition.^c(R-T) refers to the rhombohedral to tetragonal phase transition. If this is exceeded, the crystal requires repolarizing.

Abbreviations: DTGS, deuterated triglycine sulphate; TGS, triglycine sulphate; PVDF, polyvinylidene fluoride.

high dielectric constants (typically ca. 200–300), and low, but strongly frequency dependent, dielectric losses. The FOM (especially F_D) for these materials look good if the 1k Hz dielectric properties are taken (conducting a straight comparison with the other materials in Table 1) and the high dielectric constants of these materials make them very suitable for use in arrays of small detectors.

For these materials, it has been possible to quote the dielectric properties at 1 kHz and 33 Hz to illustrate the differences in FOM (especially F_D), which are obtained by going to the frequency range of interest for device applications. The F_D figures are reduced by around a factor of two. However, low-frequency dielectric loss data for many materials is hard to obtain from the literature, and therefore a direct comparison of the materials at the most relevant frequency range is not possible. This illustrates the difficulty of making valid materials comparisons simply on the basis of available data. Many studies of pyroelectric materials either fail to report the frequency at which measurements have been carried out, or specify a frequency for the dielectric measurements, which is well outside the range of interest for most devices.

Dielectric Bolometer Materials

It was noted above that, by operating a proper ferroelectric close to T_C with an electric bias field applied, very high effective pyroelectric coefficients can be obtained. Several materials have been examined in this mode, including $\text{KTa}_x\text{Nb}_{1-x}\text{O}_3$ (KTN) (Stafsud and Pines, 1971); $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) (Yokomizo *et al.*, 1970); $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) (Whatmore *et al.*, 1987; Kulwicki *et al.*, 1992); $(\text{Pb}_{0.99}\text{La}_{0.01})(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (La01-PMN) (Whatmore *et al.*, 1987); and $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ (PST) (Shorrock *et al.*, 1990). In characterizing these materials, it is necessary to measure their properties over a wide range of fields and temperatures. A typical set of properties in a BST67/33 ceramic at $0.6 \text{ V } \mu\text{m}^{-1}$ bias field is $p = 70 \times 10^{-4} \text{ cm}^{-2} \text{ K}^{-1}$, $\epsilon = 8800$ and $\tan\delta = 0.004$, giving $F_D = 124 \text{ } \mu\text{Pa}^{-1/2}$ (Kulwicki *et al.*, 1992). The field and temperature dependence of the relevant properties of BST65/35 and La01PMN ceramics have been reported by Whatmore *et al.* (1990) and for PST by Shorrock *et al.* (1990). In PST the p and ϵ are strongly peaked with temperature at low bias fields, but the peaks become lower and broader and shifted to higher temperatures at high bias fields. The effect of field on dielectric loss is to dramatically reduce it immediately below T_C and to increase it slightly above.

At low bias fields, the temperature dependence of the response and signal-to-noise FOM of dielectric bolometer materials is strongly temperature dependent in the region of T_C , as would be expected. Kulwicki *et al.* (1992) showed that in BST67/33, a second-order ferroelectric, the F_D peaks at $140 \text{ } \mu\text{Pa}^{-1/2}$ at 22°C and $0.4 \text{ V } \mu\text{m}^{-1}$ bias field. Within $\pm 2^\circ\text{C}$ from this temperature, the value falls to about one half of this figure. F_V varies similarly. This seems to make tight control of device temperature essential. However, application of higher bias fields allows this requirement to be relaxed. In PST ceramics at $5 \text{ V } \mu\text{m}^{-1}$ bias there is a much slower temperature variation, with a peak at 40°C , which is about $150 \text{ } \mu\text{Pa}^{-1/2}$. Some temperature stabilization would still be required to optimize the performance of the device, but this is not tight and could, for many applications, be achieved by heating alone, eliminating the need for a thermoelectric cooler.

Devices

Pyroelectric IR detectors containing one or two sensitive elements are used in a wide range of applications, including intruder sensing, remote light switches, spectroscopic gas analysis, flame and fire detection equipment, etc., as described by Porter (1981). Such devices typically employ LiTaO_3 single crystal or PZT-based ceramic elements at the low-cost end. The highest performance pyroelectric single- or few element devices used in Fourier Transform Infra-Red spectroscopy still typically use TGS-based single crystal materials. Linear arrays of up to 256 elements using LiTaO_3 single crystal materials for use in spectroscopy applications have been described by Norkus (2004).

Hybrid 2D arrays with a typical structure as shown in Fig. 2 have been fabricated using the Mod PZ, PST, and BST ceramics referred to in the previous section (Watton *et al.*, 1993; Kulwicki *et al.*, 1992). The ferroelectric wafer, 10–25 μm thick, is cut and polished from a hot-pressed ceramic block and has a common electrode on its top surface, which forms part of a matched thin film ($\lambda/4$) structure for radiation absorption. The rear surface has a pattern of individual element electrodes for bonding. A maximized signal is obtained by minimizing the heat loss from the individual element through three design features: The small diameter of the solder bond, typically 10 μm ; isolating the bond from the silicon read-out IC by a thick polymer layer and a narrow metal interconnection track; and isolating the detector element from its neighbors by laser etching grooves into the ceramic (reticulation). Without reticulation, heat would spread laterally between the elements, reducing the image resolution. Arrays with numbers of elements up to 388×256 have been made with an element pitch from 100 μm down to 40 μm , and groove widths are from 20 μm down to 10 μm . Noise-equivalent temperature differences in the image are typically of the order of 0.1K. Such arrays can be used for forming thermal images using radiation in the 8–14 μm band, with the array of elements placed at the focus of a germanium lens. Applications for such systems include both military and commercial areas. Publication of military use has been limited, but equipment for a Driver's Vision Enhancer and a Thermal Weapon Sight have been described (Hanson *et al.*, 1992). A major civil area, that of firefighting cameras, has been pursued by Cairns & Brother Inc., who manufactured a helmet-mounted uncooled camera based on GEC-Marconi array modules (Bennett and Matthews, 1996). Other civilian applications have included police patrol car surveillance cameras, civilian automotive driving aids, and general-purpose thermal imaging for industrial and security monitoring. The major competition for ferroelectric ceramic-based thermal imaging has come from resistance bolometer

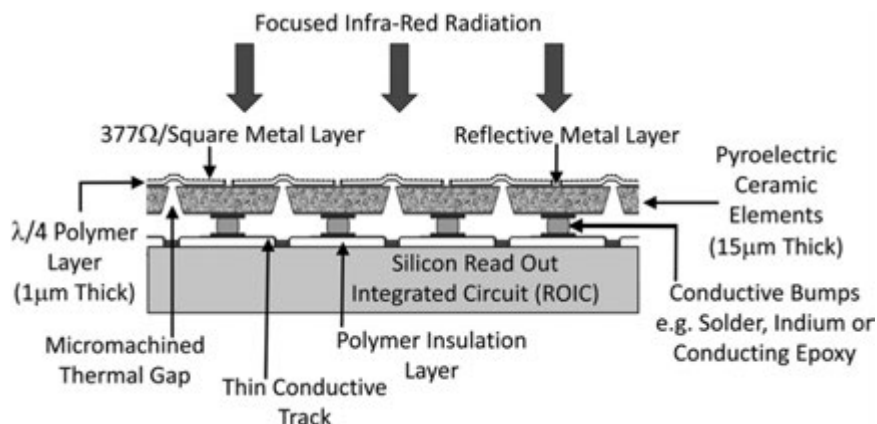


Fig. 2 Hybrid array structure using bulk pyroelectric material.

arrays using micromachined elements made from the thin films of VO_x or amorphous silicon (Niklaus *et al.*, 2008). The technology for making these lends itself to lower-cost, MEMS-based production techniques and arrays of up to 640×480 and larger with element pitches below $20 \mu\text{m}$ are now commercially available. These have displaced the hybrid ferroelectric ceramic arrays in the high-resolution thermal imaging application. However, pyroelectric hybrid arrays have certain advantages. The resistance bolometer arrays require vacuum encapsulation, which can be an expensive technology. The hybrid pyroelectric arrays do not need this. A further key advantage of the pyroelectric array is that it responds to changes in temperature, while a resistance bolometer array responds to absolute temperature. This means that a pyroelectric array placed at the image plane of a germanium lens will only see changes in the thermal image of the scene. In situations where warm objects such as people moving in a scene (perhaps for security or people-counting applications) need to be seen, rather than seeing the full thermal image, pyroelectrics are ideal because they require very little signal processing to achieve this. Low element count (e.g., 16×16 or 32×32) arrays have been very successful for applications such as fall detection in older populations (Sixsmith *et al.*, 2005) and queue-length monitoring, as well as low-cost thermal imaging (Holden, 2011).

Pyroelectric Thin Films

The use of bulk ferroelectrics in pyroelectric devices inevitably leads to situations where the material must be cut, lapped, and polished to make a thin, thermally sensitive layer. If an array of detectors is required for thermal imaging, the layer must be metallized on both faces, processed photolithographically, and bonded to a silicon read-out circuit to yield a complete hybrid array. Clearly, it would be desirable if the ferroelectric material could be deposited as a thin film onto a substrate, which would be chemically etched to leave a free-standing ferroelectric thin film, minimally supported to reduce thermal conduction from the ferroelectric to its surroundings, and thus removing the requirement for lapping and polishing. If possible, the thin film would be deposited directly onto a complete wafer of silicon chips, where it could be processed to yield an array of thin, thermally isolated structures. This requirement places a very important constraint on the temperature at which the ferroelectric is grown. The silicon circuits required for thermal imaging are complex very large scale integration (VLSI) chips, which are manufactured in silicon foundries in wafers of 6" diameter or more. It is unlikely that a general silicon foundry could accept for deposition the sorts of exotic materials discussed in the previous sections. Hence, the ferroelectric layer must be deposited on fully processed and tested wafers. However, the interconnect metallization on the chips should not be taken above about $450\text{--}500^\circ\text{C}$ for any length of time and this places an upper limit on the ferroelectric layer process temperature. The ferroelectric copolymers discussed above are interesting for this application, as they can be spun-down and cast directly onto the silicon at room temperature. These require only an anneal at ca. 150°C to develop full crystallinity. Pyroelectric arrays using P(VDF-TrFE) thin films directly deposited onto silicon have been demonstrated (Vonnunich *et al.*, 1993; Kohler *et al.*, 1998). However, it can be seen from Table 1 that the pyroelectric properties of the ferroelectric polymers are not as good as the oxide materials (modified lead zirconate titanates or the dielectric bolometer materials), which were discussed in the previous two sections. In particular, the oxides possess better properties for large arrays of small detectors (high dielectric constants and high values of F_D), but they are normally manufactured as ceramics for which the sintering temperatures are around 1200°C . Fortunately, many techniques have been researched for ferroelectric thin-film deposition, mainly for applications to nonvolatile memories (Scott and de Araujo, 1989). These include chemical solution deposition (CSD) – particularly sol-gel or metal-organic deposition (MOD), radio frequency (RF) magnetron sputtering, pulsed laser ablation deposition (PLD), and metal-organic chemical vapor deposition (MOCVD). These methods have all been well reviewed by de Araujo *et al.* (1996) and each has its own advantages and disadvantages. CSD processes tend to be relatively low cost to set up and simple to apply, with the capability for easy compositional modification, but being wet chemical processes are perhaps less acceptable in a semiconductor device processing context; sputtering and MOCVD are capital intensive processes and difficult to modify for complex film compositions, but are standard in the semiconductor industry and capable of

coating onto large-area substrates, PLD is best-suited to small-area substrates but has the advantage of being able to deposit films with complex compositions relatively quickly, as there is good correspondence between the target and the film compositions. Commercial PLD deposition systems suitable for large-area growth are becoming available.

Intrinsic Pyroelectrics

Table 2 summarizes the properties as reported recently in the literature of modified PZT thin films deposited onto Pt/Ti on Si substrates where deposition has been at temperatures below 700°C. The best F_D values are in the range 10–35 $\mu\text{Pa}^{-1/2}$ and are comparable with the properties reported for bulk ceramic pyroelectric materials. The lowest deposition temperatures reported to date have been with compositions in the PZT30/70 region. Modification of the films by doping with Mn or Nb has been shown to give significant improvements to the FOM. It has been shown that sol–gel processing can give excellent properties for films grown at 530°C or below. It can be seen from **Table 2** that RF magnetron sputtering has been used successfully to produce good-quality PZT25/75 films at nominal substrate temperatures of 450°C, although it should be noted that it is hard to get an accurate measurement of real substrate temperatures in sputtering systems because the monitoring thermocouples are usually quite remote from the substrate, which is also subject to heating from the plasma. Hence, the real growth temperature can be significantly higher than that recorded. MOCVD has not yet been used to produce such good films at temperatures below 535°C, mainly because of the problem of finding metal–organic precursors for all the constituent atoms, which will decompose at an appropriate rate at such low temperatures.

The best films on Pt/Ti/Si substrates are all polycrystalline, but tend to be strongly (111) orientated. At first sight, this may seem to be surprising, as the compositions are all tetragonal, with the polar axis along (001). However, it is found that if films are deposited with the cubic axes of the crystallites normal to the substrate plane, the tensile stresses in the film tend to force the polar axis to be in the substrate plane, reducing the net polarization and pyroelectric coefficient. Workers using other substrate systems have been able to make films with (001) normal to the film plane. For example, [Fujii et al. \(1994\)](#) have deposited $\text{Pb}_{0.9}\text{La}_{0.1}\text{TiO}_3$ at 590°C by RF magnetron sputtering epitaxially onto (100) single-crystal MgO substrates. They obtained $p = 500 \mu\text{cm}^{-2}\text{K}^{-1}$ and $F_D = 51 \mu\text{Pa}^{-1/2}$. The growth of perovskite films onto substrates other than silicon will clearly require a technology for removal of the film from the substrate and its interfacing with amplifier/multiplexer circuitry. [Fujii et al. \(1994\)](#) etched the back face of the MgO crystal substrates to locally release a portion of the films, which was electrode and patterned into individual elements prior to film release. This has been used to make linear arrays with $D^* = 3.5 \times 10^8 \text{ cm Hz}^{1/2} \text{ W}^{-1}$ at 20 Hz.

Dielectric Bolometers

As discussed above, there can be great benefits gained in pyroelectric properties, especially for thermal imaging devices, by using a ferroelectric close to T_C under an applied bias field. This has led to a drive to grow thin films of such materials. Lead scandium tantalate (PST) has been a prime candidate for such work. Complex perovskites such as this tend to be harder to crystallize into the perovskite phase than members of the PZT system close to lead titanate. There have been some extremely promising properties produced from films crystallized at relatively high temperatures on a variety of substrates. [Shorrock et al. \(1992\)](#) showed that 4 μm thick films of PST can be grown onto sapphire substrates with a 1 μm MgO coating and crystallized at 900°C. These were subsequently released by dissolution of the MgO layer in phosphoric acid to give films with $p > 2500 \mu\text{cm}^{-2}\text{K}^{-1}$, $\epsilon = 2500$, and F_D up to 110 $\mu\text{Pa}^{-1/2}$ at 4.2 $\text{V } \mu\text{m}^{-1}$ bias field. [Watton and Todd \(1991\)](#) also demonstrated PST films on sapphire substrates annealed at 900°C to yield $p \cong 5000 \mu\text{cm}^{-2}\text{K}^{-1}$, $\epsilon = 5800$, and $F_D \cong 110 \mu\text{Pa}^{-1/2}$. [Cho et al. \(1995\)](#) have demonstrated 0.85{Pb($\text{Mg}_{1/3}\text{Nb}_{2/3}$)O₃} – 0.15{Pb($\text{Zn}_{1/3}\text{Nb}_{2/3}$)O₃} films on (111)Pt-on-(100)MgO substrates. These exhibited $p \cong 150 \mu\text{cm}^{-2}\text{K}^{-1}$, $\epsilon = 1150$, and $F_D \cong 31 \mu\text{Pa}^{-1/2}$ at 3 $\text{V } \mu\text{m}^{-1}$ bias after annealing at 900°C. [Mantese et al. \(1993\)](#) produced films of $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ on yttria substrates using a MOD method, and after annealing at 1070°C, the films exhibited $p \cong 150 \mu\text{cm}^{-2}\text{K}^{-1}$ at 3 $\text{V } \mu\text{m}^{-1}$ bias. 10 μm thick films were separated from the substrates by etching and fabricated into working arrays. However, excellent though these pyroelectric properties are (and all at around 15–25°C), the films all require removal from the substrate and hybridization with a readout chip to make a working device. Thus there has been a strong drive to reduce the firing temperature to ca. 500°C so that a process fully integrated with silicon can be devised. [Watton \(1995\)](#) reported that if PST is sputtered with a large Pb excess (14%–37%), the perovskite phase can be induced to grow on Pt/Ti/Si substrates at 525–575°C, and the films possessed $p \cong 440 \mu\text{cm}^{-2}\text{K}^{-1}$, $\epsilon = 650$ –850, and F_D up to 30 $\mu\text{Pa}^{-1/2}$ at 10–15 $\text{V } \mu\text{m}^{-1}$ bias, well below the values reported for films deposited at high temperature, but still useful.

In conclusion, pyroelectric thin films can certainly be deposited directly onto silicon substrates at temperatures below 500°C and F_D values of between 10 and 35 $\mu\text{Pa}^{-1/2}$ seem to be reliably achievable using a variety of growth techniques. There may be some gains to be had in F_D (up to $> 100 \mu\text{Pa}^{-1/2}$) by using a dielectric bolometer material such as PST if a higher growth temperature can be tolerated (i.e., if the film is not to be grown onto active silicon). A hybrid process whereby the film is grown onto a separate substrate prior to linking with an active silicon circuit has been described as one way to achieve this ([Todd et al., 2000](#)).

Devices

A number of pyroelectric device structures using directly deposited thin films have been demonstrated. These include linear arrays of 128 elements with an area of $90 \times 100 \mu\text{m}^2$ and 2D arrays with 16×8 elements $400 \times 400 \mu\text{m}^2$ ([Kohler et al., 1998](#)), which

Table 2 The electrical properties of selected thin-film pyroelectric materials

Material name	Deposition method	Deposition temperature °C	p $\mu \text{ cm}^{-2} \text{ K}^{-1}$	Dielectric properties		Meas freq. Hz	Curie temp. °C	F_i $10^{-12} \text{ m V}^{-1}$	F_V $\text{m}^2 \text{ C}^{-1}$	F_D $\mu \text{ Pa}^{-1/2}$	References
				ϵ	$\tan \delta$ (%)						
PT	Sputtered	600	140	180	2.0	1000	510	52	0.033	9	(Kohli <i>et al.</i> , 1995)
PZT15/85	CSD	650	220	210	1.5	1000	455	81	0.044	15	(Kohli <i>et al.</i> , 1998)
PZT20/80	CSD	510	180	260	1.1	30	445	67	0.029	13	(Shorrocks <i>et al.</i> , 1995)
PZT25/75	CSD	510	210	340	0.7	30	430	78	0.026	17	(Shorrocks <i>et al.</i> , 1995)
PZT30/70	CSD	510	220	380	0.8	30	420	81	0.024	16	(Shorrocks <i>et al.</i> , 1995)
PZT30/70	CSD	530	211	372	1.6	33	420	78	0.024	11	(Zhang and Whatmore, 2003)
PZT30/70 -1 at% Mn	CSD	530	352	255	0.6	33		130	0.058	35	(Zhang and Whatmore, 2003)
PL07T	MOCVD	535	133	414	2.0	1000	400	49	0.013	6	(Iijima <i>et al.</i> , 1986; Roeder <i>et al.</i> , 1996)
PZT20/80-Nb0.02	CSD	650	1090	824	5.0	1000		404	0.055	21	(Han <i>et al.</i> , 2004)

Notes: Volume Heat Capacity $c' = 2.7 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$ used for all figure of merit calculations.

Abbreviations: CSD, chemical solution deposition; MOCVD, metal-organic chemical vapor deposition, PT, Lead Titanate.

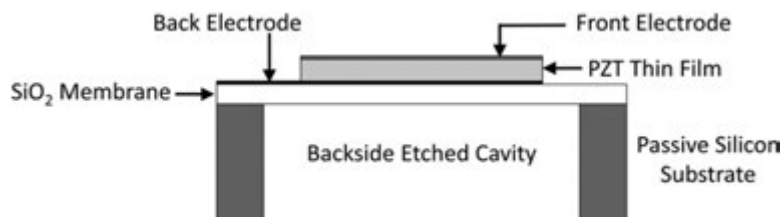


Fig. 3 Micromachined array structure using thin film pyroelectric material.

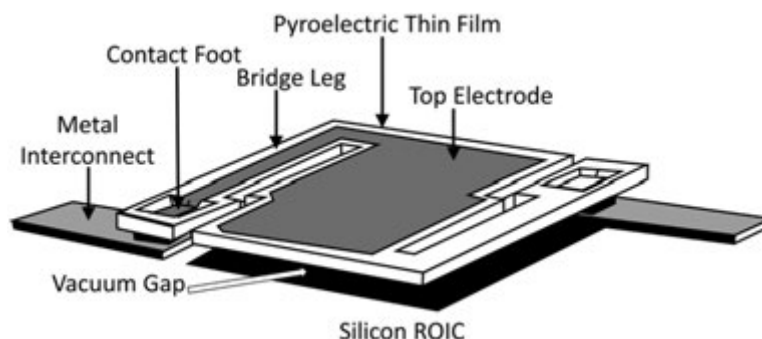


Fig. 4 Schematic of an integrated detector element employing a surface micromachined microbridge structure for good thermal isolation.

were made using both spin-coated and annealed P(VDF75-TrFE25) copolymer and sputtered PZT25/75. These were made on silicon substrates, but the silicon contained no active elements and was used as a carrier substrate that could be bulk micro-machined to release the pyroelectric elements, giving a structure of the type shown schematically in [Fig. 3](#).

For 1 mm² sensor elements, the PZT detectors showed a detectivity that was ca. $5 \times$ greater than the polymer detectors, reflecting the much higher pyroelectric coefficient and F_r of the oxide material (see [Tables 1](#) and [2](#)). It is interesting that FV and FD are similar for the two materials, which reflects the importance of selecting the appropriate FOM when comparing the likely performance of different materials in a particular sensor design. [Kohli et al., 1998](#) reported the fabrication and properties of linear arrays of 12 elements with 0.36 mm² area using sol-gel grown PZT15/85. It is interesting to note that in both of these examples, the best values of D^* obtained from the PZT detectors were very similar at $\approx 2 \times 10^8$ cm Hz^{1/2} W⁻¹. Pyreos Ltd. in the UK have commercialized pyroelectric devices based on sputtered PZT25/75 on bulk micromachined silicon and [Wojtczuk et al. \(2011\)](#) have demonstrated hand-gesture sensors using a 4×4 array from this manufacturer.

It is also possible to make integrated thin-film pyroelectric arrays using surface micromachined structures. These are advantageous because they can be manufactured with processes of the type used for making silicon-integrated circuits, without having to access the rear surface of the wafer for “back-side” etching. In principle, such structures also permit the use of the full area of the silicon for active circuitry, such as gate amplifiers and multiplexers. A typical structure for arrays with thin ferroelectric films is shown in [Fig. 4](#). The microbridge legs illustrated can provide much better thermal isolation of the element than the solder bonds of hybrid arrays shown in [Fig. 2](#). Thermal conductance through the legs can be made as low as 1–0.1 μ W/K, an improvement over the solder bond by one-to-two orders of magnitude. A disadvantage of such structures is that gas within the narrow gap beneath the active element can provide a major source of thermal leakage and thus the package must be either filled with a low thermal conductivity gas, such as xenon, or ideally evacuated to remove these effects. If radiation absorption in the microbridge itself is used, then the ferroelectric film must be ~ 1 μ m thick ($\lambda/4$ at 10 μ m). The improvement in thermal isolation achievable by integration when compared with hybrid arrays should allow some relaxation in the requirements for the ferroelectric film FOM. For example, F_D values of 20 to 30 μ Pa^{-1/2} should allow NETDs of 100 mK and below. [Todd et al. \(2000\)](#) reported that engineers at BAE Systems successfully demonstrated 256×128 arrays made with thin films of PZT30/70, as described by [Shorrocks et al. \(1995\)](#), possessing $F_D \approx 16$ μ Pa^{-1/2}. The elements showed a mode NETD of 140 mK, even before poling, in good agreement with predictions.

References

- Bennett, M.V., Matthews, I., 1996. Life-saving uncooled IR camera for use in fire-fighting applications. *Proceedings of SPIE* 2744, 549–554.
- Bhide, V.G., Hegde, M.S., Deshmukh, K.G., 1968. Ferroelectric properties of lead titanate. *Journal of the American Ceramic Society* 51, 565–568.
- Byer, R.L., Roundy, C.B., 1972. Pyroelectric coefficient direct measurement technique and application to a nsec response time detector. *Ferroelectrics* 3, 333–338.

- Choy, C.L., Leung, W.P., Xi, T.G., Fei, Y., Shao, C.F., 1992. Specific heat and thermal diffusivity of strontium barium niobate $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ single crystals. *Journal of Applied Physics* 71, 170–173.
- Cho, M.K., Kim, K.S., Chang, H.M., 1995. Preferential orientation and dielectric/pyroelectric properties of sol-gel-derived $\text{Pb}(\text{Mg,Zn})_{1/3}\text{Nb}_{2/3}\text{O}_3$ thin films. *Journal of Materials Research* 10, 2631–2641.
- DasGupta, D.K., 1991. Pyroelectricity in polymers. *Ferroelectrics* 118, 165–189.
- de Araujo, C.P., Scott, J.F., Taylor, G.W. (Eds.), 1996. *Ferroelectric Thin Films: Synthesis and Basic Properties*. Gordon and Breach.
- Felix, P., Gamot, P., Lacheau, P., Raverdy, Y., 1978. Pyroelectric, dielectric and thermal properties of TGS, DTGS and TGFB. *Ferroelectrics* 17, 543–551.
- Fujii, S., Kamada, T., Hayashi, S., *et al.*, 1994. Pyroelectric linear array IR sensors made of La-modified PbTiO_3 thin films and their applications. *Proceedings of SPIE* 2552, 612–621.
- Glass, A.M., 1968. Dielectric, thermal and pyroelectric properties of ferroelectric LiTaO_3 . *Physical Review* 172, 564–571.
- Hanson, C., Beratan, H., Owen, R., Corbin, M., McKenney, S., 1992. Uncooled thermal imaging. *Proceedings of SPIE* 1735, 17–26.
- Han, H., Song, X.Y., Zhong, J., *et al.*, 2004. Highly a-axis-oriented Nb-doped $\text{Pb}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_3$ thin films grown by sol-gel technique for uncooled infrared detectors. *Applied Physics Letters* 85, 5310–5312.
- Holden, A.J., 2011. Applications of pyroelectric materials in array-based detectors. *IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control* 58, 1981–1987.
- Iguchi, C.Y., Dos Santos, W.N., Gregorio, R., 2007. Determination of thermal properties of pyroelectric polymers, copolymers and blends by the laser flash technique. *Polymer Testing* 26, 788–792.
- Iijima, K., Takayama, R., Tomita, Y., Ueda, I., 1986. Epitaxial growth and the crystallographic, dielectric and pyroelectric properties of lanthanum-modified lead titanate thin-films. *Journal of Applied Physics* 60, 2914–2919.
- Kohler, R., Padmini, P., Gerlach, G., Hofmann, G., Bruchhaus, R., 1998. Pyroelectric IR detector arrays based on sputtered PZT and spin coated P(VDF/TrFE) thin films. *Integrated Ferroelectrics* 22, 383–392.
- Kohli, M., Huang, Y., Maeder, T., *et al.*, 1995. Processing and properties of thin film pyroelectric devices. *Microelectronic Engineering* 29, 93–96.
- Kohli, M., Seifert, A., Murali, P., 1998. Poling of pyroelectric thin films. *Integrated Ferroelectrics* 22, 453–463.
- Kulwicki, B.M., Amin, A., Beratan, H.R., Hanson, C.M., 1992. Pyroelectric imaging. In: *Proceedings of 8th International Symposium on Applications of Ferroelectrics*. IEEE Cat. No. 90CH3080-9, August 30–September 2, 1992, pp.1–10. Greenville, SC.
- Lang, S.B., 1989. Technique for the measurement of thermal-diffusivity based on the laser intensity modulation method (LIMM). *Ferroelectrics* 93, 87–93.
- Lang, S.B., 1999. The history of pyroelectricity: From ancient Greece to space missions. *Ferroelectrics* 230, 401–410.
- Lines, M.E., Glass, A.M., 1977. *Principles and Applications of Ferroelectrics and Related Materials*. Oxford: Oxford University Press.
- Liu, L.H., Wu, X., Wang, S., *et al.*, 2011. Growth and pyroelectric properties of rhombohedral $0.21\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - $0.49\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.3PbTiO_3 ternary single crystals. *Journal of Crystal Growth* 318, 856–859.
- Maciolek, R., Liu, S., 1973. Preparations and properties of low loss $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ ferroelectric single crystals. *Journal of Electronic Materials* 2, 191–200.
- Mantese, J.V., Micheli, A.L., Schubring, N.W., *et al.*, 1993. Infra-red imaging using uncooled focal plane arrays of unreticulated, $10\text{ }\mu\text{m}$ potassium tantalum niobate films. *IEEE Transaction on Electron Devices* ED-40, 320–324.
- Nakamura, M., Takekawa, S., Kitamura, K., 2010. Anisotropy of thermal conductivities in non- and Mg-doped near-stoichiometric LiTaO_3 crystals. *Optical Materials* 32, 1410–1412.
- Neumann, N., Kohler, R., Hofmann, G., 1991. Application of P(VDF TRFE) thin films in pyroelectric detectors. *Ferroelectrics* 118, 319–324.
- Niklaus, F., Vieider, C., Jakobsen, H., 2008. MEMS-based uncooled infrared bolometer arrays – A review. In: Chiao, J.C., Chen, X., Zhou, Z., Li, X. (Eds.), *Mems/Moems Technologies and Applications III*. *Proceedings of SPIE* 6836. Bellingham: SPIE International Society Optical Engineering, pp. 68360D-1–68360D-15.
- Norkus, V., 2004. Pyroelectric infrared detectors based on lithium tantalate: State of the art and prospects. In: Chatard, J.P., Dennis, P.N.J. (Eds.), *Detectors and Associated Signal Processing*. *Proceedings of SPIE* 5251. Bellingham: SPIE International Society Optical Engineering, pp. 121–128.
- Park, S.E., Shrout, T.R., 1997. Characteristics of relaxor-based piezoelectric single crystals for ultrasonic transducers. *IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control* 44, 1140–1147.
- Porter, S.G., 1981. A brief guide to pyroelectric detectors. *Ferroelectrics* 33, 193–206.
- Putley, E.H., 1970. The pyroelectric detector. In: Willardson, R.K., Beer, A.C. (Eds.), *Semiconductors and Semimetals* 5. New York: Academic, pp. 259–285.
- Putley, E.H., Watton, R., Ludlow, J.H., 1972. Pyroelectric thermal imaging devices. *Ferroelectrics* 3, 263–268.
- Remeika, J.P., Glass, A.M., 1970. Growth and ferroelectric properties of high resistivity single crystals of lead titanate. *Materials Research Bulletin* 5, 37–45.
- Roeder, J.F., Chen, I.-S., van Buskirk, P.C., Beretan, H.R., 1996. Liquid delivery MOCVD of PLT for pyroelectric detectors. In: *Proceedings of the 10th IEEE ISAF*. IEEE Cat. No. 96CH35948, pp. 227–230.
- Schossig, M., Norkus, V., Gerlach, G., 2014. Dielectric and pyroelectric properties of ultrathin, monocrystalline lithium tantalate. *Infrared Physics & Technology* 63, 35–41.
- Scott, J.F., de Araujo, C.A.P., 1989. Ferroelectric memories. *Science* 246, 1400–1405.
- Setiadi, D., Sarro, P.M., Regtien, P.P.L., 1996. A 3×1 integrated pyroelectric sensor based on VDF/TrFE copolymer. *Sensors and Actuators A: Physical* 52, 103–109.
- Shirane, G., Hoshino, S., 1951. On the phase transition in lead titanate. *Journal of the Physical Society of Japan* 6, 265–270.
- Shorrocks, N.M., Patel, A., Walker, M.J., Parsons, A.D., 1995. Integrated thin film PZT pyroelectric detector arrays. *Microelectronic Engineering* 29, 59–66.
- Shorrocks, N.M., Patel, A., Whatmore, R.W., 1992. Pyroelectric properties of thin film lead scandium tantalate. *Ferroelectrics* 133, 35–40.
- Shorrocks, N.M., Whatmore, R.W., Osbond, P.C., 1990. Lead scandium tantalate for thermal detector applications. *Ferroelectrics* 106, 387–392.
- Sixsmith, A., Johnson, N., Whatmore, R., 2005. Pyroelectric IR sensor arrays for fall detection in the older population. *Journal De Physique IV* 128, 153–160.
- Stafsud, O.M., Pines, M.Y., 1971. Characteristics of KTN pyroelectric detectors. *Journal of the Optical Society of America* 6, 1153–1155.
- Stokowski, S.E., 1976. Temperature noise and dielectric loss in pyroelectric detectors. *Applied Physics Letters* 29, 393–395.
- Sussner, H., Horne, D.E., Yoon, D.Y., 1978. New method for determining pyroelectric coefficient of thin polymer films using dielectric heating. *Applied Physics Letters* 32, 137–139.
- Tang, Y.X., Wan, X.M., Zhao, X.Y., *et al.*, 2005. Large pyroelectric response in relaxor-based ferroelectric $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ single crystals. *Journal of Applied Physics* 98(084104).
- Todd, M.A., Manning, P.A., Donohue, P.P., Brown, A.G., Watton, R., 2000. Thin film ferroelectric materials for microbolometer arrays. In: Andresen, B.F., Fulop, G.F., Strojnik, M. (Eds.), *Proceedings of SPIE Infrared Technology and Applications XXVI* 4130. Bellingham: SPIE International Society Optical Engineering, pp. 128–139.
- Vonmunch, W., Nagele, M., Rinner, M., *et al.*, 1993. P(VDF/TrFE) copolymer films for the fabrication of pyroelectric arrays. *Sensors and Actuators A: Physical* 37-38, 365–369.
- Watton, R., 1995. Ferroelectric IR bolometers – From ceramic hybrid arrays to direct thin film integration. *Ferroelectrics* 184, 141–150.
- Watton, R., Dennis, P.N., Gillham, J.P., *et al.*, 1993. IR bolometer arrays: The route to uncooled, affordable thermal imaging. *Proceedings of SPIE* 2020, 379–390.
- Watton, R., Todd, M.A., 1991. Induced pyroelectricity in sputtered lead scandium tantalate films and their merit for IR detector arrays. *Ferroelectrics* 118, 279–295.
- Whatmore, R.W., 1986. Pyroelectric materials and devices. *Reports on Progress in Physics* 49, 1335–1386.
- Whatmore, R.W., Ainger, F.W., 1983. Pyroelectric ceramic materials for uncooled IR detectors. *Proceedings of the Society of Photo-Optical Instrumentation Engineers* 395, 261–266.
- Whatmore, R.W., Osbond, P.C., Shorrocks, N.M., 1987. Ferroelectric materials for thermal IR detectors. *Ferroelectrics* 76, 351–367.
- Whatmore, R.W., Patel, A., Shorrocks, N.M., Ainger, F.W., 1990. Ferroelectric materials for thermal IR sensors – State of the art and perspectives. *Ferroelectrics* 104, 269–283.

- Whatmore, R.W., Stringfellow, S.B., Shorrocks, N.M. 1993. Ferroelectric materials for uncooled thermal imaging. In: Proceedings of SPIE's 1993 International Symposium on Optics, Imaging, and Instrumentation. vol. 2020, pp. 391–402.
- Wojtczuk, P., Armitage, A., Binnie, T.D., Chamberlain, T., 2011. PIR sensor array for hand motion recognition. Proceedings of Sensor Devices 2011: The Second International Conference on Sensor Device Technologies and Applications, pp. 99–102. Wilmington: Iaria Xps Press.
- Yokomizo, Y., Takahashi, T., Nomura, S., 1970. Ferroelectric properties of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$. Journal of the Physical Society of Japan 28, 1278–1284.
- Zhang, Q., Whatmore, R.W., 2003. Improved ferroelectric and pyroelectric properties in Mn-doped lead zirconate titanate thin films. Journal of Applied Physics 94, 5228–5233.

Superconducting Materials

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Introduction

In 1911 the Dutch physicist [Onnes \(1911\)](#) observed during studies of the electric properties of pure metals at temperatures near absolute zero (0K or -273.15°C), that the resistance of a mercury wire dropped precipitously when cooled to below 4.2K (-268.95°C). He soon recognized this to be the manifestation of a new state of matter “which on account of its extraordinary electrical properties may be called the superconducting state.”

For over 20 years after the discovery of superconductivity, this new state was believed to be just an ideal conductor that loses its resistance below a distinct temperature, the so-called critical temperature, T_c . In the year 1933, [Meissner and Ochsenfeld \(1933\)](#) discovered that magnetic fields are excluded from the inside of a superconductor even on cooling in a constant magnetic field that could not be explained by classical electrodynamics. This effect is known today as the Meissner–Ochsenfeld effect.

Bardeen *et al.* published their comprehensive theory of superconductivity in 1957 ([Bardeen *et al.*, 1957](#)). The salient point of the so-called BCS theory is the attractive electron interaction mediated by phonons. By that virtue, two electrons couple to form so-called Cooper pairs, which act in a fundamentally different way from single electrons. Being quasi-particles with integer spin, Cooper pairs follow the Bose–Einstein statistics which allows them to condense into a single quantum mechanical state, with all Cooper pairs having the same wave function. Thus, superconductivity is often referred to as a macroscopic quantum phenomenon ([Matthias *et al.*, 1965](#)). The BCS theory was very successful in predicting the critical temperature of a material and provided an explanation for the isotope effect, according to which the critical temperature shifts as a function of the isotopic mass of chemical elements.

With the discovery of materials showing transition temperatures near and above 100K, it became evident that the BCS theory would not be adequate to describe this new class of superconductors, known as high-temperature superconductors, in contrast to the term “low-temperature superconductor” which comprises all superconductors with critical temperatures below about 30K. Experiments gave evidence that the charge carriers of superconductivity are Cooper pairs. But, the question about the nature of the force that keeps the Cooper pairs together is still a matter of investigation.

Since the first observation of superconductivity in mercury, thousands of compounds and alloys were investigated with respect to their superconducting properties ([Tinkham, 1975](#)). In [Fig. 1](#) the fever curve of superconductivity is shown, which is marked by the highest critical temperature known during that time. Since 1993, several new superconductors have been found. None of them, however, have surpassed the world champion $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ exhibiting a T_c of 138K at ambient pressure, and 164K at an isostatic pressure of 23 GPa.

Type 1 Superconductors

Type 1 superconductors – also known as the “soft” superconductors – are characterized by a very sharp transition to a superconducting state at T_c , and by “perfect” Meissner–Ochsenfeld effect up to the so-called critical field, B_c . Above T_c the material becomes normal conducting. Even here, the transition is very sharp ([Fig. 2](#)). The value of B_c is temperature dependent and reaches zero at T_c . However, the magnetic field is not repelled at the surface of the superconductor, but penetrates it within a 10^{-8} – 10^{-7} m thick surface layer causing screening electric currents in the surface layer. These currents generate a magnetic field which is anti-polarized to the external field. This phenomenon is the reason for the well-known levitation effect of a permanent magnet above a superconductor, or vice versa.

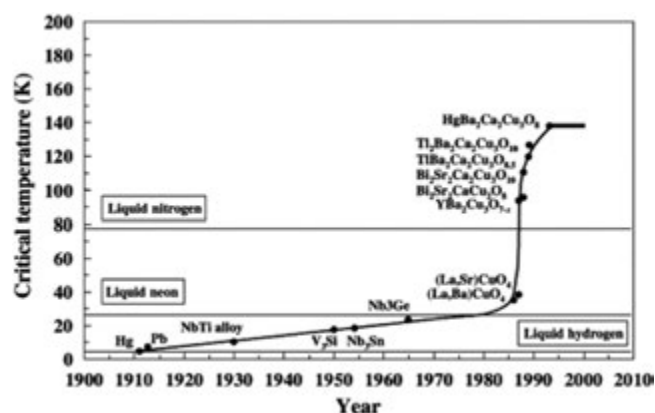


Fig. 1 Maximum critical temperature vs. time.

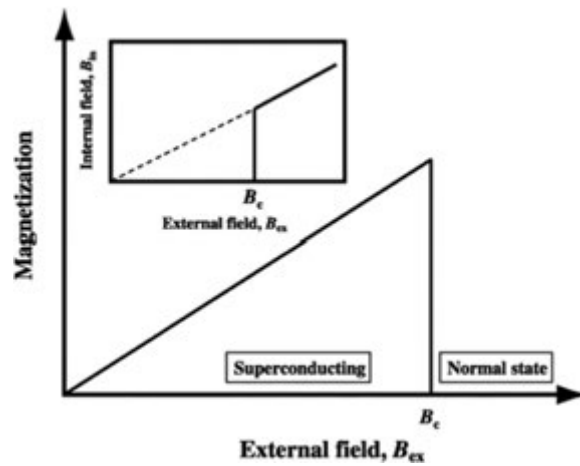


Fig. 2 Magnetization of a Type 1 superconductor vs. the external field, B_{ex} . Insert: Magnetic field within a Type 1 superconductor, B_{in} , vs. the external field, B_{ex} .

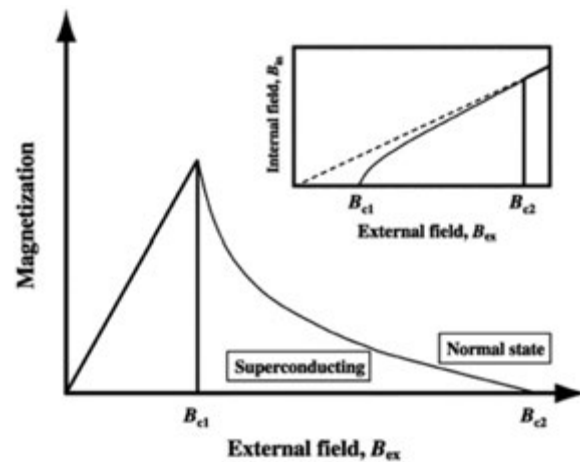


Fig. 3 Magnetization of a Type 2 superconductor vs. the external field, B_{ex} . Insert: Magnetic field within a Type 2 superconductor, B_{in} , vs. the external field, B_{ex} .

The so-called penetration depth, λ , of the external magnetic field is a material property. It also is temperature dependent and increases asymptotically towards T_c . At the particular field B_c relatively thick normal and superconducting domains running parallel to the field can coexist, known as the intermediate state.

Type 2 Superconductors

Type 2 superconductors – also known as the “hard” superconductors – differ from Type 1 in that their transition from a normal to a superconducting state is gradual across a region of “mixed state” behavior. A Type 2 superconductor exhibits a very different behavior in an external magnetic field compared to the Type 1 superconductors. At low external fields, like the Type 1 superconductor it repels the magnetic field up to the lower critical field, B_{c1} . This region is also called the “Meissner phase.” Above B_{c1} , regularly divided quantified flux vortices or flux lines enter the material up to the so-called upper critical field, B_{c2} (Fig. 3). In the region between B_{c1} and B_{c2} , superconducting and nonsuperconducting areas with trapped magnetic flux lines are present (Fig. 4). With increasing magnetic fields, the trapped flux lines move closer together and more trapped flux lines occur, so that the superconducting volume decreases and that of the nonsuperconducting increases. The region is called the “Shubnikov phase” or the mixed state. The values of B_{c1} and B_{c2} are also temperature dependent and decrease with increasing temperature. At T_c both values, B_{c1} and B_{c2} , are zero (Fig. 5).

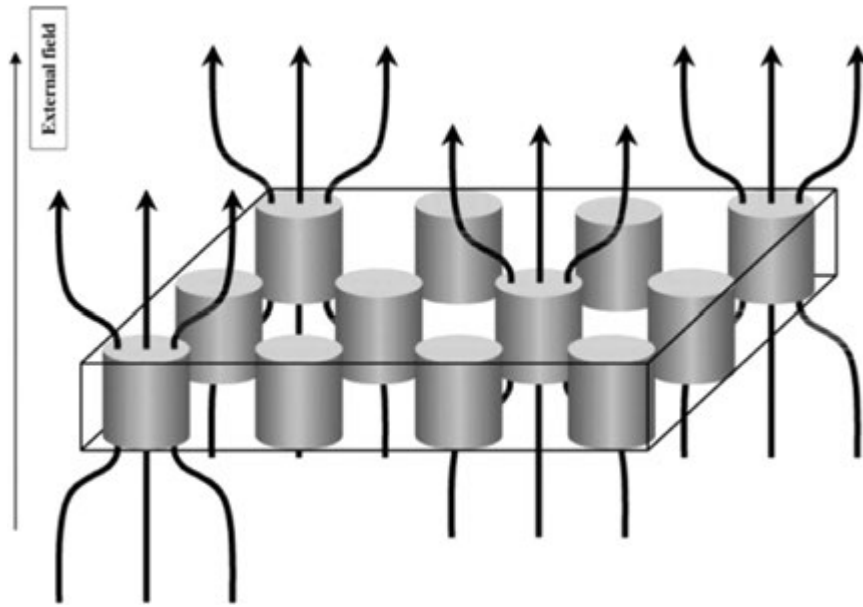


Fig. 4 Type 2 superconductor with trapped flux lines vortex.

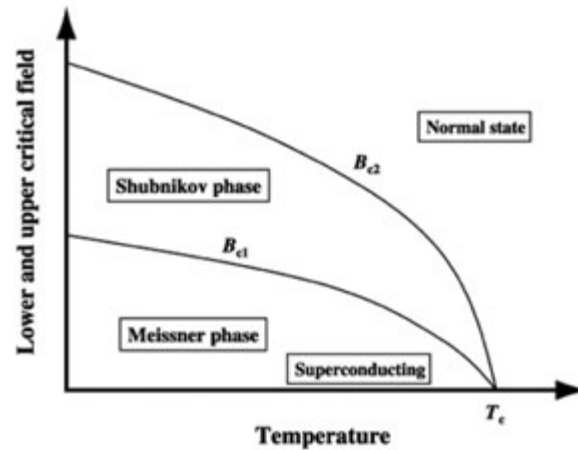


Fig. 5 Lower and upper critical field of a Type 2 superconductor vs. the temperature.

Critical Current Density

Both categories of superconductors, Types 1 and 2, can carry large electric currents up to a certain value which is called the critical current density, J_c (A cm^{-2}). Above J_c , the superconductor becomes normal conducting. J_c is dependent on both the temperature and the external magnetic field. At T_c or B_c (Type 1) or B_{c2} (Type 2) the value of J_c is zero and the superconductor becomes normal conducting (Fig. 6). Superconductors show characteristic current versus voltage behavior. At a current below J_c the voltage is zero. Above J_c , as in a metal, the voltage increases with the current (Fig. 7).

In the mixed state, when an electric current is transported through the superconductor due to the Lorentz force, the trapped flux lines can move through the superconductor causing dissipation of the current and a warming of the superconductor. This phenomenon can result in a rapid transition into the normal conducting state. Therefore, the value of J_c is significantly lower in the Shubnikov phase compared to the Meissner phase. However, the flux lines can be pinned by so-called pinning centers, which are defects with different dimensions within the superconductor. For example, point defects (zero dimension), dislocation lines (one dimension), twin planes (two dimensions), and second phases (three dimensions). The flux lines remain pinned until the Lorentz force surpasses the pinning force of the defect.

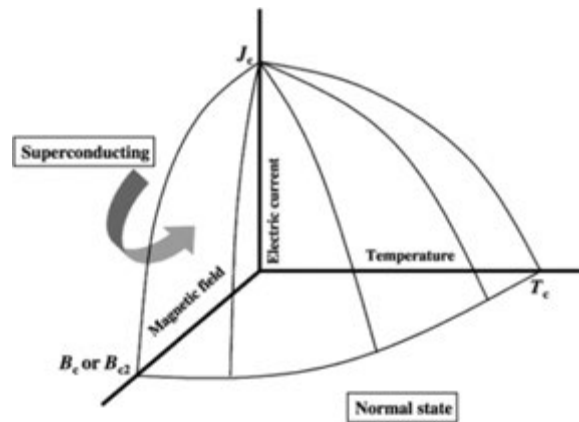


Fig. 6 Critical current density, J_c , vs. the temperature and the external magnetic field.

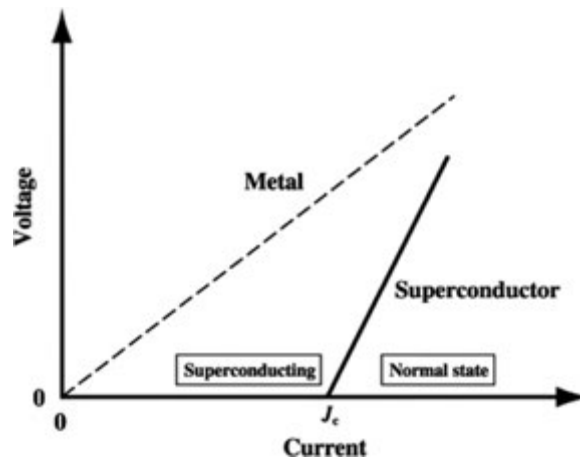


Fig. 7 Current–voltage characteristic of a superconductor.

Superconducting Materials

Except for the elements vanadium, technetium, and niobium, the Type 2 category of superconductors includes compounds and alloys. Niobium ($T_c = 9.2\text{K}$), especially when alloyed with titanium ($\text{Nb}_{0.7}\text{Ti}_{0.3}$; $T_c = 9.8\text{K}$), exhibits the highest critical temperature of all elements. Although superconductors with higher T_c are available, until now, most commercially available superconducting magnets operating below about 5 T are based on NbTi wires, due to its comparably low price and excellent manufacturing qualities. During the late 1940s and early 1950s, compounds were found with T_c values in the range of 10–20K. These compounds belong to the β -tungsten structure family, also named A15 phases or A_3B structure (Flükiger, 1991). The unit cell of the structure consists of a cube with the B atoms entering each corner of the cube. The A atoms enter the planes of the cube, and so form lines parallel to each crystallographic direction of the crystal (Fig. 8). It is believed that this extraordinary structural feature is mainly responsible for the relatively high T_c s of the compounds. Due to technological considerations with respect to processing and fabrication, only Nb_3Sn ($T_c = 18.1\text{K}$) is used for the manufacturing of wires for high field ($> 5\text{ T}$) superconducting magnets.

Superconductivity has been found in different materials (Table 1), which indicates that superconductivity is not only related to one or two structural types, but may occur everywhere.

Magnesium Diboride

MgB_2 has been found to be superconducting at a T_c of 39 K and a B_{c2} at about 11 T (Nagamatsu *et al.*, 2001). This new Type 2 superconductor has a hexagonal structure (AB_2) with $a = 3.086\text{ Å}$ and $c = 3.524\text{ Å}$. Although the compound has quite low T_c and B_{c2} values (about 15 T at 4.2K and 10 T at 20K; up to 74 T in thin films at 4.2K), it is of considerable interest for the processing of



Fig. 8 Crystal structure of A15 phases (Nb_3Sn).

Table 1 Superconducting elements, alloys, and compounds

Material	Temperature (K)	Material	Temperature (K)
<i>Elements</i>		<i>A15 phases</i>	
Carbon (C)	15	Nb_3Ge	23.2
Lead (Pb)	7.2	Nb_3Si	19
Lanthanum (La)	4.9	Nb_3Al	19
Tantalum (Ta)	4.47	Nb_3Sn	18.1
Mercury (Hg)	4.15	V_3Si	17.1
Tin (Sn)	3.72	Ta_3Pb	17
Indium (In)	3.40	V_3Ga	16.8
Thallium (Tl)	1.70	Nb_3Ga	14.5
Rhenium (Re)	1.697	V_3In	13.9
Protactinium (Pa)	1.40	<i>High-temperature superconductors</i>	
Thorium (Th)	1.38	$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$	138
Aluminum (Al)	1.175	$\text{HgBa}_2\text{CaCu}_2\text{O}_6$	124
Gallium (Ga)	1.10	$\text{HgBa}_2\text{CuO}_4$	98
Gadolinium (Gd)	1.083	$\text{Ti}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	127
Molybdenum (Mo)	0.915	$\text{TiBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$	123
Zinc (Zn)	0.85	$\text{TiBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11}$	112
Osmium (Os)	0.66	$\text{Ti}_2\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12}$	112
Zirconium (Zr)	0.61	$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	110
Americium (Am)	0.60	$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$	
Cadmium (Cd)	0.517	$\text{Bi}_2\text{Sr}_2\text{CuO}_6$	20
Ruthenium (Ru)	0.49	$\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$ (at about 5 GPa)	110
Titanium (Ti)	0.40	$\text{TmBa}_2\text{Cu}_3\text{O}_7$	90
Uranium (U)	0.20	$\text{GdBa}_2\text{Cu}_3\text{O}_7$	94
Hafnium (Hf)	0.128	$\text{YBa}_2\text{Cu}_3\text{O}_7$	93
Iridium (Ir)	0.1125	$\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_8$	70
Lutetium (Lu)	0.100	$\text{GaSr}_2(\text{Y}, \text{Ca})\text{Cu}_2\text{O}_7$	70
Beryllium (Be)	0.026	$\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$	35
Tungsten (W)	0.0154	$(\text{Nd}, \text{Sr}, \text{Ce})_2\text{CuO}_4$	35
Platinum (Pt)	0.0019	$\text{Pb}_2(\text{Sr}, \text{La})_2\text{Cu}_2\text{O}_6$	32
Rhodium (Rh)	0.000325	$\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$	38
<i>Metals and alloys</i>		<i>Various superconductors</i>	
$\text{Nb}_{0.6}\text{Ti}_{0.4}$	9.8	Cs_3C_{60}	40
Nb	9.25	MgB_2	39
Tc	7.80	$\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$	30
V	5.40	$\text{YNi}_2\text{B}_2\text{C}$	15.5
		LiTiO_2	13
		$\text{La}[\text{O}_{1-x}\text{F}_x]\text{FeP}$	4
		$\text{La}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$	26
		$\text{Pr}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$	45

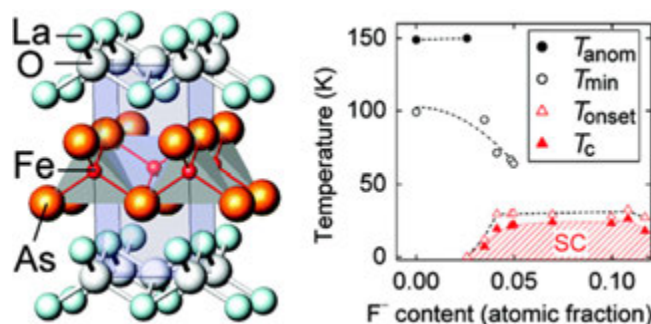


Fig. 9 The crystal structure of the iron-based layered superconductor La[O_{1-x}F_x]FeAs showing onset of superconductivity at $x = 0.3$. Reprinted with permission from Kamihara, Y., Watanabe, T., Hirano, M., Hosono, H., 2008. Iron-based layered superconductor La[O_{1-x}F_x]FeAs ($x = 0.05$ – 0.12). J. Am. Soc. 130, 3296–3297, Copyright (2008) American Chemical Society.

wires used for the construction of superconducting magnets operating at 1–2 T and 20K, due to its comparably low price and excellent workability. In addition, it is hoped that besides MgB₂ other superconducting compounds of this new class of superconductors with T_c s much higher than 39K will be found.

Iron Based Superconductors

In recent years a new class of superconducting materials were discovered that have a layered structure similar to high-temperature superconductors. These materials are based on iron phosphate or iron arsenate layers that alternate with layers consisting of the oxides of rare earth elements. These materials are named oxy-pnictides. This new class of superconducting materials have the potential for economically feasible magnetic levitation and lossless transmission of electric energy at the temperature well above that of liquid helium. First discovered in 2006 (Kamihara *et al.*, 2006) fluorine doped LaOFeP with alternating layers of Fe²⁺ P³⁻ and La³⁺ (O_{1-x}F_x)^{(2-x)-} has a T_c of only about 4K. It is obvious that fluorine doping is essential for introducing superconductivity in the material. By replacing phosphorous with arsenic the T_c jumps to 26K at a fluorine content of about 11 atom% (Kamihara *et al.*, 2008) (Fig. 9). This compound is tetragonal with $a = 0.403$ nm and $c = 0.874$ nm. The compound shows systematically decreasing lattice parameters with increasing fluorine doping at the O²⁻ site which is due to the smaller ionic radius of fluorine compared to oxygen. A major increase of T_c has been observed when lanthanum is replaced with praseodymium. The T_c of this compound increases to about 45K with an onset at 52K (Ren *et al.*, 2008). The synthesis of these materials is usually done at temperatures of 1250°C in argon atmosphere at ambient pressures using the precursor materials lanthanum arsenide or phosphide, iron arsenide or phosphide, lanthanum oxide, and lanthanum fluoride.

High-Temperature Superconducting Cuprates

Since the first high temperature superconductor (HTSC) based on copper oxide with the composition La_{0.85}Ba_{0.15}CuO₃ was found, a variety of high-temperature superconductors have been synthesized. They all share a single structural feature, namely superconducting two-dimensional sheets of CuO₂ consisting of corner-shared CuO₄ units (Park and Snyder, 1995). The sheets are separated by a nonsuperconducting layer which supplies the sheets with charge carriers. The HTSCs can be divided into three major groups: (1) REEBa₂Cu₃O_{7-x} (123 type); (2) AB₂Ca_{n-1}Cu_nO_{2n+2.5} (1223 type); (3) A₂B₂Ca_{n-1}Cu_nO_{2n+4} (2223 type) with REE = rare earth elements; A = Bi, Tl, Hg; B = Sr, Ba. The phases have a pronounced layered structure which is visible both microscopically (Fig. 10) and macroscopically (Fig. 11). Due to the significantly different parameters of the a , b , and c axis, the crystallization rate in direction of the a,b plane is about 10²–10³ times faster than in c direction.

Compared with low-temperature superconductors of Type 2, the cuprates behave very differently with respect to their superconducting properties vs. the temperature (Ginsberg, 1989; Lynn, 1990). Their resistivity transition is broader and the breadth increases rapidly with the applied field. This means that there is a region below B_{c2} where the material shows a substantial electrical resistance, although the material is superconducting with respect to quantum mechanical considerations. This region is shown in Fig. 12 between B_{c2} and the irreversibility line, B_{irr} . Below B_{irr} the resistance of the material is zero. The substantial resistance above B_{irr} corresponds to very easy flux flow.

The layered structure also implies a pronounced anisotropy of the properties, causing the so-called “two-dimensional superconductivity” parallel to the a,b plane. For example, the critical current density as well as the B_{c1} and B_{c2} values of the compounds, are significantly greater parallel to the a,b plane than parallel to the c axis (Fig. 13). In addition, due to the almost complete decoupling of the CuO₂ sheets by the nonsuperconducting (Bi, Tl, Hg)O sheets, the HTSCs behave very differently within an applied magnetic field. At temperatures below about 30K flux lines are formed above B_{c1} like in the Type 2 low-temperature superconductors. Above that temperature, the flux lines disappear and separated, almost two-dimensional, flux disks, the so-called

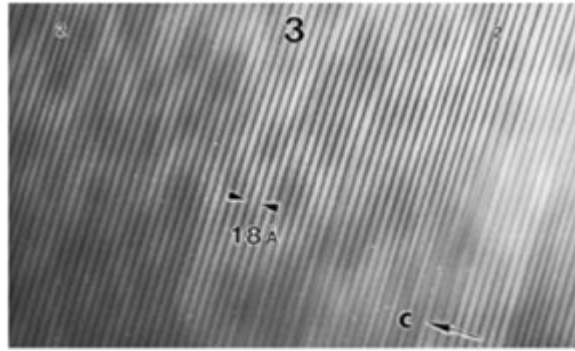


Fig. 10 Transmission electron microscopic image of a $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ crystal. Dark layers: BiO bilayers, light gray layers: $\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_7$. (3) area with $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ structure; (2) Stacking faults with $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ structure. (C) crystallographic c axis. $18 \text{ \AA}$ represent a half unit cell of $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$.

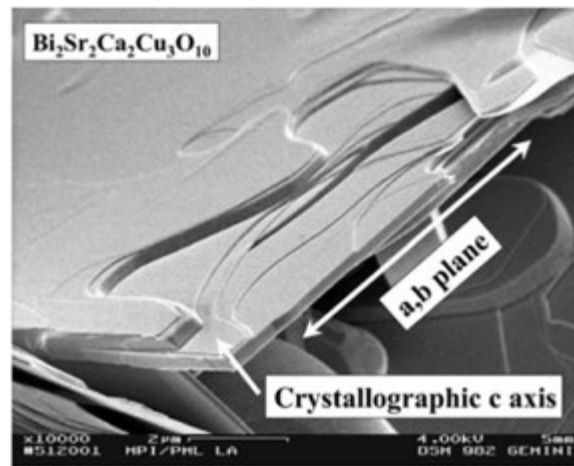


Fig. 11 Scanning electron microscopic image of a $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ crystal showing the extreme anisotropy in grain dimension.

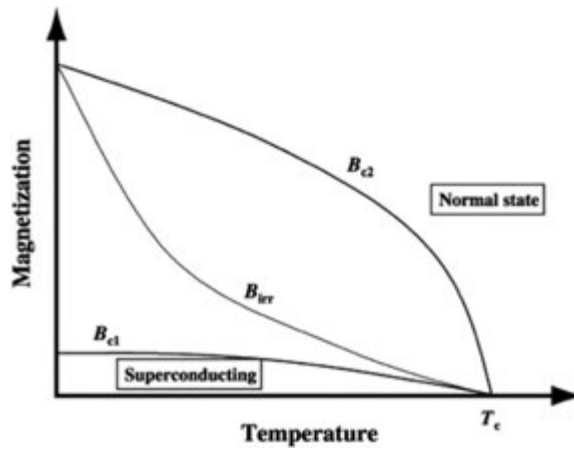


Fig. 12 B_{c1} , B_{c2} , and B_{irr} vs. the temperature.

pancake vortices, are formed within the CuO_2 sheets (Fig. 14). The coupling between the pancakes is very weak, especially at high temperatures, for example 77K (boiling point of liquid nitrogen), so that the pancakes are moving independently from the neighboring pancake of the next CuO_2 sheet when a Lorentz force is applied. Pinning of these pancakes is almost impossible and therefore, the J_c decreases significantly in an applied magnetic field (Fig. 15).

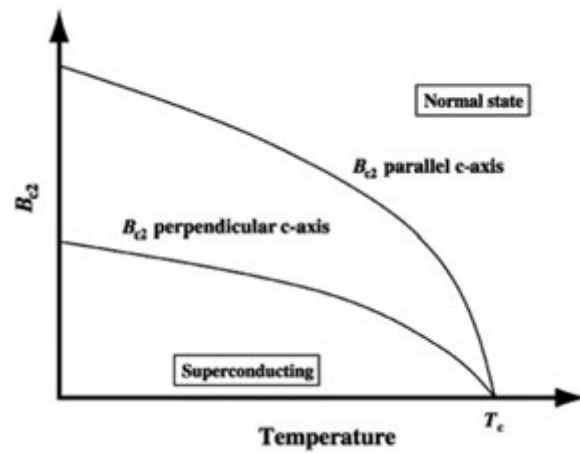


Fig. 13 Schematic drawing of the upper critical field vs. temperature parallel and perpendicular to the crystallographic c axis showing the pronounced anisotropy of the superconducting properties of the HTSCs.

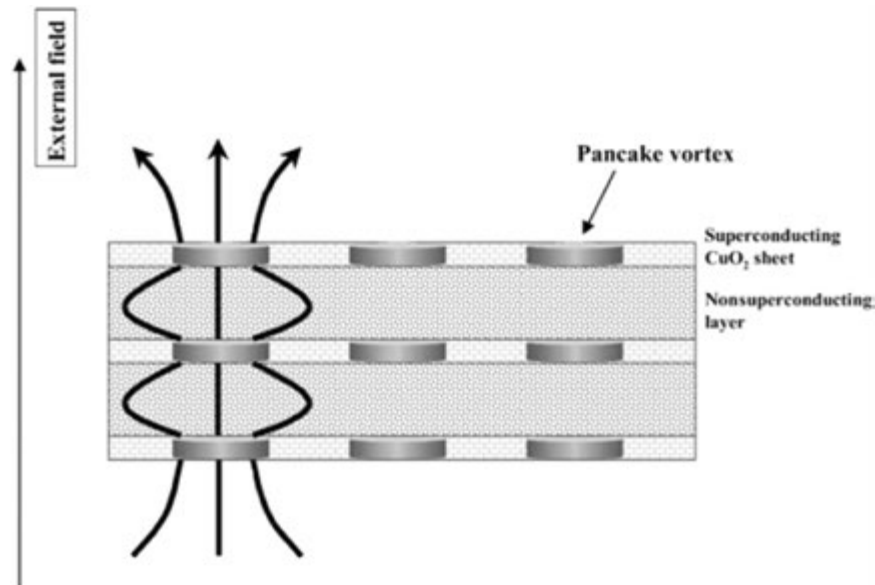


Fig. 14 Pancake vortex in a HTSC parallel to the CuO_2 sheets.

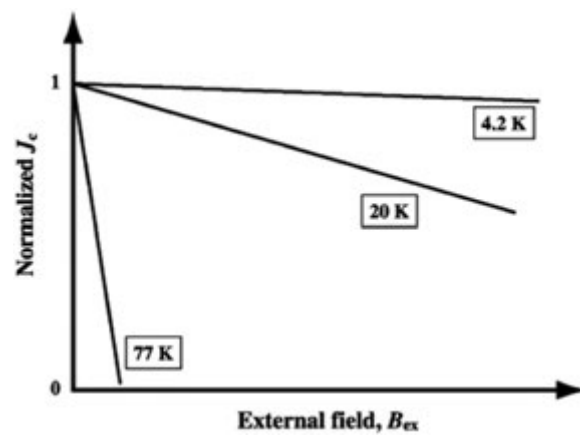


Fig. 15 Schematic drawing of the influence of the external field, B_{ex} , on the J_c value of HTSCs at different temperatures.

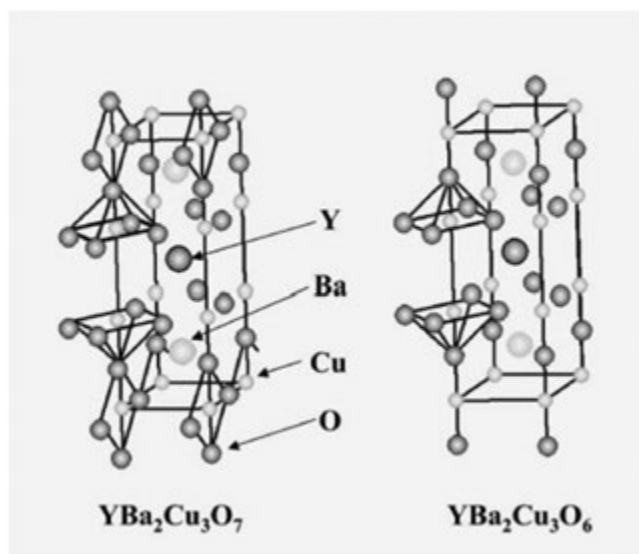


Fig. 16 Crystal structure of tetragonal, nonsuperconducting YBa₂Cu₃O₆, and orthorhombic, superconducting YBa₂Cu₃O₇.

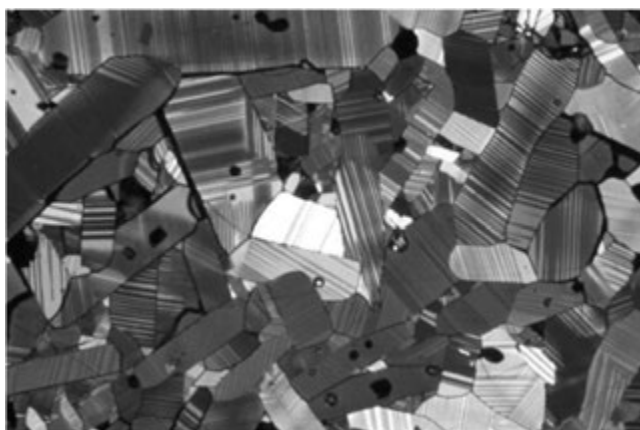


Fig. 17 Micrograph of a 123 ceramic using an optical microscope and polarized light showing the [110] twin boundaries in 123 grains.

The Compound YBa₂Cu₃O_{7-x}

One of the main important high temperature superconducting cuprates is the compound YBa₂Cu₃O_{7-x}, better known as the “123 phase” ($T_c = 93\text{K}$) (Cava, 2001). The 123 phase is characterized by a Cu–O sublattice consisting of the CuO₂ sheets parallel to the crystallographic a–b plane, and Cu–O chains parallel to the crystallographic a axis (Fig. 16). The yttrium atom enters the center of the unit cell, and separates the Cu–O sheets. At temperatures of above 700°C the compound is tetragonal with $a = 3.857 \text{ \AA}$ and $c = 11.839 \text{ \AA}$. Below that temperature, the phase becomes orthorhombic with $a = 3.885 \text{ \AA}$, $b = 3.818 \text{ \AA}$, and $c = 11.680 \text{ \AA}$ due to the introduction of excess oxygen into the Cu–O chains.

The phase transformation is combined with a formation of elastic twins parallel to the crystallographic [110] plane. This phenomenon makes it easy to distinguish between the tetragonal and orthorhombic 123 phase using a microscope and polarized light (Fig. 17). Tetragonal YBa₂Cu₃O₆ is nonsuperconducting. With increasing oxygen content the compound becomes superconducting at about YBa₂Cu₃O_{6.3}. Maximum T_c is reached at YBa₂Cu₃O_{6.93}. A further increase of the oxygen content decreases T_c .

The 1223 and 2223 Type Compounds

The compounds have layered structures parallel to the crystallographic a,b plane, consisting of (Bi,Tl, Hg)O-layers which alternate with perovskite-like B₂Ca_{n-1}Cu_nO_{1+2n} units as illustrated in Fig. 18. The Sr₂Ca_{n-1}Cu_nO_{1+2n} units contain the CuO₂ sheets which are oriented parallel to the a,b plane. The $n = 2$ phase (1212 or 2212 phase) is characterized by two CuO₂ sheets and the $n = 3$

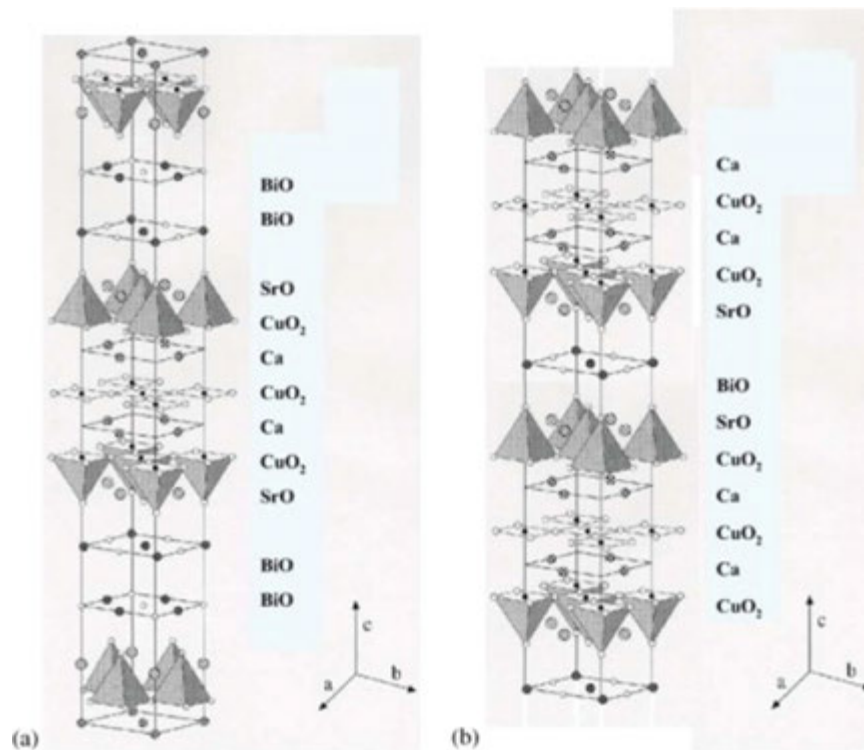


Fig. 18 (a) Crystal structure of the $A_2B_2Ca_2Cu_3O_{10}$ type HTSC with $A = \text{Bi, Tl, Hg}$, and $B = \text{Sr, Ba}$. (b) Crystal structure of the $AB_2Ca_2Cu_3O_{10}$ type HTSC with $A = \text{Tl, Hg}$, and $B = \text{Sr, Ba}$.

phase (1223 and 2223 phase) by three CuO_2 sheets, respectively. Thus, the general structure of all members of the series consist of CuO_2 sheets, that are separated by calcium (for $n > 1$) and covered in the c direction by $(\text{Ba, Sr})\text{O}$ sheets. These perovskite-like units alternate in c direction with the $(\text{Bi, Tl, Hg})\text{O}$ -layers.

The T_c s of the compounds are dependent on the oxygen content and, like the 123 phase, they exhibit a maximum T_c at a certain oxygen content. However, none of them become nonsuperconducting at low oxygen contents, and the dependence of T_c is very different from compound to compound (Majewski *et al.*, 1997a). The synthesis of the superconducting cuprates is rather straight forward and can be done in air or oxygen atmosphere using the generic oxides and carbonates (Majewski *et al.*, 1997b).

Iron Selenide Thin Films

Very recently, the discovery of superconductivity with T values up to 100K in FeSe thin films caused considerable excitement, as it opens the door to another avenue to high temperature superconductivity. Superconductivity with a T_c of up to 109K was observed in single-layer FeSe films deposited on SrTiO_3 (001) substrates (Ge *et al.*, 2015). Bulk FeSe samples were observed to have a T_c of only about 8K. However, substitution of Se with Te in the FeSe superconductor results in an increase of T_c up to 14.5K and superconductivity exists over a wide concentration range in the $\text{Fe}(\text{Se, Te})$ system, although pure FeTe is not superconducting (Liu *et al.*, 2015). Although the mechanism of high temperature superconductivity in FeSe single-layer thin films on SrTiO_3 has yet to be understood, the discovery of this novel phenomenon and the understanding of the fundamental physical mechanisms underlying this phenomenon can be the key to discovering superconductivity even at room temperature.

References

- Bardeen, J., Cooper, N.L., Schrieffer, J.R., 1957. Theory of superconductivity. *Phys. Rev.* 108 (1957), 1175–1204.
- Cava, R.J., 2001. Oxide superconductors. *J. Am. Ceram. Soc.* 83 (2001), 5–28.
- Flükiger, R., 1991. A15 compound superconductors. In *Advances in Materials Science and Engineering*. Oxford: Pergamon.
- Ge, J.-F., Liu, Z.-L., Liu, C., *et al.*, 2015. Superconductivity above 100K in single-layered FeSe films on doped SrTiO_3 . *Nat. Mater.* 14, 285–289.
- Ginsberg, D.M. (Ed.), 1989. *Physical Properties of High Temperature Superconductors*. Singapore: vol. 1, World Scientific.
- Kamihara, Y., Hiramatsu, H., Hirano, M., *et al.*, 2006. Iron-based layered superconductor: LaOFeP . *J. Am. Chem. Soc.* 128, 10012–10013.
- Kamihara, Y., Watanabe, T., Hirano, M., Hosono, H., 2008. Iron-based layered superconductor $\text{La}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$ ($x = 0.05\text{--}0.12$). *J. Am. Soc.* 130, 3296–3297.
- Liu, X., Zhao, L., He, S., *et al.*, 2015. Electronic structure and superconductivity of FeSe-related superconductors. *J. Phys. Condens. Matter* 27, 18301–18323.
- Lynn, J.W. (Ed.), 1990. *High Temperature Superconductivity*. New York: Springer.

- Majewski, P., Su, H.L., Quilitz, M., 1997a. Relationships between the chemical composition and properties of the high-temperature superconductor $\text{Bi}_{2+x}\text{Sr}_{2-y}\text{Ca}_{1+y}\text{Cu}_2\text{O}_{8+d}$. *J. Mater. Sci.* 32, 5137–5141.
- Majewski, P., Kaesche, S., Aldinger, F., 1997b. Fundamental material aspects underlying the preparation of high-temperature superconducting $(\text{Bi,Pb})_{2+x}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+d}$ ceramics. *J. Am. Ceram. Soc.* 80, 1174–1180.
- Matthias, B.T., Geballe, T.H., Compton, V.B., 1965. Superconductivity. *Rev. Mod. Phys.* 35, 1–23.
- Meissner, W., Ochsenfeld, R., 1933. Ein neuer Effekt bei Eintritt der Supraleitfähigkeit. *Naturwissenschaften* 21 (1933), 787–788.
- Nagamatsu, J., Nakagawa, N., Muranaka, T., Zenitani, Y., Akimitsu, J., 2001. Superconductivity at 39K in magnesium diboride. *Nature* 410, 63–64.
- Onnes, H.K., 1911. Further experiments with liquid helium. C. On the change of electric resistance of pure metals at very low temperatures etc. IV. The resistance of pure mercury at helium temperatures. In: *Proceedings of the KNAW*, 13 II, 1910–1911, pp. 1274–1276. Amsterdam.
- Park, C., Snyder, R.L., 1995. Structures of high-temperature cuprate superconductors. *J. Am. Ceram. Soc.* 78, 3171–3194.
- Ren, Z.A., Yang, J., Lu, W., *et al.*, 2008. Superconductivity at 52K in iron based F doped layered quaternary compound $\text{Pr}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$. *Mater. Res. Innov.* 12, 105–106.
- Tinkham, M., 1975. *Introduction to Superconductivity*. New York: McGraw-Hill, doi: 10.1016/B0-08-043152-6/01811-8. (extended edn. 1995)

Further Reading

Ginsberg, D.M. (Ed.), 1990. *Physical Properties of High Temperature Superconductors*. vol. 2, Singapore: World Scientific.

Superconductors: Borocarbides

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Superconductivity and Magnetism in Borocarbides

Superconductivity in quaternary rare-earth transition-metal borocarbides (RTBC) has been found in 1994 (Nagarajan *et al.*, 1994; Cava *et al.*, 1994). With the invention of these materials the new $\text{LuNi}_2\text{B}_2\text{C}$ -type structure (see Fig. 1), space group $14/mmm$, has been discovered which can be considered as the well-known ThCr_2Si_2 type interstitially modified by carbon. The $\text{RT}_2\text{B}_2\text{C}$ compounds are the $n = 1$ (so-called single layer) variants of $(\text{RC})_n\text{T}_2\text{B}_2$ structures where n RC layers alternate with single T_2B_2 layers. Details on the properties of these and related compounds can be found in the review articles listed in the Bibliography. Table 1 summarizes the known superconducting and non-superconducting RTBC compounds of $\text{LuNi}_2\text{B}_2\text{C}$ -type structure where R stands for 4f- and 5f-elements as well as for Sc, Y, and La. Among them $\text{YPd}_2\text{B}_2\text{C}$ has the highest superconducting transition temperature $T_c \approx 23$ K. However, no single-phase samples could be prepared of the particular compound so far. The growth of very high quality single-crystals of various RTBC almost immediately after their discovery has had a profound impact on the quality of the work performed.

For certain combinations of elements R and T , superconducting and antiferromagnetic order have been found to coexist. The magnetic moments in these materials are localized at the R -sites whereas the Ni d-electrons are nearly non-polarized. A striking feature distinguishing the superconducting RTBC from other superconductors known until 1994 is that the magnetic ordering temperature T_N is comparable with T_c (see Fig. 2), i.e., the magnetic energy is comparable with the superconducting condensation energy. Therefore, the investigation of these compounds is expected to result in new insights into the interplay of superconductivity and magnetism. The high values of T_N demand that in RTBC, different from the situation in high- T_c cuprates and the classical magnetic superconductors, exchange coupling between the rare-earth magnetic moments is the dominant magnetic interaction rather than magnetostatic interaction. Obviously the exchange is mediated by conduction electrons. Consequently, also the interaction between the magnetic moments and the conduction electrons must be relatively strong. Fig. 2 shows a linear scaling of T_N and, roughly approximated, also of T_c with the de Gennes factor $\text{DG} = (g - 1)^2(J + 1)$ of the R^{3+} Hund's rule ground state where g is the Landé factor and J is the total angular momentum. Such so-called de Gennes scaling, at the same time for T_N and T_c is due the fact that both effects, antiferromagnetism and the suppression of superconductivity, are governed by the exchange interaction of the conduction electrons with the R 4f-electrons. According to Fig. 2, $\text{YbNi}_2\text{B}_2\text{C}$ should be a superconductor becoming antiferromagnetically ordered at sufficiently low temperatures. In this compound, however, hybridization of 4f-electrons with the conduction electrons connected with correlation effects result in heavy fermion behavior and suppression of superconductivity.

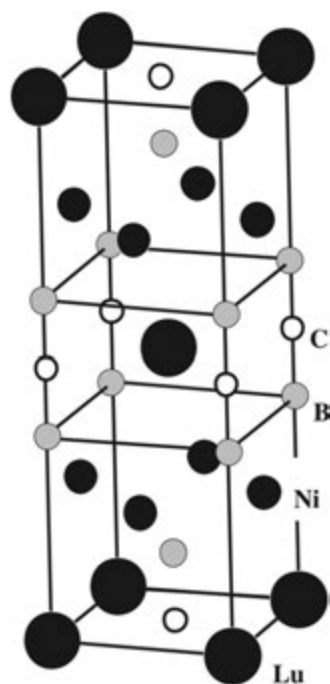


Fig. 1 $\text{LuNi}_2\text{B}_2\text{C}$ -type crystal structure.

Table 1 Compounds with the $\text{LuNi}_2\text{B}_2\text{C}$ -type structure

$\text{CeCo}_2\text{B}_2\text{C}$	$\text{HoCo}_2\text{B}_2\text{C}$	$\text{NdRh}_2\text{B}_2\text{C}$	$\text{ThRh}_2\text{B}_2\text{C}$
$\text{CeNi}_2\text{B}_2\text{C}$	$\text{HoNi}_2\text{B}_2\text{C}$	$\text{PrNi}_2\text{B}_2\text{C}$	$\text{TmNi}_2\text{B}_2\text{C}$
$\text{CePt}_2\text{B}_2\text{C}$	$\text{HoRh}_2\text{B}_2\text{C}$	$\text{PrPt}_2\text{B}_2\text{C}$	$\text{UNi}_2\text{B}_2\text{C}$
$\text{CeRh}_2\text{B}_2\text{C}$	$\text{LaIr}_2\text{B}_2\text{C}$	$\text{PtRh}_2\text{B}_2\text{C}$	$\text{URh}_2\text{B}_2\text{C}$
$\text{DyNi}_2\text{B}_2\text{C}$	$\text{LaNi}_2\text{B}_2\text{C}$	$\text{ScNi}_2\text{B}_2\text{C}$	$\text{YCo}_2\text{B}_2\text{C}$
$\text{DyPt}_2\text{B}_2\text{C}$	$\text{LaPd}_2\text{B}_2\text{C}$	$\text{SmNi}_2\text{B}_2\text{C}$	$\text{YNi}_2\text{B}_2\text{C}$
$\text{DyRh}_2\text{B}_2\text{C}$	$\text{LaPt}_2\text{B}_2\text{C}$	$\text{SmRh}_2\text{B}_2\text{C}$	$\text{YPd}_2\text{B}_2\text{C}$
$\text{ErNi}_2\text{B}_2\text{C}$	$\text{LaRh}_2\text{B}_2\text{C}$	$\text{TbNi}_2\text{B}_2\text{C}$	$\text{YPt}_2\text{B}_2\text{C}$
$\text{ErRh}_2\text{B}_2\text{C}$	$\text{LuCo}_2\text{B}_2\text{C}$	$\text{TbRh}_2\text{B}_2\text{C}$	$\text{YRu}_2\text{B}_2\text{C}$
$\text{GdCo}_2\text{B}_2\text{C}$	$\text{LuNi}_2\text{B}_2\text{C}$	$\text{ThNi}_2\text{B}_2\text{C}$	$\text{YbNi}_2\text{B}_2\text{C}$
$\text{GdNi}_2\text{B}_2\text{C}$	$\text{NdNi}_2\text{B}_2\text{C}$	$\text{ThPd}_2\text{B}_2\text{C}$	
$\text{GdRh}_2\text{B}_2\text{C}$	$\text{NdPt}_2\text{B}_2\text{C}$	$\text{ThPt}_2\text{B}_2\text{C}$	

Note: Superconductors are printed in bold face.

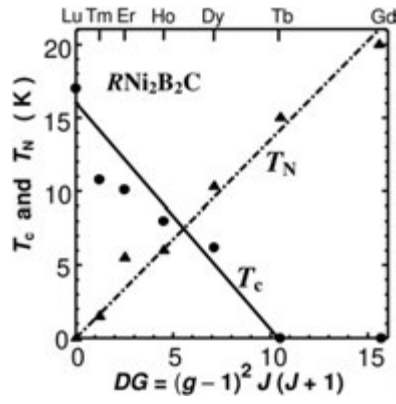


Fig. 2 Critical temperatures for superconductivity, T_c , and for antiferromagnetic ordering, T_N , of $\text{RNi}_2\text{B}_2\text{C}$ compounds with $R = \text{Lu, Tm, Er, Ho, Dy, Tb, and Gd}$. DG , g , and J are explained in the text. The straight lines represent linear approximations.

The RTBC superconductors have been classified as phonon-mediated type II superconductors in the clean limit (i.e., the mean free path of the unpaired electrons is large compared to the coherence length of the Cooper pairs). The symmetry of the superconducting gap will be discussed in the next section.

Symmetry of the Superconducting Gap

The symmetry of the superconducting order parameter is a fundamental property used to distinguish conventional from unconventional superconductors. In the latter case, the symmetry of the superconducting order parameter is lower than that of the crystal structure (the same as that of the Fermi surface). The quasiparticles in the superconducting state acquire a gap near the Fermi level reflecting the symmetry of a Cooper pair, which can be identified with the superconducting order parameter. The wave function of Cooper pairs in non-magnetic $\text{RNi}_2\text{B}_2\text{C}$ compounds is given by the product of an orbital and a spin part. In the case of singlet pairing with total spin $S = 0$, the orbital part must be of even parity and can be classified by an even total angular momentum $l = 0, 2, 4$, denoted as s -, d -, and g -wave states, respectively. Then, a pure s -wave state has no zeros (nodes) and a constant gap Δ , whereas in the more realistic extended s -wave state the gap $\Delta(k)$ changes over the Fermi surface, i.e., it becomes anisotropic. In contrast, a pure d - or g -wave state may exhibit point-like nodes.

The nature of the quasiparticle energy gap is one of the most challenging questions in the research on $\text{RNi}_2\text{B}_2\text{C}$. A few years after their discovery these compounds were assumed to be conventional s -wave superconductors with an anisotropic gap (Müller *et al.*, 2002). Later, an analysis of the upper critical field (Wang and Maki, 1998) and the field dependence of the specific heat suggested d -wave superconductivity (Nohara *et al.*, 1997). However, the strong influence of Pt substitutions for Ni on the gap (Yokoya *et al.*, 2000) quite certainly rules out such a line-node scenario.

A phenomenological model with an $(s+g)$ -wave symmetry of the gap function was proposed by Lee and Choi (2002) in order to interpret experimental data for the angle-dependent thermal conductivity (see Fig. 3(a)) and specific heat in the frame of a single band model. In particular, Maki *et al.* (2002) used the form $\Delta(k) = 1/2\Delta(1 - \sin^4\theta \cos(4\phi))$, where θ and ϕ are the polar and the azimuthal angle in the k space, respectively. This model leads to four point nodes in the energy gap located regularly in the a - b -plane and describes the angular variation of both the c -axis component of the thermal conductivity and the specific heat C in

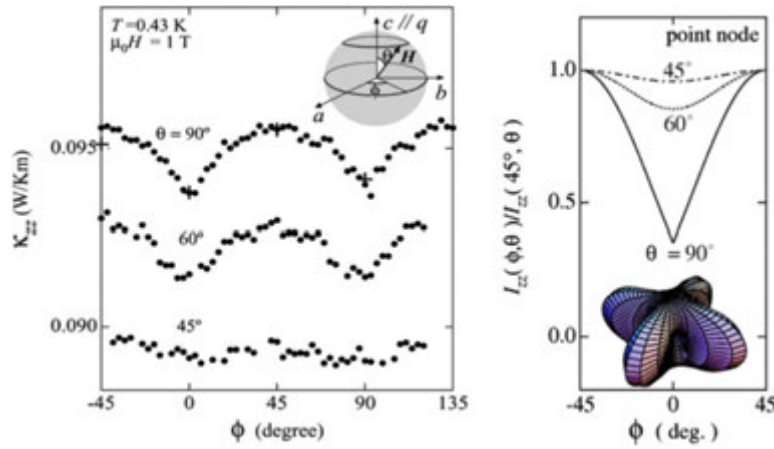


Fig. 3 Angular-dependent c-axis thermal conductivity of $\text{YNi}_2\text{B}_2\text{C}$ (a-left panel). θ and ϕ are defined in the inset. The right panel (b) shows the gap symmetry in the case of point nodes ($(s + g)$ -wave) and, additionally, the resulting angular variation of a quantity I_{zz} that is proportional to the c-axis component of the thermal conductivity. From Isawa, K., Kamata, K., Nakayima, Y., *et al.*, 2002. Gap function with point nodes in borocarbide superconductor $\text{YNi}_2\text{B}_2\text{C}$. Phys. Rev. Lett. 89, 137006.

$\text{YNi}_2\text{B}_2\text{C}$ in an in-plane magnetic field. In particular, the observed four-fold oscillations of the c-axis component of κ and C with narrow cusps (especially for $\theta = 90^\circ$) are reproduced by this model as shown in Fig. 3(b) for the thermal conductivity of $\text{YNi}_2\text{B}_2\text{C}$. A generalization for any direction of the applied field was given by Thalmeier and Maki (2003). The angle-dependent thermal conductivity was found to be strongly influenced by the presence of impurities (Yuan *et al.*, 2003; Maki *et al.*, 2004). A theoretical study by Yuan and Thalmeier (2003) has confirmed the stability of the mixed gap function. The $(s + g)$ -wave model has been described in detail by Thalmeier and Zwicknagl (2005).

An alternative explanation of the cusp-like singularity in the angle-dependent thermal conductivity and the specific heat was given by Udagawa *et al.* (2005). They calculated the field-orientational dependence of the density of states (FODOS) based on the solution of the Eilenberger equation and found rather broad minima in the point-node case. The FODOS is strongly influenced by the local Fermi surface part and its order parameter, but not so strong by the entire global nodal structure. In $\text{YNi}_2\text{B}_2\text{C}$, the Fermi surface nesting leads to a quasi two-dimensional nature of one of the conduction-electron bands. Assuming a two-band model with an isotropic superconducting coherence length, cusp-like minima are attributed to nesting effects rather than to a contribution from a nodal gap structure. A theoretical study based on the quasi-classical Eilenberger formalism (Miranović *et al.*, 2005) supported the interpretation of the rotational-field experiments. It was pointed out, however, that more detailed low-field data are required to distinguish between gap nodes and non-zero gap minima. A detailed analysis of the specific heat of $\text{YNi}_2\text{B}_2\text{C}$ has been presented by Huang *et al.* (2006). The zero-field data were compared with the predictions of different theoretical models (Fig. 4). Good agreement was found for a point-node scenario with $\Delta = \Delta_0 \sin n\theta$, where θ is the polar angle in the k space. Alternatively, an excellent description of the data is attained employing a two-band model, whereas an isotropic s-wave or line-node scenario can be ruled out. It is noted that the $(s + g)$ -wave model results in $C_p \sim T^2$ (Yuan *et al.*, 2003), which is significantly different from the usually observed T^3 dependence.

Thus, measurements of the thermal conductivity κ and the specific heat C provided first hints supporting the extended s-wave scenario in which electrons from different bands are involved in the pairing mechanism. Whereas discrepancies become visible in case of a single-band description of the experimental data within the $(s + g)$ -wave model. A large number of studies on the gap symmetry of $\text{RNi}_2\text{B}_2\text{C}$ including NMR results was summarized by Brandow (2003) who suggested strongly anisotropic s-wave superconductivity and pointed out that a single-band description might oversimplify the interpretation of experimental data due to the complex Fermi surface in $\text{RNi}_2\text{B}_2\text{C}$.

These results have been confirmed by point-contact spectroscopy (Bashlakov *et al.*, 2005, 2007), scanning tunneling spectroscopy (Martínez-Samper *et al.*, 2003; Suderow *et al.*, 2003) and photoemission spectroscopy data (Yokoya *et al.*, 2000; Baba *et al.*, 2006), too. These techniques provide a local insight, especially into the structure of the superconducting gap.

Fermi Surface in Non-magnetic Borocarbides in the Normal and Superconducting State

The knowledge of the electronic structure near the Fermi energy is a key for the understanding of mechanism of superconductivity. Band structure calculations for $\text{YNi}_2\text{B}_2\text{C}$ and $\text{LuNi}_2\text{B}_2\text{C}$ revealed a 3D band structure with rather complicated band components near the Fermi level. Experimentally, the de Haas van Alphen (dHvA) effect associated with the quantization of electron orbits in a magnetic field is a powerful tool for directly probing the Fermi surface of metals in the normal state. From dHvA oscillations on high-quality $\text{LuNi}_2\text{B}_2\text{C}$ single crystals in magnetic fields up to 32 T, several dHvA frequencies have been resolved in the normal state well above the upper critical field corresponding to five extremal Fermi-surface orbits, which are shown in Fig. 5. (Bergk *et al.*, 2008).

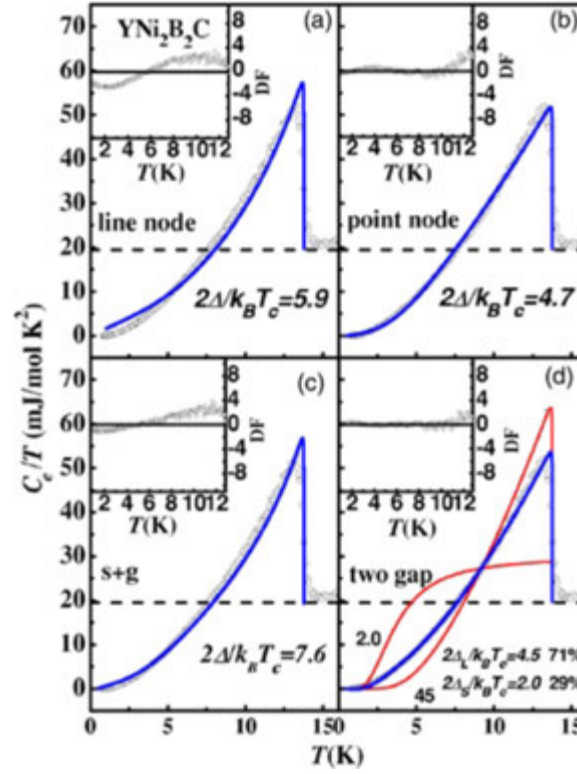


Fig. 4 Temperature-dependent electronic contribution C_e to C_p (circles) and fits (thick lines) to various models: (a) line node gap; (b) point node gap with $\Delta = \Delta_0 \sin n\theta$; (c) $(s+g)$ wave; (d) two-gap, where the thin lines show the C_e/T for the larger and the smaller gap. The respective insets show the absolute difference DF between calculation and measured data. From Huang, C.L., Lin, J.Y., Sun, C.P., *et al.*, 2006. Comparative analysis of specific heat of $\text{YNi}_2\text{B}_2\text{C}$ using nodal and two-gap models. *Phys. Rev. B* 73, 012502.

The observation of quantum oscillations in the superconducting state has been controversially discussed even more due to contradictory experimental data. The opening of a superconducting gap below H_{c2} seems to exclude the existence of quantum oscillations at first glance, because the entire Fermi surface might be disturbed by the flux line lattice. But nevertheless, dHvA oscillations have been observed in the mixed state of many type II superconductors (Harrison *et al.*, 1994 and citations within), and, in particular, in non-magnetic borocarbide superconductors (Bergk *et al.* 2008, 2012), too. Several models have been proposed to explain this behavior, but a profound theory describing quantum oscillations of elaborated Fermi surfaces down to lower fields deep inside the superconducting state is still missing.

The dHvA oscillation in the borocarbides in the mixed state are dominated by the so-called α pocket (see Fig. 5, upper panel), although the electrons of this Fermi surface sheet contribute only about 1% to the density of states. Thus, this Fermi surface plays a very minor role for the superconductivity in these compounds, which is a strong argument for a multi-band scenario.

Controversially experimental data have been reported for the α pocket in the mixed state. Both an additional damping of the dHvA signal (Goll *et al.*, 1996) and an unexpectedly small gap (Bergk *et al.*, 2012) or even an abruptly vanishing of the oscillations below B_{c2} (Ignatchik *et al.*, 2005) have been reported for the α pocket in $\text{YNi}_2\text{B}_2\text{C}$ and $\text{LuNi}_2\text{B}_2\text{C}$. Remarkably, significantly different data have been obtained with different experimental techniques, as the magnetic torque, a field-modulation or an ultrasound method, presumably because of the induced order in the flux-line lattice, when modulating the magnetic field or by applying ultrasound waves.

In order to clarify this question, quantum-oscillation data for the same $\text{YNi}_2\text{B}_2\text{C}$ single crystal were measured by the ultrasound and by the magnetic-torque method (Noessler *et al.*, 2017). By using the ultrasound method, magneto-acoustic quantum oscillations deep inside the mixed state of $\text{YNi}_2\text{B}_2\text{C}$ could be resolved. The frequency of this oscillation has been ascribed to the α pocket. Only a very weak additional damping of the dHvA data was observed below B_{c2} that was found to be consistent with the weak field inhomogeneity related to an ideal hexagonal flux-line lattice. This small damping of the dHvA signal in the mixed state was interpreted as evidence for no or a vanishingly small gap for the α pocket. In contrast, a rapidly vanishing dHvA signal was obtained below B_{c2} by the magnetic-torque method. The direct comparison between torque and ultrasound data on the same sample provides evidence that the strong damping of the torque dHvA signal below B_{c2} cannot be related to the opening of the superconducting gap of the α pocket. Instead, this effect is likely caused by a strongly distorted flux-line lattice. Whereas the persistence of the magneto-acoustic quantum oscillations down to very low fields in the mixed state points to a rearrangement of the vortices into a regular flux-line lattice under the influence of sound waves. It was argued that sound waves do not directly shake vortices as it is known from oscillating magnetic fields, but they might shake pinning centers which in return could rearrange the vortices (Noessler *et al.*, 2017).

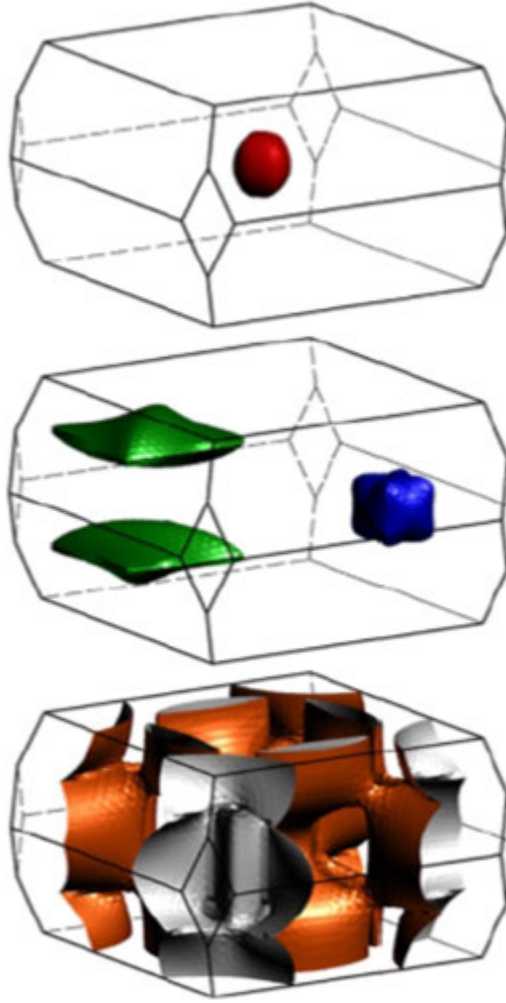


Fig. 5 Fermi surfaces (FS) in $\text{LuNi}_2\text{B}_2\text{C}$ identified from dHvA oscillations: spherical FS (upper panel), cubic and cushion-like FSs (middle panel) and branched FS (lower panel) corresponding to the dHvA frequencies F_z , F_{α} , F_{η} and F_{σ} , respectively. From Bergk, B., Petzold, V., Rosner, H., *et al.*, 2008. Anisotropic multiband many-body interactions in $\text{LuNi}_2\text{B}_2\text{C}$. *Phys. Rev. Lett.* 100, 257004.

The surprising result of an extremely small gap for the α pocket can be explained within a realistic multiband approach by a field-induced quenching of superconductivity in the α pocket well below B_{c2} . Such partial quenching of superconductivity by an external magnetic field in a multi-band superconductor was predicted for a weakly with otherwise strongly coupled bands at low temperatures (Barzykin and Gor'kov, 2007). Indeed, rather modest upper critical fields $B_{c2}^2(0)$ between 0.39 and 0.45 T were estimated for the α pocket (Noessler *et al.*, 2017) implying that superconductivity in the α pocket should be quenched at fields well below 3 T above which the dHvA oscillations could be resolved.

Upper Critical Field for Non-Magnetic Borocarbides

The upper critical field $B_{c2}(T)$ as a fundamental quantity of type-II superconductors provides insight into the coupling strength, the electronic structure, the symmetry and anisotropy of the order parameter and the presence of various disorder-related scattering processes. All these factors affect the magnitude, the shape and the anisotropy of $B_{c2}(T)$.

The reported experimental data on the upper critical field B_{c2} of $\text{YNi}_2\text{B}_2\text{C}$ and $\text{LuNi}_2\text{B}_2\text{C}$ scatter considerably due to paramagnetic signals from impurities which are difficult to avoid in the nominally non-magnetic borocarbides (Mun *et al.*, 1998). Nevertheless it has clearly been shown for both compounds that B_{c2} is anisotropic not only with respect to the tetragonal c axis and the basal plane but also within that plane (Metlushko *et al.*, 1997; Wimbush *et al.*, 2004).

The out-of-plane anisotropy can be described within the phenomenological one-band Ginzburg-Landau theory of superconductivity (Ginzburg and Landau, 1950) or its microscopic derivation from the BCS theory (Gor'kov, 1959) by an effective mass anisotropy. In the case of $\text{LuNi}_2\text{B}_2\text{C}$ the degree of the out-of-plane anisotropy of B_{c2} is nearly temperature independent and the resulting mass anisotropy, $m_c^*/m_a^* \approx 1.35$, is in good agreement with the Fermi surface anisotropy determined from band-structure calculations (Mattheiss, 1994).

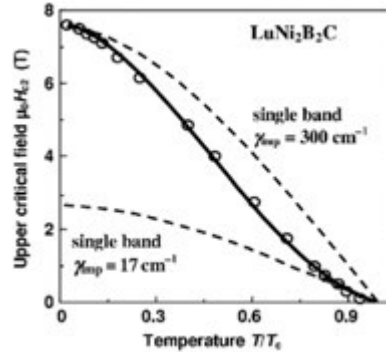


Fig. 6 $H_{c2}(T)$ of an $\text{LuNi}_2\text{B}_2\text{C}$ single crystal measured parallel to the tetragonal c -axis (●). The solid curve was calculated using a two-band model. Dashed lines: isotropic single-band model for two different scattering rates. After Shulga, S.V., Drechsler, S.L., Fuchs, G., *et al.*, 1998. Upper critical field peculiarities of superconducting $\text{YNi}_2\text{B}_2\text{C}$ and $\text{LuNi}_2\text{B}_2\text{C}$. *Phys. Rev. Lett.* 80, 1730.

The in-plane anisotropy of H_{c2} cannot be explained within the (local) GL theory, but by its non-local extension introduced by Hohenberg and Werthamer (1967). The anisotropy of the Fermi surface sheets has been assumed to cause the mentioned basal anisotropy of B_{c2} . Taking non-local corrections to H_{c2} due to the anisotropic Fermi surface into account, experimental $B_{c2}(T, \phi)$ data for $\text{LuNi}_2\text{B}_2\text{C}$ (with ϕ as the angle in the basal plane) have been described by an analytical expression (Metlushko *et al.*, 1997). In this expression, averages of the Fermi velocity are used, which can be estimated from electronic-structure calculations or taken as fitting parameters.

A special feature of the temperature dependence of B_{c2} found for the non-magnetic borocarbides $\text{YNi}_2\text{B}_2\text{C}$ and $\text{LuNi}_2\text{B}_2\text{C}$ is its positive curvature near T_c , which does not occur in the standard BCS theory. Such an upward curvature has been observed in all crystal orientations, for both, $\text{LuNi}_2\text{B}_2\text{C}$ and $\text{YNi}_2\text{B}_2\text{C}$. An example is shown in Fig. 6. It is clearly seen that the single band model cannot explain neither the large $B_{c2}(0)$ (using a reasonable impurity scattering rate of $\gamma_{\text{imp}} = 17 \text{ cm}^{-1}$) nor the positive curvature of $B_{c2}(T)$ near T_c . The anomalous S-like shape of $B_{c2}(T)$, as compared with the standard parabolic-like Werthamer-Helfand-Hohenberg (WHH) behavior, has been analyzed by Shulga *et al.* (1998) within the microscopic Eliashberg theory of superconductivity. In order to reproduce the experimental $B_{c2}(T)$ data, they considered two bands with different Fermi velocities, where one of the two Fermi velocities, v_{F1} , is considerably smaller than the Fermi-surface average of v_F . These slow electrons have a strong electron-phonon coupling and are mainly responsible for the superconductivity. It is noteworthy that the slow electrons in $\text{LuNi}_2\text{B}_2\text{C}$ and $\text{YNi}_2\text{B}_2\text{C}$ stem from nested regions on the Fermi surface, whereas in the non-superconducting compound $\text{LaNi}_2\text{B}_2\text{C}$ there is no nesting and, consequently, a smaller dispersion of v_F (Rosner *et al.*, 2001).

The two-band description of B_{c2} has been confirmed by subsequent theoretical studies (Drechsler *et al.*, 2001; Nicol and Carbotte, 2005) that are also extended on further thermodynamic properties. A similar approach using an anisotropic electron-phonon interaction spectral function (Manalo and Schachinger, 2001) also leads to good agreement with the experimental data.

In the example of Fig. 6, the experimental $B_{c2}(T)$ curve can be well reproduced by taking the velocity ratio $v_{F2}/v_{F1} \approx 4.5$ and adjusting the other input parameters of the two-band model to experimental data from the literature. Within the two-band model, both, the value $H_{c2}(0)$ and the degree of positive curvature, can be considerably varied by changing the scattering rate γ_{imp} (Shulga and Drechsler, 2001; Gurevich, 2003). As expected, in the clean limit, B_{c2} decreases with increasing interband scattering γ_{imp} . This prediction has been experimentally confirmed for pseudoquaternary $(\text{Lu}, \text{Y})\text{Ni}_2\text{B}_2\text{C}$ compounds where an increase of substitutional disorder results in a decrease of $B_{c2}(T)$ (Fuchs *et al.*, 2001).

Interplay Between Superconductivity and Magnetism in $\text{HoNi}_2\text{B}_2\text{C}$

$\text{HoNi}_2\text{B}_2\text{C}$ is one of the most interesting compounds among the borocarbide superconductors. As can be seen in Fig. 7(a), resistivity-vs.-temperature curves show a sharp transition into the superconducting state at $T_c \approx 8 \text{ K}$ in zero-magnetic field. Near-reentrant superconductivity is observed at small fields. Fig. 7(a) also shows that the temperature range near T_N where the reentrant behavior occurs does not much depend on the magnetic field indicating a magnetic phase transition at T_N . This is supported also by measurements of the specific heat C_p (see Fig. 7(b)) that shows a peak near T_N . Interestingly, two further features can be seen in Fig. 7(b) at T^* and T_M , indicating two other magnetic-ordering phenomena. On the other hand, no anomaly of C_p at T_c can be seen in Fig. 7(b). This has been attributed to the fact that the high-temperature tails of the C_p anomalies at T_N , T^* , and T_M are still higher at T_c than the expected jump in C_p associated with the superconducting transition (Canfield *et al.*, 1994).

Antiferromagnetic Order in $\text{HoNi}_2\text{B}_2\text{C}$

Three different types of antiferromagnetic order occur in $\text{HoNi}_2\text{B}_2\text{C}$ at zero magnetic field (Grigereit *et al.*, 1994; Goldman *et al.*, 1994) as was shown by elastic neutron diffraction. Upon cooling, the commensurate antiferromagnetic structure of Fig. 8(a) forms

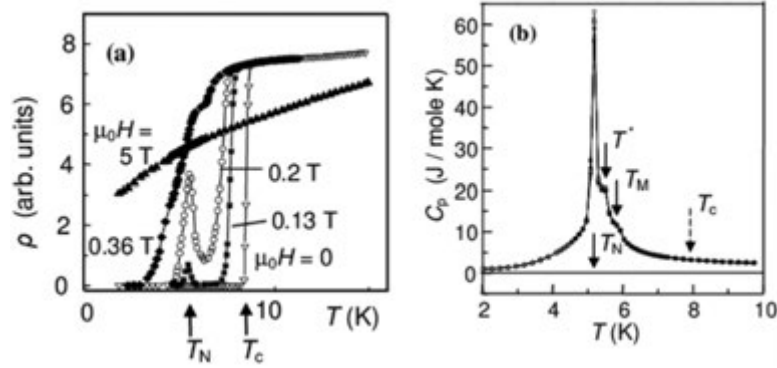


Fig. 7 (a) Resistivity vs. temperature measured at different magnetic fields H on a polycrystalline $\text{HoNi}_2\text{B}_2\text{C}$ sample. T_c is the superconducting transition temperature at $H = 0$. A near-reentrant behavior occurs around a temperature T_N . (b) Temperature dependence of the specific heat C_p of a $\text{HoNi}_2\text{B}_2\text{C}$ single crystal measured at zero magnetic field. Above the main peak of $C_p(T)$ at T_N , two additional features appear at T^* and T_M . No jump in C_p can be seen at T_c . From Müller, K.H., Schneider, M., Fuchs, G., Drechsler, S.L., 2008. Rare-earth nickel borocarbides. In: Gscheidner Jr., K.A., Bünzli, J.-C.G., Pecharsky, V.K. (Eds.), Handbook of the Physics and Chemistry of rare earths, vol. 38. Amsterdam: Elsevier, p. 175. Fig. 38.

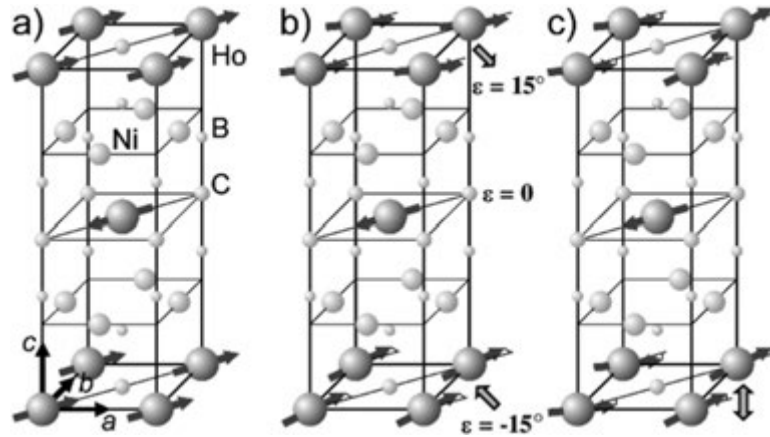


Fig. 8 Magnetic structures of $\text{HoNi}_2\text{B}_2\text{C}$ as determined by neutron scattering. (a) Commensurate antiferromagnetic. (b) Incommensurate c^* structure (spiral) with the modulation vector $\tau_2 = (0,0,0.916)$. (c) Proposed incommensurate a^* structure (after Kreyssig, A., Schneidewind, A., Loewenhaupt, M., et al., 2001. Magnetoelastic effects in rare earth nickel borocarbides. In: Müller, K.H., Narozhnyi, V.N. (Eds.), Rare Earth Transition Metal Borocarbides (Nitrides): Superconducting, Magnetic and Normal State Properties. Kluwer Academic Publishers, p. 181) with the modulation vector $\tau_3 = (0.585,0,0)$. From Müller, K.H., Schneider, M., Fuchs, G., Drechsler, S.L., 2008. Rare-earth nickel borocarbides. In: Gscheidner Jr., K.A., Bünzli, J.-C.G., Pecharsky, V.K. (Eds.), Handbook of the Physics and Chemistry of rare earths, vol. 38. Amsterdam: Elsevier, p. 175.

at $T_N \approx 5.2\text{K}$ consisting of ferromagnetic sheets in the tetragonal basal plane. Additionally, in the temperature range $T_N < T < T_c$ there is an incommensurate spiral structure along the tetragonal c axis, where the magnetic moments are ferromagnetically aligned in the a - b -plane as in the ground state. The ferromagnetic sheets in adjacent layers have a relative orientation of about 163.4° instead of 180° for the ground state (see Fig. 8(b) and (a)). Furthermore, in a small temperature range above T_N an a -axis modulated incommensurate magnetization structure occurs with a modulation vector $\tau_3 \approx (0.58,0,0)$ which is close to the nesting vector $q \approx (0.55,0,0)$ known from other borocarbide superconductors, in particular $\text{LuNi}_2\text{B}_2\text{C}$ and $\text{YNi}_2\text{B}_2\text{C}$ (see Section "Fermi Surface in Non-Magnetic Borocarbides in the Normal and Superconducting State"). The exact form of this a^* structure is still unknown. From results of neutron diffraction experiments on powder samples Kreyssig *et al.* (2001) concluded that the a^* structure has an oscillating component of magnetic moments in the a - b -plane as outlined in Fig. 8(c). Also a study by Detlefs *et al.* (2000) of metamagnetic phases suggests that the a^* structure has only magnetic moments perpendicular to the c axis.

For magnetic fields H applied perpendicular to the tetragonal c axis of $\text{HoNi}_2\text{B}_2\text{C}$ single crystals, measurements of magnetization and elastic neutron diffraction show up to three metamagnetic transitions (see Fig. 9; Canfield *et al.*, 1997). It was concluded that in a strength-of-field vs. angle-of-field phase diagram, besides the paramagnetic phase at elevated temperatures and the simple antiferromagnetic phase ($\uparrow\downarrow$) at low temperatures and low fields, two additional metamagnetic phases occur for sufficiently high fields which are denoted in Fig. 10 (left panel) by the arrow combinations $\uparrow\uparrow\downarrow$ and $\uparrow\uparrow\rightarrow$. Here it is assumed that in all of the magnetically ordered phases the local magnetic moments are directed along those $[110]$ axes that are either near parallel (arrow $\uparrow$) or near antiparallel ($\downarrow$) or near perpendicular ($\rightarrow$) to the applied field.

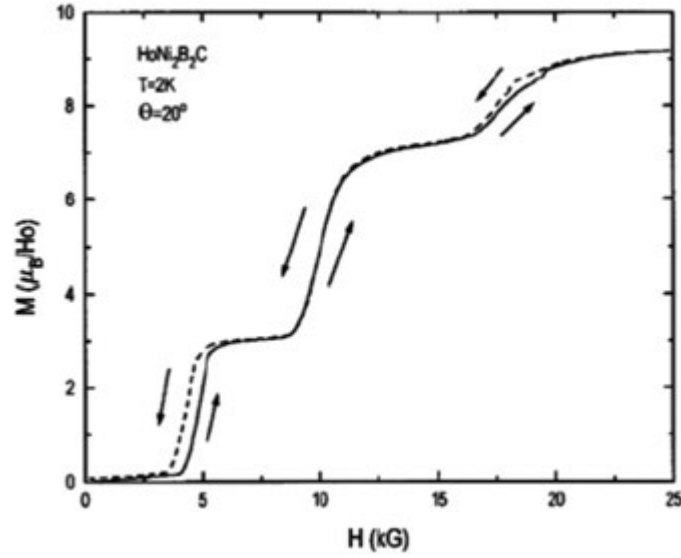


Fig. 9 Magnetization vs. applied field at $T = 2\text{K}$ for $H \perp c$ with the angle $\theta = 20^\circ$ between applied field and $[110]$ axis. Three metamagnetic transitions are observed: (1) from the simple antiferromagnetic structure $\uparrow\downarrow$ to a first metamagnetic phase $\uparrow\uparrow\downarrow$, (2) to a second metamagnetic phase $\uparrow\uparrow\rightarrow$ and (3) to the paramagnetic structure $\uparrow\uparrow$. From Canfield, P.C., Bud'ko, S.L., Cho, B.K., *et al.*, 1997. Angular dependence of metamagnetic transitions in $\text{HoNi}_2\text{B}_2\text{C}$. Phys. Rev. B 55, 970.

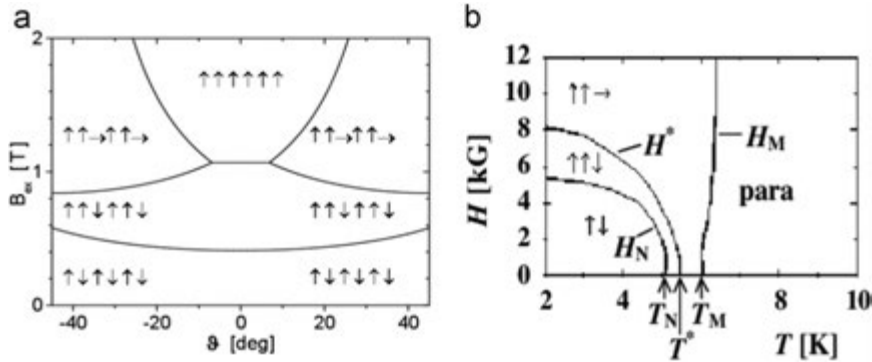


Fig. 10 Magnetic phase diagrams of $\text{HoNi}_2\text{B}_2\text{C}$. (a - left panel) H - θ phase diagram at $T = 2\text{K}$, where H is perpendicular to the c axis and has an angle θ with respect to the nearest magnetically easy $[110]$ direction. $\uparrow\downarrow$ is the antiferromagnetic phase shown in Fig. 8 (a); the metamagnetic phases $\uparrow\uparrow\downarrow$, $\uparrow\uparrow\rightarrow$ and $\uparrow\uparrow$ are described in the text (after Canfield, P.C., Bud'ko, S.L., Cho, B.K., *et al.*, 1997. Angular dependence of metamagnetic transitions in $\text{HoNi}_2\text{B}_2\text{C}$. Phys. Rev. B 55, 970). (b - right panel) Field H applied along the tetragonal a axis (i.e., $\theta = \pm 45^\circ$). Here para means the paramagnetic phase steadily changing, with increasing H , into the saturated (ferromagnetic) state $\uparrow\uparrow$ which, at low temperatures, is a metamagnetic phase. After Detlefs, C., Bourdarot, F., Burlet, P., *et al.*, 2000. Ordering wave vectors of metamagnetic states in $\text{HoNi}_2\text{B}_2\text{C}$: One dimension is not enough. Phys. Rev. B 61, R14916.

Detlefs *et al.* (2000 and, 2001) found by elastic neutron diffraction at 2K that the second metamagnetic phase ($\uparrow\uparrow\rightarrow$) has a modulation vector $\tau_3 \approx (4/7, 0, 0)$ which is close to the nesting vector $q \approx (0.55, 0, 0)$. The presence of an a^* -metamagnetic phase at 2K is supported by results of Kreyssig *et al.* (1999) who performed elastic neutron-diffraction experiments on $\text{HoNi}_2\text{B}_2\text{C}$ powders and also detected different metamagnetic phases.

The extension of the boundaries between the metamagnetic phases to the zero-field boundaries at T_N , T^* and T_M , as shown in Fig. 10 (right panel), has also been supported by specific-heat measurements by Choi *et al.* (2001) and Park *et al.* (2004). The transition at T_N is of first order. The magnetic phase transition at T^* is described as a change from an a^* -dominant phase to a c^* -dominant phase, and it cannot be excluded that it is also of first order (Park *et al.*, 2004). A first-order transition at T^* would explain the fact that both phases, a^* and c^* coexist above as well as below T^* , as has been confirmed by elastic neutron diffraction experiments on a $\text{HoNi}_2\text{B}_2\text{C}$ single crystal.

Two microscopic approaches have been presented in literature, which, until recently, had been believed to reasonably describe the magnetic phase diagram of Fig. 10(b).

Amici and Thalmeier (1998) used a quasi-one-dimensional model assuming ferromagnetically ordered Ho layers with the magnetic moments oriented perpendicular to the tetragonal c axis. The competition of the RKKY interaction along the c axis with

the crystalline electric field is analyzed in order to determine the transition between the commensurate antiferromagnetic structure and the incommensurate c^* spiral shown in Fig. 8.

The so-called clock model of Kalatsky and Pokrovsky (1998) is also a semiclassical approximation which starts with the assumption that the strong single-ion anisotropy confines the Ho magnetic moments to the four [110] directions. Both models predict the phase boundaries of Fig. 10(b) and the temperature dependence of the c -axis commensurate-to-incommensurate transition surprisingly well. However both models cannot explain the nature and origin of the a^* phase observed at zero field or at a finite field as reported by Detlefs *et al.* (2000). Possibly these problems can only be solved by a more detailed description of the RKKY interaction, taking into account the Fermi-surface-nesting features.

The field-induced first-order metamagnetic transition from the antiferromagnetic to a ferromagnetic state observed at low temperature (see Fig. 10(a)) was found to be accompanied by a giant magnetocaloric effect (MCE) (El Massalami *et al.*, 2004). For a magnetic field change of 5 T, a maximum adiabatic temperature change of $\Delta T_{\max} \sim 11$ K has been found for $\text{HoNi}_2\text{B}_2\text{C}$. A MCE has been reported for other antiferromagnetic borocarbide superconductors as $\text{DyNi}_2\text{B}_2\text{C}$ and $\text{ErNi}_2\text{B}_2\text{C}$, too (Li *et al.*, 2011). The corresponding values of the maximum adiabatic temperature change at a field change of 5 T are $\Delta T_{\max} \sim 9.7$ and 4.6 K for $R = \text{Dy}$ and Er , respectively. Remarkably, an inverse MCE, i.e., a negative temperature change ΔT due to a change of the applied magnetic field, was observed under low magnetic field ($\Delta B = 2$ T) and at low temperature for $R = \text{Ho}$, Dy and Er (Li *et al.*, 2011). Generally, this occurs in antiferromagnetic materials, in which the applied magnetic field enhances the magnetic entropy.

Reentrant and Near-Reentrant Behavior

It is generally accepted that single-phase stoichiometric $\text{HoNi}_2\text{B}_2\text{C}$ exhibits the near-reentrant behavior presented in Fig. 7(a). It is obvious that the commensurate antiferromagnetic structure of Fig. 8(a) coexists with superconductivity in $\text{HoNi}_2\text{B}_2\text{C}$. On the other hand, as can be seen in Fig. 11(a) and (c) the superconductivity is suppressed over the small temperature range where the two incommensurate magnetic structures of Fig. 8(b) and (c) occur. However, in $\text{Y}_{0.15}\text{Ho}_{0.85}\text{Ni}_2\text{B}_2\text{C}$ the situation is quite different, as shown in Fig. 11(b) and (d). Here the a^* structure again is localized at the same temperatures as the reentrant behavior but the c^* spiral exists over a broad range of temperature. Thus, the a^* structure is more closely related to the near-reentrant superconductivity in $\text{Y}_{0.15}\text{Ho}_{0.85}\text{Ni}_2\text{B}_2\text{C}$ (as well as in $\text{Lu}_{0.15}\text{Ho}_{0.85}\text{Ni}_2\text{B}_2\text{C}$, Freudenberg *et al.* (1998)) than the c^* spiral.

NiIt was theoretically shown by Machida *et al.* (1980) that if antiferromagnetic ordering is connected with Fermi surface nesting the superconducting state may be heavily disturbed. For $\text{HoNi}_2\text{B}_2\text{C}$ the strong correlation between the near-reentrant behavior and the a^* magnetic ordering has first been emphasized by Müller *et al.* (1997) and has been confirmed also by Canfield and Bud'ko (2001). The conclusion that the a^* structure is more relevant for the near-reentrant behavior in $\text{HoNi}_2\text{B}_2\text{C}$ has been further confirmed by data for $\text{Y}_{0.15}\text{Ho}_{0.85}\text{Ni}_2\text{B}_2\text{C}$.

However, Dertinger *et al.* (2001) found that the a -axis modulated structure a^* of Fig. 8 is much more sensitive to pressure, compared to the other two magnetic structures of Fig. 7, and it even disappears at relatively low values of pressure. Interestingly he observed near-reentrant behavior also at temperatures and pressures where the a^* structure had disappeared. Therefore he

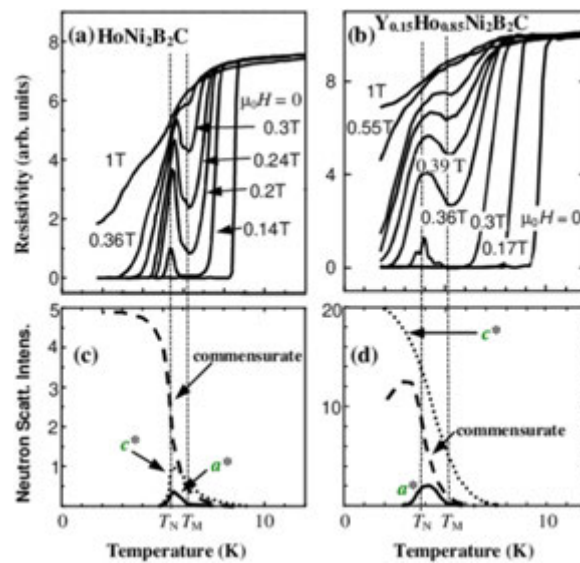


Fig. 11 (a) and (b): Resistivity vs. temperature curves for polycrystalline $\text{HoNi}_2\text{B}_2\text{C}$ and $\text{Y}_{0.15}\text{Ho}_{0.85}\text{Ni}_2\text{B}_2\text{C}$ samples, respectively, showing reentrant behavior in small magnetic fields. (c) and (d): The comparison with the neutron diffraction peak intensities shows that the a^* structure is strongly related to the reentrant behavior. T_N and T_M have been determined from the minima and the maxima, respectively, in (a) and (b); these values largely agree with T_N and T_M determined from specific heat data. From Müller, K.H., Schneider, M., Fuchs, G., Drechsler, S.L., 2008. Rare-earth nickel borocarbides. In: Gscheidner Jr., K.A., Bünzli, J.-C.G., Pecharsky, V.K. (Eds.), Handbook of the Physics and Chemistry of rare earths, vol. 38. Amsterdam: Elsevier, p. 175.

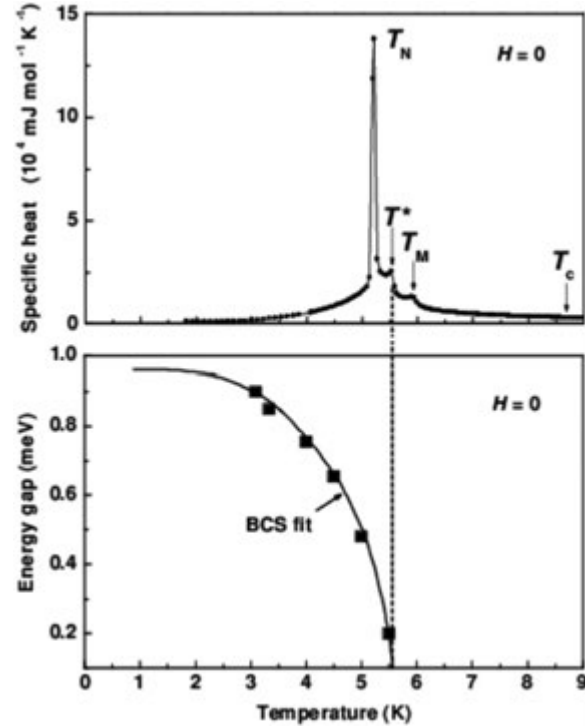


Fig. 12 High-quality $\text{HoNi}_2\text{B}_2\text{C}$ single crystal at zero magnetic field. Upper panel: specific heat with special features at temperatures T_N , T^* and T_M (as in Fig. 7(b)); Lower panel: energy gap determined by point-contact spectroscopy and fitted to the BCS gap formula. After Müller, K.H., Fuchs, G., Drechsler, S.L., *et al.*, 2007. Multiband superconductivity in $\text{HoNi}_2\text{B}_2\text{C}$. *Physica C* 460-462, 99.

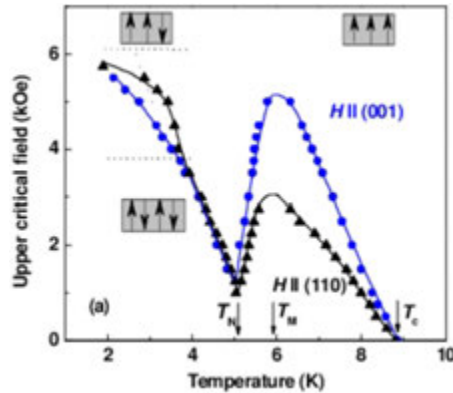


Fig. 13 Temperature dependence of the upper critical field H_{c2} of a well-annealed $\text{HoNi}_2\text{B}_2\text{C}$ single crystal measured in the [110] and [001] directions. $H_{c2}(T)$ shows a significant anisotropy above T_N and a near-reentrant behavior, i.e., $H_{c2}(T)$ has a pronounced minimum near T_N but it never disappears. The arrow combinations $\uparrow\uparrow\downarrow$, $\downarrow\downarrow\uparrow$, $\uparrow\uparrow$ correspond to a metamagnetic, the antiferromagnetic and the paramagnetic phase, respectively. After Müller, K.H., Fuchs, G., Drechsler, S.L., *et al.*, 2007. Multiband superconductivity in $\text{HoNi}_2\text{B}_2\text{C}$. *Physica C* 460-462, 99.

concluded that the near-reentrant behavior in $\text{HoNi}_2\text{B}_2\text{C}$ cannot mainly be caused by the presence of the a^* incommensurate magnetic structure. Thus further experiments have to be done to elucidate the connection between (near-) reentrant behavior and the various magnetic structures in $\text{HoNi}_2\text{B}_2\text{C}$.

Multiband Coexistence of Superconductivity and Magnetism in $\text{HoNi}_2\text{B}_2\text{C}$

As has been shown in Section “Fermi Surface in Non-Magnetic Borocarbides in the Normal and Superconducting State”, the superconducting properties of the non-magnetic borocarbides $\text{YNi}_2\text{B}_2\text{C}$ and $\text{LuNi}_2\text{B}_2\text{C}$, and in particular the behavior of the upper critical field H_{c2} , can only be understood by taking into account at least two electron bands of the Fermi surface. Thus, an

interesting question is whether such multiband concept is needed also in the case of the local-moment antiferromagnetic superconductor $\text{HoNi}_2\text{B}_2\text{C}$ and how it explains the interplay of magnetism and superconductivity in this compound (Müller *et al.*, 2007). As can be seen in Fig. 6, the transition temperature of a well prepared $\text{HoNi}_2\text{B}_2\text{C}$ single crystal has been found to be as high as $T_c = 8.8\text{K}$. However, the energy gap determined by point-contact spectroscopy can be well fitted to a BCS gap function vanishing at $T = T^* \approx 5.6\text{K}$ as shown in Fig. 12 (Naidyuk *et al.*, 2007) where the specific heat has a special feature that has been attributed to a change, with increasing temperature, from a c^* dominated to an a^* dominant magnetic phase (Park *et al.* 2004). Although the magnitude and the temperature dependence of the (small) superconducting gap in the range $T^* \leq T \leq T_c$ is not yet well investigated, gapless superconductivity (as proposed by Rybaltchenko *et al.* (1999)) cannot be excluded. The BCS-like gap (see Fig. 12) together with the isotropic $B_{c2}(T)$ observed below T_N (see Fig. 13) strongly suggests that superconductivity in the low-temperature antiferromagnetic phase survives at a pillow-like Fermi surface sheet (Drechsler *et al.*, 2004) which is isolated from the influence of the lanthanide magnetism localized at other FSSs.

A remarkable anisotropy in $B_{c2}(T)$ can be seen in Fig. 13 for a well-annealed single crystal at temperatures above T_N and even in the paramagnetic region above T_M . From a comparison of this phenomenon with the much weaker and opposite anisotropy of $B_{c2}(T)$ in $\text{YNi}_2\text{B}_2\text{C}$ (see Section "Fermi Surface in Non-Magnetic Borocarbides in the Normal and Superconducting State") it can be concluded that $B_{c2}(T)$ is smaller for H parallel to $[110]$ (compared to $[001]$; see Fig. 13) because, due to crystalline electric fields, the magnetic fluctuations have larger components in the tetragonal basal plane. Further contributions to the anisotropy of $B_{c2}(T)$ may come from anisotropic Fermi surface sheet possibly contributing to the small- (or even zero-) gap superconductivity in $\text{HoNi}_2\text{B}_2\text{C}$ at temperatures above T^* as discussed above.

To summarize, it can be concluded that a multiband scenario is indispensable for understanding the rich variety of superconducting and magnetic properties in $\text{HoNi}_2\text{B}_2\text{C}$. Many of these phenomena, in particular those occurring at temperatures between T_N and T_M , are not yet well understood.

References

- Amici, A., Thalmeier, P., 1998. Microscopic theory of magnetic phase transitions in $\text{HoNi}_2\text{B}_2\text{C}$. *Phys. Rev. B* 57, 10684.
- Baba, T., Yokoya, T., Tsuda, S., *et al.*, 2006. Laser-excited ultrahigh-resolution photoemission spectroscopy of borocarbide superconductor $\text{RNi}_2\text{B}_2\text{C}$ ($R = \text{Y}$ and Er). *Physica C* 445–448, 46.
- Barzykin, V., Gor'kov, L.P., 2007. Gapless Fermi surfaces of anisotropic multiband superconductors in a magnetic field. *Phys. Rev. Lett.* 98, 087004.
- Bashlakov, D.L., Naidyuk, Yu.G., Yanson, I.K., *et al.*, 2005. Distribution of the superconducting gap in an $\text{YNi}_2\text{B}_2\text{C}$ film studied by point contact spectroscopy. *Supercond. Sci. Technol.* 18, 1094.
- Bashlakov, D.L., Naidyuk, Yu.G., Yanson, I.K., *et al.*, 2007. Point-contact spectroscopy of the borocarbide superconductor $\text{YNi}_2\text{B}_2\text{C}$ in the normal and superconducting state. *J. Low Temp. Phys.* 147, 335.
- Bergk, B., Petzold, V., Rosner, H., *et al.*, 2008. Anisotropic multiband many-body interactions in $\text{LuNi}_2\text{B}_2\text{C}$. *Phys. Rev. Lett.* 100, 257004.
- Bergk, B., Drechsler, S.L., Canfield, P.C., Wosnitza, J., 2012. Detailed study of the de Haas-van Alphen effect in the Shubnikov state of $\text{LuNi}_2\text{B}_2\text{C}$. *Eur. Phys. J. B* 85, 57.
- Brandow, B.H., 2003. Strongly anisotropic s-wave gaps in exotic superconductors. *Philos. Mag.* 83, 2487.
- Canfield, P.C., Bud'ko, S.L., 2001. Effects of local moment magnetism on the superconducting properties of $\text{RNi}_2\text{B}_2\text{C}$ compounds. In: Müller, K.-H., Narozhnyi, V.N. (Eds.), *Rare Earth Transition Metal Borocarbides (Nitrides): Superconducting, Magnetic and Normal State Properties*. Dordrecht: Kluwer Academic Publishers, p. 33.
- Canfield, P.C., Bud'ko, S.L., Cho, B.K., *et al.*, 1997. Angular dependence of metamagnetic transitions in $\text{HoNi}_2\text{B}_2\text{C}$. *Phys. Rev. B* 55, 970.
- Canfield, P.C., Cho, B.K., Johnston, D.C., Finnemore, D.K., Hundley, M.F., 1994. Specific-heat and anisotropic superconducting and normal-state magnetization of $\text{HoNi}_2\text{B}_2\text{C}$. *Physica C* 230, 397.
- Cava, R.J., Takagi, H., Batlogg, B., *et al.*, 1994. Superconductivity at 23K in yttrium palladium boride carbide. *Nature* 367, 146.
- Choi, J.-H., Doh, H., Choi, E.-M., *et al.*, 2001. Specific heat of field-dependent magnetic orderings in $\text{HoNi}_2\text{B}_2\text{C}$. *J. Phys. Soc. Jpn.* 70, 3037.
- Dertinger, A., Dinnebier, R.E., Kreyssig, A., *et al.*, 2001. Microscopic changes in $\text{HoNi}_2\text{B}_2\text{C}$ due to thermal treatment and its effect on superconductivity. *Phys. Rev. B* 63, 184518.
- Detlefs, C., Bourdarot, F., Burlet, P., *et al.*, 2000. Ordering wave vectors of metamagnetic states in $\text{HoNi}_2\text{B}_2\text{C}$: One dimension is not enough. *Phys. Rev. B* 61, R14916.
- Detlefs, C., Bourdarot, F., Burlet, P., Bud'ko, S.L., Canfield, P.C., 2001. Magnetic structures of $\text{HoNi}_2\text{B}_2\text{C}$. In: Müller, K.-H., Narozhnyi, V.N. (Eds.), *Rare Earth Transition Metal Borocarbides (Nitrides): Superconducting, Magnetic and Normal State Properties*. Dordrecht: Kluwer Academic Publishers, p. 155.
- Drechsler, S.-L., Rosner, H., Shulga, S.V., Eschrig, H., 2001. Superconducting transition metal borocarbide. In: Drechsler, S.-L., Mishonov, T. (Eds.), *High- T_c Superconductors and Related Materials*. Dordrecht: Kluwer Academic Publishers, p. 167.
- Drechsler, S.-L., Rosner, H., Opahle, I., Shulga, S.V., Eschrig, H., 2004. Non-magnetic superconducting $\text{R}(\text{Ni,Pt})_2\text{B}_2\text{C}$ compounds ($R = \text{Y}, \text{Lu}$) in the clean and dirty limit. *Physica C* 408–410, 107.
- El Massalami, M., Takeya, H., Chaves, C.M., 2004. Isofield low-temperature specific heat of single-crystal $\text{Ho}_{1-x}\text{Y}_x\text{Ni}_2\text{B}_2\text{C}$ ($x = 0, 0.25, 0.5, 1$): Probing the magnetocaloric effect in $\text{HoNi}_2\text{B}_2\text{C}$. *Phys. Rev. B* 70, 014429.
- Freudenberger, J., Fuchs, G., Nenkov, K., *et al.*, 1998. Breakdown of de Gennes scaling in $\text{Ho}_x\text{Lu}_{1-x}\text{Ni}_2\text{B}_2\text{C}$. *J. Magn. Magn. Mater.* 187, 309.
- Fuchs, G., Müller, K.-H., Freudenberger, J., *et al.*, 2001. Influence of disorder on superconductivity in rare-earth nickel borocarbides. In: Müller, K.-H., Narozhnyi, V.N. (Eds.), *Rare Earth Transition Metal Borocarbides (Nitrides): Superconducting, Magnetic and Normal State Properties*. Dordrecht: Kluwer Academic Publishers, p. 243.
- Ginzburg, V.L., Landau, L.D., 1950. To the theory of superconductivity. *Zh. Eksp. Teor. Fiz* 20, 1064.
- Goldman, A.I., Stassis, C., Canfield, P.C., *et al.*, 1994. Magnetic pair breaking in $\text{HoNi}_2\text{B}_2\text{C}$. *Phys. Rev. B* 50, 9668.
- Goll, G., Heinecke, M., Jansen, A.G.M., *et al.*, 1996. De Haas-van Alphen study in the superconducting state of $\text{YNi}_2\text{B}_2\text{C}$. *Phys. Rev. B* 53, R8871.
- Gor'kov, L.P., 1959. Microscopic derivation of the Ginzburg-Landau equations in the theory of superconductivity. *Zh. Eksp. Teor. Fiz* 36, 1918.
- Grigereit, T.E., Lynn, J.W., Huang, Q., *et al.*, 1994. Observation of oscillatory magnetic order in the antiferromagnetic superconductor $\text{HoNi}_2\text{B}_2\text{C}$. *Phys. Rev. Lett.* 73, 2756.
- Gurevich, A., 2003. Enhancement of the upper critical field by nonmagnetic impurities in dirty two-gap superconductors. *Phys. Rev. B* 67, 184515.
- Harrison, N., Hayden, S.M., Meeson, P., *et al.*, 1994. De Haas-van Alphen effect in the vortex state of Nb_3Sn . *Phys. Rev. B* 50, 4208.
- Hohenberg, P.C., Werthamer, N.R., 1967. Anisotropy and temperature dependence of the upper critical field of type-II superconductors. *Phys. Rev.* 153, 493.
- Huang, C.L., Lin, J.-Y., Sun, C.P., *et al.*, 2006. Comparative analysis of specific heat of $\text{YNi}_2\text{B}_2\text{C}$ using nodal and two-gap models. *Phys. Rev. B* 73, 012502.
- Ignatchik, O., Coffey, T., Hagel, J., *et al.*, 2005. Magnetic quantum oscillations in the normal state of $\text{YNi}_2\text{B}_2\text{C}$. *J. Magn. Magn. Mater.* 290–291, 424.

- Kreyssig, A., Schneidewind, A., Loewenhaupt, M., *et al.*, 2001. Magnetoelastic effects in rare earth nickel borocarbides. In: Müller, K.-H., Narozhnyi, V.N. (Eds.), *Rare Earth Transition Metal Borocarbides (Nitrides): Superconducting, Magnetic and Normal State Properties*. Kluwer Academic Publishers, p. 181.
- Kalatsky, V.A., Pokrovsky, V.L., 1998. Microscopic model for the magnetic subsystem in $\text{HoNi}_2\text{B}_2\text{C}$. *Phys. Rev. B* 57, 5485.
- Kreyssig, A., Freudenberger, J., Sierks, C., *et al.*, 1999. Field and temperature dependence of magnetic order in $\text{HoNi}_2^{11}\text{B}_2\text{C}$. *Physica B* 259–261, 590.
- Lee, H.C., Choi, H.-Y., 2002. Electronic Raman scattering of (s + g)-wave superconductors: Implications for borocarbide superconductors. *Phys. Rev. B* 65, 174530.
- Li, L., Nishimura, K., Kadonaga, M., Qian, Z., Huo, D., 2011. Giant magnetocaloric effect in antiferromagnetic borocarbide superconductor $\text{RNi}_2\text{B}_2\text{C}$ (R = Dy, Ho, and Er) compounds. *J. Appl. Phys.* 110, 043912.
- Machida, K., Nokura, K., Matsubara, T., 1980. Theory of antiferromagnetic superconductors. *Phys. Rev. B* 22, 2307.
- Maki, K., Thalmeier, P., Won, H., 2002. Anisotropic s-wave superconductivity in borocarbides $\text{LuNi}_2\text{B}_2\text{C}$ and $\text{YNi}_2\text{B}_2\text{C}$. *Phys. Rev. B* 65, 140502.
- Maki, K., Won, H., Haas, St., 2004. Quasiparticle spectrum of the hybrid (s + g)-wave superconductors $\text{YNi}_2\text{B}_2\text{C}$ and $\text{LuNi}_2\text{B}_2\text{C}$. *Phys. Rev. B* 69, 012502.
- Manalo, S., Schachinger, E., 2001. Optimal spectrum for the borocarbides $\text{YNi}_2\text{B}_2\text{C}$ and $\text{LuNi}_2\text{B}_2\text{C}$. *J. Low Temp. Phys.* 123, 149.
- Martínez-Samper, P., Suderow, H., Vieira, S., *et al.*, 2003. Phonon-mediated anisotropic superconductivity in the Y and Lu nickel borocarbides. *Phys. Rev. B* 67, 014526.
- Mattheiss, L.F., 1994. Electronic properties of superconducting $\text{LuNi}_2\text{B}_2\text{C}$ and related boride carbide phases. *Phys. Rev. B* 49, 13279.
- Metlushko, V., Welp, U., Koshchev, A., *et al.*, 1997. Anisotropic upper critical field of $\text{LuNi}_2\text{B}_2\text{C}$. *Phys. Rev. Lett.* 79, 1738.
- Miranović, P., Ichioka, M., Machida, K., Nakai, N., 2005. Theory of gap-node detection by angle-resolved specific heat measurement. *J. Phys.: Condens. Matter* 17, 7971.
- Müller, K.-H., Kreyssig, A., Handstein, A., *et al.*, 1997. Magnetic structure and superconductivity in $(\text{Ho}_x\text{Y}_{1-x})\text{Ni}_2\text{B}_2\text{C}$. *J. Appl. Phys.* 81, 4240.
- Müller, K.-H., Fuchs, G., Drechsler, S.-L., *et al.*, 2007. Multiband superconductivity in $\text{HoNi}_2\text{B}_2\text{C}$. *Physica C* 460–462, 99.
- Müller, K.-H., Fuchs, G., Drechsler, S.-L., Narozhnyi, V.N., 2002. Magnetic and superconducting properties of rare earth borocarbides of the type $\text{RNi}_2\text{B}_2\text{C}$. In: Buschow, K.H. J. (Ed.), *Handbook of Magnetic Materials* 14. Amsterdam: Elsevier, p. 199.
- Mun, M.-O., Kim, M.-S., Lee, S.-I., *et al.*, 1998. Determination of the precise upper critical field of $\text{YNi}_2\text{B}_2\text{C}$ superconductor. *Physica C* 303, 57.
- Nagarajan, R., Mazumdar, Ch., Hossain, Z., *et al.*, 1994. Bulk superconductivity at an elevated temperature ($T_c \approx 12\text{K}$) in a nickel containing alloy system Y-Ni-B-C. *Phys. Rev. Lett.* 72, 274.
- Naidyuk, Yu.G., Kvintitskaya, O.E., Yanson, I.K., *et al.*, 2007. Point-contact spectroscopy of the antiferromagnetic superconductor $\text{HoNi}_2\text{B}_2\text{C}$ in the normal and superconducting state. *Phys. Rev. B* 76, 014520.
- Nicol, E.J., Carbotte, J.P., 2005. Properties of the superconducting state in a two-band model. *Phys. Rev. B* 71, 054501.
- Noessler, J., Seerig, R., Yasin, S., *et al.*, 2017. Field-induced gapless electron pocket in the superconducting vortex phase of $\text{YNi}_2\text{B}_2\text{C}$ as probed by magneto-acoustic quantum oscillations. *Phys. Rev. B* 95, (14523/1-6).
- Nohara, M., Isshiki, M., Takagi, H., Cava, R.J., 1997. Magnetic field dependence of the low-temperature specific heat of the borocarbide superconductor $\text{LuNi}_2\text{B}_2\text{C}$. *J. Phys. Soc. Jpn.* 66, 1888.
- Park, T., Salamon, M.B., Choi, E.M., Kim, H.J., Lee, S.-I., 2004. Specific heat study of the magnetic superconductor $\text{HoNi}_2\text{B}_2\text{C}$. *Phys. Rev. B* 69, 054505.
- Rosner, H., Drechsler, S.-L., Koepfner, K., Opahle, I., Eschrig, H., 2001. Electronic structure and related properties of rare earth transition metal borocarbides – LDA bandstructure analysis. In: Müller, K.-H., Narozhnyi, V.N. (Eds.), *Rare Earth Transition Metal Borocarbides (Nitrides): Superconducting, Magnetic and Normal State Properties*. Dordrecht: Kluwer Academic Publishers, p. 71.
- Rybaltchenko, L.F., Jansen, A.G.M., Wyder, P., *et al.*, 1999. Point-contact study of the magnetic superconductor $\text{HoNi}_2\text{B}_2\text{C}$. *Physica C* 319, 189.
- Shulga, S.V., Drechsler, S.-L., 2001. Eliashberg analysis of the physical properties of borocarbides. In: Müller, K.-H., Narozhnyi, V.N. (Eds.), *Rare Earth Transition Metal Borocarbides (Nitrides): Superconducting, Magnetic and Normal State Properties*. Dordrecht: Kluwer Academic Publishers, p. 393.
- Shulga, S.V., Drechsler, S.-L., Fuchs, G., *et al.*, 1998. Upper critical field peculiarities of superconducting $\text{YNi}_2\text{B}_2\text{C}$ and $\text{LuNi}_2\text{B}_2\text{C}$. *Phys. Rev. Lett.* 80, 1730.
- Suderow, H., Rodrigo, J.G., Martínez-Samper, P., *et al.*, 2003. Scanning tunneling spectroscopy in anisotropic s-wave superconductors. *Int. J. Mod. Phys. B* 17, 3300.
- Thalmeier, P., Maki, K., 2003. Thermal conductivity in superconducting borocarbides $\text{LuNi}_2\text{B}_2\text{C}$ and $\text{YNi}_2\text{B}_2\text{C}$. *Acta Phys. Polon. B* 34, 557.
- Thalmeier, P., Zwicknagl, G., 2005. Unconventional superconductivity and magnetism in lanthanide and actinide intermetallic compounds. In: Gschneidner, K.A., Jr., Bünzli, J.-C.G., Pecharsky, V.K. (Eds.), *Handbook on the Physics and Chemistry of Rare Earths* 34. Amsterdam: Elsevier, p. 135.
- Udagawa, M., Yanase, Y., Ogata, M., 2005. Effects of Fermi surface and superconducting gap structure in field-rotational experiments: A possible explanation for the cusplike singularity in $\text{YNi}_2\text{B}_2\text{C}$. *Phys. Rev. B* 71, 024511.
- Wang, G., Maki, K., 1998. Possible d-wave superconductivity in borocarbides: Upper critical field of $\text{YNi}_2\text{B}_2\text{C}$ and $\text{LuNi}_2\text{B}_2\text{C}$. *Phys. Rev. B* 58, 6493.
- Wimbush, S.C., Schultz, L., Holzapfel, B., 2004. Angular anisotropy of the upper critical field in $\text{YNi}_2\text{B}_2\text{C}$. *Physica C* 408–410, 83.
- Yokoya, T., Kiss, T., Watanabe, T., *et al.*, 2000. Ultrahigh-resolution photoemission spectroscopy of Ni borocarbides: Direct observation of the superconducting gap and a change in gap anisotropy by impurity. *Phys. Rev. Lett.* 85, 4952.
- Yuan, Q., Thalmeier, P., 2003. BCS theory for (s + g)-wave superconductivity in borocarbides $\text{Y}(\text{Lu})\text{Ni}_2\text{B}_2\text{C}$. *Phys. Rev. B* 68, 174501.
- Yuan, Q., Chen, H.-Y., Won, H., *et al.*, 2003. Impurity effects on (s + g)-wave superconductivity in borocarbides $\text{Y}(\text{Lu})\text{Ni}_2\text{B}_2\text{C}$. *Phys. Rev. B* 68, 174510.

The RABiTS Approach for Second Generation (2G) High Temperature Superconductors

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Introduction

In this chapter, we provide an overview of the Rolling Assisted Bi-axially Textured Substrate (RABiTS™) process for fabricating long length high temperature superconducting (HTS) wire based on the (RE)Ba₂Cu₃O_{7-x} materials ((RE)BCO) where RE is a rare earth. The RABiTS process is one of three template technologies developed for the roll-to-roll manufacturing of long length Second Generation (2G) HTS wire (Sathyamurthy *et al.*, 2016). All three processes rely on deposition of a continuous coating of a single-crystal-like oxide film on a flexible metal substrate which supports the growth of a highly, bi-axially textured YBCO film. The RABiTS process relies on a thermo-mechanical process to establish a cube texture in a metal foil upon which a series of epitaxial oxide layers are deposited, while the other two technologies rely on the deposition of textured oxide layers onto an un-textured metal substrate. All three approaches have been successfully scaled to roll-to-roll processes by multiple manufacturers and can be combined with either solution or vacuum based process for the deposition processes of the YBCO layer. The general architecture of the 2G HTS wire produced by these processes, illustrated in Fig. 1, consists of a bi-axially textured template (metal substrate and oxide buffer layers, a (RE)BCO layer and a protective Ag layer). Depending on the manufacturer and specific application, this structure may be enclosed in an electroplated copper layer or laminated between metal foils (Cu, SS, etc.) which serve as an electrical and mechanical stabilizer.

Cuprate-Based High Temperature Superconductors

The discovery of the cuprate based high temperature superconductor materials in 1987 marked the beginning of a world-wide effort to develop superconducting wires that could be used in liquid nitrogen. However, the complex structure and isotropic properties of the cuprate materials requires a near single crystal-like texture for the supercurrent to pass from grain-to grain.

The (RE)BCO-based high temperature superconductors have a perovskite-type crystal structure that contains two CuO₂ layers surrounding the RE atom, along with separate CuO chains oriented along the *b*-axis as shown in Fig. 2. The supercurrent passes through the CuO₂ planes, while the CuO chains function as charge reservoirs providing carriers to the CuO₂ planes. The large anisotropy produced from this planar CuO₂ structure results in supercurrent in the *a-b* plane being much greater than along the *c*-axis (Cooper and Gray, 1994; Jia *et al.*, 2011).

The coherence length, (ξ), which defines the spatial distance over which the paired superconducting electrons interact, of the (RE)BCO materials is only 1–4 nm in the *ab*-plane and less than 1 nm along the *c*-axis (Tinkham, 1996). As a result, minor distortions of the lattice periodicity, such as high angle grain boundaries, appear as planar defects that block the supercurrent flow between grains. Fundamental studies of the grain boundary mis-orientations by Dimos, Chaudhari and Mannhart established that a grain-to-grain mis-orientation of $<4^\circ$ was necessary to achieve a critical current approaching that of single crystals (Dimos *et al.*, 1990; Hilgenkamp and Mannhart, 2002). The studies also showed that at angles $>4^\circ$ the current decreased exponentially. Thus, it was established that the fabrication of the YBCO materials into wires could not be achieved with bulk polycrystalline materials, but required fabrication of a bi-axially textured layer of the material deposited over continuous lengths.

This understanding of the fundamental properties of the (RE)BCO materials led to the search for approaches to prepare continuous, single crystal-like substrates on which the (RE)BCO materials could be grown over continuous lengths. In 1991, Iijima, at Fujikura, developed the Ion Beam Assisted Deposition (IBAD) process which relies on the bombardment of an oxide film, during its vapor phase deposition, by an off-normal ion beam to sputter away unfavorable grain orientations, resulting in the deposition of a highly oriented, bi-axially textured oxide film on an un-textured substrate (Iijima *et al.*, 1991, 1992). Initial work focused on YSZ and Gd₂Zr₂O₇ films; however, most manufactures now use MgO films in which the bi-axial texture is established rapidly within the first 10 nm (Arendt and Foltyn, 2004; Ko *et al.*, 2007; Hanyu *et al.*, 2010). This layer is then covered with a layer of LaMnO₃ or CeO₂ which functions as a chemically compatible nucleation layer for the (RE)BCO (Paranthaman *et al.*, 2003).

A second approach to fabricating a textured template is based on an Inclined Substrate Deposition process developed by Hasegawa *et al.* of Sumitomo Electric Industries in 1996 (Hasegawa *et al.*, 1996). In this process, an oxide film, such as MgO, is deposited onto an un-textured metal tape at a slightly tilted angle resulting in a textured MgO layer, upon which a CeO₂ coating is deposited (Bauer *et al.*, 1999).

The RABiTS technology (which is the focus of this chapter) was developed by Goyal *et al.* at Oak Ridge National Laboratory in 1996 (Goyal, 2007; Norton *et al.*, 1996; Specht *et al.*, 1998). The process is based on generating a $\{001\} <100>$ cube texture in a metal substrate by conventional rolling deformation and recrystallization techniques, as the metal is converted into a thin tape. Although many cubic metals or alloys can be textured, face-centered cubic (FCC) materials such as Cu and Ni are the materials of choice since the thermo-mechanical deformation generates a sharp texture in which the cube plane is oriented parallel to the tape

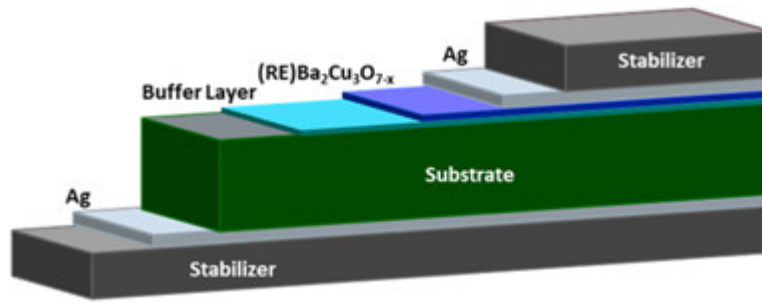


Fig. 1 General architecture of 2G HTS wire consists of the textured template (substrate and buffer layers), (RE)BCO superconducting layer, protective Ag layer and encapsulating stabilizer.

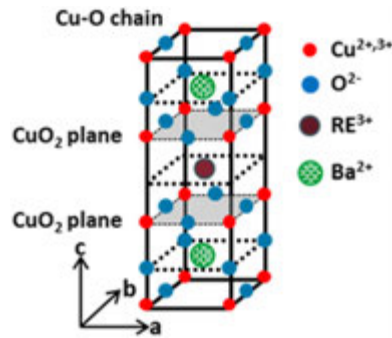


Fig. 2 Perovskite-type crystal structure of the (RE)BCO superconductor.

plane and a cube edge parallel to the rolling direction. Since the (RE)BCO is not chemically compatible with the metal substrate, it is necessary to deposit a series of epitaxial oxide layers on the substrate.

The RABiTS Template Process

In the RABiTS process, a bulk metal, usually a nickel alloy, is rolled and then annealed in an inert atmosphere to achieve a sharp cube texture with an oxide free surface that supports the growth of an epitaxial buffer layer (Goyal *et al.*, 2004, 1998). A series of oxide buffer layers are then deposited epitaxially on to the textured metal surface. The process is illustrated schematically in Fig. 3. The functions of the buffer layer are to transfer the texture of the metal substrate, prevent reaction of the metal substrate with the (RE)BCO layer and provide a surface that promotes nucleation of the (RE)BCO. The composite RABiTS structure, illustrated in Fig. 4, is generally referred to as the template for the deposition of the superconducting layer (which is generally 1–3 μm thick). The ability to produce the template in long lengths (100–1000 m) with minimal defects is an essential requirement enabling today's long length 2G wire manufacturing. The composite stack is designed to provide the degree of cube texture required for the growth of the biaxially textured YBCO while also being stable and chemically compatible with the (RE)BCO at growth conditions and amenable to formation into narrow, flexible tapes.

The RABiTS Template

The basis of the RABiTS process is the creation of a thin metallic substrate, with a sharp cube texture, that supports the growth of epitaxial oxide layers. Early R&D focused on high purity Ni substrates which can be produced with near 100% cube texture. However, pure Ni is very weak when annealed, making the high temperature roll-to-roll processing a challenge. In addition, Ni is ferromagnetic resulting in a hysteretic power loss making it less attractive for alternating current applications. Thus, research efforts rapidly focused on identifying suitable nickel alloys that would meet the following substrate requirements:

- (1) A sharp cube texture in a thin substrate with lattice parameters close to those of (RE)BCO,
- (2) Sufficient yield strength at room temperature and processing temperatures,
- (3) Oxidation resistance (no native oxide formation at conditions for buffer deposition) and
- (4) Non-magnetic.

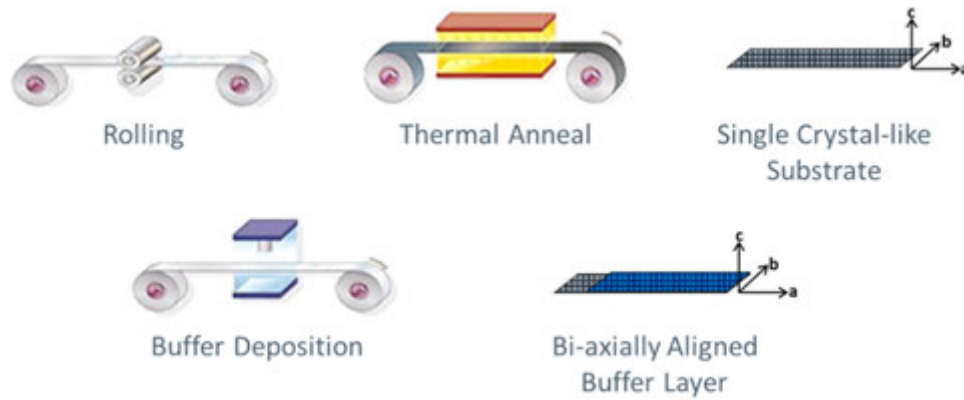


Fig. 3 Schematic illustration of the RABiTS process.

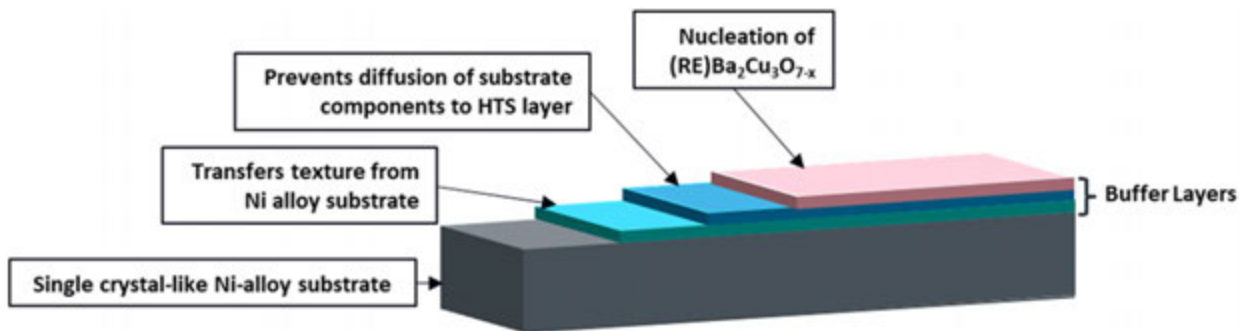


Fig. 4 Schematic cross section of an RABiTS template showing the single crystal-like metal alloy substrate and buffer layers.

The metal substrate

The choice of material for the RABiTS substrate is critical. FCC metals, such as Cu or Ni, possess a medium stacking fault energy (SFE) and form nearly single-crystal like $\{001\} \langle 100 \rangle$ foils, in which the cube axes are aligned with the principal axes of the tape, when rolled to high reductions followed by a high temperature anneal (Fig. 3). Literature on the formation of this type of texture dates to the 1920s (Goler and Sachs, 1929). Although Cu readily forms a sharp texture, it is not a useful material since it easily oxidizes under the processing conditions required for subsequent deposition of the buffer layers. Nickel is more resistant to oxidation; however, it lacks the mechanical strength required for roll-to-roll processing at elevated temperatures and, in addition, its magnetic properties produce significant ferromagnetic losses in the superconducting wire, particularly for ac applications. Thus, nickel alloys are preferred since they oxidize less easily and have higher strength at the processing temperatures.

Two Ni alloys of particular interest include NiW and NiCr (Huhne *et al.*, 2010). Both alloys form a sharp cube texture at low concentrations of W or Cr. However, even though the SFE of these alloys decreases with concentration, the ability to form a sharp cube texture deteriorates when $[W] > 5\text{--}6\text{ at\%}$ and $[Cr] > 13\text{ at\%}$ using conventional deformation and annealing processes.

Based on these requirements and suitability for supporting the epitaxial buffer growth NiW was selected as the best choice for development of the RABiTS substrate. Although the NiW alloys with a $[W] < 9.3\text{ at\%}$ are ferromagnetic, the initial work focused on a Ni-5at%W composition since it can be produced with a high cube texture using conventional rolling and annealing processes and is only weakly ferromagnetic. However, since the competing IBAD template technology is based on a non-magnetic substrate, 2G wire based on Ni-5at%W was at a competitive disadvantage in ac applications where the ferro-magnetism contributes to enhanced ac losses. As a result, Thieme at American Superconductor Corporation (AMSC) and others carried out extensive studies of the deformation mechanisms in these high concentration alloys (Sathyamurthy *et al.*, 2016). This multi-year research effort eventually led to the development of a proprietary thermo-mechanical process to that produces an excellent cube texture in the non-magnetic Ni-9at%W alloy that closely matches that in the Ni-5at%W composition.

With the optimized deformation and annealing process, a cube texture of 96%–98% is achieved over the length and width of the NiW alloy substrates with in-plane texture, $\delta\phi$, values in the range of $6.5^\circ\text{--}7^\circ$. The process is also designed to minimize the formation of other texture components, such as twins and abnormal grains, which appear as obstacles to the supercurrent flow.

An alternate approach to fabricating a textured substrate, developed by Kashima (Chubu Electric Power Co., Inc.), is based on the composite structure illustrated in Fig. 5 (Kashima *et al.*, 2012). In this approach, a non-textured metal tape, such as 316 SS or Hastelloy, is roll bonded to a thin Cu tape. The composite is then subjected to a recrystallization anneal to texture the Cu layer. A

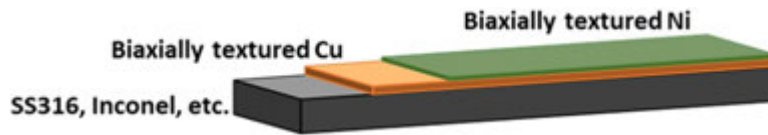


Fig. 5 Schematic illustration of a composite RABiTS substrate.

thin Ni layer is then electro-deposited onto the Cu and inherits the texture of the Cu. The Ni layer is needed to prevent the oxidation of the Cu during the buffer deposition. The advantages of the process are that the Cu forms an extremely sharp texture and that the base metal can be selected to provide the required strength for the high temperature roll-to-roll processing. Although composite is slightly magnetic due to the Ni layer, the magnetism is partially reduced during processing as Cu slowly diffuses into the Ni layer.

The buffer layers

A variety of deposition techniques have been developed for the epitaxial deposition of the buffer layers on the NiW RABiTS substrate. These include vacuum based processes such as PLD, electron beam evaporation, MOCVD, rf and reactive sputtering and non-vacuum processes such as chemical solution deposition. Among these deposition methods, chemical solution deposition may be the most cost-effective, but reactive sputtering yields the best quality film at rates amenable to large scale roll-to-roll manufacturing.

The epitaxial buffer layers play several key functions in the RABiTS template including:

- (1) *Transfer of texture from the metal substrate to the (RE)BCO layer.* In order to transfer the texture from the alloy substrate to the HTS film, the buffer layer must be able to grow epitaxially on the bare metal surface and its lattice parameters must match closely to both the substrate and the (RE)BCO film.
- (2) *A barrier to prevent metal ion diffusion from the substrate to the (RE)BCO layer during the high temperature growth.* The superconductivity of the HTS layer can be degraded by contamination with certain metal ions (i.e., little as 3% Ni substitution in the Cu site in (RE)BCO reduces the critical temperature to below 77K) (Skakle, 1998). Thus, the buffer layer must be a barrier to cation diffusion and be continuous (no cracks) and dense to provide effective chemical separation between the alloy substrate and the HTS film at the temperatures and oxygen pressures for the YBCO growth.
- (3) *A smooth, chemically inert surface for the nucleation and growth of the (RE)BCO.* The surface of the buffer must be closely lattice matched to the (RE)BCO and provide a smooth, chemically compatible surface for the YBCO nucleation.

Ideally, a single buffer layer would fulfill these requirements; however, no material has been identified that meets all the requirements and can be grown epitaxially on a Ni alloy substrate. Thus, multiple layers, each meeting at least one of the requirements, are used.

The typical buffer layer stack on the RABiTS substrate consists of three layers as shown in Fig. 4: (1) a seed layer that replicates the bi-axial texture of the substrate, (2) a barrier layer that inhibits diffusion of the substrate constituents to the (RE)BCO layer during the high temperature processing, and (3) a cap layer that is chemically compatible with the epitaxial (RE)BCO nucleation and growth. Although a variety of potential materials can be used for the buffer stack, the most common choice, and the one used by AMSC, is a three-layer stack of $\text{Y}_2\text{O}_3/\text{YSZ}/\text{CeO}_2$ deposited by reactive sputtering.

Deposition of epitaxial oxide layers on textured NiW substrates requires an understanding and control of the oxide formations during the deposition process. The deposition of the seed layer must occur on an oxide free surface, since the presence of any Ni or W oxide disrupts the epitaxial nucleation, producing a degraded or random texture which passes through to the subsequent layers. Thus, in order to nucleate the epitaxial seed layer on the NiW substrate, the deposition must occur in a pO_2 regime where the Ni and W oxides are not thermodynamically stable ($< 10^{-14}$ mTorr for W and $< 10^{-12}$ mTorr for Ni). Yttrium (along with other materials such as cerium) forms a stable, stoichiometric Y_2O_3 phase in this pO_2 regime which can be achieved with a $\text{H}_2\text{O}/\text{H}_2$ atmosphere. It should be noted that these oxides cannot be grown on NiCr alloys since Cr oxides are stable at lower oxygen pressures than Y_2O_3 .

Although Y_2O_3 can be deposited onto a clean NiW surface under these conditions, the initial nucleation frequently results in multiple in-plane c -axis orientations. The multiple in-plane orientations can be prevented by the formation of $c(2 \times 2)$ sulfur superstructure on the surface of the NiW prior to the initial Y_2O_3 nucleation. The formation of the $c(2 \times 2)$ superstructure was initially observed by Cantoni *et al.* (2001, 2003) using reflection high energy electron diffraction (RHEED) to monitor the nucleation and growth of epitaxial oxide films on textured Ni-substrates. They established that the $c(2 \times 2)$ sulfur superstructure formed prior to the nucleation of the epitaxial oxide as S impurities in the Ni diffused to the surface while heating the sample to the deposition temperature. Fig. 6 shows RHEED patterns obtained from a cube textured Ni surface with (1) no $c(2 \times 2)$ superstructure and (2) with a $c(2 \times 2)$ S superstructure. The $c(2 \times 2)$ type superstructure functions by establishing a template which promotes a single in-plane orientation during the initial nucleation. Although the initial studies were carried out on pure Ni substrates, the same mechanism occurs in NiW alloys. In manufacturing processes, the $c(2 \times 2)$ sulfur structure is typically prepared by the introduction of a S containing gas prior to the start of the oxide deposition process rather than depending on the presence of S impurities.

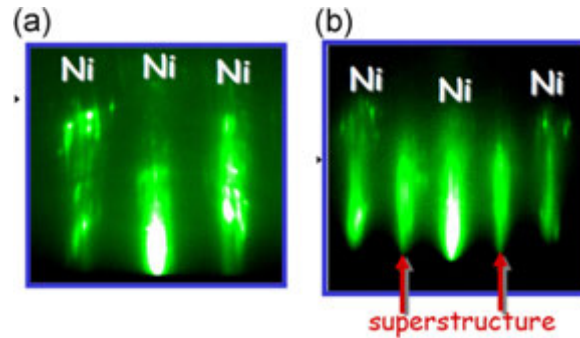


Fig. 6 RHEED patterns obtained with the incident electron beam along $\langle 100 \rangle$ for (a) clean cube textured Ni substrate surface and (b) cube textured Ni substrate surface with a $c(2 \times 2)$ S superstructure. The formation of the $c(2 \times 2)$ superstructure in (b) is indicated by the arrows.

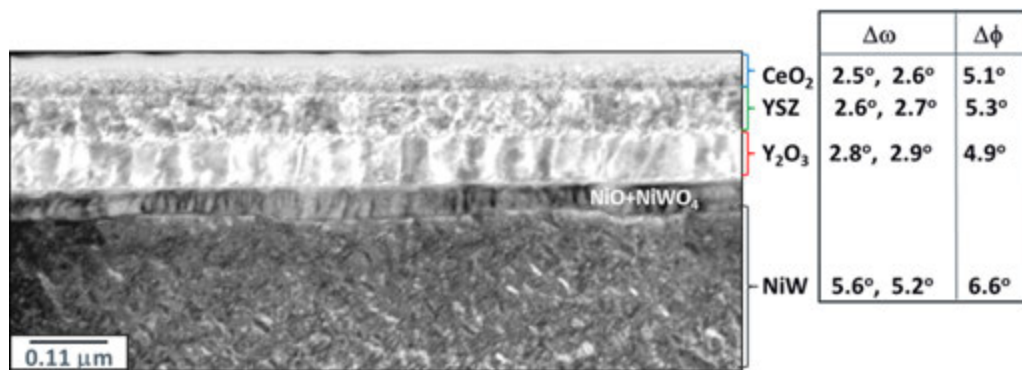


Fig. 7 TEM cross-section image of a NiW/Y₂O₃/YSZ/CeO₂ template after processing of the HTS layer. The out-of-plane ($\Delta\omega$) and in-plane ($\Delta\phi$) textures are shown for each layer. The adherent NiO-NiWO₄ formed during HTS processing.

Once the seed layer is deposited, the YSZ barrier and CeO₂ cap layers can be deposited by a variety of vacuum-based deposition techniques.

Fig. 7 shows the cross-sectional TEM image of a RABiTS template from a fully processed conductor produced by AMSC. The three buffer layers are deposited by reactive sputtering and are each ~ 75 nm thick. Typical values for the full width at half-maximum of the out-of-plane texture, $\Delta\omega$ and in-plane texture, $\Delta\phi$, for each layer are shown in **Fig. 7**. The Y₂O₃ (seed) layer replicates the texture of the Ni-W substrate. The middle YSZ (barrier) layer inhibits the diffusion of Ni and W to the (RE)BCO. The top CeO₂ (cap) layer has a texture closely matching that of the (RE)BCO layer and provides an optimized surface for the nucleation and growth of the (RE)BCO. The cross-section image in **Fig. 7** also shows the presence of a NiO-NiWO₄ layer between the Y₂O₃ and NiW. This layer forms during the conductor processing, after the preparation of the template, and is an adherent oxide that does not affect the texture or mechanical properties of the conductor.

A unique aspect of the Y₂O₃ seed layer (**Fig. 7**) is the improvement in texture, compared to the NiW substrate, which propagates through to the YSZ and the CeO₂ layers. The texture sharpening, which is unique to the PVD Y₂O₃ layer is believed to arise from lattice strain introduced during the deposition process (Cantoni *et al.*, 2009). The enhanced texture propagates through to the (RE)BCO layer significantly increasing the critical current that can be carried in the (RE)BCO layer.

Fig. 8 shows an orientation image micrograph of the CeO₂ surface of a NiW/Y₂O₃/YSZ/CeO₂ template obtained using Electron Back Scattered Diffraction. Grain boundaries with mis-orientations of $> 4^\circ$ are indicated in each image. When the in-plane and out-of-plane texture orientations are separated, it is seen that $\sim 80\%$ of the template is single crystal-like with respect to the in-plane orientation.

The ability of the oxide buffer stack to prevent diffusion of the NiW to the (RE)BCO layer is shown in **Fig. 9**. The NiW/Y₂O₃/YSZ/CeO₂ template was heated in an O₂/H₂O atmosphere at around 800°C to simulate the deposition and growth process for the (RE)BCO. The cross-section TEM and SIMS depth profile through the buffer layers, in **Fig. 9**, show that diffusion of the substrate components (Ni and W) are stopped at the YSZ layer and do not reach the (RE)BCO. It is also seen that O diffuses through the buffer stack, forming the adherent NiO-NiWO₄ layer also seen in **Fig. 7**.

A critical requirement of the RABiTS technology is the ability to produce the template in long length tapes with a consistent texture along both the length and width. In the early development of the RABiTS process, roll-to-roll x-ray analysis was used to establish that the texture was maintained uniformly across the width and length of the NiW tape. **Fig. 10** shows the pole figures

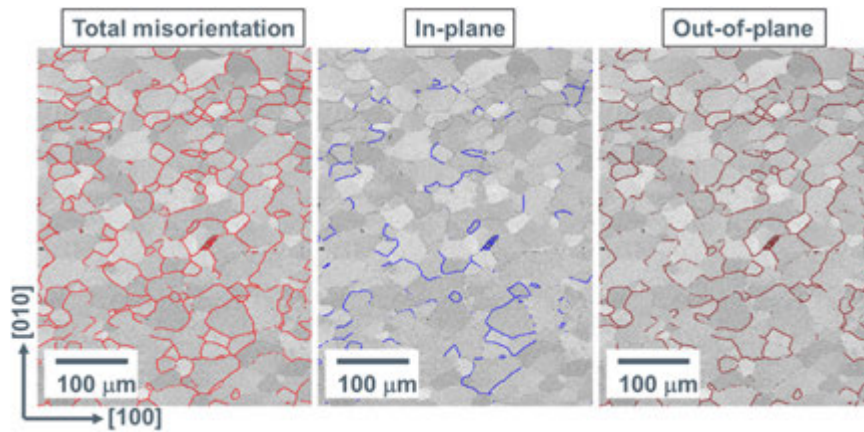


Fig. 8 Electron Back Scattered Diffraction orientation map of the CeO_2 surface of a $\text{NiW}/\text{Y}_2\text{O}_3/\text{YSZ}/\text{CeO}_2$ template showing the total mis-orientation and separated in-plane and out-of-plane mis-orientations. All grain boundary mis-orientations $>4^\circ$ are indicated.

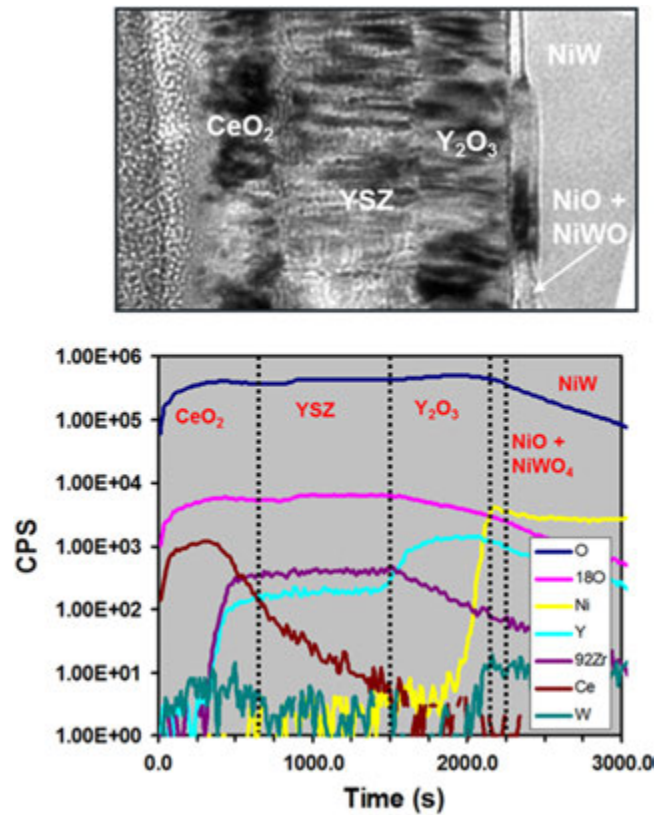


Fig. 9 TEM cross-section of a $\text{NiW}/\text{Y}_2\text{O}_3/\text{YSZ}/\text{CeO}_2$ template (top) and the SIMS profile measured through the thickness of the buffer layers (bottom) showing the extent of diffusion of the substrate components. The sample was processed in an $^{18}\text{O}_2$ environment.

(one quarter shown) of the NiW substrate and the CeO_2 cap layer measured across the width and length of a template. The data show that there is no detectable variation in the texture of either the starting substrate or the buffer layers.

Solution based processes for the buffer deposition have also been developed (Sathyamurthy *et al.*, 2004; Knoth *et al.*, 2005; Obradors *et al.*, 2006; Cordero-Cabrera *et al.*, 2007; Bäcker *et al.*, 2019). The most successful approach, used in manufacturing by Deutsche Nanoschrift, uses a two layer stack consisting of $\text{La}_2\text{Zr}_2\text{O}_7$ and CeO_2 . The $\text{La}_2\text{Zr}_2\text{O}_7$ layer functions as both the seed and barrier layers, while the CeO_2 serves as the cap layer. The oxide layers are deposited by slot die coating using metal-organic salts such as pentanedionates of La and Zr and acetates of Ce, dissolved in propionic acid and pyrolyzed at around 1000°C in a

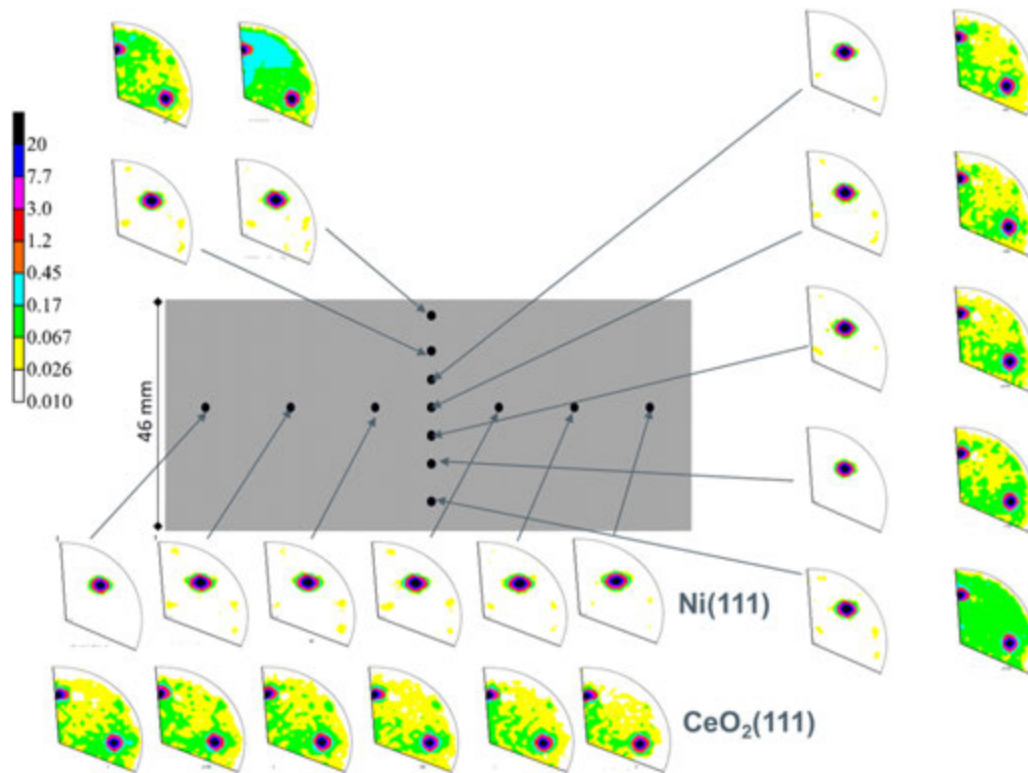


Fig. 10 Pole figures (quarter) for NiW (111) and CeO₂ (111) obtained along the length and width of a 46 mm wide NiW/Y₂O₃/YSZ/CeO₂ template showing uniformity of the texture.

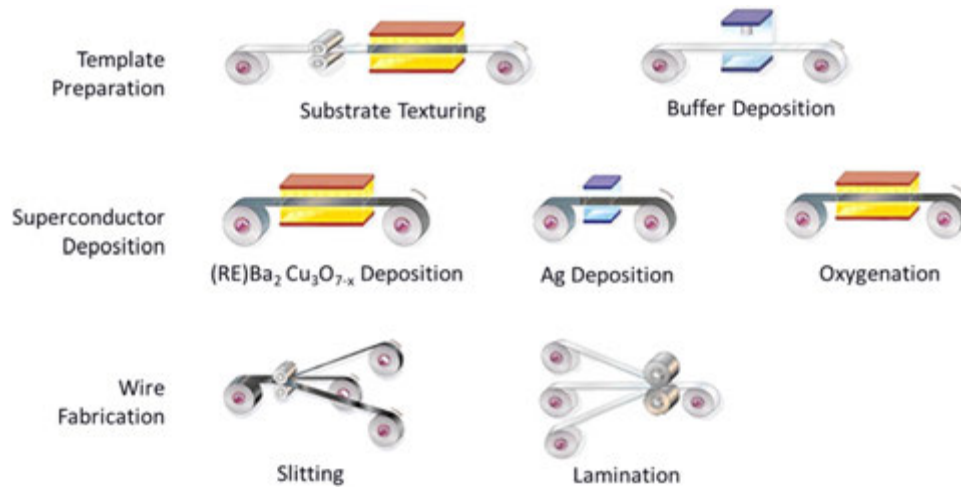


Fig. 11 Schematic diagram illustrating basic process steps for manufacturing 2G HTS wire: (1) RABiTS template fabrication, (2) superconductor deposition, and (3) wire lamination.

reducing atmosphere to prevent oxidation of the metal substrate. Although the solution-based processes are attractive for industrial coating, the NiW/La₂Zr₂O₇/CeO₂ template has not achieved the same performance in the HTS wires as the NiW/Y₂O₃/YSZ/CeO₂ template.

Roll-to-Roll Manufacturing of RABiTS-Based 2G HTS Wire

A major advantage of the RABiTS technology is the ability to produce the textured metal substrate in a wide width over long lengths. This allows the subsequent roll-to-roll processes to be carried at the same width until the strip is slit into the narrower

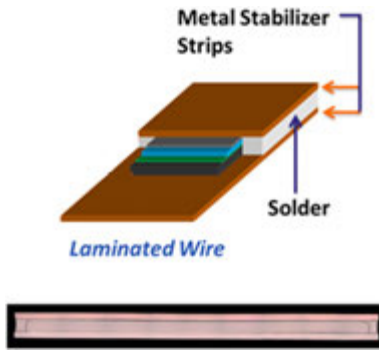


Fig. 12 Schematic illustration (top) of a laminated 2G wire showing the RABiTS template and (RE)BCO layer encapsulated between two metal lamina and a transverse cross-section micrograph (bottom) of a 4-mm wide cable wire.

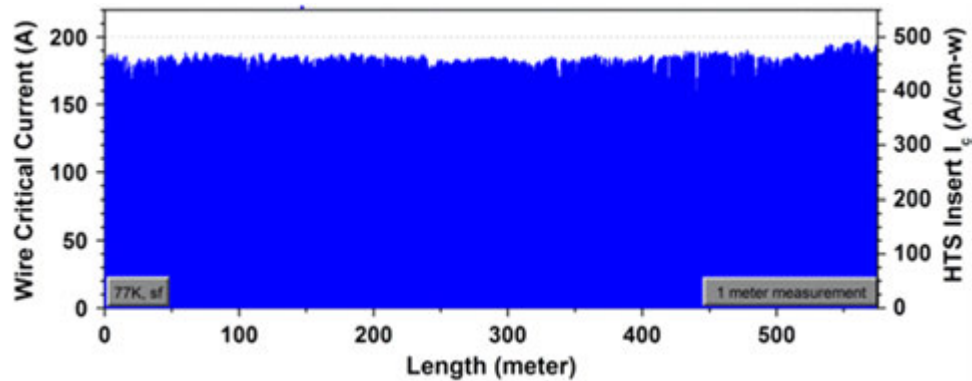


Fig. 13 Critical current measured over the length of a cable wire prepared with a RABiTS template. Courtesy of AMSC.

widths required for the actual 2G conductor. In contrast, textured IBAD templates are currently produced in a maximum width of ~ 12 mm, since the IBAD texturing process has a limited width uniformity.

AMSC and Deutsche Nanoschicht are the two major companies using the RABiTS template technology for the manufacture of 2G HTS wire. The NiW alloy (both Ni-5at%W and Ni-9at%W) is produced in multi ton quantities from a conventional melt of high purity Ni and W. The basic 2G HTS wire manufacturing process used with the RABiTS template is illustrated in Fig. 11. The process starts with a wide (~ 50 mm) NiW substrate which is rolled to ~ 75 μ m and annealed to form the cube texture. The buffer layers are then deposited onto the wide strip. The (RE)BCO layer is generally deposited by a Metal Organic Deposition slot-die coating process. After the (RE) BCO layer is completed and the surface is coated with a thin Ag layer, the wide strip is slit into multiple narrower strips which are converted into the final superconducting wire. In this conversion process, a metal foil is laminated to each side of the slit tape. The lamination process results in solder fillets on each edge of the tape, producing a hermetic seal and exceptional resistance to delamination during use. By varying the composition or thickness of the metal lamina, the normal-state electrical resistance and mechanical properties of the final wire are customized for specific applications. The basic architecture of the final wire is illustrated in Fig. 12 along with a cross-sectional micrograph of an actual wire.

This process routinely produces wires with lengths of around 0.5 km with critical currents (I_c) in excess of 150 A (> 400 A/cm-w) in a 4-mm wide conductor as shown in Fig. 13. RABiTS-based wires, primarily produced by AMSC, are being used in cable and fault current limiters (FCL) projects around the world and defense applications such as shipboard degaussing cables (Sohn *et al.*, 2010; Ryu *et al.*, 2013; HTS Cable Korea, 2011; HTS Cable, 2019; HTS Ship Degaussing Cable, 2019).

Summary

When the RABiTS technology was discovered in 1996, there was considerable doubt whether the approach could be developed into a scale able manufacturing process. However, vast advances have been achieved in the development of the RABiTS template technology over the past three decades. The technology has reached the level where the templates show a near single crystal-like texture, with most grain boundaries mis-orientations being $< 4^\circ$, allowing the growth of (RE)BCO films with critical current densities almost equal to those obtained on single crystal substrates. The initial development of the RABiTS templates was limited to ferromagnetic materials which generate ac losses in many electrical applications. However, improvements in the fundamental

understanding of the deformation science of Ni alloys have enabled the development of completely non-magnetic alloys based on Ni-9at%W. These alloys now allow the RABiTS based templates to be used for a broader range of applications.

The RABiTS process has been successfully scaled for the industrial manufacturing of 2G HTS wire by AMSC and Deutsche Nanoschicht. RABiTS templates are routinely produced in nearly defect-free lengths of nearly a kilometer and widths of ~ 50 mm. Second Generation HTS wires produced with the RABiTS technology are now manufactured in lengths exceeding 0.5 km with I_c 's at 77K, self-field in excess of 400 A/cm-w. These wires are currently being used for applications in the electrical grid (electrical cables and FCL) and in various defense applications including degaussing cables for ships.

References

- Arendt, P.N., Foltyn, S.R., 2004. Biaxially textured IBAD-MgO templates for YBCO-coated conductors. *MRS Bull.* 29, 543.
- Bäcker, M., Baumann, A., Brunkahl, O., Erbe, M., Schneller, T., 2019. Chemical Solution Deposition (CSD). In *Encyclopedia of Applied Physics*. Wiley-VCH Verlag GmbH & Co. KGaA. pp. 1–34.
- Bauer, M., Metzger, R., Semerad, R., Berberich, P., Kinder, H., 1999. Inclined substrate deposition by evaporation of magnesium oxide for coated conductors. *MRS Proc.* 585, 35.
- Cantoni, C., Christen, D.K., Feenstra, R., *et al.*, 2001. Reflection high-energy electron diffraction studies of epitaxial oxide seed-layer growth on rolling-assisted biaxially textured substrate Ni(001): The role of surface structure and chemistry. *Appl. Phys. Lett.* 79, 3077.
- Cantoni, C., Christen, D.K., Goyal, A., *et al.*, 2003. Growth of oxide seed layers on Ni and other technologically interesting metal substrates: Issues related to formation and control of sulfur superstructures for texture optimization. *IEEE Trans. Appl. Supercond.* 13, 2646.
- Cantoni, C., Specht, E.D., Goyal, A., Li, X., Rupich, M., 2009. Influence of oxygen deficiency on the out-of-plane tilt of epitaxial Y_2O_3 films on, Ni-5%W tapes. *J. Mater. Res.* 24, 520.
- Cooper, S.L., Gray, K.E., 1994. In: Ginsberg, D.M. (Ed.), *Physical Properties of High Temperature Superconductors*, Vol. IV. Singapore: World Scientific, p. 61.
- Cordero-Cabrera, M.C., Mouganie, T., Glowacki, B.A., *et al.*, 2007. Highly textured $La_2Zr_2O_7$ and CeO_2 buffer layers by ink jet printing for coated conductors. *J. Mater. Sci.* 42, 7129.
- Dimos, D., Chaudhari, P., Mannhart, J., 1990. Superconducting transport properties of grain boundaries in $YBa_2Cu_3O_7$ bi-crystals. *Phys. Rev. B* 41, 4038.
- Goler, V., Sachs, G., 1929. Walz und Rekristallizationstextur regular-flächenzentrierter Metalle III, IV. *Zeitschrift für Physik* 59, 477.
- Goyal, A., 2007. Superconducting YBCO conductors: The RABiTS approach. In: Buschow, K.H.J., Cahn, R., Flemings, M., Ilshner, B., Kramer, E., Mahajan, S., Veyssiere, P. (Eds.), *Encyclopedia of Materials: Science and Technology*, second ed. Amsterdam: Elsevier, pp. 1–5.
- Goyal, A., Budai, J., Kroeger, D.M. *et al.*, 1998. Preparing biaxially textured metal alloy article; superconductors. United States Patent No. 5,741,377.
- Goyal, A., Paranthaman, M., Schoop, U., 2004. The RABiTS approach: Using rolling-assisted biaxially textured substrates for high-performance YBCO superconductors. *MRS Bull.* 29, 552.
- Hanyu, S., Tashita, C., Hayashida, T., *et al.*, 2010. Long-length IBAD-MgO buffer layers for high performance RE-123 coated conductors by a large ion beam source. *Physica C: Supercond.* 470, 1227.
- Hasegawa, K., Fujino, K., Mukai, H., *et al.*, 1996. Biaxially aligned YBCO film tapes fabricated by all pulsed laser deposition. *Appl. Supercond.* 4, 487.
- Hilgenkamp, H., Mannhart, J., 2002. Grain boundaries in high- T_c superconductors. *Rev. Mod. Phys.* 74, 485.
- HTS Cable, 2019. Available at: <https://ir.amsc.com/news-releases/news-release-details/departement-homeland-security-signs-contract-modification-install>.
- HTS Cable Korea, 2011. Available at: <https://ir.amsc.com/news-releases/news-release-details/first-superconductor-cable-energized-koreas-power-grid>.
- HTS Ship Degaussing Cable, 2019. Available at: <https://ir.amsc.com/news-releases/news-release-details/amsc-awarded-delivery-contract-ship-protection-system-lpd-30>.
- Hühne, R., Eickemeyer, J., Sarma, V.S., *et al.*, 2010. Application of textured highly alloyed Ni–W tapes for preparing coated conductor architectures. *Supercond. Sci. Technol.* 23, 034015.
- Iijima, Y., Tanabe, N., Ikeno, Y., Kohno, O., 1991. Biaxially aligned $YBa_2Cu_3O_{7-x}$ thin film tapes. *Physica C* 185, 1959.
- Iijima, Y., Tanabe, N., Kohno, O., Ikeno, Y., 1992. In-plane aligned $YBa_2Cu_3O_{7-x}$ thin films deposited on polycrystalline metallic substrates. *Appl. Phys. Lett.* 60, 769.
- Jia, Y., Welp, U., Crabtree, G.W., *et al.*, 2011. Microstructure dependence of the c-axis critical current density in second-generation YBCO tapes. *J. Appl. Phys.* 110 (8), 083923.
- Kashima, N., Nagaya, S., Shima, K., Hoshino, H., 2012. Clad textured metal substrate for forming epitaxial thin film and thereon and method for manufacturing the same. United States Patent No. 8,147,984 B2.
- Knoth, K., Hühne, R., Oswald, S., Schultz, L., Holzappel, B., 2005. Highly textured $La_2Zr_2O_7$ buffer layers for YBCO-coated conductors prepared by chemical solution deposition. *Supercond. Sci. Tech.* 18, 334.
- Ko, K.P., Ha, H.S., Kim, H.K., *et al.*, 2007. Fabrication of highly textured IBAD-MgO template by continuous reel-to-reel process and its characterization. *Physica C: Supercond.* 463–465, 564.
- Norton, D.P., Goyal, A., Budai, J.D., *et al.*, 1996. Epitaxial $YBa_2Cu_3O_7$ on biaxially textured nickel (001): An approach to superconducting tapes with high critical current density. *Sci.* 274, 755.
- Obradors, X., Puig, T., Pomar, A., *et al.*, 2006. Progress towards all-chemical superconducting $YBa_2Cu_3O_{7-x}$ coated conductors. *J. Supercond. Sci. Tech.* 19, S13.
- Paranthaman, M., Aytug, T., Christen, D.K., *et al.*, 2003. Growth of thick $YBa_2Cu_3O_{7-δ}$ films carrying a critical current of over 230 A/cm on single $LaMnO_3$ -buffered ion-beam assisted deposition MgO substrates. *J. Mater. Res.* 18, 2055.
- Ryu, C., Jang, H., Choi, C., Kim, Y., Kim, H., 2013. Current status of demonstration and commercialization of HTS cable system in grid in Korea. In: *Proceedings of 2013 IEEE International Conference on Applied Superconductivity and Electromagnetic Devices*, October 25–27, p. 539. Beijing.
- Sathyamurthy, S., Paranthaman, M., Zhai, H.Y., *et al.*, 2004. Chemical solution deposition of lanthanum zirconate barrier layers applied to low-cost coated-conductor fabrication. *J. Mater. Res.* 19, 2117.
- Sathyamurthy, S., Thieme, C., Rupich, M.W., 2016. American superconductor: Second generation superconductor Wire – From research to power grid applications. In: Madsen, L., Svedberg, E. (Eds.), *Materials Research for Manufacturing*. Springer Series in Materials Science 224. Springer, pp. 131–165.
- Skakle, J.M.S., 1998. Crystal chemical substitutions and doping of $YBa_2Cu_3O_x$ and related superconductors. *Mater. Sci. Eng.* R23, 1.
- Sohn, S.H., Lim, J.H., Yang, B.M., *et al.*, 2010. Design and development of 500 m long HTS cable system in the KEPCO power grid, Korea. *Physica C: Supercond.* 470, 1567.
- Specht, E.D., Goyal, A., Lee, D.F., *et al.*, 1998. Cube-textured nickel substrates for high-temperature superconductors. *Supercond. Sci. Technol.* 11, 945.
- Tinkham, M., 1996. *Introduction to Superconductivity*, second ed. New York, NY: McGraw-Hill.

Ferrite Ceramics at Microwave Frequencies: Applications and Characterization

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Ferrimagnetic Materials

Basic Properties of Polycrystalline Ferrites

Ferrite materials are magnetic oxides, known as ferrimagnetic materials, which are characterized by high magnetic permeability values and insulating behavior over a wide frequency range. Their high electrical resistivity make low-loss ferrimagnets the ideal basis for passive microwave components operating over a wide range of frequencies, from 1 to 100 GHz. They are needed in devices where nonreciprocal behavior is expected, or to strengthen the interaction between a device and the electromagnetic signal. Depending on the applications, either hard or soft ferrites are used.

Ferrites have the following main physical properties

- High electrical resistivity (10^5 – 10^6 MΩ m)
- Relative dielectric constant of 11–17
- Low dielectric losses (2.10^{-4} – 15.10^{-4})
- A high magnetic susceptibility
- A Curie temperature of 200–560°C
- A saturation magnetization of 80 kA/m to 400 kA/m

Ferrites are made of oxygen ions, iron ions, and other cationic metals that may be magnetic or nonmagnetic. Their electrical resistivity is high, which makes them suitable materials for use in the microwave range. Considering their magnetic properties, in particular their magnetic saturation, magnetocrystalline anisotropy and coercive field, three types of ceramics are grouped together under the heading “ferrites.” There are spinel ferrites and iron garnets (which together constitute the soft ferrite family), and hexaferrites (which make up the hard ferrite family). Both spinel and iron garnets show low coercivity and low magnetocrystalline anisotropy, whereas hard ferrites are characterized by high coercivity and high magnetocrystalline anisotropy. The ferrite crystallographic structure, for garnets as well as for spinels and hard ferrites is formed by a close-packed pattern of oxygen anions. The magnetic materials most commonly used in the microwave frequency range are polycrystalline ceramics constituted of grains. These are divided into magnetic domains (Weiss domains) separated by domain walls (Bloch walls) (Fig. 1). The magnetic moments are kept parallel with each other by the strong energy exchange. Their spontaneous direction of magnetization is on an easy magnetization axis. This makes it possible to minimize the magnetocrystalline energy, which is commonly described by an anisotropy field. Because of the finite size of the magnetic volume, demagnetizing effects appears. This second contribution to the total magnetic energy corresponds to demagnetizing fields, which are proportional to the magnetization. The subdivision into magnetic domains lowers the total energy of the grain.

Hysteresis Loops and Magnetocrystalline Anisotropy

In its initial unmagnetized state, the magnetic structure of a polycrystalline material is subdivided into randomly distributed magnetic domains (the Weiss domains), separated from each other by domain walls (Bloch walls), as illustrated in Fig. 1. The variation of the magnetization M under the effect of an applied magnetic field H can be represented by a hysteresis loop that depicts the function $M(H)$ (Fig. 2). The magnetization process is due to a combination of domain wall bowing, unpinning, displacement, and to spin rotation. More precisely, for low values of H , the volume of those domains that are the more closely oriented along the magnetic field direction expands, at the expense of the other domains, through reversible wall movement. Then, for higher values of H , expansion occurs through irreversible wall displacements. From a magnetization value close to 80% of saturation, only one magnetic domain remains. For higher values of H , spins are rotated out of their easy direction by the applied magnetic field, leading the magnetization to reach its maximum value (the saturation magnetization).

Some of the main characteristic features of a magnetic material can be deduced from its hysteresis loop: The saturation magnetization M_s , the remanent magnetization M_R , the coercive force H_C , and the anisotropy field H_A . Hard and soft magnetic materials have different typical aspects, which also depend on their texturation (Figs. 3–4).

Among the parameters that characterize a magnetic material, the anisotropy field, H_A , is one of the most relevant because it is a measure of the magnetic hardness of the material, which has a considerable impact on the addressed frequency range of applications. The fact that magnetic properties of a material depend on the crystallographic direction along which the magnetic moments are aligned is a manifestation of the magnetocrystalline anisotropy. A first well-known example is that of magnetite Fe_3O_4 , which can be magnetized along the easy $\langle 111 \rangle$ -like directions, while the magnetization is harder along the $\langle 100 \rangle$ -like directions. A second example is that of Cobalt (Co), a hard magnetic material with hexagonal structure and uniaxial magnetocrystalline anisotropy: Co can be magnetized along the $\langle 001 \rangle$ -like directions, which define the easy directions of magnetization,

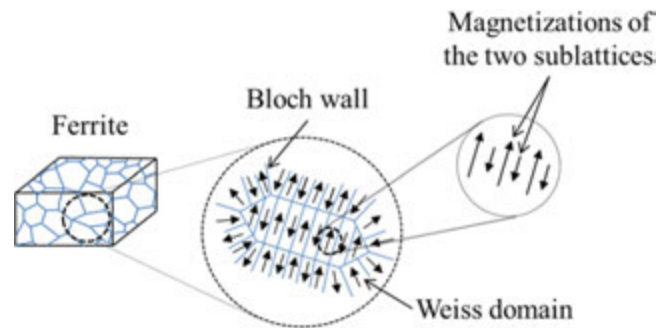


Fig. 1 Polycrystalline ferrite made of grains subdivided into magnetic domains. The grains boundaries are in blue color.

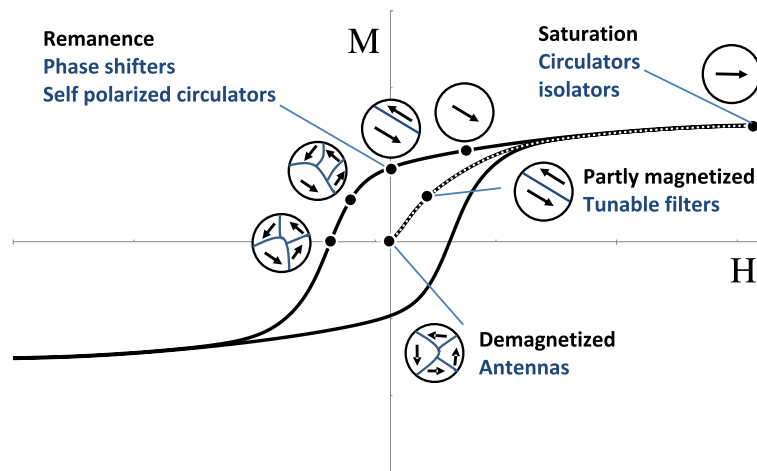


Fig. 2 Hysteresis loop, and schematic representation of magnetization by domain wall movements and by spin rotation in domains. Depending on the types of applications targeted, a given magnetic material may be used in different magnetization states.

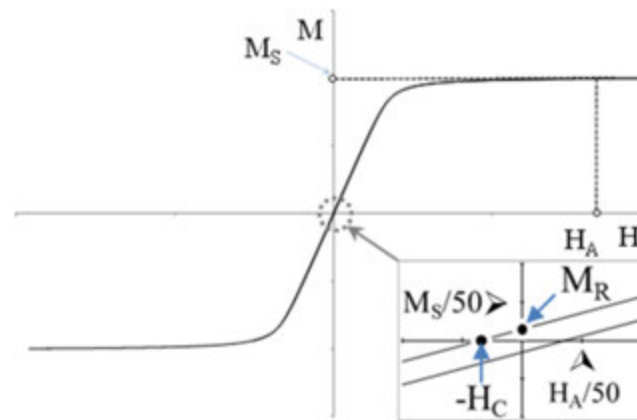


Fig. 3 Typical hysteresis loop of a soft ferrite. The inset shows how the hysteresis is closed: Remanent magnetization M_R and coercive field H_C are of the order of $M_s/50$ and $H_A/50$ or below, respectively. Low coercivity and low remanence reduce the energy loss associated with hysteresis.

but its hard directions of magnetization lie in the basal plane, along the $\langle 100 \rangle$ -like directions (Fig. 5). In any case the anisotropy field H_A is defined as the field that saturates a particle along the direction of hard magnetization. Materials that have uniaxial symmetry are not easy to demagnetize, so they are used as permanent magnets. Because the values of H_A for hard magnetic materials are typically ten times higher than those observed for spinels, spinels are referred to as soft magnetic materials. The anisotropy field H_A is a fictive field that allows to describe the anisotropy effects from the expressions of the anisotropy energy,

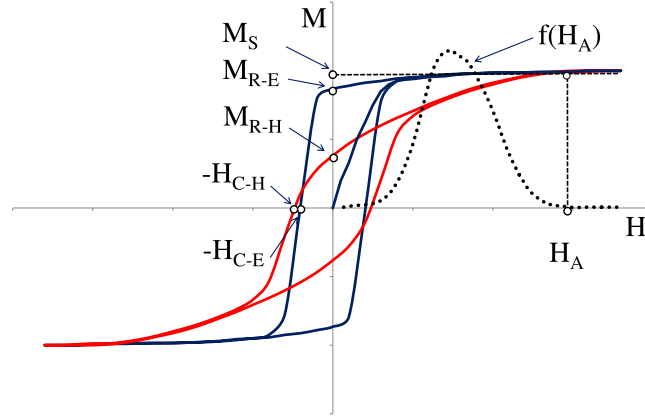


Fig. 4 Typical hysteresis loops of a hard ferrite measured along the easy axis of magnetization (blue line) and in the hard plane of magnetization (red line). Their respective remanent magnetizations M_R and coercive fields H_C are labeled correspondingly: -E for easy axis and -H for hard axis measurements. The function $f(A)$ represents the anisotropy field distribution deduced from the virgin curve, and H_A is the so-called anisotropy field (see main text for details).

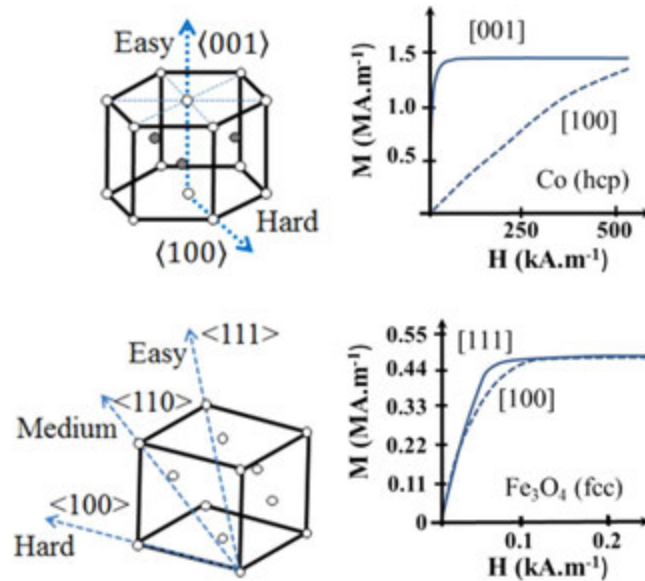


Fig. 5 Top: Crystal structure and magnetization curves (300K) of a single crystal of Cobalt. $\langle 001 \rangle$ is the easy direction of magnetization. There are six hard directions of magnetization in the basal plane, which can be deduced by hexagonal symmetry from the hard $\langle 100 \rangle$ direction. Bottom: Crystal structure and magnetization curves (300K) of a single crystal of magnetite Fe_3O_4 (only O^{2-} ions forming a face centered cubic lattice are represented). Above 130 K, $\langle 111 \rangle$ is the easy direction of magnetization, $\langle 100 \rangle$ is the hard direction of magnetization, $\langle 110 \rangle$ is the intermediate direction of magnetization.

which is itself a function of anisotropy constants (K_1 and K_2 are the anisotropy constants of first and second order, respectively). H_A is given as follows, for the various easy directions of magnetization, as a function of K_1 :

$H_A = 2K_1/\mu_0 M_S$ for the $\langle 001 \rangle$ easy axis, $H_A = -4(3K_1 + K_2)/9\mu_0 M_S$ for the $\langle 111 \rangle$ easy axis and $H_A = 2K_1/\mu_0 M_S$ for uniaxial materials (M_S is the saturation magnetization).

Factors that influence H_A in polycrystalline ferrites mainly consist of the misalignments of the magnetic grains, the magnetostatic interaction between them, and the existence of porosity. As a consequence, it is more appropriate to define an anisotropy field distribution $f(H_A)$ instead of a single anisotropy field value. This distribution can be obtained from virgin curves of magnetization (Pfeiffer, 1990). An example of $f(H_A)$ is given in Fig. 4. The highest value of the anisotropy field corresponds to the field (named H_A) at which saturation is reached, which is when the magnetizations measured along the hard and the easy directions both reach the saturation magnetization value (Fig. 5).

Depending on the types of applications targeted, a given magnetic material may be used at different magnetization states. This is illustrated in Fig. 2. With regard to the electromagnetic devices using ferrites we should mention

Table 1 Common cationic substitutions for garnets ferrites, and the associated intrinsic properties at room temperature. The presented values are taken from a number of sources, and represent what are generally taken to be the correct values for these ferrites

Rare earths and substitutions	Iron and substitutions	Doping elements	Saturation magnetization (MS, kA m ⁻¹)	Curie temperature (K)	Resonance linewidth (ΔH , A m ⁻¹)	Off resonance linewidth (ΔH_{eff} , A m ⁻¹)
Y	Fe, Al	Dy, Co	14–96	358–493	2–11.2	0.16–1.2
Y, Gd	Fe, Al	Dy, Ho	423–553	363–563	4–8	0.56–1.28
Y, Ca	Fe, Zr		156	513	0.8	1.60
Y, Ca	Fe, V, In	Dy	70	498	4.4	0.8

Table 2 Anisotropy constant K_1 and anisotropy field H_A of some common spinel ferrites

Molecular formula	Fe_3O_4 ^a	$NiFe_2O_4$ ^a	$Ni_{0.8}Fe_{2.2}O_4$ ^a	$CoFe_2O_4$ ^a	$MgFe_2O_4$ ^a	$MnFe_2O_4$ ^b	$Mg_{0.75}Mn_{0.25}Fe_2O_4$ ^c	$Mg_{0.25}Mn_{0.75}Fe_2O_4$ ^c
Anisotropy constant K_1 (kJ m ⁻³)	–11	–6.2	–3.9	200	–2.5	–3.4	–	–
Anisotropy field H_A (kA m ⁻¹)	24.3	24.4	20.8	500	–	180	20.8	16

^aValenzuela (1994).^bSrivastava and Patni (1974).^cSmit and Wijn (1959).

nonreciprocal devices (circulators, isolators, etc.), the behavior of which is based on the anisotropic permeability of the magnetic material (for this point, see Section “Microwave Passive Components Using Ferrites”). Tunable devices such as filters, resonators, and phase shifters operate on the basis of the nonlinear electromagnetic behavior of the ferrites when submitted to a dc magnetic field. Antennas can be miniaturized by using ferrites in a demagnetized state, where the magnetic permeability is high.

Soft Ferrites: Garnets Ferrites

The chemical formula for garnets is $Me_3Fe_5O_{12}$, where Me represents either a trivalent metal, such as Y, or a combination of metal ions, such as Y–Gd or Y–Gd–Al–Co. The crystal structure is orthorhombic. Among the ferrites, garnets are recommended for operating frequencies from 0.1 to 100 GHz, where they show the lowest magnetic losses ($\Delta H < 160$ A m⁻¹ (or 20 Oe)). This family includes yttrium iron garnets, yttrium aluminum garnets (YAG), calcium vanadium garnets, yttrium gadolinium garnets (Y–Gd–G), and variants with aluminum substitutions, all of which show a remarkable degree of temperature stability over –100–200°C. They are suitable for use at moderate power level. When doping with Co or Dy, YAG are usable in high-power applications. The representative properties of some garnets are listed in Table 1.

Soft Ferrites: Spinel Ferrites

The chemical formula for spinel ferrites is $MeFe_2O_4$ where Fe is trivalent ion. Me represents either a divalent metal, or a combination of divalent metal ions, such as Mn–Zn, Ni–Zn, Ni–Al, and sometimes an association of a monovalent ion (Li^+) with a trivalent ion (Fe^{3+} , Mn^{3+}). The crystal has a closed packed cubic structure. This class of spinel ferrites splits in two subclasses, depending on the frequency range addressed. First, for frequencies lower than 1 MHz, manganese–zinc ferrites are privileged, due to their high saturation magnetization (~ 480 kA m⁻¹) and low magnetic and dielectric losses ($< 3 \cdot 10^{-4}$). However, applications above 1 MHz are not to be considered due to their low electrical resistivity. The second subclass is constituted by nickel–zinc ferrites, which are suitable for use up to 500 MHz due to their high electrical resistivity (10^6 MΩ m.) The main conductivity mechanism in spinel ferrites is caused by electron hopping between Fe^{3+} and Fe^{2+} ferrite (van Uitert, 1955). For example, the effect of Fe content on the electrical resistivity of $Ni_{0.3}Zn_{0.7}Fe_{2+\delta}O_4$ ferrites is shown in Fig. 6. Iron deficient spinel ferrites show higher resistivity than stoichiometric ones, and for this reason they are highly suitable for microwave applications. In polycrystalline ferrite, grain boundaries may also play a significant role in the electrical resistivity by limiting eddy current losses.

The representative properties of some polycrystalline spinels are listed in Table 2 and in Table 3. The variations of the anisotropy constant K_1 and that of the anisotropy field H_A for some ferrites of formula $Ni_{1-x}Zn_xFe_2O_4$ (with $K_1 < 0$) and $Ni_{1-x}Zn_xCo_{0.2}Fe_2O_4$ (with $K_1 > 0$) as a function of the Zn content are presented in Fig. 7 (a) and (b) (from Mattei et al., 2015).

Hard Ferrites: Hexaferrites

The most commonly used hexaferrites include pure and substituted barium ferrites (BaO , $6Fe_2O_3$) and strontium ferrites (SrO , $6Fe_2O_3$). The crystal structure of hexaferrite is similar to that of magnetoplumbite $PbFe_{12}O_{19}$, where the Pb ion is divalent. Their

Table 3 Common cationic substitutions for spinel ferrites, and the associated intrinsic properties at room temperature. The presented values are taken from a number of sources, and represent what are generally taken to be the correct values for these ferrites

Divalent ions	Substituted trivalent ions	Saturation magnetization (M_s , kA m^{-1})	Curie temperature (K)	Resonance linewidth (ΔH , A m^{-1})	Off resonance linewidth (ΔH_{eff} , A m^{-1})
Mg, Mn	Fe	172	593	43	0.20
Mg, Mn	Fe, Al	42–160	363–563	8–20	0.17–4.20
Ni, Zn	Fe	320–400	448–473	13–27	1.20–2
Ni, Co	Fe, Al	40–240	393–858	8–72	1.60–3.20
Ni, Mg	Fe, Ti	144	773	56	> 3.60
Li, Mn	Fe	300	913	52	0.12
Li, Mn	Fe, Ti	80–230	573–773	24–46	0.12–0.72

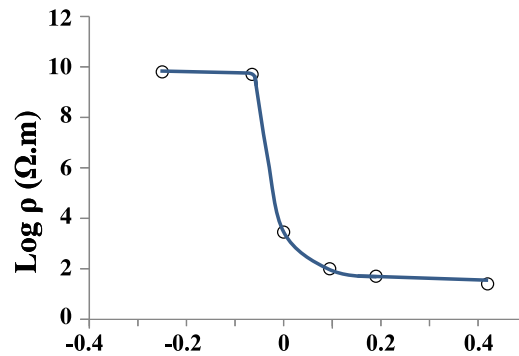


Fig. 6 The dependence of resistivity (ρ) on iron stoichiometry for a $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_{2+\delta}\text{O}_{4\pm}$ ferrite. Adapted from van Uitert, L.G., 1955. DC resistivity in the nickel and nickel zinc ferrite system. J. Chem. Phys. 23, 1883.

anisotropy fields are two or three orders of magnitude higher than that of spinels. The operational frequencies for the large range of compositionally modified hexaferrites extend from 22 to 110 GHz. Because of their high coercive field and saturation magnetization ($H_c \sim 350 - 400 \text{ kA m}^{-1}$, $M_s \sim 300 - 350 \text{ kA m}^{-1}$), hexaferrites can be used in magnetic recording applications and fabrication of permanent magnets. The best known are $\text{BaFe}_{12}\text{O}_{19}$ and $\text{SrFe}_{12}\text{O}_{19}$. Both are called “M-type hexaferrite,” as detailed below. They have uniaxial magnetic anisotropy, where the easy axis of magnetization is the crystallographic c-axis. Moreover, some compounds containing divalent ions, especially cobalt, have a plane of easy magnetization in the basal plane, or a cone of spontaneous magnetization at an angle between 0° and 90° with c-axis. The substitutions of Fe by Sc or In allow the anisotropy field to be lowered and the frequency range of applications accordingly extends from 4 to 40 GHz (Harris *et al.*, 2014).

Several other ferrimagnetic oxides are available that are derived from combinations of ferrite spinel ($\text{MeO-Fe}_2\text{O}_3$) M-hexaferrites ($\text{BaO-6Fe}_2\text{O}_3$) and Y-hexaferrites ($\text{Ba}_2^{2+}\text{Me}_2^{2+}\text{Fe}_{12}^{3+}\text{O}_{22}$). These are, with the nominal molecular formulae in brackets and where Me represents a divalent ion, W-hexaferrites ($\text{Ba}^{2+}\text{Me}_2^{2+}\text{Fe}_{16}^{3+}\text{O}_{27}$), Z-hexaferrites ($\text{Ba}_3^{2+}\text{Co}_2^{2+}\text{Fe}_{24}^{3+}\text{O}_{41}$), and U-hexaferrites ($\text{Ba}_4\text{Me}_2\text{Fe}_{36}\text{O}_{60}$). The representative properties of some hexaferrites are presented in Table 4.

Magnetic Permeability in the Microwave Range of Frequencies

The Permeability Tensor

Wave propagation in ferrites shows nonreciprocal properties arising from gyromagnetic effects, which are directly related to the precession movement of the magnetic moments. The complex phenomena involved are presented here in a simplified form.

Undamped precessions: From the atomic moment to the lossless ferrimagnetic material

We first consider an isolated atomic magnetic moment $\vec{\mu}$. When submitted to a DC magnetic field $\vec{H}$, the top of the magnetic moment comes to a precession movement around $\vec{H}$, described by the equation of movement: $\frac{d\vec{\mu}}{dt} = -\mu_0\gamma\vec{\mu} \times \vec{H}$, where $\gamma = 1.760810^4 \text{ s}^{-1}\text{T}^{-1}$, γ being the gyromagnetic ratio. This equation describes the precession of the magnetic moment. The source of $\vec{H}$ can be either an external bias field, an internal field (which can be a magnetocrystalline field or a demagnetizing field), or a combination of them. In the absence of an external magnetic field, a precession can be brought about by the internal magnetic field produced by the total magnetic anisotropy.

Table 4 Some room-temperature intrinsic properties for various hexaferrites

Molecular formula (abbreviation)	Easy directions of magnetization	Saturation magnetization (M_s , kA m ⁻¹)	Curie temperature (K)	Magnetocrystalline anisotropy field (H_a , kA m ⁻¹)
BaFe ₁₂ O ₁₉ (BaM)	Uniaxial (c-axis)	320	723	1396
SrFe ₁₂ O ₁₉ (SrM)	Uniaxial (c-axis)	345	728	1280
Ba ₂ Co ₂ Fe ₂₈ O ₄₆ (Co ₂ X)	Cone of magnetization	272	740	760
Ba ₂ Co ₂ Fe ₁₂ O ₂₂ (Co ₂ Y)	Planar anisotropy perpendicular to c-axis	184	613	760
BaCo ₂ Fe ₁₆ O ₂₇ (Co ₂ W)	Cone of magnetization or planar anisotropy	384	703	1680
Ba ₃ Co ₂ Fe ₂₄ O ₄₁ (Co ₂ Z)	Planar anisotropy perpendicular to c-axis	264	673	2240

Note: From Pullar, R.C., 2012. Hexagonal ferrites: A review of the synthesis, properties and applications of hexaferrite ceramics. Prog. Mater. Sci. 57, 1191–1334.

Turning to the case of a ferromagnetic material constituted of an assembly of magnetic moments, the DC magnetic field is supposedly large enough to bring magnetization to saturation ($\vec{M}_s$). Because the molecular field, which represents the interaction exchange, is parallel to each magnetic moment, the previous equation is validly extended to $\frac{d\vec{M}_s}{dt} = -\mu_0\gamma\vec{M}_s \times \vec{H}$, which describes the precession of the saturation magnetization. In addition, we consider that an AC magnetic field $\vec{h}$ is applied in the plane perpendicular to $\vec{H}$. As a consequence $\vec{M}_s$ is the sum of $\vec{M}$ with a variable component $\vec{m}$: $\vec{M}_s = \vec{M} + \vec{m}$. Then, within the assumption that the transverse magnetization M_x , M_y due to $\vec{h}$ is small, and thus writing $\vec{M}_s \cong \vec{M} = \text{constant}$, the equation of motion of $\vec{M}$ can be written as (Landau, 1965; Landau and Lifshitz, 1984):

$$\frac{d\vec{M}}{dt} = -\mu_0\gamma\vec{M} \times (\vec{H} + \vec{h}) \quad (1)$$

This equation is valid for an infinite medium, where no demagnetization due to the shape of the magnetic volume needs to be taken into account, and assuming that the precession is not damped. The variable component $\vec{m}$ supposedly has the same harmonic time dependance as the field $\vec{h}$ (i.e., $e^{i\omega t}$). The relationship between $\vec{m}$ and $\vec{h}$ can be written $\vec{m} = \bar{\chi}\vec{h}$, where $\bar{\chi}$ is the tensorial relative susceptibility. Solving Eq. (1), within the hypothesis framework of $|\vec{h}| \ll |\vec{H}_{DC}|$ and $|\vec{m}| \ll |\vec{M}|$, leads to the classical formulation of the susceptibility tensor $\bar{\chi}$, according to Polder (1949), or alternatively to the Polder's relative permeability tensor $\bar{\mu} = 1 + \bar{\chi}$. Its conventional expression for a magnetic field bias $\vec{H}$ arbitrarily directed along the z-direction is

$$\bar{\mu} = \begin{bmatrix} 1 + \chi & j\kappa & 0 \\ -j\kappa & 1 + \chi & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (2)$$

where

$$\chi = \frac{\omega_0\omega_m}{(\omega_0^2 - \omega_m^2)} \quad (3a)$$

$$\kappa = \frac{\omega_m\omega}{(\omega_0^2 - \omega_m^2)} \quad (3b)$$

and with $\omega_0 = \gamma|\vec{H}|$ and $\omega_m = \gamma|\vec{M}_s|$.

$\bar{\chi}$ relies on the AC magnetic field $\vec{h}$, conveyed by the electromagnetic wave, to the dynamic magnetic moment $\vec{m}$ that was generated in the material. The set of Eqs. (2) and (3) means that the energy absorption by the material from an electromagnetic wave of pulsation ω is maximal when the static field is equal to ω_0 . The gyromagnetic pulsation ω_0 is also known as the Larmor pulsation and $f_0 = \omega_0/2\pi$ is the natural ferromagnetic resonance of the ferrite. This model describes the AC susceptibility (or permeability) of a ferromagnetic material of infinite size and magnetized at saturation. However, in real situations magnetic losses are involved. This aspect will be discussed in the next section.

In the case of a ferrimagnetic material, two magnetic sublattices are present, each of which is characterized by different magnetizations and molecular fields. This situation presents a similar problem to that of two coupled oscillators. Consequently, there are two resonance frequencies, the first lying in the far infrared, which is beyond the scope of this chapter. The general expression of the second magnetic resonance frequency of the two-sublattice model has the same form as that originally obtained for the ferromagnetic case (Wangness, 1954; Smit and Wijn, 1959).

Damped precession: A dissipating behavior

In the above section our basic assumptions were firstly that the precession movement of the magnetization was undamped, secondly that the material was magnetized at saturation, and thirdly that the material has infinite dimensions. In the most general case, at least two of these assumptions are not fulfilled. Let us first consider precession damping. Interactions take place in the magnetic material, firstly inside the system of spins itself, and secondly between the system of spins and its surroundings.

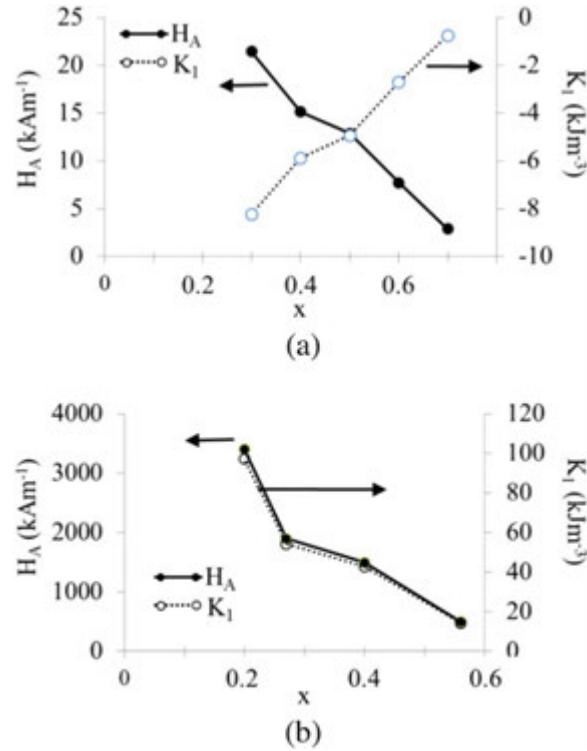


Fig. 7 Anisotropy constant K_1 (dashed line) and anisotropy field H_A (full line) for some ferrites of formula (a) $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ and (b) $\text{Ni}_{1-x}\text{Zn}_x\text{Co}_{0.2}\text{Fe}_2\text{O}_4$ as a function of the Zn content. Adapted from Mattei, J.-L., Guen, E. Le, Chevalier, A., Tarot, A.C., 2015. Experimental determination of magnetocrystalline anisotropy constants and saturation magnetostriction constants of Ni-Zn and Ni-Zn-Co ferrites intended to be used for antennas miniaturization. *J. Magn. Mater.* 374, 762–768.

These interactions cause a damping of the magnetization precession movement. Several phenomenological models introduced damping into the former relation (1), in order to reflect the existence of forces resulting in a sharper angle between the magnetic moment and the DC field (Fig. 8). This is described by the Landau–Lifschitz–Gilbert (L–L–G) equation (Landau and Lifshitz, 1935; Gilbert, 1955):

$$\frac{d\vec{M}}{dt} = -\mu_0\gamma\vec{M} \times (\vec{H} + \vec{h}) + \alpha\vec{M} \times \frac{d\vec{M}}{dt} \quad (4)$$

In this relation $\vec{H}$ is the total bias static magnetic field, and $\vec{h}$ is the magnetic field conveyed by the plane electromagnetic wave, with angular frequency ω . Coefficient α is a phenomenological factor that characterizes the damping behavior of the magnetic moments. The permeability tensor remains in the form expressed by relation (2). The diagonal and extradiagonal terms (χ and κ) can now be written as:

$$\chi = \frac{\Omega_0\omega_m}{(\Omega_0^2 - \omega_m^2)} \quad (5)$$

$$\kappa = \frac{\omega_m\omega}{(\Omega_0^2 - \omega_m^2)} \quad (6)$$

where the complex angular resonance frequency Ω_0 is written as:

$$\Omega_0 = \omega_0 + j\omega\alpha \quad \text{with } \omega_0 = \gamma H \quad (7)$$

The effect of damping on the diagonal (μ) and extradiagonal (κ) terms of the magnetic susceptibility tensor is shown in Fig. 9. The angular resonance frequency ω_R , which corresponds to the frequency at which μ'' and κ'' reach their maximum value, depends on the damping factor according to the relationship $\omega_R = \frac{\omega_0}{\sqrt{1+\alpha^2}}$.

The frequency dispersion of the permeability spectrum $\mu(f)$

For polycrystalline ferrites, the frequency dispersion $\mu(f)$ of the permeability spectrum can be assigned to and described by the superposition of two types of magnetizing processes, i.e., spin rotation and domain wall motion (Rado, 1953):

$$\mu(f) = \mu_s + \mu_{DW} = 1 + \chi_s + \chi_{DW}$$

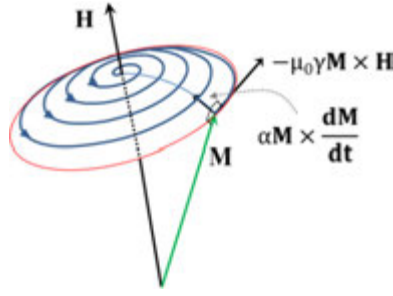


Fig. 8 Precessional dynamic of magnetization, with phenomenological damping.

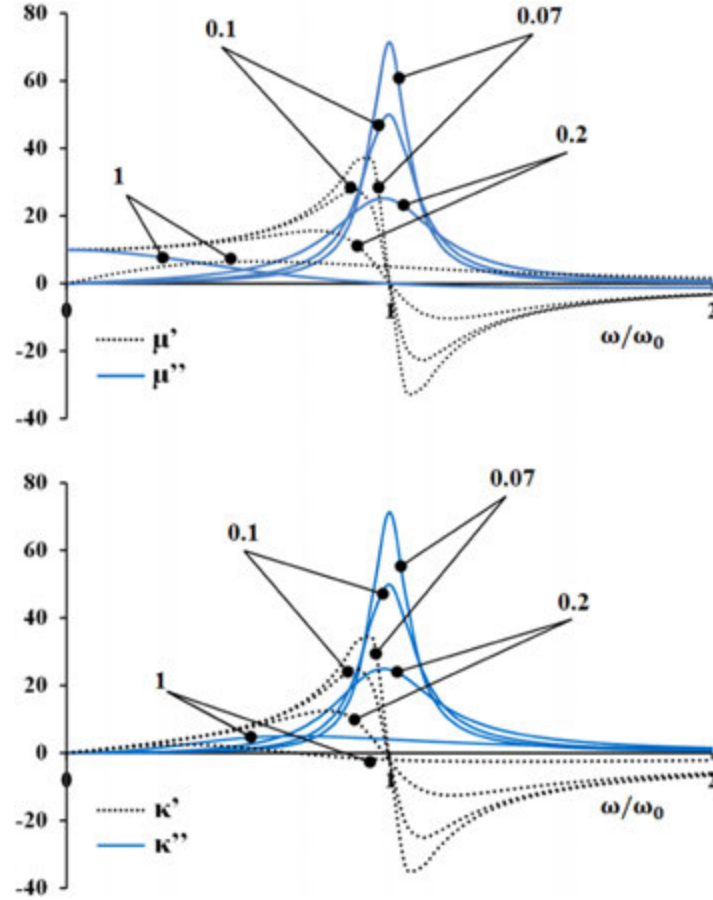


Fig. 9 Incidence of the damping factor α on the magnetic permeability spectra of $\mu(\omega/\omega_0) = 1 + \chi(\omega/\omega_0)$, and on $\kappa(\omega/\omega_0)$, where $\chi(\omega/\omega_0)$ and $\kappa(\omega/\omega_0)$ are given by Eq. (5) and Eq. (6), respectively, plotted in reduced units of angular frequency (ω_0 is the angular resonance frequency without damping). Real part (full lines) and imaginary part (dashed lines) of μ and κ are presented for different values of α (0.07, 0.1, 0.2, 1), as indicated in the figure.

The first contribution is given by the damped spin rotation. When derived from Eq. (5) and Eq. (7), the real part and imaginary part of spin-rotation susceptibility are described by Eqs. (8 and 9):

$$\chi'_S = \chi_S^{stat} \frac{\left[\left(1 - \frac{\omega^2}{\omega_0^2} (1 - \alpha^2) \right) \right]}{\left[\left(1 - \frac{\omega^2}{\omega_0^2} (1 + \alpha^2) \right) \right]^2 + 4\alpha^2 \frac{\omega^2}{\omega_0^2}} \quad (8)$$

$$\chi''_S = \chi_S^{stat} \frac{\omega}{\omega_0} \alpha \frac{\left[\left(1 + \frac{\omega^2}{\omega_0^2} (1 + \alpha^2) \right) \right]}{\left[\left(1 - \frac{\omega^2}{\omega_0^2} (1 + \alpha^2) \right) \right]^2 + 4\alpha^2 \frac{\omega^2}{\omega_0^2}} \quad (9)$$

These expressions include three parameters: The spin damping factor α , the natural angular resonance frequency ω_0 , and the DC spin-rotation susceptibility χ_s^{stat} .

The second contribution arises from magnetization process associated with domain-wall displacement. The real part and imaginary part of domain wall susceptibility are described by Eqs. (10) and (11), which were established from an analogy with the harmonic oscillator (Perekalina *et al.*, 1961; Mikami, 1973):

$$\chi'_{DW} = \chi_{DW}^{\text{stat}} \frac{\left(1 - \frac{\omega^2}{\omega_{DW}^2}\right)}{\left(1 - \frac{\omega^2}{\omega_{DW}^2}\right)^2 + \beta^2 \frac{\omega^2}{\omega_{WD}^2}} \quad (10)$$

$$\chi''_{DW} = \chi_{DW}^{\text{stat}} \frac{\beta \frac{\omega}{\omega_{DW}}}{\left(1 - \frac{\omega^2}{\omega_{DW}^2}\right)^2 + \beta^2 \frac{\omega^2}{\omega_{WD}^2}} \quad (11)$$

The involved parameters are the wall-damping factor β , the angular relaxation frequency ω_{DW} , and the DC wall susceptibility χ_{DW}^{stat} .

The angular frequency ω_R^{DW} where χ''_{DW} reaches its maximum value is given by the relation:

$$\omega_R^{\text{DW}} = \omega_{DW} \sqrt{\frac{1}{3} \left[1 - \frac{\beta^2}{2} + \sqrt{\left(\left(1 - \frac{\beta^2}{2} \right)^2 + 3} \right)} \right]}$$

The measured permeability of a $\text{Ni}_{0.5}\text{Zn}_{0.3}\text{Co}_{0.2}\text{In}_{0.02}\text{Fe}_{1.98}\text{O}_4$ polycrystalline material was fitted (Fig. 10) assuming that the permeability spectrum is the superposition of these two contributions to magnetization process. The first one was attributed to spin rotation, which is grain-size independent. Opposite, the second one, attributed to domain-wall motion, depends on the grain size (Goldman, 2006). It was observed by experimental means that the grain-size distribution presented two maxima, both over the single-domain grain size value. Accordingly, a satisfactory fit was obtained when, in addition to the spin-rotation contribution, two domain-wall contributions were involved.

In practice, even though the absorption peak that appears on the spectra of the imaginary parts of the permeability tensor components is well described by the Polder formulations if the magnetic body is saturated, the actual absorption peak is much broader in the case of a demagnetized state and is, moreover, shifted through higher frequency values for partially magnetized state. This is mainly due to two effects directly linked to the shape of the magnetic volume, and to its subdivision in magnetic domains, which were not yet taken into account. These points are addressed in the following section.

Shape-demagnetizing effects

When establishing Eq. (3), the strong hypothesis was made that the applied DC field intensity was high enough to cause the disappearance of the magnetic domains and the magnetic moment alignment in its direction. Consequently, the internal magnetic field was considered to be constant throughout the magnetic volume. Then, neither the shape of the sample nor its aspect ratio were taken into account. From a strict point of view, Polder's model is therefore valid only at the scale of the saturated ferrite of infinite size. However, the resonance frequency actually depends for a large part on the geometrical characteristics of the sample. In order to extend the validity of Polder's model to materials of finite size, Kittel took into account the shape-demagnetizing effects, which directly depend on the shape of the material (Kittel, 1951). Regarding the case of ideal ellipsoidal shaped material, the demagnetization contribution to the internal magnetic field for an isolated and uniformly magnetized volume is the dipolar-demagnetizing field $\vec{H}_d$, which is expressed as $\vec{H}_d = -\vec{N}\vec{M}$. $\vec{H}_d$ is in the opposite direction to the applied field. The diagonal demagnetization tensor $\vec{N}$ is defined so that its diagonal components verify $N_x + N_y + N_z = 1$. The N_i s are geometric factors, known as demagnetizing factors or demagnetization coefficients. At every magnetic core of finite dimensions, the demagnetizing field reduces the external field (except for a closed toroidal core of homogeneous full material submitted to an external field with the orthoradial symmetry, allowing the closure of the magnetic flux lines). For an ellipsoid with the static magnetic field in the z -direction, the internal field is uniform, and it can be written as $\vec{H}_i = \vec{H} + \vec{H}_d$ and Kittel's equation gives the resonance pulsation (also called: Ferrimagnetic resonance frequency (FMR)):

$$\omega_0 = 2\pi\mu_0\gamma \sqrt{\left(H + (N_x - N_z)M_z \right) \left(H + (N_y - N_z)M_z \right)} \quad (12)$$

Demagnetization coefficients are well-known for some ideal shapes of ferrites (Table 5). For example, the demagnetization factors of the sphere are the same in the three Cartesian directions: $N_x = N_y = N_z = 1/3$. Regarding Eq. (12), the FMR of a ferrite sphere will be similar to that of an infinite material, which is why sphere samples are used to extract the intrinsic properties of ferrites, such as their anisotropy field. For a flat cylinder with the z -axis perpendicular to its surface, $N_x = N_y = 0$ and $N_z = 1$. Following Eq. (12), the FMR will be lower than the one of an infinite material.

N_i coefficients can be rigorously calculated for ellipsoidal shapes, but only estimated for other shapes. The numerical values of demagnetizing factors have been calculated for ellipsoids (Osborn, 1945), for circular cylinders (Chen *et al.*, 1991), and for rectangular prisms (Aharoni, 1998).

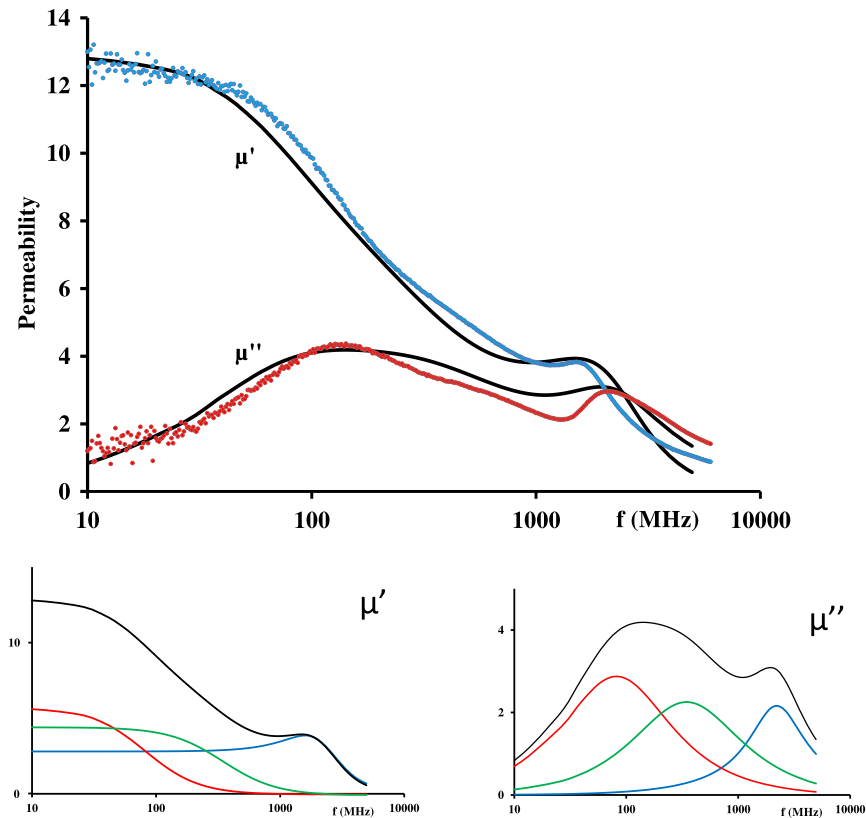
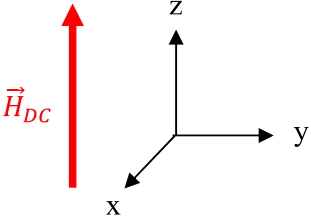


Fig. 10 Permeability spectra of a $\text{Ni}_{0.5}\text{Zn}_{0.3}\text{Co}_{0.2}\text{In}_{0.02}\text{Fe}_{1.98}\text{O}_4$ sintered ferrite. Upper figure: Experimental values are represented by symbols. Solid lines show total permeability combined with spin rotation and domain wall motion components (black lines). Their respective contributions to the total real permeability (μ') and imaginary permeability (μ'') (both shown by black lines) are detailed in the lower figures: Spin rotation (blue lines) and domain wall motion (red and green lines).

Table 5 Demagnetization coefficients for different standard shapes of ferrites

	N_x	N_y	N_z
			
Sphere	1/3	1/3	1/3
	0	0	1
	1/2	0	1/2
	0	0	1

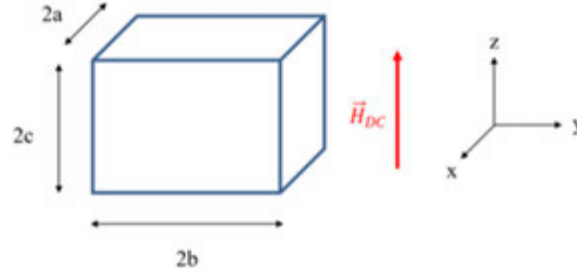


Fig. 11 Rectangular prism with a DC field applied along z-axis.

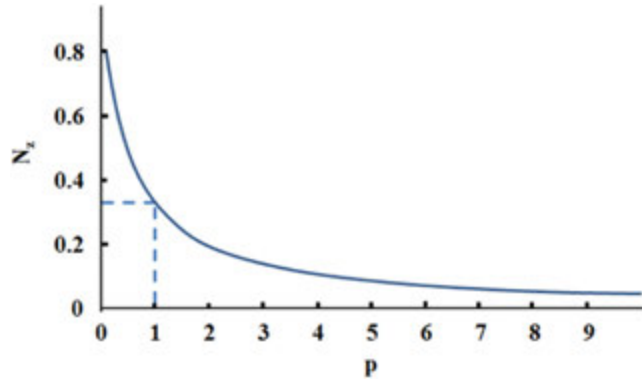


Fig. 12 Evolution of the N_z coefficient as a function of $p = c/a$ in the case of a rectangular prism with $a = b$ (calculated from Aharoni's equations).

In the case of rectangular prisms, whose dimensions are $2a$, $2b$, and $2c$ (Fig. 11), Aharoni proposed analytical formulas that make it possible to estimate demagnetization coefficients along the three Cartesian coordinates. In general, these equations are complex. In the particular case of a square cross-section, $a = b$, the N_z coefficient can be calculated using the following equations:

$$\begin{aligned} \pi N_z = & \left(p - \frac{1}{p}\right) \ln\left(\frac{\sqrt{p^2 + 2} + 1}{\sqrt{p^2 + 2} - 1}\right) + \frac{2}{p} \ln(\sqrt{2} + 1) + p \ln\left(\frac{\sqrt{p^2 + 1} - 1}{\sqrt{p^2 + 1} + 1}\right) \\ & + 2 \arctan\left(\frac{1}{p\sqrt{p^2 + 2}}\right) + \frac{2(1 - p^2)}{3p} \sqrt{p^2 + 2} + \frac{2(1 - p^3)}{3p} - \frac{2^{3/2}}{3p} \end{aligned} \quad (13)$$

where $p = c/a$.

The evolution of the N_z coefficient of a square prism ($a = b$) as a function of shape factor p calculated using Aharoni equations is shown in Fig. 12. For low values of p , the case corresponding to a flat plate, N_z is close to 1 in accordance with Table 2. The special case of a cube ($a = c$ leading to $p = 1$) leads to a value of $1/3$, similar to the case of a sphere (Fig. 12).

For a flat cylinder, a shape that is mostly used in microwave circulators, Helszajn (2008) established relationships between the thickness of a cylinder H , its radius R , and approximate demagnetizing coefficients along the three Cartesian coordinates, as follows:

$$N_z \approx 1 - \left(\frac{H}{2R}\right) \left[1 + \left(\frac{H}{2R}\right)^2\right]^{-1/2} \quad (14)$$

$$N_x \approx N_y \approx \frac{1}{2}(1 - N_z) \quad (15)$$

As an example, for a thin disk with a height $H = 0.1$ mm and a radius $R = 1.25$ mm, these formulas give $N_z = 0.959$, $N_x = N_y = 0.02$. Such a flat cylinder gives rise to a strong demagnetizing field along the z -direction so that internal field will be lower than the applied field (Fig. 13).

An ellipsoid has the property that when a uniform DC magnetic field is applied to it, the demagnetizing field is uniform throughout the sample. In practice, however, the shape of the ferrite sample is rarely an ellipsoid, and consequently nonuniformity of the internal field is frequent. Ferromagnetic bodies with arbitrary shapes do not have uniform spatial distribution of demagnetizing fields and the N_z coefficient calculated by using Aharoni formulas is only an approximation. An example of the spatial

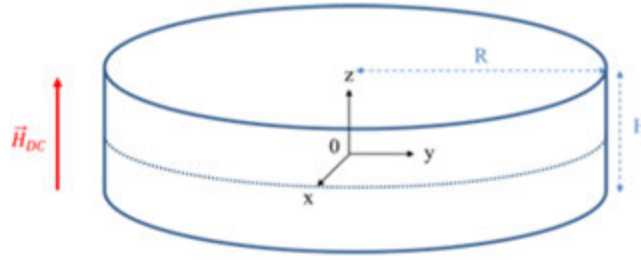


Fig. 13 Ferrite cylinder with a DC field applied along z-axis (radius R and thickness H).

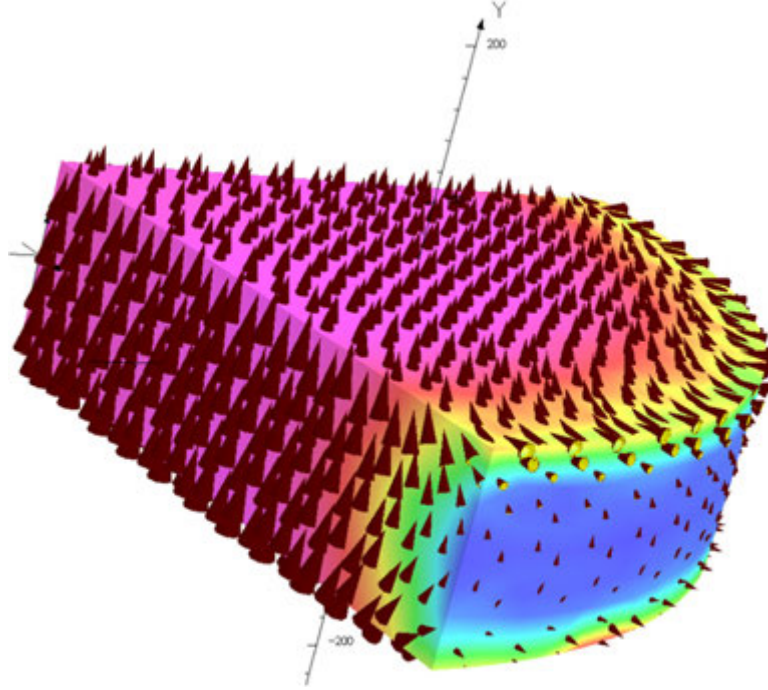


Fig. 14 Example of the spatial distribution of the internal magnetic field for a ferrite puck polarized by an uniform external magnetic field (analysis performed by using OPERA3D packages, OPERA3D, Vector Fields. Kindlington, Oxford.).

distribution of the internal magnetic field for a ferrite puck polarized by a uniform external magnetic field is presented in **Fig. 14**. If this internal field inhomogeneity is not taken into account, it may have a detrimental impact on the operations of the device that would use such a ferrite. This will be presented in greater details below.

Analytical equations making it possible to calculate the evolution of N_z coefficient as a function of the radius in a flat cylinder of ferrite under a uniform DC magnetic field were proposed by [Helszajn \(2008\)](#). In this model, two different equations are used to calculate $N_{z,center}$ at the center of the sample and $N_{z,edge}$ at its edge ([Joseph and Schlöemann, 1965](#)). This set of equations was unified by Helszajn in order to calculate the spatial distribution of N_z in a disk of ferrite.

$$N_{z,center}(r, 0) = 1 - \frac{(H/2R)}{[1 + (1 + (H/2R)^2)]^{1/2}} - \left[\frac{3(H/2R)}{[1 + ((H/2R)^2)]^{3/2}} - \frac{3(H/2R)^3}{[1 + ((H/2R)^2)]^{5/2}} \right] \left(\frac{r}{2R} \right)^2 \quad (16)$$

$$N_{z,edge}(r, 0) = \frac{1}{2} + \left(\frac{1}{\pi} \right) \tan^{-1} \left[\left(\frac{2R}{H} \right) - \left(\frac{2r}{H} \right) \right] \quad (17)$$

$$N_{z,global}(r, 0) = (N_{z,center} - N_{z,edge}) [1 - (r/R)^4] + N_{z,edge} \quad (18)$$

Fig. 15 shows the evolution of the N_z coefficient as a function of the ratio between the distance to the center r and the radius R of a ferrite disk. This calculation was performed for a flat disk of thickness $H = 0.1$ mm and radius $R = 1.25$ mm. These results demonstrate that demagnetization coefficients are strongly inhomogeneous in such ferrite disks with a strong decrease from the center of the disk ($N_z = 0.96$) to the edge ($N_z = 0.5$).

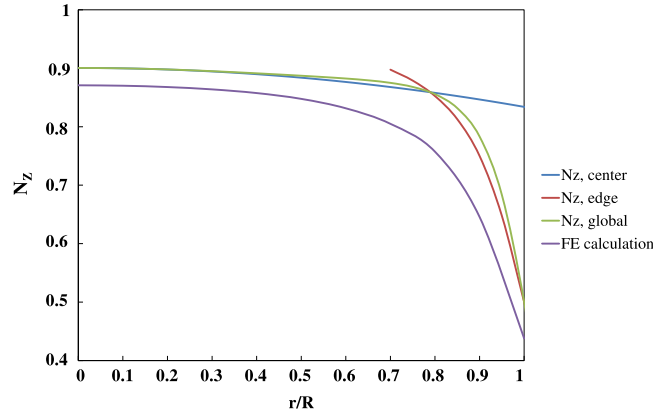


Fig. 15 Demagnetizing factor of a flat cylinder as a function of the distance to the center r/R calculated using Eqs. (8)–(10) and compared with FE simulation.

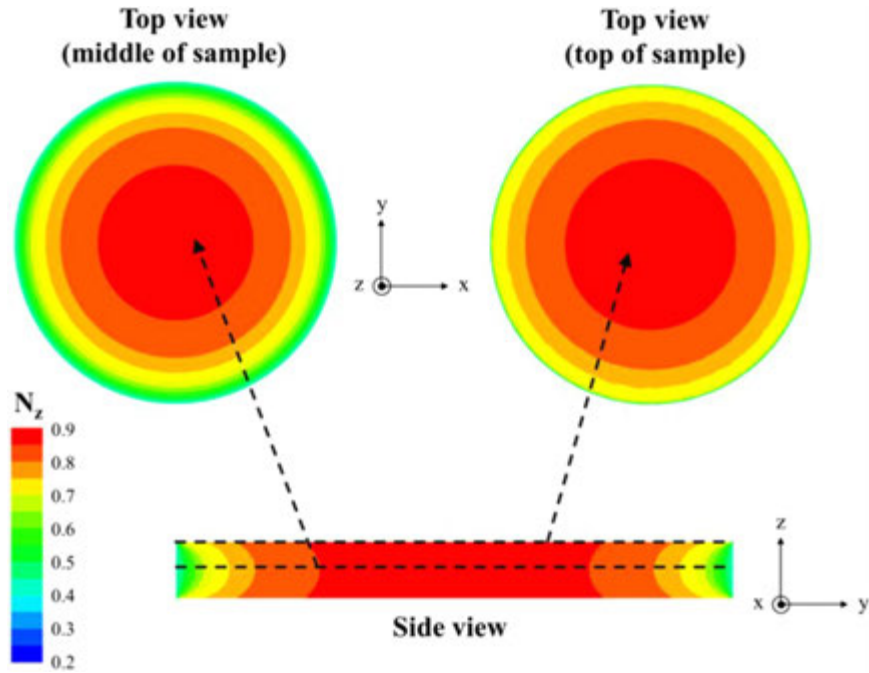


Fig. 16 Spatial distribution of the N_z coefficient in a flat disk of ferrite calculated with FE simulator.

This variation was compared with finite element calculation. The simulation was performed for a flat ferrite disk with the same geometry ($H = 0.1$ mm, $R = 1.25$ mm) and a saturation magnetization $M_s = 23,873$ A m⁻¹ under a uniform applied static magnetic field $H_{DC} = 70,000$ A m⁻¹. The variation of N_z as a function of r/R at the midheight of the disk is shown in Fig. 16. Although the trend is similar to the model proposed by Joseph, Schlöemann, and Helzasjn, one should note that the values are slightly lower.

In reality, the situation in such ferrite samples is actually more complex than a single variation of a demagnetizing field in the plane of the disk. Fig. 16 thus shows the spatial distribution of the demagnetizing coefficient N_z parallel and perpendicular to the plane of a ferrite disk. Even for a disk with a very low thickness to height ratio (H/R), one should note a nonnegligible variation of N_z along the thickness of the disk, thus inducing a different spatial distribution of N_z at the top and the middle of the sample.

The effect of shape, and thus of the demagnetizing field, can be taken into account in the calculation of dynamic permeability by using the following equations (H_{DC} applied along z -axis):

$$\mu = 1 + \frac{\omega_m(\omega_0 + \omega_m(N_y - N_z)) + j\omega\alpha\omega_m}{(\omega_0 + \omega_m(N_x - N_z))(\omega_0 + \omega_m(N_y - N_z)) - \omega^2(1 + \alpha^2) + 2j\omega\alpha\omega_0} \quad (19a)$$

$$\kappa = \frac{\omega\omega_m}{(\omega_0 + \omega_m(N_x - N_z))(\omega_0 + \omega_m(N_y - N_z)) - \omega^2(1 + \alpha^2) + 2j\omega\alpha\omega_0} \quad (19b)$$

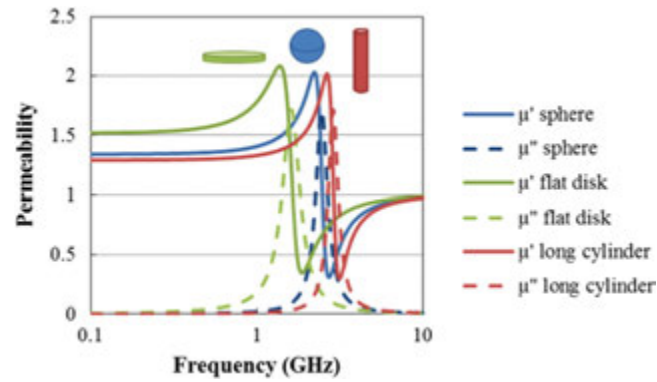


Fig. 17 Calculated permeability for different shapes of ferrite ($M_s = 23873 \text{ A m}^{-1}$, $\alpha = 0.1$, $H_{DC} = 70,000 \text{ A m}^{-1}$).

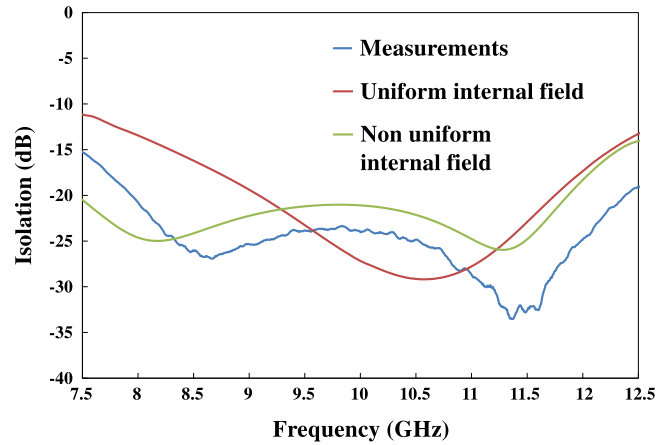


Fig. 18 Isolation of a LTCC circulator in the 7.5–12.5 GHz frequency band: Comparison between measurement, simulation with a uniform internal field and simulation with a nonuniform internal field.

As an example, permeability was calculated for different shapes of samples in the case of a ferrite (Fig. 17), with the following properties: $M_s = 23,873 \text{ A m}^{-1}$, $\alpha = 0.1$, $H_{DC} = 70,000 \text{ A m}^{-1}$. As $N_z = N_y = N_x$ for a sphere, calculated permeability is similar to that of an infinite ferrite (without taking into account shape effect); FMR is thus only dependent on the internal magnetic field. This consideration explains why spherical samples are used to extract the anisotropy field of ferrites. A flat sample (flat disk) leads to a lowering of FMR due to the effect of the strong demagnetizing fields. In contrast, long samples (a long cylinder) induce an increase of FMR due to the decrease of N_z coefficient compared with spherical samples. Moreover, the shape of the ferrite sample has an impact on the level of permeability at frequencies lower than the FMR. As an example, at 200 MHz, the permeability of a flat disk will be 1.53, and one of a long cylinder will be 1.29. The difference is greater than 18% and can lead to a frequency shift when such materials are used to fabricate antennas or filters.

Taking into account shape effect and magnetizing field inhomogeneity can be crucial in the modeling of ferrite-based devices. As an example, in [Thalakkatukulathil et al. \(2018\)](#), a microstrip circulator in low temperature cofired ceramics technology was designed and measured. This component uses a ferrite disk biased by a magnet and surrounded by a dielectric substrate. At first, the design was performed by considering a uniform internal field in the ferrite sample. Measurement showed that the bandwidth in which isolation level is lower than -15 dB was broader in measurement than in simulation (Fig. 18). Then, multiphysics simulation, which allows taking into account the nonuniformity of internal static magnetic field, was performed by coupling a magnetostatic analysis of the structure and an electromagnetic computation. Such analysis provides better agreement between simulation and measurement and demonstrates the possibility to consider the spatial inhomogeneity of internal static magnetic field in the ferrite sample in the design of ferrite-based devices.

Dynamic demagnetizing aspect: The Polder–Smit effect

In the case of a unsaturated magnetic volume, the interactions between the magnetic domains (Fig. 1) lead to dynamic demagnetizing effects.

This situation was studied by [Polder and Smit \(1953\)](#). The authors established that the AC field acting on the domains is not only constituted by the field associated with the electromagnetic wave, but also includes dynamic demagnetizing fields depending on the orientation of the domains, as well as to the material's shape. For a better understanding of the phenomenon, we will

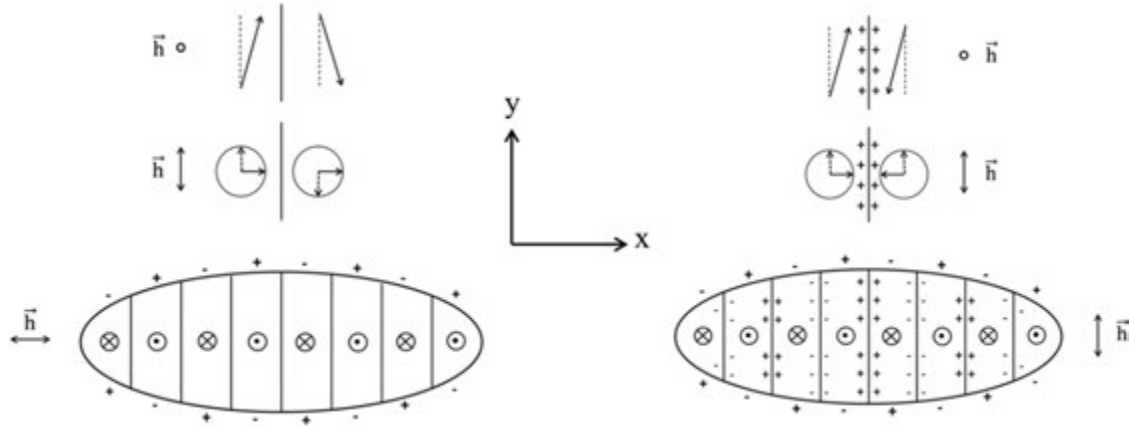


Fig. 19 Depiction of the Polder-Smith effect. Adapted from Polder, D., Smit, J., 1953. Resonance phenomena in ferrites. *Rev. Mod. Phys.* 25 (1), 89–90.

consider a demagnetized ellipsoidal material, with lamellar magnetic domains, as depicted in **Fig. 19**. From domain to domain, the magnetization points in the reverse directions are called “up” and “down.” When exposed to an AC field $\vec{h}$ the “up” and “down” magnetizations will precess in opposite way. If $\vec{h}$ is perpendicular to the magnetic walls, the normal component of magnetization $\vec{m}$ is continuous and therefore no dynamic demagnetizing field exists. However, if $\vec{h}$ is parallel to the magnetic walls, then there is no continuity of the normal component of magnetization $\vec{m}$, and a dynamic demagnetizing field appears.

The intensities of the dynamic demagnetizing fields are distributed in the range $[0, M_s]$. The corresponding resonance pulsations (or frequencies) vary between $\omega_{\min} = 2\pi\mu_0\gamma H$ and $\omega_{\max} = 2\pi\mu_0\gamma(H + M_s)$. Consequently, the χ'' peak is enlarged, meaning that the absorption is generated between these two pulsations.

Modeling the dynamic permeability of polycrystalline ferrites in any magnetization state

In actual materials nonuniformity of the internal field in ferrite prevents some regions from being saturated. Therefore other formulations of the permeability tensor are necessary to accurately predict the dynamic permeability of the ferrite medium. Different empirical models have been proposed that provide formulas for the elements of $\vec{\mu}$. [Schlömman \(1970\)](#) studied the case of a demagnetized body, the magnetic domains of which were randomly distributed along the three directions. Taking into account the magnetic domains magnetized along opposite directions, the off-diagonal elements of the tensor vanish. Then a mean permeability can be calculated. On the basis of Schlömman’s model, and assuming a magnetic body constituted of up and down magnetic domains, Igarashi and Naito calculated the permeability tensor elements ([Igarashi and Naito 1977, 1981](#)). Under the hypothesis that the magnetocrystalline field is the only contribution through the DC internal field, and also assuming that the actual frequency is far from the resonance frequency, [Rado \(1953\)](#) expressed the permeability tensor elements based on a spatial average of the magnetic domains. Starting from experimental results on the measurements of permeability tensor elements, [Green and Sandy \(1974\)](#) deduced an empirical expression of the tensor, which suits with Schlömman theory. However, the first theoretical and predictive model that allowed the determination of the permeability tensor of polycrystalline ferrites regardless of their magnetization state was proposed by [Gelin and Berthou-Pichavant \(1997\)](#) and [Gelin et al. \(2005\)](#). Thereafter [Gelin and Queffelec \(2008\)](#) introduced the generalized permeability tensor model that improved accuracy in the description of the magnetic losses phenomena. This model remains the only predictive model for the permeability tensor of polycrystalline ferrites in any magnetization state ([Guennou et al., 2007](#); [Cortes et al., 2015](#); [Le Gouellec et al., 2016](#)).

Microwave Passive Components Using Ferrites

Wave Propagation in Magnetized Ferrimagnetic Materials

The aim of this section is to briefly describe the basis of physical phenomena (usually termed Faraday effect) that is exploited by nonreciprocal microwave devices, such as circulators and isolators. A wave that propagates in a parallel manner to a static field $\vec{H}$ can be represented by two contrarotating circularly polarized components. Permeabilities can then be defined for the positive and negative rotation directions. The positive direction is clockwise when viewed in the direction of $\vec{H}$.

We consider an electromagnetic wave to be linearly polarized, with the direction of propagation directed along the static field $\vec{H}$, arbitrarily assumed to go along the z-axis. The electromagnetic field $\vec{h}$ can be divided into two components with clockwise circular polarization $\vec{h}_+$ and counterclockwise circular polarization $\vec{h}_-$ around z. An effective magnetic permeability, μ^+ and μ^- respectively, is calculated for each of them ([Epstein, 1956](#)) as follows:

$$\mu^{\pm} = \mu \pm \kappa \quad (20)$$

where μ and κ are given by [Eqs. \(5\) and \(6\)](#).

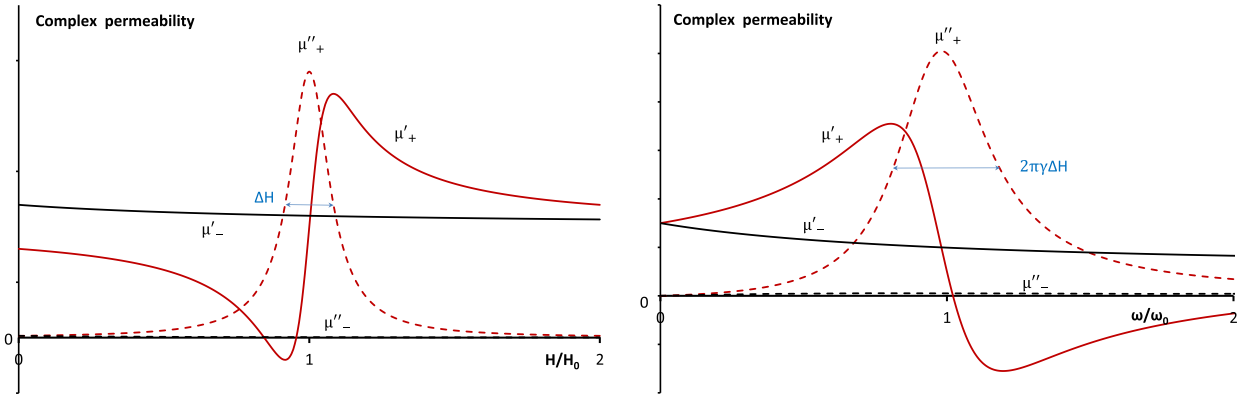


Fig. 20 Plots of the real and imaginary parts of the effective magnetic permeabilities μ^+ and μ^- as a function of the reduced field (left side) and of the reduced angular frequency (right side).

Their real and imaginary parts expressed as:

$$\mu^{+'}(\omega) = 1 + \frac{\omega_m(\omega_0 - \omega)}{(\omega_0 - \omega)^2 + \alpha^2\omega^2} \quad (21a)$$

$$\mu^{+''}(\omega) = \frac{\omega_m\alpha\omega}{(\omega_0 - \omega)^2 + \alpha^2\omega^2} \quad (21b)$$

$$\mu^{-'}(\omega) = 1 + \frac{\omega_m(\omega_0 + \omega)}{(\omega_0 + \omega)^2 + \alpha^2\omega^2} \quad (21c)$$

$$\mu^{-''}(\omega) = \frac{\omega_m\alpha\omega}{(\omega_0 + \omega)^2 + \alpha^2\omega^2} \quad (21d)$$

The plots in **Fig. 20** (right side) show that $\mu^{-''}$ is very close to zero, and that $\mu^{-'}$ remains almost constant. This demonstrates that the counterclockwise polarized wave weakly interacts with the magnetic material, whereas the propagation of the clockwise polarized wave is strongly influenced by the propagating magnetic medium.

An alternative expression is often presented that gives the complex permeability as a function of the static field. Remembering that $\omega_0 = \gamma H$ and $\omega_m = \gamma M_s$, the complex permeability μ^+ can be written as follows:

$$\mu^+(H) = 1 + \frac{\omega_m(\omega_0/\gamma - H)}{(\omega_0/\gamma - H)^2 + \frac{\Delta H^2}{4}} \quad (22a)$$

$$\mu^{+''}(H) = \frac{\omega_m \frac{\Delta H}{2}}{(H - \omega_0/\gamma)^2 + \frac{\Delta H^2}{4}} \quad (23b)$$

ΔH is the gyromagnetic line width, defined as the half-width of the resonance peak $\mu^{+''}$.

Fig. 20 shows components $\mu^{+'}$ (dispersive) and $\mu^{+''}$ (dissipative) of the permeability tensor elements, as functions of the reduced applied field (H/H_0) and of the reduced applied frequency (ω/ω_0). The medium was assumed to be magnetically saturated.

The expressions for $\mu^{-'}$ and $\mu^{-''}$ are as follows:

$$\mu^{-'}(H) = 1 + \frac{\omega_m(\omega_0/\gamma + H)}{(\omega_0/\gamma + H)^2 + \frac{\Delta H^2}{4}} \quad (24a)$$

$$\mu^{-''}(H) = \frac{\omega_m \frac{\Delta H}{2}}{(H + \omega_0/\gamma)^2 + \frac{\Delta H^2}{4}} \quad (24b)$$

Microwave Magnetic Losses

In order to measure losses at ferromagnetic resonance, experiments usually consist of power absorption measurements: A constant high frequency AC field is applied simultaneously to a DC field of variable magnitude, which should be strong enough to ensure magnetic saturation. A plot of the absorbed power as a function of the DC field magnitude, at given frequency, makes it possible to obtain the resonance peak. ΔH is the peak width at half-power, and is sometimes known as the absorption peak, or linewidth. It defines the magnetic losses at frequencies close to the magnetic gyroresonance appearing when the static magnetic field value allows an in-phase precession of the magnetic moments with the electromagnetic field h . Apart from the case of microwave-absorbing materials, which is beyond the scope of this chapter, the absorption peak ΔH should be narrow. However, in a polycrystalline material the actual internal field depends on many factors: Magnetic anisotropy, magnetization state, porosity, eddy currents, and inhomogeneous demagnetization

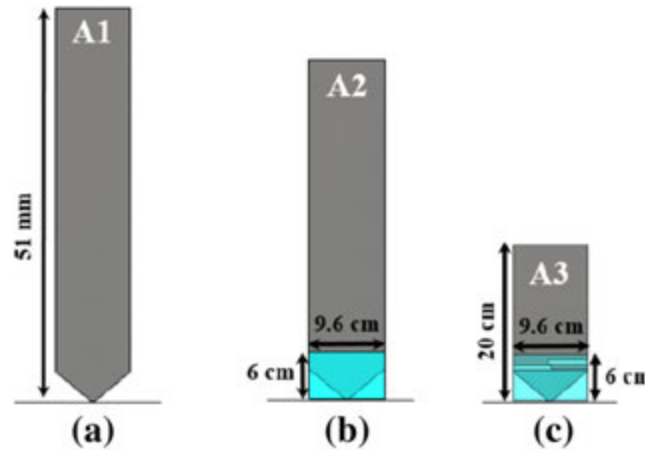


Fig. 21 Example of antenna's length reduction allowed by the use of a magnetodielectric ferrite (the ferrite is in blue color). The operating antenna frequency is 130 MHz. Various antennas topologies were studied, the more important antenna miniaturization reached 61%. Reproduced from Kabalan A., Sharaiha A., Tarot A.-C., 2019. Enhance the impact of the magneto-dielectric materials to miniaturize a planar monopole antenna. In: Proceedings of the URSI Asia-Pacific Radio Science Conference (AP-RASC), March 9–15, 2019. doi:10.23919/URSIAP-RASC.2019.8738556.

(Alvarez *et al.*, 2010). Consequently, the broadening of ΔH is due not only to the intrinsic damping of the spins (ΔH_{int}), but it contains in addition contributions from inner demagnetizing effects (ΔH_p), linked to porosity, or more generally to a residual nonmagnetic part, and to the influence of the magnetocrystalline anisotropy field H_A . Significant contributions to line width also arise from inhomogeneous demagnetization field. An expression commonly used for the total linewidth ΔH was proposed by Schlömann (1958): $\Delta H = \Delta H_{\text{int}} + 1.5pM_s + H_A$ where ΔH_{int} is the intrinsic line width and p represents the volume fraction of nonmagnetic part. The relationship between the damping factor α and ΔH_{int} , in the case of a saturated material, is $\alpha = \gamma \frac{\Delta H}{2\omega}$ (ω being the angular frequency at which ΔH is measured). In a first approximation, $H_A = \frac{K_1}{\mu_0 M_s}$, where K_1 is the first-order magnetocrystalline anisotropy constant.

However, ΔH , as defined by the Polder model of precession close to the gyroresonance, is unable to describe the full range of experimental data. This is why a complementary means to describe the magnetic losses distant from the gyroresonance is needed: An effective peak can be extrapolated from the values of the permeability away from resonance. ΔH_{eff} is the effective linewidth of the half-power peak of a Lorentz curve fitting experimental values away from the resonance. ΔH_{eff} corresponds to the off-resonance magnetic losses, and its values are lower than that of ΔH . This point will be illustrated in Section “Characterization of Magnetized Samples”.

Antenna Miniaturization

Miniaturization of electronic devices for mobile communication has led to increasing demands for the reduction of antenna dimensions. Antenna downsizing is one of today's most important challenges for antenna designers (Skrivervik *et al.*, 2001). Antenna miniaturization for wireless communication systems was first achieved through optimizing antenna design, but no other notable breakthroughs have been reported in this domain. The use of high-permittivity substrates also allow size reduction, but causes a considerable decrease in antenna efficiency and bandwidth (Hwang *et al.*, 1995; Hansen, 1982). For applications in the low-UHF frequency band (300–862 MHz), the use of magnetodielectric substrates is expected to overcome these limitations by offering larger bandwidths and improved efficiency (Hansen and Burke, 2000; Mosallaei and Sarabandi, 2004). Indeed, it has been shown (Niamien *et al.*, 2011; Niamien *et al.*, 2014) that, although the permittivity (ϵ') increases the impact of losses, as well as the stored energy, the permeability (μ') plays the opposite role by decreasing them. As a consequence, the negative impact of ϵ' on radiation efficiency and bandwidth is counterbalanced by the positive impact of μ' . Even through at frequencies lower than 30 MHz, the contribution of the domain walls to the permeability typically induces prohibitive losses. Several solutions exist that allow this problem to be avoided: Doping by Cobalt allows domain walls pinning, the use of monodomain particles may also make it possible to limit losses.

Spinel ferrites, which have $\epsilon' > 1$ and $\mu' > 1$, together with low-loss tangents (both dielectric and magnetic), are among the best candidates for antenna downsizing (Mattei *et al.*, 2011; Huitema *et al.*, 2013; Kong *et al.*, 2013; Petrov *et al.*, 2008; Kabalan *et al.*, 2019).

Fig. 21 shows the antenna's length reduction allowed by the use of a magnetodielectric ferrite (the ferrite is in blue color). In this example the operating antenna frequency is 130 MHz. In order to preserve a light weight to the device, the ferrite material was placed only where the electrical currents were large (Kabalan *et al.*, 2019) Various antennas topologies were studied, and the more important antenna downsizing reached 61% (Fig. 21(c)).

Isolators and Circulators

Nonreciprocal devices such as circulators and isolators are among the most important applications of self-biased hexaferrites (which are magnets that remain in a magnetized state in the absence of an externally applied magnetic field) in the microwave frequency range. These devices make it possible to isolate the incoming signal from the outgoing signal in transmitter/receiver

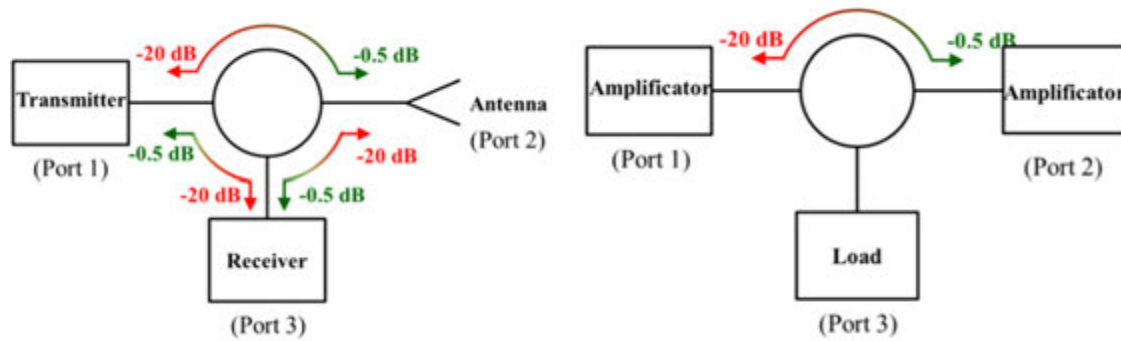


Fig. 22 Schematic representation of signal transmission through a circulator (left-hand diagram) and an isolator (right-hand diagram). For devices such as these ones, the propagation of electromagnetic waves is different in direct (port 1 to port 2) and reverse (port 2 to port 1) directions of propagation. Adapted from Harris, V.G., Sokolov, A.S., 2019 The self-biased circulator: Ferrite materials design and process considerations. *J. Supercond. Novel Magn.* 32, 97–108.

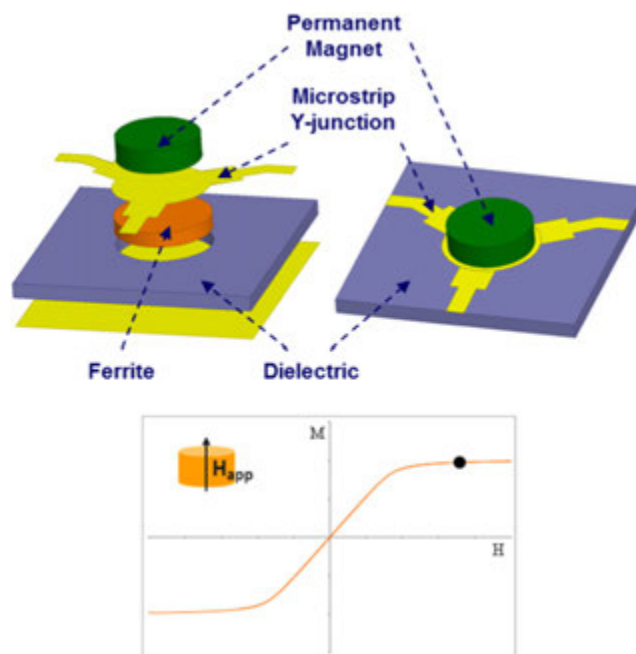


Fig. 23 Drawing of a Y-junction circulator (exploded view in the figure to the left). The ferrite puck is magnetized at saturation by the prominent bias permanent magnet.

(Tx/Rx) modules (Fig. 22). For a device such as a circulator, the propagation of electromagnetic waves is different in direct (port 1 to port 2) and reverse (port 2 to port 1) directions of propagation. Microwave systems that use a single antenna for signals emission and reception need in turn to use a circulator.

The magnetic polarization of nonreciprocal devices can be achieved through permanent magnets, placed on both sides of the ferrite (Fig. 23). However, because doing this goes against the miniaturization and lightness objectives of modern communication applications, it is highly desirable to use self-polarized hard ferrites with a reduced remanent magnetization value near $M_R/M_S = 0.85$ (Fig. 24). The device operates then at the remanent state of the ferrite. In this field, hard ferrites show great potential for integration into nonreciprocal microwave devices at frequencies from 10 to 40 GHz (Pullar, 2012; Sakai *et al.*, 2006; Harris *et al.*, 2009).

Isolators are another example of nonreciprocal microwave devices. They are used when it is necessary to isolate the device of a high-power amplifier (Fig. 22).

Microwave Characterization Methods

In this section, we summarize some characterization methods of material properties at microwave frequency. An exhaustive review of characterization methods can be found in Chen *et al.* (2004). The electromagnetic parameters of interest for microwave applications are the complex permittivity, the initial complex permeability for demagnetized materials, the complex permeability

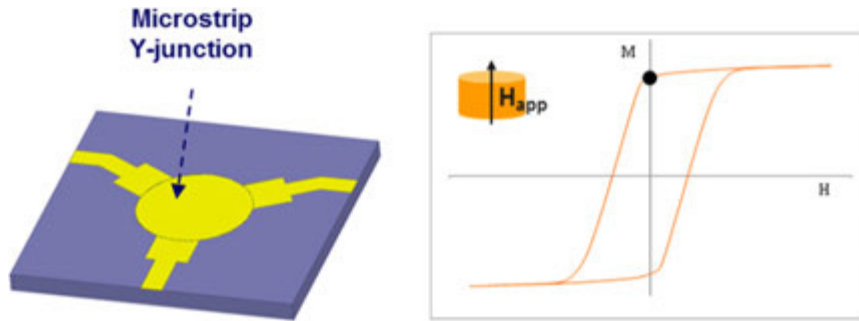


Fig. 24 Drawing of a self-biased Y-junction circulator. The self polarized hexaferrite puck (BaM type), placed below the microstrip-Y junction, is used at the remanence.

tensor, and the ferromagnetic linewidth for magnetized materials. Measurement methods for these parameters generally fall into two categories: (1) Resonant methods, which allow high accuracy but narrowband measurements and (2) nonresonant methods, which allow broadband measurements but low accuracy. All of them use network analyzers to measure S parameters of a measurement cell, which takes the form of a resonant cavity in the first case and a transmission line or waveguide in the second case.

Characterization of Demagnetized Samples

If the ferrite is demagnetized, then the sample shows isotropic properties and its permittivity and permeability are complex scalar quantities that can be determined from the measurements of two measured complex S parameters: The reflection coefficient S₁₁ and transmission coefficient S₂₁ (Baker-Jarvis, 2005). A coaxial transmission line (Fig. 25) and a rectangular waveguide are the broadband characterization methods most frequently used because analytical relationships exist between the S parameters, dimensions of the measurement cell, and electromagnetic parameters when samples completely fill the cross-section of the cell (Weir, 1974; Nicolson and Ross, 1970).

The coaxial transmission line method offers many advantages over the rectangular waveguide method. First, the frequency band is broader because there is no lower cut-off frequency in coaxial line for the transverse electromagnetic mode, and second, the sample's shape is well adapted to the magnetic field pattern avoiding demagnetizing effects. The usual measurement frequency band in coaxial method starts from 1 MHz (depending on the Vectorial Network Analyser sensibility) up to 18 GHz (the frequency of occurrence of the first higher-order mode in APC7 standard).

Fig. 26 shows the measured permittivity and permeability for a polycrystalline demagnetized nickel ferrite. The imaginary part of the initial permeability shows two maxima: The first, around 80 MHz, is associated with the domain wall motion, and the second, close to 1800 MHz, is the gyromagnetic resonance related to the anisotropy field H_k ($H_r = \gamma H_k$). The permittivity of ferrite is generally not dispersive and remains constant over the whole frequency band, with values ranging from 10 to 20 but generally remaining close to 15.

Characterization of Magnetized Samples

If the ferrite is magnetized, the sample shows anisotropic properties and the permeability becomes a complex tensor quantity with extradiagonal terms (the permittivity does not depend on the magnetic state of the sample and remains a scalar quantity). The nondiagonal permeability tensor is the most important property used in microwave devices to reach nonreciprocal behavior.

For saturated ferrites, the permeability is well described by the Polder's model. The gyromagnetic resonance linewidth ΔH is then the fundamental property used to describe the dynamic magnetic losses. Resonance linewidth ΔH is defined as the difference between the applied field values at which absorption is half of the maximum value. The standard method for measuring the resonance linewidth ΔH of ferrites is using resonant cavities as described in the IEC standard (IEC, 1982). This method is based on the cavity perturbation theory, which requires a sample's dimensions to be smaller than one quarter of the wavelength of the microwave radiation in the sample. This method is limited to a single frequency that corresponds to the resonant frequency of the measurement cavity (generally operating around 9.4 GHz).

Fig. 27 shows the absorption of the ferrite as a function of the applied magnetic field. ΔH is the linewidth of the Lorentzian curve along the experimental points near the resonance ($H_{dc} \approx H_r$). ΔH_{eff} is the linewidth of the Lorentzian curve along the experimental points outside the vicinity of the resonance ($H_{dc} \neq H_r$).

For partially magnetized ferrites, various characterization techniques have been developed to characterize the anisotropic properties of the materials. In the resonant method, the aim is to identify and control the direction of the microwave magnetic field in the cavity so that the corresponding component of the permeability tensor can be measured. Most resonant methods use

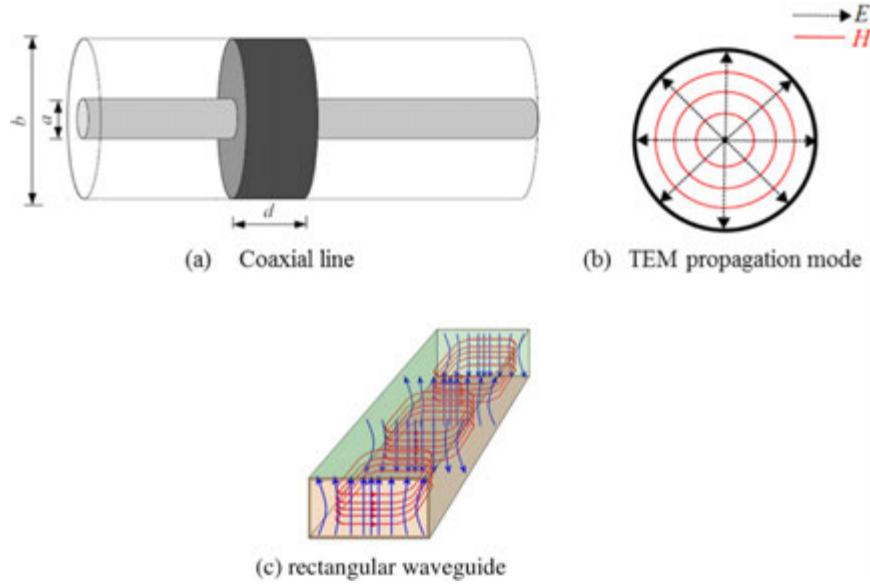


Fig. 25 Sketch and electromagnetic field pattern of coaxial transmission line (a, b).

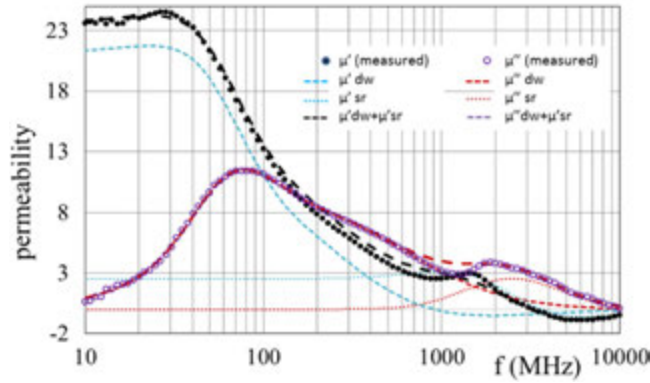


Fig. 26 Measured permeability of NiFeO material from coaxial transmission line method, and its fit by spin rotation and domain wall contributions. The labels dw and sr are for domain wall and spin rotation, respectively. Spin rotation and domain wall movements contributions to the magnetization are distinguished. The total permeability is the sum of these two contributions.

cylindrical or rectangular degenerate mode cavities or a ring resonator (Ogasawara *et al.*, 1976; Krupka and Geyer, 1996). These resonant methods only work at single or several discrete frequencies and are very suitable for low-loss materials but not pertinent at the resonance frequency where the values of losses are high.

In reflection/transmission methods, it is essential to measure more than two S parameters in order to determine the three unknown electromagnetic parameters ϵ , μ , and the extradiagonal term κ . To do this, measurement cells are asymmetrically filled to present nonreciprocal behavior taking advantage of the field displacement effect in the magnetized magnetic material.

Fig. 28 shows schemes of two methods based on (1) an asymmetrically loaded rectangular waveguide (Queffelec *et al.*, 2000) and (2) an asymmetrically loaded strip line (Lezaca *et al.*, 2010, 2011). In the latter method, the measurement cell consists of an asymmetric strip line partially filled with the material to be characterized. Two identical magnetic samples are placed above and below the metal strip. Two dielectrics with different permittivity values (ϵ_1 , ϵ_2) are placed on each side of the strip line to ensure the nonreciprocal behavior of the structure ($S_{12} \neq S_{21}$) when the magnetic sample is magnetized. In the forward direction of EM wave propagation, there is a strong wave-material interaction with dielectric 1. In the backward direction, thanks to the field displacement effect, the EM wave interacts with dielectric 2. This nonreciprocal nature of the measurement cell makes it possible to determine the diagonal component μ and extradiagonal component κ of the permeability tensor. This method is based on a full-wave analysis, taking into account higher-order modes (propagated in the loaded section and evanescent in the air sections of the measurement cell). By associating specific broadband optimization it

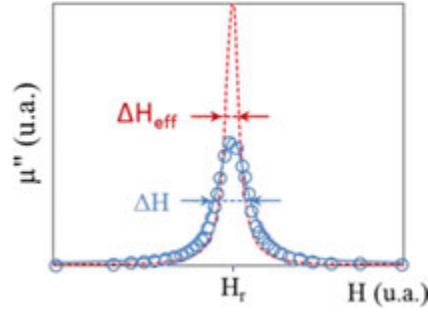


Fig. 27 Measured magnetic losses from a cavity method at 9.4GHz. ΔH is the linewidth of the Lorentzian curve near the resonance ($H_{dc} \approx H_r$). ΔH_{eff} is the linewidth of the Lorentzian curve outside the vicinity of the resonance ($H_{dc} \neq H_r$).

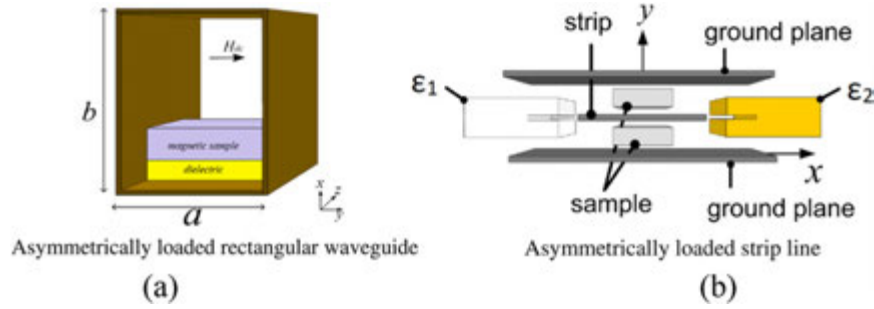


Fig. 28 Diagram of asymmetrical cells: Rectangular waveguide and strip transmission line.

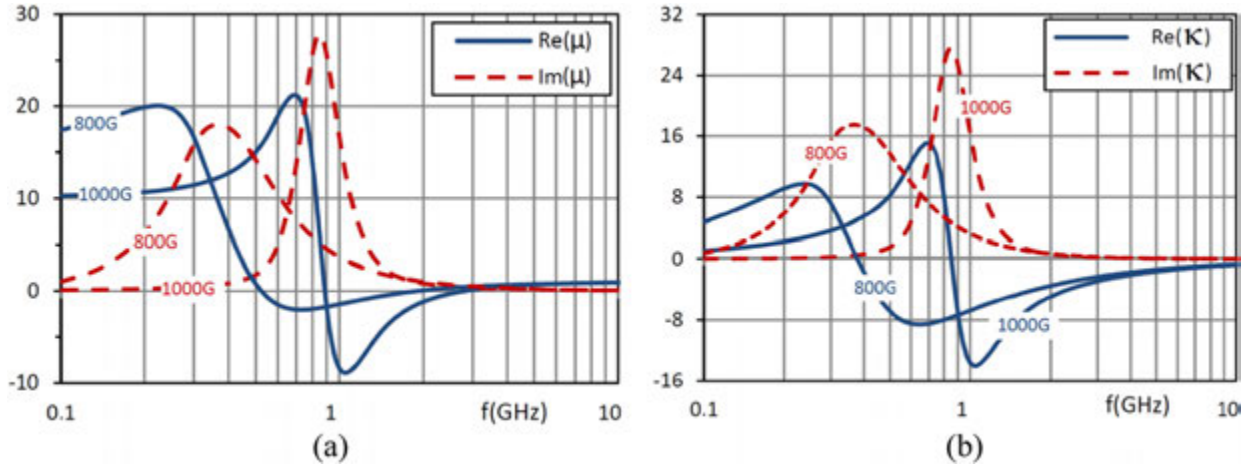


Fig. 29 Measured permeability tensor components for a garnet ferrite under applied static magnetic field up to 1000 Oe.

is possible to find the electromagnetic parameters of the unknown material while minimizing the difference between experimental and theoretical S parameters. Experimental results (Chevalier *et al.*, 2013) of the permeability tensor component μ and κ of a garnet ferrite are shown in Fig. 29.

References

- Aharoni, A., 1998. Demagnetizing factors for rectangular ferromagnetic prisms. *J. Appl. Phys.* 83, 3432–3434.
- Alvarez, G., Montiel, H., Barron, J.F., Gutierrez, M.P., Zamorano, R., 2010. Yafet–Kittel-type magnetic ordering in $\text{Ni}_{0.35}\text{Zn}_{0.65}\text{Fe}_2\text{O}_4$ ferrite detected by magnetosensitive microwave absorption measurements. *J. Magn. Magn. Mater.* 322, 348–352.

- Baker-Jarvis J., 2005. Measuring the permittivity and permeability of lossy materials: Solids, liquids, metals, building materials, and negative-index materials. In: NIST Technical Note. Report No. 1536.
- Chen, D.-X., Brug, J.A., Goldfarb, R.B., 1991. Demagnetizing factors for cylinders. *IEEE Trans. Magn.* 27, 3601–3619.
- Chen, L.F., Ong, C., Neo, C.P., Varadan, V., Varadan, V.K., 2004. *Microwave Electronics: Measurement and Materials Characterization*. Wiley & Sons.
- Chevalier, A., Cortes, J., Lezaca, J., Queffelec, P., 2013. Broadband permeability measurement method for ferrites at any magnetization state: Experimental results. *J. Appl. Phys.* 114 (17), (174904).
- Cortes J.P., Queffelec P., Chevalier A., 2015. Modeling antennas printed on magnetized substrate: Application to the design of a tunable PIFA antenna. In: *Proceedings of the 45th European Microwave Conference*, 933–936.
- Epstein, P.S., 1956. Theory of wave propagation in a gyromagnetic medium. *Rev. Mod. Phys.* 28 (1), 3–17.
- Gelin, P., Berthou-Pichavant, K., 1997. New consistent model for ferrite permeability tensor with arbitrary magnetization state. *IEEE Trans. Microw. Theory Tech.* 45 (8), 1185–1192.
- Gelin, P., Queffelec, P., Le Pennec, F., 2005. Effect of domain shapes on the dynamical behavior of polycrystalline ferrites: Application to the initial permeability. *J. Appl. Phys.* 98 (5).
- Gelin, P., Queffelec, P., 2008. Generalized permeability tensor model: Application to barium hexaferrite in a remanent state or self-biased circulators. *IEEE Trans. Magn.* 44 (1), 24–31.
- Gilbert, T.L., 1955. A Lagrangian formulation of the gyromagnetic equation of the magnetization field. *Phys. Rev.* 100 (4), 1243–1255.
- Goldman, A., 2006. *Modern Ferrite Technology*, second ed. Springer.
- Green, J.J., Sandy, F., 1974. Microwave characterization of partially magnetized ferrites. *IEEE Trans. Microw. Theory Tech.* 22 (6), 641–645.
- Guennou, A., Della, B., Quéfélec, P., Gelin, P., Mattei, J.L., 2007. Influence of the magnetic field nonuniformity on an X-band microstrip Y-junction circulator bandwidth: Theory/experiment comparison. *IEEE Trans. Magn.* 43 (6), 1642–1644.
- Hansen, R.C., 1982. Fundamental limitations in antennas. *Proc. IEEE* 69 (2), 170–182.
- Hansen, R.C., Burke, M., 2000. Antennas with magneto-dielectrics. *Microw. Opt. Technol. Lett.* 26, 75–78.
- Harris, V.G., Chen, Y., Chen, Z., Geiler, A.L., 2014. Tuning of structure and magnetic anisotropy in microwave ferrites. *J. Jpn. Soc. Powder Powder Metall.* 61 (Supplement S1), S273.
- Harris, V.G., Geiler, A., Chen, Y., *et al.*, 2009. Recent advances in processing and applications of microwave ferrites. *J. Magn. Magn. Mater.* 321.
- Helszajn, J., 2008. *The Stripline Circulator: Theory and Practice*. John Wiley and Sons.
- Huitema, L., Reveyrand, T., Mattei, J.L., *et al.*, 2013. Frequency tunable antenna using a magneto-dielectric material for DVB-H application. *IEEE Trans. Ant. Propag.* 61 (9), 4456–4466.
- Hwang, Y., Zhang, Y.P., Zheng, G.X., Lo, T.K.C., 1995. Planar inverted F antenna loaded with high permittivity materia. *Electron. Lett.* 31, 1710–1712.
- IEC, 1982. Measuring Methods for Properties of Gyromagnetic Materials Intended for Application at Microwave Frequencies. IEC 60556. IEC.
- Igarashi, M., Naito, Y., 1977. Tensor permeability of partially magnetized ferrites. *IEEE Trans. Magn.* 13 (5), 1664–1668.
- Igarashi, M., Naito, Y., 1981. Parallel component μ_z of partially magnetized microwave ferrites. *IEEE Trans. Microw. Theory Tech.* 29 (6), 568–571.
- Joseph, R.I., Schlömann, E., 1965. Demagnetizing field in nonellipsoidal bodies. *J. App. Phys.* 36 (5), 1579–1593.
- Kabalan A., Sharaiha A., Tarot A.-C., 2019. Enhance the impact of the magneto-dielectric materials to miniaturize a planar monopole antenna. In: *Proceedings of the URSI Asia-Pacific Radio Science Conference (AP-RASC)*, March 9–15, 2019. doi:10.23919/URSIAP-RASC.2019.8738556.
- Kabalan A., Sharaiha A., Tarot A.-C., 2019. Optimization of the use of magneto-dielectric materials for highly miniaturized monopole antennas. In: *Proceedings of the 13th European Conference on Antennas and Propagation (EuCAP)*, March 31–April 5, 2019.
- Kittel, C., 1951. Ferromagnetic resonance. *J. Phys. Radium* 12 (3), 291–302.
- Kong, L.B., Li, Z.W., Liu, J., *et al.*, 2013. Recent progress in some composite materials and structures for specific electromagnetic applications. *Int. Mater. Rev.* 58, 203–259.
- Krupka, J., Geyer, R.G., 1996. Complex permeability of demagnetized microwave ferrites near and above gyromagnetic resonance. *IEEE Trans. Magn.* 32 (3), 1924–1933.
- Landau, L., Lifshitz, E., 1935. On the theory of the dispersion of magnetic permeability in ferromagnetic bodies. *Phys. Z. Sowjetunion* 8, 153–169.
- Landau, L., 1965. *Collected Papers*. ter Haar, D. (Ed.), New York: Gordon and Breach, p. 101.
- Landau, L.D., Lifshitz, E.M., 1984. *Electrodynamics of Continuous Media*. Oxford: Pergamon Press.
- Le Gouellec, A., Verissimo, G., Laur, V., *et al.*, 2016. Modeling non-saturated ferrite-based devices: Application to twin toroid ferrite phase shifters. *J. Appl. Phys.* 120 (7), (073902).
- Lezaca, J.E., Queffelec, P., Chevalier, A., 2010. Generalized measurement method for the determination of the dynamic behavior of magnetic materials in any magnetization state. *IEEE Trans. Magn.* 46 (6), 1687–1690.
- Lezaca, J.E., Queffelec, P., Chevalier, A., 2011. Broadband permeability measurement method for ferrites at any magnetization state: Direct problem. *Int. J. Microw. Wirel. Technol.* 3 (3), 289–294.
- Mattei, J.-L., Guen, E. Le, Chevalier, A., Tarot, A.C., 2015. Experimental determination of magnetocrystalline anisotropy constants and saturation magnetostriction constants of Ni-Zn and Ni-Zn-Co ferrites intended to be used for antennas miniaturization. *J. Magn. Magn. Mater.* 374, 762–768.
- Mattei, J.-L., Huitema, L., Queffelec, P., *et al.*, 2011. Suitability of Ni-Zn ferrites ceramics with controlled porosity as granular substrates for mobile handset miniaturized antennas. *IEEE Trans. Magn.* 47, 3720–3723.
- Mikami, I., 1973. Role of induced anisotropy in magnetic spectra of cobalt-substituted nickel-zinc ferrites. *Jpn. J. Appl. Phys.* 12 (5), 678–693.
- Mosallaei, H., Sarabandi, K., 2004. Magneto-dielectrics in electromagnetics: Concept and applications. *IEEE Trans. Antennas Propag.* 52, 1558–1567.
- Niamien, C., Collardey, S., Sharaiha, A., Mahdjoubi, K., 2011. Compact expressions for efficiency and bandwidth of patch antennas over lossy magneto-dielectric materials. *IEEE Antennas Wirel. Propag. Lett.* 10, 63–66.
- Niamien, C., Collardey, S., Sharaiha, A., Mahdjoubi, K., 2014. Printed inverted-F antennas over lossy magneto-dielectric materials: Theoretical approach and validations. *IET Microw. Antennas Propag* 8 (7), 513–522.
- Nicolson, A., Ross, G., 1970. Measurement of the intrinsic properties of materials by time-domain techniques. *IEEE Trans. Instrum. Meas.* IM-19 (4), 377–382.
- Ogasawara, N., Fuse, T., Inui, T., Saito, I., 1976. Highly sensitive procedures for measuring permeabilities ($\mu \pm$) for circularly polarized fields in microwave ferrites. *IEEE Trans. Magn.* 12 (3), 256–259.
- Osborn, J.A., 1945. Demagnetizing factors of the general ellipsoid. *Phys. Rev.* 67, 351–357.
- Perekalina, T.M., Askochinskii, A.A., Sannikov, D.G., 1961. Resonance of domain walls in cobalt ferrite. *Sov. Phys. JETP* 13 (2), 303–307.
- Petrov, R.V., Tatarenko, A.S., Srinivasan, G., Mantese, J.V., 2008. Antenna miniaturization with ferrite-ferroelectric composites. *Microw. Opt. Technol. Lett.* 50 (12), 3154–3157.
- Pfeiffer, H., 1990. Determination of anisotropy field distribution in particle assemblies taking into account thermal fluctuations. *Phys. Status Solidi A* 118, 295–306.
- Polder, D., 1949. On the theory of ferromagnetic resonance. *Philo. Mag.* 40, 99–115.
- Polder, D., Smit, J., 1953. Resonance phenomena in ferrites. *Rev. Mod. Phys.* 25 (1), 89–90.
- Pullar, R.C., 2012. Hexagonal ferrites: A review of the synthesis, properties and applications of hexaferrite ceramics. *Prog. Mater. Sci.* 57, 1191–1334.
- Queffelec, P., Le Floch, M., Gelin, P., 2000. New method for determining the permeability tensor of magnetized ferrites in a wide frequency range. *IEEE Trans. Microw. Theory Tech.* 48 (8), 1344–1351.
- Rado, G., 1953. Magnetic spectra of ferrites. *Rev. Mod. Phys.* 25, 81.

- Sakai, T., Chen, Y., Chinnasamy, C.N., Vittoria, C., Harris, V.G., 2006. Textured Sc-doped barium-ferrite compacts for microwave applications below 20 GHz. *IEEE Trans. Magn.* 42, 3353–3355.
- Schlömann, E., 1958. Ferromagnetic resonance in polycrystalline ferrites with large anisotropy. *J. Phys. Chem. Solids* 6 (2-3), 257–266.
- Schlömann, E., 1970. Microwave behavior of partially magnetized ferrites. *J. Appl. Phys.* 41 (1), 204–214.
- Skrivervik, A.K., Zürcher, J.F., Staub, O., Mosig, J.R., 2001. PCS antenna design: The challenge of miniaturization. *IEEE Antennas Propag. Mag.* 43, 12–27.
- Smit, J., Wijn, H.P.J., 1959. *Ferrites*. Eindhoven: Philips Technical Library.
- Srivastava, C.M., Patni, M.J., 1974. Ferromagnetic relaxation processes in polycrystalline magnetic insulator. *J. Magn. Reson.* 15, 359–366.
- Thalakkatukalathil, V.V.K., Chevalier, A., Laur, V., *et al.*, 2018. Electromagnetic modeling of anisotropic ferrites – Application to microstrip Y-junction circulator design. *J. App. Phys.* 123.(234503).
- van Uitert, L.G., 1955. DC resistivity in the nickel and nickel zinc ferrite system. *J. Chem. Phys.* 23, 1883.
- Valenzuela, R., 1994. *Magnetic Ceramics*. Cambridge University Press.
- Wangsness, R.K., 1954. Magnetic resonance in ferrimagnetics. *Phys. Rev.* 93, 68.
- Weir, W.B., 1974. Automatic measurement of complex dielectric constant and permeability. *Proc. IEEE* 62 (1), 33–36.

Ferrite Magnets: Properties and Applications

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A permanent magnet is a material, which once magnetized, retains its magnetization at the temperature of use. Because permanent magnets can hardly be demagnetized, they are called “hard” magnetic materials. The magnetic properties of a permanent magnet are determined by the intrinsic magnetic properties of the compounds that constitute them. In addition, they are determined by the microstructure of the material obtained, in relation with the manufacturing process.

Ferrite permanent magnets are one of the classes of permanent magnet materials. The other ones are rare-earth transition metal magnets (Nd-Fe-B and Sm-Co) and alnicos (Fe-Ni-Al type). All these classes of permanent magnet materials lead to almost all, at least most, of the technological applications.

The importance of ferrite magnets for technological applications is due to both their low price and their reasonable magnetic performances. Barium and strontium hexaferrites have been used for several decades for their hard magnetic properties. This makes the range of applications extremely wide (electric motors, loudspeaker, toys, etc.) (Van den Broek and Stuijts, 1977). Consequently, ferrite permanent magnets occupy a dominant position in permanent magnets market, and their volume share is still growing.

This chapter deals with the magnetic properties of ferrite permanent magnets. In the first section, we compare the characteristics of ferrite permanent magnets with those of the other classes of permanent magnets, and present the structural and magnetic properties of the ferromagnetic compound that determine the properties of the magnet, the $\text{SrFe}_{12}\text{O}_{19}$ compound. In the second section, emphasis is placed on the characteristics of sintered and bonded ferrite magnet materials, in relation with the magnet processing. In the third section, the main applications of ferrite permanent magnets are presented.

Ferrite Magnets: One Class of Permanent Magnets

Permanent Magnets

Permanent magnet materials

Permanent magnets materials are magnetic materials that can keep their magnetization once they are magnetized that is, submitted to a magnetic field. These materials are denoted as hard magnetic materials. Their magnetization remains stable at the temperature of use.

The magnetic behavior of a permanent magnet material can be described by its hysteresis loop. Two different loops can be drawn, $B(H)$ or $M(H)$, where H , B and M are the external magnetic field, the magnetic flux density created in the material, and the magnetization of the material, respectively.

When the permanent magnet is placed in an external magnetic field H , small regions of the material where the magnetic moments share a common direction are created, forming magnetic domains. The polarization of the magnetic domains creates a magnetization M at the macroscopic scale. This results into the apparition in the material of a magnetic flux density B , which is related to M according to the following relation:

$$B = \mu_0(H + M)$$

Once all the magnetic domains are polarized in the same direction as that of the external magnetic field H , the maximum value of the magnetization is obtained. This value is the saturation magnetization M_s of the magnet.

When the external magnetic field is suppressed, the permanent magnet keeps a residual magnetization, which corresponds to the remnant magnetization M_r of the magnet. In the case of a perfect magnet, one would have $M_r = M_s$. In real magnets, M_r is slightly lower than M_s , due to the presence of structural defects and/or imperfect alignment of the magnetic domains.

The $M(H)$ and $B(H)$ curves are denoted hysteresis loops. These curves are shown in Fig. 1.

A wide variety of permanent magnet materials exist, for various applications. The different classes of permanent magnet materials have various properties. Some permanent magnets are ceramic, some are metallic.

Permanent magnets can be ceramic or metallic materials. They are characterized by their macroscopic (or extrinsic) magnetic properties: remnant induction field B_r , coercive field H_c (for a $\mu_0 M(H)$ loop) or BH_c (for a $B(H)$ loop), maximum energy field $(BH)_{\max}$. These properties are related to the intrinsic magnetic properties of the magnetic phases that are constitutive of the magnet: saturation magnetization M_s , anisotropy field H_A , Curie temperature T_C . The magnet properties also depend on the microstructure of the magnet: grain size and shape. Moreover, the mechanic and physico-chemical properties of the magnets strongly influence their applications.

Four families of permanent magnet materials lead to most of the applications on the market. These families are alnicos, hard ferrites, samarium-cobalt magnets and neodymium-iron-boron magnets. Other materials exist, such as martensitic hard steels, manganese-aluminum-carbon alloys, or micropowder-based magnets. However, their applications are very limited, being restricted to specific use.

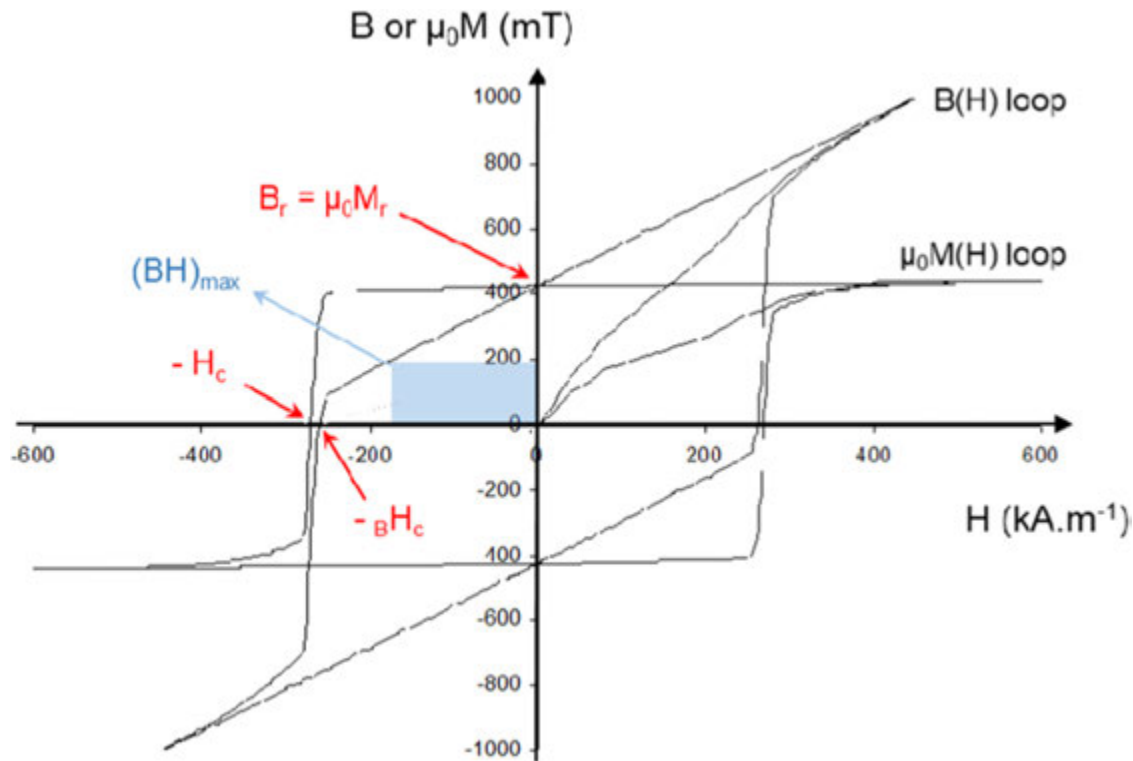


Fig. 1 Typical B(H) and M(H) hysteresis loops of a permanent ferrite magnet. For sake of clarity, the $\mu_0 M(H)$ loop is shown instead of M(H) loop, as it can be superimposed to the B(H) loop. The typical magnetic properties of a permanent magnet (remnant induction B_r , coercive field H_c and maximum energy product $(BH)_{\max}$) are evidenced in the figure.

Permanent magnet properties

Three characteristics corresponding to three magnetic properties determine the permanent magnet behavior. These parameters, that determine the choice made by the user for a given application, are all displayed in the second quadrant of the hysteresis loop. The corresponding curves are called the demagnetization curves. They are shown in [Fig. 2](#):

- the remnant induction B_r (obtained from the B(H) loop), which represents the residual induction in closed circuit, is an indication of the potential power of the magnet;
- the coercive field of magnetization H_c (obtained from the M(H) loop) which is the demagnetizing field canceling the magnetization M , is an indication of the stability of the magnet;
- the maximum energy density $(BH)_{\max}$ (obtained from the B(H) loop), which is the maximum value of the volume energy product (BH) of the magnet; it corresponds to the optimal operating point of the magnet.

The different types of magnets can be classified according to the values of B_r , H_c and $(BH)_{\max}$. Typical values of these parameters are given in [Table 1](#).

The maximum operating temperature $T_{\max}$ of a magnet is determined by its Curie temperature T_C . The Curie temperature is the temperature at which the magnetic order is broken by the thermal agitation. The corresponding values of T_C are also reported in [Table 1](#).

A comparison of the magnetic properties of the different classes of permanent magnet materials is made in [Figs. 3](#) and [4](#). Ferrite magnets have the lowest remnant induction of permanent magnets, but their coercive field is comparable to that of Sm-Co magnets ([Fig. 3](#)). Although ferrite magnets have a low maximum energy product, their operating temperature is higher than that of Nd-Fe-B magnets ([Fig. 4](#)).

The volume production of ferrite magnets makes them the most produced and most used magnets worldwide. This is due to the following reasons:

- the raw materials are not rare nor strategic;
- these materials are low cost;
- the obtained magnetic properties allowed to develop numerous applications;
- they are corrosion resistant and chemically stable in aggressive environments.

These properties make ferrite magnets appropriate for outdoor applications, and thus well suited for high volume production. One can find ferrite magnets in almost all industries: power generation, automotive, aerospace, electronic goods, military and defense ([Goldman, 2006](#)).

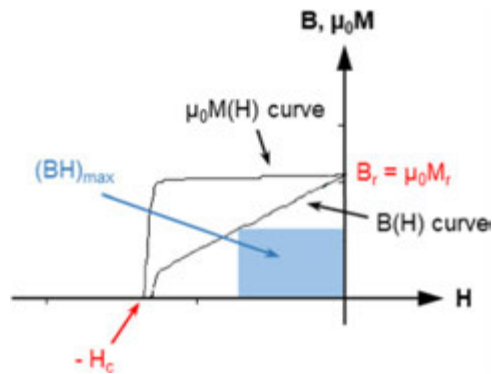


Fig. 2 Typical demagnetizing curves for a ferrite permanent magnet.

Table 1 Typical values of the main magnetic properties of different classes of magnets. The values of B_r , H_c and $(BH)_{\max}$ are given at room temperature. $T_{\max}$ correspond to the maximum temperature of use of the magnets

	B_r (T)	H_c ($\text{kA} \cdot \text{m}^{-1}$)	$(BH)_{\max}$ ($\text{kJ} \cdot \text{m}^{-3}$)	T_c ($^{\circ}\text{C}$)	$T_{\max}$ ($^{\circ}\text{C}$)
Alnico	1.1–1.3	64–103	35.8–43.8	740–860	450–540
Ferrite	0.38–0.46	200–400	25.5–40.6	450–460	250–300
Sm–Co (SmCo_5)	0.82–0.87	960–1600	135.3–151.2	700–750	250
Sm–Co ($\text{Sm}_2\text{Co}_{17}$)	0.92–1.16	490–790	159.1–254.6	800–850	450–550
Nd–Fe–B ($\text{Nd}_2\text{Fe}_{14}\text{B}$)	1.0–1.3	880–1990	199.0–310.3	310–330	80–180

Note: Rossignol, M., Yonnet, J.P., 1999. Les aimants permanents. Les matériaux magnétiques et leurs applications: Magnétisme II. Presses Universitaires de Grenoble.

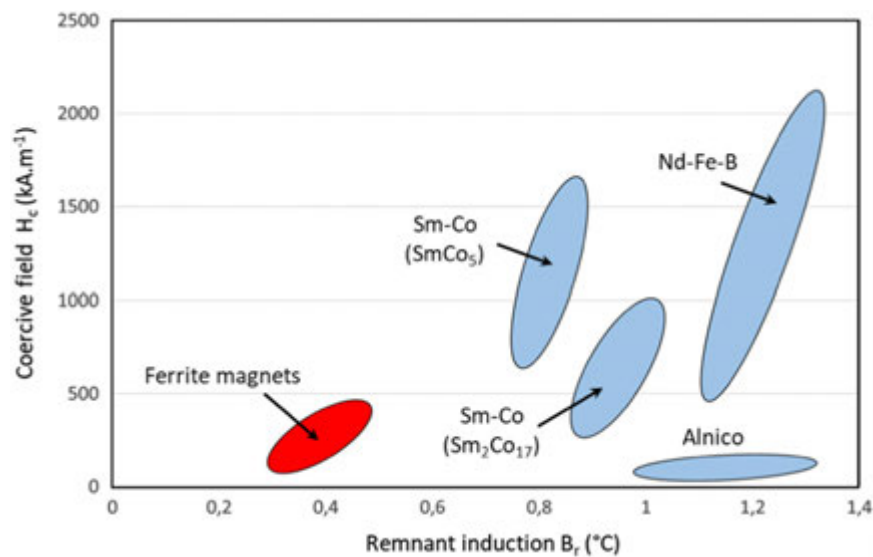


Fig. 3 Coercive field H_c vs remnant induction B_r for the different types of permanent magnet materials.

Permanent magnet market

Because raw materials used to manufacture ferrite permanent magnets are quite inexpensive compared to the other types of permanent magnets, especially rare-earth magnets, ferrite magnets are the cheapest magnets among all permanent magnet materials.

The excellent chemical stability of ferrite magnets makes them to be very well suited for high volume production such as generators, motors and loudspeakers. Consequently, low production cost and high availability of ferrite magnets make them occupy a dominant position in permanent magnets market.

The global permanent magnets market size was valued at USD19.23 billion in 2018 (Research and Markets, 2019). It is estimated to witness a compound annual growth rate of 8.3% from 2019 to 2025 (Goldman, 2006). In permanent magnets market, the volume share of ferrite magnets reached 81.1% in 2018 (Reports and Data, 2019).

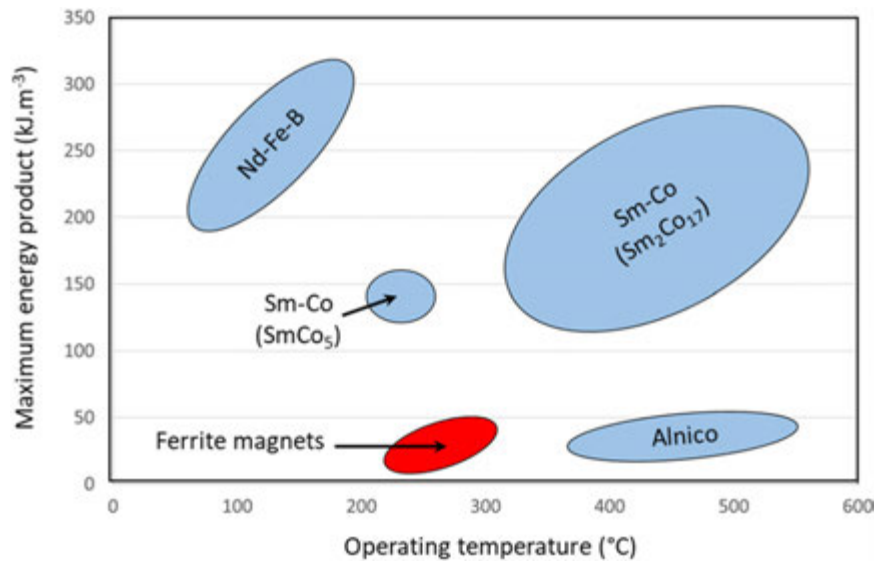


Fig. 4 Maximum energy product vs operating temperature for the different types of permanent magnet materials.

Today, the demand for permanent magnets is driven by the increasing production of electric vehicles, rising wind energy installations, and rapidly growing robotics industry. Over the coming years, an increasing application of permanent magnets is expected in automobiles to reduce dependency on fuel as well as to enhance engine power. Other future key applications of permanent magnets are energy sector and direct-drive generators. All these applications should increase the market growth over the forecast period. In this context, the ceramic ferrite magnets market is projected to register a compound annual growth rate of 6.8% in terms of value, from 2019 to reach USD12.73 Billion by 2026 (Reports and Data, 2019).

Hexaferrite Materials

Hexaferrite material exists in a natural state as lead ferrite. It has been discovered in the 1930s. Its chemical formula being $\text{PbFe}_{12}\text{O}_{19}$, it has been called magnetoplumbite. In ferrite magnets, lead is replaced:

- by barium, to obtain materials with high remnant induction field,
- by strontium, to obtain materials with high coercive field.

Ferrite permanent magnets materials were developed at the beginning of the 1950s, in the Philips Society (Went *et al.*, 1952). $\text{BaFe}_{12}\text{O}_{19}$ was introduced under the trade name Ferroxdure (Went *et al.*, 1952). An improved composition containing strontium instead of barium has been introduced for applications like permanent magnets.

Although ferrite magnets are well known for seventy years, they have been and they are still the object of an intense research, in order to increase their magnetic properties. In fact, any improvement of these properties can have significant economic consequences in relation with specific applications. This has been the case almost twenty years ago with the production of La-Co doped ferrite magnets (Taguchi *et al.*, 1996, 2000; Kools *et al.*, 2000, 2002; Grössinger *et al.*, 2000; Le Breton *et al.*, 2002, 2004; Lechevallier *et al.*, 2003, 2004; Tenaud *et al.*, 2004).

The magnetic properties of ferrite magnets are due to the intrinsic magnetic properties of the $\text{SrFe}_{12}\text{O}_{19}$ M-type hexagonal phase.

M-type hexagonal ferrites are compounds with a hexagonal structure of the magnetoplumbite $\text{PbFe}_{12}\text{O}_{19}$ type ($\text{P6}_3/\text{mmm}$ space group). The lattice parameters of the hexagonal structure are:

- $a = 0.587 \text{ nm}$ and $c = 2.301 \text{ nm}$ for $\text{PbFe}_{12}\text{O}_{19}$;
- $a = 0.588 \text{ nm}$ and $c = 2.305 \text{ nm}$ for $\text{SrFe}_{12}\text{O}_{19}$;
- $a = 0.589 \text{ nm}$ and $c = 2.319 \text{ nm}$ for $\text{BaFe}_{12}\text{O}_{19}$.

The structure of the hexagonal ferrites is derived from a stacking of close-packed oxygen/barium or strontium layers along the hexagonal c-axis with an ordering sequence of spinel (S) two-layer building units $(\text{Fe}_6\text{O}_8)^{2+}$ and three layer (R) blocks $(\text{SrFe}_6\text{O}_{11})^{2-}$ (Fig. 5). Combination of RS gives the building motif of the magnetoplumbite M-type ferrite $\text{SrFe}_{12}\text{O}_{19}$ (Kojima, 1982).

The unit cell of the $\text{SrFe}_{12}\text{O}_{19}$ structure contains two formula units that is, 2Sr^{2+} ions, 24Fe^{3+} ions and 38O^{2-} ions. Fe^{3+} ions occupy five different sites, whose geometry corresponds to the arrangement of the O^{2-} nearest neighbors around the Fe^{3+} ion: three octahedral (namely 12k, $4f_2$ and $2a$), one tetrahedral ($4f_1$) and one bipyramidal ($2b$). These five Fe sites, together with the Sr site, are displayed in Fig. 5.

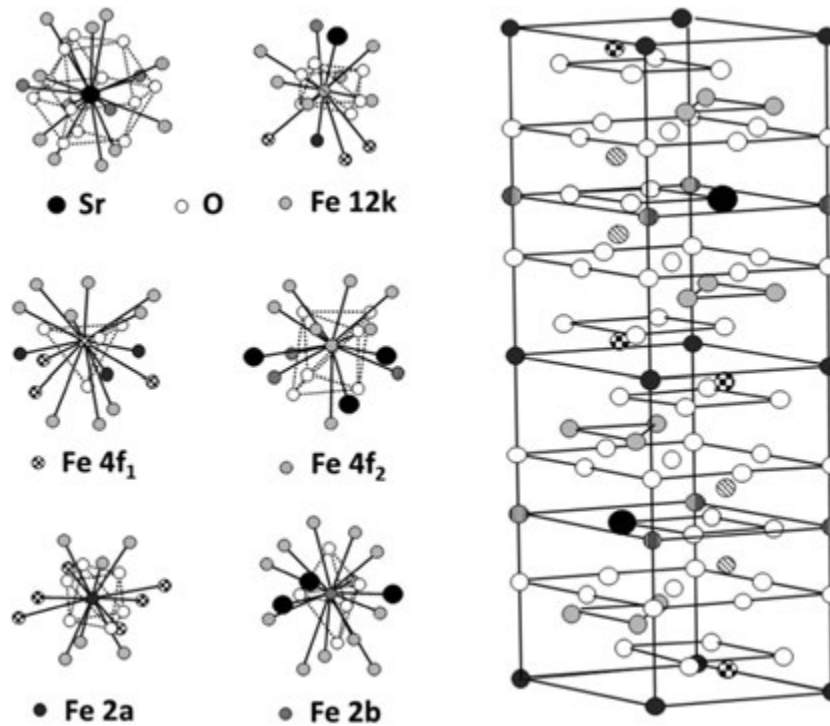


Fig. 5 Unit cell crystal structure of the hexagonal M-type phase. The Sr site and the five Fe sites are displayed. Adapted from Lechevallier, L., Le Breton, J.-M., Morel, A., Tenaud, P., 2008. *Journal of Physics: Condensed Matter* 20, 175203.

The uniaxial magneto-crystalline anisotropy of Fe^{3+} in M-type hexagonal ferrite is one of the origins of the hard magnetic properties of this material.

Some typical physical properties of the $\text{SrFe}_{12}\text{O}_{19}$ hexaferrite are:

- density 5000 kg m^{-3} ;
- resistivity $10^4 \Omega \text{ m}$;
- thermal conductivity $5.5 \text{ W m}^{-1} \text{ K}^{-1}$.

Ferrite Magnet Materials

Magnetic Properties of Ferrite Magnets

The macroscopic magnetic properties of ferrite magnets (H_c , B_r , $(BH)_{\text{max}}$) are related to the fundamental intrinsic magnetic properties of the hexaferrite $\text{SrFe}_{12}\text{O}_{19}$ compound. The intrinsic magnetic properties are:

- Curie temperature $T_C = 735\text{K}$;
- room temperature saturation magnetization $M_s = 380 \text{ kA m}^{-1}$;
- room temperature anisotropy field $H_A = 1500 \text{ kA m}^{-1}$.

In the last 20 years, numerous studies have been made to improve the magnetic properties of ferrite magnets through the improvement of the intrinsic magnetic properties of the $\text{SrFe}_{12}\text{O}_{19}$ phase. A significant improvement has been obtained when Sr and Fe were partially substituted by different cations like La–Co (Kools *et al.*, 2002; Tenaud *et al.*, 2004) or Zr–Zn (Iqbal *et al.*, 2009).

The combined substitution of La^{3+} in the Sr^{2+} site and Co^{2+} in Fe^{3+} sites lead to compositions $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}\text{Co}_x\text{O}_{19}$ (Taguchi *et al.*, 2000; Kools *et al.*, 2000). These improvements are related to the increase of the intrinsic magnetic properties of the modified M-type phase, in particular to a drastic change of the magneto-crystalline anisotropy field up to 1850 kA m^{-1} (Grössinger *et al.*, 2000). It is well known that the presence of La atoms induces an increase of the magnetocrystalline anisotropy (Lotgering, 1974). This can be related to the change of the valence state of iron ions in the 2a site from Fe^{3+} to Fe^{2+} due to the introduction of La^{3+} ion instead of Sr^{2+} ion (Lotgering, 1974; Sauer *et al.*, 1978), to compensate for the excess of positive charges.

In the case of ferrite magnets, the high density of the materials results in both high remanence and sufficient mechanical strength. With the aim to obtain a high coercivity, a small grain size is needed (about $1 \mu\text{m}$) and a narrow grain size distribution

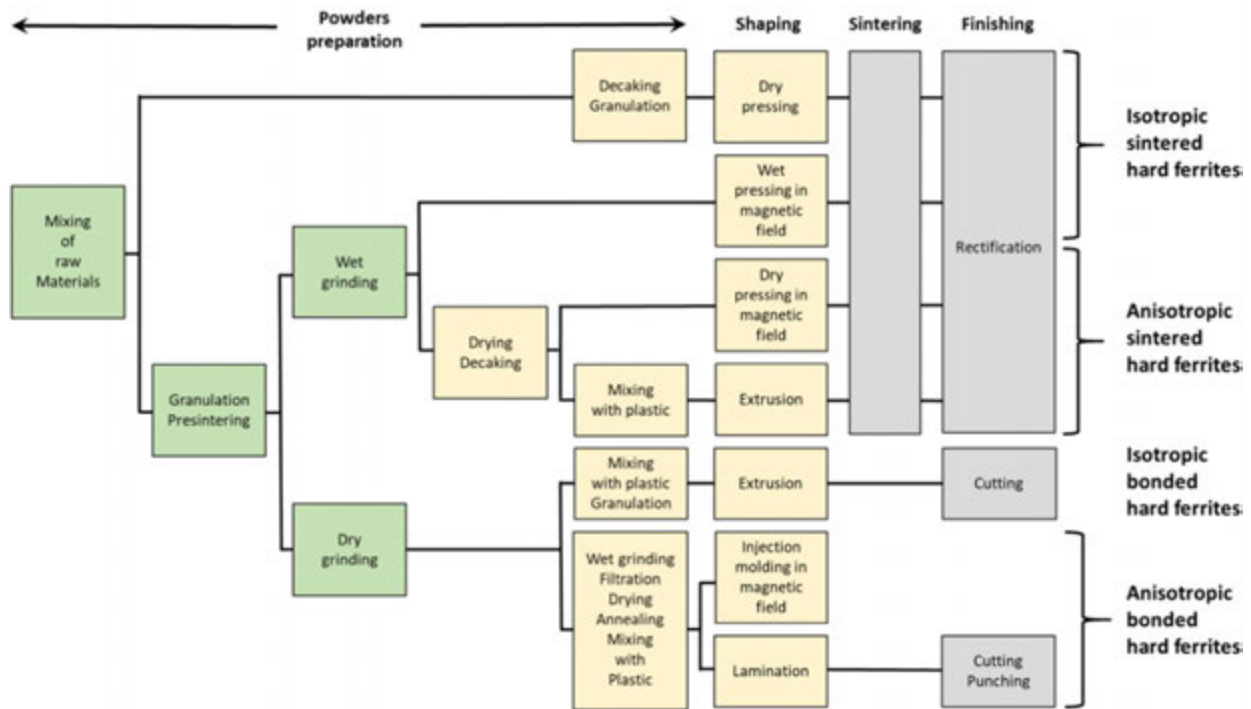


Fig. 6 The manufacture of ferrite magnets: the different steps corresponding to the processes used.

must be attained. The conventional method to obtain $\text{BaFe}_{12}\text{O}_{19}$ or $\text{SrFe}_{12}\text{O}_{19}$ hexaferrite materials is a solid state process, i.e., high temperature calcination of a mixture of $\alpha\text{-Fe}_2\text{O}_3$ and BaCO_3 or SrCO_3 .

The magnetic properties of ferrite magnets are determined by the intrinsic magnetic properties of the compounds they are based on. Their magnetic properties also strongly depend on the microstructure, which is intimately related to the manufacturing process.

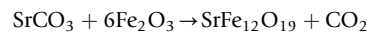
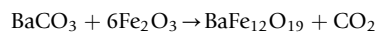
Materials Processing

The different steps of the manufacture of ferrite type magnets (both sintered and bonded magnets), depending on the processes used, are shown in **Fig. 6**. These processes are used to obtain isotropic sintered hard ferrites, anisotropic sintered hard ferrites, isotropic bonded hard ferrites or anisotropic bonded hard ferrites.

Sintered Hard Ferrites

Ceramic process

Sintered hard ferrites are obtained according to a ceramic process. In this process, raw materials (iron oxide and barium or strontium carbonate powders) are mixed with the required proportions. The mixed powder is then sintered in a high temperature furnace (1200–1300°C), to allow the raw materials to react according to the following reactions:



The obtained material is then milled in humid phase. The use of attrition milling allows obtaining micrometer-sized grains. Because this size corresponds to the mean size of the Weiss domains, the obtained grains are single domain. These powders are disaggregated and can be dry- or wet-pressed. Shaping is obtained by pressing or extrusion.

Hard ferrites offer the possibility to make oriented pressing. Ferrite crystals have an easy-axis of magnetization due to their hexagonal structure. This allows to orientate the crystals in a magnetic field during shaping, and thus to obtain materials with improved magnetic properties in the easy-axis direction. Only the single domain crystals that have a certain degree of freedom compared with the other grains can be orientated.

According to the actual milling process techniques, an orientation level of more than 90% can be obtained, which induces an increase of the remnant magnetization. As their magnetic properties are not the same in all directions, the obtained ferrites are denoted as “anisotropic” ferrites. If no magnetic field is applied during shaping, the obtained ferrites are “isotropic” ferrites.

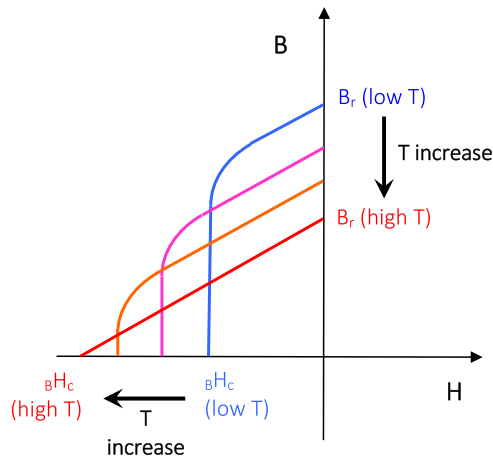


Fig. 7 Typical temperature evolution of the demagnetizing $B(H)$ curve of a sintered hard ferrite.

After shaping, sintering at temperatures of the order of 1200°C allows to obtain a densification of 90%–95%. During sintering, the dimensions of the magnets can decrease significantly. This phenomenon is denoted as shrinkage.

- (1) In the case of anisotropic ferrites, the shrinkage is anisotropic:
 - (a) a 30% shrinkage is observed in the direction of the orientation of the domains;
 - (b) a 15% shrinkage is observed in the perpendicular direction.
- (2) In the case of isotropic ferrites, the shrinkage is isotropic, from 20% to 22%.

Current grinding techniques make it possible to obtain a finer microstructure after sintering. This gives the magnet a higher coercivity.

Considering the high hardness of the ferrite material (6.5 on the Mohs scale), finishing is done by grinding with diamond grinding wheels. This allows to eliminate the asperities due to the manufacturing process. Tolerances of up to $2/100$ mm on the rectified faces can be obtained.

According to the problems encountered, related to the handling of magnetic parts during assembly, most parts are delivered unmagnetized. The magnetization is then carried out after assembly.

Properties of sintered ferrites

These properties, which are those of the obtained material, interest the user more particularly.

Chemical stability

Because sintered hard ferrites are ceramics, they are chemically stable. They are hardly dissolved and cannot be attacked by strong acids.

Their stability in time is unlimited. Indeed, the elements entering the chemical formula have saturated valence states at their most stable levels. No oxidation in the air is possible. Therefore, their magnetic properties do not degrade with time.

The chemical stability of sintered hard ferrites is the main advantage of these magnets.

Temperature coefficients

Temperature has a great influence on the properties of sintered hard ferrites. As the temperature increases, the remnant induction decreases and the magnet loses power. However, its coercive field increases and it gains stability.

The variations of the magnetic properties are typically:

- (1) remanent induction B_r : $0.2\% \text{ K}^{-1}$
- (2) coercive field H_c :
 - (a) $0.95 \text{ kA m}^{-1} \text{ K}^{-1}$ for strontium ferrite
 - (b) $0.80 \text{ kA m}^{-1} \text{ K}^{-1}$ for barium ferrite

Fig. 7 shows the typical temperature evolution of the demagnetizing $B(H)$ curve of a sintered hard ferrite.

In order to use the ferrite magnet at temperatures below 0°C , a higher coercive field than necessary at 25°C should be provided so that the operating point of the magnet remains at above the elbow of the demagnetization curve. This allows to avoid irreversible partial demagnetization of the magnet.

Dispersion of magnetic and mechanical values

The observed variations come mainly from the manufacturing process.

Table 2 Magnetic properties of high-end anisotropic sintered ferrites ($K=535$)

	B_r (mT)	H_c (kA m ⁻¹)	BH_c (kA m ⁻¹)	$(BH)_{max}$ (kJ m ⁻³)
High coercivity ferrite	385	360	285	27.3
High remanence ferrite	420	270	260	32.8

When sintering at 1200°C, the variations in the maximum temperature in industrial furnaces are of the order of $\pm 10^\circ\text{C}$. Magnetic values are sensitive to such variations. Indeed, for a variation of $+10^\circ\text{C}$ in the furnace, a variation of B_r of $+5$ mT and a variation of H_c of -12 kA m⁻¹ are observed.

During pressing, the pressed densities are dispersed. This results in a dispersion of the magnetic properties after firing. The variations for the raw parts after firing are of the order of 2.5% for B_r and 5% for H_c . The manufacturer can thus guarantee minimum values only. The automation of pressing and sintering makes it possible to reduce the dispersion of these values. This is due to the use of computerized presses and furnaces to maintain more homogeneous temperatures. The resulting part will thus be better densified and smaller.

For the same reasons, the mechanical tolerances of the raw parts of firing are about 2% due to shrinkage that the parts undergo during the densification. Thus, for a variation of $+10^\circ\text{C}$ in the oven, a variation of $+0.5\%$ is obtained for the shrinkage.

In practice, the variation of shrinkage (and therefore of the surface of the pieces) and the variation of B_r are counterbalanced to give a roughly constant flux since $\Phi = BS$.

Quality coefficient

The following quality coefficient K can be determined to characterize a given ferrite material:

$$K = B_r + 0.4H_c$$

where B_r is expressed in mT and H_c in kA m⁻¹.

The K coefficients for the range of ferrite grades are between 450 and 535. The magnetic properties and the demagnetization curves of the $K = 535$ grade are given in [Table 2](#).

Isotropic ferrites

In this type of magnets, the magnetic domains are randomly oriented. In a given direction, the remanence is almost equal to half the remanence obtained in anisotropic ferrite. These materials are therefore particularly suitable for applications for which high magnetic values are not essential or where isotropic magnetic properties are required.

The simplified manufacturing process ([Fig. 6](#)) makes these magnets particularly inexpensive. Their magnetic, electrical and physical properties are summarized in [Table 3](#).

Anisotropic ferrites

Anisotropic ferrite magnets are the most common type of ferrite magnets. Their applications are numerous. In such magnets, the orientation of the magnetic domains in a given direction makes it possible to obtain high values of the remnant induction B_r in the direction of magnetization, between 350 and 450 mT.

High remanence materials

This category includes:

- barium ferrites characterized by a relatively weak H_c coercive field, of about 150 kA m⁻¹;
- strontium ferrites characterized by an average coercive field H_c of about 250 kA m⁻¹.

The magnetic properties of a number of industrial grades are given in [Table 4](#).

High coercivity materials

These materials have a coercive field H_c of 300–500 kA m⁻¹. They are made of strontium ferrites with more or less significant additions of aluminum oxide or chromium oxide which make it possible to adjust the value of the coercive field.

The magnetic properties of a number of industrial grades are given in [Table 5](#). It should be noted that a strong coercive field can generally only be obtained at the expense of remanence.

Other ceramic materials

There are other types of ferrites that can be magnets, having magnetic properties equivalent to those of hard materials. In the ternary FeO–Fe₂O₃–BaO diagram a certain number of defined compounds have been highlighted: B, M, S, W, Y, Z. In particular, the W phase of BaFe₁₈O₂₇ composition has a magnetization saturation higher by 10%–15% than that of the BaFe₁₂O₁₉ phase. However, because of the difficulty in obtaining a pure compound, this ferrite is not industrialized.

Table 3 Room temperature magnetic properties of isotropic sintered ferrites

Magnetic property	Typical value
remnant induction B_r	220 mT
coercive field H_c	220 kA m ⁻¹
coercive field BH_c	135 kA m ⁻¹
energy density $(BH)_{\max}$	7.6 kJ m ⁻³
B_r temperature coefficient (– 4°C to 200°C)	– 0.2 (%/K)
H_c temperature coefficient (– 40°C to 200°C)	+ 0.4 (%/K)
saturation field H_{sat}	800 kA m ⁻¹
Curie temperature	450°C

Table 4 Typical magnetic properties of high remanence anisotropic sintered ferrites

	B_r (mT)	H_c (kA m ⁻¹)	BH_c (kA m ⁻¹)	$(BH)_{\max}$ (kJ m ⁻³)
Barium ferrite	400	165	160	29.5
Strontium ferrites	420	240	225	33.0
	410	275	265	41.5
	390	275	265	28.5

Table 5 Magnetic properties of high coercivity anisotropic sintered ferrites

	B_r (mT)	H_c (kA m ⁻¹)	BH_c (kA m ⁻¹)	$(BH)_{\max}$ (kJ m ⁻³)
Strontium ferrites	380	320	280	27.0
	340	335	265	21.5
	260	530	180	11.0

It is also possible to replace strontium and barium with elements such as lanthanum, or lanthanum-calcium mixtures. The magnetic properties of the materials obtained are nevertheless slightly lower than the magnetic properties of strontium or barium ferrites, the too high cost of the raw materials makes industrialization unprofitable.

However, it has been shown that the simultaneous substitution of lanthanum for strontium and iron for cobalt leads to new magnets, which result in high coercivity materials without loss of remanence (Taguchi *et al.*, 1996, 2000; Kools *et al.*, 2000, 2002; Grössinger *et al.*, 2000; Le Breton *et al.*, 2002, 2004; Lechevallier *et al.*, 2003, 2004; Tenaud *et al.*, 2004). Despite the cost of raw materials, the improvement of magnetic properties is significant and led to the industrialization of the material. These new shades of magnets are available on the market.

Bonded Ferrites

Manufacturing process

Bonded ferrites are made from ferrite powder (after presintering and dry milling) mixed with bonding agents by conventional methods in the plastics industry: extrusion, injection molding, rolling (Fig. 6).

It is possible to carry out:

- flexible magnets when the binding agent is a flexible thermoplastic;
- rigid magnets when thermosetting resins are used.

As for the sintered magnets, it is possible to obtain a magnetic anisotropy during shaping:

- by applying a magnetic field;
- or by rolling when making magnets in the form of strips or ribbons.

The manufacturing process of the bonded ferrite magnets allows the production of complex shapes, with tight tolerances. The bonded magnets can thus be folded or cut.

Magnetic properties

In a bonded ferrite magnet, the mass content of the ferrite powder can vary from 75% to 94% depending on the qualities. The density of the obtained magnet thus varies between 2500 and 3900 kg m⁻³, which is significantly lower than that of a sintered magnet. The magnetic properties of bonded ferrite magnets depend largely on the density.

Table 6 summarizes the main magnetic properties of some bonded magnets.

Table 6 Magnetic properties of some bonded ferrite magnets

	B_r (mT)	H_c (kA m ⁻¹)	BH_c (kA m ⁻¹)	$(BH)_{max}$ (kJ m ⁻³)	density (kg m ⁻³)
Anisotropic rigid magnet	240	240	175	11	3500
Isotropic rigid magnet	80	190	58	0.9	2500
	155	190	104	4.4	3900
Isotropic flexible magnet	145	190	96	3.2	3700

The dimensional tolerances without machining are of the order of $\pm 0.5\%$ for rigid magnets and $\pm 1\%$ for soft magnets.

The chemical and physical properties of the magnet are mainly related to the quality of the binding agent and to the density of the ferrite powder. In the case of bonded ferrite magnets, the chemical stability of the magnet is that of the elastomer or that of the resin. If these magnets are resistant to contact with water and mineral oils, they are quickly attacked by conventional organic solvents such as acetone, carbon tetrachloride and toluol.

Maximum operating temperatures do not exceed 100°C.

Bonded ferrite magnets are little fragile materials, unlike sintered magnets. The breaking strength is guaranteed from 30 to 150 MPa depending on the grade. These variations depend on both the binding agent and the ferrite filler.

Applications of Ferrite Permanent Magnets

Because of both their high chemical stability and their low production costs, ferrite permanent magnets remain the most used magnets today (Kramer *et al.*, 2012). They are used, often in large series, in a large number of applications where cost control remains an essential element in relation to magnetic performance. Thus, ferrite permanent magnets are used for applications when high flux density or small size are not required (Petrov and Pyrhonen, 2013). For such applications, they can be used instead of more powerful magnets with higher cost, such as rare-earth magnets.

Due to their low production costs, ferrite permanent magnets are present in a wide variety of every day life applications. They are mainly present in the motors and actuators used

- in domestic applications:
 - air conditioning system, compressor, washing machine, dryer, refrigerator, microwaves oven (rotation of the tray and fan), blender, food mixer, vacuum cleaner, hair dryer, hand dryer, electric razor, electric toothbrush, lifting pumps...
- in audio and video applications:
 - video camera (zoom, focus, tape scroll, read head motors), laser disc loader, turntables, video tape recorder (tape drive or tape drive motors), vinyl record turntables...
- in secretarial office:
 - many engines on computers, printers, photocopiers, fax...
- in automotive applications:
 - fuel pump, ABS pump, electric window regulator, electric seat, sunroof, fan, wiper, active suspension, braking, starter, door locks, air bag sensors, oil level sensors, solenoid valve sensors regulating air circulation, exhaust gas...
- in portable tools:
 - drills, screwdrivers, jigsaws, chainsaws, electric hammers, clippers...
- in medical field:
 - blood circulation pump motor, Magnetic Resonance Imaging apparatus motors, medical bed elevation motors...

Ferrite magnets are found in generators: wave power, wind turbines, turbo generators (Goldman, 2006).

Also, ferrite magnets can be found in loudspeaker coils, microphones and headphones.

References

- Goldman, A., 2006. Ferrites for Permanent Magnet Applications. In: *Modern Ferrite Technology*. Boston, MA: Springer. pp. 227–242.
- Grössinger, R., Tellez Blanco, J.C., Kools, F., *et al.* 2000. Proceedings of the 8th International Conference on Ferrites, Kyoto, Japan, p. 428.
- Iqbal, M.J., Ashiq, M.N., Gomez, P.H., 2009. *J. Alloys Comp.* 478, 736.
- Kojima, H., 1982. In: Wohlfarth, E.P. (Ed.), *Ferromagnetic Materials 3*. North-Holland Publishing Company, p. 305.
- Kools, F., Morel, A., Grössinger, R., Le Breton, J.M., Tenaud, P., 2002. *J. Magn. Magn. Mat.* 242–245, 1270.
- Kools, F., Morel, A., Tenaud, P., *et al.*, 2000. In: Abe, M., Yamazaki, Y. (Eds.), *Proceedings 8th International Conference on Ferrites*. Kyoto, Japan: Japan Society of Powder and Powder Metallurgy, p. 437.
- Kramer, M.J., Mc Callum, R.W., Anderson, I.A., Constantinides, S., 2012. *Journal of the Minerals, Metals and Materials Society* 64, 752–763.
- Le Breton, J.M., Lechevallier, L., Feng Wang, J., Harris, I.R., 2004. *J. Magn. Magn. Mater.* 272–276, 2214.
- Le Breton, J.M., Teillet, J., Wiesinger, G., *et al.*, 2002. *IEEE Trans. Magn.* 38, 2952.
- Lechevallier, L., Le Breton, J.M., Teillet, J., *et al.*, 2003. *Physica B* 327, 135.
- Lechevallier, L., Le Breton, J.M., Wang, J.F., Harris, I.R., 2004. *J. Phys. Condens. Matter* 16, 5359.

- Lotgering, F.K., 1974. *J. Phys. Chem. Solids* 35, 1633.
- Petrov, I., Pyrhonen, J., 2013. *IEEE Transactions on Industrial Electronics* 60, 2131–2138.
- Research and Markets, 2019. Permanent magnets market size, share & trends analysis report by material (ferrite, neodymium iron boron, aluminum nickel cobalt), by application, by region, and segment forecasts, 2019–2025. Report ID: 978-1-68038-058-3, Grand View Research.
- Reports and Data, 2019. Ceramic magnets market by type (soft ferrite magnet and hard ferrite magnet), grade type, by shape, by application, and segment forecasts, 2016–2026. Reports and data, report ID: RND-001514.
- Rosignol, M., Yonnet, J.P., 1999. Les aimants permanents. Les matériaux magnétiques et leurs applications: Magnétisme II. Presses Universitaires de Grenoble.
- Sauer, C., Köbler, U., Zinn, W., Stäblein, H., 1978. *J. Phys. Chem. Solids* 39, 1197.
- Taguchi, H., Minachi, Y., Masuzawa, K., Nishio, H. 2000. Proceedings of the Eighth International Conference on Ferrites. Kyoto, Japan, p. 405.
- Taguchi, H., Takeishi T., Suwa, K., Masuzawa, K., Minachi, Y., 1996. Proceedings of the 7th International Conference on Ferrites. Bordeaux, France, pp. C1–311.
- Tenaud, P., Morel, A., Kools, F., Le Breton, J.M., Lechevallier, L., 2004. *J. Alloys Comp.* 370, 331.
- Van den Broek, C.A.M., Stuijts, A.L., 1977. *Philips Tech. Rev.* 37, 157.
- Went, J.J., Rathenau, G.W., Gorter, E.W., van Oosterhout, G.W., 1952. *Rev. Tech. Philips* 13 (12), 361.

Ferrites

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Key Properties

Since their commercial introduction in 1948 by Philips, soft ferrites have found widespread use in electronic applications as inductor or transformer cores, because of their high resistivity in comparison to metallic soft-magnetic materials. This makes soft-magnetic ferrites considerably better suited for applications at frequencies ≥ 10 kHz. Soft-magnetic ferrites belong to the class of ferrites that have a cubic, spinel lattice structure. These ferrites have the structural formula MeFe_2O_4 with Me being a divalent metal ion from the 3d transition elements: manganese, iron, cobalt, nickel, copper, zinc, or combinations of these. In addition, also other ions such as Li^+ , Mg^{2+} , Cr^{3+} , Ti^{4+} , or Sb^{5+} can be incorporated in the spinel lattice. There is also a class of soft-magnetic ferrites with a hexagonal crystal structure, which has soft-magnetic properties. However, this class of soft ferrites has found limited application thus far (Kimura, 2012), and is not treated here. The reader is referred to the treatise by Smit and Wijn (1959).

The spinel-type lattice structure characterizing the conventionally applied ferrites is depicted in Fig. 1. This lattice structure has a lattice parameter a in the range 8.30–8.50 Å depending on the composition of the ferrite (Smit and Wijn, 1959). In the unit cell, of which $\frac{1}{4}$ is drawn in detail in Fig. 1, the oxygen ions (O in Fig. 1) form a close-packed face-centered cubic lattice. There are 64 possible tetrahedral (or A) and 32 possible octahedral (or B) interstices or sites in which metal ions can be incorporated. Only eight of the octahedral and 16 of the tetrahedral sites are filled with metal cations. The magnetic interactions are such that the two neighboring magnetic ions on the B-site are ferromagnetically (that is parallel) coupled, whereas the much larger coupling between the magnetic ion on the A-site and the ions on the B-sites is antiferromagnetic (antiparallel). Since, there are two ions antiparallel coupled to each magnetic ion on the A-site, a net magnetic moment still results. This gives rise to the so-called ferrimagnetism, a net magnetic moment in a magnetic material in which the dominant magnetic interaction is antiferromagnetic. This behavior can be understood on the basis of superexchange interaction between the magnetic ions as explained by Anderson (1963) and Goodenough (1963).

As shown in Fig. 1 the magnetic ions in ferrites are separated by oxygen ions, which precludes a direct exchange interaction between the magnetic ions. Since, in addition, ferrites are insulators (or very poor semiconductors) exchange interaction by itinerant electrons is also not possible. The explanation for magnetism in these oxides is that the exchange interaction between the magnetic ions is mediated by the intermediate oxygen ion through superexchange (Anderson, 1963; Goodenough, 1963). Assuming that the magnetic ions M_1 and M_2 lie on a straight line through the intermediate oxygen ion O, the magnetic superexchange interaction can be explained in the following covalent bonding picture for magnetic ions with at least a half-filled shell: one of the electrons of the oxygen p-orbital directed to the magnetic ions will be excited or transferred to the ion M_1 .

On M_1 the electron can only enter an empty orbital with its spin direction antiparallel to the magnetic moment of M_1 . The other electron of the p-orbital pointing along the $M_1\text{--O--}M_2$ bond can only be excited to the M_2 ion and lower the total energy of the system, if the magnetic moment of M_2 is oriented antiparallel to M_1 . This is so because both electrons involved originate from the same oxygen p-orbital, and thus their spins must be antiparallel according to the Pauli exclusion principle. Hence, the magnetic (spin) moments of both ions should be aligned antiparallel to obtain the lowest energy state and to fulfill the Pauli principle at the same time. More about the superexchange interaction can be found in the reviews by Anderson (1963) and Goodenough (1963). For the superexchange interaction it can be derived that it is strong and antiferromagnetic along a 180° bond, i.e., when $M_1\text{--O--}M_2$ form a straight line, while it is weak and ferromagnetic along a 90° bond. This explains that the

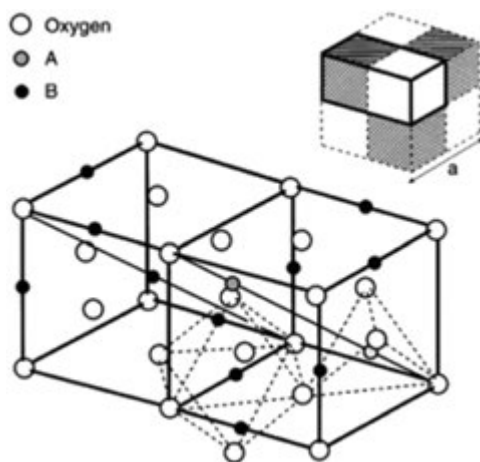


Fig. 1 The spinel lattice structure.

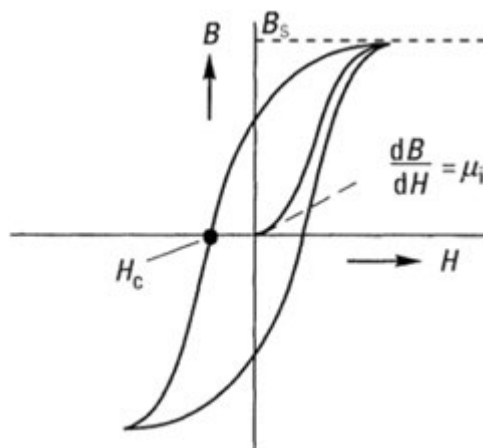


Fig. 2 A typical hysteresis loop giving the response of a magnetic material to an external field, H , as changes in induction $B = M + \mu_0 H$. At high fields the B - H loop asymptotically approaches the limit B_s due to the saturation of the magnetization at M_s , the saturation magnetization. The coercive field, H_c and the initial permeability μ_i have been indicated.

interaction between the magnetic ions on the A- and B-sites in spinel ferrites, which make an angle of around 125° (see Fig. 1), is much stronger than between those on the B-sites which make an angle of around 90° (Smit and Wijn, 1959). Thus, in ferrites the dominant magnetic interaction is the AB interaction, which is typically 15–20 times stronger than the BB interaction. This causes the magnetic moments on the A and B-sites to be antiparallel oriented whereas those on the B-sites are parallel to each other.

The net magnetic moment of spinel ferrites is thus determined by the sum of the magnetic moments of the two spins on the B-site minus the moment of the A-site. This results in typical a saturation magnetization, M_s , of spinel ferrites between 143 and 560 kA m^{-1} at 0K and 120 – 477 kA m^{-1} at room temperature (Smit and Wijn, 1959), which are lower than what can be attained in metallic magnetic materials (where the dominant magnetic interaction is ferromagnetic). Fig. 2 shows a typical magnetic hysteresis loop, which gives the response of a magnetic material to an externally applied magnetic field, H . In Fig. 2 the key parameters defining a magnetic material such as the coercivity H_c and initial permeability μ_i have been indicated. Most of the spinel ferrites, with the exception of ZnFe_2O_4 , have a Curie temperature T_c in excess of room temperature, with typical values ranging from 300°C for MnFe_2O_4 to 670°C for $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ (Smit and Wijn, 1959). This T_c of ferrites is acceptable for most applications that require typically an operating temperature of the ferrite of 80°C . In most commercial applications either MnZn-ferrites or NiZn-ferrites are used. The MnZn-ferrites have the advantage that high values of the permeability μ can be reached, whereas NiZn-ferrites offer advantageously higher values of the resistivity $\rho \approx 10^5 \Omega\text{m}$ versus $1 \Omega\text{m}$ for MnZn-ferrites. This makes NiZn-ferrites more suited for high frequency application, in particular for frequencies $\geq 1 \text{ MHz}$. For applications which require a high resistivity and low material costs, MgZn-ferrites ($\rho \approx 10^6 \Omega\text{m}$) are used. For instance, the yoke-rings in the deflection unit of cathode-ray tubes were made of MgZn-ferrites as this made it possible to wind the deflection coil directly on the ferrite yoke.

For applications the magnetic softness, characterized by the permeability $\mu = dB/dH$, is relevant as it gives the response of a ferrite to an applied magnetic field H (see Fig. 2). Depending on intrinsic properties (composition, additions) and extrinsic properties (microstructure, porosity, preparation) permeabilities of $\geq 15,000$ can be obtained. The highest permeabilities are typically reached in MnZn-ferrites with large grains, which are free from pores. NiZn-ferrites generally have lower permeabilities, in commercial applications between 100 and 1000. This is because compensation of the magneto-crystalline anisotropy, as can be done in MnZn-ferrites, is not possible in NiZn-ferrites (Smit and Wijn, 1959).

The only commercial application in which monocrystalline spinel ferrites were used on a large scale was the magnetic recording head production for videocassette recorders, VCRs. For most applications ferrites are made by ceramic processing which results in polycrystalline materials. Ceramic processing is done by mixing and calcining of oxide and carbonate powders of the constituent metals. Subsequently, the powder is pressed in the desired shape and the final processing step is a sintering process following a selected temperature profile under a carefully controlled atmosphere. Typically, the sintering temperatures needed to have the required solid state reactions proceed are 1100°C or more. Details can be found elsewhere (Smit and Wijn, 1959; Snelling, 1988).

For further information about soft ferrites the reader is referred to the book by Smit and Wijn (1959) and the review by Brabers (1995) while the book by Cox (1992) provides useful background information on the theory of their electronic properties.

Applications

Traditionally, the main application areas of soft ferrites are transformer cores, inductors, and yoke-rings in cathode-ray tubes (Snelling, 1988). Since the 1990s new applications have arisen, such as cores for induction lighting and magnetic antennas for pagers. The trend in all these applications and the driving force for ferrite development is that the operating frequency increases to achieve miniaturization. This trend is illustrated in Fig. 3 which gives the weight and operating frequency of a 100 W power supply since the 1960s. A reduction in weight from approximately 8 kg to around 100 g has been achieved. The reason that

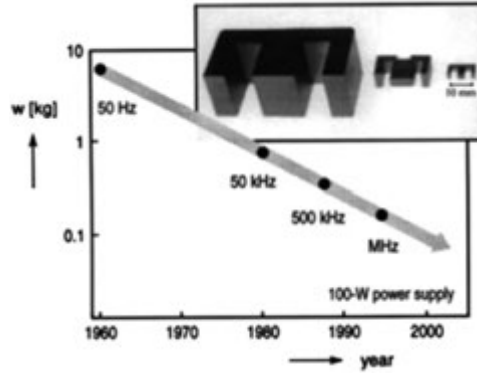


Fig. 3 The miniaturization trend in the weight of transformer cores since the 1960s. The resulting operating frequencies are indicated. The inset shows various sizes of E-cores used for transformers.

miniaturization necessitates higher operating frequencies can be understood by considering the throughput power P_{thr} of a transformer core, which can be given as:

$$P_{thr} = I_{in} \times V_{in} \quad (1)$$

with I_{in} the input current and V_{in} the input voltage. Expressing V_{in} in terms of the change of flux in time $d\Phi/dt$ gives:

$$P_{thr} = I_{in} \times Nd\Phi/dt = I_{in} \times N 2\pi f BA \quad (2)$$

with N the number of turns of the primary winding of the transformer, f the operating frequency, B the induction level in the core, and A the cross-sectional area of the core. Since the maximum induction level within the core is limited by the saturation magnetization of the ferrite, M_s , it is obvious from Eq. (2) that in order to decrease the size and hence cross-sectional area of the transformer, without sacrificing throughput power, the operating frequency f should be increased. Hence, a key aspect of modern research and development in soft ferrites is to reduce the dissipation, i.e., losses in ferrites at increasing frequencies, in the range of 100 kHz to 3 MHz.

Traditionally, three contributions to the dissipation or loss, P_{tot} , in soft ferrites are distinguished: d.c. hysteresis loss, P_h ; eddy current loss, P_e ; and residual loss, P_r . The justification for this subdivision resides in part in the differences in frequency response of each contribution, although it is to a large part phenomenological. The d.c. hysteresis loss corresponds to the dissipation incurred by cycling the d.c. B–H loop of a soft-magnetic ferrite. Through the number of times the loop is cycled per unit time, P_h depends on frequency f as $P_h = f \oint B dH$. The standard approach to limit the hysteresis loss in ferrites (Smit and Wijn, 1959; Snelling, 1988) is to facilitate domain wall movement by using ferrites with a low coercivity, H_c . This is done by selecting ferrite compositions which have a low magneto-crystalline anisotropy constant K . Ideally the ferrite should have its anisotropy compensation point, at which K passes through zero, at the required operating temperature. Typically, this is 80°C. In addition, the ferrite composition used should have a low magnetostriction constant and internal and external stress should be avoided to limit adverse magnetostriction effects. Finally, ferrites with a large grain size are used as H_c proportional to D^{-1} , with D the grain size (see van der Zaag, 1999).

The eddy current contribution is the dissipation caused by eddy currents in the ferrite. Although, due to their oxidic character, ferrites have a much higher resistivity than metallic soft-magnetic materials, their conductivity is not zero and eddy currents can occur. One can derive that the dissipation P_e is (Snelling, 1988):

$$P_e = C_e f^2 B^2 / \rho \quad (3)$$

with C_e a dimensional constant and ρ the resistivity at the measurement frequency. Hence, the P_e contribution can be separated by plotting P_{tot}/f versus f , as has been done in Fig. 4. Traditionally, the remainder of the dissipation, such as the dissipation due to ferromagnetic resonance (Snoek, 1948) has been treated as the residual loss contribution, P_r . The residual loss is thus the extra loss under a.c. measurement conditions not attributable to eddy current loss (i.e., not matching Eq. (3)). Thus, P_r has a higher than quadratic dependence on the frequency f . As Fig. 4 illustrates, at higher frequencies, both the eddy current and residual loss dominate the ferrite dissipation. Consequently, considerable work was done in the 1990s to determine and minimize the mechanisms responsible for these losses (van der Zaag, 1999).

To reduce the eddy current loss, the resistivity of ferrites should be increased. The resistivity of the ferrites used in commercial applications is determined by the resistivity of the grain boundary in these polycrystalline materials. Hence, substantial effort has been devoted to increase the grain boundary resistance by careful control of the processing conditions and by adding dopants such as Nb_2O_5 , ZrO_2 , and Ta_2O_5 besides the well-known glass-forming additions CaO and SiO_2 (Snelling, 1988). The glass formers segregate to the grain boundary to form a secondary phase, which forms an insulating layer around each grain preventing current flow from one grain to the next. At higher frequencies, also the capacitive shunting of the grain boundary impedance becomes an issue. It is thought that the addition of dopants such as Nb_2O_5 , ZrO_2 , and Ta_2O_5 play a role in reducing this effect.

The residual loss has been shown to be a dominant contribution to the dissipation of ferrites in the 500 kHz to 3 MHz frequency range. Microscopic mechanisms contributing to the residual loss are: the ferromagnetic resonance loss (Snoek, 1948)

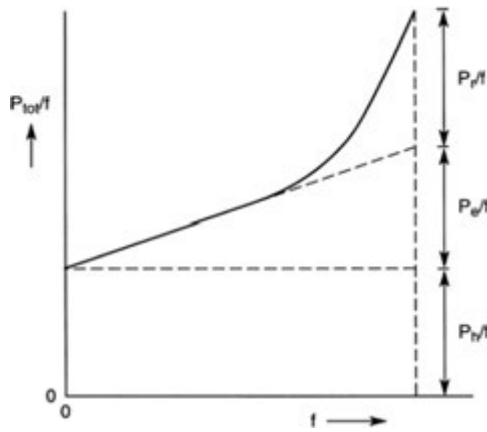


Fig. 4 Schematic diagram of the total dissipation, P_{tot} , versus the frequency, f , for soft-magnetic ferrites. The various contributing terms to the ferrite dissipation: hysteresis loss P_h , eddy current loss P_e and residual loss P_r are indicated. All terms have been scaled by the frequency.

and the intragranular domain wall loss (van der Zaag, 1999). The former is caused by excitation of the uniform spin precession in the ferrite. For this phenomenon the well-known Snoek's law applies that (Snoek, 1948):

$$(\mu_i - 1) \times f_r = \text{constant} = g/3 \pi M_s \quad (4)$$

with f_r the ferromagnetic resonance frequency and g the gyromagnetic ratio. The latter is due to domain wall movement of intragranular domain walls within the grains of a polycrystalline ferrite (van der Zaag, 1999). Both contributions can be eliminated by using a fine-grained ferrite material. In the case of the ferromagnetic resonance loss, this causes a reduction in the permeability of the ferrite and hence an upward shift of the ferromagnetic resonance (Snoek, 1948). In well-developed ferrites the ferromagnetic resonance should be above the frequency at which the ferrite is operated. The intragranular domain wall loss is eliminated by using fine-grained ferrites in which all the grains are monodomain, i.e., intragranular domain walls are absent. Such a situation occurs in fine-grained ferrites, since below a certain grain size the monodomain state has a lower magnetostatic energy than a domain state in which a magnetic domain wall is present (van der Zaag, 1999). For further reading on the subject of dissipation in ferrites the reader is referred to (Snoek, 1948; van der Zaag, 1999).

New Developments

Ferrite Films

A new development in the field of soft-ferrite research and their application is their deposition and use in thin films (see Brabers, 1995; Suzuki, 2001). Spurred by the work on high- T_c superconductors, there has been considerable improvement in the deposition of thin film oxides, making it possible to deposit thin film ferrites in the nanometer to micrometer thickness range. The interest in these thin film ferrites is driven in part by the possibility to improve integrated inductors (Suzuki *et al.*, 1996).

In the IC industry a problem is that present inductors, amongst others for RF-applications, with typical diameters of 0.2–0.8 mm are huge in comparison to the active elements on ICs. Thus, they require a too large surface area to make integration on chip economically attractive. A possible solution would be to apply a magnetic substrate or a thin magnetic film on the coil as this may result in a reduction to a $1/4$ of the area needed for the same inductance while maintaining the quality factor Q (as is illustrated in Fig. 5 by using a ferrite substrate). In view of their resistivity, which makes application at higher frequencies possible, ferrite films deposited on the integrated inductors can provide a possible solution. A problem is the high substrate temperature ($=600^\circ\text{C}$) needed to assure the formation of a ferrite film with a proper cation distribution and an adequate grain size to assure that the ferrite films have a sufficiently high permeability. Wet-chemically prepared films grown by ferrite plating at 80°C provide a useful method as permeabilities ≥ 25 have been obtained in μm thick MnZn-ferrite films in the frequency range up to 10 MHz (van der Zaag *et al.*, 1999). For approximately $0.7 \mu\text{m}$ thick NiZn-ferrite plated films permeabilities of around 80 in the 100 MHz–1 GHz range have been obtained (Obi *et al.*, 2011).

For higher frequencies in the microwave, GHz regime, the μ of MnZn-ferrite and NiZn-ferrites are too low and yttrium iron garnets (YIG) are the materials of choice. The advances made, using these YIG magnetic oxides films for microwave devices such as isolators, circulators and phase shifters has been reviewed by Harris (2011).

Another interesting trend is the work on magnetite, Fe_3O_4 , ultrathin films in view of their intrinsic fully spin-polarized electron transport for magnetoresistive sensors (Coey *et al.*, 1998; Seneor *et al.*, 1999). Fe_3O_4 is a half-metallic ferromagnet as it has a gap in the minority spin band, whereas there is no gap in the majority spin band (Brabers, 1995). Thus, for the majority spins Fe_3O_4 behaves as a metal with spin-polarized electron transport along the B-sites by hopping conduction. This property is of interest as it could be employed in magnetic tunnel junctions leading to a magnetic field sensor element with, theoretically, an infinite tunnel

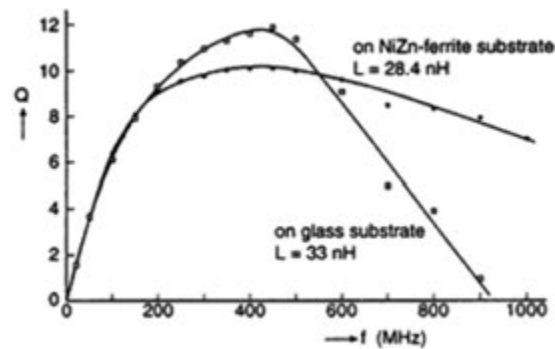


Fig. 5 The quality factor, $Q = \omega L/R$ with ω the angular frequency, L the inductance and R the resistance of the inductor, of two planar inductors, one on a glass substrate and the other on a NiZn-ferrite substrate. Although both inductors have comparable inductances ($L = 33$ and 28.4 nH) and Q , the inductor using a ferrite substrate has half the diameter, i.e., needs $1/4$ of the area.

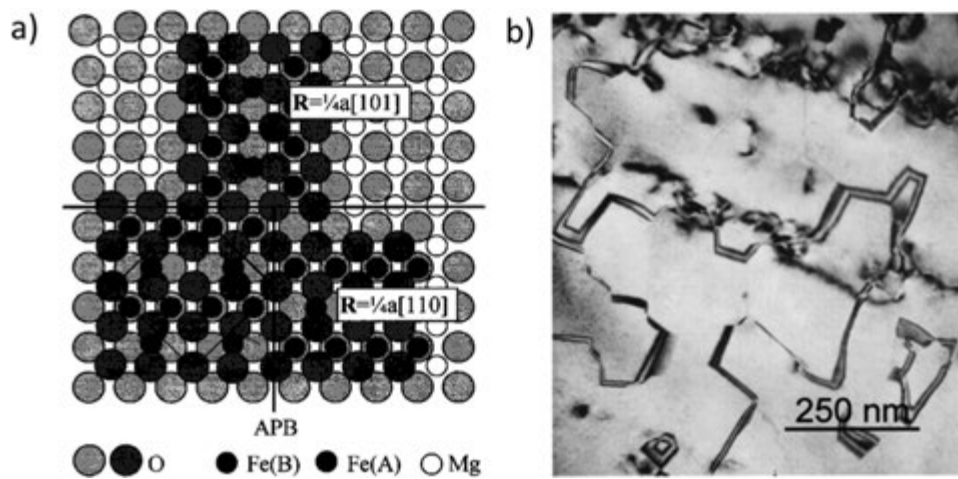


Fig. 6 (a) Anti-phase domains form when layer of a spinel, such as magnetite (Fe_3O_4), grows epitaxially on a rock salt substrate such as MgO . The domains shown are related to a reference domain by in-plane and out-of-plane shift vectors. An example of each type is shown in the drawing. A characteristic of the out-of-plane shifted domains is that the rows of octahedrally coordinated cations in atomic layers on the same level are oriented perpendicular to each other. (b) Example of antiphase boundaries (APBs) seen by transmission electron microscopy (TEM) for a 200 nm Fe_3O_4 layer grown by molecular beam epitaxy (MBE) on MgO (001). Only APBs with out-of-plane shift vectors are visible in the TEM picture. Reproduced from Hibma, T., Voogt, F.C., Niessen, L., *et al.*, 1999. Anti-phase domains and magnetism in epitaxial magnetite layers. *J. Appl. Phys.*, 85. 5291–5293, with the permission of AIP Publishing.

magneto-resistance (TMR) effect, as electrons with minority spin cannot pass the Fe_3O_4 layer. The degree to which a proper Fe_3O_4 layer can be grown in these magnetic tunnel junctions, or needs to be grown to have a positive effect on the magneto-resistance is not known precisely. The same holds for the role played by the interfaces of the Fe_3O_4 layer or antiphase boundaries (APBs). APBs arise because Fe_3O_4 has a lower symmetry and a larger unit cell, see Fig. 1, than the substrates typically used in epitaxial growth (MgO , NiO , CoO) which have a rock salt structure (Margulies *et al.*, 1997; Hibma *et al.*, 1999). Fe_3O_4 can nucleate on such a substrate in 8 unique ways, see Fig. 6(A). These different islands are not able to match up to form a continuous Fe_3O_4 layer without stacking faults, see Fig. 6(B) (Hibma *et al.*, 1999). The resulting Fe_3O_4 layer will have a continuous O_2 -sublattice, concomitant with a fragmented, discontinuous cation sublattice, giving rise to APBs.

The role of APBs in relation to the observed reduced magnetization of Fe_3O_4 thin films compared to the saturation magnetization of bulk Fe_3O_4 (Margulies *et al.*, 1997) or whether so-called “dead” magnetic interface layers caused this (van der Heijden *et al.*, 1996) has been the subject of considerable debate. The study by Chang *et al.* (2016) into the epitaxial growth of Fe_3O_4 and its interface structure has managed to elucidate this. These authors have studied the growth of ultrathin Fe_3O_4 films grown by molecular beam epitaxy (MBE) through soft X-ray absorption spectroscopy (XAS). From this experiment the following picture emerges, see Fig. 7: When depositing Fe_3O_4 , first basically a charge neutral rock salt FeO layer with 25% Fe vacancies is formed. This is a charge neutral or nonpolar layer. When depositing the second monolayer, first again such a nonpolar layer similar to the first layer is formed. However, now both monolayers can provide each the Fe^{3+} ions needed to generate the A-site Fe^{3+} ions. Since this layer is sandwiched between two layers from which the Fe^{3+} ions originate, charge neutrality is maintained. The same mechanism operates when the third monolayer is deposited. The elegant nature of this model for the growth process of Fe_3O_4 on

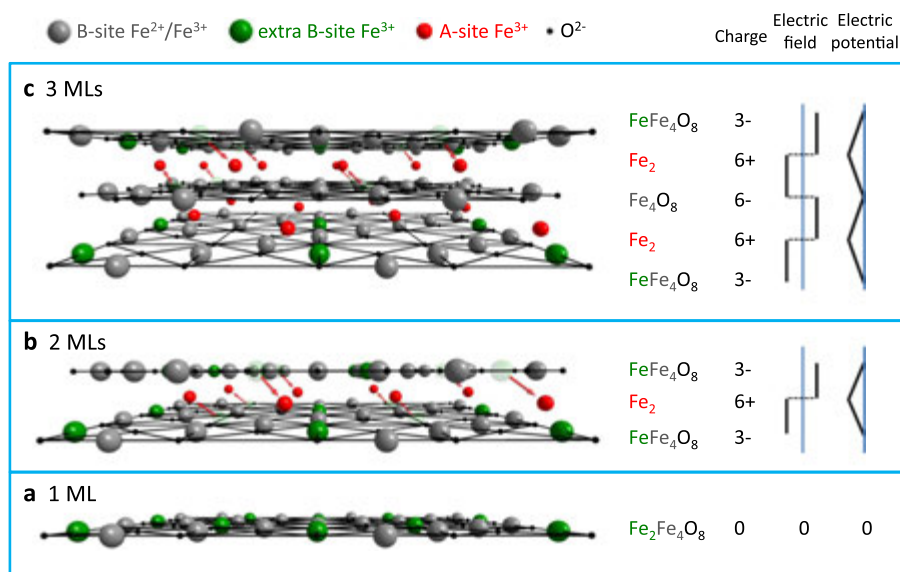


Fig. 7 Model for the growth process of polar Fe_3O_4 (001) thin films: (a) One monolayer, (b) Two monolayer and (c) Three monolayers. Reproduced from Chang, C.F., Hu, Z., Klein, S., *et al.*, 2016. Dynamic atomic reconstruction: How Fe_3O_4 thin films evade polar catastrophe for epitaxy. *Phys. Rev. X* 6, 1–7. (0401011). doi:10.1103/PhysRevX.6.041011.

rock salt substrates, such as MgO (001), is that it explains the experimental observation of the authors that Fe_3O_4 films below 6 monolayer thick lack Fe^{3+} ions compared to bulk Fe_3O_4 . Moreover, this model deals with the polar catastrophe, which would occur if one considers a simple layer-by-layer deposition of the Fe_3O_4 spinel structure (Chang *et al.*, 2016). The authors thus suggest that the Fe^{3+} ions move within the films during the deposition process to give rise to the A-site. This model for the Fe_3O_4 growth on MgO (001) seems to support the proposition of a “dead” layer model at Fe_3O_4 - MgO interface as the low amount of A-site present at the interface may lead to missing superexchange interaction at the interface which may lead to a magnetically “dead” interface. Rather than the APB approach, in which such behavior would be the consequence of superparamagnetic behavior of the antiphase domains (Voogt *et al.*, 1998).

This understanding of the growth process and interface structure of Fe_3O_4 on an epitaxial substrate may also be relevant to guide the application of ferrite layers in magnetic devices.

A first indication of an increased magneto-resistance effect due to the incorporation of Fe_3O_4 layers in magnetic tunnel junctions was reported by Seneor *et al.* (1999) and van der Zaag *et al.* (2000). More recent work has highlighted the importance of structural improvements such as the reduction of the antiphase boundary density, by using a Fe-underlayer in $\text{Fe}_3\text{O}_4/60 \text{ \AA}$ $\text{MgO}/\text{CoFe}/\text{IrMn}/\text{Ta}$ tunnel junctions grown on Al_2O_3 (0001). Importantly, this work showed that as the tunnel junctions improved, as measured by a large resistance-area product, the TMR ratio became larger and more negative, as expected for an intrinsic TMR effect. In the best tunnel junctions a TMR ratio of -26% was obtained at room temperature (Kado, 2008).

In addition, ferrite layers (XFe_2O_4 with $\text{X} = \text{Co}, \text{Ni}$ or Mn) have been studied as spin filters to cause spin polarized current in a detection layer, see the review by Moussey (2013). The problem encountered so far is that the very thin (3 nm) XFe_2O_4 spin filters suffer from thermally activated transport due to the presence of defects. Also for spin current generation for spintronic applications, magnetic insulators are of interest as these materials can generate and transmit pure spin currents with minimal dissipation from eddy currents. Thus far, most studies have applied YIG for this purpose. However, also spinel ferrite layers, such as $(\text{NiZn})_1(\text{AlFe})_2\text{O}_4$ and $\text{Mg}(\text{AlFe})_2\text{O}_4$ films, have been studied for this purpose. These films exhibit good spin pumping properties, have the advantage that they can be grown on various substrates, and have significant in-plane anisotropy, leading to high spin-wave frequencies (see, for instance, Riddiford *et al.*, 2019).

Life Sciences Applications: Magnetic Beads

Another interesting new application is the use of so-called magnetic beads in the life sciences and in *in vitro* diagnostics (Pankhurst *et al.*, 2009; Gijs *et al.*, 2010; Pamme, 2012; van Reenen *et al.*, 2014). These beads are composed of small ($< 20 \text{ nm}$) Fe_3O_4 or maghemite, $\gamma\text{-Fe}_2\text{O}_3$, nanoparticles embedded in a polymer matrix, see Fig. 8 for an example. These nanoparticles are so small that their thermal energy exceeds their magnetostatic energy at room temperature. This gives rise to superparamagnetic behavior, i.e., the beads will only exhibit magnetic behavior in an applied magnetic field. In applications, this has the advantage that bead agglomeration will only occur in an applied magnetic field. Upon removal of the field the beads will redisperse.

These beads can be functionalized by conjugation of biomolecules (such as antibodies or oligonucleotides) to the surface so that they can bind selectively specific antigens or nucleic acids fragments in a sample. Such beads have found application in *in vitro*

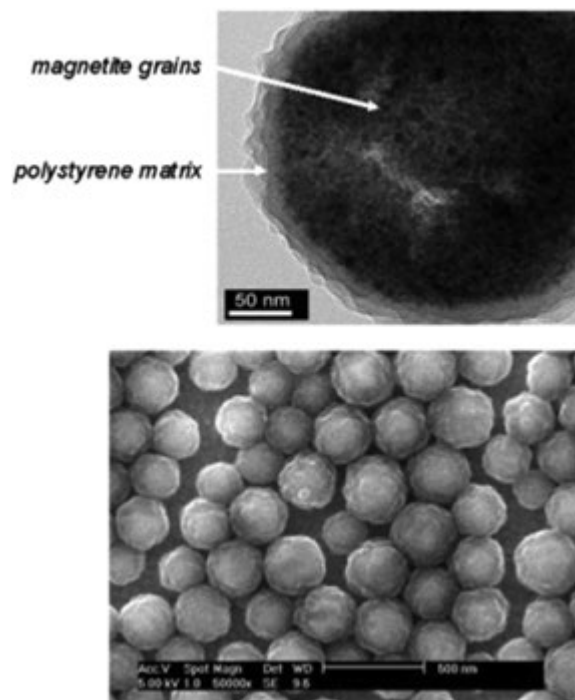


Fig. 8 Scanning electron microscope image of a magnetic bead composed of Fe_3O_4 nanoparticles embedded in a polymer matrix used in the life sciences and *in vitro* diagnostics.

diagnostics to influence or speed-up assay time through magnetic actuation (Gijs *et al.*, 2010; Pamme, 2012; Moerland *et al.*, 2019). Magnetic beads also have found application in nucleic acids purification and collection under suitable buffer conditions, when they are either silica or carboxyl coated (Hawkins *et al.*, 1994) or both.

Finally, ferrite nanoparticles are also finding use in *in vivo* applications as contrast agent in MRI and magnetic particle imaging and as agents to deliver hyperthermal treatment of tumors, where local heating is used to treat a tumor (Pankhurst *et al.*, 2009).

References

- Anderson, P.W., 1963. Chapter 2 – Exchange in insulators: Superexchange, direct exchange and double exchange. In: Rado, G.T., Suhl, H. (Eds.), *Magnetism*. New York: Academic Press.
- Brabers, V.A.M., 1995. Chapter 3 – Progress in spinel ferrite research. In: Buschow, K.H.J. (Ed.), *Handbook of Magnetic Materials*, vol. 8. Amsterdam: Elsevier, pp. 189–324.
- Chang, C.F., Hu, Z., Klein, S., *et al.*, 2016. Dynamic atomic reconstruction: How Fe_3O_4 thin films evade polar catastrophe for epitaxy. *Phys. Rev. X* 6, 1–7. doi:10.1103/PhysRevX.6.041011.
- Coe, J.M.D., Berkowitz, A.E., Balcells, L., Putris, F.F., Parker, F.T., 1998. Magnetoresistance of magnetite. *Appl. Phys. Lett.* 72, 734–736.
- Cox, P.A., 1992. *Transition Metal Oxides: An Introduction to their Electronic Structure and Properties*. Oxford: Clarendon Press, (Sections 3.4 and 5.2).
- Gijs, M.A.M., Lacharme, F., Lehmann, U., 2010. Microfluidic applications of magnetic particles for biological analysis. *Chem. Rev.* 110, 1518–1563.
- Goodenough, J.B., 1963. *Magnetism and the Chemical Bond*. New York: Wiley, pp. 165–185.
- Harris, V.G., 2011. Modern microwave ferrites. *IEEE Trans. Magn.* 48, 1075–1104.
- Hawkins, T.L., O'Connor-Morin, T., Roy, A., Sabtilan, C., 1994. DNA purification and isolation using a solid-phase. *Nucl. Acids Res.* 22, 4543–4544.
- Hibma, T., Voogt, F.C., Niessen, L., *et al.*, 1999. Anti-phase domains and magnetism in epitaxial magnetite layers. *J. Appl. Phys.* 85, 5291–5293.
- Kado, T., 2008. Large room temperature inverse magnetoresistance in tunnel junctions with a Fe_3O_4 electrode. *Appl. Phys. Lett.* 92, 092502.
- Kimura, T., 2012. Magnetoelectrical hexaferrites. *Ann. Rev. Condens. Matter Phys.* 3 (2012), 93–110.
- Margulies, D.T., Parker, F.T., Rudee, M.L., *et al.*, 1997. Origin of the anomalous magnetic behavior in single crystal Fe_3O_4 films. *Phys. Rev. Lett.* 79, 5162–5166.
- Moerland, C.P., Ijzendoorn, L.J., Prins, M.W.J., 2019. Anti-rotating magnetic particles for lab-on-chip application – A comprehensive review. *Lab. Chip* 19, 919–933.
- Moussey, J.-B., 2013. From epitaxial growth of ferrite thin to spin-polarized tunneling. *J. Phys. D Appl. Phys.* 46, 143001.
- Obi, T.O., Liu, M., Lou, J., *et al.*, 2011. Spin-spray deposited NiZn-ferrite films exhibiting $\mu'_r > 50$ at GHz range. *J. Appl. Phys.* 109 (7), 07E527-1–07E527-3.
- Pamme, N., 2012. On-chip bioanalysis with magnetic particles. *Curr. Opin. Chem. Biol.* 6, 436–443.
- Pankhurst, Q.A., Thanh, N.T.K., Jones, S.K., Dobson, J., 2009. Progress in applications of magnetic nanoparticles in biomedicine. *J. Phys. D Appl. Phys.* 42 (22), 224001.
- Riddiford, L.J., Wissler, J.J., Emori, S., *et al.*, 2019. Efficient spin current generation in low-damping $\text{Mg}(\text{AlFe})_2\text{O}_4$ thin films. *Appl. Phys. Lett.* 115, 122401.
- Seneor, P., Fert, A., Maurice, J.L., *et al.*, 1999. Large magnetoresistance in tunnel junctions with an iron oxide electrode. *Appl. Phys. Lett.* 74 (1999), 4017–4019.
- Smit, J., Wijn, H.P.J., 1959. *Ferrites*. New York: Wiley.
- Snelling, E.C., 1988. *Soft Ferrites: Properties and Application*, second ed. London: Butterworths.
- Snoek, J.L., 1948. Dispersion and absorption in magnetic ferrites at frequencies above one Mcs. *Physica* 14, 207–217.
- Suzuki, Y., 2001. Epitaxial spinel ferrite thin films. *Ann. Rev. Mater. Res.* 31, 265–289.
- Suzuki, Y., van Dover, R.B., Gyorgy, E.M., *et al.*, 1996. Structure and magnetic properties of epitaxial spinel ferrite thin films. *Appl. Phys. Lett.* 68, 714–716.

- van der Heijden, P.A.A., Bloemen, P.J.H., Gaines, J.M., *et al.*, 1996. Magnetic interface anisotropy of MBE-grown ultra-thin (001) Fe_3O_4 layers. *J. Magn. Magn. Mater.* 159, L293–L298.
- van der Zaag, P.J., 1999. New views on the dissipation in soft magnetic ferrites. *J. Magn. Magn. Mater.* 196–7, 315–319.
- van der Zaag, P.J., Bloemen, P.J.H., Gaines, J.M., *et al.*, 2000. On the construction of an Fe_3O_4 -based all-oxide spin valve. *J. Magn. Magn. Mater.* 211, 301–308.
- van der Zaag, P.J., Lubitz, P., Kitamoto, Y., Abe, M., 1999. The permeability of plated ferrite films. *IEEE Trans. Magn.* 35, 3436–3438.
- van Reenen, A., de Jong, A.M., den Toonder, J.M.J., Prins, W.J.M., 2014. Integrated lab-on-chip biosensing systems based on magnetic particle actuation – A comprehensive review. *Lab. Chip* 14, 1966–1986.
- Voogt, F.C., Palstra, T.T.M., Niesen, L., *et al.*, 1998. Superparamagnetic behavior of structural domains in epitaxial ultrathin magnetite films. *Phys. Rev. B* 57, R8107–R8110.

Multiferroic Composites

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Introduction

The intrinsic coupling of electricity and magnetism, which goes back to Michael Faraday and was unified by Maxwell equations, plays essential roles in modern physics. Among them, the coupling interaction in multiferroic materials has drawn great interest due to their promising applications in recent times. Multiferroics are defined as materials that exhibit two or more of the primary ferroic properties: ferromagnetism, ferroelectricity, ferroelasticity in the same phase (Schmid, 1994). Nowadays, the non-primary orders such as antiferromagnetism and composites of individual ferroics are also included in the multiferroics, which is more often used to refer specifically to magnetoelectric (ME) coupling (Fiebig, 2005). The ME response is the control of electric polarization by applying a magnetic field (direct ME effect) or manipulation of magnetization by applying an electric field (converse ME effect) (Nan *et al.*, 2008). These materials are extremely interesting due to their physics that one can modify the magnetic state by changing electric field, which is favored by many practical applications. There are already very good reviews of this field (Fiebig, 2005; Spaldin and Fiebig, 2005; Cheong and Mostovoy, 2007; Khomskii, 2006; Eerenstein *et al.*, 2006; Wang *et al.*, 2009; Khomskii, 2009; Nan *et al.*, 2008; Srinivasan, 2010; Wang, 2016; Tu *et al.*, 2019), here, we will cover the most emphasis of them and of course with substantial additions.

The birth of the ME effect that crystals could exhibit simultaneously more than one ferroic order probably originated with Curie (1894) in the 19th century. Debye (1926) coined the term “magnetoelectric” a few years after the first unsuccessful attempts to demonstrate the ME effect experimentally. Before the first demonstration of intrinsic ME behavior in a single-phase compound, Tellegen (1948) proposed the idea of synthesizing a composite material that exhibited a ME effect. But the real considerable investigations in this field began in 1960s after several papers were given by Landau *et al.* (2013), Dzyaloshinskii (1960) and Astrov (1960), who theoretically predicted and experimentally observed the linear ME effect of the well-known antiferromagnet Cr_2O_3 . The interest in multiferroics faded somewhat after extensive activities in 1960s and 1970s, however, the renaissance of ME multiferroics appeared in 2000s (Spaldin and Fiebig, 2005). According to the microscopic sources of ferroelectricity, multiferroics are normally divided into two groups: type-I and type-II (Khomskii, 2009). There are several different origins of ferroelectricity: lone pairs, charge ordering, etc. while the microscopic source of magnetism is mostly same: the exchange interactions between the localized electrons that lead to an equivalent localized spin, or magnetic moment. Due to the different microscopic origins of ferroelectricity and ferromagnetism in type-I multiferroics, they are independent of each other although there is a poor coupling between them. The coupling is very strong in type-II multiferroics, in which ferroelectricity is in fact caused by a type of magnetic ordering. The resurgence of the entire field of multiferroics is owing to the discovery of type-II multiferroics (Kimura *et al.*, 2003; Hur *et al.*, 2004), though they are less promising for practical applications due to the much smaller polarization in these materials. This situation also facilitates the investigations on composite multiferroics consisting of ferroelectrics and magnets in the form of multilayers and self-organized nano-structures (Ramesh and Spaldin, 2007). Recent developments in thin film growth techniques and experimental methods for observing magnetic and electric domains, together with theoretical breakthroughs in understanding ME coupling, have generated a great deal of studies on magnetoelectric multiferroics (Fiebig, 2005; Spaldin and Fiebig, 2005). However, none of the existing single-phase multiferroics materials are attractive for applications in the short term, because they are not able to combine both large and robust magnetic and electrical ordering at room temperature. By establishing two-phase composite multiferroics that consist of a ferromagnetic constituent (such as FeGaC (Liang *et al.*, 2018b; Dong *et al.*, 2018) and FeCoC (Wang *et al.*, 2019)) and a ferroelectric constituent [such as $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT)], this dilemma can be circumvented. The interaction of the elastic components between the magnetostrictive and piezoelectric constituents is the origin of magnetoelectric effects in such composites. Therefore, the emphasis of this chapter will be multiferroic or magnetoelectric composites.

Multiferroic materials play a key role in achieving strong ME coupling in multiferroic heterostructures, which has been of paramount importance for achieving multiferroic devices with large tunability. The strength of ME coupling can be represented by the two ME coupling coefficients: direct ME coupling coefficient $\alpha_{\text{direct}} = dP/dH$, and converse ME coupling coefficient $\alpha_{\text{converse}} = dM/dE$. We can obtain the contributions to the ME effect from the expansion of the free energy:

$$-F(\vec{E}, \vec{H}) = \frac{1}{2} \epsilon_0 \epsilon_{ij} E_i E_j + \frac{1}{2} \mu_0 \mu_{ij} H_i H_j + \alpha_{ij} E_i H_j + \frac{\beta_{ijk}}{2} E_i H_j H_k + \frac{\gamma_{ijk}}{2} H_i E_j E_k + \dots, \quad (1)$$

where $\vec{E}$ and $\vec{H}$ are the electric and magnetic field, respectively. $\hat{\epsilon}$ and $\hat{\mu}$ are the electric and magnetic susceptibilities. The tensor $\hat{\alpha}$, which corresponds to the induction of polarization by a magnetic field or of magnetization by an electric field, describes linear magnetoelectric coupling, while the third-rank tensors $\hat{\beta}$ and $\hat{\gamma}$ represent higher-order ME coefficients. The prefix “linear” is

generally omitted and simply referred as the “ME effect”. By differentiating F with respect to E_i , H_i , and then setting H_i , $E_i = 0$, we can easily establish ME effect in the form of $P_i(H_j)$ or $M_i(E_j)$:

$$P_i = \alpha_{ij}H_j + \frac{\beta_{ijk}}{2}H_jH_k + \dots, \quad (2)$$

$$\mu_0 M_i = \alpha_{ji}E_j + \frac{\gamma_{ijk}}{2}E_jE_k + \dots, \quad (3)$$

For the composite materials, not only the properties of the constituents but also the interaction between them can influence the properties of the composite materials that consist of two or more single-phase compounds. Three classes of effects can be distinguished (Ryu *et al.*, 2002): sum, scaling, and product properties. Therefore, the ME effect is conveniently accomplished by combining magnetostrictive and piezoelectric compounds. The ME coefficient of this type of composite can be established in a crude way as (Nan, 1994):

$$\alpha_{ME} = \frac{dE}{dH} = \frac{dS}{dH} \times k_c \times \frac{dE}{dS}, \quad (4)$$

where $\frac{dS}{dH}$, $\frac{dE}{dS}$ represent magnetostrictive and piezoelectric coefficients, respectively. k_c is denoted as the coupling coefficient between magnetostrictive and piezoelectric single-phase materials.

As for multiferroic composite architectures, there are three common structures that create strong enough coupling between them for multifunctional applications (Spaldin and Ramesh, 2019). Fig. 1(a) shows a classic ME composite consisting of ferromagnetic LuFe_2O_4 and ferroelectric LuFeO_3 multilayers developed by thin film growth techniques. Instead of horizontal layered system, a vertically mediated architecture with three-dimensional ferro- or ferrimagnetic nano-pillars embedded in a ferroelectric phase. The third structure as shown in Fig. 1(c), is the strain-induced mixed phase of particulate nano-composites.

Magnetoelectric Compositions in Composites

The multifunctional properties of multiferroic composites facilitate the development of novel electronic devices for various sensing, transduction, and antenna applications. There are several advantages for composite architectures, such as large remnant magnetizations and polarizations, as well as strong enough coupling, which allow them to be used in applications. Due to the large ME coupling coefficients, easy of fabrication and design flexibility, ME composites have been extensively studied in recent years. Different interaction structures, fabrication methods and materials of ME composites are taken into account here for developing high performance composites with strong ME coupling.

The interfacial connectivity and bonding of the piezoelectric and magnetostrictive phases have a huge influence on the strain-mediated ME coupling in the composites. The mechanical coupling coefficient k_c , which facilitates efficient strain transfer, can be used to characterize mechanical bonding between different phases. The two-phase ME composites have been generally classified as 0–3, 1–3, and 2–2 connectivity, as shown in Fig. 1, although various schemes have been proposed for designing ME composites (Palneedi *et al.*, 2016; Spaldin and Ramesh, 2019). The number here represents the dimension of the magnetostrictive and piezoelectric phases, respectively. For example, 0–3 composites are composed of magnetostrictive particles and piezoelectric matrix. In the 1–3 composites, magnetostrictive fibers/rods/tubes/wires are embed in the piezoelectric matrix. 2–2 composites consist of alternating magnetostrictive and piezoelectric laminate phases, which can be different shapes and dimensions. A variety of parameters and variables, such as geometries, layer structures and volume fraction can be altered to tailor the properties of the ME composites. The 2–2 composites are more often utilized for applications because of their simplicity of fabrication and unchanged physical characteristics of individual phases. The 2–2 composite structure, which has inherent advantages in terms of fabrication process and physical characteristics, has been confirmed from both theoretical and experimental results that it presents higher ME interactions compared to 0–3 and 1–3 structures.

Ceramic sintering, hot pressing, and spark plasma sintering (SPS) are some typical methods for synthesizing of 0–3 composites (Islam *et al.*, 2008a,b; Srinivasan *et al.*, 2004; Jiang *et al.*, 2007). By selecting individual phases, their sizes and other parameters, we can easily design the properties of 0–3 composites. However, the experimental ME response of 0–3 composites is much lower than that of theoretically calculated ones. This can be attributed to different reasons: the interdiffusion and misfit strain between the piezoelectric and magnetostrictive phases, and current leakage of the composites. Several methods such as a controlled annealing (Islam and Priya, 2006) and an insulating PZT layer (Islam *et al.*, 2008a,b) were employed to solve these problems. Readers can refer to Palneedi *et al.* (2016) for fabrication of the 1–3 type bulk ME composites since very few attempts have been made to this kind of composites. Epoxy bonding and co-firing (Ryu *et al.*, 2002; Dong *et al.*, 2006) are two most common ways for preparing bulk 2–2 laminate composites. Bilayer and sandwich structures, in which piezoelectric layer is sandwiched by two magnetostrictive layers, are usually used to prepare the 2–2 samples. The epoxy layer, for example silver epoxy, is required to be as thin as possible to acquire high performance ME composites although the mechanically soft epoxy layer can suppress the interface ME coupling. Co-firing process provides advantages of both cost-effective mass production and the interface strengthening, however, the high temperature process that is similar to 0–3 composites sintering is still detrimental to the good ME coupling. As miniaturization and multifunctionality of devices become more popular, thin film ME composites are highly desired for integrated ME devices. Improved ME coupling can be achieved in film-based composites because of the direct bonding of individual phases. Furthermore,

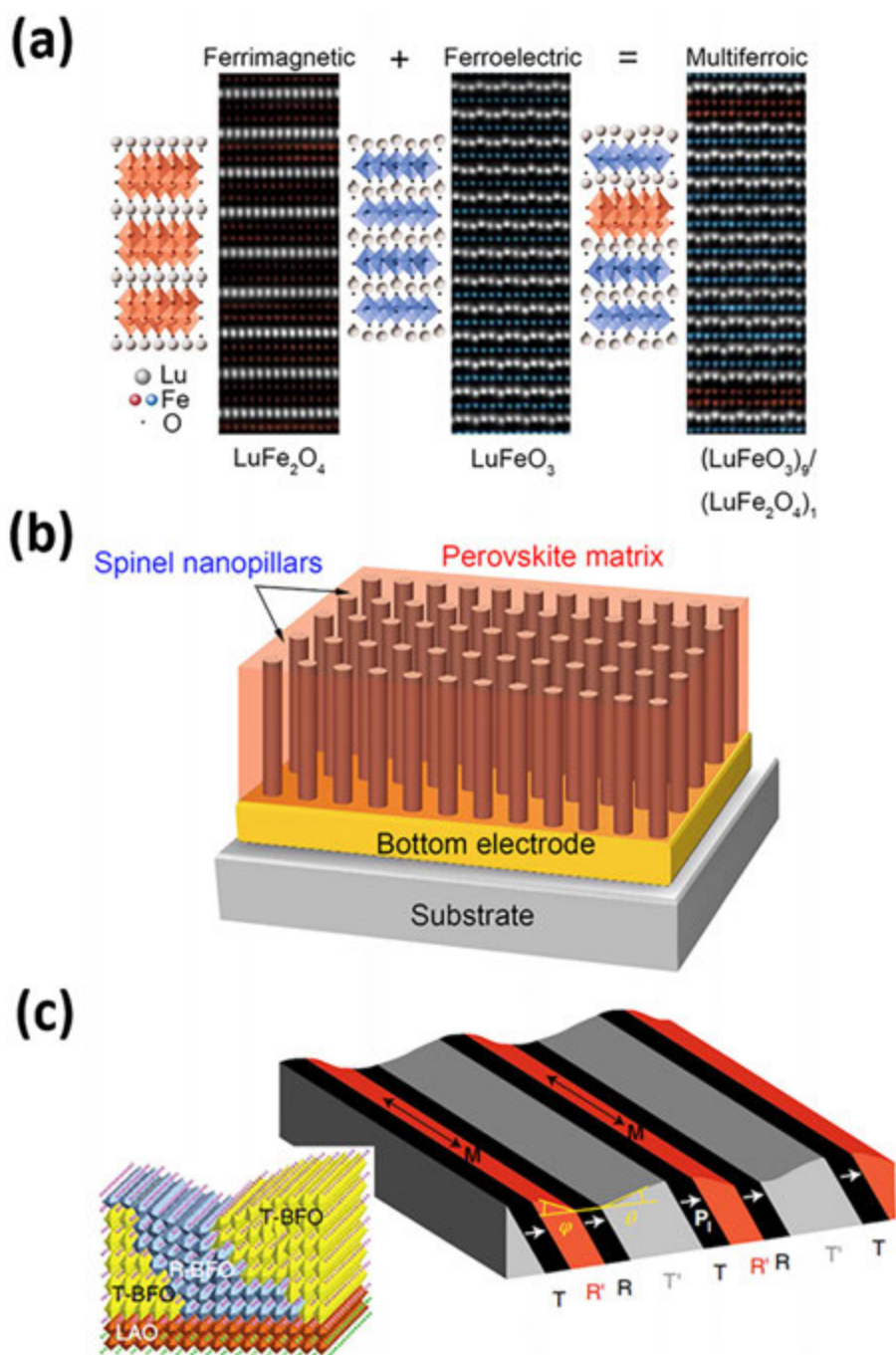


Fig. 1 Multiferroic composite architectures. (a) In classic horizontal composites, a ferroelectric material is layered with a ferro- or ferrimagnet. (b) A vertically aligned nanocomposite of a ferro/ferrimagnet embedded epitaxially in a ferroelectric phase in which coupling is mediated through three-dimensional coherent heteroepitaxy. (c) Schematics of a nanocomposite of BiFeO_3 (BFO) formed at the strain-induced morphotropic phase boundary. Reproduced from Spaldin, N., Ramesh, R., 2019. Advances in magnetoelectric multiferroics. *Nature Materials* 18 (3), 203–212.

smaller electric voltage is required for thin films than bulk samples because large electric fields can be applied to thin films. The advanced thin film deposition techniques, flexibility in the property designs, as well as interfacial strain engineering gives rise to studies on film-based ME composites. A variety of thin film ME composites have been prepared with excellent crystal epitaxy and coherent interfaces although the ME coefficients are very low in the reported papers due to substrate clamping effect. By dispersing magnetic nanoparticles into piezoelectric matrix with larger interfacial area, the ME coupling of 0–3 type composites can be boosted since the strain-mediated ME coupling (McDannald *et al.*, 2013). Though the 1–3 type ME composites, which exhibit a reduced substrate clamping effect as a result of large interfacial area, can be prepared via self-assembly process at the micro- and

nanoscale, it remains challenging to apply them in practical applications due to the difficulty on designing samples of such structures (Aimon *et al.*, 2015). Various deposition methods including physical vapor deposition (PVD), pulsed laser deposition (PLD), chemical vapor deposition (CVD), molecular beam epitaxy (MBE), spin coating, spin-spray techniques, etc., have been developed for preparing film-based 2–2 type ME composites (Sun and Srinivasan, 2012). For thick film 2–2 ME composites, several techniques such as aerosol deposition, electrodeposition, and granule spray in vacuum deposition (GSV) are employed to prepare samples. Recently, laser or light radiation, which is commonly used in printed electronics, is used to induce localized annealing effect for controlling the thermal diffusion in the nanostructured films.

The selection of appropriate piezoelectric and magnetostrictive materials is particularly significant on getting a composite with large ME coupling. Some typical piezoelectric and magnetostrictive materials used as constituents of ME composites are listed in Table 1. Among all piezoelectric materials used for bulk ME composites, the lead-based piezoelectric PMN-PT single crystal exhibits the highest piezoelectric constant, while PZT ceramics are also widely used in ongoing works because of their very low cost. Because of the extremely high Q_m , LiNbO_3 crystal could be a desired material for low-loss ME devices. But AlN seems the most favorable choice with respect to film ME devices due to the compatibility with MEMS processes although the piezoelectric response is poor. As for the piezomagnetic phase, Terfenol-D (with a giant magnetostriction) and Metglas (with a high permeability and piezomagnetic coefficient) are widely used as high-performance magnetostrictive alloys, while Ni is a good candidate for self-biased ME device (Chu *et al.*, 2018a). With respect to thin film ME composites, the largest piezomagnetic coefficients have been found in amorphous FeGaC or FeCoSiB films.

Characterization and Modeling

The development of a variety of new experimental and theoretical methods for studying time-resolved and spatial multiferroic phenomenon is discussed in this section. With the help of scanning probe techniques including piezoforce, electron scanning, conducting atomic and magnetic force microscopes (PFM, SEM, CAFM, and MFM), scanning transmission X-ray microspectroscopy (STXM), the spatial resolution of studying the spin, charge, and orbital degrees is able to approach the unit cell dimensions (Gross *et al.*, 2017; Strocov *et al.*, 2010). For the time-resolved characterization of multiferroic phenomenon, the ultrafast synchrotron X-ray is utilized to study dynamics of multiferroic composites (Orenstein, 2012).

Given that magnetoelectric composites consist of piezoelectric and magnetostrictive phases, it is crucial to evaluate the properties of these materials. There are a variety of tools that are well-known in multiferroic areas, such as vibrating sample magnetometer (VSM) for measuring magnetization and anisotropy field, ferromagnetic resonance (FMR) for measuring linewidth and Gilbert damping constant, etc. But the most significant parameters of ME composites are the magnetostriction constant of magnetic phase and piezoelectric coefficient of ferroelectric phase due to the fact that ME coupling strength is the result of a product of the piezoelectric effect and magnetostrictive effect. Owing to the prevalence of integrated ME composites devices and difficulties on characterization of thin-film piezoelectric and magnetostrictive materials, here, we introduce several characterization techniques that have been developed for evaluating these properties. In order to acquire the piezoelectric coefficients of thin films, a variety of techniques were exploited to do the measurements (Kholkin *et al.*, 1996; Dubois and Muralt, 1999a; Dufay *et al.*, 2015; Conde and Muralt, 2008; Liu *et al.*, 2002). Based on double-beam interferometer, a direct measurement of piezoelectric coefficients can be done. However, the discrimination of the true films expansion and the bimorph-like bending of the sample should be carefully taken care of. Besides, indirect extraction of piezoelectric coefficients based on different micromechanical system (MEMS) such as cantilever structures (Dufay *et al.*, 2015), surface acoustic wave (SAW) resonators (Liu *et al.*, 2002), and bulk acoustic wave (BAW) resonators (Conde and Muralt, 2008), was also proven to be effective. The tip displacement of bending-mode PZT cantilever deposited on a 16 μm -thick aluminum substrate was measured by a laser vibrometer under controlled electric field to determine the transverse piezoelectric coefficient d_{31} . A hysteresis change of both the resonance and antiresonance frequencies of thin film bulk acoustic resonator (FBAR) under applied bias was used to extract dielectric, piezoelectric, and elastic properties of the [111]-textured PZT film. The coupling factor k_t^2 of a BAW resonator can be utilized to calculate d_{33} or ε_{33} if a pure thickness mode is excited, which is same for calculating d_{31} or ε_{31} of SAW resonator. As for magnetostriction measurements, several techniques have been proposed, which can also be generally classified as either direct or indirect methods (Ekreem *et al.*, 2007). The most commonly used methods include the capacitance method based on cantilever structure (Klokholm, 1976), optical method utilizing rotating magnetic fields (Tam and Schroeder, 1989) and nano-indentation method (Shima and Fujimori, 1999). Capacitance method utilizes the tunable capacitance of the plate capacitor when thin film is on top of the cantilever, which serves as an oscillator. When a DC magnetic field is applied to the cantilever structure, a capacitance change can be induced as a consequence of deflection of the cantilever, which leads to the shift in resonant frequency of the oscillator, and therefore the magnetostriction can be derived. In optical approach, a rotating magnetic field is exploited to provide high-accuracy and non-contact measurements of the samples despite of the complex optical system. Nano-indentation method based on a commercial system is able to characterize both elastic properties and magnetostriction of thin films on top of cantilevered substrates.

By using a non-contact optical technique, Dong *et al.* (2018) recently developed a simple, compact, and sensitive system including both magnetostriction tester and delta-E tester to measure magnetostriction, piezomagnetic coefficient, and delta-E effect. The schematic of the proposed magnetostriction tester is shown in Fig. 2(a). A rotating adjustable AC magnetic field with a maximum value of 300 Oe is generated by two pairs of mutually perpendicular set Helmholtz coils with equivalent amplitude and 90° phase shift current. Similar as the cantilever method for measuring piezoelectric coefficients, the tip displacement of the

Table 1 Parameters of typical piezoelectric and piezomagnetic materials

Parameters	Piezoelectric phase					Piezomagnetic phase					
	PZT-5H	PZT-8	PMN-0.33PT (Li et al., 2010)	LiNbO ₃ (Shuxiang, 2018)	AlN film (Tsubouchi et al., 1981; Dubois and Murali, 1999b; Sanchez-Rojas et al., 2008)	Metaglas (FeSiBC) (Chu et al., 2017)	Terfenol-D (Tb _x Dy _{1-x} Fe ₂) (Chu et al., 2018b)	Ni (Chu et al., 2018b)	FeGaB film (Lou et al., 2007)	FeGaC film (Liang et al., 2018b)	FeCoSiB film (Greve et al., 2010b)
$d_{31,p}(\text{pC N}^{-1})$ or $\lambda_s(\text{ppm})$	-274	-90	-1330	-1	-2	~30	2000	-36	70	81.2	158 ^a annealed
$d_{33,p}(\text{pC N}^{-1})$ or $d_{33,m}(\text{nm A}^{-1})$	593	225	2820	21	~3.5–4	50.3	25	1.25	~88	121.3	
ϵ_r or μ_r	3400	1000	8200	30	~10	45,000	10	100	~400		
$T_C(^{\circ}\text{C})$	193	300	135	1200	>2000	395	650	630			
Q_m	65	1000	100	100,000	500						

^aThe value is estimated using Young's modulus and Poisson ratio of the film being 100 GPa and 0.3, respectively.

Note: $d_{31,p}/d_{33,p}$, transverse/longitudinal piezoelectric constant; $d_{33,m}$, longitudinal piezomagnetic constant; λ_s , saturated magnetostriction coefficient; ϵ_r , relative dielectric constant; μ_r , relative permeability; T_C , Curie temperature; Q_m , mechanical quality factor.

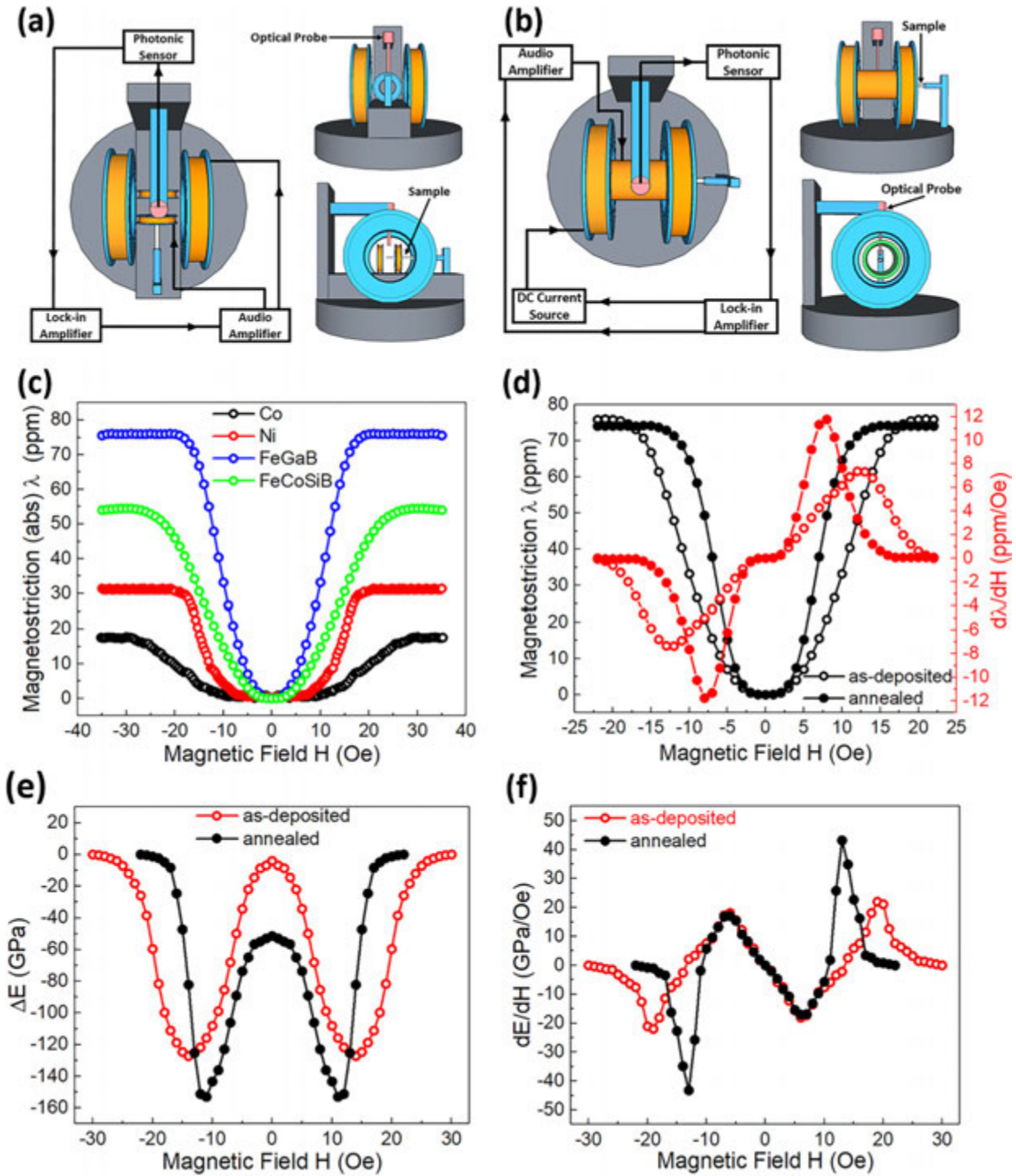


Fig. 2 (a) Schematic of the proposed magnetostriction tester in three-view. (b) Schematic of the proposed delta-E tester in three-view. (c) Measured magnetostriction with respect to magnetic field for different magnetic thin films. (d) Measured magnetostriction and piezomagnetic coefficient for as-deposited and annealed FeGaB thin films. (e) Measured delta-E effect for as-deposited and annealed FeGaB thin films. (f) Measured dE/dH for as-deposited and annealed FeGaB thin films. Reproduced from Dong, C., Li, M., Liang, X., *et al.*, 2018. Characterization of magnetomechanical properties in FeGaB thin films. *Applied Physics Letters* 113 (26), 262401.

cantilever is detected by a MTI-2000 fiber-optic sensor due to the strain change in the magnetostriction film. **Fig. 2(b)** shows the schematic of the proposed delta-E tester, which is very similar to the magnetostriction tester. Second vibration mode of the cantilever is excited by applying a 0.1 Oe AC driving field through a solenoid with the frequency swept around 1555 Hz. A DC bias magnetic field is generated by the Helmholtz coil to induce magnetic domain change in the magnetostrictive films, and thus

resulting in the change of Young's modulus. According to the modified Ruler-Bernoulli beam theorem, the change of Young's modulus can be derived by measuring the shift in resonant frequency of the cantilever. Some typical magnetostrictive films such as Ni, Co, FeGa, etc. with well-known magnetostriction values are used to calibrate the system. Fig. 2(c) shows the measured magnetostriction of some magnetostrictive thin films after system calibration and Fig. 2(d) shows the measured magnetostriction and piezomagnetic coefficient for as-deposited and annealed FeGaB thin films. The change in Young's modulus of FeGaB thin film is also measured and shown in Fig. 2(e) by using delta-E tester and Fig. 2(f) shows the derivative of Young's modulus as regard with the magnetic field (dE/dH).

For single phase multiferroic materials, first-principles (Zhong *et al.*, 1994) density functional theory (DFT) has been the standard method for modeling the behaviors of insulating magnetically ordered materials such as multiferroics, while second-principles (García-Fernández *et al.*, 2016) calculations are becoming a promising method for understanding larger systems – for example, heterostructures, domain walls, and defects (Karpinsky *et al.*, 2017). For layered multiferroic composites, a model for ME coupling in a bilayer of magnetostrictive and piezoelectric phases was proposed by Harshe *et al.* (1993) and Avellaneda and Harshé (1994) in their innovative works. Several theoretical models have been presented recently and applied to various systems, including ferrites, metals, and alloys for magnetostrictive phase and lead zirconate titanate (PZT), lead magnesium niobate-lead titanate (PMN-PT), and polyvinylidene difluoride (PVDF) for the piezoelectric phase, for low-frequency ME coupling in bilayer structures (Harshe *et al.*, 1993; Avellaneda and Harshé, 1994; Bichurin *et al.*, 2003b; Liu *et al.*, 2004). The ME voltage coefficient $\alpha_{ME} = \frac{dE}{dH}$ can be estimated by solving the elastostatic and electrostatic equations. The expression for longitudinal ME voltage coefficient can be obtained in the form of

$$\alpha_{E33} = \frac{dE_3}{dH_3} = 2 \frac{\mu_0 k v (1 - \nu) d_{31}^p q_{13}^m}{\{2d_{31}^p 2(1 - \nu) + \epsilon_{33}^p [(s_{11}^p + s_{12}^p)(\nu - 1) - \nu(s_{11}^m + s_{12}^m)]\}} \times \frac{[(s_{11}^p + s_{12}^p)(\nu - 1) - k v (s_{11}^m + s_{12}^m)]}{\{[\mu_0(\nu - 1) - \mu_{33}^m v][k v (s_{12}^m + s_{11}^m) - (s_{11}^p + s_{12}^p)(\nu - 1)] + 2q_{31}^m 2k v^2\}}, \quad (5)$$

And the transverse ME voltage coefficient is given as

$$\alpha_{E31} = \frac{dE_3}{dH_1} = \frac{-k v (1 - \nu) (q_{11}^m + q_{21}^m) d_{31}^p}{\epsilon_{33}^p (s_{12}^m + s_{11}^m) k v + \epsilon_{33}^p (s_{11}^p + s_{12}^p) (1 - \nu) - 2k d_{31}^p 2(1 - \nu)}, \quad (6)$$

Here m and p indicate the magnetostrictive and piezoelectric phases, respectively; q and d are the magnetostrictive and piezoelectric coupling coefficients, respectively; s is the compliance coefficient; ϵ is permittivity at constant stress; μ is the tensor permeability; and $\nu = v^p / (v^p + v^m)$, where v^p and v^m denote the volume of the magnetostrictive and the piezoelectric layers, respectively. Due to the strain-mediated ME coupling in multiferroic composites, the strength of ME interactions would be enhanced with orders of magnitude when the AC magnetic field is applied at frequencies corresponding to resonant modes in the ME composites, for example, electromechanical resonance (EMR) (Bichurin *et al.*, 2003a) and bending modes (Pan and Heyliger, 2003; Petrov *et al.*, 2009). The models and theories of these modes were developed in the reference mentioned above.

Applications

The interaction between the electric and magnetic phases in a multiferroic material opens up the possibility of novel devices. Wood and Austin (1974) investigated possible applications for single-phase ME materials and concluded that it was not possible for practical devices due to the weak coupling. However, multiferroic composites presented a very strong ME coupling, which have led to a great deal of applications. Here, we focus on MEMS magnetoelectric composites device applications of our group and direct readers to other reviews for bulk and other multiferroic devices. Our group has demonstrated a variety of MEMS devices based on ME composites, including magnetic-field sensors (Nan *et al.*, 2013; Chu *et al.*, 2019), tunable inductors (Gao *et al.*, 2014a,b; Chen *et al.*, 2020), band-pass and band-stop filters (Lin *et al.*, 2016; He *et al.*, 2018), and ME antennas (Nan *et al.*, 2017; Liang *et al.*, 2018a; Dong *et al.*, 2020). Regarding the bulk ME composites devices, we introduce some reviews (Nan *et al.*, 2008; Srinivasan, 2010; Spaldin and Ramesh, 2019) for consideration and some work from our group on sensors (Li *et al.*, 2017; Liang *et al.*, 2020), inductors (Lou *et al.*, 2009; Su *et al.*, 2016), isolator (Tu *et al.*, 2018), and antennas (Yang *et al.*, 2008) although no details are described here.

Magnetoelectric Sensor

It has been an open challenge in detecting weak DC and low frequencies AC magnetic fields for many years. Since the demonstration of strong ME coupling in magnetostrictive/piezoelectric ME heterostructures, exciting progress was made recently on highly sensitive magnetometers (Zhao *et al.*, 2009; Israel *et al.*, 2008). The DC magnetic field dependence of ME interaction can be utilized for DC magnetic field sensing. A self-biased ME sensor based on a 215 MHz AlN/FeGaB nano-plate resonator was demonstrated in our work. A low limit of detection for DC magnetic fields of ~ 300 pT in unshielded environment was achieved by increasing the resonance frequency of NEMS ME sensor to 215 MHz. The ME heterostructure is composed of seven Pt inter-digital electrodes on the bottom of

the AlN layer and low-loss magnetostrictive FeGaB/Al₂O₃ multilayer as the electrically floating top electrode. By diminishing substrate clamping effect, the Si substrate underneath the resonator is completely removed to achieve a strong ME coupling and high sensitivity.

The admittance curve and the Butterworth–van Dyke (BVD) model fitting of the NEMS magnetic field sensor are depicted in Fig. 3(a) showing an electromechanical resonance frequency of 215 MHz. A high quality factor of 735 and a high electro-mechanical coupling coefficient k_t^2 of 1.54% in air were extracted from the BVD model at zero bias magnetic field, which is comparable to what is typically reported in AlN nano-plate resonator (Rinaldi *et al.*, 2011). One example of the BVD equivalent electrical circuit of the resonator is shown in Fig. 3(b), in which R_s represents the resistance of metal electrodes and contact resistance, R_{op} is the parasitic resistance from substrate, C_0 denotes the device capacitance from the Pt/AlN/FeGaB stack, C_M , L_M , and R_M are the motional capacitance, inductance, and resistance, respectively. The delta-E effect, which is known as the change of Young's modulus by applying a DC bias magnetic field, results in the change in the electromechanical resonance frequency of the AlN/FeGaB heterostructure. Strong ME coupling in the NEMS ME magnetic field sensor was demonstrated in Fig. 3(c), which shows the admittance curves at various DC bias magnetic fields applied along the length direction of the resonator. As shown in Fig. 3(d), a similar trend, which first decreases and then increases with the increase of bias field, for both resonance frequency f and peak admittance amplitude Y at the resonance frequency is exhibited with DC bias magnetic field.

The resonance frequency of the magnetoelectric NEMS resonator can be expressed by

$$f_0 = \frac{1}{2W_0} \sqrt{\frac{E_{eq}}{\rho_{eq}}}, \quad (7)$$

with W_0 being the pitch of the finger electrodes forming the interdigital transducer (IDT), E_{eq} being the equivalent Young's Modulus and ρ_{eq} being the equivalent density of the resonator. By applying a DC magnetic field, a magnetostrictive strain can be induced due to the delta-E effect, and therefore a changed equivalent Young's modulus of the NEMS ME magnetic sensor. In order to measure the sensitivity of the resonator to DC magnetic fields, an extremely small magnetic field was applied to the sensor in an unshielded environment. The value of the admittance amplitude starts to scatter at 300 pT, which indicates a limit of detection

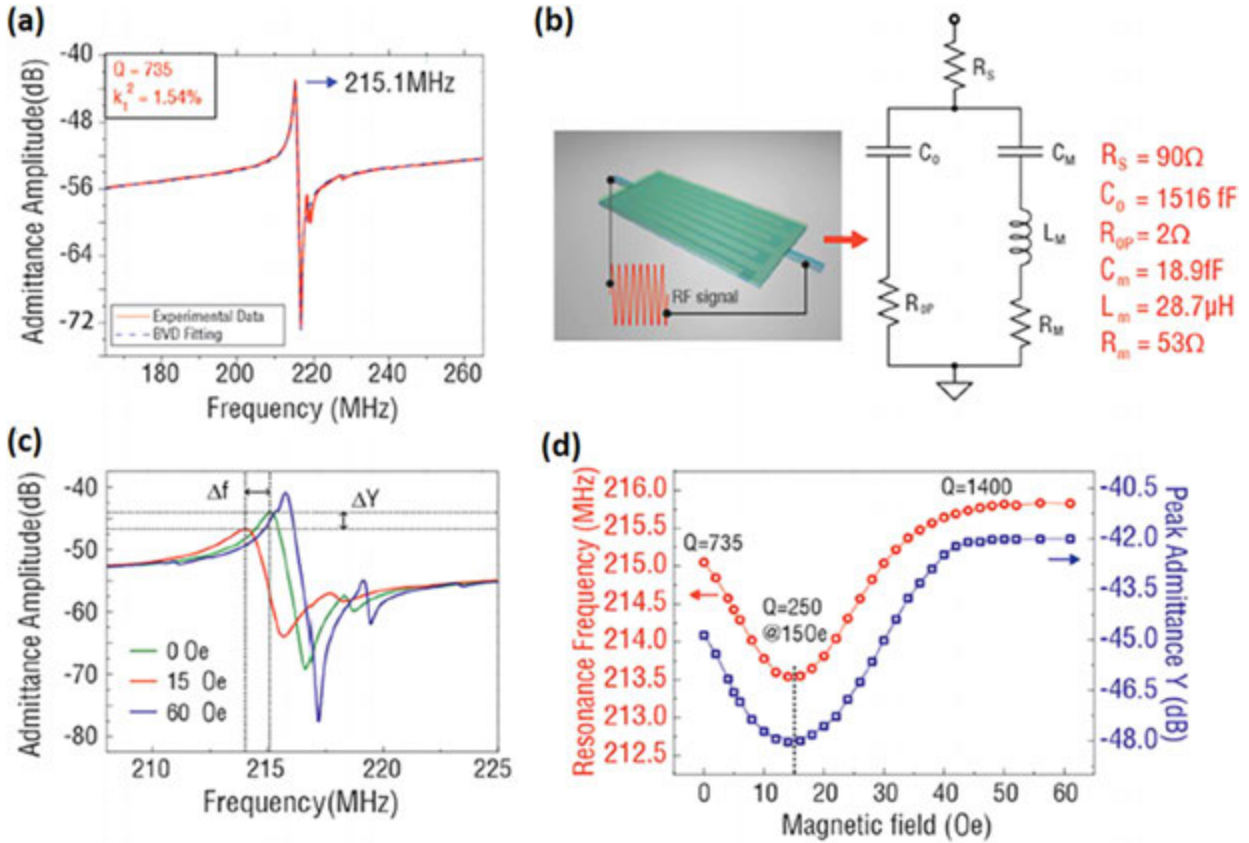


Fig. 3 (a) Admittance curve and BVD model fitting of the fabricated NEMS magnetic field sensor. (b) The BVD equivalent electrical circuit of the resonator. (c) Admittance curve of the NEMS sensor at various bias DC magnetic fields. (d) Resonance frequency and admittance amplitude at the resonance frequency as a function of DC magnetic field. Reproduced from Nan, T., Hui, Y., Rinaldi, M., Sun, N.X., 2013. Self-biased 215 MHz magnetoelectric NEMS resonator for ultra-sensitive DC magnetic field detection. Scientific Reports 3.

around 300 pT. The demonstrated RF NEMS ME magnetic sensor, which is based on the magnetic field dependence of admittance, makes it excellent self-biased magnetometer compared to conventional ME sensor that relies on the ME output voltage.

Magnetoelectric Inductor

As one of the fundamental components of electronic circuits, various inductor designs, and tuning methods have been employed in different applications. [Bedair et al. \(2012\)](#) described the design, microfabrication, and testing of integrated and continuously tuned RF copper inductors with low-power large-throw lead-zirconate-titanate (PZT) actuators. A planar solenoidal inductor, which is designed and fabricated using a two-metal MEMS process, with tunable inductance from 1 to 3.3 nH and a Q-factor of more than 20 was proposed by [Shirane et al. \(2012\)](#). A coupled inductor pair with self-inductances of 15 and 21 nH was implemented showing Q_s exceeding 40 at 800 MHz with a microfabrication technology ([Shim et al., 2012](#)). In this work, we reported novel integrated GHz magnetic inductors based on solenoid structures with FeGaB/Al₂O₃ multilayer films, which show significantly enhanced inductance and quality factor at GHz frequencies over their air core counterparts. Good high frequency performance with the inductance over 2nH and the peak quality factor close to 20 was realized in these inductors over a wide operation frequency range of DC ~ 2.5 GHz. By putting these inductors on 0.5 mm thick ferroelectric (011) cut lead magnesium niobate-lead titanate (PMN-PT) slab, we demonstrated a voltage tunable magnetoelectric inductors with a voltage tunable inductance of > 100% ([Gao et al., 2014b](#)).

Optical images of the integrated solenoid inductors are shown in [Fig. 4\(a\)](#) and [\(b\)](#) presents the schematic of tunable inductor. As presented in [Fig. 4\(c\)](#), a high voltage tunability of inductance which reaches up to 100% in about 2–3.5 GHz is achieved. And quality factor tuning corresponding to the same inductor and the same applied electric field is measured and shown in [Fig. 4\(d\)](#). Si substrate was removed by using DRIE and integrated magnetic inductor was bonded with glue to PMN-PT slab that was poled along its thickness direction. The inductance of integrated magnetic solenoid inductors can be approximated by

$$L = \frac{\mu_0 \mu_r N^2 w t_m}{l}, \quad (8)$$

in which N is the total number of turns; and w , t_m , and l are the width, thickness, and length of magnetic film, respectively. And the quality factor Q of an integrated solenoid inductor can be calculated as

$$Q = \frac{\omega \mu_0 \mu_r N t_m w_c \delta (1 - e^{-t/\delta})}{2l\rho}, \quad (9)$$

where ρ is the wire electrical resistivity, w_c , δ and t are the width, skin depth and thickness of the coil, respectively. The performance of all inductors was measured by utilizing a vector network analyzer (VNA) and an RF probing system. All the L and Q values are extracted from transmission line model with s-parameters. The applied E-field ranging from 0 to 8 kV/cm corresponding to a

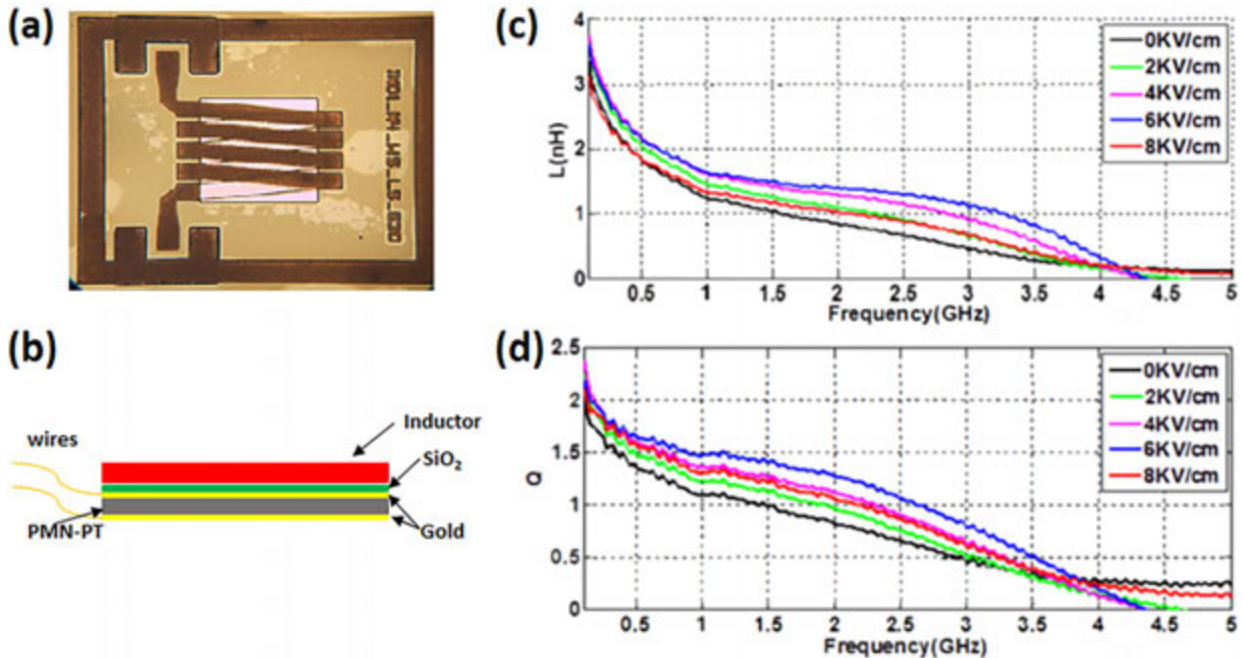


Fig. 4 (a) Optical photos of integrated magnetic inductors. (b) Schematic of tunable integrated magnetic inductor. (c) Voltage tunability for inductance of integrated inductors. (d) Voltage tunability for quality factor of integrated inductors. Reproduced from Gao, Y., Zare, S., Onabajo, M., et al., 2014b. Power-Efficient Voltage Tunable RF Integrated Magnetoelectric Inductors With FeGaB/Al₂O₃ Multilayer Films. IEEE, pp. 1–4.

voltage across the thickness direction of the PMN-PT slab from 0 to 400 V. Large inductance tunability of $> 100\%$ were achieved in these magnetoelectric inductors with an applied voltage.

Magnetoelectric Filters

Bandpass and bandstop filters are widely used to pass or suppress the signal in a specific frequency range and are critical in signal processing systems (Tu and Chang, 2005; Zhu *et al.*, 2005). Both bandpass and bandstop integrated MEMS filters based on FeGaB/Al₂O₃ magnetic multilayer films were reported in our group (Lin *et al.*, 2016; He *et al.*, 2018). FBAR structures are extensively used in RF bandpass filters, which have very high quality factor, compact size, low loss, preferable temperature stability and processing compatible with the complementary metal-oxide-semiconductor (CMOS) integrated circuit (IC) (Ruby *et al.*, 2001). Based on FBAR resonators with contour mode of transmission, an integrated tunable bandpass filter with FeGaB/AlN magnetoelectric multilayer was realized and a large frequency tunability of ~ 5 kHz/Oe and a high quality factor of 252 were achieved. Traditional ferrite-based bandstop filters mostly rely on the FMR absorption behavior of the magnetic material (Zhu *et al.*, 2009). By taking the advantage of shape anisotropy, a C-band bandstop filter, which was patterned into a slim ribbon shape and fabricated on Si wafer with FeGaB/Al₂O₃ multilayer film under a single transmission line, is reported. A self-resonance at 5 GHz with a high attenuation of over 20 dB was presented and a frequency shift from 5 to over 8.5 GHz was showed by applying a magnetic field up to 400 Oe.

As shown in the schematic of the MEMS ME bandpass filter in Fig. 5(a), the theory of FBAR bandpass filter can be explained by introducing acoustic wave. Specifically, an alternating acoustic wave due to the mechanical resonance can be induced by applying RF electric field to the MEMS resonator. When this acoustic wave transfers to port 2, the dynamic voltage or charge would be generated due to the direct piezoelectric coupling. Fig. 5(c) and (d) present measured return loss S_{11} and insertion loss S_{21} at zero bias field of MEMS ME bandpass filter with increasing magnetic fields. And the results of resonance frequency as a function of DC magnetic fields up to 200 Oe is shown in Fig. 5(b). The shift of the resonance frequency is due to delta-E effect that is the working principle of NEMS ME sensor (Nan *et al.*, 2013). The influence of magnetostrictive strain is much less than that of delta-E effect,

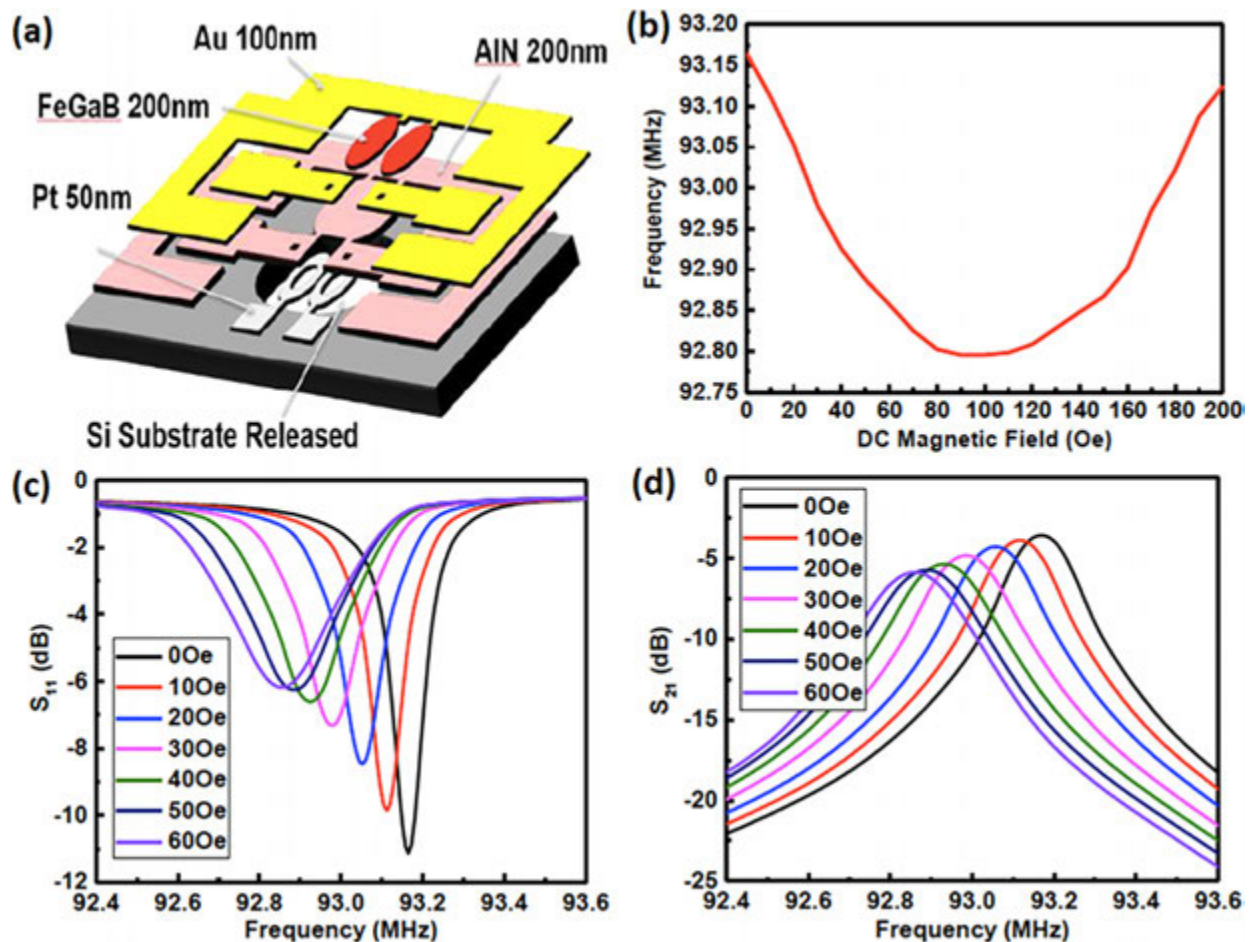


Fig. 5 (a) Schematic of the layered structure of the NEMS ME band-pass filter. (b) Resonance frequency of the NEMS ME band-pass filter as a function of DC magnetic fields. (c) S_{11} performance with different dc magnetic fields. (d) S_{21} performance with different dc magnetic fields. Reproduced from Lin, H., Nan, T., Qian, Z., *et al.*, 2016. Tunable RF Band-Pass Filters Based on NEMS Magnetoelectric Resonators. IEEE, pp. 1–4.

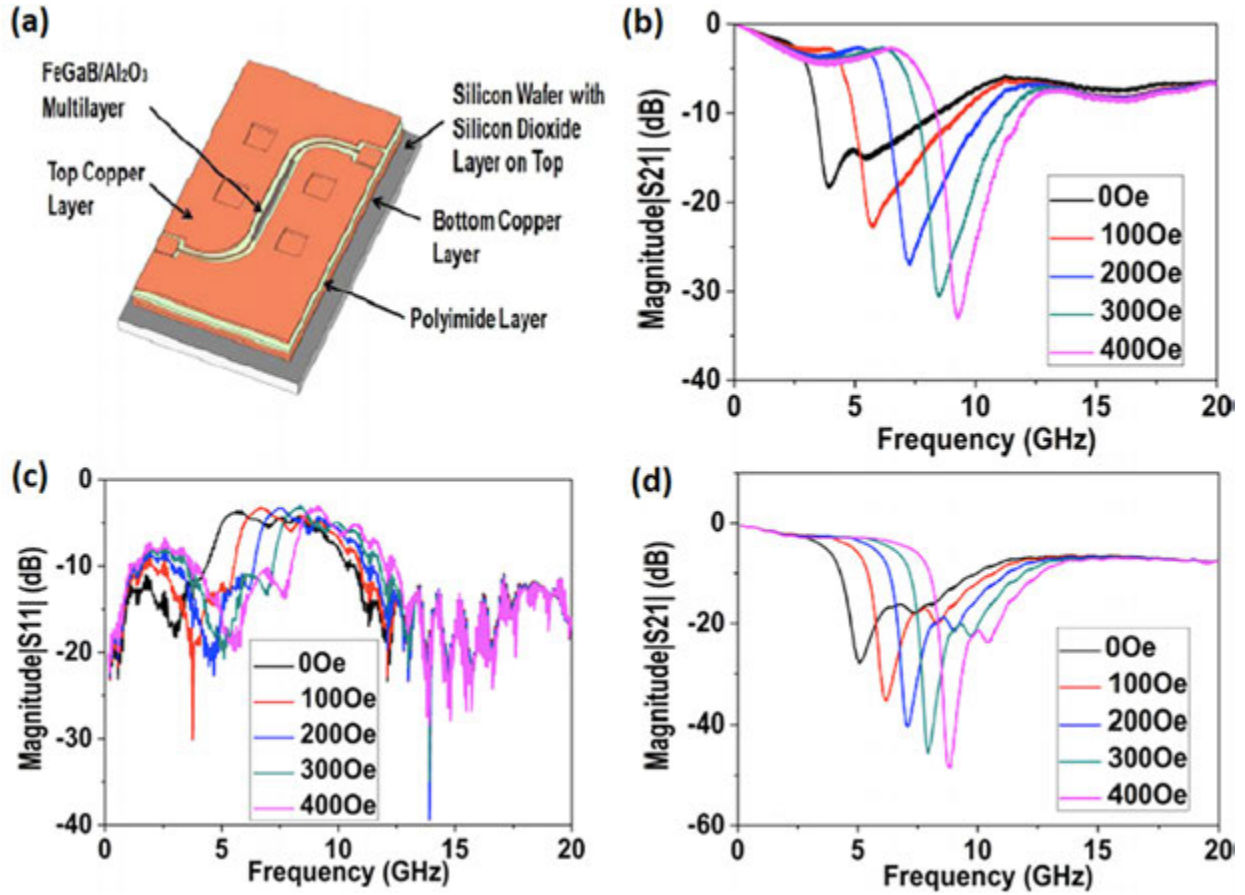


Fig. 6 (a) Schematic of the bandstop filter. (b) Measured transmission curves of the bandstop filter with 100 nm FeGaB single layer. (c) Measured reflection curves of the bandstop filter with FeGaB multilayers. (d) Measured transmission curves of the bandstop filter with FeGaB multilayers. Reproduced from He, Y., Gao, Y., Chen, H. *et al.*, 2018. Integrated tunable bandstop filter using self-biased FeGaB/Al₂O₃ multilayer thin film. *IEEE Transactions on Magnetics* 54 (9), 1–4.

since the magnetostriction constant of FeGaB of 70 ppm is much smaller than the delta-E effect induced percentage change in Young's modulus which can be up to 20%–30% (Ludwig and Quandt, 2002). The schematic of the bandstop filter device is shown in Fig. 6(a), in which the dimension of the rectangular co-planar waveguide (CPW) is 8 mm × 3.2 mm. The operating frequency corresponding to FMR frequency is determined by the external magnetic field and the in-plane uniaxial anisotropy field in this case. The FMR frequency of the magnetic material layer is given in the following equation:

$$f_{\text{FMR}} = \gamma \sqrt{(H_{\text{dc}} + H_a + (N_y - N_z)4\pi M_s)(H_{\text{dc}} + H_a + (N_x - N_z)4\pi M_s)}. \quad (10)$$

in which, γ represents the gyromagnetic ratio; H_{dc} is the applied magnetic field along the length direction; H_a denotes the anisotropy field induced by the applied field during film deposition; N_x , N_y , and N_z are the demagnetizing factors determined by the dimensions of the magnetic layer; x , y , and z are the width, height, and length direction, respectively; and M_s is the saturation magnetization.

The magnetic tunability was obtained by applying varied external magnetic fields that were parallel to the magnetic ribbon. Transmission curves of the bandstop filter with a 100 nm-thick FeGaB single layer were measured and presented in Fig. 6(b). The device shows a wide tuning range from 3.9 to 9.3 GHz with a magnetic field of up to 400 Oe. In order to reduce the insertion loss due to eddy-current effect, the magnetic material was deposited as multilayer with more periods. The results for reflection and transmission curves of the bandstop filter with multilayer structure were shown in Fig. 6(c) and (d).

Magnetoelectric Antennas

Nitsan (1977) published the very first paper, which explored the detection of RF electromagnetic radiation (EMR) from fracture of quartz-bearing rocks and other hard piezoelectric materials, that is related to ME antennas. Weldon *et al.* (2008) presented a design method for a highly integrated carbon nanotube radio transmitter in 2008, which radiates high frequency EM waves by exploiting charge on tip of the vibrating nanotube and acts like a small antenna. Besides, the acoustic wave-mediated multiferroic antennas

that are comprised of magnetostrictive/piezoelectric heterostructures was firstly proposed and described theoretically by Yao *et al.* (2015). Mateen *et al.* (2016) successfully demonstrated the wireless actuation of micro-sized silicon-based piezoelectric resonators with resonance frequencies of 36 MHz and 121 MHz at power levels of nanowatts and distance of ~ 3 feet by using conventional piezoelectric resonators. From 2017, various authors published their works on mechanical antennas of VLF and ULF frequencies by utilizing spinning magnets (Selvin *et al.*, 2017; Fawole and Tabib-Azar, 2017; Bickford *et al.*, 2017; Prasad *et al.*, 2018). Chu's limit and lower bound of the radiation quality factor were proven to be broken by the proposed spinning magnet antenna. The unprecedented demonstration of ultra-compact ME NEMS antennas was proposed by us in 2017 (Nan *et al.*, 2017) and was expected to have great impacts on our future antennas and communication systems for internet of things, wearable antennas, bio-implantable and bio-injectable antennas, smart phones, wireless communication systems, etc. The new ME antennas based on ME nano-plate resonator (NPR) and thin-film bulk acoustic resonator (FBAR), which are one to two orders of magnitude smaller than state-of-the-art compact antennas, have a novel receiving and transmitting mechanism.

COMSOL was used to design both ME NPR and FBAR based antennas in this work. The resonant bodies of these NEMS ME resonators, which are composed of piezoelectric and magnetostrictive element for the ME heterostructure, were patterned with 500 nm AlN and $[\text{Fe}_7\text{Ga}_2\text{B}_1 (45 \text{ nm})/\text{Al}_2\text{O}_3 (5 \text{ nm})] \times 10$ (hereafter termed FeGaB) thin film ME heterostructures fully suspended on a Si substrate. Efficient on-chip acoustic transduction with ultra-low energy dissipation can be achieved with the use of a NEMS resonator with an ultra-thin 500 nm AlN thin film enables. In this work, a wide range of frequencies from 60 MHz to 2.5 GHz can be realized by using a geometric design of the demonstrated ME antennas that exhibit different mode of vibrations.

NPR ME Antennas

Fig. 7(a) presents the schematic of ME NPR which has a rectangular resonating plate and the measurement structures. And the SEM image of the NPR ME resonator that consists of a single-finger bottom Pt electrode and a thin film FeGaB/AlN heterostructure is shown in Fig. 7(b). All the fabrication processes of devices in this work were compatible with CMOS microfabrication processes.

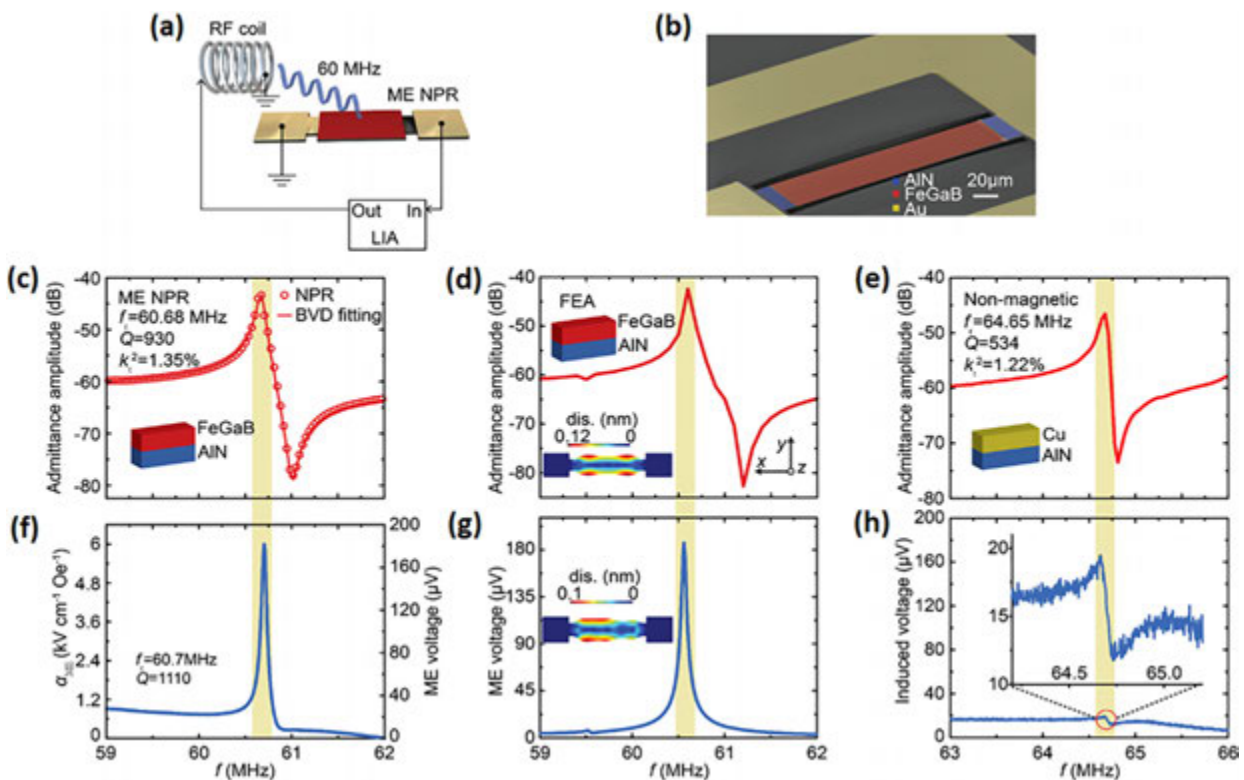


Fig. 7 ME NPR device with gigantic ME coupling. (a) Schematic of the induced ME voltage measurement setup. (b) Scanning electron microscopy (SEM) images of the fabricated ME NPR. (c) Admittance curve and MBVD model fitting of the ME NPR. The inset shows the schematic of the cross-section of the ME heterostructure. (d) Finite element analysis (FEA) of ME NPR for the admittance amplitude. The inset shows the in-plane displacement of the nano-plate at resonance peak position and its coordinate system. (e) Admittance curve of a non-magnetic control sample which has the same device design as ME NPR. The inset shows the schematic of the device cross-section. (f) ME coupling coefficient (left axis) and the induced ME voltage (right axis) versus frequency of RF magnetic field excitation. (g) FEA of ME NPR for the induced ME voltage measurement. The inset shows the in-plane displacement excited by RF magnetic field. (h) Induced voltage versus frequency for the non-magnetic device. The inset illustrates the zoomed-in view of the resonance peak area (red circle). Reproduced from Nan, T., Lin, H., Gao, Y., *et al.*, 2017. Acoustically actuated ultra-compact NEMS magnetoelectric antennas. *Nature Communications* 8 (1), 296.

The length L and width W of the rectangular resonating plate are $200\ \mu\text{m}$ and $50\ \mu\text{m}$, respectively. By fully releasing the nano-plate from the Si substrate but electrically contacted with the two anchors, we can optimize ME coupling with a minimum substrate clamping effect. As shown in Fig. 7(c), the characterization of the electrical admittance curve was presented to study the electromechanical properties of the ME NPR. By utilizing the MBVD model, an electromechanical resonance frequency $f_{r,\text{NPR}}$ of $60.68\ \text{MHz}$, a high quality factor (Q) of 930 and electromechanical coupling coefficient k_t^2 of 1.35% are given. This electromechanical resonance frequency, which can be analytically expressed as $f_{r,\text{NPR}} \sim \frac{1}{2W_0} \sqrt{\frac{E}{\rho}}$, corresponds to the contour mode of vibration excited in AlN, where W_0 is the width of the resonator pitch, E and ρ are the equivalent Young's modulus and equivalent density of the FeGaB/AlN resonator respectively. Finite element analysis (FEA) on the admittance curve of the device with the same geometry is shown in the Fig. 7(d), which is in good agreement with Fig. 7(c). The in-plane displacement distribution is shown in the inset in Fig. 7(d), which indicates a contour extensional mode of vibration. It is worth noting that the Q -factor of this NPR is much higher than the traditional LF ME heterostructures in previous reports (Srinivasan *et al.*, 2005; Greve *et al.*, 2010a; Jahns *et al.*, 2013).

As shown in Fig. 7(f), an UHFIL is used to measure the induced ME voltage of the NPR device, which is excited by an RF magnetic field (H_{rf}) with an amplitude about $60\ \text{nT}$. A clear electromechanical resonance peak is shown in the ME voltage spectrum at $60.7\ \text{MHz}$ with a peak amplitude of $180\ \mu\text{V}$. The output ME voltage spectrum measured experimentally agrees well with the FEA results with a peak amplitude of $196\ \mu\text{V}$ as shown in Fig. 7(g), the inset of which shows the simulated in-plane displacement of the ME resonator. A high ME coupling coefficient under zero DC bias magnetic field, which is expressed as $\alpha = \partial U / (\partial H_{\text{rf}} \cdot d) = 6\ \text{kV Oe}^{-1}\ \text{cm}^{-1}$, can be acquired at the electromechanical resonance frequency, where U is the induced ME voltage, and d is the thickness of AlN layer. A control sample of non-magnetic single-finger NPR has also been fabricated as a comparison and tested to confirm that the observed voltage output is due to the strain-mediated ME coupling. As shown in Fig. 7(e) inset, the non-magnetic resonator was formed by depositing a $500\ \text{nm}$ Cu thin film instead of FeGaB thin film on AlN plate. A similar admittance behavior of the Cu/AlN based control sample as the ME NPR was observed in Fig. 7(e). However, the induced voltage of the control sample operating at electromechanical resonance that is shown in Fig. 7(h) is very low under the same excitation condition ($H_{\text{rf}} = 60\ \text{nT}$), about two orders of magnitude smaller than the induced voltage in the FeGaB/AlN ME NPR.

FBAR ME Antennas

Based on the thickness resonance mode of FeGaB/AlN thin film, the UHV ME FBARs operate at $2.53\ \text{GHz}$. The active element of ME FBAR antenna is a suspended FeGaB/AlN ME circular disk with a diameter of $200\ \mu\text{m}$ as shown in Fig. 8(a) and (b). The electromechanical resonance frequency ($f_{r,\text{FBAR}}$) of the ME FBAR, which is different from ME NPR, is defined by the thickness of the

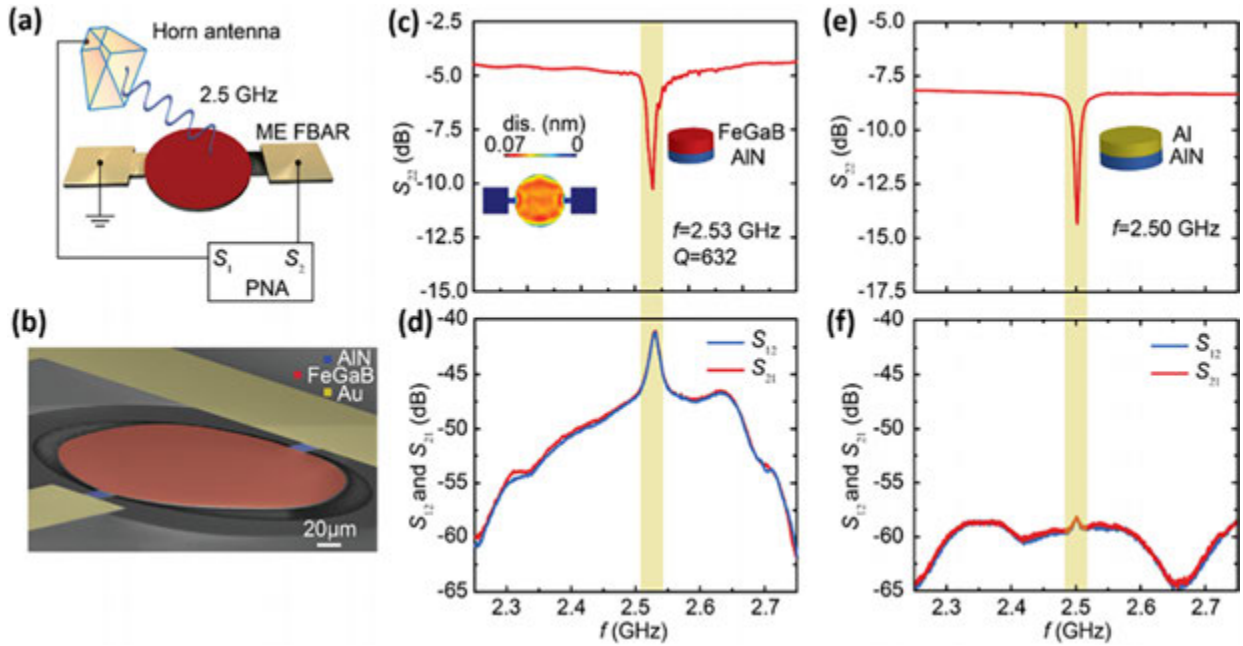


Fig. 8 ME FBAR antennas. (a) Schematic of the antenna measurement setup. (b) SEM images of the fabricated ME FBAR. (c) Return loss curve (S_{22}) of ME FBAR. The inset shows the out-of-plane displacement of the circular disk at resonance peak position. (d) Transmission and receiving behavior (S_{12} and S_{21}) of ME FBAR. (e) Return loss (S_{22}) curve of the non-magnetic Al/AlN control FBAR. (f) Transmission and receiving behavior (S_{12} and S_{21}) of the non-magnetic Al/AlN control FBAR. Reproduced from Nan, T., Lin, H., Gao, Y., *et al.*, 2017. Acoustically actuated ultra-compact NEMS magnetoelectric antennas. *Nature Communications* 8 (1), 296.

circular resonating disk and can be expressed by $f_{r,FBAR} \sim \frac{1}{2T} \sqrt{\frac{E}{\rho}}$, where T is the total thickness, E is the effective Young's modulus, and ρ is the effective density of the FeGaB/AlN heterostructure disk. Fig. 8(c) presents the measured $f_{r,FBAR}$ of 2.53 GHz, peak return loss of 10.26 dB and a Q-factor of 632 by measuring the reflection coefficient (S_{22}) of the FBAR device. The out-of-plane displacement of the FBAR is simulated and presented in Fig. 8(c) inset, which indicates a thickness extensional mode. Fig. 8(d) shows the receiving and transmitting behavior of ME FBARs that corresponds to the S_{21} and S_{12} parameters, respectively. It is obvious that S_{12} and S_{21} curves nearly overlap with each other, in which a strong resonance peak is observed at $f_{r,FBAR}$. By using the measured S_{12} data, the antenna gain of the ME FBAR is measured to be -18 dBi at $f_{r,FBAR}$ through gain comparison method. As a control device for ruling out the artificial EM coupling to the ground loop, a non-magnetic Al layer with thickness of 1000 nm was deposited to replace the 500 nm thick FeGaB multilayer for keeping the resonance frequency unchanged. Fig. 8(e) shows a similar electromechanical property of the non-magnetic control device as ME FBAR. The weak S_{21} and S_{12} resonance peaks, which are observed at 2.5 GHz in Fig. 8(f), suggest that the ME coupling effect dominates in the S_{21} and S_{12} measurement results of the ME FBAR antenna.

Challenges and Opportunities

Although lots of studies have been done on the magnetoelectric composites in the past years, there are still many challenges and opportunities that need to be addressed in the coming years. From the science point of view, understanding, modeling, and controlling of ME interaction are of critical importance for the community. Development of new mechanisms for ME composites is desired as well for approaching the limit of strength of ME coupling. From the materials point of view, large piezoelectric and magnetostrictive coefficients are always in demand for the whole multiferroic society. And in order to have high-performance and high-frequency devices, growth of thick and epitaxial films is required for stronger ME coupling. Besides, fabrication and measurements of micro/nano-magnetoelectric composites are of great interest for future applications in micro/nano-electronics. From the technology point of view, integration and scale-up with existing silicon processing flows and electronics are in particular key challenges and valuable.

The bandwidth of ME composites based devices is narrow, which limits their working frequency range, because the natural resonant peak around the resonance frequency is sharp. The broadband/wideband performance is desired for some applications such as ME antennas and is characterized by flat ME response. There are very limited efforts that have been made to this area although some papers were published (Yu *et al.*, 2005; Park *et al.*, 2009; Park and Priya, 2012; Rajaram Patil *et al.*, 2013). The bandwidth performance of a combined structure with several Terfenol-D/PZT bilayers through parallel and series connection was measured by Yu *et al.* Compared with a single bilayered structure, the frequency response to external field was much wider and the ME coupling far from the resonance ranges was significantly enhanced (Yu *et al.*, 2005). The ME response over a broad DC bias magnetic field range was found to be almost unchanged by adjusting variables that affect ME coefficient including the size and shape of laminates, the number of layers, etc. (Park *et al.*, 2009). A DC bias field is commonly needed in most conventional ME composites in order to obtain the maximum ME coefficient. Therefore, permanent magnets or electromagnets are required in the system, which result in bulky devices and electromagnetic interference. To solve these problems and facilitate ME devices miniaturization for integrated electronics and medical applications, self-biased ME composites are introduced and there is no need for DC magnetic field anymore. Zhou *et al.* recently presented a review with a comprehensive understanding of the self-biased ME composites. Readers can also refer to (Zhou *et al.*, 2016) for the properties of different types self-biased ME composites according to their working principles. All of these issues are both challenges as well as opportunities for the future applications.

References

- Aimon, N.M., Kim, D.H., Sun, X., Ross, C., 2015. Multiferroic behavior of templated BiFeO₃-CoFe₂O₄ self-assembled nanocomposites. *ACS Applied Materials & Interfaces* 7 (4), 2263–2268.
- Astrov, D., 1960. The magnetoelectric effect in antiferromagnetics. *Soviet Physics – Journal of Experimental and Theoretical Physics* 11 (3), 708–709.
- Avellaneda, M., Harshé, G., 1994. Magnetoelectric effect in piezoelectric/magnetostrictive multilayer (2–2) composites. *Journal of Intelligent Material Systems and Structures* 5 (4), 501–513.
- Bedair, S.S., Pulskamp, J.S., Meyer, C.D., *et al.*, 2012. High-performance micromachined inductors tunable by lead zirconate titanate actuators. *IEEE Electron Device Letters* 33 (10), 1483–1485.
- Bichurin, M., Filippov, D., Petrov, V., *et al.*, 2003a. Resonance magnetoelectric effects in layered magnetostrictive-piezoelectric composites. *Physical Review B* 68 (13), 132408.
- Bichurin, M., Petrov, V., Srinivasan, G., 2003b. Theory of low-frequency magnetoelectric coupling in magnetostrictive-piezoelectric bilayers. *Physical Review B* 68 (5), 054402.
- Bickford, J.A., McNabb, R.S., Ward, P.A., Freeman, D.K., Weinberg, M.S., 2017. Low Frequency Mechanical Antennas: Electrically Short Transmitters From Mechanically-Actuated Dielectrics. *IEEE*, pp. 1475–1476.
- Chen, H., Wang, X., Gao, Y., *et al.*, 2020. Integrated tunable magnetoelectric RF inductors. *IEEE Transactions on Microwave Theory and Techniques* 68 (3), 951–963.
- Cheong, S.-W., Mostovoy, M., 2007. Multiferroics: A magnetic twist to ferroelectricity. *Nature Materials* 6 (1), 13.
- Chu, Z., Shi, H., Shi, W., *et al.*, 2017. Enhanced resonance magnetoelectric coupling in (1–1) connectivity composites. *Advanced Materials* 29 (19), 1606022.
- Chu, Z., Annappureddy, V., PourhosseiniAsl, M., *et al.*, 2018a. Dual-stimulus magnetoelectric energy harvesting. *MRS Bulletin* 43 (03), 199–205.
- Chu, Z., PourhosseiniAsl, M., Dong, S., 2018b. Review of multi-layered magnetoelectric composite materials and devices applications. *Journal of Physics D: Applied Physics* 51 (24), 243001.
- Chu, Z., Dong, C., Tu, C., *et al.*, 2019. A low-power and high-sensitivity magnetic field sensor based on converse magnetoelectric effect. *Applied Physics Letters* 115 (16), 162901.

- Conde, J., Murali, P., 2008. Characterization of sol-gel $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ in thin film bulk acoustic resonators. *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control* 55 (6), 1373–1379.
- Curie, P., 1894. Sur la symétrie dans les phénomènes physiques, symétrie d'un champ électrique et d'un champ magnétique. *J. Phys. Theor. Appl.* 3 (1), 393–415.
- Debye, P., 1926. Bemerkung zu einigen neuen Versuchen über einen magneto-elektrischen Richteffect. *Zeitschrift für Physik* 36 (4), 300–301.
- Dong, C., Li, M., Liang, X., *et al.*, 2018. Characterization of magnetomechanical properties in FeGaB thin films. *Applied Physics Letters* 113 (26), 262401.
- Dong, C., He, Y., Li, M., *et al.*, 2020. A portable very low frequency (VLF) communication system based on acoustically actuated magnetoelectric antennas. *IEEE Antennas and Wireless Propagation Letters* 19 (3), 398–402.
- Dong, S., Zhai, J., Li, J., Viehland, D., 2006. Near-ideal magnetoelectricity in high-permeability magnetostrictive/piezofiber laminates with a (2–1) connectivity. *Applied Physics Letters* 89 (25), 252904.
- Dubois, M.-A., Murali, P., 1999a. Measurement of the effective transverse piezoelectric coefficient $e_{31,f}$ of AlN and $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin films. *Sensors and Actuators A: Physical* 77 (2), 106–112.
- Dubois, M.-A., Murali, P., 1999b. Properties of aluminum nitride thin films for piezoelectric transducers and microwave filter applications. *Applied Physics Letters* 74 (20), 3032–3034.
- Dufay, T., Guiffard, B., Thomas, J.-C., Seveno, R., 2015. Transverse piezoelectric coefficient measurement of flexible lead zirconate titanate thin films. *Journal of Applied Physics* 117 (20), 204101.
- Dzyaloshinskii, I.E., 1960. On the magneto-electrical effects in antiferromagnets. *Soviet Physics – Journal of Experimental and Theoretical Physics* 10, 628–629.
- Eerenstein, W., Mathur, N., Scott, J.F., 2006. Multiferroic and magnetoelectric materials. *Nature* 442 (7104), 759.
- Ekrem, N., Olabi, A., Prescott, T., Rafferty, A., Hashmi, M., 2007. An overview of magnetostriction, its use and methods to measure these properties. *Journal of Materials Processing Technology* 191 (1–3), 96–101.
- Fawole, O.C., Tabib-Azar, M., 2017. An electromechanically modulated permanent magnet antenna for wireless communication in harsh electromagnetic environments. *IEEE Transactions on Antennas and Propagation* 65 (12), 6927–6936.
- Fiebig, M., 2005. Revival of the magnetoelectric effect. *Journal of Physics D: Applied Physics* 38 (8).
- Gao, Y., Zardareh, S.Z., Yang, X., *et al.*, 2014a. Significantly enhanced inductance and quality factor of GHz integrated magnetic solenoid inductors with FeGaB/Al₂O₃ multilayer films. *IEEE Transactions on Electron Devices* 61 (5), 1470–1476.
- Gao, Y., Zare, S., Onabajo, M., *et al.*, 2014b. Power-Efficient Voltage Tunable RF Integrated Magnetoelectric Inductors With FeGaB/Al₂O₃ Multilayer Films. *IEEE*, pp. 1–4.
- García-Fernández, P., Wojdet, J.C., Iñiguez, J., Junquera, J., 2016. Second-principles method for materials simulations including electron and lattice degrees of freedom. *Physical Review B* 93 (19), 195137.
- Greve, H., Woltermann, E., Jahns, R., *et al.*, 2010a. Low damping resonant magnetoelectric sensors. *Applied Physics Letters* 97 (15), 152503.
- Greve, H., Woltermann, E., Quenzer, H.-J., Wagner, B., Quandt, E., 2010b. Giant magnetoelectric coefficients in $(\text{Fe}_{90}\text{Co}_{10})_{78}\text{Si}_{12}\text{B}_{10}\text{-AlN}$ thin film composites. *Applied Physics Letters* 96 (18), 182501.
- Gross, I., Akhtar, W., Garcia, V., *et al.*, 2017. Real-space imaging of non-collinear antiferromagnetic order with a single-spin magnetometer. *Nature* 549 (7671), 252–256.
- Harshe, G., Dougherty, J., Newnham, R., 1993. Theoretical modelling of multilayer magnetoelectric composites. *International Journal of Applied Electromagnetics in Materials* 4 (2), 145–160.
- He, Y., Gao, Y., Chen, H., *et al.*, 2018. Integrated tunable bandstop filter using self-biased FeGaB/Al₂O₃ multilayer thin film. *IEEE Transactions on Magnetics* 54 (9), 1–4.
- Hur, N., Park, S., Sharma, P., *et al.*, 2004. Electric polarization reversal and memory in a multiferroic material induced by magnetic fields. *Nature* 429 (6990), 392.
- Islam, R.A., Priya, S., 2006. Synthesis of high magnetoelectric coefficient composites using annealing and aging route. *International Journal of Applied Ceramic Technology* 3 (5), 353–363.
- Islam, R.A., Rong, C.-B., Liu, J., Priya, S., 2008b. Effect of gradient composite structure in cofired bilayer composites of $\text{Pb}(\text{Zr}_{0.56}\text{Ti}_{0.44})\text{O}_3\text{-Ni}_{0.6}\text{Zn}_{0.2}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$ system on magnetoelectric coefficient. *Journal of Materials Science* 43 (18), 6337–6343.
- Islam, R.A., Bedekar, V., Poudyal, N., Liu, J.P., Priya, S., 2008a. Magnetoelectric properties of core-shell particulate nanocomposites. *Journal of Applied Physics* 104 (10), 104111.
- Israel, C., Mathur, N., Scott, J., 2008. A one-cent room-temperature magnetoelectric sensor. *Nature Materials* 7 (2), 93.
- Jahns, R., Piorra, A., Lage, E., *et al.*, 2013. Giant magnetoelectric effect in thin-film composites. *Journal of the American Ceramic Society* 96 (6), 1673–1681.
- Jiang, Q., Shen, Z., Zhou, J., Shi, Z., Nan, C.-W., 2007. Magnetoelectric composites of nickel ferrite and lead zirconate titanate prepared by spark plasma sintering. *Journal of the European Ceramic Society* 27 (1), 279–284.
- Karpinsky, D.V., Eliseev, E.A., Xue, F., *et al.*, 2017. Thermodynamic potential and phase diagram for multiferroic bismuth ferrite (BiFeO_3). *npj Computational Materials* 3 (1), 20.
- Kholkin, A., Wüthrich, C., Taylor, D., Setter, N., 1996. Interferometric measurements of electric field-induced displacements in piezoelectric thin films. *Review of Scientific Instruments* 67 (5), 1935–1941.
- Khomskii, D., 2009. Trend: Classifying multiferroics: Mechanisms and effects. *Physics* 2, 20.
- Khomskii, D.I., 2006. Multiferroics: Different ways to combine magnetism and ferroelectricity. *Journal of Magnetism and Magnetic Materials* 306 (1), 1–8.
- Kimura, T., Goto, T., Shintani, H., *et al.*, 2003. Magnetic control of ferroelectric polarization. *Nature* 426 (6962), 55.
- Klokholt, E., 1976. The measurement of magnetostriction in ferromagnetic thin films. *IEEE Transactions on Magnetics* 12 (6), 819–821.
- Landau, L.D., Bell, J., Kearsley, M., *et al.*, 2013. *Electrodynamics of Continuous Media*. Elsevier, p. 1341.
- Li, F., Zhang, S., Xu, Z., *et al.*, 2010. Composition and phase dependence of the intrinsic and extrinsic piezoelectric activity of domain engineered $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-xPbTiO}_3$ crystals. *Journal of Applied Physics* 108 (3).
- Li, M., Dong, C., Zhou, H., *et al.*, 2017. Highly sensitive DC magnetic field sensor based on nonlinear ME effect. *IEEE Sensors Letters* 1 (6), 1–4.
- Liang, X., Chen, H., Sun, N., Lin, H., Sun, N.X., 2018a. Novel Acoustically Actuated Magnetoelectric Antennas. *IEEE*, pp. 2189–2190.
- Liang, X., Dong, C., Celestin, S.J., *et al.*, 2018b. Soft magnetism, magnetostriction and microwave properties of Fe-Ga-C alloy films. *IEEE Magnetics Letters* 10.
- Liang, X., Dong, C., Chen, H., *et al.*, 2020. A Review of Thin-Film Magnetoelastic Materials for Magnetoelectric Applications. *Sensors* 20 (5), 1532.
- Lin, H., Nan, T., Qian, Z., *et al.*, 2016. Tunable RF Band-Pass Filters Based on NEMS Magnetoelectric Resonators. *IEEE*, pp. 1–4.
- Liu, G., Nan, C.-W., Cai, N., Lin, Y., 2004. Calculations of giant magnetoelectric effect in multiferroic composites of rare-earth-iron alloys and PZT by finite element method. *International Journal of Solids and Structures* 41 (16–17), 4423–4434.
- Liu, J.-M., Pan, B., Chan, H., *et al.*, 2002. Piezoelectric coefficient measurement of piezoelectric thin films: An overview. *Materials Chemistry and Physics* 75 (1–3), 12–18.
- Lou, J., Insignares, R.E., Cai, Z., *et al.*, 2007. Soft magnetism, magnetostriction, and microwave properties of FeGaB thin films. *Applied Physics Letters* 91 (18), 182504.
- Lou, J., Reed, D., Liu, M., Sun, N., 2009. Electrostatically tunable magnetoelectric inductors with large inductance tunability. *Applied Physics Letters* 94 (11), 112508.
- Ludwig, A., Quandt, E., 2002. Optimization of the ΔE effect in thin films and multilayers by magnetic field annealing. *IEEE Transactions on Magnetics* 38 (5), 2829–2831.
- Mateen, F., Maedler, C., Erramilli, S., Mohanty, P., 2016. Wireless actuation of micromechanical resonators. *Microsystems & Nanoengineering* 2, 16036.
- McDannald, A., Staruch, M., Sreenivasulu, G., *et al.*, 2013. Magnetoelectric coupling in solution derived 3–0 type $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3\text{:xCoFe}_2\text{O}_4$ nanocomposite films. *Applied Physics Letters* 102 (12), 122905.
- Nan, C.-W., 1994. Magnetoelectric effect in composites of piezoelectric and piezomagnetic phases. *Physical Review B* 50 (9), 6082.
- Nan, C.-W., Bichurin, M., Dong, S., Viehland, D., Srinivasan, G., 2008. Multiferroic magnetoelectric composites: Historical perspective, status, and future directions. *Journal of Applied Physics* 103 (3), 1.

- Nan, T., Lin, H., Gao, Y., *et al.*, 2017. Acoustically actuated ultra-compact NEMS magnetoelectric antennas. *Nature Communications* 8 (1), 296.
- Nan, T., Hui, Y., Rinaldi, M., Sun, N.X., 2013. Self-biased 215MHz magnetoelectric NEMS resonator for ultra-sensitive DC magnetic field detection. *Scientific Reports* 3.
- Nitsan, U., 1977. Electromagnetic emission accompanying fracture of quartz-bearing rocks. *Geophysical Research Letters* 4 (8), 333–336.
- Orenstein, J., 2012. Quantum materials. *Physics Today* 65 (9), 44.
- Palneedi, H., Annareddy, V., Priya, S., Ryu, J., 2016. Status and Perspectives of Multiferroic Magnetoelectric Composite Materials and Applications. Multidisciplinary Digital Publishing Institute. p. 9.
- Pan, E., Heyliger, P.R., 2003. Exact solutions for magneto-electro-elastic laminates in cylindrical bending. *International Journal of Solids and Structures* 40 (24), 6859–6876.
- Park, C.-S., Priya, S., 2012. Broadband/wideband magnetoelectric response. *Advances in Condensed Matter Physics* 2012.
- Park, C.-S., Ahn, C.-W., Ryu, J., *et al.*, 2009. Design and characterization of broadband magnetoelectric sensor. *Journal of Applied Physics* 105 (9), 094111.
- Petrov, V., Srinivasan, G., Bichurin, M., Galkina, T., 2009. Theory of magnetoelectric effect for bending modes in magnetostrictive-piezoelectric bilayers. *Journal of Applied Physics* 105 (6), 063911.
- Prasad, M.S., Selvin, S., Tok, R.U., Huang, Y., Wang, Y., 2018. Directly Modulated Spinning Magnet Arrays for ULF Communications. *IEEE*. pp. 171–173.
- Rajaram Patil, D., Kambale, R.C., Chai, Y., *et al.*, 2013. Multiple broadband magnetoelectric response in thickness-controlled Ni/[011] Pb(Mg_{1/3}Nb_{2/3})O₃-Pb(Zr, Ti)O₃ single crystal/Ni laminates. *Applied Physics Letters* 103 (5), 052907.
- Ramesh, R., Spaldin, N.A., 2007. Multiferroics: Progress and prospects in thin films. *Nature Materials* 6 (1), 21–29.
- Rinaldi, M., Zuo, C., Van der Spiegel, J., Piazza, G., 2011. Reconfigurable CMOS oscillator based on multifrequency AIN contour-mode MEMS resonators. *IEEE Transactions on Electron Devices* 58 (5), 1281–1286.
- Ruby, R., Bradley, P., Larson, J., Oshmyansky, Y., Figueredo, D., 2001. Ultra-Miniature High-Q Filters and Duplexers using FBAR Technology. *IEEE*. pp. 120–121.
- Ryu, J., Priya, S., Uchino, K., Kim, H.-E., 2002. Magnetoelectric effect in composites of magnetostrictive and piezoelectric materials. *Journal of Electroceramics* 8 (2), 107–119.
- Sanchez-Rojas, J.L., Hernandez, J., Ababneh, A., *et al.*, 2008. Advanced Determination of Piezoelectric Properties of AIN Thin Films on Silicon Substrates. *IEEE*.
- Schmid, H., 1994. Multi-ferroic magnetoelectrics. *Ferroelectrics* 162 (1), 317–338.
- Selvin, S., Prasad, M.S., Huang, Y., Wang, E., 2017. Spinning Magnet Antenna for VLF Transmitting. *IEEE*. pp. 1477–1478.
- Shim, Y., Wu, Z., Rais-Zadeh, M., 2012. A multimetal surface micromachining process for tunable RF MEMS passives. *Journal of Microelectromechanical Systems* 21 (4), 867–874.
- Shima, T., Fujimori, H., 1999. An accurate measurement of magnetostriction of thin films by using nano-indentation system. *IEEE Transactions on Magnetics* 35 (5), 3832–3834.
- Shirane, A., Ito, H., Ishihara, N., Masu, K., 2012. Planar solenoidal inductor in radio frequency micro-electro-mechanical systems technology for variable inductor with wide tunable range and high quality factor. *Japanese Journal of Applied Physics* 51 (5S), 05EE02.
- Wu, J., Gao, X., Chen, J., *et al.*, 2018. Review of high temperature piezoelectric materials, devices, and applications. *Acta Physica Sinica* 67.207701.
- Spaldin, N., Ramesh, R., 2019. Advances in magnetoelectric multiferroics. *Nature Materials* 18 (3), 203–212.
- Spaldin, N.A., Fiebig, M., 2005. The renaissance of magnetoelectric multiferroics. *Science* 309 (5733), 391–392.
- Srinivasan, G., 2010. Magnetoelectric composites. *Annual Review of Materials Research* 40, 153–178.
- Srinivasan, G., De Vreugd, C., Laletin, V., *et al.*, 2005. Resonant magnetoelectric coupling in trilayers of ferromagnetic alloys and piezoelectric lead zirconate titanate: The influence of bias magnetic field. *Physical Review B* 71 (18), 184423.
- Srinivasan, G., DeVreugd, C., Flattery, C., Laletsin, V., Paddubnaya, N., 2004. Magnetoelectric interactions in hot-pressed nickel zinc ferrite and lead zirconate titanate composites. *Applied Physics Letters* 85 (13), 2550–2552.
- Strocov, V., Schmitt, T., Flechsig, U., *et al.*, 2010. High-resolution soft X-ray beamline ADRRESS at the Swiss Light Source for resonant inelastic X-ray scattering and angle-resolved photoelectron spectroscopies. *Journal of Synchrotron Radiation* 17 (5), 631–643.
- Su, H., Tang, X., Zhang, H., Sun, N.X., 2016. Voltage-impulse-induced nonvolatile tunable magnetoelectric inductor based on multiferroic bilayer structure. *Applied Physics Express* 9 (7), 077301.
- Sun, N.X., Srinivasan, G., 2012. Voltage Control of Magnetism in Multiferroic Heterostructures and Devices. *World Scientific*. (1240004).
- Tam, A.C., Schroeder, H., 1989. A new high-precision optical technique to measure magnetostriction of a thin magnetic film deposited on a substrate. *IEEE Transactions on Magnetics* 25 (3), 2629–2638.
- Tellegen, B.D., 1948. The gyrator, a new electric network element. *Philips Research Reports* 3 (2), 81–101.
- Tsubouchi, K., Sugai, K., Mikoshiba, N., 1981. AIN material constants evaluation and SAW properties on AIN/Al₂O₃ and AIN/Si. In: *Proceedings of the IEEE Ultrasonics Symposium*, pp. 375–380.
- Tu, C., Dong, C., Chu, Z., *et al.*, 2018. A passive isolator realized by magnetoelectric laminate composites. *Applied Physics Letters* 113 (26), 262904.
- Tu, C., Chu, Z.-Q., Spetzel, B., *et al.*, 2019. Mechanical-resonance-enhanced thin-film magnetoelectric heterostructures for magnetometers, mechanical antennas, tunable RF inductors, and filters. *Materials* 12 (14), 2259.
- Tu, W.-H., Chang, K., 2005. Compact microstrip bandstop filter using open stub and spurline. *IEEE Microwave and Wireless Components Letters* 15 (4), 268–270.
- Wang, J., 2016. *Multiferroic Materials: Properties, Techniques, and Applications*. CRC Press.
- Wang, J., Dong, C., Wei, Y., *et al.*, 2019. Magnetostriction, soft magnetism, and microwave properties in Co–Fe–C alloy films. *Physical Review Applied* 12 (3), 034011.
- Wang, K., Liu, J.-M., Ren, Z., 2009. Multiferroicity: The coupling between magnetic and polarization orders. *Advances in Physics* 58 (4), 321–448.
- Weldon, J., Jensen, K., Zettl, A., 2008. Nanomechanical radio transmitter. *Physica Status Solidi (b)* 245 (10), 2323–2325.
- Wood, V.E., Austin, A., 1974. Possible applications for magnetoelectric materials. *International Journal of Magnetism and Electromagnetism* 5 (4), 303–315.
- Yang, G.-M., Xing, X., Daigle, A., *et al.*, 2008. Electronically tunable miniaturized antennas on magnetoelectric substrates with enhanced performance. *IEEE Transactions on Magnetics* 44 (11), 3091–3094.
- Yao, Z., Wang, Y.E., Keller, S., Carman, G.P., 2015. Bulk acoustic wave-mediated multiferroic antennas: Architecture and performance bound. *IEEE Transactions on Antennas and Propagation* 63 (8), 3335–3344.
- Yu, H., Zeng, M., Wang, Y., Wan, J., Liu, J.-M., 2005. Magnetoelectric resonance-bandwidth broadening of Terfenol-D/epoxy-Pb(Zr,Ti)O₃ bilayers in parallel and series connections. *Applied Physics Letters* 86 (3), 032508.
- Zhao, P., Zhao, Z., Hunter, D., *et al.*, 2009. Fabrication and characterization of all-thin-film magnetoelectric sensors. *Applied Physics Letters* 94 (24), 243507.
- Zhong, W., Vanderbilt, D., Rabe, K., 1994. Phase transitions in BaTiO₃ from first principles. *Physical Review Letters* 73 (13), 1861–1864.
- Zhou, Y., Maurya, D., Yan, Y., *et al.*, 2016. Self-biased magnetoelectric composites: An overview and future perspectives. *Energy Harvesting and Systems* 3 (1), 1–42.
- Zhu, L., Sun, S., Menzel, W., 2005. Ultra-wideband (UWB) bandpass filters using multiple-mode resonator. *IEEE Microwave and Wireless Components Letters* 15 (11), 796–798.
- Zhu, Y., Qiu, G., Chi, K.H., Wang, B.B., Tsai, C.S., 2009. A tunable X-band band-pass filter module using YIG/GGG layer on RT/duroid substrate. *IEEE Transactions on Magnetics* 45 (10), 4195–4198.

Zinc-Oxide-Based Electronics and Photonics

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Varistors

One of the first, and most established, applications of ZnO in electronics is that of varistors for voltage surge protection in high voltage systems. Such circuits are subject to occasional transient overvoltages (from, for instance, lightning or switching) which can cause equipment failure. Varistors are devices which have a high electrical resistance for low applied voltages, which decreases as the voltage is raised. When placed in parallel with a piece of electrical equipment, varistors thus provide a circuit breaker effect at high voltages. In the case of ZnO varistors, this is achieved by means of the double Schottky junctions which form naturally at the pronounced grain boundaries in sintered ZnO powders (Fig. 1), and which act as a collection of back-to-back Zener diodes. Due to the relatively high melting point of ZnO ($\sim 1975^\circ\text{C}$), such varistors can support the heating associated with large current flow. ZnO displaced SiC as the dominant varistor material when it was discovered that doping ZnO with metal oxides (of, for instance, Bi, Pr, Co or Mn), which segregate to the grain boundaries, gives the most non-linear I/V characteristics known so far (typically showing resistivities of more than $10^{10} \Omega \text{ cm}$ below the breakdown voltage and several $\Omega \text{ cm}$ above the breakdown voltage) (Matsuoka, 1971).

Optical Filtering

Another mature use of ZnO in electronics/photonics applications is as an optical filter. Indeed, the wide bandgap ($E_g = 3.37 \text{ eV}$) that gives excellent optical transparency right across the visible spectrum also inherently blocks UV light (Fig. 2).

Based on this (along with low cost fabrication and excellent biocompatibility) ZnO has found application in UV filter coatings (e.g., for welding glasses) and as the UV blocking component in the new generation of transparent sun creams. Indeed, the latter is currently one of the biggest industrial applications of nanoparticles. This is based on ZnO's propensity for being nanostructured, combined with the fact that ZnO nanoparticles under $\sim 100 \text{ nm}$ in diameter (such as those in Fig. 3) do not scatter visible light.

ZnO coatings/pigments have also been used to boost the energy efficiency of windows/paints during hot weather by reflecting infrared (IR) solar heat and thus reducing the need for air conditioning (Fang *et al.*, 2013). This is because the plasma frequency can be engineered down (through increased doping) so as to reflect IR radiation.

Transparent Conductors

Wurtzite ZnO is also a semiconductor material with a resistivity that can be tailored from semi-insulating right through to semi-metallic by doping. Hence, under appropriate growth conditions, ZnO can be simultaneously transparent and highly electrically conducting (i.e., a "Transparent Conducting Oxide" (TCO)). TCOs are a family of degenerately-doped n-type semiconductors with resistivities under about 10^{-3} ohm cm , free-electron concentrations of the order of 10^{20} cm^{-3} and average transmittances $> 80\%$ for the whole visible range. Up till present, the most widely used TCO has been Sn-doped In_2O_3 (ITO). Doped ZnO is currently displacing ITO, however, for applications such as anti-electrostatic-discharge layers, electromagnetic interference shielding, transparent wiring, touch-sensitive panels and transparent electrical contacts (for use in flat panel displays, solar cells, light emitting diodes (LEDs) etc.) .

This is because zinc is cheaper, more abundant and less toxic than indium, while ZnO is easier to process, shows superior resistance to hydrogen plasmas and can be fabricated at lower temperatures (Gordon, 2000). Moreover, the mobilities and conductivities attainable with degenerately doped ZnO (typically with Al, Sn, Ga or Si) have become comparable with those for ITO (Fig. 4).

Doping with F, on the other hand, gives ZnO the highest optical transparency and the lowest plasma frequency of all TCOs while doping with Al can give transparencies into the mid IR (Dhakal *et al.*, 2012) (Table 1).

Solar

Many solar cell technologies employ at least one ZnO-based layer. As well as acting as transparent electrodes the ZnO layers often play a number of critical roles, including being an electron reservoir, an electron transport layer, a template/buffer for growth of the succeeding layer and a light management layer (anti-reflection (AR) and light trapping surfaces/interfaces profiting from the relatively high refractive index (2.0) of ZnO) (Fig. 5). The ZnO thickness, positioning, conductivity and morphology are thus integral to the cell design, and often represent a significant proportion of overall PV structure (& its' cost) (Fig. 6).

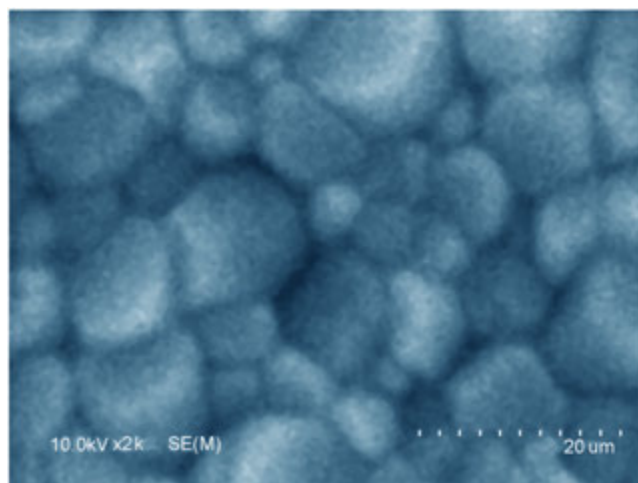


Fig. 1 Scanning electron microscope (SEM) image of a granular ZnO microstructure ($\sim 10\ \mu\text{m}$ diameter grains) with pronounced grain boundaries.

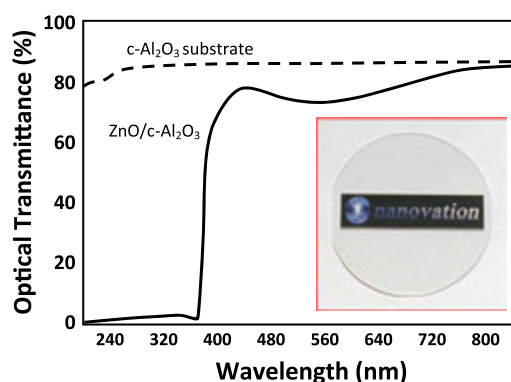


Fig. 2 Optical transmittance spectra illustrating the high intrinsic transparency in the visible range of an epitaxial ZnO film grown on a c-plane sapphire substrate.

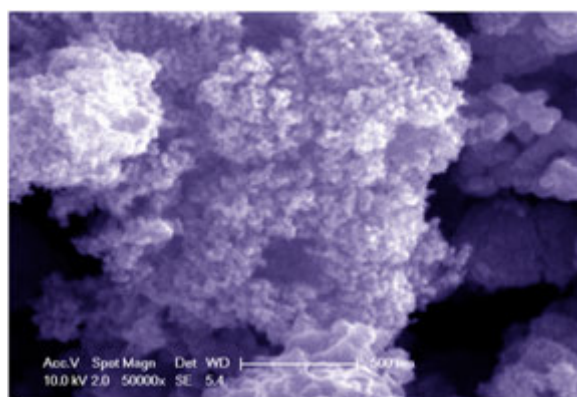


Fig. 3 SEM image of sun-cream-scale ZnO nanoparticles fabricated using a low-cost wet chemical growth approach.

As well as being the case for a number of established solar cell technologies (eg amorphous silicon (*a*-Si), polycrystalline silicon, CdTe/CdS and chalcopyrite Cu-In-Ga-Se based thin film photovoltaics), the above is also true for several emergent technologies, including hybrid inorganic/organic cells, Quantum Dot Sensitized Solar Cells (which both use ZnO nanowires for electron transport) and some variants of tandem silicon/perovskite solar cells.

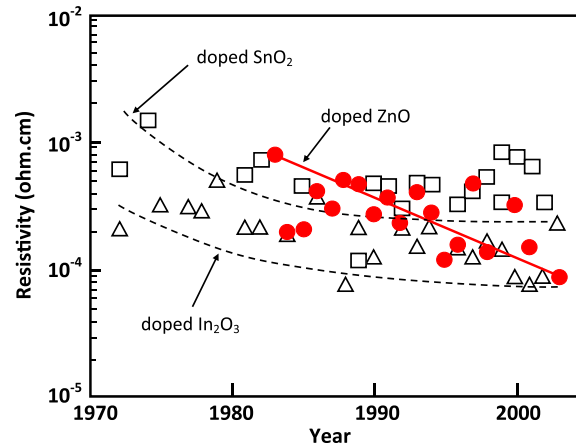


Fig. 4 The evolution of the state-of-the-art resistivity for alloys of SnO_2 , In_2O_3 and ZnO over time. After Minami, T., 2005. Transparent conducting oxide semiconductors for transparent electrodes. *Semicond. Sci. Technol.* 20, 35–44.

Table 1 Best of class crystalline materials for transparent conducting applications

Property	Material
Highest transparency	ZnO:F , Cd_2SnO_4
Highest conductivity	$\text{In}_2\text{O}_3\text{:Sn}$
Lowest plasma frequency	$\text{SnO}_2\text{:F}$, ZnO:F
Highest plasma frequency	Ag , TiN , $\text{In}_2\text{O}_3\text{:Sn}$
Highest workfunction, best contact to p-Si	$\text{SnO}_2\text{:F}$, ZnSnO_3
Lowest workfunction, best contact to n-Si	ZnO:F
Best thermal stability	$\text{SnO}_2\text{:F}$, TiN , Cd_2SnO_4
Best mechanical durability	TiN , $\text{SnO}_2\text{:F}$
Best chemical durability	$\text{SnO}_2\text{:F}$
Easiest to etch	ZnO:F , TiN
Best resistance to H plasmas	ZnO:F
Lowest deposition temperature	$\text{In}_2\text{O}_3\text{:Sn}$, ZnO:B , Ag
Least toxic	ZnO:F , $\text{SnO}_2\text{:F}$
Lowest cost	$\text{SnO}_2\text{:F}$

Note: Gordon, R.G., 2000. Criteria for choosing transparent conductors. *MRS Bull.* 25, 52–57.

Transparent/Flexible Electronics

Over recent decades, a new kind of ZnO-based TCO has emerged. These are Amorphous Oxide Semiconductors (AOS) (Hosono, 1996). Compared to wurtzite ZnO, amorphous ZnO-based alloys have lower processing temperatures, are cheaper to fabricate in large area format, are lighter and have better uniformity of properties (due, in part, to a lack of grain boundaries and related issues). Importantly, their performance is also stable/reproducible during and after repetitive bending, so they are compatible with flexible substrates/electronics.

Although AOS are not a novel class of materials (Denton *et al.*, 1954), the new generation of ZnO-based AOS exhibits enhanced carrier mobility, superior capacity for processability in air and improved thermodynamic stability compared with conventional Covalent Amorphous Semiconductors (CAS) and existing AOS (Nomura *et al.*, 2004).

Amorphous InZnO (a-IZO) is considered the most representative ternary AOS system (Wager *et al.*, 2014; Kim *et al.*, 2011). The resistivity of a-IZO can be varied very widely (from 10^{-4} to $10^8 \Omega \text{ cm}$) by controlling the cation composition and cation/oxygen stoichiometry (Kwon and Jeong, 2015). a-IZO can exhibit a mobility over $50 \text{ cm}^2/\text{Vs}$ and doping with Sn can produce even higher mobilities ($> 100 \text{ cm}^2/\text{Vs}$; Kim *et al.*, 2010) along with transparencies that are comparable with ITO (Sashabayashi *et al.*, 2003). Thus AOS are viable alternatives for use in transparent electrode applications (Minami *et al.*, 1996).

With regards to the origin of this remarkable property set, Hosono (1996) proposed, that the relatively high mobilities observed in AOS compared with CAS may be obtained because of differences in the intrinsic nature of the chemical bonding. Figs. 7 and 8 illustrate the wavefunction at the bottom of the conduction bands in CAS and AOS.

It can be seen that the hybridized sp^3 orbital overlap in CAS is highly directive. Therefore, any bond angle fluctuations would be expected to significantly alter the electronic levels, and carrier transport should be controlled by hopping between localized tail-states rather than band conduction. Thus structural randomness could greatly degrade the carrier mobility. Nomura *et al.* (2004)

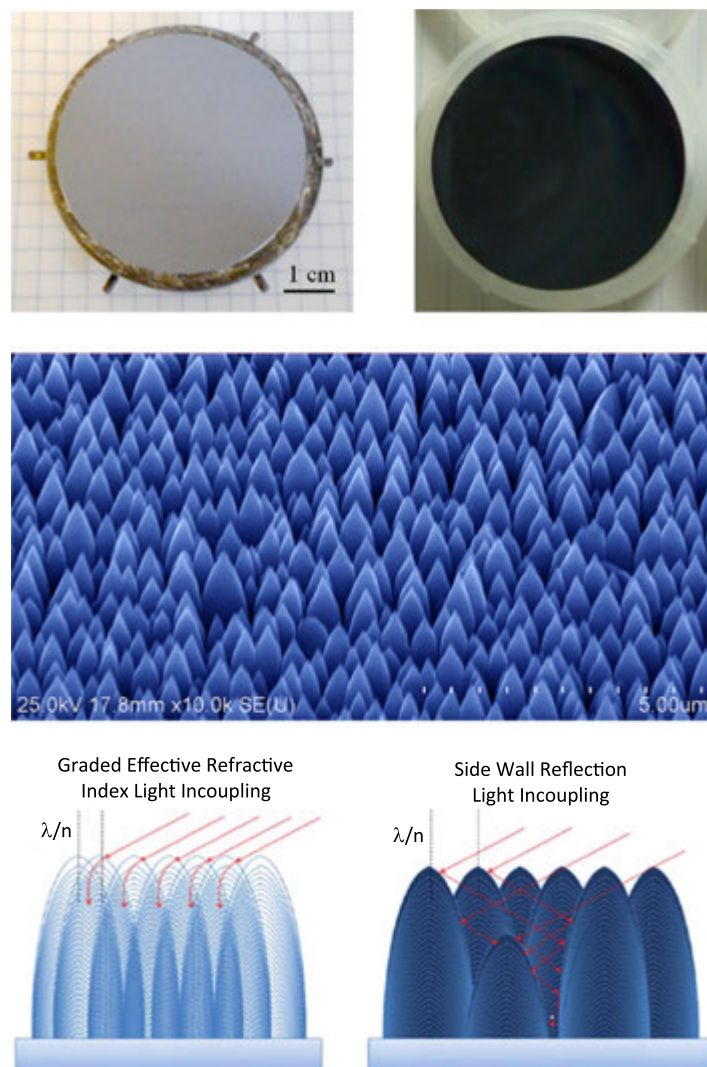


Fig. 5 The upper images show the aspect of a silicon wafer before and after coating with a ZnO moth-eye nanostructure (shown in the underlying SEM image). This sub-visible-wavelength scale of moth-eye nanostructure shows excellent high angle and broad-band AR performance by combining graded effective refractive index and nanostructure side-wall reflections so as to maximize light incoupling, as shown on the left and right, respectively, in the lower schematic. After Peres, M., Soares, M., Neves, A., Monteiro, T., Sandana, V., 2010. Morphological and optical studies of self-forming ZnO nanocolumn & nanocone arrays grown by PLD on various substrates. *Phys. Status Solidi A* 1–4. Raut, H.K., Ganesh, V.A., Nair, S., Ramakrishn, S., 2011. Anti-reflective coatings: A critical, in-depth review. *Energy Environ. Sci.* 4, 3779–3804.

explained that AOS, in contrast, have higher ionicity and the bottom of the conduction band has extended spherical s orbitals associated with the metal ion. These electronic levels have an overlap which is relatively insensitive to distortion of the metal–oxygen–metal chemical bonds. Thus strain and disorder within the material should not strongly impact the conduction. It was proposed, therefore, that AOS materials can show degenerate band conduction and superior electron mobility compared with CAS. More recently, however, this hypothesis was put into question because it was reported that trap-free mobilities are comparable for a-Si:H and AOS. Thus a more pronounced electron trapping in a-Si:H is put forward as the origin of the difference in mobility (Stewart *et al.*, 2016). Bond-angle variability (a-Si:H) and cation sublattice disorder (a-IGZO) are proposed as the respective origins of the carrier trapping.

Recently, a new generation of TFTs, employing such amorphous ZnO-alloys as channels, has been developed. Fig. 9 illustrates a typical “staggered bottom gate” oxide TFT architecture.

This is an analogy of an n-channel Metal Insulator Semiconductor Field Effect Transistor (MISFET) with an AOS substituted for both the metal gate and the semiconductor channel. Walter Shockley explained the function of MISFETs in 1950: “a very thin layer of semiconductor is placed on an insulating support. This layer of semiconductor constitutes one plate of a parallel-plate capacitor. If this capacitor is charged, with the metal plate positive, then the additional charge on the semiconductor will be represented by an increased number of electrons. Consequently, the added electrons should be free to move and should contribute to the

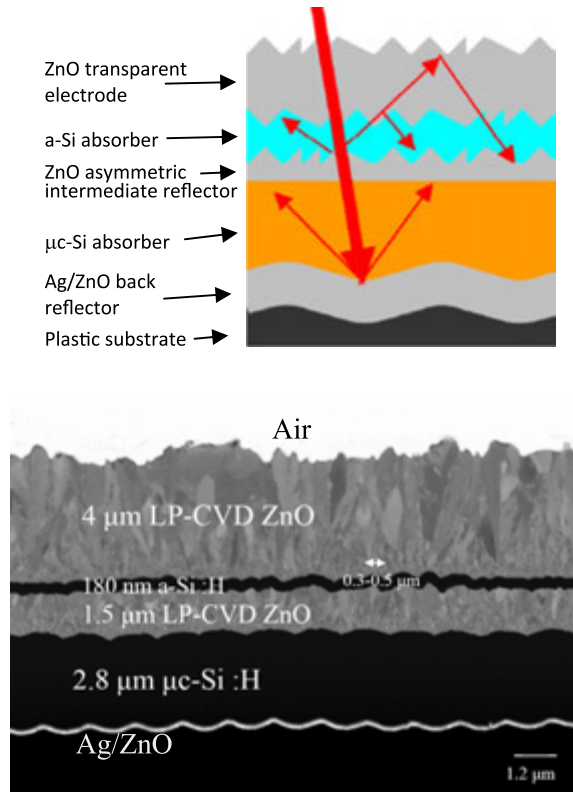


Fig. 6 A schematic and a cross-sectional electron microscope image of a high performance “micromorph” silicon tandem solar cell based on a combination of amorphous and polycrystalline silicon light harvesting layers. Of note is that (a) the ZnO-based layers represent a bigger proportion of the cell than the silicon (b) the ZnO-based layers play a number of critical light management roles (transparency, anti-reflection surfaces and light trapping interfaces) (c) the ZnO has to be an appropriate/compatible crystallographic template for the overgrowth of the succeeding silicon layer and (d) the thickness, doping/conductivity and morphology of the various ZnO layers are an integral part of the overall solar cell conception/design/realization. Reproduced from Söderström, T., Dominé, D., Feltrin, A., *et al.*, 2010. ZnO Transparent conductive oxide for thin film silicon solar cells. Proc. SPIE 7603, (76030B-8).

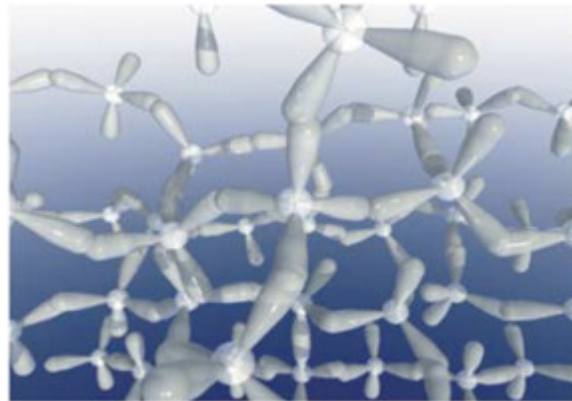


Fig. 7 Schematic of the electron orbitals at the bottom of conduction band in CAS. After Nomura, K., Ohta, H., Takagi, A., *et al.*, 2004. Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors. Nature 432, 488–492.

conductivity of the semiconductor. In this way, the conductivity in the semiconductor can be modulated by the voltage put on the capacitor plate. Since this input signal requires no power if the dielectric is perfect, power gain will result”.

Although oxide TFTs are not a novel concept (Boesen and Jacobs, 1968; Ohya *et al.*, 2001), the new generation exhibits much higher on-off ratios ($>10^8$) and channel mobilities than the hydrogenated amorphous silicon (a-Si:H) based devices which are currently used for many state-of-the-art microelectronics applications (including that of the channel in “select transistors” which

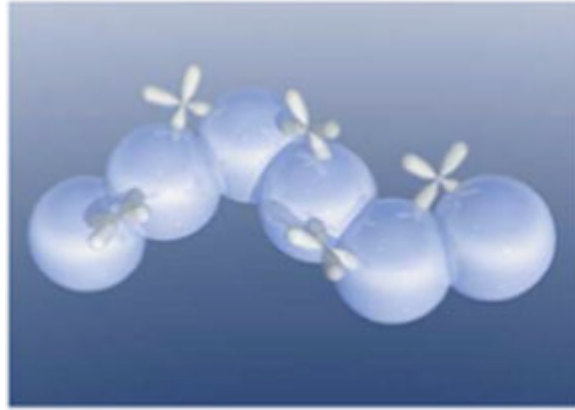


Fig. 8 Schematic of the electron orbitals at the bottom of the conduction band in ZnO-based AOS. Spheres denote metal s orbitals. The contribution of oxygen 2p orbitals is small. Overlap of neighboring s orbitals is rather large, and is not significantly affected even in an amorphous structure. After Nomura, K., Ohta, H., Takagi, A., *et al.*, 2004. Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors. *Nature* 432, 488–492.

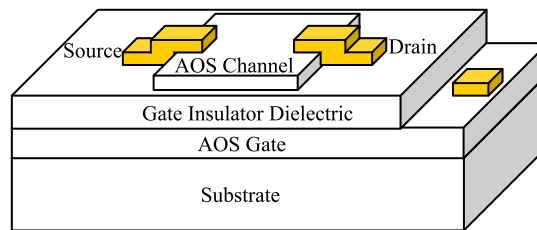


Fig. 9 Schematic of a generic “Staggered Bottom-Gate” oxide TFT. In this case, the semiconductor channel and conducting gate are both constituted of an AOS.

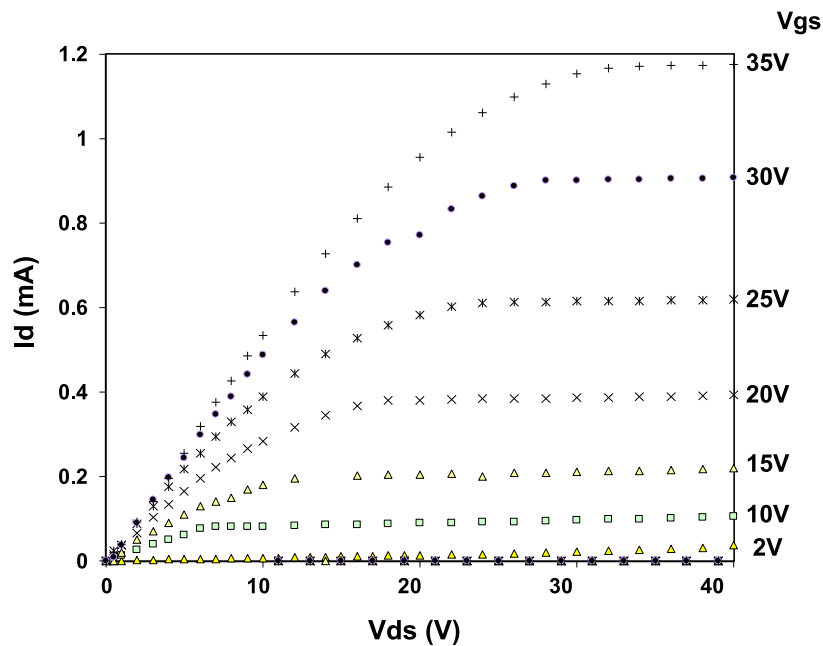


Fig. 10 Output characteristic of a ZnO channel TFT showing relatively large I_d , enhancement mode operation (no power consumption when off), good pinch off and hard saturation plateauing of I_d which indicates that the channel was depleted of carriers.

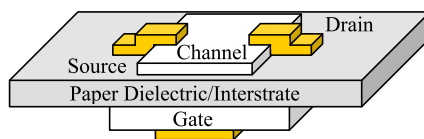


Fig. 11 Schematic of a paper “Interstrate” TFT.

transmit or block backlight for each pixel in Liquid Crystal Displays (LCD)). Another key advantage of oxide TFTs is that they are (low leakage) enhancement mode devices (Fig. 10).

This is preferable to the depletion mode alternative since circuit design is simpler and power dissipation is lower (because the off-state is the power-down state).

In contrast to TCO applications, the channels in TFTs need as low a carrier concentration as possible in order to achieve stable performance (Kwon *et al.*, 2004) - ideally $< \sim 10^{14} / \text{cm}^3$, according to Nomura *et al.* (2004). This can be achieved by introducing an extra component to a-IZO in order to suppress excessive carriers. Gallium (Ga) is the most common carrier suppressor adopted for the a-IZO system. (Nomura *et al.*, 2006; Barquinha *et al.*, 2008) and a-IGZO has become the industry standard channel for oxide TFTs.

However, gallium addition also suppresses the relatively high carrier mobility ($> 20 \text{ cm}^2/\text{Vs}$; Hosono, 2006) that can be obtained in In-rich amorphous a-IGZO (Orita *et al.*, 2001). Thus a compositional trade-off is required and state-of-the-art a-IGZO based TFTs typically have a mobility of about $12 \text{ cm}^2/\text{Vs}$ (Wager, 2016), as compared with a value of $< 1 \text{ cm}^2/\text{Vs}$ for a-Si:H. TFTs made with a-IGZO channels also offer the advantages of excellent performance when fabricated at room temperature which resolves the existing trade-off between processing temperature and device performance and allows fabrication on inexpensive heat-sensitive substrates such as transparent polymers or paper (a-Si:H fabrication temperature is too high for many flexible substrates).

As a result of these attributes a-IGZO based TFTs offer several decisive advantages over the incumbent a-Si:H based devices for use as backplane select transistors in OLED and active matrix LCD screens. The higher mobility of oxide TFTs offers increased refresh rates and the wide bandgap reduces light sensitivity (lower noise) and degradation. Improved transparencies allow more backlight to be transmitted through each pixel in LCD screens, yielding a brighter and more efficient (lower power consumption) display. This also means that the aperture ratio can be reduced, so as to give smaller pixels and thus higher resolution. Finally, ZnO based TFTs can support higher device currents. This offers possibilities for higher power operation. Since emerging in 2012, commercial a-IGZO based oxide TFTs have moved rapidly into mass production (using both physical and chemical vapor deposition fabrication) for use in phones, monitors, tablets, laptops, desktop PCs, and TVs (Wager, 2016). With regards to the future, a significant trend in oxide TFTs is towards the use of non-toxic and non-resource-critical (sustainable) materials. Hence, In- and Ga-free alternatives are being explored. a-ZnSnO (a-ZTO) in particular is showing promising results (Avis and Jang, 2011). Another active development front is that of novel device architectures. Fig. 11 shows a Metal Oxide FET (MOSFET) in which the paper acts as both the dielectric and the support, or “interstrate” (Martins *et al.*, 2008; Fortunato *et al.*, 2008) for use in oxide TFT based “e-paper” (Ito *et al.*, 2007).

A further device architecture innovation is ZnO-based Metal Semiconductor FETs (MESFETs) (Frenzel, *et al.*, 2008). These devices can operate in a lower voltage regime ($+/- 1\text{V}$) compared with MISFETs. Thus, they should be better suited to driving display pixels. A method to obtain fully transparent MESFETs devices (including all contacts) has also been developed. This methodology can be adapted to crystalline and amorphous substrates and films.

Light Emitters

A long-established, application exploiting light emission from ZnO is that of a green/blue phosphor. This is based on the efficient oxygen vacancy defect emission (peaked at about 490 nm) which is observed for zinc-rich ZnO (Fig. 12).

This phosphor was very widely used in vacuum fluorescent displays in the late 20th century but the market has waned in recent years due to the advent of novel display technologies.

More recently ZnO has been widely investigated as a potentially superior UV emitter to GaN (currently the commercially predominant wide bandgap opto-semiconductor). This is because the higher stability of the ZnO free exciton, which has a binding energy of 60 meV (compared to 21 meV for GaN) (Klingshirn, 2007) should allow much brighter UV emitters with lower threshold voltages (Gadallah *et al.*, 2013). A fundamental challenge in this respect, however, is the lack of the p-type ZnO which is necessary for the manufacture of efficient p-n junction devices (Tang *et al.*, 2017). This is because (a) it has proven difficult to incorporate and activate sufficient acceptor concentrations (the main acceptor dopants attempted have been the Group V elements N, P, As, Sb plus the Group Ia elements Li, Na, K and the Group Ib elements Ag, Cu, Au – there are various competing theories as to how the dopants act) and (b) background donors tend to compensate the acceptors because native defects (O vacancies and Zn interstitials) in combination with common impurities (such as H, Al and Ga) act as shallow donors. Advances in ZnO epitaxial growth along with the development of high quality single crystal ZnO substrates (Maeda *et al.*, 2005) and the adoption of higher purity sources have, however, helped to suppress defect densities and non-intentional impurity doping respectively and thus reduce donor compensation.

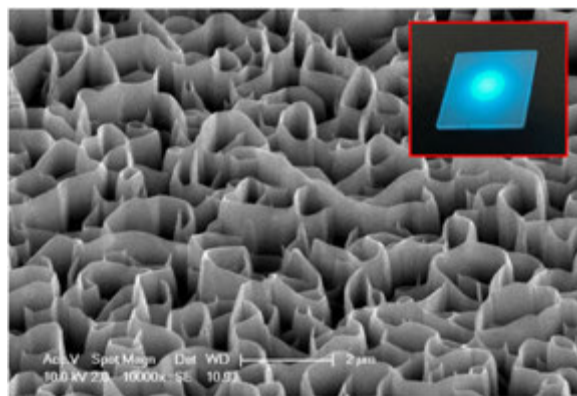


Fig. 12 SEM image of a zinc-rich ZnO nanowall sample with a photograph of the corresponding photoluminescence (inset) showing a typical green/blue emission peaked at about 490 nm.

Although many groups have nevertheless reported the development of p-type ZnO (Fan *et al.*, 2013; Tang *et al.*, 2017) allowing the demonstration of light-emitting p–n junctions (Rahman, 2019) experimental results generally show mobilities, conductivities and overall device efficiencies that are relatively disappointing. An emerging factor is that Mg alloying could facilitate the task of p-type doping. The two main reasons put forward for this are the shifting of the conduction band to higher energy acting to reduce the background donor concentration and the Zn vacancy (acceptor) concentration increasing with Mg content. In another approach, many groups have demonstrated transparent p–n junction devices using alternative p-type layers (Rahman, 2019), including p-GaN (Bayram *et al.*, 2008; Rogers *et al.*, 2006), p-NiO (Fig. 13), p-Cu₂O and p-SnO and p-Si, (Pau *et al.*, 2010; Rogers *et al.*, 2009).

These are not ideal in terms of band alignment (and, therefore, carrier injection), however, and the conductivities/mobilities of the p-type TCO are relatively low, which hinders device performance.

Sensors

The longest established use of ZnO for sensing is in gas detectors. This is because the surface and grain boundaries of ZnO are depleted of electrons because of absorbed oxygen. Exposure to oxidizing or reducing gases modulates this carrier depletion layer and hence causes the conductivity to either rise or fall (Fig. 14). The first commercial devices employed sintered ZnO powders because they were inexpensive and gave a competitive sensitivity combined with high mechanical/chemical stability and low toxicity. Recently, new generations of higher sensitivity epitaxial (Rombach *et al.*, 2016) and nanostructured ZnO gas sensors are emerging (Arafat *et al.*, 2012). The epitaxial sensors are engineered to have higher performance by presenting only the most sensitive crystallographic plane to the gas. Such epitaxial layers could also have further advantages over polycrystalline samples such as increased stability and higher sensing speed.

The nanostructured sensors, on the other hand, rely on their intrinsically large surface-to-volume ratio to provide compact, low-power devices with sub-parts-per-million (ppm) sensitivity capability for a number of molecules, including C₂H₅OH, CO, H₂, H₂O, H₂S, NH₃, NH₄, NO₂ and O₃. There has also been progress in developing innovative ZnO-based gas sensors which function at room temperature (Zhu and Zeng, 2017).

Wurtzite ZnO also offers a polar crystal structure with amongst the highest piezo-responses of any semiconductor (Triboulet, 2000). Furthermore, sputtered ZnO films show better quality and adherence to a-SiO₂/Si than alternative materials with larger piezo-responses. This capacity for monolithic integration with silicon-based electronic circuitry, along with an amenability to chemical processing, has led to ZnO being adopted for use as the piezoelectric transducer layer in surface acoustic wave (SAW) devices, which are well established for multiplexing/demultiplexing bandpass filtering for telecommunications applications: primarily cellular phones and base stations.

More recently ZnO-based SAW devices have been adopted for a whole range of sensing applications (bio, gas, humidity, UV light, pressure, chemical) (Constantinoiu and Viespe, 2020). For sensing applications, reducing or oxidative analyte molecules interact with the free electrons on the ZnO surface and thus impact the velocity of the SAW.

SAW sensors are typically based a pair of Inter-Digitated Transducers (IDTs) deposited on an piezoelectric layer. The IDTs are comprised of periodic ($\lambda/4$) metallic electrodes in the form of two intercrossing combs (Fig. 15). Their function is to convert a periodic input electrical signal into a SAW on the piezoelectric surface and then back to a periodic electrical signal at the output IDT. Changes in SAW velocity modify the transmission delay between the input and output signals.

Compared to other sensor technologies, SAW sensors offer high sensitivity, short response/recovery times, small size, low cost, and the possibility of wireless operation.

Moreover, these devices also offer the advantage that the challenges of processing, contacting and packaging ZnO based SAW devices on an industrial scale have already been mastered (Kadota, 2005).

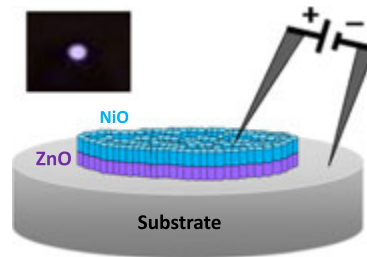


Fig. 13 Schematic of a nanostructured p-NiO/n-ZnO heterojunction with an inset image of the corresponding electroluminescence. Reproduced from Sandana, V.E., Rogers, D.J., Teherani, F.H., *et al.*, 2015. Structural, optical, electrical & morphological study of transparent p-NiO/n-ZnO heterojunctions grown by PLD. Proc. SPIE 9364, (936410-1).

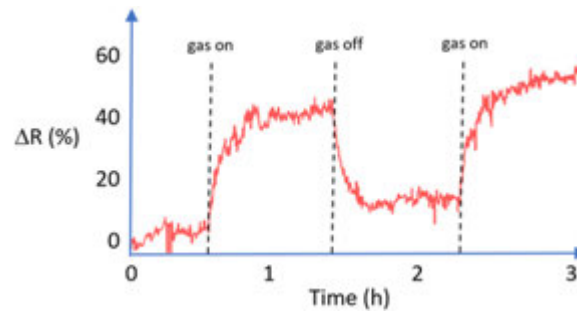


Fig. 14 The variation in electrical resistance (ΔR) with time for an epitaxial (Mg)ZnO thin film upon exposure/withdrawal of 5000 ppm CO_2 gas at 350°C (layers fabricated by Nanovation, measurements performed by A Barnabé (CIRIMAT) at U. Toulouse). The elevated temperature operation is applied in order to overcome a surface activation energy barrier and increase the reaction kinetics.

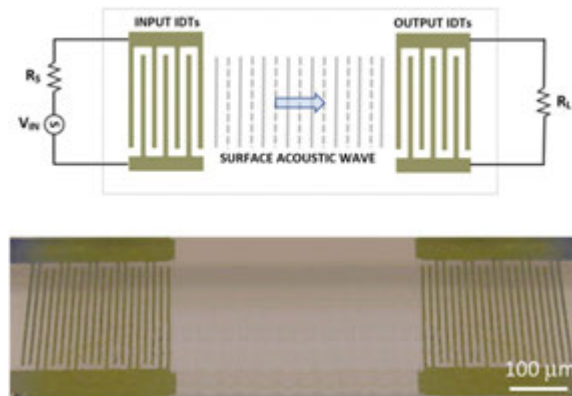


Fig. 15 Schematic and photograph of an Inter-Digitated Transducer SAW device fabricated by UV photolithography of gold contacts on a ZnO layer grown on a quartz substrate. Reproduced from Zerdali, M., Bechiri, F., Hamzaoui, S., *et al.*, 2017. Identification of acoustic waves in ZnO materials by Brillouin light scattering for SAW device applications. Proc. SPIE 10105, (1010514-1).

Recently, the use of ZnO as a UV photodetector (PD) has received much attention. This is because the bandgap can be tuned from the UVA into the UVC (solar blind region) by alloying with MgO (while maintaining the semiconducting wurtzite phase).

Current state-of-the-art (Mg)ZnO PD are usually based on Metal-Semiconductor-Metal (MSM) IDT architectures (Yang *et al.*, 2017; Rogers *et al.*, 2013). An MSM-PD is made by forming two ("back-to-back") Schottky electrodes on the surface of an n-type (Mg)ZnO layer in the form of a single IDT. Under a DC voltage bias operation one of the electrodes is always reverse biased and blocks current flow unless above-bandgap (ie UVC) light impinges on the sample so as to produce photo-generated charge carriers and increase the electrical conductivity (Fig. 16).

As well as low dark currents, such PD exhibit sharp wavelength cut-off, high speed operation, linear signal response with optical power and extremely low parasitic capacitance/noise. UVC devices, such as that in Fig. 16 are of particular interest because of their solar blindness. These characteristics make them attractive for sensing and imaging applications (e.g., aerospace, automotive, military, petroleum, flame detection and astronomy). The main challenges are to compete with alternative solid state UVC PD

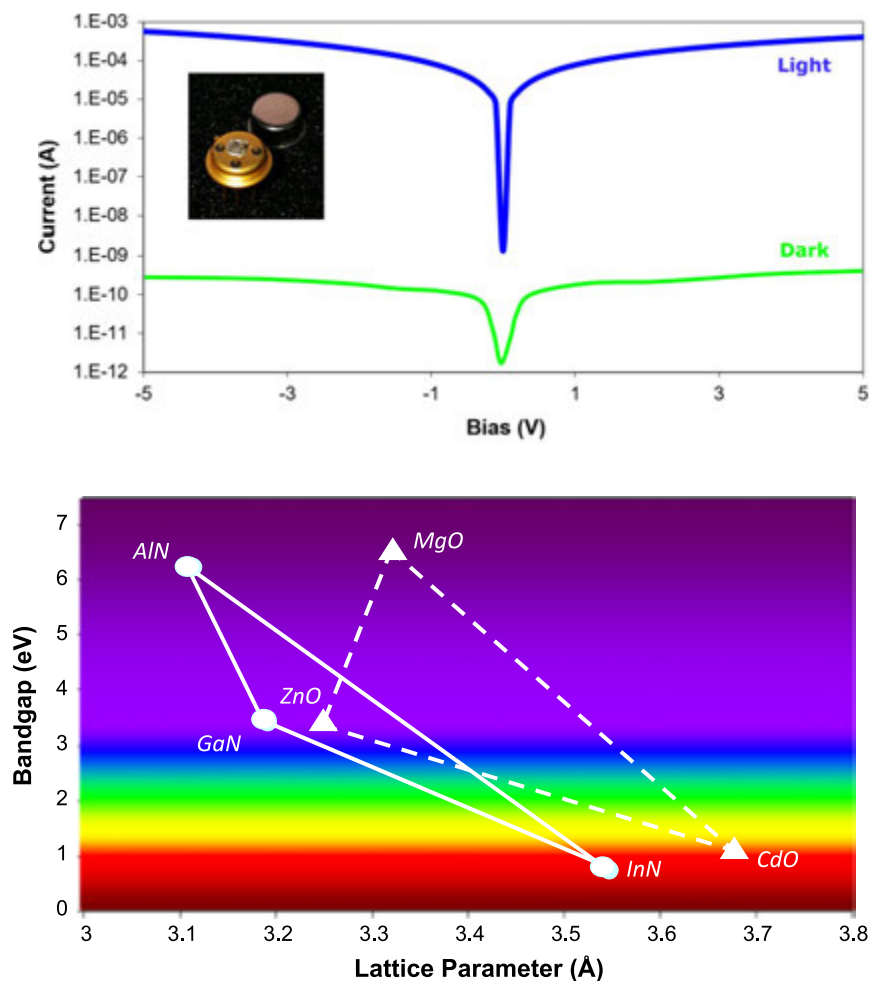


Fig. 16 The upper image shows IV characteristics for a 275 nm (Mg)ZnO MSM photodetector with/without front illumination. The lower figure compares plots of the bandgap vs. lattice constant for wurzite (Al,In)GaN and (Mg,Cd)ZnO. UV bandgap engineering of ZnO (up to 10.6 eV) can also be achieved effectively by alloying with BeO. There are toxicity and handling issues in this case, however. Reproduced from Rogers, D.J., Teherani, F.H., Sandana, V.E., *et al.*, 2018. The new oxide paradigm for solid state ultraviolet photodetectors. *Proc. SPIE 10533*, (105331P-1). Rogers, D.J., Bove, P., Sandana, E.V., Razeghi, M., Teherani, F.H., 2013. ZnO moves further into the UV. *Laser Focus World* 49 (10).

based on SiC (already available) and (Al)GaN (emerging). However, the insertion of high pass filters is necessary with SiC (bandgap engineering is not possible) and UVC (Al)GaN detectors are difficult/expensive to fabricate.

ZnO is also emerging for biosensing. As well as SAW-based sensors these can be chemoresistive, optical/plasmonic, or FET-based transducers (Pearton *et al.*, 2010). Good electrical conductivity, chemical stability, a biomimetic nature, the potential for surface functionalization, biocompatibility (the biological activity of the element to be recognized should be retained) along with a high isoelectric point, of 9.5 (which facilitates immobilization of biomolecules through an electrostatic interaction) make ZnO an attractive biosensor matrix.

Amongst these, nanostructure-based devices are very promising. Due to their small dimensions they can offer an increased sensing surface, strong binding properties, faster responses, and can boosted sensitivity (single-molecule detection in some cases) (Fig. 17).

ZnO nanostructures as biosensors have already been used to detect species including hydrogen peroxide, urea, protein, glucose, human immunoglobulin G (IgG), DNA (phosphinothricin acetyltransferase (PAT) gene), phenol, catechol or cholesterol.

Ongoing trials should pave the way to commercialization of implantable, miniature point-of-care biosensors compatible with CMOS/MEMS technology for wireless telemedicine.

Future Perspectives

With almost 9000 publications on ZnO in 2019 (Fig. 18) it is impossible to examine all the potential future applications of ZnO in this chapter.

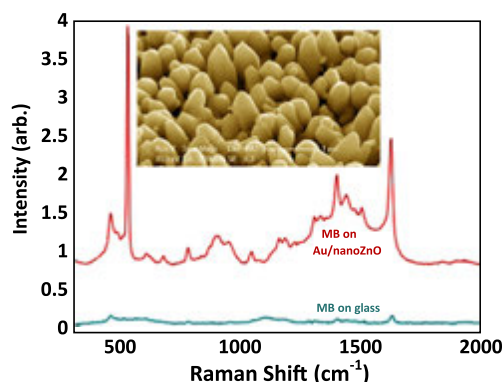


Fig. 17 Spectra showing the enhanced Raman signal response from a gold-coated nano ZnO plasmonic biosensor relative to a bare glass substrate (for Methyl Blue (MB) functionalization). Reproduced from Barbillon, G., Sandana, E., Humbert, C., *et al.*, 2017. Study of Au coated ZnO nanoarrays for surface enhanced Raman scattering chemical sensing. *J. Mater. Chem. C* 5, 3528–3535. Tang, F., Adam, P.M., Rogers, D.J., *et al.*, 2018. Sensing based on surface-enhanced raman scattering using self-forming ZnO nanoarrays coated with gold as substrates. *Proc. SPIE* 10533, (105331F-1).

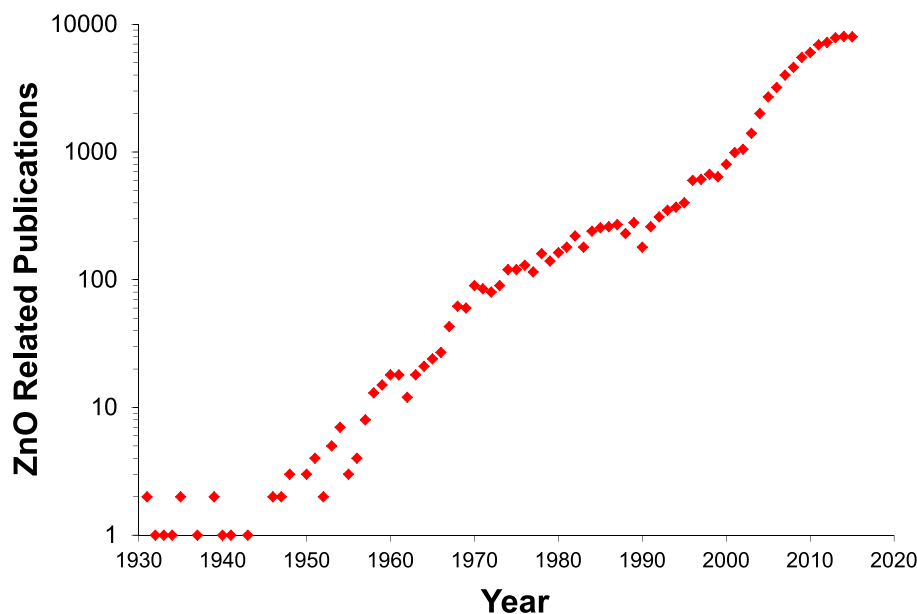


Fig. 18 The number of annual publications vs. year according to a search of the Scopus database for the term “zinc oxide” in the abstract, title or keywords.

Some promising emerging topics are memristors (Simanjuntak *et al.*, 2016), optical waveguides, nanoelectronics, electron scintillators, piezotronics, piezogenerators (Rogers *et al.*, 2012), thermoelectrics (ZnO has the highest thermoelectric figure of merit of all oxides: Ohtaki *et al.*, 2009), photoelectrochemical hydrogen generation (Harinipriya *et al.*, 2012), actuators, phononics, spintronics, infrared plasmonics (Khamh *et al.*, 2018), metamaterials etc. There is also a perspective of what may be termed extreme-condition-electronics based on ZnO's elevated high-field drift velocity (Albrecht *et al.*, 1999) and robustness for high temperature/field/radiation/frequency operation.

Also of note is that a recent Thomson-Reuters study, recorded more publications dedicated to nanostructured ZnO than to carbon nanotubes. This was attributed to the multifunctional nature of ZnO, the ease of fabricating nanostructures by various techniques (including wide-area, low cost chemical growth) and the extremely large family of nanostructure shapes that can be obtained.

Conclusions

The broad range of existing and emerging applications described above testifies to the combination of multifunctionality, market relevance and manufacturability offered by ZnO. If we can extend this to commercially viable bipolar devices in the future (homo-

or hetero-junctions) they may form the basis for brighter/low-threshold excitonic-based UV emitters and fully-integrated transparent/flexible all-oxide electronics offering novel functionality combinations such as biocompatibility, flexibility and transparency, combined with an intrinsic robustness to high temperature/power/field/radiation/frequency operation (Nozawa, 2007).

References

- Albrecht, J.D., Ruden, P.P., Limpijumrong, S., Lambrecht, W.R.L., Brennan, K.F., 1999. High field electron transport properties of bulk ZnO. *J. Appl. Phys.* 86, 6864–6867.
- Arafat, M.M., Dinan, B., Akbar, S.A., Haseeb, A.S.M.A., 2012. Gas sensors based on one dimensional nanostructured metal-oxides: A review. *Sensors* 12, 7207–7258.
- Avis, C., Jang, J., 2011. High-performance solution processed oxide TFT with aluminum oxide gate dielectric fabricated by a sol–gel method. *J. Mater. Chem.* 21, 10649–10652.
- Barquinha, P., Pereira, L., Goncalves, G., Martins, R., Fortunato, E., 2008. The effect of deposition conditions and annealing on the performance of high-mobility GIZO TFTs. *Electrochem. Solid-State Lett.* 11 (9), 248–252.
- Bayram, C., Teherani, F.H., Rogers, D.J., Razeghi, M., 2008. A hybrid green LED comprised of n-ZnO/InGaN/GaN MQW/p-GaN. *Appl. Phys. Lett.* 93, 081111.
- Boesen, G.F., Jacobs, J.E., 1968. ZnO field-effect transistor. *Proc. IEEE* 56 (11), 2094–2095.
- Constantinoiu, I., Viespe, C., 2020. ZnO metal oxide semiconductor in surface acoustic wave sensors: A review. *Sensors* 20, 5118.
- Denton, E.P., Rawson, H., Stanworth, J.E., 1954. Vanadate glasses. *Nature* 173, 1030–1032.
- Dhakal, T., Abhishek, S., Nandur, A.S., *et al.*, 2012. Transmittance from visible to mid infra-red in AZO films grown by atomic layer deposition system. *Solar Energy* 86, 1306–1312.
- Fan, J.C., Sreekanth, K.M., Xie, Z., Chang, S.L., Rao, K.V., 2013. p-Type ZnO materials: Theory, growth, properties and devices. *Prog. Mater. Sci.* 58, 874–985.
- Fang, V., Kennedy, J., Futter, J., Manning, J., 2013. A Review of Infrared Reflectance Properties of Metal Oxide Nanostructures, GNS Science Report 2013/39. Institute of Geological and Nuclear Sciences Limited.
- Fortunato, E., Correia, N., Barquinha, P., *et al.*, 2008. High-performance flexible hybrid field-effect transistors based on cellulose fiber paper. *IEEE Elec. Dev. Lett.* 29 (9), 988–990.
- Frenzel, H., Lajn, A., Brandt, M., *et al.*, 2008. ZnO metal-semiconductor field-effect transistors with Ag-Schottky gates. *Appl. Phys. Lett.* 92, 1921081–1921083.
- Gadallah, A.-S., Nomenyo, K., Couteau, C., Rogers, D.J., Léronel, G., 2013. Stimulated emission from ZnO thin films with high optical gain and low loss. *Appl. Phys. Lett.* 102, 171105.
- Gordon, R.G., 2000. Criteria for choosing transparent conductors. *MRS Bull.* 25, 52–57.
- Harinipriya, S., Usmani, B., Rogers, D.J., *et al.*, 2012. ZnO nanorod electrodes for hydrogen evolution & storage. *Proc. SPIE* 8263, (82631Y-1).
- Hosono, H., 1996. Working hypothesis to explore novel wide band gap electrically conducting amorphous oxides and examples. *J. Non-Cryst. Solids* 198–200, 165–169.
- Hosono, H., 2006. Ionic amorphous oxide semiconductors: Material design, carrier transport, and device application. *J. Non-Cryst. Solids* 352 (2006), 851–858.
- Ito, M., Kon, M., Miyazaki, C., *et al.*, 2007. Front drive display structure for color electronic paper using fully transparent amorphous oxide TFT array. *IEICE Transactions on Electronics* E90-C (11), 2105–2111.
- Kadota, M., 2005. Development of substrate structures and processes for practical applications of various surface acoustic wave devices. *Jpn. J. Appl. Phys.* 44 (6B), 4285–4291.
- Khamh, H., Sachet, E., Kelly, K., Jon-Paul Maria, J.-P., Stefan Franzen, S., 2018. As good as gold and better: Conducting metal oxide materials for mid-infrared plasmonic applications. *J. Mater. Chem. C* 6, 8326–8342.
- Kim, M.G., Kim, S.K., Ha, Y.G., *et al.*, 2010. High-performance solution-processed amorphous zinc – indium – tin oxide thin-film transistors. *J. Am. Chem. Soc.* 132 (30), 10352–10364.
- Kim, M.G., Kanatzidis, M.G., Facchetti, A., Marks, T.J., 2011. Low-temperature fabrication of high-performance metal oxide thin-film electronics via combustion processing. *Nat. Mater.* 10, 382–388.
- Klingshirn, C., 2007. ZnO: From basics towards applications. *Phys. Status Solidi (b)* 244 (9), 3027–3073.
- Kwon, J.Y., Jeong, J.K., 2015. Recent progress in high performance and reliable n-type transition metal oxide-based thin film transistors. *Semicond. Sci. Technol.* 30, 024002.
- Kwon, Y., Li, Y., Heo, Y., *et al.*, 2004. Enhancement-mode thin-film field-effect transistor using phosphorus-doped (Zn,Mg)O channel. *Appl. Phys. Lett.* 84, 2685–2687.
- Maeda, S., Sato, M., Niikura, I., Fukuda, T., 2005. Growth of 2 inch ZnO bulk single crystal by the hydrothermal method. *Semicond. Sci. Technol.* 20, 49–54.
- Martins, R., Fortunato, E., Barquinha, P., *et al.*, 2008. Write-erase and read paper memory transistor. *Appl. Phys. Lett.* 93, 2035011–2035013.
- Matsuoka, M., 1971. Nonohmic properties of zinc oxide ceramics. *Jpn. J. Appl. Phys.* 10 (6), 736–746.
- Minami, T., Kakumu, T., Takata, S., 1996. Preparation of transparent and conductive In₂O₃-ZnO films by radio-frequency magnetron sputtering. *J. Vac. Sci. Technol. A* 14, 1704.
- Nomura, K., Ohta, H., Takagi, A., *et al.*, 2004. Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors. *Nature* 432, 488–492.
- Nomura, K., Takagi, A., Kamiya, T., *et al.*, 2006. Amorphous oxide semiconductors for high-performance flexible thin-film transistors. *Jpn. J. Appl. Phys.* 45, 4303–4308.
- Nozawa, T., 2007. Transparent electronic products soon a reality. *Nikkei Electron. Asia* November, 1024–1030.
- Ohtaki, M., Araki, K., Yamamoto, K., 2009. High thermoelectric performance of dually doped ZnO ceramics. *J. Electron. Mater.* 38 (7), 1234–1238.
- Ohya, Y., Niwa, T., Ban, T., Takahashi, Y., 2001. Thin film transistor of ZnO fabricated by chemical solution deposition. *Jpn. J. Appl. Phys. Part 1* (40), 297–298.
- Orita, M., Ohta, H., Hirano, M., Narushima, S., Hosono, H., 2001. Amorphous transparent conductive oxide InGaO₃(ZnO)_m (m < 4): A Zn 4s conductor. *Phil. Mag. B* 81, 501–515.
- Pau, J., Piqueras, J., Rogers, D., *et al.*, 2010. On the interface properties of ZnO/Si electroluminescent diodes. *J. Appl. Phys.* 107, 033719.
- Pearson, S.J., Ren, F., Wang, Y.-L., *et al.*, 2010. Recent advances in wide bandgap semiconductor biological and gas sensors. *Prog. Mater. Sci.* 55, 1–59.
- Rahman, F., 2019. Zinc oxide light-emitting diodes: A review. *Opt. Eng.* 58 (1), 010901.
- Rogers, D.J., Teherani, F.H., Yasan, A., *et al.*, 2006. 375 nm electroluminescence from a ZnO/GaN:Mg/c-Al₂O₃ heterojunction light-emitting diode. *Appl. Phys. Lett.* 88, 141918.
- Rogers, D.J., Carroll, C., Bove, P., *et al.*, 2012. Energy harvesting from millimetric ZnO single wire piezo-generators. *Proc. SPIE* 8263, (82631X-1).
- Rogers, D.J., Sandana, V.E., Teherani, F.H., Razeghi, M., Drouhin, H.-J., 2009. Fabrication of nanostructured heterojunction LEDs using self-forming “Moth-Eye” arrays of n-ZnO nanocones grown on p-Si (111) by PLD 2009. *Proc. SPIE* 7217, (721708-1).
- Rogers, D.J., Bove, P., Sandana, E.V., Razeghi, M., Teherani, F.H., 2013. ZnO moves further into the UV. *Laser Focus World* 49 (10).
- Rombach, J., Papadogiannia, A., Mischob, M., *et al.*, 2016. The role of surface electron accumulation and bulk doping for gas-sensing explored with single-crystalline In₂O₃ thin films. *Sens. Actuators B* 236, 909–916.
- Sashabayashi, T., Ito, N., Nishimura, E., *et al.*, 2003. Comparative study on structure and internal stress in tin-doped indium oxide and indium-zinc oxide films deposited by r.f. magnetron sputtering. *Thin Solid Films* 445, 219–223.
- Simanjuntak, F.M., Panda, D., Wei, K.-H., Tseung-Yuen Tseng, T.Y., 2016. Status and prospects of ZnO-based resistive switching memory devices. *Nanoscale Res. Lett.* 11, 368.
- Stewart, K.A., Yeh, B.-S., Wager, J.F., 2016. Amorphous semiconductor mobility limits. *J. Non-Cryst. Solids* 432, 169–199.
- Tang, K., Shu-Lin Gu, S.-Lu., Ye, J.D., *et al.*, 2017. Recent progress of the native defects and p-type doping of zinc oxide. *Chin. Phys. B* 26, 047702.
- Triboulet, R., 2000. The scope of the ZnO growth. *Proc. SPIE* 4412, 1–8.

- Wager, J.F., 2016. Oxide TFTs: A progress report. In: *Information Display*, vol. 32, pp. 16–21.
- Wager, J.F., Yeh, B., Hoffman, R.L., Keszler, D.A., 2014. An amorphous oxide semiconductor thin-film transistor route to oxide electronics. *Curr. Opin. Solid State Mater. Sci.* 18, 53–61.
- Yang, J.-L., Ke-Wei Liu, K.-W., Shen, D.Z., 2017. Recent progress of ZnMgO ultraviolet photodetector. *Chin. Phys. B* 26 (4), 047308.
- Zhu, L., Zeng, W., 2017. Room-temperature gas sensing of ZnO-based gas sensor: A review. *Sens. Actuators A* 267, 242–261.

Varistor Electrical Properties: Microstructural Effects

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Varistors in Surge Protection

The occurrence of the transient events in the power, telecommunication, and data systems is unavoidable. The sources of such events are switching maneuvers as well as direct or indirect lightning strikes on the system infrastructure. Lightning and switching generated transient events (surges), typically lasting in the range of tens of μs to tens of ms may cause severe damage to the power system equipment, degrade wiring insulation, and destroy electronic devices.

Transient surge protectors, commonly known as Surge Arresters in the medium- (MV) and high-voltage (HV) systems, and Surge Protective Devices (SPDs) in the low-voltage (LV) systems, attempts to limit the overvoltage afflicting the electric device or power subsystem below a safe threshold, by diverting the surge current to the earthing system and largely absorbing its energy. A large portion of modern surge protective devices is based on Metal Oxide Varistors (MOVs), which exhibit highly nonlinear IV (current-voltage) characteristics conducting large currents in case of applied voltages higher than their breakdown voltage. In the contemporary surge protection industry, by MOVs, we are mainly referring to the Zinc Oxide (ZnO) varistors, as it is the case here as well.

Usually certain additional components (see Fig. 1), to the main voltage-limiting component (MOV), are necessary to guarantee their safe operation in the case of failures. In-series fuse operates and safely disconnect the MOV from the main power supply if the later one goes to the unexpected short-circuit failure. While the MOV diverts and absorbs the surge currents, an in-series thermal disconnect assembly prevents the undesirable and uncontrollable failure of the nonlinear element if the later one exhibits progressive temperature increase above the sustainable limit. The progressive temperature increase and so-called thermal runaway of the varistors usually occurs in the case of the temporary overvoltages (TOVs), and due to the aging (degradation) process of the varistors.

Temporary overvoltages are system voltages typically higher than the breakdown (nominal) voltage of the varistor, and lower than surge generated voltage spikes. Nominal or breakdown voltage of the modern varistors is usually a voltage forcing 1 mA ($\sim 10^{-5} \text{ A/cm}^2$) of current through the varistor. Temporary overvoltages can last significantly longer (in the range of seconds to hours) than lightning-induced surges.

Zinc Oxide Varistors

The groundwork of zinc oxide varistors was made in 1968 and later presented in Matsouka (1971), where the author describes zinc oxide ceramics in detail, production of it, temperature characteristics, nonlinear properties, etc. Shortly after, the zinc oxide varistors were commercialized and have become the most dominant surge protection element in the industry (Eda, 1989; Levinson, 1986; Gupta, 1990; He, 2019). Today, varistors are available in a very wide range of operating voltages, sizes, current conduction magnitudes, and energy handling capabilities. They are mainly used for protection of the electronic circuit, power, and data systems against destructive overvoltages induced by lightning strikes and switching operations, as already discussed in the previous section.

Conventional methods for the production of the ZnO based varistors are well-established with more than 40 years of industrial manufacturing. Zinc oxide varistor is a type of semiconductor ceramics produced mainly by Liquid Phase Sintering (LPS) (German et al., 2009; Arefin et al., 2009; Matsouka, 1971; Levinson, 1986; Clarke, 1999) of the ZnO powder and other metal oxide additives such as bismuth oxide (Bi_2O_3), antimony oxide (Sb_2O_3), cobalt oxide (CoO), chrome oxide (Cr_2O_3), aluminum oxide (Al_2O_3), and others, hence the name Metal Oxide Varistor (MOV). Such manufacturing methods are well defined in Matsouka (1971), May (1977), Begum (1996), and McArdle (1995). Each of the additives has its role, from the grain-growth retardants/enhancers to the nonlinearity inducers, in the forming of the varistor ceramics and its properties.

Post-sintering varistor ceramic results in a polycrystalline matrix of the doped ZnO grains surrounded by the inter-granular layer. Inter-granular layer mainly consists of the bismuth-rich phase partially, where there is no grain-to-grain boundary formed, coating the ZnO grains throughout the microstructure and forming an interconnected mesh. During the sintering process, the nonlinear IV characteristic is created on the grain-to-grain (GB) boundaries overall producing the nonlinear behavior of the

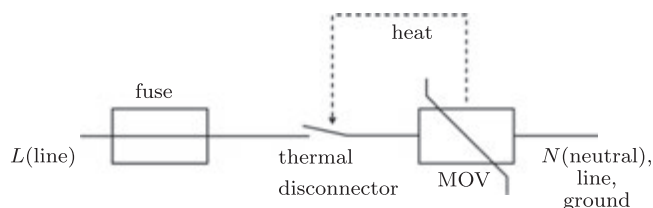


Fig. 1 Metal-Oxide Varistor (MOV) connected in series with additional components ensuring safe failure mode of surge protective devices.

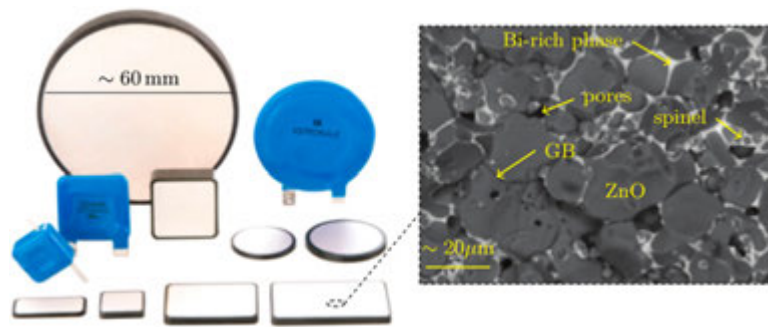


Fig. 2 Left: Different types of varistor disks used in the surge protection industry. Right: Typical varistor microstructure with the distinct regions. Grain boundary (GB) facilitates the nonlinear behavior of the varistor. ZnO grains act as a low ohmic resistance with specific resistances in the range of $0.1 - 1 \Omega \text{ cm}$. The intergranular layer acts as an insulating layer up to its melting temperature ($800\text{--}900^\circ\text{C}$) above which it melts and creates a highly conductive region. Typical grain sizes of modern varistors are in the range of $5 - 20 \mu\text{m}$. Reproduced from Matsouka, M., 1971. Non-ohmic properties of zinc oxide ceramics. Japanese Journal of Applied Physics. 10, 736–746.

varistor, i.e., voltage-dependent resistor. While the GB exhibits a nonlinear (nonohmic) behavior, the ZnO grains itself have ohmic properties with specific resistances ρ_g in the range of $0.1 - 1 \Omega \text{ cm}$ (Levinson, 1986).

Different types and shapes of the varistors are shown in Fig. 2. Varistor disks can be as well coated with epoxy resin to strengthen their surface dielectric performance. The typical polycrystalline microstructure of the varistors is also shown in Fig. 2, where distinct areas are distinguishable. Details on the varistor microstructure have been discussed extensively elsewhere (Daneu *et al.*, 2011; Matsouka, 1971; He, 2019). Typical average grain sizes of modern varistors are in the range of $5 - 20 \mu\text{m}$. Varistors with different (from nanometers to micrometers) average grain sizes are also produced (Li *et al.*, 2006; Tan *et al.*, 2009). The grain size mainly decides the varistor thickness for desired breakdown voltage and energy handling properties, thus also affecting the residual voltage and surge current rating.

The conductivity of the grains is controlled by different metal oxide additives (Meng *et al.*, 2017), and a very refined production process is required to obtain the optimal grain conductivity and GB characteristics relations. The intergranular layer, consisting mainly from the bismuth-rich phase, acts as an insulating layer up to its melting temperature ($800\text{--}900^\circ\text{C}$) above which it can melt and create a highly conductive region (Matsouka, 1971). The EDS (Energy-dispersive X-ray spectroscopy) of a typical MOV microstructure is shown in Fig. 3, where the chemical content of the microstructure phases (ZnO grain, Bi-rich and spinel phase) is given quantitatively.

In normal (constant leakage current) operation the temperature of the varistor mainly stays in the range of environment temperature. During surge absorbing transients or short duration TOVs a varistor will reach the temperatures up to $100\text{--}150^\circ\text{C}$ and safely cool down to environment temperature after the surge event. However, if the maximum absorbing energy of the varistor is exceeded, the temperatures inside the microstructure may reach melting temperature of Bi-rich phase progressively leading to the varistor failure.

The grain boundary (GB) facilitating the nonlinear behavior of the varistor is a physical junction of two ZnO grains. During the sintering process, the doping of the pure ZnO powder occurs simultaneously with the grain-growth process. This leads to the creation of the electrically active grain-to-grain junction with a diode-like behavior. The physical process governing the GB electrical characteristics have been discussed and researched extensively. However, up to this date, there is no single physical description covering all aspects of the GB characteristics (Eda, 1978, 1989; Clarke, 1999). Most accepted model is based on a double Schottky barrier (He, 2019), nonetheless failing to explain all electrical properties of the GB and all the macroscopic electrothermal performances of varistors.

As can be seen from Fig. 2, the microstructure of the varistor is highly nonuniform having both geometrical as well as electrical nonuniformities. Grains have different sizes, usually scattered in log-normal distribution, and different ohmic resistances while the grain boundaries have different breakdown voltages, different nonlinearities, and even remain purely ohmic. Nonetheless, macroscopically the varistor behaves like an electric device defined with its highly nonlinear IV characteristic.

Electrically the ZnO varistor is function-wise equivalent to the back-to-back Zener diode. The elementary model of the varistor, based on microstructure properties, can be described with the equivalent circuit shown in Fig. 4. The equivalent circuit consists of four components: (1) series resistance R_g depicting (substituting) the cumulative resistance of the varistor's grains, (2) parallel parasitic capacitance C_p depicting the cumulative GBs parasitic capacitance, (3) parallel parasitic resistance R_p depicting the cumulative GBs leakage resistance, and (4) series nonlinear voltage-dependent resistor $R(V)$, depicting the cumulative effect of the GBs. Further, the voltage-dependent resistor can be described (modeled) with the voltage-dependent current source having IV characteristic ($I(V) = I_n(V/V_n)^\alpha$) approximating the electrical behavior of GBs. Parameters V_n and I_n are varistor's breakdown voltage and current, respectively.

In practice, the V_n is evaluated at 1 mA (or $\sim 5 \times 10^{-5} \text{ A/cm}^2$) conduction current which is the typical breakdown (nominal or knee) current of the modern varistors. Parameter α defines a degree of the nonlinearity (amount of the current change in respect to the voltage change) of the varistor. In the first decades of the ZnO varistor development, the manufacturers were trying to achieve

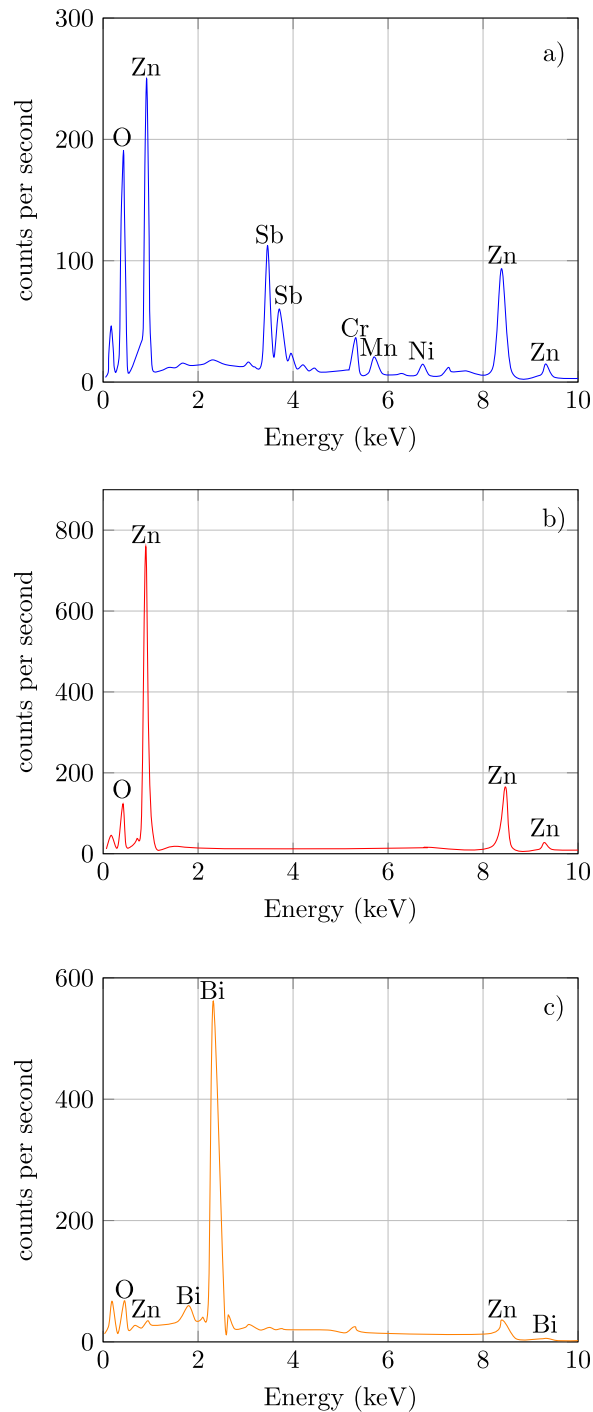


Fig. 3 Energy-dispersive X-ray spectroscopy (EDS) analysis of the microstructure chemical content of typical commercial varistor: (a) spinel (mainly $\text{Zn}_7\text{Sb}_2\text{O}_{12}$), (b) ZnO grain (mainly ZnO), and (c) Bi-rich phase (mainly Bi_2O_3). Adapted from Barrado, C., Leite, E., Bueno, P., Longo, E., Varela, J., 2004. Thermal conductivity features of ZnO-based varistors using the laser-pulse method. *Materials Science and Engineering: A*, 371, 377–381, doi:[10.1016/j.msea.2003.09.069](https://doi.org/10.1016/j.msea.2003.09.069).

high α values, approximating the ideal varistor, however, it was quickly realized that varistors with lower α values exhibit a more stable performance under TOV stress. For modern varistors, the value of α ranges from 30 to 50. Typical values of R_g , R_p , and C_p are in the range of 10 – 500 m Ω , 10 – 50 M Ω , and 1 – 100 nF, respectively. Evidently, the values of the beforementioned parameters would depend on the varistor micro- and macro-scale geometry.

In a continuous operating mode, a varistor is stressed with the voltage below its characteristic breakdown voltage, conducting currents in the range of μA . Such current is very often described, as the leakage current. When the applied voltage exceeds the

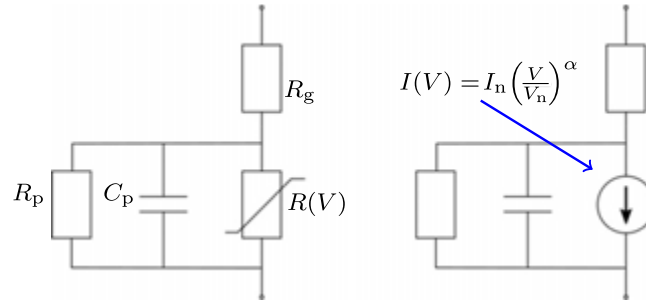


Fig. 4 A basic macroscopic model of the varistor describing both linear and nonlinear (voltage-dependent) microscopic properties. The voltage-dependent resistance can be described as voltage-dependent current source having empirical expression approximating the overall GBs IV characteristic.

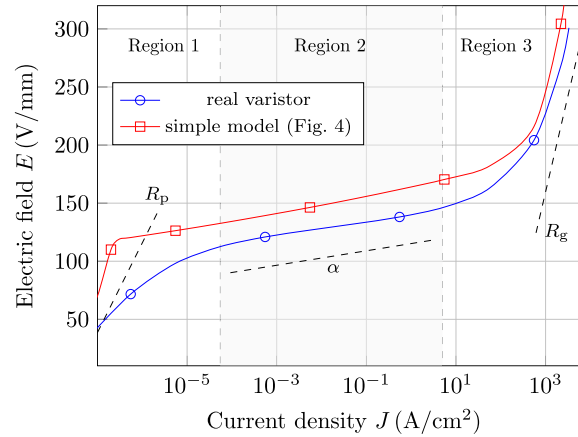


Fig. 5 JE characteristic of a typical ZnO varistor (blue-circle line). JE characteristic of a varistor's model shown in Fig. 4 (red-square line) – the characteristic is shifted in a vertical direction so as to clarify the representation.

breakdown voltage, what is the case during TOVs and surge events, the varistor becomes highly conductive capable of conducting large transient currents in the range of A to kA having very small voltage drop increase (high nonlinearity). When the voltage returns to the operating (system) level, the varistor returns to its high-resistance state again conducting leakage current.

In the case of very high overvoltages, the varistor is fully conductive and the GBs effect is minuscule, therefore the voltage drop across the varistor is mainly decided by the ohmic resistance of the varistor grains. Ohmic-capacitive leakage and ohmic grain resistances cause the linearization of the varistor characteristics at very low and very high currents. The intermediate region (above the breakdown voltage and below the high current region) is governed by the GBs, thus the nonlinear characteristics. Such behavior is represented by the varistor IV characteristic shown in Fig. 5 (red), which is also the characteristic of the varistor equivalent circuit from Fig. 4.

Conclusively, a varistor's IV characteristics can be divided into three distinct regions as follows: Region 1: pre-breakdown (leakage current) region controlled by R_p and C_p , Region 2: highly nonlinear breakdown region controlled by $I(V)$, and Region 3: up-turn region controlled mainly by R_g . However, the effect of all beforementioned processes, coupled with their scattered values, interpolates throughout the whole IV range obscuring the transition between dominant effects in the Regions 1, 2, and 3. This leads to the smoother IV characteristic of the actual varistor shown in Fig. 5 (blue). Nonlinearity degree parameter α can be calculated by the following expression

$$\alpha = \frac{\log(I_2) - \log(I_1)}{\log(V_2) - \log(V_1)}, \quad (1)$$

where (I_1, V_1) and (I_2, V_2) are set of current/voltage values (points) in the breakdown region (Matsouka, 1971; Eda, 1989; Levinson, 1986; Clarke, 1999; He, 2019). Most commonly the α is measured/evaluated by using a constant current source, where I_1 and I_2 values are set to 1 and 10 mA, respectively. For both currents the voltage drops V_1 and V_2 are read-out and by using Eq. (1) the α is calculated.

Due to the high nonlinearity and thus very large current change with respect to very small voltage change, the varistors' characteristics are often given in log-log or log-linear scale with the current on the x-axis. If the current change is given by some factor x , i.e. $I_2/I_1 = x$ then, the voltage change in the nonlinear region can be simply calculated as $V_2/V_1 = x^{1/\alpha}$.

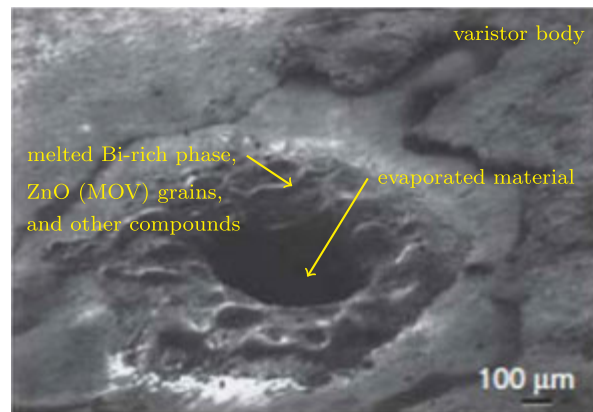


Fig. 6 Pinhole (puncture) failure of the varistor. This kind of failure results in the creation of the through-hole in the varistor body with highly conductive deposits on the hole walls. Pinhole is usually around 0.5–1 mm in diameter. Adapted from Vojta, A., Clarke, D., 1997. Microstructural origin of current localization and puncture failure in varistor ceramics. *Journal of Applied Physics*. 81, 985–993. doi:10.1063/1.364226.

Nonuniformity of Varistors Microstructure

Due to the grain microstructured nature of zinc oxide ceramics, distribution of additives and production process, the non-uniformity became an inherited property of any ZnO varistor (Modine, 2001). First to explore non-uniformity phenomena were Mizukoshi *et al.* (1983). Following their results (Eda, 1984) discussed puncture failure of ZnO varistors due to current localization caused by varistor non-uniformity. Structural non-uniformity of ZnO varistor was proven to be a key factor causing current localization inside varistor ceramics. Authors in Greuter and Blatter (1990) have experimentally shown current localization at microstructure by means of electroluminescence (Pike *et al.*, 1985). The fact that origins of “electrical” non-uniformity of ZnO varistor are not only caused by structural non-uniformity such as grains size distribution has been proven by Tao *et al.* (1987). The authors have experimentally shown that every single micro-junction in varistor ceramics presents its own electrical characteristic.

Therefore, electric current distribution inside the ZnO varistor is determined by structural non-uniformity, distribution of electrical properties of single micro-junctions and, as shown in Mizukoshi *et al.* (1983) and He and Hu (2007) as well as in this work, on the applied voltage across the varistor.

Current localization, as underlying phenomena of the pinhole failure, was further explored in Vojta and Clarke (1997), where the varistor microstructure was modeled as a uniform network of nonlinear resistors. The physical process of the pinhole failure would be discussed later, while here a quick introduction is given. Current localization leads to extensive heating in the localized current path melting it and eventually, due to the high temperatures, evaporating the material from it. After the varistor’s destruction and disconnection from the mains (in-series fuse or thermal disconnecter operates) a pinhole mode failure of the varistor manifests as an approximately 1 mm wide through-hole in the varistor body. The inner wall of the pinhole mainly consists of melted Bi-rich phase and ZnO (MOV) grains having very low ohmic resistance, thus effectively short-circuiting the varistor. The image of the cross-section of the pinhole failure mode is shown in Fig. 6.

To more explicitly represent the nonuniformity of the varistor polycrystalline structure authors in Bartkowiak *et al.* (1996) proposed a Voronoi network as a basis of composing the nonuniformly connected grid of nonlinear resistors, as shown in Fig. 7. Comparing the Voronoi network geometry and SEM (Scanning Electron Microscope) imaging of ZnO crystals as shown in Clarke (1999) and Chen *et al.* (2002), one can easily justify the use of such an approach. Authors in Bartkowiak *et al.* (1996) have used the Voronoi network as a basis for constructing a non-uniformly connected network of nonlinear resistors which, as also shown in Vojta and Clarke (1997), results in solving a set of current conservation equations by means of circuit analysis. By assigning different (distributed) threshold voltages and nonlinearity coefficients to the nonlinear resistors in the Voronoi generated network the authors in Bartkowiak *et al.* (1996) managed to combine both structural and “electrical” non-uniformity of varistor ceramics.

After this work, several contributions have been reported (Bartkowiak *et al.*, 2001; Chen *et al.*, 2002; He *et al.*, 2005; He and Hu, 2007; Long *et al.*, 2010) using numerical models with Voronoi network for analysis of ZnO varistor electrical characteristics. Current non-uniformity modeling inside ZnO varistor using Voronoi network presented by He and Hu (2007) showed current localization phenomena dependency on the applied voltage across the varistor. The results indicated that localization reaches its maximum at TOV (temporary overvoltage) region of voltage magnitudes.

Modeling of ZnO varistor with FEM (Finite Element Method) was previously reported by Lengauer *et al.* (2000). They performed FEM analysis to calculate mechanical stresses inside a ZnO disk where the disk ceramics was represented as a homogeneous solid cylinder. Authors in Frigura-Iliasa *et al.* (2010) presented an FEM model for calculation of heat losses in the varistor by assuming varistor ceramics as a homogeneous solid (as in Lengauer *et al.* (2000)). Authors in Bavelis *et al.* (2014) proposed a 3D FEM model for current distribution analysis inside a ZnO varistor by representing the grain-structured geometry with a 3D Voronoi network. A drawback of this work is that the FEM model was used only to calculate a conductance matrix of

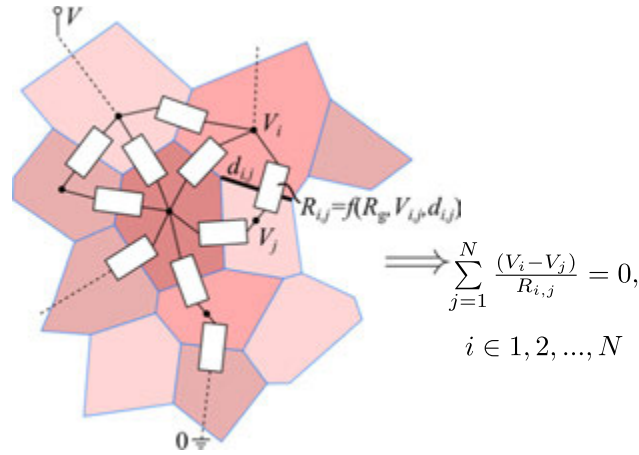


Fig. 7 Voronoi network approach in modeling of the varistors microstructure proposed by Bartkowiak *et al.* Simulation results in creating a nonuniformly connected grid of the (nonlinear) resistors of which the properties are calculated from the Voronoi network (edges lengths d_{ij}) and some empirical expressions depicting I/V characteristics behavior. N is the total number of resistors in the network and R_g ohmic grain resistance. Once the current through the network resistors R_{ij} are calculated, these values can be then represented by color code, back on Voronoi network grains, which is usually done in the literature. Reproduced from Bartkowiak, M., Mahan, G.D., Modine, F.A., *et al.*, 1996. Voronoi network model of ZnO varistors with different types of grainboundaries. *Journal of Applied Physics*. 80, 6516–6522.

ZnO grains, which was later used in a 3D nonlinear resistor network. Therefore, the presented model still results in a circuit analysis without solving for the electric field in the modeled geometry.

Energy absorption (handling) capability (EAC) of the varistors (MOVs) (Matsouka, 1971; Clarke, 1999; Eda, 1989; He, 2019) is a pivotal parameter influencing their performances as well as failure characteristics. In the early 1980s, it was realized that the EAC of the varistor fundamentally depends on its microstructure (non-) uniformity as well as stress conditions (Mizukoshi *et al.*, 1983; Kan *et al.*, 1983). In Mizukoshi *et al.* (1983) and Kan *et al.* (1983), authors have experimentally obtained the relations between varistor's uniformity, TOVs, and EACs, elucidating their quantitative cross-dependence.

To advance the understanding of the EACs, Eda (1984) has proposed a varistor model capable of solving and predicting electrothermal behavior of the varistors under specified stresses and microstructure nonuniformities. The presented model was based on the depiction of a varistor as a composite of multiple homogeneous cylinders electrically described with the same current density-electric field (JE) characteristics having different breakdown voltages. Irrespectively of the model geometrical simplicity, the obtained results had agreed well with the experimental data demonstrating severe current localization and Joule heating in the varistor body consequently leading to the pinhole (puncture) failure of the varistor under TOV conditions.

Additional work in this direction was done by Bartkowiak *et al.* (1999) presenting a model of the varistor which includes simulations of the mechanical stresses due to the rapid and nonuniform heating. This approach covered two modes of varistor failures, namely, cracking and puncture.

Cracking of the varistor is, alongside the puncture failure, a second most common mode of the varistor failure. It typically occurs when a varistor is subjected to extremely short pulses (in the range of 10 microseconds) having much larger current densities and voltage magnitudes than those conducted in the case of pinhole failure. Such stressing of the varistor causes a rapid highly nonuniform heat-related expansion of the material (mechanical shock wave) eventually resulting in the cracking of the varistor body. Fig. 8 shows the cracking mode failure, where distinct regions are observable; crack is parallel with the stressing electrical field (current conduction) and propagates through the whole varistor body. Inner walls of the crack show a violent fracture of the material without melted phase, close to the fracture a recrystallization process can also occur (He, 2019).

Fig. 9 illustrates the typical modes of the MOVs failures, as looked from above (in the voltage-applied direction). It also indicates the stressing conditions which are causing the specific failure modes. However, while a large percentage of the observed failure modes, as a function of the stressing condition, will follow the observed characteristic shown in Fig. 9, the non-disregardable uncertainty still remains on which failure will eventually occur. It is worth mentioning that a cracking failure usually does not result in the short-circuiting of the MOV, nonetheless a combination of pinhole and cracking failure may as well occur.

Previous reports (Mizukoshi *et al.*, 1983; Kan *et al.*, 1983; Eda, 1984; Ringler *et al.*, 1997; Bartkowiak *et al.*, 1999, 2001; He and Hu, 2007) have unambiguously demonstrated a voltage stress-dependent EACs of the varistors where we can observe a $\sim 50\%$ drop in EAC at TOV conditions versus the EAC levels at surge region. This deduction is also manifested in varistors' time-to-failure characteristics, exhibiting an exponential decrease for overvoltages in the range of 1.1–1.6 times the nominal voltage (Kan *et al.*, 1983; Khanmiri *et al.*, 2017). Recent large-scale experimental findings reported by Tuzek and Hinrichsen (2014) have endorsed and uphold previous experimental and simulation data.

Fig. 10 shows the varistors energy absorption capability as a function of the current densities, where a substantial increase in the EAC value at higher densities is visible. It is worth mentioning that different current waveforms are used when measuring EACs at TOV and surge regions. For TOV current magnitudes an AC source is used, where for surge current magnitudes the surge generators are used (IEC, 2011).

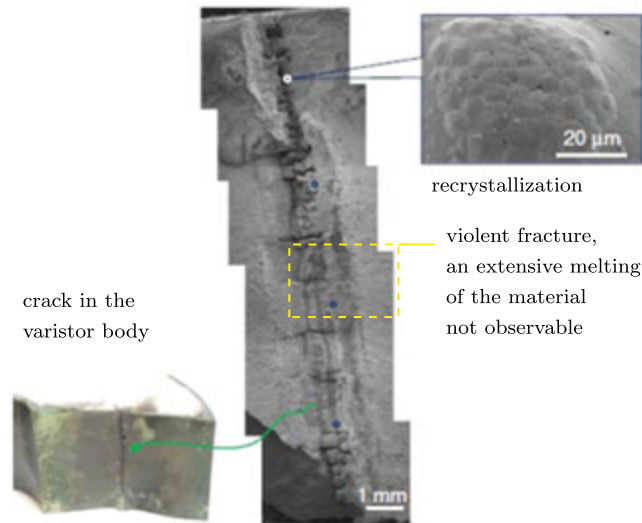


Fig. 8 Imaging of the crack cross-section within the varistor body. While here the crack resembles the pinhole failure (see Fig. 6), the width (length) of it extends throughout a much larger portion of the varistor body. Adapted from He, J., 2019. Metal Oxide Varistors: From Microstructure to Macro-Characteristics. Wiley-VCH Verlag GmbH and Co. KGaA. doi:10.1002/9783527684038.

Indubitably, as previously noted, such an undesired drop in a varistor's EACs at TOV region arises from the severe current localization in the microstructure, where the effective current-carrying (i.e. energy-absorbing) volume decreases dramatically. Quantitative evaluation of the effective volume decrease is still mainly vague; Vojta (Vojta and Clarke, 1997; Vojta *et al.*, 1996), based on simulation, sets the lowest effective volume (at highest localization) to $\sim 10\%$ and the recent IEEE C62.55–2017 (IEEE, 2017) guideline set this level to $\sim 2\%$. Due to the large scale presence of varistors in the surge protection industry, and the importance of the contemporary protection of modern power systems, the varistors nonuniformity and current localization phenomena are still the subjects of up-to-date research (Huang *et al.*, 2019; He *et al.*, 2018; Jianying *et al.*, 2018; He, 2019; Meng *et al.*, 2019; Topcagic *et al.*, 2019).

Modeling of the Varistor Microstructure

Recent research reported in Topcagic *et al.* (2018, 2019) has advanced modeling of the electrothermal phenomena within the varistor microstructure by the combination of a Voronoi network and a Finite Element Method (FEM). By employing FEM analysis authors have modeled varistor polycrystalline microstructure in 2D as well in 3D space. It is worth mentioning that, when modeling electrothermal characteristics of the MOVs former published research (Vojta and Clarke, 1997; Bartkowiak *et al.*, 1996; Bartkowiak *et al.*, 2001; Chen *et al.*, 2002; He *et al.*, 2005; He and Hu, 2007) have mainly used a 2D Voronoi network, which can be only justified by comparing it to the polished surface of the MOV (see Fig. 2). A real MOV microstructure excludes symmetries in any direction, thus a 3D Voronoi network should be used as shown in Bavelis *et al.* (2014). Nonetheless, a 3D Voronoi network fails to represent the actual sphericities of the MOV microstructure, thus the more truthful approach is to use the grain-growth model (Quey, 2019).

The unpolished SEM imaging of the typical commercial MOV surface is shown in Fig. 11. Comparing the grain structure shown in Figs 11 and 7 with those shown in Fig. 2, the difference is clearly observable justifying the usage of the grain-growth model instead of the 2D Voronoi network.

By modeling a fraction of the varistor microstructure the electrothermal behavior of the microstructure can be explored. The voltage-dependent current localization inside the modeled microstructure, for different overvoltage stresses, is shown in Fig. 12. From Fig. 12, we can also observe the modeled 3D microstructure by grain-growth algorithm presented in Quey (2019). At values of applied overvoltage stress corresponding to the leakage region, the current distribution is slightly non-uniform. When the applied overvoltage reaches a TOV range the maximum localization occurs generating the dominant percolation path. At overvoltages going from TOV to surge range, the current distributes across the whole microstructure leading to the nearly uniform distribution. The current distribution as shown in Fig. 12(c) suggests that the creation of the main percolation path, which would eventually lead to the pinhole failure, occurs on a single-grain width.

Quantitative evaluation of the current localization, indicating microstructure behavior (performances), can be described by the participation factor formerly proposed in Vojta and Clarke (1997) and described in Topcagic *et al.* (2018, 2019). The participation ratio represents the amount of microstructure volume carrying the majority of the current at a given voltage/current load. It was observed that the participation ratio is highly stress-dependent and for the microstructure as shown in Fig. 12, the participation ratio is shown in Fig. 13, indicating the occurrence of maximum localization at overvoltages ratio equal to $\sim 1.1(E/E_n \approx 1.1)$. At

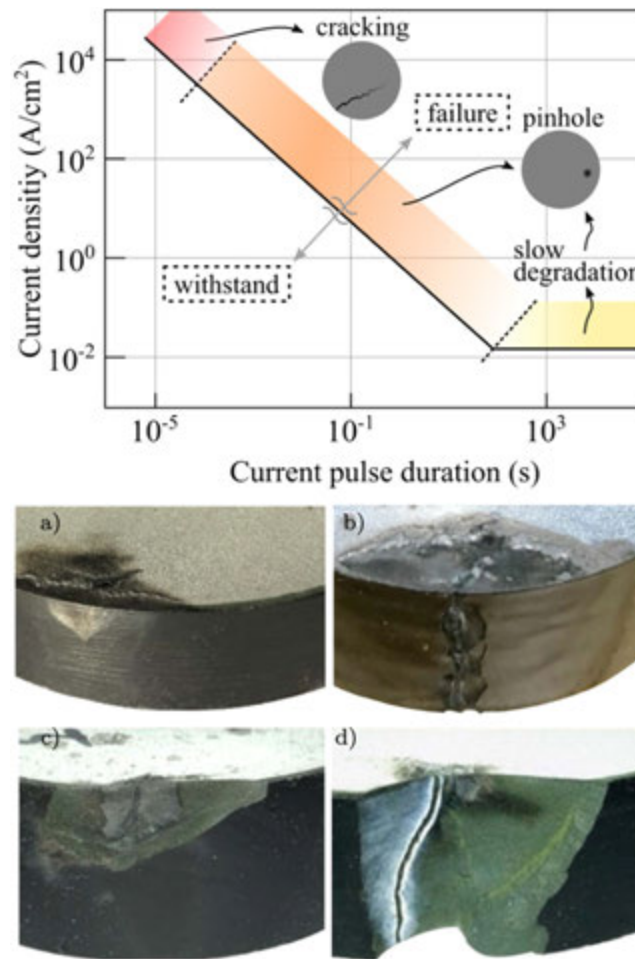


Fig. 9 Above: Illustration of the destruction modes of the varistors, looking from above onto the electrode surface with destruction modes as a function of the stressing conditions according to Eda and He. Below: Images of several typical failure modes: (a) cracking at the edge, (b) pinhole (puncturing) through the side, (c) fracturing at the inner region, and (d) fracturing and puncturing under impulse currents. Adapted from Eda, K., 1984. Destruction mechanism of ZnO varistors due to high currents. *Journal of Applied Physics*. 56, 2948–2955. He, J., 2019. Metal Oxide Varistors: From Microstructure to Macro-Characteristics. Wiley-VCH Verlag GmbH and Co. KGaA. doi:10.1002/9783527684038. Meng, P., Zhao, X., Yang, X., *et al.*, 2019. Breakdown phenomenon of ZnO varistors caused by non-uniform distribution of internal pores. *Journal of the European Ceramic Society*. 39, 4824–4830, doi:10.1016/j.jeurceramsoc.2019.06.043.

overvoltages less than 0.75, corresponding to the modeled varistor's leakage region, the participation factor is $> 80\%$ indicating slight non-uniformity, and at overvoltage ratio of 1.05 – 1.2 the participation factor drops down to only 4%. With overvoltage increase, the participation factor tends to saturation (more than 80%). The obtained results are in good agreement with previous reports (Vojta and Clarke, 1997; Topcagic *et al.*, 2018), however predicting more severe conditions, as those deduced experimentally (IEEE, 2017).

By means of the 3D model, the dynamic electrothermal behavior of the varistors microstructure can be evaluated by calculating EACs, under specified current stress. The calculation of EAC, as shown in Topcagic *et al.* (2019), has been performed by applying different overvoltage ratios (1.1–2.0) to the modeled geometry and evaluating absorbed energy up to the time at which thermal runaway starts. The results are shown in Fig. 13 indicating lowest EAC values ($\sim 500 \text{ J/cm}^3$) at TOV range and highest values ($\sim 2300 \text{ J/cm}^3$) at surge region. Clearly, such dependency of the EAC is due to the current localization within the MOV microstructure and effective volume decrease elucidated by the participation factor p . The obtained numerical results are in good agreement with experimental data previously reported in Ringer *et al.* (1997) and Khanmiri *et al.* (2017) (see Fig. 10).

As previously noted, the nonuniform current distribution raises purely from the microstructure nonuniformity without considering other factors such as difference in GBs breakdown voltages, low- α or ohmic GBs (Bartkowiak *et al.*, 2001), and the presence of pores. However, latest research (Meng *et al.*, 2019) has indicated a more important role of pores in the current conduction. Authors in Meng *et al.* (2019) have analyzed the internal structure of ZnO varistors with X-ray micro-CT technology and showed that the porosity and pore volume at the radial edge of the varistor disk is considerably higher than at other varistor areas. This observation and measurements for selected varistor specimen is shown in Fig. 14.

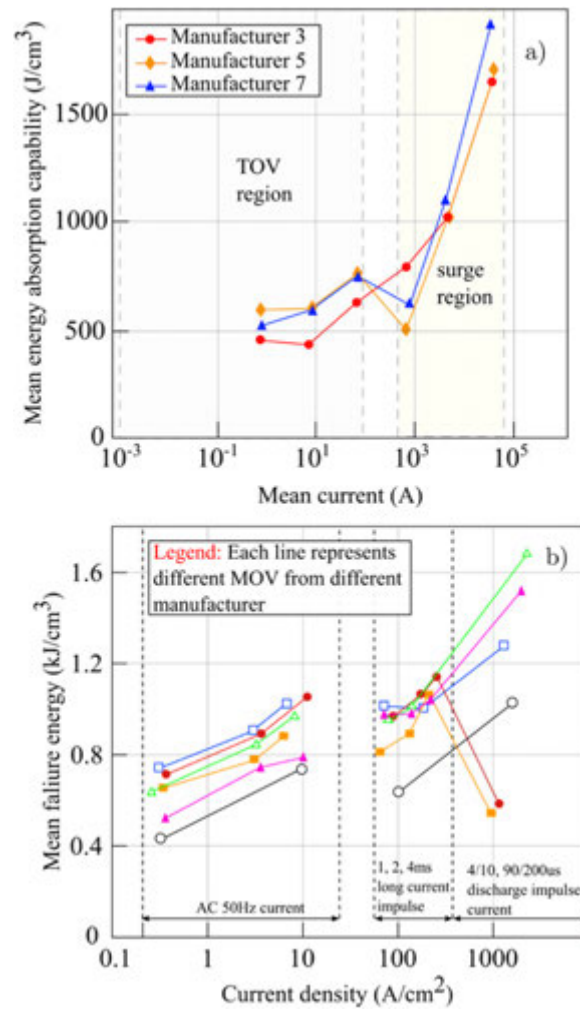


Fig. 10 Energy absorption capability as a function of the current density: (a) Experimental results reported in Ringler *et al.*, and (b) Large-scale experimental results reported in Tuczek and Hinrichsen. Reproduced from Ringler, K.G., Kirkby, P., Erven, C.C., Lat, M.V., Malkiewicz, T.A., 1997. The energy absorption capability and time-to-failure of varistors used in station-class metal-oxide surge arresters. IEEE Transactions on Power Delivery. 12, 203–212, doi:10.1109/61.568242. Tuczek, M.N., Hinrichsen, V., 2014. Recent experimental findings on the single and multi-impulse energy handling capability of metal-oxide varistors for use in high-voltage surge arresters. IEEE Transactions on Power Delivery. 29, 2197–2205, doi:10.1109/TPWRD.2013.2283911.

The influence of pores on current distribution and energy handling capability of MOVs may be of significant importance since, as experimentally shown in Meng *et al.* (2019) as well empirically deduced and recognized previously (Andoh *et al.*, 2000), the breakdown phenomenon usually occurs near the outer edge of the varistors. Authors in Meng *et al.* (2019) have used 2D Voronoi network simulations in order to study the influence of pore defect on the characteristics of the microstructure. Simulations have indicated increased voltage gradient along the simulated microstructure as the proportion of pores increased. In contrast with the increased pores proportion, the leakage current slightly decreased. Details and additional discussions are provided in Meng *et al.* (2019), while herein, we can emphasize the importance of microstructure modeling by means of electrical circuits based on nonuniform structures (Voronoi network, grain-growth (Quey, 2019; Topcagic *et al.*, 2019)), enabling important insight in the electrical behavior of the varistors microstructures.

Alongside pores it was shown by Huang *et al.* (2019) that peripheral areas (edges) of the varistor disks tend to have, even in the case of same grain sizes compared to the inner areas of the MOV disk, different GB properties, overall contributing to the slightly different IV characteristic as indicated in Fig. 15. Such difference, where we can observe down-shifted JE characteristics of the outer section of MOV disk having lower breakdown field, will cause current localization in that area producing nonuniform heat dissipation and eventually leading to the varistor failure.

Voronoi network simulations have also been proven as an effective tool in modeling of the nonlinear composite dielectrics based on ZnO micro-varistors. Nonlinear dielectrics are used (useful) for the electric stress mitigation and electric field grading in electrical insulation applications such as corona protection in rotating machines, high voltage cable joints, and cable terminations (Christen *et al.*, 2010; Donzel *et al.*, 2011; Rivenc and Lebey, 1999; Weida *et al.*, 2011; Qi *et al.*, 2004). Fig. 16 shows an illustration

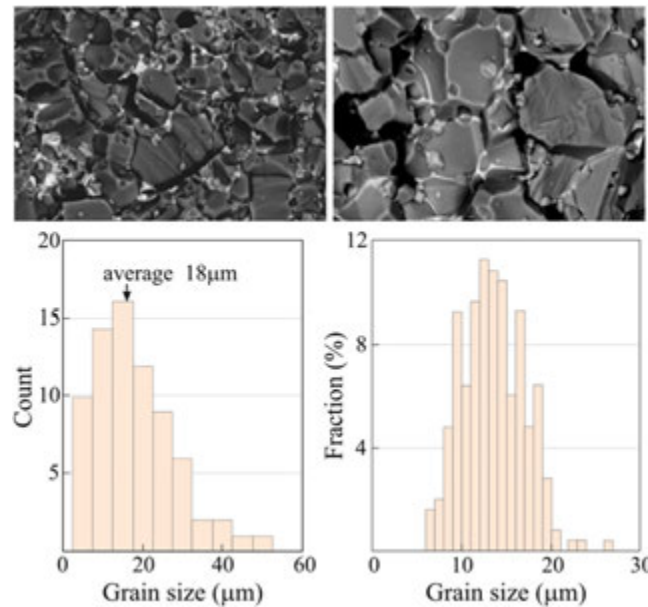


Fig. 11 Scanning Electron Microscopy (SEM) imaging the unpolished MOV surface. Grain size distributions of typical commercial varistors. Adapted from He, Y., Wei, B., Fu, Z., Dai, M., Liu, J., 2018. Mov failure modes and microstructural characteristics under operating duty tests with multiwaveform multipulse currents. *IEEE Transactions on Power Delivery*. 33, 2274–2283, doi:10.1109/TPWRD.2018.2790431. Eda, K., 1984. Destruction mechanism of ZnO varistors due to high currents. *Journal of Applied Physics*. 56, 2948–2955. Izoulet, A., Guillemet-Fritsch, S., Estournes, C., Morel, J., 2014. Microstructure control to reduce leakage current of medium and high voltage ceramic varistors based on doped ZnO. *Journal of the European Ceramic Society*. 34, 3707–3714.

of the ZnO micro-varistor based nonlinear dielectric, where a percentage of the micro-varistors is of crucial significance in optimizing and developing such materials. In that light authors in Yang *et al.* (2016a,b) discuss the percolation process and the properties of the composite dielectric by means of Voronoi network simulations. It is worth mentioning the extended possibilities of such simulations by means of 3D approach presented here and in details in Topcagic *et al.* (2019). FEM model, alongside 3D capability and proposed GB model, easily enables the electrothermal coupling, which could be used in order to investigate heat initiated degradation of composite nonlinear dielectrics.

Failure Mechanisms of the Varistors

It is well-established fact that the varistors failures, namely, pinhole and cracking can be attributed to the varistor structural and electrical nonuniformity. Pinhole failure usually occurs at TOV conditions while cracking occurs at surge currents. The mechanisms of the pinhole failure have been explored by means of simulations by Bartkowiak *et al.* (1999), Meng *et al.* (2019), He *et al.* (2005), and Topcagic *et al.* (2018, 2019) as well as others. In general, the pinhole occurs due to the extensive Joule heating at the localized current paths. This can be observed in Fig. 17, where for a given TOV load (see Fig. 18) the current conduction and localization within microstructure produce severe heat accumulation and temperature rise in the main percolation path. Such condition progressively leads to the creation of hot-spot (HT), (see Fig. 18) with temperatures above 400–500°C causing permanent varistor degradation with increased current (up to time t_f). Continuing current conduction, above the time t_f , leads to further hot-spot temperature increase eventually exceeding the melting temperature ($\sim 830^\circ\text{C}$) of intergranular Bi-rich phase. During the melting process of the Bi-rich phase, the highly conductive layer, surrounding the individual ZnO grains, is created, effectively bypassing the GBs. This is manifested in the drastic current increase clearly elucidated in the Fig. 18, which ultimately leads to the complete melting of the percolation path, i.e., MOV's pinhole failure. Evidence of this process is reported in He *et al.* (2018), where authors had observed a larger amount of the Bi-rich phase, with respect to the un-stressed MOV, in the areas of the MOV body close to the pinhole.

Experimental evidence of the Joule heating in the varistor microstructure during TOV load is shown in Fig. 19, where localization paths and extensive nonuniform Joule heating is visible. Such a load would eventually lead to the pinhole failure of the varistor. It is worth mentioning that except for the total melting of Bi-rich layer, the pinhole failure at lower conduction currents values may be initiated by the degradation of the GBs themselves, which gradually degrade by decreasing their breakdown voltages. This mechanism of degradation is contributed by migration of charge carriers within the GB depletion layer (He, 2019).

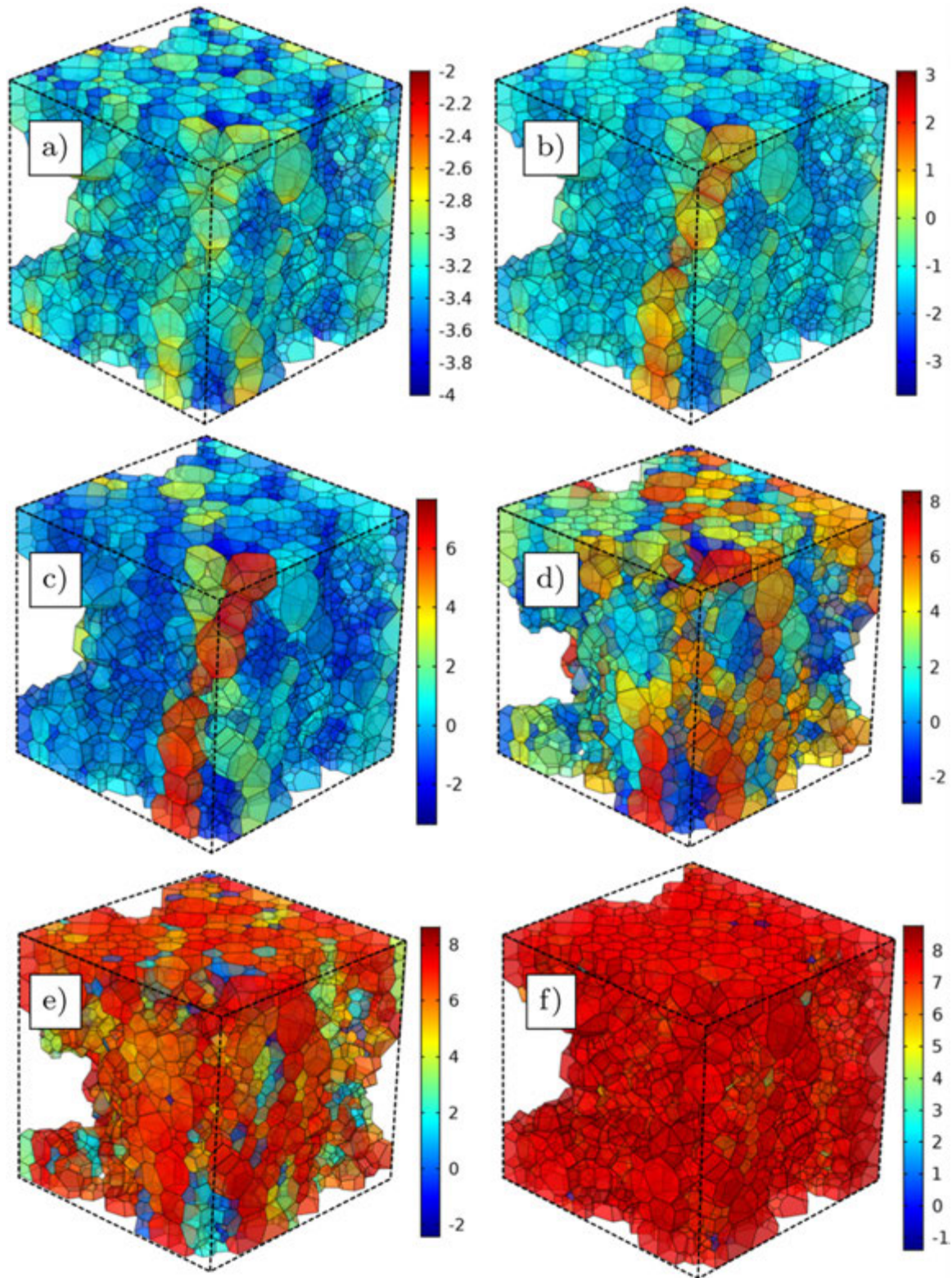


Fig. 12 Distribution of the current density $\log_{10}(|\vec{J}|)$ (in logarithmic scale) at different overvoltage ratios, which corresponds to applied electric field E divided by nominal electric field yielding $\sim 5 \times 10^{-5}$ A/cm² conduction, E/E_n as follows: (a) 0.28, (b) 1.09, (c) 1.18, (d) 1.50, (e) 1.90, and (f) 2.50, where the knee (breakdown) electrical field of the 3D model was approximately 117.0 V/mm. The creation of percolation (preferable) current paths as well as current distribution with respect to overvoltage ratio is clearly visible. Some sections of microstructure are hidden so as to show the current distribution inside the model.

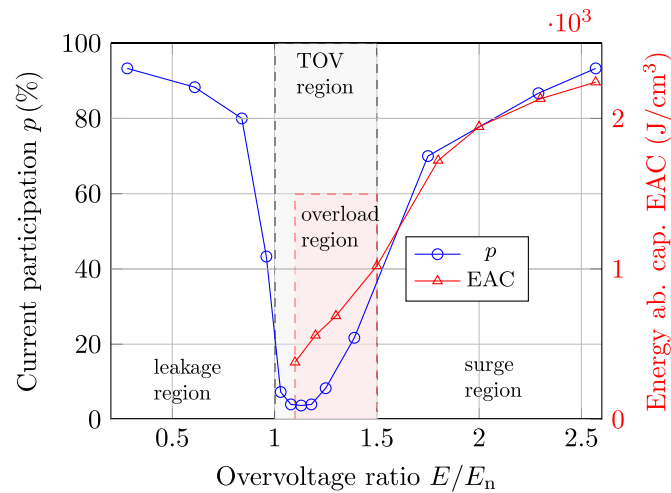


Fig. 13 Voltage-dependent grain participation factor p in respect to the applied overvoltage E/E_n . The participation ratio reaches the lowest value of $\sim 3.7\%$ at the overvoltage level equal to ~ 1.1 . Simulated voltage-dependent energy absorption capability EAC with respect to the applied overvoltage. The lowest EAC values at TOV range are in the range of $300 - 400 \text{ J/cm}^3$.

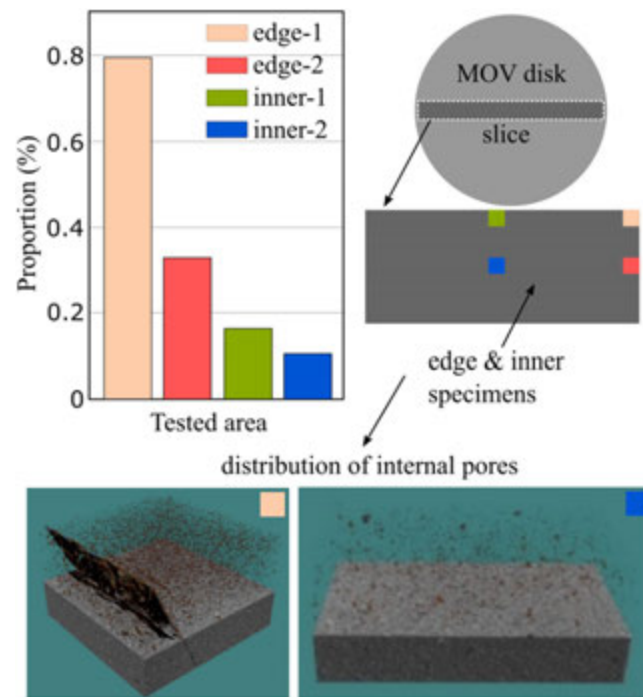


Fig. 14 The proportion of pores per specimen and 3D structure and distribution of internal pores within the region of edge-1 and inner-2. Adapted from Meng, P., Zhao, X., Yang, X. *et al.*, 2019. Breakdown phenomenon of ZnO varistors caused by non-uniform distribution of internal pores. *Journal of the European Ceramic Society*. 39, 4824–4830, doi:10.1016/j.jeurceramsoc.2019.06.043.

As possible underlying mechanism of cracking phenomena, which can also be produced by rapid heating leading to the nonuniform mechanical stress inside the microstructure as discussed by Bartkowiak *et al.* (1999) and others, however, the cracking phenomenon cannot be directly related to the current localization as it is the case in the pinhole failure mode. The reason for this is the fact that cracking failure mostly occurs during surges, which generate large overvoltages (> 2.0) on the varistors and according to the participation factor (see Fig. 13) a majority of varistor volume should participate in surge current conduction, thus excluding severe current localization.

To answer some aspects of this type of failure, authors in Meng *et al.* (2019) provide the discussion on the effect of the pores as the initiator of the cracking failure. Authors state that “the pores are insulating under low electric fields and the current through the pores is almost zero. Hence, the voltage gradient at the edge region is higher than that elsewhere.” The effects of the pores on the

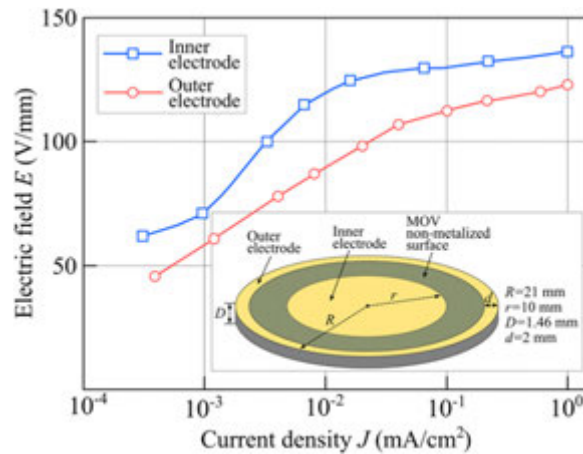


Fig. 15 *JE* characteristics of the varistor sample at room temperature for different varistor disk sections. Adapted from Huang, Y., Wu, K., Tang, Z., *et al.*, 2019. Investigation of electrical inhomogeneity in ZnO varistor ceramics based on electronic relaxations. *Ceramics International*. 45, 1110–1114, doi:10.1016/j.ceramint.2018.09.293.

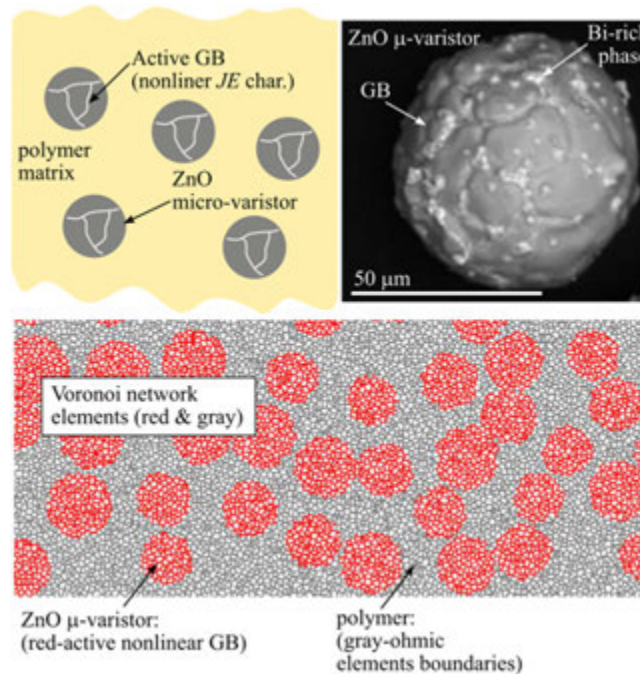


Fig. 16 Above: Illustration of composite dielectrics based on ZnO micro-varistor and an example of the micro-varistor specimen. Below: Representation of the simulation approach of such materials based on the Voronoi network. Adapted from Donzel, L., Greuter, F., Christen, T., 2011. Nonlinear resistive electric field grading part 2: Materials and applications. *IEEE Electrical Insulation Magazine*. 27, 18–29. doi:10.1109/MEI.2011.5739419. Yang, X., Hu, J., Chen, S., He, J., 2016a. Understanding the percolation characteristics of nonlinear composite dielectrics. *Scientific Reports*. 6, 30597.

varistor failures are also discussed in Danzer and Supancic (2018). It could be hypothesized that further increase of the voltage produces ionizing electrical fields on the pores initiating localized arcing. Produced arcing leads to extensive heating and mechanical pressure in the microstructure eventual leading to the cracking failure.

Surface flashovers, as the third most common varistor failure, are contributed by the edge effects on the varistor surface. The majority of the varistors have metalized electrodes, which are either sprayed on the disk surface (arc or plasma spraying) or screen printed (silver paste silk screen followed by thermal treatment). This process leads to the nonuniform edges of the electrodes, which under high overvoltages can produce highly concentrated air-ionizing electrical fields leading to the arcing on the varistors electrode edges. This phenomena is discussed, for example, in Andoh *et al.* (2000) and shown in Fig. 20.

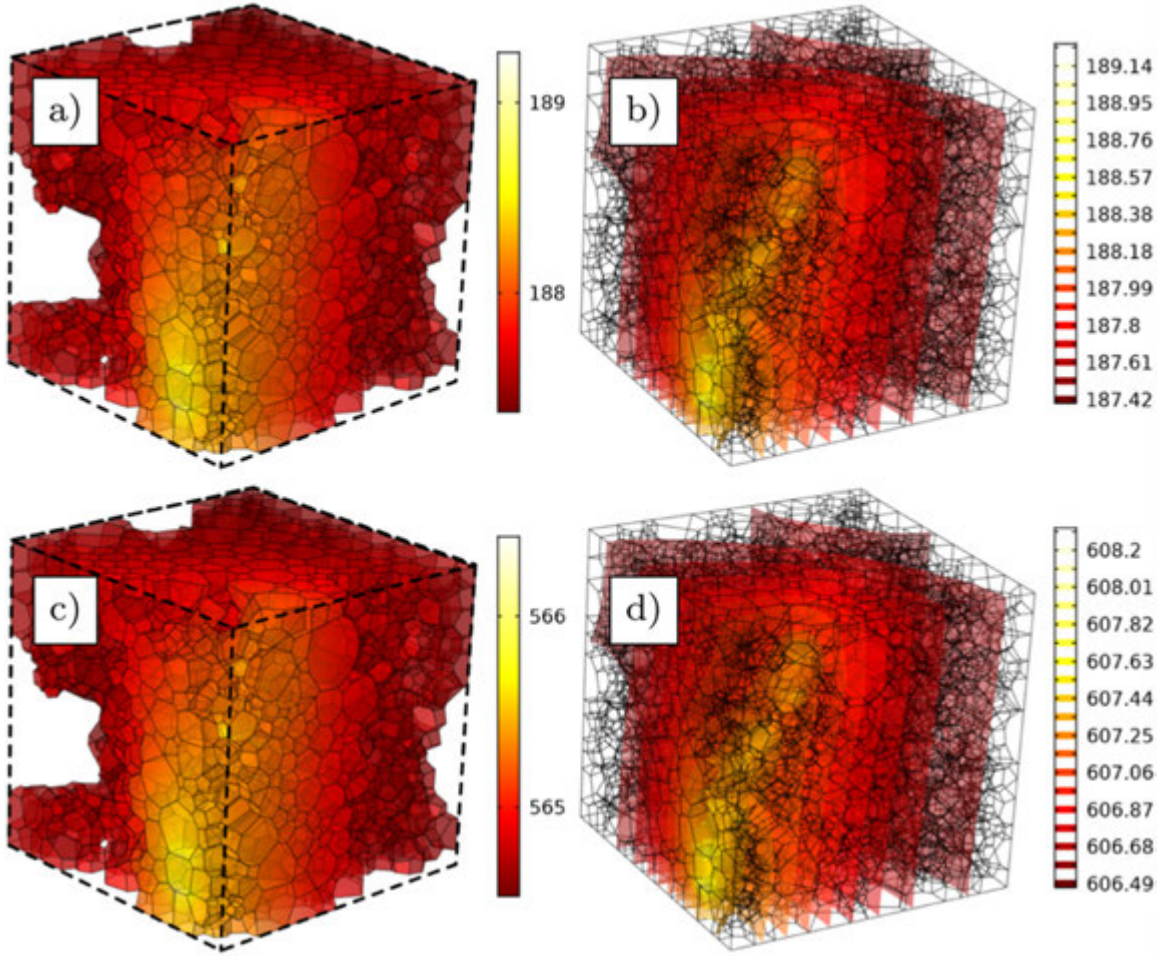


Fig. 17 Distribution of the temperature at different times under ~ 1.1 DC overload (overvoltage ratio). Creation of a pinhole failure. Figures (a) and (c) are showing temperature distribution at times t_s and t_f , respectively. Figures (b) and (d) are showing isotherm contours on times t_s and t_f , respectively. The creation of a pinhole is visible in both figures, where the isothermals clearly indicate the pinhole path. Sections of microstructure are hidden so as to show the temperature distribution within it.

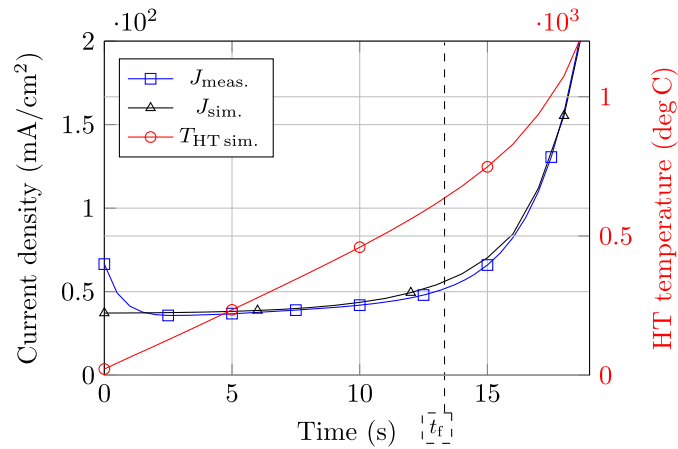


Fig. 18 Measured and simulated current conduction of the varistor under ~ 1.15 DC overload (overvoltage ratio). Simulated temperature rise of the hot spot.

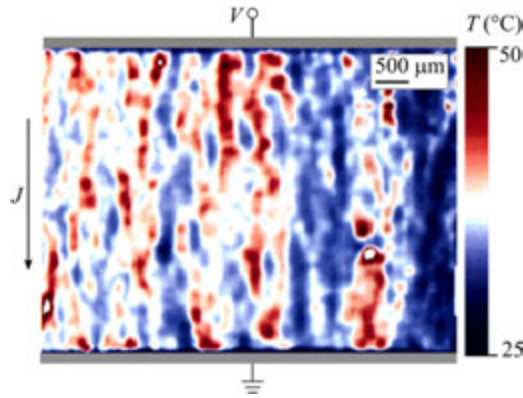


Fig. 19 Distribution of the temperature within microstructure under temporary overvoltages (TOVs). Adapted from Wang, H., Bartkowiak, M., Modine, F.A. *et al.*, 1998. Nonuniform heating in zinc oxide varistors studied by infrared imaging and computer simulation. *Journal of the American Ceramic Society*. 81. 2013–2022. doi:10.1111/j.1151-2916.1998.tb02582.x.

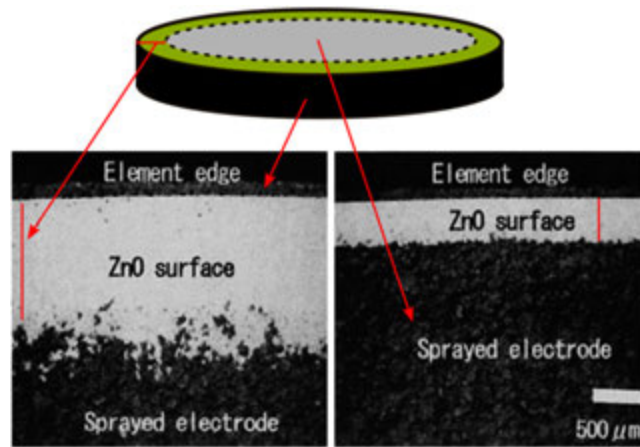


Fig. 20 SEM images of ZnO varistor disk edge with thermal sprayed aluminum electrode. Adapted from Andoh, H., Itoh, Y., Imai, T., *et al.*, 2000. Improvement of energy withstand capability in ZnO elements for surge arrester. *The Transactions of the Institute of Electrical Engineers of Japan*. A 120, 924–929.

Practical Guidelines

The decrease of the EACs of the varistors, due to the stress-dependent current localization, quantified by the participation factor (see Fig. 13), is observable during the varistor energy rating measurements. Typically, varistor's energy rating is measured by stressing it with surge currents, commonly with 8/20 or 10/350 wave according to IEC (2011), which is produced by two types of surge generators, namely, crowbar- and discharge-type generator (Schon, 2013). It can be observed that for the same peak (crest) current, the discharge-type generators impose higher stresses, i.e., varistors could not withstand the same current rating deduced (measured) on crowbar-type generators; experimentally determined impulse current ratings may differ up to 40% depending on generator type and design. The reason for this is very simple; during the wave tail of the surge current, generated by discharge-type generators, the MOV is exposed to overvoltage conditions (similar to TOV region) for long times (in several milliseconds range) determined by the over-damping impulse current circuit, whereas for crowbar-type generators the current wave-tail is interrupted typically within 2 ms. This exposure causes, according to the participation factor, additional highly-localized Joule heating on already preheated MOV, eventually leading to the puncture failure. Assuming the adiabatic heating in TOV region, the hot-spot temperature, thus the time-of-failure (see Fig. 18), can be roughly predicted applying the following expression,

$$\Delta T = \int \frac{I(V, t)V(t)}{c_p m_v \rho(V(t)/V_n)} dt, \quad (2)$$

where m_v and c_p are varistor volume and heat capacity.

The pinhole failure behavior of the MOVs under TOVs discussed in the sections above is well-recognized in the field of surge protection. The thermal runaway characteristics of the MOVs are greatly considered when dimensioning surge protection applications, where the prevention of uncontrolled MOV failure is done by the in-series thermal disconnecter and fuse. Under TOV stress the current flow through varistor vary with time in the following manner; initially, the current exhibits an exponential drop followed by quasi-stable conduction for a time duration which, depending on the magnitude of the overload stress, is followed by a rapid increase in current up to the failure of the varistor. Such behavior resembles a U-shaped current-time curve shown in Fig. 18.

Remarkably, the mathematical representation of a varistor used in the circuit analysis (LT Spice, ATP-EMPT (Dommel, 1986)) tools is still based on a static IV characteristics, thus failing to accurately predict the dynamic behavior of the varistor under TOVs. We should not confuse this with the high-frequency models of the surge arresters presented in IEEE Working Group 3.4.11 (1992), Pinceti and Giannetoni (1999) and Magro *et al.* (2004) commonly used in time-domain transients analysis.

By examining the varistor behavior under TOV conditions, authors in Topcagic *et al.* (2019) provide the dynamic model of the varistors characteristics $IV \rightarrow IVt$, based on empirical expression given as,

$$I(V, t) = \frac{1}{2} I_0(V) \left(k + \left(\frac{q_c}{q_c + q(t)} \right)^{p_q} + \left(\frac{e(t)}{e_c} \right)^{p_e} \right), \quad (3)$$

where I_0 is an initial current deduced from static IV characteristic (as, for example, well-known $I = I_n(V/V_n)^z$ or others) (Topcagic *et al.*, 2018; Khanmiri *et al.*, 2017; Chen *et al.*, 2002; Zitnik *et al.*, 2005; Abdel-Salam *et al.*, 2004), k a fitting parameter in the range of (0.8–1.2) adjusting the ratio of initial and quasi-steady-state current (see Fig. 18), q_c characteristic charge density (4), $q = \frac{1}{m_v} \int I(t) dt$ absorbed charge density, e_c characteristic energy density (4), $e = \frac{1}{m_v} \int I(t)V(t) dt$ absorbed energy density, p_q and p_e fitting powers in the range of (5–6), and m_v an MOV volume. As it is clear from the description, the parameters of the Eq. (3) must be obtained experimentally for every MOV (ceramics) type. Details of the model are discussed in Topcagic *et al.* (2019).

$$\begin{aligned} q_c &= \frac{1}{m_v} \int_0^{t_s} I(t) dt, \quad t_s = t \Big|_{\frac{dI}{dt} \approx 0}, \\ e_c &= \frac{1}{m_v} \int_0^{t_f} V(t) I(t) dt, \quad t_f = t \Big|_{I > 0 \text{ \& } I \approx I_0}. \end{aligned} \quad (4)$$

The aforementioned varistor current (initial drop and thermal runaway) response to the TOV stress, could be as well described as the initial (static) varistor's IV characteristic shift to the right, current ascending, and left, current descending direction (see Fig. 5). This deduction could be used for extending the traditional model (Epcos, 2019; Topcagic *et al.*, 2018) of the static IV characteristic into the time domain, as shown in Eq. (5),

$$\begin{aligned} \log_{10}(V) &= b_1 + b_2 \log_{10}(I/\sigma) + b_3 \exp(-\log_{10}(I/\sigma)) \\ &\quad + b_4 \exp(\log_{10}(I/\sigma)), \\ \sigma &= 1 - \frac{k}{2} + \frac{k}{2} \left(\frac{q_c}{q_c + q(t)} \right)^{p_q} + \left(\frac{e(t)}{e_c} \right)^{p_e}, \end{aligned} \quad (5)$$

where σ is a shifting operator and b_1 – b_4 fitting parameters for initial(static) varistor characteristics. Implementation of the discussed model is presented in detail in Topcagic (2019).

Conclusion

Even though ZnO varistors have been invented in the late 60s and extensively investigated the last four decades, the research on this topic is still noticeably dynamic and active. This work has very briefly covered certain aspects of varistor technology and their microstructural effects on the macroscopic electrical properties. Emphasis has been given to academic and industrial research results associated with recent advancements on varistors performance, failure modes, electromagnetic modeling and surge protection applications allowing for a deeper understanding of their dynamic electrothermal behavior. The presented research results form the basis for accomplishing future challenges:

1. Identification of real-time monitoring techniques of varistors electrical properties in order to be integrated into the next generation of smart surge protective devices in the era of modern power systems.
2. Development of enhanced energy absorption capability varistors so as to withstand long duration electromagnetic pulses with energy content higher than that of lightning strikes covering the cases of solar storms, nuclear electromagnetic pulses and power crossover of neighboring power systems.
3. Development of micro- to nano-varistor materials for smoothing the electric field at cable junctions and limiting the sheath voltages at high power applications.

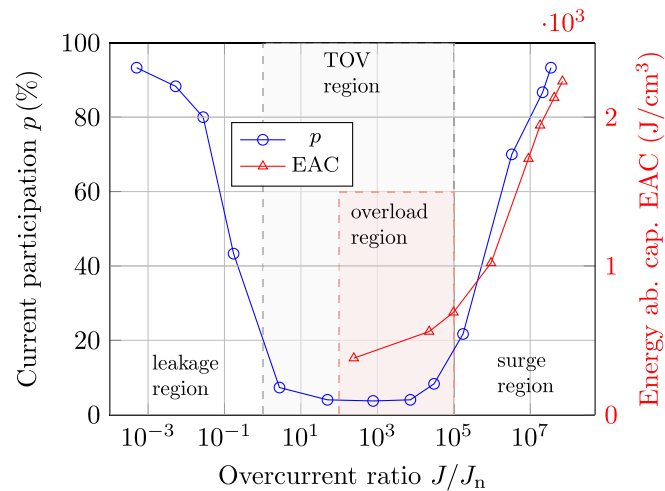


Fig. 21 Current-dependent participation factor $p(V)$ in respect to the current overload J/J_n , where J_n is a MOV's nominal (breakdown) current density corresponding to the MOV 1 mA nominal current I_n . Simulated current-dependent energy absorption capability EAC.

Appendix

The results of the participation factor p and EACs could be as well rearranged to provide the current-dependent participation factor and EACs, which may be preferential in certain calculations. This is shown in Fig. 21, where we can observe that an EACs, for complete TOV range, can be considered as constant. The difference between Figs. 13 and 21 is a consequence of the fact that a small voltage changes produce extensive current changes, thus the difference in plots' x-axis "width." The calculated EAC results, shown in Fig. 21, even more clearly indicate a good relation with the measurements (Ringler *et al.*, 1997).

References

- Abdel-Salam, M., Ahmed, N.A., Elhamd, I.S., 2004. Varistor as a surge protection device for electronic equipments. In: Proceedings of the IEEE International Conference on Industrial Technology (IEEE ICIT '04), vol. 2, pp. 688–694. doi:10.1109/ICIT.2004.1490158.
- Andoh, H., Itoh, Y., Imai, T., *et al.*, 2000. Improvement of energy withstand capability in ZnO elements for surge arrester. The Transactions of the Institute of Electrical Engineers of Japan A 120, 924–929.
- Arefin, M.L., Raether, F., Dolejš, D., Klimera, A., 2009. Phase formation during liquid phase sintering of ZnO ceramics. Ceramics International 35, 3313–3320. doi:10.1016/j.ceramint.2009.05.030.
- Bartkowiak, M., Comber, M.G., Mahan, G.D., 1999. Failure modes and energy absorption capability of ZnO varistors. IEEE Transactions on Power Delivery 14, 152–161.
- Bartkowiak, M., Comber, M.G., Mahan, G.D., 2001. Influence of nonuniformity of ZnO varistors on their energy absorption capability. IEEE Power Engineering Review 21, 69. doi:10.1109/MPER.2001.4311480.
- Bartkowiak, M., Mahan, G.D., Modine, F.A., *et al.*, 1996. Voronoi network model of ZnO varistors with different types of grain boundaries. Journal of Applied Physics 80, 6516–6522.
- Bavelis, K., Gjonaj, E., Weiland, T., 2014. Modeling of electrical transport in zinc oxide varistors. Advances in Radio Science 12, 29–34.
- Begum, S., 1996. Powder Processing Parameters and Their Influence on the Electrical Performance of ZnO Varistor. PhD Thesis. Dublin City University.
- Chen, Q., He, J., Tan, K., *et al.*, 2002. Influence of grain size on distribution of temperature and thermal stress in ZnO varistor ceramics. Science in China Series E: Technological Sciences 45, 337–347. doi:10.1360/02ye9040.
- Christen, T., Donzel, L., Greuter, F., 2010. Nonlinear resistive electric field grading part 1: Theory and simulation. IEEE Electrical Insulation Magazine 26, 47–59. doi:10.1109/MEI.2010.5599979.
- Clarke, D.R., 1999. Varistor ceramics. Journal of the American Ceramic Society 82, 485–502.
- Daneu, N., Bernik, S., Rečnik, A., 2011. Inversion boundary induced grain growth in ZnO ceramics: from atomic-scale investigations to microstructural engineering. Journal of Physics: Conference Series 326, 012003. doi:10.1088/1742-6596/326/1/012003.
- Danzer, R., Supancic, P., 2018. Failure of varistor ceramics. In: Proceedings of CIEC 16 – Torino, pp. 23–30.
- Dommel, H.W., 1986. Electro-Magnetic Transients Program (EMTP) Theory Book. Bonneville Power Administration.
- Donzel, L., Greuter, F., Christen, T., 2011. Nonlinear resistive electric field grading part 2: Materials and applications. IEEE Electrical Insulation Magazine 27, 18–29. doi:10.1109/MEI.2011.5739419.
- Eda, K., 1978. Conduction mechanism of non-ohmic zinc oxide ceramics. Journal of Applied Physics 49, 2965–2972.
- Eda, K., 1984. Destruction mechanism of ZnO varistors due to high currents. Journal of Applied Physics 56, 2948–2955.
- Eda, K., 1989. Zinc oxide varistor. IEEE Electrical Insulation Magazine 5, 28–41.
- Friguira-Iliasa, F., Vatau, D., Mihet-Popa, L., Barbulescu, C., 2010. Heat dissipation improvement for ZnO based varistors. In: Proceedings of the ICHQP.
- German, R.M., Suri, P., Park, S.J., 2009. Review: Liquid phase sintering. Journal of Materials Science 44, 1–39. doi:10.1007/s10853-008-3008-0.
- Greuter, F., Blatter, G., 1990. Electrical properties of grain boundaries in polycrystalline compound semiconductors. Semiconductor Science and Technology 5, 111–137. doi:10.1088/0268-1242/5/2/001.
- Gupta, T.K., 1990. Application of zinc oxide varistors. Journal of the American Ceramic Society 73, 1817–1840. doi:10.1111/j.1151-2916.1990.tb05232.x.
- He, J., 2019. Metal Oxide Varistors: From Microstructure to Macro-Characteristics. 2019. Wiley-VCH Verlag GmbH and Co. KGaA. doi:10.1002/9783527684038.

- He, J., Chen, S., Zeng, R., *et al.*, 2005. Electrical parameter statistic analysis and parallel coordination of ZnO varistors in low-voltage protection devices. *IEEE Transactions on Power Delivery* 20, 131–137.
- He, J., Hu, J., 2007. Discussions on nonuniformity of energy absorption capabilities of ZnO varistors. *IEEE Transactions on Power Delivery* 22, 1523–1532.
- He, Y., Wei, B., Fu, Z., Dai, M., Liu, J., 2018. Mov failure modes and microstructural characteristics under operating duty tests with multiwaveform multipulse currents. *IEEE Transactions on Power Delivery* 33, 2274–2283. doi:10.1109/TPWRD.2018.2790431.
- Huang, Y., Wu, K., Tang, Z., *et al.*, 2019. Investigation of electrical inhomogeneity in ZnO varistor ceramics based on electronic relaxations. *Ceramics International* 45, 1110–1114. doi:10.1016/j.ceramint.2018.09.293.
- IEC, 2011. IEC 61643–11:2011, Low-voltage surge protective devices, surge protective devices connected to low-voltage power systems-requirements and test methods, edition 1.0.
- IEEE, 2017. IEEE C62.55–2017 – IEEE Guide for Surge Protection of DC Power Feeds to Remote Radio Heads.
- IEEE Working Group 3.4.11, 1992. Modeling of metal oxide surge arresters. *IEEE Transactions on Power Delivery* 7, 302–309. doi:10.1109/61.108922.
- Jiaying, L., Kangning, W., Yuwei, H., 2018. Breakdown characteristics of varistor ceramics. *IntechOpen*. 59–78. doi:10.5772/intechopen.79720.
- Kan, M., Nishiwaki, S., Sato, T., Kojima, S., Yanabu, S., 1983. Surge discharge capability and thermal stability of a metal oxide surge arrester. *IEEE Transactions on Power Apparatus and Systems*. 282–288. (PAS-102).
- Khanmiri, D.T., Ball, R., Lehman, B., 2017. Degradation effects on energy absorption capability and time to failure of low voltage metal oxide varistors. *IEEE Transactions on Power Delivery* 32, 2272–2280. doi:10.1109/TPWRD.2016.2629442.
- Lengauer, M., Rubesa, D., Danzer, R., 2000. Finite element modelling of the electrical impulse induced fracture of a high voltage varistor. *Journal of the European Ceramic Society* 20, 1017–1021.
- Levinson, L.M., 1986. Zinc oxide varistors – A review. *American Ceramic Society Bulletin* 65, 639–646.
- Li, Y., Li, G., Yin, Q., 2006. Preparation of ZnO varistors by solution nano-coating technique. *Materials Science and Engineering: B* 130, 264–268. doi:10.1016/j.mseb.2006.03.010.
- Long, W., Hu, J., He, J., Liu, J., 2010. Time-domain response simulation of ZnO varistors by voronoi network with an actual grain boundary model. *Journal of the American Ceramic Society* 93, 1547–1550.
- Magro, M.C., Giannettoni, M., Pinceti, P., 2004. Validation of ZnO surge arresters model for overvoltage studies. *IEEE Transactions on Power Delivery* 19, 1692–1695. doi:10.1109/TPWRD.2004.832354.
- Matsouka, M., 1971. Non-ohmic properties of zinc oxide ceramics. *Japanese Journal of Applied Physics* 10, 736–746.
- May, J.E., 1977. Method of manufacturing a metal oxide varistor. U.S. Patent US4165351A.
- McArdle, D.M., 1995. The Effects of Powder Processing Parameters on the Microstructure and Energy Absorption Characteristics of Low Voltage ZnO Varistors. PhD Thesis. Dublin City University.
- Meng, P., Hu, J., He, J., 2017. Low-residual-voltage ZnO varistor ceramics improved by multiple doping with gallium and indium. *Materials Letters* 195, 209–212. doi:10.1016/j.matlet.2017.02.097.
- Meng, P., Zhao, X., Yang, X., *et al.*, 2019. Breakdown phenomenon of ZnO varistors caused by non-uniform distribution of internal pores. *Journal of the European Ceramic Society* 39, 4824–4830. doi:10.1016/j.jeurceramsoc.2019.06.043.
- Mizukoshi, A., Ozawa, J., Shirakawa, S., Nakano, K., 1983. Influence of uniformity on energy absorption capabilities of zinc oxide elements as applied in arresters. *IEEE Transactions on Power Apparatus and Systems* 102, 1384–1390.
- Modine, F., 2001. Varistor electrical properties: Microstructural effects. In: Buschow, K.J., Cahn, R.W., Flemings, M.C., Ilksner, B., Kramer, E.J., Mahajan, S., Veyssière, P. (Eds.), *Encyclopedia of Materials: Science and Technology*. Oxford: Elsevier, pp. 9508–9512. doi:10.1016/B0-08-043152-6/01720-4.
- Pike, G.E., Kurtz, S.R., Gourley, P.L., Philipp, H.R., Levinson, L.M., 1985. Electroluminescence in ZnO varistors: Evidence for hole contributions to the breakdown mechanism. *Journal of Applied Physics* 57, 5512–5518.
- Pinceti, P., Giannettoni, M., 1999. A simplified model for zinc oxide surge arresters. *IEEE Transactions on Power Delivery* 14, 393–398. doi:10.1109/61.754079.
- Qi, X., Zheng, Z., Boggs, S., 2004. Engineering with nonlinear dielectrics. *IEEE Electrical Insulation Magazine* 20, 27–34. doi:10.1109/MEI.2004.1367508.
- Quey, R., 2019. Neper: Polycrystal generation and meshing. Available at: <http://www.neper.info/>.
- Ringler, K.G., Kirkby, P., Erven, C.C., Lat, M.V., Malkiewicz, T.A., 1997. The energy absorption capability and time-to-failure of varistors used in station-class metal-oxide surge arresters. *IEEE Transactions on Power Delivery* 12, 203–212. doi:10.1109/61.568242.
- Rivenc, J.P., Lebey, T., 1999. An overview of electrical properties for stress grading optimization. *IEEE Transactions on Dielectrics and Electrical Insulation* 6, 309–318. doi:10.1109/94.775616.
- Schon, K., 2013. *High Impulse Voltage and Current Measurement Techniques*. New York: Springer.
- Tan, D.Q., Younsi, K., Zhou, Y., Irwin, P., Cao, Y., 2009. Nano-enabled metal oxide varistors. *IEEE Transactions on Dielectrics and Electrical Insulation* 16, 934–939. doi:10.1109/TDEI.2009.5211836.
- Tao, M., Ai, B., Dorlante, O., Loubiere, A., 1987. Different single grain junctions within a ZnO varistor. *Journal of Applied Physics* 61, 1562–1567.
- TDK Electronics (EPCOS) varistor model. Available at: <https://www.tdk-electronics.tdk.com/en/180486/design-support/design-tools/varistors/model-libraries-for-monolithic-and-multilayer-varistors>. (accessed 01.05.19).
- Topcagic, Z., 2019. Numerical Model of Current Distribution in Varistors Microstructure for Optimization of Surge Protective Devices. PhD Thesis. Ljubljana: University of Ljubljana, (Faculty of Electrical Engineering).
- Topcagic, Z., Mlakar, M., Tsovilis, T.E., 2019. Electrothermal and overload performance of metal-oxide varistors. *IEEE Transactions on Power Delivery*. 1. doi:10.1109/TPWRD.2019.2935411.
- Topcagic, Z., Tsovilis, T., Krizaj, D., 2018. Modeling of current distribution in zinc oxide varistors using voronoi network and finite element method. *Electric Power Systems Research* 164, 253–262. doi:10.1016/j.epsr.2018.08.001.
- Tuczek, M.N., Hinrichsen, V., 2014. Recent experimental findings on the single and multi-impulse energy handling capability of metal-oxide varistors for use in high-voltage surge arresters. *IEEE Transactions on Power Delivery* 29, 2197–2205. doi:10.1109/TPWRD.2013.2283911.
- Vojta, A., Clarke, D., 1997. Microstructural origin of current localization and puncture failure in varistor ceramics. *Journal of Applied Physics* 81, 985–993. doi:10.1063/1.364226.
- Vojta, A., Wen, Q., Clarke, D.R., 1996. Influence of microstructural disorder on the current transport behavior of varistor ceramics. *Computational Materials Science* 6, 51–62. doi:10.1016/0927-0256(96)00011-0.
- Weida, D., Richter, C., Clemens, M., 2011. Design of ZnO microvaristor material stress-cone for cable accessories. *IEEE Transactions on Dielectrics and Electrical Insulation* 18, 1262–1267. doi:10.1109/TDEI.2011.5976125.
- Yang, X., Hu, J., Chen, S., He, J., 2016a. Understanding the percolation characteristics of nonlinear composite dielectrics. *Scientific Reports* 6, 30597.
- Yang, X., Hu, J., He, J., 2016b. Adjusting nonlinear characteristics of ZnO-silicone rubber composites by controlling filler's shape and size. In: 2016 IEEE International Conference on Dielectrics (ICD), pp. 313–317. doi:10.1109/ICD.2016.7547607.
- Zitnik, B., Babuder, M., Muhr, M., Zitnik, M., Thottappillil, R., 2005. Numerical modelling of metal oxide varistors, In: *Proceedings of the XIVth International Symposium on High Voltage Engineering*, p. x.

Latest Trend of ZnO Multilayer Ceramic Varistors

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Introduction

ZnO varistors are used as devices to protect electronic equipment from various overvoltages such as electrostatic discharge (ESD), surges, and lightning (Matsuoka, 1971), (Koga and Sawada, 2009). In recent years, because advanced ICs with miniaturization are easily destroyed by ESD, ZnO multilayer ceramic varistors (MLCVs) are usually employed as protection devices (Koga *et al.*, 2011). The desirable characteristics are high protection performance and high stability so as not to be destroyed by overvoltage such as ESD (Koga *et al.*, 2011). In addition, today there is a need for low-capacitance MLCVs that can be used in high-frequency circuits, such as antennas for wireless communications and high-speed signal interfaces (e.g., HDMI) (Koga *et al.*, 2011). However, it is difficult in conventional MLCVs to achieve both low-capacitance and protection performance (Koga *et al.*, 2012).

In this chapter, the discovery and the mechanism of ZnO varistors are firstly mentioned, and recent issues in practical application are then showed for conventional ZnO varistors with Bi- and Pr additives. To resolve the issues, not only the new varistor material composition but also its MLCVS with a discharge cavity between internal electrodes have been developed in recent years. In addition, as shown in our recent studies, MLCVs with high nonlinearity and ESD stability can be cofired with internal electrodes of base metal. The cutting edge research on ZnO varistors is reported here.

Discovery of ZnO Varistors, and Issues of Conventional Materials

ZnO varistors were invented by Matsuoka *et al.*, and have mass produced since 1971. The discovery was made by the evaluation for bulk bodies of Ag-paste painted ZnO, which were oversintered by the oven runaway – a story that has been handed down as one of the famous examples of serendipity (Higashi and Koga, 2018). As many related papers and books have been published, you can refer to them.

Conventional ZnO varistors are divided into Bi-doped type with oxide additives (Bi, Sb, Co, etc.) and Pr-doped one with Pr oxide etc., invented by Mukae *et al.* (1979); Higashi and Koga (2018). Both types are the same level of high nonohmic ceramics, and their electric resistance considerably decreases with applied voltage. The typical V – I characteristics are shown in Fig. 1. Since the resistance (i.e., voltage) decreases rapidly by several orders of magnitude with increasing an applied voltage, a current bypass is formed with overvoltage by a varistor being connected between a signal line and ground. The voltage at which the resistivity rapidly decreases is defined as varistor voltage (i.e., breakdown voltage), which is the most important index for protection performance. In general, the voltage at a current of 1 mA is expressed as $V_{1\text{mA}}$. As an index for nonlinearity, $\alpha_{10\mu\text{A}} = V_{1\text{mA}}/V_{10\mu\text{A}}$ is often used. The value closer to 1 means that the resistance decreases rapidly by increasing of a current between 10 μA and 1 mA, and the nonlinearity is ideal. To improve the protection performance, it is necessary to lower a voltage in the high current region when overvoltage is applied. As one of the measures, lowering breakdown voltage (i.e., $V_{1\text{mA}}$) is controlled in design of MLCV. The origin of highly nonlinear characteristics around $V_{1\text{mA}}$ is responsible for Schottky barriers between ZnO grains. On the basis of the microstructure, $V_{1\text{mA}}$ is the sum of a voltage ($= V_{\text{gb}}$) per grain boundary along electric field lines between electrodes. Thus, the number of grain boundaries has been reduced by thinning between electrodes or controlling grain sizes (Koga *et al.*, 2012). However, because degradation of nonlinearity and stability occurs with decreasing $V_{1\text{mA}}$ by conventional methods, the control of $V_{1\text{mA}}$ is limited within practical characteristics (Mukae *et al.*, 1979); (Ikoma and Okumura, 1981). The results on lower-voltage

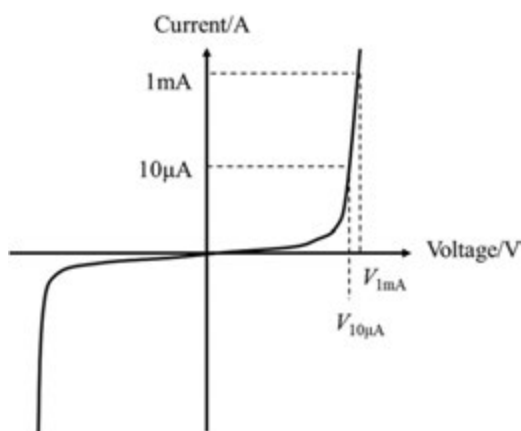


Fig. 1 V – I characteristic of varistors.

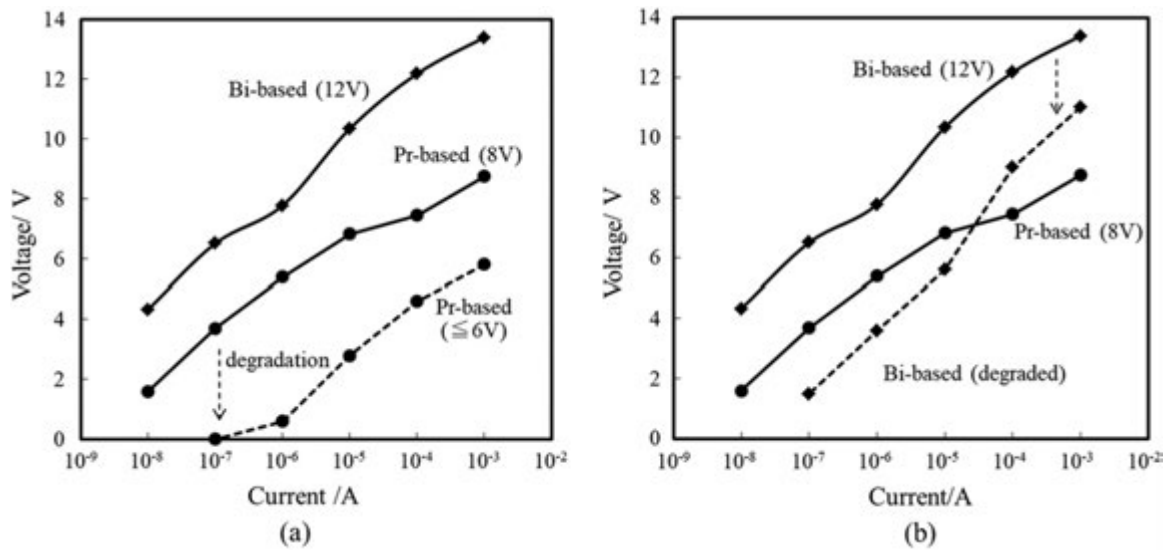


Fig. 2 V - I properties of Bi- and Pr- based MLCVs: (a) low-voltage region and (b) after applying ESD.

Table 1 Bulk and grain boundary characteristics of Bi- and Pr-doped ZnO varistors

Material system	$V_{1mA/mm}$ V	$\alpha_{10 \mu A}$ $V_{1mA}/10 \mu A$	V_{gb} V	ϕ eV	Grain size μm
Bi	760	1.18	1.78	1.15	2.7
Pr	540	1.14	1.07	0.64	2.3

limits of Pr- and Bi-based MLCVs are shown in **Fig. 2(a)** and **(b)**. As shown in **Fig. 2(a)**, nonlinearity of Bi-based MLCVs is degraded below V_{1mA} of 12 V. On the other hand, you can see that Pr-based MLCVs have high nonlinearity even down to 8 V. And more, stability against ESD is different between both types as well. Nonlinearity degradation of Bi-based MLCVs is significantly caused by ESD. On the other hand, it is clear that Pr-based MLCVs possess high ESD stability. From the results, the lower-voltage limits are found to be dependent on additives (in grain boundaries) to ZnO.

Development Direction of New Varistor Material

Detailed analysis of Bi- and Pr-doped varistors is conducted to obtain the development direction of the novel material with low-voltage characteristics and strong ESD stability. The difference of characteristics by the additives in the grain boundary compositions gives the development direction of new varistor material. Results obtained are described here.

Characteristics for Grain Boundaries in Bi/Pr-Doped ZnO Varistors

As a comparison of grain boundary characteristics between Bi- and Pr-doped types, nonlinear V - I characteristics ($V_{1mA/mm}$, $\alpha_{10 \mu A}$), average grain size, varistor voltage per grain boundary = V_{gb} (calculated from V_{1mA} and average grain size), and barrier height (ϕ) at a grain boundary are shown in **Table 1**. ϕ is determined from the change in dielectric constant due to a depletion layer at a p/n interface by using CV (capacitance-voltage) method (Ikoma and Okumura, 1981).

Grain sizes of two types are the same level of 2–4 μm , however, it is evident that V_{gb} and ϕ are considerably different between two types. Pr-doped type is approximately 40% lower V_{gb}/ϕ of 1.07 V/ 0.64 eV than 1.78 V/1.15 eV for Bi-doped, respectively. From these results, it is suggested that two types have different grain boundary characteristics even with a small amount of additives. It is likely that Pr-doped type is able to have low-voltage characteristics due to with lower V_{gb}/ϕ . Therefore, it is believed that lowering of V_{gb} is one development direction for realizing low-voltage varistors below that of Pr-doped.

Effect of Thermal Properties of Compositional Materials on ESD Stability

Because semiconductor devices such as ICs are typically vulnerable to ESD stress, a lot of knowledge has been reported on the ESD withstanding. Especially, the thermal property of the interface of the p/n junction is found to be closely related with stability to

ESD of devices (Wunsch and Bell, 1968). From the results, since nonlinearity of varistors is due to the same Schottky barriers as that of ICs, it is considered that the knowledge on ESD stability should be applicable to varistors. The equation derived from the Wunsch & Bell model is well known to be in good agreement with ESD withstanding of Schottky barriers in semiconductor devices. From this equation, capability of power withstanding per unit area of devices vs. an applied pulse width is indicated by a slope of 1/2 power, and the level of withstanding is determined by the melting point of material at an interface. On the basis of this knowledge, in the same way, ESD stability of varistors can be predicted to be improved in proportion to the melting point of the interfacial material (i.e., in grain boundaries). Melting points of compositional materials in Bi- and Pr-doped varistors are shown in Fig. 3 with those of Si in ZDs. The melting points of Bi_2O_3 and Sb_2O_3 in Bi-doped varistors are 820°C and 656°C, respectively. On the other hand, Pr_6O_{11} and Co_2O_3 in Pr-doped have melting temperatures of above 1900°C. In addition, Si in ZDs melts at about 1470°C. From their results, the melting points of interfacial materials are found to correspond well to the degree of ESD stability. Therefore, it can be seen that higher melting points of the compositions added to ZnO lead to high ESD stability in varistors (Koga et al., 2012). Furthermore, as ZnO varistors are polycrystalline ceramics, an applied voltage would be shared by each grain boundary along electric field vectors. In consequence, we believe that the lowering of the grain boundary voltage (i.e., V_{gb}) increases the number of grain boundaries, being effective in improving ESD withstanding.

Novel Low-Voltage ZnO Varistor Material With ESD Withstanding

Recently, from our studies on many varistors with lower V_{gb} and higher melting points of grain boundary compositions, we have successfully developed novel SrCoO_3 -doped ZnO varistors, which have low-voltage characteristics and strong ESD stability. The investigation of developed material is described in this section.

P-type conductive oxides, which can form Schottky barriers, are candidates for the grain boundary composition between ZnO grains of n-type semiconductor. Of those, $\text{ACoO}_{3-\delta}$ ($A = \text{Ca}, \text{Sr}, \text{and Ba}$) of perovskites in particular are P-type compounds with high melting point, and their doped ZnO is found to exhibit high nonlinearity (Koga et al., 2011, 2012). $V_{1\text{mA/mm}}$, $\alpha_{10\text{ }\mu\text{A}}$, V_{gb} and grain size of $(1-x)\text{ZnO} + x\text{ACoO}_{3-\delta}$ ($x = 0.005 \sim 0.02$) are summarized in Table 2. Precursors of $\text{ACoO}_{3-\delta}$ are prepared by solid-reaction method. They are added to ZnO powder, and mixed by ball milling method. Then, ACoO_3 -doped ZnO varistors have been produced under the optimized sintering condition so as to have high nonlinearity for each composition. As shown in Fig. 2, the new system of varistors exhibits low-voltage characteristics than those of conventional types, maintaining the same level of nonlinearity ($V_{1\text{mA/mm}} = 260\text{--}360\text{ V}$, $\alpha_{10\text{ }\mu\text{A}} = 1.27\text{--}1.4$). Furthermore, two types of varistors for $A = \text{Ca}$ and Ba have V_{gb} of 1.23 and 1.17 V, which are the intermediate values between Bi- and Pr-doped types. Whereas, it is noted that V_{gb} of SrCoO_3 -doped ZnO varistors (i.e., $A = \text{Sr}$)

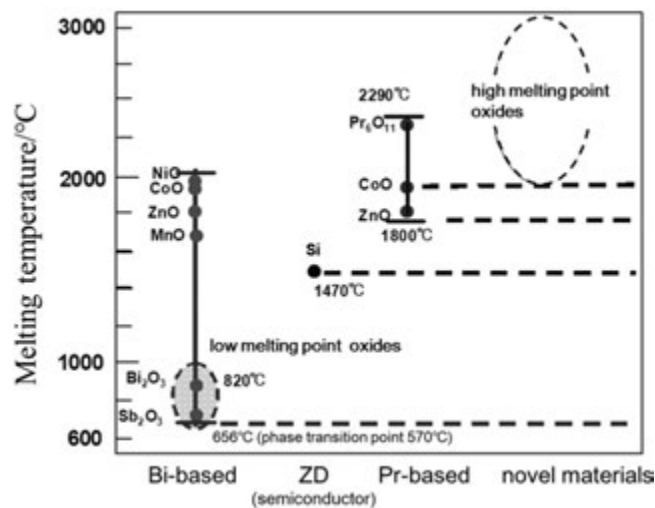


Fig. 3 Melting temperatures of each oxide in Bi/Pr-based varistor compositions and of zenor diodes.

Table 2 Characteristics of ACoO_3 -doped ZnO varistors ($A = \text{Ca}, \text{Sr}, \text{Ba}$)

A	$V_{1\text{mA/mm}}$ V	$\alpha_{10\text{ }\mu\text{A}}$ $V_{1\text{ mA}}/V_{10\text{ }\mu\text{A}}$	V_{gb} V	Grain size μm
Ca	350	1.19	1.23	3.5
Sr	360	1.19	0.81	2.3
Ba	260	1.42	1.17	7.3

is $\sim 25\%$ lower value ($= 0.81$ V) than that of Pr-based. It is evident from the result that the V_{gb} is the lowest in ZnO varistors. In addition, owing to the small grain size of $2\text{--}3\text{ }\mu\text{m}$, SrCoO₃-doped ZnO varistors are suitable for MLCVs. It is suggested from the results that electrical properties obtained from SrCoO₃-doped ZnO varistors show the possibility of low-voltage MLCVs with strong ESD stability.

MLCVs Using SrCoO₃-Doped ZnO Varistors

Multilayer SrCoO₃-doped ZnO varistors, with the size of $1.0 \times 0.5 \times 0.5$ mm in length, width, and height and $V_{1\text{mA}} = 5.6$ V (about 30% lower than 8 V of conventional MLCVs) are commercially produced. The precious metal is used as the internal electrode within MLCVs. The thickness of varistor layers between electrodes is approximately $17\text{ }\mu\text{m}$ (average number of grains: about 7 pcs.). The capacitance is designed to be 100 pF at 1 MHz, which is general in signal line applications. Fig. 4(a) and (b) shows V – I characteristics for MLCVs of SrCoO₃-doped ZnO varistors in addition to Bi- and Pr-doped types, and the change rate of $V_{1\text{mA}}$ ($\Delta V_{1\text{mA}}$) before and after ESD testing. The ESD testing for MLCVs is carried out at a peak voltage of 8 kV for waveforms under IEC 61000-4-2 standard (level 4).

MLCVs using SrCoO₃-doped ZnO varistors exhibit higher nonlinearity even in the low current region than those of conventional Bi/Pr-doped types, maintaining high insulation between 10 nA and 1 A. This is an important characteristic that leads to the reduction of leakage current when being mounted in equipment. The low-voltage V – I property should be attributed to the reduction of individual V_{gb} . From results obtained, we have confirmed that even after the ESD test, MLCVs have not only $\Delta V_{1\text{mA}}$ less than 10% but also the highest level of ESD stability. This is probably caused by the effect of increasing melting points of the grain boundary compound, which is our development direction described above. In addition, the ESD voltage is shown to be suppressed 1100 V (without MLCVs) to 80–90 V. This suppression effect can be applicable to devices that are vulnerable to ESD (i.e., LED etc.), and would lead to the expansion of a range of applications of MLCVs.

Ultralow-Capacitance MLCVs With a Discharge Cavity

High-speed communication circuits require ultralow capacitance (e.g., 0.1 pF) for devices such as MLCVs. However, lowering capacitance is usually due to the reduction of electrode area in conventional MLCVs. Thus, in case of the measure, it remains the problem that ESD stability and suppression effect cannot both be achieved with high levels. Until now, the lower limit of capacitance of conventional MLCVs has been 0.8 pF, and the suppression voltage is about 600 V at 8 kV under IEC 61000-4-2 standard. To achieve significant improvements in performance, ultralow-capacitance MLCVs ($= 0.1$ pF) have been developed, which have a discharge cavity formed by porous varistors in the internal structure (Koga *et al.*, 2012, 2013). Figs. 5 and 6 show the schematic of the structure and the ESD suppression effect at an ESD pulse voltage of 8 kV. Then, in Table 3 it is shown in comparison with the characteristics of conventional MLCVs as well. Porous SrCoO₃-doped ZnO varistor material with connected pores is formed in the region between counter electrodes. Due to the structure, an ESD pulse can be discharged in the connected pores. Furthermore, low-temperature cofired ceramics (LTCCs) with low dielectric constant ($\epsilon_r = 10$), except for the varistor region,

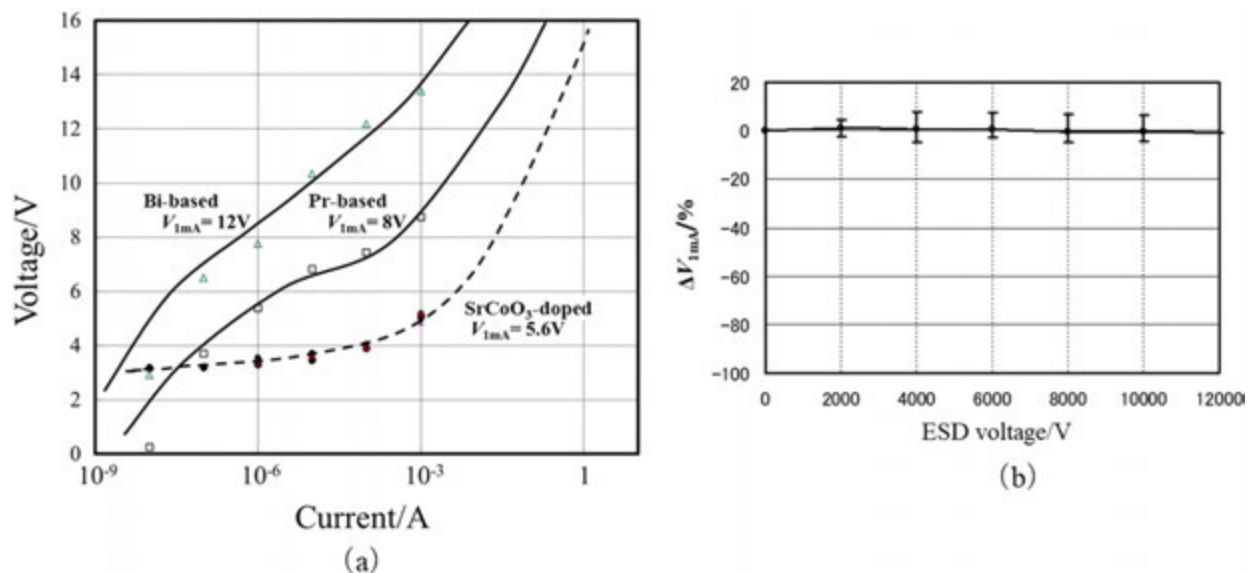


Fig. 4 Electrical properties of MLCVs of SrCoO₃-doped ZnO varistors with low varistor voltage ($V_{1\text{mA}} = 5.6$ V). (a) V – I properties and (b) $\Delta V_{1\text{mA}}$ after applying of ESD (8 kV under IEC 61000-4-2 standard [level 4]).

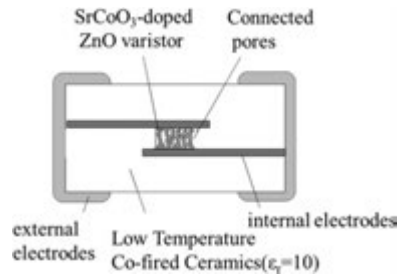


Fig. 5 Schematic of cross section of novel MLCVs with ultralow capacitance (e.g., 0.1 pF).

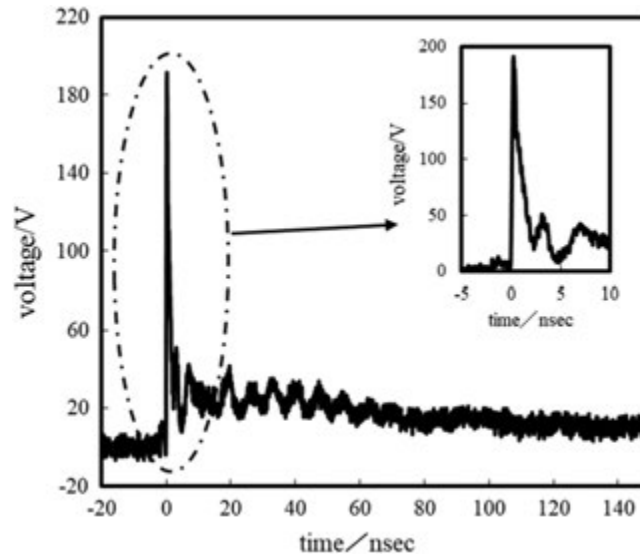


Fig. 6 Suppression wave shape for ESD at 8 kV (IEC 61000-4-2).

Table 3 Characteristics of low capacitance type of novel MLCVs

	Shape mm	Capacitance (typ.) at 1 MHz pF	Suppression voltage (typ.) at 8 kV V	ESD stability *IEC610004-2 kV
Ultralow-capacitance MLCVs (discharge type)	0.6 × 0.3 × 0.3	0.1	200	15
Conventional	1.0 × 0.5 × 0.5	0.8	600	8

are used to improve the mechanical strength and reliability as well as to reduce a stray capacitance. The device size of (length, width, and height) $0.6 \times 0.3 \times 0.3$ mm is ultracompact, and thus suitable for ICT applications.

The typical capacitance is 0.1 pF, which is reduced to about 1/8 of those of conventional MLCVs. Furthermore, the suppression effect is considerably improved from 600 V to 200 V (1100 V without MLCVs). Since $\text{SrCoO}_{3-\delta}$ contains Sr as an alkaline earth metal, it is likely that the work function is as small as 1.0–1.5 eV, which promotes discharge action during an ESD event. Therefore, in an ESD stress event, it is possible to start discharge immediately from a low-voltage level (e.g., 150 V), leading to the high suppression effect.

In the case of the conventional planar gap type, the counter electrodes wear out with every discharge and the gap distance is expanded. As the result, the suppression voltage rises. On the contrary, even after ESD pulse is repeatedly applied to the developed MLCVs (e.g., 100 times), there is no such deterioration. Since the ESD energy is almost consumed within the discharge cavity (i.e., the connected pores), the load to the varistor material results in drastically reducing.

In addition, insertion loss (I_L) is less than 0.1 dB (at 2.5 GHz), being able to operate stably even at a power level of 35 dBm. Thus, the influence on transmission characteristics can be extremely small. Due to the effect, high protection performance is obtained even for high-speed transmission lines for the antenna of mobile phones. The application of the $\text{SrCoO}_{3-\delta}$ -doped ZnO

varistor material to MLCVs with a discharge cavity has been found to give both excellent ESD suppression effect and high reliability to ESD, which have ultralow capacitance of 0.1 pF.

MLCVs Cofired With Internal Electrodes of Base Metal

In this section, we describe the new approach of realization of MLCVs with base metal as internal electrodes. As the cost of electrodes (precious metals) is very high in conventional MLCVs, the impact of application of base metal to internal electrodes should be very significant. With the minimization of adoption barriers by price, the range of applications of MLCVs is remarkably expanded. To produce MLCVs with internal electrodes of base metal, atmosphere below the equilibrium oxygen partial pressure is essential for cofiring with base metal electrode. However, Bi- and Pr-doped types cannot be used because oxygen is removed from grain boundaries, and thus nonlinearity disappears easily. On the other hand, SrCoO₃-doped ZnO varistors are found to exhibit excellent nonlinear V - I characteristics by air-annealing even after sintering in a reducing atmosphere (Higashi *et al.*, 2015). Furthermore, sufficient nonlinearity and ESD stability for practical use can be obtained from MLCVs with internal electrodes of base metal (Cu). Research on the MLCVs is described below.

Nonlinearity of SrCoO₃-doped ZnO Varistors Co-fired With Base Metal

As mentioned above, SrCoO₃-doped ZnO varistors exhibit high nonlinearity by postannealing after reduction (Higashi *et al.*, 2015). Such annealing for reducing sintered bodies is conducted also for SrTiO₃-based varistors to develop nonlinear property by

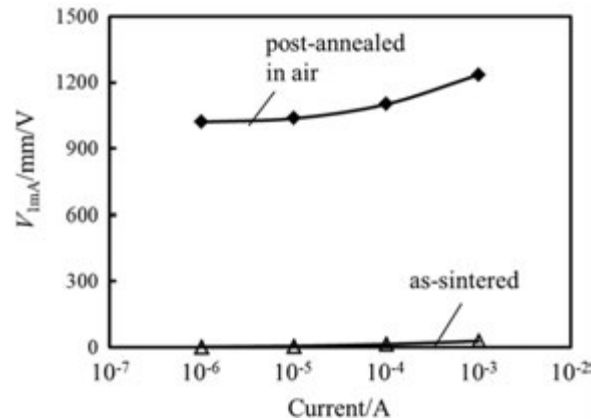


Fig. 7 V - I properties of bulk bodies of SrCoO₃-doped ZnO varistors taken from as-sintered in a reducing atmosphere and postannealed at 700°C in air.

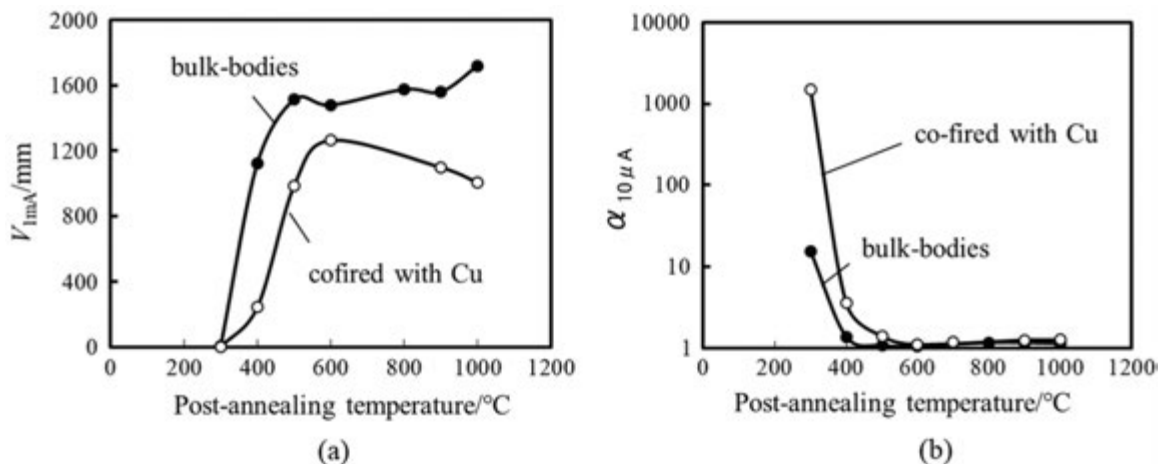


Fig. 8 Varistor properties of bulk bodies of SrCoO₃-doped ZnO varistors postannealed at various temperatures (300°C–1000°C) in N₂ (O₂ = 0.02%), (a) $V_{1mA/mm}$ and (b) $\alpha_{10 \mu A}$. Two types of sintered samples are shown: the bare bulk disk and a cofired disk with Cu on its upper and lower surfaces.

oxygen diffusion to grain boundaries (Ogasawara and Ogasawara, 1997). The nonlinearity variation by heat treatment is shown in detail here. Fig. 7 shows V - I characteristics of $\text{SrCoO}_{3-\delta}$ -doped ZnO varistors before and after air-annealing (700°C -0.5 h), which are sintered in a reducing atmosphere. As shown in the figure, the low ohmic resistance of as-sintered MLCVs changes to high nonlinear characteristics of $V_{1\text{mA/mm}} = 1240\text{ V}$ and $\alpha_{10\text{ }\mu\text{A}} = 1.19$ by annealing Higashi *et al.*, (2015). The development of nonlinearity during the annealing process is demonstrated in Fig. 8(a) ($V_{1\text{mA/mm}}$) and (b) ($\alpha_{10\text{ }\mu\text{A}}$). To examine the influence of cofiring with the base metal, cofiring with Cu electrode paste on the green compact are performed as well. Regardless of cofiring with Cu, $V_{1\text{mA/mm}}$ increases with an increase of the annealing temperature, and then saturates at around 600°C . $\alpha_{10\text{ }\mu\text{A}}$ improves to < 1.3 by annealing at above 600°C , showing excellent nonlinearity (Higashi *et al.*, 2015). The changes should be attributed to the variation state of electrical barriers formed by the diffusion of oxygen to grain boundaries. Although $V_{1\text{mA/mm}}$ of bulk bodies cofired with Cu decreases slightly by heat treatment above 600°C , the variation is relatively small (-13% at 900°C). From the result, it can be seen that annealing at about 700°C probably is effective to cause sufficient oxygen diffusion to give rise to nonlinear behavior.

Enhancement of Nonlinearity by Increasing P-Type Carriers at Grain Boundaries

It is speculated from results that heat treatment as postannealing diffuses oxygen to $\text{SrCoO}_{3-\delta}$ at grain boundaries, forming electrical barriers causing nonlinearity. Hence, $\text{SrCoO}_{3-\delta}$ should be present as p-type conductivity at interfaces between ZnO grains (n -type). To confirm the speculation, the sintered bulk bodies of $\text{SrCoO}_{3-\delta}$ were heated in a reduction atmosphere, and then air-

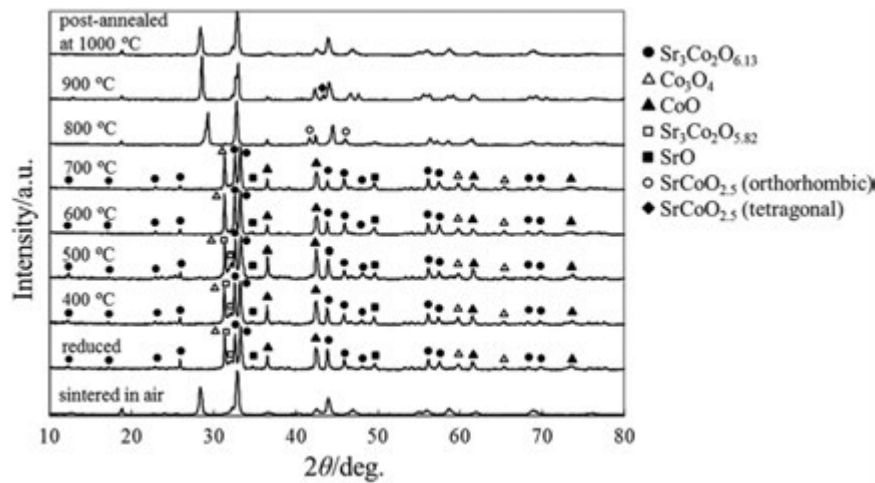


Fig. 9 Powder XRD patterns of $\text{SrCoO}_{3-\delta}$: as synthesized, reduction heat treatment, and air-annealing (400°C - 1000°C).

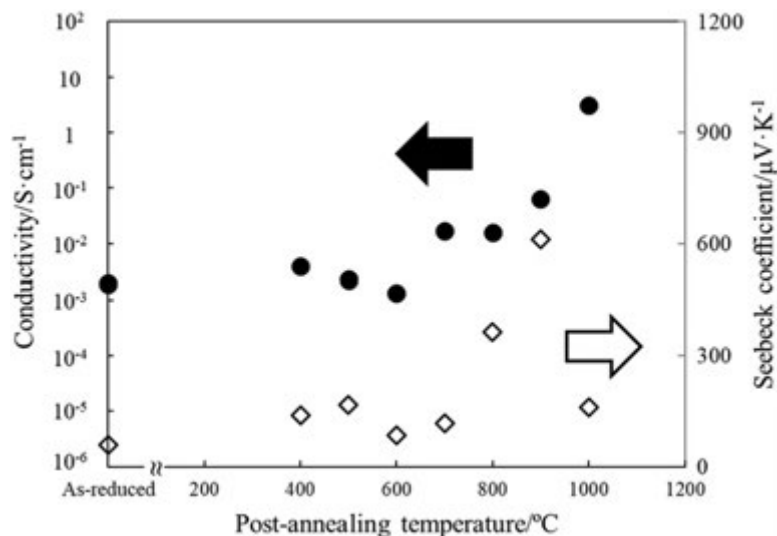


Fig. 10 Air-annealing temperature dependence of the Seebeck coefficient and conductivity of reduced $\text{SrCoO}_{3-\delta}$.

annealing was performed at 400°C–1000°C to evaluate the crystal phase, the carrier type of p/n and conductivity (Higashi and Koga, 2017).

Fig. 9 illustrates powder XRD patterns of $\text{SrCoO}_{3-\delta}$ by various heat treatments (as synthesized, reduction heat treatment, and air-annealing). Synthesized $\text{SrCoO}_{2.52}$ (hexagonal) of the perovskite type structure is mainly decomposed into $\text{Sr}_3\text{Co}_2\text{O}_{6.13}$, SrO , CoO , and Co_3O_4 by the reduction heat treatment (Higashi and Koga, 2017). However, they are resynthesized as matrix phase ($\text{SrCoO}_{2.52}$) of hexagonal with a small amount of extra two structures (orthorhombic and tetragonal as $\text{SrCoO}_{2.5}$) by annealing over 800°C (Higashi and Koga, 2017). Since the weight increases simultaneously in corresponding to the change of crystal phases, it can be seen that oxidation is responsible for reformation of $\text{SrCoO}_{2.5}$ (Higashi and Koga, 2017). Then, Fig. 10 indicates air-annealing temperature dependence of the Seebeck coefficient and conductivity of reduced $\text{SrCoO}_{3-\delta}$ (Higashi and Koga, 2017). Regardless of heat treatment, the Seebeck coefficients are all positive over the range of temperature (400°C–1000°C) studied here. It is evident from the result that annealed $\text{SrCoO}_{3-\delta}$ becomes p-type conductive by generated holes. In particular, the coefficients are found to increase sharply by twice between 700°C and 800°C. It is likely that the temperature range is in good agreement with the reformation temperature of $\text{SrCoO}_{2.52}$ (perovskite like compound) (Higashi and Koga, 2017). In addition, the conductivity shows high values of 10–1000 times that of 600°C in the temperature range of 800°C–1000°C when the $\text{SrCoO}_{2.52}$ is regenerated (1.7×10^{-2} to $3.1 \text{ S} \cdot \text{cm}^{-1}$) (Higashi and Koga, 2017). From these results, it is concluded that $\text{SrCoO}_{3-\delta}$ from compounds decomposed by reduction is regenerated by air-annealing, and the p-type carrier concentration increases with the oxidation. The increase of p-type carriers in grain boundaries should be the origin of the electrical barriers between ZnO grains (n-type), causing nonlinearity (Higashi et al., 2015); (Higashi and Koga, 2016, 2017).

MLCVs Cofired With Internal Electrodes of Base Metal

In this last section, we would like to introduce some of the results of first realizing MLCVs cofired with base metal internal electrodes by the combination of reduction sintering and oxygen diffusion control. V – I characteristics and ESD stability, which are available for practical use, could be realized for MLCVs cofired with Cu internal electrodes, using SrCoO_3 -doped ZnO varistors (Higashi et al., 2015). The device size is $1.0 \times 0.5 \times 0.5 \text{ mm}$ in length, width, and height, and the varistor-layer thickness within MLCVS is $17 \mu\text{m}$. After sintering in the same reducing atmosphere as in the evaluation of bulk disks, air-annealing is carried out at 700°C for 0.5 h. Nonlinear characteristics of $V_{1\text{mA}} = 22.4 \text{ V}$ and $\alpha_{10\mu\text{A}} = 1.44$ are obtained by the procedure process. When normalized to $V_{1\text{mA}}/\text{mm}$, it is 1320 V, which is almost the same level as that of the bulk body ($V_{1\text{mA}}/\text{mm} = 1240 \text{ V}$, $\alpha_{10\mu\text{A}} = 1.19$) (Higashi et al., 2015). Furthermore, it is confirmed that the capacitance also increases in proportion to the number of multilayers. This suggests that the function of the Cu internal electrode is effective from the expansion effect of the electrode area (Higashi et al., 2015).

Finally, we describe protection performance of the MLCVs cofired with internal electrodes of base metal. The important characteristics for ESD suppression performance, is of a large current region of above 1 A, that is, the bulk resistance of ZnO grains (Higashi and Koga, 2016). The conductivity of ZnO is due to oxygen vacancies, which significantly depend on P_{O_2} in sintering. Fig. 11 gives the relationship between P_{O_2} and ESD stability after zapping at a voltage of 8 kV. When sintered in $P_{\text{O}_2} = 1.0\text{--}1.6 \times 10^{-9} \text{ MPa}$, high ESD stability has been obtained, which gives a small $\Delta V_{1\text{mA}}$ (less than $\pm 10\%$) (Higashi et al., 2015). At higher P_{O_2} ($> 1.6 \times 10^{-9} \text{ MPa}$), Cu of the internal electrode diffuses into the ZnO grains, increasing the electrical resistance. Increasing resistance leads to cause the degradation of stability to ESD, due to heat generation after ESD stress (Higashi et al., 2015). On the other hand, in the case of low P_{O_2} below $1.6 \times 10^{-9} \text{ MPa}$, although the resistance of grains decreases, ZnO drastically evaporates by strong reduction, and the density of sintered MLCVs decreases (Higashi et al., 2015). Consequently, the internal electrodes diffuse and oxidize within MLCVs during the heat treatment, that cause the resistance deterioration in the low current region. Though practical V – I characteristics could be obtained, ZnO evaporation on the surface is one of the issues (i.e., reliability) for commercial realization of MLCVs produced by reduction sintering. Since the low density in the surface layer gives rise to the degradation of reliability such as in humidity, it is necessary to study the processing and coating to reduce the vaporization of Zn from MLCVs.

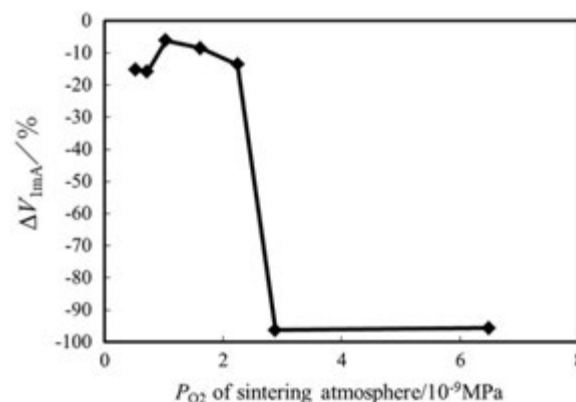


Fig. 11 The relationship between P_{O_2} and $\Delta V_{1\text{mA}}$ as ESD stability after zapping at a voltage of 8 kV.

Summary

To resolve the issues for protection from overvoltage, we have developed not only a new material system of SrCoO₃-doped ZnO varistors but also MLCVs using the same. In addition, MLCVs with base metal internal electrodes have been realized as well, for the first time. The findings obtained are listed below.

- (1) V_{gb} of SrCoO₃-doped ZnO varistor material is 30% lower than those of conventional two types of Bi/Pr-doped. The MLCVs have low-voltage characteristics ($V_{1mA} = 5.6$ V) below the conventional limit (8 V) and strong ESD stability (level 4 in IEC 61000-4-2).
- (2) For application to high-speed and high-frequency circuits, we have developed MLCVs with a discharge cavity in the structure, to give ultralow capacitance (0.1 pF), high ESD suppression effect (1100 V to 200 V), and high ESD withstanding.
- (3) V - I characteristics with practical use can be provided to MLCVs by the combination of sintering in a reducing atmosphere and air-annealing. The increase in p-type carriers of SrCoO_{3-δ} at grain boundaries should be the origin of the nonlinearity caused by air-annealing.
- (4) By the control of P_{O_2} in sintering and annealing temperature, practical V - I characteristics and ESD stability is provided to MLCVs with Cu internal electrodes.

Finally, we emphasize that recent studies reported in this paper can contribute to the development of protection performance against overvoltage. Further contributions will achieve both novel material development and device technology.

References

- Higashi, Y., Koga, E., 2016. TLP analysis of variation in ESD performance by cofiring with copper electrodes in SrCoO₃ doped-ZnO based multilayer varistors. *Journal of the Ceramic Society of Japan* 124 (6), 684–688.
- Higashi, Y., Koga, E., 2017. Relation between nonlinearity and semiconducting characteristics of SrCoO₃ additive in ZnO varistors sintered in a reducing atmosphere. *Journal of the Ceramic Society of Japan* 125 (6), 468–471.
- Higashi, Y., Koga, E., 2018. Latest R&D trends of ZnO-based multilayer ceramic varistors. *Ceramics Japan* 53 (4), 213–217.
- Higashi, Y., Hogiri, M., Koga, E., 2015. Nonlinear property of SrCoO₃-doped ZnO ceramics sintered in a reducing atmosphere and multilayer ceramic varistors with base metal electrodes. *Journal of Materials Research* 30 (15), 2300–2309.
- Ikoma, T., Okumura, T., 1981. Properties and measurements of deep levels in semiconductors. *The Journal of the Institute of Electronics, Information and Communication Engineers* 64, 195–202. (in Japanese).
- Koga, E., Sawada, N., 2009. Electrical degradation caused by electro-static discharge pulse in ZnO-based multilayer varistor. *Key Engineering Materials* 388, 15–18.
- Koga, E., Sawada, N., Amisawa, M., 2011. Multilayer varistor with low-voltage characteristics from ZnO + ACoO₃ ceramics (A = Ca, Sr and Ba). *Key Engineering Materials* 485, 249–252.
- Koga, E., Sawada, N., Amisawa, M., Minami, S., Okimoto, T., 2012. Multilayer ceramic chip varistors with low varistor voltage for ESD-protection. *Panasonic Technical Journal* 58 (1), 53–58.
- Koga, E. *et al.*, 2013. Surge Absorbing Elementus, Patent, US, 8400254 B2.
- Matsuoka, M., 1971. Nonohmic properties of zinc oxide ceramics. *Japanese Journal of Applied Physics* 10 (6), 736–746.
- Mukae, K., Tsuda, K., Nagasawa, I., 1979. Capacitance-vs-voltage characteristics of ZnO varistors. *Journal of Applied Physics* 50 (6), 4475–4476.
- Ogasawara, T., Ogasawara, M., 1997. The influence of the composition on the electrical properties of SrTiO₃ based varistor. *Journal of the Association of Materials Engineering for Resources* 10 (1), 90–96.
- Wunsch, D.C., Bell, R.R., 1968. Determination of threshold failure levels of semiconductor diodes and transistors due to pulse voltages. *Institute of Electrical and Electronics Engineers, for the Professional Technical Group on Nuclear Science* 15 (6), 244–259.

Dielectric, Ferroelectric, Antiferroelectric, Relaxor, Piezoelectric Ceramics: Definitions and Main Applications

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Introduction

The field of multifunctional applications is mainly based on dielectric ceramics, which, depending on their structure and composition, show appealing dielectric, ferroelectric, piezoelectric, and optical properties. Different types of dielectric ceramics have been developed, including thin ceramic films for microdevices. In this chapter, the dielectric crystalline media properties for different structures are defined and the main types of dielectric ceramics interesting for applications are presented. In the second section, basic concepts related to dielectrics, piezoelectric, ferroelectric, antiferroelectric, and relaxor ceramics are introduced.

The effect of crystal symmetry on the reduction of the number of independent piezoelectric moduli in piezoelectric materials is considered. It is shown that the effective properties of ferroelectric ceramics are different from those of monodomain single crystals, and that in the first approximation they can be obtained by averaging over the various orientations of the domains in the crystallites. Nonlinear properties of ferroelectric ceramics are presented.

Phase transitions in ferroelectrics and antiferroelectrics in terms of the phenomenological theory of Landau and Lifshitz (1960) are discussed, together with a brief presentation of some microscopic models and first-principles methods. The origin of the ferroelectric effect is briefly discussed, and a short discussion of ferroelectric phase transitions in the frame of the soft mode theory (Binc and Zeks, 1974) is included.

Relaxor ferroelectrics are presented. Most recent models regarding the origin, structure, and behavior of nanopolar regions are discussed.

In the third section, some of the most recent and diffused technological applications of these materials are presented.

Basic Concepts

Dielectrics

From the point of view of electrical properties, materials are divided into two categories: conductors and dielectrics. In an electric field, the first allow a flow of electric charges while the second do not allow this flow. Thus, the fundamental property of dielectrics consists in the impossibility of flowing of a continuous electrical current in them. Therefore, an electrical field can exist in the internal of a dielectric (Landau and Lifshitz, 1960). The equations governing this behavior (in the absence of magnetic field) are the classical Maxwell's equations:

$$\nabla \times \vec{E} = 0 \quad (1)$$

$$\nabla \cdot \vec{E} = \frac{\rho}{\epsilon_0} \quad (2)$$

where ρ is the total electric charge density and ϵ_0 is the permittivity of free space.

When a dielectric is introduced in an electric field, the total net charge remains null, that is $\int \rho dV = 0$. This means that average charge density for a dielectric body can be written as the divergence of a vector $-\vec{P}$ (Landau and Lifshitz, 1960):

$$\rho = -\nabla \cdot \vec{P} \quad (3)$$

$\vec{P}$ is called the polarization vector. Following Landau and Lifshitz (1960), for the determination of the physical meaning of $\vec{P}$, we consider the moment of the total dipole of all the charges inside the dielectric. Unlike the total charge, this quantity may not be null. According to the definition of the dipole moment, this quantity is the integral $\int \rho \vec{r} dV$. It can be shown that by substituting the charge density from Eq. (3) and integrating over the volume which contains the material, one obtains:

$$\int \rho \vec{r} dV = \int \vec{P} dV \quad (4)$$

Thus, the polarization vector represents the dipole moment of the volume unit of the dielectric, $\vec{P} = \rho \vec{r}$. It must be mentioned, however, that the usual definition of the macroscopic electric polarization of a crystal as the dipole per unit cell is correct only for the ionic models, where the dielectric solid is considered as formed by separated and independent polarizable units. Any attempt to apply it to covalent solids, where the electronic charge is delocalized, results into an incorrect definition (Resta, 1994).

By using Eqs. (2) and (3), Eq. (2) can be written in the form:

$$\nabla \cdot \vec{D} = 0 \quad (5)$$

where a new quantity $\vec{D}$ defined as:

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P} \quad (6)$$

has been introduced. $\vec{D}$ is called dielectric displacement and it is produced by the small displacement of the bonded charges in the electric field applied on the dielectric body.

At small values of the electric field, a linear relationship between the displacement $\vec{D}$ and the field intensity $\vec{E}$ can be considered, which in the case of an isotropic dielectric, can be written as:

$$\vec{D} = \varepsilon \vec{E} \quad (7)$$

The coefficient ε is called dielectric permittivity of the material and it is a function of its thermodynamic state. Also polarization $\vec{P}$ is proportional to the field:

$$\vec{P} = \chi \varepsilon_0 \vec{E} = (\varepsilon - \varepsilon_0) \vec{E} \quad (8)$$

The quantity $\chi = \frac{\varepsilon}{\varepsilon_0} - 1$ is called dielectric susceptibility.

In an anisotropic dielectric medium the relationship (7) becomes:

$$D_i = D_{0i} + \varepsilon_{ik} E_k \quad (9)$$

where $\vec{D}_0$ is a constant vector and ε_{ik} is the dielectric permittivity tensor. The free term $\vec{D}_0$ is not necessarily present in every crystal, since the majority of crystalline symmetry types do not allow the existence of a constant vector, therefore $D_i = \varepsilon_{ik} E_k$. The tensor ε_{ik} is symmetric, and it can be reduced to the diagonal form with an adequate choice of the coordinate system. Thus, in the general case, the tensor ε_{ik} is defined by three independent quantities ε_{11} , ε_{22} , and ε_{33} . Furthermore, depending on the symmetry of the crystal, the number of the principal values of the tensor ε_{ik} can be further reduced. For example, in crystals of the triclinic, monoclinic, and orthorhombic systems all three principal values are distinct (biaxial crystals), whereas in crystals of the tetragonal, rhombohedral, and hexagonal systems two principal values coincide thus there exists two independent principal values (uniaxial crystals). In crystals of cubic system, all three principal values of tensor ε_{ik} are equal, thus the tensor ε_{ik} reduces to a scalar, like in isotropic materials.

In dielectric materials, there are different mechanisms contributing to polarization: The shift of electronic clouds with respect to nuclei, which is the most important contribution at ultraviolet frequencies, the displacement and deformation of ions with respect to each other, occurring at infrared frequencies and the orientation of polar molecules in the field, occurring generally at microwave frequencies (Kittel, 1966).

In a variable field, there is a lag between the variation of the applied electric field and the response of polarization. Therefore, the dielectric permittivity is generally dependent on frequency, $\varepsilon = \varepsilon(\omega)$, a phenomenon that is called dispersion. The delayed response of the dielectric material with respect to the applied electric field is called dielectric relaxation. For a simple, non-interacting dipole system, it is expressed by the Debye equation:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + i\omega\tau} \quad (10)$$

where ε_∞ is the permittivity at ultrahigh frequencies and τ is the relaxation time. The real and imaginary parts of the complex dielectric permittivity $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$ are given by:

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + \omega^2\tau^2} \quad (11)$$

$$\varepsilon''(\omega) = \frac{\Delta\varepsilon \omega\tau}{1 + \omega^2\tau^2} \quad (12)$$

The ratio of the imaginary and real parts of the dielectric permittivity, $\tan \delta(\omega) = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)}$, is called dielectric loss and it represents an important quality factor for dielectric materials.

High dielectric permittivity ceramics with low dielectric loss, like SrTiO_3 , $(\text{Ba,Sr})\text{TiO}_3$, Ta_2O_5 , TiO_2 , etc., have been developed especially as thin films, for use in high capacitance devices, microwave applications, very large scale integration circuits, etc.

Piezoelectrics

In a crystal without center-of-inversion symmetry (noncentrosymmetric), an applied strain results into a net macroscopic electrical polarization, due to changes in the charge distribution produced by the applied strain. This is called direct piezoelectric effect. In piezoelectric materials also the converse effect, where the crystal is strained by the application of an electric field, is present.

Consider a dielectric medium immersed in an electric field. Generally, the internal stresses which occur in an isotropic dielectric immersed in an electric field are a quadratic effect with respect to the field (electrostrictive effect). But in piezoelectrics, these internal stresses are proportional to the first power of the electric field.

In the macroscopic theory of piezoelectricity, it is often convenient to use the electric field E_i and the stress tensor T_{ik} as independent variables. By using the thermodynamic potential for a piezoelectric medium (Landau and Lifshitz, 1960):

$$\Phi = \Phi_0 - \frac{1}{2} s_{iklm} T_{ik} T_{lm} - \frac{1}{2} \varepsilon_{ik} E_i E_k - E_i D_{i0} - d_{i,kl} E_i T_{kl} \quad (13)$$

where s_{iklm} is the elastic susceptibility (compliance) tensor and $d_{i,kl}$ is the piezoelectric strain tensor; the deformation tensor components S_{ik} and the dielectric displacement vector components D_i are expressed as:

$$S_{ik} = - \left(\frac{\partial \Phi}{\partial T_{ik}} \right)_E = s_{iklm} T_{lm} + d_{i,ik} E_l \quad (14)$$

$$D_i = - \left(\frac{\partial \Phi}{\partial E_i} \right)_T = D_{i0} + \varepsilon_{ik} E_k + d_{i,kl} T_{kl} \quad (15)$$

The above relations are the constitutive equations for the piezoelectric medium. The direct piezoelectric effect is described by the last term in the second equation, while the converse piezoelectric effect is described by the last term in the first equation. In the second equation, the term D_{i0} is related to the spontaneous polarization, which can be present in some classes of piezoelectrics, as it will be discussed later.

Before introducing other sets of constitutive equations, written for different couples of independent variables, let us see briefly which types of crystalline symmetries allow the existence of piezoelectricity and which are the effects of symmetry restrictions on the components of piezoelectric tensor.

Since $T_{kl} = T_{lk}$, it means that also $d_{i,kl}$ is symmetric in the last pair of indices. This leaves us with 18 independent components, among the 27 components of the third rank piezoelectric tensor. This number is further reduced by the crystal symmetry transformations, which must leave invariant the tensor components. A trivial result is that the material cannot be piezoelectric if it is centrosymmetric. Among the 32 crystalline classes only 20 admit piezoelectricity. These include the 10 pyroelectric classes which will be discussed later on, plus another 10 classes: D_2 belonging to the rhombic system, D_4 , D_{2d} , S_4 (tetragonal), D_3 (rhombohedral), D_6 , C_{3h} , D_{3h} (hexagonal), and T , T_d (cubic).

It is convenient to use a more concise notation, called the matrix notation, which condenses the couple of indices (kl) according to the following rules: (kl) $\rightarrow$ (k) for $k = l = 1, 2, 3$ while (kl) for $k \neq l$ transforms as follows: ((23), (31), (12)) $\rightarrow$ (4,5,6).

With these notations the constitutive equations written above become:

$$S_\alpha = s_{\alpha\beta}^E T_\beta + d_{i\alpha} E_i \quad (16)$$

$$D_i = \varepsilon_{ik}^T E_k + d_{i\beta} T_\beta \quad (17)$$

where $i = 1, 2, 3$ and $\beta = 1, 2, \dots, 6$.

The crystal symmetry operations reduce the number of independent piezoelectric moduli. The vanishing and the equality of many of the moduli in the various classes can be deduced in this way. Another approach is to transform the axes of reference of the tensor by one of the symmetry elements possessed by the crystal. After the operation, the transformed piezoelectric coefficients must remain unchanged.

By applying these rules, the independent piezoelectric moduli of all classes can be found (Nye, 1985). For example, for quartz the d_{ij} matrix is: $d_{11}, d_{12} = -d_{11}, d_{14}, d_{25} = -d_{14}, d_{26} = -2d_{11}$, all other moduli being zero. For crystals in the hexagonal 6 mm (C_{6v}) class the d_{ij} matrix is: $d_{31} = d_{32}, d_{33}, d_{15} = d_{24}$, all other moduli being zero.

As previously mentioned, three other sets of constitutive equations are derived from other thermodynamic potentials:

$$S_\alpha = s_{\alpha\beta}^E T_\beta + g_{i\alpha} D_i \quad (18)$$

$$E_i = \beta_{ik}^T D_k - g_{i\beta} T_\beta \quad (19)$$

$$T_\alpha = c_{\alpha\beta}^E S_\beta - e_{i\alpha} E_i \quad (20)$$

$$D_i = \varepsilon_{ik}^S E_k + e_{i\beta} S_\beta \quad (21)$$

$$T_\alpha = c_{\alpha\beta}^D S_\beta + h_{i\alpha} E_i \quad (22)$$

$$E_i = \beta_{ik}^S D_k - h_{i\beta} S_\beta \quad (23)$$

where $c_{\alpha\beta}$ are the elastic stiffness constants, β_{ik} are the dielectric stiffness constants, $g_{i\alpha}$ and $e_{i\alpha}$ are the piezoelectric voltage and piezoelectric stress constants, and $h_{i\alpha}$ are other piezoelectric coefficients. The superscripts E and D indicate the measurement conditions: under constant electric field or under constant charge, while T and S mean constant stress or constant strain.

The different coefficients measured under different conditions are not independent but they are related by various relationships. Thus, the following relations exist between the piezoelectric matrix coefficients (Wersing, 2008):

$$[d] = [e] [s^E] = [e^T] [g] \quad (24a)$$

$$[e] = [d] [c^E] = [e^S] [h] \quad (24b)$$

$$[g] = [h] [s^D] = [\beta^T] [d] \quad (24c)$$

$$[h] = [g] [c^D] = [\beta^S] [e] \quad (24d)$$

Detailed form of matrices can be found in Nye (1985) and IEEE Standard on Piezoelectricity (1988).

Besides the coefficients obtained from thermodynamic potentials, which represent material properties, in Eqs. (16–23), another important system of derived coefficients is represented by the electromechanical coupling factors, which describe the

strength of the conversion electrical $\leftrightarrow$ mechanical energy (IEEE Standard on Piezoelectricity, 1988). Thus:

$$k_{33}^2 = \frac{d_{33}^2}{\epsilon_{33}^T s_{33}^E} \quad (25)$$

The same type of relationship is valid also for k_{31} and k_{15} : $k_{31}^2 = \frac{d_{31}^2}{\epsilon_{33}^T s_{11}^E}$ and $k_{15}^2 = \frac{d_{15}^2}{\epsilon_{11}^T s_{55}^E}$.

The following relation is also valid: $k_{33}^2 = \frac{s_{33}^E - s_{33}^D}{s_{33}^E}$.

The piezoelectric constants are generally determined by quasistatic (Berlincourt type) methods or by the resonance method, in which samples of selected types are excited to resonance by an alternate electric field and the resonance values are used to calculate the various constants (IEEE Standard on Piezoelectricity, 1988; Wersing, 2008). The dielectric, elastic, and piezoelectric coefficients of piezoelectric ceramics are generally determined with small driving signals.

Another method consists in measuring the whole impedance spectrum of the sample and fitting the curves with parameters related to the physical properties (dielectric permittivity, elastic constants, and piezoelectric coefficients). Thus, one can use more points on the impedance curve to obtain the material properties with higher precision. Moreover, in this way it is possible to determine both the real parts as well as the imaginary parts of the coefficients (Smits, 1976).

Ferroelectrics

We discuss now the dielectric properties of crystals with a constant term $\vec{D}_0$ in Eq. (15). This constant vectorial term represents the fact that the dielectric medium is spontaneously polarized even in the absence of an external electric field. These dielectric materials are called pyroelectric. The pyroelectricity can exist only in a crystal which has a direction, that of $\vec{D}_0$ vector, which remains invariant for all the symmetry transformations. Among the 32 crystalline classes, those in which the pyroelectricity exists are triclinic (C_1), monoclinic (C_s , C_2), orthorhombic (C_{2v}), tetragonal (C_4 , C_{4v}), rhombohedral (C_3 , C_{3v}), and hexagonal (C_6 , C_{6v}) system. In a crystal of class C_1 the direction of pyroelectric vector $\vec{D}_0$ is not related to a particular crystallographic direction, for C_s this direction is in the symmetric plane, and in all the other classes the direction is along the symmetry axis. It must be mentioned that when speaking about symmetry conditions, we consider the crystalline medium as illimited. For a finite crystal, the value of its dipole moment can depend (in an ionic crystal) on the crystalline planes crossed by the sample surfaces, that is, on the fact that these planes contain ions of the same sign or are electrically neutral (Landau and Lifshitz, 1960).

In a normal pyroelectric crystal, the variation of the spontaneous polarization direction is associated with a substantial restructuring of the crystalline lattice, due to the high energy barrier between the two states. However, in some materials the positions of the atoms of the crystalline lattice in the pyroelectric phase are only slightly different from the positions in the nonpyroelectric phase. Therefore, the variation of the direction of the spontaneous polarization can occur relatively easily. These crystals are called ferroelectrics.

The ferroelectric properties of a material mainly depend on its crystalline symmetry. The direction of the spontaneous polarization (the ferroelectric axis) is already predetermined by the structure of the nonpyroelectric phase above the transition temperature. The ferroelectric axis can appear only along a well determined crystallographic direction, while in other cases the symmetry of the nonpyroelectric phase allows the occurrence of spontaneous polarization along different crystallographic directions. The appearance of polarization is always related to a decreasing of the crystal symmetry.

There are several approaches to a theory of ferroelectricity. One of these has been developed by Ginzburg in the framework of the general theory of phase transition of second order of Landau and Lifshitz (1960). It has been pointed out (Toledano and Toledano, 1987) that this approach, although phenomenologic, is still successfully employed because it is rigorous for many systems, it is a mathematically simple and flexible theory and it is strongly connected with the statistical theory of critical phenomena.

Within this approach, the dielectric polarization vector $\vec{P}$ is the order parameter whose size determines the degree of deviation of the crystalline lattice structure from the asymmetric to the symmetric phase. This means that $\vec{P}$ will be considered as an independent thermodynamic variable related to the conditions of minimization of the thermodynamic potential.

For the beginning let us consider the case of a unique ferroelectric axis. Near the transition point the order parameter $\vec{P}$ is small and the Landau expansion of the free energy density in powers of P can be considered:

$$G(T, P) = G_0(T) + \frac{1}{2}\alpha(T)P^2 + \frac{1}{4}\beta(T)P^4 + \frac{1}{6}\gamma(T)P^6 + \dots \quad (26)$$

In this expansion only even terms are considered, since the free energy density must be invariant with respect to polarization reversal in the paraelectric phase. Following the treatment in Blinc and Zeks (1974), the equilibrium spontaneous polarization values are obtained at the free energy extreme:

$$\left(\frac{\partial G(T, P)}{\partial P} \right)_{P_s} = 0 \quad (27)$$

which gives the following relation:

$$(\alpha(T) + \beta(T)P_s^2 + \gamma(T)P_s^4)P_s = 0 \quad (28)$$

The trivial solution $P_s = 0$ corresponds to the paraelectric phase. Other stable solutions are those that correspond to extreme minimum points of free energy, given by the condition:

$$\left(\frac{\partial^2 G(T, P)}{\partial P^2}\right)_{P_s} > 0 \quad (29)$$

Since the second derivative of the free energy density with respect to P is the inverse dielectric susceptibility χ^{-1} , the stability condition can be written as:

$$\chi^{-1} = \alpha(T) + 3\beta(T)P_s^2 + 5\gamma(T)P_s^4 > 0 \quad (30)$$

In the paraelectric phase, $P_s = 0$ and the condition of stability is:

$$\chi^{-1} = \alpha(T) > 0 \quad (31)$$

that is the first coefficient in the free energy expansion $\alpha(T)$ must be positive in the paraelectric phase. The limit of stability of the paraelectric phase is found at a temperature T_0 where $\alpha(T) = 0$. In the neighborhood of T_0 the coefficient $\alpha(T)$ can be developed into a Taylor series in powers of $(T - T_0)$. It is sufficient to keep only the first order term:

$$\alpha(T) = \alpha_0(T - T_0) \quad (32)$$

where α_0 is a positive constant.

From Eqs. (31) and (32), a Curie-Weiss law for the dielectric susceptibility in the paraelectric phase can be written:

$$\chi = \frac{1}{\alpha_0(T - T_0)}, \quad T > T_0 \quad (33)$$

We can further neglect the variation with temperature of β and γ coefficients. It is assumed also that $\gamma > 0$, otherwise higher order terms in Eq. (26) should be considered. Furthermore, depending on the sign of β , different variation (continuous or discontinuous) of the polarization through the transition point and temperature regions of stability for the ferroelectric phase are found.

Consider first $\beta > 0$. In this case, we can take $\gamma = 0$ without loss of significance, thus the Landau expansion of the free energy becomes:

$$G(T, P) = G_0(T) + \frac{1}{2}\alpha_0(T - T_0)P^2 + \frac{1}{4}\beta(T)P^4 \quad (34)$$

From Eqs. (27) and (29) one obtains:

$$(\alpha_0(T - T_0) + \beta P_s^2)P_s = 0 \quad (35)$$

and

$$\chi^{-1} = \alpha_0(T - T_0) + 3\beta P_s^2 \quad (36)$$

One of the solutions of Eq. (36) is $P_s = 0$, which minimizes the free energy when $T > T_0$. Other solutions corresponding to the region $T < T_0$ are obtained as:

$$P_s = \pm \left(\frac{\alpha_0}{\beta}(T_0 - T)\right)^{1/2} \quad (37)$$

From Eqs. (36) and (37), one obtains the static dielectric susceptibility below T_0 as:

$$\chi = \frac{1}{2\alpha_0(T_0 - T)}, \quad T < T_0 \quad (38)$$

The Curie-Weiss constant above T_0 is two times higher than the value below T_0 .

The stability limit of the ferroelectric phase $\chi^{-1} = 0$ is obtained at $T = T_0$ and coincides with the stability limit of the paraelectric phase. This is a second-order phase transition. Thus, for a second-order phase transition, the spontaneous polarization varies continuously through the transition temperature and increases as the square root of $T_0 - T$ (Eq. 37) below T_0 .

By substituting the solutions of Eq. (35) in the free energy (Eq. 34), the minimum values are obtained. For $T > T_0$ the free energy has one minimum at $P = 0$ while below T_0 it has two minima at $+P_s$ and $-P_s$. In Fig. 1 we show the qualitative dependence of the thermodynamic potential on polarization (a), and the spontaneous polarization and dielectric susceptibility dependences on temperature (b).

From the derivation of free energy in Eq. (34) with respect to P , we find the relationship between the electric field and the polarization (Lines and Glass, 1977):

$$\frac{\partial G(T, P)}{\partial P} = E = \alpha_0(T - T_0) + \beta P^2 \quad (39)$$

The P - E relationship describes stable states together with unstable states with negative permittivity (Lines and Glass, 1977). Only stable states and metastable states of polarization are experimentally measured, forming the so-called hysteresis curve $P(E)$ (Fig. 2). At a value of the applied field called critical field (E_c), the polarization is switched from one direction to the opposite direction. When the field is decreased to zero the polarization remains with a value called remnant polarization.

Following the treatment in Ref. (Blinic and Zeks, 1974), we consider now the case $\beta < 0$.

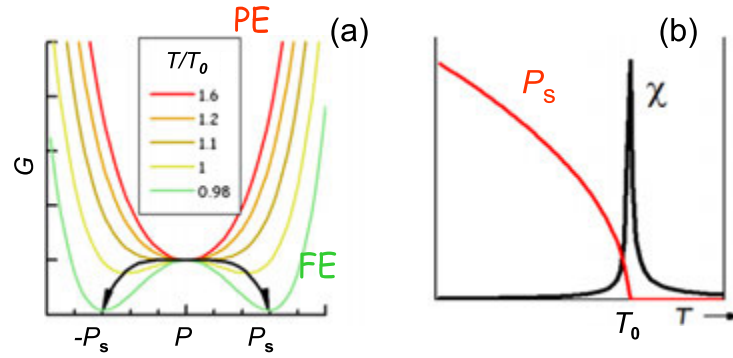


Fig. 1 (a) Free energy as a function of polarization at various temperatures; (b) dependence of spontaneous polarization and dielectric susceptibility on T , for a second order phase transition. Courtesy of F. Cordero.

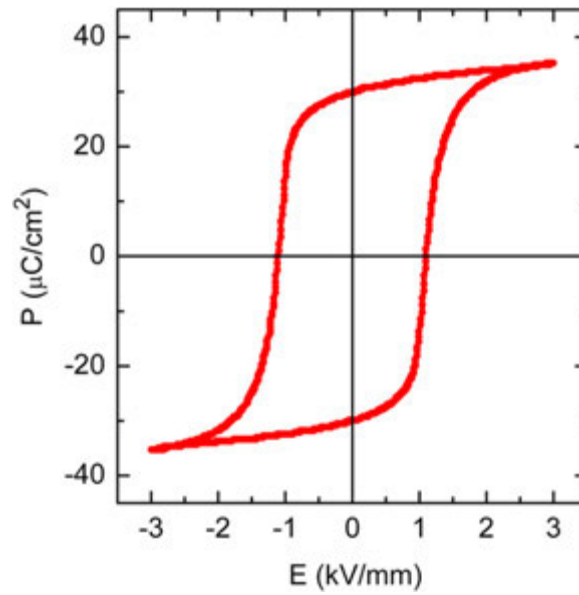


Fig. 2 Hysteresis curve measured on a ferroelectric ceramic. Modified from Craciun, F., Cordero, F., Ciuchi, I.V., Mitoseriu, L., Galassi, C., 2015. Refining the phase diagram of $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_{0.9}\text{Ti}_{0.1})_{1-x/4}\text{O}_3$ ceramics by structural, dielectric and anelastic spectroscopy investigations. *J. Appl. Phys.* 117, 184103-1-8.

Eq. (28) can be put into the form:

$$(\alpha_0(T - T_0) + \beta P_s^2 + \gamma P_s^4)P_s = 0 \quad (40)$$

In addition to the paraelectric solution $P_s = 0$, this equation has two real solutions:

$$P_s = \pm \left[-\frac{\beta}{2\gamma} \left(1 + \left(1 - \frac{4\alpha_0\gamma}{\beta^2}(T - T_0) \right)^{1/2} \right) \right]^{1/2} \quad (41)$$

$$P_s = \pm \left[-\frac{\beta}{2\gamma} \left(1 - \left(1 - \frac{4\alpha_0\gamma}{\beta^2}(T - T_0) \right)^{1/2} \right) \right]^{1/2} \quad (42)$$

The dielectric susceptibility of the ferroelectric phase is obtained by inserting the expression (41) in Eq. (30):

$$\chi^{-1} = \frac{\beta^2}{\gamma} \left(1 - \frac{4\alpha_0\gamma}{\beta^2}(T - T_0) \right)^{1/2} \left(\left(1 - \frac{4\alpha_0\gamma}{\beta^2}(T - T_0) \right)^{1/2} + 1 \right) \quad (43)$$

The stability limit of the ferroelectric phase obtained for $\chi^{-1} = 0$ gives the following limit temperature:

$$T_1 = T_0 + \frac{1}{4} \frac{\beta^2}{\alpha_0\gamma} \quad (44)$$

Thus, the stability limits of the two phases, paraelectric (T_0) and ferroelectric (T_1) are different, which is the distinctive mark of a first order phase transition. At $T = T_1$ P_s has a finite value, and there is a discontinuous variation of the spontaneous polarization through the transition point, which is another distinctive characteristic of a first order phase transition.

The second solution (42) is real only in the region $T_0 < T < T_1$ and it corresponds to a free energy maximum, therefore it is not considered.

Below T_0 the free energy has two minima corresponding to $\pm P_s$, and for $T_0 < T < T_c$ another local minimum appears at $P_s = 0$, where the ferroelectric phase is still stable and the paraelectric phase is metastable. At $T = T_c$, the free energies of the paraelectric and ferroelectric phase are equal (Blinic and Zeks, 1974; Lines and Glass, 1977). From this condition plus the minimization of free energy the transition temperature T_c is obtained as:

$$T_c = T_0 + \frac{3}{16} \frac{\beta^2}{\alpha_0 \gamma} \quad (45)$$

At T_c the dielectric susceptibility is finite and the spontaneous polarization discontinuously changes from a finite value $P_s = \left(-\frac{3\beta}{4\gamma}\right)^{1/2}$ to zero.

For $T_c < T < T_1$ the minimum at $P_s = 0$ is deeper than the two other minima at $\pm P_s$. In this region, the paraelectric phase is stable, whereas the ferroelectric phase is metastable. Above T_1 only the paraelectric phase remains.

It has been suggested (Cochran, 1960) that the phase transitions in some ferroelectrics are driven by one of the normal vibrational modes of the lattice (soft phonon) which becomes unstable. Its frequency decreases down to zero on approaching the critical temperature T_c and the frozen mode displacements become the order parameter of the transition. For a ferroelectric state, the soft phonon must be polar and must correspond to long wavelength (wavevector $q \rightarrow 0$).

One of the first models for ferroelectricity in perovskites, known as the rattling ion model, was proposed by Slater (1950). The model relies on the relative size of ions in the cell, as, for example, in the case of BaTiO_3 , where Ti ion is too small for the octahedral cage, and therefore the electrostatic forces from the other ions can displace it relatively easily from the center. However, the model cannot explain why almost all ferroelectric perovskites have B-cations with d_0 electronic configuration, like e.g., Ti^{4+} , Zr^{4+} , Nb^{5+} , Ta^{5+} , and Sc^{3+} (Cohen, 1992).

Starting from 1990, in the field of ferroelectrics new computational and experimental results have been obtained by the use of first-principles methods and of new fine experimental techniques.

First-principles methods use fundamental physics principles to compute all materials properties (Cohen, 2008). They are based on the density functional theory within the local density approximation (Cohen, 2008). First-principles calculations of the soft mode potential surface in perovskite BaTiO_3 and PbTiO_3 showed that these methods can predict the ferroelectric behavior, and the following picture of the ferroelectric instability in oxide perovskites has been established (Cohen, 2008): Long-range Coulomb forces favor off-centering, while short-range repulsive forces favor the ideal structure where the atoms are as far apart as possible. It is found that the hybridization between the B-cation d-states and the oxygen p-states reduces this repulsion, allowing the B ions to move off-center. Moreover the Pb lone-pair 6s-states also contribute to the off-centering of the Pb ions.

Actually, the most important piezoelectric materials are ferroelectric ceramics based on the Pb-containing perovskites (Helke, 2008). Different chemical modifications can be made in order to obtain the enhancement of piezoelectric and ferroelectric properties. For example, the binary solid solutions of PbTiO_3 – PbZrO_3 or $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) perovskites have demonstrated enhancement of properties at the so-called morphotropic phase boundary (MPB) where the ratio of Zr to Ti ions is nearly 53/47 (Jaffe *et al.*, 1971). At the MPB, the competition between the phases (tetragonal T and monoclinic M) is the determinant factor for properties enhancement. The Curie temperature for the MPB compositions is higher than 300°C , which allows the use of these materials at relatively high temperatures (Helke, 2008). In Fig. 3 the phase diagram of PZT, as obtained from different measurements, is shown. The dashed lines represent data taken from Jaffe *et al.* (1971) and (Noheda *et al.*, 2000).

The experimental points marked by triangles have been obtained from measurements of the dielectric and elastic susceptibility versus temperature (Cordero *et al.*, 2013). Besides the MPB between the T and M ferroelectric phases, there is another MPB between orthorhombic antiferroelectric and rhombohedral ferroelectric phases, at low Ti content.

PZT properties can be also further tailored for a broad range of applications, by doping with other elements. Usually doping elements are added in concentrations lower than 3 at%. They can be divided in two groups, and their effects can be opposite, depending on their valence. Thus, dopants with higher valency than the substituted ion act as donors and ions with lower valency act as acceptors. They are called softeners or hardeners, respectively. The charge compensation is obtained by the creation of lead or oxygen vacancies. For example, doping trivalent ions (e.g., La^{3+}) at Pb^{2+} positions or pentavalent ions (Nb^{5+}) at $\text{Zr}^{4+}/\text{Ti}^{4+}$ positions act as donors and are compensated by the formation of lead vacancies, which reduce the lattice strain. Consequently, the domain wall mobility increases, favoring domain reorientation and decreasing the coercive field (Helke, 2008). This softening effect is accompanied by enhanced dielectric permittivity, remnant polarization, and piezoelectric constants. On the other hand, acceptor doping with monovalent ions (e.g., K^+) at Pb^{2+} positions or trivalent ions (Fe^{3+}) at $\text{Zr}^{4+}/\text{Ti}^{4+}$ positions leads to the formation of oxygen vacancies. The oxygen vacancies block the domain wall movement and consequently increase the coercive field. This hardening effect leads to smaller dielectric permittivity and piezoelectric constants, but also to low dielectric and mechanical losses, which are significant quality factors for applications such as piezoelectric transformers, filters, etc.

In ferroelectric ceramics, a poling procedure is necessary in order to orient the different ferroelectric domains which form inside crystallites to minimize the depoling fields and mechanical stresses (Wersing *et al.*, 2008). In ferroelectric piezoelectrics, besides the intrinsic piezoresponse, associated with ion displacements and charge redistribution, there is also an additional extrinsic

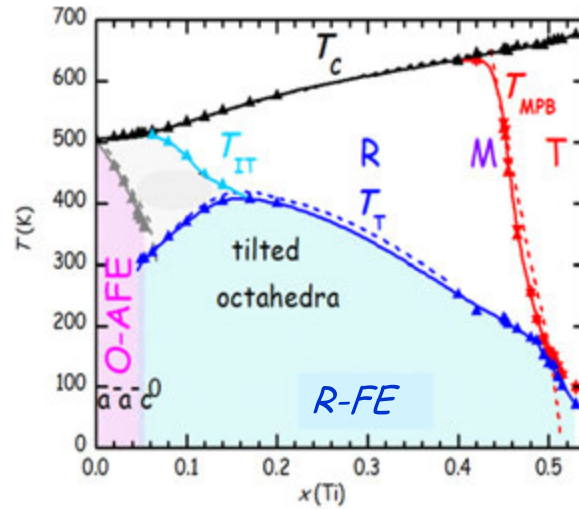


Fig. 3 Phase diagram of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$. Modified from Cordero, F., Trequattrini, F., Craciun, F., Galassi, C., 2013. Merging of the polar and tilt instability lines near the respective morphotropic phase boundaries of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$. *Phys. Rev. B* 87, 094108-1-9.

contribution resulting from non- 180° (e.g., 90°) domain wall movements (Damjanovic and Demartin, 1997). This is especially important at high intensity fields (of the order of the coercive field) where switching of domains is observed, but at low driving field the contribution is given only by reversible domain wall vibration.

In order to obtain the effective properties of poled polycrystalline ferroelectric ceramics, a simple approach is to neglect the effect of crystallite boundaries and to approximate the medium with an ensemble of domains with different orientations, where the material properties are obtained by averaging over the various orientations of the domains in the crystallites (Wersing *et al.*, 2008). Thus, in the case of the piezoelectric constants:

$$d_{iz}^* = \langle d_{iz} \rangle + \dots \quad (46)$$

By using this averaging procedure, the following expressions have been obtained for the effective piezoelectric constants (Wersing *et al.*, 2008):

$$\begin{aligned} 2d_{31}^* &= 2\langle d_{31} \rangle = (d_{31} + d_{33} - d_{15})\langle \cos \theta \rangle + (d_{31} - d_{33} + d_{15})\langle \cos^3 \theta \rangle \\ d_{31}^* &= \langle d_{33} \rangle = (d_{33} + d_{15})\langle \cos \theta \rangle + (d_{31} - d_{33} - d_{15})\langle \cos^3 \theta \rangle \\ d_{15}^* &= \langle d_{15} \rangle = (d_{33} - d_{31})\langle \cos \theta \rangle + (d_{15} - d_{33} + d_{31})\langle \cos^3 \theta \rangle \end{aligned} \quad (47)$$

where θ is the angle between the 3-axis of a domain (direction of P_3) and the 3-axis of the poled ceramic sample. The effect of the intensity of the poling electric field consists into narrowing the statistical distribution of individual polarization directions in a confined angle, which is related to the poling degree.

Thus it can be observed from these relations that depending on the degree of poling the properties of piezoelectric ceramics can be quite different from those of single domain crystallites and can vary strongly with the degree of poling that is with the intensity of the poling field.

Antiferroelectrics

Within the soft mode theory, the antiferroelectric ordering is due to the condensation of a soft mode at the Brillouin zone boundary (Blinic and Zeks, 1974). The antiferroelectric state is characterized by the appearance of two opposite sublattice polarizations and an increase in the size of the unit cell.

In simple phenomenological models of collinear antiferroelectricity, the two sublattice polarizations are equal to each other. A more complex model, where the two collinear sublattice polarizations P_+ and P_- are independent thermodynamic variables, has been developed by Kittel (1951). Thus, Kittel's model can describe ferroelectric, ferrielectric, and antiferroelectric states, depending on the specific parameters in the thermodynamic potential.

Proceeding in a parallel way to the ferroelectric case (Blinic and Zeks, 1974), the free energy density of a uniaxial antiferroelectric medium is expanded in powers of P_+ and P_- as:

$$G(T, P_+, P_-) = G_0(T) + \alpha (P_+^2 + P_-^2) + \beta P_+ P_- + \gamma (P_+^4 + P_-^4) + \dots \quad (48)$$

where higher order terms and some of the fourth order terms are neglected. This approximation is allowed if $\gamma > 0$.

The equilibrium values of the sublattice polarizations P_{+s} and P_{-s} are determined from the conditions:

$$\left(\frac{\partial G(T, P)}{\partial P_{+}} \right)_{P_{+s}, P_{-s}} = 0, \quad \left(\frac{\partial G(T, P)}{\partial P_{-}} \right)_{P_{+s}, P_{-s}} = 0 \quad (49)$$

which lead to a system of two equations for P_{+s} and P_{-s} :

$$\begin{aligned} 2\alpha P_{+s} + \beta P_{-s} + 4\gamma P_{+s}^4 &= 0 \\ 2\alpha P_{-s} + \beta P_{+s} + 4\gamma P_{-s}^4 &= 0 \end{aligned} \quad (50)$$

With further elaboration of these equations (namely by adding and subtracting them) (Blinic and Zeks, 1974), it is found that the possible solutions of the system are:

- (1) $P_{+s} = P_{-s} = 0$ paraelectric solution
- (2) $P_{+s} = P_{-s} \neq 0$ ferroelectric solution
- (3) $P_{+s} = -P_{-s} \neq 0$ antiferroelectric solution
- (4) $P_{+s} \neq -P_{-s} \neq 0$ ferrielectric solution

Following a similar procedure as for the ferroelectric case, it is found that different possible solutions are stable in different conditions. Thus, it is found that at the stability limit $2\alpha - \beta = 0$ and $2\alpha + \beta > 0$, the system transforms from the paraelectric to the antiferroelectric state. It is further assumed, similar to the ferroelectric case, that near the stability limit the coefficient $2\alpha - \beta$ can be developed into a Taylor series in powers of $(T - T_0)$, which gives:

$$\alpha(T) = \frac{1}{2}\beta + \alpha_0(T - T_0) \quad (51)$$

In these conditions, a transition from the high temperature paraelectric to the low temperature antiferroelectric phase occurs at T_0 . The antiferroelectric solution is found to be:

$$P_{+s} = -P_{-s} = \left(\frac{\alpha_0}{\gamma} (T - T_0) \right)^{1/2} \quad (52)$$

which is stable below T_0 . The stability limits of the paraelectric and antiferroelectric states coincide; therefore, the phase transition is of second order. It is found also that the ferroelectric phase is never stable but a metastable ferroelectric phase can exist for $T < T_0 - \frac{3\beta}{2\alpha_0}$ while the ferrielectric solution always corresponds to a maximum of the free energy and is never stable.

The free energy of an antiferroelectric crystal is close to that of a ferroelectric modification of the same structure (Lines and Glass, 1977). This is the origin of the high permittivity of the antiferroelectrics. The antiferroelectric phase can be switched to ferroelectric by the application of a high intensity electric field. This is called electric field-induced phase switching (Hao et al., 2014).

Fig. 4 shows the typical double hysteresis loop for an antiferroelectric ceramic (Craciun et al., 2015), where the net macroscopic remnant polarization is zero.

The forward phase switching field and the backward switching field are obtained by extrapolation. The phase switching behavior confirms that the antiferroelectric and ferroelectric states are close in energy.

However, the field-induced ferroelectric phase is not stable and can turn back to the antiferroelectric phase by the action of electric field and temperature variations.

The first reported and most known antiferroelectric is PbZrO_3 (Sawaguchi et al., 1951). For lead zirconate, the electric field-induced switching from antiferroelectric to the ferroelectric phase is obtained only at high temperatures, above 210°C (Sawaguchi et al., 1951). At room temperature, the transformation is not possible because the breakdown field is lower than the critical field

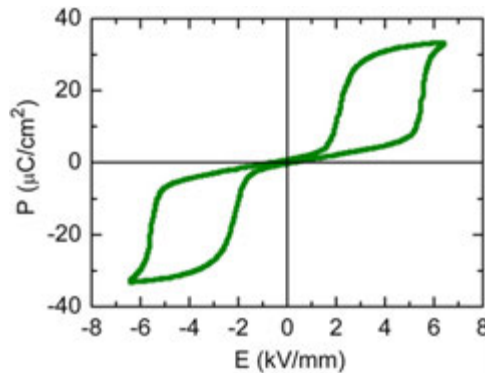


Fig. 4 Hysteresis loop for an antiferroelectric ceramic. Modified from Craciun, F., Cordero, F., Ciuchi, I.V., Mitoseriu, L., Galassi, C., 2015. Refining the phase diagram of $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_{0.9}\text{Ti}_{0.1})_{1-x/4}\text{O}_3$ ceramics by structural, dielectric and anelastic spectroscopy investigations. J. Appl. Phys. 117, 184103-1-8.

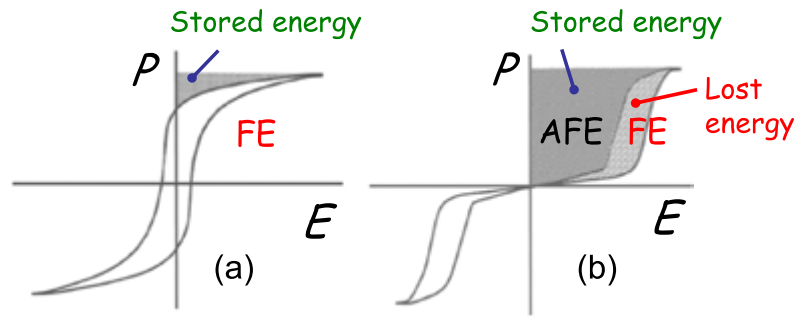


Fig. 5 Schematic illustration of the energy storage density for antiferroelectrics (b) as compared to ferroelectrics (a), as evaluated from their hysteresis loops. Modified from Hao, X., Zhai, J., Kong, L.B., Xu, Z., 2014. A comprehensive review on the progress of lead zirconate-based antiferroelectrics. *Prog. in Mater. Sci.* 63, 1–57.

for transition. Different dopants in lead zirconate are used to decrease its critical field. The most used are La^{3+} , Ba^{2+} , Ca^{2+} , and Sr^{2+} at the Pb site and Sn^{4+} , Ti^{4+} , and Nb^{5+} at the Zr site (Hao *et al.*, 2014).

Thus, by suitable doping, antiferroelectric materials with low critical field like $(\text{Pb},\text{La})(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$ (PLZST) and $\text{Pb}(\text{Zr},\text{Sn},\text{Ti},\text{Nb})\text{O}_3$ (PNZST) have been obtained (Hao *et al.*, 2013, 2014). Electric field-induced switching occurred at room temperature when the compound had tetragonal structure.

The antiferroelectric–ferroelectric field-induced transition is also a structural transition from orthorhombic or tetragonal to rhombohedral. The primitive cell volume of the ferroelectric (rhombohedral) phase is larger than the corresponding volume of the antiferroelectric (tetragonal) phase. Thus, an antiferroelectric ceramic will expand through the field-induced transformation from antiferroelectric to ferroelectric, providing a strain of nearly 1% (Hao *et al.*, 2014). Conversely, in these materials a pressure-induced transition from ferroelectric to antiferroelectric will be accompanied by huge and sharp charge release. Therefore, antiferroelectric materials have potential applications in high-strain actuators, pulsed voltage suppliers, etc. Other potential applications like pyroelectric detectors, cooling devices, and high energy capacitors are related to their enhanced response to temperature and external electric field changes.

As an example, the higher performance for energy storage in antiferroelectric materials as compared to ferroelectrics is illustrated in Fig. 5.

The energy stored per unit volume of a dielectric can be evaluated from the expression: $W = \int_0^{E_{\max}} P dE$. For hysteretic media like ferro/antiferroelectrics the useful (recoverable) energy W_r (represented by the dark gray area in Fig. 5) is the difference between the total stored energy W_s and the dissipated energy represented by the light gray area enclosed in the hysteresis loop (hysteresis loss).

The energy storage efficiency η is defined as $\eta = \frac{W_r}{W_s}$ (Hao *et al.*, 2014). For linear dielectrics where $P = \chi E \cong \epsilon E$, $W = \frac{1}{2} \epsilon E^2$. It follows that linear dielectrics, which have a small dielectric permittivity, are inferior to polar dielectrics regarding energy storage. Moreover, antiferroelectrics have superior storage performance over ferroelectrics, due to their higher recoverable energy. Progress in this field was achieved rapidly with miniaturization of thin films ($W_r = 56 \text{ J cm}^{-3}$) (Hao *et al.*, 2014).

Relaxor Ferroelectrics

Relaxor behavior can be found in materials with different compositions and structures, which generally do not show a phase transition, behaving more like glasses (Mydosh, 2015). Their common characteristic is a broad freezing transition associated with a frequency dependent maximum of some response (Cohen, 2008), be it magnetic (magnetic spin glasses (Sherrington, 2018; Vincent and Dupuis, 2018)), dielectric (dielectric glasses (Kleemann and Dec, 2018)) or elastic (strain glasses (Ji *et al.*, 2018)).

Solid solutions between ferroelectrics and dielectric relaxors, called relaxor ferroelectrics, have been intensively investigated in recent decades, due to their enhanced dielectric and piezoelectric properties. Alternatively, relaxor ferroelectrics have been obtained by doping classical ferroelectrics like PZT with different elements, e.g., La^{3+} on the A-site. A review of relaxor ferroelectrics can be found in Bokov and Ye (2006). Under field cooling, a transition from the relaxor to the ferroelectric phase is obtained. In some relaxor ferroelectric crystals like $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ (PMN–PT) and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ (PZN–PT), a huge electromechanical coupling coefficient has been obtained for compositions near the MPB (Park and Shrout, 1997) and for particular orientation of the polar axis and applied electric field. This has been attributed to the polarization rotation (Cohen, 2006).

Relaxor ferroelectrics show a broad-frequency dependent maximum in the dielectric permittivity curves measured as a function of temperature, as shown in Fig. 6. The thin lines are results of fitting with a model described in Cordero *et al.* (2005).

Different models have been proposed to explain the peculiar behavior of relaxor ferroelectrics. Almost all are related with the presence of polar nanoregions (PNRs), although they disagree when the PNRs' true origin, and especially the nature of the embedding matrix, are discussed.

Recent molecular dynamic simulations (MDS) have shown that the peculiar properties of relaxor ferroelectrics are due to the presence of a multidomain state (Takenaka *et al.*, 2017). The simulated multidomain structure of relaxor ferroelectrics have been

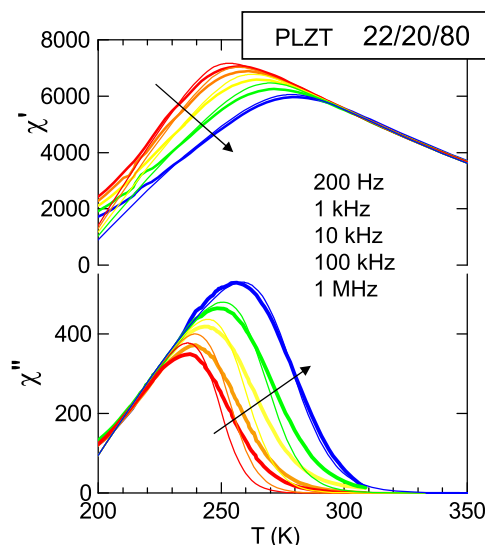


Fig. 6 Dielectric permittivity versus temperature at different frequencies for a relaxor ferroelectric. The arrows show the increasing of measurement frequencies. Modified from Cordero, F., Corti, M., Craciun, F., *et al.*, 2005. Polar and nonpolar atomic motions in the relaxor ferroelectric PLZT from dielectric, anelastic and NMR relaxation. *Phys. Rev. B* 71, 094112-1-9.

compared with experimental diffuse scattering results. More specifically, MDS of $72 \times 72 \times 72$ unit cells of 0.75PMN–0.25 PT has been made between 100 and 700 K, and the diffuse scattering intensity, which is related to the deviation of local structure from the average structure, was obtained. From the analyses of the angles between the Pb–O₁₂ dipoles along the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions, it has been found that the relaxor state consists in a multidomain disordered ferroelectric state with a very small domain size (2–10 nm) and with various low-angle domain walls separating small polar domains, without a nonpolar matrix. It has been shown that the peculiar butterfly shape of diffuse scattering patterns is a characteristic of this multidomain state. Conceptual pictures of the structural changes through the phase transitions and corresponding computed diffuse scattering patterns have been obtained. The successive phases, starting from high temperature, have been found to be: Paraelectric phase ($T > T_b$), relaxor phase with fluctuating domains ($T^* < T < T_b$), relaxor phase with static and dynamic domains ($T_f < T < T^*$), and frozen phase with static domains with very slow dynamics ($T < T_f$). An important feature is that the surrounding matrix is itself polar, but with different correlations and different dynamics (Takenaka *et al.*, 2017).

By analyzing the influence of the local environment on the Pb displacements, using the distribution of time-delay-averaged angle autocorrelation, it was found that in various environments (i.e., in subgroups with different B-cation nearest neighbors) the correlations show different dynamics and develop at different temperature (Takenaka *et al.*, 2017). In the case of PMN–PT, the Mg-rich sites decouple polarization fluctuations of the neighboring Pb sites and are therefore the cause of the small domain size. This is due to the small off-center displacement of Mg²⁺ ions arising from their large size and simple metal electronic structure. This result clearly points to a common microscopic cause of small domain size and relaxor behavior in many apparently different ferroelectric relaxors, residing in the different environment of the ferroelectric ions due to doping or due to the casual distribution of the ions.

The presence of small nanodomains in relaxors has been shown to lead to Kohlrausch–Williams–Watts dielectric relaxation and to Vogel–Fulcher type behavior for the dielectric response of relaxors (Chamberlin, 2014).

Moreover, the peculiar microstructure of the relaxor phase, which involves a high density of domain walls and the presence of a mixture of ferroelectric and paraelectric-like unit cells (Takenaka *et al.*, 2017), favors polarization rotation and gives rise to high piezoelectric response.

Applications

The main applications of the ferroelectric ceramics presented here are based on their high piezoelectric response. Indeed, as underlined in Cross and Heywang (2008), the piezoelectricity market worldwide involves a turnover of billions of dollars, covering a wide range of applications, from information and communications, to industrial automation, medical diagnostics, defense industries, etc.

The field of piezoelectric devices was boosted by the development of ferroelectric ceramics with enhanced piezoelectric properties. On the other hand, the increased market has stimulated the search for new or improved functional ceramics.

As pointed out in Cross and Heywang (2008), the number of installed piezoelectric samples in some industrial fields counts several billions, for example, in automotive applications, buzzer devices, ultrasonic imaging, high power transducers and shock wave generation, printers, ignition devices, etc.

A comprehensive list of application fields of piezoelectric ceramics can be found in [Cross and Heywang \(2008\)](#). In the category of sound and ultrasound devices, the buzzers have reached a market of several billions. They are made of ceramic tapes of soft PZT and are used for sonic alerts. Microphones and speakers based on ceramic tapes of soft PZT or PZT thin films are used in telephones, blood pressure measuring devices, etc. Ultrasonic imaging devices based on diced plates of soft PZT or PZT thin films are used in medical diagnostics. Hydroponic devices are based on PZT ceramics and composites and are used as sources or detectors for sound location.

High power transducers and shock wave generation devices have also reached a market of several billions. They are based on ceramic disks of hard PZT and are used in machining, ultrasound cleaning, lithotripsy, etc. Other applications are for atomizers made of ceramic disks of soft PZT used for oil atomizers, humidifiers, and aerosols. Air ultrasound devices made from ceramic disks of soft PZT are used for distance meters, intrusion alarms, etc.

Other applications are in the category of actuators and motors. For printers the market reached billions of installed samples ([Cross and Heywang, 2008](#)), bars, tubes or multilayer ceramics of soft PZT are used for needle drives and ink jets. For motors and transformers, rings, plates of hard PZT or soft PZT, multilayer ceramics, or even PZT thin films are used for miniaturized, compact motors and transformers.

Also bimorph actuators based on PZT multilayer ceramics are used for microelectromechanical systems like micropumps and Braille devices. Multilayer actuators based on multilayer stacks of soft PZT are used for fine positioning and optics. Injection systems based on multilayer stacks of soft PZT are employed for automotive fuel valves.

In the category of sensors, acceleration sensors based on rings or plates of soft PZT are used for automotive and medical devices. Another application field where the market has reached several billions devices is that of ignition devices based on hard PZT cylinders. These are used for gas and fuel ignition.

Adaptive devices based on various shape samples or multilayer stacks of soft PZT are used for active noise and vibration cancellation, adaptive control, etc. ([Cross and Heywang, 2008](#)).

The market for piezoelectric materials is continuously expanding, in line also with new tendencies toward the transfer and implementation of piezoelectric devices at micro- and nanoscale.

Different requirements are imposed on the employed piezoelectric ceramics used in different applications. For example, for vibrator applications, hard piezoelectric ceramics with high mechanical quality factor are preferred.

Different requirements are also imposed on the shape and dimensions of active elements used for speakers or buzzers in the domain of audible frequencies. Specific elements like unimorphs consisting of a piezoceramic plate bonded with a metallic shim, or bimorphs consisting of two piezoceramic plates bonded together, have been employed. The advantages of the piezoelectric buzzer over electromagnetic devices include high electric power efficiency and compact size. Piezoelectric speakers can have very small dimensions and weight (about 0.7 mm thickness and 0.4 g weight), with very low power consumption ([Uchino, 2017](#)).

Also in the field of ultrasonic transducers, piezoelectric ceramics show superior efficiency and have minor size than magnetostrictive materials. For these applications, piezoelectric materials with high piezoelectric constants but also high mechanical quality factor are preferred, since high power generation without heating is desired ([Uchino, 2017](#)). These transducers are widely used in sonars, ultrasonic washers, ultrasonic scanning detectors for diagnosis and therapy/surgery clinical applications, non-destructive testing, microphones, etc.

Ultrasonic imaging is one of the most developed application fields employing piezoelectric transducers, and it is also largely known due to its clinical applications ([Uchino, 2017](#)). For these imaging applications, ultrasonic transducers work for converting the electrical signal into an acoustic pulse and for converting the received echo back into an electric signal, which is registered, elaborated, and translated into useful images. The received mechanical signal carries information about the density and elasticity of the tissues. When carried out in real time, the ultrasonic imaging process allows following of moving bodies, like heart movement. The advantages of the ultrasound imaging technique over X-ray techniques is obviously related to the safety of employment.

For this type of ultrasonic transducer, besides high electromechanical coupling coefficient, high anisotropy is also desired, that is, a high ratio of the longitudinal mode coupling to the planar mode coupling, together with a large dielectric constant, which enables good electrical impedance match to the system ([Uchino, 2017](#)). Many imaging systems use multiple element array transducers. This structure allows focusing to various penetration depths, by the individual driving of the various elements and use of phase delays.

Other piezoelectric applications include sonochemistry, based on the cavitation effect in liquids. This effect is employed to transform toxic liquids into nontoxic components at ambient temperature.

Ultrasonic technology has been implemented also for transdermal drug delivery, for example, in systems for "needle-free" insulin injection ([Uchino, 2017](#)).

Other applications include piezoelectric transformers. The operation principle of a piezoelectric transformer consists of the input voltage amplification through the vibration energy transfer. The voltage rise ratio is proportional to the length/thickness ratio for a piezoceramic plate formed by a section poled on thickness and another section poled on length ([Uchino, 2017](#)). Piezoelectric transformer advantages over normal electrical transformers include smaller size and the lower noise. Multilayer-type transformers have been also developed in order to increase the voltage rise ratio. Moreover, by inverting the role of the different sections, voltage can also be decreased. This type of transformer has been developed for mobile phones and laptop computers.

Another field where piezoelectric ceramics are largely employed is in piezoelectric actuators such as high precision positioners, miniaturized ultrasonic motors, and vibration dampers. Indeed modern automation equipment requiring ultraprecise positioning

systems in the range of fractions of micrometers and minimotors smaller than 1 cm imposed the unrivaled use of piezoelectric actuators and motors, cutting out the conventional electromagnetic systems (Uchino, 2017).

Piezoelectric pulse drive motors have been also developed. They work in an on/off switching mode and are mainly used in inkjet printers. The pulse drive motor requires a low permittivity material with a quick response, thus soft PZT piezoelectric ceramics are employed.

Other important industrial applications of piezoelectric ceramics are ultrasonic motors. Electromagnetic motors cannot compete with ultrasonic motors at small size level. Indeed electromagnetic motors smaller than 1 cm have very low energy efficiency <1%. Therefore, ultrasonic motors based on piezoceramics, with high efficiency that is also independent of size, are unrivaled in the field of micromotors. The development of this field has been boosted by the urgent demand in the industry of semiconductors for very precise positioners.

Micromotors employing standing-wave type vibrations have also been developed. In this type of motor, the piezoelectric driver forms a resonating structure with another vibratory piece, when properly tuned. The efficiency of this motor can reach values as high as 90% (Uchino, 2017).

Piezoelectric ceramics are employed also in energy harvesting devices, which can recover energy from, e.g., car engines. The energy harvesting devices based on metal–ceramic composite transducers succeed to generate continuously 1 W under a force of a few tens of N and frequency of 100 Hz (Kim *et al.*, 2005). The device can perform two tasks at the same time: Vibration damping and energy harvesting.

Another important application of piezoelectric ceramics is in the field of common rail diesel injectors. The first vehicles equipped with these injectors entered into production in 2000 (Mock and Lubitz, 2008). In the first generation of piezoelectric injectors, a servohydraulic mechanism was employed to move the nozzle. Instead, for gasoline high pressure direct injectors the nozzle is actuated by a piezoactuator. The series production for this injector was begun in 2006 (Mock and Lubitz, 2008).

The use of piezoelectric ceramics in motor injection systems imposes some requirements on their properties, due to the demanding functional conditions: Drive voltage up to 200 V, large piezoelectric extension (40 μm), operating temperatures from -40°C to 160°C , a minimum life time of 10^9 cycles, etc. To fulfill these requirements piezoceramic prismatic stacks have been fabricated by multilayer technology. A few hundred ceramic sheets of about 100 μm have been sandwiched between AgPd thin electrodes with alternate polarity (Mock and Lubitz, 2008). A high effective piezoelectric coefficient of about 750 pm V^{-1} at 2 kV mm^{-1} is required. Soft PZT ceramics doped with rare earth elements at the A-site and/or Nb at the B-site are employed. Besides high piezoelectric response, these materials show also higher Curie temperature.

Conclusions

The field of functional ceramics with ferro/antiferroelectric, relaxor, and piezoelectric properties is continuously expanding, boosted by the increasing market demand. Here, we have introduced some general concepts regarding dielectric materials. The phenomenological treatment of piezoelectrics has been discussed. The effect of crystal symmetry on the reduction of the number of independent piezoelectric moduli in piezoelectric materials has been considered.

Phase transitions in ferroelectrics and antiferroelectrics have been discussed in terms of the phenomenological theory of Landau. A brief presentation of some microscopic models of ferroelectricity and first-principle methods has been given.

A discussion of the effective properties of ferroelectric ceramics has been given. It has been shown that in a first approximation they can be obtained by averaging over the various orientations of the domains in the crystallites. Nonlinear properties of ferroelectric ceramics have been introduced.

General characteristics and most recent models regarding the origin, structure, and behavior of nanopolar regions in relaxor ferroelectrics have been discussed.

The main applications of the ferroelectric ceramics based mainly on the piezoelectric properties have been presented. It has been underlined that the piezoelectricity market worldwide involves already a turnover of billions of dollars, covering a wide range of applications.

Moreover, the market for piezoelectric ceramics is continuously expanding, also in line with the new tendencies toward the transfer and implementation of piezoelectric devices at micro- and nanoscale.

References

- Blinic, R., Zeks, B., 1974. *Soft Modes in Ferroelectrics and Antiferroelectrics*. Amsterdam: North-Holland Publishing Company.
- Bokov, A.A., Ye, Z.G., 2006. Recent progress in relaxor ferroelectrics with perovskite structure. *J. Mater. Sci.* 41, 31–52.
- Chamberlin, R.V., 2014. The big world of nanothermodynamics. *Entropy* 17, 52–73.
- Cochran, W., 1960. Crystal stability and the theory of ferroelectricity. *Adv. in Phys.* 9, 387–423.
- Cohen, R.E., 1992. Origin of ferroelectricity in perovskite oxides. *Nature* 358, 136–138.
- Cohen, R.E., 2006. Relaxors go critical. *Nature* 441, 941–942.
- Cohen, R.E., 2008. First-principles theories of piezoelectric materials. In: Heywang, W., Lubitz, K., Wersing, W. (Eds.), *Piezoelectricity*. Berlin: Springer-Verlag, pp. 471–492.
- Cordero, F., Corti, M., Craciun, F., *et al.*, 2005. Polar and nonpolar atomic motions in the relaxor ferroelectric PLZT from dielectric, anelastic and NMR relaxation. *Phys. Rev. B* 71.094112-1-9.

- Cordero, F., Trequattrini, F., Craciun, F., Galassi, C., 2013. Merging of the polar and tilt instability lines near the respective morphotropic phase boundaries of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$. *Phys. Rev. B* 87.094108-1-9.
- Craciun, F., Cordero, F., Ciuchi, I.V., Mitoseriu, L., Galassi, C., 2015. Refining the phase diagram of $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_{0.9}\text{Ti}_{0.1})_{1-x/4}\text{O}_3$ ceramics by structural, dielectric and anelastic spectroscopy investigations. *J. Appl. Phys.* 117.184103-1-8.
- Gross, L.E., Heywang, W., 2008. Introduction. In: Heywang, W., Lubitz, K., Wersing, W. (Eds.), *Piezoelectricity*. Berlin: Springer-Verlag, pp. 1–5.
- Damjanovic, D., Demartin, M., 1997. Contribution of the irreversible displacement of domain walls to the piezoelectric effect in barium titanate and lead zirconate titanate ceramics. *J. Phys. Condens. Matter* 9, 4943–4953.
- Hao, X.H., Wang, Y., Zhang, L., Zhang, L.W., An, S.L., 2013. Composition-dependent dielectric and energy-storage properties in $(\text{Pb,Lu})(\text{Zr,Sn,Ti})\text{O}_3$ antiferroelectric thick films. *Appl. Phys. Lett.* 102.163903-1-4.
- Hao, X., Zhai, J., Kong, L.B., Xu, Z., 2014. A comprehensive review on the progress of lead zirconate-based antiferroelectrics. *Prog. in Mater. Sci.* 63, 1–57.
- Helke, G., 2008. Piezoelectric PZT ceramics. In: Heywang, W., Lubitz, K., Wersing, W. (Eds.), *Piezoelectricity*. Berlin: Springer-Verlag, pp. 89–130.
- IEEE Standard on Piezoelectricity, 1988. The Institute of Electrical and Electronics Engineers, New York.
- Jaffe, B., Cook, W.R., Jaffe, H., 1971. *Piezoelectric Ceramics*. London: Academic Press.
- Ji, Y., Ren, S., Wang, D., Wang, Y., Ren, X., 2018. Strain glasses. In: Lookman, T., Ren, X. (Eds.), *Frustrated Materials and Ferroic Glasses*. Switzerland: Springer Nature, pp. 183–204.
- Kim, H.W., Priya, S., Uchino, K., Newnham, R.E., 2005. Piezoelectric energy harvesting under high pre-stressed cyclic vibrations. *J. Electroceram.* 15, 27–34.
- Kittel, C., 1951. Theory of antiferroelectric crystals. *Phys. Rev.* 82, 729–732.
- Kittel, C., 1966. *Introduction to Solid State Physics*. New York: John Wiley & Sons.
- Kleemann, W., Dec, J., 2018. Relaxor ferroelectrics and related cluster glasses. In: Lookman, T., Ren, X. (Eds.), *Frustrated Materials and Ferroic Glasses*. Switzerland: Springer Nature, pp. 119–152.
- Landau, L.D., Lifshitz, E.M., 1960. *Electrodynamics of Continuous Media*. Oxford: Pergamon Press.
- Lines, M.E., Glass, A.M., 1977. *Principles and Applications of Ferroelectrics and Related Materials*. Oxford: Clarendon Press.
- Mock, R., Lubitz, K., 2008. Piezoelectric injection systems. In: Heywang, W., Lubitz, K., Wersing, W. (Eds.), *Piezoelectricity*. Berlin: Springer-Verlag, pp. 299–310.
- Mydosh, J.A., 2015. Spin glasses: redux: An updated experimental/materials survey. *Rep. Prog. Phys.* 78.052501-1-25.
- Noheda, B., Cox, D.E., Shirane, G., *et al.*, 2000. Stability of the monoclinic phase in the ferroelectric perovskite $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$. *Phys. Rev. B* 63.014103-1-9.
- Nye, J.F., 1985. *Physical Properties of Crystals*. Oxford: Oxford University Press.
- Park, S.E., Shrout, T.R., 1997. Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals. *J. Appl. Phys.* 82, 1804–1811.
- Resta, R., 1994. Macroscopic polarization in crystalline dielectrics: The geometric phase approach. *Rev. Mod. Phys.* 66, 899–915.
- Sawaguchi, E., Maniwa, H., Hoshino, S., 1951. Antiferroelectric structure of lead zirconate. *Phys. Rev.* 83, 1078.
- Sherrington, D., 2018. What can spin glass theory and analogies tell us about ferroic glasses? In: Lookman, T., Ren, X. (Eds.), *Frustrated Materials and Ferroic Glasses*. Switzerland: Springer Nature, pp. 1–30.
- Slater, J.C., 1950. The Lorentz correction in barium titanate. *Phys. Rev.* 78, 748–760.
- Smits, J.G., 1976. Iterative method for accurate determination of the real and imaginary parts of the materials coefficients of piezoelectric ceramics. *IEEE Trans. Sonics Ultrason.* SU23, 393–401.
- Takenaka, H., Grinberg, I., Liu, S., Rappe, A.M., 2017. Slush-like polar structures in single-crystal relaxors. *Nature* 546, 391–395.
- Toledano, J.C., Toledano, P., 1987. *The Landau Theory of Phase Transitions*. Singapore: World Scientific Publishing.
- Uchino, K., 2017. The development of piezoelectric materials and the new perspective. In: Uchino, K. (Ed.), *Advanced Piezoelectric Materials*. Cambridge: Woodhead Publishing (Elsevier), pp. 1–92.
- Vincent, E., Dupuis, V., 2018. Spin glasses: Experimental signatures and salient outcomes. In: Lookman, T., Ren, X. (Eds.), *Frustrated Materials and Ferroic Glasses*. Switzerland: Springer Nature, pp. 31–56.
- Wersing, W., 2008. Small signal resonance methods. In: Heywang, W., Lubitz, K., Wersing, W. (Eds.), *Piezoelectricity*. Berlin: Springer-Verlag, pp. 423–444.
- Wersing, W., Heywang, W., Beige, H., Thomann, H., 2008. The role of ferroelectricity for piezoelectric materials. In: Heywang, W., Lubitz, K., Wersing, W. (Eds.), *Piezoelectricity*. Berlin: Springer-Verlag, pp. 37–88.

Electroceramics: Modeling of Sintering, Microstructure Evolution and Functional Properties

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Introduction

One of the most challenging tasks in material science is the need to produce tailored materials with advanced characteristics for various types of modern applications in wide areas, in order to meet present and future challenges concerning the multifunctionality, mechanical and thermal stability, but also reliability, low cost, low energy budget and sustainability. The traditional trial-and-error loops during the researching and development of new materials can be substantially reduced by using modeling and simulation tools, which are able to propose predictions concerning smart materials, new structural arrangements and conditions to obtain exceptional functional properties. Computer-aided modeling is considered the most recent paradigm of scientific discovery, by completing and supporting the theoretical and experimental investigation approach. Recent advances in numerical methods, coupled with an outstanding increase of computational resources, have led to a tremendous progress in the development and integration of modeling tools to the study of a wide range of materials systems and properties (Gates and Hinkley, 2003; Thornton and Asta, 2005). Therefore, modeling and simulation are currently finding increasing applications not only in basic science concerning the fundamental aspects in materials science, but also in the industrial need of design and optimization of new materials for specific applicative demands, by strongly reducing the time and cost-intensive effort dedicated to the synthesis and characterization of materials.

The continuous trend of technological miniaturization, leading to downscaling of materials, combined with the possibility to experimentally probe the properties at various time- and length-scales, stimulated a growing interest in theoretically describing the observed properties. In this sense, the most recent trend is to integrate the numerical methods in the frame of multiscale modeling, with the final goal to predict the functional properties across relevant length- and time-scales. As schematically indicated in Fig. 1, the main theoretical approaches used to describe materials are (Yip and Short, 2013; Lubber, 2019):

- (1) *Ab-initio* (first principles) and atomistic models, which describe systems at atomic scale taking into account the electronic structure by solving the Schrödinger equation within some certain approximations without involving any empirical inputs and are able to predict real behavior of materials under controlled environment (e.g., ground state properties);
- (2) Molecular dynamics, which is a numerical method dedicated to solve the dynamic Newton equation and simulate the physical movement of atoms and molecules that are subjected to reciprocal interactions for a fixed period of time due to specific mechanical or interatomic forces (treated in quantum or classical approximation);
- (3) Mesoscale discrete models (Monte-Carlo, Ising, Potts, Heisenberg approaches) were developed for spin systems evolving with certain probability due to random variables and are able to describe some macroscopic properties or phenomena (switching in ferromagnetic or ferroelectric materials, grain growth, sintering, statistical economics, social systems, etc.) by considering discrete interactions between single elements of the system;
- (4) Micro-/meso-/macroscale models, either discrete (applied to coarser individual entities like crystallites or ceramic grains, layers, etc.) or continuous, imply a range of homogeneity at a certain scale level. Therefore, the system consists of a number of such repeating unit cells or representative volume elements (inspired from the real micro-/meso-/macroscale structure) whose properties and interactions are derived from lower scale modeling outputs or experiments and can predict average effective properties of inhomogeneous materials (ceramics, metals, composites) in a large range of length-scales. Among them, the effective field models consider the appropriate degree of freedom to describe phenomena at a given length-scale (or energy scale), while ignoring substructure and degrees of freedom at shorter distances (or at high energies). Finite differences methods are numerical tools used to solve differential equations describing materials by approximating the local derivative by finite differences. More effective, finite elements method (FEM) is a numerical tool for solving problems in physics, material science and engineering (e.g. electromagnetic field distributions, currents and heat transfer, fluid flow, etc.) which are mathematically described by complex differential equations. The method is based on the system discretization in a large number of small components (finite elements), for which simpler differential equations with specific boundary conditions are numerically solved and then the properties of the entire system are derived. FEM provides the closest description of inhomogeneous systems as multi-phase materials, composites, etc., in relationship with their microstructure and is a very useful tool to describe electrical, magnetic, thermomechanical, electromechanical, optical processes, etc. Macro-scale models are particularly useful for describing the material's behavior and predicting its response in real structures or devices. Macroscopic properties are usually described by empirical or semi-empirical physical models.

As reviewed in Ref. Iuga (2007), quantum mechanical description is necessary to characterize the electrons and collective behavior of atoms in the material at nanoscale, while at engineering scale, local gradients (of temperature, stress, fields) may be the main driving forces controlling the local materials characteristics. At intermediate scales, defects (charged defects, grain boundaries

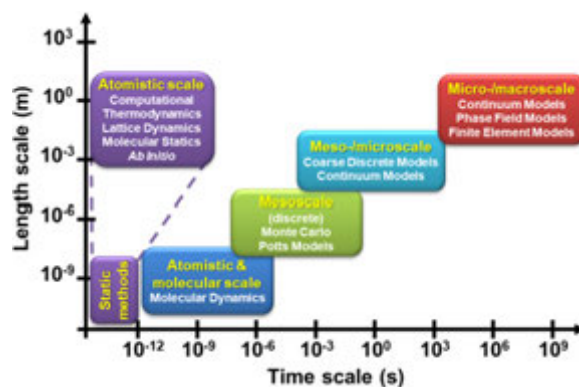


Fig. 1 Different types of models corresponding to various time and length-scales.

in ceramics, mechanical defects, dislocations, layers either localized or extended in scale) will control the microscopic (at the level of tens-hundreds of micrometers) functional properties which in turn, will ultimately determine the continuum macroscale properties.

Polycrystalline ceramics are synthetic nonmetallic inorganic compact aggregates formed by a large number of grains (single- or polycrystalline) of various shapes, size and orientations, determined by the chemical composition and processing parameters. Advanced ceramics have been mostly developed in the last four decades for high-tech specific applications, like structural, mechanical, thermal, electric or magnetic properties. Among them, electroceramics are advanced materials with a broad range of applications as insulators, inductors, superconductors, microwave dielectric resonators, electrooptic, piezo- and pyroelectric transducers and many others, whose development shows an exceptional development related both to the production of new materials and structures as well as on their miniaturization and integration in microelectronic circuits. Like in case of other materials, the functional properties of electroceramic materials depend upon their composition and nano/microstructure. But more than that, what is of highest interest is that their properties can be tuned by external stimulus such as field, temperature, stress, irradiation, chemical composition of the surrounding medium, etc. and often more than one property is present in the same structure, i.e., they show multifunctional character. Therefore, many electroceramics are active materials, whose properties are controllable by external inputs. Among the wide class of smart multifunctional materials, ferroelectric oxides brought outstanding contributions in various technological applications and in particular, in microelectronics (Xu, 1991; Bell, 2008; Bain and Chand, 2017). Their greatest engineering impact is closely related to the progressive growing knowledge in the synthesis of micro/nanostructured oxide particles, to the defect chemistry, and to the control of ceramic processing and sintering mechanisms. The most important ferroelectric oxides employed in microelectronics applications are complex oxides as BaTiO_3 -based ceramics, SrTiO_3 , $\text{Pb}(\text{Zr,Ti})\text{O}_3$ family, PbTiO_3 and its compounds, relaxors as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ or $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, LiNbO_3 or BiFeO_3 , in various structures as ceramics, thick or thin films, multilayers or complex miniaturized integrated structures.

The microstructure of ceramics is characterized by grains, grains boundaries, porosity and glass or secondary phases. To simulate the macroscopic functional properties, it is necessary firstly to build a representative geometry that incorporates the overall features of the real structures, like shape and grain size (and size distribution), pore volume fraction and their geometry and distribution, volume fraction of different phases in composites and their interconnectivity, interfaces between different phases, grain boundary thickness, etc. (Iuga, 2007; Lubner, 2019). According to the scale of modeling and for the accuracy of predicted results, inputs and validation for the models either based on experimental data or from other simulation results (as for example from first principles calculations) are necessary.

In the following, some of the main modeling approaches used to investigate and describe the properties of polycrystalline electroceramics, together with a few case studies are presented.

Models for Describing the Sintering Process and Microstructure Evolution in Electroceramics

General Aspects of Sintering

Besides the composition and phase symmetry, the material microstructure plays an important role in understanding and controlling the macroscopic responses of real materials. More specifically, for electroceramics, information about the nanoscale properties (e.g., ferroelectric domain structure, charge point defects, impurities) and microstructures (ceramic grain size and shape, texturing, nature, thickness and properties of grain boundaries, extended planar defects as dislocations, or volume defects, pores: size, shape and interconnectivity) are necessary to derive their physical and chemical macroscopic properties. Therefore, a good understanding of the microstructure evolution during the preparation steps (powder synthesis, pressing, sintering) is essential for the properties' optimization. Besides the microscopical experimental observation of ceramics, modeling the microstructures is an essential step for understanding and predicting the functional properties.

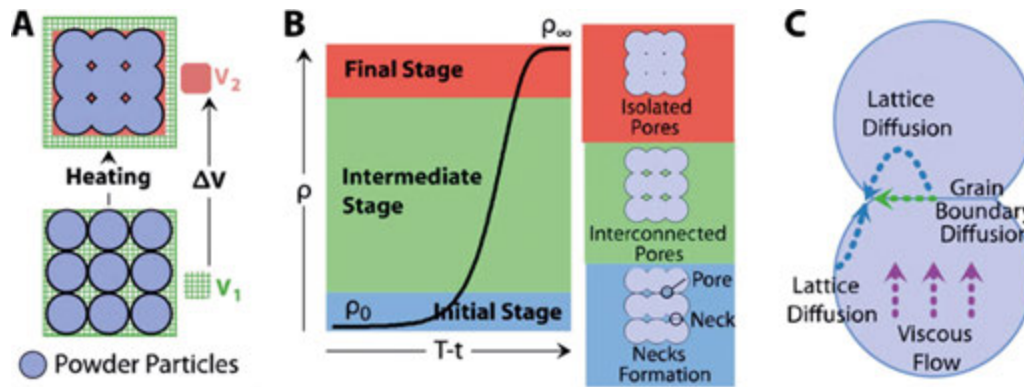


Fig. 2 Schematic representation of sintering stages and densification: A – Volume shrinkage by heating the powder compact; B – Density vs. temperature/time: ρ_0/ρ_∞ – initial/final density; C – Paths for material transport generating modification of density. Adapted from Gómez, S.Y., Hotza, D., 2018. Predicting powder densification during sintering. *Journal of the European Ceramic Society* 38 (4), 1736–1741. doi:10.1016/j.jeurceramsoc.2017.10.020, with permission.

Sintering process represents the conversion of pressed powders (green body) into a dense ceramic with controlled density and microstructure, realized by heating at high temperatures, below the melting point (Gómez and Hotza, 2018). This process takes place by the transport of material to or around the pores (lattice diffusion, grain boundary diffusion, viscous flow) under appropriate conditions of temperature, pressure and environment under the driving force related to the tendency of system to decrease its total surface and interface energy (Bordia *et al.*, 2017; Gómez and Hotza, 2018). Particle bonding, density increase and grain coarsening processes with various weights, take place during the classical sintering stages (Fig. 2).

Examples of Models Aimed to Describe the Sintering Stages and to Generate Ceramic Microstructures

Multiple efforts were dedicated to studies of sintering and microstructural evolution aimed to understand the thermodynamics and to develop appropriate models to quantify the grain growth kinetics, by considering the interplay between powder particle shape and size distribution, impurities and lattice distortions in the green body and the diffusion process, particle rearrangements, chemical reactions at interfaces, etc. Already in the middle of the 20th century the first classical description of grain growth and microstructure evolution during sintering have been proposed for the solid-state sintering, based on the idea of material flow and vacancy flow, both leading to the reduction of the free surface energy (Frenkel, 1945; Bordia *et al.*, 2017). In the next decades, various models describing the initial (Coble, 1961; Coblenz *et al.*, 1980), intermediate (Johnson, 1970; Zhao and Harmer, 1991) and final (Zhao and Harmer, 1991; Kang and Jung, 2004) stage of classical sintering were proposed. Starting from the same powder microstructure, various types of microstructures (grain size and shape, pore morphology and distribution) were generated by recent phase field complex simulations when considering the effect of anisotropic properties of powders (e.g., direction-dependent interface diffusion anisotropy, and grain orientation dependent grain boundary energy anisotropy) (Biswas *et al.*, 2018). One example showing the role of grain boundary anisotropy on the final microstructures generated by phase field simulations is presented in Fig. 3 (Biswas *et al.*, 2018).

Recently, Raether *et al.* (2019) proposed a new integrated microstructure continuous model on solid state sintering which provides highly realistic ceramic microstructures. This approach requires reasonable computer resources and show small statistical variations and includes the most important aspects of current computational microstructural models as: interface energy controlled local equilibrium structures, randomness of diffusion processes, and particle rearrangement. Fig. 4 illustrates such a simulated 3D microstructural evolution during the initial, intermediate and final stage of sintering (Raether *et al.*, 2019).

Due to the difference in the chemical potential of the atoms under curved surfaces, the atoms are transported to the particle neck entailing the redistribution of material on the surface of particles without densification (bonding), and from the particle surfaces or grain boundaries, which induces densification (shrinkage) additionally to bonding (Frenkel, 1945; Raether *et al.*, 2019). The microstructures of the intermediate and final stages of sintering are determined by phenomena as grain-boundary diffusion and lattice diffusion from the grain boundary to the pore surface which were described by kinetic (transport) equations, in which pore-grain boundary interactions and their mobilities were also considered (Frenkel, 1945; Du *et al.*, 2018; Raether *et al.*, 2019).

Not only the formation of residual porosity inherent in electroceramics, but mostly the desired porosity for specific applications is important to be described by models in which to consider the complex processes related to the variety of interactions between pores and grains. For understanding the processing parameters affecting the level and distribution of pores, the pore deformation and grain boundary migration during sintering of porous ceramics were simulated in a recent study by phase-field methods in which the variety of diffusion processes during sintering were considered (Du *et al.*, 2018; Rehn *et al.*, 2019). Therefore, pores of different shapes and sizes were considered in the simulations to investigate the grain boundary migration and pore deformations during the grain growth. Simulations show that the porous microstructure is strongly affected by the contacting

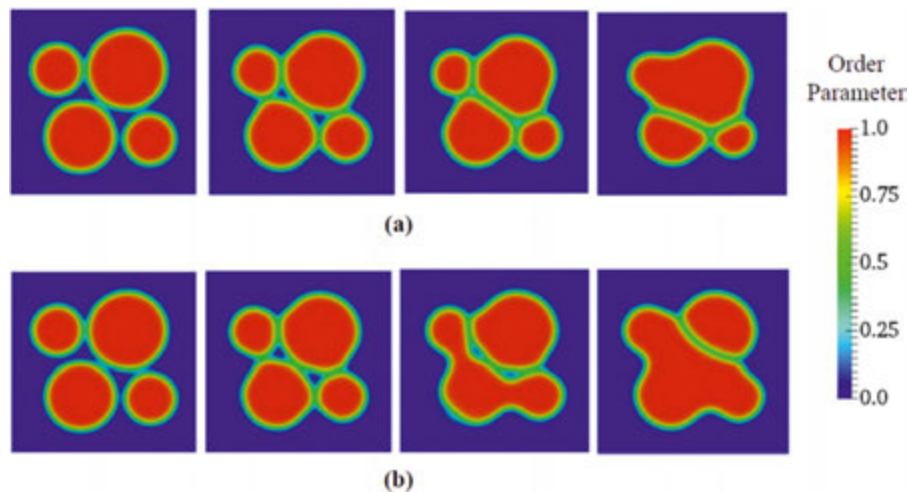


Fig. 3 Microstructural evolution during sintering of particles with different grain sizes, when considering: (a) isotropic properties, (b) anisotropic grain boundary energy. Reprinted from Biswas, S., *et al.*, 2018. Phase field modeling of sintering: Role of grain orientation and anisotropic properties. *Computational Materials Science* 148, 307–319. doi:10.1016/j.commatsci.2018.02.057, with permission.

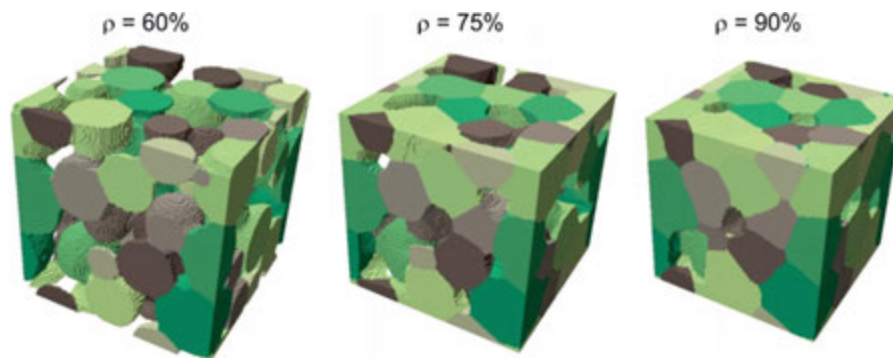


Fig. 4 3D microstructural evolution during the solid-state sintering (initial, intermediate and final stage) with a resolution of 1283 voxels. Reprinted from Raether, F., Seifert, G., Ziebold, H., 2019. Simulation of sintering across scales. *Advanced Theory and Simulations* 2 (7), 1900048. doi:10.1002/adts.201900048, with permission.

mode between pore surface and grain boundaries (Fig. 5), which is in good agreement with experimental observations of real porous ceramic microstructures.

Computational-aided design of microstructures was realized by phase field simulation for textured ferroelectric ceramics, as exemplified in Fig. 6 in which the role of template seeds configuration and corresponding grain growth for a given template composition is shown (Zhang and Liu, 2019), and a plethora of numerical approaches have been developed for generating microstructures in different types of heterogeneous composites (Cheng *et al.*, 2009; Bargmann *et al.*, 2018). An excellent overview of these methods is presented in Ref. Bargmann *et al.* (2018), in which numerical methods to describe realistic microstructures of non-porous materials as polycrystals (grains or lamellar), bi-continuous composites, matrix-inclusion composites (particle reinforced or lamellar reinforced) and porous systems as agglomerates (cellular, dilute voids), fabrics (woven and non-woven) and aggregates are reviewed.

Together with the development of new sintering techniques implemented to improve the densification, and/or suppress the grain growth (like pressure-assisted sintering, microwave sintering, two- or multi-step sintering, and electric field assisted sintering e.g., Spark Plasma Sintering SPS, etc.) (Munir *et al.*, 2006), models for specific processes involved in such sintering techniques were also proposed. Some of them, in particular ones involving highly inhomogeneous systems and describing strongly non-equilibrium processes (e.g., SPS) are still a matter of debate. More specifically, the models describing SPS processes should interconnect at least three different physical processes: the density of the sample determines the local field distribution and electrical behavior, which in turns controls the local temperature distribution who will finally govern the densification rate (Du *et al.*, 2018; Raether *et al.*, 2019; Rehn *et al.*, 2019), while simulations of the processes involved in microwave sintering requires coupling of at least three physical coupled phenomena: stationary electromagnetic waves in cavity and the local field distributions in the sample, heat transfer, and ceramic densification (Bimboim and Carmel, 1999; Bouvard *et al.*, 2010; Rybakov *et al.*, 2013).

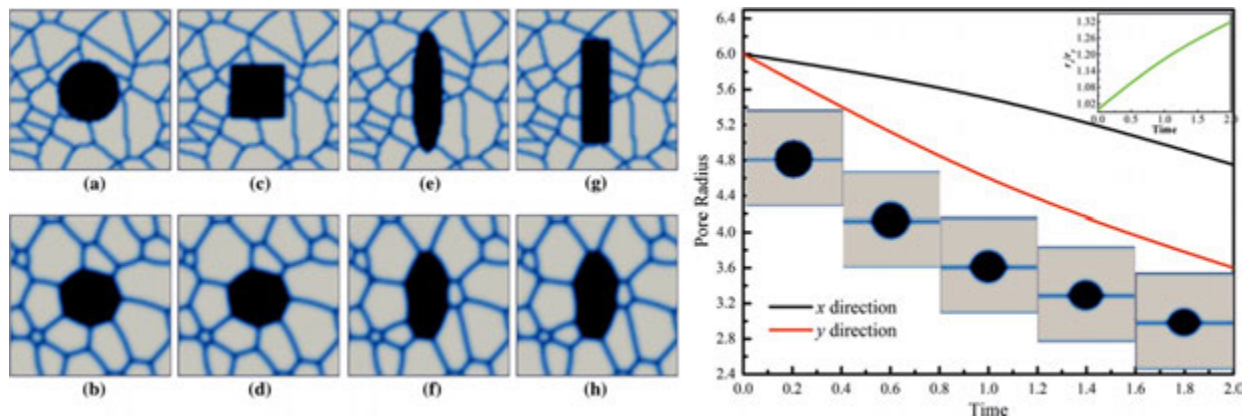


Fig. 5 Left: pore-grain morphology evolution by considering pores of different shapes: a, c, e, g – initial pore agent, b, d, f, h – final pore microstructure after 2×10^4 steps. Right: time evolution of the pore radius (initially spherical) during the sintering process. Adapted from Du, L., et al., 2018. Pore deformation and grain boundary migration during sintering in porous materials: A phase-field approach. Journal of Materials Science 53 (13), 9567–9577. doi:10.1007/s10853-018-2267-7, with permission.

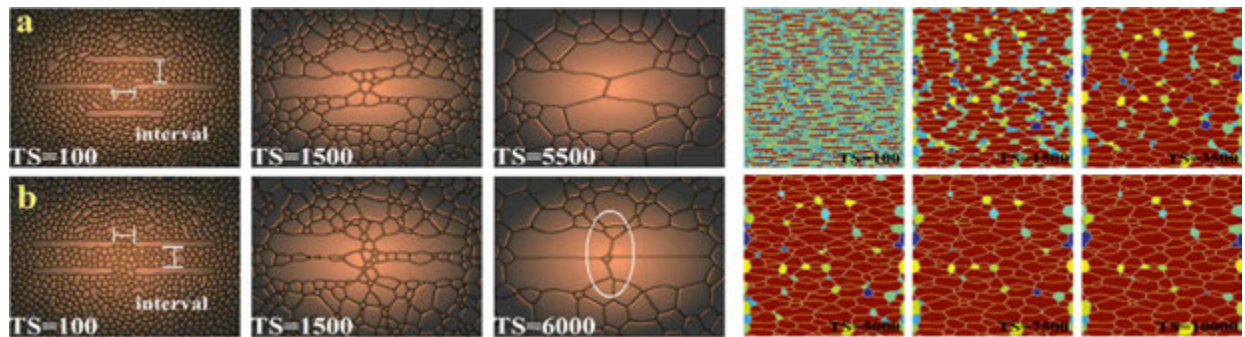


Fig. 6 Left: simulation of sintering of textured ceramics by using template seeds: grain growth at various sintering times for two types of initial template configurations. Right: microstructural evolution for a template fraction of 18.7%. Adapted from Zhang, Y., Liu, L., 2019. Computational design of microstructures of textured ferroelectric ceramics by phase field simulation. Computational Materials Science 159, 24–31. doi:10.1016/j.commatsci.2018.11.051, with permission.

The peculiar aspects of the processes involved in obtaining specific types of engineered microstructures in textured ceramics by template growth (Zhang and Liu, 2019) were also described by phase field simulations (Zhou et al., 2017b,a) and the recent interest in additive manufacturing attracted interest in developing models to produce realistic numerical microstructures (Abdeljawad et al., 2019).

Besides the physics-based models targeting simulation of the physical processes responsible for the microstructure formation and evolution (as the sintering models mentioned before) there are purely geometrical methods solely mimicking the morphology while ignoring the physical basis of the microstructure formation process. It is worth to note that together with numerically generated microstructures, real 3D ceramic microstructures can be reconstructed through experimental characterization of microstructures either by using serial sectioning techniques or based on transmissive radiation, i.e., micro-tomography (Elissalde et al., 2015; Lesseur et al., 2015; Bargmann et al., 2018). However, accurately reconstruction of 3D microstructures for a significant sample volume requires acquisition, storage and processing of a huge amount of data, so that numerically generated realistic microstructures are still applied as a good basis for modeling the functional properties of electroceramic materials.

Models for Describing the Functional Properties of Electroceramics

Effective Dielectric Properties in Inhomogeneous Ceramics: Composites and Porous Ceramics

Theoretical prediction of effective properties for multiphase materials is a very important issue not only for analyzing and optimization of material functional properties, but also for design of new material and structures. Effective medium approximations (EMA) are mesoscale approaches (discrete or continuum-type) proposing analytical or theoretical calculations of the

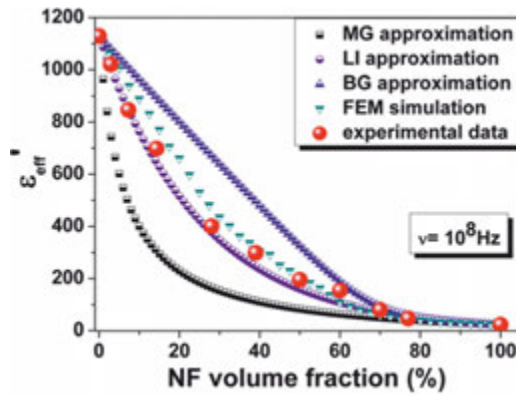


Fig. 7 Real part of the effective permittivity vs. volume filling fraction of nickel ferrite-Nb-doped PZT ceramic composites together with EMA approximations (Maxwell-Garnett, Lichtenecker and Bruggeman) and results of FEM calculations. Reprinted from Ciomaga, C.E., *et al.*, 2012. Low field permittivity of ferroelectric-ferrite ceramic composites: Experiment and modeling. *Journal of Applied Physics* 112 (9), 094103. doi:10.1063/1.4764037, with permission.

material properties in composites use an averaging of the multiple values of the composite material properties and derive approximations for the effective properties. All these EMA approaches consider the composite material to be homogeneous at macro-scale but locally inhomogeneous, being described by local relevant physical parameters and constitutive laws with boundary conditions. The dielectric properties of composites are defined by the permittivity derived from the local atomic/molecular structure of the individual constituents, but also by the composite structure. If the composite consists of two or more homogenous materials and there are boundaries between these material phases, then there are polarization mechanisms in the scale of inhomogeneities in addition to polarization mechanisms related to individual atoms and molecules. If the scale of inhomogeneities in the mixture is much smaller than the wavelength field inside the mixture (i.e., the electromagnetic field cannot “see” the inhomogeneities in the material), one can define the effective permittivity for the material. There are many classical mixing equations (e.g., Bruggeman, Maxwell-Garnett, Lichtenecker, etc.) (Sihvola, 1999; Wang and Pan, 2008) and their usefulness to predict dielectric properties of realistic di-phase composites is limited to some specific microstructures and in limited ranges of compositions. More appropriate description for realistic microstructures is provided by using local scale field calculations (Elissalde *et al.*, 2015; Lesseur *et al.*, 2015) or finite element models (FEM), as for example shown in the description of permittivity in ferroelectric-ferrite composites with different types of phase arrangement (Ciomaga *et al.*, 2012; Guzu *et al.*, 2019) or in other types of dielectric-based composites (Brosseau, 2006; Ciomaga *et al.*, 2014). For example, for nickel ferrite-PZTN ceramics, the FEM calculations provided the best approximation for describing effective dielectric constant in all the range of compositions with respect to EMA models (Fig. 7, (Ciomaga *et al.*, 2012)) because realistic microstructures were employed for calculations.

The FEM method and other types of local potential calculations (as finite difference methods or other approaches for solving Poisson local equations in discrete elements) are very useful tools to derive anisotropic dielectric properties in dielectric-based ceramic composites (see Fig. 8 (Lesseur *et al.*, 2015)) and to design ferroelectric-linear dielectric composite ceramics for tunable applications, for which a non-linear permittivity dependence on the local field is proposed for performing calculations. Tunability, i.e., the field variation of permittivity $\epsilon(E)$ is a typical non-linear dielectric property characteristic of ferroelectrics. However, ferroelectrics also possess high permittivity above 1000, while for tunability applications a permittivity of hundreds would be required (Tagantsev *et al.*, 2003). Therefore, the “dilution” with a non-linear low permittivity dielectric constant was a generally accepted approach to produce tunable composites with desired characteristics (Astafiev *et al.*, 2003). However, usually the tunability was also lost or strongly diminished by the addition of such non-linear dielectric phase. In the last few years it was clearly demonstrated by modeling that only a few specific configurations in such composites provide the required reduction of permittivity while preserving a high tunability (Padurariu *et al.*, 2016, 2017). As linear dielectric, besides other low permittivity inclusions, air pore inclusions are most effective to induce electric field fringes and to concentrate the electric field in some specific regions of the material determining a significant tunability response. However, the pore size, shape and distribution should be well controlled during the ceramic processing, because some local configurations give rise to a diminished response with respect to one of the pure ferroelectric material (Padurariu *et al.*, 2016, 2017).

Porosity is inherent to ceramic processing and usually is detrimental for the functional properties of ceramics. However, for some specific types of pore microstructures, the properties can be enhanced due to the favorable pore configurations allowing a field enhancement in some desired material regions (so called “hot spots”). For example, the role of variable amounts of anisotropic pores on the dielectric properties of PZT ceramics was investigated and the importance of pore’s shape factor was estimated by calculations (Fig. 9 (Olariu *et al.*, 2013)). It was demonstrated that the fastest decrease of permittivity versus porosity is realized for elongated pores rather than for spherical pores inclusions (Olariu *et al.*, 2013). The same trend was experimentally shown for (Ba,Sr)TiO₃ ceramics with lamellar porosity, which was also described by FEM calculations (Stanculescu *et al.*, 2015).

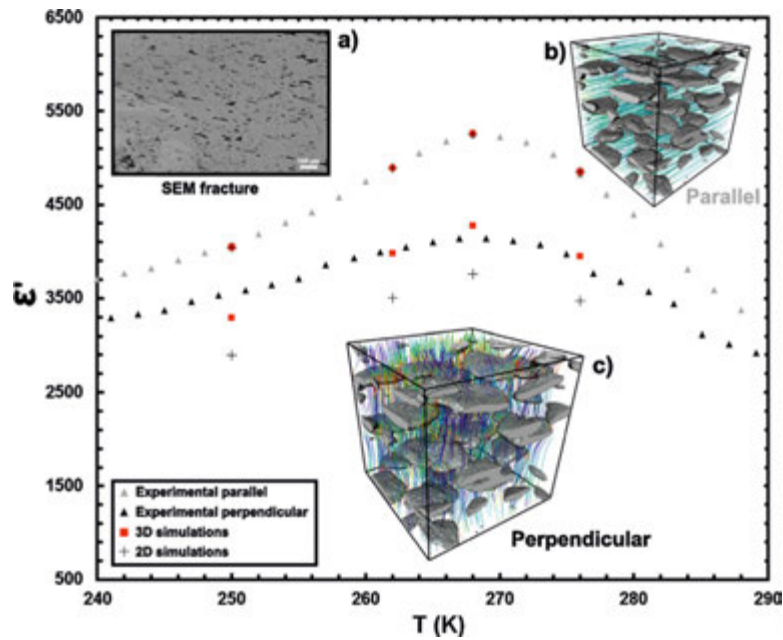


Fig. 8 Permittivity of BaSrTiO₃ ceramic composites with MgO anisotropic inclusions and calculations using real microstructures determined by XRD micro-tomography. Reprinted from Lesseur, J., *et al.*, 2015. 3D mapping of anisotropic ferroelectric/dielectric composites. *Journal of the European Ceramic Society* 35 (1), 337–345. doi:10.1016/j.jeurceramsoc.2014.07.032, with permission.

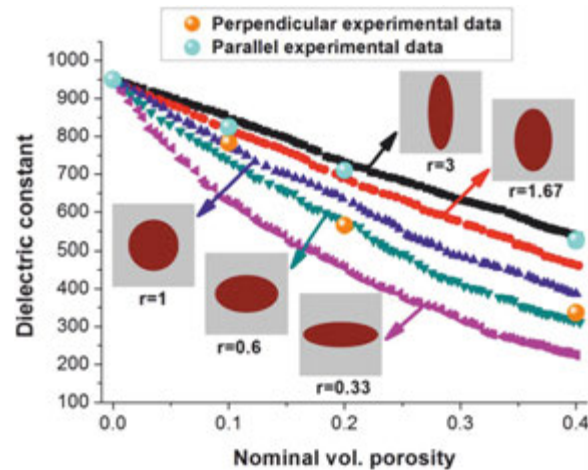


Fig. 9 Effective permittivity vs. porosity for different aspect ratios and experimental permittivity data for parallel and perpendicular configurations. Reprinted from Olariu, C.S., *et al.*, 2013. Investigation of low field dielectric properties of anisotropic porous Pb(Zr,Ti)O₃ ceramics: experiment and modeling. *Journal of Applied Physics* 114 (21), doi:10.1063/1.4837616, with permission.

Even the calculations using 2D microstructures derived from SEM imaging provide relevant qualitative results concerning the permittivity, tunability and polarization responses in ferroelectric-linear dielectric composites, it is highly important to note that only the 3D FEM modeling is the correct approach for predicting correct responses in materials with realistic microstructures (Lesseur *et al.*, 2015; Padurariu and Mitoseriu, 2016a). As clearly demonstrated in Ref. (Padurariu and Mitoseriu, 2016a), the field distributions for 2D and 3D models generated for randomly distributed phases are different (Fig. 10 – Left) and this reflects mostly on the effective nonlinear dielectric properties. Namely, the 2D approach over-estimates the tunability, providing tunability values even higher than in pure ferroelectric material at low amounts of the linear dielectric filler in ferroelectric-linear dielectric composites, and strongly under-estimates the tunability for concentrations of the linear dielectric phase above 70% (Fig. 10 – Right) (Padurariu and Mitoseriu, 2016a). Therefore, the limits of such approaches should be always critically discussed.

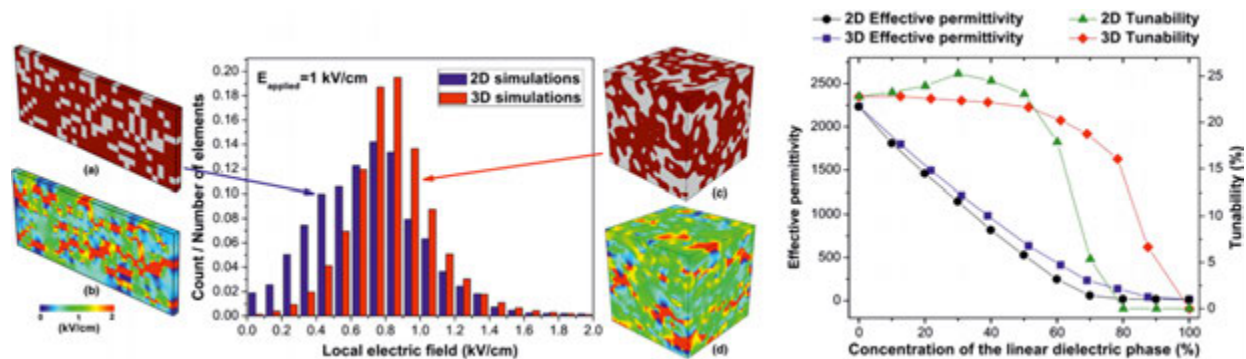


Fig. 10 Simulated 2D and 3D local field distributions for $(\text{Ba,Sr})\text{TiO}_3$ -linear dielectric composite ceramic (Left) and the corresponding computed permittivity and tunability (Right) for various concentrations of the linear dielectric phase. Adapted from Padurariu, L., Mitoseriu, L., 2016a. Comment on "The impact of composite effect on dielectric constant and tunability in ferroelectric-dielectric system". *Journal of the American Ceramic Society* 99 (11), 3816–3817. doi:10.1111/jace.14421, with permission.

Description of the Role of Defects, Interfaces, Grain Boundaries and Size Effects on the Electrical Properties of Ceramics

Defects

Defects are always present in real materials and it is necessary to understand how they affect their macroscopic (functional) properties and performances. In particular, the presence of charged defects like vacancies or substitutional ions may deteriorate a property, like for example scattering by charged defects which is known to reduce the electron mobility (Lischner, 2019). Some charged defects may also enhance properties or even introduce completely new functionality, this allowing the rational design of defect-based functionality (so called "defect engineering"), like for example in the silicon-based conventional semiconductor technology generated by doped materials. Modeling charged impurities is particularly challenging because their properties are determined by physical-chemical processes taking place on multiple length scales: charge transfer is determined by the short-ranged overlap of frontier orbitals, the screened potential of the charged defects is affected by the long-ranged dielectric response bulk material and the effective dielectric response is determined by meso- and macroscale electrical material characteristics (permittivity, conductivity). To capture such a complex interplay, multiscale theories combining first principles methods with mesoscale and coarse-grained approaches, such as interacting continuum models have been proposed (Homer, 2019; Lischner, 2019).

Grain boundaries

The topic of interface-controlled electroceramics whose electrical properties are predominantly determined by their grain boundaries is of enormous technological importance as well as high scientific interest. Their peculiar non-linear transport properties are caused by space charge layers owing to the formation of double Schottky barriers at the grain boundaries. The formation of such a charged region at the grain boundary region is a result of the discontinuity of the ionic lattice properties, Fermi level mismatch and of the difference in the adsorption (or segregation) of charged defects at the interfaces. In pure materials, intrinsic electric boundary charge arises from localized surface states for charged ions and for electrons and charged vacancies with energies different from the bulk values. The resulting boundary compositions, stoichiometry, and associated electric charges depend on the composition (purity) and processing and sintering parameters. Generally, a random grain boundary contains steps and kinks which can act as sources and sinks for ion vacancies. Therefore, the requirement for charge neutrality into the bulk gives rise to a boundary charge and an associated space charge region. When doped with aliovalent ions in solid solutions, the vacancy concentrations in the bulk and the electric charge on the boundary are affected, while heterovalent substitutions produce depleted regions at the grain boundaries and Schottky barriers (when an important difference between the bulk and grain boundary conductivity appears as result of dopants segregation at grain boundaries) (Chen and Yang, 2011; Preis and Sitte, 2015; Uriz *et al.*, 2018). Defect chemical model-based approaches (Landau lattice ferroelectric models combined with Schottky double barrier model) describing the combined ferroelectric-semiconductor character of n - doped oxides as BaTiO_3 and his solid solutions were proposed in order to derive the bulk and grain boundary resistivity as a function of temperature, dc bias, and other parameters as doping level, oxygen partial pressure or type of ferroelectric lattice or in p-doped oxides (as SrTiO_3) for the simulation of charge transport across grain boundaries under dc load (Höbling and Waser, 2002). Grain boundary engineered ceramics are essential for varistors applications (zinc oxide-based compositions or positive temperature coefficient resistive materials (PTCR) such as n-doped semiconductor BaTiO_3 ceramics), for giant permittivity materials as ceramics with semiconductor grains and high-insulating grain boundary layers or in ferrite ceramics for which the impedance and magnetic properties are strongly dependent on the nature and properties of grain boundaries.

The different electrical properties of grain boundaries with respect to their cores in non-doped ferroelectric ceramics have been usually described by using brick-layer models, as reviewed in Refs. Emelyanov *et al.* (2002); Petzelt (2010). In such ceramics, the grains have a core-shell structure (Fig. 11), with grain boundaries of variable thickness, which are considered as non-ferroelectric ("dead-layer" region) with a field-independent low-permittivity which fully isolate the ferroelectric core region (grain bulk).

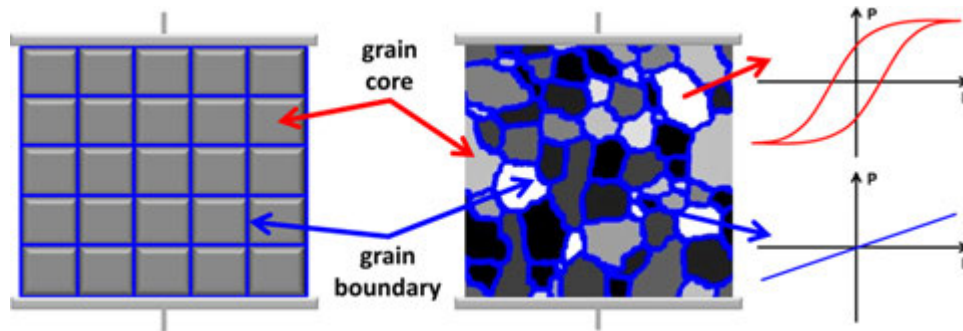


Fig. 11 “Brick layer” model for ferroelectric ceramics: linear dielectric grain boundary, ferroelectric grain core.

Therefore, any ceramic material may be described as a composite and effective field models (Emelyanov *et al.*, 2002; Polotai *et al.*, 2003; Petzelt, 2010) or numerical approaches (Padurariu *et al.*, 2012; Padurariu and Mitoseriu, 2016b; Wu *et al.*, 2016) can be employed to compute their dielectric effective properties. An important observation derived by such numerical calculations is the field inhomogeneity inside the ceramic material, even in plan-parallel capacitor configuration, which only recently started to be considered in literature.

The impact of grain boundaries on the macroscopic properties of ferroelectric ceramics is enhanced when reducing their grain size down to nanoscale (tenths of nanometers), due to the increasing weight of a large amount of grain boundaries with respect to the contribution of grain cores. Practically, all the electrical properties of nanostructured ceramics are determined to a large extent by their large number of grain boundaries. This “dilution effect” can explain the strong reduction of the effective permittivity towards the complete disappearance of the ferro-para phase transition and decrease of tunability towards a permittivity versus field linearization when reducing grain size (scale-dependent extrinsic properties). The presence of a large number of grain boundaries in nanostructured ceramics completely changes the field distribution inside the ceramic volume into a highly inhomogeneous one, as demonstrated by FEM calculations (Curecheriu *et al.*, 2010; Padurariu *et al.*, 2012; Padurariu and Mitoseriu, 2016b; Wu *et al.*, 2016). Due to the electrical boundary conditions, the highest voltage is practically applied onto the low-permittivity grain boundaries which are placed perpendicular to the field lines (Fig. 12) (Padurariu *et al.*, 2012).

Due to this effect, the permittivity is diminished and the breakdown field is much higher in nanostructured ferroelectric ceramics than in the coarse ones, as it was experimentally noticed and demonstrated by estimating the breakdown probability by phase field and FEM calculations (Fig. 13) (Cai *et al.*, 2018). Under the same applied field, the finer ceramics show a lower discharge energy density, but higher storage efficiency. Therefore, ultrafine ceramics meet the necessary requirements for being used in applications for electrostatic energy storage devices.

Grain size effects

In order to predict the role of reducing grain size on the phase transformation, polarization, tunability, switching character or piezoelectric properties as a function of grain size and of the electrical properties of core and shell components, the local field calculations by FEM approach in such core-shell (ferroelectric – linear dielectric) structures were usually completed with Landau-Devonshire – based theories (Fang *et al.*, 2010), nucleation-growth models (Boddu *et al.*, 2017) or Preisach approach (Padurariu and Mitoseriu, 2016b; Skaliukh, 2018) for switching. For example, by using a Landau-based model for the permittivity versus field dependence (Johnson approach) for the ferroelectric component, the dependence of permittivity versus applied electric field at various grain sizes for BaTiO₃ ceramics with sizes down to 100 nm was predicted, in an excellent agreement with experimental data (Fig. 14) (Padurariu *et al.*, 2012).

The electric field concentration in some specific regions such as grain boundaries, in the vicinity of pores or structural defects, gives rise to a higher probability for electrical failure (electrical breakdown) and this is detrimental in particular for high voltage applications of electroceramics, as for example for electrostatic energy storage capacity. Besides reducing ceramic grain size, in order to increase the breakdown field, it is necessary either to eliminate defects or to reduce the field concentration near defects. For these reasons, grain boundary-engineered composites formed by ferroelectric ceramic-glass core-shell structures were proposed (Wu *et al.*, 2016). In such structures, as for example in BaSrTiO₃@SiO₂, the absence of interfacial defects allows the design of higher energy storage capacity ceramics by grain boundary engineering (Wei *et al.*, 2013; Elissalde *et al.*, 2015; Wu *et al.*, 2016; Huang *et al.*, 2018).

Description of Domain Structure and Switching Properties of Ferroelectric Ceramics

The paraelectric-to-ferroelectric transition in oxide ferroelectrics is accompanied by lattice strains which cause local deformations and internal mechanical stresses, depending on the boundary constraints. The formation of regions with oriented domains (ferroelectric domain structure) separated by discontinuity regions (domain walls) takes place in order to minimize the system’s free energy, i.e., the electrostatic and internal mechanical stress contributions. The spatial distribution of domains and domain

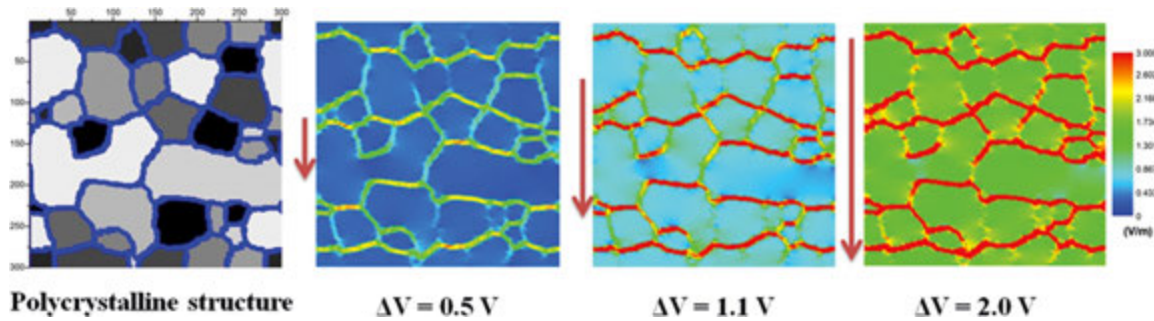


Fig. 12 Polycrystalline ceramic microstructure and the corresponding local field distribution for different applied voltages. Reprinted from Padurariu, L., *et al.*, 2012. Field-dependent permittivity in nanostructured BaTiO₃ ceramics: Modeling and experimental verification. *Physical Review B – Condensed Matter and Materials Physics* 85 (22), 1–9. doi:10.1103/PhysRevB.85.224111, with permission.

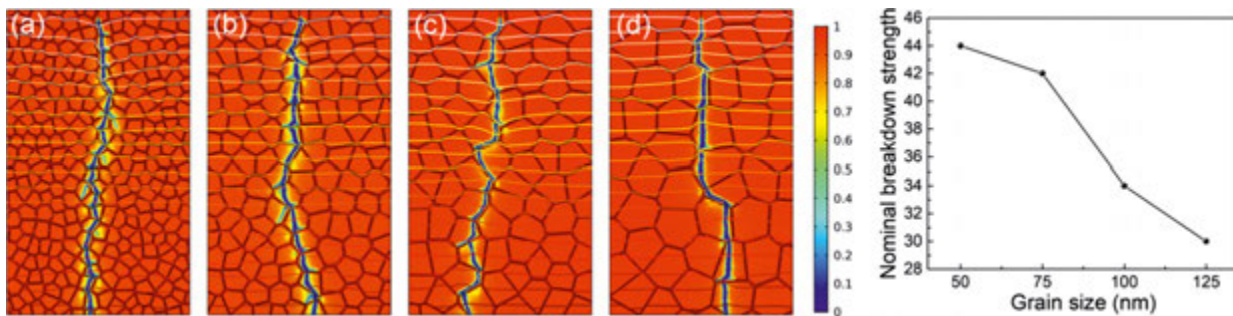


Fig. 13 Left – Simulations of the breakdown paths determined for various BaTiO₃ ceramic grain sizes: (a) 50 nm, (b) 75 nm, (c) 100 nm, (d) 125 nm; Right – Breakdown strength vs. grain size. Adapted from Cai, Z., *et al.*, 2018. Grain-size-dependent dielectric properties in nanograin ferroelectrics. *Journal of the American Ceramic Society* 101 (12), 5487–5496. doi:10.1111/jace.15803, with permission.

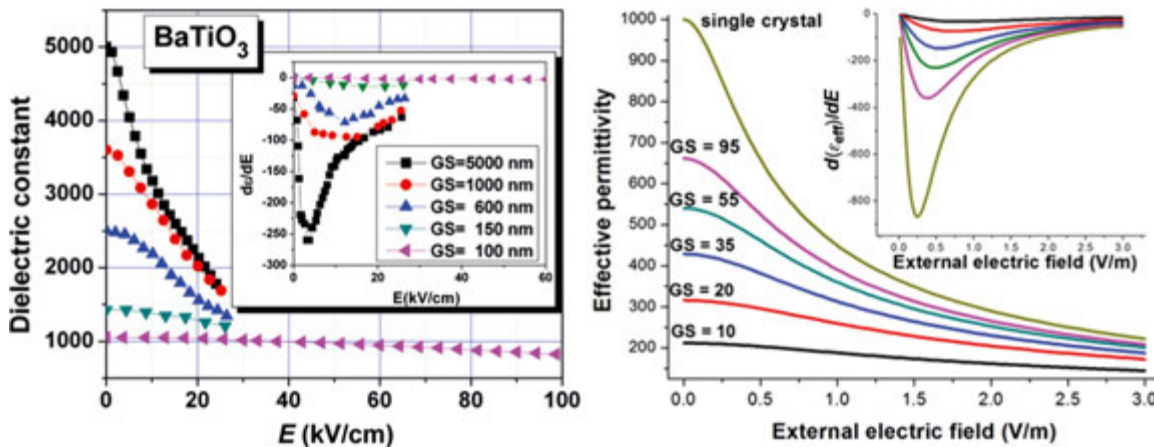


Fig. 14 Experimental (Left) and simulated (Right) permittivity vs. electric field dependence. Inset: field dependence of $d\epsilon/dE$ derivative. Adapted from Padurariu, L., *et al.*, 2012. Field-dependent permittivity in nanostructured BaTiO₃ ceramics: Modeling and experimental verification. *Physical Review B – Condensed Matter and Materials Physics* 85 (22), 1–9. doi:10.1103/PhysRevB.85.224111, with permission.

walls, their structure, patterns, mobility and defects associated to their formation strongly affect the macroscopic dielectric, piezo-, pyro- and ferroelectric properties of materials (Rödel, 2007; Weng and Wong, 2009). The artificial domain patterning is of high interest due to the possibility of exploiting engineered domain configurations to enhance properties necessary in applications like memories, sensing and actuation or energy harvesting (Weng and Wong, 2009; Muench *et al.*, 2019). Field-induced ferroelectric switching is the irreversible (hysteretic) distinctive phenomenon characteristic of ferroelectric materials, involving the nucleation of new domains and domain wall motion under applied electric fields. The ability to predict domain evolution under applied fields and/or stresses is crucial for fundamental understanding of polarization switching mechanisms in ferroelectric ceramics and for technological applications and it was mostly analyzed for single crystalline structures (Potnis *et al.*, 2010; Boddu *et al.*, 2017).

Modeling domain structure in polycrystalline ceramics with realistic microstructure is not a simple task, because it involves the description of complex movements of both ferroelectric and ferroelastic (180° , 90° , etc.) domain walls under specific electrical and mechanical boundary conditions. The three main theoretical approaches used to model the ferroelectric switching and domain structures in BaTiO_3 -like materials are: phenomenological, first-principles and force field-based methods.

The phenomenological methods (Landau-based approaches) describe the free energy of the system as a polynomial expansion of polarization, strain, temperature and external electric field without considering the atomic structure of the system. A further development are the phase-field models, additionally considering the local inhomogeneities with domain-domain interactions and long-range order electric and elastic fields (Choudhury *et al.*, 2005; Chen, 2008; Koyama and Onodera, 2009).

The first-principles methods, such as the density functional theory (DFT) have been applied for small lengths (~ 5 nm) and short time scales (~ 100 ps) only because of high computational costs, restricting investigations of hysteresis loops, sequential phase transitions and domain wall motion occurring at larger length scale (~ 10 – 100 nm) and timescale (larger than ns) (Cohen and Krakauer, 1990; Piskunov *et al.*, 2004).

Force field – based approaches (e.g., shell model, effective Hamiltonian model and bond valence) provided a higher computational speed to perform molecular dynamics (MD) simulations and allowed to compute properties of larger system and at larger time-scales, thus enabling to derive the full chemistry of ferroelectric perovskites, to evaluate the influence of surface chemistry and of oxygen defects on the ferroelectric response, to describe the succession of structural transitions, ferroelectric and thermal hysteresis loops, domain wall movement and polarization responses (Piskunov *et al.*, 2004; Akbarian *et al.*, 2019).

In polycrystalline ceramics, there are two microstructural levels to be described: grain structure (simulated by grain growth models as described in paragraph Section Models for Describing the Sintering Process and Microstructure Evolution in Electroceramics) and domain structure of each individual grain (Choudhury *et al.*, 2007), which were usually described by the inhomogeneous distribution of local polarization components of the polarization vector in the local coordinate system (Choudhury *et al.*, 2007). The total free energy of a ferroelectric polycrystalline ceramic contains the bulk free energy described as a Landau series expansion vs. local polarization terms, an elastic energy component due to the coupling between the strain-stress field (electrostriction terms), an electrostatic energy term (containing the contribution from the external applied field, dipole-dipole interaction and depolarization energy) and a gradient energy which is non-zero only around domain walls and grain boundaries (Choudhury *et al.*, 2007; Su *et al.*, 2015; Li and Wang, 2017). In such calculations, the equilibrium state is obtained when the minimum value of the free energy was reached. By using this approach, the role of grain size on the as-born domain structure (PbTiO_3 ceramic in the virgin state) (Fig. 15) or after the polycrystalline system was subjected to various field sequences (Choudhury *et al.*, 2007) or poling/depolarization processes was determined. The role of non-ferroelectric grain boundaries in

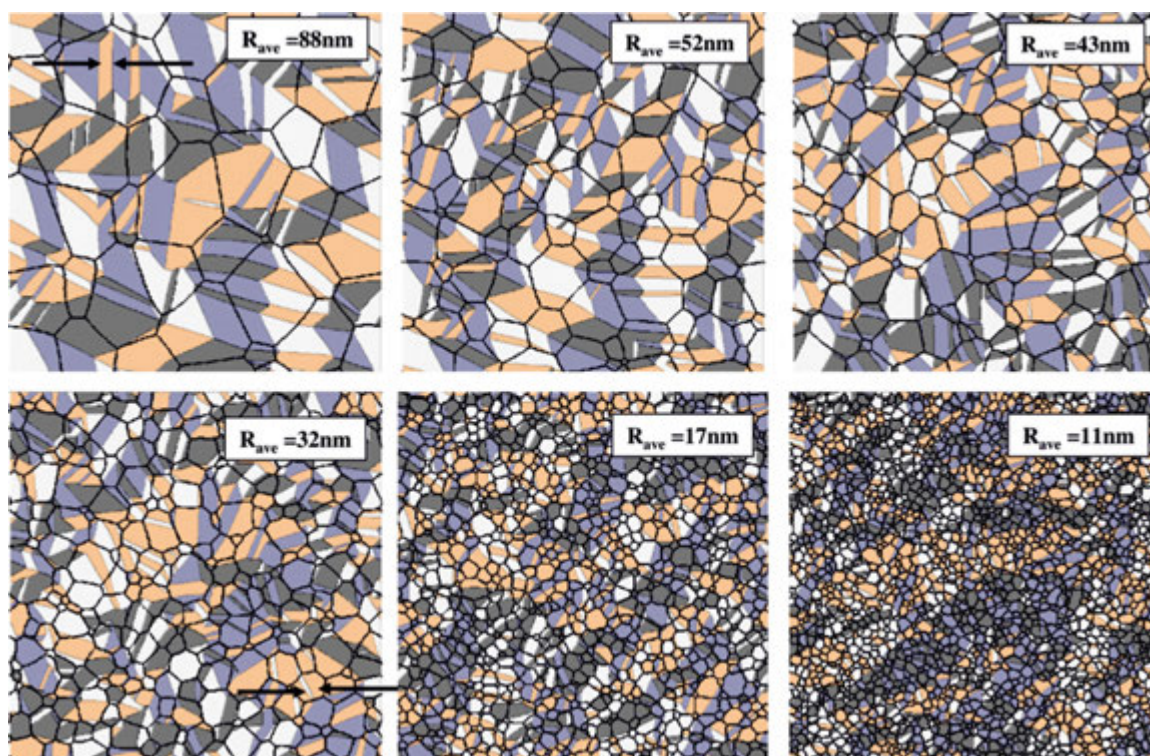


Fig. 15 Phase field simulations of domain structures in polycrystalline PbTiO_3 ceramics for various grain sizes in the range of 11–88 nm. Reprinted from Choudhury, S., *et al.*, 2007. Effect of grain orientation and grain size on ferroelectric domain switching and evolution: Phase field simulations. *Acta Materialia* 55 (4), 1415–1426. doi:10.1016/j.actamat.2006.09.048, with permission.

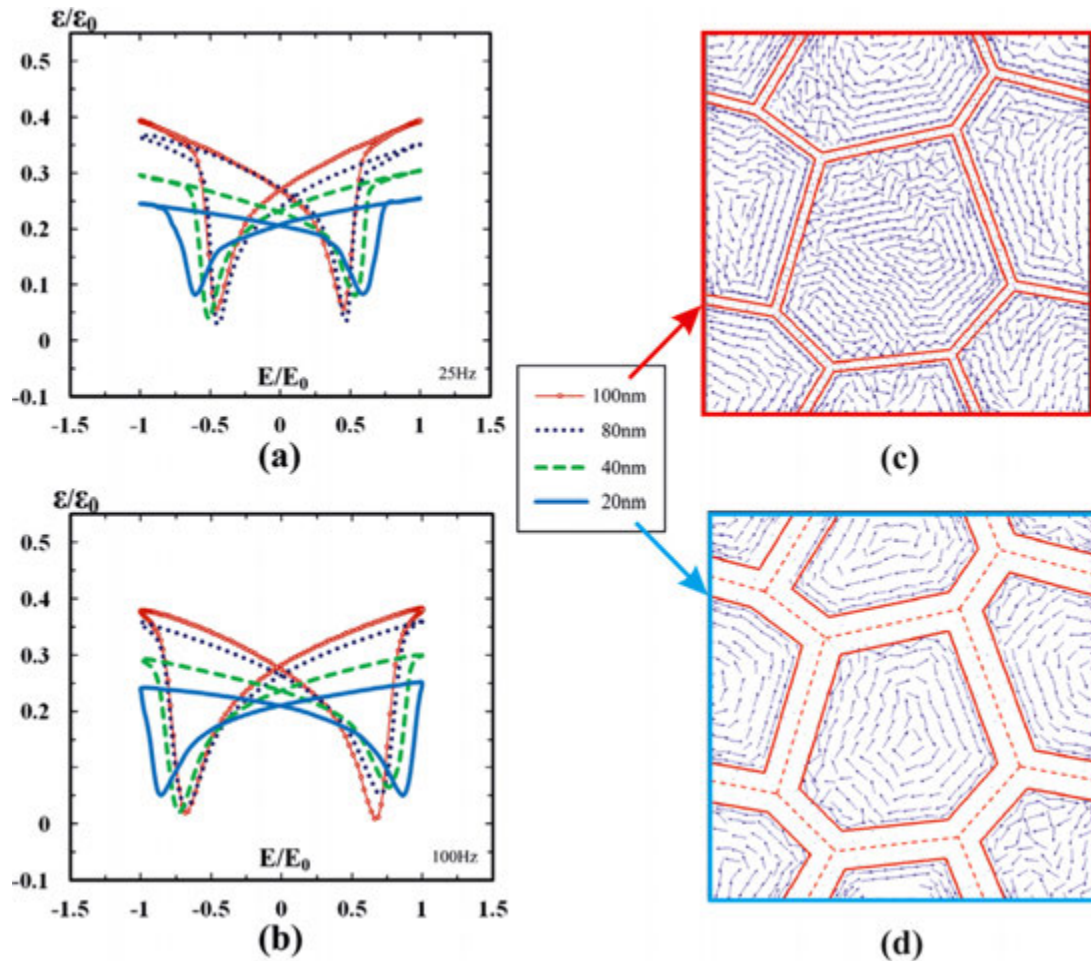


Fig. 16 Simulated grain size dependence of butterfly loops of BaTiO₃ at two frequencies by considering “dead-layer” model for grain boundaries: (a) 25 Hz, (b) 100 Hz; distribution of polarization vectors at zero field for two grain sizes: (c) 100 nm, (d) 20 nm size. Adapted from Su, Y., Liu, N., Weng, G.J., 2015. A phase field study of frequency dependence and grain-size effects in nanocrystalline ferroelectric polycrystals. *Acta Materialia* 87, 293–308. doi:10.1016/j.actamat.2015.01.015, with permission.

core-shell polycrystalline structures or in nanostructured ceramics with various grain sizes on the domain formation and on the $P(E)$ hysteresis responses were also simulated (Su *et al.*, 2015; Li and Wang, 2017).

For example, the results of such calculations show that when reducing the grain size of polycrystalline ceramics, a decrease of the polarization values and of $P(E)$ and $\varepsilon(E)$ loops area is noticed, together with modifications of local domain structures, as result of inactive non-ferroelectric grain boundaries (“dead layers”) (Figs. 16 and 17) (Su *et al.*, 2015; Li and Wang, 2017). These trends have been experimentally observed, as well.

Additionally, the polarization, strain, permittivity vs. field or stress responses under various conditions (temperature, electrical and mechanical inputs, their history or frequency) or the role of charged or dipolar defects acting as pinning centers were also simulated by using various approaches (Shu *et al.*, 2012; Su *et al.*, 2015; Li and Wang, 2017; Yang *et al.*, 2018; Zhao and Soh, 2020). In this way, both local features (e.g., the modification of domain structure at grain boundaries or around pinning centers or defects, topological structures as vortex dipolar domain structures), free energy modifications in the range of phase superposition or morphotropic phase boundaries, as well as the corresponding macroscopic average electrical or electromechanical responses (e.g., defects-induced shifts of the polarization or strain versus field loops) (Yang *et al.*, 2018) have been simulated and compared with experimental features (Fig. 18).

The most complex approach in describing polycrystalline ceramics is the hierarchical multiscale modeling which would allow the best resolution in a broad length- and time-scale, and involves a set of integrated computational methods enabling to bridge from nano to macroscale properties (Tan and Kochmann, 2017). The constitutive model with increasing complexity starts from the description of single-domain ferroelectric, then it extends to single crystals with a multiple domain structure and ends with the description of an effective polycrystalline ceramic material with its complex domain structure, as schematically represented in Fig. 19 (Tan and Kochmann, 2017).

Results from atomistic, molecular, or mesoscale simulation may feed into constitutive equations or continuum models for describing mesoscale properties (domain structures, grain boundary phenomena) and their statistical averaging will provide

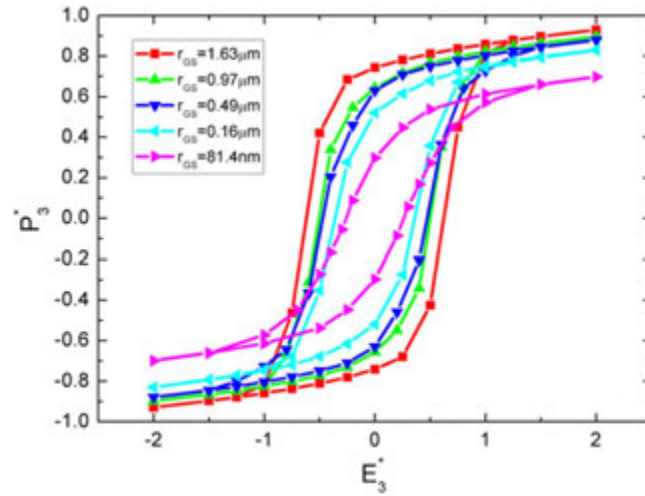


Fig. 17 Simulation of $P(E)$ response of polycrystalline ceramics for various grain sizes. The thickness of grain boundary layer was kept constant. Reprinted from Li, X., Wang, J., 2017. Effect of grain size on the domain structures and electromechanical responses of ferroelectric polycrystal. *Smart Materials and Structures* 26 (1), doi:10.1088/1361-665X/26/1/015013, with permission.

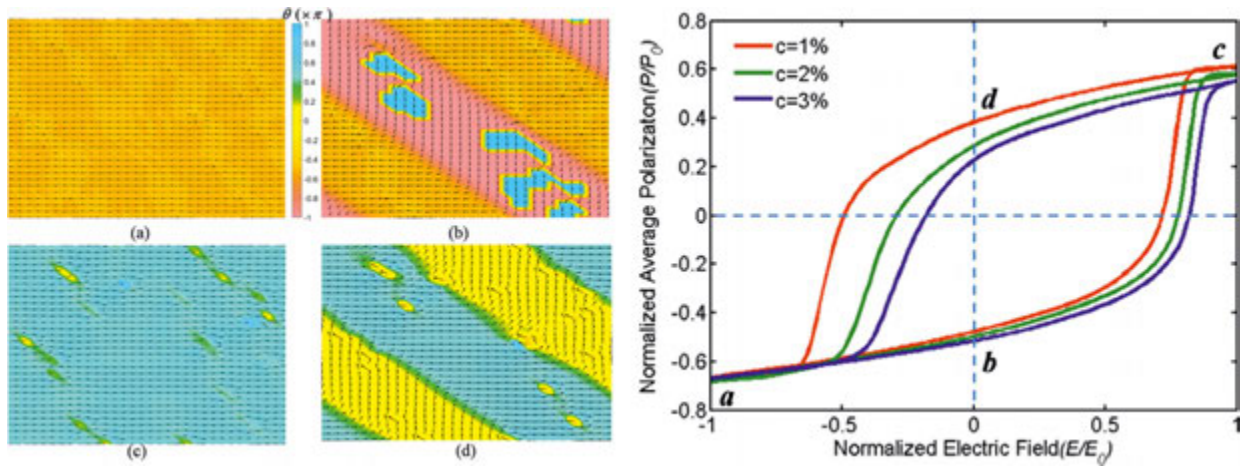


Fig. 18 Simulation of domain structure of ferroelectric ceramic by considering dipolar defects with concentration of 2% for the positions (a), (b), (c), (d) indicated on the corresponding $P(E)$ loops. Adapted from Yang, C., *et al.*, 2018. Theoretical study on local domain pinning effect due to defect dipole alignment. *Journal of Physics D: Applied Physics* 51 (41), doi:10.1088/1361-6463/aadcd4, with permission.

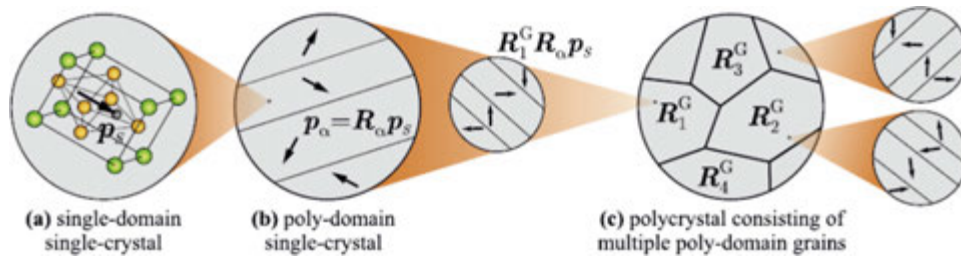


Fig. 19 Schematic representation of multi-scale modeling of tetragonal perovskite ceramics: from single domain single crystal to multi-domain polycrystals. Reprinted from Tan, W.L., Kochmann, D.M., 2017. An effective constitutive model for polycrystalline ferroelectric ceramics: Theoretical framework and numerical examples. *Computational Materials Science* 136, 223–237. doi:10.1016/j.commatsci.2017.04.032, with permission.

information about the macroscopic responses (Tan and Kochmann, 2017). The multiscale simulations could play an important role in material science and technology by providing predictive functional material properties as a result of micro- and meso-scale engineering.

Conclusions

A few examples of theoretical and modeling approaches regarding the description of ferroelectric polycrystalline ceramics, in particular ferroelectrics, have been presented. The complexity of such non-linear materials in which electrical, mechanical and thermal constraints are coupled cannot be exhaustively described by a simple modeling approach. The development of optimized approaches and computing inexpensive tools able to provide material responses describing the observed experimental properties is of high interest. Screening new or tailored electroceramic materials (in terms of chemical or crystalline phase composition, connectivity degree in composites, porosity or grain size) for exploring new or enhanced functionalities is an essential task in wide range technological areas. Optimized computational methods and simulation efforts are therefore highly necessary in order to reduce the time and costs associated to material synthesis and characterization.

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References

- Abdeljawad, F., *et al.*, 2019. Sintering processes in direct ink write additive manufacturing: A mesoscopic modeling approach. *Acta Materialia* 169, 60–75. doi:10.1016/j.actamat.2019.01.011.
- Akbarian, D., *et al.*, 2019. Understanding the influence of defects and surface chemistry on ferroelectric switching: A ReaxFF investigation of BaTiO₃. *Physical Chemistry Chemical Physics* 21 (33), 18240–18249. doi:10.1039/c9cp02955a.
- Astafiev, K.F., *et al.*, 2003. Can the addition of a dielectric improve the figure of merit of a tunable material? *Journal of the European Ceramic Society* 23 (14), 2381–2386. doi:10.1016/S0955-2219(03)00139-0.
- Bain, A.K., Chand, P., 2017. Ferroelectric ceramics: Devices and applications. In *Ferroelectrics*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA, pp. 195–306.
- Bargmann, S., *et al.*, 2018. Generation of 3D representative volume elements for heterogeneous materials: A review. *Progress in Materials Science* 96, 322–384. doi:10.1016/j.pmatsci.2018.02.003.
- Bell, A.J., 2008. Ferroelectrics: The role of ceramic science and engineering. *Journal of the European Ceramic Society* 28 (7), 1307–1317. doi:10.1016/j.jeurceramsoc.2007.12.014.
- Birnboim, A., Carmel, Y., 1999. Simulation of microwave sintering of ceramic bodies with complex geometry. *Journal of the American Ceramic Society* 82 (11), 3024–3030. doi:10.1111/j.1151-2916.1999.tb02197.x.
- Biswas, S., *et al.*, 2018. Phase field modeling of sintering: Role of grain orientation and anisotropic properties. *Computational Materials Science* 148, 307–319. doi:10.1016/j.commatsci.2018.02.057.
- Boddu, V., Endres, F., Steinmann, P., 2017. Molecular dynamics study of ferroelectric domain nucleation and domain switching dynamics. *Scientific Reports* 7 (1), 1–10. doi:10.1038/s41598-017-01002-0.
- Bordia, R.K., Kang, S.J.L., Olevsky, E.A., 2017. Current understanding and future research directions at the onset of the next century of sintering science and technology. *Journal of the American Ceramic Society* 100 (6), 2314–2352. doi:10.1111/jace.14919.
- Bouvard, D., Charmond, S., Carry, C.P., 2010. Finite element modelling of microwave sintering. In *Advances in Sintering Science and Technology*. Ceramic Transactions Series. pp. 171–180.
- Brosseau, C., 2006. Modelling and simulation of dielectric heterostructures: A physical survey from an historical perspective. *Journal of Physics D: Applied Physics* 39 (7), 1277–1294. doi:10.1088/0022-3727/39/7/S02.
- Cai, Z., *et al.*, 2018. Grain-size-dependent dielectric properties in nanograin ferroelectrics. *Journal of the American Ceramic Society* 101 (12), 5487–5496. doi:10.1111/jace.15803.
- Chen, L.Q., 2008. Phase-field method of phase transitions/domain structures in ferroelectric thin films: A review. *Journal of the American Ceramic Society* 91 (6), 1835–1844. doi:10.1111/j.1551-2916.2008.02413.x.
- Chen, Y.L., Yang, S.F., 2011. PTCR effect in donor doped barium titanate: Review of compositions, microstructures, processing and properties. *Advances in Applied Ceramics* 110 (5), 257–269. doi:10.1179/174367611Y.0000000001.
- Cheng, H., *et al.*, 2009. Monte Carlo simulation of microstructure evolution in nano-composite ceramic tool materials. *Computational Materials Science* 47 (2), 326–331. doi:10.1016/j.commatsci.2009.08.009.
- Choudhury, S., *et al.*, 2005. Phase-field simulation of polarization switching and domain evolution in ferroelectric polycrystals. *Acta Materialia* 53 (20), 5313–5321. doi:10.1016/j.actamat.2005.07.040.
- Choudhury, S., *et al.*, 2007. Effect of grain orientation and grain size on ferroelectric domain switching and evolution: Phase field simulations. *Acta Materialia* 55 (4), 1415–1426. doi:10.1016/j.actamat.2006.09.048.
- Ciomaga, C.E., *et al.*, 2012. Low field permittivity of ferroelectric-ferrite ceramic composites: Experiment and modeling. *Journal of Applied Physics* 112 (9), 094103. doi:10.1063/1.4764037.
- Ciomaga, C.E., *et al.*, 2014. Using multi-walled carbon nanotubes in spark plasma sintered Pb(Zr_{0.47}Ti_{0.53})O₃ ceramics for tailoring dielectric and tunability properties. *Journal of Applied Physics* 116 (16), 0–10. doi:10.1063/1.4900527.
- Coble, R.L., 1961. Sintering crystalline solids. I. Intermediate and final state diffusion models. *Journal of Applied Physics* 32 (5), 787–792. doi:10.1063/1.1736107.
- Coblentz, W.S., *et al.*, 1980. Initial stage solid state sintering models. A critical analysis and assessment. *Materials Science Research* 13, 141–157.
- Cohen, R.E., Krakauer, H., 1990. Lattice dynamics and origin of ferroelectricity in BaTiO₃: Linearized-augmented-plane-wave total-energy calculations. *Physical Review B* 42 (10), 6416–6423. doi:10.1103/PhysRevB.42.6416.
- Curecheriu, L., *et al.*, 2010. Grain size effect on the nonlinear dielectric properties of barium titanate ceramics. *Applied Physics Letters* 97 (24), 95–98. doi:10.1063/1.3526375.

- Du, L., *et al.*, 2018. Pore deformation and grain boundary migration during sintering in porous materials: A phase-field approach. *Journal of Materials Science* 53 (13), 9567–9577. doi:10.1007/s10853-018-2267-7.
- Elissalde, C., *et al.*, 2015. Innovative architectures in ferroelectric multi-materials: chemistry, interfaces and strain. *Journal of Advanced Dielectrics* 5 (2), 1–11. doi:10.1142/S2010135X15300017.
- Emelyanov, A.Y., *et al.*, 2002. Grain-boundary effect on the Curie-Weiss law of ferroelectric ceramics and polycrystalline thin films: Calculation by the method of effective medium. *Journal of Electroceramics* 9 (1), 5–16. doi:10.1023/A:1021665300233.
- Fang, C., *et al.*, 2010. Multishell structure and size effect of barium titanate nanoceramics induced by grain surface effects. *Physica Status Solidi (B) Basic Research* 247 (1), 219–224. doi:10.1002/pssb.200945421.
- Frenkel, J.J., 1945. Viscous flow of crystalline bodies under the action of surface tension. *J. Phys* 9, 385.
- Gates, T.S., Hinkley, J.A., 2003. Computational materials: Modeling and simulation of nanostructured materials and systems. In: *Proceedings of the 44th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference*.
- Gómez, S.Y., Holza, D., 2018. Predicting powder densification during sintering. *Journal of the European Ceramic Society* 38 (4), 1736–1741. doi:10.1016/j.jeurceramsoc.2017.10.020.
- Guzu, A., *et al.*, 2019. Functional properties of randomly mixed and layered BaTiO₃ – CoFe₂O₄ ceramic composites close to the percolation limit. *Journal of Alloys and Compounds* 796, 55–64. doi:10.1016/j.jallcom.2019.05.068.
- Höbling, T., Waser, R., 2002. Simulation of the charge transport across grain boundaries in p-type SrTiO₃ ceramics under dc load: Debye relaxation and dc bias dependence of long-term conductivity. *Journal of Applied Physics* 91 (5), 3037–3043. doi:10.1063/1.1448404.
- Homer, E.R., 2019. High-throughput simulations for insight into grain boundary structure-property relationships and other complex microstructural phenomena. *Computational Materials Science* 161 (January), 244–254. doi:10.1016/j.commatsci.2019.01.041.
- Huang, Y.H., *et al.*, 2018. From core-shell Ba_{0.4}Sr_{0.6}TiO₃@SiO₂ particles to dense ceramics with high energy storage performance by spark plasma sintering. *Journal of Materials Chemistry A* 6 (10), 4477–4484. doi:10.1039/c7ta10821d.
- Iuga, M., 2007. *Ab Initio and Finite Element Simulations of Material Properties in Multiphase Ceramics* Dissertation zur Erlangung'.
- Johnson, D.L., 1970. A general model for the intermediate stage of sintering. *Journal of the American Ceramic Society* 53 (10), 574–577. doi:10.1111/j.1151-2916.1970.tb15969.x.
- Kang, S.J.L., Jung, Y. Il, 2004. Sintering kinetics at final stage sintering: Model calculation and map construction. *Acta Materialia* 52 (15), 4573–4578. doi:10.1016/j.actamat.2004.06.015.
- Koyama, T., Onodera, H., 2009. Phase-field simulation of ferroelectric domain microstructure changes in BaTiO₃. *Materials Transactions* 50 (5), 970–976. doi:10.2320/matertrans.MC200806.
- Lesseur, J., *et al.*, 2015. 3D mapping of anisotropic ferroelectric/dielectric composites. *Journal of the European Ceramic Society* 35 (1), 337–345. doi:10.1016/j.jeurceramsoc.2014.07.032.
- Li, X., Wang, J., 2017. Effect of grain size on the domain structures and electromechanical responses of ferroelectric polycrystal. *Smart Materials and Structures* 26 (1), doi:10.1088/1361-665X/26/1/015013.
- Lischner, J., 2019. Multiscale modelling of charged impurities in two-dimensional materials. *Computational Materials Science* 160, 368–373. doi:10.1016/j.commatsci.2019.01.012.
- Luber, S., 2019. Recent progress in computational exploration and design of functional materials. *Computational Materials Science* 161, 127–134. doi:10.1016/j.commatsci.2019.01.040.
- Muench, I., Renuka Balakrishna, A., Huber, J.E., 2019. Periodic boundary conditions for the simulation of 3D domain patterns in tetragonal ferroelectric material. *Archive of Applied Mechanics* 89 (6), 955–972. doi:10.1007/s00419-018-1411-9.
- Munir, Z.A., Anselmi-Tamburini, U., Ohyanagi, M., 2006. The effect of electric field and pressure on the synthesis and consolidation of materials: A review of the spark plasma sintering method. *Journal of Materials Science* 41 (3), 763–777. doi:10.1007/s10853-006-6555-2.
- Olariu, C.S., *et al.*, 2013. Investigation of low field dielectric properties of anisotropic porous Pb(Zr,Ti)O₃ ceramics: experiment and modeling. *Journal of Applied Physics* 114 (21), doi:10.1063/1.4837616.
- Padurariu, C., *et al.*, 2017. Role of the pore interconnectivity on the dielectric, switching and tunability properties of PZTN ceramics. *Ceramics International* 43 (7), 5767–5773. doi:10.1016/j.ceramint.2017.01.123.
- Padurariu, L., *et al.*, 2012. Field-dependent permittivity in nanostructured BaTiO₃ ceramics: Modeling and experimental verification. *Physical Review B – Condensed Matter and Materials Physics* 85 (22), 1–9. doi:10.1103/PhysRevB.85.224111.
- Padurariu, L., Mitoseriu, L., 2016a. Comment on “The Impact of Composite Effect on Dielectric Constant and Tunability in Ferroelectric-Dielectric System”. *Journal of the American Ceramic Society* 99 (11), 3816–3817. doi:10.1111/jace.14421.
- Padurariu, L., Mitoseriu, L., 2016b. Local field engineering approach for tuning dielectric and ferroelectric properties in nanostructured ferroelectrics and composites. In: *Nanoscale Ferroelectrics and Multiferroics*. Chichester: John Wiley & Sons, Ltd, pp. 588–616.
- Padurariu, L., Curecheriu, L.P., Mitoseriu, L., 2016. Nonlinear dielectric properties of paraelectric-dielectric composites described by a 3D finite element method based on Landau-Devonshire theory. *Acta Materialia* 103, 724–734. doi:10.1016/j.actamat.2015.11.008.
- Petzelt, J., 2010. Dielectric grain-size effect in high-permittivity ceramics. *Ferroelectrics* 400 (1), 117–134. doi:10.1080/00150193.2010.505511.
- Piskunov, S., *et al.*, 2004. Bulk properties and electronic structure of SrTiO₃, BaTiO₃, PbTiO₃ perovskites: An ab initio HF/DFT study. *Computational Materials Science* 29 (2), 165–178. doi:10.1016/j.commatsci.2003.08.036.
- Polotai, A.V., Ragulya, A.V., Randall, C.A., 2003. Preparation and size effect in pure nanocrystalline barium titanate ceramics. *Ferroelectrics* 288, 93–102. doi:10.1080/00150190390211972.
- Potnis, P.R., Tsou, N.T., Huber, J.E., 2010. A review of domain modelling and domain imaging techniques in ferroelectric crystals. *Materials* 4 (2), 417–447. doi:10.3390/ma4020417.
- Preis, W., Sitte, W., 2015. Electrical properties of grain boundaries in interfacially controlled functional ceramics. *Journal of Electroceramics* 34 (2–3), 185–206. doi:10.1007/s10832-014-9972-7.
- Raether, F., Seifert, G., Ziebold, H., 2019. Simulation of sintering across scales. *Advanced Theory and Simulations* 2 (7), 1900048. doi:10.1002/adts.201900048.
- Rehn, V., *et al.*, 2019. Phase-field study of grain growth in porous polycrystals. *Acta Materialia* 174, 439–449. doi:10.1016/j.actamat.2019.05.059.
- Rödel, J., 2007. Effective intrinsic linear properties of laminar piezoelectric composites and simple ferroelectric domain structures. *Mechanics of Materials* 39 (4), 302–325. doi:10.1016/j.mechmat.2006.06.002.
- Rybakov, K.I., Olevisky, E.A., Krikun, E.V., 2013. Microwave sintering: Fundamentals and modeling. *Journal of the American Ceramic Society* 96 (4), 1003–1020. doi:10.1111/jace.12278.
- Shu, W., Wang, J., Zhang, T.Y., 2012. Effect of grain boundary on the electromechanical response of ferroelectric polycrystals. *Journal of Applied Physics* 112 (6), 0–16. doi:10.1063/1.4752269.
- Sihvola, A., 1999. *Electromagnetic Mixing Formulae and Applications* (IEEE Electromagnetic Waves Series, 47). London: The Institution of Electrical Engineers, (Available at: <http://amazon.com/o/ASIN/0852967721/>), (accessed 11.02.20).
- Skaliukh, A., 2018. About mathematical models of irreversible polarization processes of a ferroelectric and ferroelastic polycrystals. In *Ferroelectrics and Their Applications*. InTech. doi:10.5772/intechopen.78262.
- Stanculescu, R., *et al.*, 2015. Study of the role of porosity on the functional properties of (Ba,Sr)TiO₃ ceramics. *Journal of Alloys and Compounds* 643, 79–87. doi:10.1016/j.jallcom.2015.03.252.

- Su, Y., Liu, N., Weng, G.J., 2015. A phase field study of frequency dependence and grain-size effects in nanocrystalline ferroelectric polycrystals. *Acta Materialia* 87, 293–308. doi:10.1016/j.actamat.2015.01.015.
- Tagantsev, A.K., *et al.*, 2003. Ferroelectric materials for microwave tunable applications. *Journal of Electroceramics* 11 (1–2), 5–66. doi:10.1142/s2010135X12300022.
- Tan, W.L., Kochmann, D.M., 2017. An effective constitutive model for polycrystalline ferroelectric ceramics: Theoretical framework and numerical examples. *Computational Materials Science* 136, 223–237. doi:10.1016/j.commatsci.2017.04.032.
- Thornton, K., Asta, M., 2005. Current status and outlook of computational materials science education in the US. *Modelling and Simulation in Materials Science and Engineering* 13 (2), doi:10.1088/0965-0393/13/2/R01.
- Uriz, A.J., Buono, C., Aldao, C.M., 2018. Effects of intergranular barrier fluctuations on the electrical conductivity of polycrystalline semiconductors. *Solid State Ionics* 326, 200–204. doi:10.1016/j.ssi.2018.10.002.
- Wang, M., Pan, N., 2008. Predictions of effective physical properties of complex multiphase materials. *Materials Science and Engineering R: Reports* 63 (1), 1–30. doi:10.1016/j.mser.2008.07.001.
- Wei, X., *et al.*, 2013. Reverse boundary layer capacitor model in glass/ceramic composites for energy storage applications. *Journal of Applied Physics* 113 (2), doi:10.1063/1.4775493.
- Weng, G.J., Wong, D.T., 2009. Thermodynamic driving force in ferroelectric crystals with a rank-2 laminated domain pattern, and a study of enhanced electrostriction. *Journal of the Mechanics and Physics of Solids* 57 (3), 571–597. doi:10.1016/j.jmps.2008.11.009.
- Wu, L., Wang, X., Li, L., 2016. Enhanced energy density in core-shell ferroelectric ceramics: Modeling and practical conclusions. *Journal of the American Ceramic Society* 99 (3), 930–937. doi:10.1111/jace.14063.
- Xu, Y., 1991. *Ferroelectric Materials and their Applications*. North-Holland.
- Yang, C., *et al.*, 2018. Theoretical study on local domain pinning effect due to defect dipole alignment. *Journal of Physics D: Applied Physics* 51 (41), doi:10.1088/1361-6463/aadcd4.
- Yip, S., Short, M.P., 2013. Multiscale materials modelling at the mesoscale. *Nature Materials*, 774–777. doi:10.1038/nmat3746.
- Zhang, Y., Liu, L., 2019. Computational design of microstructures of textured ferroelectric ceramics by phase field simulation. *Computational Materials Science* 159, 24–31. doi:10.1016/j.commatsci.2018.11.051.
- Zhao, J., Harmer, M.P., 1991. Sintering kinetics for a model final-stage microstructure: A study of Al_2O_3 . *Philosophical Magazine Letters* 63 (1), 7–14. doi:10.1080/09500839108206594.
- Zhao, X.F., Soh, A.K., 2020. The grain boundary effect on electromechanical property of ferroelectric ceramics. *Scripta Materialia* 178, 313–317. doi:10.1016/j.scriptamat.2019.11.062.
- Zhou, J.E., *et al.*, 2017a. Computational study of textured ferroelectric polycrystals: Dielectric and piezoelectric properties of template-matrix composites. *Journal of Applied Physics* 121 (2), doi:10.1063/1.4973683.
- Zhou, J.E., *et al.*, 2017b. Computational study of textured ferroelectric polycrystals: Texture development during templated grain growth. *Journal of Applied Physics* 121 (6), doi:10.1063/1.4976022.

BaTiO₃-Based Ceramics: Fundamentals, Properties and Applications

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Introduction

Barium titanate, BaTiO₃, has been the first ferroelectric and piezoelectric ceramic developed for commercial applications and it is still widely used, especially as a high permittivity dielectric in multilayer ceramic capacitors (MLCCs) and as a semiconducting material in thermistors with positive temperature coefficient of resistivity (PTCR). A detailed chronology of the discovery and important scientific contributions on the understanding and use of BaTiO₃ was written by [Randall *et al.* \(2004\)](#). According to [Jaffe *et al.* \(1971\)](#) and [Haertling \(1999\)](#), there were three basic steps in the discovery and understanding of ferroelectricity and piezoelectricity in BaTiO₃ which have later paved the way to the development of the entirely new class of ferroelectric ceramic materials with perovskite structure.

The first one, the observation of an unusually high dielectric constant in barium titanate, was independently done in USA, former URSS and Japan during World War II ([Randall *et al.*, 2004](#)). The second step was the realization that the cause of the high permittivity was ferroelectricity ([Wul and Goldman, 1945](#); [von Hippel *et al.*, 1946](#)). Prior to 1940 only two ferroelectric crystals were known, Rochelle salt (potassium sodium tartrate) and potassium dihydrogen phosphate. However, BaTiO₃ has better properties, higher chemical stability and wider temperature range of operation. The third and very important step was the discovery of the “poling” process ([Grey, 1949](#); [Roberts, 1947](#)). The application of a strong electric field orients the polarization of the ferroelectric domains within the grains along the direction of the external field and this “poled” state remains even after the removal of the field. Thus, even the ceramic, despite its polycrystalline nature, behaves like a single crystal showing useful pyroelectric and piezoelectric properties. In fact, unpoled ceramics are not piezoelectrically active because the contribution of the randomly oriented grains would, on the whole, cancel out each other. This breakthrough was of fundamental importance for the large scale production and application of ferroelectric materials, as ceramics are much cheaper than single crystals and their properties, though inferior to those of single crystal, can be more easily tailored.

The crystal structure of BaTiO₃ and the origin of ferroelectricity in this compound from the cooperative ordering of the electrical dipoles arising from the deformation of the prototype perovskite cubic cell was established by [Rooksby \(1945\)](#), [Megaw \(1945\)](#), and [Kay and Vousden \(1949\)](#). The phenomenological theory of phase transitions and properties of barium titanate was introduced by [Devonshire \(1949\)](#). This thermodynamic theory was later used for describing ferroelectricity in many perovskite-type crystals and related structures. The temperature dependence of polarization, permittivity and optical properties in BaTiO₃ single crystals was determined by [Mertz \(1949\)](#), who related the observed variations to the deformations of the lattice. Later, the same author investigated the pressure and electric field dependence of the Curie temperature and interpreted the results using Devonshire's theory ([Mertz, 1950, 1953](#)). The domain structure and the domain switching, which largely affect all properties related to ferroelectricity, were studied, among the others, by [Matthias and von Hippel \(1948\)](#) and by [Merz \(1954\)](#).

The PTCR effect consists of an anomalous steep increase of resistivity of BaTiO₃ (up to 5–6 orders of magnitude) at the tetragonal to cubic phase transition temperature ([Jonker, 1964](#); [Heywang, 1971](#)) and has led to several applications as self-regulating heaters and over-current protection systems. This phenomenon is only observed in polycrystalline BaTiO₃, with the spontaneous polarization of the ferroelectric domains modifying the band-bending and, therefore, the electronic transport across the grain boundary.

In spite of more than 70 years of continuous investigation, barium titanate still attracts great attention as a model ferroelectric system and key components of materials for applications in capacitors, lead-free piezoelectric devices, ceramics and composites for energy storage ([Acosta *et al.*, 2017](#); [Yao *et al.*, 2017](#); [Palneedi *et al.*, 2018](#); [Prateek *et al.*, 2016](#)). According to Web of Science, about 15,000 papers containing “BaTiO₃” or “barium titanate” in their title have been published since 1965. The reasons behind this success are manifold: (1) simple composition and structure; (2) high stability and ease to adapt the properties to the specific application by doping, formation of solid solutions with other perovskites and tailoring of microstructure; (3) relatively simple and cheap processing especially in the case of ceramics; (4) lack of effective competitors in core applications.

Crystal Structure, Nonstoichiometry and Defect Chemistry of BaTiO₃

The BaO–TiO₂ phase diagram shown in [Fig. 1\(a\)](#) ([Lee *et al.*, 2007b](#)) presents at least 9 ternary compounds which have been proven to be useful as electroceramics, with the most important being the perovskite BaTiO₃ for its application in MLCCs and PTCR devices. [Rase and Roy \(1955\)](#) published in 1955 a phase diagram in which many phase relationships were clarified. This phase diagram was further modified by [O'Bryan and Thomson \(1974\)](#), [Negas *et al.* \(1974\)](#), [Ritter *et al.* \(1986\)](#) and, most recently, by [Lee *et al.* \(2007b\)](#).

Below 1460°C, BaTiO₃ possesses the perovskite structure. At higher temperature a hexagonal polymorph (6H-type, s.g. *P63/mmc*) with non-perovskite structure appears. The perovskite to 6H transition temperature is very sensitive to the presence of acceptor dopants, as discussed in Section “Incorporation of Transition Metal Ions and Other Acceptors”.

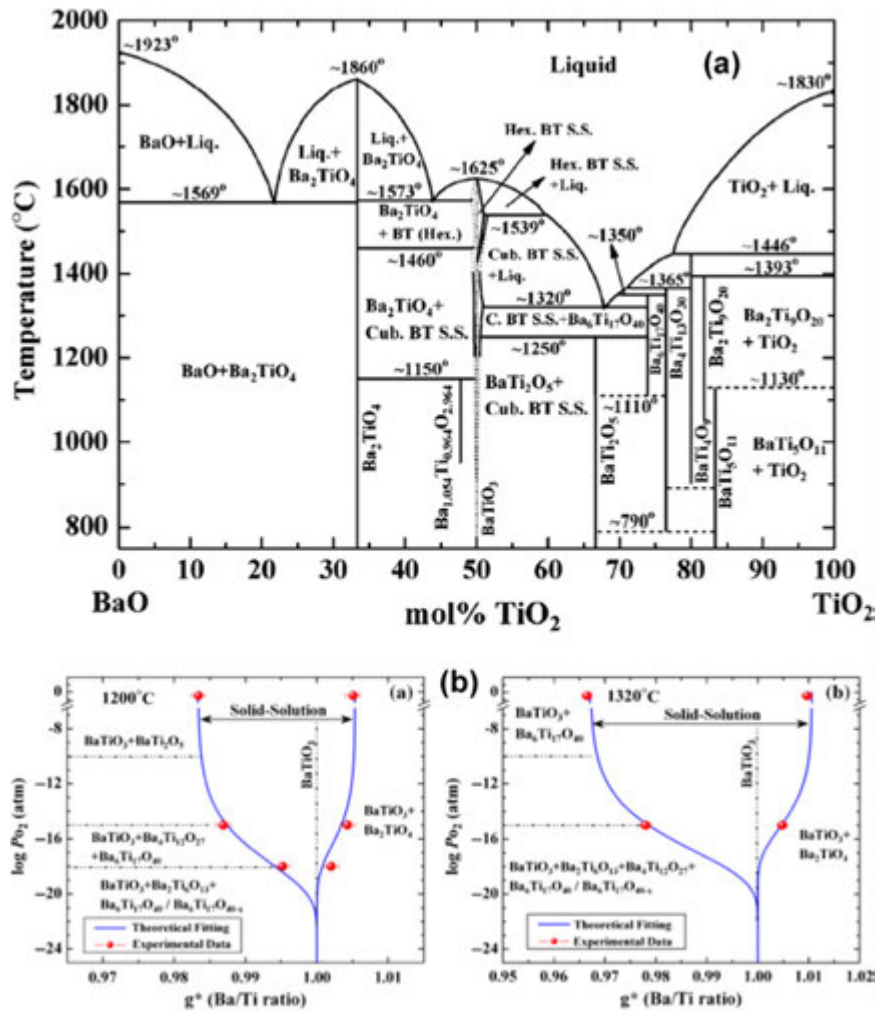


Fig. 1 (a) Pseudo-binary phase diagram of the BaO–TiO₂ system under ambient air conditions. (b) Variation of solubility regime as a function of oxygen partial pressure on the Ba- and Ti-rich sides of BaTiO₃ at 1200°C (left) and 1320°C (right). Reprinted from ref. (a) Lee, S., Liu, Z.-K., Randall, C.A., 2007b. Modified phase diagram for the barium oxide-titanium dioxide system for the ferroelectric barium titanate. *Journal of the American Ceramic Society* 90, 2589–2594, with permission of Wiley. Copyright American Ceramic Society (2007). (b) Lee, S., Randall, C.A., 2008. Comprehensive linkage of defect and phase equilibria through ferroelectric transition behavior in BaTiO₃-based dielectrics: Part 2. Defect modeling under low oxygen partial pressure conditions. *Journal of the American Ceramic Society* 91, 1753–1761, with permission of Wiley. Copyright American Ceramic Society (2008).

The perovskite form of BaTiO₃ exhibits different crystallographic variants, depending on temperature (Megaw, 1945; Kay and Vousden, 1949; Kwei *et al.*, 1993), as shown in Fig. 2. The high-temperature cubic form has the prototype ABO₃ (with Ba²⁺ as A and Ti⁴⁺ as B) perovskite structure. This is a centrosymmetric structure with Ba²⁺ at the corners, Ti⁴⁺ at the center, and the oxygen at the face centers. The titanium ion is octahedrally coordinated by six oxygen ions while Ba²⁺ has a dodecahedral coordination. At the Curie temperature, $T_C = 120\text{--}130^\circ\text{C}$, it turns from the high temperature paraelectric cubic form (*C*, *Pm* $\bar{3}$ *m*) to the ferroelectric tetragonal structure (*T*, *P4mm*). On further cooling, two other ferroelectric phases are observed: orthorhombic (*O*, *Amm*2), below $5\text{--}15^\circ\text{C}$, and rhombohedral (*R*, *R*3*m*), below -80 to $(-90)^\circ\text{C}$. Discontinuities of the small signal dielectric constant are observed at the transition temperatures (Fig. 2). All polar forms originate from a small deformation of the prototype cubic lattice arising from the off-center displacement of the Ti ion (about $0.1\text{ \AA}$ at room temperature) in the TiO₆ octahedron. Each of these variants can be thought as deformations of the cubic unit cell along an edge ([001], tetragonal), along a face diagonal ([011], orthorhombic), or along a body diagonal ([111], rhombohedral). Likewise, the orientation of the electrical dipole is [001], [011] and [111] for the *T*, *O* and *R* modifications, respectively. The cooperative, long-range ordering of the electrical dipoles gives rise to macroscopic spontaneous polarization (P_s), spontaneous lattice strain and ferroelectricity (Damjanovic, 1998). At room temperature the ratio c/a of the lattice parameters of the tetragonal cell ($a = b$, $c > a$) is 1.011, i.e., the deformation and, consequently, the spontaneous strain is of the order of 1%. At -93°C the rhombohedral angle α is 89.85° (Kwei *et al.*, 1993), i.e., there is only a deviation of 0.15° from the cubic lattice. Despite the small deformation, P_s takes significant values, up to $20\text{--}25\text{ }\mu\text{C}/\text{cm}^2$ at room temperature. The spontaneous polarization can be switched between energetically equivalent orientations

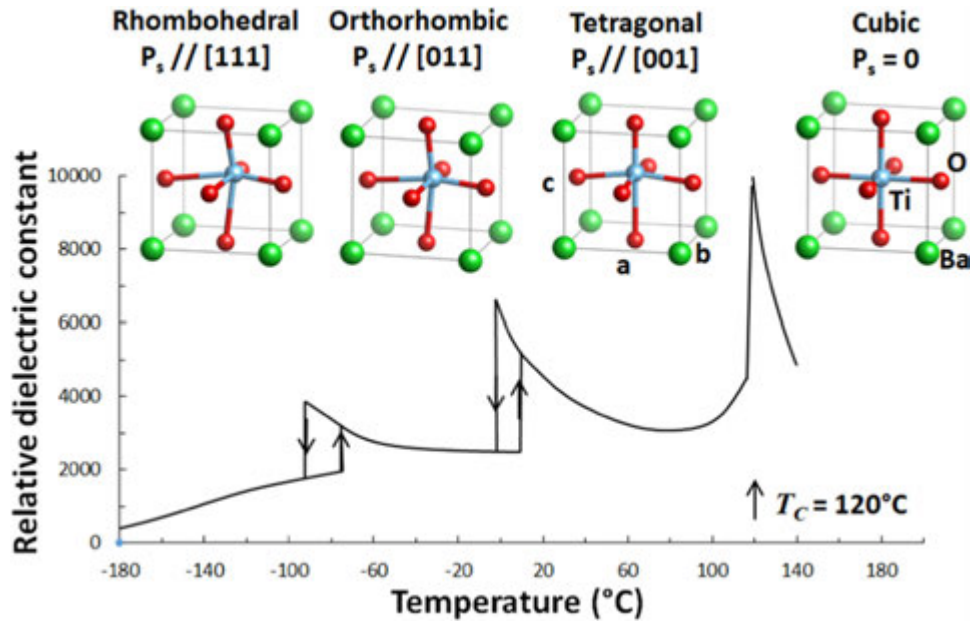


Fig. 2 (a) Temperature dependence of crystal structure and relative dielectric constant along the a-axis direction in BaTiO₃ single crystal. The Ti off center displacement is exaggerated to be better observable. Dielectric constant data from ref. Mertz, W.J., 1949. The electric and optical behavior of BaTiO₃ single-domain crystals. *Physical Review* 76, 1221–1225.

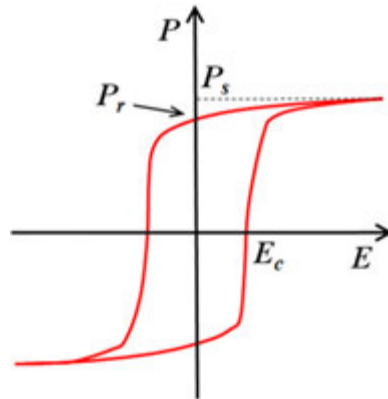


Fig. 3 Polarization (P) – electric field (E) ferroelectric polarization loop.

(6, 12 and 8 for the T, O and R phase, respectively) by means of an electric field. Polarization switching is a hysteretic process; by plotting the polarization P against the amplitude of the ac electric field E , the ferroelectric hysteresis loop is obtained (**Fig. 3**). The polarization at zero field is called remanent polarization (P_r) and the field at zero polarization is the coercive field (E_c). The switching process requires the application of a field larger than E_c . Polarization and strain are strongly coupled in ferroelectrics: a modification of the strain state determines a variation of polarization and vice versa. Because of the strong coupling between polarization and lattice strain and the often incomplete surface charge screening, the properties of ferroelectric materials are also very sensitive to the mechanical and electrical boundary conditions ([Damjanovic, 1998](#)).

Ferroelectric crystals spontaneously split into domains when cooled through the Curie temperature. Domains are regions with uniform orientation of polarization separated by domain walls. In tetragonal BaTiO₃, there are two kinds of domain walls, which separate regions with mutually antiparallel (180° walls) or perpendicular (90° walls) orientation of polarization. The other ferroelectric phases of barium titanate have a higher number of domain variants, corresponding to 3 and 4 different kinds of domain walls for the R and O phase, respectively. Domain formation occurs to minimize the elastic and electrostatic energies. In a ceramic, elastic energy in individual grains originates from the variation of lattice parameters and unit cell volume as the material crosses the paraelectric/ferroelectric transition on cooling, owing to the mechanical constraints exerted by the surrounding grains. Formation of 90° domain walls relieves the elastic energy. The electrostatic energy is associated with the depolarizing field produced by the surface charges at the termination of the material. Formation of both 90° and 180° walls relieves the electrostatic

energy. Domain walls can move under the action of an external electric field or a mechanical stress. The movement of domain walls at weak to moderate fields is one of the most important so-called extrinsic (non-lattice) contributions to the dielectric, elastic and piezoelectric properties of ferroelectric materials and may be comparable to the intrinsic effect of the lattice (Acosta *et al.*, 2017; Damjanovic, 1998). The movement of the domain walls is also responsible for the reorientation and switching of the polarization and the existence of the ferroelectric hysteresis loop.

Although for the purpose of this chapter we consider the phase transitions in BaTiO₃ as purely displacive, their actual nature has been debated. There is some evidence provided by extended X-ray absorption fine structure (EXAFS), nuclear magnetic resonance (NMR) and the pair-distribution function (PDF) investigations that the local structure of BaTiO₃ is different from the average one presented above and remains rhombohedral at all temperatures (Comes *et al.*, 1968; Kwei *et al.*, 1995; Ravel *et al.*, 1998; Zalar *et al.*, 2003; Levin *et al.*, 2014; Senn *et al.*, 2016). The results demonstrate the coexistence of displacive and order-disorder components in the phase transition mechanism. According to the eight-site model (Pirc and Blinc, 2004), the Ti ions in the paraelectric cubic phase exhibit off-center local displacement along the eight [111] directions but the average polarization is null because of the random distribution among the 8 split sites. Below the Curie temperature partial ordering occurs. Thus O, T and C long-range structures are the result of the averaging [111] displacements of octahedral Ti over 2, 4 and 8 local rhombohedral directions, respectively. Only for the rhombohedral phase the local and long-range structures are equivalent.

Lee and Randall (Lee *et al.*, 2008; Lee and Randall, 2008; Lee *et al.*, 2007a) spent a great deal of work in determining the homogeneity range of BaTiO₃ as a function of temperature and oxygen partial pressure and estimated the entropy and enthalpy of most important defect reactions. As already reported by Rase and Roy (1955), BaTiO₃ shows a non-negligible nonstoichiometry in the range 1000–1400°C. Non-stoichiometry is mainly associated to partial Schottky disorder:



where V_{Ba}'' and V_{Ti}''' denote a barium vacancy and a titanium vacancy, respectively, and $V_{\text{O}}^{\bullet\bullet}$ indicates an oxygen vacancy. Density functional theory calculations have shown that different combinations of barium vacancies, titanium vacancies and V_{Ti}''' - $V_{\text{O}}^{\bullet\bullet}$ pairs can be present in BaTiO₃ depending on processing and doping (Baker *et al.*, 2018). The homogeneity range attains the maximum width at 1320°C, the eutectic temperature of the BaO-TiO₂ system in air, with a Ba/Ti atomic ratio ranging from 0.967 to 1.01 (Lee *et al.*, 2007b, 2008). In other words, the solubility of TiO₂ in BaTiO₃ is larger than that of BaO. The nonstoichiometry within the homogeneity range of BaTiO₃ impacts on all intrinsic properties, including the Curie temperature, which can change up to 5–6°C moving throughout the solubility window, the enthalpy of transition (Lee *et al.*, 2007b, 2008; Lee and Randall, 2008; Lee *et al.*, 2007a) and the dielectric permittivity (Lee *et al.*, 2001).

At high temperature and low oxygen partial pressure, oxygen vacancies are also created by oxygen loss from the lattice of BaTiO₃ according to reaction:



where e' is an electron in the conduction band. The formation of electrons is associated to the reduction of Ti^{4+} ($3d^0$) to Ti^{3+} ($3d^1$) and the contribution of 3d orbitals to the conduction band. If n is the concentration of conducting electrons, the charge neutrality condition implies $n = 2[V_{\text{O}}^{\bullet\bullet}]$. The homogeneity range of BaTiO₃ decreases with decreasing the oxygen pressure (Lee and Randall, 2008) as the formation of oxygen vacancies in reaction (2.3) shifts reactions (2.1) and (2.2) to the left (Fig. 1(b)).

The defect chemistry of undoped barium titanate as a function of oxygen partial pressure was carefully investigated using high-temperature electrical conductivity measurements (Long and Blumenthal, 1971a,b; Chan *et al.*, 1981; Smyth, 1985) and the results could be explained by a relatively simple model. The equilibrium conductivity (Fig. 4) shows regions corresponding to the reduction regime (n -type conductivity) and the oxidation regime (p -type conductivity) below and above a conductivity minimum located at an oxygen partial pressure $p_{\text{O}_2} = p_{\text{O}_2}^0$, whose value depends on temperature. In the reduction regime the conductivity increases with decreasing p_{O_2} according to reaction (2.3). However, this reaction becomes the major source of defects only at low oxygen partial pressure, where the slope of the conductivity curve in Fig. 4 is $-1/6$. Over most of the experimental range shown in Fig. 4, the accidental acceptor impurities and their compensating oxygen vacancies are the dominant defects, and the condition of charge neutrality can be approximated by $[A'] = 2[V_{\text{O}}^{\bullet\bullet}]$, where $[A']$ represents the net concentration of acceptor impurities (see Section "Incorporation of Foreign Ions" for a more detailed discussion). Acceptor impurities, such as Al and Fe incorporated at the Ti site as well as Na and K incorporated at the Ba site usually predominates over donor impurities. If Ba/Ti $\neq$ 1 and the concentration of acceptor impurities is low, the dominating defects will be cation vacancies and oxygen vacancies (reaction (2.1) or (2.2)). Under both the above conditions, the slope of the conductivity curves in Fig. 4 is $-1/4$. In the oxidation regime above $p_{\text{O}_2}^0$, oxygen is incorporated in the perovskite lattice by reaction:



where $h^{\bullet}$ is an electron hole in the valence band. This determines an increase of the conductivity with increasing oxygen partial pressure with $+1/4$ slope in Fig. 4. Oxygen vacancies exist also in the oxidation regime owing to the presence of a net excess of acceptor impurities or nonstoichiometry.

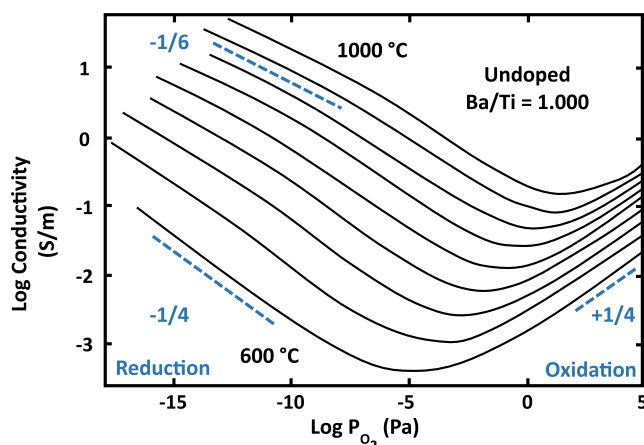


Fig. 4 Equilibrium electrical conductivity of polycrystalline BaTiO₃ at 600–1000 °C with 50 °C interval. Data from ref. Smyth, D.M., 1985. Defects and order in perovskite-related compounds. Annual Review of Material Science 15, 329–357.

Strategies for Modifying Defect Chemistry, Phase Transitions and Properties

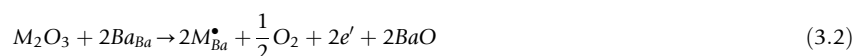
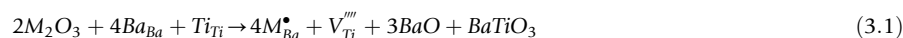
Undoped barium titanate ceramics and single crystals have limited interest for applications as their dielectric, electromechanical and optical properties show a significant temperature dependence (see the variation of dielectric constant in Fig. 2 as an example) whereas, in most cases, a better thermal stability is needed. On the other hand, the strong increase of the dielectric and piezoelectric properties approaching the phase transition temperatures (Mertz, 1953; Acosta *et al.*, 2017) would be of high interest for the fabrication of devices with better performances. The development of BaTiO₃-based materials and their use in commercial applications has been driven by the need to find a compromise between these two contrasting trends.

Chemical modification represents the most common and simple approach for tuning the phase transitions and the properties of barium titanate and other ferroelectric perovskites such as Pb(Zr,Ti)O₃, (K,Na)NbO₃ and Na_{0.5}Bi_{0.5}TiO₃. The term doping is usually used to indicate the substitution of a limited amount of parent ions, typically less than a few at%. Even a very small amount of dopant can considerably modify functional properties like the electrical conductivity and the domain wall mobility. When a substantial amount of foreign ions is incorporated in the lattice is more appropriate to refer to formation of solid solutions. Chemical modification is essential to shift the phase transition temperatures and in particular to lower T_C around room temperature and modify the nature of the phase transition. The formation of solid solutions introduces disorder and local compositional fluctuations with a decrease of the dipole correlation length, coexistence of polymorphs and diffuse phase transitions over a relatively large temperature range leading to broad permittivity peaks. Doping is also essential to impart the material a number of characteristics essential for its processing and reliability under operating conditions. Typical examples include resistance to degradation of dielectric properties during sintering in reducing atmosphere (essential for the fabrication of capacitors with non-noble metal electrodes), high insulation resistance, resistance to ageing and cycling, control of domain wall mobility. In general, the final properties are the result of a complex interplay between alteration of defect chemistry, shift and modification of phase transitions, changes in crystal structure (average and local) and polar order.

Dielectric and piezoelectric properties can also be controlled by modifying the microstructure and, in particular, by optimizing the grain size. It is well known that the permittivity and the piezoelectric activity of BaTiO₃ ceramics are maximized for a grain size of $\approx 1 \mu\text{m}$. A further strategy commonly used to improve the dielectric properties for capacitor application is the fabrication of ceramics with core-shell grains, which combines the chemical modification with the control of microstructure and formation of compositional gradients.

Incorporation of Foreign Ions

Substitution of a regular ion (Ba^{2+} or Ti^{4+}) with a foreign ion determines the formation of a point defect (Smyth, 1985). If the substituent cation has a higher positive charge than the ion it replaces (e.g., M^{3+} at the Ba site), it is termed a “donor” and will assume an effective positive charge in the oxide lattice ($M_{\text{Ba}}^{\bullet}$). This positive charge will be compensated by defects with a negative charge, most commonly cation vacancies ($V_{\text{Ti}}^{\prime\prime\prime}$, $V_{\text{Ba}}^{\prime\prime}$) or electrons (e') in the conduction band.



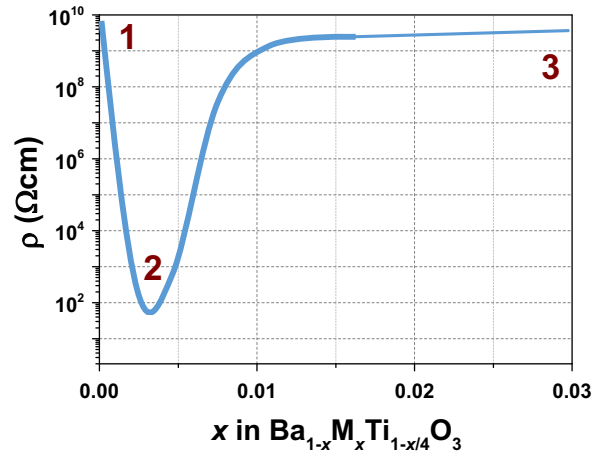
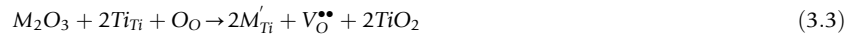


Fig. 5 Schematic representation of the room-temperature dc resistivity as a function of the trivalent dopant concentration M^{3+} for ceramics sintered in air. Adapted from ref. Morrison, F.D., Sinclair, D.C., West, A.R., 2001b. Alternative explanation for the origin of the resistivity anomaly in La-doped BaTiO₃. *Journal of the American Ceramic Society* 84, 474–476.

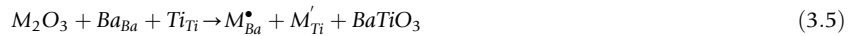
The formation of electrons is associated to the reduction of Ti^{4+} ($3d^0$) to Ti^{3+} ($3d^1$) and the contribution of 3d orbitals to the conduction band. A reaction similar to (3.1) can be written for barium vacancy compensation. According to available literature, titanium vacancies are preferred over barium vacancies as charge compensating defects especially if the dopant concentration is high (Jonker and Havinga, 1982; Chan *et al.*, 1986; Shaikh and Vest, 1986; Morrison *et al.*, 2001a). Most common donors are pentavalent ions such as Nb^{5+} , Ta^{5+} and Sb^{5+} substituting at the Ti site and large trivalent lanthanide ions (La^{3+} , Nd^{3+} , Ce^{3+} , etc.) substituting at the Ba site.

If the foreign cation has a lower charge than the regular ion it substitutes, it is called an “acceptor” and will assume an effective negative charge compensated by positively charged defects, either oxygen vacancies ($V_O^{\bullet\bullet}$) or electron holes ($h^\bullet$) in the valence band.



Common acceptors are monovalent ions (Ag^+ , Na^+ , K^+ , etc.) incorporated at the Ba site and all ions with charge lower than 4 (Li^+ , Mg^{2+} , Ca^{2+} , Ni^{2+} , Sc^{3+} , Fe^{3+} , Lu^{3+} , Yb^{3+}) and compatible ionic radius incorporated at the Ti site.

For trivalent cations with an ionic radius intermediate between Ba^{2+} and Ti^{4+} , a further incorporation mechanism, termed “self-compensation”, corresponding to the simultaneous substitution at both cation sites, exists:



Finally, when the substituent cation and the regular cation have the same charge, a neutral defect will originate.



The electrostatic interaction between defects of opposite charge can lead to the formation of defect pairs and defect clusters. These clusters, especially those formed by transition metal acceptors (Fe^{3+} , Mn^{3+} , Mn^{2+}) with a neighboring oxygen vacancy, interact with the domain walls and have a strong effect on the ferroelectric and piezoelectric properties (Jin *et al.*, 2014).

The prevailing charge compensation mechanism (cation vacancies or electrons, oxygen vacancies or holes) is determined by the formation energy of the defects, the oxygen partial pressure and the dopant concentration. For donor doping, electron compensation will prevail in reducing conditions (the Ti^{4+} ions will be progressively reduced to Ti^{3+} with decreasing oxygen activity) while titanium vacancies will dominate in oxidizing atmospheres (Makovec and Drofenik, 2000). When reaction (3.2) prevails, a plateau on the conductivity vs. oxygen pressure is observed as the number of charge carriers is determined by the donor concentration (Daniels and Härdtl, 1976; Chan and Smyth, 1984). Donor-doped BaTiO₃ ceramics sintered in air can be either semiconducting or insulating at room temperature depending on the doping level and ceramic processing conditions (Fig. 5). With increasing donor concentration, the resistivity decreases from $\approx 10^{10} \Omega \cdot cm$ of neat BaTiO₃ (point 1 in Fig. 5) down to a minimum of 10^2 – $10^1 \Omega \cdot cm$ (point 2 in Fig. 5) for a doping level of, typically, 0.2–0.3 at% (Jonker, 1964; Morrison *et al.*, 2001a). For higher doping levels the resistivity rises and the material becomes again insulating (point 3 in Fig. 5). This behavior is usually interpreted as a crossover in the charge compensation mechanism, from prevailing electron compensation to cation vacancy compensation. However, this interpretation is still controversial. Morrison *et al.* (2001a,b), on the basis of a detailed study of La-doped samples, concluded that charge compensation always occurs by cation vacancies and that semiconductivity in BaTiO₃ is determined by oxygen nonstoichiometry and reduction of Ti^{4+} to Ti^{3+} , as described by reaction (2.3). However, this conclusion was criticized by Smyth (2002), based on (1) the existence of a p_{O_2} -independent conductivity plateau proportional to the donor

concentration in donor-doped samples and (2) a reversible weight change determined by the release of excess oxygen contained in La₂O₃ (reaction (3.2)) again proportional to the donor concentration. More recent atomistic simulations have shown that oxygen loss by reaction (2.3) is much more favorable in La-doped BaTiO₃ than in the undoped material when compensation occurs by cation vacancy due to the formation of unique defect clusters involving the different point defects (Freeman *et al.*, 2013).

In the interpretation of the resistivity anomaly (Fig. 5) it should also be considered that the ceramics are not in equilibrium at room temperature and that the defect structure corresponds to that existing at an intermediate temperature between sintering temperature and room temperature. During cooling, reoxidation occurs according to the reverse of reactions (3.2) and/or (2.3) but the level and distribution of oxygen uptake on cooling and, consequently, the electrical properties depend on the sintering atmosphere, the cooling rate and the ceramic microstructure. Lowest values of resistivity are observed for coarse grained ceramics rapidly cooled. In contrast, fine grained ceramics slowly cooled tend to exhibit higher values of resistivity. However, coarse ceramics are highly heterogeneous from the point of view of resistivity, with semiconducting grains and more insulating, reoxidized grain boundaries. This heterogeneous electrical structure is at the root of the PTCR effect (Heywang, 1971). The partial reoxidation of grain boundaries determines the development/enhancement of the Schottky barriers which is required for the appearance of this non-ohmic effect. Depending on processing conditions, a fully reoxidized and insulating skin can appear on the ceramic surface (Morrison *et al.*, 2001c).

Materials with stoichiometry corresponding to reaction (3.2) sintered at low oxygen partial pressure are single phase and conducting even for large values of the dopant fraction of the order of 10 at% (Makovec and Drofenik, 2000). In this case, the donors are effectively compensated by the formation of electrons/Ti³⁺ ions.

Incorporation of Transition Metal Ions and Other Acceptors

In many cases the transition metal ions exhibit +2 and +3 charge and, due to their relatively small ionic radius, they usually substitute Ti⁴⁺ and act as acceptors. Doping of BaTiO₃ with ions of 3d transition metals, especially Fe, Mn and Co, has been widely investigated as they are quite effective as modifiers of the ferroelectric properties leading to constrained and asymmetric P (E) loops (Jin *et al.*, 2014; Hall *et al.*, 1998). The oxygen vacancies created as charge compensating defects can form defect dipoles with the acceptor ions (e.g., $Fe_{Ti}' - V_O^{\bullet\bullet}$) which stabilize the domain walls and clamp their motion ("hardening" effect) (Zhang *et al.*, 2008; Erhart *et al.*, 2007). Poled acceptor-doped BaTiO₃ ceramics can be used as highly linear piezoelectric transducers and actuators with low hysteresis and dissipation for high power/frequency applications (Zhang *et al.*, 2009). Transition metal ions and other acceptors are also quite effective (reaction (3.3)) to suppress oxygen loss and conductivity increase related to reaction (2.3) when sintering BaTiO₃ in reducing atmosphere, leading to insulating ceramics suitable for the preparation of MLCCs with non-noble metal (e.g., Ni) internal electrodes (Hagemann and Hennings, 1981).

More recently, BaTiO₃ ceramics doped with magnetic transition metal ions have attracted interest as potential multiferroic and magnetoelectric materials because of the appearance of weak magnetism (Raj *et al.*, 2008; Xu *et al.*, 2009; Lin *et al.*, 2009; Son *et al.*, 2013). However, when the dopant amount exceeds few at%, formation of the non-ferroelectric hexagonal polymorph (6H-type, s.g. *P63/mmc*) instead of the perovskite phase is observed.

Stabilization of the hexagonal modification

The perovskite/hexagonal structural transition has been investigated in some detail. In undoped BaTiO₃ the 6H polymorph is stabilized by sintering or annealing in a reducing atmosphere or quenching from a temperature above 1430–1460°C (Glaister and Kay, 1960; Kolar *et al.*, 1998; Sinclair *et al.*, 1999). The incorporation of transition metal ions (BaTi_{1-x}B_xO_{3-δ}, B = Fe, Mn, Ni, Co, Cr, Cu) stabilizes the 6H-phase below the transition temperature of 1460°C reported of pure BaTiO₃ (Fig. 1). In the case of Fe, the transition temperature decreases rapidly and attains ≈ 1300°C for $x = 0.05$ and $1150 \pm 50^\circ\text{C}$ for $x = 0.10$ (Masó *et al.*, 2006), as shown in Fig. 6. However, a mixture of 6H and perovskite phase persist at even lower temperatures. For example, for $x = 0.05$ a single phase perovskite is only obtained at temperatures ≤ 1100°C. The relative amount of the two polymorphs is very sensitive to several operating conditions, including the cooling rate, the composition of the sintering atmosphere and the annealing at temperatures below that of sintering (Langhammer *et al.*, 2000). The perovskite to 6H transformation is commonly accompanied by microstructural modifications and, in particular, by the growth of large plate-like hexagonal grains (Kolar *et al.*, 1998; Langhammer *et al.*, 2000). Stabilization of 6H-phase has been attributed to different reasons, including: (1) the formation of oxygen vacancies, (2) the Jahn-Teller effect related to specific configurations of the *d*-electrons, and (3) metal-metal bonding of cations through the face sharing octahedra existing in the 6H-phase. Since the stabilization of the hexagonal polymorph has also been observed for acceptors without *d*-electrons (Mg²⁺, Al³⁺) or with filled *d*-orbitals (Zn²⁺, Ga³⁺, In³⁺) (Keith *et al.*, 2004), the most important factor is likely to be the oxygen vacancies. However, other effects can be of some importance and, for example, can play a role in the different solubility of the acceptors. Extensive solid-solutions were reported for Fe- and Mn-doped ceramics, while for many other acceptors the maximum solubility is of the order of 10 at% (Keith *et al.*, 2004; Das *et al.*, 2014). Two series of 6H-BaTi_{1-x-y}Fe_x³⁺Fe_y⁴⁺O_{3-x/2} solid solutions with iron predominantly in the form Fe³⁺ or Fe⁴⁺ were reported by quenching from high temperatures in air or slow cooling to 200°C in oxygen, respectively (Grey *et al.*, 1998). In the first case, Fe³⁺ behaves as an acceptor and oxygen vacancy formation occurs up to $x = 0.67$ (corresponding to $\delta = 0.33$ in BaFe_xTi_{1-x}O_{3-δ}). Higher values of x resulted in the conversion of 6H in other phases. Differently, the oxidation of iron to Fe⁴⁺ avoids the formation of charge compensating defects and complete solubility exists between BaTiO₃ ($x = 0$) and BaFeO₃ ($x = 1$). The existence of two different

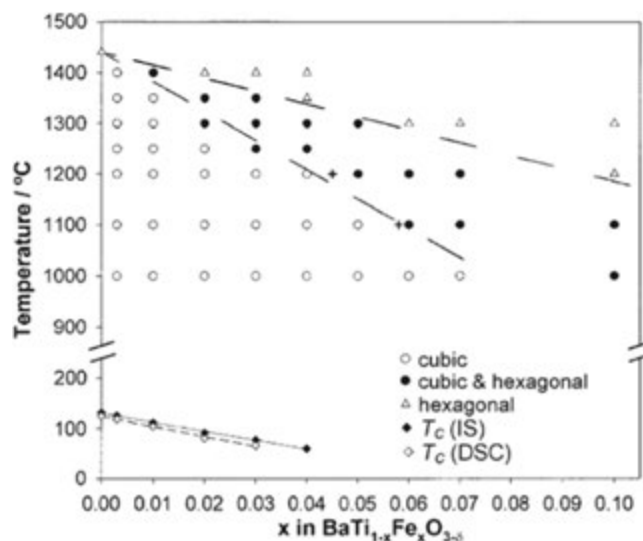


Fig. 6 Phase diagram for the solid solution $\text{BaTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$. T_C (IS) denotes Curie temperature obtained from impedance spectroscopy measurements. T_C (DSC) denotes Curie temperature obtained from differential scanning calorimetry. Reproduced from ref. Masó, N., Beltrán, H., Cordoncillo, E., Escribano, P., West, A.R., 2006. Electrical properties of Fe-doped BaTiO₃. *Journal of Materials Chemistry* 16, 1626–1633 by permission of The Royal Society of Chemistry. Copyright (2006) The Royal Society of Chemistry.

incorporation mechanisms is well evident from the opposite trend of the lattice parameters, as shown in Fig. 7. The deviation from the ideal behavior of $\text{BaTiO}_3\text{-BaFeO}_{2.5}$ and $\text{BaTiO}_3\text{-BaFeO}_3$ solid solutions indicates that iron is in a mixed valence state though one of the states predominates. The $\text{BaO-TiO}_2\text{-Fe}_2\text{O}_3$ phase diagram and the rich crystal chemistry in this system with 16 quaternary compounds were reviewed by Siegrist and Vanderah (2003). Manganese shows a behavior similar to iron as it can be incorporated at Ti site as Mn^{3+} with oxygen vacancy compensation or as Mn^{4+} or, again, in both forms depending on the annealing atmosphere and cooling rate (Miranda *et al.*, 2009).

Valence state of transition metal ions in the perovskite lattice

The oxidation number of the transition metal inside the BaTiO_3 lattice has been investigated also for low dopant concentrations (x up to 0.02) when the perovskite structure is stable. On the basis of magnetic susceptibility measurements on air-sintered ceramics, Ihrig (1978) determined that the +3 state prevails for iron, whereas manganese enters the lattice as Mn^{3+} and Mn^{4+} , and nickel is predominantly divalent. Incorporation of Cr^{4+} was suggested for chromium. The valence state of Cr, Mn and Co was found to change reversibly upon annealing at 700°C at different oxygen partial pressures (pure oxygen at 1.5×10^7 Pa, air and $\text{H}_2/\text{H}_2\text{O}$ mixture with $p(\text{O}_2) = 10^{-17}$ bar) whereas it remained constant for iron (Fe^{3+}) and nickel (Ni^{2+}) (Hagemann and Ihrig, 1979). While Cr^{4+} , Mn^{4+} and Co^{3+} prevail in pure oxygen, Cr^{3+} , Mn^{2+} and Co^{2+} predominate at low oxygen partial pressure. Similar conclusions on the valence states were attained by Hagemann and Hennings (1981) from the oxygen vacancy concentration data determined gravimetrically as a function of the oxygen partial pressure for samples containing 0.5 mol% dopant. The concentration of oxygen vacancies was fixed by the acceptor concentration (reaction (3.3)) down to $p(\text{O}_2) = 10^{-10}\text{--}10^{-12}$ Pa. At lower pressure the contribution of intrinsic vacancies from reaction (2.3) becomes increasingly important. Ozawa *et al.* (1993) measured the electrical conductivity of BaTiO_3 ceramics containing 2 at% Mn as a function of oxygen partial pressure ($10^{-10}\text{--}10^{-5}$ Pa) and concluded that at 900–1000°C, Mn^{3+} prevails at $p(\text{O}_2) < 1$ Pa, whereas Mn^{4+} predominates at higher pressure. The Electron Paramagnetic Resonance (EPR) measurements of Langhammer *et al.* (2015), (2008), Böttcher *et al.* (2011), Langhammer *et al.* (2003) generally confirmed the above trends. After sintering in air, cobalt is incorporated as a mixture of Co^{2+} and Co^{3+} , while Co^{2+} prevails after annealing in reducing atmosphere (Langhammer *et al.*, 2015). Likewise, the valence state of chromium changes from a value intermediate between +4 and +3 to +3 with decreasing oxygen partial pressure (Langhammer *et al.*, 2008). The EPR spectrum of Ni^{2+} was not detected in nickel-doped ceramics sintered in air in both the perovskite and hexagonal modifications (Böttcher *et al.*, 2011) and it was postulated that the dopant is mainly incorporated as Ni^{4+} in contrast with the results of Ihrig (1978). Copper is incorporated as Cu^{2+} after sintering in air (Langhammer *et al.*, 2003). Recent EPR results indicated that manganese behaves as an amphoteric dopant in SrTiO_3 lattice and can occupy both cation sites simultaneously as Mn^{2+} at the Sr site and $\text{Mn}^{3+}/\text{Mn}^{4+}$ at the Ti site (Maier *et al.*, 2016). This possibility should also be considered for BaTiO_3 .

Ni^{2+} and Fe^{3+} are quite effective to shift the Curie temperature down, about 30°C/at% for Ni^{2+} and 21°C/at% for Fe^{3+} , irrespective of oxygen partial pressure (Hagemann and Ihrig, 1979). Cr^{3+} and Co^{2+} are also good shifters (25 and 28°C/at%, respectively) but only in reducing atmosphere. Tetravalent chromium stabilizes the orthorhombic phase at lower temperature ($T_{\text{O/R}} = -80^\circ\text{C}$ for $x = 0$ and -105°C for $x = 0.02$) whereas most of the other ions shift the rhombohedral-orthorhombic transition to higher temperatures.

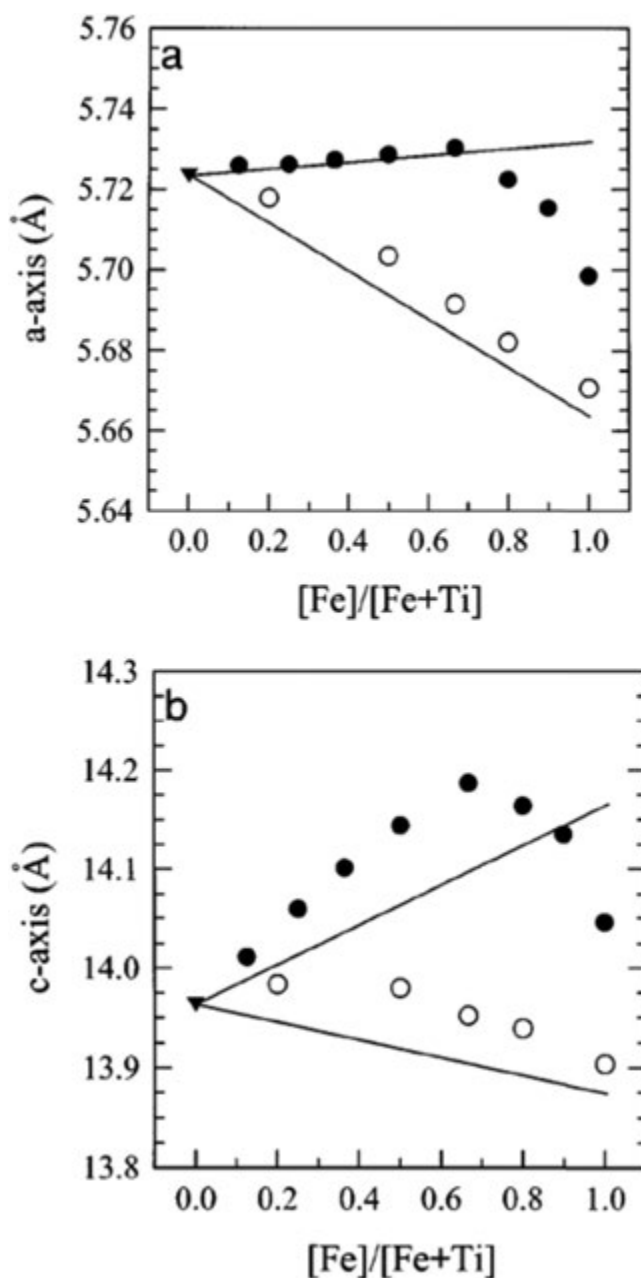


Fig. 7 Lattice parameters of 6H-BaTi_{1-x-y}Fe_x³⁺Fe_y⁴⁺O_{3-x/2} solid solution for air-quenched (filled circles) and slow-cooled in oxygen (open circles) samples after sintering in air. The lines correspond to Vegard law cell composition relationships for BaTiO₃-BaFeO_{2.5} (upper lines) and BaTiO₃-BaFeO₃ (lower lines). Reprinted from ref. Grey, I.E., Li, C., Cranswick, L.M.D., Roth, R.S., Vanderah, T.A., 1998. Structure analysis of the 6H-Ba(Ti, Fe³⁺, Fe⁴⁺)O_{3-δ} solid solution. *Journal of Solid State Chemistry* 135, 312–321, with permission from Elsevier. Copyright (1998) Academic Press.

Formation of dipolar defects

The formation of nearest neighbors acceptor-oxygen vacancy pairs, ($M'_{Ti} - V_O^{\bullet\bullet}$) and ($M''_{Ti} - V_O^{\bullet\bullet}$), was also investigated by EPR in the case of Mn- and Fe-doped BaTiO₃ and PbTiO₃ (Zhang *et al.*, 2008; Erhart *et al.*, 2007). The dipolar defects align in the direction of spontaneous polarization by oxygen vacancy motion in the MO₆ octahedron and follow the domain switching upon poling (Erhart *et al.*, 2007; Warren *et al.*, 1996). The defect dipoles do not reorient during fast field cycling but reorientation rather requires long time, high thermal energy, and high electric fields. Ordering is destroyed above T_C and is not observed in SrTiO₃. The association enthalpy was determined as -0.26 eV (Merkle and Maier, 2003) for ($Fe'_{Ti} - V_O^{\bullet\bullet}$) in SrTiO₃, meaning that most of the dipolar pairs are dissociated above 300°C. Atomistic simulations performed on SrTiO₃ indicate association enthalpies in the range -0.25 to -0.5 eV for different transition metal acceptors (Schie *et al.*, 2014). Association enthalpies of -0.2 to (-0.3) eV are reported for defect pairs involving Mn''_{Ti} , Mn'_{Ti} and Fe'_{Ti} in BaTiO₃ (Merkle and Maier, 2003).

Incorporation of Rare-Earth Ions

Trivalent rare-earths cations (RE³⁺) of the lanthanide series show a progressively smaller ionic radius moving from La³⁺ ($r^{\text{XII}} = 1.36 \text{ \AA}$) to Lu³⁺ ($r^{\text{VI}} = 0.86 \text{ \AA}$), intermediate between Ba²⁺ ($r^{\text{XII}} = 1.61 \text{ \AA}$) and Ti⁴⁺ ($r^{\text{VI}} = 0.605 \text{ \AA}$). Although the +3 state is the most stable, some lanthanides also exhibit other oxidation states: +2 (Yb, Eu, Sm) and +4 (Pr, Ce, Tb). The specific valence exhibited by these ions depends on the sintering atmosphere and on the incorporation site. The mechanism of rare-earth cation substitution in BaTiO₃ has been investigated in detail (Xue *et al.*, 1988; Buscaglia *et al.*, 2000; Tsur *et al.*, 2001; Dunbar *et al.*, 2004) as it plays a key role in determining the properties and the reliability of MLCCs fabricated with the base metal electrode technology.

Incorporation site

For trivalent cations, the incorporation site is determined by the ionic radius. Large ions such as La³⁺ ($r^{\text{XII}}: 1.36 \text{ \AA}$), Ce³⁺ ($r^{\text{XII}}: 1.34 \text{ \AA}$) and Pr³⁺ ($r^{\text{XII}}: 1.29 \text{ \AA}$) exclusively substitute at the Ba site, acting as donors, while the smaller Lu³⁺ ($r^{\text{VI}}: 0.861 \text{ \AA}$) and Yb³⁺ ($r^{\text{VI}}: 0.868 \text{ \AA}$) prefer the Ti site, acting as acceptors (Xue *et al.*, 1988; Buscaglia *et al.*, 2000; Tsur *et al.*, 2001; Dunbar *et al.*, 2004; Makovec *et al.*, 1996; Lu *et al.*, 2014). Although it is reported that Nd³⁺ ($r^{\text{VI}}: 1.27 \text{ \AA}$) preferentially substitutes at the Ba site (Shaikh and Vest, 1986; Xue *et al.*, 1988; Buscaglia *et al.*, 2000; Tsur *et al.*, 2001; Dunbar *et al.*, 2004), Hirose *et al.* (1999) have shown that the mechanism changes from Ba-site substitution to self-compensation above $x = 0.05$ when Ba/Ti = 1. For all other cations, from Sm³⁺ to Tm³⁺, the substitution site can be controlled by adjusting the Ba/Ti ratio and, for this reason, they are often indicated as “amphoteric” dopants. Consequently, provided that the maximum solubility is not exceeded, the cation will occupy the Ba site when Ba/Ti < 1, the Ti site when Ba/Ti > 1 and both sites when Ba/Ti = 1. In the latter case, charge compensation defects are not needed (self-compensation, reaction (3.5)). The correct value of Ba/Ti required for the formation of the specific single phase solid solution can be determined taking into account the stoichiometry of the incorporation reactions (3.1)–(3.5). The solubility of the RE³⁺ ions at a given site is strongly dependent on ionic radius. For example, the solubility at Ba site with titanium vacancy compensation exceeds 20 at% in the case of La³⁺ (Morrison *et al.*, 1999) but drops to 5 at% for Gd³⁺ (Ben and Sinclair, 2011) and is only of the order of 1 at% for smaller lanthanides such as Y³⁺, Dy³⁺ and Er³⁺ (Zhi *et al.*, 1999; Lee *et al.*, 2000; Buscaglia *et al.*, 2002). Opposite, the solubility of small RE ions at the Ti site is much higher, of the order of 15 at% for Ho³⁺, Dy³⁺ and Y³⁺ (Zhi *et al.*, 1999; Lee *et al.*, 2000; Buscaglia *et al.*, 2002; Makovec *et al.*, 2004; Liu and West, 2009), and then rapidly decreases with increasing ionic radius (3.75 at% for Gd³⁺). However, the incorporation of a substantial amount of acceptor ions according to reaction (3.3) determines the formation of the hexagonal polymorph of BaTiO₃, likewise trivalent and divalent transition metal ions substituting at the Ti site. According to Liu and West (2009), 6H-BaTiO₃ forms as an intermediate kinetically stabilized phase before transforming into the thermodynamically stable perovskite phase after long-time annealing at high temperatures (> 1500°C). Prolonged annealing was also required to stabilize the perovskite phase in Er-doped ceramics (Buscaglia *et al.*, 2002). In contrast, the incorporation of Fe³⁺ and other transition metal ions shifts the polymorphic phase transition at lower temperatures and annealing is ineffective. Maximum solubility of amphoteric dopants is attained when the lanthanide occupies both sites and attains 24 at% in the case of Ho³⁺ (Makovec *et al.*, 2004).

The size-dependent crystallochemical behavior of RE ions in BaTiO₃ is well reproduced by atomistic simulations especially if the formation of defect clusters driven by the electrostatic interaction between the foreign ion and the oppositely charged compensation defect is taken into account (Buscaglia *et al.*, 2001; Freeman *et al.*, 2011). Both experimental results (Jonker and Havinga, 1982; Chan *et al.*, 1986; Shaikh and Vest, 1986) and simulations indicate that the preferred compensation defects in donor-doped BaTiO₃ are titanium vacancies rather than barium vacancies.

A rapid depression of the Curie point is observed even for moderate amounts of RE³⁺. The replacement of Ba²⁺ by La³⁺, Pr³⁺ and Ce³⁺ causes a lowering of T_C at a rate of 22–24°C/at% (Lu *et al.*, 2014; Morrison *et al.*, 1999; Hwang and Han, 2001a). Incorporation of Nd³⁺ determines an even faster drop of 40°C/at% (Shaikh and Vest, 1986). However, on further reducing the ionic radius of the lanthanide, both the T_C drop rate and the solubility decrease, as observed for Gd³⁺ (Ben and Sinclair, 2011). The substitution of Ho³⁺ and Er³⁺ at the Ti site results in a lowering of T_C of 17.5 and 22.2°C/at% (Liu and West, 2009; Hwang and Han, 2001b), respectively.

The incorporation of RE³⁺ ions with intermediate size (the so-called “magic” dopants, in particular Y³⁺, Dy³⁺ and Ho³⁺) in BaTiO₃ ceramics is essential to prevent the degradation of insulating resistance and strongly improves the lifetime of MLCCs with Ni electrodes fabricated by the base-metal technology (Sakabe *et al.*, 2002; Kishi *et al.*, 2003; Mizuno *et al.*, 2007). The site occupancy of these lanthanide ions was effective for controlling the donor/acceptor dopant ratio and the microstructure. The detailed mechanism is still debated, but the amphoteric nature of the dopants certainly plays an important role.

Homovalent Substitution

BaTiO₃ forms extensive solid solutions with a number of perovskites such as CaTiO₃, SrTiO₃, PbTiO₃, BaSnO₃, BaZrO₃, BaHfO₃ and BaCeO₃ (Jaffe *et al.*, 1971; Acosta *et al.*, 2017) thus allowing the modification of phase transition temperatures, polar order and properties over a broad range of compositions.

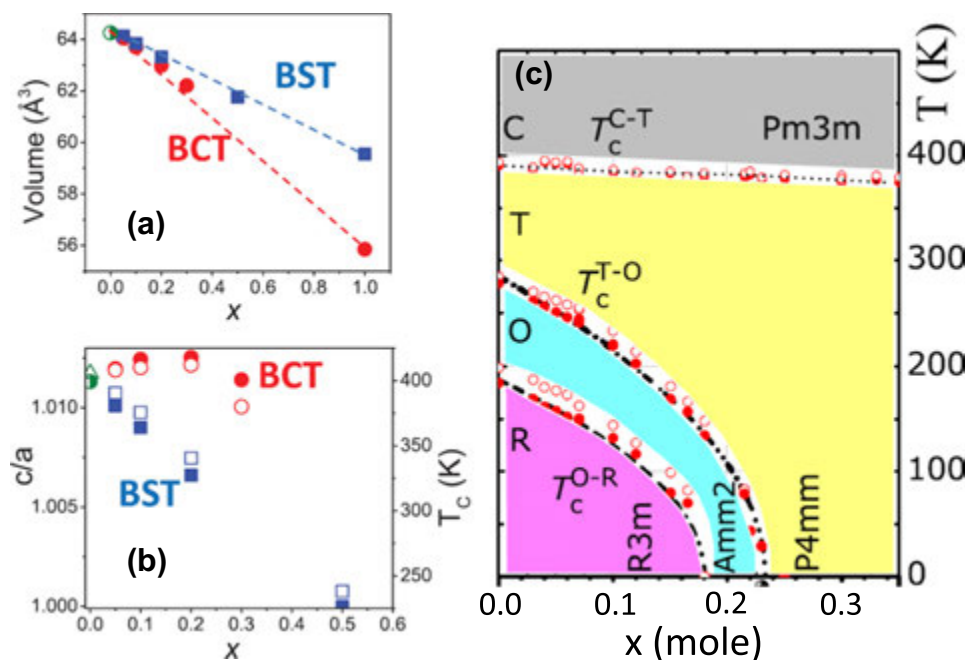


Fig. 8 Compositional dependence of (a) unit-cell volume and (b) c/a ratio (filled symbols) and T_C (open symbols) in the $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST, blue) and $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ (BCT, red) solid solutions. (c) Phase diagram of the $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ system. Reprinted from (a,b) Levin, I., Krayzman, V., Woicik, J.C., 2013. Local-structure origins of the sustained Curie temperature in (Ba,Ca)TiO₃ ferroelectrics. *Applied Physics Letters* 102, 162906, with the permission of AIP Publishing. (c) Fu, D., Itoh, M., Koshihara, S.Y., Kosugi, T., Tsuneyuki, S., 2008. Anomalous phase diagram of ferroelectric (Ba,Ca)TiO₃ single crystals with giant electromechanical response. *Physical Review Letters* 100, 227601. Copyright (2008) by the American Physical Society.

BaTiO₃-MTiO₃ solid solutions ($M = \text{Ca, Sr, Pb}$)

Despite a similar chemical behavior, Ca^{2+} and Sr^{2+} incorporated at the Ba site have a somewhat different effect on the phase transitions (Fig. 8) and properties of barium titanate which can be ascribed to their different size (Vendik and Zubko, 2000; Levin *et al.*, 2013; Fu *et al.*, 2008). The $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST) solid solution shows a continuous and almost linear decrease of T_C and c/a ratio with increasing x , until the quantum paraelectric (or incipient ferroelectric) behavior typical of SrTiO_3 is achieved ($x > 0.95$) (Jaffe *et al.*, 1971; Vendik and Zubko, 2000; Levin *et al.*, 2013). In contrast, in $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ (BCT) both T_C and c/a ratio first show a modest increase with a maximum at $x \approx 0.10$ and then decrease though they remain close to the values of BaTiO_3 (Jaffe *et al.*, 1971; Levin *et al.*, 2013; Fu *et al.*, 2008). The maximum solubility of Ca^{2+} corresponds to $x = 0.33$. Because of its smaller ionic radius ($r^{\text{XII}} = 1.34 \text{ \AA}$) in comparison to Ba^{2+} ($r^{\text{XII}} = 1.61 \text{ \AA}$), Ca^{2+} moves off-center, as revealed by EXAFS, first-principle calculations and atomistic modeling (Levin *et al.*, 2013; Fu *et al.*, 2008; Dawson *et al.*, 2014). Furthermore, the Ca^{2+} displacement amplifies the ferroelectric off-centering of Ti cations nearest to the Ca^{2+} site in a cooperative process thus enhancing ferroelectricity despite the unit cell volume decreases. Opposite, the position of Sr cations ($r^{\text{XII}} = 1.44 \text{ \AA}$) in BST is largely central. The temperatures of the O/T and R/O transitions decrease more rapidly in BCT than in BST with increasing x , showing a strong nonlinear behavior and determining the stabilization of the T phase at low temperatures. Despite its conspicuous ionic radius in octahedral coordination ($r^{\text{VI}} = 1 \text{ \AA}$), Ca^{2+} behaves as an amphoteric dopant and substitutes Ti^{4+} up to $x = 0.04$ in $\text{BaCa}_x\text{Ti}_{1-x}\text{O}_{3-x}$ causing the suppression of T_C at a rate of $22^\circ\text{C/at\%}$ (Han *et al.*, 1987; Zhang *et al.*, 2007).

While Ca^{2+} doping at the Ba site results only in a modest increase ($8\text{--}10^\circ\text{C}$) of T_C , the incorporation of Pb^{2+} determines a continuous rise of the Curie temperature up to 490°C , the T_C of PbTiO_3 (Jaffe *et al.*, 1971). Divalent lead ions tend to move off-center the PbO_{12} dodecahedron (Sághi-Szabó *et al.*, 1999) due to the stereochemically active $6s^2$ electron lone pair and, consequently, they contribute to the overall polarization and enforce the ferroelectricity of BaTiO_3 .

MgTiO_3 crystallizes with the ilmenite-type structure and Mg^{2+} preferentially substitutes at the Ti site because of its small ionic radius ($r^{\text{VI}} = 0.72 \text{ \AA}$) up to a maximum solubility of $\approx 2 \text{ at\%}$ (Su and Button, 2004). Accordingly, it is largely used as an acceptor in the fabrication of MLCCs and promotes the formation of core-shell grains (Kishi *et al.*, 1999; Kim *et al.*, 2008; Yoon *et al.*, 2009).

BaTiO₃-BaMO₃ solid solutions ($M = \text{Sn, Zr, Hf, Ce}$)

Despite the large variation of ionic radius (Sn^{4+} : $0.69 \text{ \AA}$, Zr^{4+} : $0.72 \text{ \AA}$, Ce^{4+} : $0.87 \text{ \AA}$) of cations substituting Ti^{4+} ($0.605 \text{ \AA}$), the $\text{BaM}_x\text{Ti}_{1-x}\text{O}_3$ ($M = \text{Sn, Hf, Zr, Ce}$) solid solutions exhibit a very similar behavior of the phase transitions (Shvartsman and Lupascu, 2012; Dobal *et al.*, 2001; Simon *et al.*, 2004; Dong *et al.*, 2012; Lei *et al.*, 2007; Anwar *et al.*, 2007; Li *et al.*, 2016; Canu *et al.*, 2018), exemplified by the $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ (BZT) phase diagram (Dong *et al.*, 2012) shown in Fig. 9. With increasing x , the T/C

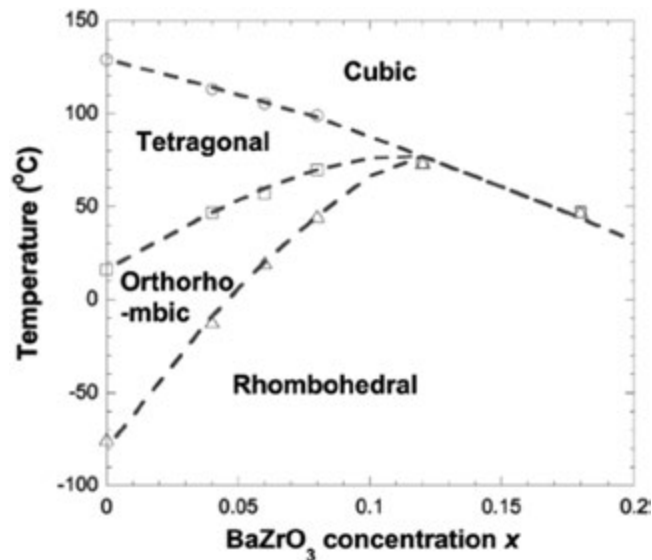


Fig. 9 Phase diagram of $x\text{BaZrO}_3-(1-x)\text{BaTiO}_3$ ceramics with $0 \leq x \leq 0.20$. Reprinted from ref. Dong, L., Stone, D.S., Lakes, R.S., 2012. Enhanced dielectric and piezoelectric properties of $x\text{BaZrO}_3-(1-x)\text{BaTiO}_3$ ceramics. *Journal of Applied Physics* 111, 084107, with the permission of AIP Publishing.

transition shifts to lower temperature while the O/T and R/T transitions move to higher temperature until they meet at the phase convergence point (x_p , T_p), giving rise to the so-called “pinched” transition. The value of x_p , 0.09–0.11, is nearly independent of specific M^{4+} cation, though some papers report $x_p \approx 0.15$ in BZT. In contrast, T_p increases with increasing the ionic radius of M^{4+} , from $\approx 320\text{K}$ (Sn) to $\approx 390\text{K}$ (Ce). When $x > x_p$, a direct and diffuse R/C transition is observed. Although the Curie temperature is depressed in comparison to undoped BaTiO_3 , the rate at which T_C decreases with increasing x depends on the size of the M^{4+} cations as shown in Fig. 10. A rapid and linear drop is observed for Sn^{4+} substitution while Ce^{4+} substitution determines a strong nonlinear behavior characterized by a decrease of T_C of only a few degrees up to $x = 0.05$ and a more rapid decay above $x = 0.10$ (Canu *et al.*, 2018). The behavior of Zr^{4+} is intermediate between Sn^{4+} and Ce^{4+} . All the considered tetravalent cations are significantly bigger than Ti^{4+} and, consequently, they have no tendency to move off-center and do not promote ferroelectric ordering. Therefore, in the case of Sn^{4+} , the linear decrease of T_C can be interpreted as a result of the dilution effect caused by the SnO_6 octahedra. However, Ce^{4+} is much bigger than Ti^{4+} and the CeO_6 octahedra are likely to determine a significant deformation and expansion of the surrounding TiO_6 octahedra enhancing the off-center displacement of Ti^{4+} and thus counterbalancing the dilution effect for low values of x (Canu *et al.*, 2018).

When the amount of M is large enough, $x = 0.19\text{--}0.22$ (≈ 0.25 for BZT), a ferroelectric to relaxor crossover occurs. In the relaxor state the average crystal structure is cubic $Pm\bar{3}m$ though at local scale it is still acentric in agreement with the existence of polar nanoregions, as discussed in Section “Phase Transition Engineering”.

Dielectric Properties

The relative dielectric constant (real part of the dielectric permittivity), ϵ' , of tetragonal BaTiO_3 single crystal is strongly anisotropic, ≈ 250 along the c -axis and ≈ 4500 on the a - b plane (Fig. 2) at room temperature. Discontinuities of ϵ' and spontaneous polarization (P_s) accompanied by hysteretic behavior are observed at the transition temperatures (Jaffe *et al.*, 1971; Mertz, 1949). The discontinuities indicate that the transitions are first-order. In ceramics these dielectric anomalies transform in peaks and the room temperature dielectric constant varies between 1000 and 5000 depending on processing, residual porosity, non-stoichiometry and grain size. The dependence of the dielectric response of BaTiO_3 ceramics on the Ba/Ti ratio was investigated by Lee *et al.* (2001). The dielectric constant attains maximum values for nearly stoichiometric compositions. In Ti-excess ceramics the permittivity drops because of the formation of a titania rich layer at the grain boundaries or $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ inclusions. In Ba-excess samples, the decrease of the dielectric constant was ascribed to the formation of Ba_2TiO_4 inclusions and the accumulation of stress around the secondary phase particles due to the different thermal expansion in comparison to BaTiO_3 (Lee *et al.*, 2007a, 2001). In any case, the above permittivity values are 100–500 times higher than those of alumina ceramics ($\epsilon' \approx 10$), common dielectrics largely used for insulating substrates. Barium titanate also shows relatively low values ($\approx 1\%$) of the loss tangent ($\tan \delta = \epsilon''/\epsilon'$, where ϵ'' is the imaginary part of permittivity), an indispensable requirement for a dielectric to be used in capacitors (Kishi *et al.*, 2003; Pan and Randall, 2010). Despite these promising properties, the permittivity of neat barium titanate strongly depends on

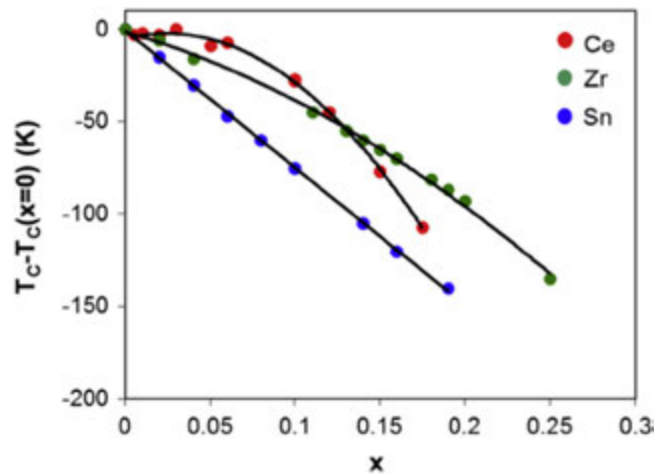


Fig. 10 Variation of the Curie temperature in the $\text{BaM}_x\text{Ti}_{1-x}\text{O}_3$ ($M = \text{Sn, Zr, Ce}$) solid solutions with respect to undoped BaTiO_3 . Reprinted from ref. Canu, G., Confalonieri, G., Deluca, M., *et al.*, 2018. Structure-property correlations and origin of relaxor behaviour in $\text{BaCe}_x\text{Ti}_{1-x}\text{O}_3$. *Acta Materialia* 152, 258–268, with permission from Elsevier. Copyright (2018) Acta Materialia Inc.

Table 1 EIA specification codes for Class II dielectrics

First marking		Second marking		Third marking	
Symbol	Low temperature limit ($^{\circ}\text{C}$)	Symbol	High temperature limit ($^{\circ}\text{C}$)	Symbol	Maximum capacitance deviation (%)
Z	+10	4	+65	A	± 1.0
Y	–30	5	+85	B	± 1.5
X	–55	6	+105	C	± 2.2
		7	+125	D	± 3.3
		8	+150	E	± 4.7
		9	+200	F	± 5.5
				P	± 10.0
				R	± 15
				S	± 22
				T	+22/–33
				U	+22/–56
				V	+22/–82

temperature and the material is not suitable for most practical applications, for which a higher thermal stability of the dielectric constant and, hence, capacitance, are desired.

The above limitations were overcome by modifying the composition and the microstructure of the material and nowadays ceramic BaTiO_3 is the most widely used dielectric material in the electronic industry (Kishi *et al.*, 2003; Pan and Randall, 2010), mainly for the fabrication of MLCCs. Barium titanate ceramics belong to Class II dielectrics with dielectric constant from 1000 to > 20000 and losses in the range 0.01–0.03 (Pan and Randall, 2010). The Electronic Industry Alliance (EIA) specification of Class II dielectrics is based on a three-character alphanumeric code. In Table 1, the first character is the low temperature operating limit, the second the high temperature limit, and the third the maximum capacitance deviation over the specified temperature range. For example, X7R means that the capacitance variation is less than $\pm 15\%$ (from its value at 25°C) between -55 and 125°C . Some commonly used MLCCs have specifications Z5U, Y5V and XNR ($N = 5-8$). The temperature dependence of permittivity can be adapted to fulfill the requirements corresponding to the given specification by two main strategies: (1) engineering the phase transitions and (2) controlling the microstructure.

Phase Transition Engineering

The incorporation of foreign ions in the BaTiO_3 lattice not only determines a shift of the phase transition temperatures as discussed in detail in Section “Strategies for Modifying Defect Chemistry, Phase Transitions and Properties” but also modifies the order of the phase transition, the width of the dielectric peak at the Curie temperature, the polar order and the frequency dispersion of permittivity. The progressive shift and broadening of the permittivity peak in $\text{BaSn}_x\text{Ti}_{1-x}\text{O}_3$ as shown in Fig. 11(a) is a representative

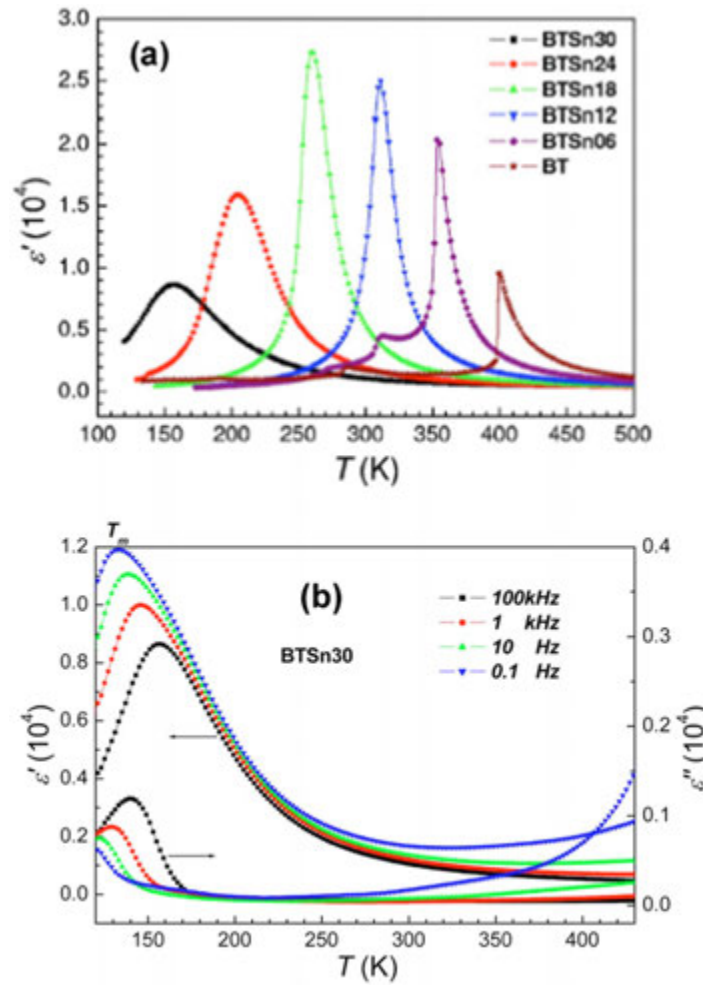


Fig. 11 (a) Temperature dependence of the relative dielectric constant (ϵ') of BaTi_{1-x}Sn_xO₃ ($x = 0, 0.06, 0.12, 0.18, 0.24, 0.30$) ceramics at 100 kHz. Composition $x = 0.12$ is close to the phase convergence point. (b) Temperature dependence of the real (ϵ') and imaginary parts (ϵ'') of the dielectric permittivity of ceramic with composition $x = 0.30$. Reprinted from ref. Lei, C., Bokov, A.A., Ye, Z.-G., 2007. Ferroelectric to relaxor crossover and dielectric phase diagram in the BaTiO₃-BaSnO₃ system. Journal of Applied Physics 101, 084105, with the permission of AIP Publishing.

example. In many heterovalent- and homovalent-substituted BaTiO₃ ceramics the dielectric behavior gradually evolves with increasing dopant concentration and a crossover to relaxor state is often observed beyond a critical dopant concentration (Shvartsman and Lupascu, 2012). The relaxor state exists in many lead-free and lead-bearing ferroelectric systems and its typical signature is the appearance of a strong frequency dispersion of the permittivity peak temperature (T_m). The maximum of both real and imaginary part of permittivity shifts at higher temperature with increasing frequency. However, the frequency dispersion is on the low-temperature side of $\epsilon'(T)$ whereas it is on the high-temperature side of $\epsilon''(T)$ (see Fig. 11(b) as an example). The frequency dependence of T_m obeys the Vogel-Fulcher law (Shvartsman and Lupascu, 2012). Relaxor behavior is attributed to the existence of polar nanodomains or polar nanoregions (PNRs) inside a highly polarizable matrix (Shvartsman and Lupascu, 2012; Burns and Dacol, 1983; Samara, 2003). The orientation of the elemental electrical dipoles, associated to the off-center displacement of the Ti⁴⁺ ions in the TiO₆ octahedra in the case of BaTiO₃-based relaxors, is highly correlated inside each nanodomain but the dipole moments of the PNRs are almost randomly oriented. The PNRs have a size of the order of a few nanometers and are highly responsive to electric fields as indicated by slim, nonlinear $P(E)$ loops. For sufficiently high fields the nanodomains can be oriented with the electric field leading to large polarization but, on removing the field, due to thermal fluctuations most nanodomains re-acquire a random orientation resulting, differently from conventional ferroelectrics, in a very small P_r . The small but nonzero P_r indicates that a weak correlation also exists among nanodomains. It should be stressed that there is no phase transition across T_m in a relaxor, indeed the PNRs exist at much higher temperatures than T_m , up to the so-called Burns temperature, T_d (Burns and Dacol, 1983). The permittivity maximum is simply a manifestation of the slowing down of dipolar motion below T_m (Samara, 2003). The average structure of a perovskite relaxor is usually cubic but at local level the spatial symmetry is broken, as indicated by Raman scattering and PDFs analysis (Hou et al., 2018). The existence of PNRs becomes apparent even in the absence of an electric field on properties depending on P^2 , for example in the deviation of the temperature dependence of refractive index and thermal expansion below T_d from the

behavior predicted for the paraelectric state (Burns and Dacol, 1983; Samara, 2003). At sufficiently low temperature (T_f), the dipolar motion freezes and the permittivity dispersion vanishes.

The dielectric properties of two families of BaTiO₃ solid solutions, BaM_xTi_{1-x}O₃ and BaTiO₃-Bi(M)O₃, which have attracted attention for application in capacitors will be discussed in some detail.

BaTiO₃-BaMO₃ solid solutions

In the case of BaM_xTi_{1-x}O₃ (M = Sn, Zr, Hf, Ce) solid solutions (Lei *et al.*, 2007; Canu *et al.*, 2018; Hennings *et al.*, 1982; Hansen *et al.*, 1998; Shvartsman *et al.*, 2009, 2008; Gao *et al.*, 2017; Kleemann *et al.*, 2013; Maiti *et al.*, 2008), the phase transition sequence (see Fig. 9 as an example), the polar order and the dielectric properties (Fig. 11) change according to the following scenario:

- (1) In the BaTiO₃-rich side of the system, T_C decreases with increasing x whereas the R/O and O/T transition temperatures rise until the three transitions merge at the phase convergence point (x_p, T_p) with $x_p \approx 0.10$, as described above. For small values of x not larger than a few at%, the T/C transition remains sharp and first order as in neat BaTiO₃. For larger x values, the permittivity peak at T_C broadens and at x_p the transition changes to second order.
- (2) The dielectric constant attains its maximum value at or close to x_p . The peak permittivity can be very high, of the order of a few tens of thousands. BZT ceramics, further modified by partial substitution of Ca at the Ba site, have maximum relative permittivity of ≈ 30000 around room temperature and a moderate temperature stability suitable for Z5U and Y5V capacitors (Hennings *et al.*, 1982; Hansen *et al.*, 1998).
- (3) For $x > x_p$, only a single R/C transition persists. The transition becomes progressively more diffuse in temperature (DPT, diffuse phase transition) as indicated by the appearance of a broad and rounded permittivity peak accompanied by some frequency dispersion. Despite the smearing of the transition, the temperature corresponding to the permittivity maximum (T_m) remains independent of frequency and can still be identified as the average T_C .
- (4) Beyond a certain substitution level x_r ($x_r = 0.20$ – 0.25 depending on M), the value of T_m starts to move at higher temperatures with increasing frequency, a typical sign of relaxor behavior. The ferroelectric to relaxor crossover occurs over a finite composition range and is not accompanied by a macroscopic phase transition (Shvartsman and Lupascu, 2012; Kleemann *et al.*, 2013). Recent broad-band dielectric spectroscopy investigations have suggested that BaZr_xTi_{1-x}O₃ compositions, especially those with $x \geq \approx 0.50$ behave like a dipolar glass rather than a typical relaxor (Filipič *et al.*, 2016; Petzelt *et al.*, 2014). Furthermore, ferroelectric order could not be induced by the application of an electric field for the composition with $x = 0.50$. The dielectric relaxation is assigned to local hopping of the off-centered Ti⁴⁺ ions in frozen BaTiO₃ clusters, whose size is rather small and cannot grow on cooling (Petzelt *et al.*, 2014).
- (5) Relaxor or dipolar glass behavior persists up to values of x very close to 1 when M = Zr as complete solid solubility exists between BaTiO₃ and BaZrO₃ (Maiti *et al.*, 2008). BaZrO₃ is a paraelectric solid with a relative dielectric constant of 37–38 at room temperature and cubic $Pm\bar{3}m$ structure up to the melting point (Akbarzadeh *et al.*, 2005). Complete solid solubility with BaSnO₃ and BaHfO₃ is also likely. In contrast, the maximum solubility of BaCeO₃ is limited and corresponds to $x = 0.33$ – 0.35 (Makovec *et al.*, 1996; Lu *et al.*, 2012).

The evolution of polar order and the decrease of dipole correlation length with composition in BaZr_xTi_{1-x}O₃ is well supported by Raman spectroscopy studies (Dobal *et al.*, 2001; Miao *et al.*, 2009; Buscaglia *et al.*, 2014). Strong Raman bands not compatible with a cubic structure were revealed for the relaxor composition $x = 0.40$ but cannot be attributed to a specific symmetry and no sign of phase transitions was detected in the range 78–398 K. The persistence of some polar bands in the Raman spectra (Buscaglia *et al.*, 2014, 2006a) far above the ferroelectric–paraelectric transition as well as measurements of acoustic emission (Dul'kin *et al.*, 2010) and refractive index (Burns and Dacol, 1982) support the existence of locally correlated displacements on the Ti sites and of polar clusters in undoped BaTiO₃ and BZT compositions $x = 0.10$ – 0.20 (Shvartsman and Lupascu, 2012). However, the dynamics of these polar clusters if compared to conventional relaxors, is much faster, reaching the THz range, and the dielectric anomaly at T_C is frequency independent in the radiofrequency region (Dul'kin *et al.*, 2010).

The local structure and polar order of BZT has been carefully investigated using X-ray absorption fine structure (XAFS) measurements as well as X-ray and neutron PDF analysis (Buscaglia *et al.*, 2014; Laulhe *et al.*, 2009; Levin *et al.*, 2011). The PDF provides direct evidence that the Ti and Zr atoms do not occupy the equivalent octahedral sites expected from the average cubic crystallographic structure of the solid solution. Because of the relatively large difference between the ionic radii of Zr⁴⁺ and Ti⁴⁺, the TiO₆ and ZrO₆ octahedra have a tendency to preserve their individuality, i.e. despite a broad bond length distribution, the average value of the Ti–O and Zr–O distances are, for most of the compositional range, similar to those observed in BaTiO₃ and BaZrO₃, respectively (Laulhe *et al.*, 2009; Levin *et al.*, 2011). This is evident in the neutron PDF because the neutron scattering factor of Ti is negative whereas those of the other involved elements is positive. This produces a “negative” peak for the Ti–O pair and a positive peak of the Zr–O pair (Laulhe *et al.*, 2009), as shown in Fig. 12. Furthermore, the X-ray PDF studies (Buscaglia *et al.*, 2014) suggest that the local structure of Ti-rich compositions is always rhombohedral with Ti displacement in the [111] pseudocubic direction, including the relaxor composition $x = 0.40$ which exhibited a cubic $Pm\bar{3}m$ diffraction pattern (from high-resolution synchrotron radiation experiments) at 100–450 K.

XAFS measurements of Levin *et al.* (2011) have revealed that for low concentrations of Ti, isolated Ti atoms in the relatively large octahedral sites of the BaZrO₃ lattice acquire centrosymmetric coordination with average Ti–O distances shorter than those in BaTiO₃. In contrast for higher concentrations of titanium, Ti atoms having one or more Ti as their B-site nearest neighbors undergo

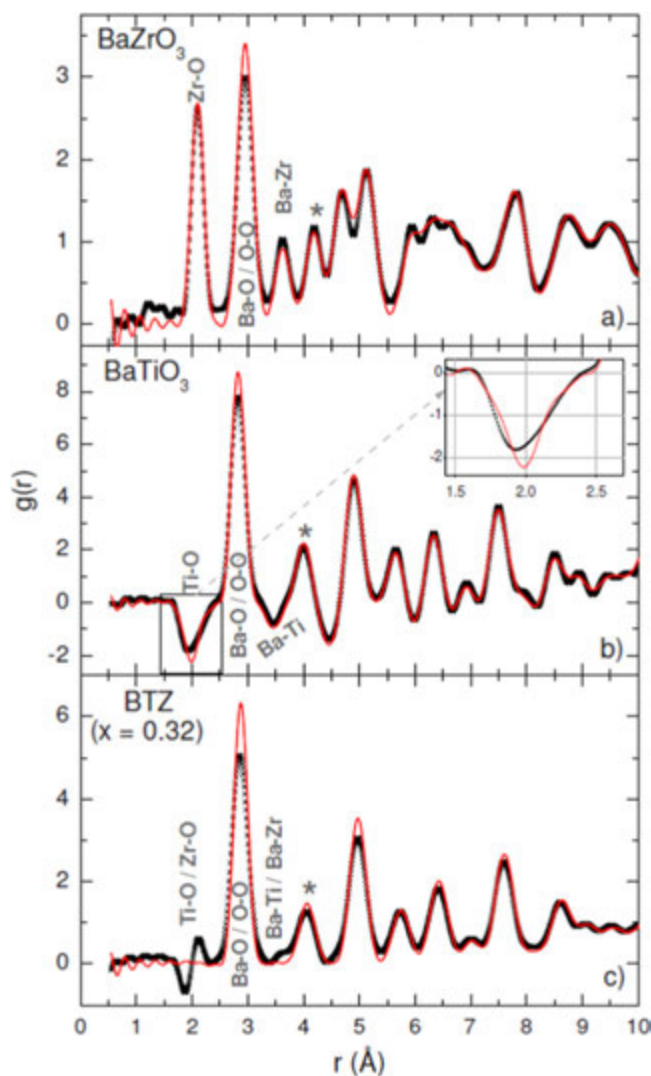


Fig. 12 Experimental pair distribution function of (a) BaZrO₃, (b) BaTiO₃, and (c) BaTi_{0.68}Zr_{0.32}O₃ at 300K (crosses), compared with the PDF calculated from their crystallographic structures (lines). Inset in figure (b): zoom on the contribution of the Ti-O pairs within the TiO₆ octahedra in BaTiO₃. Reprinted figure with permission from ref. Laulhé, C., Hippert, F., Bellissent, R., Cuello, G.J., 2009. Local structure in BaTi_{1-x}Zr_xO₃ relaxors from neutron pair distribution function analysis. *Physical Review B* 79, 064104. Copyright (2009) by the American Physical Society.

polar off-center displacements. Opposite, Zr cations are essentially in centric position. Significant deviations from a random distribution of Ti and Zr (i.e., segregation phenomena) were not detected except for compositions close to BaTiO₃.

The local structure of BaTi_{0.74}Zr_{0.26}O₃ was investigated via first-principle calculations using $3 \times 3 \times 3$ supercells (Laulhé *et al.*, 2010). While Ba and Zr off-center displacements were small and uncorrelated, Ti off-center displacement was of the same magnitude as in BaTiO₃. Notably, the direction of a Ti-atom displacement is variable and entirely determined by the distribution of the Ti and Zr atoms in the adjacent unit cells. The underlying mechanism involves local strain effects that ensue from the difference in size between the Ti⁴⁺ and Zr⁴⁺ cations. A Ti atom is no longer displaced in the direction in which its octahedral cage is compressed.

Because of the existence of a phase convergence point, BaM_xTi_{1-x}O₃ systems are of potential interest for electrocaloric cooling. Liu *et al.* (2012) have predicted that an enhanced electrocaloric effect or, in other words, a larger temperature variation ΔT , can be attained for compositions close to the convergence point since the dipole entropy increases by increasing the number of coexisting phases which is maximum at the convergence point. Experimental verification was carried out on different systems varying the composition, x . In particular, Qian *et al.* (2014) have measured a ΔT of 4.2–4.5K for $x = 0.15$ – 0.20 in BaZr_xTi_{1-x}O₃ ceramics using an electric field of $\approx 150 \text{ kV cm}^{-1}$. In the homologous systems with Hf and Sn, the temperature variation was maximized at $x = x_p$. A significant ΔT of 0.35K was obtained in BaHf_{0.11}Ti_{0.89}O₃ under an electric field of only 10 kV cm^{-1} (Li *et al.*, 2016) and a similar result was reported for BaSn_{0.105}Ti_{0.895}O₃ (Luo *et al.*, 2014).

BaTiO₃-Bi(M)O₃ solid solutions

Solid solutions between BaTiO₃ and Bi(M)O₃ compounds, such as BiScO₃, Bi(Zn_{0.5}Ti_{0.5})O₃, Bi(Mg_{0.5}Zr_{0.5})O₃, Bi(Mg_{0.5}Ti_{0.5})O₃ and Bi(Mg_{2/3}Nb_{1/3})O₃, show a common behavior and interesting dielectric properties for high-temperature capacitor applications (Beuerlein *et al.*, 2016). When the mole fraction of Bi(M)O₃ is between 0.05 and 0.15, depending on M, a transition from tetragonal *P4mm* to a pseudocubic structure is observed. Although the average structure appears cubic at X-ray and neutron diffraction, a detailed refinement performed on the (1-*x*)BaTiO₃-*x*Bi(Zn_{0.5}Ti_{0.5})O₃ compositions (*x* = 0.10, 0.20) shows that the oxygen ions and B-site cations (Ti, Zn) are displaced from the positions of the cubic perovskite lattice. PDF analysis indicates that the local structure (1–10 Å) is better described by a *P4mm* model with a *c/a* ratio of 1.014 (*x* = 0.20), close to that of BaTiO₃. However, the *c/a* ratio decreases with increasing the scale length. Beyond 3–4 nm, the structure is very close to the cubic one. The correlation between the atomic displacements is gradually lost with increasing distance and beyond a scale length corresponding to 6–8 unit cells the distortions will be almost averaged out. The introduction of Bi(Zn_{0.5}Ti_{0.5})O₃ (*x* ≥ 0.10) in the BaTiO₃ lattice introduces sufficient chemical and compositional disorder to break the long-range ferroelectric order. In contrast, for compositions *x* = 0.06 and 0.08, both the average and local structure are tetragonal although at short scale lengths (< 2 nm) the *c/a* ratio is higher than that of the average structure. The PDF analysis gives direct evidence of the existence of polar clusters for all compositions up to at least 225°C (Hou *et al.*, 2017), a temperature much higher than the Curie point of BaTiO₃.

Solid solutions with composition in the pseudocubic region exhibit relaxor behavior and a very broad permittivity peak with stable permittivity over a wide temperature range (Zeb and Milne, 2015; Ogihara *et al.*, 2009; Xiong *et al.*, 2011; Zeb and Milne, 2014a,b). The addition of Bi(M)O₃ amounts around 30–50 mol% broadens the stability range up to temperatures > 400°C as shown in Fig. 13(a). Good thermal stability at 50–350°C and 1 kHz with $\epsilon' \approx 1000$ was reported for 0.7BaTiO₃-0.3BiScO₃ although $\tan\delta$ rapidly rises above 300°C (Ogihara *et al.*, 2009). A dielectric constant of $\approx 1030 \pm 15\%$ over the temperature range 25–420°C was reported for the composition 0.7Ba_{0.8}Ca_{0.2}TiO₃-0.3Bi(Zn_{0.5}Ti_{0.5})O₃ (Zeb and Milne, 2014a) while for 0.7BaTiO₃-0.3Bi(Mg_{0.5}Zr_{0.5})O₃ ceramics ϵ' was $\approx 570 \pm 15\%$ between –20 and 430°C (Zeb and Milne, 2014b) at 1 kHz with low tangent loss (< 2%) in both cases. The temperature stability range can be further widened up to 550°C in (1-*x*)BaTiO₃-*x*Bi(Mg_{2/3}Nb_{1/3})O₃ ceramics, *x* = 0.50–0.60, (Muhammad *et al.*, 2016) while a very flat permittivity plateau of ≈ 1100 was reported for the ternary *x*BaTiO₃-(1-*x*)(0.5Bi(Zn_{1/2}Ti_{1/2})O₃-0.5BiScO₃) system (Raengthon *et al.*, 2012). Large amounts of Bi(M)O₃ often lead to inhomogeneous element distribution and formation of core-shell grains which contribute to improve the temperature stability (Ogihara *et al.*, 2009; Zeb and Milne, 2014b). Extensive formation of core-shell grains was observed in BaTiO₃-based ceramics containing only 5 mol% BiScO₃. Complete homogeneity could not be obtained even after 20 h sintering (Ogihara *et al.*, 2009).

While for the tetragonal ferroelectric phase (*x* ≤ 0.07), the Curie temperature of (1-*x*)BaTiO₃-*x*BiScO₃ ceramics decreases with increasing *x*, both *T_m* and *T_f* of compositions with pseudocubic structure (*x* > 0.07) increase with increasing *x*, though BiScO₃ is a paraelectric solid. A similar behavior was only reported for BaTiO₃-PbTiO₃ and BaTiO₃-Na_{0.5}Bi_{0.5}TiO₃ solid solutions but, in these cases, both end members are ferroelectric (Jaffe *et al.*, 1971; Datta *et al.*, 2010). A further peculiarity of the BaTiO₃-BiScO₃ system (*x* ≥ 0.10) is represented by the re-entrant relaxor behavior. By decreasing the temperature, the remanent polarization first grows from a very low level to values typical of long-range ferroelectric order and then drops again on further cooling (Bharadwaja *et al.*, 2011). This indicates that the system re-enters in a more disordered state. The maximum of remanent polarization is observed at temperatures close to *T_f*. According to Guo *et al.* (2008) and differently from most relaxors in which the PNRs emerge from the paraelectric state, polar clusters grow inside the ferroelectric matrix below *T_f*.

The Curie temperature of (1-*x*)BaTiO₃-*x*Bi(Na_{0.5}Ti_{0.5})O₃ (*x* = 0–0.30) solid solutions increased from 136°C (*x* = 0) to 214°C (*x* = 0.30) with increasing *x*. Stabilization of the tetragonal *P4mm* phase and increase of the *c/a* ratio in comparison to pure BaTiO₃ is observed over a wide temperature range, from –250°C to *T_C* (Datta *et al.*, 2010). The addition of 10% Bi(Na_{0.5}Ti_{0.5})O₃ can be used to broaden the application field of barium titanate up to 150°C. Further modification of the dielectric properties by Nb₂O₅ addition leads to ceramics with an average dielectric constant of ≈ 1600 , compatible with the X9R specification. The properties can be further modified by adding other dopants. A representative example is given in Fig. 13(b) (Chen *et al.*, 2019). Ceramics with composition (1-*x*)BaTiO₃-*x*LiTaO₃, *x* = 0.25–0.30 are also X9R compliant with ϵ' in the range 700–900 (Wang *et al.*, 2013). In addition, they can be sintered in reducing atmosphere and are, in principle, compatible with the base metal electrode technology.

In general, cofiring of Bi-containing dielectrics with base metal electrodes is quite challenging because of the reduction of Bi₂O₃ to metallic bismuth at the reduced oxygen partial pressure needed to avoid the electrode oxidation. Even cofiring with noble metal electrodes is not trivial due to the reactivity of Bi-based dielectrics and the sintering temperature has to be carefully chosen to overcome this problem (Beuerlein *et al.*, 2016).

Microstructure Control: Core-Shell Grains

Microstructure and, in particular, grain size has a strong impact on ferroelectric, dielectric and piezoelectric properties. The role of grain size has been widely investigated and will be discussed in more detail in Section “Size and Scaling Effects”. From the point of view of obtaining dielectrics with temperature-stable permittivity, a key aspect is represented by the fabrication of ceramics consisting of grains with a core-shell structure.

In general, the temperature stability can be improved by means of ceramics with non-homogeneous composition at the level of the single grains. For example, the partial interdiffusion between a BaTiO₃ core and a SrTiO₃ or BaZrO₃ shell produces grains with

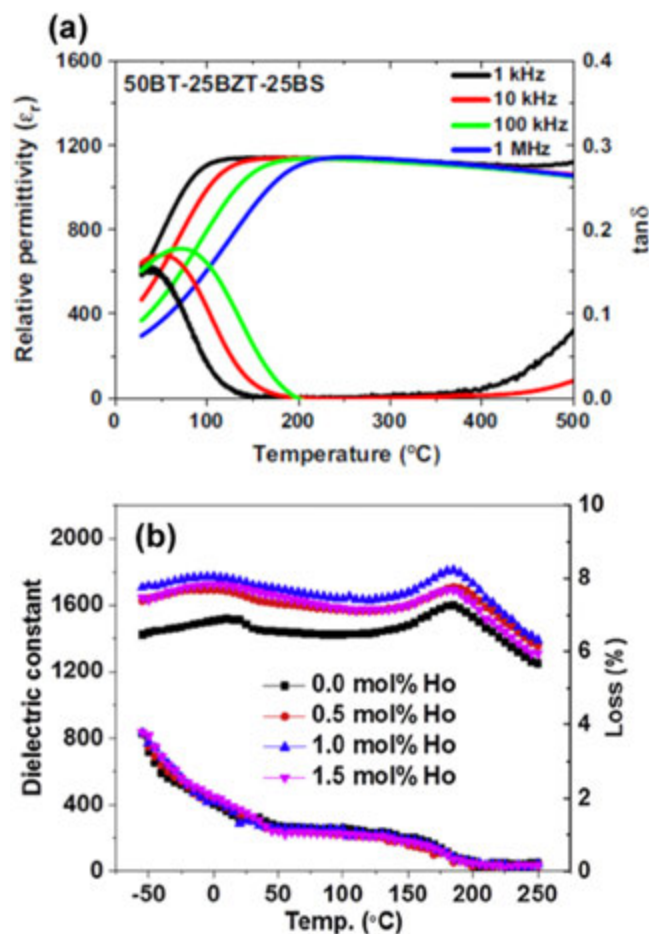


Fig. 13 Dielectric properties of BaTiO₃-Bi(M)O₃ ceramics. (a) 0.50BaTiO₃-0.25BiZn_{1/2}Ti_{1/2}O₃-0.25BiScO₃. (b) 0.9BaTiO₃-0.10Bi_{0.5}Na_{0.5}TiO₃ with 1.5 mol% Nb₂O₅ and different Ho content (frequency: 1 kHz). Reprinted from (a) Zeb, A., Milne, S.J., 2015. High temperature dielectric ceramics: A review of temperature-stable high-permittivity perovskites. *Journal of Materials Science: Materials in Electronics* 26, 9243–9255 with permission from Springer Nature GmbH. Copyright (2015) Springer Science + Business Media New York. (b) Chen, L.L., Hui, K.Z., Wang, H.X., *et al.*, 2019. Effects of Ho₂O₃ doping and sintering temperature on the core-shell structure of X9R Nb-modified BaTiO₃-(Bi_{0.5}Na_{0.5})TiO₃ ceramics. *Journal of the European Ceramic Society* 39, 3710–3715 with permission from Elsevier. Copyright (2019) Elsevier Ltd.

a radial composition gradient and, consequently, with a distribution of the Curie temperature resulting in a broad permittivity peak (Buscaglia *et al.*, 2006c; Wu *et al.*, 2015; Airimioaei *et al.*, 2017). However, the preferred microstructure for temperature-stable dielectrics belonging to XNR (N = 6–8) classes consists of a nearly pure BaTiO₃ core surrounded by a shell of more heavily doped material (Fig. 14), characterized by diffuse phase transition or relaxor behavior with a broad permittivity peak around room temperature (Jeon *et al.*, 2012). This result can be attained by controlling the Ba/Ti ratio, the amount and distribution of an appropriate dopant oxide, and grain growth (Jeon *et al.*, 2012; Armstrong *et al.*, 1989; Hennings and Schreinemacher, 1994; Chazono and Kishi, 1999). In order to obtain reliable capacitors with improved lifetime by means of the base-metal electrode technology (Ni or Cu electrodes), at least two dopants are needed (Kishi *et al.*, 2003; Sato *et al.*, 1999). A first dopant is an acceptor (Mn²⁺, Mg²⁺, Ca²⁺, etc.) added in a small amount (1–2 at%), which substitutes at the Ti site avoiding the degradation of the dielectric properties of BaTiO₃ during sintering in a reducing atmosphere. The preferred second dopant is a rare-earth ion with intermediate ionic radius (Y³⁺, Ho³⁺, Dy³⁺), which substitutes at both Ba and Ti site and is mainly confined in the shell region (Fig. 14). These rare-earths significantly improve the capacitor lifetime, hindering the degradation of the insulation resistance and, for this reason, they are often denoted as “magic” dopants (Kishi *et al.*, 2003; Sato *et al.*, 1999). The mechanism has not fully been elucidated in detail yet but it is certainly determined by the amphoteric behavior of these ions and the resulting effective control of the acceptor/donor ratio, as discussed in Section “Incorporation of Rare-Earth Ions”. Prior to the use of rare-earth dopants, BaTiO₃-Co₃O₄-Nb₂O₅ ceramics were widely investigated and used as X7R dielectrics (Hennings and Schreinemacher, 1994; Chazono and Kishi, 1999). A sintering aid, usually a powdered glass or silica, is often added to lower the sintering temperature. In most cases, the formation of the shell does not occur by solid-state diffusion of the dopant but, rather, by a dissolution-precipitation process mediated by the existence, during sintering, of a liquid phase in which the dopant oxides dissolve (Jeon *et al.*, 2012; Chazono and Kishi, 1999; Hennings and Rosenstein, 1984; Armstrong and Buchanan, 1990; Chazono and Kishi, 2000; Kim and Kang, 1999).

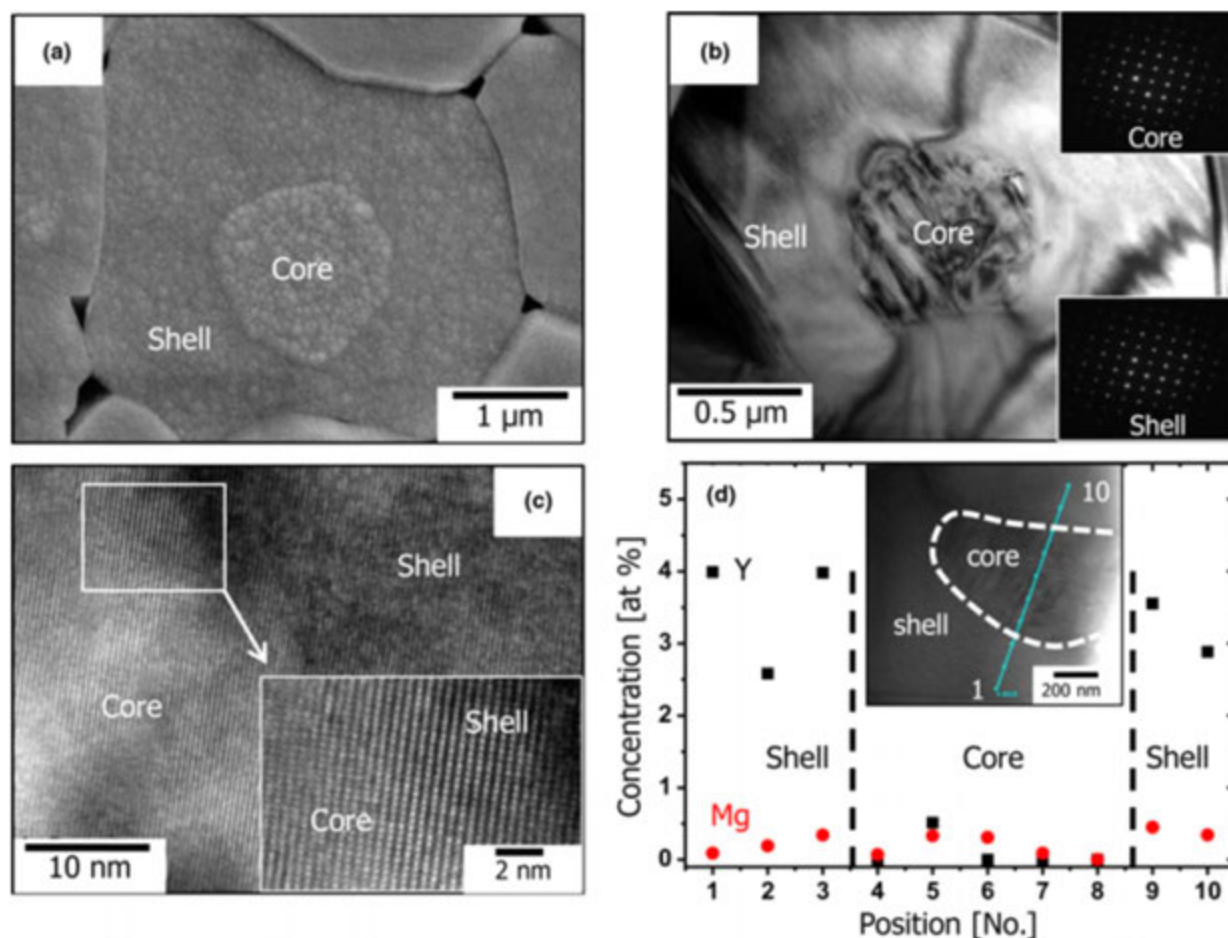


Fig. 14 (a) SEM and (b) TEM micrographs showing typical core-shell structures in a sample sintered at 1350°C in wet H₂ for 2 h; (c) HRTEM image at the interface between a core and a shell; (d) STEM/EDS line profile showing the distribution of Y and Mg. Reprinted from ref. Jeon, S.-C., Lee, C.-S., Kang, S.-L., 2012. The mechanism of core/shell structure formation during sintering of BaTiO₃-based ceramics. *Journal of the American Ceramic Society* 95, 2435–2438 with permission of Wiley. Copyright (2012) American Ceramic Society.

Microstructure control plays a crucial role on the performances of the capacitors and needs the optimization of several parameters. Sintering temperature has to be carefully optimized as variations of only 10–20°C can significantly modify the dielectric properties (Chazono and Kishi, 1999; Mizuno *et al.*, 1998) by inducing grain growth and composition homogenization. The relative amount of the dopants has also a crucial influence on the temperature stability. In BaTiO₃-Co₃O₄-Nb₂O₅ dielectrics (Chazono and Kishi, 1999, 2000), the inward diffusion of Co is no longer prevented if Nb/Co < 2, resulting in composition homogenization and collapse of the core-shell structure. In BaTiO₃ ceramics co-doped with Mg and Ho, an appropriate amount of Mg is necessary for suppressing the inward diffusion of the rare-earth ions. MgO first reacts with BaTiO₃ and forms the shell region in which Mg²⁺ substitutes at the Ti site. At higher temperature, Ho³⁺ also incorporates in the perovskite but its diffusivity is controlled by the Mg/Ho ratio (Kishi *et al.*, 1997). Likewise, the Mg/Y ratio plays a dominant role in the formation of the core-shell structure in BaTiO₃-MgO-Y₂O₃ dielectrics (Kim *et al.*, 2008). In general, a higher amount of MgO is required to suppress the grain growth and the diffusion into the core region for the larger lanthanide ions (La³⁺, Sm³⁺) compared to the intermediate size ions (Ho³⁺, Dy³⁺, Er³⁺) (Kishi *et al.*, 1999). The different behavior is related to the different incorporation site of the lanthanide ions: predominant substitution at Ba site for La³⁺ and Sm³⁺, substitution at both Ba and Ti site for Ho³⁺, Dy³⁺ and Er³⁺, as discussed in Section “Incorporation of Rare-Earth Ions”. It is worth noting that in the fabrication of MLCCs, the dielectric material is prepared by directly adding the different dopants to the BaTiO₃ powder. The lanthanide ions of intermediate size distribute between the two cation sites depending on the A/B ratio. The volumetric ratio between core and shell is also an important microstructural parameter.

A better control on the formation of the core-shell structure, especially when the grain size is in the submicron scale, can be achieved by coating the BaTiO₃ particles with a layer of the dopant oxide using a colloidal chemistry approach (Zhang *et al.*, 2011). The formation of core-shell grains is also essential to obtain X9R-compliant dielectrics (Chen *et al.*, 2019; Yao *et al.*, 2012a).

One of the main drawbacks of BaTiO₃ ceramics is the relatively low dielectric strength ($E_b \approx 90 \text{ kV cm}^{-1}$) which limits the high-field applications. A significant improvement of the breakdown field can be obtained by realizing BaTiO₃-SiO₂/glass composites with a microstructure comprising BaTiO₃ grains surrounded by a silica/glass layer at grain boundary (Zhang *et al.*, 2015;

Wang *et al.*, 2012; Liu *et al.*, 2017b; Yuan *et al.*, 2017a). Zhang *et al.* (2015) have observed a progressive increase of E_b from 90 to 280 kV cm⁻¹ with increasing silica content from 0 to 8 wt% and a parallel decrease of the dielectric constant from ≈ 4000 to ≈ 500 . The ceramics were fabricated using BaTiO₃@SiO₂ core-shell particles prepared by a Stöber-like process with different thickness of the silica shell. The existence of a continuous silica network with a low dielectric constant (≈ 4) determines a strongly nonhomogeneous distribution of the electric field. In particular, the electric field in the silica layer is higher than the applied field, whereas it is lower than the applied field in the ferroelectric cores. The higher dielectric strength of silica (≈ 400 kV cm⁻¹) and the “screening” effect of the shell results in improved insulating properties of the composite. The breakdown field further increases to ≈ 330 kV cm⁻¹ in BaTiO₃/BaTiO₃@SiO₂/BaTiO₃ multilayered thick films (Yuan *et al.*, 2017a).

The encapsulation of BaTiO₃ and Ba_{0.6}Sr_{0.4}TiO₃ particles of different diameter with an amorphous silica shell by means of a modified Stöber process, using tetraethoxysilane (TEOS) as precursor, was investigated by Elissalde *et al.* (Hornebecq *et al.*, 2004; Mornet *et al.*, 2005; Chung *et al.*, 2009, 2010). In the case of Ba_{0.6}Sr_{0.4}TiO₃ particles, the thickness of the shell can be controlled between 2 and 80 nm with high accuracy (Mornet *et al.*, 2005). Thanks to the silica shell, the sintering temperature can be decreased to $\approx 1000^\circ\text{C}$, in comparison to values of the order of 1300–1400°C required for the uncoated particles, thus avoiding grain growth. Good densification (92%) was also obtained by sintering in a microwave furnace (Chung *et al.*, 2010). Densification of BaTiO₃@SiO₂ core-shell particles by Spark Plasma Sintering and post-annealing at 800°C in air produced ceramics with a giant dielectric constant ($> 10^5$, 10 kHz) and a relatively low loss tangent (≈ 0.05) in the range 25–180°C (Chung *et al.*, 2009). The silica shell is a good dielectric and, moreover, slows down reoxidation of the inner region of the BaTiO₃ grains, which remain semiconducting after post-annealing. At low frequency ($< 10^5$ Hz) and above room temperature, the effective permittivity is controlled by the insulating grain boundary layer, whereas at higher frequency and lower temperature the contribution of grain cores predominates and the permittivity drops to values typical of BaTiO₃.

Dielectrics for Energy Storage

The main driving force for the continuous development of the MLCC technology is the large scale application of these passive components in consumer electronics. However, in the last few years there has been an increasing demand for ceramic capacitors with higher energy density for power electronic devices and pulse power applications, including hybrid and electrical vehicles. While ceramic capacitors have a high power density (fast charge/discharge performances), the energy density is relatively low and extensive studies have been undertaken to develop new dielectric materials with enhanced breakdown field and improved storage efficiency (Yao *et al.*, 2017; Palneedi *et al.*, 2018; Prateek *et al.*, 2016).

Room-temperature properties of some bulk ceramics reported in recent years (Ogihara *et al.*, 2009; Yuan *et al.*, 2018, 2017b; Zhou *et al.*, 2018; Yang *et al.*, 2017; Li *et al.*, 2017; Wang *et al.*, 2015; Wu *et al.*, 2016; Shen *et al.*, 2015; Song *et al.*, 2014, 2015; Huang *et al.*, 2015; Yang *et al.*, 2018) are summarized in Table 2. Because of the slim polarization loops (small hysteresis) and high breakdown field, BaTiO₃-Bi(M)O₃ relaxors are potential dielectric materials for energy storage. The recoverable energy density attains values up to 2–3 J cm⁻³ with efficiency of 80%–90% at fields of ≈ 200 kV cm⁻¹. Thin (15 μm thickness) BaTiO₃-BiScO₃ dielectrics exhibited superior energy storage capability at the same applied electric field, relative to commercial MLCCs (Ogihara *et al.*, 2009). The charge storage performance of BaTiO₃ ceramics is significantly lower (energy density: 0.3–0.4 J cm⁻³), because of the large hysteresis (efficiency $< 50\%$) and the inferior dielectric strength (≈ 90 kV cm⁻¹) (Zhang *et al.*, 2015; Wang *et al.*, 2012). However, the recoverable energy density can substantially be increased up to 1.2 J cm⁻³ in ceramics obtained by densification of BaTiO₃@SiO₂ core-shell particles (Zhang *et al.*, 2015), because of the enhanced dielectric strength, as previously discussed.

BaTiO₃-Bi(M)O₃ relaxors also exhibit excellent thermal stability of the energy density and efficiency. Ceramics with composition 0.85BaTiO₃-0.15Bi(Mg_{0.5}Zr_{0.5})O₃ show a decrease of energy density of only 12% from room temperature to 150°C at a field of 220 kV cm⁻¹ and energy efficiency $> 80\%$ (Yuan *et al.*, 2018). A similar stability was reported for 0.85BaTiO₃-0.15Bi(Zn_{1/2}Sn_{1/2})O₃ at 150 kV cm⁻¹, with an efficiency $> 95\%$ (Zhou *et al.*, 2018).

Ba_{1-x}Sr_xTiO₃ ceramics (Song *et al.*, 2014, 2015; Huang *et al.*, 2015; Yang *et al.*, 2018) in the paraelectric state at room temperature also show significantly enhanced energy storage density in comparison to BaTiO₃ (up to 1.3 J cm⁻³, Table 2) though the performances are inferior to the previously described BaTiO₃-based relaxors.

Tunable Dielectrics

Only a few remarks on BaTiO₃-based tunable dielectrics will be given here; for a detailed overview on tunable ferroelectrics the review paper of Tagantsev *et al.* (2003) is recommended. A typical feature of ferroelectric materials is the strong nonlinear dependence of dielectric permittivity on the applied bias electric field. This feature is described by the tunability, n , the ratio of the permittivity of the material at zero electric field, $\epsilon'(0)$, to the permittivity at a given non-zero electric field, $\epsilon'(E)$. The relative tunability is defined as $[\epsilon'(0) - \epsilon'(E)]/\epsilon'(0)$ (Tagantsev *et al.*, 2003). A variable permittivity with high tunability is attractive for the fabrication of microwave devices such as tunable dielectric resonators, tunable filters and tunable capacitors (varactors). However, the higher losses of ferroelectrics in comparison to conventional microwave dielectrics and the high voltage needed for tuning limit the use of bulk ceramic or single crystal varactors. Materials in the paraelectric state are preferred because the absence of domains reduces the losses and the hysteretic behavior. BaTiO₃-based solid solutions such as Ba_{1-x}Sr_xTiO₃, BaTi_{1-x}Zr_xO₃ and BaTi_{1-x}Sn_xO₃ ceramics show a high tunability, especially in the vicinity of phase transitions. At room temperature, the relative

Table 2 Energy storage properties of BaTiO₃-based bulk ceramics at room temperature. W_{rec} : recoverable (discharged) energy density. η : efficiency (ratio of discharged to charged energy density). E : electric field amplitude

Composition	W_{rec} ($J\ cm^{-3}$)	η (%)	E ($kV\ cm^{-1}$)	References
<i>BaTiO₃-Bi(M)O₃ solid solutions</i>				
0.85BaTiO ₃ -0.15Bi(Mg _{0.5} Zr _{0.5})O ₃	2.9	86.8	300	Yuan <i>et al.</i> (2018)
0.9BaTiO ₃ -0.1Bi(Zn _{0.5} Zr _{0.5})O ₃	2.46	86	264	Yuan <i>et al.</i> (2017b)
0.7 BaTiO ₃ -0.3 BiScO ₃	2.3 (6.1 ^a)		225 (730 ^a)	Ogihara <i>et al.</i> (2009)
0.85BaTiO ₃ -0.15Bi(Zn _{1/2} Sn _{1/2})O ₃	2.21	91.7	230	Zhou <i>et al.</i> (2018)
0.88(0.65BaTiO ₃ -0.35Bi _{0.5} Na _{0.5} TiO ₃) - 0.08Na _{0.73} Bi _{0.09} NbO ₃	1.70	82	172	Yang <i>et al.</i> (2017)
0.9BaTiO ₃ -0.1Bi(Mg _{2/3} Nb _{1/3})O ₃	1.70	90	210	Li <i>et al.</i> (2017)
0.9BaTiO ₃ -0.1Bi(Mg _{2/3} Nb _{1/3})O ₃	1.13	93	145	Wang <i>et al.</i> (2015)
0.85BaTiO ₃ -0.15Bi(Zn _{2/3} Nb _{1/3})O ₃	0.79	93.5	131	Wu <i>et al.</i> (2016)
0.91BaTiO ₃ -0.09BiYbO ₃	0.71	82.6	93	Shen <i>et al.</i> (2015)
<i>Ba_{1-x}Sr_xTiO₃ solid solution</i>				
(Ba _{0.4} Sr _{0.6})TiO ₃	1.28	–	243	Song <i>et al.</i> (2014)
(Ba _{0.4} Sr _{0.6})TiO ₃	1.15	82	190	Song <i>et al.</i> (2015)
Ba _{0.4} Sr _{0.6} TiO ₃ -5 wt%MgO	1.5	88.5	300	Huang <i>et al.</i> (2015)
Ba _{0.4} Sr _{0.6} TiO ₃ -9 wt%(Bi ₂ O ₃ -B ₂ O ₃ -SiO ₂ glass)	1.98	90.6	279	Yang <i>et al.</i> (2018)
<i>BaTiO₃</i>				
BaTiO ₃	0.38	40.3	90	Zhang <i>et al.</i> (2015)
BaTiO ₃	0.32	–	88	Wang <i>et al.</i> (2012)

^aThin layer with 15 μm thickness.

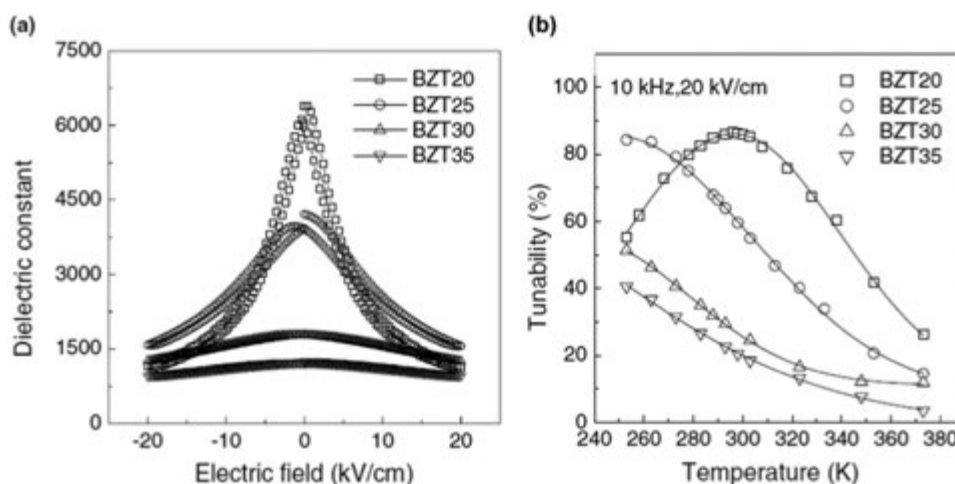


Fig. 15 (a) Dielectric permittivity vs. bias electric field and (b) relative tunability vs. temperature for different BaTi_{1-x}Zr_xO₃ ceramics ($x = 0.20-0.35$). Reprinted from ref. Tang, X.G., Chew, K.-H., Chan, H.L.W., 2004. Diffuse phase transition and dielectric tunability of Ba(Zr_yTi_{1-y})O₃ relaxor ferroelectric ceramics. *Acta Materialia* 52, 5177–5183, with permission from Elsevier. Copyright (2004) Acta Materialia Inc.

tunability at 30 $kV\ cm^{-1}$ and 10 kHz is 80% for BaZr_{0.25}Ti_{0.75}O₃ and 50% for Ba_{0.60}Sr_{0.40}TiO₃ (Zhang *et al.*, 2012). The variation of permittivity with dielectric field and of relative tunability with temperature is reported in Fig. 15 for different BaTi_{1-x}Zr_xO₃ compositions ($x = 0.20-0.35$). Compositions $x = 0.20$ and 0.25 show the maximum relative tunability (85%) at the Curie temperature (297K and 257K, respectively) (Tang *et al.*, 2004). Compositions $x = 0.30$ and 0.35 have a relaxor behavior. For many homogeneous single phase ferroelectrics, the higher the permittivity the higher the tunability but also the losses and the temperature dependence of permittivity (Tagantsev *et al.*, 2003). The correlation between tunability and losses obliges to find materials with the best trade-off between these two parameters. A guide to choose among different materials is provided by the commutation quality factor (Tagantsev *et al.*, 2003). Given an appropriate value of the quality factor required for the specific application, materials with high tunability ($n \geq 1.5$) and not too high permittivity (≤ 1000) are generally preferred. Composites between Ba_{1-x}Sr_xTiO₃ and a linear dielectric oxide, such as MgO, have been extensively investigated because the dielectric constant can be adjusted and losses lowered by changing the amount of the linear dielectric while retaining a reasonable tunability (Tagantsev *et al.*, 2003; Zhang *et al.*, 2012; Chang and Sengupta, 2002; Chung *et al.*, 2008).

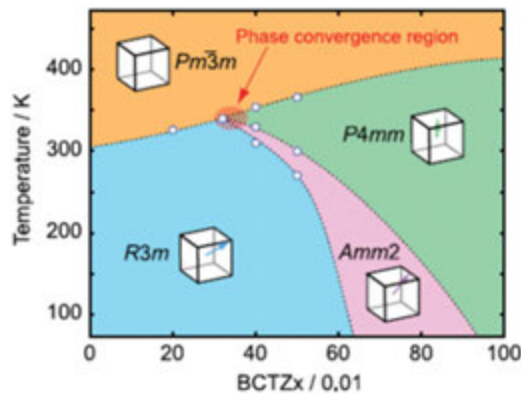


Fig. 16 $x\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3-(1-x)\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ phase diagram. Reprinted from ref. Keeble, D.S., Benabdallah, F., Thomas, P.A., Maglione, M., Kreisel, J., 2013. Revised structural phase diagram of $(\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3)-(\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3)$. Applied Physics Letters 102, 092903, with the permission of AIP Publishing.

Piezoelectric Properties

BaTiO₃ was the first oxide material to be developed as a piezoceramic (Randall *et al.*, 2004; Jaffe *et al.*, 1971; Haertling, 1999) and was used on large scale for applications in the generation of acoustic and ultrasonic vibrations, vibration detection and actuators. Typical values of the piezoelectric properties of BaTiO₃ ceramics are $d_{33} = 191$ pC/N, $d_{31} = -79$ pC/N, $d_{15} = 270$ pC/N, $k_{33} = 0.49$, $k_p = 0.38$ (Jaffe *et al.*, 1971). The piezoelectric properties of BaTiO₃, likewise dielectric permittivity, are strongly temperature dependent because of the polymorphic transitions. For most commercial purposes it is now superseded by Pb(Zr,Ti)O₃ (PZT) ceramics, with morphotropic boundary composition. PZT has superior properties, a wider temperature application range and a higher thermal stability. Undoped BaTiO₃ cannot be used for high field and high frequency applications such as the generation of ultrasonic power, because of the rapid increase of dielectric losses with increasing field. These losses arise largely from the movement of domain walls. Substitution of transition metal ion acceptors (Co^{3+} is particularly effective) at the Ti site leads to domain wall clamping and consequently to a strong reduction of the losses. As a further effect of domain wall clamping, Co^{3+} -doped BaTiO₃ shows greater resistance than PZT to depoling by compressive stresses and, consequently, it is still used in some applications despite the inferior piezoelectric activity (Jaffe *et al.*, 1971; Moulson and Herbert, 1990). The piezoelectric properties of barium titanate ceramics can be further modified by tailoring the microstructure. The influence of grain size will be discussed in Section “Size and Scaling Effects”.

In recent years, BaTiO₃-based piezoceramics have attracted a renewed interest after the publication of the paper of Liu and Ren (2009) in 2009, reporting outstanding piezoelectric properties, comparable or even superior to those of PZT at room temperature, in the $(1-x)\text{Ba}(\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_{3-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ system (BCTZ) for $x = 0.50$. The material showed $d_{33} \approx 600$ pC N⁻¹ and a large signal piezoelectric coefficient d_{33}^* (defined as the ratio of the strain and the corresponding electric field) of 1140 pm V⁻¹ at 50 kV cm⁻¹. An even higher value of d_{33}^* of 1310 pm V⁻¹ at 50 kV cm⁻¹ was reported at $x = 0.45$ by Ehmke *et al.* (2012). The high piezoelectric activity was initially attributed to the existence of a morphotropic phase boundary (MPB) between the tetragonal and the rhombohedral phase. However, Keeble *et al.* (2013), in 2013, on the basis of a careful temperature dependent XRD study of this system, demonstrated that there is not a MPB but, rather, a narrow temperature-composition region, which separates the other two crystallographic polar variants, where the orthorhombic phase is stable (see Fig. 16). A phase diagram very similar to that reported in Keeble *et al.* (2013) was constructed by Acosta *et al.* (2014) from dielectric permittivity data. Moving from low to high temperature, the same phase sequence (R-O-T-C) as in undoped BaTiO₃ is observed. However, as the presence of Zr lowers the T_C and stabilizes the R phase at higher temperature, while the effect of calcium is to shift the R/O and O/T boundaries at lower temperature, the three phase transitions are observed in a narrow (270–365 K) temperature range at $x = 0.50$. Furthermore, the different transitions meet at a phase convergence point at $x = 0.32$ – 0.35 and 333 – 337 K. The phase boundaries are not horizontal but quite slanting, this enhances the tendency to “instability” of the system, a situation quite favorable for producing high piezoelectric properties. In fact, small variations of composition or temperature stabilize one phase respect to the adjacent one, meaning that the free energy landscape is rather flat, thus promoting phase coexistence, increasing the degrees of freedom of the system and making it highly responsive to external stimuli. One possible mechanism responsible for properties enhancement is the “polarization rotation” (Damjanovic, 2005) process. Available data indicate that d_{33} features maximum values around the phase transitions when varying temperature at constant composition or composition at constant temperature (Acosta *et al.*, 2017, 2014), as shown in Fig. 17. At room temperature, Zhang *et al.* (2014) reported two maxima of d_{33} corresponding to the R/O transition at $x = 0.44$ and the O/T transition at $x = 0.50$. More generally, the highest values of d_{33} are obtained along the O/T transition, while high values of d_{33}^* are observed over a broad region around the O phase with maximum at R/O and O/T transitions. A second maximum of d_{33} is located at $x \approx 0.35$, just above room temperature and close to the R/O transition. These features are partially inherited from the $\text{BaZr}_y\text{Ti}_{1-y}\text{O}_3$ system, which shows the same behavior for $y = 0.06$ – 0.10 , with $d_{33} = 770$ pC N⁻¹ at 65°C at the O/T transition (Dong *et al.*, 2012). This further confirms that an important effect of Ca substitution is the shift the O/T phase transition to room

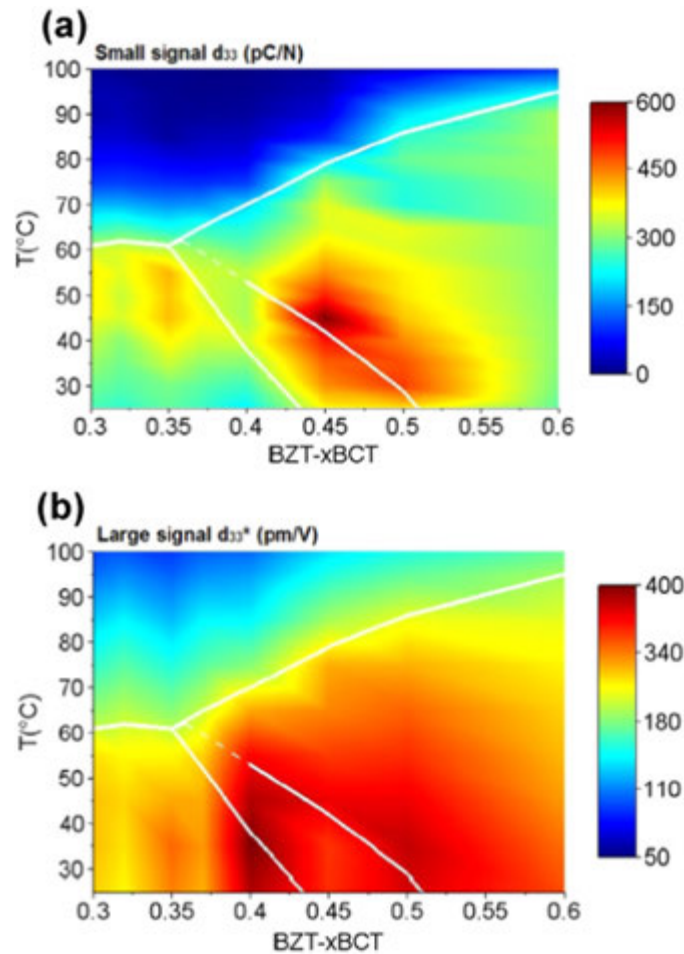


Fig. 17 Contour plot of (a) small signal d_{33} and (b) large signal d_{33}^* as a function of temperature and composition in the $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_{3-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ system. Reprinted from ref. Acosta, M., Novak, N., Jo, W., Rödel, J., 2014. Relationship between electromechanical properties and phase diagram in the $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_{3-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ lead-free piezoceramic. *Acta Materialia* 80, 48–55, with permission from Elsevier. Copyright Acta Materialia Inc. (2014).

temperature when $x = 0.50$. The origin of the large piezoelectric activity in BCTZ ceramics was investigated using the Landau-Devonshire phenomenological theory (Acosta *et al.*, 2015). Based on the combined computational and experimental results, it was concluded that a reduction in anisotropy energy (i.e., a weaker dependency of energy on the polarization orientation) accompanied by elastic softening (i.e., increase of elastic compliance) is a necessary condition for enhanced piezoelectric properties. Properties can be further maximized where a high spontaneous/remanent polarization can be retained. Despite four different phases coexist at the convergence point and the elastic compliance is comparable to that of the O/T phase boundary, a maximum in d_{33} is not observed at this composition, mainly due to the lower spontaneous/remanent polarization values determined by the small unit cell distortion.

The properties of BCTZ ceramics are highly dependent on processing, relative density, microstructure and poling conditions (Wang *et al.*, 2011; Bai *et al.*, 2015; Wu *et al.*, 2012; Praveen *et al.*, 2015; Hao *et al.*, 2012). In the case of powders prepared by solid-state reaction, factors like the precursor powder size and the calcination temperature can have a significant impact on the chemical homogeneity at local level. Differently from undoped BaTiO₃, which shows optimal values of properties in ceramics with grain size of ≈ 1 μm , the electro-mechanical constants d_{33}^* and d_{33} are maximized for a grain size of the order of 10–30 μm (Wang *et al.*, 2011; Bai *et al.*, 2015; Wu *et al.*, 2012; Praveen *et al.*, 2015; Hao *et al.*, 2012). Field cooling poling was found quite effective to improve the piezoelectric properties of BCTZ ceramics. This was attributed to the development of an internal bias field caused by the alignment of defect charge carriers, rather than higher degree of domain texture (Li *et al.*, 2013). A drawback of the BCTZ system is the relatively low T_C (70–75 °C for $x = 0.40$ and 90–95 °C for $x = 0.60$) which reduces the operating temperature range of the material. Furthermore, d_{33} decays rapidly with increasing temperature. The Curie point can be increased but at the expenses of the piezoelectric properties; for example $T_C = 114$ °C and $d_{33} = 450$ pC N⁻¹ in $(1-x)\text{Ba}(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_{3-x}(\text{Ba}_{0.8}\text{Ca}_{0.2})\text{TiO}_3$ for $x = 0.53$ (Bao *et al.*, 2010). Texturing is a common strategy to further enhancing the piezoelectric activity of ceramics by orienting the grains along a common and favorable crystallographic direction, using template grain growth. For [001] grain-oriented $(\text{Ba}_{0.94}\text{Ca}_{0.06})(\text{Ti}_{0.95}\text{Zr}_{0.05})\text{O}_3$ ceramics, a very high d_{33} of 755 pC N⁻¹ and an extremely large d_{33}^* coefficient of 2027 pm V⁻¹, along with a low strain hysteresis, were reported by Liu *et al.* (2017a).

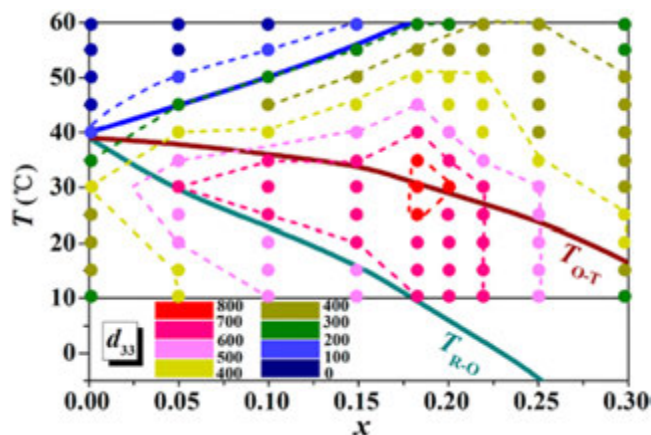


Fig. 18 Map of piezoelectric coefficient d_{33} as a function of temperature and composition in the system $(1-x)\text{Ba}(\text{Ti}_{0.89}\text{Sn}_{0.11})\text{O}_{3-x}(\text{Ba}_{0.70}\text{Ca}_{0.30})\text{TiO}_3$. Reprinted with permission from ref. Zhao, C., Wu, H., Li, F., *et al.*, 2018. Practical high piezoelectricity in barium titanate ceramics utilizing multiphase convergence with broad structural flexibility. *Journal of the American Chemical Society* 140, 15252–15260. Copyright (2018) American Chemical Society.

The family of $(\text{Ba,Ca})(\text{Ti,Sn})\text{O}_3$ (BCTS) ceramics has also been investigated in detail and shows excellent piezoelectric properties, whereas the $(\text{Ba,Ca})(\text{Ti,Hf})\text{O}_3$ (BCTH) system was less extensively explored. The phase diagrams and the general features of BCTIZ, BCTS and BCTH systems are similar (Acosta *et al.*, 2017; Keeble *et al.*, 2013; Wang *et al.*, 2014; Zhu *et al.*, 2013a,b, 2014, 2016). Low signal $d_{33} > 500 \text{ pC N}^{-1}$ and $d_{33}^* > 1000 \text{ pm V}^{-1}$ were reported for a wide range of BCTS compositions in proximity of the O/T transition and, more generally, at the polymorphic phase transitions (Zhu *et al.*, 2013a,b, 2014, 2016; Janbua *et al.*, 2017). In particular, $d_{33} = 670 \text{ pC N}^{-1}$ for $x = 0.07\text{--}0.09$ and $d_{33}^* = 1414 \text{ pm V}^{-1}$ for $x = 0.11$ were reported in $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$ ceramics (Zhu *et al.*, 2013b). A remarkable piezoelectric coefficient, $d_{33} = 697 \text{ pC N}^{-1}$, was also measured in $\text{BaSn}_x\text{Ti}_{1-x}\text{O}_3$ ceramics with composition corresponding to the phase convergence point, $x = 0.11$, with T_C of 40°C (Yao *et al.*, 2012b). However, this material has limited interest, because of the inherent thermal instability and the incorporation of Ca is essential to stabilize the tetragonal phase at higher temperature. Very recently a detailed mapping of d_{33} (Fig. 18) has revealed values higher than 600 pC N^{-1} for a large range of compositions ($x = 0.06\text{--}0.23$) in $(1-x)\text{Ba}(\text{Ti}_{0.89}\text{Sn}_{0.11})\text{O}_{3-x}(\text{Ba}_{0.70}\text{Ca}_{0.30})\text{TiO}_3$ ceramics at room temperature, with a maximum of 700 pC N^{-1} for $x = 0.18$ (Zhao *et al.*, 2018). Despite the high piezoelectric activity, the T_C of the compositions with the best properties is only $60\text{--}70^\circ\text{C}$ and, consequently, a rapid drop of d_{33} is observed with increasing temperature. BCTH ceramics generally show a reduced piezoelectric activity in comparison to BCTIZ and BCTS (Wang *et al.*, 2014; Zhao *et al.*, 2016), with higher values of d_{33} at the R/O and O/T phase boundary, up to $\approx 500 \text{ pC N}^{-1}$ in $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Hf}_{0.1}\text{Ti}_{0.9}\text{O}_3$ with a Curie temperature of $\approx 85^\circ\text{C}$.

An improvement of the piezoelectric properties of BaTiO_3 can be obtained by adding a small amount of LiF, which also lowers the sintering temperature to 1100°C , i.e. at least $200\text{--}300^\circ\text{C}$ below the temperature generally employed. Li compounds such as Li_2O , Li_2CO_3 and LiF are well-known sintering aids, which promote densification by formation of a liquid phase and growth of grains with core-shell microstructure (Randall *et al.*, 1993). Yang *et al.* (2012) showed that the addition of 4 mol% LiF leads to $d_{33} = 270 \text{ pC N}^{-1}$ and $k_p = 0.45$, though T_C is lowered to 73°C . Kimura *et al.* (2013) sintered Li-doped ceramics with improved $d_{33} = 260 \text{ pC N}^{-1}$, $k_p = 0.44$ and $T_C = 130^\circ\text{C}$ using hydrothermally-synthesized powders. In both cases, the presence of Li stabilizes the orthorhombic phase at room temperature and this can contribute to the enhancement of the piezoelectric activity. Even higher d_{33} values $> 300 \text{ pC N}^{-1}$ were measured on undoped BaTiO_3 ceramics with grain size of $\approx 50 \mu\text{m}$ sintered at $1160\text{--}1230^\circ\text{C}$ from hydrothermal powders. The poled ceramics exhibited orthorhombic or mixed tetragonal-orthorhombic structure. Optimal properties, $d_{33} = 355 \text{ pC N}^{-1}$ and $k_p = 0.40$, were obtained after sintering at 1190°C (Ma *et al.*, 2012). Coarse-grained (grain size $> 10 \mu\text{m}$) ceramics densified by spark plasma sintering featured d_{33} values up to 416 pC N^{-1} (Shen and Li, 2010). In both cases, the enhancement of piezoelectric activity was ascribed to the presence of nanodomains with thickness of few tens of nanometers. However, the origin of these nanodomains is still unclear. As discussed in the next section, maximum piezoelectric activity is usually observed in ceramics with grains size around $1 \mu\text{m}$.

Size and Scaling Effects

The properties of ferroelectric materials, including BaTiO_3 , in form of films, particles and ceramics show a significant variation with decreasing the physical dimension (thickness for films, diameter for particles and grain size for ceramics) (Shaw *et al.*, 2000; Ihlefled *et al.*, 2016). Representative examples are provided by the dielectric response and the piezoelectric activity.

Kinoshita and Yamaji (1976) first reported a progressive increase of the dielectric permittivity of BaTiO_3 ceramics with decreasing the grain size from 53 to $1.1 \mu\text{m}$. A systematic lowering of saturation polarization, piezoelectric coefficients and electromechanical coupling constants with diminishing grain size ($4\text{--}0.2 \mu\text{m}$) was described in PZT ceramics by Randall *et al.* (1998). The room

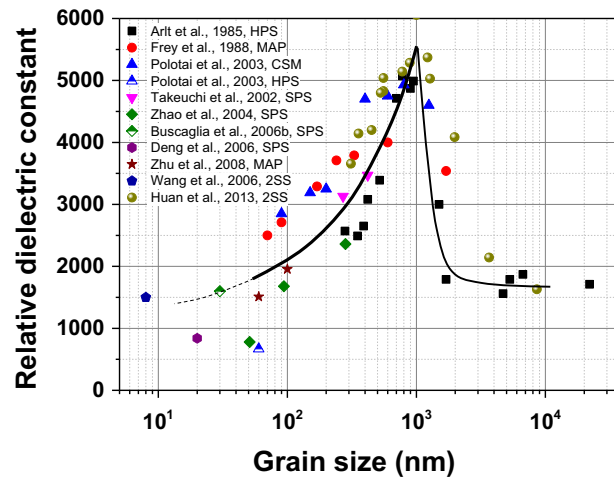


Fig. 19 Room temperature dielectric constant of BaTiO₃ ceramics as a function of grain size. Data collected from different authors. HPS, hot pressing sintering; MAP, multi-anvil press; CSM, combined sintering method; SPS, spark plasma sintering; 2SS, two-step sintering.

temperature dielectric constant of barium titanate ceramics as a function of grain size, as obtained by plotting the data reported by several authors (Arlt *et al.*, 1985; Frey *et al.*, 1998; Takeuchi *et al.*, 2002; Polotai *et al.*, 2003; Zhao *et al.*, 2004; Wang *et al.*, 2006; Buscaglia *et al.*, 2006b; Deng *et al.*, 2006; Zhu *et al.*, 2008; Huan *et al.*, 2013), is shown in Fig. 19. A pronounced maximum with $\epsilon_r = 5000$ – 6000 is observed at a grain size of $\approx 1 \mu\text{m}$. These values are 3–4 times higher than the dielectric permittivity (≈ 1500) measured in ceramics with grain size $> 10 \mu\text{m}$. The permittivity is significantly suppressed to values even lower than 1000 in ceramics with nanosized grains.

The piezoelectric coefficient d_{33} exhibits a trend similar to dielectric permittivity, with a maximum $> 500 \text{ pC N}^{-1}$ again at $\approx 1 \mu\text{m}$ (Shao *et al.*, 2008; Zheng *et al.*, 2012; Huan *et al.*, 2014; Tan *et al.*, 2015; Hoshina *et al.*, 2018) to be compared with the piezoelectric coefficient of coarse grained ceramics, 180 – 190 pC N^{-1} (Fig. 20). However, some data sets indicate the existence of a broad maximum at a grain size of 4 – $5 \mu\text{m}$.

Size and scaling effects in ferroelectric materials have received significant attention for over five decades. Besides the fundamental question of determining the critical size at which ferroelectric order vanishes, many studies have been driven by the continuous miniaturization process of virtually all active and passive electronic components, with a size reduction of the functional material inside the devices. Ferroelectric perovskites are used in different devices, including MLCCs, non-volatile memories (FERAMs) and multilayer piezoelectric transducers and actuators. A typical example of device downsizing is represented by MLCCs, widely used in consumer electronics, smartphones, hybrid and electrical vehicles. A typical multilayer capacitor is essentially a parallel connection of many stacked ceramic plate capacitors (Kishi *et al.*, 2003; Pan and Randall, 2010). The interdigitated conducting layers form the counter-electrodes for each dielectric layer. The capacitance of a MLCC is given by

$$C = \epsilon_0 \epsilon' n \frac{S}{t}$$

where S is the overlap electrode area, t the thickness of the single dielectric layer, n the number of layers and ϵ_0 the permittivity of vacuum. A reduction of the case size keeping the capacitance constant can then be obtained by decreasing the geometric parameters t and S or the lateral size of the capacitor if n is increased.

In the last 20 years the typical thickness of the dielectric layers has decreased from 10 to $0.5 \mu\text{m}$. Most of the capacitors are fabricated using the nickel inner electrodes technology, that co-fires the BaTiO₃ based dielectrics with Ni-electrode layers in a reducing atmosphere (Kishi *et al.*, 2003; Pan and Randall, 2010). Taking into account that, for reasons of long-term reliability, it is preferable to have several grains (5 – 7) spanning the thickness of each dielectric layer, the grain size of top edge MLCCs is of the order of 100 nm or even less. The dielectric constant of BaTiO₃ is significantly suppressed (< 2000) when the grain size approaches the nanoscale region and this trend continues with further reducing the grain size (Fig. 19), with a significant effect on the capacitor performance. In fact, the same depression reported for undoped ceramics is also exhibited by BaTiO₃-based dielectrics used in XNR ($N = 6$ – 9) capacitors. For example, the dielectric constant of X7R compliant ceramics decreases from ≈ 2800 to ≈ 2000 while decreasing the grain size from 460 to 120 nm (Gong *et al.*, 2014).

The scaling of properties is mainly of extrinsic origin and determined by the contribution of different types of interfaces such as grain boundaries, domain walls and other extended defects, whose concentration or volume fraction changes as the system size scales (Shaw *et al.*, 2000; Ihlefeld *et al.*, 2016). A detailed discussion of the mechanisms responsible for size and scaling effects in ferroelectrics is beyond the aim of this contribution and only some general results are summarized below. Recent reviews can be found in Ihlefeld *et al.* (2016) and Buscaglia and Randall (2020).

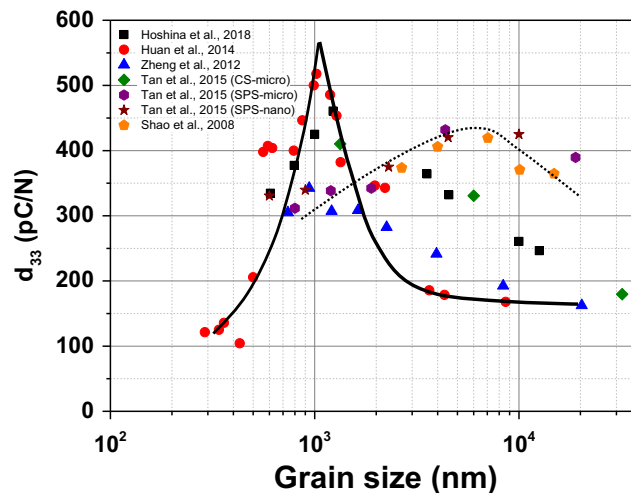


Fig. 20 Room temperature piezoelectric coefficient d_{33} of BaTiO₃ ceramics as a function of grain size. Data collected from different authors.

The domain configuration, the domain wall density and the domain wall mobility change with the grain size and this determines a dimension-dependent contribution to permittivity and piezoelectric properties. As anticipated in Section “Crystal Structure, Nonstoichiometry and Defect Chemistry of BaTiO₃”, the domain wall movement represents the major extrinsic contribution to the dielectric and piezoelectric properties at low and moderate fields (Damjanovic, 1998).

The domain configuration becomes simpler with decreasing grain size (Fig. 21). Coarse grained ceramics ($> \approx 10 \mu\text{m}$) show complex three-dimensional arrangements of 90° and 180° domain walls and their dielectric permittivity is practically constant. Below $5\text{--}7 \mu\text{m}$, the grains predominantly exhibit stripe domain patterns with domains separated by 90° walls. The domain width decreases from 0.3 to $0.4 \mu\text{m}$ to less than 100 nm in submicron ceramics. Domain walls are no longer observed when the grain size is smaller than $200\text{--}300 \text{ nm}$, and the grains mainly comprise single domains (Frey et al., 1998; Zhao et al., 2004; Buscaglia et al., 2006b; Arlt, 1990; Frey and Payne, 1996).

According to the model of Arlt et al. (1985), the permittivity of BaTiO₃ ceramics is given as the sum of two terms: the lattice contribution (assumed independent of grain size) and the domain wall contribution. When the grain size g is in the range $1\text{--}10 \mu\text{m}$, the width of the 90° domains is proportional to g^m with $m = \frac{1}{2}$ and, consequently, the dielectric permittivity increases with decreasing grain size with a $g^{-1/2}$ dependence, in agreement with the experimental data. The proportionality between the domain width and the square root of a characteristic length of the material (thickness for slabs, diameter for wires, lateral side for nanocubes) is a general property of ferroic crystals (Schilling et al., 2006, 2009) which was initially proposed by Kittel for ferromagnetic materials. When $g < 1 \mu\text{m}$, m rises to values > 1 .

In the model, the wall mobility was assumed to be independent of grain size. Later, Arlt and Pertsev (1991) predicted that the domain wall mobility is also a function of the grain size. A recent investigation using in-situ synchrotron X-ray diffraction experiments on ceramics with different grain size ($0.3\text{--}3.5 \mu\text{m}$) has provided further insight into the dependence of mobility on grain size (Ghosh et al., 2014). It was shown that the motion of 90° domain walls is greatest under both strong (above coercive) and weak (below coercive) electric fields for an intermediate grain size of $\approx 2 \mu\text{m}$. Furthermore, the domain wall motion was strongly suppressed in the ceramic with grain size of $0.3 \mu\text{m}$. The reduction of wall mobility in ferroelectric ceramics with submicron and nanometric grains is also indicated by the progressive tilting of the P(E) hysteresis loops with a reduction of both remanent and saturation polarization (Frey et al., 1998; Buscaglia et al., 2006b; Curecheriu et al., 2012). Domain reorientation and switching become increasingly more difficult as the grain size is reduced towards the single domain grain regime.

There is general consensus that the grain boundaries in BaTiO₃ and other perovskites have a non-ferroelectric character and a much lower permittivity ($\epsilon' \approx 10^2$) than the grain cores ($\epsilon' \approx 10^3$) forming a “dead-layer” region which exerts an increasing dilution effect on the dielectric properties of ceramics with decreasing grain size, especially at submicron and nanometric scale (Frey et al., 1998; Zhao et al., 2004; Buscaglia et al., 2006b; Emelyanov et al., 2002; Curecheriu et al., 2010; Padurariu et al., 2012). The low permittivity grain boundaries determine a redistribution of the electric field inside the ceramic. Finite element modeling has shown that the effective electric field is higher than the applied field in the grain boundaries perpendicular to the direction of the applied field and lower in the grain cores. This inhomogeneity increases with decreasing grain size. A main effect of electric field redistribution is the progressive decrease of the nonlinear contribution to effective permittivity and of tunability (Padurariu et al., 2012) as the grain size goes down. The effect of grain boundaries has also been investigated by phase-field simulation based on Ginzburg-Landau kinetic equation with the grain size varying from 10 to 170 nm (Su et al., 2017). At low field the monotonic decrease of dielectric permittivity with decreasing grain size is confirmed. At high field, the dielectric and piezoelectric responses are dominated by the dynamics of domain structure above the grain size of 50 nm and by the properties of the dead layer below this value. As a result, the large field permittivity and d_{33} first increase and then decrease with a maximum at $\approx 50 \text{ nm}$. The distribution of polarization in the remnant state after field removal undergoes a profound alteration with decreasing grain size, from a

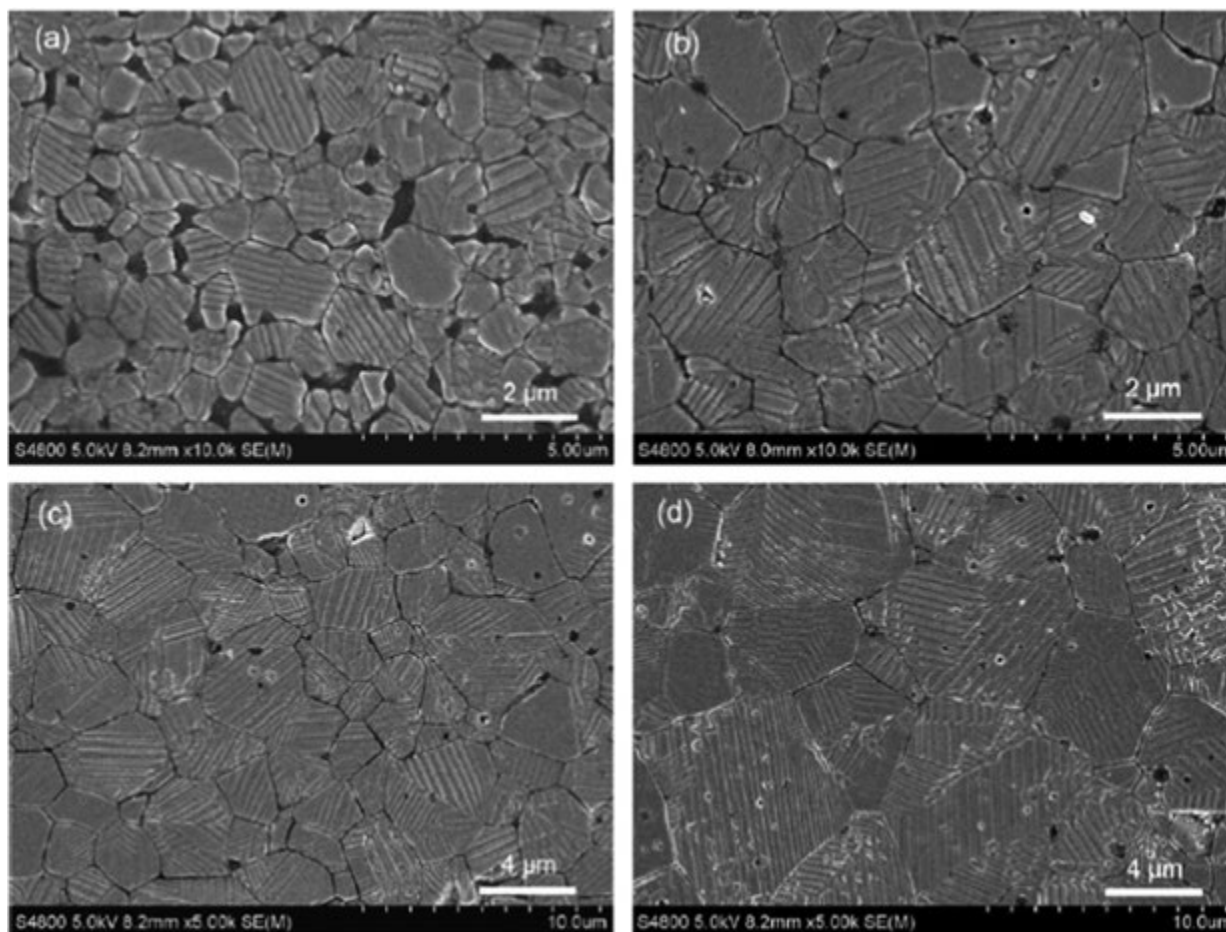


Fig. 21 SEM images of domain patterns observed in the various poled BaTiO₃ ceramics with different average grain size. (a) 0.74 μm . (b) 1.63 μm . (c) 3.95 μm . (d) 8.37 μm . A progressive evolution from simple stripe patterns to more complex domain arrangements is observed with increasing grain size. Reprinted from ref. Zheng, P., Zhang, J.L., Tan, Y.Q., Wang, C.L., 2012. Grain-size effects on dielectric and piezoelectric properties of poled BaTiO₃ ceramics. *Acta Materialia* 60, 5022–5030, with permission from Elsevier. Copyright Acta Materialia Inc. (2012).

monodomain state at 110 nm to a vortex organization at 15 nm. The change of polarization distribution is determined by the significant depolarization field associated to the “dead-layer”. A similar transition in the polarization was also predicted by [Fu and Bellaiche \(2003\)](#) in BaTiO₃ nanoparticles using a first-principles-based approach. Further experimental studies are needed to confirm these trends.

The enhancement of the dielectric strength with decreasing grains size experimentally observed ([Curecheriu et al., 2010](#)) has been elucidated by phase field modeling and ascribed to the higher breakdown energy of the grain boundaries with respect to grain cores ([Cai et al., 2018](#)). The impact of grain boundaries is also dependent on the Ba/Ti ratio. Ti-rich stoichiometries beyond the solubility limit cause the segregation of a crystalline or amorphous titania-rich layer which further amplifies the dilution effect. A significant binary oxide excess leads to the formation of secondary phase inclusions such as Ba₂TiO₄ (Ba-excess), BaTi₂O₅ and Ba₆Ti₁₇O₄₀ (Ti-excess) ([Lee et al., 2007a, 2001](#)).

Although the domain wall mobility probably plays a main role in determining the existence of the permittivity maximum in [Fig. 19](#), the dilution effect of grain boundaries gives an increasing and significant contribution to permittivity depression when the grain size is $< \approx 0.5 \mu\text{m}$ ([Frey et al., 1998](#); [Zhao et al., 2004](#)). Furthermore, the inhomogeneous distribution of the electric field in fine grained ceramics results in a decrease of the effective field in the grain core ([Padurariu et al., 2012](#)) with a negative impact on domain reorientation and switching ([Curecheriu et al., 2012](#)).

A broad dispersion of experimental data is apparent from [Figs. 19](#) and [20](#). The dispersion can be attributed to the use of powders synthesized with various methods and different precursors as well as to differences in subsequent processing, including sintering technique, sintering thermal parameters and possible post-sintering annealing treatment. The synthesis step introduces impurities of variable nature and amount as well as variability of the Ba/Ti ratio which, in turn, affects the lattice defects concentration and impacts all the properties. For example, coarse-grained ceramics sintered in the same conditions exhibited a room temperature dielectric constant in the range 950–1800, increasing the Ba/Ti molar ratio from 0.97 to 1.03 with maximum permittivity at 1.01 ([Lee et al., 2001](#)). The impact of stoichiometry can partly explain the broad dispersion of the piezoelectric

activity data, which is even larger than that of the permittivity response. Dai *et al.* (2018) systematically investigated the dependence of d_{33} on grain size for different values of the Ba/Ti ratio from 0.998 to 1.002. The maximum of d_{33} was found at a grain size of $\approx 1 \mu\text{m}$ when Ba/Ti ≥ 1 and at $\approx 4 \mu\text{m}$ when Ba/Ti < 1 , and this might justify the existence of two sets of data with a different trend in Fig. 20. Maximum piezoelectric activity ($> 500 \text{ pC/N}$) is attained at Ba/Ti = 1.

When the particle/grain size is reduced below $\approx 100 \text{ nm}$, the high fraction of surface/interface atoms produces a disturbance of the polar order, reducing the thermodynamic stability of the polar phase in comparison to the paraelectric modification, with a progressive decrease of T_C and spontaneous polarization until ferroelectricity will vanish below a critical size (Ihlefeld *et al.*, 2016; Zhong *et al.*, 1994). This phenomenon is usually referred to as “intrinsic” size effect and, along with the reduced domain wall mobility and the dilution effect of grain boundaries, will contribute to the downscaling of properties. The critical size for ferroelectricity is of the order of $\approx 10 \text{ nm}$ for isolated particles and grains in ceramics containing a low concentration of impurities and defects (Wang *et al.*, 2006; Ishikawa *et al.*, 1988; McCauley *et al.*, 1998; Polking *et al.*, 2012).

From the above discussion it is clear that multiple mechanisms combine to produce the maximization of the dielectric constant and piezoelectric properties exhibited by BaTiO₃ ceramics for an intermediate grain size and, more generally, the observed variations of properties with grain size. The size and scaling effects are further convoluted with spurious contributions related to stoichiometry, impurities and defects leading to a large dispersion of experimental data and the behavior of specific samples can be hardly understood without a comprehensive chemical and microstructural analysis.

The decline of permittivity and all other functional properties with decreasing grain size, albeit unavoidable, can be alleviated by the use of high purity precursors, a tight control of the Ba/Ti ratio and a careful processing. The coherence length and ferroelectric order will be enhanced in materials with high crystalline order, low defect concentration, absence of local strain gradients and internal stresses. A low level of impurities and a stoichiometry within the homogeneity range of the compound will decrease the effective thickness of the grain boundary layer and its dilution effect.

References

- Acosta, M., Khakpash, N., Someya, T., *et al.*, 2015. Origin of the large piezoelectric activity in $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_{3-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ceramics. *Physical Review B* 91, 104108.
- Acosta, M., Novak, N., Rojas, V., *et al.*, 2017. BaTiO₃-based piezoelectrics: Fundamentals, current status, and perspectives. *Applied Physics Reviews* 4, 041305.
- Acosta, M., Novak, N., Jo, W., Rödel, J., 2014. Relationship between electromechanical properties and phase diagram in the $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_{3-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ lead-free piezoceramic. *Acta Materialia* 80, 48–55.
- Airimioaei, M., Buscaglia, M.T., Tredici, I., *et al.*, 2017. SrTiO₃-BaTiO₃ nanocomposites with temperature independent permittivity and linear tunability fabricated using field-assisted sintering from chemically synthesized powders. *Journal of Materials Chemistry C* 5, 9028–9036.
- Akbarzadeh, A.R., Kornev, I., Malibert, C., Bellaiche, L., Kiat, J.M., 2005. Combined theoretical and experimental study of the low-temperature properties of BaZrO₃. *Physical Review B* 72, 205104.
- Anwar, S., Sagdeo, P.R., Lalla, N.P., 2007. Study of the relaxor behavior in $\text{BaTi}_{1-x}\text{Hf}_x\text{O}_3$ ($0.20 \leq x \leq 0.30$) ceramics. *Solid State Sciences* 9, 1054–1060.
- Arlt, G., 1990. Twinning in ferroelectric and ferroelastic ceramics: Stress relief. *Journal of Materials Science* 25, 2655–2666.
- Arlt, G., Pertsev, N.A., 1991. Force constant and effective mass of 90° domain walls in ferroelectric ceramics. *Journal of Applied Physics* 70, 2283.
- Arlt, G., Hennings, D., de With, G., 1985. Dielectric-properties of fine-grained barium-titanate ceramics. *Journal of Applied Physics* 58, 1619–1625.
- Armstrong, T.R., Buchanan, R.C., 1990. Influence of core-shell grains on the internal stress state and permittivity response of zirconia-modified barium titanate. *Journal of the American Ceramic Society* 73, 1268–1273.
- Armstrong, T.R., Morgens, L.E., Maurice, A.K., Buchanan, R.C., 1989. Effects of zirconia on microstructure and dielectric properties of barium titanate ceramics. *Journal of the American Ceramic Society* 72, 605–611.
- Bai, Y., Matousek, A., Tofel, P., *et al.*, 2015. (Ba,Ca)(Zr,Ti)O₃ lead-free piezoelectric ceramics – The critical role of processing on properties. *Journal of the European Ceramic Society* 35, 3445–3456.
- Baker, J.N., Bowes, P.C., Harris, J.S., Irving, D.L., 2018. Mechanisms governing metal vacancy formation in BaTiO₃ and SrTiO₃. *Journal of Applied Physics* 124, 114101.
- Bao, H.X., Zhou, C., Xue, D.Z., Gao, J.G., Ren, X.B., 2010. A modified lead-free piezoelectric BZT-xBCT system with higher T_C . *Journal of Physics D: Applied Physics* 43, 465401.
- Ben, L.B., Sinclair, D.C., 2011. Anomalous Curie temperature behavior of A-site Gd-doped BaTiO₃ ceramics: The influence of strain. *Applied Physics Letters* 98, 092907.
- Beuerlein, M.A., Kumar, N., Usher, T.-M., *et al.*, 2016. Current understanding of structure-processing-property relationships in BaTiO₃-Bi(M)O₃ dielectrics. *Journal of the American Ceramic Society* 99, 2849–2870.
- Bharadwaja, S.S.N., Kim, J.R., Ogihara, H., *et al.*, 2011. Critical slowing down mechanism and reentrant dipole glass phenomena in $(1-x)\text{BaTiO}_{3-x}\text{BiScO}_3$ ($0.1 \leq x \leq 0.4$): The high energy density dielectrics. *Physical Review B* 83, 024106.
- Böttcher, R., Langhammer, H.T., Müller, T., 2011. Paramagnetic resonance study of nickel ions in hexagonal barium titanate. *Journal of Physics: Condensed Matter* 23, 115903.
- Burns, G., Dacol, F.H., 1982. Polarization of the cubic phase of BaTiO₃. *Solid State Communications* 42, 9.
- Burns, G., Dacol, F.H., 1983. Crystalline ferroelectrics with glassy polarization behaviour. *Physical Review B* 28, 2527–2530.
- Buscaglia, M.T., Buscaglia, V., Viviani, M., Nanni, P., 2001. Atomistic simulation of dopant incorporation in barium titanate. *Journal of the American Ceramic Society* 84, 376–384.
- Buscaglia, M.T., Viviani, M., Buscaglia, V., Bottino, C., 2002. Incorporation of Er^{3+} into BaTiO₃. *Journal of the American Ceramic Society* 85, 1569–1575.
- Buscaglia, M.T., Buscaglia, V., Viviani, M., Nanni, P., Hanuskova, M., 2000. Influence of foreign ions on the crystal structure of BaTiO₃. *Journal of the European Ceramic Society* 20, 1997–2007.
- Buscaglia, V., Buscaglia, M.T., Viviani, M., *et al.*, 2006a. Grain size and grain boundary-related effects on the properties of nanocrystalline barium titanate ceramics. *Journal of the European Ceramic Society* 26, 2889–2898.
- Buscaglia, M.T., Viviani, M., Buscaglia, V., *et al.*, 2006b. High dielectric constant and frozen macroscopic polarization in dense nanocrystalline BaTiO₃ ceramics. *Physical Review B* 73, 064114.
- Buscaglia, M.T., Viviani, M., Zhao, Z., Buscaglia, V., Nanni, P., 2006c. Synthesis of BaTiO₃ core-shell particles and fabrication of dielectric ceramics with local graded structure. *Chemistry of Materials* 18, 4002–4010.
- Buscaglia, V., Randall, C.A., 2020. Size and scaling effects in barium titanate. An overview. *Journal of the European Ceramic Society*. doi:10.1016/j.jeurceramsoc.2020.01.02.

- Buscaglia, V., Tripathi, S., Petkov, V., *et al.*, 2014. Average and local atomic-scale structure in BaZr_xTi_{1-x}O₃ ($x = 0.10, 0.20, 0.40$) ceramics by high-energy x-ray diffraction and Raman spectroscopy. *Journal of Physics: Condensed Matter* 26, 065901.
- Cai, Z.M., Wang, X.H., Hong, W., *et al.*, 2018. Grain size-dependent dielectric properties in nanograin ferroelectrics. *Journal of the American Ceramic Society* 101, 5487–5496.
- Canu, G., Confalonieri, G., Deluca, M., *et al.*, 2018. Structure-property correlations and origin of relaxor behaviour in BaCe_xTi_{1-x}O₃. *Acta Materialia* 152, 258–268.
- Chan, H.M., Harmer, M.P., Smyth, D.M., 1986. Compensating defects in highly donor-doped BaTiO₃. *Journal of the American Ceramic Society* 69, 507–510.
- Chan, N.H., Smyth, D.M., 1984. Defect chemistry of donor-doped BaTiO₃. *Journal of the American Ceramic Society* 67, 285–288.
- Chan, N.H., Sharma, R.K., Smyth, D.M., 1981. Nonstoichiometry in undoped BaTiO₃. *Journal of the American Ceramic Society* 64, 556–562.
- Chang, W., Sengupta, L., 2002. MgO-mixed Ba_{0.6}Sr_{0.4}TiO₃ bulk ceramics and thin films for tunable microwave applications. *Journal of Applied Physics* 92, 3941–3946.
- Chazono, H., Kishi, H., 1999. Sintering characteristics in BaTiO₃-Nb₂O₅-Co₃O₄ ternary system: I, Electrical properties and microstructure. *Journal of the American Ceramic Society* 82, 2689–2697.
- Chazono, H., Kishi, H., 2000. Sintering characteristics in the BaTiO₃-Nb₂O₅-Co₃O₄ ternary system: II, Stability of so-called “core-shell” structure. *Journal of the American Ceramic Society* 83, 101–106.
- Chen, L.L., Hui, K.Z., Wang, H.X., *et al.*, 2019. Effects of Ho₂O₃ doping and sintering temperature on the core-shell structure of X9R Nb-modified BaTiO₃-(Bi_{0.5}Na_{0.5})TiO₃ ceramics. *Journal of the European Ceramic Society* 39, 3710–3715.
- Chung, U.C., Elissalde, C., Maglione, M., *et al.*, 2008. Low-losses, highly tunable Ba_{0.6}Sr_{0.4}TiO₃/MgO composite. *Applied Physics Letters* 92, 042902.
- Chung, U.C., Elissalde, C., Mornet, S., *et al.*, 2009. Controlling internal barrier in low loss BaTiO₃ supercapacitors. *Applied Physics Letters* 94, 072903.
- Chung, U.C., Elissalde, C., Mompou, F., *et al.*, 2010. Interface investigation in nanostructured BaTiO₃/silica composite ceramics. *Journal of the American Ceramic Society* 93, 865–874.
- Comes, R., Lambert, M., Guinier, A., 1968. The chain structure of BaTiO₃ and KNbO₃. *Solid State Communications* 6, 715–719.
- Curecheriu, L., Balmus, S.-B., Buscaglia, M.T., *et al.*, 2012. Grain size-dependent properties of dense nanocrystalline barium titanate ceramics. *Journal of the American Ceramic Society* 95, 3912–3921.
- Curecheriu, L., Buscaglia, M.T., Buscaglia, V., Zhao, Z., Mitoseriu, L., 2010. Grain size effect on the nonlinear dielectric properties of barium titanate ceramics. *Applied Physics Letters* 97, 242909.
- Dai, B., Zheng, P., Bai, W., *et al.*, 2018. Direct and converse piezoelectric grain-size effects in BaTiO₃ ceramics with different Ba/Ti ratios. *Journal of the European Ceramic Society* 38, 4212–4219.
- Damjanovic, D., 1998. Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics. *Reports on Progress in Physics* 61, 1267–1324.
- Damjanovic, D., 2005. Contributions to the piezoelectric effect in ferroelectric single crystals and ceramics. *Journal of the American Ceramic Society* 88, 2663–2676.
- Daniels, J., Härdtl, K.H., 1976. *Philips Research Reports*. 31. Philips Research Laboratories. p. 489.
- Das, S.K., Mishra, R.N., Roul, B.K., 2014. Magnetic and ferroelectric properties of Ni doped BaTiO₃. *Solid State Communications* 191, 19–24.
- Datta, K., Thomas, P.A., Roleder, K., 2010. Anomalous phase transitions of lead-free piezoelectric xNa_{0.5}Bi_{0.5}TiO₃-(1-x)BaTiO₃ solid solutions with enhanced phase transition temperatures. *Physical Review B* 82, 224105.
- Dawson, J.A., Sinclair, D.C., Harding, J.H., Freeman, C.L., 2014. A-site strain and displacement in Ba_{1-x}Ca_xTiO₃ and Ba_{1-x}Sr_xTiO₃ and the consequences for the Curie temperature. *Chemistry of Materials* 26, 6104–6112.
- Deng, X.Y., Wang, X.H., Wen, H., *et al.*, 2006. Ferroelectric properties of nanocrystalline barium titanate ceramics. *Applied Physics Letters* 88, 252905.
- Devonshire, A.F., 1949. Theory of barium titanate. *Philosophical Magazine* 40, 1040–1063.
- Dobal, P.S., Dixit, A., Katiyar, R.S., *et al.*, 2001. Micro-Raman scattering and dielectric investigations of phase transition behavior in the BaTiO₃-BaZrO₃ system. *Journal of Applied Physics* 89, 8085.
- Dong, L., Stone, D.S., Lakes, R.S., 2012. Enhanced dielectric and piezoelectric properties of xBaZrO₃-(1-x)BaTiO₃ ceramics. *Journal of Applied Physics* 111, 084107.
- Dul'kin, A.E., Petzelt, J., Kamba, S., Mojaev, E., Roth, M., 2010. Relaxor-like behavior of crystals from acoustic emission study. *Applied Physics Letters* 97, 032903.
- Dunbar, T.D., Warren, W.L., Tuttle, B.A., Randall, C.A., Tsur, Y., 2004. Electron paramagnetic resonance investigations of lanthanide-doped barium titanate: Dopant site occupancy. *The Journal of Physical Chemistry B* 108, 908–917.
- Ehmke, M.C., Ehrlich, S.N., Blendell, J.E., Bowman, K.J., 2012. Phase coexistence and ferroelastic texture in high strain (1-x)Ba(Zr_{0.2}Ti_{0.8})O_{3-x}(Ba_{0.7}Ca_{0.3})TiO₃ piezoceramics. *Journal of Applied Physics* 111, 124110.
- Emelyanov, A.Y., Pertsev, N.A., Hoffmann-Eifert, S., Böttger, U., Waser, R., 2002. Grain-boundary effect on the Curie-Weiss law of ferroelectric ceramics and polycrystalline thin films: Calculation by the method of effective medium. *Journal of Electroceramics* 9, 5–16.
- Erhart, P., Eichel, R.-A., Träskelin, P., Albe, K., 2007. Association of oxygen vacancies with impurity metal ions in lead titanate. *Physical Review B* 76, 174116.
- Filipič, C., Kutnjak, Z., Pirc, R., Canu, G., Petzelt, J., 2016. BaZr_{0.5}Ti_{0.5}O₃: Lead-free relaxor ferroelectric or dipolar glass. *Physical Review B* 93, 224105.
- Freeman, C.L., Dawson, J.A., Chen, H.-R., *et al.*, 2011. A new potential model for barium titanate and its implications for rare-earth doping. *Journal of Materials Chemistry* 21, 4861–4868.
- Freeman, C.L., Dawson, J.A., Chen, H.-R., *et al.*, 2013. Energetics of donor-doping, metal vacancies, and oxygen-loss in A-site rare-earth-doped BaTiO₃. *Advanced Functional Materials* 23, 3925–3928.
- Frey, M.H., Payne, D.A., 1996. Grain-size effect on structure and phase transformations for barium titanate. *Physical Review B* 54, 3158–3168.
- Frey, M.H., Xu, Z., Han, P., Payne, D.A., 1998. The role of interfaces on an apparent grain size effect on the dielectric properties for ferroelectric barium titanate ceramics. *Ferroelectrics* 206, 337–353.
- Fu, D., Itoh, M., Koshihara, S.Y., Kosugi, T., Tsuneyuki, S., 2008. Anomalous phase diagram of ferroelectric (Ba,Ca)TiO₃ single crystals with giant electromechanical response. *Physical Review Letters* 100, 227601.
- Fu, H.X., Bellaiche, L., 2003. Ferroelectricity in barium titanate quantum dots and wires. *Physical Review Letters* 91, 257601.
- Gao, J.H., Liu, Y., Wang, Y., *et al.*, 2017. Designing high dielectric permittivity material in barium titanate. *Journal of Physical Chemistry C* 121, 13106–13113.
- Ghosh, D., Sakata, A., Carter, J., *et al.*, 2014. Domain wall displacement is the origin of superior permittivity and piezoelectricity in BaTiO₃ at intermediate grain sizes. *Advanced Functional Materials* 24, 885–896.
- Glaister, R.M., Kay, H.F., 1960. An investigation of the cubic-hexagonal transition in barium titanate. *Proceedings of the Physical Society* 76, 763.
- Gong, H.L., Wang, X.H., Zhang, S.P., Wen, H., Li, L.T., 2014. Grain size effect on electrical and reliability characteristics of modified fine-grained BaTiO₃ ceramics for MLCCs. *Journal of the European Ceramic Society* 34, 1733–1739.
- Gray, R.B., 1949. U.S. Pat. No. US2486560A. (Transducer and Method of Making the Same).
- Grey, I.E., Li, C., Cranswick, L.M.D., Roth, R.S., Vanderah, T.A., 1998. Structure analysis of the 6H-Ba(Ti, Fe³⁺, Fe⁴⁺)O_{3-δ} solid solution. *Journal of Solid State Chemistry* 135, 312–321.
- Guo, H.Y., Lei, C., Ye, Z.-G., 2008. Re-entrant type relaxor behavior in (1-x)BaTiO_{3-x}BiScO₃ solid solution. *Applied Physics Letters* 92, 172901.
- Haertling, G.H., 1999. Ferroelectric ceramics: History and technology. *Journal of the American Ceramic Society* 82, 797–818.
- Hagemann, H.J., Ihrig, H., 1979. Valence change and phase stability of 3d-doped BaTiO₃ annealed in oxygen and hydrogen. *Physical Review B* 20, 3871–3878.
- Hagemann, H.J., Hennings, D., 1981. Reversible weight change of acceptor-doped BaTiO₃. *Journal of the American Ceramic Society* 64, 590–594.
- Hall, D.A., Ben-Omran, M.M., Stevenson, P.J., 1998. Field and temperature dependence of dielectric properties in BaTiO₃-based piezoceramics. *Journal of Physics: Condensed Matter* 10, 461–476.
- Han, Y.H., Appleby, J.B., Smyth, D.M., 1987. Calcium as an acceptor impurity in BaTiO₃. *Journal of the American Ceramic Society* 70, 96–100.

- Hansen, P., Hennings, D., Schreinemacher, H., 1998. High-K dielectric ceramics from donor/acceptor-codoped $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{1-y}\text{Zr}_y)\text{O}_3$ (BCTZ). *Journal of the American Ceramic Society* 81, 1369–1373.
- Hao, J.G., Bai, W.F., Li, W., Zhai, J.W., 2012. Correlation between the microstructure and electrical properties in high-performance $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ lead-free piezoelectric ceramics. *Journal of the American Ceramic Society* 95, 1998–2006.
- Hennings, D., Rosenstein, G., 1984. Temperature-stable dielectrics based on chemically inhomogeneous BaTiO_3 . *Journal of the American Ceramic Society* 67, 249.
- Hennings, D., Schnell, A., Simon, G., 1982. Diffuse ferroelectric phase transitions in $\text{Ba}(\text{Ti}_{1-y}\text{Zr}_y)\text{O}_3$ ceramics. *Journal of the American Ceramic Society* 65, 539.
- Hennings, D.F.K., Schreinemacher, B.S., 1994. Temperature-stable dielectric materials in the system $\text{BaTiO}_3\text{-Nb}_2\text{O}_5\text{-Co}_3\text{O}_4$. *Journal of the European Ceramic Society* 14, 463471.
- Heywang, W., 1971. Semiconducting barium titanate. *Journal of Materials Science* 6, 1214.
- von Hippel, A., Breckenridge, R.G., Chesley, F.G., Tisza, L., 1946. High dielectric constant ceramics. *Industrial & Engineering Chemistry* 38, 1097–1109.
- Hirose, N., Skakle, J.M.S., West, A.R., 1999. Doping mechanism and permittivity correlations in Nd-doped BaTiO_3 . *Journal of Electroceramics* 3, 233–239.
- Hornebecq, V., Huber, C., Maglione, M., *et al.*, 2004. Dielectric properties of pure $(\text{BaSr})\text{TiO}_3$ and composites with different grain sizes ranging from the nanometer to the micrometer. *Advanced Functional Materials* 14, 899–904.
- Hoshina, T., Hatta, S., Takeda, H., Tsurumi, T., 2018. Grain size effect on piezoelectric properties of BaTiO_3 ceramics. *Japanese Journal of Applied Physics* 57, 0902BB.
- Hou, D., Usher, T.-M., Zhou, H., *et al.*, 2017. Temperature-induced local and average structural changes in $\text{BaTiO}_{3-x}\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ solid solutions: The origin of high temperature dielectric permittivity. *Journal of Applied Physics* 122, 064103.
- Hou, D., Zhao, C., Paterson, A.R., Li, S., Jones, J.L., 2018. Local structures of perovskite dielectrics and ferroelectrics via pair distribution function analysis. *Journal of the European Ceramic Society* 38, 971–987.
- Huan, Y., Wang, X.H., Fang, J., Li, L.T., 2013. Grain size effects on piezoelectric properties and domain structure of BaTiO_3 ceramics prepared by two-step sintering. *Journal of the American Ceramic Society* 96, 3369–3371.
- Huan, Y., Wang, X.H., Fang, J., Li, L.T., 2014. Grain size effect on piezoelectric and ferroelectric properties of BaTiO_3 ceramics. *Journal of the European Ceramic Society* 34, 1445–1448.
- Huang, Y.H., Wu, Y.J., Qiu, W.J., Li, J., Chen, X.M., 2015. Enhanced energy storage density of $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{TiO}_3\text{-MgO}$ composite prepared by spark plasma sintering. *Journal of the European Ceramic Society* 35, 1469–1476.
- Hwang, J.H., Han, Y.H., 2001a. Electrical properties of cerium-doped BaTiO_3 . *Journal of the American Ceramic Society* 84, 1750.
- Hwang, J.H., Han, Y.H., 2001b. Dielectric properties of erbium doped barium titanate. *Japanese Journal of Applied Physics* 40, 676–679.
- Ihlefeld, J.F., Harris, D.T., Keech, R., *et al.*, 2016. Scaling effects in perovskite ferroelectrics: fundamental limits and process-structure-property relations. *Journal of the American Ceramic Society* 99, 2537–2557.
- Ihrig, H., 1978. The phase stability of BaTiO_3 as a function of doped 3d elements: An experimental study. *Journal of Physics C: Solid State Physics* 11, 819–827.
- Ishikawa, K., Yoshikawa, K., Okada, N., 1988. Size effect on the ferroelectric phase transition in PbTiO_3 ultrafine particles. *Physical Review B* 37, 5852–5855.
- Jaffe, B., Cook, W.R., Jaffe, H., 1971. *Piezoelectric Ceramics*. London: Academic Press.
- Janbua, W., Bongkarn, T., Kolodiazny, T., Vittayakorn, N., 2017. High piezoelectric response and polymorphic phase region in the lead-free piezoelectric $\text{BaTiO}_3\text{-CaTiO}_3\text{-BaSnO}_3$ ternary system. *RSC Advances* 7, 30166.
- Jeon, S.-C., Lee, C.-S., Kang, S.-L., 2012. The mechanism of core/shell structure formation during sintering of BaTiO_3 -based ceramics. *Journal of the American Ceramic Society* 95, 2435–2438.
- Jin, L., Li, F., Zhang, S.J., 2014. Decoding the fingerprint of ferroelectric loops: Comprehension of the material properties and structures. *Journal of the American Ceramic Society* 97, 1–27.
- Jonker, G.H., 1964. Some aspects of semiconducting barium titanate. *Solid-State Electronics* 7, 895–903.
- Jonker, G.H., Havinga, E.E., 1982. The influence of foreign ions on the crystal lattice of barium titanate. *Materials Research Bulletin* 17, 345–350.
- Kay, H.F., Vausden, P., 1949. Symmetry changes in barium titanate at low temperatures and their relation to its ferroelectric properties. *Philosophical Magazine* 40, 1019–1040.
- Keeble, D.S., Benabdallah, F., Thomas, P.A., Maglione, M., Kreisel, J., 2013. Revised structural phase diagram of $(\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3)\text{-(BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3)$. *Applied Physics Letters* 102, 092903.
- Keith, G.M., Rampling, M.J., Sarma, K., Mc. Alford, N., Sinclair, D.C., 2004. Synthesis and characterisation of doped 6H- BaTiO_3 ceramics. *Journal of the European Ceramic Society* 24, 1721–1724.
- Kim, C.-H., Park, K.-J., Yoon, Y.-J., *et al.*, 2008. Role of yttrium and magnesium in the formation of core-shell structure of BaTiO_3 grains in MLCC. *Journal of the European Ceramic Society* 28, 1213–1219.
- Kim, J.-S., Kang, S.-J.L., 1999. Formation of core-shell structure in the $\text{BaTiO}_3\text{-SrTiO}_3$ system. *Journal of the American Ceramic Society* 82, 1085–1088.
- Kimura, T., Dong, Q., Yin, S., *et al.*, 2013. Synthesis and piezoelectric properties of Li-doped BaTiO_3 by a solvothermal approach. *Journal of the European Ceramic Society* 33, 1009–1015.
- Kinoshita, K., Yamaji, A., 1976. Grain-size effects on dielectric properties in barium-titanate ceramics. *Journal of Applied Physics* 47, 371–373.
- Kishii, H., Okino, Y., Honda, M., *et al.*, 1997. The effect of MgO and rare-earth oxide on formation behavior of core-shell structure in BaTiO_3 . *Japanese Journal of Applied Physics* 36, 5954–5997.
- Kishii, H., Kohzu, N., Sugino, J., *et al.*, 1999. The effect of rare-earth (La, Sm, Dy, Ho and Er) and Mg on the microstructure in BaTiO_3 . *Journal of the European Ceramic Society* 19, 1043–1046.
- Kishii, H., Mizuno, Y., Chazono, H., 2003. Base-metal electrode-multilayer ceramic capacitors: Past, present and future perspectives. *Japanese Journal of Applied Physics* 42, 1–15.
- Kleemann, W., Miga, S., Dec, J., Zhai, J., 2013. Crossover from ferroelectric to relaxor and cluster glass in $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ ($x = 0.25\text{--}0.35$) studied by non-linear permittivity. *Applied Physics Letters* 102, 232907.
- Kolar, D., Kunaver, U., Rečnik, A., 1998. Exaggerated anisotropic grain growth in hexagonal barium titanate ceramics. *Physica Status Solidi (A)* 166, 219.
- Kwei, G.H., Lawson, A.C., Billinge, J.L., Cheong, S.-W., 1993. Structure of the ferroelectric phase of barium titanate. *Journal of Physical Chemistry* 97, 2368–2377.
- Kwei, G.H., Billinge, S.J.L., Cheong, S.W., Saxton, J.G., 1995. Pair-distribution functions of ferroelectric perovskites: Direct observation of structural ground states. *Ferroelectrics* 164, 57–73.
- Langhammer, H.T., Müller, T., Felgner, K.-H., Abicht, H.-P., 2000. Crystal structure and related properties of manganese-doped barium titanate ceramics. *Journal of the American Ceramic Society* 83, 605–611.
- Langhammer, H.T., Müller, T., Böttcher, R., Abicht, H.-P., 2003. Crystal structure and related properties of copper-doped barium titanate ceramics. *Solid State Sciences* 5, 965–971.
- Langhammer, H.T., Müller, T., Böttcher, R., Abicht, H.-P., 2008. Structural and optical properties of chromium-doped hexagonal barium titanate ceramics. *Journal of Physics: Condensed Matter* 20, 085206.
- Langhammer, T., Böttcher, R., Müller, T., Walther, T., Ebbinghaus, S.G., 2015. Defect properties of cobalt-doped hexagonal barium titanate ceramics. *Journal of Physics: Condensed Matter* 27, 295901.
- Laulhe, C., Hippert, F., Bellissent, R., Cuello, G.J., 2009. Local structure in $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ relaxors from neutron pair distribution function analysis. *Physical Review B* 79, 064104.

- Laulhé, C., Pasturel, A., Hippert, F., Kreisel, J., 2010. Random local strain effects in homovalent-substituted relaxor ferroelectrics: A first-principles study of BaTi_{0.74}Zr_{0.26}O₃. *Physical Review B* 82, 132102.
- Lee, J.K., Hong, K.S., Jang, J.W., 2001. Roles of Ba/Ti ratios in the dielectric properties of BaTiO₃ ceramics. *Journal of the American Ceramic Society* 84, 2001–2006.
- Lee, S., Randall, C.A., 2008. Comprehensive linkage of defect and phase equilibria through ferroelectric transition behavior in BaTiO₃-based dielectrics: Part 2. Defect modeling under low oxygen partial pressure conditions. *Journal of the American Ceramic Society* 91, 1753–1761.
- Lee, S., Liu, Z.-K., Kim, M.H., Randall, C.A., 2007a. Influence of nonstoichiometry on ferroelectric phase transition in BaTiO₃. *Journal of Applied Physics* 101, 054119.
- Lee, S., Liu, Z.-K., Randall, C.A., 2007b. Modified phase diagram for the barium oxide-titanium dioxide system for the ferroelectric barium titanate. *Journal of the American Ceramic Society* 90, 2589–2594.
- Lee, S., Liu, Z.-K., Randall, C.A., 2008. Comprehensive linkage of defect and phase equilibria through ferroelectric transition behavior in BaTiO₃-based dielectrics: Part 1. Defect energies under ambient air conditions. *Journal of the American Ceramic Society* 91, 1748–1752.
- Lee, W.H., Groen, W.A., Schreinemacher, H., Hennings, D., 2000. Dysprosium doped dielectric materials for sintering in reducing atmospheres. *Journal of Electroceramics* 5, 31–36.
- Lei, C., Bokov, A.A., Ye, Z.-G., 2007. Ferroelectric to relaxor crossover and dielectric phase diagram in the BaTiO₃-BaSnO₃ system. *Journal of Applied Physics* 101, 084105.
- Levin, I., Cockayne, E., Krayzman, V., *et al.*, 2011. Local structure of Ba(Ti,Zr)O₃ perovskite-like solid solutions and its relation to the bandgap behavior. *Physical Review B* 83, 094122.
- Levin, I., Krayzman, V., Woicik, J.C., 2013. Local-structure origins of the sustained Curie temperature in (Ba,Ca)TiO₃ ferroelectrics. *Applied Physics Letters* 102, 162906.
- Levin, I., Krayzman, V., Woicik, J.C., 2014. Local structure in perovskite (Ba, Sr)TiO₃: Reverse Monte Carlo refinements from multiple measurement techniques. *Physical Review B* 89, 024106.
- Li, B., Ehmke, M.C., Blendell, J.E., Bowman, K.J., 2013. Optimizing electrical poling for tetragonal, lead-free BZT-BCT piezoceramic alloys. *Journal of the European Ceramic Society* 33, 3037–3044.
- Li, J., Zhang, D., Qin, S., *et al.*, 2016. Large room temperature electrocaloric effect in lead-free BaHf_{1-x}Ti_xO₃ ceramics under low electric field. *Acta Materialia* 115, 58.
- Li, W.-B., Zhou, D., Pang, L.-X., 2017. Enhanced energy storage density by inducing defect dipoles in lead free relaxor ferroelectric BaTiO₃-based ceramics. *Applied Physics Letters* 110, 132902.
- Lin, Y.-H., Yuan, J., Zhang, S., 2009. Multiferroic behavior observed in highly orientated Mn-doped BaTiO₃ thin films. *Applied Physics Letters* 95, 033105.
- Liu, Y., Chang, Y., Li, F., *et al.*, 2017a. Exceptionally high piezoelectric coefficient and low strain hysteresis in grain-oriented (Ba,Ca)(Ti,Zr)O₃ through integrating crystallographic texture and domain engineering. *ACS Applied Materials & Interfaces* 9, 29863–29871.
- Liu, B., Wang, X., Zhang, R., Li, L., 2017b. Grain size effect and microstructure influence on the energy storage properties of fine-grained BaTiO₃-based ceramics. *Journal of the American Ceramic Society* 100, 3599–3607.
- Liu, W., Ren, X., 2009. Large piezoelectric effect in Pb-free ceramics. *Physical Review Letters* 103, 257602.
- Liu, Y., West, A.R., 2009. Ho-doped BaTiO₃: Polymorphism, phase equilibria and dielectric properties of BaTi_{1-x}Ho_xO_{3-x/2}: 0 ≤ x ≤ 0.17. *Journal of the European Ceramic Society* 29, 3249–3257.
- Liu, Z.K., Li, X., Zhang, Q.M., 2012. Maximizing the number of coexisting phases near invariant critical points for giant electrocaloric and electromechanical responses in ferroelectrics. *Applied Physics Letters* 101, 082904.
- Long, S.A., Blumenthal, R.N., 1971a. Ti-rich nonstoichiometric BaTiO₃: I, High-temperature electrical conductivity measurements. *Journal of the American Ceramic Society* 54, 515–519.
- Long, S.A., Blumenthal, R.N., 1971b. Ti-rich nonstoichiometric BaTiO₃: II, Analysis of defect structure. *Journal of the American Ceramic Society* 54, 577–583.
- Lu, D.-Y., Han, D.-D., Sun, X.-Y., 2012. Mutual solid solubility and phase equilibrium in the system BaTiO₃-BaCeO₃. *Japanese Journal of Applied Physics* 51, 071501.
- Lu, D.-Y., Sun, X.-Y., Liu, B., Zhang, J.-L., Ogata, T., 2014. Structural and dielectric properties, electron paramagnetic resonance, and defect chemistry of Pr-doped BaTiO₃ ceramics. *Journal of Alloys and Compounds* 615, 25–34.
- Luo, Z., Zhang, D., Liu, Y., *et al.*, 2014. Enhanced electrocaloric effect in lead-free BaTi_{1-x}Sn_xO₃ ceramics near room temperature. *Applied Physics Letters* 105, 102904.
- Ma, N., Zhang, B.-P., Yang, W.-G., Guo, D., 2012. Phase structure and nano-domain in high performance of BaTiO₃ piezoelectric ceramics. *Journal of the European Ceramic Society* 32, 1059–1066.
- Maier, R.A., Johnston-Peck, A.C., Donohue, M.P., 2016. (Magic Dopant) Amphoteric behavior of a redox-active transition metal ion in a perovskite lattice: New insights on the lattice site occupation of manganese in SrTiO₃. *Advanced Functional Materials* 26, 8325–8333.
- Maiti, T., Guo, R., Bhalla, A.S., 2008. Structure-property phase diagram of BaZr_{1-x}Ti_xO₃ system. *Journal of the American Ceramic Society* 91, 1769–1780.
- Makovec, D., Drofenik, M., 2000. Microstructural changes during the reduction/reoxidation process in donor-doped BaTiO₃ ceramics. *Journal of the American Ceramic Society* 83, 2593–2599.
- Makovec, D., Samardžija, Z., Kolar, D., 1996. Solid solubility of cerium in BaTiO₃. *Journal of Solid State Chemistry* 123, 30–38.
- Makovec, D., Samardžija, Z., Drofenik, M., 2004. Solid solubility of holmium, yttrium, and dysprosium in BaTiO₃. *Journal of the American Ceramic Society* 87, 1324–1329.
- Masó, N., Beltrán, H., Cordoncillo, E., Escribano, P., West, A.R., 2006. Electrical properties of Fe-doped BaTiO₃. *Journal of Materials Chemistry* 16, 1626–1633.
- Matthias, B., von Hippel, A., 1948. Domain structure and dielectric response of barium titanate single crystals. *Physical Review* 73, 1378–1384.
- McCauley, D., Newnham, R.E., Randall, C.A., 1998. Intrinsic size effects in a barium titanate glass-ceramic. *Journal of the American Ceramic Society* 81, 979–987.
- Megaw, H.D., 1945. Crystal structure of barium titanate. *Nature* 155, 484–485.
- Merkle, R., Maier, J., 2003. Defect association in acceptor-doped SrTiO₃: Case study for Fe³⁺V⁵⁺ and Mn²⁺V⁵⁺. *Physical Chemistry Chemical Physics* 5, 2297–2303.
- Mertz, W.J., 1949. The electric and optical behavior of BaTiO₃ single-domain crystals. *Physical Review* 76, 1221–1225.
- Mertz, W.J., 1950. The effect of hydrostatic pressure on the curie point of barium titanate single Crystals. *Physical Review* 77, 52–54.
- Mertz, W.J., 1953. Double hysteresis loops of BaTiO₃ at the Curie point. *Physical Review* 91, 513–517.
- Merz, W.J., 1954. Domain formation and domain wall motions in ferroelectric BaTiO₃ single crystals. *Physical Review* 95, 690–698.
- Miao, S., Pokorny, J., Pasha, U.M., 2009. Polar order and diffuse scatter in Ba(Ti_{1-x}Zr_x)O₃ ceramics. *Journal of Applied Physics* 106, 114111.
- Miranda, L., Feteira, A., Sinclair, D.C., *et al.*, 2009. Composition-structure-property relationships of 6H- and 12R-type hexagonal Ba(Mn,Ti)O_{3-δ} perovskites. *Chemistry of Materials* 21, 1731–1742.
- Mizuno, Y., Okino, Y., Kohzu, N., Chazono, H., Kishi, H., 1998. Influence of the microstructure evolution on electrical properties of multilayer capacitor with Ni electrode. *Japanese Journal of Applied Physics* 37, 5227.
- Mizuno, Y., Kishi, H., Ohnuma, K., Ishikawa, T., Ohsato, H., 2007. Effect of site occupancies of rare earth ions on electrical properties in Ni-MLCC based on BaTiO₃. *Journal of the European Ceramic Society* 27, 4017–4020.
- Mornet, S., Elissalde, C., Hornebecq, V., *et al.*, 2005. Controlled growth of silica shell on Ba_{0.6}Sr_{0.4}TiO₃ nanoparticles used as precursors of ferroelectric composites. *Chemistry of Materials* 17, 4530–4536.
- Morrison, F.D., Sinclair, D.C., West, A.R., 1999. Electrical and structural characteristics of lanthanum-doped barium titanate ceramics. *Journal of Applied Physics* 86, 6355.
- Morrison, F.D., Coats, A.M., Sinclair, D.C., West, A.R., 2001a. Charge compensation mechanisms in La-doped BaTiO₃. *Journal of Electroceramics* 6, 219.
- Morrison, F.D., Sinclair, D.C., West, A.R., 2001b. Alternative explanation for the origin of the resistivity anomaly in La-doped BaTiO₃. *Journal of the American Ceramic Society* 84, 474–476.
- Morrison, F.D., Sinclair, D.C., West, A.R., 2001c. Characterization of lanthanum-doped barium titanate ceramics using impedance spectroscopy. *Journal of the American Ceramic Society* 84, 531–538.

- Moulson, A.J., Herbert, J.M., 1990. *Electroceramics*. London: Chapman & Hall.
- Muhammad, R., Iqbal, Y., Reaney, I.M., 2016. BaTiO₃-Bi(Mg_{2/3}Nb_{1/3})O₃ ceramics for high-temperature capacitor applications. *Journal of the American Ceramic Society* 99, 2089–2095.
- Negas, T., Roth, R.S., Parker, H.S., Minor, D., 1974. Subsolidus phase relations in the BaTiO₃-TiO₂ system. *Journal of Solid State Chemistry* 9, 297–307.
- O'Bryan Jr., M., Thomson Jr., J., 1974. Phase equilibria in the TiO₂-rich region of the system BaO-TiO₂. *Journal of the American Ceramic Society* 57, 522–526.
- Ogihara, H., Randall, C.A., Trolrier-McKinstry, S., 2009. High-energy density capacitors utilizing 0.7BaTiO₃-0.3BiScO₃ ceramics. *Journal of the American Ceramic Society* 92, 1719–1724.
- Ozawa, S., Furuzawa, A., Fujikawa, N., 1993. Effect of manganese valence state on the electrical conductivity of barium titanate. *Journal of the American Ceramic Society* 76, 1191–1194.
- Padurariu, L., Curecheriu, L., Buscaglia, V., Mitoseriu, L., 2012. Field-dependent permittivity in nanostructured BaTiO₃ ceramics: Modeling and experimental verification. *Physical Review B* 85, 224111.
- Palneedi, H., Peddigari, M., Hwang, G.T., Jeong, D.Y., Ryu, J.G., 2018. High-performance dielectric ceramic films for energy storage capacitors: Progress and outlook. *Advanced Functional Materials* 28, 1803665.
- Pan, M.J., Randall, C.A., 2010. A brief introduction to ceramic capacitors. *IEEE Electrical Insulation Magazine* 26, 44–50.
- Petzelt, J., Nuzhnyy, D., Savinov, M., *et al.*, 2014. Broadband dielectric spectroscopy of Ba(Zr,Ti)₂O₇: Dynamics of relaxors and diffuse ferroelectrics. *Ferroelectrics* 469, 14–25.
- Pirc, R., Blinc, R., 2004. Off-center Ti model of barium titanate. *Physical Review B* 70, 134107.
- Polking, M.J., Han, M.G., Yourdkhani, A., *et al.*, 2012. Ferroelectric order in individual nanometre-scale crystals. *Nature Materials* 11, 700–709.
- Polotai, A.V., Ragulya, A.V., Randall, C.A., 2003. Preparation and size effect in pure nanocrystalline barium titanate ceramics. *Ferroelectrics* 288, 93–102.
- Prateek, P., Thakur, V.K., Gupta, R.K., 2016. Recent progress on ferroelectric polymer-based nanocomposites for high energy density capacitors: Synthesis, dielectric properties, and future aspects. *Chemical Reviews* 116, 4260–4317.
- Praveen, J.P., Karthik, T., James, A.R., *et al.*, 2015. Effect of poling process on piezoelectric properties of sol-gel derived BZT-BCT ceramics. *Journal of the European Ceramic Society* 35, 1785–1798.
- Qian, X.S., Ye, H.J., Zhang, Y.T., *et al.*, 2014. Giant electrocaloric response over a broad temperature range in modified BaTiO₃ ceramics. *Advanced Functional Materials* 24, 1300.
- Raengthon, N., Sebastian, T., Cumming, D., Reaney, I.M., Cann, D.P., 2012. BaTiO₃-Bi(Zn_{1/2}Ti_{1/2})O₃-BiScO₃ ceramics for high-temperature capacitor applications. *Journal of the American Ceramic Society* 95, 3554–3561.
- Raj, S., Mahadevan, P., Mandal, S., *et al.*, 2008. High temperature ferromagnetism in single crystalline dilute Fe-doped BaTiO₃. *Physical Review B* 77, 104416.
- Randall, C.A., Newnham, R.E., Cross, L.E., 2004. *History of the First Ferroelectric Oxide, BaTiO₃*. Materials Research Institute. University Park: The Pennsylvania State University.
- Randall, C.A., Wang, S.F., Laubscher, D., Dougherty, J.P., Huebner, W., 1993. Structure property relationships in core-shell BaTiO₃-LiF ceramics. *Journal of Materials Research* 8, 871–879.
- Randall, C.A., Kim, N., Kucera, J.-P., Cao, W.W., Shrout, T.R., 1998. Intrinsic and extrinsic size effects in fine-grained morphotropic-phase-boundary lead zirconate titanate ceramics. *Journal of the American Ceramic Society* 81, 677–688.
- Rase, D.E., Roy, R., 1955. Phase Equilibrium in the System BaO-TiO₂. *Journal of the American Ceramic Society* 38, 102–113.
- Ravel, B., Stern, E.A., Vedrinskii, R.I., Kraizman, V., 1998. Local structure and the phase transitions of BaTiO₃. *Ferroelectrics* 206, 407–430.
- Ritter, J.J., Roth, R.S., Blendell, J.E., 1986. Alkoxide precursor synthesis and characterization of phases in the barium-titanium oxide system. *Journal of the American Ceramic Society* 69, 155–162.
- Roberts, S., 1947. Dielectric and piezoelectric properties of barium titanate. *Phys. Rev.* 71, 890–895.
- Rooksby, H.P., 1945. Compounds of the structural type of calcium titanate. *Nature* 155, 484.
- Sághi-Szabó, G., Cohen, R.E., Krakauer, H., 1999. First-principles study of piezoelectricity in tetragonal PbTiO₃ and PbZr_{1/2}Ti_{1/2}O₃. *Physical Review B* 59, 12771–12776.
- Sakabe, Y., Hamahi, Y., Sano, H., Wada, N., 2002. Effects of rare-earth oxides on the reliability of X7R dielectrics. *Japanese Journal of Applied Physics* 41, 5668–5673.
- Samara, G.A., 2003. The relaxational properties of compositionally disordered ABO₃ perovskites. *Journal of Physics: Condensed Matter* 15, R367–R411.
- Sato, S., Nakano, Y., Sato, A., Nomura, T., 1999. Mechanism of improvement of resistance degradation in Y-doped BaTiO₃ based MLCCs with Ni electrodes under highly accelerated life testing. *Journal of the European Ceramic Society* 19, 1061–1065.
- Schie, M., Waser, R., De Souza, R.A., 2014. A simulation study of oxygen-vacancy behavior in strontium titanate: Beyond nearest-neighbor interactions. *Journal of Physical Chemistry C* 118, 15185–15192.
- Schilling, A., Adams, T.B., Bowman, R.M., *et al.*, 2006. Scaling of domain periodicity with thickness measured in BaTiO₃ single crystal lamellae and comparison with other ferroics. *Physical Review B* 74, 024115.
- Schilling, A., Byrne, D., Catalan, G., *et al.*, 2009. Domains in ferroelectric nanodots. *Nano Letters* 9, 3359–3364.
- Senn, M.S., Keen, D.A., Lucas, T.C.A., Hriljac, J.A., Goodwin, A.L., 2016. Emergence of long-range order in BaTiO₃ from local symmetry-breaking distortions. *Physical Review Letters* 116, 207602.
- Shaikh, A.S., Vest, R.W., 1986. Defect structure and dielectric properties of Nd₂O₃-modified BaTiO₃. *Journal of the American Ceramic Society* 69, 689–694.
- Shao, S.F., Zhang, J.L., Zhang, Z., *et al.*, 2008. High piezoelectric properties and domain configuration in BaTiO₃ ceramics obtained through solid-state reaction route. *Journal of Physics D: Applied Physics* 41, 125408.
- Shaw, T.M., Trolrier-McKinstry, S., McIntyre, P.C., 2000. The properties of ferroelectric films at small dimensions. *Annual Review of Materials Science* 30, 263–298.
- Shen, Z.B., Wang, X.H., Luo, B.C., Li, L.T., 2015. BaTiO₃-BiYbO₃ perovskite materials for energy storage applications. *Journal of Materials Chemistry A* 3, 18146–18153.
- Shen, Z.-Y., Li, J.-F., 2010. Enhancement of piezoelectric constant d₃₃ in BaTiO₃ ceramics due to nano-domain structure. *Journal of Ceramic Society of Japan* 118, 940–943.
- Shvartsman, V.V., Lupascu, D.C., 2012. Lead-free relaxor ferroelectrics. *Journal of the American Ceramic Society* 95, 1.
- Shvartsman, V.V., Dec, J., Xu, Z.K., *et al.*, 2008. Crossover from ferroelectric to relaxor behavior in BaTi_{1-x}Sn_xO₃ solid solutions. *Phase Transitions* 81, 1013–1021.
- Shvartsman, V.V., Zhai, J., Kleemann, W., 2009. The dielectric relaxation in solid solutions BaTi_{1-x}Zr_xO₃. *Ferroelectrics* 379, 77–85.
- Siegrist, T., Vanderah, T.A., 2003. Combining magnets and dielectrics: Crystal chemistry in the BaO-Fe₂O₃-TiO₂ system. *European Journal of Inorganic Chemistry* 8, 1483–1501.
- Simon, A., Ravez, J., Maglione, M., 2004. The crossover from a ferroelectric to a relaxor state in lead-free solid solutions. *Journal of Physics Condensed Matter* 16, 963.
- Sinclair, D.C., Skakle, J.M.S., Morrison, F.D., Smith, R.I., Beales, T.P., 1999. Structure and electrical properties of oxygen-deficient hexagonal BaTiO₃. *Journal of Materials Chemistry* 9, 1327–1331.
- Smyth, D.M., 1985. Defects and order in perovskite-related compounds. *Annual Review of Material Science* 15, 329–357.
- Smyth, D.M., 2002. The defect chemistry of donor-doped BaTiO₃: A rebuttal. *Journal of Electroceramics* 9, 179–186.
- Son, J.Y., Lee, J.-H., Song, S., Shin, Y.-H., Jang, H.M., 2013. Four-states multiferroic memory embodied using Mn-Doped BaTiO₃ nanorods. *ACS Nano* 7, 5522–5529.
- Song, Z., Liu, H., Zhang, S., *et al.*, 2014. Effect of grain size on the energy storage properties of (Ba_{0.4}Sr_{0.6})TiO₃ paraelectric ceramics. *Journal of the European Ceramic Society* 34, 1209–1217.
- Song, Z., Zhang, S., Liu, H., *et al.*, 2015. Improved energy storage properties accompanied by enhanced interface polarization in annealed microwave-sintered BST. *Journal of the American Ceramic Society* 98, 3212–3222.
- Su, B., Button, T.W., 2004. Microstructure and dielectric properties of Mg-doped barium strontium titanate ceramics. *Journal of Applied Physics* 95, 1382–1385.

- Su, Y., Kang, H., Wang, Y., Li, J., Weng, G.J., 2017. Intrinsic versus extrinsic effects of the grain boundary on the properties of ferroelectric nanoceramics. *Physical Review B* 95, 054121.
- Tagantsev, A.K., Sherman, V.O., Astafiev, K.F., Venkatesh, J., Setter, N., 2003. Ferroelectric materials for microwave tunable applications. *Journal of Electroceramics* 11, 5–66.
- Takeuchi, T., Capiglia, C., Balakrishnan, N., Takeda, Y., Kageyama, H., 2002. Preparation of fine-grained BaTiO₃ ceramics by spark plasma sintering. *Journal of Materials Research* 17, 575–581.
- Tan, Y.Q., Zhang, J., Wu, Y., *et al.*, 2015. Unfolding grain size effects in barium titanate ferroelectric ceramics. *Scientific Reports* 5, 9953.
- Tang, X.G., Chew, K.-H., Chan, H.L.W., 2004. Diffuse phase transition and dielectric tunability of Ba(Zr₁Ti_{1-x})O₃ relaxor ferroelectric ceramics. *Acta Materialia* 52, 5177–5183.
- Tsur, Y., Dumbar, T.D., Randall, C.A., 2001. Crystal and defect chemistry of rare earth cations in BaTiO₃. *Journal of Electroceramics* 7, 25–34.
- Vendik, O.G., Zubko, S.P., 2000. Ferroelectric phase transition and maximum dielectric permittivity of displacement type ferroelectrics Ba_xSr_{1-x}TiO₃. *Journal of Applied Physics* 88, 5343.
- Wang, D., Jiang, Z., Yang, B., *et al.*, 2014. Phase diagram and enhanced piezoelectric response of lead-free BaTiO₃-CaTiO₃-BaHfO₃ system. *Journal of the American Ceramic Society* 97, 3244–3251.
- Wang, P., Li, Y.X., Lu, Y.Q., 2011. Enhanced piezoelectric properties of (Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O₃ lead-free ceramics by optimizing calcination and sintering temperature. *Journal of the European Ceramic Society* 31, 2005–2012.
- Wang, S.-F., Li, J.-H., Hsu, Y.-F., *et al.*, 2013. Dielectric properties and microstructures of non-reducible high-temperature stable X9R ceramics. *Journal of the European Ceramic Society* 33, 1793–1799.
- Wang, T., Jin, L., Li, C., Hu, Q., Wei, X., 2015. Relaxor ferroelectric BaTiO₃-Bi(Mg_{2/3}Nb_{1/3})O₃ ceramics for energy storage application. *Journal of the American Ceramic Society* 98, 559–566.
- Wang, X., Zhang, Y., Son, X., *et al.*, 2012. Glass additive in barium titanate ceramics and its influence on electrical breakdown strength in relation with energy storage properties. *Journal of the European Ceramic Society* 32, 559–567.
- Wang, X.H., Deng, X.Y., Wen, H., Li, L.T., 2006. Phase transition and high dielectric constant of bulk dense nanograin barium titanate ceramics. *Applied Physics Letters* 89, 162902.
- Warren, W.L., Pike, G.E., Vanheusden, K., Dimos, D., Tuttle, B.A., 1996. Defect-dipole alignment and tetragonal strain in ferroelectrics. *Journal of Applied Physics* 79, 9250.
- Wu, J., Xiao, D., Wu, W., *et al.*, 2012. Composition and poling condition-induced electrical behavior of (Ba_{0.85}Ca_{0.15})(Ti_{1-x}Zr_x)O₃ lead-free piezoelectric ceramics. *Journal of the European Ceramic Society* 32, 891–898.
- Wu, L., Wang, X., Gong, H., *et al.*, 2015. Core-satellite BaTiO₃@SrTiO₃ assemblies for a local compositionally graded relaxor ferroelectric capacitor with enhanced energy storage density and high energy efficiency. *Journal of Materials Chemistry C* 3, 750.
- Wu, L., Wang, X., Li, L., 2016. Lead-free BaTiO₃-Bi(Zn_{2/3}Nb_{1/3})O₃ weakly coupled relaxor ferroelectric materials for energy storage. *RSC Advances* 6, 14273–14282.
- Wul, B.M., Goldman, I.M., 1945. Dielectric constants of titanates of metals of the second group. *Comptes Rendus de l'Académie des Sciences de l'URSS* 46, 139–142.
- Xiong, B., Hao, H., Zhang, S., Liu, H., Cao, M., 2011. Structure, dielectric properties and temperature stability of BaTiO₃-Bi(Mg_{1/2}Ti_{1/2})O₃ perovskite solid solutions. *Journal of the American Ceramic Society* 94, 3412–3417.
- Xu, B., Yin, K.B., Lin, J., 2009. Room-temperature ferromagnetism and ferroelectricity in Fe-doped BaTiO₃. *Physical Review B* 79, 134109.
- Xue, L.A., Chen, Y., Brook, R.J., 1988. The influence of ionic radii on the incorporation of trivalent dopants into BaTiO₃. *Materials Science and Engineering: B* 1, 193–201.
- Yang, H., Yan, F., Lin, Y., 2017. Lead-free BaTiO₃-Bi_{0.5}Na_{0.5}TiO₃-Na_{0.73}Bi_{0.09}NbO₃ relaxor ferroelectric ceramics for high energy storage. *Journal of the European Ceramic Society* 37, 3303–3311.
- Yang, H., Yan, F., Lin, Y., Wang, T., 2018. Enhanced energy storage properties of Ba_{0.4}Sr_{0.6}TiO₃ lead-free ceramics with Bi₂O₃-B₂O₃-SiO₂ glass addition. *Journal of the European Ceramic Society* 38, 1367–1373.
- Yang, W.G., Zhang, B.P., Ma, N., Zhao, L., 2012. High piezoelectric properties of BaTiO₃-xLiF ceramics sintered at low temperatures. *Journal of the European Ceramic Society* 32, 899–904.
- Yao, G.F., Wang, X.H., Wu, Y.Y., Li, L.T., 2012a. Nb-doped 0.9BaTiO₃-0.1(Bi_{0.5}Na_{0.5})TiO₃ ceramics with stable dielectric properties at high temperature. *Journal of the American Ceramic Society* 95, 614–618.
- Yao, Y.G., Zhou, C., Lv, D., *et al.*, 2012b. Large piezoelectricity and dielectric permittivity in BaTiO₃-xBaSnO₃ system: The role of phase coexisting. *Europhysics Letters* 98, 27008.
- Yao, Z.H., Song, Z., Hao, H., *et al.*, 2017. Homogeneous/inhomogeneous-structured dielectrics and their energy-storage performances. *Advanced Materials* 29, 1601727.
- Yoon, S.-H., Randall, C.A., Hur, K.-H., 2009. Effect of acceptor (Mg) concentration on the resistance degradation behavior in acceptor (Mg)-doped BaTiO₃ bulk ceramics: I. Impedance analysis. *Journal of the American Ceramic Society* 92, 1758–1765.
- Yuan, Q., Li, G., Yao, F.-Z., *et al.*, 2018. Simultaneously achieved temperature-insensitive high energy density and efficiency in domain engineered BaTiO₃-Bi(Mg_{0.5}Zr_{0.5})O₃ lead-free relaxor ferroelectrics. *Nano Energy* 52, 203–210.
- Yuan, Q., Cui, J., Wang, Y., Ma, R., Wang, H., 2017a. Significant enhancement in breakdown strength and energy density of the BaTiO₃/BaTiO₃@SiO₂ layered ceramics with strong interface blocking effect. *Journal of the European Ceramic Society* 37, 4645–4652.
- Yuan, Q., Yao, F.-Z., Wang, Y., Ma, R., Wang, H., 2017b. Relaxor ferroelectric 0.9BaTiO₃-0.1Bi(Zn_{0.5}Zr_{0.5})O₃ ceramic capacitors with high energy density and temperature stable energy storage properties. *Journal of Materials Chemistry C* 5, 9552–9558.
- Zalar, B., Laguta, V.V., Blinc, R., 2003. NMR evidence for the coexistence of order-disorder and displacive components in barium titanate. *Physical Review Letters* 90, 4.
- Zeb, A., Milne, S.J., 2014a. Low variation in relative permittivity over the temperature range 25–450°C for ceramics in the system (1-x)[Ba_{0.8}Ca_{0.2}TiO_{3-x}][Bi(Zn_{0.5}Ti_{0.5})O₃]. *Journal of the European Ceramic Society* 34, 1727–1732.
- Zeb, A., Milne, S.J., 2014b. Temperature-stable dielectric properties from 20°C to 430°C in the system BaTiO₃-Bi(Mg_{0.5}Zr_{0.5})O₃. *Journal of the European Ceramic Society* 34, 3159–3166.
- Zeb, A., Milne, S.J., 2015. High temperature dielectric ceramics: A review of temperature-stable high-permittivity perovskites. *Journal of Materials Science: Materials in Electronics* 26, 9243–9255.
- Zhang, L., Thakur, O.P., Feteira, A., 2007. Comment on the use of calcium as a dopant in X8R BaTiO₃-based ceramics. *Applied Physics Letters* 90, 142914.
- Zhang, L., Zhang, M., Wang, L., 2014. Phase transitions and the piezoelectricity around morphotropic phase boundary in Ba(Zr_{0.2}Ti_{0.8})O_{3-x}(Ba_{0.7}Ca_{0.3})TiO₃ lead-free solid solution. *Applied Physics Letters* 105, 162908.
- Zhang, L.X., Erdem, E., Ren, X.B., Eichel, R.A., 2008. Reorientation of (Mn²⁺-V⁵⁺) defect dipoles in acceptor-modified BaTiO₃ single crystals: An electron paramagnetic resonance study. *Applied Physics Letters* 93, 202901.
- Zhang, Q.W., Zhai, J.W., Kong, L.B., 2012. Relaxor ferroelectric materials for microwave tunable applications. *Journal of Advanced Dielectrics* 2, 1230002.
- Zhang, S., Lim, J.B., Lee, H.J., Shrout, T.R., 2009. Characterization of hard piezoelectric lead-free ceramics. *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control* 56, 1523–1527.
- Zhang, Y., Cao, M., Yao, Z., *et al.*, 2015. Effects of silica coating on the microstructures and energy storage properties of BaTiO₃ ceramics. *Materials Research Bulletin* 67, 70–76.
- Zhang, Y., Wang, X., Tian, Z., Hur, K.-H., Li, L., 2011. Preparation of BME MLCC powders by aqueous chemical coating method. *Journal of the American Ceramic Society* 94, 3286–3290.
- Zhao, C., Wu, H., Li, F., *et al.*, 2018. Practical high piezoelectricity in barium titanate ceramics utilizing multiphase convergence with broad structural flexibility. *Journal of the American Chemical Society* 140, 15252–15260.

- Zhao, C.L., Wu, W.J., Wang, H., Wu, J.G., 2016. Site engineering and polarization characteristics in $(\text{Ba}_{1-y}\text{Ca}_y)(\text{Ti}_{1-x}\text{Hf}_x)\text{O}_3$ lead-free ceramics. *Journal of Applied Physics* 119, 024108.
- Zhao, Z., Buscaglia, V., Viviani, M., *et al.*, 2004. Grain-size effects on the ferroelectric behavior of dense nanocrystalline BaTiO₃ ceramics. *Physical Review B* 70, 024107.
- Zheng, P., Zhang, J.L., Tan, Y.Q., Wang, C.L., 2012. Grain-size effects on dielectric and piezoelectric properties of poled BaTiO₃ ceramics. *Acta Materialia* 60, 5022–5030.
- Zhi, J., Chen, A., Zhi, Y., Vilarinho, P.M., Baptista, J.L., 1999. Incorporation of yttrium in barium titanate ceramics. *Journal of the American Ceramic Society* 82, 1345–1348.
- Zhong, W.L., Wang, Y.G., Zhang, P.L., Qu, B.D., 1994. Phenomenological study of the size effect on phase transitions in ferroelectric particles. *Physical Review B* 50, 698–703.
- Zhou, M., Liang, R., Zhou, Z., Dong, X., 2018. Novel BaTiO₃-based lead-free ceramic capacitors featuring high energy storage density, high power density, and excellent stability. *Journal of Materials Chemistry C* 6, 8528–8537.
- Zhu, J.L., Jin, C.Q., Cao, W.W., Wang, X.H., 2008. Phase transition and dielectric properties of nanograin BaTiO₃ ceramic under high pressure. *Applied Physics Letters* 92, 242901.
- Zhu, L.F., Zhang, B.P., Zhao, X.K., *et al.*, 2013a. Enhanced piezoelectric properties of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{0.92}\text{Sn}_{0.08})\text{O}_3$ lead-free ceramics. *Journal of the American Ceramic Society* 96, 241–245.
- Zhu, L.F., Zhang, B.P., Zhao, X.K., *et al.*, 2013b. Phase transition and high piezoelectricity in $(\text{Ba}, \text{Ca})(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ lead-free ceramics. *Applied Physics Letters* 103, 072905.
- Zhu, L.F., Zhang, B.P., Zhao, L., *et al.*, 2016. Large piezoelectric effect of $(\text{Ba}, \text{Ca})\text{TiO}_{3-x}\text{Ba}(\text{Sn}, \text{Ti})\text{O}_3$ lead free ceramics. *Journal of the European Ceramic Society* 36, 1017–1024.
- Zhu, L.F., Zhang, B.P., Zhao, L., Li, J.F., 2014. High piezoelectricity of BaTiO₃-CaTiO₃-BaSnO₃ lead-free ceramics. *Journal of Materials Chemistry C* 2, 4764–4771.

The PZT System

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General Introduction

Piezoelectric and ferroelectric materials are present all around us and are an integral part of our lives, even though they may, at first glance, be invisible. In our cars, fuel consumption is optimized by piezoelectric injectors and safety is enhanced by airbags controlled by accelerometers. We use, store and transport our digital data thanks to non-volatile ferroelectric memories present in our solid state hard drives and our USB keys. We communicate with the help of smartphones equipped with touch screens and using microwave filters, allowing the transfer of data to relay antennas, which also make use of ferroelectric and piezoelectric materials.

Currently, lead-based compounds such as lead zirconate titanate (PZT) constitute the best family of piezoelectric and ferroelectric materials suitable for integration into devices such as piezoelectric actuators, sensors and transducers (Holterman and Groen, 2012). These compounds present excellent piezoelectric and ferroelectric properties and are widely industrially developed.

The development of these multiple and varied applications requires materials that can be modulated in properties. The most used solution to exacerbate these properties is the addition of dopant to the PZT composition. Different types of doping are possible depending on the desired piezoelectric characteristics. Complex and very diverse doped compositions depending on the targeted applications exist on the market.

Piezoelectricity: Definition and Application

Piezoelectric Phenomenon

The piezoelectricity describes the electrical polarization phenomenon induced by a mechanical deformation in some crystals. Thus, a piezoelectric material is a material with the ability to convert mechanical energy into electrical energy and vice versa (Craciun, 2020). The direct piezoelectric effect reflects the ability of a material to generate an electrical charge when it is subjected to mechanical stress. It is interesting to note that the electric charge is proportional to this stress. At the opposite, the reverse piezoelectric effect reflects the ability of a material to deform when an electric field is applied to it. Also in this case, the deformation is proportional to the applied field (Jaffe *et al.*, 1971; Moulson and Herbert, 2003). These phenomena are schematically represented in Fig. 1.

Among the 32 crystal classes, 11 have a center of symmetry and are nonpolar. For these, the application of a stress results in a symmetrical ionic displacement and, therefore, no change in the dipole moment. The other 21 classes are non-centrosymmetric, 20 are piezoelectric. Although class 432, of cubic symmetry, is non-centrosymmetric, it exhibits elements of symmetry which, combined, exclude the existence of polar features. Among the 20 piezoelectric crystal classes, 10 are polar, that is to say they have an electrical polarization in the absence of an applied external electric field. These 10 classes are called pyroelectric because the amplitude of the dipole moment depends of the temperature. Finally, a limited number of pyroelectric materials have the additional property of having a spontaneous polarization and the direction of this polarization can be reversed under the influence of an external electric field. This last group is called ferroelectric and the PZT family belongs to it. Classification and properties of crystal systems are shown in Fig. 2.

Piezoelectric devices are largely made from polycrystalline ferroelectric ceramics. After sintering, the spontaneous polarizations of the different domains are randomly oriented. At this time, the ceramic does not exhibit any macroscopic ferroelectric property. These materials can only be used for piezoelectric applications after having been subjected to an intense electric field which preferentially aligns the polarizations of the ferroelectric domains in its direction.

The mobility of these domains allows to explain the macroscopic polarization hysteresis cycles of these materials that are shown in Fig. 3.

When the electric field is removed, the polarized ceramic tends to return to its original form. The domains reorient themselves into their initial direction more or less quickly, revealing a hysteresis. The polarization P is then a nonlinear function of the external electric field E . For large electric field values, the polarization is saturated at the spontaneous polarization $\pm P_s$. When the electric field is reduced to zero, a remanent polarization $\pm P_r$ remains in the ceramic. If the electric field is equal to $\pm E_c$ then the remanent polarization is canceled. E_c is the coercive field.

Piezoelectric Applications

Two main materials have been developed for piezoelectric applications. The first ceramic developed was barium titanate (BaTiO_3) in the 1940s. The solid solution of lead zirconate titanate was discovered in the 1950s. Today, it is the most widely used for

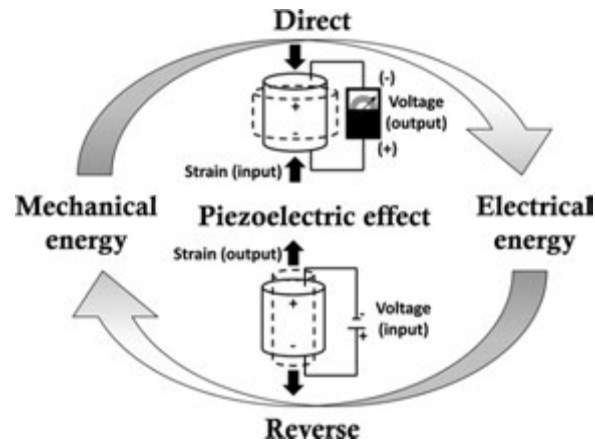


Fig. 1 Schematic representation of direct and reverse piezoelectric effect.

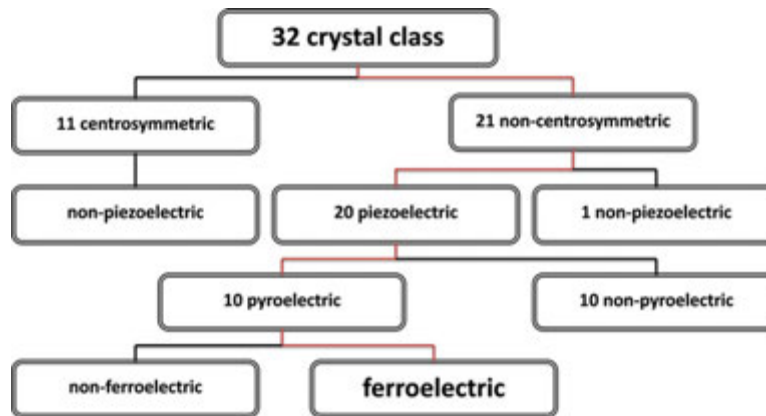


Fig. 2 Classification of crystal systems according to their piezoelectric properties.

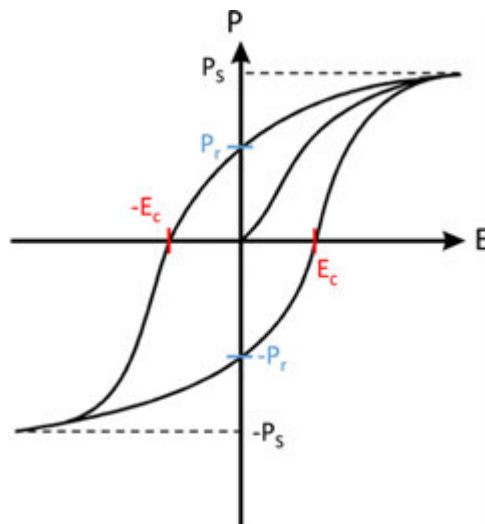


Fig. 3 Hysteresis cycle of a ferroelectric material. E electric field; P polarization; P_r remanent polarization; P_s saturation polarization; E_c coercive field.

piezoelectric applications because of its remarkable properties. Indeed, these materials have, compared to BaTiO₃, higher electromechanical coupling factor and Curie temperature allowing their use at higher temperature. Finally, due to the diversity of compositions existing in the PbZrO₃-PbTiO₃ system, PZT allows greater modulation of the properties and therefore of the applications.

These applications are very diverse due to the existence of direct and reverse effects (Moulson and Herbert, 2003). 4 major groups of applications of piezoelectric ceramics can be distinguished (Haertling, 1999):

- (1) Power generators: use of the direct effect from pressure constraints.
- (2) Pressure sensors and actuators: use of the indirect effect, slight movements are caused under the application of a field.
- (3) Generation of acoustic and ultrasonic vibrations: use of the indirect effect, the application of an alternating field generates vibrations.
- (4) Frequency control: the use of low impedance phenomenon at the resonant frequency of the material allows the selection of frequency bands.

More specifically, among the most famous applications, we find gas igniters, diesel engine injectors as well as airbag triggers using the direct piezoelectric effect but also actuators based on the reverse piezoelectric effect. Finally, mention may be made of the sensors used for reversing radar systems integrated into vehicles or echoscopy imaging systems, the operation of which is based on the two effects; direct and reverse (Holterman and Groen, 2012).

Piezoelectric Properties

Piezoelectric materials present several properties which are exploited depending the targeted applications. Their definitions are listed in this part.

Curie temperature T_c

The crystal structure of a material changes at the Curie temperature, T_c , from piezoelectric (non-centrosymmetric) to a non-piezoelectric (centrosymmetric) form. This phase change is accompanied by a peak in the dielectric constant and a complete loss of all piezoelectric properties.

Dielectric constant ϵ_r

The relative dielectric constant is defined as the ratio of the permittivity of the material ϵ^T to the permittivity of free space ϵ_0 . This is generally measured well below the mechanical resonance. The dielectric constant is derived from the static capacitance measurements at 1 kHz using a standard impedance bridge.

$$\epsilon_r = \frac{\epsilon^T}{\epsilon_0}$$

with: ϵ^T permittivity at constant stress (F/m) and ϵ_0 permittivity of free space (8.854×10^{-12} F/m).

Dielectric loss factor

The dielectric loss factor is defined as the tangent of the loss angle ($\tan \delta$). The loss factor represents the ratio of conductance to susceptance of a parallel equivalent circuit of the ceramic element. The loss factor can be measured directly using an impedance bridge.

Electromechanical coupling factor k

The electromechanical coupling factor of a piezoelectric material is a measure of the fraction of electric energy that can be converted into mechanical energy and vice versa:

$$k^2 = \frac{\text{mechanical energy converted into electric energy}}{\text{input mechanical energy}}$$

or

$$k^2 = \frac{\text{electric energy converted into mechanical energy}}{\text{input electric energy}}$$

The k_p is the electromechanical coupling factor in the radial mode (i.e., parallel to the surface of the material) and the k_t the electromechanical coupling factor in the thickness mode (i.e., perpendicular to the surface of the material).

Mechanical quality factor Q_m

The mechanical quality factor is the ratio of the reactance to the resistance in the series equivalent circuit representing the piezoelectric resonator. The Q_m factor is also related to the sharpness of the resonance frequency.

$$Q_m = \frac{f_a^2}{2\pi f_r Z_m C^T (f_a^2 - f_r^2)}$$

with: f_a anti-resonance frequency (Hz), f_r resonance frequency (Hz), Z_m minimum resonance at f_r (ohm) and C^T Capacitance of the material (F).

Alternatively, the Q_m factor can also be determined using the equation:

$$Q_m = \frac{f_r}{f_1 - f_2}$$

With: f_1 : -3 dB points from the resonance frequency f_r (Hz) and f_2 : $+3$ dB points from the resonance frequency f_r (Hz).

Piezoelectric constants d

The piezoelectric charge coefficient is the ratio of electric charge generated per unit area to an applied force (C/N or m/V).

$$d = \frac{\text{Strain developed}}{\text{Applied field}} = \frac{\text{Charge density}}{\text{Applied stress}}$$

In the d_{33} mode, the electrodes are perpendicular to the 3 axis and the applied stress or the piezoelectrically induced strain is in 3 direction.

Crystal Structure of $\text{Pb}(\text{Zr,Ti})\text{O}_3$

The lead zirconate titanate, $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) is a solid solution composed of lead zirconate PbZrO_3 and lead titanate PbTiO_3 . This solid solution exists in all chemical composition domains of the PbTiO_3 - PbZrO_3 system. PbTiO_3 , PbZrO_3 and $\text{Pb}(\text{Zr,Ti})\text{O}_3$ belong to the family of perovskite-like ABX_3 compounds.

The perovskite structure flexibility allows a wide substitution variety according the choice of the atoms on A and B sites. In particular, the relation between the lengths of the A and B sub-networks plays an important role in the determination of the material properties. This relation is characterized by the Goldschmidt tolerance factor, t (Goldschmidt, 1926).

The Goldschmidt tolerance factor measures the deviation from the ideal situation of compact stacking of atoms and gives information on the stability of the perovskite structure as a function of the A, B and X ions radius.

$$t = \frac{r_A + r_X}{(r_B + r_X)\sqrt{2}}$$

Experimentally, the perovskite structure is stable for $0.88 < t < 1.10$. This allows a large variety of substitutions on A and B sites and, therefore, the existence of a large number of compounds having this structure.

The crystalline structure of the PZT is generally represented by a cubic lattice (Fig. 4). This structure is described as a cubic stacking of cations A, bivalent with a large radius and a coordination number of 12 (Pb^{2+}). The cation B, tetravalent with a smaller radius and a coordination number of 6 is positioned in the center of the lattice (Ti^{4+} or Zr^{4+}). The O^{2-} ions occupy the center of the cube faces (Jaffe *et al.*, 1971).

The chemical composition of the PZT is defined by the X and R parameters. X corresponds to the rate of Zr^{4+} ions occupying the B site of the perovskite network and is represented by the molar ratio:

$$X = \frac{n(\text{Zr})}{n(\text{Zr}) + n(\text{Ti})}$$

The second parameter, R, characterizes the occupation rate of the A sites compared to the B sites. It is represented by the molar ratio:

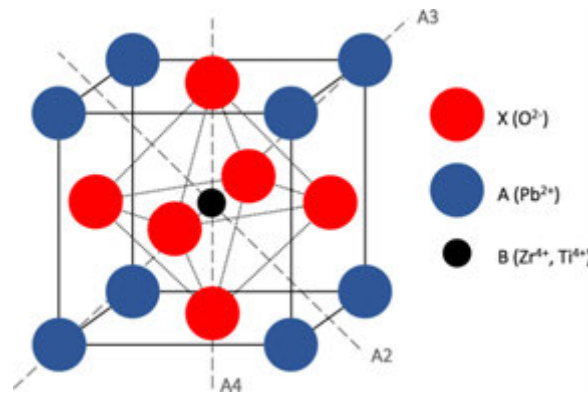


Fig. 4 Schematic representation of the perovskite structure. A2, A3 and A4 represent the deformation directions due to the displacement of the B ion into the octahedron.



Fig. 5 Bright-field (BF) TEM image showing 90° domains in 2.4 mol% Nb-doped PZT (Zr:Ti ratio: 1.095). Reproduced from: Zheng, H., Reaney, I.M., Lee, W.E., Jones, N., Thomas, H., 2001. Effects of strontium substitution in Nb-doped PZT ceramics. *Journal of the European Ceramic Society* 21, 1371–1375. doi:10.1016/S0955-2219(01)00021-8.

$$R = \frac{n(\text{Pb})}{n(\text{Zr}) + n(\text{Ti})}$$

Thus, the chemical formula of the PZT is written $\text{Pb}_R(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$.

The cubic structure for the PbTiO_3 , PbZrO_3 and $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ species is stable only at high temperature. Under this form, the PZT material present a dielectric behavior characterized by a zero electrical polarization. This is the paraelectrical state. Below this temperature, named Curie Temperature (T_C), the crystal lattice is deformed spontaneously inducing the off-centering of the B cation within its octahedron. This phenomenon generates the apparition of an electrical dipole at the lattice scale and the formation of ferroelectric domains at the microscopic scale (Fig. 5). The phase diagram PbTiO_3 - PbZrO_3 was initially presented by Jaffe *et al.* (Fig. 6).

The lead titanate adopts a tetragonal structure below $T_C = 490^\circ\text{C}$ and presents a ferroelectric behavior. At the other end of the diagram, the lead zirconate presents an orthorhombic structure below $T_C = 230^\circ\text{C}$ and exhibits a antiferroelectric behavior. In the solid solution, the substitution of the Ti^{4+} ions by the Zr^{4+} ions induces a decrease of the Curie Temperature. Below this temperature, the crystal structure and the ferroelectric characteristics of the PZT evolve with its chemical composition.

Therefore, at room temperature, for zirconium rich compositions, the orthorhombic structure and antiferroelectric behavior of the PZT material exists only up to $x = 0.94$. Below this limit, PZT adopts ferroelectric behavior but has two different crystalline structures (Shirane *et al.*, 1952): for titanium rich composition, PZT crystallizes in the tetragonal system and for an intermediate PZT enriched in zirconium, the structure is rhombohedral. The remarkable fact of this PZT solid solution is the crystal system change for the composition around $x = 0.54$. It is admitted that at this place, there is a coexistence of the two rhombohedral and tetragonal phases for the same chemical composition. This transition is called morphotropic phase boundary.

The word “domain” reflects the experimental ambiguity in developing PZT ceramics with only one composition but fluctuating perfectly between two crystalline structures. In this ideal case, the system free energy is maximum (Budimir *et al.*, 2006). As both phases are piezoelectric, an exchange term appears and the resulting properties are then exacerbated.

Many authors have attempted to define as closely as possible this morphotropic transformation zone (Guarany *et al.*, 2007; Mabud, 1980; Noheda *et al.*, 2000a,b; Ragini *et al.*, 2002). However, it is really difficult to obtain a perfect chemical homogeneity in zirconium and titanium. The slightest heterogeneity results in the shifting of the zirconium enriched zone in the rhombohedral structure and conversely of the depleted zone in the tetragonal structure.

The interest of the morphotropic zone was highlighted by Jaffe *et al.* as part of the study of the piezoelectric properties according to the chemical composition x of the PZT (Jaffe *et al.*, 1971). It is in this area that maximum piezoelectric activity is observed. The dielectric constant, the electromechanical coupling factors and the piezoelectric constants present their optimal values around $x = 0.54$.

Following Jaffe’s work, it has been shown that for well synthesized morphotropic PZT compositions, the material exhibited another stable phase (Guarany *et al.*, 2007; Noheda *et al.*, 2000a). A slight monoclinic domain appears between the rhombohedral and tetragonal zones. This domain acts as a crystallographic intermediary between the two previous zones. The updated zone of the phase diagram is presented in Fig. 7.

Synthesis Routes

In most of the applications, PZT materials are used in the form of bulk polycrystalline ceramics. The elaboration of theses ceramics is based on two fundamentals stages: the powder synthesis and the material densification. The choice of the powder fabrication

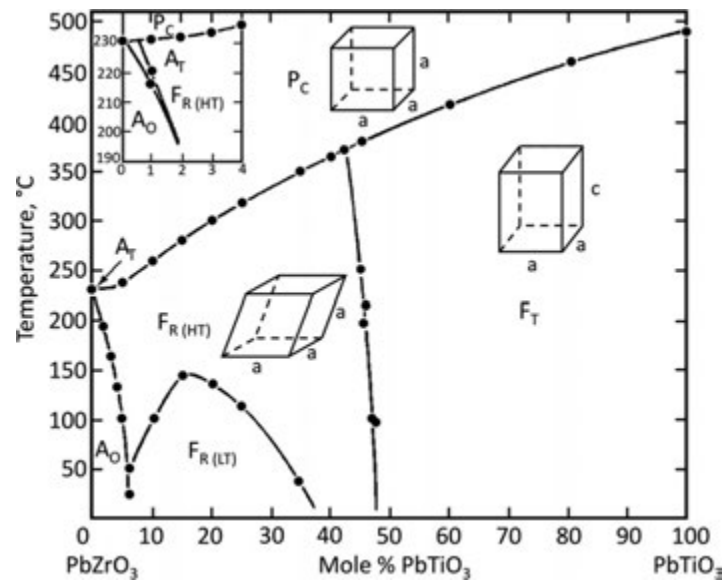


Fig. 6 Phase diagram of the PZT solid solutions. According to Jaffe *et al.*, 1971. A_0 antiferroelectric orthorhombic; A_T antiferroelectric tetragonal; $F_{R(LT)}$ ferroelectric rhombohedral low temperature; $F_{R(HT)}$ ferroelectric rhombohedral high temperature; F_T ferroelectric tetragonal; P_C paraelectric cubic.

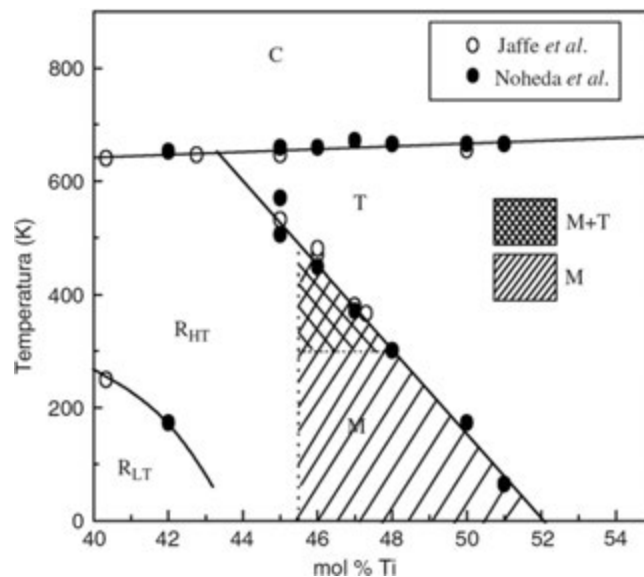


Fig. 7 Updated PZT's phase diagram around MPB. T tetragonal; M monoclinic; R_{HT} rhombohedral high temperature; R_{LT} rhombohedral low temperature; C cubic. Reproduced from: Guarany, C.A., Araújo, E.B., Silva, P.R.J., Saitovitch, H., 2007. Hyperfine interaction measurements on ceramics: PZT revisited *Physica B: Condensed Matter, Proceedings of the International Workshop "35th Anniversary of Hyperfine Interactions at La Plata" and "Humboldt Kolleg on Solid State Physics"* 389 2007 130 134. doi:[10.1016/j.physb.2006.07.039](https://doi.org/10.1016/j.physb.2006.07.039).

process is made on the basis of speed and simplicity of production and on the minimization of manufacturing costs. The most used current process is the solid state reaction of oxide precursors (Matsuo and Sasaki, 1965). Powders obtained with this synthesis route are usually sintered at temperatures around 1200°C. Other synthesis routes have been studied, especially to reduce the sintering temperature. Some examples are given from the following studies.

Texier *et al.* (2001) synthesized an Mn, Sb, W, Ni doped PZT by hydrothermal route. Dense and chemically homogeneous bulk ceramics were obtained at low temperature (950–1000°C) with comparable dielectric and piezoelectric properties ($k_p = 0.51$, $\epsilon_r = 1115$ and $d_{33} = 310$ pC/N) as for ceramics prepared by conventional way.

Nano-size powders of $Pb(Zr_{0.53}Ti_{0.47})O_3$ were fabricated by a milling coprecipitation method by Kim *et al.* (2004). Ceramics dense at 98% presenting high electromechanical coupling factor ($K_p = 0.58$) were obtained for a low sintering temperature of 900°C.

Sahoo *et al.* (2006) prepared $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ($0.48 \leq x \leq 0.54$) doped with La or Nd by wet chemical route using water soluble precursors. Sintering was performed at 1250°C and properties similar to undoped PZT were obtained for Lanthanum doped samples ($d_{33} = 273$ pC/N and $\epsilon_r = 1000$).

A sol gel auto-combustion method was used by Montanari *et al.* (2005) to synthesize highly homogeneous niobium doped PZT materials presenting nano-sized crystallites. Sintering was performed at 1100°C . Obtained piezoelectric constants were higher or comparable with those of samples obtained via traditional mixed oxide method.

Piezoelectric Properties of the PZT

At high temperature, PZT crystallizes in a cubic structure. A polarization cannot exist at this temperature. Approaching the Curie transition temperature, an elongation of the cubic lattice is observed. The symmetry then becomes rhombohedral (elongation along A3 axis) or tetragonal (elongation along A4 axis) (Fig. 4) and the PZT ceramics can be polarized.

The PZT Curie temperature varies from 230 up to 400°C depending on the composition (Wang *et al.*, 2015; Zhang *et al.*, 2005). Jaffe *et al.* (1971, 1954) showed that in the PbZrO_3 - PbTiO_3 phase diagram, some compositions present high piezoelectric properties. In particular, the dielectric constant and the electromechanical coupling factor reach their maximal values, respectively 750 and 0.40 for the morphotropic composition $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$. The mechanical quality factor has a maximum value of about 1200 for the composition $\text{Pb}(\text{Zr}_{0.48}\text{Ti}_{0.52})\text{O}_3$.

Piezoelectric properties of PZT ceramics can be modified by many factors:

- (1) The structure and the composition. The use of dopants can increase or decrease targeted properties.
- (2) External factors as mechanical strains (Algueró *et al.*, 2001), electric fields or temperature.
- (3) The lack of homogeneity and manufacturing reliability. Problems during ceramics manufacturing like lead volatilization or the appearance of parasitic secondary phases can change the properties of the ceramics (Eyraud *et al.*, 1981a; Guha *et al.*, 1988).
- (4) The aging and fatigue of the materials after polarization (Genenko *et al.*, 2015). Aging describes the gradual changes in material properties over time under external equilibrium conditions. Fatigue is characterized by a gradual change of the properties during service.
- (5) Porosity. Ferroelectric ceramics such as PZT with too low densities are hardly polarizable; most of the time, electrical breakdown occurs during the poling step leading to the destruction of the material (Jean *et al.*, 2018).

It is therefore important to control the ceramic process in order to obtain materials presenting optimized electrical properties.

PZT Properties Modification by Doping

Properties of lead titanate zirconate solid solutions can be modified by adding a small amount (1%–2% in mass) of elements called dopants. These ions substitute the Pb^{2+} ions (A site doping) or the Zr^{4+} and Ti^{4+} ions (B site doping). The valence of the dopant may be the same or different from that of the substituted ion. Different kinds of doping are possible (Jaffe *et al.*, 1971):

- (1) Isovalent substitutions: the dopant substitute ions with the same valence and almost the same size.
- (2) Substitutions with acceptor dopants: the dopant has a lower valence than the substituted ion.
- (3) Substitutions with donor dopants: the dopant has a higher valence than the substituted ion.
- (4) Substitutions with valence compensation: solid solutions are added in the system.
- (5) Multiple-valency additives: dopants with different valences but almost the same sizes are added in the system.

The dopants have different impact on the piezoelectric properties of the PZT ceramics. In this part, we will endeavor to present the bibliographic results as clearly as possible. Indeed, generally, only the intrinsic effect (structural) of the dopant is argued by the authors. In the absence of clear indications on the microstructure, extrinsic effects cannot be presented.

Most of time, studies on PZT doping are based on a “trial and error” strategy. One or more dopants are inserted into the material during the powder synthesis and/or before the sintering step and the properties are measured on the obtained ceramics. However, it is impossible to observe exactly if the dopant inserts itself in the structure, volatilize in some part or remains partially at grain boundaries. Furthermore, it is also complicated to dissociate the intrinsic effects of the dopant (insertion in the solid solution of PZT) from some extrinsic effect (i.e., modification of densification mechanisms and so on grain coarsening of the ceramic). Added to this is the impact of synthesis and sintering routes. For example, Courtois *et al.* (2006) showed that the addition of nickel had a positive impact on the mechanical quality factor during sintering of solid state synthesized powders, but a negative effect when the powder was hydrothermally synthesized.

Thus, a dopant can have an impact on the sintering, on the microstructure of the material and therefore on its properties. It can also have an intrinsic effect on the electrical properties of the PZT ceramic. All these contributions may affect final piezoelectric properties. It is then difficult for authors to clearly discriminate the different contributions of dopants for a better understanding of their effects on piezoelectric properties.

Isovalent doping

The most common isovalent substitutions are Sr^{2+} , Ca^{2+} and Ba^{2+} on the A site of the perovskite (Jaffe *et al.*, 1971). These ions have an important impact on the Curie Temperature (T_c decreases with the addition of strontium) and on the phases existence (enlargement of the quadratic phase with the addition of barium and strontium) leading to high piezoelectric properties (Kulcsar, 1959a).

Eyraud *et al.* (1981b) show important effects for addition of two dopants. Indeed, they report an increase of the electromechanical coupling factor k for a double isovalent substitution on the A site (12 at% Sr and 5 at% Ba) with conservation of the Goldschmidt factor and an increased atomic packing factor. They don't observe a noticeable decrease of the remnant polarization P_r and the mechanical quality factor Q . The improvement of the properties is attributed to the mobility of the ions on the A site.

This kind of doping is carried out in cases where relatively high piezoelectric properties are required around room temperature and no high temperature application is needed. This is typically done for materials which are used in actuator applications (Holterman and Groen, 2012).

Acceptor doping

In this case, doping is done with elements having lower valences than the substituted ions. This leads to the formation of oxygen vacancies for charge compensation and to the contraction of the crystal lattice (Jaffe *et al.*, 1971). Oxygen ions form a continuous network in the PZT cell and ions-vacancies displacement are facilitated. This acceptor-vacancy dipole is less stable than the donor-vacancy dipole. Once oriented, these dipoles will form a network stabilizing the domains structure (Moulson and Herbert, 2003). Due to the inhibition of the movements of the domain walls, dielectric constant ϵ and dielectric losses $\tan\delta$ decrease while mechanical quality factor Q_m and coercive field E_c increase. This leads to a slow-down of aging and to materials that are more difficult to polarize and depolarize. This is typical of so-called hard ceramics. The most used electron acceptor dopants are K^+ on the A site of the perovskite and Sc^{3+} , Mg^{2+} , Fe^{3+} , Co^{3+} and Cu^{2+} for the B site of the perovskite.

Moure *et al.* (1992) studied the influence of donor or acceptor dopants addition on a morphotropic PZT. More precisely, they focused on the addition of 1 at% of Fe^{3+} on the B site of the perovskite. The obtained material reaches a relative density of 98% after sintering at 1150°C for 2 h, despite a mass loss. Moure *et al.* (1992) attributed this mass loss to the evaporation of a part of the PbO. The microstructure is fine and homogeneous with a grain size around 1 μm and does not change with the increase of the sintering time. According to the authors, the control of the microstructure is due to oxygen vacancies formed as a consequence of the acceptor doping with iron. These vacancies limit the migration of the grains boundaries and thus, the grain growth. These ceramics present low dielectric losses (0.25%) and a high mechanical quality factor ($Q_m = 650$). According to Moure *et al.*, the improvement of the piezoelectric properties is linked to the diminution of the PbO present in the grain boundaries.

Fernandez *et al.* studied the impact of the iron addition on a niobium doped PZT (Fernández *et al.*, 1998). Various sintering conditions were tested with temperatures from 1070 to 1190°C and times from 1 to 8 h. The best properties were obtained for sintering at 1150°C during 2 h. According to the authors, at this temperature, the iron gets in the PZT network and plays its acceptor dopant role. Moreover, in this case, the material properties seem independent from the grains size. Indeed, the microstructure does not evolve neither with the temperature nor with the time but the electrical properties reach their highest values for sintering at 1150°C during 2 h.

Donor doping

The addition of donor dopants leads to the formation of cationic vacancies. Contrary to the oxygen vacancies, cationic vacancies present a scarce mobility. This can be explained by the anionic organization in the perovskite structure. The cations and cationic vacancies are separated by an oxygen ion which represents a considerable energetic barrier to cross to allow the cation-cationic vacancy exchange. Because of this low mobility, the donor-cationic vacancy dipole presents a stable orientation and its initial state is not affected by the spontaneous polarization or the applied field (Moulson and Herbert, 2003). Thus, this dipole does not participate in the electric response of the material.

On the other hand, this kind of doping causes a diminution of the concentration of oxygen vacancies. This leads to a decrease of the domain walls pinning phenomenon (Gerson, 1960). These domain walls will be more mobile inducing an increase of the dielectric constant ϵ and dielectric losses $\tan\delta$ and a decrease of the mechanical quality factor Q_m and the coercive field E_c . This leads to an acceleration of the aging and to materials easier to polarize and depolarize. This is typical of so-called soft ceramics (Jaffe *et al.*, 1971). The most used donor dopants are Bi^{3+} , La^{3+} and Nd^{3+} for the A site and Nb^{5+} , Sb^{5+} and W^{6+} for the B site of the perovskite.

Kulcsar works focused on dopants addition with +3 and +5 valences into PZT ceramics (Kulcsar, 1959b). He studied in particular doping with lanthanum and neodymium on A site and doping with niobium and thallium on B site of the perovskite. Kulcsar observed an increase of dielectric losses and electromechanical coupling factor but also an important increase of the dielectric constant with the addition of 1 wt% of lanthanum or neodymium. The author also observes a brutal decrease of the mechanical quality factor Q_m passing from 400 to 70. In the case of +5 valence addition, niobium has the same effect as lanthanum. In this case, optimal properties are obtained for an addition of 1 wt% of niobium. The combination of 0.5 wt% niobium and 0.5 wt% lanthanum provides material with the highest dielectric constant and electromechanical coupling factor.

Moure *et al.* studied the impact of a 4 at% Sb^{3+} doping on A site of a morphotropic PZT (Moure *et al.*, 1992). Mass losses are moderate and materials reach a relative density of 97%. The obtained materials present high electromechanical coupling factor and piezoelectric constant values ($k_p = 0.55$ and $d_{33} = 270 \text{ pC/N}$) but low mechanical quality factor ($Q_m = 100$).

Substitutions with valence compensation

The compounds used for the valence compensated substitution are of the perovskite type and form a solid solution with the PZT (Uchino, 2012). Several compounds have been studied such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, $\text{Pb}(\text{Nb}_{1/2}\text{Fe}_{1/2})\text{O}_3$, $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$, $\text{Pb}(\text{Co}_{1/2}\text{W}_{1/2})\text{O}_3$, $\text{Pb}(\text{Mn}_{1/3}\text{Sb}_{2/3})\text{O}_3$, $\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, $\text{Pb}(\text{Sb}_{1/2}\text{Nb}_{1/2})\text{O}_3$, $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$, $\text{Pb}(\text{Y}_{2/3}\text{W}_{1/3})\text{O}_3$ or $\text{Ba}(\text{Cu}_{1/2}\text{W}_{1/2})\text{O}_3$ (Dong *et al.*, 1993; Moon and Jang, 1993; Murakami *et al.*, 1995; Tapaonoi *et al.*, 1994; Uchino, 2012; Yoon *et al.*, 1997) with different effects on PZT properties.

Several results have been observed with this kind of dopants. Each solid solution has its own effect on the material. Moreover, the doping with a solid solution does not only influence the electrical properties of the material but also the sintering conditions.

Doping with $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (Moon and Jang, 1993), $\text{Ba}(\text{Cu}_{1/2}\text{W}_{1/2})\text{O}_3$ and BiFeO_3 (Dong *et al.*, 1993; Murakami *et al.*, 1995) leads to a decrease of the sintering temperature. Hence, these compounds play the role of dopant in the PZT structure but also a role of sintering aid during a part or the totality of the densification cycle. This sintering aids can be found in two forms in the sintered materials: either they enter in substitution in the PZT network and play a role as dopant or they stay in the grain boundaries. In this second case, they generally form an amorphous non ferroelectric phase (Murakami *et al.*, 1995). This secondary phase has an impact on the electrical properties and most often a drop in properties is observed with the persistence of the secondary phase.

The doping by adding a solid solution into the PZT remains a complex method. The valence of the dopant has to be taken into account to favor soft or hard piezoelectric properties. Moreover, all the ceramic process has to be adapted to control the microstructure and avoid electrical properties degradation. However, the diversity of the possible composition is an advantage that allows for a broad scanning of applications based on the exacerbated properties. For example, Moon and Jang report an increase of the dielectric constant ϵ while the mechanical quality factor Q decreases for PZT doped with $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and sintered under oxidizing atmosphere (Moon and Jang, 1993). This corresponds to the behavior of hard PZT ceramic. Dong *et al.* (1993) on the other side, observed an improvement of the mechanical quality factor Q_m while the dielectric losses $\tan\delta$ decrease for a PZT doped with $\text{Ba}(\text{Cu}_{1/2}\text{W}_{1/2})\text{O}_3$ and BiFeO_3 . This is typical from soft PZT ceramics.

Multiple-valency additives

In this case, elements with multiple valence are used as dopants. These elements can play a role of donor or acceptor according to their oxidation state (Liang and Wu, 1993). The most used elements are the chromium and the manganese.

According to Jaffe *et al.* (1971) the insertion of chromium into the PZT structure causes an increase of the mechanical quality factor Q_m , a decrease of the electromechanical coupling factor and the aging of the material. The ionic radius of chromium suggests its insertion into the B site of the perovskite. According to its oxidation state, +3 or +6, it will have an acceptor or a donor effect respectively. Chromium doped PZT ceramics are widely used as filters due to their high mechanical quality factor Q_m and the stability of the resonance and antiresonance frequencies with temperature (Uchida and Ikeda, 1967).

The PZT doping with manganese has been widely studied (Banno and Tsunooka, 1967; Cheon and Lee, 1999; Hase *et al.*, 1993; Hennings and Pomplun, 1974; Park *et al.*, 1995; Peláiz Barranco *et al.*, 2001). This dopant is known to increase the electro-mechanical coupling factor. Manganese is too small to enter in the A-site of the perovskite and therefore it fits in the B-site. In their works, Henning and Pomplun show the presence of Mn^{2+} and Mn^{3+} ions on A-site for low PbO sintering atmosphere (Hennings and Pomplun, 1974). Hase *et al.* (1993) report that for a sintering temperature below 1100°C, the manganese contributes with PbO to the formation of a secondary phase at the grain boundaries. Above 1100°C, this secondary phase disappears and the manganese is supposed to enter the PZT network. For this temperature, they also notice a strong increase of the electromechanical coupling factor.

Manganese has also been studied simultaneously with other dopants. Banno and Tsunooka studied the effect of tungsten (Banno and Tsunooka, 1967). This element contributes to the formation of soft PZT ceramics (low mechanical quality factor and low coercive field). When a second dopant, MnO_2 , is added in the tungsten doped PZT, a strong increase of the mechanical quality factor and the coercive field is observed; the ceramics become hard. Furthermore, the tungsten manganese co-doped ceramics present poor aging of the piezoelectric properties and the dielectric constant is not affected.

The effect of manganese as co-dopant with niobium has also been studied by Park *et al.* (1995). The results are the same as those of Banno and Tsunooka with a transition from soft to hard ceramic behavior. PZT doped only with niobium exhibits the behavior of a soft ceramic. When manganese is added, the equivalent resistance for the resonance frequency decreases. This phenomenon is due to a decrease of the mechanical losses which impacts the piezoelectric properties and leads to an improvement in the mechanical quality factor.

In the same way, Peláiz Barranco *et al.* (2001) observed a modification of the properties of $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.44}(\text{Cu}_{0.25}\text{Nb}_{0.75})_{0.06})\text{O}_3$ when manganese is added. They attribute the strong increase of the mechanical quality factor to the manganese ion-oxygen vacancy dipole which pins the domain walls and induces a limitation of the vibrations and thus of mechanical losses.

Cheon and Lee, for their part, studied differences between doping with chromium, manganese and chromium-manganese co-doping of $(\text{Pb}_{0.9}\text{Sr}_{0.1})(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (PSZT) (Cheon and Lee, 1999). Doping of PSZT with chromium hardens the properties, the dielectric constant and the electromechanical coupling factor decrease while the mechanical quality factor increases. Doping of PSZT with manganese leads to a decrease of the grains size and improves the dielectric constant. Finally, the properties of the PSZT co-doped with chromium and manganese are intermediate: the piezoelectric properties are close to those of Cr-PSZT and the microstructure is those of the Mn-PSZT.

Microstructure – Properties Relations

The influence of dopants on electrical properties and microstructure has been widely studied. The microstructure-properties interaction is less reported. However, relationships between microstructure and electrical properties of PZT ceramics have been studied by some research teams. Most of time, literature deals with complex PZT compositions involving several dopants.

Webster and Weston's works focused on properties of various undoped PZT ($0.495 < x < 0.559$) (Webster and Weston, 1968). They studied several sintering profiles in order to vary the final microstructure of the ceramics. They observed that the dielectric constant and the dielectric losses values decrease with the increase of the grains size, with a stabilization for grain size of 5 μm . The piezoelectric properties increase with the grain growth. A step is observed again from 5 μm for the electro-mechanical coupling factor and the remnant polarization. On the other hand, the evolution of the electromechanical quality factor seems to be linked to the composition of the ceramic. Webster and Weston explain these evolutions by the different ferroelectric domains organizations with the different microstructures. Indeed, they highlighted by SEM observations, that in the larger-sized grains ceramics the domain size is of the same order of magnitude as the grain size in the finest-grained ceramics. So, the reorientation of the domains in the ceramics with fine microstructure is more difficult. This observation allows to explain the decrease of the polarization in fine-grained materials that leads to a decrease of the piezoelectric activity. According to Webster and Weston, the decrease of the dielectric constant with the increase of the grains size is linked to the formation of internal stresses in the material when passing the Curie temperature and the paraelectric-ferroelectric phase transformation. In the case of large grains, these stresses are relaxed by the formation of 90° ferroelectric domains but, for the fine-grained materials this relaxation is almost impossible. These internal stresses participate at the extrinsic part of the dielectric constant, which results in an increase of its value. The evolution of the dielectric losses is also due to these stresses. During the charge cycling, a stress/deformation hysteresis is added to the electric field/polarization hysteresis and contributes to the dielectric losses.

The ternary system $(1-x) \text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3 - x \text{Pb}(\text{Sb}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PZT-PSN) was studied by Tapaonoi *et al.* (1994) for a substitution rate x included between 0 and 0.08. They observed that replacing PZT with PSN had no influence on the density of the ceramic pieces. On the other hand, they observed a strong decrease in grain size (5 μm to 1.9 μm) up to 3 mol% of PSN, then a stabilization of the grain size for greater substitution. The authors studied the effect of this microstructural change on the dielectric and piezoelectric properties of the ceramics. The Curie temperature and the electromechanical coupling factor k_p decrease with the PSN doping while the mechanical quality factor is improved. From these results, the authors defined an optimal composition containing 3 mol% of PSN. The grain size of the ceramics was then decreased up to 0.6–0.7 μm for this composition by grinding the powder. The study of the piezoelectric properties shows that the electromechanical coupling factor is not impacted by the decrease of the grain size. However, the piezoelectric constant d_{33} and the dielectric constant strongly decrease with the decrease of the grain size. The authors conclude that there is a grain size limit of 0.6 μm below which the decrease of the piezoelectric properties is catastrophic for the ceramics.

Randall *et al.* (1998) works focused on the evolution of the electrical properties of PZT ceramics and niobium doped PZT ceramics. Different sintering routes and conditions were applied in order to obtain grain sizes varying from 0.1 to 10 μm . The authors observed a decrease of the dielectric constant with the increase of the grains size. The remnant and maximum polarization increase with the grains size while the coercive field decrease. Randall *et al.* also observed the evolution of the lattice parameters in 0.4 mol% niobium doped PZT ceramics as a function of the grains size. The lattice distortion along the tetragonal c -axis is greatly reduced when the grain size is reduced to 1.0 μm , while the a -axis dimension is not as strongly affected. So, the crystal tetragonality, c/a , decreases as the grain size decreases. The authors attribute this result to an increase of internal stresses in materials showing a fine microstructure during the paraelectric-ferroelectric phase transition. The spontaneous unit-cell distortion is clamped in the fine-grained materials, which reduces the intrinsic polarization and also increases the internal stresses in the ceramic. The observation of the samples by transmission electron microscopy highlights the difference of configuration of ferroelectric domains with the grains size. In ceramics with grains size higher than 1 μm , different configuration of the domain in each grain exist. On the contrary, in the ceramics with submicrometer grain size, the domain configuration is unique: grains are simply striated, with the domains pinned to the grain boundary. This grain boundary/domains walls configuration complicates the domains reorientation and severely constrains the movement of domain walls. This result leads to the following consequences:

- (1) The reduction of the alignment of the ferroelectric domains leads to the reduction of the remanent polarization.
- (2) The decrease in the mobility of the domain walls leads to a reduction of the dielectric and piezoelectric coefficients.

These works are confirmed by a study of Arlt which particularly studied the influence of the microstructure on the organization of the ferroelectric domains and the properties of ferroelectric ceramics (Arlt, 1990). According to him, at the end of the sintering, during the temperature decrease, when passing the Curie temperature, each grain will deform spontaneously but will also be constrained by its neighbors. The grains deformation will be blocked and compensated by strong internal stresses. Compression stresses appear in the direction of expansion of the grains and tension stresses appear in the grains compaction direction. These internal stresses can be relaxed in the PZT by splitting the grains into ferroelectric domains. The size of these domains depends on the grain sizes according to the following relation:

$$d \sim \sqrt{g}$$

with d the domain size and g the grain size.

Arlt defines three domains arrangement modes in the ferroelectric ceramics according the grain size of the material. In case of coarse-grained ceramics, the arrangement of ferroelectric domains in a 3D network is possible. The internal stresses are insignificant. In fine-grained ceramics, the domains have a lamellar configuration and internal stresses are important. In very fine-grained ceramics (grain sizes of the same order of magnitude as the domains), the creation of domains is impossible due to too high internal stresses.

The properties of the material directly depend on its microstructural organization. Since the polarization is different on each side of the walls, the displacement of these walls under an electric field modifies the polarization. Therefore, the domain walls contribute to the different electrical properties of PZT ceramics. If the domain walls are pinned to the grain boundary or under stresses their displacement will decrease and thus, the material polarization and its properties will decrease too.

Conclusions on the Influence of Dopants and Microstructure on Electrical Properties of PZT

The electrical properties of ceramics are therefore sensitive to the chemical composition of the solid solution, to the temperature, but also to other factors. The substitutions or doping in the PZT lattice and the microstructure of the ceramic are thus essential factors.

The doping of PZT ceramics is complex. Theoretically, two main types of substitution exist and each have specific effects on the electrical properties of PZT ceramics. Donor doping generates dipoles formed by cationic vacancies and substituent ions. These dipoles have a stable orientation. They will not affect the mobility of the domain walls. The acceptor doping generates oxygen vacancies in the PZT lattice. Due to their mobility, the polarization of the "anionic vacancy-substituent ion" dipole can be changed under the influence of an external electric field. These dipoles, once oriented, will form a network stabilizing the structure of the domains resulting in the inhibition of the movements of the domain walls.

Thus, in the case of these dopants, it is the mobility of the domain walls which is the factor influencing the properties of PZT ceramics. When the mobility of the domain walls is facilitated, an increase of the dielectric constant and losses is observed while the mechanical quality factor and the coercive field are weak. The properties are reversed in the case of acceptor doping with pinned domain walls.

In reality, few of these simple mono dopants are used. The choice is rather on the use of codoping or addition of other solid solutions of perovskite structure which can form a solid solution with PZT. The preferential localization of these dopants in the PZT lattice or at the grain boundaries of the ceramic may cause a differentiation of the effects of these dopants leading to 3 possibilities. In the first case, the elements enter the PZT network and contribute to the electrical properties of the material. In the second case, the elements influence the ceramic sintering mechanisms and play the simple and unique role of sintering aids. In the third case, the integration of the dopants in the PZT lattice is partial. Thus, the dopants can be found in two forms in the sintered material. This can have a negative or a positive effect. In the case of a negative effect, the fraction of dopants remaining at the grain boundary contributes to the formation of non-ferroelectric secondary phases degrading the electrical properties of the ceramic. In the case of a positive effect, dopants can diffuse into the grains during sintering and then play the dual role of sintering aid and dopant leading to the non-precipitation of a secondary phase.

The use of solid solutions or co-doping is interesting but remains complex. It is not possible to define a precise effect of these doping. Valencies of dopants have to be taken into account in order to evaluate their influence on the electrical properties. The location of dopants is also an important factor. If they remain at the grain boundaries they will modify all the densification process, affecting the final microstructure and properties. Thus, all the ceramic process can be affected by the localization of dopants. Microstructural observations are therefore necessary for any possible conclusion on the role of each dopant.

The microstructure of a PZT ceramic is a factor controlling the domain structuring and the state of internal stresses when passing the Curie temperature. Thus, it greatly influences the dielectric and piezoelectric properties of the ceramic.

For ceramics with coarse microstructures, the organization of the domains into a 3D network is easy and domains are mobile. The stresses in the material are largely relaxed by a rearrangement of the ferroelectric domains. The polarization of the material is then facilitated and the piezoelectric activity increases. Thus, the piezoelectric properties are favored for coarse-grained ceramics. Internal stresses participate in the extrinsic part of the dielectric constant and in dielectric losses and for these coarse materials are less. It is also observed that in these coarse-grained ceramics dielectric losses and dielectric constant are low.

For ceramics with fine microstructures, the configuration of the ferroelectric domains becomes lamellar. Only 180° domains are present and the domain walls are pinned to the grain boundaries. It even seems that for a critical micron or submicron size, according to the authors, the creation of ferroelectric domains is impossible. The state of stress is high because the material could not relax them by an adequate domain structure. The polarization of the material is more difficult and the piezoelectric properties decrease. On the other hand, the contribution of the stresses to the dielectric properties being more important, the dielectric constant and the dielectric losses increase.

Conclusion

The lead zirconate titanate is therefore a material widely used in current technologies, both in the civilian field and in the military and medical fields. The main advantage of this material lies in the great modularity of its properties by the simple modification of

its composition. This particularity explains the extent of the field of application of this material. Regarding the industrial aspect, this material is widely exploited and the manufacturing processes are controlled. Regarding the aspect of research on this material, most of the phenomena have been interpreted, whether in terms of the dopants contribution or the relationships between the microstructure and the properties. Different synthesis and sintering routes have been investigated. Some questions remain about the exact nature of the morphotropic phase boundary. The situation would be idyllic if the PZT did not have the disadvantage of being largely composed of lead. As the toxicity of this element is no longer to be proven, research has been moving for the past twenty years towards alternative solutions free of lead. However, even though it is now accepted that PZT cannot be replaced by just one material, but by several depending on the targeted applications, none of the proposed candidates succeeded in achieving the performance level of PZTs. This material therefore remains the only one to be exploited at the industrial level in devices requiring piezoelectric components.

References

- Algueró, M., Cheng, B.L., Guieu, F., *et al.*, 2001. Degradation of the d_{33} piezoelectric coefficient for PZT ceramics under static and cyclic compressive loading. *Journal of the European Ceramic Society* 21, 1437–1440. [https://doi.org/10.1016/S0955-2219\(01\)00036-X](https://doi.org/10.1016/S0955-2219(01)00036-X).
- Arlt, G., 1990. The influence of microstructure on the properties of ferroelectric ceramics. *Ferroelectrics* 104, 217–227. <https://doi.org/10.1080/00150199008223825>.
- Banno, H., Tsunooka, T., 1967. Piezoelectric properties and temperature dependences of resonant frequency of $\text{WO}_3\text{-MnO}_2$ -modified ceramics of $\text{Pb}(\text{Zr-Ti})\text{O}_3$. *Japanese Journal of Applied Physics* 6.954. <https://doi.org/10.1143/JJAP.6.954>.
- Budimir, M., Damjanovic, D., Setter, N., 2006. Piezoelectric response and free-energy instability in the perovskite crystals BaTiO_3 , PbTiO_3 , and $\text{Pb}(\text{Zr,Ti})\text{O}_3$. *Physics Review B* 73.174106. <https://doi.org/10.1103/PhysRevB.73.174106>.
- Cheon, C.I., Lee, H.G., 1999. The piezoelectric properties and the stability of the resonant frequency in Mn–Cr Co-doped PSZT ceramics. *Journal of Materials Science: Materials in Electronics* 10, 81–84. <https://doi.org/10.1023/A:1008935011249>.
- Courtois, C., Crampon, J., Champagne, P., *et al.*, 2006. STEM-X-EDS analysis of morphotropic PZT ceramics: Analysis of Zr/Ti + Zr values fluctuation depending on microstructure and synthesis route of powders. *Ceramics International* 32, 767–773. <https://doi.org/10.1016/j.ceramint.2005.05.019>.
- Craciun, F., 2020. Dielectric, ferroelectric, antiferroelectric, relaxor, piezoelectric ceramics: Definitions and main applications. In *Reference Module in Materials Science and Materials Engineering*. Elsevier. <https://doi.org/10.1016/B978-0-12-803581-8.12064-8>.
- Dong, D., Xiong, M., Murakami, K., Kaneko, S., 1993. Lowering of sintering temperature of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ ceramics by the addition of BiFeO_3 and $\text{Ba}(\text{Cu}_{0.5}\text{W}_{0.5})\text{O}_3$. *Ferroelectrics* 145, 125–133. <https://doi.org/10.1080/00150199308222441>.
- Eyraud, L., Eyraud, P., Gonnard, P., Troccaz, M., 1981a. Influence of the initial lead content on the properties of doped pzt ceramics prepared by wet or dry methods. *Ferroelectrics* 34, 133–138. <https://doi.org/10.1080/00150198108238712>.
- Eyraud, L., Eyraud, P., Gonnard, P., Troccaz, M., 1981b. Properties improvement of P.Z.T. ceramics with multiple substituents. *Ferroelectrics* 31, 113–116. <https://doi.org/10.1080/00150198108201981>.
- Fernández, J.F., Moure, C., Villegas, M., *et al.*, 1998. Compositional fluctuations and properties of fine-grained acceptor-doped PZT ceramics. *Journal of the European Ceramic Society* 18, 1695–1705. [https://doi.org/10.1016/S0955-2219\(98\)00090-9](https://doi.org/10.1016/S0955-2219(98)00090-9).
- Genenko, Y.A., Glaum, J., Hoffmann, M.J., Albe, K., 2015. Mechanisms of aging and fatigue in ferroelectrics. *Materials Science and Engineering: B Electrical Fatigue* 192, 52–82. <https://doi.org/10.1016/j.mseb.2014.10.003>.
- Gerson, R., 1960. Variation in ferroelectric characteristics of lead zirconate titanate ceramics due to minor chemical modifications. *Journal of Applied Physics* 31, 188–194. <https://doi.org/10.1063/1.1735397>.
- Goldschmidt, V.M., 1926. Die gesetze der kristallochemie. *Naturwissenschaften* 14, 477–485. <https://doi.org/10.1007/BF01507527>.
- Guarany, C.A., Araújo, E.B., Silva, P.R.J., Saitovich, H. Hyperfine interaction measurements on ceramics: PZT revisited *Physica B: Condensed Matter, Proceedings of the International Workshop "35th Anniversary of Hyperfine Interactions at La Plata" and "Humboldt Kolleg on Solid State Physics"* 389 2007 130 134. [doi:10.1016/j.physb.2006.07.039](https://doi.org/10.1016/j.physb.2006.07.039).
- Guha, J.P., Hong, D.J., Anderson, H.U., 1988. Effect of excess PbO on the sintering characteristics and dielectric properties of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ -based ceramics. *Journal of the American Ceramic Society* 71, C-152–C-154. <https://doi.org/10.1111/j.1151-2916.1988.tb05038.x>.
- Haertling, G.H., 1999. Ferroelectric ceramics: History and technology. *Journal of the American Ceramic Society* 82, 797–818. <https://doi.org/10.1111/j.1151-2916.1999.tb01840.x>.
- Hase, K., Saitoh, M., Kittaka, T., Tomono, K., 1993. Electrical and mechanical properties of $\text{Pb}(\text{Zr, Ti})\text{O}_3$ ceramics related to Mn ion diffusion. *Japanese Journal of Applied Physics* 32.4227. <https://doi.org/10.1143/JJAP.32.4227>.
- Hennings, D., Pomplun, H., 1974. Evaluation of lattice site and valence of Mn and Fe in polycrystalline PbTiO_3 by electron spin resonance and thermogravimetry. *Journal of the American Ceramic Society* 57, 527–530. <https://doi.org/10.1111/j.1151-2916.1974.tb10802.x>.
- Holterman, J., Groen, P., 2012. An Introduction to Piezoelectric Materials and Components. *Stichting Applied Piezo*.
- Jaffe, B., Roth, R.S., Marzullo, S., 1954. Piezoelectric properties of lead zirconate-lead titanate solid-solution ceramics. *Journal of Applied Physics* 25, 809–810. <https://doi.org/10.1063/1.1721741>.
- Jaffe, B., Cook Jr, W.R., Jaffe, H., 1971. *Piezoelectric Ceramics*. London and New York: Academic Press. <https://doi.org/10.1016/B978-0-12-379550-2.X5001-7>.
- Jean, F., Schoenstein, F., Zaghioui, M., *et al.*, 2018. Composite microstructures and piezoelectric properties in tantalum substituted lead-free $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{1-x}\text{Ta}_x\text{O}_3$ ceramics. *Ceramics International* 44, 9463–9471. <https://doi.org/10.1016/j.ceramint.2018.02.163>.
- Kim, M.-H., Golovchanski, A., Lee, S.I., Park, T.-G., Song, T.K., 2004. Synthesis of $\text{Pb}(\text{Zr, Ti})\text{O}_3$ nanopowders by milling coprecipitation method. *Journal of Electroceramics* 13, 367–371. <https://doi.org/10.1007/s10832-004-5127-6>.
- Kulcsar, F., 1959a. Electromechanical properties of lead titanate zirconate ceramics with lead partially replaced by calcium or strontium. *Journal of the American Ceramic Society* 42, 49–51. <https://doi.org/10.1111/j.1151-2916.1959.tb09141.x>.
- Kulcsar, F., 1959b. Electromechanical properties of lead titanate zirconate ceramics modified with certain three- or five-valent additions. *Journal of the American Ceramic Society* 42, 343–349. <https://doi.org/10.1111/j.1151-2916.1959.tb14321.x>.
- Liang, C.-K., Wu, L., 1993. Microstructure and properties of Cr_2O_3 -doped ternary lead zirconate titanate ceramics. *Journal of the American Ceramic Society* 76, 2023–2026. <https://doi.org/10.1111/j.1151-2916.1993.tb08327.x>.
- Mabud, S.A., 1980. The morphotropic phase boundary in PZT solid solutions. *Journal of Applied Crystallography* 13, 211–216. <https://doi.org/10.1107/S0021889880011958>.
- Matsuo, Y., Sasaki, H., 1965. Formation of lead zirconate-lead titanate solid solutions. *Journal of the American Ceramic Society* 48, 289–291. <https://doi.org/10.1111/j.1151-2916.1965.tb14743.x>.
- Montanari, G., Costa, A.L., Albonetti, S., Galassi, C., 2005. Nb-doped PZT material by sol-gel combustion. *Journal Sol-Gel Science and Technology* 36, 203–211. <https://doi.org/10.1007/s10971-005-5290-5>.
- Moon, J.H., Jang, H.M., 1993. Effects of sintering atmosphere on densification behavior and piezoelectric properties of $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbZrO}_3$ ceramics. *Journal of the American Ceramic Society* 76, 549–552. <https://doi.org/10.1111/j.1151-2916.1993.tb03825.x>.

- Moulson, A.J., Herbert, J.M., 2003. *Electroceramics: Materials, Properties, Applications*. John Wiley & Sons.
- Moure, C., Villegas, M., Fernández, J.F., Durán, P., 1992. Microstructural and piezoelectric properties of fine grained PZT ceramics doped with donor and/or acceptor cations. *Ferroelectrics* 127, 113–118. <https://doi.org/10.1080/00150199208223356>.
- Murakami, K., Dong, D., Suzuki, H., Kaneko, S., 1995. Microanalysis of grain boundary on low-temperature sintered $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ ceramics with complex oxide additives. *Japanese Journal of Applied Physics* 34, 5457. <https://doi.org/10.1143/JJAP.34.5457>.
- Noheda, B., Gonzalo, J.A., Cross, L.E., *et al.*, 2000a. Tetragonal-to-monoclinic phase transition in a ferroelectric perovskite: The structure of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$. *Physics Review B* 61, 8687–8695. <https://doi.org/10.1103/PhysRevB.61.8687>.
- Noheda, B., Gonzalo, J.A., Guo, R., *et al.*, 2000b. The monoclinic phase in PZT: New light on morphotropic phase boundaries. *AIP Conference Proceedings* 535, 304–313. <https://doi.org/10.1063/1.1324468>.
- Park, J.-H., Kim, B.-K., Song, K.-H., Park, S.J., 1995. Piezoelectric properties of Nb_2O_5 doped and MnO_2 – Nb_2O_5 co-doped $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ ceramics. *Journal of Material Science: Materials in Electronics* 6, 97–101. <https://doi.org/10.1007/BF00188191>.
- Peláiz Barranco, A., Calderón Piñar, F., Pérez Martínez, O.P.M., Torres García, E., 2001. Effects of MnO_2 additive on the properties of PbZrO_3 – PbTiO_3 – $\text{PbCu}_{1/4}\text{Nb}_{3/4}\text{O}_3$ ferroelectric ceramic system. *Journal of the European Ceramic Society* 21, 523–529. [https://doi.org/10.1016/S0955-2219\(00\)00216-8](https://doi.org/10.1016/S0955-2219(00)00216-8).
- Ragini, R.R., Mishra, S.K., Pandey, D., 2002. Room temperature structure of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ around the morphotropic phase boundary region: A Rietveld study. *Journal of Applied Physics* 92, 3266–3274. <https://doi.org/10.1063/1.1483921>.
- Randall, C.A., Kim, N., Kucera, J.-P., Cao, W., Shrout, T.R., 1998. Intrinsic and extrinsic size effects in fine-grained morphotropic-phase-boundary lead zirconate titanate ceramics. *Journal of the American Ceramic Society* 81, 677–688. <https://doi.org/10.1111/j.1151-2916.1998.tb02389.x>.
- Sahoo, B., Jaleel, V.A., Panda, P.K., 2006. Development of PZT powders by wet chemical method and fabrication of multilayered stacks/actuators. *Materials Science and Engineering: B* 126, 80–85. <https://doi.org/10.1016/j.mseb.2005.09.045>.
- Shirane, G., Suzuki, K., Takeda, A., 1952. Phase transitions in solid solutions of PbZrO_3 and PbTiO_3 (II) X-ray study. *Journal of the Physical Society of Japan* 7, 12–18. <https://doi.org/10.1143/JPSJ.7.12>.
- Tapaonoi, C., Tashiro, S., Igarashi, H., 1994. Piezoelectric properties of fine-grained lead zirconate titanate ceramics modified with $\text{Pb}(\text{Sb}_{1/2}\text{Nb}_{1/2})\text{O}_3$. *Japanese Journal of Applied Physics* 33, 5336. <https://doi.org/10.1143/JJAP.33.5336>.
- Texier, N., Courtois, C., Traianidis, M., Leriche, A., 2001. Powder process influence on the characteristics of Mn,W,Sb,Ni-doped PZT. *Journal of the European Ceramic Society* 21, 1499–1502. [https://doi.org/10.1016/S0955-2219\(01\)00050-4](https://doi.org/10.1016/S0955-2219(01)00050-4).
- Uchida, N., Ikeda, T., 1967. Studies on $\text{Pb}(\text{Zr-Ti})\text{O}_3$ ceramics with addition of Cr_2O_3 . *Japanese Journal of Applied Physics* 6, 1292. <https://doi.org/10.1143/JJAP.6.1292>.
- Uchino, K., 2012. Designing with piezoelectric actuators. In: Guo, R., Nair, K.M., Wong-Ng, W., *et al.* (Eds.), *Morphotropic Phase Boundary Perovskites, High Strain Piezoelectrics, and Dielectric Ceramics*. John Wiley & Sons, Ltd, pp. 507–531. <https://doi.org/10.1002/9781118380802.ch45>.
- Wang, Y., Cai, K., Shao, T., Zhao, Q., Guo, D., 2015. Low-cost $(0.1\text{BiYbO}_3-0.9\text{PbTiO}_3)$ - $\text{PbZrO}_{3-x}\text{Mn}$ high Curie temperature piezoelectric ceramics with improved high-temperature performance. *Journal of Applied Physics* 117, 164102. <https://doi.org/10.1063/1.4918927>.
- Webster, A.H., Weston, T.B., 1968. The grain-size dependence of the electromechanical properties in lead zirconate titanate ceramics. *Canadian Ceramic Society Journal* 37, 41–44. <https://doi.org/10.4095/300148>.
- Yoon, S.-J., Moon, J.H., Kim, H.-J., 1997. Piezoelectric and mechanical properties of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ – $\text{Pb}(\text{Y}_{2/3}\text{W}_{1/3})\text{O}_3$ (PZT–PYW) ceramics. *Journal of Materials Science* 32, 779–782. <https://doi.org/10.1023/A:1018516608868>.
- Zhang, S., Xia, R., Lebrun, L., Anderson, D., Shrout, T.R., 2005. Piezoelectric materials for high power, high temperature applications. *Materials Letters* 59, 3471–3475. <https://doi.org/10.1016/j.matlet.2005.06.016>.

Lead-Free Piezoelectric Ceramics

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Introduction

Efforts to improve the environmental management of Waste of electrical and electronic equipment (WEEE), to contribute to a circular economy and to enhance resource efficiency, resulted in two directives issued by the European Commission. The WEEE Directive and the Restriction of Hazardous Substances Directive (RoHS1 (2003) and its revision, RoHS2 (2011)) aim at improving the collection, treatment and recovery of electronic components through recycling and reducing illegal export at their end-of-life. RoHS directive restricts the content of heavy metals, such as lead, mercury, and cadmium in electrical and electronic equipment and, more importantly, requires their substitution by safer alternatives. After the breakthrough 'Toyota' paper in 2004 revealed that Li-, Ta-, and Sb- modified sodium potassium niobate ceramics exhibit piezoelectric properties comparable to those of highly efficient and commercially most widespread lead-based piezoceramic $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) and could replace it in applications (Saito *et al.*, 2004), expectations for lead-removal increased. The adopted regulations have prompted the replacement of lead in several applications, however, a number of exemptions exist, including PZT-based technologies for which adequate lead-free alternatives are not yet available. Nonetheless, the growing awareness of environmental and health issues related to the toxic emissions of PbO from PZT-based products by evaporation during processing or its release due to improper waste disposal, combined with the threat of removing current exemptions, has triggered widespread scientific interest in developing novel efficient lead-free alternatives. The environmental concerns and related regulation were recently reviewed by Bell and Deubzer (2018).

Three main groups of lead-free perovskite ferroelectric oxides have henceforth been considered as environment-friendly alternatives to PZT piezoceramics. These include sodium potassium niobate ($(\text{K,Na})\text{NbO}_3$)-based solid solutions, most commonly $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN), sodium bismuth titanate ($\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$, NBT)-based piezoelectrics, and modified barium titanate (BaTiO_3 , BT), namely, barium calcium zirconate titanate ($(\text{Ba,Ca})(\text{Zr,Ti})\text{O}_3$, BCZT). While chemical modification of PZT, mainly donor or acceptor doping, results in a broad range of piezoelectric properties (Jaffe *et al.*, 1971), single lead-free material formulations do not exhibit the same property-diversity and cannot replace PZT. Even so, selected piezoelectric properties of individual lead-free materials are comparable to those of PZT and thus can be designed for specific applications (Rödel *et al.*, 2009, 2015; Koruza *et al.*, 2018a; Shibata *et al.*, 2018). For example, low density (KNN: 4.51 g cm^{-3} , about 55% of that of PZT) and good temperature stability make KNN-based materials good candidates for high-frequency imaging (Levassort *et al.*, 2011). Sodium bismuth titanate and related perovskite solid-solution derivatives, e.g., NBT-BT-KNN, show great potential for integration in applications where high electric-field-induced strain responses are required (Jo *et al.*, 2012; Liu and Tan, 2016; Tung *et al.*, 2019). BCZT has got exceptional piezoelectric properties suitable for actuation, however, these are obtained only within a narrow temperature window below its Curie temperature (below 100°C) (Liu and Ren, 2009). Another lead-free candidate of interest is the multiferroic and high-temperature piezoelectric BiFeO_3 or its modified formulations, such as BiFeO_3 -BT, however, it is not included in this review; please refer to Catalan and Scott (2009), Rojac *et al.* (2014, 2018), and Wang *et al.* (2018a).

Here, we briefly review the three main groups of lead-free perovskite piezoelectrics, KNN-, NBT-, and BT-based, we address the structure, phase relations, properties, synthesis and processing of these materials, link them to applications and discuss environmental and health concerns. We note that the topic of lead-free piezoceramics has been extensively covered in several reviews or books (Shrout and Zhang, 2007; Rödel *et al.*, 2009; Priya and Nahm, 2012; Coondoo *et al.*, 2013; Rödel *et al.*, 2015; Koruza *et al.*, 2018b; Rödel and Li, 2018; Wu, 2018).

Sodium Potassium Niobate

The discovery of ferroelectricity in NaNbO_3 and KNbO_3 dates back to 1949 (Matthias, 1949). Further investigations (Tennery and Hang, 1968; Jaffe *et al.*, 1971) showed that the ferroelectric orthorhombic KNbO_3 (*Amm*2) and antiferroelectric orthorhombic (*Pbma*) NaNbO_3 form a $(\text{K}_x\text{Na}_{1-x})\text{NbO}_3$ solid solution across the whole compositional range (Fig. 1(a)). The ferroelectric and piezoelectric properties peak in the proximity of the composition $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$, KNN (Egerton and Dillon, 1959). Early reports attributed this phenomenon to the formation of a morphotropic phase boundary (MPB) due to the coexistence of two orthorhombic phases at $x = 0.475$ (Tennery and Hang, 1968), and more recently at $x = 0.52$ (Dai *et al.*, 2009). The existence of the MPB has not been confirmed yet (Baker *et al.*, 2009; Tellier *et al.*, 2009).

The structure and phase transition sequence of pure KNN ceramics have been thoroughly investigated over the past decades (Shirane *et al.*, 1954; Tennery and Hang, 1968; Ahtee and Hewat, 1975; Tellier *et al.*, 2009). While a rhombohedral (*R3c*) polymorph (R) can be found at temperatures below -123°C , the crystallographic indexing of the room temperature phase is more complicated and thus often inconsistent in the literature as it depends on the selection of the appropriate unit cell, i.e., whether the initially proposed orthorhombic (*Amm*2) structure (O) with cell doubling or the perovskite type ABO_3 subcell with monoclinic (*Pm*) symmetry (M) are

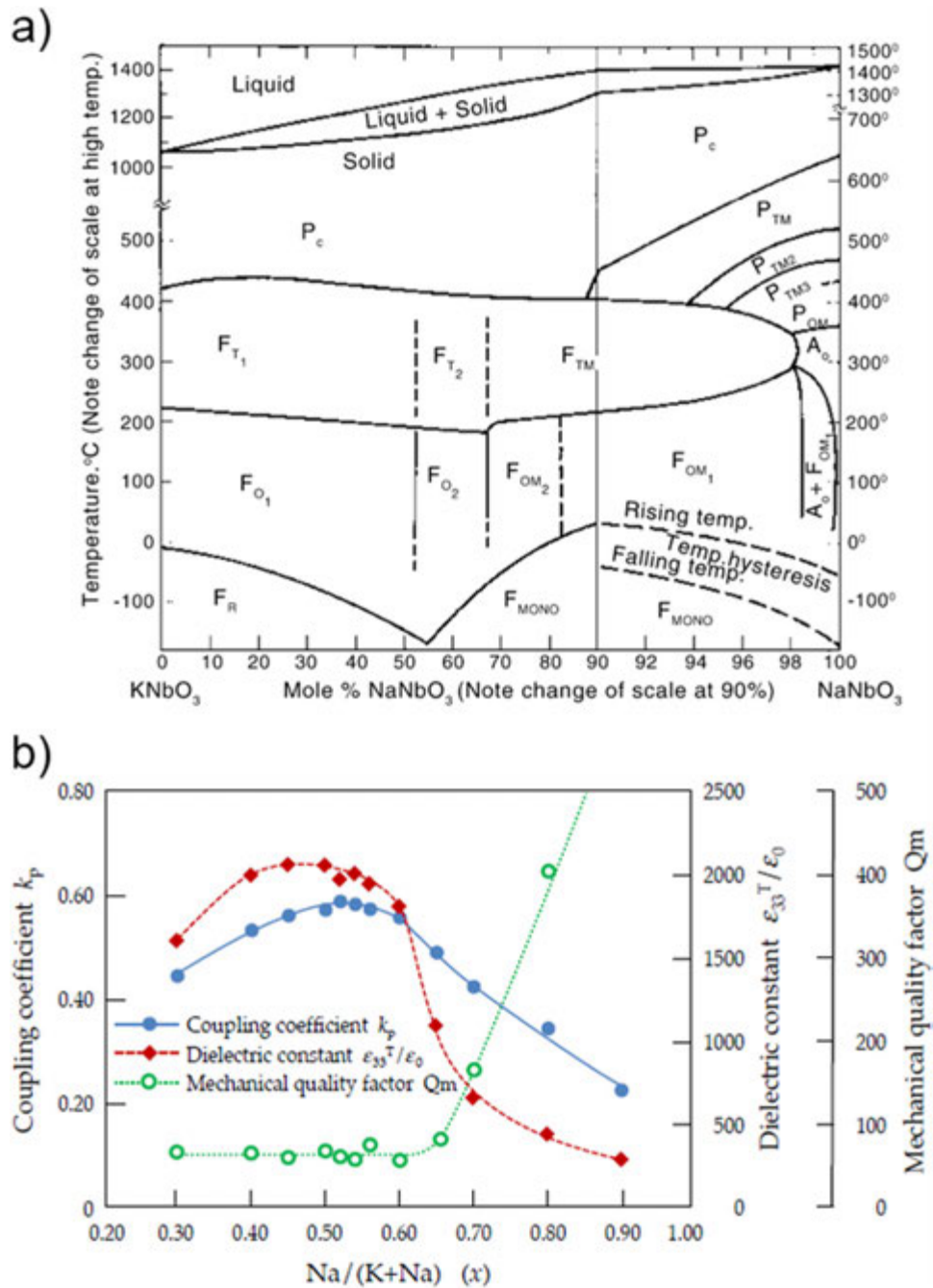


Fig. 1 (a) Pseudobinary phase diagram of the KNN solid solution. (b) Influence of the sodium/potassium ratio on the coupling coefficient, dielectric constant and mechanical quality factor of $(K_{1-x}Na_x)_{0.86}Ca_{0.04}Li_{0.02}Nb_{0.85}O_{3-6}K_{0.85}Ti_{0.85}-Nb_{1.15}O_5-BaZrO_3-Fe_2O_3-MgO$. (a) Reproduced from Jaffe, B., Cook, W.R., Jaffe, H.L., 1971. Piezoelectric ceramics. In: Roberts, J.P., Popper, P. (Eds.), Non-Metallic Solids, first ed., vol. 3. London/New York: Academic Press, with permission of Academic Press/Elsevier. (b) Reprinted from Ohbayashi, K., Matsuoka, T., Kitamura, K., *et al.*, 2017. Lead-free piezoelectric (K,Na)NbO₃-based ceramic with planar-mode coupling coefficient comparable to that of conventional lead zirconate titanate. Japanese Journal of Applied Physics 56, 061501. © 2017 The Japan Society of Applied Physics.

used. The tetragonal ($P4mm$) phase (T) is present between 200°C and ~410°C (Curie temperature, T_C) and above the T_C , pure KNN retains the cubic ($Pm\bar{3}m$) phase (C) up to its solidus temperature at 1140°C (Fig. 1(a)). Early studies of the KNN ceramics reported a piezoelectric coefficient d_{33} of ~80 pC/N (Egerton and Dillon, 1959), while values of 110–160 pC/N were achieved later with the adjustment of the Na/K ratio and by improved processing (Fukada *et al.*, 2008; Lee *et al.*, 2008; Zhang *et al.*, 2007; Zuo *et al.*, 2006), including hot-pressing (Haertling, 1967; Jaeger and Egerton, 1962) and spark-plasma sintering (Bah *et al.*, 2014; Li *et al.*, 2006).

Strategies, such as phase-boundary engineering (Wang *et al.*, 2014; Zheng *et al.*, 2017; Wang *et al.*, 2009; Xing *et al.*, 2018; Zushi *et al.*, 2013; Karaki *et al.*, 2013; Wang *et al.*, 2015a; Zhang *et al.*, 2017a), domain engineering (Yao *et al.*, 2015; Zhao *et al.*, 2018) and

additional optimization of processing (Li *et al.*, 2006; Shen *et al.*, 2017), have been employed to improve its functional properties. Among these, chemical modification aiming at the construction of phase coexistence is the most frequently used approach (Zhang and Li, 2019). KNN has been modified by doping of A- (mostly with Li, Ag, Ca, Sr, and Ba) and/or B-sites (with Ta, Sb, Ti, Zr, Mn, and other elements), by formation of solid solutions with other ABO₃ perovskites (such as LiNbO₃, LiSbO₃, LiTaO₃, CaZrO₃, CaTiO₃, BaZrO₃, BaTiO₃, (Bi,K)HfO₃, etc.) and/or by addition of transition or post-transition metal oxides (CuO, ZnO, MnO, Mn₃O₄, MnO₂, Co₂O₃, Fe₂O₃, SnO₂), and sintering aids to the stoichiometric matrix in order to overcome inherent problems related to densification and sinterability (e.g., K₄CuNb₈O₂₃, K_{5.4}Cu_{1.3}Ta₁₀O₂₉) (Matsubara *et al.*, 2004, 2005; Ando, 2012; Coondoo *et al.*, 2013; Gupta *et al.*, 2012; Hao *et al.*, 2019; Li *et al.*, 2013a; Malič *et al.*, 2015; Rödel *et al.*, 2009; Safari and Hejazi, 2012; Ohbayashi *et al.*, 2017; Xing *et al.*, 2018; Wang *et al.*, 2018b; Wu, 2018; Zheng *et al.*, 2018). It is noteworthy that the underlying origin of the property enhancement in KNN-based solid solutions (Fig. 1(b)) is not a classical MPB, as in the case of PZT, but rather a polymorphic phase transition (PPT) effect (Dai *et al.*, 2007; Zhang *et al.*, 2006), resulting from downshifting of the O/M–T and/or upshifting of R–O/M phase-transition temperatures to room temperature due to the chemical modification. Particularly, the introduction of Sb⁵⁺ proved to be a highly efficient method for raising the R–O/M transition temperature and is often used to construct a distinct phase structure featuring a R–T phase transition at room temperature, which is commonly associated with enhanced piezoelectric properties. In this regard, Sb-modified KNN solid solutions have been known for their high electromechanical performance ever since the ‘Toyota’ paper (Saito *et al.*, 2004) and are currently dominating among KNN compositions by reaching d_{33} coefficients of 570 pC/N (Xu *et al.*, 2016) and in the case of textured ceramics even 700 pC/N (Li *et al.*, 2018). The drawbacks, however, remain in Sb toxicity and reproducibility of the functional properties in such multicomponent systems. Furthermore, the issue of thermal stability of properties due to temperature sensitivity of PPT has been recently addressed with new material concepts using phase-structure engineering, e.g., constructing a diffuse phase transition over a wide temperature range (Liu *et al.*, 2018; Wang *et al.*, 2013; Yao *et al.*, 2016; Zhang *et al.*, 2017b; Wang *et al.*, 2015a; Zhang *et al.*, 2017a).

Sodium Bismuth Titanate

Discovered in the 1960s (Smolenskii *et al.*, 1960), Na_{1/2}Bi_{1/2}TiO₃ (NBT) is a relaxor ferroelectric material showing frequency dispersion of its dielectric permittivity and a broad permittivity maximum at $T_m \approx 320^\circ\text{C}$. This feature is generally assigned to the dynamic fluctuations of nanometer-scaled polar regions (Petzelt *et al.*, 2004). NBT has a complex ABO₃ perovskite structure with mixed occupancy on the A site, with Na⁺ and Bi³⁺ differing in ionic radii and charge, causing strong random elastic and electric fields on the local lattice environment (Keeble *et al.*, 2013a). In addition, the Bi³⁺ ion has 6s² lone pair electrons that tend to hybridize with the 2p orbitals of oxygen, causing strong off-centering from its cuboctahedral site (Shuvaeva *et al.*, 2005).

Different polymorphs of the perovskite structure of NBT were identified, depending on temperature, pressure and electric field (Jones and Thomas, 2002; Kreisel *et al.*, 2003). At ambient conditions NBT was long considered as rhombohedral with long-range anti-phase tilting of the oxygen octahedra and cations displaced along the $\langle 111 \rangle$ directions (R3c), although still containing platelet-like remains of the high-temperature tetragonal phase with in-phase tilted octahedra and anti-parallel cation arrangement (P4bm) (Dorset and Trolliard, 2008; Levin and Reaney, 2012; Neagu and Tai, 2017). The structure was later defined as monoclinic (Cc) on the average scale (Gorfman and Thomas, 2010; Choe *et al.*, 2018). Furthermore, displacive disorder on the bismuth-site was shown to cause heterogeneous lattice distortions, strongly related to the coherence length of the oxygen octahedral tilting (Levin and Reaney, 2012; Aksel *et al.*, 2013; Usher *et al.*, 2015; Groszewicz *et al.*, 2016).

Despite strong polarization, high relative permittivity and low dielectric losses, NBT displays rather low figures of merit for piezoelectric applications compared to lead-based materials as it exhibits a rather small piezoelectric coefficient ($d_{33} \approx 73\text{--}95$ pC/N) and large coercive field ($E_c \approx 73$ kV/cm), a moderately high depolarization temperature ($T_d \approx 200^\circ\text{C}$), and strongly hysteretic charge- and strain-responses. In order to improve its electromechanical performances, NBT is engineered by designing MPB systems. Most commonly used counterpart members are BaTiO₃ (BT) (Takenaka *et al.*, 1991) and K_{0.5}Bi_{0.5}TiO₃ (KBT), (Elkechai *et al.*, 1996), both showing an average tetragonal symmetry. Despite the general view on MPB as the coexistence of tetragonal and rhombohedral structures, local probing revealed deviations from these average symmetries (Jiang *et al.*, 2017; Datta *et al.*, 2018; Levin *et al.*, 2019). The MPB in its virgin state is rather considered as an average pseudocubic structure with nanodomain texture (i.e., at/near 0.94NBT–0.06BT (Fig. 2(a)) and 0.80NBT–0.20KBT) (Ma *et al.*, 2010; Levin *et al.*, 2013; Otoničar *et al.*, 2017). Such a metastable state with a flattened free-energy potential can easily be influenced by external fields to reach multiple stable states. Furthermore, easy switching of nanodomains and strong domain texturing cause the MPB compositions to evolve with poling into a highly oriented polar state, exhibiting enhanced polarization and strain compared to the parent members (Daniels *et al.*, 2009; Hinterstein *et al.*, 2010; Jo *et al.*, 2011; Simons *et al.*, 2011; Craciun *et al.*, 2012; Ma *et al.*, 2012; Garg *et al.*, 2013; Schader *et al.*, 2016). The obtained highly coherent long-range symmetry state at higher applied fields was assigned to the increased interatomic correlations and phase transitions, strongly influenced by the loss of Bi–O covalency (Schütz *et al.*, 2012). While the field-induced long-range order in NBT–BT is remanent, adding KNN to the NBT–BT solid solution makes ordering reversible, contributing to large field-induced strains (Jo *et al.*, 2012). The enhanced electromechanical properties at the MPBs are thus related to the progressive decoupling of strain and polarization due to competing local distortions, which stem from chemical/charge disorder at the unit cell level, strong covalent bonding between cations and oxygen and field-induced reorientation/switching of nanoscale domains.

Vast variety of NBT-based systems with numerous dopants have so far been produced with the aim to increase d_{33} , strain response and/or depolarization temperature (Dinh *et al.*, 2015; Liu and Tan, 2016; Wu, 2018; Turki *et al.*, 2019). Further efforts for improving the

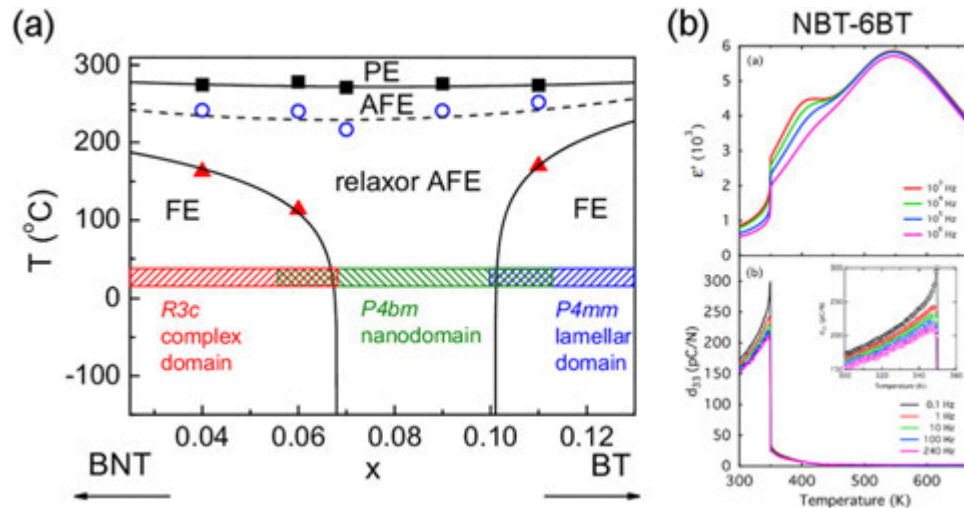


Fig. 2 (a) Partial phase diagram of the NBT–BT system in its virgin state, showing a broad morphotropic-phase region (*P4bm*) where tetragonal and/or rhombohedral long-range symmetries are induced with electric field or stress. (b) Evolution of dielectric permittivity (ϵ') and piezoelectric coefficient (d_{33}) with temperature in the poled 0.94NBT–0.06BT MPB composition; a sharp slope in permittivity curves at the temperature of depolarization coincides with a peak in d_{33} , above which the material is no longer piezoelectric. Reprinted from (a) Ma, C., Tan, X., Dul'kin, E., Roth, M., 2010. Domain structure-dielectric property relationship in lead-free $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-BaTiO}_3$ ceramics. *Journal of Applied Physics* 108, 104105, with permission of AIP Publishing. (b) Schader, F.H., Wang, Z., Hinterstein, M., Daniels, J.E., Webber, K.G., 2016. Stress-modulated relaxor-to-ferroelectric transition in lead-free $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-BaTiO}_3$ ferroelectrics. *Physical Review B* 93, 134111, with permission of AIP Publishing.

materials' functionalities have been undertaken through the role of defects (Spreitzer *et al.*, 2006; Yang *et al.*, 2018; Steiner *et al.*, 2019; Tung *et al.*, 2019) or ceramics texturing (Bai *et al.*, 2017), as well as on their integration into silicon technology (Tanaka *et al.*, 2018).

Barium Titanate

The discovery of ferroelectricity in barium titanate (BaTiO_3 , BT) at the beginning of the 2nd World War was stimulated by the need for high dielectric permittivity capacitors (Jaffe *et al.*, 1971; Haertling, 1999). Due to its excellent dielectric and ferroelectric properties, BT is still one of the most studied ferroelectrics. However, its modest piezoelectric properties, $k_p \approx 0.35$, $d_{33} \approx 190$ pC/N, and rather low T_C of 130°C (Jaffe *et al.*, 1971) could not compete with a much higher piezoelectric performance of PZT, which was discovered about 10 years later. Piezoelectric properties of BT-based materials were reviewed recently (Acosta *et al.*, 2017; Gao *et al.*, 2017, 2018).

Interest of the scientific community in piezoelectric performance of BT-based ceramics was revived in 2009 by the report on extremely high piezoelectric properties in calcium and zirconium modified BT ($(\text{Ba,Ca})(\text{Zr,Ti})\text{O}_3$, BCZT) ceramics (Liu and Ren, 2009). The respective quaternary solid solution, which had been originally studied as early as 1954 (McQuarrie and Behnke, 1954), could be treated as a quasi binary solid solution $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_{3-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (BZT– x BCT). The exceptional piezoelectric responses were reported for solid solutions in the vicinity of the optimized BZT–0.50BCT formulation with a peak d_{33} value of 620 pC/N, together with a high remanent polarization, low coercive field and high dielectric permittivity. Such high performance could not be explained by the proximity to T_C (93°C for BZT–0.50BCT), but was related to the phase boundary, i.e., MPB, between the rhombohedral BZT (R, $R3m$) and tetragonal BCT (T, $P4mm$) phases allowing many possible polarization states to coexist. At $x = 0.32$ composition of the BZT–BCT another point of phase coexistence was found at $T = 57^\circ\text{C}$, namely, between the R, T, and cubic (C, $Pm\bar{3}m$) phases, which was suggested to correspond to a tricritical point (Liu and Ren, 2009). Later studies revealed a mixture of R and T phases (Ehmke *et al.*, 2012; Haugen *et al.*, 2013), or a bridging orthorhombic phase (O, $Amm2$) between the R and T phases (Keeble *et al.*, 2013b; Acosta *et al.*, 2014). A pseudobinary BZT–BCT phase diagram and d_{33} coefficient as a function of composition and temperature are presented in Fig. 3. The phase relations and presence of a multiphase coexistence point (MCP) are topics of continued research (Keeble *et al.*, 2013a; Tian *et al.*, 2013; Zhang *et al.*, 2014; Heitmann and Rossetti, 2014; Acosta *et al.*, 2014, 2015a,b, 2017; Gao *et al.*, 2018). Transmission electron microscopy (TEM) revealed specific domain structures of individual phases of the BZT–BCT system. The off-MCP compositions, the BCT-rich T and BZT-rich R phases, were characterized by lamellar or wedge domains, respectively, while the MCP compositions, such as BZT–0.50BCT, showed nanodomains that were hierarchically arranged into larger, micron-sized domains. Furthermore, in-situ TEM studies revealed domains at the MCP to be highly susceptible to both temperature and electric field (Gao *et al.*, 2011, 2014; Guo *et al.*, 2014a; Lu *et al.*, 2014; Gao *et al.*, 2016a; Zakhozheva *et al.*, 2014, 2015), likely contributing to increased strain response. It was also found that the piezoelectric response of BZT–BCT strongly depends on the grain size (GS) (Ehmke *et al.*, 2012, 2013; Li *et al.*, 2013b; Bharathi and Varma, 2014; Guo *et al.*, 2014b; Tutuncu *et al.*, 2014; Zhang *et al.*, 2015; Bai *et al.*, 2016). In a systematic study of ceramics with GS from 0.4 to 32 μm , Hao *et al.* found that with increasing GS the phase transition temperatures decreased while the

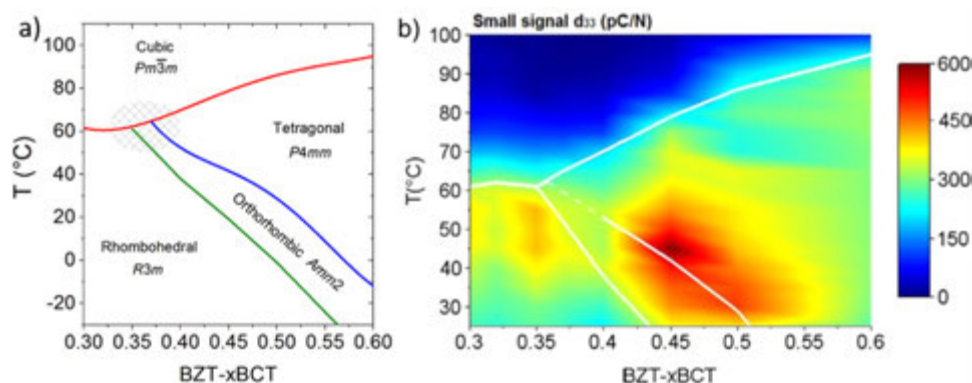


Fig. 3 (a) Partial pseudobinary phase diagram of the BZT-BCT system. The dashed area marks the phase convergence region that could not be experimentally determined. (b) Dependence of the small signal d_{33} coefficient on the BZT-BCT composition and temperature. (a) Modified after Keeble, D.S., Benabdallah, F., Thomas, P.A., Maglione, M., Kreisel, J., 2013b. Revised structural phase diagram of $(\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3)$ - $(\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3)$. *Applied Physics Letters* 102, 092903. (b) Reprinted from Acosta, M., Novak, N., Jo, W., Rödel, J., 2014. Relationship between electromechanical properties and phase diagram in the $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_{3-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ lead-free piezoceramic. *Acta Materialia* 80, 48–55, with permission of Elsevier.

physical properties (dielectric permittivity, remanent polarization, d_{33} , electromechanical coupling factors) increased, which was related to the influence of GS on the domain structure. The optimum properties were obtained for GS exceeding $10\ \mu\text{m}$ (Hao *et al.*, 2012).

Similar phase relations and high piezoelectric responses as in BZT-BCT were found in structurally analogous hafnium- and tin-substituted solid solutions (i.e., $(\text{Ba,Ca})(\text{Hf,Ti})\text{O}_3$ (Xue *et al.*, 2011); $(\text{Ba,Ca})(\text{Sn,Ti})\text{O}_3$ (Zhou *et al.*, 2012)). Doping of BZT-BCT with transition metals (e.g., Y, Cu, Zn, Cr, Mn) has been oriented towards reducing the high thermal budget and/or optimizing the functional properties (Han *et al.*, 2012; Li *et al.*, 2013c; Liu *et al.*, 2014a; Sun *et al.*, 2014; Wang *et al.*, 2015b; Chandrakala *et al.*, 2016; Xia *et al.*, 2016).

Processing

Bulk lead-free piezoelectric ceramics are most commonly prepared by solid-state synthesis, typically from metal oxide-carbonate mixtures, and sintering. In addition to conventional routes, alternative approaches have been introduced, such as solution routes and mechanochemical synthesis, or pressure-, electric field- or current-assisted sintering. The topic has been recently reviewed (Malič *et al.*, 2018; Wu, 2018).

Typical synthesis temperature ranges for KNN- and NBT-based formulations are between 700 and 900°C , for details on synthesis mechanisms refer to Malič *et al.* (2008), Aksel and Jones (2010), Kainz *et al.* (2014); Hou *et al.* (2017), and Koruza *et al.* (2016). KNN is notorious for humidity sensitivity of alkaline reagents, especially potassium carbonate, a narrow sintering range close to the solidus temperature (1140°C), difficult control of microstructure, easy appearance of secondary phases and chemical heterogeneity, especially in the case of chemical modification (Egerton and Dillon, 1959; Jaffe *et al.*, 1971; Malič *et al.*, 2015; Haugen *et al.*, 2015; Zhen and Li, 2006; Wang *et al.*, 2007; Acker *et al.*, 2010; Malič *et al.*, 2015; Radan *et al.*, 2018; Zhang and Li, 2019).

NBT requires sintering temperatures of about 1100°C to densify. Evaporation of bismuth, which contributes to coarsening of the microstructure, creation of oxygen vacancies and increased leakage current can be compensated by adding excess of bismuth oxide (Park *et al.*, 1994; Wang *et al.*, 2005; Nagata *et al.*, 2006). Note that the vapor pressure of bismuth over $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (which is close to that of PbO over PZT) is a few orders of magnitude higher than vapor pressures of sodium and potassium over respective niobates (Popović *et al.*, 2015). NBT-BT and NBT-BKT solid solutions reach high relative densities upon sintering at 1050 and 1200°C , respectively (Jo *et al.*, 2012; Kainz *et al.*, 2014; Reichmann *et al.*, 2015; Otoničar *et al.*, 2010).

Solid state synthesis of BZT-BCT takes place at temperatures of about 1200 – 1300°C , and sintering between 1300 – 1500°C . Similar as in the case of pure BT, strict control of stoichiometry is needed to avoid appearance of detrimental secondary phases. Additives or dopants such as CuO , CeO_2 , Y_2O_3 , or Bi_2O_3 were used to reduce the high sintering temperature (Chen *et al.*, 2012; Cui *et al.*, 2012, 2013; Hayati *et al.*, 2016).

Applications

The broad requirements of the various piezoelectric applications are currently being covered by chemically modifying the PZT and up to now no single lead-free composition was identified to fully replace it. However, individual benefits of lead-free systems have attracted the attention of industry and numerous prototypes/devices were reported (Shibata *et al.*, 2018).

Actuators are characterized by displacement, blocking force, and temperature operational range (Webber *et al.*, 2014). Displacement and force are increased by manufacturing multilayered structures. Due to thermodynamic incompatibility, PZT is often limited to the use of expensive Ag or Ag/Pd electrodes, which represent up to 80% of the total material cost (Randall *et al.*, 2005). Lead-free compositions can be co-fired with cheaper base-metal electrodes, such as Ni (Kawada *et al.*, 2009; Liu *et al.*, 2014b) or Cu (Gao *et al.*, 2016b; Yesner and Safari, 2018), which compensate for the costly starting ceramic materials and also have a high electromigration resistance. The displacement of lead-free actuators is inferior to their lead-based counterparts and thus higher driving voltages are required. Despite this, KNN-based actuators for ink-jet printing heads have been reported (Shimosato and Tanuma, 2012; Maruyama, 2008). Benefits of NBT-based actuators include good fatigue resistance (Zhang *et al.*, 2019; Glaum and Hoffman, 2014) and high fracture toughness (Denkhaus *et al.*, 2017), while their drawbacks are the high strain hysteresis and the need for high driving fields.

Sensors transform external mechanical stimuli (pressure, vibrations) into electrical signals and can operate at resonant or off-resonant conditions. The high and temperature-stable electromechanical coupling coefficients (k) of KNN-based compositions made them interesting for sensing, e.g., in knocking sensors, which monitor the combustion in automotive engines (Ohbayashi, 2016). In addition, individual compositions were developed to use the mechanical and thermal external stimuli for electrical power generation (Maurya *et al.*, 2018; Bowen *et al.*, 2014). These electromechanical and pyroelectric energy harvesters are desired for self-powered systems for the Internet of Things.

Transducers are used for ultrasonic imaging, sonars, and high-power applications (cleaning, welding, voltage transformers, etc.). Ultrasonic imaging benefits from the high k , good temperature stability, and low density of KNN-based piezoceramics (Levassort *et al.*, 2011). NBT-based compositions exhibit moderately high Q_m , mechanical stability, and good coupling coefficients. Unlike PZT, their performance does not degrade when driven at high vibration velocities, which enables high ultrasound intensities. They were used in Langevin-type transducers for cleaning (Tou *et al.*, 2009) or for non-destructive evaluation (Edwards *et al.*, 2007), whereas KNN-based compositions were used in ultrasonic motors (Hong *et al.*, 2015). KNN- and NBT-based materials for transducers are now available from several piezoceramic producers.

Over the past 20 years researchers have focused on developing materials with high piezoelectric performance. However, the above-listed prototypes/devices revealed the need for exploring also other application-relevant aspects, including robust processing routes, reproducibility, mechanical and thermal properties, conductivity, lifetime and cost (Koruzza *et al.*, 2018a).

Environmental and Health Concerns

KNN-based solid solutions are considered among the most promising lead-free piezoceramics (Ando, 2012; Coondoo *et al.*, 2013; Gupta *et al.*, 2012; Hao *et al.*, 2019; Hong *et al.*, 2016; Li *et al.*, 2013a; Malič *et al.*, 2015; Rödel *et al.*, 2009, 2015; Safari and Hejazi, 2012; Xing *et al.*, 2018; Wang *et al.*, 2018b; Wu, 2018; Zheng *et al.*, 2018). They are frequently described as “greener” replacements to PZT and reported as environmentally friendly compositions. However, using a systematic, well-established Life Cycle Assessment (LCA), it was recently demonstrated (Ibn-Mohammed *et al.*, 2016, 2017) that the presence of ~60 wt% Nb₂O₅ in KNN constitutes several times greater environmental damage than that of PZT, which occurs due to the methods used for extraction of niobium from its ore and purification processing. Additionally, a cost-benefit analysis of substituting PZT with KNN indicated that the initial cost of conversion to KNN is greater in comparison to PZT, mainly due to higher energy usage during production. Moreover, the authors suggested avoiding the term “environmentally friendly” for the description of KNN and other alternative piezoelectrics, at least until similar LCA studies are conducted to confirm such markings.

NBT, another potential lead-free substitute for PZT, was found to have a lower energy demand during fabrication and therefore a lower overall environmental impact than both PZT and its lead-free competitor KNN (Ibn-Mohammed *et al.*, 2018). However, the environmental profile of Bi₂O₃ precursor was shown to surpass that of PbO used for PZT according to several key environmental indicators, mostly due to additional processing and refining steps required in bismuth production. Moreover, bismuth has a higher energy cost of recycling than lead and over 90% of bismuth is obtained as a by-product of lead smelting (Krüger *et al.*, 2003), which cannot be overlooked from the perspective of potential future upscaling.

Besides environmental concerns, health-related issues of lead-free piezoceramics also need to be addressed before their potential application. For instance, although lead-based piezoceramics have excellent piezoelectric properties, they are not suitable as biomaterials due to their toxicity related to the well-known lead poisoning. On the other hand, clinical trials and in vitro studies showed that bismuth, despite being a heavy element, is not associated with significant toxicity in humans (Serfontein *et al.*, 1979; Rodilla *et al.*, 1998) and NBT–BT and BZT–BCT compositions are currently under investigation as potential biomaterials (Acosta *et al.*, 2018). Similarly, the cytotoxicity of ion-released products from KNN and Li-doped KNN was found to be low (Yu *et al.*, 2011), although slightly higher in the latter due to the release of Li (Yu *et al.*, 2012).

Summary

Triggered by increased environmental awareness and legislations, the research of lead-free piezoceramics has flourished over the past 20 years. Although the three basic material systems were already known for decades, targeted compositional and microstructural engineering has enabled to achieve excellent electromechanical properties, which are for individual compositions

comparable to the state-of-the-art PZT. In addition, this research has enabled to discover new physical phenomena and has considerably increased our understanding of e.g., crystallographic structures, phase boundaries, and relaxors. The reported prototypes and first industrial products are indicative of considerable industrial interest for these materials and continuous efforts are made to exploit the individual benefits of the selected lead-free compositions. Nevertheless, several open questions remain to be addressed in the future, including the reliability and reproducibility, cost reduction and reduction of the environmental footprint.

Acknowledgments

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References

- Acker, J., Kungl, H., Hoffmann, M.J., 2010. Influence of alkaline and niobium excess on sintering and microstructure of sodium-potassium niobate ($K_{0.5}Na_{0.5}$)NbO₃. *Journal of the American Ceramic Society* 93, 1270–1281.
- Acosta, M., Detsch, R., Grünewald, A., *et al.*, 2018. Cytotoxicity, chemical stability, and surface properties of ferroelectric ceramics for biomaterials. *Journal of the American Ceramic Society* 101, 440–449.
- Acosta, M., Khakpash, N., Someya, T., *et al.*, 2015a. Origin of the large piezoelectric activity in $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_{3-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ceramics. *Physical Review B* 91, 104108.
- Acosta, M., Novak, N., Jo, W., Rödel, J., 2014. Relationship between electromechanical properties and phase diagram in the $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_{3-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ lead-free piezoceramic. *Acta Materialia* 80, 48–55.
- Acosta, M., Novak, N., Rossetti, G.A. Jr., Rödel, J., 2015b. Mechanisms of electromechanical response in $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_{3-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ceramics. *Applied Physics Letters* 107, 142906.
- Acosta, M., Novak, N., Rojas, V., *et al.*, 2017. BaTiO₃-based piezoelectrics: Fundamentals, current status, and perspectives. *Applied Physics Reviews* 4, 041305.
- Ahtee, M., Hewat, A.W., 1975. The structures of $\text{Na}_{0.98}\text{K}_{0.02}\text{NbO}_3$ and $\text{Na}_{0.90}\text{K}_{0.10}\text{NbO}_3$ (phase Q) at room temperature by neutron powder diffraction. *Acta Crystallographica Section A* 31, 846–850.
- Aksel, E., Forrester, J., Nino, J., *et al.*, 2013. Local atomic structure deviation from average structure of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$: Combined X-ray and neutron total scattering. *Physical Review B* 87, 103113.
- Aksel, E., Jones, J.L., 2010. Phase formation of sodium bismuth titanate perovskite during solid-state processing. *Journal of the American Ceramic Society* 93, 3012–3016.
- Ando, A., 2012. Alkali niobate piezoelectric ceramics. In: Priya, S., Nahm, S. (Eds.), *Lead-Free Piezoelectrics*. New York, NY: Springer.
- Bah, M., Giovannelli, F., Schoenstein, F., *et al.*, 2014. High electromechanical performance with spark plasma sintering of undoped $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ ceramics. *Ceramics International* 40, 7473–7480.
- Bai, W., Chen, D., Li, P., *et al.*, 2016. Enhanced electromechanical properties in $\langle 001 \rangle$ -textured $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ lead-free piezoceramics. *Ceramics International* 42, 3429–3436.
- Bai, W., Chen, D., Zheng, P., *et al.*, 2017. Grain-orientated lead-free BNT-based piezoceramics with giant electrostrictive effect. *Ceramics International* 43, 3339–3345.
- Baker, D.W., Thomas, P.A., Zhang, N., Glazer, A.M., 2009. A comprehensive study of the phase diagram of $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$. *Applied Physics Letters* 95, 091903.
- Bell, A.J., Deubzer, O., 2018. Lead-free piezoelectrics – The environmental and regulatory issues. *MRS Bulletin* 43, 581–587.
- Bharathi, P., Varma, K.B.R., 2014. Grain and the concomitant ferroelectric domain size dependent physical properties of $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ ceramics fabricated using powders derived from oxalate precursor route. *Journal of Applied Physics* 116, 164107.
- Bowen, C.R., Taylor, J., Lebourbar, E., *et al.*, 2014. Pyroelectric materials and devices for energy harvesting applications. *Energy & Environmental Science* 7, 3836–3856.
- Catalan, G., Scott, J.F., 2009. Physics and applications of bismuth Ferrite. *Advanced Materials* 21, 2463–2485.
- Chandrakala, E., Paul Praveen, J., Kumar, A., James, A.R., Das, D., 2016. Strain-induced structural phase transition and its effect on piezoelectric properties of (BZT-BCT)-(CeO₂) ceramics. *Journal of the American Ceramic Society* 99, 3659–3669.
- Chen, T., Zhang, T., Wang, G., *et al.*, 2012. Effect of CuO on the microstructure and electrical properties of $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3$ piezoceramics. *Journal of Materials Science* 47, 4612–4619.
- Choe, H., Bieker, J., Zhang, N., *et al.*, 2018. Monoclinic distortion, polarization rotation and piezoelectricity in the ferroelectric $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. *IUCrJ* 5, 417–427.
- Coondoo, I., Panwar, N., Kholkin, A., 2013. Lead-free piezoelectrics: Current status and perspectives. *Journal of Advanced Dielectrics* 03, 1330002.
- Craciun, F., Galassi, C., Birjega, R., 2012. Electric-field-induced and spontaneous relaxor-ferroelectric phase transition in $(\text{Na}_{1/2}\text{Bi}_{1/2})_{1-x}\text{Ba}_x\text{TiO}_3$. *Journal of Applied Physics* 112, 124106.
- Cui, Y., Liu, X., Jiang, M., *et al.*, 2012. Lead-free $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$ -CeO₂ ceramics with high piezoelectric coefficient obtained by low-temperature sintering. *Ceramics International* 38, 4761–4764.
- Cui, Y., Yuan, C., Liu, X., Zhao, X., Shan, X., 2013. Lead-free $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$ -Y₂O₃ ceramics with large piezoelectric coefficient obtained by low-temperature sintering. *Journal of Materials Science: Materials in Electronics* 24, 654–657.
- Dai, Y.J., Zhang, X.W., Chen, K.P., 2009. Morphotropic phase boundary and electrical properties of $\text{K}_{1-x}\text{Na}_x\text{NbO}_3$ lead-free ceramics. *Applied Physics Letters* 94, 042905.
- Dai, Y., Zhang, X., Zhou, G., 2007. Phase transitional behavior in $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ -LiTaO₃ ceramics. *Applied Physics Letters* 90, 262903.
- Daniels, J.E., Jo, W., Rödel, J., Jones, J.L., 2009. Electric-field-induced phase transformation at a lead-free morphotropic phase boundary: Case study in a 93% $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ -7%BaTiO₃ piezoelectric ceramic. *Applied Physics Letters* 95, 032904.
- Datta, K., Neder, R.B., Richter, A., *et al.*, 2018. Adaptive strain prompting a pseudo-morphotropic phase boundary in ferroelectric $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -xBaTiO₃. *Physical Review B* 97, 184101.
- Denkhaus, S.M., Vögler, M., Novak, N., Rödel, J., 2017. Short crack fracture toughness in $(1-x)(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -xBaTiO₃ relaxor ferroelectrics. *Journal of the American Ceramic Society* 100, 4760–4769.
- Dinh, T.H., Bafandeh, M.R., Kang, J.-K., *et al.*, 2015. Comparison of structural, ferroelectric, and strain properties between A-site donor and acceptor doped $\text{Bi}_{1/2}(\text{Na}_{0.82}\text{K}_{0.18})_{1/2}\text{TiO}_3$ ceramics. *Ceramics International* 41, S458–S463.
- Dorcet, V., Trolliard, G., 2008. A transmission electron microscopy study of the A-site disordered perovskite $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. *Acta Materialia* 56, 1753–1761.
- Edwards, G.C., Choy, S.H., Chan, H.L.W., Scott, D.A., Batten, A., 2007. Lead-free transducer for non-destructive evaluation. *Applied Physics A-Materials Science & Processing* 88, 209–215.
- Egerton, L., Dillon, D.M., 1959. Piezoelectric and dielectric properties of ceramics in the system potassium-sodium niobate. *Journal of the American Ceramic Society* 42, 438–442.

- Ehmke, M.C., Daniels, J., Glaum, J., *et al.*, 2012. Reduction of the piezoelectric performance in lead-free $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_{3-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ piezoceramics under uniaxial compressive stress. *Journal of Applied Physics* 112, 114108.
- Ehmke, M.C., Glaum, J., Hoffman, M., Blendell, J.E., Bowman, K.J., 2013. The effect of electric poling on the performance of lead-free $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_{3-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ piezoceramics. *Journal of the American Ceramic Society* 96, 3805–3811.
- Elkechai, O., Manier, M., Mercurio, J.P., 1996. $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{--K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT-KBT) system: A structural and electrical study. *Physica Status Solidi (a)* 157, 499–506.
- Fukada, M., Saito, T., Kume, H., Wada, T., 2008. Fabrication of lead-free piezoelectric $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ ceramics by a modified solid-state reaction method. *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control* 55, 988–993.
- Gao, J., Dai, Y., Hu, X., *et al.*, 2016a. Phase transition behaviours near the triple point for Pb-free $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_{3-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ piezoceramics. *EPL* 115, 37001.
- Gao, J., Ke, X., Acosta, M., Glaum, J., Ren, X., 2018. High piezoelectricity by multiphase coexisting point: Barium titanate derivatives. *MRS Bulletin* 43, 595–599.
- Gao, L.S., Ko, S.W., Guo, H.Z., Hennig, E., Randall, C.A., 2016b. Demonstration of copper Co-fired $(\text{Na,K})\text{NbO}_3$ multilayer structures for piezoelectric applications. *Journal of the American Ceramic Society* 99, 2017–2023.
- Gao, J., Xue, D., Liu, W., Zhou, C., Ren, X., 2017. Recent progress on BaTiO_3 -based piezoelectric ceramics for actuator applications. *Actuators* 6, 24.
- Gao, J., Xue, D., Wang, Y., *et al.*, 2011. Microstructure basis for strong piezoelectricity in Pb-free $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_{3-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ceramics. *Applied Physics Letters* 99, 092901.
- Gao, J., Zhang, L., Xue, D., *et al.*, 2014. Symmetry determination on Pb-free piezoceramic $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3\text{--}0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ using convergent beam electron diffraction method. *Journal of Applied Physics* 115, 054108.
- Garg, R., Rao, B.N., Senyshyn, A., Krishna, P.S.R., Ranjan, R., 2013. Lead-free piezoelectric system $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\text{--BaTiO}_3$: Equilibrium structures and irreversible structural transformations driven by electric field and mechanical impact. *Physical Review B* 88, 014103.
- Glaum, J., Hoffman, M., 2014. Electric fatigue of lead-free piezoelectric materials. *Journal of the American Ceramic Society* 97, 665–680.
- Gorfman, S., Thomas, P.A., 2010. Evidence for a non-rhombohedral average structure in the lead-free piezoelectric material $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. *Journal of Applied Crystallography* 43, 1409–1414.
- Groszewicz, P.B., Gröting, M., Breitzke, H., *et al.*, 2016. Reconciling local structure disorder and the relaxor state in $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{--BaTiO}_3$. *Scientific Reports* 6, 31739.
- Guo, H., Voas, B.K., Zhang, S., *et al.*, 2014b. Polarization alignment, phase transition, and piezoelectricity development in polycrystalline $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3\text{--}0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$. *Physical Review B* 90, 014103.
- Guo, H., Zhou, C., Ren, X., Tan, X., 2014a. Unique single-domain state in a polycrystalline ferroelectric ceramic. *Physical Review B* 89, 100104(R).
- Gupta, S., Maurya, D., Yan, Y., Priya, S., 2012. Development of KNN-based piezoelectric materials. In: Priya, S., Nahm, S. (Eds.), *Lead-Free Piezoelectrics*. New York, NY: Springer.
- Haertling, G.H., 1999. Ferroelectric ceramics: History and technology. *Journal of the American Ceramic Society* 82, 797–818.
- Haertling, G.H., 1967. Properties of hot-pressed ferroelectric alkali niobate ceramics. *Journal of the American Ceramic Society* 50, 329–330.
- Han, C., Wu, J., Pu, C., *et al.*, 2012. High piezoelectric coefficient of Pr_2O_3 -doped $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3$ ceramics. *Ceramics International* 38, 6359–6363.
- Hao, J., Bai, W., Li, W., Zhai, J., 2012. Correlation between the microstructure and electrical properties in high-performance $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ lead-free piezoelectric ceramics. *Journal of the American Ceramic Society* 95, 1998–2006.
- Hao, J., Li, W., Zhai, J., Chen, H., 2019. Progress in high-strain perovskite piezoelectric ceramics. *Materials Science and Engineering: R: Reports* 135, 1–57.
- Haugen, A.B., Forrester, J.S., Damjanovic, D., *et al.*, 2013. Structure and phase transitions in $0.5(\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3)\text{--}0.5(\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3)$ from -100°C to 150°C . *Journal of Applied Physics* 113, 014103.
- Haugen, A.B., Madaro, F., Bjørkeng, L.-P., Grande, T., Einarsrud, M.-A., 2015. Sintering of sub-micron $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ powders fabricated by spray pyrolysis. *Journal of the European Ceramic Society* 35, 1449–1457.
- Hayati, R., Bahrevar, M.A., Ebadzadeh, T., *et al.*, 2016. Effects of Bi_2O_3 additive on sintering process and dielectric, ferroelectric, and piezoelectric properties of $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ lead-free piezoceramics. *Journal of the European Ceramic Society* 36, 3391–3400.
- Heitmann, A.A., Rossetti Jr., G.A., 2014. Thermodynamics of ferroelectric solid solutions with morphotropic phase boundaries. *Journal of the American Ceramic Society* 97, 1661–1685.
- Hinterstein, M., Knapp, M., Hölzel, M., *et al.*, 2010. Field-induced phase transition in $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ -based lead-free piezoelectric ceramics. *Journal of Applied Crystallography* 43, 1314–1321.
- Hong, C.-H., Han, H.-S., Lee, J.-S., *et al.*, 2015. Ring-type rotary ultrasonic motor using lead-free ceramics. *Journal of Sensor Science and Technology* 24, 228.
- Hong, C.-H., Kim, H.-P., Choi, B.-Y., *et al.*, 2016. Lead-free piezoceramics – Where to move on? *Journal of Materiomics* 2, 1–24.
- Hou, D., Aksel, E., Fancher, C.M., *et al.*, 2017. Formation of sodium bismuth titanate-barium titanate during solid-state synthesis. *Journal of the American Ceramic Society* 100, 1330–1338.
- Ibn-Mohammed, T., Koh, S.C.L., Reaney, I.M., *et al.*, 2016. Integrated hybrid life cycle assessment and supply chain environmental profile evaluations of lead-based (lead zirconate titanate) versus lead-free (potassium sodium niobate) piezoelectric ceramics. *Energy & Environmental Science* 9, 3495–3520.
- Ibn-Mohammed, T., Koh, S.C.L., Reaney, I.M., *et al.*, 2017. Are lead-free piezoelectrics more environmentally friendly? *MRS Communications* 7, 1–7.
- Ibn-Mohammed, T., Reaney, I.M., Koh, S.C.L., *et al.*, 2018. Life cycle assessment and environmental profile evaluation of lead-free piezoelectrics in comparison with lead zirconate titanate. *Journal of the European Ceramic Society* 38, 4922–4938.
- Jaeger, R.E., Egerton, L., 1962. Hot pressing of potassium-sodium niobates. *Journal of the American Ceramic Society* 45, 209–213.
- Jaffe, B., Cook, W.R., Jaffe, H.L., 1971. Piezoelectric ceramics. In: Roberts, J.P., Popper, P. (Eds.), *Non-Metallic Solids*, first ed., 3. London/New York: Academic Press.
- Jiang, B., Grande, T., Selbach, S.M., 2017. Local structure of disordered $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ investigated by pair distribution function analysis and first-principles calculations. *Chemistry of Materials* 29, 4244–4252.
- Jo, W., Daniels, J.E., Jones, J.L., *et al.*, 2011. Evolving morphotropic phase boundary in lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{--BaTiO}_3$ piezoceramics. *Journal of Applied Physics* 109, 014110.
- Jo, W., Dittmer, R., Acosta, M., *et al.*, 2012. Giant electric-field-induced strains in lead-free ceramics for actuator applications – Status and perspective. *Journal of Electroceramics* 29, 71–93.
- Jones, G.O., Thomas, P.A., 2002. Investigation of the structure and phase transitions in the novel A-site substituted distorted perovskite compound $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. *Acta Crystallographica* 58, 168–178.
- Kainz, T., Naderer, M., Schütz, D., *et al.*, 2014. Solid state synthesis and sintering of solid solutions of BNT-xBKT. *Journal of the European Ceramic Society* 34, 3685–3697.
- Karakı, T., Katayama, T., Yoshida, K., Maruyama, S., Adachi, M., 2013. Morphotropic phase boundary slope of $(\text{K,Na,Li})\text{NbO}_3\text{--BaZrO}_3$ binary system adjusted using third component $(\text{Bi,Na})\text{TiO}_3$ additive. *Japanese Journal of Applied Physics* 52, 09KD11.
- Kawada, S., Kimura, M., Higuchi, Y., Takagi, H., 2009. $(\text{K,Na})\text{NbO}_3$ -based multilayer piezoelectric ceramics with nickel inner electrodes. *Applied Physics Express* 2, 111401.
- Keeble, D.S., Barney, E.R., Keen, D.A., *et al.*, 2013a. Bifurcated polarization rotation in bismuth-based piezoelectrics. *Advanced Functional Materials* 23, 185–190.
- Keeble, D.S., Benabdallah, F., Thomas, P.A., Maglione, M., Kreisel, J., 2013b. Revised structural phase diagram of $(\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3)\text{--}(\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3)$. *Applied Physics Letters* 102, 092903.
- Koruz, J., Bell, A.J., Frömling, T., *et al.*, 2018a. Requirements for the transfer of lead-free piezoceramics into application. *Journal of Materiomics* 4, 13–26.
- Koruz, J., Kodumudi Venkataraman, L., Malić, B., 2018b. Chapter 3 – Lead-free perovskite ferroelectrics. In: Stojanovic, B.D. (Ed.), *Magnetic, Ferroelectric, and Multiferroic Metal Oxides*. New York: Elsevier, pp. 51–69.

- Koruza, J., Rojas, V., Molina-Luna, L., *et al.*, 2016. Formation of the core-shell microstructure in lead-free $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ - SrTiO_3 piezoceramics and its influence on the electromechanical properties. *Journal of the European Ceramic Society* 36, 1009–1016.
- Kreisel, J., Bouvier, P., Dkhil, B., *et al.*, 2003. High-pressure X-ray scattering of oxides with a nano-scaled local structure: A case study of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. *Physical Review B* 68, 14113.
- Krüger, J., Winkler, P., Lüderitz, E., Lück, M., Wolf, H.U., 2003. Bismuth, bismuth alloys, and bismuth compounds. In: Ullmann's Encyclopedia of Industrial Chemistry. Wiley.
- Lee, Y.-H., Cho, J.-H., Kim, B.-I., Choi, D.-K., 2008. Piezoelectric properties and densification based on control of volatile mass of potassium and sodium in $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ ceramics. *Japanese Journal of Applied Physics* 47, 4620–4622.
- Levassort, F., Grégoire, J.M., Lethiecq, M., *et al.*, 2011. High frequency single element transducer based on pad-printed lead-free piezoelectric thick film. In: *Proceedings of the IEEE International Ultrasonics Symposium*, p. 848.
- Levin, I., Keeble, D.S., Cibin, G., *et al.*, 2019. Nanoscale polar heterogeneities and branching Bi-displacement directions in $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. *Chemistry of Materials* 31, 2450–2458.
- Levin, I., Reaney, I.M., 2012. Nano- and mesoscale structure of $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$: A TEM perspective. *Advanced Functional Materials* 22, 3445–3452.
- Levin, I., Reaney, I.M., Anton, E.-M., *et al.*, 2013. Local structure, pseudosymmetry, and phase transitions in $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ – $\text{K}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ ceramics. *Physical Review B* 87, 24113.
- Li, B., Ehmke, M.C., Blendell, J.E., Bowman, K.J., 2013b. Optimizing electrical poling for tetragonal, lead-free BZT–BCT piezoceramic alloys. *Journal of the European Ceramic Society* 33, 3037–3044.
- Li, J., Sun, X., Zhang, X., *et al.*, 2013c. Synthesis and characterization of sol–gel derived $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_{3-x}\text{CuO}$ ceramics. *Physica Status Solidi A* 210, 533–537.
- Li, J.-F., Wang, K., Zhang, B.-P., Zhang, L.-M., 2006. Ferroelectric and piezoelectric properties of fine-grained $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ lead-free piezoelectric ceramics prepared by spark plasma sintering. *Journal of the American Ceramic Society* 89, 706–709.
- Li, J.-F., Wang, K., Zhu, F.-Y., Cheng, L.-Q., Yao, F.-Z., 2013a. $(\text{K},\text{Na})\text{NbO}_3$ -based lead-free piezoceramics: Fundamental aspects, processing technologies, and remaining challenges. *Journal of the American Ceramic Society* 96, 3677–3696.
- Li, P., Zhai, J., Shen, B., *et al.*, 2018. Ultrahigh piezoelectric properties in textured $(\text{K},\text{Na})\text{NbO}_3$ -based lead-free ceramics. *Advanced Materials* 30, 1705171.
- Liu, C., Liu, P., Kobayashi, K., Randall, C.A., 2014b. Base metal Co-fired $(\text{Na},\text{K})\text{NbO}_3$ structures with enhanced piezoelectric performance. *Journal of Electroceramics* 32, 301–306.
- Liu, H., Li, Q., Li, Y., *et al.*, 2014a. Structure evolution and electrical properties of Y^{3+} -doped $\text{Ba}_{1-x}\text{Ca}_x\text{Zr}_{0.07}\text{Ti}_{0.93}\text{O}_3$ ceramics. *Journal of the American Ceramic Society* 97, 2076–2081.
- Liu, W., Ren, X., 2009. Large piezoelectric effect in Pb-free ceramics. *Physical Review Letters* 103, 257602.
- Liu, X., Tan, X., 2016. Giant strains in non-textured $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -based lead-free ceramics. *Advanced Materials* 28, 574–578.
- Liu, Q., Zhang, Y., Zhao, L., *et al.*, 2018. Simultaneous enhancement of piezoelectricity and temperature stability in $(\text{K},\text{Na})\text{NbO}_3$ -based lead-free piezoceramics by incorporating perovskite zirconates. *Journal of Materials Chemistry C* 6, 10618–10627.
- Lu, S., Xu, Z., Su, S., Zuo, R., 2014. Temperature driven nano-domain evolution in lead-free $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ -50 $(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ piezoceramics. *Applied Physics Letters* 105, 032903.
- Ma, C., Guo, H., Beckman, S.P., Tan, X., 2012. Creation and destruction of morphotropic phase boundaries through electrical poling: A case study of lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - BaTiO_3 piezoelectrics. *Physical Review Letters* 109, 107602.
- Ma, C., Tan, X., Dul'kin, E., Roth, M., 2010. Domain structure-dielectric property relationship in lead-free $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - $x\text{BaTiO}_3$ ceramics. *Journal of Applied Physics* 108, 104105.
- Malič, B., Jenko, D., Holc, J., Hrovat, M., Kosec, M., 2008. Synthesis of sodium potassium niobate: A diffusion couples study. *Journal of the American Ceramic Society* 91, 1916–1922.
- Malič, B., Koruza, J., Hreščak, J., *et al.*, 2015. Sintering of lead-free piezoelectric sodium potassium niobate ceramics. *Materials* 8, 8117–8146.
- Malič, B., Kušcer, D., Vrabelj, M., Koruza, J., 2018. Review of methods for powder-based processing. In: Stojanovic, B.D. (Ed.), *Magnetic, Ferroelectric, and Multiferroic Metal Oxides*. New York: Elsevier, pp. 95–120.
- Maruyama, M., 2008. Tokyo Institute of Technology and Konica Minolta Succeeded in Preparing Inkjet Head Using Lead-Free Piezoelectric Ceramics (in Japanese) [Online]. Nikkei Technology Online Press Release. Available at: <https://tech.nikkeibp.co.jp> (accessed 2008).
- Matsubara, M., Yamaguchi, T., Kikuta, K., Hirano, S., 2004. Sinterability and piezoelectric properties of $(\text{K},\text{Na})\text{NbO}_3$ ceramics with novel sintering aid. *Japanese Journal of Applied Physics* 43, 7159–7163.
- Matsubara, M., Yamaguchi, T., Kikuta, K., Hirano, S., 2005. Synthesis and characterization of $(\text{K}_{0.5}\text{Na}_{0.5})(\text{Nb}_{0.7}\text{Ta}_{0.3})\text{O}_3$ piezoelectric ceramics sintered with sintering aid $\text{K}_{5.4}\text{Cu}_{1.3}\text{Ta}_{10}\text{O}_{29}$. *Japanese Journal of Applied Physics* 44, 6618–6623.
- Matthias, B.T., 1949. New ferroelectric crystals. *Physical Review* 75, 1771.
- Maurya, D., Peddigari, M., Kang, M.G., *et al.*, 2018. Lead-free piezoelectric materials and composites for high power density energy harvesting. *Journal of Materials Research* 33, 2235–2263.
- McQuarrie, M., Behnke, F.W., 1954. Structural and dielectric studies in the system $(\text{Ba},\text{Ca})(\text{Ti},\text{Zr})\text{O}_3$. *Journal of the American Ceramic Society* 37, 539–543.
- Nagata, H., Shinya, T., Hiruma, Y., *et al.*, 2006. Piezoelectric properties of bismuth sodium titanate ceramics. In: Nair, K.M., Guo, R., Bhalla, A.S., Hirano, S.-I., Suvorov, D. (Eds.), *Developments in Dielectric Materials and Electronic Devices* 167. Hoboken, NJ: John Wiley & Sons, pp. 213–221.
- Neagu, A., Tai, C.W., 2017. Local disorder in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -piezoceramic determined by 3D electron diffuse scattering. *Scientific Reports* 7, 12519.
- Ohbayashi, K., 2016. Piezoelectric properties and microstructure of $(\text{K},\text{Na})\text{NbO}_3$ - KTiNbO_5 composite lead-free piezoelectric ceramic. In: Ogawa, T. (Ed.), *Piezoelectric Materials*. IntechOpen, pp. 3–23.
- Ohbayashi, K., Matsuoka, T., Kitamura, K., *et al.*, 2017. Lead-free piezoelectric $(\text{K},\text{Na})\text{NbO}_3$ -based ceramic with planar-mode coupling coefficient comparable to that of conventional lead zirconate titanate. *Japanese Journal of Applied Physics* 56, 061501.
- Otoničar, M., Park, J., Logar, M., *et al.*, 2017. External-field-induced crystal structure and domain texture in $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - $x\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ piezoceramics. *Acta Materialia* 127, 319–331.
- Otoničar, M., Škapin, S.D., Spreitzer, M., Suvorov, D., 2010. Compositional range and electrical properties of the morphotropic phase boundary in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ system. *Journal of the European Ceramic Society* 30, 971–979.
- Park, S.-E., Chung, S.-J., Kim, I.-T., Hong, K.S., 1994. Nonstoichiometry and the long-range cation ordering in crystals of $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$. *Journal of the American Ceramic Society* 77, 2641–2647.
- Petzelt, J., Kamba, S., Fabry, J., *et al.*, 2004. Infrared, Raman and high-frequency dielectric spectroscopy and the phase transitions in $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$. *Journal of Physics: Condensed Matter* 16, 2719–2731.
- Popović, A., Bencze, L., Koruza, J., Malič, B., 2015. Vapour pressure and mixing thermodynamic properties of the KNbO_3 - NaNbO_3 system. *RSC Advances* 5, 76249–76256.
- Priya, S., Nahm, S., 2012. *Lead-Free Piezoelectrics*. New York, NY: Springer.
- Radan, K., Kmet, B., Drnovšek, S., *et al.*, 2018. Mechanochemically-assisted synthesis of lead-free piezoelectric CaZrO_3 -modified $(\text{K},\text{Na},\text{Li})(\text{Nb},\text{Ta})\text{O}_3$ -solid solution. *Ceramics* 1, 304–318.
- Randall, C.A., Kelnberger, A., Yang, G.Y., Eitel, R.E., Shrout, T.R., 2005. High strain piezoelectric multilayer actuators – A material science and engineering challenge. *Journal of Electroceramics* 14, 177–191.
- Reichmann, K., Feteira, A., Li, M., 2015. Bismuth sodium titanate based materials for piezoelectric actuators. *Materials* 8, 8467–8495.

- Rödel, J., Jo, W., Seifert, K.T.P., *et al.*, 2009. Perspective on the development of lead-free piezoceramics. *Journal of the American Ceramic Society* 92, 1153–1177.
- Rödel, J., Li, J.-F., 2018. Lead-free piezoceramics: Status and perspectives. *MRS Bulletin* 43, 576–580.
- Rödel, J., Webber, K.G., Dittmer, R., *et al.*, 2015. Transferring lead-free piezoelectric ceramics into application. *Journal of the European Ceramic Society* 35, 1659–1681.
- Rodilla, V., Miles, A.T., Jenner, W., Haworth, G.M., 1998. Exposure of cultured human proximal tubular cells to cadmium, mercury, zinc and bismuth: Toxicity and metallothionein induction. *Chemico-Biological Interactions* 115, 71–83.
- RoHS1, 2003. Directive 2002/95/EC of the European Parliament and of the European Council on the restriction of the use of certain hazardous substances in electrical and electronic equipment. *Official Journal of the European Union* L37, 19–23.
- RoHS2, 2011. Directive 2011/65/EU of the European Parliament and of the European Council on the restriction of the use of certain hazardous substances in electrical and electronic equipment. *Official Journal of the European Union* L174, 88–110.
- Rojac, T., Benčan, A., Malič, B., *et al.*, 2014. BiFeO₃ ceramics: Processing, electrical, and electromechanical properties. *Journal of the American Ceramic Society* 97, 1993–2011.
- Rojac, T., Khomyakova, E., Walker, J., Uršič, H., Benčan, A., 2018. Chapter 24 – BiFeO₃ ceramics and thick films: processing issues and electromechanical properties. In: Stojanović, B.D. (Ed.), *Magnetic, Ferroelectric, and Multiferroic Metal Oxides*. New York: Elsevier, pp. 515–525.
- Safari, A., Hejazi, M., 2012. Lead-free KNN-based piezoelectric materials. In: Priya, S., Nahm, S. (Eds.), *Lead-Free Piezoelectrics*. New York, NY: Springer, pp. 139–175.
- Saito, Y., Takao, H., Tani, T., *et al.*, 2004. Lead-free piezoceramics. *Nature* 432, 84–87.
- Schader, F.H., Wang, Z., Hinterstein, M., Daniels, J.E., Webber, K.G., 2016. Stress-modulated relaxor-to-ferroelectric transition in lead-free (Na_{1/2}Bi_{1/2})TiO₃-BaTiO₃ ferroelectrics. *Physical Review B* 93, 134111.
- Schütz, D., Deluca, M., Krauss, W., *et al.*, 2012. Lone-pair-induced covalency as the cause of temperature- and field-induced instabilities in bismuth sodium titanate. *Advanced Functional Materials* 22, 2285–2294.
- Serfontein, W.J., Mekel, R., Bank, S., Barbezat, G., Novis, B., 1979. Bismuth toxicity in man – I. Bismuth blood and urine levels in patients after administration of a bismuth protein complex (Bicitropeptide). *Research Communications in Chemical Pathology and Pharmacology* 26, 383–389.
- Shen, Z., Grüner, D., Eriksson, M., *et al.*, 2017. Ordered coalescence of nano-crystals in alkaline niobate ceramics with high remanent polarization. *Journal of Materiomics* 3, 267–272.
- Shibata, K., Wang, R.P., Tou, T., Koruza, J., 2018. Applications of lead-free piezoelectric materials. *MRS Bulletin* 43, 612–616.
- Shimosato, M., Tanuma, C., 2012. Shear-mode inkjet printhead using lead-free piezoelectric ceramic. *Toshiba Review* 67, 45.
- Shirane, G., Newnham, R., Pepinsky, R., 1954. Dielectric properties and phase transitions of NaNbO₃ and (Na,K)NbO₃. *Physical Review* 96, 581–583.
- ShROUT, T.R., Zhang, S.J., 2007. Lead-free piezoelectric ceramics: Alternatives for PZT? *Journal of Electroceramics* 19, 113–126.
- Shuvaeva, V.A., Zekria, D., Glazer, A.M., *et al.*, 2005. Local structure of the lead-free relaxor ferroelectric (K,Na_{1-x})_{0.5}Bi_{0.5}TiO₃. *Physical Review B* 71, 174114.
- Simons, H., Daniels, J., Jo, W., *et al.*, 2011. Electric-field-induced strain mechanisms in lead-free 94%(Bi_{1/2}Na_{1/2})TiO₃-6%BaTiO₃. *Applied Physics Letters* 98, 082901.
- Smolenskii, G.A., Isupov, V.A., Agranovskaya, A.I., Krainik, N.N., 1960. New materials of A^{II}B^{IV}O^{VI} type. *Soviet Physics Solid State* 2, 2982–2985.
- Spreitzer, M., Valant, M., Suvorov, D., 2006. Sodium deficiency in Na_{0.5}Bi_{0.5}TiO₃. *Journal of Materials Chemistry* 17, 185–192.
- Steiner, S., Seo, I.-T., Ren, P., *et al.*, 2019. The effect of Fe-doping on the electrical properties of Na_{1/2}Bi_{1/2}TiO₃ and 0.94 (Na_{1/2}Bi_{1/2})TiO₃-0.06 BaTiO₃. *Journal of the American Ceramic Society* 102, 5295–5304.
- Sun, H., Zhang, Y., Liu, X., *et al.*, 2014. Effects of cobalt and sintering temperature on electrical properties of Ba_{0.98}Ca_{0.02}Zr_{0.02}Ti_{0.98}O₃ lead-free ceramics. *Journal of Materials Science: Materials in Electronics* 25, 3962–3966.
- Takenaka, T., Maruyama, K., Sakata, K., 1991. Bi_{1/2}(Na_{1/2})TiO₃-BaTiO₃ system for lead-free piezoelectric ceramics. *Japanese Journal of Applied Physics* 30, 2236–2239.
- Tanaka, Y., Okamoto, S., Hashimoto, K., *et al.*, 2018. High electromechanical strain and enhanced temperature characteristics in lead-free (Na,Bi)TiO₃-BaTiO₃ thin films on Si substrates. *Scientific Reports* 8, 7847.
- Tellier, J., Malič, B., Dkhil, B., *et al.*, 2009. Crystal structure and phase transitions of sodium potassium niobate perovskites. *Solid State Sciences* 11, 320–324.
- Tennery, V.J., Hang, K.W., 1968. Thermal and X-ray diffraction studies of the NaNbO₃-KNbO₃ system. *Journal of Applied Physics* 39, 4749–4753.
- Tian, Y., Wei, L., Chao, X., Liu, Z., Yang, Z., 2013. Phase transition behavior and large piezoelectricity near the morphotropic phase boundary of lead-free (Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O₃ ceramics. *Journal of the American Ceramic Society* 96, 496–502.
- Tou, T., Hamaguchi, Y., Maida, Y., *et al.*, 2009. Properties of (Bi_{0.5}Na_{0.5})TiO₃-BaTiO₃-(Bi_{0.5}Na_{0.5})(Mn_{1/3}Nb_{2/3})O₃ lead-free piezoelectric ceramics and its application to ultrasonic cleaner. *Japanese Journal of Applied Physics* 48, 07GM03.
- Tung, P., Daniels, J.E., Major, M., *et al.*, 2019. Achieving large electric-field-induced strain in lead-free piezoelectrics. *Materials Research Letters* 7 (5), 173–179.
- Turki, O., Slimani, A., Seveyrat, L., *et al.*, 2019. Enhancement of dielectric, piezoelectric, ferroelectric, and electrocaloric properties in slightly doped (Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO₃ ceramic by samarium. *Journal of Applied Physics* 125, 174103.
- Tutuncu, G., Li, B., Bowman, K., Jones, J.L., 2014. Domain wall motion and electromechanical strain in lead-free piezoelectrics: Insight from the model system (1-x)Ba(Zr_{0.2}Ti_{0.8})O_{3-x}(Ba_{0.7}Ca_{0.3})TiO₃ using in situ high-energy X-ray diffraction during application of electric fields. *Journal of Applied Physics* 115, 144104.
- Usher, T.M., Levin, I., Daniels, J.E., Jones, J.L., 2015. Electric-field-induced local and mesoscale structural changes in polycrystalline dielectrics and ferroelectrics. *Scientific Reports* 5, 14678.
- Wang, R., Bando, H., Katsumata, T., *et al.*, 2009. Tuning the orthorhombic-rhombohedral phase transition temperature in sodium potassium niobate by incorporating barium zirconate. *Physica Status Solidi – Rapid Research Letters* 3, 142–144.
- Wang, Y., Damjanovic, D., Klein, N., Hollenstein, E., Setter, N., 2007. Compositional inhomogeneity in Li- and Ta-modified (K,Na)NbO₃ ceramics. *Journal of the American Ceramic Society* 90, 3485–3489.
- Wang, X., Liang, P., Chao, X., Yang, Z., 2015b. Dielectric properties and impedance spectroscopy of MnCO₃-modified (Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O₃ lead-free ceramics. *Journal of the American Ceramic Society* 98, 1506–1514.
- Wang, K., Malič, B., Wu, J., 2018b. Shifting the phase boundary: Potassium sodium niobate derivatives. *MRS Bulletin* 43, 607–611.
- Wang, X.X., Tang, X.G., Kwok, K.W., Chan, H.L.W., Choy, C.L., 2005. Effect of excess Bi₂O₃ on the electrical properties and microstructure of (Bi_{1/2}Na_{1/2})TiO₃ ceramics. *Applied Physics A* 80, 1071–1075.
- Wang, D., Wang, G., Murakami, S., *et al.*, 2018a. BiFeO₃-BaTiO₃: A new generation of lead-free electroceramics. *Journal of Advanced Dielectrics* 8, 1830004.
- Wang, R., Wang, K., Yao, F., *et al.*, 2015a. Temperature stability of lead-free niobate piezoceramics with engineered morphotropic phase boundary. *Journal of the American Ceramic Society* 98, 2177–2182.
- Wang, X., Wu, J., Xiao, D., *et al.*, 2014. Giant piezoelectricity in potassium-sodium niobate lead-free ceramics. *Journal of the American Ceramic Society* 136, 2905–2910.
- Wang, K., Yao, F.-Z., Jo, W., *et al.*, 2013. Temperature-insensitive (K,Na)NbO₃-based lead-free piezoelectric ceramics. *Advanced Functional Materials* 23, 4079–4086.
- Webber, K.G., Franzbach, D.J., Koruza, J., 2014. Determination of the true operational range of a piezoelectric actuator. *Journal of the American Ceramic Society* 97, 2842–2849.
- Wu, J., 2018. *Advances in Lead-Free Piezoelectric Materials*. Singapore: Springer.
- Xia, X., Jiang, X., Chen, C., *et al.*, 2016. Effects of Cr₂O₃ doping on the microstructure and electrical properties of (Ba,Ca)(Zr,Ti)O₃ lead-free ceramics. *Frontiers of Materials Science* 10, 203–210.
- Xing, J., Zheng, T., Wu, J., Xiao, D., Zhu, J., 2018. Progress on the doping and phase boundary design of potassium-sodium niobate lead-free ceramics. *Journal of Advanced Dielectrics* 8, 1830003.
- Xue, D., Zhou, Y., Bao, H., *et al.*, 2011. Large piezoelectric effect in Pb-free Ba(Ti,Sn)O_{3-x}(Ba,Ca)TiO₃ ceramics. *Applied Physics Letters* 99, 122901.

- Xu, K., Li, J., Lv, X., *et al.*, 2016. Superior piezoelectric properties in potassium–sodium niobate lead-free ceramics. *Advanced Materials* 28, 8519–8523.
- Yang, F., Li, M., Li, L., *et al.*, 2018. Defect chemistry and electrical properties of sodium bismuth titanate perovskite. *Journal of Materials Chemistry A* 6, 5243–5254.
- Yao, F.-Z., Wang, K., Cheng, L.-Q., *et al.*, 2015. Nanodomain engineered (K,Na)NbO₃ lead-free piezoceramics: Enhanced thermal and cycling reliabilities. *Journal of the American Ceramic Society* 98, 448–454.
- Yao, F.-Z., Wang, K., Jo, W., *et al.*, 2016. Diffused phase transition boosts thermal stability of high-performance lead-free piezoelectrics. *Advanced Functional Materials* 26, 1217–1224.
- Yesner, G., Safari, A., 2018. Development of a lead-free copper co-fired BNT-based piezoceramic sintered at low temperature. *Journal of the American Ceramic Society* 101, 5315–5322.
- Yu, S.-W., Kuo, S.-T., Tuan, W.-H., Tsai, Y.-Y., Su, C.-H., 2011. Ion release from three lead-free piezoelectric ceramics and their physical and cytotoxicity characteristics. *Materials Letters* 65, 3522–3524.
- Yu, S.-W., Kuo, S.-T., Tuan, W.-H., Tsai, Y.-Y., Wang, S.-F., 2012. Cytotoxicity and degradation behavior of potassium sodium niobate piezoelectric ceramics. *Ceramics International* 38, 2845–2850.
- Zakhozheva, M., Schmitt, L.A., Acosta, M., *et al.*, 2015. Wide compositional range in situ electric field investigations on lead-free Ba(Zr_{0.2}Ti_{0.8})O_{3-x}(Ba_{0.7}Ca_{0.3})TiO₃ piezoceramic. *Physical Review Applied* 3, 064018.
- Zakhozheva, M., Schmitt, L.A., Acosta, M., *et al.*, 2014. In situ electric field induced domain evolution in Ba(Zr_{0.2}Ti_{0.8})O₃–0.3(Ba_{0.7}Ca_{0.3})TiO₃ ferroelectrics. *Applied Physics Letters* 105, 112904.
- Zhang, Y., Glaum, J., Ehmke, M.C., *et al.*, 2015. The ageing and de-ageing behaviour of (Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O₃ lead-free piezoelectric ceramics. *Journal of Applied Physics* 118, 124108.
- Zhang, Y., Li, J.-F., 2019. Review of chemical modification on potassium sodium niobate lead-free piezoelectrics. *Journal of Materials Chemistry C* 7, 4284–4303.
- Zhang, H., Ma, W., Xie, B., *et al.*, 2019. (Na_{1/2}Bi_{1/2})TiO₃-based lead-free co-fired multilayer actuators with large strain and high fatigue resistance. *Journal of the American Chemical Society* 102, 6147–6155.
- Zhang, M.-H., Wang, K., Du, Y.-J., *et al.*, 2017a. High and temperature-insensitive piezoelectric strain in alkali niobate lead-free perovskite. *Journal of the American Chemical Society* 139, 3889–3895.
- Zhang, M.-H., Wang, K., Zhou, J.-S., *et al.*, 2017b. Thermally stable piezoelectric properties of (K,Na)NbO₃-based lead-free perovskite with rhombohedral-tetragonal coexisting phase. *Acta Materialia* 122, 344–351.
- Zhang, S., Xia, R., Shrout, T.R., Wang, J., 2006. Piezoelectric properties in perovskite 0.948(K_{0.5}Na_{0.5})NbO₃–0.052LiSbO₃ lead-free ceramics. *Journal of Applied Physics* 100, 104108.
- Zhang, B.-P., Zhang, L.-M., Li, J.-F., Ding, X.-N., Zhang, H.-L., 2007. Effect of sintering temperature on electrical properties of Na_{0.5}K_{0.5}NbO₃ lead-free piezoelectric ceramics prepared by normal sintering. *Ferroelectrics* 358, 188–195.
- Zhang, L., Zhang, M., Wang, L., *et al.*, 2014. Phase transitions and the piezoelectricity around morphotropic phase boundary in Ba(Zr_{0.2}Ti_{0.8})O_{3-x}(Ba_{0.7}Ca_{0.3})TiO₃ lead-free solid solution. *Applied Physics Letters* 105, 162908.
- Zhao, C., Wu, B., Wang, K., *et al.*, 2018. Practical high strain with superior temperature stability in lead-free piezoceramics through domain engineering. *Journal of Materials Chemistry A* 6, 23736–23745.
- Zheng, T., Wu, J., Xiao, D., Zhu, J., 2018. Recent development in lead-free perovskite piezoelectric bulk materials. *Progress in Materials Science* 98, 552–624.
- Zheng, T., Wu, H., Yuan, Y., *et al.*, 2017. The structural origin of enhanced piezoelectric performance and stability in lead free ceramics. *Energy & Environmental Science* 10, 528–537.
- Zhen, Y., Li, J.-F., 2006. Normal sintering of (K,Na)NbO₃-based ceramics: Influence of sintering temperature on densification, microstructure, and electrical properties. *Journal of the American Ceramic Society* 89, 3669–3675.
- Zhou, C., Liu, W., Xue, D., *et al.*, 2012. Triple-point-type morphotropic phase boundary based large piezoelectric Pb-free material-Ba(Ti_{0.8}Hf_{0.2})O₃–(Ba_{0.7}Ca_{0.3})TiO₃. *Applied Physics Letters* 100, 222910.
- Zuo, R.Z., Rödel, J., Chen, R.Z., Li, L.T., 2006. Sintering and electrical properties of lead-free Na_{0.5}K_{0.5}NbO₃ piezoelectric ceramics. *Journal of the American Ceramic Society* 89, 2010–2015.
- Zushi, J., Ariizumi, T., Kojima, S., Wang, R., Bando, H., 2013. Formation of morphotropic phase boundary in (Na_{0.5}K_{0.5})NbO₃–BaZrO₃–(Bi_{0.5}Li_{0.5})TiO₃ lead-free piezoelectric ceramics. *Japanese Journal of Applied Physics* 52, 07HB02.

Electrostrictive Ceramics and Their Applications

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Electrostriction

Electrostriction is the ability of all insulator or dielectric materials to develop mechanical deformation if subjected to an electric field. The effect is a consequence of the polarization of the ions inside the material. For insulators in standard condition, the net charge is macroscopically zero. Anyway at atomic level, the crystal is composed of positive (cation) and negative (anion) charged ions. When an electric field is applied through the material, cations and anions rearrange their relative position according to the field itself. As a consequence, the macroscopic size of the material changes. The phenomenological equations of the effect report the electrically induced strain (λ) that is proportional to the squared of the applied electric field (E) or polarization (P). In tensor notation it is expressed as:

$$\lambda_{ij} = M_{ijkl} E_k E_l,$$

or

$$\lambda_{ij} = Q_{ijkl} P_k P_l$$

where, M_{ijkl} ($\text{m}^2 \text{V}^{-2}$) and Q_{ijkl} ($\text{C}^2 \text{m}^{-4}$) are the so-called electrostriction coefficients and they are elements of a fourth-rank tensor, meaning that electrostriction takes place in all crystal symmetries (Li *et al.*, 2014). The subscripts i, j, k, l can be abbreviated for material with isotropic or cubic structure, so it is common to use the Voigt notation: M_{ij} and Q_{ij} with $i, j = 1-4$. As reported in the equations, the strain depends on the squared of the electric field ($\propto E_k E_l$). As a consequence, the distortion always develops in the same direction, regardless of the sign of E or P . Fig. 1(a) shows the parabolic field-induced strain in electrostrictive materials. As depicted in Fig. 1(b), if the applied field is not static but oscillating with a frequency f (the case of AC application), the electrostrictor material oscillates with twice the frequency $2f$ (2nd harmonic). The strain can develop either as a contraction ($M, Q < 0$) or an expansion ($M, Q > 0$), depending on the material. When an object withstands a distortion, it generates a related force or stress σ (N m^{-2}). According to Hooke's law:

$$\sigma = Y \times \lambda$$

where Y is Young's modulus, usually reported in MPa. With the same strain, hard materials with high Y develop higher stress compared to soft materials, such as rubber or polymers.

Electrostriction coefficients M and Q are related by the permittivity properties of the material:

$$M_{ijkl} = Q_{ijkl} \{\epsilon_0 (\epsilon_r - 1)\}^2$$

With ϵ_0 is the vacuum permittivity and ϵ_r is the dielectric constant of the material. The use of one coefficient or another depends on the type of material and formalism. In high permittivity dielectrics that show nonlinear polarization or hysteresis, Q is usually preferred. It is worth noticing that for the same Q value, materials with larger ϵ_r deploy larger strain. As electrostriction comes from a fundamental interaction common in all materials, it can change considerably in both magnitude and dynamics depending on the physical properties of the material. Consequently, electrostriction coefficients range across several orders of magnitude depending on the material itself, with a Q from $10^{-3} \text{ m}^4 \text{C}^{-2}$ for ferroelectrics to $10^3 \text{ m}^4 \text{C}^{-2}$ for polymers (Newnham *et al.*, 1997). Furthermore, while most of electrostrictors such as linear dielectrics, ceramics, and perovskites develop a positive strain (expansion), fluorites and polymers can have the opposite behavior (Sundar and Newnham, 1996; Newnham *et al.*, 1997; Zhang *et al.*, 1998; Li *et al.*, 2014).

In materials that are also piezoelectric, the two effects sum up and the general electromechanical effect is written as:

$$\lambda_{ij} = g_{kij} P_k + Q_{ijkl} P_k P_l$$

With g_{kij} (C m^{-2}) piezoelectric coefficient. Electrostriction can be considered as a second-order contribution of the general electromechanical coupling. Usually, the electrostrictive effect is smaller than the linear contribution by few orders of magnitude. Electrostrictive materials, however, show peculiar characteristics such as low hysteresis in the polarization-strain loop and no remnant strain, making them particularly suitable for high accuracy applications (Uchino *et al.*, 1981; Haertling, 1999; Li *et al.*, 2014).

Application

The ability of electrostrictors to convert an electric signal to mechanical distortion has been extensively used in transducing technologies (Meyer *et al.*, 2001; Restagno *et al.*, 2001; Baek *et al.*, 2011; Jones and Nenadic, 2013; Martin *et al.*, 2014). In particular, an actuator is a transducer which function is to displace an object, working as an electrostrictive motor. Actuators are used in devices that need electrical/mechanical signal conversion such as inkjet printer head, micro-pump, and noise cancellation

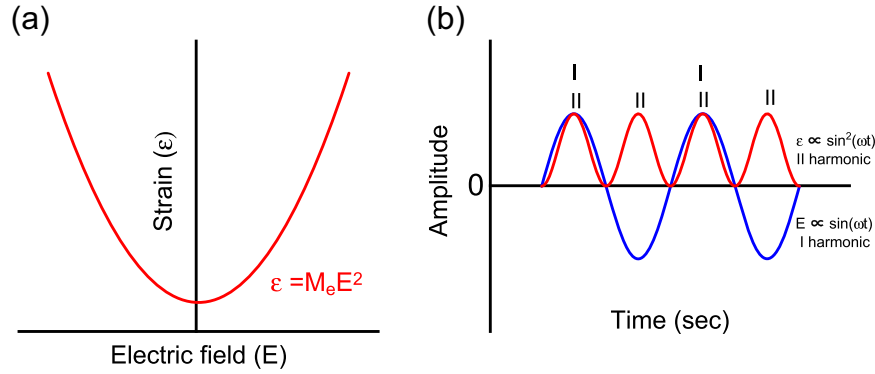


Fig. 1 (a) Strain quadratic response to electric field for electrostrictive materials. (b) Electrostriction dynamics under an applied AC field.

systems. A proper actuator should provide a significant displacement with an electric field as low as possible. Also, the performances should be stable and reproducible, allowing fine control of the actuating process. The average strain of a standard actuator is around 10^{-3} . However, this value can be improved in specific engineered devices such as multilayered actuators, or flexensional actuators (CYMBALS) (Haertling, 1999; Meyer *et al.*, 2001; Uchino, 2008). Transducers can also be used in ultrasound imaging and sensors for diagnostic and sonar devices. An electrostrictive ultrasound device can convert electrical signal in mechanical vibration, generating ultra-acoustic waves with extreme accuracy.

Piezoelectric transducers usually have higher performances. Nonetheless, electrostrictors have many advantages over piezoelectrics, such as high accuracy of the strain-field response (no hysteresis or remnant strain), low creep or aging effects, and high speed response (< 10 ms) (Newnham *et al.*, 1997). Also, they can perform at high temperature and frequency. Such features are useful in optical systems such as interferometric dilatometers and deformable mirrors.

In recent years, electrostrictor materials have been frequently included in miniaturized devices known as micro-electro-mechanical systems (MEMS) (Uchino *et al.*, 1981; Uchino, 2008). MEMS applications are several and heterogeneous: Robotics, micro-motors and electronics, biomedical devices. The preference for electrostrictors over piezoelectrics has several reasons. As in small sized devices the electric field increases, the quadratic effect becomes the main contribution to the electromechanical activity. This effect was shown in amorphous silica glass ($M \approx 10^{-21} \text{ m}^2 \text{ V}^{-2}$). In thin films with a thickness lower than $100 \text{ \AA}$, electrostriction strain is higher than piezoelectric contribution (Newnham *et al.*, 1997). This effect can be exploited in the design of materials with a zero-electromechanical coefficient, useful in devices potentially damaged by electric fields. In MEMS, the electroactive material is integrated as thin films and coupled with substrates, usually Si. Piezoelectrics are hard to integrate into these devices, because of high temperature processes and poling needed and diffusion effects often showed for lead-based piezoelectrics.

Both piezoelectric and electrostrictive materials have a limited role in pure medical application, as the best performing materials are lead-based (PZT, PMN). Moreover, these materials have been banned by the RoHS compliant of 2006, due to environmental awareness. For this reason, many efforts have been made in recent years to find a lead-free alternative.

Half of the global market of actuators is focused in MEMS application, followed by phone and digital cameras or lenses (42%), fuel injectors (5%) and ink cartridges (3.3%) (Jo *et al.*, 2012). These data are updated to 2012 when the market value was around 12 millions of dollars, the double respect to 2009 (Jo *et al.*, 2012).

Microscopic Explanation of Electrostriction

When polarized with an electric field, the ions of the material shift from their original position, causing a mechanical strain. The relative displacement of positive and negative ions should erase each other, and the net strain should be null. However, the energy required to compress an ion-pair (U_c) is usually higher than the energy needed to enlarge it (U_e) (Kittel, 2005; Li *et al.*, 2014). This is clear from the ion-pair potential respect to the equilibrium position showed in Fig. 2. Consequently, the polarization usually results in increasing of the ion-pair bond length and a positive electrostriction coefficient. Nevertheless, for some materials such as fluorites, polarization shrinks the ions-pair, causing a negative electrostriction coefficient (Sundar *et al.*, 1996; Newnham *et al.*, 1997). Also, the ion-pair potential varies depending on the material.

Considering a rigid model of $+q$ and $-q$ charged ions, the potential energy function can be described as (Uchino *et al.*, 1984; Sundar and Newnham, 1996; Li *et al.*, 2014):

$$\Delta U = U(r) - U(r_0) = f(r - r_0)^2 - g(r - r_0)^3$$

Where r is the relative distance of positive and negative ions, r_0 is the equilibrium position and f, g represent the harmonic and anharmonic contribution of the energy. Under an electric field, the strain and polarization can be calculated (Uchino *et al.*, 1984; Sundar and Newnham, 1996; Li *et al.*, 2014):

$$\lambda_1 = (3gq^2/4f^3r_0)E_1^2$$

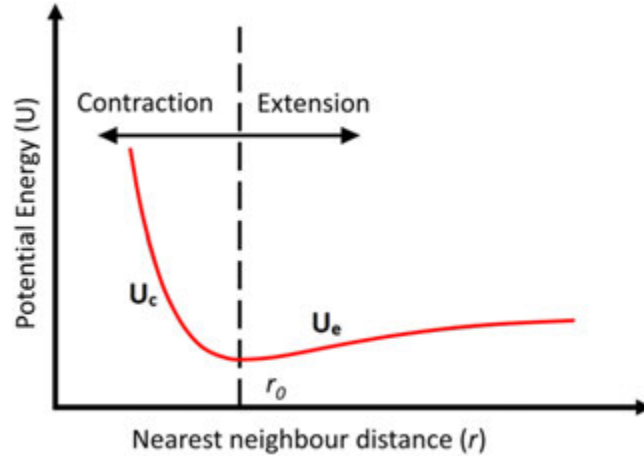


Fig. 2 Ion-pair potential in ionic crystals, r_0 is the equilibrium distance between positive and negative ions.

$$P_1 = (q^2/4\pi r_0^3)E_1$$

As well as the electrostriction coefficient:

$$Q_{11} = 12gr_0^5/fq^2$$

g/f represents the ration between anharmonic and harmonic energy contribution to the overall ion-pair potential. Therefore, high anharmonic component corresponds to high electrostriction coefficient, while f and g are associated with the material microscopic properties such as ionic radius and charge, crystal structure and symmetry. Consequently, compounds with similar microscopic environment show a similar electrostriction magnitude (Warner *et al.*, 1967; Yamada, 1972; Sundar and Newnham, 1996; Sundar *et al.*, 1996; Newnham *et al.*, 1997; Wang *et al.*, 2010; Li *et al.*, 2014).

Thermal Expansion, Newnham's Law, and Materials

In order to describe materials with different anisotropic properties, it is useful to define the hydrostatic electrostriction coefficient Q_h , as the variation of electrical susceptibility with applied hydrostatic pressure. For isotropic or cubic materials, Q_h can be written as:

$$Q_h = 0.5(d\chi/dp) \approx Q_{11} + 2Q_{12}$$

where Q_{11} and Q_{12} are the longitudinal and transverse electrostriction coefficients, respectively. Newnham carried out several studies finding an empirical relationship between macroscopic physical properties and electrostriction coefficients for several kinds of materials (Uchino *et al.*, 1981; Newnham *et al.*, 1997; Li *et al.*, 2014). Electrostriction and thermal expansion both originate from ion-pair potential anharmonicity (Uchino *et al.*, 1981). The thermal expansion coefficient can in fact be written as:

$$\alpha = \frac{3gk_b}{4f^2r_0}$$

With k_b is the Boltzmann's constant and r_0 is the cation–anion distance at equilibrium. Similarly to electrostriction, thermal expansion coefficient α is zero when the anharmonic factor g is 0. Based on Newnham results:

$$\alpha = 4.2 \times 10^{-5} Q_h^{0.5}$$

Thermal expansion and Q_h are related, as both are related to anharmonic ions potential.

Newnham also reported a connection between Q_h and elastic/dielectric effects. As a result, the vast majority of electrostrictive materials follow an empirical relationship:

$$|Q_h| \approx 2.37 \times (S/\epsilon_0 \epsilon_r)^{0.59}$$

Where S is the elastic constant, inverse of Young's modulus. **Fig. 3** shows the logarithm of the electrostriction coefficient, that depends almost linearly on $\log(S/\epsilon_0 \epsilon_r)$. Most of the materials follow this relationship, even if they show very different properties. In **Fig. 3**, we divide the plot into four areas to better group the families of materials. The center of the plot represents materials with high stiffness but low dielectric constant such as linear dielectrics and glass ceramics. The left side includes materials with high dielectric constants such as ferroelectrics and relaxors. On the right side there are polymers, with low permittivity and low stiffness. On the top, defective oxides that share the same properties of linear dielectrics do not follow Newnham's law and show two orders of magnitude higher electrostriction.

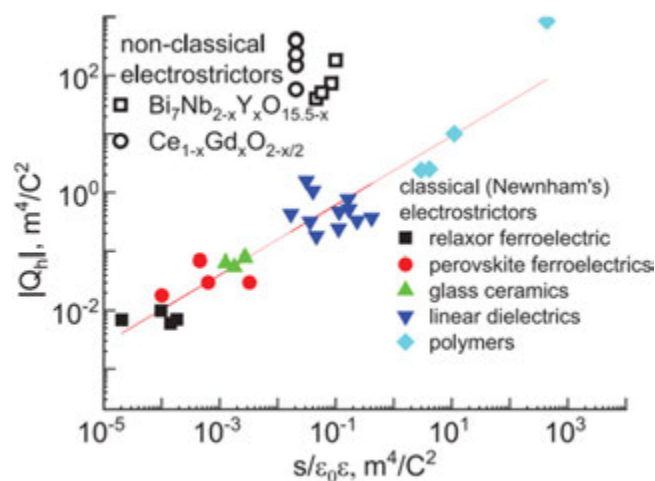


Fig. 3 Hydrostatic electrostriction coefficient for Newnham's and non-classical electrostrictors. Red line: Newnham's law. Reported with permission from Wachtel, E., Frenkel, A.I., Lubomirsky, I., 2018. Anelastic and electromechanical properties of doped and reduced ceria. *Advanced Materials* 30 (41), 1–17. doi:10.1002/adma.201707455, Copyright 2018, Wiley-VCH.

Linear Dielectrics and Glasses Ceramics

Linear dielectrics are materials which polarization depends linearly on the electric field. They can be single crystals, glasses, or ceramics (Newnham *et al.*, 1997; Yimnirun *et al.*, 2002; Li *et al.*, 2014). These materials usually have low dielectric constant ($\epsilon < 10$) and Young's modulus around $Y \approx 10^2$ GPa. Some examples are CaF_2 single crystal or AlN and ceramics, with $Q_h = 0.47$ and $0.3 \text{ m}^4 \text{ C}^{-2}$ respectively (Newnham *et al.*, 1997; Yimnirun *et al.*, 2002). Some ceramics, such as $\text{BaBi}_2\text{Nb}_2\text{O}_9$ reach high permittivity: $\epsilon \approx 400$ (Adamczyk *et al.*, 2006) and $Q_h = 0.038$ (Li *et al.*, 2014).

Perovskite Ferroelectrics and Relaxor Ferroelectrics

Ferroelectrics are materials with domains that are microscopically polarized in random directions. Like piezoelectrics, it is possible to pole ferroelectrics to enhance their performances. Perovskite ferroelectrics show higher dielectric constant respect to linear dielectrics such as SrTiO_3 ($\epsilon = 450$), PbTiO_3 ($\epsilon = 270$) and BaTiO_3 ($\epsilon = 1070$) but similar Young's modulus. The electrostriction coefficients are $Q \approx 0.04 \text{ m}^4 \text{ C}^{-2}$.

Relaxors is a family of ferroelectrics with diffuse phase transition. They show a high dielectric constant ($\epsilon \approx 10^3$) that depends strongly on both temperature and frequency (Moulson and Herbert, 2003; Heywang *et al.*, 2008; You *et al.*, 2009; Cross, 2011). Relaxor ferroelectrics are generally lead-based perovskites with $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3$ structure, where B_1 and B_2 are two different ions. These compounds are frequently used as piezoelectrics, but they also possess high electrostriction coefficient. The interest of research and industry started in the 1980 thanks to the first electrostrictive relaxors: $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN), $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) and $\text{Pb}(\text{La}_{0.09}\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ (PLZT) were studied thanks to the promising performances, with a strain up to 0.3% (Haertling, 1999; Uchino *et al.*, 1981; Blackwood and Ealey, 1993; Haertling, 1999; Moulson and Herbert, 2003; Li *et al.*, 2014). The electrostriction coefficients are about $Q_h = 0.002 \text{ m}^4 \text{ C}^{-2}$ and $M = 2 \times 10^{-18} \text{ m}^2 \text{ V}^{-2}$ for PMN (Sundar *et al.*, 1996). Lead-based piezoelectrics and electrostrictors are used in most of the transducer and actuator devices (Jo *et al.*, 2012) in which a combination of massive displacement and high mechanical reliability is needed (Uchino, 2008). Moreover, most of the relaxors are also piezoelectric, and it is possible to combine the two effects (Haertling, 1999). As said, many efforts have been made to introduce lead-free electromechanical materials, and some relaxor alternatives examples are bismuth or niobium based systems (Jo *et al.*, 2012).

Defective Oxides

Gd-doped ceria (CGO) and (Y, Nb)-stabilized $\delta\text{-Bi}_2\text{O}_3$ have been recently reported to possess high electrostrictor behavior, mostly as thin films (Korobko *et al.*, 2012, 2013; Hadad *et al.*, 2016; Santucci *et al.*, 2019). These two materials are both oxides with fluorite structure and a large amount of defects in the form of oxygen vacancies. Being ceramics, their Young's modulus is high: $Y_{\text{CGO}} = 200$ GPa, $Y_{\text{Bi}_2\text{O}_3} = 85$ GPa. They also have low dielectric constants: $\epsilon_{\text{CGO}} \approx 28$, $\epsilon_{\text{Bi}_2\text{O}_3} \approx 26\text{--}30$. The mechanism behind electrostriction in these materials is not the same, and it is related to the local geometry around the oxygen vacancies and their configuration inside grain boundaries (Li *et al.*, 2016; Kabir *et al.*, 2019).

In a pure crystal, one oxygen vacancy forms an octahedron shaped complex with six oxygen atoms. When the field is applied the octahedron withstands a rearrangement including all the oxygen atoms, amplifying the effect. For this reason, the electrostrictive coefficient results particularly high in both materials: $Q_h = 124 \text{ m}^4 \text{ C}^{-2}$ for CGO and $40\text{--}182 \text{ m}^4 \text{ C}^{-2}$ for $\delta\text{-Bi}_2\text{O}_3$. CGO and $\delta\text{-Bi}_2\text{O}_3$ do not follow the trend of Newnham's electrostrictors. Even though possessing the same mechanical/electrical

properties of linear dielectrics in fact, they place two-three orders of magnitude above similar materials. This is attributed to the particular mechanism involving oxygen vacancies. An extensive analysis of other materials with a high amount of vacancies would bring new insight of the effect, maybe showing a new trend for defective oxides.

Although too early for commercial devices, CGO showed good results as membrane and bulk (Mishuk *et al.*, 2017; Ushakov *et al.*, 2017; Kabir *et al.*, 2019). Being a non-toxic and environmentally friendly material, CGO opens new possibilities in high performance bio-compatible and medical application. CGO is also compatible with Si and ceramic electrodes (Santucci *et al.*, 2019) and does not need pre-processing or poling, making it a promising candidate for a new generation of lead-free MEMS.

Polymers

Ferroelectric polymers such as polyvinylidene fluoride (PVDF) and its copolymers, show drastically different mechanical properties respect to ceramics and glasses. Polymers are flexible, with a low density and small Young's modulus ($\approx 10^3$ MPa). They also display a low relative permittivity ($\epsilon \approx 10$) (Newnham *et al.*, 1997). Under an electric field, polymers deploy large strain of the order of 0.25% (Newnham *et al.*, 1997), with resulting electrostriction coefficients around $Q_h \approx 2 \text{ m}^4 \text{ C}^{-2}$. Particular interest has been given to polyurethane, a non-ferroelectric elastomer. Elastomers have usually very low stiffness ($Y = 40$ MPa), that allows these polymers to deploy a high strain response with high electrostriction coefficient of $Q_h \approx 10^3 \text{ m}^4 \text{ C}^{-2}$. Other polymer's properties include frequency dependence field induced strain and high Maxwell stress contribution. In terms of displacement, polymers are comparable with the best relaxor electrostrictors (PMN, PZT) (Yimnirun *et al.*, 2002). Polymers do not generate high stress because of the small Young's modulus, making them difficult to integrate with force related applications. They are however cheap and they comply with complex shapes and surfaces. Polymers are frequently used in composite technology coupled with electromechanical ceramics (Moulson and Herbert, 2003). The properties of the devices are usually engineered to the specific application, and the connectivity between the two materials has a significant role. Composites materials offer advantages in sonar and medical ultrasonic imaging, in which the polymer usually faces soft tissues (Moulson and Herbert, 2003).

Summary

Electrostriction effect is a mechanism that all materials possess and it consists of a mechanical displacement as a response to an electric field. As the strain-field relationship is squared, electrostriction distortion does not depend on the direction of the electric field and happens with twice its frequency. While usually smaller than the piezoelectric effect, electrostriction has some peculiar characteristic useful in applications such as high temperature and frequency operation. Also, electrostrictor materials do not need poling or pre-process to be fully operational. Electrostrictors are particularly suitable for MEMS. For low dimension devices, a higher electric field goes through the material, exploiting electrostrictive behavior more than piezoelectric. Also, electrostriction related strain is highly reproducible and without strain-field hysteresis. That makes electrostrictors valuable in high precision actuators.

Microscopically, electrostriction is due to the anharmonicity of ion pair potential. When the field is applied, the ions rearrange their relative position and are set apart. The species of ion and crystal structure have a major role in the magnitude of electrostriction. Elastic/dielectric properties are also related to the electromechanical activity. Particularly, $\log(Q_h)$ depends almost linearly on $\log(S/\epsilon_0\epsilon_r)$. Most of the electrostrictive materials follow this trend. The most performing materials are lead-based relaxor ferroelectrics, which possess high permittivity and Young's modulus. Polymers are also suitable for particular application thanks to high field induced strain that, however, cannot be converted in stress because polymers low Young's modulus. Defective oxides do not follow this trend: while having mechanical and electrical properties similar to linear dielectrics, they show two-three order of magnitude higher electrostriction coefficient. This is due to a peculiar effect involving oxygen vacancies and a field induced local rearrangement that amplifies the performances.

References

- Adamczyk, M., Ujma, Z., Pawełczyk, M., 2006. Dielectric properties of $\text{BaBi}_2\text{Nb}_2\text{O}_9$ ceramics. *Journal of Materials Science* 41, 5317–5322. doi:10.1007/s10853-006-0300-8.
- Baek, S.H., Park, J., Kim, D.M., *et al.*, 2011. Giant piezoelectricity on Si for. *Science* 334 (November), 958–961.
- Blackwood, G.H., Ealey, M.A., 1993. Electrostrictive behavior in lead magnesium niobate (PMN) actuators. Part I: Materials perspective. *Smart Materials and Structures* 2 (2), 124–133. doi:10.1088/0964-1726/2/2/008.
- Correia, T.M., Young, J.S., Whatmore, R.W., *et al.*, 2009. Investigation of the electrocaloric effect in a $\text{PbMg}_{2/3}\text{Nb}_{1/3}\text{O}_3$ - PbTiO_3 relaxor thin film. *Applied Physics Letters* 95, 1–4. doi:10.1063/1.3257695.
- Cross, L.E., 2011. Relaxor ferroelectrics. *Ferroelectrics* 76 (1), 241–267. doi:10.1080/00150198708016945.
- Hadad, M., Ashraf, H., Mohanty, G., Sandu, C., Murali, P., 2016. Key-features in processing and microstructure for achieving giant electrostriction in gadolinium doped ceria thin films. *Acta Materialia* 118, 1–7. doi:10.1016/j.actamat.2016.07.025.
- Haertling, G.H., 1999. Ferroelectric ceramics: History and technology. *Journal of the American Ceramic Society* 82 (4), 797–818. doi:10.1111/j.1151-2916.1999.tb01840.x.
- Heywang, W., Lubitz, K., Wersing, W., 2008. *Piezoelectricity: Evolution and Future of a Technology*. Springer.
- Jo, W., Dittmer, R., Acosta, M., *et al.*, 2012. Giant electric-field-induced strains in lead-free ceramics for actuator applications – Status and perspective. *Journal of Electroceramics* 29 (1), 71–93. doi:10.1007/s10832-012-9742-3.
- Jones, T.B., Nenadic, N.G., 2013. *Electromechanics and MEMS*. Cambridge University Press.

- Kabir, A., Santucci, S., Nong, N.V., *et al.*, 2019. Effect of oxygen defects blocking barriers on gadolinium doped ceria (GDC) electro-chemo-mechanical properties. *Acta Materialia* 174, 53–60. doi:10.1016/j.actamat.2019.05.009.
- Kittel, C., 2005. *Introduction to Solid State Physics*. John Wiley & Sons, Inc.
- Korobko, R., Patlolla, A., Kossoy, A., *et al.*, 2012. Giant electrostriction in Gd-doped ceria. *Advanced Materials* 24 (43), 5857–5861. doi:10.1002/adma.201202270.
- Korobko, R., Wachtel, E., Lubomirsky, I., 2013. Cantilever resonator based on the electrostriction effect in Gd-doped ceria. *Sensors and Actuators A: Physical* 201, 73–78. doi:10.1016/j.sna.2013.06.021.
- Li, F., Jin, L., Xu, Z., Zhang, S.J., 2014. Electrostrictive effect in ferroelectrics: An alternative approach to improve piezoelectricity. *Applied Physics Reviews* 1 (1), doi:10.1063/1.4861260.
- Li, Y.Y., Kraynis, O., Kas, J., *et al.*, 2016. Geometry of electromechanically active structures in gadolinium-doped cerium oxides. *AIP Advances* 6 (5), doi:10.1063/1.4952645.
- Martin, K., Lindsey, B.D., Ma, J.G., *et al.*, 2014. Dual-frequency piezoelectric transducers for contrast enhanced ultrasound imaging. *Sensors* 14 (11), 20825–20842. doi:10.3390/s141120825.
- Meyer, R.J., Dogan, A., Yoon, C., Pilgrim, S.M., Newnham, R.E., 2001. Displacement amplification of electroactive materials using the cymbal flextensional transducer. *Sensors and Actuators A: Physical* 87 (3), 157–162. doi:10.1016/S0924-4247(00)00489-1.
- Mishuk, E., Makagon, E., Wachtel, E., 2017. Self-supported Gd-doped ceria films for electromechanical actuation: Fabrication and testing. *Sensors and Actuators A: Physical* 264, 333–340. doi:10.1016/j.sna.2017.07.047.
- Moulson, A.J., Herbert, J.M., 2003. *Electroceramics*. Wiley. pp. 339–409. doi:10.1002/0470867965.
- Newnham, R.E., Sundar, V., Yimnirun, R., Su, J., Zhang, Q.M., 1997. Electrostriction: Nonlinear electromechanical coupling in solid dielectrics. *Journal of Physical Chemistry B* 101 (48), 10141–10150. doi:10.1021/jp971522c.
- Restagno, F., Crassous, J., Charlaix, E., Monchanin, M., 2001. A new capacitive sensor for displacement measurement in a surface force apparatus. *Measurement Science and Technology* 12 (1), 16–22. doi:10.1088/0957-0233/12/1/302.
- Santucci, S., Zhang, H.W., Sanna, S., Pryds, N., Esposito, V., 2019. Enhanced electro-mechanical coupling of $\text{TiN/Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ thin film electrostrictor. *APL Materials* 7 (7), 071104doi:10.1063/1.5091735.
- Sundar, V., Newnham, R.E., 1996. Converse method measurements of electrostriction coefficients in low-K dielectrics. *Materials Research Bulletin* 31 (5), 545–554. doi:10.1016/S0025-5408(96)00035-9.
- Sundar, V., Li, J.-F., Viehland, D., Newnham, R.E., 1996. Interferometric evaluation of electrostriction coefficients. *Materials Research Bulletin* 31 (5), 555–563.
- Uchino, K., 2008. Piezoelectric actuators 2006. *Journal of Electroceramics* 20, 301–311. doi:10.1007/s10832-007-9196-1.
- Uchino, K., Nomura, S., Cross, L.E., Newnham, R.E., Jang, S.J., 1981. Electrostrictive effect in perovskites and its transducer applications. *Journal of Materials Science* 16 (3), 569–578. doi:10.1007/BF02402772.
- Uchino, K., Nomura, S., Vedom, K., Newnham, R.E., Cross, L.E., 1984. Pressure dependence of the refractive index and dielectric constant in a fluoroperovskite, KMgF_3 . *Physical Review B* 29 (12), 6921–6925. doi:10.1103/PhysRevB.29.6921.
- Ushakov, A.D., Mishuk, E., Makagon, E., *et al.*, 2017. Electromechanical properties of electrostrictive CeO_2 :Gd membranes: Effects of frequency and temperature. *Applied Physics Letters* 110 (14), 142902.
- Wang, J.J., Meng, F.Y., Ma, X.Q., Xu, M.X., Chen, L.Q., 2010. Lattice, elastic, polarization, and electrostrictive properties of BaTiO_3 from first-principles. *Journal of Applied Physics* 108 (3), doi:10.1063/1.3462441.
- Warner, A.W., Onoe, M., Coquin, G.A., 1967. Determination of elastic and piezoelectric constants for crystals in class (3 m). *The Journal of the Acoustical Society of America* 42 (6), 1223–1231. doi:10.1121/1.1910709.
- Yamada, T., 1972. Electromechanical properties of oxygen-octahedra ferroelectric crystals. *Journal of Applied Physics* 43 (2), 328–338. doi:10.1063/1.1661117.
- Yimnirun, R., Moses, P.J., Newnham, R.E., Meyer, R.J., 2002. Electrostrictive strain in low-permittivity dielectrics. *Journal of Electroceramics* 8 (2), 87–98. doi:10.1023/A:1020543610685.
- Zhang, Q.M., Bharti, V., Zhao, X., 1998. Giant electrostriction and relaxor ferroelectric behavior in electron-irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer. *Science* 280, 2101–2104. doi:10.1126/science.280.5372.2101.

Low-Loss Ceramics in Mobile Communications

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Introduction

Low-loss ceramics in this chapter cover the low-loss dielectric or insulating ceramics for dielectric resonators, multilayer substrates, multichip modules (MCMs), and dielectric antennas. The importance of low-loss ceramics in high-frequency applications is rapidly increasing with the widespread use of these materials for mobile communications, intelligent transportation systems (ITSs), wireless local area networks (LANs), bluetooth systems, etc.

Dielectric Resonator

Dielectric Resonator Material

Study of low-loss and temperature stable dielectric ceramics focusing on microwave applications began in the 1970s, referred to as class I ceramic capacitor materials. The first practically applicable design of a dielectric resonator filter was reported in 1974. A dielectric resonator-controlled local oscillator (DRO; 11–13 GHz) for satellite broadcasting (BS) receiver was introduced in 1975. The advantages of using dielectric resonators include the miniaturization of microwave resonators resulting from the relatively high permittivity of ceramics; very high unloaded Q value owing to extremely low dielectric loss; and high temperature stability of resonant frequencies owing to the small temperature variation of the dielectric constant (O'Bryan *et al.*, 1974; Kawashima *et al.*, 1983; Wakino *et al.*, 1984; Tamura *et al.*, 1984; Zhang *et al.*, 2015; Tyagi, 2014). Moreover, the temperature coefficient of resonant frequency, τ_f , can be optimized by changing the composition of the ceramic so as to compensate for the temperature deviation in the whole system, including the surrounding circuit and components. Much effort has been concentrated on decreasing the dielectric loss of these materials. The origins and mechanism of dielectric loss at microwave and millimeter wave frequencies are discussed in the Section on Dielectric Loss.

Dielectric Properties

To satisfy the low-loss requirements, dielectric resonator materials are basically made of paraelectric ceramics. According to the classical lattice dynamics theory of ionic crystals, the complex permittivity ϵ^* at an angular frequency ω is given by the following dielectric dispersion equation, which is expressed as the superposition of electronic and ionic polarization:

$$\epsilon^*(\omega) = \epsilon(\infty) + \sum_i \frac{4\pi\rho_i \cdot \omega_i^2}{\omega_i^2 - \omega^2 - j\gamma_i\omega} \quad [1]$$

where ω_i , ρ_i , and γ_i are the eigenfrequency, strength, and damping constant, respectively, of the i th IR active lattice vibration modes, and $\epsilon(\infty)$ is the permittivity due to the electronic polarization. The summation is taken over the lattice vibrations in the unit cell. Equation [1] is resolved into real and imaginary parts as follows:

$$\epsilon'(\omega) = \epsilon(\infty) + \sum_i \frac{4\pi\rho_i \cdot \omega_i^2 \cdot (\omega_i^2 - \omega^2)}{(\omega_i^2 - \omega^2)^2 - (\gamma_i \cdot \omega)^2} \quad [2]$$

$$\epsilon''(\omega) = \sum_i \frac{4\pi\rho_i \cdot \omega_i^2 \cdot (\gamma_i \cdot \omega)}{(\omega_i^2 - \omega^2)^2 - (\gamma_i \cdot \omega)^2} \quad [3]$$

As the condition $\omega^2 \ll \omega_i^2$ holds reasonably at microwave and millimeter wave frequencies, and assuming that γ_i is not large, the following approximations are derived from eqns [2] and [3]:

$$\epsilon'(\omega) = \epsilon(\infty) + \sum_i 4\pi\rho_i \quad [4]$$

$$\frac{1}{Q} = \tan\delta = \frac{\epsilon''}{\epsilon'} = \frac{\sum_i (4\pi\rho_i \cdot \gamma_i / \omega_i^2)}{\omega(\infty) + \sum_i 4\pi\rho_i \cdot \omega} \quad [5]$$

$$Q \cdot f = \text{const} \quad [6]$$

Thus, the dielectric constant is independent of frequency and the product of Q and measured frequency is the material constant in the frequency range 10^9 – 10^{11} Hz.

Table 1 Dielectric properties of representative low-loss dielectric materials

Materials	ϵ_r	$Q \times f$ (GHz)	τ_f (ppm °C ⁻¹)	β (ppm °C ⁻¹)
MgTiO ₃ -CaTiO ₃	21	56000	0 ... 6	-0.061
Ba(Sn,Mg,Ta)O ₃	24	240000	0 ... 4	-0.009
Ba(Mg,Sb,Ta)O ₃	24	300000	0 ... 6	-0.009
Ba(Zr,Zn,Ta)O ₃	30	180000	0 ... 6	-0.006
Ba(Co,Zn,Nb)O ₃	34	120000	0 ... 8	+0.002
Ba ₂ Ti ₉ O ₂₀	38	55000	3.5	+0.020
(Zr,Sn)TiO ₄	38	60000	0 ... 6	-0.005
CaTiO ₃ -NdAlO ₃	43	47000	0	
Ba(Sm,Nd) ₂ Ti ₄ O ₁₂	82	10000	-6 ... 6	+0.024
(Ba,Pb)Nd ₂ Ti ₄ O ₁₂	92	5000	0 ... 6	-0.105
(Ba,Pb)(Nd,Bi) ₂ Ti ₄ O ₁₂	110	2500	-2 ... 8	+0.006

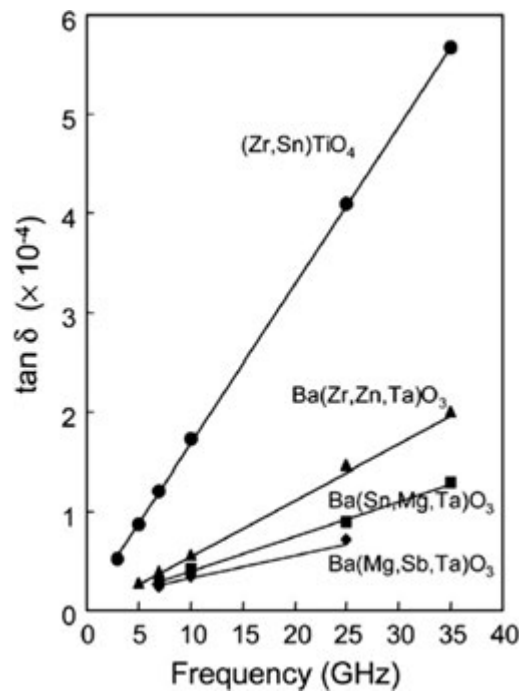
**Fig. 1** Frequency dependence of $\tan \delta$ of typical low-loss ceramics at microwave and millimeter wave frequency.

Table 1 lists the dielectric properties of dielectric resonator materials used in practice. **Fig. 1** shows the frequency dependence of $\tan \delta$ from 1 to 35 GHz for representative materials from **Table 1**. As predicted by eqn [5], $\tan \delta$ increases proportionately to frequency. These dielectric properties have been measured by the dielectric resonator method from 1 to 10 GHz (Kobayashi and Katoh, 1985) and by the specially designed TE_{01δ} mode cavity method, shown in **Fig. 2** (Ishikawa *et al.*, 1990), using a non-radiative dielectric waveguide (NRD) (Yoneyama and Nishida, 1981) from 10 to 35 GHz.

The temperature coefficient of resonant frequency, τ_f , is approximated by

$$\tau_f = -\frac{1}{2}\tau_\epsilon - \alpha \quad [7]$$

where τ_ϵ is the temperature coefficient of the dielectric constant and α is the linear thermal expansion coefficient of the dielectric specimen.

Fig. 3 shows the measured temperature dependence of resonant frequency and $\tan \delta$ for representative materials. The term β in **Fig. 3** is the coefficient of the quadratic term in the polynomial expansion equation of permittivity to temperature. Accurately controlled dielectric resonators with desired τ_f values and permittivities between 20 and 95 are available depending on the particular application.

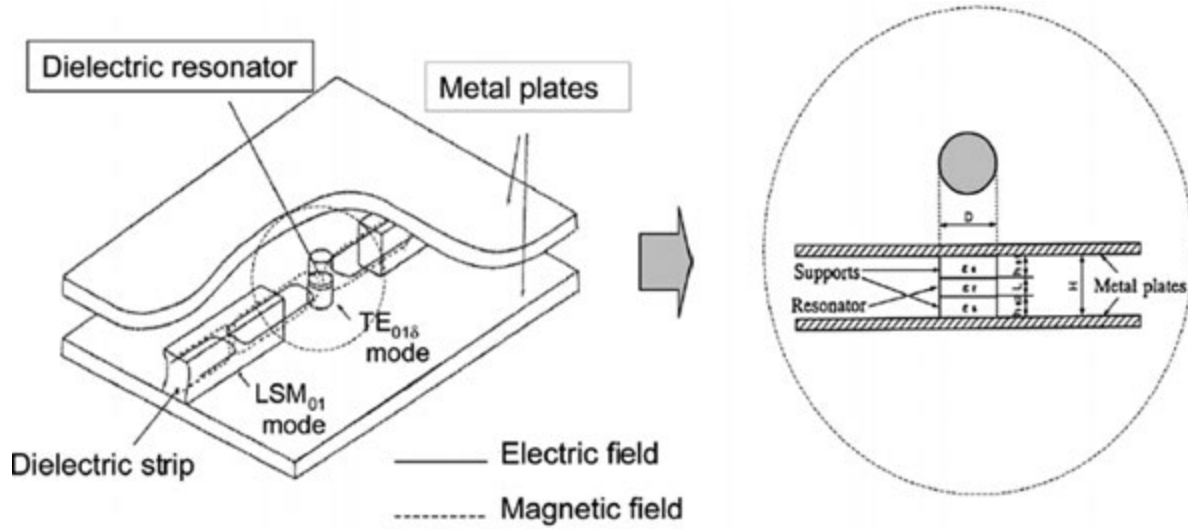


Fig. 2 Test fixture of complex permittivity at millimeter wave frequency.

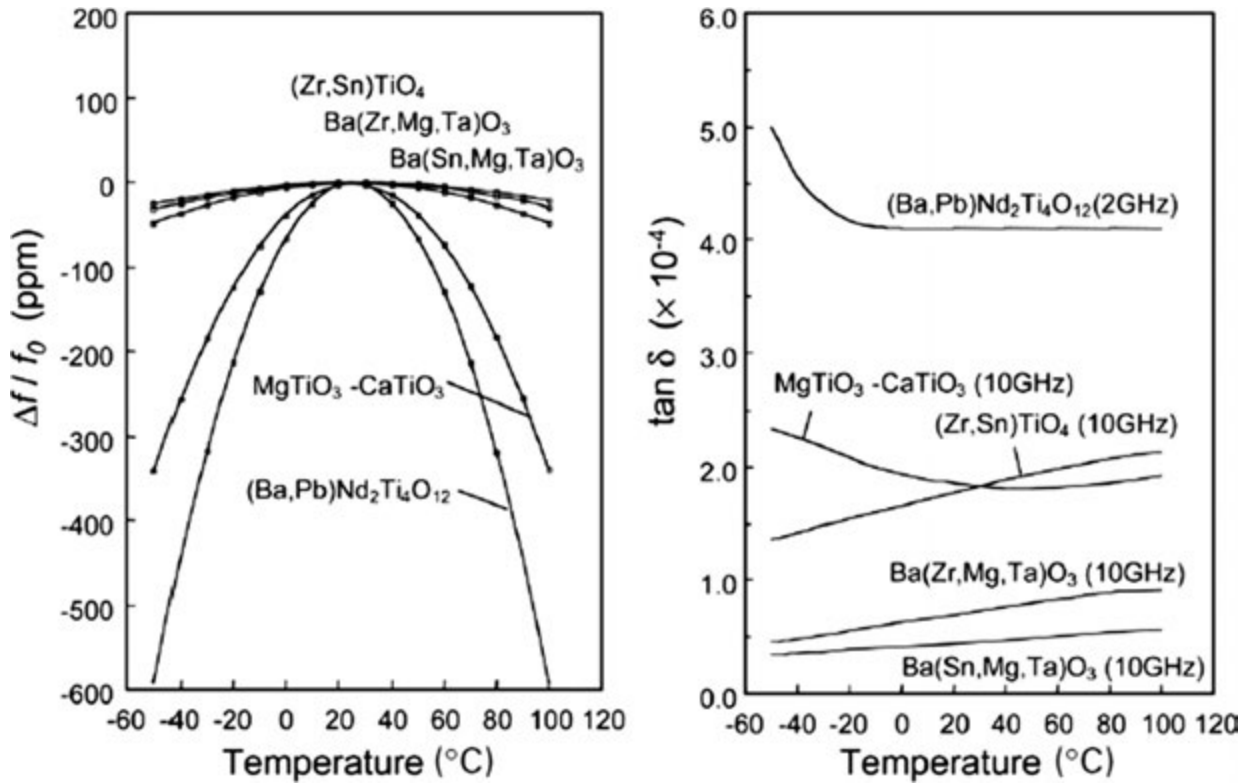


Fig. 3 Temperature dependence of resonant frequency and $\tan \delta$.

Dielectric Loss

The origin of the intrinsic damping constant γ in eqn [3] comes from the anharmonic terms due to the nonlinear property of the crystal field by which the phonons of IR active modes irreversibly convert to thermal phonons. As the phonon energy follows the Planck distribution, γ is given by (Maradudin and Fein, 1962).

$$\gamma \propto |\phi_3|^2 \times T + \dots \quad [8]$$

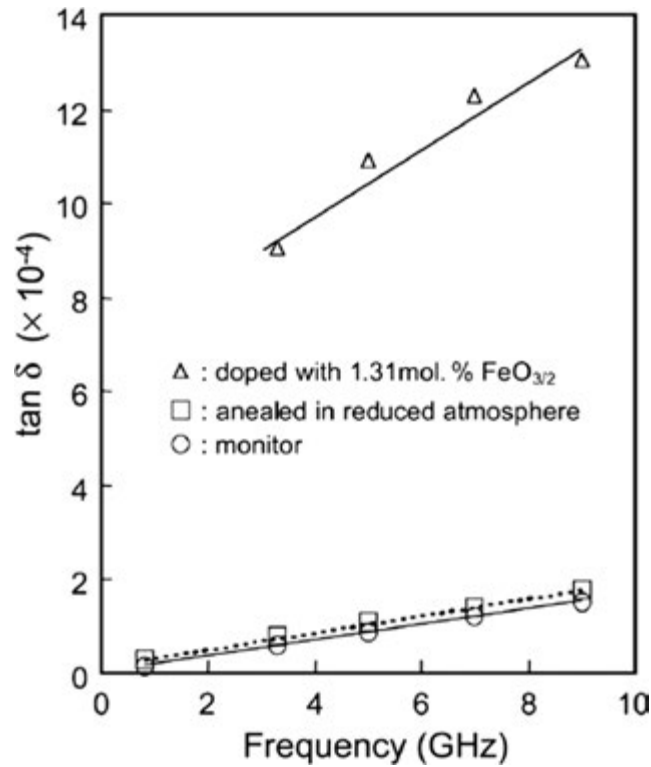


Fig. 4 Effect of oxygen vacancy and impurity on $\tan \delta$ of $(\text{Zr,Sn})\text{TiO}_4$.

where ϕ_3 is the third anharmonic term of the Hamiltonian of the crystal. Thus, the dielectric loss tangent increases in proportion to temperature if abnormal phenomena such as phase transition do not occur in the observed temperature range.

Lattice defect is another origin of $\tan \delta$ in addition to the intrinsic anharmonicity of the crystal Hamiltonian. Lattice vacancies and/or inclusions cause a deformation in crystal field and create an anharmonic term in the crystal Hamiltonian. Beside these origins, one has to consider secondary causes such as the influence of grain boundary discontinuity. **Fig. 4** shows the experimental results of investigating the effect of oxygen vacancy and impurity on $\tan \delta$ for $(\text{Zr,Sn})\text{TiO}_4$ dielectric resonator (Maradudin and Fein, 1962; Tamura, 1994). As **Fig. 4** shows, the well-prepared reference sample has the lowest $\tan \delta$ and satisfies the constant $Q \cdot f$ relationship predicted from eqn [5]. When oxygen vacancies of approximately 10^3 ppm are introduced in $(\text{Zr,Sn})\text{TiO}_4$ ceramics by annealing in a reducing atmosphere, $\tan \delta$ increases as much as 0.2×10^{-4} at every frequency, thus $Q \cdot f$ increases at lower frequency. When the specimen is doped with 1.3×10^4 ppm $\text{FeO}_{3/2}$, $\tan \delta$ increases dramatically. An oxygen vacancy and a substituted iron ion have effective charge deviations of $+2e$ and $-e$ ($-e$ is electron charge) from the defect free state, respectively, in a unit cell of $(\text{Zr,Sn})\text{TiO}_4$ crystal (Tamura, 1994; Michiura *et al.*, 1995). The random distribution of these charge defects increases $\tan \delta$ at microwave and millimeter wave frequencies (Schlömann, 1964).

In other words, how perfect the crystal lattice at the grain and space-charge free grain boundary is, is a key factor in manufacturing low-loss ceramics. Prolonged sintering over 100 h improves the Q value owing to the formation of a well-ordered superlattice structure (Kawashima *et al.*, 1983).

Applications

Dielectric resonator

Fig. 5 shows the structure and electromagnetic field distribution of the most commonly used three dominant modes (TEM, TM_{010} , and $\text{TE}_{01\delta}$) for dielectric resonators.

The TEM mode dielectric resonator is characterized by a coaxial waveguide mode field distribution with standing wave of a quarter wavelength. This mode dielectric resonator provides the most significant size reduction effect but the highest degradation of unloaded Q of the three modes.

The TM_{010} mode dielectric resonator is characterized by a TM mode field distribution along the resonator axis. This mode resonator has medium levels of unloaded Q and size reduction effect, between that of the $\text{TE}_{01\delta}$ and TEM mode resonators.

The $\text{TE}_{01\delta}$ mode dielectric resonator is characterized by a dominant TE mode field distribution, the field of which leaks at both ends of the resonator in the direction of wave propagation with rapid attenuation. Since the $\text{TE}_{01\delta}$ mode resonator has no directly attached conductor, the highest unloaded Q can be achieved using this mode.

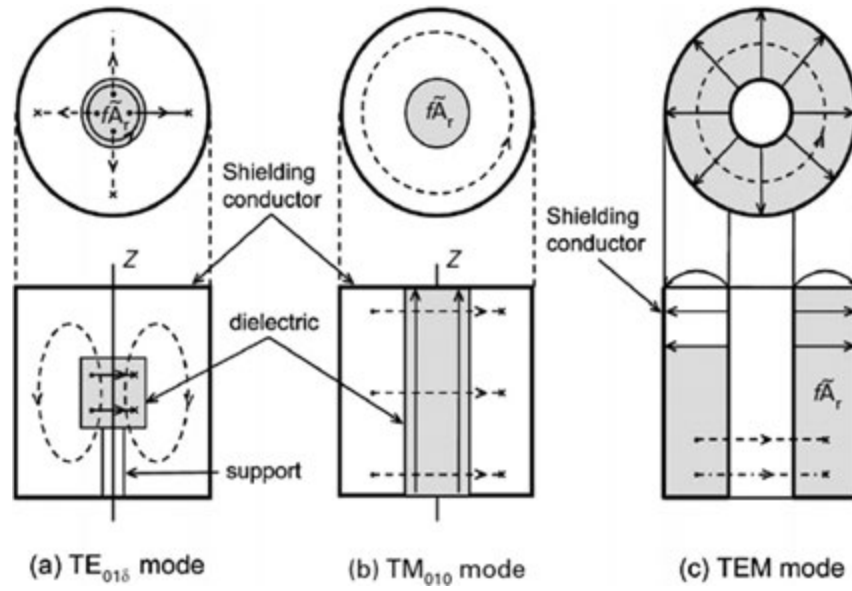


Fig. 5 Schematic structure and electromagnetic field distribution of three dominant modes TEM, TM_{010} , and $TE_{01\delta}$.

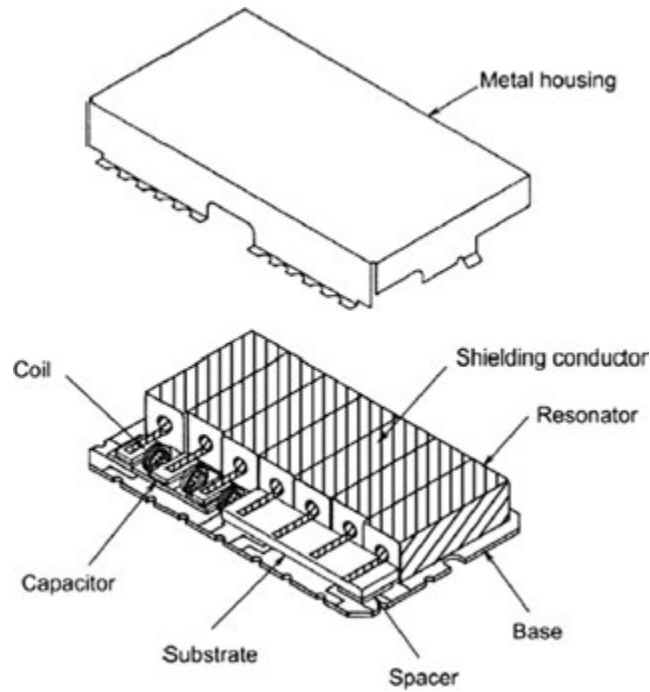


Fig. 6 Schematic structure of antenna duplexer for a mobile telephone.

Total unloaded Q , Q_u , is broken down as follows:

$$\frac{1}{Q_u} = \frac{1}{Q_d} + \frac{1}{Q_c} + \frac{1}{Q_r} \quad [9]$$

where Q_d , Q_c , and Q_r are Q factors from dielectric loss, current loss, and radiation loss, respectively. Practically, the loss owing to radiation can be neglected when the resonator is enclosed in a metallic case.

Antenna duplexer of portable telephones

Fig. 6 shows an example of an antenna duplexer. To realize the ultimate miniaturization of the device, the quarter wavelength TEM mode dielectric resonator is preferably used for this application.

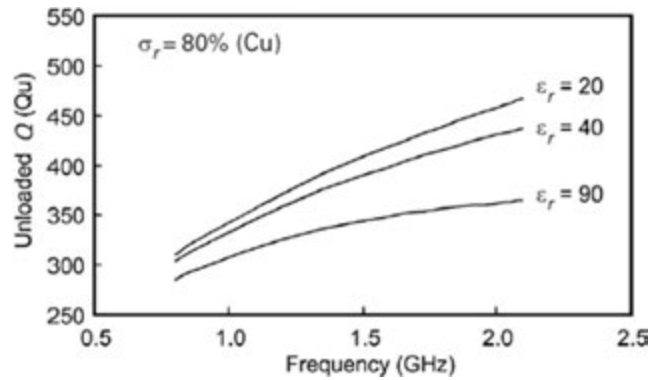


Fig. 7 Frequency dependence of unloaded Q of $\lambda/4$ TEM mode DR with 3 mm diameter.

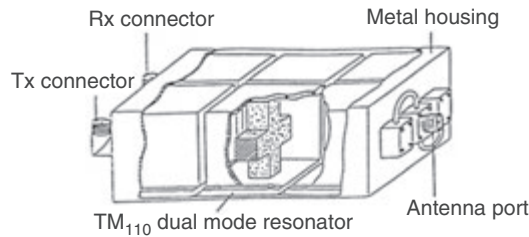


Fig. 8 TM_{010} dual-mode power filter for cellular base station.

With small-size TEM mode resonators, a large proportion of power loss comes from current loss. **Fig. 7** shows the unloaded Q of a $\lambda/4$ TEM mode dielectric resonator with an outer diameter of 3 mm. In the calculation of copper loss, the conductivity of $\sigma = 4.8 \times 10^7 \text{ Sm}^{-1}$ (approximately 80% of bulk value) is chosen, which is practically guaranteed by the firing of silver paste or by electroless copper plating.

To realize the miniaturization of filters with longer wavelength of 900 MHz band antenna duplexer, the high dielectric constant materials $(\text{Pb,Ba})\text{Nd}_2\text{Ti}_4\text{O}_{12}$ or $\text{Ba}(\text{Bi,Nd})_2\text{Ti}_4\text{O}_{12}$ with ϵ_r of 90 are widely used. For the shorter wavelength 2 GHz band, medium dielectric constant (from 20 to 40) with lower loss materials are used to obtain higher unloaded Q .

Filters in cellular base stations

With regard to the power filters for cellular base stations, as low as possible dielectric loss and nonlinear dielectric properties are required so as to prevent heat generation and interference between signal channels.

Fig. 8 shows an antenna duplexer for a cellular base station using TM_{010} dual-mode dielectric resonators (Ishikawa *et al.*, 1992). This filter can be applied for high-power operation with the help of heat transportation to the metal cavity through directly applied electrodes on the ends of the resonator body.

$(\text{Zr,Sn})\text{TiO}_4$, $\text{CaTiO}_3\text{-NdAlO}_3$, and $\text{Ba}(\text{Zr,Zn,Ta})\text{O}_3$ are used for these applications, as these materials satisfy the high ϵ_r , high Q value, and low distortion requirements.

Fig. 9 shows the measured result of the intermodulation level owing to third harmonic distortion at 800 MHz (Nishikawa *et al.*, 1989; Tamura *et al.*, 1989a). The distortion level of $(\text{Zr,Sn})\text{TiO}_4$ material is better than -140 dBc at a field intensity of $6 \times 10^4 \text{ Vm}^{-1}$, which is applicable without cross-talk problems to the filters in cellular base stations with an maximum input power of 500 W.

Millimeter wave applications

Although their dielectric constants are not very high, the complex perovskite materials based on $\text{Ba}(\text{Zn,Ta})\text{O}_3$ and $\text{Ba}(\text{Mg,Ta})\text{O}_3$ have very high Q values suitable for millimeter wave applications. **Fig. 10** shows the TE_{010} mode dielectric filter with central frequency of 30 GHz (Ishikawa *et al.*, 1997). The TE_{010} mode resonator is made of $\text{Ba}(\text{Sn,Mg,Ta})\text{O}_3$ pore-free substrate with $\epsilon_r = 24$ and has an unloaded Q of 1600.

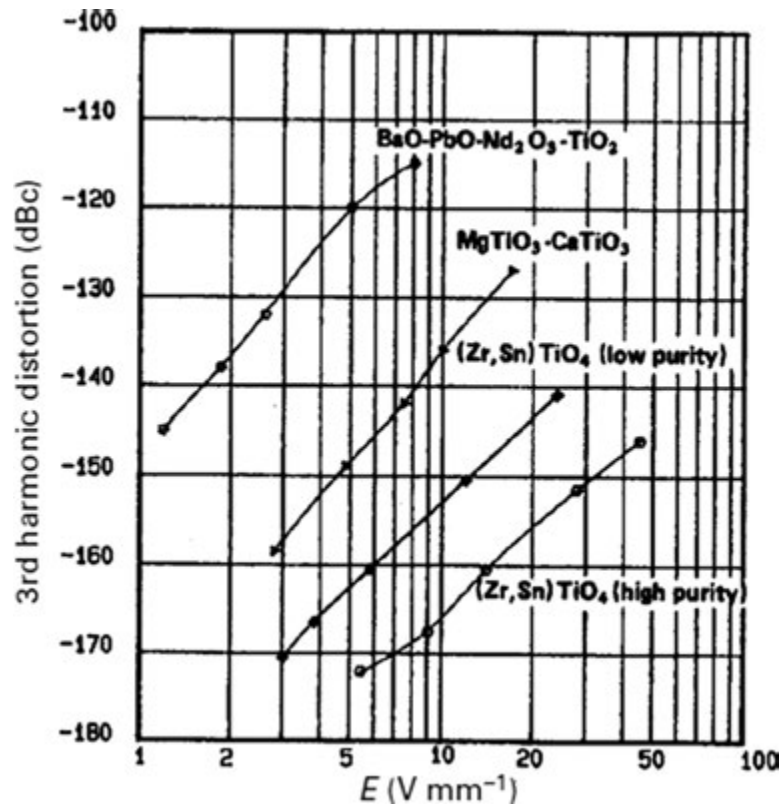


Fig. 9 Third harmonic distortion vs. electric field for low-loss ceramics.

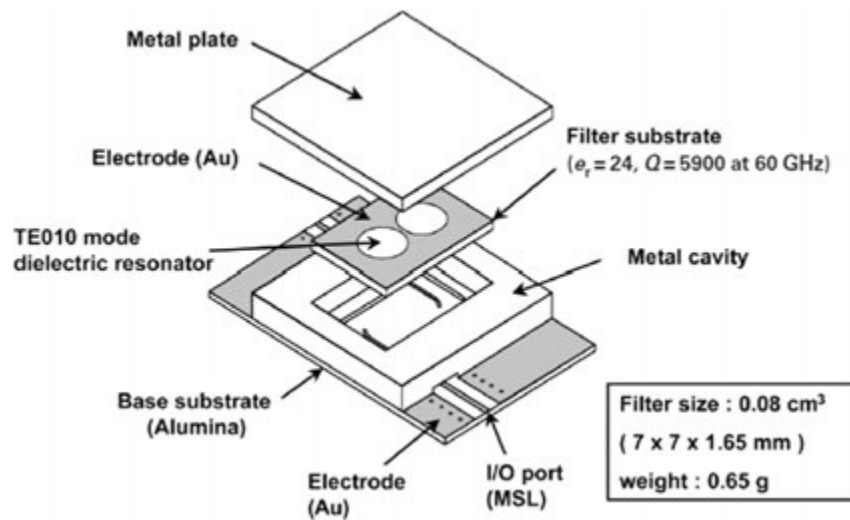


Fig. 10 Schematic structure of 30 GHz TE₀₁₀ mode filter.

Materials for high-temperature superconductivity

Much effort has been made to realize microwave filters for cellular base stations by using high-temperature superconductors. YBa₂Cu₃O_{7- δ} (YBCO) thin films on LaAlO₃ substrates are used for these applications. As shown in Fig. 11, Ba(Sn,Mg,Ta)O₃ has an extremely high $Q \cdot f$ value of 10⁶ GHz at 70 K (Tamura *et al.*, 1989b), so that this material is a promising candidate as a temperature-stable and ultralow-loss substrate for microwave circuit incorporation with high-temperature superconductors.

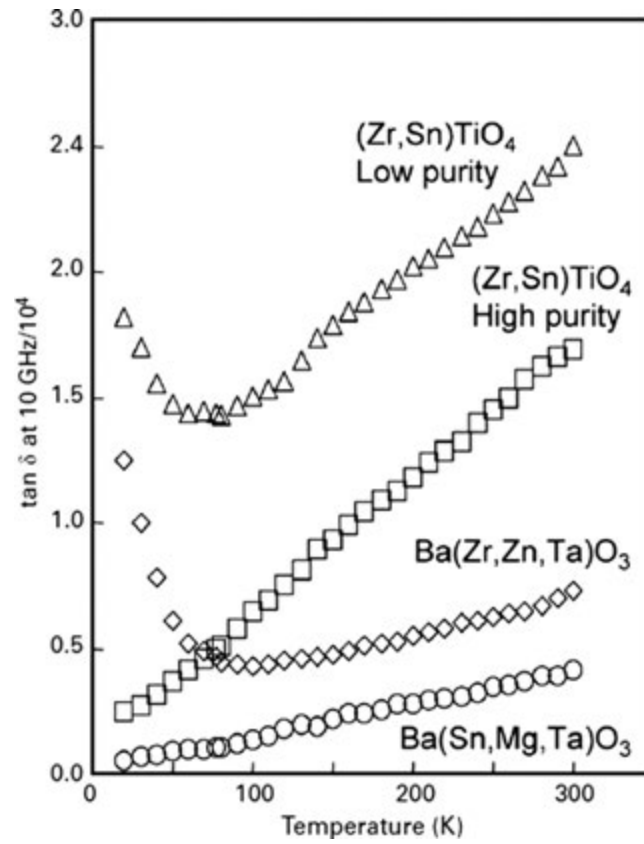


Fig. 11 $\tan \delta$ of ultralow-loss ceramics at cryogenic temperature.

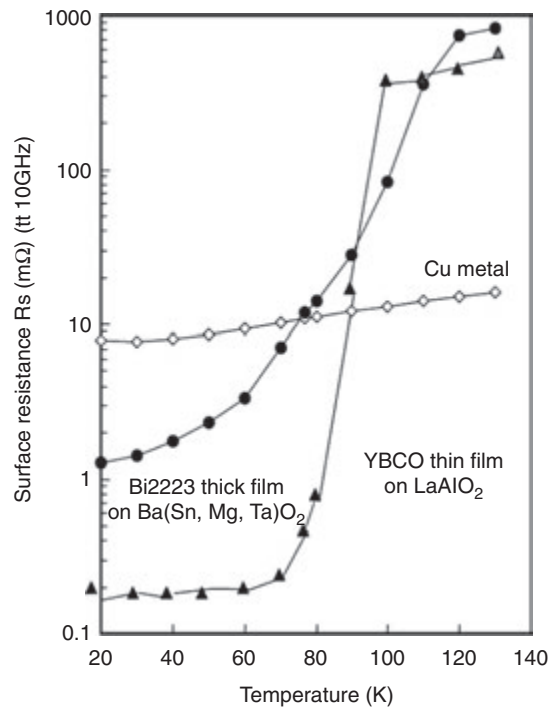


Fig. 12 Comparison of surface resistivity of Bi2223 thick film and YBCO thin film.

Fig. 12 shows the comparison of surface resistance at 10 GHz between YBCO thin film and Bi2223 thick film (Tatekawa *et al.*, 1999). Although the surface resistance obtained for Bi2223 thick films is not sufficiently low owing to the imperfect *c*-axis alignment, it has the possibility for future improvement.

Ceramic Substrates

Low-Temperature Co-Fired Ceramics

Since the major portion of power loss in high-frequency circuits is generated by current loss, owing to the finite electrical conductivity and skin effect, high conductivity metals such as silver ($6.3 \times 10^7 \text{ Sm}^{-1}$) or copper ($6.0 \times 10^7 \text{ Sm}^{-1}$) are preferred as electrode materials. Difficulties in the use of silver or copper as co-fired electrode materials are derived from their relatively low melting temperatures (silver, 962 °C; copper, 1083 °C) compared to the sintering temperature of commonly used dielectric ceramics (1300–1450 °C); another serious problem is that copper is easily oxidized during sintering in ambient atmosphere.

To overcome these difficulties, various kinds of low-temperature firable and nonreducible ceramics (so-called low-temperature co-fired ceramics, LTCCs) have been developed and put into practical use. LTCC materials can be classified (1) concerning the basic material (e.g., glass-added system and nonglass system; and (2) concerning the conductor material (e.g., copper system and silver or silver/palladium system).

Although addition of a sintering agent or glass degrades the dissipation factor and thermal conductivity somewhat, if the materials are carefully chosen, the deterioration of loss tangent can be kept within acceptable limits. Since Q_c (Q value owing to current loss) is 300–400 at most between 1 and 2 GHz, $Q_d(1/\tan \delta)$ of 1000 or more is practically applicable. Poor thermal conductivity applies some limits for high-power devices, but in practice there is no limit for low-power signal applications.

Tables 2 and 3 summarize the representative properties of several LTCC materials of several manufacturers. For miniaturization, especially at lower frequency, relatively high dielectric constant material is preferred, whereas for a high speed and/or a less distortion transmission line, lower dielectric constant material is favored. Matching of thermal expansion coefficient of substrate and the devices on that substrate should be taken in account to minimize the residual stress on relatively large devices. A good match of thermal expansion coefficient is an important factor for flip chip bonding of LSI.

Multilayer Devices Using LTCCs

Although LTCC devices, such as multilayer semidistributed LC filters, 90° couplers, power dividers, and balun, are not so highly intelligent, these simple devices are gaining favor and play important roles in sophisticated systems as key functional devices of small size, lightweight, and tuning free. Fig. 13 shows schematically the structure and the equivalent circuit of a 3 dB coupler. The structure and performance of a 5.8 GHz LC filter for the latest electronic toll collector (ETC) system are shown in Fig. 14. The dimensions of this device are 2.0 mm × 1.5 mm × 1.0 mm.

MCM

For further integration and greater miniaturization, a number of devices are combined in a multilayer substrate structure, a so-called MCM. Several grades of integrated modules with few or many devices, including ICs, are in production and contributing to miniaturization and increasing the intelligence of modules.

In analog systems, dielectric resonator duplexers have been mainly used for the antenna filter, but in a digital system, like GSM, the diode switcher can be used instead of the DR duplexer. The diode switcher has the advantages of being lighter, smaller, and cheaper than the DR duplexer. Therefore, almost all GSM cellular telephones use the diode switch. As a low-pass filter, a combination of strip lines and capacitors is embedded in the multilayer ceramic substrate, and two diodes and one resistor are mounted on the top of substrate. For active devices, silicon bare chips are mounted on the ceramic surface with die adhesive and connected with wire bond technology, or silicon flip-chip is mounted using flip-chip bonding technology. Beside these, filters and other peripheral circuits are integrated in the ceramics.

Fig. 15 shows schematically the basic concept of future three-dimensional integration by MCM.

Dielectric Antenna

Several types of distinctive antennas are now in use. By choosing an appropriate shape, size, and configuration of ceramic and conductor, dielectric antennas with acceptable characteristics can be designed for desired working frequencies. Fig. 16 shows a microstrip antenna (or patch antenna) for a global positioning system (GPS) receiver, using a high K dielectric substrate. Dielectric ceramic loaded stripline antennas have several advantages, namely small size, fairly narrow but still wide enough frequency band, and good temperature stability. GPS receivers are required to receive multiple signals from three or four different satellites

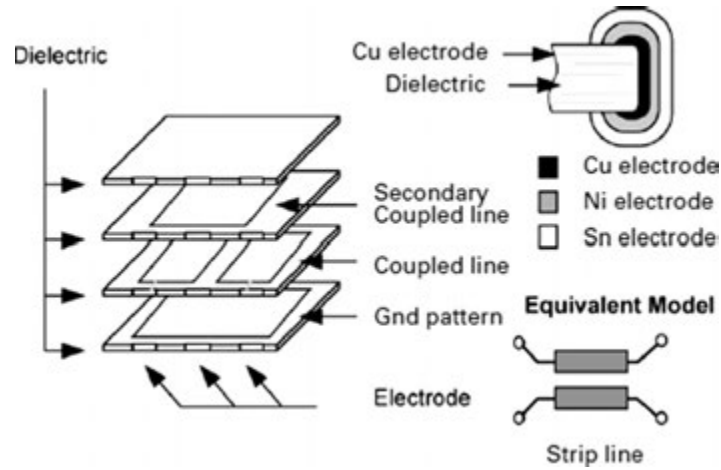
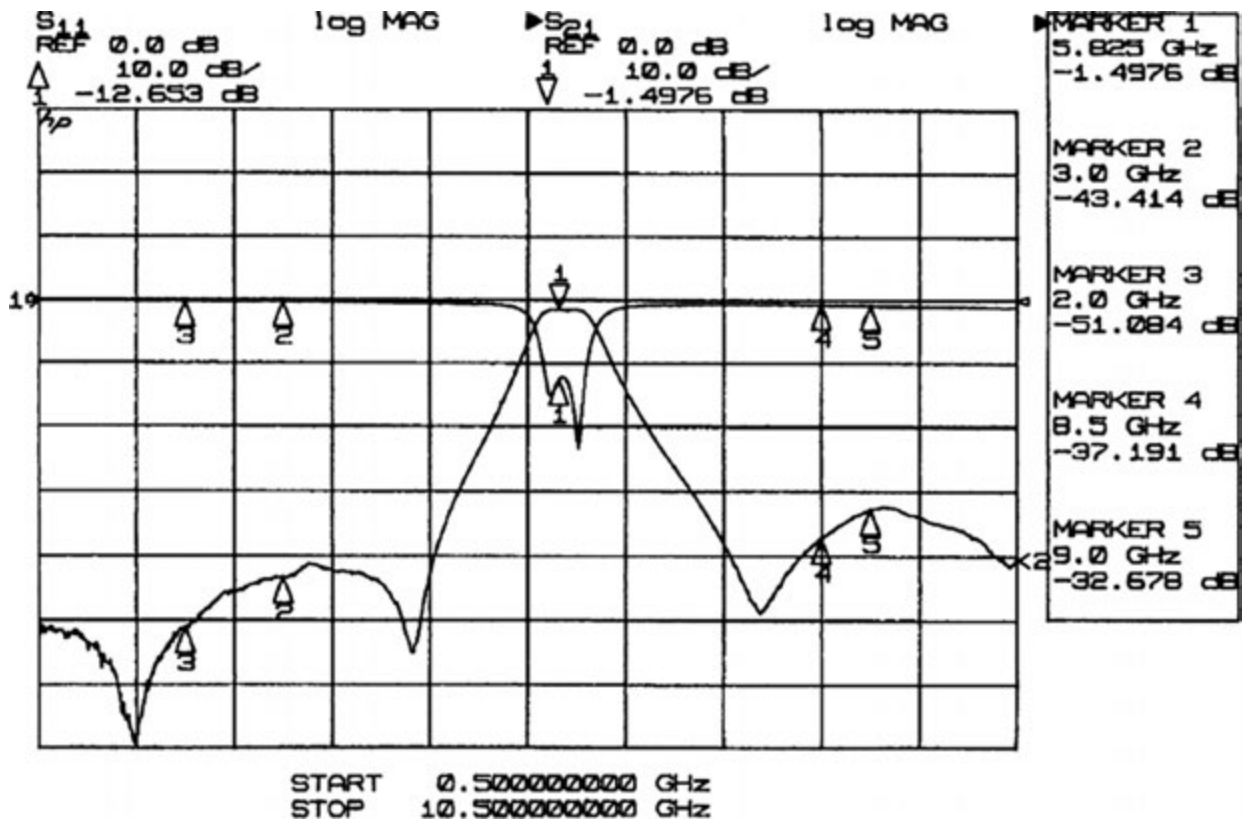
Table 2 Physical properties of LTCCs from several manufacturers

		<i>Manufacturer</i>	<i>TY</i>	<i>FJ</i>	<i>NE</i>	<i>TS</i>	<i>TD</i>	<i>KC</i>	<i>MM</i>	<i>MM</i>	<i>MM</i>
		<i>Trade name</i>	<i>LMS-2</i>	<i>MGO</i>			<i>BAS</i>			<i>T-SAM</i>	<i>CZG</i>
Ceramics	Basic composition		$\text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{B}_2\text{O}_3 - \text{CaO} - \text{MgO}$	$\text{B}_2\text{O}_3 - \text{SiO}_2 + \text{Al}_2\text{O}_3$	$\text{PbO} - \text{SiO}_2 - \text{B}_2\text{O}_3 \text{ glass} + \text{Al}_2\text{O}_3$	BaSnB_2O_3	Glass + ceramic composites	Glass + crystal	$\text{BaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{B}_2\text{O}_3 - \text{Cr}_2\text{O}_3$	$\text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{B}_2\text{O}_3 - \text{TiO}_2$	$\text{CaZrO}_2 - \text{glass}$
	Bulk density (kg ml^{-1})		2.7×10^3		3.1×10^3	4.6×10^3		$2.3 \sim 2.5 \times 10^3$	3.1×10^3	2.5×10^3	4.2×10^3
	Flexural strength (MPa)		245	201	294	132	274	167 ~ 196	157	157	212
	Thermal expansion (10^{-6} K^{-1})		4.8	4	4.2			3.0 ~ 7.0	11.6	3.3	7.0
	Thermal conductivity (W mK^{-1})		7		4.2		4.2	2.5	2.5	2.0	2.0
	Dielectric constant		6.7	4.9	7.5 (1 kHz)	9.5	7.7	5.0 ~ 5.5	6.1	6.1	25.0
	Dissipation factor ($\times 10^{-4}$)		10	20	30 (1 kHz)	5	8		7	5	5
	Voltage breakdown (kV m^{-1})			50			30		20	20	20
	Insulation resistance ($\Omega\text{-m}$)		$>10^{12}$	$>10^{14}$	2.9×10^{12}	10^{12}	5.0×10^{12}	$>10^{12}$	$>10^{10}$	$>10^{10}$	$>10^{10}$
Conductor	Materials		Cu	Cu	Ag/Pd	Ag/Pd, Au	Ag System	Cu	Cu	Cu	Cu

Table 3 Dielectric properties of typical class I ceramic capacitors

IEC type	TCC ppm °C ⁻¹	Basic composition	K	tan δ 10 ⁻⁴	IR 10 ⁺¹²
A	+100	MgTiO ₃	18	2.0	10
C	0	MgTiO ₃ -CaTiO ₃	20	2.0	10
		BaO-4TiO ₂	34	2.5	5
L	-80	BaO-TiO ₂	40	2.5	5
U	-750	TiO ₂	100	1.5	5
	-1500	CaTiO ₃	1500	3.0	5

Note: TCC, Temperature coefficient of capacitance or dielectric constant; K, Relative dielectric constant; IR, Insulating resistance.


Fig. 13 Schematic of multilayer 3 dB coupler.

Fig. 14 Frequency response of 5.8 GHz band pass filter for ETC system.

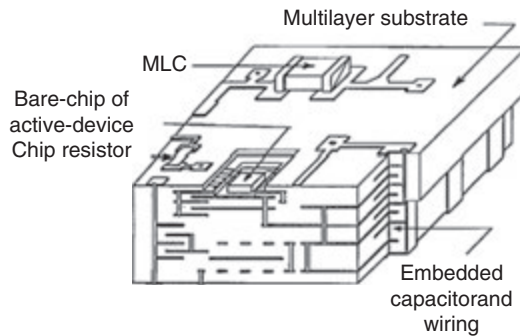


Fig. 15 Conceivable skeleton of three-dimensional MCM.

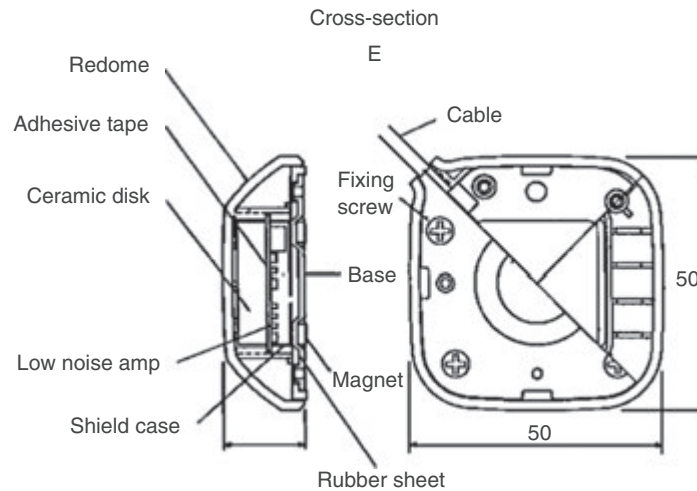


Fig. 16 Schematic structure of patch antenna for GPS receiver.

simultaneously. This antenna has axially symmetric gain characteristics around the vertical axis, so that this antenna is suitable as a multidirectional antenna.

Figs. 17 and **18** show the schematic structure and directivity data of dielectric chip antennas for mobile telephone terminals, respectively. The gain is slightly lower than that of the conventional whip antenna (so called pig-tail antenna), but it is high enough for microcell systems. This type antenna is expected to be the key device for the future miniaturization of short-range applications such as microcell handsets, small office or home LAN systems, Blue Tooth, etc.

Ceramic Capacitors

Single-Layer (Microchip) Capacitor

Most of the classical lead-type ceramic capacitors have been replaced with chip-type ones since the popularization of surface mount technology (SMT). The advantages of the chip-type over the lead-type capacitor are that it is smaller, lighter, and is better fitted to the requirement of surface mount devices (SMDs). SMT meets the demands for fully automated, flexibly controlled by computer, and much faster (less than 0.1 s per component) assembling of miniaturized equipment. Furthermore, a great advantage of chip-type components is that the parasitic inductance and stray capacitance can be reduced dramatically based on the extremely small electrode and leadless structure. Small size and less parasitic characteristics are quite effective for high-density assembling of microwave and millimeter wave equipment. In this chapter the description of lead-type devices is omitted for these reasons.

For very high frequency application, attention should be paid to the self-resonance phenomena of the capacitor and/or to the complex coupling with neighboring circuit and components. Sometimes, even a quite small inductance of signal line will cause unwanted resonance problems owing to the formation of serial or parallel parasitic LC connections in microwave or millimeter wave circuits. The lowest self-resonant frequency of a plate-type capacitor is roughly estimated by the following equations (TM_{010} mode or capacitor mode):

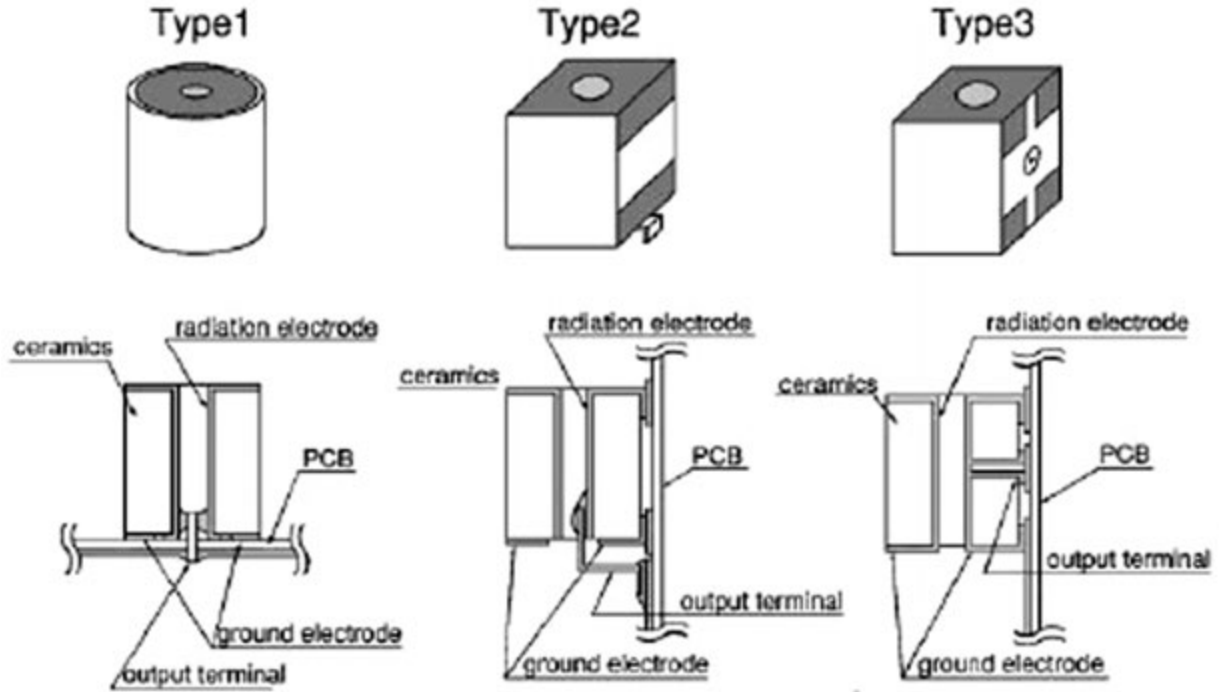


Fig. 17 Example of dielectric chip antenna.

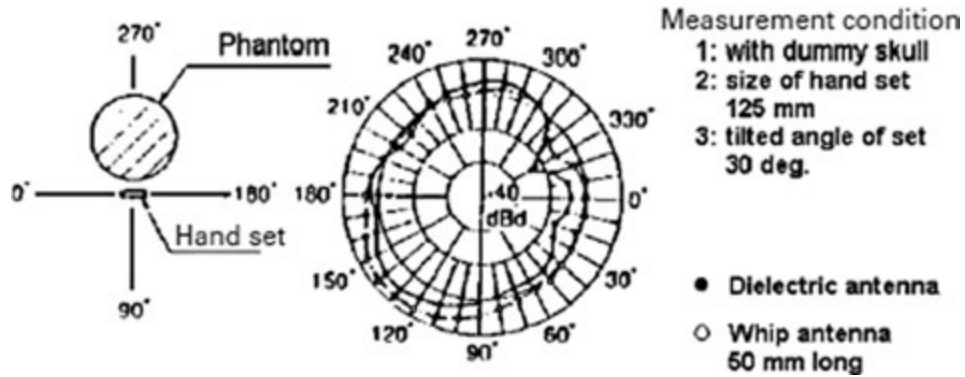


Fig. 18 Directivity data for dielectric antenna mounted on handset.

$$f_r \approx \frac{1}{2\sqrt{\epsilon_r}} \cdot \frac{c}{a} \text{ for a rectangular capacitor}$$

$$f_r \approx \frac{J_0(r)}{2\sqrt{\epsilon_r}} \cdot \frac{c}{r} \text{ for a disk - type capacitor}$$

where a , r , c , and $J_0(r)$ are the length of the longer side of the rectangular electrode, radius of the electrode of a disk capacitor, velocity of light in free space, and the first root of the first kind of Bessel function, respectively.

Since the values of $\tan \delta$ of class I ceramic capacitor materials are small enough (see Table 1) and the loss at very high frequency is largely defined by the current loss in the electrode rather than dielectric loss, the improvement of intrinsic dielectric loss is not such a critical issue for the capacitor, unlike for the dielectric resonator.

Fig. 19 shows schematically the structure of a microchip capacitor. The multielectrode array of binary aerial series is specially designed for convenience of tuning after assembling. Direct bonding to the ground plane can guarantee minimum parasitic inductance. As shown in Fig. 20, the small capacitance microchip capacitor does work over 10 GHz.

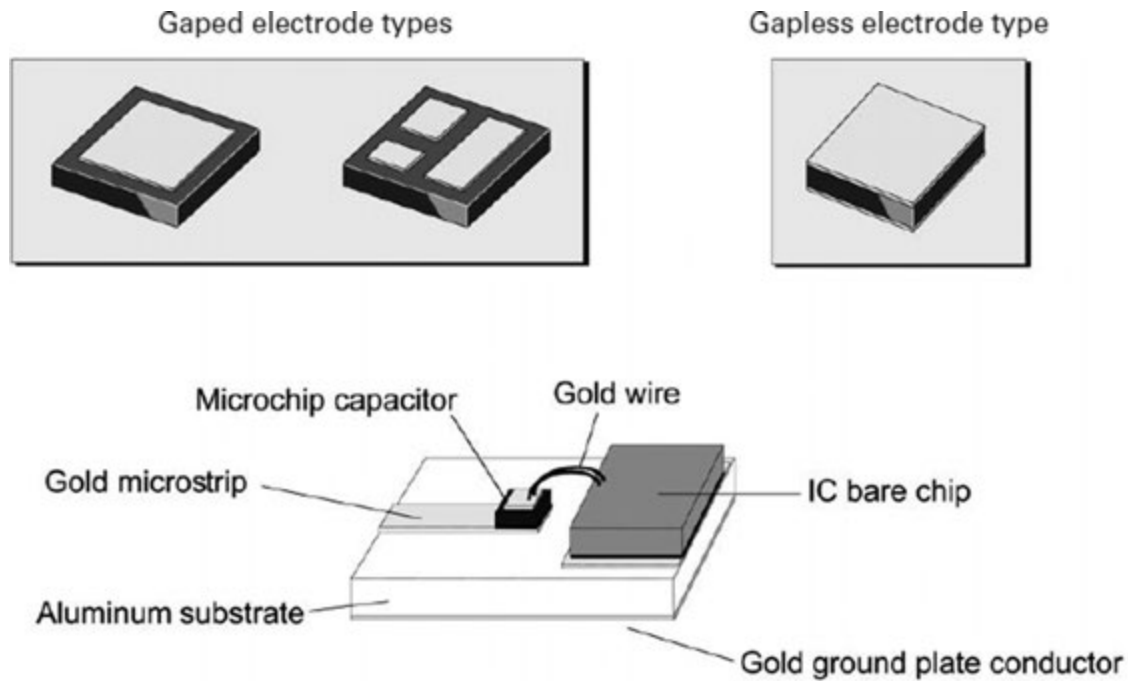


Fig. 19 Structure of microchip capacitor.

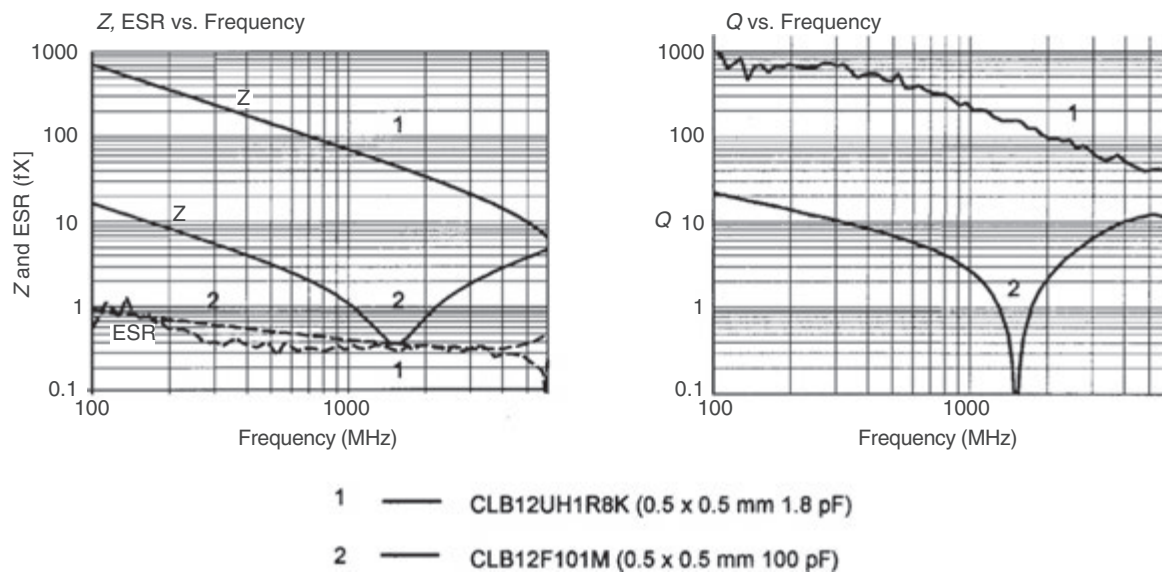


Fig. 20 Frequency characteristics of microchip capacitor.

Multilayer Ceramic Capacitor

The basic structure of an multilayer ceramic capacitor (MLC) is shown in Fig. 21. High capacitance is achieved by thin and multistacked dielectric layers, even with a small footprint. Neglecting the fringing effect, the capacitance with the given fixed effective shape and size is proportional to $1/t_1 \times (t_1 + t_2)$, where t_1 and t_2 are the thickness of the dielectric and electrode, respectively. The thickness of the active layer approaches 1–2 μm .

Originally, MLC manufacturing used platinum or palladium electrodes at the beginning of the 1940s to adapt to high-temperature and normal-atmosphere sintering. Subsequently the Ag–Pd electrode has been introduced to reduce the material cost of electrode. Since the early 1980s the electrode material is has been nickel or copper for further reduction of material cost even with the increase of processing cost for nonoxidizing sintering. Copper has the additional advantage of having higher electrical conductivity that is favorable for high Q and high-frequency applications.

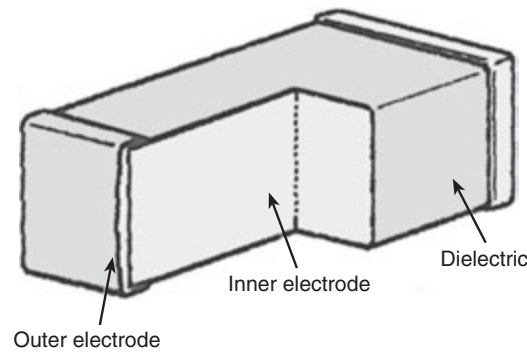


Fig. 21 Sketch of basic structure of an MLC.

Table 4 Comparison between precious metal and base metal multilayer ceramic capacitors

Electrode	Material	Pt	Pd	Ag-Pd	Ag	Ni	Cu
	Melt. temp. (°C)	1500	1450	1350	940	1500	1040
	Fire. Atm.	Air	Air	Air	Air	N ₂	N ₂
Dielectric	Material	Normal	>	>	>	Non-reducing	>
Q		Excellent	Excellent	Good	Good	Fair	Good
Ins. resit.		Excellent	Excellent	Good	Good	Fair-Good	Fair-Good
Reliability		Excellent	Excellent	Good	Fair	Good	Good

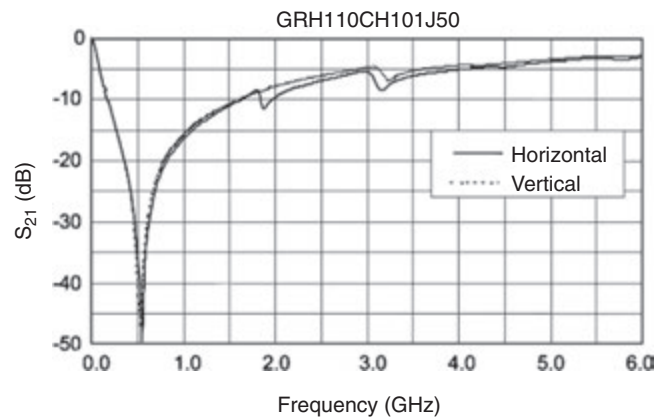


Fig. 22 Comparison of s-parameters between vertical and horizontal placing.

Table 4 summarizes the characteristics and features of different types of MLC.

As is seen in **Fig. 22**, it is worth noting that the s-parameter is different between two states; the inner electrode is placed parallel to the substrate and vertical for microwave or millimeter wave application.

References

- Ishikawa, Y., Hattori, J., Andoh, M., Nishikawa, T., 1992. 800MHz high power duplexer using TM dual-mode dielectric resonators. IEEE MTT-S Dig. II-3, 11617–11620.
- Ishikawa, Y., Hiratsuka, T., Sonoda, T., Mikami, S., 1997. V band planar type dielectric resonator filter fabricated in ceramic substrate. In: Topical Symposium on Millimeter Waves Proceeding Yokosuka Search Park, Telecom Summit, pp. 93–96.
- Ishikawa, Y., Tanaka, H., Nishida, H., Nishikawa, T., 1990. Complex permittivity measurement for millimeter wave dielectric resonator materials using NRD guide. IEICE Jpn. Tech. Rep. MW90-13, pp. 31–36.
- Kawashima, S., Nishida, M., Ueda, I., Ouchi, H., 1983. Ba(Zn,Ta)O₃ ceramic with low dielectric loss. J. Am. Ceram. Soc. 66, 421–423.
- Kobayashi, Y., Katoh, M., 1985. Microwave measurement of dielectric properties of low-loss materials by the dielectric resonator method. IEEE Trans. on MTT 33, 586–592.
- Maradudin, A.A., Fein, A.E., 1962. Scattering of neutrons by an anharmonic crystal. Phys. Rev. 128, 2589–2608.

- Michiura, N., Tatekawa, T., Higuchi, Y., Tamura, H., 1995. Role of donor and acceptor ions in the dielectric loss tangent of $(\text{Zr}_{0.8}\text{Sn}_{0.2})\text{TiO}_4$ dielectric resonator material. *J. Am. Ceram. Soc.* 78, 793–796.
- Nishikawa, T., Ishikawa, Y., Hattori, J., Ida, Y., 1989. Measurement method of intermodulation distortion of dielectric materials by using resonator method. *IEICE Jpn J27-C-1*, 650–658. (in Japanese).
- O'Bryan Jr., H.M., Thomson Jr., J., Plourde, J.K., 1974. A New BaO-TiO_2 compound with temperature-stable high permittivity and low microwave loss. *J. Am. Ceram. Soc.* 57, 450–453.
- Schlömann, E., 1964. Dielectric losses in ionic crystals with disordered charge distributions. *Phys. Rev.* 135, A413–419.
- Tamura, H., 1994. Microwave loss quality of $(\text{Zr}_{0.8}\text{Sn}_{0.2})\text{TiO}_4$. *J. Am. Ceram. Soc. Bull.* 73 (10), 92–95.
- Tamura, H., Hattori, J., Nishikawa, T., Wakino, K., 1989a. Third harmonic distortion of dielectric resonator material. *Jpn. J. Appl. Phys.* 28, 2528–2531.
- Tamura, H., Konoike, T., Wakino, K., 1984. Improved high-Q dielectric resonator with complex perovskite structure. *J. Am. Ceram. Soc.* 67, C-59–C-61.
- Tamura, H., Matsumoto, H., Wakino, K., 1989b. Low temperature properties of microwave materials. *Jpn. J. Appl. Phys.* 28 (Suppl. 28–2), 21–23.
- Tatekawa, T., Matsui, N., Kintaka, Y., Ishikawa, Y., Oota, A., 1999. Surface resistance of screen-printed Bi2223 thick films on Ag and dielectric ceramic substrates. *IEEE Trans. Appl. Supercond.* 9 (2), 1940–1943.
- Tyagi, A.K., 2014. Synthesis and characterization of ceramic dielectric resonator materials for microwave communication technology. *Procedia Mater. Sci.* 5, 1322–1331.
- Wakino, K., Minai, K., Tamura, H., 1984. Microwave characteristics of $(\text{Zr},\text{Sn})\text{TiO}_4$ and $\text{BaO-PbO-Nd}_2\text{O}_3\text{-TiO}_2$ dielectric resonator. *J. Am. Ceram. Soc.* 67, 278–281.
- Yoneyama, T., Nishida, S., 1981. Nonradiative dielectric waveguide for millimeter-wave integrated circuits. *IEEE Trans. on MTT* 29, 1188–1192.
- Zhang, Y.-D., Han, J., Liang, R., Zhou, D., 2015. Novel temperature stable Li_2TiO_3 -based microwave dielectric ceramics with low loss. *Mater. Lett.* 153, 118–120.

Further Reading

- Asami, J., *et al.*, 1991. Copper circuits on co-fired multi-layer ceramic substrate with embedded capacitors and registers. *ISHM*, pp. 402–403.
- Blodgett, J., 1980. A multi-layer ceramic multi-chip module. In: *Proceedings of the 30th Electronic Components Conference*, pp. 283–285.
- Burn, I., Porter, W.C., 1990. MLCs with copper electrodes for high frequency applications. In: *Proceedings of the 5th US-Japan Seminar on Dielectric and Piezoelectric Ceramics*, pp. 21–24.
- Frye, R., Tai, K., Lau, M., Lin, A., 1992. Silicon-on-silicon MCMs with integrated passive components. In: *Proceedings of the IEEE Multichip Module Conference*, 18–20, p. 155.
- Hagan, N.C., Henderson, J.F., Nebe, W.J., Osborne, J.J., 1989. High resolution thick film material system. *Int. J. Hybrid Microelectron.* 12 (4), 175–179.
- Kato, J., Yokotani, Y., Kagata, H., Niwa, H., 1987. Multilayer ceramic capacitor with copper electrode. *Jpn. J. Appl. Phys.* 26 (Suppl. 26–2), 90–92.
- Kawafuku, H., 1987. Characterization technique of ceramics. *Jpn. Ceram. Soc.* 135, 146.
- Keizer, P., 1994. Ceramic multicomponent module: A new approach to miniaturization. *IEEE Trans. Components, Packaging Manufact. Technol.* 17, 334–337.
- Kumagai, N., 1988. New development of multi component substrate. In: *International Microelectronics Conference*, pp. 22–26.
- Kurano, M., Shimada, Y., 1990. Shrinkage control technology for glass-ceramic substrate. In: *International Microelectronics Conference Proceedings, Tokyo*, pp. 304–311.
- Mandai, F., Ohkubo, S., 1993. Low temperature fireable ceramic material. *J. Am. Ceram. Soc., Ceramic Trans.* 32, 91–100.
- Mandai, H., 1989. Low temperature fireable electric ceramic material. *Dielectric Ceram., Am. Ceram. Soc.* 91–100.
- Mandai, H., *et al.*, 1989. Multilayer ceramic capacitors with copper electrodes. *Am. Ceram. Soc. Bull.* 68, 1671.
- Menzel, W., Schumacher, H., Schwab, W., Zhang, X., 1992. Compact multilayer filter structures for coplanar MMICs. *IEEE Microw. Guided Wave Lett.* 2 (12), 497–498.
- Messner, G., 1990. The impact of multichip modules on printed boards. Technical Paper no. A11/3, Printed Circuit World Convention 5, pp. 12–15.
- Nishigaki, S., Ikeda, T., 1991. Newly developed multilayered small size LC chip-elements for EMC noise filters made by low temperature fireable ceramics. *ISHM*, p. 511.
- Niwa, K., Imanaka, Y., Kamehara, N., Aoki, S., 1987. Crystallization of low temperature fired glass/ceramic composite. *Yogyo Kyokaishi* 95 (11), 78. (in Japanese).
- Nomura, T., Nakano, Y., Izumi, Y., 1995. Degradation of multilayer ceramics capacitors with nickel electrodes under highly accelerated life test. *Powder Powder Metall.* 42 (5), 557.
- Pillai, E.R., 1997. Coax via-a technique to reduce crosstalk and enhance impedance match at vias in high-frequency multilayer packages verified by FDTD and modeling. *IEEE Trans. Microw. Theory Tech* 45 (10), 1981–1985.
- Sakabe, Y., 1991. Technical trend of material with ceramic capacitor. *Fine Ceramics Report* 9.
- Sakabe, Y., Hamaji, Y., Omori, N., Wakino, K., Canner, J., 1991. Evaluations of strontium titanate based MLCs with copper electrode. In: *Proceedings of the Center for Dielectric Studies Symposium On Improvement of Multilayer Ceramic Reliability*, The Pennsylvania State University, pp. 102–114.
- Sakabe, Y., Kohno, Y., Yamada, Y., Canner, J.P., 1989. Low harmonic distortion ceramic multilayer capacitor. In: *Proceedings of the 39th Electronic Components Conference IEEE*, pp. 202–205.
- Sakabe, Y., Wakino, K., Canner, J., 1984. High voltage monolithic capacitors using SrTiO_3 based dielectrics. In: *Proceedings of the 4th Capacitor and Resistor Technology Symposium, Electronic Component Institute International Ltd*, p. 141.
- Sullivan, F., 1997. Low temperature co-fired ceramic applications for microwave multichip modules. In: *Proceedings of the 1997 Wireless Workshop*, pp. 50–52.
- Thelemann, T., Thust, H., 1997. Frequency behavior of ground plane via interconnections in multilayer LTCC-modules. In: *Proceedings of the International Symposium on Microelectronics, Philadelphia, PA*, pp. 350–355.
- Tosaka, M.N., *et al.*, 1984. Properties of low temperature co-fired multilayer ceramic substrate with buried passive components. In: *ISHM Proceedings*, pp. 8–62, 83–88.
- Tutt, M.N., Tserng, H.Q., Ketterson, A., 1997. A low loss, 5.5 GHz–20 GHz monolithic balun. *IEEE MTT-S Dig.* June, pp. 933–936.
- Uchikoba, F., Sato, S., Hirakata, K., Kosaka, Y., Sawamura, K., 1989. Processing and characterization of copper internal electrode multilayer capacitors. *Ceram. Trans.* 32, 101–110.
- Val, C.M., 1980. Copper dielectric interaction: A comprehensive study. *IEEE MTT-S INS NY Proc.* 77.
- Walker, V., *et al.*, 1968. Broadband stripline balun using quadrature couplers. *IEEE Trans. Microw. Theory Tech.* MTT-18, 132–133.
- Yoneda, Y., Kimura, T., Haratani, T., Asakura, K., 1997. Reliability and application of low fired multi-layer capacitor having copper inner electrode. In: *CARTS-Europe '97, 11th European Passive Components Symposium, Electronic Components Institute International Ltd*, pp. 106–113.

Small-Scale Energy Harvesting Devices for Smart Electronics

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Introduction

Novel power sources play a crucial role in the advancement of the new generation of electronic applications. Emerging small-scale modern electronic devices are lightweight and portable and have an emphasis on utilizing renewable power sources to provide sustainable solutions that have lasting user impact (Goldemberg, 2007; Wang and Song, 2006; Priya and Inman, 2009). On a large scale, geothermal, solar, nuclear, biomass, hydrogen, and wind energies are being developed as efficient renewable energy sources (Karan *et al.*, 2016). On a smaller scale, the rapid development of the internet of things (IoT) has generated tremendous number of microelectronic devices and wireless sensors that have multiple functionalities, wide-spread availability, and network connectivity (Atzori *et al.*, 2010; Gershenfeld *et al.*, 2004). In these applications, traditional power supplies based on batteries have limited lifetime, which results in a high cost of maintenance and replacement. To address this limitation, ambient energy harvesting devices based upon natural sources such as solar, thermal, magnetic field, vibrations, and bio-fuel energies have received attention to provide sustainable power sources.

Mechanical energy, including human body movements, various acoustic and vibration sources, and air/water flows are relatively abundant in our environment. These kinds of random mechanical energies are suitable for development of energy harvesters which are continuously interacting with the environments. It is advantageous to adopt a suitable energy harvesting technology depending upon the available form of energy. Different mechanical energy sources available in our surrounding useful to harvest electrical energy are summarized in Table 1.

Piezoelectricity and triboelectricity are two major energy conversion mechanisms to efficiently convert various types of wasted mechanical energies into electricity. Recently, piezoelectric nanogenerators (PENGs) (Fan *et al.*, 2009; Priya, 2007; Chung *et al.*, 2012) and triboelectric nanogenerators (TENGs) (Liu *et al.*, 2019b; Karan *et al.*, 2020) are gaining interest for energy harvesting applications, because of their reasonable energy conversion efficiency, which makes them an attractive power source for smart electronics, active sensors, and in-vivo electronic health (e-health) care (Maiti *et al.*, 2019). Magnetic fields are a ubiquitous energy source available in our surroundings with 50/60 Hz parasitic magnetic noise arising from electric power transmission cables, electronic devices, subways, manufacturing machines, etc (Ryu *et al.*, 2002; Lee *et al.*, 2020). However, the amplitude of the magnetic field strength around these sources is very low, typically less than 1 mT = 10 G. For magnetic field energy harvesting, therefore, novel approaches are required to efficiently convert low frequency and low strength magnetic fields into high electrical power. Magneto-mechano-electric (MME) generators have attracted great interest because of their capability to generate high power density from low-frequency magnetic fields (Kang *et al.*, 2018). Energy harvesting devices can capture energy from low-frequency mechanical vibrations and weak magnetic fields, based on the piezoelectric effect, triboelectric effect, and the magneto-mechano-electric effect. Device demonstrations with high efficiency and power density will enable advancement of small and smart portable electronics for wireless sensors, data transfer, and biomedical applications (Fig. 1). In the last decade, many efforts have been made towards development of novel energy harvesters that can convert small magnitude of mechanical or magnetic energy into usable electricity for powering standalone electronic systems (Wang *et al.*, 2007; Sriramdas *et al.*, 2020). However, in practice, the size of these generators should be as small as possible for ease of installation in smart electronics applications. Considering this scenario, we have focused our discussion on small-scale energy harvesting devices that have been reported in literature. The general principle for conversion of low frequency mechanical stress into electrical energy using piezoelectric/triboelectric energy harvesters is shown schematically in Fig. 2. The conversion of magnetic field to electric energy using magneto-mechano-electric energy harvester is also discussed. We illustrate the key parameters that should be taken into account for developing high performance small scale PENG/TENG/MMEG devices.

We begin with a brief overview on the importance of input energy parameters for coupling of the mechanical/vibration/magnetic field into electricity and types of constituent materials. Next, a discussion is provided on the material parameters (such as piezoelectric coupling constants d and g , electromechanical coupling factor k , triboelectric charge density Q , magnetostriction λ , etc.), elastic coupling occurring between the piezoelectric and magnetostrictive phases and fundamental properties which

Table 1 Different available mechanical energy sources to harvest electricity

Human body/motion	Infrastructures	Transportation	Industry	Environment
Breathing, blood flow, walking, flow/pressure, exhalation, finger motion, arm motion, talking jogging, etc.	Bridges, tunnels, roads, structure, farm, house, control-switch, AC system water/gas pipes etc.	Aircraft, tires, train, tracks, automobile, peddles, turbine engine, brakes, noises, vibration etc.	Motors, chillers, compressors, fans, pumps, cutting and dicing, vibrations, noise etc.	Wind, acoustic wave, ocean current/wave etc.

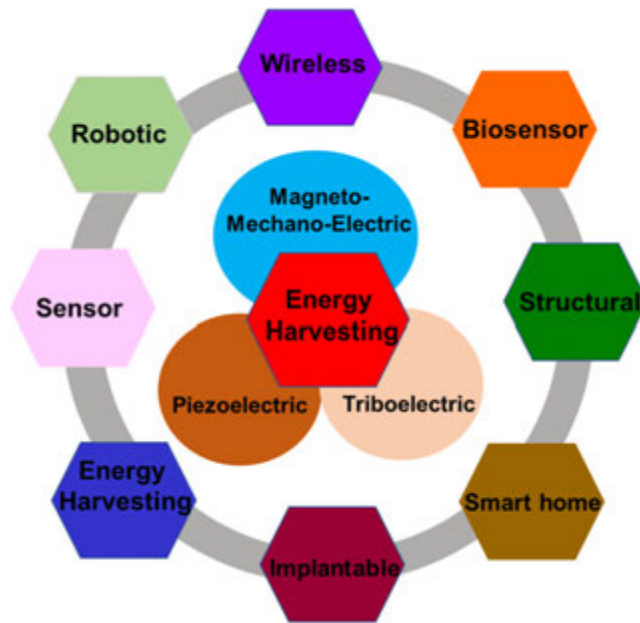


Fig. 1 Application domains for piezoelectric/triboelectric/magneto-mechano-electric energy harvesters.

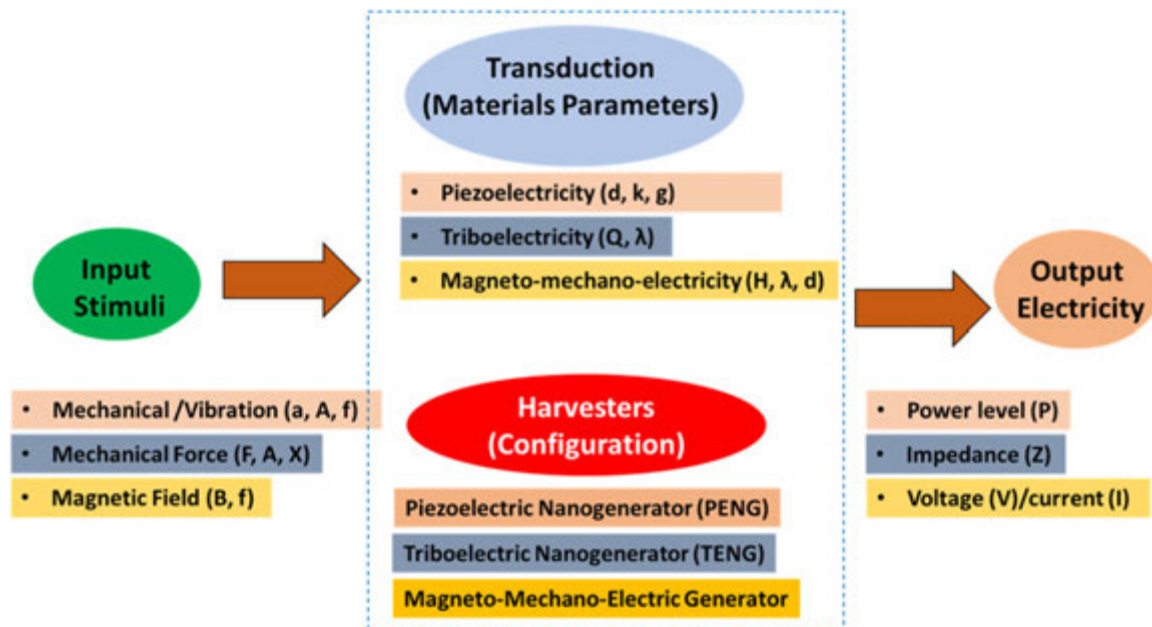


Fig. 2 Schematic diagram describing the energy flow and different parameters required for developing high performance PENG, TENG and MMEG devices.

ultimately influence the electrical properties. After that we describe the device structure for energy harvesting for various types of harvesters, output performance, impedance matching requirements and some potential applications. The power density of a harvester is dependent upon the strategies that maximize the energy capture and reduce the losses occurring at each step, namely, mechanical loss due to mismatch in mechanical impedance, and electromechanical loss depending upon the magnitude of the coupling factor. Three significant stages of energy transduction common to all the generators are: (1) transfer of input stimuli in the form of mechanical motion/magnetic field from ambient source, (2) conversion of the input energy into electrical form by direct piezoelectric/triboelectric effect in PENG or TENG and magnetic field to mechanical strain and then to electrical energy in MMEG, and (3) power management and storage of the generated electrical energy. The chapter concludes with a brief summary and future perspectives.

Transduction Mechanism

Fundamentals of Piezoelectricity

Piezoelectricity is the ability of certain crystalline materials that possess non-centrosymmetry (point group lacks an inversion center) to develop an electric charge proportional to the applied mechanical stress (direct piezoelectric effect) or develop a mechanical strain (deformation) proportional to an applied electric field (converse piezoelectric effect) (Damjanovic, 1998). According to Neumann's principle, the symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal (Nye, 1985; Newnham, 2005). Piezoelectric property can exist only in 20 non-centrosymmetric point groups. Of the 20 piezoelectric point groups, 10 point groups show the presence of spontaneous polarization (electric polarization that a substance possesses in the absence of an external electric field). These materials are termed as pyroelectric materials, in which the magnitude of the polarization varies with change in temperature. All ferroelectric crystals belong to one of these 10 polar point groups. Ferroelectrics are a subgroup of the pyroelectric family that exhibit at least two equilibrium orientations of the spontaneous polarization in the absence of an external electric field. The spontaneous polarization can be switched between the two orientations by applying an electric field (Damjanovic, 1998). It should be noted here that as-synthesized ferroelectric materials, either in the form of grain oriented polycrystalline thin films and bulk ceramics or single crystals, do not exhibit piezoelectric and pyroelectric response. The reason is that as-sintered ferroelectric ceramic or as grown thin film and single crystals usually contain randomly oriented domains. The piezoelectric effect of individual domains will cancel each other resulting in net zero polarization. Ferroelectric domains are formed below the Curie temperature in order to minimize the electrostatic energy of depolarizing fields and the elastic energy associated with mechanical constraints. Thus, ferroelectric materials need a strong electric field to induce the polar state by aligning the domains along the applied field direction (as mentioned earlier, poling process).

When the mechanical stress is applied to a piezoelectric material, an electric charge proportional to the applied stress is produced. This refers to the direct piezoelectric effect. Conversely, when electric field is applied to the same material, strain or displacement is produced proportional to the magnitude of electric field. This is called as converse piezoelectric effect. The direct piezoelectric effect can be effectively applied for an energy transducers/sensors, and the converse piezoelectric effect can be applied for the design of actuators. The general working approaches are schematically shown in Fig. 3(a)–(c). Fig. 3(a) represents the original state of the piezoelectric materials under the poling condition. The direct and converse piezoelectric effect of the piezoelectric materials is expressed by two different linear constitutive equations: (Kim *et al.*, 2011)

$$\text{Direct piezoelectric effect: } D_i = e_{ij}^{\sigma} E_j + d_{im}^d \sigma_m \quad (1)$$

$$\text{Converse piezoelectric effect: } \varepsilon_k = d_{jk}^c E_j + S_{km}^d \sigma_m \quad (2)$$

where the vector D_i signifies the dielectric displacement (unit in N/mV or C/m²), ε_k denotes the strain vector, E_j represents the applied electric field vector (unit in volts/meter), and σ_m stands for stress vector (unit in N/m²). The piezoelectric constants are the piezoelectric coefficients d_{im}^d and d_{jk}^c in m/V or C/N, the dielectric permittivity e_{ij}^{σ} in N/V² or F/m, and S_{km}^d signifies the elastic compliance matrix in m²/N. The superscripts c and d in the equation represent the converse and direct effects, respectively, and the superscript E and σ in the equation mean that the quantity is measured at constant stress and constant electric field, respectively.

The piezoelectric coefficient values can be either positive or negative, which can be calculated/measured in the direction of the applied field, well-known as the longitudinal piezoelectric coefficient, or it can be estimated in the perpendicular direction to the applied field, known as a transverse coefficient. Another piezoelectric coefficient of interest is the shear coefficient (Araujo and Soares, 2009). Since the stress and strain are symmetrical tensors, thus, the piezoelectric coefficient tensor is symmetrical in nature with respect to the same indices. In general, for longitudinal piezoelectric constant represented as d_{ij} , the subscript "i" represents the applied electric field or charge collection direction, and "j" represents the displacement or force or pressure direction. The

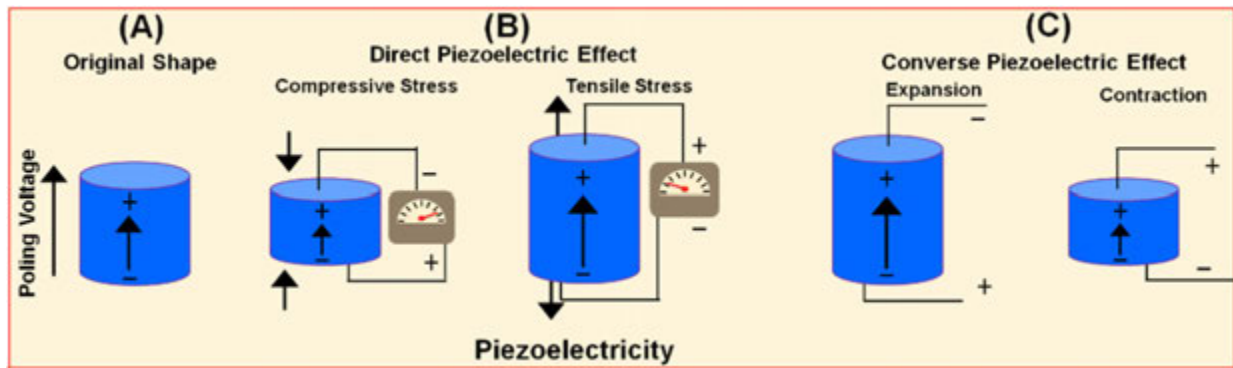


Fig. 3 Working mechanism of piezoelectric material. (A) poling process for polarizing piezoelectric materials, (B) direct piezoelectric effect, and (C) converse piezoelectric effect.

relationships for piezoelectric constants are given as:

$$d_{ij} = \left(\frac{\partial D_i}{\partial T_j} \right)^E = \left(\frac{\partial S_j}{\partial E_i} \right)^T \quad (3)$$

$$e_{ij} = \left(\frac{\partial D_i}{\partial S_j} \right)^E = - \left(\frac{\partial T_j}{\partial E_i} \right)^S \quad (4)$$

$$g_{ij} = - \left(\frac{\partial E_i}{\partial T_j} \right)^D = \left(\frac{\partial S_j}{\partial T_i} \right)^T \quad (5)$$

$$h_{ij} = - \left(\frac{\partial E_i}{\partial S_j} \right)^D = - \left(\frac{\partial T_j}{\partial D_i} \right)^S \quad (6)$$

where the first set of four terms indicates the direct piezoelectric effect and the second set of four terms represents the converse piezoelectric effect (Arnaú and Soares, 2009). There are five important material parameters for the design of piezoelectric material based applications: the piezoelectric strain constant d , the piezoelectric voltage constant g , the electromechanical coupling factor k , the mechanical quality factor Q_m , and the acoustic impedance Z (Uchino, 2010a; Zhang and Li, 2012). Each of these parameters are defined below.

Piezoelectric strain constant d : The magnitude of the induced strain x by an external electric field E is represented as: $x = dE$. The magnitude of d is an important consideration for actuator applications.

Piezoelectric voltage constant g : The induced electric field E is related to applied external stress X through the piezoelectric voltage constant g (an important figure of merit for sensor applications): $E = gX$.

Electromechanical coupling factor k : The electromechanical coupling factor k of a piezoelectric material refers to the efficiency of conversion between electrical and mechanical energy and vice-versa. This parameter is closely related to the bandwidth of resonant devices.

Mechanical quality factor Q_m : For a piezoelectric resonator, the mechanical quality factor Q_m characterizes the resonator's bandwidth relative to its center frequency: $Q_m = f_r/\Delta f$, where f_r is resonance frequency, and Δf is the frequency difference at -3 dB of the maximum admittance. A high Q_m is important for resonant applications while high Q_e (inverse of dielectric loss) is crucial for off-resonance devices.

Acoustic impedance Z : The acoustic impedance Z of a material is also related to the elastic constant and/or phase velocity through the relationship: $Z = \sqrt{\rho c}$, where ρ is the density and c is the elastic stiffness of material. Analogous to electrical impedance, the transfer of acoustic energy from one medium to another will be maximized when the two media have the same acoustic impedance.

Besides piezoelectric properties, dielectric properties are also very important in designing piezoelectric device. Dielectric constant (ϵ_r), dielectric loss ($\tan\delta$) and Curie temperature (T_c) are the most commonly characterized parameters. Dielectric constant (ϵ_r) is important for the device performance, since the capacitance is closely related to electrical impedance. Dielectric loss ($\tan\delta$) is the dissipation of energy in the form of heat. Low $\tan\delta$ is very important for high power device and sensor application. Curie temperature (T_c) represents the point above which the crystal structure becomes symmetrical and the material becomes non-piezoelectric. This point represents the maximum operating temperature for piezoelectric materials. Ferroelectric materials can be characterized by measuring their polarization as a function of applied ac electric field (P - E hysteresis loop). Remnant polarization (P_r) refers to the polarization that remains when the electric field is removed, and Coercive field (E_c) is the electric field required to reduce the polarization to zero. High E_c implies the need for high electric field to pole the sample, while low E_c materials may have low electrical stability as they can be easily depolarized.

There are mainly two approaches to achieve enhanced electric, ferroelectric and piezoelectric properties: (1) composition selection and modification through substitution/doping, and (2) microstructural design. Composition selection approach focuses on identifying binary and ternary phase diagrams that offer unique boundaries. The composition modification focuses on doping and substitutions in order to tailor the defect chemistry and phase transitions. The microstructure design focuses on the optimization of grain size and distribution, grain orientation or texture, domain size and defect organization.

Types of piezoelectric materials

Ceramic-based piezoelectric materials

The discovery of barium titanate (BaTiO_3), lead zirconate titanate ($\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$, known as PZT), and the family of materials based on these formulations, was a major breakthrough in advancing research on piezoelectric materials (Kwon et al., 2012). The PZT solid solutions with morphotropic phase boundary (MPB) have been dominating the piezoelectric industry since their discovery in 1950. MPB is an intrinsic region of a phase diagram where two or more phases coexist. The solid solution of piezoelectric materials having MPB shows enhanced piezoelectric and dielectric responses at this phase boundary. For example, the phase diagram of PZT has PbTiO_3 and PbZrO_3 as end members (Jaffe et al., 1971). Traditionally, the high piezoelectric response has been attributed to the enhanced number of polar axis in MPB composition. In a particular crystallographic symmetry, there are always a fixed number of equivalent polar axes in which the dipoles can be switched. The Ti-rich side of MPB in PZT possesses the tetragonal crystal symmetry with 6 equivalent $[001]$ directions as polar axes. However, on the Zr-rich

Table 2 Dielectric and piezoelectric properties of the various classes of piezoelectric materials

Sample	$\varepsilon_{33}^T/\varepsilon_0$	$\tan\delta$	T_c (°C)	k_{33}	k_{31}	d_{33} (pC/N)	d_{31} (10^{-3} m/N)	g_{33}	g_{31} (10^{-15} m ² /N)	Q_m	$d_{33} \times g_{33}$	$d_{31} \times g_{31}$
<i>(A) Ceramic</i>												
BT	1700	0.01	120	0.5		190		12.6			2394	
PZT-4	1200	0.003	320	0.70	−0.33	285	−122	24.8	−10.6	500	7068	1354
PZT-5A	1700	0.020	374	0.71	−0.34	374	−171	24.8	−11.4	75	9275	1949
PZT-5H	3400	0.025	195	0.75	−0.39	593	−274	19.7	−9.1	65	11,682	2496
PZT-8	1000	0.004	300	0.64	−0.30	225	−97	25.4	−10.9	1000	5715	1057
<i>(B) Polymer</i>												
PVDF	10	0.02	129	0.19	0.12	−33	16.5			4		
<i>(C) [001] Single crystal</i>												
PMN-29PT	5400	0.006	137	0.91	0.43	1540	−699	31.3	−14.2	150	48,202	9926
PMN-PZT	4850	0.005	211	0.93	0.44	1530	−718	35.6	−16.7	100	54,468	11,991
Mn-PMN-PZT	3410	0.002	203	0.92	0.45	1140	−513	37.8	−17.0	1050	43,092	8721
<i>(D) <001> Textured ceramics</i>												
PMN-PT	2591	0.006	162		0.57	1000		44			44,000	
PMN-PT-C	2820	0.006	162		0.60		411		16.5			6766
PMN-PZT	2310		211		0.60	1100				70	59,180	
Mn-PMN-PZT	1865	0.003	210		0.53	720				400		

side of the MPB, PZT with rhombohedral symmetry possesses 8 equivalent [111] directions as polar axes. Because at MPB two different phases coexist, the switching of polar axes in PZT has 14 available directions under applied E-field. This phenomenon was considered to be responsible for giving rise to high piezoelectric response at MPB. [Noheda et al. \(2000\)](#) identified the presence of bridging monoclinic phase between tetragonal and rhombohedral phase around MPB of PZT. Some well-known piezoelectric materials having MPB are $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$, $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$, and $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ - BaTiO_3 . High resolution X-ray diffraction investigations suggest that the major intrinsic contribution from both rhombohedral and tetragonal phase comes from the tilting of the P_s vectors ([Hoffmann et al., 2005](#)). The monoclinic phase with 24 permitted orientation states is expected to provide bridging polarization continuity leading to enhanced piezoelectric response ([Hoffmann et al., 2005](#)). Finding morphotropic phase boundary in a solid solution of piezoelectric materials is one of the important method to achieve high piezoelectric response. In addition, it has been shown that enhanced piezoelectric response can be related to the presence of miniaturized ferroelectric domains ($< 1 \mu\text{m}$) with high mobility ([Wada et al., 2005](#)). Wada et al. were able to synthesize miniaturized domain structure in BaTiO_3 single crystal by applying E-field along non polar [111]_c direction through a poling process conducted above T_c ([Wada et al., 2005](#)). The high piezoelectric response ($d_{31} = -230$ pC/N) observed in this system was attributed to the high density of domain walls ([Wada et al., 2005](#)). Wang et al. have performed theoretical calculations and confirmed that the enhanced piezoelectric response in the specimen with miniaturized domains was correlated with domain wall broadening under applied E-field ([Rao and Wang, 2007](#)). The enhanced piezoelectric response in non-polar directions was believed to be originated from the broadening of domain walls. Furthermore, the doping (soft and hard) of various elements in PZT has been effectively used to tune the piezoelectric response. The doping of elements like Nb^{5+} or Ta^{5+} (donor) results in “soft” PZTs (e.g., PZT-5). The enhanced piezoelectric response in soft PZT has been attributed to the ease in domain wall motion due to doping induced Pb vacancies ([Uchino, 2010b](#)). The acceptor type dopant (e.g., Fe^{3+} or Sc^{3+}) gives rise to “hard” characteristics as exemplified by PZT-8 ([Uchino, 2010b](#)). The hard PZTs have low piezoelectric response but high mechanical quality factor Q_m . This behavior of the hard PZTs has been attributed to the pinning of domain wall motion due to the presence of the doping induced oxygen vacancies ([Uchino, 2010b, 2009](#)). **Table 2** summarizes the piezoelectric, dielectric and elastic properties of typical PZTs: soft PZT-5H, semi-hard PZT-4, and hard PZT-8. Note that soft PZTs exhibit high electromechanical coupling (k), high piezoelectric coefficient (d), high relative permittivity, in comparison with hard PZTs, while Q_m is quite high in hard PZTs. Thus, soft PZTs should be used for off-resonance applications, while hard PZTs are suitable for on-resonance applications.

Lead-free perovskite materials have recently gained much attention due to the significant improvement in their physical properties. High piezoelectricity ($d_{33} \approx 416$ pC/N) was found in lead-free $(\text{K},\text{Na})\text{NbO}_3$ (KNN)-based textured ceramics having orthorhombic-tetragonal (O-T) phase boundary, which was fabricated using a reactive template grain growth (RTGG) method ([Zhang et al., 2015](#)). A series of KNN-based ceramics were demonstrated with high piezoelectric constants ($d_{33} = 490$ – 570 pC/N) by designing mixed-phase boundaries of rhombohedral (R) and tetragonal (T) phases ([Wang et al., 2018](#)). Continued investigations on the KNN-based textured ceramics have improved piezoelectric coefficient d_{33} to 700 pC/N with a large electro-mechanical coupling factor (k_p) value of 0.76 ([Moriana and Zhang, 2018](#)). Further, BT-based polycrystalline ceramics have shown a higher piezoelectric coefficient as compared to other lead-free piezoceramics. Ren et al. demonstrated a large piezoelectric coefficient ($d_{33} \approx 620$ pC/N) in lead-free $\text{Ba}(\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3$ - $(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ system with a rhombohedral-tetragonal (r-T) phase

boundary (Zhu *et al.*, 2014). Tan *et al.* reported that Sr and Nb co-modified BNT-based ceramics deliver a superior strain value ($S = 0.7\%$) (Liu and Tan, 2016).

Piezoelectric single crystals

Relaxor based ferroelectric single crystals, such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PZN-PT), have attracted extensive attention over the last 20 years due to their ultra-high piezoelectric properties (Zhang and Li, 2012). The longitudinal piezoelectric strain coefficient d_{33} and electromechanical coupling factor k_{33} , being on the order of > 1500 pC/N and 0.9, far out-performs the state-of-art polycrystalline $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) ceramics. The properties of relaxor-PT single crystals are summarized in Table 2. These properties are highly promising for various electromechanical applications. The piezoelectric response is highly dependent on the crystallographic orientation of the single crystals and it can be further improved by selecting MPB composition and substituting suitable elements on the desired lattice sites. Recently, Zhang *et al.* successfully explored derivative materials based upon Sm-doped $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (Sm-PMN-PT) single crystals having high d_{33} values in the range of 3400–4100 pC/N, with the variation below 20% over the as-grown crystal boule, which shows good property uniformity (Li *et al.*, 2019).

Textured piezoelectric ceramics

Despite the fact that single crystals have ultrahigh piezoelectric properties, as mentioned above, these materials have been facing challenges in their deployment mainly due to the high cost related to fabrication. Obtaining large size single crystals with required chemical homogeneity has been challenging. The use of single crystals is generally limited to medical imaging applications where performance considerations outweighs the materials cost. To overcome the production challenges of single crystal, textured piezoelectric ceramics with strong anisotropic properties have been developed, such as $\langle 001 \rangle$ textured PMN-PT, and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbZrO}_3\text{-PbTiO}_3$ (PMN-PZT) prepared by templated grain growth (TGG) method. Textured ceramics have shown significant improvement of piezoelectric property comparable to that of single crystal, but the cost is similar to that of traditional ceramics.

In order to obtain the textured ceramics, micro-sized template crystals are aligned in the ceramic matrix powders using tape casting method. During high temperature sintering, epitaxial growth occurs on the template seeds giving rise to textured grains (Messing *et al.*, 2004). The anisotropic shaped (whisker or platelet) template seeds should have smaller ($< 15\%$) lattice mismatch with the matrix phase for achieving high degree of texturing (Messing *et al.*, 2004). The anisotropic BT templates are synthesized using topochemical microcrystal conversion process (Liu *et al.*, 2007). These templates are used to fabricate various highly textured piezoelectric materials with excellent properties.

Polymer-based piezoelectric materials

Besides piezoelectric ceramics, there are piezoelectric polymer materials which have semi-crystalline structure, for example, polyvinylidene fluoride (PVDF), polyamides, ParyleneC, liquid crystal polymers, PVDF-TrFE block copolymer etc. The operational principle for these piezoelectric polymers is similar to that of piezoelectric ceramic materials. The semi-crystalline polymers have microscopic crystals inside matrix which are also polarized and function as dipoles as described Fig. 3. The microcrystals are distributed within an amorphous matrix. To obtain effective piezoelectricity in such materials, these small crystals should be reoriented and kept in one orientation through electrical poling or mechanical stretch process. The polyvinylidene fluoride (PVDF) material has been explored as an important piezoelectric polymer due to its high piezoelectric coefficient (20–53 pC/N) (Karan *et al.*, 2019, 2015). Correspondingly, its copolymers poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) and PVDF-TrFE have received much greater attention in the area of piezoelectric energy harvesting (Hong *et al.*, 2012). The polymers are highly attractive in some applications due to light weight, high flexibility, long-term stability and easy processing under external electric field. Among all the phases (α , β , γ , δ) of PVDF, polar β (TTTT) and semi-polar γ (T_3GT_3 G') are highly desirable due to their piezoelectric nature. Between these electrically active polar phases, the β phase is of greater importance due to its large polarization and high piezoelectric constant (Fig. 4; Martins *et al.*, 2014).

Although the piezoelectric coefficients of PVDF are not so high as compared to inorganic piezoelectric materials, its unique flexible nature renders good processing for the preparation of fibers, wires, or films, and simple integration with functional materials for better output performances. To achieve better output performance, stabilization of the polar phase in PVDF is generally done through alignment of $-\text{CH}_2/\text{CF}_2-$ dipoles using traditional electrical poling processes. The Nylon-11 nanowire, has been found to show good piezoelectric behavior with a d_{31} of up to ≈ 15 pC N^{-1} at a relatively higher temperature (up to 200°C) (Datta *et al.*, 2017). Cui *et al.* reported that direct piezoelectric responses can be generated through rationally designed piezoelectric architectural units that can be realized via additive manufacturing of highly sensitive piezo-active lattices (Cui *et al.*, 2019). Results demonstrated that PZT polymer composite fabricated using 3D printed technique have relevance for anisotropic energy harvesting.

There is another type of piezoelectric material known as voided charged polymer (VCP, sometimes called ferroelectret or piezoelectret) that contains internal gas voids. When the polymer surfaces surrounding the void are charged by electrical poling or X-ray, the space charges are created inside matrix and the VCP behaves like piezoelectric material. These polymers have very high d_{33} values. However, these piezoelectric polymers have serious life time and aging problems. The VCP is easily neutralized in extremely moist environment and the surface charge can be rapidly decayed at high temperatures. Some common piezoelectric materials with their formulations, crystalline forms, and piezoelectric coefficients are listed in Table 2.

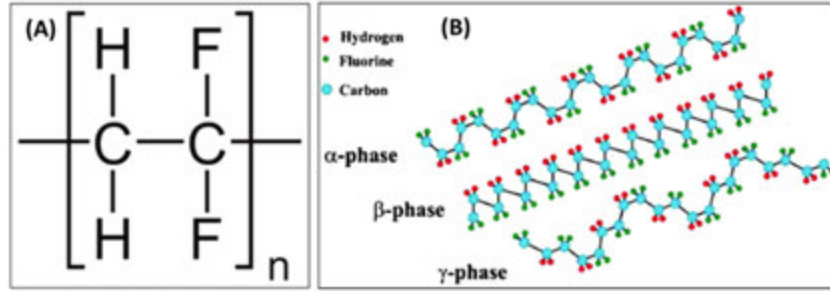


Fig. 4 (A) Chemical structure of PVDF and (B) schematic illustrations of chain conformation for α -, β -, and γ -phases in PVDF.

Selection of piezoelectric materials for energy harvesting

The transduction rate is the primary factor for the selection of piezoelectric materials. The magnitude of the transduction rate is governed by the product of piezoelectric strain constant (d) and the effective piezoelectric voltage constant (g). This can be understood by considering the electric energy available under an alternating stress excitation: (Priya *et al.*, 2019; Xu and Kim, 2012)

$$P = U_e = \frac{1}{2} CV^2 = \frac{1}{2} \epsilon_0 \epsilon_r \frac{A}{t} \left(-\frac{g \cdot F \cdot t}{A} \right)^2 \frac{1}{2} (d \cdot g) \left(\frac{F}{A} \right)^2 \cdot (At) \quad (7)$$

or energy density (u_e),

$$u_e = \frac{1}{2} (d \cdot g) \cdot \left(\frac{F}{A} \right)^2 \quad (8)$$

where F is the applied force, A is the area, and t the thickness of active piezoelectric material. This expression demonstrates that under given experimental conditions, a material with a higher $(d \cdot g)$ product is expected to generate higher power. Therefore, $d \cdot g = d^2 / \epsilon_0 \epsilon_r$ was proposed as a figure of merits (FOMs) of piezoelectric materials for energy harvesters (Islam and Priya, 2006). However, there is a challenge in achieving a high $d \cdot g$ coefficient via the composition modification in conventional piezoelectric ceramics because any increase in the piezoelectric constant (d) is always accompanied by the large increase in dielectric permittivity (ϵ); thus, high d usually shows lower g . Recently, it was found that the templated grain growth (TGG) technique yields textured PMN-PZT piezoelectric ceramics with large $(d \cdot g)$ magnitude, as shown in Fig. 5(A) and (B). This method provides more than ~ 5 times increase in the piezoelectric coefficient d , and a giant magnitude of $d \cdot g$ coefficient with value of $59\,000 \times 10^{-15} \text{ m}^2 \text{ N}^{-1}$, which is comparable to that of the single crystal counterpart and 359% higher than that of the best commercial compositions (Yan *et al.*, 2013). Using this TGG technique, two goals were achieved: (1) $\langle 001 \rangle$ texturing (grain orientation along the $\langle 001 \rangle$ crystallographic direction) of piezoelectric ceramic with engineered domain state to achieve high d and (2) realization of high $d \cdot g$ coefficient by suppressing ϵ of textured piezoelectric ceramic through the use of low ϵ templates.

Figure of merit for energy harvesting

Besides the basic piezoelectric properties (d and g), different figures of merits (FOMs) of piezoelectric materials have been proposed based on the consideration of device structures/configurations, working modes, and dimensions/scales. When it comes to resonance conditions, the effect of the loss and mechanical quality factor need to be considered. Oliver and Priya proposed a dimensionless figure of merit (DFOM), given as: (Bedekar *et al.*, 2010)

$$\text{DFOM} = \left(\frac{k_{31}^2 Q_m}{s_{11}^E} \right)_{\text{on-resonance}} \left(\frac{d_{31} g_{31}}{\tan \delta} \right)_{\text{off-resonance}} \quad (9)$$

where k_{31} is the transversal electromechanical coupling factor, Q_m is the mechanical quality factor, s_{11}^E is the elastic compliance at the constant electric field, d_{31} is the transversal piezoelectric strain constant, g_{31} is the transversal piezoelectric voltage constant, and $\tan \delta$ is the loss factor.

For micro-electromechanical systems (MEMS), where piezoelectric stress coefficients are typically used due to the constrained boundary conditions, an analogous FOM of $e \cdot h = e^2 / \epsilon_0 \epsilon_r$ is proposed. MEMS energy harvesters typically have a composite beam structure, which consists of a thin film of the piezoelectric material on an elastic substrate. Roundy *et al.* (2003) derived the expression for maximum power ($P_{\max}$) from the piezoelectric vibrational harvester as:

$$P_{\max} = \frac{1}{4} \left(\frac{e_{31}^2}{\epsilon_0 \epsilon_{33}^T} \right) \left(\frac{1 - \nu}{E_y} \right) \left(\frac{m}{\omega_0} \right) Q_{\text{tot}}^2 a_0^2 \quad (10)$$

where Poisson ratio ν , and Young's modulus E_y of the substrate material are considered besides the piezoelectric film itself. A method of delineating the contribution of material, composition, geometry, mechanical damping, and end mass to the power output of MEMS piezoelectric energy harvesters through scaling analysis is important as the power generated by the micro-scale harvesters scales down rapidly. The power generated by the MEMS piezoelectric harvester in terms of the force of excitation F_0 , proof mass m , natural frequency ω_n , and power factor Π is given by the ratio of $(F_0^2 \Pi)$ and $(m \omega_n)$. The power normalized by

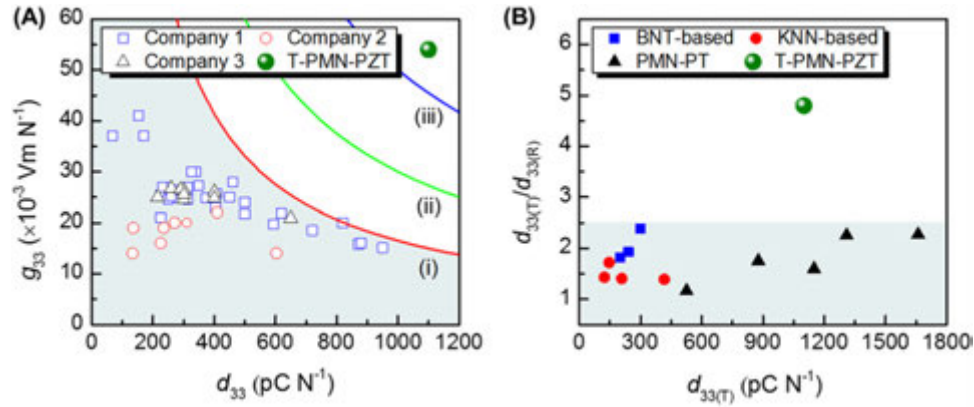


Fig. 5 (A) Comparison of g_{33} and d_{33} values of various piezoelectric ceramics. Different colored lines (i), (ii) and (iii) indicate the plots of $g_{33} \cdot d_{33} = c$ function; (i) $c = 16,500 \times 10^{-15} \text{ m}^2 \text{ N}^{-1}$, (ii) $c = 30,000 \times 10^{-15} \text{ m}^2 \text{ N}^{-1}$ and (iii) $c = 50,000 \times 10^{-15} \text{ m}^2 \text{ N}^{-1}$; (B) Comparison of $d_{33(T)}/d_{33(R)}$ ratio vs. $d_{33(T)}$ of various textured piezoelectric ceramics. The $d_{33(T)}$ and $d_{33(R)}$ represent d_{33} of textured ceramic and that of randomly oriented counterpart respectively. BNT and KNN represent $(\text{Bi}_{1-x}\text{Na}_x)\text{TiO}_3$ and $(\text{K}_{1-x}\text{Na}_x)\text{NbO}_3$ compositions respectively.

acceleration squared is decomposed as a product of five factors, namely, scaling factor S , composition factor C , inertial factor I , material factor M , and power factor P , abbreviated as SCIMP factors. This method is successfully implemented to estimate and compare the performance of different MEMS energy harvesters (Sriramdas and Pratap, 2017).

Impedance matching

Similar to the natural frequency matching with an external vibration source, the impedance of the piezoelectric energy harvester should be matched to that of an external circuit in order to maximize the power extraction. Usually, an electrical impedance matching circuit is placed between the piezoelectric generator and external loads such as a rechargeable battery and supercapacitor. Thus, the matching network should be lossless and requires that the input impedance should be matched to the output impedance. The electrical input impedance of the piezoelectric energy harvester is described as follows: (Priya *et al.*, 2019)

$$Z = 1/\omega C_0 \quad (11)$$

where ω is vibration frequency of energy harvester, and C_0 is capacitance of piezoelectric materials. The impedance matching circuit consists of a combination of capacitors, inductors and resistors in accordance with the impedance of the piezoelectric energy harvester.

Piezoelectric nanogenerator

The idea of piezoelectric nanogenerator using ZnO nanowire has been explored by Wang *et al.* (2008), Wang and Song (2006) to provide the self-powered nanotechnology, aiming at powering nanodevices/nanosystems using the energy harvested from the environment in which the systems are supposed to operate. The working principle of PENG can be explained in two different ways: the force exerted perpendicular and parallel to the axis of the nanowire materials as shown in Fig. 6(A)–(C), Wang (2011).

The working principle for the primary case (Fig. 6(A, B)) can be clarified by a vertically developed nanowire subjected to the horizontally moving tip. During application of external force by moving tip to the piezoelectric structure it gets deformed. The piezoelectric impact will generate the electric field inside the nanostructure; the extended part with the positive strain will display the positive electrical potential, while the compressed part with the negative strain will show the negative electrical potential. This is because of the relative displacement of cations and anion in the crystalline structure. Therefore, the tip of the nanowire will have an electrical signal on its surface, while the lower part of the nanowire is neutralized since it is grounded. The maximum voltage produced in the nanowire can be determined using the following equation (Wang *et al.*, 2008).

$$V_{\max} = \pm \frac{3}{4(\kappa_0 + \kappa)} [e_{33} - 2(1 + \nu)e_{15} - 2\nu e_{31}] \frac{a^3}{l^3} v_{\max} \quad (12)$$

where κ_0 is the permittivity in vacuum, κ is the dielectric constant, e_{33} , e_{15} and e_{31} are the piezoelectric coefficients, ν is the Poisson ratio, a is the radius of the nanowire, l is the length of the nanowire and $v_{\max}$ is the maximum deflection of the nanowire's tip. The electrical contact plays an important role to pump out charges in the surface of the tip. Since the ohmic contact will neutralize the electrical field generated at the tip, the Schottky contact must be formed between the counter electrode and the tip of the nanowire. In order to form an effective Schottky contact, the electron affinity (E_a) must be smaller than the work function (ϕ) of the metal composing the counter electrode. For the second case, a model with a vertically developed nanowire stacked between the ohmic contact at its base and the Schottky contact at its top is considered. At the time of applied force toward the tip of the nanowire, the uniaxial compressive is created in the nanowire. Because of the piezoelectric impact, the tip of the nanowire will have a negative piezoelectric potential, increasing the Fermi level at the tip. Since the electrons will flow from the tip to the base through the external circuit thus, the positive electrical potential will be produced at the tip. The Schottky contact will block the electrons being

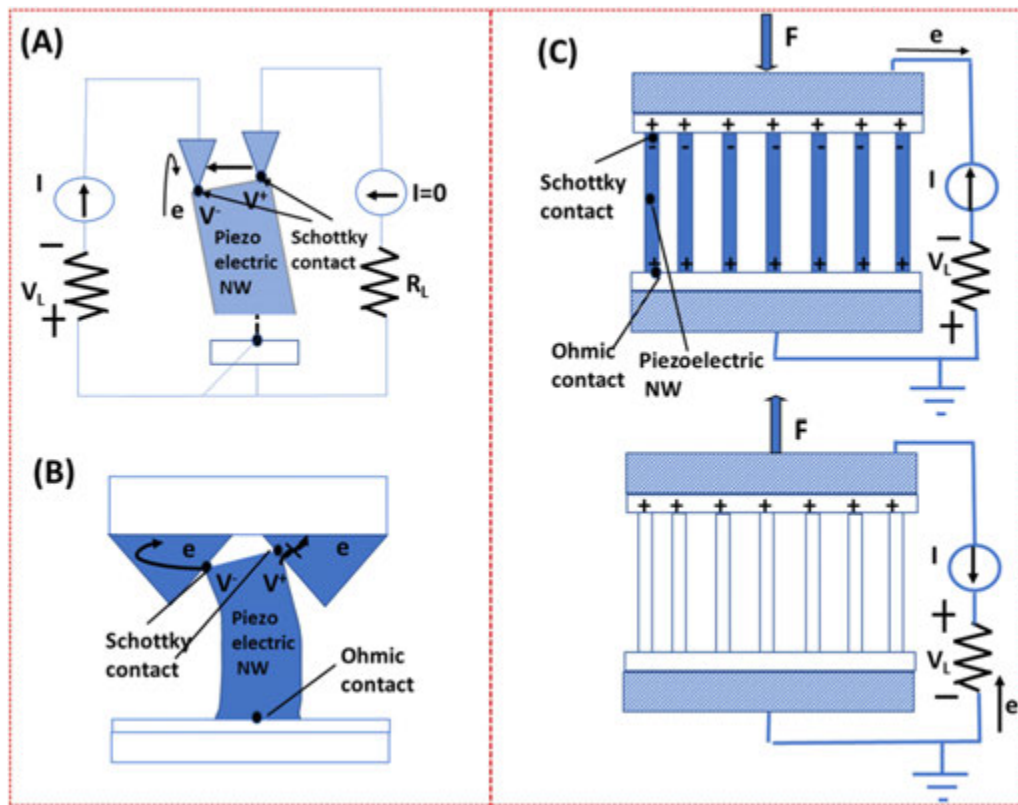


Fig. 6 The working mechanism of PENG where force is exerted perpendicular to the growing direction of nanowire. (A) An AFM tip is swept through the tip of the nanowire. (B) The nanowire is integrated with the counter electrode with AFM tip-like grating. (C) Working principle of nanogenerator where an individual nanowire is subjected to the force (F) exerted parallel to the growing direction of nanowire.

moved through the interface, hence keeping up the potential at the tip. As the force is taken out, the piezoelectric impact reduces, and the electrons will be streaming back to the top to neutralize the positive potential at the tip. In this case, an alternating current signal is generated.

Geometrical configuration

According to the configuration of piezoelectric nanostructure, most of the nanogenerators can be categorized into three types: vertical nanowire integrated nanogenerator (VNG), lateral nanowire integrated nanogenerator (LNG) and nanocomposite nanogenerators (NNG). There are few designs which do not fall into the aforementioned classes. VNG is a three dimensional design consisting of a pile of three layers (in general); base anode, vertical piezoelectric nanostructure layer, and the counter terminal. LNG is a two-dimensional arrangement comprising of three sections: the base anode, the horizontal piezoelectric nanostructure and the metal cathode for Schottky contact. In most cases, the thickness of the substrate film is much higher than the diameter of the piezoelectric nanostructure, so the individual nanostructure is exposed to the tensile strain. NNG is a three-dimensional setup comprising of three fundamental parts: the metal plate terminals, the vertical piezoelectric nanostructure and the polymer grid which fills the middle of the piezoelectric nanostructure. NNG can achieve high energy conversion effectiveness as demonstrated using unique nanogenerator designs based upon ZnO nanowires.

Fundamentals of Triboelectricity

When a given material makes contact with a dissimilar material under force, the difference in chemical potential of the two surfaces will result in a charge transfer across the interface, thereby, making surfaces of both the materials electrically charged after separation. If the electrodes are connected to external load, current will flow between them to screen out the electric field built up by the charged surfaces. As they are brought into contact again by outside mechanical stimuli, the expected potential difference on the electrodes will change and current will stream in opposite direction. A consistent AC output can be acquired by repeating this activity cycle. In other words, the device operates on the coupling of two commonly observed phenomena, contact electrification and electrostatic induction, with the former providing the static polarized charges on material surfaces and the latter driving the transformation of mechanical energy to electricity via mechanically triggered change in electric potential. The current is caused by the polarization field generated by the electrostatic charge on the surface of the dielectric material. The Maxwell's displacement

current is as follows (Wu *et al.*, 2019)

$$J_D = \frac{\partial D}{\partial t} = \varepsilon \frac{\partial E}{\partial t} + \frac{\partial P_s}{\partial t} \quad (13)$$

where, J_D is the displacement current density, D is the electric displacement vector, ε is the permittivity of the medium, E is the electric field, and P_s is the polarization field. The initial term indicates a time-varying electric field and is attached to the origin of electromagnetic waves, while the second term presents the commitment from surface polarization and is the origin of nano-generators. More specifically, in PENGs, the polarization comes from piezoelectric polarization charges generated by applied strain. -varying surface polarization as two materials in contact undergo mechanically agitated displacement. It has two electrodes connected to external load and two dielectrics for contact electrification. The surface is partially charged and the charges are non-mobile static charges, and triboelectric induced surface charge density σ_{tribo} builds up as a number of contacts between the two dielectric media and finally reaches a saturation, and it is independent of the gap distance z . The electrostatic field built by the triboelectric charges drives electrons to flow through the external load, resulting in an accumulation of free electrons in the electrode, $\pm \sigma_{\text{tr}}(z, t)$, which is a function of the gap distance $z(t)$ between the two dielectrics. The triboelectric charges build up an electrostatic field, which drives free electrons to flow through the external circuit. The corresponding displacement current can be calculated as

$$J_D = \frac{\partial D_z}{\partial t} = \frac{\partial \sigma(z, t)}{\partial t} \quad (14)$$

The displacement current is originated from the only conduction mechanism for electron transport in capacitive conduction and leads to the output current of TENG through electromagnetic waves and inductive current, rather than the direct flow of free charges across the electrodes. The current of TENG, considering the capacitive conduction model (Fig. 7(A) (ii)), is given by (Fan *et al.*, 2012)

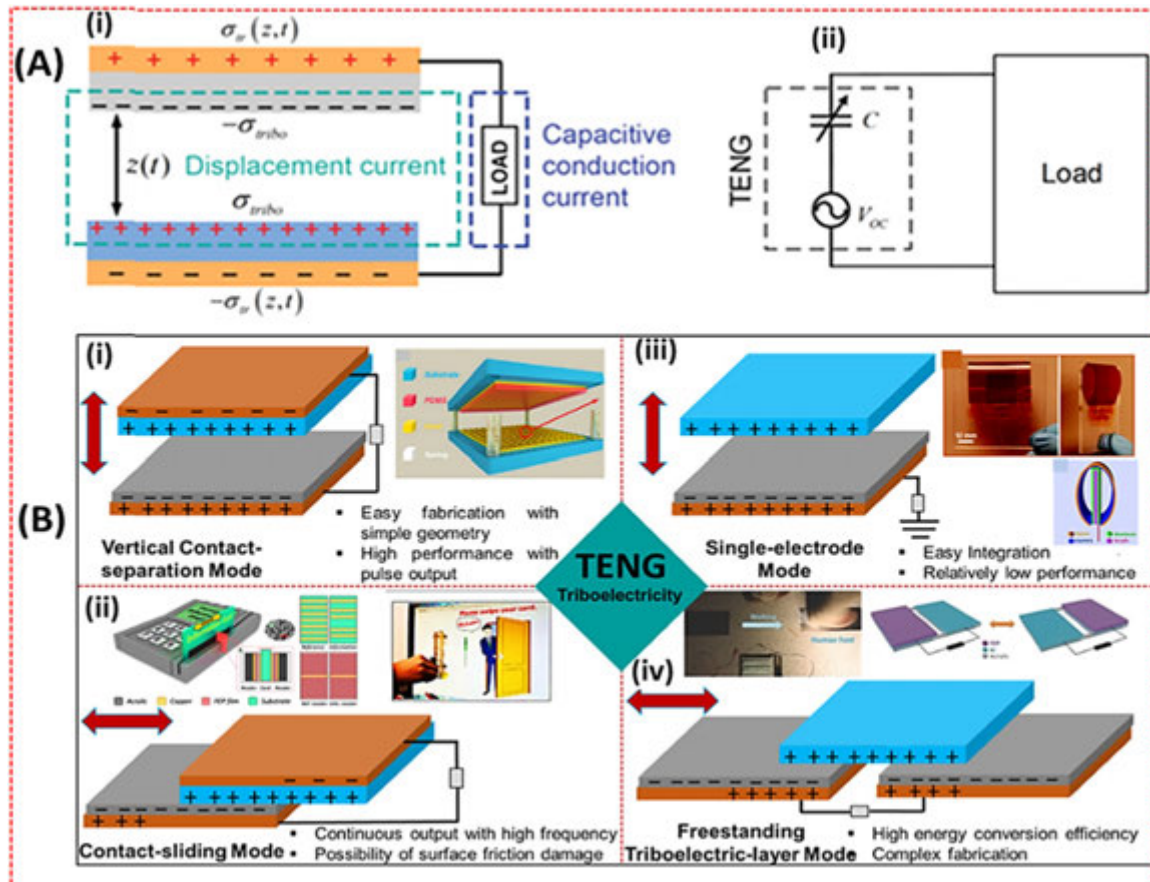


Fig. 7 (A) Theoretical models of TENG. The displacement current model of a contact-separation-mode TENG. c) The equivalent electrical circuit model of TENG. Copyright 2018, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (B) The four fundamental working modes of TENGs (i) vertical contact-separation mode, (ii) contact-sliding mode, (iii) single electrode mode and (iv) freestanding triboelectric-layer mode. Reproduced with permission from Wu, C., Wang, A.C., Ding, W., Guo, H., Wang, Z.L., 2019. *Advanced Energy Materials* 9, 1802906. Adapted with permission from Karan, S.K., Maiti, S., Lee, J.H., *et al.*, 2020. *Advanced Functional Materials* 30 (48), 2004446. Copyright 2020. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

$$I = \frac{\partial Q}{\partial t} = A \frac{\partial \sigma}{\partial t} \quad (15)$$

The mismatch of surface charge between the two electrodes of TENGs leads to the two different phenomena in the triboelectric effect. The initial part is related to the triboelectric charges that contributes to generating an output open-circuit voltage, $V_{OC}(z)$, which is a function of separation distance (z). The transferred charges (Q) contribute towards the mismatch of the fraction of electric potential. When there are no triboelectric charges, the structure behaves similar to a typical capacitor. The contribution of the transferred charges between the two electrodes is equal to $-Q/C(z)$, where C indicates the capacitance between the two electrodes. According to the electrical potential superposition principle, the total voltage between the electrodes is represented as: (Niu and Wang, 2015)

$$V = -\frac{1}{C(z)} \times Q + V_{oc}(z) \quad (16)$$

The V - Q - z relationship is the governing equation for TENGs in principle, which clearly describes its inherent capacitive nature. The separation between the materials leads to a surface charge mismatch and generates electrical potential between the two electrodes. The electrical potential promotes the current between electrodes when the external circuit is connected between the electrodes. In short-circuit (SC) conditions, the transferred charges (Q_{SC}) fully screen the electrical potential created from polarized triboelectric charges. Hence, the following equation can be derived for the short-circuit condition of the TENGs: (Niu and Wang, 2015)

$$0 = \frac{1}{C_z} Q_{sc}(z) + V_{oc}(z) \quad (17)$$

The basic fundamental relationship between Q_{SC} , C , and V_{OC} are shown by

$$Q_{SC} = C(z)V_{oc}(z) \quad (18)$$

The current transport relation of a TENG in the contact-separation mode is given as:

$$AR \frac{\partial \sigma(z, t)}{\partial t} = -\sigma(z, t)[d_1/\epsilon_1 + d_2/\epsilon_2] - H(t)[\sigma(z, t) - \sigma_T]/\epsilon_0 \quad (19)$$

where $H(t)$ indicates a function depending on the contacting rate between the two dielectrics, A indicates the electrode area, R represents the load resistance, z signifies the thickness of the film, and σ symbolizes the polarization charge density.

According to the transport relation, the displacement current, electric potential, output current, and output power can be estimated for the four basic TENG working modes. Four types of fundamental TENGs have been proposed in literature, as shown in Fig. 7. Fig. 7(B) (i) shows the vertical contact separation mode TENG, where two different dielectric film surfaces touch each other. The conducting metal films are sputtered on the bottom and top surfaces in the device. When these two different surfaces touch each other, the opposite charges are developed on both surfaces. When these two surfaces separate from each other by small gap through tiny external force, potential drop was observed. Thus, when both surface electrodes are well connected through external load, then free electrons will move from one active electrode to another to create an opposite potential in order to maintain the electrostatic field. The generated triboelectric charges will be vanished when gap is closed and electrons will flow back. The TENG generates a positive output voltage and short circuit current upon contact between the materials whereas it generates negative output voltage with negative when they are separated. The sliding or moving of the top (upper) surface on the bottom one (lower) would alter distribution of local electrical field for finite size of TENG, and thus the charged electrons on both ground and bottom electrode is exchanged to balance the potential variation of the electrode. For single electrode TENGs mode, bottom electrode part is grounded and it is used for mobile cases, since this type of TENG can move freely (Fig. 7(B) (iii)). Single electrode TENG method is operated in both ways via contact-sliding mode and contact-separation mode. If the size of the TENG is finite, an approaching or departing of the top object from the bottom one would change the local electrical field distribution, so that there are electron exchanges between the bottom electrode and the ground to maintain the potential change of the electrode. The mode can be useful for utilizing the energy from a moving object without attaching an electric connection, such as human walking, moving car, finger typing and more. For freestanding TENG mode, two symmetric electrodes are kept under a dielectric layer (Fig. 7(B) (iv)). The electrode size and gap distance among the two electrodes are of the same order as the moving object size. The movement of the moving object on the electrodes developed asymmetric charge distribution, resulting in flow of electrons among the two electrodes to adjust the local potential distribution (Fig. 7(D)) (Wang, 2015).

Parametric analysis

Charge injection depth

The triboelectric interface must have the capacitance characteristics to generate the charge in the system. The initial cause of tribological electrification depends on the presence of the internal electric fields in solid insulators. In all types of triboelectric contact modes, the charge is effective to a certain depth to form the capacitance. This depth is called the charge injection/penetration depth (λ). The capacitance characteristics in the triboelectric effect can be depicted with λ as (Pan and Zhang, 2019)

$$C = \epsilon S / 4\pi k \lambda \quad (20)$$

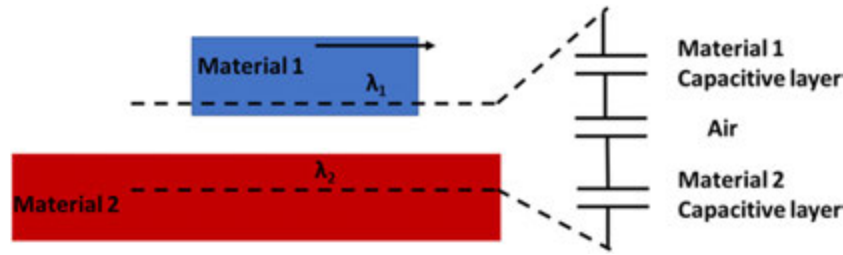


Fig. 8 The capacitive configuration for triboelectric interface.

where C is the equivalent capacitance, ε is the dielectric constant of material, and k is the electrostatic constant. The simplest configuration with the capacitance in the triboelectric interface is shown in Fig. 8.

This material-determined capacitance formed by the charge injection depth possibly interacts with interfacial air capacitance, which influence the dynamical responses of the triboelectric effect (air has breakdown voltage strength as stated by Paschen's law) (Sow *et al.*, 2013).

Surface charge density

The surface charge density σ is a parameter for quantifying the effective electric charges on both surfaces, and determines the efficiency of triboelectric devices. It serves as the basis for analyzing parameters such as the area power density and volume energy density. The surface charge and interface electrical performance is described, as in following equation: (Pan and Zhang, 2019)

$$V = f(Q) \cong f(A_{\text{eff}} \times \sigma) \quad (21)$$

where Q is the charge on the surface with an effective area of A . The accumulating charge will then introduce a voltage V . One critical point is that the final surface charge density significantly differs from the triggered charges led by the driving force of tribo-contacts. This is mainly because of charge backflow when the contact surfaces are dynamically moving farther or closer. This is a natural process in the capacitive configuration, as shown in Fig. 8.

Strategies for improving triboelectric charge density

Plenty of research efforts on TENG have been devoted to improve the triboelectric charge density, in terms of the output voltage, current, and power (Wu *et al.*, 2019). These endeavors are classified into three strategies: (1) modification in material composition, (2) improvement in effective contact area, and (3) change in environmental conditions (Fig. 9). The material modification strategy (Fig. 9(A)) is further divided into chemical surface functionalization and bulk composition manipulation. In chemical surface functionalization, the triboelectric material is modified by changing the functional groups exposed on the surface so that its charge capture capability is enhanced. In bulk composition manipulation, composite materials are generally fabricated by optimizing the material composition so that the charge-attracting or charge-trapping capability is enhanced. The second strategy for improving the triboelectric charge density (Fig. 9(B)) is based on improvement of effective contact area. The effective contact area between two solid materials is generally far from 100% due to surface roughness, and thus by simply improving the contact effectiveness, the total amount of triboelectric charges will increase even if the surface charge density where the contact electrification occurs remains unchanged. The third strategy is to introduce change in environmental conditions such as temperature and pressure (Fig. 9(C)).

The electrical output performance of a TENG is strongly depends on temperature which decreases with increasing temperature from -20 to 20°C , remained stable from 20 to 100°C , and dropped rapidly afterward. The temperature-dependent change in output charge density is attributed to the change in material permittivity and temperature-induced surface defects such as surface oxidation. As temperature, pressure also an important factor by which one can improve the triboelectric charge density of a TENG operating at high vacuum ($\approx 10^{-6}$ torr).

Choice of materials for triboelectric harvesters

Most of the materials such as metal, polymer, silk, and wood have triboelectric effect. However, the ability of a material for gaining/losing electron depends on its polarity. Wilcke (Gillispie, 2019) have proposed a triboelectric series based on order of polarity. A material towards the bottom of the series attain a more negative charge when touched to a material near the top of the series. The further away two materials are from each other on the series, the greater the charge transferred. Zou *et al.* (2019) introduced a standard method to quantify the triboelectric series for a wide range of polymers, establishing quantitative triboelectrification as a fundamental materials property. The triboelectric charge density (TECD) is measured with respect to a shape adaptable soft liquid metal to consider the ideal surface contact with the material at $20 \pm 1^\circ\text{C}$ temperature, 1 atm pressure and 0.43% relative humidity (RH). It is possible to achieve proper TECD by selecting proper materials for the fabrication of TENGs by contacting and separating with the liquid metal under same contact pressure. Using this series, one can choose a perfect triboelectric materials to fabricate proper TENG according to desired energy harvesting applications (Fig. 10).

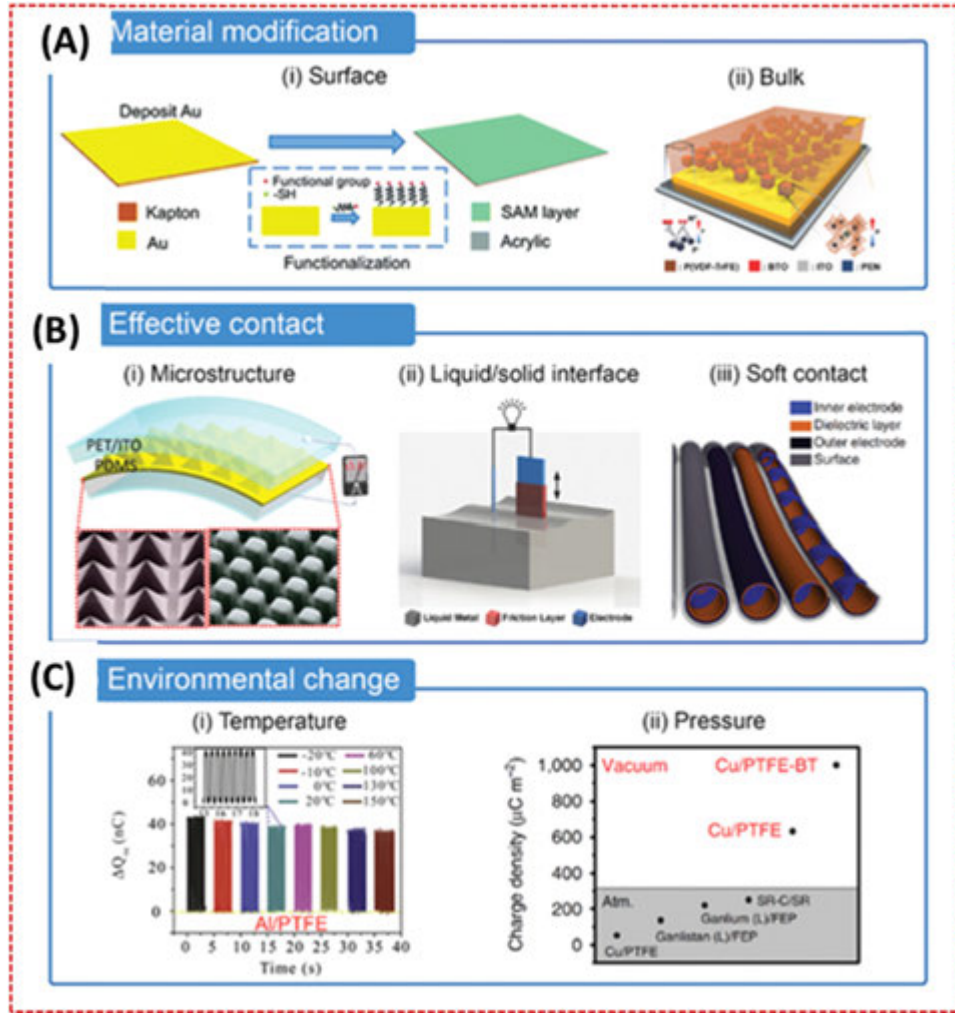


Fig. 9 Strategies for improving triboelectric charge density. (A) Material modification. (i) Chemical surface functionalization. (ii) Bulk composition manipulation. (B) Improvement in effective contact area. (i) Surface microstructure. (ii) Liquid/solid interface. (iii) Soft contact. (C) Change in environmental conditions. (i) Temperature. (ii) Pressure. Reproduced with permission from Wu, C., Wang, A.C., Ding, W., Guo, H., Wang, Z.L., 2019. *Advanced Energy Materials* 9, 1802906. Copyright 2018, Wiley-VCHS.

Figure of merit

The proposed figure of merit (FOM) for TENG consists of a structural FOM (FOM_S) and a material FOM (FOM_M) (Zi *et al.*, 2015). Cycles for maximized energy output (CMEO) method by employing instantaneous short-circuit conditions during TENG operation facilitates that cycling charge (Q_C) is equal to maximum transferred charges ($Q_{SC,max}$). The maximized energy output per cycle (E_m) from the CMEO method can be expressed by

$$E_m = 1/2 Q_{SC,max} (V_{OC,max} + V'_{max}) \quad (22)$$

where $Q_{SC,max}$, $V_{OC,max}$, and V'_{max} are all proportional to the triboelectric charge density σ . Given that the average output power and energy-conversion efficiency at the CMEO are proportional to maximum energy output (E_m)/maximum displacement (x_{max}), a dimensionless structural FOM is proposed as

$$FOM_S = (2\varepsilon_0/\sigma^2 A) \times (E_m/x_{max}) \quad (23)$$

where ε_0 is the permittivity of vacuum and A is the triboelectrification area of TENG. The term $\sigma^2 A$ is introduced in the denominator so that the effects of material properties and device size are excluded in the FOM_S . Consequently, the performance FOM is defined as

$$FOM_P = FOM_S \times \sigma^2 = (2\varepsilon_0/\sigma^2 A) \times (E_m/x_{max}) \quad (24)$$

where σ^2 can be defined as the FOM_M . The FOM_S is dependent on the maximum displacement x_{max} and can be optimized by adjusting the value of x_{max} . The $FOM_{S,max}$ for different working modes of a TENG was proposed where free standing mode has



Fig. 10 Triboelectric series of materials and their triboelectric charge density. Reproduced with permission Zou, H., Zhang, Y., Guo, L., *et al.*, 2019. Nature Communications 10, 1–9. Copyright 2019, Springer Nature.

maximum FOM and single contact mode has minimum FOM (contact freestanding triboelectric-layer mode > contact-separation mode > sliding freestanding triboelectric-layer mode > lateral-sliding mode > single-electrode contact mode).

A standard method for quantifying the triboelectric performance of a material is proposed as well. The triboelectric charge density of the test material with respect to a certain liquid metal such as Galinstan is measured. A dimensionless material FOM is defined by normalizing the triboelectric charge density from the test material with that from a reference material such as fluorinated ethylene propylene (FEP)

$$\text{FOM}_{\text{DM}} = (\sigma_N)^2 = \sigma_{\text{Material/Galinstan}}^2 / \sigma_{\text{FEP/Galinstan}}^2 \quad (25)$$

The use of liquid metal rather than solid materials is justified by the more intimate contact of a liquid–solid interface and thus less influence of surface roughness. A negative σ_N means the material is more triboelectrically positive than Galinstan, and a σ_N larger than one means it is more triboelectrically negative than FEP, and something in between means it is more negative than Galinstan but more positive than FEP.

Fundamentals of Magneto-Mechano-Electric (MME) Effect

MME generators are capable of harvesting energy from both mechanical vibrations and alternating magnetic fields because both the piezoelectric and magnetoelectric effects are present in an MME generator. The magneto-mechano-electric (MME) generators consisting of a magnetic mass on a cantilever beam structure have been promising to harvest the energy in magnetic fields through the magnetoelectric (ME) effect. However, the performance of MME generators has been enhanced by employing magnetostriction resulting in strain mediated magnetoelectric effect in the MME generators. The structure of an ME coupled MME generator is similar to that of an MME generator with the elastic layer replaced by a magnetostrictive material. In addition to the end magnetic torque, the force due to the magnetostriction further enhances the strain in the piezoelectric layer, thus increasing the power generation capability. Thus both the piezomagnetic coupling constants in magnetostrictive material and piezoelectric coupling constants in piezoelectric material simultaneously contribute to the enhancement in the power levels in magnetic field harvesters (Ryu *et al.*, 2015). MME generators are capable of harvesting energy from both mechanical vibrations and alternating magnetic fields because both the piezoelectric and magnetoelectric effects are present in an MME generator (Ryu *et al.*, 2015). To enhance the efficiency and power output of ME energy harvesters, the combination of these two techniques through MME generators is considered to be a good strategy. A dual-phase (vibration and magnetic) MME generator combines the ME coupling and piezoelectric energy harvesting mechanisms, as shown in Fig. 11. In the case of dual-phase harvester, the MME generator is simultaneously excited by an AC magnetic field (H_{ac}) generated by stray magnetic fields and ambient mechanical vibrations. In an MME generator, the AC magnetic field is converted into an electric field in two steps. In the first step, the oscillating magnetic field is converted into mechanical vibration through the magnetostriction of the magnetostrictive layer and the torque generated by a permanent magnet. In the next step, mechanical strain due to the vibration is converted into the electric field through piezoelectric material. The torque acting on a magnet of volume V , and surface S placed in a magnetic field with flux density B_{ext} is given as: (Furlani, 2001)

$$T = \int_V r \times (J_m \times B_{\text{ext}}) dv + \oint_S r \times (j_m \times B_{\text{ext}}) ds \quad (26)$$

where J_m and j_m are equivalent volume and surface current densities, respectively, and r is the vector of interest for torque computation. The force due to the torque on the beam is dependent on the beam's shape function, ϕ , in the respective mode shape and hence, the location and geometry of the magnet affect the force of excitation. The force from a permanent magnet as a function of time t , on the beam with length L , and a magnet with width w and projected area A , when placed in an external field intensity $H_1(t)$ is given by (Sriramdas *et al.*, 2020)

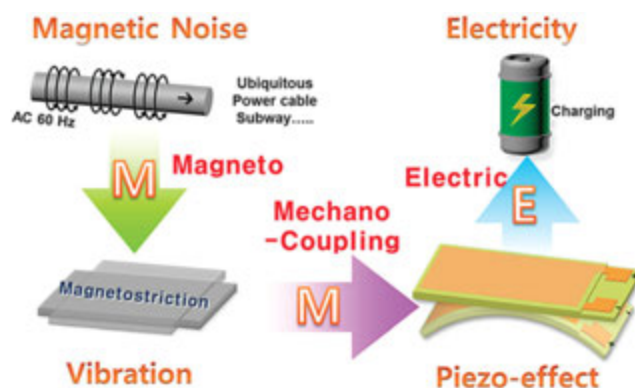


Fig. 11 The working principle and the energy transfer processes in an MME energy harvesting device. Reproduced with permission from Ryu, J., Kang, J.-E., Zhou, Y., *et al.*, 2015. *Energy & Environmental Science* 8, 2402–2408. Copyright 2014, Royal Society of Chemistry.

$$F_1 = wAB_r H_1(t) \phi(L) \quad (27)$$

where B_r is the remanent flux density of the magnet. However, the force offered by the magnetostriction in a cantilever beam is derived from the force and moment balance on an infinitesimal element of the beam using Newton's second law or Hamilton's principle (Meirovitch, 2010). The thickness of the magnetostrictive layer, t_m , elastic modulus c_{11m} and width b , and the magnetostrictive strain coupling constant d_{31m} directly increase the force of excitation due to the magnetostriction. Using the height of the neutral layer Z , the magnetostrictive force of excitation is given by

$$F_2 = c_{11m} d_{31m} b t_m \left(\frac{t_m}{2} - \bar{z} \right) \phi'(L) H_1(t) \quad (28)$$

The electromechanical coupling coefficient (Sriramdas et al., 2015) G , for the MME harvester, depends on the piezoelectric stress constant e_{31} , and the layer thickness t_p along with the magnetostrictive and adhesive layers t_m and t_a . The piezoelectric coupling coefficient G for the two-layer MME is given by,

$$G = e_{31} b \left(t_m + t_a + \frac{t_p}{2} - \bar{z} \right) \phi'_2(x)|_{x=L} \quad (29)$$

Multiple magnetostrictive layers are often used in designing MME harvesters to obtain large magnetostriction while maintaining a low frequency of resonance for the beam (Kang et al., 2018). The force of excitation due to the magnetostriction of the composite beam with piezomagnetic stress constant e_{31m} in the i^{th} layer of the magnetostrictive layer is given by

$$F_2 = b \sum_{i=1}^{2n-1} e_{31mi} t_i \left(\sum_{j=1}^{i-1} t_j + \frac{t_i}{2} - \bar{z} \right) \phi'(x)|_{x=L} H_1(t) \quad (30)$$

The forces F_1 and F_2 act simultaneously on the beam when ambient stray magnetic fields are present. These forces cause the beam to deform, thereby causing strain in the piezoelectric material. The cyclic change in the strain, results in a flow of charge from the piezoelectric material terminals when connected to an external load resistance. The MME composite transduction is a promising method of scavenging energy from magnetic fields owing to the strong ME coupling between the magnetostrictive and piezoelectric layers (Ryu et al., 2001).

Types of ME transducers

The magnetoelectric coupling effect in magnetostrictive-piezoelectric layered composites depends on the type of MME. The MME can be broadly classified into two groups of configurations (1) asymmetric transducer and (2) symmetric ME transducer. An example of an asymmetric ME transducer is a bilayer structure consisting of one magnetostrictive and one piezoelectric layer. Multiple layers of single or different magnetostrictive materials combined with one piezoelectric layer can also be described as an asymmetric ME configuration. A symmetric ME transducer consists of an even distribution of magnetostrictive (M) or piezoelectric (P) materials placed symmetrically about the neutral axis of the composite. The symmetric transducer has two distributions – MPM and PMP configurations. The symmetric transducer has significant coupling in the longitudinal vibration modes of the composite, however, the asymmetric transducer responds to the magnetic fields through the bending vibration. In both transducers, the composite responds to the magnetic field in either longitudinal or transverse direction in the respective vibration mode.

Figure of merit

The ME effect induces a magnetization M_i due to an applied electric field E_j or vice versa producing an electric polarization P_i due to an applied magnetic field H_j that can be described as follows:

$$P_i = \alpha_{ij} H_j \quad (31)$$

$$M_i = \frac{\alpha_{ji}}{\mu_0} E_j \quad (32)$$

where μ_0 is the permeability of free space and α_{ij} is the ME susceptibility tensor (Bichurin and Petrov, 2014). The tensor is a second rank tensor describing the interaction between the magnetic and electric vectors, and hence, serves as a figure of merit for ME transduction. When both electric and magnetic fields are applied to the transducer, the constitutive equations describing the coupling between the electrical and magnetic layers is described using (Bichurin et al., 2002)

$$S_i = s_{ij} T_j + d_{ik} E_k + q_{ki} H_k \quad (33)$$

$$D_k = d_{ki} T_i + \varepsilon_{kn} E_n + \alpha_{kn} H_n \quad (34)$$

$$B_k = q_{ki} T_i + \alpha_{kn} E_n + \mu_{kn} H_n \quad (35)$$

where S_i , T_j , E_k , H_k , D_k and B_k are the components of strain tensor, stress tensor, electric field, magnetic field, electric displacement, and magnetic flux density vectors. s_{ij} , d_{ki} , q_{ki} , ε_{kn} , and μ_{kn} denote the effective compliance, piezoelectric, piezomagnetic, permittivity, permeability components. The ME susceptibility tensor, α_{kn} , consists of a significant term depicted by ME voltage coefficient, α_E , depending on the type of ME transducer selected. The interface between piezoelectric and magnetostrictive layers can be represented by an interfacial coupling parameter k . The ratio of volume of piezoelectric material (p_v) to the total volume of the transducer ($p_v + m_v$) is another variable denoted by volume fraction v that is used in the optimization of α_E , where v_m is the volume of the magnetostrictive phase in the transducer. The ME susceptibility or ME voltage coefficient for a bilayer longitudinal

transducer, which has both electric and magnetic fields along direction 3 normal to the plane, is denoted by $\alpha_{E,33}$. Assuming a perfect interfacial coupling ($k = 1$), the expression for $\alpha_{E,33}$ as a function of the material properties in the respective domains denoted by a prefix m for magnetostrictive layer and p for piezoelectric layer is (Harshe *et al.*, 1993)

$$\alpha_{E,33} = \frac{-2\nu(\nu - 1)^p d_{13}^m q_{31}}{(m s_{11} + m s_{12})^p e_{33} \nu + (p s_{11} + p s_{12})^p e_{33} (1 - \nu) - 2^p d_{13}^2 (1 - \nu)} \quad (36)$$

The transverse ME coupling is observed in a bilayer transducer when the direction of the magnetic field is along the longitudinal axis (direction-1) while the electric field is along direction 3. An expression for the transverse ME voltage coefficient derived by Bichurin *et al.* (2002) considering the interfacial coupling condition k is

$$\alpha_{E,31} = \frac{-k\nu(1 - \nu)^p d_{31} (m q_{11} + m q_{21})}{(m s_{11} + m s_{12})^p e_{33} k\nu + (p s_{11} + p s_{12})^p e_{33} (1 - \nu) - 2k^p d_{13}^2 (1 - \nu)} \quad (37)$$

It may be noted that when the interfacial coupling is perfect, a similar expression is reported by Filippov *et al.* (2014). A nonlinear constitutive model for Terfenol-D magnetostrictive rods can be found in Ref. Zheng and Liu (2005) by Zheng *et al.* The effect of a bias field on the ME voltage coefficient can be described by considering the nonlinear constitutive model for the magnetostrictive material. The reader is referred to Ref. Xu *et al.* (2018), Chang and Carman (2008), Bichurin *et al.* (2017) for a more detailed discussion on the figure of merit for trilayer, multilayer and graded magnetoelectric composites.

Energy Harvesting Technologies

The current portable and wearable technology heavily relies on rechargeable batteries. But for the near future, micro/nano-systems will be widely used in health monitoring, infrastructure and environmental monitoring, internet of things and defense technologies; the traditional batteries may not meet or may not be the choice as power sources for the following reasons. First, with the increasingly miniaturized devices, the size of the total micro/nano-systems could be largely dominated by the size of the battery rather than the device itself. Second, the number and density of micro/nano-systems to be used for sensor networks could be large, thus, replacing batteries for these mobile devices is challenging and even impractical. Lastly, the power needed to drive a micro/nano-system is rather small, in the range of micro- to milli-watt range. Energy harvesting is central for powering sensors without batteries. The most promising harvesting technologies that enable powering sensors from the unused ambient energy include piezoelectric energy harvesting in the form of both cantilevers and nanogenerators, triboelectric nanogenerators, and magneto-mechano-electric generators.

Cantilever Based Piezoelectric Energy Harvester

The piezoelectric energy harvesters in the form of a cantilever are preeminent in converting mechanical energy into electrical energy. The principle of generating electrical energy from the ambient motion can be explained through the energy flow associated with the transduction process. The energy transduction is maximum at the fundamental resonance of the cantilever structure. The ambient vibration energy is transferred into the structure through the base excitation. The proof mass exchanges the kinetic energy with the potential energy stored in the beam (Hajati and Kim, 2011). At steady state the amount of energy supplied to the structure reflects the energy absorbed by the system in the form of dissipation. When a piezoelectric layer is deposited on the cantilever beam, a portion of the dissipation energy is converted into electrical energy and the remaining energy is lost in the form of mechanical dissipation. A cantilever harvester designed for a specific vibrating source has its resonance frequency tuned to match the frequency of the vibrating structure. The cantilever structure parameters such as the equivalent mass, stiffness and damping have to be evaluated to tune the resonance frequency for effective transfer of energy from the vibration source. An iterative technique for obtaining these optimal parameters at which significant energy supplied to the system is transferred to the harvesters entails the determination of bandwidth of energy absorption, and dissipation energy (Sriramdas *et al.*, 2016). The resulting frequency ratio and absorber damping ratio ensure that not only the input energy is minimum but also much of the input energy is absorbed by the harvesters. The harvester is designed with the derived optimal equivalent mass, stiffness and the damping for effective absorption of energy from the vibration source. The piezoelectric cantilever harvesters are typically designed in the form of a unimorph or a bimorph (Renaud *et al.*, 2008). In contrast to a unimorph that has a single layer of piezoelectric material, a bimorph consists of two layers of the piezoelectric material distributed either in series or parallel depending on the direction of polarization.

The basic structure of the bimorph and unimorph is shown in Fig. 12. It may be noted that the bimorph shown in Fig. 12(A) has both the piezoelectric layers connected in parallel owing to the opposing stresses during bending. When the poling direction is reversed, the two terminals have to be connected in series. A unimorph on the other hand consists of a single layer as shown in Fig. 12(B).

Performance enhancements are demonstrated using multilayer and multistep harvester configurations (Sriramdas *et al.*, 2015) consisting of several layers of piezoelectric layers. Small size energy harvesters, particularly, MEMS-scale harvesters generally consist of unimorph configuration owing to the fabrication feasibility. An end mass is etched to act as a proof mass to adjust the resonance frequency typically less than 100 Hz (Reilly *et al.*, 2009). Several parameters such as electromechanical coupling coefficient, G ,

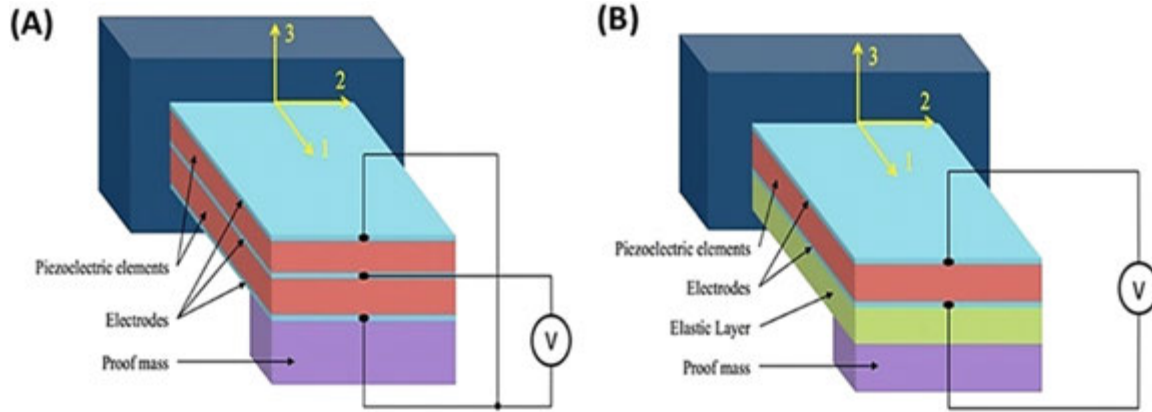


Fig. 12 (A) Bimorph structure of the piezoelectric energy harvester. (B) A unimorph configuration of the harvester with a single layer of the piezoelectric material. Reproduced with permission from Priya, S., Song, H.-C., Zhou, Y., *et al.*, 2019. *Energy Harvesting and Systems* 4, 3–39. Copyright 2017, De Gruyter.

beam stiffness, K , equivalent mass, M , damping coefficient, C , frequency of operation, ω_n , and force of excitation, F , affect the performance of the piezoelectric unimorph harvester. The differential equations governing the output from a cantilever harvester in terms of the voltage, V , and end displacement W , are

$$M\ddot{W} + C\dot{W} + KW - GV = F \quad (38)$$

$$RC_p\dot{V} + RV + V = 0 \quad (39)$$

where C_p and R are the capacitance of the harvester and the load resistance. The power from the harvester at resonance is estimated by solving the above equations for voltage and displacement and using $P = V_{rms}^2/R$. The power is optimized with respect to the load resistance R to determine the optimum harvester impedance as

$$R_{opt} = \frac{1}{C_p\omega_n} \left[\frac{2\zeta}{\sqrt{k_e^4 + 4\zeta^2}} \right] \quad (40)$$

where k_e is the coupling factor defined as $G/(\omega_n\sqrt{MC_p})$. The power developed by the piezoelectric harvester at the optimum load resistance is given by

$$P = \frac{F^2}{M\omega_n} \left(\frac{k_e^2}{8\zeta\gamma} \right) = \frac{F^2}{M\omega_n} \Pi \quad (41)$$

where $\gamma = k_e^2 + \sqrt{k_e^4 + 4\zeta^2}$. It may be noted in the expression for power that the term inside the bracket is a nondimensional quantity, called power factor, Π (Sriramdas and Pratap, 2017). The dimensionless term indicates that the power is greater when the damping ratio is small and the coupling factor is high. A relation between the damping ratio and coupling factor that maximizes the power factor is $k_e^* = 2.258 \zeta^{0.516}$. When the coupling factor and the damping ratio satisfy this relation, the power factor simplifies to $\Pi \approx \frac{1}{16\zeta}$. It may be noted that the resulting expression for power at the optimum power factor is similar to that derived in Ref. Xu (2012) when electrical and mechanical damping are equal. In order to determine the effect of geometry, inertial mass, and material properties, the expression for power is normalized with square of acceleration and the resulting terms are represented as a product of five factors namely Scaling, Composition, Inertial, Material and Power factors (SCIMP factors) (Sriramdas and Pratap, 2017). For example, the scaling factor is the product of width and cube of length. Hence, the power from a cantilever unimorph is proportional to the width and cube of length. Similarly, the other factors are used to maximize the power from the piezoelectric cantilever harvester. The optimal resistance R_{opt} is also similar to that given in the impedance matching section when the term in square brackets converges to unity for small values of coupling factor. Hence, matching the optimum load resistance is as crucial as other performance parameters to achieve the maximum power from the cantilever based piezoelectric harvesters. Aktakka *et al.* (2011) have demonstrated large acceleration (square) normalized power of $91 \mu\text{W}/\text{g}^2$ by using a thinned PZT wafer. The resonance frequency of the harvester is 154 Hz and the power generated was close to $205 \mu\text{W}$ at 1.5 g base acceleration. Thinning down PZT wafer to MEMS scale has shown promising results in another work by Janphuang *et al.* (2014). Although the power generated is small $\sim 1.6 \mu\text{W}$, the normalized power is over $160 \mu\text{W}/\text{g}^2$ at 99 Hz resonance frequency. Similar normalized power levels of $128 \mu\text{W}/\text{g}^2$ were achieved using AlN as the active piezoelectric material in the work by Andosca *et al.* (2012). It is observed that scaling and inertial factors play a significant role in microscale energy harvesters. Kuo *et al.* (2016) conducted research on transforming vibrational energy into electrical energy using a cantilever beam structure fabricated by laminating two PZT thick-film layers on both sides of a stainless-steel substrate. At 0.5 g base excitation acceleration level, generators poled for serial and parallel connections generated open-circuit output voltages (peak-to-peak) of 11.6 and 20.1 V, respectively. Under an externally applied base excitation acceleration of 1.5 g, the generator poled for parallel connection reached a maximum output voltage of 15.2 V and an output power of $423 \mu\text{W}$ at an excitation frequency of 143.4 Hz, whereas the generator

poled for serial connection achieved a maximum output voltage of 33.0 V and an output power of 413 μW at an excitation frequency of 140.8 Hz.

Piezoelectric Nanogenerator

ZnO based PENGs

The development of nanomaterials and nanotechnology led to the demonstration of the piezoelectric nanogenerator (PENG) using zinc oxide (ZnO) nanowires. Zhu *et al.* (2010) designed a flexible PENG based on lateral ZnO nanowires which are transferred to a receiving substrate to form horizontally aligned arrays. The vertically aligned ZnO NWs on Si substrates have been synthesized using physical vapor deposition method. The dense and uniform NWs have the length of $\sim 50\text{ }\mu\text{m}$, diameter of $\sim 200\text{ nm}$, and growth direction along the *c*-axis as shown in Fig. 13(A) (i). The nanogenerator can generate an open circuit output voltage to 2.03 V and short circuit current of 107 nA (Fig. 13(A) (ii)) with a peak output power density of $\sim 11\text{ mW/cm}^3$ under external mechanical force. The generated electric energy was effectively stored by utilizing capacitors, and it is successfully used to light up a light-emitting diode (LED) (Fig. 13(A) (iii)). Furthermore, by optimizing the density of the NWs on the substrate and with the use of multilayer integration, a peak output power density of $\sim 0.44\text{ mW/cm}^2$ and volume density of 1.1 W/cm^3 were predicted. Qiu *et al.* (2012) explored a cost-effective way to harvest low-frequency mechanical energy into electric power using ZnO nanorods developed on a paper substrate using low-temperature hydrothermal method (Fig. 13(B) (i)). For the fabrication, small drops of silver (Ag) paste were separately deposited on the two ends of the ZnO–paper sample to act as the electrodes. Typically, the flexible PENGs have an effective area of 0.32 cm^2 ($0.4\text{ cm} \times 0.8\text{ cm}$) and an electrode interval of 0.4 cm . One can control the electric output signal by scaling the size of the PENG device. A schematic diagram of the setup for measuring output performance is shown in Fig. 13(B) (ii). The PENG can generate an output voltage of $\sim 10\text{ mV}$ and a current of $\sim 10\text{ nA}$, which are sufficient to power up small nanoscale electronics devices (Fig. 13(B) (iii)). The measurement has been performed at a strain of 0.1% and strain rate of $5\%\text{ s}^{-1}$ with the deformation frequency of 0.33 Hz .

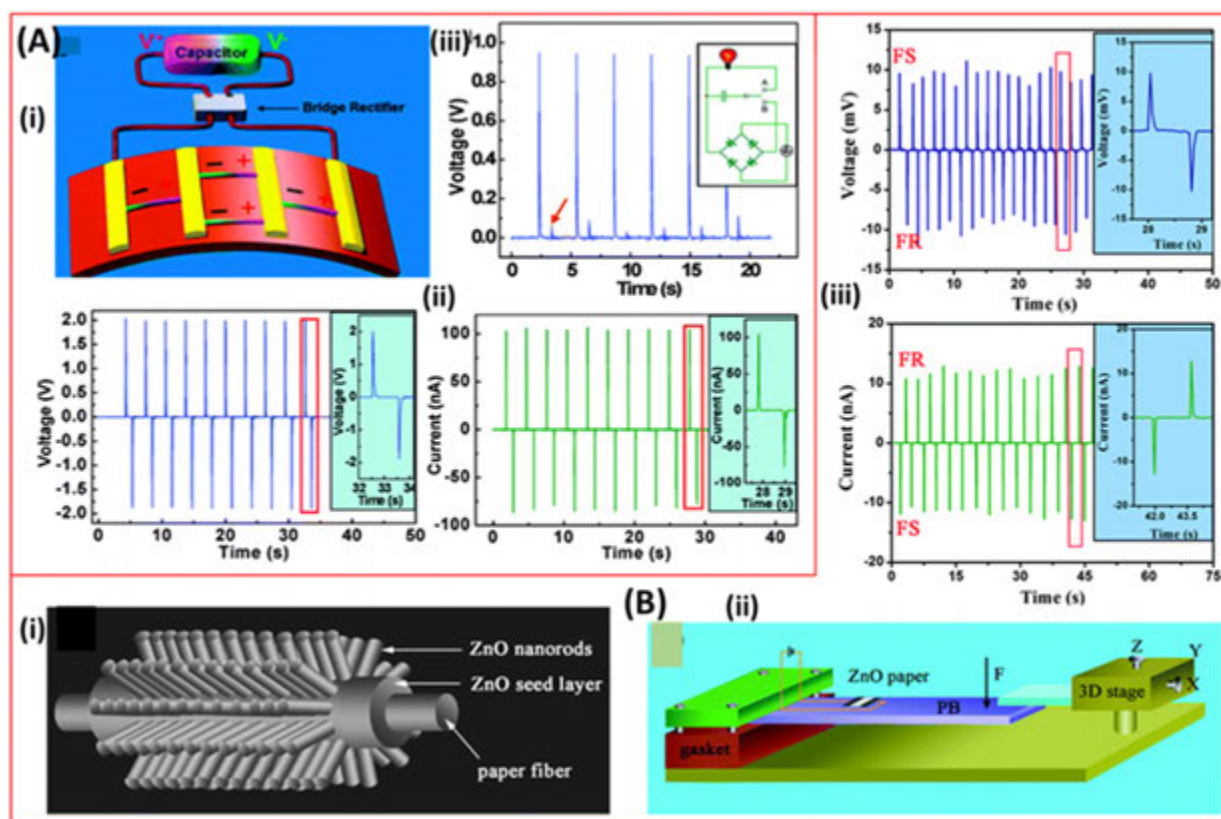


Fig. 13 Device structure and output performances of ZnO materials based nanogenerator. (A) (i) Demonstration of the output scaling-up under mechanical deformation (“+” signs indicate the polarity of the local piezoelectric potential). (ii) Open circuit voltage and short circuit current generated from the device. (iii) The electric output signal when a full wave rectifying bridge is connected to the device. (B) (i) Schematic structural depiction of an individual paper fiber grown with ZnO nanorods and (ii) a schematic diagram of the measuring setup. (iii) Output voltage and current of a ZnO–paper nanogenerator subjected to repeated cycles of fast stretching (FS) and fast releasing (FR). Reproduced with permission from Zhu, G., Yang, R., Wang, S., Wang, Z.L., 2010. *Nano Letters* 10, 3151–3155. Copyright 2010, American Chemical Society. Qiu, Y., Zhang, H., Hu, L., *et al.*, 2012. *Nanoscale* 4, 6568–6573. Copyright 2012, Royal Society of Chemistry.

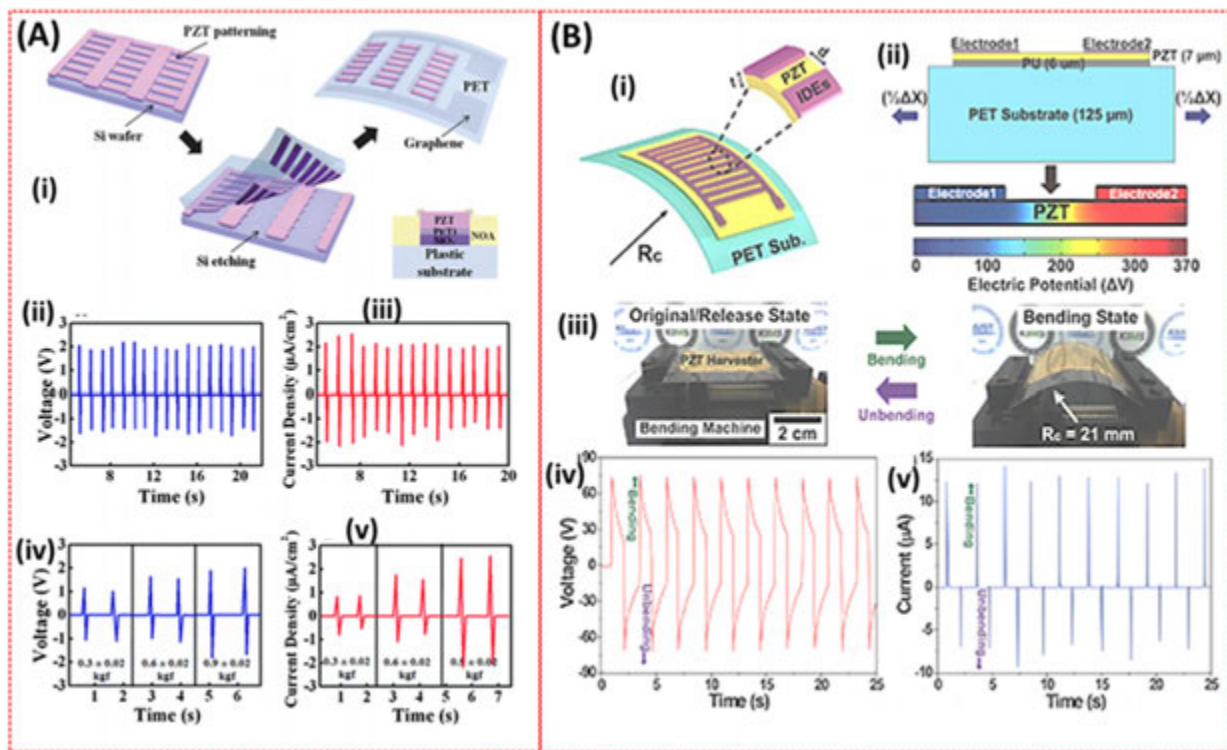


Fig. 14 (A) (i) Schematic illustration of the fabrication steps of a flexible PZT nanogenerator with graphene electrodes. (ii) The output voltage and (iii) current density of a PZT nanogenerator with doped graphene electrodes when a dynamic load was applied on top of the generator by touch. (iv) Different voltage and (v) current density signals were observed, depending on the pressure by touch. (B) A simulation model of (i) flexible PZT energy harvester with IDE (R_c : radius of curvature, t : thickness, d : IDE spacing) and (ii) the distribution of calculated piezopotential inside the AD PZT thick film (Δx : total displacement). (iii) A photograph of the flexible AD PZT harvesting device in bent and unbent states. The open-circuit voltage (iv) and short-circuit current values (v) from the flexible PZT energy harvester during periodic bending and unbending motions. Reproduced with permission from Kwon, J., Seung, W., Sharma, B.K., Kim, S.-W., Ahn, J.-H., 2012. *Energy & Environmental Science* 5, 8970–8975. Copyright 2012, Royal Society of Chemistry. Hwang, G.T., Annappureddy, V., Han, J.H., *et al.*, 2016. *Advanced Energy Materials* 6, 1600237. Copyright 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Ceramic based PENGs

The PZT material is of great interest in the scientific community for the energy harvesting due to its outstanding piezoelectric properties. Kwon *et al.* (2012) reported a practical approach for realizing high-performance PZT based flexible and semi-transparent PENG (Fig. 14(A)), where graphene acts as the electrode. The fabrication of PZT ribbon-based NGs on a PET film has been demonstrated in Fig. 14(A) (i). The PZT/Pt/Ti/SiO₂ ribbons with the desired size of 500 μm × 100 μm were created using the conventional photolithographic method. The fabricated device generated an output voltage of ~2 V, current density of ~2.2 μA cm⁻², (Fig. 14(A) (ii,iii)) resulting in a power density of ~88 mW/cm³ under an applied force of 0.9 kg f. They also have explored the change in voltage and current outputs with respect to time, by continuously increasing the compressive force in three steps, as shown in Fig. 14(A) (iv, v). Hwang *et al.* (2016) demonstrated a high-performance flexible piezoelectric energy harvester, fabricated a PZT thick film on a plastic substrate using an aerosol deposition (AD) method. Fig. 14(B) (i, ii) displays the harvester model and calculated electric potential distribution of the PZT thick film with interdigitated electrode (IDE). The flexible harvester induced an open-circuit voltage of 75 V and a short-circuit current of 14 μA due to biomechanical bending motion (Fig. 14(B) (iii, iv, v)). Moreover, the maximum output voltage of 200 V and output current of 35 μA were generated by a human finger bending motion. Qi *et al.* (2011) used a transfer printing method in which, the PENG (1 cm²) was found to generate a voltage and current output of 0.25 V and 40 nA, respectively. To increase the amplitude of strain, they further developed a stretchable PENG using integration of wavy/buckled PZT ribbons with PDMS thin film. The film can be stretched up to 8% strain and enabled its integration with a flexible structure. An output current of 60 pA was generated from the device when ten PZT ribbons were assembled all together.

Cui *et al.* (2019) reported PZT nanoparticle-based composite materials and fabricated a PENG device, which generated voltages along different angles (75°, 90° and 120°) under external applied stress. The voltage output reached up to 60 mV in the case of 75° angle. The real-time voltage output of the fabricated device was measured using different free-falling weights and reached up to 2.5 V for 100 g weight, indicating the high sensitivity of the device. The PZT based implantable energy harvesting devices powered by ultrasound is an alternative way for converting acoustic energy into electricity. A piezoelectric ultrasonic energy harvester (PUEH) based on microfabricated PZT (size of 5 mm × 5 mm) has been explored by Shi *et al.* (2016) The PUEH can generate an output power density of 0.59 μW cm⁻² to 3.75 μW cm⁻² at 1 cm distance from the ultrasound source when changing the frequency

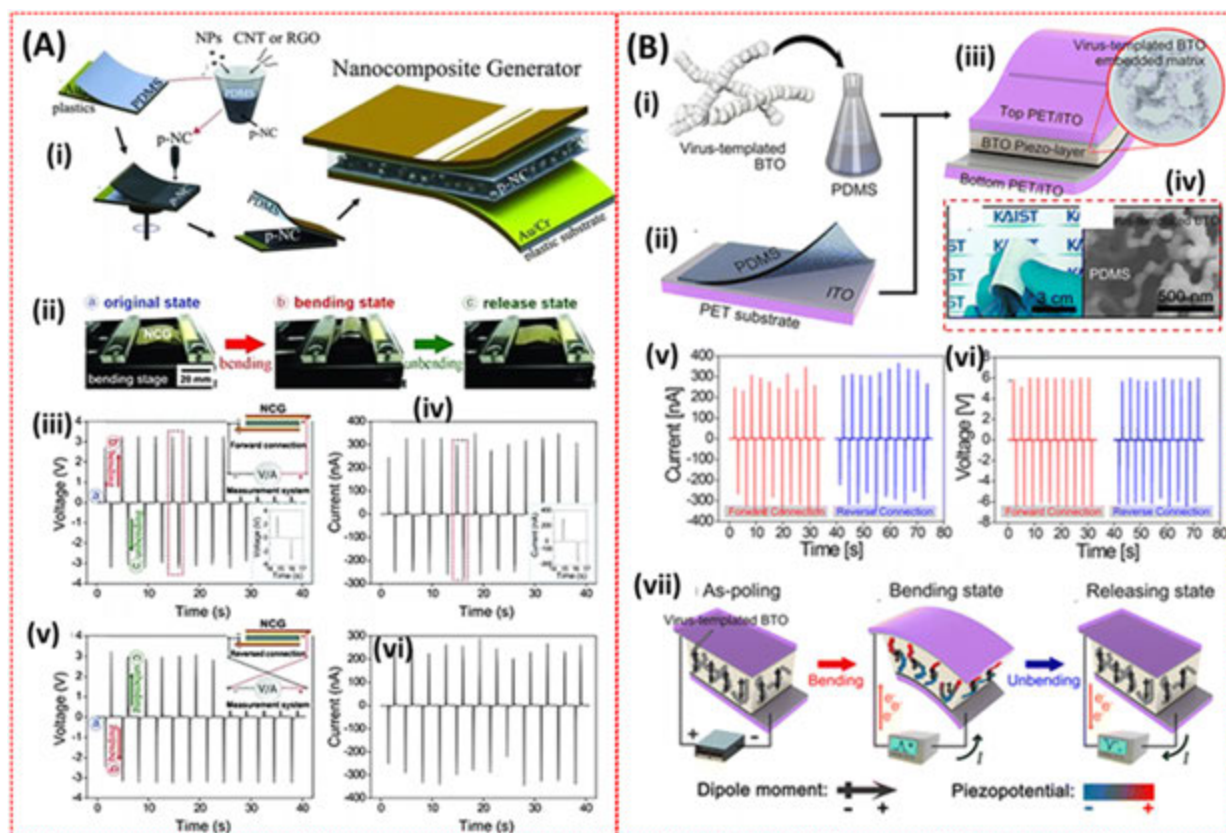


Fig. 15 (A) (i) Schematic illustration of the process for fabricating nanocomposite PENG device. (ii) Optical images of PENG devices in their original, bending, and release states. The measured (iii) output voltage and (iv) current signals of the PENG device in the forward connection during the periodic bending and unbending motions. (v) The open-circuit voltage and (vi) short-circuit current signals generated in the reverse connection. (B) (i) Schematic of fabrication process of PENG. (ii) Photograph of PENG device and SEM micrograph of BTO nanocrystal distribution inside the PDMS matrix. The generated (v) short-circuit current and (vi) open-circuit voltage signals from PENG for forward and reverse connections. (vii) The mechanism of energy harvesting from the nanogenerator device in different conditions. Reproduced with permission from Park, K.I., Lee, M., Liu, Y., *et al.*, 2013. *Advanced Materials* 24, 2999–3004. Copyright 2012, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Jeong, C.K., Kim, I., Park, K.-I., *et al.*, 2013. *ACS Nano* 7, 11016–11025. Copyright 2013, American Chemical Society.

from 250 kHz to 240 kHz of ultrasound with 1 mW/cm² intensity. The device has shown a great potential in implantable medical device applications.

The ceramic material BaTiO₃ has also received attention due to its outstanding ferroelectric properties and biocompatible characteristics, which are crucial for biomedical applications. Park *et al.* (2012) designed a nanocomposite based PENG by mixing BaTiO₃ nanoparticles and carbon nanomaterials in PDMS. They have fabricated PENG based on BaTiO₃ nanoparticles (NPs) synthesized via a hydrothermal reaction and graphitic carbons, such as single-walled and multi-walled carbon nanotubes (SW/MW-CNTs), and reduced graphene oxide (RGO) as shown in Fig. 15(A) (i). The BaTiO₃ NPs and carbon nanomaterials are dispersed in polydimethylsiloxane (PDMS) by mechanical agitation to produce a piezoelectric nanocomposite. The measured output performance of nanocomposite PENG under periodic bending and unbending motions reached up to 3 V output voltage and 270 nA current respectively, as shown in Fig. 15(A) (ii). To exclude any artifact from the external electrostatic charges, the sample was placed in a Faraday cage on an optical table and bending system is well grounded. Under the continual bending and unbending cycles, the PENG device repeatedly generates an open-circuit voltage of ~3.2 V and a short-circuit current signal of 250–350 nA; these output values are produced for a maximum horizontal displacement of 5 mm from an original 4 cm long sample at a deformation rate of 0.2 m s⁻¹. The amplitude of the output voltage generated from the PENG device increases from 0.2 V to 3.2 V after the poling process and also depends on the composition of nanomaterials, the angular bending strain, and strain rate.

A bio-inspired flexible PENG has been demonstrated using BaTiO₃ (Jeong *et al.*, 2013), where metal ion precursors, and self-assembled anisotropic BaTiO₃ nanocrystals were deposited on a viral template (Fig. 15(B) (i)). The stirred and infiltrated virus-templated BTO nanostructures are mixed with polydimethylsiloxane (PDMS) to achieve the BTO piezoelectric layer (Fig. 15(B) (i)). The indium tin oxide (ITO)-coated thick (~175 μm) polyethylene terephthalate (PET) substrate is covered with PDMS dielectric layer to prevent the electric breakdown of device. Fig. 15(B) (ii) shows the photograph of fabricated virus-templated BTO nanogenerator, which is malleable and flexible indicating that nanostructure of one-dimensional fibrous materials can be well distributed in three-dimensional active regions. The fabricated PENG device with an effective area of 2.5 × 2.5 cm² generated an output voltage

and current on the order of ≈ 6 V and ≈ 300 nA under both forward and reverse connections with measurement equipment without additional structural stabilizers, indicating that the high output is related to the nanoscale structure. The Fig. 15(B) (vii) depicts the general mechanism of energy conversion by the PENG device.

Kim *et al.* (2014) developed a “layer-by-layer” method to synthesize BaTiO₃ nanoparticles based piezoelectric thin film. The composite made by oleic acid ligands stabilized BaTiO₃ nanoparticles (NP) (> 20 nm in diameter) and polymers that were functionalized by poly(acrylic acid) (PAA). The high affinity between the $-\text{COOH}$ groups and BaTiO₃ NPs assisted the organization of the nanocomposite. The performance of these piezoelectric films was found to be precisely controlled by altering the bilayer number, nanoparticle size or inserted polymer type. As the bilayer number (n) was increased from 20 to 100, the fabricated unpoled PENG device generates the output voltage and current increased to approximately from ~ 0.1 V to ~ 1.8 V and ~ 15 nA to ~ 700 nA, respectively, under a compressive force 5.2 kg f. The influence of compressive forces on the piezoelectric performance has also been verified by measuring the output voltage and current of a device containing 100 bilayers. As the compressive force was increased from 0.8 to 5.2 kg f, the output voltage and current increased from approximately ~ 0.4 V and ~ 60 nA to ~ 1.8 V and ~ 700 nA, respectively. The results demonstrate that a degree of external compressive force can significantly affect the aligned electric dipoles and the resultant piezoelectric performance of (PAA/OA-BTONP) n multilayers without an additional poling process.

Polymer-based PENGs

PVDF and its copolymer P(VDF-TrFE) are polymeric piezoelectric material with a high piezoelectric coefficient ($d_{33} = 32.5$ pC/N) (Karan *et al.*, 2019). Sun *et al.* (2011) proposed a method for converting energy from low-speed airflow to electricity using resonant oscillation of PVDF micro-belts (Fig. 16(A)). They reduced the commercial β -phase PVDF using reactive ion etching (RIE)

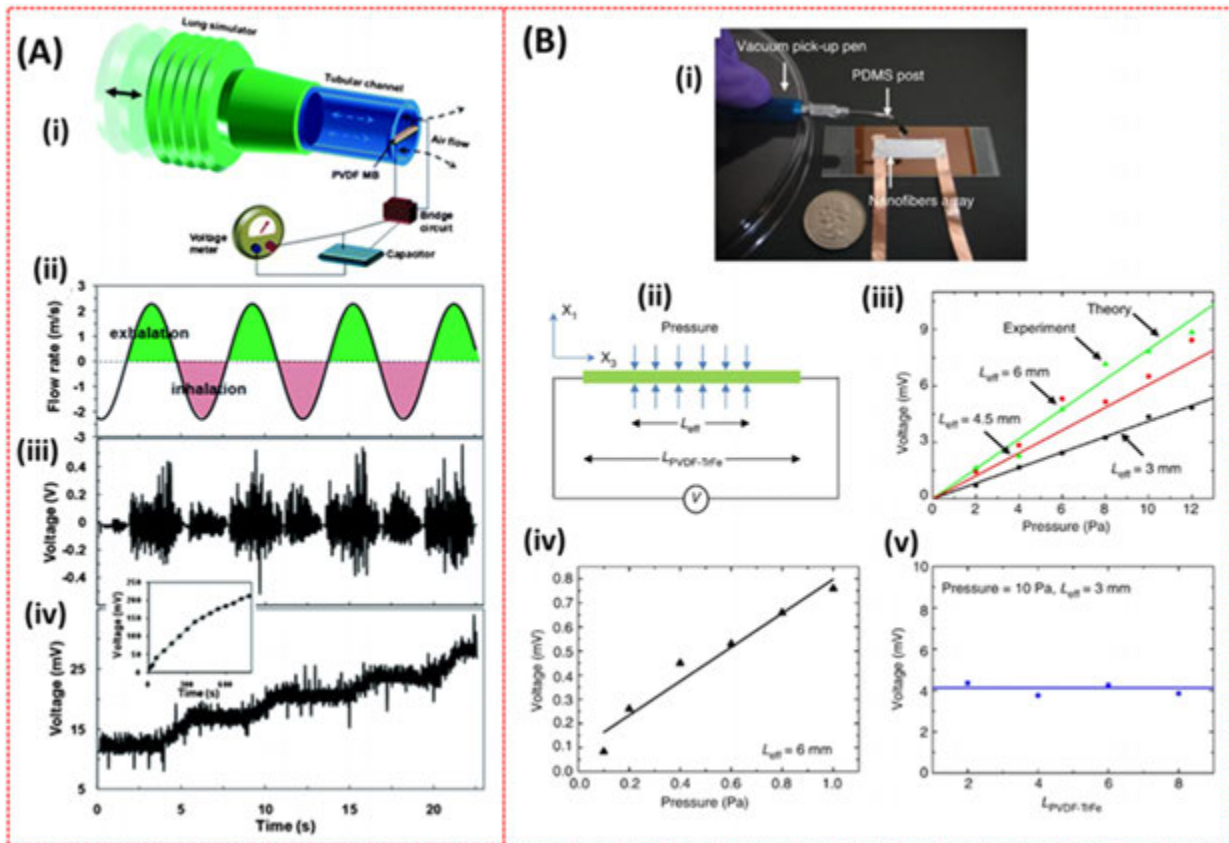


Fig. 16 (A) (i) Schematic design for simulated respiration energy harvesting. (ii) Air flow rate through a tubular channel with a matching pattern to the normal respiration of an adult. (iii) Corresponding V_{OC} measured on a PVDF MB fixed at one end of the tubular channel. (iv) Voltage increase on a capacitor that was connected to the PVDF MB through a bridge circuit. The inset shows the long-term voltage increase trend on the capacitor. (B) (i) Photograph of the measuring system for the purpose of studying the voltage response. (ii) A schematic design of an analytical model for the response of arrays of P(VDF-TrFE) fibers under applied compression $-p$ along x_1 direction over the effective contact length (L_{eff}). (iii) Experimental (symbols) and theoretical (lines) pressure response curves at different L_{eff} . (iv) Experimental (symbols) pressure response curve in the low-pressure regime (0.1–1 Pa) at $L_{\text{eff}} = 6$ mm. (v) Experimental (symbols) and theoretical (lines) response at different $L_{\text{PVDF-TrFE}}$ (applied pressure = 10 Pa, $L_{\text{eff}} = 3$ mm). Reproduced with permission from Sun, C., Shi, J., Bayerl, D.J., Wang, X., 2011. *Energy & Environmental Science* 4, 4508–4512. Copyright 2011. American Chemical Society. Persano, L., Dagdeviren, C., Su, Y., *et al.*, 2013. *Nature Communications* 4, 1–10. Copyright 2013. Springer Nature.

Table 3 The output performances of small-scale PENG devices

Piezoelectric materials	Area PENG	Output performance			References
		Voltage (V)	Current (μ A)	Power density (μ W cm ⁻²)	
PZT diaphragm and Pt electrode	5 mm $\times$ 5 mm	–	–	3.75	(Shi <i>et al.</i> , 2016)
PZT ribbons and Cr/Au electrode	–	0.001	1×10^{-6}	1.2	(Dagdeviren <i>et al.</i> , 2014)
ZnO nanowires (Length 100–500 μ m, diameter 100–800 nm)	–	0.003	0.03	–	(Yang <i>et al.</i> , 2009)
PVDF and plain Cu electrode	1 cm $\times$ 2 cm	0.26	0.2	–	(Yu <i>et al.</i> , 2016)
PMN-PT thin film and Ni electrode	1.7 cm $\times$ 1.7 cm	8.2	223	–	(Hwang <i>et al.</i> , 2014)

technique (Plasma-Therm 790, 250 W operation power). After reducing the thickness of PVDF from 26 to 11 μ m the β -phase is well-preserved without any change. For the fabrication of the device, 17 μ m thick PVDF belt was selected due to the best performance under air flow $< 2 \text{ m s}^{-1}$. For the evaluation of the device, belt was fixed at the center of a cylindrical channel with a cross-sectional area of $\sim 1 \text{ cm}^2$. One end of the channel was connected to a compressible plastic chamber that simulated the function of a lung and the other end was open (Fig. 16(A) (i)). The plastic chamber was squeezed and released every 6 s producing air flow in and out through the tunnel with a peak rate of $\sim 2.3 \text{ ms}^{-1}$ (Fig. 16(A) (ii)) and the operation provided a close simulation of typical adult's respiration. The output voltages were clearly correlated to the instantaneous flow rate and peak voltage output of ~ 0.4 – 0.5 V was detected at the highest "exhalation" flow rate of $\sim 0.5 \text{ l s}^{-1}$ (Fig. 16(A) (iii)). Due to the asymmetry of the air flow profile between inhalation and exhalation, lower output voltage was observed during inhalation cycles. The device can charge a capacitor up to $\sim 200 \text{ mV}$, after 12 min of simulated respiration, corresponding to $20 \mu\text{J}$ of electrical energy storage indicating the capability for energy harvesting through inhalation and exhalation processes.

Lin *et al.* have explored a direct-write technique utilizing near-field electrospinning to produce and place piezoelectric PVDF nanofibers on working substrates with in-situ mechanical stretching and electrical poling (Chang *et al.*, 2010). The typical electrical output of more than 50 tested nanogenerators were 5 – 30 mV and 0.5 – 3 nA. The fabricated device generated excellent output performance with good energy conversion efficiency (12.8%). Rogers *et al.* have fabricated electrospun PVDF-TrFe based self-powered PENG device for robots and sensitive impact detectors (Persano *et al.*, 2013). The device was formed simply by establishing electrical contacts to the ends of a ribbon-shaped sample of fiber arrays on a flexible polyimide (PI) support (Kapton; optimum thickness between 75 and 225 μ m), and generated large response to even minute applied pressures (Fig. 16(B) (i)). To evaluate the sensitivity quantitatively, a soft elastomer (PDMS posts) delivered well-defined levels of pressure to the arrays, while the electrical response was measured. Fig. 16(B) (iii) describes a linear variation of the output voltage with pressure. The effective contact areas between 9 and 36 mm² (squares with sides L_{eff} , Figure B(ii), with slopes between 0.41 and 0.79 mV Pa⁻¹). The devices can achieve the sensitivity of 1.1 V kPa⁻¹ in the ranges of pressure between 0.4 and 2 kPa. The devices are very sensitive to the level of response enabling accurate measurement of compressive pressures even at 0.1 Pa (Fig. 16(B) (iv)). The voltage is independent of the total length $L_{\text{PVDF-TrFe}}$ (Fig. 16(B) (v)) of the P(VDF-TrFe) fiber arrays, which is also consistent with experimental results of Fig. 16(B) (iii).

They have also fabricated the devices for measuring vibration/acceleration and orientation. The measured output voltage signal with a peak-to-peak output voltage that increases from 6 to 14 μ V generated under environmental sound pressure levels of 60–80 dB. These devices work in any orientation and can be mounted on any surface by means of transparent, skin-conformal plastic sheets. They have proved that the device can work in any orientation and can be mounted on any surface by means of transparent, skin-conformal plastic sheets. The results suggest utility in a variety of sensor- and energy harvesting components, with lightweight construction, attractive mechanical properties and potential for implementation over large areas at low cost, with application opportunities in human motion monitoring and robotics. The output performance of different small scale PENG devices is summarized in Table 3.

Triboelectric Nanogenerator

Solid-solid contact based TENGs

The TENGs harvest electrical energy from both solid–solid and liquid–solid contact. Due to their physical difference, triboelectric materials for solid–solid TENG need to have high mechanical stability for long life span and the surface of the liquid–solid contact TENG should repel water for constant liquid separation. The solid-solid contact based TENG is the common mechanism in triboelectric energy harvesting community where one solid surface contacts with another solid surface for power realization (Choi *et al.*, 2020).

A self-powered solid-solid contact based triboelectric auditory sensor (TAS) is proposed for social robotics and hearing aids by Guo *et al.* (2018). The multilayer TAS consisted of an Au-coated FEP film attached on an acrylic substrate, a spacer, and an Au-coated Kapton membrane (Fig. 17(A) (i)). The FEP-covered acrylic substrate has hole channels to reduce air damping and the Kapton membrane was fixed on the outer rim by using an annular acrylic sheet. Membrane deformation caused by acoustic waves triggers the contact and

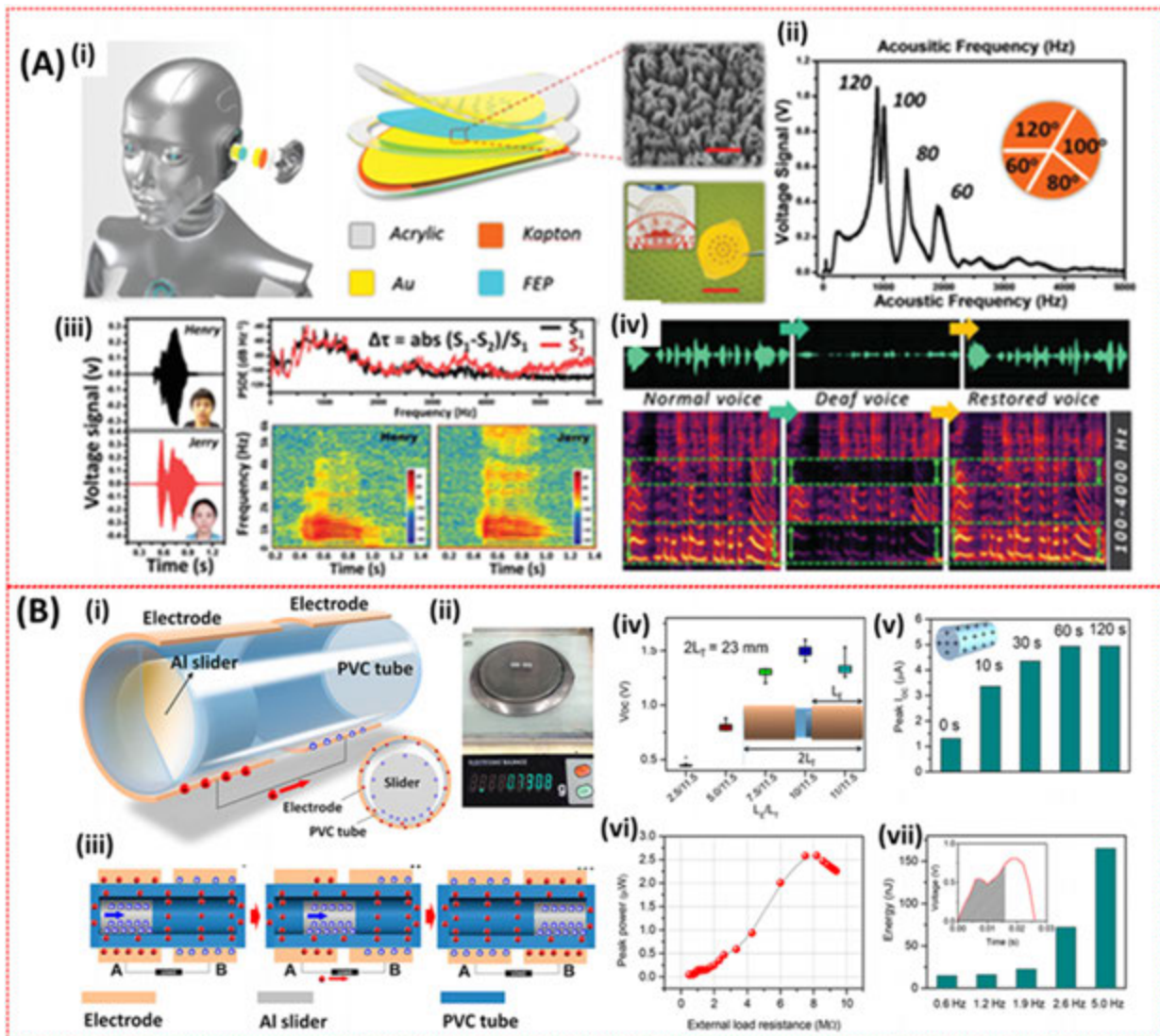


Fig. 17 (A) A triboelectric auditory sensor for social robots and hearing aids. (i) Schematics and photographs of the TAS. (ii) Broadband frequency response of the TAS with four sectorial boundaries. (iii) Security application of the TAS in voice recognition. (iv) Medical application of the TAS in hearing aids for restoring impaired frequency region. (B) Structure of a capsule TENG and its working principle. (i) Schematic illustration of the capsule TENG. The inset is a cross-sectional view. (ii) Photograph showing the weight of an as-fabricated capsule TENG. (iii) Schematics for the working principle of the capsule TENG in one-way operation. (iv) The output voltage of capsule TENGs with different electrode lengths. L_E is the length of the aluminum electrode, and $2L_T$ is the length of the tube ($2L_T = 23$ mm). (v) Increase in the generated current when the Al slider is preprocessed for different times. The inset presents a schematic diagram of the Al slider with externally introduced positive charges. (vi) Dependence of the peak power on the resistance of the external load. (vii) Electrical energies generated during a periodic vibration at a resistance of $7.5\text{ M}\Omega$ at various frequencies. The inset presents a detailed plot of the output voltage as a function of time. Reproduced with permission from Guo, H., Pu, X., Chen, J., *et al.*, 2018. *Science Robotics* 3 (20). Copyright 2018. The American Association for the Advancement of Science. Wu, C., Park, J.H., Koo, B., *et al.*, 2018. *ACS Nano* 12, 9947–9957. Copyright 2018. American Chemical Society.

separation between FEP and the membrane electrode, resulting in generating electrical outputs. The fabricated TAS device achieved an ultrahigh sensitivity of 112.4 mV dB^{-1} , which can be used for various applications such as a sound-controllable switch and an antitheft system. As shown in Fig. 17(A) (ii), a multiresonant frequency band was achieved by a TAS with four sectorial architectures, and this feature of broadband frequency response enables it to have applications in an electronic auditory system with high quality and fidelity in sound recording. Therefore, it can also be used in security systems using voice recognition. As in Fig. 17(A) (iii), the electrical signals from two different persons saying the same word “Hello” were recorded by the TAS device, and the results of power spectral density estimation (PSDE) and joint time-frequency analysis (JTFA) showed distinctive differences between the users. Fig. 17(A) (iv) shows the sound waves and corresponding acoustic spectrograms of original voices, weakened voices (-30 dB in the $207\text{--}837$ and $1594\text{--}2090\text{ Hz}$ frequency regions) played by a loudspeaker, and recorded voices by a TAS-based hearing aid system, which clearly indicates that the sound information in the impaired frequency regions was restored.

A solid-solid contact based TENG device of capsule-type has been introduced as an effective high-performance sensor by Wu *et al.* (2018). The TENG consisted of polyvinyl chloride (PVC) tube with an inner Al slider and outer PVC surface coated with Al electrodes (Fig. 17(B)). The diameter for the Al slider is smaller than that of the PVC tube for the free access inside the PVC tube, which makes it potentially more fitting for smart electronics. The maximum output is obtained when the length of the aluminum electrode is 10 mm as shown in Fig. 17(B) (iv). The electrical output of the capsule TENG can be further improved by introducing additional static charges to the Al slider. The additional static charges were introduced to the Al slider by shaking it in a polyvinylidene fluoride (PVDF) jug before sealing it in a capsule (inset of Fig. 17(B) (ii)). The short-circuit current of the capsule TENG is tested without preprocessing (0 s), as shown in Fig. 17(B) (ii). All of the static surface charges on the Al slider are generated due to the triboelectrification between the Al slider and the PVC tube because PVDF has a stronger ability to attract electrons than PVC. The peak current is seen to approach a saturation value of about $5.0 \mu\text{A}$ with increasing preprocessing time to 120 s. The output power from the capsule TENG under a vibration frequency of 5.0 Hz reached a maximum peak power of $2.6 \mu\text{W}$ at a load resistance of $7.5 \text{ M}\Omega$ (Fig. 17(B) (iii)). The highest electrical energy at a vibrational frequency of 5.0 Hz reached to 165 nJ during the periodic vibration (Fig. 17(B) (iv)). Recently, Choi *et al.* demonstrated an ordered dipole alignment in α -phase nylon-11 nanowires that can be used for the triboelectric energy harvesting. They have explored dipole alignment of non-ferroelectric polymer as-fabricated nanowires of α -phase nylon-11 (Choi *et al.*, 2020).

TENG can also be implanted inside a live animal for powering biomedical devices utilizing ambient available energies; they are termed implantable triboelectric nanogenerators (iTENGs). To power up body-implanted devices with TENGs, either bio-mechanical energy (from various types of muscular movements) or ultrasound energy transferred into the body are excellent mechanical energy sources that can generate electricity. These nanogenerators are a recent invention of modern energy harvesting and storage technologies which energize small in-vivo medical devices. Zheng *et al.* (2016a) used nanostructured polytetrafluoroethylene (n-PTFE, $50 \mu\text{m}$) as the triboelectric layer to increase the output signals as shown in Fig. 18(A) (i). A Kapton film

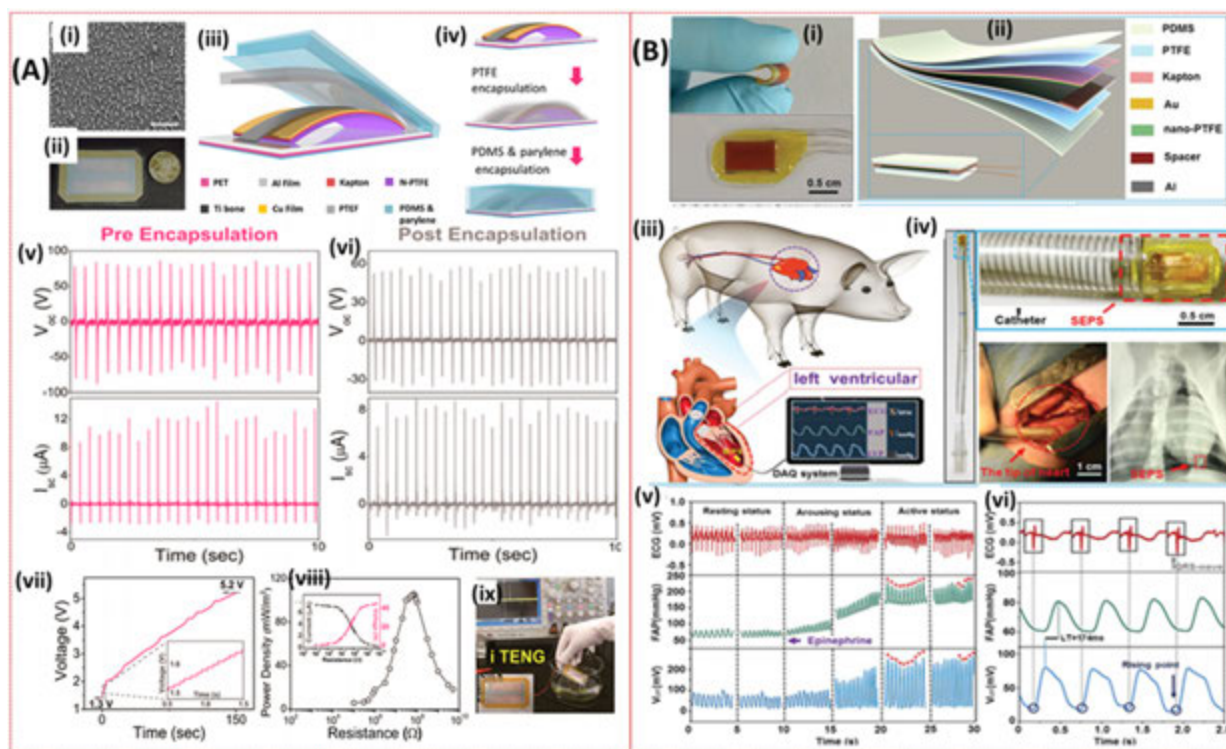


Fig. 18 (A) (i) Scanning electron microscopy image of a nanostructure on the PTFE film (scale bar: $5 \mu\text{m}$). (ii, iii) Schematic diagram and photograph of the iTENG and (iv) encapsulation process of the iTENG. (v, vi) Open-circuit voltage and short-circuit current of the iTENG before and after encapsulation. (vii) Charging curve of a $10 \mu\text{F}$ capacitor by driving the iTENG with a cyclic tapping in PBS solution (inset: large view of the plotted region, revealing the stepwise behavior of charging). (viii) Power density at different load resistances (inset: voltage and current at different load resistances). (ix) Photograph of the iTENG when applied in PBS solution. (B) (i) Photograph of the SEPS in bending and original states. (ii) Schematic illustration of the structure of the SEPS. (iii) Schematic diagram of the semaphore acquisition from the SEPS implanted into an Adult Yorkshire swine's heart. (iv) Photograph of minimally invasive surgery with a DR image of the heart implanted a device by integration with a surgical delivery system. (v) The comparison of working signals from the ECG, FAP and SEPS under different physical status. (vi) QRS waves of ECG (rectangles) absolutely corresponded to the rising points of the SEPS outputs (circles), and the leading time (LT) represents the time interval between the peaks of the two corresponding waveforms (SEPS and FAP). Reproduced with permission from Zheng, Q., Zhang, H., Shi, B., *et al.*, 2016a. ACS Nano 10, 6510–6518. Copyright 2016, American Chemical Society. Liu, Z., Ma, Y., Ouyang, H., *et al.*, 2019a. Advanced Functional Materials 29, 1807560. Copyright 2019, CWILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

(150 μm) was fixed on the n-PTFE layer to increase the flexibility of the device and an ultra-thin Al foil (100 μm) was employed as both triboelectric layer and electrode. They have developed a resilient titanium strip as the keel structure (Fig. 18(A) (ii)), which significantly enhanced the mechanical behavior of the total structure and guaranteed solid contact and separation of the iTENG. To further augment the reliability of the iTENG and to avoid adhesion in the physiological environment, parylene C was deployed on the surface as a shell structure to form a hole-free coating layer. This “layer by layer” encapsulation strategy ensured the structural stability of the iTENG and its resistance to a complex internal environment. Basically, the PDMS layer was used to ensure the flexibility of the overall device to bend conveniently in response to the tiny movements. They have tested in-vitro electrical output of the iTENG before and after encapsulation by applying a periodic external mechanical force. Ten iTENGs with a unified specification were utilized in this experiment. Before encapsulation, the voltage and current reach $\sim 90\text{ V}$ and $\sim 12\text{ }\mu\text{A}$ respectively (Fig. 18(A) (vi)). After encapsulation the iTENG has been placed in phosphate-buffered saline (PBS) to test both the output signals and the stability in a physiological solution environment. The instantaneous current drops with increasing load resistance due to ohmic loss, while the voltage builds up (Fig. 18(A) (viii)). Consequently, at a load resistance of 10 M Ω , a power density of 107 mW/m² for the iTENG was achieved. The device can charge the capacitor up to 5.2 V within 150 s. They have also tested in-vivo experiment on animal model (male adult Yorkshire porcine, 30 kg) and an electrical output voltage of up to $\sim 14\text{ V}$, and the corresponding current up to $\sim 5\text{ }\mu\text{A}$ was achieved. With a heart rate of 80 bpm, a 1 μF capacitor can charge up to 2.8 V within 200 s using iTENG.

Liu *et al.* (2019a) explored a flexible self-powered endocardial pressure sensor (SEPS) made by TENG, as shown in Fig. 18(B). The TENG has been integrated with a surgical catheter for minimally invasive implantation. To imitatively evaluate the function of the SEPS for real-time biomedical monitoring in human bodies, they have selected male adult Yorkshire pigs (40 kg) as the animal model. To achieve minimally invasive implantation, they have fabricated a delivery system by integrating the miniature SEPS with a heparin-coated polyvinyl chloride (PVC) stretchable catheter, which is widely used in cardiopulmonary bypass surgery (Fig. 18(B) (iv)). The output signals of ECG, FAP, and SEPS were documented and compared under resting, arousing and active conditions, as exhibited in Fig. 18(B) (v). At the resting status (systolic FAP < 100 mmHg), a positive voltage of $\approx 80\text{ mV}$ was obtained, with both FAP and voltage remaining constant, indicating that the miniature and flexible device exerted little interruption on the stableness of cardiac functionality. The enlarged drawing of signals at the resting status is displayed in Fig. 18(B) (vi).

Hinchet *et al.* (2019) demonstrated a transcutaneous ultrasound energy harvesting system using capacitive triboelectric technology that charges a battery from an ex-vivo condition using ultrasound (US). They explored the use of a high-frequency vibrating and implantable triboelectric generator (VI-TEG) in vivo state for harvesting US. The VI-TEG with less than 1-mm-thick (Fig. 19(A) (iii)) was developed to be implanted underneath the skin ($\approx 10\text{ mm}$) (Fig. 19(A) (i)). They prepared a thin ($\approx 50\text{ }\mu\text{m}$ thick) and large membrane of perfluoroalkoxy (PFA), which is a copolymer of tetrafluoroethylene and perfluoroethers that vibrate under the pressure of US. Such a generator confirms easy and constant operation despite the variations in environment and usage conditions. The membrane was suspended on a thin Cu electrode (3.6 cm $\times$ 3.6 cm) on a flexible printed circuit board (PCB) and coated with Au (Fig. 19(A) (ii)); the air gap was 80 mm. The preliminary mechanical and acoustic simulations showed that the US vibration cannot pass via VI-TEG because of its reflection (Fig. 19(A) (iv)). The membrane vibrated in a multimode under a US excitation of 20 kHz (Fig. 19(A) (v)), developing multiple nodes and antinodes that moved up and down. The VI-TEG works in the single-electrode mode using the primary Cu/Au electrode, a small backside reference Cu electrode, and a triboelectric PFA membrane layer.

The VI-TEG can generate voltage peaks of $\approx 25\text{ V}$ at 40 M Ω impedance and current peaks of $\approx 1.3\text{ mA}$ at 1 Ω impedance. These outcomes correspond to a root mean square (RMS) voltage of $\approx 9.71\text{ V}$ and an RMS current of $\approx 427\text{ mA}$. The VI-TEG developed 450 mA at 33 k Ω , providing a maximum power of $\approx 6.74\text{ mW}$, which is equal to $\approx 0.872\text{ mW}$ of average constant power and a power density of $\approx 5.2\text{ W m}^{-2}$.

The VI-TEG was also kept under porcine tissue which is comparable to human skin in terms of composition and anatomy to realize the in-vivo capability (Fig. 19(B) (i–iii)). Transcutaneous electronic implants are usually located at a depth of $\approx 5\text{--}10\text{ mm}$. At 0.5 cm, the VI-TEG provides output signals of more than $\approx 2.4\text{ V}$ and $\approx 156\text{ mA}$ (Fig. 19(B), iv). The lowering in the voltage and current was caused by US attenuation. At 1.0 cm under layered tissues including the skin and the fat, the VI-TEG provides output signals of more than $\approx 1.93\text{ V}$ and $\approx 98.6\text{ mA}$ (Fig. 19(B), v). The power generating performance for VI-TEG was ≈ 4.78 and ≈ 2.81 times less than that in water and the BS, respectively, under porcine tissue, because of the improved acoustic impedance and attenuation in the different layers and media structure.

Solid-liquid contact based TENGs

Solid-liquid based TENGs have several promising applications owing to their portability compared to solid-solid based TENGs. Lin *et al.* (2013) have observed a solid-liquid TENG between a patterned polydimethylsiloxane pyramid array and water. After that various systems have been demonstrated to improve the performance of the TENGs with a fast headway in nanoscale materials and micro/nano fabrication strategies. Zhang *et al.* (2021) explored a solid-liquid based TENG where triboelectric effect is produced when the fluid stream moves through a cylinder at a specific point and interacts with the internal electrode. In this concept the triboelectric charges are generated without going through the electrostatic induction process between bottom electrode and the surface in the case of TENG. Such design successfully avoids the interfacial screening effect and effectively transfers triboelectric charges based on bulk effect. The nanogenerator consists of a dielectric layer tube (Polytetrafluoroethylene (PTFE) or ethylene propylene (FEP)), an outer terminal (Cu) and an inner cathode (Al). They suggested that due to the contact of the internal electrode with the liquid, the rate of charge flow inside the tube is dominated by the volume effect instead of the interfacial effect, resulting in a higher voltage (17 times higher than the interfacial effect) and therefore boosting the power output of the device

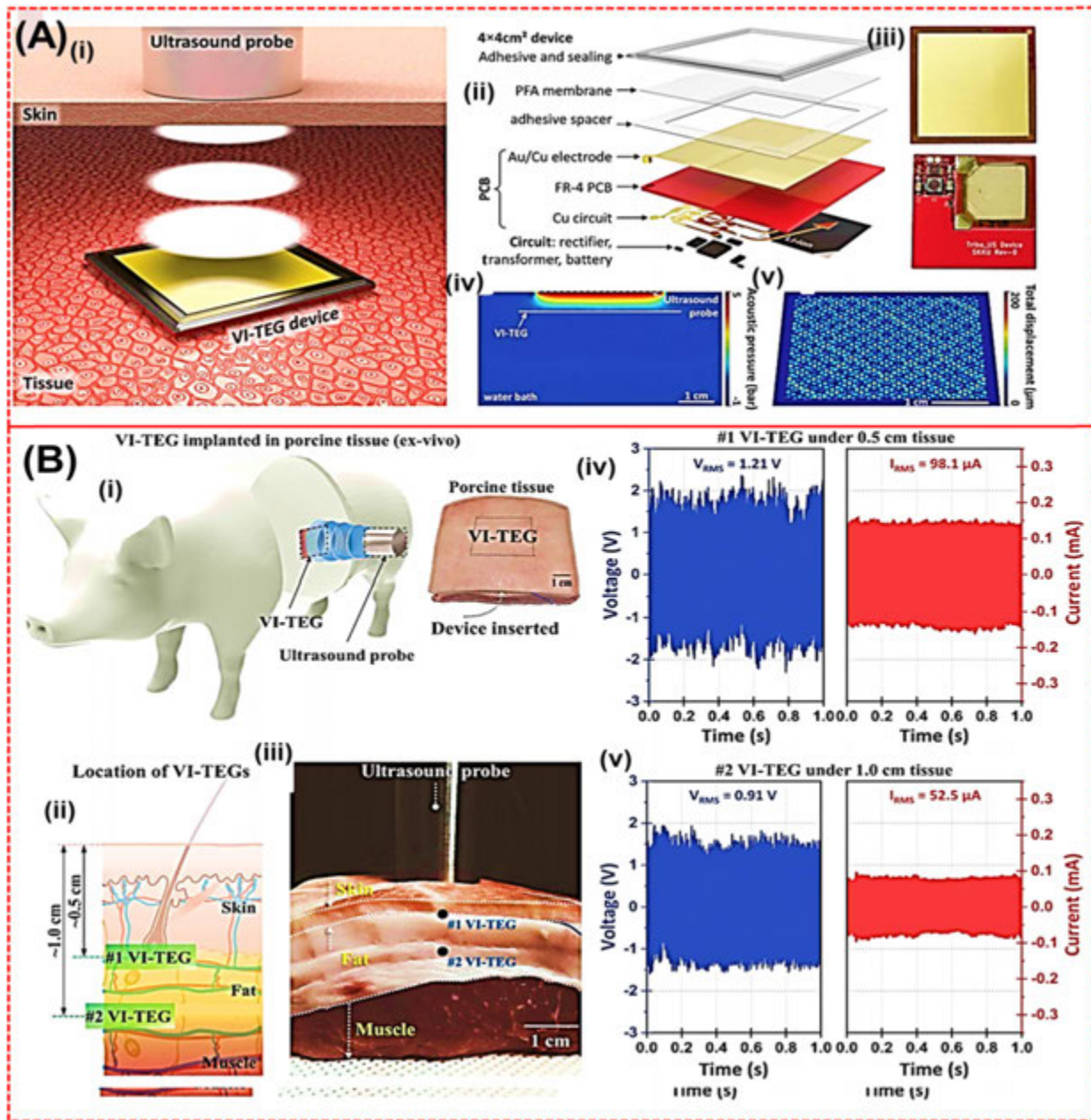


Fig. 19 Concept and design of the VI-TEG. A, (i) Illustration of US energy harvesting under skin using the VI-TEG. (ii) Exploded view of the VI-TEG structure. (iii) Front and back photo of the VI-TEG. (iv) Finite element method (FEM) simulation of US acoustic pressure propagation through water and the VI-TEG. (v) FEM simulation of the VI-TEG's vibrations in water at 5 mm under the 20 kHz US probe. (B) Schematic of the porcine ex vivo (i) and the tissue (ii) showing the location of the implanted VI-TEG. (iii) Picture of the VI-TEG implanted at 0.5 and at 1 cm under the porcine tissue. Voltage at 40 MΩ impedance, and current at 1 MΩ impedance generated by the VI-TEGs implanted at 0.5 cm (iv) and 1 cm (v) under the porcine tissue. The US probe was set at 20 kHz and 1 W cm⁻². Reproduced with permission from Hinchet, R., Yoon, H.-J., Ryu, H., et al., 2019. Science 365, 491–494. Copyright 2019, The American Association for the Advancement of Science.

(Fig. 20(A)). The fabricated device can generate an open-circuit voltage of ~904 V, which is ~17 times of its counterpart, ~52.8 V, and similar results are obtained from fluorinated (FEP) tubes. Moreover, the triboelectric output generation is also impacted by the type of flow dynamics – steady or unsteady flow. Ahn et al. (2020) studied the hydrodynamics of unsteady pipe flow and found that the output current from unsteady flow is 70 times higher than that of steady flow at a similar operating pressure (Fig. 20(B)). To increase the application scope, an unsteady type of peristaltic flow is also being used as the source of energy harvesting using the solid-liquid TENGs (Cheedarala et al., 2019). Using a peristaltic pump, liquid stream is driven through an elastomeric tubing, causing squeezing and restitution of the tubing and generating peristaltic flow, which leads to the movement of the liquid. Based

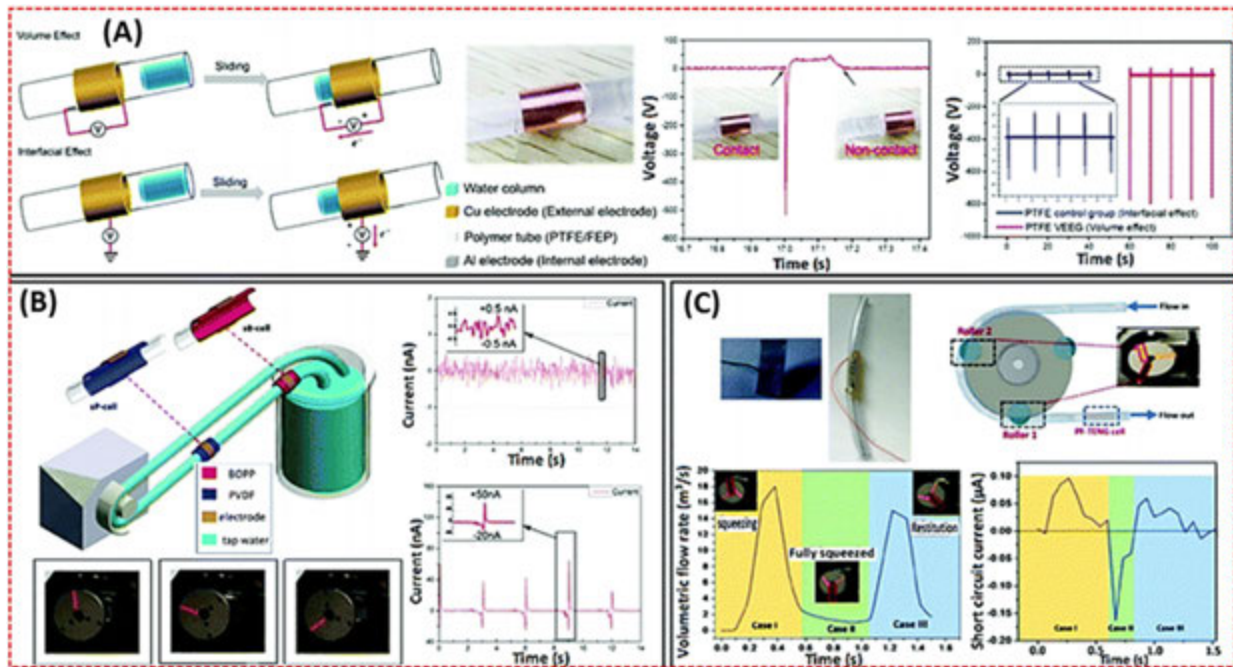


Fig. 20 Flow-based interaction mode for the fabrication of solid-liquid TENGs: (A) occurrence of the volume effect and interfacial effect when the flowing liquid contacts with the PTFE surface. (B) Effect of steady and unsteady flow on the output performance of a TENG. (C) Dependence of TENGs electrical output on the volumetric flow rate of the contact liquid. Reproduced with permission from Zhang, N., Gu, H., Lu, K., *et al.*, 2021. Nano Energy 82, 105735. Copyright 2020, Elsevier. Ahn, J.H., Hwang, J.Y., Kim, C.G., Nam, G.H., Ahn, K.K., 2020. Nano Energy 67, 104269. Copyright 2020, Elsevier. Cheedarala, R.K., Shahriar, M., Ahn, J.H., Hwang, J.Y., Ahn, K.K., 2019. Nano Energy 65, 104017. Copyright 2019, Elsevier.

Table 4 The output performances of the various small scale TENGs reported in literature

Triboelectric materials	Area of TENG	Output performance			References
		Voltage (V)	Current (μ A)	Power density (mW m^{-2})	
PDMS and Al	12 mm $\times$ 12 mm	3.73	0.14	8.44	(Zheng <i>et al.</i> , 2014)
PLGA and PCL	20 mm $\times$ 30 mm	4	1	32.6	(Zheng <i>et al.</i> , 2016b)
PTFE and Al	38 mm $\times$ 38 mm $\times$ 9.5 mm	215	660	9800	(Bai <i>et al.</i> , 2013)
PTFE and Al	25 mm $\times$ 10 mm $\times$ 1.5 mm	14	5	107	(Zheng <i>et al.</i> , 2016a)
PTFE and Kapton	30 mm $\times$ 20 mm $\times$ 1 mm	10	4	—	(Zheng <i>et al.</i> , 2016a)
PDMS and Al	30 mm $\times$ 28 mm	230	94	128 mW/cm^3	(Wang <i>et al.</i> , 2012)
PTFE and Water	100 mm $\times$ 70 mm	300	13.5	140	(Zhao <i>et al.</i> , 2018)
PMMA and Water	1000 mm^2	22	4	2.83	(Wang <i>et al.</i> , 2020)

on the change in the flow rate, the elastomeric tubing will result in three different states squeezed, fully squeezed, or fully resituated and result in different rates of charge generation and, finally, different current peaks (Fig. 20(C)).

The output performance of some small scale based TENG devices is summarized in Table 4.

Magneto-Mechano-Electric Generator

MME energy conversion has been demonstrated using a ME composite in the form of a cantilever operating at its structural resonance and converting low-frequency magnetic noise into electricity (Annapureddy *et al.*, 2016; Priya *et al.*, 2007). An ME composite with piezoelectric PMN-PZT single crystal macro-fibers and Ni magnetostrictive plate was demonstrated to generate 0.73 mW power from 0.7 mT magnetic flux density by Annapureddy *et al.* (2016). The same group explored an MME generator ($45 \times 21 \text{ mm}^2$) made by PMN-PZT single crystal fiber and Ni-based magnetostrictive materials for low power devices, wireless sensor networks, and re-charging applications (Damjanovic, 1998). The MME generator has been shown to achieve power density of $0.46 \text{ mW cm}^{-3} \text{ Oe}^{-2}$ under a weak magnetic flux density of 160 μT at 60 Hz, without an external DC magnetic field.

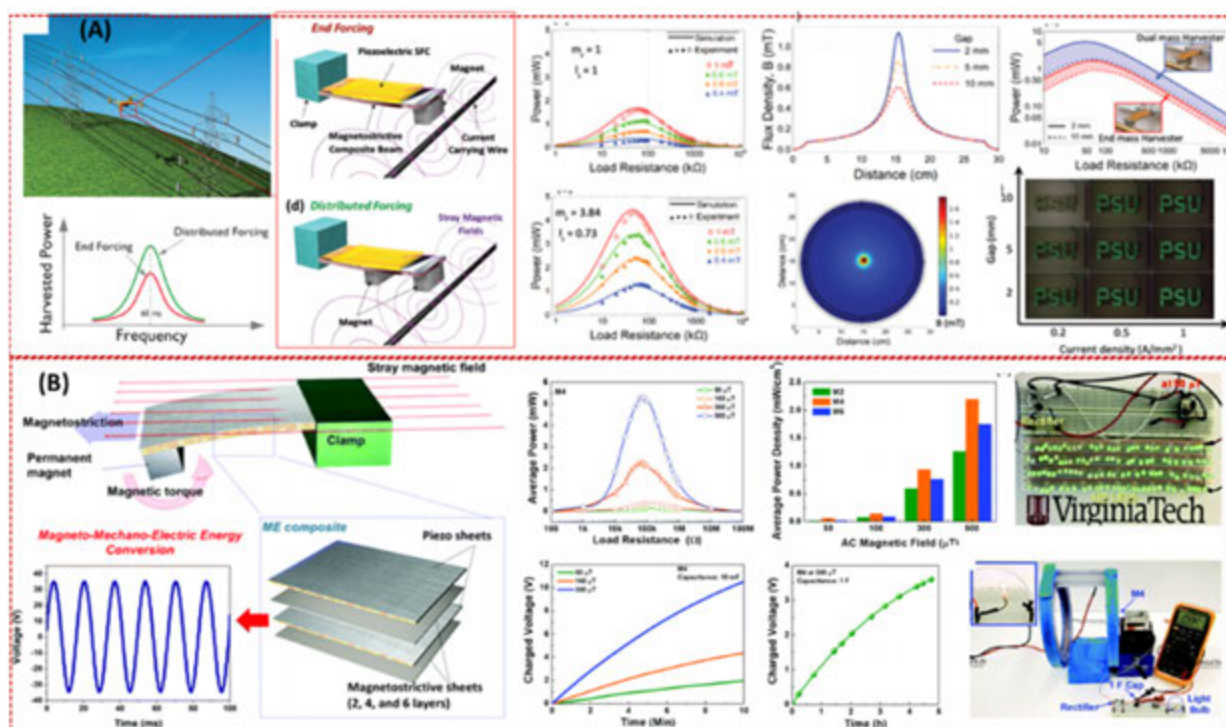


Fig. 21 (A) Schematic of end forcing and distributed forcing MME generator and the harvesting performance under magnetic field around the wire carrying current. (B) The working mechanism of the ME coupled multilayered MME generator and output performance and application demonstration. Reproduced with permission from Sriramdas, R., Kang, M.G., Meng, M., *et al.*, 2020. *Advanced Energy Materials* 10, 1903689. Copyright 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Lee, H., Sriramdas, R., Kumar, P., *et al.*, 2020. *Energy & Environmental Science* 13, 1462–1472. Copyright 2020. Royal Society of Chemistry.

Kambale *et al.* explored an MME generator with an ME structure (Kambale *et al.*, 2014), consisting of asymmetric (PZT ceramic fibers/Ni) and symmetric (Ni/PZT ceramic fibers/Ni) laminate structures. The symmetric structure developed a peak voltage of 0.3 V and an asymmetric structure developed an output of 2.5 V. The asymmetric structure developed maximum power of 6 μW at 1 Hz. Sriramdas *et al.* (2020) have demonstrated an MME harvester with large power amplification through distributed forcing (Fig. 21(A)) at a constant 60 Hz frequency. They fabricated an MME generator by adding 18 Metglas layers as magnetostrictive laminate and one layer of single-crystal fiber PMN-PZT composite. The thickness of crystal fiber was 200 μm , each Metglas layer thickness was 23 μm and the total thickness of the composite beam was 850 μm . They selected 3.96 g end mass to realize the first configuration. To obtain the fundamental frequency, 60 Hz, a mass of 7.6 g was attached at 33 mm from the clamped end which resulted in mass and length ratios of $m_r = 3.84$ and $l_r = 0.73$. In case of dual mass harvester the generated output voltage was 36.5 V, while the generated voltage was 24.7 V with just the end mass, at 1 mT flux density. Recently, Lee *et al.* (2020) have introduced a novel ME coupled MME generator (Fig. 21(B)) that provides 400% higher output power compared to the state-of-the-art, when operating at a magnetic flux density as low as 100 μT . The ME coupled MME generator develops a milliwatt power below 300 μT stray magnetic flux density. The device can also produce power under moderate to extremely low magnetic fields ($\leq 50 \mu\text{T}$), indicating its feasibility for harvesting energy for low power applications.

Kang *et al.* (2018) have explored a high-power MME harvester through amplified magneto-mechanical vibration for IoT applications (Fig. 22(A)). They fabricated MME generator using PZT as a piezoelectric layer and FBS as a magnetostrictive layer. To achieve high ME coupling, in addition to the piezomagnetic coefficient of the FBS, the overall structural design was optimized for enhancing strain amplitude in the piezoelectric macrofiber composite. To quantify the influence of strain amplitude, multilayer FBS laminates were utilized with different number of layers (5, 10, 15, and 20 layers), which resulted in different elastic stiffnesses in the overall structure. The fabricated ME coupled MME harvester with 20 layers was found to generate high electrical power of $\approx 180 \mu\text{W}_{\text{peak}}$ and $\approx 9.8 \text{ mW}_{\text{peak}}$ under an AC magnetic field of 0.1 and 1 mT, respectively. The power at 1 mT is enough to turn on 80 LED arrays and charge 10 mF capacitor. The textured Fe-Ga alloy sheet containing magnetostrictive and anisotropic PMN-PZ-PT piezoelectric single-crystal fibers based low-cost and scalable high-performance MME generator has been explored by Annpureddy *et al.* (2018) They fabricated an MME generator by covering the top and bottom of the PMN-PZT single crystal fiber composite using Cu electrodes. It is noteworthy that the Fe-Ga based MME generator demonstrated a strong ME coupling of $\alpha_{\text{ME}} = 1330 \text{ V cm}^{-1} \text{ Oe}^{-1}$, without any magnetic bias field, which is 170% larger than that of a Ni-based MME generator explored in the community. The MME generator was found to generate large DC power density of 3.22 mW/cm^3 , with high voltage of

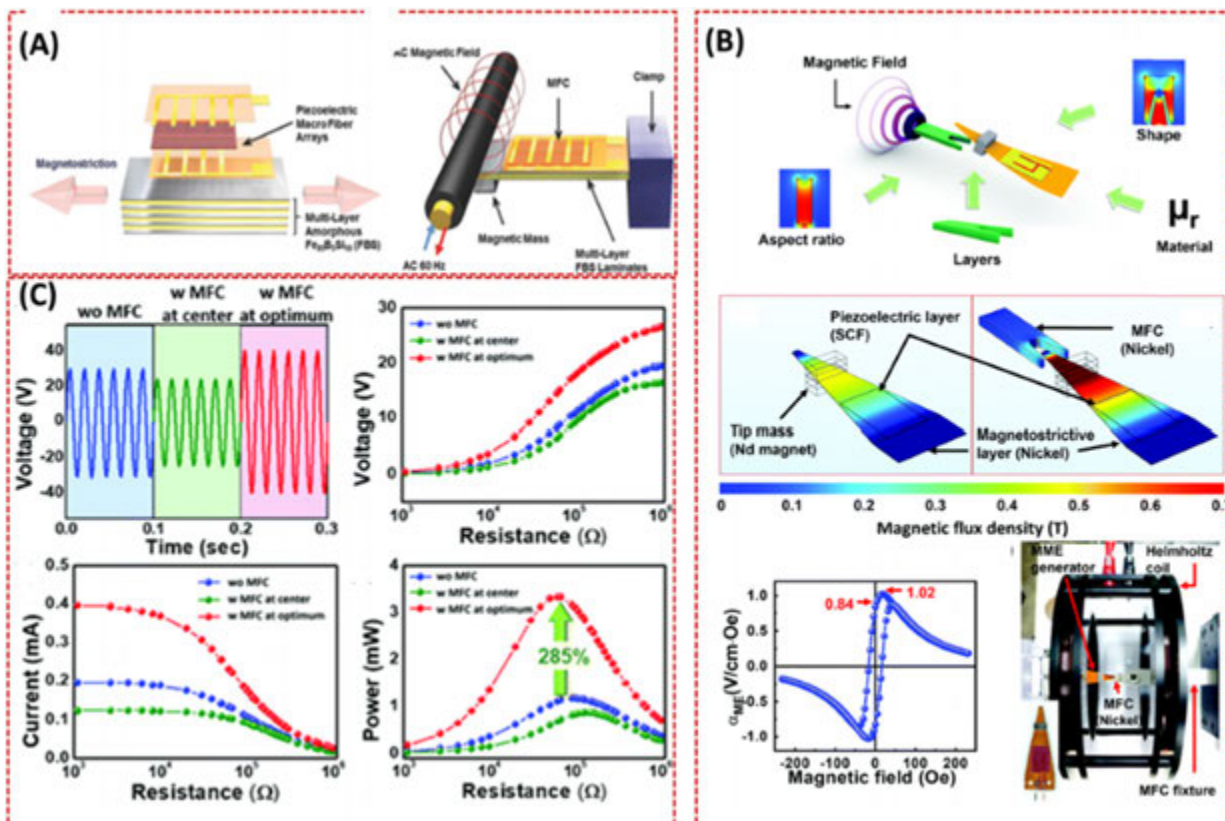


Fig. 22 (A) ME composite and energy harvesting scheme using MME harvester is shown schematically. (B) Schematic of optimized MFC concentrating the magnetic field in an MME generator, theoretical simulation model of the MFC, density distribution in the magnetostrictive layer under a magnetic field of 8 Oe, magneto-electric voltage coefficient, and measurement setup. (C) The output performance of MFC integrated MME generator. Reproduced with permission from Kang, M.G., Sriramdas, R., Lee, H., *et al.*, 2018. *Advanced Energy Materials* 8, 1703313. Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA. Weinheim. Song, H., Patil, D.R., Yoon, W.-H., *et al.*, 2020. *Energy & Environmental Science* 13, 4238–4248. Copyright 2019, Royal Society of Chemistry.

212 $V_{\text{peak-peak}}$ (>330% improvement, as compared with the Ni-based MME generator), and current of $52 \mu\text{A cm}^{-2}$ (>250% improvement) under a 60 Hz AC magnetic flux density of $700 \mu\text{T}$.

In a recent study [Song *et al.* \(2020\)](#) have introduced an MME generator made by an anisotropic 32 mode Mn-doped $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbZrO}_3\text{-PbTiO}_3$ (PMN-PZ-PT) SCF, directly integrated with a Ni cantilever structure and a NdFeB permanent magnet proof mass. They have utilized a magnetic flux concentrator (MFC) in the MME generator to increase the power density and measure output performance with and without MFC (**Fig. 22(B, C)**). The MFC can enhance the power of the MME generator by enhancing the ME coupling and magnetic forcing simultaneously, thereby influencing the intrinsic mechanism responsible for the output performance. The MME generator with the MFC was observed to generate a maximum power of 3.33 mW, which was 285% of that of the condition without the MFC (1.17 mW) under a weak magnetic field of 8 Oe ($= 8 \text{ G} = 800 \mu\text{T}$ in the air), which was sufficient to charge the 2.2 mF storage capacitor within 13 s and continuously operate an IoT sensor for a long period. They have achieved an optimum α_{ME} value of $0.84 \text{ V cm}^{-1} \text{ Oe}^{-1}$ which was obtained at $H_{\text{dc}} = 0 \text{ Oe}$, validating the intrinsic self-biasing nature of the MME generator, that eliminated the use of a DC electromagnet for additional study. The nature of self-bias of the MME generator can be assigned to the hysteretic magnetic behavior of the Ni foil, which comes from the size-dependent demagnetization effect associated with Ni foil and coercive field of the Ni foil owing to macro-sized domains with long-range ordering. The output performance of different MME generators are compared in **Table 5**.

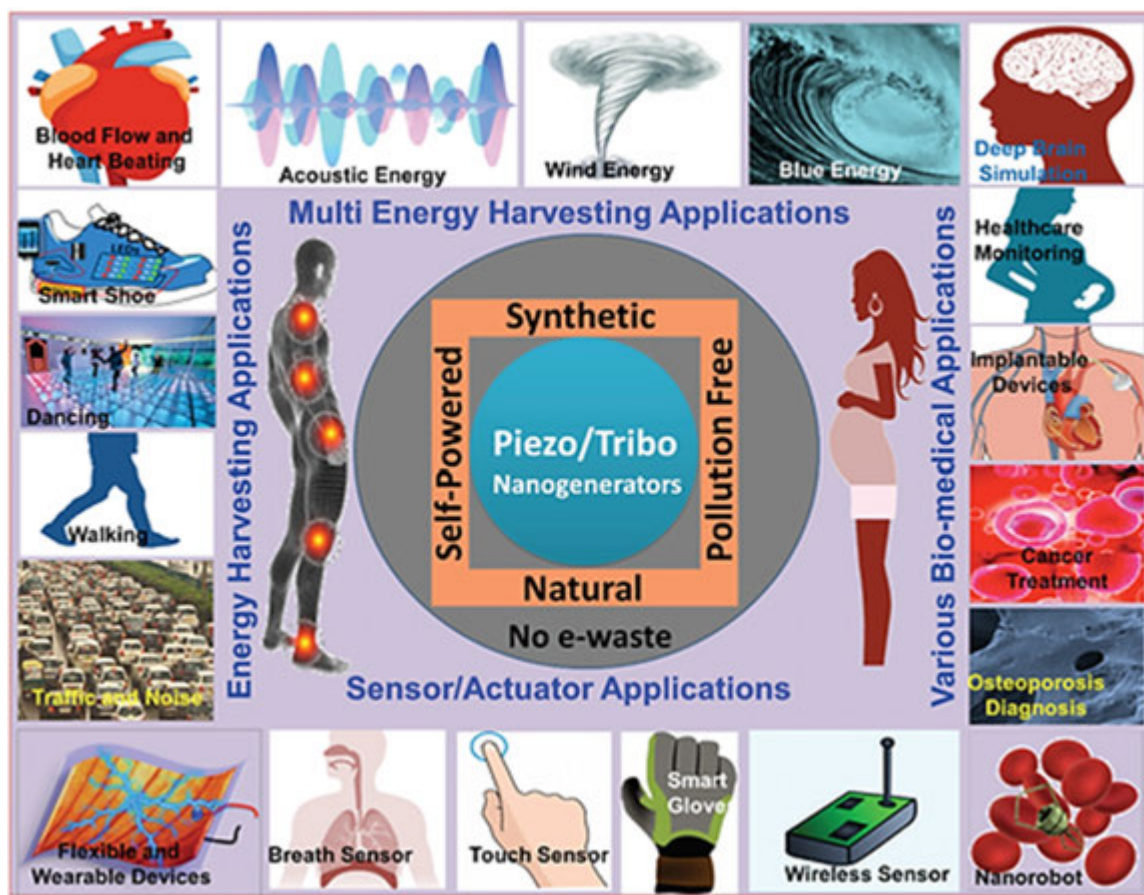
Applications

Piezo/Triboelectric nanogenerators

Mechanical energy harvesting through PENGs and TENGs has gained attention due to the diversity of designs to directly convert mechanical energy into electricity for various wearable and portable integrated applications. This energy harvesting technology can be applied in applications such as tactile sensors, resonators, medical sensors, actuators, and various portable/smart electronics. The PENGs/TENGs are relevant for future biomedical applications to detect various kinetic energies, generated from respiration or

Table 5 The performance of various MME generators reported in the literature

Materials used	Device area	Input Field	Power density	References
SCF PZT/Ni	$45 \times 21 \text{ mm}^2$	$160 \text{ } \mu\text{T}$	$46 \text{ mW cm}^{-3} \text{ Oe}^{-2}$	(Ryu <i>et al.</i> , 2015)
SCF PMN-PZT/Ni	$30 \times 12 \text{ mm}^2$	$700 \text{ } \mu\text{T}$	2.1 mW/cm^3	(Annapureddy <i>et al.</i> , 2016)
MFC PZT/Metglas	$35 \times 17 \text{ mm}^2$	1 mT	2.08 mW/cm^3	(Kang <i>et al.</i> , 2018)
SCF PMN-PZT/Metglas	$45 \times 15 \text{ mm}^2$	1 mT	2.12 mW/cm^3	(Sriramdas <i>et al.</i> , 2020)
PZT-5A/Metglas	$36 \times 31 \text{ mm}^2$	$500 \text{ } \mu\text{T}$	2.2 mW/cm^3	(Lee <i>et al.</i> , 2020)
SCF PMN-PZT/Ni	$50 \times 20 \text{ mm}^2$	$700 \text{ } \mu\text{T}$	3.2 mW/cm^3	(Annapureddy <i>et al.</i> , 2018)
SCF PMN-PZ-PT/Ni	760 mm^2	$800 \text{ } \mu\text{T}$	1.28 mW/cm^2	(Song <i>et al.</i> , 2020)

**Fig. 23** Applications of self-powered PENGs/TENGs devices to advanced technologies and biomedical engineering. Reproduced with permission from Karan, S.K., Maiti, S., Lee, J.H., *et al.*, 2020. *Advanced Functional Materials* 30, 2004446. Copyright 2020. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

heartbeat or arterial pulse movements, or even blood flow (Fig. 23). Presently, there is interest in developing in-vivo biomedical applications through biomechanical energy harvesting for the operation of implanted-medical-devices (IMDs). The harvesters enabled using a single crystalline piezoelectric PMN-PT thin film can be used as a self-powered artificial pacemaker. This material has been demonstrated in providing real-time functional electrical stimulation for stimulating the artificial heart beating in a live rat. The muscle-driven PENG can generate biomechanical energy from the heartbeat and breath of a live rat so it may be applicable for biomedical applications. The TENG can also charge the battery of a pacemaker, which is crucial for the implementation of implantable devices. Some important biomedical applications of TENGs include IMDs, cardiac monitoring sensors, laser curing systems for osteogenesis, nerve cell stimulation devices, and real-time monitoring sensors of respiratory rate, heart rate, and blood pressure.

Magneto-mechano-electric generators

MME generator can be used as a sustainable power source for IoT sensors and wireless communication systems installed in smart homes, factories, and have potential biomedical applications. ME coupled MME generator has been demonstrated to power

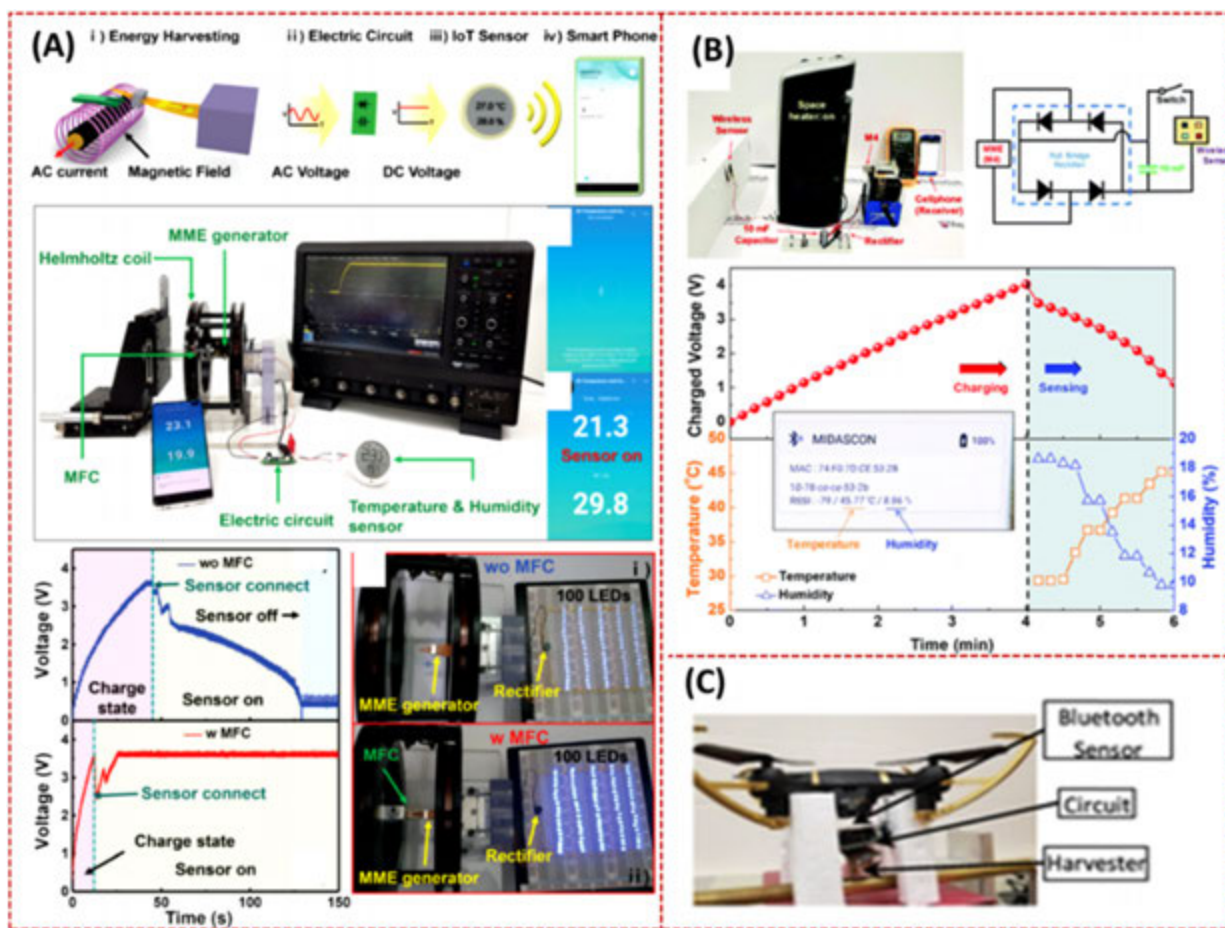


Fig. 24 Demonstration of powering smart electronics using MME generators. (A) Operation of a self-powered IoT sensor using the MME generator with the magnetic flux concentration, smartphone monitoring temperature/humidity information via a Bluetooth connection with a wireless sensor node, charging/discharging of the capacitor and powering commercial LEDs. (B) Powering an integrated sensor and a wireless data transmission system. (C) Drone can integrate with Bluetooth sensor tag, circuit and harvester for real-life applications. Reproduced with permission from Song, H., Patil, D.R., Yoon, W.-H., *et al.*, 2020. *Energy & Environmental Science* 13, 4238–4248. Copyright 2020, Royal Society of Chemistry. Lee, H., Sriramdas, R., Kumar, P., *et al.*, 2020. *Energy & Environmental Science* 13, 1462–1472. Copyright 2020, Royal Society of Chemistry. Sriramdas, R., Kang, M.G., Meng, M., *et al.*, 2020. *Advanced Energy Materials* 10, 1903689. Reproduced with permission. Copyright 2018, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

several LEDs without a capacitor, and operate multiple sensors and Bluetooth data communication systems simultaneously. The MME generator can be used for structural health monitoring (SHM) of outdoor power cables, as continuous magnetic field is present for the MME generator. MME generator has been demonstrated to power standalone IoT temperature and humidity sensors and peripheral components. The demonstration of powering smart electronics using MME generators is shown in Fig. 24. Apart from energy harvesting, the ME coupled composites find several applications in magnetic sensors, current sensors, tunable filters and resonators. On demand drug release, gastrointestinal tract examination and neural activity stimulation using ME nanoparticles are some of the potential biomedical applications. Furthermore, ME materials have potential applications in non-volatile random access memory with multiple memory states offering high memory density (Vopson, 2015). ME antenna is another possible application for transmitting data with less ohmic losses and without capacitive or inductive loadings (Petrov *et al.*, 2008). Nevertheless, ME transducers in the form of energy harvesters have been demonstrating considerable power densities even from weak and low-frequency magnetic fields. A comparative analysis of the three types of generators according to their output performance is presented in Table 6.

Remarks and Future Challenges

This chapter discussed the development of small-scale piezo/tribo/magneto-mechano-electric devices in energy harvesting and various IoT applications. The fabrication process of TENG devices is relatively simple and convenient, with low cost. The piezoelectric and MME generators can be realized with relatively easier and simpler architecture. All three techniques are of great

Table 6 Comparison of the output performance of MME generator with that of previously reported piezo/triboelectric energy harvesters

Harvesting Technique	Materials	Output Performance			Frequency (Hz)
		Voltage (V)	Current (μ A)	Power/power density	
MME Generator	Ni/PMN-PZ-PT	2.5	–	0.046 mW/cm ³	60
	Textured Fe-Ga/SCMF PMN-PZ-PT	76.5	178	3.22 mW/cm ³	60
	Ni/low-loss PMN-PZ-PT	24	120	2.1 mW/cm ³	60
Triboelectric Nanogenerator	PZT/polyethylene terephthalate	6	0.045	0.2 mW/cm ³ (peak power)	1
	PDMS/Al	230	94	128 mW/cm ³	6
	PTFE/Al	215	660	9.8 mW/cm ²	10
	Kapton/polyester	3.3	0.6	10.4 mW/cm ³ (peak power)	5
Piezoelectric Nanogenerator	PMN-PT nanobelts	6	102	0.3 mW (peak power)	–
	PZT thick film	70	12	0.2 mW	0.4
	PMN-PZT single crystals	80	17	0.26 mW	2

Note: Annapureddy, V., Na, S.-M., Hwang, G.-T., *et al.*, 2018. *Energy & Environmental Science* 11, 818–829. Bai, P., Zhu, G., Lin, Z.-H., *et al.*, 2013. *ACS Nano* 7, 3713–3719. Wang, S., Lin, L., Wang, Z.L., 2012. *Nano Letters* 12, 6339–6346.

interest in the energy harvesting community as the devices achieve excellent power densities. The studies show that the power density of small area generators depends on several parameters such as material structures, device fabrication, and impedance matching circuitry, which are essential for practical applications. Impedance matching in triboelectric harvesting technique is different from piezoelectric and MME generators, and hence, appropriate circuit development is vital to achieve higher power densities. Several demonstrations of energy harvesting and its applications towards IoT have been reported in the research community. Further developments in miniaturization to maintain higher power output, and integrated power management circuitry for charging batteries is required.

In order to develop high power density and powering electronics using the MME generator from a commercial viewpoint, some additional efforts are required such as (1) materials combination and selection criteria specific to small area harvesting, have to be established to achieve the optimum performance, (2) fundamental studies on magnetostriction based power conversion efficiency have to be examined, (3) the feasibility and biocompatibility of the integrated implantable devices is important for in-vivo studies, and (4) the novel material development using nanotechnology to achieve ultra-high sensitivity at small (micro- or nano size) scales. The small-scale energy harvesting solutions will have a tremendous impact on the application of piezoelectric, triboelectric, and magneto-mechano-electric energy harvesting for the WSNs and IoT technologies. We believe that this chapter will provide guidance not only to the beginners by introducing the essential fundamental concepts but also to the research scientific community through the state-of-the-art demonstrations and the future directions in advancing the small-scale harvesting technologies.

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Conflict of interest

The authors declare no conflict of interest.

References

- Ahn, J.H., Hwang, J.Y., Kim, C.G., Nam, G.H., Ahn, K.K., 2020. *Nano Energy* 67, 104269.
- Aktakka, E.E., Peterson, R.L., Najafi, K., 2011. *Proceedings of the 16th International Solid-State Sensors, Actuators and Microsystems Conference (TRANSDUCERS)*, Beijing, pp. 1649–1652.
- Andosca, R., McDonald, T.G., Genova, V., *et al.*, 2012. *Sensors and Actuators A: Physical* 178, 76–87.
- Annapureddy, V., Kim, M., Palneedi, H., *et al.*, 2016. *Advanced Energy Materials* 6, 1601244.
- Annapureddy, V., Na, S.-M., Hwang, G.-T., *et al.*, 2018. *Energy & Environmental Science* 11, 818–829.
- Arnau, A., Soares, D., 2009. *Piezoelectric Transducers and Applications*. Springer. pp. 1–38.
- Atzori, L., Iera, A., Morabito, G., 2010. *Computer Networks* 54, 2787–2805.

- Bai, P., Zhu, G., Lin, Z.-H., *et al.*, 2013. *ACS Nano* 7, 3713–3719.
- Bedekar, V., Oliver, J., Priya, S., 2010. *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control* 57, 1513–1523.
- Bichurin, M., Petrov, V., 2014. *Modeling of Magnetolectric Effects in Composites*. Springer.
- Bichurin, M., Petrov, V., Tatarenko, A., 2017. *Sensors* 17, 1651.
- Bichurin, M.I., Petrov, V.M., Srinivasan, G., 2002. *Journal of Applied Physics* 92, 7681–7683.
- Chang, C., Tran, V.H., Wang, J., Fuh, Y.-K., Lin, L., 2010. *Nano Letters* 10, 726–731.
- Chang, C.-M., Carman, G.P., 2008. *Journal of Intelligent Material Systems and Structures* 19, 1271–1280.
- Cheedarala, R.K., Shahriar, M., Ahn, J.H., Hwang, J.Y., Ahn, K.K., 2019. *Nano Energy* 65, 104017.
- Choi, Y.S., Kim, S.K., Smith, M., *et al.*, 2020. *Science Advances* 6.
- Chung, S.Y., Kim, S., Lee, J.H., *et al.*, 2012. *Advanced Materials* 24, 6022–6027.
- Cui, H., Hensleigh, R., Yao, D., *et al.*, 2019. *Nature Materials* 18, 234–241.
- Dagdeviren, C., Yang, B.D., Su, Y., *et al.*, 2014. *Proceedings of the National Academy of Sciences of the United States of America* 111, 1927–1932.
- Damjanovic, D., 1998. *Reports on Progress in Physics* 61, 1267–1324.
- Datta, A., Choi, Y.S., Chalmers, E., Ou, C., Kar-Narayan, S., 2017. *Advanced Functional Materials* 27, 1604262.
- Fan, F.-R., Tian, Z.-Q., Wang, Z.L., 2012. *Nano Energy* 1, 328–334.
- Fan, Z., Razavi, H., Do, J.-w., *et al.*, 2009. *Nature Materials* 8, 648–653.
- Filippov, D.A., Galichyan, T.A., Laletin, V.M., 2014. *Applied Physics A* 115, 1087–1091.
- Furlani, E.P., 2001. *Permanent Magnet and Electromechanical Devices: Materials, Analysis, and Applications*. Academic press.
- Gershenfeld, N., Krikorian, R., Cohen, D., 2004. *Scientific American* 291, 76–81.
- Gillispie, C.C., 2019. *Dictionary of Scientific Biography*. New York: Scribner, pp. 352–353.
- Goldenberg, J., 2007. *Science* 315, 808–810.
- Guo, H., Pu, X., Chen, J., *et al.*, 2018. *Science Robotics* 3 (20).
- Hajati, A., Kim, S.-G., 2011. *Applied Physics Letters* 99, 083105.
- Harshe, G., Dougherty, J.P., Newnham, R.E., 1993. *International Journal of Applied Electromagnetics in Materials* 4, 145–159.
- Hinchet, R., Yoon, H.-J., Ryu, H., *et al.*, 2019. *Science* 365, 491–494.
- Hoffmann, M.J., Kungl, H., Reszat, J.T., Wagner, S., 2005. *Polar Oxides*. Wiley-VCH Verlag GmbH & Co. KGaA. pp. 137–150.
- Hong, C.-C., Huang, S.-Y., Shieh, J., Chen, S.-H., 2012. *Macromolecules* 45, 1580–1586.
- Hwang, G.T., Park, H., Lee, J.H., *et al.*, 2014. *Advanced Materials* 26, 4880–4887.
- Hwang, G.T., Annapureddy, V., Han, J.H., *et al.*, 2016. *Advanced Energy Materials* 6, 1600237.
- Islam, R.A., Priya, S., 2006. *Applied Physics Letters* 88, 032903.
- Jaffe, B., Cook, W.R., Jaffe, H.L., 1971. *Piezoelectric Ceramics*. Academic Press.
- Janphuang, P., Lockhart, R., Uffer, N., Briand, D., de Rooij, N.F., 2014. *Sensors and Actuators A: Physical* 210, 1–9.
- Jeong, C.K., Kim, I., Park, K.-I., *et al.*, 2013. *ACS Nano* 7, 11016–11025.
- Kambale, R.C., Kang, J.-E., Yoon, W.-H., *et al.*, 2014. *Energy Harvesting and Systems* 1, 3–11.
- Kang, M.G., Sriramdas, R., Lee, H., *et al.*, 2018. *Advanced Energy Materials* 8, 1703313.
- Karan, S.K., Mandal, D., Khatua, B.B., 2015. *Nanoscale* 7, 10655–10666.
- Karan, S.K., Bera, R., Paria, S., *et al.*, 2016. *Advanced Energy Materials* 6, 1601016.
- Karan, S.K., Maiti, S., Agrawal, A.K., *et al.*, 2019. *Nano Energy* 59, 169–183.
- Karan, S.K., Maiti, S., Lee, J.H., *et al.*, 2020. *Advanced Functional Materials* 30 (48), 2004446.
- Kim, H.S., Kim, J.-H., Kim, J., 2011. *International Journal of Precision Engineering and Manufacturing* 12, 1129–1141.
- Kim, Y., Lee, K.Y., Hwang, S.K., *et al.*, 2014. *Advanced Functional Materials* 24, 6262–6269.
- Kuo, C.-L., Lin, S.-C., Wu, W.-J., 2016. *Smart Materials and Structures* 25, 105016.
- Kwon, J., Seung, W., Sharma, B.K., Kim, S.-W., Ahn, J.-H., 2012. *Energy & Environmental Science* 5, 8970–8975.
- Lee, H., Sriramdas, R., Kumar, P., *et al.*, 2020. *Energy & Environmental Science* 13, 1462–1472.
- Li, F., Cabral, M.J., Xu, B., *et al.*, 2019. *Science* 364, 264–268.
- Lin, Z.H., Cheng, G., Lin, L., Lee, S., Wang, Z.L., 2013. *Angewandte Chemie International Edition* 52, 12545–12549.
- Liu, D., Yan, Y.K., Zhou, H.P., 2007. *Synthesis of micron-scale platelet BaTiO₃*. *Journal of the American Ceramic Society* 90, 1323–1326.
- Liu, Z., Ma, Y., Ouyang, H., *et al.*, 2019a. *Advanced Functional Materials* 29, 1807560.
- Liu, W., Wang, Z., Wang, G., *et al.*, 2019b. *Nature Communications* 10, 1–9.
- Liu, X., Tan, X., 2016. *Advanced materials* 28, 574–578.
- Maiti, S., Karan, S.K., Kim, J.K., Khatua, B.B., 2019. *Advanced Energy Materials* 9, 1803027.
- Martins, P., Lopes, A.C., Lanceros-Mendez, S., 2014. *Electroactive phases of poly (vinylidene fluoride): Determination, processing and applications*. *Progress in Polymer Science* 39 (4), 683–706.
- Meirovitch, L., 2010. *Fundamentals of Vibrations*. Waveland Press.
- Messing, G.L., Trolter-McKinstry, S., Sabolsky, E.M., *et al.*, 2004. *Critical Reviews in Solid State and Materials Sciences* 29, 45–96.
- Moriana, A.D., Zhang, S., 2018. *Journal of Materiomics* 4, 277–303.
- Newnham, R.E., 2005. *Properties of Materials: Anisotropy, Symmetry, Structure*. Oxford, NY: Oxford University Press.
- Niu, S., Wang, Z.L., 2015. *Nano Energy* 14, 161–192.
- Noheda, B., Gonzalo, J.A., Cross, L.E., *et al.*, 2000. *Physical Review B* 61, 8687–8695.
- Nye, J.F., 1985. *Physical Properties of Crystals: Their Representation by Tensors And Matrices*. New York: Clarendon Press; Oxford University Press, Oxford.
- Pan, S., Zhang, Z., 2019. *Friction* 7, 2–17.
- Park, K.I., Lee, M., Liu, Y., *et al.*, 2012. *Advanced Materials* 24, 2999–3004.
- Persano, L., Dagdeviren, C., Su, Y., *et al.*, 2013. *Nature Communications* 4, 1–10.
- Petrov, R., Tatarenko, A., Pandey, S., *et al.*, 2008. *Electronics Letters* 44, 506–508.
- Priya, S., 2007. *Journal of Electroceramics* 19, 167–184.
- Priya, S., Inman, D.J., 2009. *Energy Harvesting Technologies*. Springer.
- Priya, S., Song, H.-C., Zhou, Y., *et al.*, 2019. *Energy Harvesting and Systems* 4, 3–39.
- Priya, S., Islam, R., Dong, S., Viehland, D., 2007. *Journal of Electroceramics* 19, 149–166.
- Qi, Y., Kim, J., Nguyen, T.D., *et al.*, 2011. *Nano Letters* 11, 1331–1336.
- Qiu, Y., Zhang, H., Hu, L., *et al.*, 2012. *Nanoscale* 4, 6568–6573.
- Rao, W.-F., Wang, Y.U., 2007. *Applied Physics Letters* 90.
- Reilly, E.K., Miller, L.M., Fain, R., Wright, P., 2009. *Proceedings of the PowerMEMS 2009*, 312–315.
- Renaud, M., Karakaya, K., Sterken, T., *et al.*, 2008. *Sensors and Actuators A: Physical* 145, 380–386.

- Roundy, S., Wright, P.K., Rabaey, J.M., 2003. Energy Scavenging for Wireless Sensor Networks With Special Focus on Vibrations. Springer. pp. 45–47. (Norwell).
- Ryu, J., Kang, J.-E., Zhou, Y., *et al.*, 2015. Energy & Environmental Science 8, 2402–2408.
- Ryu, J., Carazo, A.V., Uchino, K., Kim, H.-E., 2001. Japanese Journal of Applied Physics 40, 4948–4951.
- Ryu, J., Priya, S., Uchino, K., Kim, H.-E., 2002. Journal of Electroceramics 8, 107–119.
- Shi, Q., Wang, T., Lee, C., 2016. Scientific Reports 6, 24946.
- Song, H., Patil, D.R., Yoon, W.-H., *et al.*, 2020. Energy & Environmental Science 13, 4238–4248.
- Sow, M., Lacks, D.J., Sankaran, R.M., 2013. Journal of Electrostatics 71, 396–399.
- Sriramdas, R., Pratap, R., 2017. Journal of Microelectromechanical Systems 26, 679–690.
- Sriramdas, R., Rastogi, S., Pratap, R., 2016. Energy Harvesting and Systems 3, 121–131.
- Sriramdas, R., Kang, M.G., Meng, M., *et al.*, 2020. Advanced Energy Materials 10, 1903689.
- Sriramdas, R., Chiaplunkar, S., Cuduvally, R.M., Pratap, R., 2015. IEEE Sensors Journal 15, 3338–3348.
- Sun, C., Shi, J., Bayerl, D.J., Wang, X., 2011. Energy & Environmental Science 4, 4508–4512.
- Uchino, K., 2009. Ferroelectric Devices. CRC Press.
- Uchino, K., 2010a. Ferroelectric Devices. Boca Raton: CRC Press.
- Uchino, K., 2010b. Advanced Piezoelectric Materials: Science and Technology. Woodhead Publishing. p. 696.
- Vopson, M.M., 2015. Critical Reviews in Solid State and Materials Sciences 40, 223–250.
- Wada, S., Yako, K., Kakemoto, H., Tsurumi, T., Kiguchi, T., 2005. Journal of Applied Physics 98.
- Wang, B., Wu, Y., Liu, Y., *et al.*, 2020. ACS Applied Materials & Interfaces 12, 31351–31359.
- Wang, K., Malić, B., Wu, J., 2018. MRS Bulletin 43, 607–611.
- Wang, S., Lin, L., Wang, Z.L., 2012. Nano Letters 12, 6339–6346.
- Wang, X., Song, J., Liu, J., Wang, Z.L., 2007. Science 316, 102–105.
- Wang, Z.L., 2015. Faraday Discussions 176, 447–458.
- Wang, Z.L., 2011. Nanogenerators for Self-powered Devices and Systems. SMARTech Digital Repository, Georgia Institute of Technology. (ISBN: 978-1-4507-8016-2).
- Wang, Z.L., Song, J., 2006. Science 312, 242–246.
- Wang, Z.L., Wang, X., Song, J., Liu, J., Gao, Y., 2008. Piezoelectric Nanogenerators for Self-Powered Nanodevices. IEEE Pervasive Computing 7 (1), 49–55. doi:10.1109/mperv.2008.14.
- Wu, C., Park, J.H., Koo, B., *et al.*, 2018. ACS Nano 12, 9947–9957.
- Wu, C., Wang, A.C., Ding, W., Guo, H., Wang, Z.L., 2019. Advanced Energy Materials 9, 1802906.
- Xu, H., Pei, Y., Li, F., Fang, D., 2018. Journal of the Mechanics and Physics of Solids 114, 143–157.
- Xu, R., 2012. The Design of Low-Frequency, Low-g Piezoelectric Micro Energy Harvesters. Massachusetts Institute of Technology.
- Xu, R., Kim, S., 2012. Proceedings of the PowerMEMS. 464–467.
- Yan, Y., Cho, K.-H., Maurya, D., *et al.*, 2013. Applied Physics Letters 102, 042903.
- Yang, R., Qin, Y., Li, C., Zhu, G., Wang, Z.L., 2009. Nano Letters 9, 1201–1205.
- Yu, Y., Sun, H., Orbay, H., *et al.*, 2016. Nano Energy 27, 275–281.
- Zhang, N., Gu, H., Lu, K., *et al.*, 2021. Nano Energy 82, 105735.
- Zhang, S.J., Li, F., 2012. Journal of Applied Physics 111.
- Zhang, Y., Li, L., Shen, B., Zhai, J., 2015. Dalton Transactions 44, 7797–7802.
- Zhao, X.J., Kuang, S.Y., Wang, Z.L., Zhu, G., 2018. ACS Nano 12, 4280–4285.
- Zheng, Q., Shi, B., Fan, F., *et al.*, 2014. Advanced Materials 26, 5851–5856.
- Zheng, Q., Zhang, H., Shi, B., *et al.*, 2016a. ACS Nano 10, 6510–6518.
- Zheng, Q., Zou, Y., Zhang, Y., *et al.*, 2016b. Science Advances 2, e1501478.
- Zheng, X.J., Liu, X.E., 2005. Journal of Applied Physics 97, 053901.
- Zhu, G., Yang, R., Wang, S., Wang, Z.L., 2010. Nano Letters 10, 3151–3155.
- Zhu, L.-F., Zhang, B.-P., Zhao, L., Li, J.-F., 2014. Journal of Materials Chemistry C 2, 4764–4771.
- Zi, Y., Niu, S., Wang, J., *et al.*, 2015. Nature Communications 6, 1–8.
- Zou, H., Zhang, Y., Guo, L., *et al.*, 2019. Nature Communications 10, 1–9.

Multilayer Ceramic Actuators

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Piezoelectric and electrostrictive ceramic materials have become key components in smart actuator/sensor systems for use as precision positioners, miniature ultrasonic motors, and adaptive mechanical dampers. In particular, multilayer (ML) structures have been widely investigated in order to improve their reliability and to expand their applications. Developments in the USA, Japan, and Europe are compared.

Trends in Ceramic Actuators

Piezoelectric actuators are forming a new field midway between electronic and structural ceramics (Uchino, 1993, 1994, 1995b, 1996). Application fields are classified into three categories: positioners, motors, and vibration suppressors. The manufacturing precision of optical instruments such as lasers and cameras, and the positioning accuracy for fabricating semiconductor chips, which are adjusted using solid-state actuators, is of the order of 0.1 μm . Regarding conventional electromagnetic motors, tiny motors smaller than 1 cm are often required in office or factory automation equipment, and are rather difficult to produce with sufficient energy efficiency. Ultrasonic motors whose efficiency is insensitive to size are superior in the minimotor area. Vibration suppression in space structures and military vehicles using piezoelectric actuators is also a promising technology.

ML structures are mainly used for practical applications because of their low drive voltage, high energy density, quick response, and long lifetime (Yoshikawa and Shrout, 1993; Uchino, 1995a). Fig. 1 illustrates ML, multimorph, and ML-moonie structures, which will be covered in this chapter. Investigations have focused on the improvement of reliability and durability in ML actuators (MLAs).

This chapter reviews the investigations of device structures, reliability issues, and applications of MLAs, comparing the developments in the USA, Japan, and Europe.

ML Structures

Two preparation processes are possible for ML ceramic devices: one is a cut-and-bond method and the other is a tape-casting method. The tape-casting method requires expensive fabrication facilities and sophisticated techniques, but is suitable for the mass-production of thousands of pieces per month. Tape casting also provides thin dielectric layers, leading to low drive voltages of 40–100 V (Dibbern, 1995; Takada *et al.*, 1994).

An MLA with interdigital internal electrodes has been developed by Tokin (Ohashi *et al.*, 1993a,b). In contrast to the conventional electrode configuration in Fig. 1, line electrodes are printed on piezoelectric ceramic green sheets, and are stacked in such a way that alternating electrode lines are displaced by one-half pitch (see Fig. 2). This actuator generates motions at right angles to the stacking direction using the longitudinal piezoelectric effect. Long ceramic actuators up to 74 mm in length are manufactured.

A three-dimensional positioning actuator with a stacked structure has been proposed by PI Ceramic (Fig. 3), in which shear strain is used to generate x and y displacements (Bauer and Moller, 1995).

Composite actuator structures called ‘moonies’ and ‘cymbals’ have been developed at Penn State University to provide characteristics intermediate between the ML and bimorph actuators. These transducers exhibit an order of magnitude larger displacement than the ML, and much larger generative force with quicker response than the bimorph (Sugawara *et al.*, 1992; Onitsuka *et al.*, 1995). The device consists of a thin ML piezoelectric element and two metal plates with narrow moon-shaped cavities bonded together as shown in Fig. 1. A moonie $5 \times 5 \times 2.5$ mm in size can generate a 20 μm displacement under 60 V, eight times as large as the displacement of a ML of the same size (Goto *et al.*, 1992). This new compact actuator has been used to make a miniaturized laser beam scanner (Goto *et al.*, 1992). Moonie/cymbal characteristics have been investigated for various constituent materials and sizes (Tressler *et al.*, 1994; Dogan *et al.*, 1994).

Actuator Materials

Actuator materials are classified into three categories: piezoelectric, electrostrictive, and phase-change materials. Modified lead zirconate titanate (PZT, $\text{Pb}(\text{Zr,Ti})\text{O}_3$) ceramics are the leading materials for piezoelectric applications. The PLZT ($(\text{Pb,L a})(\text{Zr,Ti})\text{O}_3$) 7/62/38 compound is one such composition (Furuta and Uchino, 1986). The strain curve is shown in Fig. 4(a) (left). When the applied field is small, the induced strain, x , is nearly proportional to the field, $E(x=dE$, where d is called the piezoelectric constant). As the field becomes larger (i.e., greater than about 1 kV cm^{-1}), however, the strain curve deviates from this linear trend and

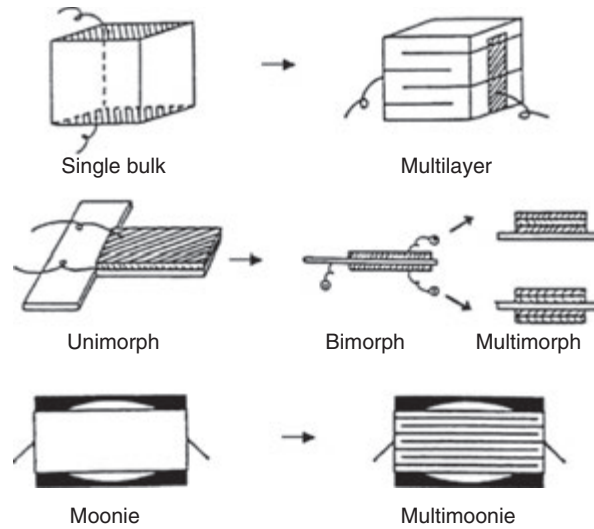


Fig. 1 Examples of multilayer, multimorph, and multilayer-moonie structures.

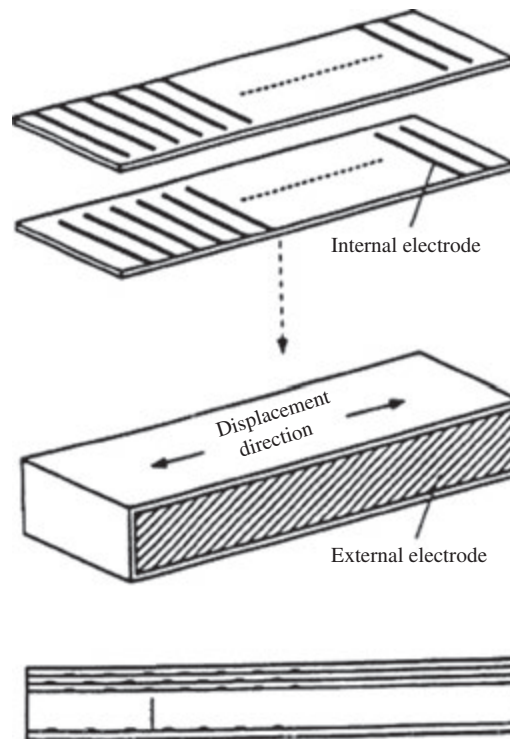


Fig. 2 Structure of an internal interdigital electrode actuator.

significant hysteresis is exhibited owing to polarization reorientation. This sometimes limits the usage of such materials in actuator applications that require nonhysteretic response.

An interesting new family of actuators has been fabricated in Germany from a barium stannate titanate system ($\text{Ba}(\text{Sn,Ti})\text{O}_3$) (von Cieminski and Beige, 1991). The useful property of $\text{Ba}(\text{Sn}_{0.15}\text{Ti}_{0.85})\text{O}_3$ is its unusual strain curve, in which the domain reorientation occurs only at low fields, and there is then a long linear range at higher fields (Fig. 4(a) (right)); i.e., the coercive field is unusually small. Moreover, this system is particularly intriguing since it contains no lead ions, an essential feature as ecological concerns grow in the future.

The second category of actuators is based on electrostriction as in PMN ($\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$)-based ceramics, developed in the USA. Although a second-order phenomenon of electromechanical coupling ($x = ME^2$, where M is the electrostrictive constant), it can be extraordinarily large (more than 0.1%) (Cross et al., 1980). An attractive feature of these materials is the near absence of

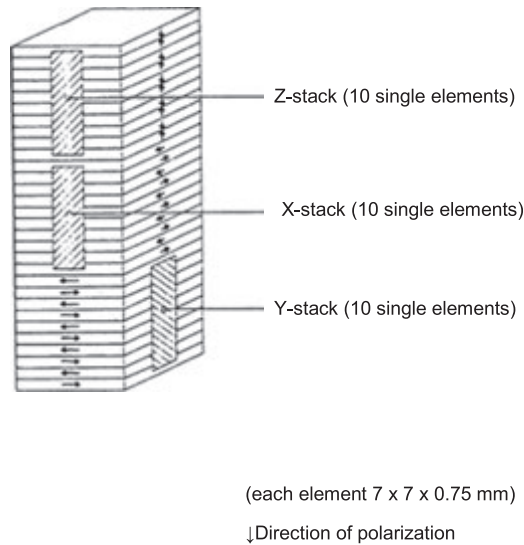


Fig. 3 Three-dimensional controllable multilayer piezoelectric actuator.

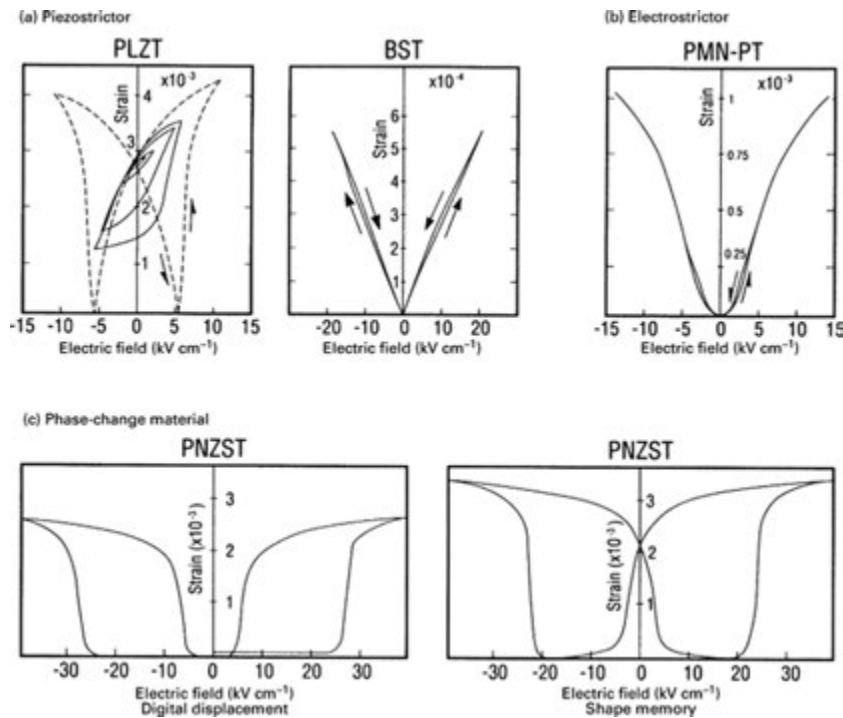


Fig. 4 Electric field-induced strains in ceramics: (a) piezoelectric $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ and $\text{Ba}(\text{Sn},\text{Ti})\text{O}_3$; (b) electrostrictive $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3},\text{Ti})\text{O}_3$; (c) phase-change material $\text{Pb}(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$.

hysteresis (**Fig. 4(b)**). The superiority of PMN over PZT has been demonstrated in a scanning tunneling microscope (STM) (Uchino, 1988). The PMN actuator can provide extremely small distortion of the image even when the probe is scanned in the opposite direction.

The third category is based on phase-change-related strains, i.e., polarization induced by switching from an antiferroelectric to a ferroelectric state (Uchino and Nomura, 1983). **Fig. 4(c)** shows the field-induced strain curves taken for the lead zirconate stannate $(\text{Pb}_{0.99}\text{Nb}_{0.02}((\text{Zr}_x\text{Sn}_{1-x})_{1-y}\text{Ti}_y)_{0.98}\text{O}_3)$ -based system. The longitudinally induced strain reaches more than 0.3%, which is much larger than that expected in normal piezoelectrics or electrostrictors. A rectangular hysteresis in **Fig. 4(c)** (left), referred to as a 'digital displacement transducer' because of the two on/off strain states, is interesting. Moreover, this field-induced transition

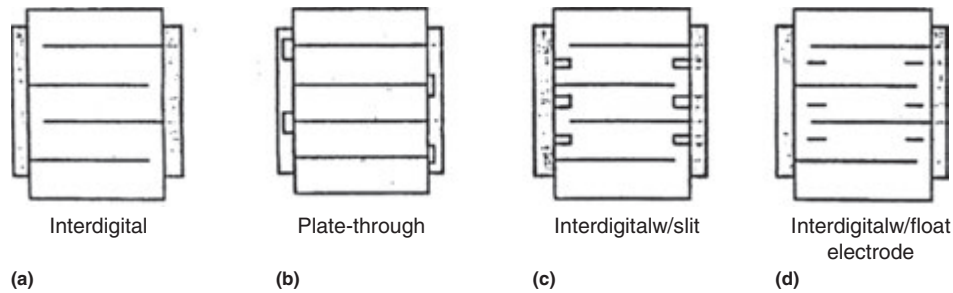


Fig. 5 Various internal electrode configurations in multilayer actuators: (a) interdigital, (b) plate-through, (c) slit-insert, and (d) float electrode.

exhibits a shape memory effect in appropriate compositions (Fig. 4(c) (right)). Once the ferroelectric phase has been induced, the material ‘memorizes’ its ferroelectric state even under zero-field conditions, although it can be erased with the application of a small reverse bias field (Furuta *et al.*, 1992). This shape memory ceramic is used in energy-saving actuators.

Reliability of MLAs

As application fields expand, the reliability and durability issues of MLAs become increasingly important. The reliability of ceramic actuators depends on a number of complex factors, which can be divided into three major categories: reliability of the ceramic itself, reliability of the device design, and the drive technique.

Compositional changes of actuator ceramics and the effect of doping are primary issues used in stabilizing the temperature and stress dependence of the induced strains. A ML piezoactuator for use at high temperatures (150 °C) has been developed by Hitachi Metal, using Sb_2O_3 -doped $(\text{Pb},\text{Sr})(\text{Zr},\text{Ti})\text{O}_3$ ceramics (Watanabe *et al.*, 1993). Systematic data on uniaxial stress dependence of piezoelectric characteristics have been collected on various navy PZT materials (Zhang *et al.*, 1996). Grain size and porosity control of the ceramics are also important in controlling the reproducibility of actuators (Okada *et al.*, 1993). Aging phenomena, especially the degradation of strain response, are, in general, strongly dependent on the applied electric field as well as on temperature, humidity, and mechanical bias stress (Sakai *et al.*, 1992).

The device design strongly affects its durability and lifetime. Silver electrode metal tends to migrate into the piezoceramic under a high electric field in high humidity. Silver–palladium alloys suppress this behavior effectively. Resistive coatings of the device should also be taken into account (Takada, 1992). To overcome electrode delamination, improved adhesion can be realized by using a mesh-type electrode or an electrode material with mixed metal and ceramic (the matrix composition) powders. Pure ceramic electrode materials have also been developed using semiconductive perovskite oxides (barium titanate-based PTCR ceramics) (Abe *et al.*, 1986). The lifetime characteristics of a MLA with applied d.c. or unipolar a.c. voltage at various temperatures (Nagata and Kinoshita, 1994, 1995b) and at various humidity levels (Nagata and Kinoshita, 1995a) have been investigated. The relationship between the logarithm of the lifetime and the reciprocal of absolute temperature shows linear characteristics similar to Arrhenius-type ones. Nevertheless, the degradation mechanism remains a critical problem.

In MLAs, reduction of the tensile stress concentration around the internal electrode edge of the conventional interdigital configuration is the central problem. Regarding the destruction mechanism of ML ceramic actuators, systematic data collection and analysis have led to considerable progress (Furuta and Uchino, 1993, 1994; Aburatani *et al.*, 1994; Wang and Singh, 1995; Cao and Evans, 1994; Schneider *et al.*, 1994; Suo, 1993; Hao *et al.*, 1996). Two typical crack patterns are generated in a conventional interdigital ML device: one is a Y-shaped crack located on the edge of an internal electrode, and the other is a vertical crack located in a layer adjacent to the top or bottom inactive layer, connecting a pair of internal electrodes.

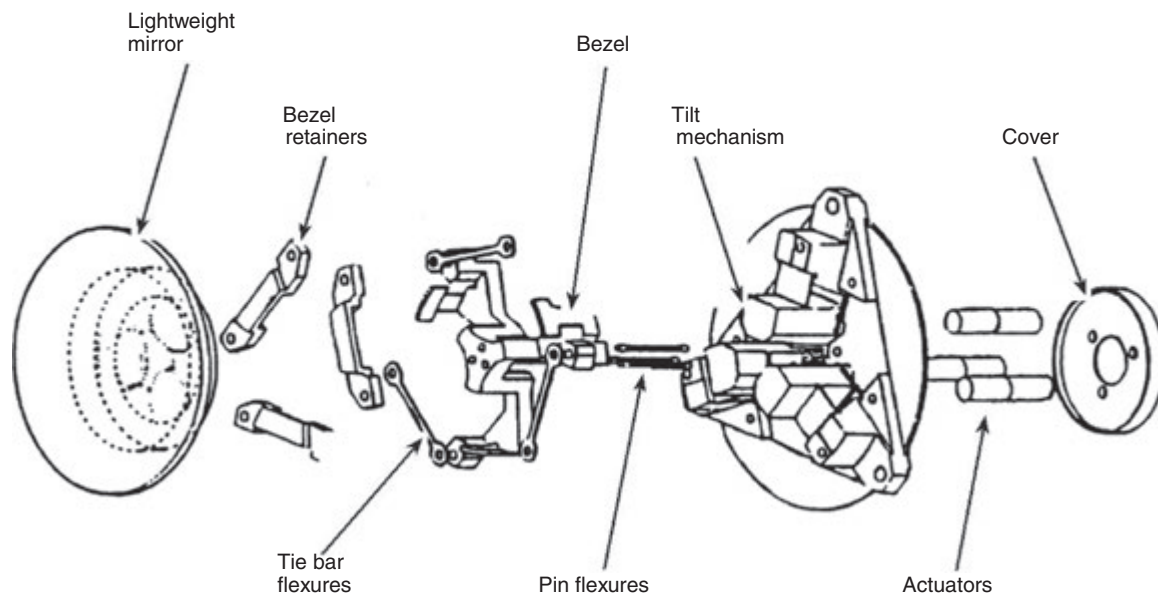
To overcome this crack problem, three electrode configurations have been proposed, as illustrated in Fig. 5: plate-through, interdigital and slit, and interdigital and float electrode types. The ‘float electrode’ type is an especially promising design, which can be fabricated using almost the same process as the conventional MLA, and leads to much longer lifetimes (Aburatani *et al.*, 1995). An empirical rule, ‘the thinner the layer, the tougher the device’ (Aburatani *et al.*, 1994; Furuta and Uchino, 1994), is also very intriguing, and will be more theoretically investigated in the near future.

Failure detection or lifetime prediction methods are expected to increase remarkably the reliability of MLAs. Acoustic emission and surface potential monitoring are promising methods (Uchino and Aburatani, 1994). A modified MLA has been developed at Pennsylvania State University containing a strain gage as an internal electrode (Sano *et al.*, 1993). This internal strain gage electrode can detect the crack initiation sensitively and monitor the field-induced strain (Aburatani and Uchino, 1996).

Regarding drive techniques for ceramic actuators, pulse drive and a.c. drive require special attention; the vibration overshoot associated with a sharp-rise step/pulse voltage causes a large tensile force, leading to delamination of the multistacked structure, while long-term application of a.c. voltage generates considerable heat. A special pulse drive technique using a mechanical bias stress is required in the first case, and heat generation can be suppressed by changing the device design. An analytical approach to the heat generation mechanism in MLAs has been reported, indicating the importance of larger surface area (Zheng *et al.*, 1996). Heat generation in piezoelectric ceramics is mainly attributed to the P–E hysteresis loss under large electric field drive (Hirose *et al.*,

Table 1 Ceramic actuator developments in the USA, Japan, and Europe (as of 2000)

	USA	Japan	Europe
Target	Military-oriented product	Mass consumer product	Laboratory equipment
Category	Vibration suppressor	Minimotor, positioner	Minimotor, positioner, vibration suppressor
Application field	Space structure military vehicles	Office equipment, cameras, precision machines, automobiles	Laboratory stage-stepper, aircraft, automobiles, hydraulic systems
Actuator size	Up-sizing (30 cm)	Down-sizing (1 cm)	Intermediate size (10 cm)
Major manufacturer	AVX/Kyocera, Morgan Matroc, Itek, Opt. Systems, Burleigh, AlliedSignal	Tokin Corp., NEC, Hitachi Metal, Mitsui-Sekka, Canon, Seiko Instruments	Philips, Siemens, Hoechst Ceram Tec., Ferroperm, Physik Instrument, Noliac

**Fig. 6** Articulating fold mirror using PMN multilayer actuators.

1995b; Takahashi *et al.*, 1995). For ultrasonic motors, antiresonance drive is preferable to resonance drive because of higher efficiency and lower heat generation for the same vibration level (Hirose *et al.*, 1995a).

Applications of MLAs

Table 1 compares a variety of ceramic actuator developments in the USA, Japan, and Europe (as of 2000). Additional details are described below.

USA

The principal target is military-oriented applications such as vibration suppression in space structures and military vehicles. Substantial increase in the size of the actuators is required for these purposes.

A typical example is found in the aircraft wing proposed by NASA (Heeg, 1993). A piezoelectric actuator is installed near the support of the wing, allowing immediate suppression of unwanted mechanical vibrations. Several publications have reported on damper and noise cancellation applications (Mather and Tran, 1993; Agrawal and Bang, 1993).

Passive dampers constitute another important application of piezoelectrics, where mechanical noise vibration is radically suppressed by the converted electric energy dissipation through Joule heat when a suitable resistance, equal to an impedance of the piezoelectric element of $1/\omega C$, is connected to the piezoelement (Uchino and Ishii, 1988).

A widely publicized application took place with the repair of the Hubble telescope launched by the Space Shuttle. ML PMN electrostrictive actuators corrected the image by adjusting the phase of the incident light wave (Fig. 6; Wada, 1993). PMN electrostrictors provided superior adjustment of the telescope image because of negligible strain hysteresis.

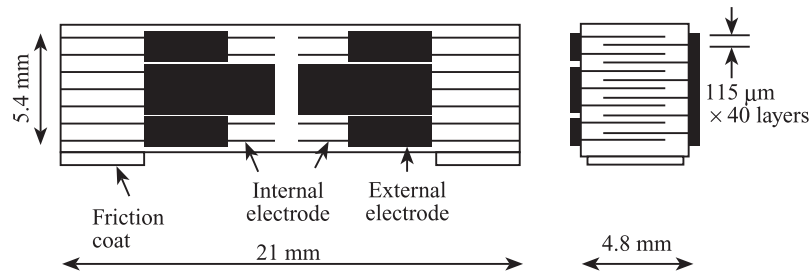


Fig. 7 Inchworm using multilayer piezoelectric actuators.

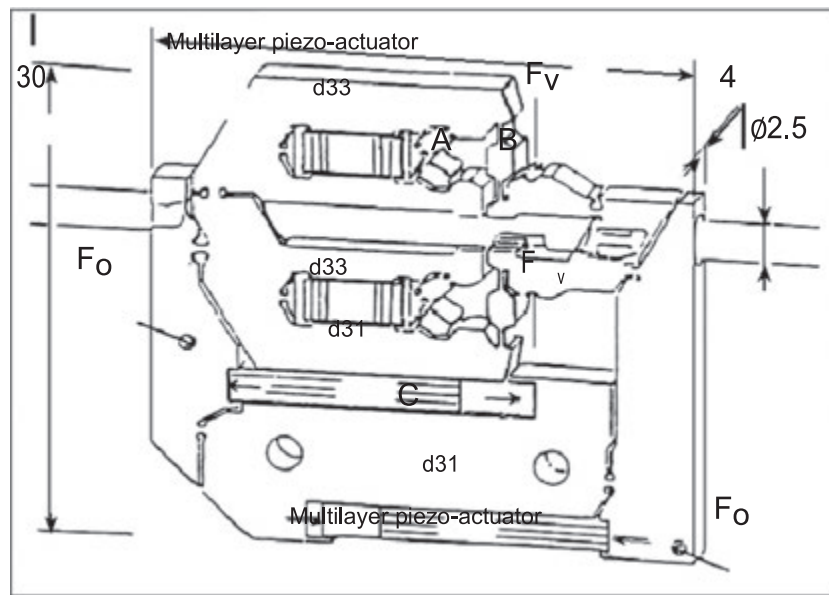


Fig. 8 Monolithic multilayer piezoelectric linear motor.

Japan

Japanese industries seek to develop mass-produced consumer products, especially minimotors and micro-positioners, aiming at applications such as office equipment and cameras/video cameras. Tiny actuators smaller than 1 cm^3 are the main focus in these products.

A dot matrix printer was the first widely commercialized product using ML ceramic actuators (Yano *et al.*, 1984). Each character formed by such a printer is composed of a 24×24 dot matrix in which a printing ribbon is impacted by a multiwire array. The printing element is composed of a ML piezoelectric device with a sophisticated hinge lever magnification mechanism. The magnification by a factor of 30 results in an amplified displacement of 0.5 mm and an energy transfer efficiency greater than 50%. A modified impact printer head has been developed by Tokin, using new interdigital internal electrode-type actuators, which has lowered production costs (Ono and Fuda, 1994). A color ink-jet printer has also been commercialized by Seiko Epson, using ML piezo-actuators (Yonekubo, 1995).

Automotive applications by Toyota Motor have been increasing. MLAs have been introduced to an electronically controlled suspension (Fukami *et al.*, 1994) and a pilot injection system for diesel engines has been developed (Abe *et al.*, 1994).

Efforts have been made to develop high-power ultrasonic vibrators as replacements for conventional electromagnetic motors. The ultrasonic motor is characterized by 'low speed and high torque,' which is contrasted with the 'high speed and low torque' of electromagnetic motors. After the invention of π -shaped linear motors (Tohda *et al.*, 1989), various modifications have been reported (Funakubo *et al.*, 1995; Saigoh *et al.*, 1995). The Mitsui Petrochemical model is of particular interest because the motor body is composed of only one component prepared by a co-firing method, as illustrated in Fig. 7 (Saigoh *et al.*, 1995). A maximum speed of 200 mm s^{-1} and a maximum thrust of 60 gf (0.6 N) has been reported for this motor.

Camera motors use a traveling elastic wave induced by a thin piezoelectric ring. A ring-type slider in contact with the 'rippled' surface of the elastic body bonded onto the piezoelectric can be driven in both directions by exchanging the sine and cosine voltage inputs. Another advantage is its thin design, making it suitable for installation in cameras as an automatic focusing device. Nearly 80% of the exchange lenses in Canon's EOS camera series have been replaced by ultrasonic motor mechanisms (Uchino, 1995c).

Intriguing research programs are underway in Japan on the vibration damping of earthquakes, using piezoelectric actuators (Shimoda *et al.*, 1992; Fujita, 1994). Active damping of a ML piezoactuator has been tested using an actual size H-type steel girder, and has been verified to be effective during earthquakes.

Europe

Ceramic actuator development has begun in Europe with a wide range of research topics. A focus of several major manufacturers is on laboratory equipment products such as laboratory stages and steppers with rather sophisticated structures.

Fig. 8 shows a walking piezomotor with four multilayer actuators by Philips (Koster, 1994). Two short actuators function as claspers while the longer two provide a proceeding distance in an inchworm mechanism. Physik Instrumente has developed more complicated two-leg type walkers (Gross, 1994).

Conclusions

The early 1980s saw the start of the intensive development of piezoelectric actuators in Japan, which then spread worldwide. The focus has been shifted to practical device applications. This chapter has reviewed several reliability issues of ML ceramic actuators as well as new actuator structures, and has compared the development of applications in the USA, Japan, and Europe.

The markets in the USA are chiefly limited to military and defense applications, and it is difficult to estimate the amount of sales. Navy needs include smart submarine skins, hydrophone actuators, and propeller noise cancellation. Smart aircraft skins are an air force objective, while the army requires helicopter rotor twisting, aeroservoelastic control, and cabin noise/seat vibration cancellation.

In Japan piezoelectric camera shutters (Minolta) and automatic focusing mechanisms in cameras (Canon), dot matrix printers (NEC), and part-feeders (Sanki) are now commercialized and mass-produced by tens of thousands of pieces per month. During commercialization, new designs and drive-control techniques of ceramic actuators have been developed. A number of patent disclosures have been generated by NEC, TOTO Corporation, Matsushita Electric, Brother Industry, Toyota Motors, Tokin, Hitachi Metal, and Toshiba.

Annual sales in 2005 (expecting the economic recovery in Japan) of ceramic actuator units, camera-related devices, and ultrasonic motors are estimated to reach \$500 million, \$300 million, and \$150 million, respectively. Regarding the final actuator-related products, \$10 billion is a realistic goal (Uchino, 1995c).

Future research trends can be divided in two ways: increasing the size of space structures and decreasing that of office equipment. Further decrease in size will also be required in medical diagnostic applications such as blood test kits and surgical catheters.

Key concerns for the future of ML ceramic actuators are 'miniaturization' and 'hybridization.' Layers thinner than 10 μm will be introduced in actuator devices replacing 100 μm sheets. Piezoelectric thin films compatible with silicon technology are a focus in microelectromechanical systems. Ultrasonic rotary motors as small as 2 mm in diameter (Flynn *et al.*, 1992) and a two-dimensional micro-optical scanner (Goto, 1994), both of which are fabricated on a silicon membrane, are good examples.

Nonuniform configurations or heterostructures of different materials, layer thickness, or electrode patterns will be adopted for practical devices. Functionally gradient piezoelectric actuators now being proto-typed indicate a new trend (Kim *et al.*, 1992).

Appendix

Fifteen years passed after authoring the above chapter. Though various researches have been explored during this period, the basic researches introduced in this chapter still remain important. Thus, in order to save the publication company's labor, the author decided to put only Appendix in this updated chapter for introducing the most essential three new researches: Pb-free piezoelectric materials, base metal (Cu) internal electrode, and diesel injection valve application.

A1 Pb-Free Piezoelectric Materials

Twenty-first century is called 'The Century of Environmental Management.' In 2006, European Community started RoHS (Restrictions on the use of certain Hazardous Substances), which explicitly limits the usage of lead (Pb) in electronic equipment. Basically, we may need to regulate the usage of PZT, most famous piezoelectric ceramics, in the future. The Japanese and European communities may experience governmental regulation on the PZT usage in these 10 years. Pb (lead)-free piezo-ceramics have started to be developed after 1999. The share of the patents for bismuth compounds (bismuth layered type and $(\text{Bi,Na})\text{TiO}_3$ (BNT) type) exceeds 61%. This is because bismuth compounds are easily fabricated in comparison with other compounds. Note that the toxicity of Bi^{3+} is not very low compared with Pb^{2+} , but that a regulation may not be proposed because this atomic element is not familiar to politicians fortunately. $(\text{Na,K})\text{NbO}_3$ (NKN) systems exhibit the highest performance because of the morphotropic phase boundary usage. Fig. A1 shows the current best data reported by Toyota Central Research Lab, where strain curves for oriented and unoriented $(\text{Na,K,Li})(\text{Nb,Ta,Sb})\text{O}_3$ ceramics are shown (Saito *et al.*, 2004). Note that the maximum strain reaches up to 1500×10^{-6} , which is equivalent to the PZT strain. Drawbacks include their sintering difficulty and the necessity of the

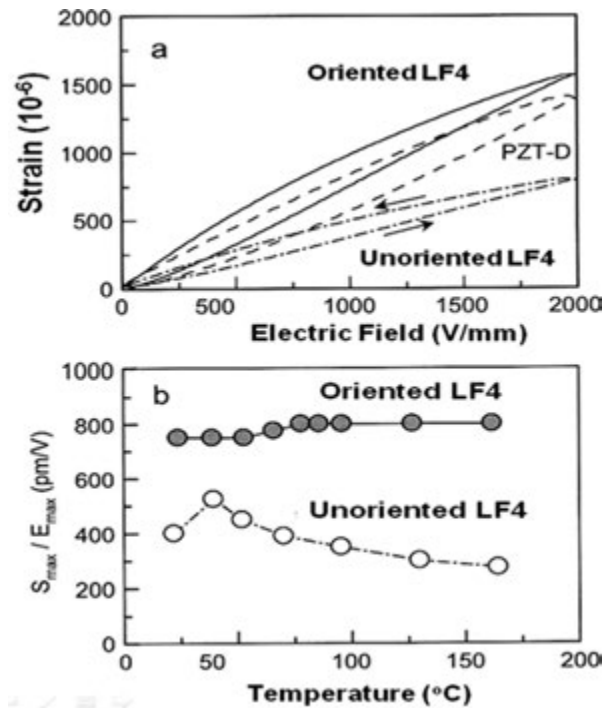


Fig. A1 Strain curves for oriented and unoriented (K,Na,Li)(Nb,Ta,Sb)O₃ ceramics.

sophisticated preparation technique (topochemical method for preparing flaky raw powder). Since the crystallographically-oriented films are obtained via the tape cast technology of flaky powders, this NKN preparation is very suitable to the ML devices. Tungsten-bronze (TB) types are another alternative choice for resonance applications, because of high Curie temperature and low loss. Refer to a review paper on Pb-free piezoelectrics by T. Takenaka (Takanaka, 2005).

Taiyo Yuden, Japan developed micro ultrasonic motors using non-Pb ML piezo-actuators (Doshida, 2009). Their composition is based on TB ((Sr,Ca)₂NaNb₅O₁₅) without heavy metal or even K (potassium seems to be a little toxic in comparison with Na). The basic piezoelectric parameters in TB ($d_{33}=55\sim80\text{ pC N}^{-1}$, $TC=300\text{ }^{\circ}\text{C}$) are not very attractive. However, once the c-axis oriented ceramics are prepared, the d_{33} is dramatically enhanced up to 240 pC N^{-1} . Further since the Young's modulus $Y_{33}^E=140\text{ GPa}$ is more than twice of that of PZT, the higher generative stress is expected, which is suitable to ultrasonic motor applications.

Taiyo Yuden developed a sophisticated preparation technology for fabricating oriented ceramics with a ML configuration: that is, preparation under strong magnetic field, much simpler than the Toyota's flaky powder preparation. Since most of piezo-ceramics are diamagnetic, the ceramic powder suspended in slurry will be aligned along its magnetically-stable axis under a strong magnetic field (such as 10 T). Because the polarization axis in their particular TB composition corresponds to the magnetically-unstable axis, they used the magnetic field parallel to the green sheet. A cut-green-sheet was rotated practically under steady magnetic field during drying period. These oriented green sheets were electroded, laminated, and sintered. They reported beautiful crystal orientation degree of the sintered product with Lotgering factor 0.9 (Doshida, 2009).

Fig. A2(a) shows their compact rotary ultrasonic motor with a piezoelectric MLA. A canti-lever rod is wobbled by a 2×2 arrayed MLA element, driven by a four-phase voltage (sine, cosine, -sine, and -cosine). They fabricated monolithic 2×2 arrayed elements with the size $2.6\times2.6\times1.1\text{ mm}^3$ including buffers with layer thickness as thin as $18\text{ }\mu\text{m}$ [Refer to Fig. A2(b) and (c)]. Because of this layer thinness and dramatic enhancement in the piezoelectric performance owing to the magnetic field alignment, the ultrasonic motor was successfully driven under only $3\text{ V}_{\text{p-p}}$ which is low enough to be adopted in mobile phones without coupling a step-up drive circuit.

A2 Cu Electrodes for ML Actuators

The internal electrode material of choice of the conventional ceramic ML devices were Ag/Pd, as it was in capacitors. However, owing to the Russian economy crisis in the late 1990s, palladium price increased dramatically with a peak in 2000, 10 times higher than 1990. Because of this raw material cost change, capacitor industries started to use Ni (Base metal) internal electrode. Though the price of Pd is stabilized now, the effort on the cheaper material usage is continuing. The piezo-actuator industry was a little behind to shift to use widely the Cu internal electrode. The piezo-industries are still using Ag/Pd or Pt for the internal electrodes. TDK-EPCOS started to commercialize the Cu embedded ML actuators for the diesel injection valve application, in which the

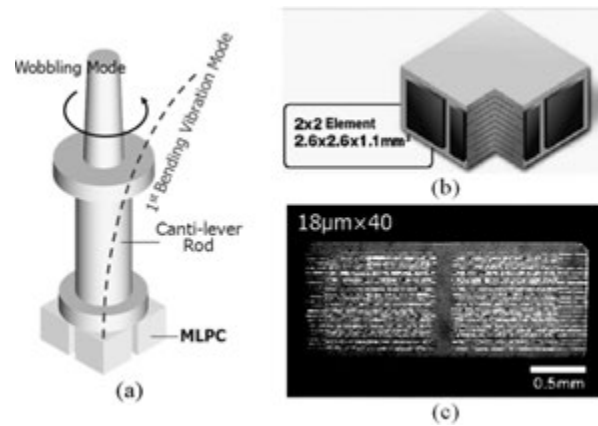


Fig. A2 (a) Compact rotary ultrasonic motor with a piezoelectric multilayer actuator, (b) 2×2 arrayed element, and (c) cross-section view of the $18 \mu\text{m}$ -layer ML element.

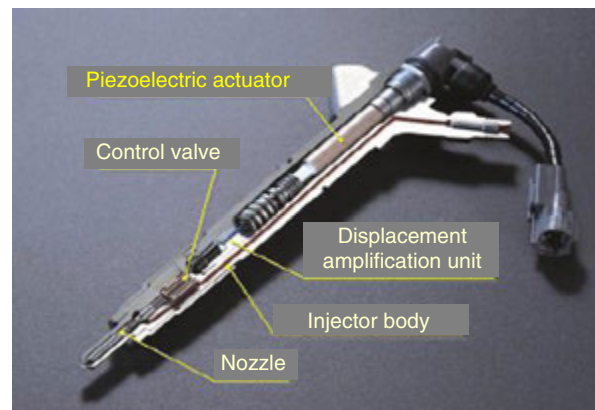


Fig. A3 Common rail type diesel injection valve with a piezoelectric multilayer actuator. [Courtesy by Denso Corporation.]

actuator cost is the major bottleneck at present (Boecking and Sugg, 2006). Another merit of the Cu electrode over Ag/Pd is the depression of the electrode metal diffusion into PZT ceramic layers.

A3 Diesel Injection Valve

Diesel engines are recommended rather than regular gasoline cars from the energy conservation and global warming viewpoint. Why? We need to consider the total energy of gasoline production; well-to-tank and tank-to-wheel. The energy efficiency, measured by the total energy required to realize unit drive distance for a vehicle (MJ km^{-1}), is of course better for high octane gasoline than diesel oil. However, since the electric energy required for purification is significant, the gasoline is inferior to diesel. As well known, the conventional diesel engine, however, generates toxic exhaust gases such as SO_x and NO_x . In order to solve this problem, new diesel injection valves were developed by Siemens, Bosch and Toyota with piezoelectric ML actuators. Fig. A3 shows a common rail type diesel injection valve (Fujii, 2005).

In order to eliminate toxic SO_x and NO_x and increase the diesel engine efficiency, high pressure fuel and quick injection control are required. In the engine one cycle (typically 60 Hz), the multiple injections should be realized in a very sharp shape (typically seven injections). For this purpose, piezoelectric actuators, specifically ML types, were adopted. The highest reliability of these devices at an elevated temperature (150°C) for a long period (10 years) has been achieved (Fujii, 2005). Note that the piezoelectric actuator is a key component to increase the burning efficiency and minimize the toxic exhaust gas elements.

References

- Abe, K., Uchino, K., Nomura, S., 1986. Barium titanate-based actuator with ceramic internal electrodes. *Ferroelectrics* 68, 215–223.
- Abe, S., Igashira, T., Sakakibara, Y., Kobayashi, F., 1994. Development of pilot injection system equipped with piezoelectric actuator for diesel engine. *J. Soc. Automot. Eng. Jpn. Rev.* 15, 201–208.

- Aburatani, H., Harada, S., Uchino, K., Furuta, A., Fuda, Y., 1994. Destruction mechanisms in ceramic multilayer actuators. *Jpn. J. Appl. Phys.* 33, 3091–3094.
- Aburatani, H., Uchino, K., 1996. Stress and fatigue estimation in multilayer ceramic actuators using an internal strain gauge. *Int. Symp. Solid-State Sensors and Actuators, SXIX-37–96. American Ceramic Society*, p. 191.
- Aburatani, H., Uchino, K., Furuta, A., Fuda, Y., 1995. Destruction mechanism and destruction detection technique for multilayer ceramic actuators. *Proc. 9th Int. Symp. Applied Ferroelectrics*, pp. 750–752.
- Agrawal, B.N., Bang, H., 1993. Active vibration control of flexible space structures by using piezoelectric sensors and actuators. *Am. Soc. Mech. Eng. Des. Eng. Div.* 61, 169–179.
- Bauer, A., Moller F., 1995. Piezo actuator special design. *Proc. 4th Int. Conf. New Actuators (Actuator '94)*. Germany, pp. 128–32.
- Boecking, F., Sugg B., 2006. Piezo Actuators: a Technology prevails with injection valves for Combustion Engines. *Proc. New Actuator 2006 (Bremen, June 14–16)*, A5.0, p. 171.
- Cao, H.C., Evans, A.G., 1994. Electric-field-induced fatigue crack growth in piezoelectrics. *J. Am. Ceram. Soc.* 77, 1783–1786.
- von Cierninski, J., Beige, H., 1991. High-signal electrostriction in ferroelectric materials. *J. Phys. D* 24, 1182–1186.
- Cross, L.E., Jang, S.J., Newnham, R.E., Nomura, S., Uchino, K., 1980. Large electrostrictive effects in relaxor ferroelectrics. *Ferroelectrics* 23 (3), 187.
- Dibbern, U., 1995. Piezoelectric actuators in multilayer technique. *Proc. 4th Int. Conf. New Actuators (Actuator '94)*. Germany, pp. 114–18.
- Dogan, A., Fernandez, J.F., Uchino, K., Newnham, R.E., 1994. New piezoelectric composite actuator designs for displacement amplification. *Proc. 4th Euro Ceramics 5*, 127–32.
- Doshida, Y., 2009. Lead-free multilayer piezo-actuators for USM. *Proc. 81st Smart Actuators/Sensors Study Committee, JTTAS*, Dec. 11, Tokyo.
- Flynn, A.M., Tavrow, L.S., Bart, S.F., *et al.*, 1992. Piezoelectric micromotors for microrobots. *IEEE J. Microelectromech. Syst.* 1, 44–51.
- Fujii, A., 2005. Multilayer piezo-actuators for diesel injection valve applications. *Proc. Smart Actuators/Sensors Study Committee, JTTAS*, Dec. 2, Tokyo.
- Fujita, T., 1994. Can piezoelectric actuators control vibrations of buildings? *New Ceram.* 7 (12), 52–55.
- Fukami, A., Yano, M., Tokuda, H., Ohki, M., Kizu, R., 1994. Development of piezo-electric actuators and sensors for electronically controlled suspension. *Int. J. Veh. Des.* 15, 348–357.
- Funakubo, T., Tsubata, T., Taniguchi, Y., *et al.*, 1995. Ultrasonic linear motor using multilayer piezo-electric actuators. *Jpn. J. Appl. Phys.* 34, 2756–2759.
- Furuta, A., Oh, K.Y., Uchino, K., 1992. Shape memory ceramics and their application to latching relays. *Sensors Mater.* 3 (4), 205–215.
- Furuta, A., Uchino, K., 1993. Dynamic observation of crack propagation in piezoelectric multilayer actuators. *J. Am. Ceram. Soc.* 76, 1615–1617.
- Furuta, A., Uchino, K., 1994. Destruction mechanism of multilayer ceramic actuators: Case of antiferroelectrics. *Ferroelectrics* 160, 277–285.
- Furuta, K., Uchino, K., 1986. Electric-field-induced strain in (Pb,Lu)(Zr,Ti)O₃ ceramics. *Adv. Ceram. Mater.* 1, 61–63.
- Goto, H., 1994. Miniature 2D optical scanner and its application to an optical sensor. *J. Opt. Technol. Contact* 32, 322–330.
- Goto, H., Imanaka, K., Uchino, K., 1992. Piezoelectric actuators for light beam scanners. *Ultrasonic Technol.* 5, 48–51.
- Gross, R., 1994. A high resolution piezo walk drive. *Proc. 4th Int. Conf. New Actuators*. Germany, pp. 190–2.
- Hao, T.H., Gong, X., Suo, Z., 1996. Fracture mechanics for the design of ceramic multilayer actuators. *J. Mech. Phys. Solids* 44, 23–48.
- Heeg, J., 1993. Analytical and experimental investigation of flutter suppression by piezoelectric actuation. *NASA Technical Paper, NASA-TP-3241*, p. 47.
- Hirose, S., Aoyagi, M., Tomikawa, Y., Takahashi, S., Uchino, K., 1995a. High-power characteristics at antiresonance frequency of piezoelectric transducers. *Proc. Ultrasonic Int.* 1–4.
- Hirose, S., Takahashi, S., Uchino, K., Aoyagi, M., Tomikawa, Y., 1995b. Measuring methods for high-power characteristics of piezoelectric materials. *Proc. Mater. Res. Soc.* 360, 15–20.
- Kim, H.S., Choi, S.C., Lee, J.K., Jung, H.J., 1992. Fabrication and piezoelectric strain characteristics of PLZT functionally gradient piezoelectric actuator by doctor blade process. *J. Korean Ceram. Soc.* 29, 695–704.
- Koster, M.P., 1994. A walking piezo motor. *Proc. 4th Int. Conf. New Actuators*. Germany, pp. 144–8.
- Mather, G.P., Tran B.N., 1993. Aircraft cabin noise reduction tests using active structural acoustic control. *American Institute of Aeronautics and Astronautics paper AIAA-93-4437*, p. 7.
- Nagata, K., Kinoshita, S., 1994. Life time of multilayer ceramic actuator at high temperature. *J. Powder Metall.* 41, 975–979.
- Nagata, K., Kinoshita, S., 1995a. Effect of humidity on life time of multilayer ceramic actuator. *J. Powder Metall.* 42, 623–627.
- Nagata, K., Kinoshita, S., 1995b. Relationship between lifetime of multilayer ceramic actuator and temperature. *Jpn. J. Appl. Phys.* 34, 5266–5269.
- Ohashi, J., Fuda, Y., Ohno, T., 1993a. Multilayer piezoelectric ceramic actuator with interdigital internal electrodes. *Jpn. J. Appl. Phys.* 32, 2412–2414.
- Ohashi, J., Fuda, Y., Ohno, T., 1993b. Multilayer piezoelectric ceramic actuator with interdigital internal electrodes. *Tokyo Tech. Rev.* 19, 55–60.
- Okada, N., Ishikawa, K., Murakami, K., Nomura, T., Ogino, M., 1993. Improving hysteresis of piezoelectric PZT actuator. *Bull. Shizuoka Univ. Electron. Sci. Grad. School* 14, 7–13.
- Onitsuka, K., Dogan, A., Tressler, J.F., *et al.*, 1995. Metal-ceramic composite transducer, the moonie. *J. Intelligent Mater. Syst. Struct.* 6, 447–455.
- Ono, Y., Fuda Y., 1994. Multilayer piezoelectric ceramic actuator with interdigital internal electrodes for impact dot-matrix printers. *Proc. 6th Symp. Electro-Magnetic Related Dynamics*, pp. 135–138.
- Saigoh, H., Kawasaki, M., Maruko, N., Kanayama, K., 1995. Multilayer piezoelectric motor using the first longitudinal and the second bending vibrations. *Jpn. J. Appl. Phys.* 34, 2760–2764.
- Saito, Y., Takao, H., Tani, T., *et al.*, 2004. Lead-free piezoceramics. *Nature* 432, 84.
- Sakai, T., Ishikiriya, M., Terai, Y., Shimazaki, R., 1992. Improvement in the durability of PZT ceramics for an actuator. *Toyota Tech. Res.* 42, 52–59.
- Sano, M., Ohya, K., Hamada, K., Inoue, Y., Kajino, Y., 1993. Multilayer piezoelectric actuator with strain gauge. *NEC Giho* 46 (10), 100–103.
- Schneider, G.A., Rostek, A., Zickgraf, B., Aldinger, F., 1994. Crack growth in ferroelectric ceramics under mechanical and electrical loading. *Proc. 4th Int. Conf. Electronic Ceramics and Applications*. Germany, pp. 1211–16.
- Shimoda, H., Ohmata, J., Okamoto, F., 1992. Seismic response control of a piping system by a semiactive damper with piezoelectric actuators. *J. Precision Eng.* Jpn. 58, 2111–2117.
- Sugawara, Y., Onitsuka, K., Yoshikawa, S., *et al.*, 1992. Metal-ceramic composite actuators. *J. Am. Ceram. Soc.* 75, 996–998.
- Suo, Z., 1993. Models for breakdown resistant dielectric and ferroelectric ceramics. *J. Mech. Phys. Solids* 41, 1155–1176.
- Takada, S., 1992. Quality improvement of multilayer piezoelectric actuator. *NEC Giho* 45, 109–113.
- Takada, S., Inoue, Y., Oya, K., Inagawa, M., 1994. 100 V DC driving type multilayer piezoelectric actuator. *NEC Giho* 47, 98–102.
- Takahashi, S., Sakaki, Y., Hirose, S., Uchino, K., 1995. Stability of PbZrO₃-PbTiO₃-Pb(Mn_{1/3}Sb_{2/3})O₃ piezoelectric ceramics under vibration-level change. *Jpn. J. Appl. Phys.* 34, 5328–5331.
- Takanaka, T., 2005. Developments and current status of lead-free piezoelectric materials. *Bull. Japan. Ceramic Soc.* 40, 586.
- Tohda, M., Ichikawa, S., Uchino, K., Kato, K., 1989. Ultrasonic linear motor using a multilayered piezoelectric actuator. *Ferroelectrics* 93, 287–294.
- Tressler, J.F., Xu, Q.C., Yoshikawa, S., Uchino, K., Newnham, R.E., 1994. Composite flextensional transducers for sensing and actuating. *Ferroelectrics* 156, 67–72.
- Uchino, K., 1988. *Ceramic Data Book '88*. Tokyo: Institute of Industrial Manufacturing Technology.
- Uchino, K., 1993. Ceramic actuators: Principles and applications. *MRS Bull.* 18, 42–48.
- Uchino, K., 1994. New piezoelectric devices for smart actuator/ sensor systems. *Proc. 4th Int. Conf. Electronic Ceramics and Applications*, pp. 179–91.
- Uchino, K., 1995a. Manufacturing technology of multilayered transducers. *Proc. Am. Ceram. Soc.* 81–93.
- Uchino, K., 1995b. Materials update: advances in ceramic actuator materials. *Mater. Lett.* 22, 1–4.

- Uchino, K., 1995c. Piezoelectric actuators/ultrasonic motors – their developments and markets. Proc. 9th Int. Symp. Applied Ferroelectrics, pp. 319–24.
- Uchino, K., 1996. Piezoelectric Actuators/Ultrasonic Motors. MA: Kluwer.
- Uchino, K., Aburatani, H., 1994. Destruction detection techniques for safety piezoelectric actuator systems. Proc. 2nd Int. Conf. Intelligent Materials, pp. 1248–56.
- Uchino, K., Ishii, T., and Ishii, 1988. Mechanical damper using piezoelectric ceramics. J. Jpn. Ceram. Soc. 96, 863–867.
- Uchino, K., Nomura, S., 1983. Electrostriction in PZT-family antiferroelectrics. Ferroelectrics 50 (1), 191–196.
- Wada, B., 1993. Summary of precision actuators for space application. JPL Document D-10659.
- Wang, H., Singh, R.N., 1995. Electric field effects on the crack propagation in a electro-strictive PMN-PT ceramic. Ferro-electrics 168, 281–291.
- Watanabe, J., Sometsugu, T., Watanabe, Y., *et al.*, 1993. Multilayer piezoelectric ceramic actuator for high temperature use. Hitachi Metal Giho 9, 59–64.
- Yano, T., Fukui, I., Sato, E., Inui, O., Miyazaki Y., 1984. Impact dot-matrix printer head using multilayer piezoelectric actuators. Proc. Electron. Commun. Soc. 1, 156.
- Yonekubo, S., 1995. Color inkjet printer by multi-layer piezo-electric actuator. J. Electron. Photo. Soc. 34, 226–228.
- Yoshikawa, S., Shrout, T., 1993. Multilayer piezoelectric actuators-structures and reliability. AIAA/ASME/ASCE/AHS/ASC Struct. Struct. Dyn. Mater. Conf. 34, 3581–6.
- Zhang, Q.M., Zhao, J.Z., Uchino, K., Zheng, J.H., 1996. Change of the weak field properties of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ piezoceramics with compressive uniaxial stresses and its links to the effect of dopants on the stability of the polarizations in the materials. J. Mater. Res. 12, 226–234.
- Zheng, J.H., Takahashi, S., Yoshikawa, S., Uchino, K., 1996. Heat generation in multilayer piezoelectric actuators. J. Am. Ceram. Soc. 79, 3193–3198.

Multilayer Glass–Ceramic/Ceramic Composite Substrates

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Historical Development

In 1943–45, Fort Monmouth Signal Laboratory developed the very first tape-casting machine and tape casting compositions (Crowley *et al.*, 1945). Later, Massachusetts Institute of Technology utilized tape casting in 1947 and reported a thin sheet of a ceramic capacitor (Howatt *et al.*, 1947). After that, the Al_2O_3 substrate was reported by Howatt in 1952 (Howatt and Metuchen, 1948). The ultimate development of multilayer glass–ceramic substrates started in the early 1970s when IBM Corporation reported Al_2O_3 , ZnZrSiO_5 and CaSiO_3 with a low melting disilicate vitreous glass phase as the first example of LTCC (Charles and Fishkill, 1967). Thereafter, the substrate technology grew with the labels of high temperature co-fired ceramics (HTCC), low-temperature co-fired ceramics (LTCC), and recently ultra-low temperature co-fired ceramics (ULTCC) technology with promising applications in most of the thrust areas of the everyday needs of society as well as in high-performance futuristic concepts.

The firing temperature and co-firing electrode usage classify multilayer glass–ceramic/ceramic composite substrates into three technologies: HTCC (1000–1600°C), LTCC (700–960°C) and ULTCC (<700°C). HTCC enables non-replaceable applications in hermetically sealed ceramic packages. LTCC/ULTCC technologies are inexpensive in terms of fabrication costs and offer a simple process that enables progress in miniaturization and the integration of advances in substrates and packages by combining functional layers and passive electronic components in one multilayer co-sinterable module. Udovic *et al.* (2001) reported the very first materials composition (tellurates) sinterable at below 700°C and later on in 2010 materials compositions were reported under the ULTCC label (Valant and Suvorov, 2001; Udovic *et al.*, 2001; Sebastian *et al.*, 2016; Yu *et al.*, 2015). Since then around 230 material compositions have been reported in this category. In 2017, Chen *et al.* (2017) developed a new tape casting slurry system with co-firability at 450°C feasible for ULTCC multilayer packaging applications. Thereafter, in subsequent years in 2017–2019, two research results were reported by Varghese *et al.* (2018, 2019) on ULTCC microwave and functional substrates co-firable at 400°C and 450°C, respectively, and by Joseph *et al.* (2019) on binder burnout and carbon emission in ULTCC tape casting compositions. In parallel with the ULTCC research, hydrothermal assisted cold sintering/upside down/room temperature ceramics/composites were opening up more and more research in substrate technology. Kähäri *et al.* (2014) reported the very first room temperature sintering process by moistening water-soluble Li_2MoO_4 with deionized water together with a uniaxial compaction pressure of 130 MPa and post-processing sintering at 120°C. Later on in 2016, Guo *et al.*, reported research on a cold sintering process with systematic studies such as the integration of nanotechnology and cold sintering processes (CSP) (Guo *et al.*, 2016a,b,c,d,e,f). They used water as a transient solvent for many of the compositions reported. Currently, many kinds of research are growing in this area for further development in device-level integration and performance studies. CSP may be applied to a very diverse range of materials such as oxides, carbonates, bromides, fluorides, chlorides and phosphates.

Tape Casting and Post-Processing

Tape casting is a casting process utilized for the manufacture of thin ceramic tapes in the thickness range of 5–500 µm from a ceramic slurry. The ceramic slurry processing consists of a series of steps such as distribution of the casting slurry on a flat carrier film and drying it using doctor blade casting technology. Fig. 1 depicts the casting flow and schematic representation of the doctor blade tape casting process. The ingredients included in the tape casting slurries are ceramics/glass–ceramic/ceramic composite powders, solvents, dispersants, plasticizers, homogenizers and binders. The tape casting schematic depicts various components such as a slurry reservoir, doctor blade and carrier film, casting direction and base substrate, followed by processes such as tape drying, peeling, lamination, etc. (Mistler and Twiname, 2000).

The laboratory tape casting process in which slurry is continuously cast on a carrier film, is represented in the schematic in Fig. 1. A mechanically and structurally stable flexible tape is produced based on the careful optimization of the slurry during different stages of the casting process. The casting stages include filler, dispersant and solvent to start with as the first step. Then, after 30 min of mixing, the plasticizers are added followed by the homogenizer and continuous milling for 12 h. The second stage is the addition of the binder to the resultant slurry together with excess solvent and continuous mixing for the next 12 h. The poured final slurry is de-aired under vacuum of 10,000 Pa for 5 min; although the duration mostly depends on the batch size of slurry for casting. Tape casting batching may differ based on surface area and particle size of the initial filler and the selection of solvents, binders, plasticizers, etc. It is better to check the viscosity of the slurry by using the spindle and cup method at 20 rpm to ensure quality control. There is a standard process in tape casting for quality control of the tape casting slurry which includes viscosity and solid loading of the final slurry, particle size distribution and sedimentation analysis. The viscosity and solid loading of the slurry checks are needed for every batch of casting slurry while the particle size and sedimentation analysis are done for the

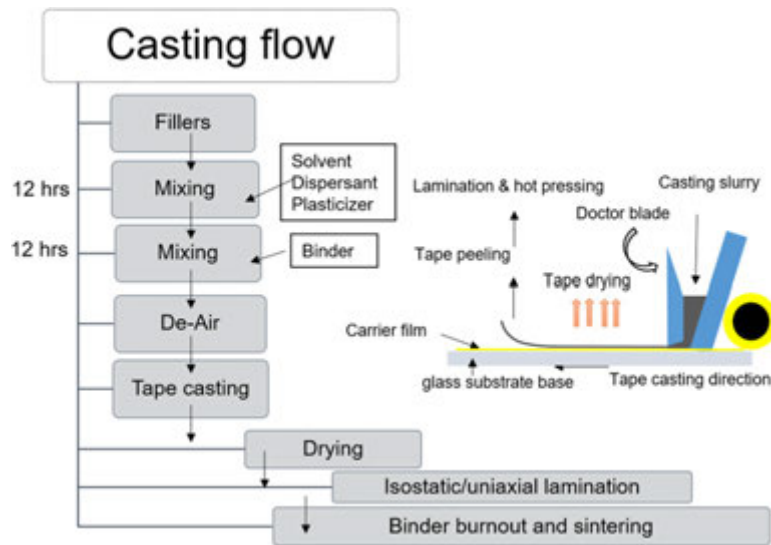


Fig. 1 The casting flow and schematic representation of the doctor blade tape casting process. Drawn by Jobin Varghese.

initial inorganic fillers and organic composition selection process. Most of the tape casting slurries show a pseudoplastic nature in viscosity measurements; that is the viscosity decreases with increase in shear rate (Mistler and Twinaime, 2000). Wonisch *et al.* (2011) reported theoretical studies on the tape casting slurry as a non-Newtonian fluid which are in the form of a continuity equation and momentum conservation equations, as shown in Eqs. (1) and (2).

$$\rho \left(\frac{\partial u}{\partial t} + u \cdot \nabla u \right) = -\nabla p + \nabla \cdot T + F \quad (1)$$

$$\frac{\partial \rho}{\partial t} = \nabla \cdot (\rho u) = 0 \quad (2)$$

where ρ is the density of slurry, u is the velocity of fluid flow, p is a stress tensor and F represents the external force. There are also several modeling approaches based on analytical and numerical approaches and these are also reported to explain the fluid flow in the tape casting process.

Finally, the resultant slurry is ready to cast. Casting is done on a silicone-coated Mylar film in a continuous tape casting setup as shown in the schematics (Fig. 1). The doctor blade gap setting and casting speed are determined based on the tape thickness required in the product. The most commonly used tape-casting solvents, binder, dispersant and plasticizers are listed in Table 1 (Mistler and Twinaime, 2000).

The selection of the inorganic powder is the first step in the preparation of the tape casting slurry. This is followed by binder and solvent selection. The binder must be dissolved in the selected solvent and the plasticizer is selected based on the choice of binder and solvent. Multiple solvent systems can also be used for the casting slurry preparation, which have the added benefit of dissolving various organics and polymers simultaneously. This provides a wider choice of different varieties of plasticizers, binder and dispersant combinations for slurry preparation. Most manufacturers prefer organic solvent-based tape casting which has a faster drying rate in comparison with aqueous casting. However, aqueous-based casting is a more environmentally friendly casting method compared to organic casting (Hotza and Greil, 1995). The drying of the cast tape is an essential stage in tape casting. Usually, an airflow of $>3.1 \text{ m}^3/\text{h}$ leads to extreme skinning on the tape (Mistler and Twinaime, 2000). Other factors such as solvent concentration, solid loading, type and concentration of binder, temperature of the drying air and thickness of the cast layer are also of concern in the drying stages (Mistler and Twinaime, 2000).

Shrinkage in drying, binder burnout and co-firing/sintering are also crucial for multilayer glass–ceramic/composite substrates. Yu *et al.* (1993) report an exciting study on the evolution of residual carbon in polyvinyl butyral (PVB) and polypropylene carbonates (PPC) on aluminum nitride (Y_2O_3 as sintering aid) tape in air and in a nitrogen atmosphere (Ym *et al.*, 1993). In these studies, the sintering temperature was $1800^\circ\text{C}/1 \text{ h}$ with binder burnout carried out at 550 and 500°C in nitrogen and air atmosphere respectively. The chapter reported on the ALN substrate fabrication in the HTCC range together with the effect of sintering on binder burnout, microstructure and thermal conductivity of the product. The typical post-processing stages after tape casting and drying are punching, via filling, conductor printing, stacking/lamination, pressing and co-firing. Punching is the process of making vias; each layer has a different via size and location based on the design. The via size depends on the thickness of the green tape: in general most manufacturers prefer a 1:1 ratio. Via filling is the process in which each layer of green tape is printed with the conductor pattern. Finally, the layers are stacked, pressed and co-fired to make electronic packages. Table 2 represents the commonly used electrode metals suitable for HTCC, LTCC and ULTCC technology with their conductivity and firing temperature.

Table 1 Commonly used tape casting slurry ingredients

<i>Solvents</i>	<i>Binder</i>	<i>Plasticizers</i>	<i>Dispersant</i>
Xylenes	Polyvinyl alcohol	(poly) Propylene glycols	Menhaden fish oil
Methyl ethyl ketone (MEK)	Polyvinyl butyral	(poly) Ethylene glycols	Polyvinyl butyral
Toluene	Cellulose acetate-Butyrate	Butyl benzyl phthalates	Phosphate ester
1,1,1 trichloroethane (TCE)	Polyacrylate esters	Dimethyl phthalates	Ethoxylate
Acetone	Polypropylene carbonates	Glycerin	Aliphatic hydrocarbons
Ethanol	Polytetrafluoroethylene	Butyl stearate	Lanolin fatty acids
Cyclohexanone	Polyurethane	Dioctyl phthalate	Linoleic acid
Butanol	Ethyl cellulose	Mixed esters phthalates	Polyisobutylene
Isopropanol	Methyl cellulose	Propylene carbonates	Polyethylene glycol
Nitropropane	Vinyl chloride acetate	Tricresyl phosphate	Sodium sulfosuccinates
Water	Polyvinyl chloride	Triethylene glycols	2-amino – 2-methyl – 1-propanol

Note: Mistler, R.E., Twinnage, E.R., 2000. Tape Casting: Theory and Practice. Ohio: The American Ceramic Society.

Table 2 Electrode metals with conductivity and firing temperature suitable for HTCC, LTCC and ULTCC applications

<i>Electrode materials</i>	<i>Applications</i>	<i>Conductivity (S/m)</i>	<i>Melting temperature (°C)</i>
Mo	HTCC	1.87×10^7	2623
W	HTCC	1.89×10^7	3422
Pt	HTCC	9.52×10^6	1768
Pd	HTCC	9.48×10^6	1554
Cu	HTCC	5.95×10^7	1083
Au	HTCC	4.51×10^7	1064
Ag	LTCC	6.30×10^7	961
Al	ULTCC	3.77×10^7	660

However, direct metal electrodes usage is limited by the application and by their co-firability with ceramics/glass–ceramics/composites. This has prompted the introduction of a better solution as composite for co-firing electrodes with better conductivity for the applications. In addition to conductivity, the adhesion between ceramic and metal electrodes, the coefficient of thermal expansion matching with that of the substrate materials or tapes and post processes such as binder burnout, shrinkage and soldering were also under consideration for a multilayer chip (MLC) electrode development process. Hence, additives such as metal alloys and low melting point conductive glasses, ceramics and metals were also considered in additive manufacturing for the preparation of conducting electrodes. As an example, some of the commercially available printable electrode pastes for multi-layer ceramic chip applications are listed in [Table 3](#). It represents some of the commercial electrode materials at various firing ranges with their usages based on ESL and Dupont products (See the web link). However, there are many companies manufacturing various electrode pastes for co-firing. The electrode pastes, which are listed below between the firing temperatures 850–980°C, are suitable for LTCC applications. The electrodes reported at less than 660°C are suitable for ULTCC applications. The electrodes with firing temperature above 1000°C are suitable for HTCC applications.

The electrode compactability also depended on many factors such as the CTE requirements, conductivity requirements, final fired thickness, surface finish of base ceramics or tapes, solderability and adhesion after firing. Typical usages of conductor electrodes in MLC (HTCC, LTCC and ULTCC) are as automotive sensors, oxygen sensors, fuel cells, SOFC (solid oxide fuel cells), solid oxide electrolyzer, SOEC (solid oxide electrolyzer cells), oxygen sensors, chemical sensors, temperature sensors, conical/planar oxygen sensors, chip resistors, SMD capacitor termination and resistance heating. Conventional tape casting and post-processing methods develop the HTCC, LTCC and ULTCC tapes but tape ingredients are varied based on processing temperatures, applications and electrode materials.

High Temperature Co-Fired Ceramic Substrates (HTCC)

HTCC is a well-known choice for hermetic packaging based on its electrical properties, high mechanical stability and good thermal conductivity. The HTCC temperature ranges from well above 1000°C to around 1600°C or more. HTCC utilizes both water-based and organic solvent systems for tape casting. The most common HTCC materials are oxides, nitrides, carbides and borides ([Sebastian and Jantunen, 2017](#)). Al_2O_3 is the most popular material for multilayer packages and substrates due to its performance consistency and continuous usage and production for years with an excellent record of success. However, other oxide materials have also been reported with claims of properties distinct from those of alumina. Most of the commercial production of HTCC tapes and materials meets the needs set by the environmental requirements such as freedom from lead, cadmium, mercury,

Table 3 Some examples of commercial electrode pastes in ESL and Dupont with materials, firing temperatures and purposes (See ESL and Dupont Webpage)

Suppliers	Codes	Materials	Firing temperature (°C) & purpose
ESL	8886-A	Alloyed gold paste (fritless)	850/1 h, ^a < 30 mΩ/sq, suitable for glazed substrates, 1–3 μm Au film
ESL	8884-G	Gold paste #	850–980/1 h, ^a 2–5 mΩ/sq with 12.5 μm fired thickness, Suitable for 96% alumina substrate
ESL	8835 (520C)	Fritted gold paste #	520/15 min, ^a 5 mΩ/sq with 10–15 μm fired thickness, suitable for LTCC, ULTCC, Al ₂ O ₃ , borosilicate, glass, soda-lime, PZT, piezo
ESL	5542	Fritless Pt conductor #	950–1300/15 min, ^a < 100 mΩ/sq with 3–7 μm fired thickness, Suitable for LTCC and HTCC
ESL	2170-A	Tungsten paste	1500–1650°C, 12.5–25 μm emulsion thickness, suitable of HTCC co-firing
ESL	9595-A	Ag/Pd	600–930/12 min, ^a 10 mΩ/sq with fired thickness of 10–15 μm, suitable for post fired ceramics
ESL	9562-G	Pt/Ag/Pd paste #	850–930/30 min, < 4 mΩ/sq with fired thickness of 12.5 μm, suitable for post fired ceramic such as Al ₂ O ₃ , AlN, etc.
ESL	599-E	Cermet Ag conductor	400–550/15 min, ^a 3–6 mΩ/sq with fired thickness of 12.5 μm, suitable for ULTCC and post fired applications
ESL	5051	Metallo-organic platinum paste #	850/12 min, ^a 3–4 mΩ/sq with fired thickness of 0.15–0.25 μm, suitable for post fired ceramics
Dupont	1187	Platable Ag paste #	800/10 min, suitable for multilayer ceramic chip applications
Dupont	4999	Solderable Ag/Pd paste #	710–750/10 min, suitable for multilayer capacitors
Dupont	5426	Ag/Pd paste	850/30 min, suitable for co-firable and chip resistors
Dupont	4899	Solderable Ag paste #	850/40 min, suitable for multilayer capacitors
Dupont	5402S	Platable Ag paste	600–620/30 min, suitable for platable C2 edge termination for chip resistors
Dupont	4933D	Ag/Pd/Pt paste #	710–780/40 min, suitable for ceramic capacitor bodies

^aElectrical resistivity # Cd/Pb/Ni/S-free.**Table 4** Alumina purity and its thermal, mechanical and dielectric properties

Properties	Al ₂ O ₃ Purity (> 99%)	Al ₂ O ₃ Purity (99%)	Al ₂ O ₃ Purity (96%–99%)	Al ₂ O ₃ Purity (94%–96%)	Al ₂ O ₃ Purity (86%–94%)	Al ₂ O ₃ Purity (80%–86%)
Density (g/cm ³)	3.75–3.95	3.76–3.94	3.71–3.92	3.60–3.90	3.40–3.90	3.30–3.60
Thermal expansion (ppm/°C)	5.4	5.4	5.1–5.4	5.1–5.4	4.9–5.5	4.5–5.5
Thermal conductivity (W/mK)	30–40	30–40	25–30	20–30	15–20	15–20
Relative permittivity (1 kHz – 100 GHz)	9–10	8.4–10.5	8.4–10.5	8.6–10.1	7.1–10	7.1–10
Dielectric loss (1 kHz – 10 GHz)	10 ^{−4} –10 ^{−3}	10 ^{−5} –10 ^{−3}	10 ^{−4} –10 ^{−3}	10 ^{−4} –10 ^{−2}	10 ^{−4} –10 ^{−2}	10 ^{−4} –10 ^{−2}
Flexural strength (MPa)	210–600	150–500	150–450	180–360	150–350	200–300
Young's modulus (GPa)	410–380	380–340	375–340	370–300	330–260	330–260
Shear modulus (GPa)	164–158	145–130	140–120	140–110	130–100	130–100
Poisson's ratio	0.27–0.24	0.26–0.24	0.25–24	0.25–0.23	0.25–0.22	0.25–22

Note: Auerkari, P., 1996. Mechanical and physical properties of engineering alumina ceramics. Tirronen, K. (Ed.), Technical Research Centre of Finland, VTT Tiedotteita-Meddelanden-Research Notes, vol. 1792, pp. 1–26. Espoo: Julkaisija-Utgivare-Publisher.

hexavalent chromium, nickel, polybrominated biphenyls, polybrominated diphenyl ether, etc. Those materials/substrates comply with controlled RoHS (Restriction of Hazardous Substances) production.

Oxide HTCCs

Alumina is available in the market in different grades for specific applications based on purity (90%–99%). It offers high strength, good thermal conductivity, hermetic, excellent electrical properties and the lowest cost of production. In some of the commercial HTCC Al₂O₃ green tapes are used with a sintering aid of 4%–8% in order to benefit from the advantages of corrosion resistance, high-temperature resistance, long life, good thermal conductivity and faster thermal compensation. The majority of HTCC production is with either black or white alumina. The material properties of the different grades of Al₂O₃ available are listed in [Table 4](#) based on Auerkari's review report in 1996 (Auerkari, 1996). Their manufacturing temperature varies between 1500–1900°C. The difference in the purity grades are due to some alloying agents or sintering aids based on applications.

In addition to alumina, BeO may be considered for multilayer packaging applications, initially because of its excellent thermal conductivity (250–330 W/mK). However, due to its disadvantages in processing and co-firing other alternative materials are also under consideration for multilayer structures. [Fig. 2](#) presents pictures of some examples of HTCC products as an aid to understanding, as presented in the Adtech Ceramics Company webpages. The customary HTCC products are amplifier housings, ceramic/metal packages, crystal packages, oscillator/SAW packages, high-frequency feedthroughs, hybrid packages, multi-chip modules, optical packages and sensor



Fig. 2 HTCC products presented in the Adtech Ceramics Company webpages. Adapted from the website <http://www.adtechceramics.com/products/htcc>.

packages. ZrSiO_4 is another important HTCC microwave substrate sinterable at 1600°C , which is reported to have a low permittivity ($\epsilon_r = 8\text{--}9.5$ at 5 GHz), low dielectric loss ($\tan \delta = 0.0003\text{--}0.0005$ at 5 GHz), moderate thermal conductivity ($\text{TC} = 14\text{--}15 \text{ W/mK}$) and an ultra-low thermal expansion coefficient ($\text{CTE} = \pm 2 \text{ ppm}/^\circ\text{C}$) (Sebastian and Jantunen, 2017). Similarly, a $0.83\text{ZnAl}_2\text{O}_4\text{--}0.17\text{TiO}_2$ based HTCC substrate is sinterable at 1500°C with a relative permittivity of 9.6 at 5 GHz, dielectric loss of 0.00084 at 5 GHz, thermal conductivity of 31.3 W/mK and CTE of $6.59 \text{ ppm}/^\circ\text{C}$ (Roshni et al., 2017). These microwave HTCC substrates are feasible for high-frequency applications. An attempt to produce a HTCC cordierite-glass substrate (at $1150^\circ\text{C}/2 \text{ h}$) is also in the literature with a low permittivity of 5 and a dielectric loss of 0.002 at 1 MHz (Mei et al., 2006).

Zirconia is another well-known material used for HTCC applications such as oxygen sensors for the automotive industry, fuel cell membranes and structural and biomedical applications. It has a high O_2 diffusivity and high toughness and strength. ZrO_2 has better optical properties than alumina, which makes it feasible for optical device applications. The high temperature stable cubic phase is satisfies for many applications due to its very high melting point of about 2370°C and crystallographic transformation from monoclinic to tetragonal at about 1170°C and from tetragonal to cubic at about 2370°C . (Prakasam et al., 2018). Yttria stabilized cubic zirconia is well known for many applications such as HTCC pressure sensors, solid oxide fuel cells and gas pumps for removing trace oxygen from gases, and its usage is more environmentally friendly due to its oxygen ion conductivity and stability in both oxidizing and reducing atmospheres. Specifically, Zr_2O with 8 mol% of Y_2O_3 has a conductivity of 0.10 S/cm at 1000°C and $3 \times 10^{-5} \text{ S/cm}$ at 400°C with an activation energy of 96 kJ/mol . Moreover, Piticescu et al. (2005) reported a zirconia pressure sensor from hydrothermally synthesized nanoscale 3.5 mol% Y_2O_3 doped ZrO_2 ceramic for use as a HTCC pressure sensor with superior mechanical stability together with high-pressure sensitivity and thermal stability. Schafbauer et al., reported testing another material starting from tape casting for the SOFCs anode support followed by a fuel cell prepared by screen printing and sintering of functional layers such as electrolyte, cathode and current collector layers. The detailed SOFCs workflow is presented in Fig. 3 based on SOFC's reported (Schafbauer et al., 2014; Snijkers et al., 2004).

For further explanation, we will briefly describe the SOFC manufacturing process from tape to device (Schafbauer et al., 2014). The SOFC's manufacturing steps include the mixing of NiO ceramic powder with fully stabilized Zr_2O with 8 mol% of Y_2O_3 (8YSZ) in the weight ratio of 60:40 as the tape casting filler with organic slurry components for the initial green tape preparation. The anode and electrolyte layer are screen-printed on the top of the green tape. The anode layer used for the present SOFC's composition is a more elegant NiO and 8YSZ screen printable paste in the same weight ratio of 60:40. Likewise, the electrolyte layer paste consists of only fine 8YSZ. Both layers have a green thickness of about $10 \mu\text{m}$. After drying the screen-printed layers, tape and screen-printed laminate are co-fired at 1400°C under air atmosphere. The sintered partial cell undergoes various reliability tests such as sintering shrinkages, curvature, electrolyte layer gas tightness and so on. Screen-printing of the cathode layer and current collector layer and its post-firing comprise the next step in the cell manufacture. The cathode paste consists of $\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_{3-\delta}$ (LSM) and 8YSZ in the weight ratio of 50:50. On the top of the double-layer cathode. LSM paste with same stoichiometry is screen-printed as the current collector layer. Finally post-firing is performed at 1100°C for

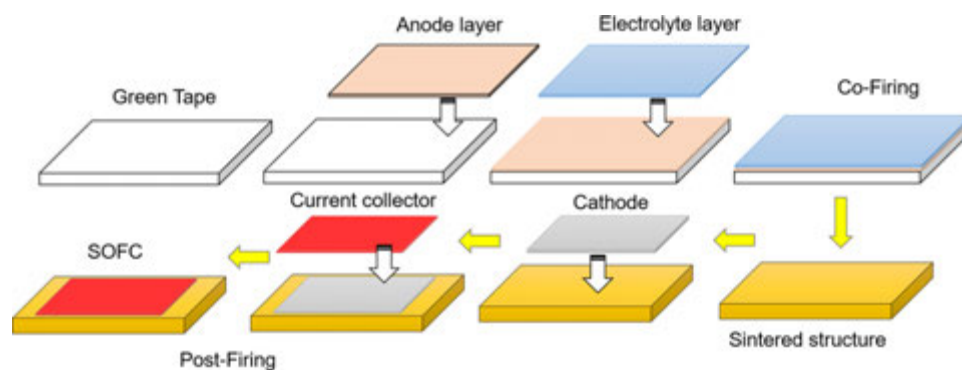


Fig. 3 Schematic representation of the detailed workflow of the SOFCs by Schafbauer *et al.* Redraw by Jobin Varghese based on Schafbauer, W., Menzler, H., Buchkremer, H.P., 2014. Tape casting of anode supports for solid oxide fuel cells at Forschungszentrum Jülich. *International Journal of Applied Ceramic Technology* 11, 125–135.

3 h. The post fired thickness of the cathode is about 15 μm and the current collector layer is about 50 μm for the manufactured SOFCs. Another intermediate temperature solid oxide fuel cell (IT-SOFCs) electrolyte material is lanthanum apatite. Santacruz *et al.* (2011) reported $\text{La}_{10}\text{AlSi}_5\text{O}_{26.5}$ ceramic tape casting sintered at 1650°C/10 h to have feasibility in future IT-SOFCs. However, research in this area is progressing for a cost-effective method of fabrication such as electrolyte plate, 3D printed electrolytes, alternate electrolyte or thin-film electrolyte with better performance for future energy needs (Wang *et al.*, 2019a,b; Feng *et al.*, 2019; Zhou *et al.*, 2019; Liu and Liu, 2019).

Sahner *et al.*, reported in 2005 an SrAl_2O_3 based HTCC gas sensor. In this study, they used SrAl_2O_3 as the HTCC substrate instead of the more commonly used alumina or zirconia. The advantages of SrAl_2O_3 over conventional alumina-based sensors is that it prevents the interaction between the gas-sensitive thick film and the substrate. Additionally, a hydrocarbon-sensing layer of strontium titanate ferrite ($\text{SrTi}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$) is post fired for gas sensor applications. Hence, the use of an additional diffusion barrier can be omitted from the conventional sensor design. In this study, SrAl_2O_3 is prepared by the conventional solid-state ceramic route with a calcination temperature of 1200°C and the laminated tape is sintered at 1400°C (Sahner *et al.*, 2005). Many more research investigations are in progress in HTCC for specific applications such as sensors for toxic contamination removal, membranes for biofuel production and antimicrobial packaging applications, where high operational stability is required (Ritter *et al.*, 2017; Song *et al.*, 2017; Luo *et al.*, 2017; Huang *et al.*, 2013).

Nitride HTCCs

Due to their excellent thermal conductivity (160 W/mK) and matching coefficient of thermal expansion compared to that of Si, HTCC AlN substrate/packages are utilized for many high heat dissipation and chip applications. Usually, Y_2O_3 ceramic is used as a sintering aid for HTCC AlN production. The sintering temperature (1400–1830°C or above) and sintering conditions of HTCC AlN may be varied to obtain maximum thermal conductivity for the applications (Joedecke *et al.*, 2009; Ym *et al.*, 1993). In general, AlN tape formulation is done with a water-free system because of its highly reactive nature with water. However, some attempts have been made for aqueous tape casting of AlN with hydrolysis inhibitors and anti-hydrolysis protective agents (Luo *et al.*, 2004; Olhero and Ferreira, 2005). In 2017, Shang *et al.* (2017) reported a new method of tape casting for AlN HTCC using gel tape casting and sintering at 1840°C in a N_2 atmosphere and they obtained a thermal conductivity of 161 W/mK. Luo *et al.* investigated the comparison of aqueous and non-aqueous tape casting of AlN substrates. The results showed that the final thermal properties of both methods did not differ much; both sintered at 1850°C/3 h. The residual carbon content was lower in the aqueous compared to the non-aqueous based HTCC AlN (Luo *et al.*, 2005). Another nitride family of materials reported for HTCC substrate applications is Si_3N_4 because of its thermal and mechanical properties. The advantages of the Si_3N_4 substrate over AlN is that it can be manufactured much thinner than AlN (Bitterlich and Heinrich, 2002). Also, the reliability of these materials has been well studied and proven by many applications (Das and Curlee, 1992; Yokota and Ibukiya, 2001). The reactivity with water is similar to that of AlN and produces an oxidized surface on reaction with water. The most common sintering aids for Si_3N_4 are Y_2O_3 and Al_2O_3 . Bitterlich and Heinrich reported an aqueous tape casting composition for Si_3N_4 . These studies covered the tape casting, lamination and post-firing of Si_3N_4 HTCC substrates. The HTCC Si_3N_4 comprised 6 wt% Y_2O_3 and 4 wt% Al_2O_3 as the major sintering aids together with other tape casting organics. The tape lamination was done at 14 MPa for 20 s at room temperature. Binder burnout was carried out at 750°C under a nitrogen atmosphere and was followed by sintering done at subsequent sintering dwells at 1100°C and 1800°C, respectively. The sintered HTCC Si_3N_4 substrate had 98% densification and a linear shrinkage of 20%–24% (Bitterlich and Heinrich, 2002).

Carbide HTCCs

The combination of high strength, hardness, creep resistance, thermal shock resistance and oxidation and acid resistance makes carbides important in HTCC applications. HTCC SiC is reported by both the aqueous and non-aqueous based tape casting routes.

Lv *et al.*, reported aqueous-based SiC HTCC tapes and substrates. The most common sintering aids for SiC, Y_2O_3 and Al_2O_3 , were used in these studies. The laminated tape binder was removed at $600^\circ C/1$ h and hot-pressed at $1850^\circ C$ for 30 min at a pressure of 25 MPa in Ar atmosphere. The final HTCC SiC substrates exhibited 98.89% densification and the flexural strength, hardness and toughness were 779.5 ± 39.2 MPa, 21.51 ± 0.70 GPa and 5.54 ± 0.26 MPa $m^{1/2}$, respectively (Lv *et al.*, 2009). Recently, Kim *et al.*, reported the joining of SiC ceramic using SiC tape by hot pressing at 1800 – $1900^\circ C$ under a pressure of 10–20 MPa in Ar atmosphere. The joined layer showed no residual stress near the join with good mechanical properties as expected (Kim *et al.*, 2019). There is also a report on the TiC based aqueous tape casting process by Zhang *et al.* (2001) but they have not studied its sintering and other properties. However, there is studies reported on its sintering behavior, microstructure, mechanical properties by pressure less sintered ultra refractory carbide using conventional powder compaction and sintering route (Silvestroni and Sciti, 2010). Major advancements in research for the carbide family of materials are progressing for ultra-high temperature ceramics (UHTCs). For example, multilayer joining of ultra refractory carbides such as ZrC, HfC and TaC with Ni/Nd/Ni trilayer is bonded by conventional solid state sintering process at multiple stages. While the bonding done with temperature of $1400^\circ C/30$ min (Silvestroni *et al.*, 2012). Recently, Vinci *et al.* (2019) reported the influence on strength of SiC fiber reinforcement in HfC/SiC composite up to $2100^\circ C$. All these researches are done by solid state approach, the results will also influence the future tape casting and firing process of Carbide HTCCs.

Boride HTCCs

Materials such as ZrB_2 , HfB_2 and Mo_2B_5 have been reported for HTCC and UHTC applications. Among these ZrB_2 was investigated by Natividad *et al.*, in 2011 due to its high melting point of $>3000^\circ C$ and low density. In addition, its mechanical and thermal properties were extensively studied for ultra-high temperature ceramics (UHTC) feasible for thermal protection systems in aerospace vehicles (Natividad *et al.*, 2011). As a UHTC material ZrB_2 has many applications such as Hall-Heroult cell cathode for electrochemical processing of aluminum, evaporation boats, crucible for handling molten metals, thermowell tube for steel refining, thermocouple sleeves for high temperature uses, nozzles and plasma electrodes (Bellosi *et al.*, 2006). On the other hand, the tape casting and binder burnout and densification have been studied and reported. In addition, ZrB_2 is utilized as similarly, Mo_2B_5 has been reported as one of the sintering aids used in the HTCC materials composition of $Al_2O_3/TiC/MoSi_2 + Mo_2B_5$ for HTCC multilayer applications (Zhang *et al.*, 1999). In addition ZrB_2 is also reinforced in ternary matrix composite due to its high melting point, hardness, excellent corrosion resistance, thermal shock resistance, high electrical and thermal conductivity (Sciti *et al.*, 2004; Guo and Kagawa, 2012). Moreover, the reinforcement of ZrB_2 in SiC matrix is found to be useful for the manufacturing of igniters and heating elements because of its satisfactory resistivity, positive temperature coefficient of electrical resistance, higher strength and toughness compared to carbides. It has good oxidation resistance up to $1200^\circ C$ (Sciti *et al.*, 2004). The approach of spark plasma sintering of Hf and Zr based borides are also investigated for cost effective production of these borides (Bellosi *et al.*, 2006). Much more research is needed for the tape casting and post-firing stages of this class of materials before real practical applications in HTCC.

Other HTCC Substrates

Several HTCC multilayer ceramics formed by the stacking of layers, or with different chemical compositions and structures, have been investigated. In particular, Al_2O_3/ZrO_2 , Al_2O_3/SiC , Si_3N_4/BN , $Al_2O_3/TiC/MoSi_2 + Mo_2B_5$, Si_3N_4/BN , $Al_2O_3/TiC/MoSi_2 + Mo_2B_5$, $Al_2O_3/MoSi_2$, $3Al_2O_3 \cdot 2SiO_2/ZrO_2$, $SiC/C/SiC$, SiN (dense)/ SiN (porous), SiC /(glass + fiber) are reported to have HTCC multilayer packaging applications (Boch *et al.*, 1986; She *et al.*, 2000; Liu and Hsu, 1996; Zhang *et al.*, 1999; Watanabe *et al.*, 2001; Park *et al.*, 2000; Clegg, 1992; Shigegaki *et al.*, 1996; Cutler *et al.*, 1996). UHTCs (Ultra High-Temperature Ceramics), a new class of materials with melting points above $3000^\circ C$, are borides, carbides and nitrides (Fahrenholtz *et al.*, 2014). These extreme temperature materials can withstand extreme environments, including the effects of temperature, chemical reactivity, mechanical stress, radiation and wear. Some of the materials under this classification are ZrB_2 , HfB_2 , TaC, ZrC, TiN, YrN and HfC. Recently, UHTCs research is focused on next generation ceramic matrix composites for combustion and harsh environments. Some of the results comprise the graphene sheet reinforced ZrB composites, spark plasma sintered Ti_3SiC_2 -carbon fiber composites, ZrB_2 reinforced with 40 vol% C fiber, 5 vol% SiC, 5 vol% $MoSi_2$, $HfSi_2$, WSi_2 composites are in the category of advancement in UHTCs (Zhang and Sanvito, 2019; Lagos *et al.*, 2019; Silvestroni *et al.*, 2019). Much uncertainty is associated with this class of materials in terms of their melting temperature and considerable research is needed in this area to establish UHTCs.

Low Temperature Co-Fired Ceramics Substrates (LTCC)

LTCC is the cost-effective and upgraded version of HTCC with firing temperatures in the range of 700 – $960^\circ C$. Likewise, HTCC conventional tape casting is the processing of LTCC substrates. The lower fabrication temperature is achieved by the additive manufacturing process of low melting point glasses, ceramics or a combination of both. The major applications of LTCC include hybrid circuits, inductors, resistors, transformers, sensors and microsystems. LTCC offers functionality such as high/low

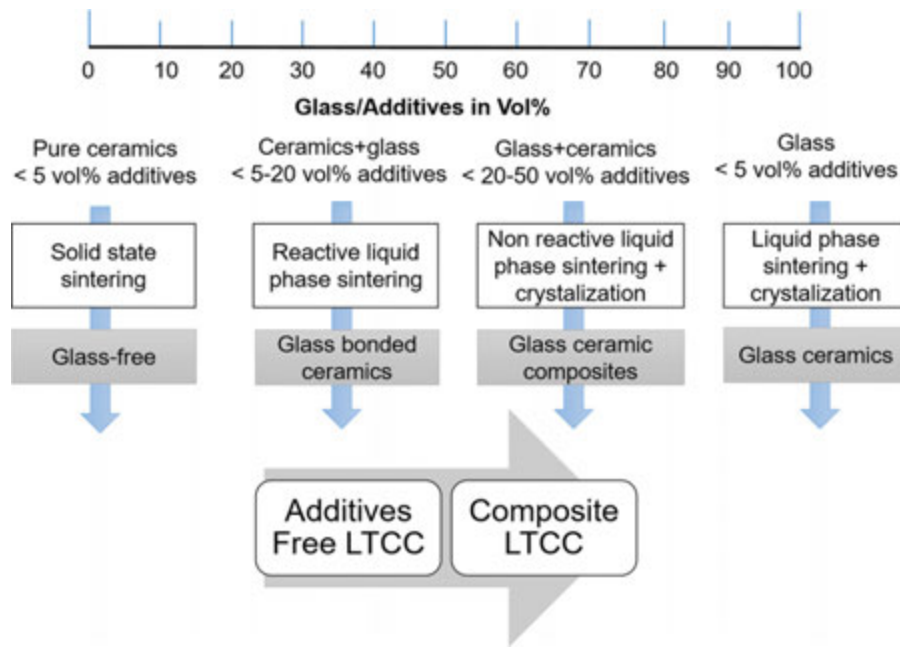


Fig. 4 LTCC composition types updated based on Rabe *et al.*, report in 2005. Redraw by Jobin Varghese based on Rabe, T., Schiller, W.A., Hochheimer, T., Modes, C., Kipka, A., 2005. Zero shrinkage of LTCC by self-constrained sintering. *International Journal of Applied Ceramic Technology* 2, 374–382.

permittivity, low dielectric loss in a single multilayer package and multi-functional features by integration and interconnections. LTCC also offers the highest interconnect density for the fabrication of 3D structures with the integration of passives such as capacitors, resistors and inductors in a single device. The tape casting and co-firing have been discussed previously in detail. Here are described some of the advances in recent research into LTCC substrates and packaging. LTCC materials have been reported with glass or without glass additives based on their co-firability with metal electrodes. In order to lower the sintering temperature many approaches have been reported such as reducing the particle size of the raw materials, chemical synthesis of the raw materials and the addition of low melting point glass/ceramics. Among these methods, low melting point glass addition is conventionally used for the fabrication of LTCC. Sebastian *et al.*, reported a detailed survey of LTCC materials sinterable at 700–950°C based on their microwave dielectric properties and their co-firability with metal electrodes. The survey listed over 1000 materials with different chemical families feasible for microwave applications (Sebastian, 2008; Sebastian and Jantunen, 2008, 2017; Sebastian *et al.*, 2015, 2016). Rabe *et al.*, describes clear LTCC ceramic types based on their raw materials, composition and sintering mechanisms. Fig. 4 presents an updated view of LTCC composition types based on the Rabe *et al.* (2005) reports.

Based on classifications, we here describe two classes: additive-free LTCC and composite LTCC. The sintering mechanisms involved in these categories are the conventional solid-state sintering reaction, reactive/non-reactive liquid phase sintering and crystallization combined with liquid-phase sintering. The subclasses of LTCC are glass-free LTCC, glass bonded ceramics, glass–ceramic composites and glass ceramics.

Additive-Free LTCC

These are the materials which are sinterable at the LTCC fabrication temperature with co-firability with metal electrode materials without any sintering aid or glass materials through additive manufacturing. There are several materials reported for additive-free LTCC but their application is limited because they lack many other required properties such as thermal conductivity, mechanical stability, matching coefficient of thermal expansion to that of electrode materials and other associated packages, temperature coefficient of resonant frequency for operation stability for the microwave substrates at high-frequency applications, durability and so on. In general, low permittivity materials are useful for LTCC microwave substrate applications whereas high permittivity materials are used for capacitive or resonating applications. The signal speed is directly proportional to the square root of the relative permittivity of the substrate and is shown in Eq. (3).

$$t_d = \frac{\sqrt{\epsilon_r}}{c} \quad (3)$$

Where, t_d is the propagation delay, c is the velocity of light and ϵ_r is the relative permittivity of the substrates. Hence, a low relative permittivity substrate is suitable for increasing the signal speed. Additive-free LTCC materials are also required for the

Table 5 Glass free LTCC materials reported with relative permittivity <10 and $Q \times f > 25,000$ GHz

Material	Sintering temperature ($^{\circ}\text{C}$)	Relative permittivity	$Q \times f$ (GHz)	τ_f (ppm/ $^{\circ}\text{C}$)
$\text{Mg}_3(\text{VO}_4)_2$	950	6.4	48,800	– 83
LiMgPO_4	950	6.6	79,100	– 60
$\text{Zn}_3\text{B}_2\text{O}_6$	925	6.7	58,500	– 58
SrCuP_2O_7	925	7.0	101,110	– 62
$\text{CaMgSi}_2\text{O}_6$	900	7.0	43,200	– 22
SrZnP_2O_7	950	7.1	52,780	– 70
MgMoO_4	900	7.1	79,100	– 46
SrZnP_2O_7	925	7.3	71,520	– 64
CaCuP_2O_7	900	7.3	71,620	– 76
CaZnP_2O_7	900	7.6	63,130	– 82
$\text{Mg}_3(\text{VO}_4)_2$	950	7.9	53,000	– 84
$\text{Nd}_2\text{Mo}_3\text{O}_{12}$	945	8.2	80,000	– 60
BaMgV_2O_7	830	8.2	37,600	– 35
$\text{Li}_2\text{Mg}_2\text{W}_3\text{O}_{12}$	720	8.4	56,700	– 73
MnMoO_4	900	8.5	54,100	– 74
LiSrBO_3	800	8.6	60,000	– 39
LiCaBO_3	800	8.7	75,000	– 150
ZnMoO_4	800	8.7	49,900	– 87
BaMoO_4	900	9.0	37,100	– 90
$\text{Mg}_3(\text{VO}_4)_2$	950	9.1	64,100	– 93
$\text{Ca}_5\text{Mg}_4(\text{VO}_4)_6$	800	9.2	53,300	– 50
BaMoO_4	900	9.3	37,200	– 79
$\text{MgCo}_2(\text{VO}_4)_2$	900	9.4	78,900	– 95
LiMgVO_4	700	9.5	34,800	– 146
$\text{Ba}_2\text{V}_2\text{O}_7$	840	9.6	30,300	– 32
BaTeO_3	800	10.0	34,000	– 54
$\text{NaCa}_2\text{Mg}_2\text{V}_3\text{O}_{12}$	915	10.0	50,600	– 47

Note: Sebastian, M.T., Ubic, R., Jantunen, H., 2015. Low-loss dielectric ceramic materials and their properties. *International Materials Reviews* 60, 392–412.

knowledge of the material properties of many advanced applications irrespective of their primary applications potential (Sebastian and Jantunen, 2008, 2017; Sebastian *et al.*, 2015).

As an example, most of the additive-free materials reported are listed in Table 5 with their sintering temperatures and microwave dielectric properties (relative permittivity <10 and $Qf < 30,000$ GHz with measurement above 1 GHz) based on Sebastian *et al.* (2015) review reports. These material families include phosphates, silicates, borates, molybdates, vanadates, tellurate and tungstates. The table is based on low permittivity materials suitable for microwave applications. Specifically, the materials in Table 5 are moderately good for microwave dielectric properties. However, most of the reported materials have a negative temperature coefficient of resonant frequency which limits the resonant frequency stability and hence their feasibility in practical applications. Moreover, mechanical properties, thermal conductivity and coefficient of thermal expansion of these materials should also be under consideration for device level fabrications.

Composite LTCC

A major class of materials reported for LTCC substrate applications is composite materials. The composite materials are prepared by the additive manufacturing process. The process includes sintering aids such as low melting point sintering ceramic oxides/glass/glass–ceramic that are used for the LTCC raw material development. In addition, chemical synthesis and reduction of the initial particle size of the raw materials were also helpful for lowering the sintering temperatures. The sintering aid selection is based on its sintering temperature and raw materials and, in the case of telecommunication applications, on its microwave dielectric properties. For example, a near zero temperature coefficient of resonant frequency of LTCC materials may be tuned by using additives such as TiO_2 (rutile) or CaTiO_3 with a very high positive temperature coefficient of resonant frequency and low dielectric loss. However, the high sintering temperature restricts its use as much as do the additives. The most common sintering aids are low melting point glasses, which allow a devitrified viscous liquid phase during the firing process to enable sintering and densification together with other additives. Al_2O_3 is the most studied material for composite LTCC substrate feasibility. Most of the commercial products also belong to the glass–ceramics group. Alumina is a major part of commercial LTCC products. The majority of LTCC feasible glasses contain Al_2O_3 , SiO_2 , B_2O_3 and MoO_3 as glass networks because of the low thermal expansion and chemical stability of SiO_2 while B_2O_3 and MoO_3 provide low melting point viscous flow. Al_2O_3 can easily form AlO_4 tetrahedron network structure while SiO_4 tetrahedra increase the connectivity, viscosity and T_g as glass network former. Other common glass network modifiers are Li_2O , Na_2O , K_2O , PbO , CaO , SrO , BaO , MgO and ZnO . Some examples of primary,

secondary and ternary glasses suitable for LTCC materials production are 99 Mole% B_2O_3 (softening point $\sim 450^\circ C$), $40B_2O_3$ – $60SiO_2$ (softening point $\sim 820^\circ C$), $50ZnO$ – $50B_2O_3$ (softening point $\sim 610^\circ C$), $30BaO$ – $60B_2O_3$ – $10SiO_2$ (softening point $\sim 627^\circ C$) and $40PbO$ – $40B_2O_3$ – $20SiO_2$ (softening point $\sim 448^\circ C$). These glasses are feasible for LTCC composition because of their low softening point, low permittivity and low dielectric loss, as is required for many applications. Additives such as glass or sintering aids are an effective way of manufacturing LTCC but in most cases they degrade the primary materials properties, such as the thermal, mechanical and electrical properties, and hence careful selection of additives is needed to develop good quality LTCC by the composite approach. Composite LTCC has been available for the last few decades and the technology is a witness of its market growth and production (Sebastian and Jantunen, 2008, 2017; Sebastian *et al.*, 2015).

Recent Advancement in LTCC Substrates

Further advances in LTCC need innovative materials, ceramic processing and the integration of upgrades into process control. One of the major drawbacks of LTCC is the sintering shrinkage that occurs in all directions, x, y and z. Another disadvantage is free sintering loss, which leads to a lack of geometric precision and hence limits the ability to produce large numbers of modules in a single LTCC. In order to compensate for these disadvantages there are a few constrained sintering mechanisms that are utilized in industry. For example, the use of green laminated tape on a sintered substrate, which prevents green tape shrinkage in the lateral direction only; in this case vertical shrinkage occurs. Another approach is a sacrificial layer on top and bottom of the laminated structure and uniaxial pressure applied during the sintering process, which prevents the lateral shrinkage to some extent. In addition, self-constrained approaches are also in the market with special casting processes and modified LTCC tapes with intermediate or separate sintering intervals. Commercial HL2000 (HeraLock) is developed based on a self-constrained sintering mechanism for shrinkage control. Hence, much research is progressing on developing a self-constrained LTCC tape which offers near zero (x, y direction) sintering shrinkages (Rabe *et al.*, 2005). Another study reports the aqueous and non aqueous fabrication of multilayer ZnO varistors for low breakdown voltage and high surge absorption. Various dopants, including Bi_2O_3 , Sb_2O_3 , Co_3O_4 , Mn_3O_4 and Cr_2O_3 are used in this research along with other organic additive for green tape casting and sintering at $900^\circ C$ (Wang *et al.*, 2008). LTCC is one of the technologies which can develop miniaturized integrated packages such as sensor and actuators. Patel *et al.*, reported a miniaturized hot plate for gas sensor applications. The design and fabrication reveal that the developed LTCC hot plate requires only 144 mW to reach a temperature of $250^\circ C$ (Patel *et al.*, 2012). A recent report discusses wet chemical porosification under alkaline conditions in LTCC for reducing the relative permittivity by embedding air in it. The chemical composition of the LTCC is unaltered by the change in the etching parameters and bath temperature which initiate the porosification processes in LTCC tapes in their fired condition (Hajian *et al.*, 2019). In addition, a 60 GHz high gain planar aperture antenna has been recently reported by Zhu *et al.*, using Ferro A6M LTCC tape for 5G applications. The LTCC A6M substrate exhibits a low permittivity of 5.9 and a dielectric loss of 0.0002 in the microwave frequency ranges (Zhu *et al.*, 2019). Microfluidics is another integrated LTCC technology for biomedical applications such as the enzymatic method of urea determination in LTCC microfluidics (Remiszewska *et al.*, 2019). Other applications are, as recently reported, dual band LTCC band pass filters, miniature electrochemical cells, integrated rectangular waveguides and LTCC monolithic microreactors (Pourzadi *et al.*, 2019; Szymanowska *et al.*, 2019; Isapour and Kouki, 2019; Alonso *et al.*, 2019). Studies on millimeter wave LTCC package research are also in progress for 5th and 6th generation telecommunication products.

Ultra-Low Temperature Co-Fired Ceramic Substrates (ULTCC)

The latest upgrade in multilayer technology is ULTCC. The ULTCC fabrication temperature is in the range of 200 – $700^\circ C$ utilizing existing doctor blade tape casting with new casting compositions. It involves two important classes based on its firing temperature and casting composition. ULTCC Category-1 and Category-2 types have firing temperatures of 200 – 400 and 400 – $700^\circ C$, respectively. There are around 250 materials reported in the literature to date which are feasible for ULTCC applications. Among this most reported materials class are molybdates, vanadates, tellurates, tungstates, phosphates, borates and their composites sinterable below $700^\circ C$ (Sebastian *et al.*, 2016; Yu *et al.*, 2015; Zhou *et al.*, 2018). Ag and Al based conducting pastes are currently available in the market for co-firing. From the beginning of 2010 to the present (2020), extensive research has focused on ULTCC worldwide. However, very little research has been done in the field of tape casting and co-firing. Chen *et al.*, in 2017 reported the very first tape casting composition for ULTCC Category 1 & 2 types, later on much more research was carried out for low and high permittivity and low dielectric loss materials using tape casting and co-firing in recent years (2018–2019). Some of them are listed in Table 6. However, there are other reports on ULTCC Category-2 tape casting and co-firing at 645 and $660^\circ C$ with existing LTCC slurry systems by Honkamo *et al.* (2009) and Zhou *et al.* (2010), respectively.

The most suitable compositions for ULTCC tape organics for both category 1 and category 2 have been studied by Varghese *et al.* (2018) and Joseph *et al.* (2019), respectively, in 2018 and 2019. Joseph *et al.* (2019) report a detailed study on binder burnout and residual carbon in ULTCC by tape casting and co-firing of $CuMoO_4$ and $CuMoO_4$ – Ag_2O ULTCC substrates in comparison with commercial LTCC tapes and substrates. Fig. 5 represents the low residual carbon ULTCC tape developed by Joseph *et al.* (2019), in 2019.

The reported tape casting slurry compositions comprise environmentally friendly organics and non-toxic binders and solvents. The cast tape exhibited low residual carbon of $<5\%$ after sintering which is comparable with commercial LTCC tapes. The

Table 6 ULTCC tape casting, co-firing and sintering reports to date

ULTCC tapes	Sintering temperature (°C)	Co-firing electrode	References
BaTiO ₃ –BBSZ	450	Ag	Chen <i>et al.</i> (2017)
Al ₂ O ₃ –BBSZ	450	Ag	Chen <i>et al.</i> (2017)
Zn ₂ Te ₃ O ₈	660	Al	Honkamo <i>et al.</i> (2009)
PZ29-GO17	450	Ag	Varghese <i>et al.</i> (2018)
Li ₂ WO ₄	650	Ag	Sasidharanpillai <i>et al.</i> (2018)
Rutile TiO ₂ -GO17	400	Ag	Varghese <i>et al.</i> (2019)
Anatase TiO ₂ -GO17	400	Ag	Varghese <i>et al.</i> (2019)
Li–Na–Al–B–Si–O glass	600	Ag	Chen <i>et al.</i> (2019)
CuMoO ₄	650	Al	Joseph <i>et al.</i> (2019)
CuMoO ₄ –Ag ₂ O	500	Al	Joseph <i>et al.</i> (2019)
CaV ₂ O ₆ -glass	650	Al	Sasidharanpillai <i>et al.</i> (2019)
Bi ₂ Mo ₂ O ₉	645	Al	Zhou <i>et al.</i> (2010)
Li ₂ MoO ₄ (LM)/[(Li _{0.5} Bi _{0.5}) _x Bi _{1–x}][Mo _x V _{1–x}]O ₄ (LBMV)	600	–	Hao <i>et al.</i> (2020)

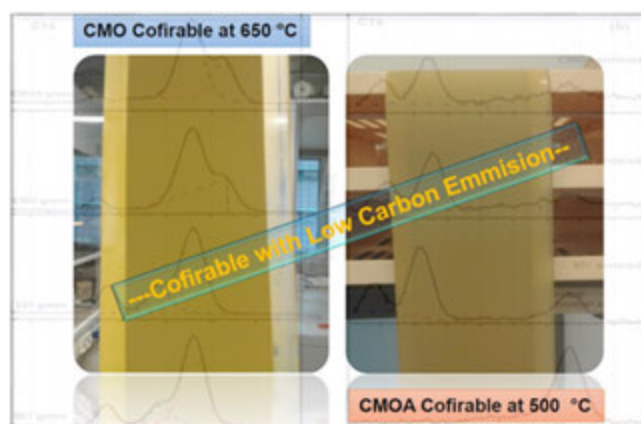


Fig. 5 ULTCC tape with low residual carbon emission reported by Joseph *et al.*, in 2019. Our own picture based on ACS copyright, Joseph, N., Varghese, J., Teirikangas, M., Vahera, T., Jantunen, H., 2019. Ultralow-temperature cofired ceramic substrates with low residual carbon for next generation microwave applications. ACS Applied Materials & Interfaces 11, 23798–23807.

developed ULTCC Category 2 materials exhibit excellent microwave dielectric loss in the range of 10^{-5} and 10^{-4} , respectively, at 10 GHz. These ULTCC substrates (CuMoO₄ and CuMoO₄-Ag₂O) are fired at 500 and 650°C. There are other reports on ULTCC substrates of Li₂WO₄ and CaV₂O₆-glass, which belongs to Category-2 with similar casting compositions and show excellent microwave dielectric properties. Varghese *et al.*, reported ULTCC Category 1 sintering of anatase and rutile TiO₂-glass at 400°C with moderately good microwave dielectric properties and near zero thermal shrinkages with an existing casting composition. In addition, they have investigated a ULTCC dual band antenna for their performance evaluation. The advantages of current developments in ULTCC over HTCC and LTCC technology are shown in Fig. 6 (Varghese *et al.*, 2019).

Recently, ULTCC tape laminated on an aluminum heat sink to isolate the substrate was reported. It has the following advantages over conventional thick film printing of the ULTCC tape. The lamination is done in one step firing, there is easy processing of cavities which is beneficial for recessed lighting, and it can produce 3D substrates for higher performing LED modules at lower cost and longer life time (Grabey *et al.*, 2016). Another important research reported on Si-ULTCC anodic bonding at 150°C, 200 V for an MEMS pressure sensor (Chen *et al.*, 2019). Moreover, very recently Hao *et al.*, presented heterogeneous multilayer dielectric ceramics of ULTCC Category-2 by self-constrained sintering. They demonstrated Li₂MoO₄ (LM) and [(Li_{0.5}Bi_{0.5})_xBi_{1–x}][Mo_xV_{1–x}]O₄ $x = 0.098$ (LBMV) tape casting and multilayer lamination and sintering at 600°C. These studies open up research to realize the solid bonding between heterogeneous materials by self-constrained sintering. Furthermore, low and high permittivity integration leads to guided electromagnetic transmission for future devices through ULTCC research (Hao *et al.*, 2020). Hereafter, much more research is needed to establish the ULTCC technology.

Cold Sintered/Upside Down/Room Temperature Ceramic Substrates (CSCC)

The most recent advance in ceramic processing is known as cold sintered co-fired ceramics (CSCC). It is a new approach to the sintering technique for ceramic and ceramic-based composites prepared by water as a transient solvent for densification at

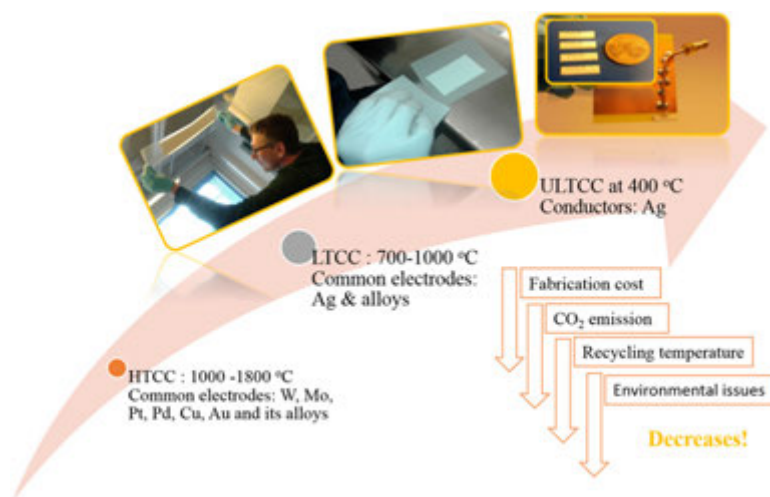


Fig. 6 Representation of the advantages of ULTCC over HTCC and LTCC technologies by Varghese *et al.*, in 2019. Our own picture based on ACS copyright 6, Varghese, J., Ramachandran, P., Sobocinski, M., Vahera, T., Jantunen, H., 2019. ULTCC glass composites based on rutile and anatase with cofiring at 400°C for high frequency applications. ACS Sustainable Chemistry & Engineering 7, 4274–4283.

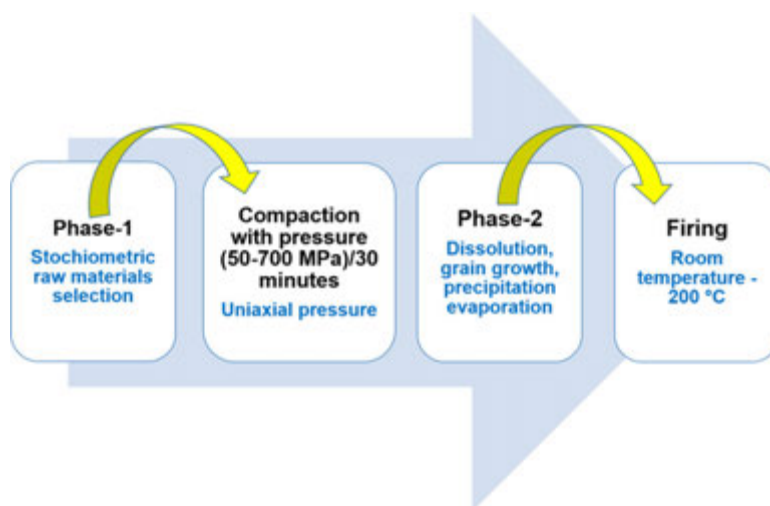


Fig. 7 Schematic flow chart of cold pressure or temperature assisted sintering process. Drawn by Jobin Varghese based on Maria, J.-P., Kang, X., Floyd, R.D., *et al.*, 2017. Cold sintering, status and prospects. Journal of Materials Research 32, 3205–3218. Guo, J., Floyd, R., Lowum, S., *et al.*, 2019. Cold sintering: Progress, challenges and future opportunities. Annual Review of Materials Research 49, 275–295.

temperatures between room temperature and 200°C. Cold sintering offers the ability for sintering by water-soluble single or mixed metal oxide ceramics such as molybdates, vanadates, tungstates, carbonates, chlorides, sulfates, fluorides, phosphates and borates with applied pressure/temperature. The integration of cold sintering with thermoplastic composites, hydrothermal assisted processes, nanotechnology, flexible-printable electroceramics devices, solid electrolytes and microwave ceramics are well studied and reported (Guo *et al.*, 2016a,b,c; Baker *et al.*, 2016; Berbano *et al.*, 2017; Kähäri *et al.*, 2014). The ferroelectric material process, capacitor material process, ceramic packaging, and semiconductor process, Li-ion cathode, magnetic materials, sputtering targets and piezoelectric materials are the current research and development fields (Guo *et al.*, 2016c,d; Polotai *et al.*, 2005; Guo *et al.*, 2016b,f, 2017, 2019). Maria *et al.*, and Guo *et al.*, reported a detailed review of cold sintering in 2017 and 2019, respectively. They discuss and review the historical background and the standard process, mechanism, applications and future prospects of the cold sintering process (Maria *et al.*, 2017; Guo *et al.*, 2019). A standard spectrum of cold sinterable ceramics includes binary, ternary, quaternary and quinary compounds like MoO_3 , Li_2CO_3 , LiFePO_4 and $\text{LiAl}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$. Fig. 7 represents the schematic flow of the cold pressure or temperature assisted sintering process (Maria *et al.*, 2017; Guo *et al.*, 2019).

The cold sintering process consists of two phases comprising compaction, consolidation, densification and crystallization during cold sintering. The compaction process is the conventional process in which particles are rearranged by sliding, grain boundary creep, etc., with partial extrusion of the liquid phase or temperature/pressure-assisted dissolution and evaporation. Mass

transport and induced nucleation happen in the pressure/temperature sintering process at the final stage of densification. Recently, Wang *et al.* (2019a,b) reported a multilayer ceramic capacitor (MLCCs) based on $(\text{Bi}_{0.95}\text{Li}_{0.05})(\text{V}_{0.9}\text{Mo}_{0.1})\text{O}_4\text{-Na}_2\text{Mo}_2\text{O}_7$ with a relative permittivity of 39, temperature coefficient of capacitance of $\pm 0.01\%$ and $\tan \delta$ of 0.01 at 1 MHz fabricated by the cold sintering process at 150°C . Another work demonstrated metallization integration in co-fired MLCs by the cold sintering process, the metals included Cu, Fe and Al co-fired with ZnO ceramics uniaxially pressed at 200 MPa pressure together with a sintering temperature of $260^\circ\text{C}/1\text{ h}$ (Beauvoir *et al.*, 2019). Nelo *et al.*, report upside down composites using a piezoelectric filler with an aqueous dispersion of lithium molybdate as binder by pressing at 250 MPa and subsequent drying at $120^\circ\text{C}/18\text{ h}$. The composites showed a moderately good voltage constant of $-33\text{ mVm}\cdot\text{N}^{-1}$ in comparison with bulk materials (Nelo *et al.*, 2019). However, there is research needed into the fundamentals and the engineering processes of cold sintering.

Summary

The chapter gives some brief historic aspects of multilayer ceramic substrate technology together with the present status of multilayer glass–ceramic/composite substrates prepared by HTCC, LTCC, ULTCC and the growth of UHTCs and cold sintering/room temperature fabrication/upside-down composite fabrications based on present and recent literature surveys. The markets and industries are in need of advanced materials and processing technology for future generations of devices based on technology demands. In addition to this, environmental and energy concerns are a challenge to the ceramic researchers to full fill future environmentally friendly ceramic utilized for circular economy.

References

- Alonso, M.B., Gómez, O., Fernández, B., *et al.*, 2019. An LTCC monolithic microreactor for the synthesis of carbon dots with photoluminescence imaging of the reaction progress. *Sensors and Actuators B: Chemical* 296, 126613. doi:10.1016/j.snb.2019.05.090.
- Auerkari, P., 1996. Mechanical and physical properties of engineering alumina ceramics. In: Tirronen, K. (Ed.), *Technical Research Centre of Finland, VTT Tiedotteita-Meddelanden-Research Notes* 1792. Espoo: Julkaisija-Utgivare-Publisher, pp. 1–26.
- Baker, A., Guo, H., Guo, J., Randall, C., 2016. Utilizing the cold sintering process for flexible-printable electroceramics device fabrication. *Journal of the American Ceramic Society* 99, 3202–3204.
- Beauvoir, T.H.D., Dursun, S., Gao, L., Randall, C., 2019. New opportunities in metallization integration in cofired electroceramics multilayers by the cold sintering process. *ACS Applied Materials & Interface* 1, 1198–1207.
- Belloso, A., Monteverde, F., Sciti, D., 2006. Fast densification of ultra-high-temperature ceramics by spark plasma sintering. *International Journal of Applied Ceramic Technology* 3, 32–40.
- Berbano, S.S., Guo, J., Guo, H., Lanagan, M.T., Randall, C.A., 2017. Cold sintering process of $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ solid electrolyte. *Journal of the American Ceramic Society* 100, 2123–2135.
- Bitterlich, B., Heinrich, J.H., 2002. Aqueous tape casting of silicon nitride. *Journal of the European Ceramic Society* 22, 2427–2434.
- Boch, P., Chartier, T., Huttepain, M., 1986. Tape casting of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ laminated composites. *Journal of the American Ceramic Society* 69, [C-192-C-192].
- Charles, M.M., Fishkill, N.Y., 1967. U.S. Patent US3540894.
- Chen, G., Ma, M., Liu, Z., *et al.*, 2019. Anodic bondable Li-Na-Al-B-Si-O glass-ceramics for Si-ULTCC heterogeneous integration. *Journal of the European Ceramic Society* 39, 2419–2426.
- Chen, M., Vahera, T., His, C., *et al.*, 2017. Tape casting system for ULTCCs to fabricate multilayer and multimat 3D electronic packages with embedded electrodes. *Journal of the American Ceramic Society* 100, 1257–1260.
- Clegg, W.J., 1992. The fabrication and failure of laminar ceramic composite. *Acta Metallurgica et Materialia* 40, 3085–3093.
- Crowley, H.L., Orange, S., Hossenlopp, A.M., Metuchen, N.J., 1945. U.S. Patent US2382136.
- Cutler, W.A., Zok, F.W., Lange, F.F., 1996. Mechanical behavior of several hybrid ceramic-matrix-composite laminates. *Journal of the American Ceramic Society* 79, 1825–1833.
- Das, S., Curlee, T.R., 1992. The cost of silicon nitride powder and the economic viability of advanced ceramics. *American Ceramic Society Bulletin* 71, 1103–1111.
- Fahrenholtz, W.G., Wuchina, E.J., Zhou, Y. (Eds.), 2014. *Ultra High Temperature Ceramics; Materials for Extreme Environmental Applications*. New Jersey: Wiley.
- Feng, Z., Liu, L., Li, L., *et al.*, 2019. 3D printed Sm-doped ceria composite electrolyte membrane for low temperature solid oxide fuel cells. *International Journal of Hydrogen Energy* 44, 13843–13851.
- Grabey, S., Shahbazi, S., Persons, R., Shahbazi, C., 2016. Evaluation of a lead-free ultra-low temperature co-fire ceramic (ULTCC) tape designed for lamination on aluminum substrates and a compatible co-firable silver conductor. *International Symposium on Microelectronics* 2016, 573–580. doi:10.4071/isom-2016-THP22.
- Guo, H., Baker, A., Guo, J., Randall, C.A., 2016a. Protocol for ultralow-temperature ceramic sintering: An integration of nanotechnology and cold sintering process. *ACS Nano* 10, 10606–10614.
- Guo, J., Berbano, S.S., Guo, H., *et al.*, 2016b. Cold sintering process of composites: Bridging the processing temperature gap of ceramic and polymer materials. *Advanced Functional Materials* 26, 7115–7121.
- Guo, J., Baker, A.L., Guo, H., Lanagan, M., Randall, C.A., 2016c. Cold sintering process: A new era for ceramic packaging and microwave device development. *Journal of the American Ceramic Society* 100, 669–677.
- Guo, H., Baker, A., Guo, J., Randall, C.A., 2016d. Cold sintering process: A novel technique for low temperature ceramic processing of ferroelectrics. *Journal of the American Ceramic Society* 99, 3489–3507.
- Guo, J., Guo, H., Baker, A.L., *et al.*, 2016e. Cold sintering: A paradigm shift for processing and integration of ceramics. *Angewandte Chemie* 55, 11457–11461.
- Guo, H., Guo, J., Baker, A., Randall, C.A., 2016f. Hydrothermal-assisted cold sintering process: A new guidance for low temperature ceramic sintering. *ACS Applied Materials & Interfaces* 8, 20909–20915.
- Guo, J., Floyd, R., Lowum, S., *et al.*, 2019. Cold sintering: Progress, challenges and future opportunities. *Annual Review of Materials Research* 49, 275–295.
- Guo, J., Guo, H., Heidary, D.S.B., Funahashi, S., Randall, C.A., 2017. Semiconducting properties of cold sintered V_2O_5 ceramics and co-sintered V_2O_5 -PEDOT: PSS composites. *Journal of the European Ceramic Society* 37, 1529–1534.
- Guo, S., Kagawa, Y., 2012. High strength zirconium diboride based composite consolidated by low temperature hot pressing. *Science and Technology of Advanced Materials* 13, 1–6. doi:10.1088/1468-6996/13/4/045007.

- Hajian, A., Müftüoğlu, D., Konegger, T., Schneider, M., Schmid, U., 2019. On the porosification of LTCC substrates with sodium hydroxide. *Composite Part B: Engineering* 157, 14–23.
- Hao, J., Yao, F.-Z., Yuan, O., *et al.*, 2020. Heterogeneous multilayer dielectric ceramics enabled by ultralow-temperature self-constrained sintering. *Journal of the American Ceramic Society* 103, 249–257. doi:10.1111/jace.16704.
- Honkamo, J., Jantunen, H., Subodh, G., Sebastian, M.T., Mohanan, P., 2009. Tape casting and dielectric properties of $\text{Zn}_2\text{Te}_3\text{O}_8$ -based ceramics with an ultra-low sintering temperature. *International Journal of Applied Ceramic Technology* 6, 531–536.
- Hotza, D., Greil, P., 1995. Review: Aqueous tape casting of ceramic powders. *Material Science & Engineering A* 202, 206–217.
- Howatt, G.N., Breckenridge, R.G., Brownlow, J.M., 1947. Fabrication of thin ceramic sheets for capacitors. *Journal of the American Ceramic Society* 30, 237–242.
- Howatt, G.N., Metuchen, N.J., 1948. U.S. Patent US2582993A.
- Huang, W., Li, X., Xue, Y., *et al.*, 2013. Antibacterial multilayer films fabricated by LBL immobilizing lysozyme and HTCC on nanofibrous mats. *International Journal of Biological Macromolecules* 53, 26–31.
- Isapour, A., Kouki, A., 2019. Vertical LTCC integrated rectangular waveguide and transitions for millimeter-wave applications. *IEEE Transactions on Microwave Theory and Techniques* 67, 868–882.
- Joedecke, B., Fritsch, M., Kretzschmar, C., Rebenklaus, L., Michaelis, A., 2009. Development of an AlN HTCC multilayer system with a tungsten cofiring metallization. In: Fraunhofer IKTS (Ed.), *Proceedings of 42nd International Symposium on Microelectronics*. California: Fraunhofer, pp. 304–308. Available at: <http://publica.fraunhofer.de/dokumente/N-131634.html>.
- Joseph, N., Varghese, J., Teirikangas, M., Vahera, T., Jantunen, H., 2019. Ultralow-temperature cofired ceramic substrates with low residual carbon for next generation microwave applications. *ACS Applied Materials & Interfaces* 11, 23798–23807.
- Kähäri, H., Teirikangas, M., Juuti, J., Jantunen, H., 2014. Dielectric properties of lithium molybdate ceramic fabricated at room temperature. *Journal of the American Ceramic Society* 97, 3378–3379.
- Kim, Y.-H., Jang, S.H., Kim, Y.-W., 2019. Joining of silicon carbide ceramics using a silicon carbide tape. *International Journal of Applied Ceramic Technology* 16, 1295–1303.
- Lagos, M.A., Pellegrini, C., Agote, N., *et al.*, 2019. Ti_3SiC_2 -Cf composite by spark plasma sintering: processing microstructure and thermo-mechanical properties. *Journal of European Ceramic Society* 39, 2824–2830.
- Liu, H., Hsu, S., 1996. Fracture behavior of multilayer silicon nitride/boron nitride ceramics. *Journal of American Ceramic Society* 79, 2452–2457.
- Liu, M., Liu, Y., 2019. Multilayer tape casting of large-scale anode-supported thin-film electrolyte solid oxide fuel cells. *International Journal of Hydrogen Energy* 44, 16976–16982.
- Luo, Q., He, B., Liang, M., Kong, A., Li, J., 2017. Continuous transesterification to produce biodiesel under HTCC/ Na_2SiO_3 /NWF composite catalytic membrane in flow-through membrane reactor. *Fuel* 197, 51–57.
- Luo, X.-J., Zhang, B.-L., Li, W.-L., Zhuang, H.-R., 2004. Preparation of aluminum nitride green sheets by aqueous tape casting. *Ceramics International* 30, 2099–2103.
- Luo, X.-J., Zhang, B.-L., Li, W.-L., Zhuang, H.-R., 2005. Comparison of aqueous and non-aqueous tape casting of aluminum nitride substrates. *Journal of the American Ceramic Society* 88, 497–499.
- Ly, Z., Zhang, T., Jiang, D., Zhang, J., Lin, Q., 2009. Aqueous tape casting process for SiC. *Ceramics International* 35, 1889–1895.
- Maria, J.-P., Kang, X., Floyd, R.D., *et al.*, 2017. Cold sintering, status and prospects. *Journal of Materials Research* 32, 3205–3218.
- Mei, S., Yang, J., Xu, X., *et al.*, 2006. Aqueous tape casting processing of low dielectric constant cordierite-based glass-ceramics-selection of binder. *Journal of the European Ceramic Society* 26, 67–71.
- Mistler, R.E., Twinn, E.R., 2000. *Tape Casting: Theory and Practice*. Ohio: The American Ceramic Society.
- Natividad, S.L., Maroto, V.R., Walker, L.S., *et al.*, 2011. Tape casting, continuous, homogenous, flexible tapes of ZrB_2 . *Journal of the American Ceramic Society* 94, 2749–2753.
- Nelo, M., Siponkoski, T., Kähäri, H., *et al.*, 2019. Upside-down composites: Fabricating piezoceramics at room temperature. *Journal of the European Ceramic Society* 39, 3301–3306.
- Olhero, S.M., Ferreira, J.M.F., 2005. Rheological characterisations of water-based AlN slurries for the tape casting process. *Journal of Material Processing Technology* 169, 206–213.
- Park, S.-Y., Saruhan, B., Schneider, H., 2000. Mullite/zirconia laminate composites for high temperature application. *Journal of the European Ceramic Society* 20, 14–15.
- Patel, C., Jadhav, A., Lone, S., *et al.*, 2012. Miniaturization of LTCC based hot plates for gas sensors application. In: *Proceedings of 1st International Symposium on Physics and Technology of Sensors (ISPTS-1)*. Pune: IEEE. doi:10.1109/ISPTS.2012.6260886.
- Piticescu, R.R., Monty, C., Millers, D., 2005. Hydrothermal synthesis of nanostructured materials: Present state and future prospects. *Sensors and Actuators B* 109, 102–106.
- Polotai, A., Breece, K., Dickey, E., Randall, C., Ragulya, A., 2005. A novel approach to sintering nanocrystalline barium titanate ceramics. *Journal of American Ceramic Society* 88, 3008–3012.
- Pourzadi, A., Isapour, A., Kouki, A., 2019. Design of compact dual-band LTCC second-order Chebyshev bandpass filters using a direct synthesis approach. *IEEE Transactions on Microwave Theory and Techniques* 67, 1441–1451.
- Prakasam, M., Valsan, S., Lu, Y., *et al.*, 2018. Nanostructured Pure and Doped Zirconia: Syntheses and Sintering for SOFC and Optical Applications. London: IntechOpen.
- Rabe, T., Schiller, W.A., Hochheimer, T., Modes, C., Kipka, A., 2005. Zero shrinkage of LTCC by self-constrained sintering. *International Journal of Applied Ceramic Technology* 2, 374–382.
- Remiszewska, E., Malecha, K., Kruk, J., *et al.*, 2019. Enzymatic method of urea determination in LTCC microfluidic system based on absorption photometry. *Sensors and Actuators B: Chemical* 285, 375–384.
- Ritter, T., Hagen, G., Kita, J., *et al.*, 2017. Self-heated HTCC-based ceramic disc for mixed potential sensors and for direct conversion sensors for automotive catalysts. *Sensors and Actuators B: Chemical* 248, 793–802.
- Roshni, S.B., Sebastian, M.T., Surendran, K.P., 2017. Can zinc aluminate-titania composite be an alternative for alumina as microelectronic substrate? *Nature Scientific Reports* 7, 1–13. (40839).
- Sahner, K., Wickles, M., Schöner, D., *et al.*, 2005. Strontium aluminate: A novel tape material for HTCC gas sensors. *Funktionskeramik* 82, 170–173. Available at: <http://www.funktionsmaterialien.de/docs/Cfi-HLK-Tagung-2005-A145>.
- Santacruz, I., Vázquez, J.M.P., Losilla, E.R., Aranda, M.A.G., 2011. Preparation of aluminium lanthanum oxyapatite tapes, $\text{La}_{10}\text{AlSi}_5\text{O}_{26.5}$, by tape casting and reaction sintering. *Journal of the European Ceramic Society* 31, 1573–1580.
- Sasidharanpillai, A., Kim, C.H., Lee, C.H., Sebastian, M.T., Kim, H.T., 2018. Environmental friendly approach for the development of ultra-low firing Li_2WO_4 ceramic tapes. *ACS Sustainable Chemistry & Engineering* 6, 6849–6855.
- Sasidharanpillai, A., Sebastian, M.T., Lee, Y., Kim, H.T., 2019. Ultra-low temperature co-fired CaV_2O_6 -glass composite ceramic substrate for microelectronics. *Journal of Materials Science: Materials in Electronics* 30, 7637–7644.
- Schafbauer, W., Menzler, H., Buchkremer, H.P., 2014. Tape casting of anode supports for solid oxide fuel cells at Forschungszentrum Jülich. *International Journal of Applied Ceramic Technology* 11, 125–135.
- Sciti, D., Melandri, C., Bellosi, A., 2004. Properties of ZrB_2 reinforced ternary composites. *Advanced Engineering Materials* 6, 775–781.
- Sebastian, M.T., 2008. *Dielectric Materials for Wireless Communication*. Amsterdam: Elsevier Science.

- Sebastian, M.T., Jantunen, H., 2017. High temperature cofired ceramic (HTCC), low temperature cofired ceramic (LTCC), and ultralow temperature cofired ceramic (ULTCC) materials. In: Sebastian, M.T., Ubig, R., Jantunen, H. (Eds.), *Microwave Materials and Applications*, 2 Volume Set, first ed. West Sussex: Wiley, pp. 355–411.
- Sebastian, M.T., Jantunen, H., 2008. Low loss dielectric materials for LTCC applications: A review. *International Materials Reviews* 53, 57–90.
- Sebastian, M.T., Ubig, R., Jantunen, H., 2015. Low-loss dielectric ceramic materials and their properties. *International Materials Reviews* 60, 392–412.
- Sebastian, M.T., Wang, H., Jantunen, H., 2016. Low temperature co-fired ceramics with ultra-low sintering temperature: A review. *Current Opinion in Solid State and Materials Science* 20, 151–170.
- Shang, Q., Wang, Z., Li, J., *et al.*, 2017. Gel-tape-casting of aluminum nitride ceramics. *Journal of Advanced Ceramics* 6, 67–72.
- She, J., Inoue, T., Ueno, K., 2000. Multilayer $\text{Al}_2\text{O}_3/\text{SiC}$ ceramic with improved mechanical behavior. *Journal of the European Ceramic Society* 20, 1771–1775.
- Shigegaki, Y., Brito, M.E., Hirao, K., Toriyama, M., Kanzaki, S., 1996. Processing of a novel multilayered siliconnitride. *Journal of the American Ceramic Society* 79, 2197–2200.
- Silvestroni, L., Melandri, C., Venkatachalam, V., *et al.*, 2019. Merging toughness and oxidation resistance in a light ZrB_2 composite. *Materials & Designs* 183, 108078. doi:10.1016/j.matdes.2019.108078.
- Silvestroni, L., Sciti, D., 2010. Sintering behavior, microstructure and mechanical properties: A comparison among pressure less sintered ultra refractory carbides. *Advances in Materials Science and Engineering* 2010, 1–11. doi:10.1155/2010/835018.
- Silvestroni, L., Sciti, D., Esposito, L., Glaeser, A.M., 2012. Joining of ultra refractory carbides. *Journal of the European Ceramic Society* 32, 4469–4479.
- Snijkers, F., Wilde, A., Mullens, S., Luyten, J., 2004. Aqueous tape casting of Yttria stabilized zirconia using natural product binder. *Journal of the European Ceramic Society* 24, 1107–1110.
- Song, X., Li, L., Geng, Z., Zhou, L., Ji, L., 2017. Effective and selective adsorption of As(III) via imprinted magnetic $\text{Fe}_3\text{O}_4/\text{HTCC}$ composite nanoparticles. *Journal of Environmental Chemical Engineering* 5, 16–25.
- Szymanowska, P., Nowak, D., Piasecki, T., 2019. Performance evaluation of miniature integrated electrochemical cells fabricated using LTCC technology. *Sensors* 19, 1314. doi:10.3390/s19061314.
- Udovic, M., Valant, M., Suvorov, D., 2001. Dielectric characterisations of ceramics from the $\text{TiO}_2\text{--TeO}_2$ system. *Journal of the European Ceramic Society* 21, 1735–1738.
- Valant, M., Suvorov, D., 2001. Processing and dielectric properties of sillenite compounds $\text{Bi}_{12}\text{MO}_{20}\text{-d}$ ($\text{M} = \text{Si, Ge, Ti, Pb, Mn, B}_{1/2}\text{P}_{1/2}$). *Journal of the American Ceramic Society* 84, 2900–2904.
- Varghese, J., Ramachandran, P., Sobocinski, M., Vahera, T., Jantunen, H., 2019. ULTCC glass composites based on rutile and anatase with cofiring at 400°C for high frequency applications. *ACS Sustainable Chemistry & Engineering* 7, 4274–4283.
- Varghese, J., Siponkoski, T., Sobocinski, M., Vahera, T., Jantunen, H., 2018. Multilayer functional tapes co-fired at 450°C : Beyond HTCC and LTCC technologies. *ACS Applied Materials & Interfaces* 10, 11048–11055.
- Vinci, A., Zoli, L., Sciti, D., *et al.*, 2019. Influence of fiber content on the strength of carbon fiber reinforced HfC/SiC composites up to 2100°C . *Journal of European Ceramic Society* 39, 3594–3603.
- Wang, W., Liu, Z., Zhang, Y., *et al.*, 2019a. A direct carbon solid oxide fuel cell stack on a single electrolyte plate fabricated by tape casting technique. *Journal of Alloys and Compounds* 794, 294–302.
- Wang, L., Tang, G., Xu, Z.-K., 2008. Comparison of water based and solvent based casting for multilayer ZnO varistors. *Journal of American Ceramic Society* 91, 3742–3745.
- Wang, D., Zhou, D., Song, K., *et al.*, 2019b. Cold sintered COG multilayer ceramic capacitors. *Advanced Electronic Materials* 5. doi:10.1002/aeml.201900025.
- Watanabe, T., Zhang, G.-J., Yue, X.-M., *et al.*, 2001. Multilayer composites in $\text{Al}_2\text{O}_3/\text{MoSi}_2$ system. *Materials Chemistry and Physics* 67, 256–262.
- Wonisch, A., Polfer, P., Kraft, T., *et al.*, 2011. A comprehensive simulation scheme for tape casting: From flow behavior to anisotropy development. *Journal of the American Ceramic Society* 94, 2053–2060.
- Ym, H., Cannon, W.R., Shamfield, D.J., 1993. Evolution of carbon during burnout and sintering of tape-cast aluminum nitride. *Journal of the American Ceramic Society* 76, 166–172.
- Yokota, H., Ibukiyama, M., 2001. A high thermal conductive β -silicon nitride substrate for power module. In: Heinrich, J.G., Aldinger, F. (Eds.), *Ceramic Materials and Components for Engine*. Weinheim: Wiley, pp. 499–504.
- Yu, H., Cannon, R., Shamfield, D.J., 1993. Evolution of carbon during burnout and sintering of tape-cast aluminum nitride. *Journal of the American Ceramic Society* 76, 166–172.
- Yu, H., Liu, J., Zhang, W., Zhang, S., 2015. Ultra-low sintering temperature ceramics for LTCC applications: A review. *Journal of Materials Science: Materials in Electronics* 26, 9414–9423.
- Zhang, J.-X., Jiang, D.-L., Tan, S.-H., Gui, L.-H., Ruan, M.-L., 2001. Aqueous processing of titanium carbide green sheets. *Journal of the American Ceramic Society* 84, 2537–2541.
- Zhang, Y., Sanvito, S., 2019. Interface engineering of graphene nano sheet reinforced ZrB_2 composites by tuning surface contacts. *Physical Review Materials* 3, 073604. doi:10.1103/PhysRevMaterials.3.073604.
- Zhang, G.-J., Yue, X.-M., Watanabe, T., 1999. $\text{Al}_2\text{O}_3/\text{TiC}/(\text{MoSi}_2 + \text{Mo}_2\text{B}_5)$ multilayer composites prepared by tape casting. *Journal of the European Ceramic Society* 19, 2111–2116.
- Zhou, D., Pang, L.-X., Wang, D.-W., Reaney, I.M., 2018. BiVO_4 based high k microwave dielectric materials: A review. *Journal of Materials Chemistry C* 6, 9290–9313.
- Zhou, D., Randall, C.A., Baker, A., *et al.*, 2010. Dielectric properties of an ultra-low-temperature cofiring $\text{Bi}_2\text{Mo}_2\text{O}_9$ multilayer. *Journal of the American Ceramic Society* 93, 1443–1446.
- Zhou, J., Zhang, L., Liu, C., *et al.*, 2019. Aqueous tape casting technique for the fabrication of $\text{Sc}_{0.1}\text{Ce}_{0.01}\text{Zr}_{0.89}\text{O}_{2+\Delta}$ ceramic for electrolyte-supported solid oxide fuel cell. *International Journal of Hydrogen Energy* 44, 21110–21114.
- Zhu, J., Yang, Y., Chu, C., Li, S., *et al.*, 2019. 60-GHz High gain planar aperture antenna using low-temperature cofired ceramics (LTCC) technology. In: *Proceedings of 2019 IEEE MTT-S International Wireless Symposium (IWS)*. Guangzhou: IEEE. doi:10.1109/IEEE-IWS.2019.8803920.

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- <http://www.adtechceramics.com/products/htcc>
Adtech Ceramics Company.
- <https://www.dupont.com/products/terminators-and-electrodes-for-capacitors.html>
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Functional Ceramics through Novel Chemical Approaches

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Chemical processing is a promising technique for the synthesis of functional ceramic thin films. Functions of ceramic thin films are predominantly determined by their crystal structure, composition, and microstructure. Precise control of these three fundamental factors is a key to developing high performance. Chemical processing via liquid sources, especially, should be focused on because they have many attractive advantages. The molecular structure of the liquid source should be designed and its reactivity optimized for the hydrolysis reaction, photoreaction and combustion, low-temperature crystallization, and the characteristic microstructure achieved in the ceramic thin film. Furthermore, chemical processing is essential for the integration of ceramic thin films into silicon semiconductors. Integration not only enhances each function, but allows the combination of multi-functions and thus provides unique performance.

Chemical Modification for Porous and Nano-Structured TiO₂ Thin Films

Poly(ethylene glycol) (PEG) can be coordinated to a structure formed by the controlled hydrolysis and polycondensation reactions of titanium tetraisopropoxide chelated with diethanolamine. From the resulting chemically modified precursor solution, anatase coatings consisting of nanometer-sized pores and grains with diameters of about 30 nm, and a preferred orientation along c-axis, can be prepared on quartz glass plates by a dip-coating method. In contrast, anatase coatings consisting of submicron-sized pores and randomly oriented grains can be prepared from the solution in which the PEG has been isolated (**Fig. 1**) (Kato *et al.*, 1996b).

The new roles of PEG in chemical processing have been confirmed. The PEG-derived organic compounds remain in a fixed position in the thin film prepared from the chemically modified titanium tetraisopropoxide solution and heated at temperatures as high as 673 K. It is not until the organic compounds decompose to carbon dioxide and the gas leaves the thin film that the nano-structure – consisting of nano-sized pores and anatase crystallites with preferred orientation – develops at 723 K (**Fig. 2**) (Kato and Nihara, 1997).

Fujishima and Honda (1972) reported that photosensitized electrolytic oxidation of water occurs on the surface of TiO₂ (rutile) single crystals. The reaction, the so-called photocatalytic reaction, was studied during the 1990s for potential application to environmental issues such as the purification and treatment of air and water. The photocatalytic reactions occurring on the surface of TiO₂ depend on this process, which starts from the absorption of light and results in photogenerated electrons and holes at the surface. The photocatalytic process is predominantly determined by the fundamental physical properties of TiO₂. Porous and nano-structured TiO₂ thin films have been examined for the photocatalytic decomposition of aqueous acetic acid, a key reaction for the purification and treatment of water. TiO₂ thin films with a thickness of 500 nm show high photocatalytic activity, which means that aqueous acetic acid (6 wt%) is decomposed in 30 min after irradiation performed using a high-pressure mercury lamp (**Fig. 3**) (Kato *et al.*, 1996a).

A photoelectrochemical solar cell based on dye-sensitized nanocrystalline TiO₂ films has been reported (O'Regan and Gratzel, 1991). The nanocrystalline TiO₂ films consisting of nanometer-sized anatase particles have enhanced geometrical surface area and a thickness of 8–12 μm . Thereby, adsorption of a large amount of the sensitizing dye followed by high energy conversion could be attained. In comparison, porous and nano-structured TiO₂ thin films with a thickness of less than 1 μm adsorb relatively large amounts of the dye and show increased photocurrent densities. This suggests that the amount of adsorbed dye could be adjusted

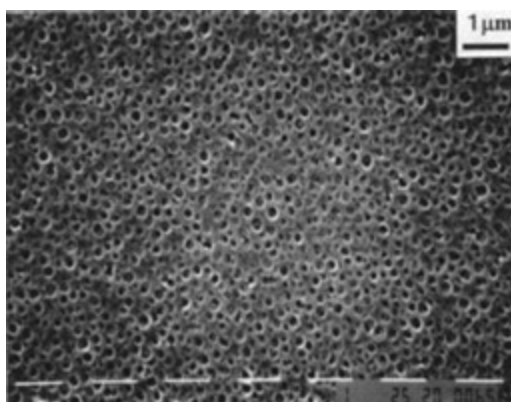


Fig. 1 Scanning electron micrograph of TiO₂ thin film prepared from the solution containing the isolated PEG.

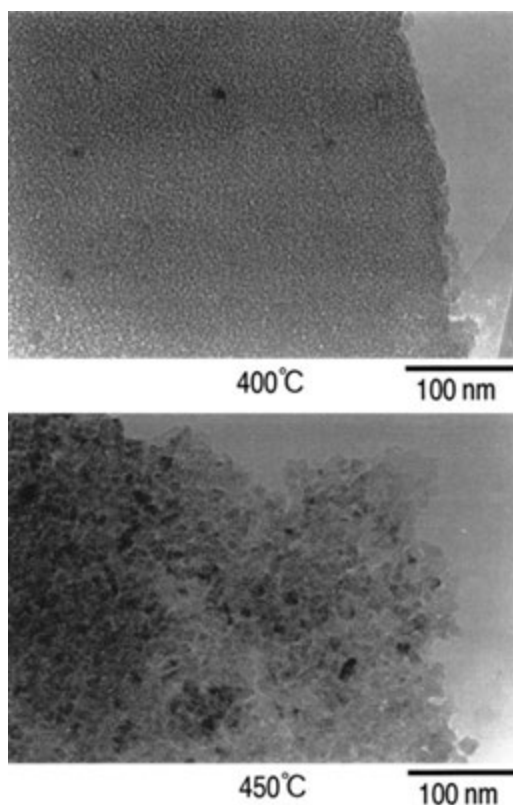


Fig. 2 Transmission electron micrographs of TiO_2 thin films prepared from the chemically modified titanium tetraisopropoxide solution with temperatures (after Kato and Niihara, 1997).

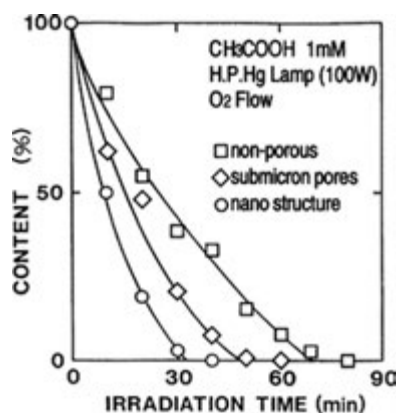


Fig. 3 Photocatalytic activity of TiO_2 thin films with various microstructures: changes in the content of acetic acid with irradiation time.

by controlling both the pore and crystallite sizes and that then even thinner TiO_2 films could show higher performances (Miki *et al.*, 1996).

Hau Ng *et al.* (2010) investigated graphene- TiO_2 nanocomposites synthesized via a solution-based method involving photocatalytic reduction of graphene oxide. Nearly 90% enhancement in the photocurrent was seen as reduced graphene oxide serves as electron collector and transporter. Additionally, the graphene- TiO_2 nanocomposite electrodes exhibited significant activity for the complete photocatalytic decomposition of 2,4-dichlorophenoxyacetic acid (2,4-D). Combined with safe, solution-based synthetic practices, the promising photocurrent and photocatalytic degradation rates provide the framework and motivation for the implementation of graphene- TiO_2 nanocomposites on larger scales. The implementation of graphene- TiO_2 nanocomposites has been shown schematically in the Fig. 4.

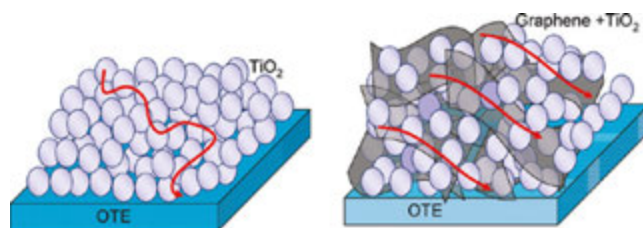


Fig. 4 Schematic diagram of the implementation of graphene-TiO₂ nanocomposites.

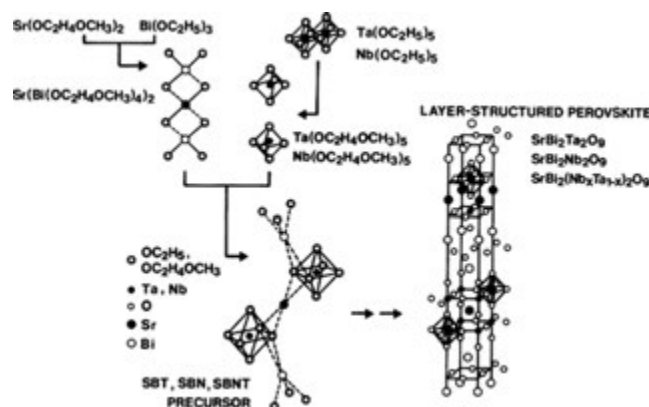


Fig. 5 Chemistry for the formation of SBT and SBN precursors (after Kato *et al.*, 1997a).

Low-Temperature Processing of Layer-Structured Perovskite Thin Films

Thin films of layer-structured perovskite compounds, such as SrBi₂Ta₂O₉ (SBT), SrBi₂Nb₂O₉ (SBN), and SrBi₂(Nb, Ta)₂O₉ (SBNT) are promising materials for nonvolatile ferroelectric memory applications due to their excellent ferroelectric properties – especially with respect to fatigue performance (Araujo *et al.*, 1995). The solid solutions SrBi₂M₂O₉ (where M is Ta or Nb), which are known as Aurivillius compounds, consist of a stack of alternating layers of oxygen octahedra (SrM₂O₇)²⁻ in the c-direction. The high spontaneous polarization is parallel to the plane of the layers (in the a-direction) because this direction contains the O–M–O chains that are known to have high capabilities for polarization, as in perovskite ferroelectrics. It is imperative for these compounds that processing temperatures are lowered to those similar to complementary metal oxide semiconductor (CMOS) technology. In addition, degradation of electrical properties is caused by bottom electrode–thin film interface reactions at relatively high temperatures.

Precursors for layer-structured perovskite thin films of SBT, SBN, and SBNT have been prepared by the reaction of a strontium–bismuth double methoxyethoxide and tantalum or niobium methoxyethoxide in methoxyethanol, followed by partial hydrolysis. Several spectroscopic techniques, such as ¹H-NMR, ¹³C-NMR, ⁹³Nb-NMR, and FTIR spectroscopy, can be used to analyze the arrangement of the metals and oxygen in the precursor molecules. The precursors contain Sr–O–M (where M is Ta or Nb) bonds (i.e., a strontium atom is connected to two MO₆ octahedra) and Sr–O–Bi bonds, with a bismuth atom bonded to the oxygen atoms of the MO₆ octahedron.

The arrangement of metal and oxygen atoms is considered similar to the layer-structured perovskite crystal sublattice (Fig. 5). As a result, the sol–gel derived SBT thin films can be crystallized by rapid thermal annealing in an oxygen atmosphere below 550 °C; they exhibit preferred {115} orientation. The crystallinity improves and the crystallite size increases with temperatures of up to 700 °C. In the case of SBN thin films, a low heating rate (2 °C min⁻¹) is necessary to control the crystallographic {115} orientation, whereas a rate of 200 °C s⁻¹ (rapid thermal annealing) produces films that exhibit c-axis orientation. The {115} SBT thin film exhibits improved ferroelectric properties when heated to 700 °C (Kato *et al.*, 1998). A SBT thin film annealed at 700 °C does not show fatigue after 10¹⁰ cycles of switching (Fig. 6).

A film deposited from the complex ethoxide solution, and then calcined at 250 °C in the mixture of water vapor and oxygen flow, contains a relatively smaller amount of the remaining alkoxy groups (Kato, 1998). It therefore crystallizes to SBT via rapid thermal annealing at temperature below 500 °C in an oxygen flow. Crystallinity improves significantly and the microstructure develops up to 650 °C. Remarkable grain growth is observed, particularly in the SBT thin film deposited from the ethanolic solution of the complex ethoxide. Film annealed at 650 °C exhibits saturated P–E hysteresis loop and improved endurance behavior.

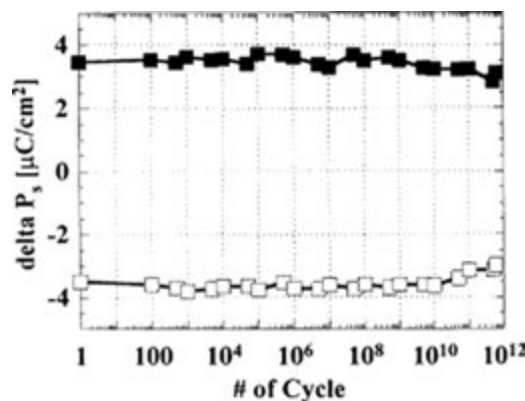


Fig. 6 Fatigue behavior of a Pt/SBT/Pt capacitor (after Kato *et al.*, 1997a).

Wang *et al.* (2013) reported a low-cost, solution-based deposition procedure utilizing nanocomposites of graphene and TiO_2 nanoparticles as the electron collection layers in meso-superstructured perovskite solar cells. The graphene nano flakes provide superior charge-collection in the nanocomposites, enabling the entire device to be fabricated at temperatures no higher than 150°C . The solar cells showed remarkable photovoltaic performance with power conversion efficiency up to 15.6%. The work demonstrates that graphene/metal oxide nanocomposites have the potential to contribute significantly toward the development of low-cost solar cells.

You *et al.* (2014) adopted a low-temperature processing technique to attain high-efficiency devices in both rigid and flexible substrates, using device structure substrate/ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ /PCBM/Al, where PEDOT:PSS and PCBM are used as hole and electron transport layers, respectively. Mixed halide perovskite, $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$, was used due to its long carrier lifetime and good electrical properties. All of these layers are solution-processed under 120°C . Based on the proposed device structure, power conversion efficiency (PCE) of 11.5% is obtained in rigid substrates (glass/ITO), and a 9.2% PCE is achieved for a polyethylene terephthalate/ITO flexible substrate.

UV-Processing of Perovskite Solid-Solution Thin Films

Potassium tantalate niobate ($\text{KTa}_x\text{Nb}_{1-x}\text{O}_3$) (KTN) has a perovskite structure, and is a solid solution of potassium tantalate (KTaO_3) and potassium niobate (KNbO_3). The ferroelectric properties of KTN can be controlled by the Ta/Nb ratio, since the Curie temperature of KTN varies almost linearly with the Ta/Nb ratio (Trieblwasser, 1959). KTN has attracted much attention for its potential application in optoelectronics and integrated optics because it has large electrooptic and nonlinear optic effects (Orlowski *et al.*, 1980). The fabrication of a KTN waveguide is one of the key techniques for its application to integrated optics.

KTN thin films have been prepared by the chemical solution deposition method. KTN precursors consist of $\text{K}[\text{Ta}(\text{OC}_2\text{H}_5)_6]$ and $\text{K}[\text{Nb}(\text{OC}_2\text{H}_5)_6]$, with interaction at a molecular level. Perovskite KTN thin films with the desired composition Ta/Nb = 65/35, 50/50, and 35/65 have been synthesized from precursor solutions by the dip-coating method. KTN thin films with {100} preferred orientation have been successfully deposited on $\text{MgO}\{100\}$ and $\text{Pt}\{100\}/\text{MgO}\{100\}$ substrates.

X-ray pole figure measurements show that grains of KTN thin films have a prominent three-dimensional regularity on $\text{MgO}\{100\}$ and $\text{Pt}\{100\}/\text{MgO}\{100\}$ surfaces. The Curie temperatures of KTN films decrease with increasing Ta/Nb ratio. Typical P-E hysteresis loops were observed for the three compositions of KTN thin films on $\text{Pt}\{100\}/\text{MgO}\{100\}$ substrates. The values of remanent polarization (P_r) of KTN thin films increase as the Ta/Nb ratio changes from 65/35 to 35/65 (Fig. 7) (Suzuki *et al.*, 1999a).

UV-processing has been used for the patterning of ceramic films. The ligands should be chosen carefully as the use of large organic ligands degrades the electrical properties of resultant films. Patterned $\text{KTa}_{0.50}\text{Nb}_{0.50}\text{O}_3$ (KTN50) thin films with a {100}-preferred orientation have been successfully crystallized at 700°C on $\text{MgO}\{100\}$ substrates. Both benzoylacetone (BZAC)-modified KTN precursor and 2-ethoxyethanol (EGMEE)-modified KTN precursor films show charge-transfer UV absorption. The decrease in CH and CO absorptions in the IR spectra for the EGMEE-modified precursor is more rapid than that in the BZAC-modified precursor. Perovskite KTN films with a prominent {100} orientation crystallize at 700°C on $\text{MgO}\{100\}$ substrates from both systems.

However, the epitaxy of KTN films from the EGMEE-modified precursor combined with UV treatment is better than that from the BZAC-modified precursor. The optical transmittance of KTN films from the EGMEE-modified precursor shows a better interference fringe than that from the BZAC-modified precursor. UV-treated KTN films on $\text{Pt}\{100\}/\text{MgO}\{100\}$ substrates are derived from the EGMEE-modified precursor reveal the highest dielectric constant and the lowest loss (Fig. 8). According to scanning electron microscopy (SEM) observation, patterned KTN films from the EGMEE-modified precursor have a smooth and pore-free surface (Suzuki *et al.*, 1999b).

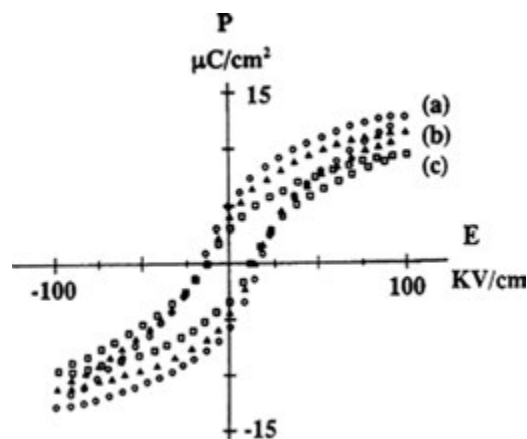


Fig. 7 P-E hysteresis curves of KTN films on Pt(100)/MgO(100) substrates at $-180\text{ }^{\circ}\text{C}$: (a) KTN35 film, (b) KTN50 film, (c) KTN65 film.

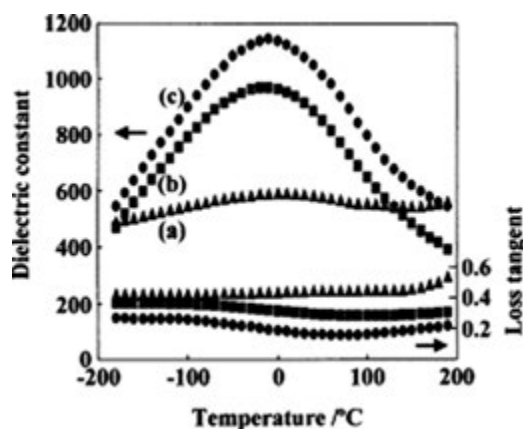


Fig. 8 Changes in dielectric constant and loss tangent with temperature for KTN50 films crystallized at $700\text{ }^{\circ}\text{C}$ on Pt(100)/MgO(100) substrates: (a) KTN50 films from BZAC-modified precursor with UV irradiation, (b) KTN 50 films from EGME-modified precursor without UV irradiation, and (c) KTN50 films from EGME-modified precursor with UV irradiation.

Taylor (2010) reported the preparation of $(1-x)$ PMN- x PT ceramics with $x=0.28 - 0.32$ in pure phase using a novel chemical solution method. The ceramics displayed better piezoelectric properties compared to those prepared by conventional solid state method. To optimize the ceramic properties, the effect of high temperature poling was investigated, and it was found that poling at high temperature degraded the piezoelectric properties due to an electric field induced phase transition. The same solution method was used to fabricate ceramics of $(1-x)$ PMN- x PT with $x=0.07$ and 0.10 which exhibit their maximum of permittivity near room temperature. A sintering temperature of $1100\text{ }^{\circ}\text{C}/4\text{hrs}$ was required in order to obtain high density, reduce dielectric losses, and increase the dielectric permittivity in order to optimize capacitive performance. The solid solution between $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) and $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ (BZT) was investigated for its structure and dielectric behavior. The addition of BZT to PMN did not change the structure significantly and it remained cubic to the solubility limit of $0.725\text{ PMN}-0.275\text{ BZT}$. The dielectric properties exhibit an increase in frequency and temperature dispersion with increasing BZT content, indicating an increase in relaxor behavior. The $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3\text{-Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ solid solution was prepared in order to explore its structure, dielectric, ferroelectric, and piezoelectric properties as a function of composition for use in high TC piezoelectric applications. The structure and properties were mapped as a function of composition to establish the ternary phase diagrams of this system for its structure, dielectric, and piezo-/ferroelectric properties.

Conclusion

Chemical modification and processing of different thin films have been discussed. KTN thin films have been prepared by the chemical solution deposition method. UV-processing has been used for the patterning of ceramic films. The epitaxy of KTN films from the EGME-modified precursor combined with UV treatment is better than that from the BZAC-modified precursor. The

optical transmittance of KTN films from the EGMEE-modified precursor shows a better interference fringe than that from the BZAC-modified precursor. Patterned KTN films from the EGMEE-modified precursor have a smooth and pore-free surface.

References

- Araujo, C.A., Cuchiari, J.D., McMillan, L.D., Scott, M.C., Scott, J.F., 1995. Fatigue-free ferroelectric capacitors with platinum electrodes. *Nature* 374, 627–629.
- Fujishima, A., Honda, K., 1972. Electrochemical photolysis of water at a semiconductor electrode. *Nature* 238, 37–38.
- Hau Ng, Y., Lightcap, I.V., Goodwin, K., MTCG-Sumura, M., Kamat, P.V., 2010. To what extent do graphene scaffolds improve the photovoltaic and photocatalytic response of TiO_2 nanostructured films. In *J. Phys. Chem. Lett. American Chemical Society*. 1, 2222–2227.
- Kato, K., 1998. Low-temperature synthesis of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ferroelectric thin films through the complex alkoxide method: effects of functional group, hydrolysis and water vapor treatment. *Jpn. J. Appl. Phys* 37, 5178–5184.
- Kato, K., Niihara, K., 1997. Roles of polyethylene glycol in the evolution of nanostructure in TiO_2 coatings. *Thin Solid Films* 298, 76–82.
- Kato, K., Torii, Y., Taoda, H., 1996a. TiO_2 coating photocatalysts with nanostructure and preferred orientation showing excellent activity for decomposition of aqueous acetic acid. *J. Mater. Sci. Lett.* 15, 913–915.
- Kato, K., Tsuge, A., Niihara, K., 1996b. Microstructure and crystallographic orientation of anatase coatings produced from chemically modified titanium tetraisopropoxide. *J. Am. Ceram. Soc.* 79, 1483–1488.
- Kato, K., Zheng, C., Dey, S.K., Torii, Y., 1997a. Chemistry of the alkoxy-derived precursor solutions for layer-structured perovskite thin films. *Integr. Ferroelectr.* 18, 225–235.
- Kato, K., Zheng, C., Finder, J.M., Dey, S.K., Torii, Y., 1998. Sol–gel route to ferroelectric layer-structured perovskite $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{SrBi}_2\text{Nb}_2\text{O}_9$ thin films. *J. Am. Ceram. Soc.* 81, 1869–1875.
- Miki, T., Igarashi, K., Taoda, H., *et al.*, 1996. Application of TiO_2 films prepared by the chemically modified alkoxide method to dye-sensitized solar cell. *Proc. Int. Symp. Optical materials technology for energy efficiency and solar energy conversion*, pp. 381–384.
- O'Regan, B., Gratzel, M., 1991. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films. *Nature* 353, 737–740.
- Orlowski, R., Boatner, L.A., Kratig, E., 1980. Photorefractive effects in the cubic phase of potassium tantalate niobate. *Opt. Commun.* 35, 45–48.
- Suzuki, K., Sakamoto, W., Yogo, T., Hirano, S., 1999a. Dielectric and pyroelectric properties of alkoxy-derived $\text{KTa}_{0.35}\text{Nb}_{0.65}\text{O}_3$ thin film. *Jpn. J. Appl. Phys* 38, 5953–5957.
- Suzuki, K., Sakamoto, W., Yogo, T., Hirano, S., 1999b. Processing of oriented $\text{K}(\text{Ta}, \text{Nb})\text{O}_3$ films using chemical solution deposition. *J. Am. Ceram. Soc.* 82, 1463–1466.
- Taylor, N.H., 2010. *Synthesis and Characterization of Complex Perovskite Solid Solutions*. Spring: Simon Fraser University.
- Triebwasser, S., 1959. Study of ferroelectric transition of solid-solution single crystal of KNbO_3 – KTaO_3 . *Phys. Rev.* 114, 63–70.
- You, J., Hong, Z., Yang, Y.M., 2014. *Low-Temperature Solution-Processed Perovskite Solar Cells with High Efficiency and Flexibility*. ACS Publications.
- Wang, J.T.-W., Ball, J.M., Barea, E.M., 2013. Low-temperature processed electron collection layers of graphene/ TiO_2 nanocomposites in thin film perovskite solar cells. In: *Nano Lett.* 14, ACS publications. pp. 724–730.

Further Reading

- Kato, K., Finder, J.M., Dey, S.K., Torii, Y., 1997b. Low-temperature crystallization and ferroelectric properties of sol–gel derived layer-structured perovskite thin films. *Integr. Ferroelectr.* 18, 237–247.
- Suzuki, K., Sakamoto, W., Yogo, T., Hirano, S., 1999c. UV processing of oriented $\text{KTa}_{0.50}\text{Nb}_{0.50}\text{O}_3$ thin films. *J. Ceram. Soc. Jpn.* 107, 1032–1036.

Overview: Bioceramics and Bioreactive Glasses

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The living being is a complex system integrating a large number of functions. Over the course of life, depending on accidents, illnesses, natural wear, etc. some functions deteriorate. Within certain limits, the body can react on its own and restore (sometimes only partially) the affected function. Nevertheless, with the global increase in aging human populations and the desire to maintain essential functions as efficiently as possible, the need for corrective procedures increases.

Among the materials likely to be involved in such procedures are metals, polymers, ceramics and glasses. Ceramics and glasses exhibit extremely varied and exceptional properties that have enabled them to be widely used for over a century in a series of various industrial fields. The use as a material in medicine has particularly accelerated over the past 50 years. From the earliest biomedical applications to date, research has also focused on understanding the relationships between composition, process, structure, texture, microstructure and resulting properties, which has enabled significant advances in terms of clinical performance.

The majority of developments are today found in the replacement or repair of hard tissue (bones, teeth), but not only. On the one hand, procedures such as total hip and knee replacements, bone reconstructions and spinal fusions, resulting from conditions such as articular cartilage degeneration and osteoporosis are today largely used. On the other hand, commercial calcium phosphate composites and glasses for bone regeneration are available, but restricted to applications that require only moderate load bearing abilities. High toughness bioinert materials are used in the articulating couple of artificial joint implants, but they do not induce direct bone/material interfaces or bond. The research is therefore focused on tough and strong materials with the ability to create a biologically relevant interface with bone.

This section of the Encyclopedia of Materials: Technical Ceramics and Glasses is specifically devoted to “*Bioceramics and Bioglasses*”. It includes five subsections:

- A. The first subsection (4 chapters) focuses on the main areas of application: after an introductory chapter describing the different properties of bones and another giving an overview of natural and synthetic bone substitutes, new trends, on the one hand in orthopedics, on the other hand in dentistry are described and discussed.
- B. The second part (5 chapters) focuses on inert bioceramics, it includes description of oxide, non oxide and carbon based materials. The two last chapters deal more precisely with zirconia (Y-TZP) and with zirconia toughened alumina composites (ZTA). Zirconia, which shows extremely favorable properties, has been primarily largely used in orthopedic. However, when the phenomenon of low temperature degradation in the presence of aqueous media was discovered, less sensible alumina-zirconia composites were tested and are now predominantly used in orthopedics, whereas TZP materials are now more and more utilized as crowns and even as implants in dentistry.
- C. The third subsection is devoted to bioreactive ceramics and glasses (7 chapters). The goal of such materials is to induce or simply to allow bone regeneration by providing (through complex mechanisms) a mineral source of calcium and phosphate to the bone/material interfaces. Calcium phosphate composites (hydroxyapatite, beta-TCP and derivatives) as well as bioreactive glasses (containing Ca and P) are restricted to applications that require only moderate load bearing abilities. After a first chapter giving an introduction on phosphate chemistry, it is successively treated: (1) a general overview of apatitic and tricalcic calcium phosphate bioceramics and (2) their applications in biomedical engineering. Ca and P are also key components of bioreactive glass compositions and of course of calcium phosphate cements (2 chapters). The 2 last chapters are focused on the use of the calcium phosphate materials in regenerative medicine and more precisely on the use of scaffolds in the regeneration of bones.
- D. The fourth part of this section aims to illustrate the progress made so far in the context of bone imitation. Most of the material processes, presented in the introductory chapter, play on the architecture and composition of ceramic and glass scaffolds. A chapter is devoted to bioactive and bioresorbable ceramic-polymer composites. The following three chapters deal with the interfaces between bones and biomaterials, either by different surface treatments, or by functionalization of the ceramic, also by projection of biomaterials on the surface of metal devices used in surgery. Another chapter presents the use of mathematical modeling to design suitable scaffolds. Finally, the last chapter illustrates very original approaches to prepare new generation bioceramics allowing an increased cellular response.
- E. The fifth subsection provides an overview of characterization techniques for bioceramics and bioreactive glasses. In four chapters, readers will have complete information on the mechanical testing of bioceramics and bioreactive glasses for both orthopedics and dentistry; a description of in vitro and in vivo tests and their biological evaluation; and finally a discussion on the clinical and biological aspects of the use of zirconia in dentistry.

Bone as a Material: Lessons From Nature

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Introduction: Bone Composition

Bone is a composite material made up of an organic phase and a mineral phase (Currey, 1984). The organic phase of bone tissue comprises a matrix formed by the collagen protein, other “non-collagenous” proteins (NCPs), water, lipids and cells, which together represent approximately 35% of the entire bone mass. The mineral phase of bone is mostly comprised of calcium and phosphorous in the form of hydroxyapatite crystals and accounts for 25% of bone volume and 65% of bone mass, and imparts mechanical integrity, compressive strength and hardness to bone tissue and thereby enables the load bearing and resistance to fracture by the skeleton. The quantity and mechanical integrity of each phase, their structural organization and interactions, determine the unique properties of bone.

Collagen

Collagen is the most abundant protein of the organic phase (90%) and forms the underlying matrix and provides a critical role in defining bone shape and structural integrity. This matrix of collagen ultimately provides the structure upon which other proteins and mineral crystals can be anchored (Glimcher, 1959).

The basic structural unit of collagen is tropocollagen, a triple helix molecule composed of three polypeptide strands (alpha chains) twisted together into a right handed coil. Covalent cross-links, comprised of pyridinium and pyrrole proteins, stabilize these collagen fibrils by forming bridges between non-helical regions and helical regions of adjacent collagen molecules. A collagen fiber is characterized by a staggered arrangement of cross-linked tropocollagen molecules, see Fig. 1. Within bone tissue these collagen fibers are organized into concentric layers known as lamellae, within which they are arranged parallel to one another. Fibrils located in adjacent lamellae are aligned at an angle of up to 90° relative to each other. This complex organization of tropocollagen molecules at the nanoscale and lamellae of collagen fibers at the microscale, determine the tensile strength, elasticity and toughness of bone (Ascenzi and Bonucci, 1976). There are approximately 28 different forms of collagen, each named with Roman numerals (I-XXVII), which are characterized by the arrangement of the tropocollagen molecules and fibrils in their collagen structure. For instance, collagen type I has a heterotrimeric structure with one polypeptide chain that is not identical to the others whereas collagen type III has a homometric triple helix structure, which is made up of three identical alpha chains. Approximately 95% of the collagen in bone is type I but type III, IV and VI are also present.

Mineral

The basic unit of bone mineral are small crystals of hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), which are formed by osteoblasts cells, when calcium and phosphate ions bind to one another in the presence of NCPs, such as osteopontin and bone sialoprotein,

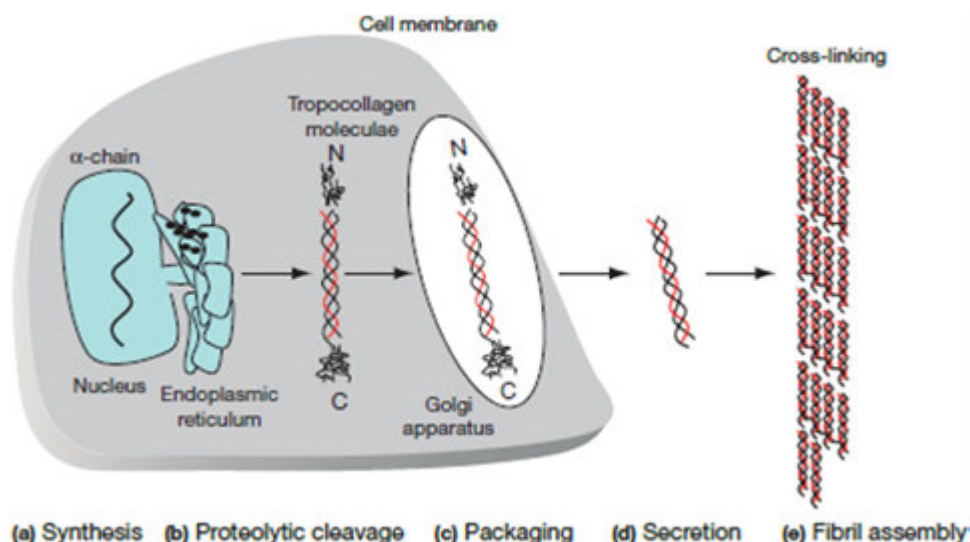


Fig. 1 Intracellular synthesis and assembly of type I collagen in the osteoblast (a)-(c) and extracellular formation of collagen fibrils (d)-(e). Reproduced from McNamara, L., 2011. Chapter 2.210 – Bone as a material. In: Ducheyne, P. (Ed.), Comprehensive Biomaterials, Oxford: Elsevier.

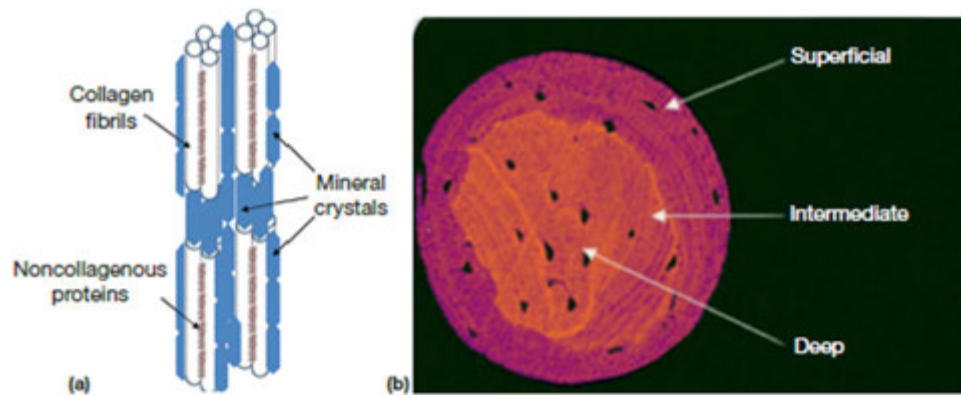


Fig. 2 (a) Distribution of mineral and noncollagenous proteins within and between collagen fibrils and (b) color-enhanced image depicting trabecular tissue mineral heterogeneity; mineral content is lower in the superficial region. Reproduced from McNamara, L., 2011. Chapter 2.210 – Bone as a material. In: Ducheyne, P. (Ed.), *Comprehensive Biomaterials*, Oxford: Elsevier.

during a process called nucleation. This nucleated hydroxyapatite crystal gradually grows in size as further calcium and phosphate ions are added to the crystal cluster overtime (Cowin, 2001). A series of gaps and channels exist within the collagen matrix providing space for deposition and growth of plate like-crystals, which are orientated parallel to the collagen fibers in the underlying matrix, see Fig. 2(A). The crystal size and distribution are dependent on the matrix dimensions and unoccupied voids throughout the structure (Cowin, 2001; Hassenkam *et al.*, 2004; Paschalis *et al.*, 1996). Studies using various microscopy techniques have observed heterogeneous mineral distribution in trabecular tissue, which is partly explained by the adaptive bone remodeling process (Brennan *et al.*, 2011a; Camacho *et al.*, 1999; Derx and Birkenhager-Frenkel, 1995; Gadeleta *et al.*, 2000; Obrant and Odselius, 1984; Roschger *et al.*, 2008). In the case of trabecular bone, this remodeling occurs at the trabecular surface ($\sim 25 \mu\text{m}$) where the tissue often has low mineral content, as remodeling does not allow adequate time for complete tissue mineralization. The tissue at the center of the trabecula is not affected by remodeling and the tissue mineral content increases overtime. This results in a heterogeneous mineral distribution throughout trabecular tissue, see Fig. 2(B).

Binding of a non-collagenous protein, called osteocalcin (see Section “Non-collagenous proteins and cells” below), to the matrix surface can prevent crystal formation through blocking nucleation sites (Boskey *et al.*, 1993; Poundarik *et al.*, 2018). The rate of mineralization can also be affected by alterations in the local ionic concentration. These processes regulate the development of inorganic mineral crystals throughout bone tissue (Cowin, 2001). The degree of bone mineral is substantially different between distinct anatomical sites and between different people, especially gender and age-dependent differences have been reported. Bone mineral content is typically increasing with age, until 60 years of age, when the mineral content begins to decrease in both men and women (Currey *et al.*, 1996), altering the stiffness and strength of bone tissue. Conversely, bone tissue with high mineral content is more brittle and susceptible to more extensive crack propagation, which in turn dramatically reduces bone toughness and impact strength. Genetic disorders which impact the organization of the underlying collagen structure can affect the mineral composition in bone tissue.

Non-Collagenous Proteins and Cells

Non-collagenous proteins make up 10% of the bone organic phase and have multiple functions in the bone extracellular matrix (ECM), which affect bone matrix formation, matrix quality and mechanical properties. These non-collagenous proteins bind adjacent collagen fibrils in mineralized tissue, via Ca^{2+} mediated bonds. They undergo reversible rupture and have been proposed to act as “sacrificial bonds” (Fig. 3), whereby the mechanical energy dissipated due to rupture prevents stresses from reaching levels that could delaminate the bone matrix and therefore contributes to bone fracture toughness (Fantner *et al.*, 2007, 2005, 2006; Hansma *et al.*, 2005; Thurner *et al.*, 2007, 2009).

Osteocalcin (OC) is the most abundant NCP in bone tissue and is known to regulate the growth of bone mineral crystals, without impairing the mineralization process involved in initial bone formation. Osteocalcin is required for bone mineral maturation (Boskey *et al.*, 1998) and reduced osteocalcin levels may contribute to decreases in bone mineral content and stiffness (Berezovska *et al.*, 2019). Osteonectin, a protein found predominantly in trabecular bone, is believed to facilitate binding between bone mineral and the collagen matrix, and is proposed to act to commence the active mineralization of bone tissue (Termine *et al.*, 1981). Osteonectin deficiency results in severely depleted trabecular bone (Ducy *et al.*, 1996), while cortical bone has compromised matrix quality (Boskey *et al.*, 2003) and decreased strength and stiffness in 3-point bending (Beamer *et al.*, 1996; Delany *et al.*, 2000). Fibronectin (FN) is a glycoprotein which is critical to bone formation and function, as it is expressed at high levels by bone forming cells (Jia *et al.*, 2002; Robey and Termine, 1985; Young, 2003). Studies suggest that FN is essential for collagen type I accumulation (Dallas *et al.*, 2005; McDonald, 1988; Sottile and Hocking, 2002) and therefore may have an impact on the quality and organization of bone collagen matrix (Singh *et al.*, 2010). Thrombospondin-2 (TSP2) has been found to play an important

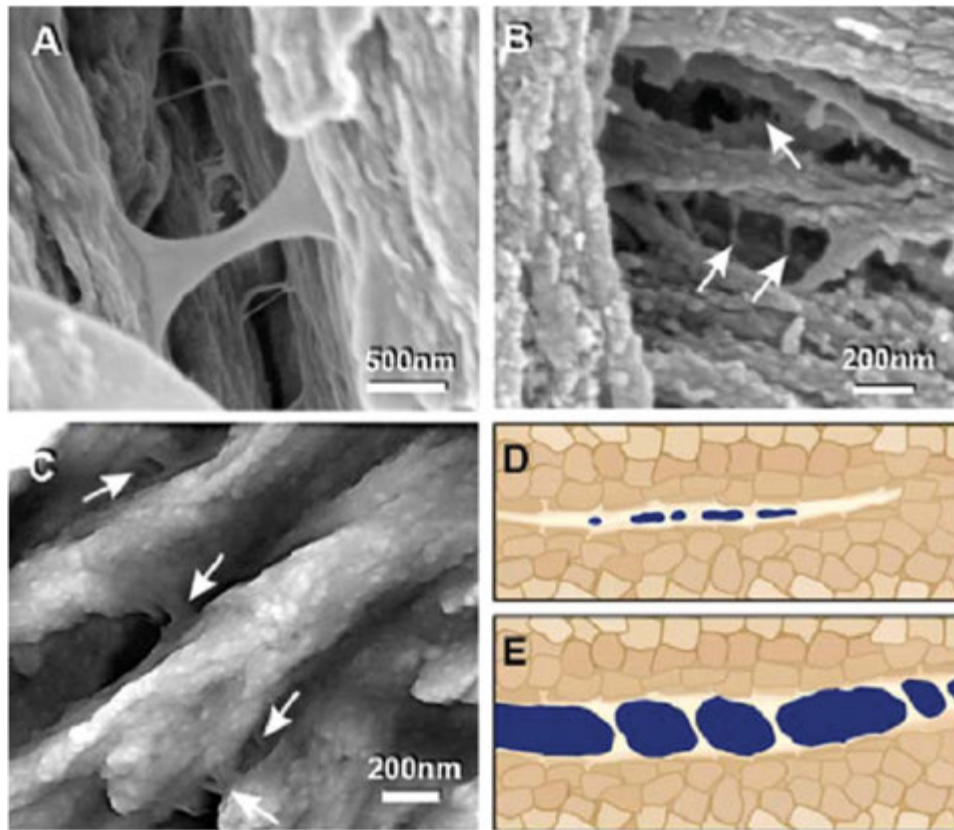


Fig. 3 High resolution Scanning Electron Micrographs (A & B) and AFM (C) show NCPs resisting fracture in bone. Schematic (D) represents the two adjacent mineralized collagen fibers successfully bind to one another via NCPs and (E) represents the NCPs resisting the formation of microcracking (open access material under the “Creative Common License CC BY-NC-SA 4.0”, see more detail at: <http://creativecommons.org/licenses/by-nc-sa/4.0/>). Reproduced from Hansma, P.K., Fantner, G.E., Kindt, J.H., *et al.*, 2005. Sacrificial bonds in the interfibrillar matrix of bone. *Journal of Musculoskeletal & Neuronal Interactions* 5, 313–315.

role in the development of the collagen matrix (Alford *et al.*, 2013; Manley *et al.*, 2015) and therefore has an impact on the mechanical integrity of bone tissue. In fact, femoral cortical bone from TSP2-deficient mice consisted of a defective organic matrix, which exhibited brittle material behavior through reduced post-yield ductility (Manley *et al.*, 2015). Recent studies have demonstrated that Osteopontin (OPN), bone sialoprotein (BSP) and dentrin matrix protein-I (DMP1) proteins, have a direct influence on the mechanical properties of bone. In fact, OPN deficiency has been shown to compromise the resistance to crack propagation, decrease the matrix elastic modulus and increase calcium variability in cortical bone (Turner *et al.*, 2010).

Bone tissue is created and its strength is sustained by a number of bone cells, which comprise approximately 5% of the tissue mass. These cells are comprised of 70% water with the remaining 30% containing varying proportions of structural and functional molecules such as proteins, DNA, and lipids.

Bone Hierarchical Organization

The intricate multiscale organization of the organic and mineral phases and the interaction between these phases, provides bone with impressive strength, stiffness and fracture toughness, while it is still a lightweight material. Bone has a complex hierarchical structure characterized by many functional units from the nanostructure to the macrostructure.

There are two types of bone tissue at the macrostructural level, cortical (or compact) bone and trabecular (or cancellous or spongy) bone, as shown in Fig. 4. Cortical bone is very dense as it has a low porosity of 5%–10%. It forms the thin protective shell surrounding the metaphysis and epiphysis of long bones, the outer shell of the vertebra, scapula and pelvis and the hollow cylindrical shaft for the diaphysis of long bone. At the micro-scale cortical bone is made up of functional units known as osteons. These are cylindrical structures that contain a central blood vessel in the Haversian canal, which is surrounded by concentric rings of osteocyte cells.

Trabecular bone, is mainly found within the metaphysis and epiphysis of long bones or within the central space of flat bones such as vertebrae, and is characterized by a high porosity (75%–95%) and a network of interconnected rods and plates called trabeculae. The majority of trabeculae are orientated along the same direction as the predominant mechanical stresses imparted on

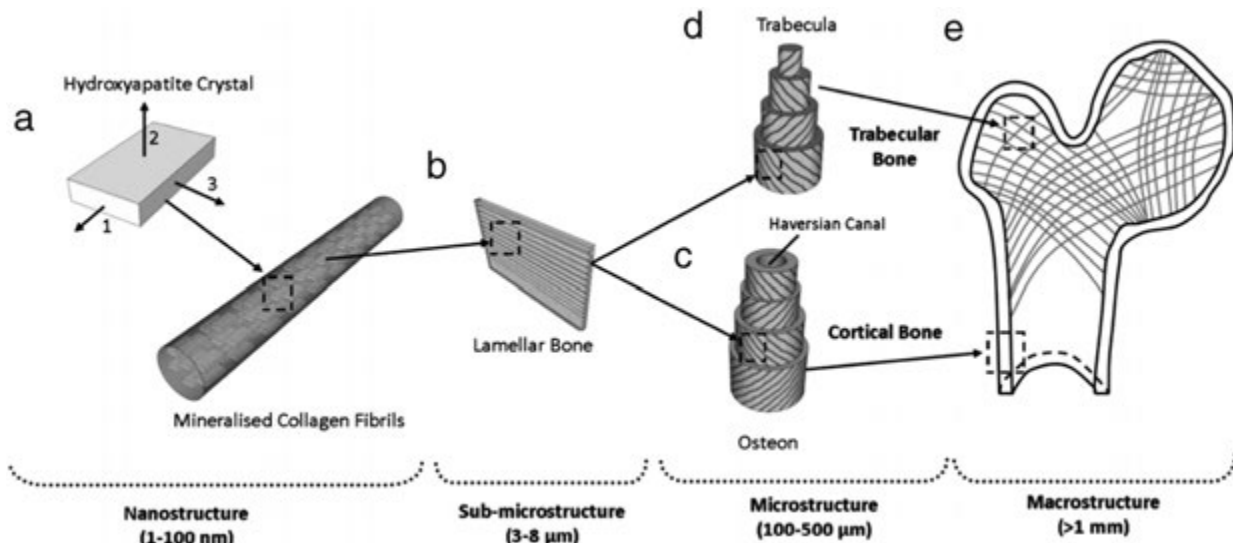


Fig. 4 Hierarchical structural of bone. Reproduced from Vaughan, T.J., McCarthy, C.T., McNamara, L.M., 2012. A three-scale finite element investigation into the effects of tissue mineralisation and lamellar organisation in human cortical and trabecular bone. *The Journal of the Mechanical Behavior of Biomedical Materials* 12, 50–62.

bone (Frost, 1994; Wolff, 1986). On this basis, it has long been proposed that trabecular bone is organised so that internal stresses are distributed to the surrounding cortical bone (Rudman *et al.*, 2006), thereby enabling structural strength while minimizing bone mass (Wolff, 1986).

Mechanical Behavior of Bone

As a consequence of the complex hierarchical structure of bone, it is necessary to examine bone at various length scales to understand its mechanical behavior, specifically by conducting whole bone, structural-level and tissue-level characterization. Whole bone testing is conducted through traditional techniques, such as 3 or 4 -point bending (Akhter *et al.*, 2001) or compression testing (Akhter *et al.*, 2001; Lane *et al.*, 2006), to approximate the bones mechanical behavior at the organ level. However, mechanical properties at the organ level are influenced by the loading direction, bone geometry (which is unique at each anatomical region) and bone mass and therefore do not provide sufficient understanding of the bone as the material level. Furthermore, whole bone testing, describes mechanical behavior at the highest level of a complex hierarchical structural and therefore does not account for local material variation.

Structural Mechanical Behavior of Bone

The structural mechanical properties of cortical and trabecular bone are highly dependent on bone mass, 3D architecture and porosity, which vary considerably depending on the anatomical location and age of the tissue. Hence, the structural mechanical properties do not represent bone mechanical behavior at the material level and are often referred to as “apparent” mechanical properties. Engineering test methods such as uniaxial tension, uniaxial compression, torsion, tensile and compressive fatigue and 3 point bending have been conducted on millimeter-scale specimens of cortical and trabecular bone, to establish the influence of porosity, microarchitecture and bone mass on the structural mechanical behavior of bone (Carter *et al.*, 1981; Chang *et al.*, 1999; Ding *et al.*, 2002; Dong and Guo, 2004; Evans, 1976; Goldstein *et al.*, 1983; Hayes and Carter, 1976; Jepsen *et al.*, 1999; Keaveny *et al.*, 1993, 1997, 1994, 1999; Kopperdahl and Keaveny, 1998; Kopperdahl *et al.*, 2000; Kotha and Guzelsu, 2003; McCalden *et al.*, 1997; Mirzaali *et al.*, 2016; Morgan *et al.*, 2001; Nicholson *et al.*, 1997; Pattin *et al.*, 1996; Schaffler and Burr, 1988; Schwiedrzik *et al.*, 2017; Wachter *et al.*, 2001; Zioupos and Currey, 1998; Zioupos *et al.*, 2001).

As a result of the alignment of collagen and organization of bone tissue, the mechanical properties of cortical bone vary with the loading direction, whereby the cortical bone material is stiffer along the long axis of bone (14–22 GPa) (Carter *et al.*, 1981; Dong and Guo, 2004; Evans, 1976; Kotha and Guzelsu, 2003; Mirzaali *et al.*, 2016; Pattin *et al.*, 1996; Reilly and Burstein, 1975; Schaffler and Burr, 1988; Zioupos and Currey, 1998; Zioupos *et al.*, 2001) when compared to the reported mechanical properties (6–10 GPa) for samples tested in the transverse direction (Dong *et al.*, 2012; Dong and Guo, 2004; Reilly and Burstein, 1975). Apparent yield strength of cortical bone has been reported as 115 MPa in compression (Mirzaali *et al.*, 2016) and 72–129 MPa in tension (Carter *et al.*, 1981; Mirzaali *et al.*, 2016). The apparent ultimate strength values reported for cortical bone indicate that the

material is more resistant to fracture under compression (205 MPa) (Reilly and Burstein, 1975) and bending (158–191 MPa) (Zioupou and Currey, 1998; Zioupou *et al.*, 2001) and is weaker under tension (93–140 MPa) (Carter *et al.*, 1981; Evans, 1976; Kotha and Guzelsu, 2003; Mirzaali *et al.*, 2016; Reilly and Burstein, 1975).

Engineering approaches have demonstrated the variability in the structural mechanical behavior of trabecular bone across anatomical sites including vertebrae, humerus, distal and proximal femur and proximal tibia (Chang *et al.*, 1999; Goldstein *et al.*, 1983; Keaveny *et al.*, 1993, 1997, 1994, 1999; Kopperdahl and Keaveny, 1998; Morgan *et al.*, 2001; Nicholson *et al.*, 1997). These studies report range of values for the apparent elastic modulus of trabecular bone (30–2600 MPa), the apparent yield strength under compression (2–21 MPa) and tension (2–16 MPa), the apparent ultimate strength in compression (1–24 MPa) and tension (2–17 MPa). This variation in the apparent mechanical behavior of trabecular bone has been correlated to bone mass, 3D microarchitecture and tissue composition, which arise due to the variable loading demands between anatomical sites. Studies have demonstrated a variation in mechanical behavior depending on the direction a load is imparted on the trabecular structure, (Nicholson *et al.*, 1997). For example, the structural elastic modulus was found to vary significantly depending on the loading direction within a single vertebral bone, with highest modulus of 165 MPa in the supero-inferior direction and lowest modulus of 43 MPa in the lateral direction (Nicholson *et al.*, 1997). It has been reported that trabecular bone has 30% higher yield strength at 21.3 MPa in compression loading compared to 15.6 MPa in tension (Keaveny *et al.*, 1994). Trabecular bone has an apparent yield strain of 0.8% (Kopperdahl and Keaveny, 1998). Compressive loading beyond yield strain, followed by unloading and reloading, results in permanent residual strains and decreased stiffness and strength (Keaveny *et al.*, 1999). Hence, solitary incidents of overloading may not cause fracture on impact but can lead to accumulation of enough permanent damage to later cause clinical fracture.

The fatigue failure of trabecular bone has been found to vary within the typical range of physiological frequencies (0.5–3 Hz), with cycles to failure as low as 20 cycles at 2.1% strain and 400,000 cycles at 0.8% strain (Michel *et al.*, 1993). Since the structural mechanical properties of bone are highly dependent on the microarchitecture and bone mass (Ding *et al.*, 2002; Mosekilde *et al.*, 1987; Wachter *et al.*, 2001), they do not describe the mechanical behavior of the bone tissue as a material.

Mechanical Behavior at Tissue level in Bone

Tissue level studies are often carried out on individual trabeculae or microscopic sections of cortical bone tissue to characterise the mechanical behavior of the tissue, independent of bone mass or architecture. Such tests can capture the influence of the composite material comprised of organic proteins, hydroxyapatite crystals and other nanoscopic constituents of bone. In general, bone tissue can be described as an anisotropic, heterogeneous non-linear material and there are significant differences in mechanical behavior of bone tissue between unique anatomical sites as a result of the adaption at the tissue composition and microstructural organization at each region to the varied daily loads exerted on the body.

Many engineering test methods have been developed to characterise bone mechanical properties at the tissue level, such as 3 point bending, torsion, buckling, cantilever bending, micro-tensile testing, micro-pillar compression, ultrasonic measurement, acoustic measurement and nanoindentation have been applied to characterise the mechanical properties of bone at the tissue level, see Fig. 5 (Ascenzi *et al.*, 1994; Ashman and Rho, 1988; Bini *et al.*, 2002; Busse *et al.*, 2009; Carretta *et al.*, 2013; Chevalier *et al.*, 2007; Choi *et al.*, 1990; Franzoso and Zysset, 2009; Giambini *et al.*, 2013; Hengsberger *et al.*, 2002; Hoffler *et al.*, 2005, 2000;

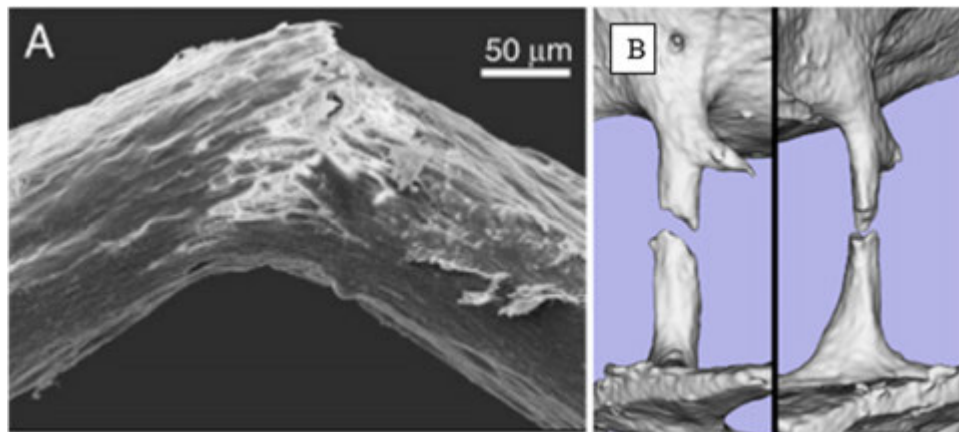


Fig. 5 (A) Fracture pattern of trabecular strut subjected to 3-point bend test. (B) Two orthogonal views of a fractured trabecular strut after micro-tensile testing image obtained using Micro-CT. Reproduced from (A) Busse, B., Hahn, M., Soltau, M., *et al.*, 2009. Increased calcium content and inhomogeneity of mineralization render bone toughness in osteoporosis: Mineralization, morphology and biomechanics of human single trabeculae. Bone 45, 1034–1043. (B) Carretta, R., Stüssi, E., Müller, R., Lorenzetti, S., 2013. Within subject heterogeneity in tissue-level post-yield mechanical and material properties in human trabecular bone. Journal of the Mechanical Behavior of Biomedical Materials 24, 64–73.

Isaksson *et al.*, 2010; Jiroušek *et al.*, 2011; Kim *et al.*, 2014; Kuhn *et al.*, 1989; Lorenzetti *et al.*, 2011; McNamara *et al.*, 2006, 2005; Mente and Lewis, 1989; Mulder *et al.*, 2007; Nicholson *et al.*, 1997; Rho, 1996; Rho *et al.*, 1997, 1993; Ryan and Williams, 1989; Schwiedrzik *et al.*, 2014; Townsend *et al.*, 1975; Turner *et al.*, 1999; Wolfram *et al.*, 2010; Zysset *et al.*, 1999). These studies have reported a wide range of elastic modulus for trabecular tissue (0.75–25 GPa), though there is less variability in the elastic modulus reported for cortical tissue (14.5–27.5 GPa).

Finite element (FE) methods can be used to estimate bone tissue elastic modulus by combining 3D reconstructions of bone, derived from high resolution micro-CT scanning, with mathematical material models (often assumed to be linear elastic). An initial estimate of tissue elastic modulus is applied to the FE bone model and iterated until the stress-strain relationship output from the computationally simulated mechanical test corresponds to experimentally obtained stress-strain data. FE studies have estimated tissue modulus to be between 2.23 and 27 GPa for trabecular bone and between 17.1 and 21.7 GPa for cortical bone (Bayraktar *et al.*, 2004; Day *et al.*, 2001; Hou *et al.*, 1998; Ladd *et al.*, 1998; Morgan *et al.*, 2003; van Rietbergen *et al.*, 1995; van Ruijven *et al.*, 2003). However these FE methods predict the elastic modulus under the assumption that bone is an isotropic material and the resulting tissue modulus is often referred to as an “effective isotropic tissue modulus” which, does not capture the complexity of the heterogeneous material.

Bone mineral content is positively correlated with the material Young’s modulus (Bourne and van der Meulen, 2004; Currey, 1984, 1988, 2003; Rho *et al.*, 1995). The heterogeneity of bone mineral distribution has been investigated. Finite element models of trabecular bone cubes were applied to study the role of the in vivo heterogeneous mineral distribution by comparing it to a hypothetical uniform mineral distribution, whereby both models would produce an identical DXA areal BMD of 0.4 gHA/cm³. An exponential relation was assumed between local mineral content and tissue level stiffness and simulated axial compression of the trabecular cube model indicated that a heterogeneous mineral distribution increased apparent stiffness (average +15%) compared to a homogenous mineral distribution (van der Linden *et al.*, 2001). Other studies have assessed the impact of incorporating material heterogeneity in FE models of bone on the predicted apparent mechanical behavior, and reported that there was a decreased trabecular stiffness (–21%)(Renders *et al.*, 2008) or both decreased and increased stiffness, depending on the extent of the heterogeneity (Jaasma *et al.*, 2002), when compared to the assumption of a homogenous distribution of mineral.

It is possible that the natural heterogeneity in trabecular tissue mineral distribution can explain a certain degree of variability in the reported elastic moduli for trabecular tissue. Furthermore, a study combining bone mineral density distribution (BMDD) analysis of quantitative backscatter SEM images and three point bending of individual human trabeculae, found that increased mineral heterogeneity resulted in significantly decreased tissue elastic modulus, yield strength, ultimate strength and bending stiffness (Busse *et al.*, 2009). It should be noted that seemingly small spatial variations in bone composition, the presence of stress-concentrations such as osteocyte lacunae, and the “cement line” interface between adjacent bone lamellae, would have a large influence on the mechanical properties of the tissue at the microscale, due to the relatively low surface to volume ratio of a trabecular element compared to macroscale testing of a cylindrical volume of trabecular bone. Furthermore, nanoindentation of individual ovine trabeculae has demonstrated tissue elastic modulus and hardness increased with distance from the superficial layer towards the core of the trabecula, (elastic modulus: superficial 17.2 GPa, intermediate 21.7 GPa, core 23.4 GPa; hardness: superficial 0.29 GPa, intermediate 0.41 GPa and core 0.47 GPa) (Brennan *et al.*, 2009). Ultrasonic and micro-tensile testing of human trabecular and cortical samples have indicated that the elastic modulus of trabecular tissue (14.8 GPa $\pm$ 1.4 and 10.4 $\pm$ 3.5 GPa, respectively) was approximately 40% lower than that of cortical bone tissue (20.7 $\pm$ 1.9 and 18.6 $\pm$ 3.5 GPa, respectively) (Rho *et al.*, 1993). However, many studies have reported elastic moduli from nanoindentation of trabecular bone tissue ranging from 17.6 to 25 GPa (Chevalier *et al.*, 2007; Giambini *et al.*, 2013; Hengsberger *et al.*, 2002; Kim *et al.*, 2014), which are similar to elastic moduli found in cortical bone. In fact, a study using acoustic measurement and nanoindentation obtained moduli from human femoral trabecular tissue of 17.50 $\pm$ 1.12 GPa and 18.14 $\pm$ 1.7 GPa respectively, which was within the range of moduli obtained in the same study from cortical tissue in the transverse (14.91 $\pm$ 0.52 GPa and 16.58 $\pm$ 0.32 GPa) and longitudinal (20.55 $\pm$ 0.21 and 23.45 $\pm$ 0.21 GPa) directions (Turner *et al.*, 1999). These findings suggest that the distinctions in the microscale arrangement of trabecular and cortical bone tissue results in different mechanical behavior at the micro- and macro-scales.

Fracture Behavior

Bone has an innate ability to sustain microdamage without allowing failure to occur at the macro-level. Everyday activities such as walking and running incur large amounts of cyclic loading on our bones over many years, which result in accumulation of microcracks within the bone tissue (Norman and Wang, 1997; Schaffler *et al.*, 1995). Fracture behavior of bone is complex due to its organization as a composite material. Fractures appear in bone in the form of macro-level cracks or diffuse microcracks, which can emerge in both normal and extreme conditions, such as creep, fatigue or impact loads (Caler and Carter, 1989; Carter and Hayes, 1977; Schaffler *et al.*, 1995; Vashishth *et al.*, 2000). It has been shown that bone microdamage mainly occurs within interstitial bone tissue and grow towards the interfaces between adjacent lamellae, which serve as energy absorbers to resist growth of macro-level cracks (Boyce *et al.*, 1998). Large cracks, which are deflected along the lamellar interfaces, are observed alongside small microcracks which accumulate and spread to absorb energy from the largest crack, in order to slow down its propagation through the bone (O’Brien *et al.*, 2005). Fracture behavior in bone is anisotropic, with large crack growth occurring longitudinally, these cracks are deflected in the tangential direction, while microcracks in the radial direction increase toughness (Zimmermann *et al.*, 2009). This anisotropic fracture behavior is influenced by the

difference of fibre orientation in the collagen matrix of adjacent lamellae, which averts crack growth from continuing along a single fibre direction, i.e. the crack can only continue alongside the fibre direction within one lamella, as the adjacent lamellae will be oriented in a different direction and therefore deflect the crack propagation, see Fig. 5 (Schaffler *et al.*, 1994). The presence of accumulated micro-damage in bone tissue causes a reduction in elastic modulus and strength (Burr *et al.*, 1998; Carter and Hayes, 1977; Schaffler *et al.*, 1995). However, remodeling of bone is essential for preventing excessive build-up of natural microdamage, in order to preserve bone strength (Burr *et al.*, 1985; Lee *et al.*, 2000). It has been found that bone toughness, or resistance to crack growth, decreases with age as the tissue becomes more mineralized (Burstein *et al.*, 1976; Nalla *et al.*, 2004; Zimmermann *et al.*, 2011). High strain rates also reduce the fracture toughness of bone through reducing its capacity for energy absorption, as low strain rates are required for microcracks to form (Schaffler *et al.*, 1989).

Bone is a Remarkably Strong and Adaptive Material

The skeletal system is a remarkable material, whose composite hierarchical design serves to provide structure to the human body, protects the internal organs and transmits movement through its series of joints in collaboration with muscles, tendons and ligaments, and is lightweight yet remarkably strong. Unlike engineering composite materials, bone is a living and adaptive material, which has the ability to constantly renew itself to maintain its strength throughout life and can also redesign itself to optimize its function in response to the demands of external loads. This renewal and adaptive nature is facilitated by dynamic cell activity that can replace aged or damaged bone with healthy bone tissue.

Bone tissue is created and its strength is sustained by osteoprogenitor, osteoblast, osteocyte, osteoclast and bone-lining cells, each of which are vital in bone modeling, repair and remodeling. Osteoprogenitors are the precursor cells necessary to enable bone formation, because they can differentiate into osteoblasts when exposed to appropriate mechanical or biochemical cues (Okazaki *et al.*, 2002). These cells are active in the growing embryo, during childhood growth, but also reside in the bone marrow, periosteum and endosteum of adults throughout life so that they can be recruited to initiate repair processes to repair fractures when necessary. Osteoblasts make and secrete unmineralized bone matrix known as osteoid, specifically by synthesizing and assembling the tropocollagen molecule (see Section “Collagen” above), where it is packaged as a triple helix of three polypeptides and two short non-helical structures at each end called telopeptides. The packaged tropocollagen molecule is secreted from the osteoblast into the extracellular matrix (ECM). Meanwhile the non-helical telopeptide ends are removed by proteinases, which promotes aggregation of many tropocollagen molecules in the ECM. Bone lining cells are quiescent osteoblasts that line endosteal surfaces, which are known to be involved in bone remodeling by signaling to osteocytes and promoting osteoclast differentiation (Kollet *et al.*, 2006; Matsuo and Irie, 2008).

Osteocytes, which are the most abundant bone cell, are terminally differentiated. These cells play a role in remodeling, are mechanosensory and also can regulate calcium content in bone by remodeling their surrounding matrix (Bonewald, 2011). Osteoclasts are multinucleated, motile cells and are the only cells capable of resorping bone matrix when it is necessary to remove damaged or aged bone tissue during bone remodeling or repair.

Bone formation at any stage of life, occurs in one of two forms, intramembranous ossification or endochondral ossification. Endochondral ossification is carried out in embryonic long bones, the growth plate of immature bone and during fracture healing. Mesenchymal stem cells (MSCs) are differentiated into cartilage cells, called chondroblasts and create a cartilage matrix to serve as a template for bone development (Ortega *et al.*, 2004). The chondroblasts differentiate into chondrocytes, which promotes mineralization of the cartilage template, before they undergo programmed cell death, known as apoptosis. Empty cavities in the mineralized collagen template, previously occupied by chondrocytes, are infiltrated by blood vessels, which encourage the recruitment of osteoclasts and osteoblasts (Collin-Osdoby, 1994; Gerber and Ferrara, 2000; Sumpio *et al.*, 2002). The osteoclasts remove the underlying cartilage template and the osteoblasts replace it with new bone tissue. During early development, secondary ossification occurs at the end of long bones, which undergo vascularization and form a cartilage layer called the growth plate. Bone growth continues through childhood, by means of endochondral ossification at the growth plate, causing long bones to gradually increase in length. At a certain point in adulthood, this growth plate fuses and mineralizes into bone tissue, thus ending growth at the bone site.

During embryonic development, flat bones such as the clavicle and the skull are formed by intramembranous ossification. These bones do not require a cartilage template to initiate bone formation. Instead MSCs gather together to form an aggregate material which serves as a basic template for ossification. The MSCs differentiate into osteoblasts and deposit immature bone tissue, which is then calcified into woven bone and with continued remodeling cycles the tissue increases in strength and hardness (Chung *et al.*, 2004; Cowin, 2001; Kanczler and Oreffo, 2008).

Bone in Ageing and Disease: Osteoporosis

The mechanical integrity of bone becomes compromised during ageing or pathological diseases, such as osteoporosis. Increases in cortical porosity with aging has been found account for 76% of a reduction in the apparent material strength (McCalden *et al.*, 1993), while the apparent elastic modulus is reported to have a negative power relationship with porosity (Schaffler and Burr, 1988). The porosity predominantly affects the elastic modulus and shear modulus in the longitudinal direction, whereas it has

been found to be unrelated to the apparent behavior in the transverse direction (Dong and Guo, 2004). The apparent mechanical behavior of trabecular bone decreases during ageing, with almost 10% decrease in modulus and strength in the human femur and spine per annum (McCalden *et al.*, 1997). As people age there is a gradual loss of bone mass, but this process is more dramatic and accelerated during osteoporosis. This bone loss is a result of an imbalance in the bone remodeling process whereby excessive bone resorption occurs without satisfactory bone formation to replenish the lost tissue. As a consequence the bone structure is depleted, the mechanical integrity is reduced and susceptibility to fracture is increased. Severe fractures in advanced ageing result in immobility, pain, deformity and, potentially, a reduced quality of life.

Osteoporosis primarily occurs in postmenopausal women, with 40% of women over 50 at risk (Melton *et al.*, 2005) and produces the second most significant health threat in women after breast cancer, with an osteoporotic fracture increasing the risk of mortality by 10%–20% within a year of injury (Cummings and Melton, 2002; Melton *et al.*, 2005). Although, there is an link between decreased bone mass and reduction in mechanical strength of bone structures during osteoporosis, as demonstrated in testing of bone from animal models of the disease (Brennan *et al.*, 2012; Kennedy *et al.*, 2009), it is incorrect to assume the bone loss occurs systemically throughout the trabecular structure. In fact, a recent study has shown that while there is loss of trabecular struts in early stages in a rat model of osteoporosis, the struts that remain have increased thickness in the long term (Waarsing *et al.*, 2006).

Furthermore, loss of bone mass accounts for only 60% of the increase in bone fragility during osteoporosis (Ammann and Rizzoli, 2003). Thus, it has become increasingly clear that the heterogeneity of trabecular structure and bone tissue composition must also be a causative factor in the increased fracture risk. Studies have produced conflicting reports on the changes to bone tissue mineral content during osteoporosis, some observed unchanged or decreased mineral content in osteoporotic tissue (Guo and Goldstein, 2000; Li and Aspden, 1997), while others reveal and increase in tissue level mineral and increased heterogeneity of mineral distribution (Busse *et al.*, 2009). Osteoporosis has also been shown to affect the collagen content in bone tissue, with alterations occurring in the nature and quantity of collagen cross-links (Batge *et al.*, 1992; Mansell and Bailey, 2003). Increased heterogeneity of the mineralized collagen matrix, may potentially have a significant contribution to the risk of fracture in osteoporotic tissue by means of altered load distribution within the trabecular structure.

The impact of osteoporosis on tissue level mechanical properties has been investigated using bone tissue from osteoporotic humans and animal models, which simulates the conditions of postmenopausal osteoporosis. These studies have produced conflicting reports on the effect of osteoporosis on tissue elastic moduli, with nanoindentation studies indicating there is no change in stiffness of the lumbar vertebra (Guo and Goldstein, 2000) and proximal tibia of ovariectomised rats (Maimoun *et al.*, 2012) and the proximal femur of ovariectomised sheep in a model of long term osteoporosis (Brennan *et al.*, 2011b) compared to age-matched controls. Further nanoindentation studies and a three-point bending study reported decreased elastic modulus in osteoporotic tissue from the human iliac crest (Tjhia *et al.*, 2011) and vertebrae (Busse *et al.*, 2009; Kim *et al.*, 2014), lumbar vertebrae from ovariectomized rats (Maimoun *et al.*, 2012) and the proximal femur of ovariectomised sheep (Brennan *et al.*, 2009). However, another nanoindentation study and a micro-tensile study have reported increased stiffness in the human proximal humerus (Molino *et al.*, 2019) and the proximal tibia of ovariectomised rats (McNamara *et al.*, 2006). Aside from the possible contribution of differences between the experimental technique and anatomical site used in these studies, the variability of the reported effects of osteoporosis on tissue-level mechanical behavior may be a strong indication of the increased material heterogeneity in bone tissue due to osteoporosis.

Lessons From Nature: Natural and Synthetic Biomaterials That Mimic Bone

As described above, bone is a unique and complex material that exhibits exceptional biological and physical properties, but disease and ageing impair the tissue and so alternative materials have been explored for various applications including medical devices to replace degenerative bones or as materials that encourage bone repair within the body.

Metallic biomaterials were the first class of material considered to replace damaged bone, particularly in development of orthopedic implants to treat fractures and degenerative conditions such as osteoarthritis and osteoporosis. Stainless steel, cobalt chromium and titanium have been widely used in orthopedic implants (prosthetic hips, knees) because they provide high strength, fracture toughness, hardness, corrosion resistance and are biocompatible (Disegi and Eschbach, 2000; Ratner *et al.*, 2004). However, these materials exhibit substantially higher elastic moduli and so bear the load, and in doing so by-pass regions of bone in terms of force/stress transmission. Bone tissue is intricately linked to the mechanical demands, and bone cells activate a biological response known as “stress-shielding” to remove bone tissue in the absence of sufficient stress. Stress-shielding is a complication of orthopedic implants that can ultimately cause implant loosening and require revision surgery (Glassman *et al.*, 2006; Sumner, 2015; Uthoff and Finnegan, 1983). Moreover, metallic implants often need to be modified to prevent corrosion and wear, which can release toxic metallic ions that activate inflammation, and coated in proteins to encourage cell attachment for (osseo)integration of the implant (Bekmurzayeva *et al.*, 2018; Rony *et al.*, 2018). Porous metallic foams have thus been developed to enhance the match of the material properties to bone and prevent stress-shielding, and also to provide physical space for cell infiltration and osseointegration (Krishna *et al.*, 2007; Ryan *et al.*, 2006). These have been recently vastly improved by the accessibility of additive manufacturing techniques, such as rapid prototyping, selective laser sintering, selective laser melting, and electron beam melting, which facilitate production of complex porous structures (Lopez-Heredia *et al.*, 2008; Yuan *et al.*, 2019).

Bioactive ceramic materials, such as hydroxyapatite (HA) and tricalcium phosphate (β -TCP), exhibit certain mechanical properties and chemical composition that are similar bone (LeGeros, 2002, 2008), and for this reason they have been widely used

to replace bone tissue for orthopedic implants to overcome the issue of stress-shielding. These ceramics are biocompatible and bioactive, meaning that their composition enables degradation and release of calcium and phosphate ions that facilitate and induce bone formation by the host (osteoconduction, osteoinduction) (Barrere *et al.*, 2006; Rosa *et al.*, 2003). Hydroxyapatite can be processed to form porous structures that mimic bone microarchitecture using various approaches including ceramic foaming, polymeric sponges, gel casting, microwave processing and electrophoretic deposition (Li *et al.*, 2002; Sopyan *et al.*, 2007). However, ceramic materials are more brittle than bone and so are unsuited to skeletal locations where high impact loading is anticipated. Moreover, unfavorable cell behavior can arise, such as necrosis, if nutrients cannot reach the interior of ceramic materials. Calcium containing silica glasses also exhibit high strength, degradability and bioactivity (Jell and Stevens, 2006; Stevens, 2008), whereas marine species such as coral, sea urchins and sea sponges exhibit properties of bone because they produce calcium carbonate skeletons and these exhibit a natural porosity (Battistella *et al.*, 2012; Ivankovic *et al.*, 2010; Lekakou *et al.*, 2008; Mena *et al.*, 1979; Supronowicz *et al.*, 2011). Other ceramics like aluminum oxide, zirconium oxide or more recently silicon nitride or carbide are biologically inert and are used as permanent prosthesis material like hip or knee joints. Their main advantages compared to metallic or polymeric materials are their higher wear and corrosion resistance. More details are presented in other Encyclopedia chapters, these from Piconi and Tamperi on bioinert oxide ceramics and from Hampshire on non-oxide bioceramics.

Tissue engineering is a field that combines principles of biology and engineering to develop functional substitutes for damaged tissues (Langer and Vacanti, 1993). Naturally derived organic materials, such as collagen, glycosaminoglycans, gelatin, chitosan, silk fibrin, and elastin, have been widely used for bone tissue engineering (Dawson *et al.*, 2008; Harley and Gibson, 2008) because they mimic the organic components of the extracellular matrix and are biocompatible but also encourage cell attachment and matrix production (Harley and Gibson, 2008). Collagen-based scaffolds are widely used, due to the abundance and importance of the collagen protein in vivo for regulating bone cell growth and matrix production (Ben-David *et al.*, 2011; Chen *et al.*, 2007; Mullen *et al.*, 2013). Similarly, gelatin (denatured collagen) has been widely explored (Ben-David *et al.*, 2011; Jones and Cartmell, 2006). Glycosaminoglycans are proteins that exist in bone tissue and play a functional role in terms of providing attachment cues for bone cells, water retention and shock adsorption, and these have been added to collagen scaffolds at various concentrations to increase cell attachment and differentiation (Byrne *et al.*, 2008; Farrell *et al.*, 2007; Farrell *et al.*, 2006; Keogh *et al.*, 2010; Tierney *et al.*, 2009a,b). Elastin is also a naturally occurring organic protein that has been incorporated into collagen scaffolds to promote osteogenic differentiation and mineralization (Amruthwar and Janorkar, 2013; Çelebi *et al.*, 2012). However, natural polymers only serve to expedite or enhance the healing process by bone cells but they exhibit poor mechanical properties and so are not appropriate for applications where the load bearing function of bone requires immediate restoration. Chemical crosslinking of collagen/gelatin has been explored to address this limitation, but can only enhance the properties within the kPa range (Haugh *et al.*, 2011), and as such these materials remain deficient for implantation in load bearing locations.

Synthetic polymers (polylactic acid, polyglycolic acid) have been explored due to their availability, biocompatibility and the fact that their mechanical, physical and biological properties can be controlled to suit various applications (Gunatillake and Adhikari, 2003) (MacArthur and Oreffo, 2005; Yang *et al.*, 2004; Yang *et al.*, 2001), for example by altering the monomer ratios in copolymers (Murphy *et al.*, 2013). However, synthetic polymers also exhibit poor mechanical properties and can release acidic by-products and stimulate adverse tissue and inflammatory reactions (Murphy *et al.*, 2013).

Composite scaffolds have been explored to overcome the limitations of low mechanical stiffness of polymer based scaffolds and the brittle nature of ceramics/glasses. A variety of biologically enhanced ceramic and glass materials have been developed by combining them with bioactive materials such collagen, gelatin, RGD peptides, PCL, PLA, and these have been shown to simultaneously stimulate bone regeneration while having superior mechanical properties to polymers (Dawson *et al.*, 2008; Germanier *et al.*, 2006; Kanungo *et al.*, 2008; Lyons *et al.*, 2014; Tan *et al.*, 2014; Xu *et al.*, 2010; Yang *et al.*, 2004; Zhou *et al.*, 2007).

References

- Akhter, M.P., Cullen, D.M., Gong, G., Recker, R.R., 2001. Bone biomechanical properties in prostaglandin EP1 and EP2 knockout mice. *Bone* 29, 121–125.
- Alford, A.I., Golicz, A.Z., Cathey, A.L., Reddy, A.B., 2013. Thrombospondin-2 facilitates assembly of a type I collagen-rich matrix in marrow stromal cells undergoing osteoblastic differentiation. *Connective Tissue Research* 54, 275–282.
- Ammann, P., Rizzoli, R., 2003. Bone strength and its determinants. *Osteoporosis International* 14, 13–18.
- Amruthwar, S.S., Janorkar, A.V., 2013. In vitro evaluation of elastin-like polypeptide-collagen composite scaffold for bone tissue engineering. *Dental Materials* 29, 211–220.
- Ascanzi, A., Bonucci, E., 1976. Relationship between ultrastructure and "pin test" in osteons. *Clinical Orthopaedics and Related Research*, 275–294.
- Ascenzi, A., Baschieri, P., Benvenuti, A., 1994. The torsional properties of single selected osteons. *Journal of Biomechanics* 27, 875–884.
- Ashman, R.B., Rho, J.Y., 1988. Elastic modulus of trabecular bone material. *Journal of Biomechanics* 21, 177–181.
- Barrere, F., van Blitterswijk, C.A., de Groot, K., 2006. Bone regeneration: Molecular and cellular interactions with calcium phosphate ceramics. *International Journal of Nanomedicine* 1, 317–332.
- Batge, B., Diebold, J., Stein, H., Bodo, M., Muller, P.K., 1992. Compositional analysis of the collagenous bone matrix. A study on adult normal and osteopenic bone tissue. *European Journal of Clinical Investigation* 22, 805–812.
- Battistella, E., Mele, S., Foltran, I., *et al.*, 2012. Cuttlefish bone scaffold for tissue engineering: A novel hydrothermal transformation, chemical-physical, and biological characterization. *Journal of Applied Biomaterials & Functional Materials* 10, 99–106.
- Bayraktar, H.H., Morgan, E.F., Niebur, G.L., *et al.*, 2004. Comparison of the elastic and yield properties of human femoral trabecular and cortical bone tissue. *Journal of Biomechanics* 37, 27–35.
- Beamer, W.G., Donahue, L.R., Rosen, C.J., Baylink, D.J., 1996. Genetic variability in adult bone density among inbred strains of mice. *Bone* 18, 397–403.
- Bekmurzayeva, A., Duncanson, W.J., Azevedo, H.S., Kanayeva, D., 2018. Surface modification of stainless steel for biomedical applications: Revisiting a century-old material. *Materials Science and Engineering C: Materials for Biological Applications* 93, 1073–1089.

- Ben-David, D., Kizhner, T.A., Kohler, T., *et al.*, 2011. Cell-scaffold transplant of hydrogel seeded with rat bone marrow progenitors for bone regeneration. *Journal of Cranio-Maxillofacial Surgery* 39, 364–371.
- Berezovska, O., Yildirim, G., Budell, W.C., *et al.*, 2019. Osteocalcin affects bone mineral and mechanical properties in female mice. *Bone* 128, 115031.
- Bini, F., Marinuzzi, A., Marinuzzi, F., Patanè, F., 2002. Microtensile measurements of single trabeculae stiffness in human femur. *Journal of Biomechanics* 35, 1515–1519.
- Bonewald, L.F., 2011. The amazing osteocyte. *Journal of Bone and Mineral Research: The official Journal of the American Society for Bone and Mineral Research* 26, 229–238.
- Boskey, A.L., Maresca, M., Ullrich, W., *et al.*, 1993. Osteopontin-hydroxyapatite interactions in vitro: Inhibition of hydroxyapatite formation and growth in a gelatin-gel. *Bone and Mineral* 22, 147–159.
- Boskey, A.L., Gadaleta, S., Gundberg, C., *et al.*, 1998. Fourier transform infrared microspectroscopic analysis of bones of osteocalcin-deficient mice provides insight into the function of osteocalcin. *Bone* 23, 187–196.
- Boskey, A.L., Moore, D.J., Amling, M., Canalis, E., Delany, A.M., 2003. Infrared analysis of the mineral and matrix in bones of osteonectin-null mice and their wildtype controls. *The Journal of Bone and Mineral Research* 18, 1005–1011.
- Bourne, B.C., van der Meulen, M.C., 2004. Finite element models predict cancellous apparent modulus when tissue modulus is scaled from specimen CT-attenuation. *Journal of Biomechanics* 37, 613–621.
- Boyce, T.M., Fyhrie, D.P., Glatkowski, M.C., Radin, E.L., Schaffler, M.B., 1998. Damage type and strain mode associations in human compact bone bending fatigue. *Journal of Orthopaedic Research* 16, 322–329.
- Brennan, M.A., Gleeson, J.P., Browne, M., *et al.*, 2011a. Site specific increase in heterogeneity of trabecular bone tissue mineral during oestrogen deficiency. *European Cells and Materials* 21, 396–406.
- Brennan, O., Kennedy, O.D., Lee, T.C., *et al.*, 2011b. The effects of estrogen deficiency and bisphosphonate treatment on tissue mineralisation and stiffness in an ovine model of osteoporosis. *Journal of Biomechanics* 44, 386–390.
- Brennan, O., Kennedy, O.D., Lee, T.C., *et al.*, 2009. Biomechanical properties across trabeculae from the proximal femur of normal and ovariectomised sheep. *Journal of Biomechanics* 42, 498–503.
- Brennan, O., Kulwaba, J.S., Lee, T.C., *et al.*, 2012. Temporal changes in bone composition, architecture, and strength following estrogen deficiency in osteoporosis. *Calcified Tissue International* 91, 440–449.
- Burr, D.B., Turner, C.H., Naick, P., *et al.*, 1998. Does microdamage accumulation affect the mechanical properties of bone? *Journal of Biomechanics* 31, 337–345.
- Burr, D.B., Martin, R.B., Schaffler, M.B., Radin, E.L., 1985. Bone remodeling in response to in vivo fatigue microdamage. *Journal of Biomechanics* 18, 189–200.
- Burstein, A.H., Reilly, D.T., Martens, M., 1976. Aging of bone tissue: Mechanical properties. *Journal of Bone and Joint Surgery* 58, 82–86.
- Busse, B., Hahn, M., Soltan, M., *et al.*, 2009. Increased calcium content and inhomogeneity of mineralization render bone toughness in osteoporosis: Mineralization, morphology and biomechanics of human single trabeculae. *Bone* 45, 1034–1043.
- Byrne, E.M., Farrell, E., McMahon, L.A., *et al.*, 2008. Gene expression by marrow stromal cells in a porous collagen-glycosaminoglycan scaffold is affected by pore size and mechanical stimulation. *Journal of Materials Science: Materials in Medicine* 19, 3455–3463.
- Caler, W.E., Carter, D.R., 1989. Bone creep-fatigue damage accumulation. *Journal of Biomechanics* 22, 625–635.
- Camacho, N.P., Rinnerthaler, S., Paschalis, E.P., *et al.*, 1999. Complementary information on bone ultrastructure from scanning small angle X-ray scattering and Fourier-transform infrared microspectroscopy. *Bone* 25, 287–293.
- Carretta, R., Stüssi, E., Müller, R., Lorenzetti, S., 2013. Within subject heterogeneity in tissue-level post-yield mechanical and material properties in human trabecular bone. *Journal of the Mechanical Behavior of Biomedical Materials* 24, 64–73.
- Carter, D.R., Hayes, W.C., 1977. Compact bone fatigue damage: a microscopic examination. *Clinical Orthopaedics and Related Research*. 265–274.
- Carter, D.R., Caler, W.E., Spengler, D.M., Frankel, V.H., 1981. Fatigue behavior of adult cortical bone: The influence of mean strain and strain range. *Acta Orthopaedica Scandinavica* 52, 481–490.
- Çelebi, B., Cloutier, M., Balloni, R., Mantovani, D., Bandiera, A., 2012. Human elastin-based recombinant biopolymers improve mesenchymal stem cell differentiation. *Macromolecular Bioscience* 12, 1546–1554.
- Chang, W.C., Christensen, T.M., Pinilla, T.P., Keaveny, T.M., 1999. Uniaxial yield strains for bovine trabecular bone are isotropic and asymmetric. *Journal of Orthopaedic Research* 17, 582–585.
- Chen, D.C., Lai, Y.L., Lee, S.Y., Hung, S.L., Chen, H.L., 2007. Osteoblastic response to collagen scaffolds varied in freezing temperature and glutaraldehyde crosslinking. *Journal of Biomedical Materials Research Part A* 80, 399–409.
- Chevalier, Y., Pahr, D., Allmer, H., Charlebois, M., Zysset, P., 2007. Validation of a voxel-based FE method for prediction of the uniaxial apparent modulus of human trabecular bone using macroscopic mechanical tests and nanoindentation. *Journal of Biomechanics* 40, 3333–3340.
- Choi, K., Kuhn, J.L., Ciarelli, M.J., Goldstein, S.A., 1990. The elastic moduli of human subchondral, trabecular, and cortical bone tissue and the size-dependency of cortical bone modulus. *Journal of Biomechanics* 23, 1103–1113.
- Chung, U.-I., Kawaguchi, H., Takato, T., Nakamura, K., 2004. Distinct osteogenic mechanisms of bones of distinct origins. *Journal of Orthopaedic Science: Official Journal of the Japanese Orthopaedic Association* 9, 410–414.
- Collin-Osdoby, P., 1994. Role of vascular endothelial cells in bone biology. *Journal of Cellular Biochemistry* 55, 304–309.
- Cowin, S.C., 2001. *Bone Mechanics Handbook*, second ed. CRC Press.
- Cummings, S.R., Melton, L.J., 2002. Epidemiology and outcomes of osteoporotic fractures. *The Lancet* 359, 1761–1767.
- Currey, J.D., 1984. Effects of differences in mineralization on the mechanical properties of bone. *Philosophical Transactions of the Royal Society B: Biological Sciences* 304, 509–518.
- Currey, J.D., 1988. The effect of porosity and mineral content on the Young's modulus of elasticity of compact bone. *Journal of Biomechanics* 21, 131–139.
- Currey, J.D., 2003. Role of collagen and other organics in the mechanical properties of bone. *Osteoporosis International* 14 (Suppl 5), S29–S36.
- Currey, J.D., Brear, K., Zioupos, P., 1996. The effects of ageing and changes in mineral content in degrading the toughness of human femora. *Journal of Biomechanics* 29, 257–260.
- Dallas, S.L., Sivakumar, P., Jones, C.J., *et al.*, 2005. Fibronectin regulates latent transforming growth factor-beta (TGF beta) by controlling matrix assembly of latent TGF beta-binding protein-1. *Journal of Biological Chemistry* 280, 18871–18880.
- Dawson, J.I., Wahl, D.A., Lanham, S.A., *et al.*, 2008. Development of specific collagen scaffolds to support the osteogenic and chondrogenic differentiation of human bone marrow stromal cells. *Biomaterials* 29, 3105–3116.
- Day, J.S., Ding, M., van der Linden, J.C., *et al.*, 2001. A decreased subchondral trabecular bone tissue elastic modulus is associated with pre-arthritis cartilage damage. *Journal of Orthopaedic Research* 19, 914–918.
- Delany, A., Amling, M., Priemel, M., *et al.*, 2000. Osteopenia and decreased bone formation in osteonectin-deficient mice. *Journal of Clinical Investigation* 105, 915–923.
- Derkx, P., Birkenhager-Frenkel, D.H., 1995. A thionin stain for visualizing bone cells, mineralizing fronts and cement lines in undecalcified bone sections. *Biotechnic & Histochemistry* 70, 70–74.
- Ding, M., Odgaard, A., Linde, F., Hvid, I., 2002. Age-related variations in the microstructure of human tibial cancellous bone. *Journal of Orthopaedic Research* 20, 615–621.
- Disegi, J.A., Eschbach, L., 2000. Stainless steel in bone surgery. *Injury* 31 (Suppl 4), 2–6.
- Dong, X.N., Guo, X.E., 2004. The dependence of transversely isotropic elasticity of human femoral cortical bone on porosity. *Journal of Biomechanics* 37, 1281–1287.
- Dong, X.N., Acuna, R.L., Luo, Q., Wang, X., 2012. Orientation dependence of progressive post-yield behavior of human cortical bone in compression. *Journal of Biomechanics* 45, 2829–2834.

- Ducy, P., Desbois, C., Boyce, B., *et al.*, 1996. Increased bone formation in osteocalcin-deficient mice. *Nature* 382, 448–452.
- Evans, F.G., 1976. Mechanical properties and histology of cortical bone from younger and older men. *The Anatomical Record* 185, 1–11.
- Fantner, G.E., Hassenkam, T., Kindt, J.H., *et al.*, 2005. Sacrificial bonds and hidden length dissipate energy as mineralized fibrils separate during bone fracture. *Nature Materials* 4, 612–616.
- Fantner, G.E., Oroudjev, E., Schitter, G., *et al.*, 2006. Sacrificial bonds and hidden length: Unraveling molecular mesostructures in tough materials. *Biophysical Journal* 90, 1411–1418.
- Fantner, G.E., Adams, J., Turner, P., *et al.*, 2007. Nanoscale ion mediated networks in bone: Osteopontin can repeatedly dissipate large amounts of energy. *Nano Letters* 7, 2491–2498.
- Farrell, E., O'Brien, F.J., Doyle, P., *et al.*, 2006. A collagen-glycosaminoglycan scaffold supports adult rat mesenchymal stem cell differentiation along osteogenic and chondrogenic routes. *Tissue Engineering* 12, 459–468.
- Farrell, E., Byrne, E.M., Fischer, J., *et al.*, 2007. A comparison of the osteogenic potential of adult rat mesenchymal stem cells cultured in 2-D and on 3-D collagen glycosaminoglycan scaffolds. *Technology and Health Care* 15, 19–31.
- Franzoso, G., Zysset, P.K., 2009. Elastic anisotropy of human cortical bone secondary osteons measured by nanoindentation. *Journal of Biomechanical Engineering* 131, 021001.
- Frost, H.M., 1994. Wolff's Law and bone's structural adaptations to mechanical usage: An overview for clinicians. *The Angle Orthodontist* 64, 175–188.
- Gadeleta, S.J., Boskey, A.L., Paschalis, E., *et al.*, 2000. A physical, chemical, and mechanical study of lumbar vertebrae from normal, ovariectomized, and nandrolone decanoate-treated cynomolgus monkeys (*Macaca fascicularis*). *Bone* 27, 541–550.
- Gerber, H.-P., Ferrara, N., 2000. Angiogenesis and bone growth. *Trends in Cardiovascular Medicine* 10, 223–228.
- Germanier, Y., Tosatti, S., Brogini, N., Textor, M., Buser, D., 2006. Enhanced bone apposition around biofunctionalized sandblasted and acid-etched titanium implant surfaces – A histomorphometric study in miniature pigs. *Clinical Oral Implants Research* 17, 251–257.
- Giambini, H., Wang, H.-J., Zhao, C., *et al.*, 2013. Anterior and posterior variations in mechanical properties of human vertebrae measured by nanoindentation. *Journal of Biomechanics* 46, 456–461.
- Glassman, A.H., Bobyn, J.D., Tanzer, M., 2006. New femoral designs: Do they influence stress shielding? *Clinical Orthopaedics and Related Research* 453, 64–74.
- Glimcher, M.J., 1959. Molecular biology of mineralized tissues with particular reference to bone. *Reviews of Modern Physics* 31, 359–393.
- Goldstein, S.A., Wilson, D.L., Sonstegard, D.A., Matthews, L.S., 1983. The mechanical properties of human tibial trabecular bone as a function of metaphyseal location. *Journal of Biomechanics* 16, 965–969.
- Gunatillake, P.A., Adhikari, R., 2003. Biodegradable synthetic polymers for tissue engineering. *European Cells & Materials Journal* 5, 1–16.
- Guo, X.E., Goldstein, S.A., 2000. Vertebral trabecular bone microscopic tissue elastic modulus and hardness do not change in ovariectomized rats. *Journal of Orthopaedic Research: Official Publication of the Orthopaedic Research Society* 18, 333–336.
- Hansma, P.K., Fantner, G.E., Kindt, J.H., *et al.*, 2005. Sacrificial bonds in the interfibrillar matrix of bone. *Journal of Musculoskeletal & Neuronal Interactions* 5, 313–315.
- Harley, B.A.C., Gibson, L.J., 2008. In vivo and in vitro applications of collagen-GAG scaffolds. *Chemical Engineering Journal* 137, 102–121.
- Hassenkam, T., Fantner, G.E., Cutroni, J.A., *et al.*, 2004. High-resolution AFM imaging of intact and fractured trabecular bone. *Bone* 35, 4–10.
- Haugh, M.G., Murphy, C.M., McKiernan, R.C., Altenbuchner, C., O'Brien, F.J., 2011. Crosslinking and mechanical properties significantly influence cell attachment, proliferation, and migration within collagen glycosaminoglycan scaffolds. *Tissue Engineering Part A* 17, 1201–1208.
- Hayes, W.C., Carter, D.R., 1976. Postyield behavior of subchondral trabecular bone. *Journal of Biomedical Materials Research* 10, 537–544.
- Hengsberger, S., Kulik, A., Zysset, P., 2002. Nanoindentation discriminates the elastic properties of individual human bone lamellae under dry and physiological conditions. *Bone* 30, 178–184.
- Hoffler, C.E., Moore, K.E., Kozloff, K., *et al.*, 2000. Heterogeneity of bone lamellar-level elastic moduli. *Bone* 26, 603–609.
- Hoffler, C.E., Guo, X.E., Zysset, P.K., Goldstein, S.A., 2005. An application of nanoindentation technique to measure bone tissue Lamellae properties. *The Journal of Biomechanical Engineering* 127, 1046–1053.
- Hou, F.J., Lang, S.M., Hoshaw, S.J., Reimann, D.A., Fyhrie, D.P., 1998. Human vertebral body apparent and hard tissue stiffness. *Journal of Biomechanics* 31, 1009–1015.
- Isaksson, H., Nagao, S., Małkiewicz, M., *et al.*, 2010. Precision of nanoindentation protocols for measurement of viscoelasticity in cortical and trabecular bone. *Journal of Biomechanics* 43, 2410–2417.
- Ivankovic, H., Tkalec, E., Orlic, S., Ferrer, G.G., Schauerl, Z., 2010. Hydroxyapatite formation from cuttlefish bones: Kinetics. *Journal of Materials Science: Materials in Medicine* 21, 2711–2722.
- Jaasma, M.J., Bayraktar, H.H., Niebur, G.L., Keaveny, T.M., 2002. Biomechanical effects of intraspecimen variations in tissue modulus for trabecular bone. *Journal of Biomechanics* 35, 237–246.
- Jell, G., Stevens, M.M., 2006. Gene activation by bioactive glasses. *Journal of Materials Science: Materials in Medicine* 17, 997–1002.
- Jepsen, K.J., Davy, D.T., Krzyrow, D.J., 1999. The role of the lamellar interface during torsional yielding of human cortical bone. *Journal of Biomechanics* 32, 303–310.
- Jia, L., Young, M.F., Powell, J., *et al.*, 2002. Gene expression profile of human bone marrow stromal cells: High-throughput expressed sequence tag sequencing analysis. *Genomics* 79, 7–17.
- Jiroušek, O., Němeček, J., Kytýř, D., *et al.*, 2011. Nanoindentation of trabecular bone-comparison with uniaxial testing of single trabecula. *Chemické Listy*.
- Jones, G., Cartmell, S.H., 2006. Optimization of cell seeding efficiencies on a three-dimensional gelatin scaffold for bone tissue engineering. *The Journal of Applied Biomaterials & Biomechanics* 4, 172–180.
- Kanczler, J., Oreffo, R., 2008. Osteogenesis and angiogenesis: The potential for engineering bone. *European Cells and Materials* 15, 100–114.
- Kanungo, B.P., Silva, E., Van Vliet, K., Gibson, L.J., 2008. Characterization of mineralized collagen-glycosaminoglycan scaffolds for bone regeneration. *Acta Biomaterialia* 4, 490–503.
- Keaveny, T.M., Wachtel, E.F., Kopperdahl, D.L., 1999. Mechanical behavior of human trabecular bone after overloading. *Journal of Orthopaedic Research* 17, 346–353.
- Keaveny, T.M., Borchers, R.E., Gibson, L.J., Hayes, W.C., 1993. Trabecular bone modulus and strength can depend on specimen geometry. *Journal of Biomechanics* 26, 991–1000.
- Keaveny, T.M., Wachtel, E.F., Ford, C.M., Hayes, W.C., 1994. Differences between the tensile and compressive strengths of bovine tibial trabecular bone depend on modulus. *Journal of Biomechanics* 27, 1137–1146.
- Keaveny, T.M., Piniella, T.P., Crawford, R.P., Kopperdahl, D.L., Lou, A., 1997. Systematic and random errors in compression testing of trabecular bone. *Journal of Orthopaedic Research* 15, 101–110.
- Kennedy, O.D., Brennan, O., Rackard, S.M., *et al.*, 2009. Effects of ovariectomy on bone turnover, porosity, and biomechanical properties in ovine compact bone 12 months postsurgery. *Journal of Orthopaedic Research* 27, 303–309.
- Keogh, M.B., Fj, O.B., Daly, J.S., 2010. A novel collagen scaffold supports human osteogenesis-applications for bone tissue engineering. *Cell and Tissue Research* 340, 169–177.
- Kim, G., Cole, J.H., Boskey, A.L., Baker, S.P., Van Der Meulen, M.C.H., 2014. Reduced tissue-level stiffness and mineralization in osteoporotic cancellous bone. *Calcified Tissue International* 95, 125–131.
- Kollet, O., Dar, A., Shviti, S., *et al.*, 2006. Osteoclasts degrade endosteal components and promote mobilization of hematopoietic progenitor cells. *Nature Medicine* 12, 657–664.
- Kopperdahl, D.L., Keaveny, T.M., 1998. Yield strain behavior of trabecular bone. *Journal of Biomechanics* 31, 601–608.

- Kopperdahl, D.L., Pearlman, J.L., Keaveny, T.M., 2000. Biomechanical consequences of an isolated overload on the human vertebral body. *Journal of Orthopaedic Research* 18, 685–690.
- Kotha, S.P., Guzelsu, N., 2003. Tensile damage and its effects on cortical bone. *Journal of Biomechanics* 36, 1683–1689.
- Krishna, B.V., Bose, S., Bandyopadhyay, A., 2007. Low stiffness porous Ti structures for load-bearing implants. *Acta Biomaterialia* 3, 997–1006.
- Kuhn, J.L., Goldstein, S.A., Choi, R., *et al.*, 1989. Comparison of the trabecular and cortical tissue moduli from human iliac crests. *Journal of Orthopaedic Research* 7, 876–884.
- Ladd, A.J., Kinney, J.H., Haupt, D.L., Goldstein, S.A., 1998. Finite-element modeling of trabecular bone: comparison with mechanical testing and determination of tissue modulus. *Journal of Orthopaedic Research* 16, 622–628.
- Lane, N.E., Yao, W., Balooch, M., *et al.*, 2006. Glucocorticoid-treated mice have localized changes in trabecular bone material properties and osteocyte lacunar size that are not observed in placebo-treated or estrogen-deficient mice. *The Journal of Bone and Mineral Research* 21, 466–476.
- Langer, R., Vacanti, J.P., 1993. Tissue engineering. *Science* 260, 920.
- Lee, T.C., O'Brien, F.J., Taylor, D., 2000. The nature of fatigue damage in bone. *International Journal of Fatigue* 22, 847–853.
- LeGeros, R.Z., 2002. Properties of osteoconductive biomaterials: Calcium phosphates. *Clinical Orthopaedics and Related Research*. 81–98.
- LeGeros, R.Z., 2008. Calcium phosphate-based osteoinductive materials. *Chemical Reviews* 108, 4742–4753.
- Lekakou, C., Lamprou, D., Vidyarthi, U., Karopoulou, E., Zhdan, P., 2008. Structural hierarchy of biomimetic materials for tissue engineered vascular and orthopedic grafts. *Journal of Biomedical Materials Research* 85, 461–468.
- Li, B., Aspden, R.M., 1997. Material properties of bone from the femoral neck and calcar femorale of patients with osteoporosis or osteoarthritis. *Osteoporosis International* 7, 450–456.
- Li, S.H., De Wijn, J.R., Layrolle, P., de Groot, K., 2002. Synthesis of macroporous hydroxyapatite scaffolds for bone tissue engineering. *Journal of Biomedical Materials Research* 61, 109–120.
- Lopez-Heredia, M.A., Sohier, J., Gaillard, C., *et al.*, 2008. Rapid prototyped porous titanium coated with calcium phosphate as a scaffold for bone tissue engineering. *Biomaterials* 29, 2608–2615.
- Lorenzetti, S., Carretta, R., Müller, R., Stüssi, E., 2011. A new device and method for measuring the elastic modulus of single trabeculae. *Medical Engineering & Physics* 33, 993–1000.
- Lyons, F.G., Gleeson, J.P., Partap, S., Coghlan, K., O'Brien, F.J., 2014. Novel microhydroxyapatite particles in a collagen scaffold: A bioactive bone void filler? *Clinical Orthopaedics and Related Research* 472, 1318–1328.
- MacArthur, B.D., Oreffo, R.O., 2005. Bridging the gap. *Nature* 433, 19.
- Maimoun, L., Brennan-Speranza, T.C., Rizzoli, R., Ammann, P., 2012. Effects of ovariectomy on the changes in microarchitecture and material level properties in response to hind leg disuse in female rats. *Bone* 51, 586–591.
- Manley, E., Perosky, J.E., Khoury, B.M., *et al.*, 2015. Thrombospondin-2 deficiency in growing mice alters bone collagen ultrastructure and leads to a brittle bone phenotype. *Journal of Applied Physiology* 119, 872–881.
- Mansell, J.P., Bailey, A.J., 2003. Increased metabolism of bone collagen in post-menopausal female osteoporotic femoral heads. *The International Journal of Biochemistry & Cell Biology* 35, 522–529.
- Matsuo, K., Irie, N., 2008. Osteoclast–osteoblast communication. *Archives of Biochemistry and Biophysics* 473, 201–209.
- McCalden, R.W., McGeough, J.A., Court-Brown, C.M., 1997. Age-related changes in the compressive strength of cancellous bone. The relative importance of changes in density and trabecular architecture. *The Journal of Bone and Joint Surgery* 79, 421–427.
- McCalden, R.W., McGeough, J.A., Barker, M.B., Court-Brown, C.M., 1993. Age-related changes in the tensile properties of cortical bone. The relative importance of changes in porosity, mineralization, and microstructure. *Journal of Bone and Joint Surgery* 75, 1193–1205.
- McDonald, J.A., 1988. Extracellular matrix assembly. *The Annual Review of Cell and Developmental Biology* 4, 183–207.
- McNamara, L.M., Prendergast, P.J., Schaffler, M.B., 2005. Bone tissue material properties are altered during osteoporosis. *Journal of Musculoskeletal & Neuronal Interactions* 5, 342–343.
- McNamara, L.M., Ederveen, A.G.H., Lyons, C.G., *et al.*, 2006. Strength of cancellous bone trabecular tissue from normal, ovariectomized and drug-treated rats over the course of ageing. *Bone* 39, 392–400.
- Melton, L.J., Chrischilles, E.A., Cooper, C., Lane, A.W., Riggs, B.L., 2005. How many women have osteoporosis? *Journal of Bone and Mineral Research* 20, 886–892.
- Mena, F., Pacheco, P., Aguayo, D., Martinez, G., Grosvenor, C.E., 1979. Reflex regulation of autonomic influences upon the oxytocin-induced contractile response of the mammary gland in the anesthetized rat. *Endocrinology* 104, 751–756.
- Mente, P.L., Lewis, J.L., 1989. Experimental method for the measurement of the elastic modulus of trabecular bone tissue. *Journal of Orthopaedic Research* 7, 456–461.
- Michel, M.C., Guo, X.D.E., Gibson, L.J., McMahon, T.A., Hayes, W.C., 1993. Compressive fatigue behavior of bovine trabecular bone. *Journal of Biomechanics* 26, 453–463.
- Mirzaali, M.J., Schwedrzik, J.J., Thawichai, S., *et al.*, 2016. Mechanical properties of cortical bone and their relationships with age, gender, composition and microindentation properties in the elderly. *Bone* 93, 196–211.
- Molino, G., Dalpozi, A., Ciapetti, G., *et al.*, 2019. Osteoporosis-related variations of trabecular bone properties of proximal human humeral heads at different scale lengths. *The Journal of the Mechanical Behavior of Biomedical Materials* 100, 103373.
- Morgan, E.F., Bayraktar, H.H., Keaveny, T.M., 2003. Trabecular bone modulus-density relationships depend on anatomic site. *Journal of Biomechanics* 36, 897–904.
- Morgan, E.F., Yeh, O.C., Chang, W.C., Keaveny, T.M., 2001. Nonlinear behavior of trabecular bone at small strains. *Journal of Biomechanical Engineering* 123, 1–9.
- Mosekilde, L., Mosekilde, L., Danielsen, C.C., 1987. Biomechanical competence of vertebral trabecular bone in relation to ash density and age in normal individuals. *Bone* 8, 79–85.
- Mulder, L., Koolstra, J.H., den Toonder, J.M.J., van Eijden, T.M.G.J., 2007. Intratrabecular distribution of tissue stiffness and mineralization in developing trabecular bone. *Bone* 41, 256–265.
- Mullen, C.A., Haugh, M.G., Schaffler, M.B., Majeska, R.J., McNamara, L.M., 2013. Osteocyte differentiation is regulated by extracellular matrix stiffness and intercellular separation. *The Journal of the Mechanical Behavior of Biomedical Materials* 28, 183–194.
- Murphy, C.M., O'Brien, F.J., Little, D.G., Schindeler, A., 2013. Cell-scaffold interactions in the bone tissue engineering triad. *European Cells & Materials Journal* 26, 120–132.
- Nalla, R.K., Krucz, J.J., Kinney, J.H., Ritchie, R.O., 2004. Effect of aging on the toughness of human cortical bone: Evaluation by R-curves. *Bone* 35, 1240–1246.
- Nicholson, P.H.F., Cheng, X.G., Lowet, G., *et al.*, 1997. Structural and material mechanical properties of human vertebral cancellous bone. *Medical Engineering & Physics* 19, 729–737.
- Norman, T.L., Wang, Z., 1997. Microdamage of human cortical bone: incidence and morphology in long bones. *Bone* 20, 375–379.
- O'Brien, F.J., Taylor, D., Clive Lee, T., 2005. The effect of bone microstructure on the initiation and growth of microcracks. *Journal of Orthopaedic Research* 23, 475–480.
- Obrant, K.J., Odselius, R., 1984. Electron microprobe analysis and histochemical examination of the calcium distribution in human bone trabeculae: A methodological study using biopsy specimens from post-traumatic osteopenia. *Ultrastructural Pathology* 7, 123–131.
- Okazaki, R., Inoue, D., Shibata, M., *et al.*, 2002. Estrogen promotes early osteoblast differentiation and inhibits adipocyte differentiation in mouse bone marrow stromal cell lines that express estrogen receptor (ER) α or β . *Endocrinology* 143, 2349–2356.
- Ortega, N., Behonick, D.J., Werb, Z., 2004. Matrix remodeling during endochondral ossification. *Trends in Cell Biology* 14, 86–93.
- Paschalis, E.P., DiCarlo, E., Betts, F., *et al.*, 1996. FTIR microspectroscopic analysis of human osteonal bone. *Calcified Tissue International* 59, 480–487.
- Pattin, C.A., Caler, W.E., Carter, D.R., 1996. Cyclic mechanical property degradation during fatigue loading of cortical bone. *Journal of Biomechanics* 29, 69–79.

- Poundarik, A.A., Boskey, A., Gundberg, C., Vashishth, D., 2018. Biomolecular regulation, composition and nanoarchitecture of bone mineral. *Scientific Reports* 8, 1191.
- Ratner, B.D., Hoffman, A.S., Schoen, F.J., Lemons, J.E., 2004. *Biomaterials Science: An introduction to materials in medicine*, third ed. Elsevier.
- Reilly, D.T., Burstein, A.H., 1975. The elastic and ultimate properties of compact bone tissue. *Journal of Biomechanics* 8, 393–405.
- Renders, G.A., Mulder, L., Langenbach, G.E., Van Ruijven, L.J., Van Eijden, T.M., 2008. Biomechanical effect of mineral heterogeneity in trabecular bone. *Journal of Biomechanics* 41, 2793–2798.
- Rho, J.-Y., Ashman, R.B., Turner, C.H., 1993. Young's modulus of trabecular and cortical bone material: Ultrasonic and microtensile measurements. *Journal of Biomechanics* 26, 111–119.
- Rho, J.-Y., Hobatho, M.C., Ashman, R.B., 1995. Relations of mechanical properties to density and CT numbers in human bone. *Medical Engineering & Physics* 17, 347–355.
- Rho, J.-Y., 1996. An ultrasonic method for measuring the elastic properties of human tibial cortical and cancellous bone. *Ultrasonics* 34, 777–783.
- Rho, J.-Y., Tsui, T.Y., Pharr, G.M., 1997. Elastic properties of human cortical and trabecular lamellar bone measured by nanoindentation. *Biomaterials* 18, 1325–1330.
- Robey, P.G., Termine, J.D., 1985. Human bone cells in vitro. *Calcified Tissue International* 37, 453–460.
- Rony, L., Lancigu, R., Hubert, L., 2018. Intraosseous metal implants in orthopedics: A review. *Morphologie* 102, 231–242.
- Rosa, A.L., Beloti, M.M., van Noort, R., 2003. Osteoblastic differentiation of cultured rat bone marrow cells on hydroxyapatite with different surface topography. *Dental Materials* 19, 768–772.
- Roschger, P., Paschalis, E.P., Fratzl, P., Klaushofer, K., 2008. Bone mineralization density distribution in health and disease. *Bone* 42, 456–466.
- Rudman, K.E., Aspden, R.M., Meakin, J.R., 2006. Compression or tension? The stress distribution in the proximal femur. *Biomedical Engineering Online* 5, 12.
- Ryan, G., Pandit, A., Apatsidis, D.P., 2006. Fabrication methods of porous metals for use in orthopaedic applications. *Biomaterials* 27, 2651–2670.
- Ryan, S.D., Williams, J.L., 1989. Tensile testing of rodlike trabeculae excised from bovine femoral bone. *Journal of Biomechanics* 22, 351–355.
- Schaffler, M.B., Burr, D.B., 1988. Stiffness of compact bone: Effects of porosity and density. *Journal of Biomechanics* 21, 13–16.
- Schaffler, M.B., Radin, E.L., Burr, D.B., 1989. Mechanical and morphological effects of strain rate on fatigue of compact bone. *Bone* 10, 207–214.
- Schaffler, M.B., Choi, K., Milgrom, C., 1995. Aging and matrix microdamage accumulation in human compact bone. *Bone* 17, 521–525.
- Schaffler, M.B., Pitchford, W.C., Choi, K., Riddle, J.M., 1994. Examination of compact bone microdamage using back-scattered electron microscopy. *Bone* 15, 483–488.
- Schwidetzky, J., Raghavan, R., Burki, A., *et al.*, 2014. In situ micropillar compression reveals superior strength and ductility but an absence of damage in lamellar bone. *Nature Materials* 13, 740–747.
- Schwidetzky, J.J., Mirzaali, M.J., Thaiwichai, S., *et al.*, 2017. Response to the commentary on mechanical properties of cortical bone and their relationships with age, gender, composition and microindentation properties in the elderly. *Bone* 105, 312–314.
- Singh, P., Carraher, C., Schwarzbauer, J.E., 2010. Assembly of fibronectin extracellular matrix. *The Annual Review of Cell and Developmental Biology* 26, 397–419.
- Sopyan, I., Mel, M., Ramesh, S., Khalid, K.A., 2007. Porous hydroxyapatite for artificial bone applications. *Science and Technology of Advanced Materials* 8, 116–123.
- Sottile, J., Hocking, D.C., 2002. Fibronectin polymerization regulates the composition and stability of extracellular matrix fibrils and cell-matrix adhesions. *Molecular Biology of the Cell* 13, 3546–3559.
- Stevens, M.M., 2008. Biomaterials for bone tissue engineering. *Materials Today* 11, 18–25.
- Sumner, D.R., 2015. Long-term implant fixation and stress-shielding in total hip replacement. *Journal of Biomechanics* 48, 797–800.
- Sumpio, B.E., Timothy Riley, J., Dardik, A., 2002. Cells in focus: Endothelial cell. *The International Journal of Biochemistry & Cell Biology* 34, 1508–1512.
- Supronowicz, P., Gill, E., Trujillo, A., *et al.*, 2011. Human adipose-derived side population stem cells cultured on demineralized bone matrix for bone tissue engineering. *Tissue Engineering Part A* 17, 789–798.
- Tan, S., Fang, J.Y., Yang, Z., Nimni, M.E., Han, B., 2014. The synergetic effect of hydrogel stiffness and growth factor on osteogenic differentiation. *Biomaterials*.
- Termine, J.D., Kleinman, H.K., Whitson, S.W., *et al.*, 1981. Osteonectin, a bone-specific protein linking mineral to collagen. *Cell* 26, 99–105.
- Turner, P.J., Erickson, B., Jungmann, R., *et al.*, 2007. High-speed photography of compressed human trabecular bone correlates whitening to microscopic damage. *Engineering Fracture Mechanics* 74, 1928–1941.
- Turner, P.J., Chen, C.G., Ionova-Martin, S., *et al.*, 2010. Osteopontin deficiency increases bone fragility but preserves bone mass. *Bone* 46, 1564–1573.
- Turner, P.J., Lam, S., Weaver, J.C., Morse, D.E., Hansma, P.K., 2009. Localization of phosphorylated serine, osteopontin, and bone sialoprotein on bone fracture surfaces. *The Journal of Adhesion* 85, 526–545.
- Tierney, C.M., Haugh, M.G., Liedl, J., *et al.*, 2009a. The effects of collagen concentration and crosslink density on the biological, structural and mechanical properties of collagen-GAG scaffolds for bone tissue engineering. *The Journal of the Mechanical Behavior of Biomedical Materials* 2, 202–209.
- Tierney, C.M., Jaasma, M.J., O'Brien, F.J., 2009b. Osteoblast activity on collagen-GAG scaffolds is affected by collagen and GAG concentrations. *Journal of Biomedical Materials Research Part A* 91, 92–101.
- Tjha, C.K., Odvina, C.V., Rao, D.S., *et al.*, 2011. Mechanical property and tissue mineral density differences among severely suppressed bone turnover (SSBT) patients, osteoporotic patients, and normal subjects. *Bone* 49, 1279–1289.
- Townsend, P.R., Rose, R.M., Radin, E.L., 1975. Buckling studies of single human trabeculae. *Journal of Biomechanics* 8, 199–201.
- Turner, C.H., Rho, J., Takano, Y., Tsui, T.Y., Pharr, G.M., 1999. The elastic properties of trabecular and cortical bone tissues are similar: Results from two microscopic measurement techniques. *Journal of Biomechanics* 32, 437–441.
- Uthoff, H.K., Finnegan, M., 1983. The effects of metal plates on post-traumatic remodelling and bone mass. *Journal of Bone and Joint Surgery - Series B* 65, 66–71.
- van der Linden, J.C., Birkenhager-Frenkel, D.H., Verhaar, J.A., Weinans, H., 2001. Trabecular bone's mechanical properties are affected by its non-uniform mineral distribution. *Journal of Biomechanics* 34, 1573–1580.
- van Rietbergen, B., Weinans, H., Huiskes, R., Odgaard, A., 1995. A new method to determine trabecular bone elastic properties and loading using micromechanical finite-element models. *Journal of Biomechanics* 28, 69–81.
- van Ruijven, L.J., Giesen, E.B., Farella, M., van Eijden, T.M., 2003. Prediction of mechanical properties of the cancellous bone of the mandibular condyle. *Journal of Dental Research* 82, 819–823.
- Vashishth, D., Koontz, J., Qiu, S.J., *et al.*, 2000. In vivo diffuse damage in human vertebral trabecular bone. *Bone* 26, 147–152.
- Waarsing, J.H., Day, J.S., Verhaar, J.A.N., Edervae, A.G.H., Weinans, H., 2006. Bone loss dynamics result in trabecular alignment in aging and ovariectomized rats. *Journal of Orthopaedic Research* 24, 926–935.
- Wachter, N.J., Augat, P., Mentzel, M., *et al.*, 2001. Predictive value of bone mineral density and morphology determined by peripheral quantitative computed tomography for cancellous bone strength of the proximal femur. *Bone* 28, 133–139.
- Wolff, J., 1986. *Concept of the law of bone remodelling*. In *The Law of Bone Remodelling*. Berlin, Heidelberg: Springer Berlin Heidelberg.
- Wolfram, U., Wilke, H.-J., Zysset, P.K., 2010. Rehydration of vertebral trabecular bone: Influences on its anisotropy, its stiffness and the indentation work with a view to age, gender and vertebral level. *Bone* 46, 348–354.
- Xu, C., Su, P., Wang, Y., *et al.*, 2010. A novel biomimetic composite scaffold hybridized with mesenchymal stem cells in repair of rat bone defects models. *Journal of Biomedical Materials Research Part A* 95, 495–503.
- Yang, X.B., Roach, H.I., Clarke, N.M., *et al.*, 2001. Human osteoprogenitor growth and differentiation on synthetic biodegradable structures after surface modification. *Bone* 29, 523–531.
- Yang, X.B., Bhatnagar, R.S., Li, S., Oreffo, R.O., 2004. Biomimetic collagen scaffolds for human bone cell growth and differentiation. *Tissue Engineering* 10, 1148–1159.
- Young, M.F., 2003. Bone matrix proteins: Their function, regulation, and relationship to osteoporosis. *Osteoporosis International* 14 (Suppl 3), S35–S42.

- Yuan, L., Ding, S., Wen, C., 2019. Additive manufacturing technology for porous metal implant applications and triple minimal surface structures: A review. *Bioactive Materials* 4, 56–70.
- Zhou, Y., Chen, F., Ho, S.T., *et al.*, 2007. Combined marrow stromal cell-sheet techniques and high-strength biodegradable composite scaffolds for engineered functional bone grafts. *Biomaterials* 28, 814–824.
- Zimmermann, E.A., Schaible, E., Bale, H., *et al.*, 2011. Age-related changes in the plasticity and toughness of human cortical bone at multiple length scales. *Proceedings of the National Academy of Sciences of the United States of America* 108, 14416.
- Zimmermann, E.A., Launey, M.E., Barth, H.D., Ritchie, R.O., 2009. Mixed-mode fracture of human cortical bone. *Biomaterials* 30, 5877–5884.
- Ziopoulos, P., Currey, J.D., 1998. Changes in the stiffness, strength, and toughness of human cortical bone with age. *Bone* 22, 57–66.
- Ziopoulos, P., Currey, J.D., Casinos, A., 2001. Tensile fatigue in bone: Are cycles-, or time to failure, or both, important? *Journal of Theoretical Biology* 210, 389–399.
- Zysset, P.K., Edward Guo, X., Edward Hoffer, C., Moore, K.E., Goldstein, S.A., 1999. Elastic modulus and hardness of cortical and trabecular bone lamellae measured by nanoindentation in the human femur. *Journal of Biomechanics* 32, 1005–1012.

Overview of Substitutes for Bone Replacement: Natural and Synthetic Products

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Introduction

Organ replacement has long been a source of concern for humans. In particular, needs in the field of bone tissue engineering are currently increasing especially because of the aging population and the democratization of extreme sports. Bone-grafting procedures annually performed in the world are estimated at about a few million (Bohner *et al.*, 2012).

Bone is a connective tissue associating a fibrous organic matrix essentially made of collagen and a mineral part, more or less porous, comparable to a poorly crystallized calcium phosphate apatite, ensuring the rigidity of the bone tissue. The bone is in perpetual remodeling under the action of osteoblast cells, responsible for its formation and mineralization and osteoclast cells, contributing to its resorption. This continual renewal mechanism confers to the bone self-healing properties (Thomas *et al.*, 2008). Nevertheless, in some critical situations due to trauma or diseases and resulting in significant bone loss, the natural remodeling process is not sufficient to ensure the total restoration of the damaged tissues and justifies the use of external input. The concept of replacing missing bone tissue has emerged for centuries with traces of orthopedic treatments found in Pre-Columbian and Egyptian civilizations (de Grado *et al.*, 2018).

The replacement by natural biological materials was thus firstly considered. Nowadays, these transplants come from the patient himself (autograft), from another patient (allograft), or from an animal (xenograft). The autogenous graft is often viewed by surgeons as the gold standard. The use of autografts is thus quite widespread in order to prevent the risk of pathologies transmission induced by foreign grafts. Nevertheless, several major drawbacks, as additional surgery, limited quantity, inappropriate shape, chronic pain and infection risks, lead hospital practitioners to consider other techniques. Consequently, the use of bone substitute engineered products has widely expanded in the last decades. An essential criterion for the substitute is the absence of cytotoxic effect for the organism. This characteristic is called biocompatibility and was defined in 1987 by Williams as “the ability of a material to perform with an appropriate host response in a specific application” (Williams, 1987). Scientists have then enriched the vocabulary of bone tissue engineering by involving other more specific notions as osseointegration, osteoconduction, osteoinduction, bioresorption, *etc.* In addition to natural origin materials, several families of synthetic materials can meet some of these relevant criteria and thus be considered for bone substitution: metals and metal alloys, ceramics and glasses, polymers and composites (Ratner *et al.*, 2013). Biomaterials for bone substitution were classified according to the different phenomena observed at the bone/material interface. Three generations were thus defined. The materials of the first generation can be qualified as biotolerant but bioinert. The second and third generations gather all the bioactive materials with a distinction between osteoconductive ones in case of second generation and osteoinductive ones for the third generation (Hench, 1991; Cao and Hench, 1996; Bongio *et al.*, 2010). In the case of critical bone defects, reconstruction often uses several categories of materials. Indeed, the defect filling is ensured by bioactive materials of second or even third generation, while the support of the host bone/substitute combination, during healing, is ensured by inert fixations made of first generation materials.

This review provides an overview of materials from natural and synthetic origin, specifically in the field of bioceramics and bioglasses, applied to bone substitution and the developmental multidisciplinary approaches currently considered to improve the integration and bioactivity of these bone implants. This document is divided into three sections corresponding respectively to the different tracks used by researchers and suppliers to influence the biological performance of the implants. These are the chemical composition of the materials, the physical shape of the implants and the functionalization of the biomaterials.

Material Composition

Natural Origin

Autografts

The specific properties of an ideal bone substitute are being biocompatible, bioresorbable, osteoconductive, osteoinductive, structurally similar to bone, porous, mechanically resistant, easy to use, safe, and cost-effective (de Grado *et al.*, 2018). Regarding these specifications, autologous graft or autograft is the only type of graft to meet them all and that's why it is still the gold standard for bone filling. Indeed, taken from an anatomical site and transplanted to another site within the same individuals, the autologous bone graft can integrate more quickly and completely in the host bone with a progressive resorption followed by a replacement by a new viable bone (Wang and Yeung, 2017a; Shin *et al.*, 2015). Moreover, autografts may retain some cell viability and are considered to promote bone healing mainly through osteogenesis and/or osteoconduction. In addition, no rejection problem or disease transmission is expected after implantation of autologous grafts (Shin *et al.*, 2015). This kind of graft can be harvested either from intraoral or extra-oral donor sites. Intraoral donor sites include edentulous ridges, extraction sockets, mandibular ramus, symphysis, maxillary tuberosity, *etc.* Popular sources of extra-oral donor sites are the tibia, iliac crest, and calvarium (Shin *et al.*, 2015).

There are different types of commonly used autologous grafting like cancellous, cortical or vascularized autograft then bone marrow aspirate and platelet-rich plasma (Roberts and Rosenbaum, 2012).

Generally, cancellous bone is the most commonly used form of autologous bone grafting. Its superior osteogenic potential is due to the presence of high concentrations of osteoblasts and osteocytes. In addition, its large trabecular surface area encourages revascularization and incorporation at the recipient site. Unlike cancellous bone, whose low density provides little mechanical support, cortical bone possesses excellent structural integrity. However, its dense, highly organized structure is a limit for the supply of osteoblasts, osteocytes and other cellular progenitors leading to limited osteogenic and osteoinductive properties. In vascularized grafts, the graft's osteocytes and other osteoprogenitor cells are preserved. This may increase the graft's osteogenic potential and prevent the initial loss of graft strength seen with non-vascularized cortical grafts. Harvesting of such a vascularized bone graft requires the preservation of its nutrients, metaphyseal and/or additional perforating vessels, such as arteries and veins, in neighboring vessels upon delivery to the recipient site. Although bone marrow aspirate, which is the spongy tissue inside some of human larger bones, are less commonly employed than cancellous or cortical grafts, it has been shown to be effective in the treatment of bone defects and nonunions in some cases. Obtained from bone marrow aspiration, it is injected as a viscous fluid at the defective site but don't provide any structural support. Finally, platelet-rich plasma (PRP) is an autologous suspension of platelets prepared from whole blood *via* double-centrifugation techniques. PRP is rich in several key growth factors due to its high concentrations of platelets. Growth factors are polypeptides that act locally as modulators of cellular activities and naturally occur within a healthy bone matrix or are expressed during fracture healing. The combination of synthetic bone substitutes with bone-active growth factors is promising to achieve an optimal bone healing. Currently, a few biological factors like bone morphogenetic proteins (BMPs), fibroblast growth factors (FGF), vascular endothelial growth factors (VEGF), parathyroid hormone (PTH) and platelet-rich plasma (PRP) have been studied and clinically tested. In PRP, platelets are activated with calcium chloride after their extraction from the patients' blood and can be applied to the site of injury. (Roberts and Rosenbaum, 2012; Shin *et al.*, 2015).

As mentioned above, only autograft currently meets all the properties of an ideal bone graft especially an osteoconductive matrix, osteogenic cells and osteoinductive proteins. The lack of immune response is also a major advantage of this technique. However, the drawbacks of the autograft related to the harvesting process, including donor site complication and pain, increased blood loss, increased operative time, potential for donor site infection and limited volume of material available have been too extensively reported (Roberts and Rosenbaum, 2012; Wang and Yeung, 2017a; de Grado *et al.*, 2018).

Allografts

Allogeneic bone grafting or allografts refer to bone taken from human corpses, treated sterile and transplanted to a recipient (Roberts and Rosenbaum, 2012). Given the limitation of autologous bone grafts, bone allograft is considered the best alternative to autografts and has been used effectively in many circumstances, especially for patients with low healing potential, non-union established and extended comminution after fractures (Wang and Yeung, 2017a).

Due to its possibility to be machined and customized, allograft is present in a variety of forms, including osteochondral, cortical, cancellous and highly processed bone derivatives such as demineralized bone matrix (DBM) (Roberts and Rosenbaum, 2012; Wang and Yeung, 2017a). This kind of graft can exhibit osteoconductive and sometimes osteoinductive potential depending on the preparation process. In most of the cases, allografts do not include viable cells and are therefore not osteogenic, except for bone marrow allograft transplant, which can be employed in fracture healing (Roberts and Rosenbaum, 2012). Finally, compared to autografts, allografts are found to be immunogenic and demonstrate a higher failure rate (Wang and Yeung, 2017a).

Allograft has become a popular alternative to autologous bone grafting due to the lack of morbidity at the donor site, the reduction in surgical time and the general success of the results (Roberts and Rosenbaum, 2012). Nevertheless, the major drawbacks of allografts are the risk of disease transmission and the high costs of such material. Indeed, a risk of disease transmission exists like, for example cases of HIV or hepatitis B and C transmissions have been reported. The transmission of any other kind of viruses is not to be excluded even if procedures have been significantly improved by the development of modern tissue banks and improvement in processing technology. (de Grado *et al.*, 2018; Wang and Yeung, 2017a; Roberts and Rosenbaum, 2012). In addition to ethical issues, high production costs have to be considered because allografts need to be treated and sterilized before to be stored and clinically used. This could represent a significant cost contrary to the absence of storage during a autogenous bone graft procedure (de Grado *et al.*, 2018).

Cancellous allografts

Mostly supplied in the form of cuboid blocks, cancellous allografts are the most common types of commercial allogeneic grafts. Due to the poor mechanical properties they confer and their relatively weak capacity to promote healing, spongy allografts are mainly applied in the increase of spinal fusion and the filling material for cavitory skeletal defects. Indeed, compared to autografts, they are a relatively poor promoter of healing due to their preparation process. A similar but slower sequence of events occurs in the process of incorporating allografts compared to autograft. Unlike incorporation of autologous cancellous graft, an inflammatory response from the local host results in the incorporation of cancellous allograft, leading to the production of an encapsulated layer of fibrous tissue around the graft. During this time, the allografts remain trapped and are never completely absorbed several years after the transplant (Roberts and Rosenbaum, 2012; Wang and Yeung, 2017a; Goldberg and Akhavan, 2005).

Cortical allografts

In addition to being readily available, cortical allografts provide rigid structural support and can be used in conjunction with multiple other fracture repair techniques. Like cortical autografts, they can be used to fill large defects and allow sometimes early weight bearing even before bony incorporation. Indeed, they can be placed in areas requiring immediate load-bearing resistance due to their resistance to compressive strength. For this reason, cortical allografts are a commonly employed in spine procedures and are also frequently used to provide stabilization to the femoral shaft in the setting of periprosthetic hip fractures (Roberts and Rosenbaum, 2012).

Usually, transplanted allografts are frozen or freeze-dried products free from marrow and blood because of immune responses and safety reasons. Like cancellous allograft, cortical allograft incorporation involves an initial inflammatory response and is also preceded by creeping substitution in a similar way than its autogenous counterpart. In general, the process is initiated by osteoclastic resorption and followed by the sporadic formation of new apposition bones by osteoconduction (Wang and Yeung, 2017a; Roberts and Rosenbaum, 2012; Goldberg and Akhavan, 2005).

Demineralized bone matrix (DBM)

Demineralized bone matrix (DBM) is a kind of highly processed allograft derivative with at least 40% of the mineral content of the bone matrix removed by acid treatment, while collagens, proteins and growth factors remain (Boyce *et al.*, 1999). Thus, it can be considered as an artificial allograft and is available in the form of lyophilized powder, crushed granules, chips, dough, gels or injection mixture of DBM with autologous bone marrow (Connolly, 1995).

DBM is a popular supplement to vertebral fusion procedures, nonunion of grafts and filling of bone defects. Its osteoinductive properties are greater than those of cancellous or cortical allografts. Indeed, the osteoinductive property of DBM is mainly determined by the remaining growth factors, which are directly correlated with preparation techniques. Techniques involving alcohol, acetic acid, lactic acid and nitric acid have been demonstrated to have a detrimental effect on osteoinductivity. That is why most of the commercially available DBM today is washed with hydrochloric acid. Concerning DBM osteoconductivity, it is conferred by providing a framework for cell populating and for generating new bone after the demineralization treatment. In addition, some modern DBM preparations are mixed with cortical and/or cancellous bone chips to provide additional osteoconductive properties. Like the autogenic graft, the incorporation of DBM starts with growth factors triggering a cascade of endochondral ossification and leading to new bone formation at the implantation site (Roberts and Rosenbaum, 2012; Goldberg and Akhavan, 2005; Wang and Yeung, 2017b).

No immunological rejection is present with DBM because the antigenic surface structure of the bone is destroyed during its acid demineralization. The use of DBM prevents donor site morbidity and comparable pain intensity has been shown after the surgical procedure compared to autograft procedures. Despite a suitable availability, demineralized bone matrix is more expensive than an iliac crest bone autograft procedure and its mechanical properties are quite low. Thereby, DBM is not currently used as a stand-alone bone substitute but preferentially for filling purposes (de Grado *et al.*, 2018; Campana *et al.*, 2014; Kinney *et al.*, 2010; Pieske *et al.*, 2009).

Xenografts

Another alternative to autograft could be the use of xenogenic bone or xenografts. Xenograft bone substitutes have their origin from a species other than human, such as bovine or porcine bone and corals which can be freeze dried or demineralized and deproteinized. They are usually only distributed as a calcified matrix after several treatments (de Grado *et al.*, 2018; Campana *et al.*, 2014; Wang and Yeung, 2017a).

Among xenograft materials, coral based xenografts have been approved to be used as bone substitutes in 1992 by the Food and Drug Administration (FDA), which is the national health product regulatory agency in the United States (de Grado *et al.*, 2018). Indeed, corals have interconnected pores and a skeleton quite similar to cortical and spongy bones. Madreporite and/or milleporite type of corals are harvested and treated to become “coral derived granules” (CDG) and other types of coralline xenografts. Coral-based substitutes are mainly calcium carbonate while natural human bone is made of hydroxyapatite (HA) along with calcium phosphate and carbonate. A large proportion of fluorides, useful in the context of grafting to promote bone development, can also be found in coralline materials. Further, the coral material can remain in its calcium carbonate state or either be transformed industrially into hydroxyapatite through a hydrothermal process. Its calcium carbonate form has the advantage of a better resorption of the graft by the natural bone while its transformation to hydroxyapatite yields to a non-resorbable xenograft. Coralline HA can be used as growth factors carrier, such as BMP (Bone Morphogenetic Proteins), TGF- β (Transforming Growth Factor-beta), or FGF (Fibroblast Growth Factor). It can be found in different aspects like granules or blocks and it is able to provide immediate support, rapid ingrowth and healing of cancellous bones. Despite its slow resorption, it does not induce adverse effects. In addition, coralline HA is osteoconductive, may show excellent bone binding capacity, avoids donor site morbidities and is unlikely to promote disease transmission or the risk of deep infections. The main problems of coralline hydroxyapatite are minimal remodeling due to high crystallinity coupled with its insoluble nature and the fact that osteoclasts cannot absorb it, so that these implants live in the implantation site throughout their life (de Grado *et al.*, 2018; Campana *et al.*, 2014; Wang and Yeung, 2017a; Roberts and Rosenbaum, 2012).

Even if xenografts present interesting advantages like the easy availability, the osteoconductivity, the good mechanical properties and low costs, the same limitations than allografts persist. Indeed, there is still a risk of immunogenicity problems and disease transmission concerning the porcine endogenous retrovirus (PERV) and the bovine spongiform encephalopathy (BSE).

Finally, patients beliefs can be a restriction on the acceptance and the use of this technique by the medical team (de Grado *et al.*, 2018; Campana *et al.*, 2014).

Synthetic Origin

In order to avoid all the limitations of the above-mentioned autografts, allografts and xenografts, in particular the severe shortage of natural bone grafts faced with an aging population, the use of synthetic bone substitutes is becoming more and more popular (de Grado *et al.*, 2018; Wang and Yeung, 2017a).

For the engineering of synthetic bone substitutes, the first input to be considered is the raw material. Currently, bioceramics, bioactive glass, polymers or combinations thereof are the most commonly available synthetic materials for bone substitutes (Wang and Yeung, 2017a; Roberts and Rosenbaum, 2012).

Bioceramics

1st generation: Inert bioceramics

The first objective in the research of ceramic materials for bone substitutes, starting in the 1950s, is to use inert materials which have no reaction with living tissues. This first generation is formed by inert ceramics with the most well-known examples, zirconia (ZrO_2 , zirconium dioxide) and alumina (Al_2O_3 , aluminum oxide) which are primarily used in the fabrication of femoral heads. However, these inert ceramics experiment foreign body reactions in a similar way to what happens with metallic and polymeric biomaterials. Therefore, even if they are biocompatible, they will give rise to a foreign body surrounding the implant by an acellular collagen capsule which will isolate it from the body. In this way, an inert ceramic does not form a bonding to bone and will never transform itself into bone (Vallet-regí, 2010; Hench, 1991). Yet, release of substances from zirconia and alumina implants to the surrounding tissue is very low and neither local nor systemic effects have been reported (Li and Hastings, 2016).

Oxide ceramics like alumina and zirconia exhibit superior mechanical properties, corrosion and wear resistance. Indeed, they are stable even in the most invasive industrial and biomedical environments. Their high strength, excellent corrosion and wear resistance and stability, non-toxicity and biocompatibility *in vivo* make them adequate candidates for load-bearing hard tissue replacements and fixation implants in dentistry and surgery. Alumina bioceramics are in the pure aluminum oxide form and their most established example of bone substitute application is the total hip endoprosthesis with a combination of metallic stem, ceramic ball and ultra-high molecule weight polyethylene (UHMWPE). On another side, zirconia bioceramics are partially stabilized by additional oxides like yttrium oxide, calcium oxide or magnesium oxide and are mostly used in hip ball and dental implants. Alumina and zirconia can also be both used for alveolar ridge reconstruction, maxillofacial reconstruction, as bone substitutes and in ophthalmology, knee prosthesis, bone screws as well as other applications as dental biomaterials, such as dental crown core, post, bracket and inlay (Li and Hastings, 2016).

Concerning mechanical properties of oxide bioceramics, alumina is mechanically weaker than zirconia although it is chemically more stable. Moreover, the phase changes in zirconia produce a unique ceramic material having much higher strength and higher fracture toughness compared with alumina and other ceramics. Indeed, as first discovered by Garvie *et al.* (1975), an increase of both strength and fracture toughness can be obtained by utilizing the zirconia tetragonal-monoclinic phase transformation induced by the presence of the stress field ahead of a crack. During this transformation, the variation in volume and the shear deformation developed in the reaction are recognized as opposing the opening of the crack and therefore acting to increase the resistance to crack propagation. As a consequence, zirconia resulting excellent mechanical properties allow to design implants with increased long-term clinical performance (Li and Hastings, 2016; Garvie *et al.*, 1975).

2nd generation: Bioactive bioceramics

Later in the advancement of ceramic research for bone applications, in the 1980s, the new trend became the manufacturing of ceramics implants that react with the environment and produce newly formed bone. The search for bioactive ceramics yielded to promising results with ceramics that can react with the physiological fluids forming biological-type apatite. Further, in the presence of living cells, this apatite can form new bone. Among these bioactive ceramics, calcium phosphate (CaP) and calcium sulfate are effective and well-known materials. These bioactive ceramics form the second generation of bioceramics. For medical applications, these materials are provided in several formats: powder, porous pieces, dense pieces, injectable mixtures and coatings. They have excellent features in terms of biocompatibility and bioactivity, but their mechanical properties are really poor (Hench, 1991; Vallet-regí, 2010; Wang and Yeung, 2017a).

Calcium phosphate

Calcium phosphate (CaP) is the common name of a family of minerals containing calcium cations (Ca^{2+}) together with orthophosphate (PO_4^{3-}), metaphosphate (PO_3^-), or pyrophosphate ($\text{P}_2\text{O}_7^{4-}$) anions, and sometimes hydrogen (H^+) or hydroxide (OH^-) ions. They are the principal form of calcium found in bovine milk and blood and the major inorganic constituent of bone and tooth enamel (Eliaz and Metoki, 2017). Calcium phosphate compounds used in bone grafting include monocalcium phosphate, dicalcium phosphate, tricalcium phosphate (both alpha- and beta- crystalline forms), hydroxyapatite and tetracalcium phosphate (Roberts and Rosenbaum, 2012). These synthetic materials can be processed in both dense and porous forms in bulk, as well as in the forms of powders, granules, cements/pastes, scaffolds or coatings as a function of the

biomedical applications. Common commercially available forms of CaP are porous implants, non-porous dense implants and granular particles with pores (Habraken *et al.*, 2016; Wang and Yeung, 2017a).

Most common CaP synthesis methods can be separated in different categories: dry methods, wet methods, high temperature processes or synthesis from biogenic sources (Sadat-Shojai *et al.*, 2013). Dry methods do not use a solvent, unlike wet methods, and can be performed in two main ways: solid-state synthesis and mechanochemical process. The main advantages of these methods are the possibility to produce highly crystalline CaP from relatively inexpensive raw materials. However, the large size of particles in the case of solid-state synthesis and the low phase purity in the case of mechanochemical process are major drawbacks (Sadat-Shojai *et al.*, 2013). Unlike dry methods, wet methods have conventionally been applied to the preparation of CaP particles having a nanosized structure with a regular morphology. Indeed, wet chemical methods have the advantages in precise control over the morphology and size of particles. Aqueous solutions of various sources for phosphate and calcium ions are employed and CaP crystals are normally produced by precipitation. Wet processes can be performed by a number of technical routes classified into six groups: conventional chemical precipitation, hydrolysis method, sol-gel method, hydrothermal method, emulsion method, and sonochemical method. Nevertheless, difficulties in controlling the crystallinity and phase purity of nanoparticles, some technical issues and time-consuming details make some wet procedures unsuitable for scaling up to produce large quantities of CaP (Sadat-Shojai *et al.*, 2013; Canillas *et al.*, 2017a,b). In order to have a better control on the phase purity, high-temperature processes can be used to avoid undesirable CaP phases while producing CaP with high crystallinity and good chemical homogeneity. Currently, two possible routes for CaP high-temperature synthesis are combustion method and pyrolysis process. Yet, the main disadvantages are a poor control over the processing variables and generation of the secondary aggregates (Sadat-Shojai *et al.*, 2013; Canillas *et al.*, 2017a,b). Finally, biogenic sources mainly bone waste, eggshells, exoskeleton of marine organisms, naturally derived biomolecules, and biomembranes can be employed to produce CaP. The extraction of biominerals from biowastes is an interesting process due to the economic and environmental benefits of waste recovery. In addition, some extracted ceramics present some superior characteristics like a better acceptance by the living organs, because of its physicochemical similarity to the human bone apatite. In a near future, this approach is expected to attract more attention, especially to overcome the current drawbacks. Indeed, some of these waste materials can be exclusively used to produce CaP blocks or particles of large size (Sadat-Shojai *et al.*, 2013).

Depending on the forms and requirements needed for CaP materials, different techniques can be used. Processing of ceramic pieces normally consist in two steps, the shaping and the following sintering. Most common shaping methods include: uniaxial compaction, isostatic pressing, granulation, slip casting, gel casting, freeze casting, atomization, polymer replication, extrusion, low pressure injection, slurry, dipping or thermal spraying. Also, the shaping of CaP can be realized during cooling and solidification of previously melted raw materials. The second step, sintering, is a processing step to consolidate the shaped forms. During the sintering of CaP, different processes take place. First water, carbonates and remaining volatile chemicals from synthesis are removed. Second, shrinkage occurs as a consequence of the removal of these gases while powders densify, and grain size increases. There are also some chemical changes and chemical decomposition depending the CaP species. Conventionally, sintering is carried out in electric furnaces with quite long thermal cycles. However, alternative sintering methods such as hot isostatic pressing, microwave, spark plasma sintering or rate-controlled sintering have been proposed in order to obtain improved mechanical properties, by minimizing grain growth and shrinkage during sintering (Canillas *et al.*, 2017a,b; Eliaz and Metoki, 2017).

Among the CaP family, hydroxyapatite and tricalcium phosphate are the most studied and used for biomedical applications due to their excellent properties allowing them to promote rapid bone formation on their surface and assure fast bone healing (Wang and Yeung, 2017a; de Grado *et al.*, 2018; Eliaz and Metoki, 2017; Habraken *et al.*, 2016).

Hydroxyapatite (HA)

Hydroxyapatite (HA) is one of the most studied CaP compounds and has the specific formula $(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2)$. Its Ca/P ratio is 1.67 and it is part of the apatite family, which includes crystalline compounds with crystalline hexagonal lattice. Hydroxyapatite accounts for nearly 70% of the mineral content of teeth and bone but it is present in a substituted form. Indeed, pure, stoichiometric HA never occurs in biological systems. In fact, mineral species like carbonate, silicate, magnesium as well as other ions can replace hydroxyl or phosphate groups in the apatite structure (Campana *et al.*, 2014; de Grado *et al.*, 2018; Eliaz and Metoki, 2017; Wang and Yeung, 2017a).

Hydroxyapatite is recognized as a good bone graft material since it is a bioactive substance forming a strong chemical bond with host bone tissue. In addition to its bioactivity, HA is also osteoconductive, non-toxic, non-immunogenic and has similar mechanical properties compared to the cancellous bone. HA ceramic parts can be manufactured with a macroporosity and pore interconnectivity to allow the adhesion, proliferation, differentiation of osteoprogenitor cells, the revascularization and subsequently ingrowths of new bone after implantation (Campana *et al.*, 2014; de Grado *et al.*, 2018).

Because of its chemical similarity with the biological mineral in bone and teeth, HA is widely employed in different clinical uses from augmenting atrophic alveolar ridges to repairing long bone defects, non united bone fractures, middle ear prostheses, spinal fusions, and craniofacial repair. Moreover, hydroxyapatite has also been used in dental surgery, biomolecular and drug delivery, as well as for coating on orthopedic and dental implants (Eliaz and Metoki, 2017).

However, the major drawback of hydroxyapatite is its very low *in vivo* resorption. Its relatively high Ca/P ratio and its crystallinity delay its resorption rate leading to its retention at least up to 3 years after implantation. This could be an issue since the remaining hydroxyapatite grafts could compromise the intrinsic strength of the new-formed bone at the defect site. Indeed, it

has been shown that mechanical properties of HA grafts generally decrease by 30%–40% *in situ* after being implanted for several months (Wang and Yeung, 2017a; de Grado *et al.*, 2018; Campana *et al.*, 2014).

Tricalcium phosphate (TCP)

Tricalcium phosphate belongs to the whitlockite family characterized by the general formula $(\text{Ca,Mg})_3(\text{PO}_4)_2$. TCP can be found as three poly-morph phases: β , α and α' . Both α -TCP and β -TCP are used in clinics for bone repair and remodeling applications. Indeed, while β -TCP is mainly used for the manufacturing of biodegradable bioceramics shaped as dense or macro-porous granules and blocks, the more soluble and reactive α -TCP is mainly used as a fine powder in the preparation of calcium phosphate cements (Carrodegua and De Aza, 2011; Canillas *et al.*, 2017a,b; Wang and Yeung, 2017a; de Grado *et al.*, 2018).

Especially β -TCP has been widely studied since its discovery in 1920 and has largely been used as a bone substitute for more than 25 years, mainly for orthopedics and dentistry applications. It presents excellent properties like biocompatibility, osteoconductivity and bioresorption. Indeed, with its chemical formula of $\text{Ca}_3(\text{PO}_4)_2$ and a Ca/P ratio of 1.5, β -TCP is characterized by a better resorption *in vivo* compared to hydroxyapatite. Typically, β -TCP grafts are gradually resorbed by osteoclasts and replaced by remodeled bone in weeks after implantation. For this reason, TCP is one of the most effective materials for filling bone defects caused by trauma and benign tumors since it serves as a temporary support for bone healing. Moreover, the presence of a porous interconnected structure may accelerate the bone remodeling ability of β -TCP by facilitating the colonization of osteogenic cells and nutrients *via* an enhanced capillarity (de Grado *et al.*, 2018; Wang and Yeung, 2017a; Eliaz and Metoki, 2017).

Some current clinical uses of tricalcium phosphate are spine fusion, open-wedge tibial osteotomy, contained bone defects, hand surgery, oral/periodontal procedures and drug carriers. The use of β -TCP has shown really few complications like infection or nonunion. Nevertheless, this material presents some drawbacks like its unpredictable bioresorption and its poor mechanical properties. Indeed, β -TCP mechanical properties are still inferior to cancellous bone or bone allografts ones in most cases (de Grado *et al.*, 2018; Eliaz and Metoki, 2017; Wang and Yeung, 2017a; Canillas *et al.*, 2017a,b).

Biphasic calcium phosphate (BCP)

Since 1985, the term BCP describes bioceramics consisting of a mixture of HA and β -TCP phases. This kind of mixtures is widely used in commercial ceramic in order to combine the advantages of both calcium salts. Indeed, this association presents all the advantages of both components like osteoconductivity, biocompatibility, safety and promotion of bone formation. However, the main profit of BCP is the possibility to control the bioresorption. Of course, as mentioned above, the resorption of β -TCP is faster than the resorption of hydroxyapatite due to its smaller Ca/P ratio. Yet, HA presents better mechanical properties than β -TCP with average compressive resistances of 160 and 100 MPa, respectively. So, the combination of both allows, on one hand, a faster resorption and a higher bone ingrowth rate than using HA alone. On the other hand, it confers better mechanical properties and a more controlled resorption than β -TCP alone (de Grado *et al.*, 2018; Wang and Yeung, 2017a; Canillas *et al.*, 2017a,b).

BCP with different HA/ β -TCP ratios can be produced to adjust the dissolution rate and mechanical properties. Biphasic calcium phosphate can be useful as implant coatings or can be prepared in compact form or porous forms with interconnected macropores to mimic the cancellous bone structure. Some compositions are commercially available as bone graft or bone substitute biomaterials for orthopedic, maxillofacial and dental applications. Sometimes, they can be associated with bone marrow aspirate which then provides enhanced osteogenic properties. Despite the improvement of mechanical properties by the mixing of β -TCP and HA, the strength of BCP ceramics is still lower than cortical bone compression strength, which is between 150 and 200 MPa (de Grado *et al.*, 2018; Wang and Yeung, 2017a; Canillas *et al.*, 2017a,b).

Doped CaP

Some strategies have been considered in order to improve the mechanical and biological properties of synthetic calcium phosphate. One of them consists of doping calcium phosphate with different dopants. The first type of doping involves cationic substitution, where monovalent, bivalent and multivalent cations replace Ca^{2+} into the CaP lattice sites. The most well-known examples are Mg^{2+} , Sr^{2+} , Zn^{2+} or Ag^+ . A second type of doping implies the anionic substitution, where hydroxyl and/or phosphate sites are substituted by anionic species like F^- , Cl^- , OH^- , CO_3^{2-} or PO_4^{3-} . Usually present as traces, these ions can affect the lattice parameters, the crystallinity, the dissolution kinetics and other physical properties of CaP (Tite *et al.*, 2018; Adzila *et al.*, 2012; Boanini *et al.*, 2010).

These dopants are used for different reasons. First of all, doping of synthetic CaP can be useful to mimic the natural mineral bone composition which is an apatite characterized by small dimensions, low crystallinity and non-stoichiometric composition containing significant amount of CO_3^{2-} ions. Another role of dopant substitution is the possibility to increase the thermal stability of some CaP phases. The most famous example is the thermal stabilization of β -TCP. Indeed, there is a main difficulty concerning the sintering of β -TCP since it undergoes a phase transformation to α form around 1150°C. This phase transformation is accompanied by a sudden dilatometric expansion leading to mechanical stresses inducing cracks within the ceramic part. This phase transformation limits the mechanical reliability of TCP ceramics sintered above the transformation temperature. To avoid these difficulties, it has been shown that the addition of dopants like Mg^{2+} , Zn^{2+} and Sr^{2+} can stabilize the β -TCP phase and postpone its problematic allotropic transition to higher temperatures. Finally, ionic substitution serves also to optimize cell-material interactions of calcium phosphate and strengthening their mechanical properties. Indeed, the presence of minerals and traces of metal elements can aid bone growth and accelerate bone formation and resorption *in vivo*. Some ions have also been reported able to eliminate the bacterial presence around the CaP graft. Concerning the improvement of mechanical properties, the

substitution of calcium by other cations can increase the strength of some chemical bonds, shrink the lattice volume and strengthen the CaP mechanical behavior (Tite *et al.*, 2018; Boanini *et al.*, 2010; Adzila *et al.*, 2012; Champion, 2013).

CaP cements

Calcium phosphate cements (CPCs) were invented in 1986 by Brown and Chow in order to extend the adaptability and moldability of calcium phosphate bone substitutes. CaP cements consist of a calcium phosphate powder which is mixed with a liquid, usually an aqueous curing agent, to form a workable paste. CPCs can be easily injected to fill bone defects with various shapes and then solidified through an isothermal hardening reaction whose duration varies from 15 to 80 min depending on the formulation. After solidification and depending of its composition, the bioresorbable CPC can stay in the body for up to 2 years without resorption, to support bone healing. The possibility to fill complex bone cavity with such CaP pastes is the main advantage of CPC. Indeed, they allow avoiding gaps between the bone and the implant. In addition, some CPC compositions are injectable and absolutely useful in minimal invasive procedures such as vertebroplasty and kyphoplasty (de Grado *et al.*, 2018; Wang and Yeung, 2017a; Canillas *et al.*, 2017a,b).

According to the composition, properties of CPCs like their feasibility, setting reaction and biodegradation can change. Currently, two types of CPC can be distinguished. The first type is apatitic CPCs which are viscous with a relatively poor injectable ability. Nevertheless, the setting reaction can occur at the physiological pH value and the mechanical properties are slightly better than the second type of CaP cements, brushite CPCs. Indeed, the brushite CPCs demonstrate high but sometimes unpredictable degradability. However, they are feasible for injection and solidify quickly at a low pH value. In the same way as the other calcium phosphate substitutes, CPCs are biocompatible and osteoconductive but brittle leading occasionally to some complications (de Grado *et al.*, 2018; Wang and Yeung, 2017a).

Calcium sulfate

Another kind of commonly used synthetic material for bone substitutes is calcium sulfate. Also known as plaster of Paris, calcium sulfate (CaSO_4) is an osteoconductive and biodegradable ceramic applied in filling void defects since 1892. Indeed, it offers lots of advantages like being osteoconductive, non-allergenic, inexpensive and available in different forms. Its preparation consists of heating gypsum with a patented alpha-hemihydrate crystal structure and it can be manufactured into hard pellets or injectable viscous fluids that harden *in vivo* (de Grado *et al.*, 2018; Wang and Yeung, 2017a).

The main characteristic of calcium sulfate is its fast resorption, even faster than CaP phases like α / β -TCP. Indeed, it resorbs in 1–3 months *in vivo* after implantation and it creates porosity while stimulating bone ingrowth. This makes calcium sulfate the most rapidly absorbed synthetic bone substitute available. Its rapid resorption in addition to its lack of macroporous structure and weak mechanical properties make calcium sulfate an inappropriate material to support early functional rehabilitation. Actually, the resorption of calcium sulfate is faster than the deposition of new bone causing a non optimal fusion between the implant and the implantation site. For these reasons, calcium sulfate is more used to fill small bone defects with rigid internal fixation or as a support or a vehicle for local antibiotics or growth factors delivery. Indeed, calcium sulfate is a convincing choice of material for a combination with other synthetic bone substitutes because of its easy preparation and its low cost (de Grado *et al.*, 2018; Wang and Yeung, 2017a; Roberts and Rosenbaum, 2012).

Bioglasses

Bioactive glasses or bioglasses is a group of synthetic silicate-based ceramics. At the time of their discovery in 1970s, the Bioglass® composition was 45 wt% silicon dioxide (SiO_2), 24.5 wt% sodium oxide (Na_2O), 24.5 wt% calcium oxide (CaO) and 6 wt% phosphorus pentoxide (P_2O_5). Afterwards, some additives like potassium oxide (K_2O), magnesium oxide (MgO) and boric oxide (B_2O_3) were added to obtain a more stable composition (de Grado *et al.*, 2018; Wang and Yeung, 2017a).

Like the CaP and calcium sulfate ceramics, bioglasses are biocompatible, osteoconductive, do not induce any inflammatory response and often present a porous structure promoting resorption and bone ingrowths. Indeed, after implantation, a strong physical bonding takes place between bioglasses and host bones probably caused by the leaching and the accumulation of silicon and the formation of hydroxycarbonate apatite (HCA) layer on the surface of the glass. In fact, the surface of the bioglasses, subjected to an aqueous solution or to body fluids, starts to dissolve and transforms into a layer of gel rich in silica- $\text{CaO}/\text{P}_2\text{O}_5$ which then mineralizes into hydroxycarbonate apatite in a few hours. Hydroxycarbonate apatite is similar to bone mineral and interacts with collagen fibrils to create a bond with the host bone. This thin HCA film absorbs proteins, attracts osteo-progenitor cells and is partially replaced by bone through a creep substitution process. Bioglasses undergo relatively fast *in vivo* resorption and can be completely resorbed in six months. The greater the porosity, the faster the resorption following deposition of the new bone (Jones, 2013; de Grado *et al.*, 2018; Wang and Yeung, 2017a; Rahamana *et al.*, 2011).

Dissolution products of the glass, soluble silica and calcium ions, stimulate osteogenic cells to produce bone matrix and confer osteoinductive properties to bioglasses. Unlike CaP ceramics which are only osteoconductive because they support new bone growth, bioglasses are osteoconductive as well as osteoinductive. Indeed, they support new bone growth along the bone-implant interface as well as within the implant away from the bone-implant interface (Jones, 2013; Rahamana *et al.*, 2011).

Currently, there are several types of bioactive glass: the conventional silicates, such as Bioglass® 45S5, phosphate-based glasses and borate-based glasses. Phosphate glasses present very high solubility and it is possible to control this solubility by manipulating their composition. Borate glasses have really encouraging clinical results of healing of chronic wounds, they are easily to process and they show a faster degradation than silica-based bioglasses (Jones, 2013; de Grado *et al.*, 2018).

Different methods are available to prepare porous bioactive glass scaffolds. The conventional melt-quenching route consists in forming glass particles of a “melt-derived” glass into a construct with the desired architecture and geometry. After this shaping step, a mechanically reliable 3-D network with interconnected porosity is formed by the sintering of the structure where the particles are bond together. Other methods like sol-gel processing, electrospinning or processing of a viscous melt have also been used to prepare foldable scaffolds of bioactive glass (Jones, 2013; Rahamana *et al.*, 2011).

Concerning bioglasses biomedical applications, the original Bioglass 45S5 has been widely used to repair bone defects in the jaw and in orthopedics. However, bioglasses are quite brittle with low mechanical strength and decreased fracture resistance. For these reasons, bioactive glass porous scaffolds can only be used in sites where there is little load or only compressive load, for examples in the reconstruction of facial defects (de Grado *et al.*, 2018; Jones, 2013; Wang and Yeung, 2017a; Rahamana *et al.*, 2011).

Polymers

Compared to other bone substitute materials, polymers possess drastically different physical, mechanical and chemical properties. Polymers are macromolecules composed of covalently bonded monomers with a glass transition temperature that makes them quite flexible. Both natural and synthetic polymers can be used for bone repair applications (Campana *et al.*, 2014; Prakasam *et al.*, 2017).

Well-known natural polymers are starch, chitosan, derivatives of hyaluronic acid, collagen, fibrin gels and silk. The most used and important is collagen and can be found in bone. Indeed, bone is a composite mostly made of collagen and carbonate substituted hydroxyapatite arranged in a highly organized hierarchical structure which has a strong effect on the bone mechanical properties. Although collagen can be employed alone in some cases, it is mainly used in combination with other materials such as with bioceramics like hydroxyapatite. Actually, this kind of composite made with ceramic and collagen can combine benefits of both materials, especially in terms of mechanical properties. On one hand, the ductile properties of collagen help to increase the poor fracture toughness of bioceramics while the additions of ceramic particles to collagen give higher stability and resistance. In addition, such composites have been proved to be biocompatible and show better osteoconductive properties compared to the corresponding pure materials. Moreover, for surgical applications, the addition of collagen to a ceramic structure can provide shape control, spatial adaptation, increased particle and defect wall adhesion, and the capability to favor clot formation and stabilization. The main objective in the manufacturing of collagen-ceramic is to mimic the bone composition in order to reduce bacterial infections and risks of implant rejection. Some collagen-ceramic composites are already available in the market and suitable for spinal fusions. However, further studies are needed to assess the efficiency of such composites compared to other bone substitute materials (Campana *et al.*, 2014; Lawson and Czernuszka, 1998; de Grado *et al.*, 2018).

Concerning synthetic polymers for bone substitutes, they can be nondegradable or biodegradable depending on the composition. The most used nondegradable polymer is poly(methyl methacrylate) (PMMA) which is employed in orthopedics for 60 years. It is still currently a key material and one of the most enduring materials in orthopedic surgery due to its non-biodegradable and nonresorbable properties. PMMA is mainly used as cements for its high mechanical property and feasibility for handling. Actually, PMMA cements are of the most extended used materials for articular prosthesis fixation and vertebroplasty. Indeed, this polymer is rigid, biologically inert, relatively inexpensive, easy to obtain and minimally resorbed. This kind of cements can be prepared by mixing powdered methyl methacrylate polymer and liquid methyl methacrylate monomer, which polymerize during an exothermic reaction. This exothermic reaction can induce excessive heat and may potentially damage adjacent tissues. The main drawbacks of PMMA are its lack of bioactivity, its lack of replacement by new bone and its long-term susceptibility to infection or rejection (de Grado *et al.*, 2018; Campana *et al.*, 2014; Wang and Yeung, 2017a; Pryor *et al.*, 2009).

With the ability to be resorbed by the body, degradable polymers like poly lactic acid (PLA), poly glycolic acid (PGA), poly- β -hydroxybutyrate (PHB), poly lactic-co-glycolide (PLGA) and poly(ϵ -caprolactone) have the advantage of enhancing bone healing without remaining into the body. Depending on the type of polymer chain arrangement and its crystallinity/amorphous nature, the degradation rate can be modified. PCL, PGA and PLA are used for craniomaxillofacial fixation, sutures, interference screws, fixation plates and pins and for meniscus. However, these polymers lack mechanical strength and their degradation rate is not well controlled in addition to their tendency to induce inflammation reactions in the acidic medium. Moreover, they do not promote new bone growth and may rather inhibit it. An exception could be the PCL which is considered as a promising polymer since it is being used to enhance bone ingrowth and regeneration in the treatment of bone defects. Yet, its current slow degradation time limits its clinical use. Nevertheless, biodegradable polymers can be used as standalone devices, as extenders of autografts/allografts or as bioactive molecules or growth factors carriers. Current polymer-based bone substitutes exist in different forms but they are mainly studied in the field of tissue engineering for their manufacturing with macropores and micropores or also in the shape of thick membranes (de Grado *et al.*, 2018; Campana *et al.*, 2014; Wang and Yeung, 2017a; Sabir *et al.*, 2009; Prakasam *et al.*, 2017).

Composites

Finally, the different materials mentioned above can be associated and combined to form composites as explained with collagen and hydroxyapatite Section “Polymers”. A vast range of composite materials exists for bone repair applications. They differ by the components chosen and to the way they are assembled and processed. The main kinds of composites materials are organic/inorganic fiber composites, bioglass/polymer composites, hydrogel composites, polymer-polymer composites, multiphase ceramics and ceramic/polymer composites. Among them, biocomposites consisting of an inorganic dispersed phase in a polymer matrix are widely studied for their extremely promising properties as bone substitutes. The selection of components obviously

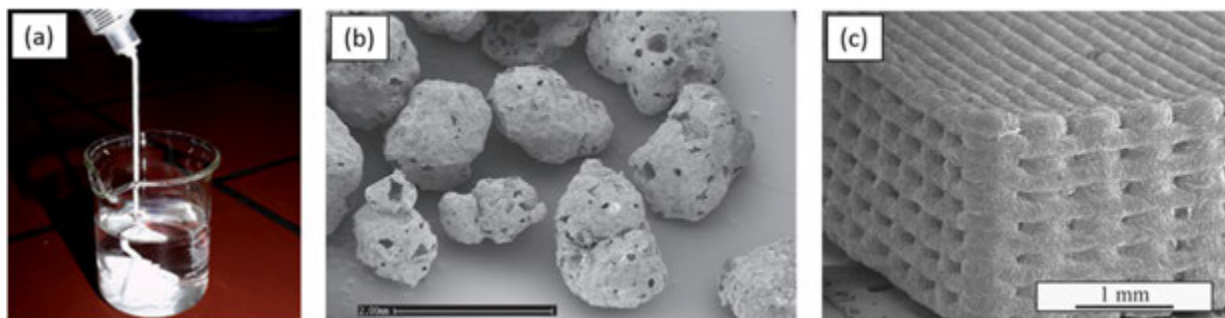


Fig. 1 The most used bone graft substitutes forms: (a) cements/pastes, (b) granules and (c) porous blocks/scaffolds; (a) and (b); (c). Reproduced from (a) and (b) Bohner, M., 2010. Resorbable biomaterials as bone graft substitutes. *Materials Today* 13 (1–2), 24–30. [https://doi.org/10.1016/S1369-7021\(10\)70014-6](https://doi.org/10.1016/S1369-7021(10)70014-6). (c) Miranda, P., *et al.*, 2006. Sintering and robocasting of β -tricalcium phosphate scaffolds for orthopaedic applications. *Acta Biomaterialia* 2, 457–466.

depends on the intended application, especially if the bone substitute is used or not in load-bearing areas or if it must be resorbable or not. Nevertheless, there is a main objective in biocomposites fabrication which consists in the reinforcement of a relatively low-modulus polymer with a high-modulus, high-strength reinforcing inorganic material. It is performed by using the plastic flow of the polymeric material under stress to transfer the load to the inorganic phase. In this way, a composite with a higher strength and modulus than the polymer alone and better toughness and process ability than the pure inorganic material can be produced. Biocomposites properties depend on the relative volume fraction of each of the phases and the way they are processed. The most commonly used polymers in combination with inorganic materials are chitosan, silk, gelatin, alginate, saturated poly- α -hydroxy esters, including PLA and PGA, their copolymer PLGA and PCL. These polymers can be mixed with inorganic powders or scaffolds like CaP, calcium sulfate or bioglasses. Due to their porosity and cell adhesion ability, biomaterial composites present a promising role in drug delivery. In addition, the manufacturing of inorganic/polymer composites also allows to mimic the bone structure and might receive higher demand in future for this reason (Grøndahl *et al.*, 2017; de Grado *et al.*, 2018; Bongio *et al.*, 2010; Kashirina *et al.*, 2019).

Finally, another type of composite is starting to get attention: the combination of synthetic materials with xenografts called xenohybrid. Indeed, it is becoming interesting in research as well as in industrial and clinical practices. This kind of composite presents high similarity with human cancellous bone and possesses higher bioactivity. Moreover, there is the possibility to tailor the degradation rate of the material and to incorporate active biomolecules. Although some studies pretend that this combination provides enhanced clinical performance, there is a need of more clinical data to further develop the properties of such materials. The major issue with the use of xenografts remains the alteration of both mechanical and biological performances through the cleaning and sterilization process (Haugen *et al.*, 2020; Ferracini *et al.*, 2019).

Comparison Natural Synthetic

Natural materials such as autograft, allograft, xenograft, demineralized bone matrix or natural polymers have been used beside synthetic materials like ceramics, bioglasses or polymers in bone repair applications. Although synthetic materials possess regenerative effects and are highly useful to solve the natural bone substitutes limitations, their lack of osteoinductive properties is a major issue. Indeed, most bone graft substitutes, especially synthetic ceramics and cements, do not possess any osteoinductive property. In fact, their ability of bone healing essentially comes from their osteoconductive properties. Yet, when the ideal implant site environment is disturbed, the absence of osteoinduction and the presence of bone growth factors can lead to delayed union or non-union. Actually, it has been proven that the presence of osteoinductive factors at the site of bone injury during bone healing is of great importance. For this reason, more and more researches focus on direct application of bone-active growth factors or combine them with synthetic biomaterials in order to achieve a maximal osteogenic effect. One of the most promising approaches is the incorporation of such active biomolecules into manufactured porous scaffolds to combine osteoconductivity and resorbability. These researches lead to the development of a new bone substitute's generation. This point is developed in the Section "Materials Functionalization and Drug Delivery Systems" (Wang and Yeung, 2017b; Schallenger *et al.*, 2014; Giannoudis *et al.*, 2007; Giannoudis *et al.*, 2008; Sheikh *et al.*, 2019).

Unlike synthetic materials, some human-derived bone substitutes like demineralized bone matrix (DBM) can possess osteoinductive properties and exhibit superior bone regeneration ability. In the case of DBM, it is due to the presence of native growth factors preserved and exposed through the demineralization process. However, the increasing demand of bone repair materials and the as-mentioned limitations of human-derived materials create a need to continue the development of new biomaterials or the improvement of known bone substitutes. Currently, autologous bone graft would be still the best choice for many bone repair applications but the relatively high donor morbidity and the limited amount which can be harvested are major issues. Allografts can avoid these limitations even if they present very variable osteoinductive properties and a risk of diseases transmission. Accordingly, future researches will be more focused on synthetic bone grafts especially for the optimization of grafts

stability, handling and biological properties (Zimmermann and Moghaddam, 2011). In addition to the material composition, one of the main challenges is the designing and the manufacturing of bone substitutes with favorable shapes, architectures and porosity for proper bone regeneration and vascularization. Indeed, biological properties and implant integration do not only depend on material composition but also on implant physical form (Schallenger *et al.*, 2014; Sheikh *et al.*, 2019; Wang and Yeung, 2017a).

Implants Physical Shape

The bone substitute materials may take a variety of forms, including pellets, granules, wedges, blocks/scaffolds, cements/pastes, putties, membranes and disks. The choice of the formulation depends of the application, the type of bone defect, the site and the geometry of the implantation site, the clinicians' preferences or the availability of the material. The as-mentioned types of formulations can be used as bone filler to assist and support the healing of bone defects too large to spontaneously heal. Actually, the most used bone graft substitutes are in the form of granules, cements/pastes or porous blocks/scaffolds (Bohner, 2010, 2014) (Fig. 1).

Granules

In the form angular or spherical particles, this type of bone substitute shape is the most used mainly due to its low cost, easy manufacturing and its quite fast bone ingrowths. The main advantage of granules is their ability to fill any defect form especially widely open defects where they can migrate during and after surgery. An optimal filling can be achieved by adjusting the granules characteristics like their morphology, shape, porosity, microstructure and size. Typically, irregular morphologies can cause undesirable *in vivo* inflammatory reactions leading to slower bone growth. For this reason, smooth geometries are preferred are superior. Even if spherical particles present a better flowability than angular granules to fill even small effects, they present high packing densities. This can limit the size of the space between the granules, so that bone growth is reduced as well as resorption due to smaller porosities and a larger amount of material. Thus, most of the current commercial products are angular with a size varying between 0.1 and 5 mm. This range of size is a compromise for an easy insertion in bone defects and a relatively simple handling of the granules during the surgery.

Bone filler granules can be produced by various techniques, depending on the material composition. Some of them are the crushing of blocks, hydrothermal conversion of natural corals, dripping, drip casting, gel casting and stirring mixtures of immiscible liquids. Block crushing can form granules of irregular shapes and sizes, which requires additional sieving and grinding procedures to obtain appropriate sizes and a more regular shape. Contrariwise, granules made by dripping, drip casting, gel casting and stirring mixtures of immiscible liquids present adequate spherical or near-spherical shapes.

Concerning the application of granules, small ones (< 1 mm) are preferably used in dental products while larger ones (> 1 mm) are more useful in orthopedics (Bohner, 2010, 2014; Hsu *et al.*, 2007).

Pastes/Cements/Putties

Pastes/cements and putties are the most suitable materials for the filling of closed defects since they can be directly injected with minimally invasive techniques. They can avoid the issues linked with the use of granules such as difficult handling, time-consuming filling and falling granules outside the defect. Indeed, injectable and/or moldable bone substitute formulations have been developed with the most used approaches consisting of mixing a polymer matrix with ceramic powders or granules. Two types of formulations can be distinguished as a function of hardening or non hardening properties. Typically, non hardening injectable pastes are called putties while pastes that harden are considered to be cements.

Most of the time, cements hardening after implantation by a setting reaction provide a better mechanical stability than putties by the physical entanglement of the materials. However, putties are characterized by a higher handling compared to hardening pastes (Bohner, 2010, 2014).

Cements

Among the different cement compositions, polymer- and mineral-based cements are the most famous. Concerning polymer-based cements, PMMA is widely used to anchor joint replacement prosthesis and to augment bone even if it presents some drawbacks. Indeed, this material is not resorbable and presents a toxicity leading to hypotension as well as a high exothermicity causing bone and tissue necrosis. Currently, alternative polymeric compositions and improvements to PMMA cements are studied to overcome these problems (Bohner, 2010, 2014).

Mineral-based cements mainly consist of ceramic-based cements composed of calcium sulfate, calcium silicate and/or calcium phosphate. Nowadays, almost 50 compositions are available by mixing the different materials. In order to obtain adequate injectable cements, different parameters such as the setting time, the setting rate, the injectability and the cohesion have to be optimized. Typically, the setting time should be close to 10 min while the setting rate should allow the end of the setting reaction shortly after the setting time. Moreover, cements must present the ability to be injected without a solid-liquid phase separation

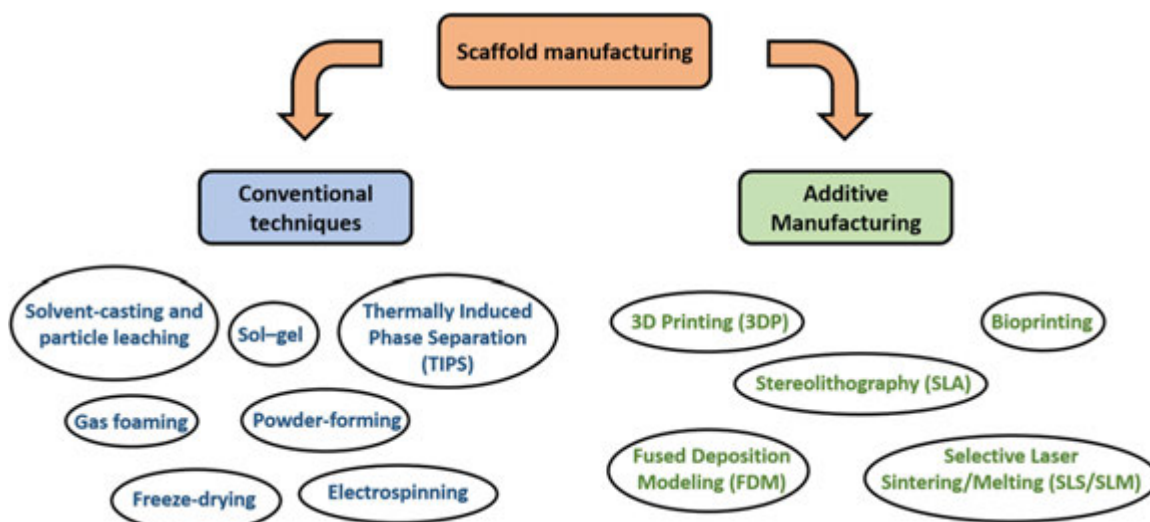


Fig. 2 The main scaffold manufacturing techniques for biomaterials.

(injectability) and to keep its physical integrity during setting (cohesion). The hardening of such ceramic-based cements starts first with the dissolution of the reagent in the aqueous phase and second in the nucleation and growth of crystals. During this process, a large excess of water is often employed leading to highly porous cements with a pore size depending of the entangled crystals. Usually, these cements only contain micropores due to the micrometer-sized crystals. The absence of macropores can slow down the blood vessel and tissue ingrowths at the implantation site because it is only possible after the cement resorption. The entanglement of crystals after the hardening reaction lead to a quite high stability under compression but ceramic-based cements are brittle and weak, especially under tension and shear (Bohner, 2010; Habraken *et al.*, 2016; Bohner, 2014).

Putties

Most putties are prepared by mixing a polymer matrix and ceramic powders or granules. The polymer phase serves as a glue material for the solid particles. There are different examples in the literature like a mix of β -TCP granules with a sodium alginate solution or chitosan used to bond hydroxyapatite particles. Pure organic compositions also exist with, for example, PMMA and demineralized bone used alone to act as sealant in case of bleeding in bone. On the other hand, pure mineral compositions include, similarly to cements, hydraulic cements such as calcium sulfate and calcium phosphate cements. Some developments have been carried out to obtain putties made of nano- or micro-sized calcium phosphate particles and water. The absence of hardening reactions in putties allow them to be used in closed as well in open bone defects (Bohner, 2010, 2014).

Blocks/Scaffolds

Probably the most presently studied type of bone substitute formulation; blocks/scaffolds are generally used to fill large bone defects or defects with very well-defined geometries. Compared to other bone graft formulations, blocks/scaffolds offer different advantages. Although granules usually have better bone ingrowths, scaffolds present a higher mechanical stability and an easier handling than a pile of granules. Moreover, the well-defined geometry of scaffolds can avoid issues linked with possible uncontrollable extrusions of cements/putties. Indeed, in some cases, pastes can be extruded beyond the bone defects boundaries leading to their no-dissolution or to the damaging of surrounding tissues (Bohner, 2014).

Scaffolds can be used alone as acellular systems or combined with active molecules as vehicles for cells and/or drugs, as a function of the area and the severity of the bone defect. Scaffolds are commonly used alone in trauma, spine fusion markets or in dentistry. Indeed, wedges are often applied in knee osteotomy while cages are used for inter-vertebral body fusion. On another side, combinations of scaffolds with active molecules and/or stem cells are mainly employed in orthobiologics, typically substances used to help injuries to heal more quickly. These combinations can improve the bone implant integration and the promotion of bone formation. Currently, two great fields of applications are studied where the use of scaffolds could be beneficial. The first one, personalized medicine, requires personalized fabrication of synthetic implants and the second one, bone tissue engineering, needs to produce 3D scaffolds with complex tailored architecture (Champion *et al.*, 2017; Ho-shui-ling *et al.*, 2019).

In general, blocks/scaffolds are highly porous in order to provide fast bone ingrowth and rapid integration of the graft. Indeed, a scaffold is typically defined as an artificial structure used to support three-dimensional tissue formation where new cells can migrate and new vessels can form. An ideal bone scaffold should allow or improve cell viability, attachment, proliferation and homing, osteogenic differentiation, vascularization, host integration and, where necessary, load bearing. Moreover, it is vital to produce scaffolds quite similar to the natural environment, with multi-functional properties and efficient in terms of cost and

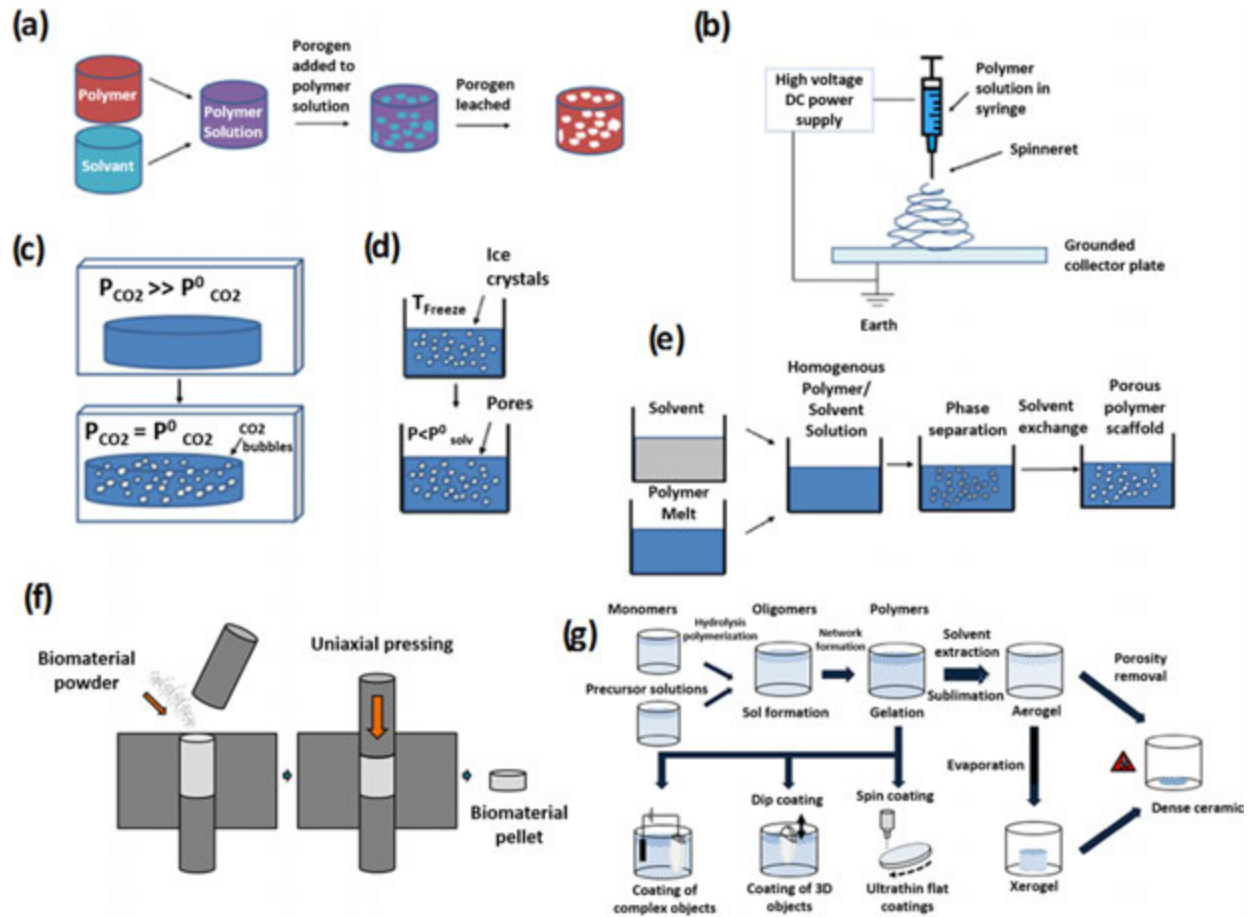


Fig. 3 Common conventional scaffold fabrication techniques. (a) Solvent casting-particle leaching process (b) Electrospinning (c) Gas foaming (d) Freeze-drying (e) Phase separation (f) Powder forming and (g) Sol-gel. (a) – (e) Reproduced from Turnbull, G., *et al.*, 2018. 3D bioactive composite scaffolds for bone tissue engineering. *Bioactive Materials* 3, 278–314; (g) Owens, G.J., *et al.*, 2016. Sol – gel based materials for biomedical applications. *Progress in Materials Science* 77, 1–79.

clinical use. Indeed, implants should enable easy handling during surgeries with minimal preparatory procedures allowing industrial sterilization and reproducibility at lower cost.

Optimizations of scaffolds characteristics are so needed to meet these ideal requirements. Among them, bone substitutes architecture, including geometry and porosity, particularly draws the attention of researchers. It has been proven that scaffolds architecture and micro-architecture are of critical importance for bone regeneration. Typically, scaffolds should have distributed, interconnected pores and display a high porosity in order to ensure cell penetration, vascular ingrowth and nutrient diffusion, as well as waste products elimination. In addition, the mean pore size must be controlled to ensure proper cell colonization. Although the critical pore size range can vary as a function of cell and tissue type, a pore size comprised between 200 and 500 μm is considered optimal for bone regeneration and vascularization. Sometimes, pore sizes superior to 300 μm are recommended in order to enhance bone formation and the formation of capillaries (Roseti *et al.*, 2017; Bohner, 2014; Alaribe *et al.*, 2016).

Scaffolds manufacturing

Different technologies exist to manufacture porous scaffolds and they can be classified in to main categories: conventional and Additive Manufacturing (AM) techniques (Fig. 2).

Conventional techniques

Typically, in conventional manufacturing, scaffolds are produced by subtractive methods where an initial block is modified and shaped to the desired final form. Conventional technologies include solvent casting and particle leaching, freeze-drying, thermally induced phase separation, gas foaming, powder-forming, sol-gel, and electrospinning (Turnbull *et al.*, 2018; Roseti *et al.*, 2017; Thavornyutikarn *et al.*, 2014).

Solvent-casting and particle leaching

First, solvent-casting and particle leaching consist in the dissolution of a polymer solution in a solvent with uniformly distributed salt particles of a specific size (**Fig. 3(a)**). After evaporation of the solvent, it remains a salt particles-embedded matrix, which is then immersed in water. The contact with water leads to the leaching out of the salt and this allows producing a highly porous structure. This process presents different advantages like an ease to perform, low equipment costs while producing high scaffold porosity with the possibility to tune pore size. Nevertheless, the scaffold shapes that can be produced are quite simple and limited to sheets and tubes. Finally, some residual solvent can stay inside the structure leading to some harmful effects on biological species (Turnbull *et al.*, 2018; Roseti *et al.*, 2017; Thavorniyutikarn *et al.*, 2014).

Freeze-drying

Another widely used process in scaffold manufacturing is the freeze-drying process or lyophilization. In a similar way than solvent-casting, a synthetic polymer is dissolved into a suitable solvent before being frozen and solidified (**Fig. 3(d)**). After, the solvent is evaporated *via* sublimation producing a dry scaffold with an interconnected porous structure. The main benefit of freeze-drying is the low used temperatures allowing the incorporation of biological factors sensitive to high temperatures. Even if the pore size is simple to control, it usually leads to the production of irregular small size pores. Besides, this technique involves quite long process durations, high-energy consumption and the use of cytotoxic solvents (Turnbull *et al.*, 2018; Roseti *et al.*, 2017; Thavorniyutikarn *et al.*, 2014).

Thermally induced phase separation (TIPS)

Low temperatures are also applied in the Thermally Induced Phase Separation (TIPS) process. In this technique, a polymer solution is quenched and goes through a liquid-liquid phase separation to form a polymer-rich phase and phase poor in polymer (**Fig. 3(e)**). After solidification of the first one, the polymer poor phase is removed, leaving a very porous nanometric fiber network. As for the freeze-drying process, low temperatures involved in the TIPS are a plus for the possible incorporation of bioactive molecules (Turnbull *et al.*, 2018; Roseti *et al.*, 2017; Thavorniyutikarn *et al.*, 2014).

Gas foaming

In order to limit or avoid the use of organic solvents possibly cytotoxic, the gas foaming technique employs relatively inert gas-foaming agents like carbon dioxide or nitrogen (**Fig. 3(c)**). These agents are useful to produce sponge-like structures with an average pore size in the range of 30–700 μm and porosity up to 85%. Typically, molded biodegradable polymers are pressurized until saturation with water or fluoroform to introduce many bubbles into the polymer. Indeed, these bubbles are responsible for sponge-like structure obtained at the end of the process. In contrary to freeze-drying and TIPS, gas foaming includes the use of high temperatures during compression molding. Moreover, this technique usually leads to close, non-interconnected porous structures as well as nonporous skin layer at the scaffold surface (Turnbull *et al.*, 2018; Roseti *et al.*, 2017; Thavorniyutikarn *et al.*, 2014).

Powder-forming

The most well-known process to manufacture porous ceramic scaffolds is the powder-forming. In powder-forming processes, ceramic particles are put in suspensions with water or ethanol forming a slurry (**Fig. 3(f)**). This slurry is then used to produce green bodies by different ways. Dry or wet processes are available depending of the manufacturing conditions. Among them, the replication technique is particularly suitable to produce scaffolds with controlled shape and porosity. Commonly, it consists in the dispersion of ceramic slurry within a template, usually polymer foam with the desired macrostructure. Further, the drying of the solvent and the thermal decomposition of the template lead to the green body. Finally, the densification of the green part allows obtaining a scaffold with controllable pore size, high porosity and interconnectivity (Roseti *et al.*, 2017; Thavorniyutikarn *et al.*, 2014; Canillas *et al.*, 2017a,b).

Sol-gel

In addition to the as-mentioned processes, sol-gel technique can also be used to create ceramic or glass materials in the form of ultra-fine or spherical shaped powders, thin-film coatings, ceramic fibers, microporous inorganic membranes, monolithic parts and highly porous aerogels. The inorganic polymerization of metal alkoxides is employed in this process (**Fig. 3(g)**). Typically, the first step is the formation of a sol by the addition of a surfactant to the solid loading. This step is then followed by condensation and gelation reactions to form the gel. The sol-gel process is highly useful for the obtaining of scaffolds with controlled shape with a high purity at quite low temperatures. However, the major issue with scaffolds made by the sol-gel process is the low mechanical strength in most cases (Mahony and Jones, 2008; Roseti *et al.*, 2017; Thavorniyutikarn *et al.*, 2014).

Electrospinning

Finally, the electrospinning technique can be used to create nanofibrous architectures by the assembling of fine fibers (**Fig. 3(b)**). Indeed, by means of electrical charges and a syringe pump, it is possible to draw fibers up to the nanometer scale and use a collector to build structures. Actually, a polymer solution, loaded or not with particles (ceramic or bioglass for example), is placed into a container with a millimeter size nozzle and subjected to electric field. The generated electric field provokes the ejection of a charged liquid jet that is then elongated, projected and deposited on the collector. After evaporation of the solvent, ultra-thin fibers remain on the collector forming nanofibrous architecture with high surface area to volume ratios. This characteristic can help to

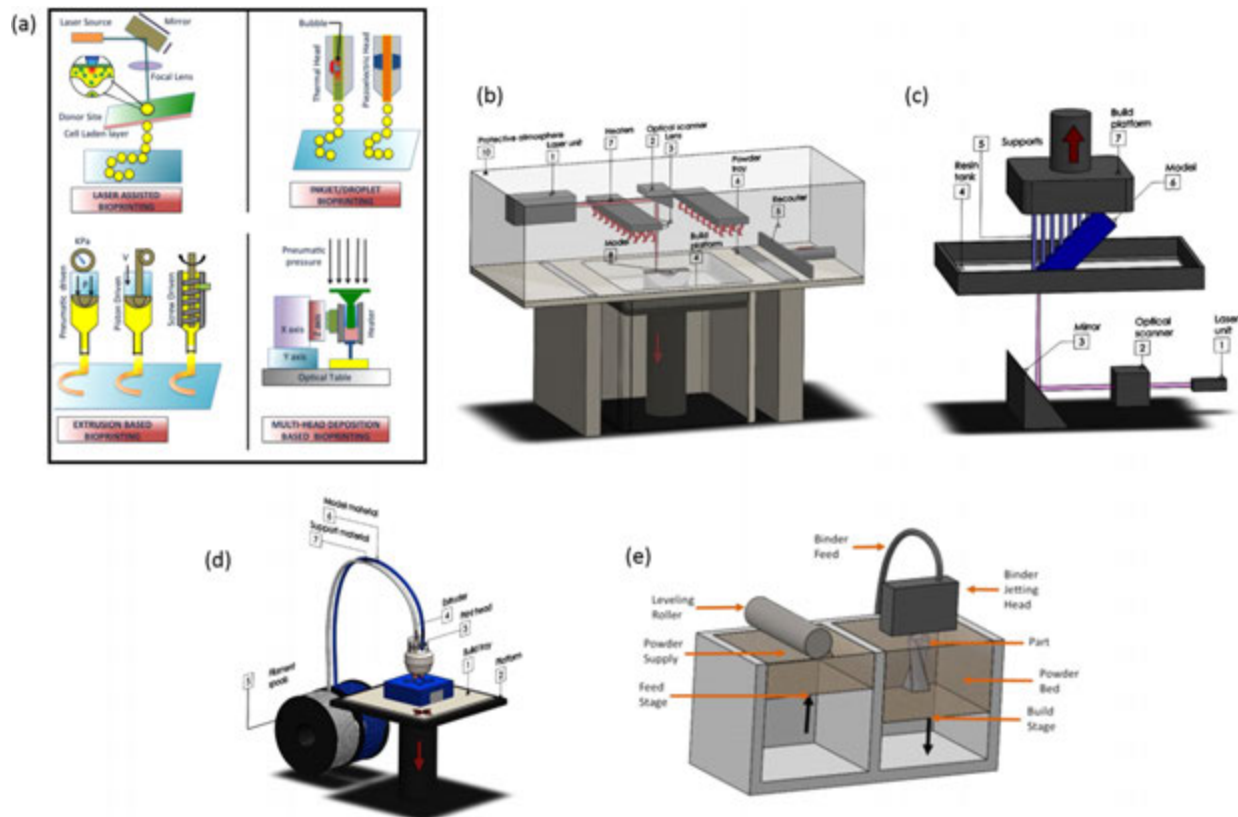


Fig. 4 Common Additive Manufacturing techniques for biomaterial scaffolds fabrication. (a) Bioprinting (b) Selective Laser Sintering/melting (c) Stereolithography (d) Fused Deposition Modeling (e) 3D Printing; (a) Reproduced from Dwivedi, R., Mehrotra, D., 2020. 3D Bioprinting and Craniofacial Regeneration. Craniofacial Research Foundation. <https://doi.org/10.1016/j.jobcr.2020.08.011>. (b) – (d) Turnbull, G., *et al.*, 2018. 3D bioactive composite scaffolds for bone tissue engineering. *Bioactive Materials* 3, 278–314. (e) Szymczyk-Ziółkowska, P., *et al.*, 2020. A review of fabrication polymer scaffolds for biomedical applications using additive manufacturing techniques. *Biocybernetics and Biomedical Engineering* 40, 624–638.

functionalize the fibers with different bioactive species. The use of organic solvents is a major disadvantage of electrospinning with the possibility of residual cytotoxic traces (Demir *et al.*, 2002; Roseti *et al.*, 2017; Thavorniyutikarn *et al.*, 2014).

The main challenge in the manufacturing of porous scaffolds by conventional technologies is the control of the shapes, geometries and internal architecture of produced parts. Most of conventional techniques cannot produce fully continuous interconnectivity and uniform pore morphology within a scaffold. Moreover, the lack of reproducibility inherent to some manual-based processes is a drawback to control scaffolds parameters like the pore size, pore geometry and spatial distribution. In addition, most conventional fabrication methods are using toxic organics as solvent or porogens and their residues in the scaffold can lead to severe inflammatory responses. To counter these limits, Additive Manufacturing methods have been developed and their use is increasing within the medical field. Indeed, AM techniques allow a more punctual and accurate control of porosity, pore size and, globally, of internal architecture. Therefore, biomaterials parts with reproducible properties can be produced and a better imitation of the natural bone tissue structure can be achieved. The main objective is to produce porous scaffolds with appropriate controlled pore size and high interconnectivity to promote cell penetration, tissue ingrowth, nutrients delivery and rapid vascular invasion while providing a proper mechanical integrity and degradation (Roseti *et al.*, 2017; Thavorniyutikarn *et al.*, 2014; Chartier *et al.*, 2015).

Additive manufacturing

Rapid prototyping, additive manufacturing, solid free form fabrication or 3D printing is defined by ASTM F2792-12a as the process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies (Zocca *et al.*, 2015).

Different technologies are grouped under this term like Stereolithography (SLA), Fused Deposition Modeling (FDM), Selective Laser Sintering/Melting (SLS/SLM), 3D Printing (3DP) and Bioprinting. In all these processes, an object is created from a virtual model by adding material layer by layer. Among the AM techniques, liquid-, paste-, and powder-based processes can be distinguished (Turnbull *et al.*, 2018; Roseti *et al.*, 2017; Thavorniyutikarn *et al.*, 2014; Zocca *et al.*, 2015).

Stereolithography

The first invented Additive Manufacturing technique is the stereolithography, or SLA for Stereo-Lithography Apparatus, by which a solid object is formed by successively print thin layers of an ultraviolet (UV) curable material one on top of each other (Fig. 4(c)). Typically, a SLA machine consists of a tank of photo-sensitive liquid resin, a moveable built platform, an UV light source and a dynamic mirror system. Two types of stereo-lithography setups exist at the moment: the bottom-up and the top-down approaches. The main difference between the two processes is the position of the light source with respect to the resin tank. The light source is placed above the tank in the bottom-up process while the light comes from under the tank in the top-down approach. Moreover, there are two different types of light source. The classic light source is a UV laser beam scanning the resin bed to produce the final part. The more recent UV source is a DLP (Digital light projection) device where a digital mirror device (DMD) is made of up to several millions of mirrors that can be independently switched on or off. The SLA process can fabricate 3D scaffolds from polymers, bioceramics and composites. Indeed, biodegradable polymers such as poly(propylene fumarate) (PPF), photo-cross-linkable PCL, PDLA, vinyl esters and photocrosslinkable poly(ester anhydride) are successfully printed with this technique. In addition to the fabrication of hydrogel polymer scaffolds, SLA is also used to build a ceramic network using a photo-sensitive polymer as a binder. For this purpose, a liquid photosensitive resin is filled with ceramic particles with a solid content in the range of 20–50 vol percentages. The addition of a solid loading can lead to high viscosities introducing some difficulties to the process. After printing, debinding and sintering steps are needed to obtain ceramic-based scaffolds.

The main benefits of the stereolithography process are the freedom of designing structures, the ability to build parts of various sizes and a good surface finish. The spatial resolution is usually approximately 50 μm which is a very high accuracy and resolution compared to other Additive Manufacturing processes. SLA is suitable to create well-defined scaffolds with controlled interconnected porosity. However, there are still some limitations related to the use of photo-sensitive material and the debinding step usually highly time-consuming. The shrinkage of the polymer during the polymerization process can also alter the final shape of the printed part. A major issue is the possible cytotoxicity caused by photo-sensitive resins employed in the medical field. To counter these problems, more and more researches are focused on the development of alternative resins with a better debinding behavior and that possess a better biocompatibility *in vivo* (Roseti *et al.*, 2017; Thavornnyutikarn *et al.*, 2014; Zocca *et al.*, 2015; Melchels *et al.*, 2010).

Fused deposition modeling

Probably the most-well known additive manufacturing technique, the Fused Deposition Modeling (FDM) process uses molten thermoplastic materials to print desired shapes. In this process, the material is extruded from a nozzle and deposited onto a base platform following the 3D model (Fig. 4(d)). After the deposition of a layer, the platform or the nozzle moves to print other layers until the obtaining of the final object. This technique is quite useful to manufacture 3D scaffolds with controllable pore size and porosity by playing with the parameters like the material deposition amount, the spacing between the extruded filaments and the height interval. The FDM process is able to print scaffolds with a wide range of materials from polymers to ceramics and composites. Among polymers, PCL, PLA, PLGA and poly(butylene terephthalate) (PBT) are easily printed with this technique. Concerning the manufacturing of bioceramic scaffolds, there are two ways to use FDM to produce porous parts. The first method is called the fused deposition of ceramics (FDC) and uses a filament made of a thermoplastic polymer, a ceramic powder and a binder. After the printing, the 3D green ceramic part is debinded to remove the thermoplastic polymer as well as the binder and the part is densified by sintering. The other way to manufacture ceramic scaffolds with FDM is an indirect method called the lost mold technique. It uses an FDM machine to produce polymer molds with a negative structure of the intended network. After the mold printing, a ceramic slurry is cast into the mold and solidifies. The obtained object is then heated to remove the organics after the final sintering process to consolidate the ceramic network.

In the same way as ceramics, composite scaffolds combining polymers with bioglasses and ceramics can also be manufactured by the FDM process. The most studied compositions are PCL/HA, PCL/TCP and PCL with S53P4 bioactive glasses. Due to its low cost, the absence of organic solvent, the ability to form a fully interconnected porous 3D architecture and the ease of the process, especially the absence of object cleaning after printing, the FDM technique is an ideal way to produce biocompatible scaffolds. Indeed, it allows a flexible fabrication of interconnected porous scaffolds with the possibility to introduce compositional or morphological variation across the printed parts. Although FDM is highly reproducible, there are some limitations linked with the effect of high temperatures on raw material. Unlike SLA, its resolution is quite low because of the limited extruded filament diameter. Finally, the raw material selection is limited due to their shaping in the form of filaments with specific size. Preformed fibers need to have consistent size and properties to feed through the rollers and nozzle during printing. In order to overcome FDM issues, different processes derived from FDM have been optimized to improve the printing of porous scaffolds. These techniques include multi-head deposition system (MHDS), low-temperature deposition manufacturing (LDM), precision extruding deposition (PED), pressure-assisted microsyringe (PAM), robocasting and 3DBioplotter® system. (Roseti *et al.*, 2017; Thavornnyutikarn *et al.*, 2014).

Selective laser sintering/melting

The Selective Laser Sintering/Melting or SLS/SLM process is a powder-based technology and consists in binding together powder particles in thin layers with a high-power laser (Fig. 4(b)). Typically, the laser beam is able to fuse selected regions of the powder bed onto a surface forming a material layer. Then next layers of the material are deposited on the top of the bed by a roller and the process is repeated until the part is completed. In this process, the particle size and shape of the feedstock powder are major

parameters because they influence powder flowability and the final scaffold product. Due to low compaction forces present in the powder after the sintering process, printed structures have an internally porous structure suitable for a bone scaffolds. Therefore, SLS has been used polymers, metals and ceramics to produce tissue-engineered parts. Polymers PCL and poly-3-hydroxybutyrate (P3HB) have been successfully printed by SLS while manufacturing bioceramics directly present some difficulties. Indeed, the fast heating and cooling rates associated with the high-energy laser are not optimal to shape ceramic powders. Concerning composites, the most studied compositions are PCL/HA, PCL/TCP and poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV)/TCP. In SLS, it is a challenge to find the optimal combination of the process parameters like powder composition, particle size, laser power, powder bed temperature, scan speed, scan spacing, and part orientation. Indeed, all of them influence the mechanical properties of the final printed scaffold.

The main advantage of SLS is the fact there is no need of additional supporting structures for the model during printing because unprocessed powders serve as a support. Moreover, this process does not use organic solvents or any toxic chemicals. Nevertheless, the relatively high laser temperatures and the heat transfer reactions induce some limitations. First, the heat can be harmful for polymers with possible degradation during the process. The direct laser sintering of ceramics is complicated by their poor resistance to thermal shock and the short interaction time between laser and powder limits the densification. For the production of complex-shaped prototypes or large prototypes by SLS processing, it is quite time-consuming. In addition, the powder trapped inside the small holes and pores can be sometimes impossible to remove. This can lead to the blocking of cellular ingrowth and to inflammatory reactions if the part is used as an implant. Finally, similar to SLA, the shape and size of the final printed part can be different from the 3D model due to shrinkage during the printing process (Roseti *et al.*, 2017; Thavornyutikarn *et al.*, 2014; Zocca *et al.*, 2015).

3D printing

The 3D printing or 3DP is an ink-jet printing technique based on the selective spraying of a liquid binder onto the layer of the powder bed. The binder merges particles together to form a solid layer (Fig. 4(e)). After the printing of a layer, the powder bed is lowered to spread a new powder layer with a roller and the process can continue until the formation of the final object. The printed parts are embedded inside not fused powders which need to be removed to reveal the final object. This process is suitable to create complex 3D scaffolds by using a broad variety of materials, including polymer, hydrogels, ceramics and composites. PLGA scaffolds were created by this technique as well as hydrogels parts made of PEG/collagen/PDL, PEO/PCL and starch/cellulose. In fact, 3D printing is the only solid-phase AM technique able to manufacture hydrogel scaffolds. However, due to their lack of mechanical strength, a post-treatment step involving infiltration and monomers crosslinking is necessary to produce stable pieces. In the same way as the SLS technique, ceramic-based scaffolds can be manufactured with 3DP systems even if a heat treatment is required to obtain higher densities in the final parts. The most tested bioceramic powders are hydroxyapatite and β -TCP. Bioglass powders and polymer/ceramic composites are also widely studied like PLGA/TCP and PCL/TCP combinations.

The 3D printing process presents several advantages like cheap raw materials, high build speeds and the absence of additional support structure similar to SLS. Moreover, unlike SLS, 3DP does not require the use of heat making possible the incorporation of biologically active molecules or thermosensitive compounds. Despite these benefits, the limited resolution and accuracy of this technique are major drawbacks. It is mainly due to weak bonds between particles leading to relatively poor strength of the parts. In addition, large sizes of powder particles cause rough surface finishes of objects. Similar to the SLS process, the removal of trapped powder particles inside small cavities can be difficult and these residues may be harmful to cells and tissues. Finally, there is still the issue of the shrinkage and distortion that can occur during printing and sintering steps (Roseti *et al.*, 2017; Thavornyutikarn *et al.*, 2014).

Bioprinting

Bioprinting is one of the latest developed additive manufacturing processes and can overcome some of the challenges met with conventional scaffolds manufacturing processes. Typically, conventional methods do not allow controlling cell distribution with accuracy and then cannot produce homogeneous scaffolds. In bioprinting, small units of cells and biomaterials are dispensed together with micrometer precision to build complex structures like tissues or organs (Fig. 4(a)). To date, bioprinting has been mostly used to process hydrogels and different types of cells. The current main technologies used for bioprinting are inkjet, microextrusion and laser-assisted printing. Inkjet printing delivers controlled volumes of a liquid ink to predefined locations onto a substrate in order to build the final construct. In this technique, thermal or acoustic forces are used to eject drops of liquid. The main limitation of inkjet bioprinting is that the biological material has to be in a liquid form to enable droplet formation and the liquid must form a solid 3D structure after deposition. Microextrusion works in a similar way than extrusion processes mentioned above with a robotically controlled extrusion of a material, which is deposited onto a substrate by a microextrusion head. Contrary to inkjet printing, microextrusion usually leads to beads or cords rather than liquid droplets. The major benefits of this technique are its ability to deposit high cell densities and the wide range of available materials. Many researches are now focused on increasing print resolution and speed which are the main limitations of microextrusion. In laser-assisted bioprinting, laser pulses are focused on a "ribbon" made of a laser-energy-absorbing layer and a layer of biological material. The laser generates a high-pressure bubble that propels cell-containing materials toward the collector substrate. Despite interesting advantages like the absence of nozzle avoiding clogging and its compatibility with a wide range of cells, rapid gelation kinetics are required to achieve high resolution and high shape fidelity. In all these three bioprinting processes, the most important factors are surface resolution, cell viability and the biological materials used for printing. Bioprinting is considered as promising approach in the field of

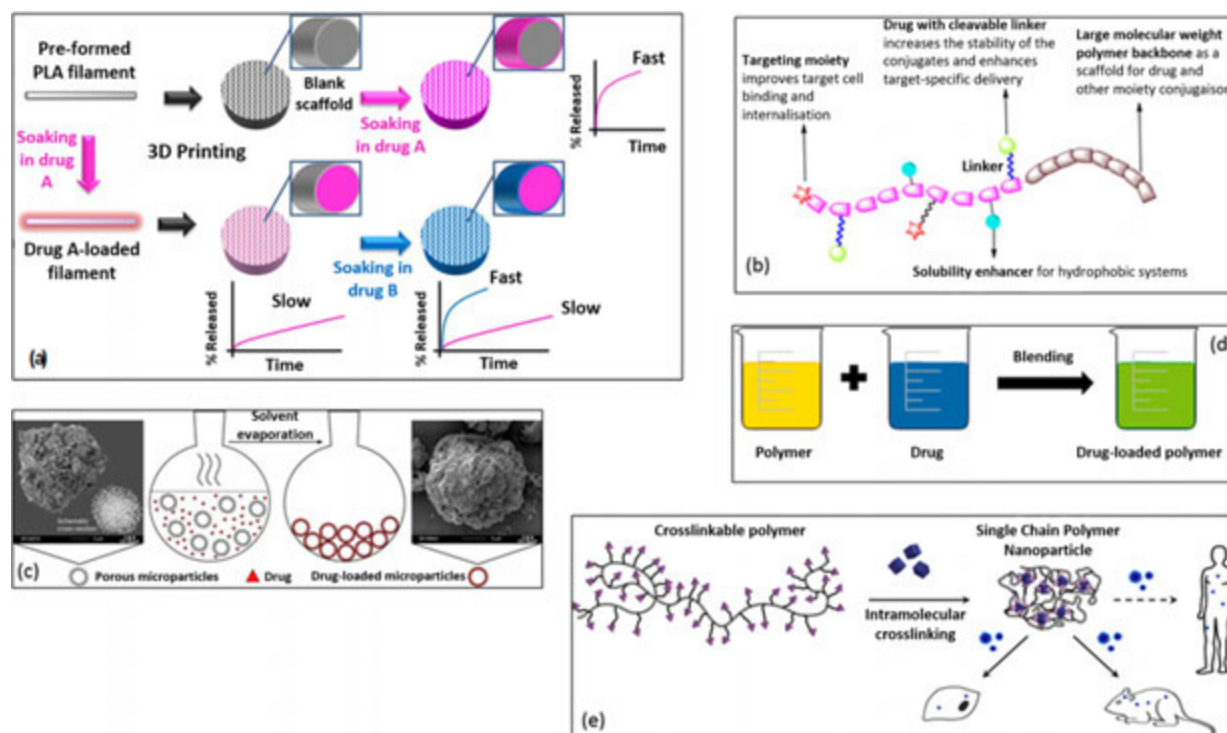


Fig. 5 Drug loading techniques in polymer scaffolds: (a) soak loading; (b) the drug-polymer conjugation; (c) pre-loading in nano/microparticles; (d) blend loading and (e) site-specific binding of the drug to the polymer. Reproduced from (a) Farto-Vaamonde, X., *et al.*, 2019. Post-manufacture loading of filaments and 3D printed PLA scaffolds with prednisolone and dexamethasone for tissue regeneration applications. *European Journal of Pharmaceutics and Biopharmaceutics* 141 (May), 100–110. <https://doi.org/10.1016/j.ejpb.2019.05.018>. (b) Marasini, N., Haque, S., Kaminskas, L.M., 2017. Current opinion in colloid & interface science polymer-drug conjugates as inhalable drug delivery systems: A review. *Current Opinion in Colloid & Interface Science* 31, 18–29. <https://doi.org/10.1016/j.cocis.2017.06.003>. (c) Preisig, D., *et al.*, 2014. Drug loading into porous calcium carbonate microparticles by solvent evaporation. *European Journal of Pharmaceutics and Biopharmaceutics* 87 (3), 548–558. <https://doi.org/10.1016/j.ejpb.2014.02.009>. (e) Kröger, A.P.P., Paulusse, J.M.J., 2018. Single-chain polymer nanoparticles in controlled drug delivery and targeted imaging. *Journal of Controlled Release* 286 (August), 326–347. <https://doi.org/10.1016/j.jconrel.2018.07.041>.

regenerative medicine to address the need for tissues and organs suitable for transplantation (Roseti *et al.*, 2017; Pina *et al.*, 2017; Murphy and Atala, 2014).

To conclude with scaffolds manufacturing techniques, Additive Manufacturing processes like SLA, FDM, SLS/SLM, 3DP and Bioprinting offer some benefits over conventional fabrication techniques. Indeed, they allow high flexibility in shape and size, precise control over spatial distribution and porosities, high reproducibility and customized design for specific medical applications. Moreover, a broad variety of biomaterials can be shaped with Additive Manufacturing. For the time being, SLA and FDM are widely studied to produce and optimize the manufacturing of scaffold architectures for bone tissue engineering applications. In fact, these two processes currently present the best characteristics for scaffolds fabrication. SLA has the best accuracy and surface quality while FDM allows versatile fabrication in lay-down pattern and good structural integrity. The proper fusion bonding between individual materials layers involved in these techniques is the reason why they can produce 3D structures with good mechanical integrity throughout the entire scaffold compared to powder-based systems.

Additive Manufacturing processes are probably going to replace conventional fabrication techniques for biomaterials scaffolds fabrication due to the poor control of the internal and external architecture, pore morphology, pore size, pore interconnectivity and overall porosity involved in these classic processes (Thavornyutikarn *et al.*, 2014; Roseti *et al.*, 2017).

Materials Functionalization and Drug Delivery Systems

As mentioned above, most of synthetic bone graft substitutes do not possess osteoinductive properties as natural-derived materials like demineralized bone matrix. This can be problematic in situations where the ideal graft environment is disturbed with an absence of bone growth factors secretion. Therefore, providing osteoinductive properties to graft substitutes is one of the major challenges of the recent and futures researches besides implant composition, structure and bioresorbability. The final objective is to design and develop temporary bone scaffolds able to deliver bioactive molecules and drugs or cells to the injury site and

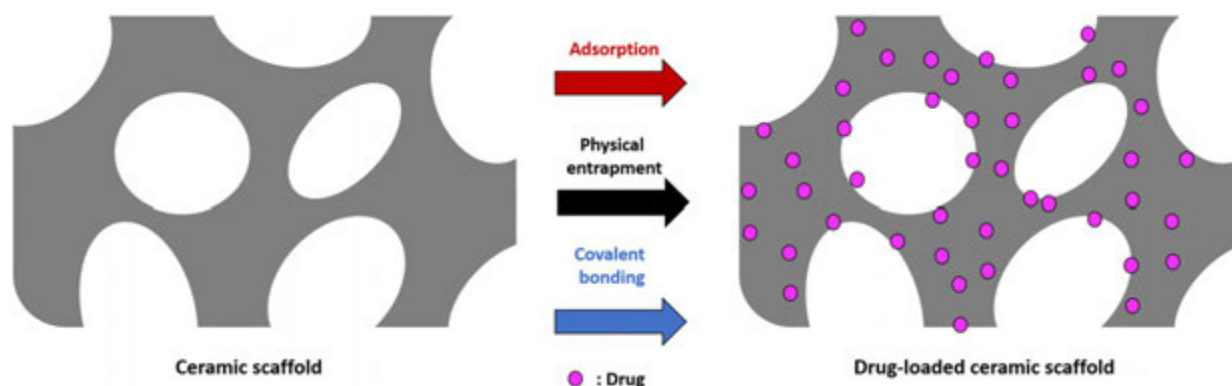


Fig. 6 Techniques to load biomimetic ceramics with therapeutic agents/drugs.

promote the healing and tissue regeneration while concomitantly preventing pathology. For this purpose, the capacity for a scaffold to direct cell behavior can be improved through the controlled delivery of bioactive molecules like growth factors, stem cells, drugs and proteins. Indeed, these molecules can positively influence the bone mass by stopping the action of inhibitors and thereby have a positive effect on bone mass (Wang and Yeung, 2017b; Lin *et al.*, 2019; Alaribe *et al.*, 2016; Haugen *et al.*, 2020; Bongio *et al.*, 2010; Giannoudis *et al.*, 2007).

Different strategies are considered to boost bone repair like the application of biologically active molecules and the seeding of scaffolds with stem cells to create bone tissue engineered structures. The administration of such biomolecules has showed promising results in some preclinical and clinical models for the promotion of bone formation and repair. Moreover, the use of biodegradable scaffolds is preferred due to their contribution to the release of loaded bioactive molecules. According to the wide literature on the topic, combining resorbable scaffolds for tissue regeneration with drugs is a suitable strategy to improve tissue regeneration. In fact, such association combines different advantages. The first one is a local drug delivery with improved bioavailability allowing to reduce adverse effects with respect to systemic drug administration. Secondly, this allows a continuing drug release without interruption. Finally, there is the possibility to associate two or more drugs/bioactive molecules in a single scaffold in order to extend the current clinical utilities (Campana *et al.*, 2014; Wang and Yeung, 2017b; Alaribe *et al.*, 2016; Haugen *et al.*, 2020; Ho-shui-ling *et al.*, 2019).

Two important requirements for drug-releasing scaffolds are the appropriate dose providing over the suitable therapeutic time and the controlled biodegradability rate of the scaffold material. The first requirement needs to be tuned to dynamically match the physiological needs of the tissue regeneration. Similarly, scaffold degradation rate is crucial to control the drug release and should be synchronized with the rate of tissue growth (Giannoudis *et al.*, 2007; Kwong and Harris, 2008; Ho-shui-ling *et al.*, 2019; Alaribe *et al.*, 2016; Haugen *et al.*, 2020; de Grado *et al.*, 2018; Turnbull *et al.*, 2018; Diaz-Rodriguez *et al.*, 2018).

According to the as-cited requirements, polymers, ceramics and their composites are suitable materials for making drug-releasing scaffolds due to their properties. On one side, polymers possess a tunable biodegradation rate due to hydrolytically unstable linkages in their backbone in addition to being mostly biocompatible. Both natural and synthetic polymers can be associated with bioactive molecules which can be covalently bound to polymers or physically entrapped inside a polymer matrix. In both cases, the polymer degrades releasing bioactive molecules in the physiological environment. There are different forms of polymeric scaffolds for drug delivery from 3D porous matrices to electrospun nanofibrous matrices, nanoparticles, porous microspheres and thermosensitive hydrogels. The load of drugs in polymer scaffolds can be achieved by different techniques and the most common one is the blend loading which involves a previous blend of the polymer and the drug (Fig. 5(d)). Usually, the blending is made by mixing solutions of the polymer and the previously prepared drug in a common solvent. This strategy allows for the drug to be incorporated during the formation of the scaffold. The other well-known drug loading processes are soak loading (Fig. 5(a)), site-specific binding of the drug to the polymer (Fig. 5(e)), pre-loading in nano/micro-particles (Fig. 5(c)), and drug polymer conjugation (Fig. 5(b)). In the soak loading process, drugs are embedded in a pre-fabricated drug-free scaffold by submerging the scaffold in a solution of the drug until its loading. For the site-specific binding, polymers which present functional groups with affinity to drugs can build strong drug-polymer interactions for the loading. The pre-loading in nano/microparticles method consists of loading the drug in small polymer particles, and then confining it within the scaffold polymer networks during pre- or post- fabrication. Finally, the drug-polymer conjugation allows to bind the drug and the polymer in a covalent manner for a precise control of the quantity of the incorporated drug. Several parameters like the polymer-drug compatibility, the preparation method of the scaffold, drug stability, the final application, and the desired drug release rate are involved in the choice of the process. The drug release can then be controlled by various processes as a function of loading approach. These processes imply diffusion, polymer erosion or degradation, and swelling of polymer followed by diffusion. They can all take place simultaneously or not (Calori *et al.*, 2020; Kwong and Harris, 2008; Ho-shui-ling *et al.*, 2019; Alaribe *et al.*, 2016; Sabir *et al.*, 2009; Dorati *et al.*, 2017).

On the other hand, ceramic materials have also the ability to biodegrade (*e.g.*, CaP, bioglasses and calcium sulfate) and release bioactive molecules at a controlled rate. Actually, the incorporation of therapeutic molecules to bioceramics could enhance their

performance by ensuring tissue repair, treatment, and/or preventing post implantation pathologies or diseases by the controlled local delivery of loaded therapeutic agents. Multidimensional and hierarchical ceramics structures allow increasing the surface area of drug-releasing scaffolds and promoting proteins adsorption. Moreover, the incorporation of therapeutic molecules within the structure of bioceramics enables the administration of poorly water-soluble drugs without the need of any kind of additives. This combination can lead to a local and long-term effective drug release with ceramic resorption at the target site. In order to do so, different techniques are available to load biomimetic ceramics with therapeutic molecules: adsorption, physical entrapment, and covalent bonding (Fig. 6). Physical adsorption, which is a superficial phenomenon, is one of the most commonly used mechanisms to dope biomimetic ceramics with therapeutic molecules. This approach is clearly influenced by surface characteristics of the biomaterials as well as the drug loading capacity and release. High scaffold-specific surface areas allow the loading biomolecules without the use of aggressive treatments. However, surface adsorption doesn't usually achieve a long-term retention of drugs due to the weak interactions between biomaterials and therapeutic molecules. The second technique consists in trapping therapeutic molecules into the structure of the material during their manufacturing. The key of this process is an optimal homogenization of the drug inside the scaffold matrix to avoid the burst release. This category of loading processes requires a multistep approach that complicates the synthesis of the scaffold. The last approach to produce drug-loaded ceramics scaffolds is the covalent bonding of therapeutic molecules. It can achieve stable and durable incorporation for up to several months and avoid the burst release (Dorati *et al.*, 2017; Chindamo *et al.*, 2020; Lin *et al.*, 2019; Ho-shui-ling *et al.*, 2019; Alaribe *et al.*, 2016; Diaz-Rodriguez *et al.*, 2018).

The study of drug-releasing scaffolds is a promising area for both polymers and ceramics. Indeed, the incorporation of therapeutic molecules or cell attachment to these systems can allow to increase the performance and so the potential applicability of the scaffolds. Researches are focused on the finding of the biomaterial or a combination of biomaterials with optimum properties to support tissue regeneration, and to obtain drug delivery systems able to modulate drug release. For that, the dreamed drug-loaded scaffolds must meet the following conditions: a local drug delivery with improved bioavailability and reduced adverse effects with respect to systemic drug administration, a sustained drug release and the ability of combining two or more drugs in a single scaffold. There have been continued advances towards the further development of the field where new materials and combinations of materials, as well as improved scaffold designs and novel processing techniques have been investigated for drug-delivery.

Still, there is a lack of a large amount of biological information to fully understand the *in vitro* and *in vivo* performance of such scaffolds in specific applications. Finally, too few clinical trials are made on these studied systems due to strict regulations. In order to limit the gap between academic research and commercial reality more efforts must be made to achieve an application and clinical use (Bohner, 2014; Mourin and Boccaccini, 2010; Bagherifard, 2017; Alaribe *et al.*, 2016; Diaz-Rodriguez *et al.*, 2018).

Conclusion

The twentieth and beginning of twenty-first century brought considerable advances in the field of bone tissue engineering. The growing and never-ending needs coupled with the motivation of the researchers for innovation, have contributed intensively to develop more and more smart strategies for bone substitution. Future research should be based on interdisciplinary and convergence of several sciences and technologies, for simultaneous optimization of chemical composition control, shaping methods and functionalization routes.

References

- Azila, S., Murad, M., Sopyan, I., 2012. Doping metal into calcium phosphate phase for better performance of bone implant materials. *Recent Patents on Materials Science* 5 (January), 18–47. Available at: <http://www.eurekaselect.com/openurl/content.php?genre=article&issn=1874-4648&volume=5&issue=1&spage=18>.
- Alaribe, F.N., *et al.*, 2016. Scaffolds from biomaterials advantages and limitations in bone and tissue engineering. *Biologia* 71 (4).
- Bagherifard, S., 2017. Mediating bone regeneration by means of drug eluting implants: from passive to smart strategies. *Materials Science and Engineering C* 71, 1241–1252. <https://doi.org/10.1016/j.msec.2016.11.011>.
- Boanini, E., Gazzano, M., Bigi, A., 2010. Ionic substitutions in calcium phosphates synthesized at low temperature. *Acta Biomaterialia* 6 (6), 1882–1894. <https://doi.org/10.1016/j.actbio.2009.12.041>.
- Bohner, M., 2010. Resorbable biomaterials as bone graft substitutes. *Materials Today* 13 (1–2), 24–30. [https://doi.org/10.1016/S1369-7021\(10\)70014-6](https://doi.org/10.1016/S1369-7021(10)70014-6).
- Bohner, M., 2014. *Bone Substitute Materials*, third ed. Elsevier. doi:10.1016/B978-0-12-801238-3.00224-5.
- Bohner, M., Galea, L., Doebelin, N., 2012. Calcium phosphate bone graft substitutes: Failures and hopes. *Journal of the European Ceramic Society* 32 (11), 2663–2671.
- Bongio, M., *et al.*, 2010. Development of bone substitute materials: From “biocompatible” to “instructive”. *Journal of Materials Chemistry* 20 (40), 8747–8759.
- Boyce, T., Edwards, J., Scarborough, N., 1999. Allograft bone: The influence of processing on safety and performance. *Orthopedic Clinics of North America* 30 (4), 571–581.
- Calori, I.R., *et al.*, 2020. Polymer scaffolds as drug delivery systems. *European Polymer Journal* 129.109621. <https://doi.org/10.1016/j.eurpolymj.2020.109621>.
- Campana, V., *et al.*, 2014. Bone substitutes in orthopaedic surgery : From basic science to clinical practice. *Journal of Materials Science: Materials in Medicine* 25 (10), 2445–2461.
- Canillas, M., *et al.*, 2017a. Calcium phosphates for biomedical applications. *Boletín de la Sociedad Española de Cerámica y Vidrio* 56 (3), 91–112. <https://doi.org/10.1016/j.bsecv.2017.05.001>.
- Canillas, M., *et al.*, 2017b. Processing of hydroxyapatite obtained by combustion synthesis. *Boletín de la Sociedad Española de Cerámica y Vidrio* 56 (5), 237–242. <https://doi.org/10.1016/j.bsecv.2017.05.002>.
- Cao, W., Hench, L.L., 1996. Bioactive materials. *Ceramics International* 22 (6), 493–507.

- Carrodegua, R.G., De Aza, S., 2011. α -Tricalcium phosphate: Synthesis, properties and biomedical applications. *Acta Biomaterialia* 7 (10), 3536–3546. <https://doi.org/10.1016/j.actbio.2011.06.019>.
- Champion, E., 2013. Sintering of calcium phosphate bioceramics. *Acta Biomaterialia* 9 (4), 5855–5875. <https://doi.org/10.1016/j.actbio.2012.11.029>.
- Champion, E., *et al.*, 2017. Chapter 14 – Advanced processing techniques for customized ceramic medical devices. In: Palmero, P., Cambier, F., Barra, E. De (Eds.), *Advances in Ceramic Biomaterials*. Woodhead Publishing, pp. 433–468.
- Chartier, T., *et al.*, 2015. Additive manufacturing to produce complex 3D ceramic parts. *Journal of Ceramic Science and Technology* 6, 95–104.
- Chindamo, G., *et al.*, 2020. Bone diseases: Current approach and future perspectives in drug delivery systems for bone targeted therapeutics. *Nanomaterials* 10.
- Connolly, J.F., 1995. Injectable bone marrow preparations to stimulate osteogenic repair. *Clinical Orthopaedics and Related Research* 313.
- de Grado, G.F., *et al.*, 2018. Bone substitutes: A review of their characteristics, clinical use, and perspectives for large bone defects management. *Journal of Tissue Engineering* 9. 2041731418776819.
- Demir, M.M., *et al.*, 2002. Electrospinning of polyurethane fibers. *Polymer* 43 (11), 3303–3309.
- Díaz-Rodríguez, P., Sánchez, M., Landin, M., 2018. Drug-loaded biomimetic ceramics for tissue engineering. *Pharmaceutics* 10, 1–20.
- Dorati, R., *et al.*, 2017. Biodegradable scaffolds for bone regeneration combined with drug-delivery systems in osteomyelitis therapy. *Pharmaceutics* 10.
- Eliaz, N., Metoki, N., 2017. Calcium phosphate bioceramics: A review of their history, structure, properties, coating technologies and biomedical applications. *Materials* 10.
- Ferracini, R., *et al.*, 2019. Composite Xenohybrid bovine bone-derived scaffold as bone substitute for the treatment of tibial plateau fractures. *Applied Sciences* 9 (13), 2675.
- Garvie, R.C., Hannink, R.H., Pascoe, R.T., 1975. Ceramic steel? *Nature* 258, 703–704.
- Giannoudis, P.V., *et al.*, 2008. The diamond concept – Open questions. *Injury* 39 (Suppl. 2), S5–S8.
- Giannoudis, P.V., Einhorn, T.A., Marsh, D., 2007. Fracture healing: The diamond concept. *Injury* 38 (Suppl. 4), S3–S6.
- Goldberg, V.M., Akhavan, S., 2005. Biology of bone grafts. In: Lieberman, J.R., Friedlaender, G.E. (Eds.), *Bone Regeneration and Repair: Biology and Clinical Applications*. Springer, pp. 57–65.
- Grøndahl, L., Jack, K.S., Goonasekera, C.S., 2017. *Composite Materials for Bone Repair*, second ed. Elsevier Ltd. doi:10.1016/B978-0-08-100752-5.00005-6
- Habraken, W., *et al.*, 2016. Calcium phosphates in biomedical applications: Materials for the future? *Materials Today* 19 (2), 69–87. <https://doi.org/10.1016/j.mat.2015.10.008>.
- Haugen, H.J., *et al.*, 2020. Bone grafts : which is the ideal biomaterial ? *Journal of Clinical Periodontology* 46, 92–102.
- Hench, L.L., 1991. Bioceramics: From concept to clinic. *Journal of the American Ceramic Society* 74 (7).
- Ho-shui-ling, A., *et al.*, 2019. Bone regeneration strategies: Engineered scaffolds, bioactive molecules and stem cells Current stage and future perspectives. *Biomaterials*. 143–162.
- Hsu, Y.H., Turner, I.G., Miles, A.W., 2007. Fabrication and mechanical testing of porous calcium phosphate bioceramic granules. *Journal of Materials Science: Materials in Medicine*. 1931–1937.
- Jones, J.R., 2013. Review of bioactive glass: From Hench to hybrids. *Acta Biomaterialia* 9 (1), 4457–4486. <https://doi.org/10.1016/j.actbio.2012.08.023>.
- Kashirina, A., *et al.*, 2019. Biopolymers for bone substitutes: A review. *Biomaterials Science* 7, 3961–3983.
- Kinney, R.C., *et al.*, 2010. Demineralized bone matrix for fracture healing : Fact or fiction ? *Journal of Orthopaedic Trauma* 24 (3), 52–55.
- Kwong, F.N.K., Harris, M.B., 2008. Recent developments in the biology of fracture repair. *Journal of the American Academy of Orthopaedic Surgeons* 16 (11), 619–625.
- Lawson, A.C., Czernuszka, J.T., 1998. Collagen-calcium phosphate composites. *Proceedings of the Institution of Mechanical Engineers, Part H: Journal of Engineering in Medicine* 212, 413–425.
- Li, J., Hastings, G.W., 2016. Chapter 5 – Oxide bioceramics : Inert ceramic materials in medicine and dentistry. In: Murphy, W., Black, J., Hastings, G. (Eds.), *Handbook of Biomaterial Properties*. Springer, pp. 339–352.
- Lin, K., *et al.*, 2019. 3D printing of bioceramic scaffolds-barriers to the clinical translation: From promise to reality, and future perspectives. *Materials* 12.
- Mahony, O., Jones, J.R., 2008. Porous bioactive nanostructured scaffolds for bone regeneration: A sol-gel solution. *Nanomedicine* 3 (2), 233–245.
- Melchels, F.P.W., Feijen, J., Grijpma, D.W., 2010. Biomaterials A review on stereolithography and its applications in biomedical engineering. *Biomaterials* 31 (24), 6121–6130. <https://doi.org/10.1016/j.biomaterials.2010.04.050>.
- Mourin, V., Boccaccini, A.R., 2010. Bone tissue engineering therapeutics : Controlled drug delivery in three-dimensional scaffolds. *Journal of the Royal Society Interface* 7 (43), 209–227.
- Murphy, S.V., Atala, A., 2014. 3D bioprinting of tissues and organs. *Nature Biotechnology* 32 (8), 773–785. <https://doi.org/10.1038/nbt.2958>.
- Peske, O., *et al.*, 2009. Autologous bone graft versus demineralized bone matrix in internal fixation of ununited long bones. *Journal of Trauma Management & Outcomes* 3, 1–8.
- Pina, S., *et al.*, 2017. Biofunctional ionic-doped calcium phosphates: Silk fibroin composites for bone tissue engineering scaffolding. *Cells Tissues Organs* 204 (3–4), 150–163.
- Prakasam, M., *et al.*, 2017. Biodegradable materials and metallic implants – A review. *Journal of Functional Biomaterials* 8 (4), 44. <http://www.mdpi.com/2079-4983/8/4/44>.
- Pryor, L.S., *et al.*, 2009. Review of bone substitutes. *Craniofacial Trauma & Reconstruction* 2 (3), 151–160.
- Rahamana, M.N., *et al.*, 2011. Bioactive glass in tissue engineering. *Acta Biomaterialia* 7 (6), 2355–2373.
- Ratner, B.D., *et al.*, 2013. Introduction – Biomaterials science: An evolving, multidisciplinary endeavor. In: Ratner, B.D., Schoen, F.J., Hoffman, A.S., Lemons, J.E. (Eds.), *Biomaterials Science: An Introduction to Materials in Medicine*, third ed. Academic Press, pp. xxv–xxxix.
- Roberts, T.T., Rosenbaum, A.J., 2012. Bone grafts, bone substitutes and orthobiologics. *Organogenesis* 8 (4), 114–124.
- Roseti, L., *et al.*, 2017. Scaffolds for bone tissue engineering: State of the art and new perspectives. *Materials Science and Engineering C* 78, 1246–1262. <https://doi.org/10.1016/j.msec.2017.05.017>.
- Sabir, M.I., Xu, X., Li, L., 2009. A review on biodegradable polymeric materials for bone tissue engineering applications. *Journal of Materials Science* 44, 5713–5724.
- Sadat-Shojai, M., *et al.*, 2013. Synthesis methods for nanosized hydroxyapatite with diverse structures. *Acta Biomaterialia* 9 (8), 7591–7621. <https://doi.org/10.1016/j.actbio.2013.04.012>.
- Schallenger, M.A., *et al.*, 2014. Comparison of the osteogenic potential of osteoselect demineralized bone matrix putty to novabone calcium-phosphosilicate synthetic putty in a cranial defect model. *The Journal of Craniofacial Surgery* 25 (2), 657–661.
- Sheikh, Z., *et al.*, 2019. Natural and synthetic bone replacement graft materials for dental and maxillofacial applications. *Advanced Dental Biomaterials*. 347–376.
- Shin, S.Y., *et al.*, 2015. Periodontal Regeneration: Current Therapies. Elsevier Inc. doi:10.1016/B978-0-12-397157-9.00040-0.
- Thavornvutikarn, B., *et al.*, 2014. Bone tissue engineering scaffolding: Computer-aided scaffolding techniques. *Progress in Biomaterials* 3, 61–102.
- Thomas, T., Martin, A., Lafage-Proust, M.-H., 2008. Physiologie du tissu osseux. */data/traite/ap/14-40315/*.
- Tite, T., *et al.*, 2018. Cationic substitutions in hydroxyapatite: Current status of the derived biofunctional effects and their in vitro interrogation methods. *Materials* 11, 1–62.
- Turnbull, G., *et al.*, 2018. 3D bioactive composite scaffolds for bone tissue engineering. *Bioactive Materials* 3, 278–314.
- Vallet-regí, M., 2010. Evolution of bioceramics within the field of biomaterials. *Comptes Rendus Chimie* 13, 174–185.
- Wang, W., Yeung, K.W.K., 2017a. Bone grafts and biomaterials substitutes for bone defect repair: A review. *Bioactive Materials* 2 (4), 224–247. <https://doi.org/10.1016/j.bioactmat.2017.05.007>.
- Wang, W., Yeung, K.W.K., 2017b. Bone grafts and biomaterials substitutes for bone defect repair: A review. *Bioactive Materials* 2 (4), 224–247. <https://doi.org/10.1016/j.bioactmat.2017.05.007>.
- Williams, D.F. (Ed.), 1987. *Definitions in biomaterials: Proceedings of a Consensus Conference of the European Society for Biomaterials*, Chester, England. Amsterdam; New York: Elsevier. [March 3-5, 1986].
- Zimmermann, G., Moghaddam, A., 2011. Allograft bone matrix versus synthetic bone graft substitutes. *Injury* 42, S16–S21. <https://doi.org/10.1016/j.injury.2011.06.199>.
- Zocca, A., *et al.*, 2015. Additive manufacturing of ceramics: Issues, potentialities, and opportunities. *Journal of the American Ceramic Society* 98 (7), 1983–2001.

New Trends in Ceramics for Orthopedics

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State of the Art

Ceramics were successfully introduced in orthopedics at the end of the 1960s. Ceramics, in contrast to metals or polymers do not suffer corrosion or hydrolysis. Moreover, their resistance to wear makes them ideal for bearing devices. So far, the major industrial applications of bio-ceramics have been femoral heads and cups, hydroxyapatite coatings in total hip arthroplasty, and bioactive ceramics as bone fillers. Ceramics can be chosen either for their inertia and wear properties (for joint prostheses), or for their affinity with bone tissues, which favors bone adhesion and bone in-growth. They are therefore separated in two groups: 'bio-inert' and 'bio-active' ceramics.

Currently used bio-inert ceramics, i.e., micro-structured alumina, yttria stabilized zirconia, and mostly now zirconia-toughened alumina composites give satisfactory results. Their major biomedical application concerns Total Hip Replacement (THR), especially for the femoral head and acetabular cup components. Nowadays, the main issue for THR is the generation of wear debris, produced mainly by the acetabular component ([Campbell et al., 2004](#)). The standard artificial joints consist of a polymer cup made of ultrahigh molecular weight polyethylene (UHMWPE), placed in the acetabulum via a metal-back component, and a metal (stainless steel or cobalt chromium alloy) ball affixed to a metal stem introduced in the femur. Any use of the joint, such as walking, results in cyclic articulation of the polymer cup against the metal ball. During the reciprocating motion of normal joint use, UHMWPE fibrils are then released, mostly by adhesive wear, to form submicrometer-sized wear debris. This results in billions of tiny polymer particles being shed into the surrounding synovial fluid and tissues. The biological interaction with small particles in the body then becomes critical. It is currently believed that the UHMWPE particles generated at the contact surfaces enter the periprosthetic tissues where they trigger macrophages reaction. Then macrophages release pro-inflammatory cytokines that stimulate osteoclastic bone resorption, leading to osteolysis and eventual loosening of the prosthesis and a need for revision. This has led to the development and use of alternative surfaces for hip articulation such as ceramic-UHMWPE, metal-metal and ceramic-on-ceramic couplings. In the case of metal-metal coupling the amount of ion release can be very detrimental for the surrounding tissues. The use of bio-ceramic materials, in comparison to metal alloy structural implants, reduces wear rate of the polyethylene components and produces negligible amounts of metal ion release. Due to the low roughness exhibited by ceramic heads (typically lower than few nanometers) and their good wettability, abrasion is reduced significantly if ceramic femoral heads are used with acetabular cups made of polyethylene and almost completely avoided when using ceramic femoral heads together with ceramic cup inserts.

The clinical success associated to the use of ceramic led to the implantation of more than 3.5 million alumina components, more than 600,000 zirconia femoral heads worldwide since 1990, and more than 8 million zirconia toughened alumina components, with a strongly growing market (i.e., more than 25% growth for the alumina-alumina coupling between 2002 and 2004). There are many reports on fracture rates associated with ceramics. Important references have been compiled elsewhere ([Campbell et al., 2004](#)). If, in the pioneering days, the fracture rate was quite high (up to 13% for some series), the in vivo failure rate reported by the producer of BioloX® alumina is today below 0.01% ([Willmann, 2000](#)). A comparable failure rate was claimed by the producer of Prozyr® zirconia heads ([Cales, 2000](#)) before the critical event of 2001, discussed below. For more current ZTA ceramics, such as BioloX® Delta the failure rate is even lower, below 1 in 100,000 ([Ruys, 2019](#)).

Even though the clinical follow up with current alumina ceramics is very good, it must be kept in mind that their use has been restricted so far to a limited number of designs of hip components, for which the mechanical loading is less demanding. As an example, 22 mm heads are not currently manufactured using alumina ceramics, for reliability reasons. Alumina is not used for Total Knee Replacement (TKR), where ceramics could also improve the wear properties. Alumina-alumina coupling also exhibits a significant increase of failure ratios. This is again related to its modest mechanical properties. In the 90's, Yttria-Stabilized Zirconia became a popular alternative to alumina as structural ceramic because of substantially higher fracture toughness and strength. The use of zirconia has opened the way towards new implant designs that were not possible with alumina, more brittle. An example is the use of zirconia for 22 mm heads, and the development of zirconia knees by some companies. Biomedical grade zirconia exhibits the best mechanical properties of single phase oxide ceramics: this is the consequence of phase transformation toughening, which increases its crack propagation resistance. The stress – induced phase transformation involves the transformation of metastable tetragonal grains to the monoclinic phase at the crack tip. It is accompanied by volume expansion and induces compressive stresses which hinder crack propagation. On the other hand, due to this meta – stability, zirconia is prone to aging in the presence of water ([Chevalier, 2006](#)). Zirconia manufacturers considered this problem as a minor issue until 2001, when roughly 400 failures of zirconia heads were reported within a very short period (See Relevant Websites section). The failure origin is now associated to an accelerated aging in two particular batches. Even if limited in time and number, and clearly identified to be process controlled, these events have had a catastrophic impact for the use of zirconia, some surgeons returning to other solutions. More important, some clinical reports show that zirconia can exhibit a progressive ageing degradation even under 'normal' situation, which limits the long-term stability of zirconia.

For these different reasons, there is a trend to develop stronger and more reliable ceramics that should expand the field of application of bio-inert ceramics in orthopedics.

Unlike bio-inert ceramics, the requirements for bio-active ceramics are to provide favorable surfaces for bone adhesion and bone in-growth (Hench, 1998). On the other hand, the specifications in terms of load-bearing capability are less demanding. The bio-active ceramics are thus based on calcium phosphate materials (mainly hydroxyapatite, HAP, and tri-calcium phosphate, TCP), because their composition is close to the mineral part of bone.

Since the early 1980s, the most important application of bio-active ceramics has been the coating of orthopedic metal implants, at locations where a strong interface with bone is required. This is the case of some parts of the femoral stems and acetabular metal-backs for the hip joints and tibial and femoral components for the knee joints. These systems represent successful alternatives to cemented prostheses, especially for young and active people, and are therefore generally associated to ceramic-ceramic couplings. If clinical studies show a benefit concerning the early fixation of un-cemented implants compared to cemented artificial joints, no influence on implant lifetime has been measured so far (See Relevant Websites section). If most of current bio-active coatings are made of plasma-sprayed hydroxyapatite, new developments include new materials and/or new processes (Campbell, 2003). Newest approaches (i.e., biomimetic coatings) open the way to incorporate biologically active agents.

In the mid 1980s, the osteo-conductive properties of calcium phosphate led to their use as synthetic bone grafts, as an alternative to auto-grafts and xeno-grafts (Hench, 1998). Indeed, as compared to auto-grafts, synthetic bone substitute involve less invasive surgery (a two step operation is necessary for the former) and are available in large quantities. As compared to xeno-grafts, the risk of rejection is much less important, and the transmission of diseases is avoided. Most of current bone substitutes are porous pieces of biphasic calcium phosphates, i.e., HAP-TCP composites (Daculsi *et al.*, 2003). A careful control of the architecture (volume and morphology of the macro and micro-porosities) is a key issue for a successful implant, as the macroporosity controls the access of the tissues and biological fluids to the volume of the substitute, and the microporosity the adhesion of the cells and the resorption rate of the calcium phosphate (thus the availability of Ca and P ions for bone reconstruction). The fast *in-vivo* resorption rate of TCP, as compared to HAP, allows controlling the overall degradation rate of the HAP-TCP composite, and thus adapting the material to the patient (faster resorption for patients with faster bone reconstruction). The synthetic bone substitutes US market was about 280 million USD in 2015, with an expected 20% yearly increase (Bone Graft Substitutes Market).

Although they offer very good clinical results, some limitations still exist. The optimization of the micro- and macro- porosities and their effect on biological properties are not always taken into account, which results in a large variability of physico-chemical properties among current commercial substitutes. Another strong limitation is their brittleness associated to low toughness and slow crack growth sensitivity (Benaqqa *et al.*, 2005), which restricts their use to non-load bearing applications, and makes them difficult to handle during surgery. Last but not least, their bioactivity should be increased in order to promote a faster and better bone reconstruction. We should keep in mind that the nanostructure of natural HAP crystals leads to a specific area of bone around 50–100 m²/g, to compare with 1 m²/g for most synthetic bone substitutes (grain size being generally higher than 1 µm).

New Progresses on Bio-Inert Ceramics

From Alumina to Plastic Alumina-Zirconia Composites

The first used bio-inert ceramics, i.e., alumina and zirconia, give good clinical results, especially compared to metals and polymers. New generations of ceramics for orthopedics should meet the need for a larger range of devices and a better reliability. The state of the art, described above has shown the limit of alumina in terms of mechanical performance and of zirconia in terms of long-term stability. Zirconia-Toughened alumina (ZTA) usually performs better than alumina in terms of mechanical strength, at least equaling the strength of zirconia while presenting a much better physico-chemical stability under *in vivo* conditions. As a result, ZTA is now the reference ceramic materials for the fabrication of hip replacement balls and cups. Major ceramic companies are developing such materials, of which a comprehensive state of the art is presented by Piconi (2017). Among them, the Biolox® Delta material developed by Ceramtec AG (Plochingen, Germany) has become the most implanted ceramic material in orthopedics (with more than 8 million components). It consists of approximately 75% aluminum oxide, the basis for hardness and wear resistance, and approximately 25% zirconium oxide, for improved mechanical properties (See Relevant Websites section). A strength value higher than 1150 MPa is reported associated with a toughness value of 8.5 MPa√m. Other zirconia-alumina composites are already commercialized but did not reach comparable market penetration. For example, the alumina-toughened zirconia (ATZ, 80% tetragonal zirconia polycrystals and 20% alumina) Bio-Hip®, developed by Metoxit AG (Thayngen, Switzerland), has a bending strength of up to 2000 MPa, and a toughness of 8 MPa√m. Two materials commercialized by Mathys Orthopädie GmbH are also worth mentioning: a ZTA (Symarec) and an ATZ (Ceramys), both with interesting balance between strength and hardness. Table 1 summarizes some typical mechanical properties of current alumina-zirconia composites, compared to monoliths.

However, the major parameter controlling ceramics lifetime is their sensitivity to Slow Crack Growth (SCG) and delayed failure, which is not taken into account in the sole strength and toughness data. As a general trend, the susceptibility of ceramics to SCG is discussed on the basis of a V (crack velocity) versus K_I (stress intensity factor) diagram (K_I representing the stresses at the tip of a crack or any pre-existing defect such as a pore, a scratch, etc, in the ceramic). Recently, the presence of a threshold in the stress intensity factor, below which no crack propagation occurs, has been the subject of important research in the ceramic field. This

Table 1 Mechanical properties of current alumina-zirconia composites, compared to monoliths

Material	Alumina BioloX®	Zirconia Prozyr®	ZTA (BioloX delta®)	ATZ (Ziradent®)	Pseudo-plastic ceramic (Evocera®)
K_{IC} (MPa $\sqrt{m}$)	4	6	8.5	8	8–14
Flexural Strength (MPa)	800	2000	1384	> 1300	500–700
Yield strength (MPa)					400
Young modulus (GPa)	400	200	398	~ 220	
Hardness (Vickers)	1500	1200	1900	1400	

ZTA: zirconia-toughened alumina.

ATZ: alumina-toughened zirconia.

*All information and data correspond to the present state of our knowledge concerning the properties of the ceramics. They are given by the producers and may not be measured using comparable setups, therefore they are given only as orders of magnitudes.

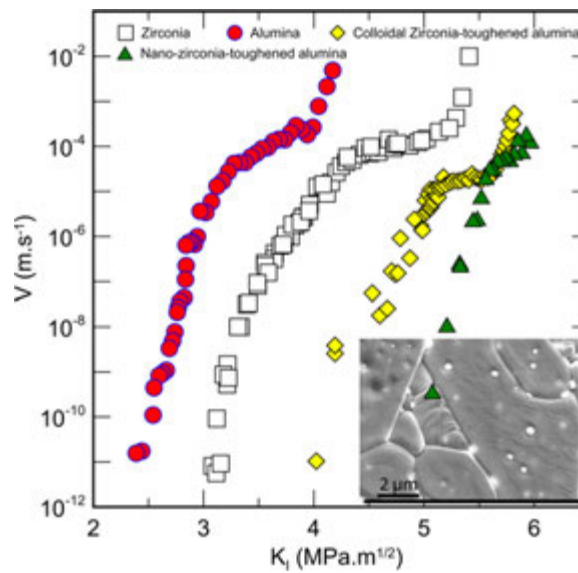


Fig. 1 V- K_I curves of biomedical grade alumina and zirconia and of two generations of alumina – zirconia composites. The insert shows the microstructure of a novel composite with nanometric zirconia particles inside the alumina grains (nano-zirconia toughened alumina).

threshold corresponds to equilibrium with null crack velocity. For ceramic joint prostheses for example, this threshold, K_{I0} , determines a safety range of use. **Fig. 1** represents the overall V- K_I curves of biomedical grade alumina, zirconia and an alumina – 10 vol% zirconia composite obtained by a modified colloidal route (De Aza *et al.*, 2002). It shows the significant improvement brought by these composites on both K_{IC} and K_{I0} .

The addition of alumina to zirconia at least reduces drastically ageing kinetics. It is shown that strength of BioloX delta® for example does not decrease even when repeatedly steam sterilized. However, ‘no decrease in strength’ does not mean necessary ‘no ageing’, since other manifestations of ageing are grain pull out and roughening. Some studies have been devoted to ageing in alumina–zirconia systems, and they show that, even if limited and possibly reduced to zero, some degree of degradation can be observed, depending on microstructural features. However the consequences of ageing in alumina-zirconia composites seem less important than in zirconia monoliths. As an example, we showed in a previous work (Pecharroman *et al.*, 2003) that ageing could be significant in a 3Y-TZP–alumina composite above 16 vol% zirconia (see **Fig. 2**). This critical content was related to the percolation threshold above which a continuous path of zirconia grains allowed transformation to proceed. Any extrapolation to other laboratory scale or industrial composites could be hazardous, but it shows again how ageing must be checked carefully prior to clinical development of a given alumina–zirconia composite.

Towards Pseudo-Plastic Ceramics

The reinforcement in conventional alumina – zirconia composites is due to the zirconia phase transformation toughening mechanism. Other sources of reinforcements can be expected in nano-structured ceramics and composites, such as the development of a compressive residual stress field due to the homogeneous distribution of second phase nanoparticles in a matrix. This is the case of a composite, where zirconia nanoparticles are evenly distributed into a micron size alumina matrix (Chevalier *et al.*, 2005). Those zirconia particles are mainly (> 70%) intragranular, with almost perfect spherical shape (diameter ranging from 30 nm to 150 nm).

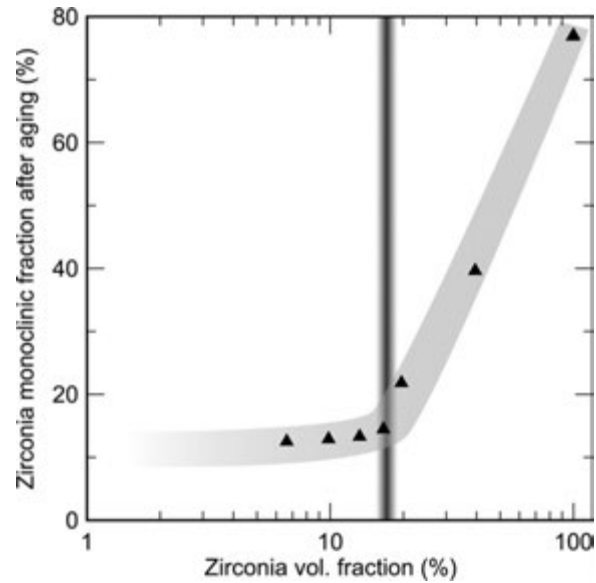


Fig. 2 Aging behavior of alumina – zirconia composites : zirconia monoclinic fraction observed after 40 h aging at 140°C versus zirconia content in the composite.

These particles are well below the critical size for phase transformation. This composite was developed in the framework of Bioker project (FP5 – Contract n° G5RD-CT-2001-00483). The V-K_i curve of this composite, containing only 1.6 vol% of zirconia nanoparticles, is compared to alumina and zirconia monoliths, and to the previous microstructured composite on Fig. 1. The nanostructured composite exhibits a peculiar behavior, i.e., its toughness is very high (50% higher than alumina, with the addition of only 1.6 vol% of zirconia!) and its sensitivity to Slow Crack Growth is much lower than for the other materials (ratio of threshold to toughness close to a covalent ceramic). This leads to a threshold value twice that of a standard biomedical grade alumina.

The literature is still sparse concerning mechanical properties of nanostructured ceramics and composites, especially in regards to orthopedic applications (in which field nanostructured ceramics are not yet on the market). However, some recent works (Lee *et al.*, 2003) show a significant improvement of both wear resistance and toughness associated to the use of dispersion of nanometer sized particles in a micrometer size matrix. This kind of materials is usually called ‘micro- nano’ composites, and can be processed via classical sintering methods. The process of ‘real’ nano- composites (both phases being less than 100 nm) is now possible via new sintering techniques such as Spark Plasma Sintering. However, their potential for orthopedic applications is still speculative.

One can also take advantage of Zirconia tetragonal-to-monoclinic phase transformation to fabricate pseudo-plastic ceramics (Chevalier *et al.*, 2020). This is one of the most interesting advances in the field these last years. This pseudo-plastic effect rises from the transformation-induced plasticity allowed by the t-m transformation, and was first observed in ceria-stabilized zirconia (Ce-TZP). Recently, an optimized material was proposed. It’s composed of 84 vol% ZrO₂ doped with 11 mol% of Ceria, 8 vol% Al₂O₃ and 8 vol% SrAl₁₂O₁₉ platelets. Together with an adequate sintering schedule (setup to offer a grain size and phase assemblage favoring the t-m transformation a little below room temperature (– 42°C)), this results in an excellent tolerance to flaw (as illustrated in Fig. 3 that shows almost no decrease of strength in the presence of defects as large as 150 µm) related to a plastic strain to failure of ~0.5%. However this is at the cost of a largely reduced strength (~400 MPa).

Although no applications of this material are on the market, it is available from the Doceram company under the tradename EvoCera® (EVOCERA), and is believed to be an excellent candidate for the fabrication of dental implants.

New Implant Designs

The benefit arising from alumina – zirconia composites and nano-structured materials permitted to develop new hip implant designs that are in the scope of orthopedic surgeons, to increase the quality of life of patients:

- Thinner acetabular cup wall for ceramic-ceramic making the procedure as conservative regarding bone removal as the current metal-metal solution. Ceramic/ceramic implants are currently much bulkier than the equivalent metal component.
- Small heads (22 mm, 28 mm) with longer neck length than currently available for surgeons.
- Hip resurfacing implants, making surgery much less invasive than today.

These last years, three concepts also emerged and are marketed:

- Femoral and tibial component of primary, total knee replacements (TKR).
- Anatomically-contoured heads for hip implants (tradename Biolox contoura® (Varadarajan *et al.*, 2013).

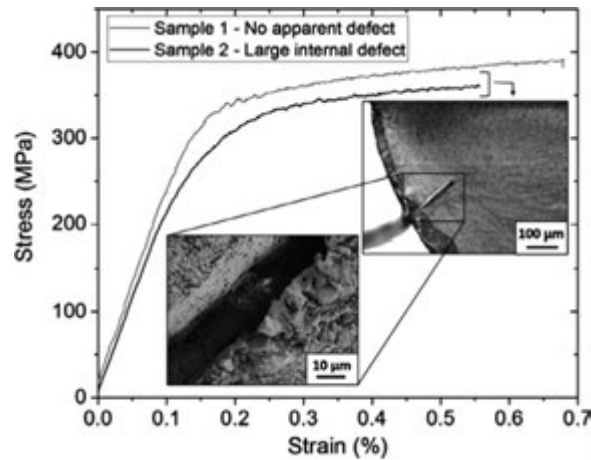


Fig. 3 Stress-strain curve of a pseudo-plastic ceramic with and without defect. From Chevalier, J., Liens, A., Reveron, H., *et al.*, 2020. Forty years after the promise of «ceramic steel?»: Zirconia-based composites with a metal-like mechanical behavior. *Journal of the American Ceramic Society* 103, 1482–1513.

- Systems for revision surgery (specifically ball head exchange), in which a titanium sleeve is used between the remaining stem and the new ceramic ball, to accommodate small geometric defects of the stem and avoid its replacement (*Biolog Option® System*).

Improved Testing Methods

As can be seen above, most biomedical ceramics are characterized by their strength, toughness, hardness, sometimes by their resistance to slow crack growth or hydrothermal ageing. Additionally, their resistance to friction and wear are fully characterized, using hip simulator that reproduces the gait movements, including now the shocks due to microseparation and relocation of the head in the insert in the case of hip prostheses components (Al-Hajjar *et al.*, 2013).

However, most testing procedures measure a given property individually: interactions between the different properties are seldom taken into account. A few studies start to consider the interactions between wear and hydrothermal ageing (Gremillard *et al.*, 2013; Perrichon *et al.*, 2017; Al-Hajjar *et al.*, 2019) and show the existence of an acceleration of ageing on the most loaded areas, as well as an acceleration of wear on the areas most degraded by ageing. These two degradation processes are thus symbiotic and should be studied as such.

Current Developments on Bio-Active Ceramics

Two physical properties of bio-active ceramics control their overall behavior, thus are key parameters for optimum biological performance. These are the interconnecting macro-porosity and an appropriate micro-porosity. The literature is still very sparse on these points, although their control is quite easy (Bignon *et al.*, 2003).

In the previous decade, macroporosity ($> 100 \mu\text{m}$) is generally obtained through the incorporation, in the green ceramic body, of a volatile phase (i.e., polymer), which is burnt during a thermal treatment at intermediate temperature. The amount and size of this porogen agent directly controls the size of the macro-pores, and more important their interconnections. The characterization of these interconnections can be obtained via mercury intrusion porosimetry measurements or image analysis (an example being images obtained with X-ray tomography).

Additive manufacturing techniques are now particularly useful to address both an optimization of the characteristics of the macroporosity (Charbonnier *et al.*, 2020; Magnaudeix *et al.*, 2016) and of the external shape of the scaffold, enabling the fabrication of personalized bone substitutes (Brie *et al.*, 2013), potentially leading to accelerated recovery and spectacular aesthetic results (Fig. 4).

Micro-porosity ($< 2 \mu\text{m}$) is controlled by the sintering procedure: higher temperatures and sintering times decrease the volume, and to lower extent the size of micro-porosity. The size of the micro-porosity is mainly related to the grain size of the ceramic powder prior sintering. Nanostructured ceramic powders could open the possibility to obtain pores with a sub-micrometer size and to increase specific surface.

Although the effect of interconnections between macro-pores is clearly established (i.e., faster proliferation of cells and subsequent bone in-growth), the role of micro-porosity is not yet completely established. Some results show that the micro-porosity is beneficial for cell adhesion and even invasion (Bohner *et al.*, 2017) and to some extent to osteo-induction (Habibovic *et al.*, 2005). This should still be an important field of research.

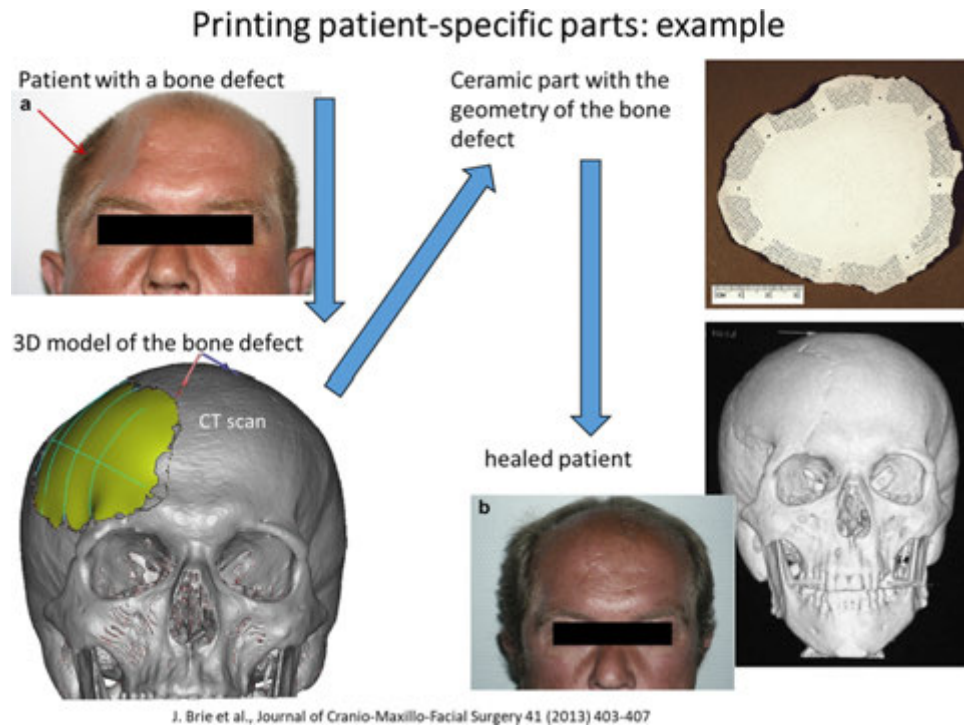


Fig. 4 Fabrication steps of patient-specific implants. From Brie, J., Chartier, T., Chaput, C., *et al.*, 2013. A new custom made bioceramic implant for the repair of large and complex craniofacial bone defects. *Journal of Cranio-Maxillo-Facial Surgery* 41, 403–407. doi:10.1016/j.jcms.2012.11.005.

As an alternative to biphasic calcium phosphates, there is a renewed interest on the use of bioactive glasses, in the form of porous architectures for bone substitution applications (Chen *et al.*, 2006). Bioactive glasses, such as 45S5 Bioglass®, which was developed more than 20 years ago, meet the criteria to be used as bone substitutes: they are osteo-conductive, bioactive, and at least partially resorbable. The major advantage of bio-active glasses is the formation, in contact with body fluids, of a carbonated apatite layer, with physico-chemical features close to natural bone hydroxyapatite (Hench, 1998). This apatite is characterized by nanometer size, non-stoichiometric and partially amorphous grains. In addition to the possible modification of micro-porosity via sintering temperatures and macro-porosity via porogen addition, bio-active glasses offer the opportunity to tailor their bio-activity and mechanical properties via crystallization process. Indeed, at intermediate temperature, i.e., between glass transition and melting temperatures (around 550°C and 1000°C for Bioglass®) the crystallinity ratio can be varied from 0 to almost 100% and the size of the crystals from nanometric to micrometric values. Therefore, ‘ideal’ resorbable scaffolds offering a range of porosity between nanometers and hundreds of micrometers, with large specific surface, can be obtained with bioactive glasses. There is still very few clinical uses of porous bioactive glasses as monolithic materials in orthopedics. However, they are available as granules or putty (for ex. Glassbone® Putty). They are also used as bioactive loads in PLA-bioactive glasses composites: some orthopedic fixation devices take advantage of the good mechanical properties and of the resorbability of the composite (for ex: LockActiv® interference screws).

In addition to be a “physical” substrate for bone formation, porous ceramic bone substitutes can sustain other functionalities. Mainly, they can locally release biologically active substances with controlled kinetics. Research is conducted mainly on two kinds of substances: antibiotics to avoid inflammation around the implant (Hasegawa *et al.*, 2004), and growth factors (Williams, 2006) such as Bone Morphogenetic Protein to enable a faster growth of bone. The key factor controlling the drug release is the way the drug is held in the implant. Much work is dedicated to include drugs in resorbable polymers. The release rate is then controlled by either the resorption rate of the polymer or the diffusion of the drug through the polymer. The polymer can then be added to a ceramic matrix, or mixed with calcium phosphate or bioactive glass powder to produce a polymer matrix composite (Tampieri *et al.*, 2003). Another possibility is to include directly the drug in the pores of the porous ceramic implant. Such systems allow tunable release rate for periods arranging from hours (Polak *et al.*, 2017) to several weeks (Dash and Cudworth, 1998), the release rate depending on the structure of the porosity (size and connectivity of the micropores) and on the drug physical properties (mainly diffusion coefficient and adhesion energy with the bone substitute).

Due to the continuous release and precise location, the efficiency of the antibiotics is optimum with very small doses (but locally almost constant and higher than the Minimum Inhibitory Concentration for the most common pathogenic agents). It has been shown also that bone substitutes loaded with growth factors present a bone growth rate that can be fourfold this of non-loaded substitutes. The addition of a drug-delivery functionality to bone substitutes can be considered as very promising for faster healing. However, the higher cost of such Drug Delivery Implants still impedes their clinical use.

One can go a step further into complexity, by synthesizing implantable materials that are partly living tissues. After Williams (2006), “tissue engineering is the creation of new tissue for the therapeutic reconstruction of the human body, by the deliberate and controlled stimulation of selected target cells, through a systematic combination of molecular and mechanical signals”. In other words, artificially building new tissues requires a delicate combination of starting material (cells) and interactions with the biological reactor. The presence of a scaffold mimicking the Extra Cellular Matrix can be considered as an essential factor, from both mechanical and molecular points of view. Indeed, the scaffold should not only provide the place for the cells to live, but also favors the different cellular process that have to take place (differentiation, proliferation, building of new ECM...). To our knowledge, such scaffolds do not yet exist.

Calcium phosphate ceramics are candidates for such applications, because of their ability, when combined with molecules such as Recombinant Human Bone Morphogenetic Proteins (rhBMP2), to induce bone formation even in ectopic sites (Kroese-Deutmann *et al.*, 2005). Much research is also devoted to polymer matrix composites (loaded with calcium phosphate particles, BMPs and possibly cells), an interesting way to produce the scaffold being to use 3D printing, rapid prototyping or similar techniques to control exactly its morphology and the distribution of the different components.

Conclusion

The aim of this paper was to review current research and development on ceramics for orthopedics. Alumina-zirconia composites are brought to the market as an answer to alumina brittleness and zirconia aging. Furthermore, new processing technologies open the way towards nanostructured ceramics and composites that are expected to exhibit improved mechanical performances.

Concurrently, bio-active ceramics bone substitutes are increasingly associated to organic materials and biological agents, to improve bone in-growth. Bone tissue engineering is still far from daily use, but concrete trends can be distinguished.

References

- Alfatto, S., Testoni, M., Cacciari, G.L., Toni, A., 1999. A mixed oxides prosthetic ceramic ball heads. Part II: effect of the zirconia fraction on the wear of ceramic on ceramic joints. *Biomaterials* 20, 1925–1929.
- Al-Hajjar, M., Fisher, J., Tipper, J.L., Williams, S., Jennings, L.M., 2013. Wear of 36-mm BIOLOX(R) delta ceramic-on-ceramic bearing in total hip replacements under edge loading conditions. *Proceedings of the Institution of Mechanical Engineers, Part H: Journal of Engineering in Medicine* 227, 535–542.
- Al-Hajjar, M., Gremillard, L., Begand, S., *et al.*, 2019. Combined wear and ageing of ceramic-on-ceramic bearings in total hip replacement under edge loading conditions. *Journal of Mechanical Behaviour of Biomedical Materials* 98, 40–47.
- Benaqqa, C., Chevalier, J., Saadaoui, M., Fantozzi, G., 2005. Slow crack growth behaviour of hydroxyapatite ceramics. *Biomaterials* 26, 6106–6112.
- Bignon, A., Chouteau, J., Chevalier, J., *et al.*, 2003. Effect of micro- and macroporosity of bone substitutes on their mechanical properties and cellular response. *Journal of Materials Science: Materials in Medicine* 14, 1089–1097.
- BioloX Option® System. Available at: <https://www.ceramtec.com/bioloX/products/hip/bioloX-option/>. (accessed on 18.06.20).
- Bohner, M., Baroud, G., Bernstein, A., *et al.*, 2017. Characterization and distribution of mechanically competent mineralized tissue in micropores of β -tricalcium phosphate bone substitutes. *Materials Today* 20 (3), 106–115. doi:10.1016/j.mattod.2017.02.002.
- Bone Graft Substitutes Market. Available at: <https://www.grandviewresearch.com/industry-analysis/bone-grafts-substitutes-market>, (accessed on 08.06.20).
- Brie, J., Chartier, T., Chaput, C., *et al.*, 2013. A new custom made bioceramic implant for the repair of large and complex craniofacial bone defects. *Journal of Cranio-Maxillo-Facial Surgery* 41, 403–407. doi:10.1016/j.jcms.2012.11.005.
- Cales, B., 2000. Zirconia as a sliding material: Histologic, laboratory, and clinical data. *Clinical Orthopaedics and Related Research* 379, 94–112.
- Campbell, A.A., 2003. Bioceramics for implant coatings. *Materials today* 6, 26–30.
- Campbell, P., Shen, F.-W., McKellop, H., 2004. Biologic and tribologic considerations of alternative bearing surfaces. *Clinical Orthopaedics and Related Research* 418, 98–111.
- Charbonnier, B., Manassero, M., Bourguignon, M., *et al.*, 2020. Custom-made macroporous bioceramic implants based on triply-periodic minimal surfaces for bone defects in load-bearing sites. *Acta Biomaterialia* 109, 254–266. doi:10.1016/j.actbio.2020.03.016.
- Chen, Q.Z., Thompson, I.D., Boccaccini, A.R., 2006. 45S5 bioglass®-derived glass-ceramic scaffolds for bone tissue engineering. *Biomaterials* 27, 2414–2425.
- Chevalier, J., Deville, S., Fantozzi, G., *et al.*, 2005. Nanostructured ceramic oxides with a slow crack growth resistance close to covalent materials. *Nanoletters* 5, 1297–1301.
- Chevalier, J., 2006. What future for zirconia as a biomaterial? *Biomaterials* 27, 535–543.
- Chevalier, J., Gremillard, L., 2007. New trends in ceramics for orthopedics. In: Buschow, K.H.Jürgen, Cahn, Robert W., Flemings, Merton C., Iltschner, Bernhard, Kramer, Edward J., Mahajan, Subhash, Veyssi re, Patrick (Eds.), *Encyclopedia of Materials: Science and Technology*. Elsevier, pp. 1–8. doi:10.1016/B978-008043152-9.02148-5.
- Chevalier, J., Liens, A., Reveron, H., *et al.*, 2020. Forty years after the promise of “ceramic steel?”: Zirconia-based composites with a metal-like mechanical behavior. *Journal of the American Ceramic Society* 103, 1482–1513.
- Daculsi, G., Laboux, O., Malard, O., Weiss, P., 2003. Current state of the art of biphasic calcium phosphate bioceramics. *Journal of Materials Science: Materials in Medicine* 14, 195–200.
- Dash, A.K., Cudworth, G.C., 1998. Therapeutic applications of implantable drug delivery systems. *J. Pharmacological and toxicological methods* 40, 1–12.
- De Aza, A.H., Chevalier, J., Fantozzi, G., Schehl, M., Torrecillas, R., 2002. Crack growth resistance of alumina, zirconia and zirconia toughened alumina ceramics for joint prostheses. *Biomaterials* 23, 937–945.
- EVOCERA. Available at: <https://www.moeschter-group.com/en/materials/evocera/>. (accessed 19.06.20).
- Glassbone® Putty. Available at: <http://noraker.com/products/glassbone-putty-en/>. (accessed on 30.06.20).
- Gremillard, L., Martin, L., Zych, L., *et al.*, 2013. Combining aging and wear to assess the durability of zirconia-based ceramic heads for total hip arthroplasty. *Acta Biomaterialia* 9 (7), 7545–7555.
- Habibovic, P., Yuan, H., Van Der Valk, C.M., *et al.*, 2005. 3D Microenvironment as essential element for osteoinduction by biomaterials. *Biomaterials* 26, 3565–3575.
- Hasegawa, M., Sudo, A., Komlev, V.S., Barinov, S.M., Uchida, A., 2004. High release of antibiotic from a novel hydroxyapatite with bimodal pore size distribution. *Journal of Biomedical Materials Research - Part B Applied Biomaterials* 70 (2), 332–339.
- Hench, L., 1998. Bioceramics. *Journal of the American Ceramic Society* 81, 1705–1727.

- Kroese-Deutmann, H.C., Quinten Ruhé, P., Spauwen, P.H.M., Jansen, J.A., 2005. Bone-inductive properties of rhBMP-2 loaded porous calcium phosphate cement implants inserted at an ectopic site in rabbits. *Biomaterials* 26, 1131–1138.
- Lee, S.W., Morillo, C., Lira-Olivares, J., *et al.*, 2003. Tribological and microstructural analysis of $\text{Al}_2\text{O}_3/\text{TiO}_2$ nanocomposites to use in the femoral head of hip replacement. *Wear* 255, 1040–1044.
- LockActiv® Interference Screws. Available at: <http://noraker.com/products/lock-activ-en/>. (accessed on 30.06.20).
- Magnaudeix, A., Usseglio, J., Lasgorceix, M., *et al.*, 2016. Quantitative analysis of vascular colonisation and angio-conduction in porous silicon-substituted hydroxyapatite with various pore shapes in a chick chorioallantoic membrane (CAM) model. *Acta Biomaterialia* 38, 179–189. doi:10.1016/j.actbio.2016.04.039.
- Pecharroman, C., Bartolome, J.F., Requena, J., *et al.*, 2003. Percolative mechanism of ageing in zirconia containing ceramics for biomedical applications. *Advanced Materials* 15, 507–511.
- Perrichon, A., Reynard, B., Gremillard, L., *et al.*, 2017. A testing protocol combining shocks, hydrothermal ageing and friction, applied to Zirconia Toughened Alumina (ZTA) hip implants. *Journal of Mechanical Behaviour of Biomedical Materials* 65, 600–608.
- Piconi, C., 2017. Ceramics for joint replacement: Design and application of commercial bearings. In: Palmero, P., De Barra, E., Cambier, F. (Eds.), *Advances in Ceramic Biomaterials*. Woodhead Publishing Series in Biomaterials, pp. 129–179.
- Polak, S.J., Lee, J.S., Murphy, W.L., *et al.*, 2017. Microstructural control of modular peptide release from microporous biphasic calcium phosphate. *Materials Science and Engineering C* 72, 268–277. doi:10.1016/j.msec.2016.11.054.
- Ruys, A., 2019. Alumina bearings in orthopedics: Present and future. In: Ruys, A. (Ed.), *Alumina Ceramics*. Woodhead Publishing Series in Biomaterials, pp. 179–223. doi:10.1016/b978-0-08-102442-3.00007-5.
- Tampieri, A., Celotti, G., Landi, E., *et al.*, 2003. Porous phosphate-gelatin composites as bone grafts with drug delivery functions. *Journal of Materials Science: Materials in Medicine* 14, 623–627.
- Varadarajan, K.M., Duffy, M.P., Zumbunn, T., *et al.*, 2013. Next-generation soft-tissue-friendly large-diameter femoral head. *Seminars in Arthroplasty* 24, 211–217. TKR. Available at: <https://www.ceramtec.com/biolox/products/knee/>. (accessed on 19.06.20).
- Williams, D.F., 2006. To engineer is to create: The link between engineering and regeneration. *Trends in Biotechnology* 24, 4–8.
- Willmann, G., 2000. Ceramic femoral head retrieval data. *Clinical Orthopaedics and Related Research* 379, 173–177.

Relevant Websites

- www.ceramtec.com
CeramTec.
The Ceramic Experts.
- www.anaes.fr
Haute Autorité de Santé.
Portail HAS Professionnels.
- www.prozyr.com
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New Trends in Ceramics for Dentistry

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Introduction

The human tooth is essentially an inorganic/organic composite material, characterized by a complex hierarchical structure, which is responsible of its unique physical, mechanical and optical properties. A deep understanding of the relationship between the composition, the structure and the properties of human teeth is necessary for correctly designing restorative dental materials and products.

Basically, the bulk of the dental tissue is composed by thick, mineralized dentin, covered by a protective layer, the highly mineralized enamel. These two layers are joined by the so-called dentin-enamel junction (DEJ) (McKittrick *et al.*, 2010). The root, mainly composed by dentin, is attached to the bony socket through a cementum. The inner part of teeth is composed by a non-mineralized soft tissue, the dental pulp that also contains nerves and the vascular system to provide connection with the surrounding tissues (Goldberg *et al.*, 2012; McKittrick *et al.*, 2010).

Dentin and enamel differ on their chemical composition and micro/macro-structure.

Dentin contains 40–45 vol% mineral phase (apatite crystals), 30 vol% organic matter (collagen and other proteins) and 20–25 vol% water. Enamel is richer in mineral phase (~ 92 vol%), with a smaller fraction of organic material (2 vol%) and water (6 vol%) (Goldberg *et al.*, 2012; McKittrick *et al.*, 2010).

Dentin's architecture is mainly formed by tubules (~ 1.5 μm in diameter), surrounded by highly mineralized apatite (0.5–1 μm in thickness) rods, which extend from the DEJ to the pulp (Halgas *et al.*, 2013; Cuy *et al.*, 2002). Enamel is mainly composed ~ 5 μm keyhole-shaped structures known as prisms (Lu *et al.*, 2012), which extend from the DEJ to the tooth surface. Fig. 1 depicts the characteristic microstructures of both dentin and enamel tissues of human tooth (Chan *et al.*, 2011).

Due to different compositions and structures, dentin and enamel are characterized by different mechanical properties and therefore show different roles during the mastication process. Dentin, located between the crown and the root, has the role of distributing the load across the teeth; enamel, the hardest tissue in human's body, protects the dentine from fracture and wear damage during load-bearing function, and acts as the cutting and grinding surface during mastication. For this reason, teeth are required to have high hardness and stiffness to support the mastication load, while a certain fracture toughness is required as well, to limit cracks and brittle fracture.

Mechanical properties of dental and enamel structures are frequently determined by nanoindentation tests, able to provide hardness and stiffness data. Halgas *et al.* (2013) performed a systematic investigation of dental mechanical properties by moving from the enamel occlusal surface to dentin tissue, passing through the DEJ. Nanoindentation tests proved that tooth is characterized by the highest hardness and indentation modulus in the enamel layer, and specifically in correspondence to the occlusal surface. Here, in fact, the hardness and modulus were about 6.5 GPa and 90 GPa, respectively. These values decreased to about 3.5 GPa and 75 GPa, respectively, in the areas closed to DEJ. Crossing the DEJ, a further sharp reduction was observed, since hardness and indentation modulus were about 1 GPa and 20 GPa, respectively, in the dentin region. Here, such values were almost constant and independent from the indentation area. Cuy *et al.* (2002) performed a deeper investigation of the enamel mechanical properties, and confirmed that the hardness and the elastic modulus were higher at the enamel surface and decreased significantly in correspondence of the DEJ. These authors correlated the variations in mechanical properties to changes in enamel chemical composition and microstructure (enamel prisms orientation). In particular way the chemical composition played the major role, since it was found a Ca and P enrichment at the enamel surface, suggesting a higher degree of mineralization in this area. In spite the sharp variation of mechanical properties in correspondence of the DEJ, this interface has a key role on the overall performance: it is very durable, and able to inhibit the propagation of cracks from the enamel to the dentin as well as to keep the tooth integrity during masticatory actions (Imbeni *et al.*, 2005).

Ceramics should satisfy some requirements to be clinically approved as dental materials, which include mechanical properties, biocompatibility and aesthetical properties. Some of these requirements, such as those related to mechanical performance and biocompatibility, have been addressed by specific standards. In particular way, the standard ISO 6872–2015 can be considered a reference for some physical and mechanical properties. Here, besides specific definitions of dental ceramic products, ceramics are classified into Type I, which includes ceramic products in the form of powders, pastes, or aerosols, and Type II, which are all other forms of ceramic products. In addition, the required minimal mechanical (flexural strength and fracture toughness) and chemical (solubility) properties for the different ceramic products are given, in agreement with their intended chemical use. To make an example, the recommended minimum flexural strength and fracture toughness of a monolithic ceramic for single-unit anterior prostheses, veneers, inlays, or onlays adhesively cemented are 50 MPa and 0.7 MPa $\sqrt{\text{m}}$, respectively, whereas the solubility should be < 100 $\mu\text{g}/\text{cm}^2$. For the determination of the flexural strength, three testing methods are recommended by this standard: three- and four-point bending and biaxial flexure (piston-on-three-ball); the recommended fracture toughness method is the Single-edge V-Notch Beam (SEVNB) test.

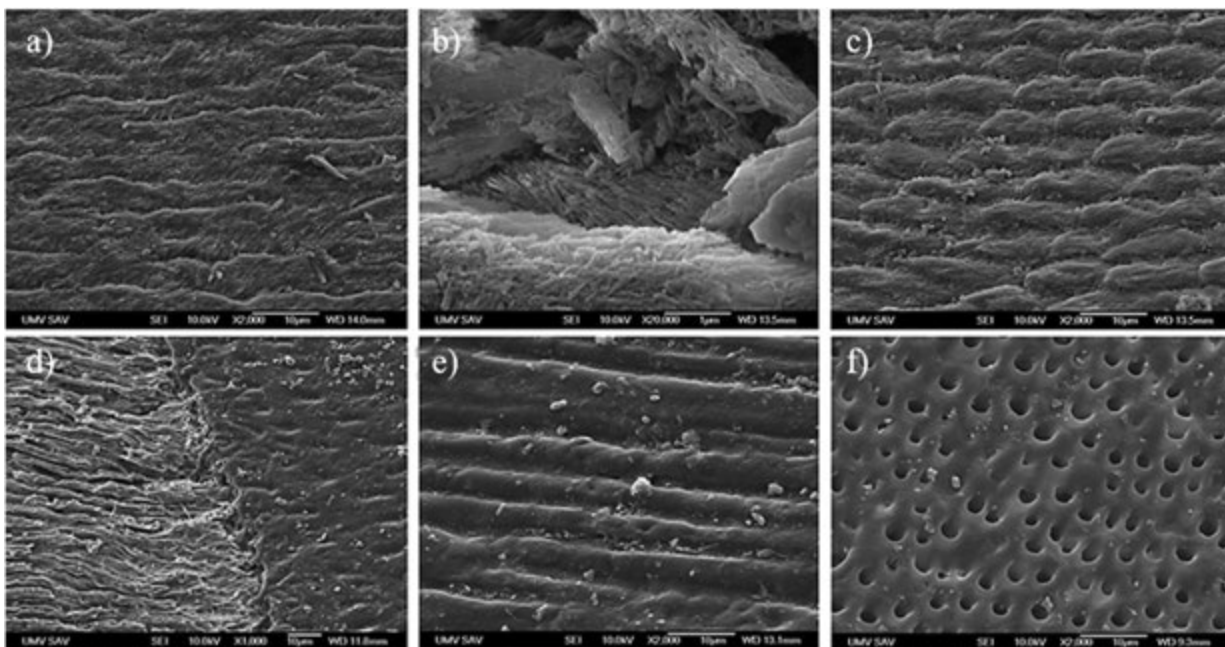


Fig. 1 Typical microstructures of enamel and dentin tissues of the human tooth (cross section observations). Occlusal (a) and central (c) areas of enamel with typical prismatic structure of enamel rods; higher-magnification of enamel prism, showing apatite crystals (b); DEJ between enamel (left) and dentin (right) (d); parallel (e) and vertical (f) sections of dentine: tubules are visible in (e). Reproduced from Halgas, R., Dusza, J., Kaiferova, J., Kovacsova, L., Markovska, N., 2013. Nanoindentation testing of human enamel and dentin. *Ceramics – Silikáty* 57, 92–99.

The evaluation of biocompatibility of the dental medical devices is described in the standard ISO 7405–2018, even if it is not specific for ceramic materials and products. This standard provides a clear guide to select the most proper testing method - both *in-vitro* (cytotoxicity) and *in-vivo* (animal) tests - according to the contact nature and duration as well as to the dental device type. When possible, for ethical issues, *in-vitro* testing should be preferred to *in-vivo* ones, and for this reason the optimization of laboratory protocols aimed to mimic as much as possible the clinical practice is currently in course. *In-vitro* tests offer several advantages as compared to *in-vivo* ones: lower cost, higher reproducibility, no legal and ethical issues. By exposing the synthetic dental materials to different physiological fluids and/or cell cultures, it is possible to gain information about cytotoxicity, inflammatory responses, anti-bacterial properties or cell differentiation capability of the dental material itself (De Souza Costa *et al.*, 2014). A recent approach deals with the use of an artificial pulp chamber, allowing the contact of the pulpal surface of the prosthetic material with the culture media. In these tests, it is also very important to properly select the cell lineages, to possibly apply 3D culture models and properly select volumes and concentrations of cell cultures to approach as much as possible the clinical conditions (De Souza Costa *et al.*, 2014). *In-vivo* tests – performed to observe the response of the synthetic material to living tissues – involve the use of animals, thus involving ethical and legal controversies. Moreover, the information obtained by these tests can be affected by the species, age and gender of the animal used, the results could be difficult to interpret and not easily transferred to human beings.

A further important requirement for dental ceramics is the esthetics, meaning the color and the optical property of the material, trying to match as much as possible the natural dental issue. Since there is no standard defining the color, proper measuring systems are normally used. One of them, named CIE $L^*a^*b^*$ seems proper to characterize non-self-luminous objects. In this system, the color is given by three coordinates, where L^* gives the degree of brightness, a^* the redness/greenness and b^* the yellowness/blueness. These parameters can be evaluated by a spectrophotometer, allowing to quantify which is the mean color difference between two materials (*i.e.*, natural and synthetic tooth). The standard of clinically acceptable ΔE^* was determined as 3.7 (Kim *et al.*, 2014).

The physical, mechanical and esthetic requirements of all-ceramic dental materials restrict the choice to few compositions. In the following paragraphs, the current and mainly used materials for all-ceramic restorations are discussed, by summarizing their main characteristics, advantages over other solutions, current issues. Is to overcome such issues that new solutions – in terms of both materials and technologies, are nowadays under development, and they will be here discussed as well. Therefore, this contribution aims at providing some guidelines for the design and development of innovative all-ceramic products and at indicating the new directions that the research in the field of all-ceramics restorative materials is moving in.

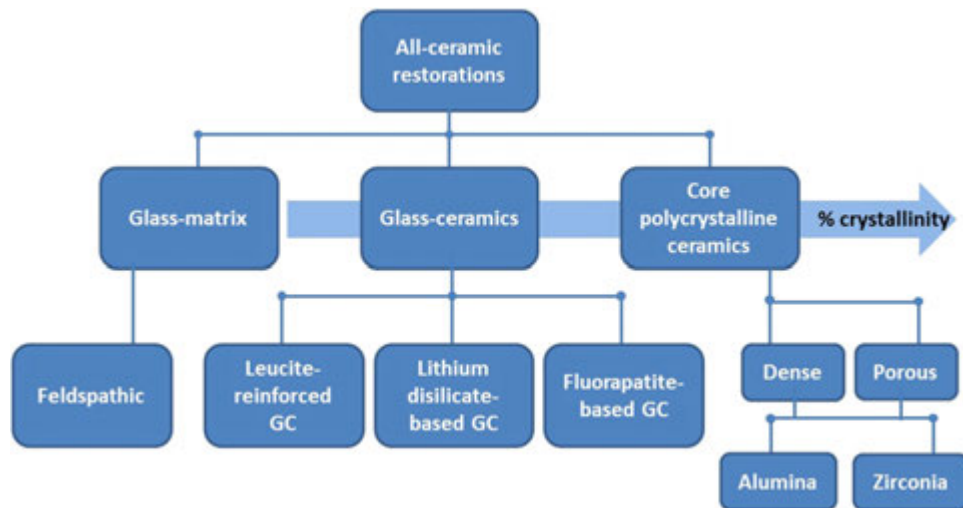


Fig. 2 Classification of all-ceramic materials for dental restoration. Adapted from Ho, G.W., Matinlinna, J.P., 2011. Insights on ceramics as dental materials. Part I: Ceramic material types in dentistry. *Silicon* 3, 109–115.

All-Ceramic Dental Materials: State of the Art

According to the classification proposed in [Fig. 2](#), all-ceramic restorations can be distinguished into glass-matrix, glass-ceramics and polycrystalline ceramics, where not only the chemical composition but also the degree of crystallinity and the particle size can affect both the biomechanical properties and esthetics. In fact, highly esthetic ceramics contain a significant amount of glassy phase, but their strength is much lower than polycrystalline materials ([Kelly and Denry, 2008](#)).

The most traditional all-ceramic restorative material is the feldspathic one, which basically contain silica glassy phase (silica or silicate ≥ 15 wt%) ([Ho and Matinlinna, 2011](#)) and is commonly known as “porcelain”, which is referred to a mixture of quartz, kaolin and feldspar in a specific compositional range ([Babu et al., 2015](#)). All three components play specific roles: kaolin acts as a binder between the ceramics particles, but – due to its opaque appearance, its content in the mixture should be limited ($< 4\%$) ([Ho and Matinlinna, 2011](#)). Feldspar provides most of the glassy phase, while quartz acts as a reinforcement, since its structure does not change during the sintering process. Besides high chemical resistance and biocompatibility, the major advantage of this type of material is the very pleasing esthetics, since color and shade match those of natural dental tissue, and make it fine for veneers and inlays/onlays ([Ho and Matinlinna, 2011](#)).

Glass-ceramics or particle-filled glasses differ from traditional feldspathic materials due to higher degree of crystallinity, which improve their mechanical properties. During firing, a progressive crystallization occurs, thus leading to a material with 50 up to near 100% crystalline phase, with the remaining amorphous phase filling the porosity, and contributing to increase the density. Current glass-ceramic dental materials include three main compositions: leucite-reinforced glass-ceramics, lithium disilicates and fluorapatite-based ceramics ([Gracis et al., 2015](#)). The main advantages of the first two compositions rely on the higher mechanical properties as compared to porcelain, which widen their application to anterior/posterior teeth, crowns, all-ceramic bridges ([Ho and Matinlinna, 2011](#)). In particular way, leucite-based ceramic is characterized by flexural strength of about 120 MPa and fracture toughness of $1.6\text{--}1.8\text{ MPa}\sqrt{\text{m}}$, while lithium disilicate shows a flexural strength in the range 350–450 MPa and fracture toughness in the range $2.8\text{--}3.5\text{ MPa}\sqrt{\text{m}}$ ([Ho and Matinlinna, 2011](#)). Thanks to lithium-disilicate glass-ceramics, it is now possible to produce all-ceramic partial dentures made of three elements ([Kern et al., 2012](#)). Fluorapatite is mainly used for its chemical and structural similarity to hydroxyapatite, which provide excellent biocompatibility, besides a possible fluoride release ([Gineste et al., 1999](#)) able to stimulate new bone formation ([Rodríguez-Lorenzo and Gross, 2003](#)).

However, in spite the improvement in mechanical properties shown by the glass-ceramics, glass-containing dental materials still show poor strength in load-bearing conditions. For this reason, a different approach has been developed, in which such esthetic ceramics are used in combination with a stronger and tougher core, made of polycrystalline alumina or zirconia. In such a way, structural and optical properties are both achieved in dental restorations. Biomedical-grade alumina was introduced in the medical market (especially for orthopedics) starting from the 60's, due to its excellent biocompatibility, high hardness and wear resistance and good flexural strength (in the range 400–580 MPa) ([McEntire et al., 2015](#)). However, due to low fracture toughness ($3.3\text{--}4.2\text{ MPa}\sqrt{\text{m}}$) ([McEntire et al., 2015](#)) and poor reliability, alumina ceramics were progressively substituted by zirconia ceramics, characterized by an impressive flexural strength (700–1500 MPa, [McEntire et al., 2015](#)) and high/very high fracture toughness (in the range $4\text{--}20\text{ MPa}\sqrt{\text{m}}$, [McEntire et al., 2015](#)) as it will be deepened in Section “Monolithic Restorations: From Y-TZP to Innovative Zirconia-Based Compositions”. A different approach, but still dealing with polycrystalline core ceramics, consists on producing glass-infiltrated ceramics, still with the aim of further increasing the reliability of those dental materials. In this case, a porous core made by a polycrystalline ceramic is infiltrated by a proper glass, creating an interpenetrating structure and

providing an effective mechanism to limit crack propagation thanks to the glassy phase (Ho and Matinlinna, 2011). These ceramics are mainly used in substructures for anterior or posterior single crown and short span anterior partial dentures (Ho and Matinlinna, 2011).

In spite the several advances reached by dental ceramics over the years, the achievement of all the main requirements in a single material is still challenging. For this reason, new solutions are currently under development, and those related to all-ceramic materials and related technologies are briefly discussed in the following (Fornabaio *et al.*, 2017).

All-Ceramic Dental Materials: New Frontiers in Materials and Processing

Monolithic Restorations: From Y-TZP to Innovative Zirconia-Based Compositions

The development of layered ceramics, consisting on an esthetic ceramic applied on a polycrystalline core, presents a major issue related to chipping and delamination of the low-strength porcelain veneer as respect to the high-strength core (Silva *et al.*, 2017). The residual thermal stresses arising during cooling from high-temperature firing are the main reason for chipping and delamination phenomena (Al-Amleh *et al.*, 2014).

For this reason, monolithic restorations based on polycrystalline structural ceramics, like zirconia, were introduced (Malkondu *et al.*, 2016). The basic idea is to avoid veneering, since the monolithic material should provide both mechanical performance and esthetics. The best candidate ceramic material for this new approach is zirconia, ZrO_2 . As previously mentioned, zirconia is characterized by an exceptional flexural strength and fracture toughness, deserving the title of “ceramic steel” (Garvie *et al.*, 1975). The remarkable properties of this ceramic are mainly ascribable to the tetragonal-to-monoclinic (*t-to-m*) zirconia phase transformation. In fact, zirconia exists into three polymorphs: from room temperature to about 1170°C, the stable phase is the monoclinic one; the tetragonal structure exists between 1170°C and 2370°C, and the cubic phase above this last temperature and till the melting point (2680°C). Therefore, during cooling from the sintering temperature, a spontaneous *t-to-m* transformation occurs, which is accompanied by a significant volume expansion ($\sim 5\%$), thus leading to the failure of the ceramic pieces. In order to overcome such a problem, the high-temperature polymorphs of zirconia are stabilized by proper dopants, such as yttrium oxide (Scott, 1975). In such a way, during cooling, the high-temperature tetragonal phase can be retained at room temperature in a metastable state. Under an applied stress, metastable tetragonal grains can transform again to monoclinic ones: the consequent volume expansion gives rise to a compressive field exerted on the crack, hindering its propagation and avoiding the catastrophic failure of the ceramic. Such toughening transformation is the main mechanism responsible of the high strength and toughness of zirconia ceramics (Hannink *et al.*, 2000). Ytria-stabilized polycrystalline tetragonal zirconia (Y-TZP) started to be used as a biomedical material in the 90's, especially for orthopedic implants, to overcome the intrinsic brittleness of alumina ceramics and increase the reliability of biomedical ceramic devices (El-Ghani and Sherief, 2016). Only recently, monolithic Y-TZP was introduced in the dental market, its success again due to its outstanding mechanical properties. In spite characterized by high strength and hardness, recent investigations showed no serious damage by wear on the antagonist dental tissue (which could be either natural enamel or a ceramic material), or at least comparable to that induced by other more traditional restorative ceramics (Silva *et al.*, 2017).

Compared to the glass-based dental materials, the esthetics of polycrystalline Y-TZP is of lower quality. In order to achieve a higher translucency, the current strategies include increasing the zirconia purity and the fired density, decreasing the grain size and structural defects, or also increasing the amount of cubic zirconia. Lack of translucency in ceramics is mainly due to light scattering effects from grain boundaries and defects. Moreover, in not cubic structure, birefringence occurs, *i.e.*, the occurrence of different refractive indexes, depending to the crystallographic orientation. In order to minimize the birefringence, the grain size should be decreased below a critical value (Zhang, 2014). The addition of cubic zirconia, characterized by isotropic optical properties, is effective in increasing the translucency as well. Thanks to such strategies, it is possible now to use monolithic Y-TZP also in esthetic regions (Silva *et al.*, 2017).

However, a serious drawback affects Y-TZP materials, which is the so-called low temperature degradation (LTD), also known as *ageing* (Lughi and Sergo, 2010). When exposed to temperature body and in presence of moisture, a spontaneous *t-to-m* transformation could occur, even if not triggered by a propagating crack. Such uncontrolled transformation can lead to catastrophic effects, such as loss of strength, generation of micro-cracks or even to the failure of the device (Chevalier *et al.*, 2009). Although the LTD mechanisms are still not completely clear, the degradation mechanism seems to be favored by the presence of yttrium in the zirconia lattice (Bartolomé *et al.*, 2004) creating oxygen vacancies. In fact, in presence of moisture, OH^- groups can move from the surface to the bulk of the material through grain boundary diffusion, filling the oxygen vacancies of the zirconia lattice and destabilizing the metastable tetragonal phase (Lawson, 1995). LTD had a catastrophic effect on Y-TZP heads used in hip prostheses, leading to the premature failure of a consistent number of ceramic heads in a very short period of time (between 2000 and 2002), and causing the immediate withdrawn of zirconia balls from the orthopedic market (Lughi and Sergo, 2010). In the case of Y-TZP for monolithic restorations, the results concerning its ageing behavior are still controversial (Flinn *et al.*, 2017; Pereira *et al.*, 2016; Adabo *et al.*, 2015; Cattani-Lorente *et al.*, 2011) and deserve further investigations.

However, in order to limit or completely avoid this issue, current research is focusing on alternative zirconia dopants as well as to the development of innovative zirconia-based composites. As the undesired transformation is triggered by oxygen vacancies, the choice of alternative stabilizers, having a tetravalent cation, to substitute Zr^{4+} in the zirconia lattice is a proper strategy. Therefore,

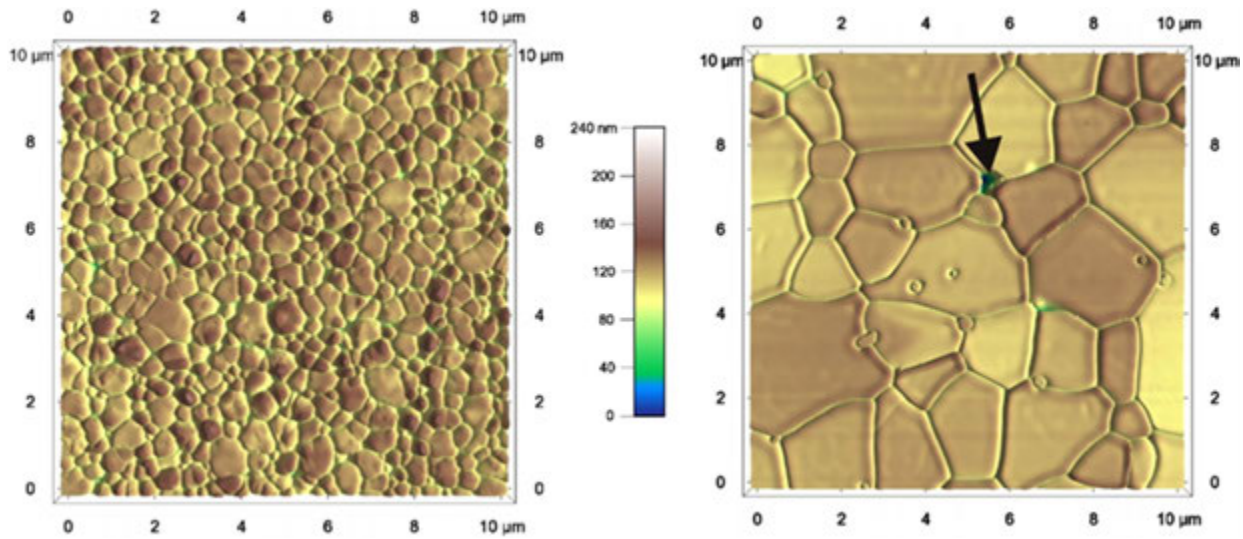


Fig. 3 Atomic Force Microscopy (AFM) images of the microstructures of 3Y-TZP (left) and 12Ce-TZP (right) after thermal etching. The arrow points to a location with a probable grain pull-out. Reprinted with permission from Kohorst, P., Borchers, L., Stempel, J., *et al.*, 2012. Low-temperature degradation of different zirconia ceramics for dental applications. *Acta Biomaterialia* 8, 1213–1220.

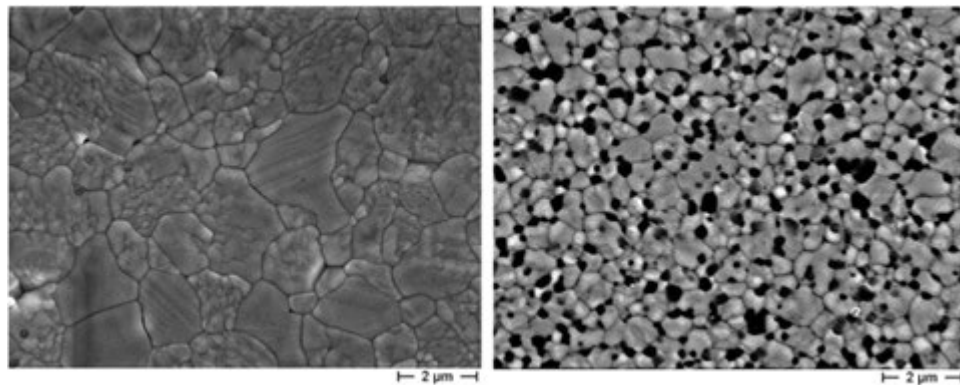


Fig. 4 Field emission scanning electron microscope (FESEM) microstructures of Ce-TZP (left) and Ce-TZP/16vol%Al₂O₃ composite (right), both sintered at 1450°C for 1 h.

most attention is now focused on the development of CeO₂-stabilized zirconia, referred to as Ce-TZP, in which CeO₂ is normally added in the 8–12 mol% range (Tsukuma and Shimada, 1985). The improved stability towards ageing of Ce-TZP compared to Y-TZP has been already demonstrated in literature (Deville *et al.*, 2005), showing safe conditions during clinical use.

The addition of CeO₂ to a zirconia lattice induces a significant grain growth, as shown in Fig. 3 which compares the sintered microstructures of Y-TZP and Ce-TZP materials (Kohorst *et al.*, 2012). We can observe that, under proper sintering conditions, it is possible to achieve fully dense and highly homogeneous materials. However, a significant difference in grain size characterizes these two materials, since Y-TZP is characterized by an average size of 500 nm, while Ce-TZP presents a micron-sized microstructure, whose average size is 1.8 μm (Kohorst *et al.*, 2012). Moreover, grains pull-out (black arrow in Fig. 3) and some residual porosity could be observed as well.

As expected, the coarsened microstructure in Ce-TZP leads to a decrease of mechanical properties as compared to Y-TZP. In fact, the former material was characterized by a flexural strength of 495 ± 11 MPa, the latter of 1740 ± 151 MPa. However, when exposed to ageing conditions (hydrothermal treatment, at 134°C and 3 bar), Y-TZP showed a progressive and significant decrease in strength by increasing the ageing time. On the opposite, no significant strength variation in Ce-TZP was detected (Kohorst *et al.*, 2012).

In order to increase the flexural strength, many papers underline the beneficial effect of adding second-phase particles, such as alumina (Ban *et al.*, 2008). Due to the pinning effect exerted by fine-grained and homogeneously distributed Al₂O₃ particles, it is possible to retain the zirconia grain growth during sintering, and to achieve a significantly finer microstructure. Fig. 4 compares the microstructures of pure Ce-TZP (left) and of the same material added with 16 vol% Al₂O₃ (right), both sintered under the same

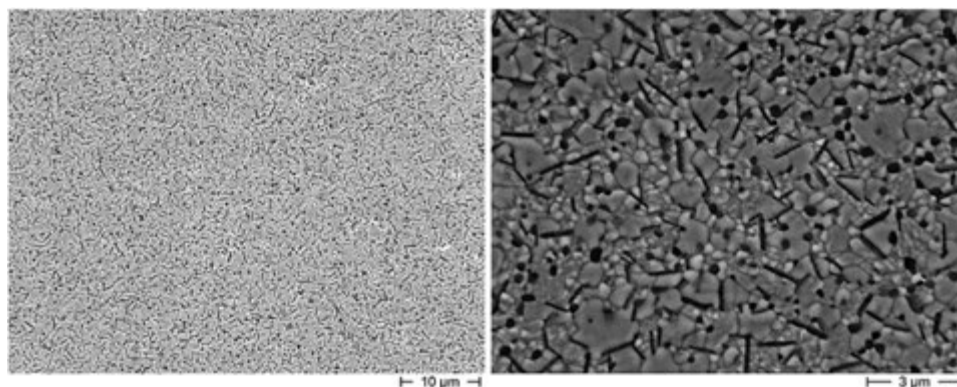


Fig. 5 Typical microstructure of a triphasic composite having composition Ce-TZP/16vol%Al₂O₃/16vol%SrAl₁₂O₁₉, developed by the authors and co-workers. The high density and microstructural homogeneity of phase distribution is evident in the lower-magnification image (left), while the powder morphology is evidenced in the higher-magnification image (right).

conditions (1450°C/1 h). We can observe the key role exerted by the fine-grained and homogeneously distributed Al₂O₃ particles in providing an effective retention of the zirconia grain size (Fornabaio *et al.*, 2015). Besides refining the microstructure, the addition of the hard and stiff alumina phase induces an overall enhancement of Ce-TZP mechanical properties, especially the flexural strength and the hardness. On the other hand, the *t*-to-*m* toughening transformation is hindered, leading to a decrease of the composite fracture toughness as compared to pure Ce-TZP.

For this reason, the last generation of tough and strong zirconia-based ceramics are designed as multi-phase composites, where besides Al₂O₃, a further second-phase is added, characterized by elongated or rod-like morphology, and able to further increase the material fracture toughness by additional crack deflection and crack bridging mechanisms (Cutler *et al.*, 1994; Miura *et al.*, 1994; Palmero *et al.*, 2015; Apel *et al.*, 2012; Kern, 2014). As a consequence, strong, tough and stable zirconia materials can be successfully obtained. In this field, a key role is played by the manufacturing, since in order to achieve fine and controlled microstructures in such complex composites, all processing steps – from powder synthesis to final sintering, have to be properly controlled (Palmero *et al.*, 2011, 2014). In Reveron *et al.* (2017) the fine tuning of the ceria content inside the zirconia matrix and the fine microstructural refinement achieved thanks to the addition of two kinds of second-phases, fine and rounded Al₂O₃ particles and elongated SrAl₁₂O₁₉, allowed to achieve outstanding mechanical properties. In Fig. 5, a typical microstructure of this triphasic materials, developed by the Author and co-workers in the frame of Longlife European Project “Advanced multifunctional zirconia ceramics for long-lasting implants”, grant agreement no 280741, is depicted. In the lower magnification image (left), it is possible to observe the fully dense and highly homogeneous microstructure obtained, with a perfect distribution of the all the phases in the composite materials. In the higher magnification image (right), it is possible to appreciate the different morphologies which characterize this composite materials, with both fine-grained round Al₂O₃ particles and rod-like SrAl₁₂O₁₉ particles, both homogeneously embedded in a fine-grained CE-TZP matrix.

In fact, the material was characterized by very high flexural strength (> 1 GPa) and fracture toughness (> 10 MPa√m), besides high stability against ageing. Even more, due to transformation toughening, the material showed a certain plasticity before failure. Such metal-like behavior was responsible of the exceptional Weibull modulus ($m \cong 60$) which characterized this material. High mechanical performance, *in vivo* stability and reliability make this innovative composite suitable for biomedical applications, in particular way in dental restoration. However, Ce-TZP does not present translucency and the presence of ceria imparts a certain yellowish coloration, making this solution at the moment suitable only for implants and for restorations for non-esthetic regions.

Functionally Graded Ceramics

In search of proper esthetics besides good mechanical properties, a new strategy implies the development of functionally graded materials (FGM), which can be considered an evolution of layered ceramics and glass-infiltrated ceramics (Zhang *et al.*, 2010, 2012). The concept behind FGM is to provide a gradual change in the structure or in the compositions, and thus in the material functionality. In order to join mechanical performance and esthetics, Zhang and Kim (2009) developed an Y-TZP/glass graded structure. The glass composition was designed in order to match the coefficient of thermal expansion (CTE) of Y-TZP. In particular way, it consisted on a silica-alumina glass containing K, Na, Ca and Tb oxides in proper concentration. To produce the graded structure, Y-TZP was pre-sintered in order to create a porous template for the glass. The top and bottom surfaces of the porous pellet were covered with powdered glass, and the system was heated at 1450°C/2 h, in order to have infiltration and densification at the same time. The process succeeded in the development of the desired graded structure, as shown in Fig. 6: on both surfaces a residual glass layer was detected (a), while moving toward the inner part a compositional gradation was observed, with a progressive decrease of the glassy phase and an increase in the zirconia amount, up to the achievement of a dense Y-TZP core (b). No phase transformation was observed after infiltration and sintering: in fact, tetragonal zirconia was the only crystalline phase detected in the final material. As a consequence of composition gradual change, a progressive variation of mechanical properties

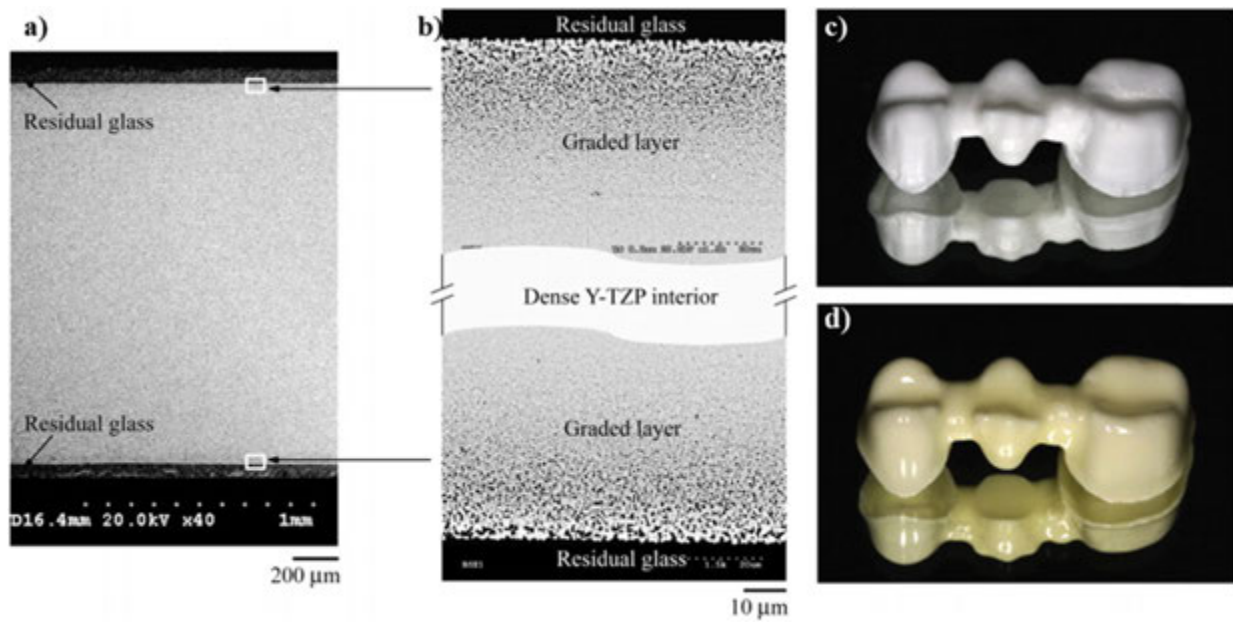


Fig. 6 Scanning electron microscope (SEM) images showing cross-section (polished) glass-infiltrated Y-TZP materials, after sintering at $1450^{\circ}\text{C}/2\text{ h}$. (a) Low magnification image showing the presence of residual glass layer ($\sim 50\text{ }\mu\text{m}$ thick) at both the top and bottom surfaces. (b) Higher magnification image of the inserts (white boxes) of (a), still showing the outer surface residual glass layer (black), which gradually decrease in the graded glass-zirconia layer, and the dense Y-TZP core. Digital photographs showing veneering surfaces of a “traditional” (c) and glass-infiltrated (d) three-unit Y-TZP framework, both sintered at $1450^{\circ}\text{C}/2\text{ h}$. Reprinted with permission from Zhang, Y., Kim, J.-W., 2009. Graded structures for damage resistant and aesthetic all-ceramic restorations. *Dental Materials* 25, 781–790.

was achieved as well: in particular way, both the elastic modulus and the hardness showed the lowest values in correspondence to the external residual glass. However, by moving from the surface towards the inner core, both increased in a progressive way. In the core, the elastic modulus and hardness were 3.5 and 2.1 times those of the glassy phase. The digital photographs in Fig. 5 show the appearance of glass-infiltrated (c) and monolithic (d) Y-TZP materials, both sintered at $1450^{\circ}\text{C}/2\text{ h}$. In the former case, we can observe that the material is characterized by proper optical properties, in term of translucency and shade, while the un-filtrated material shows a white and completely opaque appearance.

The FGM approach was also exploited by Fabris *et al.* (2017) to overcome the issue related to the generation of thermal residual stresses generated within layered dental ceramics. In the traditional technology, the external glassy veneer is directly fired onto the polycrystalline core, at high temperature. During cooling, significant thermal residual stresses are created, due to the CTE mismatch between the core and the external layer. In addition, the differences in elastic modulus between the same two layers can lead to stress generation during the masticatory activity, thus creating microcracks. Such issues are the major responsible of catastrophic failure of dental ceramics, as well of chipping of the veneer layer (Fabris *et al.*, 2017). Through mathematic models, the residual stresses in three different structures were calculated. The first was a traditional bilayer structure (glass veneer – polycrystalline ceramic core); the second was a trilayer structure, with an additional layer between veneer and core having an intermediate composition; the last one was a FGM in which a graded interlayer was considered between veneer and core. As expected, the bilayer system was characterized by the highest thermal residual stress, while both multilayer structures showed significantly lower stress.

FGM seems to be an effective strategy to avoid delamination and fracture of the layered ceramics, and to improve their overall mechanical properties and esthetics. Besides simulations (Fabris *et al.*, 2017) and laboratory-scale developments, efforts are in course to bring this technology to the market. An example is provided by Abu Kasim *et al.* (2013) who patented three types of multilayered composite materials based on zirconia, alumina, hydroxyapatite and titanium, to develop newly designed functionally graded dental posts.

Le Ferrand *et al.* (2015) proposed a very innovative method to develop functionally graded materials, characterized by a complex architecture, able to better mimic the natural living tissues. The method is based on magnetically assisted slip casting. As in traditional slip casting, a ceramic suspension is poured into a porous gypsum mold of a pre-defined and even complex geometry. Thanks to capillary forces, the liquid is extracted by the porous mold, and a cake is formed at its surface. By progressively changing the composition of the ceramic slurry cast into the gypsum mold, it is possible to achieve a compositional gradation. Even more, in this work, the ceramic slurry was added with alumina platelets, previously functionalized by paramagnetic Fe_3O_4 nanoparticles. Thanks to the application of a magnetic field during the slip casting process, it was possible to orient the platelets, and achieve the desired textured microstructure. This approach has been applied by the authors to mimic the structure of a human molar. For the dentin tissue, the suspension was made by a mixture of isotropic alumina particles and functionalized alumina

platelets; for the enamel, the isotropic alumina particles were partially replaced by silica particles. In such a way, during sintering, silica particles generated a glassy phase which filled the residual porosity in the alumina structure, and provided a denser and harder external layer. In addition, by applying a proper magnetic field, it was possible to orient the alumina platelets, and precisely with a perpendicular orientation to the external surface in the enamel-like layer, and parallel to the same surface in the dentin-like layer.

Innovative Manufacturing

The use of CAD-CAM (computer-aided design/computer-aided manufacturing) systems in the dental market is now a well consolidated process. It is a kind of subtractive process, in which material is progressively removed from a blank or a green part, according to a defined design. Its success is mainly due to the fact that the process is less time-consuming as respect to traditional manufacturing methods: with CAD-CAM process, in fact, it is possible to use high-speed grinding to shape dental crowns. Moreover, it allows a perfect design of the digital dental restoration, characterized by accuracy and precision and customized on the patient's clinical requirement. Still important, prediction of the final outcome is possible as well. In spite of being used for almost 30 years, a continuous evolution of the process and systems occurs, in terms of both equipment and processable materials, moving from traditional porcelain to esthetic ceramics, polycrystalline ceramics and composites (Silva *et al.*, 2017). The major drawback of this manufacturing method is the huge amount of waste produced, which could reach 90% of the prefabricated block (Silva *et al.*, 2017). Therefore, alternative processing methods have been developed, to provide a more efficient and sustainable production of dental restorations. In particular way, new additive methods have been developed and some of them adapted to the dental materials manufacturing. In spite of different 3D printing processes are nowadays available on the market, few technology allows the fabrication of all-ceramic materials, and precisely inkjet printing (also known as robocasting) and stereolithography.

An example is provided by the work of Ebert *et al.* (2009) who used direct inkjet printing to develop zirconia dental materials. The ink was prepared starting from a boehmite sol, to which zirconia nanoparticles were added, besides dispersants. The slurry was used to fill the standard cartridge of a modified commercial printer and to develop the 3D structure through layer by layer processing. The printed material was dried and further sintered at 1450°C/2.5 h, resulting in a high final density (96.9% of the theoretical density) and a quite homogeneous microstructure. Flexural strength and fracture toughness were 763 MPa and 6.7 MPa√m, respectively, while the Weibull modulus was 3.5. The low reliability of the developed parts was mainly imputed to the presence of large defects induced during the printing process.

In stereolithography process, a ceramic powder (up to 50 vol%) is mixed with a low-viscosity UV-curable monomer, to get the feedstock paste. During the process, reticulation of the polymer occurs, thus allowing to build 3D structures made of "green" ceramic layers. A proper thermal debinding is then required to remove the organic fraction, followed by high-temperature sintering to consolidate the ceramic structure (Lian *et al.*, 2018). By exploiting this technology, Dehurtevent *et al.* (2017) developed alumina dental ceramics, by investigating the role of the Al₂O₃ particle size (either sub-micrometric and micrometric) and solid loading in the monomer. The best results were achieved by using the larger-size particles, at the highest solid loading, yielding density and flexural strength comparable to materials obtained by traditional subtractive method. Digital images of the dental materials produced are presented in Fig. 7. In spite of the results achieved suggest that stereolithography could be an evaluable alternative the

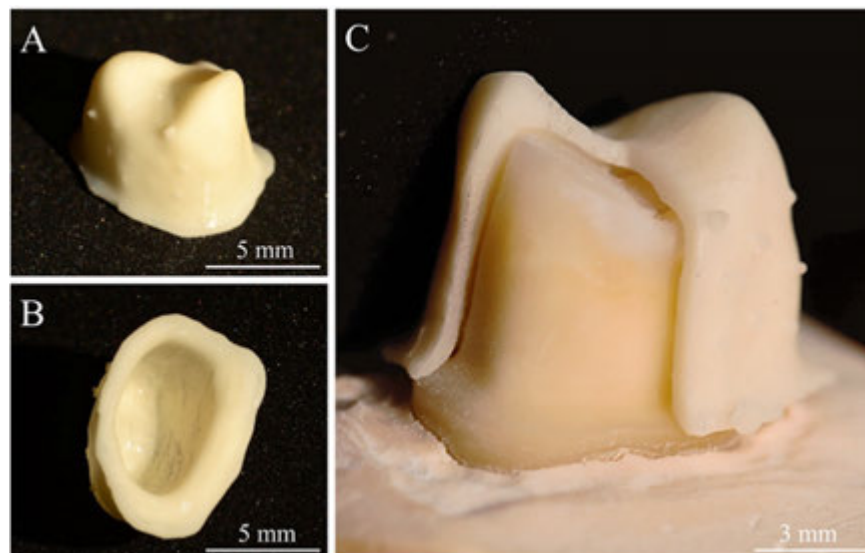


Fig. 7 Digital images of stereolithography-manufactured alumina dental crown framework: external (A) and internal (B) views. Crown framework in place on an all-ceramic crown preparation (C). Reprinted from Dehurtevent, M., Robberecht, L., Hornez, J.-C., *et al.*, 2017. Stereolithography: A new method for processing dental ceramics by additive computer-aided manufacturing. *Dental Materials* 33, 477–485, with permission.

standard procedures, the authors underlined the need of more studies on the subject. The major drawback consists on the significant shrinkage experienced by the materials during debinding and sintering. Moreover, the authors observed a not-isotropic shrinkage, unlike subtractive-processed materials. Such anisotropy, besides the presence of residual uncured monomers and unsuitable curing strategies, may induce distortion's and cracks in the pieces, particularly when complex-shapes have to be processed.

Conclusions and Perspectives

The use of ceramics in the dental market is continuously increasing, as they outperform other class of materials mainly in terms of biocompatibility, chemical stability and key mechanical properties such as hardness and wear resistance. However, challenges remain in the development of all-ceramic dental restoration which could satisfy both mechanical performance and esthetics in long-lasting solutions. In fact, the traditional approach of applying an esthetic, predominantly glassy layer (the so-called veneer) on the surface of a polycrystalline structural ceramic show chipping and delamination and major drawbacks. For this reason, new solutions, materials and technology are currently under development. The directions for current and future research are depicted in this contributions, still restricting the discussion to all-ceramics solutions.

In this frame, two main strategies are being followed. The former approach focuses on the design and development of innovative compositions for all-ceramic monolithic restorations. Here in fact, most attention is nowadays focused on monolithic yttria-stabilized zirconia, which presents exceptional flexural strength, high fracture toughness and good esthetics, therefore suitable for implants and prosthesis in the posterior part of the mouth, subjected to the highest stresses. However, the risk of *in-vivo* degradation is leading the research to find innovative solutions, in terms of zirconia dopants, second-phases, and manufacturing methods able to provide reliable and long-lasting ceramics. The second approach, which intends to mimic the natural dental tissue architecture, focuses on the design and development of functionally graded ceramics. This approach is being exploited with the main purpose of producing a glass-ceramic compositionally graded structure, to avoid neat interfaces between the veneer and ceramic core, and therefore limit chipping and delimitation issues.

Furthermore, some very recent papers demonstrate the feasibility of using additive manufacturing techniques as possible alternative to subtractive methods, such the CAD-CAM based standard process. If successful, these methods could lead to higher productivity and lower waste, as well as the possibility to manufacture complex-shape bridges or other dental components, which are currently difficult to produce with other techniques.

References

- Abu Kasim, N.H., Madfa, A.A., Abd Shukor, M.H., *et al.*, 2013. Metal-Ceramic Dental Post. Patent no. WO2013043039 (A2).
- Adabo, G.L., Mariscal, E.M., Hatanaka, G.R., 2015. Flexural strength and microstructure of anterior/monolithic zirconia after low-temperature aging. *Dental Materials* 31, 48–49.
- Al-Amleh, B., Waddell, J.N., Lyons, K., Swain, M.V., 2014. Influence of veneering porcelain thickness and cooling rate on residual stresses in zirconia molar crowns. *Dental Materials* 30, 271–280.
- Apel, E., Ritzberger, C., Courtois, N., *et al.*, 2012. Introduction to a tough, strong and stable Ce-TZP/MgAl₂O₄ composite for biomedical applications. *Journal of the European Ceramic Society* 32, 2697–2703.
- Babu, P.J., Alla, R.K., Alluri, V.R., Datla, S.R., Konakanchi, A., 2015. Dental ceramics: Part I – An overview of composition, structure and properties. *American Journal of Materials Engineering and Technology* 3, 13–18.
- Ban, S., Sato, H., Suehiro, Y., Nakanishi, H., Nawa, M., 2008. Biaxial flexure strength and low temperature degradation of Ce-TZP/Al₂O₃ nanocomposite and Y-TZP as dental restoratives. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 87, 492–498.
- Bartolomé, J.F., Montero, I., Díaz, M., *et al.*, 2004. Accelerated aging in 3–mol%-yttria stabilized tetragonal zirconia ceramics sintered in reducing conditions. *Journal of the American Ceramic Society* 87, 2282–2285.
- Cattani-Lorente, M., Scherrer, S.S., Ammann, P., Jobin, M., Wiskott, H.W.A., 2011. Low temperature degradation of a Y-TZP dental ceramic. *Acta Biomaterialia* 7, 858–865.
- Chan, Y.L., Ngan, A.H.W., King, N.M., 2011. Nano-scale structure and mechanical properties of the human dentine-enamel junction. *Journal of the Mechanical Behavior of Biomedical Materials* 4, 785–795.
- Chevalier, J., Gremillard, L., Virkar, A.V., Clarke, D.R., 2009. The tetragonal-monoclinic transformation in zirconia: Lessons learned and future trends. *Journal of the American Ceramic Society* 92, 1901–1920.
- Cutler, R.A., Lindemann, J.M., Ulvensøen, J.H., Lange, H.I., 1994. Damage-resistant SrO-doped Ce-TZP/Al₂O₃ composites. *Materials Design* 15, 123–133.
- Cuy, J.L., Mann, A.B., Livi, K.J., Teaford, M.F., Weihs, T.P., 2002. Nanoindentation mapping of the mechanical properties of human molar tooth enamel. *Archives of Oral Biology* 47, 281–291.
- De Souza Costa, C.A., Heblinh, J., L.S. Scheffel, D., *et al.*, 2014. Methods to evaluate and strategies to improve the biocompatibility of dental materials and operative techniques. *Dental Materials* 30, 769–784.
- Dehurtevent, M., Robberecht, L., Hornez, J.-C., *et al.*, 2017. Stereolithography: A new method for processing dental ceramics by additive computer-aided manufacturing. *Dental Materials* 33, 477–485.
- Déville, S., El Attaoui, H., Chevalier, J., 2005. Atomic force microscopy of transformation toughening in ceria-stabilized zirconia. *Journal of the European Ceramic Society* 25, 3089–3096.
- Ebert, J., Özkol, E., Zeichner, A., *et al.*, 2009. Direct inkjet printing of dental prostheses made of zirconia. *Journal of Dental Research* 88, 673–676.
- El-Ghani, O.S.A., Sherief, A.H., 2016. Zirconia based ceramics, some clinical and biological aspects: review. *Future Dental Journal* 2, 55–64.
- Fabris, D., Souza, J.C.M., Silva, F.S., *et al.*, 2017. Thermal residual stresses in bilayered, trilayered and graded dental ceramics. *Ceramics International* 43, 3670–3678.
- Flinn, B.D., Raigrodski, A.J., Mancil, L.A., Toivola, R., Kuykendall, T., 2017. Influence of aging on flexural strength of translucent zirconia for monolithic restorations. *Journal of Prosthetic Dentistry* 117, 302–309.

- Fornabaio, M., Palmero, P., Traverso, R., *et al.*, 2015. Zirconia-based composites for biomedical applications: Role of second phases on composition, microstructure and zirconia transformability. *Journal of the European Ceramic Society* 34, 4039–4049.
- Fornabaio, M., Reveron, H., Adolfsson, E., *et al.*, 2017. Design and development of dental ceramics: Examples of current innovations and future concepts. In: Palmero, P., Cambier, F., De Barra, E. (Eds.), *Advances in Ceramic Biomaterials: Materials, Devices and Challenges*, Woodhead Publishing 1st ed. pp. 355–389.
- Garvie, R.C., Hannink, R.H., Pascoe, R.T., 1975. Ceramic steel? *Nature* 258, 703–704.
- Gineste, L., Gineste, M., Ranz, X., *et al.*, 1999. Degradation of hydroxylapatite, fluorapatite, and fluorhydroxyapatite coatings of dental implants in dogs. *Journal of Biomedical Materials Research* 48, 224–234.
- Goldberg, M., Kulkarni, A.B., Young, M., Boskey, A., 2012. Dentin: Structure, composition and mineralization: The role of dentin ECM in dentin formation and mineralization. *Frontiers in Bioscience* 3, 711–735.
- Gracis, S., Thompson, V.P., Ferencz, J.L., Silva, N.R., Bonfante, E.A., 2015. A new classification system for all-ceramic and ceramic-like restorative materials. *International Journal of Prosthodontics* 28, 227–235.
- Halgas, R., Dusza, J., Kaiferova, J., Kovacsova, L., Markovska, N., 2013. Nanoindentation testing of human enamel and dentin. *Ceramics – Silikáty* 57, 92–99.
- Hannink, R.H.J., Kelly, P.M., Muddle, B.C., 2000. Transformation toughening in zirconia-containing ceramics. *Journal of the American Ceramic Society* 83, 461–487.
- Ho, G.W., Matinlinna, J.P., 2011. Insights on ceramics as dental materials. Part I: Ceramic material types in dentistry. *Silicon* 3, 109–115.
- Imbeni, V., Kruzic, J.J., Marshall, G.W., Marshall, S.J., Ritchie, R.O., 2005. The dentin-enamel junction and the fracture of human teeth. *Nature Materials* 4, 229–232.
- Kelly, J.R., Denry, I., 2008. Stabilized zirconia as structural ceramic: An overview. *Dental Materials* 24, 289–298.
- Kern, F., 2014. A comparison of microstructure and mechanical properties of 12Ce-TZP reinforced with alumina and in situ formed strontium- or lanthanum hexaaluminate precipitates. *Journal of the European Ceramic Society* 34, 413–423.
- Kern, M., Sasse, M., Wolfart, S., 2012. Ten-year outcome of three-unit fixed dental prostheses made from monolithic lithium disilicate ceramic. *Journal of the American Dental Association* 43, 234–240.
- Kim, J.H., Kim, K.-B., Kim, W.-C., Kim, H.-Y., Kim, J.H., 2014. Evaluation of the color reproducibility of all-ceramic restorations fabricated by the digital veneering method. *Journal of Advanced Prosthodontics* 6, 71–78.
- Kohorst, P., Borchers, L., Stempel, J., *et al.*, 2012. Low-temperature degradation of different zirconia ceramics for dental applications. *Acta Biomaterialia* 8, 1213–1220.
- Lawson, S., 1995. Environmental degradation of zirconia ceramics. *Journal of the European Ceramic Society* 15, 485–502.
- Le Ferrand, H., Bouville, F., Niebel, T.P., Studard, A.R., 2015. Magnetically assisted slip casting of bioinspired heterogeneous composites. *Nature Materials* 14, 1172–1181.
- Lian, Q., Sui, W., Wu, X., Yang, F., Yang, S., 2018. Additive manufacturing of ZrO₂ ceramic dental bridges by stereolithography. *Rapid Prototyping Journal* 24, 114–119.
- Lu, C., Nakamura, T., Kroach, C.S., 2012. Effective property of tooth enamel: Monoclinic behaviour. *Journal of Biomechanics* 45, 1437–1443.
- Lughi, V., Sergio, V., 2010. Low temperature degradation –aging– of zirconia: A critical review of the relevant aspects in dentistry. *Dental Materials* 26, 807–820.
- Malkond, O., Tinastepe, N., Akan, E., Kazazoglu, E., 2016. An overview of monolithic zirconia in dentistry. *Biotechnology & Biotechnological Equipment* 30, 644–652.
- McEntire, B.J., Bal, B.S., Rahaman, M.N., Chevalier, J., Pezzotti, G., 2015. Ceramics and ceramic coatings in orthopaedics. *Journal of the European Ceramic Society* 35, 4327–4369.
- McKittrick, J., Chen, P.-Y., Tomblato, L., *et al.*, 2010. Energy absorbent natural materials and bioinspired design strategies: A review. *Materials Science and Engineering C* 30, 331–342.
- Miura, M., Hongoh, H., Yogo, T., Hirano, S., Fujii, T., 1994. Formation of plate-like lanthanum- β -aluminate crystal in Ce-TZP matrix. *Journal of Materials Science* 29, 262–268.
- Palmero, P., Fornabaio, M., Montanaro, L., *et al.*, 2015. Towards long lasting zirconia-based composites for dental implants. Part I: Innovative synthesis, microstructural characterization and in vitro stability. *Biomaterials* 50, 38–46.
- Palmero, P., Naglieri, V., Spina, G., Lombardi, M., 2011. Microstructural design and elaboration of multiphase ultra-fine ceramics. *Ceramics International* 37, 139–144.
- Palmero, P., Montanaro, L., Reveron, H., Chevalier, J., 2014. Surface coating of oxide powders: A new synthesis method to process biomedical grade nano-composites. *Materials* 7, 5012–5037.
- Pereira, G., Silvestri, T., Camargo, R., *et al.*, 2016. Mechanical behavior of a Y-TZP ceramic for monolithic restorations: Effect of grinding and low-temperature aging. *Materials Science and Engineering C* 63, 70–77.
- Reveron, H., Fornabaio, M., Palmero, P., *et al.*, 2017. Towards long lasting zirconia-based composites for dental implants: Transformation induced plasticity and its consequence on ceramic reliability. *Acta Biomaterialia* 48, 423–432.
- Rodríguez-Lorenzo, L.M., Gross, K.A., 2003. Encapsulation of apatite particles for improvement in bone regeneration. *Journal of Materials Science: Materials in Medicine* 14, 939–943.
- Scott, H.G., 1975. Phase relationships in the zirconia-yttria system. *Journal of Materials Science* 10, 1527–1535.
- Silva, L.H.D., Lima, E., Miranda, R.B.P., *et al.*, 2017. Dental ceramics: A review of new materials and processing methods. *Brazilian Oral Research* 31, 133–146.
- Tsukuma, K., Shimada, M., 1985. Strength, fracture toughness and Vickers hardness of CeO₂-stabilized tetragonal ZrO₂ polycrystals (Ce-TZP). *Journal of Materials Science* 20, 1178–1184.
- Zhang, Y., 2014. Making yttria-stabilized tetragonal zirconia translucent. *Dental Materials* 30, 1195–1203.
- Zhang, Y., Kim, J.-W., 2009. Graded structures for damage resistant and aesthetic all-ceramic restorations. *Dental Materials* 25, 781–790.
- Zhang, Y., Chai, H., Lawn, B.R., 2010. Graded structures for all-ceramic restorations. *Journal of Dental Research* 89, 417–421.
- Zhang, Y., Sun, M.-J., Zhang, D., 2012. Designing functionally graded materials with superior load-bearing properties. *Acta Biomaterialia* 8, 1101–1108.

Oxide Ceramics for Biomedical Applications

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Introduction

The biomedical applications of oxide ceramics today are related to two main field:

- (1) Orthopedic joint replacements, where oxide ceramics are used for the manufacture of components of the bearing, i.e., ball heads and inserts for hip replacements, femoral (condylar) component for knee replacements, glenoid head in shoulder replacements, etc.
- (2) Dentistry, where oxides are used in dental implants either in the production of crown, bridges and fixed partial dentures obtained by CAD/CAM from ceramic blanks.

The use of oxide ceramics in orthopedic joint replacements for several peculiar characteristics of these materials that can be summarized as follows:

- (1) Biological safety of the material, of its debris and of its degradation products, if any;
- (2) Chemical stability in the long term: absence of corrosion/ion release;
- (3) Suitability of the mechanical properties to assure the component expected behavior;
- (4) Physical stability: very low wear, absence of swelling, stiffness under load;
- (5) High surface finish achievable;
- (6) Scratching resistant surface;
- (7) Suitability for the geometrical design of the components;
- (8) Workability by common mechanical tooling;
- (9) Contained production costs.

The oxide ceramics in use today in joint replacements are aluminum oxide (alumina, α -Al₂O₃, corundum), alumina matrix composites (AMCs) and stabilized zirconium dioxide (zirconia, YTZP). So far, alumina has been replaced progressively by alumina-zirconia composites in orthopedics because of the better mechanical behavior of these ceramics that allow higher flexibility in device design joined to higher reliability of ceramic components, while zirconia (YTZP) and alumina-toughened zirconia (ATZ) are today the oxide of reference in dentistry.

Alumina was the first oxide introduced in clinical use. In orthopedics, it became the “ceramic” and in scientific papers the use of the term “ceramic” without any other specification to indicate alumina is accepted. Nevertheless, this may result confusing because of the many ceramics that are, have been used in clinics or are under development for use in joint replacements besides alumina (e.g., Y-TZP, Mg-PSZ, Si₃N₄, ZTA, ATZ, etc).

A few number companies are manufacturing ball heads for THRs worldwide. While some of them are among the pioneers in this field and operate in the orthopedics market since a long, other are newcomers attracted by the growing diffusion of ceramics in arthroplasty. The Medical Products Division of CeramTec GmbH (Plochingen, Germany) deliver about 80% of the worldwide demand. For a detailed description, the reader may refer to a former work of the senior author (Piconi, 2017).

Although the main use of oxide ceramics is in components of joint replacement bearings, new applications are emerging in dentistry (Piconi *et al.*, 2008, 2014; Piconi and Sprio, 2018). In dentistry, zirconia (Y-TZP) is today the oxide ceramic of reference for the production of load bearing devices.

The Development of Oxide Ceramics in Biomedical Applications

It is known that the first patent on the use of an oxide ceramic (alumina) as a biomaterial is made in a 1932 patent by Rock (1933), but it had no practical consequences. In the early times, the development of oxide ceramics in biomedical applications had as reference bone substitutes, but since the studies of Boutin *et al.*, it was targeted on the components of bearings for Total Hip Replacements (THRs).

First clinical use of alumina was in Cerosium, a material developed by Smith in the USA. It was a porous (65 vol%) aluminosilicate loaded by epoxy resin, intended to be implanted to replace large defects on the long bones (Smith, 1992).

However, the real start took place about the mid-1960, when the company Degussa GmbH (Düsseldorf, Germany) introduced into the market its powder Degussit Al23, the first high-purity, high-alumina ceramic precursor that allowed obtaining ceramic parts suitable for medical applications within the human body by high temperature sintering.

Using Degussit Al23 Sandhaus, a Swiss dentist, developed its CBS dental implant, a device that had pretty good clinical outcomes (Sandhaus, 1969). It can be hypothesized that information about this device stimulated the interest of Dr. Pierre Boutin, an orthopedic surgeon with practice in Pau, France. With the help of one of his patient who was a top manager in a ceramic workshop nearby Dr. Boutin developed in 1970 the first ceramic-ceramic bearing for Total Hip Replacement (THR) (Boutin, 1972).

Shortly after, researchers in Keramishe Werk Hermsdorf (KWH, Hermsdorf, Germany) launched the development of alumina unicompartimental tibial plateau replacements (Glien, 1980). These devices that are the first ceramic devices used in the knee joint, were implanted by prof. Langer in Jena (Langer and Blumentritt, 1987; Langer, 2002). In the same years, prof. Hironobu Oonishi, a pioneer in the development of ceramic devices, launched the development of the first Total Knee Replacement (TKR). This device (the so-called KOM-1) – made by the company Kyocera (Kyoto, Japan) – were formed by an alumina femoral component articulating on a polyethylene insert hosted on an alumina tibial plateau, and were implanted cementless in 134 patients. (Oonishi, 1990, 2006) Kyocera developed also unicompartimental knee replacements that showed high success rate at controls made at an average 42 months after surgery (24–68 months) (Atsui *et al.*, 1997).

Since then several other TKR design based on alumina were developed in Japan, such as the Low Friction Anatomical (LFA-1), the Yokohama Medical Ceramic Knee (YMCK), the Bisurface knee replacement, and the Kyoto Ceramics-1 (KC-1). (Solarino *et al.*, 2017).

There were several failure in the first series of Boutin's implants. In these devices both the alumina cup, both the metallic stem were fixed to the host bone by cement, while the ceramic ball head was fixed by epoxy glue to a cylindrical trunnion at the extremity of the stem. Both the bone cementation both the glue degradation were at the origin of the failures.

The research program launched in Germany to develop alumina ceramic components for THR applications had as reference two key concepts:

- (1) To achieve direct-to-bone fixation both of the cup and the stem (although some version of the implants were designed for cement fixation too);
- (2) To connect the ceramic head to the stem by a Morse-like taper connection.

Especially relevant is the introduction of the Morse Taper connection, which marked a milestone in arthroplasty, opening the way to modularity in joint replacements (Hernigou *et al.*, 2013).

The clinical results from the early alumina-alumina ceramic designs proved to be mixed at best. Because of the design of some implants and of the poor quality of some materials, alumina ball-heads experienced an unacceptable rate of failure on the first years of clinical use (Piconi *et al.*, 1999).

Nevertheless, this early clinical experience with alumina ceramic component in THR allowed assessing that:

- (1) The wear rate of these early alumina ceramic bearings was very low in comparison with metal-polyethylene bearings (2.6 $\mu\text{m}/\text{year}$ for the cup; 5.4 $\mu\text{m}/\text{year}$ for the head);
- (2) The application of these components in younger patients reduced complications related to aseptic loosening of the components thereby reducing drastically the incidence of clinical complications (Piconi and Streicher, 2013).

Due to implant failures, several manufacturers that undertook the production of alumina ceramics for medical applications withdrew from the market in the early 1980s. The ones committed to pursue the development of ceramic joint replacements started a process aimed to:

- (1) Increase the mechanical properties of the products increasing density and decreasing the grain size,
- (2) Develop tough ceramics.

The first approach led about 1995 to the present generation of high purity alumina, obtained by selected precursors by a manufacturing process carried out in the framework of a Total Quality System. Technological improvements (Hot Isostatic Pressing, laser marking, and proof testing) allowed obtaining alumina ceramics with bending strength about double the one of the early materials (Piconi and Streicher, 2013).

The other approach was based on the discovery of the phase transformation toughening in partially stabilized zirconia (PSZ) by Garvie *et al.* (1975) and shortly after in tetragonal zirconia polycrystal (TZP) by Gupta *et al.* (1977).

The development of ball heads for THR by Yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) in clinical applications is due to the work of the team lead by two French scientists, Bernard Calés and Pascal Christel. Fostered by the company Ceramiques Techniques Desmarquest, (Everux, France) (Christel *et al.*, 1988; Calés and Stefani, 1995; Piconi and Maccauro, 1999).

YTZP allowed a larger flexibility in design of ceramic components for joint replacement overcoming the limitations due to the mechanical properties of Alumina. Nevertheless, YTZP is a complex material that may exhibit different properties and varying stability depending on processing and on the conditions of use. This led to mixed performance records in clinics (Piconi *et al.*, 2007). Finally, the worldwide product withdrawal of zirconia ball heads on 2001, although interesting only two lots of a single manufacturer, led to the practical abandonment of YTZP in joint replacement (Piconi *et al.*, 2006).

This created a technological gap, leaving unattended the demand for several innovative devices made out oxide ceramics, whose design needs a material with mechanical behavior improved with respect to alumina. The development of the composite ceramic known by the tradename BIOLOX®delta gave a new momentum to the whole field (Burger, 1997). This composite is constituted by an alumina matrix containing a homogeneous dispersion of fine zirconia grains and of zirconium aluminate platelets. It is today the reference material in ceramic joint replacements. In addition, it has allowed the development of several new ceramic devices, and opened the way to a new class of oxide ceramic composites now under development worldwide.

Alumina

Chemical-Physical and Mechanical Properties

Among the seven forms of alumina known, only alpha- alumina, or corundum, is suitable for use as bio- material due to its high stability. Alpha-alumina (known also as corundum, or emery if containing impurities), is forming in nature several gemstones, e.g., ruby red in color for the presence of chromium, or sapphire, blue in color due to titanium. Alpha-alumina is aluminum metal in its highest oxidative state: then, no more oxidative reactions are possible, the chemical and physical stability of the material being the maximum achievable. The strong ionic and covalent chemical bonds between Al^{3+} and O^{2-} are giving to the material an high melting point, hardness, and resistance to the attack of strong inorganic acids, like e.g., orthophosphoric, or hydrofluoric acid (Piconi, 2011).

Alpha-alumina has a crystal structure, formed by h.c.p. layers of oxygen atoms, with two-thirds of octahedral sites occupied by aluminum atoms. The surface layer of O^{2-} anions allow the chemisorption on the surface of OH^+ groups, then the bonding of water molecules or proteins. In other words, the surface has an high wettability, higher e.g., of several metallic alloys, allowing to establish a fluid film at the interface in the joints of arthroprostheses' bearings using ceramic components. Joined to the high hardness of alumina (2000–2200 GPa), the wettability of the surface is making this ceramic the ideal material for the components of the arthroprostheses joints (Oonishi *et al.*, 1999; Rieger, 2001; Piconi, 2011).

To achieve the mechanical properties required by the specifications of a medical-grade alumina (ISO, 6474), ceramics must have almost no porosity, very high density, fine grain size, and high grain size homogeneity. Poor control of the micro- structural properties, or a level of impurities of such high concentration that it could lower the stability of the material in vivo (Walter, 1992) were probably the initiators of the failures that were observed in the first years of clinical use of alumina. Because of the use of starting materials of better purity, developments in ceramic processing, and the introduction of proof testing in quality control of ball-heads these failures have been eliminated. Coupled with the use of high- purity powder, the introduction into the manufacturing process of hot isostatic pressing (e.g., 1400°C, 1000 bar) after sintering of the ball-heads allows ceramics with a typical grain size below 2 μm and a further reduction in porosity to be obtained (Richter *et al.*, 1998). The most evident effect of such improvements is the increase in mechanical properties of medical-grade alumina, e.g., the bending strength that was increased in the period 1970–90 from 400 MPa to about 630 MPa. The introduction of proof testing in final control allows the elimination of all the components presenting defects undetectable by conventional methods. In a proof test, ball-heads are submitted for a short time to loads several times the maximum expected in service. All the components that fail below a preset threshold stress level are eliminated. The proof stress levels and hold time are functions of the expected life- time of the component, and are identified on the basis fracture mechanics theory. (Piconi, 2011).

Alumina is sensitive to cyclic loading, as under these conditions flaws (e.g., residual pores, large grain boundaries) may grow and reach a critical size. In the presence of water, the water molecules that permeate the material through the open porosity can enhance the growth of subcritical cracks in alumina (Dörre and Hubner, 1984). During production of materials that have to operate in the physiological environment, it is then very important to obtain a high-density, pore- free structure. The interaction of water with the impurities or the additives plays an important role in stability. To limit grain growth during sintering, it is common to introduce in the material small quantities of MgO (<0.1 mol%) as a sintering aid. Care must be taken in controlling the amount of MgO , as excess may induce the formation of foreign phases in Al_2O_3 , and to control the concentration of impurities like SiO_2 and NaO that can form leachable glassy phases at grain boundaries. Also, the reaction between CaO impurities and water can cause fatigue failure of alumina components (Dörre and Hubner, 1984; Rieger, 2001; Walter, 1992).

Alumina Biocompatibility

Extraction procedures performed by media suitable for cell culture have shown the absence of release from alumina, and a very low cellular reactivity. Alumina has shown a very low degree of cell stimulation towards macrophage and lymphocytes: macrophages incorporating alumina particles still exhibit an excellent chemotactic response, showing the low toxicity of ceramic particles.

When implanted in soft tissues, alumina ceramics (disks, cylinders) are surrounded by a layer of connective tissue. This pseudomembrane transforms progressively in a layer of connective tissue. After the implant of alumina ceramics in bone in nonloaded conditions, fast bone formation is observed in close contact with the ceramic implant without fibrous interposition, the implant remaining stable in time due to surface texture, which is penetrated by cell dendrites. There is no chemical bonding: alumina is a “nearly inert” material. A proteoglycan layer is present at the bone–biomaterial interface. Micromotions of the implant increase the thickness of the fibrous capsule. Bone apposition at the interface is enhanced by the stresses due to loading.

The tissue reaction to the injection of alumina particles in several animal sites is characterized by the presence of granulocytes and lymphocytes in a quantity lower than the ones observed after the injection of metals. In comparison to metal and polyethylene, alumina elicits the weakest tissue response: it has been noted that alumina particles do not induce the fibrosis observed after injection of polymers or metals.

The carcinogenic reaction observed in long-term experiments (3.5 years) after the implant of alumina ceramics appears nonspecific and related more to surface geometry than to any other reaction. No carcinogenic reaction is observed after the injection subcutaneous of alumina powder in Sprague–Dawley rats (Dörre and Hubner, 1984; Christel *et al.*, 1988; Gross *et al.*, 1988; Christel, 1992; Li and Hastings, 1998).

Wear of Alumina

The hardness of α -alumina is in the range 2000–2200 HV. The high hardness of alumina implies the low wear of components of the joint, and high resistance to scratching. By diamond polishing it is possible to obtain a very fine surface finish: the typical surface of ball-heads is characterized by $R_a = 0.02 \mu\text{m}$, $R_t = 0.5 \mu\text{m}$. Coupled with a very fine surface finish, this contributes to lowering the risk of abrasive wear due to surface defects of the ball-head (Rieger, 2001).

In hip simulators tests, alumina has shown a volume wear of 1/2000 that of UHMWPE. The clinical wear of alumina THR bearings has proved to be lower than that of bearings using metal ball-heads. In alumina–alumina joints it has been observed that the wear and friction decreases with time: this is due to the formation of a double layer of water and carboxylic acids chemisorbed on the surface of alumina ceramics in vivo. The stability of this layer during the service of the joint depends on the sphericity of the components (typical sphericity deviation $\pm 0.2 \mu\text{m}$), and on the clearance existing between the ball-head and the socket. It should be noted that the ceramic particulate due to wear has proved to be very well tolerated by the organism: local and systemic reactions to ceramic wear debris are reduced, in comparison to those observed in the presence of metal and UHMWPE debris (Böhler *et al.*, 1999; Fischer *et al.*, 1999; Fischer *et al.*, 2006).

Zirconia

The introduction in arthroplasty of zirconia was made to exploit the toughness of this material, called by its discoverers a “ceramic steel” (Garvie *et al.*, 1975). The attention was initially devoted to Partially Stabilized Zirconia (PSZ). Several PSZs have been tested as ceramic biomaterials, especially Mg-PSZ, which biocompatibility has been extensively tested in vitro and in vivo with favorable results. Nevertheless, most of the development in arthroplasty shifted towards Yttria-stabilized Tetragonal Zirconia Polycrystal (Y-TZP) (Gupta *et al.*, 1977) than become the standard material for clinical applications, whose characteristics identified by the standard ISO 13356.

Namely, Mg-PSZ has some drawbacks relevant to biomedical applications. Mg-PSZ is characterized by grain sizes in the range 30–40 μm and by residual porosity. This can negatively influence the wear rate of UHMWPE sockets that are coupled with zirconia ball-heads. In addition, the complexity of the thermal cycle and the higher sintering temperature of Mg-PSZ, which is higher than that of Y-TZP (1800°C versus 1400°C), has to be taken into account, as it may constitute a technologic drawback (Calés and Stefani, 1995; Piconi and Maccauro, 1999).

Due to the advantages of Y-TZP over alpha-alumina many manufacturers worldwide introduced zirconia components into the market, with variable quality. More than 600,000 Y-TZP ball head for THR were sold by the year 2001 when took place the worldwide withdrawal of the products made by Saint Gobain – Advanced Ceramics Desmarquest who was the main zirconia heads manufacturer. The withdrawal was issued following the unexpected high rate of fracture that took place in two ball head batches processed by the new tunnel furnace introduced in the production line to increase its throughput (Piconi *et al.*, 2006). This event created a lack of confidence in zirconia ball heads whose outcomes in the clinical setting – as shown by the analysis of the literature (Piconi *et al.*, 2007) – had been mixed at the best. Moreover, the low thermal conductivity of zirconia (about one tenth the one of alumina), (see Table 1) joined to its relatively low hardness does not allow the manufacture of ceramic-ceramic bearings. For all these reasons today zirconia has been almost abandoned in orthopedics. The use of Y-TZP is limited to one Total Knee Replacement (TKR) in clinical use in Japan, while Magnesia-Partially Stabilized Zirconia (Mg-PSZ) is used in some niche products. On the other hand, Y-TZP has found a wide field of application in dentistry, as reported elsewhere in this text (Piconi *et al.*, 2014).

Chemical-Physical and Mechanical Properties

Zirconia is a well-known polymorph that occurs in three forms: monoclinic (M), cubic (C), and tetragonal (T). Pure zirconia is monoclinic at room temperature, and is stable up to 1170°C. Above this temperature it transforms into the tetragonal and then into the cubic phase at 2370°C. On cooling, a T–M transformation takes place in a temperature range of about 100°C below

Table 1 Selected behavior of oxide ceramics currently used in joint replacements

Property	Alumina (1970s)	Y-TZP	Mg-PSZ	Alumina (BIOLOX [®] forte)	BIOLOX [®] delta AMC	Ceramys [®] ATZ
Al ₂ O ₃ content (vol%)	99.1–99.6	–	–	> 99.8	80	20
ZrO ₂ content (vol%)	–	> 99	> 99	–	17	80
Density (g/cm ³)	3.90–3.95	6.02	5.5	3.97	4.37	5.51
Thermal Conductivity (W/mK)	30	2.5	3	–	–	–
Hardness (HV)	1800	1200	1500	2000	1760	1500
Flexural strength (MPa)	> 300	1000	400–650	630	1390	1039
Fracture Toughness (MPa m ^{1/2})	3.5	4.5	12.5	4.5	> 6	7.4
Young Modulus (GPa)	380	210	210	407	–	–

Source: Adapted from Piconi, C., 2017. Ceramics for joint replacement: Design and application of commercial bearings. In: Palmero, P., Cambier, F., De Barra, E. (Eds.), *Advances in Ceramic Biomaterials*. Duxford: Woodhead, pp. 129–179.

1070°C, associated with a volume expansion of some 3%–4%. Stresses generated by the expansion originate cracks in pure zirconia ceramics that, after sintering in the range 1500–1700°C, break into pieces during cooling to room temperature. The addition of “stabilizing” oxides, like CaO, MgO, CeO₂, and Y₂O₃, to pure zirconia allows the generation of a multiphase material known as partially stabilized zirconia (PSZ), which has a microstructure at room temperature formed by cubic zirconia containing monoclinic and tetragonal zirconia precipitates as minor phase. The homogeneous and fine distribution of the tetragonal phase within the cubic matrix improves the mechanical strength of PSZ, as the precipitates are able to transform to monoclinic when the constraint exerted on them by the matrix is relieved, i.e., by a crack advancing in the material. An enhancement in toughness is obtained, because the energy associated with crack propagation is dissipated both in the T–M transformation and in overcoming the compression stresses due to the volume expansion. In this case, the stress field associated with expansion due to the phase transformation acts in opposition to the stress field that promotes the crack propagation. The development of tetragonal metastable precipitates may be obtained by the addition of some 8 mol% of MgO to ZrO₂. This allows the formation of a fully cubic microstructure at 1800°C, and the nucleation within the matrix of a tetragonal metastable phase during controlled cooling and aging.

PSZ can also be obtained in the ZrO₂–Y₂O₃ system. However, the main interest in using yttria as a stabilizing oxide is due to the fact that in this system it is also possible to obtain ceramics formed by tetragonal grains at room temperature, called Yttria-stabilized Tetragonal Zirconia Polycrystals (YTZPs).

YTZP materials, containing some 2–3 mol% Y₂O₃, are almost completely constituted by tetragonal grains some hundreds of nanometers in size (less than 0.5 µm), the balance being some cubic phase. The fraction of tetragonal phase retained at room temperature is dependent on the size of grains, on the yttria content, and on the constraint exerted on them by the matrix. The mechanical properties of YTZP ceramics depend on such parameters.

It is very important in YTZP materials to consider the metastable nature of the tetragonal grains. A critical grain size exists, depending the yttria concentration, above which spontaneous T–M transformation of grains takes place, whereas this transformation would be inhibited in a too fine grained structure. Special attention must be devoted to avoid the presence of silica in zirconia ceramics that are to be used as biomaterials. Silica is sometimes used as a sintering additive to limit grain growth and to achieve full density at temperatures lower than 1500°C. SiO₂ and Al₂O₃ may be introduced also during powder processing before firing. The formation of aluminosilicate glasses in the grain boundaries may deplete the concentration of the stabilizing oxide Y₂O₃ in the grains, leading to a loss of stability of the tetragonal phase.

In Mg-PSZ magnesium silicates like enstatite (MgSiO₃) and forsterite (Mg₂SiO₄) may form at grain boundaries, lowering the MgO content in the grains and promoting the formation of monoclinic phase. The leaching of the glassy phase in wet environments adds a further factor in depleting the stability of the material.

Radioactive impurities in zirconia

The ores that are used for the production of the chemicals used in the powder production are associated to Uranium (²³⁸U), thorium (²³²Th) and the nuclides of their decay chains. Especially uranium and zirconia have a wide miscibility interval (International Atomic Energy Agency, 2007). These radioactive nuclides can be contained only as traces in the high purity powders that are used for the production of medical grade YTZPs (Bavbek *et al.*, 2014). The issue of zirconia radioactivity was raised about 1990, by the papers of Hopf, *et al.* that observed very high contents of radioactive isotopes in zirconia powders used as radiopacifiers in bone cements, quite different from the one suitable for fine ceramics (Hopf *et al.*, 1989, 1990). Nevertheless, these papers raised the attention on the issue of zirconia radioactivity, although measures performed on the ball heads for hip replacements were showing specific activities lower than 10 Bq/Kg, then much lower than the one of the human body (about 50 Bq/Kg) (Calès and Peille, 1990; Cieur *et al.*, 1992).

The gamma activity of the powders used in the production of YTZP ceramics zirconia was object of an extensive screening in view of their use as precursors of ceramic biomaterials. The variability of the content in gamma emitters among the different powders on the market was put in evidence (Capannesi *et al.*, 1992) as well as the effectiveness of the processes used for the purification of zirconium chemicals leading to in high purity materials with the specific activity lower than the one of human body (Piconi and Casarci, 2000). In addition, Tests performed in zirconia samples are demonstrating that doses of ionizing energy due to the prolonged use of the zirconia components are below that limits stated by the International Commission on Radiological Protection (Porstendörfer *et al.*, 1996).

Stability in Zirconia Ceramics

The metastability of the tetragonal phase that is the key of the interesting mechanical properties of zirconia is also the origin of its main drawback. In wet environments zirconia ceramics undergo the spontaneous transformation of the metastable tetragonal phase into monoclinic. The transformation, which starts on the surface and progresses into the material bulk, decreases the density of the material, and induces micro- and macrocracking. As the phase transformation progresses, one may observe the reduction in strength and toughness of the ceramic.

None of the models proposed to explain comprehensively the spontaneous T–M transformation in YTZP (Lawson, 1995; Chevalier *et al.*, 2007; Lughì and Sergo, 2010). The reaction of water with yttria to form Y(OH)₃ scavenging the stabilizer from Y-TZP grains is the mechanism was proposed by Lange *et al.* (1986) while Yoshimura *et al.* (1987) proposed a model based on a

cascade of events started by the reaction of water with Zr-O chemical bonds, leading to t-m transformation. The most recent theory, proposed by *Chevalier et al. (2009)* takes into account the reaction between O_2^- from water dissociation and oxygen vacancies in the YTZP lattice as origin of the LTD.

It is worthwhile noting that the rate of strength degradation is not the same for all TZP ceramics. Reduction in grain size and/or increase in concentration of stabilizing oxide decrease the transformation rate. Moreover, internal residual stresses, flaw population and distribution play a relevant role on this behavior. As the extent of strength degradation of YTZPs in wet environments depends on material microstructure, it can be controlled by choice of the material manufacturing process and by the precursors selected for ceramic manufacture. This makes the stability of YTZPs a characteristic peculiar to each material and of its manufacturing technology (*Chevalier et al., 2009*).

The lack of stability in wet environments may affect not only the mechanical properties of zirconia ceramics, but also the wear of UHMWPE sockets that are usually coupled to zirconia ball-heads, because of the increase in roughness that take place at the material surface. The design of precursors (e.g., yttria coating of zirconia grains) can limit this problem as well as the use of small quantities of alumina as an additive (*Lawson, 1995; Piconi et al., 1997, 1998; Palmero et al., 2014*).

Zirconia Biocompatibility

Zirconia has proved to be biologically safe in the cytotoxicity and cytocompatibility tests performed in vitro using fibroblasts 3T3 and L929, human lymphocytes, human osteoblasts, HUVEC, and macrophages (*Piconi and Maccauro, 1999; Piconi et al., 2014*).

The results of in vivo tests show the absence of local or systemic toxic effects after the implantation of zirconia ceramics, in spite of the differences among materials, shape of samples, site of implantation, and evaluation method selected. Samples have been implanted for different times into muscles or bone of different animals, as well as after powder injection in mice. During tests, especially in the early postoperative phase, connective tissue is frequently observed at the bone-ceramic interface.

Carcinogenicity and teratogenicity has been carefully studied in medical grade zirconia because high radioactivity levels were observed in some experimental zirconia ceramics in the late 1980s. This originated rumors about risks in using zirconia in medical devices, but it has been demonstrated that the precursors of medical-grade zirconia conforming to ISO 13356 standard reach specific activity levels similar to the one of human body (about 40 Bq/kg), due to the natural abundance of ^{90}K in blood, muscles and marrow. (*Capannesi et al., 1992; Porstendörfer et al., 1996; Piconi et al., 2014; Bavbek et al., 2014*).

Carcinogenesis is not observed after intra-peritoneal injection in mice, or after implant of disk and tubes in rabbit muscles. Also the absence of aberration of the chromosomal patterns in cells co-cultured on zirconia plates has been reported (*Piconi and Maccauro, 1999*). Carcinogenicity tests (Ames test) and teratogenicity tests (cellular chromosome aberrations) in the presence of $ZrO_2 + Y_2O_3$ doped with 0.5 ppm UO_2 have been performed in vitro, both with negative results. (*Covacci et al., 1999*).

Alumina-Zirconia Composites

The abandon of zirconia in 2001 opened a technological gap in orthopedics. At the turn of the century, it was clear that there was the need of for additional sizes, increased reliability and longevity of ceramic components in arthroplasty. This pushed the industry to develop higher strength composite ceramic materials. Researcher then turned their attention towards different zirconia-toughened ceramics, and significant results were obtained in the development of composites having alumina as main component identified as Zirconia-Toughened Alumina (ZTA) either having zirconia as main constituent, then called Alumina-Toughened Zirconia (ATZ).

The first one introduced into the market about 2002 was the alumina matrix composite (AMC) BIOLOX®delta, made by CeramTec GmbH, (Plochingen, Germany) (*Burger and Richter, 2001*).

The basic concept throughout its development was to preserve the excellent properties of alumina as an implantable ceramic material and to increase its mechanical properties, specifically its fracture toughness. The resulted in a material formed by a fine grained high purity alumina matrix (approximately 80 vol%) combined with three different oxides in order to achieve the desired enhanced properties. The balance of the material mass is constituted by evenly dispersed YTZP zirconia particles with an average grain size of roughly 0.27 μm (17 vol%) and by a complex zirconium aluminate phase with a maximum length of approximately 5 μm and an aspect ratio of 5–10.

Two mechanism are concurring to toughen and to reinforce this composite: the phase transformation of YTZP triggered by the tensile stresses in proximity of a crack tip is an effective energy dissipative mechanism. Moreover, the volume expansion associated to the transformation has to win the high stiffness of the alumina matrix and then has to overcome an higher energy threshold. The resulting compressive stresses field is high efficient in blocking further advance of the crack in the microstructure. The elongated zirconium aluminate crystals nucleated into the composite microstructure during sintering acting as short fibers give a further contribution both to reinforce both to toughen further the material. Chromium oxide is added giving the material its characteristic pink color.

A different approach was followed by researchers working in Mathys Orthopedic (Ermsdorf, Germany, now) who developed a material mostly constituted by zirconia (Ceramics®). In this composite zirconia is present as transformable YTZP both as untransformable cubic zirconia, that with the minor constituent alumina is forming the matrix of the composite (*Begand et al., 2005; Schneider et al., 2008*).

Alumina-Toughened Zirconia (ATZ) composite for orthopedic joint replacement was presented on 2005 by Begand *et al.* (2005) and was introduced in the orthopedic market on 2007 by Mathys Orthopédie (Bettlach, Switzerland) under the tradename Ceramys®. As reported by Schneider *et al.* (2008) large part of this material (about 60 vol%) is tetragonal zirconia, the balance being cubic and some monoclinic.

The mechanical behavior of the material reported by these Authors are remarkable. Nevertheless, due to the permanence of concerns on zirconia, the diffusion of ATZ in arthroplasty seems limited. Kyocera (Kyoto, Japan) followed an original approach developing a ZTA (BioCeram® AZ209) in which zirconia was stabilized in the tetragonal state by residual stresses only (Clarke *et al.*, 2016). More recently, this company presented a further ZTA reinforced by platelet-like alumina crystals (BioCeram® AZUL™) owing its tradename to its characteristic blue color due to the presence of Cobalt among its additives (Ikeda *et al.*, 2017).

Orthopedic Applications

The large part of oxide ceramic in orthopedic applications are ball heads and inserts for THR bearings. Today, ceramic bearings are introduced in shoulder joint replacements, while ceramic knee replacement are already in clinical use, although still in a limited number. Kyocera Medical (Kyoto, Japan) – which is a pioneer in this field – is making femoral condyles in zirconia (Y-TZP) that are implanted in Japan since 2001. In Europe, only CeramTec (Plochingen, Germany) is manufacturing alumina-zirconia composite components for the knee implants produced by Lima Corporate (Villanova di San Daniele, Italy) and by Peter Brehm (Weisendorf, Germany).

It is well known that the use of ceramic bearings minimizes at the best possible with present technology the wear debris released from the joint. In addition, the cytotoxicity of the ceramic debris is the minimum among the different materials (polymers, metals) used in joint replacement bearings (Fisher *et al.*, 2006). A low wear is especially relevant in joint replacements, because of the osteolysis due to the body reactions to wear debris and the consequent aseptic loosening of the implants is still among the main reasons of revision surgeries. Because of the low wear, joint replacements with ceramic bearings are especially suitable for more active patients, as well as for the younger ones with longer life expectations (Black, 1997).

So far, alumina represents a minor share (15%–20%) of the market of ball heads and inserts for Total Hip Replacements (THR) while the use of zirconia (Y-TZP) in THR ball heads has been practically abandoned since 2001 (Piconi *et al.*, 2007). Also in the knee alumina has left place to YTZP or zirconia-alumina composites, that are “the ceramic” in orthopedic today. The main manufacturer worldwide (CeramTec GmbH, Plochingen, Germany) claims to have sold by mid-2019 more than ten million ball heads and inserts for THR made out BIOLOX®delta Alumina Matrix Composite (AMC) and more than five millions made out the former BIOLOX® alumina. Thanks to the improved mechanical properties of BIOLOX®delta in comparison to the ceramics formerly used, as illustrated in Table 1 in the following, it was possible to develop ceramic components for joint replacements with design more challenging than in the past.

The different composite ceramics now on the market are not only providing a reduction in wear of the bearing, but also higher reliability. Massin *et al.* (2014) reported the data of the French National Agency for Medicines and Health Products Safety (ANSM) on the fracture frequencies of BIOLOX®delta inserts (0.025%) and of ball heads (0.0013%), that are closely matching the 0.001% (1/100.000) for heads and 0.021% for inserts reported as resulting by the manufacturer's records. that (Sentuerk *et al.*, 2016).

Oxide Ceramic in Total Hip Replacements

Notwithstanding the high number of Total Hip Replacements presently offered by the implants manufacturers on the orthopedic market worldwide, their design is based on several common features, depicted in Fig. 1. The femoral component is constituted by a stem to be inserted in the femoral canal hosting at its proximal extremity a ball head, the head (ceramic or metal) is articulating into the acetabular component of the implant (the cup, the socket) constituted by an insert (ceramic or polymeric) fixed into a metallic shell. Both the stem both the cup may be cemented into bone, either positioned cementless.

As remarked in the Introduction, the taper connection developed for the head-stem in THR by the German researchers in the early 1970 made possible the modularity now widely used in a number of joint replacements. The taper connection allows modular design, e.g., a stem may host metallic or ceramic heads, while a modular acetabular socket that can host ceramic or polyethylene inserts. The number of available sizes give rise to a family of bearings, providing the selection of the wear couple that suits better the needs and the anatomy of the patients.

Ceramic heads are classified by external diameter, neck length and taper type and size. The standard series of ball head diameters is 28, 32, 36, 40, 44 mm. For any diameter the depth internal of the conical bore can be selected in four steps, identified by the resulting neck length of the implant, i.e., + 5 (XL, Extra Long neck), + 3.5 mm (L, Long neck), 0 mm (M, Medium neck) and – 3.5 mm (S, Short neck). Whatever the ball type, the taper connection transfers the loads due to patient activity to the ceramic head generating two main tensile stresses in the ceramic head, e.g., in the head dome, and homoradial (hoop) stresses close to the taper surface. (Andrisano *et al.*, 1990; Middleton *et al.*, 1994; Weisse *et al.*, 2003).

The taper fitting more common in Europe is the so-called 12/14. It is noted that this denomination is not corresponding to the real geometry of the taper, whose angle, length, upper and lower base diameter may differ largely among the different implant systems. In addition, implants of different models made by the same manufacturer may have different design of the taper



Fig. 1 Schematic of a THR with ceramic-on-ceramic bearing joint. Reprinted from Piconi, C., 2017. Ceramics for joint replacement: Design and application of commercial bearings. In: Palmero, P., Cambier, F., De Barra, E. (Eds.), *Advances in Ceramic Biomaterials*. Duxford: Woodhead, pp. 129–179.

connection. Calés and Stefani (1998) analyzed 20 different taper design, observing significant variations between the top of the trunnion with respect to the center of the ball head and of the distance between the top of the trunnion and the bore rim, both parameters resulting relevant for the stress distribution within the ball head. In addition, the variability among the tapers of the different implant systems are enhanced by the machining tolerances and by the surface finish of the taper itself, that are specific to each manufacturer and to each THR system (Munir *et al.*, 2015). In consequence of the many variables that characterize each taper, it is evident that coupling between stem and head shall not be made at random, but carefully following the instructions given by the implant manufacturer.

In the large majority of hip replacement systems now on the market also the acetabular components (the socket, the cup) have modular design, consisting in a metallic shell (the metal back) hosting a ceramic or UHMWPE insert (or inlay) fitted into the shell by a taper connection. Whatever the design of the implant system, the mechanical interlock between the liner and the metal back has to assure the stability of the insert, that once seated into the metal back has to resist to pull out, to torsion moments, to lever out moment due to the forces exerted on it during its clinical use.

To the extent of this chapter, heads are ceramic, but the use of metallic heads (usually CoCr-Alloy) is widespread and also all-polyethylene cups are in clinical use. Consequently, THR bearings are categorized as Hard-on-Hard or Hard-on-Soft bearings.

The choice of the bearing couple marks the difference among Countries: while in the EU, Japan, Korea there is a prevalence of the use of ceramic heads while in the USA and Australia the CoCr-alloy is the material of choice for THR heads. In the acetabular side cross-linked UHMWPE [XLPE] are the material more used worldwide, but in France and in Korea ceramic-on-ceramic is the preferred bearing, as depicted in Fig. 2. It is note that the market is evolving very fast, and the use of ceramic heads in arthroplasty is growing, especially in couple with XLPEs.

The hard-on-soft configuration is traditional in THR since 1960, when Sir John Charley selected Ultra High Molecular Weight Polyethylene (UHMWPE) for the acetabular component of Low Friction Arthroplasty, after the first attempts made with polytetrafluoroethylene (PTFE) resulted in a series of failures. The UHMWPE debris generated by the wear of the bearing were identified as the origin of the cascade of events leading to aseptic loosening of the implants since a long (Willert and Semlitsch, 1977). The increase in number of hip arthroplasties performed in more active patients has enhanced the relevance of the risk of complications related to wear debris. As put in evidence in the introductory part of this section, several ceramics can be used for the ball heads and a number of polymeric materials that can be used for the articular surface of the cup.

Current hard-on-soft solution is to couple ceramic ball heads are coupled to cross-linked polyethylene.

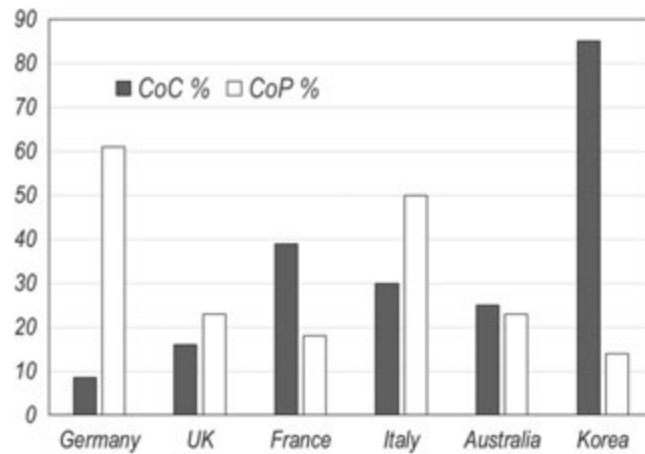


Fig. 2 Use of ceramic components in total hip replacements in selected countries (CoC: ceramic-on-ceramic bearing. CoP: ceramic-on-polyethylene bearing). Reprinted from Piconi, C., 2017. Ceramics for joint replacement: Design and application of commercial bearings. In: Palmero, P., Cambier, F., De Barra, E. (Eds.), *Advances in Ceramic Biomaterials*. Duxford: Woodhead, pp. 129–179.

A number of investigations were carried out to improve the tribological behavior of UHMWPE, e.g., by the introduction of second phases (e.g., glass fibers, carbon fibers). Today, the solution that is widespread in arthroplasty consists in improving the mechanical properties of UHMWPE by the increase of the cross-linking of the molecular chains. Several cross-linked polyethylenes were developed with different process and clinical results, as comprehensively illustrated by Brach del Prever *et al.* (2009) and by Oral and Muratoglu (2016).

Artificial joints are to be designed to enable the whole range of physiological movements (flexion, extension, abduction, adduction and rotation) then THR are currently designed to allow a Range of Motion (ROM) of at least 120°. The increase in diameter may allow ROM of 135–140°, and then 36 or 40 mm bearings are now usual in many THR systems. The higher ROM decrease the risk of impingement of the cup rim on the stem neck (Willmann *et al.*, 2000) while increase the “jumping distance” of the joint, e.g., the displacement necessary to dislocate permanently the head from the socket. This is especially relevant for young and active patients, or for patients demanding high joint mobility due to their resting position (squatting).

The main drawback of the increased bearing diameter is the increase of the overall diameter of the socket. This is negative for the patient’s bone stock, both for the suitability of the implant for smaller anatomies (e.g., female or Asian patients). In consequence, to limit the thickness of the cup is necessary to limit by limiting the thickness of the shell and of the insert, without compromising the stiffness of the whole cup, is a challenging task in the design of the implant (Dold *et al.*, 2016).

In the light of the above, the use of ceramic in larger bearings is very interesting, because of low friction of ceramic-on-ceramic surface that do not lead to increase in wear or torque for bigger head diameter.

ZTA composites (BIOLOX®delta) are making feasible the design of cementless all-ceramic cups. In addition, it has been demonstrated in animal models the effectiveness of treatment giving bone bonding behavior to the external surface of ceramic cups, thus achieving osseointegration of the device (Schreiner *et al.*, 2002, 2012; Theelke *et al.*, 2009).

Oxide Ceramic Hip Resurfacing

The resurfacing of the femoral head is an interesting alternative to THR for high activity patients, because it is bone-sparing and reducing dislocation risk. Nevertheless, its survivorship in female patients is lower than in males because of the reduced head size, especially is lower than 50 mm.

The alternative is to make hip resurfacing devices by ceramics.

During the 1970s Locke and Stärk (Rosenthal Technik Lauf, Germany) developed several very innovative alumina devices. Remarkable is the femoral head resurfacing alumina femoral cup to be coupled with an alumina uncemented cup. (Salzer *et al.*, 1978). The outcomes of these devices was unsatisfactory. Today, thanks to improved design and materials the prototypes of ceramic resurfacing devices are under development, as reported recently in several works (Dickinson *et al.*, 2011; Pandorf and Preuss, 2019; Vogel *et al.*, 2019). A ceramic resurfacing device made out the alumina matrix composite BIOLOX®delta (CeramTec, Plochingen, Germany) is depicted in Fig. 3.

Oxide Ceramic Knee Joint Replacements

The issue of wear is becoming more and more relevant in knee replacements because the number of implants performed each year is growing, and more and more young patients are today candidates for the implant of a knee replacement. The use of a ceramic in knee replacement has several potential advantages; first, an improved lubrication of the articulating surface due to the high



Fig. 3 Ceramic hip resurfacing. Courtesy: Medical products Division, CeramTec GmbH, Plochingen, Germany.

wettability of ceramic surface by the synovia liquid and then a lower wear rate of the PE liner on the tibial component. A further reason for the selection of ceramics in knee replacements is linked to the growing incidence of allergic reactions to metal ions, and of the wide metallic surface that patients may develop for the presence of different metallic implants in several anatomical districts of the body. The Australian Orthopedic Register shows that about 2% of TKR revision surgeries is due to “metal related pathologies” (Australian Orthopedic Association, 2016). The subject is still debated (Münch *et al.*, 2015; Middleton and Toms, 2016; Innocenti *et al.*, 2017; Saccomanno *et al.*, 2019). However, it has been noted that 15 in 23 different TKR systems used clinically in the UK had a “anallergic” version obtained by ceramization of the metallic components, both version having identical design and size (Ajwani and Charalambous, 2016).

A reduction in PE wear can also be expected for the better scratching resistance of the ceramic surfaces, in comparison to metallic alloys, that will save the status of the polished articulating surfaces. (Solarino *et al.*, 2017) Moreover, the use of ceramic devices is reducing the artifacts in CT – scans of the joint after surgery (Kasperek *et al.*, 2019).

The development of ceramic knee replacements

Although the first use of alumina in the knee is due to the prof. Langer who used unicompartimental tibial plateau replacements in Jena, (Langer and Blumentritt, 1987; Langer, 2002) the development of ceramic Total Knee Replacement (TKR) was started in Japan on 1970s by the late prof. Hironobu Oonishi, a pioneer in the development of ceramic devices. These TKRs (the so-called KOM-1) – made by the company Kyocera (Kyoto, Japan) – were formed by an alumina femoral component articulating on a polyethylene insert hosted on an alumina tibial plateau, and were implanted cementless in 134 patients. (Oonishi, 1990, 2006) Kyocera developed also unicompartimental knee replacements that showed high success rate at controls made at an average 42 months after surgery (24–68 months) (Atsui *et al.*, 1997).

Since then several other TKR design based on alumina were developed in Japan, such as the Low Friction Anatomical (LFA-1), the Yokohama Medical Ceramic Knee (YMCK), the Bisurface knee replacement designed by the University of Kyoto all made by the company Kyocera (Kyoto, Japan), and the Kyoto Ceramics-1 (KC-1) (Solarino *et al.*, 2017).

Other researchers focused their work on the development of TKRs with zirconia femoral components. Payten and Ben Nissan (Payten and Ben Nissan, 2000), reported the design of a modular knee replacement in its femoral component Mg-PSZ inserts clipped on the metallic baseplate. Experimental THR with YTZP femoral condyles gave unsatisfactory short-outcomes in 20 patients in the University Hospital Motol (Praha, Czech Republic), and the development of these devices looks abandoned by now (Vavřík *et al.*, 2008; Veigl *et al.*, 2011).

Preliminary results of clinical trials carried out in the USA on TKRs with Y-TZP condyles are reported in the literature, but these studies looks have been uneventful so far (Blaise *et al.*, 2002; Bal *et al.*, 2005). The contemporary development of femoral components for knee arthroplasty made out the AMC BIOLOX®delta (CeramTec, Plochingen, Germany) may have contributed to the dismissal of these projects (Heimke *et al.*, 2002).

So far, BIOLOX®delta components are used in two different knee replacements, the Multigen Plus Total Knee Replacement designed by LIMA Corporate (San Daniele del Friuli, Italy) (Dalla Pria *et al.*, 2006) and the BPK-S designed by Peter Brehm (Weisendorf, Germany).



Fig. 4 The multigen total knee replacement with ceramic femoral component (Courtesy CeramTec GmbH, Medical Products Division, Plochingen, Germany). Reprinted from Piconi, C., 2017. Ceramics for joint replacement: Design and application of commercial bearings. In: Palmero, P., Cambier, F., De Barra, E. (Eds.), *Advances in Ceramic Biomaterials*. Duxford: Woodhead, pp. 129–179.



Fig. 5 The BPH-S total knee replacement with ceramic femoral component and tibial tray (Courtesy CeramTec GmbH, Medical Products Division, Plochingen, Germany). Reprinted from Piconi, C., 2017. Ceramics for joint replacement: Design and application of commercial bearings. In: Palmero, P., Cambier, F., De Barra, E. (Eds.), *Advances in Ceramic Biomaterials*. Duxford: Woodhead, pp. 129–179.

The more striking difference between the two devices is in the tibial component. In the Multigen Plus – depicted in [Fig. 4](#) - it consists in a monoblock XLPE component, while in the BPK-S – depicted in [Fig. 5](#) - a BIOLOX®delta tibial tray hosts a semi-constrained XLPE insert, with a stump in its inferior part articulating with the tray to control its motion. The clinical and

radiological outcomes and survival rate of both devices are comparable to other metallic TKA systems (Bergschmidt *et al.*, 2015; Meier *et al.*, 2016).

Oxide Ceramics in Shoulder Joint Replacement

Besides hip and knee replacements here is today a new interest for using ceramic components in shoulder replacement, as the glenoid component of the implant. The replacement of the shoulder joint with ceramic devices has been attempted in the past. The device described in the US Patent issued by Zeibig and Locke is an alumina “three-part implant...for an upper arm bone” (Zeibig and Locke, 1976). Sim *et al.* reported the implant of a ceramic humeral component (Rosenthal, Lauf, Germany) after resection due to bone tumor (Sim *et al.*, 1980). Later, Huckstep and Sherry reported the use in three cases the implant of shoulder replacement with alumina head for limb salvage due to bone tumor (Huckstep and Sherry, 1996).

The development achieved in the last years in shoulder replacements stimulated the interest for using ceramic components in Total Shoulder Replacement (TSR) systems. The component of reference is the glenoid head. Several models are on the market, the one manufactured by CeramTec is illustrated in Fig. 6. Enomoto (2001) reported the short term results of 11 cementless artificial humeral head replacement performed between 1993 and 2000 using alumina-ceramics head Physio-shoulder system (Kyocera, Japan), while a glenoid ball head coupled to a ceramic humeral insert is used in the Unic® TSR (Evolutis®, Brennon, France). Ceramic glenoids or ceramic humeral heads are also used in the TSRs of the Affinys® system (Mathys Orthopedie, Bettlach, Switzerland) (Bell and Coghlan, 2014).

Oxide Ceramics in Ankle Joint Replacements

First attempts for using alumina in an ankle joint replacement were made in Japan since the early 1980s. The TNK total ankle replacement – that has tibial and the talar components made out high density alumina – was introduced in the Japanese market by Kyocera (Kyoto, Japan) in the early 1990 and it is still in clinical use. In TNK, the tibial component hosts a UHMWPE insert on the articular surface. The bone-contacting surfaces of the tibial and talar components are coated with alumina beads, forming a porous surface aimed to achieve the cementless fixation of the implant by bone ingrowth. The review of clinical experience with two successive generations of TNK devices demonstrated that improved results could be achieved using cement to stabilize the implants in situ (Nishikawa *et al.*, 2004; Takakura *et al.*, 2004). More recently, osteonecrosis of the talus has been treated with alumina patient-specific talar replacements (Taniguchi *et al.*, 2015).



Fig. 6 Ceramic glenoid head (Courtesy Medical Products Division, Ceramtec GmbH, Plochingen, Germany). Reprinted from Piconi, C., 2017. Ceramics for joint replacement: Design and application of commercial bearings. In: Palmero, P., Cambier, F., De Barra, E. (Eds.), *Advances in Ceramic Biomaterials*. Duxford: Woodhead, pp. 129–179.

Oxide Ceramics in Finger Joint Replacements

Several prosthetic implants have been designed to treat the proximal interphalangeal and metacarpophalangeal joints affected by post traumatic conditions or rheumatoid arthritis.

The literature mentions a ceramic device only, the Orthosphere® (Wright Medical, Austin TX). This device, consisting is a zirconia sphere, was used in the interpositional arthroplasty of the thumb carpometacarpal joint, as reported by Calandruccio and Jobe (Calandruccio and Jobe, 1997).

Oxide Ceramics in Disk Replacement

Ceramics devices are used in spine arthrodesis (the synthesis of two or more adjacent vertebral bodies) and in spine arthroplasty by Total Disk Replacements (TDR). The main advantage of TDR over arthrodesis consists in the preservation of the relative motion of the vertebral bodies. So far.

A further TDR with ceramic components is the the Discocerv™ (Scient'x, Voisin Le Bretonneaux, France) intended to replace disks in the cervical spine (C2–C7). It is formed by two titanium alloy (Ti-6Al-4V) endplates which external profile fits into the native disk space. In their interior there is the bearing, formed by a convex alumina disk articulating on a concave Y-TZP disk. (Ramadan *et al.*, 2007; Enan *et al.*, 2011).

A further TDR using PEEK-ceramic bearing with design based on the KineFlex® 11C Cervical TDR (SpinalMotion, Mountain View, CA, USA) has been tested. This device is formed by two PEEK endplates hosting between them a mobile zirconia-toughened alumina ceramic core (CeraSurf1-p; CoorsTek1 Medical, Grand Junction, CO, USA) (Siskey *et al.*, 2016).

References

- Ajwani, S.H., Charalambous, C.P., 2016. Availability of total knee arthroplasty implants for metal hypersensitivity patients. *Knee Surgery & Related Research* 28, 312–318.
- Andrisano, A.O., Dragoni, E., Strozzi, A., 1990. Axsymmetric mechanical analysis of ceramic heads for total hip replacement. *Proceedings of the Institution of Mechanical Engineers Part H Journal of Engineering in Medicine*. 157–167.
- Atsui, K., Tateishi, H., Futani, H., Maruo, S., 1997. Ceramic unicompartmental knee arthroplasty for spontaneous osteonecrosis of the knee joint. *Bulletin of the Hospital for Joint Diseases* 56, 233–236.
- Australian Orthopaedic Association, 2016. National Joint Replacement Registry. Annual Report. Adelaide: AOA.
- Bal, B.S., Greenberg, D.D., Aleto, T.J., 2005. Primary total knee replacement with a zirconia ceramic femoral component. In: D'Antonio, J.A., Dietrich, M. (Eds.), *Bioceramics and Alternative Bearings in Joint Arthroplasty*. Darmstadt: Steinkopff, pp. 83–190.
- Bavbek, A.B., Özcan, M., Eskitascioglu, G., 2014. Radioactive potential of zirconium-dioxide used for dental applications. *Journal of Applied Biomaterials & Functional Materials* 12, 35–40.
- Begand, S., Oberbach, T., Glien, W., 2005. ATZ: A new material with a high potential in joint replacement. *Key Engineering Materials* 284–286, 983–986.
- Bell, S.N., Coghlan, J.A., 2014. Short stem shoulder replacement. *International Journal of Shoulder Surgery* 8, 72–75.
- Bergschmidt, P., Bader, R., Ganzer, D., *et al.*, 2015. Prospective multi-centre study on a composite ceramic femoral component in total knee arthroplasty: Five-year clinical and radiological outcomes. *The Knee* 22, 186–191.
- Black, J., 1997. Prospects for alternate bearing surfaces in total replacement arthroplasty of the hip. In: Puhl, W. (Ed.), *Performance of the Wear Couple Biolox Forte in Hip Arthroplasty*. Stuttgart: Enke, pp. 2–10.
- Blaise, L., Webb, J., Calés, B., 2002. Mechanical analysis of a knee prosthesis with a zirconia femoral component. *Orthopaedic Proceedings* 84-B.(14).
- Böhler, M., Mochida, Y., Bauer, Th.W., Salzer, M., 1999. Analysis of wear debris particles from alumina on alumina ceramic THA. In: Sedel, L., Willmann, G. (Eds.), *Reliability and Long-Term Results of Ceramics in Orthopedics*. Stuttgart: Thieme, pp. 57–59.
- Boutin, P., 1972. Arthroplastie totale de la hanche par protheses en alumine fritté. *Revue de Chirurgie Orthopédique et Réparatrice* de 58, 230–246.
- Brach del Prever, E.M., Bistolfi, A., Bracco, P., Costa, L., 2009. UHMWPE for arthroplasty: Past or future? *Journal of Orthopaedics and Traumatology* 10, 1–8.
- Burger, W., 1997. Umwandlungs- und plateletverstärkte Aluminiumoxidmatrixwerkstoffe. *Keramische Zeitschrift* 49, 1067–1070.
- Burger, W., Richter, H.G., 2001. High strength and toughness alumina matrix composites by transformation toughening and *in situ* platelet reinforcement (ZPTA). *The new generation of bioceramics*. In: Giannini, S., Moroni, A. (Eds.), *Bioceramics 13*. Zurich: Trans Tech, pp. 545–548.
- Calandruccio, J.H., Jobe, M.T., 1997. Arthroplasty of the thumb carpometacarpal joint. *Semin Arthroplasty* 82, 135–147.
- Calés, B., Stefani, Y., 1995. Yttria stabilized zirconia for improved orthopedic prostheses. In: Wise, D.L., Trantolo, D.J., Altobelli, D.E., *et al.* (Eds.), *Encyclopedic Handbook of Biomaterials and Bioengineering*. New York: Dekker, pp. 415–452.
- Calés, B., Stefani, Y., 1998. Risks and advantages in standardization of bores and cones for heads in modular hip prostheses. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 43, 62–68.
- Calés, B., Peille, C.N., 1990. Radioactive properties of ceramic hip joint heads. In: Heimke, G. (Ed.), *Bioceramics 2*. Köln: Deutsche Keramische Gesellschaft, pp. 152–159.
- Capannesi, G., Piconi, C., Sedda, A.F., Greco, F., 1992. Radioactivity measurements of zirconia powders. In: Ravaglioli, A., Krajewski, A. (Eds.), *Bioceramics and the human body*. Amsterdam: Elsevier, pp. 211–217.
- Chevalier, J., Gremillard, L., Deville, S., 2007. Low temperature degradation of zirconia: An implication for biomedical implants. *Annual Review of Materials Research* 37, 1–3.
- Chevalier, J., Gremillard, L., Virkar, A.V., Clarke, D.R., 2009. The tetragonal–monoclinic transformation in zirconia: Lessons learned and future trends. *Journal of the American Ceramic Society* 92, 1901–1920.
- Christel, P.S., 1992. Biocompatibility of surgical grade dense polycrystalline alumina. *Clinical Orthopaedics and Related Research* 282, 10–18.
- Christel, P.S., Meunier, A., Dorlot, J.-M., *et al.*, 1988. Biomechanical compatibility and design of ceramic implants for orthopedic surgery. In: Ducheyne, P., Lemons, J.E. (Eds.), *Bioceramics: Material Characteristics Versus In Vivo Behavior*. New York: Academy of Sciences, pp. 234–256.
- Cieur, S., Heindl, R., Robert, A., 1992. Radioactivity of a femoral head of zirconia ceramics. In: Hulbert, J.E., Hulbert, S.F. (Eds.), *Bioceramics 3*. Terre Haute: Rose-Hulman Inst. of Technology, pp. 152–159.
- Clarke, I.C., Lazennec, J.Y., Smith, E.J., *et al.*, 2016. Ceramic-on-ceramic bearings: Simulator wear compared to clinical retrieval data. In: Sonntag, R., Kretzer, J.P. (Eds.), *Material for Total Joint Arthroplasty*. London: Imperial College Press, pp. 85–132.
- Covacci, V., Bruzese, N., Maccauro, G., *et al.*, 1999. In vitro evaluation of the mutagenic and carcinogenic power of high purity zirconia ceramic. *Biomaterials* 20, 371–376.

- Dalla Pria, P., Giorgini, L., Kuntz, M., Pandorf, T., 2006. Ceramic knee design. In: Benazzo, F., Falez, F., Dietrich, M. (Eds.), *Bioceramics and Alternative Bearings in Joint Arthroplasty*. Darmstadt: Steinkopff, pp. 115–123.
- Dickinson, A.S., Browne, M., Wilson, K.C., Jeffers, J.R.T., Taylor, A.C., 2011. Pre-clinical evaluation of ceramic femoral head resurfacing prostheses using computational models and mechanical testing. *Proceedings of the IMechE, Part H: Journal of Engineering in Medicine* 225, 866–876.
- Dold, P., Pandorf, T., Flohr, M., Preuss, R., Bone, M.C., 2016. Acetabular shell deformation as a function of shell stiffness and bone strength. *Proceedings of the IMechE, Part H: Journal of Engineering in Medicine* 230 (4), 259–264.
- Dörre, E., Hubner, H., 1984. *Alumina, Processing, Properties and Applications*. Heidelberg: Springer.
- Enan, A., Abu-Hegazy, M., Abo-Hegy, M., Al-Kerdany, A., 2011. Single level cervical arthroplasty with the discocerv prosthesis: A preliminary report. *Acta Orthopaedica Belgica* 77 (2), 224–229.
- Enomoto, E., 2001. Cementless artificial humeral head replacement for a comminuted proximal humeral fracture. *Katakansetsu* 25, 487–490.
- Fischer, J., Ingham, E., Stone, M.H., *et al.*, 1999. Wear and debris generation in artificial hip joints. In: Sedel, L., Willmann, G. (Eds.), *Reliability and Long-Term Results of Ceramics in Orthopedics*. Stuttgart: Thieme, pp. 78–81.
- Fischer, J., Jin, Z., Tipper, J., Stone, M., Ingham, E., 2006. Tribology of alternative bearings. *Clinical Orthopaedics and Related Research* 453, 25–34.
- Garvie, R.C., Hannink, R.H.J., Pascoe, R.T., 1975. Ceramic Steel? *Nature* 258, 703–704.
- Glien, W., 1980. Entwicklung und Produktion biokeramischer Implantate. *Hermesdorfer Technische Mitteilungen* 77, 2452–2458.
- Gross, U., Schmitz, H.-J., Strunz, V., 1988. Surface activity of bioactive glass, aluminum oxide and titanium in a living environment. In: Ducheyne, P., Lemons, J.E. (Eds.), *Bioceramics: Material Characteristics Versus In Vivo Behavior*. New York: Academy of Sciences, pp. 2011–2026.
- Gupta, T.K., Bechtold, J.H., Kuznicki, R.C., Cadoff, L.H., Rossing, B.R., 1977. Stabilization of tetragonal phase in polycrystalline zirconia. *Journal of Materials Science* 12, 2421–2426.
- Heimke, G., Leyen, S., Willmann, G., 2002. Knee arthroplasty: Recently developed ceramics offer new solutions. *Biomaterials* 23, 1539–1551.
- Hernigou, P., Queinnee, S., Flouzat Lachaniette, C.H., 2013. One hundred and fifty years of history of the Morse taper: From Stephen A. Morse in 1864 to complications related to modularity in hip arthroplasty. *International Orthopaedics* 37, 2081–2088.
- Hopf, Th., Hopf, Ch., Göbel, B., 1990. About radioactivity of some PMMA bone cements. *Acta Orthopaedica Belgica* 56, 443–444.
- Hopf, Th., Sherr, O., Göbel, B., Hopf, Ch., 1989. Vergleichende tierexperimentelle Untersuchung zur Gewebsverträglichkeit und Messungen der radioaktivität verschiedener Röntgenkontrastmittel. *Zeitschrift für Orthopädie und Unfallchirurgie* 127, 620–624.
- Huckstep, R.L., Sherry, E., 1996. Replacement of the proximal humerus in primary bone tumours. *ANZ Journal of Surgery* 66, 97–100.
- Ikedo, J., Murakami, T., Sasaki, T., *et al.*, 2017. Wear and corrosion resistance of low temperature degradation FreeCZTA for artificial joint. *Key Engineering Materials* 720, 296–300.
- Innocenti, M., Vieri, B., Melani, T., Paoli, T., Carulli, C., 2017. Metal hypersensitivity after knee arthroplasty: Fact or fiction? *Acta BioMedica* 2 (88, Supp.), 78–83.
- International Atomic Energy Agency, 2007. *Radiation Protection and NORM Residue Management in the Zircon and Zirconia Industries*. Safety Reports Series No. 51. Vienna: International Atomic Energy Agency.
- Kasperek, M.F., Töpker, M., Lazar, M., *et al.*, 2019. Dual-energy CT and ceramic or titanium prostheses material reduce CT artifacts and provide superior image quality of total knee arthroplasty. *Knee Surgery, Sports Traumatology, Arthroscopy* 27 (5), 1552–1561.
- Lange, F.F., Dunlop, G.L., Davis, B.I., 1986. Degradation during ageing of transformation toughened ZrO_2 - Y_2O_3 materials at 250°C. *Journal of the American Ceramic Society* 69, 237–240.
- Langer, G., 2002. Ceramic tibial plateau of the 70s. In: Garino, J.P., Willmann, G. (Eds.), *Bioceramics in Joint Arthroplasty*. Stuttgart: Thieme, pp. 128–130.
- Langer, G., Blumentritt, S., 1987. Our ceramic endoprotheses programme – Investigations and results. In: Vincenzini, P. (Ed.), *Ceramics in Clinical Applications*. Amsterdam: Elsevier, pp. 313–319.
- Lawson, S., 1995. Environmental degradation of zirconia ceramics. *Journal of the European Ceramic Society* 15, 485–502.
- Li, J., Hastings, G.W., 1998. Oxide bioceramics: Inert ceramic materials in medicine and dentistry. In: Black, J., Hastings, G.W. (Eds.), *Handbook of Biomaterial Properties*. London: Chapman and Hall, pp. 340–354.
- Lughi, V., Sergio, V., 2010. Low temperature degradation -aging- of zirconia: A critical review of the relevant aspects in dentistry. *Dent Mater* 26, 807–820.
- Massin, P., Lopes, R., Masson, B., *et al.*, 2014. Does BIOLOX® delta ceramic reduce the rate of component fractures in total hip replacement? *Orthopaedics & Traumatology: Surgery & Research* 100, S317–S321.
- Meier, E., Gelse, K., Trieb, K., *et al.*, 2016. First clinical study of a novel complete metal-free ceramic total knee replacement system. *Journal of Orthopaedic Surgery and Research* 11, 21–28.
- Middleton, J., Pande, G.N., Richter, H.G., Willmann, G., 1994. Investigation into the mechanical reliability of ceramic femoral heads for hip joints. *Journal of Materials Science: Materials in Medicine* 5, 503–506.
- Middleton, S., Toms, A., 2016. Allergy in total knee arthroplasty: A review of the facts. *The Bone & Joint Journal* 98-B, 437–441.
- Münch, H.J., Jacobsen, S.S., Olesen, J.T., *et al.*, 2015. The association between metal allergy, total knee arthroplasty, and revision. *Acta Orthopaedica* 13, 1–6.
- Munir, S., Walter, W.L., Walsh, W.R., 2015. Variations in trunnion surface topography between different commercially available hip replacement stems. *Journal of Orthopaedic Research* 33, 98–105.
- Nishikawa, M., Tomita, T., Fujii, M., *et al.*, 2004. Total ankle replacement in rheumatoid arthritis. *International Orthopaedics* 28, 123–126.
- Oonishi, H., 1990. Knee and ankle joint replacements. In: Heimke, G. (Ed.), *Osseo-Integrated Implants*. Boca Raton: CRC Press, pp. 171–186.
- Oonishi, H., Oonishi, H., Kim, S.C., *et al.*, 2006. Ceramic knee arthroplasty: Advanced clinical experiences of 26 years. *Semin Arthroplasty* 17, 134–140.
- Oonishi, H., Amino, H., Ueno, M., Yunoki, H., 1999. Concepts and design with ceramics for total hip and knee replacement. In: Sedel, L., Willmann, G. (Eds.), *Reliability and Long-Term Results of Ceramics in Orthopedics*. Stuttgart: Thieme, pp. 7–28.
- Oral, E., Muratoglu, O.K., 2016. Crosslinked polyethylene. In: Sonntag, R., Kretzer, J.P. (Eds.), *Materials for Total Joint Arthroplasty*. London: Imperial College Press, pp. 133–182.
- Palmero, P., Montanaro, L., Reveron, H., Chevalier, J., 2014. Surface coating of oxide powders: A new synthesis method to process biomedical powders. *Materials* 7, 5012–5037.
- Pandorf, T., Preuss, R., 2019. Determination of the minimum clearance of ceramic resurfacing systems. *Orthopaedic Proceedings* 4 (101-B, Suppl), 15.
- Payten, W.M., Ben Nissan, B., 2000. Development of a modular ceramic knee prosthesis. In: Wise, D., Trantolo, D.J., Lewandrowski, K.-U., *et al.* (Eds.), *Biomaterials Engineering and Devices: Human Applications* 2. Totowa: Humana Press, pp. 309–336.
- Piconi, C., 2011. Alumina. In: Ducheyne, P., Healey, K.E., Hutmacher, D.W., Grainger, D.W., Kirkpatrick, C.J. (Eds.), *Comprehensive Biomaterials* 1. Amsterdam: Elsevier, pp. 73–94.
- Piconi, C., 2017. Ceramics for joint replacements: Design and applications of commercial bearings. In: Palmero, P., Cambier, F., De Barra, E. (Eds.), *Advances in Ceramic Biomaterials*. Duxford: Woodhead, pp. 129–179.
- Piconi, C., Maccauro, G., 1999. Zirconia as a ceramic biomaterial. *Biomaterials* 20, 1–25.
- Piconi, C., Casarci, M., 2000. Purification of chemicals for the production of biomedical grade Y-TZP ceramics. In: Rammlair, D., Mederer, J., Oberthur, R.B., Petinghaus, H. (Eds.), *Applied Mineralogy*. Rotterdam: Balkema, pp. 205–207.
- Piconi, C., Streicher, R., 2013. Forty years of ceramic-on-ceramic THR bearings. *Semin Arthroplasty* 24, 188–192.

- Piconi, C., Sprio, S., 2018. Zirconia implants: Is there a future? *Current Oral Health Reports* 5, 186–193.
- Piconi, C., Burger, W., Richter, H.G., *et al.*, 1997. New Y-TZP powders for biomedical applications. *Journal of Materials Science: Materials in Medicine* 8, 113–118.
- Piconi, C., Labanti, M., Magnani, G., *et al.*, 1999. Analysis of a failed alumina THR ball head. *Biomaterials* 20, 1637–1646.
- Piconi, C., Maccauro, G., Pilloni, L., *et al.*, 2006. On the fracture of a zirconia ball head. *Journal of Materials Science: Materials in Medicine* 17, 289–300.
- Piconi, C., Rimondini, L., Cerroni, L., 2008. *La Zirconia in Odontoiatria*. Milano: Elsevier Masson.
- Piconi, C., Kosmac, T., Condò, S.G., 2014. Alumina- and zirconia-based ceramics for load bearing applications. In: Shen, J.Z., Kosmac, T. (Eds.), *Advanced Ceramics for Dentistry*. Waltham: Butterworth-Heinemann, pp. 219–253.
- Piconi, C., Burger, W., Richter, H.G., Cittadini, A., Maccauro, G., 1998. Y-TZP ceramics for artificial joint replacements. *Biomaterials* 19, 1489–1494.
- Piconi, C., Maccauro, G., Angeloni, M., Rossi, B., Learmonth, I.D., 2007. Zirconia heads in perspective: A survey of zirconia outcomes in total hip replacement. *HIP International* 17, 119–130.
- Porstendörfer, J., Reineking, A., Willert, H.G., 1996. Radiation risk estimation based on activity measurements on zirconium oxide implants. *Journal of Biomedical Materials Research* 32, 663–667.
- Ramadan, A.S., Mitulescu, A., Schmitt, P., 2007. Total cervical disc replacement with the discocerv® (cervidisc evolution) cervical prosthesis: Early results of a second generation. *The European Journal of Orthopaedic Surgery and Traumatology* 217, 513–520.
- Richter, H.G., Willmann, G., Weick, K., 1998. Improving the reliability of the ceramic on ceramic wear couple in THR. In: Jacobs, J.J., Craig, T.L. (Eds.), *Alternative Bearing Surfaces in Total Joint Replacement*. West Conshohocken: American Society for Testing and Materials., pp. 173–185.
- Rieger, W., 2001. Ceramics in orthopedics – 30 years of evolution and experience. In: Rieker, C., Oberholzer, S., Wyss, U. (Eds.), *World Tribology Forum in Arthroplasty*. Bern: Hans Huber, pp. 283–294.
- Rock, M., 1933. German Pat. DRP 583.589 Künstliche Ersatzteile für das Innere und Aussere des Menschliche und Tierische Körpers.
- Saccomanno, M.F., Sircana, G., Masci, G., *et al.*, 2019. Allergy in total knee replacement surgery: Is it a real problem? *World Journal of Orthopedics* 10 (2), 63–70.
- Salzer, M., Knahr, K., Locke, H., Stärk, N., 1978. Cement-free bioceramic double-cup endoprosthesis of the hip-joint. *Clinical Orthopaedics and Related Research* 134, 80–86.
- Sandhaus, S., 1969. *Nouveaux aspects de l'implantologie*. Paris: Prelat.
- Schneider, L., Begand, S., Kriegel, R., *et al.*, 2008. Low-temperature aging behavior of alumina-toughened zirconia. *Journal of the American Ceramic Society* 91, 3613–3618.
- Schreiner, U., Schroeder-Boersch, H., Schwarz, M., Scheller, G., 2002. Verbesserung der knöchernen Integration bioinertter Keramiken durch Modifikation der Oberfläche – Ergebnisse eines Tierversuchs. *Biomedizinische Technik* 47, 164–168.
- Schreiner, U., Schulze, A., Scheller, G., Apruzzese, C., Schwarz, M.L., 2012. Osteointegration zementfreier Hüftpfannen aus Keramik. *Zeitschrift für Orthopädie und Unfallchirurgie* 150, 32–39.
- Sentuerk, U., von Roth, P., Perka, C., 2016. Ceramic on ceramic arthroplasty of the hip. *The Bone & Joint Journal* 98-B (2 Suppl A), 14–17.
- Sim, F.H., Chao, E.Y., Pritchard, D.J., Salzer, M., 1980. Replacement of the proximal humerus with a ceramic prosthesis: A preliminary report. *Clinical Orthopaedics and Related Research* 146, 161–174.
- Siskey, R., Ciccarelli, L., Lui, M.K., Kurtz, S.M., 2016. Are PEEK-on-ceramic bearings an option for total disc arthroplasty? An in vitro tribology study. *Clinical Orthopaedics and Related Research* 474 (11), 2428–2440.
- Smith, L.W., 1992. Ceramic-plastic material as a bone substitute. *Clinical Orthopaedics and Related Research* 282, 4–9.
- Solarino, G., Piconi, C., De Santis, V., Piazzolla, A., Moretti, B., 2017. Ceramic knee arthroplasty: Ready to Go? *Joints* 5 (4), 224–228.
- Takakura, Y., Tanaka, Y., Kumai, T., Sugimoto, K., Ohgushi, H., 2004. Ankle arthroplasty using three generations of metal and ceramic prostheses. *Clinical Orthopaedics and Related Research* 424, 130–136.
- Taniguchi, A., Takakura, Y., Tanaka, Y., *et al.*, 2015. An alumina ceramic total talar prosthesis for osteonecrosis of the talus. *Journal of Bone and Joint Surgery* 97, 1348–1353.
- Theelke, B., Kuntz, M., Eichhorn, S., *et al.*, 2009. Development of osseointegrative ceramic coatings based on ZPTA– mechanical characterization and influence on the substrate. In: Kim, S. (Ed.), *Bioceramics 22*. Seoul: Korean Society for Biomaterials, pp. 145–149.
- Vavřík, P., Landor, I., Denk, F., 2008. Clinical evaluation of the ceramic femoral component used for reconstruction of total knee replacement. *Acta chirurgiae orthopaedicae et traumatologiae Čechoslovaca* 75, 436–442.
- Veigl, D., Vavřík, P., Pokorný, D., *et al.*, 2011. Comparison of in vivo characteristics of polyethylene wear particles produced by a metal and a ceramic femoral component in total knee replacement. *Acta chirurgiae orthopaedicae et traumatologiae Čechoslovaca* 78, 49–55.
- Vogel, D., Liebelt, M., Kalkowsky, F., *et al.*, 2019. Mechanical and numerical characterization of ceramic femoral components for hip resurfacing arthroplasty. *Proceedings of the IMechE, Part H: Journal of Engineering in Medicine* 233 (9), 883–891.
- Walter, A., 1992. On the material and the tribology of alumina– alumina couplings for hip joint prostheses. *Clinical Orthopaedics and Related Research* 282, 31–46.
- Weisse, B., Zahner, M., Weber, W., Rieger, W., 2003. Improvement of the reliability of ceramic hip joint implants. *Journal of Biomechanics* 36, 1633–1639.
- Willert, H.G., Semlitsch, M., 1977. Reactions of the articular capsule to wear products of artificial joint prostheses. *Journal of Biomedical Materials Research* 11, 157–164.
- Willmann, G., Brodbeck, A., Richter, H.G., 2000. Untersuchung von explantierten BIOLOX Köpfen: analyse der metallische Abdrücke in der konischen Bohrung. In: Willmann, G., Zweimüller, K. (Eds.), *Bioceramics in Hip Joint Replacements*. Stuttgart: Thieme, pp. 81–87.
- Yoshimura, M., Noma, T., Kawabata, K., Somiya, S., 1987. Role of water on the degradation process of Y-TZP. *Journal of Materials Science Letters* 6, 465–467.
- Zeibig, A., Locke, H., 1976. Ceramic Implant. U.S. Pat. 3979779.

Non-Oxide Ceramics as Biomaterials

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Silicon Nitride

Introduction

Silicon nitride is the name given to a family of structural ceramics that is used for high temperature and wear resistant applications which include turbocharger rotors, glow plugs, bearings, cutting tools, valves and certain refractory components (Riley, 2000; Petzow and Herrmann, 2002; Hampshire, 2016). Silicon nitride, general stoichiometric formula Si_3N_4 , may be formed as a dense ceramic at temperatures in the range 1750–1900°C by hot pressing (HPSN), pressureless sintering (SSN), hot isostatic pressing (HIPing) or gas pressure sintering (GPS) which results in a ceramic with high flexural strengths (600–1200 MPa), high fracture resistance, high thermal shock resistance, high creep resistance, high hardness, and excellent resistance to erosion.

Silicon nitride may also be formed as a microporous ceramic by reaction bonding which involves nitridation of silicon powder compacts at 1200–1400°C during which silicon nitride crystals grow within the pre-existing pores of the silicon powder compact (Moulson, 1979). The original dimensions of the component remain virtually unchanged during nitriding (linear shrinkage <0.1%), allowing complex shapes to be machined to their final size either before nitriding in the ceramic green state or after partial nitriding at 1000–1200°C to make the material stronger. The final product is known as RBSN (Reaction Bonded Silicon Nitride) (Ziegler *et al.*, 1987) and contains up to 25% microporosity which limits its mechanical strength (200–250 MPa) for certain engineering applications. By addition of oxide additives to silicon powder compacts prior to nitriding, a dense form of silicon nitride may be subsequently produced by sintering the RBSN at ~1750°C, the resulting ceramic known as Sintered Reaction Bonded Silicon Nitride (SRBSN) (Mangels and Tennenhouse, 1980). However, the presence of porosity may be beneficial for biomedical applications. The amount of porosity within a ceramic implant is an important design parameter. Low porosity implants with reasonable fracture toughness are essential for load bearing applications whereas high porosity or graded porosity devices would be advantageous for bone fixation (McEntire *et al.*, 2015).

Sintering of pure silicon nitride is quite difficult because self-diffusivity is low and species only become sufficiently mobile for sintering at temperatures where the decomposition of silicon nitride commences (>1850°C). Thus, alternative approaches were developed by the use of densification additives to create the conditions for liquid phase sintering. Oxide additives ($\text{Al}_2\text{O}_3 + \text{Y}_2\text{O}_3$ or $\text{RE}_2\text{O}_3 - \text{RE} = \text{Rare Earth}$) are mixed with α -silicon nitride powder before forming of the green ceramic into a component shape. Firing is carried out at sintering temperatures of 1750–1900°C where reaction of the additives with silica present on the Si_3N_4 particle surfaces and some of the nitride itself occurs to form an oxynitride liquid which promotes densification by solution-precipitation (Riley, 2000; Hampshire, 2016). The α - Si_3N_4 dissolves in the liquid and is precipitated as the β -form of Si_3N_4 which grows as prismatic hexagonal rod-like crystals that eventually impinge on each other forming an interlocking microstructure of high aspect ratio β -grains and intergranular glass films (Sun *et al.*, 1998; Hampshire and Pomeroy, 2012). By varying the type and amounts of the mixed additives, the chemistry of the grain boundary phase is modified and this has a significant effect on the grain size and aspect ratios of the β - Si_3N_4 grains, resulting in a range of materials with tailored strength and fracture toughness (typically $\geq 6 \text{ MPa m}^{1/2}$). An advancing crack has to take a more complex high energy route through the ceramic and continued crack propagation is restricted by grain bridging and pull-out in the crack wake. This reduces tensile stresses at the crack-tip resulting in increasing resistance to crack propagation as the crack extends, a phenomenon referred to as R-curve behavior (Fünfschilling *et al.*, 2009).

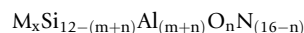
SiAlONs

Other members of the silicon nitride family are the SiAlONs which are solid solutions of Si, Al, O, and N, based on the silicon nitride structure. β' -SiAlON is formed when oxygen replaces nitrogen in the β - Si_6N_8 structure while, at the same time, silicon is replaced by aluminum to maintain charge neutrality (Jack and Wilson, 1972). The solid solution composition is



with z values in the range 0–4.2 and the structure retains the 6:8 metal: non-metal ratio of β - Si_6N_8 . β' -sialons still require the use of sintering additives such as Y_2O_3 and other RE_2O_3 in order to densify the ceramic (Ekström and Nygren, 1992). Microstructures are similar to β - Si_3N_4 with elongated hexagonal grains of β' -sialon but a reduced amount of intergranular glass phase.

Similarly, α' -SiAlONs (α') are based on the α - $\text{Si}_{12}\text{N}_{16}$ unit cell with general composition (Hampshire *et al.*, 1978):



In α' -SiAlON, partial replacement of Si^{4+} by Al^{3+} occurs if, at the same time, charge compensation is effected by the accommodation of other ions, $\text{M} = \text{Li}^+, \text{Ca}^{2+}, \text{Y}^{3+}$, or other rare earth lanthanide ions (Ln^{3+}), in the two interstitial sites (x) in the unit cell. x (<2) is determined by the valence (v) of the M^{v+} ion. As with β' , oxide additives are used as densification aids but they also provide M^{v+} ions for stabilization of α' (Mandal, 1999).

The two SiAlON phases, α' and β' , can coexist depending on the sintering additives used. Therefore, there are more variables to be used as design parameters for SiAlON ceramics and the amount of α' -SiAlON can be varied from 0% to 100% continuously and the type and amount of intergranular phase can also be modified by using mixed additives. These are usually combinations of CaO and two rare earth lanthanide oxides which allow more easier densification but on subsequent heat treatment, the final properties of the SiAlON ceramics can be tailored so that when high hardness is needed, α' -SiAlON content is increased and when higher toughness is required, then additive chemistry is changed to give predominantly β' -SiAlON (Calis Acikbas *et al.*, 2012). These ceramics are already available as cutting tools or refractories and are being developed as wear parts.

Silicon Nitride as a Biomedical Material

During the late 1980s, the effect of an in vitro and in vivo investigation of silicon nitride (RBSN) on rabbit skeletal cells and tissue was carried out (Howlett *et al.*, 1989). Segmental femoral Si_3N_4 endoprostheses were implanted in each of three adult rabbits and the osseous reactions monitored during their natural life. Each implant was enclosed by a stable cuff of bone within four months of implantation and remained unchanged during the rest of the animal's life. Autopsies confirmed the radiographic observations and tissue adjacent to each prosthesis was morphologically normal.

At around the same time, some of the same authors (Sorrell *et al.*, 2004) were involved in a human clinical trial in Australia to determine the capability of silicon nitride as an arthrodesis device in the lumbar spine. 30 patients with long-term spinal degeneration problems underwent anterior interbody fusion of the lower spine using reaction bonded silicon nitride intervertebral spacers. A control population of 10 underwent the same procedure using autologous bone. After 5 years, there were no significant differences in patient satisfaction or rates of union between the autologous bone grafts and the RBSN implants, but there was a significant reduction in interspace collapse with the silicon nitride implants. After 10 years, progressive degeneration was observed in 13 of 16 cases assessed which were thought likely to be the result of stress shielding due to elastic modulus mismatch.

Evidence from another study (Kue *et al.*, 1999) showed that reaction bonded silicon nitride has a non-toxic, biocompatible ceramic surface for the propagation of functional human bone cells in vitro.

Given the excellent combination of mechanical and tribological properties of dense silicon nitride, investigations of other properties critical in biomedical environments were examined such as cytotoxicity, wetting behavior, chemical stability in aqueous media, including simulated body fluid (SBF) and wear rates in physiological solutions with a view to developing silicon nitride components for orthopedic applications (Bal and Rahaman, 2012). Not only is silicon nitride non-toxic, but the material encourages cell adhesion, normal proliferation and differentiation. Cell growth, viability and morphology on silicon nitride were comparable with Ti, and polished Si_3N_4 surfaces appeared to promote cell growth.

Prosthetic hip and knee replacement bearings require biomaterials with low wear rates and favorable frictional coefficients that remain stable in vivo for their service life. Silicon nitride wear couples showed low sliding wear rates both in phosphate-buffered saline (PBS) and in bovine serum compared with the other tested wear couples (Olofsson *et al.*, 2012). Tribofilms were built up on silicon nitride surfaces in both environments, controlling the friction and wear characteristics. Under these test conditions, the contact surfaces of silicon nitride become ultra-smooth as a result of tribochemical polishing and the friction becomes very low at increasing sliding distances.

In view of the possibility of using silicon nitride as a ceramic for structural orthopaedic implants, another study (Mazzocchi and Bellosi, 2008; Mazzocchi *et al.*, 2008) investigated three different silicon nitride based materials: (1) 90.0 vol% Si_3N_4 + 10.0 vol% bioglass, (2) 91.3 vol% Si_3N_4 + 8.7 vol% MgO, and (3) a $\text{Si}_3\text{N}_4/\text{TiN}$ composite with 65.0 vol% matrix (93 wt% Si_3N_4 + 2 wt% Al_2O_3 + 5 wt% Y_2O_3) + 35.0 vol% TiN. Some critical features for biomedical applications were investigated: (i) the wetting behavior against aqueous media, including physiological solutions; (ii) the chemical stability in water and in physiological solutions; and (iii) the wear resistance, measured under experimental procedures that simulate the conditions typical of the hip joint prosthesis. For the $\text{Si}_3\text{N}_4/\text{TiN}$ composite material, some oxidation of TiN affected the friction coefficient but for the monolithic silicon nitrides, friction coefficients were found to be lower than results reported in the literature and the wear resistance is an order of magnitude higher than those reported for other ceramics used for hip joints. The results indicated that silicon nitride was a suitable biomaterial for bone substitution in load bearing prostheses.

Porous silicon nitride-based ceramics, with pore structures similar to that of trabecular bone consisting of an interconnected macroporous network, were prepared by a replica method with polyurethane sponge as pore forming agent (Bodišová *et al.*, 2013). Two porous ceramics were prepared: (1) air-sintered silicon nitride (following burn-out of the polyurethane) and (2) sintered reaction-bonded silicon nitride. No oxide sintering additives were used. Using the same characterization methods as for human bone samples, the pore size distributions in the most important dimensional regions, i.e., under 50 nm and over 100 μm were measured and found to be similar to that of the bone, especially in the air-sintered silicon nitride ceramics. Likewise, the mechanical properties of the air-sintered silicon nitride were very close to those of bone. In the case of sintered reaction-bonded silicon nitride further optimization is required in terms of enhancing the meso- and nano-pore contents and decreasing the hardness and elastic modulus values. The non-cytotoxicity of both forms of porous silicon nitride was confirmed by MTT proliferation test.

Bacteriostasis studies have been conducted on silicon nitride which was compared with titanium (Ti) and polyether ether ketone (PEEK) using five separate nosocomial bacterial strains in vitro (Gorth *et al.*, 2012). Lower amounts of biofilm formation (up to 90%) and fewer live bacteria were consistently found on Si_3N_4 than either of the other two biomaterials. As might be expected, PEEK generated the highest amount of biofilm and harbored the most live bacteria. They postulated that reasons for the observed differences



Fig. 1 Silicon nitride bioceramic components for joint and spinal reconstruction. Courtesy of SINTX Technologies, Salt Lake City, Utah, USA.

were likely due to: (i) improved hydrophilicity of the ceramic in comparison to the moderately and highly hydrophobic metal and polymer, respectively; (ii) chemical moieties on the surface of Si_3N_4 including charged amino and silanol species of SiNH_3^+ , SiOH_2^+ , SiO^- , SiNH_2 , and SiOH , all of which may act to repel microbial attachment; and (iii) a micro-textured surface for Si_3N_4 , which may also prevent biofilm formation. These features were not observed with the other two biomaterials.

The rigid and permanent fixation of an alloplastic medical device with native bone is referred to as osseointegration and is just as important as wear resistance. Samples of silicon nitride implanted in tibias of rabbits were evaluated eight weeks after implantation (Guedes e Silva *et al.*, 2008). The Si_3N_4 and the adjacent bone tissue were analyzed by scanning electron microscopy in order to verify the bone growth around the implants and its morphology and the interaction between the implant and the bone. Bone growth had occurred mainly in the cortical areas. In another study of a highly porous ($\sim 72\%$) silicon nitride (Anderson and Olsen, 2010), osseous penetration of up to 3 mm was observed with excellent vascularization twelve weeks after implantation in an ovine model.

The extents of osseointegration of silicon nitride, PEEK, and titanium were compared in Wistar rats (Webster *et al.*, 2012). Silicon nitride had improved osseointegration over the other two biomaterials at all times up to 3 months post-operatively. New bone formation in the surgical area around the implants was 69% for Si_3N_4 and only 24% for PEEK and 36% for Ti. When implants were pre-inoculated with 104 *Staphylococcus epidermidis*, new bone formation (after 3 months) was 41% for Si_3N_4 and only 21% for PEEK and 26% for Ti. Live bacteria were identified around PEEK (88%) and Ti (21%) implants, whereas none were present on the silicon nitride.

Silicon Nitride Biomedical Devices

Silicon nitride components for biomedical applications, as shown in Fig. 1, are now being manufactured by SINTX Technologies, formerly Amedica Corporation (Salt Lake City, UT, USA). FDA certification has been approved for various products, including ceramic interbody vertebrae fusion devices for cervical and thoracic spine surgery. The company is also developing silicon nitride for new biomedical devices for the spine, dental, oral maxillofacial, podiatry, and arthroplasty markets. The silicon nitride is densified using ~ 6 wt% Y_2O_3 and ~ 4 wt% Al_2O_3 as additives and is sintered in nitrogen at $> 1700^\circ\text{C}$ for ~ 3 h, followed by hot-isostatic pressing $> 1650^\circ\text{C}$ under a nitrogen pressure of > 200 MPa for ~ 2 h.

Fully dense silicon nitride, under development as bearings for hip and knee joint replacements, was found (Bal *et al.*, 2009; Rahaman and Xiao, 2018) to be chemically stable when subjected to accelerated aging for 100 h at 120°C and 0.1 MPa steam in a surgical autoclave. X-ray analysis showed no measurable difference in phase composition following treatment and flexural strength remained within 1 standard deviation (± 36 MPa) of the mean strength (936 MPa). In addition, Si_3N_4 exhibits excellent radiographic visibility as a partially-radiolucent material (Rahaman and Xiao, 2018).

The surface texture and chemistry of these silicon nitride materials has been tailored by applying thermal, chemical, and mechanical treatments, to yield ultra-smooth or highly fibrous surface structures that lead to enhanced osseointegration and bacterial resistance without compromising bulk mechanical properties (Bock *et al.*, 2015). Smooth surfaces are required for bearings in hip and knee arthroplasty because conforming surfaces result in higher contact area between components and hence lower stresses and wear rates. In contrast, surface roughness can markedly influence the response of cells *in vitro* and *in vivo* for implants intended for osseointegration and bacteriostasis. The treatments included grinding and polishing, etching in aqueous hydrofluoric acid, and heating in nitrogen or air. The treated surfaces were characterized using a variety of techniques to assess morphology, surface chemistry and phase composition, surface charging and wetting behavior.

The surface of as-fabricated Si_3N_4 exhibited anisotropic and stochastically oriented β - Si_3N_4 grains covered with a thin $\text{Si}_2\text{N}_2\text{O}$ -like passivation layer, strong negative charging at biologic pH, and moderate hydrophilicity that improved over time as capillary forces drew water into the spaces between the surface grains. Etching in HF produced a surface composition with a higher N/Si and a lower

O/Si ratio than as-fabricated materials – which exhibited strong negative surface charging at homeostatic pH and moderate hydrophilicity.

Thermal treatment in N_2 produced a surface coated in crystalline β -SiALON precipitates whose concentration decreased as a function of depth up to 90 μm . Thermal treatment in an oxidizing atmosphere resulted in a surface composition effectively the same as amorphous SiO_2 . It also exhibited extremely low wetting angles and charging behavior that mimicked pure silica. The isoelectric points of these variously treated samples increased with decreasing O/Si and with increasing N/Si atomic ratios, as the surfaces transitioned from resembling pure SiO_2 to pure Si_3N_4 .

It was considered that both oxidation and thermal treatment under N_2 might offer interesting advantages for orthopaedic implants due to the observed extreme hydrophilicity. The large negative surface charge at homeostatic pH observed for the as-fabricated Si_3N_4 may contribute to its bacteriostatic and osteointegrative behavior. The significant increase in the surface charge for the oxidized material may lead to an enhancement of these properties over what has already been observed for the as-fabricated material. Further, the surface chemistry of silica is well-understood, lends itself to tailored modification, and has already been shown to be an ideal scaffold for bone on-growth. A material that exhibits the flexibility of silica's surface chemistry with the desirable bulk mechanical properties of dense silicon nitride could be readily engineered and adapted to several implant applications. Thus, this potential for modification of silicon nitride surfaces to enhance cell metabolism and possibly promote faster healing in bone repair devices led to further studies of the effects of surface chemistry of silicon nitride on biological interactions (Pezzotti, 2018, 2019).

Effect of Surface Chemistry of Silicon Nitride on Biological Interactions

Certain bioceramics can release or adsorb molecules that support metabolic chemistry and stimulate cells to replicate and function efficiently. In particular, Pezzotti *et al.* (2017a) cite the promising in vitro performance of Si_3N_4 bioceramics with emphasis on its reciprocity with living cells. The importance of elemental silicon in bone development and the bioactivity of silicate glasses are well known (Jones, 2013). Silicon is directly incorporated into hydroxyapatite by ionic substitution. Nitrogen from amino acids is essential for protein synthesis, bone growth, and tissue repair. Cells assimilate and transform water, carbon dioxide (CO_2), and N-containing species – ammonium (NH_4^+), nitrate (NO_3^-), and di-nitrogen (N_2) – into complex biomolecules. Thus when silicon nitride is used as a biomaterial, these N-containing species are all available for biological interactions.

Pezzotti and co-workers have undertaken a number of studies (Pezzotti *et al.*, 2016, 2017a,b; Pezzotti, 2018) the aims of which were to obtain new insights into the biological interactions between Si_3N_4 , with different surface chemistries, and living cells. As with previous investigations, they varied the parameters of thermal treatments on silicon nitride and observed the modifications of its surface chemistry. The treated ceramics were subjected to (1) in vitro tests to examine the treated surface's interaction with relevant proteins, human cells and nosocomial bacteria and (2) in vivo experiments to examine the performance of the modified surfaces in complex, living systems.

Over a 7 day testing period, the in vitro behavior of osteosarcoma cells in the presence of silicon nitride samples with modified surface chemistry was greatly improved in terms of cell differentiation, attachment, proliferation, and apatite formation (Pezzotti *et al.*, 2016). A post-sintering annealing cycle under a N_2 atmosphere resulted in an atypical surface modification of Si_3N_4 with the formation of some unusual Si–Y–Al–O–N phases. Samples exposed to this annealing treatment produced 40% increase in (hydroxy-)apatite formation when compared with as-fired Si_3N_4 and 100% increase when compared with a biomedical Ti alloy. The enhanced apatite formation was shown to preferentially occur at locations corresponding to the mixture of Si–Y–Al–O–N phases and originated from a high density of positively charged surface groups, including both nitrogen vacancies (V_N^{3+}) and N–N bonds (N^{4+}) formed during annealing.

In a further study (Pezzotti *et al.*, 2017b), two short term intervertebral spinal spacers – a Si_3N_4 cervical implant and a PEEK lumbar device – with comparable in vivo service were retrieved and evaluated. The amount of bone growth within the Si_3N_4 implant was found to be orders of magnitude greater than in the PEEK implant. Spectroscopic analyses, including Raman, XPS and FT-IR, consistently demonstrated an important “chemical fingerprint” for the bone grown by human osteoblasts in the neighborhood of the Si_3N_4 surface. This included a modified form of bony apatite in which $(\text{SiO}_4)^{4-}$ tetrahedra and N^{3-} ions substituted for $(\text{PO}_4)^{3-}$ tetrahedra and OH^- ions, respectively. The availability and release of Si and N atoms at the surface of Si_3N_4 and their favorable biological interaction increases the metabolic activity of osteoblasts, which in turn results in rapid and efficient bone growth. These data suggest that, in contrast to traditional bioinert devices such as PEEK, solid Si_3N_4 stimulates human cells to produce a “chemically modified” bony apatite, and provides local healing at least comparable to synthetic hydroxyapatite and anti-resorptive drugs. This opens the possibility of promoting faster healing in a new generation of high-performance bone repair devices.

Pezzotti (2018) reported that the peculiar surface chemistry of bulk Si_3N_4 bioceramic in an aqueous environment has the potential to reduce implant-associated bacterial infections. Similar to the antibacterial effect exerted by reactive oxygen species (ROS) from TiO_2 , reactive nitrogen species (RNS), such as nitrous oxide (N_2O), nitric oxide (NO), and peroxyxynitrite (OONO) in Si_3N_4 , severely affect bacterial metabolism and lead to their lysis. Functioning as a spontaneous NO donor, the Si_3N_4 surface provides a slow and constant release of such a potent bactericidal agent. A spike in NO concentration was directly monitored in living bacteria after 24 h exposure to Si_3N_4 substrates, which coincided with the beginning of DNA degradation observed by in situ Raman spectroscopy. After 48 h, the DNA of bacteria showed complete destruction on Si_3N_4 . RNS developed on Si_3N_4 substrates were more efficient in inducing bacterial lysis than ROS developed on TiO_2 .

Pezzotti (2019) considers that the use of silicon nitride in biomedical applications has been an “unexpected gift”. While it retains all of its engineered mechanical properties, it has unusual surface chemistry such that when it is immersed in an aqueous environment, slow elution of Si and N from its surface enhances healing of soft and osseous tissue, inhibits bacterial proliferation and even eradicates viruses. He poses the question: “How can this unique bioceramic be both friendly to mammalian cells while concurrently destroying invasive pathogens?” This unparalleled characteristic can be explained by the pH-dependent kinetics of two species – NH_4^+ and NH_3 – both of which are leached from the wet Si_3N_4 surface. A deeper understanding of the chemical interactions of bioceramics with living tissue will ultimately lead to new therapeutic strategies.

Fabrication Techniques

Rahaman and Xiao (2018) have reviewed recent developments in the design, processing, and evaluation of silicon nitride implants for biomedical applications. Si_3N_4 components are manufactured using conventional ceramic fabrication methods, such as die and cold isostatic pressing, injection molding and slip casting. Some of these allow near-net-shape fabrication of complex shapes whereas some often require post-fabrication diamond machining to produce the requisite shape and dimensions which can be costly.

Some biomedical implants may require a composite architecture composed of a dense (outer) region to provide strength to support physiological loads and a porous (inner) region with the requisite porosity and pore size for bone infiltration and integration with host bone. Conventional forming methods are limited in their ability to produce microstructures with a controlled spatial distribution of porosity and the requisite pore size to facilitate osseointegration. In comparison, additive manufacturing techniques such as robocasting can provide better control of the shape and architecture of silicon nitride green parts. Robocasting is a colloidal-based method based on computer-controlled layer-by-layer deposition of a highly concentrated suspension (slurry or paste) through a nozzle of diameter $\sim 100\text{ }\mu\text{m}$ to $\sim 1\text{ mm}$. Thus, additive manufacturing methods could provide a viable route for creating custom orthopaedic implants with the desired shape, architecture, and precise dimensions.

Summary – Silicon Nitride

Silicon nitride has been shown to have very interesting and unique properties. It can be created with a smooth or microrough surface topography, and its surface chemistry can be varied from a silica-rich to a predominantly N-rich composition, which can influence the response of cells, tissues, and bacteria in vivo. Si_3N_4 implants have shown attractive osseointegration and anti-microbial activity in vivo. Commercially, it has been developed for spinal reconstruction devices but its use in orthopaedic applications has so far not been realised commercially. This is due partly to the long and costly process of approval by various regulatory authorities. It should also be noted that silicon nitride requires a different and more costly process for manufacture, i.e., sintering at higher temperatures than oxides and under a nitrogen atmosphere and, with higher hardness, it is more difficult to machine. However, the development of silicon nitride devices in orthopedics is expected to be realised in the near future.

Silicon Carbide

SiC exists in many polymorphic forms called polytypes where the coordination between Si and C is always tetrahedral and the structures differ only in the sequence of identical layers of Si atoms coordinated to four C atoms (Pandey and Krishna, 1975). β -SiC adopts the cubic zinc blende structure whereas the other common polymorphs have a hexagonal structure, related to the Wurtzite crystal structure and, for historical reasons, are collectively referred to as α -SiC. Silicon carbide has been developed as an engineering ceramic with excellent high-temperature strength, good oxidation and thermal shock resistance, high hardness, and low specific weight. Because of its strong covalent bonding character, as with silicon nitride, SiC requires the use of sintering additives and external pressure to enable densification.

Both α - and β -SiC powders can be densified at temperatures of 1850–2000°C with the addition of Al_2O_3 and Y_2O_3 which involves liquid-phase-sintering (Lee and Kim, 1994). With α -SiC, the microstructure consisted of equiaxed SiC grains, whereas with β -SiC, a platelike grain structure resulted from the grain growth associated with the $\beta \rightarrow \alpha$ -SiC phase transformation during sintering. As grain size increased for the sintered SiC from α -SiC powder, fracture toughness increased slightly whereas for the sintered SiC from β -SiC powder, fracture toughness increased significantly which was attributed to crack bridging and crack deflection by the platelike α -SiC grains.

Silicon carbide ceramics have been considered as potential materials for biomedical applications (Rade *et al.*, 2013). SiC showed good wetting properties but bioactivity, estimated on the basis of hydroxyapatite formation in simulated body fluid, was only achieved by surface modification. Much of the literature is concerned with property assessments of SiC rather than biomedical aspects.

Biomorphic SiC can be fabricated by controlled pyrolysis of wood to obtain a carbon scaffold and subsequent reactive infiltration with molten silicon at 1550°C to obtain the silicon carbide scaffold. Through this process, the microstructure of the final SiC product mimics that of the starting material with porosity ranging from 30% to 70% and resembles the cellular microstructure and mechanical characteristics of the bone (González *et al.*, 2003). It can be coated with bioglass for potential implant applications.

Cell morphology, proliferation, and osteogenic activity were successfully evaluated in biomorphic SiC scaffolds with MC3T3-E1 pre-osteoblasts up to 28 days (López-Álvarez *et al.*, 2013). After one day of incubation cells appeared closely attached to the SiC

ceramics with the flattened morphology typical of healthy osteoblasts starting to colonize the pores. On the 7th day of incubation several layers of cells covered the surface without any sign of cytotoxicity. Finally, after 28 days of cell culture micrographs showed a pre-mineralized extracellular matrix with a complex network of filopodia.

One problem facing the medical community today is the lack of biocompatible materials that are also capable of electronic operation. Such devices are currently implemented using silicon technology, which either has to be hermetically sealed so it cannot interact with the body or the material is only stable in vivo for short periods of time. For long term use (for example, permanent implanted devices such as glucose sensors, brain-machine-interface devices) a more robust material that the body does not recognize and reject as a foreign material is needed. Silicon carbide may be just such a material that will allow the development of advanced biomedical devices never thought possible for long-term use in vivo. SiC is a wide-band-gap semiconductor biocompatible material that offers higher power densities and lower energy losses, enabling lighter, more compact and higher efficiency products for biocompatible and long-term in vivo applications ranging from heart stent coatings to neurological implants and sensors (Saddow, 2016).

References

- Anderson, M.C., Olsen, R., 2010. Bone ingrowth into porous silicon nitride. *Journal of Biomedical Materials Research* 92A, 1598–1605.
- Bal, B.S., Khandkar, A., Lakshminarayanan, R., *et al.*, 2009. Fabrication and testing of silicon nitride bearings in total hip arthroplasty. *Journal of Arthroplasty* 24, 110–116.
- Bal, B.S., Rahaman, M.N., 2012. Orthopedic applications of silicon nitride ceramics. *Acta Biomaterialia* 8 (8), 2889–2898.
- Bock, R.M., McEntire, B.J., Bal, B.S., *et al.*, 2015. Surface modulation of silicon nitride ceramics for orthopaedic applications. *Acta Biomaterialia* 26, 318–330.
- Bodišová, K., Kašiarová, M., Domanická, M., *et al.*, 2013. Porous silicon nitride ceramics designed for bone substitute applications. *Ceramics International* 39, 8355–8362.
- Calis Acikbas, N., Yurdakul, H., Mandal, H., *et al.*, 2012. Effect of sintering conditions and heat treatment on the properties, microstructure and machining performance of α - β -SiAlON ceramics. *Journal of the European Ceramic Society* 32, 1321–1327.
- Ekström, T., Nygren, M., 1992. SiAlON ceramics. *Journal of the American Ceramic Society* 75 (2), 259–276.
- Fünfschilling, S., Fett, T., Hoffmann, M.J., *et al.*, 2009. Bridging stresses from R-curves of silicon nitrides. *Journal of Materials Science* 44, 3900–3904.
- González, P., Serra, J., Liste, S., *et al.*, 2003. New biomorphic SiC ceramics coated with bioactive glass for biomedical applications. *Biomaterials* 24 (26), 4827–4832.
- Gorth, D.J., Puckett, S., Ercan, B., *et al.*, 2012. Decreased bacteria activity on Si₃N₄ surfaces compared with peek or titanium. *International Journal of Nanomedicine* 7, 4829–4840.
- Guedes e Silva, C.C., König, B., Carbonari, M.J., *et al.*, 2008. Bone growth around silicon nitride implants – An evaluation by scanning electron microscopy. *Materials Characterization* 59, 1339–1341.
- Hampshire, S., 2016. Chapter 5 – Silicon nitride ceramics. In: Ohji, T., Singh, M. (Eds.), *Engineered Ceramics: Current Status and Future Prospects*. Hoboken, NJ: John Wiley & Sons, pp. 79–97.
- Hampshire, S., Park, H.K., Thompson, D.P., Jack, K.H., 1978. α -Sialon ceramics. *Nature* 274, 880–882.
- Hampshire, S., Pomeroy, M.J., 2012. Grain boundary glasses in silicon nitride: A review of chemistry, properties and crystallisation. *Journal of the European Ceramic Society* 32, 1925–1932.
- Howlett, C.R., McCartney, E., Ching, W., 1989. The effect of silicon nitride ceramic on rabbit skeletal cells and tissue. An in vitro and in vivo investigation. *Clinical Orthopaedic and Related Research* 244, 293–304.
- Jack, K.H., Wilson, W.I., 1972. Ceramics based on the Si-Al-O-N and related systems. *Nature Physical Sciences* 238 (80), 28–29. (London).
- Jones, J.R., 2013. Review of bioactive glass: From Hench to hybrids. *Acta Biomaterialia* 9, 4457–4486.
- Kue, R., Sohrabi, A., Nagle, D., Frondoza, C., Hungerford, D., 1999. Enhanced proliferation and osteocalcin production by human osteoblast-like MG63 cells on silicon nitride ceramic discs. *Biomaterials* 20, 1195–1201.
- Lee, S.K., Kim, C.H., 1994. Effects of α -SiC vs. β -SiC starting powders on microstructure and fracture toughness of SiC sintered with Al₂O₃-Y₂O₃ additives. *Journal of the American Ceramic Society* 77, 1655–1658.
- López-Álvarez, M., Rodríguez-Valencia, C., Serra, J., González, P., 2013. Bio-Inspired ceramics: Promising scaffolds for bone tissue engineering. *Procedia Engineering* 59, 51–58.
- Mandal, H., 1999. New developments in α -SiAlON ceramics. *Journal of the European Ceramic Society* 19, 2349–2357.
- Mangels, J.A., Tennenhouse, G.J., 1980. Densification of reaction bonded silicon nitride. *American Ceramic Society Bulletin* 59, 1216–1222.
- Mazzocchi, M., Bellosi, A., 2008. On the possibility of silicon nitride as a ceramic for structural orthopaedic implants. Part I: processing, microstructure, mechanical properties, cytotoxicity. *Journal of Materials Science: Materials in Medicine* 19, 2881–2887.
- Mazzocchi, M., Gardini, D., Traverso, P.L., Faga, M.G., Bellosi, A., 2008. On the possibility of silicon nitride as a ceramic for structural orthopaedic implants. Part II: chemical stability and wear resistance in body environment. *Journal of Materials Science: Materials in Medicine* 19, 2889–2896.
- McEntire, B.J., Bal, B.S., Rahaman, M.N., Chevalier, J., Pezzotti, G., 2015. Ceramics and ceramic coatings in orthopaedics. *Journal of the European Ceramic Society* 35, 4327–4369.
- Moulson, A.J., 1979. Review – Reaction-bonded silicon nitride: Its formation and properties. *Journal of Materials Science* 14, 1017–1051.
- Olofsson, J., Grehk, T.M., Berlind, T., *et al.*, 2012. Evaluation of silicon nitride as a wear resistant and resorbable alternative for total hip joint replacement. *Biomaterials* 2 (2), 94–102.
- Pandey, D., Krishna, P., 1975. Influence of stacking faults on the growth of polytype structures. II. Silicon carbide polytypes. *Philosophical Magazine* 31 (5), 1133–1148.
- Petzow, G., Herrmann, M., 2002. Silicon nitride ceramics. In: Jansen, M. (Ed.), *High Performance Non-Oxide Ceramics II*. Berlin Heidelberg: Springer-Verlag, pp. 47–167.
- Pezzotti, G., 2018. A spontaneous solid-state NO donor to fight antibiotic resistant bacteria. *Materials Today Chemistry* 9, 80–90.
- Pezzotti, G., 2019. Silicon nitride: A bioceramic with a gift. *ACS Applied Material Interfaces* 11 (30), 26619–26636.
- Pezzotti, G., Marin, E., Adachi, T., *et al.*, 2017a. Bioactive silicon nitride: a new therapeutic material for osteoarthritis. *Nature Scientific Reports* 7, 4484. doi:10.1038/srep44848.
- Pezzotti, G., McEntire, B., Bock, R.M., *et al.*, 2016. In situ spectroscopic screening of osteosarcoma living cells on stoichiometry-modulated silicon nitride bioceramic surfaces. *ACS Biomaterials Science and Engineering* 2 (7), 1121–1134.
- Pezzotti, G., Oba, N., Zhu, W., *et al.*, 2017b. Human osteoblasts grow transitional Si/N apatite in quickly osteointegrated Si₃N₄ cervical insert. *Acta Biomaterialia* 64, 411–420.
- Rade, K., Martinčič, A., Novak, S., Kobe, S., 2013. Feasibility study of SiC-ceramics as a potential material for bone implants. *Journal of Materials Science* 48, 5295–5301.
- Rahaman, M., Xiao, W., 2018. Silicon nitride bioceramics in healthcare. *International Journal of Applied Ceramic Technology* 15, 861–872.
- Riley, F.L., 2000. Silicon nitride and related materials. *Journal of the American Ceramic Society* 83 (2), 245–265.

- Saddow, S., 2016. Chapter 1 – Silicon carbide materials for biomedical applications. In: Saddow, S. (Ed.), *Silicon Carbide Biotechnology: A Biocompatible Semiconductor for Advanced Biomedical Devices and Applications*, second ed. London: Elsevier, pp. 1–25.
- Sorrell, C.C., Hardcastle, P.H., Druitt, R.K., Howlett, C.R., McCartney, E., 2004. Results of 15-year clinical study of reaction-bonded silicon nitride intervertebral spacers. In *Proceedings of the 7th World Biomaterials Congress*. Sydney: Australian Society for Biomaterials, p. 1872.
- Sun, E.Y., Becher, P.F., Plucknett, K.P., *et al.*, 1998. Microstructural design of silicon nitride with improved fracture toughness: ii. Effects of yttria and alumina additives. *Journal of the American Ceramic Society* 81 (11), 2831–2840.
- Webster, T.J., Patel, A.A., Rahaman, M.N., Bal, B.S., 2012. Anti-infective and osteointegration properties of silicon nitride, poly(ether ether ketone), and titanium implants. *Acta Biomaterialia* 8 (12), 4447–4454.
- Ziegler, G., Heinrich, J., Wötting, G., 1987. Relationships between processing, microstructure and properties of dense and reaction-bonded silicon nitride. *Journal of Materials Science* 22, 3041–3086.

Carbon in Biomedical Engineering

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Introduction

Carbons are ubiquitous materials that are easily recognizable in a wide variety of forms, such as graphite and diamond. Each type of carbon has a specific atomic structure and mechanical properties. As carbon is prevalent in all living organisms, it seemed natural to examine the material for potential use in biomedical engineering. It has long been established that medically relevant carbons do not elicit an adverse reaction in the host tissue, and conversely, the host environment does not have a harmful effect on the carbon material.

Carbons were first studied as a biomaterial in the late 1960s, when pyrolytic carbon was used for a component of mechanical heart valve implants. Since then, two other types of carbon have also been used in biomedical applications. Vitreous (glassy) carbon has been used as an electrode material for pacemakers (Beyersdorf *et al.*, 1988), neural implants (Vomero *et al.*, 2019) and glucose biosensors (Castrignanò *et al.*, 2016), to name a few. Also, in the past, vapor-deposited carbon has been coated onto vascular grafts (Aebischer *et al.*, 1988; Bernex *et al.*, 1992).

Pyrolytic carbon has emerged as a material that is extensively used in biomedical engineering. It is also referred to as low temperature isotropic, or LTI carbon. Pyrolytic carbon is a coating that is applied to a substrate, typically graphite. The coating is approximately 0.1–1 mm thick. Pyrolytic carbon has been alloyed with approximately 7% silicon (Si) to enhance the strength and hardness of the material, which improves wear resistance. While the Si-alloyed material is successful in cardiovascular and orthopedic practices, unalloyed pyrolytic carbon is most often used in biomedical applications today.

Structure of Pyrolytic Carbon

Pyrolytic carbon has a crystal structure that is loosely similar to that of graphite. The structure of graphite consists of carbon atoms arranged in planar hexagonal arrays (Bokros, 1977). Strong covalent bonds exist between the atoms in the basal plane. The planar arrays are stacked in an ordered ABAB sequence to produce a hexagonal close-packed crystal lattice. The carbon atoms between adjacent planes are bound by weaker van der Waals bonds (Bokros, 1977; More *et al.*, 2013).

In contrast to graphite, pyrolytic carbon has a turbostratic structure. The basal planes are warped and contain defects, such as missing carbon atoms. The crystallites are relatively small. The layers within the crystallites lie roughly parallel to one another, but the atoms in one layer may have no additional relationship to those in other layers of the same crystallite. The stacking of the planes is haphazard, and thus there is very little order in the direction perpendicular to the planes. This results in higher bonding strengths between the planes, and contributes to enhanced mechanical properties such as fatigue resistance and wear resistance (Bokros, 1977; More *et al.*, 2013; Tian *et al.*, 1993).

Fabrication of Pyrolytic Carbon

Pyrolytic carbon is often deposited as a coating, with a thickness of 0.1–1 mm, onto a graphite substrate (Bellemère, 2018; More *et al.*, 2013) through a process called pyrolysis. During this procedure, ceramic particles are placed into a vertical tube reactor. A flow of inert gas, such as argon, nitrogen or helium, causes the particles to levitate, creating a fluidized bed. The substrate to be coated is added into the fluidized bed, which is then heated to 1500°C. A hydrocarbon gas such as propane or methane is passed through the bed and, due to the high temperature, the hydrocarbon is thermally decomposed, or pyrolyzed. As a result, carbon atoms are deposited onto the substrate, where they coalesce to form the coating (Bellemère, 2018; More *et al.*, 2013).

Mechanical Properties of Pyrolytic Carbon

The mechanical properties of pyrolytic carbon make it an ideal material for medical applications. Its modulus of elasticity ranges from 20 to 29 GPa, which is similar to that of cortical bone (18–20 GPa) (Bellemère, 2018; More *et al.*, 2013). As a result, the carbons are mechanically compatible with bone. The stresses are distributed more equally between carbon and bone while minimizing areas of stress concentration, thus preventing stress shielding and the associated bone weakening and loss.

Pyrolytic carbon is not susceptible to fatigue failure (Bellemère, 2018; Bernex *et al.*, 1992; More *et al.*, 2013). During cyclical testing, the material does not fail at stresses below the fatigue limit. However, at stresses above the fatigue limit, the material fails during the first cycle of loading. Thus, the fatigue limit is equal to the static strength (Beyersdorf *et al.*, 1988; Shim, 1974). The inherent resistance of pyrolytic carbon to fatigue failure is related to the lack of mobile defects in the turbostratic structure of the

materials, which, when present, provide a mechanism for fatigue crack propagation. Because of this behavior, pyrolytic carbon is suitable for use in applications that experience cyclic loads, such as artificial heart valves and joint replacement devices.

The hardness of a material serves as an indication of wear resistance. Materials with higher hardness numbers are more resistant to wear. Pyrolytic carbon has a hardness of 236 DPH (More *et al.*, 2013), and therefore exhibits excellent wear resistance.

Biocompatibility of Pyrolytic Carbon

Carbon, in general, displays good biocompatibility with the human body, as the element is naturally abundant in the biological system. More specifically, pyrolytic carbon possesses excellent biocompatibility in blood, and in soft and hard tissues.

The proper functioning of blood flow through the cardiovascular system depends on a precise balance between blood proteins and cells. Any slight change in this balance can lead to blood coagulation. Most foreign materials, when placed in contact with blood, will induce coagulation. However, pyrolytic carbon has demonstrated good to excellent thromboresistance, and may interact with blood without inducing clot formation (Bokros, 1977). Pyrolytic carbon is a hydrophobic material which promotes protein adsorption, resulting in a protein layer on the surface (Bellemère, 2018). The thromboresistance of pyrolytic carbon is confirmed by many years of success with pyrolytic carbon mechanical heart valve implants.

Pyrolytic carbon also exhibits excellent biocompatibility in both soft and hard tissues. Bone has been shown to grow up to the surface of the material without an intervening fibrous capsule, thus fixation can occur via direct bone apposition. Pyrolytic carbon does not induce a foreign body reaction or inflammatory response in adjacent tissue. Furthermore, it does not elicit a systemic response in the major organs, tissues, blood and urine.

Many materials are inert in the body in bulk form, but in particulate form induce a severe inflammatory reaction. Pyrolytic carbon particles, however, induce a minimal, passive response. Carbon particulates on the order of one micron provoke no inflammatory reaction when injected into the peritoneal cavity and placed surgically into the knee joints of rats (Helbing *et al.*, 1977). The particles migrate from the site of implantation through the lymphatic system and accumulate in the lymph nodes. There is no apparent damage to the lungs, liver, spleen, lymph nodes, or kidneys.

Applications of Biomedical Carbons

Cardiovascular Applications

As a result of excellent thromboresistance and good mechanical properties, carbons have been used in cardiovascular applications, primarily in mechanical heart valves. The heart beats an average of 38 million times a year, and therefore the materials used to fabricate mechanical heart valves must be able to withstand cyclic stress and wear, while minimizing clot formation. Today, over 182,000 heart valves are replaced annually, the majority of which contain pyrolytic carbon components.

In 1969, pyrolytic carbon was first used in artificial heart valves with a caged ball design (Gott *et al.*, 2003). The ball was made of pyrolytic carbon while the cage was composed of titanium. The implant was eventually discontinued when the pyrolytic carbon ball was found to erode the titanium struts. In the early 1970s, non-tilting disc valves with pyrolytic carbon occluders were introduced, however they were also discontinued due to the wear of the fabric covering the titanium housing (Gott *et al.*, 2003). Additionally in the early 1970s, the first mechanical heart valves with a pyrolytic carbon tilting convex disc occluder were created (Gott *et al.*, 2003). Subsequent designs included those in which the disc was contained by prongs or via a guide strut through the center of the disc. Several mechanical valves with pyrolytic carbon tilting disc occluders are currently still in use, including one design in which the housing is also made of pyrolytic carbon. In 1977, the pyrolytic carbon bileaflet valve design, consisting of two semi-circular leaflets, was introduced (Gott *et al.*, 2003). When the leaflets open, a central and two peripheral channels are created for blood flow. The implant was the first mechanical heart valve in which all components (housing and leaflets) were made of pyrolytic carbon. This implant design is the most commonly used for mechanical heart valves (Bloomfield, 2002).

Pyrolytic carbon mechanical valves are widely used for the replacement of the aortic (Saito *et al.*, 2016; Chan *et al.*, 2010; Chambers *et al.*, 2013; Bouchard *et al.*, 2014) and mitral (Saito *et al.*, 2016; Chan *et al.*, 2010; Chambers *et al.*, 2013; Murana *et al.*, 2018; Bouchard *et al.*, 2014) valves. Studies have compared the mortality rate between aortic valve replacement and mitral valve replacement. Early mortality rate (within 30 days of implantation) ranged from 0.9% to 4.4% for aortic valve replacement, and from 2.2% to 7.9% for mitral valve replacement (Saito *et al.*, 2016; Chan *et al.*, 2010; Chambers *et al.*, 2013; Bouchard *et al.*, 2014). Late mortality rate ranged from 16.9% to 30.8% for aortic valve replacement, and from 31.0% to 38.9% for mitral valve replacement (Saito *et al.*, 2016; Bouchard *et al.*, 2014). Furthermore, aortic valve replacement demonstrated a lower valve-related mortality rate (5.2% to 8.8%) compared to that for the mitral valve replacement (11.0% to 12.3%) (Saito *et al.*, 2016; Bouchard *et al.*, 2014). Regarding hemorrhaging, the five-year freedom from bleeding was 93.6% (Chan *et al.*, 2010) and the 30-year freedom from bleeding was 95.6% (Saito *et al.*, 2016) for aortic valve replacement. With respect to mitral valve replacement, the five-year freedom from bleeding was 95.7% (Chan *et al.*, 2010) and the 30-year freedom from bleeding was 93.0% (Saito *et al.*, 2016). Considering blood clotting, the five-year freedom from thromboembolism was 96.5% (Chan *et al.*, 2010) and the 30-year freedom from thromboembolism was 88.6% (Saito *et al.*, 2016) for aortic valve replacement. The five-year freedom from thromboembolism with mitral valve replacement was 97.7% (Chan *et al.*, 2010), while the 30-year freedom from thromboembolism was

79.8% (Saito *et al.*, 2016). In general, while both valve replacements have excellent outcomes at intermediate and long-term follow-up, the aortic valve replacement performs better than the mitral valve replacement.

Pyrolytic carbon bileaflet mechanical valves have also been used for double valve replacements, in which both the aortic and mitral valves are replaced (Saito *et al.*, 2016; Chambers *et al.*, 2013). Long-term studies found that the early mortality rate with a double valve replacement ranged from 3.6% to 4.3% (Saito *et al.*, 2016; Chambers *et al.*, 2013), while the late mortality rate was 35.2% and the valve-related mortality rate was 9.2% (Saito *et al.*, 2016). The linearized late mortality rate was 4.1% per patient-year, while the linearized valve-related rate was 1.8% per patient-year (Chambers *et al.*, 2013). With respect to the incidence of hemorrhage and clotting, the 30-year freedom from excessive bleeding was 90.4%, and the 30-year freedom from thromboembolism was 80.8%. These values were significantly less than with aortic valve replacement alone, at $p < 0.05$ and $p < 0.0001$, respectively (Saito *et al.*, 2016). Thus, double valve replacement demonstrated very good outcomes but did not perform as well as single valve replacement.

Although uncommon, pyrolytic carbon bileaflet valves have been used for the replacement of the tricuspid valve (Zhu *et al.*, 2018). In this study of 265 cases, thrombosis of the valve was noted in 3.8% of the replacements, however in the majority of the cases the cause was due to the inappropriate use of anticoagulants. Three implants had to be replaced due to thrombosis. The survival rate was 89.2% after five years and 86.6% after 10 years, though only two deaths were associated with valve complications. Overall, the long-term outcomes for replacement of the tricuspid valve with a pyrolytic carbon bileaflet valve were good.

Orthopedic Applications

Hand and wrist implants

Pyrolytic carbon implants have been used extensively in the replacement of the small joints of the hand and wrist. The primary reason for the replacement of these joints is arthritis, although trauma can result in the placement of an implant. The proximal interphalangeal (PIP) joint of the hand is the third most common site for osteoarthritis, and when conservative treatments are no longer effective, surgical intervention includes arthrodesis or arthroplasty. While the gold standard for PIP joint arthroplasty is replacement with a silicone implant, pyrolytic carbon prostheses have increasingly been used. The implant is a two-component semi-constrained device. The proximal component is bicondylar in design, while the distal component has two concave surfaces to articulate against the proximal component. The implant is press-fit and allows for bone growth up to the implant.

Clinical studies on the use of pyrolytic carbon PIP implants have demonstrated that, in general, patients experience a significant decrease in pain both at rest and during activity at medium-term and long-term follow-up (Wagner *et al.*, 2018; Wijk *et al.*, 2010; Daecke *et al.*, 2012; Chung *et al.*, 2009; Ono *et al.*, 2012; Herren *et al.*, 2006; Tagil *et al.*, 2014; Watts *et al.*, 2012; Reissner *et al.*, 2014; Mashhadi *et al.*, 2012; Sweets and Stern, 2011; Bravo *et al.*, 2007; Tuttle and Stern, 2006; Adams *et al.*, 2012). Additionally, there was general patient satisfaction with the outcomes (Wijk *et al.*, 2010; Chung *et al.*, 2009; Ono *et al.*, 2012; Tagil *et al.*, 2014; Desai *et al.*, 2014; Sweets and Stern, 2011; Tuttle and Stern, 2006) and range of motion was unchanged in the majority of the studies (Wagner *et al.*, 2018; Wijk *et al.*, 2010; Daecke *et al.*, 2012; Chung *et al.*, 2009; Ono *et al.*, 2012; Nunley *et al.*, 2016; Branam *et al.*, 2007; Herren *et al.*, 2006; Tagil *et al.*, 2014; Dickson *et al.*, 2015b; Watts *et al.*, 2012; Mashhadi *et al.*, 2012; Bravo *et al.*, 2007; Tuttle and Stern, 2006). Sweets and Stern (2011), however, found that the range of motion of the PIP joint significantly improved from pre-operative measurements to approximately one-year post-operatively, but then decreased to below pre-operative values at a mean final follow-up of 55 months. With respect to grip strength, most of the research suggests that, after pyrolytic carbon PIP joint arthroplasty, there is no change in strength (Wagner *et al.*, 2018; Wijk *et al.*, 2010; Daecke *et al.*, 2012; Chung *et al.*, 2009; Ono *et al.*, 2012; Nunley *et al.*, 2016; Branam *et al.*, 2007; Tagil *et al.*, 2014; Bravo *et al.*, 2007).

Complication rates associated with pyrolytic carbon PIP joint arthroplasty are reportedly higher than those related to silicone PIP implants (Squiteri and Chung, 2008; Chan *et al.*, 2013). Common complications include loosening of the implant (Daecke *et al.*, 2012; Nunley *et al.*, 2016; Branam *et al.*, 2007; Herren *et al.*, 2006; Tagil *et al.*, 2014; Dickson *et al.*, 2015b; Watts *et al.*, 2012; Sweets and Stern, 2011; Bravo *et al.*, 2007; Tuttle and Stern, 2006; Adams *et al.*, 2012), dislocation of the implant (Daecke *et al.*, 2012; Chung *et al.*, 2009; Ono *et al.*, 2012; Branam *et al.*, 2007; Sweets and Stern, 2011; Tuttle and Stern, 2006), joint stiffness (Dickson *et al.*, 2015b; Watts *et al.*, 2012; Desai *et al.*, 2014), joint instability (Dickson *et al.*, 2015b; Watts *et al.*, 2012; Mashhadi *et al.*, 2012; Bravo *et al.*, 2007) and persistent pain (Wijk *et al.*, 2010; Nunley *et al.*, 2016; Tagil *et al.*, 2014; Bravo *et al.*, 2007). Squeaking of the implant has been reported (Chung *et al.*, 2009; Ono *et al.*, 2012; Branam *et al.*, 2007; Dickson *et al.*, 2015b; Watts *et al.*, 2012; Mashhadi *et al.*, 2012; Desai *et al.*, 2014; Sweets and Stern, 2011; Tuttle and Stern, 2006), however this did not appear to affect the performance of the device and patient satisfaction. Reviews of the literature indicate that there is no evidence to replace the silicone PIP implant with a pyrolytic device as the gold standard for treatment (Squiteri and Chung, 2008; Chan *et al.*, 2013).

Pyrolytic carbon implants have also been used to replace the metacarpophalangeal (MCP) joint of the hand. An early clinical study of the use of pyrolytic carbon to replace this joint demonstrated that at long-term follow-up (average 11.7 years post-operative), range of motion (ROM) was increased by an average of 13 degrees with no resorption of bone (Cook *et al.*, 1999). Pyrolytic carbon was found to be a suitable material for the replacement of the MCP joint. Since then, further clinical studies have shown that, in general, patients experience a decrease in pain (Nunez and Citron, 2005; Parker *et al.*, 2007; Parker *et al.*, 2006; Dickson *et al.*, 2015a; Aujla *et al.*, 2017) at both medium-term and long-term follow-up. Many of the studies also indicated an increase in pinch and grip strengths (Nunez and Citron, 2005; Parker *et al.*, 2007; Parker *et al.*, 2006; Wall and Stern, 2013; Simpson-White and Chojnowski, 2014; Dickson *et al.*, 2015a), and an increased satisfaction with functionality and appearance (Nunez and Citron, 2005; Parker *et al.*, 2007, 2006; Wall and Stern, 2013; Simpson-White and Chojnowski, 2014; Dickson *et al.*, 2015a; Aujla *et al.*, 2017). The literature presents

conflicting data regarding change in ROM after MCP joint replacement with pyrolytic carbon implants, but increases in ROM were more often observed at longer follow-up periods (Wall and Stern, 2013; Simpson-White and Chojnowski, 2014; Aujla *et al.*, 2017). Complications associated with pyrolytic carbon MCP joint implants include extensor tendon pathology (Parker *et al.*, 2007, 2006; Wall and Stern, 2013; Houdek *et al.*, 2015), stiffness (Parker *et al.*, 2007; Wall and Stern, 2013; Houdek *et al.*, 2015; Dickson *et al.*, 2015a), subluxation or dislocation of the implant (Parker *et al.*, 2007, 2006; Dickson *et al.*, 2015a), and implant fracture (Simpson-White and Chojnowski, 2014; Houdek *et al.*, 2015; Dickson *et al.*, 2015a).

The use of pyrolytic carbon implants to replace the trapeziometacarpal joint in the wrist has been explored. Hemiarthroplasty implants have been used in which the proximal aspect of the first metacarpal is replaced (Vitale *et al.*, 2017; Martinez de Aragon *et al.*, 2009; Caudwell *et al.*, 2018), however long-term follow-up has not been conducted. Medium-term studies have shown that there is an increase in grip strength (Vitale *et al.*, 2017; Martinez de Aragon *et al.*, 2009), radial abduction (Vitale *et al.*, 2017), and oppositional and appositional pinch (Vitale *et al.*, 2017; Martinez de Aragon *et al.*, 2009). However, revision surgery can result from subluxation, displacement or fracture of the implant (Vitale *et al.*, 2017; Martinez de Aragon *et al.*, 2009; Caudwell *et al.*, 2018), loosening (Martinez de Aragon *et al.*, 2009), pain (Martinez de Aragon *et al.*, 2009), and bone fracture (Martinez de Aragon *et al.*, 2009). At a mean follow-up of 6.5 years, there was no significant difference in grip or pinch strength between the operated and contralateral sides (Caudwell *et al.*, 2018). Furthermore, when compared to a suspensionplasty procedure, there was a significantly higher number of major complications and joint revision surgery when pyrolytic carbon hemiarthroplasty implants were used to treat arthritis of the joint (Vitale *et al.*, 2017). More research on pyrolytic carbon hemiarthroplasty implants for the replacement of the trapeziometacarpal joint is necessary.

Pyrolytic carbon interposition implants have also been studied for the treatment of arthritis of the trapeziometacarpal joint (Colgate-Stone *et al.*, 2011; Szalay *et al.*, 2013; Barrera-Ochoa *et al.*, 2014; Agout *et al.*, 2016). In this case, the implant is used to replace the trapezium after a trapeziectomy. While the implant results in a significant decrease in symptoms and pain (Colgate-Stone *et al.*, 2011), and patients are satisfied with the outcomes (Barrera-Ochoa *et al.*, 2014), complications such as implant dislocation and persistent pain do occur (Colgate-Stone *et al.*, 2011; Szalay *et al.*, 2013; Barrera-Ochoa *et al.*, 2014). In the early stages of investigating pyrolytic carbon as an interposition implant to replace the trapezium, the superiority of the pyrolytic carbon implant was not able to be proved. Given the high cost of the implant, high learning curve for the surgical technique and extended surgery time, surgeons at the time discontinued the use of the implant in their practice (Colgate-Stone *et al.*, 2011; Szalay *et al.*, 2013). However, a study that looked at the interposition implant with a minimum 10-year follow-up period (average 10.5 years) found that grip strength, key pinch strength, and pain levels improved considerably, and that the vast majority of patients were satisfied with the device (Agout *et al.*, 2016).

Although less frequently, pyrolytic carbon implants have been used to replace other small bones or joints in the wrist. Early results from the replacement of the scaphotrapeziotrapezoid joint with a pyrocarbon interposition implant, either circular (Pegoli *et al.*, 2006) or rectangular (Gauthier *et al.*, 2017) in shape, indicate improvement in pain, symptoms, and strength. However, longer-term studies with a greater sample size are needed. Preliminary studies on the replacement of the radiocarpal and midcarpal joints with an olive-shaped pyrocarbon interposition implant as a primary or revision procedure have been reported (Daruwalla *et al.*, 2012; Bellemère *et al.*, 2012a,b; Pierrart *et al.*, 2012). In the procedure, the implant replaces the lunate, proximal two-thirds of the scaphoid and a small section of the head of the capitate. Early results from these studies indicate high satisfaction with the device and considerable improvement in pain and function, but little, if any, change in mobility and grip strength. Further studies with a larger sample size and longer follow-up are warranted on this implant. Finally, an ovoid-shaped pyrocarbon interposition implant with adaptive mobility that occurs with motion of the wrist has been studied for the replacement of the proximal pole of the scaphoid in cases of nonunion due to avascular necrosis (Gras *et al.*, 2012; Aribert *et al.*, 2019), scaphoid nonunion advanced collapse (SNAC) wrist (Daruwalla *et al.*, 2013; Santos *et al.*, 2018; Aribert *et al.*, 2019), and radioscapoid osteoarthritis (Daruwalla *et al.*, 2013; Aribert *et al.*, 2019). With follow-up ranging from an average 1.6–10 years, the results are encouraging. Improvement in pain (Gras *et al.*, 2012; Daruwalla *et al.*, 2013; Santos *et al.*, 2018; Aribert *et al.*, 2019) and function (Gras *et al.*, 2012; Daruwalla *et al.*, 2013; Aribert *et al.*, 2019) were reported. In long-term follow-up studies, an increase in grip strength was noted (Gras *et al.*, 2012; Aribert *et al.*, 2019), however the grip strength was less than that on the contralateral side at shorter follow-up periods (Daruwalla *et al.*, 2013; Santos *et al.*, 2018).

Shoulder implants

The pyrolytic carbon interposition shoulder arthroplasty (PISA) is a relatively new implant to replace the humeral head. It consists of a graphite sphere coated with pyrolytic carbon, and is placed freely within a cavity created in the proximal aspect of the humerus. It was developed in response to the poor performance of metallic humeral heads of hemi-shoulder arthroplasties that articulate with the glenoid cavity. This innovative implant was used in a study of 61 patients who presented with primary osteoarthritis, avascular necrosis, or post-instability or post-fracture secondary osteoarthritis (Garret *et al.*, 2017). At a mean follow-up of 26.8 months, improvements in pain, activity, mobility and strength were noted. However, radius of curvature and the free positioning of the implant were noted as potential causes of failure. A longer term study (mean follow-up of 42.8 months) using the same implant was conducted in 10 patients who presented with advanced collapse of the humeral head after post-fracture avascular necrosis (Hudek *et al.*, 2017). Patient satisfaction was high and the function of the shoulder was excellent. The study found that the collapse of the humeral head was a good indication for the use of PISA implants. Studies with longer follow-up periods and greater sample sizes are needed to fully assess the success of the implant.

A hemi-shoulder arthroplasty was evaluated for the replacement of the humeral head (Garret *et al.*, 2019). The implant consisted of a pyrolytic carbon humeral head on a cobalt-chromium taper that connected to a convertible humeral stem. The study of 61 patients included 37 individuals with primary osteoarthritis, 11 with osteonecrosis, 11 with secondary osteoarthritis and two with rheumatoid arthritis. With a mean follow-up of 25.9 months, there was improvement in both pain and activity level. However, the outcomes were based on the etiology of the shoulder pathology. Replacement due to atraumatic osteonecrosis and post-instability secondary osteoarthritis produced satisfactory results, while those for post-traumatic osteonecrosis and post-traumatic secondary osteoarthritis resulted in poor outcomes. Patients with rheumatoid arthritis were satisfied with the surgery, although the outcomes were not exceptional. More research is needed on this implant.

Carbon Fibers

Carbon fibers are lightweight, high strength, flexible, biocompatible and chemically stable. They are produced by pyrolyzing organic precursor fibers such as pitch, polyacrylonitrile (PAN) and rayon (Migliaresi, 2013). The fibers can be used alone or as part of a composite material. Composites are a combination of two or more materials that, when used together, significantly improve the performance of the material. They consist of a matrix material and fiber material, which can be the same or different materials. Carbon fiber reinforced polymers have been used in cardiovascular, spinal, dental and orthopedic applications.

Carbon fiber reinforced polyetheretherketone (CFR-PEEK) is a material that is used frequently in biomedical applications. PEEK is a polymer with excellent biocompatibility, high strength, chemical resistance and a modulus of elasticity similar to that of cortical bone. The addition of carbon fibers to PEEK further increases the mechanical strength of the material. The type of carbon fiber has an effect on the static and fatigue behavior of CFR-PEEK (Bonnheim *et al.*, 2019). Composites with PAN carbon fibers had a significantly higher modulus of elasticity and ultimate tensile strength compared to those with pitch carbon fibers. For both types of fibers, these properties were significantly greater than that for unreinforced PEEK. Additionally, both types of CFR-PEEK composites experienced brittle failure, while PEEK alone underwent some degree of plastic deformation before failure. With respect to fatigue behavior, PAN CFR-PEEK was more resistant to fatigue crack propagation, compared to pitch CFR-PEEK and PEEK alone.

Common orthopedic applications of CFR-PEEK include fracture fixation plates, such as those used for the repair of distal fibula fractures (Wilson *et al.*, 2016) and distal radius fractures (Mugnai *et al.*, 2018; Gallagher *et al.*, 2019). The material has also been investigated for use as intramedullary nails for musculoskeletal tumors (Piccioli *et al.*, 2017) and in total knee arthroplasty (Koh *et al.*, 2019). Spinal applications include pedicle screws for spinal fusion (Lindtner *et al.*, 2018). Finally, CFR-PEEK has been investigated for use in dental applications such as abutment screws (Neumann *et al.*, 2014; Schwitalla *et al.*, 2018).

Conclusion

Carbon has been shown to be mechanically and chemically suitable for use in the human body. Both pyrolytic carbon and carbon fibers have been widely used in biomedical applications. As fabrication techniques are continuously refined and improved, the properties of the material will be enhanced and new applications will be explored.

References

- Adams, J., Ryall, C., Pandyan, A., *et al.*, 2012. Proximal interphalangeal joint replacement in patients with arthritis of the hand. A meta-analysis. *Journal of Bone and Joint Surgery* 94B, 1305–1312.
- Aebischer, P., Goddard, M.B., Sassen, H.F., Hunter, T.J., Galletti, P.M., 1988. Tissue reaction to fabrics coated with turbostratic carbon: subcutaneous versus vascular implants. *Biomaterials* 9, 80–85.
- Agout, C., Ardouin, L., Bellemère, P., 2016. A ten-year prospective outcome study of Pi2 pyrocarbon spacer arthroplasty in carpometacarpal joint osteoarthritis. *Hand Surgery and Rehabilitation* 35, 255–261.
- Aribert, M., Bouju, Y., Chaise, F., *et al.*, 2019. Adaptive Proximal Scaphoid Implant (APSI): 10-year outcomes in patients with SNAC wrists. *Hand Surgery and Rehabilitation* 38, 34–43.
- Aujla, R.S., Sheikh, N., Dival, P., Bhowal, B., Dias, J.J., 2017. Unconstrained metacarpophalangeal joint arthroplasties. A systematic review. *Bone and Joint Journal* 99-B, 100–106.
- Barrera-Ochoa, S., Vidal-Tarrason, N., Correa-Vazquez, E., *et al.*, 2014. Pyrocarbon interposition (PyroDisk) implant for trapeziometacarpal osteoarthritis: Minimum 5-year follow-up. *Journal of Hand Surgery* 39, 2150–2160.
- Bellemère, P., 2018. Pyrocarbon implants for the hand and wrist. *Hand Surgery and Rehabilitation* 37, 129–154.
- Bellemère, P., Maes-Clavier, C., Loubesac, T., Gaisne, E., Kerjean, Y., 2012a. Amandys® implant: Novel pyrocarbon arthroplasty for the wrist. *Chirurgie de la Main* 31, 176–187.
- Bellemère, P., Maes-Clavier, C., Loubesac, T., *et al.*, 2012b. Pyrocarbon interposition wrist arthroplasty in the treatment of failed wrist procedures. *Journal of Wrist Surgery* 1, 31–38.
- Bernex, F., Mazzucotelli, J.P., Roudiere, J.L., *et al.*, 1992. In vitro endothelialization of carbon-coated Dacron vascular grafts. *International Journal of Artificial Organs* 15, 172–180.
- Beyersdorf, F., Schneider, M., Kreuzer, J., *et al.*, 1988. Studies of the tissue reaction induced by transvenous pacemaker electrodes. I. Microscopic examination of the extent of connective tissue around the electrode tip in the human right ventricle. *Pacing and Clinical Electrophysiology* 11, 1753–1759.
- Bloomfield, P., 2002. Choice of heart valve prosthesis. *Heart* 87, 583–589.
- Bokros, J.C., 1977. Carbon biomedical devices. *Carbon* 15, 355–371.

- Bonnheim, N., Ansari, F., Regis, M., Bracco, P., Pruitt, L., 2019. Effect of carbon fiber type on monotonic and fatigue properties of orthopedic grade PEEK. *Journal of the Mechanical Behavior of Biomedical Materials* 90, 484–492.
- Bouchard, D., Mazine, A., Stevens, L.-M., *et al.*, 2014. Twenty-year experience with the CarboMedics mechanical valve prosthesis. *Annals of Thoracic Surgery* 97, 816–823.
- Branam, B.R., Tuttle, H.G., Stern, P.J., Levin, L., 2007. Resurfacing arthroplasty versus silicone arthroplasty for proximal interphalangeal joint osteoarthritis. *Journal of Hand Surgery* 32A, 775–788.
- Bravo, C.J., Rizzo, M., Hormel, K.B., Beckenbaugh, R.D., 2007. Pyrolytic carbon proximal interphalangeal joint arthroplasty: results with minimum two-year follow-up evaluation. *Journal of Hand Surgery* 32A, 1–11.
- Castrignanò, S., Valetti, F., Gilardi, G., Sadeghi, S.J., 2016. Graphene oxide-mediated electrochemistry of glucose oxidase on glassy carbon electrodes. *Biotechnology and Applied Biochemistry* 63, 157–162.
- Caudwell, M., Bayne, G., Page, R.S., 2018. Anatomic pyrocarbon hemiarthroplasty for thumb carpometacarpal osteoarthritis in patients under 65 years: Mid term results. *Journal of Hand Surgery* 23, 469–473.
- Chambers, J.B., Pomar, J.L., Mestres, C.A., Palatianos, G.M., 2013. Clinical event rates with the On-X bileaflet mechanical heart valve: A multicenter experience with follow-up to 12 years. *Journal of Thoracic and Cardiovascular Surgery* 145, 420–424.
- Chan, K., Ayeni, O., McKnight, L., *et al.*, 2013. Pyrocarbon versus silicone proximal interphalangeal joint arthroplasty: A systematic review. *Plastic and Reconstructive Surgery* 131, 114–124.
- Chan, V., Jamieson, W.R.E., Lam, B.-K., *et al.*, 2010. Influence on the On-X mechanical prosthesis on intermediate term major thromboembolism and hemorrhage: A prospective multicenter study. *Journal of Thoracic and Cardiovascular Surgery* 140, 1053–1058.
- Chung, K.C., Ram, A.N., Shauver, M.J., 2009. Outcomes of pyrolytic carbon arthroplasty for the proximal interphalangeal joint. *Plastic and Reconstructive Surgery* 123, 1521–1532.
- Colgate-Stone, T.J., Garg, S., Subramanian, A., Mani, G.V., 2011. Outcome analysis of trapezectomy with and without pyrocarbon interposition to treat primary arthrosis of the trapeziometacarpal joint. *Hand Surgery* 16, 49–54.
- Cook, S.D., Beckenbaugh, R.D., Redondo, J., *et al.*, 1999. Long-term follow-up of pyrocarbon metacarpophalangeal implants. *Journal of Bone and Joint Surgery* 81, 635–647.
- Daecke, W., Kaszap, B., Martini, A.K., *et al.*, 2012. A prospective, randomized comparison of 3 types of proximal interphalangeal joint arthroplasty. *Journal of Hand Surgery* 37A, 1770–1779.
- Daruwalla, Z.J., Davies, K.L., Shafighian, A., Gillham, N.R., 2012. Early results of a prospective study on the pyrolytic carbon (pyrocarbon) Amandys® for osteoarthritis of the wrist. *Annals of the Royal College of Surgeons in England* 94, 496–501.
- Daruwalla, Z.J., Davies, K.L., Shafighian, A., Gillham, N.R., 2013. An alternative treatment option for scaphoid nonunion advanced collapse (SNAC) and radioscapoid osteoarthritis: early results of a prospective study on the pyrocarbon adaptive proximal scaphoid implant (APSI). *Annals of the Academy of Medicine of Singapore* 42, 278–284.
- Desai, A., Gould, F.J., Mackay, D.C., 2014. Outcome of pyrocarbon proximal interphalangeal joint replacement. *Hand Surgery* 19, 77–83.
- Dickson, D.R., Badge, R., Nuttall, D., *et al.*, 2015a. Pyrocarbon metacarpophalangeal joint arthroplasty in noninflammatory arthritis: Minimum 5-year follow-up. *Journal of Hand Surgery* 40, 1956–1962.
- Dickson, D.R., Nuttall, D., Watts, A.C., *et al.*, 2015b. Pyrocarbon proximal interphalangeal joints arthroplasty: Minimum five-year follow-up. *Journal of Hand Surgery* 40, 2142–2148.
- Gallagher, E.A., Lamorinière, S., McGarry, P., 2019. Finite element investigation into the use of carbon fibre reinforced PEEK laminated composites for distal radius fracture fixation implants. *Medical Engineering and Physics* 67, 22–32.
- Garret, J., Godenèche, A., Boileau, P., *et al.*, 2017. Pyrocarbon interposition shoulder arthroplasty: Preliminary results from a prospective multicenter study at 2 years of follow-up. *Journal of Shoulder and Elbow Surgery* 26, 1143–1151.
- Garret, J., Harly, E., Le Huec, J.-C., *et al.*, 2019. Pyrolytic carbon humeral head in hemi-shoulder arthroplasty: Preliminary results at 2-year follow-up. *JSES Open Access* 3 (1), 37–42.
- Gauthier, E., Truffandier, M.-V., Gaisne, E., Bellemère, P., 2017. Treatment of scaphotrapezotrapezoid osteoarthritis with the Pyrocardan® implant: results with a minimum follow-up of 2 years. *Hand Surgery and Rehabilitation* 36, 113–121.
- Gott, V.L., Alejo, D.E., Cameron, D.E., 2003. Mechanical heart valves: 50 years of evolution. *Annals of Thoracic Surgery* 76, S2230–S2239.
- Gras, M., Wahegaonkar, A.L., Mathoulin, C., 2012. Treatment of avascular necrosis of the proximal pole of the scaphoid by arthroscopic resection and prosthetic semireplacement arthroplasty using the pyrocarbon adaptive proximal scaphoid implant (APSI): Long-term functional outcomes. *Journal of Wrist Surgery* 1, 159–164.
- Helbing, G., Wolter, D., Neugebauer, R., Coldewey, J., 1977. The reaction of tissue to friction particles of LTI-carbon and carbon fibres reinforced carbon in the knee joint of the rat. *Third Annual Meeting of the Society for Biomaterials*. 151.
- Herren, D.B., Schindele, S., Goldhahn, J., Simmen, B.R., 2006. Problematic bone fixation with pyrocarbon implants in proximal interphalangeal joint replacement: Short-term results. *Journal of Hand Surgery* 31B, 643–651.
- Houdek, M.T., Wagner, E.R., Rizzo, M., Moran, S.L., 2015. Metacarpophalangeal joint arthroplasty in the setting of trauma. *Journal of Hand Surgery* 40, 2416–2420.
- Hudek, R., Werner, B., Abdelkawi, A.F., Gohlke, F., 2017. Pyrocarbon interposition shoulder arthroplasty in advanced collapse of the humeral head. *Orthopäde* 46, 1034–1044.
- Koh, Y.-G., Park, K.-M., Lee, J.-A., *et al.*, 2019. Total knee arthroplasty application of polyetheretherketone and carbon-fiber-reinforced polyetheretherketone: A review. *Materials Science & Engineering C* 100, 70–81.
- Lindtner, R.A., Schmid, R., Nydegger, T., Kenschake, M., Schmoelz, W., 2018. Pedicle screw anchorage of carbon fiber-reinforced PEEK screws under cyclic loading. *European Spine Journal* 27, 1775–1784.
- Martinez de Aragon, J.S., Moran, S.L., Rizzo, M., Reggin, K.B., Beckenbaugh, R.D., 2009. Early outcomes of pyrolytic carbon hemiarthroplasty for the treatment of trapezial-metacarpal arthritis. *Journal of Hand Surgery* 34A, 205–212.
- Mashhadi, S.A., Chandrasekharan, L., Pickford, M.A., 2012. Pyrolytic carbon arthroplasty for the proximal interphalangeal joint: Results after minimum 3 years of follow-up. *Journal of Hand Surgery* 37E, 501–505.
- Migliaresi, C., 2013. Composites. In: Ratner, B.D., Hoffman, A.S., Schoen, F.J., Lemons, J.E. (Eds.), *Biomaterials Science: An Introduction to Materials In Medicine*, third ed. Oxford: Elsevier, Inc, pp. 223–241.
- More, R.B., Haubold, A.D., Bokros, J.C., 2013. Pyrolytic carbon for long-term medical implants. In: Ratner, B.D., Hoffman, A.S., Schoen, F.J., Lemons, J.E. (Eds.), *Biomaterials Science: An Introduction to Materials In Medicine*, third ed. Oxford: Elsevier, Inc, pp. 209–222.
- Mugnai, R., Tarallo, L., Capra, R., Catani, F., 2018. Biomechanical comparison between stainless steel, titanium and carbon-fiber reinforced polyetheretherketone volar locking plates for distal radius fractures. *Orthopaedics & Traumatology: Surgery & Research* 104, 877–882.
- Murana, G., Alfonsi, J., Savini, C., *et al.*, 2018. On-X mitral valve replacement: A single-centre experience in 318 patients. *Interactive CardioVascular and Thoracic Surgery* 27, 836–841.
- Neumann, E.A.F., Villar, C.C., França, F.M.G., 2014. Fracture resistance of abutment screws made of titanium, polyetheretherketone, and carbon fiber-reinforced polyetheretherketone. *Brazilian Oral Research* 28, 1–5.
- Nunez, V.A., Citron, N.D., 2005. Short-term results of the Ascension™ pyrolytic carbon metacarpophalangeal joint replacement arthroplasty for osteoarthritis. *Chirurgie de la Main* 24, 161–164.
- Nunley, R.M., Boyer, M.J., Goldfarb, C.A., 2016. Pyrolytic carbon arthroplasty for posttraumatic arthritis of the proximal interphalangeal joint. *Journal of Hand Surgery* 31A, 1468–1474.

- Ono, S., Shauver, M.J., Chang, K.W.C., Chung, K.C., 2012. Outcomes of pyrolytic carbon arthroplasty for the proximal interphalangeal joint at 44 months mean follow-up. *Plastic and Reconstructive Surgery* 129, 1139–1150.
- Parker, W., Moran, S.L., Hormel, K.B., Rizzo, M., Beckenbaugh, R.D., 2006. Nonrheumatoid metacarpophalangeal joint arthritis. Unconstrained pyrolytic carbon implants: indications, technique, and outcomes. *Hand Clinics* 22, 183–193.
- Parker, W.L., Rizzo, M., Moran, S.L., Hormel, K.B., Beckenbaugh, R.D., 2007. Preliminary results of nonconstrained pyrolytic carbon arthroplasty for metacarpophalangeal joint arthritis. *Journal of Hand Surgery* 32A, 1496–1505.
- Pegoli, L., Zorli, I.P., Pivato, G., Berto, G., Pajardi, G., 2006. Scaphotrapezotrapezoid joint arthritis: A pilot study of treatment with the scaphoid trapezium pyrocarbon implant. *Journal of Hand Surgery* 31B, 569–573.
- Piccioli, A., Piana, R., Lisanti, M., *et al.*, 2017. Carbon-fiber reinforced intramedullary nailing in musculoskeletal tumor surgery: a national multicentric experience of the Italian orthopaedic society (SIOT) bone metastasis study group. *Injury* 48S3, S55–S59.
- Pierrart, J., Bourgade, P., Mamane, W., Rousselon, T., Masmejean, E.H., 2012. Novel approach for posttraumatic panarthritis of the wrist using a pyrocarbon interposition arthroplasty (Amandys®): Preliminary series of 11 patients. *Chirurgie de la Main* 31, 188–194.
- Reissner, L., Schindele, S., Hensler, S., Marks, M., Herren, D.B., 2014. Ten year follow-up of pyrocarbon implants for proximal interphalangeal joint replacement. *Journal of Hand Surgery* 39E, 582–586.
- Saito, S., Tsukui, H., Iwasa, S., *et al.*, 2016. Bileaflet mechanical valve replacement: an assessment of outcomes with 30 years of follow-up. *Interactive CardioVascular and Thoracic Surgery* 23, 599–607.
- Santos, F.L., Ferreira, A., Grazina, R., *et al.*, 2018. APSI scaphoid hemiarthroplasty – Long-term results. *Revista Brasileira de Ortopedia* 53, 582–588.
- Schwitalla, A.D., Zimmermann, T., Spintig, T., *et al.*, 2018. Maximum insertion torque of a novel implant-abutment-interface design for PEEK dental implants. *Journal of the Mechanical Behavior of Biomedical Materials* 77, 85–89.
- Shim, H.S., 1974. The behavior of isotropic pyrolytic carbons under cyclic loading. *Biomaterials, Medical Devices, and Artificial Organs* 2, 55–65.
- Simpson-White, R.W., Chojnowski, A.J., 2014. Pyrocarbon metacarpophalangeal joint replacement in primary osteoarthritis. *Journal of Hand Surgery* 39E, 575–581.
- Squitieri, L., Chung, K.C., 2008. A systematic review of outcomes and complications of vascularized toe joint transfer, silicone arthroplasty, and pyrocarbon arthroplasty for posttraumatic joint reconstruction of the finger. *Plastic and Reconstructive Surgery* 121, 1697–1707.
- Sweets, T.M., Stern, P.J., 2011. Pyrolytic carbon resurfacing arthroplasty for osteoarthritis of the proximal interphalangeal joint of the finger. *Journal of Bone and Joint Surgery* 93, 1417–1425.
- Szalay, G., Meyer, C., Scheufens, T., *et al.*, 2013. Pyrocarbon spacer as a trapezium replacement for arthritis of the trapeziometacarpal joint. A follow-up study of 60 cases. *Acta Orthopaedica Belgica* 79, 648–654.
- Tagil, M., Geijer, M., Abramo, A., Kopylov, P., 2014. Ten years' experience with a pyrocarbon prosthesis replacing the proximal interphalangeal joint. A prospective clinical and radiographic follow-up. *Journal of Hand Surgery* 39E, 587–595.
- Tian, C.L., Hetherington, V.J., Reed, S., 1993. A review of pyrolytic carbon: Application in bone and joint surgery. *Journal of Foot and Ankle Surgery* 32, 490–498.
- Tuttle, H.G., Stern, P.J., 2006. Pyrolytic carbon proximal interphalangeal joint resurfacing arthroplasty. *Journal of Hand Surgery* 31A, 930–939.
- Vitale, M.A., Hsu, C.C., Rizzo, M., Moran, S.L., 2017. Pyrolytic carbon arthroplasty versus suspensionplasty for trapezial-metacarpal arthritis. *Journal of Wrist Surgery* 6, 134–143.
- Vomero, M., Mondragon, N.C., Stieglitz, T., 2019. Electrochemical characterization and surface analysis of activated glassy carbon neural electrodes. In: *Proceeding of the Annual International Conference of the IEEE Engineering in Medicine and Biology Society (EMBC)*. pp. 3923–3926.
- Wagner, E.R., Weston, J.T., Houdek, M.T., *et al.*, 2018. Medium-term outcomes with pyrocarbon proximal interphalangeal arthroplasty: A study of 170 consecutive arthroplasties. *Journal of Hand Surgery* 43, 797–805.
- Wall, L.B., Stern, P.J., 2013. Clinical and radiographic outcomes of metacarpophalangeal joint pyrolytic carbon arthroplasty for osteoarthritis. *Journal of Hand Surgery* 38A, 537–543.
- Watts, A.C., Hearnden, A.J., Trail, I.A., *et al.*, 2012. Pyrocarbon proximal interphalangeal joint arthroplasty: Minimum two-year follow-up. *Journal of Hand Surgery* 37A, 882–888.
- Wijk, U., Wollmark, M., Kopylov, P., Tagil, M., 2010. Outcomes of proximal interphalangeal joint pyrocarbon implants. *Journal of Hand Surgery* 35A, 38–43.
- Wilson, W.K., Morris, R.P., Ward, A.J., Carayannopoulos, N.L., Panchbhavi, V.K., 2016. Torsional failure of carbon fiber composite plates versus stainless steel plates for comminuted distal fibula fractures. *Foot & Ankle International* 37, 548–553.
- Zhu, X., Luo, Y., Zhang, E., *et al.*, 2018. Ten-year experience of tricuspid valve replacement with the St. Jude medical valve. *Scientific Reports* 8, 16654.

Yttria-Stabilized Zirconia as a Biomaterial: From Orthopedic Towards Dental Applications

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Introduction

Zirconia was introduced in orthopedics in 1984, in the form of a magnesia-stabilized ceramic (Mg-PSZ for *Partially Stabilized Zirconia*) to answer the problem of alumina brittleness and the risk of failure of femoral heads in total hip replacement (THR) procedures. Mainly USA and Australia developed a Mg-PSZ orthopedic zirconia, which has never been used in large-scale clinical trials. In the late 1980s, yttria-stabilized zirconia containing 3 mol% of Y_2O_3 (3Y-TZP for *Tetragonal Zirconia Polycrystal*) rapidly took its place in the orthopedic field, especially due to its higher strength (more than 1000 MPa, i.e., at least twice that of Mg-PSZ). The impressive strength of 3Y-TZP compared to Mg-PSZ results from the microstructural refinement (typically tetragonal grains of size <500 nm compared to 30–40 μm for the cubic grains of Mg-PSZ) because 3Y-TZP ceramics can be sintered at lower temperatures (1400°C versus 1800°C for Mg-PSZ). As will be discussed below, 3Y-TZP zirconia also takes advantage of phase transformation toughening, which increases its crack propagation resistance. From the early 1990s to 2002, more than 600,000 hip femoral heads made of 3Y-TZP were implanted worldwide. The most important manufacturers were Saint Gobain Desmarquest (SGD) in France, Kyocera in Japan, Metoxit in Switzerland and Morgan Technical Ceramics in UK. At that time, biomedical grade 3Y-TZP femoral heads were considered as the most promising alternative to alumina for THR.

The main toughening mechanism in stabilized zirconia is the stress-induced tetragonal-to-monoclinic (*t-m*) phase transformation. Briefly and schematically, at the crack-tip, the transformation of the metastable tetragonal phase to the stable monoclinic one is accompanied by a lattice expansion that induces compressive stresses, hindering the crack propagation. At a macroscopic level, this results in an apparent increase of the toughness (K_{IC}) of the ceramic material. Therefore, the toughness of 3Y-TZP is about twice that of alumina (5–8 MPa $\sqrt{m}$ versus 3–4 MPa $\sqrt{m}$, respectively). Due to these major advantages, 3Y-TZP allowed producing smaller femoral heads that were not possible to manufacture with alumina (e.g., 22 mm in diameter) and the development of knee prostheses or hip resurfacing implants. However, from the early 1990s some critical points regarding 3Y-TZP began to be reported, such as its potential radioactivity, the negative effect of steam sterilization procedures on the surface roughness and its questionable stability in contact with water or body fluids. This last fact, better known as Low Temperature Degradation (LTD) or “aging” led to 3Y-TZP abandon in the orthopedic field in the early 2000s. To date, numerous reports show that LTD was the responsible for a series of 3Y-TZP femoral heads fractures (Chevalier, 2006; Chevalier *et al.*, 2009).

As regards the zirconia radioactivity issues, they were induced by the fact that zirconia oxide (ZrO_2 or Baddeleyite) is always found associated to other minerals and natural radionuclides (uranium, radium and thorium). Even if during the processing of the powder such elements are eliminated, the level of purification depends on the powder manufacturer. As some special zirconia powders used as radiopacifier in PMMA cements showed significant radioactive impurities, the competition between alumina and zirconia powder producers strongly stimulated the controversy for a while until other works demonstrated that zirconia ceramics made from highly purified powders exhibited radioactivity levels much below the natural background (Piconi and Maccauro, 1999). Today, international standards specify radioactivity limits of Y-TZP ceramics used for implants to below 200 Bq/Kg (International Organization for Standardization, 2016a). Current developed pure Y-TZP powders show values of 20–50 Bq/Kg, which is clearly below this benchmark.

The most relevant problem remains the stability of zirconia in the presence of water or body fluids, a matter that has caused concern in the orthopedic field, when negative effects of sterilization or premature failures started to be reported. The degradation of zirconia ceramics became well known in the ceramic community after the initial studies of Kobayashi (Kobayashi *et al.*, 1981), who discovered a serious limitation of Y-TZP ceramics for applications at temperatures close to 250°C. During aging or LTD, a spontaneous tetragonal to monoclinic (*t-m*) zirconia phase transformation of grains on any surface in contact with water, water vapor, or body fluid occurs. It means that no external applied stress is needed to start the process. This transformation of surface grains is accompanied by a volume expansion of 3–5 vol% leading to surface-roughening, grain-pull-out and microcracking. 3Y-TZP aging was first thought to be very limited and well-controlled near the ambient temperature. However, in 1997 the US Food and Drug Administration (FDA) reported on the negative effect of steam sterilization procedures applied in zirconia implants (134°C, 2 bars pressure) on their surface roughness. This sterilization procedure is since then forbidden for zirconia. More importantly, in 2001, the FDA announced that firms distributing orthopedic implants were recalling series of Prozyr® 3Y-TZP ball heads made by SGD (Evreux, France). In fact, hundreds of femoral heads failed in recently-implanted patients. The origin of the failures was later related to an accelerated *t-m* phase transformation that occurred in only certain batches. Even though limited in numbers and duration, the production of zirconia femoral heads declined by 90% between 2001 and 2002 and never recovered. This failure episode had a strong negative impact on the use of yttria-stabilized zirconia in orthopedics. Since then, monolithic 3Y-TZP was abandoned in this area, for the benefit of alumina-matrix composites (e.g., Biolox Delta®), which roughly speaking combine the stability of the alumina matrix and a reinforcement by dispersed zirconia grains (very often yttria-stabilized). The same 3Y-TZP ceramic, in which further powder improvements were made to achieve a better aging resistance, as it

is the case with some alumina addition (e.g., zirconia Tosoh E-grades), has become a successful dental material, for the manufacturing of implants and external restorations (crowns, bridges and dentures by CAD-CAM processing of pre-sintered blanks).

“Pro- orthopedic or biomedical zirconia” supporters claim that only 3Y-TZP allows specific designs of implants that would fail with more brittle alumina and composites. They also rightly claim that the 3Y-TZP femoral heads failure rate before 2001 was exceptionally low and that its aging sensitivity can be controlled by a careful monitoring of the processing (powder synthesis, shaping, sintering and post-treatment steps) and/or composition. The “con- orthopedic or biomedical zirconia” advocates, and they are to a certain extent also right, claim that it is unsatisfactory to implant an “unstable” material in the body. Around the mid-2000s, the available clinical retrieval studies did not fully assess this issue. Moreover, their results were somewhat controversial: some results showed excellent behavior of some femoral heads after several years in-vivo, while others showed enhanced roughening associated with severe wear and osteolysis around the implant (Clarke *et al.*, 2003). The aim of this update is therefore to describe based on recent factual knowledge, the major advantages (i.e., crack resistance) and drawbacks (i.e., aging resistance) of yttria-stabilized zirconia ceramics to understand its behavior and why it was abandoned in orthopedics, but immediately introduced in the dental field. Particular emphasis is given to the phase-transformation toughening, the aging phenomenon and the optical properties because they remain the critical points for the future of zirconia in dentistry and in some other niche biomedical applications.

After this introduction, the chapter is divided in three additional sections, a general discussion and some concluding remarks. Section “Main Features of Yttria-Stabilized Zirconia” provides an overview of the key chemical, physical and mechanical properties of Y-TZP. Section “Aging Process and its Consequence on Zirconia-Based Biomedical Implants” shows the nature and importance of LTD in the field of biomedical ceramics. Section “Optical Properties of Yttria-Stabilized Zirconia” analyzes the optical properties of yttria-stabilized zirconia and the impact of novel rich-yttria composition (stabilizer and dopants) on the mechanical resistance and aging. The fifth section discusses the past, the present and the future of biomedical-grade zirconia and ends with a brief conclusion.

Main Features of Yttria-Stabilized Zirconia

Zirconia is a well-known polymorph that occurs in three crystallographic forms: monoclinic (m), tetragonal (t) and cubic (c), at ambient pressure. As shown in Fig. 1, pure zirconia is monoclinic at ambient temperature and pressure. This phase is stable up to 1170°C. Above this temperature, it transforms to the tetragonal phase and then to the cubic one at 2370°C. The cubic phase is stable up to the melting point of 2680°C.

As zirconia products are usually sintered in the 1350–1550°C range, a reverse t–m transformation of the sintered bodies (if made of pure zirconia) occurs during cooling. As pointed out earlier, the t–m transformation is associated with a volume expansion of 3–5%. This inevitably leads to large stresses and cracking upon cooling from the sintering temperature, which prohibits the use of pure zirconia in manufacturing dense products (unless they would be sintered at temperatures lower than 1170°C by non-conventional processes). In order to overcome this problem, additives such as calcia (CaO), magnesia (MgO), yttria (Y₂O₃) or ceria (CeO₂) must be added to zirconia to preserve the material in either the tetragonal (t) or the cubic (c) phase after cooling to room temperature. Biomedical grade zirconia is usually stabilized with 3 mol% Y₂O₃ and its requirements such density (> 6 g/cm³) and grain size (< 0.6 μm) are reported by standards (International Organization for Standardization, 2016a). The addition of stabilizers, here 3 mol% of yttria, maintains the t phase at ambient temperature, therefore in a metastable state. Today, 3 mol% yttria-stabilized zirconia (3Y-TZP) is the most commonly manufactured powder in the ZrO₂-Y₂O₃ system for biomedical use. However, due to the growing interest in using yttria-stabilized zirconia in dental restorations, newer Y-rich zirconia generations (4Y, 5Y, etc.) have been also produced industrially.

Most of the properties of Y-TZP ceramics can be predicted from the ZrO₂-Y₂O₃ equilibrium phase diagram shown in Fig. 1. After sintering, 3Y-TZP is very often described as fully tetragonal zirconia. However, depending on the sintering conditions (temperature and time), it rather consists of a mixture of yttria-poor t and yttria-rich c phases. The phase diagram gives the composition and content at the equilibrium at high temperature (lever rule). After cooling, the t + c phases can be retained. However, again, the phase diagram shows that the metastable t phase will have the tendency to go back to the m stable state. In other words, the reverse t–m transformation is expected to occur at ambient temperature if the energy-barrier for the t–m transformation is lowered. This will depend on the microstructure (mainly on grain size and phase content) and on external parameters, e.g., external applied stresses or environment.

The T–M Phase Transformation

Solid-state phase transformations can be classified as diffusional (so called “civilian”) and diffusionless (so-called “military” or martensitic) depending on the mechanism by which transformation takes place. Martensitic transformations were first described in steels and then in shape memory alloys. There are considered as diffusionless as the movement of each atom involved in the transformation is less than one interatomic spacing, i.e., these transformations do not require long-range movements of atoms. Because of its key role on the mechanical behavior of zirconia, the most studied zirconia phase transformation is the t–m martensitic phase change. This transformation can be induced by a change in the temperature (i.e., during cooling) or by the action of a mechanical stress over the metastable tetragonal phase (case of stabilized zirconia). The t–m transformation temperatures and stresses are mainly dependent on zirconia composition and grain sizes, but can also be affected by other factors such as internal residual stresses. The t–m transformation is reversible and exhibits

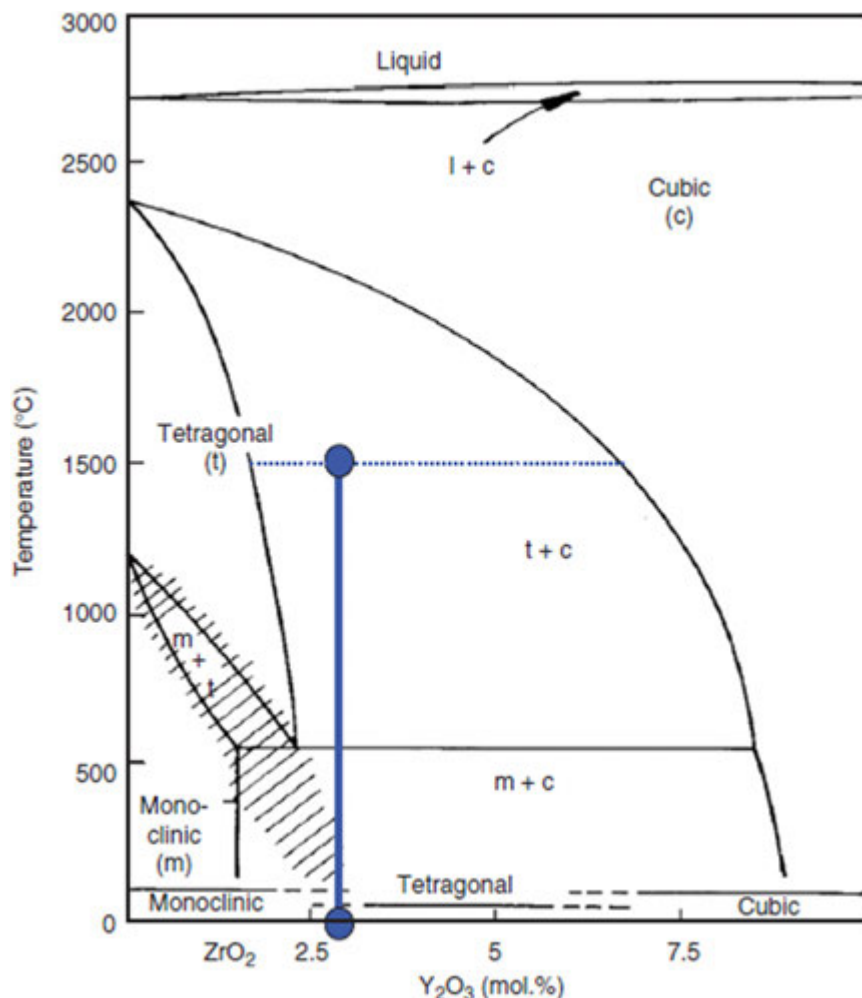


Fig. 1 $\text{Y}_2\text{O}_3\text{-ZrO}_2$ equilibrium phase diagram. The vertical blue line represents the composition of 3Y-TZP. The dashed blue horizontal line shows the composition of 3Y-TZP ceramics (t + c phases) at high temperature. Adapted from Scott, H.G., 1975. Phase relationships in the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ system. *Journal of Materials Science* 10, 1527.

hysteresis, in other words the t-m transformation takes place at lower temperature than the m-t one (Bansal and Heuer, 1972). In pure zirconia, the m-t transformation occurs at 1170°C during heating, while the reverse t-m transformation begins at 950°C upon cooling. The stabilization of zirconia with yttria shifts the hysteresis cycle to lower temperatures so the t-m transformation occurs below the ambient temperature for a bulk 3Y-TZP. As the transformation takes place by a cooperative movement of a large number of atoms (shear process) without atomic diffusion, it can occur at any temperature and keeping the same chemical composition. The velocity of the transformation may reach that of sound in the solid. A further consequence of the diffusionless nature of the martensitic transformation is that the change in crystal structure is achieved by a homogeneous deformation of the parent phase on particular crystallographic planes and directions. Macroscopically, the transformation is easily localized because the shape of the transformed region changes, the strain being a combination of shear and dilatational, parallel and normal to the habit plane as described in Fig. 2.

Generally, martensitic transformations lead to less volume change as compared to the shear components. In zirconia, the shear strain is about 0.15–0.17 and the volume change (dilatational strain) near 0.05 (i.e., 5%) (Deville *et al.*, 2004). The t-m zirconia phase transformation leads, therefore, to shear strain and significant volume increase. In metastable zirconia and especially in 3Y-TZP, the t-m transformation can occur in the bulk or at the surface of the material. In the bulk, when induced by applied stresses, the transformation leads to the positive effect of toughening since the localized t-m transformation hinders the propagation of cracks. At the surface, especially in contact with water or body fluids, the spontaneous transformation leads to the negative effect of aging (i.e., increased roughness and microcracking).

Toughening Mechanism in Transformable Zirconia

The metastable nature of tetragonal grains was the basis for the development of zirconia as a “tough” ceramic in the 1970s and 1980s. Garvie *et al.* (1975) showed in their famous paper “Ceramic steel?” that the mechanical strength of zirconia was improved

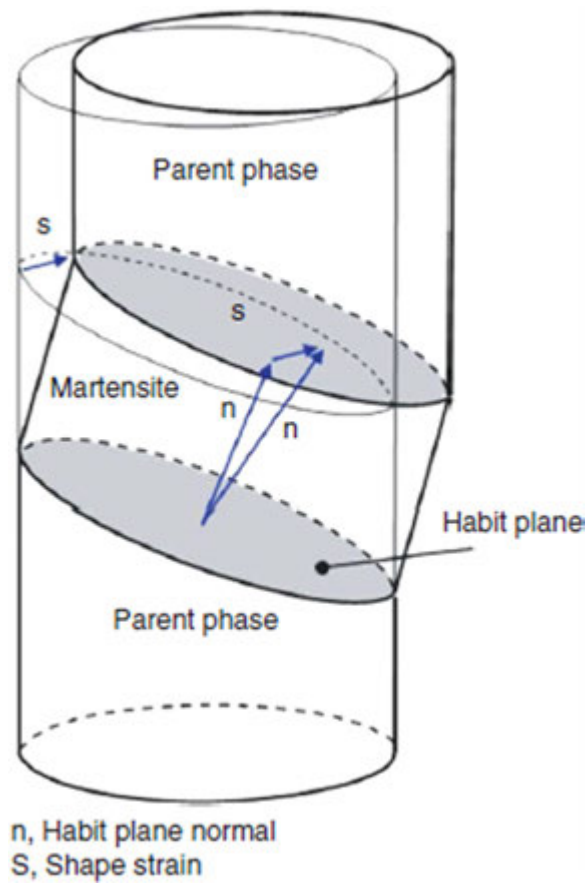


Fig. 2 Schematic representation of habit plane and shape strain for a martensitic transformation.

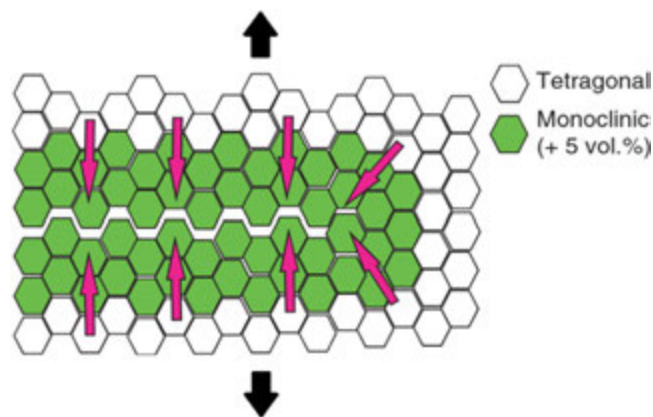


Fig. 3 Schematic drawing of the transformation zone around a propagating crack, leading to compressive stresses and subsequent shielding stress intensity factor.

by the t-m transformation that takes place around a propagating crack. The large stresses appearing around a crack lead to the t-m transformation ("process zone"). When a crack propagates, the stress field at the crack tip associated with the volume expansion due to the transformation (compressive stresses) acts against the tensile applied stress field, shielding the crack propagation as illustrated in **Fig. 3**. This t-m phase transformation, usually triggered by shear and/or hydrostatic tensile stresses, leads to a significant increase of the strength due to the increase of the work of fracture.

Transformation toughening was first described in steels showing a TRIP effect (TRIP for *Transformation-Induced-Plasticity*) and wear resistant cast irons (Gerberich *et al.*, 1968). McMeeking and Evans (1982) developed modeling of phase-transformation

toughening in brittle materials at the beginning of the 1980s. Giving a comprehensive review of toughening mechanism is beyond the scope of this chapter. The interested reader may refer to the book “Transformation Toughening of Ceramics” (Green *et al.*, 1989).

The stress-induced t-m phase transformation leads to a shielding K_{Ish} of the applied stress intensity factor K_I . This means that the real stress intensity factor at the crack-tip $K_{I_{tip}}$ is lower than that applied by the external forces, according to

$$K_{I_{tip}} = K_I - K_{Ish} \quad (1)$$

So, the higher the applied stress intensity factor, the higher the shielding stress intensity factor due to the phase transformation, as confirmed experimentally on 3Y-TZP ceramics (Chevalier *et al.*, 1999a). The toughening capability of a given zirconia depends on the critical local stress leading to t-m phase transformation (σ_m^c). The microstructure and composition will play a major role on transformation toughening, since σ_m^c mainly depends on the grain size and the nature and amount of phase stabilizer. Some studies report that about 70%–80% of the applied stress intensity factor is actually reduced at the crack-tip with grain size ranging between 0.5 and 1 μm . The variation of the toughness in biomedical grade 3Y-TZP ceramics ranges from 5 to 8 $\text{MPa}\sqrt{\text{m}}$ for grain sizes of 0.3–1.2 μm (above 1.2 μm , 3Y-TZP is no longer stable). As discussed earlier, typical biomedical alumina exhibits lower toughness values (3–4 $\text{MPa}\sqrt{\text{m}}$) and this was one of the reason for introducing 3Y-TZP ceramics in orthopedics, so to overcome the problem of alumina brittleness.

Today it is well known that ceramic materials are susceptible to slow crack propagation at K_I values under K_{IC} . This behavior is mainly observed in oxide ceramics, for which ionic bonds can react with water at the crack tip. The slow-crack propagation depends on the applied load but can also be sensitive to the environment (atmosphere, chemical species), the temperature and other variables. That means that under “appropriate or specific” conditions, cracks can grow at relatively low stresses. Since it is impossible to completely avoid introducing imperfections and microcracks during the processing of bioceramics, cracks may grow in a slow manner before causing catastrophic failure, without any warning signal. All the aspects of slow crack growth (SCG) in ceramics are covered in the book by Lawn (1993).

As a general trend, slow crack growth is described based on a V (crack velocity) versus K_I (stress intensity factor) diagram. Slow crack growth in ceramics is attributed to stress-assisted corrosion at the crack-tip, or any pre-existing defect in the material. It is indeed the combined effect of high stresses at the crack-tip and the presence of water or body fluid molecules, which reduce surface energy at the crack-tip, thus inducing crack propagation in a slow manner. Over the years, the presence of a threshold in the stress intensity factor (K_{I0}), under which no crack propagation occurs, has been the subject of important research in the ceramic field. The threshold corresponds to crack equilibrium with a null crack velocity, thus propagation does not occur below this. For ceramic joint prostheses, this threshold determines a safety range of use. Above the threshold K_{I0} , three stages are generally observed in oxide ceramics. Each stage can be fitted by a phenomenological power-law relation, in the form

$$V = A \cdot K_I^n \quad (2)$$

where A and n are the slow crack growth parameters associated with the material and the environment conditions. Fig. 4 represents the V – K_I curves of biomedical grade alumina and zirconia ceramics.

Region I depends strongly on external variables, applied stress, temperature, and chemical concentration. In this region, the environmental species react with the ceramic bonds in the crack front-tip. This region is therefore reaction-rate controlled. Region II is insensitive to applied stress, suggesting a transport process in which the active environmental species are increasingly unable to keep pace with the crack front tip as K_I increases. This region depends on the diffusion of the corrosive species from the environment to the crack-tip. Region III is associated with fast fracture and then with K_{IC} . The toughness (K_{IC}) and threshold (K_{I0}) of zirconia are superior to that of alumina. The difference in crack resistance is, however, larger for large stress intensity factors, since the larger the applied K_I the larger the reinforcement. The higher crack resistance of zirconia, compared to alumina, associated with a lower grain size (typically 0.5 μm for zirconia, 2 μm for alumina) leads to a significant increase of the strength. For example, 3Y-TZP strength values as high as 2 GPa have been reported, compared to 600 MPa for alumina.

Phase Transformation by Grinding

In transformable zirconia ceramics such as 3Y-TZP, surface grinding or polishing is sufficient to induce t–m transformation on the surface. This transformation generates a thin surface layer of monoclinic phase, which places the surface of the material in a compressive state. The thickness and features of this layer depends mainly on the severity of the surface treatment, but also on the grain size and composition of the ceramic. It can reach a few tens of microns for surfaces machined under “severe” conditions, with compressive stresses of hundreds of MPa. For example, in 3Y-TZP ceramics (grain size 320 nm), grinding with water at 300 rpm and 80 μm disk produced three different transformed layers (Minguella *et al.*, 2020). A top layer of 300 nm depth containing in-situ recrystallized nano-grains of 10–20 nm in size and microcracks extending parallel to the surface, a second region of $\sim 1 \mu\text{m}$ depth made of plastically deformed grains in a direction parallel to the surface and finally, a layer of bulk-like 3Y-TZP grains of 4 μm in depth in which monoclinic laths were observed. Regarding residual compressive stresses, they can extend below the surface until a depth of approximately 5 μm , decreasing progressively and reaching a maximum of 700 MPa. Compressive stresses can improve the strength (e.g., from 1200 to 1300 MPa in biaxial bending) as reported by Muñoz-Tabares *et al.* (2011) and have a positive effect in the so-called hydrothermal degradation process. For example, ground 3Y-TZP can be safe from hydrothermal degradation (131°C-96 h in autoclave) due to the formation of a tetragonal refined-top layer, as proposed by Muñoz-Tabares and Anglada (2012).

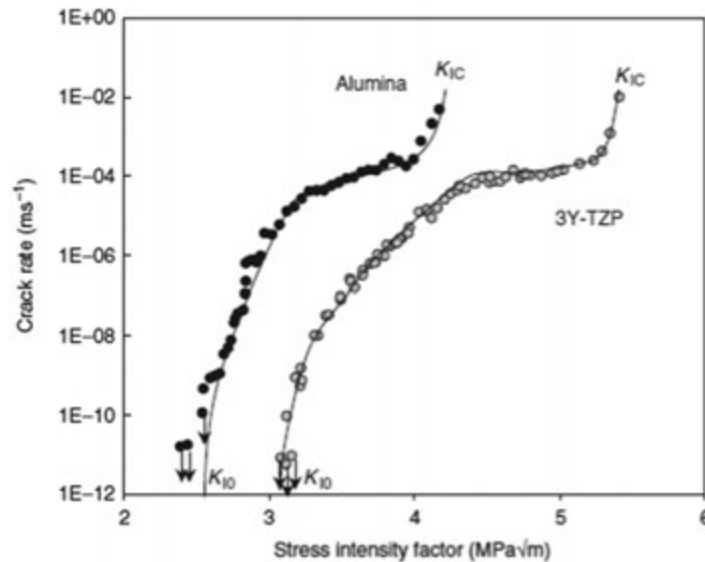


Fig. 4 Crack rate versus stress intensity factor of biomedical grade alumina and zirconia ceramics.

However, it is necessary to keep in mind that heavily ground samples may also display degraded mechanical behavior and poor aging resistance, both resulting from a complex balance between residual stress field and surface microcracking.

The use of 3Y-TZP for developing biomedical devices is explained by the fact that, compared to alumina, 3Y-TZP ceramics exhibit higher resistance to slow crack growth and higher strengths (especially if machined because the apparent toughness can reach $20 \text{ MPa}\sqrt{\text{m}}$). Hence, the ultimate compressive load of 3Y-TZP femoral ball heads can be 2–2.5 times higher than that of alumina ball heads of the same diameter and neck length (Piconi and Maccauro, 1999). So, if the use of 3Y-TZP stopped in orthopedics early 2000s, is without any doubt because of its sensitivity to aging. Paradoxically, the main advantage of zirconia, i.e., its phase transformation capacity, can also be its main drawback when t-m transformation takes place at the surface in an uncontrolled manner. It is also important to understand at this stage that giving a monoclinic content at the surface as an indicator of “damage” is not correct as t-m associated to grinding and surface treatments may be positive while negative if associated to water-assisted aging. The decrease (or increase) of mechanical properties related to t-m transformation is thus a balance between the beneficial compressive stresses and the negative microcracking effect.

Aging Process and its Consequence on Zirconia-Based Biomedical Implants

Giving a comprehensive review of the aging mechanism would again considerably extend the scope of this chapter. The readers not familiar with this field can refer to the excellent review of Lawson (1995) or a more recent overview (Chevalier, 2006). The excitement created by Y-TZP materials in the 1980s was already dampened by the phenomenon of aging (Kobayashi *et al.*, 1981). The authors revealed that Y-TZP ceramics could suffer a slow, t-m phase transformation at the surface in contact with humid atmosphere, followed by microcracking and a loss in strength. Following this work, a series of works were published with an attempt to understand the basic micromechanisms behind the t-m transformation and to reduce this detrimental phenomenon. The main features of this so-called “Low Temperature Degradation” (LTD) are the following:

- (1) Transformation proceeds most rapidly at temperatures of $200\text{--}300^\circ\text{C}$ and is time dependent;
- (2) Water or water vapor enhances the transformation;
- (3) Transformation proceeds from the surface to the bulk of zirconia materials;
- (4) Higher stabilizing content or finer grain size increase the resistance to transformation;
- (5) Processing conditions affect the aging behavior;
- (6) Surface post-treatments such grinding and polishing can modify the resistance to aging.

Several models proposed mechanisms by which the presence of water could promote t-m transformation. Sato and Shimada (1985) have proposed a chemisorption of water to form Zr-OH at the surface of zirconia, which results in the accumulation of strain energy able to trigger the t-m transformation. Yoshimura *et al.* (1987) further refined this model proposing the chemisorption of water as the key mechanism for having aging but attributing the accumulation of stresses to the migration of OH species at the surface and into the zirconia lattice. The diffusion of OH is promoted by the presence of oxygen vacancies in the lattice of yttria (yttria and zirconia being tri- and tetravalent cations, respectively). This could explain the different LTD behavior of Y-TZP versus Ce-TZP ceramics (cerium being tetravalent, only fewer oxygen vacancies are present, which gives rise to a much better aging resistance). Other models postulated a reaction between H_2O and yttria (Y_2O_3) to form Y(OH)_3 compound, leading to a

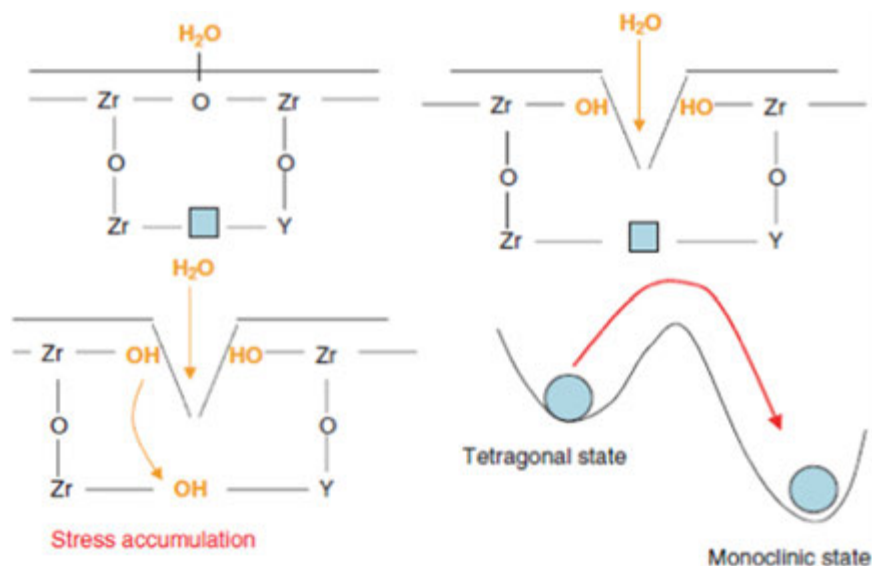


Fig. 5 Model for the increase in internal stresses due to water chemisorption and diffusion of OH^- in the lattice. Adapted from Yoshimura, M., Noma, T., Kawabata, K., Somiya, S., 1987. Role of water on the degradation process of Y-TZP. *Journal of Materials Science Letters* 6, 465–467.

depletion of the stabilizer content and consequently to t-m transformation. However, today, the depletion of Y_2O_3 during LTD is considered unlikely and the fundamental role of internal stresses model of Yoshimura is the most accurate in its description of the different features of LTD. This model is schematically represented in Fig. 5.

When the stresses due to the diffusion of OH^- species reach a critical level in the lattice, then a grain or a part of it can undergo phase transformation. Transformation starts first in isolated grains located on the surface in contact with water, body fluids or water vapor (e.g., under autoclave conditions). The initial transformation of specific tetragonal grains (nucleation sites) can be related to their metastability degree (either to a larger grain size and/or lower yttria content), their orientation from the surface, the presence of residual stresses or even of the cubic phase, often neglected in most of the experimental works despite its critical influence (Chevalier *et al.*, 2004). As shown in Fig. 6, the nucleation of the transformation leads then to a cascade of events occurring neighbor to neighbor. The transformation of one grain leads to a volume increase thus stressing up the neighboring grains and results in microcracking. This offers a path for the water to penetrate deeper into the specimen, triggering new nucleation and growth sites for t-m.

The transformation occurs, therefore, by a nucleation and growth process, often described by Mehl–Avrami–Johnson laws (Chevalier *et al.*, 1999b). The growth stage depends on several microstructural features such as porosity, residual stresses, grain size, etc. Several studies have been performed to investigate the aging kinetics of 3Y-TZP ceramics at ambient temperature and under accelerated conditions (in autoclave, e.g., at $134^\circ C$, 2 bars). However, if all show some amounts of t-m phase transformation, the kinetics data are strongly scattered due to differences in the processing (dispersing, shaping, sintering) affecting the grain size, composition, residual stresses and density and in the post-processing steps (cutting, grinding, polishing, chemical etching, sandblasting, etc.). This fact led to misunderstanding and some zirconia producers stated that products manufactured with biomedical 3Y-TZP were safe, while competitors and scientific works declared at the same time the contrary. Again, some works showed excellent behavior of 3Y-TZP femoral heads after several years in-vivo, while others showed enhanced roughening associated with severe wear and osteolysis around the implant, as consequence of aging. This is once more due to differences in the processing from one supplier to another. During the short history of 3Y-TZP in orthopedics, many varieties have come into existence -black/white zirconia, HIPed heads, non-HIPed heads- and all showed different LTD resistance. The consequences of aging process on the long-term performance of zirconia implants can be: (1) the roughening of the surface that leads to increased wear and (2) microcracking that leads to grain pull-out, the generation of particle debris and, possibly, premature failure when microcracked, damaged zones reach the critical size for slow crack growth to proceed.

At this stage of the chapter, it is important to recall the main facts related to the failures of some Prozyr® femoral heads already implanted. By mid-1998, Saint Gobain Demarquest (SGD) had made thousands of femoral balls with very low failure rates. However, in 2001 catastrophic head fracture were reported (Clarke *et al.*, 2003; Maccauro *et al.*, 2004) linked to a Prozyr® batch in which fracture rates as high as 42% occurred 21–46 months after surgery. At that time, it was said by the manufacturer that failure occurred via “unexpected” and accelerated aging process observed in only some batches of Prozyr® femoral heads. It is clear today that these failures were caused by an “unusual” accelerated aging of the cone region of the heads due to a change carried-out in the sintering step by SGD. In fact, in 1998, a change from a batch to a continuous flow tunnel furnace produced slightly modifications of microstructure and density, leading to a decrease in aging resistance. These relatively small changes in density were undetectable by the quality control but thorough analysis showed that the inner core of the ball was not as dense as usual and could contain percolating porosity; the change in the manufacturing process was the reason for the sudden increase of Prozyr® failure rates. This critical situation led to SGD to pull 3Y-TZP femoral heads off the market. In 2001, considering that small changes

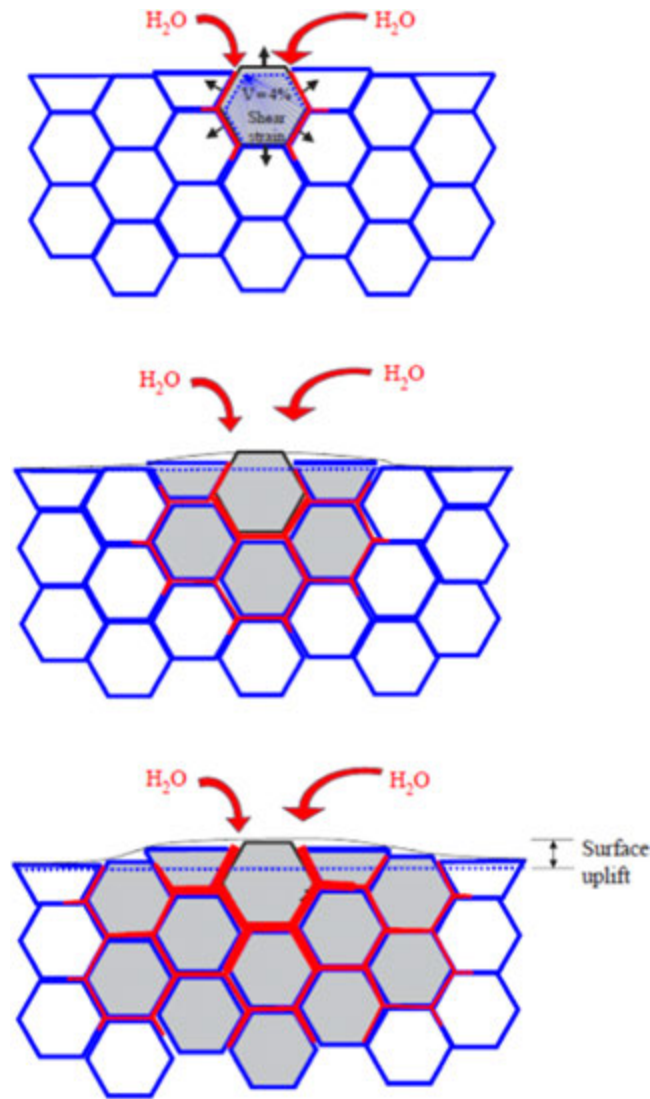


Fig. 6 Schematic aging representation showing the nucleation of t-m in a grain at the surface, the t-m transformation propagation from neighbor to neighbor, accompanied with surface uplift and microcracking. Transformed grains are gray and penetration of water paths in red. From Chevalier, J., 2006. What future for zirconia as a biomaterial?. In: Leong, K. (Ed.), *Biomaterials*, vol. 27. Elsevier, pp. 535–543.

in the processing could induce similar dramatic events in other 3Y-TZP implants, European and American regulatory agencies recalled thousands of 3Y-TZP femoral balls. By 2002, all Prozyr® sales stopped and SGD retired from the medical field.

The crisis of 2001 emphasized the importance of accurate process control for such metastable zirconia implants, but should not lead to any conclusion about the behavior of a zirconia in the body. Maybe more critical are the reports that showed surface degradation of zirconia implants, or strong osteolysis. Haraguchi *et al.* (2001) reported for the first time, two cases of a surface degradation (roughening and microcracking) caused by t-m phase transformation. The zirconia used in this work, presumably processed by Kyocera, satisfied the requirement later specify in standards, that is, maximum amount of monoclinic phase after accelerated aging in autoclave at 134°C under a pressure of 0,2 MPa for a period of 5 h < 25% (International Organization for Standardization, 2016a). However, the authors measured monoclinic contents of 20% and 30% in both heads after a short period of 3 or 6 years of implantation, respectively. They also reported a strong increase in roughness, growing from 6 nm to 120 nm. Another paper from Catledge *et al.* (2003) confirmed the degradation of surface properties for some explanted zirconia heads that had undergone various degrees of phase transformation, ranging from 0% to ~78% monoclinic content after 62 months in service. The hardness dropped from 18 GPa to 11 GPa for high transformation fractions, which indicates extensive microcracking in the transformed regions. Contrasting with these poor clinical experiences, other authors also reported a better behavior of zirconia femora heads, at least at middle-term follow-up (Caton *et al.*, 2004). For instance, 22 mm diameter zirconia heads implanted for 45 months showed less than 10% monoclinic content, with apparently neither increase in roughness or grain pull-out. These different clinical experiences and events have shown that LTD was relevant in-vivo and may lead to failure of implants after a short duration. They also have confirmed the strong variability of zirconia femoral heads with regard to aging resistance. As discussed earlier, main parameters affecting LTD are the density (open porosity offers

water molecules easy access to the bulk), grain size (finer grain size increase the stability of zirconia, so the resistance to t-m transformation), the homogeneity of microstructure/phase distribution (negative effect of residual cubic phase) and the residual stresses (positive effect if tensile on the surface).

Fortunately, it is now possible to assess the sensitivity against aging of biomedical grade zirconia prior to be implanted. Due to the thermally activated character of the t-m transformation, accelerated aging tests in autoclave were standardized. It is proposed for example that autoclaving 1 h at 134°C under vapor steam (0.2 MPa) has roughly the same effect as few years in-vivo. Nevertheless, it must be known that depending on the apparent activation energy used for extrapolating LTD kinetics, the results may vary and that such accelerated aging tests do not take into account possible coupling effects on the aging kinetics. For example, increased aging kinetics in 3Y-TZP femoral heads has been observed when accelerating aging tests were coupled with wear tests (Douillard *et al.*, 2012; Gremillard *et al.*, 2013). There is still a great need of more advanced studies on zirconia aging, with particular interest in finding the correlation between compositional and microstructural features, post-treatment procedures, wear, cyclic loading, shocks and LTD resistance by developing new accelerated tests in-vitro and in-vivo. Recently, Wei and Gremillard (2018) proposed a new protocol to predict the aging behavior of 3Y-TZP from microstructural parameters (grain size, yttria partitioning and monoclinic, tetragonal and cubic amounts) able to allow adapting the sintering conditions in order to maximize the LTD resistance. However, it is not yet known whether shear, tensile or compressive stresses could induce/hinder aging, thus affecting its kinetics.

Currently, the main features of zirconia LTD are well known and there are different tools and standards to assess the aging resistance of a given Y-TZP before its use as a medical implant material. Moreover, 3Y-TZP aging-resistant compositions containing small amounts of alumina (i.e., 0.25 wt%) or partially to fully-stabilized zirconia with higher yttria content have been first developed at the laboratory scale (Zhang *et al.*, 2014) but are now available commercially (e.g., Tosoh TZ-3Y-E with 0.1–0.4 wt% Al_2O_3 , TZ-8Y with 8 mol% Y_2O_3). The improved 3Y-TZP LTD resistance when adding small quantities of alumina is linked to the segregation of Al^{3+} at the grain boundaries and the heterogeneous distribution of Y^{3+} . In Y-rich systems, the improved aging resistance is due to the full stabilization of the cubic phase, as in 8Y-FSZ ceramics (FSZ for *Fully Stabilized Zirconia*). The better understanding of LTD phenomenon and microstructural features effect has allowed yttria-stabilized zirconia to take off in the dental field, first as crowns, then as implants (Ren *et al.*, 2011; Li *et al.*, 2019b) as shown in Fig. 7.

To date there is no alarming report on the resistance to aging of yttria-stabilized zirconia used in dentistry, except in a few pre-clinical trials and research works involving special implants in which a new surface design or new surface treatments have been applied (Sanon *et al.*, 2015).

Optical Properties of Yttria-Stabilized Zirconia

Although 3Y-TZP zirconia is the strongest ceramic oxide in terms of flexural strength (typically > 1 GPa) and resistance to fracture (toughness of 5–8 $\text{MPa}\sqrt{\text{m}}$), other ceramics in the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ system containing up to 8 mol% of yttria have emerged driven by dental restorative applications. Their optimized esthetic properties and the advances made in CAD/CAM technologies allow the realization of dental crowns and frameworks based on several Y-stabilized zirconia, which can be also colored to match the patient teeth's coloring. Depending on the content of yttria, these new ceramics can be opaque, "highly-translucent" or "ultra-translucent" and characterized by different structural features but also lower strength as compared to 3Y-TZP. However, they exhibit a better resistance to aging as predicted by the phase diagram of Fig. 1, since the higher the stabilizer amount, the higher the "stable" cubic phase content.

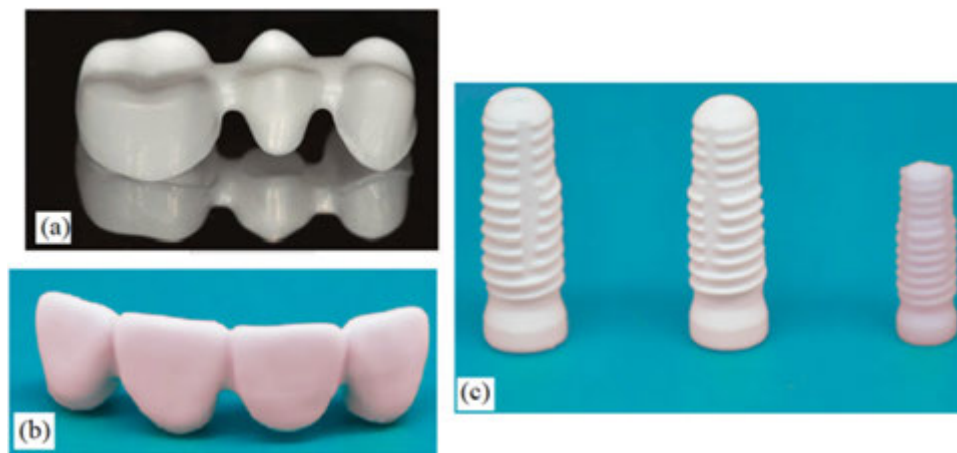


Fig. 7 Illustrations of full-ceramic crowns, fixed-partial denture or bridges and implants made of 3Y-TZP by (a) CAD/CAM and (c, d) stereolithography 3D printing; the corresponding change of size of implant after printing, debinding and sintering is shown. Adapted from Kyraiou, V., Pelekanos, S., Eliades, G., 2012. Identification of monoclinic phase in CAD/CAM zirconia FPD frameworks. *European Journal of Esthetic Dentistry: Official Journal of the European Academy of Esthetic Dentistry* 7, 418–429, and Li, H., Song, L., Sun, J., Ma, J., Shen, Z., 2019b. Dental ceramic prostheses by stereolithography-based additive manufacturing: Potentials and challenges. *Advances in Applied Ceramics: Structural, Functional and Bioceramics* 118, 30–36.

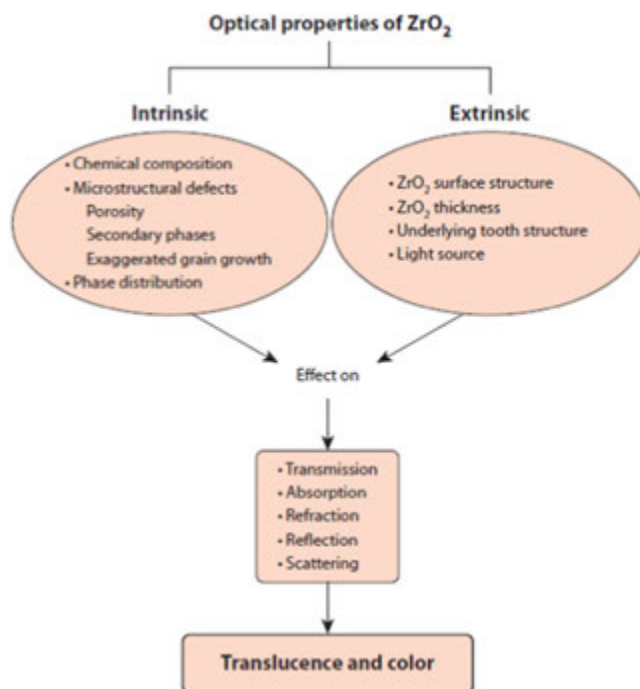


Fig. 8 Effect of intrinsic and extrinsic factors on optical properties of Y-TZP dental zirconia. From Shahmiri, R., Christopher, O., Hart, J., Sorrell, C.C., 2018. Optical properties of zirconia ceramics for esthetic dental restorations: A systematic review. *Journal of Prosthetic Dentistry* 119, 36–46.

As shown in Fig. 8, the color and appearance of monolithic Y-TZP zirconia dental restorations depend on intrinsic and extrinsic characteristics. Color matching and improved translucency is achieved by adding small amounts of dopants such as Fe₂O₃, Pr₂O₃, Al₂O₃, LaAl₂O₃ etc.

There are several other parameters, which may be varied to improve the esthetic; the interested reader may refer to the review papers proposed by Shahmiri *et al.* (2018) and Kontonasaki *et al.* (2020). Zirconia materials developed for dental applications typically contain 2–3 mol% of yttria (<15% cubic phase), 4–5 mol% of yttria (>50% cubic phase) or 6–8 mol% of yttria (up to 100% of cubic phase). The grain sizes range from 200 nm to 1500 nm. For 3Y-TZP, the refractive index is low (2.214) but that of birefringence is high (0.038), leading to greater scattering that can alter the color and increase the opacity. On the other hand, fully-stabilized-zirconia materials (FSZ with 100% of cubic phase) exhibit lower refractive index (e.g., 2.177 for 9 mol% of yttria) and no birefringence, which markedly improve translucency. However, in Y-rich ceramics the strength and toughness diminish because cubic zirconia does not undergo stress-induced transformation. Therefore, a compromise must be found in order to adapt the stabilizer content to the required properties, so the mechanical resistance versus esthetic depending on the application (e.g., restoration of the posterior or frontal regions of the mouth). In general, opaque zirconia (e.g., compositions close to 3Y-TZP) offers significantly greater strength (800–1000 MPa) and is indicated for the posterior regions of the mouth, while ultra-translucent zirconia (e.g., 5Y-PSZ) has lower mechanical properties (typically 500 MPa) but more natural esthetic appearance (required in the front part of the mouth). Even so, the strength of 5Y-PSZ (e.g., 500 and 900 MPa for Zpex Smile/Tosoh and Lava Esthetic/3M ESPE, respectively) is still higher than that observed in lithium disilicate (LS2) glass-ceramics (400–500 MPa for IPS e.max/Ivoclar Vivadent) (Zhang and Lawn, 2018).

Efforts are underway to further improving the esthetic and the mechanical properties of Y-TZP zirconia, for example, by incorporating small quantities of other oxides. Fig. 9 shows the effect of dopants (Al₂O₃, La₂O₃) on the mechanical, LTD and optical properties of 3Y and 5Y systems as reported by Zhang *et al.* (2015, 2016). The incorporation of alumina (0.05–0.25 wt% Al₂O₃) and/or 0.2 mol% La₂O₃ certainly enhances 3Y-TZP translucency and aging resistance but can also decrease mechanical properties. Co-doping 3Y-TZP with small amounts of alumina and lanthania leads to the segregation of Al³⁺ and La³⁺ at the zirconia grain boundaries. Segregation seems to be a key factor to design hydrothermally stable and high-translucent Y-TZP ceramics, while maintaining excellent mechanical properties.

Final Discussion: The Past, the Present and the Future of Y-TZP Zirconia in the Biomedical Field

The problem caused by selected batches of Prozyr® femoral heads in 2001 and the wide variability of research/clinical results regarding 3Y-TZP aging behavior highlighted the lack of precise specifications to ensure excellent long-term behavior of biomedical zirconia at that time. Since then, the mechanisms behind LTD and the effects of coupling different solicitations (biological,

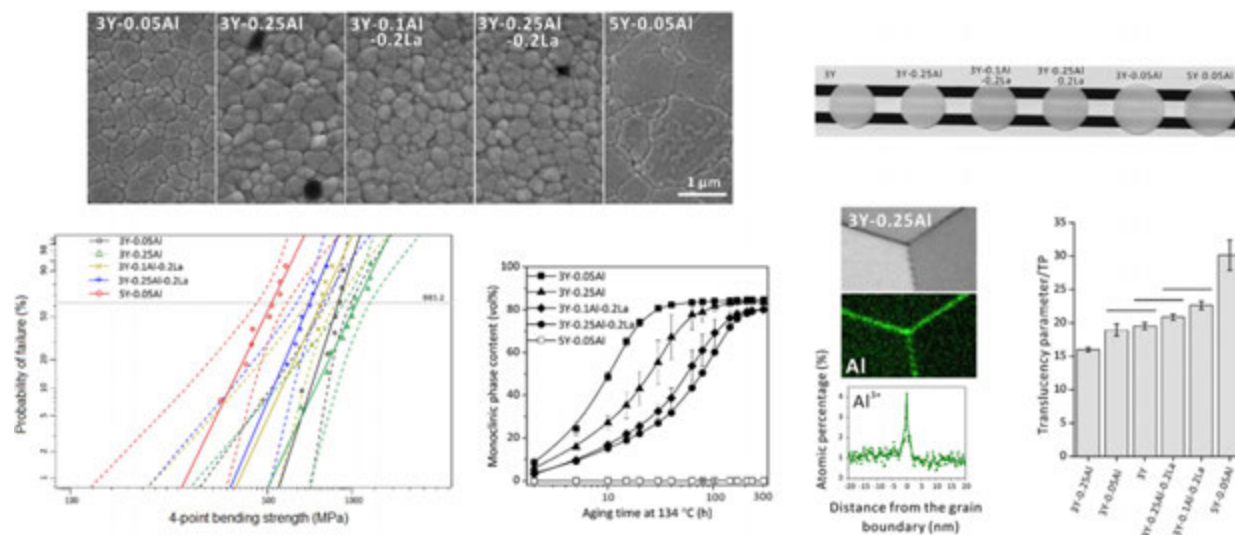


Fig. 9 Microstructure, Weibull plot for 4-point bending, Monoclinic phase transformed during accelerated aging tests and translucency parameters of highly translucent Y-TZP ceramics containing 3(3Y) and 5(5Y) mol% of Y_2O_3 , with 0.25, 0.1 or 0.05 wt% of Al_2O_3 (referred to as 0.25Al, 0.1Al and 0.05Al) or 0.2 mol% of La_2O_3 (referred as 0.2 La). Adapted from Zhang, F., Vanmeensel, K., Batuk, M., *et al.*, 2015. Highly-translucent, strong and aging-resistant 3Y-TZP ceramics for dental restoration by grain boundary segregation. *Acta Biomaterialia* 16, 215–222. Zhang, F., Inokoshi, M., Batuk, M., *et al.*, 2016. Strength, toughness and aging stability of highly-translucent Y-TZP ceramics for dental restorations. *Dental Materials* 32, e327–e337.

mechanical, wear, etc.) and microstructural/compositional features have been studied in depth. Today, we can better predict the aging of zirconia end products thanks to existing standardized procedures (proposed by ISO and ASTM standards since 2008) and other more complex tests that are currently being developed on a laboratory scale. These standards have been inspired in research works which have shown for instance that one hour of autoclave treatment at 134 °C had theoretically the same effect as few years in vivo, allowing to assess the aging sensitivity of a given zirconia in shorter times (Chevalier *et al.*, 1999b). However, even if enormous progress has been made on this aspect, recommendations of current standards (International Organization for Standardization, 2015a) need still to be revised (e.g., less than 25% of t-m transformation after 5 h of accelerated aging at 134 °C and 0.2 MPa). For instance, according to the standard for dental ceramics (International Organization for Standardization, 2015b) recommendations are made for samples having followed a specific surface preparation (i.e., grinded to 30–40 μm and then polished to 15–20 μm) which gives surface finishing/residual stresses very different from those observed in final dental products on in other biomedical devices. Standards have already been revised in the past following advances in the research field. For example, the first guidelines fixed the maximum grain size in biomedical-grade 3Y-TZP to a linear intersection distance of 0.6 μm but as numerous studies clearly showed a dramatic decrease of aging resistance above a linear intersect of 0.4 μm, the standard limit was modified accordingly. In current versions of standards, X-ray diffraction (XRD) allows to quantify the t-m transformation. However, in our opinion this technique is not enough alone and should be coupled to other ones for better characterizing the transformation, for example optical interferometry, atomic force microscopy and scanning electron microscopy of aged cross-sections (Chevalier *et al.*, 1999b; Deville *et al.*, 2004).

3Y-TZP started to be used in the dental field right after being “banished” from orthopedics, in which alumina-based composites containing zirconia become the standard. As in the case of orthopedics, zirconia ceramics were introduced as an alternative to alumina, first for manufacturing crowns, frameworks and abutments and then dental implants. The aging of 3Y-TZP dental materials could be an issue if lessons learned from the past are not taken into account. Let us recall here that it was the issue of break in series of Prozyr® femoral heads in 2001 that highlighted the coupled phenomena (aging, microstructure, slow-crack growth), contributing in this manner to their knowledge. If we had the knowledge of today on this subject 20 years ago, prostheses and femoral heads in zirconia would be currently among the safest on the market! By paying attention to the processing and post-treatments of dental materials and their impacts (which are now relatively well known), one can therefore guard against reckless risks.

Particular attention must be paid to dental implants where the roughness of their surface must be increased to improve osseointegration. Some studies start to report premature failure of zirconia dental implants (Scherer *et al.*, 2019) and restorations (Oilo and Arola, 2018) that have mainly been related to surface defects (where stress concentrations would be induced) or to design issues (due to the erroneous tendency to copy what is done on titanium implants). On the basis of available results, adapted protocols and quality controls have to be implemented to guarantee very precisely the main characteristics of dental zirconia (density, composition, grain size, grinding and polishing states, surface flaws and modifications, implant/restoration design, shape of threads, etc.), thus minimizing the risk of failure.

There is a room for further technical progress of currently available dental Y-TZP ceramics. For implants, the use of 3Y-TZP is preconized in order to be able to withstand the complex and high stresses to which they are subjected. Two-pieces dental implant

systems seem to be more desirable for technical reasons, although more challenging because of limitations related to connections. For external restorations, the zirconia-yttria composition can be adapted to the location in the mouth always taking into account the trade-off between esthetic and mechanical properties. Other dopants can also be added in order to improve the optical properties (i.e., transparency and color to match the aspect of the remaining natural teeth). Further innovation in additive manufacturing (AM) technologies could enable novel designs and solutions that are presently too high-cost. Digital dentistry is one of the fastest growing areas of AM technology and possible applications include the fabrication of crowns, bridges, dentures, models, surgical guides, implants and other orthodontic materials. Recently, some works have reported the use of ceramic stereolithography in manufacturing 3Y-TZP bridges, crowns, teeth and implants (Li *et al.* 2019a,b; Lian *et al.*, 2019). Nevertheless, important challenges as the reliability of the process, surface finishing, processing-defects and ceramic debinding/densification procedures must be overcome in order to implement an AM productive solution. Novel ultra-translucent and colored monolithic Y-TZP zirconia ceramics present considerably improved esthetic and translucency, better aging resistance but lower strength. They have to be further evaluated both *in vitro* and *in vivo* for their long-term potential behavior.

Taking advantage of its superior mechanical properties, novel Y-TZP biomedical applications are also being developed in the field of neuro-stimulation and heart's implantation, as biocompatible containers of electronic modules. Thin (40 μm), very flexible and near IR-transparent foils are used for housing ultra-thin implantable neuro-stimulators which contain an infrared photovoltaic module able to recharge the device without external wiring (Chevalier and Gremillard, 2017). Once again, an absolute vigilance must be paid to the LTD phenomenon, due to the very thin thicknesses of the parts implemented here and, above all, to the degree of criticality of these types of applications (Le Coadou *et al.*, 2015).

Conclusion

Zirconia and especially 3Y-TZP is the toughest ceramic oxide first used in orthopedics and then in the dental field due to its major advantages in terms of reliability versus crack propagation and delayed failure and consequently in terms of freedom to design. Even if the LTD remains a point of vigilance, zirconia 3Y-TZP will always keep a place of choice in the biomaterial field, thanks to its mechanical properties not yet equaled by another ceramic and to its very fine microstructure, which allows developing special optical properties.

If we look at the past, the failure episodes of Prozyr® femoral heads in 2001 which banned the use of 3Y-TZP in orthopedics have also opened a controversial debate about the future of zirconia as a biomaterial, which has helped deepen understanding of LTD. The unpleasant incidents, even if dramatic in some aspects, have led the scientific and orthopedic community to study the behavior of zirconia, especially with respect to aging *in vitro* and *in vivo*. Current knowledge shows that the strong variability of the degradation of zirconia *in vitro* and *in vivo* is related to the strong influence of processing and post-treatment procedures on aging kinetics. Early failure rates in some dental devices as reported in the past show that the 3Y-TZP sensitivity to undergo t-m transformation and its brittleness as a ceramic (even if tougher than alumina or glass-ceramics) remain the most critical factors in the dental field. It may seem that dental implant failures are less critical than failures in orthopedics, but it must be remembered here that the surgical procedure for retrieving a broken dental implant often involves a bone graft, additional healing times, discomfort for the patient and extra-costs, but more importantly, that all these health problems are now preventable.

Even if we know today how to avoid LTD and its consequences, new clinical studies and coupling test procedures are necessary in order to better identify the set of relevant technical and biological factors, which would seriously affect the durability of Y-TZP bioceramics. Certainly, 3Y-TZP ceramics and novel rich-yttria compositions can be excellent materials of choice in the area of dental restoration if all the variables linked to the processing and post-processing of the material are perfectly mastered. At the present as in the past, the future of zirconia as biomaterial will depend on the ability to control materials characteristics (which can be supplier-dependent) and applied post-treatments (sintering, polishing, grinding, etc.). For example, the hydrothermal stability limits for using zirconia as a biomaterial are standardized, but standard's guidelines do not include the effect of surface preparation on the aging resistance (International Organization for Standardization, 2016a). In other words, existing standards are useful for investigating the "intrinsic" sensitivity to aging of a given zirconia, but it may not give relevant information on the aging kinetics of "real" dental devices. Efforts must be made to develop new tests and normative procedures capable of taking into account surface modifications applied to the real products or devices and the coupled effect of the environment and the mechanical, chemical and biological stresses. We can certainly be more positive today about the future of Y-TZP as biomaterial compared to our position a decade ago. Although LTD remains to be monitored with precision, today we have all the knowledge to avoid it in the range of temperature and time compatible with most applications. Thus, thanks to its exceptional mechanical properties, the ease of implementation of CAD-CAM technologies and the tunability of optical properties, the future of the zirconia stabilized with yttria in the biomedical field, especially in the dental field, still looks very promising!

References

- Bansal, G.K., Heuer, A.H., 1972. On a martensitic phase transformation in Zirconia (ZrO_2) – I. Metallographic evidence. *Acta Metallurgica* 20, 1281–1289.
- Catledge, S.A., Cook, M., Vohra, Y., *et al.*, 2003. Surface crystalline phases and nanoindentation hardness of explanted zirconia femoral heads. *Journal of Materials Science: Materials in Medicine* 14, 863–867.

- International Organization for Standardization, 2015a. ISO 13356:2015 Implants for Surgery-Ceramic Materials Based on Yttria-stabilized Tetragonal Zirconia (Y-TZP). Geneva: ISO.
- International Organization for Standardization, 2015b. ISO 6872:2015 Dentistry-cERamic Materials. Geneva: ISO.
- Caton, J., Bouraly, J.P., Reynaud, P., Merabet, Z., 2004. Phase transformation in zirconia heads after THA myth or reality. In: Proceedings of the 9th BIOLOX Symposium, Paris, pp. 73–74.
- Chevalier, J., 2006. What future for zirconia as a biomaterial? In: Leong, K. (Ed.), *Biomaterials* 27. Elsevier, pp. 535–543.
- Chevalier, J., Gremillard, L., 2017. Chapter 1.6 - Zirconia as a biomaterial. In: Ducheyne, P. (Ed.), *Comprehensive Biomaterials II*, second ed. Elsevier, pp. 123–144.
- Chevalier, J., Olagnon, C., Fantozzi, G., 1999a. Subcritical crack propagation in 3Y-TZP ceramics, static and cyclic fatigue. *Journal of the American Ceramic Society* 82, 3129–3138.
- Chevalier, J., Drouin, J.M., Cales, B., 1999b. Low temperature aging of Y-TZP ceramics. *Journal of the American Ceramic Society* 82, 2150–2154.
- Chevalier, J., Gremillard, L., Virkar, A.V., Clarke, D.R., 2009. The tetragonal-monoclinic transformation in zirconia: Lessons learned and future Trends. *Journal of the American Ceramic Society* 92, 1901–1920.
- Chevalier, J., Deville, S., Münch, E., Jullian, R., Lair, F., 2004. Critical effect of cubic phase on aging in 3 mol% yttria-stabilized zirconia ceramics for hip replacement prosthesis. *Biomaterials* 25, 5539–5545.
- Clarke, I., Manaka, M., Green, D., *et al.*, 2003. Current status of zirconia used in total hip implants. *Journal of Bone and Joint Surgery* 85-A, 73–84.
- Deville, S., Guenin, G., Chevalier, J., 2004. Martensitic transformation in zirconia. Part I: Nanometer scale prediction and measurement of transformation induced relief. *Acta Materialia* 52, 5697–5707.
- Douillard, T., Chevalier, J., Descamps-Mandine, A., *et al.*, 2012. Comparative ageing behaviour of commercial, unworn and worn 3Y-TZP and zirconia-toughened alumina hip joint heads. *Journal of the European Ceramic Society* 32, 1529–1540.
- Garvie, R., Hannink, J., Pascoe, R., 1975. Ceramic steel? *Nature* 258, 703–704.
- Gerberich, J.W., Hemings, P.L., Merz, M.D., Zackay, V.F., 1968. Preliminary toughness results on TRIP steel. *Transactions of American Society for Metals* 61, 843–847.
- Green, D., Hannink, R., Swain, M., 1989. *Transformation Toughening of Ceramics*. Boca Raton, FL: CRC Press.
- Gremillard, L., Martin, L., Zych, L., *et al.*, 2013. Combining ageing and wear to assess the durability of zirconia-based ceramic heads for total hip arthroplasty. *Acta Biomaterialia* 9, 7545–7555.
- Haraguchi, K., Sugano, N., Nishii, T., *et al.*, 2001. Phase transformation of a zirconia ceramic head after total hip arthroplasty. *Journal of Bone and Joint Surgery* 83-B, 996–1000.
- Kobayashi, K., Kuwajima, H., Masaki, T., 1981. Phase change and mechanical properties of ZrO_2 - Y_2O_3 solid electrolyte after aging. *Solid State Ionics* 3/4, 489–495.
- Kontonasaki, E., Giasimakopoulos, P., Rigos, A.E., 2020. Strength and aging resistance of monolithic zirconia: An update to current knowledge. *Japanese Dental Science Review* 56, 1–23.
- Lawn, B., 1993. *Fracture of Brittle Solids*, second ed. Cambridge: Cambridge University Press.
- Lawson, S., 1995. Environmental degradation of zirconia ceramics. *Journal of the European Ceramic Society* 15, 485–502.
- Le Coadou, C., Karst, N., Emieux, F., *et al.*, 2015. Assessment of ultrathin yttria-stabilized zirconia foils for biomedical applications. *Journal of Materials Science* 50, 6197–6207.
- Li, H., Song, L., Sun, J., Ma, J., Shen, Z., 2019a. Stereolithography-fabricated zirconia dental prostheses: concerns based on clinical requirements. *Advances in Applied Ceramics: Structural, Functional and Bioceramics*. 236–243. doi:10.1080/17436753.2019.1709687.
- Li, H., Song, L., Sun, J., Ma, J., Shen, Z., 2019b. Dental ceramic prostheses by stereolithography-based additive manufacturing: Potentials and challenges. *Advances in Applied Ceramics: Structural, Functional and Bioceramics* 118, 30–36.
- Lian, Q., Wu, X., Li, D., *et al.*, 2019. Accurate printing of a zirconia molar crown bridge using three-part auxiliary supports and ceramic mask projection stereolithography. *Ceramic International* 45, 18814–18822.
- Maccauro, G., Piconi, C., Burger, W., *et al.*, 2004. Fracture of a Y-TZP ceramic femoral head, analysis of a fault. *Journal of Bone and Joint Surgery* 86B, 1192–1196.
- McMeeking, R., Evans, A., 1982. Mechanics of transformation toughening in brittle materials. *Journal of the American Ceramic Society* 65, 242–246.
- Minguela, J., Slawik, S., Mücklich, F., *et al.*, 2020. Evolution of microstructure and residual stresses in gradually ground polished 3Y-TZP. *Journal of the European Ceramic Society* 40, 1582–1591.
- Muñoz-Tabares, J.A., Anglada, M., 2012. Hydrothermal degradation of ground 3Y-TZP. *Journal of the European Ceramic Society* 32, 325–333.
- Muñoz-Tabares, J.A., Jiménez-Piqué, E., Reyes-Gasga, J., Anglada, M., 2011. Microstructural changes in ground 3Y-TZP and their effect on mechanical properties. *Acta Materialia* 59, 6670–6683.
- Oilo, M., Arola, D., 2018. Fractographic analyses of failed one-piece zirconia implant restorations. *Dental Materials* 34, 922–931.
- Piconi, C., Maccauro, G., 1999. Review: zirconia as a ceramic biomaterial. *Biomaterials* 20, 1–25.
- Ren, L., Janal, M.L., Zhang, Y., 2011. Sliding contact fatigue of graded zirconia with external esthetic glass. *Journal of Dental Research* 90, 1116–1121.
- Sanon, C., Chevalier, J., Douillard, T., *et al.*, 2015. A new testing protocol for zirconia dental implants. *Dental Materials* 31, 15–25.
- Sato, T., Shimada, M., 1985. Transformation of yttria-doped tetragonal ZrO_2 polycrystal by annealing in water. *Journal of the American Ceramic Society* 68, 356–359.
- Scherrer, S., Mekki, M., Crottaz, C., *et al.*, 2019. Translational research on clinically failed zirconia implants. *Dental Materials* 35, 368–388.
- Shahmiri, R., Christopher, O., Hart, J., Sorrell, C.C., 2018. Optical properties of zirconia ceramics for esthetic dental restorations: A systematic review. *Journal of Prosthetic Dentistry* 119, 36–46.
- Wei, C., Gremillard, L., 2018. Towards the prediction of hydrothermal ageing of 3Y-TZP bioceramics from processing parameters. *Acta Materialia* 144, 245–256.
- Yoshimura, M., Noma, T., Kawabata, K., Somiya, S., 1987. Role of water on the degradation process of Y-TZP. *Journal of Materials Science Letters* 6, 465–467.
- Zhang, F., Vanmeensel, K., Inokoshi, M., *et al.*, 2014. 3Y-TZP ceramics with improved hydrothermal degradation resistance and fracture toughness. *Journal of the European Ceramic Society* 34, 2453–2463.
- Zhang, F., Vanmeensel, K., Batuk, M., *et al.*, 2015. Highly-translucent, strong and aging-resistant 3Y-TZP ceramics for dental restoration by grain boundary segregation. *Acta Biomaterialia* 16, 215–222.
- Zhang, F., Inokoshi, M., Batuk, M., *et al.*, 2016. Strength, toughness and aging stability of highly-translucent Y-TZP ceramics for dental restorations. *Dental Materials* 32, e327–e337.
- Zhang, Y., Lawn, B.R., 2018. Novel zirconia materials in dentistry. *Critical Reviews in Oral Biology and Medicine* 92, 140–147.

ZTA Ceramics for Biomedical Applications

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Introduction

Total hip replacement (THR) surgery during which a worn natural hip joint is removed and replaced by a prosthesis was introduced by Dr. Charnley in 1960 (Campbell and Rothman, 1971) and has become a standard procedure with approximately 500,000 cases every year and an annual growth rate of a few percent (Rahaman *et al.*, 2007). Total knee replacement (TKR) is quickly catching up due to higher annual growth rates. The human hip is an enarthrosis (ball and socket joint). Indications are either cases of arthrosis or – less frequently – fracture, e.g., due to severe accidents (Crawford and Murray, 1997).

The natural enarthrosis is removed and replaced by a synthetic pairing (the prosthesis). The joint region of the femur is cut off and a metal stem (typically a titanium alloy) is inserted in the femur (by cementation or press-fit). The joint region in the pelvic bone is also machined away and a metal cup is implanted. The metal stem and cup are often surface structured and coated in order to promote safe long term fixation in the surrounding bone (Rahaman *et al.*, 2007).

The joint as such is represented by a ball fixed on a conical taper on the stem and a socket insert in the metal cup. The classical solution is metal balls of, e.g., cobalt chromium alloy and polymer counterparts of very stable ultrahigh molecular weight polyethylene (UHMWPE) (Geerdink *et al.*, 2006). Highly crosslinked polymers offer higher wear resistance but suffer from inherent brittleness (Bradford *et al.*, 2004). The lifetime of these standard prostheses is limited by wear of the metal/polymer pairings, which can either destroy the polymer or cause aseptic loosening of the joint by release of wear debris. Other negative effects are corrosion of the metal and release of metal ions. The lifetime strongly depends on the weight and mobility of the patient and may be individually very different; the estimated average lifetime of such a joint is in the range between 10 and 20 years (Crawford and Murray, 1997). It is reported that ~25% of implants fail prematurely (Emery *et al.*, 1997). Morell carried out an in detail analysis of a fractured alumina ball head (Morell *et al.*, 2012).

The motivation for introducing ceramics to THR was therefore mainly the reduction of wear in the artificial joint and thereby to avoid the risks and cost of revision surgery (Lavernia *et al.*, 1995). The extremely hard ceramics do not wear themselves, are well wetted by the synovial fluid and – if properly machined – also cause much less wear in the polymer counterpart (Willmann, 1996).

Biomedical grade alumina was the first material used in THR since the 1970s (Boutin *et al.*, 1988). Alumina while being hard and abrasion resistant is also relatively brittle ($K_{IC} \sim 3\text{--}4 \text{ MPa}\sqrt{\text{m}}$). Over the last 20 years, the continuous improvement of material and manufacturing processes has led to a reduction of the failure rate of the alumina balls by reducing the number and size of defects (Willmann, 1996).

Yttria stabilized tetragonal zirconia polycrystals (Y-TZP) was introduced in the 1990s to overcome the brittleness of alumina (Christel, 1989). Y-TZP is much stronger and tougher than alumina. However Y-TZP being a non-equilibrium compound suffers from low temperature degradation (LTD). This was discovered first by Kobayashi *et al.* (1980) for higher temperatures. It was however not considered relevant for materials operating at low temperature in the living environment. In the 1990s, the failure of a large number of components in vivo and the subsequent revision surgeries and claims for damage together with an FDA (Food and Drug Administration) recall of zirconia femoral heads in 2001 led to an early end of the promising developments in Y-TZP prostheses (Chevalier *et al.*, 2007). As a matter of fact the new generation of ageing resistant Y-TZP materials was already under development and close to market introduction at this time (Burger *et al.*, 1997).

The need for a tougher and stronger material with high LTD resistance initiated the development of zirconia toughened alumina (ZTA) materials. The performance of Y-TZP and ZTA materials exposed to ageing and wear has been investigated in detail (Gremillard *et al.*, 2013). Today the world's top-selling ceramics (BioloX Delta® by CeramTec, Germany) for hip prostheses is a zirconia toughened composite (ZTC) which besides zirconia alumina and yttria contains small amounts of chromium and strontium oxides (Kuntz, 2006). The basic recipe had originally been developed for cutting tool applications under the abbreviation DC25 (25 mass % which correspond to 18 vol% zirconia) but was then found to be an excellent material for THR (Burger and Richter, 2001). As the patent had expired a few years ago, other manufacturers started manufacturing materials of similar composition. A summary on recent developments in biomedical grade ZTA is given by Kurtz *et al.* (2014).

An important point which deserves to be mentioned in this review is the regulatory environment imposed by government organizations such as the FDA in the USA or the corresponding organizations in other countries. They were regulatory procedures introduced to protect the patients and ensure a constant and reliable quality of medical products. For this purpose, all manufacturing procedures of a medical product brought successfully to the market and certified by these agencies are fixed. Any later changes of materials procedures etc., are subject to a re-assessment. As such re-assessments are costly and time consuming, products are seldom changed unless a serious reason is given (e.g., superior competitor product or, fundamental improvements in materials technology) which justifies the effort. The industry is therefore rather conservative. The same measures taken to protect the patients are somewhat conflicting towards innovations in the field.

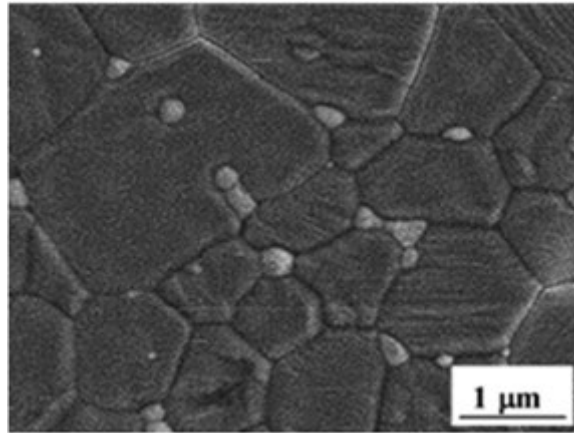


Fig. 1 Microstructure of alumina – 5 vol% zirconia (AZ5) made by mixing and milling.

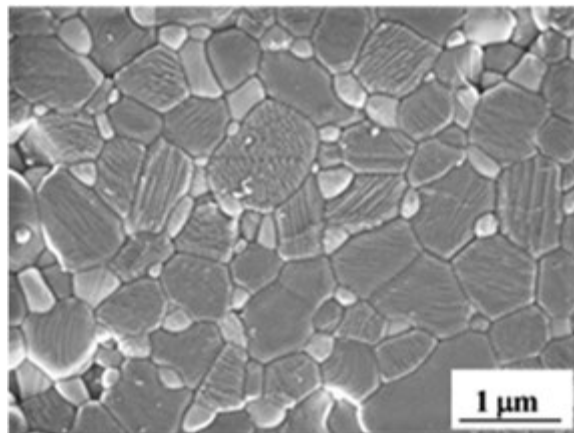


Fig. 2 Microstructure of alumina – 10 vol% zirconia (AZ10) made by mixing and milling.

ZTA – The Basics on the Materials

ZTA is a composite ceramic containing a zirconia dispersion in an alumina matrix. This combination boosts mechanical and tribological properties compared to alumina ([Wang and Stevens, 1989](#)). Depending on the amount of zirconia particles, their size, dispersion quality, zirconia stabilizer content (if any) and stabilizer type as well as firing conditions, a very wide broad range of properties can be realized in ZTA materials. In this context, it is beneficial to understand the role of the zirconia dispersion and the basic reinforcement concepts applied in ZTA. The reinforcement mechanisms in pure ZTA are transformation toughening, microcracking, and residual stress due to thermal mismatch of the phases and the fraction of transformed (monoclinic) zirconia.

Tailoring of the Microstructure

The effects of zirconia addition on the microstructure of ZTA materials were studied in detail by [Lange \(1982\)](#). They found out that zirconia is an efficient grain growth inhibitor for the alumina matrix. However, zirconia grains must be so numerous as to block all 4-junctions and thereby prevent coalescence of alumina grains. The threshold defined by [Lange and Hirlinger \(1984\)](#) is at ~ 7 vol% zirconia. It should however be considered that the effect will depend on the starting grain size of the alumina and zirconia and the quality of mixing of the two phases. The finer the zirconia phase and the better its dispersion degree the more stable will the microstructure be towards overfiring.

Figs. 1–4 show ZTA materials with zirconia fractions of 5–24 vol% ([Kern, 2010, 2012a, 2013; Kern et al., 2016](#)). All materials are based on the same 300 nm α -alumina by addition of nanoscale zirconia by mixing and milling and subsequent hot pressing (unpublished images, authors own work). It becomes clear that in AZ5 not all 4 junctions can be blocked and that in addition to

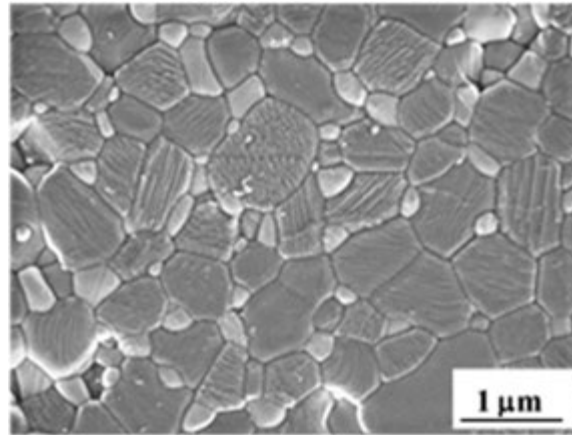


Fig. 3 Microstructure of alumina – 17 vol% zirconia (AZ17) made by mixing and milling.

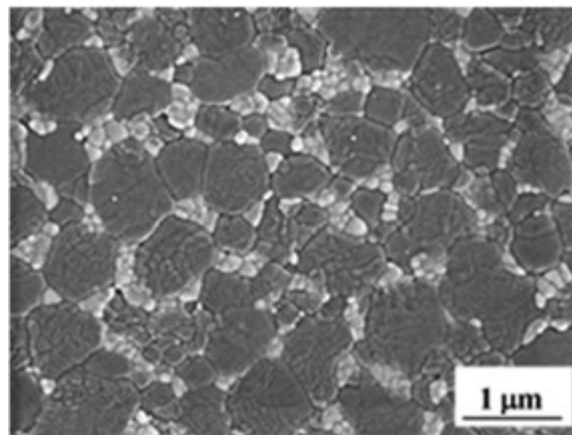


Fig. 4 Microstructure of alumina – 24 vol% zirconia (AZ24) made by mixing and milling.

zirconia grains at the grain boundaries some zirconia grains were trapped inside alumina particles due to grain growth of the matrix. In AZ10, these intragranular zirconia grains become rare and completely disappear at higher zirconia contents. In AZ17 (a typical biomedical grade composition) and even more pronounced in AZ24 (already out of biomedical grade specification), aggregation of zirconia grains is clearly visible.

Obtaining a perfect dispersion is therefore a matter of powder choice and proper choice of processing parameters. The problem was identified quite early and theoretically described by [Garvie \(1985\)](#) and [Garvie and Swain \(1985\)](#). The zirconia dispersion may be divided in three fractions. The first consist of oversize grains which transform to monoclinic during cooling from sintering temperature and are no longer available for transformation toughening. However, they may provide some toughness by inducing microcracking of the ceramic. The second fraction refers to undersized grains with a diameter lower than a critical size D_C^I which do not transform at all even if exposed to stress. What remains as an exploitable size fraction for transformation toughening are grains ranging from diameters D_C^I (lower limit) to the critical grain size D_C . The exploitable size range is surprisingly small. [Garvie \(1985\)](#) and [Garvie and Swain \(1985\)](#) calculated values between 380 and 460 nm. [Naglieri et al. \(2013a\)](#) showed that the range depends on the zirconia content and may range from 435 to 485 nm for alumina – 5 vol% unstabilized zirconia to 465–565 nm for alumina – 10 vol% unstabilized zirconia. In case of stabilized zirconia such values will be shifted towards larger grain sizes.

Distribution of zirconia and prevalence of isolated grains is also important for the aging (LTD) characteristics of zirconia materials. Transformed grains can trigger the transformation of adjacent grains (no matter if stress – or LTD-induced) ([Chevalier, 2006](#)). ZTA compositions below the percolation threshold in which the zirconia grains are not in contact (for grains of equal size $\sim 16\%$ zirconia content) are therefore considered LTD stable while such with higher contents will be prone to degrade. This consideration has led to the restriction of the maximum zirconia fraction in biomedical grade ZTA to <30 mass% ~ 22 vol%.

Materials made by mixing and milling react very sensitively to changes in dispersion conditions ([Heijman et al., 2002](#)). The initial approach to solve this problem was to make alumina–zirconia powders by sol–gel method which is feasible but extremely

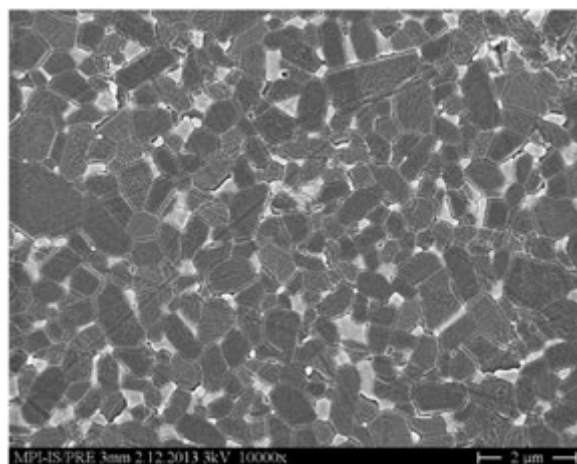


Fig. 5 Microstructure of alumina – 10 vol% zirconia (AZ10) made by powder coating.

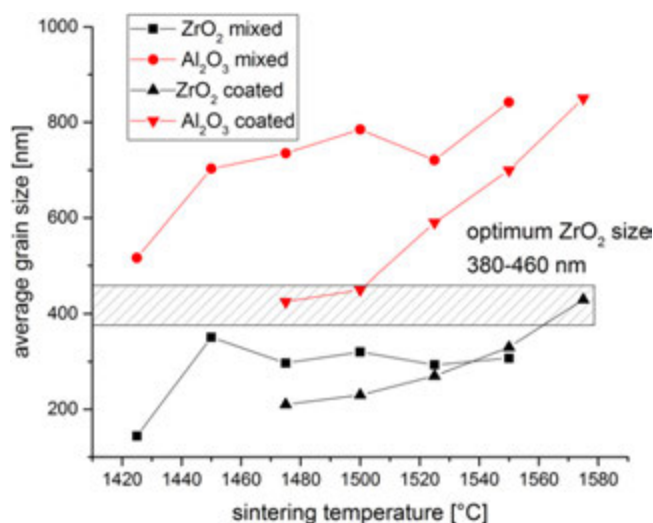


Fig. 6 Grain size of alumina and zirconia grains in AZ10 materials produced by mixing and milling vs. powder coating depending on sintering temperature.

uneconomical compared to a mixing and milling approach (Messing and Kumagai, 1989; Srdić and Radonjić, 1997). Later, it was proposed to crystallize zirconia particles on the surface of commercially available alumina powders by a wet chemical method (named surface coating process) (Palmero *et al.*, 2014).

The efficiency of this latter approach to obtain zirconia dispersions with a narrower zirconia grain size distribution was successfully demonstrated in various studies. Materials showed enhanced toughness and resistance to subcritical crack growth due to the higher transformable zirconia fraction and the LTD resistance was also enhanced (Deville *et al.*, 2003; Palermo *et al.*, 2009; Naglieri *et al.*, 2013a; De Aza *et al.*, 2003). Fig. 5 shows the microstructure of a AZ10 material made from a zirconia coated alumina powder sintered at 1525°C/3 h in air (Authors own work, related to: Kern *et al.*, 2015). Fig. 6 shows the grain sizes of alumina and zirconia in AZ10 ceramics made by mixing and milling and by surface coating process (Kern *et al.*, 2015; Kern, 2016). Evidently the alumina matrix and the zirconia dispersion are much finer in case of the “coated” starting powder. However, it is also seen that the zirconia grain size is in both cases at the lower end of the optimum range. This would also explain the moderate toughness of both materials (3.8–4.7 MPa√m for the coated, 4–5 MPa√m for the mixed ZTA). To the authors’ knowledge the concept was never technically implemented. The main causes were most probably regulatory ones, i.e., the need for a complete re-assessment of the production cycles and concerns about the up-scalability of the concept from lab to production size. The heat treatment of the coated powders is a tricky procedure to ensure a homogeneous crystallization of the zirconia nanoparticles on the alumina powder (Naglieri *et al.*, 2010). Another important point to be considered is the progress in conventional mixing and milling processes which today are capable to produce ZTA qualities far superior to the reference materials presented in the studies. Dispersion quality also affects the efficiency of reinforcement mechanisms as shown in the following paragraph.

Reinforcement Mechanisms

Typically, there are three basic reinforcement mechanisms in ZTA materials.

Residual stress fields result from different thermal expansion coefficients and elastic properties of alumina and zirconia phases. Besides these “regular” residual stresses, there is an additional stress increment exerted by zirconia grains which have transformed from tetragonal to monoclinic during cooling from high-temperature sintering (Gregori *et al.*, 1999).

Residual stress can be relieved and additional fracture surface can be created by microcracking. The effects may happen prior to loading (existing microcracks) or occur during loading by a superposition of residual and working stress. Residual stress – tensile or compressive – may initiate or impede microcracking.

Finally, there is transformation toughness, where transformation of tetragonal zirconia grains can be triggered by applied stress. This results in a martensitic tetragonal to monoclinic transformation associated with volume expansion of 4%–5% and shear. In contrast to Y-TZP, which transforms predominantly dilating, the transformation of isolated zirconia particles in ZTA may exploit both dilatation and shear and result in high transformation efficiency.

Microcracking

The first ZTA materials that were introduced by Claussen, exclusively exploited the concept of microcracking (Claussen, 1976). The materials contained a large fraction of large unstabilized zirconia particles which transformed to tetragonal during sintering and re-transformed to monoclinic during cooling down. As the $t \rightarrow m$ transformation of zirconia is associated with volume expansion and shear, the expanding zirconia particles exert tensile tangential stresses in the surrounding matrix. These stresses scale with r^3 (r = particle size) and may lead to circumferential microcracks (Evans and Faber, 1981). When a proceeding crack interacts with these microcracks, the fracture energy is dissipated by creating higher fracture surface which leads to an enhanced fracture resistance. While the toughness increase can be quite significant, these “pre-existing microcracks” – depending on the microstructure – may lead to a damaged microstructure and a loss of strength (Claussen, 1976). Microcracks may moreover create voids into which synovial fluid may penetrate and induce subcritical crack growth (Chevalier, 2006). Therefore, this toughening mechanism in its pure form is not suitable for biomedical grade ZTA.

Transformation toughening

In order to exploit this mechanism, it is necessary that the zirconia dispersed particles are largely tetragonal and transformable. As shown by Lange (1982) and Heuer *et al.* (1982), the transformability depends on zirconia particle size, zirconia particle content, and zirconia stabilizer content. Moreover, the shape and crystallinity of the zirconia particles, their location and the question if they form a percolating network are crucial. The transformation toughness ΔK_{IC}^T of the composite can be roughly calculated using a slightly modified formalism according to McMeeking and Evans (1982).

$$\Delta K_{IC}^T = X \cdot V_z \cdot V_m \cdot E \cdot \sqrt{c \cdot \varepsilon_T / (1 - \nu)} \quad (1)$$

(X : transformation efficiency, V_z : zirconia content, V_m : transformed fraction, c = transformation zone size, ε_T : expansion due to phase transformation, ν : Poisson’s ratio, E : Young’s modulus).

Interaction of different effects makes the exact quantification however very complicated.

Small amounts of <10 vol% fine and well distributed zirconia particles can be added without the need to add stabilizer (typically yttria) (Lange, 1982). Transformation of these isolated zirconia particles can only be triggered by stress. Martensite plates formed in one zirconia particle cannot trigger transformation in adjacent grains, the shear component of the transformation is reduced by self-accommodation: a formation of twin shaped monoclinic domains in the grains (Lee *et al.*, 1994). In such a case, the maximum transformation efficiency is obtained (dilatation and shear component fully exploited, $X \sim 0.5$, such as in magnesia stabilized zirconia Mg-PSZ) (Kelly and Rose, 2002). As the transformability of an inclusion is size-related, the challenge in these materials is to produce materials with an almost monodisperse zirconia fraction which transforms at a defined stress. Still due to the limited zirconia content V_z (typically 10–20 vol%), the achievable toughness increase is moderate.

In ZTA materials containing larger fractions of zirconia, the zirconia particles are no longer isolated and one transforming particle may trigger transformation in an adjacent grain. The percolation threshold for this transition theoretically is in the range of 15–17 vol% zirconia (Balberg *et al.*, 2004). In this case the transformation efficiency should be drastically reduced as then transformation should become largely dilating ($X = 0.22$). Moreover, it becomes necessary to stabilize the zirconia dispersion with, e.g., yttria to prevent re-transformation to monoclinic during cooling (Sommer *et al.*, 2012a,b). The beneficial effect of the increase in V_z is therefore partially offset by the reduction of X (see Eq. (1)). The maximum toughness is typically achieved for compositions close to the percolation point. Other stabilizers than yttria never gained any importance for biomedical grade ZTA. ZTAs with ceria stabilized zirconia dispersions (12Ce-TZP) would require zirconia grain sizes of 1.5–2 μm to overcome the constraint of the alumina matrix (Grain size 3–4 μm) and become sufficiently transformable (Becher *et al.*, 1993).

A combined effect of microcracking and transformation stress is transformation induced microcracking (Shin *et al.*, 1999). In this case, microcracks (non-preexisting) are formed under applied load when the applied stress triggers transformation of tetragonal zirconia grains. Contrary to preexisting microcracks, the material contains initially no flaws and shows no progressive damage as long as the applied stress is low (under regular operation conditions) but is able to provide a toughness boost in catastrophic loading situations.

Residual stress

Without phase transformation, the inclusion of a high CTE tetragonal zirconia grain into a low CTE alumina matrix results in compressive stress for the matrix and tensile stress for the inclusion: e.g., in a ZTA containing 25 wt% of entirely tetragonal zirconia, the alumina matrix is under a hydrostatic compressive stress of 225 MPa (Gregori *et al.*, 1999). The direct dispersion toughening effect of the high CTE dispersion is however negligible due to the fine grain microstructure of biomedical ZTA (Taya *et al.*, 1990). Applied and residual stress are additive. Such a situation – a matrix under compressive stress – is beneficial to achieve high strength. Moreover, the tensile stress on the tetragonal zirconia dispersion – the composite in total is stress neutral – should facilitate its stress induced transformation.

In “real” ZTA materials, the latter effect is difficult to realize as keeping the entire dispersion tetragonal (considering a certain width of zirconia grain size distribution) practically requires severe over-stabilization. Such materials, e.g., with a dispersion of 3Y-TZP are typically strong but not tough as the tetragonal phase is mostly not transformable. In ZTA materials in which the zirconia partially re-transforms during cooling a certain monoclinic content is created associated by volume expansion. This volume expansion leads to tensile stress in the matrix, which counteracts the effect of the CTE mismatch (Gregori *et al.*, 1999). It was shown that an equilibrated strength-toughness characteristic is reached in a state where the matrix is stress neutral, i.e., a situation where CTE and transformation related volume expansion equilibrates (at ~22% monoclinic). The toughness maximum is typically obtained for a ZTA with an alumina matrix under slight tensile stress. Data from studies on hot pressed and pressureless sintered ZTA with biomedical grade recipe (17 vol% zirconia) support this assumption (Sommer *et al.*, 2012b; Kern *et al.*, 2016; Yildirim and Kern, 2019).

The state of residual stress not only affects the mechanical properties. Machining characteristics and behavior in as-implanted state are also strongly influenced. In an alumina matrix under tensile stress (at relative monoclinic zirconia contents of >25%), breakout of grains is facilitated. The detrimental effect to machinability was detected when trying to machine understabilized alumina – 17 vol% zirconia (Kern *et al.*, 2016). Pezzotti *et al.* (2008) showed that samples with low monoclinic content in as manufactured state formed a high fraction monoclinic after aging in vivo so that grain detachment was facilitated. Reviewing the properties of the biomedical grade materials of the leading manufacturer (higher phase stability after LTD in recent study by Pezzotti *et al.* (2010)) compared to earlier one by the same author (Pezzotti *et al.*, 2010) indicates that in recent years the manufacturer tended to retain a higher tetragonal phase content and sacrifice some toughness by finer microstructure and/or higher stabilizer content in favor of enhanced long term phase stability.

Third phases

Further “reinforcement phases” can be introduced into ZTA. Two leading companies use zirconia toughened composites (ZTC) which contain a few percent of in situ formed strontium hexaaluminate ($\text{SA6} = \text{SrAl}_{12}\text{O}_{19}$), a phase with an elongated plate or rod shape in addition to the zirconia dispersion. Despite the fact that these ZTCs do have extraordinarily high strength, the simplistic explanation that the effect is due to crack bridging and crack deflection which is put forward by the manufacturers (Kuntz, 2006) may be challenged due to basic fracture mechanics considerations (He *et al.*, 1994). Hexaaluminates have lower Young’s modulus than the alumina matrix (Schmid *et al.*, 1999), therefore a crack proceeding in the alumina matrix will never be deflected at a strong alumina SA6/interface hit orthogonally by the crack, this may happen only if the platelets are hit under a very flat angle. Still, the SA6 has higher CTE than alumina which should slightly increase toughness and the slightly lower elastic constraint may improve transformability of the zirconia dispersion. For ZTA containing 24 vol% zirconia (1.4Y) reinforced with cerium hexaaluminate ($\text{CeAl}_{11}\text{O}_{18} = \text{CA6}$), no crack deflection was found. Still the platelet reinforced materials had higher toughness and resistance to subcritical crack growth, however at lower strength and toughness (Kern, 2013). For material with 10 vol% unstabilized zirconia and 5 vol% platelet addition, abnormal grain growth and a shift from an inter-type to an intra-inter type microstructure at high sintering temperatures were observed (Kern, 2012b). Usually, any additional separate and insoluble phase may change the residual stress distribution and restrict grain growth which helps maintaining a fine microstructure during firing (Kim and Kriven, 2008; Palermo *et al.*, 2011a).

In order to develop a ZTA material with tailored strength-toughness characteristics for a demanding application such as biomedical implants, it is important to know that depending on material design and processing conditions all reinforcement effects are operative simultaneously.

The Set of Requirements and the Resulting Current Standard ISO6474-2

The effective requirements to ZTA implants are different with respect to the patient, his activity, his weight and the type of articulated joint (hip, knee, shoulder, etc.). In the case of hip, the requirements are definitely lower than in case of the knee. The ball/socket joint in the hip is preferably loaded compressively. However, a modern prosthesis system is based on a conical taper with press-fit of the ball-head; i.e., by this combination, the ball-head is under tensile stresses. Therefore, high mechanical strength properties are required for the ball-head. The joint (ball and socket joint) is in plane contact, so that the contact pressure per unit area is relatively low. In fact, the experience with the first generation of alumina THR prostheses – which had only moderate strength – leads to the assumption that the vast majority of implanted components survived. Regular loading conditions can be endured over long periods by alumina joints with proven track record which are less strong (~400–500 MPa) and less fracture

resistant ($K_{IC} < 4 \text{ MPa}\sqrt{\text{m}}$) than biomedical grade ZTA (Willmann, 1996). It should however be noted that 30 years ago hip implants were typically implanted to older patients with a lower level of activity.

Point or line load can however occur when the ball is withdrawn from the socket and chafing over the edge of the ceramic socket when slipping back (Uribe *et al.*, 2013). In case of ceramic/ceramic pairings, this can cause (even if it happens much less frequently than the regular loading) much more severe stripe wear and in rare cases, even chipping of the edge of the socket may occur. In case of larger balls, this effect can be reduced, as the articulation angle is larger for larger joints. While wear and release of wear debris is an important failure criterion for ceramic/polymer joints, the wear in ceramic/ceramic pairs is negligible. Rahaman *et al.* (2007) quoted wear rates of $200 \mu\text{m}/\text{year}$ for Co-Cr/UHMWPE, this value is reduced to $< 100 \mu\text{m}/\text{year}$ for alumina or zirconia articulating. Alumina/alumina couples show wear rates of $< 5 \mu\text{m}/\text{year}$. Similar tendencies which are however not comparable due to different wear units were obtained by El-Hajjar *et al.* (2013). They found a wear of $0.74 \text{ mm}^3/10^6$ cycles for alumina/alumina, $0.14 \text{ mm}^3/10^6$ cycles for ZTA/ZTA and $0.06 \text{ mm}^3/10^6$ cycles for ATZ/ATZ all ceramic joints.

Attaching the ball on the metal stem is a safe procedure as soon as the surgery procedures by the implant manufacturers are carried out properly. Moisture or any kind of debris such as small bone fragments in the gap between cone and ball must in any case be avoided. The latter cause tensile stress which can reduce the strength of the taper/ball combination drastically.

The knee is the most demanding component. The loading conditions are line or point load. It should be specified that the femoral and tibia part can be made of ceramics. They are, however, separated by a rotating or fixed UHMWPE polymer insert which drastically reduces the Hertzian load due to its low elastic modulus. Metal knee implants are relatively thin walled, which is no problem due to the ductility of the material. Extensive removal of tissue for implantation is to be avoided. The available space is limited which requires a design with low wall thickness and consequently a ceramic material with superior strength. Fixation of a ceramic knee implant is a tricky procedure even for skilled surgeons as the standard procedure for metal components – driving by impact – has to be carried out with utmost care to avoid damage. For this reason, no producer ever dared to commercialize knee implants made of alumina, the application of ceramic knee joints required materials with a higher strength and an improved fracture resistance. These prerequisites are only possible with ZTA or zirconia (Y-TZP). Requirements to knee implants are included in the standard DIN EN ISO 21536:2009. In the meantime, the first successful clinical studies were published. Meier *et al.* (2016) reported burst strength of 11.8–13.5 kN for the tibia part of the prosthesis made of BioloX Delta®.

Besides the mechanical stability, any material containing zirconia is viewed suspiciously since a couple of zirconia joints failed by LTD in the 1990s (Chevalier, 2006; Piconi *et al.*, 2006). LTD was discovered by Kobayashi years before but nobody seriously considered that the effect would happen with measurable speed at blood heat (Kobayashi *et al.*, 1980). Anyway due to some imperfections along the process chain of implant manufacturing, it happened and many patients suffered from sudden joint failure and the need to endure surgery once again. The claims for damage were severe and yttria stabilized zirconia was more or less banned for endoprosthesis applications even though newly developed recipes showed drastically improved LTD stability. Testing for LTD, a spontaneously happening phase transformation from tetragonal to monoclinic in contact with polar liquids (water, body fluids) has become a standard for qualifying biomedical grade ZTA materials. This includes not only the phase transformation as such but also mechanical tests, wear tests and fatigue tests after accelerated hydrothermal ageing. The requirements to ZTA materials are summarized in ISO standard 6474-2. Besides X-Ray diffraction and RAMAN spectroscopy tests to analyze the changes in the phase composition recently more sophisticated methods were applied. Pezzotti (2014) showed by cathodoluminescence measurements that the oxygen sub-lattice in alumina and zirconia (3Y-TZP) materials behave completely different if exposed to water over a long time. While alumina creates oxygen vacancies which can then be occupied by cations of lower valence such as Ca^{2+} and Mg^{2+} , Y-TZP actually eliminates a part of oxygen vacancies introduced by stabilizing with Y^{3+} – with the well-known detrimental consequences regarding LTD resistance. For alumina/zirconia composites, Pezzotti stated a strong influence of minor amounts of dopants such as chromia and titania (present in products by different manufacturers) which may have a strong and adverse influence on the phase stability and thereby the LTD resistance of ZTA.

Table 1 shows a selection of the most important requirements to composition, microstructure, and mechanical properties. Concerning the composition, besides the typical ingredients alumina, zirconia, and yttria to stabilize the zirconia phase, further constituents may be contained including projected additives (such as chromia, titania, or strontium oxide to create hexaaluminate platelets) but also allows a certain amount of impurities which are typically contained in the starting powders.

At first sight, these minimum requirements are just slightly better than a high quality alumina. It should however be mentioned that the best biomedical grade ZTA materials by far outperform the standard.

Manufacturing

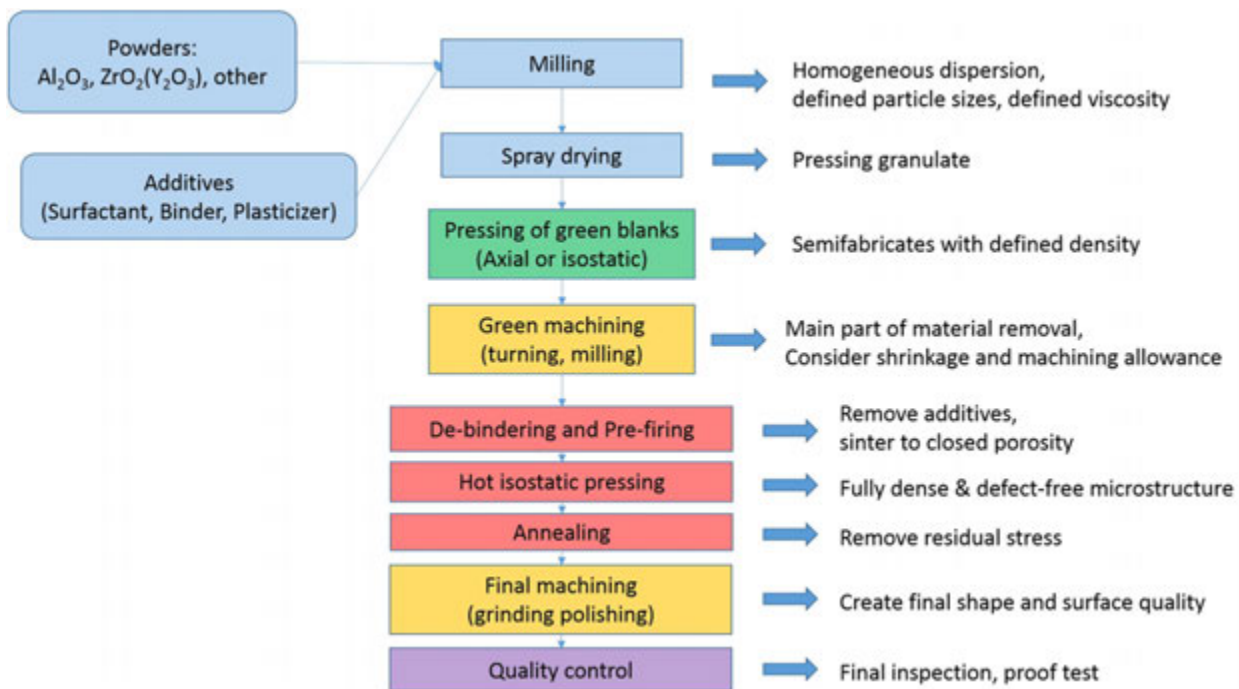
Despite the fact that several alternative routes have been tried to manufacture biomedical grade ZTA, the prevalent shaping technology is pressing of blanks and subsequent green machining. The complete process chain is shown in Fig. 7. The processing steps are strongly correlated to each other, so that the previous steps influence the subsequent ones. Therefore, inaccuracies or introduction of defects in one step may lead to detrimental consequences in the following steps which may result in insufficient quality or to increase in effort in the subsequent operations. As final machining represents the most costly part of the chain, all previous process steps must be carried out in such a way as to minimize the final machining effort.

Implants for, e.g., hip or knee are biomedical components and are therefore subject to strict regulations (e.g., by FDA). This means that once the material is authorized the whole production cycle is fixed and cannot be altered without re-approval by the

Table 1 Requirements according to ISO6474-2 type X

Property	Requirements acc. ISO6474-2
Density	$\geq 99\%$ of theoretical
Alumina grain size	$\leq 1.5 \mu\text{m}$
Zirconia grain size	$\leq 0.6 \mu\text{m}$
Bending strength	$\geq 600 \text{ MPa}$
Fracture resistance	$\geq 4 \text{ MPa}\sqrt{\text{m}}$
Vickers hardness	$\geq 16 \text{ GPa}$
Young's modulus	$\geq 320 \text{ GPa}$
Cyclic fatigue	No failure at 10^7 cycles at 400 MPa load
Hydrothermally aged strength	$\geq 600 \text{ MPa}$, $< 20\%$ strength loss compared to as processed condition
Hydrothermally aged fatigue	No failure at 10^7 cycles at 320 MPa load
Hydrothermally aged wear	$\leq 20\%$ wear increase compared to as processed condition
Composition	60–90 wt% alumina 10–30 wt% ZrO_2 ($< 5\% \text{ HfO}_2$) $< 10 \text{ wt}\%$ projected additives 0.2 wt% Impurities such as, e.g., SiO_2 , CaO , Na_2O

Note: Data extracted from ISO standard ISO6474-2.

**Fig. 7** Process chain for manufacturing of biomedical grade ZTA.

regulatory agency. Due to high effort of time and money re-approvals are in most cases economically not justified and, therefore, very rare.

Typically submicron size alumina and nanoscale zirconia are used as starting powders. Depending on the zirconia fraction, a stabilization of the zirconia with yttria is required (at $> 10 \text{ vol}\%$ zirconia) (Lange, 1982). Besides the main mandatory constituents some manufacturers add “projected additives” such as magnesium oxide, titanium oxide, strontium oxide and chromium oxide either to control grain growth, form second phases such as hexaaluminates or to stabilize zirconia (Pezzotti, 2014).

As structural homogeneity (i.e., a homogeneous dispersion of zirconia in the microstructure) is a crucial property, the compounding procedure is the key to achieve the desired properties such as mechanical strength and LTD resistance.

Mixing and milling steps represent the state of the art, here the challenge is to develop a surfactant system appropriate for the mixed suspensions containing powders of different surface chemistry. Fig. 8 shows some examples of Zeta potential curves of some alumina and zirconia powders (Yildirim and Kern, 2019). It can be seen that the alumina (APA0.5, green) and one of the zirconia powders (partially stabilized 2Y-TZP, IN-2Y, red) show almost identical trends, a point of zero charge at $\text{pH} = 5.5$ and sufficient

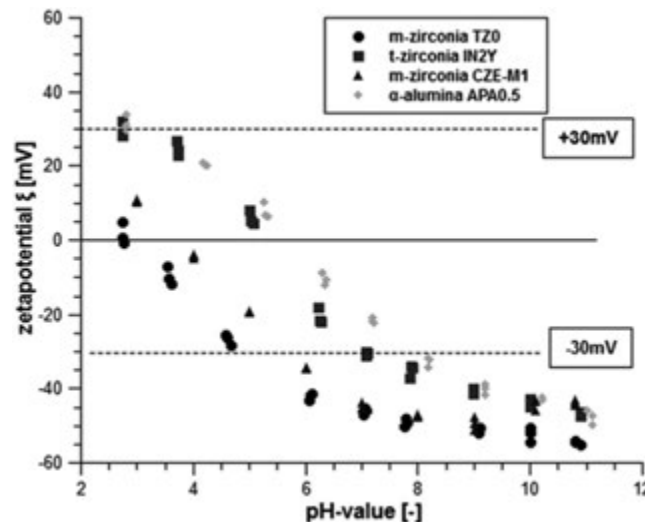


Fig. 8 Zeta potential of some alumina and zirconia powders. Redrawn, two data sets added Yildirim, N., Kern, F., 2019. Mechanical properties and ageing resistance of slip cast and pressurelessly sintered ZTA – The influence of composition and heat treatment conditions. *Sci. Sinter.* 51 (3), 1–14.

stability ($\zeta > 130 \text{ mV I}$) at $\text{pH} > 7.5$, while the two other monoclinic zirconia powders (TZ0 and CZE-M1) exhibit a point of zero charge at $\text{pH} = 3\text{--}3.5$ and a sufficient stability at $\text{pH} > 5.5$. Some of the projected additives such as magnesia and strontium oxide have a very basic character which would negatively affect the suspension stability. They may be added as aluminates (e.g., MgAl_2O_4) or zirconates (e.g., SrZrO_3) (Cutler *et al.*, 1991) as these ternary phases have a more favorable surface chemistry. Leriche and coworkers have shown that while yttria free recipes can also be dispersed in the acidic regime, yttria containing recipes should be prepared in the alkaline regime ($\text{pH} 10\text{--}11$) to avoid partial solubilization of yttria (Leriche *et al.*, 1992).

A good overview on organic additives for ceramics processing was recently published by Aimable and Chartier (2020). Today either commercially available electrosteric dispersants such as polyacrylates supplied under the brand names Darvan C-N by Vanderbilt minerals or Dolapix from Zschimmer & Schwarz are used or manufacturers have their own proprietary recipes.

At the technical scale, the compounding step is performed with batches of hundreds of kilograms of powder, which are mixed and milled in agitator bead mills with Y-TZP milling media. For this purpose, the powder blends are dispersed in de-ionized water using the aforementioned dispersants and milled, either by recirculation of the dispersion over the milling chamber of the bead mill, or by oscillating the suspension between two stirred storage tanks. The latter method is more complicated but offers the opportunity to adjust a narrower residence time distribution and thereby a potentially better homogeneity.

The stabilized suspension is blended with the other additives such as binders and plasticizers. The binders – typically either polyvinylalcohol (PVA) or acrylates – are required to provide the sufficient green strength for handling and green machining. Plasticizers make the ready-to-press-powder more compliant. The ready-to-press-powder is subsequently manufactured by spray drying to produce a granulate with an average diameter of $\sim 60\text{--}80 \mu\text{m}$, a more or less spherical shape, good free flowing properties and a well-defined bulk density (Naglieri *et al.*, 2013b). This well-defined bulk density is mandatory as in the subsequent pressing processes the metering of the granulate – at least in case of axial pressing is performed volumetrically.

Dry pressing is carried out either by uniaxial pressing which leads to cylindrical blank shapes or by cold isostatic pressing (CIP) which is capable to produce a roughly pre-shaped ball geometry. During the pressing process, it is necessary that the granules are completely crushed. In fact, remaining granule artefacts left in the microstructure of the green compact can produce detrimental effects in the mechanical properties of the sintered pieces. In order to minimize density gradients and resulting shape inaccuracies, uniaxial pressing is carried out by double sided pressing in steel molds, where the punches are often cemented carbide materials to reduce wear. CIP can be carried out either by wet- or dry bag technology. For mass production, typically dry-bag pressing is carried out in pre-shaped compressible polymer molds (e.g., polyurethane) which are capable to manufacture shapes very close to the desired final shape.

Fig. 9 shows how a cold isostatic pressed spherical green body is placed on a tray by a vacuum-assisted handling system after removing it from the press. As can be seen, apart from a ring-shaped seam the green compact is an almost perfect sphere.

Moreover, the green density of the pressed blanks has to be adjusted within an extremely narrow range with respect to the subsequent machining operations. This requires a strict control of the recipes for the pressing granulate and the protocols for the pressing parameters. Both uniaxial and isostatic pressing have their pros and cons.

Uniaxial pressed cylindrical blanks are much easier to mount and green machine due to their well-defined dimensions. It should however be considered that density distribution in an uniaxially pressed cylinder is always inhomogeneous, the top and bottom which were in contact with the punches are denser than the material in the center (press-neutral-zone). Therefore, by this pressing method, the machine parameters have to be adjusted that the press neutral zone is shifted within the cylindrical part to

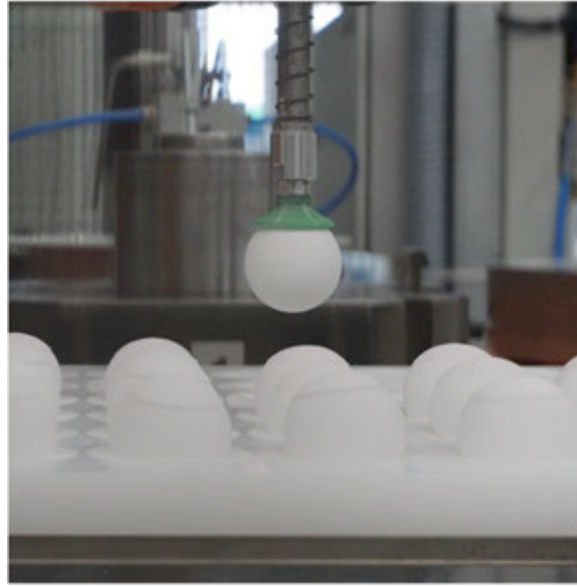


Fig. 9 Near net-shape cold isostatic pressed green bodies. Image courtesy of Mathysmedical (CH).



Fig. 10 Green machining of a ball. Image courtesy of Mathysmedical (CH).

the very low end. Clamping shall take place at the very low end of the cylinder. This approach finally guarantees a homogeneous green density for the final part after machining.

CIPed blanks (especially made by wet-bag processes) have more irregular shapes which makes correct mounting on the turning machines a bit more complicated. However, using CIPed blanks saves a lot of precious raw material as the blank already has a pre-shape. For a ball of 40 mm final diameter, it may be estimated that considering a loss fraction of 50% starting from axially pressed and only 15% if starting from near net shape CIP blanks, the material saved amounts to ~ 40 g per piece (taking into account that 1 kg of ready-to-press powder in production is about EUR 100.–, savings by isostatic near-*net*-shape pressing are significant).

Fig. 10 shows the green machining (turning) of a ball. Machining is made in dry state, and milling dust has to be extracted by suction. Due to the highly abrasive character of the green compact typically diamond coated milling tools are used. [Klocke *et al.* \(1997\)](#) showed that despite the higher price of diamond coated tools compared to plain cemented carbide tools, the cost per machined piece can be cut by factor of three. As besides the machining of the outer contour the conical taper also has to be machined out, it is necessary to change the clamping from left to right after finishing the milling operation from one side. Typically, automated lathes equipped with two opposite clamping units and automatic tool changer are used. Proper selections of tools, clamping devices and machining strategies are essential to obtain defect-free green-machined semi fabricates ([Margarindo *et al.*, 2017](#)). Contrary to manufacturing of less demanding structural ceramic parts, recycling of the milling dust is not possible due to the inherent risk of contaminating the ready-to-press powder with debris from the cutting tools. The economic challenge in

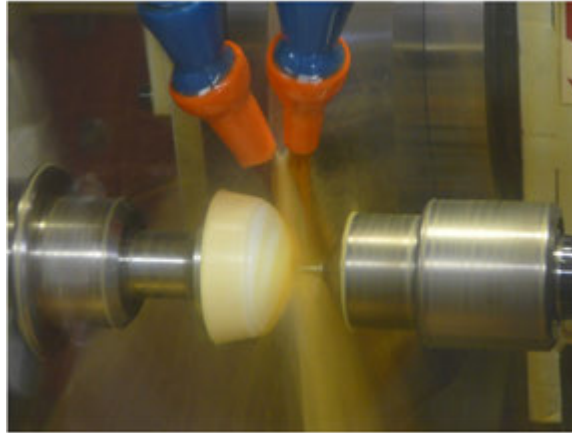


Fig. 11 Grinding of a ceramic liner. Image courtesy of Mathysmedical (CH).

green machining is to create a geometry extremely close to the final shape (considering sintering shrinkage) so that final machining can be reduced to a minimum.

Non rotationally-symmetric parts require more complex machining operations. Especially complex shaped surfaces of knee-implants could not be economically machined until very fast program-controlled 5-axis milling machines were set up which were capable to machine complex shapes and create a smooth enough surface. Near-*net*-shape technologies capable to form such complex geometries would be highly desirable to cut production cost and reduce waste. Technologies considered were slip casting (Naglieri *et al.*, 2013a), direct coagulation casting (DCC) (Graule *et al.*, 1995) and application of ceramic injection molding (Abou El-Ezz *et al.*, 2011). However, to date no net-shaping technology was developed that was able to produce components for THR and TKR of the required strength and reliability.

Machined components are typically automatically mounted on suitable kiln furniture, balls are typically sintered on spherical sockets.

In order to meet the high requirements concerning strength, toughness, wear resistance and LTD resistance, the ceramics should be almost perfectly defect-free and have a fine-grained and extremely homogeneous microstructure (Chevalier *et al.*, 2007, 2009). The heat treatment is typically multi-stage process combining atmospheric sintering and hot-isostatic pressing ("sinter-HIP"). In the first sintering cycle under atmospheric conditions, the first step is burning out of the organic additives at low temperature ($\sim 600^\circ\text{C}$). After debinding, the components are sintered to closed porosity; i.e., density above $\sim 94\%$. Preferably, the density of the pre-fired ceramic part should be between 96% and 98%. Depending on recipes this requires a sintering temperature of $\sim 1400\text{--}1500^\circ\text{C}$. Basically it is no problem to fully densify alumina-zirconia composites with submicron size microstructure below 1500°C by pressureless sintering in air (Palmero *et al.*, 2011b). In the next step, these pre-fired ceramics are transferred into a hot isostatic press. As the pre-firing has created a gas-tight microstructure, the sinter-HIP cycle can be carried out without the need to apply a pressure transducing shell as in classical HIP. Applied pressures are typically in the range of 100 MPa, the atmosphere is typically argon. The temperatures are approximately in the same range as in pre-firing. This pressure assisted sintering cycles is vastly capable to remove remaining structural defects (Bocanegra-Bernal *et al.*, 2009).

The benefit of post-HIPing was manifested in a drastic increase in reliability. According to a report of CeramTec, the failure rate of Biolox® (alumina) femoral heads decreased from 0.026% to 0.004% from the first generation of relatively coarse grained pressureless sintered alumina femoral heads to the third generation of post-HIPed fine grained materials (Willmann, 1996). As the reducing atmosphere creates oxygen vacancies and as the pressure assisted sintering may create residual stresses typically a third heat treatment cycle is carried out under atmospheric conditions to re-oxidize and anneal the ceramics. It has to be stated that the major benefit achieved with HIPing has to be seen in combination with proof-testing.

Now the materials are ready for final machining. Fig. 11 shows the grinding of the outer side of a ceramic liner (pelvic part). Due to the high hardness and abrasion resistance of ZTA materials, this requires the use of diamond tools for grinding and diamond suspensions for polishing. Compared to alumina machining of the hard, tough and fine grained ZTA material is much more challenging. The transition from ductile to brittle in grinding of ceramics is observed at a value of

$$h_{crit} = 0.15(E/H) \cdot (E/K_{IC})^2 \quad (2)$$

(with E = Young's modulus, H = Vickers hardness, K_{IC} = fracture resistance). To obtain brittle behavior which enables machining at high speed, a typical biomedical grade ZTA ($E = 356 \text{ GPa}$, $H = 18 \text{ GPa}$, $K_{IC} = 6 \text{ MPa}\sqrt{\text{m}}$) requires an advance rate h_{crit} three times higher than a typical biomedical grade alumina ($E = 385 \text{ GPa}$, $H = 18 \text{ GPa}$, $K_{IC} = 3.5 \text{ MPa}\sqrt{\text{m}}$). This increases the requirements to machines and tools drastically (Klocke and König, 2005). At the same time, it should be considered that even though brittle conditions are required for acceptable machining speed during the roughing step, machining in the brittle regime always means a damaging of the surface. As ZTA contains transformable tetragonal zirconia, there is always a phase transformation



Fig. 12 Measurement of the geometry by tactile method. Image courtesy of Mathysmedical (CH).

of the zirconia from tetragonal to monoclinic in the processed zone under roughing conditions (Denkena *et al.*, 2017). Such a transformed zone is typically under high compressive stress and desired for many mechanical engineering applications. The correlation between residual stress, strength and machining is very complex and non-linear (Xu *et al.*, 2010).

In contrast, in case of ZTA for biomedical applications a machining induced phase transformation is not desired in the final component as it is feared that existing monoclinic phase nucleates subsequent low temperature degradation processes. Proper adjustment of machining parameters, choice of tool geometries, cooling liquids and lubricants is required to achieve the necessary surface quality for a ceramic-polymer or all ceramic couple and to avoid machining induced LTD processes. Hence, there are no publications giving details on this special issue, and the knowledge generated in the companies in this field over generations that gives power over competitors was always kept secret. It is known that even companies with decades of experience in machining alumina or zirconia had a hard time machining the hard and tough ZTA material and it took time and financial effort to process a set of appropriate and profitable machining parameters.

Quality control has become an integral part of the production cycle in order to persistently guarantee the specified material properties and in order to meet the requirements of the regulatory agencies. Fig. 12 shows the tactile measurement of the taper geometry of ceramic balls.

Different companies use various exactly specified test protocols including, e.g., automated measurement of geometrical tolerances, optical inspection, application of fluorescent crack detection solvents, regular measurement of randomly picked control samples and proof tests in which every single component is checked with a specified load which exceeds the load expected in application. Failure of a single component in the proof test may lead to a blocking of the whole production batch until the reason for failure is detected. Laser marking of the manufactured components allows traceability of the components.

Conclusion

Biomedical grade ZTA materials have today reached a high degree of reliability and maturity. Manufacturing cycles were successively refined over the last two decades allowing to manufacture materials with very high strength, abrasion resistance and LTD stability. This has allowed for extending the range of applications from the classical total hip arthroplasty to the knee which is mechanically more demanding, the shoulder and other smaller joints. However, it is difficult to predict what the next stage of development will be, a modified more sophisticated ZTA ceramic or a completely different material system such as silicon nitride which has recently entered the market.

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References

- Abou El-Ezz, M., Kern, F., Gadow, R., 2011. Ageing behavior of injection-molded ZTA ceramics as a function of stabilizer content. *J. Ceram. Sci. Tech.* 02 (04), 191–196.
- Aimable, A., Chartier, T., 2020. Organic additives for ceramics processing. In: *Reference Module in Materials Science and Engineering*. Springer. doi:10.1016/B978-0-12-803581-8.11768-0.
- Balberg, I., Azuley, D., Toker, D., Millo, O., 2004. Percolation and tunneling in composite materials. *Int. J. Mod. Phys. B* 18 (15), 2091–2121.
- Becher, P., Alexander, K.B., Bleier, A., *et al.*, 1993. Influence of ZrO_2 grain size and content on the transformation response of Al_2O_3 - ZrO_2 (12 mol% CeO_2) system. *J. Am. Ceram. Soc.* 76 (3), 657–663.
- Bocanegra-Bernal, M.H., Domínguez-Rios, C., García-Reyes, A., *et al.*, 2009. Hot isostatic pressing (HIP) of α - Al_2O_3 submicron ceramics pressureless sintered at different temperatures: Improvement in mechanical properties for use in total hip arthroplasty (THA). *Int. J. Refract. Met. Hard Mater.* 27, 900–906.
- Boutin, P., Christel, P., Dorlot, J.M., *et al.*, 1988. The use of dense alumina-alumina ceramic combination in total hip replacement. *J. Biomed. Mater. Res.* 22 (12), 1203–1232.
- Bradford, L., Baker, D., Riess, M.D., Pruitt, L.A., 2004. Fatigue crack propagation resistance of highly crosslinked polyethylene. *Clin. Orthop.* 429, 68–72.
- Burger, W., Richter, H.G., Piconi, C., *et al.*, 1997. New Y-TZP powders for medical grade zirconia. *J. Mat. Sci. Mater. Med.* 8, 113–118.
- Burger, W., Richter, H.G., 2001. High strength and toughness alumina matrix composites by transformation toughening and 'in situ' platelet reinforcement (ZPTA) – The new generation of bioceramics. *Key Eng. Mat.* 192–195, 545–548.
- Campbell, R.E., Rothman, R.H., 1971. Charnley low-friction total hip replacement. *Am. J. Roentgenol. Radium. Ther. Nucl. Med.* 113 (4), 634–641.
- Chevalier, J., 2006. What future for zirconia as a biomaterial? *Biomaterials* 27, 535–543.
- Chevalier, J., Gremillard, L., Deville, S., 2007. Low-temperature degradation of zirconia and implications for biomedical implants. *Annu. Rev. Mater. Res.* 37, 1–32.
- Chevalier, J., Gremillard, L., Virkar, A.V., Clarke, D.R., 2009. The tetragonal-monoclinic transformation in zirconia: Lessons learned and future trends. *J. Am. Ceram. Soc.* 92 (9), 1901–1920.
- Christel, P.S., 1989. Zirconia: The second generation of ceramics for total hip replacement. *Bull. Hosp. Joint Dis. Orthop. Inst.* 49, 170–177.
- Claussen, N., 1976. Fracture toughness of Al_2O_3 with an unstabilized ZrO_2 dispersed phase. *J. Am. Ceram. Soc.* 59 (1–2), 49–51.
- Crawford, R.W., Murray, D., 1997. Total hip replacement: Indications for surgery and risk factors for failure. *Ann. Rheum. Dis.* 56, 455–457.
- Cutler, R.A., Mayhew, R.J., Prettyman, K.M., Virkar, A.V., 1991. High-toughness Ce-TZP/ Al_2O_3 ceramics with improved hardness and strength. *J. Am. Ceram. Soc.* 74 (1), 179–186.
- De Aza, A.H., Chevalier, J., Fantozzi, G., Schehl, M., Torrecillas, R., 2003. Slow-crack-growth behavior of zirconia-toughened alumina ceramics processed by different methods. *J. Am. Ceram. Soc.* 86 (1), 115–120.
- Denkena, B., Busemann, S., Gottwik, L., Grove, T., Wippermann, A., 2017. Material removal mechanisms in grinding of mixed oxide ceramics. *Procedia CIRP* 65, 70–77.
- Deville, S., Chevalier, J., Fantozzi, G., *et al.*, 2003. Low-temperature ageing of zirconia-toughened alumina ceramics and its implication in biomedical implants. *J. Eur. Ceram. Soc.* 23, 2975–2982.
- El-Hajjar, M., Jennings, L.M., Begand, S., *et al.*, 2013. Wear of novel ceramic-on-ceramic bearings under adverse and clinically relevant hip simulator conditions. *J. Biomed. Mater. Res. B Appl. Biomater.* 101 (8), 1456–1462.
- Emery, D.F.G., Clarke, H.J., Grover, M.L., 1997. Stanmore total hip replacement in younger patients: Review of a group of patients under 50 years of age. *J. Bone Joint Surg.* 79 (2), 240–246.
- Evans, A.G., Faber, K.T., 1981. Toughening of ceramics by circumferential microcracking. *J. Am. Ceram. Soc.* 64 (7), 394–398.
- Garvie, R.C., 1985. Thermodynamic analysis of the tetragonal to monoclinic transformation in a constrained zirconia microcrystal – Part 2 In the presence of an applied stress. *J. Mat. Sci.* 20, 3479–3486.
- Garvie, R.C., Swain, M.V., 1985. Thermodynamics of the tetragonal to monoclinic phase transformation in constrained zirconia microcrystals – Part 1 In the absence of an applied stress field. *J. Mat. Sci.* 20, 1193–1200.
- Geerdink, C.H., Grimm, B., Ramakrishnan, R., *et al.*, 2006. Crosslinked polyethylene compared to conventional polyethylene in total hip replacement: Pre-clinical evaluation, in vitro testing and prospective clinical follow-up study. *Acta Orthop.* 77 (5), 719–725.
- Graule, T.J., Gauckler, L.J., Bader, F.H., 1995. Direct coagulation casting (DCC): Fundamentals of a new forming process for ceramics. *Ceram. Trans.* 51, 457–461.
- Gregori, G., Burger, W., Sergio, V., 1999. Piezo-spectroscopic analysis of the residual stresses in zirconia-toughened alumina ceramics: The influence of the tetragonal-to-monoclinic transformation. *Mat. Sci. Eng. A* 271, 401–406.
- Gremillard, L., Martin, L., Zych, T., 2013. Combining ageing and wear to assess the durability of zirconia-based ceramic heads for total hip arthroplasty. *Acta Biomater.* 9, 7545–7555.
- He, M.H., Evans, A.G., Hutchinson, J.W., 1994. Crack deflection at an interface between dissimilar elastic materials – The role of residual stresses. *Int. J. Solids Struct.* 31 (24), 3443–3455.
- Heijman, M.J.G.W., Benes, N.E., ten Elshof, J.E., Verweij, H., 2002. Quantitative analysis of the microstructural homogeneity of zirconia-toughened alumina composites. *Mat. Res. Bull.* 37, 141–149.
- Heuer, A.H., Claussen, N., Kriven, W.M., Ruhle, M., 1982. Stability of tetragonal ZrO_2 particles in ceramic matrices. *J. Am. Ceram. Soc.* 65 (12), 642–650.
- Kelly, P.M., Rose, L.R.F., 2002. The martensitic transformation of ceramics – Its role in transformation toughening. *Prog. Mat. Sci.* 67, 463–557.
- Kern, F., 2010. Microstructure and mechanical properties of hot-pressed alumina – 5 vol% zirconia nanocomposites. *J. Ceram. Sci. Tech.* 2 (1), 69–74.
- Kern, F., 2012a. Sintering conditions, microstructure and properties of alumina 10 vol% zirconia nanocomposites. *J. Ceram. Sci. Tech.* 3 (1), 1–8.
- Kern, F., 2012b. Structure-property relations in alumina–zirconia nanocomposites reinforced with in situ formed cerium hexaaluminate precipitates. *Scr. Mater.* 67, 1007–1010.
- Kern, F., 2013. Effect of In situ-formed cerium hexaaluminate precipitates on properties of alumina -24 vol% Zirconia (1.4Y) composites. *J. Ceram. Sci. Tech.* 04 (04), 177–186.
- Kern, F., 2016. Neue Oxidkeramiken und Nanocomposites für Hochleistungsanwendungen. Habilitation Thesis. Aachen: Shaker Verlag.
- Kern, F., Koummarasy, S., Gadow, R., 2016. The Influence of stabilizer concentration on the mechanical properties of alumina – 17 vol% zirconia (0.6Y-2Y) composites. *J. Ceram. Sci. Tech.* 07 (03), 295–300.
- Kern, F., Palmero, P., Marro, F.G., Mestra, A., 2015. Processing of alumina–zirconia composites by surface modification route with enhanced hardness and wear resistance. *Ceram. Int.* 41, 889–898.
- Kim, D.Y., Kriven, W.M., 2008. Processing and characterization of multiphase ceramic composites – Part II: Triplex composites with a wide sintering temperature range. *J. Am. Ceram. Soc.* 91 (3), 793–798.
- Klocke, F., Gerent, O., Schippers, C., 1997. Machining of advanced ceramics in the green state. *CFI/Ber. DKG* 74 (6), 288–290.

- Klocke, F., König, W., 2005. *Fertigungsverfahren 2 – Schleifen, Honen, Läppen*. Berlin Heidelberg: Springer-Verlag.
- Kobayashi, K., Kuwajima, H., Masaki, T., 1980. Phase change and mechanical properties of $\text{ZrO}_2\text{-Y}_2\text{O}_3$ solid electrolyte after ageing. *Solid State Ion* 3–4, 489–493.
- Kuntz, M., 2006. Validation of a new high performance alumina matrix composite for use in total joint replacement. *Semin. Arthroplast. JSES* 17, 141–145.
- Kurtz, S.M., Kocagöz, S., Arnhold, C., *et al.*, 2014. Advances in zirconia toughened alumina biomaterials for total joint replacement. *J. Mech. Behav. Biomed. Mater.* 31, 107–114.
- Lange, F.F., 1982. Transformation toughening – Part 4: Fabrication, fracture toughness and strength of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ composites. *J. Mater. Sci.* 17, 247–254.
- Lange, F.F., Hirlinger, M.M., 1984. Hindrance of grain growth in Al_2O_3 by ZrO_2 inclusions. *J. Am. Ceram. Soc.* 64 (3), 164–168.
- Lavernia, C.J., Drakeford, M.K., Tsao, A.K., *et al.*, 1995. Revision and primary hip and knee arthroplasty. A cost analysis. *Clin. Orthop. Relat. Res.* 311, 136–141.
- Lee, B.T., Hiraga, K., Shindo, D., Nishiyama, A., 1994. Microstructure of pressureless-sintered $\text{Al}_2\text{O}_3\text{-24vol% ZrO}_2$ composite studied by high-resolution electron microscopy. *J. Mater. Sci.* 29, 959–964.
- Leriche, A., Moortgat, G., Cambier, F., *et al.*, 1992. Preparation and characterization of a dispersion toughened ceramic for thermomechanical use (ZTA). Part I: Material preparation. Characterization of microstructure. *J. Eur. Ceram. Soc.* 9, 169–176.
- Margarindo, A., Purquerio, B.M., Foschini, C.R., Fortulan, C.A., 2017. Influence of the green-machining parameters on the mechanical properties of alumina rods. *Int. J. Adv. Manuf. Technol.* 88, 3475–3484.
- McMeeking, R., Evans, A.G., 1982. Mechanics of transformation-toughening in brittle materials. *J. Am. Ceram. Soc.* 65 (5), 242–246.
- Meier, E., Gelse, K., Trieb, K., *et al.*, 2016. First clinical study of a novel complete metal-free ceramic total knee replacement system. *J. Orthop. Surg. Res.* 11 (21), 1–7.
- Messing, G., Kumagai, M., 1989. Low-temperature sintering of seeded sol-gel-derived, ZrO_2 -toughened Al_2O_3 composites. *J. Am. Ceram. Soc.* 42 (1), 40–44.
- Morell, R., Danzer, R., Milošev, I., Trebše, R., 2012. An assessment of in vivo failures of alumina ceramic total hip joint replacements. *J. Eur. Ceram. Soc.* 32, 3073–3084.
- Naglieri, V., Gutknecht, D., Garnier, V., *et al.*, 2013b. Optimized slurries for spray drying: Different approaches to obtain homogeneous and deformable alumina-zirconia granules. *Materials* 21, 5382–5397.
- Naglieri, V., Joly-Pottuz, L., Chevalier, J., Lombardi, M., Montanaro, L., 2010. Follow-up of zirconia crystallization on a surface modified alumina powder. *J. Eur. Ceram. Soc.* 30, 3377–3387.
- Naglieri, V., Palmero, P., Montanaro, L., Chevalier, J., 2013a. Elaboration of alumina-zirconia composites: Role of the zirconia content on the microstructure and mechanical properties. *Materials* 6, 2090–2102.
- Palmero, P., Kern, F., Lombardi, M., Gadow, R., 2011b. Role of immiscible and miscible second phases on the sintering kinetics and microstructural development of nano-crystalline $\alpha\text{-Al}_2\text{O}_3$ -based materials. *Ceram. Int.* 37, 3547–3556.
- Palmero, P., Montanaro, L., Reveron, H., Chevalier, J., 2014. Surface coating of oxide powders: A new synthesis method to process biomedical grade nano-composites. *Materials* 7, 5012–5037.
- Palmero, P., Naglieri, V., Chevalier, J., Fantozzi, G., Montanaro, L., 2009. Alumina-based nanocomposites obtained by doping with inorganic salt solutions: Application to immiscible and reactive systems. *J. Eur. Ceram. Soc.* 29, 59–66.
- Palmero, P., Naglieri, V., Spina, G., Lombardi, M., 2011a. Microstructural design and elaboration of multiphase ultra-fine ceramics. *Ceram. Int.* 37, 139–144.
- Pezzotti, G., 2014. Bioceramics for hip joints: The physical chemistry viewpoint. *Materials* 7 (6), 4367–4410.
- Pezzotti, G., Saito, T., Takahashi, Y., Fukatsu, K., Sugano, N., 2010. Surface topology of advanced alumina/zirconia composite femoral head as compared with commercial femoral heads made of monolithic zirconia. *J. Am. Ceram. Soc.* 94 (3), 945–950.
- Pezzotti, G., Yamada, K., Sakahura, S., Pitto, R.P., 2008. Raman spectroscopic analysis of advanced ceramic composite for hip prosthesis. *J. Am. Ceram. Soc.* 91 (4), 1199–1206.
- Piconi, C., Maccauro, G., Piloni, L., *et al.*, 2006. On the fracture of a zirconia ball head. *J. Mat. Sci. Mater. Med.* 17, 289–300.
- Rahaman, M.H., Yao, A., Bal, B.S., Garini, J.P., Ries, M.D., 2007. Ceramics for prosthetic hip and knee joint replacement. *J. Am. Ceram. Soc.* 90 (7), 1965–1988.
- Schmid, C., Luccini, E., Sbaizero, O., Maschio, S., 1999. The Synthesis of calcium or strontium hexaluminate added ZTA composite ceramics. *J. Eur. Ceram. Soc.* 19, 1741–1746.
- Shin, Y.S., Rhee, J.W., Kang, S.J.L., 1999. Experimental evaluation of toughening mechanism in alumina-zirconia composites. *J. Am. Ceram. Soc.* 82 (5), 1229–1232.
- Sommer, F., Landfried, R., Kern, F., Gadow, R., 2012a. Mechanical properties of zirconia toughened alumina with 10–24 vol% 1.5 mol% Y-TZP reinforcement. *J. Eur. Ceram. Soc.* 32 (15), 3905–3910.
- Sommer, F., Landfried, R., Kern, F., Gadow, R., 2012b. Mechanical properties of zirconia toughened alumina with 10–24 vol% 1Y-TZP reinforcement. *J. Eur. Ceram. Soc.* 32 (16), 4177–4184.
- Srdić, V.V., Radonjić, L., 1997. Transformation toughening in sol-gel-derived alumina-zirconia composites. *J. Am. Ceram. Soc.* 80 (8), 2056–2060.
- Taya, M., Hayashi, S., Kobayashi, A.S., Yoon, H.S., 1990. Toughening of a particulate-reinforced ceramic-matrix composite by thermal residual stress. *J. Am. Ceram. Soc.* 73 (5), 1382–1391.
- Uribe, J., Geringer, J., Gremillard, L., Reynard, B., 2013. Degradation of alumina and zirconia toughened alumina (ZTA) hip prostheses tested under microseparation conditions in a shock device. *Tribol. Int.* 63, 151–157.
- Wang, J., Stevens, R., 1989. Review zirconia-toughened alumina (ZTA) ceramics. *J. Mater. Sci.* 24, 3421–3440.
- Willmann, G., 1996. Development in medical grade alumina during the last two decades. *J. Mater. Process. Technol.* 56, 168–176.
- Xu, H.H.K., Jahanmir, S., Ives, L.K., 2010. Effect of grinding on strength of tetragonal zirconia and zirconia toughened alumina. *Mach. Sci. Tech.* 1 (1), 49–66.
- Yildirim, N., Kern, F., 2019. Mechanical properties and ageing resistance of slip cast and pressurelessly sintered ZTA – The influence of composition and heat treatment conditions. *Sci. Sinter.* 51 (3), 1–14.

Phosphates

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Introduction

Phosphates are materials containing oxoanions of phosphorus (V), ranging from the simple orthophosphate group PO_4^{3-} through ring and chain anions to infinite networks. Oxoanions of phosphorus in lower oxidation states such as phosphite, HPO_3^{2-} , are also known. Many solid phosphates have been prepared or are found as minerals. Their diversity results from variations in the phosphate species, the large number of cations to which they may be coordinated, and the presence of other anions or molecules, notable H_2O . Their chemistry and properties are similar to those of solid silicates (see *Acid Catalysts, Clays, and Zeolites*). Background information on the chemistry of phosphates and related phosphorus species can be found in [Corbridge \(1974\)](#) and [Kanazawa \(1989\)](#).

Phosphate Anions

Solid phosphates are conveniently classified according to the anions they contain. Orthophosphates contain isolated phosphate tetrahedrons, but these can also be linked through P–O–P bridges to give a range of condensed phosphate anions ([Fig. 1](#)) ([Durif, 1995](#)).

Orthophosphates, (di)Hydrogen Phosphates

The orthophosphate (often shortened to “phosphate”) group, PO_4^{3-} , is the most common phosphorus oxoanion. All four oxygen atoms are usually coordinated to cations in solid orthophosphates leading to strongly bonded, extended structures. The acid orthophosphate

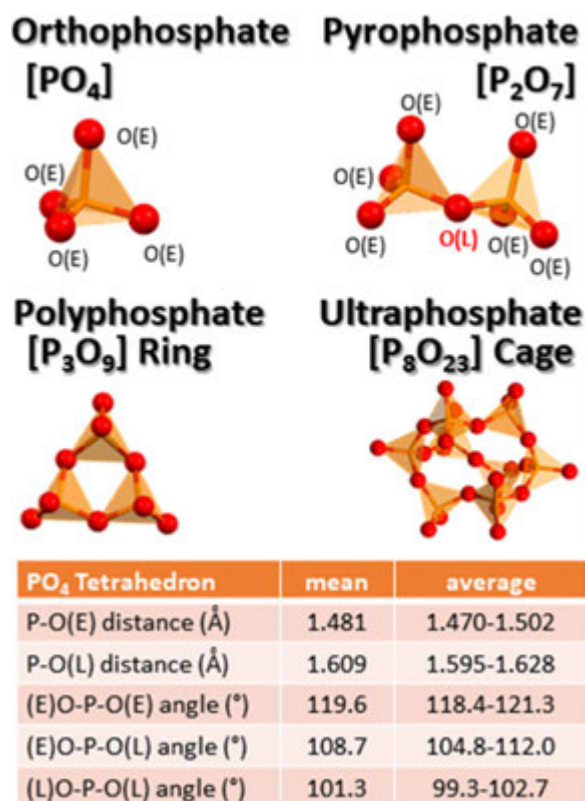


Fig. 1 Isolated P – O Structures Including Ortho, Pyro, Poly, and Ultra Phosphates. Description of the Geometry of the Basic Unit of the PO_4 Tetrahedron.

anions hydrogen phosphate, HPO_4^{2-} , and dihydrogen phosphate, H_2PO_4^- , are also found in many materials. Almost every metallic element forms an orthophosphate, and a range of oxidation states is stabilized for transition elements, e.g., from V^{II} to V^{V} in $\text{NaV}^{\text{II}}\text{V}^{\text{III}}_2(\text{PO}_4)_3$, $\text{V}^{\text{III}}\text{PO}_4$, $\text{V}^{\text{IV}}\text{O}(\text{H}_2\text{PO}_4)_2$, and $\text{V}^{\text{V}}\text{OPO}_4$. Mixed anion orthophosphates are sometimes found, e.g., $\text{Ca}_2(\text{PO}_4)\text{F}$, $\text{Fe}_2(\text{PO}_4)\text{O}$, $\text{LiMn}(\text{PO}_4)(\text{OH})$, and $\text{Ca}_5(\text{PO}_4)_2(\text{SiO}_4)$. Solid solutions in which the orthophosphate group is partially substituted by orthoarsenate, vanadate, and silicate groups further extend the range of possible phases.

Pyrophosphates, Diphosphates

The pyrophosphate anion $\text{P}_2\text{O}_7^{4-}$, consists of two phosphate tetrahedrons linked through a common oxygen atom. This bridging oxygen does not coordinate even to highly charged cations. Pyrophosphates are also known as “Diphosphates”. They often result from thermal treatment of orthophosphates. Many pyrophosphates are known and variations in composition and structure are similar to those for the orthophosphates.

Polyphosphates

Linking phosphate tetrahedra into chains through two vertices results in polyphosphate anions, $\text{P}_n\text{O}_{3n+1}^{(n+2)-}$, also known as oligophosphates. Finite chains containing up to six tetrahedra have been found in the solid state. They become less common with increasing n . Cyclophosphates (cyclopolyphosphates), $\text{P}_n\text{O}_{3n}^{n-}$, contain rings of up to 12 tetrahedra, but those with three, four, and six units are most common. Infinite catenaphosphates chains, $(\text{PO}_3^-)_\infty$, are formed at high temperatures. Polyphosphates sometimes adopt layered structures which can intercalate molecules in the interlamellar spaces, e.g., organic amines are intercalated by the triphosphates $\text{MH}_2\text{P}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Al}, \text{Cr}, \text{Mn}, \text{Fe}$).

Ultraposphates

These contain two- and three-connected phosphate tetrahedra and have stoichiometry $\text{P}_n\text{O}_{3n-1}^{(n-2)-}$, where $n = 4, 5, 6$, and 8. The unique cage phosphate anion $\text{P}_8\text{O}_{23}^{6-}$ is the only example of a molecular ultraposphate anion. The other species form infinite framework anions in which charge-compensating cations reside. Ultraposphates are anhydrous, as the P–O–P bridges between three-connected phosphate tetrahedra are susceptible to hydrolysis. The lanthanide ultraposphates MP_5O_{14} are notable laser materials.

Mixed-Anion Phosphates

The Mixed-Anion Phosphates (MAP) contain two kinds of phosphoric anions having different degrees of condensation. Pyrophosphates-orthophosphates are the main family of MAP. These phases are crystallized mainly e.g., $\text{LiMg}_3(\text{PO}_4)(\text{P}_2\text{O}_7)$ (Kim *et al.*, 2015) or amorphous e.g., $(\text{Ca}_y\text{Na}_z\text{H}_{3+y-2y-z})(\text{PO}_4)_{1-x}(\text{P}_2\text{O}_7)_x \cdot n\text{H}_2\text{O}$ (Soulié *et al.*, 2016).

Preparation of Solid Phosphates

Preparative routes for solid phosphates are typical of those used in materials chemistry. Reactions in which cations and phosphate anions are combined can take place in solution under normal or hydrothermal pressures, or by direct combination at high temperatures to overcome kinetic barriers. Hydrothermal, flux growth, and chemical vapor transport techniques are used to facilitate crystal growth. Transformations of phosphates into new structures can be achieved thermally or through ion-exchange reactions.

Solution and Hydrothermal Methods

Many phosphates of soluble cations, e.g., alkali and alkaline earth metals, ammonium, can be deposited from aqueous solutions, and this method can be used for crystal growth. Acid phosphates such as KDP (KH_2PO_4) (see Section “Ferroics”) may be prepared by partial neutralization of phosphoric acid with metal hydroxides or carbonates. Insoluble phosphates can be precipitated by mixing cation and phosphate solutions and condensed phosphates can be prepared from polyphosphoric acids, made by adding a small amount of water to P_2O_5 . The solubility of phosphates of highly charged cations increases with temperature and pressure, and so hydrothermal conditions are used to obtain more crystalline products, as well as many phases not formed at atmospheric pressure (see *Hydrothermal Synthesis*). This method is also used to grow large single crystals of materials such as KTP (see Section “Nonlinear Optical Materials”). Microporous metal phosphates are prepared in hydrothermal bombs using hydrated cations or quaternary ammonium species as templates to direct the porous framework (see Section “Microporous Materials”). Ion-exchange reactions in solution can be used to modify phosphates containing mobile cations, e.g., treatment of the cyclophosphate $\text{AgP}_6\text{O}_{18} \cdot \text{H}_2\text{O}$ with aqueous NaCl gives $\text{NaP}_6\text{O}_{18}$.

Thermal Treatments and Flux Growth

Heating well-ground mixtures of a metal oxide or salt and P_2O_5 or a phosphate source such $NH_4H_2PO_4$ is a convenient route to many anhydrous phosphates and gives a good control of stoichiometry. Gentle heating of hydrated phosphates gives many anhydrous materials and further thermal decomposition often yields new phases; in particular, dehydration of acid phosphates can result in condensed phosphate anions. Many phosphates melt congruently enabling crystals to be grown by slow cooling and phosphate glasses can be obtained via a rapid quench. Excess phosphate or water may be added to promote flux growth of crystals, e.g., lanthanide ultraphosphate crystals, MP_5O_{14} , are grown by cooling $M_2O_3 - P_2O_5 - H_2O$ melts from 400 to 500°C to room temperature.

Vapor Transport

Chemical vapor transport (see *Chemical Vapor Deposition*) can be used for a variety of anhydrous metal phosphates at temperatures around 1000°C using Cl_2 or I_2 as the carrier gas, through the formation of volatile halides and oxyhalides. This has been used to grow crystals of several phosphates, e.g., $TiPO_4$, $Fe_2P_2O_7$, RhP_3O_9 .

Sol-Gel Methods

Sol-gel methods using phosphate alkoxide precursors $(PO(OR)_3)$ (Livage *et al.*, 1992) or other sol-gel methods (Styskalik *et al.*, 2017) are reported in the literature. Nevertheless, the synthesis of phosphate glasses by sol-gel methods is still a challenge. The difficulty is induced by the undesired precipitation (quick hydrolysis) instead of reaching a gelation step considered as necessary to obtain glasses. Other precursor like $(PO(OH)_{2x}(OBu^n)_{2-2x})$ (with $x = 0$ or 1) has also been studied (Pickup *et al.*, 2007) in order to control hydrolysis.

Characterization of Phosphates

Solid phosphates range from being highly crystalline to glassy and the usual structural techniques of X-Ray or neutron diffraction and electron microscopy can be used to characterize them. Vibrational and NMR spectroscopies are both very useful for studying solid phosphates, especially poorly crystalline materials (Brow, 2000).

Both IR and Raman spectroscopies are used to study the vibrations of P–O bonds in solid phosphates (Rey *et al.*, 2014; Rulmont *et al.*, 1991). The features in the P–O stretching region (700–1400 cm^{-1}) are of greatest diagnostic use. Pyro- and polyphosphates are distinguished from orthophosphates by the vibrations of the P–O–P bridges, and the (–P–O–) rings in cyclo n phosphates give characteristic vibrations in the 600–850 cm^{-1} region.

NMR spectroscopy is extremely useful for studying phosphates (Kirkpatrick and Brow, 1995), as the ^{31}P nucleus has a spin of 1/2 and is 100% abundant. The magic angle spinning technique (MASNMR) is used to obtain highly resolved spectra from solid phosphates. The isotropic ^{31}P chemical shifts move to high-field values with increasing connectivity of phosphate tetrahedra and increasing charge on the coordinated cations, enabling different local environments in disordered materials to be identified. Paramagnetic cations can give a large contact or pseudocontact shift and may broaden the ^{31}P resonance. MASNMR can also be used to study kinetic processes, such as the crystallization of the solid phosphates from solution.

Phosphate Materials

Many phosphate structures are rigid, resistant to chemical attack, and can be thermally stable up to temperatures above 1000°C, giving rise to useful structural properties such as hosting mobile ions or molecules. Low absorption in the UV-visible region results in uses as optical materials. Many solid phosphates occur as minerals and biominerals. Main classes of phosphate materials are described below.

Fast Ion Conductors

Appreciable ionic conductivity is found in open framework or layered materials containing mobile cations (see section “Fast Ion Conductors”). A variety of crystalline phosphates are good ionic conductors, notably NASICON (NA Super Ionic CONductor) solid solutions $Na_{1+x}Zr_2(PO_4)_{3-x}(SiO_4)_x$ (Fig. 2) which have very high sodium ion conductivities in the range $1.8 < x < 2.2$. Many ion-exchanged derivatives and substituted NASICON frameworks are known, e.g., $AM_2(PO_4)_3$ ($A = Na, Ca, Sr, Ba$; $M = Ti, Mo$).

Many phosphates form layered structures (see Section “Intercalation Hosts and Ion Exchangers”) leading to high cation mobilities within the interlamellar spaces. Hydrated acid phosphates have high hydrogen ion conductivities, e.g., conductivities of 10^{-3} – $10^{-5} \Omega^{-1} cm^{-1}$ in $\alpha - Zr(HPO_4)_2 \cdot H_2O$ at room temperature. (The dispersion in these values reflects slight variations in the water content, as proton exchange between H_3O^+ cations enhances the conductivity.) Very high conductivities of $\sim 10^{-2} \Omega^{-1} cm^{-1}$ at 300K are also found in hydrogen uranyl phosphate.

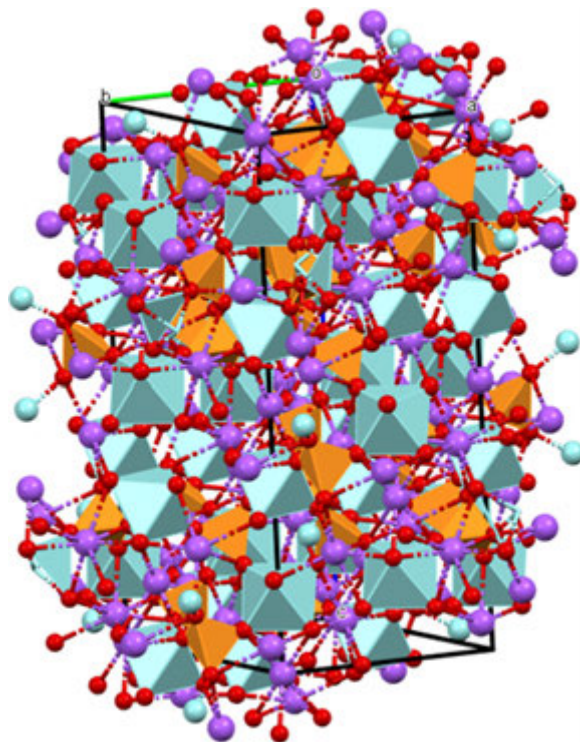


Fig. 2 The structure of NASICON, $\text{Na}_{1+x}\text{Zr}_2(\text{PO}_4)_{3-x}(\text{SiO}_4)_x$, typifies the features of many metal phosphate materials. A rigid framework of corner-sharing ZrO_6 octahedra (cyan) and phosphate/silicate tetrahedral (orange) contains a network of connected pores through which the sodium cations (purple) migrate.

Fast ion-conducting surface phase in LiFePO_4 controlled off-stoichiometry (e.g., $\text{LiFe}_{1-2y}\text{P}_{1-y}\text{O}_{4-\delta}$, $y = 0.05$) allows to create battery materials for ultrafast charging and discharging (full battery discharge in 10–20 s) (Kang and Ceder, 2009). Improved LiFePO_4 is a commercial battery material whose practical capacity (165 mAh g^{-1}) and whose rate capability 60%–80% is excellent (Etacheri *et al.*, 2011).

Rapid cooling of phosphate melts gives glasses, some of which have appreciable ionic conductivities (Martin, 1991). $\text{M}_2\text{O} - \text{P}_2\text{O}_5$ glasses ($\text{M} = \text{Li, Na, K, Rb, Cs, Ag}$) containing at least 30% M_2O are stable and have high M ion conductivities which are enhanced by the addition of M halides. It has been proposed that microphase separation occurs in $\text{AgPO}_4 - \text{AgI}$ glasses giving small regions of highly conducting $\alpha\text{-AgI}$. The glassy matrix suppresses the structural phase change that quenches the ionic conductivity of AgI below 146°C . The superionic glasses formed by doping AgI into glasses are also noted $\text{AgI}_x(\text{AgPO}_3)_{1-x}$ (Sidebottom, 2000).

Intercalation Hosts and Ion Exchangers

Many phosphates adopt layered structures in which strong M–O–P bonding is present within rigid layers, but only weak electrostatic or hydrogen bonding occurs between layers. Ions can diffuse in two dimensions within the interlamellar spaces leading to appreciable ionic conductivities, described above, and the ability to exchange ions with the surrounding media for use, e.g., in water softening, trapping of toxic metals. Molecules can also be intercalated into the interlamellar spaces leading to applications in catalysis, molecular separation, and properties resulting from oriented molecules, e.g., nonlinear optics (see *Acid Catalysts*, *Acid Catalysts* and *Metal Chain Compounds*). Useful layered phosphates, such as those described below, typically contain high-valence metals such as zirconium, vanadium, or uranium.

α -Zirconium phosphate, $\alpha - \text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, adopts a layered structure in which the hydrogen phosphate groups use three unprotonated oxygens to bond to zirconium while the P–OH groups hydrogen bond to the water molecules in the interlamellar spaces (Clearfield, 1991; Pet'kov, 2012). The layers can adjust their spacing or stacking pattern to adjust to external conditions and any intercalated species. This leads to a diverse chemistry as one or both of the hydrogens can be exchanged by monovalent and divalent cations, and these phases can show various degrees of hydration. Polar molecules such as amines can be reversibly intercalated into $\alpha - \text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, which can act as an acid catalyst for their reactions. Amine-intercalated $\alpha - \text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and other layered phosphates can be pillared with the Keggin ion $\text{Al}_{13}\text{O}_4(\text{OH})_{12} \cdot \text{H}_2\text{O}^{7+}$ or chromium acetate polymers. Isostructural $\text{M}^{\text{IV}}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ materials are obtained with $\text{M} = \text{Ti, Hf, Ce, and Sn}$, and analogous layered phosphonates $\text{M}^{\text{IV}}(\text{RPO}_3)_2 \cdot \text{H}_2\text{O}$ contain organic (R) groups between the inorganic layers in place of the OH groups in the hydrogen phosphates. Gamma compound with two chemically distinct types of phosphate group (Clayden, 1987) $\gamma - \text{M}^{\text{IV}}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ are found for $\text{M} = \text{Zr, Ti}$ (Nilchi *et al.*, 2004).

Vanadyl phosphate, α - VOPO_4 , is one of a series of layered oxosalts MOXO_4 ($\text{M}=\text{V}, \text{Nb}, \text{Ta}, \text{Mo}$; $\text{X}=\text{P}, \text{As}, \text{S}$) (Jacobson, 1992). Each vanadyl (VO^{3+}) group is coordinated by four phosphate groups and vice versa. Weak $\text{V}=\text{O}\cdots\text{V}=\text{O}$ interactions hold the layers together, which enables one equivalent of Lewis base molecules to be intercalated through coordination to the vanadyl group. $\text{VOPO}_4\cdot\text{L}$ derivatives are formed with $\text{L}=\text{H}_2\text{O}, \text{ROH}, \text{Py}$, etc. Cross-linked layers are found in $\text{VOPO}_4\cdot(4, 4 - \text{bipyridine})_{1/2}$. Cation insertion reactions occur under mildly reducing conditions giving a variety of $\text{M}_x\text{VOPO}_4\cdot n\text{H}_2\text{O}$ derivatives, e.g., $\text{Na}_{0.2}\text{VOPO}_4\cdot 2\text{H}_2\text{O}$. This results in a decrease in the interlayer spacing due to the electrostatic attraction between the anionic layers and the inserted cations.

Similar uranyl phosphate layers are found in hydrogen uranyl phosphate (HUP), $\text{HUO}_2\text{PO}_4\cdot 4\text{H}_2\text{O}$. The two-dimensional network of hydrogen-bonded water molecules lying between the layers accommodates the extra proton, which gives rise to very high proton conductivities (see Section "Fast Ion Conductors"). HUP and other members of the torbenite group of minerals can undergo cation exchange, e.g., autunite, $\text{Ca}(\text{UO}_2\text{PO}_4)_2\cdot n\text{H}_2\text{O}$, reversibly exchanges Ca^{2+} for K^+ , Ba^{2+} , Mn^{2+} , Cu^{2+} , and Mg^{2+} in aqueous solutions (Pet'kov, 2012).

Microporous Materials

An enormous number of microporous metal phosphates (Yu and Xu, 2003) can be prepared, in which large cavities and channels are enclosed within a strongly bonded $\text{M}-\text{O}-\text{P}$ framework. Such materials can have zeolitic properties, enabling ions and molecules to be adsorbed and react within the pores (see *Acid Catalysts, Organic-Inorganic Composite Crystals, and Zeolites*). Infinite networks of alternating PO_4 and MO_4 tetrahedra analogous to silicate structures are formed with divalent and trivalent M . Aluminophosphates (AlPOs) with $\text{M}=\text{Al}$ are most common (Wilson and Flanigen, 1989) but tetrahedral structures with $\text{M}^{3+}=\text{B}^{3+}$, Ga^{3+} , and Fe^{3+} are also known. $\text{M}^{2+}=\text{Be}^{2+}$, Mg^{2+} , Co^{2+} , and Zn^{2+} give anionic tetrahedral networks. These materials are obtained by a hydrothermal route with organic molecules such as amines or alkylammonium ions as structure-directing agents (SDAs) (Castro et al., 2010; Yu and Xu, 2006). A notable AlPO is the very large-pore material VPI-5 containing one-dimensional channels. The connecting windows have diameters of 12 Å enabling the structure to reversibly sorb large molecules such as $(\text{C}_4\text{F}_9)_3\text{N}$. Further variation of the structural and catalytic properties of AlPOs is obtained by the substitution of aluminum by silicon or metal cations, e.g., magnesium, manganese, iron, cobalt, or zinc. These give the possibility of framework redox activity (e.g., $\text{Fe}^{2+}/\text{Fe}^{3+}$) in catalysis as well as the usual Brønsted acidity.

Oxidation Catalysts

Several transition metal phosphate systems catalyze mild oxidations of organic molecules (Monceaux and Courtine, 1991). Catalysis takes place at particle surfaces through transition metal redox couples. V^{IV} and V^{V} phosphates catalyze the selective oxidation of linear C_4 hydrocarbons to maleic anhydride through the in situ formation of $(\text{VO})_2\text{P}_2\text{O}_7$. The structure of the initial vanadium phosphate is important in determining the morphology and catalytic activity of the $(\text{VO})_2\text{P}_2\text{O}_7$ particles. Highly active, platey microcrystallites can be prepared through the topotactic decomposition of the layered precursor $\text{VOHPO}_4\cdot 1/2\text{H}_2\text{O}$. A similar catalysis of the oxidative dehydrogenation of isobutyric acid to methacrylic acid occurs at the surface of mixed-valent $\text{Fe}^{2+}/\text{Fe}^{3+}$ phosphates.

The NASICON-type phase $\text{CuTi}_2(\text{PO}_4)_3$ catalyzes the oxidation of propylene to acrolein and alcohol dehydrogenations. The open titanium phosphate framework enables copper ions to diffuse to the surface giving surface growths of copper metal or oxides which catalyze the reaction (see *Supported Catalysts*).

Cobalt-Phosphate (Co-Pi) are used for water oxidation Catalyst (Kanan et al., 2008). High surface Co-Pi oxygen evolving catalysts form as thin films on conducting surfaces when aqueous solutions of Co^{2+} salts are electrolyzed in the presence of phosphate. Electrode prepared from Co-Pi achieves a current density of 100 mA cm^{-2} for water oxidation at 442 mV overpotential (Esswein et al., 2011).

Ferroics

Ferroics can be switched between two or more oriented states under appropriate forces. The charge separation present in metal phosphates gives rise to electric dipoles that can result in ferroic properties for which the switching forces are electrical or mechanical (Quarton, 1991). Ferroelectrics possess a net polarization due to parallel ordering of local dipoles; this requires an acentric crystal structure. The members of the potassium dihydrogen phosphate (KDP) family, MH_2PO_4 ($\text{M}=\text{Na}, \text{K}, \text{Rb}, \text{Cs}$), are archetypal ferroelectrics. In KDP the net polarization results from the ordering of asymmetric $\text{P}-\text{O}-\text{H}\cdots\text{O}-\text{P}$ hydrogen bonds below $T_c = 123\text{K}$. Additional $\text{N}-\text{H}\cdots\text{O}-\text{P}$ hydrogen bonding in $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP) gives a slightly different ordering of the acidic protons in which the dipoles cancel out; this is an antiferroelectric phase.

Ferroelectricity also arises in $\text{AM}_2(\text{PO}_4)_3$ types ($\text{A}=\text{Li}-\text{Cs}, \text{Ag}, \text{Cu}$; $\text{M}=\text{Ce}, \text{Th}, \text{U}$) through A cation displacements and in AMPO_4 materials (e.g., $\text{A}=\text{Rb}, \text{Cs}$; $\text{M}=\text{Mg}, \text{Co}, \text{Zn}$) through coupled rotations of the MO_4 and phosphate tetrahedrons. Piezoelectricity, a stress-induced polarization, is found in KDP-type materials and ADP was formerly used in submarine applications to emit and receive ultrasonic waves.

Nonlinear Optical Materials

Materials having a bulk polarization (i.e., ferroelectric phases) may be used for nonlinear optical processes such as second harmonic generation and electro-optic switching (see *Molecular Nonlinear Optical Materials*). KTP, described below, is a very efficient nonlinear material (Hagerman and Poeppelmeier, 1995; Satyanarayan *et al.*, 1999). The KDP materials described in the previous section are inferior to KTP but find use in electro-optics as they are very transparent over a wide frequency range.

The structure of potassium titanyl phosphate, KTiOPO_4 , consists of helical chains of TiO_6 octahedrons interlinked by orthophosphate groups to give a framework containing channels in which K^+ ions reside. The Ti^{4+} ions are displaced away from the centers of the octahedra due to the formation of dipolar $\text{Ti}=\text{O}$ “titanyl” groups, resulting in a net hyperpolarizability. KTP is an efficient second harmonic generator, converting the near-IR emission of Nd-YAG lasers (1064 nm) into blue-green light of twice the frequency (532 nm). It may also be used for optical frequency mixing, in electro-optic modulation devices and optical waveguides. Good-quality single crystals of KTP are grown from $\text{K}_2\text{O}-\text{P}_2\text{O}_5$ fluxes or hydrothermally. Cation-exchanged ATiOPO_4 derivatives ($\text{A}=\text{Ag}, \text{Na}, \text{Rb}, \text{Cs}, \text{Tl}, \text{NH}_4$) have been prepared to modify the nonlinear properties.

Phosphors and Laser Materials

These both require a non-absorbing host containing a low concentration of optically active centers. Phosphors contain absorption and emission centers; fluoroapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, doped with antimony and manganese is very efficient and is used as a coating in fluorescent lamps to convert 254 nm mercury UV radiation into visible light. $\text{Na}_3(\text{Ce}_{0.65}\text{Tb}_{0.35})(\text{PO}_4)_2$ and lanthanide-doped $\text{Zn}_3(\text{PO}_4)_2$ are also efficient phosphors. Polyphosphate glasses such as NaPO_3 or $\text{Al}(\text{PO}_3)_3$ containing < 1% neodymium dopant are used in high-gain or high-power laser applications (Campbell and Suratwala, 2000; Marion and Weber, 1991); other lanthanide like Europium are studied (Babu *et al.*, 2007). $\text{NdP}_5\text{O}_{14}$ and other lanthanide ultraphosphates have been extensively researched as laser materials. The large cation-cation separations in these lattices enable stoichiometric $\text{NdP}_5\text{O}_{14}$ to lase without excessive fluorescence quenching. Other neodymium phosphate laser crystals are the cyclotetraphosphates $\text{MNdP}_4\text{O}_{12}$ ($\text{M}=\text{Li}, \text{Na}, \text{K}$) and the orthophosphates $\text{M}_3\text{Nd}(\text{PO}_4)_2$ ($\text{M}=\text{Na}, \text{K}$).

Negative Thermal Expansion Ceramics

There has been much recent interest in materials showing negative thermal expansion. They are generally neutral frameworks made up of rigid metal and oxoanion (here phosphate) polyhedra. Heating these materials excites the transverse (bending) $\text{M}-\text{O}-\text{P}$ vibrations with little expansion of the $\text{M}-\text{O}$ and $\text{P}-\text{O}$ bonds. Hence the $\text{M}-\text{P}$ distance decreases with rising temperature, leading to an overall negative expansion in several materials. Zero thermal expansion composites are made by combining these phases with normal (positive) expansion materials. Examples of phosphates showing negative thermal expansion are the diphosphate-divanadate solid solutions $\text{ZrP}_{2-x}\text{V}_x\text{O}_7$ and the microporous aluminophosphate AlPO-17 which shows a particularly large effect (Attfield and Sleight, 1998). Zirconium tungsten phosphate $\text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2$ (ZWP) exhibits the property of NTE of approximately $-5 \times 10^{-6} \text{ K}^{-1}$ from room temperature to 1073K (Watanabe *et al.*, 2008). Some phases $\text{A}_{5-qx}\text{M}_x\text{Zr}(\text{PO}_4)_3$ (N is the 4-, 3-, 2- valent element; $q = 4, 3, \text{ or } 2$; and $5 - qx \geq 1$) which are member of the $\text{NaZr}_2(\text{PO}_4)_3$ (NZP) family of materials have a near-zero net thermal anisotropy (Orlova *et al.*, 2002).

Minerals

Several hundred phosphate minerals are known, virtually all of which are orthophosphates. The important mineral apatite, ideally $\text{Ca}_5(\text{PO}_4)_3\text{X}$ ($\text{X}=\text{F}, \text{Cl}, \text{OH}$), is found in igneous pegmatite rocks and hydrothermal veins. Poorly crystalline or amorphous phosphorite sediments made from the hard remains of marine organisms are the principal commercial source of phosphates, although apatites are also mined. Treatment of phosphate minerals with sulfuric acid yields “superphosphate” fertilizer and phosphoric acid treatment gives “triple superphosphate”, rich in $\text{Ca}(\text{H}_2\text{PO}_4)_2$. Other soluble fertilizers such as ammonium phosphates are obtained from these products. Many of the f-block elements are extracted from phosphate minerals, notably monazite. Torbenite minerals related to HUP (see Section “Intercalation Hosts and Ion Exchangers”) are sources of uranium.

Biomaterials

Phosphates are found in soft organic tissues as phosphate esters, and in hard tissues, notably bones and teeth, which are composites of an organic matrix and biomineralized apatites (Videau and Dupuis, 1991). These apatite phases have Ca/P ratios of 1.6–1.8 and often incorporate other cations (Na^+ , K^+ , Mg^{2+}) or anions (F^- , Cl^- , CO_3^{2-} , citrate). A variety of synthetic calcium phosphates have been investigated as biomaterials for implants (de Groot, 1993; Rey *et al.*, 2017). $\text{Ca}_3(\text{PO}_4)_2$ (TCP) and a mixture of TCP and Hydroxyapatite named biphasic calcium phosphate (BCP) can be used as a biodegradable bone substitute which is gradually replaced by autogenous bone (de Grado *et al.*, 2018). Less degradable apatite implants can attach to natural bone with less inflammation. Calcium phosphate cement are powder mixture of tetracalcium phosphate (TTCP) or dicalcium phosphate anhydrous (DCPA) or dihydrated (DCPD) or TCP or other phases which react in the presence of water (Kenny and Buggy, 2003).

Hydroxyapatite is coated on metallic osteoarticular implant by plasma spray in order to increase the osteointegration (Sun *et al.*, 2001). Bioinert zinc phosphate cements are used in prosthetic dental applications (Herschke *et al.*, 2006).

Summary

An enormous number of solid phosphate materials can be found or synthesized and many still wait to be discovered. They are generally durable, nontoxic, and have a wide range of actual and potential materials applications. Future developments may include new microporous catalysts, structural materials such as zero expansion ceramics, and improved biomaterials.

References

- Attfield, M.P., Sleight, A.W., 1998. Exceptional negative thermal expansion in AlPO_4 -17. *Chem. Mater.* 10, 2013–2019. doi:10.1021/cm9801587.
- Babu, S.S., Babu, P., Jayasankar, C.K., *et al.*, 2007. Optical absorption and photoluminescence studies of Eu^{3+} -doped phosphate and fluorophosphate glasses. *J. Lumin.* 126, 109–120. doi:10.1016/j.jlumin.2006.05.010.
- Brow, R.K., 2000. Review: The structure of simple phosphate glasses. *J. Non-Cryst. Solids* 263–264, 1–28. doi:10.1016/S0022-3093(99)00620-1.
- Campbell, J.H., Suratwala, T.I., 2000. Nd-doped phosphate glasses for high-energy/high-peak-power lasers. *J. Non-Cryst. Solids* 263–264, 318–341. doi:10.1016/S0022-3093(99)00645-6.
- Castro, M., Seymour, V.R., Carnevale, D., *et al.*, 2010. Molecular modeling, multinuclear NMR, and diffraction studies in the templated synthesis and characterization of the aluminophosphate molecular sieve STA-2. *J. Phys. Chem. C* 114, 12698–12710. doi:10.1021/jp104120y.
- Clayden, N.J., 1987. Solid-state nuclear magnetic resonance spectroscopic study of γ -zirconium phosphate. *J. Chem. Soc. Dalton Trans.* 1877–1881. doi:10.1039/DT9870001877.
- Clearfield, A., 1991. Layered and three-dimensional phosphates of tetravalent elements. *Eur. J. Solid State Inorg. Chem.* 28, 37–56.
- Corbridge, D.E.C., 1974. *The Structural Chemistry of Phosphorus*. Amsterdam: Elsevier Scientific Publishing Company.
- de Grado, G.F., Keller, L., Idoux-Gillet, Y., *et al.*, 2018. Bone substitutes: A review of their characteristics, clinical use, and perspectives for large bone defects management. *J. Tissue Eng.* doi:10.1177/20417731418776819.
- de Groot, K., 1993. Clinical applications of calcium phosphate biomaterials: A review. *Ceram. Int.* 19, 363–366. doi:10.1016/0272-8842(93)90050-2.
- Durif, A., 1995. *Crystal Chemistry of Condensed Phosphates*. United States: Springer. doi:10.1007/978-1-4757-9894-4.
- Esswein, A.J., Surendranath, Y., Reece, S.Y., Nocera, D.G., 2011. Highly active cobalt phosphate and borate based oxygen evolving catalysts operating in neutral and natural waters. *Energy Environ. Sci.* 4, 499–504. doi:10.1039/C0EE00518E.
- Etacheri, V., Marom, R., Elazari, R., Salitra, G., Aurbach, D., 2011. Challenges in the development of advanced Li-ion batteries: A review. *Energy Environ. Sci.* 4, 3243–3262. doi:10.1039/C1EE01598B.
- Hagerman, M.E., Poeppelmeier, K.R., 1995. Review of the structure and processing-defect-property relationships of potassium titanyl phosphate: A strategy for novel thin-film photonic devices. *Chem. Mater.* 7, 602–621. doi:10.1021/cm00052a004.
- Herschke, L., Rottstegge, J., Lieberwirth, I., Wegner, G., 2006. Zinc phosphate as versatile material for potential biomedical applications Part 1. *J. Mater. Sci. Mater. Med.* 17, 81–94. doi:10.1007/s10856-006-6332-4.
- Jacobson, A.J., 1992. Intercalation reactions of layered compounds. In: Cheetham, A.K., Day, P. (Eds.), *Solid State Chemistry: Compounds*. Oxford, New York: Oxford University Press, pp. 182–233.
- Kanan, M.W., Surendranath, Y., Nocera, D.G., 2008. Cobalt-phosphate oxygen-evolving compound. *Chem. Soc. Rev.* 38, 109–114. doi:10.1039/B802885K.
- Kang, B., Ceder, G., 2009. Battery materials for ultrafast charging and discharging. *Nature* 458, 190–193. doi:10.1038/nature07853.
- Kanazawa, T., 1989. *Inorganic Phosphate Materials*. Tokyo: Kodansha/Amsterdam: Elsevier.
- Kenny, S.M., Buggy, M., 2003. Bone cements and fillers: A review. *J. Mater. Sci. Mater. Med.* 14, 923–938. doi:10.1023/A:1026394530192.
- Kim, S.-C., Lee, M.-S., Kang, J., Kim, Y.-I., Kim, S.-J., 2015. Crystal structure and ion conductivity of a new mixed-anion phosphate $\text{LiMg}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$. *J. Solid State Chem.* 225, 335–339. doi:10.1016/j.jssc.2015.01.011.
- Kirkpatrick, R.J., Brow, R.K., 1995. Nuclear magnetic resonance investigation of the structures of phosphate and phosphate-containing glasses: A review. *Solid State Nucl. Magn. Reson.* 5, 9–21. doi:10.1016/0926-2040(95)00042-0.
- Livage, J., Barboux, P., Vandenborre, M.T., Schmutz, C., Taulelle, F., 1992. Sol-gel synthesis of phosphates. *J. Non-Cryst. Solids* 147–148, 18–23. doi:10.1016/S0022-3093(92)90586-1.
- Marion, J., Weber, M., 1991. Phosphate laser glasses. *Eur. J. Solid State Inorg. Chem.* 28, 271–287.
- Martin, S.W., 1991. Ionic conduction in phosphate glasses. *J. Am. Ceram. Soc.* 74, 1767–1784. doi:10.1111/j.1151-2916.1991.tb07788.x.
- Monceaux, L., Courtine, P., 1991. Phosphorus in mild oxidation catalysts. *Eur. J. Solid State Inorg. Chem.* 28, 233–251.
- Nilchi, A., Ghanadi Maragheh, M., Khanchi, A., Farajzadeh, M.A., Aghaei, A.A., 2004. Synthesis and ion-exchange properties of crystalline titanium and zirconium phosphates. *J. Radioanal. Nucl. Chem.* 261, 393–400. doi:10.1023/B:JRN.0000034876.90837.f0.
- Orlova, A.I., Kemenov, D.V., Pet'kov, V.I., *et al.*, 2002. Ultralow and negative thermal expansion in zirconium phosphate ceramics. *High Temp. High Press.* 34, 315–322. doi:10.1068/hjtr025.
- Pet'kov, V.I., 2012. Complex phosphates formed by metal cations in oxidation states I and IV. *Russ. Chem. Rev.* 81, 606. doi:10.1070/RC2012v081n07ABEH004243.
- Pickup, D.M., Guerry, P., Moss, R.M., *et al.*, 2007. New sol-gel synthesis of a $(\text{CaO})_{0.3}(\text{Na}_2\text{O})_{0.2}(\text{P}_2\text{O}_5)_{0.5}$ bioresorbable glass and its structural characterisation. *J. Mater. Chem.* 17, 4777–4784. doi:10.1039/B709955J.
- Quarton, M., 1991. Dielectric monophosphates. *Eur. J. Solid State Inorg. Chem.* 28, 289–301.
- Rey, C., Combes, C., Drouet, C., *et al.*, 2017. Bioactive calcium phosphate compounds: Physical chemistry. In *Reference Module in Materials Science and Materials Engineering*. Elsevier. doi:10.1016/B978-0-12-803581-8.10171-7.
- Rey, C., Marsan, O., Combes, C., *et al.*, 2014. Characterization of calcium phosphates using vibrational spectroscopies. In: Ben-Nissan, B. (Ed.), *Advances in Calcium Phosphate Biomaterials*, Springer Series in Biomaterials Science and Engineering. Springer Berlin Heidelberg, pp. 229–266.
- Rulmont, A., Cahay, R., Liegeoisduyckaerts, M., Tarte, P., 1991. Vibrational spectroscopy of phosphates – Some general correlations between structure and spectra. *Eur. J. Solid State Inorg. Chem.* 28, 207–219.
- Satyanarayan, M.N., Deepthy, A., Bhat, H.L., 1999. Potassium titanyl phosphate and its isomorphs: Growth, properties, and applications. *Crit. Rev. Solid State Mater. Sci.* 24, 103–191. doi:10.1080/10408439991329189.
- Sidebottom, D.L., 2000. Influence of cation constriction on the ac conductivity dispersion in metaphosphate glasses. *Phys. Rev. B* 61, 14507–14516. doi:10.1103/PhysRevB.61.14507.

- Soulié, J., Gras, P., Marsan, O., *et al.*, 2016. Development of a new family of monolithic calcium (pyro)phosphate glasses by soft chemistry. *Acta Biomater.* 41, 320–327. doi:10.1016/j.actbio.2016.05.030.
- Styskalik, A., Skoda, D., Barnes, C.E., Pinkas, J., 2017. The power of non-hydrolytic sol-gel chemistry: A review. *Catalysts* 7, 168. doi:10.3390/catal7060168.
- Sun, L.M., Berndt, C.C., Gross, K.A., Kucuk, A., 2001. Material fundamentals and clinical performance of plasma-sprayed hydroxyapatite coatings: A review. *J. Biomed. Mater. Res.* 58, 570–592. doi:10.1002/jbm.1056.
- Videau, J., Dupuis, V., 1991. Phosphates and biomaterials. *Eur. J. Solid State Inorg. Chem.* 28, 303–343.
- Watanabe, H., Tani, J., Kido, H., Mizuuchi, K., 2008. Thermal expansion and mechanical properties of pure magnesium containing zirconium tungsten phosphate particles with negative thermal expansion. *Mater. Sci. Eng. A* 494, 291–298. doi:10.1016/j.msea.2008.04.037.
- Wilson, S.T., Flanigen, E.M., 1989. Synthesis and characterization of metal aluminophosphate molecular sieves. In: *Zeolite Synthesis*. ACS Symposium Series. American Chemical Society, pp. 329–345.
- Yu, J., Xu, R., 2006. Insight into the construction of open-framework aluminophosphates. *Chem. Soc. Rev.* 35, 593–604. doi:10.1039/B505856M.
- Yu, J., Xu, R., 2003. Rich structure chemistry in the aluminophosphate family. *Acc. Chem. Res.* 36, 481–490. doi:10.1021/ar0201557.

Apatitic and Tricalcic Calcium Phosphate-Based Bioceramics: Overview and Perspectives

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Introduction

Calcium phosphates represent a major class of biominerals found in a variety of living organisms, and strategies are developed to prepare synthetic analogs for biomedical applications such as bone regeneration but also in other (nano)medicine domains as for cell therapy. While nanocrystalline, non-stoichiometric apatites mimic bone mineral and dentin, and exhibit a high (surface) bioactivity, stoichiometric hydroxyapatite (HA) is thermally/thermodynamically very stable and approaches more the composition of tooth enamel. Besides apatitic compounds, other calcium phosphate (CaP) phases are also particularly relevant to biomedical applications such as bone repair, like tricalcium phosphates (TCPs, especially the high temperature α and β forms or the low temperature forms, amorphous TCP and apatitic TCP). These various compounds, apatitic and tricalcic, are the most used CaP phases to-date in the biomedical field, and may offer a large panel of bioceramic-based systems with diverse characteristics (mechanical, biological, chemical, thermodynamic...) so as to comply with clinical needs. One main applicative domain is certainly the production of resorbable or non-resorbable bone implants, which may also associate drugs and other active agents. In this chapter, an overview will be given on both apatitic and tricalcic CaP compounds, in terms of structure, synthesis and processing routes, physicochemical characterization and main biological properties. Biphasic systems such as HA/ β -TCP, also known as biphasic calcium phosphate (BCP) bioceramics, will also be addressed. Finally, some conclusive remarks and perspectives are given.

Apatitic Ceramics

Overview

Apatites are a large group of minerals sharing a similar crystallography and responding to the general formula $M_{10}(XO_4)_6Y_2$ (Elliott, 1994). For biomedical applications, however, the metallic cations M mostly represent calcium – although a wealth of substitutions may occur – and XO_4 mainly stands for phosphate groups. In this context, the reference apatitic compound is stoichiometric hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, denoted HA. This compound is not naturally encountered in vivo, except that tooth enamel exhibits a mineral composition that approaches it despite some carbonation and a few residual ion vacancies. HA is however one key ceramic compound for the setup of bone substitutes and is widely used at a clinical scale, especially when non-resorbable scaffolds are needed. In bone, dentin and synthetic biomimetic analogs obtained by soft chemistry (typically temperature lower than 100°C and in the absence of high-temperature calcination), in contrast, the apatitic phase is clearly non-stoichiometric with vacancies in Ca^{2+} and OH^- sites, and part of the PO_4^{3-} ions are also protonated as HPO_4^{2-} divalent anions and substituted by carbonate ions (B-type). A-type carbonate ions can also be present in substitution of some OH^- ions, although to a limited amount (Gomez-Morales *et al.*, 2013). This non-stoichiometry confers a thermodynamic metastability (Rollin-Martinet *et al.*, 2013), but also an associated greater reactivity/bioactivity. Reviews of apatitic compounds have been reported (Combes *et al.*, 2016; Dorozhkin, 2009; Gomez-Morales *et al.*, 2013; LeGeros, 1991, 2008; Sakae *et al.*, 2015). A general chemical formula can be written to approximate the global composition of these compounds: $Ca_{10-x}(PO_4)_6-x(HPO_4, CO_3)_x(OH)_{2-x}$. This overall formula points to a Ca/P (+ C) molar ratio lower than the stoichiometric value of 1.67; however it does not depict in detail the complex sub-structure of biological and biomimetic nanocrystalline apatites which exhibit, on the surface of their nanocrystals, a hydrated ionic layer which is non-apatitic (ion organization within this layer does not correspond to the apatite array) (see below). This layer has a low Ca/P (+ C) ratio, potentially close to 1, and contains labile ions that can be easily exchanged with ions from the surrounding fluids and take an active part in molecular adsorption processes (Cazalbou *et al.*, 2005; Eichert *et al.*, 2005; Rey *et al.*, 2014). The high reactivity of these compounds can then be modulated thanks to appropriate associations with ions and (bio) molecules to offer additional functionalities to the derived bioceramics, thus opening a large variety of medical applications in the field of bone regeneration, but also in (nano)medicine.

Structure

Apatite compounds – and in particular calcium phosphate ones – generally crystallize in the hexagonal $P6_3/m$ space group (sometimes monoclinic $P2_1/b$ as in the case of chlorapatite for example) (Elliott, 1994). Hydroxyapatite, for instance, exhibits typical unit cell parameters close to $a = 9.418 \text{ \AA}$ and $c = 6.881 \text{ \AA}$, leading to a theoretical density of about 3.16 (Kay *et al.*, 1964; Rey *et al.*, 2011). The 3D organization of the atoms in the unit cell is based on a compact-like arrangement of phosphate groups and some interstitial sites are occupied by calcium and hydroxide ions. This organization generates two types of so-called channels, often denoted Ca(1) and Ca(2) in relation to the location of the calcium atoms. In particular, the axis of the

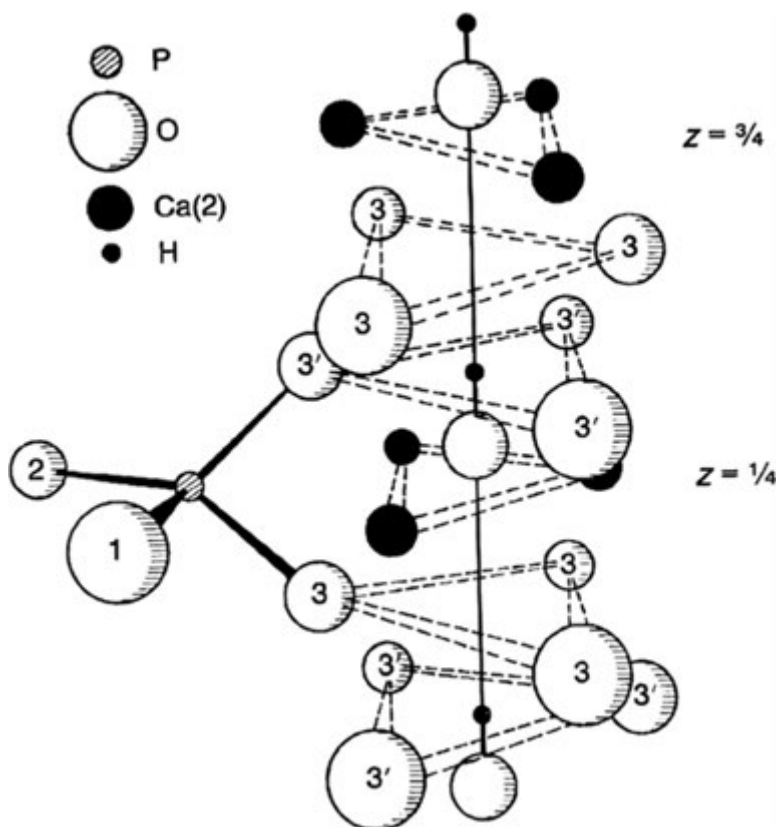


Fig. 1 Representation of part of the hydroxyapatite structure: Ca(2) apatitic channels along the c-axis, hosting the OH⁻ ions. From Elliott, J.C., 1994. *Structure and Chemistry of the Apatites and other Calcium Orthophosphates*. Amsterdam: Elsevier Science.

Ca(2) channels (Fig. 1) can accommodate a variety of anions (e.g., OH⁻, Cl⁻, F⁻, A-type CO₃²⁻, peroxides...) but also small molecules (e.g., glycine), and these confined species can take part in exchange reactions as in chromatography setups although specific conditions need to apply for such exchanges to take place.

The 3D cohesion of the apatite ionic crystal is maintained by strong electrostatic interactions between the cations and anions attracting each other. The phosphate ions are large entities that convey stability to the structure, therefore vacancies in phosphate site have not been reported; only substitutions by other ions such as carbonates CO₃²⁻ (B-type carbonates) or other large ions can be undergone in phosphate sites. Nonstoichiometry can thus solely be linked to vacancies in cationic sites (replacement of Ca²⁺) and in monovalent anionic sites (replacement of OH⁻). The clear impact of Ca/OH vacancies on the stability of the crystal was evaluated on the basis of calorimetry experiments (Rollin-Martinet *et al.*, 2013). These ions can also be substituted by a wealth of others. Common cationic substituents can be bioactive ions such as Mg²⁺, Sr²⁺, Cu²⁺, Zn²⁺, among others, or inert like Na⁺, but also toxic ones like Pb²⁺ or Cd²⁺. Again, these ions being potentially different in size, charge, affinity for oxygen, etc., their substitution in the apatitic lattice will generate modifications in their thermodynamic properties (Drouet, 2015).

Synthesis and Processing Routes

Two situations should be differentiated (Drouet *et al.*, 2017), whether well-crystallized or nanocrystalline apatites are considered, as this will dictate the synthesis and processing route to carry out.

Well-crystallized apatites

Well-crystallized apatites, such as stoichiometric HA, may only be obtained upon heating, e.g., close to water boiling temperature, and this is often accompanied by a thermal post-treatment in dry conditions for improving its crystallinity and/or densification rate. Sintering indeed allows increasing drastically the mechanical strength of obtained bioceramics or at least precursor forms (e.g., granules) (Khalil *et al.*, 2007; Kobayashi *et al.*, 2006; Raynaud *et al.*, 2002). Stoichiometric HA remains stable up to typically ~1250°C without major alteration, unless very low water pressure conditions are used, leading to partial dehydration from 850°C generating oxyapatite (Trombe and Montel, 1978).

Such well-crystallized apatite can be typically prepared by neutralization, in stoichiometric amounts, of phosphoric acid by calcium hydroxide (lime) or another calcium source such as calcium nitrate (where the nitrates will be subsequently eliminated upon washing and calcination). When using lime as precursor, however, attention should be paid as this compound has a strong

tendency to partially dehydrate in variable proportions, thus making arduous the stoichiometric assessment of the number of moles of calcium. One solution is to pre-calcine (e.g., at 600°C) the lime prior to synthesis and weigh the desired amount after cooling down to room temperature in a desiccator. Then, any post-rehydration is inconsequential on the synthesis outcome. Other phosphate precursors can also be used, such as di-ammonium hydrogenphosphate. In any case, fixing the pH to alkaline conditions, e.g., pH 10 via ammonia addition, will facilitate the obtainment of stoichiometric HA. Solid state reactions can also be used to prepare HA, e.g., 1000°C (Suchanek and Yoshimura, 1998), starting from a phosphate and a calcium precursor such as calcium carbonate.

The stoichiometry of prepared HA, for which a Ca/P ratio of 1.67 is expected (within experimental uncertainty) may be verified by calcination for 15 h at 1000°C (ISO 13779-3:2008), via X-ray diffraction (XRD) analysis where only the HA phase should be detected. The presence of β -TCP besides the HA phase would depict a situation where under-stoichiometric apatite $\text{Ca}_{10-x}(\text{PO}_4)_{6-x}(\text{HPO}_4)_x(\text{OH})_{2-x}$ is obtained, with a Ca/P ratio between 1.50 and 1.67. Note that for even lower Ca/P ratios (< 1.50) calcination would lead to a mixture of β -TCP and calcium pyrophosphate $\text{Ca}_2\text{P}_2\text{O}_7$. The residual presence of CaO, after 15 h of calcination at 1000°C, detected by XRD would indicate in contrast that calcium was initially present beyond the stoichiometric amount. Traces of CaO can also be assessed by a pink coloration upon contact with a phenolphthalein solution. The residual CaO can however be eliminated by a washing procedure.

Well-crystallized, stoichiometric HA can be processed in different forms in view of bioceramic usages, and especially as bone substitutes such as dense or porous scaffolds, granules, coatings on metal prostheses... In porous structures (Meurice *et al.*, 2012; Sopyan *et al.*, 2007), macropore interconnection (typically in the range 300–500 μm) are bound to allow cell colonization and favor osteointegration (Karageorgiou and Kaplan, 2005; Lu *et al.*, 1999; Mastrogiacomo *et al.*, 2006). Such pores can be obtained via pore-forming agents (e.g., NaCl, CaCO_3 , glucose, paraffin...) that will be either washed away or eliminated by calcination during a subsequent heating process (Chevalier *et al.*, 2008; Descamps *et al.*, 2009; Tancrét *et al.*, 2006; Walsh and Tanaka, 2001). Other approaches such as stereolithography, freeze casting or else the transformation of naturally-porous biological calcium carbonates into calcium phosphate can be used (Charrière *et al.*, 2003; Gonzalez-McQuire *et al.*, 2005; Liu, 1997; Meurice *et al.*, 2012; Walsh *et al.*, 2005).

HA is also widely used in the field of implant coatings. Today and since the mid-1980s, HA is indeed used, from a commercial viewpoint, as starting precursor to feed plasma spray guns to deposit hydroxyapatite (although partially decomposed) onto prosthetic devices such as hip implants (Sun *et al.*, 2001) in order to favor their osteointegration (Buser *et al.*, 1991; Jarcho, 1986).

Nanocrystalline apatites

The preparation of bone-like nanocrystalline, non-stoichiometric apatites (also called biomimetic when prepared close to physiological conditions) can only be carried out at low temperature, in solution. This can typically be done by double decomposition of a calcium and a phosphate precursor, or by hydrolysis of an unstable CaP compound (Gomez-Morales *et al.*, 2013; Markovic *et al.*, 2011). In these conditions, the obtained apatite compounds (provided that they are not heated too high due to their metastability) exhibit very similar features to bone apatite. Synthesis of carbonated or non-carbonated biomimetic nanocrystalline apatites can thus be done this way (Grunenwald *et al.*, 2014b; LeGeros, 1994; Vandecastelaere *et al.*, 2012). For carbonation, a carbonate-containing precursor such as NaHCO_3 has to be added in the phosphate precursor medium.

Suspensions or “gels” of nanocrystalline apatites are obtained upon filtration (and washing) of the precipitating medium, and their drying leads to ceramic pieces, although characterized by limited mechanical strength (Sarda *et al.*, 1999). Bone-like apatite can also be the final product after the setting of calcium phosphate cements, whether the latter is based on the hydrolysis of a precursor CaP phase e.g., α -TCP (Ginebra, 1997) or on acid-base reaction (Constantz, 1995). Calcium carbonate may also be associated to CaP-based cement formulations (Combes *et al.*, 2006) to obtain carbonated nanocrystalline apatite biomimetic cements and/or modulate their resorption in vivo.

It is also possible to prepare 3D scaffolds via a consolidation step. However, again, low/moderate temperatures need to be applied so as to prevent the degradation of the metastable nanocrystals and their bone-like features such as hydration and nanosized dimensions. Flash sintering such as spark plasma sintering (SPS) carried out at low temperature (e.g., 150°C) has been proved to be an effective way to consolidate nanocrystalline apatites while preserving these appealing nanocrystals characteristics (Drouet *et al.*, 2006; Grossin *et al.*, 2010; Ortali *et al.*, 2018). These cold sintering approaches revealed that it was possible to use the intrinsic water contained in the samples (within the hydrated surface layer) to consolidate apatite nanocrystals, via the merging of the surface layers of adjacent nanocrystals. The role of the hydrated layer in assisting the sintering of iodate-containing HA crystals was also shown (Coulon *et al.*, 2016). A similar type of “cold fusion” is probably likewise involved in the case of enamel formation (Daculsi *et al.*, 1984). Mechanical properties after SPS consolidation become attractive for non-load-bearing sites in orthopedics and dentistry, e.g., with a Young modulus in the range 12–37 GPa, close to cortical bone (7–30 GPa). Mineral-organic composites involving nanocrystalline apatite can also be prepared, where a polymer can typically modulate mechanical properties and/or allow the formation of (macro)porous scaffolds, whether obtained by SPS (Brouillet *et al.*, 2015) or via other methods such as freeze-casting (Schardosim *et al.*, 2017).

Nanocrystalline apatite coatings on implants can be obtained by soft chemistry routes such as electrodeposition or dip-coating in apatite suspensions (Abe *et al.*, 1990; Autefage *et al.*, 2009; Blackwood and Seah, 2009; Chai and Ben-Nissan, 1999), and results pointed to the osteoinductive character of such biomimetic apatite (Autefage, 2009). More recently, cold spray was shown as another low temperature processing approach for the realization of nanocrystalline apatite coatings (Kergourlay *et al.*, 2016), while preserving the appealing characteristics of the initial nanocrystals.

Finally, the nanometer scale of bio-inspired apatites allows for the preparation of individualized apatite nanoparticles relevant to cell therapy/(nano)medicine (Drouet *et al.*, 2015; Iafisco *et al.*, 2012; Welzel *et al.*, 2004), and applications in the fields of oncology, hematology, dermatology, transfection and medical imaging (typically via lanthanide substitution in the apatite lattice (Al-Kattan *et al.*, 2010; Mondéjar *et al.*, 2007)) are being developed.

In all cases, whether in the form of gels/pastes, coatings, particles or scaffolds, the high reactivity of apatite nanocrystals makes it possible to convey additional functions such as antibacterial, antitumor, luminescence etc., via ion substitutions/exchanges or molecular adsorption/grafting (biomolecules, drugs...).

Physicochemical Characterization

Various complementary techniques can be used to characterize CaP compounds such as apatites, and also permit to distinguish between bone-like apatites and well-crystallized, stoichiometric HA (Drouet, 2013). While X-ray diffraction allows getting information on the crystalline features of HA or the apatitic core of biomimetic apatites, for example to estimate the mean crystallite dimensions, it does not convey direct information on the non-apatitic disordered layer from the nanocrystals surface which has an amorphous-like character (although some degree of organization exists as seen by vibrational spectroscopy). Electron microscopy such as (HR)TEM or (FEG)SEM have also to be used with caution, unless in cryogenic conditions (Drouet *et al.*, 2018a), as crystal damage can be provoked upon beam (and high vacuum) exposure (Bres *et al.*, 2014).

In contrast, vibrational spectroscopy techniques (FTIR, Raman) appear very well suited to analyze apatitic compounds, and they allow exploring the local chemical environment of ions within the structure. Very specific features (Fig. 2) have for example been reported to exist in bone apatite or in biomimetic synthetic counterparts, e.g., by FTIR spectroscopy (Boskey and Mendelsohn, 2005; Drouet *et al.*, 2018b; Miller *et al.*, 2001; Paschalis *et al.*, 2011; Rey *et al.*, 1989a,b, 1991a,b,c, 1990) which do not appear in stoichiometric HA. Some relationship with the IR spectrum of octacalcium phosphate (OCP) $\text{Ca}_8(\text{PO}_4)_6(\text{HPO}_4)_2 \cdot 5\text{H}_2\text{O}$ can also be unveiled (Fowler *et al.*, 1993). These features permit to evidence the presence or absence of a hydrated non-apatitic layer on the nanocrystals. The signature of non-apatitic (surface) HPO_4^{2-} ions around 534 cm^{-1} is one such signature. Also, the degree of hydroxylation can be scrutinized by looking at the OH libration band at 632 cm^{-1} . A lower OH⁻ signal and the presence of HPO_4^{2-} ions is then a clear evidence of the non-stoichiometry of the sample. Raman spectroscopy can also be used to detect non-apatitic signatures on apatite nanocrystals (Crane *et al.*, 2006). In microscopy setup, Raman spectroscopy also allows drawing mappings and may be used directly in aqueous media (e.g., in cell culture medium). FTIR (and Raman) spectroscopies also allow distinguishing apatitic compounds from other CaP phases such as dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, DCPD) or OCP, or even amorphous CaP which leads to large, nearly monocomponent bands in the ν_3 and $\nu_4(\text{PO}_4)$ domains. A review on vibrational spectroscopy features of CaP compounds has been recently published (Rey *et al.*, 2014c). Another spectroscopy technique particularly informative for CaP compounds including apatites is solid state nuclear magnetic resonance (NMR), especially regarding the elements P, H, C, Ca and F (Arends *et al.*, 1987; Beshah *et al.*, 1990; Laurencin *et al.*, 2010; Roufosse *et al.*, 1984; Yesinowski, 1998; Yi *et al.*, 2013). This technique allowed confirming results obtained by other methods such as vibrational spectroscopies, regarding the existence of a disordered CaP hydrated layer on the surface of bone apatite nanocrystals or their biomimetic counterparts (Sfihi and Rey, 2002; Jäger *et al.*, 2006; Von Euw *et al.*, 2017, 2019; Wu *et al.*, 2002).

Chemical analyses are also key for a thorough characterization of such samples. Cationic contents can be measured by ICP or atomic absorption spectrometry, or else complexometry (e.g., with EDTA) although the latter is not specific to a given type of cation. Methods based on particle beams such as particle-induced X-ray emission (PIXE) can also be employed (Jallot and Moretto, 2006; Loong *et al.*, 2000), e.g., to obtain element mappings, but they request the use of heavy equipment. Phosphates can be titrated by UV-visible spectrophotometry of a phospho-vanado-molybdenic complex (Charlot, 1974). The carbonation level can be chemically assessed from coulometry (Huffman, 1977) or directly from FTIR spectrometry analyses (Grunenwald *et al.*, 2014a).

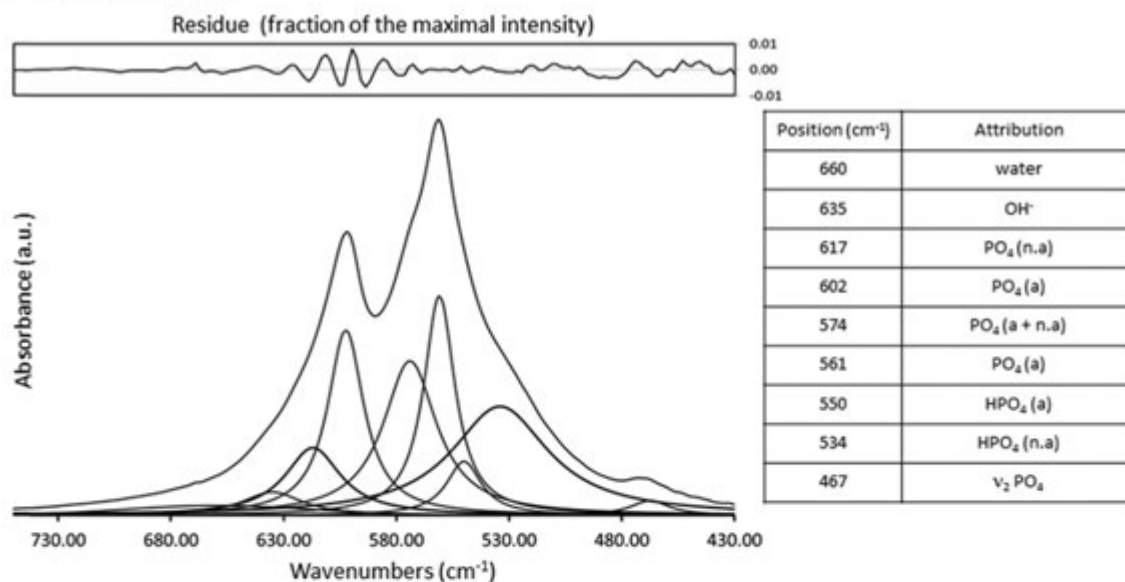
Surface analysis techniques can also be used to complement the physicochemical characterization, such as atomic force microscopy (AFM) (McElderry *et al.*, 2013; Onuma *et al.*, 1995; Robinson *et al.*, 2005; Ramirez Rodriguez *et al.*, 2016), X-ray photoelectron spectroscopy (XPS) (Lu *et al.*, 2000; Takadama *et al.*, 2001) or electron paramagnetic resonance (EPR) (Fattibene and Callens, 2010).

Biological Properties

The biological response of implanted materials (typically in terms of bioactivity, tissue integration, degradation...) is directly linked to their physicochemical features.

Due to its high stability, stoichiometric HA is the most stable CaP compound in physiological conditions (Brown and Kornberg, 2004). As such, it is characterized by a low solubility *in vivo* leading to a slow bioresorption: it may be considered as "non bioresorbable" and adhered osteoclasts were reported to have difficulties to spread and form resorption pits (Redey *et al.*, 1999). In contrast, biomimetic nanocrystalline apatites are expected to resorb significantly faster due to their lower thermodynamic stability (Rollin-Martinet *et al.*, 2013) leading to a higher solubility. Upon maturation however, their dissolution by osteoclasts was reported (Kim *et al.*, 2001) to decrease *in vitro* as the amount of labile (hydrogen)phosphate decreases on the apatite nanocrystals: the more mature the nanocrystals, the less resorbable.

a) $\nu_4\text{PO}_4$ domain



b) $\nu_3\text{PO}_4$ domain

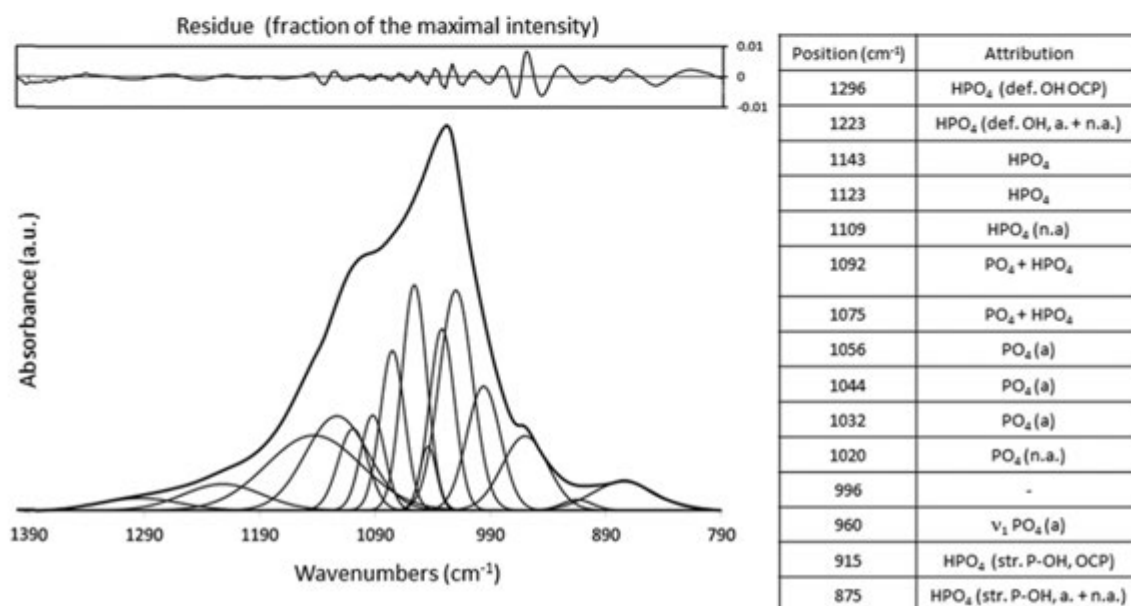


Fig. 2 Example of IR spectral decompositions (non-carbonated biomimetic apatite matured 1 day): (a) In the $\nu_4\text{PO}_4$ domain: the central zone corresponding to the 574 cm^{-1} band contains most probably an important contribution of non-apatitic (n.a) species. The best defined peaks and the thinnest ones can be attributed to apatitic (a) phosphates by reference to well-crystallized apatites. The non-apatitic phosphates (PO₄ and HPO₄), leading to wider bands, are only apparent on the sides of the envelope, where peaks attributed to apatitic phosphates have a relatively low intensity. (b) In the $\nu_3\text{PO}_4$ domain: attributions are based on those of Fowler for OCP and those proposed by Paschalis *et al.* Although the $\nu_3\text{PO}_4$ bands are the most intense from phosphate ions in IR spectroscopy, the various components are here significantly less well resolved than in the $\nu_4\text{PO}_4$ domain. The decomposition is not unique and remains more difficult to assess; moreover, no correspondence has been quantitatively established so far. Adapted from Fowler, B.O., Markovic, M., Brown, W.E., 1993. Octacalcium phosphate. 3. Infrared and Raman vibrational spectra. *Chemistry of Materials* 5, 1417–1423. Paschalis, E.P., Mendelsohn, R., Boskey, A.L., 2011. Infrared assessment of bone quality: A review. *Clinical Orthopaedics and Related Research* 469, 2170–2178. Drouet, C., Grossin, D., Combes, C., *et al.*, 2018b. Apatites biomimétiques Des biomimétiques aux analogues de synthèse pour le biomédical. *Techniques de l'Ingénieur*. IN227v1.

Despite their relevance to the clinic, to date only a limited amount of *in vivo* data is available on nanocrystalline apatite systems for which the development has occurred more recently. While HA is bioactive but “only” osteoconductive, the additional osteoinductivity of apatite nanocrystals deposited as a coating on BCP granules was nonetheless demonstrated intramuscularly in

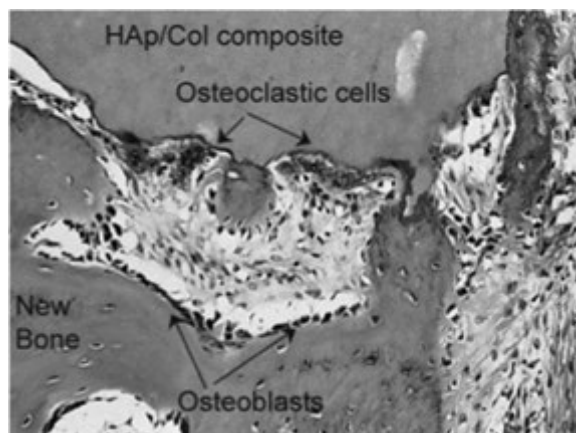


Fig. 3 Example of HA/collagen composite implantation data: optical microphotograph of H-E stained cross section at 12 weeks after implantation in beagle's tibia. Osteoclastic cells (multinucleated giant cells) resorbed the composite and created Howship's-like lacunae and osteoblasts formed new bone at surrounding of the composite. From Kikuchi, M., Ikoma, T., Itoh, S., *et al.*, 2004a. Biomimetic synthesis of bone-like nanocomposites using the selforganization mechanism of hydroxyapatite and collagen. *Composites Science and Technology* 64, 819–825.

the sheep, and the study also showed that an almost doubled amount of BMP-2 growth factor could be associated to the coated granules for accelerating bone regrowth (Autefage, 2009; Autefage *et al.*, 2009). Coatings of stoichiometric HA obtained by plasma spray are, on the other hand, commercially and clinically available (let us however remind that part of the HA phase has decomposed and only partially recomposed into HA in the torch), and although non osteoinductive, they were shown to allow improved osteointegration (De Groot *et al.*, 1987).

In vitro, the behavior of (rat) osteoblasts and (human) mesenchymal stem cells (MSC) was scrutinized and compared between sintered and biomimetic CaP (Sadowska *et al.*, 2017). Both types of cells were found to be sensitive to the ionic modifications undergone in the culture medium upon immersion of bone-like apatite, leading to a decrease in proliferation rate compared to sintered HA, especially of MSC. Higher alkaline phosphatase (ALP) activity for both cell types was also noticed for biomimetic apatite, pointing to a promotion of the osteoblast phenotype. The inflammatory response of HA particles with different morphologies was also investigated *in vitro* (using primary human polymorphonuclear cells (PMNCs), mononuclear cells (MNCs), and human dermal fibroblasts (hDFs)) or *in vivo* (subcutaneously in mice) (Pujari-Palmer *et al.*, 2016). A 2-fold decrease in viability was observed after exposure to HA particles of fiber morphology on PMNCs and hDFs, while MNC viability decreased 5-fold after treatment with dot-like particles. Also, a greater level of reactive oxygen species (ROS) was reached with the fibers in both PMNCs and MNCs, and the highest degree of apoptosis on all these cell types. Moreover, greater capsule thickness was noted subcutaneously in mice after exposure to fibers and dots morphologies.

In the form of self-supported scaffolds, apatitic systems were shown to exhibit bone regeneration ability, and bone-like apatite was again shown to have superior properties. For example, Mg-doped and MgCO_3 – cosubstituted materials were found to enhance MSC and osteoblast-like cells (MG63) in terms of adhesion, proliferation and metabolic activation compared to stoichiometric HA (Landi *et al.*, 2006). Ionic doping can also provide specific features. The effect of several inorganic substituents has been reviewed (Yang *et al.*, 2010). For example, Ag-doped apatites were shown to exhibit antibacterial and antifungal properties (Ciobanu *et al.*, 2013). Moreover, MG63 osteoblast-like cells cultivated on bone-like doped apatites showed that the presence of Mg^{2+} and Sr^{2+} promoted proliferation and expression of collagen I, and that the presence of Mn^{2+} ions had a noticeable positive effect on osteocalcin production (Bracci *et al.*, 2009).

Porosity is another factor with a direct effect on bone regrowth: porous HA scaffolds with micro-channels (25–30 μm) have been for example implanted in dogs, unveiling an increase in bone density compared to non-porous HA (Ren *et al.*, 2018). *In vitro*, a significant promotion of human placenta-derived mesenchymal stem cell (hPMSC) on osteogenic differentiation and maturation of osteoblasts was also pointed out by the authors for these porous HA scaffolds. This effect is postulated as being related to larger protein adsorption capabilities as well as promoting facilitated expression of osteogenic genes. Microporosity modulates the particle surface topography and this was reported to be impactful on cell proliferation and ALP activity (Rosa *et al.*, 2002).

As mentioned previously, combinations are also possible with organic components such as (bio)polymers, and this strategy may allow approaching even further the natural composition and/or architecture of bone while providing adequate conditions for bone repair (Itoh *et al.*, 2000; Kikuchi *et al.*, 2004a; Kim *et al.*, 2005; Tampieri *et al.*, 2003, 2011). Facilitated formation of bony tissue was reported, for example in view of osteochondral use (Itoh *et al.*, 2002; Kon *et al.*, 2010), and its resorption/neof ormation upon bone cell activity can be followed (Fig. 3). At a cellular level, the presence of polymers such as chitosan may improve cell proliferation (Kong *et al.*, 2005). The *in vivo* resorption rate of the organic component should however be selected carefully so as to avoid a too high foreign-body reaction and allow time for new bone tissue formation/apposition (Rovira *et al.*, 1993).

Mini-invasive surgery can be obtained using cement formulations (Burguera *et al.*, 2006; Knaack, 1998), and bone-like apatite can be the final product after cement setting. Advantages over more massive pieces are also their possible injectability and easier and better filling of bone defects with complex geometries. Their biocompatibility and bone repair abilities have been well documented (Bohner, 2010; Laschke *et al.*, 2007; Theiss *et al.*, 2005; von Rechenberg *et al.*, 2013).

Beyond bone applications, apatite (nano)particles can also be used in “(nano)medicine” for cell or tissue therapy (Drouet *et al.*, 2015; Iafisco *et al.*, 2012; Stefanic *et al.*, 2017; Welzel *et al.*, 2004), in particular due to their mimicry to bone apatite leading to highly biocompatible systems. Application fields may be wide and are in the process of being investigated. This is all the more relevant that ionic substitutions and/or molecular adsorptions can lead to tailored nanosystems with additional functionalities relevant to the targeted uses. Examples of applications are transfection, intracellular drug delivery in the fields on oncology (Adamiano *et al.*, 2018; Epple *et al.*, 2010; Iafisco *et al.*, 2016; Meshkini and Oveisi, 2017; Sarda *et al.*, 2018), hematology (Stefanic *et al.*, 2017), medical imaging (Al-Kattan *et al.*, 2010, 2014; Altinoglu *et al.*, 2008; Doat *et al.*, 2003; Guo *et al.*, 2008; Gómez-Morales *et al.*, 2018; Mondéjar *et al.*, 2007; Morgan *et al.*, 2008). The requirement of individualized circulating nanoparticles faces the question of the control of agglomeration, which is usually obtained via an organic corona adsorbed around the nanoparticles. Keeping in mind the biomedical requirements, only biocompatible organic agents can be selected to form this corona. Some phosphate/phosphonate compounds have for example been proposed with 2-aminoethyl phosphate (AEP) or phosphonated polyethyleneglycol (PEGp) (Al-Kattan *et al.*, 2010; Bouladjine *et al.*, 2009; Drouet *et al.*, 2015) as well as DNA (Mondéjar *et al.*, 2007; Welzel *et al.*, 2004), and other organics like citrates (Delgado-Lopez *et al.*, 2012; Gómez-Morales *et al.*, 2018). Among associations with active (bio)molecules/drugs, various studies have already been reported involving for instance cell-targeting agents like antibodies (Iafisco *et al.*, 2012) or folic acid (Drouet *et al.*, 2015; Sarda *et al.*, 2018), or else chemotherapeutic drugs like doxorubicin (Iafisco *et al.*, 2016) or methotrexate (Sarda *et al.*, 2018), potentially added in these latter studies to super-paramagnetic properties via Fe doping. Internalization in cells appears to happen via endocytosis, and the acidic conditions (pH 4–5) existing in endo(lyso)somes are thus bound to allow the progressive dissolution of apatite and consecutive drug release, which is associated to the release of natural metabolites such as calcium and phosphate ions.

Tricalcium Phosphate-Based Ceramics

Overview

Since the first trials of implantation of tricalcium phosphate (TCP: $\text{Ca}_3(\text{PO}_4)_2$) compounds, as a suspension, in animals (Albee, 1920), tricalcium phosphate beta (β -TCP) has become one of the first calcium phosphate phases to be used as bioceramics for bone substitution and repair due to its stability at high temperature and easiness of processing as ceramics (Jarcho *et al.*, 1979; Metsger *et al.*, 1982; Nery *et al.*, 1975). β -TCP-based ceramics have been commercialized for a long time and they are one of the major bioresorbable synthetic bone substitutes in use in today's practice of orthopedic and maxillofacial surgeons for the reconstruction of all kinds of bone defects (augmentation of alveolar ridge defects, sinus reconstruction and bone reconstruction following injuries or diseases (Horch *et al.*, 2006; Le Huec *et al.*, 1997; Nakagawa *et al.*, 2006; Ogoose *et al.*, 2005; Szabo *et al.*, 2005)). Today, several TCP phases are used as bioceramics (Table 1): the β -TCP phase which is the most widely used TCP compound, the metastable high-temperature phase α -TCP but also the amorphous tricalcium phosphate (*am*-TCP) and the apatitic tricalcium phosphate (*ap*-TCP); *am*-TCP and *ap*-TCP playing both an important role in coatings on metallic prosthesis and in calcium phosphate cements (Combes and Rey, 2010). TCPs are involved in many bone substitute materials in the form of dense or porous ceramics, coatings on metallic prosthesis, cements and composites.

Structures

Am-TCP has been shown to exhibit a local order studied in detail by Posner *et al.* (Betts and Posner, 1974a,b; Posner and Beebe, 1975). They proposed a model based on the agglomeration of cluster units of 9.5 Å of diameter and with a $\text{Ca}_9(\text{PO}_4)_6$ chemical

Table 1 TCP phases involved in several forms of bioceramics and their related properties

TCP phases	Chemical formula	Forms of bone substitute materials	Main TCP properties involved
α -TCP	$\alpha\text{-Ca}_3(\text{PO}_4)_2$	Cements, Coatings, composites	Dissolution & hydrolysis of α -TCP, <i>ap</i> -TCP and <i>am</i> -TCP; Bioresorbability; Reactivity/provider of Ca^{2+} and PO_4^{3-}
β -TCP	$\beta\text{-Ca}_3(\text{PO}_4)_2$	Ceramics, cements, coatings, composites, scaffolds for tissue engineering	ions (cement setting reaction); Release of ions with biological activity; Mechanical properties (composites)
<i>ap</i> -TCP (Ca-deficient apatite with equal amount of HPO_4^{2-} and OH^- : Ca/P = 1.5)	$\text{Ca}_9(\text{PO}_4)_{6-x}(\text{HPO}_4)_x(\text{OH})_x$	Cements, coatings, composites	
<i>am</i> -TCP (amorphous TCP)	$\text{Ca}_3(\text{PO}_4)_2, \text{nH}_2\text{O}$	Cements, coatings, composites	

Adapted from Rey, C., Combes, C., Drouet, C., Somrani, S., 2008. Chapter 15 – Tricalcium phosphate based ceramics. In: Kokubo, T. (Ed.), *Bioceramics and their Clinical Applications*. CRC & Woodhead Publishing Limited, pp. 326–366.

composition. The stability of Posner's clusters has been confirmed by theoretical calculations (Trebourg *et al.*, 2000). They consist in a central column of Ca^{2+} ion surrounded by six oxygen atoms arising from six phosphate groups and stabilized with eight additional Ca^{2+} ions distributed at the periphery. These clusters seem to constitute a basic building unit of several calcium phosphate phases (apatite, OCP, and crystalline TCPs). The presence of water is an intrinsic feature of am-TCP which should correspond to a hydrated TCP phase ($\text{Ca}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$) involving two types of bound water: loosely bound water molecules and the ones inside the amorphous particles which are tightly bound (Eanes, 1970; Sedlak and Beebe, 1974).

Ap-TCP is the low-temperature crystalline form derived from the crystallization in aqueous environment of am-TCP associated with an internal hydrolysis of phosphate groups (Heughebaert and Montel, 1982; Heughebaert, 1977) according to the following chemical equation: $\text{PO}_4^{3-} + \text{H}_2\text{O} \rightarrow \text{HPO}_4^{2-} + \text{OH}^-$ and leading to a crystalline apatite with equal amount of HPO_4^{2-} and OH^- , and consequently with a Ca/P ratio equal to 1.5.

The two major crystalline phases of TCP involved in bioceramics are α and β -TCP. β -TCP is a stable TCP phase which crystallizes in the rhombohedral system (space group $R3c$) with 21 formula units $\text{Ca}_3(\text{PO}_4)_2$ per hexagonal unit cell (Dickens *et al.*, 1974; Elliott, 1994). An interesting structural feature of β -TCP is the presence of columns of ions (anions and cations) parallel to the c -axis. It is worthwhile noting that a great amount of calcium ions (generally reported up to 15%) in β -TCP can be substituted by Mg^{2+} ions without major structure alteration, leading to a Mg- β -TCP phase (Clement *et al.*, 1989). Other bivalent cations can substitute for calcium in β -TCP: Zn^{2+} and Sr^{2+} being among the most interesting ones (Bigi *et al.*, 1997; Ito *et al.*, 2005). Zn^{2+} can substitute for calcium up to 20% and Sr^{2+} up to 80%. β -TCP incorporating some Na^+ ions ($\text{Ca}_{10}\text{Na}(\text{PO}_4)_7$ and up to 2.11% Na^+), has also been synthesized (Obadia *et al.*, 2011).

α -TCP is a metastable TCP phase crystallizing in the $P2_1/a$ monoclinic space group. The unit cell comprises 24 formula $\text{Ca}_3(\text{PO}_4)_2$ units (Mackay, 1953). As for β -TCP, α -TCP structure is also characterized by the presence of columns of ions (Ca^{2+} and PO_4^{3-}) parallel to the c -axis (Mathew *et al.*, 1977). A structural relationship with apatite can be derived by the replacement of cation columns with anion columns as described by Elliott (1994). Ionic substitutions in α -TCP have been less investigated than in β -TCP. Mostly, Zn^{2+} has been reported to substitute for Ca^{2+} (Ito *et al.*, 2001) and silicate for phosphate (Reid *et al.*, 2006; Sayer *et al.*, 2003).

TCP Powders Synthesis

The production of TCP-based ceramics requires first the synthesis of TCP precursor powder and then powder processing to produce cohesive bioceramics (dense or macroporous ceramics, coatings, cements or composites) for bone substitution applications.

Generally, two different TCP powder synthesis routes can be distinguished depending on the amorphous or crystalline TCP phases to be prepared: precipitation in solution (wet route) under controlled experimental conditions (pH, temperature, ion concentrations...) to synthesize the low-temperature phases (am- and ap-TCP), and the dry high-temperature route in particular, but not exclusively, for the synthesis of α - and β -TCP.

Synthesis of am-TCP

Am-TCP can be prepared by various solution-mediated routes. One of the most convenient preparation methods is by double decomposition, in aqueous media at ambient temperature and pH close to 10, between a calcium salt solution and a hydro-genphosphate salt solution (Heughebaert, 1977; Somrani *et al.*, 2005). It can also be obtained in hydroalcoholic medium (Lebugle *et al.*, 1986; Rodrigues and Lebugle, 1998); and the presence of ethanol in the precipitation medium influences the composition of the amorphous phase, especially its HPO_4^{2-} content and Ca/P ratio (Fellah and Layrolle, 2009; Rodrigues and Lebugle, 1998). A sol-gel route in ethanol was also reported to synthesize am-TCP with various Ca/P ratios which then will control the CaP crystalline phase formed after heating, typically at 1100°C in air for 5 h (Fellah and Layrolle, 2009). The main difficulties in the preparation of am-TCP are related to its instability and reactivity. Generally, am-TCP cannot be obtained at neutral or slightly acidic pH. However, it can be stabilized by various mineral ions or organic molecules which can be added in the precipitating and/or washing solutions (Holt *et al.*, 1989). Due to its reactivity and rather high water content, precipitated am-TCP is generally freeze-dried and stored at -18°C to prevent any further evolution. Dry, heated am-TCP can however be stored at room temperature.

Am-TCP can also be obtained by a dry high-temperature route, through rapid quenching of melted calcium phosphate (Ranz, 1996). However, in practice other anions such as O^{2-} are also observed in such high temperature amorphous phase, increasing its Ca/P atomic ratio (> 1.5) especially in plasma sprayed coatings of HA.

Am-TCP can also easily incorporate "foreign" ions through ionic substitutions (carbonate, Mg^{2+} , pyrophosphate, Ag^+ ...) with ions from the preparation solutions (Greenfield and Eanes, 1972).

Synthesis of ap-TCP

This compound is formed from the crystallization of am-TCP in aqueous medium. An internal hydrolysis of PO_4^{3-} phosphate ions occurs according to the following chemical reaction (Heughebaert, 1977; Heughebaert and Montel, 1982): $\text{PO}_4^{3-} + \text{H}_2\text{O} \rightarrow \text{HPO}_4^{2-} + \text{OH}^-$ leading to a crystalline apatite with equal amount of HPO_4^{2-} and OH^- according to the chemical formula $\text{Ca}_9(\text{PO}_4)_{6-x}(\text{HPO}_4)_x(\text{OH})_x$ corresponding to a non-stoichiometric calcium deficient hydroxyapatite family (Rey *et al.*, 2007).

Ap-TCP can be prepared by the methods described for am-TCP powder synthesis, except for the drying step which has to be carried out in an oven at 80°C in order to allow the internal hydrolysis and crystallization to occur (Heughebaert, 1977; Lebugle *et al.*, 1986). Several ionic substitutions are possible in ap-TCP as in other apatitic compounds.

Synthesis of α - and β -TCP

α -TCP and β -TCP phases can be obtained by a suitable high-temperature treatment of am-TCP and/or ap-TCP or, more generally, any mixture of calcium phosphate salts with the appropriate Ca/P ratio (Vallet-Regi *et al.*, 1997). A thermal treatment of am-TCP and ap-TCP phases at 900°C, in air for several hours, leads indeed to the formation of β -TCP with a high purity. α -TCP and β -TCP powders cannot be directly precipitated in aqueous systems but recently pure β -TCP platelet crystals were obtained within minutes at moderate temperature (150°C) by precipitation in ethylene glycol (Galea *et al.*, 2014).

α -TCP is generally obtained by heating β -TCP above 1125°C (the transition temperature for $\beta \rightarrow \alpha$ phase), followed by rapid quenching. It is interesting to note that α -TCP can also be obtained transitorily by heating am-TCP at temperatures lower than 1125°C (between 630 and 700°C), but this method leads generally to a product containing traces of β -TCP (Carrodeguas and De Aza, 2011; Eanes, 1970; Somrani *et al.*, 2003).

TCP-Ceramics Processing

Dense and macroporous ceramics

TCP powder sintering has been less studied than that of HA. The main difficulty in sintering β -TCP ceramic is related to the transition temperature of the β -TCP phase to the α -TCP phase which is accompanied by crystal expansion generating mechanical stresses and consequently cracks within the ceramics (Champion, 2013). For pure TCP, this transition occurs at 1125°C, however it can be shifted toward higher temperature in the presence of trace element impurities such as Mg, Fe, Mn and Zn thus facilitating the sintering process at higher temperatures. Another issue is related to the fact that the reverse transformation from α to β -TCP during ceramic cooling at room temperature does not occur in the same conditions as the initial transformation. Grain growth and reversible conversion into α -TCP is enhanced above 1250°C which compromises the densification and mechanical properties of the ceramic. Usually β -TCP powders are sintered between 1100°C and 1250°C depending on the characteristics of the initial powder and the expected final density of the ceramic (Fig. 4). Densification starts at about 750°C and the highest sintering rate is reached at about 950–1000°C (Champion, 2013). The composition of the initial powder is also a determinant parameter: an excess of calcium (Ca/P > 1.52) facilitates the transformation into α -TCP and Ca/P < 1.42 led to the formation of calcium

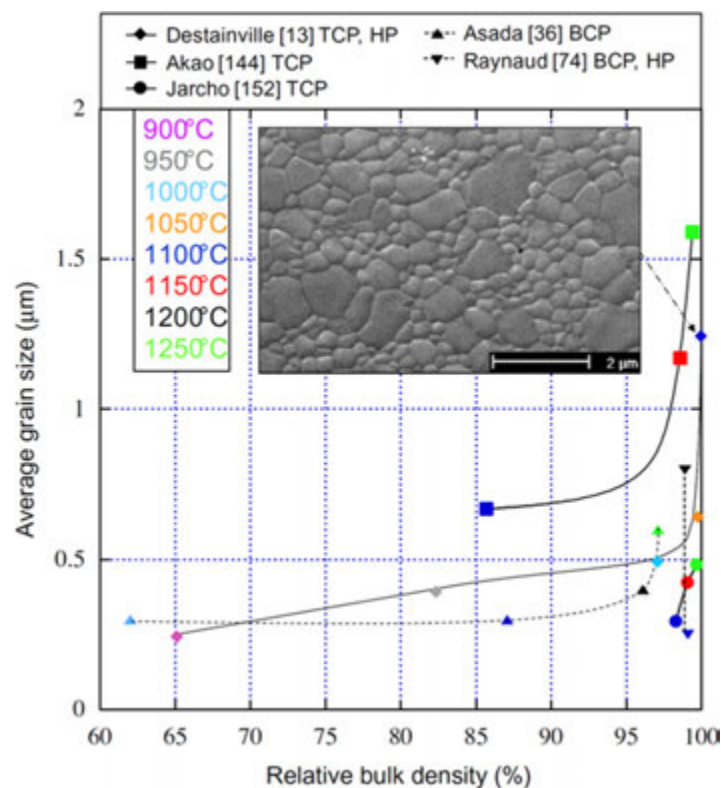


Fig. 4 Review on sintering trajectories of β -TCP and BCP ceramics. From Champion, E., 2013. Sintering of calcium phosphate bioceramics. *Acta Biomaterialia* 9, 5855–5875.

pyrophosphate (β -Ca₂P₂O₇) inclusions which slows down the sintering process. Addition of calcium pyrophosphate in the range 0.5–3 wt% enables sintering of β -TCP at higher temperature (1200°C) without transformation into α -TCP; the ceramic obtained has a relative density of 95% (Ryu *et al.*, 2002). Sintering conditions were shown to have an impact on the mechanical behavior of β -TCP ceramics (Wang *et al.*, 2004).

Hot pressing (HP) sintering and non-conventional sintering by SPS of pure β -TCP have been investigated with the objective to lower the sintering temperature while avoiding phase transformation (Drouet *et al.*, 2006; Zhang *et al.*, 2008).

α - and β -TCP biphasic ceramics with controlled α/β ratio can be prepared by reactive sintering of hydroxyapatite (HA) and dicalcium phosphate mixtures impregnated either with Mg-acetate or Mg-nitrate solution stabilizing the β -TCP phase (Famery *et al.*, 1994).

Several methods have been developed to prepare macroporous TCP-based bioceramics with interconnected pores (ranging between 150 and 400 μ m in diameter) allowing cell seeding and/or migration, vascularization and bone ingrowth and also a control of ceramic resorption: ceramic foams (using hydrogen peroxide, carbon dioxide...), solid/solid reaction, ceramic slurry impregnation of polymer porosifier skeletons which leave macropores by heating at temperature below 200°C (sponge, scaffold of PMMA beads...), ice-templating and more recently additive manufacturing like robocasting or microstereolithography. In addition, the preparation of macroporous β -TCP blocks using α -TCP-oil emulsions and sintering at 1250 °C has been reported (Bohner, 2000). Porous α -TCP ceramic can be prepared using replica of porous structure (polyurethane sponge) and conventional sintering of β -TCP above 1100°C (Kitamura *et al.*, 2004). The macroporous TCP bioceramics exhibit generally a low resistance to compression, roughly related to their porosity, which does not allow their direct use in load-bearing applications. The pore volume rarely exceeds 50% (Park *et al.*, 2012; Sous *et al.*, 1998) but can occasionally reach 80%; in addition to the mechanical behavior, it determines the rate of resorption and cellular rehabilitation.

Cements

Currently, the second most important use of TCP compounds is in ionic self-setting cements able to set and harden in a living body and most of them can be injected. Despite their poor mechanical properties, they offer a number of advantages and are increasingly used in clinical practice. Various TCP phases (am-, α - or β -TCP) are involved in many calcium phosphate cement compositions, already commercialized or not. Especially, am- and α -TCP are involved in several cement compositions due to their fast hydrolysis reactions leading to poorly crystalline apatite crystals formation (often similar to ap-TCP) and entanglement responsible for cement hardening. α -TCP has been shown to be stabilized by the presence of silicon which prevents the $\beta \rightarrow \alpha$ reverse transformation during cooling (Mestres *et al.*, 2012). Both Si-doped α -TCP and α -TCP hydrolyze to a calcium-deficient hydroxyapatite during cement setting and hardening, but the setting rate of Si- α -TCP based cement proved to be slower than with α -TCP based cement (Motisuke *et al.*, 2017). Biphasic HA/ β -TCP cement has been prepared with different phase ratios from self-setting α -TCP/ β -TCP pastes (Gallinetti *et al.*, 2014). Also, the association of α -TCP cement with gelatin increases the cement setting rate and its mechanical properties (Bigi *et al.*, 2004). β -TCP is the main constituent of DCPD cements and sometimes used as inert additive in other types of CaP cements. One of the main drawbacks compared to ceramic blocks is the preparation of the paste and (most generally) the absence of macropores allowing cell rehabilitation, but the main advantage is their ability to fill any kind of bone defects and their injectability allowing mini-invasive surgical procedures. Although the hardening reactions are generally correctly described *in vitro*, the alterations of these reactions *in vivo* are not well known when the cement paste is in contact with body fluids, and the diffusion of mineral ions and/or organic additives from the cement to adjacent tissues.

Coatings

Although formed in several coating processes, especially in plasma sprayed HA, TCP compounds have not yet been commercialized as thermal coatings. Low temperature deposition involving am- and ap-TCP-like compounds (Barrere *et al.*, 2004) has been proposed. Several authors studied β -TCP coating on bioinert bioceramics (zirconia) or metals/alloys (magnesium alloys, titanium, gold) to improve their *in vitro* and *in vivo* biological properties. Stefanic *et al.* used a wet deposition route followed by a thermal treatment at a temperature ranging between 800 and 1200°C which could control the β -TCP coating topography and physicochemical properties (dissolution, protein adsorption capacity, bioactivity in SBF) (Stefanic *et al.*, 2014). Other authors also implemented wet routes for preparing the metallic surfaces (alkali treatment) and then formed the β -TCP coating in a super-saturated calcium phosphate solution or by electrodeposition using a β -TCP suspension both followed by a heat treatment at 400°C (Chai *et al.*, 2012; Chen *et al.*, 2014; Jiang *et al.*, 2015; Pang *et al.*, 2018). β -TCP coating was also reported to be obtained by RF magnetron sputtering or plasma spray (Lim *et al.*, 2018; Lin *et al.*, 2001).

Composites

TCP compounds (mainly α -, β -TCP and am-TCP) are also used as mineral ions releasing substances in polymer materials although such composites have received little commercialized applications. Many types of polymeric materials have been proposed mainly degradable natural or synthetic polyesters (polylactic, polyglycolic acids, poly- ϵ -caprolactones, etc.) and natural polymers or proteins (collagen, chitosan, alginate,...) (Aunoble *et al.*, 2006; Kikuchi *et al.*, 2004b; Luginbuehl *et al.*, 2005; Matsuno *et al.*, 2006; Van Den Vreken *et al.*, 2006; Zhang and Zhang, 2001). The advantages of these associations have not always been demonstrated (Ekholm *et al.*, 2006).

Main Physicochemical Properties of TCP Phases

Several TCP physicochemical properties of interest for TCP ceramics processing (thermal properties) and their interaction with biological fluids (solubility and evolution in aqueous medium) and bone tissue (see in the Section “Biological Properties”) will be presented in the next section.

Solubility

All TCPs are considered as more soluble than stoichiometric hydroxyapatite, however a precise solubility product has not yet been determined in the case of am- and ap-TCP. For the latter compound it depends probably on the hydrolysis ratio and its stoichiometry. A broad range of data on the solubility of am-TCP is available; some of the reported values could have been altered due to the hydrolysis reaction of this very unstable phase. The most relevant values reported are related to the work of Somrani *et al.* (2005). As expected, this phase is much more soluble than the crystalline TCP phases.

The solubility behavior of α - and β -TCP has been fully investigated (Fowler and Kuroda, 1986; Gregory *et al.*, 1974). As a general trend, the solubility of these phases was found to decrease in the order α -TCP > β -TCP > Ca-deficient apatites > HA (Ducheyne *et al.*, 1993). Considering the general concept that biological resorbability of calcium phosphates is determined by their solubility, all TCPs are bioresorbable (LeGeros, 1991).

Substituted β -TCP, containing Zn and Mg, have been shown to exhibit a lower solubility than the non-substituted one depending on the substitution ratio (Ito *et al.*, 2002). Additionally, the kinetics of dissolution of β -TCP seems very sensitive to the presence of foreign ions in the solution, especially Mg^{2+} and Zn^{2+} , and a concentration of Zn^{2+} as low as $2 \times 10^{-6} \text{ mol L}^{-1}$ has been shown to completely inhibit its dissolution (Tang *et al.*, 2001). For a given ion-doping molar content, Mg-doped β -TCP was reported to be more soluble than Zn-doped β -TCP (Li *et al.*, 2009b). Recently, the dissolution properties of non-doped and Mg-doped β -TCP dense ceramics in acidic solution (pH 4.4) have been compared, demonstrating the key role of doping (especially Mg-doping) and grain orientation on the process and kinetics of resorption (Gallo *et al.*, 2019).

TCP phases evolution in aqueous medium

When immersed in solution, α -TCP and am-TCP show a strong tendency to evolve towards a more stable phase through a hydrolysis process for which solution parameters such as pH, ion concentrations and temperature are known to play a major role. In alkaline and neutral pH conditions, am-TCP progressively transforms into non-stoichiometric hydroxylated apatites (Eanes and Meyer, 1977). The presence of some ionic species such as Mg^{2+} , CO_3^{2-} , $\text{P}_2\text{O}_7^{4-}$ which inhibit apatite crystal growth was shown to delay this hydrolysis process (LeGeros *et al.*, 2005). The hydrolytic conversion rate of am-TCP into apatite depends strongly on the temperature (Heughebaert, 1977; Somrani *et al.*, 2005) which thus controls the setting reaction of am-TCP based cements (Knaack, 1998).

α -TCP hydrolyzes also rapidly in aqueous solution (Monma, 1980; Monma *et al.*, 1981). The hydrolysis products are generally OCP and non-stoichiometric apatite, although dicalcium phosphate anhydrous (DCPA or monetite) and dicalcium phosphate dihydrate (DCPD or brushite) can also form.

In contrast, β -TCP does not show a tendency to hydrolyze rapidly in solution at physiological temperatures. This behavior can be linked to its solubility product below that of blood plasma (larger value of $-\log [K_{sp}]$) in contrast to the other TCP phases and particularly α - and am-TCP (Rey *et al.*, 2008).

Thermal stability of TCP phases

No variation of the Ca/P ratio of TCP phases can occur on heating. Among the TCP phases, α -TCP is known as the high-temperature stable form in the 1125°C to 1430°C temperature range (Welch and Gutt, 1961). Under 1125°C, β -TCP is the stable TCP phase. ap-TCP can be seen as the low-temperature crystalline form of am-TCP (e.g., upon drying at 80°C). On heating at temperatures higher than 750°C, this phase transforms into β -TCP (Destainville *et al.*, 2003). Am-TCP is a quite unstable phase and hydrolyzes easily into ap-TCP in the presence of small amounts of water at room temperature. Am-TCP remains however amorphous when heated up to ca. 630°C (Eanes, 1970). Above this temperature, it crystallizes first into the metastable α -TCP generally associated with small fractions of β -TCP at 800°C, and then into pure β -TCP. However, am-TCP enriched with Mg (or containing other elements stabilizing the β -TCP phase such as Fe and Zn) transforms directly into the β -TCP phase without the intermediary formation of α -TCP.

Surface properties of TCP

Only few data are available to-date on the surface properties of TCP phases, despite their high involvement in the biomaterials field. Regarding the literature concerning the surface properties or reactivity of TCPs, most studies deal with either adsorption or ion exchange processes, but the elucidation of the corresponding mechanisms and the relationship with intrinsic surface properties of the TCP phases involved are only rarely addressed.

The effect of recombinant human transforming growth factor-beta1 (rhTGF-beta1) adsorbed onto TCP-coated implants (0.3 μg of rhTGF-beta1) was followed in a dog model (Lin *et al.*, 2001). The adsorption of various proteins on β -TCP and other calcium phosphates was also investigated (Ohta *et al.*, 2001). The total number of calcium sites on β -TCP was found to be significantly smaller than on the other calcium phosphates tested, including hydroxyapatite. The association of bisphosphonate with β -TCP and a mixture of HA and β -TCP has been investigated (Josse *et al.*, 2005). A high amount of zoledronate was associated

with β -TCP powders and the released concentration of phosphate in solution was shown to be directly related to the amount of zoledronate loaded on β -TCP.

Biological Properties

In vitro cell tests on TCPs

Many cell culture studies on TCP ceramics have been published involving osteoblast, osteoclast and bone cell precursors. Often these studies have been made on poorly characterized TCP samples (grain size, impurities, microstructure, surface roughness); moreover they implied different cell lines and different methodologies. It is therefore not possible to correlate these rather large sets of data and to link the observations with physical-chemical characteristics of the materials. In addition, alterations of TCPs surface ceramics in cell culture media have been reported which are susceptible to modify cell behavior during the course of the experiments. A follow-up of the mineral composition of the cell culture medium and a re-analysis of the ceramic surface after cell culture could probably clear up some contradictory results.

It has been generally observed that TCP ceramics are not cytotoxic on contact with extract fluids. In the presence of TCP particles, which could be released from cement powders or from resorbing ceramics, the osteoblast cell behavior depends strongly on the amount and size of particles. Massive amounts of small particles impair cell growth (Pioletti *et al.*, 2000; Sun *et al.*, 1997) and may cause cell death whereas small amounts of α -TCP powders have been shown to favor osteoblast proliferation and expression, which is possibly related to the release of mineral ions, especially calcium and phosphate ions, acting directly on cells (Ehara *et al.*, 2003). Osteoblast cell cultures on composite samples (biphasic calcium phosphates, TCP and collagen or polymers) give generally better results than on the raw materials. Ion-substituted TCP (Zn- β -TCP, Mg- β -TCP, Si- α -TCP cement) have also been claimed to improve osteoblast attachment and proliferation sometimes related to an optimal ion substitution ratio (Camire *et al.*, 2006; Ito *et al.*, 2000; Singh *et al.*, 2014), compared to the pure TCP. The role of surface energy and topography of β -TCP on the osteoblast cells has also been studied *in vitro* (dos Santos *et al.*, 2008, 2009).

It has been shown that CaP material characteristics (composition, solubility, grain size and crystallinity) as well as surface features (topography, roughness, pore size, wettability and surface energy) influence osteoclasts adhesion and resorption activity but only very few data have been published concerning osteoclast behavior on TCP phases. Some authors failed to observe any activity on the surface of α - and β -TCP despite alterations of the calcium and phosphate concentration in the cell culture medium (Doi *et al.*, 1999). A possible reason for this failure could be the ion release, and probably the existence of an alkaline surface reaction related to the surface hydrolysis, inhibiting osteoclast activity. In other cases, however, osteoclast attachment and resorption activity has been described, evidencing a much stronger degradation of β -TCP than HA (de Bruijn *et al.*, 1994; Monchau *et al.*, 2002), related to the rate of dissolution of the calcium phosphates. Such data seem in agreement with *in vivo* studies. Recently, Gallo *et al.* compared the results of an osteoclast resorption assay with a dissolution test of β -TCP samples in acidic conditions (Gallo *et al.*, 2019).

The possible use of α -, β - and Zn-containing β -TCP as scaffolds for bone tissue engineering has been investigated using bone marrow cells (Dong *et al.*, 2002; Ikeuchi *et al.*, 2003; Jensen *et al.*, 2015; Kim *et al.*, 2017; Niemeyer *et al.*, 2004). These ceramics have been shown to exhibit good biological properties favoring cell adhesion, proliferation and differentiation. Implants seeded with precursor cells have shown the ability to generate bone tissues in non-osseous sites (Kasten *et al.*, 2005) and the rate of bone healing has been shown to be higher using cell-seeded ceramics.

In vivo studies

The literature on *in vivo* studies agrees generally on the relation between the degradation rate of TCPs and their dissolution kinetics including structural and microstructural parameters such as crystal size, particle size and porosity/pore size of the ceramics (Duan *et al.*, 2017; Lapczynska *et al.*, 2014; Zhang *et al.*, 2014). α -TCP has been shown to be more easily resorbed than β -TCP *in vivo* (Yamada *et al.*, 2007) and Zn- and Mg-substituted β -TCPs exhibit generally a lower resorption rate *in vivo* related to the effects of the substitutions on the solubility (Ito *et al.*, 2002). Hydrolysis into less soluble compounds may occur rapidly *in vivo*, especially for am- and α -TCP, affecting their biodegradation.

Generally bone formation is observed on degraded β -TCP and α -TCP implant surface on contact with the materials and sometimes at a distance of the ceramic surface (Galois and Mainard, 2004; Kihara *et al.*, 2006; Neo *et al.*, 1998). This behavior could be related to the resorbability of TCP implants which could occur at different rates from that of bone formation, possibly because of the involvement of different resorption processes, and the inability of TCP to promote apatite nucleation.

In some cases, an osteoinductive behavior of raw β -TCP has been suggested (Tsukanaka *et al.*, 2015; Yuan *et al.*, 2001) however other authors have reached opposite conclusions. Association of growth factors such as BMP (bone morphogenetic protein) with TCP ceramics provides however an osteoinductive behavior (Wu *et al.*, 1992).

The main difficulty concerning especially α -TCP and am-TCP is their evolution *in vivo*. These are rarely considered but they have probably a strong impact on their biological behavior. In addition to histological investigations, physical-chemical characterization of the retrieved implants should be performed for better apprehending the modifications undergone and the surrounding bone neoformation.

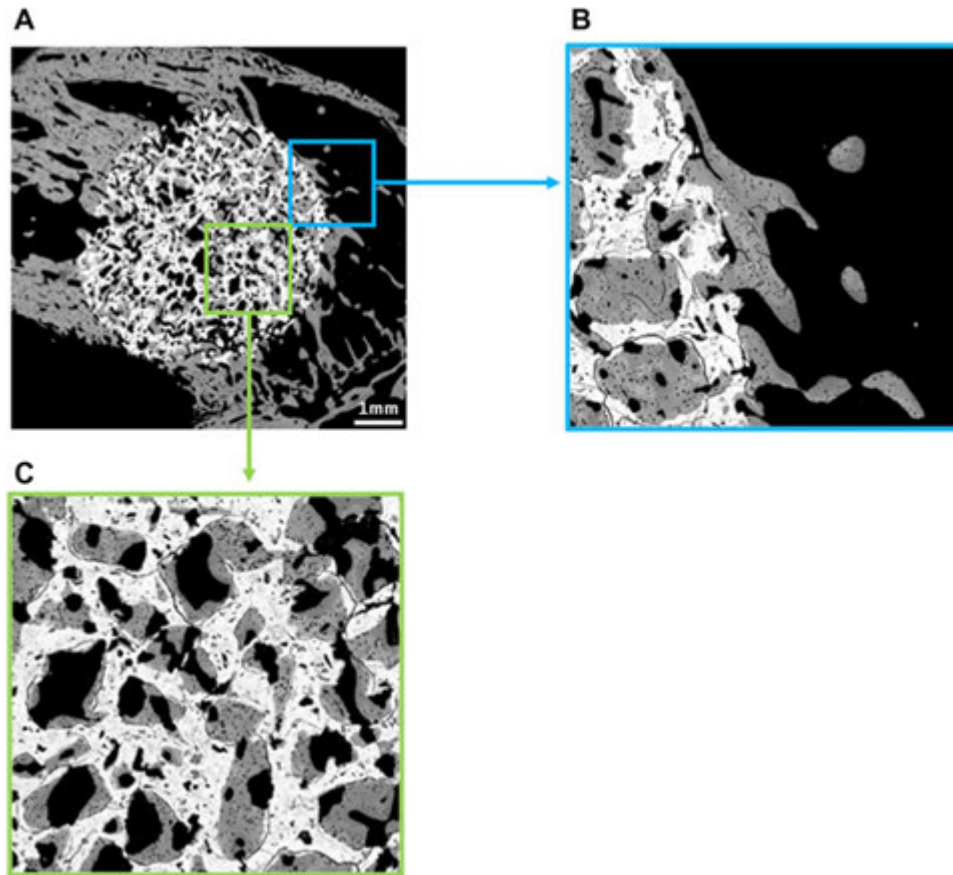


Fig. 5 SEM micrographs of macroporous BCP ceramic (mean pore diameter: 565 μm ; total porosity: 50%) implanted 12 weeks in critical bone defect (rabbit femur) (A) showing bone ingrowth in the pores both at the periphery (B) and within the implant (C). BCP (white); native and newly formed bone (gray); non mineralized tissue (black). From Bouler, J.M., Pilet, P., Gauthier, O., Verron, E., 2017. Biphasic calcium phosphate ceramics for bone reconstruction: A review of biological response. *Acta Biomaterialia* 53, 1–12.

Biphasic Calcium Phosphate Ceramics: HA/ β -TCP

Biphasic calcium phosphate (BCP) ceramics associating a rather soluble calcium phosphate phase, β -TCP, with a more stable phase, HA, allow a better control of bioactivity and biodegradation rate thanks to their physicochemical characteristics (HA/ β -TCP ratio, micro- and macroporosity and the interconnection of pores) and have proven to be efficient in numerous clinical indications especially in the form of macroporous granules or monoliths (Fig. 5) (Bouler *et al.*, 2017; Daculsi *et al.*, 2003; LeGeros *et al.*, 2003). The HA/ β -TCP ratio is known as the main parameter controlling not only the bioresorption rate but also the biological properties of BCP ceramics through the effect of the released ions on bone progenitor cells. The properties of BCP ceramics vary depending on the sintering process and parameters which control the microstructure, phase composition and crystal defects within the ceramic (Bouler *et al.*, 2000).

BCP with different HA/ β -TCP ratios can be prepared by mechanical mixing and co-sintering of HA and β -TCP powders in desired quantities or by chemical methods producing calcium-deficient apatites ($\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}$) followed by sintering. The ability of BCP to be sintered is lower than that of the separated HA or β -TCP phases; a higher temperature (for example at least 1250°C) is needed to sinter dense BCP ceramics (Bouler *et al.*, 2000). To avoid β -TCP to α -TCP transformation in this temperature condition, magnesium oxide is commonly added to stabilize the β -TCP phase (Ryu *et al.*, 2004). The BCP composition obtained after sintering depends on the calcium deficiency of the unsintered biological or synthetic calcium-deficient apatite and on the sintering temperature.

The HA/ β -TCP ratio of BCP ceramics controls both the ceramic resorption rate and the release of ions in the environment of bone cells which could also trigger the biological properties.

BCP macroporous ceramics are processed by gel casting or addition of sacrificial organic particles (polymer, naphthalene, sucrose particles...), to be degraded by a thermal treatment before sintering, depending on the targeted porosity and final mechanical strength, and then sintered at high temperature. Sintering of BCP at lower temperature has been investigated by conventional and microwave sintering leading to microporous ceramics, but the sintering is not completed (Li *et al.*, 2009a). Micro and macroporous BCP ceramics are expected to present better biological properties.

To improve BCP granules handling, their association with a hydrosoluble polymer or silanized hydroxypropyl methyl cellulose gel allows obtaining a non self-hardening or self-hardening injectable bone substitute, respectively (Struillou *et al.*, 2011). Other associations of BCP granules with fibrin glue to obtain a composite or with other calcium phosphate phases to obtain a self-setting cement have also been investigated (Saffarzadeh *et al.*, 2009).

Conclusion and Perspectives

Two main families of calcium phosphate compounds are particularly investigated for biomedical applications, and especially for bone repair: apatites (involving not only stoichiometric HA but also non-stoichiometric/biomimetic phases) and tricalcium phosphates. The most recent developments aim at proposing new processing routes and improving their biological properties. Three main axes are specially investigated: their substitution with bioactive ions, their combination with active molecules, and their association with cells in the scope of tissue engineering. The ion-substituted route leads to compounds which have shown interesting advanced properties and it is probable that they will receive an industrial development in future years. One of the main advantages of these inorganic materials is their low cost and stability to sterilization procedure and their excellent storage properties. Local delivery of active (bio)molecules including growth factors from composite materials based on apatite or TCPs ceramics is widely investigated. Despite a high cost and uncertainties on stability of such biologically active molecules, they will probably appear on the market for some dedicated applications, especially in the case where bone repair potential is impaired and in old patients; regulatory aspects are however particularly drastic with the use of growth factors. A difficulty in the case of BMP-containing HA or TCP bioceramics is indeed the need of a high concentration of growth factor, much higher than physiological doses. There are probably progresses to be made in the optimization of growth factor release and control and also probably in considering the associations of several active molecules with complementary and/or synergistic activities. Because of their resorbability, porous TCP ceramics have been used with success for tissue engineering of bone tissue. Despite the cost of tissue engineering strategy, apatitic and TCP-based scaffolds are widely studied and developed for the personalized repair of critical size defects in bone tissue especially considering the very recent development of additive manufacturing for bioceramics processing. Beyond bone repair, other medical domains are also emerging such as (nano)medicine and cell therapy where bio-inspired CaP compounds can cumulate a high tailorable reactivity and an intrinsic biocompatibility.

Summary

Calcium phosphates (CaPs) are biominerals found in living organisms. Synthetic analogs can be prepared for biomedical applications like bone substitution and (nano)medicine. Biomimetic nanocrystalline apatites exhibit a high bioactivity while stoichiometric hydroxyapatite (HA) is thermodynamically very stable. Other CaPs are also relevant to medicine like tricalcium phosphates (TCPs, especially the high temperature α and β forms or the low temperature forms, amorphous TCP and apatitic TCP). These apatitic and tricalcic compounds are the most used CaPs in the biomedical field, and offer a large panel of bioceramic-based systems with diverse characteristics (mechanical, biological, chemical, thermodynamic...) to comply with clinical needs.

References

- Abe, Y., Kokubo, T., Yamamuro, T., 1990. Apatite coating on ceramics, metals and polymers utilizing a biological process. *Journal of Materials Science: Materials in Medicine* 1, 233–238.
- Adamiano, A., Iafisco, M., Sandri, M., *et al.*, 2018. On the use of superparamagnetic hydroxyapatite nanoparticles as an agent for magnetic and nuclear in vivo imaging. *Acta Biomaterialia* 73, 458–469.
- Albee, F.H., 1920. Studies in bone growth – Triple calcium phosphate as a stimulus osteogenesis. *Annals of Surgery* 71, 32–39.
- Al-Kattan, A., Dufour, P., Dexpert-Ghys, J., Drouet, C., 2010. Preparation and physicochemical characteristics of luminescent apatite-based colloids. *Journal of Physical Chemistry C* 114, 2918–2924.
- Al-Kattan, A., Santran, V., Dufour, P., Dexpert-Ghys, J., Drouet, C., 2014. Novel contributions on luminescent apatite-based colloids intended for medical imaging. *Journal of Biomaterials Applications* 28, 697–707.
- Altinoglu, E.I., Russin, T.J., Kaiser, J.M., *et al.*, 2008. Near-infrared emitting fluorophore-doped calcium phosphate nanoparticles for in vivo imaging of human breast cancer. *ACS Nano* 2, 2075–2084.
- Arends, J., Christoffersen, J., Christoffersen, M.R., *et al.*, 1987. A calcium hydroxyapatite precipitated from an aqueous solution. An international multimethod analysis. *Journal of Crystal Growth* 84, 515–532.
- Aunoble, S., Clement, D., Frayssinet, P., Harmand, M.F., Le Huec, J.C., 2006. Biological performance of a new beta-TCP/PLLA composite material for applications in spine surgery: In vitro and in vivo studies. *Journal of Biomedical Materials Research – Part B: Applied Biomaterials* 91, 416–422.
- Auféage, H., 2009. Rôle ostéoinducteur d'un revêtement d'apatite carbonatée nanocristalline sur des céramiques de phosphate de calcium. PhD thesis. Toulouse, France: Institut National Polytechnique de Toulouse.
- Auféage, H., Briand-Mesange, F., Cazalbou, S., *et al.*, 2009. Adsorption and release of BMP-2 on nanocrystalline apatite-coated and uncoated hydroxyapatite/beta-tricalcium phosphate porous ceramics. *Journal of Biomedical Materials Research – Part B: Applied Biomaterials* 91, 706–715.
- Barrere, F., Snel, M.M., van Blitterswijk, C.A., de Groot, K., Layrolle, P., 2004. Nano-scale study of the nucleation and growth of calcium phosphate coating on titanium implants. *Biomaterials* 25, 2901–2910.
- Beshah, K., Rey, C., Glimcher, M.J., Shimizu, M., Griffin, R.G., 1990. Solid state C-13 and proton NMR studies of carbonate-containing calcium phosphates and enamel. *Journal of Solid State Chemistry* 84, 71–81.

- Betts, F., Posner, A.S., 1974a. A structural model for amorphous calcium phosphate. *Transactions of the American Crystallographic Association* 10, 73–84.
- Betts, F., Posner, A.S., 1974b. X-ray radial distribution study of amorphous calcium phosphate. *Materials Research Bulletin* 9, 353–360.
- Bigi, A., Bracci, B., Panzavolta, S., 2004. Effect of added gelatin on the properties of calcium phosphate cement. *Biomaterials* 25, 2893–2899.
- Bigi, A., Foresti, E., Gandolfi, M., Gazzano, M., Roveri, N., 1997. Isomorphous Substitutions in B-Tricalcium Phosphate: the Different Effects of Zinc and Strontium. *Journal of Inorganic Biochemistry* 66, 259–265.
- Blackwood, D.J., Seah, K.H.W., 2009. Electrochemical cathodic deposition of hydroxyapatite: Improvements in adhesion and crystallinity. *Materials Science and Engineering: C* 29, 1233–1238.
- Bohner, M., 2000. Calcium phosphate emulsions: Possible applications. *Key Engineering Materials* 192–195, 765–768.
- Bohner, M., 2010. Design of ceramic-based cements and putties for bone graft substitution. *European Cells & Materials Journal* 20, 1–12.
- Boskey, A.L., Mendelsohn, R., 2005. Infrared spectroscopic characterization of mineralized tissues. *Vibrational Spectroscopy* 38, 107–114.
- Bouladjine, A., Al-Kattan, A., Dufour, P., Drouet, C., 2009. New advances in nanocrystalline apatite colloids intended for cellular drug delivery. *Langmuir* 25, 12256–12265.
- Bouler, J.M., LeGeros, R.Z., Daculsi, G., 2000. Biphasic calcium phosphates: Influence of three synthesis parameters on the HA/beta-TCP ratio. *Journal of Biomedical Materials Research* 51, 680–684.
- Bouler, J.M., Pilet, P., Gauthier, O., Verron, E., 2017. Biphasic calcium phosphate ceramics for bone reconstruction: A review of biological response. *Acta Biomaterialia* 53, 1–12.
- Bracci, B., Torricelli, P., Panzavolta, S., *et al.*, 2009. Effect of Mg²⁺, Sr²⁺, and Mn²⁺ on the chemico-physical and in vitro biological properties of calcium phosphate biomimetic coatings. *Journal of Inorganic Biochemistry* 103, 1666–1674.
- Bres, E.F., Reyes-Gasga, J., Rey, C., Michel, J., 2014. Probe size study of apatite irradiation in stem. *European Physical Journal-Applied Physics* 67.
- Brouillet, F., Laurencin, D., Grossin, D., *et al.*, 2015. Biomimetic apatite-based composite materials obtained by spark plasma sintering (SPS): Physicochemical and mechanical characterizations. *Journal of Materials Science: Materials in Medicine* 26, 1–11.
- Brown, M.R.W., Kornberg, A., 2004. Inorganic polyphosphate in the origin and survival of species. *Proceedings of the National Academy of Sciences of the United States of America* 101, 16085–16087.
- de Bruijn, J.D., Bovell, Y.P., Davies, J.E., van Blitterswijk, C.A., 1994. Osteoclastic resorption of calcium phosphates is potentiated in postosteogenic culture conditions. *Journal of Biomedical Materials Research* 28, 105–112.
- Burguera, E.F., Xu, H.H., Weir, M.D., 2006. Injectable and rapid-setting calcium phosphate bone cement with dicalcium phosphate dihydrate. *Journal of Biomedical Materials Research Part B-Applied Biomaterials* 77B, 126–134.
- Buser, D., Schenk, R.K., Steinemann, S., *et al.*, 1991. Influence of surface characteristics on bone integration of titanium implants. A histomorphometric study in miniature pigs. *Journal of Biomedical Materials Research* 25, 889–902.
- Camire, C.L., Saint-Jean, S.J., Mochales, C., *et al.*, 2006. Material characterization and in vivo behavior of silicon substituted alpha-tricalcium phosphate cement. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 76, 424–431.
- Carrodegua, R.G., De Aza, S., 2011. alpha-Tricalcium phosphate: synthesis, properties and biomedical applications. *Acta Biomaterialia* 7, 3536–3546.
- Cazalbou, S., Eichert, D., Ranz, X., *et al.*, 2005. Ion exchanges in apatites for biomedical application. *Journal of Materials Science: Materials in Medicine* 16, 405–409.
- Chai, C.S., Ben-Nissan, B., 1999. Bioactive nanocrystalline sol-gel hydroxyapatite coatings. *Journal of Materials Science: Materials in Medicine* 10, 465–469.
- Chai, H., Guo, L., Wang, X., *et al.*, 2012. In vitro and in vivo evaluations on osteogenesis and biodegradability of a beta-tricalcium phosphate coated magnesium alloy. *Journal of Biomedical Materials Research Part A* 100, 293–304.
- Champion, E., 2013. Sintering of calcium phosphate bioceramics. *Acta Biomaterialia* 9, 5855–5875.
- Charlot, G., 1974. *Chimie analytique quantitative. Vol I - methodes chimiques et physico-chimiques, vol II - methodes selectionnees d'analyse chimique des elements* (Masson).
- Charrière, E., Lemaire, J., Zysset, P., 2003. Hydroxyapatite cement scaffolds with controlled macroporosity: Fabrication protocol and mechanical properties. *Biomaterials* 24, 809–817.
- Chen, Z., Mao, X., Tan, L., *et al.*, 2014. Osteoimmunomodulatory properties of magnesium scaffolds coated with beta-tricalcium phosphate. *Biomaterials* 35, 8553–8565.
- Chevalier, E., Chulia, D., Pouget, C., Viana, M., 2008. Fabrication of porous substrates: A review of processes using pore forming agents in the biomaterial field. *Journal of Pharmaceutical Sciences* 97, 1135–1154.
- Ciobanu, C.S., Iconaru, S.L., Chifiriuc, M.C., *et al.*, 2013. Synthesis and antimicrobial activity of silver-doped hydroxyapatite nanoparticles. *BioMed Research International* 2013, 10.
- Clement, D., Tristan, J.M., Hamad, M., Roux, P., Heughebaert, J.C., 1989. The Mg²⁺/Ca²⁺ substitution in beta-tricalcium ortho-phosphate. *Journal of Solid State Chemistry* 78, 271–280.
- Combes, C., Rey, C., 2010. Amorphous calcium phosphates: Synthesis, properties and uses in biomaterials. *Acta Biomaterialia* 6, 3362–3378.
- Combes, C., Bareille, R., Rey, C., 2006. Calcium carbonate-calcium phosphate mixed cement compositions for bone reconstruction. *Journal of Biomedical Materials Research, Part A* 79, 318–328.
- Combes, C., Cazalbou, S., Rey, C., 2016. Apatite Biominerals. *Minerals* 6, 1–25.
- Constantz, B.R., 1995. Skeletal repair by in situ formation of the mineral phase of bone. *Science* 267, 1796–1798.
- Coulon, A., Laurencin, D., Grandjean, A., *et al.*, 2016. Key parameters for spark plasma sintering of wet-precipitated iodate-substituted hydroxyapatite. *Journal of the European Ceramic Society* 36, 2009–2016.
- Crane, N.J., Popescu, V., Morris, M.D., Steenhuis, P., Ignelzi, M.A., 2006. Raman spectroscopic evidence for octacalcium phosphate and other transient mineral species deposited during intramembranous mineralization. *Bone* 39, 434–442.
- Daculsi, G., Menanteau, J., Kerebel, L.M., Mitre, D., 1984. Length and shape of enamel crystals. *Calcified Tissue International* 36, 550–555.
- Daculsi, G., Laboux, O., Malard, O., Weiss, P., 2003. Current state of the art of biphasic calcium phosphate bioceramics. *Journal of Materials Science: Materials in Medicine* 14, 195–200.
- De Groot, K., Geesink, R., Klein, C., Serekian, P., 1987. Plasma sprayed coatings of hydroxylapatite. *Journal of Biomedical Materials Research* 21, 1375–1381.
- Delgado-Lopez, J.M., Iafisco, M., Rodriguez, I., *et al.*, 2012. Crystallization of bioinspired citrate-functionalized nanoapatite with tailored carbonate content. *Acta Biomaterialia* 8, 3491–3499.
- Descamps, M., Hornez, J.C., Leriche, A., 2009. Manufacture of hydroxyapatite beads for medical applications. *Journal of the European Ceramic Society* 29, 369–375.
- Destainville, A., Champion, E., Bernache-Assollant, D., Laborde, E., 2003. Synthesis, characterization and thermal behavior of apatitic tricalcium phosphate. *Materials Chemistry and Physics* 80, 269–277.
- Dickens, B., Schroeder, L.W., Brown, W.E., 1974. Crystallographic studies of the role of Mg as a stabilizing impurity in β -Ca₃(PO₄)₂. The crystal structure of pure β -Ca₃(PO₄)₂. *Journal of Solid State Chemistry* 10, 232–248.
- Doat, A., Fanjul, M., Pellé, F., Hollande, E., Lebugle, A., 2003. Europium-doped bioapatite: A new photostable biological probe, internalizable by human cells. *Biomaterials* 24, 3365–3371.
- Doi, Y., Iwanaga, H., Shibutani, T., Moriwaki, Y., Iwayama, Y., 1999. Osteoclastic responses to various calcium phosphates in cell cultures. *Journal of Biomedical Materials Research* 47, 424–433.
- Dong, J., Uemura, T., Shirasaki, Y., Tateishi, T., 2002. Promotion of bone formation using highly pure porous beta-TCP combined with bone marrow-derived osteoprogenitor cells. *Biomaterials* 23, 4493–4502.

- Dorozhkin, S.V., 2009. Nanodimensional and nanocrystalline apatites and other calcium orthophosphates in biomedical engineering, biology and medicine. *Materials* 2, 1975–2045.
- Drouet, C., 2013. Apatite formation: Why it may not work as planned, and how to conclusively identify apatite compounds. *BioMed Research International* 2013.490946
- Drouet, C., 2015. A comprehensive guide to experimental and predicted thermodynamic properties of phosphate apatite minerals in view of applicative purposes. *The Journal of Chemical Thermodynamics* 81, 143–159.
- Drouet, C., Largeot, C., Raimbeaux, G., *et al.*, 2006. Bioceramics: Spark plasma sintering (SPS) of calcium phosphates. *Advances in Science and Technology* 49, 45–50.
- Drouet, C., Al-Kattan, A., Choimet, M., *et al.*, 2015. Biomimetic apatite-based functional nanoparticles as promising newcomers in (nano)medicine: Overview of 10 years of initiatory research. *Journal of General Practice and Medical Diagnosis*. 1–9.
- Drouet, C., Leriche, A., Hampshire, S., *et al.*, 2017. Chapter 2 – Types of ceramics: material class. In: Palmero, P., Cambier, F., Barra, E. De (Eds.), *Advances in Ceramic Biomaterials*. Woodhead Publishing, pp. 21–82.
- Drouet, C., Aufray, M., Rollin-Martinet, S., *et al.*, 2018a. Nanocrystalline apatites: The fundamental role of water. *American Mineralogist* 103, 550–564.
- Drouet, C., Grossin, D., Combes, C., *et al.*, 2018b. Apatites biomimétiques Des biomimétiques aux analogues de synthèse pour le biomédical. *Techniques de l'Ingénieur*. IN227v1
- Duan, R., Barbieri, D., Luo, X., *et al.*, 2017. Variation of the bone forming ability with the physicochemical properties of calcium phosphate bone substitutes. *Biomaterials Science* 6, 136–145.
- Ducheyne, P., Radin, S., King, L., 1993. The effect of calcium phosphate ceramic composition and structure on in vitro behavior. I. Dissolution. *Journal of Biomedical Materials Research* 27, 25–34.
- Eanes, E.D., 1970. Thermochemical studies on amorphous calcium phosphate. *Calcified Tissue Research* 5, 133–145.
- Eanes, E.D., Meyer, J.L., 1977. The maturation of crystalline calcium phosphates in aqueous suspensions at physiologic pH. *Calcified Tissue Research* 23, 259–269.
- Ehara, A., Ogata, K., Imazato, S., *et al.*, 2003. Effects of alpha-TCP and TetCP on MC3T3-E1 proliferation, differentiation and mineralization. *Biomaterials* 24, 831–836.
- Eichert, D., Combes, C., Drouet, C., Rey, C., 2005. Formation and evolution of hydrated surface layers of apatites. *Key Engineering Materials* 284–286, 3–6.
- Ekhölm, M., Hietanen, J., Tulamo, R.M., *et al.*, 2006. The copolymer of epsilon-caprolactone-lactide and tricalcium phosphate does not enhance bone growth in mandibular defect of sheep. *Journal of Materials Science: Materials in Medicine* 17, 139–145.
- Elliott, J.C., 1994. *Structure and Chemistry of the Apatites and other Calcium Orthophosphates*. Amsterdam: Elsevier Science BV.
- Eppe, M., Ganesan, K., Heumann, R., *et al.*, 2010. Application of calcium phosphate nanoparticles in biomedicine. *Journal of Materials Chemistry* 20, 18–23.
- Famery, R., Richard, N., Boch, P., 1994. Preparation of α - and β -tricalcium phosphate ceramics, with and without magnesium addition. *Ceramics International* 20, 327–336.
- Fattibene, P., Callens, F., 2010. EPR dosimetry with tooth enamel: A review. *Applied Radiation and Isotopes* 68, 2033–2116.
- Fellah, B.H., Layrolle, P., 2009. Sol-gel synthesis and characterization of macroporous calcium phosphate bioceramics containing microporosity. *Acta Biomaterialia* 5, 735–742.
- Fowler, B.O., Kuroda, S., 1986. Changes in heated and in laser-irradiated human tooth enamel and their probable effects on solubility. *Calcified Tissue International* 38, 197–208.
- Fowler, B.O., Markovic, M., Brown, W.E., 1993. Octacalcium phosphate. 3. Infrared and Raman vibrational spectra. *Chemistry of Materials* 5, 1417–1423.
- Galea, L., Bohner, M., Thuering, J., *et al.*, 2014. Growth kinetics of hexagonal sub-micrometric beta-tricalcium phosphate particles in ethylene glycol. *Acta Biomaterialia* 10, 3922–3930.
- Gallinetti, S., Canal, C., Ginebra, M.P., Ferreira, J., 2014. Development and characterization of biphasic hydroxyapatite/beta-TCP cements. *Journal of the American Ceramic Society* 97, 1065–1073.
- Gallo, M., Le Gars Santoni, B., Douillard, T., *et al.*, 2019. Effect of grain orientation and magnesium doping on β -tricalcium phosphate resorption behavior. *Acta Biomaterialia* 89, 391–402.
- Galois, L., Mainard, D., 2004. Bone ingrowth into two porous ceramics with different pore sizes: An experimental study. *Acta Orthopaedica Belgica* 70, 598–603.
- Ginebra, M.P., 1997. Setting reaction and hardening of apatitic calcium phosphate cement. *Journal of Dental Research* 76, 905–912.
- Gomez-Morales, J., Lafisco, M., Delgado-Lopez, J.M., Sarda, S., Drouet, C., 2013. Progress on the preparation of nanocrystalline apatites and surface characterization: Overview of fundamental and applied aspects. *Progress in Crystal Growth and Characterization of Materials* 59, 1–46.
- Gómez-Morales, J., Verdugo-Escamilla, C., Fernández-Penas, R., *et al.*, 2018. Luminescent biomimetic citrate-coated europium-doped carbonated apatite nanoparticles for use in bioimaging: Physico-chemistry and cytocompatibility. *RSC Advances* 8, 2385–2397.
- Gonzalez-McQuire, R., Green, D., Walsh, D., *et al.*, 2005. Fabrication of hydroxyapatite sponges by dextran sulphate/amino acid templating. *Biomaterials* 26, 6652–6656.
- Greenfield, D.J., Eanes, E.D., 1972. Formation chemistry of amorphous calcium phosphates prepared from carbonate containing solutions. *Calcified Tissue Research* 9, 152–162.
- Gregory, T.M., Moreno, E.C., Patel, J.M., Brown, W.E., 1974. Solubility of beta-Ca₃(PO₄)₂ in the system Ca(OH)₂-H₃PO₄-H₂O at 5, 15, 25 and 37°C. *Journal of Research of the National Bureau of Standards* 78A, 667–674.
- Grossin, D., Rollin-Martinet, S., Estournès, C., *et al.*, 2010. Biomimetic apatite sintered at very low temperature by spark plasma sintering: Physico-chemistry and microstructure aspects. *Acta Biomaterialia* 6, 577–585.
- Grunenwald, A., Keyser, C., Sautereau, A.M., *et al.*, 2014a. Revisiting carbonate quantification in apatite (bio)minerals: A validated FTIR methodology. *Journal of Archaeological Science* 49, 134–141.
- Grunenwald, A., Keyser, C., Sautereau, A.M., *et al.*, 2014b. Adsorption of DNA on biomimetic apatites: Toward the understanding of the role of bone and tooth mineral on the preservation of ancient DNA. *Applied Surface Science* 292, 867–875.
- Guo, Y., Shi, D., Lian, J., *et al.*, 2008. Quantum dot conjugated hydroxylapatite nanoparticles for in vivo imaging. *Nanotechnology* 19, 175102.
- Heughebaert, J.-C., Montel, G., 1982. Conversion of amorphous tricalcium phosphate into apatitic tricalcium phosphate. *Calcified Tissue International* 34, 103–108.
- Heughebaert, J.C., 1977. Contribution à l'étude de l'évolution des orthophosphates de calcium précipités amorphes en orthophosphates apatitiques.
- Holt, C., Van Kemenade, M.J.J.M., Nelson, L.S., *et al.*, 1989. Amorphous calcium phosphates prepared at pH 6.5 and 6.0. *Materials Research Bulletin* 24, 55–62.
- Horch, H.H., Sader, R., Pautke, C., *et al.*, 2006. Synthetic, pure-phase beta-tricalcium phosphate ceramic granules (Cerasorb) for bone regeneration in the reconstructive surgery of the jaws. *International Journal of Oral and Maxillofacial Surgery* 35, 708–713.
- Huffman, E.W.D., 1977. Performance of a new automatic carbon dioxide coulometer. *Microchemical Journal* 22, 567–573.
- lafisco, M., Varoni, E., Di Foggia, M., *et al.*, 2012. Conjugation of hydroxyapatite nanocrystals with human immunoglobulin G for nanomedical applications. *Colloids and Surfaces B: Biointerfaces* 90, 1–7.
- lafisco, M., Drouet, C., Adamiano, A., *et al.*, 2016. Superparamagnetic iron-doped nanocrystalline apatite as a delivery system for doxorubicin. *Journal of Materials Chemistry B* 4, 57–70.
- Ikeuchi, M., Ito, A., Dohi, Y., *et al.*, 2003. Osteogenic differentiation of cultured rat and human bone marrow cells on the surface of zinc-releasing calcium phosphate ceramics. *Journal of Biomedical Materials Research Part A* 67, 1115–1122.
- Ito, A., Kawamura, H., Miyakawa, S., *et al.*, 2002. Resorbability and solubility of zinc-containing tricalcium phosphate. *Journal of Biomedical Materials Research* 60, 224–231.
- Ito, A., Otsuka, M., Kawamura, H., *et al.*, 2005. Zinc-containing tricalcium phosphate and related materials for promoting bone formation. *Current Applied Physics* 5, 402–406.
- Ito, A., Ojima, K., Naito, H., Ichinose, N., Tateishi, T., 2000. Preparation, solubility and cytocompatibility of zinc-releasing calcium phosphates ceramics. *Journal of Biomedical Materials Research* 50, 178–183.
- Ito, A., Kamo, M., Ichinose, N., Sogo, Y., Sakurai, T., 2001. Fabrication and in-vitro biocompatibility of zinc-containing α -tricalcium phosphate. *Key Engineering Materials* 218–220, 183–186.

- Itoh, S., Kikuchi, M., Takakuda, K., *et al.*, 2000. The biocompatibility and osteoconductive activity of a novel hydroxyapatite/collagen composite biomaterial, and its function as a carrier of rhBMP-2. *Journal of Biomedical Materials Research* 54, 445–453.
- Itoh, S., Kikuchi, M., Takakuda, K., *et al.*, 2002. Implantation study of a novel hydroxyapatite/collagen (Hap/col) composite into weight bearing sites of dogs. *Journal of Biomedical Materials Research* 63, 507–515.
- Jäger, C., Welzel, T., Meyer-Zaika, W., Epple, M., 2006. A solid-state NMR investigation of the structure of nanocrystalline hydroxyapatite. *Magnetic Resonance in Chemistry* 44, 573–580.
- Jallot, E., Moretto, P., 2006. Characterisation, by the PIXE method, of trace elements during physicochemical reactions at the periphery of bioactive glass pastilles in contact with biological fluids. *Instrumentation Science and Technology* 34, 405–416.
- Jarcho, M., 1986. Biomaterial aspects of calcium phosphates. Properties and applications. *Dental Clinics of North America* 30, 25–47.
- Jarcho, M., Salsbury, R.L., Thomas, M.B., Doremus, R.H., 1979. Synthesis and fabrication of beta-tricalcium phosphate (Whitlockite) ceramics for potential prosthetic applications. *Journal of Materials Science* 14, 142–150.
- Jensen, J., Kraft, D.C., Lysdahl, H., *et al.*, 2015. Functionalization of polycaprolactone scaffolds with hyaluronic acid and beta-TCP facilitates migration and osteogenic differentiation of human dental pulp stem cells in vitro. *Tissue Engineering Part A* 21, 729–739.
- Jiang, T., Guo, L., Ni, S., Zhao, Y., 2015. Upregulation of cell proliferation via Shc and ERK1/2 MAPK signaling in SaOS-2 osteoblasts grown on magnesium alloy surface coating with tricalcium phosphate. *Journal of Materials Science: Materials in Medicine* 26, 158.
- Josse, S., Fauchoux, C., Soueidan, A., *et al.*, 2005. Novel biomaterials for bisphosphonate delivery. *Biomaterials* 26, 2073–2080.
- Karageorgiou, V., Kaplan, D., 2005. Porosity of 3D biomaterial scaffolds and osteogenesis. *Biomaterials* 26, 5474–5491.
- Kasten, P., Vogel, J., Luginbuhl, R., *et al.*, 2005. Ectopic bone formation associated with mesenchymal stem cells in a resorbable calcium deficient hydroxyapatite carrier. *Biomaterials* 26, 5879–5889.
- Kay, M.I., Young, R.A., Posner, A.S., 1964. Crystal structure of hydroxyapatite. *Nature* 204, 1050–1052.
- Kergourlay, E., Grossin, D., Cinca, N., *et al.*, 2016. First cold spraying of carbonated biomimetic nanocrystalline apatite on Ti₆Al₄V: Physical–chemical, microstructural, and preliminary mechanical characterizations. *Advanced Engineering Materials* 18, 496–500.
- Khalil, K.A., Kim, H.Y., Kim, S.W., Kim, K.W., 2007. Observation of toughness improvement of the hydroxyapatite bioceramics densified using high-frequency induction heat sintering. *International Journal of Applied Ceramic Technology* 4, 30–37.
- Kihara, H., Shiota, M., Yamashita, Y., Kasugai, S., 2006. Biodegradation process of alpha-TCP particles and new bone formation in a rabbit cranial defect model. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 79, 284–291.
- Kikuchi, M., Ikoma, T., Itoh, S., *et al.*, 2004a. Biomimetic synthesis of bone-like nanocomposites using the selforganization mechanism of hydroxyapatite and collagen. *Composites Science and Technology* 64, 819–825.
- Kikuchi, M., Koyama, Y., Yamada, T., *et al.*, 2004b. Development of guided bone regeneration membrane composed of beta-tricalcium phosphate and poly (L-lactide-co-glycolide-co-epsilon-caprolactone) composites. *Biomaterials* 25, 5979–5986.
- Kim, H.M., Kim, Y.S., Woo, K.M., *et al.*, 2001. Dissolution of poorly crystalline apatite crystals by osteoclasts determined on artificial thin-film apatite. *Journal of Biomedical Materials Research* 56, 250–256.
- Kim, H.W., Knowles, J.C., Kim, H.E., 2005. Porous scaffolds of gelatin-hydroxyapatite nanocomposites obtained by biomimetic approach: Characterization and antibiotic drug release. *Journal of Biomedical Materials Research* 74B, 686–698.
- Kim, W.J., Yun, H.-S., Kim, G.H., 2017. An innovative cell-laden α -TCP/collagen scaffold fabricated using a two-step printing process for potential application in regenerating hard tissues. *Scientific Reports* 7, 3181.
- Kitamura, M., Ohtsuki, C., Iwasaki, H., *et al.*, 2004. The controlled resorption of porous alpha-tricalcium phosphate using a hydroxypropylcellulose coating. *Journal of Materials Science: Materials in Medicine* 15, 1153–1158.
- Knaack, D., 1998. Resorbable calcium phosphate bone substitute. *Journal of Biomedical Material Research* 43, 399–409.
- Kobayashi, S., Kawai, W., Wakayama, S., 2006. The effect of pressure during sintering on the strength and the fracture toughness of hydroxyapatite ceramics. *Journal of Materials Science: Materials in Medicine* 17, 1089–1093.
- Kon, E., Delcogliano, M., Filardo, G., *et al.*, 2010. Orderly osteochondral regeneration in a sheep model using a novel nano-composite multilayered biomaterial. *Journal of Orthopaedic Research* 28, 116–124.
- Kong, L., Gao, Y., Cao, W., *et al.*, 2005. Preparation and characterization of nano-hydroxyapatite/chitosan composite scaffolds. *Journal of Biomedical Materials Research Part A* 75, 275–282.
- Landi, E., Tampieri, A., Mattioli-Belmonte, M., *et al.*, 2006. Biomimetic Mg- and MgCO₃-substituted hydroxyapatites: Synthesis characterization and in vitro behaviour. *Journal of the European Ceramic Society* 26, 2593–2601.
- Lapczyna, H., Galea, L., Wust, S., *et al.*, 2014. Effect of grain size and microporosity on the in vivo behaviour of beta-tricalcium phosphate scaffolds. *European Cells & Materials* 28, 299–319.
- Laschke, M.W., Witt, K., Pohlemann, T., Menger, M.D., 2007. Injectable nanocrystalline hydroxyapatite paste for bone substitution: In vivo analysis of biocompatibility and vascularization. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 82, 494–505.
- Laurencin, D., Wong, A., Chrzanowski, W., *et al.*, 2010. Probing the calcium and sodium local environment in bones and teeth using multinuclear solid state NMR and X-ray absorption spectroscopy. *Physical Chemistry Chemical Physics* 12, 1081–1091.
- Le Huec, J.C., Lespriet, E., Delavigne, C., *et al.*, 1997. Tri-calcium phosphate ceramics and allografts as bone substitutes for spinal fusion in idiopathic scoliosis as bone substitutes for spinal fusion in idiopathic scoliosis: Comparative clinical results at four years. *Acta Orthopaedica Belgica* 63, 202–211.
- Lebugle, A., Zahidi, E., Bonel, G., 1986. Effect of structure and composition on the thermal decomposition of calcium phosphates (Ca/P = 1.33). *Reactivity of Solids* 2, 151–161.
- LeGeros, R.Z., 1991. Calcium Phosphates in Oral biology and medicine. *Monographs in Oral Science* 15, 1–201.
- LeGeros, R.Z., 1994. Biological and synthetic apatites. In: Brown, O.W., Constantz, B. (Eds.), *Hydroxyapatite and Related Materials* 3. Boca Raton: CRC Press.
- LeGeros, R.Z., 2008. Calcium phosphate-based osteoinductive materials. *Chemical Reviews* 108, 4742–4753.
- LeGeros, R.Z., Mijares, D.Q., Park, J., *et al.*, 2005. Amorphous calcium phosphates (ACP): Formation and stability. *Key Engineering Materials* 284–286, 7–10.
- LeGeros, R.Z., Lin, S., Rohanizadeh, R., Mijares, D., LeGeros, J.P., 2003. Biphasic calcium phosphate bioceramics: Preparation, properties and applications. *Journal of Materials Science: Materials in Medicine* 14, 201–209.
- Li, B., Chen, X., Guo, B., *et al.*, 2009a. Fabrication and cellular biocompatibility of porous carbonated biphasic calcium phosphate ceramics with a nanostructure. *Acta Biomaterialia* 5, 134–143.
- Li, X., Ito, A., Sogo, Y., Wang, X., LeGeros, R.Z., 2009b. Solubility of Mg-containing beta-tricalcium phosphate at 25°C. *Acta Biomaterialia* 5, 508–517.
- Lim, H.P., Park, S.W., Yun, K.D., *et al.*, 2018. Novel beta-TCP coated titanium nanofiber surface for enhanced bone growth. *Journal of Nanoscience and Nanotechnology* 18, 853–855.
- Lin, M., Overgaard, S., Glerup, H., Soballe, K., Bunger, C., 2001. Transforming growth factor-beta1 adsorbed to tricalciumphosphate coated implants increases peri-implant bone remodeling. *Biomaterials* 22, 189–193.
- Liu, D.-M., 1997. Fabrication of hydroxyapatite ceramic with controlled porosity. *Journal of Materials Science: Materials in Medicine* 8, 227–232.
- Loong, C.K., Rey, C., Kuhn, L.T., *et al.*, 2000. Evidence of hydroxyl-ion deficiency in bone apatites: An inelastic neutron-scattering study. *Bone* 26, 599–602.

- Lu, H.B., Campbell, C.T., Graham, D.J., Ratner, B.D., 2000. Surface characterization of hydroxyapatite and related calcium phosphates by XPS and TOF-SIMS. *Analytical Chemistry* 72, 2886–2894.
- Lu, J.X., Flautre, B., Anselme, K., *et al.*, 1999. Role of interconnections in porous bioceramics on bone recolonization in vitro and in vivo. *Journal of Materials Science: Materials in Medicine* 10, 111–120.
- Luginbuehl, V., Wenk, E., Koch, A., *et al.*, 2005. Insulin-like growth factor I-releasing alginate-tricalciumphosphate composites for bone regeneration. *Pharmaceutical Research* 22, 940–950.
- Mackay, A.L., 1953. A preliminary examination of the structure of α - $\text{Ca}_3(\text{PO}_4)_2$. *Acta Crystallographica* 6, 743–744.
- Markovic, S., Veselinovic, L., Lukic, M.J., *et al.*, 2011. Synthetical bone-like and biological hydroxyapatites: A comparative study of crystal structure and morphology. *Biomedical Materials* 6.045005.
- Mastrogiovanni, M., Scaglione, S., Martinetti, R., *et al.*, 2006. Role of scaffold internal structure on in vivo bone formation in macroporous calcium phosphate bioceramics. *Biomaterials* 27, 3230–3237.
- Mathew, M., Schroeder, L.W., Dickens, B., Brown, W.E., 1977. The crystal structure of α - $\text{Ca}_3(\text{PO}_4)_2$. *Acta Crystallographica B* 33, 1325–1333.
- Matsuno, T., Nakamura, T., Kuremoto, K., *et al.*, 2006. Development of beta-tricalcium phosphate/collagen sponge composite for bone regeneration. *Dental Materials Journal* 25, 138–144.
- McElderry, J.-D.P., Zhu, P., Mroue, K.H., *et al.*, 2013. Crystallinity and compositional changes in carbonated apatites: Evidence from ^{31}P solid-state NMR, Raman, and AFM analysis. *Journal of Solid State Chemistry* 206, 192–198.
- Meshkini, A., Oveisi, H., 2017. Methotrexate-F127 conjugated mesoporous zinc hydroxyapatite as an efficient drug delivery system for overcoming chemotherapy resistance in osteosarcoma cells. *Colloids Surf B Biointerfaces* 158, 319–330.
- Mestres, G., Le Van, C., Ginebra, M.P., 2012. Silicon-stabilized alpha-tricalcium phosphate and its use in a calcium phosphate cement: Characterization and cell response. *Acta Biomaterialia* 8, 1169–1179.
- Metsger, D.S., Driskell, T.D., Paulsrud, J.R., 1982. Tricalcium phosphate ceramic – A resorbable bone implants – Review and current state. *Journal of the American Dental Association* 105, 1035–1038.
- Meurice, E., Leriche, A., Hornez, J.-C., *et al.*, 2012. Functionalisation of porous hydroxyapatite for bone substitutes. *Journal of the European Ceramic Society* 32, 2673–2678.
- Miller, L.M., Vairavamurthy, V., Chance, M.R., *et al.*, 2001. In situ analysis of mineral content and crystallinity in bone using infrared micro-spectroscopy of the $\nu(4)$ PO_4 -vibration. *Biochimica Et Biophysica Acta-General Subjects* 1527, 11–19.
- Monchau, F., Lefèvre, A., Descamps, M., *et al.*, 2002. In vitro studies of human and rat osteoclast activity on hydroxyapatite, β -tricalcium phosphate, calcium carbonate. *Biomolecular Engineering* 19, 143–152.
- Mondejar, S.P., Kovtun, A., Eppe, M., 2007. Lanthanide-doped calcium phosphate nanoparticles with high internal crystallinity and with a shell of DNA as fluorescent probes in cell experiments. *Journal of Materials Chemistry* 17, 4153–4159.
- Monma, H., 1980. Preparation of octacalcium phosphate by the hydrolysis of α -tricalcium phosphate. *Journal of Materials Science* 15, 2428–2434.
- Monma, H., Ueno, S., Kanazawa, T., 1981. Properties of hydroxyapatite prepared by the hydrolysis of tricalcium phosphate. *Journal of Chemical Technology and Biotechnology* 31, 15–24.
- Morgan, T.T., Muddana, H.S., Altinoglu, E.I., *et al.*, 2008. Encapsulation of organic molecules in calcium phosphate nanocomposite particles for intracellular imaging and drug delivery. *Nano Letters* 8, 4108–4115.
- Motisque, M., Mestres, G., Renó, C.O., *et al.*, 2017. Influence of Si substitution on the reactivity of α -tricalcium phosphate. *Materials Science and Engineering: C* 75, 816–821.
- Nakagawa, N., Saegusa, Y., Abe, S., Miura, Y., Yoshiya, S., 2006. The effectiveness of RA wrist fusion using Beta-TCP without autogenous iliac bone grafting: a report of four cases. *The Journal of Hand Surgery* 11, 71–75.
- Neo, M., Herbst, H., Voigt, C.F., Gross, U.M., 1998. Temporal and spatial patterns of osteoblast activation following implantation of beta-TCP particles into bone. *Journal of Biomedical Materials Research* 39, 71–76.
- Nery, E.B., Lynch, K.L., Hirthe, W.M., Mueller, K.H., 1975. Bioceramic implants in surgically produced infrabony defects. *Journal of periodontology* 46, 328–347.
- Niemeyer, P., Krause, U., Fellenberg, J., *et al.*, 2004. Evaluation of mineralized collagen and alpha-tricalcium phosphate as scaffolds for tissue engineering of bone using human mesenchymal stem cells. *Cells Tissues Organs* 177, 68–78.
- Obadia, L., Julien, M., Quillard, S., *et al.*, 2011. Na-doped beta-tricalcium phosphate: Physico-chemical and in vitro biological properties. *Journal of Materials Science: Materials in Medicine* 22, 593–600.
- Ogose, A., Hotta, T., Kawashima, H., *et al.*, 2005. Comparison of hydroxyapatite and beta tricalcium phosphate as bone substitutes after excision of bone tumors. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 72, 94–101.
- Ohta, K., Monma, H., Tkahashi, S., 2001. Adsorption characteristics of proteins on calcium phosphates using liquid chromatography. *Journal of Biomedical Materials Research* 55, 409–414.
- Onuma, K., Ito, A., Tateishi, T., Kameyama, T., 1995. Growth kinetics of hydroxyapatite crystal revealed by atomic force microscopy. *Journal of Crystal Growth* 154, 118–125.
- Ortali, C., Julien, I., Vandenheide, M., Drouet, C., Champion, E., 2018. Consolidation of bone-like apatite bioceramics by spark plasma sintering of amorphous carbonated calcium phosphate at very low temperature. *Journal of the European Ceramic Society* 38, 2098–2109.
- Pang, D., He, L., Wei, L., Zheng, H., Deng, C., 2018. Preparation of a beta-tricalcium phosphate nanocoating and its protein adsorption behaviour by quartz crystal microbalance with dissipation technique. *Colloids and Surfaces B: Biointerfaces* 162, 1–7.
- Park, J.-H., Bae, J.-Y., Shim, J., Jeon, I., 2012. Evaluation of suitable porosity for sintered porous β -tricalcium phosphate as a bone substitute. *Materials Characterization* 71, 103–111.
- Paschalis, E.P., Mendelsohn, R., Boskey, A.L., 2011. Infrared assessment of bone quality: A review. *Clinical Orthopaedics and Related Research* 469, 2170–2178.
- Pioletti, D.P., Takei, H., Lin, T., *et al.*, 2000. The effects of calcium phosphate cement particles on osteoblast functions. *Biomaterials* 21, 1103–1114.
- Posner, A.S., Beebe, R.A., 1975. The surface chemistry of bone mineral and related calcium phosphates. *Seminars in Arthritis and Rheumatism* 4, 267–291.
- Pujari-Palmer, S., Chen, S., Rubino, S., *et al.*, 2016. In vivo and in vitro evaluation of hydroxyapatite nanoparticle morphology on the acute inflammatory response. *Biomaterials* 90, 1–11.
- Ramírez Rodríguez, G.B., Delgado López, J.M., Iafisco, M., *et al.*, 2016. Biomimetic mineralization of synthetic collagen-like peptide: A bottom-up approach to design advanced nanocomposite scaffolds for tissue engineering. *Frontiers in Bioengineering and Biotechnology*. doi:10.3389/fbioe.2016.01.02747.
- Ranz, X., 1996. Développement et caractérisation de dépôts d'apatite obtenus par projection plasma sur prothèses orthopédiques. PhD thesis. Toulouse, France: Institut National Polytechnique de Toulouse.
- Raynaud, S., Champion, E., Bernache-Assollant, D., Thomas, P., 2002. Calcium phosphate apatites with variable Ca/P atomic ratio I. Synthesis, characterisation and thermal stability of powders. *Biomaterials* 23, 1065–1072.
- von Rechenberg, B., Genot, O.R., Nuss, K., *et al.*, 2013. Evaluation of four biodegradable, injectable bone cements in an experimental drill hole model in sheep. *European Journal of Pharmaceutics and Biopharmaceutics* 85, 130–138.
- Redey, S.A., Razzouk, S., Rey, C., *et al.*, 1999. Osteoclast adhesion and activity on synthetic hydroxyapatite, carbonated hydroxyapatite and natural calcium carbonate: Relationship to surface energies. *The Journal of Bone and Mineral Research* 45, 140–147.
- Reid, J.W., Tuck, L., Sayer, M., Fargo, K., Hendry, J.A., 2006. Synthesis and characterization of single-phase silicon-substituted α -tricalcium phosphate. *Biomaterials* 27, 2916–2925.
- Ren, X., Tuo, Q., Tian, K., *et al.*, 2018. Enhancement of osteogenesis using a novel porous hydroxyapatite scaffold in vivo and vitro. *Ceramics International* 44, 21656–21665.

- Rey, C., Lian, J., Grynpas, M., *et al.*, 1989b. Non-apatitic environments in bone mineral: FT-IR detection, biological properties and changes in several disease states. *Connective Tissue Research* 21, 267–273.
- Rey, C., Combes, C., Drouet, C., *et al.*, 2014. Surface properties of biomimetic nanocrystalline apatites; applications in biomaterials. *Progress in Crystal Growth and Characterization of Materials* 60, 63–73.
- Rey, C., Marsan, O., Combes, C., *et al.*, 2014c. Characterization of calcium phosphates using vibrational spectroscopies. In: Ben-Nissan, B. (Ed.), *Advances in Calcium Phosphate Biomaterials*. London: Springer, pp. 229–266.
- Rey, C., Collins, B., Goehl, T., Glimcher, M.J., 1989a. The carbonate environment in bone mineral. A resolution-enhanced fourier transform infrared spectroscopy study. *Calcified Tissue International* 45, 157–164.
- Rey, C., Shimizu, M., Collins, B., Glimcher, M.J., 1990. Resolution-enhanced Fourier transform infrared spectroscopy study of the environment of phosphate ions in the early deposits of a solid phase of calcium phosphate in bone and enamel, and their evolution with age. I: Investigations in the ν_4 PO_4 domain. *Calcified Tissue International* 46, 384–394.
- Rey, C., Renugopalakrishnan, V., Collins, B., Glimcher, M.J., 1991a. Fourier transform infrared spectroscopic study of the carbonate ions in bone mineral during aging. *Calcified Tissue International* 49, 251–258.
- Rey, C., Shimizu, M., Collins, B., Glimcher, M.J., 1991c. Resolution-enhanced fourier-transform infrared-spectroscopy study of the environment of phosphate ion in the early deposits of a solid-phase of calcium-phosphate in bone and enamel and their evolution with age. 2. Investigations in the ν_3 PO_4 domain. *Calcified tissue international* 49, 383–388.
- Rey, C., Combes, C., Drouet, C., Somrani, S., 2008. Chapter 15 – Tricalcium phosphate based ceramics. In: Kokubo, T. (Ed.), *Bioceramics and their Clinical Applications*. CRC & Woodhead Publishing Limited, pp. 326–366.
- Rey, C., Combes, C., Drouet, C., Grossin, D., 2011. Bioactive ceramics: Physical Chemistry. In *Comprehensive Biomaterials*. Elsevier. pp. 187–221.
- Rey, C., Renugopalakrishnan, V., Shimizu, M., Collins, B., Glimcher, M.J., 1991b. A resolution-enhanced Fourier Transform Infrared spectroscopic study of the environment of the CO_3^{2-} ion in the mineral phase of enamel during its formation and maturation. *Calcified Tissue International* 49, 259–268.
- Rey, C., Combes, C., Drouet, C., Stihl, H., Barroug, A., 2007. Physico-chemical properties of nanocrystalline apatites: implications for biominerals and biomaterials. *Materials Science and Engineering C* 27, 198–205.
- Robinson, C., Connell, S., Brookes, S.J., *et al.*, 2005. Surface chemistry of enamel apatite during maturation in relation to pH: Implications for protein removal and crystal growth. *Archives of Oral Biology* 50, 267–270.
- Rodrigues, A., Lebugle, A., 1998. Influence of ethanol in the precipitation medium on the composition, structure and reactivity of tricalcium phosphate. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 145, 191–204.
- Rollin-Martinet, S., Navrotsky, A., Champion, E., Grossin, D., Drouet, C., 2013. Thermodynamic basis for evolution of apatite in calcified tissues. *The American Mineralogist*.
- Rosa, A.L., Beloti, M.M., Van Noort, R., Hatton, P.V., Devlin, A.J., 2002. Surface topography of hydroxyapatite affects ROS17/2.8 cells response. *Pesquisa Odontologica Brasileira* 16, 209–215.
- Roufosse, A.H., Aue, W.P., Roberts, J.E., Glimcher, M.J., Griffin, R.G., 1984. Investigation of the mineral phases of bone by solid-state phosphorus-31 magic angle sample spinning nuclear magnetic resonance. *Biochemistry* 23, 6115–6120.
- Rovira, A., Bareille, R., Lopez, I., *et al.*, 1993. Preliminary report on a new composite materials made of calcium phosphate, elastin peptides and collagens. *Journal of Materials Science-Materials in Medicine* 4, 372–380.
- Ryu, H.S., Hong, K.S., Lee, J.K., *et al.*, 2004. Magnesia-doped HA/ β -TCP ceramics and evaluation of their biocompatibility. *Biomaterials* 25, 393–401.
- Ryu, H.-S., Youn, H.-J., Sun Hong, K., *et al.*, 2002. An improvement in sintering property of β -tricalcium phosphate by addition of calcium pyrophosphate. *Biomaterials* 23, 909–914.
- Sadowska, J.-M., Guillem-Marti, J., Montufar, E.B., Espanol, M., Ginebra, M.-P., 2017. Biomimetic versus sintered calcium phosphates: The in vitro behavior of osteoblasts and mesenchymal stem cells. *Tissue Engineering Part A* 23, 1297–1309.
- Saffarzadeh, A., Gauthier, O., Bilban, M., Bagot D'Arc, M., Daculsi, G., 2009. Comparison of two bone substitute biomaterials consisting of a mixture of fibrin sealant (Tisseel) and MBCP (TricOs) with an autograft in sinus lift surgery in sheep. *Clinical Oral Implants Research* 20, 1133–1139.
- Sakae, T., Nakada, H., LeGeros, J.P., 2015. Historical review of biological apatite crystallography. *Journal of Hard Tissue Biology* 24, 111–122.
- dos Santos, E.A., Farina, M., Soares, G.A., Anselme, K., 2008. Surface energy of hydroxyapatite and beta-tricalcium phosphate ceramics driving serum protein adsorption and osteoblast adhesion. *Journal of Materials Science: Materials in Medicine* 19, 2307–2316.
- dos Santos, E.A., Farina, M., Soares, G.A., Anselme, K., 2009. Chemical and topographical influence of hydroxyapatite and beta-tricalcium phosphate surfaces on human osteoblastic cell behavior. *Journal of Biomedical Materials Research Part A* 89, 510–520.
- Sarda, S., Iafisco, M., Pascaud-Mathieu, P., *et al.*, 2018. Interaction of folic acid with nanocrystalline apatites and extension to methotrexate (antifolate) in view of anticancer applications. *Langmuir* 34, 12036–12048.
- Sarda, S., Tofighi, A., Hobatho, M.C., Lee, D., Rey, C., 1999. Associations of low temperature apatite ceramics and proteins. *Phosphorus Research Bulletin* 10, 208–213.
- Sayer, M., Stratilatov, A.D., Reid, J., *et al.*, 2003. Structure and composition of silicon-stabilized tricalcium phosphate. *Biomaterials* 24, 369–382.
- Schardosim, M., Soulie, J., Poquillon, D., *et al.*, 2017. Freeze-casting for PLGA/carbonated apatite composite scaffolds: Structure and properties. *Materials Science and Engineering C: Materials for Biological Applications* 77, 731–738.
- Sedlak, J.M., Beebe, R.A., 1974. Temperature programmed dehydration of amorphous calcium phosphate. *Journal of Colloid and Interface Science* 47, 483–489.
- Stihl, H., Rey, C., 2002. 1-D and 2-D double heteronuclear magnetic resonance study of the local structure of type B carbonate fluoroapatite. In: Fraissard, J., Lapina, O. (Eds.), *Magnetic Resonance in Colloid and Interface Science*. Kluwer Academic Publishers, pp. 409–418.
- Singh, S.S., Roy, A., Lee, B.E., Banerjee, I., Kumta, P.N., 2014. MC3T3-E1 proliferation and differentiation on biphasic mixtures of Mg substituted beta-tricalcium phosphate and amorphous calcium phosphate. *Materials Science & Engineering C-Materials for Biological Applications* 45, 589–598.
- Somrani, S., Rey, C., Jemal, M., 2003. Thermal evolution of amorphous tricalcium phosphate. *Journal of Materials Chemistry* 13, 888–892.
- Somrani, S., Banu, M., Jemal, M., Rey, C., 2005. Physico-chemical and thermochemical studies of the hydrolytic conversion of amorphous tricalcium phosphate into apatite. *Journal of Solid State Chemistry* 178, 1337–1348.
- Sopyan, I., Mel, M., Ramesh, S., Khalid, K.A., 2007. Porous hydroxyapatite for artificial bone applications. *Science and Technology of Advanced Materials* 8, 116–123.
- Sous, M., Bareille, R., Rouais, F., *et al.*, 1998. Cellular biocompatibility and resistance to compression of macroporous β -tricalcium phosphate ceramics. *Biomaterials* 19, 2147–2153.
- Stefanic, M., Milacic, R., Drazic, G., *et al.*, 2014. Synthesis of bioactive beta-TCP coatings with tailored physico-chemical properties on zirconia bioceramics. *Journal of Materials Science: Materials in Medicine* 25, 2333–2345.
- Stefanic, M., Ward, K., Tawfik, H., *et al.*, 2017. Apatite nanoparticles strongly improve red blood cell cryopreservation by mediating trehalose delivery via enhanced membrane permeation. *Biomaterials* 140, 138–149.
- Struillou, X., Boutigny, H., Badran, Z., *et al.*, 2011. Treatment of periodontal defects in dogs using an injectable composite hydrogel/biphasic calcium phosphate. *Journal of Materials Science: Materials in Medicine* 22, 1707–1717.
- Suchanek, W., Yoshimura, M., 1998. Processing and properties of hydroxyapatite-based biomaterials for use as hard tissue replacement implants. *Journal of Materials Research* 13, 94–117.
- Sun, J.S., Tsuang, Y.H., Liao, C.J., *et al.*, 1997. The effects of calcium phosphate particles on the growth of osteoblasts. *Journal of Biomedical Materials Research* 37, 324–334.

- Sun, L.M., Berndt, C.C., Gross, K.A., Kucuk, A., 2001. Material fundamentals and clinical performance of plasma-sprayed hydroxyapatite coatings: A review. *Journal of Biomedical Materials Research* 58, 570–592.
- Szabo, G., Huys, L., Coulthard, P., *et al.*, 2005. A prospective multicenter randomized clinical trial of autogenous bone versus beta-tricalcium phosphate graft alone for bilateral sinus elevation: Histologic and histomorphometric evaluation. *The International Journal of Oral & Maxillofacial Implants* 20, 371–381.
- Takadama, H., Kim, H.-M., Kokubo, T., Nakamura, T., 2001. XPS study of the process of apatite formation on bioactive Ti–6Al–4V alloy in simulated body fluid. *Science and Technology of Advanced Materials* 2, 389–396.
- Tampieri, A., Celotti, G., Landi, E., *et al.*, 2003. Biologically inspired synthesis of bone-like composite: Self-assembled collagen fibers/hydroxyapatite nanocrystals. *Journal of Biomedical Materials Research* 67, 618–625.
- Tampieri, A., Sprio, S., Sandri, M., Valentini, F., 2011. Mimicking natural bio-mineralization processes: A new tool for osteochondral scaffold development. *Trends in Biotechnology* 29, 526–535.
- Tancr t, F., Boulter, J.M., Chamouss t, J., Minois, L.M., 2006. Modelling the mechanical properties of microporous and macroporous biphasic calcium phosphate bioceramics. *Journal of the European Ceramic Society* 26, 3647–3656.
- Tang, R., Wu, W., Haas, M., Nancollas, G., 2001. Kinetics of dissolution of beta-tricalcium phosphate. *Langmuir* 17, 3480–3485.
- Theiss, F., Apelt, D., Brand, B.A., *et al.*, 2005. Biocompatibility and resorption of a brushite calcium phosphate cement. *Biomaterials* 26, 4383–4394.
- Treboux, G., Layrolle, P., Kanzaki, N., Onuma, K., Ito, A., 2000. Existence of Posner's cluster in vacuum. *The Journal of Physical Chemistry A* 104, 5111–5114.
- Trombe, J.C., Montel, G., 1978. Some features of the incorporation of oxygen in different oxidation state in the apatitic lattice-1 on the existence of calcium and strontium oxyapatites. *Journal of Inorganic and Nuclear Chemistry* 40, 15–21.
- Tsukanaka, M., Fujibayashi, S., Otsuki, B., Takemoto, M., Matsuda, S., 2015. Osteoinductive potential of highly purified porous beta-TCP in mice. *Journal of Materials Science: Materials in Medicine* 26, 132.
- Vallet-Reg , M., Gordo, M., Ragel, C.V., Caba as, M.Y., Rom n, J.S., 1997. Synthesis of ceramic-polymer-drug biocomposites at room temperature. *Solid State Ionics* 101–103, 887–892.
- Van Den Vreken, N.M., Pieters, I.Y., De Maeyer, E.A., *et al.*, 2006. Apatite formation in composites of alpha-TCP and degradable polyesters. *Journal of Biomaterials Science, Polymer Edition* 17, 953–967.
- Vandecastelaere, N., Rey, C., Drouet, C., 2012. Biomimetic apatite-based biomaterials: On the critical impact of synthesis and post-synthesis parameters. *Journal of Materials Science: Materials in Medicine* 23, 2593–2606.
- Von Ew, S., Aji , W., Chan-Chang, T.H.C., *et al.*, 2017. Amorphous surface layer versus transient amorphous precursor phase in bone – A case study investigated by solid-state NMR spectroscopy. *Acta Biomaterialia* 59, 351–360.
- Von Ew, S., Wang, Y., Laurent, G., *et al.*, 2019. Bone mineral: New insights into its chemical composition. *Scientific Reports* 9, 8456.
- Walsh, D., Tanaka, J., 2001. Preparation of a bone-like apatite foam cement. *Journal of Materials Science: Materials in Medicine* 12, 339–343.
- Walsh, D., Boanini, E., Tanaka, J., Mann, S., 2005. Synthesis of tri-calcium phosphate sponges by interfacial deposition and thermal transformation of self-supporting calcium phosphate films. *Journal of Materials Chemistry* 15, 1043–1048.
- Wang, C.X., Zhou, X., Wang, M., 2004. Influence of sintering temperatures on hardness and Young's modulus of tricalcium phosphate bioceramic by nanoindentation technique. *Materials Characterization* 52, 301–307.
- Welch, J.H., Gutt, W., 1961. 874. High-temperature studies of the system calcium oxide–phosphorus pentoxide. *Journal of the Chemical Society*. 4442–4444.
- Welzel, T., Radtke, I., Meyer-Zaika, W., Heumann, R., Eppe, M., 2004. Transfection of cells with custom-made calcium phosphate nanoparticles coated with DNA. *Journal of Materials Chemistry* 14, 2213–2217.
- Wu, C.H., Hara, K., Ozawa, H., 1992. Enhanced osteoinduction by intramuscular grafting of BMP-beta-TCP compound pellets into murine models. *Archives of Histology and Cytology* 55, 97–112.
- Wu, Y.T., Ackerman, J.L., Kim, H.M., *et al.*, 2002. Nuclear magnetic resonance spin-spin relaxation of the crystals of bone, dental enamel, and synthetic hydroxyapatites. *Journal of Bone and Mineral Research* 17, 472–480.
- Yamada, M., Shiota, M., Yamashita, Y., Kasugai, S., 2007. Histological and histomorphometrical comparative study of the degradation and osteoconductive characteristics of alpha- and beta-tricalcium phosphate in block grafts. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 82, 139–148.
- Yang, L., Perez-Amodio, S., Barr re-de Groot, F.Y.F., *et al.*, 2010. The effects of inorganic additives to calcium phosphate on in vitro behavior of osteoblasts and osteoclasts. *Biomaterials* 31, 2976–2989.
- Yesinowski, J.P., 1998. Nuclear magnetic resonance spectroscopy of calcium phosphates. In: Amjad, Z. (Ed.), *Calcium Phosphates in Biological and Industrial Systems*. Dordrecht: Kluwer Academic Publisher, pp. 103–143.
- Yi, H., Balan, E., Gervais, C., *et al.*, 2013. A carbonate-fluoride defect model for carbonate-rich fluorapatite. *American Mineralogist* 98, 1066–1069.
- Yuan, H., de Bruijn, J.D., Li, Y., *et al.*, 2001. Bone formation induced by calcium phosphate ceramics in soft tissue of dogs: a comparative study between porous alpha-TCP and beta-TCP. *Journal of Materials Science: Materials in Medicine* 12, 41456.
- Zhang, F., Lin, K., Chang, J., Lu, J., Ning, C., 2008. Spark plasma sintering of macroporous calcium phosphate scaffolds from nanocrystalline powders. *Journal of the European Ceramic Society* 28, 539–545.
- Zhang, J., Luo, X., Barbieri, D., *et al.*, 2014. The size of surface microstructures as an osteogenic factor in calcium phosphate ceramics. *Acta Biomaterialia* 10, 3254–3263.
- Zhang, Y., Zhang, M., 2001. Synthesis and characterization of macroporous chitosan/calcium phosphate composite scaffolds for tissue engineering. *Journal of Biomedical Materials Research* 55, 304–312.

Calcium Phosphates in Biomedical Engineering

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Introduction

Apatite was the first calcium phosphate recognized as mineral specie. It was discovered in 1786 by Abraham Gottlob and named by him as “Apatao”. From the ancient greek that means “to mislead” because it had previously been confused for other minerals, namely beryl, tourmaline, chrysolite, amethyst, fluorite, etc. Nowadays, apatite is the name for a group of minerals with the same crystallographic structure. In the case of calcium phosphates (CaP), the term “apatite” involves CaP with Ca/P ratios within 1.5–1.67. The main CaP phases and their corresponding formulas are summarized in [Table 1](#). CDHA, HA, FA, and OA belong to the apatite’s group while MCPM, MCPA, DCPD, and DCPA belong to the acid phosphates group. CaP are an interesting family of compounds in many fields of science and technology, including geology, chemistry, biology and medicine due to their natural abundance and their presence in the living organism ([Dorozhkin, 2013a](#)). The present chapter will be focused on the revision of CaP uses for biomedical applications and their progresses in the biomaterials field thanks to the advances achieved in their synthesis and processing and making them capable of addressing new challenges of medicine.

Calcium Phosphates in the Field of Biomaterials

CaP are of a special importance since they are the most important inorganic constituents of hard tissues in vertebrates. In the form of a poor crystalline, non-stoichiometric, ion-substituted calcium-deficient hydroxyapatite (CDHA, commonly referred to as “biological apatite”), CaP are present in bones, teeth and tendons of mammals to give these organs stability, hardness and function ([Dorozhkin, 2013a](#)). That is why these CaP are characterized by being biocompatible what makes them extremely interesting for medical applications.

CaP have been widely studied from a biological, structural, and morphological point of view and nowadays, they are commonly applied in orthopedic and maxillofacial application as well as in dentistry due to biocompatible and osteoinductive properties apart from their biocompatibility ([Dorozhkin, 2013a](#)).

Especially in the field of bone restoration and regeneration applications, the research in CaP has been driven due ageing challenge faced by the actual society. It is well known that all the tissues suffer a progressive deterioration with age. In bone tissue, this process is named osteoporosis. It is a worldwide disease which mainly affects to humans older than 50. The process is especially severe in women because of the menopause. It can result in bone fractures which involve patient disability or even death in the worst cases. Moreover, the use of new transports and the practice of extreme sports during the last decades have increased the number of accidents whose assistance involves orthopedic surgery. For these reasons, it has been experienced an increase in the demand of bone grafts and advances in surgical practice.

The first in vivo tests performed with CaP as artificial material to repair defects created surgically were made in 1920 by the surgeon Fred Houdlette Albee, who can be considered the father of bone grafts. However, it won’t be until 1960 when the interest for ceramics as potential bone grafts has grown owing to their biomechanical properties. The first goal of bioceramics was to replace part of bones, so the requirement was that the physiological environment must tolerate them. They must be able to resist the mechanical loads of implanted individuals in physiological conditions during years of use ([Sastre et al., 2004](#)).

Table 1 Summary of CaP phases, their corresponding Ca/P molar ratios, abbreviations and formulas

Ca/P atomic ratio	Compound	Typical abbreviations	Chemical formula
0.5	Monocalcium phosphate monohydrate	MCPM	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$
0.5	Monocalcium phosphate anhydrous	MCPA or MCP	$\text{Ca}(\text{H}_2\text{PO}_4)_2$
1.0	Dicalcium phosphate dihydrate, Brushite	DCPD	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$
1.0	Dicalcium phosphate anhydrous, Monetite	DCP, DCPA	CaHPO_4
1.33	Octacalcium phosphate	OCP	$\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$
1.5	β -Tricalcium phosphate	β -TCP	$\beta\text{-Ca}_3(\text{PO}_4)_2$
1.5	α -Tricalcium phosphate	α -TCP	$\alpha\text{-Ca}_3(\text{PO}_4)_2$
1.2–2.2	Amorphous calcium phosphates	ACP	$\text{Ca}_x\text{H}_y(\text{PO}_4)_z \cdot n\text{H}_2\text{O}$ $n = 3 - 4.5$; 15%–20% H_2O
1.5–1.67	Calcium-deficient hydroxyapatite	CDHA or Ca-def HA	$\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}$ ($0 < x < 1$)
1.67	Hydroxyapatite	HA or HAp	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$
1.67	Fluorapatite	FA or FAp	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$
1.67	Oxyapatite	OA, OAp or OXA	$\text{Ca}_{10}(\text{PO}_4)_6\text{O}$
2	Tetracalcium phosphate	TetCP	$\text{Ca}_4(\text{PO}_4)_2\text{O}$

In addition, implants need to fix to the surrounded tissue so bone bonding is also a mandatory requirement. In 1967, Prof. Hench started his research through the modification of the chemical composition of ceramics and glasses to provide then chemical reactivity in contact with the physiological media, with the aim to promote bone bonding. The concept of bioactivity appears. In 1971 appeared the first bioactive glass, named Bioglass® and in 1984 Hench and Wilson include the Hydroxyapatite (HA) inside of the bioactive ceramics group. Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), has been widely used in the field because its chemical composition is quite similar to mineral phase of bones. It has an ionic character and its crystalline structure can be described as a hexagonal packaging of oxygen atoms where cations are placed on the tetrahedral and octahedral sites (Sastre *et al.*, 2004).

Due to the chemical similarity of CaP and the inorganic phase of bones and teeth, they possess bone-bonding ability. For this reason, they have been processed as coatings in the surface of load-bearing implants.

Furthermore, beyond replacing the lost bone, the new challenges facing science is regeneration (Peppas and Langer, 1994). New concepts such as biodegradation, resorption or osteoinduction appear. Modern grafts should act as temporal support for cells and promote bone regeneration while material is resorbed. Then, biodegradability is also an essential property. It is possible to design CaP-based materials with controlled biodegradation rate. Biodegradability is mandatory and HA is a very stable phase under the physiological conditions, which is translated into a low solubility and slow resorption kinetics. Then tricalcium phosphates (TCP) appears. It is the biodegradable CaP par excellence (Sastre *et al.*, 2004). It belongs to the Whitlockites family which correspond to the general formula $(\text{Ca,Mg})_3(\text{PO}_4)_2$. Most of the bioresorbable ceramics, with the exception of plaster or wollastonite (de Aza *et al.*, 1994, 2000), are based on CaP. Their biodegradability increases following the sequence $\text{HA} \ll \beta\text{-TCP} < \alpha\text{-TCP}$.

Moreover, since for cells it is difficult to organize themselves in big defects, nowadays, CaP are designed as three dimensional (3D) porous structures to promote cell colonization, vascularization, and bone formation. (Canillas *et al.*, 2017) For this reason, regeneration has also promoted the need to develop porous 3D structures and has focused the interest of the studies in the development of processing methods to manufacture CaP scaffolds. With the development of additive manufacturing technologies, 3D printing means a revolution in the biomaterials field. In report titled "The disruptive nature of 3D printing" published in the European Commission, the importance of the 3D printing technologies for the development of CaP 3D structures for bone regeneration applications is highlighted. Due to the necessity to produce 3D structures adapted to the requirements and sizes of patients, additive manufacturing allows the manufacture of personalized implants in short times. In the same report the authors point to bioprinting, and specially of hard tissues, as the research placed at the forefront (Bonneau and Yi, 2017).

Finally, recent studies are also focused in the physicochemical properties of CaP. Apart from their chemical composition, particle shape and size or the porous morphology have been studied as key parameters in the cell osteogenesis. The objective of these studies is the development of more biomimetic materials (Barba *et al.*, 2018). Finally, apart from bone substitution and regeneration applications, they have been also suggested as vehicles of drugs, peptides or ADN molecules (Parent *et al.*, 2017).

Synthesis and Processing

Synthesis

As it was previously mentioned CaP are minerals present in the nature and in the hard tissues of vertebrates. The constituting building blocks of bone are composites of biological apatite and molecules of collagen. Calcified tissues, such as bone or dentin contain ~70 wt% apatite and ~20 wt% collagen (Vallet-Regí and González-Calbet, 2004).

Nano-sized CaP represent the basic inorganic building blocks of bones and teeth of mammals. Collagen molecules are self-assembled into fibrils with a periodicity of 67 nm and 40 nm gaps between the ends. Within these gaps, biological apatite takes place and grows in the form of tiny nano-sized plate-like crystals with specific crystalline orientation along the c-axes in parallel to the long axes of the collagen fibrils. This in vivo process of biological apatite formation is named biological mineralization or biomineralization. Biomineralization is the natural method of synthesis of CaP. During this process, organized assemblies of organic macromolecules regulate nucleation, growth and morphology of inorganic crystals. Nanodimensional apatite achieves two main functions: nanometer sizes of mineral particles ensure the optimum strength and maximum tolerance of flaws; moreover, it is a storage of calcium and orthophosphate ions which are available for a wide variety of metabolic functions thanks to the so-called remodeling process. It consists on the constant resorption and formation of biological apatite which are controlled by osteoclasts and osteoblasts respectively.

Apart of biomineralization, the origin of CaP used for medical application can be natural, for example, calcined bovine HA or carboxyhydroxyapatite from the eggshells, and/or synthetic. Most common synthesis methods are based on thermal treatment in solid state (Lin *et al.*, 2014). But there is also a wide range of synthesis methods inspired on the bottom-up approach. The wet chemical precipitation is the most used. Morphology, phase formation and crystallinity of precipitated apatites have been studied in relation with temperature, calcium concentration or pH. Other method commonly used in the synthesis of nanosize CaP is the hydrothermal. Fine-grained single crystals, characterized by high purity, controlled morphology and narrow size distribution can be obtained. Alternative bottom-up synthesis methods can be such as sol-gel (Costa *et al.*, 2012) or solution combustion method (Canillas *et al.*, 2017). The latter allows the design of the shape and size of particles by the control of the redox environment.

Moreover, methods based on the natural nucleation and growth of nanocrystalline apatite between self-assembled collagen fibrils, have been also developed based on the biological apatite formation in mammals. This process has been simulated using macromolecules as templating agents. Precipitation of nanosized apatites from aqueous solutions has been carried out, for

example, in the presence of dissolved polyacrylic acid (Liou *et al.*, 2005), polyvinyl alcohol, amino acids or gelatin. The aim of this type of synthesis is the obtention of biocomposites with structure and mechanical properties similar to bones. It also allows the obtention of complex morphologies. An interesting example is a pH-induced self-assembly peptide-amphiphile, to obtain nanostructured fibrous scaffolds by cross-linking, and following mineralization. C-axes of CDHA crystals grow aligned with the long axes of the fibers similar to biological apatite in bones (Dorozhkin, 2013b).

Most of the CaP synthesized are composed by HA, TCP or mixtures of those. TCP presents three poly-morphs: β , α and α' , from the lowest to the highest stability temperatures and being the last one total reversible in both senses. (Carrodegua and de Aza, 2011) In case of α and β , pure phases as well as controlled mixtures may be obtained with adequate thermal treatment and amount of Mg. $\beta \rightarrow \alpha$ Ca₃(PO₄)₂ transition temperature is increased with Mg (Mg₃(PO₄)₂) and Mg and Si (CaMg(SiO₃)₂) content. (Carrodegua *et al.*, 2010) Moreover, β -TCP phase can be also stabilized with partial Ca substitution for Sr and Zn and α -TCP with partial PO₄³⁻ substitution for SiO₄⁴⁻. (Wang *et al.*, 2018; Bandyopadhyay *et al.*, 2012) Whatever of these phases, possess higher solubility than HA (HA < β -TCP < α -TCP) according with the literature. The vast majority of CaP bioceramics are based on HA both types of TCP and multiphase formulations thereof.

The term BCP (Biphasic Calcium Phosphates) is referring to mixtures of CaP phases. In order to obtain the optimum in vivo bioresorbability this kind of mixture are used. Usually balance of a more stable phase and a more soluble phase are used with the aim to control the bioresorbability. Different biphasic mixtures of HA and β -TCP and α -TCP phases has been considered and also triphasic formulations were included. In fact, the preparation of pure chemicals is difficult and expensive, so CaP bioceramics are multiphasic mixtures where there are one or two major phases. In general, physico-chemical properties of biphasic, triphasic and multiphasic CaP bioceramics depend on the relative amounts of the components. (Daculsi *et al.*, 2009) The most important advantages of biphasic, triphasic and multiphasic CaP bioceramics is the control of the in vivo resorption as well as bioactivity by manipulation of the phase ratios. (Yamada *et al.*, 1997) BCP products with different or similar HA/ β -TCP ratios have been manufactured and they are commercially available as bone graft or bone substitute biomaterials for orthopedic, maxillofacial and dental applications.

Finally, self-setting formulations have drawn great attention due to their easily handling and their biomimetic physicochemical properties with the inorganic phase of bones. Self-setting CaP formulations are mixtures of CaP powders and aqueous solutions such as distilled water, SBF, aqueous solutions of sodium orthophosphates, H₃PO₄ or citric acid. Self-setting process goes through two possible reactions: acidic-base or hydrolysis. In the first case, CaP with relatively acidic behavior reacts with relatively basic one to produce a relatively neutral compound. The second type consists on the hydrolysis of metastable CaP in aqueous media. In both cases, when CaP are placed in the aqueous environment they dissolve and a process of mass transport takes place until supersaturated microenvironment is created with regards to the final product. Crystals obtained by precipitation grow and form microneedles and micropellets of CDHA and DCPD, which provide rigidity to the hardened material (Ginebra *et al.*, 2010).

Depending of the product obtained after setting, cements are divided in two main types: apatite forming formulations and brushite forming formulations. In case of apatite-forming formulations, the products of the setting reaction are poorly crystalline HA, CDHA, or carbonate apatite, if the setting reaction occurs in presence of carbonates. It is thought that the similar chemistry of those products and biological apatite is responsible of their excellent in vivo resorption.

In addition, the setting process occurs at pH values close to the physiological and it contributes to their good biocompatibility. Solubility of these formulations in aqueous solutions is expected to be similar to that of bone mineral. Solubility increases when pH is slightly acid. Moreover, controlled dissolution can be improved by osteoclast. Furthermore, crystals obtained can be easily detached, especially after dissolution and it makes the ingestion by osteoclast and other cells easier. Regarding to the setting time, which is increased on in vivo conditions, it is quite long for apatite forming formulations. It can involve technical complications and, for this reason, an interesting goal consists on decrease their setting time. Different approaches have been suggested, for example, by reducing the amount of liquid phase as low as possible or using additives like H₃PO₄ to decrease the pH and promote the dissolution of CaP.

In the case of brushite forming formulations, the major product of the setting reaction is DCPD. These setting reactions occur by acidic-base process. DCPD precipitates mainly at pH below 6. Consequently, the reaction environments in these formulations are always slightly acidic. Apart from its biocompatibility, Brushite presents higher solubility compared with CDHA. It is translated in a faster degradation and quickly resorption in vivo. The disadvantage is the short setting time that makes its injectability complicated. For this reason, one of the main goals consists on decrease the viscosity.

Finally, monetite based formulations have been developed by acidic-base process to be applied as granulates which provide a 3D structure (Padilla *et al.*, 2015). Inside of brushite cements, monetite has also take great attention. Cements for Monetite-HA mixtures have been developed with the aim to control bioresorption rates.

Processing

As other formulations, CaP might be processed in both dense and porous forms in bulk, as well as in the forms of powders, granules, scaffolds, or coatings. Depending of the requirements they have to be processed in different ways. For example, improved mechanical properties require dense materials while cell colonization, bone regeneration, and vascularization require 3D porous structures such as scaffolds or granules. Powders can be used, for example as raw materials to obtain self-setting formulations or inks for 3D printing. Nanosized particles can be used not only to obtain dense materials but also for drug delivery systems or gene therapy (Parent *et al.*, 2017).

Processing normally consist in two steps, conformation, considering the specifications of the component to produce, and following sintering. Most common shape forming methods include: uniaxial compaction, isostatic pressing, granulation, slip casting, gel casting,

freeze casting, spray drying, polymer replication, extrusion, low pressure injection, dipping or thermal spraying. Also, shaping can be carried out during cooling and solidification of previously melted raw materials. It has to be noted that shape forming of any ceramic products require a proper selection of the raw materials in terms of particle sizes distribution. Sintering is a processing step with great interest to consolidate the shaped forms. During the sintering of CaP, different processes take place in CaP compositions: dihydroxylation, decarbonation, volatile chemicals removal, shrinkage and grain size growth. Chemical changes such as chemical decomposition of acidic orthophosphates by water loss also take place. To obtain improved mechanical properties grain growth and remaining porosity must be minimized during the sintering (Laasri *et al.*, 2010). For this reason, sintering methods such as hot isostatic pressing, microwave, spark plasma sintering or rate controlled sintering have been suggested.

Polymeric-ceramic composites were designed with the objective to get similar mechanical properties to bones since they are a composite material of collagen and hydroxyapatite. Moreover, they have increased the processing possibilities for ceramics. These kinds of composites have been widely studied and developed for biomedical applications. The main reasons to add a polymeric phase are: the improvement of the mechanical properties regarding to the brittleness of ceramics, their easy manufacture as 3D structures and the possibility to include drugs or molecules in their matrix and their ability to control their drug delivering rate. Ceramic powders, granulates or 3D structures can be coated or embed in a polymer matrix. Polymeric processing methods such as freeze-thawing, photopolymerization, melt-extrusion, have been used in the processing of polymeric-ceramic composites (Canillas *et al.*, 2017).

Furthermore, bone regeneration applications need the manufacturing of implants with interconnected porosities, complex geometries and specific sizes. Nowadays, CaP implants with even more complex geometries can be developed thanks to the computer-aided design and additive manufacturing technologies. For example, a digital image of a bone defect in a patient can be used to develop a three-dimensional (3D) structure. The computer reduces the model to slices or layers and 3D structures are constructed layer-by-layer (de Aza *et al.*, 1994). CaP or composites of those with polymers and hydrogels can be printed by using different 3D technologies: VAT polymerization (such as stereolithography), power bed fusion (laser sintering), material extrusion (robocasting or fused deposition modeling) or binder jetting. In many cases, a second sintering step is required involving the sacrifice of the polymer phase (Zhang *et al.*, 2019).

Last advances in robocasting have developed 3D CaP structures with polymer cores to improve mechanical properties. Coaxial needle is used to produce log-pile structures of hollow rods which are following filled with a polymer phase. (Paredes *et al.*, 2019). Moreover, the development of 3D structures with self-setting formulations by robocasting have avoided the sintering step and the manufacturing of more biomimetic structures (Raymond *et al.*, 2018).

New developments on Selected Laser Sintering (SLS) and Selected Laser Melting (SLM) are, just now, enabling ceramic based scaffolds without the need for a second sintering stage (Trombetta *et al.*, 2017).

Moreover, biomedical systems are already capable to print proteins and cells so current research interest mainly resides in the bioprinting of organs and tissues and bioprinting of hard tissues such as bone and tendons have received a special attention (Bonneau and Yi, 2017). Usually, the bioinks are composed by a hydrogel which contains cell or proteins in its matrix. Current 3D bioprinting technologies are based on: extrusion, stereolithography, inject and laser assisted (Derakhshanfar *et al.*, 2018). While extrusion based bioprinting is being widely studied, laser assisted bioprinting present interesting advantages: it is able to print volumes in the range of picolitres increasing the precision and high cell viability due to the last developments. For example, Blaser Assisted Laser Induced Forward Transfer (BA-LIFT) have extraordinary decreased the cell death due to the laser effects. Current studies are directed to the bioprint of hard tissues include CaP in the matrix of these hydrogels.

Properties and Applications

It was previously described that CaP is chemically similar with mammalian bones and teeth. In addition to their biocompatibility, one of their major features is their bioactivity. For these reasons, CaP are used in medicine for different medial applications related with hard tissue such as bone augmentation, dental fillings and periodontal treatments, implant fixations or vertebroplasty and kyphoplasty (Lewis, 2006).

There have been different developments in CaP ceramics and these advances have required the development of CaP-based materials with different characteristics and properties. For example, in 1950 self-setting abilities of CaP are discovered and in early 1980 CaP cements awake the interest of the biomaterials science community because of their suitable properties for bone repair, augmentation and regeneration but also because of their easy handling and injectability. Setting times, viscosity are important parameters for injectability (Ginebra, 2008) but also in the manufacture of 3D structures where the rheology studies had focused the attention of researchers.

Graham and van der Eb introduce a novel application in 1973 (Graham and van der Eb, 1973), when they demonstrated the capability of CaP to condense DNA and the transfection efficiency was increased with a relatively simple procedure. They are also suggested as drug delivery systems or for alternative tissue engineering purposes. CaP appear to be promising carriers of growth factors, bioactive peptides and various types of cells. In the 1990s, a multitude of papers about the use of CaP scaffolds as controlled drug delivering systems were published.

In other hand, first CaP coatings, films and layers appeared about 1975. Until that time, CaP had been limited to non-load bearing applications, since they are mechanically brittle. However, surface of any implant is always the first part to interact cells and surrounding tissues and, for this reason, the surface properties play a key role. Then CaP are suggested to be placed onto the surface of mechanically strong but bioinert or biotolerant materials (non bioactive), suitable for load bearing applications. CaP

improves biocompatibility and, consequently, prevents encapsulation, osteoconductivity, but mainly improves the bioactivity of the implants, facilitating their bonding to the bones. The objective of the coatings is to obtain the desired surface properties through changes in the surface of the material, but maintaining unchanged their bulk. The attempt to combine these requirements resulted in a discipline named surface engineering. Cohesion and adhesion of the coating to the substrate are key parameters studied in this discipline. Also fatigue, elastic modulus and hardness are important properties for the applications of coatings. Also the crystallinity, the solubility rate, the topography and the interaction with proteins and cells play important roles in the success of the coating (Surmenev *et al.*, 2014).

Nanosized CaP were introduced in 1994. Both a greater viability and a better proliferation of various types of cells have been detected on smaller crystals of CaP. These effects have been related with a higher surface-to-volume ratio, reactivity and biomimetic morphologies of the nanosized particles. Recent advances suggest that this is a natural selection, since the nanostructured materials promote specific interactions with proteins. For all these reasons, nano-sized and nanocrystal line forms of CaP have a great potential for bone repair and augmentation but also as drug delivery systems. Synthesis and development of nanomaterials, their singular properties and sophistication have revolutionized numerous research fields. They can develop more complex functions and be designed to mimic the physicochemical properties of natural materials (Surmenev *et al.*, 2014).

Finally, the great challenge that these materials face in their medical application is regeneration rather than tissue replacement (Li *et al.*, 2013). In the late 1990s applications of CaP in tissue engineering began. As previously described, CaP present suitable properties for the tissue engineering applications such as biocompatibility, biodegradability, bioactivity, high affinity for drugs, proteins and cells and possible osteoinductivity. Moreover, since the main goal in tissue engineering is to create tissues and organs *de novo* and cells need a support to be organized in a 3D disposition, one of the main trials has been the development of 3D porous structures which simulate the extracellular matrix. New developments to manufacture 3D porous structures soar. However, porosity decreases the mechanical resistance. This is an important parameter when implants are directed to regenerate bone tissue and it is a big challenge in the field. In the forefront, the bioprinting of hard tissues face two main challenges: the printing technology and curing methods after printing have been compatible with the viability of cells.

Final Remarks

Since humanity discovered the presence of CaP in living organisms, these compounds aroused great interest from the scientific community. The physico-chemical and biological properties of CaP have widely studied. They have been encouragingly postulated as bone grafts due to their similar chemical composition to bones, biocompatibility and bioactivity properties. While first bone grafts only pretended to substitute bone damaged or bone lost, the modern bone grafts pursue the bone regeneration by mimicking body's own self-repairing abilities. This new generation of bone grafts acts as temporal substrate for bone cells but they must biodegrade with the time to give the way to new bone tissue formed. Osteoinduction and biodegradation or bioresorption are new properties required. Also the obtention of 3D structures with interconnected macro and micro porosity are mandatory. CaP possess attractive biological properties in terms of biocompatibility, bioactivity, bioresorbability, and osteoinductivity. In addition, advances in other research fields such as, materials engineering (nanotechnology or 3D printing technologies), tissue engineering (bioprinting), surface engineering, and alternative applications such as drug delivery or gene therapy, have driven the research of CaP as biomaterials. For example, due to their ceramic nature, which confers brittleness, CaP were limited to non-load bearing applications. However, they have been also suggested as coatings to provide bioactivity over metallic implants for load-bearing applications. In other hand, CaP self-setting formulations offered the possibility to be easy handling, minimal invasion and capability to adopt required shapes. Also, CaP have been suggested as vehicles for drug delivery systems (antibiotics, anti-inflammatories, growth factors, etc.) and ADN or ARN transfection. In other hand, several polymer-ceramic composites have been developed and studied to decrease the brittleness of ceramics, provide bioactivity to the polymers and aid the controlled release of drugs. Finally, 3D printing technologies have revolutionized the manufacture of scaffolds and bone grafts. Last advances have proposed 3D printing of self-setting CaP formulations. The current interest is focused in the bioprinting of hard tissues which involves 3D printing of composite materials, usually hydrogel-CaP composite, and cells or proteins.

To conclude, CaP continue playing an important role in the research of medical devices for Biomedical Engineering.

References

- Bandyopadhyay, A., Petersen, J., Fielding, G., Banerjee, S., Bose, S., 2012. ZnO, SiO₂, and SrO doping in resorbable tricalcium phosphates: Influence on strength degradation, mechanical properties, and in vitro bone–cell material interactions. *J. Biomed. Mater. Res. B Appl. Biomater.* 100, 2203–2212.
- Barba, A., Maazouz, Y., Diez-Escudero, A., *et al.*, 2018. Osteogenesis by foamed and 3D printed nanostructures calcium phosphates scaffolds: Effect of pore architecture. *Acta Biomater.* 79, 135–147.
- Bonneau, V., Yi, H., 2017. The Disruptive Nature of 3D Printing: Digital Transformation Monitor. European Commission. Available at: <https://ec.europa.eu/growth/tools-databases/dem/monitor/category/3d-printing>.
- Canillas, M., Pena, P., de Aza, A.H., Rodríguez, M.A., 2017. Calcium phosphates for biomedical applications. *Bol. Soc. Esp. Ceram. Vidr.* 56, 91–112.
- Carrodegas, R.G., de Aza, S., 2011. α -Tricalcium phosphate: Synthesis, properties and biomedical applications. *Acta Biomater.* 7, 3536–3546.
- Carrodegas, R.G., de Aza, A.H., García-Páez, I., de Aza, S., Pena, P., 2010. Revisiting the phase-equilibrium diagram of the Ca₃(PO₄)₂–CaMg(SiO₃)₂ system. *J. Am. Ceram. Soc.* 93, 561–569.

- Costa, D.O., Dixon, S.J., Rizkalla, A.S., 2012. One - and three-dimensional growth of hydroxyapatite nanowires during sol-gel-hydrothermal synthesis. *ACS. Appl. Mater. Interfaces* 4 (3), 1490–1499.
- Daculsi, G., Jegoux, F., Layrolle, P., 2009. The micro macroporous biphasic calcium phosphate concept for bone reconstruction and tissue engineering. In: Basu, B., Katti, D. S., Kumar, A. (Eds.), *Advance Biomaterials: Fundamentals Processing and Applications*. New York: Wiley-American Ceramic Society, pp. 101–142.
- de Aza, P.N., Guitian, F., de Aza, S., 1994. Bioactivity of wollastonite ceramics: In vitro evaluation. *Scr. Metall. Mater.* 31, 1001–1005.
- de Aza, P.N., Luklinska, Z.B., Martínez, A., *et al.*, 2000. Morphological and structural study of pseudo-wollastonite implants in bone. *J. Microsc.* 197, 60–67.
- Derakhshanfar, S., Mbeleck, R., Xu, K., *et al.*, 2018. 3D bioprinting for biomedical devices and tissue engineering: A review of recent trends and advances. *Bioact. Mater.* 3, 144–156.
- Dorozhkin, S.V., 2013a. A detailed history of calcium orthophosphates from 1770s till 1950. *Mater. Sci. Eng. C* 33, 3085–3110.
- Dorozhkin, S.V., 2013b. Nanodimensional and nanocrystalline calcium orthophosphates. *Int. J. Chem. Mater. Sci.* 1, 105–174.
- Ginebra, M.P., 2008. Calcium phosphate bone cements. In: Deb, S. (Ed.), *Orthopaedic BONE Cements*. Cambridge: Woodhead Publishing Ltd, pp. 206–230.
- Ginebra, M.P., Español, M., Montufar, E.B., Pérez, R.A., Mestres, G., 2010. New processing approaches in calcium phosphate cements and their applications in regenerative medicine. *Acta Biomater.* 6, 2863–2873.
- Graham, F.L., van der Eb, A.J., 1973. A new technique for the assay of infectivity of human adenovirus 5 DNA. *Virology* 52, 456–467.
- Laasri, S., Taha, M., Laghizil, A., Hlil, E.K., Chevalier, J., 2010. The effect of densification and dihydroxylation on the mechanical properties of stoichiometric hydroxyapatite bioceramics. *Mater. Res. Bull.* 45, 1433–1437.
- Lewis, G., 2006. Injectable bone cements for use in vertebroplasty and kyphoplasty: State-of-the-art review. *J. Biomed. Mater. Res. B* 76, 456–468.
- Li, X., Wang, L., Fan, Y., *et al.*, 2013. Nanostructured scaffolds for bone tissue engineering. *J. Biomedical Mater. Res. A* 101A, 2424–2435.
- Lin, K., Wu, Ch., Chang, J., 2014. Advances in synthesis of calcium phosphate crystals with controlled size and shape. *Acta Biomater.* 10, 4071–4102.
- Liou, S.C., Chen, S.Y., Liu, D.M., 2005. Manipulation of nanoneedle and nanosphere apatite/poly-(acrylic acid) nanocomposites. *J. Biomed. Mater. Res. B Appl. Biomater.* 73, 117–122.
- Padilla, S., García de Castro, A., Garzón-Gutiérrez, A., *et al.*, 2015. Novel nanostructured Zn-substituted monetite based biomaterial for bone regeneration. *J. Nanomed. Nanotechnol.* 6.
- Paredes, C., Pajares, A., Miranda, P., 2019. Development by robocasting and mechanical characterization of hybrid HA/PCL coaxial scaffolds for biomedical applications. *J. Eur. Ceram. Soc.* 39, 4375–4383.
- Parent, M., Baradari, H., Champion, E., Damia, C., Viana-Trecant, M., 2017. Design of calcium phosphate ceramics for drug delivery applications in bone diseases: A review of the parameters affecting the loading and release of the therapeutic substance. *J. Control. Release* 252, 1–17.
- Peppas, N.A., Langer, R., 1994. New challenges in biomaterials. *Science* 263, 1715–1720.
- Raymond, S., Maazouz, Y., Montufar, E.B., *et al.*, 2018. Accelerated hardening of nanotextured 3D-plotted self-setting calcium phosphate inks. *Acta Biomater.* 75, 451–462.
- Sastre, R., de Aza, S., San Román, J., 2004. *Biomateriales*. Spain: Faenza Editrice Iberica.
- Surmenev, R.A., Surmeneva, M.A., Ivanova, A.A., 2014. Significance of calcium phosphate coatings for the enhancement of new bone osteogenesis – A review. *Acta Biomater.* 10, 557–579.
- Trombetta, R., Inzana, J.A., Schwarz, E.M., Kates, S.L., Awad, H.A., 2017. 3D printing of calcium phosphate ceramics for bone tissue engineering and drug delivery. *Ann. Biomed. Eng.* 45, 23–44.
- Vallet-Regí, M., González-Calbet, J.M., 2004. Calcium phosphates as substitution of bone tissues. *Prog. Solid State Chem.* 32, 1–31.
- Wang, J., Qian, J., Xu, W., *et al.*, 2018. Effects of $\text{Sr}^{2+}/\text{Zn}^{2+}$ co-substitution on crystal structure and properties of nano- β -tricalcium phosphate. *Ceram. Int.* 44, 6096–6103.
- Yamada, S., Heymann, D., Boulter, J.M., Daculsi, G., 1997. Osteoclastic resorption of calcium phosphate ceramics with different hydroxyapatite/ β -tricalcium phosphate ratios. *Biomaterials* 18, 1037–1041.
- Zhang, L., Yang, G., Johnson, B.N., Jia, X., 2019. Three-dimensional (3D) printed scaffold and material selection for bone repair. *Acta Biomater.* 84, 16–33.

Bioceramics in Regenerative Medicine

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Introduction

The ability of bones to self-heal and regenerate has been intensively studied since ancient times ([Hippocrates and Adams, 1939](#)). Indeed, bones and hard tissues including the cartilage and teeth are of key importance for the human life, in terms of mobility, manipulation, chewing, and thus it is today one of the most demanding issues in medicine. The bone physiological healing response is active toward a complete and effective regeneration only in case of small defects, while critical-size and load-bearing bony regions require the transplantation of bone substitutes. Given its importance, it was estimated that bone represents nowadays the second most common transplanted tissue after blood, with the iliac crest autologous graft being most used ([Shegarfi and Reikeras, 2009](#)).

Given the limited availability, risk of site morbidity and immune responses related to the use of autografts and allografts from donors, a great deal of research effort has been devoted in the last decades to the development of synthetic scaffolds, aiming to drive and sustain the bone regeneration process. A wide consensus is today consolidated toward the concept of “biomimetics”, that is the intrinsic ability of a synthetic material to closely reproduce the chemical composition, physical properties, and architecture of native tissues, with the purpose to create 3-D environments able to deliver signals stimulating cell chemotaxis and specific differentiation of autologous stem cells ([Tampieri et al., 2011](#)).

As the major component of bone tissue is a calcium phosphate, namely a ceramic material, the term *bioceramics* refers to the class of materials investigated for bone repair and regeneration. In the last decades, the research on regenerative bioceramics has greatly expanded, with the purpose to achieve the optimal composition, multi-scale structure, and mechanical performance.

In this respect, this chapter describes the main features requested for ceramic bone scaffolds and the most recent approaches to develop regenerative bioceramics, with particular respect to bioactive ceramic nanoparticles and their functionalization, 3-D porous ceramics and self-hardening injectable ceramic pastes and cements. Furthermore, the chapter explores recent advances in additive manufacturing techniques that, in spite of technological difficulties, are considered as a major approach to obtain implantable, personalized devices with organized and tailored porosity. Finally, the chapter gives an overview on some clinical results encouraging further research in the field.

Requirements for Regenerative Bioceramics: Physicochemical, Morphological, and Mechanical Aspects

The interaction of biomaterials with living tissues is driven by multiple factors acting in a synergistic fashion. Particularly, it is today well known that, in their adhesion to a foreign substrate, stem cells respond to environmental conditions dictated by the substrate composition, pH, nano-texture, multi-scale porosity, and mechanical behavior such as elasticity and toughness under physiological multi-modal loading.

The composition of a scaffold is important because it can induce specific cell response by biochemical recognition. Bone tissue composition includes about 70% of hydroxyapatite (HA) and 30% of collagen by weight ([Biltz and Pellegrino, 1969](#)). For this reason, calcium phosphates (CaPs) closely mimic the bone tissue and provide higher osteoblasts adherence and proliferation when compared to other materials ([Stevens et al., 2008](#)). A very high number of calcium phosphate bio-devices have been developed in the past decades, mainly for orthopedic, maxillofacial, and dental applications ([Thamaraiselvi and Rajeswari, 2003](#)). Hydroxyapatite, the most stable crystalline CaP at physiological pH, can be obtained by a multitude of synthesis approaches, particularly as ion-doped phases to improve the compositional mimicry with bone and enhance bioactivity/bioresorbability and, in turn, enhanced osteoconduction and osteoinduction ([Turnbull et al., 2018](#); [Wang and Yeung, 2017](#); [Gomes et al., 2018](#); [Basu and Basu, 2019](#); [Iafisco et al., 2018](#); [Shahrezaee et al., 2018](#)). The bioresorbability of calcium phosphates is greatly related to their microstructure and is enhanced if low temperature syntheses are used. On the other hand, high-temperature sintering processes may improve the mechanical performance of bioceramics, but limiting their bioresorbability ([Dorozhkin, 2010a](#); [Prakasam et al., 2015](#)). In general, the biological in vitro and in vivo performance of a scaffold designed for regenerative medicine are related to the composition, as when a biomaterial is implanted in living tissues a layer of water molecules rapidly forms on its surface, influencing the deposition of the subsequent layer of proteins, finally guiding the interaction of the scaffold with the surrounding cells ([Wilson et al., 2005](#); [Othman et al., 2018](#)).

Besides the composition, the nano- and micro-architecture of scaffolds is a critical factor in encouraging cell viability and promoting tissue ingrowth, as shown by previous studies reporting enhanced adhesion of cells to the scaffold by tailoring micro- and nano-features of the scaffold surface such as the surface area and roughness ([Wang and Yeung, 2017](#); [Meco and Lampe, 2018](#); [Ashworth et al., 2018](#); [Bružauskaitė et al., 2016](#)). Scaffold porosity must be precisely engineered to obtain features making cells migration and proliferation favorable. Despite a wide range of studies have been performed to investigate the best range of porosity for a bone scaffold, the precise tuning of pore size and shape still comes demanding. The mean pore size determines the

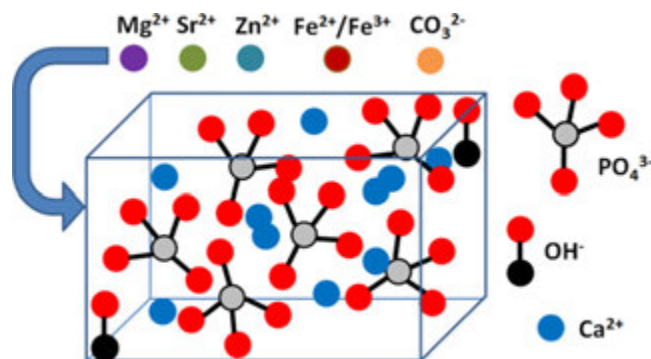


Fig. 1 Crystalline structure of Hydroxyapatite with examples of ionic substitutions.

surface area of the scaffold: among ceramic bodies presenting the same overall porosity extent, a decreased pore size reflects in an increased availability of scaffold ligands toward a more stable interaction with the surrounding cells with improved cell-scaffold anchoring and osteogenic effects (Rouahi *et al.*, 2006). However, a too small pore size can complicate the migration of cells into the scaffold. It was shown that scaffolds implanted in vivo with pore sizes close to 300 μm promote osteogenesis due to higher permeability and potential for vascularization, whereas smaller pore sizes are more favorable for chondrogenesis (Kuboki *et al.*, 2001; Walthers *et al.*, 2014). Therefore, the best compromise is to present a multi-scale porosity to cells, i.e., macro-pores allowing cell and osteon ingrowth in vivo, and micro-pores to encourage cell-scaffold ligand interactions. A key factor is the pore interconnection that is mandatory to improve the diffusion of oxygen and nutrients and outwards diffusion of waste products from the scaffold. Also, interconnected porosity favors the confluence of new bone tissue from the external to the inner parts of the scaffold and promotes vasculogenesis, i.e., the formation of a well-developed vascular network for blood circulation.

The porosity extent and pore architecture are strictly related to the scaffold mechanics. In fact, porosity supports osteointegration that gives mechanical stability while also having significant relevance on the final mechanical performance of the bone-scaffold construct. Such performance is relevant for the activity of bone cells: the transfer of dynamic, complex biomechanical forces by the macroscopic scale to the cell level activate mechano-regulatory effects involving complex biochemical reactions which are key in influencing bone tissue growth, cellular differentiation, and bone remodeling (Isaksson *et al.*, 2008). In the lack of bio-competent mechanical response, cells may be stimulated to detach from the substrate or to differentiate away from an osteogenic lineage toward an undesirable morphology (Boccaccio *et al.*, 2011). Thus, bone regeneration process is highly affected by the mechanical loading and the stress distribution along the scaffold, favoring or inhibiting the cell differentiation.

Based on these premises, the take-home message is that the ideal scaffold for bone regeneration should be provided with bone-mimicking composition and a multi-scale porous structure able to transfer the mechanical forces in a fashion similar as the natural bone. This is a major challenge for material scientists, considering the possible alteration of the desired phase composition due to the ceramic processing and, also, considering that the scaffold mechanical stiffness and porosity are directly conflicting other physical properties, with mechanical strength inversely related to increasing scaffold porosity (Chan and Leong, 2008).

Methods for Bioceramic Synthesis

Bioactive Nanoparticles: Imparting Biofunctionalities by Specific Ion Doping

Human hard tissues are basically composed of poorly crystalline carbonate-substituted nanosized apatites (CHA), with the exception of enamel, which has a high degree of crystallinity (Combes *et al.*, 2016; Dorozhkin, 2009; Gómez-Morales *et al.*, 2013; Iafisco *et al.*, 2014a; Rey *et al.*, 2007; Tampieri *et al.*, 2016). Biologic bone apatites are non-stoichiometric (Ca/P ratio less than 1.67) and calcium-deficient (i.e., they also show Ca vacancies) and incorporate ions substituting calcium, phosphorous and hydroxyl (i.e., Mg^{2+} , CO_3^{2-} , Sr^{2+} , Na^+ , K^+ , SiO_4^{4-}) in the crystal lattice, in very varying extent, depending on the state of the bone metabolism (see Fig. 1).

This is in contrast with the stoichiometric hydroxyapatite phase (i.e., $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), which is stable and poorly soluble at physiological conditions. Among heterovalent substituting ions in biological HA, carbonate (CO_3^{2-}) is the most abundant (2–8 wt% De Groot, 1983), and partially enters both in the phosphate (PO_4^{3-}) site (B-type CHA) and the OH^- site (A-type CHA) of the HA structure. Such substitution depends on the degree of bone maturation, where the newly formed bone contains prevalently B-type carbonation and the mature bone is mostly carbonated in A position (Boskey, 2006). B-type carbonated hydroxyapatites showed improved solubility, collagen deposition in vitro and reabsorption in vivo and enhanced activity for cell adhesion, when compared with stoichiometric HA and/or to A-type CHA (Landi *et al.*, 2008a; Boskey, 2006). Among other foreign ions present in the biologic apatite, magnesium (Mg^{2+}) has the marked property of increasing the nucleation kinetics of HA on collagen fibrils but, in the meantime, hampering crystal growth, thus generating nano-size HA nuclei, strongly enhancing the bioavailability of the mineral phase. In fact, magnesium is found in much higher concentrations in young and newly formed mineralized tissues and is considered

today as a fundamental element governing the first stages of bone formation (Bigi *et al.*, 1992). Trace elements present in the natural bone such as silicon are essential for healthy skeletal development in higher biological organisms (Pietak *et al.*, 2007), in particular for its role in the crosslinks between collagen and proteoglycans that stabilizes the new bone matrix and prevents enzymatic degradation (Carlisle, 1970). Strontium ions (Sr^{2+}) elicit great interest because it can regulate the activity of osteoblasts and osteoclasts by activating signaling pathways through a cation-sensing receptor (CaSR) present in both these cell lines (Takaoka *et al.*, 2010; Querido *et al.*, 2016; Marie *et al.*, 2001), thus helping to equilibrate the bone turnover. For this reason, the doping with Sr^{2+} ions elicits great interest to fabricate bioceramics able to promote bone healing in the presence of metabolic diseases such as osteoporosis (Cianferotti *et al.*, 2013; Fogelman and Blake, 2005). Interestingly, several ions and molecules can modulate bone remodeling by activating or inhibiting such CaSR, which may be considered a promising strategy for the treatment of bone diseases (Cianferotti *et al.*, 2015). A significant association has been also found between bone density and the intake of Mg, an essential micronutrient with a wide range of metabolic functions, including the maintenance of osteoporotic bone integrity (Castiglioni *et al.*, 2013).

In this context, the enhancement of the *in vivo* bioactivity and biodegradability of calcium phosphate phase was also investigated by the preparation of calcium phosphate nanoparticles (CaP NPs) by using a vast range of methods, including sol-gel, solution spray drying, hydrothermal process, precipitation techniques, solid-state reaction, and biomimetic deposition (Karimi *et al.*, 2016; Manuel *et al.*, 2004; Okada and Furuzono, 2012; Owens *et al.*, 2016). The use of biomimetic synthesis conditions (e.g., body-like synthesis temperature) helps to maintain a poorly developed and disordered nanocrystal structure allowing the entrapment of ions naturally present in the physiological environment into the structure of the mineral phase (Tampieri and Sprio, 2016; Bohner *et al.*, 2013; Iafisco and Degli Esposti, 2018). As a general rule of thumb, the ions of one element can extensively replace those of another in ionic crystals when their radii differ by no more than 15% and their charges by no more than ± 1 , provided that electrical neutrality is maintained (Goldschmidt, 1926). In general, substitution can be limited by poor structure flexibility and by the different electronegativities of the competing ions, which form bonds of different ionic behavior. Multiple ion doping has been also extensively explored. For example, the synthesis of HA powders co-substituted by silicon and other ions in anionic (carbonate) or cationic sites (magnesium) was carried out by neutralization of a calcium hydroxide suspension (calcium source) by an orthophosphoric acid solution (phosphate source) in aqueous environment, with the addition of suitable salts of the substituting ions (Sprio *et al.*, 2008; Iafisco *et al.*, 2014b). It was demonstrated that co-substitution is limited by the competition arising between ions attempting to occupy the same crystallographic site (Mg and Sr for Ca, for instance). Multiple doping was also used to investigate antibacterial ability, such as gallium or Zn, proving an effective antibacterial effect against some bacterial strains, without reducing the viability of human cells (Ballardini *et al.*, 2018; Sprio *et al.*, 2019).

CaP NPs are often developed as starting materials for the fabrication of 3-D scaffolds. However, several applications of CaP NPs as a bio-device include cell transfection, gene silencing, drug delivery, biomedical imaging (Epple *et al.*, 2010), and also for cardiac delivery of MicroRNAs (Mauro *et al.*, 2016). In this respect, functionalization processes to decorate the surface of HA or to induce specific crystallization pathways are widely explored.

Approaches for Biomimetic Functionalization of Bioceramics

Among bioceramics, synthetic hydroxyapatites exhibit excellent biological properties such as biocompatibility, bioactivity, lack of toxicity or inflammatory and immunologic responses, and also a relatively high bioresorbability (Degli Esposti *et al.*, 2018). These properties can be significantly enhanced by improving their biomimetism, that is, by preparing them with similar dimensions, morphology, surface, and chemical characteristics as for biological ones. In recent years, hydroxyapatites with different stoichiometry, size and morphology have been generated and the effects of varying synthesis conditions on stoichiometry, crystallinity and morphology have been investigated and elucidated (Dorozhkin, 2010b; Roveri *et al.*, 2008; Sadat-Shojai *et al.*, 2013).

The significant role of surface in biological phenomena such as protein adsorption and bone cell adhesion to implanted bioceramics has been put forward in the last years highlighting that the capability to tailor surface structure at the micro- and nanoscale level may boost the possibility to elicit specific responses from cells in addition to optimizing the *in vivo* response (Norton *et al.*, 2006). The surface properties of hydroxyapatite govern the affinity and the binding mechanisms between biological macromolecules (e.g., proteins) and the hydroxyapatite surface, which indirectly determines the interactions between bone cells and implanted biomaterials (see structural model in Fig. 2). The surface properties ultimately play a pivotal role in determining the success of bioceramics as bone implant and/or drug carrier (Lee *et al.*, 2014). Modifications of the surface properties can occur through the addition of new functional molecules or by a direct modification of the surface by physical techniques (e.g., photolithography). Roughness, surface charge, surface energy, wettability, microporosity, and crystallinity can be nowadays perfectly tailored by using several methodologies.

In general, surface modification of bioceramics based on hydroxyapatite by the addition of new molecules may be classified as physical or chemical functionalization. Direct immobilization or physical immobilization is the simplest way to impregnate molecules onto the hydroxyapatite surface. In this case, functional molecules are adsorbed via weak non-covalent interactions, such as electrostatic, van der Waals, hydrogen bonding, and/or hydrophobic interactions (Gómez-Morales *et al.*, 2013).

One of the most exploited methods for chemical (i.e., covalent) functionalization of bioceramics with bioactive molecules is the reaction of surface hydroxyl groups with substituted alkoxysilanes (Russo *et al.*, 2014). Silanol groups from hydrolyzed silicon alkoxides are able to condense with the hydroxyl groups of the orthophosphate scaffold, while the alkyl chain bears the functional group that can be exploited for further functionalization. Amine functional groups are extensively used for surface

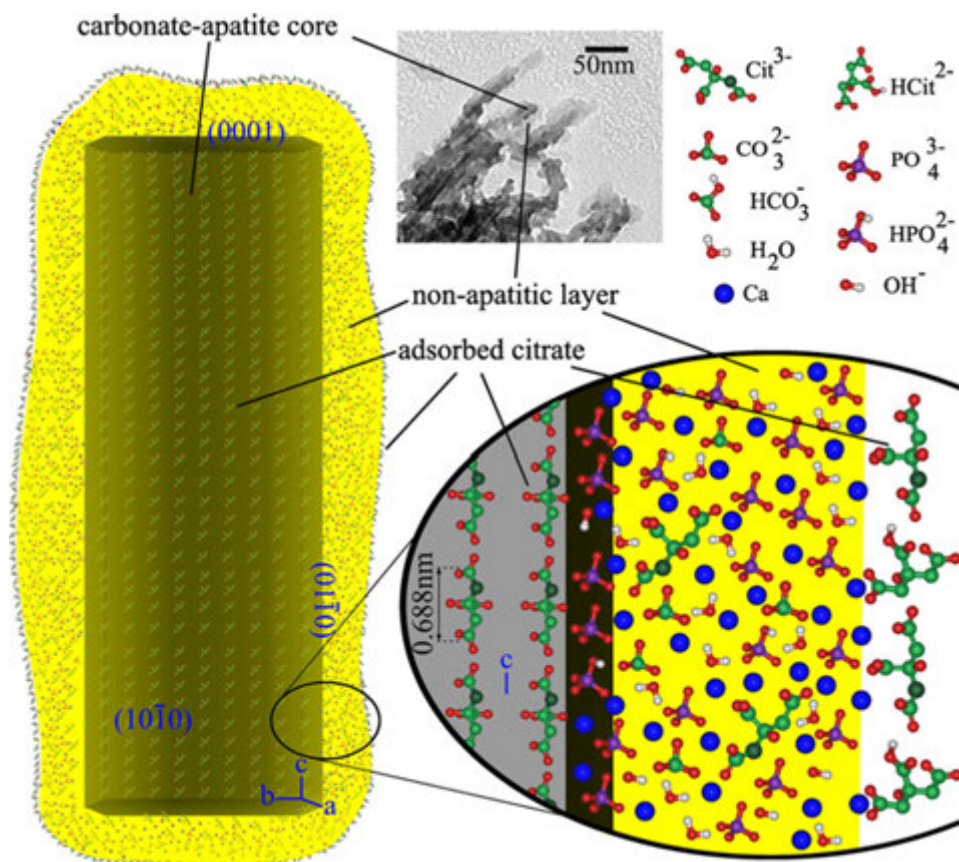


Fig. 2 Proposed model of the apatite nanoparticle composed of a well-ordered apatite core covered by a non-apatitic hydrated layer composed of ionic species, including citrate, and structural water. TEM image shows this layered structure. From Delgado-López, J.M., Iafisco, M., Rodríguez, I., *et al.*, 2012. Crystallization of bioinspired citrate-functionalized nanoapatite with tailored carbonate content. *Acta Biomaterialia* 8, 3491–3499.

functionalization because they are quite versatile and particularly suited for condensation reaction to the corresponding amides; in this respect, (3-aminopropyl)triethoxysilane (APTES) is one of the most widely used reagents. The silanol groups at one end of hydrolyzed APTES can form a binding with OH groups exposed on the material surface, while its amine group can be exploited for further covalent derivatization with organic (bio)molecules.

Taking into account the biomimetic concept, the most promising methods for the design of optimized structural and surface features are those that take inspiration from the architecture of biological tissues to improve biological affinity of the bioceramics with other materials, such as, for instance, the immobilization of biological relevant molecules on the surface of bioceramics.

For example, it was shown that hydroxyapatite pre-coated with the biomimetic arginine-glycine-aspartic acid (Arg-Gly-Asp; RGD) peptides then over-coated with serums increased mesenchymal stem cell (MSC) attachment and spreading on HA, compared to either coating alone (Sawyer *et al.*, 2005). Interestingly, the added stimulatory effect of RGD and serum on MSCs was only observed when HA was coated with low concentrations of RGD. The authors suggested that at high densities, RGD changed the conformation of absorbed osteogenic proteins (e.g., fibronectin) such that the proteins did not engage or fully activate cell surface receptor.

Recently, citrate molecules strongly bound to the surface of bone apatites (1 molecule per every 2 nm²) have been identified by advanced solid-state NMR and proposed to be responsible for the inhibition of crystal thickening and also for the stabilization of nanocrystals within the collagen matrix (Hu *et al.*, 2010). NMR studies have revealed that citrate represents 5.5 wt% of the organic matrix of bone (Hu *et al.*, 2010). Due to its excellent chemical and biochemical properties, like its excellent Ca-complexing power and its bioavailability, citrate has been molecules for the preparation of synthetic hydroxyapatite nanoparticles that incorporated the molecules to their surfaces (Lopez-Macipe *et al.*, 1998). The strong effect of citrate on hydroxyapatite crystallization has been studied using complementary techniques such as X-ray diffraction (XRD) and synchrotron X-ray Wide Angle total scattering (WAXTS) (Delgado-López *et al.*, 2014), atomic force microscopy (AFM) (Delgado-López *et al.*, 2014; Jiang *et al.*, 2008), solid-state nuclear magnetic resonance (ssNMR) (Hu *et al.*, 2010), IR and Raman spectroscopy (Delgado-López *et al.*, 2012), and high resolution transmission electron microscopy (TEM/HRTEM) (Sakhno *et al.*, 2015).

These studies have proved that citrate plays a dual role in HA crystallization. First, citrate drives the growth of HA via an amorphous precursor, and second citrate induces a non-classical oriented aggregation of the nanocrystals (Chatzipanagis *et al.*, 2016; Delgado-López *et al.*, 2014; Iafisco *et al.*, 2015). Furthermore, during crystallization early HA nanocrystals undergo an oriented

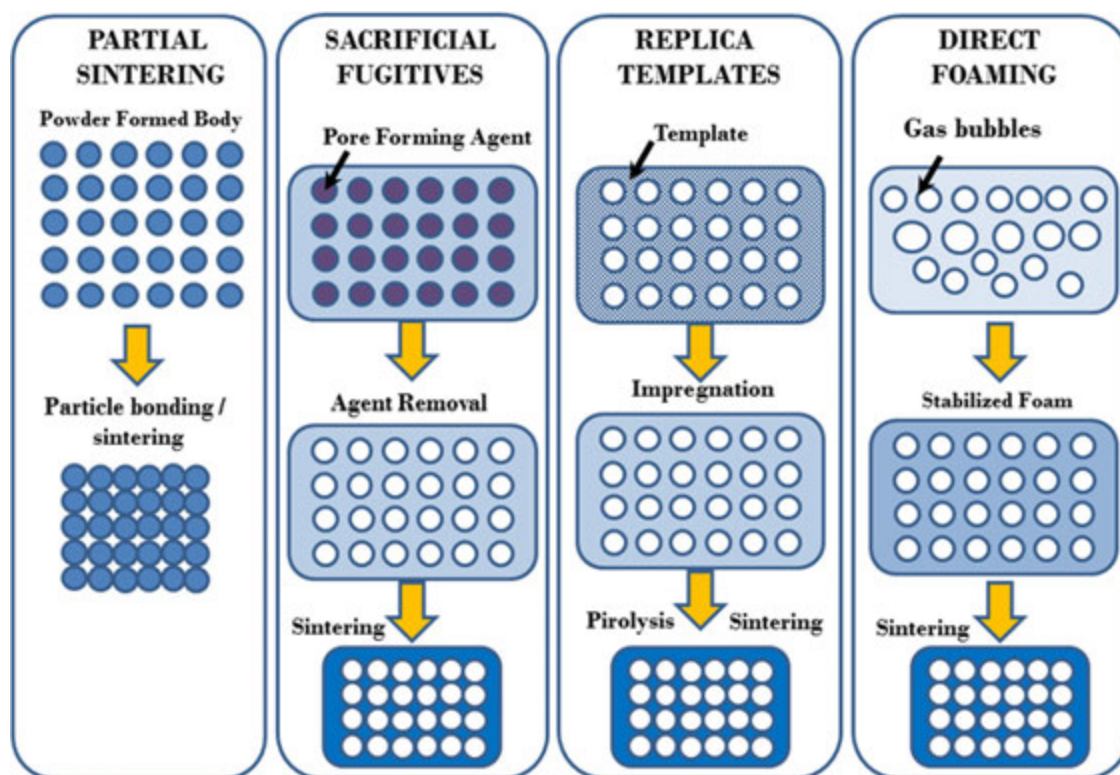


Fig. 3 Schematic representation of the four main approaches to fabricate macroporous ceramics.

aggregation by attachment of the citrate-free (0 0 0 1) faces (Iafisco *et al.*, 2015). The consequence is that hydroxyapatite nanocrystals synthesized in presence of citrate usually are nanoplatelets 80–100 nm long, 30–50 nm wide, and 5–10 nm thick. Citrate-functionalized HA nanocrystals have excellent biocompatibility and colloidal stability and have been tested for drug delivery, imaging, coating of metallic prostheses, and many other applications (Di Mauro *et al.*, 2016; Miragoli *et al.*, 2018; Martínez-Casado *et al.*, 2015; Delgado-López *et al.*, 2013).

3-D Forming Technologies to Fabricate Scaffolds with Tailored Porosity and Mechanics

The ability of a scaffold to successfully regenerate a bone defect is greatly related to the combination of key properties including chemistry, morphology, pore size, microstructure, and mechanical performance (Bose *et al.*, 2013). In this respect, solid metal implants are characterized by very different mechanical properties if compared to the surrounding bone tissue, leading to local bone-implant mismatch and bone resorption, possibly inducing stress shielding effect (when a substantial difference between the Young's modulus of bone and implant occur Arifin *et al.*, 2014) or implant failure. In fact, it was demonstrated that insufficient load transfer from the implant to the surrounding bone may result in bone reabsorption with relative loosening of the prosthetic implant (Dujovne *et al.*, 1993). This concept can be related also to the mechanotransduction, that is, the process by which bone cells convert mechanical energy, including gravity, tension, compression, and shear stresses, into biochemical signals, to maintain adult bone health and homeostasis. Despite the knowledge about the precise molecular pathways underlying such mechanotransduction phenomena is still matter of intense research, it is clear that the mechanical performance of an implanted scaffold play a vital role toward the long-term successful bone-implant construct (Stroe *et al.*, 2013; Yavropoulou and Yovos, 2016).

Non-porous bioceramics exhibit high mechanical strength, but their clinical use is very limited because of the impossibility to induce bone ingrowth into such material and to achieve substantial osteointegration (Gauthier *et al.*, 1998), as shown, for example, in various cranioplasty procedures (Sprio *et al.*, 2016b). Hence, a great deal of research effort is being devoted in the development of porous bioceramics (Lew *et al.*, 2012). They can be made by a variety of methods, including partial sintering, sacrificial fugitives, replica templates and direct foaming (Turnbull *et al.*, 2018; see Fig. 3):

- (1) *Partial sintering* of bioceramic powders involves high-temperature sintering to control the diffusion or evaporation condensation of atoms induced by heat. In this case, the final porosity is the result of a thermal treatment adequately terminated before a full densification occurs. The features of the final structure are mainly influenced by the size of starting powders as well as the high-temperature treatment, which directly impact on the degree of interaction between grains, thus determining also the final mechanical strength of the structure (Ohji and Fukushima, 2012; Ersoy *et al.*, 2015).

- (2) *Sacrificial fugitives* can be mixed with ceramic raw powders as pore forming agents. These components are generally classified into synthetic organic matters (e.g., polymer beads, organic fibers, etc.), natural organics (potato starch, cellulose, cotton, etc.), metallic and inorganic matters (nickel, carbon, fly ash, glass particles, etc.) and liquid (water, gel, emulsions, etc.). The sintering process provokes the burning out of these additives and creates pores in the consolidated ceramic structure (Ohji and Fukushima, 2012). In this case, the critical step refers to the homogeneity of the dispersion of the fugitive with the ceramic powders (Landi *et al.*, 2008b).
- (3) *The replica technique* is a valuable approach to fabricate macroporous bioceramics with interconnected porosity and open cell walls. The process begins with the impregnation of a porous or cellular structure (e.g., the most frequently used template is porous polymeric sponge, such as polyurethane or cellulose (Tampieri *et al.*, 2001)) with ceramic slurries showing appropriate viscosity and fluidity in order to achieve a homogeneous ceramic layer over the sponge walls. Finally, the as-obtained ceramic-impregnated templates are adequately dried, thermally treated to decompose the organic sponges and sintered to achieve the complete densification of the structure.
- (4) *The direct foaming method* is an interesting template-free technique to obtain porous bioceramics, involving the inclusion of gases into ceramic slurry, followed by adequate stabilization. This process is particularly promising, especially due to the absence of organic phases to be eliminated during thermal consolidation, thus preventing possible structural damaging and penalization of the final mechanical properties (Stuart *et al.*, 2006). A key factor is the development of ceramic slurries with optimal rheological properties, so that they can be dried and physically stabilized upon pouring into pre-shaped containers, while maintaining shape, size, and distribution of the air bubbles that can be controlled to optimize overall porosity and mechanics for load bearing applications (Dapporto *et al.*, 2016).

In a different approach, the method adopts liquid phases to form a channel-like porosity, typical of cortical bone, by freeze-drying. The porous channels run from the bottom to the top of the samples during freezing/heating cycles, and the pores assume an anisotropic arrangement along the solidification plane with size and distribution controlled by changing the freezing temperature gradient through the process (Landi *et al.*, 2008b).

Injectable Bioceramic Pastes and Cements

When surgery on complex-shape bone defects or voids is requested, the implantation of 3-D massive scaffolds might not be the optimal solution, so that injectable and self-hardening biomaterials would be the elective candidate. Bone cements represent an injectable and self-hardening type of materials basically produced by mixing two phases, a powder and a liquid; upon mixing, the material is injected into the body, while the resulting paste progressively hardens into a solid mass (Ginebra *et al.*, 2012; Zhang *et al.*, 2014).

In the 1960s, a self-curing polymethylmethacrylate (PMMA) formulation was used for the first time to fix the femoral stem and the acetabular component in place (Charnley, 1960). However, given the significant drawbacks affecting the use of PMMA cements for bone regeneration (Vaishya *et al.*, 2013), calcium phosphate cements (CPCs) are investigated since the 1980s, when they were firstly developed by Brown and Chow (1983) and LeGeros and Cholley (1982). In these CaPs, the hardening reaction is based on the dissolution and precipitation of calcium phosphate phases into apatitic phases during hardening and it takes place at physiological temperature, avoiding heat peaks. The absence of exothermic phenomena allows also the incorporation of drugs and biological molecules, making them good candidates for drug delivery applications (Ginebra *et al.*, 2012). The ideal CPCs should be characterized by: easy preparation, full injectability, absence of phase separation during extrusion, in vivo hardening times to guarantee an adequate mechanical support, absence of disintegration upon immersion in physiological fluids, absence of shrinkage during setting, no toxicity, radio-opacity to follow the material during in vivo implantation.

In this respect, a lot of formulations have been developed with the aim to fulfill specific requirements for bone augmentation (Aral *et al.*, 2008), reinforcement of osteoporotic bones (Libicher *et al.*, 2006), fixation of metallic implants to weakened bone (Ooms *et al.*, 2003), spinal fractures and vertebroplasty (Lewis, 2006).

The CPCs leading to the formation of HA or calcium deficient HA (CD-HA) can be classified in two main categories, which are summarized in Fig. 4: (1) Single component, in which a single calcium phosphate compound, alpha-tricalcium phosphate (α -TCP), undergoes hydrolysis to CD-HA without varying the Ca/P ratio, according to (Ginebra *et al.*, 1999); (2) Multicomponent CPCs, in which two or more calcium phosphates, some more acidic and the other basic, set following an acid-base reaction. The basic component is normally tetracalcium phosphate (TTCP), and the most widely studied acidic reactants are either dicalcium phosphate anhydrous (DCPA) or dicalcium phosphate dihydrate (DCPD). The Ca/P ratio of the final HA depends on the ratio between TTCP and the acidic component (Ginebra *et al.*, 2012; O'Neill *et al.*, 2017).

Compared to acrylic bone cements or other polymeric injectable biomaterials, CPCs have the ability to form a direct bond with bone, and their osteoconductivity. In addition, they can be resorbable, with a resorption rate that depends on their composition and microstructural features. However, the main limitation of porous CPCs is mainly related to difficult injectability, poor mechanical performance, and brittleness, which has limited their applicability to bone anatomical sites not subjected to high mechanical loading. Several methods to reduce the phase separation of CaP materials during extrusion have been established, which include: increasing the liquid-to-powder ratio and injection rate, reducing plastic limit, and increasing the viscosity of the liquid component or the repulsive force between particles (Ginebra *et al.*, 2012; Zhang *et al.*, 2014). A significant challenge is the control of the rheology of concentrated suspensions or pastes (such as CPCs) as it is the result of

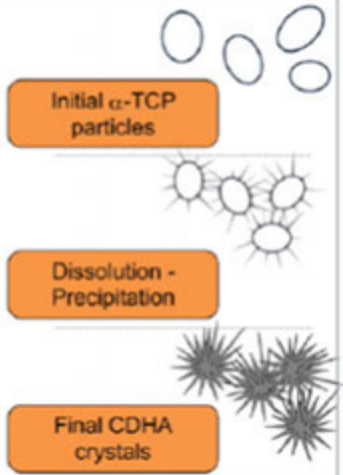
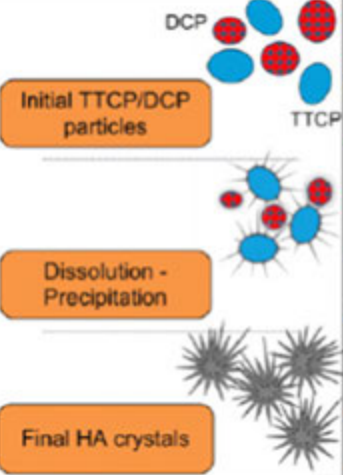
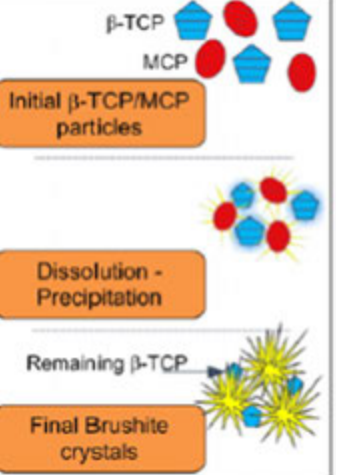
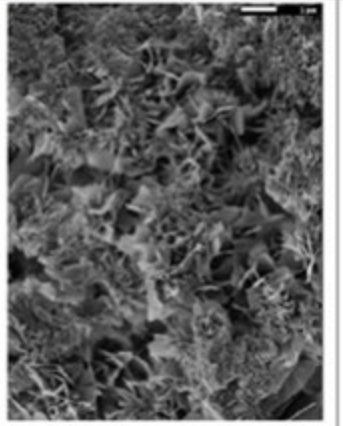
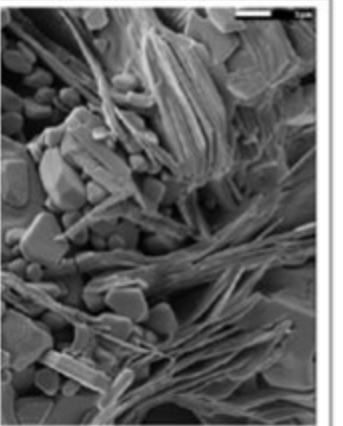
	Apatitic Cement		Brushitic Cement
	Single Component	Multiple Components	
Reactives	α -TCP	TTCP + DCPA/DCPD	β -TCP + MCPM/MCPA
Reaction	$3\alpha\text{-Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{O} \rightarrow \text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})$	$2\text{Ca}_4(\text{PO}_4)_2\text{O} + 2\text{CaHPO}_4 \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	$\beta\text{-Ca}_3(\text{PO}_4)_2 + \text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + 7\text{H}_2\text{O} \rightarrow 4\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$
Type of Reaction	Hydrolysis	Acid-Base	Acid-Base
Setting mechanism and crystal morphology			
		APATITE BRUSHITE	

Fig. 4 Classification of calcium phosphate cements, with examples of the most common formulations. From Ginebra, M.P., Canal, C., Espanol, M., Pastorino, D., Montufar, E.B., 2012. Calcium phosphate cements as drug delivery materials. *Advanced Drug Delivery Reviews* 64, 1090–1110.

complicate interactions among the powder particles and between the powder particles and the liquid component. Despite the huge amount of experiments reported in literature, the optimal tuning of the multitude of processing parameters is still a critical issue (O'Neill *et al.*, 2017).

An elective approach to prepare CPCs is based on the use of $\alpha\text{-Ca}_3(\text{PO}_4)_2$ as a metastable inorganic precursor for subsequent transformation into self-hardening hydroxyapatite cement in vivo. In this respect, cell-instructive properties can be implemented by doping with bioactive ions, commonly Sr^{2+} ions (Schumacher and Gelinsky, 2015), obtaining injectable devices able to locally release Sr^{2+} ions and modulate the activity of osteoblast and osteoclast cells. Furthermore, the addition of natural polymers to a CPC matrix is a recent strategy to improve several properties relevant for the cement processing, injectability and performance (Perez *et al.*, 2012). A recent study investigated a CPC formulation enriched with sodium alginate to improve the cement flowability during extrusion, mechanical properties and osteoinductive properties in vitro (Montesi *et al.*, 2017) and bone penetration in vivo, using a rabbit model (Sprio *et al.*, 2016a; see Fig. 5).

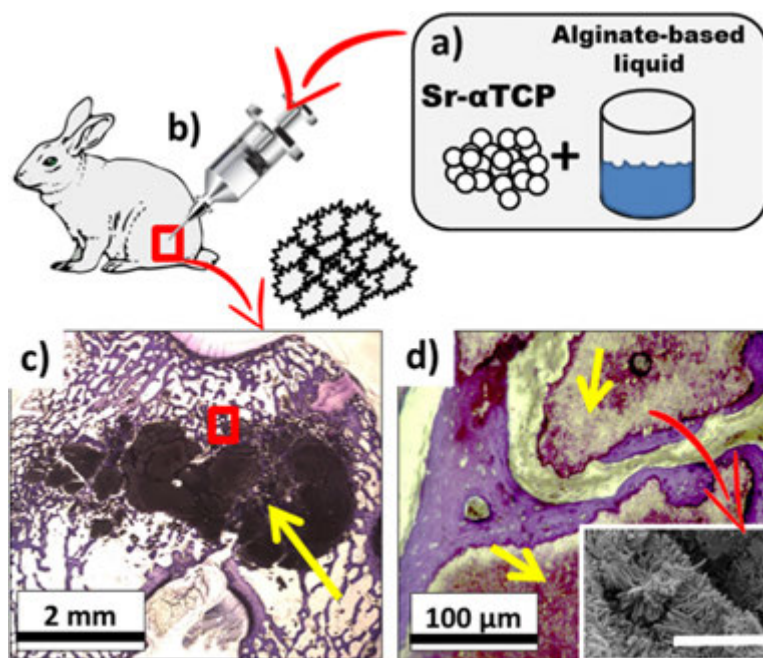


Fig. 5 Schematic representation of the alginate-containing CPC. After mixing of the powder and the liquid (a), a homogeneous paste was obtained and delivered by a syringe (b), leading to the rapid formation of apatitic crystal with a flaky to needle-like morphology (c). The paste was extruded into rabbit femoral condyle defects and hardening in vivo occurred. At 1 month after implantation (c), the bone cement (yellow arrows) revealed effective osteointegration and tight junctions with the surrounding lamellar bone tissue (d, inset scale bar: 1 μ m). From Sprio, S., Dapporto, M., Montesi, M., *et al.*, 2016a. Novel osteointegrative Sr-substituted apatitic cements enriched with alginate. *Materials* 9.

The future of CPCs relies on formulations including polymeric additives to achieve the injectability and setting behavior desired by clinicians, while providing the material with improved compression strength, reduced fragility, higher porosity, and bone-like viscoelasticity in the long term.

Additive Manufacturing of Bioceramic Scaffolds

The multi-scale features of a scaffold, i.e., pore size, shape, and interconnectivity, are difficult to be fully controlled with most of described approaches (Bose *et al.*, 2013). A claimed method to design and fabricate complex-shape structures is given by Additive Manufacturing (AM) that is a computer-aided process including slurry-based, powder-based, and bulk solid-based methods (Chen *et al.*, 2019). The general AM approach can be declined in a variety of 3-D manufacturing methods, namely vat polymerization, powder bed fusion, material extrusion, and binder jetting (Trombetta *et al.*, 2017; Ferrage *et al.*, 2016; see Fig. 6).

In particular, the *vat polymerization* (e.g., stereolithography) involves the polymerization of a photo-curable liquid polymer at the surface of a vat by a low-power ultraviolet (UV) light source; the *powder bed fusion* (e.g., laser sintering) employs a laser or electron beam to achieve selective thermal binding layer-by-layer of materials; the *material extrusion* deals with any process in which materials are deposited as continuous strands through a nozzle in an incremental layer-by-layer 3-D structure upon solidification of the extruded material, while the binder jetting selectively deposits one or more binding solutions from inkjets to induce the particles consolidation. In general, the adoption of 3-D printing technology may permit the control of scaffold shape and geometry but also a more precise tuning of fine features such as interconnected porosity, pore size, and distribution.

The possibility of manufacturing customized implants without shape limitations makes 3-D printing valuable for medical applications, especially for facial and reconstructive surgery (Hsieh *et al.*, 2017). Initially developed as a rapid prototyping method, 3-D printing technologies have been continuously evolving since the 1980s (Huang *et al.*, 2012). In the specific case of bioceramic scaffolds, the consolidation of the structure can be obtained by means of low-temperature or high-temperature post-processing treatments after the printing (Trombetta *et al.*, 2017). High-temperature sintered calcium phosphates, such as hydroxyapatite (HA), beta-tricalcium phosphate (β -TCP), have been employed to develop robocasted scaffolds for bone tissue engineering (Fu *et al.*, 2011; Franco *et al.*, 2010). However, the intrinsic low biodegradability of these high-temperature bioceramics represents a serious concern when considering its application in bone tissue engineering, where the scaffold must be degraded and progressively replaced by new bone. A possible approach to cope with such concern could be the development of self-setting ceramic ink that avoids the sintering step in the robocasted ceramic scaffolds. In this case, this process may allow the fabrication of biomimetic scaffolds, with chemical and microstructural features that are much closer to the mineral phase of bone than the high-temperature robocasted ceramics, and particularly with a higher resorption rate than sintered hydroxyapatite scaffolds. In addition, the low-temperature setting offers a valuable platform for the incorporation of biologically active molecules that can be used to promote

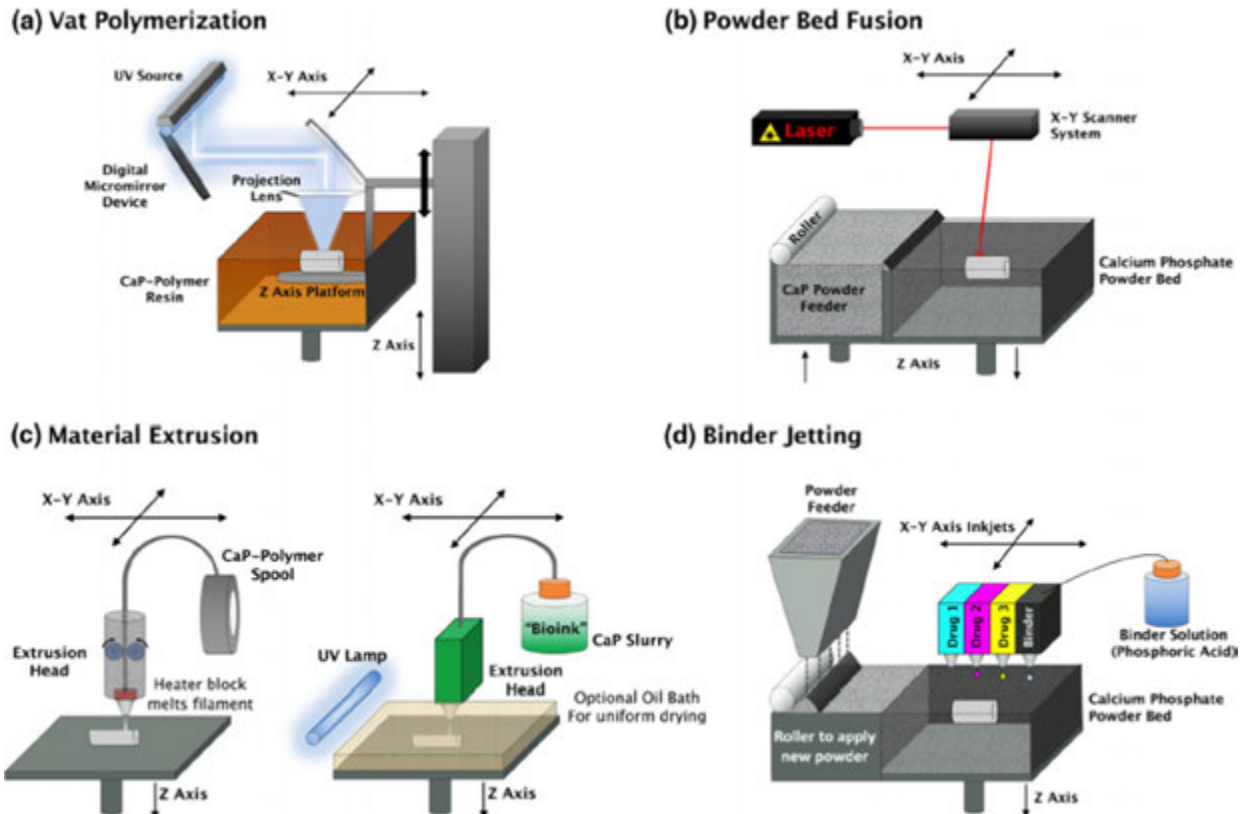


Fig. 6 Schematic depiction of the major technologies used in 3-D printing or composite calcium phosphate scaffolds for bone regeneration and drug delivery. From Trombetta, R., Inzana, J.A., Schwarz, E.M., Kates, S.L., Awad, H.A., 2017. 3-D printing of calcium phosphate ceramics for bone tissue engineering and drug delivery. *Annals of Biomedical Engineering* 45, 23–44.

osteinduction of the implant. This approach was successfully adopted by preparing self-setting formulations in some studies (Lode *et al.*, 2014; Maazouz *et al.*, 2014), even if more research is required to tune the rheology of the paste, thus improving the printing spatial resolution and the mechanical performance of the final scaffold (Xu *et al.*, 2017). In particular, the capability to extrude the material is a very critical aspect, especially if the reactivity of the particles modifies the rheological behavior over time, considerably reducing the possibility of continuous printing processes. One of the strategies to increase the injectability of calcium phosphate cements is the addition of a water-soluble polymer in the liquid phase, for example, gelatine (Montufar *et al.*, 2010) or sodium alginate (Sprio *et al.*, 2016a). The optimization of low-temperature self-hardening CPCs may broaden the applicability of this technique to potentially have in-hospital patient specific bone grafts, allowing surgeons to obtain ready-to-use bone grafts for a rapid treatment of emergency cases (Ginebra *et al.*, 2018).

Despite the various benefits and applications, a critical aspect of 3-D printing is represented by the intrinsically inanimate characterization of the printed scaffolds, as only the initial state is considered. In this respect, a more recent technique was introduced, called “4-D-Bioprinting”, where the additional dimension is represented by the time, intended as the responsiveness of the material, evolving overtime after implantation (Gao *et al.*, 2016).

Preclinical and Clinical Testing of Bioceramics

Bioceramics were extensively tested in the last decades for bone regeneration in both pre-clinical and clinical scenarios (Daculsi *et al.*, 2014). A large variety of commercial bioceramic bone substitutes have been developed; however, the major cruciality is represented by the difficult achievement of all the prerequisites for bone reconstruction. On the basis of the specific clinical scenario, bioceramics have to be mechanically competent, or injectable and self-hardening, or also shapeable. The results of animal experiments and clinical follow up studies showed that bioinert ceramics are characterized by high mechanical strength and minimal or no tissue reaction, confirming their cytocompatibility, but without any bonding with the bone. Conversely, bioglasses and glass ceramics exhibited nontoxicity, chemical bond to bone and osteoinductive property, while calcium phosphate ceramics exhibit nontoxicity, bioresorption ability and osteoinductive property (Thamaraiselvi and Rajeswari, 2003).

Porous HA scaffolds have been tested in different animal studies (Ciocca *et al.*, 2013; Woodard *et al.*, 2007) and clinical cases (Edwards and Ousterhout, 1987; Stefini *et al.*, 2015). In this latter cases, one of the most demanded clinical need in bone tissue

engineering refers to the regeneration of large skull defects (Sprio *et al.*, 2016b). A great deal of research effort has been devoted to the development of different biomaterials, including titanium, acrylic meshes as well as calcium phosphate-based bone grafts. Despite some interesting features in terms of shaping capability and mechanical performance, some drawbacks have been also reported, in terms of enhanced cold/heat conduction or hypersensitivity in contact with metals (Hanasono *et al.*, 2009; Lee *et al.*, 2009). In this respect, such inert materials also exhibit poor osteogenic and osteoconductivity, so that extensive penetration of the surrounding bone cells in the implant is severely compromised. In the last decades, hydroxyapatite-based porous scaffolds also came into clinical practice, basically due to possibility to customize the shape with the patient's defect, improved biocompatibility and biomimetic features. The hydrophilic character of HA favors cell attachment to the surface of the implanted scaffold, while the capability to produce HA scaffolds with open and interconnected multiscale porosity induced extensive bone ingrowth into the pores (Karageorgiou and Kaplan, 2005). Furthermore, histological examinations evidenced extensive bone penetration, particularly along the epidural surfaces (Boyde *et al.*, 1999). The improved biocompatibility in vivo of HA was also demonstrated by the absence of allergic reactions, infections, and morbidity during a two-years follow-up retrospective study (Staffa *et al.*, 2012). Indeed, nosocomial and post-operative infections are becoming a pandemic problem, due to the increasing bacterial resistance to antibiotic drugs, so that the use of implantable biomaterials effective to limit the biofilm formation is becoming imperative. Recent results report that calcium phosphates, particularly substituted HA phases, can be elective to elicit antimicrobial effect against a wide spectrum of infective strains, basing only on compositional and crystallinity features (Ballardini *et al.*, 2018; Sprio *et al.*, 2019).

Future Perspectives in the Fabrication of Regenerative Bioceramics

In the last decades, considerable advances were done in material science to replace inert, potentially toxic material with bioceramics permitting safer and improved long-term performance. Nevertheless, in spite of some relevant clinical success, several needs remain unmet so that the development of effective regenerative bioceramics is still an open challenge. A critical issue is surely the difficulty to overcome the so-called "death valley" from the lab to the patient bed and translate new biomaterials to clinics. From a scientific perspective, new fabrication approaches may enable a new generation of smart and multi-functional devices to reach the difficult goal to obtain porous materials showing bio-competent chemistry, structure and mechanics at the same time. In particular, new approaches for the thermal consolidation of bioceramics (e.g., conventional or pressureless spark plasma sintering, microwave sintering) can help to tune the nano and microstructural features of particles and grains, preventing their uncontrolled growth, toward adequate mechanical performance to promote long-term interaction between the scaffold and the surrounding load-bearing bone tissue. Furthermore, the research on CaP bone cements is highly active nowadays and promising to give new injectable biomaterials with enhanced bioactivity and mechanics, particularly for bone regions difficult to access by 3-D solid scaffolds and, also, to replace acrylic materials in spinal and neurosurgical applications. In this respect, new advances are envisaged also in additive manufacturing applied to self-hardening ceramic pastes, to overcome existing technological limitations and achieve 3-D scaffolds with highly complex structures that are impossible to be fabricated with conventional manufacturing methods.

Finally, the occurrence of post-op infections often hampers a positive clinical outcome. In this respect, the synthesis of bioceramics intrinsically provided with antibacterial and osteoinductive properties is an emerging research topic that promises to give findings, fundamental for clinical applications and substantially contributing to solve many of still unmet clinical needs.

References

- Aral, A., Yalcin, S., Karabuda, Z.C., *et al.*, 2008. Injectable calcium phosphate cement as a graft material for maxillary sinus augmentation: An experimental pilot study. *Clinical Oral Implants Research* 19, 612–617.
- Arifin, A., Bakar, A., Muhamad, N., Syarif, J., Ramli, M.I., 2014. Material processing of hydroxyapatite and titanium alloy (HA/Ti) composite as implant materials using powder metallurgy: A review. *Materials & Design* 55, 165–175.
- Ashworth, J.C., Mehr, M., Buxton, P.G., Best, S.M., Cameron, R.E., 2018. Optimising collagen scaffold architecture for enhanced periodontal ligament fibroblast migration. *Journal of Materials Science: Materials in Medicine* 29, 166.
- Ballardini, A., Montesi, M., Panseri, S., *et al.*, 2018. New hydroxyapatite nanophases with enhanced osteogenic and anti-bacterial activity. *Journal of Biomedical Materials Research Part A* 106, 521–530.
- Basu, S., Basu, B., 2019. Doped biphasic calcium phosphate: Synthesis and structure. *Journal of Asian Ceramic Societies* 7, 265–283.
- Bigi, A., Foresti, E., Gregorini, R., *et al.*, 1992. The role of magnesium on the structure of biological apatites. *Calcified Tissue International* 50, 439–444.
- Biltz, R.M., Pellegrino, E.D., 1969. The chemical anatomy of bone. I. A comparative study of bone composition in sixteen vertebrates. *Journal of Bone and Joint Surgery* 51, 456–466.
- Boccaccio, A., Ballini, A., Pappalettere, C., *et al.*, 2011. Finite element method (FEM), mechanobiology and biomimetic scaffolds in bone tissue engineering. *International Journal of Biological Sciences* 7, 112–132.
- Bohner, M., Tadier, S., van Garderen, N., *et al.*, 2013. Synthesis of spherical calcium phosphate particles for dental and orthopedic applications. *Biomater* 3.e25103.
- Bose, S., Vahabzadeh, S., Bandyopadhyay, A., 2013. Bone tissue engineering using 3D printing. *Materials Today* 16, 496–504.
- Boskey, A., 2006. Mineralization, structure and function of bone. In: Seibel, M., Robins, S., Bilezikian, J. (Eds.), *Dynamics of Bone and Cartilage Metabolism*. Elsevier, pp. 201–212.
- Boyde, A., Corsi, A., Quarto, R., Cancedda, R., Bianco, P., 1999. Osteoconduction in large macroporous hydroxyapatite ceramic implants: Evidence for a complementary integration and disintegration mechanism. *Bone* 24, 579–589.

- Brown, W.E., Chow, L.C., 1983. A new calcium phosphate setting cement. *Journal of Dental Research* 62, 672.
- Bružauskaitė, I., Bironaitė, D., Bagdonas, E., Bernotienė, E., 2016. Scaffolds and cells for tissue regeneration: Different scaffold pore sizes-different cell effects. *Cytotechnology* 68, 355–369.
- Carlisle, E.M., 1970. Silicon: A possible factor in bone calcification. *Science* 167, 279–280.
- Castiglioni, S., Cazzaniga, A., Albisetti, W., Maier, J.A.M., 2013. Magnesium and osteoporosis: Current state of knowledge and future research directions. *Nutrients* 5, 3022–3033.
- Chan, B.P., Leong, K.W., 2008. Scaffolding in tissue engineering: General approaches and tissue-specific considerations. *European Spine Journal* 17 (Suppl 4), 467–479.
- Charnley, J., 1960. Anchorage of the femoral head prosthesis to the shaft of the femur. *Journal of Bone and Joint Surgery* 42-B, 28–30.
- Chatzipanagis, K., Iafisco, M., Roncal-Herrero, T., et al., 2016. Crystallization of citrate-stabilized amorphous calcium phosphate to nanocrystalline apatite: A surface-mediated transformation. *CrystEngComm* 18.
- Chen, Z., Li, Z., Li, J., et al., 2019. 3D printing of ceramics: A review. *Journal of the European Ceramic Society* 39, 661–687.
- Cianferrotti, L., D'Asta, F., Brandi, M.L., 2013. A review on strontium ranelate long-term antifracture efficacy in the treatment of postmenopausal osteoporosis. *Therapeutic Advances in Musculoskeletal Disease* 5, 127–139.
- Cianferrotti, L., Gomes, A.R., Fabbri, S., Tanini, A., Brandi, M.L., 2015. The calcium-sensing receptor in bone metabolism: From bench to bedside and back. *Osteoporosis International* 26, 2055–2071.
- Ciocca, L., Donati, D., Ragazzini, S., et al., 2013. Mesenchymal stem cells and platelet gel improve bone deposition within CAD-CAM custom-made ceramic HA scaffolds for condyle substitution. *Biomed Research International* 2013, 1–10.
- Combes, C., Cazalbou, S., Rey, C., 2016. Apatite biominerals. *Minerals* 6, 34.
- Daculsi, G., Aguado, E., Miramond, T., 2014. Essential requirements for resorbable bioceramic development: Research, manufacturing, and preclinical studies. In: Antoniac, I.V. (Ed.), *Handbook of Bioceramics and Biocomposites*. Cham: Springer International Publishing.
- Dapporto, M., Sprio, S., Fabbri, C., Figallo, E., Tampieri, A., 2016. A novel route for the synthesis of macroporous bioceramics for bone regeneration. *Journal of the European Ceramic Society* 36, 2383–2388.
- De Groot, K., 1983. *Bioceramics of Calcium Phosphate*, 1, *Biocompatibility of Clinical Implant Materials*, vol. 1, CRC Press. Boca Raton, Florida. 199–224.
- Degli Esposti, L., Carella, F., Adamiano, A., Tampieri, A., Iafisco, M., 2018. Calcium phosphate-based nanosystems for advanced targeted nanomedicine. *Drug Development and Industrial Pharmacy* 44, 1223–1238.
- Delgado-López, J.M., Iafisco, M., Rodríguez-Ruiz, I., Gómez-Morales, J., 2013. Bio-inspired citrate-functionalized apatite thin films crystallized on Ti–6Al–4V implants pre-coated with corrosion resistant layers. *Journal of Inorganic Biochemistry* 127, 261–268.
- Delgado-López, J.M., Iafisco, M., Rodríguez, I., et al., 2012. Crystallization of bioinspired citrate-functionalized nanoapatite with tailored carbonate content. *Acta Biomaterialia* 8, 3491–3499.
- Delgado-López, J.M., Frison, R., Cervellino, A., et al., 2014. Crystal Size, Morphology, and Growth Mechanism in Bio-Inspired Apatite Nanocrystals. *Advanced Functional Materials* 24, 1090–1099.
- Di Mauro, V., Iafisco, M., Salvarani, N., et al., 2016. Bioinspired negatively charged calcium phosphate nanocarriers for cardiac delivery of MicroRNAs. *Nanomedicine* 11, 891–906.
- Dorozhkin, S.V., 2009. Nanodimensional and nanocrystalline apatites and other calcium orthophosphates in biomedical engineering, biology and medicine. *Materials* 2, 1975–2045.
- Dorozhkin, S.V., 2010a. Calcium orthophosphates as bioceramics: State of the art. *Journal of Functional Biomaterials* 1, 22–107.
- Dorozhkin, S.V., 2010b. Nanosized and nanocrystalline calcium orthophosphates. *Acta Biomaterialia* 6, 715–734.
- Dujovne, A.R., Bohn, J., Krygier, J.J., Miller, J.E., Brooks, C.E., 1993. Mechanical compatibility of noncemented hip prostheses with the human femur. *The Journal of Arthroplasty* 8, 7–22.
- Edwards, M.S., Ousterhout, D.K., 1987. Autogenic skull bone grafts to reconstruct large or complex skull defects in children and adolescents. *Neurosurgery* 20, 273–280.
- Epple, M., Ganesan, K., Heumann, R., et al., 2010. Application of calcium phosphate nanoparticles in biomedicine. *Journal of Materials Chemistry* 20, 18–23.
- Ersay, N.M., Aydoğdu, H.M., Değirmenci, B.Ü., Çökük, N., Sevimay, M., 2015. The effects of sintering temperature and duration on the flexural strength and grain size of zirconia. *Acta Biomaterialia Odontologica Scandinavica* 1, 43–50.
- Ferrage, L., Bertrand, G., Lenormand, P., Grossin, D., Ben-Nissan, B., 2016. A review of the additive manufacturing (3DP) of bioceramics: Alumina, zirconia (PSZ) and hydroxyapatite. *Journal of the Australian Ceramic Society* 53.
- Fogelman, I., Blake, G.M., 2005. Strontium ranelate for the treatment of osteoporosis. *British Medical Journal* 330, 1400–1401.
- Franco, J., Hunger, P., Launey, M.E., Tomsia, A.P., Saiz, E., 2010. Direct write assembly of calcium phosphate scaffolds using a water-based hydrogel. *Acta Biomaterialia* 6, 218–228.
- Fu, Q., Saiz, E., Tomsia, A.P., 2011. Bioinspired strong and highly porous glass scaffolds. *Advanced Functional Materials* 21, 1058–1063.
- Gao, B., Yang, Q., Zhao, X., et al., 2016. 4D bioprinting for biomedical applications. *Trends Biotechnology* 34, 746–756.
- Gauthier, O., Boulter, J.M., Aguado, E., Pilet, P., Daculsi, G., 1998. Macroporous biphasic calcium phosphate ceramics: Influence of macropore diameter and macroporosity percentage on bone ingrowth. *Biomaterials* 19, 133–139.
- Ginebra, M.P., Canal, C., Espanol, M., Pastorino, D., Montufar, E.B., 2012. Calcium phosphate cements as drug delivery materials. *Advanced Drug Delivery Reviews* 64, 1090–1110.
- Ginebra, M.-P., Espanol, M., Maazouz, Y., Bergez, V., Pastorino, D., 2018. Bioceramics and bone healing. *EFORT Open Reviews* 3, 173–183.
- Ginebra, M.-P., Fernández, E., Driessens, F.C.M., Planell, J.A., 1999. Modeling of the hydrolysis of α -tricalcium phosphate. *Journal of the American Ceramic Society* 82, 2808–2812.
- Goldschmidt, V.M., 1926. Die Gesetze der Kristallochemie. *Naturwissenschaften* 14, 477–485.
- Gomes, S., Vichery, C., Descamps, S., et al., 2018. Cu-doping of calcium phosphate bioceramics: From mechanism to the control of cytotoxicity. *Acta Biomaterialia* 65, 462–474.
- Gómez-Morales, J., Iafisco, M., Delgado-López, J.M., Sarda, S., Drouet, C., 2013. Progress on the preparation of nanocrystalline apatites and surface characterization: Overview of fundamental and applied aspects. *Progress in Crystal Growth and Characterization of Materials* 59, 1–46.
- Hanasono, M.M., Goel, N., DeMonte, F., 2009. Calvarial reconstruction with polyetheretherketone implants. *Annals of Plastic Surgery* 62, 653–655.
- Hippocrates, Adams, F., 1939. *The Genuine Works of Hippocrates*. Baltimore: Francis Adams, Williams & Wilkins, pp. 8–9.
- Hsieh, T.Y., Dedhia, R., Cervenka, B., Tollefson, T.T., 2017. 3D printing: Current use in facial plastic and reconstructive surgery. *Current Opinion in Otolaryngology & Head and Neck Surgery* 25, 291–299.
- Huang, S., Liu, P., Mokasdar, A., Hou, L., 2012. Additive manufacturing and its societal impact: A literature review. *The International Journal of Advanced Manufacturing Technology*. 1191–1203.
- Hu, Y.-Y., Rawal, A., Schmidt-Rohr, K., 2010. Strongly bound citrate stabilizes the apatite nanocrystals in bone. *Proceedings of the National Academy of Sciences* 107 (52), 22425–22429.
- Iafisco, M., Degli Esposti, L., 2018. Fluoride-doped amorphous calcium phosphate nanoparticles as a promising biomimetic material for dental remineralization. *Scientific Reports* 8, 17016.

- Iafisco, M., Degli Esposti, L., Ramírez-Rodríguez, G.B., *et al.*, 2018. Fluoride-doped amorphous calcium phosphate nanoparticles as a promising biomimetic material for dental remineralization. *Scientific Reports* 8, 17016.
- Iafisco, M., DelgadoLópez, J.M., Drouet, C., 2014a. Nanocrystalline apatites: Synthesis, physical-chemical and thermodynamic characterization. In: *Apatite: Synthesis, Structural Characterization and Biomedical Applications. Geology and Mineralogy Research Developments*. New York: Nova Science Publishers, pp. 49–80.
- Iafisco, M., Ramírez-Rodríguez, G.B., Sakhno, Y., *et al.*, 2015. The growth mechanism of apatite nanocrystals assisted by citrate: Relevance to bone biomineralization. *CrystEngComm* 17, 507–511.
- Iafisco, M., Ruffini, A., Adamiano, A., Sprio, S., Tampieri, A., 2014b. Biomimetic magnesium-carbonate-apatite nanocrystals endowed with strontium ions as anti-osteoporotic trigger. *Materials Science & Engineering C* 35, 212–219.
- Isaksson, H., van Donkelaar, C.C., Huiskes, R., Ito, K., 2008. A mechano-regulatory bone-healing model incorporating cell-phenotype specific activity. *Journal of Theoretical Biology* 252, 230–246.
- Jiang, W., Pan, H., Cai, Y., *et al.*, 2008. Atomic force microscopy reveals hydroxyapatite—citrate interfacial structure at the atomic level. *Langmuir* 24, 12446–12451.
- Karageorgiou, V., Kaplan, D., 2005. Porosity of 3D biomaterial scaffolds and osteogenesis. *Biomaterials* 26, 5474–5491.
- Karimi, M., Hesaraki, S., Alizadeh, M., Kazemzadeh, A., 2016. Synthesis of calcium phosphate nanoparticles in deep-eutectic choline chloride–urea medium: Investigating the role of synthesis temperature on phase characteristics and physical properties. *Ceramics International* 42, 2780–2788.
- Kuboki, Y., Jin, Q., Takita, H., 2001. Geometry of carriers controlling phenotypic expression in BMP-induced osteogenesis and chondrogenesis. *Journal of Bone and Joint Surgery* 83-A (Suppl 1), S105–S115.
- Landi, E., Sprio, S., Sandri, M., Celotti, G., Tampieri, A., 2008a. Development of Sr and CO₃ co-substituted hydroxyapatites for biomedical applications. *Acta Biomaterialia* 4, 656–663.
- Landi, E., Valentini, F., Tampieri, A., 2008b. Porous hydroxyapatite/gelatin scaffolds with ice-designed channel-like porosity for biomedical applications. *Acta Biomaterialia* 4, 1620–1626.
- Lee, W.-H., Loo, C.-Y., Rohanizadeh, R., 2014. A review of chemical surface modification of bioceramics: Effects on protein adsorption and cellular response. *Colloids and Surfaces B: Biointerfaces* 122, 823–834.
- Lee, S.C., Wu, C.T., Lee, S.T., Chen, P.J., 2009. Cranioplasty using polymethyl methacrylate prostheses. *Journal of Clinical Neuroscience* 16, 56–63.
- LeGeros, R.Z., Cholley, A.S.A., 1982. Apatitic calcium phosphates: Possible dental restorative materials. *Journal of Dental Research* 61, 343.
- Lewis, G., 2006. Injectable bone cements for use in vertebroplasty and kyphoplasty: State-of-the-art review. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 76, 456–468.
- Lew, K.S., Othman, R., Ishikawa, K., Yeoh, F.Y., 2012. Macroporous bioceramics: A remarkable material for bone regeneration. *Journal of Biomaterials Applications* 27, 345–358.
- Libicher, M., Hillmeier, J., Liegibel, U., *et al.*, 2006. Osseous integration of calcium phosphate in osteoporotic vertebral fractures after kyphoplasty: Initial results from a clinical and experimental pilot study. *Osteoporosis International* 17, 1208–1215.
- Lode, A., Meissner, K., Luo, Y., *et al.*, 2014. Fabrication of porous scaffolds by three-dimensional plotting of a pasty calcium phosphate bone cement under mild conditions. *Journal of Tissue Engineering and Regenerative Medicine* 8, 682–693.
- Lopez-Macipe, A., Gomez-Morales, J., Rodriguez-Clemente, R., 1998. Nanosized hydroxyapatite precipitation from homogeneous calcium/citrate/phosphate solutions using microwave and conventional heating. *Advanced Materials* 10, 49.
- Maazouz, Y., Montufar, E.B., Guillem-Marti, J., *et al.*, 2014. Robocasting of biomimetic hydroxyapatite scaffolds using self-setting inks. *Journal of Materials Chemistry B* 2, 5378–5386.
- Marie, P.J., Ammann, P., Boivin, G., Rey, C., 2001. Mechanisms of action and therapeutic potential of strontium in bone. *Calcified Tissue International* 69, 121–129.
- Manuel, C., Foster, M., Monteiro, F., *et al.*, 2004. Preparation and characterization of calcium phosphate nanoparticles. *Key Engineering Materials* 254–256, 903–906.
- Martínez-Casado, F.J., Iafisco, M., Delgado-López, J.M., *et al.*, 2015. Bioinspired citrate–apatite nanocrystals doped with divalent transition metal ions. *Crystal Growth & Design* 16, 145–153.
- Mauro, V.D., Iafisco, M., Salvarani, N., *et al.*, 2016. Bioinspired negatively charged calcium phosphate nanocarriers for cardiac delivery of MicroRNAs. *Nanomedicine* 11, 891–906.
- Meco, E., Lampe, K.J., 2018. Microscale architecture in biomaterial scaffolds for spatial control of neural cell behavior. *Frontiers in Materials* 5.
- Miragoli, M., Ceriotti, P., Iafisco, M., *et al.*, 2018. Inhalation of peptide-loaded nanoparticles improves heart failure. *Science Translational Medicine* 10, (eaan6205).
- Montesi, M., Panseri, S., Dapporto, M., Tampieri, A., Sprio, S., 2017. Sr-substituted bone cements direct mesenchymal stem cells, osteoblasts and osteoclasts fate. *PLoS One* 12.
- Montufar, E.B., Traykova, T., Schacht, E., *et al.*, 2010. Self-hardening calcium deficient hydroxyapatite/gelatin foams for bone regeneration. *Journal of Materials Science: Materials in Medicine* 21, 863–869.
- Norton, J., Malik, K.R., Darr, J.A., Rehman, I., 2006. Recent developments in processing and surface modification of hydroxyapatite. *Advances in Applied Ceramics* 105, 113–139.
- Ohji, T., Fukushima, M., 2012. Macro-porous ceramics: Processing and properties. *International Materials Reviews* 57, 115–131.
- Okada, M., Furuzono, T., 2012. Hydroxylapatite nanoparticles: Fabrication methods and medical applications. *Science and Technology of Advanced Materials* 13.064103.
- O'Neill, R., McCarthy, H.O., Montufar, E.B., *et al.*, 2017. Critical review: Injectability of calcium phosphate pastes and cements. *Acta Biomaterialia* 50, 1–19.
- Ooms, E., Wolke, J.G., van der Waerden, J.P., Jansen, J.A., 2003. Use of injectable calcium-phosphate cement for the fixation of titanium implants: An experimental study in goats. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 66, 447–456.
- Othman, Z., Pastor, B., van Rijt, S., Habibovic, P., 2018. Understanding interactions between biomaterials and biological systems using proteomics. *Biomaterials* 167.
- Owens, G.J., Singh, R.K., Foroutan, F., *et al.*, 2016. Sol–gel based materials for biomedical applications. *Progress in Materials Science* 77, 1–79.
- Perez, R.A., Kim, H.W., Ginebra, M.P., 2012. Polymeric additives to enhance the functional properties of calcium phosphate cements. *Journal of Tissue Engineering* 3.
- Pietak, A.M., Reid, J.W., Stott, M.J., Sayer, M., 2007. Silicon substitution in the calcium phosphate bioceramics. *Biomaterials* 28, 4023–4032.
- Prakasam, M., Locs, J., Salma-Ancane, K., *et al.*, 2015. Fabrication, properties and applications of dense hydroxyapatite: A review. *Journal of Functional Biomaterials* 6, 1099–1140.
- Querido, W., Rossi, A.L., Farina, M., 2016. The effects of strontium on bone mineral: A review on current knowledge and microanalytical approaches. *Micron* 80, 122–134.
- Rey, C., Combes, C., Drouet, C., Sfihi, H., Barroug, A., 2007. Physico-chemical properties of nanocrystalline apatites: Implications for biominerals and biomaterials. *Materials Science and Engineering: C* 27, 198–205.
- Rouahi, M., Gallet, O., Champion, E., *et al.*, 2006. Influence of hydroxyapatite microstructure on human bone cell response. *Journal of Biomedical Materials Research Part A* 78, 222–235.
- Roveri, N., Palazzo, B., Iafisco, M., 2008. The role of biomimetism in developing nanostructured inorganic matrices for drug delivery. *Expert Opinion on Drug Delivery* 5, 861–877.
- Russo, L., Taraballi, F., Lupo, C., *et al.*, 2014. Carbonate hydroxyapatite functionalization: A comparative study towards (bio)molecules fixation. *Interface Focus* 4.
- Sadat-Shojai, M., Khorasani, M.-T., Dinpanah-Khoshdargi, E., Jamshidi, A., 2013. Synthesis methods for nanosized hydroxyapatite with diverse structures. *Acta Biomaterialia* 9, 7591–7621.
- Sakhno, Y., Ivanchenko, P., Iafisco, M., Tampieri, A., Martra, G., 2015. A step toward control of the surface structure of biomimetic hydroxyapatite nanoparticles: Effect of carboxylates on the {010} P-rich/Ca-rich facets ratio. *The Journal of Physical Chemistry C* 119, 5928–5937.

- Sawyer, A.A., Hennessy, K.M., Bellis, S.L., 2005. Regulation of mesenchymal stem cell attachment and spreading on hydroxyapatite by RGD peptides and adsorbed serum proteins. *Biomaterials* 26, 1467–1475.
- Schumacher, M., Gelinsky, M., 2015. Strontium modified calcium phosphate cements – Approaches towards targeted stimulation of bone turnover. *Journal of Materials Chemistry B* 3, 4626–4640.
- Shahrezaee, M., Raz, M., Shishehbor, S., *et al.*, 2018. Synthesis of magnesium doped amorphous calcium phosphate as a bioceramic for biomedical application: In vitro study. *Silicon* 10, 1171–1179.
- Shegarfi, H., Reikeras, O., 2009. Review article: Bone transplantation and immune response. *Journal of Orthopaedic Surgery* 17, 206–211.
- Sprio, S., Dapporto, M., Montesi, M., *et al.*, 2016a. Novel osteointegrative Sr-substituted apatitic cements enriched with alginate. *Materials* 9.
- Sprio, S., Fricia, M., Maddalena, G.F., Nataloni, A., Tampieri, A., 2016b. Osteointegration in cranial bone reconstruction: A goal to achieve. *Journal of Applied Biomaterials & Functional Materials* 14, 470–476.
- Sprio, S., Preti, L., Montesi, M., *et al.*, 2019. Surface phenomena enhancing the antibacterial and osteogenic ability of nanocrystalline hydroxyapatite, activated by multiple ions doping. *ACS Biomaterials Science & Engineering* 5 (11), 5947–5959.
- Sprio, S., Tampieri, A., Landi, E., *et al.*, 2008. Physico-chemical properties and solubility behaviour of multi-substituted hydroxyapatite powders containing silicon. *Materials Science and Engineering: C* 28, 179–187.
- Staffa, G., Barbanera, A., Faiola, A., *et al.*, 2012. Custom made bioceramic implants in complex and large cranial reconstruction: A two-year follow-up. *Journal of Cranio-Maxillofacial Surgery* 40, E65–E70.
- Stefini, R., Zanotti, B., Nataloni, A., *et al.*, 2015. The efficacy of custom-made porous hydroxyapatite prostheses for cranioplasty: Evaluation of postmarketing data on 2697 patients. *Journal of Applied Biomaterials & Functional Materials* 13, e136–e144.
- Stevens, B., Yang, Y., Mohandas, A., Stucker, B., Nguyen, K.T., 2008. A review of materials, fabrication methods, and strategies used to enhance bone regeneration in engineered bone tissues. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 85B, 573–582.
- Stroe, M.C., Crolet, J.M., Racila, M., 2013. Mechanotransduction in cortical bone and the role of piezoelectricity: A numerical approach. *Computer Methods in Biomechanics and Biomedical Engineering* 16, 119–129.
- Stuart, A.R., Gonzenbach, U.T., Tervoort, E., Gauckler, L.J., 2006. Processing routes to macroporous ceramics: A review. *Journal of the American Ceramic Society* 89, 1771–1789.
- Takaoka, S., Yamaguchi, T., Yano, S., Yamauchi, M., Sugimoto, T., 2010. The calcium-sensing receptor (CaR) is involved in strontium ranelate-induced osteoblast differentiation and mineralization. *Hormone and Metabolic Research* 42, 627–631.
- Tampieri, A., Celotti, G., Sprio, S., Delcogliano, A., Franzese, S., 2001. Porosity-graded hydroxyapatite ceramics to replace natural bone. *Biomaterials* 22, 1365–1370.
- Tampieri, A., Iafisco, M., Sprio, S., *et al.*, 2016. Hydroxyapatite: From nanocrystals to hybrid nanocomposites for regenerative medicine. In: Antoniac, I.V. (Ed.), *Handbook of Bioceramics and Biocomposites*. Cham: Springer International Publishing.
- Tampieri, A., Sprio, S., 2016. *Bio-Inspired Regenerative Medicine: Materials, Processes, and Clinical Applications*. Jenny Stanford Publishing.
- Tampieri, A., Sprio, S., Sandri, M., Valentini, F., 2011. Mimicking natural bio-mineralization processes: A new tool for osteochondral scaffold development. *Trends in Biotechnology* 29, 526–535.
- Thamaraiselvi, T., Rajeswari, S., 2003. Biological evaluation of bioceramic materials – A review trends. *Trends in Biomaterials & Artificial Organs* 18.
- Trombetta, R., Inzana, J.A., Schwarz, E.M., Kates, S.L., Awad, H.A., 2017. 3D printing of calcium phosphate ceramics for bone tissue engineering and drug delivery. *Annals of Biomedical Engineering* 45, 23–44.
- Turnbull, G., Clarke, J., Picard, F., *et al.*, 2018. 3D bioactive composite scaffolds for bone tissue engineering. *Bioactive Materials* 3, 278–314.
- Vaishya, R., Chauhan, M., Vaish, A., 2013. Bone cement. *Journal of Clinical Orthopaedics and Trauma* 4, 157–163.
- Walters, C.M., Nazemi, A.K., Patel, S.L., Wu, B.M., Dunn, J.C.Y., 2014. The effect of scaffold macroporosity on angiogenesis and cell survival in tissue-engineered smooth muscle. *Biomaterials* 35, 5129–5137.
- Wang, W., Yeung, K.W.K., 2017. Bone grafts and biomaterials substitutes for bone defect repair: A review. *Bioactive Materials* 2, 224–247.
- Wilson, C., Clegg, R., Leavesley, D., Percy, M., 2005. Mediation of biomaterial–cell interactions by adsorbed proteins: A review. *Tissue Engineering* 11, 1–18.
- Woodard, J.R., Hilldore, A.J., Lan, S.K., *et al.*, 2007. The mechanical properties and osteoconductivity of hydroxyapatite bone scaffolds with multi-scale porosity. *Biomaterials* 28, 45–54.
- Xu, H.H.K., Wang, P., Wang, L., *et al.*, 2017. Calcium phosphate cements for bone engineering and their biological properties. *Bone Research* 5, 17056.
- Yavropoulou, M.P., Yovos, J.G., 2016. The molecular basis of bone mechanotransduction. *Journal of Musculoskeletal and Neuronal Interactions* 16, 221–236.
- Zhang, J., Liu, W., Schnitzler, V., Tancret, F., Bouler, J.M., 2014. Calcium phosphate cements for bone substitution: Chemistry, handling and mechanical properties. *Acta Biomaterialia* 10, 1035–1049.

Bioactive Glasses and Glass-Ceramics

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Introduction: The Genesis of Bioactive Glasses and the Concept of Glass-Tissue Interfacial Bond

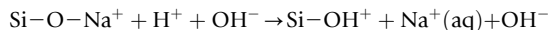
The concept of “bioactive” or “surface-active” glass was first introduced by Larry L. Hench at the University of Florida in the late 1960s when his research team developed the so-called 45S5 glass composition (45% SiO₂, 24.5% CaO, 24.5% Na₂O, and 6.0% P₂O₅ wt%), which was able to tightly bond to living bone (Hench *et al.*, 1971). The 45S5 glass was then tradenamed as Bioglass®, has been marketed for various dental and orthopedic applications, and has been used in hundreds of thousands of human patients (Hench, 2006). This has led to a considerable effort towards understanding the fundamental science that governs the physico-chemical, thermal and biomedical properties of bioactive glasses based on – or inspired by – the 45S5 formulation, so that novel glasses with enhanced biological efficacy could be designed (Table 1).

The chemical nature of the bond between the tissue and the material considerably enhances the interfacial adhesion of the implant; at the same time, the reactivity – strongly dependent on solubility – of bioactive materials is typically limited to their surface owing to the progressive “passivation” of the surface layer, which does not allow further degradation to progress rapidly to the bulk material. Therefore, a stable interface can be formed and maintained long enough to favor further cellular interactions in vivo and to induce the controlled growth of mature tissues.

Bioactive glasses can thus be intended as an ideal compromise between bio-inert materials (e.g., alumina and zirconia) and completely biodegradable materials such as α - or β -tricalcium phosphates, which undergo full dissolution upon exposure to physiological fluids and may be totally replaced with living tissues.

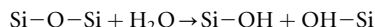
The mechanism of bioactivity and bone bonding of 45S5 glass has been first described by Hench and then confirmed by other authors (Hench, 1988; Greenspan, 1999). A hydroxycarbonate apatite (HCA) layer is generally believed to form on the surface of bioactive glasses upon contact with aqueous solutions (e.g., simulated body fluid (SBF) or physiological fluids) as a result of a sequence of reactions similar to the processes of conventional silicate glass corrosion:

- (1) Ionic exchange between Ca²⁺ and Na⁺ ions in the material and H⁺ and H₃O⁺ ions coming from the surrounding environment. Silanol bonds (Si–OH) are established on the surface of the glass. An increase of the solution pH is observed due to the release of alkaline ions and a silica gel layer forms on the surface of the glass. The chemical reaction can be described as follows:



This reaction occurs within a few minutes of exposure to SBF or body fluids. The surface layer is depleted of alkaline cations and is characterized by a net superficial negative charge. (PO₄)³⁻ ions, too, can be released into the surrounding fluids.

- (2) Breaking of O–Si–O bonds due to the high value of local pH determines, leading to the breaking of the silica network. Soluble silica is released in the form of Si(OH)₄ and the silanol groups are exposed on the surface of the glass in direct contact with the solution:



It has been demonstrated that the soluble silica released has a great impact on the proliferation of cells responsible for the formation of new bone in the adjacent area of the glass surface (Christodoulou *et al.*, 2005).

- (3) Silanol groups condensation and re-polymerization of an amorphous silica gel layer having poor content of Na⁺ and Ca²⁺ cations. The thickness of this layer typically varies between 1 and 2 μm . An increase in the proportion of bridging oxygens was observed during leaching. The surface of the material is characterized by a diffused micro-porosity, with an average pore size in the range of 3–5 nm and an effective surface area of up to 100 m²/g.

Table 1 Examples of bioactive silicate, borate and phosphate glass compositions (wt%)

Glass name	Production	SiO ₂	P ₂ O ₅	B ₂ O ₃	Na ₂ O	K ₂ O	CaO	MgO
45S5 Bioglass®	Melting	45	6	–	24.5	–	24.5	–
S53P4	Melting	53	4	–	23	–	20	–
13-93	Melting	53	4	–	6	12	20	5
Biosilicate®	Melting	48.5	4	–	23.75	–	23.75	–
CEL2	Melting	43.8	6.9	–	15.0	6.1	23.6	4.6
13-93B1	Melting	34.4	3.8	19.9	5.8	11.7	19.5	4.9
13-93B3	Melting	–	3.7	56.6	5.5	11.2	18.5	4.6
ICEL2	Melting	1.9	66.4	–	9.7	3.9	15.2	2.9
58S	Sol-gel	58.2	9.2	–	–	–	32.6	–
70S30C	Sol-gel	71.4	–	–	–	–	28.6	–

- (4) Ca^{2+} and $(\text{PO}_4)^{3-}$ ions, coming from both the material and the surrounding fluids, migrate through the silica gel layer towards the material surface. As a result, an amorphous calcium phosphate (ACP) layer forms on the top of the silica gel.
- (5) Hydroxyl and carbonate groups are incorporated from the solution while the process of dissolution of the glass continues starting from the surface. The ACP layer crystallizes to HCA. The resulting surface is very similar to the nano-crystalline mineral phase of the bone tissue from both compositional and structural viewpoints, and this allows the direct anchoring of the implant to the living tissue.

The five reaction stages described above may occur both *in vitro* and *in vivo*. If the glass is implanted in the body, the biological mechanism of bonding to bone involves adsorption of growth factors onto the surface HCA layer, followed by attachment, proliferation and differentiation of osteoprogenitor cells. Upon further degradation and conversion of the glass into HCA, osteoblasts can produce extracellular matrix composed of collagen microfibrils that mineralizes with nanocrystalline HCA on the surface of the implant.

45S5 glass was proved to be an excellent material and considered for long time as the “gold standard” bone substitute. However, it suffers from several drawbacks owing to (1) limited ability in sintering because it starts crystallizing before viscous flow takes place, (2) slow degradation kinetics which make it difficult to match the formation rate of new tissue, (3) abrupt pH variations in the biological microenvironment due to the increase in the concentration Na^+ and Ca^{2+} ions, especially in the short term when the release is faster (Jones, 2013). These are the reason why other glass compositions have been developed over the years (Table 1).

Bioactivity was demonstrated not only in silicate but also in borate and phosphate glass systems (Rahaman *et al.*, 2011). However, silicate glasses have always received higher attention in comparison to the other two classes of bioactive glasses mainly due to their higher chemical and thermal stability, which allows easy synthesis and processing of these glasses and provides flexibility to tailor their chemical compositions in order to achieve the desired properties. It has also been reported that the release of silica species from bioactive glasses in the range of 0.1 ppm to 100 ppm elicits a stimulatory effect on the osteoblast viability and promotes the expression of a range of genes involved in bone formation (Christodoulou *et al.*, 2005).

Several studies on the chemical dissolution of different melt-derived silicate glasses have led to the establishment of an empirical model that describes the relationship between glass composition and bioactivity (Ogino *et al.*, 1980). Specifically, silicate glasses with SiO_2 content varying between 45 and 52 wt% exhibited the highest bioactivity and were able to bond to both bone and soft collagenous tissues within 5–10 days. Melt-derived bioactive glasses and glass-ceramics containing 55–60 wt% of SiO_2 require a longer time to form a bond with bone and cannot bond to soft tissues. Glass compositions with more than 60 wt% of SiO_2 bond neither to bone nor to soft tissues, do not promote the formation of a surface layer of HCA and form a non-adherent fibrous interfacial capsule. It is worth pointing out that this composition-bioactivity relationship has been determined for glasses synthesized through melt-quenching route and may not be considered valid for sol-gel glasses: in fact, HCA was observed to form on the surface of gel-derived glasses with 90 mol% of SiO_2 after immersion in SBF (Li *et al.*, 1991). These differences in the bioactivity of melt-quenched and sol-gel glasses are due to the different surface chemistry of the two systems (presence of an inherent mesoporosity and high specific surface area in the materials synthesized by wet route) (Izquierdo-Barba and Vallet-Regi, 2015).

Production Processes and Types of Bioactive Glasses

Bioactive glasses can be produced by “conventional” melt-quenching route or sol-gel process. The melt-quenching route is conceptually easy but requires that the glass composition is properly designed in order to facilitate the melting process/casting into molds and to satisfy the reaction/bioactivity criteria in the biological fluids. On the other hand, the sol-gel method allows the expansion of the compositional range without compromising the system bioactivity; furthermore, it permits obtaining a high-purity product (no problems of contamination from the crucible material) and using a lower processing temperature (calcination temperatures are significantly lower than those required for melting).

Melt-Derived Bioactive Glasses

At present, the most-commonly used melt-derived bioactive glasses in clinics are 45S5, 13-93, and S53P4 (Table 1). In principle, the melting process of bioactive glasses is similar to that used for common soda-lime glasses for everyday applications. Melting of reagents (typically oxides and carbonates) is carried out at high temperatures (1200–1550°C) in an electrically-heated furnace. Process parameters (e.g., dwelling time at the melting temperature) is properly set in order to obtain a homogeneous and bubble-free melt. Platinum crucibles are the best choice to avoid contamination of the melt in biomedical applications; use of a cap is useful to limit the loss of boron, phosphorous and fluorine that tend to vaporize during high-temperature melting. Multiple melting steps may also be performed to reach ultra-high levels of homogeneity of the final product.

The available “dry” forming routes for (bioactive) glasses, according to the final product, include direct casting into molds, quenching into water to obtain a “frit” to further crush, or drawing into continuous fibers from a pre-form that was heated above the glass transition temperature (T_g).

After being ground and sieved, glass powders can also be heat-treated well above T_g in order to allow the sintering of particles into a porous architecture (scaffold) or to obtain a coating on a surface.

Crystallization is a critical aspect in view of the compositional range of melt-derived bioactive glasses since the thermal treatments, which are used for example to allow consolidation of the particles, could promote devitrification if carried out above the onset crystallization temperature (T_x). The presence of crystalline phases can significantly slower down the formation rate of the HCA layer on the material surface; nevertheless, it was reported that, even after full devitrification (100% of crystallinity), systems such as 45S5 Bioglass® still maintain a residual bioactivity (Peitl *et al.*, 1996; Arstila *et al.*, 2007).

Over the last years, considerable efforts have been addressed to developing melt-derived bioactive glasses that can undergo high-temperature thermal treatments without devitrification, in order to obtain, for example, good sinterability while maintaining good HCA-forming ability. In this regard, a successful example is the 13-93 glass composition which has a quite large sinterability window ($T_x - T_g$) and is approved for clinical use in Europe and USA (Rahaman *et al.*, 2017).

Bioactive silicate glasses

When Larry Hench started designing the formulation of a glass implant that could potentially bond to bone, he decided to use a quaternary silicate system containing both calcium and phosphorus, which are the main constituents of bone apatite. As a result, the 45S5 composition has a high Ca-to-P ratio and a relatively low melting temperature to allow easy casting into molds.

Addition of other oxides to the original 45S5 composition allowed further modulating the properties of bioactive glasses, such as dissolution rate and therapeutic effects via ion release (Hoppe *et al.*, 2011). It is impressive that, although more than 50 years have been passed since the discovery of 45S5 composition, intense research is still ongoing about this glass system and its medical applications in orthopedics, dentistry, and even soft tissue repair (Hench, 2006).

The main technological limitation of 45S5 glass concerns its small hot-working range: in fact, T_g and T_x of Bioglass® are very close, which limits the possibility of sintering by viscous flow without (partial) crystallization (Baino and Fiume, 2018) and leads to the decrease of apatite-forming capability. The glass S53P4, which is clinically used for maxillofacial surgery (Stoor *et al.*, 2010) and orbital floor repair (Peltola *et al.*, 2008) especially in Europe, also exhibits an easy tendency to crystallize upon heating (Massera *et al.*, 2012). More complex systems have a better stability against devitrification: for example, 13-93 has been proved to be bioactive and to have a larger sinterability window than Bioglass® due to the introduction of a higher amount of silica (53 wt%) together with K_2O and MgO , which are known to increase the hot-working range of glasses (Brink *et al.*, 1997). Fully amorphous 13-93 porous scaffolds mimicking the architectural and mechanical properties of cancellous bone were fabricated by the sponge replica method (Fu *et al.*, 2008), while robocasting was useful to produce strong 13-93 structures for load-bearing applications (cortical bone repair) (Liu *et al.*, 2013).

Very promising foam-like scaffolds, in terms of bone architectural biomimicry, bone-like mechanical properties and HCA-forming ability, were produced by applying the sponge replica method to melt-derived CEL2 glass powder (Vitale-Brovarone *et al.*, 2009a).

A very popular melt-derived bioactive glass in South America is Biosilicate®, which is clinically used not only for bone repair but also for the treatment of dentinal hypersensitivity, the replacement of middle ear small bones and the production of orbital implants for enucleated patients (Crovace *et al.*, 2016).

Bioactive borate glasses

Borate and borosilicate glasses are more reactive than silicate systems in contact with aqueous media such as body fluids, hence they are less durable and can convert faster to HCA than traditional SiO_2 -based bioactive materials. The bioactivity mechanism is conceptually similar to that of silicate glasses and involves the formation of a borate-rich gel layer instead of the silica gel. The rate of glass conversion into HCA can be modulated by tailoring the glass composition, thus varying the reaction time from hours to months (Huang *et al.*, 2006).

Borate-based glasses are appealing from a technological viewpoint as they have a lower T_g than silicate materials; glass transition can be tailored and increased by adding alkali and alkali-earth oxides in proper amounts. In general, borate glass products can be sintered more easily and in a more controlled way than silicate-based ones because of their ability to readily undergo viscous flow (Balasubramanian *et al.*, 2018).

Glasses in which SiO_2 was partially or totally replaced by B_2O_3 were found to be more reactive than their silicate counterparts (e.g., 45S5 Bioglass®) and to promote faster bone growth in vivo (Fu *et al.*, 2010). Particles of a SiO_2 -free borate glass were totally converted into HCA in less than four days; on the contrary, borosilicate glasses still maintained a silica-rich core after several weeks (Huang *et al.*, 2006). Bioactive borate and borosilicate glasses are also able to stimulate angiogenesis, which is key for promoting bone healing (Bi *et al.*, 2013).

An issue concerning the in vivo use of bioactive borate glasses is that high concentrations of $(BO_3)^{3-}$ ions is toxic to cells. Some in vitro biocompatibility tests have revealed that borate glasses can be cytotoxic if the tests are carried out in static conditions (Fu *et al.*, 2009). On the contrary, when the same tests were carried out in dynamic conditions or in vivo, no significant cytotoxic effect was detected due to the dilution of borate ions. In this regard, a threshold concentration for boron has been reported (0.65 mM) under which there was no toxic effect to cells and, thus, borate glass scaffolds could successfully support osteoblastic cell growth and differentiation. Safer conditions for cell culture/implantation in the body could be achieved by inducing HCA formation on the glass prior to cell seeding via pre-immersion in SBF (Fu *et al.*, 2009).

Having a larger sinterability window, borate glasses are more amenable to be processed than silicate ones and this property is very advantageous for obtaining high-quality sintered products. In this regard, Fu *et al.* (2009) used the sponge replica method to fabricate 13-93B1 glass scaffolds with 3D porous network mimicking the trabecular architecture of human bone (porosity 72 vol%, pore size ranging from 200 to 500 μm) and acceptable mechanical properties for osseous defect repair (compressive strength about 6.4 MPa). However, the same authors reported that the fast conversion of these borate scaffolds into

HCA was associated to the simultaneous decrement of mechanical properties during immersion in SBF (the compressive strength decreased to about 1 MPa within 1 month).

Recently, borate glasses have also been proposed in the form of micro-sized fibers for applications in wound dressing due to their pro-angiogenic properties associated to the release of boron and calcium ions (Balasubramanian *et al.*, 2018).

Bioactive and resorbable phosphate glasses

In the context of tissue healing, “restitutio ad integrum” is not possible if the biomaterial used to support the regenerative process does not completely dissolve once it has performed its function. In this regard, bioactive SiO₂-based glasses do not possess this ability – which means that residual silicate material will persist indefinitely in the body – unless they are synthesized in the form of nanoparticles (Vichery and Nedelec, 2016). However, fully-resorbable biomedical glasses can be obtained if P₂O₅ is used as a former oxide. Phosphate glasses are prone to congruently and totally dissolve over time in aqueous media, such as body fluids, and their dissolution rate can be varied from a few hours to some months by properly modifying the composition (Abou Neel *et al.*, 2009a). The low stability of phosphate glasses is due to the asymmetry of the structural tetrahedral unit [PO₄] and the easy hydration of P–O–P bond. The dissolution of these glasses is regulated by two interdependent stages: (1) surface hydration associated to Na⁺/H⁺ ion exchange and (2) rupture of the phosphate network due to breakage of P–O–P bonds in the hydrated layer. Metal oxides, such as TiO₂ (Abou Neel and Knowles, 2008), CuO (Abou Neel *et al.*, 2005) or Fe₂O₃ (Patel and Knowles, 2006), can be added to the composition in order to modulate (typically decrease) the dissolution kinetics of phosphate systems.

Being resorbable, phosphate glasses can be used as inorganic temporary platforms for the controlled release of biologically-active and therapeutic ions (Lakhkar *et al.*, 2013). In this regard, a number of antibacterial elements such as silver, copper, zinc and gallium were incorporated in the phosphate glass network and gradually released during the glass dissolution. It is worth pointing out that the ion release profile is much more linear in phosphate glasses compared to partially-resorbable silicate systems (Franks *et al.*, 2000). Phosphate glasses can also be drawn into fibers due to their relatively low T_g: under this form, they have been proposed for soft tissue engineering applications such as nerve (Vitale-Brovarone *et al.*, 2012) and muscle regeneration (Shah *et al.*, 2005), where the implantation of a tissue-like fibrous construct is key to guide cell growth.

Phosphate glasses have also been proposed for the fabrication of resorbable scaffolds for bone tissue engineering. For example, the composition of the silicate glass CEL2 was modified to obtain a phosphate glass named ICEL2 (Table 1), in which the molar percentages of the former oxides P₂O₅ and SiO₂ were inverted (Leonardi *et al.*, 2010). This phosphate glass showed a high tendency to dissolve in vitro when soaked in aqueous media like distilled water, SBF or TRIS (up to 75% of mass was lost over immersion for 4 months). Apart from being resorbable, ICEL2-derived porous glass-ceramic scaffolds produced by sponge replication (Vitale-Brovarone *et al.*, 2011) or polyethylene burn-off (Bretcanu *et al.*, 2014) also exhibited apatite-forming properties: in fact, small HCA agglomerates were observed to form on the scaffold struts in vitro in spite of the progressive dissolution of the material, which promoted stem cells to attach and differentiate into osteoblasts.

Phosphate glasses were also proposed as carriers for the local release of strontium, which is known to have anti-resorptive effects on bone tissue, thereby being effective in the treatment of osteoporosis (Peng *et al.*, 2009). In fact, the human body absorbs strontium in bones as if it is calcium due to the similarities between strontium and calcium ions. It was also reported that the replacement of Na₂O with SrO (up to 5 mol%) can significantly increase the dissolution rate of the phosphate glass, along with glass density and glass transition temperature (Abou Neel *et al.*, 2009b). This was due to the fact that SrO generates modifications in the glass network, increasing the number of Q¹ and Q³ units and decreasing the Q² ones. The increased dissolution rate produces the proportional increase in the release of Na⁺, Ca²⁺ and phosphate anions (e.g., (PO₄)³⁻) in the solution. On the contrary, the concentration of Sr²⁺ ions is proportional to the concentration of SrO in the glass and not to the dissolution rate. The control of the dissolution rate is useful to limit the change of pH in the solution (physiological value about 7.4) since a too fast or too large variation in the pH might be toxic for cells.

Sol-Gel Bioactive Glasses and Hierarchical Materials

While melt-derived silicate glasses cannot be bioactive if SiO₂ exceeds 60 wt%, glasses produced by sol-gel process still retain an excellent apatite-forming ability in spite of having a silica content up to 90 mol% (Li *et al.*, 1991). The exceptional bioactivity of these glasses relies on their inherent nano-texture associated to a high specific surface area (typically well above 50 m²/g), which governs the dissolution mechanism and leads to a significantly faster ion exchange with body fluids in comparison to melt-derived systems with analogous composition (specific surface area less than 0.5 m²/g) (Izquierdo-Barba and Vallet-Regi, 2015).

The sol-gel process is a chemistry-based (or “wet”) synthesis route in which the polymerization reaction of a solution containing precursors of the metal oxides leads to the gelation of the sol at room temperature. Biomedical sol-gel glasses are typically produced by hydrolysis and poly-condensation of alkoxyde precursors (e.g., tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS)) followed by aging and drying at room temperature (Baino *et al.*, 2018). The oxide composition of sol-gel glasses is typically simpler as compared to melt-derived ones as the addition of high amounts of modifiers (e.g., Na₂O), needed to lower the melting temperature and facilitate glass processing, can be avoided in this case.

The sol-gel process can be summarized in five sequential stages (Hench and West, 1990). During step 1 (mixing), reagents are mixed together at room temperature to induce the formation of covalent bonds between the elements. Hydrolysis and poly-condensation occur simultaneously until homogenization of the solution is achieved. The step 2 (gelation) is associated to an

increase of viscosity due to the formation of a 3D interconnected network. The step 3 (aging) leads to a decrease of porosity as well as a remarkable improvement of mechanical strength. The liquid phase (alcohols) is removed during the step 4 (drying), which can be performed at a moderately high temperature (typically less than 200°C), and the obtained dry gel is finally stabilized by thermal treatment above 600°C (step 5).

Sol-gel glasses exhibit an typical nanoporous texture (mean pore size within 10–30 nm) which inherently derives from the synthesis process (Jones *et al.*, 2006). Smaller nanopores (typically 2–20 nm) with a well-defined symmetry and ordered arrangement could be obtained by incorporating supramolecular chemistry in the sol-gel process, leading to the advent of the so-called “ordered mesoporous materials”. For this purpose, surfactants are used to build micelles (above a critical concentration) due to the hydrophilic-hydrophobic features of those molecules, around which the silicate glass network can self-organize. In 1992, surfactant-templated pure amorphous SiO₂ was first synthesized and applied as a molecular sieve by researchers of the Mobil Oil Corporation (Kresge *et al.*, 1992) and, a decade later, Vallet-Regi *et al.* (2001) pioneered the biomedical use of these ordered mesoporous microspheres as a drug delivery system since small biomolecules could be hosted in the mesopores.

Interestingly, it was observed that mesoporous silica could promote the nucleation of HCA when soaked in SBF (Izquierdo-Barba *et al.*, 2005). This is in apparent contrast with the bioactivity mechanism suggested by Hench (1988), since there are no cations that can be released from the amorphous silica network and exchanged with ions from the solution to activate the apatite-forming mechanism. The bioactivity of mesoporous SiO₂ is still under debate but a partial explanation of the experimental evidence can be attributed to the role played by the unique textural properties of mesoporous materials: in fact, the ultrahigh specific surface area (well above 100 m²/g) seems to govern the material reactivity in aqueous media more crucially than the composition (Izquierdo-Barba and Vallet-Regi, 2015).

Hierarchical systems comprising a coating of pure-silica mesoporous microspheres (e.g., SBA-15, MCM-41) deposited onto the struts of bioactive glass-ceramic macroporous foams (large pore size within 50–500 µm) were developed as multifunctional implants for the simultaneous treatment of infections (via the controlled release of drugs from the mesopores) and acceleration of bone regeneration (via the glass bioactivity and bone growth inside the macropores) (Cauda *et al.*, 2008, Vitale-Brovarone *et al.*, 2009b).

Mesoporous bioactive glasses (MBGs), produced by incorporating additional oxides in the silica network, have been the topic of intense research over the last years. MBGs are typically more bioactive than melt-derived and “conventional” sol-gel-derived glasses due to the ultrahigh specific surface area which accelerates the ion-exchange reaction between glass and biological fluids (Wu and Chang, 2012).

MBGs were extensively proposed as highly-versatile platforms for the controlled release of both drugs and small amounts of metallic cations eliciting a therapeutic effect (Wu and Chang, 2014, Kargozar *et al.*, 2018a).

The fabrication of hierarchical MBG scaffolds exhibiting macro-mesoscale porosities is a difficult task due to two main reasons: (1) mesoporous materials are highly brittle due to the inherent mesoporosity and (2) the temperatures used to process MBGs cannot be increased too much (typically within 500–700°C) in order to preserve the mesoporous texture, thereby resulting in suboptimal densification. Co-templating strategies combining sponge replication (formation of large macropores) with surfactant-assisted sol-gel process (formation of mesopores) allowed fabricating scaffolds with appealing hierarchical porous structure but poor mechanical properties (compressive strength within 50–300 kPa (Wu *et al.*, 2010) versus 2–12 MPa for cancellous bone). Stronger hierarchical MBG scaffolds (compressive strength up to 16 MPa) having a grid-like structure of macro-sized channels and small mesopores on the struts were recently fabricated by applying additive manufacturing technologies, such as 3D printing (Zhang *et al.*, 2014).

Biological Role of Doping Elements

The exceptional versatility of bioactive glasses in term of physico-chemical and biological properties greatly relies on their composition, which can be finely designed and tailored to achieve the desired effect (e.g., fast resorption, quick HCA-forming kinetics). For instance, it was widely shown that the addition of monovalent and bivalent modifiers (e.g., K₂O, Na₂O, CaO, and MgO) is useful to decrease the thermal and chemical stability of the glass, resulting in an increase of the HCA-formation ability in silicate glasses (Brink *et al.*, 1997) and the resorption kinetics in phosphate glasses (Abou Neel *et al.*, 2009a). Furthermore, small amounts of metallic elements can be embedded in the glass composition so that, once released, can elicit an appropriate therapeutic effect at the implantation site (Kargozar *et al.*, 2018b). A summary of the biological effects elicited by the ionic species released from bioactive glasses is reported in Table 2.

Although the research field on ion-driven therapies is very challenging and potentially offers unique advantages – e.g., the use (and abuse) of antibiotics can be replaced by the controlled release of antibacterial cations, thus overcoming the problem of bacterial resistance (Kargozar *et al.*, 2018a) –, there are some issues suggesting caution in applying ion-releasing materials in clinics. In fact, some ions can be toxic to healthy cells even if released at low concentrations and their long-term effects *in vivo* still are partially unknown. A typical case is represented by Co²⁺ ions, which have been incorporated in bioactive glasses to promote angiogenesis (Kargozar *et al.*, 2017a; Wu *et al.*, 2011) but, concurrently, may interfere with cell metabolism and play a role in carcinogenesis and tumor growth (Littmann *et al.*, 2018).

Bioactive Glass-Based Products and Clinical Applications

Bioactive glasses, given their physical properties, stiffness and HCA-forming ability *in vitro* and *in vivo*, have been traditionally proposed for applications in contact with bone in orthopedics and dentistry (Tables 3 and 4).

Table 2 Biological role of the ionic dissolution products released from bioactive glasses

Therapeutic ion	Biological effects	Mechanism of action
Monovalent	Silver (Ag^+)	Antibacterial activity • Block of the respiration and electron transfer as well as collapse of the proton motive force in bacteria • Leakage of massive proton through the bacteria cell membrane
	Lithium (Li^+)	Osteogenesis • Activation of Wnt/Catenin signaling pathway • Stimulation of Col1, Runx2, ALP, and bone sialoprotein
	Fluoride (F^-)	Osteogenesis • Promotion of Akt and GSK3β phosphorylation and activation of the canonical Wnt/β-catenin signaling pathway • Stimulation of the expression of bone differentiation markers of COL1A1, ALP, and osteonectin
Divalent	Calcium (Ca^{2+})	Osteogenesis • Promotion of SMAD signaling pathway Angiogenesis • Increase of the expression of genes involved in angiogenesis including PDGF, EGF, IGF-I, bFGF, and VEGF • Induction of EC proliferation
	Strontium (Sr^{2+})	Osteogenesis • Activation of Wnt/Catenin signaling pathway • Up-regulation of genes expression of Runx-2, BMP-2, OCN, OPN, BSP, and Col1, ALP activity and matrix mineralization • Enhancement of the attachment, proliferation, and differentiation of osteoblastic cells • Reduction of osteoclast activity
	Manganese (Mn^{2+})	Osteogenesis • Up-regulation of Runx-2 and OPN
	Magnesium (Mg^{2+})	Antibacterial activity • Generation of ROS and inhibition of bacteria germination
		Osteogenesis • Activation of Notch1 signaling pathway
		Angiogenesis • Over-expression of COL10A1 gene
	Zinc (Zn^{2+})	Osteogenesis • Stimulation of PKC/MAPK signaling pathways
		Antibacterial activity • Enhancement of ROS production and damage to DNA, RNA and proteins • Destabilization of bacterial membranes
	Copper (Cu^{2+})	Anti-inflammatory activity • Decrease of the expression of TNF-α, IL-1β, and VCAM by inhibition of NF-κB activation via A20 and PPAR-α pathways
		Osteogenesis • Activation of bone metabolism via the action as a cofactor for lysyl oxidase • Inhibition of bone resorption through the action as a cofactor for superoxide dismutase
		Angiogenesis • Stabilization of nuclear HIF-1α simulating hypoxia, thereby activating proangiogenic factors VEGF, bFGF, TNF-α, and IL-1
Trivalent	Cobalt (Co^{2+})	Antibacterial activity • Attachment to the bacteria plasma membrane, causing lethal changes in the cell membrane such as disruption of membrane integrity inevitably
		Angiogenesis • Induction of HIF and thereby up-regulation of angiogenic factors VEGF and bFGF
	Cerium (Ce^{3+})	Osteogenesis • Activation of TGF-β/BMP and Smad1/5/8 signaling pathway and thereby up-regulation of genes of Runx 2, Col 1, BMP2, ALP, and OCN
	Gallium (Ga^{3+})	Antibacterial activity • Increase of the levels of ROS in the cerium-incubated bacteria cells, resulting in DNA, RNA, and protein damages
		Osteogenesis • Inhibition of the differentiation and resorbing activity of osteoclasts
	Boron (as BO_3^{3-} in biofluids)	Antibacterial activity • Inhibition of essential biological reactions in bacteria
Tetravalent	Silicon (as SiO_4^{4-} in biofluids)	Osteogenesis • Activation of MAPK signal pathway
		Angiogenesis • Up-regulation of VEGF and TGF-β1 genes
	Iron (Fe^{3+})	Osteogenesis • Activation of MAPK signal pathway
		Angiogenesis • Up-regulation of Runx2, ALP, and BMP2 genes
	Europium (Eu^{3+})	Angiogenesis • Overexpression of angiogenic genes of CD31, MMP9, VEGFR1/2, and PDGFRα/b
Pentavalent	Phosphorus (as PO_4^{3-} in biofluids)	Osteogenesis • Activation of BMP2 signaling pathway
	Niobium (Nb^{5+})	Angiogenesis • Induction of endothelial cell (EC) homing, cell polarization, migration
Pentavalent	Phosphorus (as PO_4^{3-} in biofluids)	Osteogenesis • Stimulation of the expression of matrix gla protein (MGP)
	Niobium (Nb^{5+})	Angiogenesis • Stimulation of pro-angiogenic FOXC2, osteopontin, and VEGFa • Enhancement of VEGF secretion

Table 3 Chronological development of bioactive glass products in medicine

Year	Achievement/application
1969	Invention of the 45S5 glass composition (45S5 Bioglass®) by Larry Hench
1977	Treatment of ear diseases by using Ceravital® glass-ceramics (replacement of middle ear small bones)
1978	Investigation of bioactive glass biocompatibility in the eye (cornea)
1985	Approval by Food and Drug Administration (FDA) in the USA of the first 45S5 Bioglass® implant (MEP®) for middle ear small bone replacement
1987	Treatment of liver cancer by using insoluble radioactive glasses
1988	Clinical use of the 45S5 Bioglass®-based Endosseous Ridge Maintenance Implant (ERMI) in human patients
1993	FDA approval of PerioGlas (45S5 Bioglass® particulate) for bone and dental repair
1998	First use of bioactive glasses in peripheral nerve repair
1999	FDA approval of radioactive glasses (TheraSphere®) for cancer treatment
2000	First use of bioactive glasses in wound healing
2002	FDA approval of Medpor®-Plus™ (polyethylene/45S5 Bioglass® porous orbital implant) for use in enucleated patients.
2003	Introduction of Zn-containing antibacterial bone/dental cements
2004	First use of bioactive glasses in lung tissue engineering
2004	Advent of mesoporous bioactive glass (MBG) as a drug delivery system
2005	First use of bioactive glasses in skeletal muscle and ligament repair
2005	First use of bioactive glasses in the treatment of gastrointestinal ulcers
2010	First use of bioactive glasses in cardiac tissue engineering
2011	Commercialization of a cotton-candy borate bioactive glass for wound healing in veterinarian medicine.
2012	First use of bioactive glasses in embolization of uterine fibroids
2012	First use of bioactive glasses in spinal cord repair
2018	First use of radioactive glasses (TheraSphere®) in patients with metastatic colorectal carcinoma of the liver

Table 4 Examples of bioactive glass products available on the market

Glass name or system	Commercial products and notes	Manufacturer
45S5	NovaBone® Putty and NovaBone® Dental Putty: moldable glass-based paste injectable into the bone/dental defect site by a syringe NovaBone® particulate (90–710 µm) for orthopedics NovaBone® Morsels (porous granulate) for bone repair PerioGlas® particulate (90–710 µm) for repairing jaw bone defects NovaBone® porous blocks for bone repair Biogran® particulate (300–360 µm) for bone repair NovaMin® particulate and BioMin for tooth enamel remineralization and dentinal hypersensitivity prevention	Novabone (USA); Mo-Sci Corp. (USA); Biomet 3i (USA); BioMin Technologies (UK)
45S5 + polyethylene	Porous composite orbital implant (Medpor-Plus™) for enucleation	Porex Surgical Inc (USA)
S53P4	Particulate for maxillofacial repair and custom-made monolithic plates for the repair of orbital floor fractures (BoneAlive®)	Abmin Technologies Ltd/Vivoxid (Finland); Mo-Sci Corp. (USA)
13-93	Cast monolithic implants, quenched frit, rods, fibers, disks, granules and micro-sized powders for bone repair	Mo-Sci Corp. (USA)
13-93B3	Cotton-candy fibrous scaffolds (DermaFuse™/Mirragen™) for wound healing	Mo-Sci Corp. (USA), Avalon Medical (USA)
70S30C	Sol-gel powder for bone repair	MedCell (UK)
Y ₂ O ₃ -Al ₂ O ₃ -SiO ₂ glass	Insoluble microspheres (TheraSphere®) for the treatment of liver cancer by embolization combined with local radiotherapy	BTG International Ltd (USA)

In the last decades, bone repair has become a major clinical and socioeconomic need due to the demographics associated with aging populations throughout the world (Clegg *et al.*, 2013); therefore, the availability of bioactive materials able to regenerate bone avoiding tissue transplantation is dramatically attractive.

The first bioactive glass product used in clinics dates back to 1980s, when melt-derived small blocks of 45S5 glass were implanted in the middle ear of deaf patients to recover sound conduction (Merwin, 1986). In the same years, 45S5 glass conical implants were also experimented as artificial dental roots in humans (Stanley *et al.*, 1997). Both products, albeit providing quite successful results from a clinical viewpoint, underwent progressive disuse as surgeons prefer to cut or shape the implant intraoperatively to match better the patient's anatomy, which is impossible with rigid pre-formed implants. At present, bioactive glasses are mainly used in the form of particles, granules or injectable putties that can be easily pressed into the bone site of concern: common applications of biomedical glasses include repair of traumatic or congenital osseous defects, bone

reconstruction following bone cancer removal, vertebral fusion, treatment of spinal osteomyelitis, tooth enamel remineralization, and prevention of dentinal hypersensitivity (Jones *et al.*, 2016). Glass-ceramics are of particular interest in dentistry for use in both dental root/alveolar bone surgery (if bioactive) and restorative/esthetic applications (if inert) (Montazerian and Zanutto, 2017).

Bioactive glass powder is often used as a raw material to fabricate three-dimensional (3D) scaffolds with an interconnected network of macropores mimicking the trabecular architecture of cancellous bone (Baino *et al.*, 2019a). Scaffolds are typically produced either by using a sacrificial material/template that acts as a pore-forming agent (e.g., open-cell polymeric sponge, plant-derived porous structures, starch and polyethylene grains), or by implementing additive manufacturing techniques (e.g., robocasting). Other strategies to obtain bioactive glass scaffolds include the freezing of glass particle suspensions and the foaming of a sol followed by thermal consolidation. Very innovatively, some researchers have tried applying sustainable approaches to the synthesis of bioactive glass scaffolds using “eco-friendly” raw materials. In this regard, natural marine sponges (Boccardi *et al.*, 2016) or stale bread (Fiume *et al.*, 2019) were proven to be inexpensive and suitable templates to produce bioactive glass foams mimicking the pore-strut architecture of cancellous bone.

Bioactive glasses are generally unsuitable for load-bearing applications due to their relatively poor mechanical properties (high brittleness, low bending strength, low fracture toughness); however, they can be applied as surface coatings on strong/tough implants to combine the adequate mechanical properties of the substrate with the high bioactivity of the glass, along with – in some cases – additional extra-functionalities like antibacterial properties and/or drug release (Baino and Verné, 2017). Research on this topic is still ongoing as there are some open challenges from a technological viewpoint; one of the most crucial is that the consolidation of bioactive glass coatings on metallic prostheses requires high-temperature sintering of the glass layer, with the associated risk of metal oxidation and glass/metal thermal expansion coefficient mismatch.

Bioactive glass fibers can be obtained by conventional drawing from a preform or even electrospinning to produce porous mats (Hong *et al.*, 2010). Furthermore, glass micro- or nano-sized particles can be incorporated in soft polymeric matrices to fabricate bioactive composites, that are very useful for interfacial hard/soft tissue engineering applications (Kargozar *et al.*, 2018c).

Recently, bioactive glasses have also been experimented in some novel applications in contact with soft tissues with very promising results (Table 3). Hench's 45S5 Bioglass® was reported to promote angiogenesis both in vitro and in vivo (rat model) (Gerhardt *et al.*, 2011). This property is peculiar of other glass compositions, too, such as 13-93B3 glass that was proved to be highly-effective in accelerating wound healing in both animals and humans (Wray, 2011). 13-93B3 glass resorbable fibers, which mimic the microstructure of a fibrin clot, have a high content of calcium that favors the migration of epidermal cells and, therefore, can promote the regeneration of skin even in diabetic patients for whom conventional treatment with drugs is unsuccessful. Angiogenesis can be further enhanced if this glass is doped with copper, as demonstrated in a rat subcutaneous model (Bi *et al.*, 2013). Application of these materials is currently approved for use in veterinary medicine only.

Commercial products comprising Ag-doped resorbable phosphate glass embedded in polymeric matrices are also used in clinics for preventing and combatting infections in wound dressing applications due to the sustained release of Ag⁺ ions.

The pro-angiogenic ability of bioactive glasses is also helpful in ophthalmology: in fact, 45S5 Bioglass®-coated porous polyethylene orbital implants, which replace the ocular globe in enucleated patients, could be invaded by vascularized connective tissue (fibrovascularization) more rapidly compared to the glass-free porous polymer (Baino *et al.*, 2019b).

Some special types of insoluble radioactive glasses are used for the treatment of liver cancer (Day, 2012). In a typical treatment, Y₂O₃-Al₂O₃-SiO₂ glass microspheres (mean particle diameter 25 or 30 μm, about 50 mol% of Y₂O₃ in the composition) are injected into the patient's bloodstream to lodge in the capillary bed of the liver, which is a highly-vascularized organ. Before arterial infusion, the glass beads are exposed to neutrons to create ⁹⁰Y, a radioisotope that has a short half-life (64 h) and decays to stable ⁹⁰Zr through emitting β-rays. As a result, a localized dosage of up to 15,000 rad can be locally delivered to kill cancer cells, with high benefits to the patient (3000 rad is the maximum dosage allowed under external radiotherapy). Apart from being used in the treatment of hepatocellular carcinoma for many years, radioactive glass microspheres have recently shown promise to combat kidney cancer and metastatic liver cancer in other organs, too.

Magnetite-containing melt-derived bioactive glasses as well as MBGs have also been proposed for the treatment of bone cancer via hyperthermia (Kargozar *et al.*, 2019).

Some examples of clinically-approved products based on bioactive glasses are reported in Table 4. Furthermore, there are a number of emerging applications in contact with non-calcified tissues and soft organs (Table 3) that have not reached yet clearance for clinical use, including cardiac tissue regeneration, artificial lungs, epithelial restitution in gastric mucosa and intestine, peripheral nerve regeneration and corneal repair (Miguez-Pacheco *et al.*, 2015; Baino *et al.*, 2016; Kargozar *et al.*, 2017b). These novel experimental studies are contributing to further expand the use of glass in medicine and stimulate unconventional research, which could have a great impact on human life and health.

References

- Abou Neel, E.A., Ahmed, I., Pratten, J., Nazhat, S.N., Knowles, J.C., 2005. Characterisation of antibacterial copper releasing degradable phosphate glass fibres. *Biomaterials* 26, 2247–2254.
- Abou Neel, E.A., Chrzanowski, W., Pickup, D., *et al.*, 2009b. Structure and properties of strontium-doped phosphate-based glasses. *J. R. Soc. Interface* 6, 435–446.

- Abou Neel, E.A., Knowles, J.C., 2008. Physical and biocompatibility studies of novel titanium dioxide doped phosphate-based glasses for bone tissue engineering applications. *J. Mater. Sci. Mater. Med.* 19, 377–386.
- Abou Neel, E.A., Pickup, D.M., Valappil, S.P., Newport, R.J., Knowles, J.C., 2009a. Bioactive functional materials: A perspective on phosphate-based glasses. *J. Mater. Chem.* 19, 690–701.
- Arstila, H., Hupa, L., Karlson, K., Hupa, M., 2007. In vitro bioactivity of partially crystallised glasses. *Glass Technol. Eur. J. Glass Sci. Technol. A* 48, 196–199.
- Baino, F., Fiume, E., 2018. Quantifying the effect of particle size on the crystallization of 45S5 bioactive glass. *Mater. Lett.* 224, 54–58.
- Baino, F., Fiume, E., Barberi, J., *et al.*, 2019a. Processing methods for making porous bioactive glass-based scaffolds – A state-of-the-art review. *Int. J. Appl. Ceram. Technol.* 16, 1762–1796.
- Baino, F., Fiume, E., Miola, M., Verné, E., 2018. Bioactive sol-gel glasses: Processing, properties, and applications. *Int. J. Appl. Ceram. Technol.* 15, 841–860.
- Baino, F., Novajra, G., Miguez-Pacheco, V., Boccaccini, A.R., Vitale-Brovarone, C., 2016. Bioactive glasses: Special applications outside the skeletal system. *J. Non-Cryst. Solids* 432, 15–30.
- Baino, F., Verné, E., 2017. Glass-based coatings on biomedical implants: A state-of-the-art review. *Biomed. Glasses* 3, 1–17.
- Baino, F., Verné, E., Fiume, E., *et al.*, 2019b. Bioactive glass and glass-ceramic orbital implants. *Int. J. Appl. Ceram. Technol.* 16, 1850–1863.
- Balasubramanian, P., Buttner, T., Miguez-Pacheco, V., Boccaccini, A.R., 2018. Boron-containing bioactive glasses in bone and soft tissue engineering. *J. Eur. Ceram. Soc.* 38, 855–869.
- Bi, L., Rahaman, M.N., Day, D.E., *et al.*, 2013. Effect of bioactive borate glass microstructure on bone regeneration, angiogenesis, and hydroxyapatite conversion in a rat calvarial defect model. *Acta Biomater.* 9, 8015–8026.
- Boccardi, E., Philippart, A., Melli, V., *et al.*, 2016. Bioactivity and mechanical stability of 45S5 bioactive glass scaffolds based on natural marine sponges. *Ann. Biomed. Eng.* 44, 1881–1893.
- Bretcanu, O., Baino, F., Verné, E., Vitale-Brovarone, C., 2014. Novel resorbable glass-ceramic scaffolds for hard tissue engineering: From the parent phosphate glass to its bone-like macroporous derivatives. *J. Biomater. Appl.* 28, 1287–1303.
- Brink, M., Turunen, T., Happonen, R., Yli-Urpo, A., 1997. Compositional dependence of bioactivity of glasses in the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{MgO}-\text{CaO}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$. *J. Biomed. Mater. Res.* 37, 114–121.
- Cauda, V., Fiorilli, S., Onida, B., *et al.*, 2008. SBA-15 ordered mesoporous silica inside a bioactive glass-ceramic scaffold for local drug delivery. *J. Mater. Sci. Mater. Med.* 19, 3303–3310.
- Christodoulou, I., Buttery, L.D., Saravanapavan, P., *et al.*, 2005. Dose- and time-dependent effect of bioactive gel-glass ionic-dissolution products on human fetal osteoblast-specific gene expression. *J. Biomed. Mater. Res. B* 74, 529–537.
- Clegg, A., Young, J., Iliffe, S., Rikkert, M.O., Rockwood, K., 2013. Frailty in elderly people. *Lancet* 381, 752–762.
- Crovace, M.C., Souza, M.T., Chinaglia, C.R., Peitl, O., Zanotto, E.D., 2016. Biosilicate® – A multipurpose, highly bioactive glass-ceramic. In vitro, in vivo and clinical trials. *J. Non-Cryst. Solids* 432, 90–110.
- Day, D.E., 2012. Glasses for radiotherapy. In: Jones, J.R., Clare, A.G. (Eds.), *Bio-Glasses: An Introduction*, first ed. New York: Wiley, pp. 203–228.
- Fiume, E., Serino, G., Bignardi, C., Verné, E., Baino, F., 2019. Bread-derived bioactive porous scaffolds: An innovative and sustainable approach to bone tissue engineering. *Molecules* 24, 2954.
- Franks, K., Abrahams, I., Knowles, J.C., 2000. Development of soluble glasses for biomedical use. Part I: In vitro solubility measurement. *J. Mater. Sci. Mater. Med.* 11, 609–614.
- Fu, H., Fu, Q., Zhou, N., *et al.*, 2009. In vitro evaluation of borate-based bioactive glass scaffolds prepared by a polymer foam replication method. *Mater. Sci. Eng. C* 29, 2275–2281.
- Fu, Q., Rahaman, M.N., Bal, B.S., Brown, R.F., Day, D.E., 2008. Mechanical and in vitro performance of 13-93 bioactive glass scaffolds prepared by a polymer foam replication technique. *Acta Biomater.* 4, 1854–1864.
- Fu, Q., Rahaman, M.N., Bal, B.S., *et al.*, 2010. Bioactive glass scaffolds with controllable degradation rates for bone tissue engineering applications. II. In vitro and in vivo biological evaluation. *J. Biomed. Mater. Res.* 95, 172–179.
- Gerhardt, L.C., Widdows, K.L., Erol, M.M., *et al.*, 2011. The pro-angiogenic properties of multi-functional bioactive glass composite scaffolds. *Biomaterials* 32, 4096–4108.
- Greenspan, D.C., 1999. Bioactive glass: Mechanism of bone bonding. *Tandläkartidn. Ark* 91, 1–32.
- Hench, L.L., Splinter, R.J., Allen, W.C., Greenlee, T.K., 1971. Bonding mechanisms at the interface of ceramic prosthetic materials. *J. Biomed. Mater. Res.* 5, 117–141.
- Hench, L.L., 1988. Bioactive ceramics. *Ann. N. Y. Acad. Sci.* 523, 54–71.
- Hench, L.L., West, J.K., 1990. The sol-gel process. *Chem. Rev.* 90, 33–72.
- Hench, L.L., 2006. The story of bioglass. *J. Mater. Sci. Mater. Med.* 17, 967–978.
- Hong, Y., Chen, X., Jing, X., *et al.*, 2010. Preparation, bioactivity, and drug release of hierarchical nanoporous bioactive glass ultrathin fibers. *Adv. Mater.* 22, 754–758.
- Hoppe, A., Guldal, N.S., Boccaccini, A.R., 2011. A review of the biological response to ionic dissolution products from bioactive glasses and glass-ceramics. *Biomaterials* 32, 2757–2774.
- Huang, W., Day, D., Kittiratanapiboon, K., Rahaman, M., 2006. Kinetics and mechanisms of the conversion of silicate (45S5), borate, and borosilicate glasses to hydroxyapatite in dilute phosphate solutions. *J. Mater. Sci. Mater. Med.* 17, 583–596.
- Izquierdo-Barba, I., Ruiz-Gonzalez, L., Doadrio, J.C., Gonzalez-Calbet, J., Vallet-Regi, M., 2005. Tissue regeneration: A new property of mesoporous materials. *Solid State Sci.* 7, 983–989.
- Izquierdo-Barba, I., Vallet-Regi, M., 2015. Mesoporous bioactive glasses: Relevance of their porous structure compared to that of classical bioglasses. *Biomed. Glasses* 1, 140–150.
- Jones, J.R., Brauer, D.S., Hupa, L., Greenspan, D.C., 2016. Bioglass and bioactive glasses and their impact on healthcare. *Int. J. Appl. Glass Sci.* 7, 423–434.
- Jones, J.R., Lee, P.D., Hench, L.L., 2006. Hierarchical porous materials for tissue engineering. *Philos. Trans. A Math. Phys. Eng. Sci.* 364, 263–281.
- Jones, J.R., 2013. Review of bioactive glass: from Hench to hybrids. *Acta Biomater.* 9, 4457–4486.
- Kargozar, S., Baino, F., Hamzehlou, S., Hill, R.G., Mozafari, M., 2018b. Bioactive glasses entering the mainstream. *Drug Discov. Today* 23, 1700–1704.
- Kargozar, S., Hamzehlou, S., Baino, F., 2017b. Potential of bioactive glasses for cardiac and pulmonary tissue engineering. *Materials* 10, 1429.
- Kargozar, S., Lotfibakhshaei, N., Ai, J., *et al.*, 2017a. Strontium- and cobalt-substituted bioactive glasses seeded with human umbilical cord perivascular cells to promote bone regeneration via enhanced osteogenic and angiogenic activities. *Acta Biomater.* 58, 502–514.
- Kargozar, S., Montazerian, M., Hamzehlou, S., Kim, H.W., Baino, F., 2018a. Mesoporous bioactive glasses: Promising platforms for antibacterial strategies. *Acta Biomater.* 81, 1–19.
- Kargozar, S., Mozafari, M., Hamzehlou, S., Kim, H.W., Baino, F., 2019. Mesoporous bioactive glasses (MBGs) in cancer therapy: Full of hope and promise. *Mater. Lett.* 251, 241–246.
- Kargozar, S., Mozafari, M., Hill, R.G., *et al.*, 2018c. Synergistic combination of bioactive glasses and polymers for enhanced bone tissue regeneration. *Mater. Today Proc.* 5, 15532–15539.
- Kresge, C., Leonowicz, M., Roth, W., Valtruli, J., Beck, J., 1992. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature* 359, 710–712.
- Lakhkar, N.J., Lee, I.H., Kim, H.W., *et al.*, 2013. Bone formation controlled by biologically relevant inorganic ions: Role and controlled delivery from phosphate-based glasses. *Adv. Drug Deliv. Rev.* 65, 405–420.

- Leonardi, E., Ciapetti, G., Baldini, N., *et al.*, 2010. Response of human bone marrow stromal cells to a resorbable $P_2O_5-SiO_2-CaO-MgO-Na_2O-K_2O$ phosphate glass-ceramic for tissue engineering applications. *Acta Biomater.* 6, 598–606.
- Li, L., Clark, A.E., Hench, L.L., 1991. An investigation of bioactive glass powders by sol-gel processing. *J. Biomed. Mater. Res. Appl. Biomater.* 2, 231–239.
- Littmann, E., Autefage, H., Solanki, A.K., *et al.*, 2018. Cobalt-containing bioactive glasses reduce human mesenchymal stem cell chondrogenic differentiation despite HIF-1 α stabilization. *J. Eur. Ceram. Soc.* 38, 877–886.
- Liu, X., Rahaman, M.N., Hilmas, G.E., Bal, B.S., 2013. Mechanical properties of bioactive glass (13-93) scaffolds fabricated by robotic deposition for structural bone repair. *Acta Biomater.* 9, 7025–7034.
- Massera, J., Fagerlund, S., Hupa, L., Hupa, M., 2012. Crystallization mechanism of the bioactive glasses, 45S5 and S53P4. *J. Am. Ceram. Soc.* 95, 607–613.
- Merwin, G.E., 1986. Bioglass middle ear prosthesis: preliminary report. *Ann. Otol. Rhinol. Laryngol.* 95, 78–82.
- Miguez-Pacheco, V., Hench, L.L., Boccaccini, A.R., 2015. Bioactive glasses beyond bone and teeth: Emerging applications in contact with soft tissues. *Acta Biomater.* 13, 1–15.
- Montazerian, M., Zanotto, E.D., 2017. Bioactive and inert glass-ceramics. *J. Biomed. Mater. Res. A* 105, 619–639.
- Ogino, M., Ohuchi, F., Hench, L.L., 1980. Compositional dependence of the formation of calcium phosphate films on bioglass. *J. Biomed. Mater. Res.* 14, 55–64.
- Patel, A., Knowles, J.C., 2006. Investigation of silica-iron-phosphates glasses for tissue engineering. *J. Mater. Sci. Mater. Med.* 17, 937–944.
- Peitl, O., LaTorre, G.P., Hench, L.L., 1996. Effect of crystallization on apatite layer formation of bioactive glass 45S5. *J. Biomed. Mater. Res.* 30, 509–514.
- Peltola, M., Kinnunen, I., Aitasalo, K., 2008. Reconstruction of orbital wall defects with bioactive glass plates. *J. Oral Maxillofac. Surg.* 66, 639–646.
- Peng, S., Zhou, G., Luk, K.D., *et al.*, 2009. Strontium promotes osteogenic differentiation of mesenchymal stem cells through the Ras/MAPK signaling pathway. *Cell. Physiol. Biochem.* 23, 165–174.
- Rahaman, M.N., Day, D.E., Bal, B.S., *et al.*, 2011. Bioactive glass in tissue engineering. *Acta Biomater.* 7, 2355–2373.
- Rahaman, M.N., Xiao, W., Fu, Q., Huang, W., 2017. Review – Bioactive glass implants for potential application in structural bone repair. *Biomed. Glasses* 3, 56–66.
- Shah, R., Sinanan, A.C.M., Knowles, J.C., Hunt, N.P., Lewis, M.P., 2005. Craniofacial muscle engineering using a 3-dimensional phosphate glass fibre construct. *Biomaterials* 26, 1497–1505.
- Stanley, H.R., Hall, M.B., Clark, A.E., *et al.*, 1997. Using 45S5 bioglass cones as endosseous ridge maintenance implants to prevent alveolar ridge resorption: A 5-year evaluation. *Int. J. Oral Maxillofac. Implants* 12, 95–105.
- Stoor, P., Pulkkinen, J., Grenman, R., 2010. Bioactive glass S53P4 in the filling of cavities in the mastoid cell area in surgery for chronic otitis media. *Ann. Otol. Rhinol. Laryngol.* 119, 377–382.
- Vallet-Regi, M., Ramila, A., Del Real, R.P., Perez-Pariente, J., 2001. A new property of MCM-41: Drug delivery system. *J. Chem. Mater.* 13, 308–311.
- Vichery, C., Nedelec, J.M., 2016. Bioactive glass nanoparticles: From synthesis to materials design for biomedical applications. *Materials* 9, 288.
- Vitale-Brovvarone, C., Bairo, F., Miola, M., *et al.*, 2009b. Glass-ceramic scaffolds containing silica mesophases for bone grafting and drug delivery. *J. Mater. Sci. Mater. Med.* 20, 809–820.
- Vitale-Brovvarone, C., Bairo, F., Verné, E., 2009a. High strength bioactive glass-ceramic scaffolds for bone regeneration. *J. Mater. Sci. Mater. Med.* 20, 643–653.
- Vitale-Brovvarone, C., Ciapetti, G., Leonardi, E., *et al.*, 2011. Resorbable glass-ceramic phosphate-based scaffolds for bone tissue engineering: Synthesis, properties and in vitro effects on human marrow stromal cells. *J. Biomater. Appl.* 26, 465–489.
- Vitale-Brovvarone, C., Novajra, G., Lousteau, J., *et al.*, 2012. Phosphate glass fibres and their role in neuronal polarization and axonal growth direction. *Acta Biomater.* 8, 1125–1136.
- Wray, P., 2011. "Cotton candy" that heals. *Am. Ceram. Soc. Bull.* 90, 24–31.
- Wu, C., Chang, J., 2012. Mesoporous bioactive glasses: Structure characteristics, drug/growth factor delivery and bone regeneration application. *Interface Focus* 2, 292–306.
- Wu, C., Chang, J., 2014. Multifunctional mesoporous bioactive glasses for effective delivery of therapeutic ions and drug/growth factors. *J. Control. Rel.* 193, 282–295.
- Wu, C., Zhang, Y., Zhu, Y., Friis, T., Xiao, Y., 2010. Structure-property relationships of silk-modified mesoporous bioglass scaffolds. *Biomaterials* 31, 3429–3438.
- Wu, C., Zhou, Y., Fan, W., *et al.*, 2011. Hypoxia-mimicking mesoporous bioactive glass scaffolds with controllable cobalt ion release for bone tissue engineering. *Biomaterials* 33, 2076–2085.
- Zhang, J., Zhao, S., Zhu, Y., *et al.*, 2014. Three-dimensional printing of strontium-containing mesoporous bioactive glass scaffolds for bone regeneration. *Acta Biomater.* 10, 2269–2281.

Calcium Phosphate Cements

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Introduction

Recent advances in medicine have supported generations of people to live longer. With age comes diminishing quality of bone and hence bone disease and fracture become increasingly more prevalent. In order to aid with fracture fusion and regeneration, bone grafting techniques such as autogenous and allogeneous bone grafts are employed. Their primary functions are to provide structural support to the fracture site and enhance biological fracture repair.

The gold standard in bone grafting are autogenous bone grafts that involve the use of bone harvested from the patient's own body which is seeded with living cells and growth factors. The limitations associated with this technique are significant and include the fact that autogenous bone grafting requires a second surgical site which may result in donor site morbidity, increased post-operative pain and limited supply of bone.

The alternative, allogeneous bone grafting is when bone is harvested from a cadaver. Although this to some degree overcomes the limited supply, there is a significant increase in the transmission of disease and infection from the donor bone and also a risk of rejection. Donor bone has to undergo sterilization to limit these factors however it has an adverse effect on bone strength and biological factors (Zhang *et al.*, 2013).

The limitations associated with the above techniques hence underline the need for a suitable alternative which is free from limitation and disease. The scope of this chapter explores the use of calcium phosphate cements (CPCs) as a suitable alternative which may be used as a bone grafting substitute.

Calcium phosphate cements and their application as a bone cement have been of continuing interest since their introduction to dentistry in 1983 by Brown and Chow (1983) of the American Dental Association. Brown and Chow studied the use of CPCs as a remineralizing paste for the repair of dental carious lesions. By investigating the setting reactions of tetracalcium phosphate (TTCP), dicalcium phosphate anhydrous (DCPA) and dicalcium phosphate dihydrate (DCPD), Brown and Chow inadvertently uncovered a new self-setting orthopedic bone cement consisting solely of calcium phosphates which precipitate a hydroxyapatite (HA) by-product. This was deemed a momentous discovery as hydroxyapatite is the major mineral component of bone and hence the cement will be highly compatible with both soft and hard tissue (Chow and Takagi, 2001).

The CPC setting reaction is a dissolution-precipitation reaction whereby the combination of a powder and liquid phase results in the formation of a cement paste which sets in situ as a solid mass. The initial reaction sees the dissolution of calcium and phosphate ions which work to supersaturate the solution with respect to calcium and phosphate ions leading to the precipitation of the thermodynamically favored calcium orthophosphate phase via a nucleation and crystal growth process. The entanglement of these precipitated needles like crystals of HA is responsible for the hardening of the cement.

According to Hak (2007), the attractiveness of CPCs as an alternative to autogenous bone grafts stems from their bioactive, biocompatible, osteoconductive, and osteointegrative abilities. CPCs promote ingrowth of new living bone and house the ability to display early biological properties similar to that of HA. Studies have confirmed that CPCs once set are incorporated into the bone remodeling cycle and hence undergo osteoclastic resorption, followed by angiogenesis and new bone formation (Bohner, 2000).

In recent years as summarized by Chow *et al.* (1991), there has been a resurgence of interest in optimizing calcium phosphate cements with relation to the setting reaction in order to comply with clinical requirements. At present, calcium phosphate cements are restricted to non-/low-load bearing applications due to their weak mechanical properties. Examples include stabilization of craniofacial surgical sites, and maxillofacial void defect filling. CPCs' weak mechanical properties can be attributed to the highly porous nature of the cement. It has been discussed by Ambard and Muenninghoff (2006) that reduction of the cement's porosity would adversely compromise the cements osteoconductive properties and its ability to be incorporated into the bone remodeling cycle. Other parameters of interest as discussed by Ginebra *et al.* (2004), Fernández *et al.* (1998) and various other published authors include injectability and molding capabilities, powder/liquid ratio, and pH and solubility.

Bone graft substitutes are designed to be osteoconductive i.e., promote either on growth and/or ingrowth of newly formed bone and are traditionally used in conjunction with either/or a potent biologic stimulus or internal and external fixation methods. Currently on the market there are copious amounts of different bone graft substitutes which vary considerably in terms of structural strength, chemical composition and both resorption and remodeling rates. It is therefore paramount for surgical staff to fully understand the differences in order to optimize their use in specific clinical situations (Hak, 2007).

Bone graft substitutes are indicated for filling bone voids and defects where mechanical stability is not its primary function. As stated above, because of their limited structural stability, they are used in conjunction with traditional fixation methods (Hak, 2007).

The ideal biomaterial would exhibit good mechanical stability, be biocompatible and easily shaped and molded for esthetic purposes. According to Henslee *et al.* (2012), calcium phosphate cements display all these qualities.

Table 1 Crystallographic data for known calcium phosphates

<i>CaP</i>	<i>Space group</i>	<i>Unit cell parameters (a, b, c in Å, α, β, γ in °)</i>	<i>Z</i>	<i>Density (g/cm³)</i>
MCPM	Triclinic $\bar{P}\bar{1}$	$a = 5.6261(5), b = 11.889(2), c = 6.4731(8)$ $\alpha = 98.633(6), \beta = 118.262(6), \gamma = 83.344(6)$	2	2.23
MCPA	Triclinic $\bar{P}\bar{1}$	$a = 7.5577(5), b = 8.2531(6), c = 5.5504(3)$ $\alpha = 109.87(1), \beta = 93.68(1), \gamma = 109.15(1)$	2	2.58
DCPD	Monoclinic Ia	$a = 5.812(2), b = 15.180(3), c = 6.239(2)$ $\beta = 116.42(3)$	4	2.32
DCPA	Triclinic $\bar{P}\bar{1}$	$a = 6.190(1), b = 6.627(2), c = 6.9982(2)$ $\alpha = 96.34(2), \beta = 103.82(2), \gamma = 88.33(2)$	4	2.89
OCP	Triclinic $\bar{P}\bar{1}$	$a = 19.693(4), b = 9.523(2), c = 6.835(2)$ $\alpha = 90.15(2), \beta = 92.54(2), \gamma = 108.65(1)$	1	2.61
α – TCP	Monoclinic $P2_1/a$	$a = 12.887(2), b = 27.280(4), c = 15.219(2)$ $\beta = 126.20(1)$	24	2.86
β – TCP	Rhombohedral $R\bar{3}cH$	$a = b = 10.439(1), c = 37.375(6)$ $\gamma = 120$	21	3.07
HA	Monoclinic $P2_1/a$ or hexagonal $P6_3/m$	$a = 9.84214(8), b = 2a, c = 6.8814(7)$ $\gamma = 120$ (monoclinic)	4	3.16
		$a = b = 9.4302(5), c = 6.8911(2)$ $\gamma = 120$ (hexagonal)	2	
TTCP	Monoclinic $P2_1$	$a = 7.023(1), b = 11.986(4), c = 9.473(2)$ $\beta = 90.90(1)$	4	3.05

Note: Dorozhkin, S., 2009b. Calcium orthophosphates in nature, biology and medicine. Materials 2, 399–498.

Calcium Phosphate Salts

Calcium Orthophosphates (CaPs) can be considered as salts of either primary ($H_2PO_4^-$), secondary (HPO_4^{2-}) or tertiary (PO_4^{3-}) phosphate ions and the counter ion Calcium (Ca^{2+}). They are further distinguished by their Calcium to Phosphate ratio, 0.5–2.0 and their crystal structure influencing their physiochemical characteristics and applicability to use as a bone substitute. CaPs can be generally divided between high temperature formation and low temperature precipitate materials. High temperature materials (FA, OA, TTCP, α and β -TCP) are typically formed at temperatures above 1000°C. The solution precipitated materials of Calcium Deficient Hydroxyapatite (CDHA), Dicalcium Phosphate Anhydrous and Dihydrate (DCPA, DCPD), Monocalcium Phosphate Anhydrous and Monohydrate (MCPA, MCPM), Octocalcium Phosphate (OCP) and Hydroxyapatite (HA) are obtained at low temperatures. Typically the phase formed is dependent on the solution pH, supersaturation as well as reaction rate, and typically it is these low temperature precipitate formed calcium phosphate salts that are utilized in the setting reaction of a calcium phosphate cement.

Dorozhkin (2007) states that the primary parameters of interest for calcium phosphate salts are molar Ca/P ratio, solubility and basicity/acidity as these parameters correlate significantly with solution pH. A lower Ca/P molar ratio indicates a more acidic and water-soluble calcium phosphate salt. It has been noted by Bohner (2000) that subtle alterations in the structure and composition of calcium phosphate compounds has a significant effect on their in vivo behavior. The in vivo degradation of a calcium phosphate is largely dependent on their solubility. If the solubility of the calcium phosphate salt is less than that of the mineral component of bone, an extremely slow degradation rate will be observed whereas the opposite is noted if the solubility is greater than that of the mineral component of bone. The following are the most commonly used calcium phosphate salts and their properties (Table 1).

Monocalcium phosphate monohydrate (MCPM) is the most acidic and water-soluble calcium phosphate compound. At temperatures above 100°C, it transforms into MCPA. Due to its high acidity and solubility, MCPM is never found in biological calcifications. However, MCPM is used in some calcium phosphate biomedical applications.

Monocalcium phosphate anhydrous (MCPA) is the anhydrous form of MCPM. It crystallizes under similar conditions as MCPM but at temperatures above 100°C. Like MCPM, MCPA never appears in calcified tissue. Currently it is not used for any biomedical applications.

Dicalcium phosphate dihydrate (DCPD) can be easily crystallized from aqueous solutions. DCPD transforms into dicalcium phosphate anhydrite at temperatures above 80°C. It is metastable and can be converted into the following CaPs: DCPA at pH < 6; OCP at pH 6–7; CDHA at pH > 7 (Bohner, 2000). *In vivo*, DCPD is converted into precipitated HA or biodegraded and replaced by bone. Inflammatory responses may occur when large amounts of DCPD are converted to precipitated HA (PHA) *in vivo*, this is due to the large amount of acid released as shown in the following reaction (Albee, 1920):



DCPD is of biological importance because it is often found in pathological calcifications. It has been detected in fracture callus, bone and kidney stones. It is also sometimes considered a precursor of HA in bone. DCPD is biocompatible, biodegradable and osteoconductive, and thus is used in calcium phosphate cements for biomedical applications.

Dicalcium phosphate anhydrous (DCPA) is the anhydrous form of DCPD. DCPA, like DCPD, can be crystallized from aqueous solutions but at 100°C. Unlike DCPD, DCPA occurs in neither normal nor pathological calcifications. DCPA powder has been tested *in vivo* and has proven to be biocompatible and biodegradable. It is used in calcium phosphate cements.

Octacalcium phosphate (OCP) crystals are triclinic and they consist of alternating apatite layers and hydrated layers. These two layers are linked to each other by Van der Waals and hydrogen bonds. OCP is often found as an intermediate phase during the precipitation of the thermodynamically more stable calcium phosphates like HA, from aqueous solutions. OCP plays an important role in the *in vivo* formation of apatitic biominerals. OCP is also biocompatible, biodegradable and osteoconductive.

Tricalcium phosphate (TCP) exists in two major distinct phases: α -TCP and β -TCP phases. α -TCP crystallizes in the monoclinic space group, and β -TCP crystallizes in the rhombohedral space group. Despite their similar chemical composition, their different crystallographic features give different resorption features: α -TCP is more soluble than β -TCP, and it is obtained after heating the β -TCP to more than 1170°C.

β -TCP is the “true calcium orthophosphate” of the stoichiometric composition $\text{Ca}_3(\text{PO}_4)_2$. It can be obtained through the thermal treatment above 650°C of an equimolar amount of DCPD and PHA (Precipitated hydroxyapatite) at Ca:P ratio of 1.67 and subsequent calcination (Eliaz, 2012). β -TCP cannot be precipitated from solution, but may only be prepared by calcination. At temperatures above 1170°C it transforms into the high temperature phase α -TCP (Dorozhkin, 2009b). Being the stable phase at room temperature, β -TCP is less soluble in water than α -TCP. Pure β -TCP never occurs in biological calcifications. β -TCP is degradable and can be used in combination with HA as a biphasic calcium phosphate (BCP) as a bone substitute.

α -TCP has exactly the same chemical composition as β -TCP but has a different crystallographic structure. α -TCP is more reactive in aqueous systems than β -TCP and can be hydrolyzed to a mixture of other calcium phosphates. It never occurs in biological calcifications and has a limited application in medicine in calcium phosphate cements.

Amorphous calcium phosphate (ACP) is often encountered as a transient phase during the formation of calcium phosphates in aqueous systems. Usually ACP is the first phase that is precipitated from a supersaturated solution prepared by rapid mixing of solutions containing calcium and phosphate ions. The chemical composition of ACP depends on the pH of the solution and the concentrations of the calcium and phosphate ions. Biologically, ACP is found in soft-tissue pathological calcifications. ACP is sometimes used in calcium phosphate cements.

Calcium deficient hydroxyapatite (CDHA) can be easily prepared by the simultaneous addition of calcium and phosphate containing solutions into boiling water, followed by boiling the suspension for several hours. During this time, the initially precipitated OCP or ACP (depending on pH) is transformed into CDHA (Dorozhkin, 2009b). Unsubstituted CDHA does not exist in biological calcifications; it occurs only with ionic substitutions, i.e., sodium for calcium, carbonate for phosphate. This substituted CDHA forms dahllite “the biological apatite” which is the main inorganic component of animal and human normal and pathological calcifications. Therefore, CDHA is a very promising compound for the manufacture of artificial bone substitutes.

Hydroxyapatite (HA) is highly crystalline and is the most stable and least soluble of all calcium orthophosphates. Pure HA crystallizes in the monoclinic space group $P2_1/b$ (Elliott *et al.*, 1973). However, at temperatures above 250°C, there is a monoclinic to hexagonal phase transition in HA (Elliott, 1994). Some impurities, like partial substitution of hydroxide by fluoride or chloride ions, stabilize the hexagonal structure of HA at ambient temperature. For this reason, the very rare single crystals of natural HA always exhibit a hexagonal space group (Elliott, 1994). Pure HA never occurs in biological systems, however, because of the chemical similarities to bone mineral, HA is widely used as a coating for orthopedic and dental implants.

Precipitated hydroxyapatite (PHA) chemistry is very complex. PHA can have a Ca:P ratio from 1.50 to 1.67 (Brown and Martin, 1999). PHA with a Ca:P molar ratio of 1.50 is often called calcium-deficient (CDHA) or tricalcium phosphate (TCP). TCP has almost the same chemical composition as β -TCP but has a different crystalline structure. PHA is obtained by precipitation in an aqueous solution above pH 7 (Bohner, 2000). PHA crystals are poorly crystalline and of submicron dimensions however PHA has a very large specific surface area. Therefore, PHA is very similar to the apatite present in bone. According to literature the solubility of PHA varies by up to 20% depending on the method of preparation (Bohner, 2000). The solubility of PHA increases with a decrease in Ca:P ratio, a decrease in crystallinity and a decrease in crystal size. Depending on Ca:P ratio, on heating above 700°C, PHA degrades into the following (Bohner, 2000):

Table 2 IR and Raman peak positions of hydroxyapatite

IR ^a	Raman ^a		Assignment
3572	3572 m		OH stretch
1087	1075 s	1046 s	} ν_3 PO ₄
~1072 sh ^a	1061 w,sh	1039 m	
1046	1053 sh	1028 s	
~1032 sh			
	962 vs		ν_1 PO ₄
962		948 m	
	641 vw		OH libration
630		630 vw	
	615 m		} ν_4 PO ₄
601	608 s	593 s	
571		580 s	
	447 s		} ν_2 PO ₄
474		432 s	
~462 sh			
	376 w		lattice mode
	333 w ^b		Ca ₃ -(OH) "ν ₁ stretch"
~355 sh			} Ca-PO ₄ lattice modes
343	306 w ^b		
	289 w ^b	175 w	
	267 w ^b	157 w	
	237 w	153 w	
~290	222 w	140 w	
~275	206 w	132 w	
~228	196 w	114 w ^c	

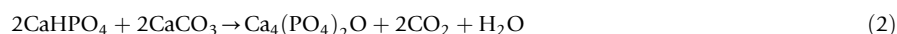
Abbreviations: vs: very sharp, vw: very weak, w: weak, m: medium, s: strong, vs: very strong, sh: shoulder.

Note: Elliott, J.C., 1994. Structure and chemistry of the apatites and other calcium orthophosphates.

In: Elliott, J.C. (Ed.), Studies in Inorganic Chemistry. Elsevier.

- (1) Ca:P = 1.50 PHA → β - TCP
- (2) Ca:P = 1.50–1.67 PHA → mixture of β - TCP and HA
- (3) Ca:P = 1.67 PHA → HA

Tetracalcium phosphate (TTCP) is the most basic calcium orthophosphate. However, its solubility in water is higher than that of HA. TTCP cannot be precipitated from aqueous solutions, and thus can only be prepared by a solid-state reaction above 1300°C, for example, by heating homogenized, equimolar quantities of DCPA and CaCO₃. This reaction should be carried out in a dry atmosphere to prevent uptake of water and formation of HA (Dorozhkin, 2009b):



TTCP is not very stable in aqueous solutions, it slowly hydrolyzes to HA and calcium hydroxide. Consequently, TTCP is never found in biological calcifications. TTCP is the most soluble calcium phosphate below a pH of 5. It is also the most basic calcium phosphate. In medicine, TTCP is widely used for the preparation of various self-setting calcium phosphate cements. It is bio-compatible but despite its high solubility it is poorly biodegradable.

Hydroxyapatite

Up to 70% of bone is made up of an inorganic mineral called hydroxyapatite, which includes calcium phosphate, calcium carbonate, calcium fluoride, calcium hydroxide and citrate (Ooi *et al.*, 2007). Hydroxyapatite is predominantly crystalline. The properties of hydroxyapatite, both natural and synthetic, vary widely. Hydroxyapatite being the crystalline component of bone, is the most commonly used calcium phosphate in implant/bone filler fabrication. Synthetic HA has such chemical similarity to bone

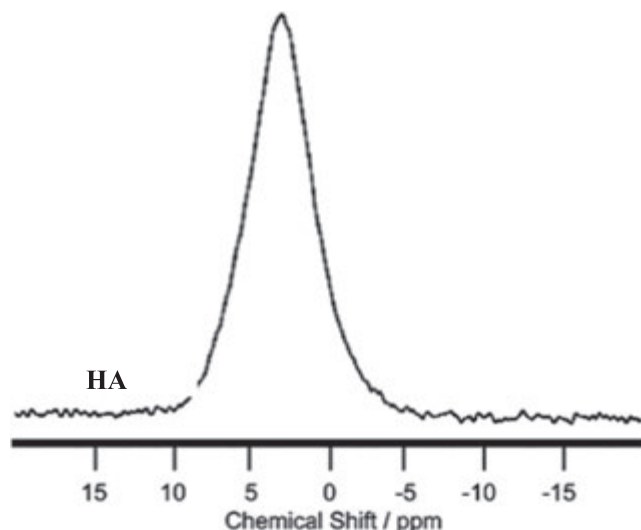


Fig. 1 ^{31}P MAS NMR of Hydroxyapatite showing resonance at 2.8 ppm relative to 85% H_2PO_4 . Reproduced from Chappell, H., Duer, M., Groom, N., Pickard, C., Bristowe, P., 2008. Probing the surface structure of hydroxyapatite using NMR spectroscopy and first principles calculations, *Physical Chemistry Chemical Physics*. 10 600–606.

mineral that it will induce a biological response similar to the one generated during bone remodeling. Hydroxyapatite is one of the few materials that are classified as bioactive, meaning it will support bone ingrowth and osseointegration when used in orthopedic, dental and maxillofacial applications. The key properties of synthetic HA are (1) its ability to integrate in bone structures and support bone ingrowth, without breaking down or dissolving, (2) HA is a thermally unstable compound, decomposing at temperatures from about 800–1200°C depending on its stoichiometry, (3) generally speaking dense hydroxyapatite does not have the mechanical strength to enable it to succeed in long term load bearing applications (Dorozhkin, 2009b).

Hydroxyapatite has a similar structure to octacalcium phosphate (OCP) ($\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4$) and there is a strong relationship between these two compounds.

The nucleation of hydroxyapatite depends upon reaction conditions. In highly supersaturated solutions at neutral or alkali pH conditions, it was shown that amorphous calcium phosphate first forms which then transforms to OCP which then hydrolyzes to Hydroxyapatite (Elliott, 1994). In studies where seeded crystals were added to calcium phosphate solutions with altering conditions showed that the rate of crystal growth is largely determined by the degree of the supersaturation of the surrounding solution (Moreno *et al.*, 1977; Moreno and Varughese, 1981). Kinetic analysis showed that linear growth rate was dependent on the square of the degree of supersaturation of the solution (Moreno *et al.*, 1977; Moreno and Varughese, 1981).

Infrared and Raman spectroscopy techniques can be used for identification of phases within a sample (Table 2).

NMR Spectroscopy of HA

In ^1H MAS NMR of hydroxyapatite at 500.13 MHz and a spinning speed of 7.3 kHz a sharp resonance was present at 0.2 ppm relative to trimethyl silane which was attributed to the proton in the OH^- group, a second resonance at 5.6 ppm was identified which was attributed to surface adsorbed water (Yesinowski and Eckert, 1987). ^{43}Ca MAS NMR has been performed on hydroxyapatite samples in an attempt to distinguish between the two Ca sites with Ca(I) located at -1.8 ± 0.8 ppm and Ca(II) at 11.2 ± 0.8 ppm (Laurencin *et al.*, 2008). ^{31}P MAS NMR studies were also carried out on hydroxyapatite at 68 MHz and a spinning speed of 2.5 kHz and gave a resonance at 2.8 ppm relative to 85% H_3PO_4 . The authors also produced a number of calcium-deficient apatites with Ca/P – 1.46 & 1.58. These also gave resonances at 2.8 ppm indicating no difference in peak position with changing stoichiometry (Rothwell *et al.*, 1980) (Fig. 1).

X-ray Diffraction of HA

The XRD pattern below is that of Hydroxyapatite. The characteristic peaks are the triplet peaks around 32 degrees 2 theta (31.7 (211)), 32.1 (112 and 32.8 (300)° 2θ). There is also a characteristic line at 25.8 (002)° 2θ (Fig. 2).

Octacalcium Phosphate

Octacalcium phosphate (OCP) has the chemical formula $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$. Octacalcium phosphate, which is structurally similar to hydroxyapatite, is a possible precursor in the formation of apatitic calcium phosphate minerals in bones and teeth (Brown and Chow, 1990). OCP is more soluble and less stable at physiological conditions than hydroxyapatite. The similarity of

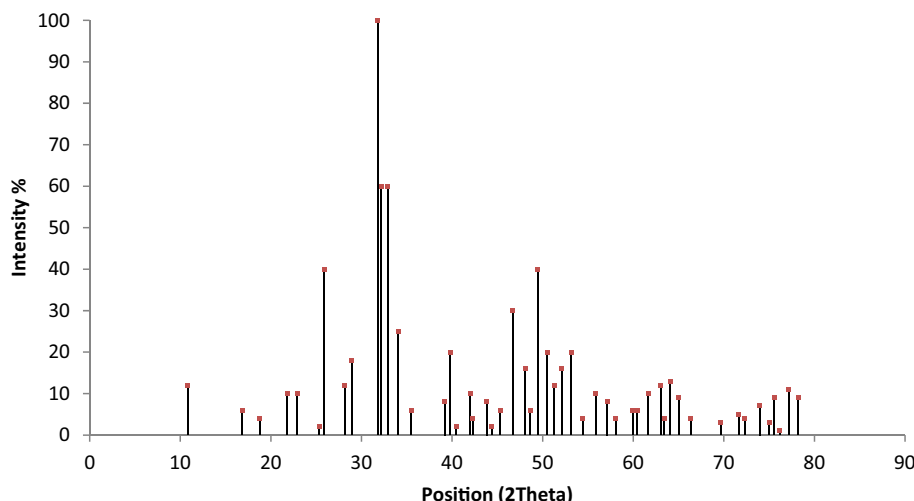


Fig. 2 X-ray Diffraction pattern and relative intensities of Hydroxyapatite. JCPDC ref code 009-0432.

the apatite layer in OCP and the apatite structure in HA provides geometrically favorable conditions for phase transformation from OCP to HA. OCP tends to convert to HA not only in an in vitro environment, but also as an implant in bone defects. This intermediary, however, is thought to be pH dependent. OCP will be an intermediate phase before hydroxyapatite formation at pH between 5.0 and 9.0 whereas if reaction conditions are above pH 9.0 then hydroxyapatite will precipitate directly (Chow, 2000). It has been proposed that the transformation of OCP to HA follows a dissolution-precipitation process (Elliott, 1994). Solid state transformation of OCP to HA has also been suggested in the work of (Nakamura *et al.*, 2006) where the transformation was induced by electron beam irradiation in TEM and the crystal structure change was observed using bright field images, electron diffraction and high resolution microscopy. Studies have shown that resorption of OCP is followed by replacement of newly formed bone (Markovic and Chow, 2010).

Crystals of OCP are typically small and plate-like. The crystals are triclinic, space group P1, with cell parameters $a = 19.692 \text{ \AA}$, $b = 9.523 \text{ \AA}$, $c = 6.835 \text{ \AA}$, $\alpha = 90.15^\circ$, $\beta = 92.54^\circ$, $\gamma = 108.65^\circ$ and $z = 2$. The crystal structure of OCP is described as an alternative stacking of apatite layers and hydrated layers along its [100] direction (Chow and Takagi, 2001). The apatite layer is approximately 1.1 nm thick and is alternating with the water layers which are approximately 0.8 nm thick, parallel to (100) and are a clear feature of the OCP structure (Elliott, 1994) (Fig. 3).

The apatite like layer provides an explanation for the similarities seen in the lattice parameters of OCP and HA ($a = 9.4176$, and $c = 6.8814 \text{ \AA}$). This apatite layer is made of alternating sheets of phosphate ions with Ca^{2+} ions. The water layer consists of phosphate ions more widely spaced than the apatite later and Ca^{2+} ions with a slightly variable amount of water molecules between them. The constituent ions in the OCP structure are distributed between these two layers differently. Six Ca^{2+} ions and two of the six phosphates are located in the apatite layer. The water layer is made of two Ca^{2+} ions and a single phosphate ion. This leaves three phosphate ions which are located in the junction between the apatite and water layers. Two of the phosphate ions are protonated, the phosphate ion in the water layer and one of the phosphate ions located at the inter layer junction (Elliott, 1994).

NMR Spectroscopy of OCP

^1H MAS NMR performed at 500 MHz and a spinning speed of 7.8 kHz showed the presence of a chemical shift at 13 ppm referenced to trimethyl silane and this was assigned to an acidic proton of a HPO_4^{2-} ion located in the junction between the apatite and water layers. The other HPO_4^{2-} located in the water layer was not found. The failure to find a clearly resolved resonance was attributed to positional disorder of this ion and overlap with resonances with the structural water found in OCP. Chemical shifts at 1.1 and 1.5 ppm were detected and were assigned to protons on an isolated water molecule found in the OCP water layer. At 5.5 ppm there was an intense spinning sideband pattern that was assigned to relatively immobile structural water groups. The intensity of this resonance was attributed to a more mobile water species either in the OCP water later or on the OCP surface. ^1H MAS NMR studies performed on thermally dehydrated OCP (a process known to induce OCP to HA transformation) gave a resonance at 0.2 ppm which was attributed to the OH^- found in HA. This was attributed to as evidence of the theory that the structural water in OCP can relocate themselves to a nearby PO_4^{3-} to form HPO_4^{2-} and OH^- in a dehydration reaction of OCP to form HA (Elliott, 1994).

A ^{31}P MAS NMR study performed on OCP (121 MHz, spinning speed 6 kHz) prepared through a reaction of sodium phosphate monobasic dihydrate ($\text{H}_2\text{NaPO}_4 \cdot 2\text{H}_2\text{O}$) and calcium nitrite tetrahydrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. The OCP sample gave four resonances relative to 85% H_3PO_4 and -0.2 , 2.0 , 3.3 and 3.7 ppm. The resonance at 0.2 ppm was assigned to P5 and P6; the resonance at 2.0 ppm was P3; 3.3 ppm was P2 and P4; lastly 3.7 ppm was attributed to P1. Phosphates labeled P1–4 are the PO_4^{3-} ions in the OCP structure and P5 & P6 are the HPO_4^{2-} ions (Tsai *et al.*, 2010; Tseng *et al.*, 2004; Davies *et al.*, 2012) (Fig. 4).

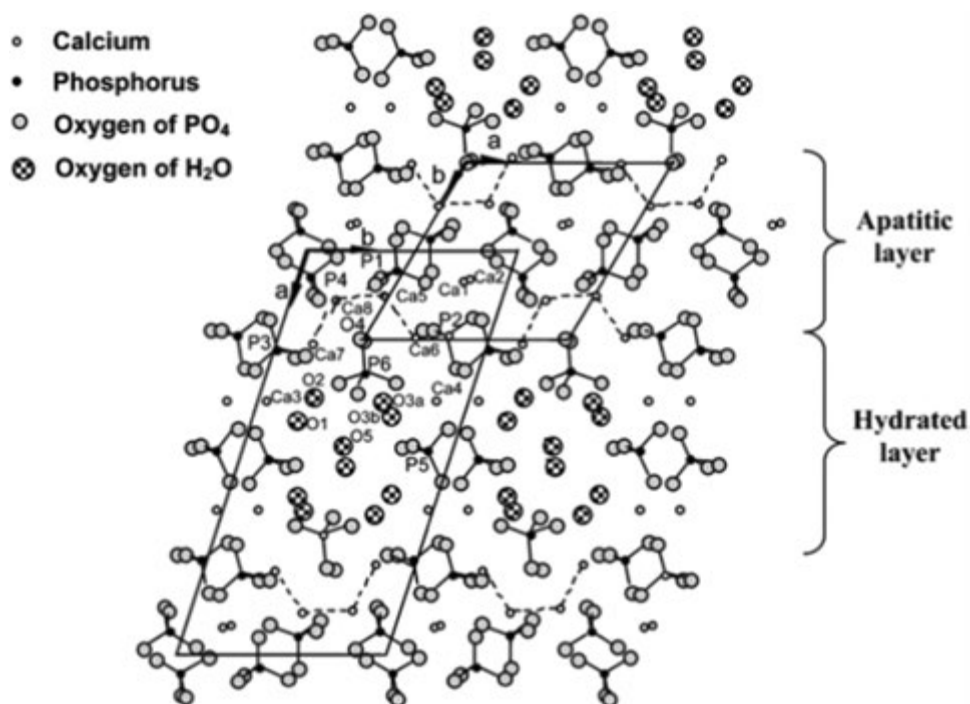


Fig. 3 Crystal structure of octacalcium phosphate. Reproduced from Cazalbou, S., Combes, C., Eichert, D., Rey, C., 2004. Adaptive physico-chemistry of bio-related calcium phosphates. *Journal of Materials Chemistry* 14, 2148–2153.

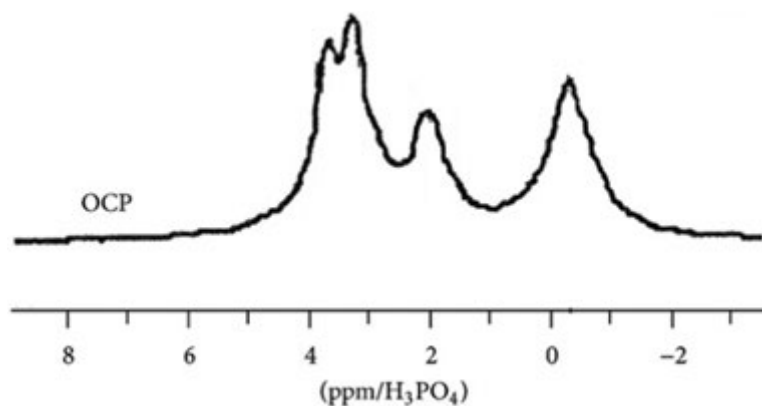


Fig. 4 ^{31}P MAS NMR of Octacalcium Phosphate showing resonances at -0.2 , 2.0 , 3.3 and 3.7 ppm relative to $85\% \text{H}_2\text{PO}_4$. Adapted from Drouet, C., 2013. Apatite formation: Why it may not work as planned, and how to conclusively identify apatite compounds *BioMed Research International* 2013, 490946.

X-Ray Diffraction

Fig. 5 shows the reference XRD pattern of OCP. Given the similarities between the pattern for OCP and HA, the only diffraction line where OCP can be distinguished from HA is the diffraction line at $4.7^\circ 2\theta$, which in highly crystalline OCP will give an intense diffraction line.

Dicalcium Phosphate Dihydrate

Brushite or dicalcium phosphate dihydrate (DCPD) ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) was discovered in 1865 in phosphatic guano in the Caribbean. It is proposed that Brushite is an intermediate for apatite formation, indeed if Brushite is placed into a pH solution outside of its solubility range then apatite will form (Elliott, 1994).

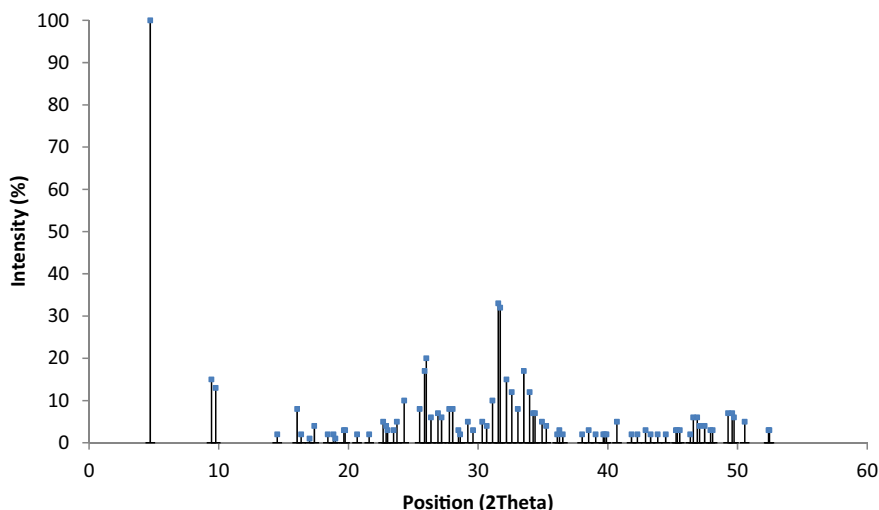


Fig. 5 X-ray Diffraction pattern and relative intensities of Octacalcium Phosphate. JCPDC ref code 026-1056.

Structure

DCPD is monoclinic, space group *1a* with lattice parameters $a = 5.812 \pm 0.002$, $b = 15.180 \pm 0.003$, $c = 6.239 \pm 0.002$ Å and $\beta = 116^\circ 25' \pm 2'$. Four formula units are present per unit cell with an asymmetric unit $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, none of the 5 hydrogen atoms are related by symmetry (Curry and Jones, 1971). The structure of DCPD consists of columns that are parallel to the short diagonal of the (010) face of the unit cell, of alternating Ca^{2+} and PO_4^{3-} ions. The columns are joined together to form corrugated sheets, a conspicuous feature of the structure. The sheets have the composition CaHPO_4 and are linked together by water molecules. Similarly structured sheets are also notable found in the structure of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (Elliott, 1994).

Hydrolysis of DCPD will ultimately lead to formation of HA. However, unlike the relationship between OCP and HA, DCPD is not a pseudomorph of HA (Elliott, 1994). Where the transformation of OCP to HA goes via a solid state phase transition, the single crystal unit is altered chemically to give the formula of HA. In DCPD to HA transformation the route of formation is through dissolution of DCPD then precipitation of HA which can go via OCP as an intermediate depending upon reaction conditions.

DCPD will transform to OCP if in a solution with a pH range 6.2–7.4 and at a temperature within 25–37°C (Tung *et al.*, 1985). If reaction conditions have a higher pH or temperature than this then it is believed that HA will precipitate directly. The reason for this is that the precipitation and growth rate of HA is slow if the pH or temperature is not high; this is in contrast to OCP which has a lower solubility than DCPD and will form readily in mild conditions.

Below are the IR and Raman frequencies for DCPD. DCPD can be distinguished from its bands at 875 cm^{-1} (IR) and 880 cm^{-1} (Raman), which are P-O(H) stretching (Table 3).

NMR Spectroscopy of Dicalcium Phosphate Dihydrate

^{31}P MAS NMR (2 kHz, spinning speed) ^1H decoupled at 68 MHz studies performed on DCPD samples have shown a resonance at 1.7 ppm relative to 85% H_2PO_4 . ^1H MAS NMR studies have shown resonances at 6.4 and 10.4 ppm referenced to trimethyl silane which were attributed to structural water and acidic protons respectively. This was performed at both 200 and 500 MHz with a spinning speed up to 8 kHz (Miquel *et al.*, 1990) (Fig. 6).

X-Ray Diffraction Dicalcium Phosphate Dihydrate

DCPD can be distinguished from OCP and HA by its peak at $11.607^\circ 2\theta$ as shown in Fig. 7.

In Vivo use of Calcium Phosphates

All calcium phosphates are osteoconductive which means bone bonds directly to the surface without an intervening soft tissue layer (Williams, 1987). Osteoconduction helps to increase the activity of bone forming cells – osteoclasts. This osteoconductive property of calcium phosphates, combined with suitable porosity, provides a powerful bone growth scaffold.

The first in vivo use of calcium phosphates has been shown to date back to the 1920s, when tricalcium phosphate (TCP) was implanted to test its efficacy as a bone substitute. The data compared bone fractures with bone loss, and showed that bone growth and union, when injected with calcium phosphate, healed faster than did the controls without its use (Dorozhkin, 2009a; Chow, 2009). Over the next few decades various calcium phosphate particles were implanted into animal specimens to test their effect on

Table 3 IR and Raman peak positions of DCPD

<i>IR</i>	<i>Raman</i>	<i>Assignment</i>
3547 s		O-H Stretching of water
3492 s		
3295 s		
3171 s		O-H Stretching
2964 sh		
2386 w		
2270 vw		
2128 vw		
1720 sh		2875 = 1750
1651 s		H ₂ O Bending
1218 s		O-H In-plane bending
1141 s	1119 w 1083 m	
1066 s	1060 m	PO Stretching
1006 sh		P-O(H) Stretching H ₂ O Libration
998 s	998 vs	
875 s	880 m	
795 s	784 w,br	
665 m		PO Bending
578 s	588 m	
530 s	525 m	
	414 m	
	383 m	H ₂ O Translation
	323 w	PO Bending
	280 w	
	209 m	
	179 w	Lattice vibration
	144 m	
	112 w	

Note: Elliott, J.C., 1994. Structure and chemistry of the apatites and other calcium orthophosphates. In: Elliott, J.C. (Ed.), *Studies in Inorganic Chemistry*. Elsevier.

Abbreviations: vw, very weak, w, weak, m, medium, s, strong, vs, very strong, br, broad, sh, shoulder.

healing with hydroxyapatite (HA) being implanted into rats and guinea pigs for testing in 1951 (Bohner *et al.*, 2000b; Dorozhkin, 2009a). Despite these early experiments however, it was not until the early 1970s that the stigma and fear of utilizing non inert materials within the physiological environment was challenged by researchers who investigated the implantation of soda lime-phosphate silicate glass compositions in the femurs of rats (Hench, 1991; Pattanayak *et al.*, 2011). These implanted bioactive materials were investigated, synthesized and characterized. The results indicated that the materials bonded to the living bone without forming interfacial scar tissue. Extensive toxicity studies on these materials have demonstrated a high degree of biocompatibility, minimal if any inflammatory response or foreign body response and no evidence of local or systemic toxicity. This is because calcium and phosphate ions are the most common ions in the body and these compounds allow direct bonding of soft tissue or bone cells. Since then, focus on these bioactive materials has increased significantly, with the idea of developing calcium phosphate based cements being investigated Brown and Chow (1983).

Calcium Phosphate Cements (CPCs)

The development of the first self-setting calcium phosphate cement was reported in 1987 by Chow (Chow and Takagi, 2001), (Sanzana *et al.*, 2008), (Chow, 2009). These pastes were based on the solubility properties of calcium phosphates being greater than HA in the physiological environment.

One of the great challenges facing modern medicine is to replace old, deteriorating bone with a material that can function for the remaining years of the patient's life and, ideally, be replaced by new bone. This is the theory behind the development of calcium phosphate cements, which are resorbable biomaterials and are designed to gradually degrade over a determined period of time and be replaced by naturally forming host tissue, resulting in a very thin or non-existing interfacial bond. The aim of CPC's is

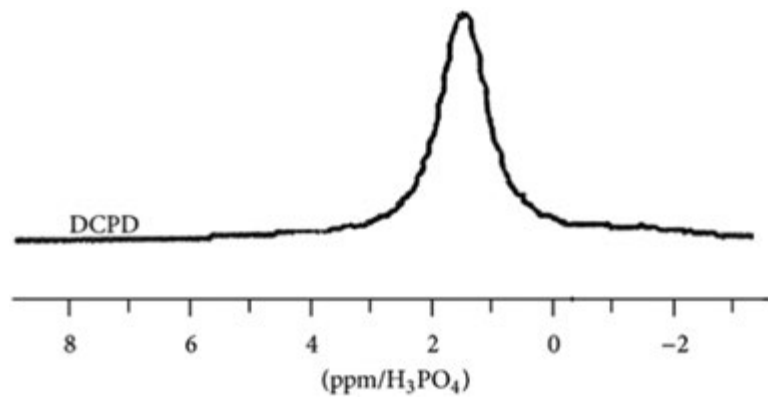


Fig. 6 ^{31}P MAS NMR of dicalcium phosphate dihydrate showing resonance at 1.7 ppm relative to 85% H_2PO_4 . Adapted from Drouet, C., 2013. Apatite formation: Why it may not work as planned, and how to conclusively identify apatite compounds. *BioMed Research International* 2013, 490946.

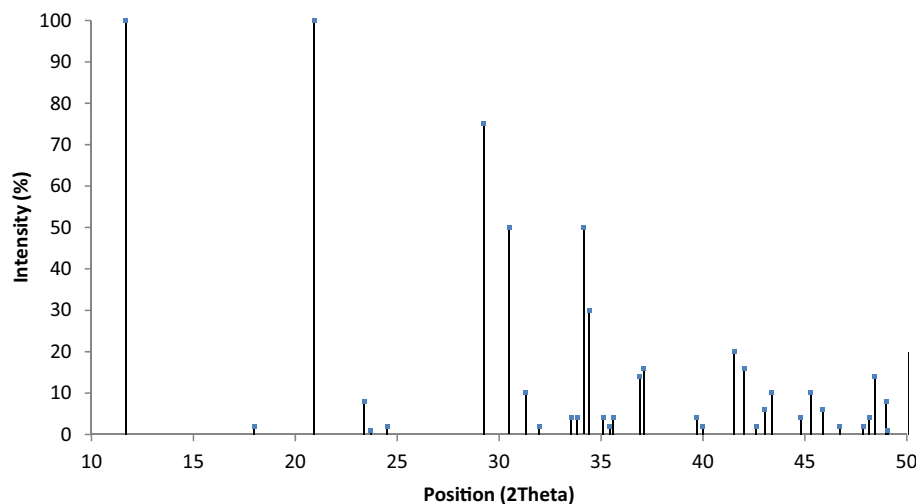


Fig. 7 X-ray Diffraction pattern and relative intensities of dicalcium phosphate dihydrate. JCPDC ref code 009-0077.

to disturb bone functions and properties as little as possible and to behave temporarily in a manner similar to that of bone. These CPC's must form and reproduce the structure, crystallinity, morphology and composition of bone crystals (Hench, 1991; Dorozhkin, 2009a, 2010).

Calcium phosphate cements are synthetic bone graft materials that consist essentially of only calcium phosphate compounds and are capable of self-setting to a hard mass. Synthetic, self-setting, CPC's generally consist of a powder and an aqueous liquid, which are mixed, resulting in a paste-like consistency. They can be molded and even injected via syringe before they harden in situ with fast setting times. This hardening occurs without excessive heat production and at favorable pH levels. Also CPC's allow the surgeon to shape and implant the bioactive bone substitute material on a patient-specific base in real time. This versatility is a key distinguishing characteristic of CPC's from prefabricated calcium orthophosphate granules or blocks. Upon mixing, the powder dissolves in the aqueous solution and new forms of crystals precipitate, the reaction proceeds until all reactive calcium phosphate compounds react. Cement hardening occurs with the entanglement of calcium phosphate crystals, hence leading to a highly porous structure. CPC's exhibit bioactive behavior and integrate into the bone structure by a physiochemical bond as part of bone remodeling process.

The advantages of CPCs include being injectable, moldable and the ability to adapt to the bone defects. They also exhibit excellent biocompatibility and osteoconductive properties. However, because of their limited compressive strength, they are limited to non-load bearing applications such as maxillofacial surgery, the repair of cranial defects and dental fillings. In 1996 the FDA cleared the first calcium phosphate cement for clinical use for non-load bearing applications called BoneSource™ Hydroxyapatite Cement (Friedman *et al.*, 1998; Xu *et al.*, 2007). This self-setting bioactive CPC forms biocompatible precipitated HA as the end product and is, in small defects, gradually replaced by new bone over time, without a loss in volume.

Table 4 Commercial compositions of calcium phosphate cements

Company	Cement/ name	Components	End product
ETEX	a-BSM Embarc Biobon	Powder: ACP (50%), DCPD (50%); Solution: H ₂ O (unbuffered saline solution)	Apatite
Stryker-Leibinger Corp	BoneSourc HydroSet	Powder: TetCP (73%), DCPD (27%); Solution: H ₂ O, Na ₂ HPO ₄ , NaH ₂ PO ₄	Apatite
Teknimed	Cementek Cementek LV	Powder: α -TCP, TetCP, Na Glycerophosphate; Solution: H ₂ O, Ca(OH) ₂ , H ₃ PO ₄ Powder: α -TCP, TetCP, Na Glycerophosphate, dimethylsiloxane; Solution: H ₂ O, Ca(OH) ₂ , H ₃ PO ₄	Apatite
Biomet	Calcion Mimix	Powder: α -TCP (61%), DCP (26%), CaCO ₃ (10%), HAP (3%); Solution: H ₂ O, Na ₂ HPO ₄ Powder: TetCP, α -TCP, C ₅ H ₅ O ₇ Na · 2H ₂ O	Apatite
Mitsubishi materials	Biopex	Powder: α -TCP, TetCP, DCPD, HAP, Mg ₃ (PO ₄) ₂ , NaHSO ₃ ; Solution: H ₂ O, sodium succinate, sodium chondroitin sulfate	Apatite
	Biopex-R	Powder: α -TCP (75%), TetCP (18%), DCPD (5%), HA (2%); Solution: H ₂ O, sodium succinate, sodium chondroitin sulfate	
Kyphon	KyphOs	Powder: α -TCP (77%), Mg ₃ (PO ₄) ₂ (14%), MgHPO ₄ (4.8%), SrCO ₃ (3.6%); Solution: H ₂ O (NH ₄) ₂ HPO ₄	Apatite
Shanghai Rebone Biomaterials Co, Ltd	Rebone	Powder: TetCP, DCPD; Solution: H ₂ O	Apatite
Synthes-Norian	Norian SRS Norian CRS	Powder: α -TCP (85%), CaCO ₃ (12%), MCPM (3%); Solution: H ₂ O, Na ₂ HPO ₄	Apatite
Kasios	Eunobone	Powder: β -TCP (98%), Na ₄ P ₂ O ₇ , (2%); Solution: H ₂ O, H ₃ PO ₄ , H ₂ SO ₄	DCPD
Synthes	ChronOs inject	Powder: β -TCP, MCPM, MgHPO ₄ · 3H ₂ O, Na ₂ H ₂ P ₂ O ₇ ; Solution: NaH ₂ PO ₄ , H ₂ O, sodium hyaluronate	DCPD

Note: Böhner, M., Gbureck, U., Barralet, J.E., 2005. Technological issues for the development of more efficient calcium phosphate bone cements: A critical assessment. *Biomaterials*, 26, 6423–6429.

Biodegradation/Bioresorption of Calcium Phosphate Cements and Replacement by New Bone

Biodegradation is the process caused by the action of living systems whereby a material is broken down into its simpler components. Resorption of bone in vitro or in vivo has been described as cell-mediated degradation of the inorganic and organic phases of bone (Barrère *et al.*, 2006). The process of biodegradation/bioresorption of CaP materials results in physicochemical changes after contact with the biological environment. The physical changes may include disintegration, loss of mechanical strength, loss of density, and change in porosity. The chemical changes include reduction in the pH of the implant environment causing partial dissolution of the material. Chemical changes may also include elevation in the concentrations of calcium and phosphate ions in the environment leading to the formation of other CaP phases. CPCs are bioactive which means they can form a chemical bond with the bone tissue, resulting in a strong bone/material interface. Biodegradation/bioresorption of the material is believed to be related to the solubility of the CaP materials. CaP materials of different composition differ in their crystallographic structure and therefore in their internal bonding strength which is reflected in their stability and solubility or dissolution properties. Even CaP materials of identical composition but different crystallographic structure i.e., α -TCP and β -TCP, vary in their dissolution properties in vitro and also vary in their extent of biodegradation. The differences in biodegradation/biodissolution of CaP materials of similar composition but of different crystallinity may be associated with crystal sizes and the amount of lattice defects present. Smaller crystals will dissolve more readily than larger crystals of the same composition due to the larger surface area exposed to the biological environment.

In theory, calcium phosphate cement may be substituted by bone depending on its formulation and particle size. Apatite CPC was implanted as a paste into the femoral bone of dogs for 3 and 6 months. Histology was performed on thin un-decalcified sections. No foreign body reaction, no inflammation and no necrosis were found. It was found that new bone was formed directly on the resorption line of the calcium phosphate cement whereby a creeping substitution of cement by bone had taken place (Yuan *et al.*, 2000). Osteoclast like cells resorbed the cement as if the cement was bone and replaced the cement with new bone. This is an important property, as the cement could provide short-term biologically desirable properties and then be replaced by new bone. Bone substitution depends on porosity, crystallinity, chemical composition, particle size and powder/liquid (P/L) ratio of the cement.

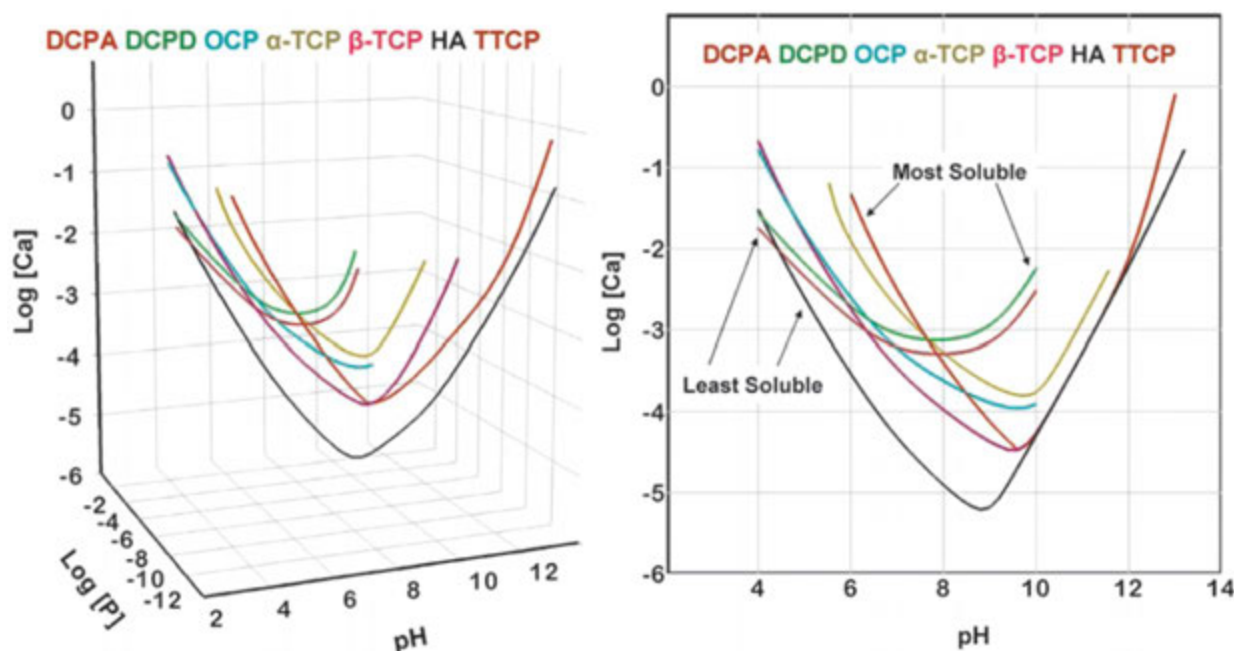


Fig. 8 Solubility phase diagram in 3d and 2d. Reproduced from Chow, L.C., 2009. Next generation calcium phosphate-based biomaterials, *Dental Materials Journal* 28, 1–10.

Solubility of Calcium Phosphates in Calcium Phosphate Cements

Extensive research on new CPC compositions has shown that cementation can occur in mixtures containing a wide variety of calcium phosphate compounds (Chow and Eanes, 2001). Table 4 shows a list of calcium phosphates which have been used as cement ingredients, some of which have been shown to be products in other cement systems. The calcium phosphates in Table 4 are listed in order of increasing Ca/P molar ratio. This is also the order of increasing basicity. Solubility is one of the most important properties of calcium phosphate compounds. The solubility of a CaP determines the equilibrium of almost all ambient-temperature chemical reactions in which calcium phosphates are involved. Gravimetric solubility, defined as the mass of a solid that can dissolve into a unit volume of solution, is a simple way of describing solubility. However, this quantity can change significantly with pH and other solution parameters so is not suitable to describe the solubility properties of CaPs. A more fundamental parameter for describing solubility is the thermodynamic solubility product constant, K_{sp} . K_{sp} is defined as the equilibrium constant for a solid substance dissolving in an aqueous solution. It represents the level at which a solute dissolves in solution. The more a substance dissolves, the higher the K_{sp} value it has.

The reactions between calcium phosphate compounds that occur in an aqueous environment can be described as dissolution/precipitation reactions. Upon mixing, the calcium phosphates dissolve and precipitate into a less soluble form of CaP. During the precipitation reaction, the CaP crystals grow and become entangled, thus providing mechanical rigidity to the cement. For example, in the TTCP/DCPA cement paste, dissolution of TTCP and DCPA in water leads to a solution composition that is highly supersaturated with respect to calcium and phosphate, resulting in HA precipitation. Such reactions are driven by the solubilities of the reactants and product for a given composition.

Solubility is described as the amount of a solid that can dissolve into a unit volume of solution. For calcium phosphates, this quantity can change by several orders of magnitude with changes in pH and concentrations of acids and bases (Chow, 2009). A solubility phase diagram is shown in Fig. 8. Each curve in the diagram, known as a solubility isotherm, can be calculated from the solubility product constant (K_{sp}) of the compound (Table 4). The isotherm describes the solubility of a salt, expressed as the total calcium and total phosphate concentrations of the saturated solution as a function of pH. The phase diagram is also shown in a two dimensional graph, in which a salt whose isotherm lies below that of another salt is less soluble (more stable). The point where two isotherms cross is known as a singular point. The solution at the singular point is simultaneously saturated with respect to both salts.

The setting reactions may be understood by analysing the solubility of the individual cement components such as TTCP and DCPA. The solubility phase diagram showing the solubility curves of TTCP, DCPA and HA is given in Fig. 9.

Over a range of pH, HA is the least soluble salt with DCPA becoming the least soluble when the pH falls below 4.2. TTCP is the most soluble salt at pH below 9. The relative stability of TTCP and DCPA is a major driving force for the setting reactions with both considerably more soluble than HA at pH above 4.2. As a result, a solution saturated with respect to TTCP (or DCPA) is supersaturated with calcium and phosphate ions leading to HA precipitation (Chow and Takagi, 2001). If the solubility of a calcium phosphate e.g. Hydroxyapatite, is less than the mineral part of bone, it degrades very slowly if at all. However, if the

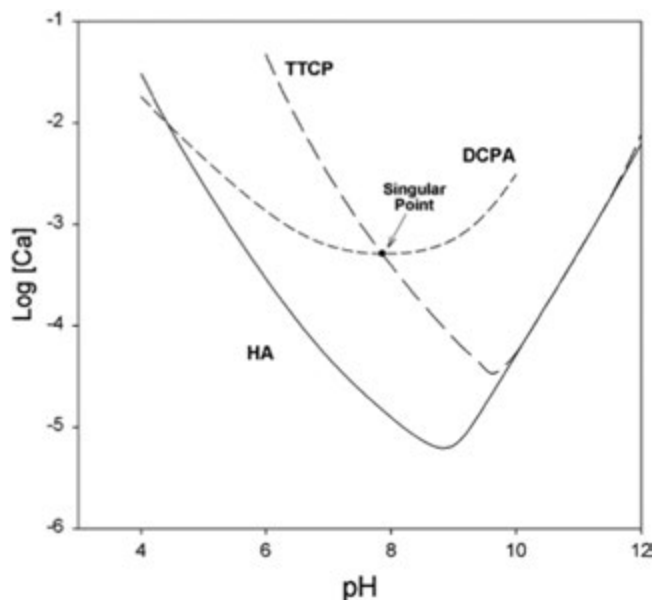


Fig. 9 Solubility ternary system, $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$, at 25°C showing solubility isotherms of TTCP, DCPA and HA. Reproduced from Chow, L.C., Takagi, S., 2001. A natural bone cement – A laboratory novelty led to the development of revolutionary new biomaterials, *Journal of Research of the National Institute of Standards and Technology* 106, 1029–1033.

solubility of a CaP is greater than that of the mineral part of bone it is degraded. Therefore, using the different solubility isotherms of CaP at pH 7.0 the in vivo degradation rate of CaP can be predicted to be in the order of (Chow, 2009):

$$\text{MCPM} > \text{TTCP} \approx \alpha\text{-TCP} > \text{DCPD} > \text{DCP} > \text{OCP} > \beta\text{-TCP} > \text{PHA} > \text{HA}$$

Initially, the setting reaction of CPC starts with dissolution of the calcium phosphate salts in the aqueous system. This dissolution supplies the Ca and P ions, which precipitate in the form of HA with the reaction occurring under isothermic conditions and physiological pH. After initial setting, needle-like crystals enlarge epitaxially and are responsible for the adherence and interlocking of the crystalline grains, which result in hardening. As CPC forms HA in an aqueous environment at body temperature, it results in a relatively low crystallinity HA that is more similar to biological apatites than non-resorbable sintered/ceramic HA formed at high temperatures (Carey *et al.*, 2005).

As mentioned previously, HA is the most stable compound over a wide pH range. For this reason, most neutral pH CPC formulations would form HA or similar apatitic phases such as Ca-deficient HA or carbonated HA. TTCP and DCPA are the most soluble salts and for this reason they were used in the first HA-forming CPC, thus providing the greatest driving force for the HA-forming reaction. As the only calcium phosphate salt with a Ca/P ratio higher than that of HA, TTCP can be combined with lower Ca/P ratio calcium phosphate salts such as DCPA to formulate a mixture that has the stoichiometry of HA. As long as both DCPA and TTCP are present in excess and the dissolution of these two salts is greater than the rate of HA formation, the solution remains near the singular point of pH 8 for these two salts. Thus, during HA formation, the pH of the cement will be only slightly higher than physiological pH which may contribute to high biocompatibility. It should be noted, however, that Figs. 8 and 9 are representative of equilibrium conditions and do not provide information on the kinetics of the dissolution/precipitation process.

The cement setting reaction determines the intermediate and the final products that will be formed in a CPC. Consequently, the type and rate of reaction phases formed and morphologies and thus determines the mechanical and biological properties of the cement. Formation of different calcium phosphate phases as the major cement product offers an effective means for formulating CPCs with a range of in vivo resorption rates. Different formulations will result in various pH conditions depending on the setting reaction. A CPC with a desired pH can be tailored to gain compatibility with components such as osteoinductive factors, antibiotics etc.

There are two classes of CPC's which exist: HA/Apatite forming and DCPD forming cements. Both have excellent biocompatibility and have excellent potential for their common applications.

Apatite and DCPD Forming CPCs

DCPD cements have a higher rate of resorbability, which is believed to be due to DCPD being more soluble than HA (Dorozhkin, 2009b). DCPD cements have been shown to resorb faster than apatite cements and as a result, DCPD cements suffer from a rapid decrease in strength, though overall strength of implanted bone increases due to bone ingrowth (Nishimura *et al.*, 1991).

Apatite cements have better material properties than DCPD cements. DCPD cements have short setting times (~ 30 s) compared to apatite cements (10 min) (Mirtchi *et al.*, 1989). The short setting time of DCPD cements is often considered a

disadvantage as the surgeon will not have sufficient time for the paste to be loaded into the implantation device and implanted before the material sets, making it difficult to use these cements clinically. Attempts to lengthen the setting time include using less soluble reactants, addition of pyrophosphates which have been shown to inhibit setting. One thing which does not appear to have been documented much is the effect of particle size which hypothetically could be used to manipulate setting times.

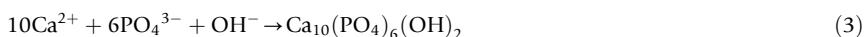
Apatite cements appear to have wider clinical use than DCPD cements. Currently there are 18 different formulations (Bohner *et al.*, 2005) of apatite cements compared to 3 DCPD cement formulations (Tamimi *et al.*, 2012). This poses the question of why DCPD cements are less popular regardless of their faster resorbability and high initial strength. Dorozhkin (2009b) suggests that the reason for this imbalance is simply that apatite cements were developed before DCPD cements meaning there is a great amount of research done on apatite cements. Therefore, there is large scope for the development of DCPD cements.

Chemistry of Setting in Calcium Phosphate Cements

The most important property of CPC is the cement setting reaction. The nature of the cement products and the physical and biological properties of the hardened cement are determined by the cement setting reaction.

Hydroxyapatite Cement

As previously mentioned, HA cements are the most common and most commercially used group of CPCs. HA cements were the first composition developed by Brown and Chow in 1986 and the setting reaction is shown below.

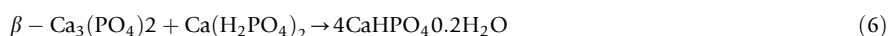
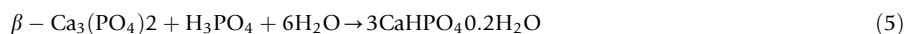
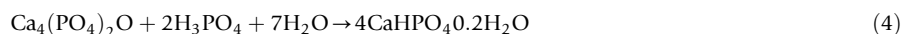


This simplified reaction highlights the ions which are required for HA formation. Ca^{2+} and PO_4^{3-} ions are usually delivered in the form of various calcium phosphate salts. A pH above 7 is required to provide a source of OH^- ions during the setting reaction.

Brushite (DCPD) Cements

DCPD cements were discovered and developed after the discovery of apatite cements in 1987 by two independent research groups, Mirtchi and Lemaitre (Mirtchi *et al.*, 1989). The first DCPD cements were prepared by mixing MCPM and β -TCP and adding water. The resulting paste was shown to set via an exothermic reaction.

Setting reaction: There are a number of different reactions to form DCPD cements, a selection of these are listed below.



There are 4 steps involved in the setting mechanism for DCPD, (1) the constituents of the cement starting material powder dissolve in water; (2) the dissolved ions form a super-saturated gel; (3) nucleation of DCPD crystals occurs within the gel phase; (4) crystal growth from the nucleated small crystals, these crystals interlock giving a hard set cement (Tamimi *et al.*, 2012). DCPD is soluble above pH 6, therefore DCPD can only precipitate at pH < 6. In cement systems containing β -TCP and MCPM as reactants, studies have shown that over the course of setting, initially the MCPM starts to dissolve which causes a rapid decrease in pH to 2.5 (Bohner *et al.*, 2005, 1997) and then pH increases during the setting reaction to pH 5. The pH in the cement system can be altered (pH 2.5–6) by using different ratios of each of the starting materials; if more MCPM is used the pH will remain low even after setting has completed whereas if excessive β -TCP is used the pH can be almost neutral at pH 6 (Bohner *et al.*, 1997).

Another study by Bohner *et al.* examined a cement reaction where MCPM was replaced with orthophosphoric acid. This system showed good control over reactivity and composition, faster preparation, longer setting times and higher tensile strengths. However, the pH of orthophosphoric acid is lower than that of MCPM resulting in a pH of 2.5 in the cement system both during setting and after the setting reaction is complete. This low pH raises concerns in relation to biocompatibility and potential inflammation (Bohner *et al.*, 1997).

Setting Rate/Reaction Rate

The setting rate of CPCs is a very important handling property because it directly affects the clinical procedure. Too early a setting reaction limits the time the surgeon can spend applying and sculpting the cement, whereas too late a setting reaction results in a longer operating procedure which increases risk to the patient. A number of strategies exist to modify the setting rate of cements, for example, changing the particle size of the reagents, adding a nucleating phase or dissolving accelerators or retarders into the liquid phase (Bohner, 2010). Adding a neutral phosphate such as disodium hydrogen phosphate or sodium dihydrogen phosphate to the liquid phase reduces setting time. In the case of a paste containing dicalcium phosphate and tetracalcium phosphate,

this is possible because the formation of HA and the dissolution of dicalcium phosphate during the setting reaction occur in a linear fashion, thus avoiding early formation of HA. This is important because HA formed early during the setting reaction of the original formulation engulfs unreacted dicalcium phosphate particles (Dorozhkin, 2009a). Therefore, dicalcium phosphate cannot dissolve because it becomes isolated from the solution and thus the setting reaction is slower.

Factors Affecting the Setting Reaction, Paste Stability and Injectability

Although the chemical reactions depend on the chemical composition of the system, setting and hardening of the cement paste is predominantly controlled by the dissolution and precipitation processes in the cement system. A number of additional factors have been reported to influence the resulting CPC setting properties. The modification of parameters such as using additives, varying the Ca/P molar ratio, the powder/liquid ratio in the system, and the particle sizes, specific surface areas and morphology of the cement components, will result in a material that can be tailored to specific clinical requirements and applications. Of particular importance is how such factors can be used to control setting time, for example, a setting reaction that is too fast limits the period during which the surgeon can apply the cement, whereas a setting reaction that is too slow prevents the surgeon from closing the defect and hence extending the overall procedure duration.

The injectability of CPCs is of crucial importance for surgical procedures utilizing minimally invasive procedures or for delivery of the cement into a very narrow space, and is related to the ability of a paste to remain homogeneous under pressure and avoid filter-pressing. Currently, injectable CPC products are delivered as two components consisting of a powder and aqueous liquid, which are mixed in the operating room. After mixing, the paste like cement is injectable and malleable for a few minutes, depending on the type of cement, temperature, etc. and, following injection, the cement hardens in situ.

In addition to a large number of parameters relating to CPC composition (e.g., particle size and shape, particle size distribution, powder/liquid ratio, liquid viscosity, etc.), the injectability of a setting cement depends strongly on the post-mixing time interval relative to the cement setting time. Hence, premixed CPCs that do not harden until being placed into the defect are an advantage.

Use of additives

Through incorporation of setting accelerators such as phosphoric acid into the liquid phase, the setting time of the product can be greatly reduced while additives such as citric acid ensure a desirable initial working time prior to rapid hardening due to impedance of the dissolution-precipitation reactions in the cement. These additives promote dissolution of the solids by lowering the solution pH resulting in an increased rapid cement hardening setting time in the range of 10–15 min (Chow, 2009; Dorozhkin, 2009a).

Used as a hardening accelerator, MCPM has been observed to dissolve quickly in water and, through precipitation, form phosphoric acid and small crystals of DCPD throughout the paste, thus promoting HA formation and paste hardening.

The inclusion of additives such as propylene glycol produces a soft paste that significantly increases the injectability of the CPC. With the addition of citrate ions to the cement paste, there is a chemical interaction between the additive and the calcium phosphate particles. This interaction can modify the particle interactions and hence the physico-chemical properties of the cement, in particular the injectability. The same citrate ions have previously been highlighted as they modify the setting reaction and postpone the full hydrolysis of the calcium phosphate.

Ca/P molar ratio

The Ca/P ratio of the cement system is controlled by the relative amounts of MCPM, DCPA and TTCP present in the two pastes with a decrease in the Ca/P ratio resulting in an increased setting reaction rate. Ishikawa (2014) suggested the formation of nearly stoichiometric HA (Ca/P ratio of 1.66) when excess TTCP was present and formation of Ca-deficient HA when excess DCPA was present in the TTCP + DCPA cement. As described in Chow *et al.* (2005), HA formed in neutral or mildly acidic pH conditions is expected to have a Ca/P ratio of approximately 1.5. Accordingly an overall Ca/P ratio of 1.5 in the formulation should lead to the situation that HA is the only cement product. A Ca/P ratio of > 1.33 is believed to yield HA as the major phase in the product. Although stoichiometrically the Ca/P molar ratio in TTCP is 2, a Ca/P molar ratio of 1.9 is usually targeted for TTCP manufacture to avoid the formation of calcium oxide (Chow *et al.*, 2005).

By decreasing the TTCP/DCPA ratio from Brown and Chow's (1983) traditional ratio of 1 to 0.33 (yielding overall Ca/P ratios of 1 and 1.33), Xu *et al.* (2007) increased the CPC dissolution rate by 40% compared with the CPC control ratio of 1 without compromising the setting time or the strength and modulus which exceeded those of natural cancellous bone. In contrast, a significant decrease in strength and modulus was observed in the increased ratios of 2 and 3. Xu *et al.* (2007) selected the TTCP/DCPA ratios of 2 and 3, as a ratio of 1 results in stoichiometric HA and a ratio of 0.5 results in Ca-deficient HA, which has a faster dissolution rate than stoichiometric HA (Matsuya *et al.*, 2000). Similar results were also reported by Hirayama *et al.* (2008).

Powder/liquid ratio

The powder/liquid ratio is hugely influential on both the paste handling characteristics and the setting reaction as it determines the water content in the cement available for reaction. The liquid phase can be water, saline, or other physiological like fluid. A phosphate containing solution can be used for a shortened working time with a non-aqueous but water-miscible liquid such as

glycerol or polyethylene glycol for applications that require a longer working time. Water plays an important role in cements as initially, it is involved as a dissolution medium for the calcium phosphates and secondly, it is involved in the formation of DCPD or OCP. Nevertheless, it is important to note that the quantity of water actually needed by the overall formation of the cement is relatively small (Lacout *et al.*, 1996).

The P/L ratio affects the injectability of the paste. A study by Khairoun *et al.* (1998) observed that the paste injectability increases with an increasing L/P ratio from 0.35 to 0.40, thus decreasing viscosity of the paste (i.e., varies inversely with its viscosity). When a paste, which is a two component mixture of a finely divided ceramic powder and a liquid is submitted to a pressure gradient, the liquid may flow faster than the solid, resulting in local changes in the solid dispersion. This previously mentioned phenomenon of filter-pressing may have a knock on effect on the paste injectability. In addition, the powder/liquid ratio also affects the mass amount of calcium phosphate components in a given volume of the paste. This in turn, contributes to the paste viscosity and the porosity and strength of the hardened cement mass. It also affects the overall Ca/P ratio of the formulation.

pH and temperature

An important in vivo characteristic of HA-forming CPC is that it does not dissolve spontaneously in a normal physiological fluid environment, yet it is resorbable under cell-mediated acidic conditions. The pH, presence of water, time and temperature all have a strong effect on the decomposition of DCPD to DCPA with a study by Bohner *et al.* (2000a,b) confirming low pH and high temperature trigger this decomposition. An increase in acidity has also been shown to accelerate the cement setting reaction and therefore to decrease the setting time (Bohner *et al.*, 2000a). The solubility of the injectable CPC is similar to that of bone mineral, meaning it will be relatively insoluble at neutral pH and increasingly soluble as pH decreases. This is an important characteristic of normal bone mineral that facilitates controlled dissolution by osteoclasts as the cells causes a lowering of the pH at the site where bone will be dissolved.

Mechanical injection device

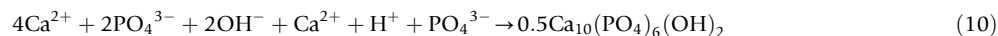
Currently available CPCs are mixed by hand and to be injected, the cement paste must be transferred into the appropriate delivery system, usually a syringe. Khairoun *et al.* (1998) defined “injectability” to mean the percentage by weight of the part of the amount of paste which could be extruded from such a syringe, either by hand or by force of 100 N maximum. The use of additives can decrease the extrusion force required for the cement paste. Modification of the injection device, such as shorter cannulas with a larger diameter, as well as small injection rates, favors a good injectability.

Particle size

Handling properties and tissue response are highly dependent on the setting reaction of the cement. The setting reaction is based on a dissolution-precipitation reaction and the entanglement of the precipitated calcium phosphate crystals, therefore particle size has an influence on the setting reaction. For example, the larger the particle size the smaller the surface area. A small surface area will slow the rate of dissolution, leading to a longer setting time. In this case, where this cement consists of multiple calcium phosphates – TTCP and DCPA, it is especially important to regulate the particle size since the balanced supply of Ca^{2+} and PO_4^{3-} is important for the precipitation of Hydroxyapatite. Both TTCP and DCPA can supply Ca^{2+} and PO_4^{3-} ions as shown in Eqs. 8 and 9 (Ishikawa, 2014).



Then Ca^{2+} and PO_4^{3-} are precipitated as hydroxyapatite crystals as shown in Eq. (10)



The overall reaction can be expressed as shown in Eq. (11)



However, TTCP and DCPA supply different Ca/ PO_4 molar ratios. TTCP which has a Ca/P ratio of 2.0 supplies a larger amount of Ca^{2+} for the formation of Hydroxyapatite which has a Ca/P ratio of 1.67. DPCA which has a Ca/P ratio of 1.0 supplies less Ca^{2+} for the formation of HA. Therefore, TTCP and DCPA should dissolve at the same rate for the formation of HA, however, if the particle sizes of both TTCP and DCPA are the same, the dissolution of each will not occur at the same rate. When the dissolution rates of TTCP and DCPA are compared, TTCP dissolves quickly, while the dissolution rate of DCPA is slow.

Table 5 summarizes the setting reaction of a TTCP/DCPA cement with their different particle sizes. As shown in this table, cement consisting of small TTCP and large DCPA does not set. The mechanical strength of the cement increases with increasing TTCP/DPCA particle diameter ratio. The cement with a large TTCP and a small DCPA results in the highest mechanical strength. Where small TTCP is combined with large DCPA, TTCP dissolves quickly as it has a larger specific surface area. Dissolution of TTCP supplies more Ca^{2+} ions and increases pH. At high pH, apatite is still the most stable phase, thermodynamically. However, too high a supersaturation results in the formation of amorphous calcium phosphate or small apatite crystals which are too small to interlock with each other, resulting in a lower mechanical strength. As mentioned previously, TTCP dissolves faster than DCPA,

Table 5 Setting reaction of a TTCP/DCPA cement with varying particle sizes

Average particle diameter (μm)		Ratio of the average particle diameter of TTCP/DCPA	Compressive strength (MPa)
TTCP	DCPA		
1.6	11.9	0.13	0 (no setting)
12.4	11.9	1.04	7.1 ± 1.0
1.6	0.9	1.78	21.8 ± 4.4
12.4	0.9	13.78	51.0 ± 4.5

Note: Ishikawa, K., 2014. Calcium phosphate cement. Ben - Nissan, B. (Ed.), *Advances in Calcium Phosphate Biomaterials*. Springer.

therefore, the combination of a large TTCP with a small DCPA is necessary in the formation of HA. The use of larger TTCP with smaller DCPA allows the appropriate amount of supersaturation and thus is the key to TTCP-DCPA cements.

The supply of Ca^{2+} and PO_4^{3-} by the dissolution of TTCP and DCPA results in a supersaturated solution with respect to HA. Therefore, Ca^{2+} and PO_4^{3-} are precipitated as HA crystals. The precipitation reaction results in the decrease of the Ca^{2+} and PO_4^{3-} concentration, which elicits further dissolution of the TTCP and DCPA. The dissolution-precipitation continues until all the TTCP and DCPA are consumed. The precipitated HA crystals interlock with each other to set and harden.

As previously mentioned, a reduction in particle size produces a significant decrease in both initial and final setting times and an acceleration of the rate of cement hardening or hydration of the curing. With a decrease in powder size, a significant increase in the rate of the reaction is observed (Ginebra *et al.*, 2004). According to Chow *et al.*, the optimum particle size for TTCP ranges from 1 to 80 μm with median = 17 μm approximately. DCPA powder should be in the range of 0.4–3 μm , with median = 1 μm approximately.

The particle size of the powder phase is a key factor that contributes to the cement properties and must be considered to optimize the cement for the given clinical requirements. Optimization and control of the particle size could avoid the need to incorporate other additives which may hinder the mechanical properties or potentially compromise the bone cement biocompatibility (Ginebra *et al.*, 2004). However, it is important to note that too fine a particle size has the potential to affect the product injectability due to thick paste formation.

The main ingredients of the calcium phosphate cement in this study are TTCP, DCPA and MCPM. As previously mentioned, TTCP powder is synthesized from a solid-state reaction between equimolar amounts of commercially available CaHPO_4 (DCPA) and calcium carbonate, CaCO_3 , which are mixed and heated at 1500°C for 6 h in a furnace followed by quenching at room temperature (Carey *et al.*, 2005). Typically, the mixture is ground and ball milled to obtain TTCP particles with sizes ranging from approximately 1 to 80 μm , with a median of 17 μm . DCPA powder is commercially sourced and has particle sizes ranging from 0.4 to 3 μm , with a median of 1 μm (Carey *et al.*, 2005). MCPM is also commercially sourced, however, being a highly soluble compound, the particle size of MCPM is not regarded as a critically important factor (Chow, 2008).

As DCPA is the least reactive of the compounds in the DCPA + TTCP reaction, it is desirable to use smaller DCPA and larger TTCP particles to ensure the reaction can proceed with the desired stoichiometry. Chow (2008), also noted that larger DCPA particles are not desirable as they do not have a sufficient surface area to match the high reaction rate of TTCP, leading to a large amount of unreacted DCPA in the system resulting in a product with a lower strength.

Reduction of the particle size can be achieved during reagent manufacture through the powder milling process, in turn resulting in an increased powder surface area. These modifications alter the surface area of the powder available for contact with the liquid, thus affecting the dissolution rate of the phosphate and calcium ions from the solid particles. This increases the reactivity rate of the CPC reagents, thus, decreasing the setting time and increasing cement hardening (Barralet *et al.*, 2002; Ginebra *et al.*, 2004; Bohner, 2007).

A more regular or equiaxed morphology particle has been reported to improve injectability and Ishikawa (2003) have observed that cements based on TTCP-DCPA-water mixtures were more injectable when TTCP particles were round and not irregular in shape although this morphology has a direct influence on the surface area.

Ginebra *et al.* (2004) investigated the influence of particle size on the final structure of the cement at the micro and nanoscale range with results showing that the higher specific surface area produced by the reduction in particle size, strongly accelerated the hydrolysis of the α -TCP into Ca-deficient HA. They also reported that the reduction of the particle size produces a substantial decrease of the setting time and accelerates the hardening of the cement without significantly affecting the final strength attained.

A decrease in particle size has also been reported to improve injectability and Ishikawa (2003) have observed that cements based on TTCP-DCPA-water mixtures were more injectable when TTCP particles were round and not irregular in shape. It is also desirable that the particles are deagglomerated to allow for an increased viscosity and improved injectability as the heavier agglomerated particles may cause blockages in the cannula during injection at the defect site.

In summary, the optimization of the particle size and specific surface area of the powder phase can vary the properties (setting time, hardness, morphology, porosity etc.) of the final cement product. Therefore, particle size is a crucial parameter in the development of a calcium phosphate based bone substitute and thus will be a major focus in the course of this project. Beyond Ishikawa *et al.*, there is very little published data on actual particle size.

Mechanical Properties

A limiting factor of calcium phosphate cements is their mechanical properties. They are very brittle and have low impact resistance and relatively low tensile strength. Porosity is one of the main reasons for their low strength. The presence of pores makes it easy for macro and micro cracks to propagate through the material, thus reducing the mechanical properties of the cement. Porosity may be controlled by adjusting the particle size and the powder to liquid ratio. On the other hand, a certain level of porosity is desired to allow for bone ingrowth into the set cement. Other factors affecting strength are the materials used in the solid phase, particle size, incorporation of filler materials in the solid phase, powder to liquid ratio, and various liquid phases. The theory behind the use of filler particles is that if a strong filler is present in the matrix, it may stop crack propagation. However, the presence of filler particles will reduce the porosity of the material and therefore, decrease bone ingrowth into the cement. A reduction in the bone ingrowth into the cement will lead to a slower resorption rate and thus slower bone substitution. The addition of polymers and composites to cement formulations has been tried in an attempt to increase strength which proved successful, however, the formation of HA was reduced thus leading to a reduction in the biocompatibility of the cement. Research shows that it is difficult to increase the strength of the cement without compromising its bioactivity. Target values for mechanical properties of calcium phosphate cements have not been determined. However, the targets would depend on the location of the cement in the body, the type of loading expected to be experienced by the cement, the type of bone into which it is placed and the amount and direction of the forces applied. In general, the mechanical properties of the cement should match those of the material being replaced.

Bone Void Filler Applications

Calcium phosphate cements are most commonly used to fill bone defects or voids. These may arise when large sections of bone have had to be removed (e.g., bone cancers) or when bone augmentations are required (e.g., maxillofacial reconstructions or dental applications). The bone filler is used to reinforce porous bone to give better support for screws and plates in fracture fixation. It can also provide a scaffold and encourage the rapid filling of the void by naturally forming bone and provides an alternative to bone grafts.

Calcium phosphate cements are promising materials for both dental and orthopedic applications due to their self-setting nature, mouldability, biocompatibility, lack of any by-products and their potential for being replaced by new bone. The ability to be molded in place is an important property of calcium phosphate cements due to the complexity of some bone defects/voids. The area of interest in this research is in craniomaxillofacial applications. The use of calcium phosphate cements in this area is logical as there is little or no stress generated in these conditions. The ability to mold the material during placement is advantageous for cosmetic reasons.

Premixed Formulations

Most of the currently available CPCs are in the form of a powder and a liquid that are mixed immediately before use. In the clinical situation, the ability of the surgeon to properly mix the cement and then place the cement paste in the defect within the prescribed time is a crucial factor in achieving optimum results. Thus, the need for a premixed cement paste is evident. A premixed cement paste would be stable in the package and harden only after being placed in the defect. This can be achieved by combining calcium phosphate powders with a non-aqueous paste. When this paste is placed into the defect diffusion of water from the surrounding tissues would cause the paste to harden and form a cement. However, this technique is not always suitable, for example, for large defects the amount of diffusion of water is not sufficient to cause hardening across the entire cross section of the defect/implant. To combat this issue, dual-paste premixed cement formulations were developed. Such a system can be devised by preparing a non-aqueous paste and an aqueous paste with calcium phosphate powders suspended in both pastes. The two pastes would be kept separate in the packaging. When the two pastes are mixed together in the defect, diffusion of water from the surrounding tissues and also water from the aqueous paste will cause the cement to harden. The dual-paste system hardens more rapidly and uniformly than the single-paste system due to the provision of water in the aqueous paste. In general, premixed calcium phosphate cements have lower mechanical properties, possibly due to the volume taken up by the non-aqueous liquid. Research and improvements on this aspect of premixed formulations are on-going.

Existing Products

Bone substitutes are being increasingly used in craniomaxillofacial (CMF) surgery. A wide variety of bone substitutes have been employed over the past 50 years. The three most common apatite forming cements used in the CMF area are Norian CRS (Synthes, Paoli, PA), BoneSource (Stryker, Kalamazoo, MI) and Mimix (W.Lorenz Surgical, Jacksonville, FL). A comparison of these cements is summarized in [Table 6](#). It is important to note that the compressive strength obtained for these products may not be comparable due to variance in compressive strength test methods which may result in an overestimation of the strength of the material.

Table 6 Comparison of the properties of calcium phosphate cements

	<i>Norian CRS</i>	<i>Bonesource</i>	<i>Mimix</i>
Base Component	MCPM, TCP, Calcium carbonate	TTCP	TTCP
Compressive Strength (MPa)	30	50	22
Resorbability	Complete	Minimal	Minimal
Pore diameter (μm)	0.03	0.002–0.005	211
Initial setting time (min)	10	10–15	3.4
Final setting time	1 h	4 h	4–6 min
Sets in a moist environment	Yes	No	Yes
Osteoconductive	Yes	Yes	Yes

Note: Pryor, L.S., Gage, E., Langevin, C.-J., *et al.*, 2009. Review of bone substitutes. *Craniofacial Trauma & Reconstruction* 2, 151–160.

Norian CRS Bone Cement™

Norian CRS bone cement is a pliable calcium phosphate cement that is mixed *in vivo* to form dahllite, a carbonated apatite, once set. Originally approved by the FDA for use in distal radius fractures (Pryor *et al.*, 2009), it has also been used broadly in craniofacial surgery. Norian CRS bone cement is prepared by mixing sodium phosphate solution with MCPM, TCP and calcium carbonate to form a bone putty. This putty begins to harden in 2 min during an exothermic reaction that may reach as high as 42°C and is set in 10 min. Maximum strength is not achieved until 24 h (Pryor *et al.*, 2009). In a recent study of Norian by Zins *et al.* reconstructed skull bone defects in sheep showed excellent osteointegration, but almost no osteoconductivity over the course of 12 months (Zins *et al.*, 2008). Drop tests resulted in fractures in the center of the construct rather than at the interface. Norian is slowly absorbed over time and is not intended for use in load-bearing areas.

Bone Source™

Bone Source is a self-setting calcium phosphate cement originally approved for use in filling burr holes and cranial defects well as the augmentation and restoration of bone contour in the craniofacial skeleton. It is prepared by mixing calcium phosphate salts including TTCP in a sodium phosphate buffer, forming a putty that remains malleable for approximately 20 min (Pryor *et al.*, 2009). Bone Source hardens into HA, and like other HA cements, is very slowly absorbed over time. It is not intended to fill defects over 25 cm² and lacks sufficient strength for load bearing applications.

Mimix Bone Void Filler™

Mimix, like Bone Source, achieved FDA clearance for use in filling burr holes and craniotomy defects and in smoothing facial skeleton contour abnormalities over a surface area no larger than 25 cm². The cement is prepared by mixing dry components of calcium phosphate powder, including TTCP, and sodium citrate dehydrate with an anhydrous citric acid solution. As it cures, Mimix hardens into HA and is mildly exothermic. Mimix Quickset is rapidly prepared, remains malleable for 3–4 min, and is completely set in 4–6 min.

HydroSet™

HydroSet is a calcium phosphate cement that comes in a powder and liquid form which is mixed and loaded into a syringe by the user. It is an injectable, sculptable and fast-setting bone substitute. Its design function is a fast-setting cement indicated to fill bony voids or gaps that are not intrinsic to the stability of the bony structure. HydroSet™ was specifically formulated to provide exceptional wet-field environment characteristics and remodels to natural bone through osteoclastic resorption and new bone formation. As HydroSet™ cement sets the reaction that occurs does not release any heat that could potentially damage the surrounding tissue thus increasing the products desirability.

HydroSet™ powder consists of three powder components: dicalcium phosphate dihydrate (DCPD) tetracalcium phosphate (TTCP), and tri-sodium citrate. And a liquid phase that is water based with polyvinylpyrrolidone (PVP), and sodium phosphate [Na₂HPO₄]. Once set, HydroSet can be drilled and tapped to augment the placement of provisional hardware. This powder and liquid requires mixing by the surgeon prior to use which introduces the possibility of inconsistent mixing by the surgeon and paste hardening/setting prior to insertion into bone defect.

Drawbacks of Existing Products

The main drawback associated with most of the existing products on the market is that, in clinical use, the surgeon needs to have the CPC powder and liquid mixed properly and thoroughly in a short period of time. The paste needs to be transferred into a

delivery device before it is injected into the defect before the paste hardens. The requirement of on-site powder-liquid mixing increases the time spent in surgery. It may also raise concerns about insufficient and inhomogeneous mixing, thus compromising the strength of the material, and inconsistencies between operators causing unpredictable variations. Also, over mixing after precipitation starts will lead to the breaking up of the interlocking structure which will compromise the mechanical properties. The surgeon must anticipate when wound closure is going to be required and call for cement mixing to commence approximately 7 mins prior to this point. If there is a delay in the anticipated closure time this may result in wasted material. To circumvent such problems, it is desirable to have CPC that are in the form of a dual-paste premixed self-hardening calcium phosphate cement system which is stable as provided but hardens only after being introduced to the bone defect and positioned properly. Such premixed types of product eliminate variability and also reduce time spent in the operating room.

Critical Assessment of Current Literature on Calcium Phosphate Cements

After reviewing the literature it became apparent that there are considerable differences in protocol when producing and analysing calcium phosphate cements.

Immersion Media

The immersion media used to store calcium phosphate cement samples varies greatly, some solutions include physiological-like solution (PLS), simulated body fluid (SBF), Tris buffer and deionised water. Each of these solutions will have a different effect on the immersed cements in terms of setting chemistry and reaction rate. PLS contains calcium and phosphate ions which will increase the reaction rate of a cement compared to the same cement immersed in an alternative media. SBF contains ions such as Mg^{2+} and Cl^- . Mg^{2+} has been shown to inhibit apatite formation (Giocondi *et al.*, 2010). The pH of deionised water may affect the reaction rate of cement samples also and does not adequately represent the conditions the cement would be exposed to in vivo. Tris buffer is a solution which does not contain any other ions which may interfere with the reaction rate of the cement but does not mimic the in vivo conditions as at the defect site, intraoperative levels of Ca^{2+} and PO_4^{3-} are non-zero, but are difficult to predict. PLS contains Ca^{2+} and PO_4^{3-} ions and can, therefore, represent in vivo conditions to some extent. For this reason, and for the purpose of comparison to literature, PLS, buffered to pH ~ 7.2 was the immersion media of choice used in this study.

Compressive Strength

Compressive strength measurement does not accurately represent the forces seen on the cement in vivo. Flexural strength may be a more appropriate technique to imitate the forces seen on the cement once implanted, but is difficult to measure due to brittleness and porosity of these materials. Another issue with compressive strength measurements is the tendency for researchers to manipulate their samples to give higher strengths. This is achieved by applying a load to the cement while it is in the mold, during setting, producing denser samples, thus, resulting in samples with a higher compressive strength when compared to samples which are simply loaded into the mold by hand. Applying a load to the cement while in the mold does not represent conditions observed by the cement in vivo. It is rarely outlined in publications whether or not a load was applied to the samples, making comparison difficult.

Characterization

Traditional methods of characterization of calcium phosphate cements include XRD, SEM and FTIR. A few studies have used ^{31}P MAS NMR to characterize cement phase but these are in the minority (Legrand *et al.*, 2009). There are a number of issues with relying on XRD for phase identification; due to the similarity of the HA and OCP crystal structure there is only one diffraction line different between the two phases. This line appears in OCP at $4.7^\circ 2\theta$. Many researchers scan from $10^\circ 2\theta$ and therefore miss this diffraction line, hence missing the presence of OCP. If an investigator does scan from $3^\circ 2\theta$ it is still possible that the OCP phase will be missed. This is because the plane associated with the 4.7° peak is so small it can easily be missed by the x-ray if the crystal is not in the correct orientation. Similarly with FTIR, many of the absorption bands for HA and OCP are very close or overlapping and make phase identification extremely difficult. Using optical methods such as SEM for phase identification can also prove difficult as there are many conflicting publications on the morphology of specific phases due to differences in formulation/production techniques.

Conclusions

Calcium phosphate cements have become established materials for clinical bone substitute and augmentation applications due to their key characteristic of presenting an osteoconductive interface to the native tissue and typically exhibiting an absence of foreign body response and fibrous encapsulation. Furthermore, such materials may exhibit bio-resorption in vivo with replacement by newly

grown bone. The rate and extent of this behavior is determined by both the chemistry of the CPC system (brushite forming cements show greater bioresorbability than HA forming cements) and also the anatomical site of implantation and the defect size. Pre-mixed dual paste type formulations offer superior handling and placement characteristics as well as more consistent homogeneity and thus more predictable properties in vivo, but generally at the expense of mechanical strength due to the presence of the suspension vehicle components of the paste systems. These dual paste systems also offer the potential for the addition of bioactive or pharmaceutical agents to the cement system which will be a focus for future development of these materials. Of continuing interest for the future is the development of formulations with unique properties tailored for specific anatomical sites/surgical techniques, and more generally efforts will continue to address their principal disadvantage and clinical limitation ie low strength and brittle behavior via the modification of formulations to a more composite nature via the incorporation of polymeric/bio-polymeric components aimed at conferring toughness and strength, yet retaining the osteoconductive properties and also the bio-resorption potential where appropriate.

References

- Albee, F.H., 1920. Studies in Bone Growth. *Annals of Surgery* 71, 32–39.
- Ambard, A.J., Muenninghoff, L., 2006. Calcium phosphate Cement: Review of mechanical and biological properties. *Journal of Prosthodontics* 15 (5), 321–328.
- Barralet, J.E., Gaunt, T., Wright, A.J., Gibson, I.R., Knowles, J.C., 2002. Effect of porosity reduction by compaction on compressive strength and microstructure of calcium phosphate cement. *Journal of Biomedical Materials Research* 63, 1–9.
- Barrère, Van Blitterswijk, C.A., K, D.G., 2006. Bone regeneration: Molecular and cellular interactions with calcium phosphate ceramics. *International Journal of Nanomedicine* 1, 317–332.
- Bohner, M., 2000. Calcium orthophosphates in medicine: From ceramics to calcium phosphate cements. *Injury* 31 (Suppl. 4), 37–47.
- Bohner, M., 2007. Reactivity of calcium phosphate cements. *Journal Materials Chemistry* 17, 3980–3986.
- Bohner, M., 2010. Design of ceramic-based cements and putties for bone graft substitution. *European Cells and Materials* 20, 1–12.
- Bohner, M., Gbureck, U., Barralet, J.E., 2005. Technological issues for the development of more efficient calcium phosphate bone cements: A critical assessment. *Biomaterials* 26, 6423–6429.
- Bohner, M., Van Landuyt, P., Merkle, H.P., Lemaître, J., 1997. Composition effects on the pH of a hydraulic calcium phosphate cement. *Journal of Materials Science: Materials in Medicine* 8, 675–681.
- Bohner, M., Merkle, H.P., Landuyt, P.V., Trophard, G., Lemaître, J., 2000a. Effect of several additives and their admixtures on the physico-chemical properties of a calcium phosphate cement. *Journal of Materials Science: Materials in Medicine* 11, 111–116.
- Bohner, M., Merkle, H.P., Lemaître, J., Tre, J., 2000b. In vitro aging of a calcium phosphate cement. *Journal of Materials Science: Materials in Medicine* 11, 155–162.
- Brown, P.W., Martin, R.I., 1999. An analysis of hydroxyapatite surface layer formation. *The Journal of Physical Chemistry B* 103, 1671–1675.
- Brown, W.E., Chow, L.C., 1983. A new calcium phosphate setting cement. *Journal of Dental Research* 62, (672).
- Brown, W.E., Chow, L.C., 1990. Dental Restorative Cement Pastes. US 07/051, 739.
- Carey, L.E., Xu, H.H.K., Simon JR, C.G., Takagi, S., Chow, L.C., 2005. Premixed rapid-setting calcium phosphate composites for bone repair. *Biomaterials* 26, 5002–5014.
- Chow, L.C., Takagi, S., Constantino, P.D., Friedman, C.D., 1991. Self setting calcium phosphate cements. *Material Research Society* 179, 3–24.
- Chow, L.C., 2000. Calcium phosphate cements: Chemistry, properties and applications. In: Calvert, P., Kokubo, T., Levy, R.J., Scheid, C.R. (Eds.), *Mineralization in Natural and Synthetic Biomaterials*, vol. 599. MRS Online.
- Chow, L.C., 2008. Formulation Development of HydroSet II - Report of Results of Collaborative Research between American Dental Association Foundation and Howmedica International. Stryker Corporation.
- Chow, L.C., 2009. Next generation calcium phosphate-based biomaterials. *Dental Materials Journal* 28, 1–10.
- Chow, L.C., Takagi, S., 2001. A natural bone cement—A laboratory novelty led to the development of revolutionary new biomaterials. *Journal of Research of the National Institute of Standards and Technology* 106, 1029–1033.
- Chow, L.C., Eanes, E.D., 2001. Octacalcium Phosphate. Switzerland: Karger.
- Chow, L.C., Markovic, M., Frukhtbeyn, S.A., Takagi, S., 2005. Hydrolysis of tetracalcium phosphate under a near-constant-composition condition—effects of pH and particle size. *Biomaterials* 26, 393–401.
- Curry, N.A., Jones, D.W., 1971. Crystal structure of brushite, calcium hydrogen orthophosphate dihydrate: A neutron-diffraction investigation. *Journal of The Chemical Society A: Inorganic, Physical, Theoretical*. 3725–3729.
- Davies, E., Duer, M.J., Ashbrook, S.E., Griffin, J.M., 2012. Applications of NMR crystallography to problems in biomineralization: Refinement of the crystal structure and ^{31}P solid-state NMR spectral assignment of octacalcium phosphate. *Journal Of The American Chemical Society* 134, 12508–12515.
- Dorozhkin, S.V., 2007. Calcium orthophosphates. *Journal of Materials Science* 42, 1061–1095.
- Dorozhkin, S., 2009a. Calcium orthophosphate cements and concretes. *Materials* 2, 221–291.
- Dorozhkin, S., 2009b. Calcium orthophosphates in nature, biology and medicine. *Materials* 2, 399–498.
- Dorozhkin, S.V., 2010. Bioceramics of calcium orthophosphates. *Biomaterials* 31, 1465–1485.
- ELIAZ, N., 2012. Degradation of Implant Materials, London: Springer.
- Elliott, J.C., 1994. Structure and chemistry of the apatites and other calcium Orthophosphates. In: Elliott, J.C. (Ed.), *Studies in Inorganic Chemistry*. Elsevier.
- Elliott, J.C., Mackie, P.E., Young, R.A., 1973. Monoclinic hydroxyapatite. *Science* 180, 1055–1057.
- Friedman, C.D., Costantino, P.D., Takagi, S., Chow, L.C., 1998. BoneSource™ hydroxyapatite cement: a novel biomaterial for craniofacial skeletal tissue engineering and reconstruction. *Journal of Biomedical Materials Research* 43, 428–432.
- Fernandez, E., Gil, F.J., Best, S.M., *et al*, 1998. Improvement of the mechanical properties of new calcium phosphate bone cements in the $\text{CaHPO}_4\text{--}\alpha\text{-Ca}_3(\text{PO}_4)_2$ system: Compressive strength and microstructural development. *Journal of Biomedical Materials Research* 41, 560–507.
- Ginebra, M.P., Driessens, F.C.M., Planell, J.A., 2004. Effect of the particle size on the micro and nanostructural features of a calcium phosphate cement: A kinetic analysis. *Biomaterials* 25, 3453–3462.
- Giocondi, J.L., El-Dasher, B.S., Nancollas, G.H., Orme, C.A., 2010. Molecular mechanisms of crystallization impacting calcium phosphate cements. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* 368, 1937–1961.
- Hak, D.J., 2007. The use of osteoconductive bone graft substitutes in orthopaedic trauma. *The Journal of the American Academy of Orthopaedic Surgeons* 15 (9), 525–536.
- Hench, L.L., 1991. Bioceramics: From concept to clinic. *Journal of the American Ceramic Society* 74, 1487–1510.
- Hirayama, S., Takagi, S., Markovic, M., Chow, L.C., 2008. Properties of calcium phosphate cements with different tetracalcium phosphate and dicalcium phosphate anhydrous molar ratios. *Journal of Research of the National Institute of Standards and Technology* 113, 311–320.

- Henslee, A., Gwak, D., Mikos, A., Kasper, F., 2012. Development of a biodegradable bone cement for craniofacial applications. *Journal of Biomedical Materials Research Part A* 100 (9), 2252–2259.
- Ishikawa, K., 2003. Effects of spherical tetracalcium phosphate on injectability and basic properties of apatitic cement. *Key Engineering Materials* 240, 369–372.
- Ishikawa, K., 2014. Calcium phosphate cement. In: Ben - Nissan, B. (Ed.), *Advances in Calcium Phosphate Biomaterials*. Springer.
- Khairoun, I., Boltong, M.G., Driessens, F.C.M., Planell, J.A., 1998. Some factors controlling the injectability of calcium phosphate bone cements. *Journal of Materials Science: Materials in Medicine* 9, 425–428.
- Lacout, J.L., Mejdoubi, E., Hamad, M., 1996. Crystallization mechanisms of calcium phosphate cement for biological uses. *Journal of Materials Science: Materials in Medicine* 7, 371–374.
- Laurencin, D., Wong, A., Dupree, R., Smith, M.E., 2008. Natural abundance ^{43}Ca solid-state NMR characterisation of hydroxyapatite: Identification of the two calcium sites. *Magnetic Resonance in Chemistry* 46, 347–350.
- Legrand, A.P., Sfihi, H., Lequeux, N., Lemaître, J., 2009. ^{31}P Solid-State NMR study of the chemical setting process of a dual-paste injectable brushite cements. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 91B, 46–54.
- Markovic, M., Chow, L.C., 2010. An octacalcium phosphate forming cement. *National Institute of Standards and Technology* 115, 257–265.
- Matsuya, S., Takagi, S., Chow, L.C., 2000. Effect of mixing ratio and pH on the reaction between $\text{Ca}_4(\text{PO}_4)_2\text{O}$ and CaHPO_4 . *Journal of Materials Science-Materials in Medicine* 11, 305–311.
- Miquel, J.L., Facchini, L., Legrand, A.P., *et al.*, 1990. Characterisation and conversion study into natural living bone of calcium phosphate bioceramics by solid state NMR spectroscopy. *Clinical Materials* 5, 115–125.
- Mirtchi, A.A., Lemaître, J., Hunting, E., 1989. Calcium phosphate cements: Action of setting regulators on the properties of the β -tricalcium phosphate-monocalcium phosphate cements. *Biomaterials* 10, 634–638.
- Moreno, E.C., Varughese, K., 1981. Crystal growth of calcium apatites from dilute solutions. *Journal of Crystal Growth* 53, 20–30.
- Moreno, E.C., Zahradnik, R.T., Glazman, A., Hwu, R., 1977. Precipitation of hydroxyapatite from dilute solutions upon seeding. *Calcified Tissue Research* 24, 47–57.
- Nakamura, T., Yamashita, K., Neo, M., 2006. TEM examinations of OCP/HA transformation. *Key Engineering Materials* 309–311, 191–194.
- Nishimura, N., Yamamuro, T., Taguchi, Y., *et al.*, 1991. A new bioactive bone cement: Its histological and mechanical characterization. *Journal of Applied Biomaterials* 2, 219–229.
- Ooi, C.Y., Hamdi, M., Ramesh, S., 2007. Properties of hydroxyapatite produced by annealing of bovine bone. *Ceramics International* 33, 1171–1177.
- Pattanayak, D.K., Rao, B.T., Rama Mohan, T.R., 2011. Calcium phosphate bioceramics and bioceramic composites. *Journal of Sol-Gel Science and Technology* 59, 432–447.
- Pryor, L.S., Gage, E., Langevin, C.-J., *et al.*, 2009. Review of bone substitutes. *Craniofacial Trauma & Reconstruction* 2, 151–160.
- Sanzana, E.S., Navarro, M., Macule, F., *et al.*, 2008. Of the in vivo behavior of calcium phosphate cements and glasses as bone substitutes. *Acta Biomaterialia* 4, 1924–1933.
- Rothwell, W.P., Waugh, J.S., Yesinowski, J.P., 1980. High-resolution variable-temperature phosphorus- ^{31}P NMR of solid calcium phosphates. *Journal of the American Chemical Society* 102, 2637–2643.
- Tamimi, F., Sheikh, Z., Barralet, J., 2012. Dicalcium phosphate cements: Brushite and monetite. *Acta Biomaterialia* 8, 474–487.
- Tsai, T.W.T., Chou, F.-C., Tseng, Y.-H., Chan, J.C.C., 2010. Solid-state ^{31}P NMR study of octacalcium phosphate incorporated with succinate. *Physical Chemistry Chemical Physics* 12, 6692–6697.
- Tseng, Y.-H., Zhan, J., Lin, K.S.K., Mou, C.-Y., Chan, J.C.C., 2004. High resolution ^{31}P NMR study of octacalcium phosphate. *Solid State Nuclear Magnetic Resonance* 26, 99–104.
- Tung, M.S., Chow, L.C., Brown, W.E., 1985. Hydrolysis of dicalcium phosphate dihydrate in the presence or absence of calcium fluoride. *Journal Dental Research* 64, 2–5.
- Williams, D.F., 1987. Definitions in Biomaterials: Proceedings of a Consensus Conference of the European Society for Biomaterials, Chester, England, March 3-5, 1986. New York: Elsevier.
- Xu, H.H.K., Carey, L.E., Simon Jr., C.G., Takagi, S., Chow, L.C., 2007. Premixed calcium phosphate cements: Synthesis, physical properties, and cell cytotoxicity. *Dental Materials* 23 (4), 433–441.
- Yesinowski, J.P., Eckert, H., 1987. Hydrogen environments in calcium phosphates: Proton MAS NMR at high spinning speeds. *Journal of the American Chemical Society* 109, 6274–6282.
- Yuan, H., Li, Y., De Bruijn, J.D., De Groot, K., Zhang, X., 2000. Tissue responses of calcium phosphate cement: A study in dogs. *Biomaterials* 21, 1283–1290.
- Zhang, J., Liu, W., Schnitzler, V., Tancket, F., Bouler, J.M., 2013. Review: Calcium phosphate cements (CPCs) for bone substitution: Chemistry, handling and mechanical properties. *Acta Biomaterialia* 1, 1–41.
- Zins, J.E., Moreira-Gonzalez, A., Parikh, A., *et al.*, 2008. Biomechanical and histologic evaluation of the Norian craniofacial repair system and Norian craniofacial repair system fast set putty in the long-term reconstruction of full-thickness skull defects in a sheep model. *Plastic and Reconstructive Surgery* 121, 271e–282e.

Bone Regeneration With Ceramics Scaffold

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Introduction

The skeletal system is an elaborate structure built for movement and protection while simultaneously having a role in breathing, metabolism, cell production, and even sound transmission. These functions are highly specific and each one of them requires a specialized type of bones (Ott, 2017). All of them have the ability to constantly remodel themselves, which makes them capable to correct small injuries or defects, especially if the patient is young and healthy. Problems do occur in larger fractures and in older patients where the remodeling ability is diminished and the porosity of the bone is increased. Bone diseases commonly affect aging bone when systemic diseases like osteoporosis, osteoarthritis, or bone cancer/metastasis become more frequent. It is estimated that several hundred million people worldwide are affected by musculoskeletal conditions, making it a severe medical problem (Baroli, 2009). As a result, bone is the second most transplanted tissue after blood (Shegarfi and Reikeras, 2009), but the availability of bone transplants is limited, they are expensive and have several drawbacks. Therefore, the solution to this problem is sought in bone substitute/regeneration materials which can improve the outcome of the clinical treatment and ensure the long-term lifespan of the implant.

Bone Composition, Structure, and Mechanical Properties

From a materials science standpoint, bone can be considered an organic-inorganic composite with a complex, hierarchical structure. Bone biomineralization starts by osteoblasts secretion of an unmineralized organic matrix that will guide the mineral deposition, which will develop into hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HA), a form of calcium phosphate (CaP). The complexity of bone structure is represented in **Fig. 1** where different levels of organizations are denoted. The first level represents the major components, i.e., collagen, HA, and water. Although more than 200 proteins can be found in the bone, about 90% of protein content consists of collagen type I, folded in a triple helix structure. Thin, small and plate-like nanocrystals of HA attach to these fibers (Weiner and Wagner, 1998). Fibers control the growth of the crystals and organize themselves in layers to form fibrils. As the crystals continue to grow, they compress the fibers and join in sheet-like form. These sheets can be parallel (lamellar bone) or cylindrical (osteon). Osteon is the basic structural unit of a bone structure and will form diverse microstructures, based on the location and the function of a bone. All osteoblasts found between the sheets will modify into osteocytes (bone cells involved in bone remodeling, signal transmission, and calcium removal) (Ott, 2017).

Cancellous (or trabecular, spongy) bone can be found as an internal porous structure for example in long bone ends or in the vertebrae. It is well vascularized and here the blood-forming (haematopoietic) occurs. The spongy structure also helps in the optimization of the bone weight and ease of movement, reducing stress caused by jumping or running. Cortical, more dense bone is usually surrounding the cancellous bone and provides a mechanically more robust structure, built for endurance ([Dorozhkin, 2012](#)).

The composition of mature bones varies depending on the bone type from about 50% to 90% mineral, 5% to 40% organic matrix, and 50% to 90% water (Boskey and Robey, 2013; Ott, 2017). As an essential part of our locomotive system, bones can on average withstand around 4 MPa stress during daily activities, with a mean load of a hip joint up to 3000 N (Dorozhkin, 2018a).

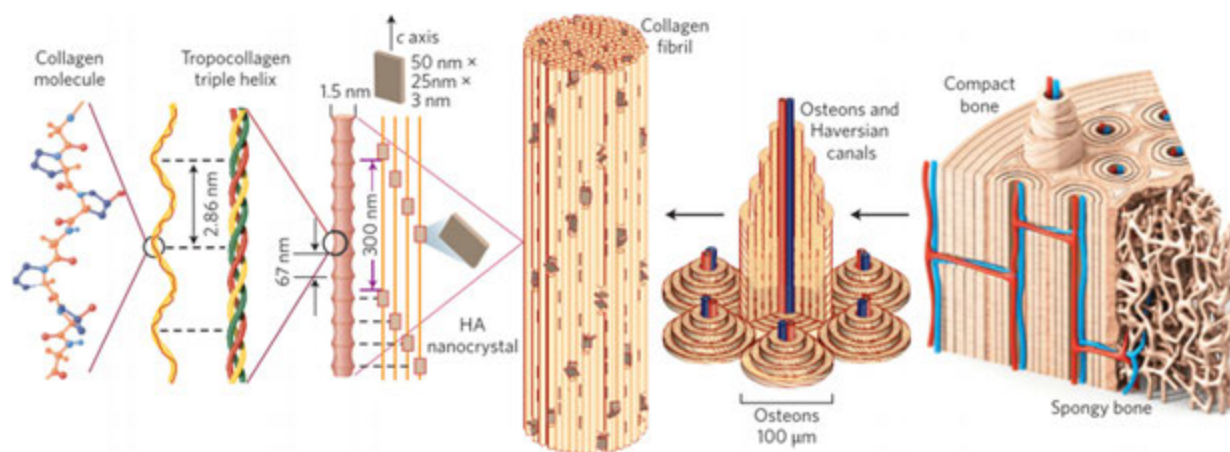


Fig. 1 The hierarchical structure of bone. Figure reprinted with permission from Wegst, U.G.K., Bai, H., Saiz, E., Tomsia, A.P., Ritchie, R.O., 2015. Bioinspired structural materials. *Nat. Mater.* 14, 23–36. doi:[10.1038/nmat4089](https://doi.org/10.1038/nmat4089).

Bone Implant Materials

For the material to be successfully used in bone replacement or regeneration it should be: (Alvarez-Urena *et al.*, 2017; Shanmugam and Sahadevan, 2018):

- *Biocompatible* – non-harmful to the patient regarding its phases, surface properties, chemical reactions, mechanical load, and closeness of fit as well as non-immunogenic (without causing severe inflammation or implant rejection);
- *Bioactive* – able to bond directly to the bone and to form strong inosculation interface between a tissue and the implant which can resist a relative displacement between the two progressing bone formations and enhance the success rate of the restoration;
- *Osteoinductive* – able to trigger the start of bone regeneration by promoting the mitogenesis of undifferentiated mesenchymal cells, leading to the formation of osteoprogenitor cells that have the osteogenic capacity;
- *Osteoconductive* – able to direct bone growth by triggering fibrovascular tissue and osteoprogenitor cells invasion of a porous structure, often acting as a temporary scaffold, which will be replaced with a newly formed bone;
- *Biodegradable* – capable of being broken down into non-harmful products during the regeneration process in a proper period (which differs with the age of the patient).

Also, implant material must be sterile, should not trigger the development of teratomas or cancers, and can't be radioactive.

The surgical procedure of introducing new bone or substitute implant material into a defect, or around it, with the intent of helping bone healing is called bone grafting (Xiao *et al.*, 2013). Depending on the source of the bone grafts they can be classified as autografts, allografts, xenografts, and alloplastic grafts.

Autograft

Autograft (autologous or autogenous bone) is a bone tissue taken from the same organism in which it will be implanted. This material has native components and can promote healing by inducing cells to trigger new bone growth without the risk of disease transmission. Autograft can be utilized for relatively small procedures and it requires additional surgery, at a harvesting site that commonly stays painful after surgery. Further complications like infections, nerve injury, fractures, or hematoma are commonly associated with harvesting an autograft (Carlisle and Fischgrund, 2009).

Allograft

An allograft is a bone taken from one patient and placed into another one. There is no additional surgery for the same patient as in autograft, but allograft is not genetically identical, which can lead to immunogenic reactions and it presents a risk of disease transmission. This risk can be reduced with treatments like demineralization and lyophilization. Common complications associated with allografts are unwanted resorption, pain in the site of the repair, high rejection rate, prolonged inflammatory response, reduced biomechanical properties and greater variability than autograft (Carlisle and Fischgrund, 2009; Zhang *et al.*, 2019).

Xenograft

A xenograft is a material taken from one species and placed in another one, such as marine biominerals taken from corals or shellfish and used as a bone graft. Most commonly used xenografts are from a bovine or porcine bone that are lyophilized/demineralized and deproteinized before grafting. In comparison to the allograft, they are relatively inexpensive and readily available materials, but they still carry all risks of allografts, including ethical concerns. Furthermore, bovine xenograft degrades quicker than bone, induces a greater immune response and its osteogenicity is low (Dorozhkin, 2012).

Alloplastic Graft

Alloplastic (or synthetic) bone graft is made from synthetic materials. Such material is disease-free, there is no concern about immunological compatibility, it can be sterilized and is easily available (Dorozhkin, 2012). Examples of alloplastic grafts are diverse metallic or ceramics components, commonly shaped into some form of scaffolds.

Scaffolds

An optimal solution for bone regeneration is sought in scaffolds. Bone tissue scaffold is a 3D biomaterial that provides architecture and environment for bone tissue to develop and grow, guiding the spatially and temporally complex process of bone regeneration (De Witte *et al.*, 2018). 3D scaffolds should mimic the natural extracellular matrix (ECM) in its structure, surface topographies (from nano- to microscale), and mechanical properties (Wu *et al.*, 2014). They can also serve as carriers for different biologically active molecules, including growth factors, antibiotics, or gene therapy, among others (Kolk *et al.*, 2012; Roseti *et al.*, 2017).

To successfully perform their function, scaffolds need to fulfill several biological, mechanical, structural and technological requirements (Abbasi *et al.*, 2020; Amini *et al.*, 2012; Chen *et al.*, 2018; Darus *et al.*, 2018; De Witte *et al.*, 2018; Gittens *et al.*, 2014; O'Brien, 2011; Roseti *et al.*, 2017; Wu *et al.*, 2014):

- *Biological* – as all biomaterials, scaffolds should primarily be non-immunogenic, bioactive, biocompatible, and provide an environment in which cells can normally function (adhere, proliferate, differentiate, migrate, and produce new matrix). A scaffold should be biodegraded and synchronously replaced by newly formed tissue while providing enough mechanical support, and, when possible, release beneficial ions like calcium, strontium or magnesium, without toxic by-products. The rate of bone healing greatly varies with the age and health of the bone, so scaffold should be designed according to these conditions.
- *Mechanical* – scaffolds should mimic the mechanical properties of the bone as close as possible. Mechanical properties of scaffolds usually match the properties of human cancellous bone with compressive strength of 2–12 MPa and modulus between 0.1 and 5 GPa.
- *Structural* – scaffold should have an interconnected porous structure to enable proper cell growth and migration, nutrient flow, vascularization, and spatial organization, as well as interlocking between the scaffold and surrounding tissue which ensures long-term stable fixation of the scaffold. The recommended range for pore size is from 150 to 500 μm so osteoblasts can enter, nutrients and waste products can diffuse, while material integrity is not compromised. Overall porosity should be in the range 50% to 90%, which is challenging for the structure that needs to have great mechanical strength. A scaffold must be properly placed and fixated with the bone on the macroscale, which demands optimal properties of its surface (mechanics, porosity, grain size, roughness, chemistry, etc.) for the bone regenerative cells attachment and growth, i.e., for the onset of the new bone mineralization. At the microscale, the type of proteins that will adsorb will depend on the implant surface properties and can result in both, inflammation or healing. Those proteins will be recognized by the cell membrane receptors, which means that the implant surface must be precisely constructed since this can significantly influence the cell response. At the nanoscale, different features like nanopits, nanoislands, nanogrooves or nanotubes can significantly influence the cell response.
- *Technological* – for scaffolds to be successfully implemented in practice, all of their properties should meet corresponding regulatory requirements. The process of their production should be cost-effective and reproducible at a large scale. This also includes a sterilization procedure, i.e., it should be possible to sterilize scaffolds by usual industrial procedures. They also should be easy to handle in practice since complex preparation procedures should be avoided during operation. As well, they should enable a minimally invasive implantation procedure.

In the following articles materials and techniques used for bioceramics scaffold productions are presented.

Ceramics Materials for Bone Regeneration

Different materials are used for producing scaffolds, depending on their intended use. Metals are material of choice for load-bearing application. However, metals are not bioactive or biodegradable, they release toxic ions and are subjected to corrosion and wear. This commonly results in problems like dislocations or fibrous capsule production which can cause implant rejections (Ghassemi *et al.*, 2018). On the other hand, polymers have good biocompatibility and ductility, their bioresorption can be tailored, but their poor mechanical strength and degradation by-products can be a problem. Bioceramics are emerging as bioactive, biodegradable, and mechanically stiff materials that could overcome some of the difficulties of metals and polymers. However, they could have low strength and brittleness, as well as a slow degradation rate (Chocholata *et al.*, 2019).

In general, ceramics are considered as polycrystalline non-metallic inorganic materials with good compressive strength and inertness. Examples are silicates, metallic oxides, carbides, sulfides, refractory hydrides, selenides or natural structures like bone, teeth, etc. Bioceramics are ceramics specially developed for biomedical applications like bone fillers, implant coatings, scaffolds, etc. (Alvarez-Urena *et al.*, 2017; Xiao *et al.*, 2013). Like all ceramics, bioceramics are hard but brittle, wear-resistant, chemically stable, electrically, and thermally insulating. The key properties in which bioceramics differ between themselves are degradability and bioactivity (Xiao *et al.*, 2013). The first generation of bioceramics materials was developed to serve as a mechanical support for the damaged site. They are biocompatible but inert, so that material does not trigger an immune response, with major materials in use being alumina and zirconia (Yu *et al.*, 2015). The ability of some bioceramics (bioglasses, glass ceramics, HA) to stimulate bone regeneration and form a strong interface with the bone spurred the development of second generation of bioceramics, the bioactive and bioresorbable materials (Yu *et al.*, 2015). Bioactive materials are materials of choice for small defects or mechanically non-demanding bones (e.g., cranial) but their usage is limited by brittleness. Most recently, bioresorbable materials came to focus as the ideal substitute for the bone, since they do not just substitute but also regenerate the injured part of the bone. Such materials do not cause disease transfer or immunological problems and some can be used as drug-delivery systems. Unfortunately, their mechanical properties are weak, and their degradation rate is hard to predict (Dorozhkin, 2018b). Porous materials are more beneficial for cell attachment and growth, but their load-bearing ability is tenfold times lower than cancellous bone. Only ceramic materials that have similar values to the cortical bone is dense bioactive ceramics (Fig. 2(a)). This dense ceramics refers to HA with tensile strength ranging from 40 to 200 MPa and Young's modulus from 80 to 110 GPa, but its fracture toughness is low, approx. $1.2 \text{ MPa m}^{1/2}$ (Dorozhkin, 2012; Farid, 2019).

The third generation of bioceramics incorporates instructive cues for inducing favorable cell response. The examples are highly porous scaffolds or scaffolds loaded with cells, genes or growth factors (Yu *et al.*, 2015). Differences in ceramics bioactivity

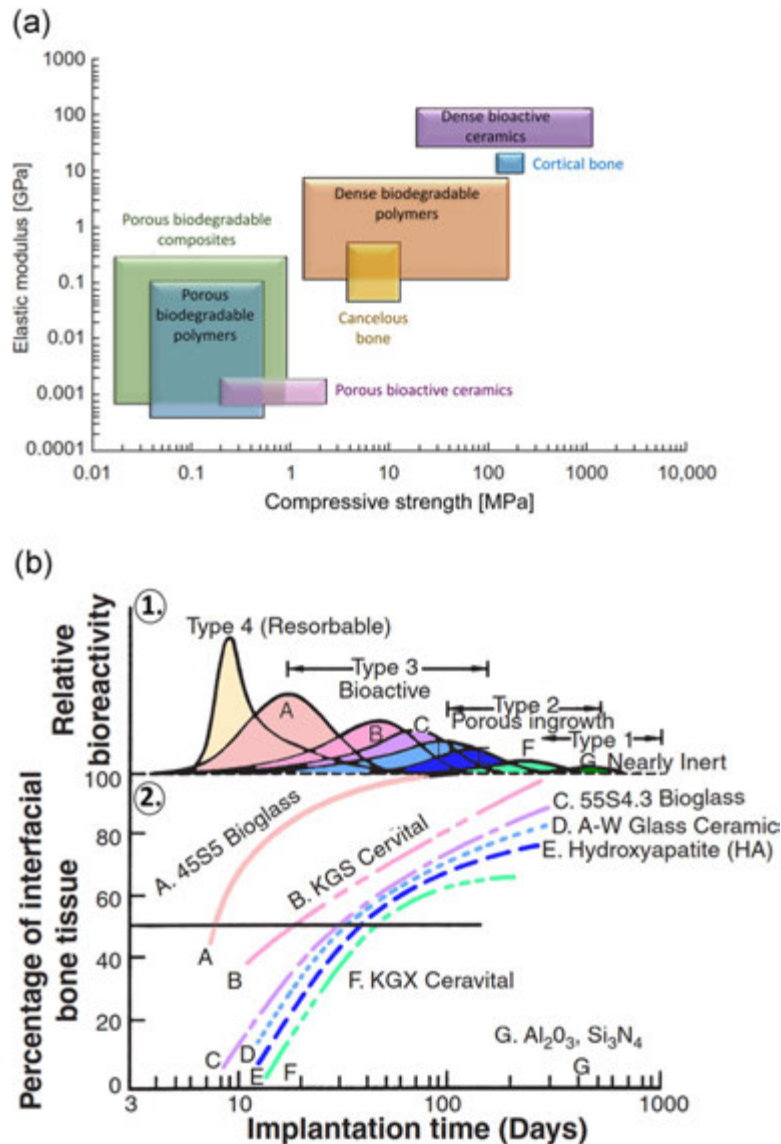


Fig. 2 (a) Mechanical properties of biomaterials for bone tissue applications compared with properties of cortical and cancellous bone, (b) Bioactivity spectra of bioceramics implants: (1) relative rate of bioreactivity, (2) time dependence of bone bonding at an implant interface. Adapted with permission from: (a) Varanasi, V.G., Velten, M.F., Odatsu, T., *et al.*, 2017. Chapter 9 – Surface modifications and surface characterization of biomaterials used in bone healing. In: Bose, S., Bandyopadhyay, A. (Eds.), *Materials for Bone Disorders*. Academic Press, pp. 405–452. doi:10.1016/B978-0-12-802792-9.00009-4. (b) Ratner, B.D., 2008. *Biomaterials Science: An Introduction to Materials in Medicine*. Amsterdam: Elsevier, Acad. Press.

are represented in Fig. 2(b) where relative bioreactivity (1) is correlated with the interfacial bond formation rate between implants and bone (2).

Bioinert Bioceramics

Bioinert bioceramics were used for the bone tissue replacement to produce load-bearing material that will serve to permanently replace bone. Bioinert bioceramics are considered as standard support for mechanically strenuous sites like hips or knees. Commonly used materials are alumina, zirconia, carbons, sintered HA, calcium alumina oxides, and silicon nitrides. Alumina ceramics is made from aluminum oxide (Al_2O_3) and commonly used in bioceramics, orthopedic and dental applications since it has a high hardness (> 20 GPa), corrosion resistance, and excellent wear, but it is brittle (Drouet *et al.*, 2017). Zirconia (ZrO_2) in its partially stabilized form is an alternative for alumina with better mechanical properties, making it highly usable as a dental implant material, especially as a composite with alumina, calcium oxide, magnesia or yttria, but its degradation can be problematic (Shanmugam and Sahadevan, 2018). Other commonly used bioinert ceramics for bone implants are silicon nitride or

diamond-like carbon, to name a few. The lack of bond formation between the tissue and bioinert ceramics materials can lead to a nonadherent fibrous capsule that causes loosening and implant failure (Hench, 1991). As a solution, materials with porous structures were suggested, where tissue can lock and bond with the implant. However, the porous structure has lower mechanical stability which leads to another set of problems to solve. Silicon nitrides and carbides have good mechanical properties and are nontoxic, but expensive to produce so currently their scaffolds are in the development phase (Drouet *et al.*, 2017).

Bioactive Bioceramics

Bioactive materials are chemically similar to the bone. This enables them to bond with the bone and trigger a natural repair mechanism of the bone tissue. Common bioactive ceramics are bioactive glass ceramics, HA, and calcium silicates. Bioactive glass can trigger new bone formation by releasing the calcium and phosphorus ions that can be utilized in a bone reconstruction procedure. It is used in larger cranial defects but it can also be shaped for use in a microsurgical environment for small bones like the middle ear or spine. However, particles or granules are preferred form which can be pressed into diverse shapes and used as fillers or spacers (Al Tamami *et al.*, 2020; Cottrill *et al.*, 2020; Drouet *et al.*, 2017). Since bioglass is unsuitable for load-bearing implants it is mostly used as a coating, for example of alumina hip joint cups or titanium alloys that usually increase osteointegration (Dmoušek *et al.*, 2012).

Most praised glass-ceramics is apatite-wollastonite (A/W) system (Cerabone®, Ceravital®) a combination of silica phosphate glass-ceramics that is biocompatible, bioactive and has a significantly higher toughness, strength, elastic modulus and stability so it can be used even in some load-bearing applications (Kokubo, 2008). Components like glass-ionomer cements (GICs) are commonly used as restorative materials in dentistry, for example as a composite of calcium-fluoroaluminosilicate glass particles and polyacrylic acid (Gremillard and Tadier, 2017). Such mixtures partially dissolve glass which releases ions and provoke cement forming in a matter of minutes.

HA has an optimal chemical composition, but its brittleness is much higher than the bone due to the lack of organic matrix, especially if it is used in the porous form (Karageorgiou and Kaplan, 2005).

Bioresorbable Bioceramics

The most advanced approach is to use resorbable implant materials that can biodegrade in a time needed for natural bone tissue to regenerate and replace the implant. The distinction between bioactive and bioresorbable bioceramics is sometimes in their structure: dense HA is bioactive and will last for 5–7 years in the organism, while porous HA will be resorbed within 1 year (Goto *et al.*, 2001; Raucci *et al.*, 2016). The rate of biodegradation is hard to accurately control because the resorption rate depends on diverse factors. Also, the strength of these materials is commonly insufficient to produce sufficient support during the regeneration procedure.

The most investigated bioresorbable bone substitute materials are different forms of CaPs, tunable osteoinductive and osteoconductive materials that are easy to produce (Drouet *et al.*, 2017). Commonly used forms are tricalcium phosphate (TCP, $\text{Ca}_3(\text{PO}_4)_2$), calcium-deficient hydroxyapatite (CDHA, $\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-y}$, $0 < x < 1$), HA, and bi- or triphasic CaP (diverse combinations of TCP and HA). TCP-based ceramics (both α - and β -form) are often used as coatings on metallic prostheses, dental restorative materials, or small bone replacements. β -TCP is among the most frequently used bone substitutes in orthopedics and dentistry since it is bioresorbable in comparison to the HA-based ceramic. Biphasic calcium phosphate ceramics and triphasic ceramics are slowly replacing the use of β -TCP in Europe and are commonly referred to as calcium phosphate ceramics (Dorozhkin, 2016).

Another material that encourages bone regeneration and serves as a temporary bone substitute is calcium sulfate hemihydrate (CS, plaster of Paris / gypsum). CS is already used as injectable repair for smaller bone defects (Kelly and Wilkins, 2004). Calcium carbonate from organisms like corals can also be used for conversion to carbonate apatites, as an osteoconductive material with a structure similar to trabecular bone. Unfortunately, it has reduced biodegradation and mechanical properties, while the availability of the corals also remains a challenge (Damien and Revell, 2004).

Bioceramics in Organic-Inorganic Composites

The bones' exceptional properties are a consequence of them being organic-inorganic composites. In an effort to mimic the bone to a higher extent, organic-inorganic composites consisting of bioceramics and polymers are being developed. Such materials utilize the advantages of both classes of materials (osteoconductivity and sustained release of bioceramics, tailored degradability and controlled release of polymers) while minimizing their drawbacks. Structure and volume ratio of polymers and arrangement of bioceramics within polymer matrix are key parameters that enable tailoring of composite properties. Among the most investigated composites are those with poly(α -hydroxy ester)s and copolyesters of the lactic and glycolic acid, collagen and gelatin (Alvarez-Urena *et al.*, 2017).

Scaffolds Processing Techniques

Several techniques can be used to produce ceramics scaffolds with different structural features. Generally they are divided into conventional and additive manufacturing techniques.

Conventional Techniques

Conventional techniques are based on a top-down approach, starting from large solids and fabricating them into smaller, complex objects. Complex porous 3D structures are especially demanding to produce by conventional techniques and often the control of pore architecture is not satisfactory (Butscher *et al.*, 2011).

Principles of some of the most commonly used conventional techniques are:

- *Solvent casting and particulate leaching* – thick paste, consisting of water soluble porogen (i.e., salt), ceramics powder, and organic solvent or polymer solution is poured in a mold and left to dry. Porogen is leached by keeping the scaffolds in water for a specific period. After leaching, the scaffold is sintered to obtain mechanical strength. The control over pore size is achieved through the size of porogen particles (Darus *et al.*, 2018; Roy *et al.*, 2017).
- *Thermally-induced phase separation* – the slurry is prepared by mixing the ceramics powder with a dioxane/water mixture. Frequently, a polymer is added to the slurry. The slurry is heated to 15–20°C above the determined cloud point and then quenched at the desired water bath temperature. To obtain a porous structure, the sample is freeze-dried and subsequently sintered. Scaffolds with anisotropic pore structures, tubular morphology and porosity up to 95% are obtained (Roy *et al.*, 2017). The scaffold porosity can be controlled by freezing rate, temperature, and polymer concentration (Thavornmyutikarn *et al.*, 2014).
- *Polymer bead* – polymer beads of specific sizes are mixed with ceramics powder and compacted. Obtained samples are heated at around 550°C to burn off the polymer and subsequently sintered at higher temperatures. The pore size is controlled with the size of polymer beads. (Roy *et al.*, 2017).
- *Freeze casting* – a stable aqueous ceramics slurry containing appropriate dispersant and binder amounts is prepared and unidirectionally frozen to obtain a solid 3D component. Water is removed by freeze-drying to retain the scaffold's shape and integrity. The dried scaffold is sintered. (Darus *et al.*, 2018; Roy *et al.*, 2017).
- *Gas foaming* – in situ gas-forming agent is added to the stable ceramics slurry which is cast to the desired geometry. During the setting, formed CO₂ gas escapes the system and this creates interconnected pores in the ceramics. This technique was developed to avoid organic, cytotoxic solvents (Roseti *et al.*, 2017; Roy *et al.*, 2017).
- *Sol-gel technique* – this technique is based on the polymerization of metal aloxides. The precursor is mixed with water to form sols through hydrolysis and condensation. Addition of surfactants and catalyst results in foaming of the sol and beginning of condensation. Foamed sols are transferred to the molds and turned into gel after sealing for a while. Thermal treatment densifies the matrix (Zhu *et al.*, 2020).
- *Gel casting* – fluid and castable slurry is prepared by dispersing ceramics powder in an aqueous solution of monomer, cross-linker, free radical initiator and catalyst. The slurry is poured in a mold and in situ polymerized gel forms which immobilizes ceramics particles in the shape of the mold. Still wet object is removed from the mold and dried in controlled conditions. An obtained dry green body is strong enough to be machined. Binder is removed by heating and the sintering is used to improve mechanical properties (Yang *et al.*, 2011).
- *Electrospinning* – electrospinning is a technique for producing nanofibrils of different materials. The method is based on electrostatic repulsion between the surface charges to form a nanofiber. A drop of solution or a melt is held at the end of the capillary by its surface tension. Applying a high electrostatic voltage results in distortion of the drop into a conical jet. When the voltage becomes high enough a stable liquid jet is ejected from the tip of the cone. It dries during the jet traveling in the air, and ultra-fine fibers with a high surface-to-volume ratio are formed and collected on electrically grounded targets (Balu *et al.*, 2014).
- *Sacrificial mold* – polymer foam is coated with ceramics slurry and the polymer is removed by suitable heating (Roy *et al.*, 2017).

Advantages and disadvantages of these methods are given in Table 1, while examples of the scaffolds produced by these methods are given in Fig. 3.

Additive Manufacturing

With conventional techniques, it is not always easy to achieve strict control over pore size, interconnectivity, and geometry. This in turn means, that scaffolds produced in that manner cannot specifically and adequately improve cell growth and tissue regeneration (Ma *et al.*, 2018). Additive manufacturing (AM, sometimes called rapid prototyping) techniques offer a solution to this problem.

Additive manufacturing is a family of technologies capable of generating 3D objects directly from digital data (Parra-Cabrera *et al.*, 2018). The core concept of all of these technologies is the rapid and seamless transition between a computer model and its physical realization (Gibson *et al.*, 2010). Commercial AM technologies create a 3D object by depositing multiple 2D layers on top of each other. They differ in materials that can be used, how layers are formed, and ways of their bonding (Parra-Cabrera *et al.*, 2018).

AM methods have overcome limitations of conventional bioceramics processing methods in control of the shapes, geometry, and internal architecture of the scaffolds, without the usage of toxic organic solvents. A scaffold is made by deposition of overlying layers which enables stricter control of porosity, pore size, and mechanical properties. These methods also enable the preparation of scaffolds with two or more materials. Combined with medical imaging of the place of injury they enable the production of scaffolds matching the specific patient's needs (Hammel *et al.*, 2014; Roseti *et al.*, 2017). Also, these techniques enable the design of the personalized scaffold structure matching the surrounding tissue of the specific patient and accounting for the differences in

Table 1 Comparison of advantages and disadvantages of conventional ceramic production techniques

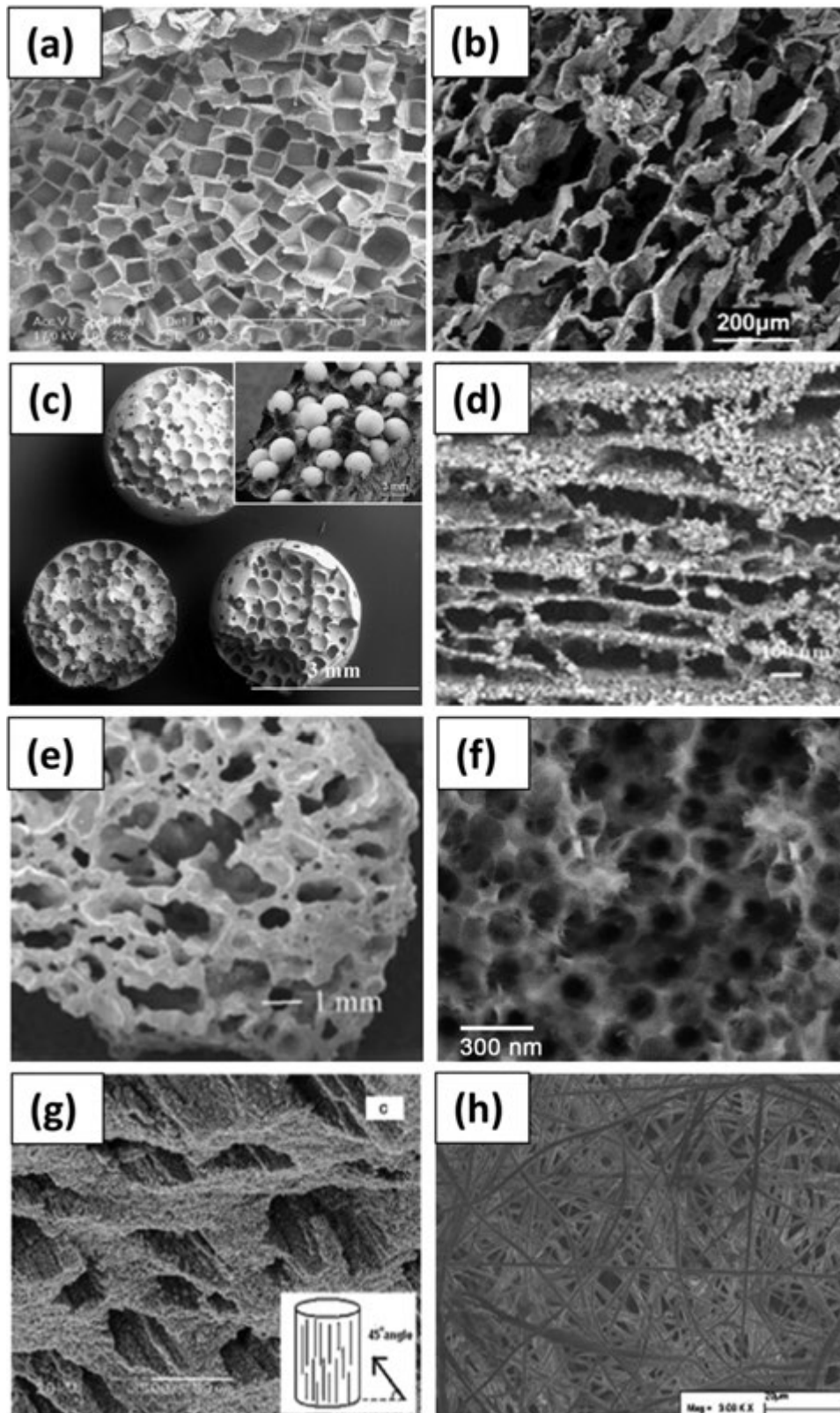
Technique	Advantages	Disadvantages
<i>Solvent casting and particulate leaching</i>	● simple production ● easy method ● control of pore size and porosity	● toxic solvent and porogen residue ● decreased activity of bioinductive molecules ● no pharmacological agents can be added ● weak mechanical properties
<i>Thermally-induced phase separation</i>	● anisotropic pore structure with tubular morphology ● high porosity (up to 95%) ● control of pore size and structure ● low probability of the defects	● complex and expensive processing ● poor mechanical properties ● not suitable for seeding cells or bone tissue growth (pore sizes 10 – 100 μm) ● use of organic solvents
<i>Polymer bead</i>	● simple inexpensive process	● small scale production ● poor mechanical properties ● unable to form complex geometry
<i>Freeze casting</i>	● high mechanical strength ● environmentally friendly	● a complex process requiring special and costly instrumentation ● poor control over pore geometry and distribution ● long processing time
<i>Gas foaming</i>	● inexpensive process ● no organic cytotoxic solvents ● good for preparing large samples ● eliminates the use of chemical solvents	● a complex process ● poor mechanical properties ● limited dimension accuracy ● possibility of closed pore structure ● poor control over pore size, distribution, and interconnectivity ● restrained inclusion of cells and bioactive molecules
<i>Sacrificial mold or powder</i>	● a simple and inexpensive process ● good control over pore interconnectivity	● poor compressive strength
<i>Sol-gel technique</i>	● highly mesoporous structure ● high purity ● low cost	● poor mechanical properties ● large content of nanoporosity
<i>Gel casting</i>	● near-net shape ● high homogeneity ● good interconnectivity when combined with foaming	● slurry rheology and homogeneity
<i>Electrospinning</i>	● large surface areas ● superior mechanical properties ● large scale production ● very thin fibers ● simple and inexpensive technique	● inadequate control of scaffold architecture, pore network, and size ● suboptimal 3D scaffolds ● organic solvents may be required ● limited mechanical properties

Note: Babaie, E., Bhaduri, S.B., 2018. Fabrication aspects of porous biomaterials in orthopedic applications: A review. *ACS Biomater. Sci. Eng.* 4, 1–39. doi:10.1021/acsbomater.7b00615. Chocholata, P., Kulda, V., Babuska, V., 2019. Fabrication of scaffolds for bone-tissue regeneration. *Materials* 12, 568. doi:10.3390/ma12040568. Darus, F., Isa, R.M., Mamat, N., Jaafar, M., 2018. Techniques for fabrication and construction of three-dimensional bioceramic scaffolds: Effect on pores size, porosity and compressive strength. *Ceram. Int.* 44, 18400–18407. doi:10.1016/j.ceramint.2018.07.056. Ribas, R.G., Schatkoski, V.M., Montanheiro, T.L., *et al.*, 2019. Current advances in bone tissue engineering concerning ceramic and bioglass scaffolds: A review. *Ceram. Int.* 45, 21051–21061. doi:10.1016/j.ceramint.2019.07.096. Roseti, L., Parisi, V., Petretta, M., *et al.*, 2017. Scaffolds for Bone. *Tissue Eng.: State Art New Perspect. Mater. Sci. Eng. C* 78, 1246–1262. doi:10.1016/j.msec.2017.05.017. Roy, M., Bandyopadhyay, A., Bose, S., 2017. Ceramics in bone grafts and coated implants. In: Bose, S., Bandyopadhyay, A. (Eds.), *Materials for Bone Disorders*, Elsevier. pp. 265–314. doi:10.1016/B978-0-12-802792-9.00006-9. Thavorniyutikarn, B., Chantarapanich, N., Sitthiseriratip, K., Thouas, G.A., Chen, Q., 2014. Bone tissue engineering scaffolding: Computer-aided scaffolding techniques. *Prog. Biomater.* 3, 61–102. doi:10.1007/s40204-014-0026-7. Turnbull, G., Clarke, J., Picard, F., *et al.*, 2018. 3D bioactive composite scaffolds for bone tissue engineering. *Bioactive Mater.* 3, 278–314. doi:10.1016/j.bioactmat.2017.10.001.

tissue structure connected with age, health, or the condition of the surrounding bone (Hammel *et al.*, 2014). AM methods may be applied directly from intended ceramics materials or indirectly using molds. Principles of the most frequently used AM methods are described below, while the main advantages and disadvantages of different AM techniques are given in Table 2.

Direct techniques utilize ceramics powder, colloidal solution, or paste to directly build the desired structure. The benefit of these techniques is that powder bed supports successive layers, due to which spanning elements are more easily fabricated. Among most commonly used techniques are (Bose *et al.*, 2015; Hammel *et al.*, 2014; Parra-Cabrera *et al.*, 2018; Roseti *et al.*, 2017):

- **Stereolithography** – is a 3D printing technique based on the selective solidification of photopolymer resins using a UV light source. 3D objects are processed by subsequent deposition of 2D layers which are solidified either by scanning a laser over a surface of the resin or by projecting the entire slice. For manufacturing ceramics objects, photopolymerizable suspensions of ceramics powders are used. After creating a green part (the part before sintering), a cross-linked polymer binder is burned-out and the remaining object is sintered to improve mechanical properties. To prevent crack formation, deformation, or shrinkage caused by polymer removal the cured ceramics green part must have density 50% or higher.



- *Extrusion based methods* – a movable extrusion head is used to selectively deposit material to form layers. An example of this technique is robocasting which was originally developed for ceramics materials. In robocasting, a highly concentrated suspension of the material of interest and a solvent are deposited layer-by-layer through a syringe-type nozzle. Ensuring adequate viscosity of suspension enables that layers keep their shape until drying. When printing ceramics, the dried object is usually heated to remove additives and to increase mechanical stability. Fused deposition modeling works in the same manner, the difference being that a thermoplastic polymer is extruded through a heated nozzle. Fused deposition of ceramics is the modification of this method used to process 3D ceramics structures. It uses thermoplastic polymer mixture, which includes a binder, plasticizer, and dispersant, as a ceramics powder carrier. Using multiple extruders in parallel enables incorporating different materials in different parts of the object, with a discrete transition between materials.
- *Powder bed-based methods* – manufacturing starts by spreading a thin layer of powder (around 100 μm thick) across the building area using a counter-rotating leveling roller. Layers are created by selectively binding particles in the powder layer. Binding of ceramics powders is usually done by selective deposition of the liquid binder by inkjet printhead. Alternatively, a dry binder can be mixed with the powder, and binder activator is printed. After printing ceramics objects are usually heated to evaporate binder and to sinter the object. The first commercial powder bed-based method is selective laser sintering. This method uses a high-power laser to fuse powder particles in thin layers that are built on top of each other. Before laser sintering, the powder is preheated just below the melting/transition point to minimize thermal distortion and facilitate the fusion of the new layer to the previous one. The focused CO_2 laser beam is directed on a power bed in the pattern according to CAD design. Surrounding powder remains loose and serves as a support for the subsequent layer. After one layer is processed, the platform is lowered and the next layer of powder is spread until the desired object is made.
- *Inkjet 3D printing* – binder jetting machine distributes a layer of powder onto a platform. Subsequently, liquid droplets of bonding agent are deposited onto the powder by inkjet printer, bonding the particles together. After the layer is finished, the platform is lowered and the next layer is produced. 3D printing can be also used to print sacrificial mold, in this way aqueous binder can be used and porogen size is not limited. However, limitations are high density packing of porogen in complex features and restrictions on the shape or feature design.
- *Bioprinting* – small units of cell and biomaterials are dispensed together with micrometer precision to form tissue-like structures. Extrusion-based and laser-based bioprinting can be used for producing ceramics or composite scaffolds. In extrusion-based bioprinting continuous filaments of material are dispensed using a piston or pneumatic pressure to fabricate 2D or 3D structures. Laser-based bioprinters use a pulsed laser to transfer materials to a receiving substrate.

Examples of the scaffolds produced by AM are given in Fig. 4.

Drawbacks of direct methods are that the feature size is limited by the resolution of the machine, scaffold material must be compatible with AM process and sometimes smooth surfaces are created which do not provide a good environment for the cells. Also, liquid or powder residues may be left behind in the scaffold and the size of the printed components may be restricted due to the lack of strength (Hammel *et al.*, 2014). A possible solution is indirect technique. A mold of negative architecture is made of polymer or wax by AM. The ceramics slurry is cast into the mold which is removed by heating. The remaining ceramics scaffold is then sintered to the required density.

Advanced Applications of Scaffolds

Expanded interaction surfaces of porous implants are built for the flow of nutrients and cell attachment, but they can be loaded with diverse substances and used for targeted delivery with prolonged release of e.g., particles, therapeutics, polymers, or even living cells. The active components can be delivered in various forms, from powders, granules, spheres, pastes, fibers, tubes, and

Fig. 3 Typical pore morphologies of ceramics scaffolds created by conventional techniques: (a) 40% nanohydroxyapatite/nylon 6,6 composite scaffold fabricated by solvent casting/particulate leaching, (b) poly(α -hydroxyl acids)/hydroxyapatite composites prepared by thermally-induced phase separation, (c) fracture facies of hydroxyapatite (HA) macroporous beads prepared using polymer bead technique, inset shows PMMA beads in fracture facies of calcium carbonate scaffolds, (d) β -tricalcium phosphate (β -TCP) scaffolds fabricated using freeze casting technique, (e) calcium deficient hydroxyapatite scaffold obtained by gas foaming, (f) porous calcium silicate obtained by sol-gel technique, (g) porous ceramics with unidirectional pore channels fabricated by freeze-gel casting technique, (h) composite methylene chloride and dimethylformamide mats with 30% HA-TCP obtained by electrospinning. Reprinted with permission from: (a) Mehrabian, M., Nasr-Esfahani, M., 2011. HA/nylon 6,6 porous scaffolds fabricated by salt-leaching/solvent casting technique: Effect of nano-sized filler content on scaffold properties. *Int. J. Nanomed.* 2011, 1651–1659. doi:10.2147/IJN.S21203. (b) Zhang, R., Ma, P.X., 1999. Poly(α -hydroxyl acids)/hydroxyapatite porous composites for bone-tissue engineering. I. Preparation and morphology. *J. Biomed. Mater. Res.* 44, 446–455. (c) Descamps, M., Hornez, J.C., Leriche, A., 2009. Manufacture of hydroxyapatite beads for medical applications. *J. Eur. Ceram. Soc.* 29, 369–375. doi:10.1016/j.jeurceramsoc.2008.06.008. (d) Darus, F., Isa, R.M., Mamat, N., Jaafar, M., 2018. Techniques for fabrication and construction of three-dimensional bioceramic scaffolds: Effect on pores size, porosity and compressive strength. *Ceram. Int.* 44, 18400–18407. doi:10.1016/j.ceramint.2018.07.056. (e) Almirall, A., Larrecq, G., Delgado, J.A., *et al.*, 2004. Fabrication of low temperature macroporous hydroxyapatite scaffolds by foaming and hydrolysis of an α -TCP paste. *Biomaterials* 25, 3671–3680. doi:10.1016/j.biomaterials.2003.10.066. (f) Papynov, E.K., Shichalin, O.O., Apanasevich, V.I., *et al.*, 2019. Synthetic CaSiO_3 sol-gel powder and SPS ceramic derivatives: “In vivo” toxicity assessment. *Prog. Nat. Sci. Mater. Int.* 29, 569–575. doi:10.1016/j.pnsc.2019.07.004. (g) Yang, J., Yu, J., Huang, Y., 2011. Recent developments in gelcasting of ceramics. *J. Eur. Ceram. Soc.* 31, 2569–2591. doi:10.1016/j.jeurceramsoc.2010.12.035. (h) Patilola, A., Collins, G., Livingston Arinze, T., 2010. Solvent-dependent properties of electrospun fibrous composites for bone tissue regeneration. *Acta Biomater.* 6, 90–101 doi:10.1016/j.actbio.2009.07.028.

Table 2 Features of different additive manufacturing techniques

Technique	Parameters	Advantages	Disadvantages
<i>Stereolithography, SLA</i>	● layer thickness: 1 μm for specimen volume < 35 mm^3 ● smallest feature indirect 366 μm, direct 1 – 70 μm	● high accuracy ● complex 3D structures ● easy removal of photopolymer by heating ● fine control over pore size and shape	● photo-polymerization of materials ● photocurable materials ● expensive materials and equipment ● support material needed ● slow process ● extensive and laborious postprocessing ● toxic uncured resins ● difficult to fabricate larger scaffolds with complex internal structure
<i>Fused deposition modeling, FDM</i>	● layer thickness: 250 – 370 μm ● smallest feature rod diameter 260 – 700 μm	● high porosity ● complete pore interconnectivity ● control of pore size ● macro-shape control ● no support material needed ● no residual powder ● good compressive strength ● solvent-free	● high processing temperature ● limited variety of materials ● pore inconsistency ● thermoplastic polymers required ● mechanical anisotropy
<i>Selective laser sintering, SLS</i>	● layer thickness: 76 – 100 μm ● smallest feature 45 – 100 μm	● complex structures ● independent control of porosity and pores size ● wide range of materials ● solvent-free ● no support material needed ● good mechanical properties	● high processing temperature ● limited to small pore sizes ● low accuracy ● high cost ● low surface quality ● low mechanical strength ● slow printing speed ● powder residue ● toxic organic solvent ● low mechanical strength ● limited to small pore sizes ● low surface quality ● risk of entrapment of unbound powder ● low accuracy ● difficult depowdering process
<i>3D printing</i>	● layer thickness: slurry 20 – 100 μm, dry powder 50 μm ● smallest feature 350 – 500 μm	● easy process ● high porosity ● independent control of the size of the pores and porosity ● macro shape control ● wide range of materials ● no support material needed ● possibility of printing without sintering ● cost efficient	● high processing temperature ● limited to small pore sizes ● low accuracy ● high cost ● low surface quality ● low mechanical strength ● slow printing speed ● powder residue ● toxic organic solvent ● low mechanical strength ● limited to small pore sizes ● low surface quality ● risk of entrapment of unbound powder ● low accuracy ● difficult depowdering process
<i>Robocasting</i>	● layer thickness: 225 – 750 μm ● smallest feature rod diameter 200 – 400 μm	● high accuracy ● no support material needed ● combination of materials possible ● simple and economic ● no entrapment of particles into pores ● high fabrication speed ● applicable to a wide range of bio-ceramics	● material limitations ● slow process ● expensive process ● geometry restricted ● low accuracy ● limited to logpire structures ● easy to sag and collapse during printing ● precise control of rheology required

Note: Butscher, A., Böhner, M., Hofmann, S., Gauckler, L., Müller, R., 2011. Structural and material approaches to bone tissue engineering in powder-based three-dimensional printing. *Acta Biomater.* 7, 907–920. doi:10.1016/j.actbio.2010.09.039. Chocholata, P., Kulda, V., Babuska, V., 2019. Fabrication of scaffolds for bone-tissue regeneration. *Materials* 12, 568. doi:10.3390/ma12040568. Lin, K., Sheikh, R., Romanazzo, S., Roohani, I., 2019b. 3D printing of bioceramic scaffolds – Barriers to the clinical translation: From promise to reality, and future perspectives. *Materials* 12, 2660. doi:10.3390/ma12172660.

wires to films, coatings, hydrogels, or whole blocks, combined into innovative biomaterials that can advance bone regeneration process. They can be added into the finished porous scaffolds, deposited on its surface, or integrated into the scaffold during its formation. The combinations of two or more of these options are common. Fig. 5. summarizes most used substances that can be integrated with bone regeneration scaffolds.

Scaffolds With Particles

Biodegradable CaP and silica-based scaffolds release ions like calcium or silicone which can stimulate osteoblasts to increase bone growth. This beneficial effect can be enhanced by the incorporation of ions like lithium, silver, strontium, magnesium, etc., in the scaffolds. Such substitutions also influence the degradation rate, mechanical and biological properties like antibacterial activity

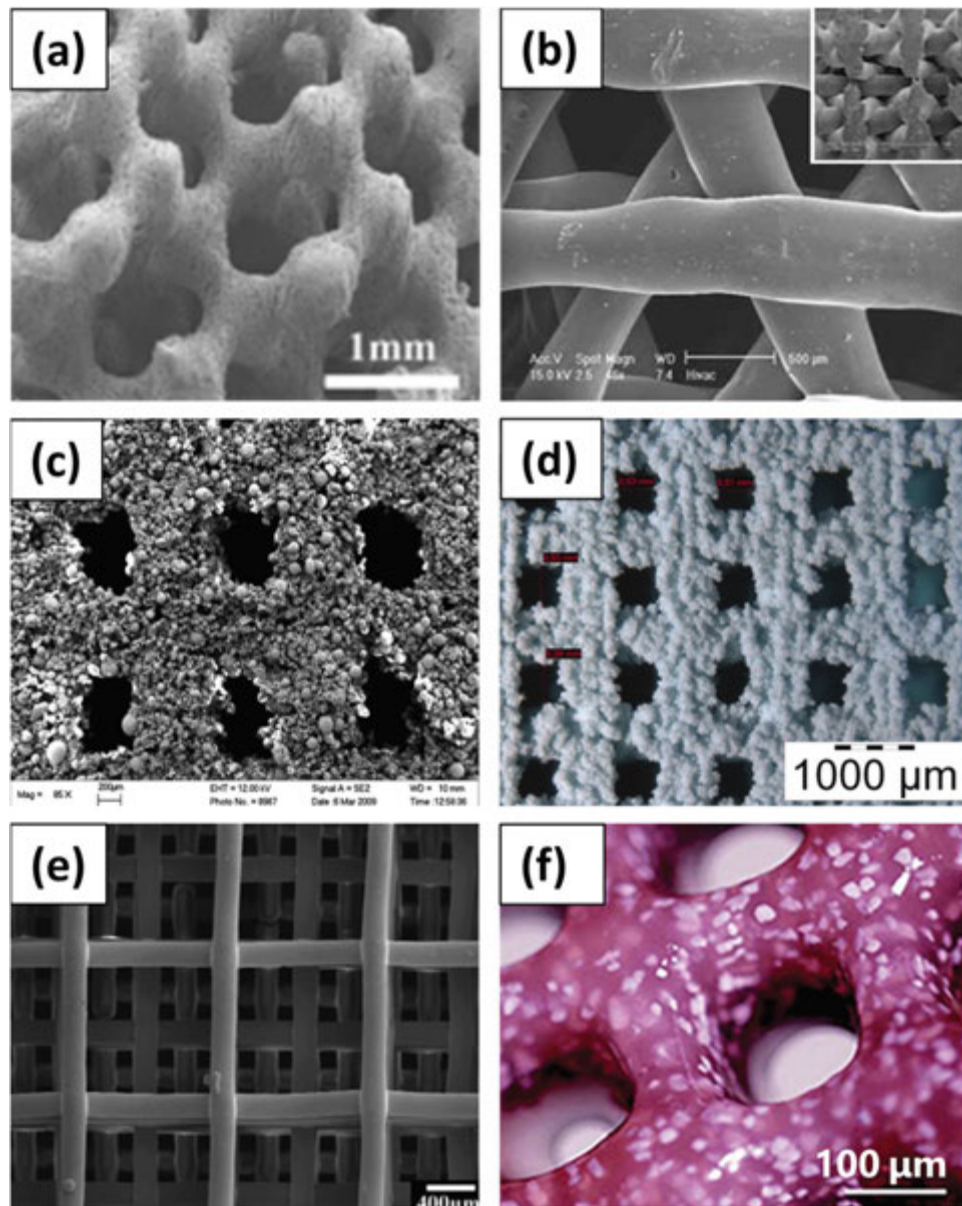


Fig. 4 Additive manufacturing techniques for ceramics scaffold production: (a) calcium phosphate (CaP) ceramics printed using stereolithography-based additive manufacturing (b) polycaprolactone – tricalcium phosphate scaffold printed using fused deposition modeling, (c) (CaP)/poly(hydroxybutyrate-co-hydroxyvalerate) scaffold fabricated using selective laser sintering, (d) 3D printed hydroxyapatite scaffold, (e) glass scaffold printed using robocasting, (f) porous bioprinted scaffolds containing mesenchymal stem cells and ceramic particles with plasmid DNA encoding BMP-26. Advanced applications for bone regeneration. Reprinted with the permission from: (a) Wei, Y., Zhao, D., Cao, Q., *et al.*, 2020. Stereolithography-based additive manufacturing of high-performance osteoinductive calcium phosphate ceramics by a digital light-processing system. *ACS Biomater. Sci. Eng.* 6, 1787–1797. doi:[10.1021/acsbomaterials.9b01663](https://doi.org/10.1021/acsbomaterials.9b01663). (b) Zhou, Y., Hutmacher, D.W., Varawan, S.-L., Lim, T.M., 2007. In vitro bone engineering based on polycaprolactone and polycaprolactone-tricalcium phosphate composites. *Polym. Int.* 56, 333–342. doi:[10.1002/pi.2138](https://doi.org/10.1002/pi.2138). (c) Duan, B., Wang, M., Zhou, W.Y., *et al.*, 2010. Three-dimensional nanocomposite scaffolds fabricated via selective laser sintering for bone tissue engineering. *Acta Biomater.* 6, 4495–4505. doi:[10.1016/j.actbio.2010.06.024](https://doi.org/10.1016/j.actbio.2010.06.024). (d) Warnke, P.H., Seitz, H., Warnke, F., *et al.*, 2010. Ceramic scaffolds produced by computer-assisted 3D printing and sintering: characterization and biocompatibility investigations. *J. Biomed. Mater. Res. B Appl. Biomater.* 93B, 212–217. doi:[10.1002/jbm.b.31577](https://doi.org/10.1002/jbm.b.31577). (e) Fu, Q., Saiz, E., Tomsia, A.P., 2011. Direct ink writing of highly porous and strong glass scaffolds for load-bearing bone defects repair and regeneration. *Acta Biomater.* 7, 3547–3554. doi:[10.1016/j.actbio.2011.06.030](https://doi.org/10.1016/j.actbio.2011.06.030). (f) Datta, P., Ozbolat, V., Ayan, B., Dhawan, A., Ozbolat, I.T., 2017. Bone tissue bioprinting for craniofacial reconstruction. *Biotechnol. Bioeng.* 114, 2424–2431. doi:[10.1002/bit.26349](https://doi.org/10.1002/bit.26349).

(Bose *et al.*, 2013). Alternatively, particles of titanium, alumina, iron oxide, silica, or carbon (graphene) can also be used to tune ion release and/or to improve the mechanical properties of the scaffolds (Canal and Ginebra, 2011). Apart from different composition, nanomaterials of different morphologies can be used (Erceg *et al.*, 2020).

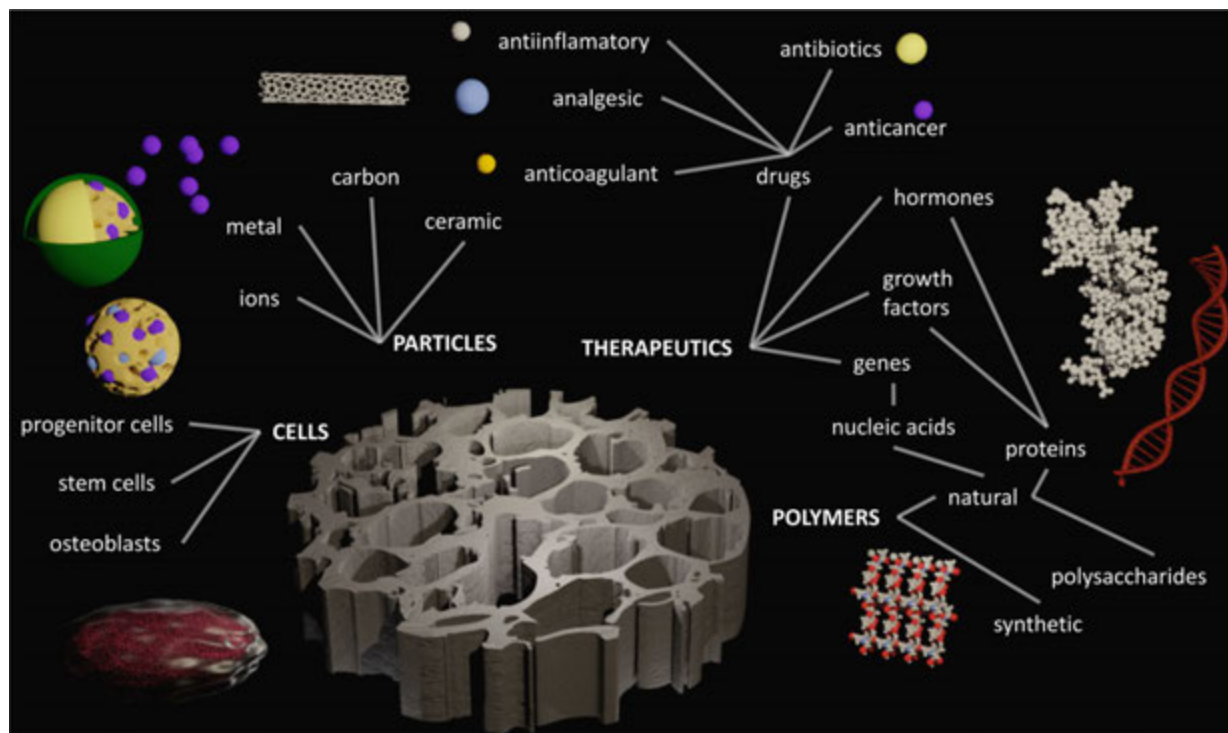


Fig. 5 Schematic representation of substances commonly integrated into bone scaffolds. The main components for integration are diverse particles. From ions and nanoparticles to mesoscale spheres or carbon nanofibers, therapeutics (diverse drugs, hormones, growth factors or genes), polymers (natural or synthetic) and cells (mostly diverse forms of stem or progenitor cells).

Scaffolds With Therapeutics

Drug release scaffolds

Scaffolds can also serve as a structure that can co-deliver substances like drugs, supplements or growth factors. This enables local regulation of pain or reduction of the infection at the site. Delivery of different drugs like bisphosphonates, aspirin, ibuprofen, gentamicin, vancomycin, methotrexate, cisplatin, doxorubicin, gentamicin sulfate, cefoperazone sodium and flomoxef was tested (Habracken *et al.*, 2007; Porter *et al.*, 2009; Rödel *et al.*, 2018). Commonly used carriers are mesoporous silica, silica-based glasses, CaP beads or coatings, injectable CaP, TCP/alginate beads, injectable HA, or gypsum, silicon dioxide, etc. All these materials are used to encapsulate drugs and to prolong their release. Drug release depends on the composition of the inorganic phase, its porosity, specific surface area, topography, degradation rate, etc. (Dorozhkin, 2018b; Rödel *et al.*, 2018). Furthermore, it is possible to utilize glass-ceramics in processes like localized heating aimed to destroy malignant tumorous cells which, in comparison to the classical treatments, have minimal damage to the rest of the body (Wang *et al.*, 2017). However, the homogenous drug loading is a challenge, as is controlling the rate of simultaneous drug release. Common problems are burst release in the first hours or days after the surgery (that could cause overdosage), the release of drugs by both diffusion and degradation (that causes problems with determination of appropriate dosage), degradation of an active ingredient during processing, etc. (Parent *et al.*, 2017). The resorption rate must be comparable with the specific bone regeneration rate, which can spread from a few months up to 2 years (Dorozhkin, 2018b). In the meantime, the scaffold must endure all mechanical stresses that the bone in question is normally enduring.

Growth factors

Growth factors such as bone morphogenetic proteins (BMPs), transforming growth factor (TGF) and insulin growth factor (IGF) were tested in diverse bone defects with good results regarding the accelerated bone defect filling, resorption of the implant and bone remodeling in general (Arcos and Vallet-Regí, 2013; Shi *et al.*, 2020). They also stimulate cell recruitment and differentiation and are currently used in treatments, but not without the concerns (Shi *et al.*, 2020). Observations of long term effects on patients suggest the possibility of some factors like BMPs to produce tumors, immune responses, infections, etc. Therefore, caution with dosage is recommended (Schmidt-Bleek *et al.*, 2016). Loading of growth factor into bioceramics scaffolds can be achieved by physical entrapment and nanoparticle encapsulation (De Witte *et al.*, 2018).

Hormones

Osteoporosis is more common in women after menopause because estradiol activity is lowered. This hormone affects mineral resorption and bone loss, so targeted delivery of estradiol using diverse bone scaffolds improves bone formation (Cinebra *et al.*,

2006; Shi *et al.*, 2020). Similar results were obtained with prostaglandin and parathyroid hormone that both stimulate bone formation but could increase the risk of later cancer development. Mesoporous materials, like mesoporous silicas, are considered as good materials for both hormones and growth factors delivery (Vallet-Regí and Ruiz-Hernández, 2011).

Gene therapy

Gene transfer technology includes application of nucleic acids for therapeutic purposes. Research is focused on RNA interference-based therapy (to replace pathogenic genes) or replacing growth factors/hormones with genes (that will encode for these factors). They are usually based on the release from different polymer matrices or particulate ceramics containing gene vector complexes. For example, a combination of chemically modified mRNA (encoding for BMP-2 protein) and biphasic calcium phosphate granules (Balmayor *et al.*, 2016). Unfortunately, in this stage of research high dosages are required which causes safety and immunogenic concerns (Dang *et al.*, 2018; Shi *et al.*, 2020).

Scaffolds with polymers

Scaffolds with polymers commonly include both natural and synthetic polymers, or their combinations. The most used natural polymers are proteins (collagen, albumin, elastin, silk fibroin, fibronectin, osteocalcin, etc.) and polysaccharides (gelatin, chitosan, alginate, cellulose), while synthetic degradable polymers commonly include polylactic, polyglycolide or poly(lactic-co-glycolic) acid, polycaprolactone and their diverse combinations in a form of copolymers (Bharadwaz and Jayasuriya, 2020; Garg *et al.*, 2012). They can be combined with materials like nanoparticulate CaP or silica-based materials into nanocomposites and serve as injectable nanofillers or part of the scaffold coatings (Bharadwaz and Jayasuriya, 2020).

Proteins like collagen, osteocalcin, sialoprotein, and osteopontin have a good affinity for calcium ions and can interact with HA where they can regulate the formation and growth of the crystals (Shi *et al.*, 2020).

Because of versatility, storage capacity, and good bioactivity of the polymers, the most probable solution to the controlled release of therapeutics will be ceramics scaffolds combined with polymers. With the proper setup of their properties (e.g. porosity, charge, strength, bioactivity, biodegradability or cell adhesion) drug release could be much better regulated (Ghassemi *et al.*, 2018; Polo-Corrales *et al.*, 2014).

Scaffolds with living cells

Novel studies are focused on the implantation of scaffolds with cells (freshly isolated or cultured), implantation of tissues grown in vitro from cells and scaffolds using donor cells, or direct implantation of a scaffold that will simulate body to promote local repair. Nanoparticulate form of bioactive ceramics is popular for these scaffolds because, in that form, they can easily be combined with living cells. The activity of cells can be modulated with the modification of scaffold nanotopography (Zhu *et al.*, 2020). The nanostructures that can be used for better bone remodeling should have following properties: the grains below 100 nm in size, the boundaries of the grains enhance cell adhesion, differentiation and growth. Such nanoceramics have outstanding physical, chemical, and mechanical properties and are easily shaped. This is especially interesting in combination with titanium, silver, aluminum or HA nanoparticles that exhibit antibacterial activity, enhanced adhesion of osteoblasts, and lower the adhesion of fibroblasts (which favor fibrous encapsulation) (Affatato *et al.*, 2006; Wagner *et al.*, 2006; Webster, 2001).

Combining CaPs with different reinforcement agents and cells from the human body could produce material that can satisfy most of the above-listed demands. For example, resorbable CaP scaffolds seeded with cells, or stem cell bi- and tri-culture are of great significance in the regeneration of dental, craniofacial and orthopedic defects in clinical practice (Lin *et al.*, 2019a; Wang *et al.*, 2014).

Scaffolds Which Introduce Stimulus

Materials that can exhibit different physical stimuli that could enhance tissue repair and regeneration are lately coming into the focus.

Graphene and its derivatives (graphene oxide, reduced graphene oxide, carboxyl graphene oxide), carbon nanotubes and quantum dots are non-degradable materials which, in addition to conductivity, possess excellent thermal, mechanical and optical properties. Initially, they were used to enhance mechanical properties, but presently their conductivity is investigated for enhancement of tissue regeneration. However, no conclusive results can be found about their cytotoxicity and their ultimate fate in vivo (Aslankoohi *et al.*, 2019).

Magnetic bioceramics show great potential as devices for bone healing and on-demand release of drugs or biomolecules using ferrimagnetism, ferromagnetism or superparamagnetism (Xu and Gu, 2014). If magnetic mesoporous silica or HA doped $\text{Fe}^{2+}/\text{Fe}^{3+}$ materials are used, the local increase in temperature can be achieved, that will destroy cancerous cells, while producing minimal (and often temporary) damage to surrounding body cells (Drouet *et al.*, 2017; Tampieri *et al.*, 2012).

Implantation of scaffolds can disturb natural signaling pathways due to their rigidity for signal conduction. Piezoelectric materials capable of generating and transferring the signals according to the changes in their environment are emerging as a possible solution (Jacob *et al.*, 2018). Numerous piezoelectric materials are available, while in bone tissue engineering only particulate form of piezoelectric barium titanate, boron nitride or zinc oxide had stimulating effects without significant problems regarding toxicity (Aslankoohi *et al.*, 2019; Jacob *et al.*, 2018).

Conclusion and Future Directions

Bioceramics scaffolds are promising materials for enhancing our abilities to repair bone tissue. A variety of materials and methods available for producing these scaffolds offer a wide range of possibilities in treating rather complex diseases and traumas. For example, the damage caused by cancer can be overwhelming for the organism to cure by itself, but using early detection methods and quick reaction with appropriate medical implants that can simultaneously cure and replace damaged tissue offer new hope to many patients. Several challenges remain to be solved to fully exploit the advantages of bioceramics scaffolds. Extended life expectancy of the population increases the severity of premature implant failure. The problem of resistant bacterial strains significantly affects implantation procedures and the solution for successful infection control still needs to be found. Mechanical properties of ceramics are still an issue, especially for biodegradable materials which require to retain needed mechanical support while being degraded and replaced with the new bone. With further development, trauma patients could have a better recovery rate with less pain and inflammations due to the locally delivered drugs, and even without the need for a second surgery for implant removals.

Exciting new fields where bioceramics scaffolds have high potential are personalized medicine and development of nanoceramics. In personalized medicine living cells are combined with the ceramics scaffolds. Stem cell research in this field has already provided good results in *in vivo* experiments. Nanoceramics research is focused on providing a suitable nanoscale environment for cells to further enhance bone growth with appropriate material for fast bone regeneration.

Constant advances in manufacturing technologies, especially additive manufacturing, are enabling that such advanced materials more successfully reach medical practice.

References

- Abbasi, N., Hamlet, S., Love, R.M., Nguyen, N.-T., 2020. Porous scaffolds for bone regeneration. *J. Sci. Adv. Mater. Devices* 5, 1–9. doi:10.1016/j.jsamd.2020.01.007.
- Affatato, S., Torrecillas, R., Taddei, P., *et al.*, 2006. Advanced nanocomposite materials for orthopaedic applications. I. A long-term *in vitro* wear study of zirconia-toughened alumina. *J. Biomed. Mater. Res. B Appl. Biomater.* 78B, 76–82. doi:10.1002/jbm.b.30462.
- Al Tamami, N., Bawazeer, N., Fieux, M., Zaouche, S., Tringali, S., 2020. Tolerance and safety of 45S5 bioactive glass used in obliteration procedures during middle ear surgery: Preliminary results. *Am. J. Otolaryngol.* 102542. doi:10.1016/j.amjoto.2020.102542.
- Alvarez-Urena, P., Kim, J., Bhattacharyya, S., Ducheyne, P., 2017. Chapter 6.1 – Bioactive Ceramics and Bioactive Ceramic Composite Based Scaffolds ☆. In: Ducheyne, P. (Ed.), *Comprehensive Biomaterials II*. Elsevier, pp. 1–19. doi:10.1016/B978-0-12-803581-8.10136-5.
- Amini, A.R., Laurencin, C.T., Nukavarapu, S.P., 2012. Bone tissue engineering: Recent advances and challenges. *Crit. Rev. Biomed. Eng.* 40, 363–408. doi:10.1615/CritRevBiomedEng.v40.i5.10.
- Arcos, D., Vallet-Regí, M., 2013. Bioceramics for drug delivery. *Acta Mater* 61, 890–911. doi:10.1016/j.actamat.2012.10.039.
- Aslankooi, N., Mondal, D., Rizkalla, A.S., Mequanint, K., 2019. Bone repair and regenerative biomaterials: Towards recapitulating the microenvironment. *Polymers* 11, 1437. doi:10.3390/polym11091437.
- Balmayor, E.R., Geiger, J.P., Koch, C., *et al.*, 2016. Modified mRNA for BMP-2 in combination with biomaterials serves as a transcript-activated matrix for effectively inducing osteogenic pathways in stem cells. *Stem Cells Dev.* 26, 25–34. doi:10.1089/scd.2016.0171.
- Balu, R., Singaravelu, S., Nagiah, N., 2014. Bioceramic nanofibres by electrospinning. *Fibers* 2, 221–239. doi:10.3390/fib2030221.
- Baroli, B., 2009. From natural bone grafts to tissue engineering therapeutics: brainstorming on pharmaceutical formulative requirements and challenges. *J. Pharm. Sci.* 98, 1317–1375. doi:10.1002/jps.21528.
- Bharadwaz, A., Jayasuriya, A.C., 2020. Recent trends in the application of widely used natural and synthetic polymer nanocomposites in bone tissue regeneration. *Mater. Sci. Eng. C* 110, 110698. doi:10.1016/j.msec.2020.110698.
- Bose, S., Fielding, G., Tarafder, S., Bandyopadhyay, A., 2013. Understanding of dopant-induced osteogenesis and angiogenesis in calcium phosphate ceramics. *Trends Biotechnol.* 31, 594–605. doi:10.1016/j.tibtech.2013.06.005.
- Bose, S., Vahabzadeh, S., Ke, D., Bandyopadhyay, A., 2015. Additive Manufacturing of Ceramics. In: Bandyopadhyay, A., Bose, S. (Eds.), *Additive Manufacturing*. CRC Press, pp. 143–184. doi:10.1201/b18893.
- Boskey, A.L., Robey, P.G., 2013. Chapter 6 – The composition of bone. In: Maine, M.D. (Ed.), *Primer on the Metabolic Bone Diseases and Disorders of Mineral Metabolism*. Wiley, pp. 49–58. doi:10.1002/9781118453926.ch6.
- Butscher, A., Bohner, M., Hofmann, S., Gauckler, L., Müller, R., 2011. Structural and material approaches to bone tissue engineering in powder-based three-dimensional printing. *Acta Biomater.* 7, 907–920. doi:10.1016/j.actbio.2010.09.039.
- Canal, C., Ginebra, M.P., 2011. Fibre-reinforced calcium phosphate cements: A review. *J. Mech. Behav. Biomed. Mater.* 4, 1658–1671. doi:10.1016/j.jmbbm.2011.06.023.
- Carlisle, E.R., Fischgrund, J.S., 2009. Chapter 27 – Bone graft and fusion enhancement. In: Errico, T.J., Lonner, B.S., Moulton, A.W. (Eds.), *Surgical Management of Spinal Deformities*. Philadelphia: W.B. Saunders, pp. 433–448. doi:10.1016/B978-141603372-1.50030-5.
- Chen, X., Fan, H., Deng, X., *et al.*, 2018. Scaffold structural microenvironmental cues to guide tissue regeneration in bone tissue applications. *Nanomaterials* 8, 960. doi:10.3390/nano8110960.
- Chocholata, P., Kulda, V., Babuska, V., 2019. Fabrication of scaffolds for bone-tissue regeneration. *Materials* 12, 568. doi:10.3390/ma12040568.
- Cottrill, E., Pennington, Z., Lankipalle, N., *et al.*, 2020. The effect of bioactive glasses on spinal fusion: a cross-disciplinary systematic review and meta-analysis of the preclinical and clinical data. *J. Clin. Neurosci.* 78, 34–46. doi:10.1016/j.jocn.2020.04.035.
- Damien, E., Revell, P.A., 2004. Coralline hydroxyapatite bone graft substitute: A review of experimental studies and biomedical applications. *J. Appl. Biomater. Biomech.* 2, 65–73. [PMID 20803439].
- Dang, M., Saunders, L., Niu, X., Fan, Y., Ma, P.X., 2018. Biomimetic delivery of signals for bone tissue engineering. *Bone Res.* 6, 25. doi:10.1038/s41413-018-0025-8.
- Darus, F., Isa, R.M., Mamat, N., Jaafar, M., 2018. Techniques for fabrication and construction of three-dimensional bioceramic scaffolds: Effect on pores size, porosity and compressive strength. *Ceram. Int.* 44, 18400–18407. doi:10.1016/j.ceramint.2018.07.056.
- De Witte, T.-M., Fratila-Apachitei, L.E., Zadpoor, A.A., Peppas, N.A., 2018. Bone tissue engineering via growth factor delivery: From scaffolds to complex matrices. *Regen. Biomater.* 5, 197–211. doi:10.1093/rb/rby013.
- Dorozhkin, S.V., 2012. *Calcium Orthophosphates: Applications in Nature, Biology, and Medicine*. CRC Press, Taylor & Francis Group.
- Dorozhkin, S.V., 2016. Multiphasic calcium orthophosphate (CaPO₄) bioceramics and their biomedical applications. *Ceram. Int.* 42, 6529–6554. doi:10.1016/j.ceramint.2016.01.062.

- Dorozhkin, S.V., 2018a. Current state of bioceramics. *J. Ceram. Sci. Technol.* 9 (4), 353–370. doi:10.4416/JCST2018-00026.
- Dorozhkin, S.V., 2018b. Chapter 13 – Calcium-orthophosphate-based bioactive ceramics. In: Thomas, S., Balakrishnan, P., Sreekala, M.S. (Eds.), *Fundamental Biomaterials: Ceramics*. Woodhead Publishing Series in Biomaterials. Woodhead Publishing, pp. 297–405. doi:10.1016/B978-0-08-102203-0.00013-5.
- Drnovšek, N., Novak, S., Dragin, U., *et al.*, 2012. Bioactive glass enhances bone ingrowth into the porous titanium coating on orthopaedic implants. *Int. Orthop.* 36, 1739–1745. doi:10.1007/s00264-012-1520-y.
- Drouet, C., Leriche, A., Hampshire, S., *et al.*, 2017. Chapter 2 – Types of ceramics: Material class. In: Palmero, P., Cambier, F., De Barra, E. (Eds.), *Advances in Ceramic Biomaterials*. Woodhead Publishing, pp. 21–82. doi:10.1016/B978-0-08-100881-2.00002-6.
- Erceg, I., Selmani, A., Gajović, A., *et al.*, 2020. Calcium phosphate formation on TiO₂ nanomaterials of different dimensionality. *Colloid. Surf. A: Physicochem. Eng. Asp.* 593, 124615. doi:10.1016/j.colsurfa.2020.124615.
- Farid, S.B.H., 2019. *Bioceramics: For Materials Science and Engineering*. Elsevier.
- Garg, T., Singh, O., Arora, S., Murthy, R., 2012. Scaffold: A novel carrier for cell and drug delivery. *Crit. Rev. Ther. Drug Carrier Syst.* 29, 1–63. doi:10.1615/critrevtherdrugcarriersyst.v29.i1.10.
- Ghassemi, T., Shahroodi, A., Ebrahimzadeh, M.H., *et al.*, 2018. Current concepts in scaffolding for bone tissue engineering. *Arch. Bone Jt. Surg.* 6, 90–99. [PMID: 29600260].
- Gibson, I., Rosen, D.W., Stucker, B., 2010. *Additive Manufacturing Technologies*. Boston, MA: Springer, doi:10.1007/978-1-4419-1120-9.
- Ginebra, M.P., Traykova, T., Planell, J.A., 2006. Calcium phosphate cements as bone drug delivery systems: A review. *J. Control. Release* 113, 102–110. doi:10.1016/j.jconrel.2006.04.007.
- Gittens, R.A., Olivares-Navarrete, R., Schwartz, Z., Boyan, B.D., 2014. Implant osseointegration and the role of microroughness and nanostructures: Lessons for spine implants. *Acta Biomater.* 10, 3363–3371. doi:10.1016/j.actbio.2014.03.037.
- Goto, T., Kojima, T., Iijima, T., *et al.*, 2001. Resorption of synthetic porous hydroxyapatite and replacement by newly formed bone. *J. Orthop. Sci.* 6, 444–447. doi:10.1007/s007760170013.
- Gremillard, L., Tadier, S., 2017. Chapter 1 – Materials for hard tissue applications: An overview. In: Palmero, P., Cambier, F., De Barra, E. (Eds.), *Advances in Ceramic Biomaterials*. Woodhead Publishing, pp. 3–20. doi:10.1016/B978-0-08-100881-2.00001-4.
- Habraken, W.J.E.M., Wolke, J.G.C., Jansen, J.A., 2007. Ceramic composites as matrices and scaffolds for drug delivery in tissue engineering. *Adv. Drug Deliv. Rev.* 59, 234–248. doi:10.1016/j.addr.2007.03.011.
- Hammel, E.C., Ighodaro, O.L.-R., Okoli, O.I., 2014. Processing and properties of advanced porous ceramics: An application based review. *Ceram. Int.* 40, 15351–15370. doi:10.1016/j.ceramint.2014.06.095.
- Hench, L.L., 1991. Bioceramics: From concept to clinic. *J. Am. Ceram. Soc.* 74, 1487–1510. doi:10.1111/j.1151-2916.1991.tb07132.x.
- Jacob, J., More, N., Kalia, K., Kapusetti, G., 2018. Piezoelectric smart biomaterials for bone and cartilage tissue engineering. *Inflamm. Regen.* 38, doi:10.1186/s41232-018-0059-8.
- Karageorgiou, V., Kaplan, D., 2005. Porosity of 3D biomaterial scaffolds and osteogenesis. *Biomaterials* 26, 5474–5491. doi:10.1016/j.biomaterials.2005.02.002.
- Kelly, C.M., Wilkins, R.M., 2004. Treatment of benign bone lesions with an injectable calcium sulfate-based bone graft substitute. *Orthopedics* 27, s131–s135. [PMID: 14763545].
- Kokubo, 2008. Chapter 13 – Bioactive glass-ceramics. In: Kokubo, T. (Ed.), *Bioceramics and Their Clinical Applications*, Woodhead Publishing Series in Biomaterials. Woodhead Publishing, pp. 284–301.
- Kolk, A., Handschel, J., Drescher, W., *et al.*, 2012. Current trends and future perspectives of bone substitute materials – From space holders to innovative biomaterials. *J. Cranio-Maxillofac. Surg.* 40, 706–718. doi:10.1016/j.jcms.2012.01.002.
- Lin, Y., Huang, S., Zou, R., *et al.*, 2019a. Calcium phosphate cement scaffold with stem cell co-culture and prevascularization for dental and craniofacial bone tissue engineering. *Dent. Mater.* 35, 1031–1041. doi:10.1016/j.dental.2019.04.009.
- Ma, H., Feng, C., Chang, J., Wu, C., 2018. 3D-printed bioceramic scaffolds: from bone tissue engineering to tumor therapy. *Acta Biomater.* 79, 37–59. doi:10.1016/j.actbio.2018.08.026.
- O'Brien, F.J., 2011. Biomaterials & scaffolds for tissue engineering. *Mater. Today* 14, 88–95. doi:10.1016/S1369-7021(11)70058-X.
- Ott, S.M., 2017. Chapter 2 – Bone biology and effects of pharmaceutical intervention on bone quality. In: Bose, S., Bandyopadhyay, A. (Eds.), *Materials for Bone Disorders*. Academic Press, pp. 29–82. doi:10.1016/B978-0-12-802792-9.00002-1.
- Parent, M., Baradari, H., Champion, E., Damia, C., Viana-Trecant, M., 2017. Design of calcium phosphate ceramics for drug delivery applications in bone diseases: A review of the parameters affecting the loading and release of the therapeutic substance. *J. Control. Release* 252, 1–17. doi:10.1016/j.jconrel.2017.02.012.
- Parra-Cabrera, C., Achille, C., Kuhn, S., Ameloot, R., 2018. 3D printing in chemical engineering and catalytic technology: Structured catalysts, mixers and reactors. *Chem. Soc. Rev.* 47, 209–230. doi:10.1039/C7CS00631D.
- Polo-Corrales, L., Latorre-Esteves, M., Ramirez-Vick, J.E., 2014. Scaffold design for bone regeneration. *J. Nanosci. Nanotechnol.* 14, 15–56. doi:10.1166/jnn.2014.9127.
- Porter, J.R., Ruckh, T.T., Popat, K.C., 2009. Bone tissue engineering: A review in bone biomimetics and drug delivery strategies. *Biotechnol. Prog.* 25, 1539–1560. doi:10.1002/btpr.246.
- Raucci, M.G., Giugliano, D., Ambrosio, L., 2016. Fundamental properties of bioceramics and biocomposites. In: Antoniac, I.V. (Ed.), *Handbook of Bioceramics and Biocomposites*. Cham: Springer International Publishing, pp. 35–58. doi:10.1007/978-3-319-12460-5_3.
- Rödel, M., Meininger, S., Groll, J., Gbureck, U., 2018. Chapter 7 – Bioceramics as drug delivery systems. In: Thomas, S., Balakrishnan, P., Sreekala, M.S. (Eds.), *Fundamental Biomaterials: Ceramics*. Woodhead Publishing, pp. 153–194. doi:10.1016/B978-0-08-102203-0.00007-X.
- Roseti, L., Parisi, V., Petretta, M., *et al.*, 2017. Scaffolds for Bone. *Tissue Eng.: State Art New Perspect. Mater. Sci. Eng. C* 78, 1246–1262. doi:10.1016/j.msec.2017.05.017.
- Roy, M., Bandyopadhyay, A., Bose, S., 2017. Ceramics in bone grafts and coated implants. In: Bose, S., Bandyopadhyay, A. (Eds.), *Materials for Bone Disorders*. Elsevier, pp. 265–314. doi:10.1016/B978-0-12-802792-9.00006-9.
- Schmidt-Bleek, K., Willie, B.M., Schwabe, P., Seemann, P., Duda, G.N., 2016. BMPs in bone regeneration: Less is more effective, a paradigm-shift. *Cytokine Growth Factor Rev.* 27, 141–148. doi:10.1016/j.cytogfr.2015.11.006.
- Shanmugam, K., Sahadevan, R., 2018. Chapter1 – Bioceramics — An introductory overview. In: Thomas, S., Balakrishnan, P., Sreekala, M.S. (Eds.), *Fundamental Biomaterials: Ceramics*. Woodhead Publishing, pp. 1–46. doi:10.1016/B978-0-08-102203-0.00001-9.
- Shegarfi, H., Reikeras, O., 2009. Review article: Bone transplantation and immune response. *J. Orthop. Surg.* 17, 206–211. doi:10.1177/230949900901700218.
- Shi, C., Wu, T., He, Y., Zhang, Y., Fu, D., 2020. Recent advances in bone-targeted therapy. *Pharmacol. Ther.* 207, 107473. doi:10.1016/j.pharmthera.2020.107473.
- Tampieri, A., D'Alessandro, T., Sandri, M., *et al.*, 2012. Intrinsic magnetism and hyperthermia in bioactive Fe-doped hydroxyapatite. *Acta Biomater.* 8, 843–851. doi:10.1016/j.actbio.2011.09.032.
- Thavornyutikarn, B., Chantarapanich, N., Sitthiseripatip, K., Thouas, G.A., Chen, Q., 2014. Bone tissue engineering scaffolding: computer-aided scaffolding techniques. *Prog. Biomater.* 3, 61–102. doi:10.1007/s40204-014-0026-7.
- Vallet-Regí, M., Ruiz-Hernández, E., 2011. Bioceramics: From bone regeneration to cancer nanomedicine. *Adv. Mater.* 23, 5177–5218. doi:10.1002/adma.201101586.
- Wagner, V., Dullaart, A., Bock, A.-K., Zweck, A., 2006. The emerging nanomedicine landscape. *Nat. Biotechnol.* 24, 1211–1217. doi:10.1038/nbt1006-1211.
- Wang, P., Zhao, L., Chen, W., *et al.*, 2014. Stem cells and calcium phosphate cement scaffolds for bone regeneration. *J. Dent. Res.* 93, 618–625. doi:10.1177/0022034514534689.
- Wang, X., Li, T., Ma, H., *et al.*, 2017. A 3D-printed scaffold with MoS₂ nanosheets for tumor therapy and tissue regeneration. *NPG Asia Mater.* 9, e376. doi:10.1038/am.2017.47.
- Webster, T.J., 2001. Nanophase Ceramics: The Future Orthopedic and Dental Implant Material. In *Advances in Chemical Engineering*. Academic Press, pp. 125–166.

- Weiner, S., Wagner, H.D., 1998. The material bone: Structure-mechanical function relations. *Annu. Rev. Mater. Sci.* 28, 271–298. doi:10.1146/annurev.matsci.28.1.271.
- Wu, S., Liu, X., Yeung, K.W.K., Liu, C., Yang, X., 2014. Biomimetic porous scaffolds for bone tissue engineering. *Mater. Sci. Eng. R Rep.* 80, 1–36. doi:10.1016/j.mser.2014.04.001.
- Xiao, Z., Wang, Z., Yang, B., Zhang, X., 2013. Bioceramic scaffolds. In: Ma, P.X. (Ed.), *Biomaterials and Regenerative Medicine*. Cambridge: Cambridge University Press, pp. 151–182. doi:10.1017/CBO9780511997839.013.
- Xu, H.-Y., Gu, N., 2014. Magnetic responsive scaffolds and magnetic fields in bone repair and regeneration. *Front. Mater. Sci.* 8, 20–31. doi:10.1007/s11706-014-0232-1.
- Yang, J., Yu, J., Huang, Y., 2011. Recent developments in gelcasting of ceramics. *J. Eur. Ceram. Soc.* 31, 2569–2591. doi:10.1016/j.jeurceramsoc.2010.12.035.
- Yu, X., Tang, X., Gohil, S.V., Laurencin, C.T., 2015. Biomaterials for bone regenerative engineering. *Adv. Healthc. Mater.* 4, 1268–1285. doi:10.1002/adhm.201400760.
- Zhang, H., Yang, L., Yang, X.-G., *et al.*, 2019. Demineralized bone matrix carriers and their clinical applications: An Overview. *Orthop. Surg.* 11, 725–737. doi:10.1111/os.12509.
- Zhu, L., Luo, D., Liu, Y., 2020. Effect of the nano/microscale structure of biomaterial scaffolds on bone regeneration. *Int. J. Oral Sci.* 12, 1–15. doi:10.1038/s41368-020-0073-y.

Further Reading

- Almirall, A., Larrecq, G., Delgado, J.A., *et al.*, 2004. Fabrication of low temperature macroporous hydroxyapatite scaffolds by foaming and hydrolysis of an α -TCP paste. *Biomaterials* 25, 3671–3680. doi:10.1016/j.biomaterials.2003.10.066.
- Datta, P., Ozbolat, V., Ayan, B., Dhawan, A., Ozbolat, I.T., 2017. Bone tissue bioprinting for craniofacial reconstruction. *Biotechnol. Bioeng.* 114, 2424–2431. doi:10.1002/bit.26349.
- Descamps, M., Hornez, J.C., Leriche, A., 2009. Manufacture of hydroxyapatite beads for medical applications. *J. Eur. Ceram. Soc.* 29, 369–375. doi:10.1016/j.jeurceramsoc.2008.06.008.
- Duan, B., Wang, M., Zhou, W.Y., *et al.*, 2010. Three-dimensional nanocomposite scaffolds fabricated via selective laser sintering for bone tissue engineering. *Acta Biomater.* 6, 4495–4505. doi:10.1016/j.actbio.2010.06.024.
- Fu, Q., Saiz, E., Tomsia, A.P., 2011. Direct ink writing of highly porous and strong glass scaffolds for load-bearing bone defects repair and regeneration. *Acta Biomater.* 7, 3547–3554. doi:10.1016/j.actbio.2011.06.030.
- Mehrabanian, M., Nasr-Esfahani, M., 2011. HA/nylon 6,6 porous scaffolds fabricated by salt-leaching/solvent casting technique: Effect of nano-sized filler content on scaffold properties. *Int. J. Nanomed.* 2011, 1651–1659. doi:10.2147/IJN.S21203.
- Papynov, E.K., Shichalin, O.O., Apanasevich, V.I., *et al.*, 2019. Synthetic CaSiO_3 sol-gel powder and SPS ceramic derivatives: “In vivo” toxicity assessment. *Prog. Nat. Sci. Mater. Int.* 29, 569–575. doi:10.1016/j.pnsc.2019.07.004.
- Ratner, B.D., Hoffman, A.S., Schoen, F.J., Lemons, J.E. (Eds.), 2008. *Biomaterials science: An introduction to materials in medicine*, Second ed. Elsevier, Academic Press.
- Varanasi, V.G., Veltin, M.F., Odatsu, T., *et al.*, 2017. Chapter 9 – Surface modifications and surface characterization of biomaterials used in bone healing. In: Bose, S., Bandyopadhyay, A. (Eds.), *Materials for Bone Disorders*. Academic Press, pp. 405–452. doi:10.1016/B978-0-12-802792-9.00009-4.
- Warnke, P.H., Seitz, H., Warnke, F., *et al.*, 2010. Ceramic scaffolds produced by computer-assisted 3D printing and sintering: Characterization and biocompatibility investigations. *J. Biomed. Mater. Res. B Appl. Biomater.* 93B, 212–217. doi:10.1002/jbm.b.31577.
- Wegst, U.G.K., Bai, H., Saiz, E., Tomsia, A.P., Ritchie, R.O., 2015. Bioinspired structural materials. *Nat. Mater.* 14, 23–36. doi:10.1038/nmat4089.
- Wei, Y., Zhao, D., Cao, Q., *et al.*, 2020. Stereolithography-based additive manufacturing of high-performance osteoinductive calcium phosphate ceramics by a digital light-processing system. *ACS Biomater. Sci. Eng.* 6, 1787–1797. doi:10.1021/acsbiomaterials.9b01663.
- Zhang, R., Ma, P.X., 1999. Poly(α -hydroxyl acids)/hydroxyapatite porous composites for bone-tissue engineering. I. Preparation and morphology. *J. Biomed. Mater. Res.* 44, 446–455. doi:10.1002/(sici)1097-4636(19990315).
- Zhou, Y., Hutmacher, D.W., Varawan, S.-L., Lim, T.M., 2007. In vitro bone engineering based on polycaprolactone and polycaprolactone–tricalcium phosphate composites. *Polym. Int.* 56, 333–342. doi:10.1002/pi.2138.

Advanced Processes for the Design of Customized Ceramic Medical Devices

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Introduction

Various materials have been used to treat musculoskeletal deficiencies for more than 50,000 years of human existence. The early ones were aesthetic or functional devices designed to repair cranial injuries, replace teeth or limbs (Pietrzak, 2008). The first known ceramic medical device could refer to a toe prosthesis worn by a 3000-year-old Egyptian woman (Wagle, 1994). Today, autograft is considered as the gold standard in bone surgery. But, its harvesting can induce medical complications such as pain or infections (Heary *et al.*, 2002) and it may even be impossible due to limited available amounts, possibly not sufficient for defect filling, or insufficient quality. Besides, the architectural design, shape and size, of such implants are often unsatisfying because it cannot be adapted to the bone defect. To overcome these drawbacks and limitations, there is a growing demand for synthetic bone graft substitutes that may be customized on demand. Among the materials used, a first generation of biocompatible ceramic for medical devices appeared from the early 1960s, mainly made of alumina and/or zirconia. These ceramics present a high chemical and biological inertia associated with specific properties such as high strength, hardness and wear, and friction resistance. They can be used as load-bearing implants. Twenty years later, a second generation of medical ceramics arose, essentially made of calcium phosphates, which interacts with the surrounding living tissues and presents superior biological properties of bioactivity or bioresorbability. These two generations of ceramics are commonly used in a wide range of applications for bone tissue repair in orthopedics, maxillofacial surgery and dentistry. Nevertheless, there is an increasing need for advanced customized devices to treat various osseous pathologies for which there is still no fully satisfactory solution at present. This is particularly the case of the repair or reconstruction of large bone defects resulting for trauma, infectious diseases, cancer, or malformations.

Thus, ceramics are the subject of continuous efforts of research and development to extend their medical applications. The primary role of ceramic bone graft substitutes is to restore the injured function: food grinding, locomotion, protection of vital organs, etc. In addition to this fundamental role, two kinds of customizations can be highlighted.

- (1) The bone repair and regeneration itself, which requires the production of 3D scaffolds with complex tailored architecture. This architecture must include a network of interconnected pores at the microscopic scale (size < 1 mm) allowing the scaffold colonization by newly formed bone tissues. This approach directs to bone tissue engineering and regenerative medicine.
- (2) In some situations, aesthetic criteria have to be taken into account, such as in dental applications or for cranio-maxillofacial implants, for which the macroscopic design of the prosthesis has to be defined according to an individualized approach, which directs to personalized medicine.

Therefore, a multiscale approach to design advanced ceramic devices is required. To this end, emerging computer aided design and computer aided manufacturing (CAD/CAM) of ceramic parts appears to be the only technologies that can be implemented (Champion *et al.*, 2017). Conventional ceramic processing techniques suffer from limitation or inability to produce near-net-shape parts with highly complex design. Thus, the development of customized ceramics is a great challenge to provide new high-performance medical ceramics and extend their fields of applications to improve healthcare of populations. This chapter focuses on the main approaches implemented for the shaping of such advanced bioceramic devices.

Digital Manufacturing Processes: Towards Automization of Customized Fabrication

Digital manufacturing systems have been developed from the early 1950s for aerospace and automotive applications. Developments in the biomedical field began during the 1980s. CAD/CAM of customized ceramic devices involves three fundamental steps (Fig. 1): (1) acquisition of patient images of the pathological tissue using various imaging or scanning technologies (e.g., optical images, magnetic resonance imaging, computed tomography...), (2) transformation of images in digital data using a CAD software allowing 3D reconstruction and manipulation of data to simulate the medical device and set up of a digital file (e.g., Standard Tessellation Language – STL – file), to order the manufacturing machine, (3) shaping of the ceramic part by CAM using the processed data.

CAD/CAM can be applied to quite any ceramic part production using either subtractive machining (SM) or additive manufacturing (AM) technologies. Subtractive manufacturing technologies are based on the fabrication of a part by removing matter from bulk material. They have been widely used to produce metal or polymer parts and much less so for ceramic ones, mainly because of their high brittleness. Since the 1980s, new technologies of additive manufacturing appear. AM, in opposition to SM, is a process of joining materials to make parts from 3D model data, usually layer upon layer (ISO/ASTM, 2015). AM technologies were also developed initially to produce metal or polymers prototypes or parts. Some of these AM technologies, detailed above, have been adapted to shape three-dimensional ceramic parts from those set up for polymers or metals (Chartier *et al.*, 2015). The main subtractive and additive digital manufacturing technologies are summarized in Fig. 2.

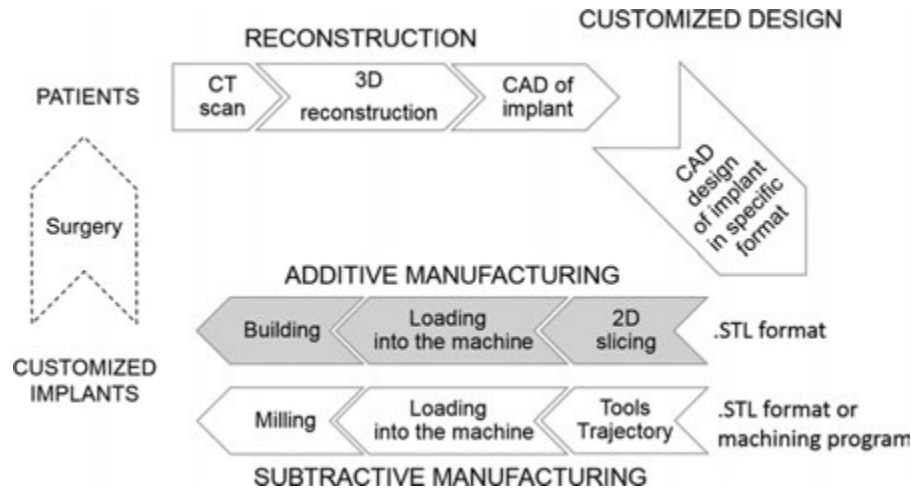


Fig. 1 Flowchart of CAD/CAM of a ceramic medical device.

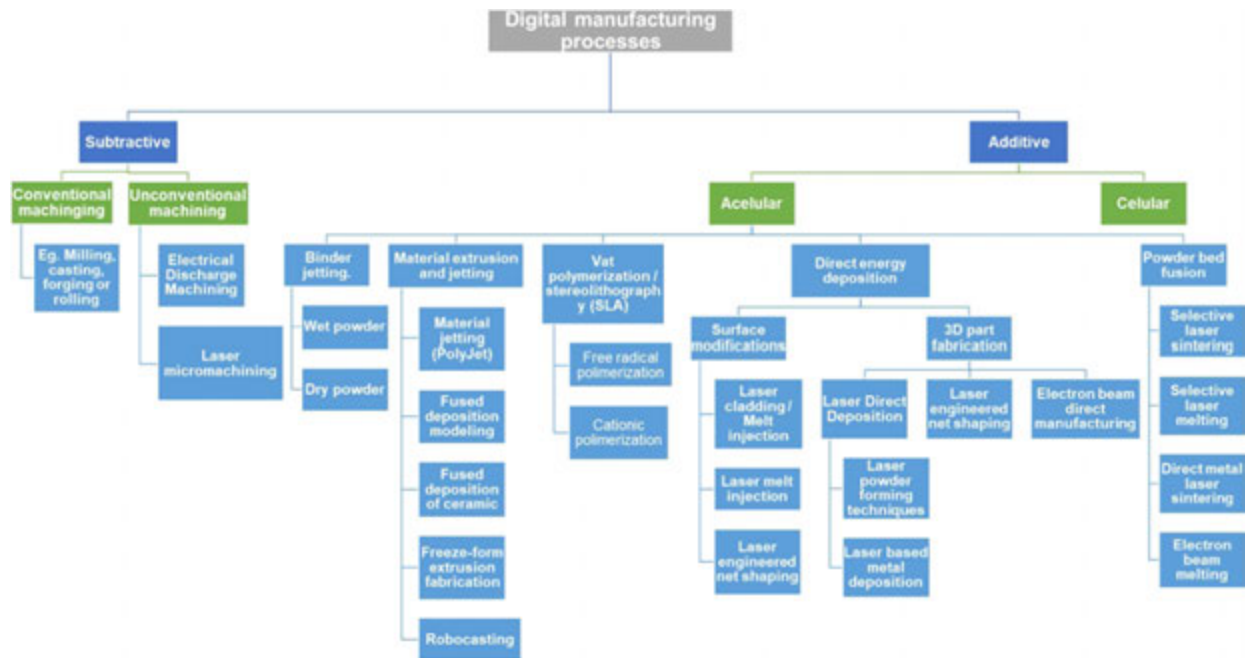


Fig. 2 Main manufacturing technologies. Reproduced from Galante, R., Figueiredo-Pina, C.G., Serro, A.P., 2019. Additive manufacturing of ceramics for dental applications: A review. Dent. Mater. 35, 825–846. Copyright © 2019, with permission from Elsevier.

In the medical field, the use of SM to shape ceramic parts is almost restricted to the dental field. AM is more generally investigated and applied in all areas of bone surgery, including orthopedics and maxillo-facial surgery. This chapter will be more specifically devoted to these AM technologies for the processing of ceramic medical devices. A very short focus will be dedicated to SM and AM for dental applications.

Four main AM technologies implementing CAD/CAM approach can be used to produce complex 3D ceramic parts (Chartier *et al.*, 2015). They have become of an increasing interest due to the wide possibilities they offer for the on-demand fabrication of customized implants for bone repair or scaffolds for the emerging bone tissue engineering. These technologies are particularly adapted to the rapid production of devices for personalized medicine. Thus, the contribution of the biomedical field to AM applications is strong with about 17% share in 2016 (Javaid and Haleem, 2018).

Whatever the AM technologies, the use of a STL file format, defined as a "file format for model data describing the surface geometry of an object as a tessellation of triangles used to communicate 3D geometries to machines in order to build physical parts" (ISO/ASTM, 2015), is required in order to facetize the CAD model so that it can be processed by the digital tools dedicated to additive manufacturing (Chartier *et al.*, 2018). The CAD design of the implant is sliced into 2D layers of the desired thickness, then imported into the additive manufacturing system. Finally, implants or scaffold with patient-specific geometries and/or

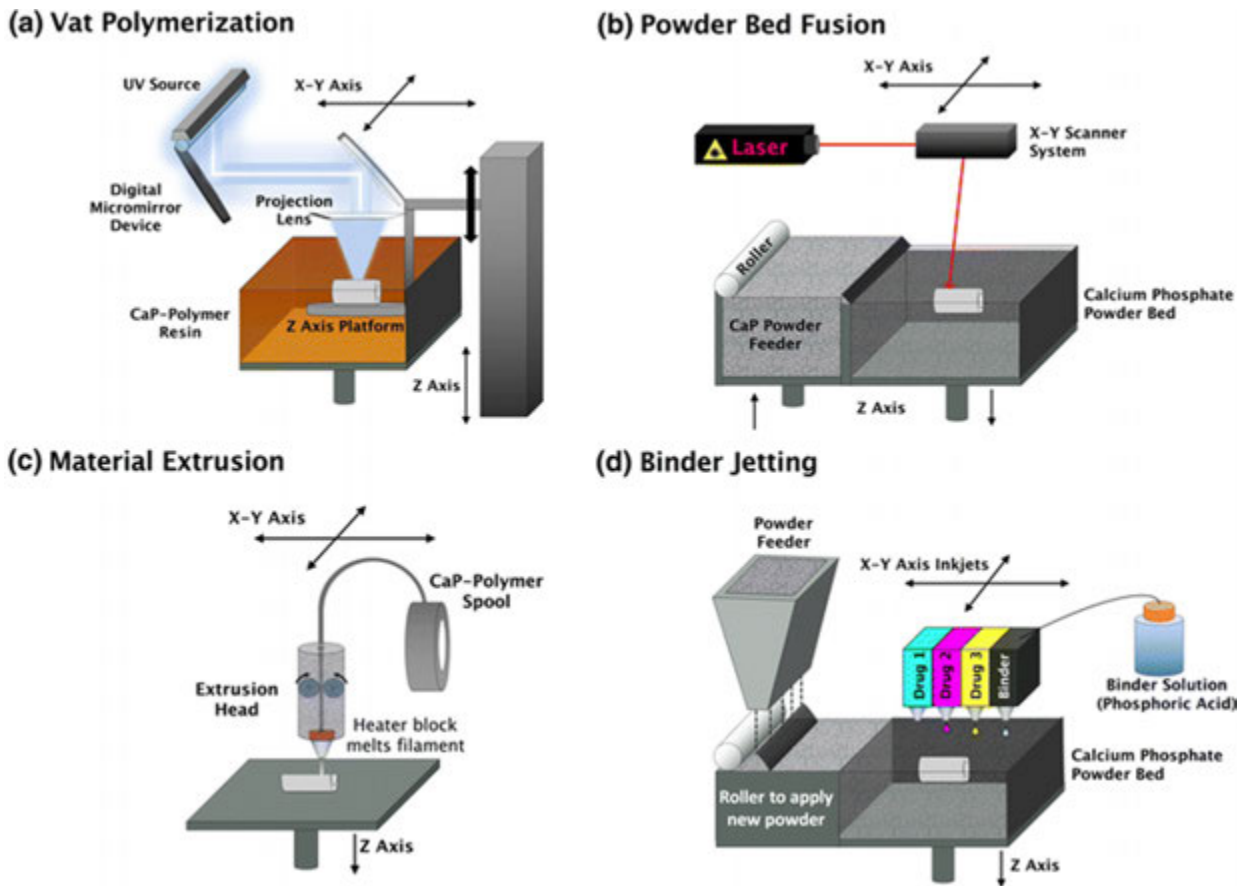


Fig. 3 Schematic depiction of the major AM technologies used to produce customized ceramic medical devices. Reproduced from Trombetta, R., Inzana, J.A., Schwarz, E.M., Kates S.L., Awad, H.A., 2017. 3D printing of calcium phosphate ceramics for bone tissue engineering and drug delivery. *Ann. Biomed. Eng.* 45, 23–44. Copyright © 2016, with permission of Springer Nature.

controlled multi-scale porosity are shaped layer-by-layer. The AM technologies used, for ceramic parts shaping are detailed in **Fig. 3**. They are classified in four categories according to the feedstock and the working principle: stereolithography (SLA) or vat photopolymerization, selective laser sintering (SLS) or powder bed fusion, robocasting (RB) or material extrusion and three-dimensional printing (3DP) or binder jetting (Brunello *et al.*, 2016; Champion *et al.*, 2017; Huttmacher *et al.*, 2004; Melchels *et al.*, 2010; Mota *et al.*, 2015; Trombetta *et al.*, 2017; Zocca *et al.*, 2015).

The resolution that can be achieved with these different AM technologies is superior to 500 μm , stereolithography having the best resolution (**Fig. 4**). This makes possible the achievement of personalized implants with sufficient dimensional precision but also of scaffolds containing pores with typical size of about 500 μm to allow new bone tissue ingrowth in the porous network of the scaffold.

Customized Bone Graft Substitutes and Scaffolds for Bone Tissue Engineering

A brief overview of the four most commonly used AM technologies, i.e., SLA, SLS, RB, and 3DP, is described hereafter and examples of bioceramic implants or scaffolds are provided. For each technology, illustrations of recent advances in printed bioceramic devices and their targeted medical applications are listed in **Table 1**. For further reading, a brief review, not reproduced here, listing a table of 40 chronologically arranged primary applications of additive manufacturing as used for medical purposes can be found elsewhere (Javaid and Haleem, 2018).

Vat Polymerization

Vat polymerization, also known as "stereolithography" (SLA), is an AM process based on the photopolymerization of selected areas of a photo-curable ceramic suspension (i.e., containing ceramic powder and a mixture of photosensitive monomers), previously spread on a building platform by way of a scraper, by applying a low-power ultra-violet (UV) light source or a laser beam (Chartier *et al.*, 2015). Once a layer of suspension exposed to beam becomes hardened according to the geometric patterns defined by the 2D slices of the CAD file, the subsequent layers are sequentially cured and linked together to form a solid green part.

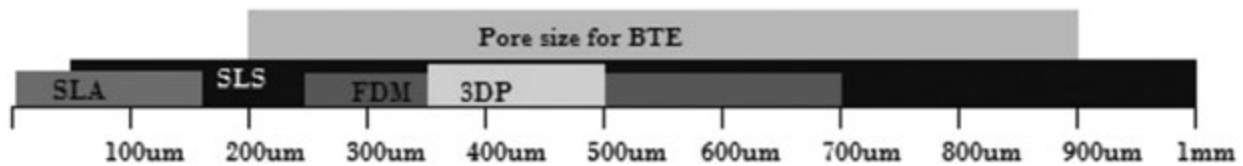


Fig. 4 Comparison of resolution ranges. Reproduced from Moreno, A.P.M., Vrech, S.M., Sanchez, M.A., Rodriguez, A.P., 2019. Advances in additive manufacturing for bone tissue engineering scaffolds. *Mater. Sci. Eng. C* 100, 631–644. Copyright © 2019, with permission of Elsevier.

Table 1 Additive manufacturing technologies, materials and medical applications

AM techniques	Materials	References	Applications
Vat polymerization	HA	(Brie <i>et al.</i> , 2013)	Craniofacial surgery: large bone defects (more than 25 cm ²)
	Silicon substituted HA	(Lasgorceix <i>et al.</i> , 2016)	Bone substitute
Powder bed fusion	BCP (biphasic calcium phosphate)	(Shuai <i>et al.</i> , 2013)	Tissue engineering
	PEEK (poly(ether-ether-ketone)/HA composite	(Tan <i>et al.</i> , 2003)	
	Functional graded scaffolds of HDPE (high-density polyethylene)/HA	(Salmoria <i>et al.</i> , 2013)	
	PCL (poly-ε-caprolactone)/HA scaffolds	(Knutson <i>et al.</i> , 2015)	Spinal surgery: cervical interbody fusion cage
		(Kang <i>et al.</i> , 2013)	Spinal surgery: lumbar interbody fusion cage
		(Eosoly <i>et al.</i> , 2010)	Tissue engineering
Material extrusion	PVA (polyvinyl alcohol)/HA composite	(Wiria <i>et al.</i> , 2007)	Tissue engineering
	Al ₂ O ₃	(Chua <i>et al.</i> , 2004)	
		(Tang <i>et al.</i> , 2011)	
	HA	(Dellinger <i>et al.</i> , 2007)	Orthopaedic
		(Simon <i>et al.</i> , 2007)	
	TCP (tricalcium phosphate)	(Michna <i>et al.</i> , 2005)	Orthopaedic
Binder jetting		(Miranda <i>et al.</i> , 2006)	
		(Martinez-Vázquez <i>et al.</i> , 2010)	
	HA	(Leukers <i>et al.</i> , 2005; Seitz <i>et al.</i> , 2005; Warne <i>et al.</i> , 2010)	Bone tissue engineering
		(Fierz <i>et al.</i> , 2008)	
		(Irsen <i>et al.</i> , 2006)	
	TCP doped with ZnO and SiO ₂	(Fielding <i>et al.</i> , 2012)	Orthopaedic surgery: tibial cage
	TCP	(Tarafder <i>et al.</i> , 2013)	
		(Barralet <i>et al.</i> , 2009; Gbureck <i>et al.</i> , 2007)	
		(Castilho <i>et al.</i> , 2017)	
	BCP (biphasic calcium phosphate)	(Castilho <i>et al.</i> , 2014)	Bone tissue engineering
	Functional graded scaffolds of Al ₂ O ₃ /Y-TZP	(Gingter <i>et al.</i> , 2015)	

The consolidated part thus shaped, unpolymerized suspension is removed and further thermal treatments of debinding and sintering are required to obtain a dense ceramic part.

The accuracy of SLA directly relates to the beam size. But, a highly focused beam that has to scan the surface to be polymerized on each layer would increase significantly the processing time so that scanning methods generally use beam larger than 100 µm in diameter. Such a resolution is sufficient to produce customized devices at the macroscopic scale to match the defect size and individualized aesthetic criteria but lacks of precision to develop scaffolds which porous architecture must be tailored at the microscopic scale. To overcome this limitation, integral microstereolithography (µSLA) method, derived from stereolithography, can be advantageously implemented (Bertsch *et al.*, 2003; Chartier *et al.*, 2015). In this case, the surface that must be polymerized can be integrally irradiated by a UV light that passes through a dynamic mask produced by a digital micro-mirror device (DMD) and reproducing the 2D pattern of the CAD slice. This method allows to increase the resolution without time consuming consequence.

Applications

The possibilities for using SLA method have particularly emerged for biomedical applications (Melchels *et al.*, 2010) but it is still mainly focused on polymer models fabrication (D'Urso *et al.*, 2000; Provaggi *et al.*, 2017; Sodian *et al.*, 2002). Indeed, direct shaping of ceramic parts by vat photopolymerization remains a difficulty because it requires specific suspension formulation containing high amount of ceramic powder and having specific rheological behaviour. The scattering of incident photons of the ceramic particles

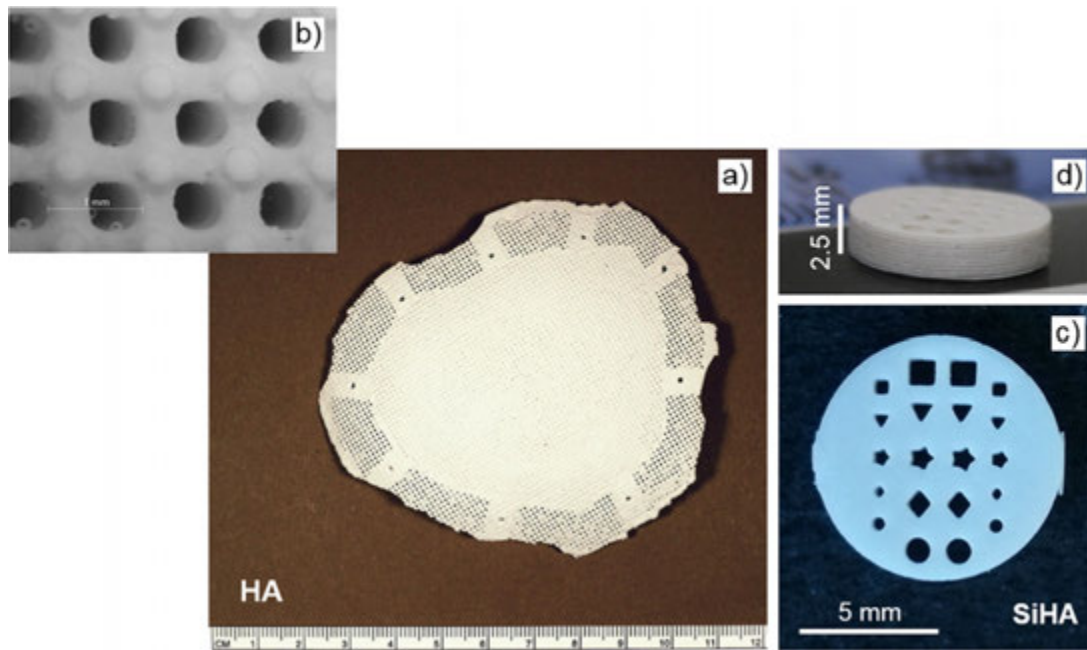


Fig. 5 HA cranial implant with macro-porous areas located at the periphery up to about 1 cm shaped by SLA: (a) Overview, (b) zoom on the macro-porosity. Silicon substituted hydroxyapatite scaffolds shaped by μ SLA: (c) Top view and (d) Side view. Reproduced from: (a) and (b) Brie, J., Chartier, T., Chaput, C., *et al.*, 2013. A new custom made bioceramic implant for the repair of large and complex craniofacial bone defects. *J. Craniomaxillofac. Surg.* 41, 403–407. Copyright © 2013, with permission from Elsevier. (c) and (d) Magnaudeix, A., Usseglio, J., Lasgorceix, M., *et al.*, 2016. Quantitative analysis of vascular colonisation and angio-conduction in porous silicon-substituted hydroxyapatite with various pore shapes in a chick chorioallantoic membrane (CAM) model. *Acta Biomater.* 38, 179–189. doi:10.1016/j.actbio.2016.04.039. Copyright © 2016, with permission from Elsevier.

reduces the resolution. To overcome these difficulties linked to the presence of a high amount of ceramic particles, indirect AM can be implemented. The approach is to shape a “negative” sacrificial polymer mould of the ceramic part, usually by SLA or 3DP, and to cast the ceramic suspension in this mould. Further heat treatment to burn the mould and sinter the ceramic part is applied (Skoog *et al.*, 2014; Charbonnier *et al.*, 2016; Chu *et al.*, 2001). Nevertheless, vat polymerization has been the first implemented AM to produce directly commercially available calcium phosphate bioceramic devices by for bone repair. Example of large craniofacial implants made in hydroxyapatite is given in Fig. 5. Such implants are produced using CAD/CAM from patient scanner (Brie *et al.*, 2013). Their “lace-like” periphery allows to match the bone defect and to have a close contact with the native bone tissue of the patient. One of the major difficulties in the production of large size and complex shape devices is to control and take account of the deformations and shrinkages that will occur during the post-sintering of the part in order to design and shape the green part at the required dimensions. Additional cylindrical macropores (Fig. 5(b)) or about 500 μ m in diameter are produced on the periphery of the implant, while the implant core is much thicker and fully dense to preserve good mechanical properties on the long term. After implantation, these macropores are colonized by newly formed bone, which results in a perfect osseointegration of the implant.

Concerning these macropores, reaching a high resolution to design their geometry is all the more important because cell behaviour is known to depend of the surface topography of the scaffold through curvature driven growth (Bidan *et al.*, 2013). Following the works of Bidan *et al.* (2013) on the influence of surface curvature, various scaffold designs have being investigated including graded porosity (Petit *et al.*, 2017), or different pore shapes and hierarchical structures (Guyot *et al.*, 2014; Gariboldi and Best, 2015; Ma *et al.*, 2018). A reliable production of model scaffolds by μ SLA with high dimensional resolution that takes account of the phenomenon of overcure due to light scattering and of the shrinkage of ceramics during post-sintering has been developed (Lasgorceix *et al.*, 2016). It permits to reach a dimensional precision of about 20 μ m and the design of pores with complex geometries (Fig. 5(c) and (d)). Investigation of bone cell colonization and vascularization of these macropores showed that the geometry of pore cross-section affected greatly the biological behaviour (Magnaudeix *et al.*, 2016; Rüdrieh *et al.*, 2019). Concave surfaces and angles associated to triangular or rhombus cross-sections greatly enhanced bone cell colonization, vascularization and blood vessels guidance (Fig. 6). Comparatively, convex angles or circular geometries were much lesser colonized and square cross-sections were the worse probably due to their long flat surfaces.

Powder Bed Fusion

Powder bed fusion is defined, in ISO/ASTM (2015) standard, as an AM process in which thermal energy selectively fuses regions of a powder bed. Among powder bed fusion category, Selective Laser Sintering (acronym SLS) process is the most widely used

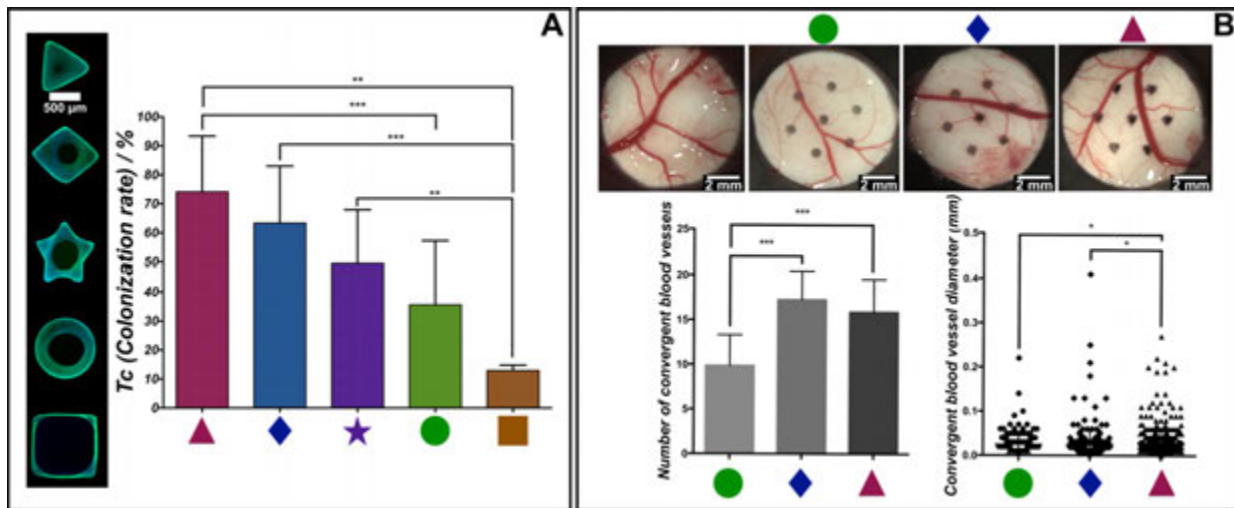


Fig. 6 (A) In vitro colonization of Si-HA scaffold macropores by MC3T3-E1 pre-osteoblast cells after 7 days, (B) Ex ovo analysis of blood vessel colonization in Si-HA scaffolds. (A) Adapted from Magnaudeix, A., Usseglio, J., Lasgorceix, M., *et al.*, 2016. Quantitative analysis of vascular colonisation and angio-conduction in porous silicon-substituted hydroxyapatite with various pore shapes in a chick chorioallantoic membrane (CAM) model. *Acta Biomater.* 38, 179–189. doi:10.1016/j.actbio.2016.04.039. Copyright © 2019, with permission of Elsevier. (B) Rüdrieh, U., Lasgorceix, M., Champion, E., *et al.*, 2019. Pre-osteoblast cell colonization of porous silicon substituted hydroxyapatite bioceramics: Influence of microporosity and macropore design. *Mat. Sci. Eng. C.* 97, 510–528. Copyright © 2016, with permission from Elsevier.

for developing bioceramic scaffolds. SLS is based on the formation of a ceramic part by applying a heating source, usually Nd:YAG or CO₂ laser beam with a wavelength suitable for the chemical composition of the raw material (Ferrage *et al.*, 2017), on selected areas of ceramic powder bed, previously spread on a building platform through a roller, to build each layer by sintering. The local powder densification can be done by directly sintering the ceramic powder. However, due to the low adsorption of ceramic materials at the wavelength of classical laser sources, SLS is more frequent performed on a blend of the ceramic powder with a binder phase which is melted by the laser source. The ceramic parts thus shaped, the unbound powder is removed and a post-consolidation process of sintering at high temperature is required to achieve fully densified ceramic devices.

Applications

Concerning bioceramics, only some works report the use of an experimental SLS system to fabricate bioceramic devices made of the most used ceramic materials: zirconia, alumina (Ferrage *et al.*, 2017) or hydroxyapatite (Cruz *et al.*, 2005) or biphasic calcium phosphate (BCP) (Shuai *et al.*, 2013). The low number of available studies can be explained by the challenging to fuse ceramic particles together by a laser beam. In fact, as mentioned above the use of a thermoplastic polymer functioning as a binder material is suggested to able the ceramic powder fusion (Duan *et al.*, 2010; Eosoly *et al.*, 2010). Barlow and Vail (1994) have also patented a shaping method based on an indirect SLS technique to produce ceramics parts from polymer-bound alumina. This alternative, called iSLS for indirect SLS (Deckers *et al.*, 2014) consists of mixing “sacrificial” polymer binder with ceramic powder allowing the “glueing” of ceramic particles together during the laser scanning before being burned during a debinding thermal cycle. The resulting ceramic part is then sintered. For example, Tang *et al.* (2011) used a slurry composed of alumina powder coated with PVA to produce dense bioceramic parts more easily (Table 1).

In the context of bone tissue engineering, iSLS method has been employed by some groups (Table 1) to develop directly composite materials composed of a biocompatible polymer matrix and hydroxyapatite filler, including PEEK (poly(ether-ether-ketone)) (Tan *et al.*, 2003), PVA (poly(vinyl alcohol)) (Chua *et al.*, 2004), PCL (poly(ϵ -caprolactone)) (Wiria *et al.*, 2007), or HDPE (high-density polyethylene) (Salmoria *et al.*, 2013). The biocomposite blend of PVA/HA were for example dedicated to craniofacial and joint defect applications (Chua *et al.*, 2004) whereas pure polymer material was preferred to produce lower stiffness scaffolds with high resolution for soft tissue engineering applications such as cardiac tissue (Chia and Wu, 2015).

The fabrication of designed porous biodegradable intervertebral fusion cages has been the subject of particular attention by for reducing revision spinal surgeries in order to avoid post-operative complications. 3D printed bioresorbable cervical cages (Knutsen *et al.*, 2015) and lumbar cages (Kang *et al.*, 2013) have thus been produced using SLS method with PCL/HA mixture. An example of composite scaffold produced by SLS is given in Fig. 7. Though the resolution of SLS is good enough at the macroscopic scale to produce personalized implants, one of its main limitation is the relatively low accuracy at the microscopic scale, which unlike μ SLA, does not allow the design of complex pore shapes for the production of bioceramic scaffolds (see Figs. 5 and 7).

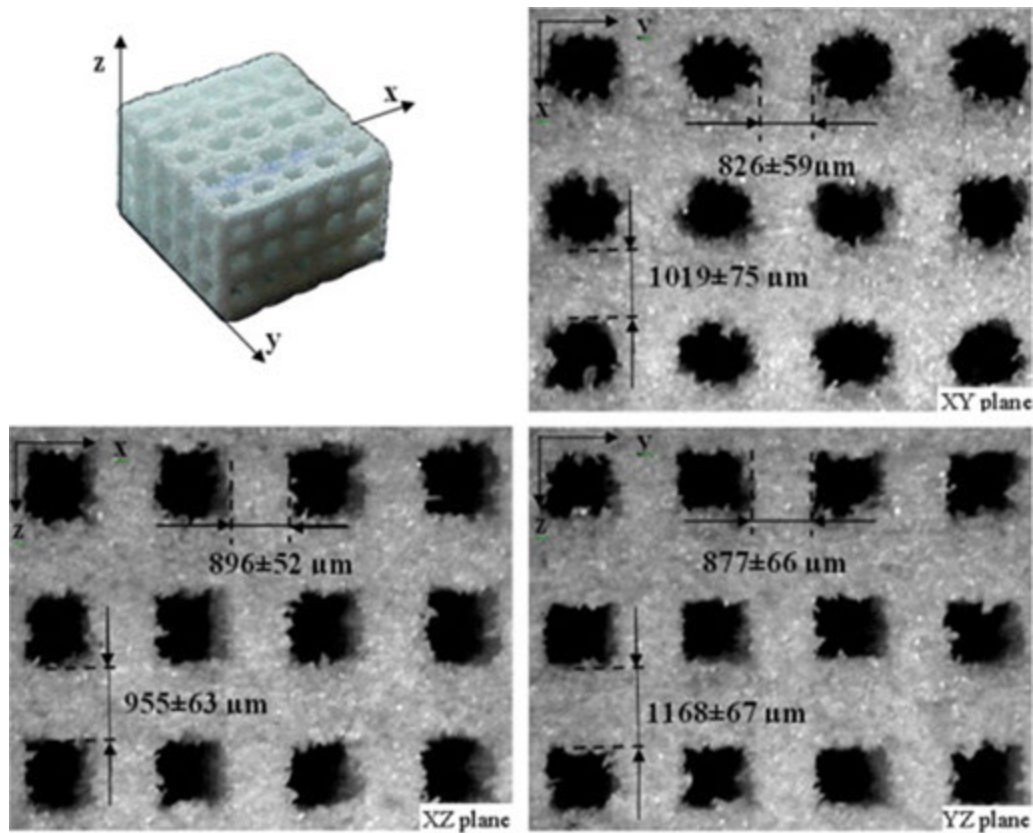


Fig. 7 Surface of hydroxyapatite/poly- ϵ -caprolactone scaffolds produced by SLS method in the three principle planes, with strut sizes (average $\pm$ standard deviation). Reproduced from Eosoly, S., Brabazon, D., Lohfeld, S., Looney, L., 2010. Selective laser sintering of hydroxyapatite/poly- ϵ -caprolactone scaffolds. *Acta Biomater.* 6, 2511–2517. Available at: <https://doi.org/10.1016/j.actbio.2009.07.018>. Copyright © 2010, with permission from Elsevier.

Material Extrusion

According to ISO/ASTM (2015), material extrusion is defined as AM process in which material is selectively dispensed through a nozzle or orifice. Among the material extrusion process, robocasting (RB) method based on robotic deposition of a viscous paste by means of continuous extrusion through a nozzle onto a construction platform is the most commonly used for ceramics shaping. This method, unlike AM technologies mentioned above, does not require a post-shaping step of feedstock removing. In fact, green bodies can be directly debinded and sintered to consolidate the scaffolds. Through RB, ceramic scaffolds can be built up with good mechanical characteristics. However, the accuracy remains conditioned by the diameter and the geometry of the nozzle, which are restrictive parameters. Moreover, material extrusion can only produce “continuous” rods that do not allow the shaping of very complex geometries. Hence, this AM process has been not largely preferred to design scaffolds with tailored architectures.

Applications

Some research groups have lately implemented and developed the fabrication of tailor-made calcium phosphate ceramic parts by extrusion techniques based on HA and/or β -TCP slurries (Dellinger *et al.*, 2007; Simon *et al.*, 2007; Martínez-Vázquez *et al.*, 2010; Michna *et al.*, 2005; Miranda *et al.*, 2006) in particular for orthopaedic applications due to their potential in load-bearing bone tissue engineering applications (Miranda *et al.*, 2008). Example of scaffold that can be produced by RB is given in Fig. 8.

Binder Jetting

Binder jetting is defined, in ISO/ASTM (2015) standard, as an AM process in which a liquid bonding agent is selectively deposited to join powder materials. Binder jetting technology also known as “three-dimensional printing” (3DP) or “direct ink printing” (DIP) is based on the printing of a pattern by selective deposition of liquid binder solution droplets, through a print-head, onto a thin layer of powder, previously spread by roller, thus binding the particles together. The surrounding unglued powder, serving as support, is then removed and the remaining green part is consolidated at high temperature to obtain a dense ceramic body.

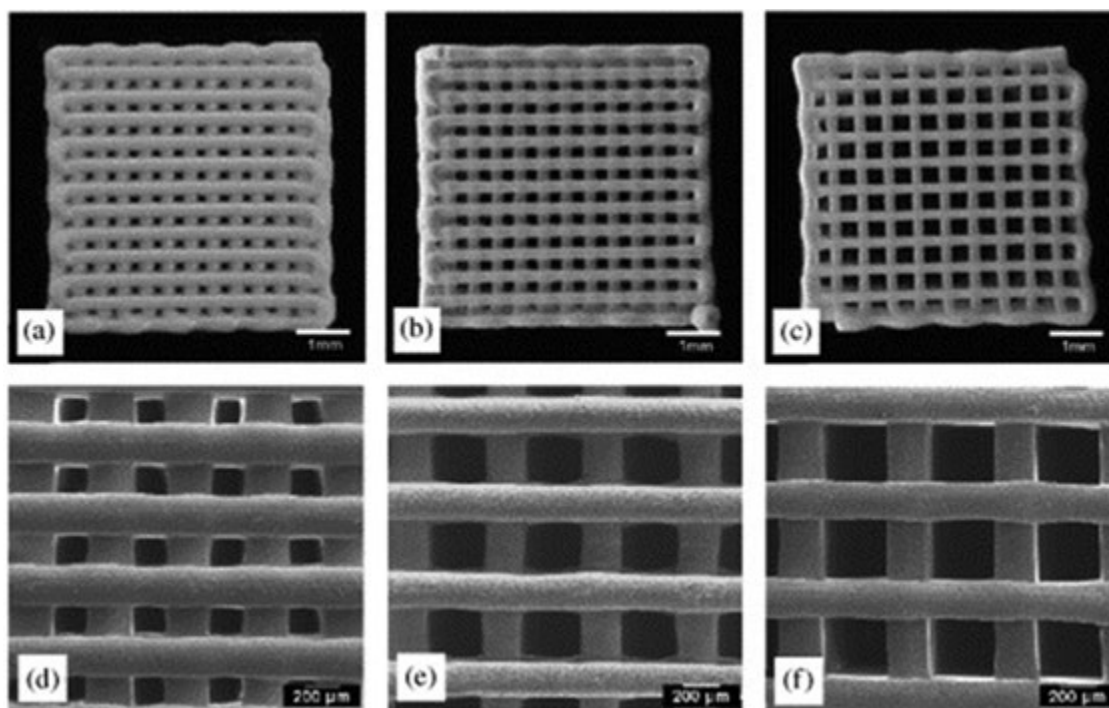


Fig. 8 Optical images of 3-D periodic hydroxyapatite scaffolds with varying minimum separation distance between rods of: (a) 250 μm , (b) 350 μm , and (c) 500 μm . And the corresponding SEM images (d–f) (top surface). Reproduced from Michna, S., Wu, W., Lewis, J.A., 2005. Concentrated hydroxyapatite inks for direct-write assembly of 3-D periodic scaffolds. *Biomaterials* 26, 5632–5639. doi:10.1016/j.biomaterials.2005.02.040. Copyright © 2005, with permission from Elsevier.

Applications

In the field of ceramic medical devices, some specimens have been built using powder-binder systems from calcium phosphate powders.

Seitz *et al.* produced HA scaffolds by jetting different nature of polymeric binder fluids to bond calcium phosphate particles, hydroxyapatite (HA) and/or tricalcium phosphate (β -TCP), together. Water soluble polymer blend (Schelofix) (Leukers *et al.*, 2005; Seitz *et al.*, 2005; Warnke *et al.*, 2010), water-based polymer binder solution (Fierz *et al.*, 2008), or an aqueous PVA solution (Irsen *et al.*, 2006) was used in these cases. 3D printed tricalcium phosphate tissue engineering scaffolds were also shaped with commercial organic water based binder (Fielding *et al.*, 2012; Tarafder *et al.*, 2013).

Gbureck *et al.* (2007) focused their works on the fabrication of calcium phosphate implants by printing process which consisted of a hydraulic setting reaction with a mixture based on phosphoric acid as liquid printing phase. By this way, brushite (DCPD), hydroxyapatite (HA) (Barralet *et al.*, 2009; Gbureck *et al.*, 2007), biphasic calcium phosphates (BCPs) ceramics containing hydroxyapatite (HA), and tricalcium phosphate (TCP) in varying ratios (Castilho *et al.*, 2014) and tricalcium phosphate (TCP) (Castilho *et al.*, 2017) scaffolds were shaped to substitute complex bone defects. For example, tricalcium phosphate scaffolds were developed to design resorbable cages (Fig. 9) for tibial region (Castilho *et al.*, 2017).

In terms of biomedical applications, another fabrication strategy was implemented by Gingter *et al.* to shape functionally graded system made of bioinert and/or bioactive ceramics. Their works focused on the production of innovative structures based on $\text{Al}_2\text{O}_3/\text{Y-TZP}$ by direct inkjet printing. The structures were built by means of two independently thermal printheads, one dedicated to alumina ink and the other one to yttria stabilized zirconia. Thus, DIP technology allows for creating graded ceramic bodies with varying material composition in several directions.

Dental Applications

CAD/CAM was implemented first, more than 25 years ago, in dentistry for the production of various fixed prosthetic restorations and has become a well established technology commonly used in this medical field (Lee and Lee, 2017). The main requirements for such applications are presented in Fig. 10. They include chemical inertia, mechanical reliability and durability associated with aesthetics criteria. During the past, according to the criteria, porcelain-fused-to-metal was considered as the standard for dental restorations. Nowadays, the demand for more aesthetic led to the production of all-ceramic restorations and the main ceramic materials commonly used to this purpose (Fig. 11) are resin matrix ceramics, silicate ceramics, alumina or zirconia (Conejo *et al.*, 2017).

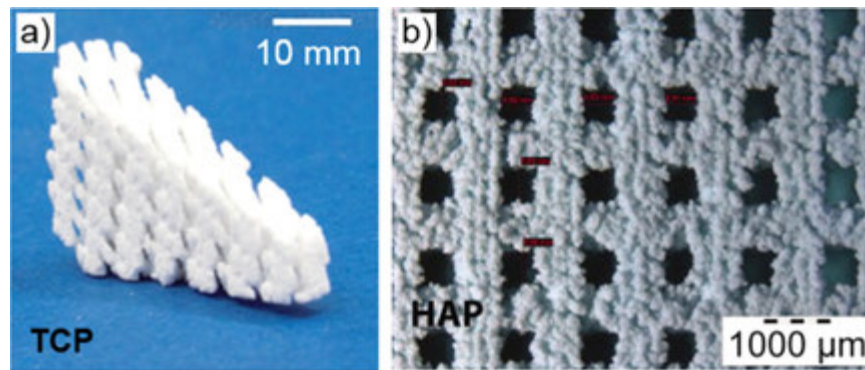


Fig. 9 Views of scaffolds produced by 3D printing and sintering. (a) Ceramic cage made of TCP and (b) HA scaffolds. Reproduced from (a) Castilho, M., Rodrigues, J., Vorndran, E., *et al.*, 2017. Computational design and fabrication of a novel bioresorbable cage for tibial tuberosity advancement application. *J. Mech. Behav. Biomed. Mater.* 65, 344–355. Available at: <https://doi.org/10.1016/j.jmbbm.2016.08.036>. Copyright © 2017, with permission from Elsevier. Warnke, P.H., Seitz, H., Warnke, F., *et al.*, 2010. Ceramic scaffolds produced by computer-assisted 3D printing and sintering: Characterization and biocompatibility investigations. *J. Biomed. Mater. Res. B Appl. Biomater.* 93, 212–217. Available at: <https://doi.org/10.1002/jbm.b.31577>. Copyright © 2010, with permission from John Wiley & Sons.

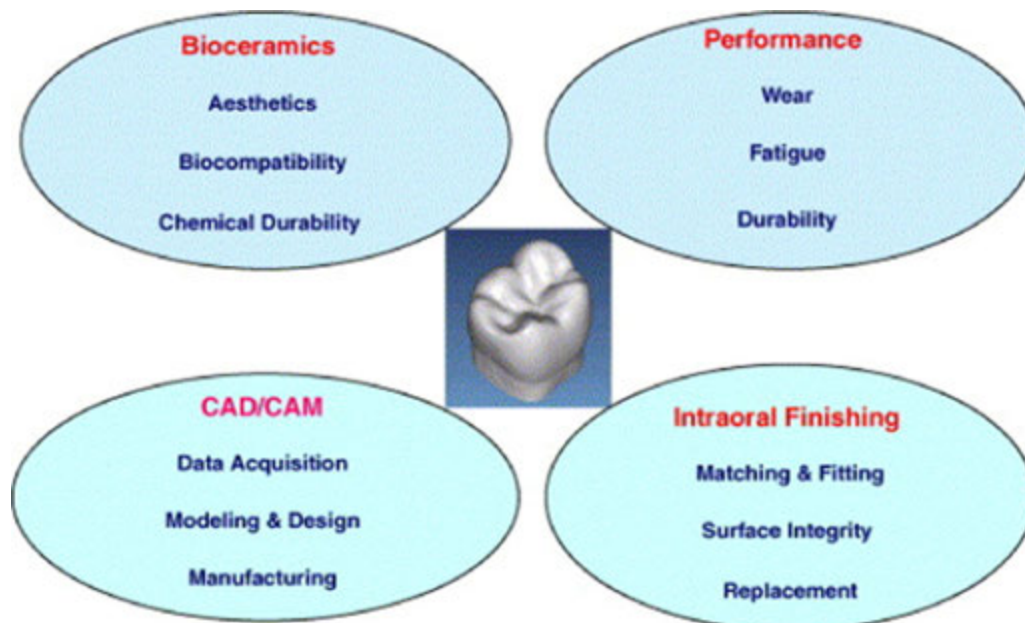


Fig. 10 Requirements in the applications of customized ceramics for dental restorations. Reproduced from Yin, L., Song, X.F., Song, Y.L., Huang, T., Li, J., 2006. An overview of in vitro abrasive finishing & CAD/CAM of bioceramics in restorative dentistry. *Int. J. Mach. Tools Manuf.* 46, 1013–1026. Available at: <https://doi.org/10.1016/j.ijmachtools.2005.07.045>. Copyright © 2006, with permission from Elsevier.

CAD/CAM dental devices are usually produced by subtractive manufacturing (Fig. 1) based on milling of pre-sintered or fully sintered blocks mostly using 3–5 axis systems (Galante *et al.*, 2019). The advantage of sintered blocks is that the device can be milled directly at the final dimensions, which is generally the case except for alumina and zirconia. For these later oxides, pre-sintered blocks are used because they would be too difficult to machine after full sintering due to their very high hardness. This method requires that the shrinkage occurring during post-sintering treatment must be taken in account in the initial size and design of the milled part. These CAD/CAM technologies are now commercially available for the production of dental devices at the level of the chairside in a dental practice so that they can be widely spread (Blatz and Conejo, 2019). The main drawbacks of subtractive technologies relates to the processing cost of the manufacturing units and milling tools and to the waste of material upon machining (Azari and Nikzad, 2009).

Additive manufacturing (AM) technologies may constitute an alternative to overcome these problems and produce at lesser cost (Javaid and Haleem, 2018; Silva *et al.*, 2017). However, probably due to the difficulties linked to the direct shaping of ceramics by AM, few works have been devoted to these new approaches. Only 11 original research papers were published up to now (source Scopus, July 2019, using the following keywords: “additive manufacturing”, “dentistry” and “ceramic”). Attempts to

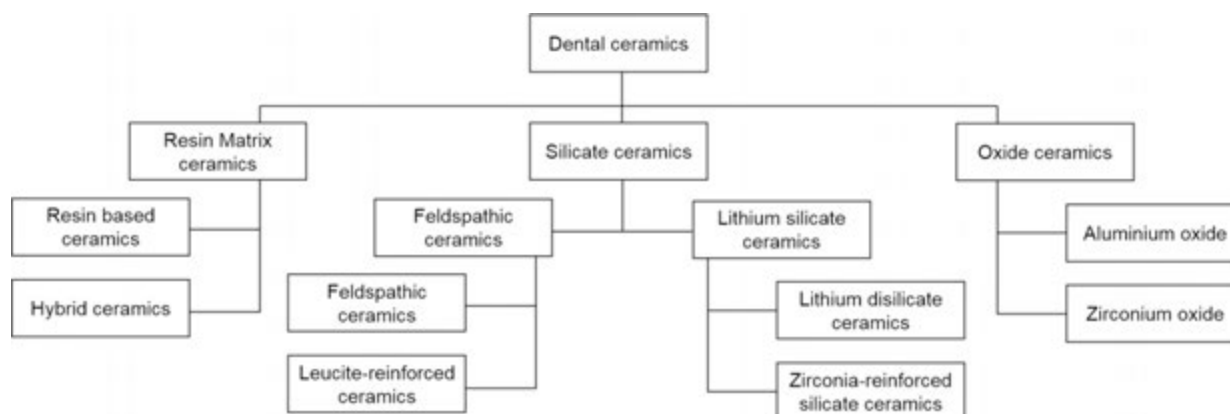


Fig. 11 Classification of ceramic materials used in dental applications. Reproduced from Conejo, J., Nueesch, R., Vonderheide, M., Blatz, M.B., 2017. Clinical performance of all-ceramic dental restorations. *Curr. Oral Health Rep.* 4, 112–123. Available at: <https://doi.org/10.1007/s40496-017-0132-4>. Copyright © 2017, with permission from Springer Nature.



Fig. 12 3Y-TZP (Teragonal zirconia polycrystals) bridge framework (sintered) shaped by direct inkjet printing. Reproduced from Emre, O., Zhang, W., Ebert, J., Telle, R., 2012. Potentials of the "direct inkjet printing" method for manufacturing 3Y-TZP based dental restorations. *J. Eur. Ceram. Soc.* 32, 2193–2201. Copyright © 2012, with permission from Elsevier.

shape zirconia crowns (Fig. 12) by 3D printing (Ebert *et al.*, 2009; Emre *et al.*, 2012; Li *et al.*, 2019) have been made but difficulties remain to produce reliable ceramic parts without defects (large processing flaws, cracks, ...) so that improvements are required in view of reliable processing (Alghazzawi, 2016).

Concluding Remarks

CAD/CAM technologies appear promising to produce custom-made ceramic medical devices for personalized medicine or bone tissue engineering. These versatile technologies appear of particular interest to this niche market but there are few commercially available products. Several points can be put forward to explain these current limitations and challenges remain in the future developments of ceramic medical devices (Singh and Ramakrishna, 2017).

- The technologies themselves remain young and under development. Research effort and improvements, mainly in the feed-stock and process parameters to ensure a reliable and cost-effective production, are still a necessity. This is noticeably the case of for the production of mechanically resistant ceramic devices for load-bearing applications.
- The biological behaviour at the interface materials/living tissues must be better understood to provide rational of scaffolds design. The current trends include the use 3D bioreactors and cell co-cultures to provide a more physiological model than the classical 2D static cell cultures (Champion *et al.*, 2017). At the scientific research level combined approaches, especially by implementing AM manufacturing and biofabrication are also rising to improve the biological performances of implants and scaffolds (Giannitelli *et al.*, 2015).
- A wide variety in the protocols, formulations, procedures either in the processing or in the characterizations of devices under development can be found in the available literature so that it is difficult to acquire reliable knowledge. Thus, there is a crucial need for rationalization with approaches including standardizations and certifications. Finally, as it has been the case in

dentistry with CAD/CAM subtractive manufacturing of restorative dental devices, CAD/CAM to produce customized implants or scaffolds for bone tissues surgery will have to reach hospital centers and the surgeons to get involved in the designing for additive manufacturing (Gibson and Srinath, 2015). These last points appear to be key factor to achieve in the transfer of these technologies from research to viable end-user applications.

References

- Alghazzawi, T.F., 2016. Advancements in CAD/CAM technology: Options for practical implementation. *J. Prosthodont. Res.* 60, 72–84. doi:10.1016/j.jpor.2016.01.003.
- Azari, A., Nikzad, S., 2009. The evolution of rapid prototyping in dentistry: A review *Rapid Prototyp. J* 15, 216–225. doi:10.1108/13552540910961946.
- Barlow, J.W., Vail, N.K., 1994. A method for producing high-temperature parts by way of low-temperature sintering. US Patent 5, 284–695.
- Barralet, J., Gbureck, U., Habibovic, P., et al., 2009. Angiogenesis in calcium phosphate scaffolds by inorganic copper ion release. *Tissue Eng. Part A* 15, 1601–1609. doi:10.1089/ten.tea.2007.0370.
- Bertsch, A., Jiguet, S., Bernhard, P., Renaud, P., 2003. Microstereolithography: A review. *Mater. Res. Soc. Symp. Proc.* 758.
- Bidan, C.M., Kommareddy, K.P., Rimpler, M., Kollmannsberger, P., Fratzl, P., 2013. Geometry as a factor of tissue growth: Towards shape optimization of tissue engineering scaffolds. *Adv. Healthc. Mater.* 2, 186–194.
- Blatz, M.B., Conejo, J., 2019. The current state of chairside digital dentistry and materials. *Dent. Clin.* 63, 175–197. doi:10.1016/j.cden.2018.11.002.
- Brie, J., Chartier, T., Chaput, C., et al., 2013. A new custom made bioceramic implant for the repair of large and complex craniofacial bone defects. *J. Craniomaxillofac. Surg.* 41, 403–407. doi:10.1016/j.jcms.2012.11.005.
- Brunello, G., Sivoletta, S., Meneghello, R., et al., 2016. Powder-based 3D printing for bone tissue engineering. *Biotechnol. Adv.* 34, 740–753. doi:10.1016/j.biotechadv.2016.03.009.
- Castilho, M., Moseke, C., Ewald, A., et al., 2014. Direct 3D powder printing of biphasic calcium phosphate scaffolds for substitution of complex bone defects. *Biofabrication* 6, 015006. doi:10.1088/1758-5082/6/1/015006.
- Castilho, M., Rodrigues, J., Vorndran, E., et al., 2017. Computational design and fabrication of a novel bioresorbable cage for tibial tuberosity advancement application. *J. Mech. Behav. Biomed. Mater.* 65, 344–355. doi:10.1016/j.jmbbm.2016.08.036.
- Champion, E., Magnaudeix, A., Pascaud-Mathieu, P., Chartier, T., 2017. Chapter 14 – Advanced processing techniques for customized ceramic medical devices. In: Palmero, P., Cambier, F., Barra, E.D. (Eds.), *Advances in Ceramic Biomaterials*. Woodhead Publishing, pp. 433–468. Available at: <http://dx.doi.org/10.1016/B978-0-08-100881-2.00015-4>.
- Charbonnier, B., Laurent, C., Marchat, D., 2016. Porous hydroxyapatite bioceramics produced by impregnation of 3D-printed wax mold: Slurry feature optimization. *J. Eur. Ceram. Soc.* 36, 4269–4279.
- Chartier, T., Dupas, C., Lasgorceix, M., et al., 2015. Additive manufacturing to produce complex 3D ceramic parts. *J. Ceram. Sci. Technol.* 6, 95–104.
- Chartier, T., Pateloup, V., Chaput, C., 2018. Élaboration de pièces céramiques par fabrication additive [www Document]. Ref TIP589WEB – Verres Céramiques. Available at: <https://www-techniques-ingenieur-fr/base-documentaire/materiaux-th11/ceramiques-42578210/elaboration-de-pieces-ceramiques-par-fabrication-additive-n4807/> (accessed 19.07.2019).
- Chia, H.N., Wu, B.M., 2015. Recent advances in 3D printing of biomaterials. *J. Biol. Eng.* 9, 4. doi:10.1186/s13036-015-0001-4.
- Chu, T.-M.G., Halloran, J.W., Hollister, S.J., Feinberg, S.E., 2001. Hydroxyapatite implants with designed internal architecture. *J. Mater. Sci. Mater. Med.* 12, 471–478.
- Chua, C.K., Leong, K.F., Tan, K.H., Wiria, F.E., Cheah, C.M., 2004. Development of tissue scaffolds using selective laser sintering of polyvinyl alcohol/hydroxyapatite biocomposite for craniofacial and joint defects. *J. Mater. Sci. Mater. Med.* 15, 1113–1121. doi:10.1023/B:JMSM.0000046393.81449.a5.
- Conejo, J., Nueesch, R., Vonderheide, M., Blatz, M.B., 2017. Clinical performance of all-ceramic dental restorations. *Curr. Oral Health Rep.* 4, 112–123. doi:10.1007/s40496-017-0132-4.
- Cruz, F., Simões, J., Coole, T., Bocking, C., 2005. Direct manufacture of hydroxyapatite based bone implants by selective laser sintering. Presented at the Virtual Modelling and Rapid Manufacturing – Advanced Research in Virtual and Rapid Prototyping, pp. 119–125.
- da Silva, L.H., de Lima, E., de Paulo Miranda, R.B., et al., 2017. Dental ceramics: A review of new materials and processing methods. *Braz. Oral Res.* 31. doi:10.1590/1807-3107bor-2017.vol31.0058.
- Deckers, J., Meyers, S., Kruth, J.P., Vleugels, J., 2014. Direct selective laser sintering/melting of high density alumina powder layers at elevated temperatures. *Phys. Procedia*, 8th Int. Conference on Laser Assisted Net Shape Engineering, 56, 117–124. doi:10.1016/j.phpro.2014.08.154.
- Dellinger, J.G., Cesarano, J., Jamison, R.D., 2007. Robotic deposition of model hydroxyapatite scaffolds with multiple architectures and multiscale porosity for bone tissue engineering. *J. Biomed. Mater. Res. A* 82, 383–394. doi:10.1002/jbm.a.31072.
- Duan, B., Wang, M., Zhou, W.Y., et al., 2010. Three-dimensional nanocomposite scaffolds fabricated via selective laser sintering for bone tissue engineering. *Acta Biomater.* 6, 4495–4505. doi:10.1016/j.actbio.2010.06.024.
- D'Urso, P.S., Effeney, D.J., Earwaker, W.J., et al., 2000. Custom cranioplasty using stereolithography and acrylic. *Br. J. Plast. Surg.* 53, 200–204. doi:10.1054/bjps.1999.3268.
- Ebert, J., Özkol, E., Zeichner, A., et al., 2009. Direct inkjet printing of dental prostheses made of zirconia. *J. Dent. Res.* 88, 673–676. doi:10.1177/0022034509339988.
- Emre, O., Zhang, W., Ebert, J., Telle, R., 2012. Potentials of the "direct inkjet printing" method for manufacturing 3Y-TZP based dental restorations. *J. Eur. Ceram. Soc.* 32, 2193–2201.
- Eosoly, S., Brabazon, D., Lohfeld, S., Looney, L., 2010. Selective laser sintering of hydroxyapatite/poly- ϵ -caprolactone scaffolds. *Acta Biomater.* 6, 2511–2517. doi:10.1016/j.actbio.2009.07.018.
- Ferrage, L., Bertrand, G., Lenormand, P., Grossin, D., Ben-Nissan, B., 2017. A review of the additive manufacturing (3DP) of bioceramics: Alumina, zirconia (PSZ) and hydroxyapatite. *J. Aus. Ceram. Soc.* 53, 11–20.
- Fielding, G.A., Bandyopadhyay, A., Bose, S., 2012. Effects of silica and zinc oxide doping on mechanical and biological properties of 3D printed tricalcium phosphate tissue engineering scaffolds. *Dent. Mater. Off. Publ. Acad. Dent. Mater.* 28, 113–122. doi:10.1016/j.dental.2011.09.010.
- Fierz, F., Beckmann, F., Huser, M., et al., 2008. The morphology of anisotropic 3D-printed hydroxyapatite scaffolds. *Biomaterials* 29 (28), 3799–3806.
- Galante, R., Figueiredo-Pina, C.G., Serro, A.P., 2019. Additive manufacturing of ceramics for dental applications: A review. *Dent. Mater.* 35, 825–846. doi:10.1016/j.dental.2019.02.026.
- Gariboldi, M.I., Best, S.M., 2015. Effect of ceramic scaffold architectural parameters on biological response. *Front. Bioeng. Biotechnol.* 3, 151. doi:10.3389/fbioe.2015.00151.
- Gbureck, U., Hölzel, T., Doillon, C.J., Müller, F.A., Barralet, J.E., 2007. Direct printing of bioceramic implants with spatially localized angiogenic factors. *Adv. Mater.* 19, 795–800. doi:10.1002/adma.200601370.
- Giannitelli, S.M., Mozetic, P., Trombetta, M., Rainer, A., 2015. Combined additive manufacturing approaches in tissue engineering. *Acta Biomater.* 24, 1–11.
- Gibson, I., Srinath, A., 2015. Simplifying medical additive manufacturing: Making the surgeon the designer. *Procedia Technol.* 20, 237–242. (In: Proceedings of the 1st International Design Technology Conference, DESTech2015, Geelong).
- Gingter, P., Wätjen, A., Kramer, M., Telle, R., 2015. Functionally graded ceramic structures by direct thermal inkjet printing. *J. Ceram. Sci. Technol.* 6, 119–124.
- Guyot, Y., Papantoniou, I., Chai, Y.C., et al., 2014. A computational model for cell/ECM growth on 3D surfaces using the level set method: a bone tissue engineering case study. *Biomech. Model. Mechanobiol.* 13, 1361–1371. doi:10.1007/s10237-014-0577-5.

- Heary, R.F., Schlenk, R.P., Sacchieri, T.A., Barone, D., Brotea, C., 2002. Persistent iliac crest donor site pain: Independent outcome assessment. *Neurosurgery* 50, 510–517. doi:10.1097/00006123-200203000-00015.
- Hutmacher, D.W., Sittlinger, M., Risbud, M.V., 2004. Scaffold-based tissue engineering: Rationale for computer-aided design and solid free-form fabrication systems. *Trends Biotechnol.* 22, 354–362. doi:10.1016/j.tibtech.2004.05.005.
- Irsen, S.H., Leukers, B., Höckling, C., Tille, C., Seitz, H., 2006. Bioceramic granulates for use in 3D printing: Process engineering aspects. *Mater. Werkst.* 37, 533–537. doi:10.1002/mawe.200600033.
- ISO/ASTM., 2015. ISO/ASTM 52900:2015, Additive manufacturing – General principles – Terminology. ASTM F2792-10e1 (2012). Available at: <https://www.iso.org/standard/69669.html>.
- Javadi, M., Haleem, A., 2018. Additive manufacturing applications in medical cases: A literature based review. *Alex. J. Med.* 54, 411–422. doi:10.1016/j.ajme.2017.09.003.
- Kang, H., Hollister, S.J., La Marca, F., Park, P., Lin, C.-Y., 2013. Porous biodegradable lumbar interbody fusion cage design and fabrication using integrated global-local topology optimization with laser sintering. *J. Biomech. Eng.* 135, 1010131–1010138. doi:10.1115/1.4025102.
- Knutsen, A.R., Borkowski, S.L., Ebramzadeh, E., et al., 2015. Static and dynamic fatigue behavior of topology designed and conventional 3D printed bioresorbable PCL cervical interbody fusion devices. *J. Mech. Behav. Biomed. Mater.* 49, 332–342. doi:10.1016/j.jmbbm.2015.05.015.
- Lasgorceix, M., Champion, E., Chartier, T., 2016. Shaping by microstereolithography and sintering of macro-micro-porous silicon substituted hydroxyapatite. *J. Eur. Ceram. Soc.* 36, 1091–1101.
- Lee, S.J., Lee, J.D., 2017. Digital impressions for implant-supported fixed dental prostheses. *Curr. Oral Health Rep.* 4, 136–141. doi:10.1007/s40496-017-0135-1.
- Leukers, B., Güllkan, H., Irsen, S.H., et al., 2005. Hydroxyapatite scaffolds for bone tissue engineering made by 3D printing. *J. Mater. Sci. Mater. Med.* 16, 1121–1124. doi:10.1007/s10856-005-4716-5.
- Li, H., Song, L., Sun, J., Ma, J., Shen, Z., 2019. Dental ceramic prostheses by stereolithography-based additive manufacturing: Potentials and challenges. *Adv. Appl. Ceram.* 118, 30–36. doi:10.1080/17436753.2018.1447834.
- Ma, H., Feng, C., Chang, J., Wu, C., 2018. 3D-printed bioceramic scaffolds: From bone tissue engineering to tumor therapy. *Acta Biomater.* 79, 37–59.
- Magnaudeix, A., Usseglio, J., Lasgorceix, M., et al., 2016. Quantitative analysis of vascular colonisation and angio-conduction in porous silicon-substituted hydroxyapatite with various pore shapes in a chick chorioallantoic membrane (CAM) model. *Acta Biomater.* 38, 179–189. doi:10.1016/j.actbio.2016.04.039.
- Martínez-Vázquez, F.J., Perera, F.J., Miranda, P., Pajares, A., Guiberteau, F., 2010. Improving the compressive strength of bioceramic robocast scaffolds by polymer infiltration. *Acta Biomater.* 6, 4361–4368. doi:10.1016/j.actbio.2010.05.024.
- Melchels, F.P.W., Feijen, J., Grijpma, D.W., 2010. A review on stereolithography and its applications in biomedical engineering. *Biomaterials* 31, 6121–6130. doi:10.1016/j.biomaterials.2010.04.050.
- Michna, S., Wu, W., Lewis, J.A., 2005. Concentrated hydroxyapatite inks for direct-write assembly of 3-D periodic scaffolds. *Biomaterials* 26, 5632–5639. doi:10.1016/j.biomaterials.2005.02.040.
- Miranda, P., Pajares, A., Saiz, E., Tomsia, A.P., Guiberteau, F., 2008. Mechanical properties of calcium phosphate scaffolds fabricated by robocasting. *J. Biomed. Mater. Res. A* 85, 218–227. doi:10.1002/jbm.a.31587.
- Miranda, P., Saiz, E., Gryn, K., Tomsia, A.P., 2006. Sintering and robocasting of beta-tricalcium phosphate scaffolds for orthopaedic applications. *Acta Biomater.* 2, 457–466. doi:10.1016/j.actbio.2006.02.004.
- Mota, C., Puppi, D., Chiellini, F., Chiellini, E., 2015. Additive manufacturing techniques for the production of tissue engineering constructs. *J. Tissue Eng. Regen. Med.* 9, 174–190. doi:10.1002/term.1635.
- Petit, C., Montanaro, L., Palmero, P., 2017. Functionally graded ceramics for biomedical application: Concept, manufacturing, and properties. *Int. J. Appl. Ceram. Technol.* 15, 820–840.
- Pietrzak, W.S., 2008. Musculoskeletal and wound treatment through the ages: A brief historical tour. In: Pietrzak, W.S. (Ed.), *Musculoskeletal Tissue Regeneration: Biological Materials and Methods, Orthopedic Biology and Medicine*. Totowa, NJ: Humana Press, pp. 3–17. Available at: http://doi.org/10.1007/978-1-59745-239-7_1.
- Provaggi, E., Leong, J.J.H., Kalaskar, D.M., 2017. Applications of 3D printing in the management of severe spinal conditions. *Proc. Inst. Mech. Eng. H* 231, 471–486. doi:10.1177/0954411916667761.
- Rüdrich, U., Lasgorceix, M., Champion, E., et al., 2019. Pre-osteoblast cell colonization of porous silicon substituted hydroxyapatite bioceramics: Influence of microporosity and macropore design. *Mat. Sci. Eng. C* 97, 510–528.
- Salmoria, G.V., Fancello, E.A., Roesler, C.R.M., Dabbas, F., 2013. Functional graded scaffold of HDPE/HA prepared by selective laser sintering: Microstructure and mechanical properties. *Int. J. Adv. Manuf. Technol.* 65, 1529–1534. doi:10.1007/s00170-012-4277-y.
- Seitz, H., Rieder, W., Irsen, S., Leukers, B., Tille, C., 2005. Three-dimensional printing of porous ceramic scaffolds for bone tissue engineering. *J. Biomed. Mater. Res. B Appl. Biomater.* 74, 782–788. doi:10.1002/jbm.b.30291.
- Shuai, C., Li, P., Liu, J., Peng, S., 2013. Optimization of TCP/HAP ratio for better properties of calcium phosphate scaffold via selective laser sintering. *Mater. Charact.* 77, 23–31. doi:10.1016/j.matchar.2012.12.009.
- Singh, S., Ramakrishna, S., 2017. Biomedical applications of additive manufacturing: Present and future. *Curr. Opin. Biomed. Eng.* 2, 105–115. doi:10.1016/j.cobme.2017.05.006.
- Simon, J.L., Michna, S., Lewis, J.A., et al., 2007. In vivo bone response to 3D periodic hydroxyapatite scaffolds assembled by direct ink writing. *J. Biomed. Mater. Res.* 83A, 747–758.
- Skoog, S.A., Goering, P.L., Narayan, R.J., 2014. Stereolithography in tissue engineering. *J. Mater. Sci. Mater. Med.* 25, 845–856. doi:10.1007/s10856-013-5107-y.
- Sodian, R., Loebe, M., Hein, A., et al., 2002. Application of stereolithography for scaffold fabrication for tissue engineered heart valves. *ASAIO J.* 46 (2), 12–16. doi:10.1097/00002480-200201000-00004.
- Tan, K.H., Chua, C.K., Leong, K.F., et al., 2003. Scaffold development using selective laser sintering of polyetheretherketone-hydroxyapatite biocomposite blends. *Biomaterials* 24, 3115–3123. doi:10.1016/S0142-9612(03)00131-5.
- Tang, H.-H., Chiu, M.-L., Yen, H.-C., 2011a. Slurry-based selective laser sintering of polymer-coated ceramic powders to fabricate high strength alumina parts. *J. Eur. Ceram. Soc.* 31, 1383–1388. doi:10.1016/j.jeurceramsoc.2011.02.020.
- Tarafer, S., Balla, V.K., Davies, N.M., Bandyopadhyay, A., Bose, S., 2013. Microwave-sintered 3D printed tricalcium phosphate scaffolds for bone tissue engineering. *J. Tissue Eng. Regen. Med.* 7, 631–641. doi:10.1002/term.555.
- Trombetta, R., Inzana, J.A., Schwarz, E.M., Kates, S.L., Awad, H.A., 2017. 3D printing of calcium phosphate ceramics for bone tissue engineering and drug delivery. *Ann. Biomed. Eng.* 45, 23–44. doi:10.1007/s10439-016-1678-3.
- Wagle, W.A., 1994. Toe prosthesis in an Egyptian human mummy. *Am. J. Roentgenol.* 162, 999–1000. doi:10.2214/ajr.162.4.8141038.
- Warnke, P.H., Seitz, H., Warnke, F., et al., 2010. Ceramic scaffolds produced by computer-assisted 3D printing and sintering: Characterization and biocompatibility investigations. *J. Biomed. Mater. Res. B Appl. Biomater.* 93, 212–217. doi:10.1002/jbm.b.31577.
- Wiria, F.E., Leong, K.F., Chua, C.K., Liu, Y., 2007. Poly- ϵ -caprolactone/hydroxyapatite for tissue engineering scaffold fabrication via selective laser sintering. *Acta Biomater.* 3, 1–12. doi:10.1016/j.actbio.2006.07.008.
- Zocca, A., Colombo, P., Gomes, C.M., Günster, J., 2015. Additive manufacturing of ceramics: Issues, potentialities, and opportunities. *J. Am. Ceram. Soc.* 98, 1983–2001. doi:10.1111/jace.13700.

Bioactive and Biodegradable Polymer-Based Composites

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Introduction

Polymer-based biocomposites are a fundamental class of materials developed in the course of the past decades in response to the need for novel biomaterials that could be used in diverse biomedical applications, from orthopedic fixation devices to engineered scaffolds for the growth of cells and tissues (tissue engineering) (Boccaccini *et al.*, 2010). Although these materials find application in several fields of life sciences, in this chapter the focus will be on their use in tissue engineering (Gritsch *et al.*, 2017), with particular emphasis on the regeneration of bone (Amini *et al.*, 2012; Ning, 2016).

Tissue engineering (TE) is an interdisciplinary field that combines know-how from materials science, chemistry, biology and medicine to create artificial constructs, named “scaffolds”, that are able to support the regeneration of tissues while being gradually eroded and resorbed (Gough and Boccaccini, 2007; Hutmacher, 2006; Henkel *et al.*, 2013). TE represents a complex challenge that requires the fine tailoring of numerous parameters in order to create a functional interface between the artificial construct (scaffold) and the body (Gritsch *et al.*, 2017; Hutmacher, 2006). A candidate material for tissue engineering scaffolds has to fulfill several key physicochemical and biological requirements: it has to be biocompatible and non-immunogenic, have adequate mechanical properties to match the target tissue, exhibit porous structure to facilitate cell invasion and vascularization and be suitable for sterilization (Henkel *et al.*, 2013). But most importantly, especially in the case of bone, it has to have two key properties: controlled biodegradability (Van De Velde and Kiekens, 2002) and bioactivity (Kokubo and Takadama, 2006; Maçon *et al.*, 2015).

The chief difference between tissue engineering and conventional medical approaches is moving from what is called a “replacement” strategy, in which a medical device aims to restore a severed tissue only in its function but not its physiology, to a “repair and regeneration” approach, whose goal is to temporarily restore function to allow the defective tissue to regenerate and reestablish a physiological-like situation both morphologically and functionally (Henkel *et al.*, 2013). In this sense, biodegradability is an essential feature of scaffolds: regeneration cannot be achieved using materials that once implanted will permanently remain within the body (Van De Velde and Kiekens, 2002; Basnett *et al.*, 2017). Tissue engineering scaffolds shall be designed using mainly biodegradable materials, and biodegradable polymers in particular (Van De Velde and Kiekens, 2002; Rezwan *et al.*, 2006). Biodegradable polymers are a specific class of polymers with a tailorable ability to be progressively broken down by living organisms and environmental conditions *in vivo* (Hutmacher, 2006; Basnett *et al.*, 2017). In particular, if the degradation by-products are compounds that can be processed and eliminated through physiological pathways, the polymer will be deemed bioresorbable (Li, 2017). For instance, polylactic acid is broken down by hydrolysis into lactic acid moieties that can be readily converted into CO₂ by the Krebs cycle (Vert *et al.*, 1992). In general, there are several ways biodegradability can operate, mainly through hydrolytic, temperature-mediated, radiation-mediated and enzymatic degradations (Van De Velde and Kiekens, 2002). In a typical *in vivo* scenario, scaffolds will be mostly degraded by hydrolysis and enzymes (Vert *et al.*, 1992; Nelson and Cox, 2004): accurate material design will allow control over these phenomena and the development of a construct that has matching degradation and tissue in-growth rates (Hutmacher, 2006; Henkel *et al.*, 2013). In this way, the scaffold is effectively removed by the body while new tissue is forming (Fig. 1).

Filler candidates for the fabrication of composites for tissue engineering must possess another important biological property that is in fact tightly linked to their biodegradability: bioactivity. Bioactivity (or bioreactivity) is defined in this context as the ability of a material to successfully interact and bond with a target living tissue (Maçon *et al.*, 2015; Hench, 2015; Hench *et al.*, 1971). The term gained importance starting from the late 1960s, when it was first linked to the interesting properties of a novel class of materials: bioactive glasses (BGs) (Jones, 2013). BGs are a family of inorganic materials with several different compositions, most of which are able to create a strong bond with bone thanks to their ability to dissolve *in vivo* and to form hydroxyapatite, the natural mineral phase of bone on their surfaces (Jones, 2013). As a consequence, although the definition of bioactivity does not mention specific target tissues and a bioactive material could have properties that go beyond its ability to mineralize, the term “bioactivity” is still associated to the ability of a material to trigger biomineralization (Mahabadi and Alexandru, 2006; Miguez-Pacheco *et al.*, 2015). This verbal ambiguity is an interesting topic of debate and it was discussed in a recent review paper (Mahabadi and Alexandru, 2006). In this chapter, we will still refer to bioactivity in bone-specific terms as the ability of a material to trigger the deposition of hydroxyapatite either *in vivo* or in simulated body fluid (SBF) as an acellular bioactivity test (Kokubo and Takadama, 2006; Maçon *et al.*, 2015; Fujibayashi *et al.*, 2003).

Since most polymers available for biomedical applications lack intrinsic bioactivity (Rezwan *et al.*, 2006; Gritsch *et al.*, 2019), exception made for some natural polymers, e.g., silk-derived proteins (Marelli *et al.*, 2012b; Griffanti *et al.*, 2019), the idea of combining a biodegradable and often bioresorbable polymeric matrix with a bioactive inorganic filler is naturally an ideal and straight-forward approach to obtain a biomaterial combining biodegradability and bioactivity (Boccaccini *et al.*, 2010; Rezwan *et al.*, 2006; Baino *et al.*, 2015). The preparation of composite is achieved either by solvent-based or melting-based mixing of a bioactive

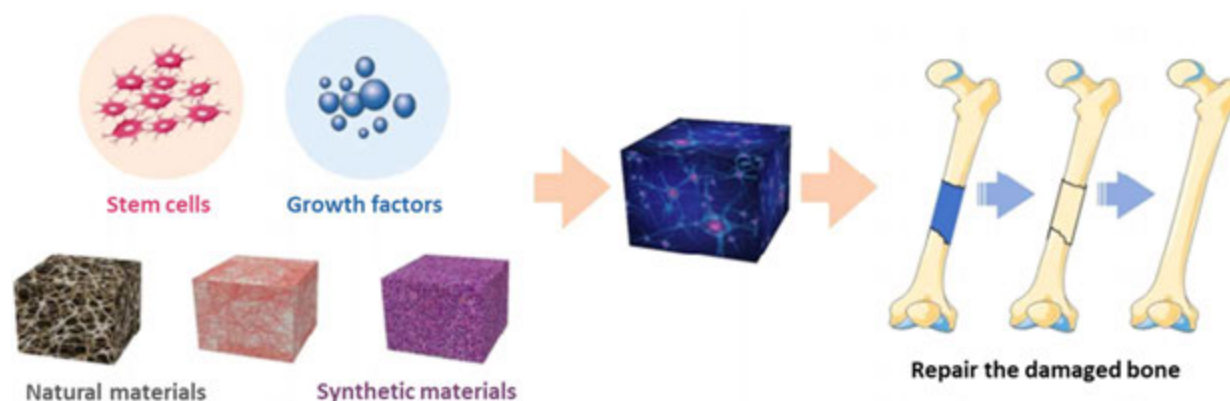


Fig. 1 The concept of regenerative medicine and the key elements for successful bone tissue engineering. Figure adapted from reference Hao, Z., Song, Z., Huang, J., *et al.*, 2017. *Biomater. Sci.* 5, 1382–1392, with permission of RCS publishing.

filler of desired size and aspect ratio (e.g., particles, fibers) with the biodegradable matrix polymer (Chen *et al.*, 2008), as identified more than 15 years ago (Rezwan *et al.*, 2006). The final properties of the composite will be a complex combination of the ones of the two materials. They depend on several factors, including filler homogeneity and size, interface properties between the two phases and filler-to-matrix ratio (Rezwan *et al.*, 2006; Chen *et al.*, 2008). The underlying relationship between these properties and the overall physicochemical and biological behavior of the final material is subject of study within the theory of composites material, as discussed in-depth elsewhere (Milton, 2002). Polymer-based composites with bioactive fillers as TE scaffolds are considered as an alternative to current therapies for bone reconstruction, which heavily rely on autologous tissue (Amini *et al.*, 2012; Henkel *et al.*, 2013). Autografts are well-studied and effective, but suffer from a number of disadvantages, mainly their limited availability and the need for invasive harvesting (Campana *et al.*, 2014). Polymer-based biocomposites have been long studied as a promising alternative to autografts and a possible solution to keep up with the increasing annual demand for bone grafts: for instance, bone disorder-related annual costs are expected to hit \$2.5 billion this year in the USA (Amini *et al.*, 2012).

This chapter offers an overview on traditional and recent materials and technologies developed for the production of bioactive and biodegradable polymer-based composites for bone tissue engineering. The most important bioactive glasses and bioceramics, as well as relevant polymers used in the field, will be listed and described in terms of properties, advantages and disadvantages. The most widely studied and promising approaches to process such composites and to fabricate them into scaffolds will be then outlined, from traditional protocols of particulate leaching all the way to the most cutting-edge techniques, such as bioplotting or 3D melt electrospinning writing. The development of nanocomposites will be also discussed highlighting the advantages of nanostructured composites. Recent relevant investigations and the most promising organic/inorganic combinations will be highlighted and discussed with special attention to their clinical translation potential, limitations of current technologies and possible directions for future developments.

Bioactive Ceramic Phases

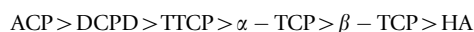
Among other beneficial properties (e.g., mechanical properties enhancement), the filler phase in biocomposites has the main role of providing bioactivity to the system (Baino *et al.*, 2015; Milton, 2002). As previously discussed, bioactivity is defined in this case as the ability of a material to successfully bond to bone tissue by promoting biomineralization (Hench, 2015; Hench *et al.*, 1971).

In this section, the two main groups of bioactive fillers used in biomedical composites will be discussed: calcium phosphates (Ambard and Mueninghoff, 2006; Rahaman, 2014) and bioactive glasses (Jones, 2013; Rahaman, 2014; Rahaman *et al.*, 2011). Due to their similarity to the inorganic component of bone, the most common bioactive ceramics used in clinical applications are inspired by calcium phosphates (CaPs) (Siddiqui *et al.*, 2018). CaPs are a family of several inorganic materials with diverse properties depending on their composition and crystallinity, making them a straightforward and versatile choice for bone tissue engineering and regeneration. The current main alternative to calcium phosphates are bioactive glasses (BGs) (Rahaman, 2014). BGs have been proposed as an attractive alternative to CaPs because of their superior biological properties (Jones, 2013). Due to their faster degradation kinetics and more complex ion release profile, BGs have been correlated with improved gene expression, regulation of growth factor secretion and enhanced physiological regeneration processes, such as osteogenesis and angiogenesis (Brauer, 2015; Valerio *et al.*, 2004; Jell and Stevens, 2006). These properties were confirmed even in the presence of sole BGs, without addition of growth factors (Valerio *et al.*, 2004). Finally, beyond the CaPs and BGs families, other types of bioceramics have been investigated to impart bioactivity to polymeric materials. Among these, the most relevant are (1) metal oxides, such as titanium (Santiago-Medina *et al.*, 2015) and magnesium oxides (Hickey *et al.*, 2014), (2) non-phosphate calcium-containing inorganics, mainly wollastonite and other calcium silicates (Wu and Chang, 2013; Sanmartin de Almeida *et al.*, 2018) and (3) carbon nanotubes (Tanaka *et al.*, 2017).

Calcium Phosphates

General characteristics

Calcium phosphates are a natural choice in the development of biocomposites for bone tissue engineering applications due to their similarity to the mineral phase of bone. Combining a polymer (collagen, for instance) with a calcium phosphate is a straightforward approach to mimic natural bone tissue (Marelli *et al.*, 2011). However, calcium phosphate is a rather general term, which identifies a wide family of materials that differ in properties depending on their specific composition and structure (Rahaman, 2014). Several forms of CaPs are investigated as biomaterials: both amorphous (Skrtic *et al.*, 2003; Zhao *et al.*, 2011) (ACP) and crystalline CaPs with different formulas (Rahaman, 2014; LeGeros, 2002; Mattioli-Belmonte *et al.*, 2012), mainly hydroxyapatite (HA) (Subuki *et al.*, 2018), artificial surrogate of the natural mineral phase of bone with ideal formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, beta-tricalcium phosphates (Liu and Lun, 2012) (β -TCP, $\text{Ca}_3(\text{PO}_4)_2$) and composites of the two, usually referred to as biphasic calcium phosphates (BCP) (Dasgupta, 2018). Other formulations include tetracalcium phosphates (TTCP, $\text{Ca}_4(\text{PO}_4)_2\text{O}$) (Moseke and Gbureck, 2010), alpha-tricalcium phosphates (Carrodegua and Aza, 2011) (α -TCP, a polymorph of β -TCP) and dicalcium phosphate dehydrate (Burguera *et al.*, 2006) (DCPD, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). The ratio of calcium to phosphate (Ca/P) is normally used as an effective indicator to discriminate between different formulations (Rahaman, 2014). In general, CaPs share similar biocompatibility, low-toxicity and low-immunogenicity (Jeong *et al.*, 2019). In addition, calcium phosphate ceramics are usually osteoconductive (Ripamonti, 1996; Yuan *et al.*, 2001; Yamasaki and Sakai, 1992), though not osteoinductive (Rahaman, 2014). In fact, although some studies suggested that several CaPs (e.g., HA, β -TCP, BCP) have the ability to form bone in non-osseous sites, no conclusive evidence was collected to date (LeGeros, 2008). Osteoinductivity depends on numerous factors, such as the chemical composition, surface topography and macrostructure of the biomaterial (Rahaman, 2014). Pore size, structure and porosity in particular play a key role: both macro- and mesoporosity and the concavity of macropores have been linked with the ability of certain CaPs to entrap pro osteogenic growth factors (e.g., bone morphogenic protein, BMP), increasing their local concentration and ultimately enhancing the behavior of osteoprogenitor cells in situ (Reddi, 2000; Jin *et al.*, 2000; De Groot, 1998). The complexity of the phenomenon determines that osteoinductivity is most likely a property that depends on several concurring factors and cannot be defined as an intrinsic property of materials (Reddi, 2000). In parallel, bioactivity and osteoconductivity are generally considered intrinsic properties of CaPs and are deemed similar throughout the formulation spectrum of these materials (Samavedi *et al.*, 2013). Nevertheless, some differences are present. These are mostly related to the degradation kinetics of CaPs, which can highly change in relation to their composition and environmental conditions, ultimately impacting on bioactivity (Jeong *et al.*, 2019; Samavedi *et al.*, 2013). The composition and structures used in biomedical applications are the ones that are stable in aqueous media at physiological temperature (37°C). Fixing these conditions, the main parameter that will rule the degradation kinetics of a specific CaP will be the environmental pH (Rahaman, 2014). For instance, at physiological pH (7.4) the most stable CaP phase will be HA (Samavedi *et al.*, 2013), which should not come as a surprise, given that, as already mentioned, CaP normally crystallize as HA in bones. Other forms of CaPs will follow an order of increasing solubility as follows:



As a general rule, the lower the Ca/P ratio, the more acidic and water soluble the bioceramics will be (Dorozhkin, 2011). Tetracalcium phosphates are an exception to this rule, as they have the highest Ca/P ratio, (2.0), but degrade faster than HA (Ca/P = 1.67) (Rahaman, 2014). HA has the second highest Ca/P ratio and the slowest degradation kinetics among biologically relevant calcium phosphates (Rahaman, 2014). The stability of HA in body fluids can be further increased by substitution of hydroxyl ions in the lattice with fluorine, obtaining fluorapatite (FA) (Daas *et al.*, 2018).

Hydroxyapatite

The use of HA as a biomaterial dates back to the 1950s, when this calcium phosphate was used as inert bone filler, owing to its stability in vivo and its similarity to bone (Rahaman, 2014). Only later the biological reactivity of HA was better explained and exploited in medical sciences (Rahaman, 2014). Since HA has such a similar structure to the mineral phase of bone, which composes circa 69wt% of bone tissue, its use can be considered as one of first examples of a biomimicry approach in biomedical engineering (Jeong *et al.*, 2019). HA has a crystalline structure with cations and anions organized in a hexagonal lattice. The mechanical properties of HA depend on several variables, including crystal size, porosity, density, sintering or phase composition (Pielichowska and Blazewicz, 2010). The range of bending, compressive, and tensile strength values of HA are 38–250, 120–150, and 38–300 MPa, respectively (Fu *et al.*, 2011). The Young's modulus of dense HA can highly vary depending on porosity and impurities and it usually sits within a range of 35–120 GPa (Rahaman, 2014; Fu *et al.*, 2011). Other relevant mechanical properties of HA are a Weibull's modulus typical of brittle materials (i.e., 5–18), and a Vicker's hardness of 3–7 GPa (Pielichowska and Blazewicz, 2010). In general, the mechanical properties of HA are linked to its microstructure and, as such, can be improved by designing harvesting and production protocols that optimize grain fineness to obtain a densely sintered body in the final material. HA can be either of natural or artificial origin. It can be prepared artificially using a number of synthesis routes (e.g., wet precipitation, hydro-/solvo- thermal processing or sol-gel chemistry), as described in detail elsewhere (Pielichowska and Blazewicz, 2010). Natural HA is instead commonly harvested from bovine bone or obtained by processing coral minerals. The latter case consists in turning calcite (CaCO_3) into HA by a hydrothermal treatment in presence of ammonium phosphate (250°C at 100 bar pressure) (Rahaman, 2014) (Fig. 2).

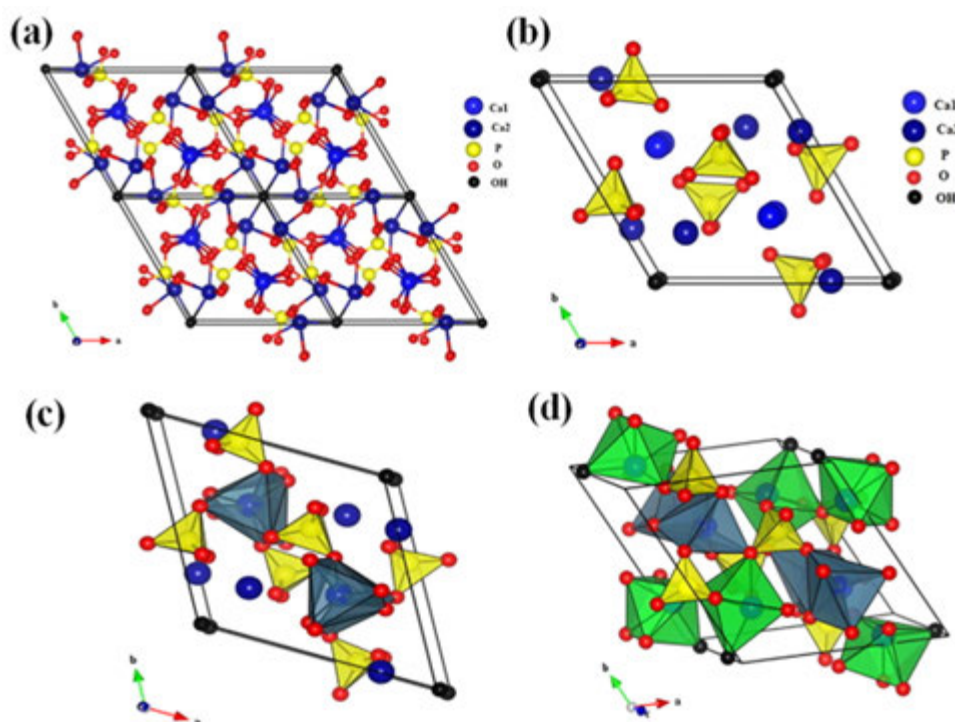


Fig. 2 Crystalline structure of the unit cell of HA. Picture (a) shows the overall projection according to plan (001). The other insets show (b) the arrangement of octahedrons [Ca(1)O₆], (c) octahedral [Ca(1)O₆] and tetrahedral [PO₄] and (d) octahedral [Ca(1)O₆] and [Ca(2)O₆] together with tetrahedral [PO₄], respectively. Figure reproduced from reference Fihri, A., Len, C., Varma, R.S., Solhy, A., 2017. *Coord. Chem. Rev.* 347, 48–76, with permission of Elsevier.

Materials obtained following these routes maintain the natural three dimensional macrostructure of natural HA (i.e., an interconnected macroporosity similar to trabecular bone) and are usually characterized by consistent variations in formulation (Jeong *et al.*, 2019). As a matter of fact, HA in general is prone to elemental substitution such as Mg, Sr or CO₃ (Graziani *et al.*, 2018). This property leads to the fact that harvesting pure natural HA is nearly impossible, a great complication for process reproducibility (Jeong *et al.*, 2019). In turn, the substitution of ions or atomic clusters in synthetic HA is a well-established approach to modify the properties of the material and enhance it with diverse beneficial physicochemical and therapeutic effects (Graziani *et al.*, 2018; Ratnayake *et al.*, 2017; Cacciotti, 2016; Tite *et al.*, 2018). For example, silicon can substitute calcium ions, enhancing osteoid calcification during the early stages of mineralization even in trace amounts (Sprio *et al.*, 2008; Gibson *et al.*, 1999; Thian *et al.*, 2006). Si-substituted HA has increased bioactivity and can release Si ions that are demonstrated to stimulate osteogenesis (see section on Bioactive Glasses below) (Thian *et al.*, 2006). Copper, strontium, selenium and zinc ions have been also successfully substituted into the HA lattice and it was demonstrated that such substitutions can have several therapeutic effects, promoting osteogenesis and angiogenesis or having antimicrobial properties (Ratnayake *et al.*, 2017; Tite *et al.*, 2018; Mouriño *et al.*, 2012).

Tricalcium phosphates

Beside HA, TCP is the second main calcium phosphate used in medical devices, with several products using this material already on the market, mostly in the field of orthopedic fixation and bone fillers (Rahaman, 2014; Liu and Lun, 2012). TCPs are also widely studied as fillers for tissue engineering composite scaffolds (Samavedi *et al.*, 2013). There are two relevant polymorphs of TCP that are stable at atmospheric pressure. The main phase stable at room temperature is β -TCP. This polymorph can be produced by heating at 800–1000°C a precursor of ACP previously synthesized by precipitation (Liu and Lun, 2012). By applying a thermal treatment at $\sim 1125^\circ\text{C}$, the β -polymorph can be turned in more soluble and reactive α -TCP. This is a type of TCP that undergoes rapid direct hydrolysis upon contact with water, turning from a liquid slurry into solid HA, a characteristic that makes α -TCP an ideal candidate material for in situ setting and injectable bone cements (Carrodeguas and Aza, 2011). The more stable β -TCP, on the other hand, is most commonly used as constituent material for tissue engineering scaffolds with lower degradation rates and superior mechanical properties (Liu and Lun, 2012). Similarly to HA, TCPs can be used as carriers of dopant ions. It was demonstrated that substitution is an effective strategy to stabilize the β -phase and to increase the sinterability of β -TCP without the occurring of unwanted polymorphs (Bose *et al.*, 2011). Ions and ion clusters can also modify the overall physicochemical, mechanical, and biological properties of the final material. Some relevant examples are magnesium and strontium. The inclusion

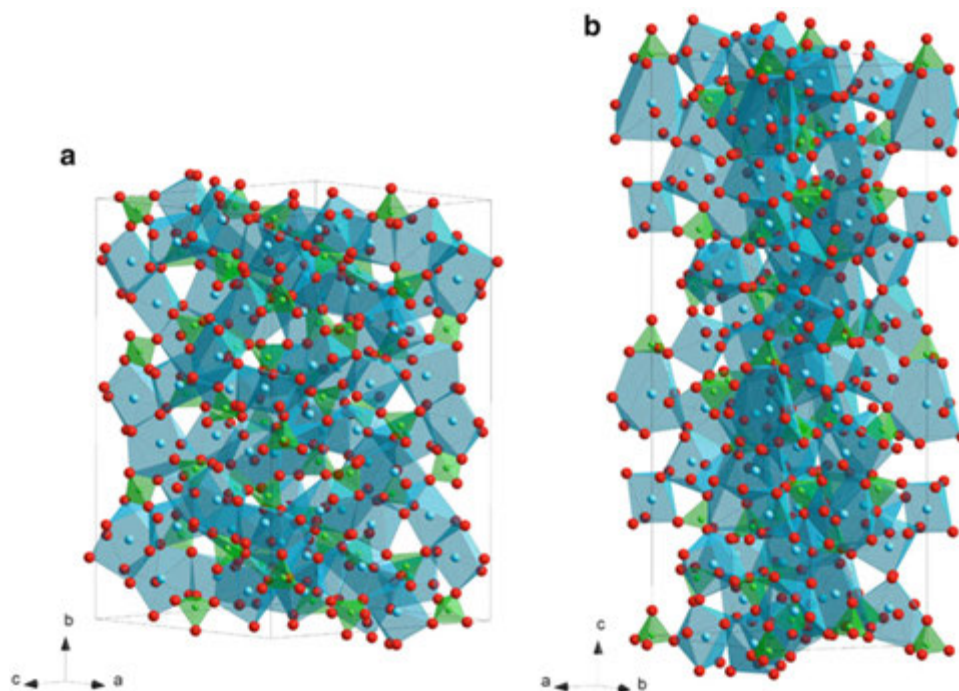


Fig. 3 Crystal structures of α -TCP (a) and β -TCP (b). Picture reproduced from reference Goto, T., Katsui, H., 2015. *Interface Oral Health Science* 2014. Tokyo: Springer, pp. 103–115, with permission of Elsevier.

of these two ions within the TCP lattice was found to significantly improve phase stability and degradation rate while at the same time eliciting a positive effect on the growth of bone cells (Habibovic and Barralet, 2011) (Fig. 3).

In general, HA and TCP can be considered materials with complementary properties: HA is typically almost non-degradable and mechanically stronger than TCP, which in turn degrades faster and has inferior mechanical strength (Rahaman, 2014). In case intermediate properties are needed, a common viable strategy is to combine the two materials into an appropriate formulation of biphasic calcium phosphate (BCP) (Legeros *et al.*, 2003). The degradation rate of BCP can be controlled by varying its HA/ β -TCP ratio. In particular, the higher the HA/ β -TCP ratio the slower the degradation will be (Rahaman, 2014; Legeros *et al.*, 2003). Several methods are available for the production of BCP, mainly thermal treatment of Ca-deficient HA above 700°C, hydrolysis of DCPD and direct wet precipitation of calcium nitrate and diammonium phosphate (Kivrak and Taş, 2005).

Bioactive Glasses

General characteristics

The use of glasses for biomedical applications started in the late 1960s, when Professor Larry Hench and collaborators reported for the first time the unique ability of a specific silicate-based glass formulation (i.e., 45S5, later named Bioglass®) to form a strong bond to bone (Kivrak and Taş, 2005). 45S5 bioactive glass (BG) is based on a three-dimensional glass-forming SiO_2 network (45wt%) containing 24.5% Na_2O , 24.5% CaO and 6% P_2O_5 (in weight). It has high reactivity and high degradation rate in water. Over the course of the years, several other types of bioactive glasses were synthesized (Table 1) (Jones, 2013). Initially, novel compositions were developed by synthesizing small variations from the initial 45S5 formulation. In particular, the addition of glass modifiers (K_2O , MgO) was investigated to tailor the processing and physicochemical properties of the glass (Hench *et al.*, 1971). More recently, research has also focused on the doping of BGs with additional elements with attractive biological properties and therapeutic effects (biologically active ions) (Mouriño *et al.*, 2012). In addition, other glass-forming networks have been increasingly investigated. The possibility to synthesize glasses with borate and phosphate networks was demonstrated and proved itself to be a very promising strategy for the preparation of novel bioactive glasses, which expands BG applications to wound healing and soft tissue engineering (Miguez-Pacheco *et al.*, 2015).

Bioactive glasses are traditionally synthesized by conventional melt-quenching (Jones, 2013). Typically this process involves glass precursors in proper amounts to be decarbonated at around 950°C, then molten in a crucible above 1400°C and finally fast quenched in water (to retain the amorphous structure and avoid crystallization). The frit is then ground to powder. Alternatively, several formulations of bioactive glass can be produced via sol-gel method (Arcos and Vallet-Reg, 2010; Baino *et al.*, 2018a). This approach consists of the formation of a silica network by acidic- or alkali-catalyzed hydrolysis, condensation and polymerization of low molecular precursors at or near room temperature. The solution of precursors will progressively polymerize and turn into a gel that can then be dried by simple solvent casting. Sol-gel bioactive glasses possess properties that are not characteristic of similar

Table 1 Compositions (in wt%) of some notable silicate, borate and phosphate bioactive glasses

	Name	SiO ₂ (wt%)	CaO (wt%)	Na ₂ O (wt%)	P ₂ O ₅ (wt%)	K ₂ O (wt%)	MgO (wt%)	B ₂ O ₃ (wt%)
Silicate	45S5	45.0	24.5	24.5	6.0	–	–	–
	13–93	53.0	20.0	6.0	4.0	12.0	5.0	–
	58S	58.2	32.6	–	9.2	–	–	–
	70S30C	71.4	28.6	–	–	–	–	–
	S53P4	53.0	20.0	23.0	4.0	–	–	–
	6P53B	52.7	18.0	10.3	6.0	2.8	10.2	–
	ICIE16 (Elgayar <i>et al.</i> , 2005)	48.0	32.9	6.6	2.5	10.0	–	–
Borate	13–93B1	34.4	19.5	5.8	3.8	11.7	4.9	19.9
	13–93B3	–	18.5	5.5	3.7	11.1	4.6	56.6
	0106-B2	25.0	22.6	5.9	4.0	12.0	5.5	25.0
Phosphate	Meta (Bitar <i>et al.</i> , 2004) (O/P = 3)	–	34.2	6	59.8	–	–	–
	Invert (Walter <i>et al.</i> , 2001)	–	26.7	14.9	41.5	–	16.9	–

melt-based formulations (Jones, 2013). Most importantly, they have intrinsic mesoporosity (i.e., pore size of 5–20 nm) (Baino *et al.*, 2018a) and can be directly processed into desired shapes and structures during the sol phase (e.g., by electrospinning) (Kim *et al.*, 2006). The absence of high temperatures and the mesoporous structure make sol-gel bioactive glasses ideal for the loading and delivery of drugs and delicate and sensitive biomolecules (Baino *et al.*, 2017). It also allows for the formation of organic/inorganic hybrids, a novel category of materials attracting ever-growing interest thanks to their unique properties (Jones, 2013; Hench and Jones, 2015; Poologasundarampillai and Maçon, 2017). On the downside, sol-gel glasses usually have lower mechanical strength and higher degradation rates compared to melt-quenched ones, possibly due to the higher porosity intrinsic of the sol-gel route, and are generally considered not suitable for high load bearing applications (Jones, 2013). Similarly, as fillers in biocomposites, they are not normally used to increase mechanical properties, but to bring high bioactivity, drug delivery capability and other biologically relevant features to the polymeric matrix (Hench and Jones, 2015).

Silicate bioactive glasses

As previously described, the field of bioactive glasses in biomedical applications started with silicate bioactive glasses and with the formulation called 45S5 in particular, the first glass produced specifically to form a strong bond with bone. Through the decades, 45S5 Bioglass® was thoroughly studied, processed and combined with other materials, including poly(lactic acid) and poly (caprolactone) (Boccaccini *et al.*, 2010; Rezwan *et al.*, 2006), collagen (Vargas *et al.*, 2013) and alginate (Leite *et al.*, 2016; Sarker *et al.*, 2016) to make TE scaffolds. The mechanism of BG bioactivity has been also described in detail (Hoppe *et al.*, 2011; Fiume *et al.*, 2018). Briefly, 45S5 Bioglass® and other silicate BGs bond to bone thanks to the formation of a carbonate-substituted HA layer (HCA) at the surface of the glass upon contact with body fluids. HCA is highly similar to bone native minerals and it is thought to foster the adsorption of growth factors and, in turn, the guidance of cell adhesion, proliferation and differentiation into osteoblasts (Hoppe *et al.*, 2011). These cells will be triggered by the biological surroundings to produce bone ECM (collagen), which will then mineralize at the interface, progressively and seamlessly linking the material and the tissue together while the glass degrades. In particular, in the case of 45S5 BG, bioactivity is well correlated with some key compositional features of the glass: (1) a low SiO₂ content that determines lower chemical durability compared to silicate glasses; (2) high content of network modifiers (Na₂O and CaO) that reduces the network connectivity (NC) and consequently increases the degradation rate and, finally, (3) high CaO/P₂O₅ ratio (Hoppe *et al.*, 2011). 45S5 BG degrades relatively quickly (Jones, 2013). Its degradation products can be metabolized by the organism and as such the material can be called bioresorbable. The main by-products are cations (Na⁺ and Ca²⁺) that are naturally present in the body and silicon compounds, most probably silicic acid, Si(OH)₄ (Hench and Jones, 2015). The latter was most likely proved harmless, as in vivo studies on rabbit showed that it is excreted in soluble form via urine (Lai *et al.*, 2002). In spite of its strong asset of beneficial properties, 45S5 BG comes with some limitations, mostly in terms of processability. In fact, the thermal treatment of Bioglass® is challenging due to the narrow window of temperature between the glass transition temperature (T_g) and the onset of crystallization (Chen *et al.*, 2006). Heating Bioglass® often causes its partial crystallization into combeite, resulting in a glass-ceramic (Rahaman, 2014). This devitrification is a non-controlled phenomenon that can irregularly cause the decrease of mechanical properties, reduced degradation rate and reduced rate of conversion to HA (“slower” bioactivity, sometimes incomplete conversion to HA) (Rahaman, 2014). Processing methods that use high temperatures, such as extrusion-based techniques (composite extrusion, fused deposition modeling), will have to take into account this problem and try minimizing its repercussions. Another disadvantage of 45S5 BG is that in some cases its high reactivity and dissolution rate can determine a local raise in pH that could hinder its biocompatibility (Cirraldo *et al.*, 2018a). For these and other reasons, research has focused in the past decades on the identification of other formulations of silicate bioactive glasses that could tackle the limitations of the original composition when needed (Elgayar *et al.*, 2005). For instance, the notable 13–93 composition was developed by Brink *et al.* increasing the SiO₂ fraction (53wt%) and decreasing the remaining components (20wt% CaO, 6wt% Na₂O and 4wt% P₂O₅) to allow for the addition of two additional network modifiers, namely K₂O (12wt%) and MgO (5wt%) (Sharmin *et al.*, 2017; Brink, 1997). Compared to 45S5, 13–93 bioactive glass degrades and converts to HA at a slower rate.

However, it has better processing properties, in particular it can be processed by viscous flow sintering creating sintered structures without relevant crystallization (Brink, 1997). In terms of biological properties, there is no significant difference between the two silicate bioactive glasses. Studies confirmed that several cell types (e.g., MC3T3-E1 or MLO-A5) have similar proliferation and differentiation toward an osteoblast phenotype when in contact with either glass formulations (Brown *et al.*, 2008). Similarly, 6P53B glass (52.7wt% SiO₂, 18wt% CaO, 10.3wt% Na₂O, 6wt% P₂O₅, 10.2wt% MgO and 2.8wt% K₂O) is another notable Mg- and K-containing BG formulation with increased silica content, which was developed aiming at reduced degradation rate and enhanced processability (Pazo *et al.*, 1998). It is particularly used for the production of inorganic scaffolds by additive manufacturing (robocasting). Simpler compositions, such as 58S (58.2wt% SiO₂, 32.6wt% CaO and 9.2wt% P₂O₅) and 70S30C (71.4wt% SiO₂, 28.6wt% CaO), are also widely studied and were initially developed in relation to the sol-gel method, as compositions with fewer elements, and especially fewer network modifiers, are more reproducible (Jones, 2013). Finally, it is important to mention the S53P4 BG composition, another well-known BG (53wt% SiO₂, 20wt% CaO, 23wt% Na₂O and 4wt% P₂O₅), closely related to 45S5 BG and currently commercialized under the name BonAlive® (McAndrew *et al.*, 2013).

Borate bioactive glasses

In alternative to silicon oxide, boron oxide can be also used as a network former. Starting from the 13–93 silicate glass composition, the silica fraction was replaced with boron either partially (e.g., 13–93B1, 34.4wt% SiO₂, 19.9wt% B₂O₃, 19.5wt% CaO, 5.8wt% Na₂O, 3.8wt% P₂O₅, 4.9wt% MgO and 11.7wt% K₂O) or completely (i.e., 13–93B3, 56.6wt% B₂O₃, 18.5wt% CaO, 5.5wt% Na₂O, 3.7wt% P₂O₅, 4.6wt% MgO and 11.1wt% K₂O) (Fu *et al.*, 2010a,b). Compared to silicate bioactive glasses, borate formulations are less chemically durable and degrade faster once in contact with body fluids (Fu *et al.*, 2010b). This behaviour determines that borate bioactive glasses usually have a higher conversion rate to HA, compared to 13–93 or even 45S5 BGs (Liu *et al.*, 2013), but at the same time it raises concerns about possible toxic effects: high release of (BO₃)³⁻ ions is known to be cytotoxic (Landolph, 1985), as in vitro studies on murine MLO-A5 cells have confirmed (Fu *et al.*, 2010a). Fortunately, ion concentration reaches dangerous levels only when observed in static in vitro models. Boron blood concentration levels were monitored in a rabbit tibiae model and were found to be far below the toxicity level (Zhang *et al.*, 2010b). In addition, no adverse nephrotoxic or hepatotoxic effect due to 13–93B3 was assessed when testing glass granules in vivo in a subcutaneous rat model (Rahaman, 2014). Non-toxic borate ion concentrations were actually associated with therapeutic effects both in terms osteogenesis and angiogenesis, thanks to their activation of MAPK signaling (Capati *et al.*, 2016) and upregulation of VEGF and TGF-β1 growth factors (Dzondo-Gadet *et al.*, 2002), respectively. To further strengthen the safety of borate bioactive glasses, the possibility to manipulate and control their degradation behavior was investigated. In particular, it was observed that the glass degradation rate can be significantly reduced by increasing the silicate content and it is maximized in purely borate glasses (Fu *et al.*, 2010b). Compositional variations can also be useful to introduce in the glass trace elements that favor bone growth, angiogenesis or tackle bacterial colonization. For instance, 13–93B3 was doped with 0.4wt% CuO and implanted in a rat subcutaneous site, finding that the addition of copper can effectively enhance angiogenesis (Bi *et al.*, 2012). Thanks to their highly tailorable degradability and ease of manufacture borate bioactive glasses are a novel very promising alternative to silicate-based ones. As a matter of fact, medical devices based on this class of glasses are already on the market: a non-woven wound healing mash (Mirragen®) was recently developed and commercialized by ETS Wound Care, USA (Bi *et al.*, 2012). The device also recently obtained FDA clearance. The mash is specifically developed for chronic wounds and can support and improve skin regeneration thanks both to its fibrous structure and the quick release of therapeutic ions from high degradation rate borate glass (Fiume *et al.*, 2018; Baino *et al.*, 2018b).

Phosphate bioactive glasses

In recent years, the synthesis and applications of phosphate bioactive glasses have been also explored (Brauer, 2012; Knowles, 2003). Phosphate bioactive glasses are based on the glass-forming properties of P₂O₅ using CaO and Na₂O as primary modifiers (Brow, 2000). They are usually divided in three families depending on the phosphate content: ultraphosphate glasses, with more than 50 mol% of P₂O₅ (2.5 < O/P < 3), metaphosphate glasses, with a P₂O₅ content of 50 mol% (O/P = 3) and polyphosphate glasses when the phosphate content is lower than 50 mol% (O/P > 3) (Knowles, 2003). In addition, so-called invert glasses can be produced with less than 33.3 mol% phosphate (Walter *et al.*, 2001). In these glasses, the network is formed by orthophosphates and pyrophosphates and the fraction of complementary elements (e.g., calcium, sodium) is higher than the phosphate content. Invert glasses offer a possible compositional solution to reduce glass hydrolysis, however they are difficult to manufacture due to their narrow processing window (Walter *et al.*, 2001). Likewise other bioinorganic platforms, phosphate-based glasses can be used as therapeutic ion carrier by selective doping with specific trace elements within the network (e.g., copper, boron, strontium or selenium) (Łapa *et al.*, 2019).

Phosphate bioactive glasses are constituted by the main elements of the mineral phase of bone (calcium and phosphate) and, as such, they offer a strategy to avoid the long term persistence of network formers (e.g., silicon) in vivo (Knowles, 2003). They are highly resorbable (they are often deemed “soluble”) (Navarro *et al.*, 2005) and versatile in terms of degradation rate, which can be vastly tailored by changing the chemical composition (Sharmin *et al.*, 2017). In addition, they are characterized by good processability, in particular by melt fiber drawing (Rinehart *et al.*, 1999; Muñoz-Senovilla *et al.*, 2017; Massera *et al.*, 2014). However, differently to the more common silicate ones, phosphate glasses are generally characterized by relatively faster and more acidic degradation (i.e., local pH lowers significantly during dissolution in buffer solutions) (Rinehart *et al.*, 1999). Some formulations of phosphate glasses, especially ternary CaO–Na₂O–P₂O₅, are characterized by very fast degradation (i.e., within 7 days) and great

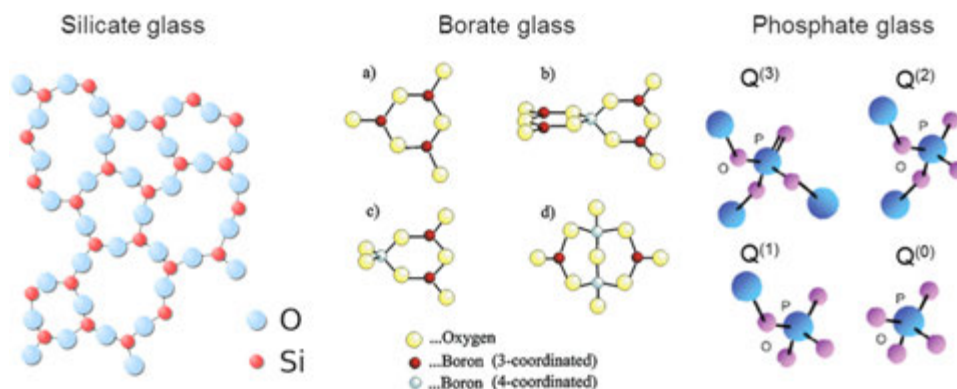


Fig. 4 Schematic representation of the network structure of silicate, borate and phosphate glasses (left to right).

reduction in local pH (Salih *et al.*, 2000; Ahmed *et al.*, 2004). However, as typical for most bioactive glass systems, these issues can be solved by compositional modifications (Abou Neel *et al.*, 2008). Most remarkably, studies showed that the weight loss and release of ions from phosphate glasses follow a steady linear trend, compared to the burst/plateau release trend of silicate networks (Rahaman, 2014). The linear release of ions is considered a key difference between phosphate and silicate bioactive glasses and a strong asset of the former (Fig. 4).

Other bioactive ceramics

Besides calcium phosphates and bioactive glasses, numerous other materials are being investigated as bioactive fillers of polymer-based biocomposites for bone tissue engineering. A typical approach is to use other calcium-containing ceramics, mainly calcium silicates or calcium carbonates. Diopside ($\text{CaMgSi}_2\text{O}_6$), akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$), bredigite ($\text{Ca}_7\text{MgSi}_4\text{O}_{16}$) and, above all, wollastonite (CaSiO_3) were reported as main calcium silicate alternatives to CaPs and BGs in bone tissue engineering, especially thanks to their superior mechanical properties (Wu and Chang, 2013; No *et al.*, 2017). In particular, the interest in the use of wollastonite grew in the past decade due to higher reported bioactivity compared to other silicates (Wu and Chang, 2013). Several reports demonstrate the possibility to use this calcium silicate for the preparation of inorganic 3D porous scaffolds as well as of biocomposites (Li and Chang, 2005a; Ye *et al.*, 2008; Mostafa and Zaki, 2015). Similarly to other bioceramics, wollastonite degrades releasing calcium and silicon ions, which are known to be able to enhance osteogenic and angiogenic differentiation and to trigger biomineralization (i.e., bioactivity), as demonstrated by several studies both in vitro and in vivo (Wu and Chang, 2013). As mentioned above, calcium carbonates (calcite and aragonite) were also investigated as possible biomaterials for tissue engineering, owing to their bioactivity and resorbability (Peng *et al.*, 2016; Lopez-Heredia *et al.*, 2017). In particular, a promising calcium carbonate-based material of natural origin is nacre. Nacre can be obtained from mussels. It structurally consists of an inorganic aragonite lamellar phase dispersed within an organic matrix. Previous studies demonstrated its biocompatibility, bioactivity and osteoconductivity. Most remarkably, nacre has outstanding mechanical properties that can be ascribed to its highly organized structure that makes it highly competitive against other bone tissue engineering biomaterials. The use of bulk nacre as well as of composites of it with polymers (e.g., various saturated poly- α -hydroxy esters, polyhydroxyalkanoates) were explored and recently reviewed elsewhere (Gritsch *et al.*, 2019; Deville *et al.*, 2006; Gerhard *et al.*, 2017).

Due to its bioresorbability and its important role in bone remodeling and skeleton development, magnesium and its oxide (MgO) were also investigated as bioactive filler to a polymer phase (Hickey *et al.*, 2014; Diba *et al.*, 2014). Mg ions have been linked to a number of important physiological events. They seem to have an effect in increasing differentiation towards the osteogenic phenotype and regulating the activity of osteoblast integrins and their ability to attach to the substrate. In particular, Mg^{2+} can bond to integrins α subunits, modulating cell affinity to the biomaterial surface (Wong *et al.*, 2014). Besides the possibility of substituting Mg ions within the networks of previously described bioceramics (e.g., Mg-HA, Mg-diopside or Mg-containing bioactive glasses), magnesium has been explored as a possible filler both as metallic or MgO micro- and nanoparticles (Hickey *et al.*, 2014; Diba *et al.*, 2014; Wong *et al.*, 2014; Nasri-Nasrabadi *et al.*, 2018). Magnesium microparticles introduced in a polycaprolactone matrix, for example, were found to increase both the native mechanical properties and bioactivity of the polymer (Suryavanshi *et al.*, 2017). Magnesium oxide offers further advantages, as it is known to be an effective antibacterial agent with significantly easier handling and higher shelf life compared to the bare metal. Interestingly, MgO was found to be more biologically effective when formed as particles compared to the bulk, making it an ideal candidate as filler for bioresorbable composites (Hickey *et al.*, 2014).

Another relevant oxide reported as filler in biocomposites is titanium dioxide (TiO_2) (Gerhardt *et al.*, 2007; Wei *et al.*, 2008; Haldorai, 2018; Kim *et al.*, 2014b). Titanium oxide naturally forms on titanium surfaces when in contact with body fluids. It has excellent biocompatibility and it can regulate osteoblast differentiation. The actual mechanism of action is still under investigation and it is not clear whether osteoblast differentiation is affected by the titanium oxide itself or by oxygen released from the material (Santiago-Medina *et al.*, 2015). Some authors suggest that oxygen tension can increase in presence of titanium oxide and that it can

have a strong effect on osteoblast differentiation (Nicolaije *et al.*, 2012). Results seem to confirm that hypoxia shifts differentiation from the osteogenic to the chondrogenic phenotype (Heppenstall *et al.*, 1976). In general, the influence of TiO₂ on the gene expression of osteoblast cells was confirmed (Santiago-Medina *et al.*, 2015; Salim *et al.*, 2004). However, the effect of titanium oxide goes beyond chemotaxis: physical factors such as roughness and other microstructural features play a particularly important role in determining the biological properties of this material (Santiago-Medina *et al.*, 2015). For instance, when combined with poly(D,L-lactic acid) (PDLLA) (Gerhardt *et al.*, 2007; Wei *et al.*, 2008), TiO₂ was found to improve the nanometric features and roughness of the polymer alone, resulting in a nanometric topography that resembles the one of native bone (Gerhardt *et al.*, 2007). This difference in topography was linked with an increase in HA formation and with increased osteoblast adhesion on the surface of composite specimens with high TiO₂ loading. No bioactivity was assessed either on the polymer alone, on TiO₂ nanoparticles or on composites with low filler content (Gerhardt *et al.*, 2007). This suggests that high nanoparticle content, determining an increase in surface roughness, may improve both cell adhesion and bioactivity. Similar promising results were obtained with natural polymers, such as chitosan (Haldorai, 2018) and silk fibroin (Kim *et al.*, 2014b).

In the past decade, carbon nanotubes (CNTs) have emerged as a very promising candidate biomaterial, fostering rich literature on the topic (Li *et al.*, 2010; Sahithi *et al.*, 2010; Zhang *et al.*, 2010a; Beg *et al.*, 2011). They are a relatively recent class of nanomaterials discovered in 1991 (Iijima, 1991), an allotrope of carbon consisting of an hexagonal lattice bent on itself to form a hollow cylinder. Among their several other applications, it was demonstrated that CNTs can be used by themselves for the fabrication of pure-CNTs scaffolds, as reported for instance by Tanaka *et al.* (2017), where the group reported the production of porous constructs by foaming. As an alternative, CNTs can be incorporated into a composite with either polymeric (Magiera *et al.*, 2017; Kaur *et al.*, 2017) or inorganic (Bai *et al.*, 2010; Boccaccini *et al.*, 2007) matrices. These composites generally have highly increased mechanical properties compared to the native polymer, thanks to the outstanding tensile strength and flexibility of CNTs, but at the same time high integrity and low brittleness owing to the bonding capability of the polymer (e.g., polycaprolactone or polypropylenefumarate, see following section) (Mattioli-Belmonte *et al.*, 2012). Despite their remarkable physical properties, one reason that prevented the spreading of investigation on CNTs is the concern that exists regarding their safety (Padmanabhan and Kyriakides, 2015; Ema *et al.*, 2016). The debate over their biocompatibility is indeed still open, as some studies reported possible cytotoxic effects upon degradation (Francis and Devasena, 2018), while others endorse their biological compatibility, even showing improvements in terms of cell adhesion and proliferation (Kaur *et al.*, 2017; Cheng *et al.*, 2013). Further investigations will have to look more in-depth at this controversial point in order to understand what will be the future of CNTs in biomaterials science.

Biodegradable Polymer Matrices

The matrix of a composite tissue engineering scaffold is responsible for holding together the structure, bonding the filler particles/fibers, while at the same time providing a suitable substrate for cell attachment and proliferation. Several different materials and combinations of them have been proposed over the years, each one with properties that suit specific applications and with synergies with specific bioceramics. Generally speaking, biodegradable polymers are divided into two categories depending on their origin: synthetic or natural. Synthetic polymers, principally saturated and unsaturated polyesters, have the advantage of complete control over key properties like degradation kinetics, mechanical behavior or pore structure and size. However, they usually are hydrophobic and biologically inert. On the other hand, natural polymer mimic closely the structure or even the composition of the ECM. They are high in water content, bioresorbable, biocompatible and usually more biologically active (i.e., can elicit specific responses from cells) than synthetic polymers. Yet, their origin and the need to extract them from natural sources imply that they are (1) less available, (2) with more irregular physical properties and (3) more often immunogenic, in comparison with synthetic polymers. In this section, the key synthetic and natural polymers for the production of biocomposites are listed and their properties discussed. In particular, the reasons to combine them into composites and the bioceramics they were combined with will be mentioned.

Synthetic Polymers

Saturated poly- α -hydroxy esters

Saturated poly- α -hydroxy esters are probably the most widespread family of synthetic biodegradable polymers used in the fabrication of biocomposites for tissue engineering and other biomedical applications (Li, 2017; Zhou *et al.*, 2012; Habraken *et al.*, 2007). The most notable examples of this class are linear polymers synthesized from glycolic acid, lactic acid (both L and D stereoisomers) and ϵ -caprolactone monomers, or copolymers of the above. Their popularity is due to their biocompatibility, their tailorable mechanical and degradation properties and their versatility (Li, 2017; Vert *et al.*, 1992; Girones Molera *et al.*, 2012). The possibility to synthesize a wide range of copolymers makes saturated poly- α -hydroxy esters a very powerful toolbox for the fabrication of polymers with very diverse properties by varying the molecular weight, the monomers and the stereoregularity (Vert *et al.*, 1992, 1994). In addition, they are easy to process through a wide spectrum of typical forming methods, such as film casting, foaming, fiber spinning and most thermoforming approaches (e.g., extrusion, injection molding) (Gritsch *et al.*, 2019). Thanks to their convenient mechanism of degradation and processability, these bioresorbable polymers are approved by the FDA for use in

various devices in contact with body fluids and are currently under commercial use in several medical applications (Lunt, 1998; Malikmammadov *et al.*, 2018). The main mechanism of biodegradation of saturated poly- α -hydroxy esters consists of de-esterification through hydrolytic degradation (Schwach and Vert, 1999). Once in contact with body fluids, the polymer uptakes water and the reaction is catalyzed by both acids and alkalies in solution. Polyester hydrolysis can be also autocatalyzed by the terminal carboxylic acids of the polymer chains. Most importantly for medical applications, the degradation by-products of these polymers can be readily disposed by the organism through physiological pathways, mainly by the citric acid cycle (CAC). Degradation kinetics are affected by a wide range of parameters, including chemical structure, molecular weight (MW), polydispersity (PD), crystallinity, additives, device size and morphology, mechanical stress/strain, processing techniques and environmental conditions (Vert *et al.*, 1992, 1994). For instance, for both poly(glycolide-co-lactide) and poly(DL-lactide) the degradation kinetics highly vary depending on the content of L- and D-lactic acid monomers (Kimura, 2009). In spite of their several advantages, this class of polymer presents a major drawback: especially for thick structures, degradation tends to proceed heterogeneously and from the bulk of the materials (Grizzi *et al.*, 1995). Bulk erosion is very dangerous, as it can cause premature failure of the device, abrupt release of by-products and quick pH drop, which in turn can trigger a strong inflammatory response (Schwach and Vert, 1999; Grizzi *et al.*, 1995). Generally, the phenomenon is thought to be caused by a joint effect of the adsorption of degraded oligomers into the inner side of the device, the autocatalytic effect of carboxylic end groups of the polymer and the neutralization of surface pH by the buffer (both in vitro and in vivo) (Schwach and Vert, 1999; Siparsky *et al.*, 1998).

The acidic degradation of PLA, PGA, PCL and their copolymers poses significant limits to their use in biomaterials science, as the materials have been implicated in adverse tissue reactions, especially in the case of massive devices (Ramot *et al.*, 2016; Narayanan *et al.*, 2016). In the last decades, research focused on the identification of possible strategies to reduce autocatalysis and pH decrease of these polyesters in order to enhance their biocompatibility and control their degradation. Review papers are available, discussing in-depth how to tackle the consequence of the hydrolysis of saturated poly- α -hydroxy esters (Valentina *et al.*, 2017; Shasteen and Choy, 2011). Among other possible approaches, a major cost-effective strategy is to prepare composites combining these polymers with bioinorganic species such as bioactive glasses (Boccaccini *et al.*, 2010; Blaker *et al.*, 2005; Conoscenti *et al.*, 2018) and calcium phosphates (Rezwan *et al.*, 2006; Zhou *et al.*, 2012; Danoux *et al.*, 2014). In fact, the possibility of counteracting the acidic degradation of many biodegradable polymers is one of the main reasons that justifies the use of composites. PLA- and PGA-based polymers are probably the most widely studied materials in this sense. Several isomers of PLA and copolymers with PGA were combined with an array of different bioactive glasses, including 45S5 (Eqtesadi *et al.*, 2016b; Rezabeigi *et al.*, 2016; Simpson *et al.*, 2015), 13–93 (Xiao *et al.*, 2017; Eqtesadi *et al.*, 2016a) and doped compositions (e.g., strontium) (Lee *et al.*, 2019), calcium phosphates (Zhou *et al.*, 2012; Danoux *et al.*, 2014; Shin *et al.*, 2018) and silicates (Su *et al.*, 2017), metal oxides (Marra *et al.*, 2016) and carbon based nanomaterials (Gonçalves *et al.*, 2017). Similarly, PCL has been also combined with several different phases using various techniques, as thoroughly summarized in a recent review (Hajiali *et al.*, 2018).

Polypropylene fumarate

Polypropylene fumarate (PPF) is, just like PLA or PGA, a linear polyester based on propylene glycol and fumaric acid, a component of the CAC (Yan *et al.*, 2011). Contrarily to saturated poly- α -hydroxy esters, PPF has the advantage of containing unsaturated bonds (Kasper *et al.*, 2009). These C–C double bonds allow for crosslinking of the polymer into a covalent network either alone or in combination with other moieties (e.g., N-vinyl pyrrolidone, poly(ethylene glycol)-dimethacrylate) (Kasper *et al.*, 2009; He *et al.*, 2000). Molecular weight distribution, unsaturation ratio and crosslinking degree of PPF can be controlled in order to tailor its degradation rate and mechanical properties. In addition, when combined with appropriate initiators, PPF can be used for the development of injectable platforms for in situ crosslinking (He *et al.*, 2000). The molecular characteristics of PPF will be key in shaping the material depending on the specific application: high MW and polydispersity PPF can reach very high viscosities before crosslinking and be very hard to handle and mold into shape. The complexity in processability is generally considered one of the major drawbacks of this family of polymers (Rezwan *et al.*, 2006). In terms of degradation, PPF is degraded hydrolytically similarly to saturated poly- α -hydroxy esters into biocompatible by-products that can be readily removed from the body through physiological pathways. Compared to saturated polyesters, PPF is characterized by lower acidification upon degradation and as such it is a very promising strategy to overcome the drawbacks of PLA-based technologies (Rezwan *et al.*, 2006; Kasper *et al.*, 2009). As a matter of fact, several PPF-based approaches were explored aiming at its biomedical application for orthopedic implants, tissue engineering scaffolds and controlled drug delivery (Cai *et al.*, 2019). In particular, in the context of tissue engineering and regenerative medicine, PPF and its composites have been investigated for the development of injectable substitutes, combining this very promising polymer with bioactive ceramic particles, β -TCP and HA in particular (Diez-Pascual, 2017; Westbrook, 2016). However, in spite of the encouraging results obtained so far, PPF has been investigated to a lesser extent, in comparison with the extensive research published on composites of saturated poly- α -hydroxy esters.

Biodegradable polyurethanes

Polyurethanes (PU) are a family of polymers composed of monomers linked together by carbamate, or urethane bonds (Burke and Hasirci, 2004; Sobczak, 2015). They are mostly thermosetting and as such unsuitable for temperature-based fabrication techniques (Hasirci and Aksoy, 2007). There are however studies reporting the synthesis of thermoplastic polyurethanes that can be, for example, extruded and 3D printed (Mi *et al.*, 2014; Cui *et al.*, 2019). In a typical synthesis, a polyisocyanate or an isocyanate-terminated prepolymer is reacted with a polyol to give an alternating chain copolymer of the two. In the case of polyurethane for bone grafts, the polyisocyanates used are most frequently either lysine- or hexamethylene diamine-derived, as they offer good

performance with lower toxicity compared to standard aromatic polyisocyanates (Hasirci and Aksoy, 2007). The degradability of polyurethanes depends on their chemical structure. There are non-biodegradable, inert PU as well as highly biodegradable ones. In particular, it is the polyol component that determines greatly the degradation rate of the final cured polymer (Hasirci and Aksoy, 2007). For instance, polyurethanes based on polycarbonate hydrolytically degrade slower than the ones based on polyethers, which in turn degrade slower than polyester-based PU (Hasirci and Aksoy, 2007). The advantage of polyurethanes in bone tissue engineering is to have a very versatile platform that permits the exploration of diverse properties depending on the specific selected chemistry. The product of polyurethane synthesis can in fact be finely tailored in its properties by mindful control of the initial reagents. Polyurethanes offer a superior solution in terms of synthesis-tailored mechanical and degradation properties, non-toxic degradation by-products and drug carrying capability (Burke and Hasirci, 2004). Their setting behavior makes them ideal candidates for the development of injectable biomaterials. Furthermore, they possess the intrinsic ability to be formed into porous foams, ideal for tissue engineering, by simple synthesis in presence of water (Guelcher *et al.*, 2004). Bioactive fillers can be added to the polymer in order to create a biocomposite with superior properties. In particular, promising results have been obtained combining polyurethanes with 45S5 bioactive glass (Ryszkowska *et al.*, 2010), HA (Cui *et al.*, 2019), fluorapatite (Asefnejad *et al.*, 2011), β -TCP (Aguilar-Perez *et al.*, 2018) and titanium particles (Aguilar-Perez *et al.*, 2018).

Natural Polymers

Polypeptides

Among natural polymers, polypeptides seem a natural choice: protein-based biomaterials tend to fold and self-assemble on a molecular level, forming a growth substrate that offers better mimicking of the natural ECM compared to synthetic polymers (Curry *et al.*, 2016). Polypeptide biopolymers are traditionally animal-sourced, although recombinant varieties are also studied (Yang *et al.*, 2004; Wu *et al.*, 2017). They are characterized by competitive bioresorbability and bioadhesion. In addition, owing to the hierarchical organization typical of proteins, they offer cues to cells on many different levels: from ligand motifs in their primary structure (e.g., RGD sequences) to topographical signaling of secondary to quaternary structures (Curry *et al.*, 2016). Polypeptides are also very versatile in terms of functionalization and engineering of biologically responsive materials, thanks to their numerous reactive groups and possible biological responses (e.g., binding metal ions and ligands) (Tallawi *et al.*, 2015; Mas-Moruno, 2018; Gómez-Guillén *et al.*, 2011).

Being the main component of the extracellular matrix, collagen is perhaps the most frequently studied polypeptide for tissue engineering scaffolds (Lee *et al.*, 2001). Collagen is mainly synthesized by fibroblasts and it makes up for 25%–35% of the whole-body protein weight content and 90% of the organic component of the bone ECM (Gelse, 2003). There are approximately twenty-nine known types of collagen (Ricard-Blum, 2011). Among these, type I collagen is the most commonly used, thanks to its higher availability and lower immunogenicity (Ricard-Blum, 2011). The main beneficial properties of collagen are that it is intrinsically biocompatible, biodegradable and with a good potential to stimulate cell proliferation and differentiation both in vitro and in vivo (Lee *et al.*, 2001). In terms of disadvantages, collagen tends to cause possible antigenic responses (Lynn *et al.*, 2004). It also have poor dimensional stability due to swelling in vivo and low mechanical properties, especially for load bearing scaffolds. Although stability and mechanical properties can be improved via crosslinking (physical, chemical or enzymatic, described in detail elsewhere (Meyer, 2019)), they usually are insufficient for its stand-alone application. Composite approaches are great strategies to increase mechanical properties while developing a structure that more closely resembles native bone (i.e., collagen + hydroxyapatite), especially when using bioinspired calcium phosphates (Curry *et al.*, 2016). However, the composite approach for collagen does not avoid immunogenicity (Zhang *et al.*, 2018). A possible way to overcome this issue is to use gelatin. Gelatin is denatured collagen produced mainly from type I collagens of different origin: bovine, porcine and, in more recent years, fish, sea urchin, jellyfish and bird feet (Liu *et al.*, 2015). Since the primary structure of collagens of different origin will be not exactly the same, the composition of gelatin can vary. However, all varieties are principally composed of proline, hydroxyproline and glycine with smaller traces of other amino acids (Liu *et al.*, 2015). Regardless of the amino acid composition, the denaturation process destroys the supramolecular fibrillary structure of collagen, which is thought to be responsible for its immunogenicity (Lynn *et al.*, 2004). This results in gelatin being non-immunogenic, but also determines a drop in mechanical properties and stability in aqueous environments. In fact, gelatin dissolves in water within a few hours and for effectively using it, its stabilization via crosslinking, most commonly with aldehydes, carbodiimide (EDC) chemistry or genipin, is required (Yahia *et al.*, 2015). For instance, Lacroix *et al.* (2014) prepared composites of 75S25C bioactive glass and gelatin crosslinked using glutaraldehyde. Porous constructs were prepared using poly(methyl metacrylate) (PMMA) beads as porogen agent and they showed similar bioactivity to pure bioactive glass scaffolds, but with higher compressive strength. Other examples of filler phases for gelatin are HA (Landi *et al.*, 2008), β -TCP (Takahashi *et al.*, 2005) and different formulations of bioactive glasses, including nano-sized sol-gel derived bioactive glass (64.5wt% SiO₂, 29.5wt% CaO, 6.5wt% P₂O₅) (Hafezi *et al.*, 2012) and Mg- and Zn- doped BGs (Raz *et al.*, 2018). Usually, gelatin-based scaffolds are produced by freeze-drying. In some remarkable cases, the high dissolution rate of gelatin seems to naturally increase the native bioactivity of collagen, as some studies report increases in biomineralization after addition of gelatin to a PLLA matrix (Magiera *et al.*, 2017). Additionally, the high-throughput production of gelatin is a relative simple process to implement, making it more available and cost-effective than non-denatured collagen (Liu *et al.*, 2015).

In alternative to collagen-based biopolymers, silk derivatives are highly studied for biomedical applications in diverse tissues (Bhattacharjee *et al.*, 2017; Farokhi *et al.*, 2018). Silk is a protein-based natural material produced mainly by *Lepidoptera* larvae and

adult web arthropod spinners. As a biomaterial, silk can be used for the preparation of textile-based braided scaffolds and grafts (Bhattacharjee *et al.*, 2017; Catto *et al.*, 2014). In particular, in the context of bone regeneration, remarkable results were obtained when silk braided structures were correlated with spatially regulated formation of hydroxyapatite following a mineralization mechanism that resembled the one of collagen type I in bone (He *et al.*, 2013). Although notable results were attained using native silk, studies tend to agree that for biomedical applications the separation of silk in its two constitutive compounds, fibroins and sericins, seems to give better and more tailorable results, owing to the completely different nature of the two protein families that can be individually engineered. Generally, fibroin proteins are the major constituent of silk (72%–81% of a cocoon). It is a hydrophobic glycoprotein that, as such, is insoluble in water. Fibroin molecules are in fact very stable owing to their ability to establish a high number of intermolecular hydrogen bonds. Dissolution can be achieved by disruption of these H-bonds using chaotropic agents, most commonly lithium bromide, and by subsequent dialysis (Lu *et al.*, 2011). Fibroin has a semi-crystalline structure in which two phases coexist: highly ordered crystalline antiparallel β -sheet domains (silk I) interposed by loose regions of mixed α -helix, β -sheet and random coiling (silk II) (Cilurzo *et al.*, 2011; Qi *et al.*, 2017). The mechanical properties of fibroin are highly dependent on the ratio between the two phases: while a higher silk I content contributes to strength and toughness, silk II makes fibroin more flexible and elastic (Qi *et al.*, 2017). Most interestingly, the ratio between silk I and II can be controlled through well-established and scalable processes (e.g., methanol conditioning to increase silk I content, water vapor annealing to increase silk II) (Lu *et al.*, 2011). The possibility of tailoring the secondary structure of fibroin, and therefore its degradation and mechanical properties, makes it a more processable and tailorable biomaterial for tissue engineering, as compared to native silk (Cilurzo *et al.*, 2011). Additionally, fibroin is also known to have minimal immunogenicity, high cytocompatibility and to directly regulate several signaling pathways responsible for osteogenic differentiation (Farokhi *et al.*, 2018; Santin *et al.*, 1999). Nonetheless, the osteogenic potential of fibroin was deemed not sufficient and additional strategies have to be developed to achieve substantial bone growth (Farokhi *et al.*, 2018). For instance, bioactive, osteopromotive components should be associated with silk fibroin to overcome its drawbacks (Farokhi *et al.*, 2018; Kim *et al.*, 2014a). The combinations of fibroin with either hydroxyapatite (Farokhi *et al.*, 2018) or bioactive glasses (Du *et al.*, 2019) are current main research trends as regards this biopolymer, with comprehensive reviews available on both topics (Farokhi *et al.*, 2018; Midha *et al.*, 2018). Other explored approaches include the addition of carbon nanotubes (Ayutsede *et al.*, 2006) or TiO₂ (Kim *et al.*, 2014b) for mechanical toughening.

Parallel to fibroin, sericin can also be isolated from silk cocoons. Contrary to fibroin, sericin is hydrophilic. Its structure is composed by two subunits: α - and β -sericin, they organize mainly into random coils with minor elements in β -sheet conformation (Padamwar and Pawar, 2004). Although it is traditionally considered as a waste product of the purification of fibroin, recent studies pointed out the favorable properties of sericin and suggest further investigation to use it in biomedical sciences (Kunz *et al.*, 2016; Yooyod *et al.*, 2016). Research efforts to date have been negligible due to immunogenicity concerns for the use of this protein (Kunz *et al.*, 2016). Nevertheless, recent reports support the idea that, as long as it is used in absence of fibroin, antigenic responses subsequent to sericin exposure are minimal (Wang *et al.*, 2015). Owing to its hydrophilicity, antibacterial and antioxidative properties and UV-protective ability, sericin was proposed as wound dressing/skin protection biomaterial (Ersel *et al.*, 2016; Qi *et al.*, 2018). Higher hydrophilicity in particular is known to induce greater collagen synthesis, as compared to fibroin. Sericin also showed promising results for bone regeneration. When used alone, it can be used for the preparation of biomimetic composites, since it spontaneously induces hydroxyapatite nucleation provided that the β -sheet content is high when immersed in a metastable calcium phosphate solution (Zhang *et al.*, 2014; Takeuchi *et al.*, 2005; Li *et al.*, 2016). In parallel, sericin can also promote the secretion of tumor necrosis factor- α (TNF- α), an important growth factor associated with osteogenesis (Jo *et al.*, 2017). In a more traditional composite approach, sericin was also proposed as matrix for bone tissue engineering composite scaffolds in combination with calcium phosphates, resulting in constructs with high adhesive properties, improved cell viability and increased osteoblast differentiation (Vedakumari *et al.*, 2020). Similar results were obtained when applying sericin as a coating on titanium implants: adhesion, proliferation and differentiation of osteoblast cells were enhanced in presence of the protein (Nayak *et al.*, 2013).

Polysaccharides: chitosan, cellulose, starch, alginate, pectin

Naturally derived polysaccharides are widely studied for the fabrication of a variety of tissue engineering composite scaffolds (Pacheco *et al.*, 2018). They have similar properties to polypeptides: they are biocompatible and biodegradable. However, they are usually obtained from more accessible and available sources and, as a consequence, can be produced cost-effectively in higher quantity (e.g., cellulose and chitin are the first and second most common biopolymers on the planet, respectively). Notable representatives of this category are chitin, chitosan, cellulose, alginate, starch and pectin, among others. Natural polysaccharide biopolymers can be sourced from animals (chitin, chitosan), plants (cellulose, alginate, pectin, starch) or microorganisms (cellulose) (Schuerch, 1985).

Chitosan is a semicrystalline, partly deacetylated derivative of chitin, a major structural component of the exoskeleton of crustaceans as well as the carbohydrate skeleton of fungi. It is composed of randomly organized glucosamine and N-acetyl glucosamine units (the ratio between deacetylated and acetylated monomers is defined as degree of deacetylation) (Zargar *et al.*, 2015). Chitosan is not found in mammals or other vertebrates, but nonetheless it has ideal properties for biomedical applications (Levengood and Zhang, 2014). It is mildly hydrophilic (i.e., contact angle ~ 70 – 80°), biocompatible, intrinsically antibacterial and mucoadhesive. It is known to modulate the activity of inflammatory cells to promote wound healing and the activity of blood cells towards hemostasis (Cheung *et al.*, 2015). In addition, the foreign body response and risk of fibrous encapsulation upon in vivo implantation of chitosan is minimal (Archana *et al.*, 2013). Most of its properties are thought to be due to its rich content of amines and its cationic nature at neutral pH and can be effectively tailored by controlling the molecular weight and degree of deacetylation (Zargar *et al.*, 2015). The high amount of reactive residues (both primary amines and hydroxyls) also determine that

chitosan can be readily functionalized and modified according to the need (Mourya and Inamdar, 2008). The solvent and melt blending of chitosan with other polymers has been also studied in-depth. Remarkably, it was demonstrated that imidazole- or methyl pyrrolidinone-modified chitosans are osteoconductive in vivo and can promote bone regeneration (Muzzarelli *et al.*, 1993). Other than with chemical functionalization, the osteoconductivity of chitosan for its use in bone tissue engineering can be also enhanced by means of inorganic fillers (Levengood and Zhang, 2014). Rich literature is available about the combination of chitosan with bioceramics, with a clear focus on the use of several forms of calcium phosphates, mainly hydroxyapatite (Brun *et al.*, 2014; Pighinelli and Kucharska, 2013; Lei *et al.*, 2017; Ramahdita *et al.*, 2018) and tricalcium phosphates (Kuo *et al.*, 2009; Viswanathan *et al.*, 2019; Puvaneswary *et al.*, 2015; Liu *et al.*, 2006). The combination with several formulations of bioactive glasses (Martins *et al.*, 2018; Luz and Mano, 2012; Caridade *et al.*, 2013; Liverani *et al.*, 2018) and with oxides of titanium (Hal-dorai, 2018), magnesium (Sanuja *et al.*, 2014; Praffulla and Bubbly, 2018) silver and zinc (Motshekga *et al.*, 2015) were also investigated and reported with very promising results both in terms of physicochemical and biological properties.

The use of cellulose as biocompatible and abundant material for tissue engineering scaffolds was also proposed (Hickey and Pelling, 2019). Cellulose is a homopolymer of β (1-4) linked D-glucose and it is the most common biopolymer on Earth (Sharma *et al.*, 2019), a tremendous economic advantage compared to other biomaterials. It is currently mainly extracted from plant lignocellulose, although the use of bacterial cellulose was recently proposed and it is now rising as a promising strategy for the development of scaffolds (Torgbo and Sukyai, 2018). Compared to plant-derived cellulose, bacterial cellulose has higher purity, better structural properties, water absorption and mechanical strength, all avoiding the polluting processes necessary to extract cellulose from lignocellulose (Jang *et al.*, 2017). Furthermore, bacterial cellulose is directly synthesized in the form of nanofiber networks, a strong asset for its biomedical application: the material as prepared already presents an ideal topography for cell growth and attachment, as previously demonstrated (Reiniati *et al.*, 2017; Lin and Dufresne, 2014). It is also mechanically strong and characterized by high stability in vivo, owing to the absence of enzymes that can break its backbone. Because of these and other beneficial properties, BC was proposed as possible scalable and cost-effective biomaterial for several applications, including artificial blood grafts, wound dressings, or artificial skin (Hickey and Pelling, 2019; Torgbo and Sukyai, 2018; Esa *et al.*, 2014). Nevertheless, due to its high stability, the biodegradability of cellulose is very low and so it is its biological activity after implantation. Recent studies tried to investigate possible approaches to control and tailor the degradability of cellulose and enhance its properties for its application as bone tissue engineering scaffolds. The combination with additional polymers (e.g., chitosan, gelatin, fibroin, PEG) (Chakrabarty and Teramoto, 2018) and the use of biomolecules were both explored (e.g., osteogenic growth peptide, vascular endothelial growth factor) (Courtenay *et al.*, 2018). However, the main strategy adopted seems to be the fabrication of biocomposites using graphene oxide (Luo *et al.*, 2018), carbon nanotubes (Ioniță *et al.*, 2018) and, above all, hydroxyapatite (Saska *et al.*, 2011). HA fillers can be introduced into bacterial cellulose mainly via three routes: (1) in situ, that is by adding HA during bacterial synthesis, (2) by impregnation or (3) by dissolution of BC and subsequent solvent casting (Sharma *et al.*, 2019). Research performed so far on HA-bacterial cellulose composites has shown how this class of composites can effectively create an environment that promotes cell adhesion and migration, fostering a well-integrated growth of bone without significant immune response or chronic inflammation (Saska *et al.*, 2011).

Another widely used polysaccharide in bone tissue engineering is alginate, second only to chitosan and its derivatives. Alginate is composed of a random sequence of guluronic and mannuronic acid monomers. It is obtained from seaweed, brown algae in particular (e.g., several species of *Laminaria*, *Ascophyllum nodosum*, and *Macrocystis pyrifera*) which are highly available at low cost (Lee and Mooney, 2012). The purification process consists of an alkali extraction treatment, filtration and precipitation of alginate by CaCl_2 . The alginate calcium salt can be converted into alginic acid through a treatment with HCl (Dusseault *et al.*, 2006). Alginate is biodegradable, biocompatible, non-toxic and non-immunogenic. It can also be easily processed into hydrogels, microspheres, microcapsules, sponges, foams and fibers (Lee and Mooney, 2012). Many of these fabrication techniques rely on the property of alginate of being physically crosslinkable in presence of divalent cations, most interestingly calcium ions. In fact, the polysaccharide chains can organize themselves around the cations to form a so-called egg box network (Li *et al.*, 2007). Alginate is also versatile in terms of chemical modifications thanks to carboxylic moieties present at each monomer. Chemical functionalization can be used to tailor biodegradability, mechanical properties, gelation kinetics or cell behavior, among other properties. On the downside, alginate tends to resist protein adsorption upon contact with body fluids and impedes cell adhesion, a property known as antifouling. Chemical modification and composite fabrication are two main strategies used to overcome this characteristic of the polysaccharide (Venkatesan *et al.*, 2014, 2015). Composites of alginate with bioactive glass (Mishra *et al.*, 2009), calcium silicates (Wu *et al.*, 2011), TiO_2 (Naik *et al.*, 2016) and hydroxyapatite (Lin and Yeh, 2004) all proved to be viable options to increase the mechanical properties, bioactivity and cell response of pure alginate.

For the design of injectable bone fillers for tissue regeneration, pectin and its composites are the natural materials of choice (Munarin *et al.*, 2011; Lara-Espinoza *et al.*, 2018). Pectin is a polysaccharide similar to alginate, but with a more complex structure, comprising several types of oligosaccharide monomers based on galacturonic acid. It shares with alginate the ability to form an egg-box structure in presence of calcium ions, but the transition between crosslinked and soluble pectin forms can be modulated easier and without harsh conditions (e.g., high temperature or pH) by controlling the presence of counter ions (e.g., sodium), making pectin an ideal choice for tunable drug or cell carriers. In addition, certain groups found in pectin, such as rhamnogalacturonans (disaccharides of galacturonic acid and rhamnose with various side chains), were confirmed to have an influence in determining the beneficial properties of the overall material (Sousa *et al.*, 2015; Mikshina *et al.*, 2015). For instance, pectin was found to have an ability to trigger growth and differentiation of mammalian bone cells proportional to its content short chain rhamnogalacturonan moieties (Munarin *et al.*, 2011; Park *et al.*, 2013). Finally, it was demonstrated that pectin-based gel

microspheres physically crosslinked with calcium ions can be bioactive, promoting biomineralization by increasing the nucleation rate of the bone mineral phase (Munarin *et al.*, 2011).

Starch, or amyllum, is another relevant natural polysaccharide used as biomaterial (Salgado *et al.*, 2004). It has a very simple structure of repetitive glucose units linked by glycosidic bonds, either in a linear helix (amylose, 20–25 wt%) or in a branched fashion (amylopectin, 75–80 wt%). Starch is produced by most green plants as a form of energy storage and, as such, is highly available at low cost, making it an ideal candidate for scalable, environmentally friendly biomedical applications. In fact, it was proposed as an alternative to current polymers used in tissue engineering. Thanks to its adequate mechanical and degradation properties, starch is a potential candidate in the development of bone fillers, drug delivery carriers and tissue engineering scaffolds (Pacheco *et al.*, 2018). It also has promising biological properties: it is non-toxic, it does not cause excessive inflammatory responses and it supports the growth and proliferation of osteoblasts with physiological-like protein expression (Salgado *et al.*, 2004; Gomes *et al.*, 2001, 2002). In parallel, the lack of bioactivity can be overcome preparing composites of starch with HA as filler (Mirab *et al.*, 2018).

Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHA) are another family of aliphatic polyesters (Basnett *et al.*, 2017). They are naturally synthesized by microorganisms, mainly bacteria, cultured in presence of unbalanced nutrient concentrations. Some relevant examples of this class of polymers are poly-3-hydroxybutyrate (PHB), copolymers of 3-hydroxybutyrate and 3-hydroxyvalerate (PHBV), poly-4-hydroxybutyrate (P4HB), copolymers of 3-hydroxybutyrate and 3-hydroxyhexanoate (PHBHHx) and poly-3-hydroxyoctanoate (PHO) (Goonoo *et al.*, 2017; Chen and Wu, 2005). Similarly to saturated poly- α -hydroxy esters, these polymers are biodegradable through hydrolysis, thermoplastic and highly processable (Basnett *et al.*, 2017). Their unique synthesis route, together with high processability and tailorability, make them very attractive candidates for the development of biomedical devices and tissue engineering scaffolds. Their use as matrix for the fabrication of biocomposites has been extensively investigated, with a particular focus on the combination between PHAs and hydroxyapatite (Ng *et al.*, 2019). High HA loading was however found to be not ideal due to lack of interaction between the two phases of the composite (Misra *et al.*, 2006). Other approaches include the use of (1) wollastonite (Li and Chang, 2005b), owing to its high mechanical properties; and (2) bioactive glasses, which thanks to their alkaline degradation products can help controlling hydrolysis and reducing possible inflammation. One strength of PHAs is their high tailorability depending on the desired application; they can be blended, surface modified or combined with other polymers (Rezwan *et al.*, 2006). The fabrication of composites is also a viable and highly explored route. In particular, blending among different types of PHAs is known to be a very effective strategy to dramatically adapt material properties and biocompatibility to specific needs (Chen and Wu, 2005; Doi *et al.*, 1995). Compared to other polyesters, PHAs seem to present fewer concerns in terms of their degradation. For instance, in a notable *in vivo* example, PHB was correlated with the induction of favorable response from bone tissue without evidence of chronic inflammatory response even after 12 months from implantation (Doyle *et al.*, 1991). During the whole implantation period, the material did not suffer major structural failures and promoted the formation of new highly organized bone tissue. However, the industrialization of this very promising family of materials is jeopardized by their limited availability and the difficulty of their extraction from the raw bacterial culture product. This fabrication step can be time-consuming and expensive, often requiring high quantity of halogenated solvents. To date, PHAs extraction seems to be a major bottleneck for the industrial scale-up and the possibility to achieve high throughput production of these polymers (Chen and Wu, 2005; Verma *et al.*, 2003). Nevertheless, the fabrication of composites with PHAs is already widely explored using mainly HA (Tong *et al.*, 2010), bioactive glasses (Zhou and Yu, 2014), wollastonite (Li and Chang, 2005a,b) and metal oxides (Anžlovar *et al.*, 2018).

Scaffold Fabrication Techniques and State of the Art

In addition to the bulk properties of the material used, tissue engineering scaffolds have to be designed bearing in mind another important characteristic: their morphology. A complex and hierarchical 3D porous architecture is fundamental to guarantee the homogeneous development of new tissue for a number of reasons. First of all, micrometric pores (circa 400 μm) allow cell infiltration through the scaffold, both upon seeding and in second instance during proliferation and migration. Additionally, wide pores support the spreading of vessels, the diffusion of nutrients, the removal of metabolic waste and the even distribution of newly formed extracellular matrix (ECM) during tissue development (Perez and Mestres, 2016). Smaller pores and roughness are thought to influence cell behavior, too. Specifically, surface topographical features can stimulate cell membrane integrins and other receptors, ultimately regulating cellular processes such as migration, proliferation and gene transcription (Nguyen *et al.*, 2016). The presence of combined hierarchical micro- and nanometric topographical features is considered a fundamental requirement for successful tissue engineering scaffolds and it has been studied in-depth for decades (Jeon *et al.*, 2014; Jin and Kim, 2014; Gritsch *et al.*, 2017). In particular, a plethora of material processing techniques have been optimized and are currently available to fabricate porous biocomposite scaffolds. A recent critical review by Garg *et al.* (2012) offers a comprehensive overview about the pro and cons of scaffolds and their respective fabrication techniques (Fig. 5).

Scaffold fabrication techniques are usually classified using mainly two rationales: (1) top-down and bottom-up methods, or (2) traditional and non-traditional fabrication techniques (Subia *et al.*, 2010). In particular, the first classification is based on the nature of the fabrication approach: top-down methods are processes that remove portions of the initial material bulk to obtain the final structure (e.g., particulate leaching, freeze-drying). Conversely, bottom-up approaches are the ones in which the structure is

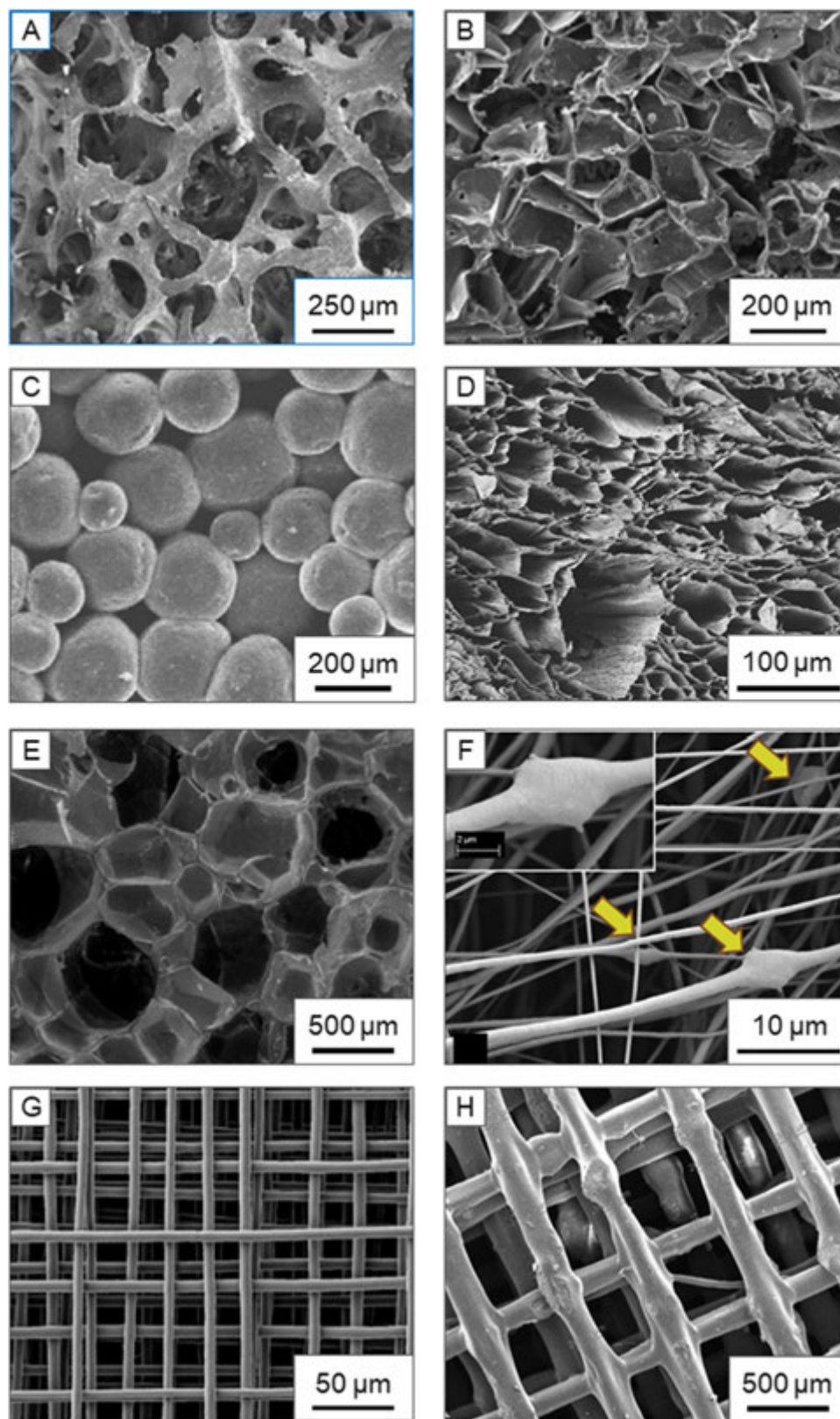


Fig. 5 The physiological structure of cancellous bone (A) compared to the typical morphologies obtained with current scaffold fabrication techniques: solvent casting/particulate leaching (B), microsphere sintering (C), thermally induced phase separation (D), supercritical CO₂ foaming (E), electrospinning (F), melt electrospinning writing (G) and 3D printing (H). SEM micrographs reproduced from references Rezwan, K., Chen, Q. Z., Blaker, J.J., Boccaccini, A.R., 2006. *Biomaterials* 27, 3413–3431. Liverani, L., Lacina, J., Roether, J.A., *et al.*, 2018. *Bioact. Mater.* 3, 55–63. Spencer, C., Jonathan, P., Janice, M., Ralph, S., 2016. *Front. Bioeng. Biotechnol.*, doi:[10.3389/conf.FBIOE.2016.01.00145](https://doi.org/10.3389/conf.FBIOE.2016.01.00145). Mou, Z.-L., Zhao, L.-J., Zhang, Q.-A., Zhang, J., Zhang, Z.-Q., 2011. *J. Supercrit. Fluids* 58, 398–406, with permission of the respective publishers.

progressively built using smaller building blocks (e.g., 3D printing, electrospinning). Often a combination of the two approaches leads to the best results as it allows the simultaneous formation of features at different resolutions and thus the creation of a more complex and hierarchical structure (Biswas *et al.*, 2012). This makes it often hard to conclusively classify a scaffold fabrication technique into one of the two categories. In the following sections, current main fabrication techniques for the preparation of biocomposite scaffolds for tissue engineering are presented and discussed in terms of their benefits and disadvantages.

Solvent Casting/Particulate Leaching

The most traditional and straight-forward technique to prepare composite scaffolds is probably solvent casting (SC). In this process, a polymer is dissolved in a proper solvent, mixed with the filler to create a homogeneous suspension and cast in a desired mold for solvent evaporation. This method allows for the fabrication of bulk films, but it can also be performed in combination with a particulate leaching (PL) step to obtain porous features. In a typical top-down SC/PL method, a porogen agent insoluble in the solvent is added during the preparation of the mixture and leached from the scaffold by dissolution in a second solvent that dissolves the porogen but not the main composite structure. SC/PL is an inexpensive and widely studied technique to readily prepare tissue engineering scaffolds without the need for a complex apparatus. However, it has several disadvantages, including limited control of pore distribution and interconnectivity and extensive use of solvents, which could potentially remain in the final product and cause toxicity. Solvent consumption can be reduced if the solvent blending between polymer and filler is replaced by melt blending: the filler and the porogen are mixed with the molten polymer. This method successfully avoids the use of solvents to dissolve the polymer for the matrix. However, it does not overcome the limits of this technique in terms of porosity control and solvent consumption during the leaching process. The state of the art on SC/PL has been recently reviewed by Prasad *et al.* (2017).

Microsphere Sintering

Microsphere sintering is a traditional bottom-up scaffold fabrication technique to create a porous interconnected 3D construct starting from polymeric microspheres produced with various methods (e.g., emulsification, polymer spraying) and sifted to a desired size range (Singh *et al.*, 2008). During this step, particles of a bioactive filler can be dispersed within the polymer in order to create composite microspheres. Microsphere sintering takes its name from its similarity to ceramic sintering: the polymer microspheres are poured in a three dimensional mold, compacted and heated slightly above their glass transition temperature without applying pressure in order to partially fuse them and create a porous network. Subcritical CO₂ was also used as an alternative sintering agent (Singh *et al.*, 2010). The structures that can be obtained by this technique are well interconnected. However, high porosity (> 70%) as well as fine control over the final morphology are hard to achieve (Chu and Liu, 2008). Nevertheless, the mild processing conditions of microsphere sintering still make this technique very interesting and particularly suitable for the preparation of scaffolds with a release capability for therapeutic molecules. In fact, since the drug can be loaded homogeneously within the polymer during microsphere preparation, the incorporation efficiency will be higher than the one obtained by simple adsorption and, likewise, the delivery will be better controlled over time (Singh *et al.*, 2008). The drug delivery potential of microsphere sintering determined that PLGA is the principal polymer used for this technique. Composite TiO₂/PLGA porous scaffolds prepared using this technique were proposed by Wang *et al.* (2010) using composite microspheres prepared by emulsion in PVA. The sintering was performed at 90°C for 2 h. The resulting constructs showed improved cell adhesion, probably due to a protein selection phenomenon mediated by TiO₂, which favored fibronectin and bovine serum albumin adsorption on the surface of the scaffold, promoting in turn the interaction between the biomaterial and the membrane integrins of osteoblasts. The filler also regulated the activity of osteoblasts, promoting ALP activity and calcium secretion.

Finally, microsphere sintering can also be used to prepare a negative sacrificial template to combine with SC/PL (Bossard *et al.*, 2018). Briefly, a three-dimensional structure is prepared as described above using an easily leachable material. A suspension of polymer and filler is then infiltrated through the cavities of the sintered construct. Infiltration can be vacuum-aided or improved by centrifugation, among others. After complete evaporation of the solvent, the microspheres can be leached out using a proper solvent to obtain a composite cast of the negative template. The combination of microsphere sintering with SC/PL was demonstrated fabricating porous hybrid scaffolds consisting of PCL and 75S25C BG. Using this combined technique, it was possible on one hand to obtain a more controlled and interconnected pore distribution than simple SC/PL, while at the same time achieving higher porosity than simple sintering (Bossard *et al.*, 2018). The scaffolds were also biologically tested *in vitro* and *in vivo*. Results showed that they can promote osteoblast adhesion and differentiation *in vitro*. In parallel, micro-computed tomography (μ CT) measurements of *in vivo* implantation demonstrated that PCL/BG resulted in higher bone ingrowth compared to a commercial xenograft used as control. Histological data also revealed ongoing vascularization and bone remodeling, confirming that the scaffolds offer a promising alternative to current technologies (Granel *et al.*, 2019).

Thermally Induced Phase Separation (TIPS)

Thermally induced phase separation (TIPS) identifies a group of traditional top-down processes to fabricate porous composite scaffolds that overcome the porosity constraints of previously described methods (Mannella *et al.*, 2015; Barroca *et al.*, 2010; Helen *et al.*, 2007). Typically, TIPS consists of the solvent blending of a polymer with an insoluble inorganic filler and subsequent rapid

quenching of the mixture at temperatures below the limit of solubility of the polymer. This quick transition solidifies the solvent and causes a phase separation forcing the polymer and the particles into the remaining interstitial spaces. TIPS is then coupled with a freeze-drying step to sublimate the solvent and obtain a highly porous composite scaffold with full pore interconnectivity (Maquet *et al.*, 2004). The pore distribution of scaffolds obtained by TIPS/FD is characterized by a typical strong anisotropy: the pores follow the direction and shape of solvent crystals that solidified according to the applied gradient of temperature (Barroca *et al.*, 2010). This determines that controlling the freezing parameters has great impact on the size, shape and direction of the pores, allowing to ultimately tailor the final structure of the scaffold to the specific application need. The polymer, the solvent, the ratio between the two and the presence of third moieties in the mixture are other relevant parameters that determine the morphology of the construct. A porogen can also be added, combining TIPS/FD with PL to obtain a highly hierarchical porosity with maximized interconnectivity (Kim *et al.*, 2012a). TIPS/FD was widely applied to the processing of PDLLA-based composite scaffolds. Rich literature is available on the phase separation fabrication of PDLLA/Bioglass® porous scaffolds and their characterization in terms of porous morphology, mechanical properties, in vitro short and long term degradation, bioactivity and cell culture with different cell phenotypes (Blaker *et al.*, 2005; Verrier *et al.*, 2004; Maquet *et al.*, 2003; Blaker *et al.*, 2011). Similar scaffolds were used to investigate the ability of these constructs to promote adhesion, proliferation and ECM-secretion of primary annulus fibrosus cells seeded on them, in view of their application as treatment for damaged intervertebral disc. Remarkably, the results showed that PDLLA/Bioglass® porous scaffolds provide the adequate cues for cells, enhancing their proliferation and promoting the production of glycosaminoglycans and collagens of both types I and II. Above all, type II collagen is particularly important for the formation of physiological-like cartilage tissue (Bernhard and Vunjak-Novakovic, 2016). The technique is also highly promising for the processing of chitosan/hydroxyapatite composites. As demonstrated by Lei *et al.* (2017), HA disperses with particularly high homogeneity within chitosan solutions. The authors prepared a Sr-HA/chitosan nanocomposite with three-dimensional interconnected macroporosity (100–400 μm) which gave remarkably positive results when biologically tested in vitro. Sr-HA nanocrystals were found to significantly improve the proliferation and osteogenic differentiation of human bone marrow mesenchymal stem cells. In particular, the release of strontium ions from the composite enhanced ALP activity, ECM mineralization and the expression of osteogenic-related COL-1 and ALP genes. The authors also highlighted the presence of an optimum level of strontium substitution at which a synergic effect between strontium and calcium ions is established, leading to the strongest combination of bioactive and osteogenic properties (Lei *et al.*, 2017).

Supercritical CO₂ Foaming

Although it is widely used in tissue engineering thanks to its versatility, TIPS has the disadvantage of relying on solvents that present concerns in terms of toxicity and waste management. For these reasons, in recent years authors suggested foaming by means of supercritical fluids, and of supercritical CO₂ in particular, as a promising strategy to reduce the use of solvents (Reverchon *et al.*, 2008; Kim *et al.*, 2012b). Thanks to its unique physical properties, non-toxicity, low cost, liquid-like density, gas-like viscosity and very low surface tension, supercritical CO₂ is an ideal medium to impart porosity to polymers. Furthermore, since the supercritical temperature and pressure values are relatively mild ($T_c = 31.5^\circ\text{C}$ and $P_c = 75.8\text{ bar}$), this process can be used to impregnate materials with biomolecules, such as growth factors, that would be degraded or denatured by other fabrication techniques (Davies *et al.*, 2008). In a typical supercritical CO₂ foaming protocol for a PLGA/ β -TCP composite (Yang *et al.*, 2010), the desired amount of polymer and filler are mixed, put in a mold and compressed. The filled molds are then fed into the reactor. Afterwards, the temperature is raised, the reactor chamber purged with N₂ and then filled with CO₂ at a desired pressure. Temperature/pressure conditions are kept constant over a period of time to allow foaming and finally the chamber is vented. Li *et al.* (2019) used this type of protocol to prepare porous composite scaffolds with a PLGA matrix and a mesoporous bioactive glass (MBG, composition 79.5wt% SiO₂, 14wt% CaO and 6.5wt% P₂O₅) particulate filler. The authors used the advantage of the mild processing conditions of supercritical CO₂ foaming to also introduce the proangiogenic lipid FTY720. With a simultaneous sustained release of the lipid and ions from the MBG, the composite scaffolds were found to favor cell adhesion and proliferation, but most importantly to promote in vitro osteogenic differentiation of bone marrow stromal cells while also upregulating the expression of HIF-1 α via the activation of the Erk1/2 pathway, a key element for the mediation of osteo- and angiogenesis. These promising results were further scrutinized in vivo in a critical-sized rat calvarial bone defect. Vascularized bone regeneration was observed in presence of FTY/MBG/PLGA scaffolds, in particular an increase in the formation of type H new vessels was observed in newly formed bone tissue, possibly as a consequence of a synergistic effect between FTY720 lipid and therapeutic ions release. This achievement is particularly relevant, since it is well-known how effective bone regeneration must be coupled with equally effective angiogenesis in order to obtain physiological-like new tissue. Supercritical CO₂ processing is an environmentally friendly technique with a high potential for the development of tissue engineering porous scaffolds with controlled drug release. In addition, protocols for supercritical CO₂ foaming are very simple and reproducible, which is a strong asset in view of clinical application and commercialization. However, compared to TIPS, it requires specific equipment to be performed (e.g., a high pressure reactor) and, as such, has higher associated costs (Carfi Pavia *et al.*, 2013).

Electrospinning

Beginning in the early 1990s, many research groups started to investigate the suitability of a novel technique for the fabrication of non-woven fibers with significantly smaller diameters compared to traditional fiber fabrication techniques (Jiang *et al.*, 2014;

Huang *et al.*, 2003). The technique had been popularized as electrospinning by Reneker and Rutledge (Doshi and Reneker, 1995) and quickly gained relevance as an important approach to fabricate scaffolds for the regeneration of many tissues, including skin, muscle, nerves, bone and blood vessels (Agarwal *et al.*, 2008). The rapid spreading of interest over electrospinning in the biomedical field is due to the high potential of this technique to mimic the complex range of morphological features of the natural ECM (Bagbi *et al.*, 2018). In fact, a typical electrospun structure features well interconnected porosity and nano- and microscale topographical cues that were demonstrated to effectively guide cell proliferation and migration and facilitate the formation of new functional tissue (Tong *et al.*, 2010). Electrospinning consists of applying a high-voltage electric field (10–20 kV) between the needle of a syringe delivering a polymer solution and a collecting plate in front of it. This electric force overcomes the surface tension of the droplet on the top of the needle creating a so-called Taylor cone and a thin polymer jet diffusing from the needle to the collector. While the jet elongates and thins, the solvent evaporates and forms polymer fibers. Owing to its high versatility, with electrospinning it is possible to achieve diverse fiber features using a relatively simple apparatus. This is because the properties of electrospun constructs can be radically influenced by carefully adjusting process parameters: solution (i.e., viscosity, conductivity, surface tension), electrospinning (voltage, flow rate, needle-collector distance) and ambient parameters (temperature, humidity, air flow) among others (Jiang *et al.*, 2014; Kolbuk *et al.*, 2015). With specific sets of these properties it is possible to refine fiber topography, obtaining for instance porous or hollow fibers. The shape of the collector and its relative movement to the needle also play an important role, allowing to control fiber direction and to fabricate non randomized structures, such as aligned fibers (Subramanian *et al.*, 2011; Jose *et al.*, 2012) or hollow cylinders (Marelli *et al.*, 2012a). In recent developments, electrospinning was also combined with sol-gel chemistry for the spinning of inorganic sols and the fabrication of fully inorganic fibers (Choi *et al.*, 2003) or polymer/ceramic hybrids, as recently reported by Pirzada *et al.* (2012), who successfully produced silica/poly (vinyl alcohol) hybrid electrospun fibers. Most importantly, electrospinning is often combined with a composite approach. In fact, the addition of particles of a second phase was confirmed as a viable strategy to prepare non-woven fibrous composite scaffolds with enhanced properties, especially in terms of bioactivity (Agarwal *et al.*, 2008; Labbaf *et al.*, 2018; Liverani *et al.*, 2017; Noh *et al.*, 2010; Liverani *et al.*, 2014). For instance, various types of bioactive glass were solvent mixed with PCL using class III benign solvents (formic and acetic acid) and electrospun. The tested BGs included microparticles of commercially available Vitryxx® (45wt % SiO₂, 24.5wt% CaO, 24.5wt% Na₂O and 6wt% P₂O₅) and nano-sized 45S5 BG (Liverani *et al.*, 2018) as well as custom formulations of mesoporous bioactive glasses (MBGs), such as calcium-containing silica nanoparticles (MCM-41) (Liverani *et al.*, 2017) and silver-doped MGB (composition 77wt% SiO₂, 18.5wt% CaO, 1.5wt% P₂O₅ and 3wt% Ag₂O) (Ciraldo *et al.*, 2018b). Other relevant combinations reported for electrospinning are PHBV/HA (Ito *et al.*, 2005), gelatin/ZnO (Münchow *et al.*, 2015) and fibroin/HA (Kim *et al.*, 2014a), among many others (Baji and Mai, 2017). The composite approach applied to electrospinning is progressively gaining importance as an effective strategy to introduce the advantages of bioceramics into the ECM-like morphology of polymer fiber mats. Liverani *et al.* (2018) confirmed that embedding BG particles in PCL/chitosan fibers did not hinder the bioactivity of the former, while Labbaf *et al.* (2018) tested a similar PCL/BG system using a sol-gel derived 58S formulation. The authors found that PCL/58S could be a promising candidate biomaterial for dental pulp tissue engineering, given that dental pulp stem cells were found to optimally adhere and proliferate on the substrate while mineralization, measured by alizarin red, was significantly increased compared to a positive control (i.e., tissue culture polystyrene, TCPS).

Additive Manufacturing (AM)

The term Additive Manufacturing (AM), also known as Solid Free-form Fabrication (SFF) or Rapid Prototyping (RP), identifies a broad category of both top-down and bottom-up non-traditional techniques for scaffold fabrication (Hutmacher, 2006; Li *et al.*, 2015; Calignano *et al.*, 2019). In AM, a construct is precisely recreated layer by layer following a previously developed computer aided design (CAD). There are countless AM approaches, usually divided into seven categories: material extrusion, material jetting, binder jetting, sheet lamination, VAT photo-polymerization, powder bed fusion and direct energy deposition.

Currently (Li *et al.*, 2015; Singh and Ramakrishna, 2017), the most studied methods to manipulate polymer-based bio-composites are either laser-based techniques such as (1) stereolithography (SLA), in which fluid resin is first evenly distributed on a platform, irradiated with a desired pattern, photo-polymerized, recoated with the following layer and so on; or (2) selective laser sintering (SLS), where a focused laser heats powder deposited layer by layer, causing sintering of the particles and formation of a desired pattern. Alternatively, nozzle-based approaches are explored, mostly (3) fused deposition modeling (FDM), a technique based on spatially-controlled extrusion in the three dimensions, (4) solvent-based 3D printing, using for example fibroin and MBG (Du *et al.*, 2019) or polycaprolactone and 13-93B3 (Kolan *et al.*, 2019), and (5) bioplotting, similar to 3D printing, but with ink dispensing inside a liquid medium with matching density that allows for fabrication without need of additional support. In contrast to other AM techniques, bioplotting is more versatile and can be used to process a wide variety of different materials, as well as to directly print cells within the ink. Among these, one of the principal candidates is alginate. Alginate-based bioinks are particularly relevant owing to the possibility to precisely tailor the gelation process in presence of divalent cations (see paragraph “Polysaccharides: chitosan, cellulose, starch, alginate, pectin”). Generally, calcium sulfate (CaSO₄) is used as source of calcium for crosslinking, owing to its ideal solubility compared to other calcium salts (e.g., CaCl₂), resulting in higher working times (Lee and Mooney, 2012). A bioactive filler, usually hydroxyapatite (Gao and Cui, 2016), is added in order to increase both the mechanical and biological properties of the biopolymer. To improve the homogeneity and the dispersion of the filler proper dispersants are usually added to the ink, for instance poly(vinyl alcohol) (Bendtsen *et al.*, 2017) or sodium citrate (You *et al.*, 2018). Typical

results show these setups are effective in protecting cells during the printing process and are characterized by good biological performance. You *et al.* (2018), for instance, demonstrated the ideal properties of an alginate/hydroxyapatite bioprinted scaffold for its application in osteochondral tissue engineering: the presence of the bioactive filler homogeneously dispersed within the polysaccharide (thanks to the addition of sodium citrate) was linked to increases in ALP activity, mineralization and collagen type X secretion by chondrocytes seeded during printing. Scaffolds were also subcutaneously implanted *in vivo* in a murine model, confirming the higher mineralization potential of composites compared to alginate alone (Fig. 6).

Thanks to its ability to crosslink *in situ*, PPF is also a promising candidate for scaffold additive manufacturing. In a recent case study, Trachtenberg *et al.* (2017) investigated the combination of this attractive biodegradable polymer with HA nanoparticles, aiming to obtain an accurate fabrication process resulting in scaffolds with robust compressive mechanical properties. Their results confirmed that it was possible to obtain PPF/HA 3D printed porous scaffolds with complete interconnectivity, measured by μ CT. Most remarkably, the process permits fine tailoring of the amount of HA layer-by-layer by simply varying the composition of the ink. This in turn results in scaffolds with a HA gradient that can better mimic the structure of physiological bone, and especially the one of the osteochondral tissue at the interface between bone and cartilage. Buyuksungur *et al.* (2017) also explored the potential of PPF in biomedical additive manufacturing, in particular using fused deposition modeling. The polymer was printed in combination with PCL and nano-sized HA (nHA) in order to improve and tailor the hydrophilicity of the scaffolds. Results confirmed that nHA significantly increased the compressive modulus and promoted cell adhesion compared to pure PCL. The addition of PPF, in parallel, improved the proliferation rate of bone marrow stem cells seeded onto the scaffolds. Furthermore, the composite scaffolds showed improved mineralization (alizarin red assay) and ALP activity as well as increased expression of relevant genes for osteogenesis (COL1 and RUNX2). These variations were mostly linked to the presence of the bioceramic filler. *In vivo* characterization and histological observations in a rabbit model confirmed the potential of PCL/PPF/HA composite scaffolds: improved tissue regeneration and mineralization were assessed for the biocomposites compared to a PCL control and, most remarkably, the stiffness of the final tissue/scaffold construct was found to be similar to the one of healthy bone samples.

AM techniques can also be used indirectly to prepare a sacrificial negative template that will be then infiltrated with a desired scaffolding biomaterial and made porous by leaching of the printed material (Calignano *et al.*, 2019). The indirect approach has the strong benefit of allowing the use of polymers optimized specifically for AM without the constraint of its biological properties (Calignano *et al.*, 2019). Regardless of the specific method, both direct and indirect AM are continuously gaining more resonance as effective ways to fabricate scaffolds thanks to their unique benefits of total control over scaffold architecture, high accuracy in structure reproduction and virtually complete interconnectivity. This can possibly lead to customized design of scaffolds, depending on the need of each patient (Egan, 2019). However, research still has to be performed in particular to expand the portfolio of available materials for these techniques as well as the current resolution limitation within micrometric ranges (Dalton *et al.*, 2015).

Melt Electrospinning Writing

Recently, a new technique has been proposed, which combines the versatility and accuracy of additive manufacturing techniques with the higher resolution of traditional electrospinning: melt electrospinning writing (MEW), described by its creators as a technique to bridge the gap between solution electrospinning and direct writing additive manufacturing processes (Muerza-Cascante *et al.*, 2014; Brown *et al.*, 2016). It consists of the melt electrospinning of polymer fibers toward an automated stage collector that moves according to the speed of the melt electrospinning jet and controls where fibers deposit. MEW is a high resolution and high throughput AM approach that allows fabrication of highly porous fiber scaffolds with submicrometric morphological features and total control on the final structure of the construct (Wunner *et al.*, 2018; Hrynevich *et al.*, 2018; McColl *et al.*, 2018; Wunner *et al.*, 2019). Due to its recent development, though, not many polymers have been demonstrated to be suitable for MEW. The recognized benchmark polymer for this technique is polycaprolactone (McColl *et al.*, 2018; Hochleitner *et al.*, 2015). This polymer was used alone, but also combined with bioactive inorganics, for the fabrication of composites for tissue engineering. By adding strontium-doped bioactive glass to PCL fibers, for instance, it was possible to induce ion release during cell culture, ultimately triggering the deposition of HCA on the scaffolds while enhancing the adhesion and proliferation of MC3T3-E1 pre-osteoblasts *in vitro*, compared to PCL-only scaffolds. Results also highlighted how cells had increased alkaline phosphatase activity as well as improved differentiation toward the osteoblast phenotype, demonstrating their potential in the development of artificial bone grafts.

Current MEW research is extending the range of available polymers to produce scaffolds, using for example poly(2-ethyl-2-oxazoline) (Ren *et al.*, 2014), poly(L-lactide-*co*- ϵ -caprolactone-*co*-acryloyl carbonate) (Chen *et al.*, 2016) or poly(urea-siloxane) (Hochleitner *et al.*, 2018). More remarkably, block polymers of racemic PDLLA and poly(ethylene glycol) were developed to be processed into biocomposite MEW structures, as demonstrated by Hochleitner *et al.* (2015). PLA-PEG-PLA has been successfully melt electrospun in combination with melt-derived micro-sized 45S5 Bioglass®.

Summary and Current Challenges

Properties of Bioactive and Biodegradable Polymer-Based Composites

Biocomposites consisting of a biodegradable polymeric matrix and an inorganic bioactive phase are a major class of biomaterials studied in the past two decades for diverse applications in medicine, in particular in the field of tissue engineering. Conventional

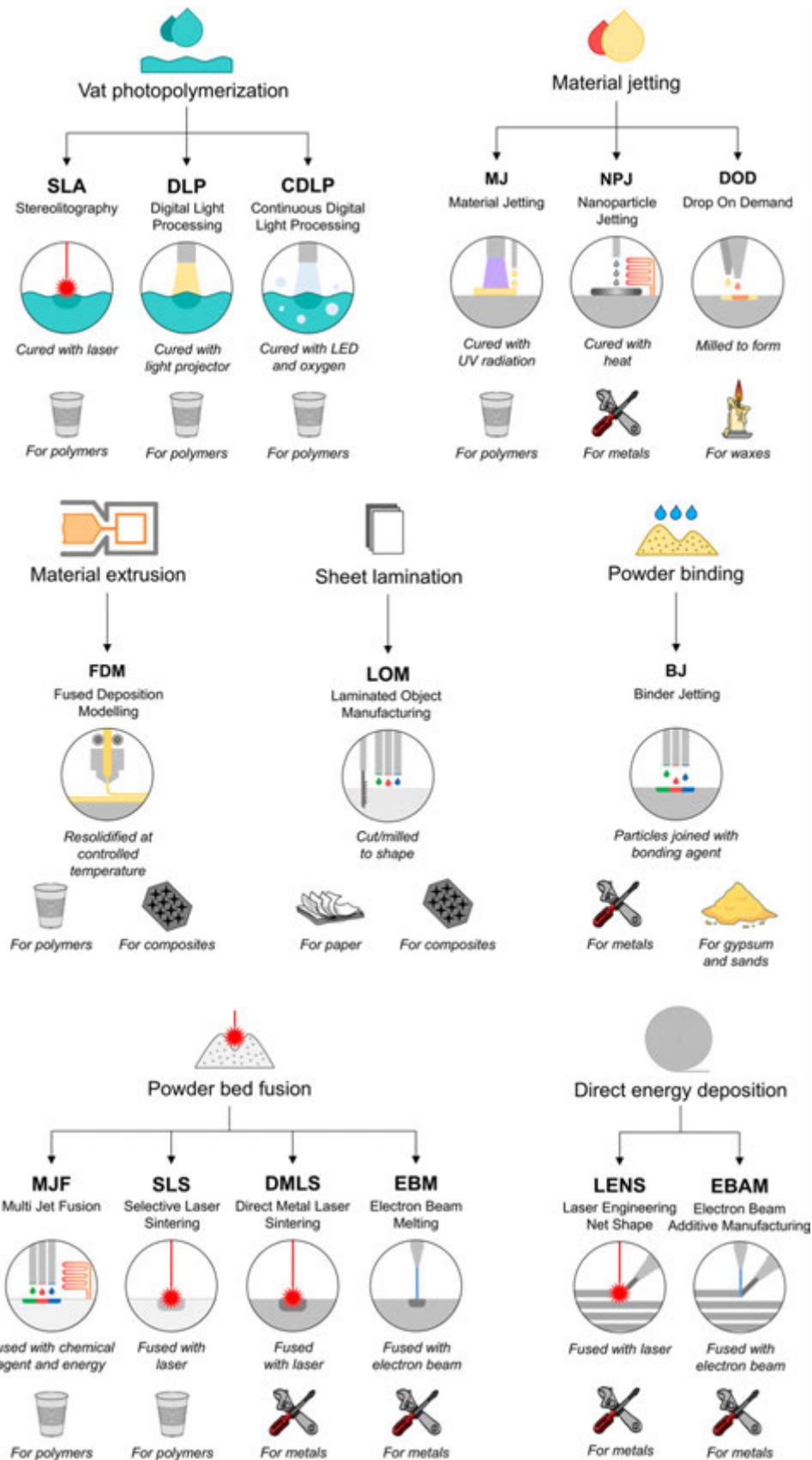


Fig. 6 Diagram summarizing the different types of additive manufacturing techniques currently in use and the materials they are particularly relevant for each method.

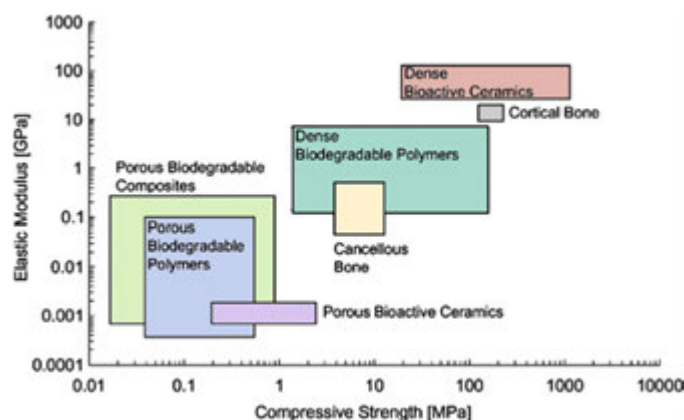


Fig. 7 Elastic modulus versus compressive strength ranges of biodegradable polymers, bioactive ceramics, both dense and porous, and composites thereof. Porosities of the porous scaffolds are $>75\%$ and mostly interconnected. Figure is adapted from reference Rezwan, K., Chen, Q.Z., Blaker, J.J., Boccaccini, A.R., 2006. *Biomaterials* 27, 3413–3431, with permission of Elsevier.

material processing techniques have been adapted and improved with the specific aim of incorporating bioactive fillers into three-dimensional, porous and interconnected polymeric networks. These constructs are specifically engineered to support the growth of new tissue, promote its mineralization (i.e., bioactivity) and degrade with properly tailored kinetics. This chapter offered a summary on the main current biodegradable polymers, inorganic bioactive fillers and fabrication methods used, together with an overview of the current achievements and state of the art in the field. Nevertheless, several challenges remain to be tackled. In particular, Rezwan *et al.* (2006) identified four major materials science trends/challenges that current and future research should focus on in order to advance laboratory research to clinically relevant devices. First of all, in spite of all the extensive research developed for decades on the topic, the mechanical strength of most artificial scaffolds is still significantly lower than that of cancellous bone and even more in the case of cortical bone. This determines strong limits in both the size and type of bone defects that can be treated to date. When comparing the elastic modulus and the compressive strength of dense bioactive ceramics, biodegradable polymers and monophasic as well as composite porous scaffolds to those of cancellous and cortical bone, it can be observed that the required properties are reached by few dense polymers and bioactive ceramics. Porous scaffolds, on the other hand, are weaker than bone (at least one order of magnitude) and have generally insufficient mechanical strength. This mismatch between the bulk properties of materials and composites and the properties of their porous structures is one of the current key limitations of this type of tissue engineering scaffolds. As discussed in this here, the composite approach is usually an effective strategy to improve the mechanical properties of scaffolds. However, the increase is often lower than desired, most probably due to low interfacial bonding between the two phases. The use of surface functionalizations and/or surfactants are main strategies under investigation to achieve further improvement in scaffold mechanical properties (Fig. 7).

Secondly, the surface properties of scaffolds should be engineered in order to optimize cell response. Chemical modifications are extensively investigated and used to modify and improve the biological performance of currently developed tissue engineering constructs. Cell response can be tailored and promoted by altering the protein adsorption behavior of materials when in contact with body fluids (e.g., antifouling), as well as by adding new functionalities that can beneficially communicate with cells (for instance, integrins, laminins, RGD proteins and several growth factors including vascular endothelial growth factor, bone morphogenetic proteins, transforming growth factor beta and insulin-like growth factor). Grafting biologically active moieties onto biomaterials and especially biocomposites is a vast and highly promising field that has given successful results so far, as reported in previous reviews (Tallawi *et al.*, 2015; Mas-Moruno, 2018). From a materials science point of view, the use of such biomolecules introduces limits in terms of processability: harsh conditions such as high temperatures, extreme levels of pH and even the presence of certain moieties (e.g., calcium) can degrade the biomolecule and make it inactive. This will have to be taken into account when designing composite materials containing proteins and growth factors. For instance, microsphere sintering and sol-gel based techniques are considered to be highly promising fabrication methods for GF-containing scaffolds.

Finally, the long-term degradation and mechanical behavior of composites as well as their *in vivo* and preclinical biological performance need further investigation. In particular, better analytical models have to be developed in order to study and predict the behavior of biocomposites once implanted in a patient. In addition to that, in recent years another trend has gained importance: stem cell encapsulation/delivery within the composite scaffold, in particular in relation to additive manufacturing techniques, which seems to be a promising strategy to achieve better tissue regeneration compared to acellular approaches (Gasperini *et al.*, 2014).

The Advantage of Nanocomposites

The previous paragraph has discussed possible future trends in the optimization of the properties of conventional biocomposites. An alternative route to enhance the properties of this class of materials increased in popularity in recent years: the development of

nanocomposites. The use of nanoparticles and nanofibers over conventional micro-sized fillers has recently become feasible by advances in synthesis methods, especially in sol-gel based techniques for the fabrication of nanoscale bioactive glass. The advantages of bioactive glass nanoparticles or nanofibers over micro-sized ones have been demonstrated very promising, thanks to their larger surface area, increased solubility and reactivity (Misra *et al.*, 2008). For instance, Caridade *et al.* (2013) observed how the inclusion of nano-sized Bioglass® in a chitosan matrix resulted in higher bioactivity, and thus higher surface reactivity, than control composites with a conventional micron-sized filler. In addition, nano-sized fillers introduce nanotopographic surface features in composite scaffolds, increasing their hierarchical porosity and roughness and, in turn, optimizing the response of cells cultured on them (Gritsch *et al.*, 2017). Nanoscale surface features can in fact promote cell adhesion, motility and differentiation. Studies have also confirmed that nanotopography can enhance selective protein adsorption of fibronectin, vitronectin and several other peptides associated with successful cell attachment (Verma *et al.*, 2011; Dvir *et al.*, 2011). Furthermore, oriented topographic patterns can further guide the movement and growth of cells through contact guidance. In this way, it can be possible to obtain highly anisotropic tissues, such as tendons, nerves or muscle fibers (Nguyen *et al.*, 2016). Nanocomposites are particularly investigated for bone tissue engineering, dentistry (i.e., dentin regeneration) as well as in cartilage and osteochondral regeneration, as described in a previous review paper (Boccaccini *et al.*, 2010). The combination of biodegradable polymers, both synthetic and natural, with nanoscale bioactive fillers, bioactive glasses in particular, is emerging as a powerful strategy towards a new generation of enhanced bioactive materials with substantial advantages in terms of material homogeneity, reactivity and biological response compared to conventional composites with μm -scale fillers. The research on these materials is expected to expand in the future. In particular, increasing processing approaches for inorganic nanostructured bioactive materials will increase their possible applications. Possible identified directions of future research are the investigation on injectable osteoconductive biomaterials, thin coatings and self-assembling nanocomposites as well as the optimization of the micro/nano-scale spatial control of surface bioactivity (Boccaccini *et al.*, 2010; Gritsch *et al.*, 2017). In parallel, both in vivo response and clinical effectiveness of bionanocomposites still need to be tested and fully validated, with particular attention to be put in clarifying the health and safety concerns associated with the long-term use of nanomaterials (Alpaslan and Webster, 2014).

Concluding Remarks

Polymer-based composites consisting of a biodegradable polymer as matrix and a bioactive filler are a major class of materials used for the development of scaffolds for hard tissue repair. These materials offer a synergic combination of a glass/ceramic with tissue bonding properties (i.e., bioactive) coupled with the ease of processing of biocompatible degradable polymers formed into a three-dimensional structure. Countless materials and processing strategies have been proposed in the past decades and are currently available and still under investigation. In this chapter, the main materials available, together with the most applied and promising fabrication techniques have been listed and described. These biodegradable and bioactive biocomposites combine several key properties for their successful application in tissue engineering: interconnected porosity, ideal structure and topography, bioactivity, biodegradability and the possibility of biomolecule incorporation. It was shown how being able to accurately tailor all the several variables at play, such as materials and their processing, fabrication techniques, grafting of biomolecules and, in some cases, encapsulation of cells, is key for a successful device. However, at the same time, several limitations remain to be addressed, mainly the need for improved mechanical properties, more accurate tailoring of the cell response and better analytic tools to investigate and predict the long-term behavior of biocomposite scaffolds. Many challenges are still ahead, but with them also many opportunities for biomaterials research.

References

- Abou Neel, E.A., O'Dell, L.A., Smith, M.E., Knowles, J.C., 2008. *J. Mater. Sci. Mater. Med.* 19, 1669–1679.
- Agarwal, S., Wendorff, J.H., Greiner, A., 2008. *Polymer* 49, 5603–5621.
- Aguilar-Perez, F.J., Vargas-Coronado, R., Cervantes-Uc, J.M., *et al.*, 2018. *J. Biomater. Appl.* 33, 11–22.
- Ahmed, I., Lewis, M., Olsen, I., Knowles, J.C., 2004. *Biomaterials* 25, 491–499.
- Alpaslan, E., Webster, T.J., 2014. *Int. J. Nanomed.* 9, 7–12.
- Ambard, A.J., Muenninghoff, L., 2006. *J. Prosthodont.* 15, 321–328.
- Amini, A.R., Laurencin, C.T., Nukavarapu, S.P., 2012. *Crit. Rev. Biomed. Eng.* 40, 363–408.
- Anžlovar, A., Kržan, A., Žagar, E., 2018. *Arab. J. Chem.* 11, 343–352.
- Archana, D., Dutta, J., Dutta, P.K., 2013. *Int. J. Biol. Macromol.* 57, 193–203.
- Arcos, D., Vallet-Reg, M., 2010. *Acta Biomater.* 6, 2874–2888.
- Asefnejad, A., Behnamghader, A., Khorasani, T.M., Farsadzadeh, B., 2011. *Int. J. Nanomed.* 6, 93–100.
- Ayutsede, J., Gandhi, M., Sukigara, S., *et al.*, 2006. *Biomacromolecules* 7, 208–214.
- Bagbi, Y., Pandey, A., Solanki, P.R., 2018. *Nanoscale Mater. Water Purif.* 275–288.
- Bai, Y., Neupane, M.P., Park, I.S., *et al.*, 2010. *Mater. Sci. Eng. C* 30, 1043–1049.
- Baino, F., Novajra, G., Vitale-Brovarone, C., 2015. *Front. Bioeng. Biotechnol.* 3, 202.
- Baino, F., Fiume, E., Miola, M., Verné, E., 2018a. *Int. J. Appl. Ceram. Technol.* 15, 841–860.
- Baino, F., Hamzehlou, S., Kargozar, S., 2018b. *J. Funct. Biomater.* 9, 25.
- Baino, F., Fiorilli, S., Vitale-brovarone, C., 2017. *Bioeng.* 4(1), 1–18.
- Baji, A., Mai, Y.-W., 2017. *Nanofiber Composites for Biomedical Applications*. Elsevier. pp. 55–78.

- Barroca, N., Daniel-Da-Silva, A.L., Vilarinho, P.M., Fernandes, M.H.V., 2010. *Acta Biomater.* 6, 3611–3620.
- Basnett, P., Ravi, S., Roy, I., 2017. *Science and Principles of Biodegradable and Bioresorbable Medical Polymers*. Elsevier.
- Beg, S., Rizwan, M., Sheikh, A.M., *et al.*, 2011. *J. Pharm. Pharmacol.* 63, 141–163.
- Bendtsen, S.T., Quinnell, S.P., Wei, M., 2017. *J. Biomed. Mater. Res. Part A* 105, 1457–1468.
- Bernhard, J.C., Vunjak-Novakovic, G., 2016. *Stem Cell Res. Ther.* 7, 56.
- Bhattacharjee, P., Kundu, B., Naskar, D., *et al.*, 2017. *Acta Biomater.* 63, 1–17.
- Bi, L., Jung, S., Day, D., *et al.*, 2012. *J. Biomed. Mater. Res. Part A* 100A, 3267–3275.
- Biswas, A., Bayer, I.S., Biris, A.S., *et al.*, 2012. *Adv. Colloid Interface Sci.* 170, 2–27.
- Bitar, M., Salih, V., Mudera, V., Knowles, J.C., Lewis, M.P., 2004. *Biomaterials* 25, 2283–2292.
- Blaker, J.J., Nazhat, S.N., Maquet, V., Boccaccini, A.R., 2011. *Acta Biomater.* 7, 829–840.
- Blaker, J.J., Maquet, V., Jérôme, R., Boccaccini, A.R., Nazhat, S.N., 2005. *Acta Biomater.* 1, 643–652.
- Boccaccini, A.R., Chicatun, F., Cho, J., *et al.*, 2007. *Adv. Funct. Mater.* 17, 2815–2822.
- Boccaccini, A.R., Erol, M., Stark, W.J., *et al.*, 2010. *Compos. Sci. Technol.* 70, 1764–1776.
- Bose, S., Tarafder, S., Banerjee, S.S., Davies, N.M., Bandyopadhyay, A., 2011. *Bone* 48, 1282–1290.
- Bossard, C., Granel, H., Wittrant, Y., *et al.*, 2018. *Biomed. Glasses* 4, 108–122.
- Brauer, D.S., 2012. *Bio-Glasses*. Chichester: John Wiley & Sons, Ltd, pp. 45–64.
- Brauer, D.S., 2015. *Angew. Chemie - Int. Ed.* 54, 4160–4181.
- Brink, M., 1997. *J. Biomed. Mater. Res.* 36, 109–117.
- Brow, R.K., 2000. *J. Non. Cryst. Solids* 263–264, 1–28.
- Brown, R.F., Day, D.E., Day, T.E., *et al.*, 2008. *Acta Biomater.* 4, 387–396.
- Brown, T.D., Dalton, P.D., Huttmacher, D.W., 2016. *Prog. Polym. Sci.* 56, 116–166.
- Brun, V., Guillaume, C., Mechiche Alami, S., *et al.*, 2014. *Biomed. Mater. Eng.* 24, 63–73.
- Burguera, E.F., Xu, H.H.K., Weir, M.D., 2006. *J. Biomed. Mater. Res. Part B Appl. Biomater.* 77B, 126–134.
- Burke, A., Hasirci, N., 2004. *Polyurethanes in biomedical applications*. In: Hasirci, N., Hasirci, V. (Eds.), *Biomaterials From Molecules to Engineered Tissue*. Springer, pp. 83–101.
- Buyuksungur, S., Endogan Tanir, T., Buyuksungur, A., *et al.*, 2017. *Biomater. Sci.* 5, 2144–2158.
- Cacciotti, I., 2016. Cationic and anionic substitutions in hydroxyapatite. In: Antoniac, I.V. (Ed.), *Handbook of Bioceramics and Biocomposites*. Springer, pp. 145–211.
- Cai, Z., Wan, Y., Becker, M.L., Long, Y.-Z., Dean, D., 2019. *Biomaterials* 208, 45–71.
- Calignano, F., Galati, M., Iuliano, L., Minetola, P., 2019. *J. Healthc. Eng.* 9748212. doi:10.1155/2019/9748212.
- Campana, V., Milano, G., Pagano, E., *et al.*, 2014. *J. Mater. Sci. Mater. Med.* 25, 2445–2461.
- Capati, M.L.F., Nakazono, A., Igawa, K., *et al.*, 2016. *Biol. Trace Elem. Res.* 174, 300–308.
- Carfi Pavia, F., La Carrubba, V., Brucato, V., 2013. *Polym. Bull.* 70, 563–578.
- Caridade, S.G., Merino, E.G., Alves, N.M., *et al.*, 2013. *J. Mech. Behav. Biomed. Mater.* 20, 173–183.
- Carrodeguas, R.G., Aza, S. De, 2011. *Acta Biomater.* 7, 3536–3546.
- Catto, V., Farè, S., Freddi, G., Tanzi, M.C., 2014. *ISRN Vasc. Med.* 2014, 1–27.
- Chakrabarty, A., Teramoto, Y., 2018. *Polymers* 10 (5), doi:10.3390/polym10050517.
- Chen, a.R., Roether, Q., Boccaccini, J.A., 2008. *Top. Tissue Eng.* 4, 1–27.
- Chen, F., Hochleitner, G., Woodfield, T., *et al.*, 2016. *Biomacromolecules* 17, 208–214.
- Chen, G.-Q., Wu, Q., 2005. *Biomaterials* 26, 6565–6578.
- Chen, Q.Z., Thompson, I.D., Boccaccini, A.R., 2006. *Biomaterials* 27, 2414–2425.
- Cheng, Q., Rutledge, K., Jabbarzadeh, E., 2013. *Ann. Biomed. Eng.* 41, 904–916.
- Cheung, R.C.F., Ng, T.B., Wong, J.H., Chan, W.Y., 2015. *Mar. Drugs* 13, 5156–5186.
- Choi, S.S., Lee, S.G., Im, S.S., Kim, S.H., Joo, Y.L., 2003. *J. Mater. Sci. Lett.* 22, 891–893.
- Chu, P.K., Liu, X., 2008. *Biomaterials Fabrication and Processing Handbook*. CRC Press. p. 720.
- Cilurzo, F., Gennari, C.G.M., Selmin, F., *et al.*, 2011. *Int. J. Pharm.* 414, 218–224.
- Cirraldo, F.E., Boccardi, E., Melli, V., Westhauser, F., Boccaccini, A.R., 2018a. *Acta Biomater.* 75, 3–10.
- Cirraldo, F.E., Liverani, L., Gritsch, L., Goldmann, W.H., Boccaccini, A.R., 2018b. *Materials* 11, 692.
- Conoscenti, G., Carfi Pavia, F., Cirraldo, F.E., *et al.*, 2018. *J. Mater. Sci.* 53. doi:10.1007/s10853-017-1743-9.
- Courtenay, J.C., Sharma, R.I., Scott, J.L., 2018. *Molecules* 23 (3). doi:10.3390/molecules23030654.
- Cui, Z., Zheng, Z., Su, C., *et al.*, 2019. *J. Mater. Sci.* 54, 11231–11242.
- Curry, A.S., Pensa, N.W., Barlow, A.M., Bellis, S.L., 2016. *Matrix Biol.* 52–54, 397–412. doi:10.1016/j.matbio.2016.02.011.
- Daas, I., Badr, S., Osman, E., 2018. *J. Contemp. Dent. Pract.* 19, 306–312.
- Dalton, P.D., Muerza-Cascante, M.L., Huttmacher, D.W., 2015. *Tissue engineering scaffold design and fabrication via melt electrospinning*. In: Mitchell, G.R. (Ed.), *Electrospinning: Principles, Practice and Possibilities*. RCS Publishing, pp. 100–120.
- Danoux, C.B., Barbieri, D., Yuan, H., *et al.*, 2014. *Biomater* 4. e27664.
- Dasgupta S., 2018. *SM J of Orthop.* 4(1), 1–12. doi:10.15406/atropa.2017.02.00049.
- Davies, O.R., Lewis, A.L., Whitaker, M.J., *et al.*, 2008. *Adv. Drug Deliv. Rev.* 60, 373–387.
- De Groot, K., 1998. *Tissue Eng.* 4, 337–341.
- Deville, S., Saiz, E., Nalla, R.K., Tomsia, A.P., 2006. *Adv. Sci. Technol.* 49, 148–152.
- Diba, M., Goudouri, O.-M., Tapia, F., Boccaccini, A.R., 2014. *Curr. Opin. Solid State Mater. Sci.* 18, 147–167.
- Diez-Pascual, A., 2017. *Polymers* 9, 260.
- Doi, Y., Kitamura, S., Abe, H., 1995. *Macromolecules* 28, 4822–4828.
- Dorozhkin, S.V., 2011. *Biomater* 1, 121–164.
- Doshi, J., Reneker, D.H., 1995. *J. Electrostat.* 35, 151–160.
- Doyle, C., Tanner, E.T., Bonfield, W., 1991. *Biomaterials* 12, 841–847.
- Du, X., Wei, D., Huang, L., *et al.*, 2019. *Mater. Sci. Eng. C* 103, 109731.
- Dusseault, J., Tam, S.K., Ménard, M., *et al.*, 2006. *J. Biomed. Mater. Res. Part A* 76A, 243–251.
- Dvir, T., Timko, B.P., Kohane, D.S., Langer, R., 2011. *Nat. Nanotechnol.* 6, 13–22.
- Dzondo-Gadet, M., Mayap-Nzietchueng, R., Hess, K., *et al.*, 2002. *Biol. Trace Elem. Res.* 85, 23–33.
- Egan, P.F., 2019. *Materials* 12, 2355.
- Elgayar, I., Aliev, A.E., Boccaccini, A.R., Hill, R.G., 2005. *J. Non. Cryst. Solids* 351, 173–183.
- Ema, M., Gamo, M., Honda, K., 2016. *Regul. Toxicol. Pharmacol.* 74, 42–63.
- Eqtessadi, S., Motealleh, A., Pajares, A., Guiberteau, F., Miranda, P., 2016a. *J. Non Cryst. Solids* 432, 111–119.

- Egtesadi, S., Motealleh, A., Perera, F.H., Pajares, A., Miranda, P., 2016b. *Mater. Lett.* 163, 196–200.
- Ersel, M., Uyanikgil, Y., Karbek Akarca, F., *et al.*, 2016. *Med. Sci. Monit.* 22, 1064–1078.
- Esa, F., Tasirin, S.M., Rahman, N.A., 2014. *Agric. Agric. Sci. Procedia* 2, 113–119.
- Farokhi, M., Mottaghitalab, F., Samani, S., *et al.*, 2018. *Biotechnol. Adv.* 36, 68–91.
- Fiume, E., Barberi, J., Verné, E., Bairo, F., 2018. *J. Funct. Biomater.* 9, 24.
- Francis, A.P., Devasena, T., 2018. *Toxicol. Ind. Health* 34, 200–210.
- Fu, Q., Rahaman, M.N., Bal, B.S., *et al.*, 2010a. *J. Biomed. Mater. Res. Part A* 95A, 172–179.
- Fu, Q., Rahaman, M.N., Fu, H., Liu, X., 2010b. *J. Biomed. Mater. Res. Part A* 95A, 164–171.
- Fu, Q., Saiz, E., Rahaman, M.N., Tomsia, A.P., 2011. *Mater. Sci. Eng. C* 31, 1245–1256.
- Fujibayashi, S., Neo, M., Kim, H.-M., Kokubo, T., Nakamura, T., 2003. *Biomaterials* 24, 1349–1356.
- Gao, G., Cui, X., 2016. *Biotechnol. Lett.* 38, 203–211.
- Garg, T., Singh, O., Arora, S., Murthy, R.S.R., 2012. *Crit. Rev. Ther. Drug Carr. Syst.* 29, 1–63.
- Gasparin, L., Mano, J.R., Reis, R., 2014. *Soc. Interface* 11, 20140817.
- Gelse, K., 2003. *Adv. Drug Deliv. Rev.* 55, 1531–1546.
- Gerhard, E.M., Wang, W., Li, C., *et al.*, 2017. *Acta Biomater.* 54, 21–34.
- Gerhardt, L.-C., Zell, G.M.R., Boccaccini, A.R., 2007. *J. Mater. Sci. Mater. Med.* 18, 1287–1298.
- Gibson, I.R., Best, S.M., Bonfield, W., 1999. *J. Biomed. Mater. Res.* 44, 422–428.
- Girones Molera, J., Mendez, J.A., San Roman, J., 2012. *Curr. Pharm. Des.* 18, 2536–2557.
- Gomes, M.E., Salgado, A., Reis, R.L., 2002. *Polymer Based Systems on Tissue Engineering, Replacement and Regeneration*. Dordrecht: Springer, pp. 221–249.
- Gomes, M.E., Reis, R.L., Cunha, A.M., Blitterswijk, C.A., de Bruijn, J.D., 2001. *Biomaterials* 22, 1911–1917.
- Gómez-Guillén, M.C., Giménez, B., López-Caballero, M.E., Montero, M.P., 2011. *Food Hydrocoll.* 25, 1813–1827.
- Gonçalves, C., Gonçalves, I., Magalhães, F., Pinto, A., 2017. *Polymers* 9, 269.
- Goonoo, N., Bhaw-Luximon, A., Passanha, P., Esteves, S.R., Jhurry, D., 2017. *J. Biomed. Mater. Res. - Part B Appl. Biomater.* 105, 1667–1684.
- Gough, J.E., Boccaccini, A.R., 2007. *Tissue Engineering Using Ceramics and Polymers*. Elsevier.
- Granel, H., Bossard, C., Collignon, A.-M., *et al.*, 2019. *ACS Appl. Bio Mater.* 2 (8), 3473–3483. doi:10.1021/acsabm.9b00407.
- Graziani, G., Boi, M., Bianchi, M., 2018. *Coatings* 8, 269.
- Griffanti, G., Jiang, W., Nazhat, S.N., 2019. *Biomater. Sci.* 7, 1064–1077.
- Gritsch, L., Meng, D., Boccaccini, A.R., 2017. Chapter 20 – Nanostructured biocomposites for tissue engineering scaffolds. In: Ambrosio, L. (Ed.), *Biomedical Composites*. Elsevier, pp. 501–542.
- Gritsch, L., Conoscenti, G., La Carrubba, V., Noeaid, P., Boccaccini, A.R., 2019. *Mater. Sci. Eng. C* 94, 1083–1101.
- Grizzi, I., Garreau, H., Li, S., Vert, M., 1995. *Biomaterials* 16, 305–311.
- Guelcher, S. a., Patel, V., Gallagher, K., *et al.*, 2004. *AIChE Annu. Meet. Conf. Proc.* 30, 1087–1089.
- Habibovic, P., Barralet, J.E., 2011. *Acta Biomater.* 7, 3013–3026.
- Habraken, W.J., Wolke, J.G., Jansen, J.A., 2007. *Adv. Drug Deliv. Rev.* 59, 234–248.
- Hafezi, F., Hosseinejad, F., Fooladi, A.A.I., *et al.*, 2012. *J. Mater. Sci. Mater. Med.* 23, 2783–2792.
- Hajiali, F., Tajbakhsh, S., Shojaei, A., 2018. *Polym. Rev.* 58, 164–207.
- Haldorai Y., 2018. *Indian J. Fibre Text.* 43, 464–473.
- Hasirci, N., Aksoy, E.A., 2007. *High Perform. Polym.* 19, 621–637.
- He, P., Sahoo, S., Ng, K.S., *et al.*, 2013. *J. Biomed. Mater. Res. - Part A* 101 A, 555–566.
- He, S., Yaszemski, M.J., Yasko, A.W., Engel, P.S., Mikos, A.G., 2000. *Biomaterials* 21, 2389–2394.
- Helen, W., Merry, C.L.R., Blaker, J.J., Gough, J.E., 2007. *Biomaterials* 28, 2010–2020.
- Hench, L.L., 2015. *J. Mater. Sci. Mater. Med.* 26, 86.
- Hench, L.L., Jones, J.R., 2015. *Front. Bioeng. Biotechnol.* 3, 194. doi:10.3389/fbioe.2015.00194.
- Hench, L.L., Splinter, R.J., Allen, W.C., Greenlee, T.K., 1971. *J. Biomed. Mater. Res.* 5, 117–141.
- Henkel, J., Woodruff, M.A., Epari, D.R., *et al.*, 2013. *Bone Res.* 1, 216–248.
- Heppenstall, R.B., Goodwin, C.W., Brighton, C.T., 1976. *J. Bone Jt. Surg. - Ser. A* 58, 1153–1156.
- Hickey, D.J., Ercan, B., Chung, S., *et al.*, 2014. 2014 40th Annual Northeast Bioengineering Conference (NEBEC). IEEE. pp. 1–2.
- Hickey, R.J., Pelling, A.E., 2019. *Front. Bioeng. Biotechnol.* doi:10.3389/fbioe.2019.00045.
- Hochleitner, G., Jüngst, T., Brown, T.D., *et al.*, 2015. *Bioprinting* 7, 035002.
- Hochleitner, G., Fürsattel, E., Giesa, R., *et al.*, 2018. *Macromol. Rapid Commun.* 39, 1800055.
- Hoppe, A., Güldal, N.S., Boccaccini, A.R., 2011. *Biomaterials* 32, 2757–2774.
- Hrynevich, A., Elçi, B., Haigh, J.N., *et al.*, 2018. *Small* 14, 1800232.
- Huang, Z.-M., Zhang, Y.-Z., Kotaki, M., Ramakrishna, S., 2003. *Compos. Sci. Technol.* 63, 2223–2253.
- Hutmacher, D.W., 2006. *Biomater. Silver Jubil. Compend.* 175–189.
- Iijima, S., 1991. *Nature* 354, 56–58.
- Ioniță, M., Crică, L.E., Voicu, S.I., *et al.*, 2018. *Carbohydr. Polym.* 183, 50–61.
- Ito, Y., Hasuda, H., Kamitakahara, M., *et al.*, 2005. *J. Biosci. Bioeng.* 100, 43–49.
- Jang, W.D., Hwang, J.H., Kim, H.U., Ryu, J.Y., Lee, S.Y., 2017. *Microb. Biotechnol.* 10, 1181–1185.
- Jell, G., Stevens, M.M., 2006. *J. Mater. Sci. Mater. Med.* 17, 997–1002.
- Jeon, H.J., Simon, C.G., Kim, G.H., 2014. *J. Biomed. Mater. Res. - Part B Appl. Biomater.* 102, 1580–1594.
- Jeong, J., Kim, J.H., Shim, J.H., Hwang, N.S., Heo, C.Y., 2019. *Biomater. Res.* 23, 4.
- Jiang, T., Carbone, E.J., Lo, K.W.H., Laurencin, C.T., 2014. *Prog. Polym. Sci.* 46, 1–24.
- Jin, G.Z., Kim, H.W., 2014. *Tissue Eng. Regen. Med.* 11, 284–290.
- Jin, Q.-M., Takita, H., Kohgo, T., *et al.*, 2000. *J. Biomed. Mater. Res.* 51, 491–499.
- Jo, Y.-Y., Kweon, H., Kim, D.-W., *et al.*, 2017. *Sci. Rep.* 7, 15589.
- Jones, J.R., 2013. *Acta Biomater.* 9, 4457–4486.
- Jose, R.R., Elia, R., Firpo, M.A., Kaplan, D.L., Peattie, R.A., 2012. *J. Mater. Sci. Mater. Med.* 23, 2679–2695.
- Kasper, F.K., Tanahashi, K., Fisher, J.P., Mikos, A.G., 2009. *Nat. Protoc.* 4, 518–525.
- Kaur, T., Kulanthavel, S., Thirugnanam, A., Banerjee, I., Pramanik, K., 2017. *Biomed. Mater.* 12 (2), 025012. doi:10.1088/1748-605X/aa5f76.
- Kim, H., Che, L., Ha, Y., Ryu, W., 2014a. *Mater. Sci. Eng. C* 40, 324–335.
- Kim, J.H., Sheikh, F.A., Ju, H.W., *et al.*, 2014b. *Int. J. Biol. Macromol.* 68, 158–168.
- Kim, H.W., Kim, H.E., Knowles, J.C., 2006. *Adv. Funct. Mater.* 16, 1529–1535.
- Kim, J.J., Jin, G.Z., Yu, H.S., *et al.*, 2012a. *Mater. Sci. Eng. C* 32, 2545–2551.

- Kim, S.H., Jung, Y., Kim, S.H., 2012b. *Tissue Eng. Part C Methods* 19, 181–188.
- Kimura, Y., 2009. *Polym. J.* 41, 797–807.
- Kivrak, N., Taş, A.C., 2005. *J. Am. Ceram. Soc.* 81, 2245–2252.
- Knowles, J.C., 2003. *J. Mater. Chem.* 13, 2395.
- Kokubo, T., Takadama, H., 2006. *Biomaterials* 27, 2907–2915.
- Kolan, K.C.R., Semon, J.A., Bromet, B., Day, D.E., Leu, M.C., 2019. *Int. J. Bioprinting* 5, 3.
- Kolbuk, D., Guimond-Lischer, S., Sajkiewicz, P., Maniura-Weber, K., Fortunato, G., 2015. *Int. J. Polym. Mater. Polym. Biomater.* 64, 365–377.
- Kunz, R.I., Brancalhão, R.M.C., de, L., Ribeiro, F.C., Natali, M.R.M., 2016. *Biomed. Res. Int.* 2016, 1–19.
- Kuo, S.M., Chang, S.J., Niu, G.C.-C., *et al.*, 2009. *J. Appl. Polym. Sci.* 112, 3127–3134.
- Labbaf, S., Houreh, A.B., Rahimi, M., *et al.*, 2018. *Biomed. Glasses* 4, 123–130.
- Lacroix, J., Jallot, E., Lao, J., 2014. *Chem. Eng. J.* 256, 9–13.
- Lai, W., Garino, J., Ducheyne, P., 2002. *Biomaterials* 23, 213–217.
- Landi, E., Valentini, F., Tampieri, A., 2008. *Acta Biomater.* 4, 1620–1626.
- Landolph, J.R., 1985. *Am. J. Ind. Med.* 7, 31–43.
- Łapa, A., Cresswell, M., Jackson, P., Boccaccini, A.R., 2019. *Adv. Appl. Ceram.* 1–14.
- Lara-Espinoza, C., Carvajal-Millán, E., Baladrán-Quintana, R., López-Franco, Y., Rascón-Chu, A., 2018. *Molecules* 23, 942.
- Lee, C.H., Singla, A., Lee, Y., 2001. *Int. J. Pharm.* 221, 1–22.
- Lee, K.Y., Mooney, D.J., 2012. *Prog. Polym. Sci.* 37, 106–126.
- Lee, S., Matsugaki, A., Kasuga, T., Nakano, T., 2019. *J. Biomed. Mater. Res. Part A* 107, 1031–1041.
- Legeros, R.Z., Lin, S., Rohanizadeh, R., Mijares, D., Legeros, J.P., 2003. *J. Mater. Sci. Mater. Med.* 14, 201–209.
- LeGeros, R.Z., 2002. *Clin. Orthop. Relat. Res.* 81–98.
- LeGeros, R.Z., 2008. *Chem. Rev.* 108, 4742–4753.
- Lei, Y., Xu, Z., Ke, Q., *et al.*, 2017. *Mater. Sci. Eng. C* 72, 134–142.
- Leite, Á.J., Sarker, B., Zehnder, T., *et al.*, 2016. *Biofabrication* 8, 035005.
- Levengood, S.K.L., Zhang, M., 2014. *J. Mater. Chem. B* 2, 3161.
- Li, H., Chang, J., 2005a. *Polym. Degrad. Stab.* 87, 301–307.
- Li, H., Chang, J., 2005b. *J. Control. Release* 107, 463–473.
- Li, L., Fang, Y., Vreeker, R., Appelqvist, I., Mendes, E., 2007. *Biomacromolecules* 8, 464–468.
- Li, S., Song, C., Yang, S., *et al.*, 2019. *Acta Biomater.* 94, 253–267.
- Li, W., Cai, Y., Zhong, Q., *et al.*, 2016. *J. Mater. Chem. B* 4, 340–347.
- Li, X., Fan, Y., Watari, F., 2010. *Biomed. Mater.* 5 (2). doi:10.1088/1748–6041/5/2/022001.
- Li, Y., Li, D., Lu, B., Gao, D., Zhou, J., 2015. *Rapid Prototyp. J* 21, 747–762.
- Li S., 2017. *Science and Principles of Biodegradable and Bioresorbable Medical Polymers: Materials and Properties*. Woodhead Publishing, pp. 37–78.
- Lin, H.-R., Yeh, Y.-J., 2004. *J. Biomed. Mater. Res.* 71B, 52–65.
- Lin, N., Dufresne, A., 2014. *Eur. Polym. J.* 59, 302–325.
- Liu, B., Lun, D., 2012. *Orthop. Surg.* 4, 139–144.
- Liu, D., Nikoo, M., Boran, G., Zhou, P., Regenstein, J.M., 2015. *Annu. Rev. Food Sci. Technol.* 6, 527–557.
- Liu, H., Li, H., Cheng, W., *et al.*, 2006. *Acta Biomater.* 2, 557–565.
- Liu, X., Rahaman, M.N., Day, D.E., 2013. *J. Mater. Sci. Mater. Med.* 24, 583–595.
- Liverani, L., Abbruzzese, F., Mozetic, P., *et al.*, 2014. *Asia-Pacific J. Chem. Eng.* 9, 407–414.
- Liverani, L., Lacina, J., Roether, J.A., *et al.*, 2018. *Bioact. Mater.* 3, 55–63.
- Liverani, L., Boccardi, E., Beltran, A.M., Boccaccini, A.R., 2017. *Polymers* 9 (10). doi:10.3390/polym9100487.
- Lopez-Heredia, M.A., Łapa, A., Mendes, A.C., *et al.*, 2017. *Mater. Lett.* 190, 13–16.
- Lu, Q., Zhang, B., Li, M., Zuo, B., Kaplan, D.L., 2011. *Biomacromolecules*. 1080–1086.
- Lunt, J., 1998. *Polym. Degrad. Stab.* 59, 145–152.
- Luo, H., Dong, J., Yao, F., *et al.*, 2018. *Nano-Micro Lett.* 10, 42.
- Luz, G.M., Mano, J.F., 2012. *Biomed. Mater.* 7, 054104.
- Lynn, A.K., Yannas, I.V., Bonfield, W., 2004. *J. Biomed. Mater. Res* 71B, 343–354.
- Maçon, A.L.B., Kim, T.B., Valliant, E.M., *et al.*, 2015. *J. Mater. Sci. Mater. Med.* 26, 1–10.
- Magiera, A., Markowski, J., Menaszek, E., Pilch, J., Blazewicz, S., 2017. *J. Nanomater.* 2017, 1–11.
- Mahabadi, H.K., Alexandru, L., 2006. *Can. J. Chem.* 63, 221–222.
- Malikmammadov, E., Tanir, T.E., Kiziltay, A., Hasirci, V., Hasirci, N., 2018. *J. Biomater. Sci. Polym. Ed.* 29, 863–893.
- Mannella, G.A., Conoscenti, G., Carfi Pavia, F., La Carrubba, V., Brucato, V., 2015. *Mater. Lett.* 160, 31–33.
- Maquet, V., Boccaccini, A.R., Pravata, L., Nottingher, I., Jérôme, R., 2003. *Biomed Mater Res A* 66A, 335–346.
- Maquet, V., Boccaccini, A.R., Pravata, L., Nottingher, I., Jérôme, R., 2004. *Biomaterials* 25, 4185–4194.
- Marelli, B., Ghezzi, C.E., Mohn, D., *et al.*, 2011. *Biomaterials* 32, 8915–8926.
- Marelli, B., Achilli, M., Alessandrino, A., *et al.*, 2012a. *Macromol. Biosci.* 12, 1566–1574.
- Marelli, B., Ghezzi, C.E., Alessandrino, A., *et al.*, 2012b. *Biomaterials* 33, 102–108.
- Marra, A., Silvestre, C., Duraccio, D., Cimmino, S., 2016. *Int. J. Biol. Macromol.* 88, 254–262.
- Martins, T., Moreira, C.D.F., Costa-Júnior, E.S., Pereira, M.M., 2018. *Biomed. Glas.* 4, 45–56.
- Mas-Moruno, C., 2018. *Peptides and Proteins as Biomaterials for Tissue Regeneration and Repair*. Elsevier. pp. 73–100.
- Massera, J., Ahmed, I., Petit, L., Aallos, V., Hupa, L., 2014. *Mater. Sci. Eng. C* 37, 251–257.
- Mattioli-Belmonte, M., Vozzi, G., Whulanza, Y., *et al.*, 2012. *Mater. Sci. Eng. C* 32, 152–159.
- McAndrew, J., Efrimescu, C., Sheehan, E., Niall, D., 2013. *Ir. J. Med. Sci.* 182, 509–511.
- McColl, E., Groll, J., Jungst, T., Dalton, P.D., 2018. *Mater. Des.* 155, 46–58.
- Meyer, M., 2019. *Biomed. Eng. Online* 18, 24.
- Mi, H.Y., Jing, X., Salick, M.R., Peng, X.F., Turng, L.S., 2014. *Polym. Eng. Sci.* 54, 2947–2957.
- Midha, S., Kumar, S., Sharma, A., *et al.*, 2018. *Biomed. Mater.* 13, 055012.
- Miguez-Pacheco, V., Hench, L.L., Boccaccini, A.R., 2015. *Acta Biomater.* 13, 1–15.
- Mikshina, P.V., Petrova, A.A., Faizullin, D.A., Zuev, Y.F., Gorshkova, T.A., 2015. *Biochem* 80, 915–924.
- Milton, G.W., 2002. *The Theory of Composites*. Cambridge: Cambridge University Press.
- Mirab, F., Eslamian, M., Bagheri, R., 2018. *Biomed. Phys. Eng. Express*. doi:10.1088/2057–1976/aad74a.
- Mishra, R., Basu, B., Kumar, A., 2009. *J. Mater. Sci. Mater. Med.* 20, 2493–2500.

- Misra, S.K., Mohn, D., Brunner, T.J., *et al.*, 2008. *Biomaterials* 29, 1750–1761.
- Misra, S.K., Valappil, S.P., Roy, I., Boccaccini, A.R., 2006. *Biomacromolecules* 7, 2249–2258.
- Moseke, C., Gbureck, U., 2010. *Acta Biomater.* 6, 3815–3823.
- Mostafa, N.Y., Zaki, Z.I., 2015. *Int. J. Chem. Sci.* 13, 80–96.
- Motshekga, S.C., Ray, S.S., Onyango, M.S., Momba, M.N.B., 2015. *Appl. Clay Sci.* 114, 330–339.
- Mourinho, V., Cattalini, J.P., Boccaccini, A.R., 2012. *J. R. Soc. Interface* 9, 401–419.
- Mourya, V.K., Inamdar, N.N., 2008. *React. Funct. Polym.* 68, 1013–1051.
- Muerza-Cascante, M.L., Haylock, D., Huttmacher, D.W., Dalton, P.D., 2014. *Tissue Eng. Part B Rev.* 21, 187–202.
- Munarin, F., Guerreiro, S.G., Grellier, M.A., *et al.*, 2011. *Biomacromolecules* 12, 568–577.
- Münchow, E.A., Albuquerque, M.T.P., Zero, B., *et al.*, 2015. *Dent. Mater.* 31, 1038–1051.
- Muñoz-Senovilla, L., Muñoz, F., Tricot, G., Ahmed, I., Parsons, A.J., 2017. *J. Mater. Sci.* 52, 9166–9178.
- Muzzarelli, R.A.A., Biagini, G., Bellardini, M., *et al.*, 1993. *Biomaterials* 14, 39–43.
- Naik, K., Chandran, V.G., Rajashekar, R., Waigankar, S., Kowshik, M., 2016. *J. Biomater. Appl.* 31, 387–399.
- Narayanan, G., Vernekar, V.N., Kuyinu, E.L., Laurencin, C.T., 2016. *Adv. Drug Deliv. Rev.* 107, 247–276.
- Nasri-Nasrabadi, B., Kaynak, A., Heidarian, P., *et al.*, 2018. *Polym. Adv. Technol.* 29, 2553–2559.
- Navarro, M., Ginebra, M.P., Planell, J. a., Barrias, C.C., Barbosa, M. a., 2005. *Acta Biomater.* 1, 411–419.
- Nayak, S., Dey, T., Naskar, D., Kundu, S.C., 2013. *Biomaterials* 34, 2855–2864.
- Nelson, D.L., Cox, M.M., 2004. *Lehninger Principles of Biochemistry*, fourth ed. W.H. Freeman & Company.
- Ng, H.-M., Bee, S.-T., Tin Sin, L., Ratnam, C.T., Rahmat, A.R., 2019. *Polym. Rev.* 59, 187–239.
- Nguyen, A.T., Sathe, S.R., Yim, E.K.F., 2016. *J. Phys. Condens. Matter* 28, 183001.
- Nicolaije, C., Koedam, M., van Leeuwen, J.P.T.M., 2012. *J. Cell. Physiol.* 227, 1309–1318.
- Ning, C., 2016. *Biomaterials for bone tissue engineering*. In: Poitout, D.G. (Ed.), *Biomechanics and Biomaterials in Orthopedics*, second ed. Springer, pp. 35–57.
- No, Y., Li, J., Zreiqat, H., 2017. *Materials* 10, 153.
- Noh, K.T., Lee, H.Y., Shin, U.S., Kim, H.W., 2010. *Mater. Lett.* 64, 802–805.
- Pacheco, D.P., Marcello, E., Bloise, N., *et al.*, 2018. *Curr. Org. Chem.* 22, 1222–1236.
- Padamwar, M.N., Pawar, A.P., 2004. *J. Sci. Ind. Res.* 63, 323–329.
- Padmanabhan, J., Kyriakides, T.R., 2015. *Wiley Interdiscip. Rev. Nanomed. Nanobiotechnol.* 7, 355–370.
- Park, S.N., Tae Noh, K., Jeong, Y.-I., *et al.*, 2013. *Exp. Mol. Med.* 45, e8.
- Pazo, A., Saiz, E., Tomsia, A.P., 1998. *Acta Mater.* 46, 2551–2558.
- Peng, Y., Sun, H.-Y., Wang, Z.-C., *et al.*, 2016. *Chemotherapy* 61, 32–40.
- Perez, R.A., Mestres, G., 2016. *Mater. Sci. Eng. C. Mater. Biol. Appl.* 61, 922–939.
- Pielichowska, K., Blazewicz, S., 2010. *Adv. Polym. Sci.* 232, 97–207.
- Pighinelli, L., Kucharska, M., 2013. *Carbohydr. Polym.* 93, 256–262.
- Pirzada, T., Arvidson, S.A., Saquing, C.D., Shah, S.S., Khan, S.A., 2012. *Langmuir* 28, 5834–5844.
- Poolagasundarampillai, G., Maçon, A.L.B., 2017. *RSC Smart Mater.* 286–302.
- Prafulla S, Bubbly S, 2018. *AIP Conf. Proc.* 030168.
- Prasad, A., Sankar, M.R., Katiyar, V., 2017. *Mater. Today Proc.* 4, 898–907.
- Puvaneswary, S., Talebian, S., Raghavendran, H.B., *et al.*, 2015. *Carbohydr. Polym.* 134, 799–807.
- Qi, C., Xu, L., Deng, Y., *et al.*, 2018. *Biomater. Sci.* 6, 2859–2870.
- Qi, Y., Wang, H., Wei, K., *et al.*, 2017. *Int. J. Mol. Sci.* 18 (3). doi:10.3390/ijms18030237.
- Rahaman, M.N., 2014. Chapter 3 – Bioactive ceramics and glasses for tissue engineering. In: Boccaccini, A.R., Ma, P.X. (Eds.), *Tissue Engineering Using Ceramics and Polymers*, second ed. Elsevier, pp. 67–114.
- Rahaman, M.N., Day, D.E., Sonny Bal, B., *et al.*, 2011. *Acta Biomater.* 7, 2355–2373.
- Ramahdita, G., Puspita, D.M., Albab M.F., *et al.*, 2018. *AIP Conf. Proc.* 020006.
- Ramot, Y., Zada, M.H., Domb, A.J., Nyska, A., 2016. *Adv. Drug Deliv. Rev.* 107. doi:10.1016/j.addr.2016.03.012.
- Ratnayake, J.T.B., Mucalo, M., Dias, G.J., 2017. *J. Biomed. Mater. Res. Part B Appl. Biomater* 105, 1285–1299.
- Raz, M., Moztaazadeh, F., Kordestani, S.S., 2018. *Silicon* 10, 667–674.
- Reddi, A.H., 2000. *Tissue Eng.* 6, 351–359.
- Reiniati, I., Hrymak, A.N., Margaritis, A., 2017. *Crit. Rev. Biotechnol.* 37, 510–524.
- Ren, J., Blackwood, K.A., Doustgani, A., *et al.*, 2014. *J. Biomed. Mater. Res. Part A* 102, 3140–3153.
- Reverchon, E., Cardea, S., Rapuano, C., 2008. *J. Supercrit. Fluids* 45, 365–373.
- Rezabeigi, E., Wood-Adams, P.M., Drew, R.A.L., 2016. *J. Biomed. Mater. Res. Part B Appl. Biomater.* 105 (8), 2433–2442.
- Rezwan, K., Chen, Q.Z., Blaker, J.J., Boccaccini, A.R., 2006. *Biomaterials* 27, 3413–3431.
- Ricard-Blum, S., 2011. *Cold Spring Harb. Perspect. Biol.* 3. a004978.
- Rinehart, J.D., Taylor, T.D., Tian, Y., Latour, R.A., 1999. *J. Biomed. Mater. Res.* 48, 833–840.
- Ripamonti, U., 1996. *Biomaterials* 17, 31–35.
- Ryszkowska, J.L., Auguścik, M., Sheikh, A., Boccaccini, A.R., 2010. *Compos. Sci. Technol.* 70, 1894–1908.
- Sahithi, K., Swetha, M., Ramasamy, K., Srinivasan, N., Selvamurugan, N., 2010. *Int. J. Biol. Macromol.* 46, 281–283.
- Salgado, A.J., Coutinho, O.P., Reis, R.L., 2004. *Tissue Eng.* 10, 465–474.
- Salih, V., Franks, K., James, M., *et al.*, 2000. *J. Mater. Sci. Mater. Med.* 11, 615–620.
- Salim, A., Nacamuli, R.P., Morgan, E.F., Giaccia, A.J., Longaker, M.T., 2004. *J. Biol. Chem.* 279, 40007–40016.
- Samavedi, S., Whittington, A.R., Goldstein, A.S., 2013. *Acta Biomater.* 9, 8037–8045.
- Sanmartín de Almeida, M., de G.V., Fernandes, O., de Oliveira, A.M., Granjeiro, J.M., 2018. *J. Int. Med. Res.* 46, 2537–2548.
- Santiago-Medina, P., Sundaram, P.A., Diffoot-Carlo, N., 2015. *Int. J. Dent.* 2015, 1–9.
- Santin, M., Motta, A., Freddi, G., Cannas, M., 1999. *J. Biomed. Mater. Res.* 46, 382–389.
- Sanuja, S., Agalya, A., Umapathy, M.J., 2014. *Int. J. Polym. Mater. Polym. Biomater.* 63, 733–740.
- Sarker, B., Li, W., Zheng, K., Detsch, R., Boccaccini, A.R., 2016. *ACS Biomater. Sci. Eng.* 2, 2240–2254.
- Saska, S., Barud, H.S., Gaspar, A.M.M., *et al.*, 2011. *Int. J. Biomater.* 2011, 1–8.
- Schuerch, C., 1985. *Bioactive Polymeric Systems*. Boston, MA: Springer, pp. 365–386.
- Schwach, G., Vert, M., 1999. *Int. J. Biol. Macromol.* 25, 283–291.
- Sharma, A., Thakur, M., Bhattacharya, M., Mandal, T., Goswami, S., 2019. *Biotechnol. Reports* 21. e00316.
- Sharmin, N., Gu, F., Ahmed, I., Parsons, A.J., 2017. *J. Tissue Eng.* 8.
- Shasteen, C., Choy, Y. Bin, 2011. *Biomed. Eng. Lett.* 1, 163–167.

- Shin, D.Y., Kang, M.-H., Kang, I.-G., Kim, H.-E., Jeong, S.-H., 2018. *J. Biomater. Appl.* 32, 1360–1370.
- Siddiqui, H., Pickering, K., Mucalo, M., 2018. *Materials* 11, 1813.
- Simpson, R.L., Nazhat, S.N., Blaker, J.J., *et al.*, 2015. *J. Mech. Behav. Biomed. Mater.* 50, 277–289.
- Singh, M., Morris, C.P., Ellis, R.J., Detamore, M.S., Berkland, C., 2008. *Tissue Eng. Part C Methods* 14, 299–309.
- Singh, M., Sandhu, B., Scurto, A., Berkland, C., Detamore, M.S., 2010. *Acta Biomater.* 6, 137–143.
- Singh, S., Ramakrishna, S., 2017. *Curr. Opin. Biomed. Eng.* 2, 105–115.
- Siparsky, G.L., Voorhees, K.J., Miao, F., 1998. *J. Environ. Polym. Degrad.* 6, 31–41.
- Skrtic, D., Antonucci, J.M., Eanes, E.D., 2003. *J. Res. Natl. Inst. Stand. Technol.* 108, 167.
- Sobczak, M., 2015. *Polym. Plast. Technol. Eng.* 54, 155–172.
- Sousa, A.G., Nielsen, H.L., Armagan, I., Larsen, J., Sørensen, S.O., 2015. *Food Hydrocoll.* 47, 130–139.
- Sprio, S., Tampieri, A., Landi, E., *et al.*, 2008. *Mater. Sci. Eng. C* 28, 179–187.
- Su, C.-J., Tu, M.-G., Wei, L.-J., *et al.*, 2017. *Materials* 10, 501.
- Subia, B., Kundu, J., Kundu, S.C., 2010. Chapter 7 – Biomaterial scaffold fabrication techniques for potential tissue engineering applications. In: Eberli, D. (Ed.), *Tissue Engineering*. InTech.
- Subramanian, A., Krishnan, U.M., Sethuraman, S., 2011. *Biomed. Mater.* 6, 25004.
- Subuki I., Adnan N., Sharudin R.W., 2018. *AIP Conf. Proc.* 020019.
- Suryavanshi, A., Khanna, K., Sindhu, K.R., Bellare, J., Srivastava, R., 2017. *Biomed. Mater.* 12, 055011.
- Takahashi, Y., Yamamoto, M., Tabata, Y., 2005. *Biomaterials* 26, 3587–3596.
- Takeuchi, A., Ohtsuki, C., Miyazaki, T., *et al.*, 2005. *J. R. Soc. Interface* 2, 373–378.
- Tallawi, M., Rosellini, E., Barbani, N., *et al.*, 2015. *J. R. Soc. Interface* 12.
- Tanaka, M., Sato, Y., Zhang, M., *et al.*, 2017. *Nanomaterials* 7, 46.
- Thian, E.S., Huang, J., Vickers, M.E., *et al.*, 2006. *J. Mater. Sci.* 41, 709–717.
- Tite, T., Popa, A.C., Balescu, L.M., *et al.*, 2018. *Materials* 11 (11). doi:10.3390/ma11112081.
- Tong, H.-W., Wang, M., Li, Z.-Y., Lu, W.W., 2010. *Biomed. Mater.* 5, 54111.
- Torgbo, S., Sukyai, P., 2018. *Appl. Mater. Today* 11, 34–49.
- Trachtenberg, J.E., Placone, J.K., Smith, B.T., Fisher, J.P., Mikos, A.G., 2017. *J. Biomater. Sci. Polym. Ed.* 28, 532–554.
- Valentina, I., Harouti, A., Fabrice, L., Vincent, V., Roberto, P., 2017. *AIP Conf. Proc.* 1914. doi:10.1063/1.5016801.
- Valerio, P., Pereira, M.M., Goes, A.M., Leite, M.F., 2004. *Biomaterials* 25, 2941–2948.
- Van De Velde, K., Kiekens, P., 2002. *Polym. Test.* 21, 433–442.
- Vargas, G.E., Haro Durand, L.A., Cadena, V., *et al.*, 2013. *J. Mater. Sci. Mater. Med.* 24, 1261–1269.
- Vedakumari, S.W., Jayalakshmi, R., Sanjayan, C.G., *et al.*, 2020. *Polym. Bull.* 77, 475–481. doi:10.1007/s00289-019-02754-7.
- Venkatesan, J., Niithya, R., Sudha, P.N., Kim, S.-K., 2014. *Adv. Food Nutr. Res.* 73, 45–57.
- Venkatesan, J., Bhatnagar, I., Manivasagan, P., Kang, K.-H., Kim, S.-K., 2015. *Int. J. Biol. Macromol.* 72, 269–281.
- Verma, S., Domb, A.J., Kumar, N., 2011. *Nanomedicine* 6, 157–181.
- Verma, S., Bhatia, Y., Valappil, S.P., Roy, I., 2003. *Arch. Microbiol.* 179, 66–69.
- Verrier, S., Blaker, J.J., Maquet, V., Hench, L.L., Boccaccini, A.R., 2004. *Biomaterials* 25, 3013–3021.
- Vert, M., Mauduit, J., Li, S.S., 1994. *Biomaterials* 15, 1209–1213.
- Vert, M., Li, S.M., Spenlehauer, G., Guerin, P., 1992. *J. Mater. Sci. Mater. Med.* 3, 432–446.
- Viswanathan, N., Kumar, I.A., Meenakshi, S., 2019. *Int. J. Biol. Macromol.* 133, 811–816.
- Walter, G., Vogel, J., Hoppe, U., Hartmann, P., 2001. *J. Non. Cryst. Solids* 296, 212–223.
- Wang, Y., Shi, X., Ren, L., *et al.*, 2010. *J. Biomed. Mater. Res. Part B Appl. Biomater.* 9999B.
- Wang, Z., Zhang, Y., Zhang, J., *et al.*, 2015. *Sci. Rep.* 4, 7064.
- Wei, J., Chen, Q.Z., Stevens, M.M., Roether, J.A., Boccaccini, A.R., 2008. *Mater. Sci. Eng. C* 28, 1–10.
- Westbrook, E.G., 2016. *Nano Life* 06, 1642011.
- Wong, H.M., Chu, P.K., Leung, F.K.L., *et al.*, 2014. *Prog. Nat. Sci. Mater. Int.* 24, 561–567.
- Wu, C., Chang, J., 2013. *Biomed. Mater.* 8, 032001.
- Wu, C., Fan, W., Gelinsky, M., *et al.*, 2011. *J. R. Soc. Interface* 8, 1804–1814.
- Wu, Y., Kang, Z., Tian, Z., Wu, M., Wang, J., 2017. *Polymers* 9, 669.
- Wunner, F.M., Wille, M.L., Noonan, T.G., *et al.*, 2018. *Adv. Mater.* 30, 1706570.
- Wunner, F.M., Eggert, S., Maartens, J., *et al.*, 2019. *3D Print. Addit. Manuf.* 6, 82–90.
- Xiao, W., Zaeem, M.A., Li, G., Sonny Bal, B., Rahaman, M.N., 2017. *J. Mater. Sci.* 52, 9039–9054.
- Yahia, L.H., Chirani, N., Gritsch, L., *et al.*, 2015. *J. Biomed. Sci.* 4 (2), doi:10.4172/2254-609X.100013.
- Yamasaki, H., Sakai, H., 1992. *Biomaterials* 13, 308–312.
- Yan, J., Li, J., Runge, M.B., *et al.*, 2011. *J. Biomater. Sci. Polym. Ed.* 22, 489–504.
- Yang, C., Hillas, P.J., Báez, J.A., *et al.*, 2004. *BioDrugs* 18, 103–119.
- Yang, C., Kang, Y.-Q., Liao, X.-M., *et al.*, 2010. *Front. Mater. Sci. China* 4, 314–320.
- Ye, L., Chang, J., Ning, C., Lin, K., 2008. *J. Biomater. Appl.* 22, 465–480.
- Yooyod, M., Ross, G.M., Limpeanchob, N., *et al.*, 2016. *Eur. Polym. J.* 81, 43–52.
- You, F., Chen, X., Cooper, D.M.L., Chang, T., Eames, B.F., 2018. *Biofabrication* 11, 015015.
- Yuan, H., Yang, Z., de Bruijn, J.D., de Groot, K., Zhang, X., 2001. *Biomaterials* 22, 2617–2623.
- Zargar, V., Asghari, M., Dashti, A., 2015. *ChemBioEng Rev.* 2, 204–226.
- Zhang, D., Wu, X., Chen, J., Lin, K., 2018. *Bioact. Mater.* 3, 129–138.
- Zhang, H.P., Wang, X.Y., Min, S.J., *et al.*, 2014. *Ceram. Int.* 40, 985–991.
- Zhang, X., Jia, W., Gu, Y., *et al.*, 2010b. *Biomaterials* 31, 5865–5874.
- Zhang, Y., Bai, Y., Yan, B., 2010a. *Drug Discov. Today* 15, 428–435.
- Zhao, J., Liu, Y., Sun, W.-B., Zhang, H., 2011. *Chem. Cent. J.* 5, 40. doi:10.1186/1752-153X-5-40.
- Zhou, H., Lawrence, J.G., Bhaduri, S.B., 2012. *Acta Biomater.* 8, 1999–2016.
- Zhou, M., Yu, D., 2014. *Mol. Med. Rep.* 10, 508–514.

Surface Treatment of Bioceramics

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General Introduction

Bioceramics is the term for ceramics used in biological environments especially for bone or dental substitution (Paul *et al.*, 2010). Even if they are mainly used in orthopedics and dentistry, they are also used in drug delivery applications. The most commonly used ceramics are calcium phosphates (CaPs) in the form of α or β -tricalcium phosphate or hydroxyapatite, silicates like 45S5 Bioglass®, alumina, porcelain and zirconia (Bose *et al.*, 2018). The surface of these implanted materials is subject to a large kind of species from water, biomolecules to dissolved ions and also external stimuli. Typically, the integration ability of bioceramics into a biological medium is determined by the interaction between these external factors and the material surface. The ultimate goal of bioceramics engineering is to enhance as much as possible this integration of the manufactured ceramics. By consequence, it is necessary to first study and promote the interactions between the synthetic material and the body environment (Kurella and Dahotre, 2005; Soon *et al.*, 2016).

It is known that material surface properties could be really different from the bulk properties. There is always a balance when choosing an appropriate material between these two kinds of properties. A material could be totally suitable for a specific application in terms of bulk properties while its surface biological interactions are unsuitable or even incompatible. Therefore, surface modification is able to maintain the key bulk properties of the material while only modifying the surface. By this way, it is not necessary to change the bulk material to increase the biocompatibility (Kurella and Dahotre, 2005; Bose *et al.*, 2018). Moreover, even if a ceramic compound is intrinsically biocompatible, an abundance of studies all over the world proved that the surface properties and so the biointegration can be enhanced by surface modification (Soon *et al.*, 2016). Finally, the main objective of the surface modification of a biomaterial is to create a specific chemical and physical environment that offers a favorable cellular (Bose *et al.*, 2018) and bacterial response (Tuson and Weibel, 2013) in the biological medium.

Typically, the surface properties known to affect the interactions between a solid biomaterial and a biological environment are the surface energy, surface charge, wettability, surface chemistry and the surface topography (Soon *et al.*, 2016; Fig. 1).

These influential properties are discussed in more detail in the next section for all kind of biomaterials like polymers, metals, ceramics and composites. Indeed, these different materials are submitted to the same conditions into the biological environment when they are implanted. Therefore, the influence and the role of surface properties on biological interactions are quite similar for each kind of material.

Influential Surface Properties for Biocompatibility

Surface Energy

As defined by Murthy (2011), surface energy is the work required to increase unit surface area at constant temperature, pressure and composition. It is the manifestation of intermolecular forces due the unbalanced molecular forces existing with the molecules at the surface of liquid or solid. Indeed, these surface molecules are not subject to the same number of forces than the molecules inside the phase (liquid or solid) and therefore possess additional energy. When two condensed phases are in contact, the interfacial energy is defined as the additional free energy between these two phases. These surface and interfacial energies are essential due to their ability to widely influence the material behavior in different conditions. For example, the wettability, another important surface property which has an important role in determining the biocompatibility, adsorption processes and adhesion in biomaterials, is highly dependent on the surface energy and surface tension (Murthy, 2011; Van Krevelen and Te Nijenhuis, 2009).

Therefore, the modification of the surface energy by surface treatments can help to improve the biocompatibility. In several studies, it has been hypothesized that high surface energy is more appropriate for bone implants like titanium or ceramics. Higher surface energy means higher wettability which can enhance the interactions between the implant surface and the biological environment. Indeed, an increase in the cell spreading is observed on the substrates with higher surface energy (Zhao *et al.*, 2005).

Surface Charge

Obviously, electrostatic forces have a determinant role in cells attachment on biomaterials surfaces. When two different phases are in contact, this leads to some ionic interactions at the interface. The charge accumulation resulting from these interactions forms the electrostatic potential. Several parameters are used to describe this surface potential but the most used is the zeta potential (Metwally and Stachewicz, 2019). Zeta potential is defined as the potential difference between the medium and the stationary layer of fluid attached to the particle (Barba *et al.*, 2019). Even if zeta potential can be very useful, it only gives indirect information about the surface potential as it measures the net charge of material immersed in a liquid solution. Other methods like KPFM

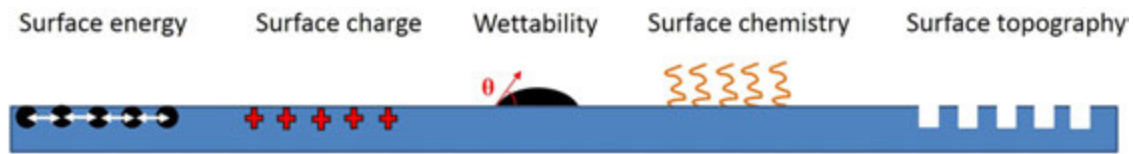


Fig. 1 Surface properties affecting interactions between a solid biomaterial and a biological environment.

(Kelvin Probe Force Microscope), EFM (Electrostatic Force Microscope) or XPS (X-ray Photoelectron Spectroscopy) techniques can provide direct measurement of charge distribution without liquid immersion (Metwally and Stachewicz, 2019).

Several researches studied the charge impact on cells (human endothelial cells, osteoblast-like fibroblast, and neural cell). It was found that surface charge is predominant in the step of adhesion between cells and biomaterials surface and especially in the initial stages of cell attachment. In addition, its role is critical for the cell differentiation signaling. It has also been shown that positive charges are more beneficial for the cell attachment. Indeed, positive charges activate the immune system supporting tissue regeneration and the positively charged surfaces adsorb more proteins. It is not surprising because most of the existed cells and their corresponding adhesion proteins are negatively charged (Fig. 2; Lotfi *et al.*, 2013; Metwally and Stachewicz, 2019).

Therefore, surface charge can be used to control cells and enhance their attachment and proliferation. The complete study of the influence of surface potential on the cells-surface interaction could help to develop functional implantable biomaterials for different applications like regenerative medicine. For now, the different mechanisms involved in the control of cells activities via surface charge are still at an early stage of understanding. Indeed, these interactions between cells and surfaces are complex and need extended investigation in connection with other surface properties like topography, wettability and surface chemistry (Lotfi *et al.*, 2013; Metwally and Stachewicz, 2019).

Wettability

Wettability corresponds to the ease of spreading of liquid on the surface. This ability is directly related to the intermolecular forces between the phases in contact (Agrawal *et al.*, 2017). Typically, wettability can be estimated by contact angle measurements. Contact angle of the surface is defined as the angle formed by the intersection of solid-liquid and liquid-vapor interface. This angle is obtained by putting a drop of liquid on a flat material surface and by drawing a tangent along the liquid-vapor interface. The contact angle is used to represent the final shape of the drop and can describe the interaction between the liquid and the material surface. A contact angle higher than 90° indicates that wetting of the surface is not preferred. In this case, the liquid remains on the surface without spreading. On the contrary, when the contact angle is smaller than 90° , the wetting is favored and the liquid can spread on the surface. The terms hydrophobic and hydrophilic are used when water is used as liquid. Typically, in the scientific community, the definition is that a surface is hydrophilic when its static water contact angle is smaller than 90° and hydrophobic when the angle is more than 90° (Fig. 3).

Some surfaces can be qualified as superhydrophobic or superhydrophilic, if they exhibit water contact angles higher than 145° or lower than 10° , respectively. Water droplets immediately roll on the superhydrophobic surfaces while water simply lies as a flat film on superhydrophilic surfaces (Law, 2014; Otitoju *et al.*, 2017).

The wettability is a key factor in the cell adhesion and protein adsorption on a biomaterial surface. Indeed, some studies claim that enhancing the hydrophilicity of a surface can improve its interactions with the biological species especially for wound healing and osseointegration. Some improvements in the bone implant contact have been made with hydrophilic surfaces and osteoblasts cells exhibiting higher level of differentiation markers on these surfaces (Soon *et al.*, 2016). Moreover, it has also been proved that cells requiring substratum adhesion for proliferation prefer hydrophilic surfaces with water contact angle less than 60° . Therefore, the improvement of the attachment, proliferation and differentiation of cells like osteoblasts on a biomaterial surfaces is possible by increasing its hydrophilicity (Wu *et al.*, 2015).

Surface Topography

Surface topography is defined by surface orientation and roughness and is characterized by a succession of peaks and valleys (Goriainov *et al.*, 2014). Like wettability, surface topography has a real impact on cells adhesion, proliferation and differentiation on a surface. Indeed, there is a phenomenon called surface guidance that allows shaping cell morphology by changing the physical environment, especially the surface topography (Goriainov *et al.*, 2014). Roughness, which is the measure of the finely spaced micro-irregularities on the surface texture, is commonly used to quantify the topography (Choudhury and Chinchani, 2016). Roughness values can be obtained by several methods like Atomic Force Microscopy (AFM), Confocal Laser Scanning Microscopy, scanning interferometry or scatterometry. Although, it is delicate to compare roughness values obtained from different techniques because surface roughness changes as a function of scanning scale (Gong *et al.*, 2018). Distinct roughness levels can be observed depending on the average height deviation, S_a , which expresses, as an absolute value, the difference in height of each point compared to the average of the surface, according to ISO 25178-1:2016 (Geometrical product specifications – Surface texture: Areal – Part 1: Indication of surface texture). Typically, in the study reported by Goriainov *et al.* (2014), rough surfaces is defined as the average height deviation is higher than $2\text{ }\mu\text{m}$, moderately rough surfaces when S_a is between $1\text{--}2\text{ }\mu\text{m}$, minimally rough surfaces

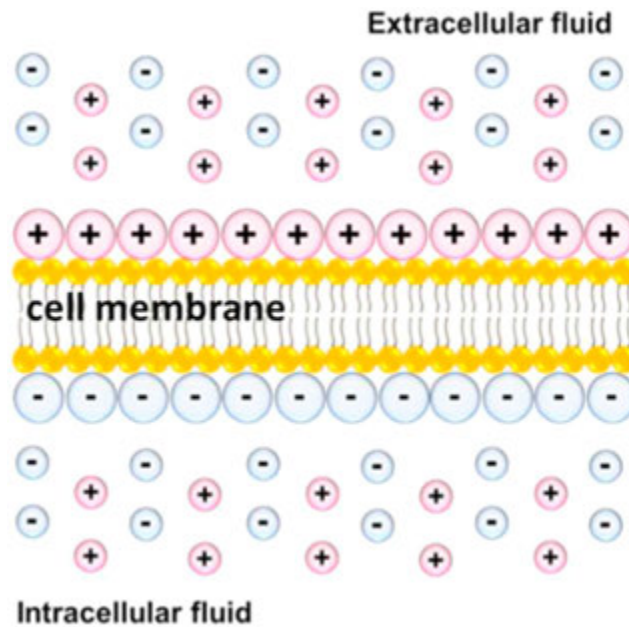


Fig. 2 Schematic of cell membrane potential showing charge accumulation on both sides of cell membrane. Adapted from Metwally, S., Stachewicz, U., 2019. Surface potential and charges impact on cell responses on biomaterials interfaces for medical applications. *Materials Science and Engineering C* 104, 109883. doi:10.1016/j.msec.2019.109883.

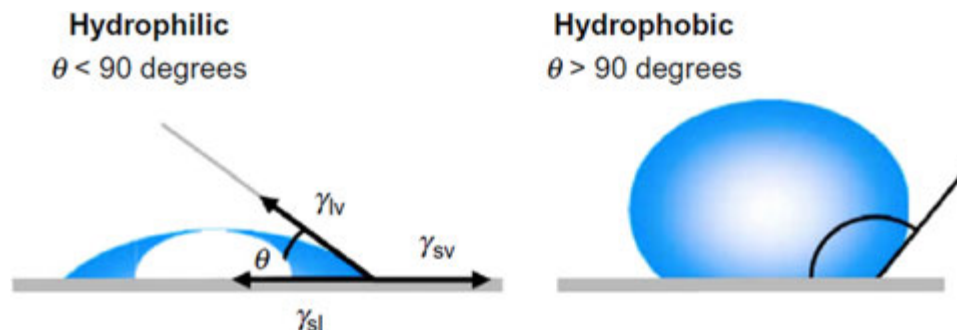


Fig. 3 Schematic representation of contact angles formed by a liquid droplet on a solid surface and three different interfacial tensions: solid-liquid (γ_{sl}), liquid-vapor (γ_{lv}) and solid-vapor (γ_{sv}). Adapted from Agrawal, G., Negi, Y.S., Pradhan, S., Dash, M., Samal, S.K., 2017. Wettability and contact angle of polymeric biomaterials. In: *Characterization of Polymeric Biomaterials*. Elsevier Ltd. doi:10.1016/B978-0-08-100737-2.00003-0.

when Sa is between 0.5–1 μm and smooth surfaces when the value is lower than 0.5 μm . Among these roughness levels, moderate surface roughness seems to be an optimal range to promote the biological integration of an implant. Indeed, moderately rough surfaces have been associated experimentally with stronger bone responses in vitro and in vivo besides with a better cell attachment. Excessively rough surfaces are characterized by very long distances between their peaks and so cells can perceive them as flat. The consequence is that flat surfaces can cause excessive cells flattening and then compromise their nutrition. Therefore, specific topographical modifications can be introduced to modify the roughness of a biomaterial surface in order to improve its interactions with cells and the biological environment.

Surface Chemistry

There is no doubt there is a strong dependence of cell adhesion and proliferation on substrate surface chemistry. Indeed, studies over the years showed that the surface chemical composition is primordial for protein adsorption and subsequent cell adhesion. The chemical structure on the surface can also guide cells fate and affect their shape (Liu *et al.*, 2007). Some particular surface functional groups like hydroxyl or carboxyl can particularly stimulate adhesion and proliferation of cells. Calcium phosphates are well known for their interaction with bone through protein adsorption and their ability to enhance cell attachment, spreading and osteoblast differentiation with some chemical surface impregnation like Mg, S, P, Sr, F and Ca (Goraiainov *et al.*, 2014). As well as

the chemical composition, particle size and crystallinity can also affect interactions between biomaterial surfaces and the biological environment. Generally, the smaller the particles sizes, the higher the total surface area and then the greater number of available binding sites for biomolecules interaction (Lee *et al.*, 2014). About the crystallinity, materials with lower crystallinity have higher solubility so the ionic strength can be increased in the surrounding medium. Biomolecules undergo structural conformational changes in high ionic strength media exposing more polar ionized charges on the surface. This phenomenon promotes a higher adsorption rate on the biomaterial surfaces with low crystallinity (Lee *et al.*, 2014). Therefore, chemical composition has an important role to play on the improvement of biomaterials biological interactions. It is possible to enhance surface behavior by some chemical modifications like coating, substitution, functionalization or incorporation. These different chemical treatments are discussed in detail in a next section. Nevertheless, it is a challenge in some cases to clearly separate cause and effect in the cell-adhesion/proliferation process of surface chemistry from all other surface properties. Indeed, most of surface properties are linked to each other. For example, surface wettability is a direct function of both surface chemical composition and surface topography (Liu *et al.*, 2007; Lee *et al.*, 2014).

Surface Modification Techniques

Even if surface properties discussed in the previous section are described for all types of biomaterials, this section is focused on surface modification techniques of bioceramics. Due to their properties (hardness, brittleness, great strength, stiffness, resistance to corrosion, resistance to wear and low density), ceramics surfaces need some special requirements to be treated (Patel and Gohil, 2012). Typically, surface modification techniques can be classified in two categories: physical and chemical modifications. On one hand, physical modifications provoke a change in the topography or morphology of the surface with no theoretical change of the chemistry of the surface. Techniques like machining, grinding, sandblasting, etching, polishing or laser texturing can produce such physical modifications. On the other hand, chemical treatments change the chemistry of the surface to enhance surface properties by UV light treatment, coatings, biofunctionalization or self-assembly (Bose *et al.*, 2018). Sections below describe the main physical and chemical surface modification techniques for biomaterials with the focus on ceramics.

Physical Modifications

Machining and Grinding

Typically when a biomaterial surface did not undergo any subsequent finishing, it is just called a machined surface. Most of the time, bioceramic parts are manufactured to get the final desired shape and are subject to cleaning, decontamination, passivation and sterilization (Elias, 2011). The two main methods to manufacture ceramics are cutting and grinding. These mechanical processes remove unnecessary parts of a material by sinking the cutting edge of a tool into a workpiece. In cutting, machining is performed by a cutting tool that has a cutting edge of the desired shape (Ohnishi *et al.*, 2015). The conventional cutting methods include diamond saw blade cutting, abrasive wheel cutting, wire saw cutting and mechanical mounting but some modern techniques have been developed over the years to minimize cracks and damages. Among these new techniques, there are wire electrical discharge machining, laser beam machining, abrasive water jet machining and hybrid machining (Rakshit and Das, 2019) (Fig. 4).

On the other hand, grinding is performed by large numbers of abrasive grains scattered on the outer surface of the grinding wheel. Many abrasives are suitable for the wheel surface but the physical properties of diamond make it an excellent candidate for ceramics grinding. Grinding can produce high shape accuracy, dimensional precision and can be used to create an appropriate roughness on a material surface (Ohnishi *et al.*, 2015).

Due to the extreme properties of ceramics, it is often a challenge to machine them. Indeed, ceramics are more susceptible to fracture during manufacturing processes because of their high hardness and brittleness. The surface can be highly influenced by the action and the types of cutting or the grinding tools. In most cases, machined surfaces present unwanted patterns of grooves from the manufacturing process, likely to influence in an uncontrolled way the interactions between the material and the biological medium (Fig. 5). Therefore, a finishing step usually follows the ceramics machining to optimize surface properties (Elias, 2011).

Sandblasting

Sandblasting or air-abrasion is one of the most common methods used for surface preparation. This technique has the advantage to create homogenous and anisotropic surfaces even on hard materials like ceramics or glasses. Indeed, it creates scratch-like irregularities using a high-speed stream of solid particles propelled by compressed air to remove unfavorable contaminants, increase surface energy, bonding surface area, and surface roughness (Fig. 6).

Alumina particles are usually used for their low cost, hardness, and needle-like shape but fractures can happen sometimes due to its brittle behavior. It is possible to tailor the obtained topography by varying parameters such particle size, particle shape, kinetic energy, pressure or impact angle. Moreover, the solid particles have to be clean as well as uniform-sized for the preparation of proper surfaces and the choice of the different parameters must avoid excessive damage to the material surface (Ebnesajjad, 2014; Soon *et al.*, 2016; Papageorgiou and Pandis, 2017).

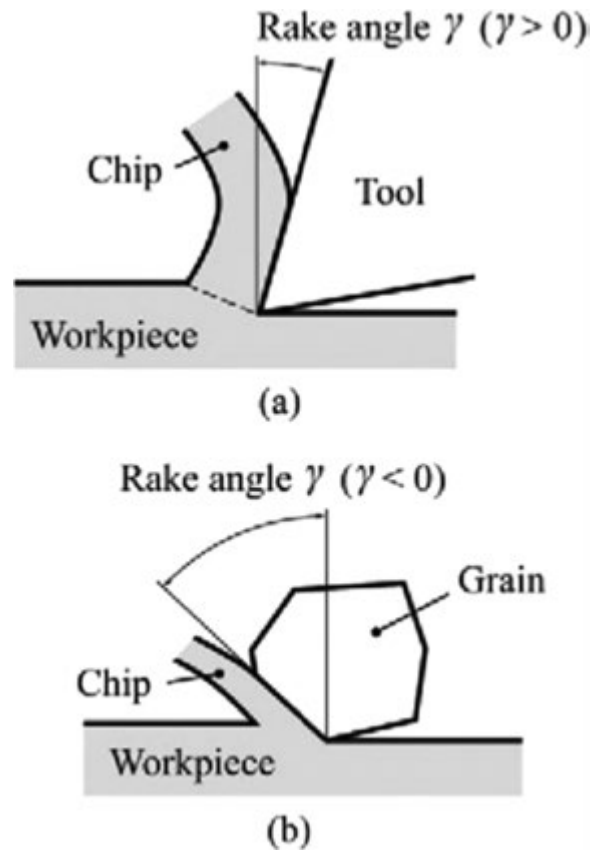


Fig. 4 Representation of (a) Cutting and (b) Grinding. Reproduced from Ohnishi, O., Suzuki, H., Uhlmann, E., *et al.*, 2015. Chapter 4 – Grinding. In: Handbook of Ceramics Grinding and Polishing, second ed. Boston: William Andrew Publishing. pp. 133–233. doi:[10.1016/B978-1-4557-7858-4.00004-2](https://doi.org/10.1016/B978-1-4557-7858-4.00004-2).

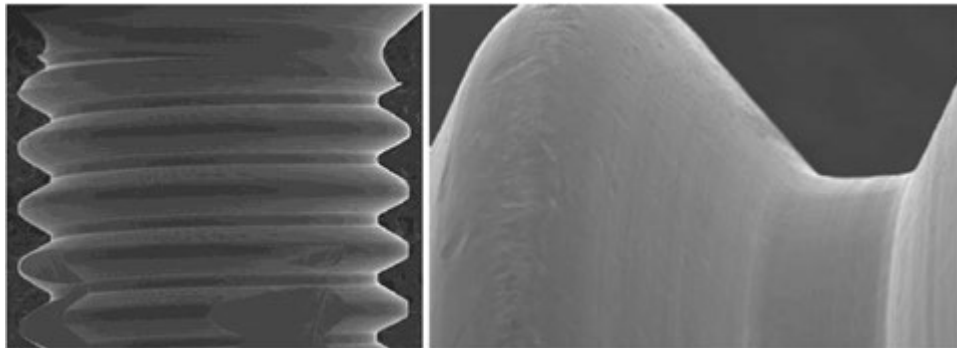


Fig. 5 Surface morphology of machined dental implant, showing the grooves left by the manufacturing tools. Reproduced from Elias, C.N., 2011. Factors affecting the success of dental implants. In: Implant Dentistry – A Rapidly Evolving Practice. doi:[10.5772/18746](https://doi.org/10.5772/18746).

It has been shown by Nothdurft *et al.* (2015) that a rougher surface obtained by sandblasting has favored the adhesion of fibroblast on zirconia. Nevertheless, the use of sandblasting can alter the surface chemistry by alumina contamination but this issue can be resolved by acid etching treatment. Indeed, this technique, discussed in the following section, can allow to remove surface residues (Soon *et al.*, 2016).

Chemical Etching

Chemical etching is a complementary surface modification technique to machining and sandblasting to its capability to induce a fine roughness sometimes up to the nanoscale. Most of the chemicals used for etching are acids like hydrofluoric acid, nitric acid or

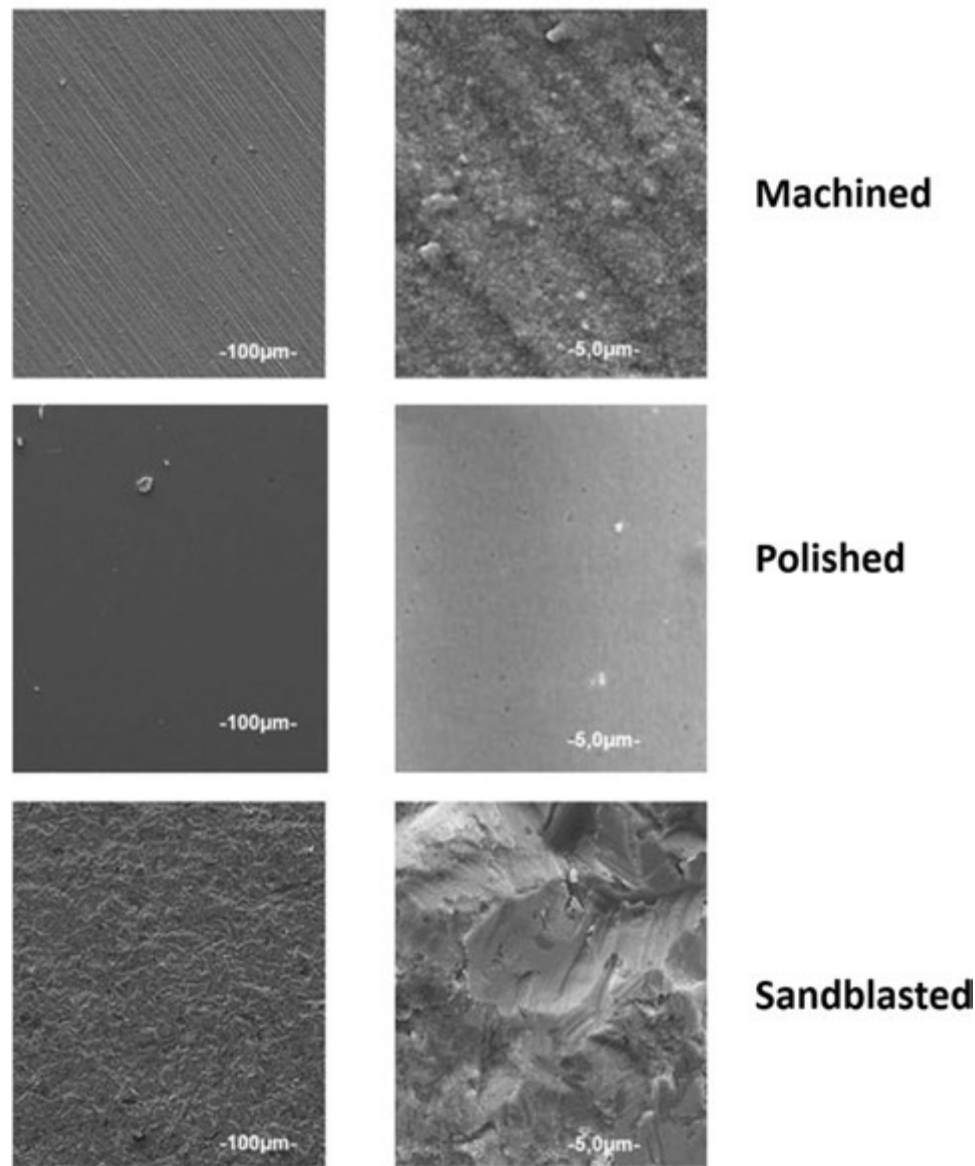


Fig. 6 Scanning electron microscopic views of zirconia with three different surface topographies (machined, polished, and sandblasted) under 500 and 10,000 magnifications. Adapted from Nothdurft, F.P., Fontana, D., Ruppenthal, S., *et al.*, 2015. Differential behavior of fibroblasts and epithelial cells on structured implant abutment materials: A comparison of materials and surface topographies. *Clinical Implant Dentistry and Related Research* 17, 1237–1249. doi:10.1111/cid.12253.

sulfuric acid. Nevertheless, some mixtures of potassium hydroxide and sodium hydroxide have also been used. Acid etching can produce some sharp edges on the treated surface (Fig. 7) but it can be smoothened by a following heat treatment.

The different parameters that influence the obtained topography are prior surface treatments, composition of acid mixture, temperature and treatment time (Fig. 8). Distinct types of topographies can be achieved by varying these parameters (Soon *et al.*, 2016; Flamant *et al.*, 2016).

This technique has some advantages like the obtaining of a homogeneous roughening of the material regardless its shape and size. Moreover, it can limit the risk of material delamination due to its absence of applied stress. On the other hand, some chemical changes can be induced by the presence of acids. These changes can modify the interactions between the ceramic material surface and the biological environment (Soon *et al.*, 2016). Some studies have investigated the effect of chemical etching on cells behavior. For example, Depprich *et al.* (2008) have shown that primary bovine osteoblasts are able to attach, proliferate and differentiate on acid-etched zirconia surfaces. Moreover, Ito *et al.* (2013) showed that the combination of sandblasting and acid etching can lead to an increase in the proliferation rate of osteoblast-like cells.

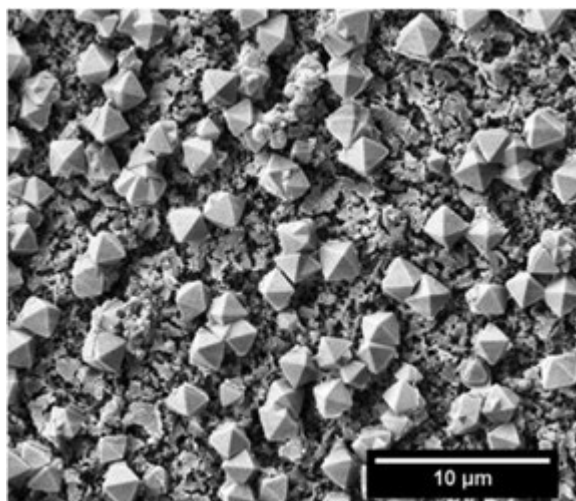


Fig. 7 Scanning electron microscopic observations of a zirconia surface after etching in HF 40% for 2 h. Reproduced from Flamant, Q., Marro, F.G., Rovira, J.J.R., Anglada, M., 2016. Hydrofluoric acid etching of dental zirconia. Part 1: Etching mechanism and surface characterization. *Journal of the European Ceramic Society* 36, 121–134. doi:[10.1016/j.jeurceramsoc.2015.09.021](https://doi.org/10.1016/j.jeurceramsoc.2015.09.021).

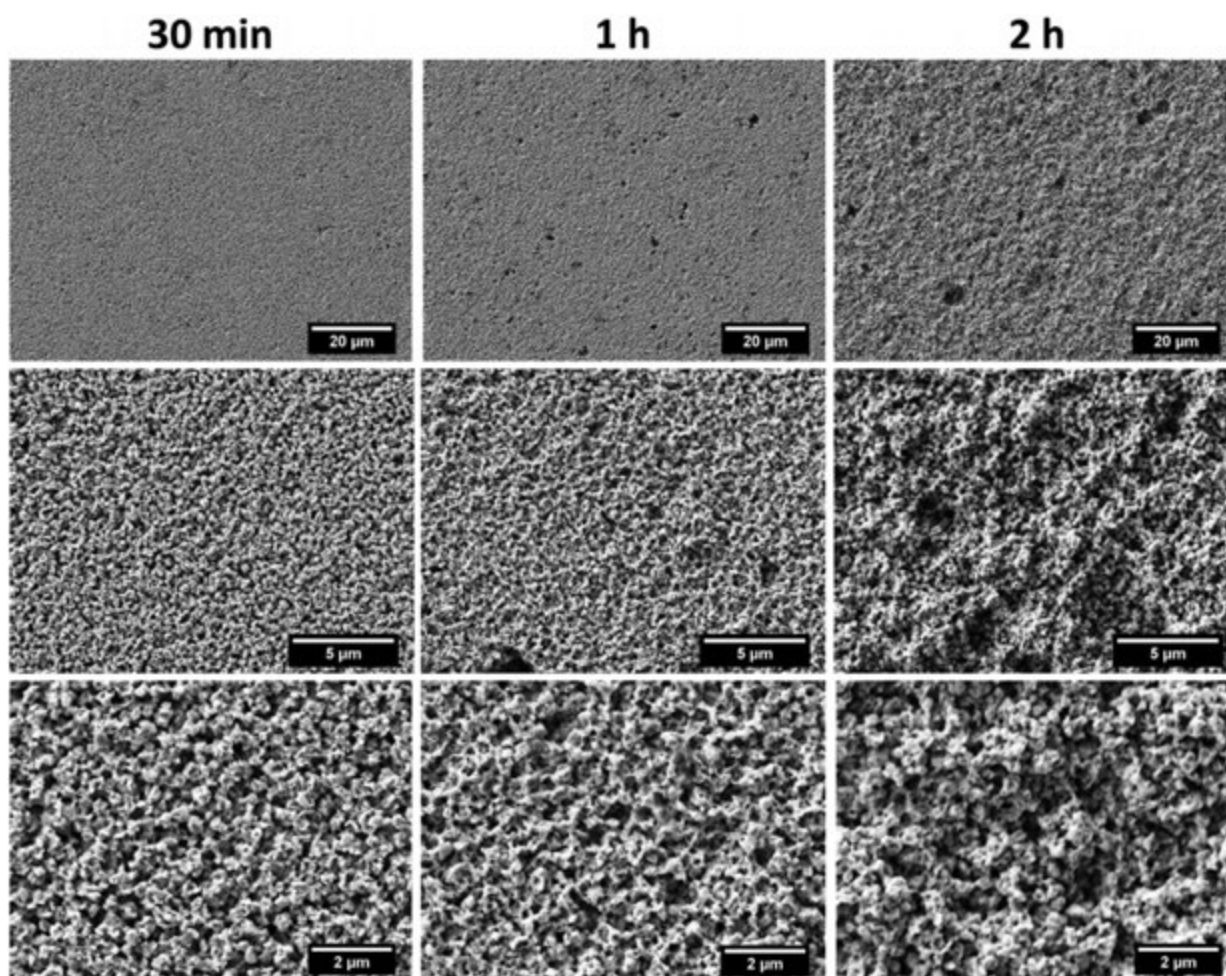


Fig. 8 Scanning electron microscopic observations of zirconia surfaces at different magnifications and for different etching times in HF 40%. Reproduced from Flamant, Q., Marro, F.G., Rovira, J.J.R., Anglada, M., 2016. Hydrofluoric acid etching of dental zirconia. Part 1: Etching mechanism and surface characterization. *Journal of the European Ceramic Society* 36, 121–134. doi:[10.1016/j.jeurceramsoc.2015.09.021](https://doi.org/10.1016/j.jeurceramsoc.2015.09.021).

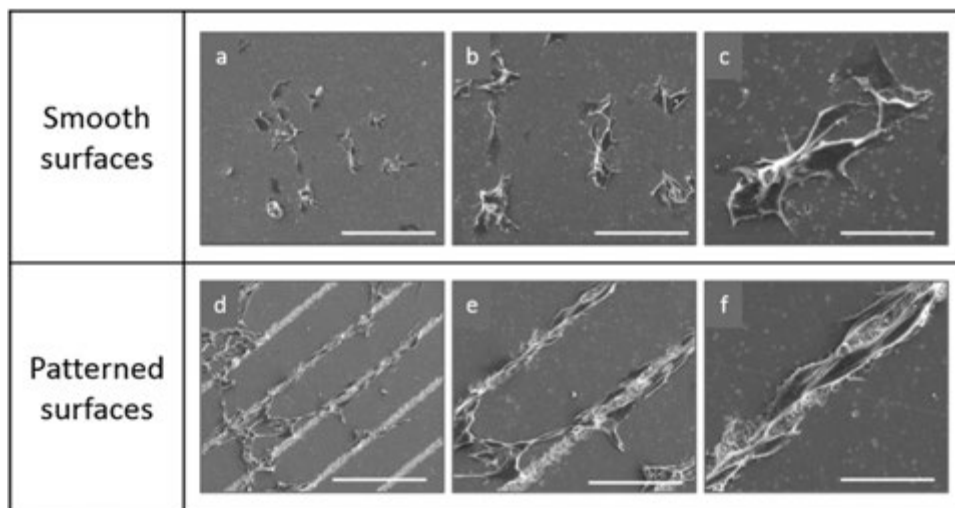


Fig. 9 SEM micrographs of MG63 osteoblastic cells adhering on sintered β -TCP substrates, one day after seeding: smooth surfaces (a–c) and laser patterned surfaces (d–f); scale bar: 200 μ m (a, d), 100 μ m (b, e) and 40 μ m (c, f). Reproduced from Lasgorceix, M., Grenho, L., Fernandes, M.H., *et al.*, 2018. Femtosecond laser impact on calcium phosphate bioceramics assessed by micro-Raman spectroscopy and osteoblastic behaviour. *Journal of the European Ceramic Society* 38 (16), 5545–5553. doi:10.1016/j.jeurceramsoc.2018.07.048.

Polishing

Contrary to sandblasting and etching that create some surface roughness, polishing allows producing mirror-like surface with fine particle abrasives and soft pads. Indeed, it occurs by the sliding frictions between particles and the treated surface. Typically, the polisher travels across the work surface against which particles of abrasives are forced to the point of contact (Kasai, 2003). Silicon carbide polishing paper and diamond or silica suspensions are often used with a polishing machine to polish ceramic surfaces (Soon *et al.*, 2016).

Osteoblast cells are known to show good adhesion and proliferation on rough surfaces, but opposite behavior can be observed with other types of cells. For example, epithelial cells are known to attach better to a smoother/polished surface than to a rough surface. In addition to its ability to produce a very smooth surface, polishing can also serve to clean the implant surface. Indeed, mechanical treatment like polishing can theoretically clean without altering material chemical and physical properties. Nevertheless, there are always some surface modifications and contaminations due to abrasive suspensions used in the process (Soon *et al.*, 2016). Usually, polishing is applied as a surface preparation stage to obtain reproducible smooth surfaces before further treatment (Lasgorceix *et al.*, 2018).

Laser Treatment

Laser treatment of biomaterials has been widely studied over the past few years to improve surface properties and to investigate the effect of the surface patterning on cells behavior (Jeong *et al.*, 2011; Liang *et al.*, 2012; Shukla *et al.*, 2016). For ceramics, some studies show that the changes induced by laser treatments on different materials improve the wettability compared to untreated material (Lasgorceix *et al.*, 2018). In some cases, it has been observed a modification of the cellular response on laser treated surfaces, in particular cell guidance phenomena (Fig. 9).

Light amplification by stimulated emission of radiation (LASER) is a source of coherent electromagnetic radiation that can be applied to modify the surface of various materials from ceramics to metals and polymers. Due to the high power density generated, laser sources can melt, heat, create patterns and grooves or chemically modify the material surface. Depending on the laser parameters and the target material, laser treatments effects can affect only the surface or have also an effect deeper in the material. This last characteristic is interesting because it is possible to change surface properties without any effect on bulk ones. The major advantages of laser treatments are the rapidity and the absence of contact between the material and the laser that avoids any risk of surface contamination (Kurella and Dahotre, 2005; Soon *et al.*, 2016). About the treatment of ceramics, depending on the laser process parameters, it can cause only texturing of the surface to change the topography or it can involve modification of microstructure, grain refinement, phase transformations, mixing of multiple materials, and formation of composites on the surface (Kurella and Dahotre, 2005). Indeed, Samant *et al.* (2008) showed that repetition rate, scanning speed and pulse width of the laser can influence the interdendritic porosity and grain size of treated alumina. In the case of laser texturing, it is possible to create some complex periodic surface structures that can enhance properties involved in biocompatibility like protein adsorption and cell/surface interactions. Indeed, the use of a laser has the potential to produce uniform 3D micrometer and submicrometer structures with high resolution. Therefore, laser treatment of biomaterials can become a strong alternative to conventional

photolithographic processes in biomedical surface engineering (Kurella and Dahotre, 2005; Shukla *et al.*, 2016). The interaction between a laser beam and a solid ceramic material is quite complex and is still under investigation. Indeed, there are a large number of laser–matter interaction parameters such as laser pulse duration, wavelength, angular divergence, spot size and energy, physical properties of solid matter, surrounding environment composition, and pressure (Semerok *et al.*, 2002). Of course, different kinds of lasers are available to vary the processing parameters depending of the treated material. For texturing applications, CO₂, Nd: YAG, Ti: sapphire and UV lasers (excimers) are reported to be used for biomaterials. Moreover, it has been proved that femtosecond lasers have advantages over nanosecond and picosecond lasers for the treatment of biomaterials due to their higher precision, a reduced heat-affected zone and smaller amount of debris around the treated spot (Vorobyev and Guo, 2009). Indeed, it is preferable to limit the heat produced by the laser to treat thermal sensitive materials. Even if the benefits of laser-induced periodic surface structures on surface properties are becoming more evident throughout the scientific community, very few works have been conducted on surface structuring of ceramics in relation to its applicability in the biomedical sector. Therefore, laser surface structuring of bioceramics need further studies to understand fully the effects of nanosecond, picosecond and femtosecond lasers on the biocompatibility of treated ceramics (Semerok *et al.*, 2002; Kurella and Dahotre, 2005; Shukla *et al.*, 2016).

Other Techniques

Physical surface modification techniques cited above are the most currently used for ceramics. Indeed, this list is not exhaustive and more and more innovative techniques are being developed to optimize surface properties of biomaterials. Some examples are electron beam texturing, photolithography, ion beam texturing or electric arc texturing. Nevertheless, these methods present some limitations. Electron and ion beam processing need to be processed in vacuum chambers which means shape and size limitations for samples. Moreover, the use of these two techniques is expensive. Photolithography, on the other hand, is an extremely time-consuming multistage process compared to methods like laser treatments (Kurella and Dahotre, 2005).

Chemical Modifications

Ultraviolet Light Treatment

UV light treatment has been proven to enhance integration of bone implants due to this influence on the hydrophilicity. Indeed, the effect of UV light on titanium surfaces has been shown to improve their bioactivity and osteoconductive ability. This is possible by an increase of protein adsorption together with an osteogenic cell attachment and proliferation. This phenomenon is called “UV light-mediated photofunctionalization” and is associated with the photochemical and photocatalytic removal of hydrocarbons onto the material treated surface (Aita *et al.*, 2009). Same observations can be made for ceramics since Tuna *et al.* (2015) have shown that UV treatment of zirconia induced profound alterations in the surface physicochemical properties. Indeed, UV treated surfaces were converted from hydrophobic to hydrophilic status and a significant decrease in surface carbon content was observed. Similar results were also found by Att *et al.* (2009) with UV light treated zirconia disks. A treatment of 48 h substantially increased their capacity for attachment, spread, and proliferation of rat bone marrow-derived osteoblasts. The increased osteoblasts affinity for the UV-treated zirconia surfaces was already distinguishable within the first hours of seeding (Fig. 10).

Nevertheless, mechanisms involved in the modification of zirconia surface properties during UV treatment are not yet fully understood. Moreover, there is a need for further studies to determine the impact of these alterations on the surface biocompatibility (Tuna *et al.*, 2015; Soon *et al.*, 2016). Finally, this kind of UV treatment is mostly studied with zirconia ceramics and it could be interesting to investigate this surface modification technique with other bioceramics.

Coating

Coating of implant is one of the strategies used to enhance biocompatibility and osseointegration without changing the bulk material. Indeed, biomaterial coatings can be really useful to inhibiting bacterial colonization and to enhancing the attachment of tissue cells on the surface (Soon *et al.*, 2016). Coating technique consists in the covering of a surface with the same material or with a bioactive material (Chevalier *et al.*, 2011). In the case of a coating of the same material, it is usually realized to incorporate some porosity on the surface in order to promote osseointegration or even to allow bone in-growth (Fig. 11). To achieve a porous surface, the bioceramic implants are coated with slurry containing ceramic powder, like zirconia or calcium phosphate, and a pore-former. Sintering of the implants is performed to fully densify after the application of the coating. During this step, the pore-former burns off and leaves a porous surface. However, this way is sometimes complex in case of difficult control of the processing that can lead to poor mechanical properties and ageing resistance (Sennerby *et al.*, 2005; Chevalier *et al.*, 2011).

Besides, coating with bioactive ceramics is widely used to improve surface properties of metals like titanium or other inert ceramics. Calcium phosphates (CaP) are the best candidate for coating material due to their good biocompatibility, osseointegration and osteoconduction. The presence of a bioactive CaP coating can help to establish a stable interface between the implant and the bone besides with blocking the diffusion of toxic elements from the bulk implant into the body. Moreover, it can reduce the friction coefficient between the implant and its biological surroundings and enhance bone growth around the graft. Many

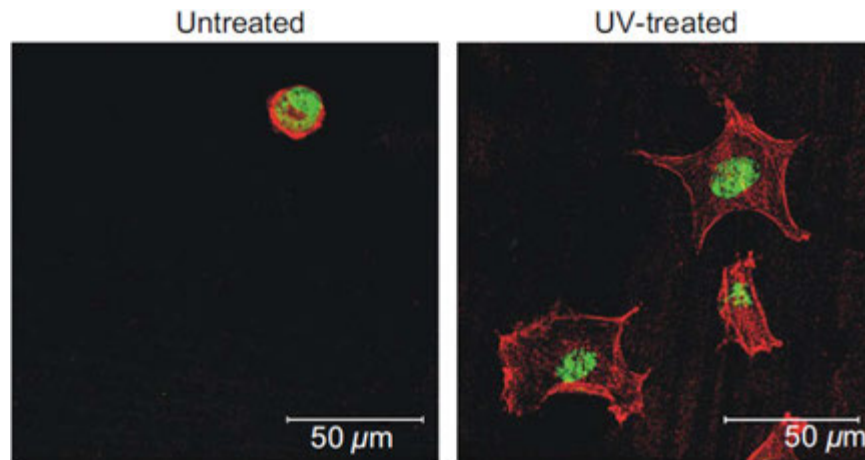


Fig. 10 Increased osteoblast affinity of zirconia disks by UV light treatment. Initial spread and cytoskeletal arrangement of rat bone marrow-derived osteoblasts 3 h after seeding onto untreated and UV-treated zirconia surfaces. Representative confocal microscopic images with dual staining of DAPI for nuclei (green) and rhodamine phalloidin for actin filaments (red). Adapted from Att, W., Takeuchi, M., Suzuki, T., *et al.*, 2009. Enhanced osteoblast function on ultraviolet light-treated zirconia. *Biomaterials* 30 (7), 1273–1280. doi:[10.1016/j.biomaterials.2008.11.024](https://doi.org/10.1016/j.biomaterials.2008.11.024).

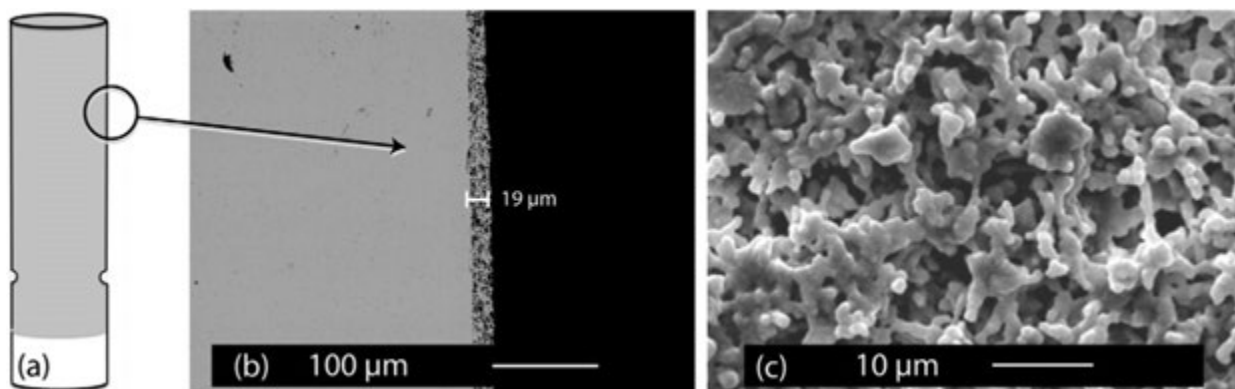


Fig. 11 Geometry of the zirconia cylindrical samples, with emphasis on the zone coated with the porous layer in grey (a), cross-section of a sample in a zone coated with the porous layer (b) and microstructure of the porous coating (c). Reproduced from Chevalier, J., Loh, J., Gremillard, L., Meille, S., Adolfson, E., 2011. Low-temperature degradation in zirconia with a porous surface. *Acta Biomaterialia* (7), 2986–2993. doi:[10.1016/j.actbio.2011.03.006](https://doi.org/10.1016/j.actbio.2011.03.006).

processes exist to prepare synthetic CaP coatings such as plasma spraying, high-velocity oxygen-fuel, thermal spraying, sputter coating, radio-frequency magnetron sputtering, pulsed laser deposition, ion-beam deposition, frit enameling, hot isostatic pressing, metallic-organic chemical vapor deposition and electrodeposition (Eliaz and Metoki, 2017). Among these processes, plasma spray is currently the most common technique used commercially for coating implants with CaP, due to its versatility. This technique provides a high deposition rate and low cost. In this process, a high-frequency arc is ignited between an anode and a tungsten cathode. The gas flowing through between the electrodes is ionized and a plasma plume is developed. The spray material is injected as a powder outside of the gun nozzle into the plasma plume. There, it is melted and hurled by the gas onto the substrate surface. The molten and semi-molten particles rapidly solidify on impact against the substrate, and an integral layer is built-up by the overlaying of many particles. The relatively high temperatures involved in this kind of processes present some drawbacks like CaP phase transformation as well as the difference of thermal expansion coefficients between the bulk and the coating materials. Therefore, coatings present sometimes a lack of adherence to the substrate and process residual stresses may provoke delamination.

To avoid the problems related to high temperatures, the sol-gel process can be used and it is the simplest technique to manufacture thin films less than 1 µm. Indeed, it can be carried out at room temperature, and therefore, high temperature complications can be spared. Sol-gel coating can produce various materials with special functions and involves the formation of solid materials from solution. This is mainly inorganic compounds mixed in solutions of monomeric, oligomeric, polymeric or colloidal precursors. There are typically five stages during the sol-gel process. The first one is the production of a homogenous solution of the sol-gel precursors. Second, the addition of a suitable reagent, like water, is necessary to form a sol. The third step

consists in changing the sol to gel by poly-condensation. After, the gel can be shaped to get the final preferred shape such as thin films or fibers. The last step is the sintering of the shaped gel to obtain the desired ceramic material. This method has some advantages like an excellent adhesion, a good corrosion resistance, high purity material production, low sintering temperatures, process simplicity and the ability to coat complex shapes. Nevertheless, these advantages do not come alone. Indeed, the sol-gel process presents a high permeability, a low wear-resistance and a difficult porosity control. Moreover, the cost of raw materials is quite high that limits its industrial utilization (Eliaz and Metoki, 2017).

The choice of coating process is important but the surface preparation is crucial for the CaP coating properties. Indeed, a pre-treatment of a metallic or ceramic implant before coating with CaP allows to increase the adhesion strength, to control the corrosion rate, to increase nucleation kinetics, to control the structure, the porosity and the morphology of the coating, to improve the bioactivity and osseointegration of the coating, etc. Moreover, surface pre-treatments can also affect performance and longevity of the implant. Thus, different practices exist with their own advantages. Among the used surface pre-treatments, there are for example mechanical grinding, chemical etching, grit blast, soaking with NaOH or heat treatment (Eliaz and Metoki, 2017).

Post-treatments after coating are also widely applied to optimize coating properties. Most of the time, it is necessary to convert CaP phases with lower Ca/P ratio to hydroxyapatite or other calcium phosphate with a higher Ca/P ratio. Contrary to preparation methods, only two post-treatments are used commercially: sintering and soaking in an alkaline solution. The two methods can take several hours and produce different surface morphologies. Indeed, the sintering post-treatment generates preferably flake-like morphology compared to chrysanthemum-like structures obtained with the alkaline post-treatment. It has been shown that the crystallinity is increased by these two post-treatments but even more with sintering (Eliaz and Metoki, 2017).

Coating of materials is an interesting way to optimize implant surface properties in order to guide the integration of the graft. Calcium phosphate coatings can help for bone-implant bonding. Nevertheless, several flaws like variation in coating/implant bond strength can cause a poor coating stability and adhesion to the substrate. New techniques for depositing CaP-based coating on medical implants are constantly being developed to solve these different issues and to minimize the possibility of failure and delamination. Finally, it is well known that CaP based coatings with a higher dissolution rate enhance osteoblast response but their fast dissolution limits their stability. Therefore, there is also some progress to make with CaP coating materials (Soon *et al.*, 2016; Eliaz and Metoki, 2017).

Biofunctionalization

Compare to CaP coatings, biofunctionalization or biomimetic surface modification consists in the immobilization of biomolecules like proteins, enzymes and peptides onto the implant surface. This organic anchorage can alter the biochemical properties and the biological responses of the surface and the attached molecules. Indeed, the immobilization of charged biomolecules like proteins onto biomaterials can be oriented in a manner that is optimal for binding to their respective biological charged sites. With biofunctionalization, lots of drugs or proteins could be fixed onto the surface of biomaterials and minimize some biointegration drawbacks. Typically, there are three main kinds of biomimetic surface modification: direct or physical immobilization, chemical immobilization and bioaffinity immobilization (Lee *et al.*, 2014; Soon *et al.*, 2016).

The simplest way to impregnate biomolecules onto a ceramic surface (e.g., a CaP surface) is the direct immobilization or physical immobilization (Fig. 12). Proteins are adsorbed via weak non-covalent interactions like electrostatic, van der Waals, hydrogen bonding, and/or hydrophobic interactions. It is possible to modulate the environmental conditions around the material to regulate its capacity for protein adsorption. Physical immobilization allows some advantages such as the structural preservation of protein molecules and its applicability to most types of native surfaces. However, the binding affinities of proteins are usually quite low because of the non-specific character nature of this physical immobilization. Moreover, the blockage of binding sites and non-specific interaction of proteins with their surroundings can cause low adsorption or loss of protein activity (Lee *et al.*, 2014).

On the other hand, chemical immobilization approach consists of modifying the surface energy, charge, and composition of a material to attach proteins through covalent bonds (Fig. 12). Different methods are available for this achievement like covalent immobilization of organic functional groups, ion-bombardment, sol-gel, and treatment with acid/alkaline. Some examples of linkers that can bind proteins onto the surface of CaP are silanes, mercaptans and catechol. These linkers are able to connect with the side chain functional groups of proteins like amines, carboxylates, thiols or hydroxyls. Even if this kind of biofunctionalization allows strong links, this could be a drawback and a limit for the release of the attached proteins. Moreover, it is not a selective technique due to the presence of many functional groups on proteins (Lee *et al.*, 2014).

The last way to carry out biofunctionalization is called bioaffinity immobilization. This consists of the immobilization of a biomolecule via bioaffinity interactions with other biomolecules. In most cases, such bioaffinity immobilization is not wanted because it can lead to the biomolecule inactivation. Indeed, active sites can be blocked with this kind of interaction and cause the inactivation. Nevertheless, bioaffinity immobilization of biomolecules onto a ceramic substrate can also improve the biological activity (Lee *et al.*, 2014). The most famous example is the arginine-glycine-aspartate (RGD) which is a widely used adhesive peptide. Actually, many adhesive proteins are found to possess RGD as their cell recognition site (Soon *et al.*, 2016). In recent studies, RGD-peptide has been successfully immobilized on zirconia and hydroxyapatite surfaces and enhanced the biocompatibility of the material. Methods like hydrothermal treatment and silanization are used to optimize this immobilization (Lee *et al.*, 2014; Soon *et al.*, 2016).

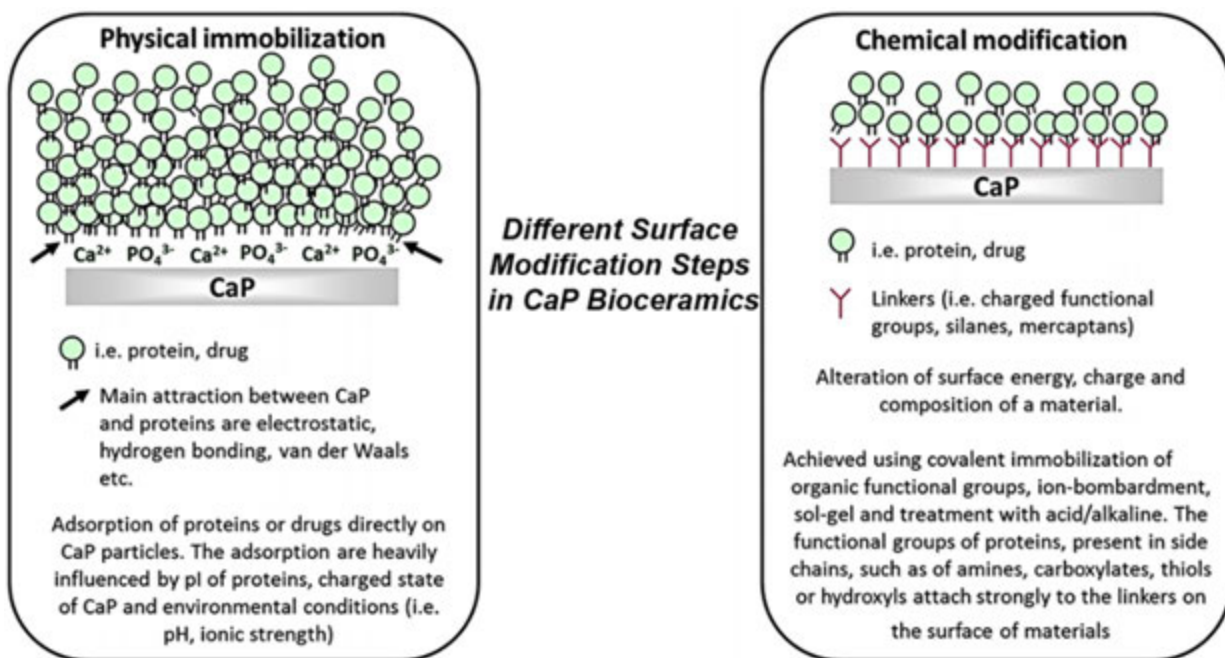


Fig. 12 Types of surface modification processes commonly used for modifying CaP particles to achieve optimal protein or drug adsorption and cells–CaP interactions. Reproduced from Lee, W.H., Loo, C.Y., Rohanizadeh, R., 2014. A review of chemical surface modification of bioceramics: Effects on protein adsorption and cellular response. *Colloids and Surfaces B: Biointerfaces* 122, 823–834. doi:10.1016/j.colsurfb.2014.07.029.

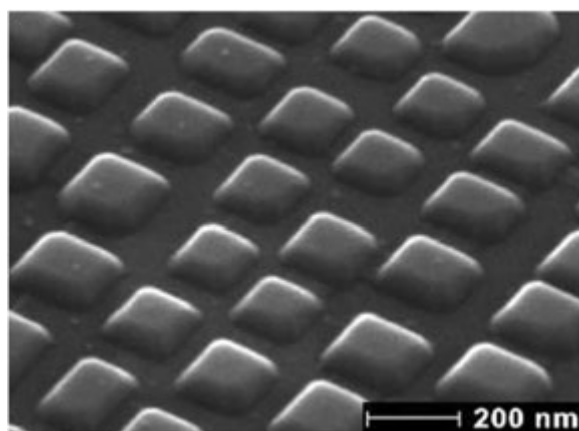


Fig. 13 Scanning electron microscopy (SEM) image of self-ordered nanostructure on the (001) surface of YSZ. The inset fast Fourier transform of the SEM image shows evidence of the periodicity. Adapted from Rauscher, M.D., Andrew Boyne, A., Dregia, S.A., Akbar, S.A., 2008. Self-assembly of pseudoperiodic arrays of nanoislands on YSZ-(001). *Advanced Materials* 20 (9), 1699–1705. doi:10.1002/adma.200701383.

Self-Assembly

Another quite new technique for surface modification is self-assembly. This is defined as the autonomous process by which components organize into patterns or structures without external intervention (Whitesides and Grzybowski, 2002). Self-assembling processes involve components from the molecular to the planetary scale and many different kinds of interactions in both nature and technologies. This kind of techniques can be of great interest because it is one of few practical strategies for making nanostructures. Typically, two main kinds of self-assembly exist for the moment. On one hand, static self-assembly involves systems that are at global or local equilibrium. It does not dissipate energy contrary to dynamic self-assembly. In dynamic self-assembly, the formation of structures or patterns takes place with interactions that only occur if the system is dissipating energy (Whitesides and Grzybowski, 2002).

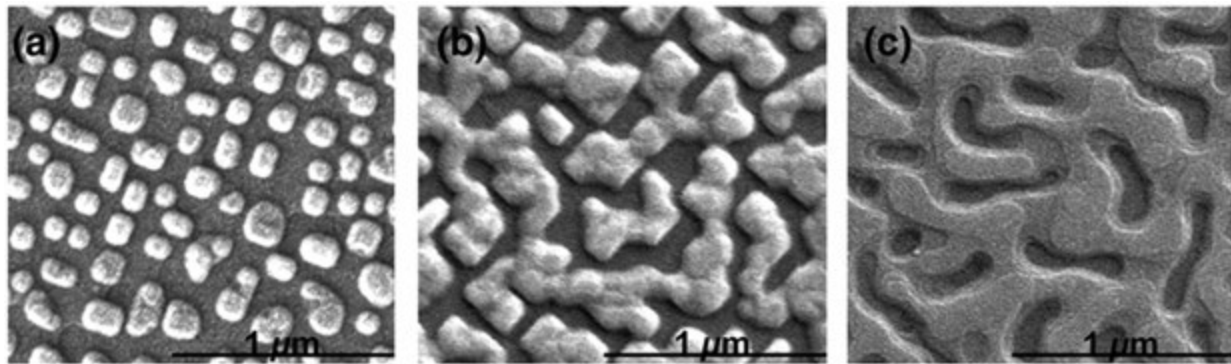


Fig. 14 Scanning electron microscopy of nanofeatures manufactured using GDC/YSZ system: (a) islands, (b) connected islands, and (c) pits. Reproduced from Parikh, K.S., Rao, S.S., Ansari, H.M., *et al.*, 2012. Ceramic nanopatterned surfaces to explore the effects of nanotopography on cell attachment. *Materials Science and Engineering C* 32 (8), 2469–2475. doi:10.1016/j.msec.2012.07.028.

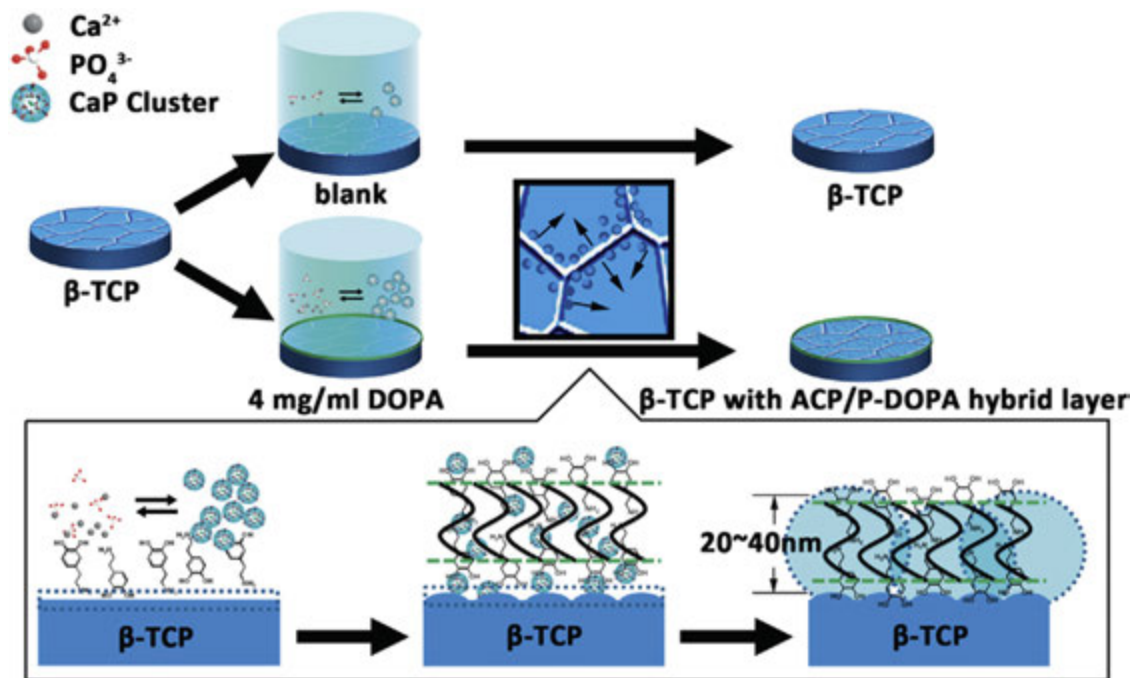


Fig. 15 Schematic representation of the formation mechanism of Ca-P/polydopamine composite nanolayer on the surface of β -TCP ceramics. Reproduced from Wu, C., Han, P., Liu, X., *et al.*, 2014. Mussel-inspired bioceramics with self-assembled Ca-P/polydopamine composite nanolayer: Preparation, formation mechanism, improved cellular bioactivity and osteogenic differentiation of bone marrow stromal cells. *Acta Biomaterialia* 10 (1), 428–438. doi:10.1016/j.actbio.2013.10.013.

There are different examples of this process applied with ceramics such as CaP or zirconia. Rauscher *et al.* (2008) have succeeded in depositing a gadolinia-doped ceria (GDC) on yttrium stabilised zirconia with pseudoperiodic-array of nanoislands on the surface after thermal treatment (Fig. 13). Such nanopatterned surfaces (Fig. 14) were shown by Parikh *et al.* (2012) to exhibit satisfying cellular responses such as remarkable changes in cell spreading and cytoskeletal protein distribution.

About CaP, Wu *et al.* (2014) inspired themselves from mussels to prepare a uniform CaP/polydopamine composite nanolayer on the surface of β -tricalcium phosphate bioceramics by soaking β -TCP bioceramics in Tris-dopamine solution (Fig. 15). This formed self-assembled CaP/polydopamine composite nanolayer significantly enhances the surface roughness and hydrophilicity of β -TCP ceramics and stimulates the attachment, proliferation, alkaline phosphate activity and bone-related gene expression of human bone marrow stromal cells.

Surface Treatment Perspectives

Finally, as explained in this chapter, the major goal of bioceramic implants is their proper osteointegration into a bioenvironment. For that, it has been shown that the implant surface is determinant. Many surface modification techniques exist to optimize the implant integration. The future of surface modification techniques on ceramics is promising but a lot of work has still to be done. Indeed, there are many contradicting results in the scientific community and more comprehensive researches have to be carried out to uncover complex mechanisms behind surface properties and cellular response. Moreover, current surface modifications techniques have to be improved in order to produce optimized bioceramic surfaces. In that case, surface modification will be a way to improve the reliability of bioceramic implantation for humans.

References

- Agrawal, G., Negi, Y.S., Pradhan, S., Dash, M., Samal, S.K., 2017. Wettability and contact angle of polymeric biomaterials. In: *Characterization of Polymeric Biomaterials*. Elsevier Ltd. doi:10.1016/B978-0-08-100737-2.00003-0.
- Aita, H., Hori, N., Takeuchi, M., *et al.*, 2009. The effect of ultraviolet functionalization of titanium on integration with bone. *Biomaterials* 30 (6), 1015–1025. doi:10.1016/j.biomaterials.2008.11.004.
- Att, W., Takeuchi, M., Suzuki, T., *et al.*, 2009. Enhanced osteoblast function on ultraviolet light-treated zirconia. *Biomaterials* 30 (7), 1273–1280. doi:10.1016/j.biomaterials.2008.11.024.
- Barba, A.A., Bochicchio, S., Dalmoro, A., *et al.*, 2019. Polymeric and lipid-based systems for controlled drug release: an engineering point of view. In: *Nanomaterials for Drug Delivery and Therapy*. Elsevier Inc. doi:10.1016/B978-0-12-816505-8.00013-8.
- Bose, S., Robertson, S.F., Bandyopadhyay, A., 2018. Surface Modification of Biomaterials and Biomedical Devices using Additive Manufacturing. *Acta Biomaterialia*. 6–22. doi:10.1016/j.actbio.2017.11.003.
- Chevalier, J., Loh, J., Gremillard, L., Meille, S., Adolfsen, E., 2011. Low-temperature degradation in zirconia with a porous surface. *Acta Biomaterialia*. (7), 2986–2993. doi:10.1016/j.actbio.2011.03.006.
- Choudhury, S.K., Chinchani, S., 2016. Finish machining of hardened steel. In: *Comprehensive Materials Finishing 1*. Elsevier Science. doi:10.1016/B978-0-12-803581-8.09149-9.
- Deppe, R., Ommerborn, M., Zipprich, H., *et al.*, 2008. Behavior of osteoblastic cells cultured on titanium and structured zirconia surfaces. *Head and Face Medicine* 4, 1–9. doi:10.1186/1746-160X-4-29.
- Ebnesajjad, S., 2011. Chapter – 7 Surface Preparation of Thermoplastics, Thermosets, and Elastomers. In: *Handbook of Adhesives and Surface Preparation*. 107–134. doi:10.1016/B978-1-4377-4461-3.10007-0.
- Elias, C.N., 2011. Factors affecting the success of dental implants. In: *Implant Dentistry – A Rapidly Evolving Practice*. doi:10.5772/18746.
- Eliaz, N., Metoki, N., 2017. Calcium phosphate bioceramics: A review of their history, structure, properties, coating technologies and biomedical applications. *Materials* 10. doi:10.3390/ma10040334.
- Flamant, Q., Marro, F.G., Rovira, J.J.R., Anglada, M., 2016. Hydrofluoric acid etching of dental zirconia. Part 1: Etching mechanism and surface characterization. *Journal of the European Ceramic Society* 36, 121–134. doi:10.1016/j.jeurceramsoc.2015.09.021.
- Gong, Y., Xu, J., Buchanan, R.C., 2018. Surface roughness: A review of its measurement at micro-/nano-scale. *Physical Sciences Reviews* 3 (January), doi:10.1515/psr-2017-0057.
- Goriainov, V., Cook, R., Latham, J.M., Dunlop, D.G., Oreffo, R.O.C., 2014. Bone and metal: An orthopaedic perspective on osseointegration of metals. *Acta Biomaterialia* 10 (10), 4043–4057. doi:10.1016/j.actbio.2014.06.004.
- Ito, H., SASAKI, H., SAITO, K., *et al.*, 2013. Response of osteoblast-like cells to zirconia with different surface topography. *Dental Materials Journal* 32 (1), 122–129. doi:10.4012/dmj.2012-208.
- Kurella, A., Dahotre, N.B., 2005. Review paper: Surface modification for bioimplants: The role of laser surface engineering. *Journal of Biomaterials Applications*. doi:10.1177/0885328205052974.
- Kasai, T., 2003. Lapping and polishing technology. In: *Handbook of Advanced Ceramics*, pp. 611–627. doi: 10.1016/B978-012654640-8/50017-1. (1–2).
- Jeong, Y.H., Son, I.B., Choe, H.C., 2011. Formation of surface roughness on the Ti-35Nb-xZr alloy using femtosecond laser for biocompatibility. *Procedia Engineering* 10, 2393–2398. doi:10.1016/j.proeng.2011.04.394.
- Lasgorceix, M., Grenho, L., Fernandes, M.H., *et al.*, 2018. Femtosecond laser impact on calcium phosphate bioceramics assessed by micro-Raman spectroscopy and osteoblastic behaviour. *Journal of the European Ceramic Society* 38 (16), 5545–5553. doi:10.1016/j.jeurceramsoc.2018.07.048.
- Law, K.Y., 2014. Definitions for hydrophilicity, hydrophobicity, and superhydrophobicity: Getting the basics right. *Journal of Physical Chemistry Letters* 5, 686–688. doi:10.1021/jz402762h.
- Lee, W.H., Loo, C.Y., Rohanizadeh, R., 2014. A review of chemical surface modification of bioceramics: Effects on protein adsorption and cellular response. *Colloids and Surfaces B: Biointerfaces* 122, 823–834. doi:10.1016/j.colsurfb.2014.07.029.
- Liang, C., Wang, H., Yang, J., *et al.*, 2012. Biocompatibility of the micro-patterned NiTi surface produced by femtosecond laser. *Applied Surface Science* 261, 337–342. doi:10.1016/j.apsusc.2012.08.011.
- Liu, X., Lim, J.Y., Donahue, H.J., *et al.*, 2007. Influence of substratum surface chemistry/energy and topography on the human fetal osteoblastic cell line hFOB 1.19: Phenotypic and genotypic responses observed in vitro. *Biomaterials* 28, 4535–4550. doi:10.1016/j.biomaterials.2007.06.016.
- Lotfi, M., Nejib, M., Naceur, M., 2013. Chapter 8 – Cell adhesion to biomaterials: Concept of biocompatibility. *Advances in Biomaterials Science and Biomedical Applications*. 207–240. doi:10.5772/53542.
- Metwally, S., Stachewicz, U., 2019. Surface potential and charges impact on cell responses on biomaterials interfaces for medical applications. *Materials Science and Engineering C* 104, 109883. doi:10.1016/j.msec.2019.109883.
- Murthy, N.S., 2011. Techniques for analyzing biomaterial surface structure, morphology and topography. *Surface Modification of Biomaterials: Methods Analysis and Applications*. 232–255. doi:10.1016/B978-1-84569-640-5.50009-9.
- Nothdurft, F.P., Fontana, D., Ruppenthal, S., *et al.*, 2015. Differential behavior of fibroblasts and epithelial cells on structured implant abutment materials: A comparison of materials and surface topographies. *Clinical Implant Dentistry and Related Research* 17, 1237–1249. doi:10.1111/cid.12253.
- Ohnishi, O., Suzuki, H., Uhlmann, E., *et al.*, 2015. Chapter 4 – Grinding. In: *Handbook of Ceramics Grinding and Polishing second ed*. Boston: William Andrew Publishing. pp. 133–233. doi:10.1016/B978-1-4557-7858-4.00004-2.
- Otitoju, T.A., Ahmad, A.L., Ooi, B.S., 2017. Superhydrophilic (superwetting) surfaces: A review on fabrication and application. *Journal of Industrial and Engineering Chemistry* 47, 19–40. doi:10.1016/j.jiec.2016.12.016.
- Papageorgiou, S.N., Pandis, N., 2017. Clinical evidence on orthodontic bond failure and associated factors. In: *Orthodontic Applications of Biomaterials*. Elsevier Ltd. doi:10.1016/B978-0-08-100383-1.00012-6.

- Parikh, K.S., Rao, S.S., Ansari, H.M., *et al.*, 2012. Ceramic nanopatterned surfaces to explore the effects of nanotopography on cell attachment. *Materials Science and Engineering C* 32 (8), 2469–2475. doi:10.1016/j.msec.2012.07.028.
- Patel, N.R., Gohil, P.P., 2012. A review on biomaterials: Scope, applications & human anatomy significance. *International Journal of Emerging Technology and Advanced Engineering* 2 (4), (ISSN 2250-2459).
- Paul, W., Sharma, C.P., Chitra, S., 2010. Inorganic Nanoparticles for Targeted Drug Delivery, pp. 204–235. doi:10.1533/9781845699802.
- Rakshit, R., Das, A.K., 2019. A review on cutting of industrial ceramic materials. *Precision Engineering* 59, 90–109. doi:10.1016/j.precisioneng.2019.05.009.
- Rauscher, M.D., Andrew Boyne, A., Dregia, S.A., Akbar, S.A., 2008. Self-assembly of pseudoperiodic arrays of nanoislands on YSZ-(001). *Advanced Materials* 20 (9), 1699–1705. doi:10.1002/adma.200701383.
- Samant, A.N., Paital, S.R., Dahotre, N.B., 2008. Process optimization in laser surface structuring of alumina. *Journal of Materials Processing Technology* 203 (1–3), 498–504. doi:10.1016/j.jmatprotec.2007.10.055.
- Semerok, A., Sallé, B., Wagner, J.F., Petite, G., 2002. Femtosecond, picosecond, and nanosecond laser microablation: Laser plasma and crater investigation. *Laser and Particle Beams* 20 (1), 67–72. doi:10.1017/S0263034602201093.
- Sennerby, L., Dasmah, A., Larsson, B., Iverhed, M., 2005. Bone tissue responses to surface-modified zirconia implants: A histomorphometric and removal torque study in the rabbit. *Clinical Implant Dentistry and Related Research* 7 (Suppl. 1), 13–20. doi:10.1111/j.1708-8208.2005.tb00070.x.
- Shukla, P., Waugh, D.G., Lawrence, J., Vilar, R., 2016. Laser surface structuring of ceramics, metals and polymers for biomedical applications: A review. In: *Laser Surface Modification of Biomaterials: Techniques and Applications*. Elsevier Ltd. doi:10.1016/B978-0-08-100883-6.00010-1.
- Soon, G., Pingguan-Murphy, B., Lai, K.W., Akbar, S.A., 2016. Review of zirconia-based bioceramic: surface modification and cellular response. *Ceramics International* 42 (11), 12543–12555. doi:10.1016/j.ceramint.2016.05.077.
- Tuna, T., Wein, M., Swain, M., Fischer, J., Att, W., 2015. Influence of ultraviolet photofunctionalization on the surface characteristics of zirconia-based dental implant materials. *Dental Materials* 31 (2), e14–e24. doi:10.1016/j.dental.2014.10.008.
- Tuson, H.H., Weibel, D.B., 2013. Bacteria-surface interactions. *Soft Matter* 9 (17), 4368–4380. doi:10.1039/c3sm27705d.
- Van Krevelen, D.W., Te Nijenhuis, K., 2009. Interfacial energy properties. In: *Properties of Polymers*, pp. 229–244. doi:10.1016/b978-0-08-054819-7.00008-x.
- Vorobyev, A.Y., Guo, C., 2009. Femtosecond laser surface structuring of biocompatible metals. In: *Proceedings of the Commercial and Biomedical Applications of Ultrafast Lasers IX*, vol. 7203, p. 720300. doi:10.1117/12.809593.
- Whitesides, M., Grzybowski, B., 2002. Self-assembly at all scales. *Journal of the Chemical Society, Perkin Transactions* 77 (9), 746. Available at: <http://science.sciencemag.org/>.
- Wu, C., Han, P., Liu, X., *et al.*, 2014. Mussel-inspired bioceramics with self-assembled Ca-P/polydopamine composite nanolayer: preparation, formation mechanism, improved cellular bioactivity and osteogenic differentiation of bone marrow stromal cells. *Acta Biomaterialia* 10 (1), 428–438. doi:10.1016/j.actbio.2013.10.013.
- Wu, C.C., Wei, C.K., Ho, C.C., Ding, S.J., 2015. Enhanced hydrophilicity and biocompatibility of dental Zirconia ceramics by oxygen plasma treatment. *Materials* 8, 684–699. doi:10.3390/ma8020684.
- Zhao, G., Schwartz, Z., Wieland, M., *et al.*, 2005. High surface energy enhances cell response to titanium substrate microstructure. *Journal of Biomedical Materials Research – Part A* 74, 49–58. doi:10.1002/jbm.a.30320.

Chemical Functionalization of Calcium Phosphate Bioceramic Surfaces

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Introduction

The reconstruction of bone defects, especially in the cases of large osseous defects, remains a significant clinical issue (Marchat *et al.*, 2013). These defects could result from trauma, malformations, cancer or other pathologies such as osteomyelitis or osteoporosis, and the current approaches, including autografts, allografts or synthetic biomaterials, are not satisfactory. In the field of bone substitution, bone autograft is considered as the gold standard because it contains the extracellular matrix (ECM), growth factors and osteocompetent cells, which are essential to support the induction and growing of new bone (Giannoudis *et al.*, 2007, 2008). Nevertheless, their use is limited by the narrow amount of bones able to be autografted, their shape and their size that cannot always be adapted to the defect geometry, and by an excessive graft resorption. Furthermore, the bone samplings induce pain, infections, hemorrhages and an increase of morbidity. While allografts may avoid the mentioned drawbacks, they are inclined towards transmitting infectious diseases that also limit their use (Hinsenkamp *et al.*, 2012). This is the reason why synthetic bone substitutes fulfilling a well-defined function and having, in some cases, strong interactions with host tissues have been developed.

The first generation of biomaterials (*i.e.*, bioinert materials) appeared in the 1960s and followed the advances in medicine and biomechanics. Their interaction with the living tissues is limited to the formation of a very thin fibrous layer of encapsulation, and they remain chemically stable even after several years of implantation. The improvement of biointegration has led to a second generation of bioactive and/or biodegradable biomaterials. Bioactive materials are bound to the host tissues and interact positively with it, and biodegradable materials are replaced by living tissue after a few weeks or months of implantation (Hench and Polak, 2002). Due to a chemical composition close to the bone mineral calcium phosphates, such as hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) or beta-tricalcium phosphate (β -TCP, $\text{Ca}_3(\text{PO}_4)_2$), are classified among them and they are used since the early 1980s (Jarcho, 1981). This chemico-physical analogy with bone gives to porous calcium phosphate based bioceramics (CPC) specific properties. When shaped to the form of scaffolds or granules, they are highly biocompatible and osteoconductive as they allow the adhesion, the proliferation and the differentiation of cells on their surface (Elliott, 1994). CPC may indeed have two types of porosity: a micro-porosity (pore diameters less than 10 μm), which is involved in the phenomena of exchanges with biological fluids, and a macro-porosity (pore diameters from a few tens to a few hundred micrometers), which is a determining factor for vascular invasion and cellular colonization of substrates (Burg *et al.*, 2000). The new bone tissue grows from the host bone and penetrates within the interconnected macro-pore network of scaffolds or within the interstitial voids; the resorption of substitutes will be then driven by their chemical composition. However, osteoconduction phenomenon is limited, this bone ingrowth only occurs up to about 1 cm from the bone apposition (Petite *et al.*, 2000). While they are osteoconductive, CPC are not or weakly osteoinductive (Bose and Tarafder, 2012); therefore full-bone repair is restricted to defects of small dimensions. As a result, since the early 2000s, research has been focused on the development of the third generation of bioceramics, which are able to interact strongly with the host bone tissues. The interactions between biomaterials and living tissues are crucial from the adhesion of progenitor cells to their differentiation into mature actors of bone healing. The current conception of what the ideal bone biomaterial should be and what biological properties it should have taken into account this integrated vision of the physiology of the bone repair (Vishwakarma *et al.*, 2016; Lopes *et al.*, 2018). Ideal bone substitutes have to stimulate the bone repair through the induction of bone cell differentiation (osteoinductive materials), which is mandatory and needs the existence of an efficient vascularization. They also have to be embedded into the natural bone to insure the mechanical and functional integrity of the bone structure, *i.e.*, to have osteointegrative properties (Chen *et al.*, 2016).

Among the biomolecules employed for biomaterial surface functionalization, we will focus on the biomimetic approach employing molecules that are produced by cells or their synthetic derivatives. Then we will present the different routes of functionalization of CPC with a focus on the covalent immobilization based on the use of anchors, cross-linkers and specific chemical reactions. Finally, we will expose the main *in vitro* and *in vivo* experiments performed to evaluate the added-value of CPC functionalization.

Molecules to Stimulate Biological Events

The biological events occurring during the bone repair and following a bone substitute implantation consist of coordinated and sequential processes involving cellular actors from three distinct physiological systems: immune, vascular and skeletal (Fig. 1). So, the molecules being tethered to biomaterial surfaces are intended first to target mainly monocytes and macrophages for the osteoimmunomodulatory (OIM) strategies. The second target is the osteogenic cells and functional osteoblasts originated from the differentiation of mesenchymal stem cells (MSC). All these cells are directly addressed by adhesive, proliferative and/or osteogenic

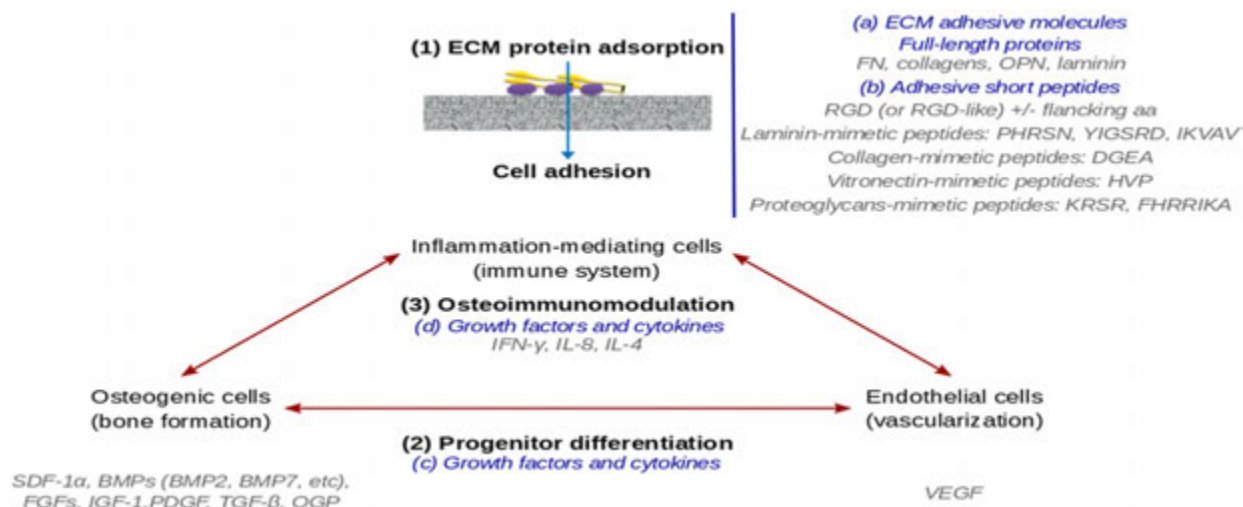


Fig. 1 Schematic representation of strategies and natural molecules used to chemically functionalize CPC. (1) The first event to occur after material implantation is the adsorption of extracellular matrix (ECM) proteins, which allow cell adhesion. In order to mimicry this event, molecules that can be tethered with biomaterials are ECM-related molecules *i.e.*, (a) full-length proteins or (b) short peptides. Another category of natural molecules used is growth factors (GF) and cytokines (CK) that can trigger either (2) specific progenitor differentiation into mature bone (osteogenesis) or endothelial cells (angiogenesis and vascularization) or (3) osteoimmunomodulation that consists of activating macrophages, effector cells of the innate immune response, in order they secrete communicating molecules able to stimulate processes involved in bone repair.

molecules. In addition, stimulation of endothelial cell activities will allow to theoretically improving the biomaterial vascularization. The proteins that belong to the extracellular matrix are essential players (Hankenson *et al.*, 2015) in the initiation of the coordinated biological events leading to bone rehabilitation. The coordination of the associated cells activities, whatever their type and the physiological system to which they belong, lies on the secretion of extracellular signaling molecules. They are mainly growth factors (GF) and cytokines (CK) and they could be pharmacologically triggered (Hankenson *et al.*, 2015). GF and CK are freely released by cells, but can also be trapped into the ECM meshwork by interaction with resident proteins (*e.g.*, fibronectine, heparin) and released during the ECM remodeling. Different strategies can be followed to stimulate either of these systems.

Adhesive Proteins From ECM and Derivatives: Enhancement of Cell Adhesion, Proliferation and Activities

The first event to occur just after a biomaterial implantation, and before interaction with cells is the absorption of ECM proteins from interstitial liquid and blood ((1) in Fig. 1) (Wilson *et al.*, 2005). Then ECM proteins elicit the cell attachment, adhesion and spreading (Chen *et al.*, 2018). The cell function, phenotype and physiological activities will be modulated depending on the cell nature. The selective adhesion of cells to such proteins is mainly performed through the integrins. They are transmembrane heterodimeric receptors, constituted by the assembly of one α and one β subunits (18 and 8 isoforms exist for each subunit type, respectively). This leads to one of the 24 known combinations with differential affinities toward the ECM proteins (their ligands) that are distributed regarding to the cell types. These combinations are associated with the regulation of specific cell functions (cytoskeleton remodeling, cell survival, proliferation or differentiation) through interactions with the intracellular molecular regulators (Marie *et al.*, 2014; Kechagia *et al.*, 2019). To improve osteointegrative properties of biomaterials, standard strategies take advantage of the adhesive properties of bone ECM proteins (osteopontin, bone sialoprotein, fibronectine, type I collagen, vitronectin, *etc.*) to enhance cell adhesion and further cellular activities (Shekaran and Garca, 2010; Chen *et al.*, 2018). The following section presents references corresponding to reviews or examples of works using these strategies but it is far to be exhaustive.

Biomaterials can be functionalized with full ECM adhesive proteins such as fibronectin (Fn) (Kawashita *et al.*, 2016) or type I collagen (Hennessy *et al.*, 2009). Whereas most of the cells are sensitive to Fn or collagens, functionalization with other ECM adhesive molecules like laminin is more common to increase adhesion of endothelial and/or neural cells. The majority of investigations carrying out this functionalization strategy are based on the use of synthetic short RGD (Arg-Gly-Asp) peptides, discussed recently in Huettner *et al.* (2018). The RGD motif, identified in Fn by Pierschbacher and Ruoslahti (1984), is shared by numerous ECM proteins and is the shortest active amino acid (aa) sequence recognized by their associated integrin receptors. Short aa sequence is easily synthesized and less immunogen than full length proteins. This is why tethering of RGD to biomaterial surface by absorption or covalent immobilization is widely used in the literature (for example Durrieu *et al.* (2004)). In full-length proteins, aa flanking the RGD motif modulates the strength of its recognition by each integrin complex subtype. This consequently alters the attachment and the subsequent behavior of cells. Modifications of the RGD motif by adding other aa were done to obtain more specific cell responses by triggering specific $\alpha\beta$ integrin heterodimers (see Huettner *et al.* (2018) for a review). The cell responses will be modulated by the density of molecular tethering and by the kind of stimulated integrins (Perlin *et al.*, 2008; Chollet *et al.*, 2009) and also by the density of full length ECM proteins such as the Fn (Matsui *et al.*, 2015).

While RGD and its derivatives are the preferential choices for functionalizing biomaterials with adhesive peptides, other short aa adhesive sequences may be used (Wang *et al.*, 2017). Fn functional domains derivatives such as type II Fn domains (Pereira *et al.*, 2017) or the ninth type III Fn domain PHRSN may be employed (Redick *et al.*, 2000). The impact of this latter short aa sequence on cell adhesion was evaluated on many polymers and titanium substrates while being often co-attached with an RGD motif for a stronger cell response (Chen *et al.*, 2013; Pramono *et al.*, 2016; Aye *et al.*, 2018). Surface functionalization with a DGEA motif, derived from collagen, can enhance the differentiation process of osteogenic progenitors (Mehta *et al.*, 2015). YIGSRD and IKVAV, respectively derived from laminin and elastin, are also considered, alone or in combination with other sequences to improve their efficiency, especially by enhancing the adhesion of endothelial, muscular or neural cells (dos Santos *et al.*, 2019; Peng *et al.*, 2019). Another way to enhance osteoblast adhesion has been to conjugate KRSR, a peptide mimicking the proteoglycan domains recognized by heparin, to nanocrystalline hydroxyapatite (Nelson *et al.*, 2006). A recent new kind of modified mimetic peptides called elastin-like recombinamers was designed to combine the advantages of adhesive peptides with antifouling properties (Ciofani *et al.*, 2013). They were proven to have interesting biological properties in a context of bone regeneration both *in vivo* and *in vitro* (Tejeda-Montes *et al.*, 2014) but to our knowledge they have not been used yet to functionalize calcium phosphate based materials.

The choice of ECM protein mimetic peptide to enhance cell adhesion can be crucial since some are stimulating the exclusive adhesion of a specific cell type. The targeting of specific integrin receptors to trigger adhesion of a given cell type can be successfully achieved through screening procedures. Recently Kanie *et al.* have defined short active aa sequences from type IV collagen that differentially enhance the specific adhesion of endothelial or smooth muscle cells (Kanie *et al.*, 2012).

Growth Factors and Cytokines: Inducing Specific Cell Behaviors

GF and CK are signaling molecules produced by cells to regulate the behavior of targeted cells in the vicinity of the emitting cells (paracrine communication) that can be of the same cell type (autocrine signaling). Due to the specific chemotactic, proliferative or differentiating effects induced by these molecules, and their relatively small size, GF and CK constitute an attractive way for functionalization (Lee *et al.*, 2011; Tollemar *et al.*, 2016). Moreover, immobilization allows for a local administration with a limited diffusion and avoids supraphysiologic doses that may limit side effects associated to a broader delivery of GF (Hajimiri *et al.*, 2014). The potential efficacy and specificity of GF allow for the development of complex strategies to create smart biomaterials ((2) to (3) in Fig. 1). Indeed, in response to GF stimulation, receptor cells can in turn secrete other GF and CK, inducing further responses. The choice and the design of GF-functionalized biomaterials for bone tissue engineering are discussed in (Przekora, 2019).

Stimulating Bone Cells: Regulation of Osteogenic Differentiation

To make an osteoinductive material, the obvious strategy is to use molecules that are physiologically involved in the regulation of osteogenic differentiation. The GF molecules involved in osteogenesis that are likely to be used for material improvement are well known (Linkhart *et al.*, 1996; Lee *et al.*, 2011; Ripamonti *et al.*, 2006). The first inducible process is the homing of the osteogenic precursors MSC (Fiedler *et al.*, 2002) to the material surface (Andreas *et al.*, 2014). To this purpose, the linkage of a chemotactic GF such as the human PDGF-BB (platelet-derived growth factor-BB) (Phipps *et al.*, 2012) or the SDF-1 α (stromal derived factor 1 α – also known as CXCL12) allows the recruitment of MSC to the material surfaces (Shen *et al.*, 2016; Zhang *et al.*, 2018). To enhance efficiency, GF stimulating stem cell recruitment can be co-attached with osteogenic GF such as bone morphogenic proteins (BMP) (Ratanavaraporn *et al.*, 2011; Shen *et al.*, 2016), which are able to stimulate together both stem cell recruitment and the induction of osteogenesis (Lowery and Rosen, 2018). For example, SDF-1 α is able to modulate the effect of BMP-2 (Hosogane *et al.*, 2010). BMP are frequently employed, as illustrated by the extensive literature that may be found about their use. BMP2 has been the most widely chosen for this purpose (*e.g.*, (Damia *et al.*, 2019; Lin *et al.*, 2019a)). The use of BMP2 and BMP7/OP-1 (osteogenic protein 1) has indeed been approved by the FDA (Food & Drug administration) for the treatment of spinal fusion and bone defects (Hustedt and Blizzard, 2014; Mckie *et al.*, 2014). However, BMP2 was associated to serious adverse effects and medical concerns that limits its clinical use, which even led to an FDA warning in 2008 (James *et al.*, 2016). This point requires a profound reconsideration about how to use it (Bialy *et al.*, 2017). It has been demonstrated that the way a GF is linked to the material surface affect its biological effects (Suliman *et al.*, 2015). In this respect, K. Anselme *et al.* have compared the effects of three BMP (BMP2, BMP6 and BMP7) associated with a human Fn for the functionalization of TiHA surfaces (Brigaud *et al.*, 2017). Some mimetic shorter peptides have also been proven to be efficient on osteogenic cell activities *in vitro* (Zouani *et al.*, 2010). Their benefit lies in that they reproduce at least a part of BMP2, BMP7 or BMP9, known as “knuckle epitope” (Saito *et al.*, 2003), which corresponds to the ligand domain recognized by the BMPRII (BMP type II receptor). The shorter size of such peptides should enhance their effect and efficiency by limiting possibilities of misfolding or misorientation when anchored to the surfaces of materials (Zouani *et al.*, 2010).

Other osteogenic GF of interest for inducing osteogenic differentiation are the members of the FGF (fibroblast growth factor) family (Feito *et al.*, 2010; de la Concepción Matesanz *et al.*, 2012), IGF-1 (insulin-like growth factor 1) (Gao *et al.*, 2015), TGF- β (transforming growth factor β) (Gu *et al.*, 2016) and PDGF (platelet-derived growth factor) (Raghavendran *et al.*, 2016; Bateman *et al.*, 2005; Kämmerer *et al.*, 2016; Santana and Santana, 2015) that can be combined with BMP2 (Thoma *et al.*, 2016; Kim *et al.*, 2013).

Recently, some studies have focused on a short natural peptide present in the bone ECM that have similar properties as a GF, namely the OGP (osteogenic growth peptide) (Policastro and Becker, 2015; Moore *et al.*, 2010).

Stimulating Endothelial Cells: Pro-Angiogenic Growth Factors

Vascularization of biomaterials is an important concern that conditions the success of the bone repair (Hu and Olsen, 2016). Just as in the case of osteogenesis, angiogenesis, which is the formation of new blood vessels from existing ones, can be regulated by several GF and CK molecules (Bayer *et al.*, 2015). The GF the most employed for this purpose is the VEGF (vascular endothelial growth factor) (Hu and Olsen, 2016). Whereas the stimulation of vascularization by CK may be indirectly achieved through the stimulation of innate immune cells or osteogenic precursors, the direct approach consists in the functionalization (adsorption or covalent route) by GF directly acting on endothelial cells (García and García, 2015). Hence, by stimulating production of VEGF by osteogenic cells, BMP such as BMP2 and BMP4 can be considered as angiogenic growth factors in multicellular systems (Deckers *et al.*, 2002; Kuttappan *et al.*, 2018).

Osteoimmunomodulation: Stimulating Messenger Immune Cells to Control Bone Healing

A strong immune response is harmful to the patient and can lead to serious adverse events until complete failure of the implantation (Anderson *et al.*, 2008). However, the existence of a basal immune response is necessary and conditions the success of the subsequent tissue repair (Horwood, 2015). Osteoimmunomodulation (OIM) is based on the foreign body reaction (FBR) occurring after a bone substitute implantation. The FBR, is a natural event induced by the hematoma formation following the blood vessel injuries after the surgical intervention. Extravasated innate immune cells (monocytes, macrophages) are activated by ECM proteins adsorbed on the fibrin-rich blood clot and on the biomaterial surface, and adhere onto it (Lin *et al.*, 2019b). The essential role of immunity and macrophages in bone repair is known to be crucial (Horwood, 2015). Therefore, guided bone regeneration by OIM (detailed in (Sridharan *et al.*, 2015; Chen *et al.*, 2016; Julier *et al.*, 2017; Spiller *et al.*, 2015)) is a relevant strategy that has recently been described. By controlling the activation of immune cells (mainly macrophages) to trigger the adequate secretion of immune signaling molecules, this strategy aims to induce and accelerate bone repair. By creating a favorable micro-environment where osteogenic and endothelial progenitors can be recruited, OIM should favor their proliferation, promote or even efficiently induce their differentiation. Depending on the local molecular micro-environment, macrophages can be activated and oriented according to two distinct and complementary secretory profiles (phenotypes) called M1 and M2 (Murray, 2017). The pro-inflammatory and pro-angiogenic M1 polarization (*i.e.*, its phenotypic orientation) is an early process induced by pro-inflammatory molecules such as interferon- γ (IFN- γ) or pro-inflammatory interleukins (IL, *e.g.*, IL-8). CK and GF released by M1 macrophages (*e.g.*, IL-1 β , prostaglandin E2 or SDF-1 α) are able to recruit and stimulate MSC (Pajarinen *et al.*, 2019). Occurring later, the switch to M2 polarization, globally anti-inflammatory, pro-healing, and favoring matrix deposition and tissue remodeling, is essential for bone healing (Mantovani *et al.*, 2012; Vi *et al.*, 2015; Chen *et al.*, 2016; Vishwakarma *et al.*, 2016). It can be induced by exposing macrophages to interleukins such as IL-4, IL-10, which will secrete in turn TGF- β , PDGF-BB, VEGF, and IGF-1. Therefore the macrophage polarization may be induced by a functionalized material (Sridharan *et al.*, 2015). This field gains in interest, as demonstrated by the special issue of the review Biomaterial published in March 2019, edited by Goodman and Ouyang (2019). The main advantage is the amplification of the signal by the synergy of GF and CK products, triggering then both osteogenesis and angiogenesis. Somehow, this strategy will work as a potent “multi-functionalization”. But the biggest difficulty is to act finely in order not to induce an unfavorable immune reaction leading to chronic inflammation, which could range from the formation of a fibrous capsule to a chronic inflammatory reaction and finally to the biomaterial rejection (Anderson *et al.*, 2008). Some recent examples of osteoimmunomodulation triggering osteogenesis and angiogenesis to enhance osteointegration *in vitro* and *in vivo* can be found in the literature. A first category of studies consists in the functionalization, *i.e.*, the macrophages polarization, with a unique molecule such as IL-8 or IL-4 (Lin *et al.*, 2019a; Yin *et al.*, 2019). Interestingly, more complex system have been developed to tune M1-to-M2 macrophage polarization (Alvarez *et al.*, 2016; Spiller *et al.*, 2015). To this end, (Spiller *et al.*, 2015) have engineered decellularized bovine bones. Their strategy has been on one hand to adsorb IFN- γ in order to first activate the macrophages towards the M1 phenotype by a fast release (Li *et al.*, 2008). And on the other hand they have covalently attached IL-4 to have a slow release and an induction of the M2 phenotype afterwards. A similar strategy was followed by (Alhamdi *et al.*, 2019) and by Li *et al.* (2008).

Chemical Functionalization Routes of CPC

The aim of the chemical functionalization is to improve the biological behavior of CPC by the addition of biomolecules (*i.e.*, full-length proteins or short aa sequences). While the behavior of the biomolecules could be slightly modulated, the receptor-ligand interactions have to be preserved by the functionalization (Rahmany and Dyke, 2013) whatever the chemical functionalization routes is. The following section summarizes of the routes employed for CPC different chemical functionalization, but does not precise the one used for a define biomolecule.

Substrate/Protein Interactions

The chemical functionalization routes of CPC are commonly classified according to the resulting strength of the substrate/protein interactions. Adsorption corresponding to direct interactions between the targeted biomolecule and the substrates and covalent immobilization employing intermediate molecules have to be distinguished.

Functionalization by proteins is commonly carried out by immersing the calcium phosphate substrate into an aqueous solution leading to the absorption of the targeted molecule (Hennessey *et al.*, 2009; Kawashita *et al.*, 2016). The characterization of biomolecule adsorption on solid surfaces is well documented in Migliorini *et al.* (2018) and in Thyparambil *et al.* (2015). When occurring, the adsorption phenomenon is influenced by the experimental conditions used (pH, ionic strength, temperature, *etc.*) and the surface properties of the substrate. Protein adsorption typically increases with roughness, microporosity, charge surface, crystallinity and specific surface area of the substrates (Lee *et al.*, 2014). Generally, the bindings between the adsorbed molecules and the adsorbent are ensured by weak electrostatic interactions, *i.e.*, Van der Waals forces (Debye forces $< 1 \text{ kJ mol}^{-1}$, Keesom interactions $\sim 3 \text{ kJ mol}^{-1}$ and London dispersion forces in the $1\text{--}10 \text{ kJ mol}^{-1}$ range), or hydrogen bonds ($20\text{--}40 \text{ kJ/mol}$) (Fig. 2(a)). This physisorption, which could be modeled (for example (Capriotti *et al.*, 2007)) does not result in any alteration of the protein molecular structure, as no irreversible bond is formed and no change in the chemical functions of the molecule occurs. However it may induce an aggregation and a fibrillation of the protein (Pellenc *et al.*, 2006) or a modification, certainly reversible, of its secondary structure (Paul and Sharma, 2008; Iafisco *et al.*, 2010; Matsui *et al.*, 2015). Finally, physisorption generates mono – or a multi-layer adsorptions (Wang *et al.*, 2012) and leads to a fast and not well controlled release over time (Parent *et al.*, 2016). Nevertheless, it is possible to obtain a mono-layer of strongly adsorbed molecules. In this case, adsorption is accompanied by changes in the distribution of the electronic charges and of the adsorbed molecules leading to ionic bonds (Roussière *et al.*, 2008). This is particularly the case of bisphosphonates (BP) that are able to chemisorb onto calcium phosphates. These stable analogous of pyrophosphate groups ($\text{P}_2\text{O}_7^{4-}$) are characterized by a P–C–P bond linking of two phosphonate groups and they are resistant to enzymatic hydrolysis. Their characteristic chemical structure allows them to get bound to the bone mineral and thus to influence the activity of the cells responsible for bone remodeling (their biological activity is related to their side chains), as illustrated by their use in osteoporosis treatments (Russell, 2007). Due to their affinity for calcium phosphates and the various ending functions of their side chains, the BP can be used as intermediate molecules (Fig. 2(b)) to modify the surface of CaP implants by biologically active molecules (Schuessele *et al.*, 2009; Yewle *et al.*, 2012) but the anchoring of BP requires reactive surfaces with large specific surface areas (Pascaud *et al.*, 2013) which is not the case of CPC for which the specific surface areas are much lower than $5 \text{ m}^2 \text{ g}^{-1}$.

In the case of the CPC, which need thermal treatment during the shaping process and which present low specific surface areas, the most relevant route is the “covalent immobilization” one. Based on the establishment of strong ionic-covalent bonds between the molecule of interest and the surface of the substrate, it may be carried out after their sintering. Chosen by several research teams, it is reported to offer advantages including the control of the surface density and the release kinetics of the bio-molecules.

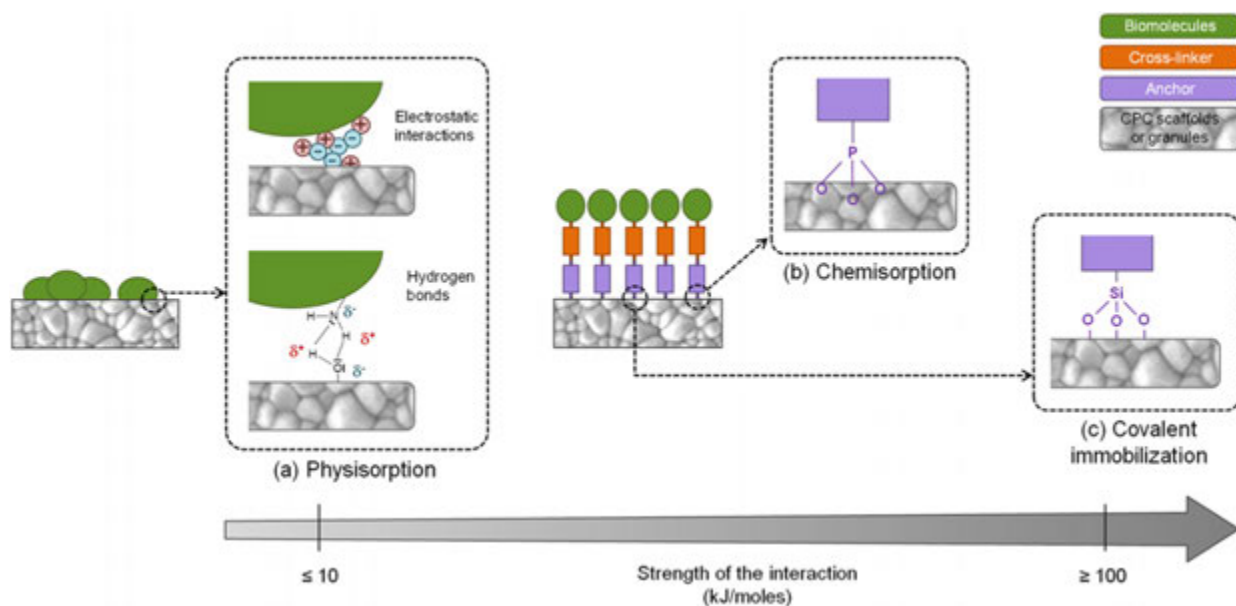


Fig. 2 Drawing summarizing the different approaches for the functionalization of calcium phosphate bioceramics with: (a) physisorption, where the binding of biomolecules is ensured by low electrostatic interactions or hydrogen bonds, (b) chemisorption using bisphosphate molecules and (c) covalent immobilization using silanes. In these last two routes, bisphosphonates and silanes are utilized as anchors and require a reactive terminal function (*e.g.*, an amine) allowing the addition of the spacer and then the protein or peptide sequence.

Most of the protocols are based on approaches involving three steps: (1) the surface modification of the substrate surface using silane as anchor to provide reactive functions, (2) the addition of a bi-functional molecule (cross-linker) and finally (3) the immobilization of biomolecules (Fig. 2(c)). The control of the silanization step must make it possible to control the surface density of the biomolecule and therefore its biological activity.

Functionalization by “Covalent Immobilization”

Silanization

Silanization, developed by Plueddemann (1982), is frequently used to modify the surface of an inorganic substrate by providing a strong substrate/organic molecule bond. Silanization is a simple and inexpensive technique applicable to different types of materials: colloidal particles, porous materials, flat surfaces, polymer-reinforced composite materials. Firstly developed to modify the surface of metal oxides and glasses, it was then adapted to other types of substrates having hydroxyl surface groups. The silanes that are used for functionalization have a general formula of $R_nSiX_{(4-n)}$ where R refers to a non-hydrolyzable chain, X to a hydrolyzable group and the functionality term indicates the number of hydrolyzable X groups. A surface silanization reaction is a competition between the reactions resulting from the hydrolysis of the X groups: their homocondensation (or oligomerization) leading to the formation of oligomers and then to a 3D network and their heterocondensation onto surface hydroxyl groups of the substrates (Fig. 3). Their mechanisms are similar and mainly influenced by the pH, the nature of the solvent (aqueous or organic), the reaction time and temperature, the silane concentration and the nature of its carbon chains (functionality, length and functions) and finally the chemistry and the topography of the substrates (Howarter and Youngblood, 2006; Böhmeler et al., 2011; Siniscalco et al., 2019).

Since the beginning of 2000, the silanization is widely employed for the chemical modification of calcium phosphates to provide primary amine free functions for the subsequent immobilization of biomolecules like short aa sequences or full-length proteins. The amine-terminal functions will later react, *via* nucleophilic addition, with specific groups like aldehyde functions for example (see the subsection hereafter). Consequently, the density and distribution of the biomolecules will be directly determined by those of the anchor agent and the biological properties of the biomaterial will depend on the initial silanization. Thus, a good knowledge of this first step is of prime importance. While the reaction conditions have a strong influence on the silanization,

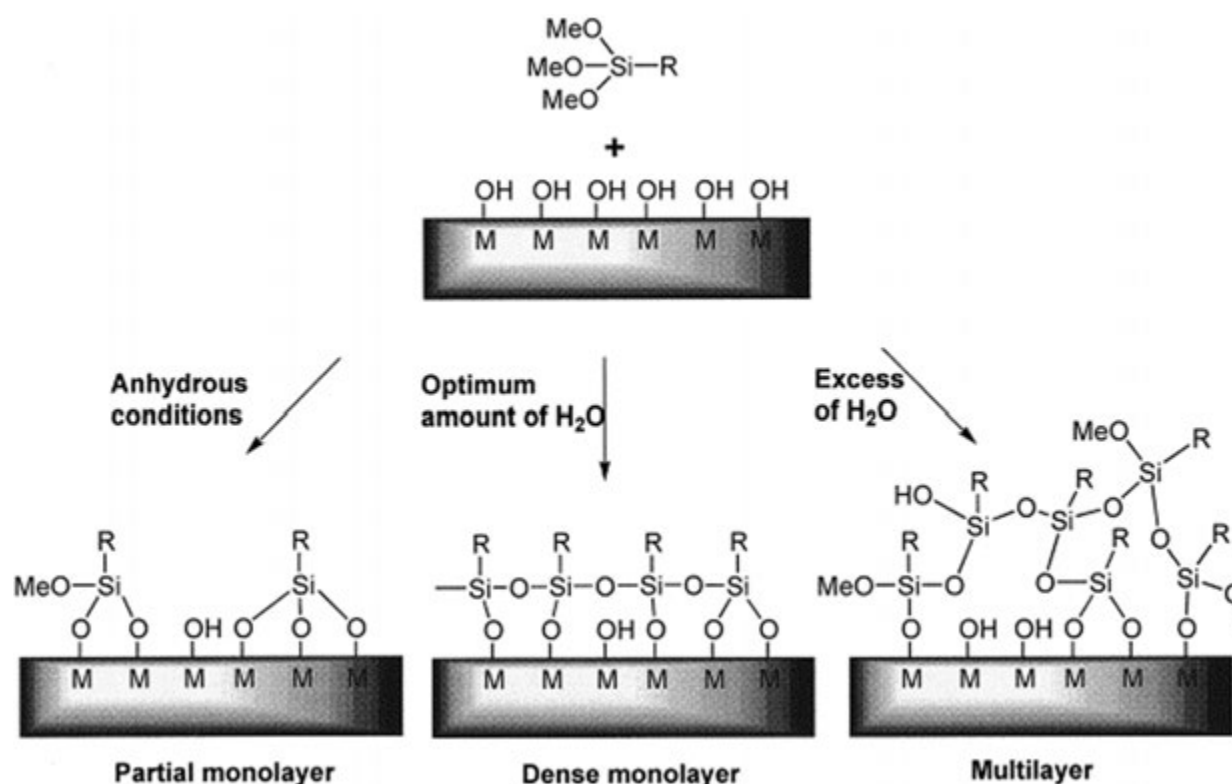


Fig. 3 Schematic representation of the water influence on the surface modification of an oxide surface by an silane (organotrimethoxysilane): (left) anhydrous conditions lead to heterocondensation whereas (middle) homocondensation, and then (right) 3D network, will result from an excess of water. Mutin, P., Guerrero, G., Vioux, A., 2003. Organic-inorganic hybrid materials based on organophosphorus coupling molecules: From metal phosphonates to surface modification of oxides. *Comptes Rendus Chimie* 6, 1153–1164. doi:10.1016/j.crci.2003. Copyright from Elsevier undergoing.

silane and substrates affect it also. The APTES (3-aminopropyltriethoxysilane) is the most employed silane for silanization of biomaterials (Durrieu *et al.*, 2004; Swan *et al.*, 2005; Zurlinden *et al.*, 2005; Balasundaram *et al.*, 2006; Nelson *et al.*, 2006; Wang *et al.*, 2008; Detsch *et al.*, 2009; Acharya *et al.*, 2012; Poli *et al.*, 2019; Damia *et al.*, 2019) but leads to polymerization. The impact of the R non-hydrolyzable chain can be assessed at the surface of model such as a silicone wafer. Böhmler *et al.* have shown that compared to APTES, the molecular assembly is better in the case of AHAPS (N-(6-aminoethyl)-aminopropyltrimethoxysilane) – which presents long and non-alkyl chains (Böhmler *et al.*, 2011). Nevertheless, the folding or reversal of the silane molecule significantly affects the accessibility of the amine-terminal groups and therefore the possibility of a subsequent binding of the biomolecules.

Most of the investigations have been devoted to prove the presence of the molecule on the ceramic surface and to determine the quantity of it. To access to the constituent elements, the organic modifiers and the chemical composition of the surface after functionalization, spectroscopic methods such as energy-dispersive spectroscopy, secondary ion mass spectrometry, infrared spectroscopy (FTIR) or attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS) are often used (Treccani *et al.*, 2013). Thermogravimetry analyzes (TGA) coupled with mass spectroscopy (MS) are employed for the study of the interaction strength between the attached organic groups and the surface and estimate the quantity of immobilized molecules (Damia *et al.*, 2019). In parallel, the spatial repartition and coverage of the ceramic surface by silane molecules can be investigated by Raman mapping. Recently, silanization of hydroxyapatite ceramics has been studied by Siniscalco *et al.* (2019). In a biological point of view, silicate substituted hydroxyapatite (SiHA, $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{SiO}_4)_x(\text{OH})_{2-x}$) are of a great interest as silicon is known to influence the strength, the formation and the calcification of the bone tissue (Carlisle, 1970; Carlisle, 1972). In a chemical point of view, silicate groups can provide preferential sites on the ceramic surface *via* Si–O–Si covalent bonding between CPC and silane molecules (Ek *et al.*, 2003). The Raman maps (Fig. 4) show, whatever the silane and the substrates are, the presence of hillocks evidencing polymerization and/or aggregation of the molecules. But the spots are more intense on SiHA than on HA highlighting the substrate influence. The fact that APMES (3-aminopropyltrimethoxysilane, $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{OCH}_2\text{CH}_3$), which has only one hydrolysable group, leads to relatively intensive spots suggests a dimerization of the molecules. This indicated that there is an interaction between the protonate amine function and the substrate surface, which has been mentioned by several authors (Böhmler *et al.*, 2011; Michelot *et al.*, 2015). So, it is necessary to ensure that the free amine functions required by the following functionalization steps are not all engaged in the silanization reaction. In the case of for RDG motif, Chollet *et al.* have demonstrated an activity for surface densities in the order of $10^{-12} \text{ mol mm}^{-2}$ (Chollet *et al.*, 2009). With this aim, Poli *et al.* have set up sensitive quantification of amine-terminal functions in non-acid media. Two methods have been developed: a modification of the Kaiser method and an adduct method able to quantify primary amine functions down to the $1.0 - 10^{-8} \text{ mol g}^{-1}$ ($\sim 2.0 - 10^{-8} \text{ mol m}^{-2} = 2.0 - 10^{-14} \text{ mol mm}^{-2}$) (Poli *et al.*, 2014).

Immobilization of the Biomolecules

As mentioned above, covalent immobilization routes are based on approaches involving three blocks: (1) a silane presenting free amine function, (2) a cross-linker/spacer and finally (3) the biomolecules of interest (Fig. 2). While the role of the silane is to ensure the junction between the inorganic substrate and the organic structure, the cross-linker agent links the silane to the biomolecule and provides a suitable spacing (Massia and Hubbell, 1991). Two approaches can be distinguished: the “grafting from” approach based on the successive bonding of molecules from the bioceramic surface to the biomolecule and the “grafting to” approach that allows the bonding of a functional building. The latter is constituted by the spacer and the biomolecule of interest, directly onto a silanized surface. Anyway, whatever the approach is, they are based on the same reactions.

The first type of reaction corresponds to the formation of imine bonds between the silane and the crosslinker and between the crosslinker and the targeted protein (or short aa sequence) as illustrated by the left part of Fig. 5. This bond results from the condensation of primary amine and aldehyde functions. Dialdehyde molecules like glutaraldehyde (GA) react with the free amine functions present on the silanized surface, then they will get bound to the biomolecules *via* their amine-terminal groups (Hermanson, 2013; Treccani *et al.*, 2013; Hajimiri *et al.*, 2015). This “grafting from” approach is relatively easy to set up but glutaraldehyde is potentially toxic.

The second group of reactions leads to the formation of amide bonds between the silane and the crosslinker and generally requires the activation of the targeted biomolecule. These reactions need anhydrous solvent and a long set-up. The stable amide bond results from the reaction between the amine-terminal function of the silane with a succinimide function, frequently N-Hydroxysuccinimide (NHS) (Perlin *et al.*, 2008). This approach is illustrated in Fig. 5 (right part) that presents the EDC/NHS strategy (Treccani *et al.*, 2013). The biomolecule is activated by a reaction between its carboxylic acid group and the EDC (1-ethyl-3-(3-diméthylaminopropyl)carbodiimide); then the obtained molecule (O-acylisourea intermediate) reacts with the NHS to provide a reactive NHS-ester function (Durrieu *et al.*, 2004; Schuessle *et al.*, 2009; Poli *et al.*, 2019). Another common possibility is to use the specific reaction between the C=C double bond of maleimide function and the thiol function ($-\text{SH}$) (Lowe, 2014) of the cysteine amino-acid present in the protein or added to the short aa sequence. Different succinimide/maleimide crosslinker agents may be used, offering a large range of possibilities in terms of chain length and approach, *i.e.*, “grafting from” (*e.g.*, (Balasundaram *et al.*, 2006)) *versus* “grafting to” (*e.g.*, (Poli *et al.*, 2019)): SMP (N-succinimidyl-3-maleimidopropionate) (Nelson *et al.*, 2006; Balasundaram *et al.*, 2006), NHS-PEG₆-maleimide (succinimidyl-[(N-maleimidopropionamido)-hexaethyleneglycol] ester) (Damia *et al.*, 2019; Poli *et al.*, 2019). But when all cysteine are linked by disulfide bridges, thiol groups are unavailable to

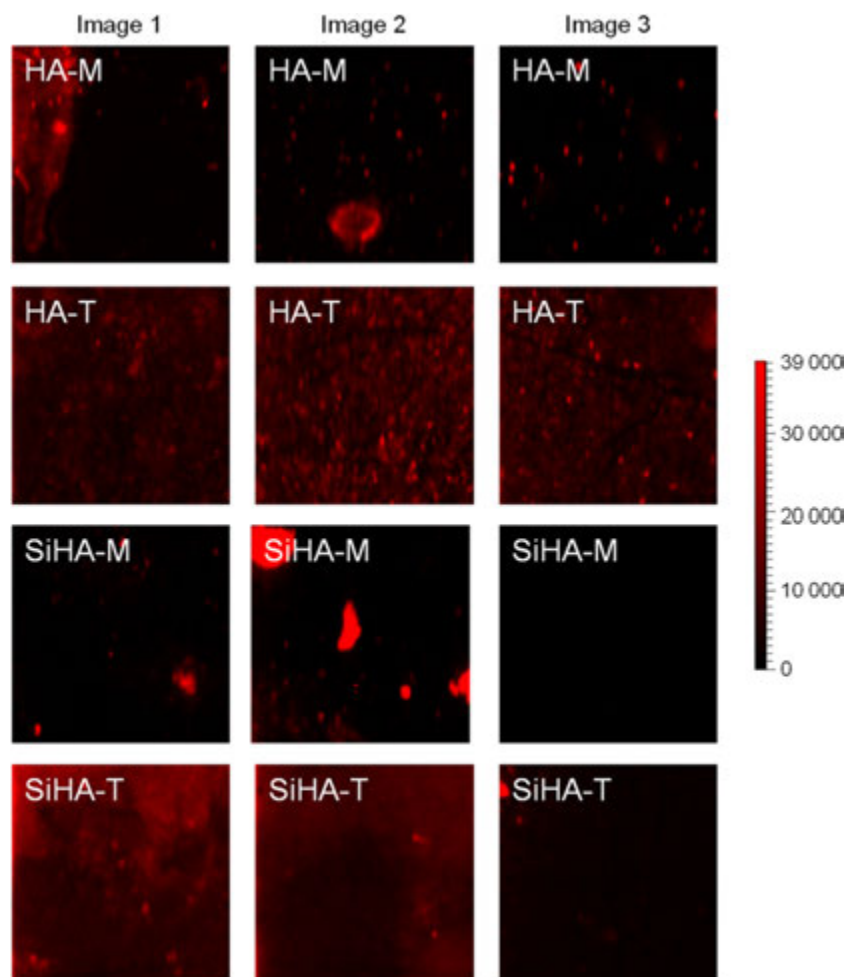


Fig. 4 Raman maps of silanized HA ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and SiHA ($\text{Ca}_{10}(\text{PO}_4)_5.6(\text{SiO}_4)_{0.4}(\text{OH})_{1.6}$) polished ceramics. The two silanes use are the 3-aminopropyltrimethoxysilane (APTES noted M, $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{OCH}_2\text{CH}_3$) and the 3-aminopropyltriethoxysilane (APTES notes T, $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2(\text{OCH}_2\text{CH}_3)_3$). Raman mapping was performed using an inVia Reflex Renishaw Raman spectrophotometer (streamline mode, $\lambda = 532 \text{ nm}$), 50 LWD objective. The maps were reconstructed according to the integrated intensity of the CH modes of both CH_3 and CH_2 units from 2760 to 3060 cm^{-1} . To give an overview of surface properties, three maps of $150\text{--}150 \mu\text{m}^2$ are presented for each condition. Reproduced with permission from Siniscalco, D., Dutreilh-Colas, M., Hjezi, Z., *et al.*, 2019. Functionalization of Hydroxyapatite Ceramics: Raman Mapping Investigation of Silanization. *Ceramics* 2 (2), 372–384. doi:10.3390/ceramics2020029. Copyright © 2019, with permission from MDPI under CC BY 4.0.

react with maleimide function. So in the case of the immobilization of protein that contains no free cysteine amino acid, a thiolation of the protein is required. Traut's reagent is classically used as it reacts with primary amines (of the protein) to form thiols function. The thiol-maleimide coupling will be promoted in anhydrous media, *e.g.*, in the presence of dimethylsulfoxide (DMSO) or dimethylformamide (DMF). Indeed, in aqueous medium with pH above 8, maleimide functions react with amines of arginine or lysine rather than with the thiol group (Brewer and Riehm, 1967). Finally, other crosslinker agents could be used such as a bis-N-hydroxysuccinimide ester of suberic acid (Wang *et al.*, 2008), p-phenylenediisothio-cyanate (Detsch *et al.*, 2009), polyethylene glycol disuccinimidyl succinate (PEG-(SS) 2) (Acharya *et al.*, 2012) or heparin (Goonasekera *et al.*, 2015).

Biological Activity of CPC Functionalized

In vitro and *in vivo* evaluations purpose to evaluate the added-value of functionalization regarding osteointegration and/or angiogenesis stimulation. Most of the authors *in vitro* evaluate the as-obtained biomaterials with osteoblast precursors or human umbilical vein endothelial cells (HUVEC). Nevertheless, as the differentiation of cells is wanting, mesenchymal stem cells (MSC) are more and more utilized since the 2000s. For *in vivo* experiments, the models used are mostly small animal models with *subcutaneous* or bone site implantations depending on the aim, *i.e.*, increasing CPC osteointegration or favoring osteoinduction (Kohli *et al.*, 2018).

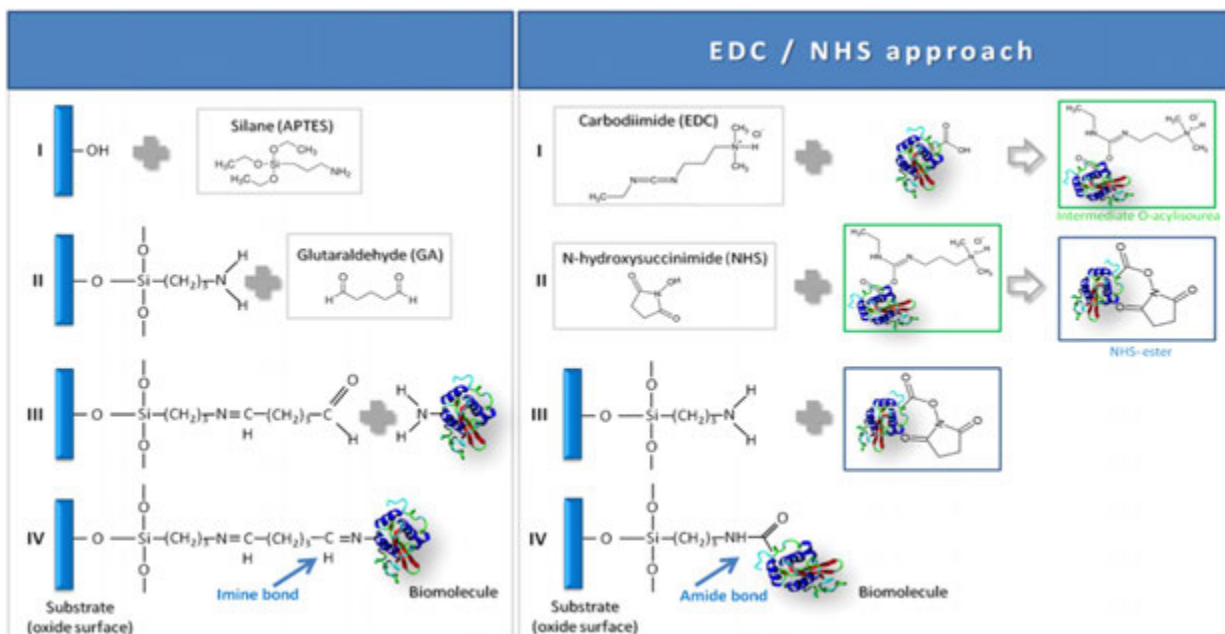


Fig. 5 Schematic showing the covalent immobilization of biomolecules by glutaraldehyde (GA) and EDC/NHS approaches onto amino-terminated surfaces. Reproduced with permission from Treccani, L., Klein, T.Y., Meder, F., Pardun, K., Rezwani, K., 2013. Functionalized ceramics for biomedical, biotechnological and environmental application. *Acta Biomaterialia* 9, 7115–7150. doi:10.1016/j.actbio.2013.03.036. Copyright © 2019, with permission from Elsevier.

In Vitro Evaluation: Adhesiveness and Differentiation

In the beginning of the third generation of biomaterials, the main aim was to increase the cell adhesion. The results presented in this section focus only on chemical functionalization done on CPC materials. Depending on the nature of the attached molecule, cell response has been evaluated from 30 min to 14 even 21 days in culture. Attachment and subsequent adhesion process are relatively short (from 30 min to 24 h), beyond this period the quantitative modifications of cell population *in vitro* are mainly due to cell proliferation events.

As mentioned previously, in comparison with full-length proteins, short aa sequences are less immunogenic, easily synthesized and immobilized onto CPC surfaces, especially by the covalent route. This is why RDG motifs were widely studied: for instance in 2002, Itoh *et al.* have adsorbed E₇PRGDT peptides onto HA ceramics and shown that the peptide stimulated cell attachment and increased DNA content and ALP activity (Itoh *et al.*, 2002). Among the numerous works done on covalent immobilization, the ones of Durrieu *et al.* have to be mentioned (Durrieu *et al.*, 2004). They have indeed shown that it is possible to strongly immobilize RDG sequences on CPC substrates (HA) and they have also highlighted the impact of their sequences on the cell attachment. Cyclo-peptides (c-DfKRG) have been found attractive since they favor cell attachment in short incubation times (3 h) whereas linear RGD peptides (GRGDSPC) allow it at long incubation times (24 h). Later on, it has been shown that RDG sequences improve cell differentiation of murine bone marrow-derived cells line ST-2 (Detsch *et al.*, 2009) and the proliferation of MC3T3-E1 cells (Poli *et al.*, 2019). Interestingly, they also enhance the adhesion of HUVEC. Organic ligands containing cRGDfK as integrin-recognition motif and a pyrogallol unit as anchoring moiety to bioceramics have been adsorbed onto HA and β -tricalcium phosphate (β -TCP) ceramics (Borcard *et al.*, 2012). Functionalized β -TCP ceramics are particularly promising for HUVEC adhesion and adsorption of human proteins, which confirms that the behavior of the RDG motifs used is strongly influenced by the substrate (Perlin *et al.*, 2008). Anyway, the potential of cell-adhesion peptides like RGD in tissue engineering does not reach the end (Huettner *et al.*, 2018).

Concerning full-length ECM proteins, Fn has been shown to act very early in the interaction between cell and material surfaces. When adsorbed at the surface of HA or HA/ β -TCP ceramics, Fn enhance, *in vitro*, the attachment and the adhesion of osteoblastic cells or dermal fibroblasts (Hindié *et al.*, 2014; Kawashita *et al.*, 2016; Matsui *et al.*, 2015; Pendergrass *et al.*, 2012). Moreover, (Kawashita *et al.*, 2016) and (Hindié *et al.*, 2014) have shown that the cell average length or spreading is increased in presence of Fn. When adsorbed, the extent of efficacy of the adhesive effect is dependent on the amount of Fn coated (Matsui *et al.*, 2015) and enhances on a calcium phosphate based ceramic surfaces in comparison with other materials such as alumina, glass or polystyrene (Hindié *et al.*, 2014). The rate of cell proliferation compared to uncoated substrates is not or very slightly ameliorated (Li *et al.*, 2008; Kawashita *et al.*, 2016). Finally, the osteoblastic differentiation evidenced by the activity of the mineralization-associated enzyme alkaline phosphatase (ALP) is not modified by the presence of Fn (Kawashita *et al.*, 2016). Beside Fn, the other ECM protein frequently studied is type I collagen. A study has evidenced that the adhesive properties of collagen has greater influence

than Fn on rat adipose derived stromal cells when adsorbed on HA/ β -TCP 70:30 substrates (Li *et al.*, 2008). In the same approach as the ones used for RDG sequences, Hennessy *et al.* have compared the effect of collagen I and its mimetics short peptides (DGEA or GFOGER) when adsorbed onto HA disks (Hennessy *et al.*, 2009). Collagen and its derivative have a positive effect on expression of osteogenic markers (osteocalcin) and on the enzymatic activity of mineralization-associated alkaline phosphatase, suggesting that they improve osseointegration of HA by stimulating osteoblastic differentiation of MSC rather than their adhesion. However, Wang *et al.* have obtained different results with no effect on cell adhesion and proliferation of cells seeded on porous HA coated with collagen *versus* HA bare scaffolds (Wang *et al.*, 2016). Finally, the case of MEPE (matrix extracellular phospho-glycoprotein), a non-collagenous ECM acid phosphoprotein, is notable (Acharya *et al.*, 2012). The results obtained *in vitro* for the free peptide on human BMSCs (on mineralization) and the expression of the osteogenic marker genes have been confirmed *in vivo*: functionalized HA/ β -TCP particles have been found to enhance bone regeneration in the calvaria defect model in mice.

Biological effect of chemotactic GF on progenitor cells can be evidenced *in vitro* by transwell or Boyden chamber assays. The fast release of SDF-1 α immobilized with alginate and coated onto porous HA scaffolds elicited a strong migration of bone marrow MSC and a good attachment of the cells. However, SDF-1 α does not seem to influence the cell differentiation behavior (Zhang *et al.*, 2018), which is in accordance with other assays performed with non-ceramic materials (Shen *et al.*, 2016). Concerning BMP2, the osteogenic differentiation is dependent of the functionalization route (*i.e.*, adsorption or covalent immobilization) and on the substrate nature. This is directed related to its release kinetics that can be evaluated by biochemical dosages using spectrophotometry (Feito *et al.*, 2010), ELISA (Wernike *et al.*, 2010; Dou *et al.*, 2019) or radiolabeled GF for PDGF-BB (Bateman *et al.*, 2005), VEGF (Wernike *et al.*, 2010; Crouzier *et al.*, 2011) and BMP2, both *in vitro* (Crouzier *et al.*, 2011) and *in vivo* (Tazaki *et al.*, 2009). The release of VEGF immobilized at the surface of BCP disks has been tested alone and in presence of murine bone marrow cells. No modification has been observed except when the osteoclastic differentiation has been induced, in this case the VEGF release was promoted (Wernike *et al.*, 2010). Concerning BMP2, the retention of its biological activity after adsorption or covalent immobilization onto material surface has been tested using a light-promoted reporter system. It is active when BMP2 associated intracellular signaling cascade is activated and effective in responsive cell lines, C2C12 myoblasts or murine mesenchymal cells (Crouzier *et al.*, 2011; Damia *et al.*, 2019). BMP2 has been demonstrated to not or slightly positively affect cell adhesion and proliferation of C2C12 cells (Abarrategi *et al.*, 2012; Crouzier *et al.*, 2011). Elsewhere BMP2 strongly affects the activity of ALP whether it is directly adsorbed to the surface of ceramic materials (Wang *et al.*, 2016), or immobilized using a polyelectrolyte multilayer film (Crouzier *et al.*, 2011). Regarding the use of FGFs in an osteogenesis induction purpose, FGF-1 or FGF-2 adsorbed on silicated HA scaffolds have enhanced adhesion and proliferation of human osteoblastic cells without inducing cell death, associated with the activation of a specific molecular pathway involving the modification of the intracellular flux of calcium (Feito *et al.*, 2010; Wang *et al.*, 2016). PDGF-BB adsorbed on β -TCP also strongly induces the proliferation of human primary osteoblasts (Bateman *et al.*, 2005). Importantly, in the latter case, there exists a synergy between the adsorbed PDGF and the substrate where the cell proliferation is stimulated. Direct or indirect strategies aiming at enhancing biomaterial vascularization use to test the capacity of endothelial cells to proliferate and migrate. *In vitro*, HUVEC are used most of the time. Cell proliferation and migration are both hallmarks of endothelial cell activation enabling new blood vessels to be built. Hence, it has been shown that they are stimulated by VEGF immobilized onto HA, BCP and β -TCP surfaces. VEGF has also been shown to efficiently induce HUVEC differentiation, which has been tested by the mean of tubulogenesis assays, with a better effect obtained with β -TCP over HA (Chen *et al.*, 2015). In the same study, it has also been shown that VEGF promote the secretion of pro-angiogenic factors by human fibroblasts. Finally activation of endothelial cells by angiogenic GF is reflected by the expression of genes and proteins associated with angiogenesis such as the VEGF receptor KDR, or the NO producing enzyme eNOS (Chen *et al.*, 2015; Li *et al.*, 2018).

In Vivo Osteogenic and Osteointegrative Properties

In vivo, osteogenicity of chemically functionalized scaffolds is often tested by histomorphometric analysis of the scaffold after an ectopic implantation for a duration of at least 14 days (subcutaneous or intramuscular) in small animal models such as mice, rats and rabbits (see *e.g.*, (Liang *et al.*, 2005; Saito *et al.*, 2004)). The efficiency of ceramic (HA, substituted or not, β -TCP or BCP with different HA/TCP ratio) functionalization with adsorbed or covalently immobilized BMP2 is reflected by an increase of ALP activity in tissues surrounding the implant (Alam *et al.*, 2001; Liang *et al.*, 2005; Levengood *et al.*, 2010). An absence or a slight presence of connective or fibrous tissue, an infiltration of active immune cells and the presence of ectopic bone formation (Alam *et al.*, 2001; Tazaki *et al.*, 2009; Crouzier *et al.*, 2011) associated with the formation of blood neo-vessels (Liang *et al.*, 2005) and marrow cavities (Abarrategi *et al.*, 2012; Liang *et al.*, 2005) can be observed. Moreover Liang *et al.* have observed the action of BMP2 on the homing of endogenous MSC to the site of implantation, although this phenomenon seems to be delayed on the non-functionalized scaffold (Liang *et al.*, 2005). The quicker the BMP2 is released, the weaker the osteogenicity is (Tazaki *et al.*, 2009; Crouzier *et al.*, 2011). Conversely to Tazaki *et al.*, Alam *et al.* (Alam *et al.*, 2001) have found that when BMP2 is immobilized on porous HA the induction of new bone formation is stronger than with BCP having various HA/TCP ratios. In all the cases, no or slight ectopic bone formation was demonstrated *in vivo* for all scaffolds alone (Alam *et al.*, 2001). In the study of Lin *et al.* (2019a), the nature of the surface of the scaffold has been found to influence the amount of bone formation after subcutaneous implantation in rats. *In vivo* a sequential release with a burst of VEGF and a more sustained liberation of BMP2 leads to a better osteogenesis (subcutaneous site in the rat model), in comparison with scaffolds loaded only with an osteogenic GF such as BMP2 (Dou *et al.*, 2019).

Osteointegrative properties can be evaluated by implantation in long bone (*e.g.*, tibia), calvaria or mandibulae defects (Saito *et al.*, 2006; Abarrategi *et al.*, 2012; Schopper *et al.*, 2008). Positive osteointegrative effects of BMP2 have been shown in dogs with respect to the dose (Yuan *et al.*, 2001). By sequential injection of fluorescent dyes that accumulate on the site of the new mineralized bone apposition, the positive effect of BMP2 in the enhancement of bone formation kinetics *in vivo* has been assessed by Schnettler *et al.* (2008) and Schopper *et al.* (2008). The improvement of osteointegration has been preserved by BMP-2 mimetic peptide deriving from the “knuckle sequence” (Saito *et al.*, 2006). Nevertheless the kinetics of bone formation presented in the rodent models suggest that ectopic formation in small animals is not representative of the ones occurring in larger mammals (Pearce *et al.*, 2007; Hollister and Murphy, 2011; Evans, 2011). Interestingly, after having validated the osteogenicity of BMP2 coated HA ceramic scaffolds in an ectopic site in rabbit, in order to test the osteointegrative properties of their system, Abarrategi *et al.* have compared two different animal models, rabbit and minipigs, in orthotopic implantation assays (Abarrategi *et al.*, 2012). The study puts in light the enhancement of osteointegration of HA scaffolds when associated with BMP2 in comparison to bare HA and to the absence of implant, whatever the animal model is. Better qualitative (bone neoformation, histological structure with presence of blood vessels and bone marrow) and quantitative (amount of bone neo-formation) results have been obtained in presence of BMP2. The study of Abarrategi *et al.* has not evidenced any impact of the scaffold nature upon osteointegration in minipigs. BCP particles coated with PDGF have shown a better osteogenicity in a human model of alveolar bone ridge augmentation (Santana and Santana, 2015). Positive results with the same approach have been also described in a dog model of bone defect (Irokawa *et al.*, 2010). However in a model of rat calvarial defect, the implantation of commercial ceramic bone substitutes (β -TCP and HA) adsorbed with PDGF have given mixed results compared to bare CPC with no or few differences (Luvizuto *et al.*, 2016; de Oliveira *et al.*, 2017).

The stimulation of neovascularization has elicited scaffold colonization by new blood vessels (size and density). In this study, dual releases systems have been used, in which VEGF was adsorbed onto the surface of ceramic HA/collagen composite scaffolds associated with BMP2 loaded in carboxymethyl chitosan microspheres (Dou *et al.*, 2019). The nature of the material employed modifies the biological response, hence the impact of VEGF on β -TCP is superior than on HA. As evidenced by immunofluorescence stainings, more micro-vascular vessels are formed on the scaffold implantation site and more angiogenic factors are produced by resident cells in response to release of VEGF (Chen *et al.*, 2015; Wernike *et al.*, 2010). In this work, two complementary methods have been used: the intravenous injection of FITC-dextran allowing the visualization of vascular network by fluorescence microscopy and a quantitative microscopic analysis using a specific histological index, which is the functional capillary density (FCD) defined as the total length of the erythrocyte perfused capillaries per area (Wernike *et al.*, 2010). The dosage of markers associated with bone and vascular differentiation in tissues around/in the scaffolds give also quantitative information about the efficiency of the employed strategy (Wallner *et al.*, 2015).

Bone pathologies due to the aging of the population are a major problem. In this context, GF-modified scaffolds are promising for the cure of diseases like osteoporosis. Hence, Plaza *et al.* have tested fibronectin-coated HA in a steroid-induced osteoporotic rabbit model with positive results (Plaza *et al.*, 2016). In addition, Wallner *et al.* have used a model of critical defect in diabetic mice (Wallner *et al.*, 2015). Gu *et al.* have tested HA functionalized with TGF-beta and IGF-1 for cervical intervertebral fusion in goat on a 12-week time. The fusion was efficiently achieved in the group implanted with GF-coated HA (Gu *et al.*, 2016).

Lastly the OIM strategies employing chemically grafted GF and/or CK have been, to our knowledge, done with hydrogels or polymer-based materials with positive results *in vitro* and *in vivo*. However, Li *et al.* have sequentially activated human primary macrophages *in vitro* towards the M1 phenotype and then they have switched to the M2 phenotype (Li *et al.*, 2018). This has been assessed by the detection of specific markers and the identification of backsecreted GF and CK (VEGF, PDGF and SDF-1 α). IFN- γ has been adsorbed on composite scaffolds made with calcium silicate and β -TCP. On one hand, the burst release of IFN- γ aims at stimulating M1 activation, and the silicon released from material degradation to obtain M2-polarized macrophages. This allows for the activation of HUVEC cells without altering cell viability *in vitro*. The structures have been proven to be osteogenic *in vivo* with good vascularization, which is promising regarding the novelty of this strategy.

Conclusion

The goal of the chemical functionalization of calcium phosphate bioceramics is to develop the third generation of biomaterials aiming an improvement of the interactions between the biomaterial and its environment. The library of well-characterized natural or derived molecules available for improving the biological properties of biomaterials for bone tissue engineering is rather large. The possibility of synergistic effects associated with the combination of different molecules further increases the possibilities. The choice of associated molecules obviously depends on the targeted biological mechanism. It should be noted that the association of a type of molecule with a given type of material has to be taken into consideration. The works presented here claim to promote the adhesion, the proliferation and the differentiation of the bone cells or to induce angiogenesis, a prerequisite for viable bone growth. So proteins and short aa sequences involved in cell adhesion, osteogenesis and angiogenesis processes are deployed. The routes of functionalization are various and mostly based either on direct adsorption or on covalent immobilization using different agents. Adsorption is relatively well referenced (proteins/substrate interactions, modeling of protein conformations) but questions remain concerning the “bond” between CPC substrates and silane in “covalent immobilization”. Anyway, whatever the chosen route, the targeted biomolecule will be modified. The conformation is modified by the adsorption mechanism and the functions of the covalent immobilization, so its behavior has to be carefully evaluated. Moreover, to be close to the “reality”,

the release kinetics of the biomolecules must be determined in bone physiological conditions, *i.e.*, with a very low flow. The promising approach of osteoimmunomodulation (OIM) is gaining an increasing interest. It is indeed mostly tested on CPC, using their chemico-physical and topography properties to trigger immune cell activation instead of chemical functionalization routes. Therefore, a synergy gathering both these strategies has to be investigated. To conclude, the present chapter and the related results (*in vitro* and *in vivo* experimentations) highlight that functionalized CPC are promising prospects for the induction of bone regrowth after surgery. However, since these devices are intended to be used in humans, the regulatory aspects should be considered at each stage of the development of these materials.

References

- Abarrategi, A., Moreno-Vicente, C., Martínez-Vázquez, F.J., *et al.*, 2012. Biological properties of solid free form designed ceramic scaffolds with BMP-2: In vitro and in vivo evaluation. *PLoS One* 7. e34117. doi:10.1371/journal.pone.0034117.
- Acharya, B., Chun, S.-Y., Kim, S.-Y., *et al.*, 2012. Surface immobilization of MEPE peptide onto HA/upbeta-TCP ceramic particles enhances bone regeneration and remodeling. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 100B (3), 841–849. doi:10.1002/jbm.b.32648.
- Alam, M.I., Asahina, I., Ohmamiuda, K., *et al.*, 2001. Evaluation of ceramics composed of different hydroxyapatite to tricalcium phosphate ratios as carriers for rhBMP-2. *Biomaterials* 22 (12), 1643–1651. doi:10.1016/s0142-9612(00)00322-7.
- Alhamdi, J.R., Peng, T., Al-Naggar, I.M., *et al.*, 2019. Controlled M1-to-M2 transition of aged macrophages by calcium phosphate coatings. *Biomaterials* 196, 90–99. doi:10.1016/j.biomaterials.2018.07.012.
- Alvarez, M.M., Liu, J.C., Santiago, G.T.-d., *et al.*, 2016. Delivery strategies to control inflammatory response: Modulating M1-M2 polarization in tissue engineering applications. *Journal of Controlled Release* 240, 349–363. doi:10.1016/j.jconrel.2016.01.026.
- Anderson, J.M., Rodríguez, A., Chang, D.T., 2008. Foreign body reaction to biomaterials. *Seminars in Immunology* 20 (2), 86–100. doi:10.1016/j.smim.2007.11.004.
- Andreas, K., Sittlinger, M., Ringe, J., 2014. Toward in situ tissue engineering: Chemokine-guided stem cell recruitment. *Trends in Biotechnology* 32 (9), 483–492. doi:10.1016/j.tibtech.2014.06.008.
- Aye, S.-S., Li, R., Boyd-Moss, M., *et al.*, 2018. Scaffolds formed via the non-equilibrium supramolecular assembly of the synergistic ECM peptides RGD and PHSRN demonstrate improved cell attachment in 3D. *Polymers* 10 (7), 690. doi:10.3390/polym10070690.
- Balasundaram, G., Sato, M., Webster, T.J., 2006. Using hydroxyapatite nanoparticles and decreased crystallinity to promote osteoblast adhesion similar to functionalizing with RGD. *Biomaterials* 27 (14), 2798–2805. doi:10.1016/j.biomaterials.2005.12.008.
- Bateman, J., Intini, G., Margarone, J., *et al.*, 2005. Platelet-derived growth factor enhancement of two alloplastic bone matrices. *Journal of Periodontology* 76 (11), 1833–1841. doi:10.1902/jop.2005.76.11.1833.
- Bayer, E., Gottardi, R., Fedorchak, M., Little, S., 2015. The scope and sequence of growth factor delivery for vascularized bone tissue regeneration. *Journal of Controlled Release* 219, 129–140. doi:10.1016/j.jconrel.2015.08.004.
- Bialy, I.E., Jiskoot, W., Nejadnik, M.R., 2017. Formulation, delivery and stability of bone morphogenetic proteins for effective bone regeneration. *Pharmaceutical Research* 34 (6), 1152–1170. doi:10.1007/s11095-017-2147-x.
- Böhmle, J., Ploux, L., Ball, V., Anselme, K., Ponche, A., 2011. Necessity of a thorough characterization of functionalized silicon wafers before biointerface studies. *The Journal of Physical Chemistry C* 115 (22), 11102–11111. doi:10.1021/jp201377n.
- Borcard, F., Staedler, D., Comas, H., *et al.*, 2012. Chemical functionalization of bioceramics to enhance endothelial cells adhesion for tissue engineering. *Journal of Medicinal Chemistry* 55 (18), 7988–7997. doi:10.1021/jm301092r.
- Bose, S., Tarafder, S., 2012. Calcium phosphate ceramic systems in growth factor and drug delivery for bone tissue engineering: A review. *Acta Biomaterialia* 8 (4), 1401–1421. doi:10.1016/j.actbio.2011.11.017.
- Brewer, C.F., Riehm, J.P., 1967. Evidence for possible nonspecific reactions between N-ethylmaleimide and proteins. *Analytical Biochemistry* 18 (2), 248–255. doi:10.1016/0003-2697(67)90007-3.
- Brigaud, I., Agniel, R., Leroy-Dudal, J., *et al.*, 2017. Synergistic effects of BMP-2, BMP-6 or BMP-7 with human plasma fibronectin onto hydroxyapatite coatings: A comparative study. *Acta Biomaterialia* 55, 481–492. doi:10.1016/j.actbio.2017.04.013.
- Burg, K.J., Porter, S., Kellam, J.F., 2000. Biomaterial developments for bone tissue engineering. *Biomaterials* 21 (23), 2347–2359. doi:10.1016/S0142-9612(00)00102-2.
- Capriotti, L.A., Beebe, T.P., Schneider, J.P., 2007. Hydroxyapatite surface-induced peptide folding. *Journal of the American Chemical Society* 129 (16), 5281–5287. doi:10.1021/ja070356b.
- Carlisle, E.M., 1970. Silicon: A possible factor in bone calcification. *Science* 167 (3916), 279–280.
- Carlisle, E.M., 1972. Silicon: An essential element for the chick. *Science* 178 (4061), 619–621.
- Chen, S., Guo, Y., Liu, R., *et al.*, 2018. Tuning surface properties of bone biomaterials to manipulate osteoblastic cell adhesion and the signaling pathways for the enhancement of early osseointegration. *Colloids and Surfaces B: Biointerfaces* 164, 58–69. doi:10.1016/j.colsurfb.2018.01.022.
- Chen, X., Sevilla, P., Aparicio, C., 2013. Surface biofunctionalization by covalent co-immobilization of oligopeptides. *Colloids and Surfaces B: Biointerfaces* 107, 189–197. doi:10.1016/j.colsurfb.2013.02.005.
- Chen, Y., *et al.*, 2015. Enhanced effect of upbeta-tricalcium phosphate phase on neovascularization of porous calcium phosphate ceramics: In vitro and in vivo evidence. *Acta Biomaterialia* 11, 435–448. doi:10.1016/j.actbio.2014.09.028.
- Chen, Z., Klein, T., Murray, R.Z., *et al.*, 2016. Osteoimmunomodulation for the development of advanced bone biomaterials. *Materials Today* 19 (6), 304–321. doi:10.1016/j.mattod.2015.11.004.
- Chollet, C., Chanseau, C., Remy, M., *et al.*, 2009. The effect of RGD density on osteoblast and endothelial cell behavior on RGD-grafted polyethylene terephthalate surfaces. *Biomaterials* 30 (5), 711–720. doi:10.1016/j.biomaterials.2008.10.033.
- Ciofani, G., Genchi, G.G., Liakos, I., *et al.*, 2013. Human recombinant elastin-like protein coatings for muscle cell proliferation and differentiation. *Acta Biomaterialia* 9 (2), 5111–5121. doi:10.1016/j.actbio.2012.10.016.
- Crouzier, T., Sailhan, F., Becquart, P., *et al.*, 2011. The performance of BMP-2 loaded TCP/HAP porous ceramics with a polyelectrolyte multilayer film coating. *Biomaterials* 32 (30), 7543–7554. doi:10.1016/j.biomaterials.2011.06.062.
- Damia, C., Marchat, D., Lemoine, C., *et al.*, 2019. Functionalization of phosphocalcic bioceramics for bone repair applications. *Materials Science and Engineering: C* 95, 343–354. doi:10.1016/j.msec.2018.01.008.
- de Oliveira, J.C.S., Okamoto, R., Sonoda, C.K., *et al.*, 2017. Evaluation of the osteoinductive effect of PDGF-BB associated with different carriers in bone regeneration in bone surgical defects in rats. *Implant Dentistry* 26 (4), 559–566. doi:10.1097/id.0000000000000580.
- de la Concepción Matesanz, M., Feito, M.J., Ramírez-Santillán, C., *et al.*, 2012. Signaling pathways of immobilized fgf-2 on silicon-substituted hydroxyapatite. *Macromolecular Bioscience* 12 (4), 446–453. doi:10.1002/mabi.201100456.

- Deckers, M.M.L., van Bezooijen, R.L., van der Horst, G., *et al.*, 2002. Bone morphogenetic proteins stimulate angiogenesis through osteoblast-derived vascular endothelial growth factor α . *Endocrinology* 143 (4), 1545–1553. doi:10.1210/endo.143.4.8719.
- Dietsch, R., Dieser, I., Deisinger, U., *et al.*, 2009. Biofunctionalization of dispense-plotted hydroxyapatite scaffolds with peptides: Quantification and cellular response. *Journal of Biomedical Materials Research Part A* 92 (2), 493–503. doi:10.1002/jbm.a.32386.
- dos Santos, B.P., Garbay, B., Pasqua, M., *et al.*, 2019. Production, purification and characterization of an elastin-like polypeptide containing the Ile-Lys-Val-Ala-Val (IKVAV) peptide for tissue engineering applications. *Journal of Biotechnology* 298, 35–44. doi:10.1016/j.jbiotec.2019.04.010.
- Dou, D., Zhou, G., Liu, H., *et al.*, 2019. Sequential releasing of VEGF and BMP-2 in hydroxyapatite collagen scaffolds for bone tissue engineering: Design and characterization. *International Journal of Biological Macromolecules* 123, 622–628. doi:10.1016/j.ijbiomac.2018.11.099.
- Durrieu, M.C., *et al.*, 2004. Grafting RGD containing peptides onto hydroxyapatite to promote osteoblastic cells adhesion. *Journal of Materials Science: Materials in Medicine* V15 (7), 779–786.
- Ek, S., Iiskola, E.I., Niinistö, L., *et al.*, 2003. Atomic layer deposition of a high-density aminopropylsiloxane network on silica through sequential reactions of γ -aminopropyltriethoxysilanes and water. *Langmuir* 19 (25), 10601–10609.
- Elliott, J., 1994. *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates*. Amsterdam: Elsevier.
- Evans, C.H., 2011. Barriers to the clinical translation of orthopedic tissue engineering. *Tissue Engineering Part B: Reviews* 17 (6), 437–441. doi:10.1089/ten.teb.2011.0228.
- Feito, M.J., Lozano, R.M., Alcaide, M., *et al.*, 2010. Immobilization and bioactivity evaluation of FGF-1 and FGF-2 on powdered silicon-doped hydroxyapatite and their scaffolds for bone tissue engineering. *Journal of Materials Science: Materials in Medicine* 22 (2), 405–416. doi:10.1007/s10856-010-4193-3.
- Fiedler, J., Röderer, G., Günther, K.-P., Brenner, R.E., 2002. BMP-2, BMP-4, and PDGF-bb stimulate chemotactic migration of primary human mesenchymal progenitor cells. *Journal of Cellular Biochemistry* 87 (3), 305–312. doi:10.1002/jcb.10309.
- Gao, T., Zhang, N., Wang, Z., *et al.*, 2015. Biodegradable microcarriers of poly(lactide-co-glycolide) and nano-hydroxyapatite decorated with IGF-1 via polydopamine coating for enhancing cell proliferation and osteogenic differentiation. *Macromolecular Bioscience* 15 (8), 1070–1080. doi:10.1002/mabi.201500069.
- Garcia, J.R., Garcia, A.J., 2015. Biomaterial-mediated strategies targeting vascularization for bone repair. *Drug Delivery and Translational Research* 6 (2), 77–95. doi:10.1007/s13346-015-0236-0.
- Giannoudis, P.V., Einhorn, T.A., Marsh, D., 2007. Fracture healing: The diamond concept. *Injury* 38 (Suppl. 4), S3–S6. doi:10.1016/S0020-1383(08)70003-2.
- Giannoudis, P.V., Einhorn, T.A., Schmidmaier, G., Marsh, D., 2008. The diamond concept – Open questions. *Injury* 39 (Suppl. 2), S5–S8. doi:10.1016/S0020-1383(08)70010-X.
- Goodman, S., Ouyang, H.-W., 2019. *Novel Molecular and Cellular Strategies to Optimize Bone Healing*. Amsterdam: Elsevier.
- Goonasekera, C.S., Jack, K.S., Bhakta, G., *et al.*, 2015. Mode of heparin attachment to nanocrystalline hydroxyapatite affects its interaction with bone morphogenetic protein-2. *Biointerphases* 10 (4), 04A308. doi:10.1116/1.4933109.
- Gu, Y., Zhang, F., Lineaweaver, W.C., *et al.*, 2016. In vivo study of hydroxyapatite-coated hat type cervical intervertebral fusion cage combined with IGF-I and TGF- β 1 in the goat model. *Clinical Spine Surgery* 29 (5), E267–E275. doi:10.1097/bsd.0b013e3182781d52.
- Hajimiri, M., Shahverdi, S., Kamalinia, G., Dinarvand, R., 2014. Growth factor conjugation: Strategies and applications. *Journal of Biomedical Materials Research Part A* 103 (2), 819–838. doi:10.1002/jbm.a.35193.
- Hajimiri, M., Shahverdi, S., Kamalinia, G., Dinarvand, R., 2015. Growth factor conjugation: Strategies and applications. *Journal of Biomedical Materials Research* 103 (2), 819–838. doi:10.1002/jbm.a.35193.
- Hankenson, K., Gagne, K., Shaughnessy, M., 2015. Extracellular signaling molecules to promote fracture healing and bone regeneration. *Advanced Drug Delivery Reviews* 94, 3–12. doi:10.1016/j.addr.2015.09.008.
- Hench, L.L., Polak, J.M., 2002. Third-generation biomedical materials. *Science* 295, 1014–1017. doi:10.1126/science.1067404.
- Hennessy, K.M., Pollot, B.E., Clem, W.C., *et al.*, 2009. The effect of collagen I mimetic peptides on mesenchymal stem cell adhesion and differentiation, and on bone formation at hydroxyapatite surfaces. *Biomaterials* 30 (10), 1898–1909. doi:10.1016/j.biomaterials.2008.12.053.
- Hermanson, G.T., 2013. *Bioconjugate Techniques*, third ed. New York: Academic Press.
- Hindí, M., Camand, E., Agniel, R., *et al.*, 2014. Effects of human fibronectin and human serum albumin sequential adsorption on preosteoblastic cell adhesion. *Biointerphases* 9 (2), 029008. doi:10.1116/1.4867598.
- Hinsenkamp, M., Muylle, L.C., Eastlund, T., *et al.*, 2012. Adverse reactions and events related to musculoskeletal allografts: Reviewed by the world health organisation project NOTIFY. *International Orthopaedics* 36 (3), 633–641. doi:10.1007/s00264-011-1391-7.
- Hollister, S.J., Murphy, W.L., 2011. Scaffold Translation: Barriers Between Concept and Clinic. *Tissue Engineering Part B: Reviews* 17 (6), 459–474. doi:10.1089/ten.teb.2011.0251.
- Horwood, N.J., 2015. Macrophage polarization and bone formation: A review. *Clinical Reviews in Allergy & Immunology* 51 (1), 79–86. doi:10.1007/s12016-015-8519-2.
- Hosogane, N., Huang, Z., Rawlins, B.A., *et al.*, 2010. Stromal derived factor-1 regulates bone morphogenetic protein 2-induced osteogenic differentiation of primary mesenchymal stem cells. *The International Journal of Biochemistry & Cell Biology* 42 (7), 1132–1141. doi:10.1016/j.biocel.2010.03.020.
- Howarter, J.A., Youngblood, J.P., 2006. Optimization of silica silanization by 3-aminopropyltriethoxysilane. *Langmuir* 22 (26), 11142–11147. doi:10.1021/la061240g.
- Hu, K., Olsen, B.R., 2016. The roles of vascular endothelial growth factor in bone repair and regeneration. *Bone* 91, 30–38. doi:10.1016/j.bone.2016.06.013.
- Huettner, N., Dargaville, T.R., Forget, A., 2018. Discovering cell-adhesion peptides in tissue engineering: Beyond RGD. *Trends in Biotechnology* 36 (4), 372–383. doi:10.1016/j.tibtech.2018.01.008.
- Hustedt, J.W., Blizzard, D.J., 2014. The controversy surrounding bone morphogenetic proteins in the spine: A review of current research. *The Yale Journal of Biology and Medicine* 87, 549–561.
- Iafisco, M., Sabatino, P., Lesci, I.G., *et al.*, 2010. Conformational modifications of serum albumins adsorbed on different kinds of biomimetic hydroxyapatite nanocrystals. *Colloids and Surfaces B: Biointerfaces* 81 (1), 274–284. doi:10.1016/j.colsurfb.2010.07.022.
- Irokawa, D., Ota, M., Yamamoto, S., Shibukawa, Y., Yamada, S., 2010. Effect of β tricalcium phosphate particle size on recombinant human platelet-derived growth factor-BB-induced regeneration of periodontal tissue in dog. *Dental Materials Journal* 29 (6), 721–730. doi:10.4012/dmj.2010-033.
- Itoh, D., Yoneda, S., Kuroda, S., *et al.*, 2002. Enhancement of osteogenesis on hydroxyapatite surface coated with synthetic peptide (EEEEEEPRGDT) in vitro. *Journal of Biomedical Materials Research* 62 (2), 292–298.
- James, A.W., LaChaud, G., Shen, J., *et al.*, 2016. A review of the clinical side effects of bone morphogenetic protein-2. *Tissue Engineering Part B: Reviews* 22 (4), 284–297. doi:10.1089/ten.teb.2015.0357.
- Jarcho, M., 1981. Calcium phosphate ceramics as hard tissue prosthetics. *Clinical Orthopaedics and Related Research* 157, 259–278.
- Julier, Z., Park, A.J., Briquez, P.S., Martino, M.M., 2017. Promoting tissue regeneration by modulating the immune system. *Acta Biomaterialia* 53, 13–28. doi:10.1016/j.actbio.2017.01.056.
- Kämmerer, P.W., Schiegnitz, E., Palarie, V., *et al.*, 2016. Influence of platelet-derived growth factor on osseous remodeling properties of a variable-thread tapered dental implant in ~vivo. *Clinical Oral Implants Research* 28 (2), 201–206. doi:10.1111/clr.12782.
- Kanie, K., Narita, Y., Zhao, Y., *et al.*, 2012. Collagen type IV-specific tripeptides for selective adhesion of endothelial and smooth muscle cells. *Biotechnology and Bioengineering* 109 (7), 1808–1816. doi:10.1002/bit.24459.
- Kawashita, M., Hasegawa, M., Kudo, T.-A., *et al.*, 2016. Effect of fibronectin adsorption on osteoblastic cellular responses to hydroxyapatite and alumina. *Materials Science and Engineering: C* 69, 1268–1272. doi:10.1016/j.msec.2016.08.034.
- Kechagia, J.Z., Ivaska, J., Roca-Cusachs, P., 2019. Integrins as biomechanical sensors of ~the microenvironment. *Nature Reviews Molecular Cell Biology*. doi:10.1038/s41580-019-0134-2.

- Kim, S.E., Yun, Y.-P., Lee, J.Y., *et al.*, 2013. Co-delivery of platelet-derived growth factor (PDGF-BB) and bone morphogenic protein (BMP-2) coated onto heparinized titanium for improving osteoblast function and osteointegration. *Journal of Tissue Engineering and Regenerative Medicine* 9 (12), E219–E228. doi:10.1002/term.1668.
- Kohli, N., Ho, S., Brown, S.J., *et al.*, 2018. Bone remodelling in vitro: where are we headed? A review on the current understanding of physiological bone remodelling and inflammation and the strategies for testing biomaterials in vitro. *Bone* 110, 38–46. doi:10.1016/j.bone.2018.01.015.
- Kuttappan, S., Mathew, D., Jo, J.-I., *et al.*, 2018. Dual release of growth factor from nanocomposite fibrous scaffold promotes vascularisation and bone regeneration in rat critical sized calvarial defect. *Acta Biomaterialia* 78, 36–47. doi:10.1016/j.actbio.2018.07.050.
- Lee, K., Silva, E.A., Mooney, D.J., 2011. Growth factor delivery-based tissue engineering: General approaches and a review of recent developments. *Journal of The Royal Society Interface* 8 (55), 153–170. doi:10.1098/rsif.2010.0223.
- Lee, W.-H., Loo, C.-Y., Rohanizadeh, R., 2014. A review of chemical surface modification of bioceramics: effects on protein adsorption and cellular response. *Colloids and Surfaces B: Biointerfaces* 122, 823–834. doi:10.1016/j.colsurfb.2014.07.029.
- Levengood, S.K.L., Polak, S.J., Poellmann, M.J., *et al.*, 2010. The effect of BMP-2 on micro- and macroscale osteointegration of biphasic calcium phosphate scaffolds with multiscale porosity. *Acta Biomaterialia* 6 (8), 3283–3291. doi:10.1016/j.actbio.2010.02.026.
- Li, T., Peng, M., Yang, Z., *et al.*, 2018. 3D-printed IFN- γ -loading calcium silicate- β -tricalcium phosphate scaffold sequentially activates M1 and M2 polarization of macrophages to promote vascularization of tissue engineering bone. *Acta Biomaterialia* 71, 96–107. doi:10.1016/j.actbio.2018.03.012.
- Li, X., Yao, J., Yang, X., Tian, W., Liu, L., 2008. Surface modification with fibronectin or collagen to improve the cell adhesion. *Applied Surface Science* 255 (2), 459–461. doi:10.1016/j.apsusc.2008.06.105.
- Liang, G., Yang, Y., Oh, S., *et al.*, 2005. Ectopic osteoinduction and early degradation of recombinant human bone morphogenetic protein-2-loaded porous β -tricalcium phosphate in mice. *Biomaterials* 26 (20), 4265–4271. doi:10.1016/j.biomaterials.2004.10.035.
- Lin, X., Hunziker, E.B., Liu, T., Hu, Q., Liu, Y., 2019a. Enhanced biocompatibility and improved osteogenesis of coralline hydroxyapatite modified by bone morphogenetic protein 2 incorporated into a biomimetic coating. *Materials Science and Engineering: C* 96, 329–336. doi:10.1016/j.msec.2018.11.017.
- Lin, D., Chai, Y., Ma, Y., *et al.*, 2019b. Rapid initiation of guided bone regeneration driven by spatiotemporal delivery of IL-8 and BMP-2 from hierarchical MBG-based scaffold. *Biomaterials* 196, 122–137. doi:10.1016/j.biomaterials.2017.11.011.
- Linkhart, T.A., Mohan, S., Baylink, D.J., 1996. Growth factors for bone growth and repair: IGF, TGF β and BMP. *Bone* 19, 1S–12S.
- Lopes, D., Martins-Cruz, C., Oliveira, M.B., Mano, J.F., 2018. Bone physiology as inspiration for tissue regenerative therapies. *Biomaterials* 185, 240–275. doi:10.1016/j.biomaterials.2018.09.028.
- Lowe, A.B., 2014. Thiol–ene “click” reactions and recent applications in polymer and materials synthesis: A first update. *Polymer Chemistry* 5, 4820–4870. doi:10.1039/C4PY00339J.
- Lowery, J.W., Rosen, V., 2018. The BMP pathway and its inhibitors in the skeleton. *Physiological Reviews* 98 (4), 2431–2452. doi:10.1152/physrev.00028.2017.
- Luvizuto, E.R., Tangl, S., Dobsak, T., *et al.*, 2016. Effect of recombinant PDGF-BB on bone formation in the presence of β -tricalcium phosphate and bovine bone mineral matrix: A pilot study in rat calvarial defects. *BMC Oral Health* 16 (1), doi:10.1186/s12903-016-0210-3.
- Mantovani, A., Biswas, S.K., Galdiero, M.R., Sica, A., Locati, M., 2012. Macrophage plasticity and polarization in tissue repair and remodelling. *The Journal of Pathology* 229 (2), 176–185. doi:10.1002/path.4133.
- Marchat, D., Zymelka, M., Coelho, C., *et al.*, 2013. Accurate characterization of pure silicon-substituted hydroxyapatites powders synthesized by a new precipitation route. *Acta Biomaterialia* 9, 6992–7004.
- Marie, P.J., Ha?, E., Saidak, Z., 2014. Integrin and cadherin signaling in bone: Role and potential therapeutic targets. *Trends in Endocrinology & Metabolism* 25 (11), 567–575. doi:10.1016/j.tem.2014.06.009.
- Massia, S.P., Hubbell, J.A., 1991. An RGD spacing of 440 nm is sufficient for integrin α V β 3-mediated fibroblast spreading and 140 nm for focal contact and stress fiber formation. *The Journal of Cell Biology* 114 (5), 1089–1100.
- Matsui, N., Nozaki, K., Ishihara, K., Yamashita, K., Nagai, A., 2015. Concentration-dependent effects of fibronectin adsorbed on hydroxyapatite surfaces on osteoblast adhesion. *Materials Science and Engineering: C* 48, 378–383. doi:10.1016/j.msec.2014.12.042.
- Mckie, J., Qureshi, S., Iatridis, J., *et al.*, 2014. Trends in bone morphogenetic protein usage since the U.S. Food and Drug Administration advisory in 2008: What happens to physician practices when the food and drug administration issues an advisory? *Global Spine Journal* 4, 71–76. doi:10.1055/s-0033-1363515.
- Mehta, M., Madl, C.M., Lee, S., Duda, G.N., Mooney, D.J., 2015. The collagen I mimetic peptide DGEA enhances an osteogenic phenotype in mesenchymal stem cells when presented from cell-encapsulating hydrogels. *Journal of Biomedical Materials Research Part A* 103 (11), 3516–3525. doi:10.1002/jbm.a.35497.
- Michelot, A., Sarda, S., Audin, C., *et al.*, 2015. Spectroscopic characterisation of hydroxyapatite and nanocrystalline apatite with grafted aminopropyltriethoxysilane: Nature of silane–surface interaction. *Journal of Materials Science* 50 (17), 5746–5757. doi:10.1007/s10853-015-9122-x.
- Migliorini, E., Weidenhaupt, M., Picart, C., 2018. Practical guide to characterize biomolecule adsorption on solid surfaces (Review). *Biointerphases* 13 (6), 06D303. doi:10.1116/1.5045122.
- Moore, N.M., Lin, N.J., Gallant, N.D., Becker, M.L., 2010. The use of immobilized osteogenic growth peptide on gradient substrates synthesized via click chemistry to enhance MC3T3-E1 osteoblast proliferation. *Biomaterials* 31 (7), 1604–1611. doi:10.1016/j.biomaterials.2009.11.011.
- Murray, P.J., 2017. Macrophage polarization. *Annual Review of Physiology* 79 (1), 541–566. doi:10.1146/annurev-physiol-022516-034339.
- Nelson, M., Balasundaram, G., Webster, T.J., 2006. Increased osteoblast adhesion on nanoparticulate crystalline hydroxyapatite functionalized with KRSR. *International Journal of Nanomedicine* 1 (3), 339–349.
- Pajarinen, J., Lin, T., Gibon, E., *et al.*, 2019. Mesenchymal stem cell-macrophage crosstalk and bone healing. *Biomaterials* 196, 80–89. doi:10.1016/j.biomaterials.2017.12.025.
- Parent, M., Magnaudeix, A., Delebassee, S., *et al.*, 2016. Hydroxyapatite microporous bioceramics as vancomycin reservoir: Antibacterial efficiency and biocompatibility investigation. *Journal of Biomaterials Applications* 31 (4), 488–498. doi:10.1177/0885328216653108.
- Pascaud, P., Gras, P., Coppel, Y., Rey, C., Sarda, S., 2013. Interaction between a bisphosphonate, tiludronate, and biomimetic nanocrystalline apatites. *Langmuir* 29, 2224–2232.
- Paul, W., Sharma, C., 2008. Tricalcium phosphate delayed release formulation for oral delivery of insulin: a proof-of-concept study. *Journal of Pharmaceutical Sciences* 97 (2), 875–882. doi:10.1002/jps.21012.
- Pearce, A.I., Richards, R.G., Milz, S., Schneider, E., Pearce, S.G., 2007. Animal models for implant biomaterial research in bone: A review. *European Cells & Materials* 13, 1–10.
- Pellenc, D., Giraudier, S., Champion, E., *et al.*, 2006. Removal of surface by-products from sintering hydroxyapatite: Effect of a chelation treatment on fibronectin adsorption and cell adhesion. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 76B, 136–142.
- Pendegrass, C.J., El-Husseiny, M., Blunn, G.W., 2012. The development of fibronectin-functionalised hydroxyapatite coatings to improve dermal fibroblast attachment in vitro. *The Bone & Joint Journal* 94-B (4), 564–569. doi:10.1302/0301-620x.94b4.27698.
- Peng, G., Yao, D., Niu, Y., Liu, H., Fan, Y., 2019. Surface modification of multiple bioactive peptides to improve endothelialization of vascular grafts. *Macromolecular Bioscience* 19 (5), 1800368. doi:10.1002/mabi.201800368.
- Pereira, A.M., Machado, R., da Costa, A., *et al.*, 2017. Silk-based biomaterials functionalized with fibronectin type II promotes cell adhesion. *Acta Biomaterialia* 47, 50–59. doi:10.1016/j.actbio.2016.10.002.
- Perlin, L., MacNeil, S., Rimmer, S., 2008. Production and performance of biomaterials containing RGD peptides. *Soft Matter* 4 (12), 2331. doi:10.1039/b801646a.
- Petite, H., Viateau, V., Bensaid, W., *et al.*, 2000. Tissue-engineered bone regeneration. *Nature Biotechnology* 18 (9), 959–963. doi:10.1038/79449.

- Phipps, M.C., Xu, Y., Bellis, S.L., 2012. Delivery of platelet-derived growth factor as a chemotactic factor for mesenchymal stem cells by bone-mimetic electrospun scaffolds. *PLoS One* 7 (7), e40831. doi:10.1371/journal.pone.0040831.
- Pierschbacher, M.D., Ruoslahti, E., 1984. Cell attachment activity of fibronectin can be duplicated by small synthetic fragments of the molecule. *Nature* 309 (5963), 30–33. doi:10.1038/309030a0.
- Plaza, J.Q., Garzón, L.B., Gimenez, B.B., *et al.*, 2016. Application of calcium phosphates and fibronectin as complementary treatment for osteoporotic bone fractures. *Injury* 47, S15–S21. doi:10.1016/s0020-1383(16)30601-5.
- Plueddemann, E., 1982. *Silane Coupling Agents*. New York: John Wiley & Sons.
- Poli, E., Chaleix, V., Damia, C., *et al.*, 2014. Efficient quantification of primary amine functions grafted onto apatite ceramics by using two UV–vis spectrophotometric methods. *Analytical Methods* 6, 9622–9627. doi:10.1039/C4AY02012J.
- Poli, E., Magnaudeix, A., Damia, C., *et al.*, 2019. Advanced protocol to functionalize CaP bioceramic surface with peptide sequences and effect on murine pre-osteoblast cells proliferation. *Bioorganic & Medicinal Chemistry Letters* 29 (9), 1069–1073. doi:10.1016/j.bmcl.2019.03.002.
- Policastro, G.M., Becker, M.L., 2015. Osteogenic growth peptide and its use as a bio-conjugate in regenerative medicine applications. *Wiley Interdisciplinary Reviews: Nanomedicine and Nanobiotechnology* 8 (3), 449–464. doi:10.1002/wnan.1376.
- Pramono, S., Pugdee, K., Suwanprateep, J., Koontongkaew, S., 2016. Sandblasting and fibronectin-derived peptide immobilization on titanium surface increase adhesion and differentiation of osteoblast-like cells (MC3T3-E1). *Journal of Dental Sciences* 11 (4), 427–436. doi:10.1016/j.jds.2016.07.004.
- Przekora, A., 2019. The summary of the most important cell-biomaterial interactions that need to be considered during in vitro biocompatibility testing of bone scaffolds for tissue engineering applications. *Materials Science and Engineering: C* 97, 1036–1051. doi:10.1016/j.msec.2019.01.061.
- Raghavendran, H.R.B., Mohan, S., Genasan, K., *et al.*, 2016. Synergistic interaction of platelet derived growth factor (PDGF) with the surface of PLLA/Col/HA and PLLA/HA scaffolds produces rapid osteogenic differentiation. *Colloids and Surfaces B: Biointerfaces* 139, 68–78. doi:10.1016/j.colsurfb.2015.11.053.
- Rahmany, M.B., Dyke, M.V., 2013. Biomimetic approaches to modulate cellular adhesion in biomaterials: A review. *Acta Biomaterialia* 9 (3), 5431–5437. doi:10.1016/j.actbio.2012.11.019.
- Ratanavaraporn, J., Furuya, H., Kohara, H., Tabata, Y., 2011. Synergistic effects of the dual release of stromal cell-derived factor-1 and bone morphogenetic protein-2 from hydrogels on bone regeneration. *Biomaterials* 32 (11), 2797–2811. doi:10.1016/j.biomaterials.2010.12.052.
- Redick, S.D., Settles, D.L., Briscoe, G., Erickson, H.P., 2000. Defining fibronectin's cell adhesion synergy site by site-directed mutagenesis. *The Journal of Cell Biology* 149 (2), 521–527. doi:10.1083/jcb.149.2.521.
- Ripamonti, U., Ferretti, C., Heliotis, M., 2006. Soluble and insoluble signals and the induction of bone formation: Molecular therapeutics recapitulating development. *Journal of Anatomy* 209 (4), 447–468. doi:10.1111/j.1469-7580.2006.00635.x.
- Roussière, H., Fayon, F., Alonso, B., *et al.*, 2008. Reaction of zoledronate with β -tricalcium phosphate for the design of potential drug device combined systems. *Chemistry of Materials* 20, 182–191. doi:10.1021/cm702584d.
- Russell, R., 2007. Bisphosphonates: Mode of action and pharmacology. *Pediatrics* 119, 150–162.
- Saito, A., Suzuki, Y., Kitamura, M., *et al.*, 2006. Repair of 20-mm long rabbit radial bone defects using BMP-derived peptide combined with an upalpha-tricalcium phosphate scaffold. *Journal of Biomedical Materials Research Part A* 77A (4), 700–706. doi:10.1002/jbm.a.30662.
- Saito, A., Suzuki, Y., Ogata, S.-I., Ohtsuki, C., Tanihara, M., 2003. Activation of osteo-progenitor cells by a novel synthetic peptide derived from the bone morphogenetic protein-2 knuckle epitope. *Biochimica et Biophysica Acta (BBA) – Proteins and Proteomics* 1651 (1–2), 60–67. doi:10.1016/s1570-9639(03)00235-8.
- Saito, A., Suzuki, Y., Ogata, S.-I., Ohtsuki, C., Tanihara, M., 2004. Prolonged ectopic calcification induced by BMP-2-derived synthetic peptide. *Journal of Biomedical Materials Research* 70A (1), 115–121. doi:10.1002/jbm.a.30071.
- Santana, R., Santana, C., 2015. A clinical comparison of guided bone regeneration with platelet-derived growth factor extend ash enhanced bone ceramic versus autogenous bone block grafting. *The International Journal of Oral & Maxillofacial Implants* 30 (3), 700–706. doi:10.11607/jomi.3529.
- Schnettler, R., Knöss, P.D., Heiss, C., *et al.*, 2008. Enhancement of bone formation in hydroxyapatite implants by rhBMP-2 coating. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 90B (1), 75–81. doi:10.1002/jbm.b.31255.
- Schopper, C., Moser, D., Spassova, E., *et al.*, 2008. Bone regeneration using a naturally grown HA/TCP carrier loaded with rh BMP-2 is independent of barrier-membrane effects. *Journal of Biomedical Materials Research Part A* 85A (4), 954–963. doi:10.1002/jbm.a.31525.
- Schuessele, A., Mayr, H., Tessmar, J., Goeferich, A., 2009. Enhanced bone morphogenetic protein-2 performance on hydroxyapatite ceramic surfaces. *Journal of Biomedical Materials Research Part A* 90 (4), 959–971.
- Shekaran, A., Garca, A.J., 2010. Extracellular matrix-mimetic adhesive biomaterials for bone repair. *Journal of Biomedical Materials Research Part A* 96A (1), 261–272. doi:10.1002/jbm.a.32979.
- Shen, X., Zhang, Y., Gu, Y., *et al.*, 2016. Sequential and sustained release of SDF-1 and BMP-2 from silk fibroin-nanohydroxyapatite scaffold for the enhancement of bone regeneration. *Biomaterials* 106, 205–216. doi:10.1016/j.biomaterials.2016.08.023.
- Siniscalco, D., Dutreilh-Colas, M., Hjezi, Z., *et al.*, 2019. Functionalization of hydroxyapatite ceramics: Raman mapping investigation of silanization. *Ceramics* 2 (2), 372–384. doi:10.3390/ceramics2020029.
- Spiller, K.L., Nassiri, S., Witherell, C.E., *et al.*, 2015. Sequential delivery of immunomodulatory cytokines to facilitate the M1-to-M2 transition of macrophages and enhance vascularization of bone scaffolds. *Biomaterials* 37, 194–207. doi:10.1016/j.biomaterials.2014.10.017.
- Sridharan, R., Cameron, A.R., Kelly, D.J., Kearney, C.J., O'Brien, F.J., 2015. Biomaterial based modulation of macrophage polarization: A review and suggested design principles. *Materials Today* 18 (6), 313–325. doi:10.1016/j.mattod.2015.01.019.
- Suliman, S., Xing, Z., Wu, X., *et al.*, 2015. Release and bioactivity of bone morphogenetic protein-2 are affected by scaffold binding techniques in vitro and in vivo. *Journal of Controlled Release* 197, 148–157. doi:10.1016/j.jconrel.2014.11.003.
- Swan, E.E.L., Popat, K.C., Desai, T.A., 2005. Peptide-immobilized nanoporous alumina membranes for enhanced osteoblast adhesion. *Biomaterials* 26 (14), 1969–1976. doi:10.1016/j.biomaterials.2004.07.001.
- Tazaki, J., Murata, M., Akazawa, T., *et al.*, 2009. BMP-2 release and dose-response studies in hydroxyapatite and beta-tricalcium phosphate. *Bio-Medical Materials and Engineering* 19, 141–146. doi:10.3233/BME-2009-0573.
- Tejeda-Montes, E., Klymov, A., Nejadnik, M.R., *et al.*, 2014. Mineralization and bone regeneration using a bioactive elastin-like recombinamer membrane. *Biomaterials* 35 (29), 8339–8347. doi:10.1016/j.biomaterials.2014.05.095.
- Thoma, D.S., Cha, J.-K., Sapata, V.M., *et al.*, 2016. Localized bone regeneration around dental implants using recombinant bone morphogenetic protein-2 and platelet-derived growth factor-BB in the canine. *Clinical Oral Implants Research* 28 (11), 1334–1341. doi:10.1111/clr.12989.
- Thyparambil, A.A., Wei, Y., Latour, R.A., 2015. Experimental characterization of adsorbed protein orientation, conformation, and bioactivity. *Biointerphases* 10 (1), 019002.
- Tollemar, V., Collier, Z.J., Mohammed, M.K., *et al.*, 2016. Stem cells, growth factors and scaffolds in craniofacial regenerative medicine. *Genes & Diseases* 3 (1), 56–71. doi:10.1016/j.gendis.2015.09.004.
- Treccani, L., Klein, T.Y., Meder, F., Pardun, K., Rezwani, K., 2013. Functionalized ceramics for biomedical, biotechnological and environmental applications. *Acta Biomaterialia* 9 (7), 7115–7150. doi:10.1016/j.actbio.2013.03.036.
- Vi, L., Baht, G.S., Whetstone, H., *et al.*, 2015. Macrophages promote osteoblastic differentiation in vivo: Implications in fracture repair and bone homeostasis. *Journal of Bone and Mineral Research* 30 (6), 1090–1102. doi:10.1002/jbmr.2422.
- Vishwakarma, A., Bhise, N.S., Evangelista, M.B., *et al.*, 2016. Engineering immunomodulatory biomaterials to tune the inflammatory response. *Trends in Biotechnology* 34 (6), 470–482. doi:10.1016/j.tibtech.2016.03.009.

- Wallner, C., Schira, J., Wagner, J.M., *et al.*, 2015. Application of VEGFA and FGF-9 enhances angiogenesis, osteogenesis and bone remodeling in type 2 diabetic long bone regeneration. *PLoS One* 10 (3), e0118823. doi:10.1371/journal.pone.0118823.
- Wang, C., Liu, Y., Fan, Y., Li, X., 2017. The use of bioactive peptides to modify materials for bone tissue repair. *Regenerative Biomaterials* 4 (3), 191–206.
- Wang, H., Wu, G., Zhang, J., *et al.*, 2016. Osteogenic effect of controlled released rhBMP-2 in 3D printed porous hydroxyapatite scaffold. *Colloids and Surfaces B: Biointerfaces* 141, 491–498. doi:10.1016/j.colsurfb.2016.02.007.
- Wang, K., Zhou, C., Hong, Y., Zhang, X., 2012. A review of protein adsorption on bioceramics. *Interface Focus* 2 (3), 259–277. doi:10.1098/rsfs.2012.0012.
- Wang, V., Misra, G., Amsden, B., 2008. Immobilization of a bone and cartilage stimulating peptide to a synthetic bone graft. *Journal of Materials Science: Materials in Medicine* 19 (5), 2145–2155. doi:10.1007/s10856-007-3306-0.
- Wernike, E., Montjovent, M.O., Liu, Y., *et al.*, 2010. VEGF incorporated into calcium phosphate ceramics promotes vascularisation and bone formation in vivo. *European Cells and Materials* 19, 30–40. doi:10.22203/ecm.v019a04.
- Wilson, C.J., Clegg, R.E., Leavesley, D.I., Pearcy, M.J., 2005. Mediation of biomaterial-cell interactions by adsorbed proteins: A review. *Tissue Engineering* 11 (1–2), 1–18. doi:10.1089/ten.2005.11.1.
- Yewle, J.N., Wei, Y., Puleo, D.A., Daunert, S., Bachas, L.G., 2012. Oriented immobilization of proteins on hydroxyapatite surface using bifunctional bisphosphonates as linkers. *Biomacromolecules* 13 (6), 1742–1749. doi:10.1021/bm201865r.
- Yin, X., Li, Y., Yang, C., *et al.*, 2019. Alginate/chitosan multilayer films coated on IL-4-loaded TiO₂ nanotubes for modulation of macrophage phenotype. *International Journal of Biological Macromolecules* 133, 503–513. doi:10.1016/j.ijbiomac.2019.04.028.
- Yuan, H., De Bruijn, J.D., Zhang, X., Van Blitterswijk, C.A., De Groot, K., 2001. Use of an osteoinductive biomaterial as a bone morphogenetic protein carrier. *Journal of Materials Science: Materials in Medicine* 12, 761–766.
- Zhang, B., Li, H., He, L., *et al.*, 2018. Surface-decorated hydroxyapatite scaffold with on-demand delivery of dexamethasone and stromal cell derived factor-1 for enhanced osteogenesis. *Materials Science and Engineering: C* 89, 355–370. doi:10.1016/j.msec.2018.04.008.
- Zouani, O.F., Chollet, C., Guillotin, B., Durrieu, M.-C., 2010. Differentiation of pre-osteoblast cells on poly(ethylene terephthalate) grafted with RGD and/or BMPs mimetic peptides. *Biomaterials* 31 (32), 8245–8253. doi:10.1016/j.biomaterials.2010.07.042.
- Zurlinden, K., Laub, M., Jennissen, H., 2005. Chemical functionalization of a hydroxyapatite based bone replacement material for the immobilization of proteins. *Materialwissenschaft und Werkstofftechnik* 36, 820–827. doi:10.1002/mawe.200500978.

Thermally Sprayed Materials for Biomedical Applications

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Introduction

Surface functionalization in biomedicine and in tissue engineering has become an expanding field with steadily growing in complexity and involved methods during the last decades. Especially for artificial implants, surface functionalization by chemical or physical treatments or by applying functional coatings has reached a level where chemical composition, release kinetics, resorption behavior, and tissue reaction provoked by a specific surface bioactive behavior can be exactly tuned on a molecular level. Development progresses as new scientific insights arise. The complexity is not at last a demanding challenge as the field is a truly interdisciplinary one, bringing together experts from rather different fields of knowledge: Cell biologists, surgeons, dentists, material, process engineers, physicists, and chemists.

Nearly all available modern surface treatment technologies are involved to alter and functionalize surfaces of surgical instruments, functional implants like electrodes, staying in the human body permanently or non-permanently, that is permanent implants (endoprosthetic devices) as well as exoprosthesis. Besides tailoring the chemical composition of a surface, surface topology is the second important key of surface functionalization, especially for implants that are in direct contact with living tissue. Surface structuring using electrochemical etching, laser engraving, and plasma treatment or mechanical treatments adjusts the amount and size of a specific pore structure or specially formed roughness cavities. This enables tissue to grow into and anchor on the artificial implant surface.

Surface Functionalization for Biomedical Applications

The material diversity used for coatings comprises more or less all known material types like metals, oxides, non-oxides, calcium phosphate based materials, bioglasses, polymers, and amorphous carbons. This fact is also reflected by the multiplicity of surface coating and treatment techniques to chemically and physically tailored surfaces. [Table 1](#) summarizes most common surface coating and treatment techniques and lists some typical application examples.

Thermal Spray Process

Thermal Spraying (TS) is a thermo-kinetic deposition process and involves intensive heat and mass transfer during coating deposition by melting and acceleration of a solid feedstock. It comprises a whole group of different spray methods and can be divided according to the type of energy source used, either being of electrical or autogenous nature. It also includes some special processes. An overview is given in [Fig. 1](#). In principle, every material that shows a congruent melting behavior without decomposition can be thermally sprayed. This is especially true for most metals, oxide ceramics, some carbides, some polymers, and metal ceramic based composite materials (so called cermets). It is also valid for many bioceramics or bioinspired materials, like calcium phosphate based materials and many derived composite materials.

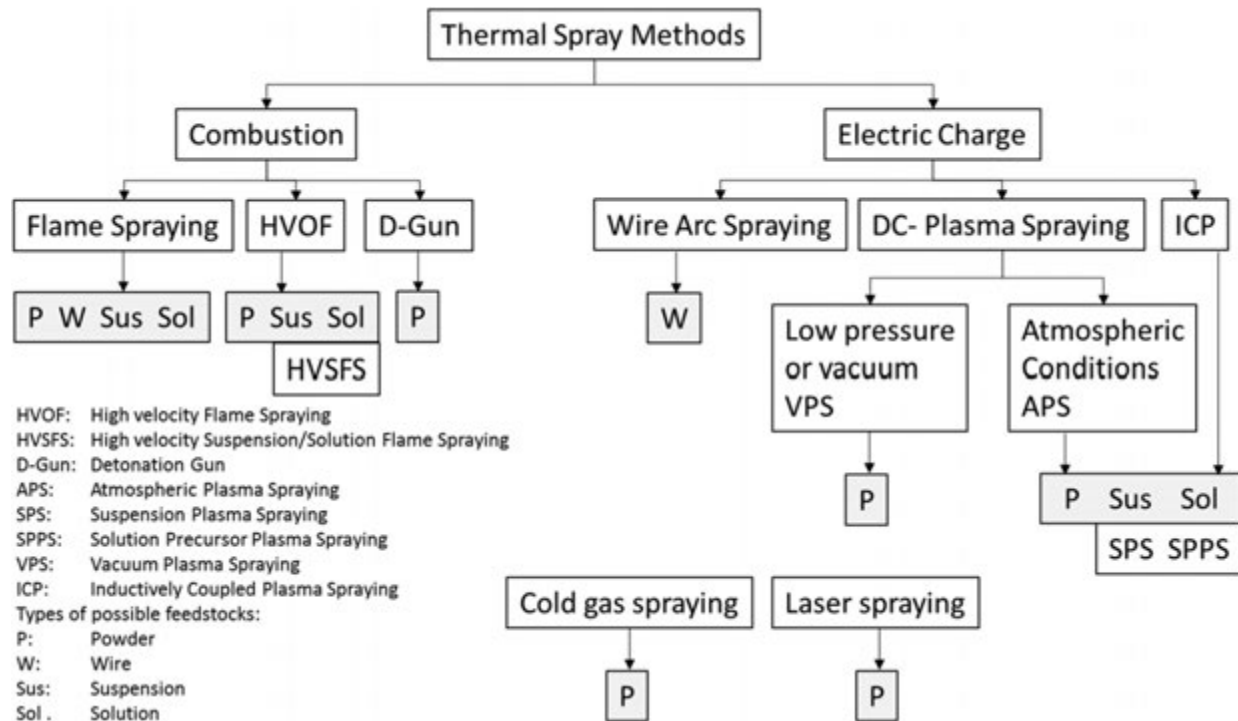
Thermal spraying shows some technical parallels to welding processes, especially when metal feedstocks in form of powders, wires, or rods are involved. From a historical point of view, both techniques were indeed developed in parallel. However, there are some important differences between welding and thermal spraying. In welding the substrate will always be heated above melting point to form a melt bath and alloying of substrate and coating will occur near the surface. This is not the case in thermal spraying. The substrate temperature will only rise to a moderate or intermediate level in the range of 100–300°C, to name typical numbers. By simultaneous cooling techniques, using compressed air or liquid CO₂, it can even be kept below 100°C. This allows for coating of thermally sensible substrates like polymers (PEEK, CFRP, etc.). In most cases, thermal spray coatings need a properly roughened surface to form appropriate adhesion through a mechanical clamping of the individual spray particles that form the final coating. Of course there may also exist diffusion zones on a microscopic level that contribute to adhesion, but substrate and coating material are clearly distinguishable on the interface.

Flame spraying was invented in the beginning of the 20th century and widely used for spraying metals (powders and wires), whereas atmospheric plasma spraying (APS) was primarily used for aerospace applications in the 1960s and entered a broader industrial level starting in the 1980s. The principle setup of a single cathode plasma spray torch is shown in [Fig. 2](#).

However, APS quickly emerged as a versatile and robust coating technology capable of spraying all kind of refractory materials like refractory metals and oxides. The absence of fuel gases and oxygen insures low chemical alteration of the sprayed feedstock. Further variations of this process include vacuum plasma spraying in evacuated chambers (refer to [Fig. 3](#)). This technology allows for spraying of materials that strongly tend to oxidize under ambient conditions. A good example is titanium (Ti), a well-known material that is widely used as coatings in biomedical applications as well. Biocompatible metals and bioceramic coatings are typically applied by vacuum and atmospheric plasma spraying (VPS and APS) techniques and the related manufacturing chains.

Table 1 Examples for surface coating and treatment techniques

Surface process	Coating type	Material examples	Typical substrates	Typical application examples
Thermal spraying (TS)	Thick film 50–100 μm	HAp, TCP, Ti	Ti, Ti-alloys, stainless steel, oxide ceramics, PEEK	Joint replacement implants: Improve bone ingrowth
Physical vapor deposition (PVD)	Thin film 1–5 μm	TiN, ZrN	CoCrMo, stainless steel	Artificial joints: Wear and corrosion protection
Chemical vapor deposition (CVD)		Amorphous carbon DLC	CoCrMo, stainless steel	Artificial joints: Wear and corrosion protection
Electrochemical deposition (ED)		HAp, TCP, Ti	Ti, Ti-alloys	Mainly for dental implant, dental root surface
Sol-gel		HAp		
Electrophoretic deposition		HAp		
Electrolytic plasma oxidation	Surface conversion	TiO ₂		

**Fig. 1** Classification of thermal spray process types according to the type of energy source used, together with appropriate feedstock types (P, W; Sus and Sol).

Flame spraying on the other hand further developed in the later 1980s, when high velocity flame spraying (HVOF) appeared as a new spray method producing high particle velocities. HVOF produces a supersonic jet of combustion gas. Injection of fine powders leads to supersonic particle speed as well, resulting in well adherent and dense coatings. In most industrial applications however, HVOF is used to spray metal and cermet coatings for demanding wear and corrosion protection applications. The typical setup of a HVOF torch is outlined in Fig. 4.

Feedstocks for thermal spraying are mostly available as fine powders or engineered agglomerates, but also as rods and wires depending on the characteristics of the underlying spray material. With the turn of the millennium, a new type of feedstock caught interest within the thermal spray community. Liquid feedstocks opened up a new field of applications and material compositions. Suspension spraying either uses the plasma spraying or flame spray process, called suspension plasma spraying (SPS) and high velocity suspension flame spraying (HVSFS), respectively. In order to spray a liquid feedstock appropriately, modifications in the feeder system as well as in the torch injection and combustion chamber have to be done (see Fig. 5). Analogous to suspension spraying, a liquid feedstock containing a liquid precursor (for instance salts, metal-organics, etc.) can be sprayed, interestingly leading also to fine grained but splat like structures in the coating. As to be discussed in Section “Examples of Research and Development Topics”, liquid feedstock spraying has become one of the central approaches for creating novel biomaterial coatings using SPS and HVSFS. The use of liquid sub-micron and nanoscale suspensions of ceramic powders and the injection through the combustion chamber with subsequent expansion of the particle loaded hot gas jet towards the substrate allows a completely

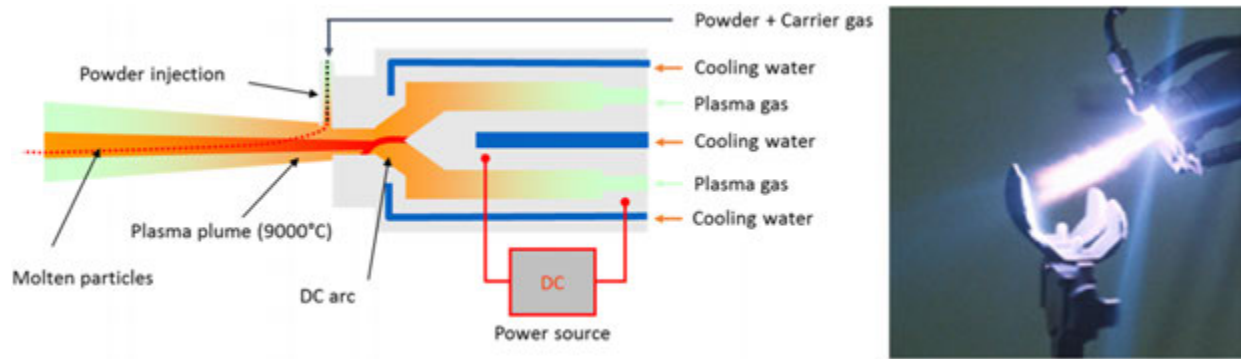


Fig. 2 Right: Principle setup of a single cathode plasma spray torch with radial powder injection typically used for spraying biomaterials. Left: Plasma-coating of knee implant. Image taken from Stryker Orthopedics, 2012.



Fig. 3 Outline of a vacuum plasma spray (VPS) facility typically used for spray coating of porous Ti and HAp on bone implants. Reproduced with permission from AMT AG, Kleindöttingen, Switzerland. www.amt-ag.com.

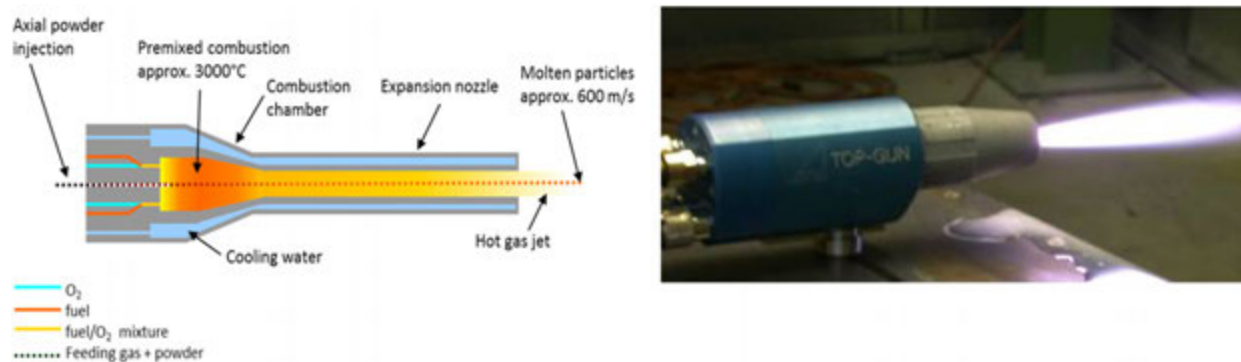


Fig. 4 Typical setup of a HVOF torch to spray powders. With a modification of the injection-part, it is also feasible for suspension spraying. Image source IFKB, University of Stuttgart, 2019.

different thermal and dwell time management of the core process. As a result novel thin solid layers with high density and good adhesion as well as with very fine microstructure can be obtained.

Thermal spraying in general produces coatings regarded as thick coatings typically in a range starting at 50 μm and going up to several 100 μm . Some technical applications demand even thicker coatings, entering the mm range. One of the best examples is TBC coatings, composed of yttria-stabilized zirconia applied in the hot section of gas turbines. Plasma spraying is one of the most successful methods to fulfill this demand, as the coatings exhibit a certain level of fine distributed pores and multi lamellar structures, somehow reducing the stiffness and brittleness of the material, therefore allowing higher coating thickness. The porosity however, is beneficial especially when applied as a TBC material, as it further reduces the thermal conductivity within the coating material. On the other

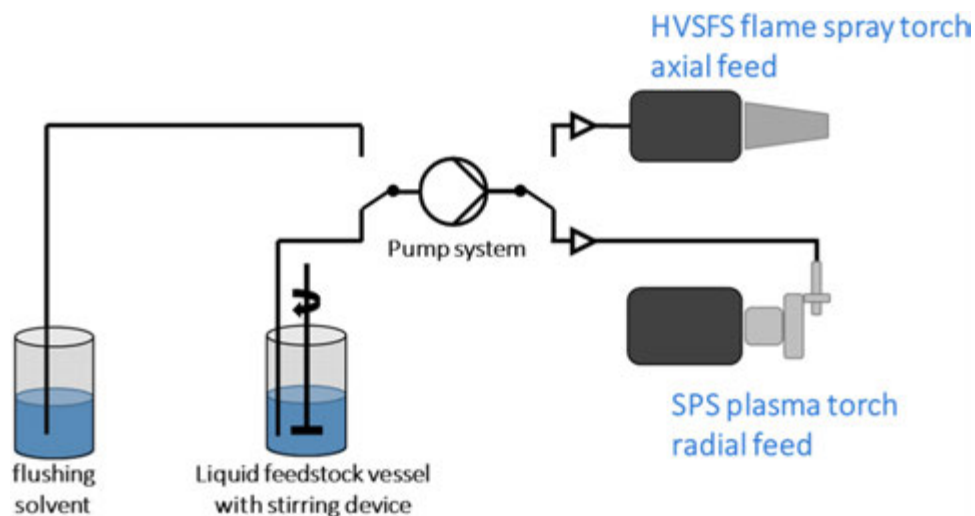


Fig. 5 Schematic setup for suspension spraying either using the HVOF or the APS process.

hand, by spraying nano- and μ -sized particle containing suspensions using SPS or HVSFS, a downscaling of coatings became possible, as splat dimensions are one to two magnitudes smaller compared to standard APS spray processes. Covering and uniformly structured coatings in the range of 10–50 μm become possible recently, opening up new application fields and coating properties.

Thermal Spraying of Biomaterials

Thermal spraying of biomaterials dates back to the 1970s of the last centuries. First applications reported in literature were CaP coated tooth implants and APS was the preferred coating method. In 1986, plasma spray coatings for the stem of hip endoprotheses in hip joint arthroplasty were introduced to accelerate and improve their ingrowth behavior. The biocompatibility of these coatings enabled the press fit type of hip operation in comparison to the traditional cementation. Coatings on other implant types like shoulder and knee joint replacement parts followed during the ongoing decades. VPS techniques became the preferred method for coating of bone implants with titanium and subsequent top coatings. Recently PEEK implants for spinal therapy (anterior cervical discectomy and fusion) are successfully plasma-spray-coated (Robotti, 2012). Typical application fields are depicted in Fig. 6.

At present, atmospheric plasma spraying and vacuum plasma spraying using specially manufactured spray powders are the two processes to apply various biocompatible materials on metal and polymer implant bodies. Mostly used spray materials in commercially available applications are titanium (Ti) or hydroxyapatite (HAp).

By studying the current literature, research has promising results using suspensions to extend the material palette by introducing bioglasses and glass ceramics. The use of fine grade submicron or even nano-sized powders allows for some new types of coating structures: Either being thin and dense or open porous. Suspension spraying, using either the plasma or the high velocity flame spray process are under intensive research. An overview is given in Table 2.

Classification of Biomaterials Used in Thermal Spray Applications

Every artificial material that enters the body causes a specific reaction of the human body, depending on its chemical nature. Especially metals can undergo a corrosive attack in the body induced by the surrounding fluids and tissues. This can cause severe toxic or allergenic reactions by the body leading to inflammation that may imply a serious health threat for the patient. A second reason is a mechanical attack of joints or joint parts that produces wear debris that distributes into the surrounding tissue. Corrosion and wear can, of course overlay, thus potentiating their effects.

However, regarding the case that none of these problems would occur and the material stays intact, most materials can be classified into four groups showing a typical behavior in or towards living tissue. The material classification is summarized in Fig. 7. Bioceramics, however, represent a special group of materials and were found to be suitable as a thermal spray feedstock as they show a rather stable melting behavior. Most materials used as thermal spray coatings are classified as bio-inert or bioactive. Table 3 gives a summary of thermally sprayed materials, which can be practically divided into four groups:

- (1) calcium phosphates;
- (2) oxides;
- (3) metals, predominantly Ti; and
- (4) bioglasses and glass-ceramics.

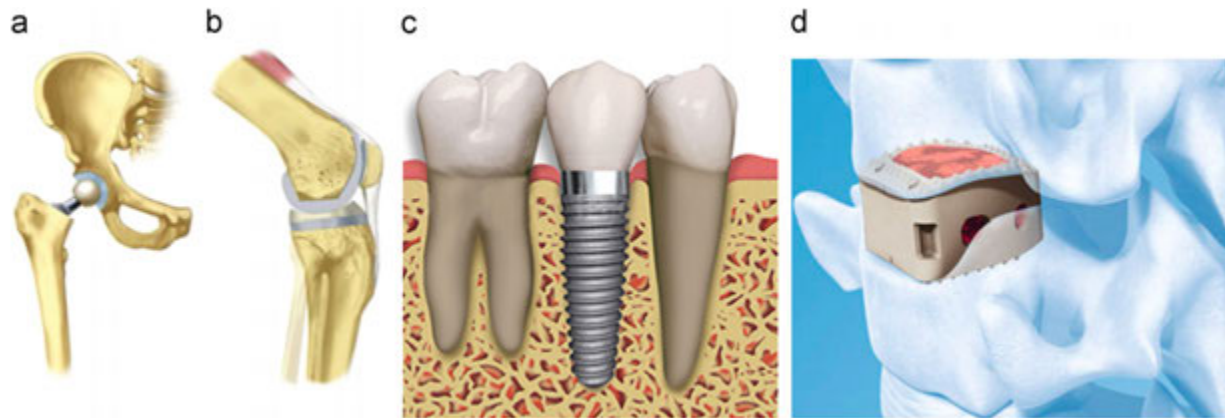


Fig. 6 Typical application fields where thermally sprayed biomaterial coatings are in use. Implants for hip and knee joint replacement ((a) and (b)). Dental implants (c). Cervical interbody fusion cage (d). Reproduced with permission from (a) and (b) Klinikum Garmisch-Partenkirchen/endogap Klinik für Gelenkersatz, www.endogap.de. (c) Image taken from <http://morganheightsdental.com>. (d) Image taken from <http://www.medicaexpo.com/prod/depu-synthes/product-79814-631391.html>.

Table 2 Overview of relevant thermal spray methods used for biomedical applications

Spray method	Short	Energy source	Feedstock type	Typical particle velocities ($m\ s^{-1}$)	Particle size range (μm)	Typical materials sprayed	Remarks
Atmospheric plasma spraying	APS	Electric arc	Powder	200–300	30–150	HAp, TCP, TiO_2 , certified spray powders	Standard industrial procedure. Different porosity levels
Vacuum plasma spraying	VPS	Electric arc	Powder	300–400	30–150	HAp, TCP, Ti, certified spray powders	Standard industrial procedure. Different porosity levels
(Atmospheric) Suspension plasma spraying	SPS	Electric arc	Suspension	200–300	From μ to nano-scaled particles	HAp, TiO_2	Under development. Openporous coatings
High velocity flame spraying	HVOF	Combustion	Powder	600–800	20–50	HAp, TCP, TiO_2	Under development. Dense coatings
High velocity suspension flame spraying	HVSFS	Combustion	Suspension	600–800	From μ to nano-scaled particles	HAp, TCP, TiO_2 , bioglasses	Under development. Dense coatings

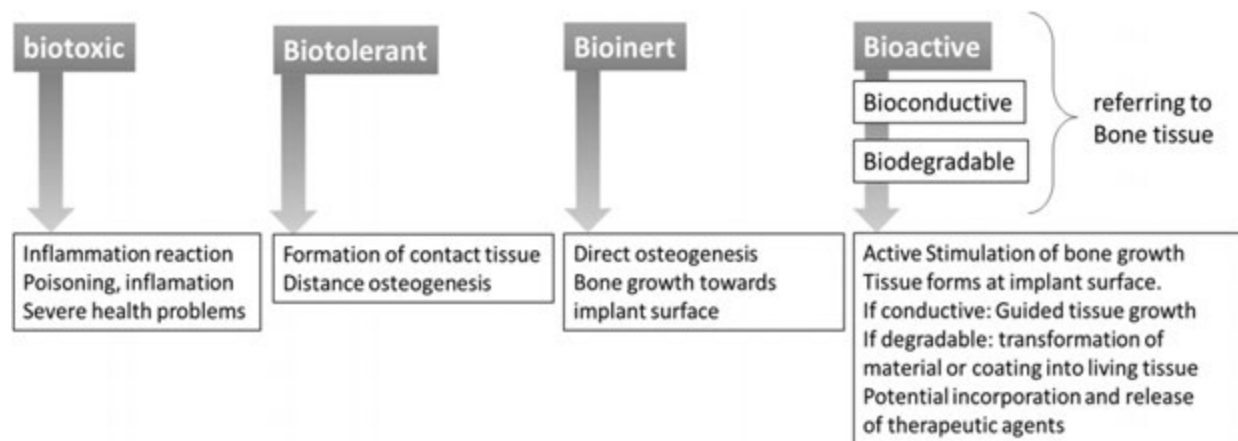


Fig. 7 Classification of materials regarding their biological behavior in contact with living (bone) tissue.

Table 3 Overview of biomaterials used in thermal spray based biomedical applications

Material	Composition	Material type	Biorelated properties
Hydroxyapatite	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	Calcium phosphate (CaP)	Bioactive, bioconductive, porous ingrowth
Tricalcium phosphate	$\text{Ca}_3(\text{PO}_4)_2$	Calcium phosphate (CaP)	Bioactive, bioresorbable
Titania	TiO_2 , TiO_{2-x}	Oxide, suboxide	Bioinert
Titanium	Ti	Metal	Bioinert, porous ingrowth
Bioglasses and glass-ceramics (AW, 45S5, GB14, ...)	General composition: $[\text{SiO}_2]_x [\text{P}_2\text{O}_5]_y [\text{CaO}]_z [\text{Na}_2\text{O}]_v [\text{K}_2\text{O}]_w [\text{MgO}]_w \dots$	Si, P-glasses	Bioactive, bioresorbable

Table 4 Calcium phosphates used for thermal spray coatings

Name	Chemical composition	Abbreviation	Ca:P ^a molar ratio	Solubility at 37°C ^b [$-\log(K_s)$]
Dicalcium phosphate, brushite	$\text{CaHPO}_4/\text{CaHPO}_4 \cdot 2(\text{H}_2\text{O})$	C ₂ P	1	7.02/6.63
Tricalcium phosphate	α , β , γ – $\text{Ca}_3(\text{PO}_4)_2$	C ₃ P	1.5	25.5 (α), 29.5 (β)
Hydroxyapatite	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	HA, HAp	1.67	117.2
Tetracalcium phosphate	$\text{Ca}_4\text{O}(\text{PO}_4)$	C ₄ P	2	37–42

^aJuhasz (2012).^bEliasz (2017).

All four groups are discussed in more details in the following Sections “Calcium Phosphate Based Bioceramics”, “Bioglasses”, “Glass-Ceramics”, “Oxides”, “Titanium”.

Calcium Phosphate Based Bioceramics

By far the most prominent group of biomaterials are calcium phosphate based ceramics. Calcium phosphates (CaP) have Ca^{2+} and phosphate groups $(\text{PO}_4)^{3-}$ or $(\text{PO}_3\text{H})^{2-}$ as their main constituents, in some cases further modified by $(\text{OH})^-$ groups or organized in a hydrated form. Well known representatives are: Tricalciumphosphate (TCP) and hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, usually abbreviated as HA or HAp. It is closely linked to the fluorapatite, where $(\text{OH})^-$ is replaced by F^- , forming $\text{Ca}_5(\text{PO}_4)_3\text{F}$. It has a chemical composition that is very close to the composition of the mineral phase of natural bone. However, the natural bone mineral has a slightly lower Ca:P ratio than 1.67 (therefore, non-stoichiometric) and integrates further elements like Na, Mg, F, etc. In dense form (for instance sintered or as a dense coating), it is rather stable in biological surroundings, showing very low solubility or resorption.

TCP exists in three polymorphs, named α , α' and β . The rhombohedral β -form is the stable room temperature phase and the monoclinic α - and hexagonal α' are the two high temperature forms. TCP is bioresorbable with a lower density and a relatively higher solubility of the metastable α and α' forms.

Dicalcium phosphate (C₂P) and Tetracalcium phosphate (C₄P) are further chemical compounds that belong to this group. As summarized and depicted in Table 4, the Ca/P ratio is one of the important factors, as it determines the solubility of the CaP and thus its chemical behavior in a biological surrounding, primarily its bioresorbability.

It should be emphasized here that solubility in general is strongly dependent of the surrounding medium (its pH value, physiological composition and temperature) as well as the morphological structure of the CaP material, will say: Grade of crystallinity, grade of porosity, and amount of exchange surface. It should be noted that an amorphous structure shows a significantly higher solubility than crystalline phases. This partial solubility is of high importance for the reaction with osteoblasts at the phase boundary after operation and during the convalescence period.

CaP based materials are widely used as cements, pastes, and as filler application in dental repair and bone healing and bone replacement procedures. TCP and HAp coatings, often applied by thermal spraying, are widely used in orthopedic, dental and maxillofacial applications (see sections “Examples of Commercially Available Applications” and “Examples of Research and Development Topics”). As they are chemically similar to the mineral component of human bone and hard tissue, they support bone ingrowth and osseointegration, because they are able to form a direct bond to the surrounding hard tissue. It is generally agreed in clinical practise, that these materials are able to shorten the healing process in patients with metal-based implants. TCP is mainly used as a bioresorbable material in certain applications. It dissolves and is replaced on site by natural bone tissue within some weeks. HAp remains more stable as a coating and may be resorbed/transformed to natural bone tissue on a month or year time scale. In any case, it should be understood that the coating is more than just a compatible bond to the remaining bone structure but to some extent a bioactive materials that transforms to natural bone, thereby enhancing the mechanical bond of a prosthetic device to the surrounding hard tissue.

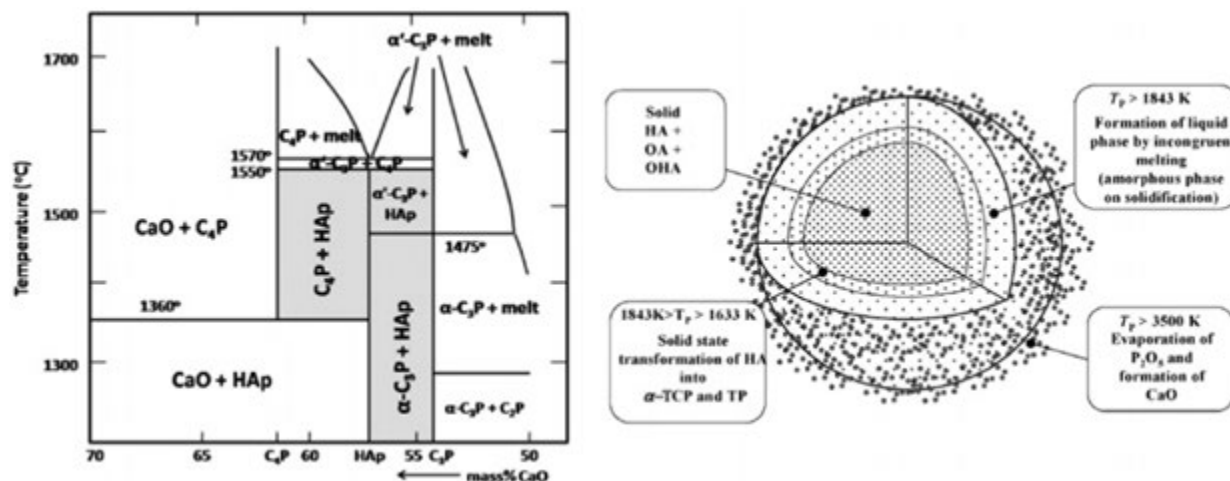


Fig. 8 Left side: CaO/CaP phase diagram showing possible routes for formation of CaP species depending on CaO content and temperature. Right side: Molten HAp particle in plasma spray process with formation of byproducts due to thermal decomposition reactions that occur inflight. Reproduced from (Left side) Heimann, R.B., 2013. Structure, properties and biomedical performance of osteoconductive bioceramic coatings. *Surface and Coatings Technology* 233, 17–38. (Right side) Dyshlovenko, S., 2004. Numerical simulation of hydroxyapatite powder behaviour in plasma jet. *Surface and Coatings Technology* 179, 110–117.

Most calcium phosphates, especially HAp can be synthesized in many ways using precipitation reactions, sol–gel processes, flame synthesis, or by extraction from animal bone based natural sources. The same is true for applicable coating methods. HAp coatings can be fabricated using several PVD techniques, by sol–gel method, electrophoretic deposition and last, but not least by the use of thermal spray processes, namely plasma (APS, VPS) or flame spraying (FS, HVOF, HVSFS), using exclusively fabricated HAp spray powders and engineered suspensions.

Thermal spraying of HAp or TCP always leads to the formation of accompanying species due to molecular fragmentation. The reason for that is that the spray material undergoes phase transitions by melting, partial evaporation, and subsequent quenching process with high cooling rates on the substrate. As these phase transitions do not occur under thermodynamic equilibrium conditions, there is always a certain probability to obtain a mixed phase coating product, including metastable species. On the other side this diversity gives an additional tool to the materials engineering to tailor the bioresorption and biocompatibility. Although the main phase in the coating consists of crystalline HAp, the material partially undergoes a thermal decomposition by spalling off OH[−] and P₂O₅[−] groups (refer to Fig. 8). This leads to the formation of further species like α-TCP, oxyapatite (OA) and oxyhydroxyapatite (OHA) that can be found in the coating. At high temperature levels, possibly the formation of undesired CaO is enabled. The high cooling rates lead to a certain amount of amorphous phase, as can be recognized. For instance in XRD spectra.

Bioglasses

The invention of bioglasses dates back to 1969 when Larry Hench and co-workers published first results about the high compatibility and bioactive behavior of specific types of reactive silicon-based glasses, also containing Na₂O, CaO, P₂O₅ as main constituents. The first commercially available bioglass was called 45S5 Bioglass® and had a unique composition of 45% SiO₂, 24.5% Na₂O, 24.4% CaO, and 6% P₂O₅. Bioglasses are generally highly reactive and bioresorbable. This is also reflected by the high Ca:P ratio. For 45S5, it is in the range of 5. In simulated body fluid and in adequate in vivo environment, their surface transforms to dense Hap surface reaction layers. This beneficial effect is exploited for the transformation of porous bioglass structures to Hap or the stimulation and ingrowth of natural bone and hard tissue in various implant structures.

The production of such glasses is according to standard glass manufacturing routes. A key issue is the high purity of the material that has to be maintained throughout the entire manufacturing route. The manufacturing of medical parts includes sintering of components, tempering, and injection molding by use of glass powder containing feedstocks with subsequent tempering. Thermal spraying of glass powders is possible, especially by using flame spray processes.

Soon after publication of the first type of the 45S5 glass, Hench, D. Day and others were developing further variants of bioglasses, using the basic constituents (SiO₂, Na₂O, CaO, P₂O₅). It can be regarded as a kind of chemical construction kit (Hench, 1991). Fig. 9 illustrates that a tailoring of bioglasses is possible in a wide composition range depicted as A, where the glass composition is able to form a direct bone contact. Other compositions (For instance region S in Fig. 9) favor soft tissue formation at the interface. The basic formulation can be further enhanced by adding further oxides like potassium (K₂O) or magnesium oxides (MgO). Thereby, constituents may act as network former or network modifier. Addition of P₂O₅, for instance acts as a network former and integrates into the Si–O tetrahedral network. Na⁺, K⁺, and Ca²⁺ for instance act as network modifiers. At

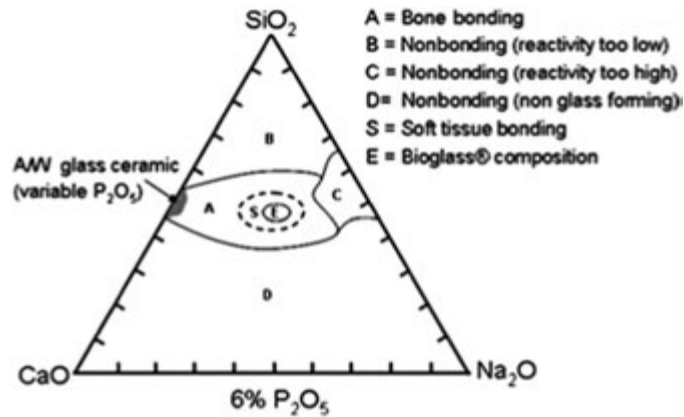


Fig. 9 Three phase diagram showing different regions and describes their typical behavior when in contact with living bone tissue. Image reproduced from Hench, L.L., 1991. Bioceramics: From concept to clinic. *Journal of the American Ceramic Society* 74 (7), 1487–1510.

Table 5 Chemical composition of different bioglasses that are commercially available or that are under investigation. Main constituents are highlighted

Designation	Inventor / Manufacturer	SiO ₂	P ₂ O ₅	CaO	CaF ₂	MgO	K ₂ O	Na ₂ O
45S5 bioglass	L. L. Hench	45	6.0	24.5				24.5
A-W bioglass	Kokubo et al.	34	16.2	44.7	0.5	4.6		
Bio-K	University of Modena, Italy	40	5.3	21.8			33.1	
Bioglass	Colorobbia, Italy	47.3	15.2	26.8	1.5	2.5		4.90

Table 6 Chemical composition of blood plasma (Plasma) and simulated body fluid (SBF) according to the formula of Kokubo. Values are given as ion concentration in mmol/l

	pH	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	HCO ₃ ⁻	HPO ₄ ²⁻	SO ₄ ²⁻
Plasma	7.2 ÷ 7.4	142.0	5.0	1.5	2.5	103.0	27.0	1.0	0.5
SBF	7.2 ÷ 7.4	142.0	5.0	1.5	2.5	147.8	4.2	1.0	0.5

Note: Kokubo, T., 2006. How useful is SBF in predicting in vivo bone bioactivity? *Biomaterials* 27, 2907–2915. Ha, S.-W., 1998. In vitro testing of plasma sprayed hydroxyapatite coatings. *Journal of the American Ceramic Society* 81 (1), 81–88.

present, some dozens of commercially available bioglass types exist and much more are under investigation in research labs. Four well-known examples are shown in [Table 5](#) including the 45S5 type.

The bioactivity of bioglasses is closely linked to their specific dissolution behavior in living tissue. Systematic research of the complex kinetic and chemistry uses so-called simulated body fluid (SBF) tests to observe dissolution and precipitation reactions occurring when a bioglass material is exposed to body like environment, the typical composition is given in [Table 6](#). By immersion of bioglass samples or coated surfaces into the solution and by tracking composition as well as the precipitation reactions that will occur on the glass surface as a function of time (in days or weeks), the reaction behavior of a specific bioglass composition can be characterized. Bioactive behavior involves some typical steps including:

- Fast dissolution of cations out of the glass and replacement by H ions. Thereby the pH value of the solution increases.
- Loss of silica in the glass network and subsequently formation of a silica layer on the surface.
- Migration of cations (Ca²⁺, PO₄³⁻) to the bioglass surface through the silica rich layer forming amorphous CaO/P₂O₅ rich films.
- Crystallization and forming of HAp / HCA layer (HCA: Carbonated hydroxyapatite).

For a more detailed description of the mechanism, please refer to [Hench \(1993\)](#). Despite its excellent bioactive properties, the major disadvantages of bioactive glasses are their low mechanical strength and low fracture toughness. These characteristics restrict their use to a few applications, that is as fillers in dental bone repair. To improve the mechanical performance, bioactive glass-ceramics have been developed.

Glass-Ceramics

Glasses that contain a certain amount of crystalline phase dispersed in their glassy matrix are called glass-ceramics. The kind and amount of crystalline phase and thus the final properties of the glass-ceramic material can be controlled by the initial glass composition as well as by a controlled heat treatment. Some types of glass ceramics are based on calcium alkali orthophosphates $\text{Ca}_2\text{KNa}(\text{PO}_4)_2$ and degrade faster than TCP. The most well-known commercially bioactive glass-ceramics are Ceravital®, Bioverit®, and A/W Cerabone® (for composition refer to Table 7).

Ceravital® is composed of a glassy phase, containing devitrite and apatite crystals. The main application of this glass-ceramic is as substitute of the ossicular chain in the middle ear. In addition to the glassy phase, Bioverit® is composed of apatite and mica crystals, which are responsible for its excellent machinability. Bioverit® implants are mainly used as spinal spacers and in head and neck surgery. The A/W Cerabone® glass-ceramic is composed of an apatite matrix reinforced by needle-like wollastonite crystals, possessing highest fracture toughness values among all of the bioactive glass-ceramics. Among other applications, A/W Cerabone® has been used as iliac crest bone graft with great success. It is also known as A/W glass-ceramic and contains crystalline phases of apatite and β -wollastonite in a glassy matrix. It was originally developed by Kokubo in the late 1980s (Kokubo, 1993).

All three mentioned glass-ceramics are composed of an apatite-like crystalline phase, which is much less soluble than bioglass, for instance 45S5. Although glass-ceramics in general exhibit a better mechanical performance than bioglasses, their bioactivity level is lower than of pure bioglasses but higher than typical crystalline CaP ceramics like HAp. This has been investigated in a famous comparative study by Hench (1991) and results are summarized in a rather popular graphic shown in Fig. 10.

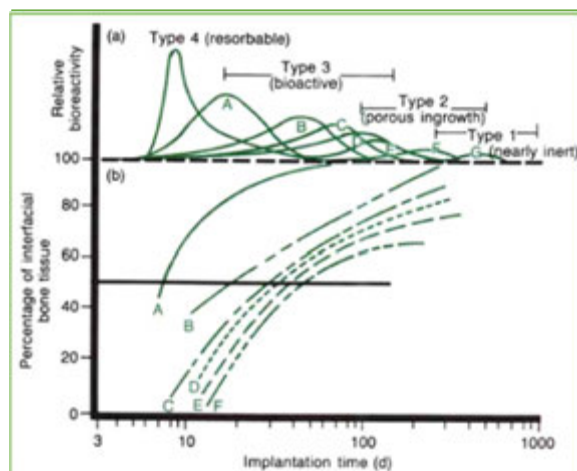
Bioglasses and glass-ceramics can both be sprayed using plasma and flame spray techniques. Although not yet established in clinical practice, both material groups are under intensive investigation as promising candidates for bioactive coatings mainly for bone implants.

Oxides

Spraying oxides using plasma or flame spray methods is a well-established method to manufacture thick and well adherent oxide based coatings on metal substrates for many industrial applications. Oxides to be considered for medical applications are titanium oxide (TiO_2), zirconium oxide (ZrO_2), and aluminum oxide (Al_2O_3). These materials are regarded as bio-inert and support the formation of direct bone tissue contact in dental or bone implants. Recent studies showed a distinct osteoconductivity for TiO_2 coatings. For most medical applications, these oxide materials (Al_2O_3 and ZrO_2) are not used as coatings but as sintered bodies.

Table 7 Chemical compositions of some popular glass-ceramics

Designation	Commercial name	Reference	SiO_2	$\text{Ca}(\text{PO}_3)_2$	CaO	K_2O	MgO	P_2O_5	Na_2O
KSG	Ceravital®	Ohtsuki (1991)	46	16	33				5
A-W glass ceramic	A/W Cerabone®	Rabiee (2019)	34.2	16.2	44.9	0.5	46	16.3	
GB14	GB14	Berger (1995)			30.67	14.32	2.45	43.14	9.42



- (A) 45S5 Bioglass@
- (B) KGS Ceravital
- (C) 55S4.3 Bioglass
- (D) A/W glass-ceramic
- (E) HAp
- (F) KGX Ceravital
- (G) $\text{Al}_2\text{O}_3\text{-Si}_3\text{N}_4$

Fig. 10 Comparison of the bioactive behavior for different biomaterials: Bioglasses (A, C) glass ceramics (B, D, F); HAp (E), ceramic composite (G). Image reproduced from Hench, L.L., 1991. Bioceramics: From concept to clinic. *Journal of the American Ceramic Society* 74 (7), 1487–1510.

This is not the case for titanium oxide, as it exhibits very interesting features when applied as a coating (Liang, 2019). TiO_2 coatings can be created employing many different manufacturing routes like PVD, CVD, sol-gel, anodizing techniques, and plasma or flame spraying techniques. Each method creates unique surface structures and different crystalline phase compositions. TiO_2 exists in two main crystalline phases, anatase and rutile (brookite, a third phase is of minor importance). They often coexist in different ratios and strongly determine the physical and chemical behavior of the coating. For medical applications, this is for instance the wetting behavior against aqueous media. It is well known that TiO_2 as anatase exhibits a strong photocatalytic activity when irradiated using visible light or, with an even stronger effect, using UV-A. This can change wettability of the surface from hydrophobic to hydrophilic when irradiated. For implants, especially for dental roots, the wetting with blood plasma is crucial for accelerated protein adsorption and further promotion of osteoblast cell growth and subsequent osseointegration.

Titanium

Although titanium is a metal, it should be considered in this context, as it is widely used in thermal spray applications on bone implants. Titanium generally is regarded as a bio-inert material showing excellent biocompatibility as it always forms a thin oxide layer on its surface. Titanium with high purity (Grade 2 and Grade 3) or titanium alloys for instance Ti6Al4V are also widely used as load bearing structural bone replacements due to its high cycle fatigue behavior (see Section “Involved Substrates”).

Production of high purity titanium powder, which is used in medical technology is performed in two routes: (1) HDH process and (2) gas atomized (molten bath). HDH stands for hydratio–dehydration, which means that through the addition of hydrogen, the source material becomes brittle and can be crushed mechanically. After this process step, the material is then returned to its original metal state by a thermal process under high vacuum that thermally removes the hydrogen (dehydration).

Spraying of porous titanium is currently performed in a vacuum plasma spray process on bone implant structures namely on hip joint implants (femur side). As Ti powder shows a highly chemical reactivity towards oxygen, resulting in exothermal oxidation reaction the entire spray process is restricted to vacuum processes.

Involved Substrates

Thermal spraying is a flexible and versatile coating technology and can be performed on many types of substrates. Among these are all kind of metals, some polymers, all kind of ceramics (silicate, oxide, or non-oxide based), glasses, even a wood surface can be metal or ceramic coated.

In medical applications, thermal spraying is predominantly used to coat permanent implant structures made from metal, polymer, or ceramic materials, with metal bone implants being the main application at present. A number of R&D activities investigate the possibilities to apply coatings on ceramic and polymer substrates for new implant products. In Table 8, most common substrate materials are summarized together with their predominant applications. For metal implants, there exist three main applications, dental implants, bone joint replacement (hip, knee, shoulder, finger, etc.), and spinal implants. Oxide ceramics like alumina or zirconia based materials are mostly used as composites for instance stabilized zirconia (YSZ) as dental routes or zirconia toughened alumina (ZTA) as joint parts in hip, shoulder and knee. PEEK is a material that has been recently introduced as implant for instance in spinal replacement.

Table 8 Implant materials that are suitable for thermal spray coating process

Material type	Material	Main implant applications	Remarks
Metal	Ti grade 2,3,4	Hip and knee joints; dental implants	For less mechanically loaded implant parts. High corrosion resistance
	Ti6Al4V	Hip and knee joints; dental implants	Used for mechanically highly loaded parts
	CoCrMo alloy	Hip and knee joints; dental implants	Used for mechanically highly loaded parts
	Stainless steel 316 L	Hip and knee joints	Nowadays gradually replaced by CoCrMo and Ti
Oxides	ZTA	Sphere for hip joint Cap for hip joint Knee joint	Needs high precision tooling Mounted in metal case Under development
	YSZ	Dental implant	As an alternative to Ti
Polymers	PEEK	Lumbar cages	Mainly spinal implants
	PDLLA Poly-D, L lactic acid	Resorbable screws, plates and foils	Mainly used in maxillofacial surgery
	PLLA Poly-L lactic acid		

Examples of Commercially Available Applications

Dental roots made from Ti were among the first implants that where plasma spray coated using HAp and titanium oxide (Heimann, 2015) (Straumann, Basel CH). Although many other surface treatments of Ti based dental implants exist nowadays on the market, plasma spraying of HAp and TiO_2 is still one of the chosen methods and under further research (van Oirschot, 2016), including clinical studies on patients (Palarie, 2012). In most cases, only the root section that is in direct contact to bone tissue is surface treated (Fig. 11).

Nowadays hip and knee joint implants are the most common application for plasma spraying. All joint implants in general consist of a joint pair that replaces the natural joint. Hip and knee joints are the ones that have to bear highest mechanical load. A durable fixation is of great importance.

In case of the hip joint, it is the femur rod that is anchored in the open cut femur bone. The counterpart is the acetabular shell that is fixated in the pelvis. To fixate the femur rod, two clinical methods have been established in clinical practise and are used alternatively. The first method fixates the implant by cementing it into the bone. This is performed by using polymethylmethacrylate (PMMA) as a glue between bone and implant. In this case, a coating of the implant is not necessary and would not have any benefit. The second method is based on a mechanical fixation of the implant called press-fit by mechanically pressing it into the laid open femur cavity. In this case, the bone tissue is in close contact with the implant surface and in this case bioactive coatings are applied to improve the ingrowth process by active stimulation of bone tissue growth at the implant surface. This leads to a durable connection between implant and bone within some weeks. Plasma spraying (APS and VPS) is the preferred method used on commercial implants. Porous Ti and/or HAp are applied on Ti alloy and CoCr-based implants. Hip implants exist in a wide variety of geometries and designs that are chosen to meet the specific anatomical and clinical conditions of the individual patient. One example of a set of hip implant parts that are plasma spray coated with HAp is shown in Fig. 12.

Knee joints are also inserted pairwise as femur and tibia sided bearings. The strategy is comparable to hip joint replacements, regarding implant materials (Ti alloys, CoCrMo) as well as coating materials. Bioactive coatings are applied to all bone contacting surfaces of the tibia and femur bearing component respectively (refer to Fig. 13). However, most manufacturers also provide sets for cement fixation. In this case, bioactive coatings are not applied. In this case, open porous surfaces are favored by using for instance sintered metal beads or plasma-sprayed Ti (refer to Fig. 14).



Fig. 11 Calcium phosphate plasma spray-coated dental implants. Image taken from www.nationalelfservice.net/dentistry/restorative-dentistry.



Fig. 12 Set of hip joint implants. Left: HAp plasma spray-coated hip implant (femur side). Right: HAp coated acetabular shell (pelvis side). Images reproduced with permission from: BIO - VAC ESPAÑA S.A. Coatings for surgical implants, Paterna (Valencia), Spain, www.biovac.es.



Fig. 13 Knee joint implants. Left: Complete set of three part prosthesis consisting of two coated bearing parts and polymer patella made from ultra high molecular weight polyethylene (UHMWPE). Right: Plasma-sprayed side of the tibia bearing part. Images reproduced with permission from Marle, Nogent, France. www.marle.fr.

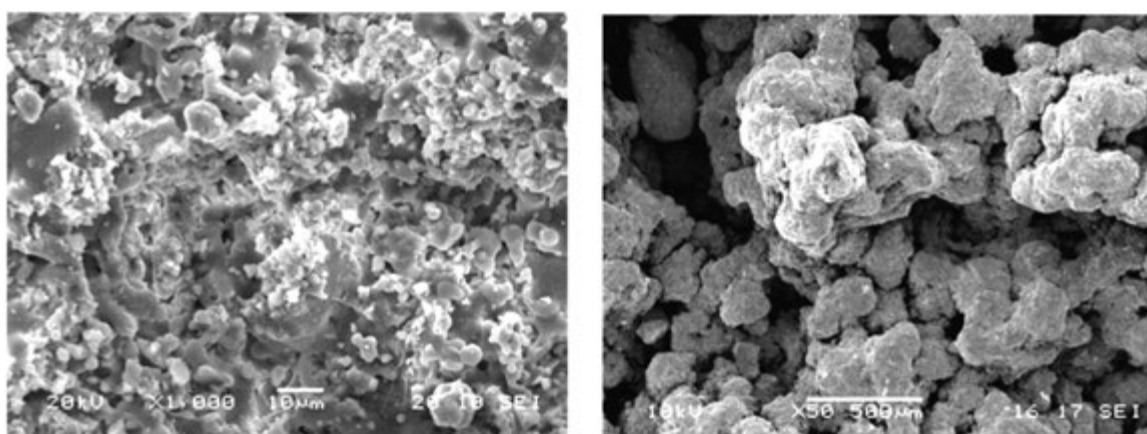


Fig. 14 Typical microstructure of plasma sprayed HAp and Ti coating surfaces in SEM, showing the openporous structure. Left: HAp coating surface (sprayed using APS). Right: Ti coating surface (sprayed using VPS). Images reproduced with permission from EUROCOATING S.p.A., Ciré-Pergine (TN), Italy, www.eurocoating.biz/products-services/coating-solutions/plasma-spray-coatings.

Examples of Research and Development Topics

In the last section, some R&D results that were published in recent years are presented, dealing with thermal spraying for biomedical applications.

TCP Coatings on PDLLA Implants

Bioresorbable polymer implants fabricated from poly (D, L-lactic) acid (PDLLA) are often used in maxillofacial surgery as an alternative to Ti implants. The material is a completely amorphous bioresorbable polymer, degraded within the human body into lactic acid by hydrolysis. Compared to titanium, it shows significantly lower mechanical values (bending strength), but in situations where less mechanical load is expected, it can be a valuable alternative, since it is resorbable and thus eliminates the need for a secondary operation that is needed for implant removal.

Biocompatibility of these implants are nevertheless not completely satisfactory, because it is difficult, to properly adjust degradation behavior of the material. A too fast degradation in vivo can lower the pH value in the surrounding tissue, thus leading to irritations and inflammatory reactions. Therefore new composite devices are demanded. Thermally sprayed tricalcium phosphate (TCP) coatings can significantly increase the biocompatibility of resorbable polymer implants and helps to better match the resorption rate of the implant with the bone-healing rate. The manufacturing process of suitable β -TCP powders to be used in atmospheric plasma spraying (APS) via spray-dry granulation and thermal spray coating on bioresorbable PDLLA implant samples were demonstrated (Baccalaro, 2009). An example of uncoated and plasma-coated plates is shown in Fig. 15.

The TCP coating prevents direct PDLLA/bone-tissue contact thus and acts as a dissolution barrier as it degrades more slowly therefore preventing a too fast degradation of the PDLLA material. The plasma spray coating shows a good adhesion and even

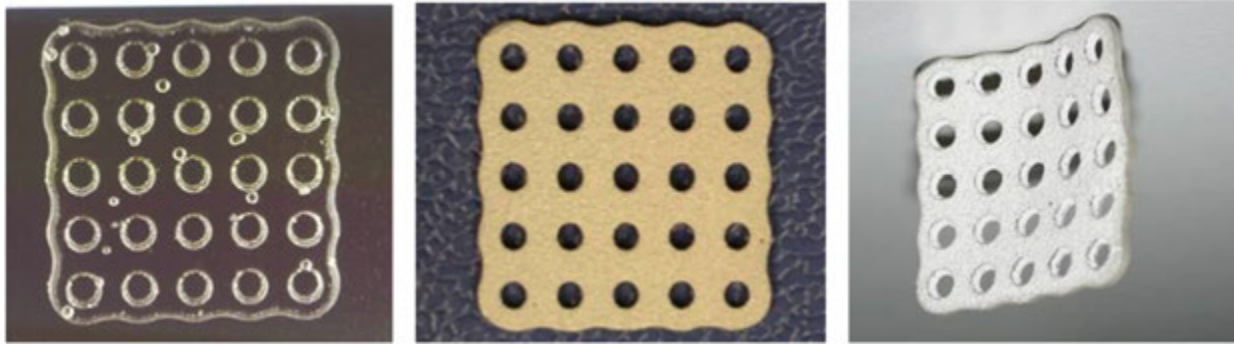


Fig. 15 Left: Uncoated PDLLA plate. Center: TCP plasma-coated PDLLA sample. Right: Demonstration of plastic deformation of coated sample. See text for details. Image source IFKB University of Stuttgart.

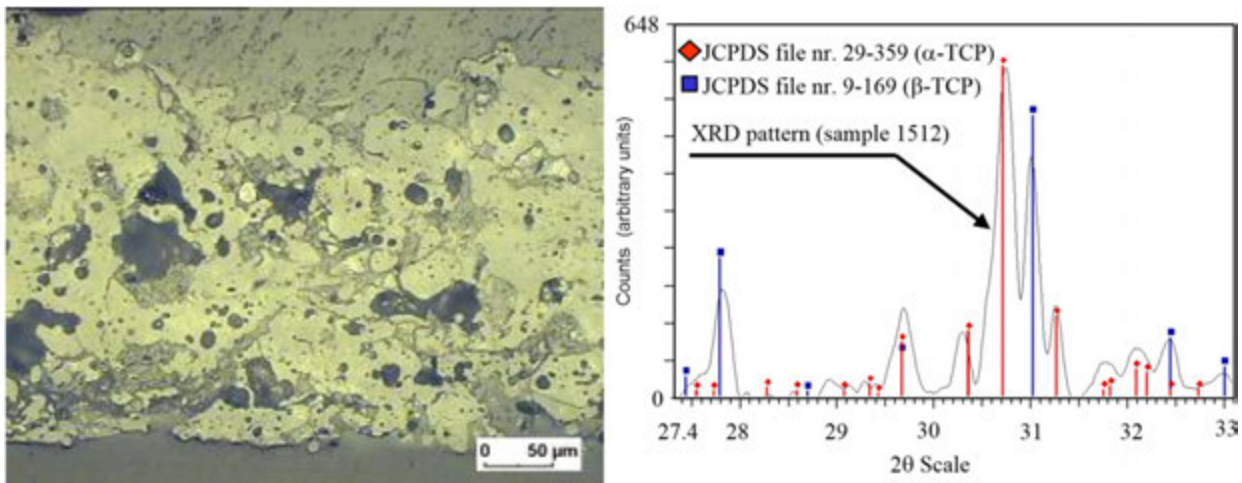


Fig. 16 Left: Light microscope image of plasma sprayed TCP on PDLLA substrate. Right: XRD spectrum of plasma sprayed TCP. See text for details. Image source IFKB University of Stuttgart.

allows for a deformation of the PDLLA implant during surgery. This can be done by the surgeon on-site by mildly warming up the PDLLA material. It becomes soft and can be bended to match geometrical constraints when doing bone reconstruction in maxillofacial surgery. **Fig. 16** (left side) shows a light microscope image of plasma sprayed TCP showing a well-formed connection of the ceramic to the PDLLA polymer interface. The coating porosity level can be adjusted by plasma spray parameters as well as the phase composition that can range from pure α to a α/β mixed phase (refer to **Fig. 16**, right side). Both values affect the resorbability of the TCP material (resorption rate α -TCP > β -TCP).

Ceramic Coatings on Dental Zirconia Implants

Ceramic dental implants have been introduced in recent years as an alternative to Ti implants mainly for two reasons: Increasing esthetic standards especially for teeth implants and increasing incidence of titanium allergies that exist in a percentage of patients and ask for metal free implants.

Among ceramic materials, zirconia has been the choice as it exhibits excellent biocompatibility and tissue integration, low affinity to plaque, and favorable biomechanical properties. Unquestionable is the high esthetic level that is reached by a zirconia ceramic implant, as it resembles the natural teeth material in any optical aspects. However, a drawback came, when early failures were reported to be significantly higher for zirconia implants than for titanium implants. Technical failure as a result of fracture of the material is also a major concern and material development is still going on. Integration of the material into the bone also is an issue as the implant surface is rather smooth and osseointegration is not as fast as in Ti implants. However, a mechanical roughening of the implant surface is critical, as it may affect the material toughness of the ceramic due to implementation of surface defects.

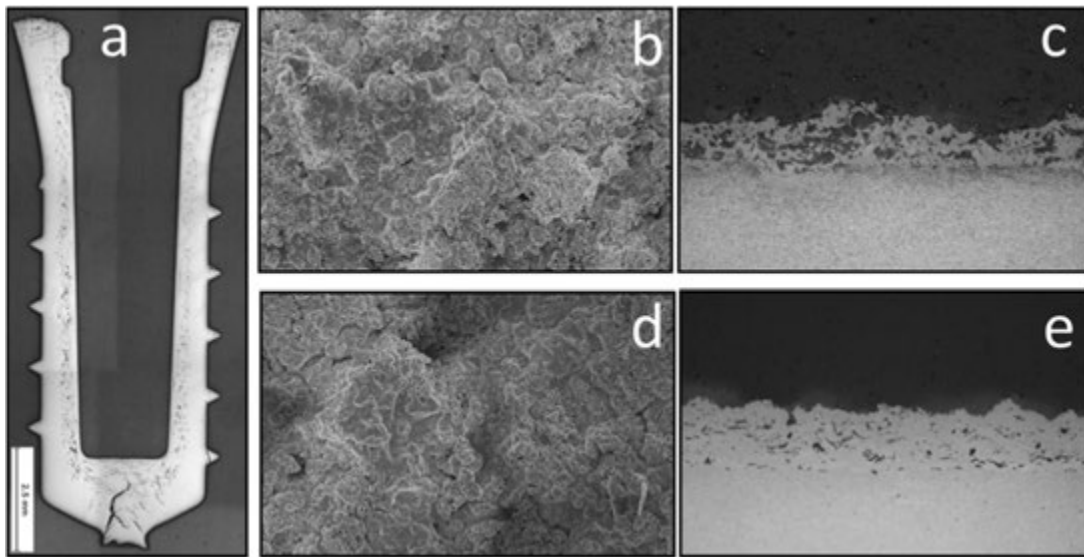


Fig. 17 (a) Cross-section of a zirconia test body for coating tests. (b) and (c) Surface and top section of ZrO_2 plasma spray coating on a zirconia substrate pre-sintered at 1300°C . (d) and (e) Surface and top section of ZrO_2 plasma spray coating after final sintering at 1500°C . See details in text. Image source (a): IFKB University of Stuttgart. (b)–(e) Reproduced from Stiegler, N., 2012. Biokeramische Schichten auf Implantaten durch thermokinetische Beschichtungsverfahren: Thermisches Spritzen von Biomaterialien. In: Gadow, R. (Ed.), *Forschungsberichte des Instituts für Fertigungstechnologie keramischer Bauteile*, Universität Stuttgart. Aachen: Shaker Verlag. (ISBN 3844014799).

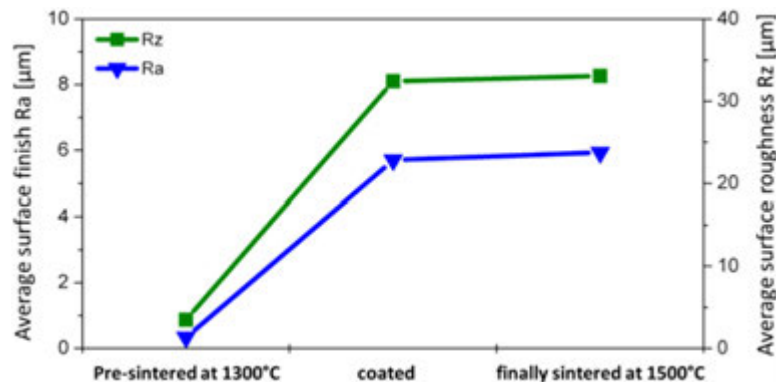


Fig. 18 Comparison of achieved surface roughness values on plasma-spray-coated ceramic samples before coating in pre-sintered state, after coating on pre-sintered body and after final sintering at 1500°C . Data reproduced from Stiegler, N., 2012. Biokeramische Schichten auf Implantaten durch thermokinetische Beschichtungsverfahren: Thermisches Spritzen von Biomaterialien. In: Gadow, R. (Ed.), *Forschungsberichte des Instituts für Fertigungstechnologie keramischer Bauteile*, Universität Stuttgart. Aachen: Shaker Verlag (ISBN 3844014799)

A possible approach to achieve a rough surface without mechanical treatment was done in a study by applying a plasma spray coating directly on a pre-sintered ceramic body (cross-section shown in Fig. 17(a)). As a mechanical activation of the ceramic surface is not allowed, the coating is performed at elevated temperatures to achieve sufficient adhesion. When final sintering the coated ceramic body at 1500°C , a post densification and increased bonding of the plasma sprayed coating can be observed (refer to Fig. 17(c) and (e)). As depicted in Fig. 18, the roughness values could be significantly increased by this procedure. No change of roughness occurred after final sintering of the samples.

However, it should be kept in mind that when sintering oxide ceramics a significant shrinkage occurs, setting the coating under compressive stress. This can be avoided by choosing an appropriate temperature in the pre-sintering process. In this study 1300°C was found to be high enough to avoid delamination. Coated and sintered flat samples were mechanically analyzed in respect of coating adhesion and mechanical failure of the YSZ ceramic. It was found that the coating process did not affect bending strength and that values were comparable to uncoated samples (in the range of 700 MPa). Coating adhesion was measured on flat samples and reached 55 MPa after sintering. As a conclusion, plasma spraying proved as a reliable process to shape ceramic implant surfaces to a desired structure. Meanwhile industry is offering implant parts made from oxide ceramic and PEEK that are directly coated with a porous Ti coating using VPS (Keramik and PEEK, 2019).

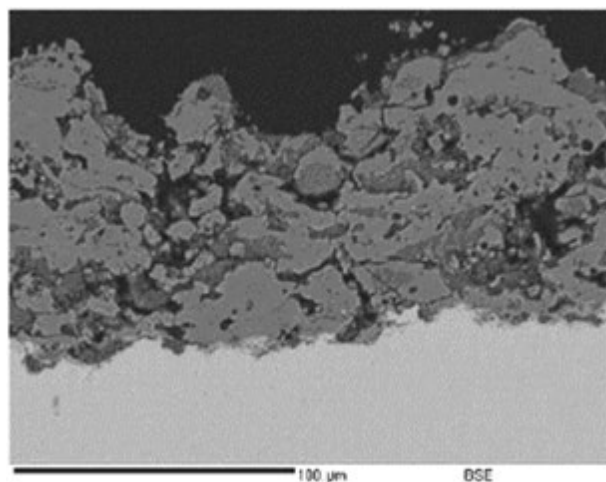


Fig. 19 SEM (BSE) cross-section image of an SPS sprayed HAp coatings showing its typical open porous structure. See text for details. Image reproduced from Łatka, L., 2010. Mechanical properties of suspension plasma sprayed hydroxyapatite coatings submitted to simulated body fluid. *Surface and Coatings Technology* 205 (4), 954–960.

Suspension Spraying of CaP Materials

Since the introduction of suspension-based spraying around the millennium, there was an increasing interest among the research community to develop bioceramics coatings for implant applications. The main goal was to fabricate thin, homogeneous, high quality layers to overcome some of the drawbacks observed in plasma spraying, namely the degradation of HAp and formation of by-products (OHA, OA TCP amorphous CaP, etc.). Suspension spraying also offers new microstructures, namely the formation of nano-structured coatings with a tailored crystallinity. This became possible by direct processing of nano-powders (Jaworski, 2008, 2010). First activities started in the 1990s by plasma spraying of HAp using ICP technology (Bouyer, 1997). Since then, the research activity in this field accelerated, reflected in an enormous publication activity (Killinger, 2011, 2015).

Suspension plasma spraying of CaP materials based on submicron or nanoparticle containing suspensions were intensively studied by Pawlowski *et al.* (Podlesak, 2010; Jaworski, 2008; Łatka, 2010). Morphology of SPS HAp coatings show a typical porous and inhomogeneous structure (refer to Fig. 19) consisting of different areas: (1) unmelted sintered particle form agglomerate zones; (2) molten particles generate splats; and (3) rounded droplets depending on size, impact velocity and temperature. Inhomogeneities are mainly due to different trajectories and thermal histories of droplets within plasma jet when injected radially. A typical coating structure is shown in in vitro testing in SBF (refer to Table 6) shows increased dissolution due to the rather high specific surface area. Selective dissolution of amorphous zones and formation of carbonated hydroxyapatite (HCA) inside pores and defects can be observed.

HVSFS was introduced in 2007 as an alternative coating process for spraying of CaP materials (Gadow, 2010). Like in SPS processing of nano and submicron powders dispersed in suspension is possible. The process is capable to form dense and well adherent coatings of HAp, TCP and bioglass materials. Examples are shown in Fig. 20. The coatings were sprayed using submicron- and nano-scaled feedstocks reaching a film thickness of 20 μm in one spray path. Coating adhesion was in the range of 20 MPa.

In vitro SBF tests showed that higher coating density slows down dissolution tendency compared to SPS coatings. However re-precipitated HAp can be observed but is strongly affected by degree of crystallinity of the coating (Bolelli, 2015). Bioglass coatings also show a higher activity in SBF. In direct comparison to SPS coatings, it can be stated that SPS form silica gel and HAp within the porous coating volume whereas HVSFS coatings form a compact layer of silica gel and HAp layers on top.

In vitro cell tests were performed on HVSFS HAp and 45S5 bioglass coatings using MG63 cells (refer to Bernstein, 2011; Altomare, 2011). Fig. 21 shows SEM images of MG63 cells adhered to the bioglass coating surface after 3 and 7 days for comparison. It was found that no toxic products were released by the coating. Human osteosarcoma cells could well adhere and proliferate onto the surface of 45S5 bioglass. The formulation thus maintains its biofunctionality, when sprayed via HVSFS.

HVSFS Spraying of Metal Doped CaP Materials

An interesting approach is the creation of antibacterially active coatings on implants. This can be acquired for instance by implementation of antibacterial agents like metals into a coating. Release of the agent is then either promoted by bio-erosion of the coating or due to a high surface area if the coating is porous. Some metal ion (Ag) doped HAp spray powders are already available on the market (Medicoat AG, 2019). Another approach is using suspension spraying where metal ions in

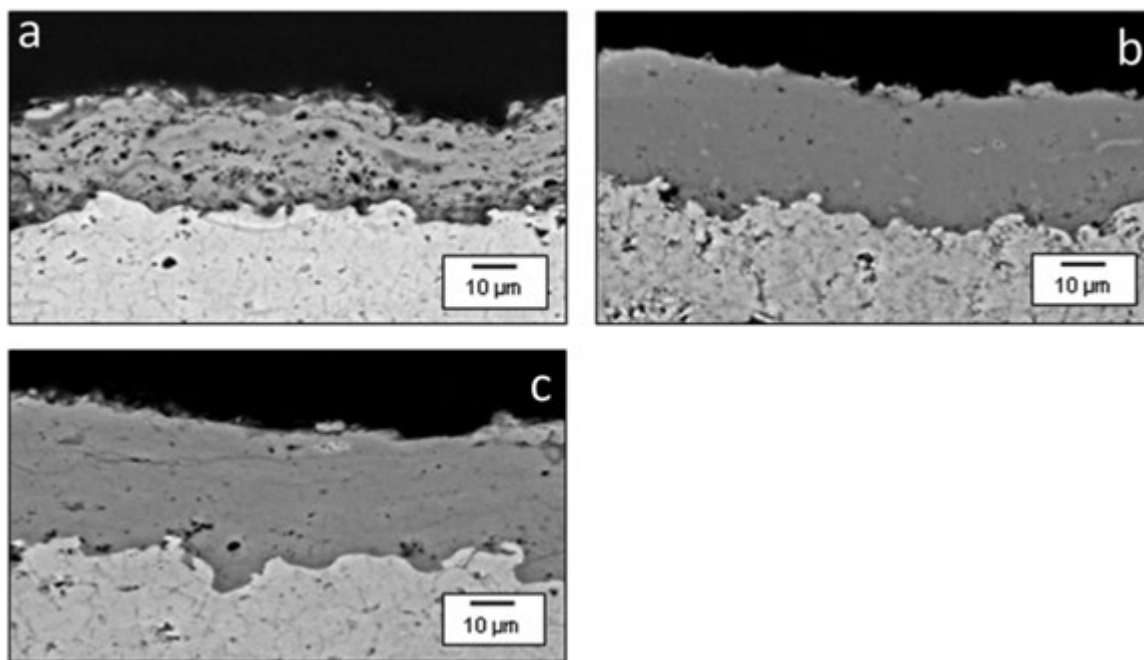


Fig. 20 SEM images of HVSFS sprayed CaP coatings using HVSFS. (a) Bio-K coating, (b) HAp coating, (c) TCP coating. Images reproduced from Bellucci, D., 2011. Optimisation of high velocity suspension flame sprayed (HVSFS) bioactive coatings on Ti substrates by DoE approach. In: Marple, B.R., Agarwal, A., Hyland, M.M., *et al.* (Eds.), *Proceedings of the International Thermal Spray Conference*. New York: Springer-Verlag. (ISBN 978-1-4614-4367-4).

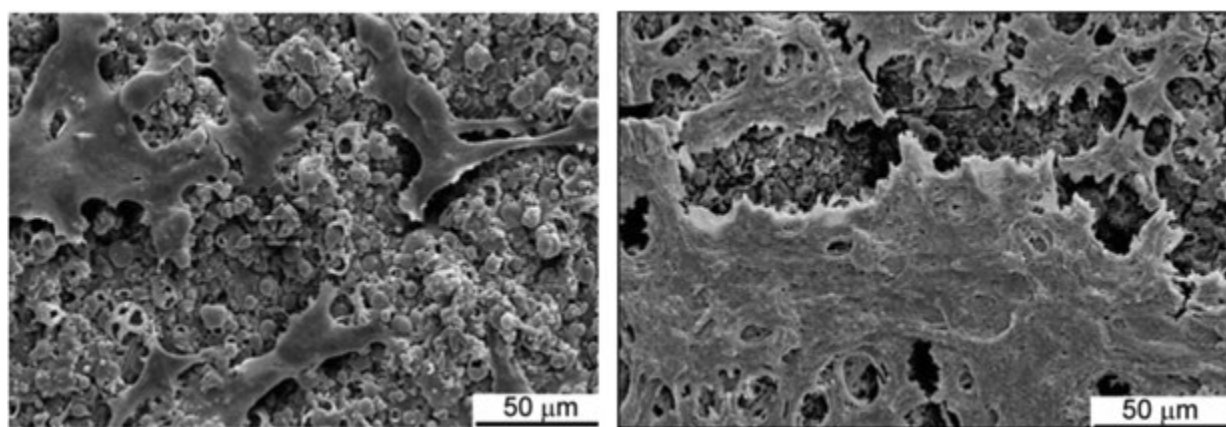


Fig. 21 SEM image of HVSFS sprayed 45S5 bioglass coatings covered with living MG63 cells after 3 days (Left) and 7 days (Right). Images reproduced from Altomare, L., 2011. Microstructure and in-vitro behaviour of 45S5 bioglass coatings deposited by high velocity suspension flame spraying (HVSFS). *Journal of Materials Science: Materials in Medicine* 22 (5), 1303–1319.

form of ultrafine powders or as a salt can be directly mixed with CaP based powders in the liquid feedstock. This is described in Krieg (2017). Suspensions containing HAp, TCP, bioglass, and GB14 were prepared and doped using Cu, Bi, and Ag. Coatings were fabricated using HVSFS and analyzed regarding their metal ion distribution in the coating. It could be shown that a distribution of nano crystals in the CaP matrix is possible (refer to Fig. 22). In vitro cell tests confirm the biocompatibility of the coatings.

In vivo investigations were recently performed by the G.E.R.N. at the Universitätsklinik in Freiburg, Germany. Titanium rods were HVSFS coated and implanted into the femur condyle of rabbits. As an example, Fig. 23 shows the histologic section of HVSFS coated Ti-rod implant after 24 weeks implantation period near the coating interface region. TCP doped with Cu was applied as a coating material. Similar results were achieved using HAp, GB14, and bioglass as a coating material. The image clearly shows a tight connection of the bone tissue to the coating surface and proves the good biocompatibility of the coatings. However, further investigations are necessary to interpret the histological results.

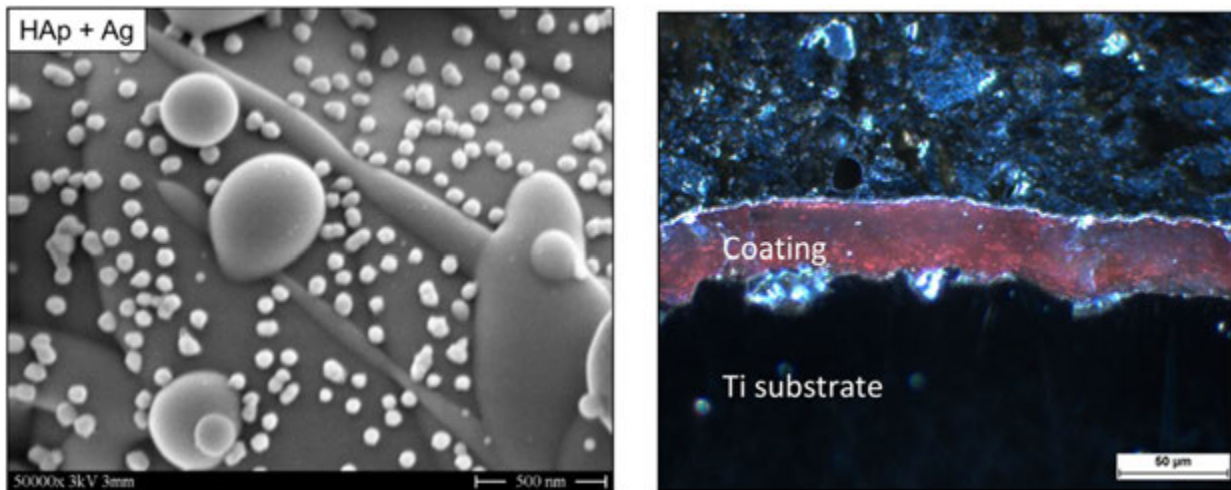


Fig. 22 Left: SEM image of a surface of metal (Ag) doped HAp coating. Nano crystallites of metal are visible within the HAp spray coated matrix. Right: Light microscope cross-section image of HVSFS sprayed HAp coating doped with Cu. Image source IFKB, University of Stuttgart.



Fig. 23 Histologic section of HVSFS coated Ti-rod implant in femur condyle of rabbit animal. Image shows the interface region with bone tissue, HVSFS coating (TCP + Cu dopant), Ti metal implant after 24 weeks. Images reproduced with permission from Dr. Anke Bernstein G.E.R.N. Freiburg, Germany, 2019.

Conclusion and Summary

Functionalization of bone implant surfaces is the major subject of thermally sprayed CaP and Ti based coating materials. A fast ingrowth and a good and long lasting bone–tissue connection are the major goals of this strategy. Bioresorbable coatings can even more stimulate bone ingrowth and tissue formation directly occurring on the implant surface. It is unquestioned that TS coatings have been impressively successful in fulfilling these goals for many decades.

However, there are still remaining issues related to load bearing implants mainly in hip joint replacement. One of the major problems is the loosening of load bearing implants due to a bone remodeling. This is provoked by the altered stress distribution caused by stress shielding of the metal implant. Although the process may take many years, it eventually leads to a progressive depletion of bone tissue and finally to the loosening of the implant. So the problem is not addressed to the interface or the coating itself, but to the mechanical properties of the implant, that causes the stress shielding. To solve the problem, new implant materials have to be found that resemble the mechanical properties of the bone in terms of mechanical stiffness (Young modulus), fatigue strength and density. An interesting approach was done in the late 1990s, when fiber reinforced PEEK materials were under evaluation as an alternative to metal materials for hip implants (Ha, 1997). The material shows distinct advantages compared to metal implants. It behaves artifact-free in radiographic imaging, the lower modulus of elasticity better matches that of bone and fatigue strength is greater than most metal implants. Although the material showed promising results in mechanical testing, a problem remained that could not fully satisfactory solved so far: The proper design of the PEEK surface to ensure the same quality of ingrowth behavior like seen from metal implants. Although used nowadays in several applications like internal and external fixation structures (Scholz, 2011), it has not yet replaced load bearing metal materials in hip implant applications. New concepts for an improved implant–bone interface are necessary and need to be developed.

Functionalization of implant surfaces by adding active agents (antibiotics, growth factors, etc.) that are released post-operative into the surrounding tissue is another concept that is under intense research. One example for this concept, that uses thermally sprayed coatings has been presented in the last section (metal-doped coatings).

Direct fixation of ceramic implants by thermal spray application of bio-inert or bioactive coatings on zirconia or alumina-based implants in knee and hip joints is another field under current development. By a direct anchoring of the ceramic implant to the human bone (for instance pelvis, femur, etc.), metal connecting pieces are becoming fully redundant.

More applications of thermally sprayed coatings are useful in general tissue engineering and flexible scaffolds. Thermally sprayed oxide and bioceramic coatings on various flat and even flexible substrates have shown their promising potential for cell growth in tissue engineering not only with respect to prosthetic devices and a focus on osteoblast and stem cells growth but also for liver cells, skin and cartilage. These in vivo or in vitro cell growth concepts are a further issue of interdisciplinary scientific cooperation with ceramists.

References

- Altomare, L., 2011. Microstructure and in-vitro behaviour of 45S5 bioglass coatings deposited by high velocity suspension flame spraying (HVSFS). *Journal of Materials Science: Materials in Medicine* 22 (5), 1303–1319.
- Baccalaro, M., 2009. Manufacturing of thermally sprayed tricalcium phosphate (TCP) coatings for biomedical applications. In: Mizuno, M. (Ed.), *Advances in Bioceramics and Biocomposites: A Collection of Papers Presented at the 29th International Conference on Advanced Ceramics and Composites*, Jan 23–28, 2005, Cocoa Beach, FL. John Wiley & Sons, pp. 11–16.
- Berger, G., 1995. *Bioceramics*. vol. 8. Oxford: Pergamon, pp. 453–456.
- Bernstein, A., 2011. Investigations on vitro behaviour of ceramic coatings deposited by high velocity suspension flame spraying. *Key Engineering Materials* 493–494, 530–534.
- Bolelli, G., 2015. Comparison between suspension plasma sprayed and high velocity suspension flame sprayed bioactive coatings. *Surface and Coatings Technology* 280, 232–249.
- Bouyer, E., 1997. Suspension plasma spraying of hydroxyapatite. *JOM* 49 (2), 58–62.
- Eliaz, N., 2017. Calcium phosphate bioceramics: A review of their history, structure, properties, coating technologies and biomedical applications. *Materials* 10 (4), doi:10.3390/ma10040334. www.mdpi.com/journal/materials.
- Gadow, R., 2010. Hydroxyapatite coatings for biomedical applications deposited by different thermal spray techniques. *Surface and Coatings Technology* 205 (4), 1157–1164.
- Ha, S.-W., 1997. Topo-graphical characterization and microstructural interface analysis of vacuum-plasma-sprayed titanium and hydroxyapatite coatings on carbon fibre-reinforced poly (etheretherketone). *Journal of Materials Science: Materials in Medicine* 8 (12), 891–896.
- Heimann, R., 2016. Plasma-sprayed hydroxylapatite-based coatings: Chemical, mechanical, microstructural, and biomedical properties. *Journal of Thermal Spray Technology* vol. 25 (5), 827–850.
- Heimann, R.B., 2015. *Bioceramics – A historical perspective*. In *Bioceramic Coatings for Medical Implants: Trends and Techniques*. Weinheim: Wiley VCH, pp. 1–10. (ISBN: 978-3-527-33743-9).
- Hench, L.L., 1991. *Bioceramics: From concept to clinic*. *Journal of the American Ceramic Society* 74 (7), 1487–1510.
- Hench, L.L., 1993. Bioactive glasses. In: Hench, L.L., Wilson, L. (Eds.), *An Introduction to Bioceramics: Advanced Series in Ceramics 1*. World Scientific, pp. 41–62.
- Jaworski, R., 2008. Synthesis and preliminary tests of suspension plasma spraying of fine hydroxyapatite powder. *Journal of Thermal Spray Technology* 17 (5–6), 579–584.
- Jaworski, R., 2010. Recent developments in suspension plasma sprayed titanium oxide and hydroxyapatite coatings. *Journal of Thermal Spray Technology* 19 (1–2), 240–247.
- Medicoat AG, 2019. Antibakterielles Hydroxylapatit Pulver. Mägenwil: Medicoat AG, Available at: <http://www.medicoat.ch/spritzpulver/antibakterielles-hydroxylapatit-pulver/>.
- Juhász, J.A., 2012. Bioactive ceramics: Processing, structures and properties. *Journal of Materials Science* 47 (2), 610–624.
- Killinger, A., 2011. Review on new developments in suspension and solution precursor thermal spray processes. *Journal of Thermal Spray Technology* 20, 677–695. doi:10.1007/s11666-011-9639-8.
- Killinger, A., 2015. Status and future trends in suspension spray techniques. In: Espallargas, N. (Ed.), *Future Development of Thermal Spray Coatings: Types, Designs, Manufacture and Applications*. Woodhead Publishing and Elsevier, pp. 81–122. (ISBN: 9780857097699).
- Keramik & PEEK, 2019. Feste Verankerung durch poröse Titan-Plasma-Beschichtungen auf Metall. Image Brochure F-TPS-290513. Rostock: DOT GmbH, Available at: <http://www.dot-coating.de/beschichtungen/ortho/tps-beschichtungen>.
- Kokubo, T., 1993. A/W glass-ceramic: Processing and properties. In: Hench, L.L., Wilson, J. (Eds.), *An Introduction to Bioceramics*. World Scientific, pp. 75–88.
- Krieg, P., 2017. High velocity suspension flame spraying (HVSFS) of metal doped bioceramic coatings. *Bioactive Materials* 2, 162–169.
- Łatka, L., 2010. Mechanical properties of suspension plasma sprayed hydroxyapatite coatings submitted to simulated body fluid. *Surface and Coatings Technology* 205 (4), 954–960.
- Liang, L., 2019. Osteoblast response to different UVA-activated anatase implant coatings. *Advanced Materials Interfaces* 6, 1–13. 1801720. doi:10.1002/admi.201801720.
- Ohtsuki, C., 1991. Apatite formation on the surface of ceravital-type glass-ceramic in the body. *Journal of Biomedical Materials Research* 11, 1363–1370.
- Oldani, C., 2012. Titanium as a biomaterial for implants. In: Fokter, S.K. (Ed.), *Recent Advances in Arthroplasty*. IntechOpen. doi:10.5772/1445.
- Palarie, V., 2012. Early outcome of an implant system with a resorbable adhesive calcium-phosphate coating – A prospective clinical study in partially dentate patients. *Clinical Oral Investigations* 16 (4), 1039–1048.
- Podlesak, H., 2010. Advanced microstructural study of suspension plasma sprayed hydroxyapatite coatings. *Journal of Thermal Spray Technology* 19 (3), 657–664.
- Rabiee, M., 2019. *Introduction to Nanomaterials in Medicine*. Morgan & Claypool Publishers.
- Robotti, P., 2012. Chapter 9 – Thermal plasma spray deposition of titanium and hydroxyapatite on polyaryletheretherketone implants. In: Kurtz, S.M. (Ed.), *Plastics Design Library, PEEK Biomaterials Handbook*. William Andrew Publishing, pp. 119–143. (ISBN 9781437744637).
- Scholz, M.-S., 2011. The use of composite materials in modern orthopaedic medicine and prosthetic devices: A review. *Composites Science and Technology* 71, 1791–1803.
- Stiegler, N., 2012a. High-velocity suspension flame sprayed (HVSFS) hydroxyapatite coatings for biomedical applications. *Journal of Thermal Spray Technology* 21 (2), 275–287.
- van Noort, R., 1987. Ti: The Implant Material of Today. *Journal of Materials Science* 22 (11), 3801–3811.
- van Oirschot, B.A., 2016. A systematic review on the long-term success of calcium phosphate plasma-spray-coated dental implants. *Odontology* 104 (3), 347–356. doi:10.1007/s10266-015-0230-5.

Design of Tissue Engineering Scaffold by Means of Mathematical Modeling

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Introduction

In a nutshell, tissue engineering aims at equipping biological tissues with a suitable substrate for tissue regeneration. Thereby, the need for regeneration may have to do with the preceding removal of malfunctioning or pathological tissue. Although tissue engineering is relevant to more or less all biological tissues, this chapter focuses on bone tissue. In bone tissue engineering, a scaffold structure is typically implanted into the patient, taking over the function of removed bone tissue. There, it fulfills two main functions. On the one hand, it is supposed to act as replacement material, taking thus over the load-bearing role of bone tissue. On the other hand, it may also provide the substrate on which new bone tissue can grow. In a best-case scenario, growth of new bone tissue is accompanied by the gradual dissolution of the synthetic tissue engineering scaffold. Hence, in the long-run, the affected tissue becomes again a completely natural material. The related technologies and methods have been developed and honed over several decades, with a number of textbooks and review papers documenting the time course and the evolution of the respective state of the art ([Hutmacher, 2000](#); [Hollister, 2005](#); [Rezwan et al., 2006](#); [Lanza et al., 2007](#); [Williams, 2008](#); [O'Brien, 2011](#); [Geris, 2013](#)).

Adequate integration into the targeted physiological environment requires bone tissue engineering scaffolds to fulfill several requirements. The most important, commonly known ones are biocompatibility, osteoconductivity, biodegradability, and mechanical competence. In particular, the term biocompatibility describes that scaffold materials must not cause any harm to the targeted physiological environment. In other words, it is paramount to not use materials which cause, e.g., inflammations or other adverse reactions. Furthermore, scaffolds should stimulate the regeneration of bone tissue. For that purpose, they must be suitable for hosting bone growth-promoting cells and growth factors, and they must be sufficiently porous, in order to provide enough physical space for substantial ingrowth of bone tissue. If a scaffold material features these characteristics, it is referred to as osteoconductive. The aforementioned desired behavior of dissolving upon substantial ingrowth of new bone tissue is known as biodegradability. Once sufficient amounts of new bone tissue have been formed, degradation and eventual disappearance of the scaffold structure is desirable, as it has then fulfilled the purpose of providing temporary support and is no longer needed. Clearly, the involved degradation processes must not occur too fast, as then the required load-bearing capacity would not be provided anymore. This leads to the last of the above-listed requirements, namely mechanical competence. Bone is often concerned with load-bearing tasks, which is why bone tissue engineering scaffolds must exhibit suitable mechanical properties.

While the first three requirements – biocompatibility, osteoconductivity, and biodegradability – are mainly a matter of choosing appropriate materials, mechanical competence is clearly a topic which can benefit from predictive engineering methods. The scaffold material has to sustain the mechanical loading to which it is subjected, thus it must not be too soft. However, the biochemical processes related to bone regeneration are partly governed by the deformation characteristics of the scaffold ([Simmons et al., 2001](#); [Robling et al., 2006](#); [Jacobs et al., 2010](#)). This implies that for optimal integration of the scaffold into its bony vicinity, it must not be too stiff either, otherwise the biochemical processes involved cannot be initiated or maintained through the prevalent mechanobiological couplings. In the long run, the consequence would be potentially adverse, and phenomena such as stress shielding could occur, which may lead to bone degeneration in the proximity of the implant ([Engh et al., 1987](#)). For that reason, designing scaffold materials and structures with the just right stiffness (that is, not too soft and not too stiff), which is the mechanical property determining the elastic deformation behavior, is a delicate task. In this respect, nowadays much stressed terms come into play, namely patient-specific design or precision medicine, meaning that a scaffold is implanted which fits as well as possible to the biological and mechanical environment which can be found precisely in a specific patient.

Standardly, experimental methods are employed in order to scrutinize new scaffold materials and structures regarding their suitability as to replace a respective piece of bone. While biocompatibility, osteoconductivity, and biodegradability can be tested reasonably well by means of experimental methods, it is extremely challenging to study the mechanical properties of bone tissue engineering materials and structures, in particular when taking into consideration that these properties actually evolve over time. For those reasons, following a more comprehensive approach has been suggested as remedy ([Geris, 2013](#)). In particular, utilizing the predictive capabilities of computational modeling, while also integrating data provided by experimental research and clinical studies, promises to provide a predictive assessment of materials and structures in terms of their performance when applied as bone replacement material. This chapter presents a brief overview of the current state of the art in this field.

A Survey on Mathematical Models Used in Bone Tissue Engineering

The conventional state of the art in the field largely comprises some kind of high-resolution imaging modality by means of which the input for large-scale numerical studies is produced. In particular, the most popular imaging method is clearly computed tomography (CT) or micro-computed tomography (micro-CT), which yields information concerning the three-dimensional distribution of

attenuation coefficients, in terms of attenuation coefficient-proportional gray values. By employing suitable thresholding, the sought-after geometry of the scaffold structure can be deduced (Rüeggsegger *et al.*, 1996).

The mechanical behavior of tissue engineering structures is typically described by a set of partial differential equations. In order to solve such systems of coupled equations, numerical methods are usually employed. A number of different modeling techniques is available for discretizing the shape of the modeled domain and for solving the resulting equations, including the classical Finite Element (FE) method, boundary element methods, meshless methods, isogeometric methods, and more. The most widespread method is undoubtedly the FE method, which is probably due to the fact that commercial FE software is widely available and easy to use. The complexity of the numerical models and the computational costs arising for the simulations depends on the morphology of the studied scaffold. If the latter exhibits some sort of periodicity, so-called unit cell models can be easily created, see e.g. (Adachi *et al.*, 2006; Huttmacher and Singh, 2008; Lacroix *et al.*, 2009; Olivares *et al.*, 2009; Melchels *et al.*, 2010; Sturm *et al.*, 2010; Dias *et al.*, 2012; Truscetto *et al.*, 2012), and Fig. 1(A) for an exemplary model. For irregular microstructures, the aforementioned micro-CT data is often the basis for generation of a corresponding FE model, see e.g. (Jaecques *et al.*, 2004; Porter *et al.*, 2005; Williams *et al.*, 2005; Lacroix *et al.*, 2006; Sandino *et al.*, 2008; Lacroix *et al.*, 2009; Milan *et al.*, 2009; Voronov *et al.*, 2010; Sandino and Lacroix, 2011), and Fig. 1(C). However, the related computation time is substantial, causing severe restrictions as to the applicability of such modeling strategies in clinical environments. As a remedy, so-called numerical multi-scale models have been suggested, where the FE models are comparably coarse, and information from lower observation scales is integrated in homogenized fashion. This strategy is particularly useful if certain domains within the numerical model are subjected to a dynamic evolution, as it is the case if bone tissue is formed in the pore spaces of a scaffold structure (Sanz-Herrera *et al.*, 2008, 2009a,b), see e.g. Fig. 1(B).

From a conceptual point of view, large-scale numerical modeling can be applied to study a wide range of different aspects relevant in bone tissue engineering, including the assessment of local effects occurring in response to physiological mechanical loading, the simulation of the pore fluid movement, see e.g., Fig. 1(D), or the bone regeneration performance over time. The significance of these simulations is directly related to the reliability of the input parameters fed into the numerical model. This concerns in particular the mechanical properties. The simplest approach in this respect is to assume homogeneous material properties, thereby neglecting any material heterogeneities. Clearly, this approach is based on a quite strong simplification, and potentially entails inadequate simulation results, as demonstrated in (Dejaco *et al.*, 2012). Furthermore, simplified empirical laws can be used for relating the distribution of gray values resulting from CT scanning to a corresponding distribution of material properties. Unarguably, this approach may work well for a certain material, whereas it may be completely wrong for another material.

This chapter is however not focusing on the standard methods mentioned above – respective review articles and textbooks can be found straightforwardly in the open literature. Instead, the remainder of the chapter presents a selection of alternative and complementing approaches, which could further improve the applicability of mathematical models in clinical practice.

Homogenization of Mechanical Properties Based on Continuum Micromechanics

As described briefly further below, continuum micromechanics is a theoretical concept particularly well suited for bone tissue and also bone replacement materials. Within the framework of continuum micromechanics, a material is considered to be macro-homogeneous, but micro-heterogeneous. If the characteristic length of such micro-heterogeneities, termed d , is significantly smaller than the characteristic length of a volume element containing them, termed l_{RVE} , this volume element is referred to as *representative volume element* (RVE). Thereby, “significantly smaller” is not precisely defined, but it has been shown that l_{RVE} must be at least 2–3 times larger than d (Drugan and Willis, 1996). Furthermore, l_{RVE} must be significantly smaller than the characteristic lengths of the geometry making up the structure composed of the material defined by the RVE, termed L , and of the loading acting onto this structure, termed P . Practically, this requirement is satisfyingly fulfilled if L and P are at least 5–10 times larger than l_{RVE} (Kohlhauser and Hellmich, 2013). Typically, the microstructure of the material contained in an RVE is way too complex for describing it in detail. Instead, so-called material phases, which are assumingly homogeneous (in an approximative sense), are introduced. The material phases are chosen such that they exhibit known physical properties, such as volume fractions or mechanical properties, and a variety of different phase morphologies can be established, thereby allowing for considering different phase shapes, or interactions between the considered material phases.

If separation of scales is fulfilled, as described above, continuum micromechanics provides mathematical tools for scaling mechanical properties known on the scale of individual material phases up to scale of the macroscopic material, based on combining Eshelby's matrix-inclusion problem (Eshelby, 1957) with stress and strain volume averaging laws. In this chapter, all mathematical details related to deriving the related homogenization schemes are omitted, and the interested reader is referred to pertinent literature (Hill, 1963, 1965a,b; Suquet, 1997; Zaoui, 2002; Dormieux, 2005).

The very basis for using continuum micromechanics models in the field of bone tissue engineering was laid by developing respective models for bone tissue. First attempts focused on homogenizing bone stiffness (Hellmich and Ulm, 2002; Fritsch and Hellmich, 2007; Vass *et al.*, 2018), based on which subsequently strength homogenization approaches were developed (Fritsch *et al.*, 2009; Morin *et al.*, 2017). Based on very similar modeling considerations, micromechanics models were developed for bone tissue engineering materials, comprising hydroxyapatite-based biomaterials in general (Fritsch *et al.*, 2010) or very specific, hydroxyapatite-based granules applied in dental engineering (Scheiner *et al.*, 2016a,b). Furthermore, it could be demonstrated how biomaterials can be modeled in a poromicromechanical framework, thereby allowing to study the influence of the respectively chosen poromechanical configuration on the macroscopic strength estimates (Fritsch *et al.*, 2013).

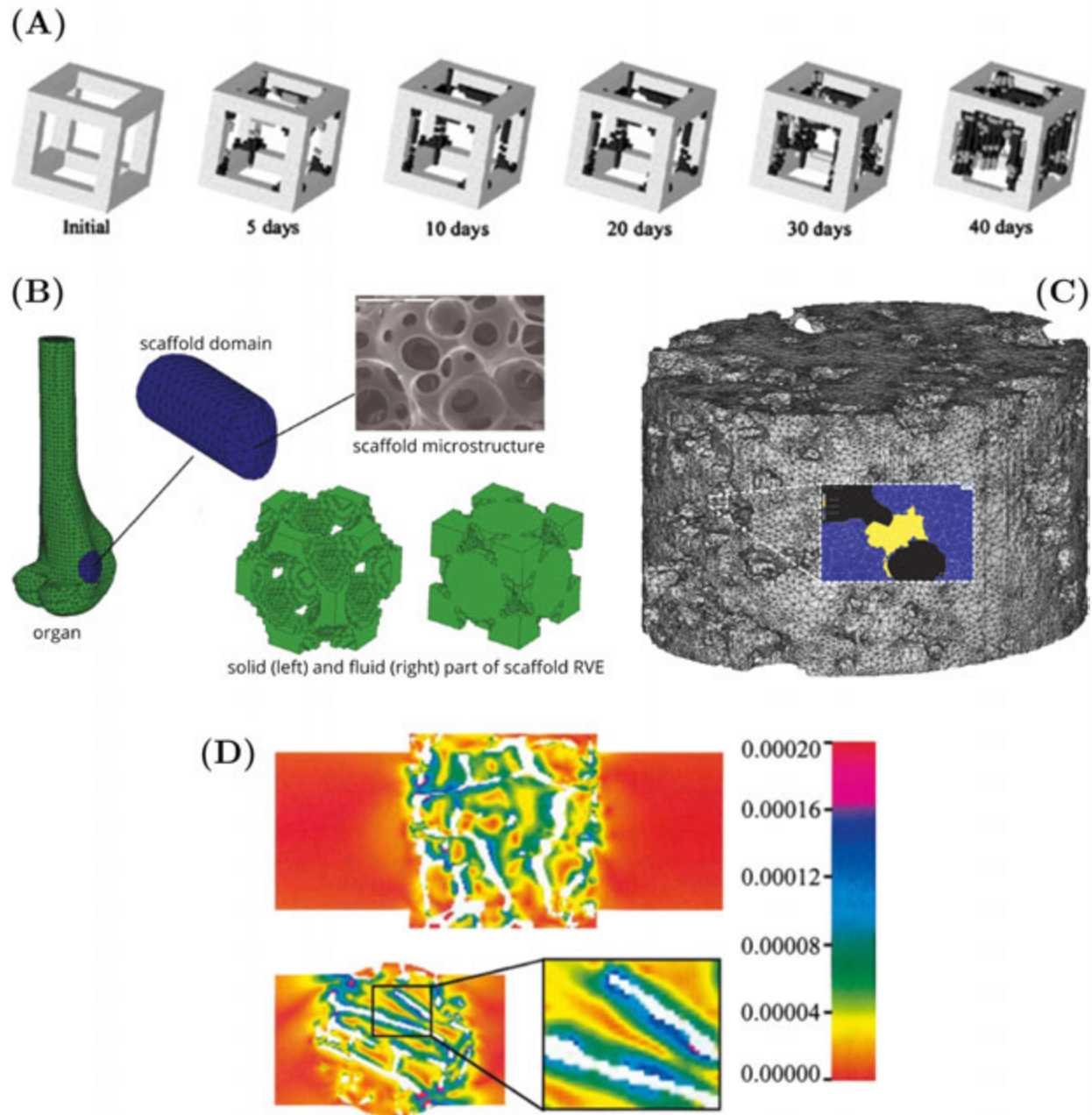


Fig. 1 Results of numerical simulations set up for assessing the performances of bone replacement materials; (A) Development of bone regeneration over 40 days, based on a unit cell model, (B) Numerical multi-scale model including a scaffold implanted in a rabbit distal femur, (C) 3D micro-FE model of a calcium phosphate-based tissue engineering material, with the magnified region showing the distribution of tensile and compressive stresses due to uniaxial compression, and (D) the shear stresses caused by fluid flow in the pores of a scaffold sample, during a perfusion test. Reprinted from (A) Adachi, T., Osako, Y., Tanaka, M., Hojo, M., Hollister, S.J., 2006. Framework for optimal design of porous scaffold microstructure by computational simulation of bone regeneration. *Biomaterials* 27 (21), 3964–3972. (B) Sanz-Herrera, J.A., García-Aznar, J.M., Doblaré, M.M., 2008. Micro-macro numerical modelling of bone regeneration in tissue engineering. *Computer Methods in Applied Mechanics and Engineering* 197 (33–40), 3092–3107. (C) Lacroix, D., Chateau, A., Ginebra, M.P., Planell, J.A., 2006. Micro-finite element models of bone tissue-engineering scaffolds. *Biomaterials* 27 (30), 5326–5334. (D) Porter, B., Zauel, R., Stockman, H., Guldberg, R., Fyhrie, D., 2005. 3-D computational modeling of media flow through scaffolds in a perfusion bioreactor. *Journal of Biomechanics* 38 (3), 543–549.

Clearly, this method can be applied and adapted to any hierarchically organized material fulfilling the separation-of-scales-requirement. This is particularly true for *hard* materials, for which the existing theoretical concepts, see also the references above, can be straightforwardly considered. For *soft* tissues, the equations describing the constitutive behavior of the materials must be reasonably extended and adapted, owing to the potentially arising large deformations which are not encountered in hard tissues.

Bone Tissue Systems Biology Approaches

Keeping in mind that bone replacement materials serve the purpose of allowing for or stimulating bone regeneration in the vicinity of the respective tissue engineering scaffold, it would be a desirable goal to actually predict how well a specific material or a specific structure would perform before inserting it into the patient's body. To that end, understanding the process of bone regeneration is key.

Bone regeneration is a complicated biological process (Petite *et al.*, 2000; Lieberman and Friedlaender, 2005). Essentially, the growth of new bone tissue in the pore spaces of bone tissue engineering scaffolds comprises numerous biochemically and mechanically stimulated mechanisms. First, they cause addition of bone tissue by mononuclear cells called osteoblasts, deriving from mesenchymal stem cells. In more detail, osteoblasts lay down osteoid to fill this cavity, a substance consisting mainly of collagen type I. Over time, osteoid gets mineralized, with the bone mineral mainly consisting of carbonated hydroxyapatite. Since the greater part of bone mineral is formed very fast (within a few days), osteoblasts are often, for simplicity, referred to as bone-forming cells, without explicitly mentioning the intermediate step of osteoid secretion. Hence, initiation of bone regeneration requires the attraction of such stem cells to the pore spaces of the implanted scaffold, and creation of a milieu which facilitates the required differentiation processes.

Once the scaffold is (at least partly) covered with bone tissue, also remodeling events take place, implying that the bone tissue is removed by multinuclear cells called osteoclasts, deriving from hematopoietic stem cells. More precisely, osteoclasts attach themselves to the bone surface, thereby creating an acidic environment in order to dissolve the bone matrix, thus leaving behind a resorption cavity. This cavity is subsequently filled with new bone tissue by osteoblasts. Moreover, osteocytes, a third cell type found in bone, has been identified as bone remodeling "conductor". In particular, osteocytes are former osteoblasts that have been "buried" in newly secreted osteoid. Osteocytes are the most abundant cell type in bone tissue, and they are considered to be capable of sensing changes in their environment, particularly concerning the mechanical loading. There is ample evidence that osteocytes transduce these changes into biochemical signals, which, in turn, lead to corresponding changes of cellular activities in the bone microenvironment.

As for the exact biochemical regulatory pathways, the discovery of the receptor activator of nuclear factor kappa beta (RANK) and its ligand (RANKL) allowed for understanding the interplay between osteoblasts and osteoclasts. Namely, binding of RANKL, which is produced by both osteoblasts and osteocytes, to RANK, which is a transmembrane protein found on osteoclasts, is required for differentiation of osteoclasts. Furthermore, osteoprotegerin (OPG), a protein which is produced by osteoblasts, is a so-called decoy receptor, as it also binds to RANKL and thereby prevents osteoclastogenesis. Furthermore, the parathyroid hormone (PTH) influences the RANK-RANKL-OPG pathway, through promoting the production of RANKL and inhibiting the production of OPG. Transforming growth factor beta (TGF-beta), in turn, promotes the differentiation of osteoblast progenitor cells, inhibits the differentiation of osteoblast precursor cells, and promotes the apoptosis of osteoclasts. The list of factors contributing to the regulation of the bone cells could be easily extended by further proteins and hormones (such as nitric oxide, prostaglandins, vitamin D, corticosteroids, interleukins, calcitonin, or the Wnt beta-catenin pathway, just to mention a few), see (Robling *et al.*, 2006; Jacobs *et al.*, 2010; Bonewald, 2011) for respective review articles.

Mechanical excitation of bone cell activities is a heavily debated field, and several hypotheses have been brought forth over the years, including direct stretching of the cell-surrounding bone matrix, the hydrostatic pressure to which the cells are exposed, the fluid flow in the bone pore spaces, or microcracks emerging as result of local overloading (Robling *et al.*, 2006; Jacobs *et al.*, 2010). Also the exact consequences of changing mechanical loading, in terms of the mechanotransductive response, are not completely resolved. Experimentally confirmed hypotheses include the increase of osteoblast proliferation due to increased mechanical loading (with respect to "normal" loading conditions), and the increase of RANKL production due to decreased mechanical loading.

The above sketched regulatory mechanisms of bone formation and resorption have not yet been considered at all in the context of computational models of bone regeneration. The addition of bone tissue is usually considered based on simple laws, mostly involving scalar representatives of the location-dependent mechanical loading as functional argument, see e.g., (Adachi *et al.*, 2006), while biological details are completely neglected. The latter deficit could be eradicated by integrating into the structural simulations of bone tissue engineering scaffold systems biology-based bone models of the bone metabolism, see e.g., (Lemaire *et al.*, 2004; Pivonka *et al.*, 2008, 2010; Graham *et al.*, 2013; Scheiner *et al.*, 2013; Pastrama *et al.*, 2018). These models allow for consideration of cell populations, different developmental stages along the cell lineages, and regulation of cell differentiation, proliferation, and apoptosis processes by biochemical factors. The fundamental mathematical tools for such models are (ordinary or partial) differential equations. For example, in (Pivonka *et al.*, 2008, 2010), a set of three coupled ordinary differential equations is proposed, each of which represents the evolution a specific cell population. Solving these equations (which is and usually has to be done numerically, by means of approximating algorithms) gives then access to the developments of the considered cell populations over time. In some references (Scheiner *et al.*, 2013; Pastrama *et al.*, 2018), bone systems biology models are furthermore coupled with a bone micromechanics model for estimating the local mechanical stimulus perceived at the cell level, in order to include a physically meaningful argument for biomechanical regulation of the bone cell activities.

Utilization of Micromechanics for Quantification of Mechanobiological Stimuli

Let us tie in with the above-raised argument concerning the utilization of micromechanical models for quantifying the mechanical stimulus acting onto the cells driving bone regeneration. It could be shown that the hydrostatic pore pressures in the pore spaces of bone can be reliably predicted (Scheiner *et al.*, 2016c); fluid flow in the canaliculi and lacunae, occurring in response to macroscopic mechanical loading, can be estimated by downscaling related pressure gradients to the relevant pore spaces, see e.g., (Estermann and Scheiner, 2018); and microcracking can be introduced by taking into account suitable failure criteria defining the

onset of cracking events in the bone matrix (Fritsch *et al.*, 2009; Morin *et al.*, 2017). Furthermore, other mechanisms hypothesized to trigger bone cell activities, such as piezoelectric excitation (Ahn and Grodzinsky, 2009) can be also covered by multi-scale, micromechanics-inspired modeling approaches (Dunn and Taya, 1993).

X-Ray Physics-Based Analysis of CT Data

In biomedical practice, studying tissues or whole organs by means of an X-ray-based method is a common standard. When aiming at revealing the three-dimensionally distributed geometry and composition of such a tissue, computed tomography (CT) is usually applied. In order to process the information collected by means of CT scans properly, revisiting the theoretical foundation is crucial.

During a CT scan, X-rays are sent through the studied object, and the reduction of the X-ray intensity upon passing through the object, referred to as attenuation, is measured. By varying the direction of the X-ray as well as the position of the source of the X-ray, a comprehensive set of attenuation data is gathered. The Radon transform (Radon, 1917) is then utilized, in order to process the attenuation behavior in terms of the three-dimensional distribution of attenuation coefficients. Usually, the attenuation coefficients are expressed in terms of gray values which are proportional to the attenuation coefficients. Depending on the setting of the tomograph, corresponding resolutions can be achieved, typically in the range of a few micrometers. Thus, the studied object is then reflected in the CT data as an assembly of voxels (which are cubic domains whose side length is defined via the resolution); and each voxel is characterized by a constant gray value, representing the average attenuation coefficient within this voxel.

Using the CT data as basis for reconstructing the exact shape and geometry of the scanned objects, e.g., for building corresponding numerical models, is an often applied strategy. However, it has been shown in the past years that additionally, information concerning the composition of the material making up individual voxels can be extracted. To that end, the proportionality of the recorded attenuation coefficients to the voxel density is utilized. Taking into consideration that the voxel density, in turn, is proportional to the volume fractions of the materials contained within the voxels, the composition of the voxels can be straightforwardly deduced. The resulting field of material compositions can, in further consequence, be fed into micro-mechanical homogenization schemes, in order to obtain also a field of mechanical properties, discussed in the previous section, see e.g., (Hellmich *et al.*, 2008; Scheiner *et al.*, 2009; Dejaco *et al.*, 2012; Czenek *et al.*, 2014; Szlczak *et al.*, 2019).

For the sake of demonstration, Fig. 2(A) shows the gray value distribution in a cross-section of a granular, hydroxyapatite-based biomaterial obtained by means of micro-CT scanning. Analyzing the distribution of gray values as described above gives then access to the corresponding distribution of volume fractions of the constituents, i.e., of hydroxyapatite and of air pores. Considering the micro-morphology of the studied material suggests employing Mori-Tanaka-type stiffness homogenization. Feeding the resulting distribution of elastic constants into a structural model allows for simulation of the mechanical behavior of one of these granules when subjected to physiologically relevant mechanical loading, such as uniaxial compression, see Fig. 2(B) and (C). Comparison of these two images clearly underpins the importance of taking into account the heterogeneous distribution of mechanical properties, as was done in the simulation behind Fig. 2(B), instead of simply assuming, for simplicity average mechanical properties which are constant for all voxels, see Fig. 2(C).

Further Modeling Strategies

The above-presented modeling strategies appear to be a valuable set of computational tools which should (at least) be considered when facing the task of developing a model for some kind of tissue engineering application. However, the story does certainly not end at this point. Hence, this section is devoted to presenting further methods which have proved useful.

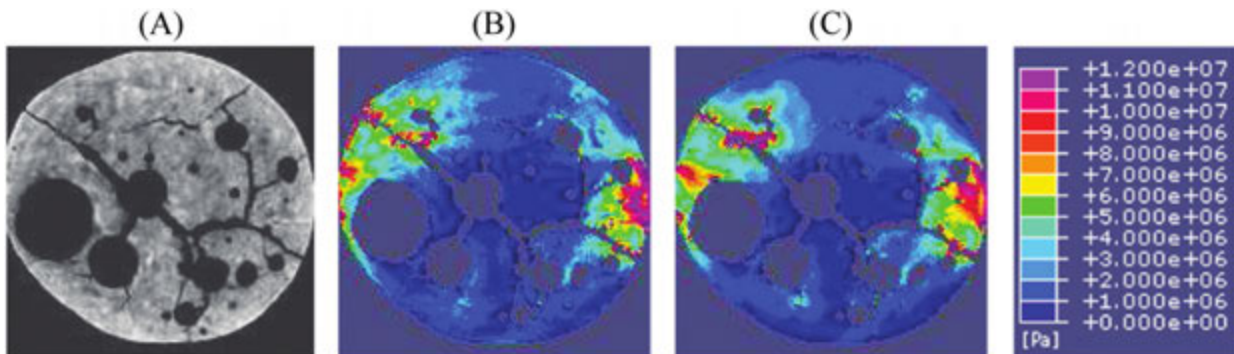


Fig. 2 (A) Gray value distribution in a cross-section of a granular, hydroxyapatite-based biomaterial, obtained by means of micro-CT scanning; distribution of the deviatoric stress norms resulting from FE simulations considering uniaxial compression, with load initiation occurring on the lateral sides of the granule, for (B) heterogeneous and (C) homogeneous stiffness properties. Reprinted from Dejaco, A., Komlev, V.S., Jaroszewicz, J., Swieszkowski, W., Hellmich, C., 2012. Micro CT-based multiscale elasticity of double-porous (pre-cracked) hydroxyapatite granules for regenerative medicine. *Journal of Biomechanics* 45, 1068–1075.

Two mechanisms are of particular interest in tissue engineering, in order to make sure that the inserted material blends in well into the physiological environment: dissolution of the scaffold and growth of new biological tissue. In order to anticipate how well a particular tissue engineering material performs, mathematical models were developed. e.g., a set of simple equations was introduced in (Chen *et al.*, 2011), essentially comprising degradation kinetics laws of the polymer under investigation, a hydrolysis law, and Fick's second law of diffusion. An extended diffusion-convection-reaction modeling framework was proposed in (Akalp *et al.*, 2016), extended by constitutive laws of the studied hydrogel, and some additional laws for defining the underlying material parameters. A somewhat simplified approach was taken in (Byrne *et al.*, 2007), where a fixed dissolution rate governs the temporal change of the studied scaffold within a large-scale numerical model. A similar approach was pursued in (Nava *et al.*, 2013), however for the growth of newly formed tissue in a bioreactor environment. The growth rate was considered to be dependent on the shear stress to which the particular location on the scaffold was subjected, and on the oxygen concentration. A set of equations reflecting the detailed stoichiometry of dissolution was presented in (Sanz-Herrera *et al.*, 2018), showing that dissolution (and also growth) do not need to rely on phenomenological equations but can also be modeled in minute detail.

Molecular dynamics is a modeling concept which has turned out to be well suited for assessing the biocompatibility of tissue engineering materials, see e.g., (Katti *et al.*, 2008; Sarmadi *et al.*, 2017). Molecular dynamics can also be employed for studying the absorption/desorption behavior of relevant factors onto the biomaterial surface (Huang *et al.*, 2018), or the interaction of biomaterials with its environment (Gopalakrishnan and Subramanian, 2011). Furthermore, the mechanical properties of composites on very small length scales has been studied by molecular dynamics simulations, see e.g., (Ebrahimi *et al.*, 2013).

In order to make the production process of biomaterials as predictable as possible, mathematical models have been used. Examples range from very basic computer-aided design (which is not necessarily mathematical modeling per se, but which can be extended by models for optimizing the eventually arising structure) (Mironov *et al.*, 2003) to more complicated models of the electrospinning process, comprising transport laws; mass, momentum, and charge balance equations; and a comprehensive set of constitutive equations (Wan *et al.*, 2004).

Assessing the processes governing the development of biological tissues in their physiological environments is very difficult (if not impossible). As a remedy, bioreactors are used. Bioreactors aim at creating a realistic replica of the physiological environment, and allow for inserting testing and monitoring equipment, improving the knowledge as to the exact conditions around the tissue under examination. Mathematical models were proposed for the sake of, firstly, reproducing the processes inside the bioreactor, and of, secondly, optimizing the scaffold's performance (Chung *et al.*, 2007; Couet and Mantovani, 2012). Furthermore, mathematical models were developed for optimizing the bioreactors themselves as well (Hidalgo-Bastida *et al.*, 2012).

Conclusions and Outlook

The mathematical modeling strategies in this contribution are supposed to provide an outlook as to how computer simulations may support patient-specific design of tissue engineering scaffolds may look like in the future. It goes without saying that the interested reader should not restrict her- or himself to the presented methods and references, but should probably consider this chapter as basis for looking deeper into the vast realm of mathematical modeling in biomedical engineering in general, and in tissue engineering in particular.

In order to make predictive computer simulations actually applicable in clinical practice, additional efforts are certainly necessary and will keep researchers busy for years to come. These efforts should probably focus, on the one hand, on improving the physical and biological foundation of the models, and on improving the current state of the art in the field, from a theoretical point of view. On the other hand, establishing mathematical models as credible tool among medical doctors is a second grand challenge. To that end, particular emphasis should be laid on experimental and clinical validation of the models, and on developing simulation tools such that they are eventually quickly applicable by non-experts as well. If these challenges are successfully met, chances are good that mathematical modeling will become a standard technology in tissue engineering in the foreseeable future.

References

- Adachi, T., Osako, Y., Tanaka, M., Hojo, M., Hollister, S.J., 2006. Framework for optimal design of porous scaffold microstructure by computational simulation of bone regeneration. *Biomaterials* 27 (21), 3964–3972.
- Ahn, A.C., Grodzinsky, A.J., 2009. Relevance of collagen piezoelectricity to „Wolff's law": A critical review. *Medical Engineering and Physics* 31 (7), 733–741.
- Akalp, U., Bryant, S.J., Vernerey, F.J., 2016. Tuning tissue growth with scaffold degradation in enzyme-sensitive hydrogels: A mathematical model. *Soft Matter* 12, 7505–7520.
- Bonewald, L.F., 2011. The amazing osteocyte. *Journal of Bone and Mineral Research* 26 (2), 229–238.
- Byrne, D.P., Lacroix, D., Planell, J.A., Kelly, D.J., Prendergast, P.J., 2007. Simulation of tissue differentiation in a scaffold as a function of porosity, Young's modulus and dissolution rate: Application of mechanobiological models in tissue engineering. *Biomaterials* 28, 5544–5554.
- Chen, Y., Zhou, S., Li, Q., 2011. Mathematical modeling of degradation for bulk-erosive polymers: Applications in tissue engineering scaffolds and drug delivery systems. *Acta Biomaterialia* 7, 1140–1149.
- Chung, C.A., Chen, C.W., Chen, C.P., Tseng, C.S., 2007. Enhancement of cell growth in tissue-engineering constructs under direct perfusion: Modeling and simulation. *Biotechnology and Bioengineering* 97, 1603–1616.
- Couet, F., Mantovani, D., 2012. Optimization of culture conditions in a bioreactor for vascular tissue engineering using a mathematical model of vascular growth and remodeling. *Cardiovascular Engineering and Technology* 3, 228–236.

- Czenek, A., Blanchard, R., Dejaco, A., *et al.*, 2014. Quantitative intravoxel analysis of microCT-scanned resorbing ceramic biomaterials – Perspectives for computer-aided biomaterial design. *Journal of Materials Research* 29 (23), 2757–2772.
- Dejaco, A., Komlev, V.S., Jaroszewicz, J., Swieszkowski, W., Hellmich, C., 2012. Micro CT-based multiscale elasticity of double-porous (pre-cracked) hydroxyapatite granules for regenerative medicine. *Journal of Biomechanics* 45, 1068–1075.
- Dias, M.R., Fernandes, P.R., Guedes, J.M., Hollister, S.J., 2012. Permeability analysis of scaffolds for bone tissue engineering. *Journal of Biomechanics* 45 (6), 938–944.
- Dormieux, L., 2005. *Applied Micromechanics of Porous Media*. Wien New York: Springer Verlag.
- Drugan, W.R., Willis, J.R., 1996. A micromechanics-based nonlocal constitutive equation and estimates of representative volume element size for elastic composites. *Journal of the Mechanics and Physics of Solids* 44 (4), 497–524.
- Dunn, M.L., Taya, M., 1993. Micromechanics predictions of the effective electroelastic moduli of piezoelectric composites. *International Journal of Solids and Structures* 30, 161–175.
- Ebrahimi, S., Montazeri, A., Rafii-Tabar, H., 2013. Molecular dynamics study of the interfacial mechanical properties of the graphene-collagen biological nanocomposite. *Computational Materials Science* 69, 29–39.
- Engh, C.A., Bobyn, J.D., Glassman, A.H., 1987. Porous-coated hip replacement. The factors governing bone ingrowth, stress shielding, and clinical results. *Bone & Joint Journal* 69-B (1), 45–55.
- Eshelby, J., 1957. The determination of the elastic field of an ellipsoidal inclusion, and related problems. *Proceedings of the Royal Society of London Series A: Mathematical and Physical Sciences* 241, 376–396.
- Estermann, S.J., Scheiner, S., 2018. Multiscale modeling provides differentiated insights to fluid flow-driven stimulation of bone cellular activities. *Frontiers in Physics* 6.76
- Fritsch, A., Hellmich, C., 2007. 'Universal' microstructural patterns in cortical and trabecular, extracellular and extravascular bone materials: Micromechanics-based prediction of anisotropic elasticity. *Journal of Theoretical Biology* 244 (4), 597–620.
- Fritsch, A., Hellmich, C., Dormieux, L., 2009. Ductile sliding between mineral crystals followed by rupture of collagen crosslinks: Experimentally supported micromechanical explanation of bone strength. *Journal of Theoretical Biology* 260 (2), 230–252.
- Fritsch, A., Hellmich, C., Dormieux, L., 2010. The role of disc-type crystal shape for micromechanical predictions of elasticity and strength of hydroxyapatite biomaterials. *Philosophical Transactions of the Royal Society London A* 368, 1913–1935.
- Fritsch, A., Hellmich, C., Young, P., 2013. Micromechanics-derived scaling relations for poroelasticity and strength of brittle porous polycrystals. *Journal of Applied Mechanics* 80 (2), 020905.
- Geris, L., 2013. *Computational Modeling in Tissue Engineering*. Springer-Verlag Berlin Heidelberg.
- Gopalakrishnan, R., Subramanian, V., 2011. Interaction of collagen with carbon nanotube: A molecular dynamics investigation. *Journal of Biomedical Nanotechnology* 7, 186–187.
- Graham, J.M., Ayati, B.P., Holstein, S.A., Martin, J.A., 2013. The role of osteocytes in targeted bone remodeling: A mathematical model. *PLOS One* 8 (5), e63884.
- Hellmich, C., Ulm, F.J., 2002. Micromechanical model for ultra-structural stiffness of mineralized tissues. *Journal of Engineering Mechanics* 128 (8), 898–908.
- Hellmich, C., Kober, C., Erdmann, B., 2008. Micromechanics-based conversion of CT data into anisotropic elasticity tensors, applied to FE simulations of a mandible. *Annals of Biomedical Engineering* 36 (1), 108–122.
- Hidalgo-Bastida, A., Thirunavukkarasu, S., Griffith, S., Cartmell, S.H., Naire, S., 2012. Modeling and design of optimal flow perfusion bioreactors for tissue engineering applications. *Biotechnology and Bioengineering* 109, 1095–1099.
- Hill, R., 1963. Elastic properties of reinforced solids: Some theoretical principles. *Journal of Mechanics and Physics of Solids* 11 (5), 357–372.
- Hill, R., 1965a. Continuum micro-mechanics of elastoplastic polycrystals. *Journal of Mechanics and Physics of Solids* 13 (2), 89–101.
- Hill, R., 1965b. A self-consistent mechanics of composite materials. *Journal of Mechanics and Physics of Solids* 13 (4), 213–222.
- Hollister, S.J., 2005. Porous scaffold design for tissue engineering. *Nature Materials* 4 (7), 518–524.
- Huang, B., Lue, Y., Li, T., *et al.*, 2018. Molecular dynamics simulations of adsorption and desorption of bone morphogenetic protein-2 on textured hydroxyapatite surfaces. *Acta Biomaterialia* 80, 121–130.
- Hutmacher, D.W., 2000. Scaffolds in tissue engineering bone and cartilage. *Biomaterials* 21 (24), 2529–2543.
- Hutmacher, D.W., Singh, H., 2008. Computational fluid dynamics for improved bioreactor design and 3D culture. *Trends in Biotechnology* 26 (4), 166–172.
- Jacobs, C.R., Temiyasathit, S., Castillo, A.B., 2010. Osteocyte mechanobiology and pericellular mechanics. *Annual Review of Biomedical Engineering* 12, 369–400.
- Jaecques, S.V.N., Van Oosterwyck, H., Muraru, L., *et al.*, 2004. Individualised, micro CT-based finite element modelling as a tool for biomechanical analysis related to tissue engineering of bone. *Biomaterials* 25 (9), 1683–1696.
- Katti, K.S., Katti, D.R., Dash, R., 2008. Synthesis and characterization of a novel chitosan/montmorillonite/hydroxyapatite nanocomposite for bone tissue engineering. *Biomedical Materials* 3, 034122.
- Kohlhauser, C., Hellmich, C., 2013. Ultrasonic contact pulse transmission for elastic wave velocity and stiffness determination: Influence of specimen geometry and porosity. *Engineering Structures* 47, 115–133.
- Lacroix, D., Planell, J.A., Prendergast, P.J., 2009. Computer-aided design and finite-element modelling of biomaterial scaffolds for bone tissue engineering. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* 367 (1895), 1993–2009.
- Lacroix, D., Chateau, A., Ginebra, M.P., Planell, J.A., 2006. Micro-finite element models of bone tissue-engineering scaffolds. *Biomaterials* 27 (30), 5326–5334.
- Lanza, R., Langer, R., Vacanti, J.P., 2007. *Principles of Tissue Engineering*. Elsevier Academic Press.
- Lemaire, V., Tobin, F.L., Greller, L.D., Cho, C.R., Suva, L.J., 2004. Modeling of the interactions between osteoblast and osteoclast activities in bone remodeling. *Journal of Theoretical Biology* 229 (3), 293–309.
- Lieberman, J.R., Friedlaender, G.E., 2005. *Bone Regeneration and Repair*. Humana Press.
- Melchels, F.P.W., Bertoldi, K., Gabbriellini, R., *et al.*, 2010. Mathematically defined tissue engineering scaffold architectures prepared by stereolithography. *Biomaterials* 31 (27), 6909–6916.
- Milan, J.L., Planell, J.A., Lacroix, D., 2009. Computational modelling of the mechanical environment of osteogenesis within a polylactic acid-calcium phosphate glass scaffold. *Biomaterials* 30 (25), 4219–4226.
- Mironov, V., Boland, T., Trusk, T., Forgacs, G., Markwald, R.R., 2003. Organ printing: Computer-aided jet-based 3D tissue engineering. *Trends in Biotechnology* 21, 157–161.
- Morin, C., Vass, V., Hellmich, C., 2017. Micromechanics of elastoplastic porous polycrystals: Theory, algorithm, and application to osteonal bone. *International Journal of Plasticity* 91, 238–267.
- Nava, M.N., Raimondi, M.T., Pietrabbisa, R., 2013. A multiphysics 3D model of tissue growth under interstitial perfusion in a tissue-engineering bioreactor. *Biomechanics and Modeling in Mechanobiology* 12, 1169–1179.
- O'Brien, F.J., 2011. Biomaterials and scaffolds for tissue engineering. *Materials Today* 14 (3), 88–95.
- Olivares, A.L., Marsal, E., Planell, J.A., Lacroix, D., 2009. Finite element study of scaffold architecture design and culture conditions for tissue engineering. *Biomaterials* 30 (30), 6142–6149.
- Pastrama, M.I., Scheiner, S., Pivonka, P., Hellmich, C., 2018. A mathematical multiscale model of bone remodeling, accounting for pore space-specific mechanosensation. *Bone* 107 (208), 221.
- Petite, H., Viateau, V., Bensaid, W., *et al.*, 2000. Tissue-engineered bone regeneration. *Nature Biotechnology* 18 (9), 959–963.
- Pivonka, P., Zimak, J., Smith, D.W., *et al.*, 2008. Model structure and control of bone remodeling: A theoretical study. *Bone* 43 (2), 249–263.

- Pivonka, P., Zimak, J., Smith, D.W., *et al.*, 2010. Theoretical investigation of the role of the RANK-RANKL-OPG system in bone remodeling. *Journal of Theoretical Biology* 262 (2), 306–316.
- Porter, B., Zauel, R., Stockman, H., Guldberg, R., Fyhrie, D., 2005. 3-D computational modeling of media flow through scaffolds in a perfusion bioreactor. *Journal of Biomechanics* 38 (3), 543–549.
- Radon, J., 1917. Über die Bestimmung von Funktionen durch ihre Integralwerte längs gewisser Mannigfaltigkeiten [On the determination of functions from their integrals along certain manifolds]. *Berichte der Sächsischen Akademie der Wissenschaften* 29, 262–277.
- Sezwan, K., Chen, Q.Z., Blaker, J.J., Boccaccini, A.R., 2006. Biodegradable and bioactive porous polymer/inorganic composite scaffolds for bone tissue engineering. *Biomaterials* 27 (18), 3413–3431.
- Robling, A.G., Castillo, A., Turner, C.H., 2006. Biomechanical and molecular regulation of bone remodeling. *Annual Review of Biomedical Engineering* 8, 455–498.
- Rüeggsegger, P., Koller, B., Müller, R., 1996. A microtomographic system for the nondestructive evaluation of bone architecture. *Calcified Tissue International* 58, 24–29.
- Sandino, C., Lacroix, D., 2011. A dynamical study of the mechanical stimuli and tissue differentiation within a CaP scaffold based on micro-CT finite element models. *Biomechanics and Modeling in Mechanobiology* 10 (4), 565–576.
- Sandino, C., Planell, J.A., Lacroix, D., 2008. A finite element study of mechanical stimuli in scaffolds for bone tissue engineering. *Journal of Biomechanics* 41 (5), 1005–1014.
- Sanz-Herrera, J.A., García-Aznar, J.M., Doblaré, M.M., 2008. Micro-macro numerical modelling of bone regeneration in tissue engineering. *Computer Methods in Applied Mechanics and Engineering* 197 (33–40), 3092–3107.
- Sanz-Herrera, J.A., García-Aznar, J.M., Doblaré, M., 2009a. A mathematical approach to bone tissue engineering. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* 367 (1895), 2055–2078.
- Sanz-Herrera, J.A., García-Aznar, J.M., Doblaré, M., 2009b. On scaffold designing for bone regeneration: A computational multiscale approach. *Acta Biomaterialia* 5 (1), 219–229.
- Sanz-Herrera, J.A., Soria, L., Reina-Romo, E., Torres, Y., Boccaccini, A.R., 2018. Model of dissolution in the framework of tissue engineering and drug delivery. *Biomechanics and Modeling in Mechanobiology* 17, 1331–1341.
- Sarmadi, M., Shamloo, A., Mohseni, M., 2017. Utilization of molecular dynamics simulation coupled with experimental assays to optimize biocompatibility of an electrospun PCL/PVA scaffold. *PLOS One* 12, e0169451.
- Scheiner, S., Sinibaldi, R., Pichler, B., *et al.*, 2009. Micromechanics of bone tissue-engineering scaffolds, based on resolution error-cleared computer tomography. *Biomaterials* 30 (12), 2411–2419.
- Scheiner, S., Pivonka, P., Hellmich, C., 2013. Coupling systems biology with multiscale mechanics, for computer simulations of bone remodeling. *Computer Methods in Applied Mechanics and Engineering* 254, 181–196.
- Scheiner, S., Komlev, V.S., Gurin, A.N., Hellmich, C., 2016a. Multiscale mathematical modeling in dental tissue engineering: Towards computer-aided design of a regenerative system based on hydroxyapatite granules, focusing on early and mid-term stiffness recovery. *Frontiers in Physiology* 7 (383), 1–18.
- Scheiner, S., Komlev, V.S., Hellmich, C., 2016b. Strength increase during ceramic biomaterial-induced bone regeneration: A micromechanical study. *International Journal of Fracture* 202 (2), 217–235.
- Scheiner, S., Pivonka, P., Hellmich, C., 2016c. Poromicromechanics reveals that physiological bone strains induce osteocyte-stimulating lacunar pressure. *Biomechanics and Modeling in Mechanobiology* 15 (1), 9–28.
- Simmons, C.A., Meguid, S.A., Pilliar, R.M., 2001. Differences in osseointegration rate due to implant surface geometry can be explained by local tissue strains. *Journal of Orthopaedic Research* 19 (2), 187–194.
- Sturm, S., Zhou, S., Mai, Y.W., Li, Q., 2010. On stiffness of scaffolds for bone tissue engineering – A numerical study. *Journal of Biomechanics* 43 (9), 1738–1744.
- Suquet, P.M., 1997. *Continuum Micromechanics*. Wien New York: Springer Verlag.
- Szlazak, K., Vass, V., Hasslinger, P., *et al.*, 2019. X-ray physics-based CT-to-composition conversion applied to a tissue engineering scaffold, enabling multiscale simulation of its elastic behavior. *Materials Science and Engineering: C* 95, 389–396.
- Truscello, S., Kerckhofs, G., Van Bael, S., *et al.*, 2012. Prediction of permeability of regular scaffolds for skeletal tissue engineering: A combined computational and experimental study. *Acta Biomaterialia* 8 (4), 1648–1658.
- Vass, V., Morin, C., Scheiner, S., Hellmich, C., 2018. Review of “universal” rules governing bone composition, organization, and elasticity across organizational hierarchies. In: Pivonka, P. (Ed.), *Multiscale Mechanobiology of Bone Remodeling and Adaptation* 578. Cham: Springer, pp. 175–229.
- Voronov, R., VanGordon, S., Sikavitsas, V.I., Papavassiliou, D.V., 2010. Computational modeling of flow-induced shear stresses within 3D salt-leached porous scaffolds imaged via micro-CT. *Journal of Biomechanics* 43 (7), 1279–1286.
- Wan, Y.-Q., Guo, Q., Pan, N., 2004. Thermo-electro-hydrodynamic model for electrospinning process. *International Journal of Nonlinear Sciences and Numerical Simulation* 5, 5–8.
- Williams, D.F., 2008. On the mechanisms of biocompatibility. *Biomaterials* 29 (20), 2941–2953.
- Williams, J.M., Adewunmi, A., Schek, R.M., *et al.*, 2005. Bone tissue engineering using polycaprolactone scaffolds fabricated via selective laser sintering. *Biomaterials* 26 (23), 4817–4827.
- Zaoui, A., 2002. Continuum micromechanics: Survey. *Journal of Engineering Mechanics* 128 (8), 808–816.

Unconventional, Nature-Inspired Approaches to Develop Bioceramics for Regenerative Medicine

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Introduction

The term biomaterial includes all materials or systems proposed for clinical applications to replace part of a living system or to function in intimate contact with living tissues. Materials science researchers and engineers are exploring this complex domain, as it requires consideration of biocompatibility, i.e., acceptance of the artificial implant by the surrounding tissues and, in the frame of Regenerative Medicine, assessment on bioactivity, bio-reabsorbability and ability to be integrated and remodeled. Such a research field requires interdisciplinary approaches and robust knowledge of chemistry, biology and mechanics, in order to cope with the complex chemical composition, multiscale structure and biological functions of the organ to be replaced/regenerated. In fact, after decades of attempts to develop biomaterials able to effectively regenerate tissues/organs, most of them failed in their task and today the need of a radically new approach is commonly recognized. In this scenario, the chapter describes new frontiers in biomaterial development, fed by novel nature-inspired approaches, and able to circumvent the limitations of the current ceramic technology. Thus it will be illustrated how the biomineralization process, by which nature builds innumerable biologic structures, could be used to obtain scaffolds for regeneration of bone and also complex anatomical regions such as the osteochondral and periodontal tissues. We will show recent developments for load-bearing scaffolds fabrication by using a revolutionary biomorphic transformation process, able to convert a natural hierarchically organized structure in fully ceramic and bioactive devices retaining the original 3-D multiscale structure and the unique damage tolerant performance. Finally, it will be shown how such new bio-devices can be powered by functionalization with magnetic doping and/or nanoparticles, to obtain on-demand activation of bio-functionalities. Particularly, the recent development of a biocompatible, bioactive superparamagnetic apatite is described, as a tool very promising to apply novel safer therapies in nanomedicine and to boost the endogenous potential of debilitated patients.

The “Biomimetic Approach”

The term biomimicry, entered in the scientific language in 1982, refers to a “new science that studies nature’s models and then imitates or takes inspiration from natural designs and processes to solve human problems”. Such a new tendency in material science suggests looking to Nature as a “Model and Mentor” and emphasizes sustainability as one of the main objective (Benyus, 1997). Indeed, materials found in nature combine many inspiring properties such as sophistication, miniaturization, hierarchical organizations, hybridation, resistance and adaptability. Differently, using a classic design approach, some properties turn out to be exclusive, such as for instance strength and toughness where strong materials are brittle and tough materials are relatively weak. However, natural materials with complex and hierarchical morphology and structure that span from nano- to macro-scales are both strong and tough. Generally, natural materials utilize very basic chemical components but such molecular building blocks are organized into complex architectures that give rise to exceptional mechanical properties: bone, nacre, teeth and woods are great examples of damage tolerant materials (Wegst *et al.*, 2014). The exceptional resistance to fracture of bone is due to complex deformation and toughening mechanisms that operate at different size scales i.e., from the nanoscale structure of protein molecules to macroscopic hierarchic architectures (Launey *et al.*, 2010). Recently, one of the most successful approach in designing and developing biomaterials for regenerative medicine is the biomimetic approach that is the effort to mimic the whole characteristics of the native tissue/organ. More specifically, the idea embodied in the concept of “biomimetics” is that the physico-chemical and morphological features of implanted biomaterials must be, by themselves, signals able to stimulate cell chemotaxis and colonization by autologous cells that work to remodel the original tissue/organ. In this way, the human body can be considered as a natural bioreactor able to guide appropriate tissue regeneration starting from a biomimetic scaffold without artificial addition of cells or other biological factors but simply recalling autologous cells and preserving the physiologic equilibrium and homeostasis, thanks to the reproduction of biologic environmental cues. In the practice of tissue/organ regeneration, the use of scaffolds is required particularly when it comes to regenerate large bone defects, since cells need a bioactive and bioresorbable bridge to start the remodeling cascade leading to a complete regeneration of the missing tissue and avoiding bad clinical outcomes such as non-union phenomena.

To this aim, nanocrystalline calcium phosphates (CaPs) exhibiting multiple ionic substitutions (e.g., Mg^{2+} , CO_3^{2-} , Sr^{2+}) are well reputed as the best in class materials for bone regeneration and have been extensively investigated in the past decade. Unlike stoichiometric hydroxyapatite (HA) that is only composed of Ca, PO_4 and OH, biological HA incorporates in its lattice several ions present in the physiological environment through ionic substitution or interstitial adsorption (see Fig. 1). This incorporation of doping ions is a dynamic process, changing in function of the age and physiological condition of the individuals; it modifies

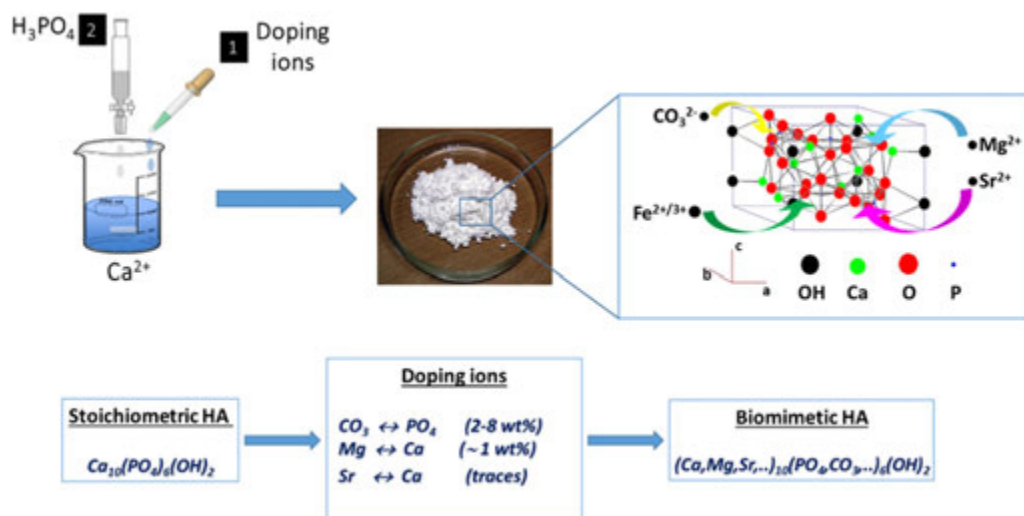


Fig. 1 Scheme of the synthesis and composition of a biomimetic hydroxyapatite.

several structural and physico-chemical HA parameters, such as reticular constant, crystal's morphology and size, crystallinity, thermal stability and solubility and thus affects decisively the phase bioactivity (Sprio *et al.*, 2008; Iafisco *et al.*, 2014a).

Among doping ions, CO_3^{2-} ions can occupy two different sites of the apatite lattice. B-substitution occurs at the PO_4^{3-} site, influencing the surface polarity and thus improving the osteoblasts adhesion and is typical of young and immature bones; conversely, carbonation in site A refers to partial substitution of OH^- , which increases the stability of mineral phase and in fact, it is more typical of mature bone tissue. Incorporation of Mg^{2+} ions influences the HA bioavailability, decreasing the crystallinity and promoting the nucleation and new apatite nuclei. Substitution of Calcium with Sr^{2+} ions has been largely studied thanks to its ability to restore the bone turnover balance, this is important for the treatment of osteoporotic bone fractures. Some positive results on the efficacy of local release of strontium were obtained in recent studies based on titanium implants functionalized with strontium or coated with strontium-substituted HA. (Li *et al.*, 2010). Combined substitution of Calcium with Fe^{2+} and Fe^{3+} ions were recently studied to endow HA with unique superparamagnetic ability and generate a new biocompatible and bio-resorbable FeHA nanophase, characterized by multiple functionality and high safety (Sprio *et al.*, 2008; Tampieri *et al.*, 2012). In particular, FeHA exhibits high magnetization under external static magnetic fields, in spite of very low amounts of secondary iron oxides, so that it can also exhibit excellent biocompatibility and bioresorbability (Panseri *et al.*, 2012; Panseri *et al.*, 2016).

Such bioactive ceramics are chemically unstable in physiologic environment, they are able to exchange bioactive ions with the surrounding environment and instruct cells to specific tasks, so that they might be considered as "inorganic metabolic phases". The production of biomimetic, bioactive CaPs has been carried out using several methods (Sprio *et al.*, 2008; Iafisco *et al.*, 2014b), but the final product is a fine powder that has to be subsequently treated with forming and sintering techniques to obtain 3-D porous devices. In fact, the scaffold should exhibit interconnected, multiscale porosity: large pores (200–400 μm) to ensure cell colonization, and a diffuse nano, micro-porosity for exchange of nutrients and waste products. Moreover, such features have to be associated with adequate mechanical performance withstanding physiological mechanical forces. Nevertheless, the conventional approaches for material processing do not allow accurate control of crystal and compositional changes, particularly during the high temperature consolidation process, so that irreversible crystal growth and alteration of bioactive chemical compositions and crystal structures occur, leading to reduction of the material's bioactivity and cell-instructive ability (Tampieri *et al.*, 2003). The fabrication of bio-functional 3-D ceramics retaining bioactive chemistry and nanostructure poses significant challenges. In fact, the current processing to consolidate inorganic materials with relevant mechanical performance requires the use of sintering treatments, which normally degrade the bio-active metastable phases and, in case of HA, induce the expulsion of doping ions and the re-crystallization process.

In attempting to preserve the relevant physico-chemical and biological properties of synthetic bioactive HA, when obtained as 3-D scaffolds, previous studies investigated different nature-inspired technologies either with a bottom-up or with a top-down approach. In the first case, the application of a biomineralization process represents the translation of the natural nano-technological process responsible for the natural bone and tooth formation, where a bio-organic macromolecule assembles into complex 3-D architecture and drive the heterogeneous nucleation of apatite nano-phase. When carried out by laboratory procedures, the mineralization of artificially assembled natural polymers generates hybrid-composites endowed with high similarity with natural mineralized tissue and superior biological performances. Such a process could be reproduced by exploiting the ability of collagen molecules to assemble into fibrils and thicker fibers by pH variation, that contemporary induces HA nuclei formation at the interface, at body temperature (Fig. 2). The biomineralization process activates multi-scale control mechanisms, thanks to the information stored in the complex structure of collagen macromolecule; particularly, chemical, structural and morphological mechanisms are activated and control the nanosize and crystal orientation of the nucleated mineral phase which can maintain

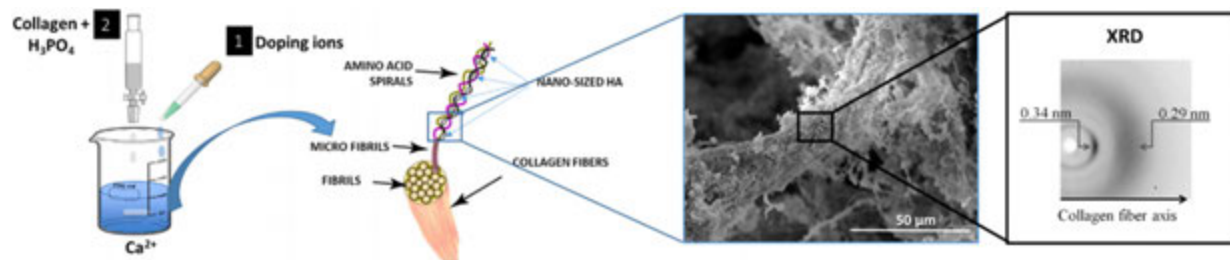


Fig. 2 (left) Scheme of the biomineralization collagen fibers; (right) Scanning electron microscopy and X-ray diffraction of biomineralized collagen fibers.

high instability level and capability of dynamic ion exchange. In particular, during Collagen fibers' self-assembly, the molecules of tropocollagen leave a regular array of 40-nm gaps within each periodic unit and such zones are called hole zones. The mineral phase of hard tissues preferentially nucleates exactly in these sites, and grow under the control exerted by the interaction with non-collagenous acidic macromolecules present in the hole zones and linking carboxylate groups and Ca^{2+} ions of the mineral phase. Specifically, the growth of the apatite-like nuclei is confined to very thin lamellae (45 nm in length, 20 nm in width and $\sim 2\text{--}3$ nm in thickness) with specific crystal orientation, as revealed by XRD analysis in flat chamber (see Fig. 2). A reflection very narrow and enhanced in intensity corresponding to the [002] plane refers to a preferential growth of the hexagonal apatite lattice along its c axis, thus favouring exposure of the ab face. Previous studies reported that proteins such as osteocalcin and osteopontin, present in the extracellular matrix and active in the bone formation and remodeling process, are chemically affine with the ab plane of hydroxyapatite (Mann, 2001). Therefore, it appears that biomineralization process could generate hybrid HA/Collagen constructs mimicking physico-chemical features of the immature bone tissue from the macro to the sub-nano scale, as instructive guides for bone regeneration.

The obtained hybrid gels can be treated by freeze-drying or freeze casting, thus generating scaffolds with high compositional and structural similarity with natural bony tissue and also graded structures resembling complex anatomical regions like the osteochondral and periodontal ones (Sprio *et al.*, 2014). The final product of such a process is a fibrous, porous construct able to deform elastically in liquid media, thus showing remarkable adaptability to any bone tissue defects but at the same time, inability to retain its original volume under compressive forces so that its use is so far limited to non load-bearing defects. Biomineralization is among the first attempts to exploit the unique features of biologic processes to fabricate scaffolds retaining physicochemical and architectural features typical of native tissues (Sprio *et al.*, 2016; Murray *et al.*, 2012). In this respect, the following paragraphs illustrate some examples of biomimetic hybrid scaffolds addressed to regeneration of multifunctional anatomical regions such as the articular joint and the periodontium, i.e., scaffolds prepared in graded fashion to regenerate simultaneously different tissues characterized by increasing mineralization extent.

Hybrid Scaffolds for the Regeneration of Multifunctional Anatomical Regions

Biomimetic Scaffolds for Osteochondral Regeneration

Osteoarthritis (OA), the most common form of arthritis, is a serious disease affecting the joints and is the fastest growing cause of disability worldwide (Vos *et al.*, 2012; Kingsbury *et al.*, 2014). Recent evidence suggests that we are moving towards a worldwide OA epidemic, particularly in Europe, where OA is estimated to affect >40 million people, (Buckwalter *et al.*, 1993) with a prevalence directly associated with ageing (Hutmacher, 2000; Hutmacher *et al.*, 2000; Martin *et al.*, 2000; Barbour *et al.*, 2017; Ethgen and Reginster, 2004; Hootman *et al.*, 2016; Henderson *et al.*, 2007).

The regeneration of osteoarticular regions affected by OA is thus one of the most demanding clinical needs nowadays and a target of high impact for biomaterials science and regenerative medicine. So far, most of attempts to regenerate osteochondral tissue in patients affected by OA or osteochondral defects have not resulted in a stable and reproducible restoration of joint function (Knutsen *et al.*, 2004; Kraeutler *et al.*, 2018; Cao *et al.*, 2003). An issue hampering the development of scaffold for osteochondral regeneration is the need to treat simultaneously the articular cartilage surface and the underlying subchondral bone. Even if various therapeutic approaches have been developed to treat osteochondral defects, none of them has proved yet to ensure long-lasting regeneration. One of the most promising strategies consists in the generation of hybrid scaffolds with graded composition and structure, obtained by the combination of distinct but integrated layers corresponding to the cartilage and bone regions (Chen *et al.*, 2011; Panseri *et al.*, 2012; Tampieri *et al.*, 2011; Sprio *et al.*, 2018). Among these approaches, the biomineralization process is particularly interesting, as it is able to activate a complex sequence of phenomena occurring at the molecular level and guiding the nucleation of nano-nuclei of CaP phases on self-assembling collagen fibers mimicking the process occurring *in vivo*. The high compositional and structural mimicry of the hybrids with the natural tissues is the basis of excellent bioactivity and bioresorbability, which can occur through cell and enzymatic activity. Very important, favouring the natural metabolic processes, the use of hybrid biomimetic devices can prevent any adverse effects related to foreign body reactions and this is very important particularly for aged patients, for which tissue regeneration is somewhat hampered by reduced endogenous potential.

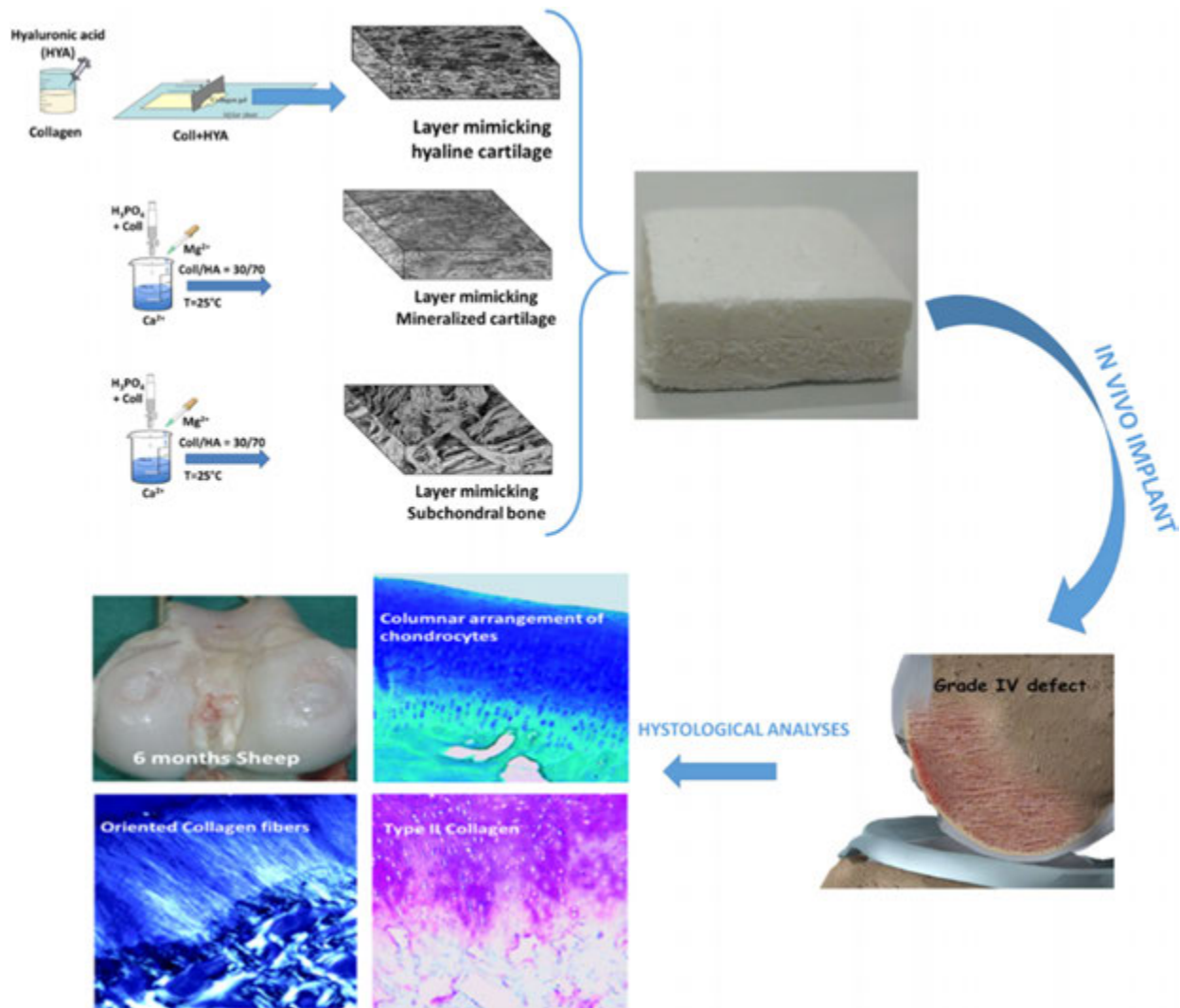


Fig. 3 (up) Sketch about the synthesis of hybrid device for osteochondral defect and (down) histology analysis of in vivo implant of hybrid osteochondral scaffold at six months of follow-up in sheep showing well-oriented collagen fibers, formation of type II collagen and columnar orientation of chondrocytes.

The biomineralization process rises interest also due to its flexibility in achieving hybrid constructs with different compositions, fiber orientation and texture, porosity extent and stiffness (Sprio *et al.*, 2008), acting on few key parameters during synthesis, crosslinking and freeze-drying process in a relatively simple fashion. A previous study showed how the biomineralization process was directed to obtain scaffolds with graded composition, porosity and morphology, in order to reproduce different histological areas in the osteochondral tissue. Therefore, by simply varying the degree of mineralization and the alignment of collagen fibers different hydrogels with specifically designed features were engineered into three-layered devices reproducing the sub-chondral bone (mineralization extent = 60–70 wt%), mineralized cartilage (mineralization extent = 30–40 wt%), and the hyaline cartilage (mineralization extent = 0 wt%) as Fig. 3 shows (Tampieri *et al.*, 2003). Freeze drying processes can be applied to guide the water sublimation and the fiber alignment thus generating dried fibrous constructs with tailored and oriented porosity extent. The non-mineralized collagen layer reproduced the typical columnar-like structure of the articular cartilage, with the fibers converging towards the external surface and form horizontal flat ribbons, thus resembling the morphology of the *lamina splendens* (Sprio *et al.*, 2008; Kon *et al.*, 2010). Bio-hybrid graded composites have demonstrated enhanced cell proliferation with very spread cell morphology, as well as high osteoinductivity and regenerative potential. In fact, they were able to differentially support cartilage and bone tissue formation in both the cartilaginous and bony layers, as demonstrated by comparative in vivo study carried out on adult sheep, where hydroxyapatite/collagen graded composites have been implanted on femoral condyles (Haumschild and Haumschild, 2009). In particular, histological evaluation showed the formation of new hyaline-like tissue and good integration of scaffolds with host cartilage, with a strong proteoglycan staining and columnar rearrangement of chondrocytes, and an underlying well-ordered sub-chondral trabecular bone (Fig. 3).

Biomimetic Scaffolds to Treat Periodontal Diseases

Periodontitis is an inflammatory disease affecting the tooth, it is extremely widespread worldwide and has a prevalence that is similar to cardiovascular disease and diabetes (Williams *et al.*, 2008; Dye, 2012), estimated as 25%–47% (Hajishengallis, 2010). Periodontitis is widespread, particularly among the elderly, attributed to accumulated exposure to different type of foods, medications and physical environments but, on the basis of recent studies, it is also related to a change in susceptibility with ageing (Bartold *et al.*, 2000). Severe periodontitis is characterized by tissue resorption involving both the alveolar bone and cementum, which provokes the tooth loss. The current approaches for the treatment of periodontal diseases are mostly based on preservative and conservative approaches. However ever-increasing attention has been focused on regenerative therapies, rather than resective surgery, to establish guided periodontal regeneration which, to date, is considered the only successful therapeutic approach to stimulate the activity of multiple cell lineages active in the oral environment (e.g., osteoblasts, cementoblasts, dentinoblasts, endothelial (Linde and Goldberg, 1993; Maeda *et al.*, 2014; Bodineau *et al.*, 2009)) and to promote the formation of new dental tissues with appropriate texture and biomechanical competence. The oral environment is particularly prone to infections and in this respect, it was observed that aged people have higher levels of some Gram-negative bacilli, such as *Pseudomonas aeruginosa*, *Klebsiella pneumoniae*, and *Enterobacter*, as compared with young individuals that could affect the incidence of periodontitis in the elderly (Sprio *et al.*, 2018).

Giving the great complexity of the cell interactions and cross-talk in dental tissues, it is very hard to contrive effective regenerative approaches, even if a scaffold is adopted. In this respect, the use of biomimetic hybrid scaffolds can be promising since they can recapitulate relevant features of native tissues, and possibly instruct the cells only by virtue of physicochemical, topological and structural properties (Lee *et al.*, 2014). To this purpose, the biomineralization process was applied to fabricate hybrid graded scaffolds recapitulating the physico-chemical, morphological and structural features of the different periodontal tissues (see Fig. 4). The strategy was based on the creation of a multi-layer construct with different region-specific pore/channel sizes and material composition (Sprio *et al.*, 2018; Bortolomai *et al.*, 2019), related to the periodontal ligament, the cementum, and the alveolar bone.

The bottom layer mimicking alveolar bone has been obtained as a hybrid porous construct made of Mg, CO₃-doped hydroxyapatite nano-crystals nucleated on self-assembling collagen fibrils and retaining very low, bone-like, crystallinity degree. To enhance cell differentiation, the mineral phase was partially doped with Fe²⁺/Fe³⁺ ions, as a tool providing magnetic signals to activate osteoblast cells. The middle layer mimicking periodontal ligament (PDL) is composed of a collagen membrane obtained by tape-casting technique matched with an air-drying process under environmental condition. This process permitted to maintain

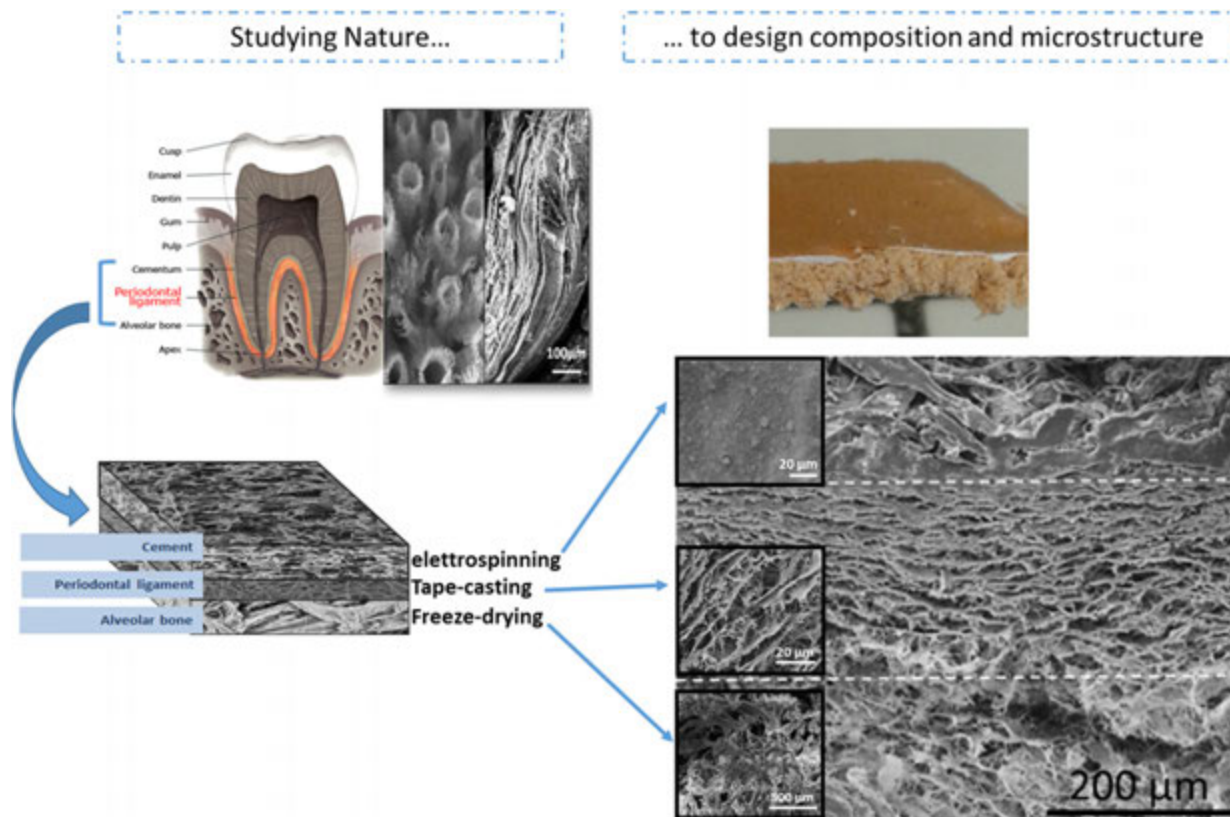


Fig. 4 Bio-inspired approach to fabricate biomimetic periodontal scaffolds.

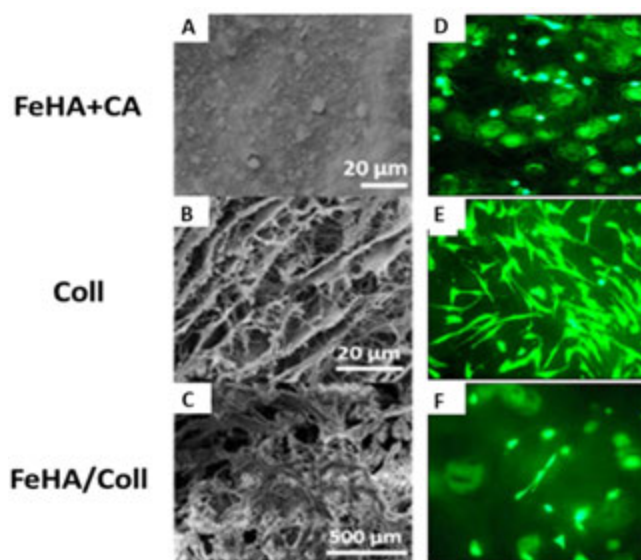


Fig. 5 Live&Dead of cells into different periodontal regions.

a thin and highly porous central area, relevant to promote extensive vascularization and diffusion of nutrients to the cementum layer. 1,4-Butanediol diglycidyl ether (BDDGE) was selected as a cross-linking agent to increase the stability of PDL and to promote the formation of bridges through covalent links between the collagen fibers (Krishnakumar *et al.*, 2018; Sandri *et al.*, 2016; Goncalves *et al.*, 2005). The top layer mimicking the cementum was composed of ion doped hydroxyapatite mixed with cellulose acetate (CA), and deposited by electrospinning to obtain a fibrous structure with mineralization degree $\sim 50\%$, able to form bundles around the fibers of the PDL, and with high density of tight pores, all features relevant for anchoring the tooth to its alveolus and for entrapping cementoblasts (Ho *et al.*, 2009; Maredziak *et al.*, 2016). Thanks to these unique structural properties and biomimetic composition, the scaffold showed excellent cytocompatibility and viability as Fig. 5 highlights.

Emerging Technologies for Regeneration of Load-Bearing Segmental Bones: Biomorphic Transformation of Natural Structures

The hybrid scaffolds obtained by biomineralization process are fibrous, porous and able to deform elastically in liquid media, thus showing remarkable adaptability to tissue defects, and particularly effective in regeneration of complex anatomical region but, at the same time, unable to retain its original volume under compressive forces. To design scaffolds with mechanical strength enabling application in critical size bone defects, bioactive ceramic powders have been used in association with biocompatible and bio-erodible polymers. The as-obtained printable pastes have been also used for the fabrication of 3-D porous scaffolds by additive manufacturing techniques (Rezwan *et al.*, 2006). However, besides the scarce compositional and mechanical similarity with bone tissue, polymer-based scaffolds often exhibit non-enzymatic dissolution profiles for which acidic and harmful by-products can be released, altering cell metabolism and vitality thus jeopardizing tissue healing (Liu *et al.*, 2006). Furthermore, the regeneration of large bone defects is much more demanding than a simple bone cavity or a non-load bearing bony region. In fact, in combination with bioactive composition and porous morphology, the mechanical properties play a key role, because of the need to withstand multi-modal mechanical stimuli whereas stimulating cells to produce new bone tissue. The bone ability to cope with mechanical forces is strongly related to its complex hierarchical architecture, as occurs in the majority of bio-structures, giving unusual and superior performance in comparison with any artificial materials (Wongmaneerung *et al.*, 2009; Roulland *et al.*, 2005; Qian *et al.*, 2013; Cazalbou *et al.*, 2005). Such peculiar structure allows an efficient distribution of the mechanical loads from the macroscale down to the smallest trabeculae, where strain-sensing mechanisms exhibited by the osteocyte cells can take place and activate the permanent bone remodeling process (Iafisco *et al.*, 2014a; Limonov and Richard, 2016; Sprio *et al.*, 2008). Unfortunately, the fabrication of functional 3-D inorganic materials retaining nanostructure poses significant challenges and activate degradation phenomena (Wongmaneerung *et al.*, 2009; Roulland *et al.*, 2005; Limonov and Richard, 2016). A very relevant case study is given by nanocrystalline calcium phosphates (CaPs) exhibiting multiple ionic substitutions (e.g., Mg^{2+} , CO_3^{2-} , and Sr^{2+}), which are well known as the elective phases to develop scaffolds for bone regeneration (Rey *et al.*, 1989; Dahl *et al.*, 2001; Bertinetti *et al.*, 2009). Although, when in the form of nano-powders, the synthesis of such bioactive ceramics is not a critical task (Iafisco *et al.*, 2014a; Sprio *et al.*, 2008), its development in form of 3-D scaffolds, endowed with adequate mechanical performance, is a challenge that the scientific community is intensively facing. In fact, current fabrication methods do not allow accurate control of crystal and compositional changes, particularly during the consolidation process, where irreversible crystal growth and chemical stabilization occurs, reducing the scaffold bioactivity (Tampieri *et al.*, 2011). Furthermore, the current processes for the development

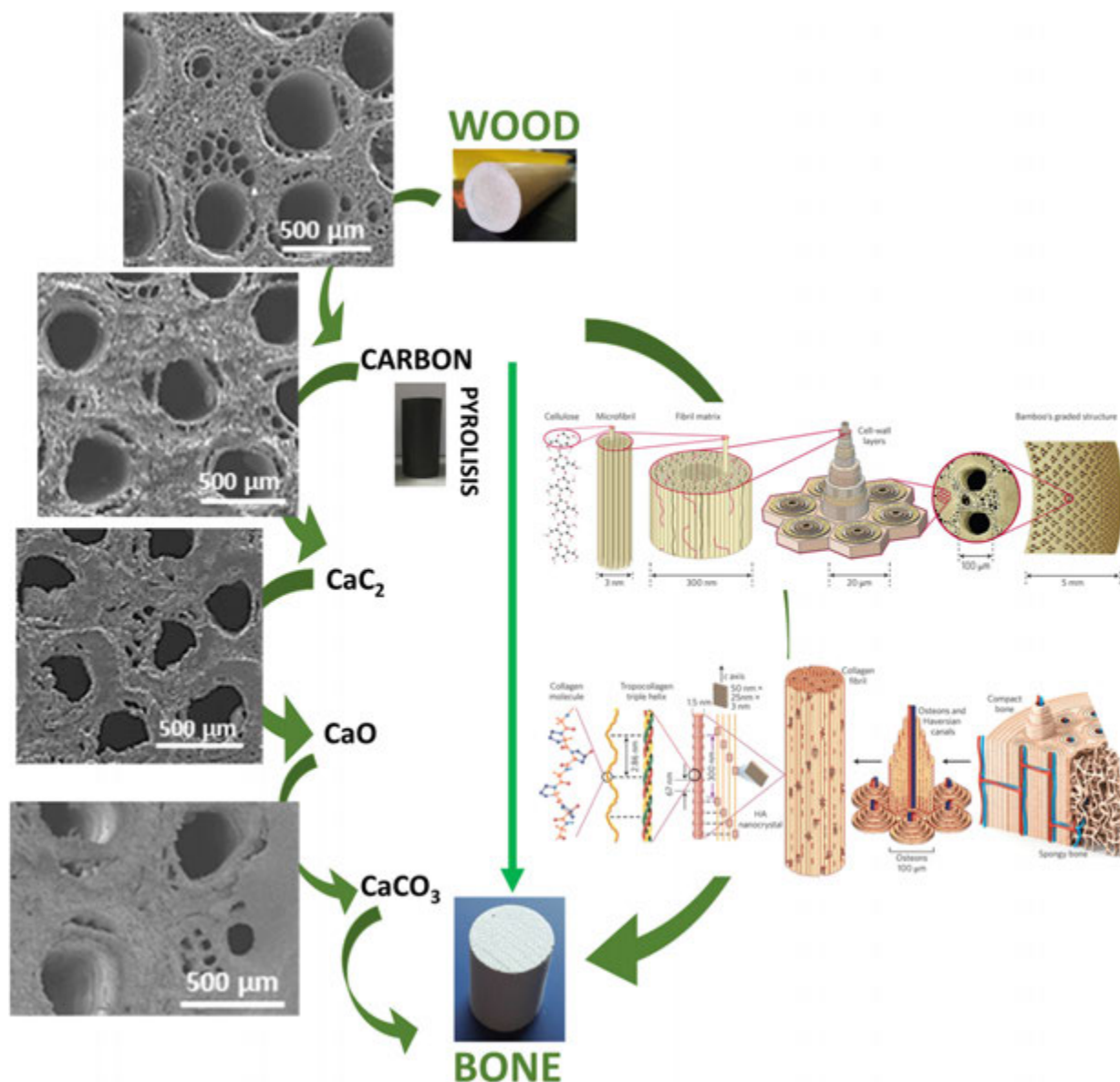


Fig. 6 Scheme of (left) single steps of synthesis and (right) the multi-scale structure of wood and bone tissue.

of inorganic scaffold do not allow the generation of complex organized hierarchical structure, mimicking the natural ones (Schumacher and Gelinsky, 2015; Zhang *et al.*, 2014). In this view, striving to generate 3-D bodies with unique features, new technological approaches are needed, moving away from conventional protocols based on ceramic powder synthesis-processing-forming-sintering, towards chemical processes governed by concomitant nucleation/growth/assembling phenomena directly occurring in the 3-D state and giving bio-functional phases already consolidated in 3-D bodies with adequate porous structure. Nature can be a source of inspiration for the development of hierarchically structured biomaterials following a top-down approach (Limonov and Richard, 2016; Rezwani *et al.*, 2006). Indeed, the nano-sized building blocks forming the natural biological tissue is one of the bases of their self-organization ability and needs to be replaced by synthetic materials with controlled composition, structure and organization on multiple length scales (Suryanarayana, 1999). Following this approach, natural wood have been selected as starting point: it is, indeed, a cellular structure made of fiber bundles interconnecting channel-like porous areas with hollow tubes, and it can be considered as the elective template in starting the preparation of a new bone scaffold characterized by a biomimetic hierarchical composition and structure, exhibiting also a remarkable combination of high strength, stiffness and toughness at low density (Tampieri *et al.*, 2009). In Fig. 6 is illustrated a recent approach in which, a wooden structure, mimicking the osteon structure of the compact bone, was transformed into large bioactive, mechanically competent bone scaffolds by a multi-step process consisting in heterogeneous reactions established between reactive gases in the supercritical state and the solid 3-D templates.

Cylindrical wood pieces (*Calamus manna*) were preliminarily pyrolyzed at 1000°C to achieve a porous carbon body. The obtained body was then transformed into calcium carbide by heterogeneous reaction with gaseous calcium and then, oxidized at calcium oxide. Then, the subsequent transformation into highly reactive CaCO_3 precursor was carried out under wet conditions, by reaction with supercritical, hydrated CO_2 at high gas pressure. The heterogeneous reactions between CO_2 gas in supercritical state and solid biomorphic CaO templates, allowed the kinetic control of the temperature- and time-dependent grain growth and made possible to maintain the primitive composition and nanostructure at the basis of desired functional performances (Beruto and Botter, 2000). The final conversion into biomimetic, multi-doped hydroxyapatite, was obtained by hydrothermal reaction at conditions permitting the conversion of the template into a 3D body made of nano-twinned lamellar hydroxyapatite with hierarchical multi-scale porous architecture inherited by the natural wood template. Such a process could be carried out by thorough kinetic control of the temperature- and time-dependent grain growth making possible to retain high reactivity in the intermediate precursors and allow the achievement of the desired phase as a 3-D scaffold with bioactive composition and damage-tolerant mechanical performance. In fact, it was found that the uncontrolled grain growth of CaCO_3 and the lowering of specific surface area led to a poorly reactive phase affecting the subsequent transformation of CaCO_3 into hydroxyapatite by the hydrothermal method.

A bioreactor study was made, as a clinically-reflective approach for initial in vitro screening. The results highlighted a significant effect of the biomorphic scaffold on the up-regulation of various genes involved in both early (BMP2, Runx2 and ALP) and late (OPN and Col15a1) stages of osteogenic commitment (Orlando *et al.*, 2013; Thurner *et al.*, 2010), when compared to a porous sintered apatite scaffold (Fig. 7).

In vivo tests confirmed the excellent osteoinductive ability of the biomorphic scaffold, showing well developed bone tissue in ectopic site 12 weeks after subcutaneous implantation in rabbits. The histological analyses show both osteogenesis, osteoclastogenesis and angiogenesis, with abundant woven bone structures and a neovascular network penetrating through the scaffold and, further, the presence of active osteoclasts into surface depressions at the new woven bone surface report on bone resorption, typical of normal bone remodeling (see Fig. 8).

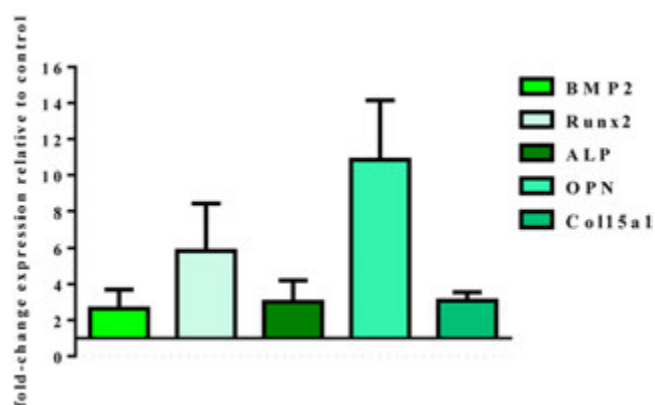


Fig. 7 Relative quantification ($2^{-\Delta\Delta\text{Ct}}$) of gene expression after 14 days of dynamic cell culture. Fold-change expression of the target genes induced by B-HA samples in respect to S-HA samples, used as a calibrator, are shown in the graph. Two-way ANOVA analysis indicated statistical difference between the samples with $p \leq 0.0001$. Reproduced from Tampieri, A., Ruffini, A., Ballardini, *et al.*, 2019. Heterogeneous chemistry in the 3-D state: An original approach to generate bioactive, mechanically-competent bone scaffolds. *Biomaterials Science* 7, 307–321.

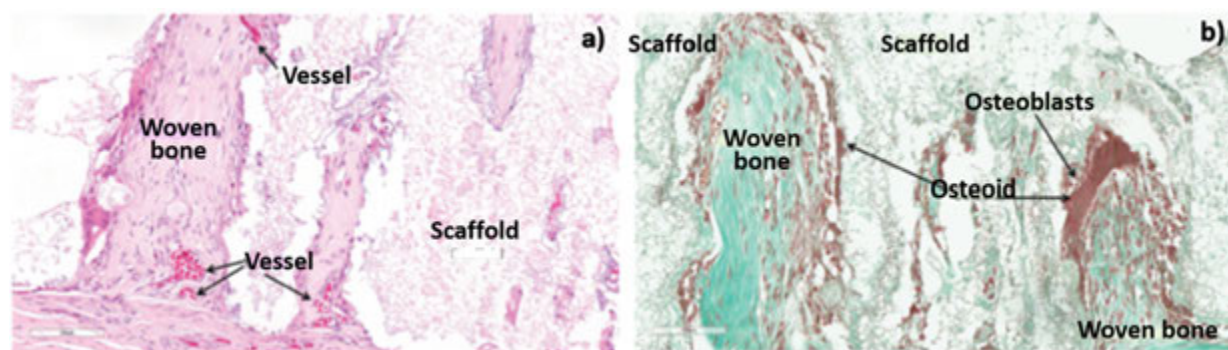


Fig. 8 Histological analysis of the biomorphic scaffold implanted subcutaneously in a rabbit model after 12 weeks. (a) Hematoxylin-eosin stain and (b) Goldner's Trichrome stain. Magnification $20\times$. Reproduced from Tampieri, A., Ruffini, A., Ballardini, *et al.*, 2019. Heterogeneous chemistry in the 3-D state: An original approach to generate bioactive, mechanically-competent bone scaffolds. *Biomaterials Science* 7, 307–321.



Fig. 9 X-ray image of a biomorphic bone scaffold implanted in critical metatarsus defect in sheep.

Particularly, the multi-scale porous structure, closely reproducing the lymphatic system of natural woods, is a key feature to promote vascular development throughout the whole scaffold. Recent results highlighted that the cross talk between endothelial and mesenchymal stem cells can be stimulated by such a biomimetic structure, very relevant to support bone and vascular regeneration, particularly in long bone segments, where the lack of vascularization is a major concern. Besides, the scaffold was implanted in critical size, load-bearing bone defect in a sheep model, showing excellent mechanical properties and adaptability to long bone defects, as shown in the radiography in **Fig. 9**, and ability to induce complete bone remodeling.

The obtained results highlighted how heterogeneous chemical processes carried out under unusual experimental conditions permitting the strict control of reaction kinetics in the 3D state permit to transform natural structures into inorganic devices inheriting their complex 3-D geometries, optimized in millions of years of evolution for optimal functional and mechanical performance.

Furthermore, such a hierarchic pore structure was found to be the source of outstanding, damage-tolerant mechanical performance, unusual for pure ceramics. In particular, the extremely intricate organization and interconnection of the channel-like pores of the biomorphic apatite effectively hinders crack propagation so that the fracture dynamics of the biomorphic ceramic under compression results very close to that of the starting wooden template and, also, to the one of natural bone tissue. Besides, the channel porosity of the wooden template closely resembling the osteon structure of compact bone, yields anisotropic mechanical properties that also results in flexure strength higher than compression strength, which is quite uncommon for ceramics, but very interesting in the view of application as scaffold for long bone segments where not only compressive forces but also the flexural ones, can be relevant.

These outstanding results report on the association of unique physicochemical and mechanical properties, obtained only thanks to a fabrication process revolutionizing the previous ceramic approaches. This is encouraging for the future development of functional 3-D ceramics so far prevented by inherent technological limitations. The excellent cell-instructive ability of the biomorphic scaffold, as induced by a bioactive scaffold recapitulating chemistry, nanostructure, structure and mechanics of the natural bone, demonstrates the validity of the “biomimetic concept” and – most importantly – suggests that biomimetic scaffolds alone can favor metabolic processes yielding tissue regeneration without the aid of additional growth factors, bioactive molecules and cells. This has a great impact on translational processes where it will be possible to avoid complex regulatory and storage issues, thus drastically shortening the time required for translation “from the bench to patient” and reducing the healthcare costs.

Magnetic Scaffold to Boost Tissue Regeneration

Previous studies show that the decrease in the regenerative potential in the elders or in presence of degenerative diseases is related to functional changes in adult stem cells with ageing. Such modifications include ability to proliferate, to form single cell-derived colonies and also differentiation capacity. Indeed, osteogenic and chondrogenic differentiation of stem cells undergo significant impairment with ageing, that negatively impact on new tissue formation (Hou *et al.*, 2013). Since biomimetic scaffolds are intended to effectively drive bone tissue regeneration, also providing progressive replacing of the scaffold itself with new healthy tissue (bio-resorption process), the patients’ metabolism plays an important role in the regulation of the kinetics and extent of new tissue formation. For this reason, metabolic diseases, as well as the degenerative conditions induced by aging, are a concern because the healing of damaged or missing tissues is significantly reduced. Since the occurrence of degenerative diseases is expected

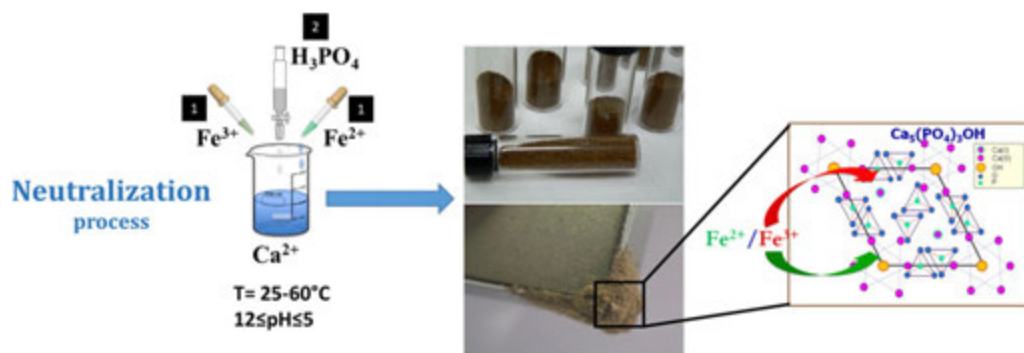


Fig. 10 Scheme of the synthesis and macroscopic view of iron-doped hydroxyapatite.

to steadily rise in the next decades, the need to treat an ever increasing number of patients with impaired endogenous potential pushes the Material Science research towards new therapeutic approaches to boost cell functions and tissue regeneration. The use of drug delivery systems to release bioactive molecules directly in situ is a hot research topic in materials science. Particularly, the possibility to activate and control the release by remote signaling to obtain on demand delivery in temporally and spatially defined fashion, is a target extremely relevant, to improve the effectiveness and personalization of the therapy.

In this respect, recent studies report that the use of weak magnetic fields can be beneficial as remote signaling to permit non-invasive control of biomedical devices in vivo. The use of magnetic materials in nanomedicine is raising a steadily growing interest, due to the numerous possible applications including cancer therapy by hyperthermia, magnetic resonance imaging and other theranostic approaches based on the guiding of magnetic NPs to specific targeted areas in vivo and their use as nano-probes. This represents a very interesting and promising tool for new personalized therapies (Meng *et al.*, 2013, 2010; Mertens *et al.*, 2014; Panseri *et al.*, 2013; Shan *et al.*, 2013; Lewinski *et al.*, 2008). However, the currently used superparamagnetic iron oxides NPs (SPION, i.e.: mainly magnetite and maghemite) exhibit long-term toxicity by progressive accumulation in soft tissues and organs such as liver and kidney (Singh *et al.*, 2010; Tampieri *et al.*, 2012). Recent studies developed a new biocompatible and bioresorbable superparamagnetic phase by doping the hydroxyapatite lattice with $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions in the two independent crystal sites of calcium (FeHA) (Tampieri *et al.*, 2011) (see Fig. 10).

This approach was attempted with the purpose of creating Fe-rich sublattices in the HA crystal, whose interaction could induce superparamagnetic behavior as Fig. 10 illustrates. Previous studies based on computer simulations had indicated that both divalent and trivalent Fe ions could be introduced in the HA lattice at different Ca crystal sites (Jiang *et al.*, 2002). Hence, the synthesis of superparamagnetic Fe-doped HA was carried out in conditions of pH and temperature preventing the oxidation of Fe^{2+} and the crystallization of undesired magnetite phase. The analysis of the crystal changes in respect to Fe doping confirms the substitution of Ca^{2+} in the lattice. Further studies (Iannotti *et al.*, 2017) reported on the segregation of Fe^{3+} on the surface of the HA crystals where they induce the heterogeneous nucleation of maghemite nanocrystals in very few amount (i.e., $\sim 2-3$ wt%). The distribution of the Fe ions in the apatitic and non-apatitic regions of HA structure confer complex magnetic properties enabling unique bio-functionalities (Tampieri *et al.*, 2012).

Thanks to the close similarity with the mineral bone composition, FeHA exhibits very good biocompatibility and enhanced cell proliferation and differentiation, if compared to the un-doped HA. Very interestingly, this effect was significantly increased when a static magnetic field was applied (Panseri *et al.*, 2012; Clavijo-Jordan *et al.*, 2012; Patricio *et al.*, 2019).

As reported in Fig. 11, FeHA is an excellent candidate in nanomedicine and regenerative medicine because its features can be customized changing size, morphology and combining with different polymers. Three different applications have been investigated: (1) the development of magnetic nanobeads suitable for the transportation of bioactive molecules; (2) the possibility to internalize it in cells; (3) the biomineralization of FeHA into collagen fibers to create magnetic hybrid scaffold for tissue engineering.

- (1) The possibility offered by the biomineralization process to generate nano-composites with superparamagnetic properties opens to the possible development of hybrid carriers with enhanced functionality, by using single or blended bio-polymeric matrices (Patricio *et al.*, 2017; Campodoni *et al.*, 2016). In particular, alginate is attractive due to its ability to bind to different monovalent ions, generally to create water soluble products, or bivalent ions such as Ca^{2+} , to create insoluble hydrogel, film, beads, nanoparticles thanks to the linking with Mannuronic and Guluronic units, that yields a typical “egg-box” structure (De and Robinson, 2003; Chen *et al.*, 2006; Zhao *et al.*, 2012; Eiselt *et al.*, 2000).

In particular, Campodoni *et al.* followed a biomineralization approach to synthesize a superparamagnetic hybrid nano beads consisting of Fe-doped apatite nanocrystals nucleated onto alginate polymeric matrices (Alg-FeHA). Starting from Alg-FeHA, superparamagnetic hybrid nanobeads (MHNs) were formed by a subsequent emulsification by oil-in-water technique. Importantly, the amount of alginate results very low, thus not affecting the magnetization values of MHNs in respect to the free magnetic nanoparticle. MHNs can be activated and deactivated by varying the intensity and the frequency of external magnetic fields; moreover, it is possible to guide them in specific therapeutic site where they can eventually release on

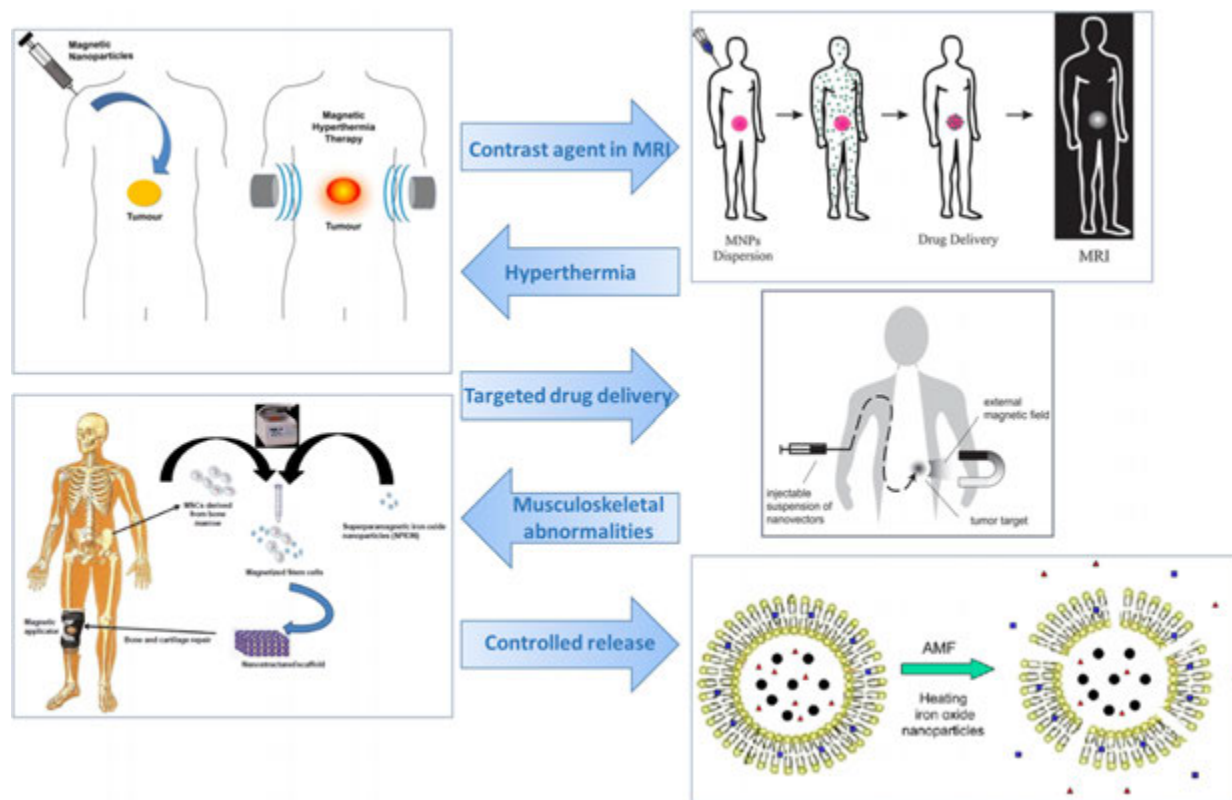


Fig. 11 An overview about the different applications in which magnetic materials can be exploited.

demand the relevant payload. Indeed, the design and magnetic ability of these particles enables enhanced drug protection against early degradation, as well as to avoid undesired or passive release inside of the target cells (Campodoni *et al.*, 2016). Hybrid magnetic devices can be also obtained in the form of hollow micro-nano spheres (Gloria *et al.*, 2013; Iafisco *et al.*, 2013; Nappini *et al.*, 2011) enabling multiple functionalization, by taking advantage of the active surface sites of the polymer and the mineral phase. Interestingly, their bioactivity can be tailored by the amount of FeHA phase so that they displayed good biocompatibility with bone marrow mesenchymal stem cells, and their proliferation was enhanced by higher amounts of FeHA phase. These magnetic materials have potential uses as building blocks for the preparation of scaffolds able to release different therapeutics on demand by remote activation through alternate magnetic fields. Such a stimulus can be dosed to obtain mild effect (magneto-shaking), permitting to deliver the payload with controllable kinetics or to trigger hyperthermia effect by which spheres can be disrupted thus releasing the bioactive agent (Liu *et al.*, 2016) in a more intense fashion, to provide a boosting effect. These approaches are still at their infancy but the growing interest in obtaining more effective and stimuli-responsive devices for regenerative medicine will definitely push deeper research in the field (Plouffe *et al.*, 2015).

- (2) As an alternative to drug delivery, magnetic fields can be used for cell manipulation and guiding to specific target sites. Magnetic-based cell separation technology is a recent approach, aimed to improve the selection, sorting and handling of stem cells, which can be the basis of personalized cell and gene therapies (Tampieri *et al.*, 2003). Such approach can be used to improve the effectiveness of implanted scaffolds, which is particularly relevant for tissue regeneration in the elderly (Sprio *et al.*, 2014). In fact, since ageing implies a reduced number and activity of stem cells, the cell population of implanted scaffolds can be impaired and ineffective, thus resulting in low extent of new tissue formation. The use of magnetic NPs open new scenarios in this respect; in fact, a key limiting factor in the regeneration of extended bone defects is the inability of cells to self-propagate in the inner part of the scaffold and to establish new bone and vascular tissue (Ganguly and Puri, 2010). Recent studies show that it is possible to locally guide the migration of magnetic NPs and NP-labeled cells through the use of an externally applied magnetic field gradient (Amer *et al.*, 2017). In this respect, FeHA NPs showed to be easily incorporated into cells by endocytosis, thus obtaining “magnetic cells” without negatively affecting the cell behavior (e.g., proliferation, morphology, differentiation). Besides the beneficial effect given by enhanced scaffold population, this approach can greatly widen the perspective of application of cell therapies, since magnetic guiding with biocompatible NPs can help to improve the cell retention and viability post-injection that are among the most critical obstacles facing clinical translation (Amer *et al.*, 2017).
- (3) The achievement of biocompatible nano-biomaterials with magnetic properties opens new perspectives not only in nano-medicine, as described above, but also in Regenerative Medicine with the development of new biomedical devices with ability of remote activation and switching of high socio-economic impact. Indeed, the development of scaffolds enhancing

bone regeneration by remote magnetic activation is an emerging concept in Regenerative Medicine (Assiotis *et al.*, 2012), since it has been demonstrated that weak magnetic or pulsed electromagnetic fields are effective in promoting bone fracture healing, spinal fusion and bone ingrowth in animal models (Chalidis *et al.*, 2011; Glazer *et al.*, 1997; Grace *et al.*, 1998; Yan *et al.*, 1998; Panseri *et al.*, 2012). Moreover, several previous works have demonstrated that magnetic scaffolds have a positive effect on osteoinductivity with and without application of external magnetic forces. However, the incorporation of magnetic phases into ceramic bone scaffolds is made difficult by the need of consolidating green ceramic bodies by a high temperature treatment that often provokes oxidation of superparamagnetic iron oxides and losing of magnetic properties (Tampieri *et al.*, 2014). In this respect a bio-inspired fabrication process such as biomineralization (see previous paragraph) permitted to retain the fine physicochemical features determining enhanced bioactivity in FeHA and to develop 3-D magnetic hybrid scaffolds with mineralization extent that could be tailored from cartilage to bone-like level (Banobre-Lopez *et al.*, 2011), thus permitting its application as a magnetic scaffold, very promising to boost regeneration of critical size bone and osteochondral defects.

Future Perspectives

Under the pressure of still unmet industrial and societal needs requiring smart materials and devices, material science is today experiencing great impulses, with the purpose to discover new ways for fabrication of smart 3-D bioceramics. A prominent target is the achievement of consolidated bodies by low energy processes, aiming to retain nanostructure and biofunctional ability typical of nanocrystalline, metastable phase compositions. In future decades, material scientists will be called to explore completely new pathways based on chemical reactions carried out in non-equilibrium conditions rather than under stable thermodynamic regimes.

A main general concept emerging today in Material Science is to draw inspiration from Nature to obtain functional 3-D ceramics: to this purpose, the hydrophobic features of lotus flower, the adhesive ability of geckos, the inimitable mechanical properties of web spider and the dynamically active mechanical response of organisms such as the Echinoderms are just some examples that scientists will try to mimic. Particularly, the achievement of materials able of complex and adaptive mechanical performance is among the hardest challenges for biomaterial scientists. In fact, in Regenerative Medicine it is increasingly evident that, besides chemical recognition by cells, appropriate dynamic mechanical stimulation is key to activate and support the formation and maturation of new load-bearing tissues. The development of such new devices could open to regeneration of complex anatomical regions subjected to loading. Particularly relevant in this respect are the osteochondral tissues of the joints which, in modern life, are frequently subjected to degenerative pathologies and thus seriously jeopardize the mobility and quality of life of an ever increasing number of aged patients. In this respect, new mechanically active scaffolds could be the key to stimulate the simultaneous regeneration of bone and the articular cartilage in large degenerated regions, targeting the achievement of a completely resorbable “Bioprosthesis” completely replacing the invasive metal-based prosthesis.

Another growing field in biomaterial science is the development of functional nanoparticles for nanomedicine. Today, the use of toxic metal or metal oxide NPs is pushing scientists to complex approaches for creating bio-friendly interfaces with cells. On the other hand, NPs are called to function as active devices for theranostics, that is bio-sensors and drug deliverers. Biomimetic and bioactive ceramic nanoparticles are emerging as relevant candidates to replace metal-based devices, thanks to their chemical affinity with human hard tissues, ability to directly induce a positive cell response by chemical recognition, and to their reabsorbability, thus opening to safer applications and ability to provide clearer response for disease detection. This has great relevance for more targeted and personalized applications in nanomedicine and can respond to urgent needs related to the ageing of the population, envisaged to reach the maximum peak within the incoming two decades.

References

- Amer, M.H., Rose, F.R.A.J., Shakesheff, K.M., Modo, M., White, L.J., 2017. Translational considerations in injectable cell-based therapeutics for neurological applications: Concepts, progress and challenges. *npj Regenerative Medicine* 2, 23.
- Assiotis, A., Sachinis, N.P., Chalidis, B.E., 2012. Pulsed electromagnetic fields for the treatment of tibial delayed unions and nonunions. A prospective clinical study and review of the literature. *Journal of Orthopaedic Surgery and Research* 7, 24.
- Banobre-Lopez, M., Pineiro-Redondo, Y., De Santis, R., *et al.*, 2011. Poly(caprolactone) based magnetic scaffolds for bone tissue engineering. *Journal of Applied Physics* 109.
- Barbour, K.E., Helmick, C.G., Boring, M., Brady, T.J., 2017. Vital signs: Prevalence of doctor-diagnosed arthritis and arthritis-attributable activity limitation – United States, 2013–2015. *Morbidity and Mortality Weekly Report* 66, 246–253.
- Bartold, P.M., McCulloch, C.A., Narayanan, A.S., Pitaru, S., 2000. Tissue engineering: A new paradigm for periodontal regeneration based on molecular and cell biology. *Periodontol* 24, 253–269.
- Benyus, J.M., 1997. *Biomimicry: Innovation Inspired by Nature*. New York: Morrow.
- Bertinetti, L., Drouet, C., Combes, C., *et al.*, 2009. Surface characteristics of nanocrystalline apatites: Effect of Mg surface enrichment on morphology, surface hydration species, and cationic environments. *Langmuir* 25, 5647–5654.
- Beruto, D.T., Botter, R., 2000. Liquid-like H₂O adsorption layers to catalyze the Ca (OH)₂/CO₂ solid–gas reaction and to form a non-protective solid product layer at 20°C. *Journal of the European Ceramic Society* 20, 497–503.
- Bodineau, A., Folliquet, M., Segulier, S., 2009. Tissue senescence and modifications of oral ecosystem in the elderly: Risk factors for mucosal pathologies. *Current Aging Science* 2, 109–120.

- Bortolomai, I., Sandri, M., Draghici, E., *et al.*, 2019. Gene modification and three-dimensional scaffolds as novel tools to allow the use of postnatal thymic epithelial cells for thymus regeneration approaches. *Stem Cells Translational Medicine* 8 (10), 1107–1122.
- Buckwalter, J.A., Woo, S.L., Goldberg, V.M., *et al.*, 1993. Soft-tissue aging and musculoskeletal function. *Journal of Bone and Joint Surgery* 75, 1533–1548.
- Campodoni, E., Adamiano, A., Dozio, S.M., *et al.*, 2016. Development of innovative hybrid and intrinsically magnetic nanobeads as a drug delivery system. *Nanomedicine* 11, 2119–2130.
- Cao, T., Ho, K.H., Teoh, S.H., 2003. Scaffold design and in vitro study of osteochondral coculture in a three-dimensional porous polycaprolactone scaffold fabricated by fused deposition modeling. *Tissue Engineering* 9 (Suppl. 1), S103–S112.
- Cazalbou, S., Eichert, D., Ranz, X., *et al.*, 2005. Ion exchanges in apatites for biomedical application. *Journal of Materials Science: Materials in Medicine* 16, 405–409.
- Chalidis, B., Sachinis, N., Assiotis, A., Maccauro, G., 2011. Stimulation of bone formation and fracture healing with pulsed electromagnetic fields: Biologic responses and clinical implications. *International Journal of Immunopathology and Pharmacology* 24, 17–20.
- Chen, H., Ouyang, W., Lawuyi, B., Prakash, S., 2006. Genipin cross-linked alginate-chitosan microcapsules: Membrane characterization and optimization of cross-linking reaction. *Biomacromolecules* 7, 2091–2098.
- Chen, J., Chen, H., Li, P., *et al.*, 2011. Simultaneous regeneration of articular cartilage and subchondral bone in vivo using MSCs induced by a spatially controlled gene delivery system in bilayered integrated scaffolds. *Biomaterials* 32, 4793–4805.
- Clavijo-Jordan, V., Kodibagkar, V.D., Beeman, S.C., Hann, B.D., Bennett, K.M., 2012. Principles and emerging applications of nanomagnetic materials in medicine. *Wiley Interdisciplinary Reviews Nanomedicine and Nanobiotechnology* 4, 345–365.
- Dahl, S., Allain, P., Marie, P., *et al.*, 2001. Incorporation and distribution of strontium in bone. *Bone* 28, 446–453.
- De, S., Robinson, D., 2003. Polymer relationships during preparation of chitosan–alginate and poly-L-lysine–alginate nanospheres. *Journal of Controlled Release* 89, 101–112.
- Dye, B.A., 2012. Global periodontal disease epidemiology. *Periodontol* 58, 10–25.
- Eiselt, P., Yeh, J., Latvala, R.K., Shea, L.D., Mooney, D.J., 2000. Porous carriers for biomedical applications based on alginate hydrogels. *Biomaterials* 21, 1921–1927.
- Ethgen, O., Reginster, J.Y., 2004. Degenerative musculoskeletal disease. *Annals of the Rheumatic Diseases* 63, 1–3.
- Ganguly, R., Puri, I.K., 2010. Microfluidic transport in magnetic MEMS and bioMEMS. *Wiley Interdisciplinary Reviews Nanomedicine and Nanobiotechnology* 2, 382–399.
- Glazer, P.A., Heilmann, M.R., Lotz, J.C., Bradford, D.S., 1997. Use of electromagnetic fields in a spinal fusion. A rabbit model. *Spine* 22, 2351–2356.
- Gloria, A., Russo, T., D'Amora, U., *et al.*, 2013. Magnetic poly(epsilon-caprolactone)/iron-doped hydroxyapatite nanocomposite substrates for advanced bone tissue engineering. *Journal of the Royal Society Interface* 10. (20120833).
- Goncalves, P.F., Sallum, E.A., Sallum, A.W., *et al.*, 2005. Dental Cementum Reviewed: Development, Structure, Composition, Regeneration and Potential Functions.
- Grace, K.L., Revell, W.J., Brookes, M., 1998. The effects of pulsed electromagnetism on fresh fracture healing: osteochondral repair in the rat femoral groove. *Orthopedics* 21, 297–302.
- Hajishengallis, G., 2010. Too old to fight? Aging and its toll on innate immunity. *Molecular Oral Microbiology* 25, 25–37.
- Haumschild, M.S., Haumschild, R.J., 2009. The importance of oral health in long-term care. *Journal of the American Medical Directors Association* 10, 667–671.
- Henderson, I., Lavigne, P., Valenzuela, H., Oakes, B., 2007. Autologous chondrocyte implantation: Superior biologic properties of hyaline cartilage repairs. *Clinical Orthopaedics and Related Research* 455, 253–261.
- Ho, S.P., Yu, B., Yun, W., *et al.*, 2009. Structure, chemical composition and mechanical properties of human and rat cementum and its interface with root dentin. *Acta Biomaterialia* 5, 707–718.
- Hootman, J.M., Helmick, C.G., Barbour, K.E., Theis, K.A., Boring, M.A., 2016. Updated projected prevalence of self-reported doctor-diagnosed arthritis and arthritis-attributable activity limitation among US adults, 2015–2040. *Arthritis & Rheumatology* 68, 1582–1587.
- Hou, R., Zhang, G., Du, G., *et al.*, 2013. Magnetic nanohydroxyapatite/PVA composite hydrogels for promoted osteoblast adhesion and proliferation. *Colloids and Surfaces B: Biointerfaces* 103, 318–325.
- Hutmacher, D.W., 2000. Scaffolds in tissue engineering bone and cartilage. *Biomaterials* 21, 2529–2543.
- Hutmacher, D.W., Hutmacher, D.W., Teoh, S.H., *et al.*, 2000. Design and Fabrication of a 3D Scaffold for Tissue Engineering Bone. Agrawal, C.M., Parr, J., Lin, S. (Eds.), West Conshohocken, PA: ASTM International.
- Iafisco, M., Sandri, M., Panseri, S., *et al.*, 2013. Magnetic bioactive and biodegradable hollow Fe-doped hydroxyapatite coated poly(L-lactic) acid micro-nanospheres. *Chemistry of Materials* 25, 2610–2617.
- Iafisco, M., Delgado López, J.M., Drouet, C., 2014a. Nanocrystalline Apatites: Synthesis, Physical-Chemical and Thermodynamic Characterization.
- Iafisco, M., Ruffini, A., Adamiano, A., Sprio, S., Tampieri, A., 2014b. Biomimetic magnesium–carbonate-apatite nanocrystals endowed with strontium ions as anti-osteoporotic trigger. *Materials Science and Engineering: C* 35, 212–219.
- Iannotti, V., Adamiano, A., Ausanio, G., *et al.*, 2017. Fe-doping-induced magnetism in nano-hydroxyapatites. *Inorganic Chemistry* 56, 4446–4458.
- Jiang, M., Terra, J., Rossi, A., *et al.*, 2002. Fe²⁺/Fe³⁺ substitution in hydroxyapatite: Theory and experiment. *Physical Review B* 66, 224107.
- Kingsbury, D.J., Bader-Meunier, B., Patel, G., *et al.*, 2014. Safety, effectiveness, and pharmacokinetics of adalimumab in children with polyarticular juvenile idiopathic arthritis aged 2 to 4 years. *Clinical Rheumatology* 33, 1433–1441.
- Knutsen, G., Engebretsen, L., Ludvigsen, T.C., *et al.*, 2004. Autologous chondrocyte implantation compared with microfracture in the knee. A randomized trial. *Journal of Bone and Joint Surgery* 86-a, 455–464.
- Kon, E., Delcogliano, M., Filardo, G., *et al.*, 2010. Orderly osteochondral regeneration in a sheep model using a novel nano-composite multilayered biomaterial. *Journal of Orthopaedic Research* 28, 116–124.
- Kraeutler, M.J., Belk, J.W., Purcell, J.M., McCarty, E.C., 2018. Microfracture versus autologous chondrocyte implantation for articular cartilage lesions in the knee: A systematic review of 5-year outcomes. *American Journal of Sports Medicine* 46, 995–999.
- Krishnakumar, G.S., Gostynska, N., Dapporto, M., *et al.*, 2018. Evaluation of different crosslinking agents on hybrid biomimetic collagen-hydroxyapatite composites for regenerative medicine. *International Journal of Biological Macromolecules* 106, 739–748.
- Launey, M.E., Buehler, M.J., Ritchie, R.O., 2010. On the mechanistic origins of toughness in bone. *Annual Review of Materials Research* 40, 25–53.
- Lee, C.H., Hajibandeh, J., Suzuki, T., *et al.*, 2014. Three-dimensional printed multiphase scaffolds for regeneration of periodontium complex. *Tissue Eng Part A* 20, 1342–1351.
- Lewinski, N., Colvin, V., Drezek, R., 2008. Cytotoxicity of nanoparticles. *Small* 4, 26–49.
- Li, Y., Li, Q., Zhu, S., *et al.*, 2010. The effect of strontium-substituted hydroxyapatite coating on implant fixation in ovariectomized rats. *Biomaterials* 31, 9006–9014.
- Limonov, M.F., Richard, M., 2016. Optical Properties of Photonic Structures: Interplay of Order and Disorder. CRC Press.
- Linde, A., Goldberg, M., 1993. Dentinogenesis. *Critical Reviews in Oral Biology & Medicine* 4, 679–728.
- Liu, D., Yang, F., Xiong, F., Gu, N., 2016. The smart drug delivery system and its clinical potential. *Theranostics* 6, 1306–1323.
- Liu, H., Slamovich, E.B., Webster, T.J., 2006. Less harmful acidic degradation of poly (lactic-co-glycolic acid) bone tissue engineering scaffolds through titania nanoparticle addition. *International Journal of Nanomedicine* 1, 541.
- Maeda, H., Tomokiyo, A., Wada, N., *et al.*, 2014. Regeneration of the periodontium for preservation of the damaged tooth. *Histology & Histopathology* 29, 1249–1262.
- Mann, S., 2001. Biomimeralization: Principles and Concepts in Bioinorganic Materials Chemistry. Oxford University Press.
- Mareziak, M., Marycz, K., Tomaszewski, K.A., Kornicka, K., Henry, B.M., 2016. The influence of aging on the regenerative potential of human adipose derived mesenchymal stem cells. *Stem Cells International*. (2152435). doi:10.1155/2016/2152435.
- Martin, I., Obradovic, B., Treppo, S., *et al.*, 2000. Modulation of the mechanical properties of tissue engineered cartilage. *Biorheology* 37, 141–147.
- Meng, J., Zhang, Y., Qi, X., *et al.*, 2010. Paramagnetic nanofibrous composite films enhance the osteogenic responses of pre-osteoblast cells. *Nanoscale* 2, 2565–2569.

- Meng, J., Xiao, B., Zhang, Y., *et al.*, 2013. Super-paramagnetic responsive nanofibrous scaffolds under static magnetic field enhance osteogenesis for bone repair in vivo. *Scientific Reports* 3, 2655.
- Mertens, M.E., Hermann, A., Bühren, A., *et al.*, 2014. Iron oxide-labeled collagen scaffolds for non-invasive MR imaging in tissue engineering. *Advanced Functional Materials* 24, 754–762.
- Murray, C.J., Vos, T., Lozano, R., *et al.*, 2012. Disability-adjusted life years (DALYs) for 291 diseases and injuries in 21 regions, 1990–2010: A systematic analysis for the Global Burden of Disease Study 2010. *Lancet* 380, 2197–2223.
- Nappini, S., Bonini, M., Bombelli, F.B., *et al.*, 2011. Controlled drug release under a low frequency magnetic field: Effect of the citrate coating on magnetoliposomes stability. *Soft Matter* 7, 1025–1037.
- Orlando, B., Giacomelli, L., Ricci, M., Barone, A., Covani, U., 2013. Leader genes in osteogenesis: A theoretical study. *Archives of Oral Biology* 58, 42–49.
- Panseri, S., Cunha, C., D'Alessandro, T., *et al.*, 2012. Intrinsically superparamagnetic Fe-hydroxyapatite nanoparticles positively influence osteoblast-like cell behaviour. *Journal of nanobiotechnology* 10, 32.
- Panseri, S., Russo, A., Sartori, M., *et al.*, 2013. Modifying bone scaffold architecture in vivo with permanent magnets to facilitate fixation of magnetic scaffolds. *Bone* 56, 432–439.
- Panseri, S., Sandri, M.M., Iafisco, M., *et al.*, 2016. Magnetic labelling of mesenchymal stem cells with iron-doped hydroxyapatite nanoparticles as tool for cell therapy. *Journal of Biomedical Nanotechnology* 12 (5), 909–921.
- Patrício, T.M.F., Panseri, S., Montesi, M., *et al.*, 2019. Superparamagnetic hybrid microspheres affecting osteoblasts behaviour. *Materials Science and Engineering: C* 96, 234–247.
- Patrício, T.M.F., Panseri, S., Sandri, M., Tampieri, A., Sprio, S., 2017. New bioactive bone-like microspheres with intrinsic magnetic properties obtained by bio-inspired mineralisation process. *Materials Science and Engineering: C* 77, 613–623.
- Plouffe, B.D., Murthy, S.K., Lewis, L.H., 2015. Fundamentals and application of magnetic particles in cell isolation and enrichment: A review. *Reports on progress in physics* 78, 016601.
- Qian, S., Zhu, K., Pang, X., *et al.*, 2013. Influence of sintering temperature on electrical properties of $(K_{0.4425}Na_{0.52}Li_{0.0375})(Nb_{0.8825}Sb_{0.07}Ta_{0.0475})O_3$ ceramics without phase transition induced by sintering temperature. *Journal of Advanced Ceramics* 2, 353–359.
- Rey, C., Collins, B., Goehl, T., Dickson, I., Glimcher, M., 1989. The carbonate environment in bone mineral: A resolution-enhanced Fourier transform infrared spectroscopy study. *Calcified Tissue International* 45, 157–164.
- Rezwani, K., Chen, Q.Z., Blaker, J.J., Boccaccini, A.R., 2006. Biodegradable and bioactive porous polymer/inorganic composite scaffolds for bone tissue engineering. *Biomaterials* 27, 3413–3431.
- Roulland, F., Allainmat, G., Pollet, M., Marinel, S., 2005. Low temperature sintering of the binary complex perovskite oxides $xBa(Zn_{1/3}Ta_{2/3})O_3 + (1-x)Ba(Mg_{1/3}Ta_{2/3})O_3$. *Journal of the European Ceramic Society* 25, 2763–2768.
- Sandri, M., Filardo, G., Kon, E., *et al.*, 2016. Fabrication and pilot in vivo study of a collagen-BDDGE-elastin core-shell scaffold for tendon regeneration. *Frontiers in Bioengineering and Biotechnology* 4, 52.
- Schumacher, M., Gelinsky, M., 2015. Strontium modified calcium phosphate cements – Approaches towards targeted stimulation of bone turnover. *Journal of Materials Chemistry B* 3, 4626–4640.
- Shan, D., Shi, Y., Duan, S., *et al.*, 2013. Electrospun magnetic poly(L-lactide) (PLLA) nanofibers by incorporating PLLA-stabilized Fe_3O_4 nanoparticles. *Materials Science and Engineering C: Materials for Biological Applications* 33, 3498–3505.
- Singh, N., Jenkins, G.J., Asadi, R., Doak, S.H., 2010. Potential toxicity of superparamagnetic iron oxide nanoparticles (SPION). *Nano Review* 1.
- Sprio, S., Tampieri, A., Landi, E., *et al.*, 2008. Physico-chemical properties and solubility behaviour of multi-substituted hydroxyapatite powders containing silicon. *Materials Science and Engineering: C* 28, 179–187.
- Sprio, S., Sandri, M., Iafisco, M., *et al.*, 2014. Chapter 9 – Composite biomedical foams for engineering bone tissue. In: Netti, P.A. (Ed.), *Biomedical Foams for Tissue Engineering Applications*. Woodhead Publishing.
- Sprio, S., Fricia, M., Maddalena, G.F., Nataloni, A., Tampieri, A., 2016. Osteointegration in cranial bone reconstruction: A goal to achieve. *Journal of Applied Biomaterials & Functional Materials* 14, 470–476.
- Sprio, S., Campodoni, E., Sandri, M., *et al.*, 2018. A graded multifunctional hybrid scaffold with superparamagnetic ability for periodontal regeneration. *International Journal of Molecular Sciences* 19.
- Suryanarayana, C., 1999. *Non-Equilibrium Processing of Materials*. Elsevier.
- Tampieri, A., Sprio, S., Sandri, M., Valentini, F., 2011. Mimicking natural bio-mineralization processes: A new tool for osteochondral scaffold development. *Trends Biotechnology* 29, 526–535.
- Tampieri, A., Celotti, G., Landi, E., *et al.*, 2003. Biologically inspired synthesis of bone-like composite: Self-assembled collagen fibers/hydroxyapatite nanocrystals. *Journal of Biomedical Materials Research A* 67, 618–625.
- Tampieri, A., Sprio, S., Ruffini, A., *et al.*, 2009. From wood to bone: Multi-step process to convert wood hierarchical structures into biomimetic hydroxyapatite scaffolds for bone tissue engineering. *Journal of Materials Chemistry* 19, 4973–4980.
- Tampieri, A., D'Alessandro, T., Sandri, M., *et al.*, 2012. Intrinsic magnetism and hyperthermia in bioactive Fe-doped hydroxyapatite. *Acta Biomaterialia* 8, 843–851.
- Tampieri, A., Iafisco, M., Sandri, M., *et al.*, 2014. Magnetic bioinspired hybrid nanostructured collagen-hydroxyapatite scaffolds supporting cell proliferation and tuning regenerative process. *ACS Applied Materials & Interfaces* 6, 15697–15707.
- Turner, P.J., Chen, C.G., Ionova-Martin, S., *et al.*, 2010. Osteopontin deficiency increases bone fragility but preserves bone mass. *Bone* 46, 1564–1573.
- Vos, T., Flaxman, A.D., Naghavi, M., *et al.*, 2012. Years lived with disability (YLDs) for 1160 sequelae of 289 diseases and injuries 1990–2010: A systematic analysis for the Global Burden of Disease Study 2010. *Lancet* 380, 2163–2196.
- Wegst, U.G.K., Bai, H., Saiz, E., Tomsia, A.P., Ritchie, R.O., 2014. Bioinspired structural materials. *Nature Materials* 14, 23.
- Williams, R.C., Barnett, A.H., Claffey, N., *et al.*, 2008. The potential impact of periodontal disease on general health: A consensus view. *Current Medical Research and Opinion* 24, 1635–1643.
- Wongmaneeerung, R., Yimnirun, R., Ananta, S., 2009. Fabrication and characterization of perovskite ferroelectric PMN/PT ceramic nanocomposites. *Journal of Materials Science* 44, 5428–5440.
- Yan, Q.C., Tomita, N., Ikada, Y., 1998. Effects of static magnetic field on bone formation of rat femurs. *Medical Engineering & Physics* 20, 397–402.
- Zhang, J., Liu, W., Schnitzler, V., Tancrét, F., Boulter, J.M., 2014. Calcium phosphate cements for bone substitution: chemistry, handling and mechanical properties. *Acta Biomaterialia* 10, 1035–1049.
- Zhao, D., Zhuo, R.-X., Cheng, S.-X., 2012. Alginate modified nanostructured calcium carbonate with enhanced delivery efficiency for gene and drug delivery. *Molecular BioSystems* 8, 753–759.

Assessment of Mechanical Properties of Bioceramics

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Introduction

Ceramics are characterized by strong atomic bonds and in consequence exhibit a high stiffness expressed by a high value of Young's modulus and a brittle behavior which means without plastic deformation. Ceramics present a low tensile strength and a high compressive strength. The mechanical behavior is very sensitive to the presence of surface or volume flaws like grooves and pores. Ceramics have also a high hardness and so exhibit a good wear resistance. Owing to all these mechanical properties and their bio-inertia, aluminum, and zirconium oxides and composites are commonly used as structural parts like hip joint, knee prosthesis, dental implant. Contrarily, other ceramics such as calcium phosphate, carbonate or silicate, whose chemical composition is close to that of natural bone, are rather used for their osteoconductive properties as bone repairing material. In this paper, the mechanical behavior of these ceramics is largely described.

Mechanical Behavior

Elastic Behavior

The elastic modulus or Young's modulus depends on the bond stiffness and the interatomic distance. Ceramics exhibit two bond types: ionic and covalent which have a high bond stiffness. So, the elastic modulus of ceramics is rather high. Diamond has a Young's modulus equal to 1000 GPa, alumina 390 GPa, zirconia 205 GPa, hydroxyapatite 110 GPa, and glass 70 GPa.

The elastic modulus decreases with increasing the volume fraction of porosity P following the empirical equation:

$$E = E_0(1 - 1.9P + 0.9P^2) \quad (1)$$

where E_0 is the elastic modulus of the dense material.

So, the elastic modulus of alumina decreases from 390 GPa to 100 GPa for a volume fraction porosity equal to 40%.

The elastic modulus decreases equally when microcracks appear.

Hardness

Due to the strong interatomic bonds, ceramics exhibit high hardness. Diamond is the hardest material (Vickers hardness $HV = 9000$), alumina $HV = 2300$, zirconia $HV = 1400$. The hardness as the elastic modulus depends on the porosity.

Mechanical Strength

The mechanical strength of ceramics exhibits large variations and depends on the grain size, porosity, reinforcement mechanisms. The ceramics are brittle and thus, the mechanical strength depends essentially on the flaw (or crack) size. This size is related to the microstructure obtained after fabrication (pores, flaws, cracks). The strength variation is related to the size distribution of the flaws. This variation can be described by using a statistical function and the empirical Weibull approach is very often used. This approach based on the weakest link gives the failure probability as a function of stress σ and volume V of ceramic

$$P(V) = \exp\left[-V\left(\frac{\sigma - \sigma_u}{\sigma}\right)^m\right] \quad (2)$$

σ_u = stress below which failure has zero probability, σ_0 = normalizing parameter and m = Weibull modulus.

The Weibull modulus reflects the width of the strength distribution. The higher m is, the lower is the strength variation. Values of m between 5 and 20 are often obtained. An example of such a distribution for alumina is given by the Fig. 1 (the Weibull modulus m is about 20). Practically, the strength variability must be reduced and highest m values must be obtained.

As for elastic modulus, the mechanical strength decreases with increasing the volume fraction of porosity. For alumina, the bending strength can vary from 300 MPa down to 50 MPa for an alumina with 30% porosity. The decrease can be described by the following empirical equation:

$$\sigma = \sigma_0 \exp(-\alpha P) \quad (3)$$

with σ = mechanical strength for dense ceramic.

α = constant (in the range 4–7).

So, porous ceramics exhibit low mechanical strength.

This effect of porosity is very significant for the use of calcium phosphate bone substitutes and has a detrimental influence on the mechanical strength which influences the device handiness for surgeons. Fig. 2 shows the variation of compressive strength of two bone

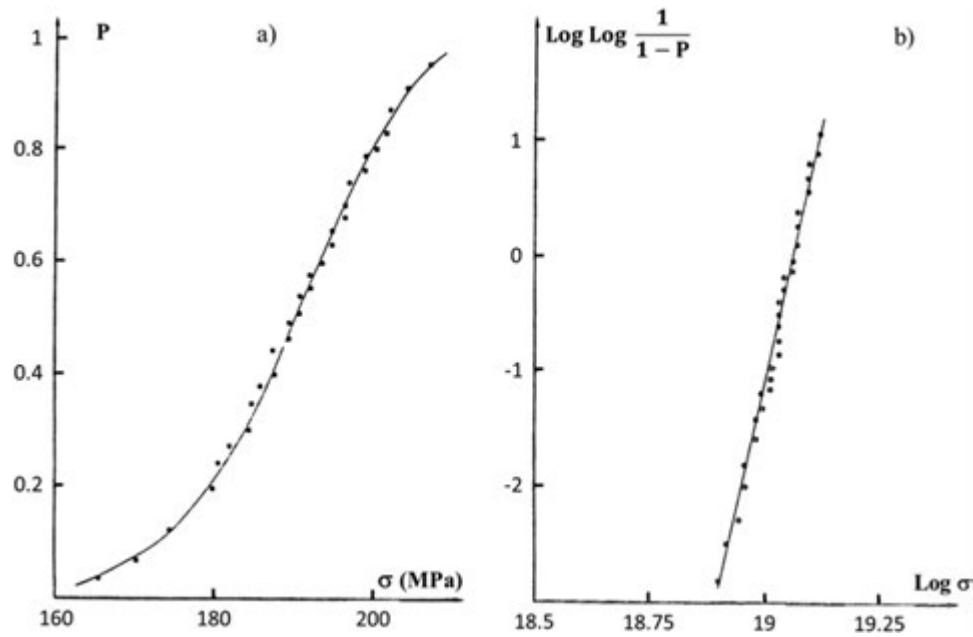


Fig. 1 (a) Failure probability of alumina as a function of 4-points bending stress; (b) Weibull analysis (Eq. (2): the slope is equal to m).

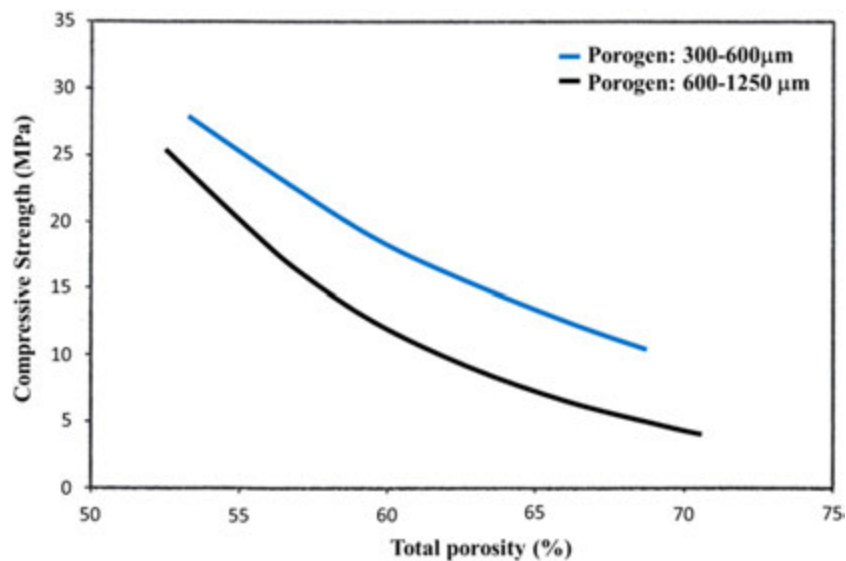


Fig. 2 Compressive strength versus pore volume fraction for bone substitutes processed with 300–600 μm and 600–1250 μm porogen particles. From Bignon, A., Chouteau, J., Chevalier, J., *et al.*, 2003. Effect of micro- and macroporosity of bone substitutes on their mechanical properties and cellular response. *Journal of Materials Science: Materials in Medicine* 14, 1089–1097.

substitutes constituted of hydroxyapatite (HAP) and β -tricalcium phosphate (β -TCP) with a weight ratio of 70:30 processed with two sizes of porogen particles (300–600 μm and 600–1250 μm) and sintered at 1125°C during 15 h (Bignon *et al.*, 2003). Two types of pores must be considered: micro- and macroporosities, the last ones being of major importance, ceramics being sensitive to the largest defects. The results obtained for the two porogen particle sizes are well described by Eq. (3) but with different α parameters ($\alpha = 2$ and 4 for 300–600 μm and 600–1250 μm sizes, respectively). The largest defects being macropores, the strength of 600–1250 μm ceramics is lower. The strength depends also on the grain size and the presence of micropores: the larger the grain size, the lower the strength.

Toughness

Based on fracture mechanics, the fracture toughness of a brittle ceramic corresponding to the crack growth resistance can be evaluated by the critical stress intensity factor K_{IC} given by the Griffith criterion

$$K_{IC} = \sigma_f Y a_c^{1/2} \quad (4)$$

where σ_f = fracture strength, a_c = critical flaw size and Y = non dimensional geometrical factor.

The fracture toughness of ceramics is in the range 1–10 MPa m^{1/2} and the presence of flaws or cracks with a size of the order of some μm is responsible for the ceramic failure.

Very often, the toughness increases with crack growth and the fracture behavior is described by a crack growth resistance curve (R-curve), representing the stress intensity factor K_R with the crack extension Δa . Generally, K_R increases with a decreasing slope from an initial value (intrinsic fracture toughness) up to a plateau. The crack becomes unstable when the strength σ_f is reached with $K=K_R$ and $dK/da=dK_R/da$. So, the strength improvement of ceramics is related to the slope of the R-curve and the early part of this R-curve.

In order to improve the mechanical properties, particularly toughness, several mechanisms of reinforcement can be used (Fantozzi and Chevalier, 2020): phase transformation, microcracking, crack deflection, crack bridging, and fiber or whisker reinforcement.

Microstructural Toughening

Concerning bioceramics, the most important used reinforcement mechanisms are grain (crack) bridging and transformation toughening. These toughening mechanisms act as crack-shielding mechanisms due to the closure stresses acting in the wake of the propagating crack. The resulting R-curve as a function of crack propagation Δa can be written as follows:

$$K_R(\Delta a) = K_0 + K_{sh}(\Delta a) \quad (5)$$

where K_0 = intrinsic fracture toughness, K_{sh} = toughening increment.

The toughening increment is higher for phase transformation (up to 15 MPa m^{1/2}) than for grain bridging (2–5 MPa m^{1/2}).

Grain (Crack) Bridging

This reinforcement occurs when a crack meets a grain (or a particle) without breaking it. An example of grain bridging in alumina is shown by Fig. 3. The crack-tip shielding is due to elastic and interfacial frictional stresses which reduce the crack opening. This shielding results in a reduction of the effective stress intensity factor and thus enhances the material toughness. The grain bridging magnitude depends on the grain size and aspect ratio. Elongated grains enhance the frictional bridging and pull-out and result in a more significant R-curve behavior. Fig. 4 shows such an effect for coarse grained alumina (El Attaoui *et al.*, 2005) which exhibits a higher fracture resistance when the grain size increases.

The increase of fracture toughness must lead to an increase of fracture strength following Eq. (4) if the critical flaw size is constant. But generally, for monolithic ceramics the flaw size varies as the grain size: $a_c = \alpha d_{\max}$, $d_{\max}$ = maximum grain size and α = constant (between 5 and 10). So, the increase of flaw size is more important than the increase of fracture toughness and thus the fracture strength decreases very often when the grain size increases. As a result, fine grain alumina ceramics exhibit better mechanical strength than coarse grain ones.

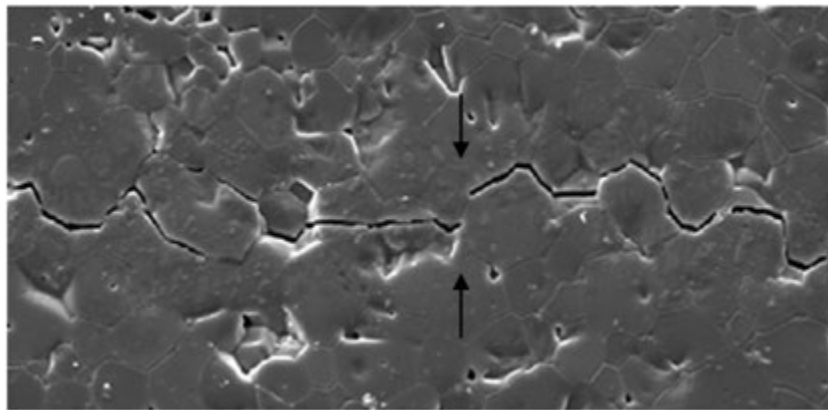


Fig. 3 SEM micrograph of grain bridging in alumina. From Fantozzi, G., Saadaoui, M., 2014. Toughness, fatigue and thermal shock of ceramics: Microstructural effects. In: Sarin, V.K., Llanes, L., Mari, D. (Eds.), *Comprehensive Hard Materials*. Elsevier, pp. 299–319.

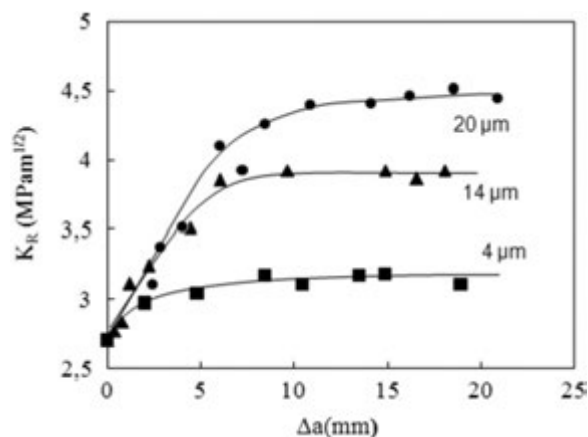


Fig. 4 K_R curves for alumina with different grain sizes. From Fantozzi, G., Saadaoui, M., 2014. Toughness, fatigue and thermal shock of ceramics: Microstructural effects. In: Sarin, V.K., Llanes, L., Mari, D. (Eds.), *Comprehensive Hard Materials*. Elsevier, pp. 299–319.

Transformation Toughening

Increase in mechanical strength and fracture toughness can be obtained by stress-induced phase transformation (Green *et al.*, 1989). The most significant results are observed for a large variety of zirconia-toughened ceramics (ZTC) which can be classified into different types following their microstructure (Hannink *et al.*, 2000):

- (1) Toughened ceramics with tetragonal zirconia particles in a ceramic matrix: the most known is zirconia toughened alumina (ZTA).
- (2) Partially stabilized zirconia (PSZ) constituted of tetragonal precipitates dispersed in a cubic zirconia matrix, obtained by doping with some stabilizers (as magnesia).
- (3) Tetragonal zirconia polycrystals (TZP) with the tetragonal phase retained at room temperature by addition of a stabilizer. The most commons are Y-TZP and Ce-TZP ceramics with yttria and ceria stabilizers respectively.

Transformation toughening is linked to the stress-induced martensitic tetragonal (t) to monoclinic (m) transformation of zirconia grains or particles which takes place in the wake of the crack. This phase transformation occurs with a volume increase (about 5%) and a shear strain which lead to the appearance of compressive stresses shielding the crack tip and hindering the crack opening. Therefore, the crack propagation needs an increase of the applied stress intensity factor in order to overcome the shielding contribution K_{sh} (Eq. (5)). The crack growth resistance increases and reaches a plateau corresponding to a steady-state transformation zone.

The increase of the transformation toughening is related to the stability of the tetragonal phase which depends on microstructural characteristics such as particle or grain size. There is a critical stress for transformation σ_c , the higher the grain size is, the lower is σ_c and therefore the higher are the volume fraction of transformed particles and the toughness increase. But, if the grain size becomes higher than a critical size, spontaneous transformation occurs during cooling and most grains or particles are transformed before crack propagation and the toughening disappears.

Phase transformation in ZTC is often accompanied by other mechanisms such as microcracking or grain bridging which can contribute also to the toughening.

Mechanical Properties of ZTC

Some mechanical properties of different ZTC are given in the Table 1.

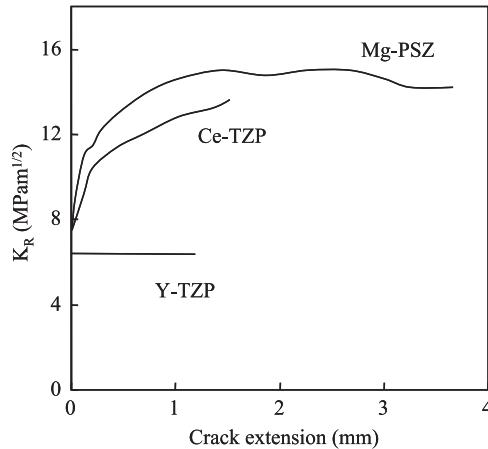
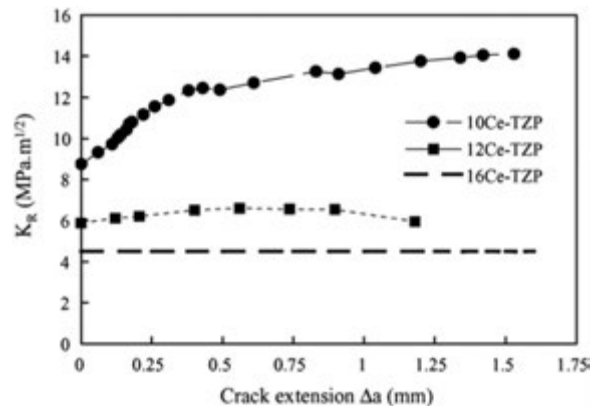
Crack growth resistance curves of some ZTC are shown in Fig. 5. It can be noticed that higher R-curve effect is observed for the Mg-PSZ or Ce-TZP ceramics.

Some interesting combinations of mechanical strength and fracture toughness have been obtained with Ce-TZP ceramics or composites (Touaiher *et al.*, 2018; El Attaoui *et al.*, 2007). As shown by Fig. 6, a strong R-curve behavior is observed for a ceria content of the order of 10–11 mol%, which is due to an autocatalytic phase transformation. If the ceria content is too high, the level of transformability is lower because the tetragonal phase is more stable and then the toughness is lower. Fig. 7 shows the autocatalytic transformation zone for the 10Ce-TZP ceramic observed during a crack propagation observed by double torsion test.

The variation of the mechanical strength versus the fracture toughness of Y-TZP, Ce-TZP, or Mg-PSZ ceramics is shown in Fig. 8. Y-TZP ceramics largely used for biomedical applications exhibit high strength (~ 1 GPa) with a moderate toughness. Besides, Ce-TZP or Mg-PSZ present high toughness with a moderate strength (~ 500 MPa). The fracture of high strength ceramics is governed by the intrinsic flaws whereas the high toughness ceramics exhibit a strength limited by the t-m transformation, the

Table 1 Mechanical properties of ZTC

Ceramic	Mg-PSZ	Y-TZP	ZTA	Ce-TZP
Density (g cm^{-3})	5.75	6.05	4–5	6.1–6.2
σ_f (MPa)	500–700	1000–1500	600–1000	400–800
K_{IC} ($\text{MPa m}^{1/2}$)	6–9	8–12	6–10	6–15
E (GPa)	185–205	200	250–350	190–200
Hardness HV (GPa)	11–12	12	16–18	7–13

**Fig. 5** K_R curves for different zirconia toughened ceramics. From Hannink, R.H.J., Kelly, P.M., Muddle, B.C., 2000. Transformation toughening in zirconia-containing ceramics. *Journal of the American Ceramic Society* 83, 461–487.**Fig. 6** K_R curves of Ce-TZP ceramics. From El Attaoui, H., Saadaoui, M., Chevalier, J., Fantozzi, G., 2007. Static and cyclic crack propagation in Ce-TZP ceramics with different amounts of transformation toughening. *Journal of the European Ceramic Society* 27, 483–486.

transformation zone size becoming comparable or larger than the intrinsic flaws and the strength is insensitive to the initial flaw size.

So, new Ce-TZP based composites have been developed recently with a microstructure refinement in order to improve the mechanical strength: Ce-TZP/alumina, Ce-TZP/ MgAl_2O_4 nanocomposites and platelets reinforced Ce-TZP composites with alumina and strontium or lanthanum aluminate (Touaiher *et al.*, 2018).

The Ce-TZP with 11.5 mol% CeO_2 , 8 vol% alumina, 8 vol% strontium aluminate exhibits a fracture toughness of $10.6 \text{ MPa m}^{1/2}$ with a bending strength higher than 700 MPa. Furthermore, this material does not present low temperature degradation.

Concerning ZTA ceramics, the reinforcement depends on the volume fraction of transforming particles, the particle size and the yttria content. Fracture toughness presents a maximum with increased zirconia content. This maximum occurs for higher zirconia content when the particle size decreases and is shifted towards high volume fraction as the yttria content increases. ZTA exhibit values of fracture toughness up to $10 \text{ MPa m}^{1/2}$ and mechanical strength up to 1 GPa.



Fig. 7 Transformation zone observed during crack propagation of a 10Ce-TZP ceramic. From El Attaoui, H., Saadaoui, M., Chevalier, J., Fantozzi, G., 2007. Static and cyclic crack propagation in Ce-TZP ceramics with different amounts of transformation toughening. *Journal of the European Ceramic Society* 27, 483–486.

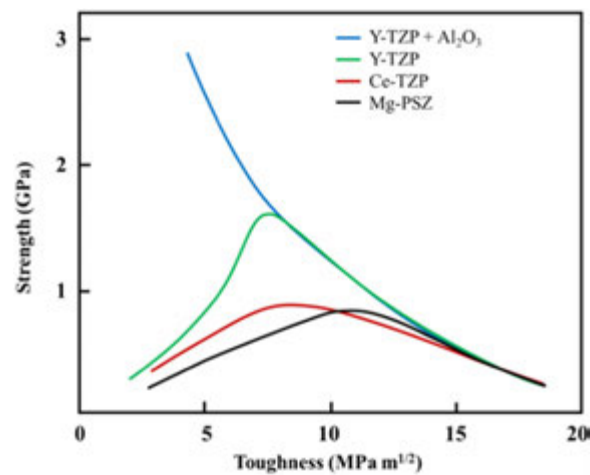


Fig. 8 Relation mechanical strength-fracture toughness for ZTC ceramics. From Swain, M.V., Rose, L.R.F., 1986. Strength limitations of transformation-toughened zirconia alloys. *Journal of the American Ceramic Society* 69, 511–518.

Subcritical Crack Growth

For many ceramics, the presence of a reactive environment provokes cracks to grow at a stress intensity factor lower than the fracture toughness K_c and can lead to delayed fracture. The basic mechanism responsible for this slow crack growth is the stress-enhanced chemical interaction between environmental species (as water) and the crack tip bonds, the crack growth rate being determined by the reaction kinetics. This slow crack growth is linked to the stress intensity factor K_I by a power law between the crack growth rate and K_I : Eq. (6) K_I^n

$$V = da/dt = A K_I^n \quad (6)$$

With A and n = constants depending on the material, cracking region and environment-ceramic interaction.

The lifetime prediction for ceramic components can be deduced from this slow crack growth rate by determining the time necessary to reach the critical flaw size given by Eq. (4) corresponding to the applied stress σ .

Typical V - K_I curves are shown in Fig. 9 for a 3Y-TZP zirconia doped with 3 mol% of Y_2O_3 . Under vacuum, water and air conditions, the presence of a threshold below which there is no propagation can be noticed. The V - K_I curve in air comprises three stages. For the stage I (low crack growth rates), the rate-limiting mechanism is the reaction between the ceramic and corrosive molecules (water) at the crack tip provoking the fracture of ceramic bonds. The stage II is controlled by the transport of molecules from the crack mouth up to the crack tip. The stage III takes place for higher crack rates and corresponds to the fracture of ceramics bonds without reaction with environment. In water, only the stage I occurs and under vacuum stage III appears for a stress intensity factor near K_{IC} .

The sensitivity of ceramic to stress assisted corrosion and slow crack growth is related to the aptitude of reaction with water and it is strongly linked to ionic fraction of the bond (higher the ionic fraction, higher the sensitivity).

For polycrystalline ceramics, the slow crack growth behavior is linked strongly to the microstructure, especially for reinforced ceramics.

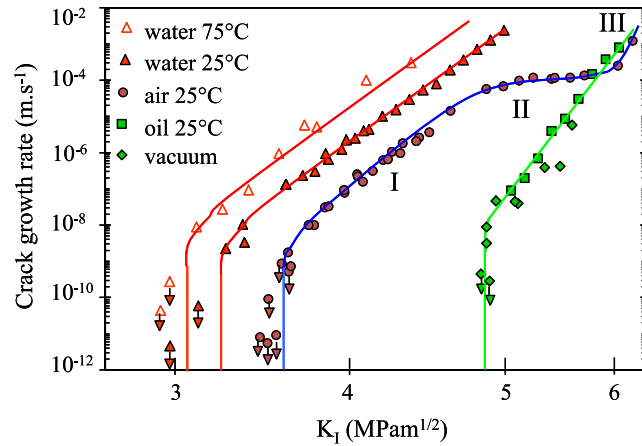


Fig. 9 Crack velocity V - K_I curves of a Y-TZP zirconia. From Chevalier, J., Fantozzi, G., 2005. Slow crack propagation in ceramics at the nano- and micro-scale: Effect of microstructure. In: Bradt, R.C., Munz, D., Sakai, M., White, K.W. (Eds.), *Fracture Mechanics of Ceramics 14*. New York: Springer, pp. 173–190.

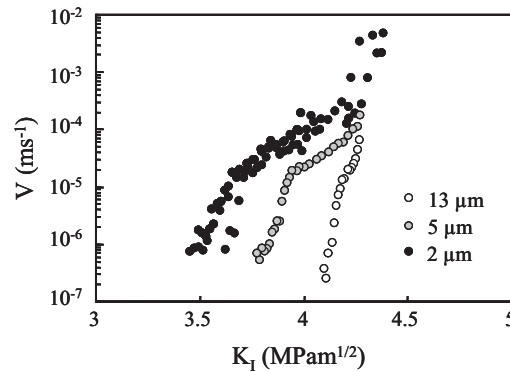


Fig. 10 Crack velocity V - K_I curves for three alumina with different grain sizes. From Ebrahimi, M.E., Chevalier, J., Fantozzi, G., 2000. Slow crack growth behavior of alumina ceramics. *Journal of Materials Research* 15, 142–147.

The driving force for slow crack growth corresponds to the effective crack tip stress intensity factor K_{tip} taking into account the crack shielding K_{sh} due to the reinforcement:

$$K_{tip} = K_I - K_{sh} \quad (7)$$

For non-transforming ceramics, the grain size has a significant effect on slow crack growth due to the grain bridging reinforcement. By increasing the grain size, the shielding effect of bridging increases. **Fig. 10** shows the V - K_I curves obtained in air for three polycrystalline alumina with different grain sizes.

The slow crack growth controlled by stress corrosion is very sensitive to the stress intensity factor in the stage I and when the grain size increases, the V - K_I curve is shifted toward higher stress intensity factor with a higher slope of the power law. Moreover, the threshold is higher for the coarse grained alumina than for the fine grained alumina.

It can be noticed that the shielding effect of grain bridging is observed only for the intergranular mode of fracture and for largest grain size, a shift of the V - K_I curve towards low stress intensity factor occurs corresponding to the appearance of a transgranular fracture mode without grain bridging effect (Ebrahimi *et al.*, 2000).

For zirconia toughened ceramics, the effect of phase transformation toughening on the slow crack growth must be taken into account. The transformation zone size increases with the applied stress and thus the shielding stress intensity factor is proportional to the applied stress intensity factor:

$$K_{sh} = C_{sh} K_I \quad (8)$$

C_{sh} is a parameter which increases with the material transformability.

The intrinsic mechanism of slow crack growth can be attributed to a stress corrosion mechanism at the crack tip and is given by

$$V = A_0 K_{tip}^n \quad (9)$$

A_0 = intrinsic parameter.

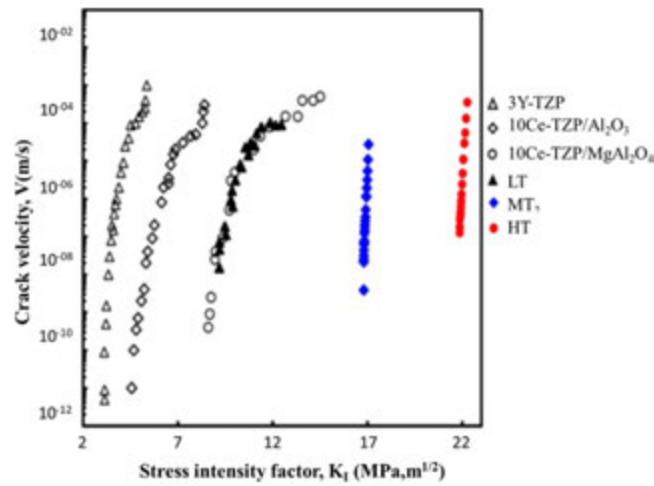


Fig. 11 Crack velocity V - K_I curves of Ce-TZP composites. From Touaiher, I., Saadaoui, M., Chevalier, J., Preiss, L., Reveron, H., 2018. Fracture behavior of Ce-TZP/alumina/aluminate composites with different amounts of transformation toughening. Influence of the testing methods. Journal of the European Ceramic Society 38, 1778–1789.

So, from Eqs. (7), (8) and (9), the V - K_I law when zirconia particles exhibit phase transformation becomes:

$$V = A_0(1 - C_{sh})^n K_I^n \quad (10)$$

The transformation toughening effect on slow crack growth shifts the V - K_I law towards the high stress intensity factors. C_{sh} depends on the stability of the tetragonal phase.

The slow crack growth curves of Ce-TZP zirconia composites are shown in Fig. 11 and compared with 3Y-TZP, Ce-TZP/alumina nanocomposite, and Ce-TZP/magnesium aluminate spinel (Touaiher *et al.*, 2018).

The Ce-TZP composites contain 8 vol% alumina and 8 vol% strontium hexa-aluminate with a CeO_2 stabilizer content of 11 and 11.5 mol%. One composite HT (sintered at 1500°C) corresponding to the lower ceria content (11 mol%) exhibits a large transformation zone, the LT composite (sintered at 1450°C) corresponds to the higher ceria content (11.5 mol%) and presents a lower transformability and the third one MT (11.5 mol%, sintered at 1500°C) exhibits a medium transformability.

For the MT and HT composites, the V - K_I curve is shifted toward very high toughness values, corresponding to a high value of C_{sh} (Eq. (8)): the higher the transformability, the higher the V - K_I shift and the threshold intensity factor K_{I0} . Transformation toughening requires zirconia particles with a size between the critical size for spontaneous transformation and the critical size for stress induced transformation.

Fig. 12 shows the microstructure of two ZTA composites (De Aza *et al.*, 2003): the first one A-10Z corresponds to a narrow distribution of nano-size zirconia particles (10 vol%) distributed in a micrometer alumina matrix.

The particle sizes between 100 and 600 nm correspond to the maximum amount of transformation toughening and the V - K_I curve is shifted toward higher K_I values, compared to alumina and Y-TZP (Fig. 13). The A-2.5Z nanocomposites obtained with 2.5 vol% zirconia nanoparticles exhibit a peculiar behavior: both fracture toughness and threshold are increased. The size of zirconia particles (< 100 nm) is below the critical size for the stress induced transformation and so, there is no transformation toughening. The reinforcement of this composite is due to a compressive residual stress field in the matrix which hinders the crack front opening.

Among ceramics for medical applications, hydroxyapatite is a good candidate in orthopedics owing to the composition similar to the mineral part of bones and teeth. Slow crack growth behavior of dense hydroxyapatite has been investigated by Benaqqa *et al.* (2005). Fig. 14 shows the V - K_I curve determined in air for a hydroxyapatite with a grain size of 2 μm . The slow crack growth occurs below the toughness (0.9 MPa $m^{1/2}$), presents a threshold around 0.6 MPa $m^{1/2}$ and exhibits the classical three stages I, II, and III consistent with the stress corrosion by water molecules observed in oxide ceramics. Stage I has a primordial importance since slow crack rates rule the lifetime in service.

Cyclic Fatigue

Ceramics are sensitive to cyclic fatigue, especially if they exhibit a significant crack growth resistance (R-curve). Cyclic loading enhances slow crack growth compared to static loading: crack growth rates can be several orders of magnitude higher than those obtained with a static loading. The crack growth rate is very sensitive to the maximum applied stress intensity factor K_{max} (high value of the exponent m) compared to the stress intensity factor range ΔK . It is given by the modified Paris law:

$$da/dt = A(\Delta K)^p K_{max}^m \quad (11)$$

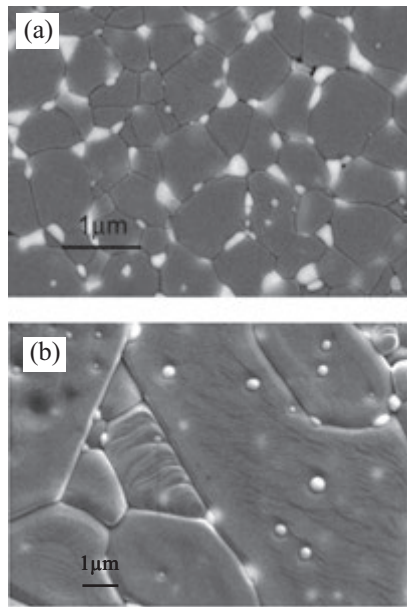


Fig. 12 SEM micrographs showing the microstructure of the A-10Z (a) and A-2.5Z (b) composites. From De Aza, A.H., Chevalier, J., Fantozzi, G., Schehl, M., Torrecillas, R., 2003. Slow crack growth behavior of zirconia-toughened alumina ceramics processed by different methods. *Journal of the American Ceramic Society* 86, 115–120.

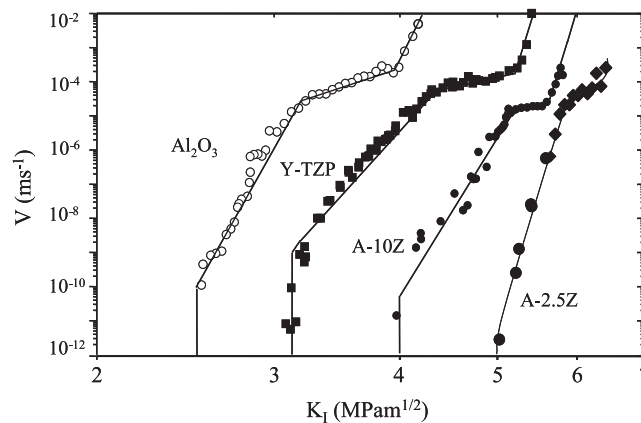


Fig. 13 Crack velocity V - K_I curves for alumina, 3Y-TZP zirconia and composites A-10Z and A-2.5Z. From De Aza, A.H., Chevalier, J., Fantozzi, G., Schehl, M., Torrecillas, R., 2003. Slow crack growth behavior of zirconia-toughened alumina ceramics processed by different methods. *Journal of the American Ceramic Society* 86, 115–120.

Moreover, the threshold below which no crack propagation occurs is much smaller for cyclic loading compared with static loading. The intrinsic response to static or cyclic loading is the same, but a degradation of the reinforcement takes place during cyclic loading. The cyclic loading behavior is linked to the microstructural aspects of the reinforcement.

For non-transforming ceramics, the toughening is due essentially to crack bridging. During cyclic loading, there is a degradation of the bridging zone and a decrease of the shielding capacity. Accumulation of frictional-wear damage at the grain/matrix interface and reduction of frictional sliding resistance of partially debonded grains diminish bridging stresses and thus enhance crack growth rates under cyclic loading (Ritchie *et al.*, 2000).

Fig. 15 shows an example of such degradation for a coarse grained alumina (20 μm) exhibiting a significant R-curve behavior shown in Fig. 4. The specimen is first monotonically loaded until fully bridged crack was formed (plateau of the R-curve). Then the specimen is submitted to cyclic mode during 10,000 cycles with a maximum load lower than the load reached at the end of the monotonic loading. The degradation can be quantified by the drop of K_R without crack growth. Then after an incubation period, cyclic fatigue crack growth is initiated with an increase of K_R due to new bridging zones. A new steady-state equilibrium is reached taking into account the balance between the shielding effect of bridging during fatigue crack propagation and the cyclic degradation. The plateau value after cyclic fatigue is lower, the bridging effect being less effective than during monotonic loading.

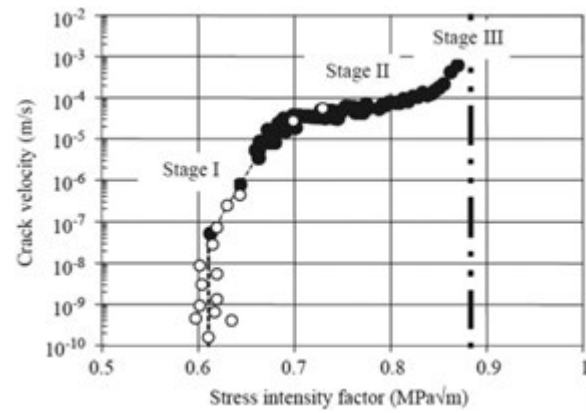


Fig. 14 Crack velocity V - K_I curves of hydroxyapatite in air. From Benaqqa, C., Chevalier, J., Saadaoui, M., Fantozzi, G., 2005. Slow crack growth behavior of hydroxyapatite ceramics. *Biomaterials* 26, 6106–6112.

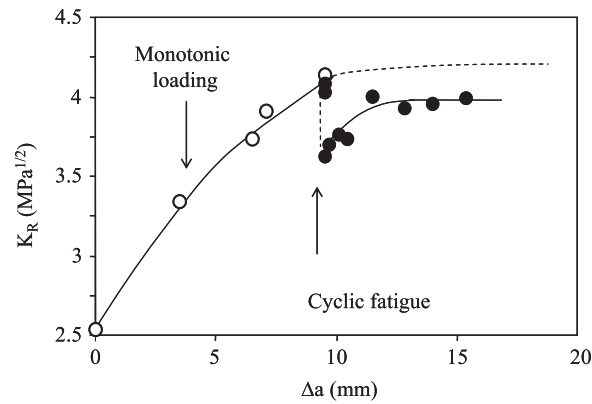


Fig. 15 Degradation of the reinforcement by cyclic loading in 20 μm grain size alumina. From Fantozzi, G., Saadaoui, M., 2014. Toughness, fatigue and thermal shock of ceramics: Microstructural effects. In: Sarin, V.K., Llanes, L., Mari, D. (Eds.), *Comprehensive Hard Materials*. Elsevier, pp. 299–319.

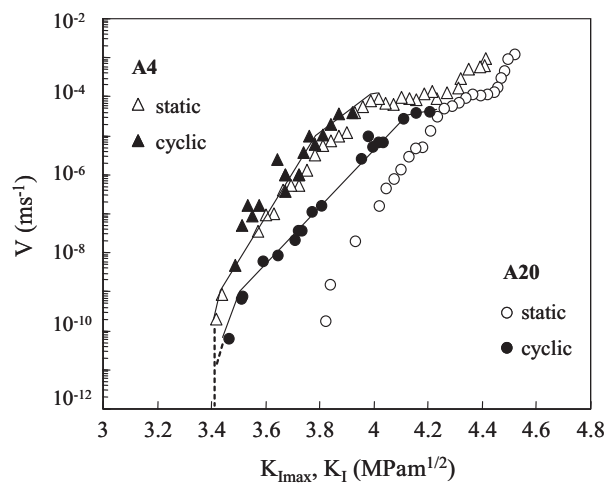


Fig. 16 Crack growth rate as a function of the maximum applied stress intensity factor K_{max} during cyclic loading for A4 and A20 alumina compared to the static V - K_I curves. From Fantozzi, G., Saadaoui, M., 2014. Toughness, fatigue and thermal shock of ceramics: Microstructural effects. In: Sarin, V.K., Llanes, L., Mari, D. (Eds.), *Comprehensive Hard Materials*. Elsevier, pp. 299–319.

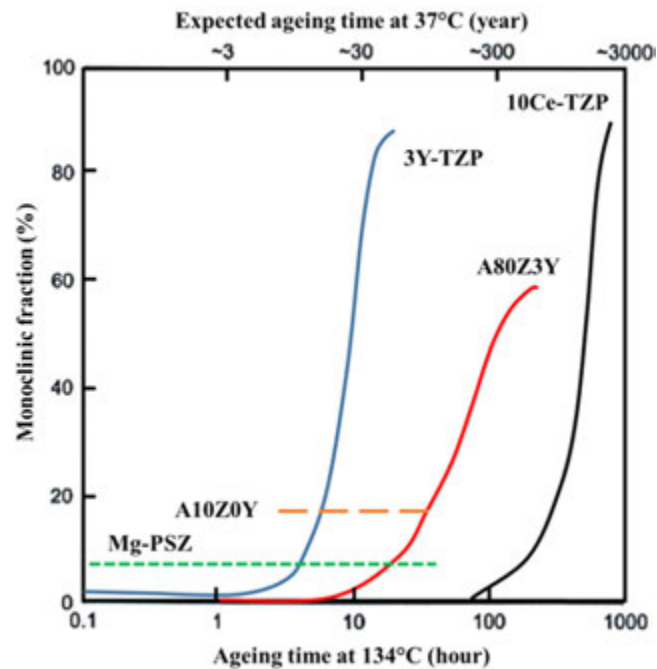


Fig. 17 Low temperature degradation kinetics of zirconia toughened ceramics measured at 134°C. From Chevalier, J., Gremillard, L., Virkar, A.V., Clarke, D.R., 2009. The tetragonal-monoclinic transformation in zirconia: Lessons learned and future trends. *Journal of the American Ceramic Society* 92, 1901–1920.

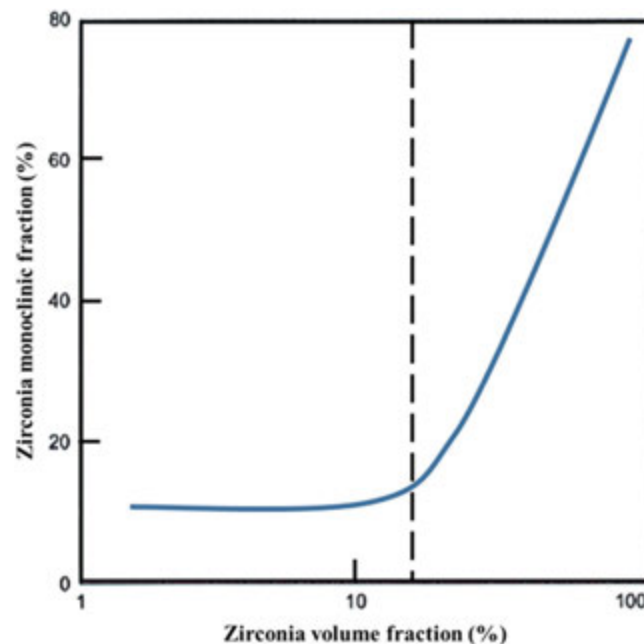


Fig. 18 Monoclinic fraction versus zirconia content in zirconia toughened alumina composites after 40 h at 140°C in steam. From Chevalier, J., Gremillard, L., Virkar, A.V., Clarke, D.R., 2009. The tetragonal-monoclinic transformation in zirconia: Lessons learned and future trends. *Journal of the American Ceramic Society* 92, 1901–1920.

Steady state crack growth rates as a function of $K_{\max}$ during cyclic loading for two alumina (A4 and A20 with respective grain size of 4 and 20 μm) are shown in Fig. 16 (the static loading results are also shown for comparison).

For the fine grained alumina which has a small R-curve effect (Fig. 4), the cyclic fatigue effect is very limited whereas for the coarse grained alumina the crack growth rate becomes higher up to several orders of magnitude in the low crack growth rate

region. The difference between the static and the cyclic loading is due to the shielding degradation during cyclic fatigue. The threshold for the cyclic loading tends toward the fine grain one. The benefit of crack bridging disappears for low cyclic load.

The same effect of cyclic fatigue was observed for Ce-TZP ceramics by *El Attaoui et al.* (2007). Several fatigue mechanisms intervene: wedge effect due to debris, bridging degradation, modification of the shielding effect of the transformation zone.

Low Temperature Degradation

The zirconia-toughened ceramics are very interesting materials but some particular zirconia ceramics exhibit a low temperature degradation in the presence of moisture. They suffer a slow t-m transformation at the sample surface in the presence of moisture which leads to microcracking strength loss. This phenomenon, presented as Achilles heel, was largely described by *Chevalier et al.* (2009).

The main features of the low temperature degradation are summarized as follows (*Chevalier et al.*, 1999; *Déville et al.*, 2003):

- (1) Transformation proceeds rapidly at 200–300°C and is time dependent.
- (2) Water or water vapor enhance the transformation.
- (3) The degradation is due to the t-m transformation accompanied by microcracking.
- (4) Transformation proceeds from the surface to the bulk of zirconia ceramics.
- (5) Higher stabilizing content or finer grain size increase the resistance to transformation.

The mechanisms responsible of the low temperature degradation are not firmly established. **Fig. 17** shows the low temperature ageing kinetics of different zirconia ceramics (*Chevalier et al.*, 2009) measured at 134°C in steam autoclave: 10Ce-TZP, Mg-PSZ, 3Y-TZP, A10Z0Y, and alumina-toughened zirconia (A80Z3Y) (The expected ageing times at 37°C are also indicated). The results show that ceria-doped zirconia have a better behavior than 3Y-TZP ceramics. It can be also noticed that alumina reinforced with a low content of zirconia is very resistant to low temperature degradation as the Mg-PSZ ceramics. For the ZTA ceramics, the transformation t-m occurs when the zirconia content exceeds the percolation threshold (~ 16 vol fraction) as shown by **Fig. 18**.

References

- Benaqqa, C., Chevalier, J., Saadaoui, M., Fantozzi, G., 2005. Slow crack growth behaviour of hydroxyapatite ceramics. *Biomaterials* 26, 6106–6112.
- Bignon, A., Chouteau, J., Chevalier, J., *et al.*, 2003. Effect of micro- and macroporosity of bone substitutes on their mechanical properties and cellular response. *Journal of Materials Science: Materials in Medicine* 14, 1089–1097.
- Chevalier, J., Cales, B., Drouin, J.M., 1999. Low-temperature aging of Y-TZP ceramics. *Journal of the American Ceramic Society* 82, 2150–2154.
- Chevalier, J., Fantozzi, G., 2005. Slow crack propagation in ceramics at the nano- and micro-scale: Effect of microstructure. In: Bradt, R.C., Munz, D., Sakai, M., White, K.W. (Eds.), *Fracture Mechanics of Ceramics* 14. New York: Springer, pp. 173–190.
- Chevalier, J., Gremillard, L., Virkar, A.V., Clarke, D.R., 2009. The tetragonal-monoclinic transformation in zirconia: Lessons learned and future trends. *Journal of the American Ceramic Society* 92, 1901–1920.
- De Aza, A.H., Chevalier, J., Fantozzi, G., Schehl, M., Torrecillas, R., 2003. Slow crack growth behavior of zirconia-toughened alumina ceramics processed by different methods. *Journal of the American Ceramic Society* 86, 115–120.
- Déville, S., Chevalier, J., Fantozzi, G., *et al.*, 2003. Low-temperature ageing of zirconia-toughened alumina ceramics and its implication in biomedical implants. *Journal of the European Ceramic Society* 23, 2975–2982.
- Ebrahimi, M.E., Chevalier, J., Fantozzi, G., 2000. Slow crack growth behavior of alumina ceramics. *Journal of Materials Research* 15, 142–147.
- El Attaoui, H., Saadaoui, M., Chevalier, J., Fantozzi, G., 2005. Quantitative analysis of crack shielding degradation during cyclic fatigue of alumina. *Journal of the American Ceramic Society* 88, 172–178.
- El Attaoui, H., Saadaoui, M., Chevalier, J., Fantozzi, G., 2007. Static and cyclic crack propagation in Ce-TZP ceramics with different amounts of transformation toughening. *Journal of the European Ceramic Society* 27, 483–486.
- Fantozzi, G., Chevalier, J., 2020. Ceramic matrix composites with roughly equiaxed reinforcements: Microstructure and mechanical behavior. In: *Encyclopedia of Materials: Technical Ceramics and Glasses*. Elsevier.
- Fantozzi, G., Saadaoui, M., 2014. Toughness, fatigue and thermal shock of ceramics: Microstructural effects. In: Sarin, V.K., Llanes, L., Mari, D. (Eds.), *Comprehensive Hard Materials*. Elsevier, pp. 299–319.
- Green, D.J., Hannink, R.H.J., Swain, M.V., 1989. *Transformation Toughening of Ceramics*. Boca Raton, FL: CRC Press.
- Hannink, R.H.J., Kelly, P.M., Muddle, B.C., 2000. Transformation toughening in zirconia-containing ceramics. *Journal of the American Ceramic Society* 83, 461–487.
- Ritchie, R.O., Gilbert, C.J., McNaney, J.M., 2000. Mechanics and mechanisms of fatigue damage and crack growth in advance materials. *International Journal of Solids and Structures* 37, 311–329.
- Swain, M.V., Rose, L.R.F., 1986. Strength limitations of transformation-toughened zirconia alloys. *Journal of the American Ceramic Society* 69, 511–518.
- Touaiher, I., Saadaoui, M., Chevalier, J., Preiss, L., Reveron, H., 2018. Fracture behavior of Ce-TZP/alumina/aluminate composites with different amounts of transformation toughening. Influence of the testing methods. *Journal of the European Ceramic Society* 38, 1778–1789.

Mechanical Properties of Dental Ceramics

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Introduction

Due to the specific type of chemical bonding, most ceramics are characterized by their biocompatibility, color stability, chemical durability, temperature resistance, wear resistance and ability to be formed into precise shapes, all of which make them very well suited for applications in dentistry. Indeed, during the past two decades, numerous types of ceramics and processing methods have been introduced, being one of the fastest growing areas in dental materials research and development. Dental ceramics comprise a wide variety of materials that reaches from silicate glasses, porcelain, glass-ceramics to dense polycrystalline sintered oxide ceramics and can be classified into different groups by their principal crystal phase and/or matrix phase, as shown in [Table 1](#). Note that a “composite” refers to a different material in the ceramic and dentistry field. A ceramic composite is a combination of two or more ceramic phases, such as ceramic particles or fibers embedded in a ceramic matrix; whereas a dental composite normally refers to a resin composite in which ceramic particles or fibers are embedded in a polymer matrix. Dental ceramics can be formed into inlays, onlays, veneers, crowns, and more complex fixed dental prostheses (FDPs). As a load-bearing part, the mechanical performance is one of the most important factors that a dental prosthesis has to fulfill in order to ensure its intended functions effectively and safely over extended periods of time. The mechanical properties comprise the elastic and/or plastic response of a material to deformation, crack growth or fracture under an applied force/pressure and the induced stresses, and can be expressed in units of stress and/or strain.

Ceramics are brittle in nature and the fracture of ceramics occurs with very limited plastic strain (commonly less than a few parts per thousand). They may fracture without warning when bended excessively or when quickly heated and cooled (i.e., under thermal shock conditions). The flexural or bending strength, that well resembles the stress condition of dental prosthesis as shown in [Fig. 1](#), is an important parameter to design the dental component. However, the strength of a ceramic is not an inherent material property since it varies under different conditions (processing route, specimen dimensions, specimen shapes, stress cycles, surface quality and the environment). In parallel, an adequate fracture toughness that describes the crack growth resistance of brittle materials is a true material-dependent property, and is an important requirement of any dental ceramic. This chapter introduces the basic principles of brittle fracture and fracture statistics. The mechanical resistance to fracture of different dental ceramics in correlation with their microstructure will be discussed. There are also questions on why dental restorations may fracture after a few years of service but not during the first month or year of clinical service? The mastication cyclic loading-unloading force in the oral cavity must somehow have reduced the mechanical resistance of the prosthetic material, due to the very slow but steady propagation of inherent flaws/cracks at loads that are smaller than the initial fracture load. This causes a loss of strength with time, and among the different mechanisms, fatigue and chemically-assisted slow crack growth are important phenomena for dental ceramics.

Fracture Mechanisms

While ceramics can exhibit a brittle or ductile behavior over different temperature ranges, brittle fracture mechanisms are inevitably the most important mechanism of failure of ceramics for dental applications close to room temperature conditions. In this case, flaws play a dominating role in their mechanical behavior. The early work of Griffith has shown that small cracks in glass can reduce the strength to only 1% of its theoretical strength ([Griffith and Taylor, 1921](#)). Flaws cannot be completely avoided and can be generated during processing or in service such as during sintering, handling of the green body, machining, contact damage, or corrosion. The flaws of different sizes can be located on the surface or dispersed in the bulk material, behaving like cracks. The propagation of such cracks in general leads to sudden and unexpected failure, i.e., catastrophic failure. Although mechanisms such as phase transformation, microcracking, crack deflection, crack bridging and pull-out can provide some resistance to crack propagation, they are less effective as compared to plastic deformation.

Cracks grow if the reduction of the stored elastic energy associated with the crack growth is larger than or equal to the additional surface energy needed to create the new free surfaces ([Griffith and Taylor, 1921](#)). Linear elastic fracture mechanisms based on stress (Irwin) or energy (Griffith) criteria can be used to describe the fracture of brittle ceramics assuming that the crack tip is infinitely sharp and embedded in an elastic continuum ([Lawn, 2010](#)). Under type I failure mode, which is the most important geometry for the failure of ceramics with an applied tensile stress that is perpendicular to the crack plane, a crack will propagate when the stress intensity factor (K_I) reaches or exceeds a critical value K_{IC} .

$$K_I = \sigma Y \sqrt{a} \geq K_{IC} \quad (1)$$

The stress intensity factor K_I describes the elastic stress field near the tip of a crack, σ is the applied stress and a the crack length. The factor Y is a dimensionless constant that depends on the geometry of the specimen and the crack, and on the gradients of the

Table 1 Overview of representative dental ceramics

	<i>Material</i>	<i>Composition</i>	<i>Trade name</i>
<i>Ceramics with a glass phase (Silicate ceramic)</i>	Feldspathic ceramic	About 40% Feldspar filled aluminosilicate glass	Dentsply Sirona CEREC Blocs Dentsply Sirona CEREC Blocs (Polychromatic) VITABLOCS Mark II VITABLOCS TriLuxe forte VITABLOCS RealLife
	Leucite glass-ceramic	40%–50% Leucite filled (aluminosilicate) glass	3 M Paradigm C Dentsply Sirona Cerec Bloc C In IPS Empress CAD IPS Empress CAD Multi Dentsply Sirona Cergo Press, Ceram Ceram Press IPS Empress Esthetic IPS e.max ZirPress VITA PM 9
	Lithium silicate glass-ceramic	70% lithium (alumino) (di)silicate filled glass	IPS e.max CAD IPS e.max Press Dentsply Sirona Celtra Duo VITA Suprinity PC Dentsply Sirona Celtra Press Straumann n!ce
	Glass-infiltrated ceramic	70% particle (Zirconia/ Spinel/Alumina) filled glass	In-Ceram Spinel In-Ceram Zirconia In-Ceram Alumina
	Alumina	Al ₂ O ₃	Procera Alumina InCoris Al
<i>Ceramics without a glass phase (polycrystalline oxide ceramic)</i>	Zirconia	3Y-TZP, 4–6Y-PSZ	Vita In-Ceram Al 3 M Lava Zirconia Esthetic 3M Lava Plus Dentsply Sirona Cercon base ht DMG LuxaCam Zirkon Ivoclar Vivadent IPS e.max ZirCAD Dentsply Sirona inCoris ZI Dentsply Sirona inCoris TZI Straumann zircon (ZrO ₂) VITA YZ T, HT, ST, XT Wieland Zenostar Zr NanoZr
	Ceramic composite	ATZ, Ce-TZP/Al ₂ O ₃	
	Polymer-infiltrated ceramic (glass matrix based)	Feldspatic-ceramic network infiltrated with polymer	VITA Enamic
<i>Hybrid and resin ceramics with the addition of polymers</i>	Resin composite (polymer matrix based)	Polymer matrix filled with about 60–80 wt% ceramic nanoparticles/nanoclusters.	3 M LAVA Ultimate Restorative DMG LuxaCam Composite COLTENE BRILLIANT Crios Ivoclar Vivadent Tetric CAD

Note: 3Y-TZP: 3 mol% yttria-stabilized tetragonal zirconia polycrystalline; 4-6Y-PSZ: 4–6 mol% yttria partially stabilized zirconia; ATZ: Alumina toughened zirconia; Ce-TZP/Al₂O₃: Ceramic composite based on ceria-stabilized zirconia with alumina.

Data sources: Kelly, J.R., 2008. Dental ceramics: what is this stuff anyway? *Journal of the American Dental Association*, 139, 4S–7S. Kern, M., Thompson, V. P., Beuer, F., *et al.*, 2017. All-Ceramics at a Glance, third English ed. Germany: AG Keramik. Zhang, F., Reveron, H., Spies, B.C., *et al.*, 2019. Trade-off between fracture resistance and translucency of zirconia and lithium-disilicate glass ceramics for monolithic restorations. *Acta Biomaterialia*, 91, 24–34.

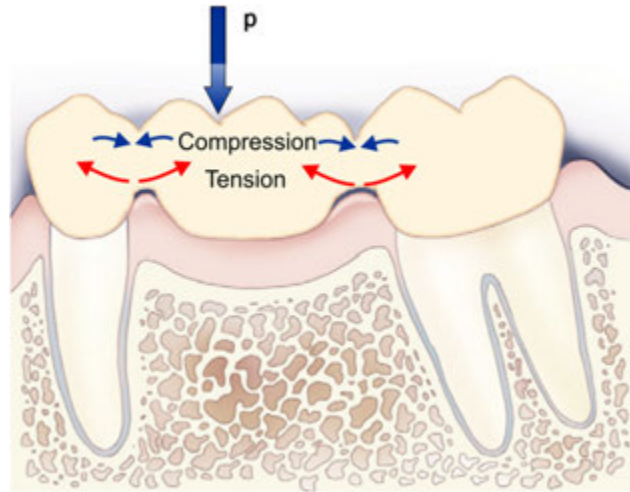


Fig. 1 Stresses induced in a three-unit bridge under an applied force. Adapted from Figure 4-1, Mechanical properties of Dental Materials, Anusavice, K., Shen, C., Rawls, H.R., 2013. Phillips' Science of Dental Materials. twelfth ed. The Netherlands: Elsevier. Copyright (2013), with permission from Elsevier.

stress field. Flaws in ceramic materials are usually very small in comparison to the specimen dimensions, and Y is independent of the crack length with $Y = \sqrt{\pi}$ for an internal flaw and $Y = \sqrt{\pi/2}$ for a surface flaw. K_{IC} , the critical value of K_I , i.e., the fracture toughness, at which the crack will propagate and lead to fracture is in principle an intrinsic material property. K_{IC} under plane stress conditions in mode I is defined as:

$$K_{IC} = (EG_c)^{1/2} \quad (2)$$

where E is the Young's modulus and G_c the energy absorbed per unit area of crack propagation, i.e., the strain energy release rate.

According the above mechanism, the fracture strength of ceramics can be written as

$$\sigma_f = \frac{K_{IC}}{Y\sqrt{a_c}} \quad (3)$$

This expression shows that the fracture strength depends linearly on the fracture toughness K_{IC} and is inversely proportional to the square root of the critical flaw size a_c . It also shows that there are two ways to improve the strength of dental ceramics, either by increasing the fracture toughness which is a true material property and/or controlling the defect size which is more processing-related.

The strength of ceramics is often determined in a bending test. Tensile testing of ceramics and glasses is rarely done due to the high expense of specimen fabrication and the difficulties of performing tensile tests without introducing bending stresses and damaging contact stresses during gripping. Compressive stresses of ceramics are often reported but ceramics rarely fail under compressive stresses. The fracture strength of dental ceramics can be measured by four-point bending, three-point bending and biaxial strength testing of rectangular specimens according to the ISO, 6872:2015 standard (ISO, 6872, 2015). The probability of finding a large defect is higher in a larger specimen and the average strength of larger ceramic specimen is therefore lower than that of smaller specimens. Surface machining and contact damage can induce critical defect on the surface. The measured fracture stress varies as well with the specimen shape. Since the size and location of the critical defect in each ceramic specimen can be different, the strength of a batch of ceramic specimens generally has a large scatter. Under these conditions, one might wonder whether a specific dental prosthesis made from a certain dental ceramic will indeed have the reported strength. The reported strength typically represents the average value and the standard deviation of a range of strength data, while a strength probability analysis is necessary to describe and design dental ceramics. The statistic nature of the strength of ceramics components can be treated by Weibull statistics. Weibull analyses are based on the weakest link hypothesis which assumes that flaws in the specimen do not interact with each other (Danzer, 1992). The two-parameter Weibull distribution that is generally used for the strength of dental ceramics can be described as (ISO, 6872, 2015):

$$P_f = 1 - \exp \left[- \left(\frac{\sigma}{\sigma_0} \right)^m \right] = 1 - P_s \quad (4)$$

where P_f is the failure probability which can be determined by $P_f = i - 0.5/N$ with i = rank in strength and N = number of specimens in the batch. P_s is the survival probability. m is the shape parameter or Weibull modulus and σ_0 is the characteristic strength, a scaling parameter at which $P_f = 1 - \exp(-1) \approx 63.2\%$. Fig. 2 shows a typical Weibull distribution plot of a zirconia ceramic for illustrative purposes.

The Weibull plot can be used to determine the failure or survival probability of a sample under a given load with the specific shape, size and processing conditions for which the Weibull plot was generated. In addition to the mean and characteristic strength, the Weibull modulus can be used as a factor in the design of dental restorations that are made from brittle ceramics. For example, if a dental application specifies that 2% ceramic restoration failures can be accepted, the strength data can be tested and

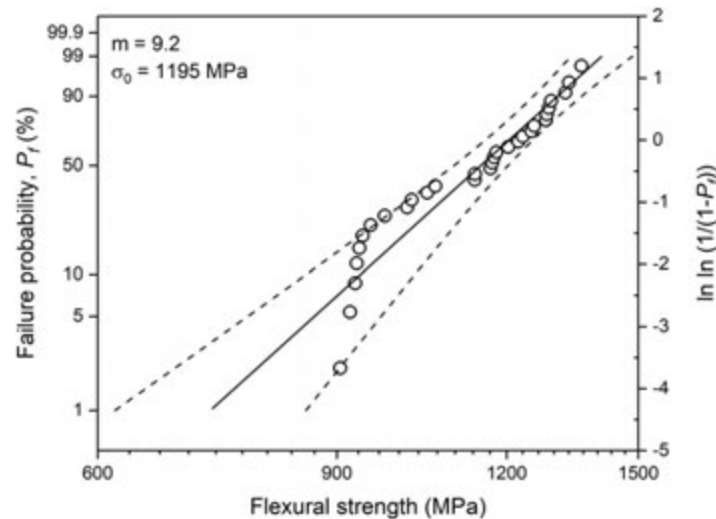


Fig. 2 Weibull diagram of failure probability versus strength for the four-point bending strength measured on a 3 mol% yttria-stabilized zirconia. The axes are scaled to represent the Weibull distribution as a straight line and the slope of $\ln \ln (1/(1-P_f))$ versus $\ln \sigma$ is the Weibull modulus (m). Dashed lines indicate the borders of the combined 95% confidence intervals.

Weibull analysis can be used to estimate the stress level that matches this 2% failure rate in order to optimize the design or the dimensions of restorations and/or restricting the conditions of use so that no location within the restoration would be loaded above the failure stress. Another important parameter is the Weibull modulus (m), which depends on the flaw distribution in ceramics and indicates the scatter of the strength data. A high Weibull modulus reflects a low variation in measured strength values and a reduced probability that flaws will interact to weaken a brittle material. Engineered ceramics typically have a Weibull modulus of 5–20, whereas ductile metals such as aluminum can have a high m value of about 100 (Lambrigger, 1997; Gong *et al.*, 2020; Meyers and Chawla, 2008).

A large number of specimens needs to be tested in order to determine accurate values for the Weibull parameters (Weibull modulus and Weibull scale parameter, i.e., characteristic strength), especially for the Weibull modulus (Davies, 2017). ISO 6872 requires to prepare at least 10 and preferably 30 specimens, but usually a minimum of 30 samples is required to obtain an acceptable estimation precision of the Weibull modulus (Wu *et al.*, 2001; Davies, 2017). It can be observed from Fig. 3 that the confidence intervals of the Weibull modulus get rapidly narrower with increased specimen number, especially for $n < 30$. A sample number of about 30 is the turning point of gaining the precision and, when the sample size is higher than 100, the difference in gaining more precision become small with a confidence of higher than 90% (McLean and Hartsock, 1989).

Although the Weibull modulus of strength data obtained under fast fracture conditions can be used to determine the reliability and fracture probability of ceramics over time, other factors such as cyclic loading and environmentally-assisted subcritical crack growth can occur in dental ceramics. Existing cracks may propagate subcritically under external loads, resulting in a “time-dependent” strength and affecting the reliability of dental ceramic components. Therefore, it would be more useful if the data for Weibull analysis are obtained under test conditions that closely simulate clinical conditions, including cyclic fatigue and oral fluid conditions.

Strength and Toughness of Dental Ceramics

The International Organization for Standardization (ISO) provided the recommended values of flexural strength and fracture toughness for ceramic dental prostheses and restorations with respect to their intended clinical use, as specified in ISO, 6872:2015 and recalled in Table 2. The flexural strengths of different dental ceramics are shown in Fig. 4 and the fracture principles introduced above are valid for all these materials. It is clear that the mechanical properties of dental ceramics vary over a wide range with a strength from 60 MPa to more than 1000 MPa (Zhang *et al.*, 2019). Along with the required mechanical properties, the clinical use of different dental ceramics is also guided by the optical properties of the dental ceramics itself with high translucency being emphasized as one of the primary parameters in controlling optical appearance. It is widely known that the ceramics having better esthetics/translucency in general are less strong, and vice versa (see Fig. 5). Glass-ceramics are more brittle but more translucent and are normally used in low load-bearing areas, whereas polycrystalline ceramics are stronger and tougher but more opaque and typically used in posterior highly stressed areas. In recent years, ceramic dental implants are attracting more and more interest as well but only zirconia ceramics and zirconia-based ceramic composite materials fulfill the mechanical requirements to be used as dental implant and abutment, as specified in ISO 13356. More details are summarized in Tables 2 and 3 shows the general mechanical properties and indications for use of various dental ceramics.

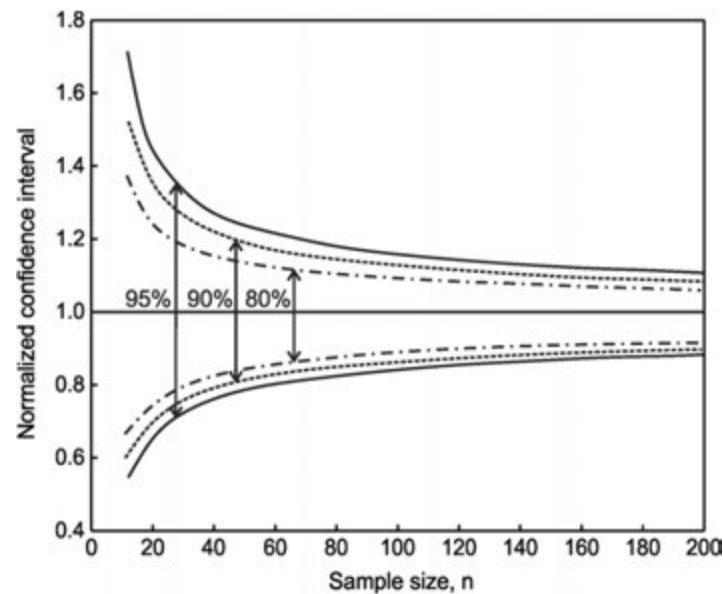


Fig. 3 Confidence intervals for the Weibull modulus versus sample size. Adapted from Wu, D., Li, Y., Zhang, J., *et al.*, 2001. Effects of the number of testing specimens and the estimation methods on the Weibull parameters of solid catalysts. *Chemical Engineering Science* 56, 7035–7044. Copyright (2001), with permission from Elsevier.

Table 2 Minimum required value for mean flexural strength and fracture toughness of ceramics for fixed prostheses by intended clinical use

<i>Recommended clinical indications</i>	<i>Flexural strength (MPa)</i>	<i>Fracture toughness (MPa m^{1/2})</i>
Monolithic ceramic for single-unit anterior prostheses, veneers, inlays, or onlays adhesively cemented. Ceramic for coverage of a metal framework or a ceramic substructure.	50	0.7
Monolithic ceramic for single-unit anterior or posterior prostheses adhesively cemented. Partially or fully covered substructure ceramic for single-unit anterior or posterior prostheses adhesively cemented.	100	1.0
Monolithic ceramic for single-unit anterior or posterior prostheses and for three-unit prostheses not involving molar restoration adhesively or non-adhesively cemented. Partially or fully covered substructure for single-unit anterior or posterior prostheses and for three-unit prostheses not involving molar restoration adhesively or non-adhesively cemented.	300	2.0
Monolithic ceramic for three-unit prostheses involving molar restoration. Partially or fully covered substructure for three-unit prostheses involving molar restoration.	500	3.5
Monolithic ceramic for prostheses involving partially or fully covered substructure for four or more units or fully covered substructure for prostheses involving four or more units.	800	5.0

Note: Adapted from ISO 6872, 2015. ISO 6872:2015. Dentistry – Ceramic Materials. ISO 6872.

Ceramics With a Glass Phase

Feldspathic porcelain is made from molten mixtures of pure natural feldspars. Its amorphous structure consists of a disordered network of polymer-like chains made of silica tetrahedra linked together by sharing common oxygen atoms (Kelly, 2008). Feldspathic porcelains with predominantly glass phase are very brittle with low strength, limiting their use to low-stress applications. Many efforts have been made to add filler particles to the base glass composition to improve the mechanical properties. The fillers can be crystalline but also particles of high-melting glasses that are stable at the sintering temperature of the ceramic material. If the ceramic particles are formed by a precipitation process through a nucleation and growth heat treatment, the materials are referred to as glass-ceramics, like leucite (KAlSi_2O_6) reinforced glass-ceramics and lithium (di)silicate ($\text{Li}_2\text{Si}_2\text{O}_5$ or Li_2SiO_3) glass-ceramics. The strength enhancement in leucite reinforced glass-ceramic is attributed to a good dispersion of the fine leucite crystals as well as the tangential compressive stresses that are developed around the crystals upon cooling because of the difference in coefficient of thermal expansion (CTE) between leucite crystals and glassy matrix. As such, crack deflection becomes an active toughening mechanism improving the toughness and strength (Denry *et al.*, 1996; Fu *et al.*, 2020; Apel *et al.*, 2008). Regarding lithium (di)silicate glass-ceramic, as compared to leucite reinforced glass-ceramic, a larger fraction (up to 70%) of

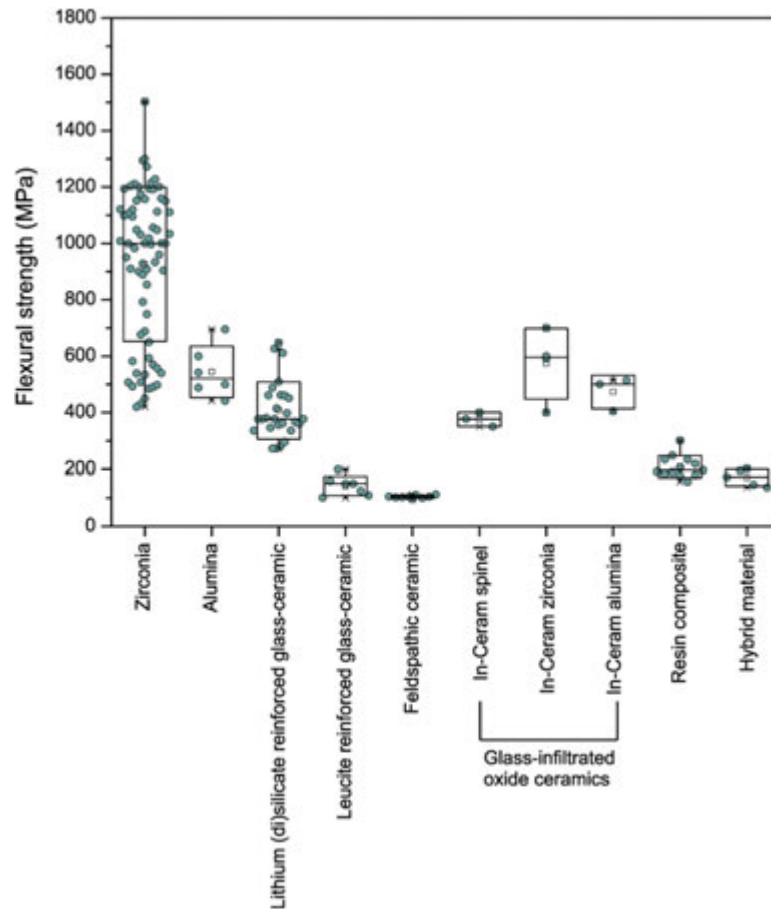


Fig. 4 Flexural strength range of dental ceramics. The upper and lower quantile in the box diagram represent 25% and 75% of the data, respectively. Reprinted from Zhang, F., Reveron, H., Spies, B.C., *et al.*, 2019. Trade-off between fracture resistance and translucency of zirconia and lithium-disilicate glass ceramics for monolithic restorations. *Acta Biomaterialia* 91, 24–34. Copyright (2019), with permission from Elsevier.

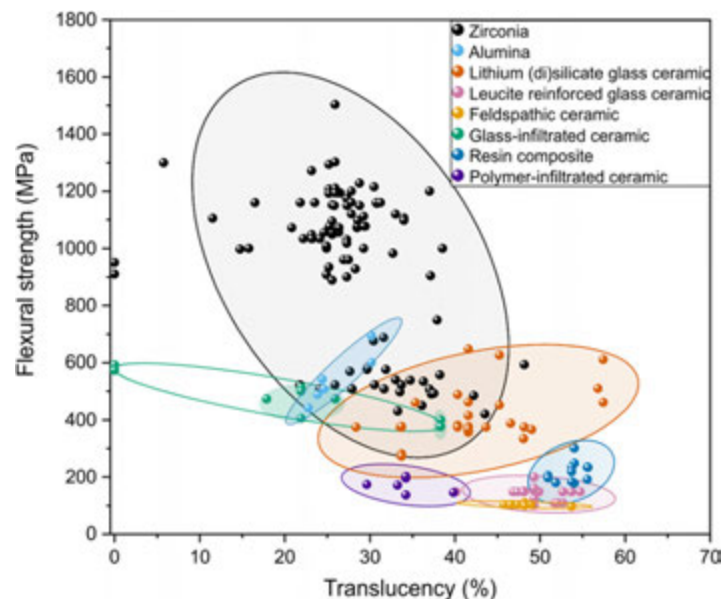


Fig. 5 Strength versus translucency map for CAD/CAM dental ceramics. Reprinted from Zhang, F., Reveron, H., Spies, B.C., *et al.*, 2019. Trade-off between fracture resistance and translucency of zirconia and lithium-disilicate glass ceramics for monolithic restorations. *Acta Biomaterialia* 91, 24–34. Copyright (2019), with permission from Elsevier.

Table 3 General mechanical properties and indications for use of dental ceramics. σ flexural strength, K_{IC} fracture toughness, E Young's modulus, H hardness

Material		Crystalline phase	Mechanical properties				Primary application	Contraindications
			σ (MPa)	K_{IC} (MPa m ^{1/2})	E (GPa)	H (GPa)		
Ceramics with a glass phase	Feldspathic porcelain	Amorphous glass	60–70	0.9–1.3	70	6	Metal-ceramic veneers Anterior laminate veneers	Inlays, onlays, crowns, and bridges (except as metal-ceramic veneers)
	Leucite glass-ceramic (IPS Empress)	KAlSi ₂ O ₆	160	1.3	65	6.2	Anterior single-unit crowns Anterior laminate veneers	High-stress situations Bridges
	Lithium disilicate glass-ceramic (IPS e.max)	Li ₂ Si ₂ O ₅	360–400	2.3–2.8	95	5.8	Anterior and premolar crowns Anterior three-unit bridges Premolar crowns	High-stress posterior situations Bridges involving molar teeth
	Glass-infiltrated spinel	MgAl ₂ O ₄	400	2.7	185	–	Anterior crowns	Anterior bridges Posterior crowns and bridges
	Glass-infiltrated alumina	Al ₂ O ₃	500	3.9	280	11	Anterior and posterior crowns	Anterior veneers Posterior crowns and bridges High translucency needed
	Glass-infiltrated alumina/Zirconia	Y-TZP	600	4.4	258	11	Posterior crowns Posterior bridge substructures up to three units	Anterior veneers and crowns Where high translucency needed
Ceramics without a glass phase (polycrystalline oxide ceramic)	Alumina	Pure Al ₂ O ₃	400–700	≈ 3.5	270–380	16	Core ceramic for crowns Low-stress anterior bridges	Anterior veneers High-stress posterior bridges
	Zirconia	Pure 3Y-TZP	900–1400	5–8	205–210	12	Posterior crowns Posterior bridge substructures up to 5 units Implant	Anterior veneers, crowns, and bridges High translucency is needed
		Pure 4–6Y-PSZ	400–800	2.5–4.0	205–210	12	Anterior and premolar crowns Anterior three-unit bridges Premolar crowns Posterior crowns Posterior bridge (depending on the specific zirconia grade)	Depending on the specific zirconia grade
		Ce-TZP/Al ₂ O ₃ (Ceramic composite)	1290	8.6	245	12	Posterior crowns and bridge substructures Implant	Anterior veneers, crowns, and bridges High translucency is needed
Natural tooth	Enamel	About 90% hydroxyapatite	261–288	0.6–1.5	70–100	3–5	–	–
	Dentin	About 70% hydroxyapatite	232–305	3.1	15–30	0.6	–	–

Data sources: Anusavice, K., Shen, C., Rawls, H.R., 2013. Phillips' Science of Dental Materials, twelfth ed. The Netherlands: Elsevier. Shen, J.Z., Kosmac, T., 2014. Advanced Ceramics for Dentistry, The Netherlands: Elsevier. Zhang, F., Reveron, H., Spies, B.C., *et al.*, 2019. Trade-off between fracture resistance and translucency of zirconia and lithium-disilicate glass ceramics for monolithic restorations. *Acta Biomaterialia* 91, 24–34. Chevalier, J., Liens, A., Reveron, H., *et al.*, 2019. Forty years after the promise of "ceramic steel?": Zirconia-based composites with a metal-like mechanical behavior. *Journal of the American Ceramic Society* 103, 1482–1513. Ban, S., 2008. Reliability and properties of core materials for all-ceramic dental restorations. *Japanese Dental Science Review* 44, 3–21.

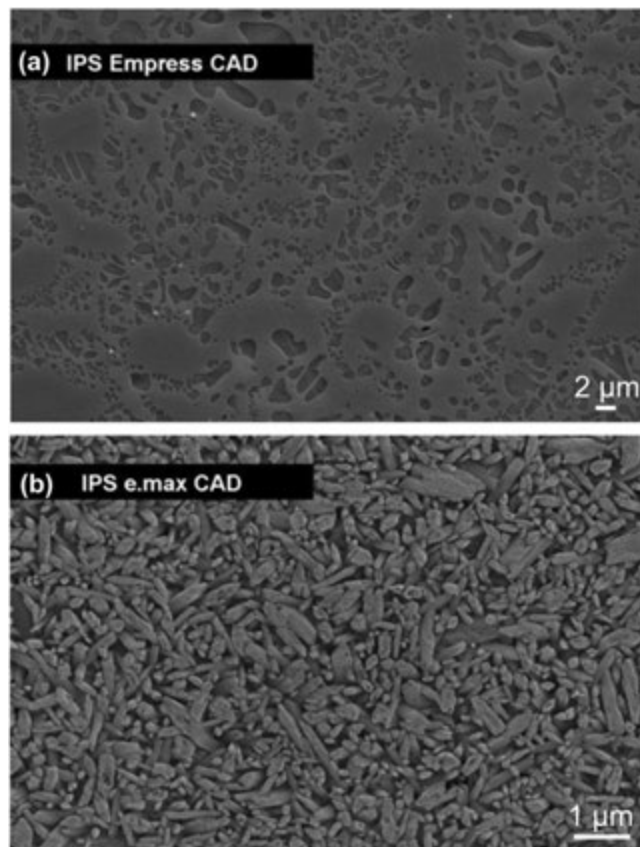


Fig. 6 (a) Leucite reinforced glass-ceramic (IPS Empress[®] CAD, Ivoclar Vivadent AG) shows lamina-like, irregular-shaped leucite crystals. Surface was etched with 3% HF for 10 s (b) Interlocked microstructure of lithium disilicate glass-ceramic (IPS e.max[®] CAD, Ivoclar Vivadent AG). The glass phase has been removed by acid etching with 40% HF vapor for 30 s, leaving needle-like lithium disilicate crystals. Adapted from Ritzberger, C., Apel, E., Höland, W., *et al.*, 2010. Properties and clinical application of three types of dental glass-ceramics and ceramics for CAD-CAM technologies. *Materials* 3, 3700–3713.

cross-linked fine rod-like elongated crystals are used to reinforce the glassy matrix and multiple crack deflections are attributed to an improved crack resistance and concomitantly higher strength and toughness (Zhang *et al.*, 2019; Ritzberger *et al.*, 2010; Fu *et al.*, 2020; Apel *et al.*, 2008; Belli *et al.*, 2018) (Fig. 6). Glass-infiltrated ceramics consist of a porous pre-sintered ceramic core that is infiltrated with a low-viscosity lanthanum aluminosilicate glass fired at 1100°C for 4–6 h to eliminate porosity and increase strength. In-Ceram[®] glass-infiltrated oxide materials are available in three variations subsequently veneered with an esthetic porcelain: a spinel core, an alumina core, or an alumina-zirconia core and all of them are primarily crystalline with successively increasing bending strength and decreasing translucency. Glass-infiltrated oxide ceramics are nowadays no longer used in dentistry.

Polycrystalline Oxide Ceramics and Ceramic Composites Without Glass Phase

Alumina was early introduced in dentistry and has been subjected to continuous development processes. The main effort to improve its strength from less than 400 MPa to more than 600 MPa was achieved by defect-control, e.g., proper selection of raw materials, powder processing, sintering, etc. However, alumina is still quite brittle without very efficient toughening mechanisms. Since the introduction of tougher and stronger zirconia ceramics, pure alumina is no longer used as dental ceramic. In very recent years, a lot of effort is given to produce bioinspired alumina-based materials using platelet-shaped alumina particles. Nacre-like “brick-and-mortar” structures have been successfully fabricated (Munch *et al.*, 2008; Bouville *et al.*, 2014; Le Ferrand *et al.*, 2015), giving rise to a remarkable crack resistance (fracture toughness above 20 MPa m^{1/2}, 7 times higher than the toughness of typical alumina ceramics).

Zirconia ceramics, in particular 3 mol% yttria-stabilized tetragonal zirconia polycrystalline (3Y-TZP) ceramics can have a fracture toughness of 5–8 MPa m^{1/2} and a flexural strength of 900–1400 MPa, the highest ever reported for any dental ceramic, enabling the fabrication of multi-unit FDPs for stress-bearing posterior dentition. Pure zirconia is a polymorphic material that occurs in three different forms depending on temperature: monoclinic (m) at room temperature, tetragonal (t) above 1170°C, and cubic (c) beyond 2370°C. The phase transitions are reversible and accompanied with a volume expansion of about 0.5% in the case of the c to t transformation and about 4% for the t to m transformation. Furthermore, zirconia can be stabilized at room

temperature as cubic and/or tetragonal polymorph, depending on the stabilizer type (CaO, MgO, Y_2O_3 , CeO_2 , etc.) and their quantity (Kelly and Denry, 2008). If transformable tetragonal phase is present within a matrix of cubic zirconia, one refers to partially stabilized zirconia (PSZ). If zirconia is fully tetragonal, one refers to Tetragonal Zirconia Polycrystals (TZP). The most interesting property of zirconia ceramics originates from the fact that tetragonal zirconia is metastable at room temperature and can be transformed to a stable monoclinic phase by shear and/or hydrostatic tensile stresses. When a crack propagates, the concentrated tensile stress field at the crack tip enables t-m transformation and the associated volume expansion generates localized compressive stresses which act against the applied stress intensity factor and inhibit crack propagation (Hannink *et al.*, 2004). This process can significantly increase the toughness of zirconia ceramics due to an enhanced crack growth resistance (i.e., R-curve behavior), see Fig. 7.

Among the different zirconia ceramics, yttria-stabilized tetragonal zirconia polycrystals that normally contain 3 mol% yttria (3Y-TZP) are today the benchmark materials for dental clinical applications due to their high strength, fine grain size and good wear properties. They are recommended for framework materials in porcelain-veneered crowns and FDPs in posterior and anterior regions. 3Y-TZP has also been promoted as an alternative for titanium implants and abutments due to the natural coloration, higher wear and corrosion resistance, improved biocompatibility and lower affinity to bacterial plaque and peri-implantitis (Pieralli *et al.*, 2017). When compared to alumina, not only the higher bending strength and fracture toughness, but also the lower hardness and elastic modulus of zirconia are more attractive for use in dentistry. While dense alumina has a hardness of about 16 GPa, the hardness of Y-TZP is lower, which is a clear advantage in the adjustment of coronal parts by machining. Another advantage of zirconia over alumina is the substantially lower elastic modulus (200 GPa versus 380 GPa), which implies lower elastic stresses between the natural dentine and the prosthetic work.

However, classic dental 3Y-TZP that normally contains 0.25 wt% alumina is relatively opaque and needs to be veneered with a quite thick layer of feldspathic porcelain in order to meet the patient's individual tooth characteristics. The trend towards monolithic ceramic restorations, in order to avoid the difficulties with the veneering ceramics, i.e., the clinically rather regularly encountered chipping of bi-layered zirconia ceramics (zirconia substrate with veneering top layer), has requested zirconia ceramics to be more translucent. Therefore, several generations of more translucent yttria-stabilized zirconias have been introduced in dentistry, either based on a reduced light-scattering alumina content to as low as 0.05 wt% and/or increased yttria content. Partially stabilized zirconia (PSZ) containing 4–6 mol% yttria however have a lower toughness, strength and reliability (see Fig. 8) due to a reduced transformability with increased non-transformable cubic ZrO_2 content and less-transformable tetragonal zirconia (Zhang *et al.*, 2019; Zhang and Lawn, 2018; Zhang *et al.*, 2020b) and faster crack growth. It is also noteworthy that although zirconia stabilized with 3 mol% yttria is referred to as 3Y-TZP, it in fact is a mixture of *t*- and about 15 wt% *c*- ZrO_2 .

Nevertheless, zirconia transformation toughening can be exploited to improve the mechanical properties of ceramics in different ways, in particular in alumina toughened zirconia (ATZ) composite materials. In contrast to orthopedics, ceramic composites have not yet found much applications in dentistry, probably because such a ceramic composite is opaque and thus not appreciated from an esthetic point of view. One alumina-zirconia composite was however already introduced in dentistry, i.e., NANOZR® (Panasonic Electric Works, Osaka, Japan). It is a nanocomposite based on the research of Nawa *et al.* (1998). The optimized material consists of 10 mol% Ce-TZP matrix and 30 vol% of alumina, and characterized by an interpenetrating microstructure, in which nano-sized alumina grains are trapped inside the zirconia grains. NANOZR® ATZ has a comparable strength as 3Y-TZP, but a higher fracture toughness (Table 3) and higher resistance to slow crack growth under static and cyclic loading conditions (De Aza *et al.*, 2002).

Slow Crack Growth (SCG) and Fatigue

In the section above, we focused on the basic mechanical properties of brittle ceramics, as measured on specimens tested at a fast rate assuming that fracture would occur after the application of a load. This is appropriate since standards for dental ceramics solely require minimum mechanical properties that are measured under fast fracture conditions. However, this should not be

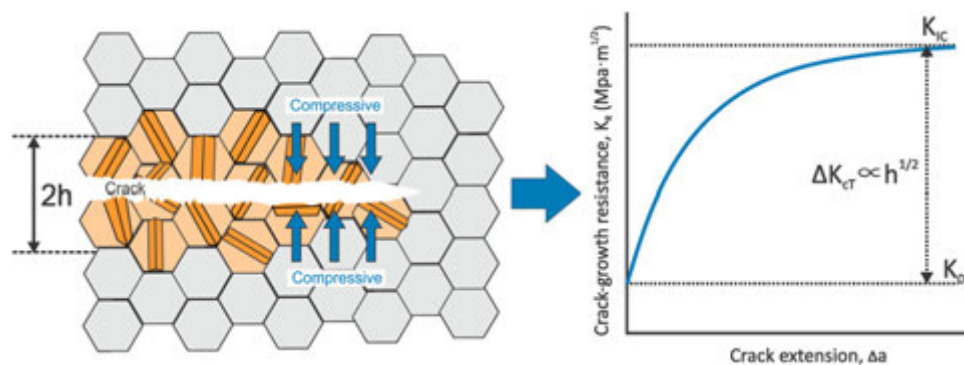


Fig. 7 Illustration of the transformation toughening effect and crack resistance (K_R) as a function of the crack extension (Δa). h is the transformation zone width and transformation toughness enhancement (ΔK_{CT}) is proportional to $h^{1/2}$.

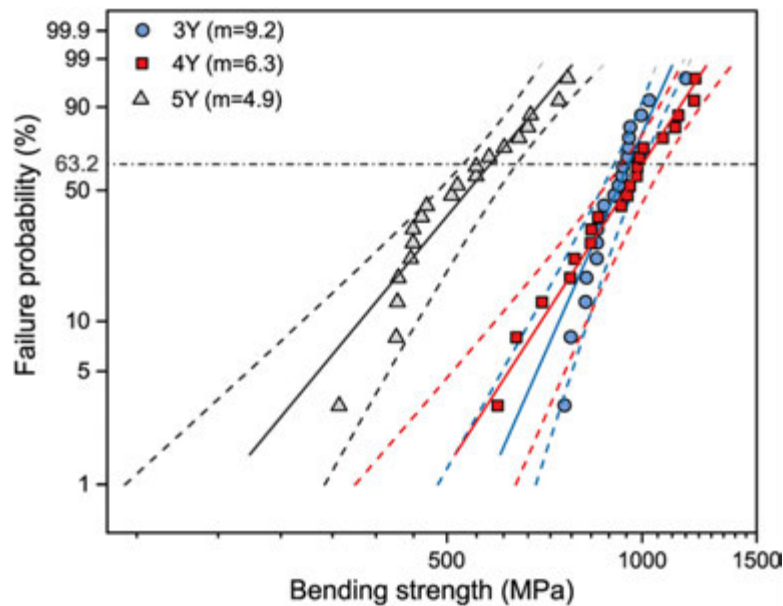


Fig. 8 Weibull plot with 95% confidence bands for the four-point bending strength of zirconia ceramics stabilized with 3 mol% (3Y), 4 mol% (4Y) and 5 mol% (5Y) yttria. The characteristic strength (failure probability of 63.2%) is marked by the horizontal line. Reprinted from Zhang, F., Reveron, H., Spies, B.C., *et al.*, 2019. Trade-off between fracture resistance and translucency of zirconia and lithium-disilicate glass ceramics for monolithic restorations. *Acta Biomaterialia* 91, 24–34. Copyright (2019), with permission from Elsevier.

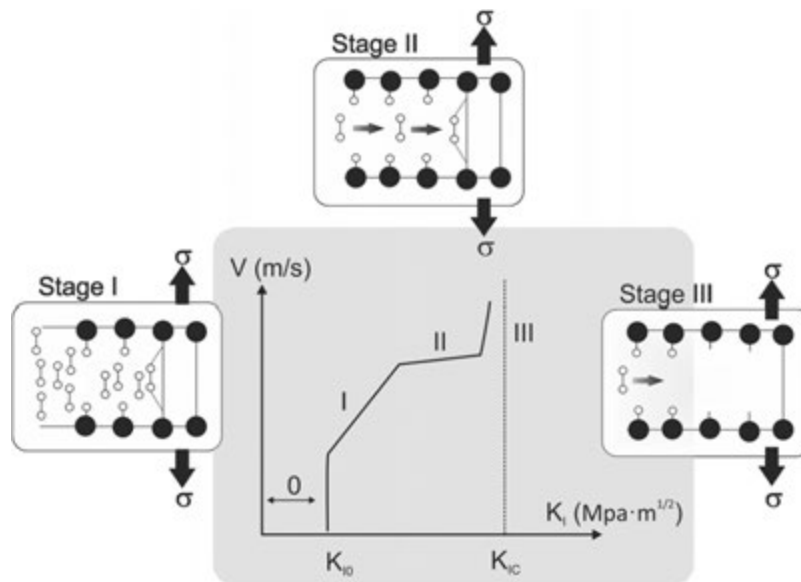


Fig. 9 The different crack growth velocity regions observed in $V-K_I$ curves. Region 0 is the safe region. Region I (low V) is strongly influenced by the reaction between the ceramic and the corrosive environmental species. Region II (intermediate V) is much less sensitive to K_I . Region III (high V) is associated with fast fracture and corresponds to the commonly reported fracture toughness (K_{IC}). Adapted from De Aza, A.H., Chevalier, J., Fantozzi, G., *et al.*, 2002. Crack growth resistance of alumina, zirconia and zirconia toughened alumina ceramics for joint prostheses. *Biomaterials* 23, 937–945. Chevalier, J., Olagnon, C., Fantozzi, G., 2004. Subcritical crack propagation in 3Y-TZP ceramics: Static and cyclic fatigue. *Journal of the American Ceramic Society* 82, 3129–3138. Copyright (2002), with permission from Elsevier.

considered sufficient for safe use in patients, since the humid environment and cyclic loading in the oral environment can degrade the restoration load-bearing capacity over time (Ritchie, 1999; Lawn, 2010).

Chemically-assisted slow crack growth or subcritical crack growth (SCG) occurs due to the presence of water molecules (or other corrosive species, like ammonia or polar solvents). This process is known as static fatigue, which promotes breakage of the strained ionic-covalent bonds at the crack tip or any pre-existing defect due to a stress corrosion reaction, and initiates crack propagation at stress intensities (K_I) below the material fracture toughness (K_{IC}) (Chevalier *et al.*, 2004; Lawn, 2010). The

relationship between the crack growth velocity (V) and the stress intensity factor (K_I) can be used to describe the susceptibility of ceramics to SCG (Chevalier *et al.*, 2004; Lawn, 2010; Swain, 2014). Fig. 9 shows a schematic of a V - K_I diagram which features four (0, I, II and III) different stages with distinct mechanisms for a given environment. In each stage, a power law ($V = \alpha K_I^n$) can fit the speed at which cracks propagate when stressed, where α and n are constants dependent on the material properties and environmental variables. If the crack propagation parameters (α and n) are known for each stage, it is possible to estimate the durability or lifetime of a component. Furthermore, the presence of a threshold (K_{I0}) in the stress intensity factor provides the basis for the safety design of a load-bearing material. The threshold (K_{I0}) corresponds to a crack equilibrium below which no crack propagation will occur, representing a more intrinsic toughness property than the widely used fracture toughness (i.e., critical stress intensity factor), K_{IC} . The higher the K_{I0} threshold, the higher the reliability and consequently longer lifetime. Moreover, a higher slope of the V - K_I/K_{IC} curve indicates that the ceramic is less sensitive to time-dependent failure, as SCG occurs under larger applied K_I/K_{IC} values. Considering the fact that the oral cavity is a complex environment with a fluctuating temperature, high acidic environment (low pH), bacteria, etc., SCG which results from the combined effect of high stresses at the crack tip and the presence of water molecules that induce crack propagation in a subcritical manner can be important for dental ceramics. Fig. 10 shows the V - K_I diagrams measured by the double torsion method under static and cyclic loading conditions for two currently popular dental ceramic systems, namely lithium disilicate and zirconia ceramics with different translucency levels. This shows that dental ceramic materials are indeed susceptible to slow crack propagation at K_I values below K_{IC} . Independent on the K_{IC} and yttria content, zirconia stabilized by different yttria contents show a similar relative susceptibility to SCG under static loading (parallel shift of V - K_I curves), while having a significant higher SCG resistance than lithium disilicate glass-ceramic ($K_{I0,static}/K_{IC}$ of lithium disilicate

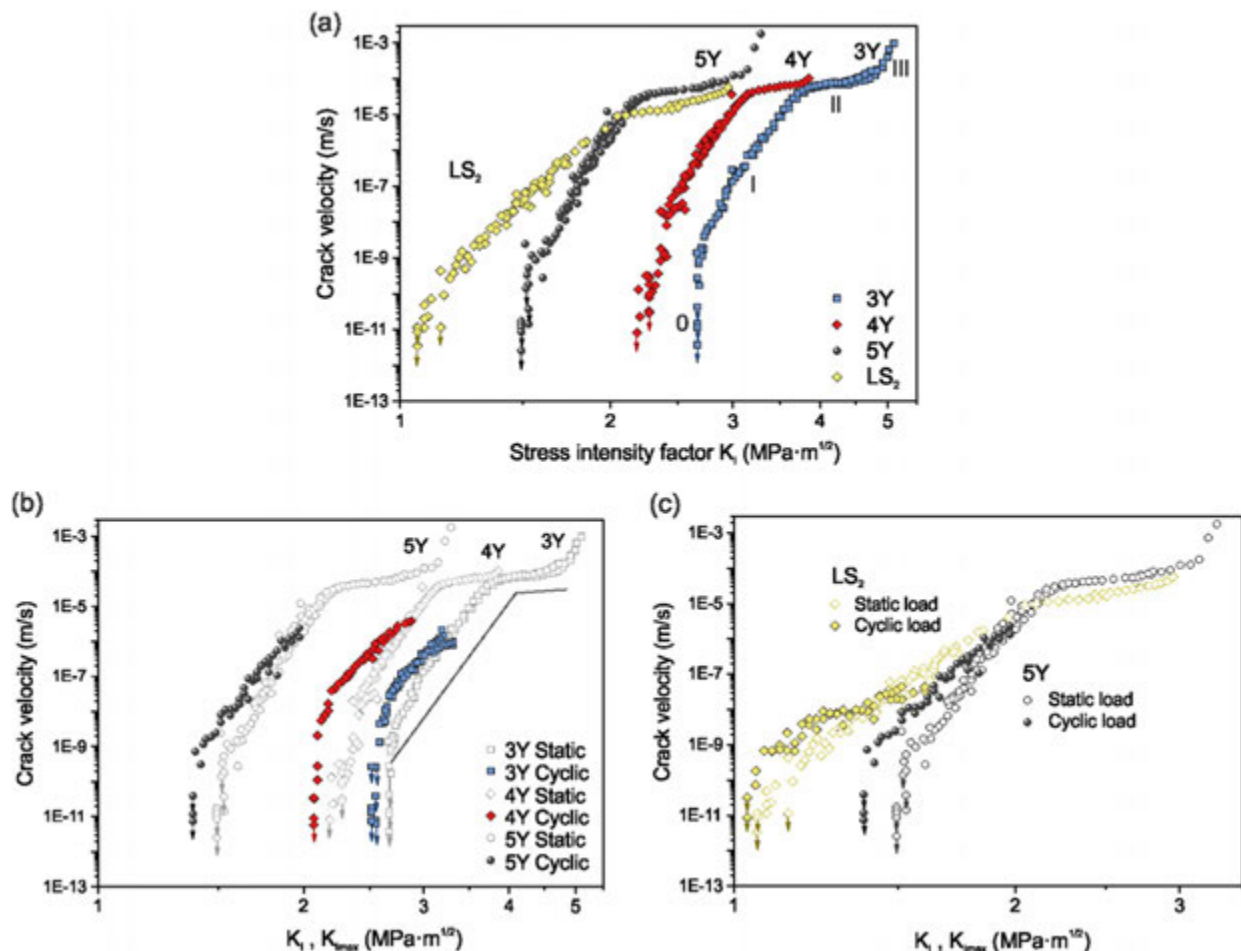


Fig. 10 Slow crack growth: (a) V - K_I curves under static loading in air for lithium disilicate glass-ceramic (LS_2 , IPS e.max CAD) and three high-translucent zirconia ceramics (3Y, 3 mol% yttria-stabilized tetragonal zirconia; 4Y, 4 mol% yttria-stabilized zirconia; 5Y, 5 mol% yttria-stabilized zirconia). The different crack-velocity regions (stage III, stage II, stage I and stage 0, i.e., threshold K_{I0}) are marked in the 3Y curve. (b) Effect of cyclic loading (10 Hz, $R = P_{min}/P_{max} = K_{I,min}/K_{I,max} = 0.1$) on V - K_I curves of the three zirconia ceramics, presented as V - $K_{I,max}$. The black dashed line represents the estimated V - $K_{I,max}$ curve if there would be no cyclic degradation in 3Y. (c) Comparison of V - $K_I/K_{I,max}$ curves of 5Y zirconia and LS_2 glass-ceramic under static and cyclic fatigue. Reprinted from Zhang, F., Reveron, H., Spies, B.C., *et al.*, 2019. Trade-off between fracture resistance and translucency of zirconia and lithium-disilicate glass ceramics for monolithic restorations. *Acta Biomaterialia* 91, 24–34. Copyright (2019), with permission from Elsevier.

glass-ceramic ~ 0.4 smaller than that of zirconia ceramics). The ceramics with glass phases are indeed generally more susceptible to SCG than polycrystalline ceramics without a glass phase (Borba *et al.*, 2011; Wendler *et al.*, 2018; Olagnon *et al.*, 2006; Gonzaga *et al.*, 2011).

Moreover, in addition to the chemically-assisted SCG, mechanical fatigue by cyclic loading is also important (Zhang *et al.*, 2013). In general, cyclic loading lowers the load-bearing capability and accelerates crack growth in brittle ceramics by degrading the extent of crack-tip shielding toughening mechanisms (Ritchie, 1999). These can involve transformation toughening, crack bridging, crack deflection or combinations thereof (Launey and Ritchie, 2009). Fig. 10 illustrates that the crack growth rates under cyclic loading are accelerated with smaller K_{I0} as compared to static crack growth at equivalent stress intensities, independent on the ceramic type and toughening mechanisms. Furthermore, in addition to the flexure load as shown before in Fig. 1, contact damage is of great importance for dental restorations as well. Although the contact stresses at the surface are mainly compressive during chewing activity, tensile stresses can locally occur especially by biting on a hard object with large curvature. Various damage modes are identified in clinically fractured crowns and bridges, and different types of cracks including radial cracks, cone cracks and edge chipping cracks may initiate from the contact zone at the occlusal surface, at the cementations surface as well as from the margins (Fig. 11) (Zhang and Lawn, 2019; Zhang *et al.*, 2013). These damages maybe not be deep, but they are cumulative and can act as a failure origin especially under cyclic fatigue conditions for both veneered and monolithic restorations. Contact testing using sphere indenters on flat specimen is proposed to simulate occlusal and intaglio damage (Zhang and Lawn, 2019). Fig. 12

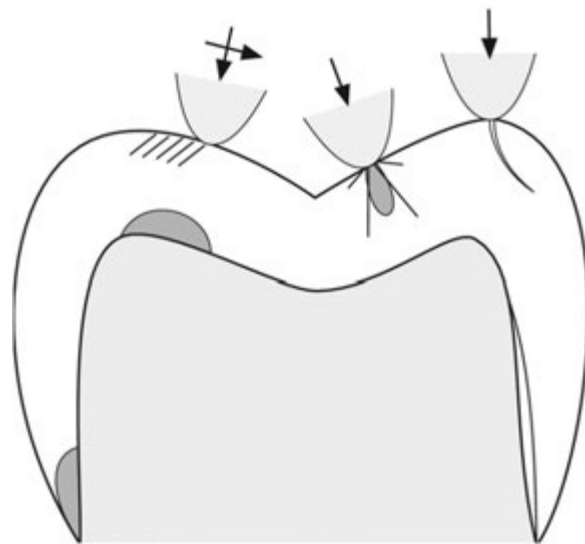


Fig. 11 Various damage modes in ceramic crown at occlusal and cementations surfaces from axial, sliding and edges contacts. Reprinted from Zhang, Y., Lawn, B.R., 2019. Evaluating dental zirconia. *Dental Materials* 35, 15–23. Copyright (2019), with permission from Elsevier.

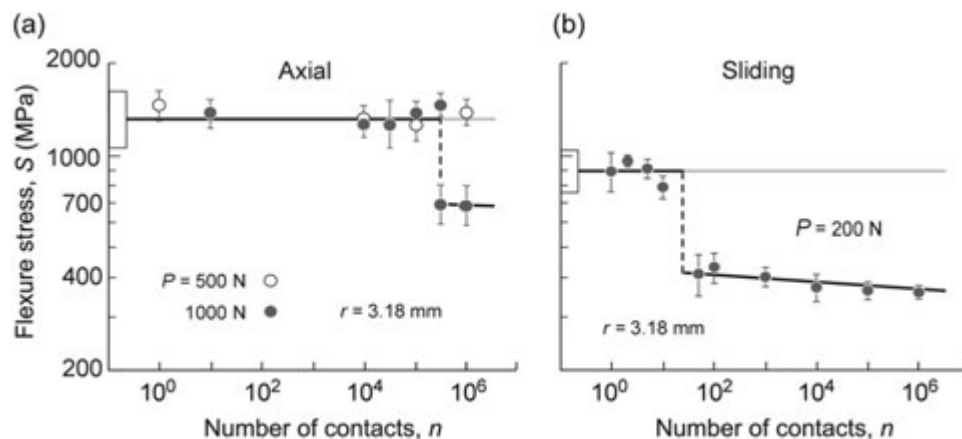


Fig. 12 Strength of 3Y-TZP zirconia after occlusal damage from cyclic contacts with sphere of 3.18 mm radius in water under axial and sliding loading. Data points for specimens on the lower solid lines are failures from contact sites. Boxes at left axis are strengths of un-indented specimens (standard deviation bounds). Reprinted from Zhang, Y., Lawn, B.R., 2019. Evaluating dental zirconia. *Dental Materials* 35, 15–23. Copyright (2019), with permission from Elsevier.

shows the remaining strength of 3Y-TZP zirconia ceramics after cyclic contact at the occlusal surface with sphere indenter of 3.18 mm radius under axial and sliding loads in water condition. Importantly, the strength degradation is larger for sliding loading condition after a relatively small numbers of cycles and at a much lower contact load than that for axial loading condition, due to the accumulation of surface attrition and the formation of macroscopic cracks in quasi-plastic mode (Zhang and Lawn, 2019; Jung *et al.*, 2000). The strength degradation is determined by the numbers of cycles but not by the contact time, emphasizing the importance of mechanical fatigue (as opposed to time-temperature chemically-assisted SCG) for dental ceramics especially for relatively tougher ceramics (Zhang *et al.*, 2013; Kim *et al.*, 1999). Fatigue tests using clinically relevant ceramic configurations that take the contact cyclic loading, SCG and environment into consideration are needed to better predict the lifetime of dental ceramics. With respect to the fatigue testing of dental zirconia implants, ISO standard 14801 addresses the topic but it is mainly dedicated to titanium-based implants. An experimental setup for a dynamic fatigue procedure is prescribed and it is required to cyclic fatigue test the final market-ready product with an angulation of 30° to the vertical axis along with a simulated alveolar bone recession of 3 mm (ISO 14801, 2017). However, other environmental factors like hydrothermal aging are not considered. ISO 13356 examines the hydrothermal aging of standardized bending bars with polished surface zirconia test specimens subjected to humidity at 134°C and 0.2 MPa for 5 h. The adaption and combination of both ISO 14801 and ISO 13356 standards using a chewing simulator can be proposed as laboratory test to check a priori the reliability of zirconia implants (Zhang *et al.*, 2020a).

Conclusions

Dental ceramics comprise a wide variety of materials ranging from glasses to dense polycrystalline ceramics with properties varying over a broad range and there is no single material perfectly suited for all clinical applications. This chapter tried to introduce the mechanical properties of different dental ceramics. Their initial strength and toughness are summarized to guide the choice of the most appropriate material for a specific clinical requirement. Since dental ceramics fracture in a brittle way with a large scatter in strength values, the strength distribution needs to be statistically approached to assess the material reliability. On the other hand, cracks or preexisting flaws in ceramics may subcritically and slowly propagate under a load that is lower than the fracture strength, lowering the load-bearing capability of dental ceramics over time and resulting in a “time-dependent” strength. Chemically-assisted slow crack growth, hydrothermal aging and fatigue testing need to be considered to design the dental ceramics, preferably under testing conditions that closely mimic the clinical application.

References

- Apel, E., Deubener, J., Bernard, A., *et al.*, 2008. Phenomena and mechanisms of crack propagation in glass-ceramics. *Journal of the Mechanical Behavior of Biomedical Materials* 1, 313–325.
- Belli, R., Wendler, M., Cicconi, M.R., *et al.*, 2018. Fracture anisotropy in texturized lithium disilicate glass-ceramics. *Journal of Non-Crystalline Solids* 481, 457–469.
- Borba, M., de Araujo, M.D., Fukushima, K.A., *et al.*, 2011. Effect of the microstructure on the lifetime of dental ceramics. *Dental Materials* 27, 710–721.
- Bouville, F., Maire, E., Meille, S., *et al.*, 2014. Strong, tough and stiff bioinspired ceramics from brittle constituents. *Nature Materials* 13, 508–514.
- Chevalier, J., Olagnon, C., Fantozzi, G., 2004. Subcritical crack propagation in 3Y-TZP ceramics: Static and cyclic fatigue. *Journal of the American Ceramic Society* 82, 3129–3138.
- Danzer, R., 1992. A general strength distribution function for brittle materials. *Journal of the European Ceramic Society* 10, 461–472.
- Davies, I.J., 2017. Confidence limits for Weibull parameters estimated using linear least squares analysis. *Journal of the European Ceramic Society* 37, 5057–5064.
- De Aza, A.H., Chevalier, J., Fantozzi, G., *et al.*, 2002. Crack growth resistance of alumina, zirconia and zirconia toughened alumina ceramics for joint prostheses. *Biomaterials* 23, 937–945.
- Denry, I.L., Mackert Jr., J.R., Holloway, J.A., Rosenstiel, S.F., 1996. Effect of cubic leucite stabilization on the flexural strength of feldspathic dental porcelain. *Journal of Dental Research* 75, 1928–1935.
- Fu, L., Engqvist, H., Xia, W., 2020. Glass-ceramics in dentistry: A review. *Materials* 13, 1049.
- Gong, J., Deng, B., Jiang, D., 2020. The efficiency of normal distribution in statistical characterization of the experimentally measured strength for ceramics. *Journal of Materials Engineering and Performance*. doi:10.1007/s11665-020-05352-1
- Gonzaga, C.C., Cesar, P.F., Miranda Jr., W.G., Yoshimura, H.N., 2011. Slow crack growth and reliability of dental ceramics. *Dental Materials* 27, 394–406.
- Griffith, A.A., Taylor, G.I., 1921. VI. The phenomena of rupture and flow in solids. *Philosophical Transactions of the Royal Society of London. Series A, Containing Papers of a Mathematical or Physical Character* 221, 163–198.
- Hannink, R.H.J., Kelly, P.M., Muddle, B.C., 2004. Transformation toughening in zirconia-containing ceramics. *Journal of the American Ceramic Society* 83, 461–487.
- ISO 14801, 2017. Dentistry - Implants - Dynamic Loading Test for Endosseous Dental Implants. DIN EN ISO 14801. pp. 1–15.
- ISO 6872, 2015. ISO 6872:2015. Dentistry – Ceramic Materials. ISO 6872.
- Jung, Y.G., Peterson, I.M., Kim, D.K., Lawn, B.R., 2000. Lifetime-limiting strength degradation from contact fatigue in dental ceramics. *Journal of Dental Research* 79, 722–731.
- Kelly, J.R., 2008. Dental ceramics: What is this stuff anyway? *Journal of the American Dental Association* 139, 4S–7S.
- Kelly, J.R., Denry, I., 2008. Stabilized zirconia as a structural ceramic: An overview. *Dental Materials* 24, 289–298.
- Kim, D.K., Jung, Y.G., Peterson, I.M., Lawn, B.R., 1999. Cyclic fatigue of intrinsically brittle ceramics in contact with spheres. *Acta Materialia* 47, 4711–4725.
- Lambrigger, M., 1997. Evaluation of Weibull master curves of zirconia ceramics and zirconia/alumina composites. *Journal of Materials Science Letters* 16, 924–926.
- Launey, M.E., Ritchie, R.O., 2009. On the fracture toughness of advanced materials. *Advanced Materials* 21, 2103–2110.
- Lawn, B., 2010. *Fracture of Brittle Solids*, second ed. Cambridge: Cambridge University Press.
- Le Ferrand, H., Bouville, F., Niebel, T.P., Studart, A.R., 2015. Magnetically assisted slip casting of bioinspired heterogeneous composites. *Nature Materials* 14, 1172–1179.
- McLean, A.F., Hartsock, D.L., 1989. Design with Structural Ceramics. In: Wachtman, J.B. (Ed.), *Treatise on Materials Science & Technology*. San Diego: Elsevier.
- Meyers, M.A., Chawla, K.K., 2008. *Mechanical Behavior of Materials*. Cambridge: Cambridge university press.
- Munch, E., Launey, M.E., Alem, D.H., *et al.*, 2008. Tough, bio-inspired hybrid materials. *Science* 322, 1516–1520.

- Nawa, M., Bamba, N., Sekino, T., Niihara, K., 1998. The effect of TiO_2 addition on strengthening and toughening in intragranular type of 12Ce-TZP/ Al_2O_3 nanocomposites. *Journal of the European Ceramic Society* 18, 209–219.
- Olagnon, C., Chevalier, J., Pauchard, V., 2006. Global description of crack propagation in ceramics. *Journal of the European Ceramic Society* 26, 3051–3059.
- Pieralli, S., Kohal, R.J., Jung, R.E., *et al.*, 2017. Clinical outcomes of zirconia dental implants: A systematic review. *Journal of Dental Research* 96, 38–46.
- Ritchie, R.O., 1999. Mechanisms of fatigue-crack propagation in ductile and brittle solids. *International Journal of Fracture* 100, 55–83.
- Ritzberger, C., Apel, E., Höland, W., *et al.*, 2010. Properties and clinical application of three types of dental glass-ceramics and ceramics for CAD-CAM technologies. *Materials* 3, 3700–3713.
- Swain, M.V., 2014. Impact of oral fluids on dental ceramics: What is the clinical relevance? *Dental Materials* 30, 33–42.
- Wendler, M., Belli, R., Valladares, D., *et al.*, 2018. Chairside CAD/CAM materials. Part 3: Cyclic fatigue parameters and lifetime predictions. *Dental Materials* 34, 910–921.
- Wu, D., Li, Y., Zhang, J., *et al.*, 2001. Effects of the number of testing specimens and the estimation methods on the Weibull parameters of solid catalysts. *Chemical Engineering Science* 56, 7035–7044.
- Zhang, F., Reveron, H., Spies, B.C., *et al.*, 2019. Trade-off between fracture resistance and translucency of zirconia and lithium-disilicate glass ceramics for monolithic restorations. *Acta Biomaterialia* 91, 24–34.
- Zhang, F., Meyer Zur Heide, C., Chevalier, J., *et al.*, 2020a. Reliability of an injection-moulded two-piece zirconia implant with PEKK abutment after long-term thermo-mechanical loading. *Journal of the Mechanical Behavior of Biomedical Materials* 110, 103967.
- Zhang, F., Van Meerbeek, B., Vleugels, J., 2020b. Importance of tetragonal phase in high-translucent partially stabilized zirconia for dental restorations. *Dental Materials* 36, 491–500.
- Zhang, Y., Lawn, B.R., 2018. Novel zirconia materials in dentistry. *Journal of Dental Research* 97, 140–147.
- Zhang, Y., Lawn, B.R., 2019. Evaluating dental zirconia. *Dental Materials* 35, 15–23.
- Zhang, Y., Sailer, I., Lawn, B.R., 2013. Fatigue of dental ceramics. *Journal of Dentistry* 41, 1135–1147.

Biological Assessment of Bioceramics: In Vitro and In Vivo Tests

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Bioceramics are biocompatible materials widely used in the mineralized tissues, with proven usefulness in replacement and regeneration strategies. Inert bioceramics (e.g., alumina and zirconia) are unable to induce an interfacial behavior with the host tissue, being encapsulated by a thin layer ofacellular collagen at the tissue interface. Otherwise, bioactive bioceramics (e.g., hydroxyapatite, tricalcium phosphate, bioglasses, and ceramic composites) are actively involved in interfacial events with complex ionic, molecular and cellular underlying mechanisms, ultimately leading to a direct chemical bonding with the surrounding tissues. Active bioceramics may present themselves with varying degrees of bioresorbable behavior, with an active role in the bone metabolic activities, being progressively partial or completely replaced by the host tissue (Ginebra *et al.*, 2018).

Bioactivity is closely related with the chemical and physical properties of the material itself but is greatly modulated by the processing route, sterilization process, presentation form (bulk, particulate, 3D scaffolds) and porosity (dense, porous), endowing the prepared material sample with a different physic-chemical profile. More advanced strategies involving the addition of physiological relevant biomolecules and cells, may further tailor the bioactivity to elicit specific tissue responses for particular clinical settings.

In most repair and regenerative approaches, the bioceramic is set up to remain in the implanted bone for a long period. Studying the initial tissue interactions and the later biological behavior, usually progressing to a steady state that ensures the continuous performance of the material, is a lengthy and challenging task. This is expected, taking into account that a bioactive material is implanted in a complex and highly dynamic tissue undergoing constant modeling and remodeling activities.

The development of bioactive ceramics with endless possibilities for modulating and tailoring their bioactivity demands mandatory evaluation of the biological response to ensure material safety and efficacy. This follows progressively complex in vitro and in vivo approaches, prior moving to clinical trials and marketing. This chapter summarizes the commonly used in vitro and in vivo methodologies to assist in the biological evaluation of a biomaterial targeted for bone replacement and regeneration. For a better understanding, basic concepts of the bone metabolism and bone tissue/material interaction are also briefly considered.

Bone Tissue-Biomaterial Interaction

Bone is a connective tissue consisting of a calcified extracellular matrix (~90%) and a cellular component (~10%). Cortical bone, heavy mineralized (up to 80% of the skeleton), forms the outer layer of bones, while the inner parts contain trabecular bone imbibed in marrow (Teti, 2011). The bone matrix is a composite component. Around 60% is mineralized by the presence of calcium phosphate in the form of hydroxyapatite, $(\text{Ca}_5[\text{PO}_4]_2\text{OH})$, and the organic component is mostly collagen type I (85%–90%), including also non-collagenous proteins (~10%), lipids and glycosaminoglycans. The matrix is permeated with a well-organized network of osteocytes, terminally differentiated osteoblasts, while the quiescent bone surfaces are covered by a monolayer of bone lining cells (also, osteoblastic lineage cells). Bone is continuously being remodeled by the concerted actions of the bone resorbing osteoclasts and the bone forming osteoblasts. Together, the inorganic and the organic content, and also the structural organization in cortical and trabecular bone, give the tissue its performance in resisting torque, compression and shear stress (Teti, 2011).

Bone modeling and remodeling are highly regulated by a complex interplay of local and systemic modulators, involving autocrine, paracrine and endocrine mechanisms translated through key intracellular signaling pathways. Bone modeling is an unbalanced process in which bone resorption and bone formation can occur independently to allow harmonic growth and adaptation to mechanical loading (Langdahl *et al.*, 2016). Conversely, bone remodeling is a homeostatic renewal process, in which the resorption of old or damaged bone is coupled, spatially and temporally, to the formation of the same amount of new bone. Each year, approximately 5% of cortical bone and 20% of trabecular bone are remodeled ensuring metabolic homeostasis and functional integrity. Additionally, bone is a source of a variety of molecules involved in local and systemic metabolic activities, as calcium and phosphate homeostasis, kidney function and energy metabolism, being thus considered an endocrine organ.

Bone tissue deals with the implanted biomaterial as a foreign body, triggering multi-directional, temporal and spatial immune responses, hopefully leading to positive outcomes on the biomaterial integration and long-term stability. This process involves three key players – the material, the immune system mediators and cells, and the bone cells (Franz *et al.*, 2011; Chen *et al.*, 2016).

Immediately after implantation, proteins from surrounding blood and interstitial fluids (e.g., fibrinogen, complement proteins, vitronectin, and fibronectin) adsorb to the material surface within seconds forming a transient surface matrix. This elicits the activation of the coagulation cascade and the complement system, ending up with the formation of a thrombus. Simultaneously, an acute inflammatory reaction is set up involving the recruitment and the activation of neutrophils and other polymorphonuclear leucocytes that release proteolytic and reactive oxygen species, attempting to degrade the material. After a short time (~two days), these initially recruited inflammatory cells undergo apoptosis. Following, degranulation of activated mast cells release pro-inflammatory cytokines

and other mediators amplifying the immune reaction. This paracrine environment promotes the recruitment of monocytes and their differentiation into macrophages, with also a rich cytokine pattern release. These events are accompanied by the revascularization of the injured tissue, ensuring the availability of nutrients, immune and bone precursor cells, bioactive molecules and, also, the removal of the waste products resulting from the intense cellular and molecular activity.

Simultaneously to this host response, the material can also have a dynamic behavior, a process related to its bioactivity. In contact with the body fluids and the local acidic environment elapsing from the inflammatory process, bioactive bioceramics release calcium and phosphate ions (and other ions, depending of the chemical composition) and even material debris to the surroundings. The interacting host response (with plenty of bioactive molecules) and material surface reactivity (associated to the on-going dissolution/precipitation events) lead to a progressive surface conditioning, which can positively modulate the recruitment, adhesion and differentiation of osteoblastic precursors. As a result, differentiated osteoblasts on the material surface produce an immature bone tissue, which later undergoes remodeling by the concerted action of osteoblasts and osteoclasts. Through all these events, some initially entrapped bioactive bioceramics are further degraded being partial or totally replaced by bone. Constant remodeling, driven by functional loading and mechanical strain, sensed by the osteocyte communication system in the mineralized matrix, ensures the long-term metabolic and functional performance of the regenerated tissue (Ginebra *et al.*, 2018).

In Vitro Cell Culture Models for Bioceramics' Biological Characterization

In vitro testing of bioceramics involves the use of cell culture systems that attempt to be representative of the bone metabolic cellular and molecular activities. However, bone is a rather complex tissue encompassing a dynamic interaction of several cell types and a mineralized collagenous matrix, to cope with the constant and variable mechanical load associated to locomotion. Trying to recreate the bone physiology in vitro is a challenging task, never fully achieved. As such, cell culture systems are constantly being improved to better accomplish more representative models (Scheinplug *et al.*, 2018). Nevertheless, relatively basic methodologies continue to be routinely used providing relevant information, as long as they are focused on specific objectives.

In vitro models aim to provide information on the cytocompatibility and specific bone cells' functionality upon contacting with the material. As normal bone metabolism encompasses dynamic events of bone formation and bone resorption, the material performance is usually evaluated through the response elicited in the behavior of osteoblastic and osteoclastic cells. Single-cell culture systems evaluate the response of each of these cell types associated to the interfacial cellular and molecular events and underlying intracellular mechanisms. However, the complex and reciprocal cellular interactions occurring during normal bone remodeling are not analyzed. Co-culture systems of bone cells, particularly involving osteoblasts and osteoclasts, are required to evaluate such behavior. Single-cell cultures or co-cultures are routinely established in 2D conditions. In this setting, cells are seeded directly on the bioceramics or they are exposed to the materials' extracts/leaching products. These models lack the tridimensional nature of the cell-to-cell and cell-matrix interactions. Several 3D cell culture methodologies are described, and continuously improved, to better elucidate the material/bone cells/matrix interactions (Scheinplug *et al.*, 2018). Bioceramics in particulate form might be analyzed in scaffold-free 3D spheroid cultures that can be generated from a mixture of the particles and single or multiple bone cells. This system evaluates relevant interactions in a 3D environment. Porous bioceramic scaffolds naturally provide a 3D environment for in vitro testing (Laranjeira *et al.*, 2009; Meurice *et al.*, 2016). Further, both 2D and 3D models are also able to incorporate dynamic flow conditions using bioreactors with varying degrees of complexity and, additionally, allow mechanical loading during cell/material culturing (Owen and Reilly, 2018).

The selection of the cell system, i.e., cancerous or immortalized cell lines versus primary cells, is obviously relevant, being targeted to the research purpose (Czekanska *et al.*, 2012). Cell lines have several advantages, mainly related to the high expansion potential and reproducibility. They also express several molecular and functional markers of normal cells. As such, these cells might be quite useful to screen large amounts of material samples (bulk, particulate), providing rapid and reproducible feed-back information in the different stages of the material development process. As the major limitation, they do not express a normal phenotypic differentiation. As such, cell lines/immortalized cells normally display a behavior associated with certain stages of the phenotypic development. In some contexts, this turns up to be useful, helping in the characterization of the underlying mechanisms elicited by the biomaterial in the different stages of phenotype development, assisting in targeted research objectives. However, the non-physiological behavior of the cell lines raises concerns regarding translational value of these systems (Czekanska *et al.*, 2014).

Animal and human primary cells constitute the most adequate tool for having more representative models, as they are able to display the complete phenotypic differentiation behavior. Animal (mostly, rat and mouse) bone cell cultures are frequently used and main advantages include accessibility, various collection locations and control of the donor animal in terms of age, weight and gender. Rat bone cells are very useful in some research settings, due to the known genome with the availability of all genetic and molecular tools to analyze the mechanisms underlying the elicited biomaterial response (Czekanska *et al.*, 2012). However, due to inter-species differences, human primary cells provide more representative models (Czekanska *et al.*, 2012, 2014). Limitations are associated with the availability of biological samples for culture establishment, sampling locations and reproducibility of cell behavior, due to donor-related variability (age, gender, health status, medication, etc.).

The culture medium and the culture time are crucial in cell culture testing (Yoshimura *et al.*, 2017). Several standardized media are available to feed single-cell cultures. Even so, there is a great variability in media composition, mainly due to the addition of varying targeted supplements. The culture time should be settled according to the research purposes, i.e., to analyze specific cellular interfacial events, and it varies greatly. This scenario is further complicated for co-cultured cells (Zhu *et al.*, 2018). Each cell type has

specific in vitro growth needs and distinct temporal differentiation processes. Also, the reciprocal direct-contact/paracrine interactions influencing both cell types need to be considered for appropriate and representative in vitro systems, might also hamper results comparison and the translational usefulness of these systems.

Bioactive bioceramics are characterized by a high surface reactivity when in contact with the aqueous biological environment, forming a strong bonding with the bone tissue. In vivo, due to the continuous fluid flow, the initial burst ion release (calcium and phosphate ions, other ions present in the material composition) is soon followed by a dynamic ionic exchange at the material/fluid interface, with dissolution/precipitation events, leading to the formation of a biological-like hydroxyl-carbonate-apatite layer, similar to the mineral phase of the bone. This apatite layer also contains bioactive molecules precipitated from the surroundings, during these exchange events. These favored conditions allow for cell adhesion, proliferation and differentiation of bone cells, resulting in strong bonding with the bone tissue (El-Rashidy *et al.*, 2017). In vitro, in the static cell culture environment, the high surface reactivity of some bioceramics is problematic. For high reactive bioceramics, the initial burst ion release results in a high ionic concentration in the material surface vicinity, with relevant changes in the pH and the osmotic conditions, creating a localized cytotoxic microenvironment that prevents cell adhesion and/or causes cell death (Dias *et al.*, 2005). To overcome this, preconditioning the material prior to cell seeding is routinely used. Establishing the appropriate protocol is challenging, as it depends on the material composition, surface features and formulation.

Preconditioning consists in the immersion of the material sample, for a certain period, in an aqueous solution, before cell seeding. Media frequently include TRIS buffer, an organic buffer solution, simulated body fluid (SBF), with similar ion concentration to that of human plasma, and commonly used culture media, i.e., Alpha Minimum Essential Medium (α -MEM) and Dulbecco's Modified Eagle's Medium (DMEM), supplemented or not with serum. The preconditioning protocol might be performed in one step or two steps (using the same or a different immersion medium), and with or without medium refreshing. Preconditioned surfaces are more cytocompatible due to the already stabilized ion release together with the formation of an apatite-like layer, favoring cell adhesion, proliferation and differentiation. A comprehensive review on this issue was recently published (Ciraldo *et al.*, 2018). Performing the cell culture studies in dynamic fluid flow conditions further allows a continuous dilution of the released species, being more representative of the in vivo conditions (Karadjian *et al.*, 2019).

The Osteoblast and Bone Formation – In vitro Models

The osteoblasts are present in the active bone remodeling surfaces, being in charge for synthesizing the extracellular organic matrix and assisting in its mineralization. Mature osteoblasts are basophilic, mononuclear and polygonal cells and exhibit the features of a protein-producing cell, i.e., well-developed rough endoplasmic reticulum, prominent Golgi complex and chromatic nucleus with large nucleolus.

Osteoblasts originate from pluripotent mesenchymal stem cells (MSCs) recruited from neighboring microenvironment. Development of the osteoblast phenotype involves a complex spatial-temporal endocrine, paracrine and autocrine regulation, with a variety of hormones and a large number of growth factors and cytokines being engaged in this process (Hayrapetyan *et al.*, 2015; Blair *et al.*, 2017). Runx2 is the key transcription factor in the nuclear environment responsible for the commitment of pluripotent MSCs into the osteoblastic cell lineage, being the master regulator for the expression of downstream key genes, as collagen type I, alkaline phosphatase, osteopontin, bone sialoprotein and osteocalcin, at an early stage of osteoblastic differentiation (Liu and Lee, 2013). Runx2 has also a role in the expression of Osterix, a later key transcription factor essential for the final stages of osteoblast differentiation (Liu and Lee, 2013). Several pathways are involved in the osteoblast differentiation sequence. Among them, TGF- β /BMP, Wnt/ β -catenin, hedgehog (Hh) and Notch pathways play pivotal roles (Hayrapetyan *et al.*, 2015; Hojo *et al.*, 2015; Majidinia *et al.*, 2018).

Osteoblast differentiation proceeds along a temporal sequence, moving from osteoprogenitors, pre-osteoblasts, to fully mature osteoblasts. This process involves initial active cell proliferation, accompanied by the synthesis of the collagenous organic matrix (the osteoid), matrix maturation and organization (during which cell growth does not occur), and matrix mineralization. This reciprocal and functionally coupled relationship between proliferation and differentiation is tightly coupled and regulated to support normal bone formation.

In each bone forming site, osteoblasts form tight junctions and produce an organized organic matrix, a complex protein mixture, secreted in a specific order, composed mainly by collagen type I (~88%), glycoproteins (e.g., fibronectin, osteonectin, osteopontin and bone sialoprotein), γ -carboxyglutamic acid containing proteins (e.g., osteocalcin and matrix gla-protein), enzymes (e.g., alkaline phosphatase, collagenases, other proteinases), proteoglycans, proteolipids and a number of growth factors (e.g., fibroblastic growth factors (FGFs), insulin-like growth factors (IGFs), TGF- β s, BMPs). Alkaline phosphatase (ALP), an enzyme present in the plasma membrane, is expressed at the preosteoblast stage and osteocalcin is highly expressed in mature osteoblasts, being considered, respectively, early and later major osteoblastic markers. During this process, a variety of biomolecules is incorporated in the osteoid but also disseminates into the local microenvironment, having paracrine effects.

Following organic matrix maturation, mineralization is initiated in small cytoplasmic membrane vesicles rich in ALP - with a key role in the initiation of the process, by providing phosphate ions. The vesicles also contain proteins and phospholipids with calcium-binding ability, and the deposition of calcium phosphate occurs within the vesicles and, subsequently, continuous in the extra-vesicular space. Here, crystals of hydroxyapatite fill the inter-collagen fibrils' spaces of the osteoid and, upon the formation of stable mineral "critical nucleus", crystal growth becomes a faster physic-chemical driven process (Hayrapetyan *et al.*, 2015).

The half-life of the osteoblast is approximately three months and they have three destinations, namely apoptosis, becoming lining cells or being entrapped in the matrix, in lacunar spaces, converted into osteocytes.

Osteoblastic cell cultures

Animal- and human-derived primary cells, induced osteoblasts from pluripotent stem cells, and immortalized and osteosarcoma cell lines, with their associated advantages and limitations, all have been used to address the dynamic cell-bioceramic material interfacial behavior (Czekanska *et al.*, 2012, 2014; Mata *et al.*, 2015).

The human osteosarcoma cell lines MG-63 and SaOs-2, and the mouse MC3T3-E1 cell line are frequently used. MG-63 cells are arrested in the pre-osteoblast stage, constituting essentially a proliferative and poor differentiated cell population. Otherwise, SaOs-2 cells are differentiated cells, presenting high levels of alkaline phosphatase and easy matrix mineralization. MC3T3-E1 mouse cells are representative of a pre-osteoblastic phenotype being able to differentiate into mature osteoblasts. They exhibit cellular proliferation senescence (as primary cells), but inter-species differences need to be accounted, i.e., dissimilarities in the proliferation rate, temporal expression of osteoblastic markers and mineralized matrix features, compared to human primary cells (Czekanska *et al.*, 2012; Hwang and Horton, 2019). Primary animal cells (mostly, from rat and mouse) are able to display the complete osteoblastic proliferation/differentiation pathway (although, senescence occurs progressively with cell passaging). Due to species-related differences, results extrapolation to human primary cells needs to be cautious (Czekanska *et al.*, 2012).

Primary human cells replicate the development of the osteoblastic phenotype, being the more representative model to evaluate cell-material interactions (Scheinpflug *et al.*, 2018). Cultures of primary osteoblast-lineage cells might be established from several sources. Embryonic stem cells (ESCs) are pluripotent cells, highly proliferative in the undifferentiated stage, and able to undergo osteogenic differentiation. Major concerns include ethical constraints, safety issues and tight control of in vitro conditions to modulate the osteogenic behavior (Korkusuz *et al.*, 2016; Scheinpflug *et al.*, 2018). For these reasons, mesenchymal stromal cells (MSCs), that can be isolated from several adult tissues avoiding ethical controversy, are considered to be a suitable cell source for in vitro model systems (Scheinpflug *et al.*, 2018). MSCs have multi-lineage differentiation potential in vitro, are relatively easy to isolate, expand and differentiate into the osteoblastic lineage using standard cell culture techniques and, additionally, are endowed with versatile paracrine features useful to co-cultured cell models. However, they undergo rapid senescence after few passages (Geissler *et al.*, 2012). MSCs can be isolated from several sources including bone marrow, umbilical cord, adipose tissue, dental pulp, among others (Gao *et al.*, 2017). They are characterized by the common stem cells attributes, but differ in several features such as colony-forming ability, proliferation rate, multilineage differentiation potential and on the proteome and transcriptome pointing to a site-specific phenotype for MSCs (Al-Nbaheen *et al.*, 2013; Akintoye *et al.*, 2006). Regarding this, bone marrow-derived MSCs (mostly isolated from bone marrow discarded in orthopedic procedures) are the most commonly used (Gao *et al.*, 2017). In vitro, medium supplementation with dexamethasone, β -glycerophosphate and ascorbic acid favors the osteoblastic differentiation (Coelho and Fernandes, 2000; Langenbach and Handschel, 2013).

Upon seeding, cells contact immediately with the material, via the transitory protein layer formed in the material surface (coming from the serum-supplemented culture medium). The initial interactions are followed by cell adhesion and cytoplasm spreading, a process mediated by specific integrins, transmembrane proteins that interact with the protein-conditioned material surface and the cytoskeleton. This implies the proper re-organization of the F-actin cytoskeleton with the establishment of focal adhesion zones, leading to the acquisition of a cell morphology fitting on the material surface topography. This initial behavior is crucial for the subsequent cell proliferation, movement and differentiation (Carvalho *et al.*, 2018; Lasgorceix *et al.*, 2018). Characterization of the cell-material response involves a variety of parameters, from the initial interaction to the completion of the osteoblastic phenotype, based on the normal osteoblast biology, and is exemplified in Fig. 1.

Testing a biomaterial with osteoblastic cell cultures is expected to assist in selecting promising materials to be further assessed in animal models. Related to this, a multicenter review study was conducted to analyze the correlation between routinely used in vitro assays (cell adhesion, viability, proliferation; cell differentiation; mineralization assay) with the in vivo outcomes of bone regeneration in early stage (small animal) models, for a wide range of bone regeneration materials (Hulsart-Billström *et al.*, 2016). This study evidenced a poor correlation between the in vitro observations and the in vivo regenerative outcomes. The great variability of used protocols certainly contributed to this discrepancy. Also, it evidenced the need in having a more complete assessment of the cell response, by focusing in other bone cell types and more representative models of the bone biology.

The Osteoclasts and Bone Resorption – In Vitro Models

Osteoclasts (1%–2% of bone cells) are motile multinucleated cells that resorb the bone matrix. They differentiate from hematopoietic myeloid lineage precursors, a process regulated by a variety of systemic and local factors, and complex intracellular signaling (Boyce *et al.*, 2012). Osteoclast precursors are present in the bone marrow and in the blood (here, as post-mitotic cells) being recruited to bone remodeling sites and subsequently differentiated into osteoclasts. Two cytokines are essential in osteoclastogenesis: macrophage colony-stimulating factor (*m*-CSF) and receptor activator of nuclear factor kappa-B ligand (RANKL).

Initially, M-CSF is needed for the proliferation and survival of osteoclast progenitors. Following, the expression of the receptor activator of nuclear factor kappa-B (RANK) characterizes the population committed to differentiate into osteoclasts. Upon the binding of this receptor to its ligand, RANKL, the precursor cells initiate a maturation process, involving the fusion of the mononuclear cells to form multinucleated and polarized cells, able to activate their resorptive mechanisms. RANK-RANKL binding

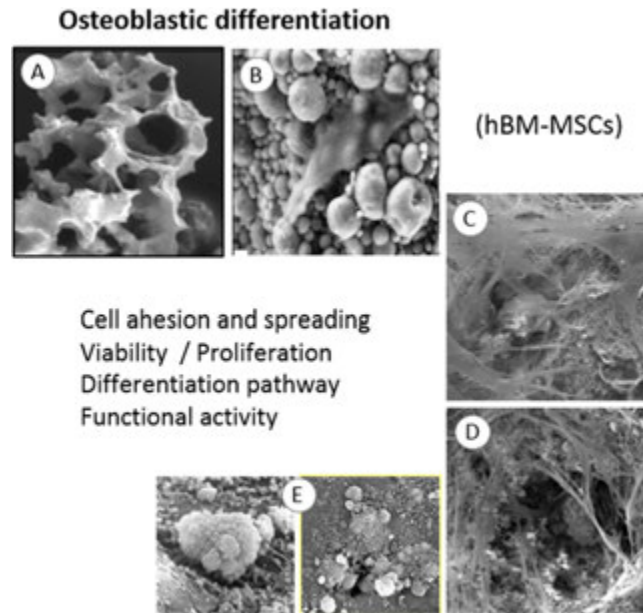


Fig. 1 Osteoblastic differentiation of human bone marrow-derived mesenchymal stromal cells (hBM-MSCs) cultured on a porous 3D bioceramic scaffold for 28 days: SEM images – (A) scaffold, (B) cell adhesion and spreading, (C) cell proliferation and pore migration, matrix formation, and (D) matrix mineralization inside the porous structure. (E): Illustrative images of matrix mineralization by hBM-MSCs cultured on two hydroxyapatite samples for 28 days.

triggers the activation of several signaling molecules, namely nuclear factor kappa beta (NF- κ B) and, finally, nuclear factor of activated T-cells 1 (NFATc1), the transcription factor critical for osteoclastogenesis; it translocate to the nucleus and promotes the expression of osteoclast-specific genes, such as tartrate-resistant acid phosphatase (TRAP), β 3 integrins, calcitonin receptors and cathepsin K (Teti, 2011). RANKL/RANK signaling also stimulates the capacity of osteoclasts to resorb bone and decreases osteoclasts apoptosis. Co-stimulatory mechanisms mediated by the osteoclast membrane immunoreceptors osteoclast-associated receptor (OSCAR) and triggering receptor expressed on myeloid cells 2 (TREM2) seem also to be important for osteoclastogenesis through the activation of NFATc1 (Boyce *et al.*, 2012).

Bone resorption involves the adhesion of multinucleated osteoclasts to the bone matrix, mainly through the binding of membrane receptors, especially β 3 integrins, to recognition sites on matrix proteins, leading to the formation of an actin-rich ring, defining and sealing the area to be resorbed. Inside the sealing zone, the re-organization of the cytoplasm allows the formation of a ruffled border membrane that greatly increases the surface area in contact with the matrix; additionally, polarized trafficking of endosomes and lysosomes to the ruffled border also occurs.

The resorption of the bone matrix is accomplished in two phases, i.e., dissolution of the mineral content, followed by the degradation of the organic components. The resorption lacuna is highly acidic which is attained by the combined actions of vacuolar ATPases and chloride channels in the ruffled border, that, respectively, pump protons and chloride ions into the lacuna. Hydrochloric acid is formed and dissolves the hydroxyapatite mineral phase, making the organic matrix available for proteolytic degradation by endosomal metalloproteinases and lysosomal proteinases (especially cathepsin K). Digested matrix proteins are taken up by endocytosis through the ruffled border, transported across the cytoplasm, and released by exocytosis into the extracellular space (transcytosis). Cytoplasmic vesicles, containing the specific enzyme TRAP, fuse with the transcytotic vesicles to destroy the endocytosed material. Osteoclasts have an average half-life of two weeks and die by apoptotic processes, regulated by paracrine mechanisms (Boyce *et al.*, 2012).

Osteoclastic cell cultures

Several osteoclastic lineage cells are used to establish appropriate cell culture models. They include cancerous/immortalized cell lines and animal- or human-derived osteoclastic precursors.

Precursor cells can be isolated from blood mononuclear cells (PBMCs), typically via density gradient centrifugation, by adhesion selection. The monocytes (osteoclast precursors) can be further isolated from PBMCs by using magnetic-activated cell sorting (positive CD14 and CD45 cells). Bone marrow consisting of supporting stroma and hematopoietic tissue may also provide osteoclast precursors present in the hematopoietic fraction. Additionally, two cell lines are frequently used. The human monocytic cell line THP-1 (derived from a boy with acute monocytic leukemia) and the murine leukemic monocyte macrophage cell line RAW264.7. In vitro, osteoclastogenesis is achieved by the exposure of precursor cells to M-CSF and RANKL (due to their roles in this process), added to serum-supplemented standardized culture media and a convenient culture time. RAW264.7 cells only

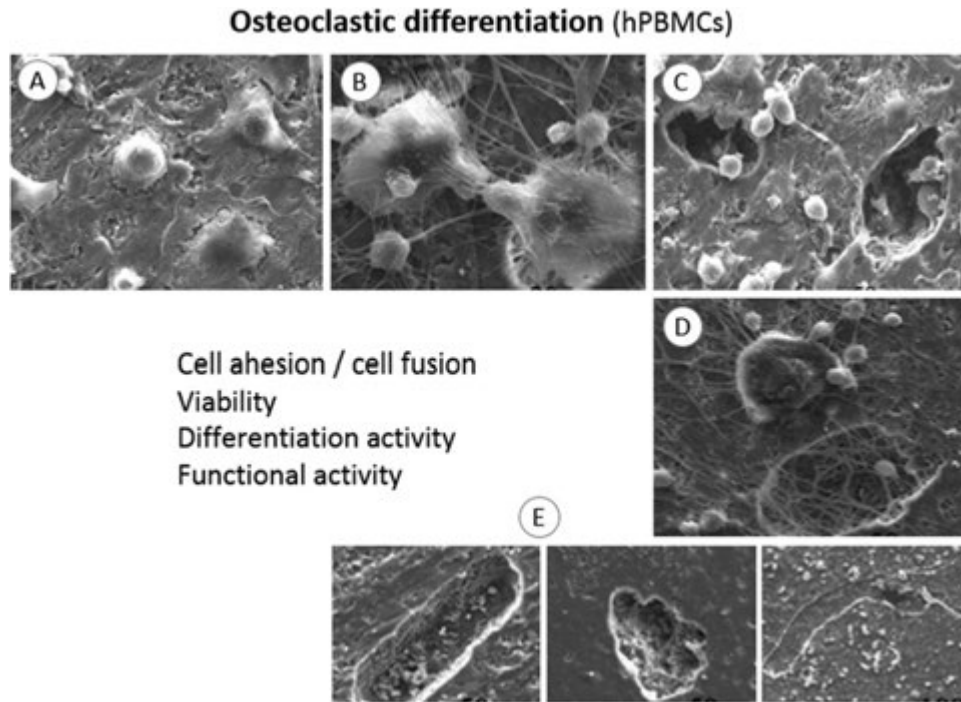


Fig. 2 Osteoclastic differentiation of human peripheral blood mononuclear cells (hPBMCs) cultured on a hydroxyapatite bulk substrate for 21 days: SEM images – (A) osteoclasts over the material surface, (B) osteoclast-osteoclast communication, (C) resorption pits, (D) resorption pits still showing remains of the organic collagenous matrix, and (E) illustrative images of resorption pits and a resorption trail on the hydroxyapatite substrate.

require RANKL exposure. Differentiation of human PBMCs is routinely used to assess the osteoclastogenesis and osteoclasts functional activity (Owen and Reilly, 2018; Costa-Rodrigues *et al.*, 2011).

For bioceramic testing, precursor cells are seeded on the material surface and cultured in appropriate conditions. Precursors adhere to the material through specific integrins and characterization of the elicited osteoclastic response takes into account the morphological features, differentiation of the precursor cells, and functionality of the mature osteoclasts. On the material surface, mature osteoclasts are easily identified by the presence of several nuclei and the typical circular F-actin cytoskeleton arrangement needed for the formation of the sealing zone. For the osteoclastic differentiation, markers commonly evaluated include the expression/secretion of integrin $\beta 3$ and integrin αv , RANK and calcitonin receptors, and the enzymes cathepsin K and TRAP. Functional activity is analyzed by the formation of resorption pits in the ceramic surface. For the underlying mechanisms, relevant signaling pathways' activation are assessed (Costa-Rodrigues *et al.*, 2016), Fig. 2.

The Bone Remodeling Cycle – In Vitro Models

Bone remodeling occurs in specific and specialized vascularized entities, the bone remodeling compartments, likely formed by an extension of the bone lining cells, which provide the structural basis for coupling and regulating the cellular activity. Remodeling requires a functional cohort of cells, the basic multicellular unit (BMU), which involves the coordinated action of bone cells, i.e., lining cells, osteocytes, osteoclasts and osteoblasts, and endothelial cells to support angiogenesis (Teti, 2011), Fig. 3. It comprises four major distinct but overlapping phases – activation, resorption, reversal, and formation.

Activation is the event that converts a defined resting surface into a remodeling site. The induction signal appears to be determined by the matrix through the osteocyte communication network (the bone sensing system), by detecting mechanical and biochemical stimuli (e.g., micro-damage, ischemic events). Transduction of these signals, via paracrine modulation, leads to the appropriate cellular activity at the bone surface (Bonewald, 2011).

As a result, osteoclast precursors are recruited from the surrounding marrow or the bloodstream, and differentiate into active osteoclasts. Bone lining cells that secrete M-CSF and RANKL, and the osteocytes – major producers of RANKL – have a role in this process. Osteoblast-lineage cells also secrete OPG, a key regulator of osteoclastogenesis. Osteoclasts attach to the bone matrix, resorb a portion of the underlying matrix and form a resorption lacuna – a process completed in few days. Osteoclast apoptosis is subsequently activated, liberating the remodeling area. Ending of this phase is related with several factors, i.e., increased local calcium and phosphate concentration (resulting from the degradation of the bone matrix), release of factors from the degraded matrix, signals from the osteocytes, among others (Boyce *et al.*, 2012).

The reversal phase, lasting 7–14 days, begins with the appearance of a heterogeneous population of macrophage-like mononuclear cells in the resorption lacunae. The lacuna is leveled by the removal of the matrix debris left behind during the

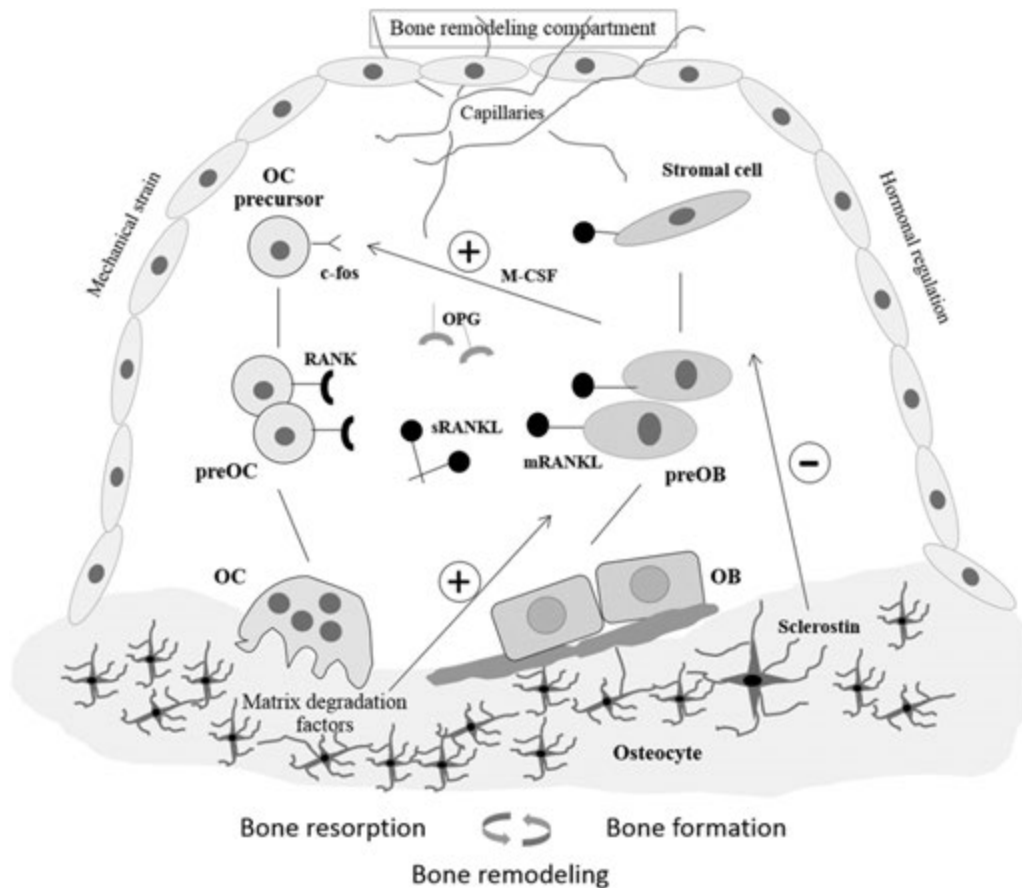


Fig. 3 Simplified view of the cellular and humoral interactions within the RANK/RANKL/OPG signaling in the bone remodeling compartment. OB: osteoblast; OC: osteoclast.

osteoclast activity, and a cement line enriched in proteoglycans, appears, demarcating the edge at which osteoclasts stopped their activity. This is a critical period between bone resorption and bone formation, with a role in the coupling of the two processes. Reversal cells may release relevant factors for the following bone formation phase, and/or might contribute to the formation of the cement line that may play a role in guiding osteoblasts during the bone formation phase (Teti, 2011).

Subsequently, osteoblast precursors are recruited to the resorption lacuna and differentiate into osteoblasts. A variety of factors with osteoblastic anabolic effect, released from the bone matrix during the resorption phase (e.g., TGF β , BMPs, PDGF, FGFs, IGFs), play a role in this process. Also, osteoclasts modulate osteoblastic cell behavior through several mechanisms, including the secretion of sphingosine 1-phosphate, the ephrinB2/EphB2/B4 and semaphorin/plexin signaling (Owen and Reilly, 2018). The functional osteoblasts lay down a collagenous organic matrix, the osteoid, that later becomes mineralized by the deposition of hydroxyapatite. This is a slow phase, taking three to four months, during which the more mature osteoblasts are entrapped in the organic matrix, becoming osteocytes. At the end of the formation phase, the resorption lacuna is completely filled with new bone, without any changes in the total bone amount. The mechanisms involved in the termination of this phase are unclear, but the major signal is very likely released by the osteocytes embedded in the mineralized matrix. Osteocytes secrete sclerostin that prevents the activation of the Wnt signaling, an important osteoblast inducer.

The strict control of bone remodeling is achieved by a complex bone-cell and humoral crosstalk. Extracellular vesicles (exosomes) play a key role in cellular crosstalk. The vesicles carry a variety of key molecules, i.e., BMPs, non-collagenous matrix proteins, RANKL and OPG, and an array of microRNAs that can modulate the differentiation and activity of bone cells (Yin *et al.*, 2017; Gao *et al.*, 2017). The role of circulating microRNAs must also be accounted (Yin *et al.*, 2017).

The adult skeleton has approximately 1–2 million active remodeling sites at any given time, replacing a volume of $\sim 0.025 \text{ mm}^3$, in each microsite. The lifespan of a single BMU is about 6–9 months, during which several generations of osteoclasts and osteoblasts are formed. The rate of remodeling of the skeleton, as a whole, is 5%–10% per year. Imbalance between resorption and formation compromises bone homeostasis, leading to bone metabolic disorders (Teti, 2011).

Co-culture models of osteoblastic and osteoclastic cells

In vitro models of bone remodeling require the communication between osteoblastic and osteoclastic cells (Goers *et al.*, 2014; Zhu *et al.*, 2018). Several protocols are used in co-culture models, to math distinct research purposes, however all within two

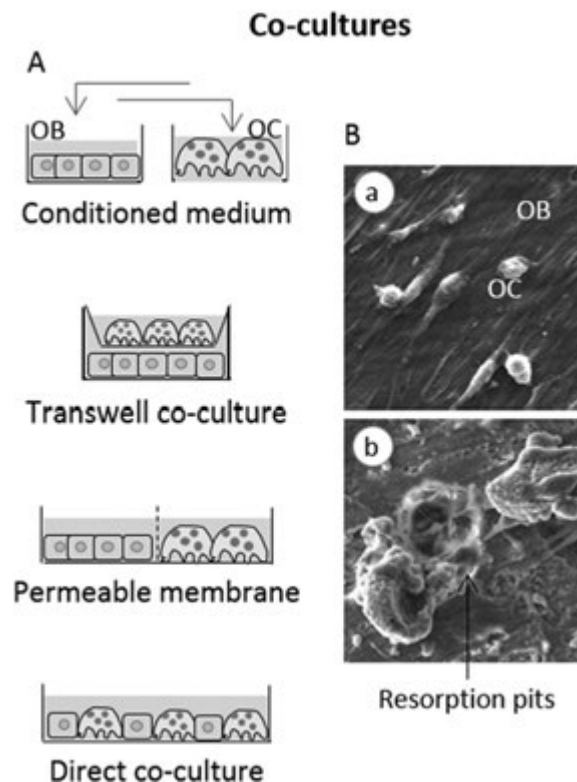


Fig. 4 (A) Representative co-culture models; (B), co-cultured human bone marrow-derived mesenchymal stromal cells (hBM-MSCs) and human peripheral blood mononuclear cells (hPBMCs) on the surface of a bulk hydroxyapatite substrate, for 21 days. SEM images showing the osteoclasts interacting with the continuous osteoblastic cell layer (a) and the resorption pits on the co-cultured surface (b). OB: osteoblast; OC: osteoclast.

approaches, i.e., the simultaneous cultivation of two (or more) cell populations allowing direct (via gap junctions) or indirect (via paracrine pathways) communication with each other (Roeder *et al.*, 2011), Fig. 4.

The direct methodologies imply the culture of both cell types on the same surface, with a defined/optimized cell-cell ratio (Costa-Rodrigues *et al.*, 2012). Here, both the effects of cell-to-cell contact and soluble factors are involved. However, conventional normalization methods for parameters such as mitochondrial activity, expression of genes and protein or DNA content, do not differentiate between the different cell types. Other approaches are used to visualize cell organization, quantify the number of cells and evaluate the differentiation of each cell type. Fluorogenic staining and phenotype immunofluorescence staining, and cell separation by cell sorting are useful tools in this scenario (Zhu *et al.*, 2018).

In the indirect co-culture models, one of the cell types is cultured on the material surface and exposed to the conditioned medium from the other cell type culture (performed in standard tissue culture plates or also on the material surface). Another approach requires a permeable membrane to separate the two cell types in the culture reservoir, but allowing the exchange of soluble factors. With this kind of set up it is possible to have the material samples cultured with distinct single cell types separated by the membrane, and to analyze the reciprocal paracrine interactions on each population (Zhu *et al.*, 2018). Using a transwell insert in the culture reservoir, the material surface may be seeded with one of the cell types, and the permeable membrane with the other cell type, also characterizing the behavior of each cell population.

The common osteoblastic and osteoclastic cell types used in the monoculture models, and referred previously, are commonly used to establish co-culture models. A great variability of combinations of the two cell types have been described (Owen and Reilly, 2018). In general, primary osteoblast-lineage cells and monocyte-derived osteoclasts are more representative models, especially, for long-term studies, because of the normal phenotype differentiation. Human mesenchymal stromal cells (hMSCs, normally from bone marrow) and peripheral blood monocytes (PBMCs) are recognized cell populations targeted to analyze the interactions of osteoblastic and osteoclastic cells. This system has the advantage of avoiding the use of phenotype-inducer supplements because of the reciprocal cell differentiation induction (Schulze *et al.*, 2018). As mentioned before, other primary cells, especially rodent cells, are also used to overcome the limitations of using human cells, namely regarding availability and donor variables (Czekanska *et al.*, 2012). Also, osteoblastic and osteoclastic cell lines are used to analyze the reciprocal phenotype interactions, being useful models to address particular targets (Zhu *et al.*, 2018; Owen and Reilly, 2018).

The reported culture media are highly variable in their formulation, due to the distinct requirements of the two cell types, the experimental approach and the research purpose (Baker, 2016; Owen and Reilly, 2018). Nevertheless, in a variety of studies,

osteogenic-induced conditions usually include supplementation with dexamethasone, β -glycerophosphate and ascorbic acid, while osteoclastogenic medium is typically supplemented with M-CSF and RANKL. However, these compounds are not always included or even needed, and other molecules may be added, such as Vitamin D, parathyroid hormone and retinoids (Owen and Reilly, 2018). The appropriate/optimized culture media formulation is determined by the osteoblastic- and the osteoclastic-lineage cells that are used (immortalized cell lines, cancerous cell lines or primary cells and their origin) and the research purpose (short- or long-term interactions, intended cell characterization). In the direct co-culture procedures, the compatibility of the cell types in culture, their seeding protocols (cell ratio, order, simultaneous or temporal spaced seeding) and particular supplements' needs, must be accounted for proper medium selection (Zhu *et al.*, 2018).

Characterization of the cellular behavior involves a panel of methodologies addressing several aspects related to cell adhesion and spreading, re-organization of the cytoskeleton during the initial cell-material interactions, rate and pattern of cell growth, phenotype differentiation markers and functional activity. The appropriate methodologies are conditioned by the co-culture set up, Fig. 4.

Multi-culture models

Bone remodeling requires proper blood supply and, thus, incorporating vascularization (in vitro, microvascular endothelial cells) appears interesting to mimic remodeling.

Tri-culture models involving osteoblasts, osteoclasts and endothelial cells have been established and results showed mutual phenotype interactions in terms of viability, proliferation and functional activity, compared to single- or two-cell type cultures (Pagani *et al.*, 2018; Grémare *et al.*, 2019). In the same line, a tetra-culture model was described involving endothelial cells, MSCs, MSCs differentiated into osteoblasts and osteoclast mononuclear precursors, showing that the presence of endothelial cells had a positive effect on the osteogenic and osteoclastogenic differentiation, with all the four cell types having synergic effects (Bongio *et al.*, 2016).

Immune Cells Involved in Bone Remodeling

The immune system and the bone tissue are closely related, sharing a variety of cytokines, receptors, signaling pathways and transcription factors (Chen *et al.*, 2016). The initial immune response elicited by the biomaterial, strongly depending on its physicochemical profile, is an essential player in the outcome of the material osteointegration/replacement and long-term performance. Abnormal immune response leads to an imbalance between osteoclastogenesis and osteogenesis, resulting in poor remodeling, normally favoring bone loss and implant failure. Characterization of the immune response elicited by the material should be included in a standard evaluation protocol (Chen *et al.*, 2016).

Complex immune cellular and humoral crosstalk modulates osteoclastogenesis and osteogenesis through three major cytokines associated to these events, M-CSF, RANKL and OPG. During normal bone remodeling, T and B-lymphocytes cooperate in the process of basal bone turnover to maintain bone homeostasis. RANKL is expressed by activated T-cells and neutrophils, and, in turn, B-lineage cells are the major source of bone marrow-derived OPG (Pacifci, 2010). A variety of immune mediators elicits indirect effects on osteoclastogenesis and osteogenesis, acting through the M-CSF/RANKL/OPG axis. IL-1, TNF- α , IL-6 and oncostatin promote, alone or in combination, osteoclast differentiation and function. Otherwise, TGF- β , IFN- γ , IL-17, BMP-2, and VEGF favor osteogenesis and bone formation.

Among the immune cells, macrophages have multiple roles in the bone healing. These cells are broadly classified into M1 and M2 phenotypes, based on their distinct biological profile. In a simple view, the pro-inflammatory M1 subtype (producing osteoclastogenic cytokines), appears to be dominant in the early stages of the repair process during the acute inflammatory reaction. The M2 subtype plays a more relevant role during the mid- to late stages of the process and, by releasing different cytokine patterns, might lead to either the formation of a fibrocapsule or the formation of new bone, at the bone-implant interface (Chen *et al.*, 2016). Conversely, bone cells also modulate immune cells. For instance, osteoclasts secrete TNF, IL-1 and IL-6, amplifying osteoclastogenesis and inflammation, and activated MSCs can induce the macrophage phenotype M2, decreasing inflammation and stimulating the healing process (Yiostalo *et al.*, 2012).

In vitro, biomaterials can be assessed in the presence of immune cells (e.g., neutrophils, mast cells, monocytes/macrophages), to analyze reciprocal interactions, applying the usual cell culture/material methodologies. Culture models using macrophages are a relevant tool due to the important role of this cell type in the bone repair process (Rayahin and Gemeinhart, 2017; Huang *et al.*, 2018). However, in a more integrated view, in vitro evaluation of the osteoimmunomodulation properties of bioceramics is more challenging. Proper models should incorporate the interactions between biomaterials, bone cells and immune cells, thereby involving indirect and direct co-culture systems (Chen *et al.*, 2016; Kohli *et al.*, 2018). In the simplest indirect co-culture protocols, the biomaterial is first cultured with immune cells and the attained conditioned medium is further used to feed osteoblastic and osteoclast cells to evaluate the effects on osteogenesis and osteoclastogenesis, respectively. A more representative model is the use of a transwell insert in the culture reservoir. Here, the immune cells can be cultured in indirect contact with the materials and the bone cells, allowing the simultaneous interaction of the three players, and to characterize separately the two cell types in culture. The co-culture of immune and bone cells on the biomaterial surface was also described, but this method appears to have poor reproducibility and the characterization of each cell populations implies troublesome methods of cell sorting.

In vivo Models for Bioceramics' Biological Characterization

A wide range of animal models has been commonly used in bone tissue-related research, as a platform to address and characterize the biological response of ceramic-based biomaterials, at the molecular, cellular and tissue level, further assisting on the characterization of the biocompatibility, osteoconductivity/osteoinductivity/osteoinductivity, mechanical functionality and degradation process of developed bioceramics. By assisting on the translation of in vitro outputs into clinical testing, experimental animal models allow a further understanding of the healing/regeneration process, establishing a controlled and standardized research setting for translational data validation. Herein, we approach and discuss the commonly used animal species and defect models for the characterization of bioceramics and related biomaterials for bone tissue application.

Animal Species

Established literature overview supports the use of distinct animal species in orthopedic-related research, including the rat (36%–38%), rabbit (13%–19%), mouse (15%–26%), sheep (11%), dog (9%), goat (4%), primates (3%) with the remaining including less used models as the pig, sheep and cat (O'Loughlin *et al.*, 2008; Martini *et al.*, 2001). From a biological point of view, no single model provides a fulfilled and representative comparison to the bone healing process of humans, with a wide variation in anatomical, biochemical and biomechanical characteristics of the bone tissue and related healing process, attained between species and individual strains (Aerssens *et al.*, 1998). As so, each model should be carefully selected in order to address adequately a particular research question, normally sustaining a progressive research approach, starting from small animals (as mice, rats and rabbits) into a higher phylogenetic complexity (as with dogs, goats, pigs, or sheep), in accordance with guidelines for market approval of ISO standards and regulatory agencies' policies.

The selection of a particular animal model is thus a determinant step in the study protocol establishment, and should entail the biochemical and microstructural characteristics of the bone tissue, as well as those of the healing process. Macrostructural differences, in gross anatomy and cortical/cancellous distribution should further be acknowledged, as they can influence the biomechanical parameters that greatly modulate the healing outcome. Age and endocrine status are further variables that can have a significant impact on the outcome of bone repair and regeneration, and thus are important to define and control (Muschler *et al.*, 2010). Other factors that should be taken into consideration throughout the study design regarding animal selection include animal size, cost for acquisition and maintenance, availability, ethical/social acceptability, easy of manipulation, staff familiarity and technical capacity, biomarkers availability, among others (Auer *et al.*, 2007; Pearce *et al.*, 2007). In addition, and according to regulatory standards, one should further consider the dimensions of the test biomaterials/constructs, number of implants per animal, duration of the biological evaluation and attained biological differences between species (Ghasemi-Mobarakeh *et al.*, 2019).

Rodent models

Rodents embrace a wide group of strains of both mice and rats, being characterized by significant dissimilarities of metabolic and structural characteristics of the skeleton, as comparing to humans. It is of mention the modeling-driven skeletal organization, the open growth plates at long bones' epiphysis, the absence of organized Harversian systems, predominance of cortical bone and limited cortical remodeling or secondary osteon formation (Pearce *et al.*, 2007; Erben, 1996). Notwithstanding, cancellous implant studies can still be conducted at the distal femur and proximal tibia locations, regardless of the established size limitations for multiple implant evaluation (Gomes and Fernandes, 2011). Nonetheless, multi implants can be placed on the calvarial bone considering sub-critical size defects and the predominant cortical organization of parietal bones (Gomes and Fernandes, 2011).

Rodents further present a high bone growth rate, established throughout the largest portion of life expectancy, thus continuing significantly after maturity, with the onset of puberty being disassociated from the process of growth plate closure contrariwise to other species (Kilborn *et al.*, 2002). Rodents also report an increased mineral density of the cancellous and cortical bone, as comparing to humans and other species – high levels at the trabecular structure might be related to the fewer but thicker *trabeculae*, while increased cortical density might be associated with the decreased intracortical remodeling, as comparing to higher species (Jerome and Peterson, 2001; Bagi *et al.*, 2011).

On the other hand, rodents, given their small size, low cost of either acquisition and maintenance, and easy manipulation, are broadly considered for first-line models for in vivo assessment of bone tissue regenerative strategies, given the well-established models, wide availability of biomarkers and comparative background data (Gomes and Fernandes, 2011). In addition, rodent species are well defined genetically, and can further be easily manipulated in order to address molecular approaches within the research purposes. In this context, immunocompromised mice and rats can be used for the biological assessment of tissue engineering constructs composed of allogenic and xenogenic constituents (McGovern *et al.*, 2018).

Rabbits

Rabbits are small mammals of the *Leporidae* family and *Lagomorpha* order, frequently used in bone-related research since they are easily available, are easy to house and manipulate and display a convenient size. Long bones, such as the tibia and femur, as well as the calvaria, are favorite locations for both cortical and cancellous implant studies – with the tibia being the most easily accessible and the femur allowing for adequate internal fixation (Burkholder *et al.*, 2012). Skeletal maturation – which is attained at the relative young age of 6 months – allows for the biocompatibility assessment in cancellous bone at the femoral condyles, and

also, contrariwise to rodents, at the calvarial location, with monocortical and bicortical defects being established and widely applied in research. Additionally, rabbits, as compared to rodents, present a more secondary osteonal remodeling, more similar to the process attained in the human bone (Muschler *et al.*, 2010), and are considered young adults at the time of epiphysis closure (Kilborn *et al.*, 2002).

Structurally, significant differences exist between rabbits' bones and those of human, regarding both shape and size, and as also in terms of biomechanical loading, given the distinct posture and movement of both species. Bone structure of rabbits' long bones relies on a primary longitudinal distribution of osteons, parallel with the long axis surrounding the medullary canal and periosteum. Rabbits also report a fast bone turnover, as comparing to other species, with a significant intracortical Haversian remodeling (Castañeda *et al.*, 2006) - which can be less representative of the human healing process. Rabbits, as rodents, present a higher cortical bone mineral density as comparing to higher models, possibly related to the reduced intracortical remodeling verified in these species (Bagi *et al.*, 2011), which further justifies a higher fracture resistance of the long bones, attaining values similar to that of humans (Wang *et al.*, 1998).

Dogs

Canine species are broadly used for the biocompatibility assessment of bone regenerative approaches, particularly within the dental and craniofacial field, considering the anatomical and tissue similarity, as well as the ability to develop periodontitis and peri-implantitis disease models similar to the human conditions (Albuquerque *et al.*, 2012; Berglundh *et al.*, 2003). Structurally, dogs and humans bones share numerous similarities including the formation of secondary osteons, cortical remodeling, as well as similar organic and inorganic composition. Haversian structure embraces 3–5 lamellar concentric rings, and relatively small Haversian canals in proportion to the osteon size (Morris, 2007).

Comparatively, a structure closely to that of the human bone is attained, with eventually a small dimension of the osteon diameter of dogs. Additionally, dogs' bone tissue is characterized by the existence of plexiform (laminar) bone in the close vicinity to the periosteum and endosteum – an histological type associated to rapidly growing animals and seldom observed in human children during large growth spurts (Cattaneo *et al.*, 2009). This tissue is structured more rapidly than secondary osteons, and characterized by a “brick wall” effect, elapsing from the radial, circumferential and longitudinal organization of primary osteons with rectangular vascular spaces, and rarely alternating lamellar bone layers (Hillier and Bell, 2007; Mulhern and Ubelaker, 2001). Additional differences are related with the higher trabecular turnover rates in dogs, averaging $2\text{--}5 \times$ times as compared to humans (Reichert *et al.*, 2009). Apposition and remodeling rates seem to vary significantly between bones of the same animal, as well as between breeds (Huja and Beck, 2008).

Pigs

Pigs have also been largely used within bone-related research given the established anatomical, morphological and biochemical similarities with the human bone. Notwithstanding, these animals may be difficult to manipulate, given their high end body weight and more aggressive behavior, being often disregarded in the favor of goats and sheep. Accordingly, miniature pigs and micropigs have been developed in order to prevail over these limitations, with significant success (Wang *et al.*, 2007; Ruehe *et al.*, 2009).

In pigs, tibias and femurs are proportionally small, considering animal weight and structure, which can preclude the assessment of multiple human-size implants; however, calvarial bone and the maxilla can be effectively considered for translational applications. Pigs' bones present a great similarity to human's bones regarding structure, mineral density and mineral concentration, remodeling – occurring both at trabecular and intra-cortical locations – and healing – with the regeneration rate being the most close to the one of humans (Reichert *et al.*, 2009). A lamellar bone microstructure, resembling those of humans, has also been described, despite the denser trabecular organization (Wancket, 2015). In immature animals, the presence of plexiform bone is also abundant within cortical locations of long bones (Hillier and Bell, 2007).

Sheep and goat

Sheep and goat are embraced as reliable models for the assessment of translational bone regenerative therapies, given the adequate dimensions of long bones and biomechanical loading, and similar body weight to humans (Martini *et al.*, 2001; Kruyt *et al.*, 2004). The macrostructure of the bone tissue is quite similar to that of humans in both sheep and goat, however, the tissue is essentially structured by primary bone with osteons presenting less than 100 μm , while humans present a broadly secondary bone organization (Jordana *et al.*, 2016). Further, both species present a non-uniformly distributed Haversian organization throughout individual bones, being these systems particularly concentrated at specific bone sectors (e.g., cranial portion of the tibial diaphysis) (Dias *et al.*, 2018).

Sheep, up to 3–4 years of age, present a predominant plexiform bone structure, with secondary remodeling not occurring prior to the 7–9 years of age (Li *et al.*, 2015). Mature animals present a high trabecular bone density, superior to that of humans up to 2 times, further associated with an increased bone strength and higher bone ingrowth rate (Willie *et al.*, 2004). Notwithstanding, significant differences seem to be associated with the anatomical location (Liebschner, 2004). Immature animals, on the other hand, are characterized by a low-density trabecular structure that is broadly flexible given the increased collagenous content (Nafei *et al.*, 2000). Goats broadly report a metabolic rate and remodeling rate at the bone tissue, similar to that of humans (Pearce *et al.*, 2007), with a sequence of bone ingrowth similar to the one described for sheep (Pearce *et al.*, 2007).

The experimental manipulation of ruminants implies specific considerations regarding handling and housing, given their size, as well as through the perioperative period, namely throughout anesthesia and ventral recumbence position (Dias *et al.*, 2018).

Non-human primates (NHPs)

NHPs are widely characterized and used models within bone tissue applications, given the high genetic homology with humans and similarity on gait, posture, skeleton and bone tissue structure, organization and osteonal remodeling (Jerome and Peterson, 2001). Used species include African green monkeys, (*Cercopithecus aethiops*), Rhesus macaque (*Macaca mulatta*), and baboon (*Papio hamadryas*) as well as marmosets. NHPs are particularly relevant models within bone implant research in which the biomechanical component is not adequately mimicked by other species – anatomical locations such as the femur, ileum, vertebral bodies, ribs' cortex, mandible and calvarial are commonly considered. However, long bones-related assessment are broadly appropriately matched for distinct large models, as those from NHPs may be too small to support human translational implants, given the inferior total body weight and proportional bone size of the most commonly used species, only baboons approach the humans' skeletal size range (Muschler *et al.*, 2010). Furthermore, it has been presumed that NHPs' models allow for the most extrapolative and clinical predictable research for the assessment of immunological and biological response, given the similarity in the biological milieu, anatomy, endocrine and major systems' functionality. However, attained response outputs seem to be as heterogeneous, or even more, than those attained with quadrupeds' models, substantially diminishing this argument (Muschler *et al.*, 2010). NHPs-based research is also significantly expensive due to the price of animal acquisition and critical-care maintenance. Furthermore, substantial social and ethical issues should be largely acknowledged on the experimental use of these animals.

Models of Ectopic Bone Formation

Prior to the characterization of bioceramics within an orthotopic bone model, a first-stage evaluation is generally conducted within an ectopic model. Ectopic derives from the greek word *ektos* (away from a place), and refers to the process of ossification/mineralization in an anatomical location distinct from its usual origin – i.e., the bone tissue. Ectopic bone formation is normally evaluated in small animal models (rodents and rabbits) and allows the evaluation of the biological response in the absence of bone-specific growth factors, and endogenous local or recruited bone forming cells and related precursors, sustaining a particularly controlled milieu for the evaluation of the in vivo experimental bone formation (Scott *et al.*, 2011). It is further assayed in the absence of biomechanical stimulation – eventually some compressive forces may be established, depending on the construct/implant size, and particularly on the kidney capsule model – thus minimizing bone-stimulating mechanotransduction (Scott *et al.*, 2011). Data analysis may also be hindered by the eventual resorption of the newly formed ectopic bone (Eyckmans and Luyten, 2006).

Ectopic assessment is of particular relevance for the characterization of osteoinductive structures, or tissue engineering constructs containing bone-forming cells or related growth factors. Different anatomical locations have been used with success, including intramuscular, subcutaneous, and kidney capsule locations.

Ectopic models are relatively economic and cost-effective, yielding fast and potentially translational results that allow for the research progression into more clinically relevant approaches (Eyckmans and Luyten, 2006; Scott *et al.*, 2011). Usually, constructs or biomaterials are implanted in the defined anatomical region and, after an appropriate period of time, are excised with the neighboring tissue and examined through imagiological and histological techniques to address the existence and characteristics of newly formed bone tissue (Scott *et al.*, 2011). Diffusion chambers may be used to assay fast releasing substances. While small animals are generally preferred, established differences on the attained biological response exist between species (Westhauser *et al.*, 2017; Eyckmans and Luyten, 2006).

Subcutaneous implantation

The implantation in subcutaneous tissue is the simplest experimental procedure for ectopic evaluation that can be established in any common animal model. Rodents are generally preferred for economic reasons, as well as the lax skin that facilitates the accommodation of large volume implants and availability of genetic-manipulated and immunodeficient models that allow heterogenic and xenogenic assessment.

Incisions are normally conducted on the dorsum, minimizing the risk for the animal to remove the stiches and sutures (Hoogstraten-Miller and Brown, 2008). Care should be taken regarding the physical identification of the implant/biomaterial, as throughout the healing period, grown tissues mimic the surrounding subdermal tissues. The lax skin of rodents also allows for implant/biomaterial migration, which can difficult its recover upon the end of the implantation period.

Subcutaneous location is also characterized by the general absence of bone-forming precursor or mature cells – as in comparison to the intramuscular location in which resident precursor cells might differentiate into the osteogenic lineage upon adequate stimulation – which can be an advantage or a hindrance, depending on the experimental protocol and study objectives. Additionally, a reduced blood flow and vascularization is attained in subcutaneous locations, as comparing to intramuscular, or the kidney capsule model. As so, a decreased bone formation is normally attained in the subcutaneous model, as comparing to other target model locations (Habibovic and de Groot, 2007; Yang *et al.*, 1996).

Intramuscular implantation (muscle pouch)

Intramuscular implantation, as the subcutaneous location, can be largely applied to a vast range of animal models, despite the preference for the use of rodents (Asatrian *et al.*, 2014). In these animals the hind limb is a preferred location, allowing for the use of larger implants, while the lower leg, on the other hand, entails the use of smaller implants but facilitates palpation and surface identification (Scott *et al.*, 2011). In large animals, the dorsal musculature is generally preferred (Willie *et al.*, 2004).

Intramuscular implantation is associated with an increased bone formation process, given the verified activation of BMP-signaling cascade and other osteogenic-signaling pathways upon the established muscle injury, for implant/biomaterial placement (Asatrian *et al.*, 2014). One must further considered the recruitment/activation of muscle-related precursor cell populations (e.g., satellite cells) that can, upon adequate stimulation, induce the local osteogenic process. An atraumatic surgical procedure, embracing a blunt-dissection approach is thus required to minimize tissue activation.

Kidney capsule implantation

The kidney capsule implantation model, due to its technical/surgical difficulty, is less used than prior ectopic models. Implant/biomaterials are to be placed between the renal parenchyma and the capsule of the kidney, either by injection or following incision – given the creation of adequate space by blunt dissection. Care should be given to keep the capsule intact ensuring adequate implant confinement (Cunha and Baskin, 2016).

Renal capsule implantation is associated with supra-physiological blood flow and nutrient supply to the implant, which may significantly increase the bone formation response, as comparing to other ectopic models (Scott *et al.*, 2011). Implant size must be critically selected to prevent capsule damage and is generally inferior to that used in intramuscular and subcutaneous approaches. Also regarding size, large-volume implants can induce compressive forces which may influence the biological outcome (Scott *et al.*, 2011).

Models of Orthotopic Bone Formation

Orthotopic models are broadly used for the assessment of the efficacy and biosafety of new biomaterials/tissue engineering products or bone regenerative procedures, with investigational procedures being established in or around the bone tissue. Orthotopic derives from the greek work *orthos*, that refers to “right, straight” defining an approach on the correct anatomical location, in this case, the bone tissue. Different approaches can be employed within this context, being either non-surgical (e.g., injection of materials into long bones’ periosteum) or surgical (e.g., a calvarial drilled defect or long bone segmental defect, with materials grafted on the defect site) (McGovern *et al.*, 2018). The most commonly approaches include the calvarial/mandibular defect, the long bone segmental defect, partial cortical defect and cancellous bone defect, with the former two being the most widely used and following addressed (Bigham-Sadeh and Oryan, 2015).

Calvarial/mandibular bone defects

The calvaria bone defect is commonly conducted in small animals (i.e., rodents and rabbits) (Gomes and Fernandes, 2011) despite its successful application in larger animal models (Szpalski *et al.*, 2010). The calvarial defect is a well-established and adequate model given the macrostructure of the calvarial bone, allowing the establishment of uniform and standardized defects that can be easily characterized through imagiological or histological techniques, with minor influence of neighboring structures. Further, the calvarial approach allows for an adequate surgical access and biomaterial/construct implantation in different animal models, given the support provided by the dura mater and associated tissues. However, this defect model does not allow for the bone healing process under physiological mechanical loading, which might be of relevance for particular applications (Gomes and Fernandes, 2011). Overall, it is a widely used model, so vast amount of background data is available, which thus facilitates data analysis and comparison (Spicer *et al.*, 2012).

Briefly, a full-thickness anteroposterior mid-sagittal incision is created and a flap is subsequently raised and retracted to expose the calvarial bone. A standardize circular defect is following established, usually with a trephine burr under copious irrigation, involving the complete thickness of the bone – normally the parietal. Care must be given to prevent dura damage by periodically checking osteotomy depth, for which a neural or periosteal elevator can be used. The drilled bone disk is then carefully elevated and biomaterials/constructs are implanted in the volume of the created defect. Following, the periosteum is repositioned and sutured, and the overlying muscular tissue and skin flap are positioned and sutured, Fig. 5.

When establishing a surgical bone defect, the overall dimensions of the defect is a critical point that needs to be copiously considered. Critical size defects (CSDs) have been classically defined as those intra-osseous located, that present the smallest size, for a given bone and species, that are not able to heal spontaneously throughout the lifetime of the animal (Schmitz and Hollinger, 1986). These were developed to model human nonunions, establishing defects that were unable to heal on their own. Subsequently, the definition was revised to the defects in which the bone regeneration was inferior to 10%, throughout animals lifetime (Hollinger and Kleinschmidt, 1990). Despite widely disseminated, these concepts seem to lack functionality, given the majority of studies are of limited duration and do not extend over the animals’ lifetime (Cooper *et al.*, 2010). As so, a more functional approach on CSDs definition relies on an established defect that does not heal over the duration of the study, leaving behind the idea of “smallest size bone defect” and concept of “lifetime of the animal” (Gosain *et al.*, 2000).

Even in this context, there is a wide range of dimensional variation of the CSD according to each species, further considering a wide variation according to the weight, age and strain, of a given species (Schmitz *et al.*, 1990). Circular defects, established with

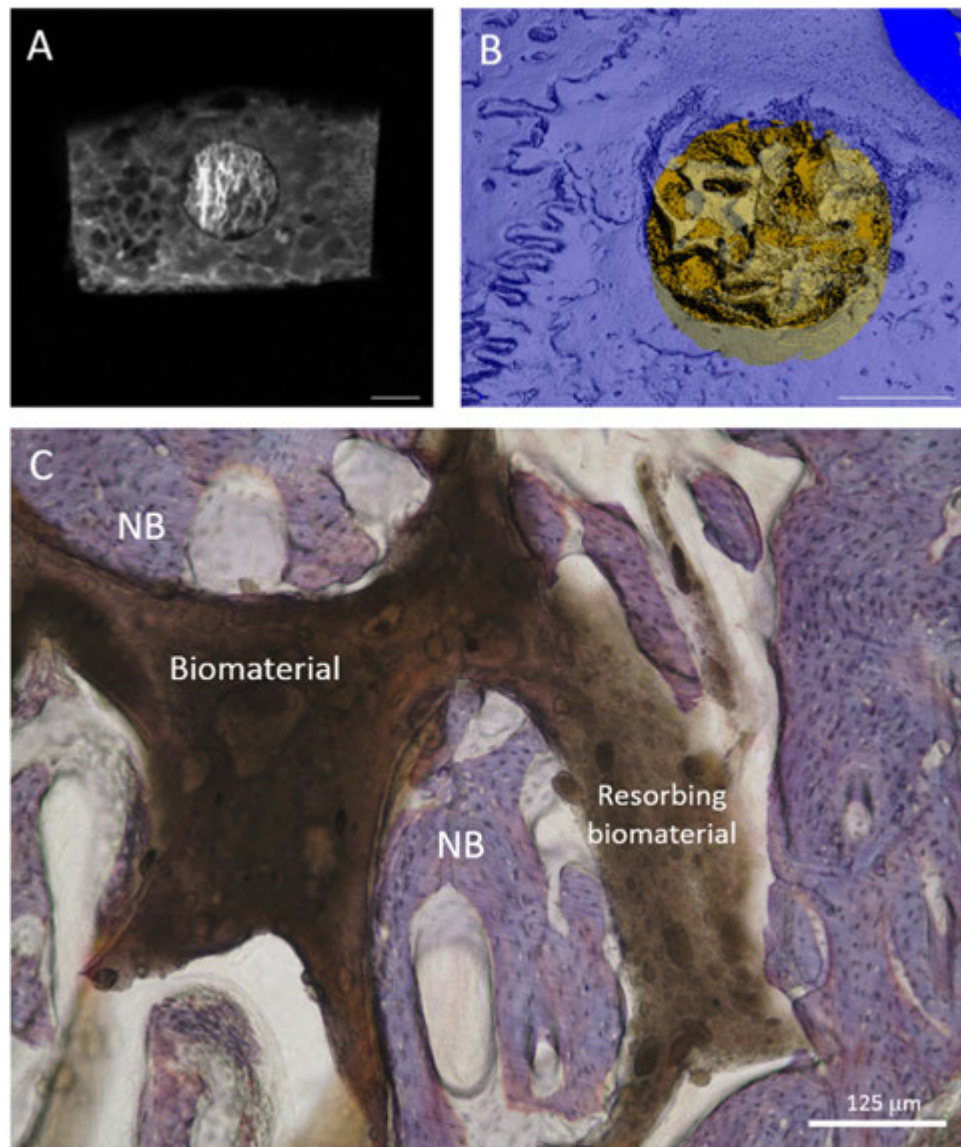


Fig. 5 Regeneration of rabbit calvaria defects. (A), radiographic image of a 5 mm calvaria defect implanted with a bioceramic scaffold for 3 months; (B), microtomographic 3D reconstruction of a 5 mm calvaria defect implanted with a bioceramic scaffold (orange) for 3 months. Note the newly formed bone tissue at the defect volume (yellow); (C), histological section of a 5 mm calvaria defect implanted with a bioceramic scaffold for 3 months. Note the close interaction of the newly formed bone tissue (NB) with the biomaterial and the progressive resorption of the implanted scaffold. Scale bar of A and B correspond to 2.5 mm.

trephine burrs, have been widely conducted, given the consistency and easiness of the surgical procedure. Still, other defect configurations, ranging from oval, square, rectangular and trapezoidal have further been reported, broadly by the use of reciprocating saw or round dental burs (Mardas *et al.*, 2014).

In the mouse model, 3, 4, and 5 mm in diameter parietal defects were found to be critical sized in the adult, whereas significant healing was seen regardless of the size of the defect, in juvenile mice (Aalami *et al.*, 2004), leading to the overall acknowledgment that defects larger than 5 mm in diameter are critical size in nature for this species (Ning *et al.*, 2017).

In the rat, there has been controversy on the established CSD dimensions. Broadly, 5 mm in diameter are most commonly used, and were shown, after 12 months of healing, to allow for a minimal bone formation at the defect margin (Bosch *et al.*, 1998). The 5 mm defect allows the establishment of 2 defects per animal allowing a paired split design experiment, and the avoidance of the sagittal suture within the defect limits, which can alter the healing process (Gomes and Fernandes, 2011). On the other hand, some reports shown an increased healing at the defect margin with 5 mm defects, further advocating the use of 8 mm for CSDs (Hollinger and Kleinschmidt, 1990; Gomes and Fernandes, 2011).

In the rabbit, calvaria defects are generally located in the parietal, frontal or both bones, and the vast majority of studies employs a 15 mm diameter circular defect (Delgado-Ruiz *et al.*, 2018). Interestingly, the defect dimensions seems to have a direct influence on

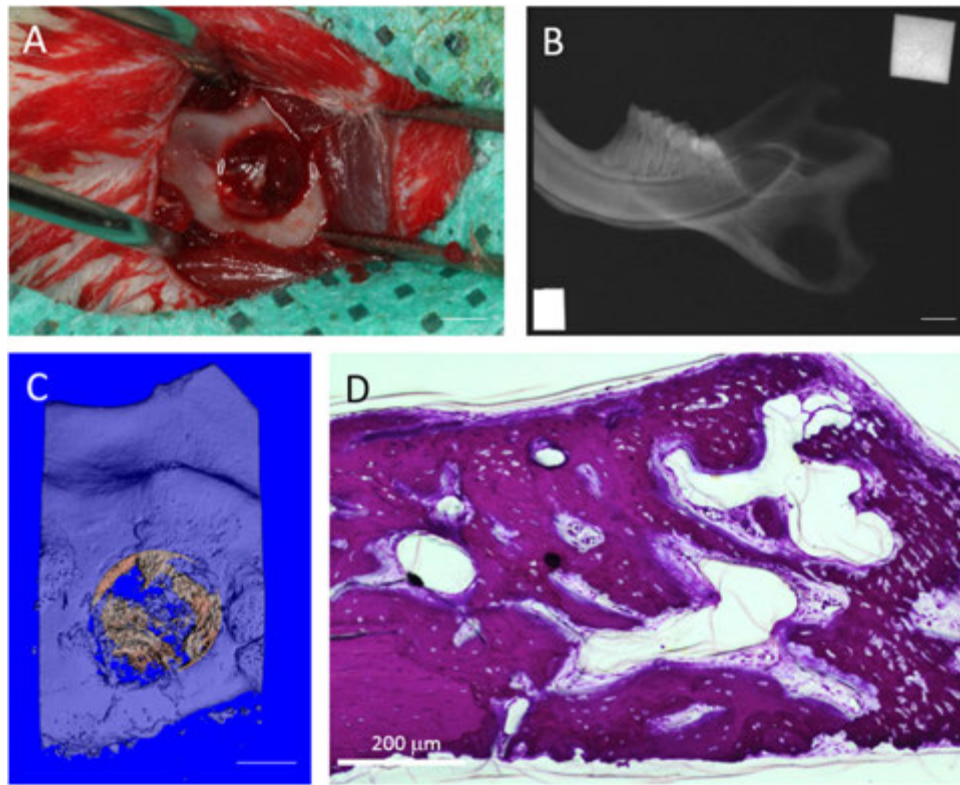


Fig. 6 Regeneration of rat mandibular defects. (A) Intraoperative image of the establishment of a critical size defect (CSD) at the rat mandible (5 mm in diameter); (B) radiographic image of a 5 mm calvaria CSD defect, healed for 3 months; (C) microtomographic 3D reconstruction of a 5 mm mandibular CSD defect, implanted with bioceramic nanoparticles for 3 months. Note the newly formed bone tissue at the defect volume (pink), interspersed with particles remnants; (D) histological section of a 5 mm mandibular CSD defect, implanted with bioceramic nanoparticles for 3 months. Note the newly formed bone tissue with a cancellous organization. Scale bar of A, B, and C correspond to 2.5 mm.

the regenerative outcome, with defects larger than 15 mm sustaining an increased healing with longer regenerative periods (Delgado-Ruiz *et al.*, 2015, 2018). Defect smaller than 15 mm can also be considered CSDs, depending on the time of assessment (Delgado-Ruiz *et al.*, 2015). A similar size range has been established as CSDs in pigs and minipigs calvarial bone. Calvarial CSDs have been further established for other species, particularly the dog (20 mm diameter defects (Cui *et al.*, 2007)), sheep (22 mm diameter defects (Viljanen *et al.*, 1997)) and some NHPs, such as monkeys (15 mm diameter defects) (Brierly *et al.*, 2016).

In addition to the calvaria, the mandible can be also used for the establishment of circular full thickness (through-and-through) defects, offering an increased content of cancellous bone between the cortical structures. Furthermore, mandible offers the possibility to establish physiological biomechanical loading throughout the healing process, further mimicking a translation application, particular to dental and craniofacial-related applications, Fig. 6.

Whether rodents and rabbits have narrow and small mandibles, continuous (circular) defects are most commonly employed than segmental defects that further require adequate stabilization. CSDs for rat mandible have been established to be of 5 mm in diameter (Arosarena and Collins, 2003), a dimension similar to those established for rabbits (He *et al.*, 2008). In minipigs, at the lower border of the mandible, full-thickness 8 mm full thickness defects were established as critical size (Mardas *et al.*, 2014). Larger animal models report CSDs of increased dimensions – for instance in the dog, 20 mm defects have been established to be critical size (Cui *et al.*, 2007), while in sheep, 22 mm diameter defects are acknowledged to be CSDs (Brierly *et al.*, 2016).

Segmental bone defects

Long-bone segmental defects have been established, in distinct animal models, embracing the removal of a defined segment from a determined site of the bone. Globally, the established defect should allow the biomaterial/construct to be characterized under similar conditions to that required for clinical application (Gugala *et al.*, 2007). As for the calvarial/mandibular defect, and in order to create and reinforce the bone healing ability of nonunions, the segmental defect must be of enough dimensions to preclude the direct bone healing – bridging of the defect – that is, a critical size defect (CSD). As a rule of thumb, the defect should be 2–2.5 times the diameter of the long bone's shaft (Gugala *et al.*, 2007). Furthermore, other factors should be taken into the consideration for segmental CSDs' establishment, including the definition of species, age, anatomical location, presence of periosteum, biomechanical loading, endocrine and systemic condition, and as significantly different from calvarial/mandibular circular defects, the fixation process for the defect stabilization.

Distinct anatomical locations (e.g., tibia, femur, radius, ulna and humerus) have been considered, which further difficult comparative analysis of the data, given the established healing differences on the bone tissue itself, or supporting tissues, as the periosteum (Fuji *et al.*, 2006). Fundamentally, segmental defects can be established through osteotomy or trauma. Osteotomy endorses the use of a drill/burr or saw to remove surgically the defined section of the bone, from a predetermined location, establishing a high consistency between replicates (Reichert *et al.*, 2009). Alternatively, and in order to more closely mimic trauma-related clinical scenario, the defect can be created with a 3-point bending device, commonly employed for experimental fracture establishment, creating a sharp cut edge, injuring both the bone and involving soft tissues. This approach originates a larger variability on the established defects (Li *et al.*, 2015).

Ideally, a segmental bone defect should mimic clinical translational conditions, allow for adequate defect fixation, permit early biomechanical loading and facilitate the biological processes of healing (Horner *et al.*, 2010).

Within the mice, representatively, femoral mid-diaphysis 3.5–4 mm defects sustain the absence of bridging, with endochondral ossification at the defect margins and intramembranous ossification at mid-portion following biomaterials/constructs implantation (Tiyapatanaputi *et al.*, 2004; Manassero *et al.*, 2016). Alternative models have been created with reduced defect dimensions (e.g., 1.8 mm) but increased periosteum stripping, further highlighting the relevance of the periosteum on assisting bone healing (Garcia *et al.*, 2008). Radial defects (CSD – 4 mm) have also been largely used due to the attained high stability achieved by the ulnar support (Ning *et al.*, 2017).

In the rat, segmental CSDs of the tibia have been established within the 4–5 mm range, and between 5 and 10 mm within the femur (Garcia *et al.*, 2013). In the mandible, 5 × 5 mm full-thickness defects were found to correspond to CSDs (Arosarena and Collins, 2003). In the rabbit, CSDs of long bone have been found to range from 10 to 20 mm, in different long bone such as the humerus, radius, ulna, tibia and femur and mandible (Lu and Rabie, 2003; Zhao *et al.*, 2016; Crigel and Balligand, 2002) and significantly larger (50 mm), at the ribs (Liu *et al.*, 2016). For dogs, commonly used CSDs range from 20 to 70 mm in the femur (Jewell *et al.*, 2015), between 20 and 25 mm in the radius and ulna, and between 35 and 50 mm within the mandible (Marei *et al.*, 2018). In minipigs, critical size mandibular segmental defects have been determined as 60 mm and 20 mm, with and without periosteum stripping, respectively (Ma *et al.*, 2009), whether long bones CSDs seem to range within 25–30 mm. In sheep, used models rely on femoral CSDs ranging from 25 to 50 mm, tibial CSDs ranging from 20 to 50 mm, with the 30 mm defect being the most used (Jewell *et al.*, 2015; Lammens *et al.*, 2017).

The process of fixation is another fundamental aspect regarding the selection of segmental bone defects. It is expected that experimental fixation within animal models mimics the clinical scenario, allowing for sufficient defect stabilization that endorses bone healing (Reichert *et al.*, 2009). This is of additional relevance for load-bearing defects, as comparing to those established in naturally supported bones such as the radius or fibula. Internal fixation devices, such as intramedullary rods, screws and bone plates, or external devices as external fixators or cast and splints, are commonly used. Still, the vast majority of approaches are not originally designed for the application in experimental animal models, and its possible effect on the modulation of the healing process is largely unknown.

Conclusion

In vitro and in vivo evaluation of bioceramics is needed throughout the all process of material development, although with distinct meanings, aiming to end up with a safe and effective product for bone regeneration. In vitro assays, targeted for the evaluation of a bone regenerative material, inform on the bone cells' differentiation and functional activity at the bone cells/material interface. Further, downstream mechanisms underlying the elicited response might be analyzed in controlled and defined cell culture/material conditions needed to unveil molecular signaling pathways. However, the structural, metabolic and functional complexity of the bone tissue calls for appropriate in vivo experimentation to assess the bone regenerative efficacy of the biomaterial together with its local and systemic safety. In this way, the in vitro testing is expected to function as a reliable pre-screening to guide subsequent studies through the biomaterial testing pipeline.

The wide variability of the in vitro methodologies related with the cell type and passage, culture protocols, evaluated parameters and inferred results significance can result in significant data discrepancy, compromising its usefulness for predicting in vivo outcomes and, therefore, to guide on the further appropriate animal testing. Similar reasoning is applied to the in vivo testing, namely the results translation from the small animals to the large animal models and from the preclinical studies into clinical trials. Nevertheless, as a whole, in vitro and in vivo testing should provide reliable information for rapid and safe translation to the clinical setting. The predictability of these assays is continuously being improved due to the constant development of testing methodologies, together with standardization and validation strategies.

References

- Aalami, O., Nacamuli, R., Lenton, K., *et al.*, 2004. Applications of a mouse model of calvarial healing: Differences in regenerative abilities of juveniles and adults. *Plastic and Reconstructive Surgery* 114, 713–720.
- Aerssens, J., Boonen, S., Lowet, G., Dequeker, J., 1998. Interspecies differences in bone composition, density, and quality: Potential implications for in vivo bone research. *Endocrinology* 139, 663–670.

- Akintoye, S., Lam, T., Shi, S., *et al.*, 2006. Skeletal site-specific characterization of orofacial and iliac crest human bone marrow stromal cells in same individuals. *Bone* 38, 758–768.
- Al-Nbaheen, M., Vishnubalaji, R., Ali, D., *et al.*, 2013. Human stromal (mesenchymal) stem cells from bone marrow, adipose tissue and skin exhibit differences in molecular phenotype and differentiation potential. *Stem Cell Reviews and Reports* 9, 32–43.
- Albuquerque, C., Morinha, F., Requicha, J., *et al.*, 2012. Canine periodontitis: The dog as an important model for periodontal studies. *Veterinary Journal* 121, 299–305.
- Arosarena, O., Collins, W., 2003. Defect repair in the rat mandible with bone morphogenetic protein 5 and prostaglandin E1. *Archives of OtolaryngologyHead & Neck Surgery* 129, 1125–1130.
- Asatrian, G., Chang, L., James, A., 2014. Muscle pouch implantation: an ectopic bone formation model. *Methods in Molecular Biology* 1213, 185–191.
- Auer, J., Goodship, A., Arnoczky, S., *et al.*, 2007. Refining animal models in fracture research: Seeking consensus in optimising both animal welfare and scientific validity for appropriate biomedical use. *BMC Musculoskeletal Disorders* 8, 72.
- Bagi, C., Berryman, E., Moalli, M., 2011. Comparative bone anatomy of commonly used laboratory animals: Implications for drug discovery. *Comparative Medicine* 61, 76–85.
- Baker, M., 2016. Reproducibility: Respect your cells. *Nature* 537, 433–435.
- Berglundh, T., Abrahamsson, I., Lang, N., Lindhe, J., 2003. De novo alveolar bone formation adjacent to endosseous implants: A model study in the dog. *Clinical Oral Implants Research* 14, 251–262.
- Bigham-Sadegh, A., Oryan, A., 2015. Selection of animal models for pre-clinical strategies in evaluating the fracture healing, bone graft substitutes and bone tissue regeneration and engineering. *Connective Tissue Research* 56, 175–194.
- Blair, H., Larrouette, Q., Li, Y., *et al.*, 2017. Osteoblast differentiation and bone matrix formation in vivo and in vitro. *Tissue Engineering Part B: Reviews* 23, 268–280.
- Bonewald, L., 2011. The amazing osteocyte. *Journal of Bone and Mineral Research* 26, 229–238.
- Bongio, M., Lopa, S., Gilardi, M., Bersini, S., Moretti, M., 2016. A 3D vascularized bone remodeling model combining osteoblasts and osteoclasts in a CaP nanoparticle-enriched matrix. *Nanomedicine* 11, 1073–1091.
- Bosch, C., Melsen, B., Vargervik, K., 1998. Importance of the critical-size bone defect in testing bone-regenerating materials. *Journal of Craniofacial Surgery* 9, 310–316.
- Boyce, B., Rosenberg, E., Papp, A., Duong, L., 2012. The osteoclast, bone remodelling and treatment of metabolic bone disease. *European Journal of Clinical Investigation* 42, 1322–1341.
- Brierly, G., Tredinnick, S., Lynham, A., Woodruff, M., 2016. Critical sized mandibular defect regeneration in preclinical in vivo models. *Molecular Biology Reports* 2, 83–89.
- Burkholder, T., Linton, G., Hoyt, R.J., 2012. The rabbit as an experimental model. In: Suckow, M., Stevens, K., Wilson, R. (Eds.), *The Laboratory Rabbit, Guinea Pig, Hamster, and Other Rodents*. Amsterdam: Academic Press.
- Carvalho, A., Cangeiro, L., Oliveira, V., *et al.*, 2018. Femtosecond laser microstructured Alumina toughened Zirconia: A new strategy to improve osteogenic differentiation of hMSCs. *Applied Surface Science* 435, 1237–1245.
- Castañeda, S., Largo, R., Calvo, E., *et al.*, 2006. Bone mineral measurements of subchondral and trabecular bone in healthy and osteoporotic rabbits. *Skeletal Radiology* 35, 34–41.
- Cattaneo, C., Porta, D., Gibelli, D., Gamba, C., 2009. Histological determination of human origin of bone fragments. *Journal of Forensic Sciences* 54, 1–3.
- Chen, Z., Klein, T., Murray, R., *et al.*, 2016. Osteoimmunomodulation for the development of advanced bone biomaterials. *Materials Today* 19, 304–321.
- Cirraldo, F., Boccardi, E., Melli, V., Westhauser, F., Boccaccini, A., 2018. Tackling bioactive glass excessive in vitro bioreactivity: Preconditioning approaches for cell culture tests. *Acta Biomaterialia* 75, 3–10.
- Coelho, M., Fernandes, M.H., 2000. Human bone cell cultures in biocompatibility testing. Part II: Effect of ascorbic acid, β -glycerophosphate and dexamethasone on osteoblastic differentiation. *Biomaterials* 21, 1095–1102.
- Cooper, G., Mooney, M., Gosain, A., *et al.*, 2010. Testing the critical size in calvarial bone defects: Revisiting the concept of a critical-size defect. *Plastic and Reconstructive Surgery* 125, 1685–1692.
- Costa-Rodrigues, J., Carmo, S., Inês, P., *et al.*, 2016. Osteoclastogenic differentiation of human precursor cells over micro- and nanostructured hydroxyapatite topography. *Biochimica et Biophysica Acta – General Subjects* 1860, 825–835.
- Costa-Rodrigues, J., Fernandes, A., Fernandes, M.H., 2011. Spontaneous and induced osteoclastogenic behaviour of human peripheral blood mononuclear cells and their CD14⁺ and CD14⁺ cell fractions. *Cell Proliferation* 44, 410–419.
- Costa-Rodrigues, J., Fernandes, A., Lopes, M., Fernandes, M.H., 2012. Hydroxyapatite surface roughness: Complex modulation of the osteoclastogenesis of human precursor cell. *Acta Biomaterialia* 8, 1137–1145.
- Crigel, M., Balligand, M., 2002. Critical size defect model on the femur in rabbits. *Veterinary and Comparative Orthopaedics and Traumatology* 15, 158–163.
- Cui, L., Liu, B., Liu, G., *et al.*, 2007. Repair of cranial bone defects with adipose derived stem cells and coral scaffold in a canine model. *Biomaterials* 28, 5477–5486.
- Cunha, G., Baskin, L., 2016. Use of sub-renal capsule transplantation in developmental biology. *Differentiation* 91, 4–9.
- Czekanska, E., Stoddart, M., Ralphs, J., Richards, R., Hayes, J., 2014. A phenotypic comparison of osteoblast cell lines versus human primary osteoblasts for biomaterials testing. *Journal of Biomedical Materials Research Part A* 102, 2636–2643.
- Czekanska, E., Stoddart, M., Richards, R., Hayes, J., 2012. In search of an osteoblast cell model for in vitro research. *European Cells & Materials* 24, 1–17.
- Delgado-Ruiz, R., Guirado, J.C., Romanos, G., 2018. Bone grafting materials in critical defects in rabbit calvariae. A systematic review and quality evaluation using ARRIVE guidelines. *Clinical Oral Implants Research* 29, 620–634.
- Delgado-Ruiz, R., Calvo-Guirado, J., Romanos, G.E., 2015. Critical size defects for bone regeneration experiments in rabbit calvariae: systematic review and quality evaluation using ARRIVE guidelines. *Clinical Oral Implants Research* 26, 915–930.
- Dias, I., Camassa, J., Bordelo, J., *et al.*, 2018. Preclinical and translational studies in small ruminants (sheep and goat) as models for osteoporosis research. *Current Osteoporosis Reports* 16, 182–197.
- Dias, A., Trigo Cabral, A., Lopes, M., Santos, J., Fernandes, M.H., 2005. In vitro studies of calcium phosphate glass ceramics with different solubility using human bone marrow cells. *Journal of Biomedical Materials Research Part A* 74, 347–355.
- El-Rashidy, A., Roether, J., Harhaus, L., Kneser, U., Boccaccini, A., 2017. Regenerating bone with bioactive glass scaffolds: a review of in vivo studies in bone defect models. *Acta Biomaterialia* 62, 1–28.
- Erben, R., 1996. Trabecular and endocortical bone surfaces in the rat: modeling or remodeling? *Anatomical Records* 246, 39–46.
- Eyckmans, J., Luyten, F., 2006. Species specificity of ectopic bone formation using periosteum-derived mesenchymal progenitor cells. *Tissue Engineering* 12, 2203–2213.
- Franz, S., Rammelt, S., Scharnweber, D., Simon, J., 2011. Immune responses to implants – A review of the implications for the design of immunomodulatory biomaterials. *Biomaterials* 32, 6692–6709.
- Fujii, T., Ueno, T., Kagawa, T., Sakata, Y., Sugahara, T., 2006. Comparison of bone formation ingrafted periosteum harvested from tibia and calvaria. *Microscopy Research and Technique* 69, 580.
- Gao, C., Peng, S., Feng, P., Shuai, C., 2017. Bone biomaterials and interactions with stem cells. *Bone Research* 21, 17059.
- Garcia, P., Histing, T., Holstein, J., *et al.*, 2013. Rodent animal models of delayed bone healing and non-union formation: A comprehensive review. *European Cells & Materials* 26, 1–12.
- Garcia, P., Holstein, J., Maier, S., *et al.*, 2008. Development of a reliable non-union model in mice. *Journal of Surgical Research* 147, 84–91.
- Geissler, S., Textor, M., Kuhnisch, J., *et al.*, 2012. Functional comparison of chronological and in vitro aging: Differential role of the cytoskeleton and mitochondria in mesenchymal stromal cells. *PLoS One* 7, e52700.

- Ghasemi-Mobarakeh, L., Kolahreez, D., Ramakrishna, S., Williams, D., 2019. Key terminology in biomaterials and biocompatibility. *Current Opinion in Biomedical Engineering* 10, 45–50.
- Ginebra, M.-P., Montserrat, E., Maazouz, Y., Bergez, V., Pastorino, D., 2018. Bioceramics and bone healing. *EFORT Open Reviews* 3, 173–183.
- Goers, L., Freemont, P., Polizzi, K., 2014. Co-culture systems and technologies: Taking synthetic biology to the next level. *Journal of the Royal Society Interface* 11, (20140065).
- Gomes, P., Fernandes, M.H., 2011. Rodent models in bone-related research: The relevance of calvarial defects in the assessment of bone regeneration strategies. *Laboratory Animals* 45, 14–24.
- Gosain, A., Song, L., Yu, P., *et al.*, 2000. Osteogenesis in cranial defects: Reassessment of the concept of critical size and the expression of TGF- β isoforms. *Plastic and Reconstructive Surgery* 106, 360–371.
- Grémare, A., Aussel, A., Bareille, R., *et al.*, 2019. A unique tri-culture model to study osteoblasts, osteoclasts and endothelial cells interactions. *Tissue Engineering Part C: Methods* 25.
- Gugala, Z., Lindsey, R., Gogolewski, S., 2007. New approaches in the treatment of critical-size segmental defects in long bones. *Macromolecular Symposia* 253, 147–161.
- Habibovic, P., de Groot, K., 2007. Osteoinductive biomaterials – Properties and relevance in bone repair. *Journal of Tissue Engineering and Regenerative Medicine* 1, 25–32.
- Hayrapetyan, A., Jansen, J., van Den Beucken, J., 2015. Signaling pathways involved in osteogenesis and their application for bone regenerative medicine. *Tissue Engineering Part B: Reviews* 21, 75–87.
- He, H., Yan, W., Chen, G., Lu, Z., 2008. Acceleration of de novo bone formation with a novel bioabsorbable film: a histomorphometric study in vivo. *Journal of Oral Pathology & Medicine* 37, 378–382.
- Hillier, M., Bell, L., 2007. Differentiating human bone from animal bone: A review of histological methods. *Journal of Forensic Sciences* 52, 249–263.
- Hojo, H., Ohba, S., Chung, U., 2015. Signaling pathways regulating the specification and differentiation of the osteoblast lineage. *Regenerative Therapy* 1, 57–62.
- Hollinger, J., Kleinschmidt, J., 1990. The critical size defect as an experimental model to test bone repair materials. *Journal of Craniofacial Surgery* 1, 60–68.
- Hoogstraten-Miller, S., Brown, P., 2008. Techniques in aseptic rodent surgery. *Current Protocols in Immunology* 82, 1.12.1–1.12.14.
- Horner, E., Kirkham, J., Wood, D., *et al.*, 2010. Long bone defect models for tissue engineering applications: Criteria for choice. *Tissue Engineering Part B: Reviews* 16, 263–271.
- Huang, Y., Wu, C., Zhang, X., Chang, J., Dai, K., 2018. Regulation of immune response by bioactive ions released from silicate bioceramics for bone regeneration. *Acta Biomaterialia* 66, 81–92.
- Huja, S., Beck, F., 2008. Bone remodeling in maxilla, mandible, and femur of young dogs. *Anatomical Records* 291, 1–5.
- Hulsart-Billström, G., Dawson, J., Hofmann, S., *et al.*, 2016. A surprisingly poor correlation between in vitro and in vivo testing of biomaterials for bone regeneration: Results of a multicentre analysis. *European Cells & Materials* 24, 312–322.
- Hwang, P., Horton, J., 2019. Variable osteogenic performance of MC3T3-E1 subclones impacts their utility as models of osteoblast biology. *Scientific Reports* 9, 8299.
- Jerome, C., Peterson, P., 2001. Nonhuman primate models in skeletal research. *Bone* 29, 1–6.
- Jewell, E., Rytlewski, J., Anglen, J., *et al.*, 2015. Surgical fixation hardware for regeneration of long bone segmental defects: Translating large animal model and human experiences. *Clinical Reviews in Bone and Mineral Metabolism* 13, 222–231.
- Jordana, X., Marín-Moratalla, N., Moncunill-Solè, B., Nacarino-Meneses, C., Köhler, M., 2016. Ontogenetic changes in the histological features of zonal bone tissue of ruminants: A quantitative approach. *Comptes Rendus Palevol* 15, 255–266.
- Karadjian, M., Essers, C., Tsilakidis, S., *et al.*, 2019. Biological properties of calcium phosphate bioactive glass composite bone substitutes: Current experimental evidence. *International Journal of Molecular Sciences* 20, 305.
- Kilborn, S., Trudel, G., Uthoff, H., 2002. Review of growth plate closure compared with age at sexual maturity and lifespan in laboratory animals. *Journal of the American Association for Laboratory Animal Science* 41, 21–26.
- Kohli, N., Ho, S., Brown, S., *et al.*, 2018. Bone remodelling in vitro where are we headed? A review on the current understanding of physiological bone remodeling and inflammation and the strategies for testing biomaterials in vitro. *Bone* 110, 38–46.
- Korkusuz, P., Kose, S., Zubeyde Kopru, C., 2016. Biomaterial and stem cell interactions: Histological biocompatibility. *Current Stem Cell Research & Therapy* 11, 475–486.
- Kruyt, M., Dhert, W., Yuan, H., *et al.*, 2004. Bone tissue engineering in a critical size defect compared to ectopic implantations in the goat. *Journal of Orthopaedic Research* 22, 544–551.
- Lammens, J., Maréchal, M., Geris, L., *et al.*, 2017. Warning about the use of critical-size defects for the translational study of bone repair: Analysis of a sheep tibial model. *Tissue Engineering Part C: Methods* 23, 694–699.
- Langdahl, B., Ferrari, S., Dempster, D., 2016. Bone modeling and remodeling: potential as therapeutic targets for the treatment of osteoporosis. *Therapeutic Advances in Musculoskeletal Disease* 8, 225–235.
- Langenbach, F., Handschel, J., 2013. Effects of dexamethasone, ascorbic acid and β -glycerophosphate on the osteogenic differentiation of stem cells in vitro. *Stem Cell Research & Therapy* 4, 117.
- Laranjeira, M., Dias, A., Santos, J., Fernandes, M.H., 2009. In vitro biological characterization of macroporous 3D Bonelike structures prepared through a 3D machining technique. *Materials Science and Engineering C* 29, 930–935.
- Lasgorceix, M., Grenho, L., Fernandes, M., *et al.*, 2018. Femtosecond laser impact on calcium phosphate bioceramics assessed by micro-Raman spectroscopy and osteoblastic behaviour. *Journal of the European Ceramic Society* 38, 5545–5553.
- Liebschner, M., 2004. Biomechanical considerations of animal models used in tissue engineering of bone. *Biomaterials* 25, 1697–1714.
- Liu, F., Chen, K., Hou, L., *et al.*, 2016. Determining the critical size of a rabbit rib segmental bone defect model. *Regen Biomater* 3, 323–328.
- Liu, T., Lee, E., 2013. Transcriptional regulatory cascades in Runx2-dependent bone development. *Tissue Engineering Part B: Reviews* 19, 254–263.
- Li, Y., Chen, S.-K., Li, L., *et al.*, 2015. Bone defect animal models for testing efficacy of bone substitute biomaterials. *Journal of Orthopaedic Translation* 3, 95–104.
- Lu, M., Rabie, A., 2003. Microarchitecture of rabbit mandibular defects grafted with intramembranous or endochondral bone shown by micro-computed tomography. *British Journal of Oral and Maxillofacial Surgery* 41, 385–391.
- Majidinia, M., Sadeghpour, A., Yousefi, B., 2018. The roles of signaling pathways in bone repair and regeneration. *Journal of Cell Physiology* 233, 2937–2948.
- Manassero, M., Decambon, A., Thong, B.H., *et al.*, 2016. Establishment of a segmental femoral critical-size defect model in mice stabilized by plate osteosynthesis. *Journal of Visualized Experiments*. e52940.
- Mardas, N., Dereka, X., Donos, N., Dard, M., 2014. Experimental model for bone regeneration in oral and cranio-maxillo-facial surgery. *Journal of Investigative Surgery* 27, 32–49.
- Marei, H., Mahmood, K., Almas, K., 2018. Critical size defects for bone regeneration experiments in the dog mandible: a systematic review. *Implant Dentistry* 27, 135–141.
- Martini, L., Fini, M., Giavaresi, G., Giardino, R., 2001. Sheep model in orthopedic research: A literature review. *Comparative Medicine* 51, 292–299.
- Mata, D., Oliveira, F., Neto, M., *et al.*, 2015. Smart electroconductive bioactive ceramics to promote in situ electrostimulation of bone. *Journal of Materials Chemistry B* 3, 1831–1845.
- Ma, J.-L., Pan, J.-L., Tan, B.-S., Cui, F.-Z., 2009. Determination of critical size defect of minipig mandible. *Journal of Tissue Engineering and Regenerative Medicine* 3, 615–622.
- McGovern, J., Griffin, M., Hutmacher, D., 2018. Animal models for bone tissue engineering and modelling disease. *Disease Models and Mechanisms* 11, (dmm033084).
- Meurice, E., Bouchart, F., Hornez, J., *et al.*, 2016. Osteoblastic cells colonization inside beta-TCP macroporous structures obtained by ice-templating. *Journal of the European Ceramic Society* 36, 2895–2901.

- Morris, Z., 2007. Quantitative and Spatial Analysis of the Microscopic Bone Structures of Deer, Dog, and Pig. Master's Thesis. Louisiana State University.
- Mulhern, D., Ubelaker, D., 2001. Differences in osteon banding between human and nonhuman bone. *Journal of Forensic Sciences* 46, 220–222.
- Muschler, G., Raut, V., Patterson, T., 2010. The design and use of animal models for translational research in bone tissue engineering and regenerative medicine. *Tissue Engineering Part B: Reviews* 16, 123–145.
- Nafei, A., Danielsen, C., Linde, F., Hvid, I., 2000. Properties of growing trabecular ovine bone, part I: Mechanical and physical properties. *The Journal of Bone and Joint Surgery* 82, 910–920.
- Ning, B., Zhao, Y., Buza Iii, J., *et al.*, 2017. Surgically-induced mouse models in the study of bone regeneration: current models and future directions. *Molecular Medicine Reports* 15, 1017–1023.
- Owen, R., Reilly, G., 2018. In vitro models of bone remodeling and associated disorders. *Frontiers in Bioengineering and Biotechnology* 6, 134.
- O'Loughlin, P., Morr, S., Bogunovic, L., *et al.*, 2008. Selection and development of preclinical models in fracture-healing research. *Journal of Bone and Joint Surgery* 90 (Suppl 1), 79–84.
- Pacifici, R., 2010. The immune system and bone. *Archives of Biochemistry and Biophysics* 503, 41–53.
- Pagani, S., Torricelli, P., Veronesi, F., *et al.*, 2018. An advanced tri-culture model to evaluate the dynamic interplay among osteoblasts, osteoclasts, and endothelial cells. *Journal of Cellular Physiology* 233, 291–301.
- Pearce, A., Richards, R., Milz, S., Schneider, E., Pearce, S., 2007. Animal models for implant biomaterial research in bone: A review. *European Cells & Materials* 13, 1–10.
- Rayahin, J.E., Gemeinhart, R.A., 2017. Activation of macrophages in response to biomaterials. In: Kloc, M. (Ed.), *Macrophages. Results and Problems in Cell Differentiation*. Springer.
- Reichert, J., Saifzadeh, S., Wullschlegel, M., 2009. The challenge of establishing preclinical models for segmental bone defect research. *Biomaterials* 30, 2149–2163.
- Roeder, I., Loeffler, M., Glauche, I., 2011. Towards a quantitative understanding of stem cell–niche interaction: Experiments, models, and technologies. *Blood Cells, Molecules, and Diseases* 46, 308–317.
- Ruehe, B., Niehues, S., Heberer, S., Nelson, K., 2009. Miniature pigs as an animal model for implant research: bone regeneration in critical-size defects. *Oral Surgery, Oral Medicine, Oral Pathology, Oral Radiology, and Endodontology* 108, 699–706.
- Scheinpflug, J., Pfeiffenberger, M., Damerau, A., *et al.*, 2018. Journey into bone models: A review. *Genes* 9, 247.
- Schmitz, J., Hollinger, J., 1986. The critical size defect as an experimental model for craniomandibulofacial nonunions. *Clinical Orthopaedics and Related Research* 205, 299–308.
- Schmitz, J., Schwartz, Z., Hollinger, J., Boyan, B., 1990. Characterization of rat calvarial nonunion defects. *Cells Tissues Organs* 138, 185–192.
- Schulze, S., Wehrum, D., Dieter, P., Hempel, U., 2018. A supplement-free osteoclast–osteoblast co-culture for pre-clinical application. *Journal of Cellular Physiology* 233, 4391–4400.
- Scott, M., Levi, B., Askarinam, A., *et al.*, 2011. Brief review of models of ectopic bone formation. *Stem Cells and Development* 21, 655–667.
- Spicer, P., Kretlow, J., Young, S., *et al.*, 2012. Evaluation of bone regeneration using the rat critical size calvarial defect. *Nature Protocols* 7, 1918–1929.
- Szpalski, C., Barr, J., Wetterau, M., Saadeh, P.B., Warren, S.M., 2010. Cranial bone defects: Current and future strategies. *Neurosurgical Focus* 29 (6), E8.
- Teti, A., 2011. Bone development: Overview of bone cells and signaling. *Current Osteoporosis Reports* 9, 264–273.
- Tiyapatanaputi, P., Rubery, P., Carmouche, J., *et al.*, 2004. A novel murine segmental femoral graft model. *Journal of Orthopaedic Research* 22, 1254–1260.
- Viljanen, V., Lindholm, T., Gao, T., Lindholm, T., 1997. Low dosage of native allogeneic bone morphogenetic protein in repair of sheep calvarial defects. *International Journal of Oral and Maxillofacial Surgery* 26, 389–393.
- Wancket, L., 2015. Animal models for evaluation of bone implants and devices: Comparative bone structure and common model uses. *Veterinary Pathology* 52, 842–850.
- Wang, S., Liu, Y., Fang, D., Shi, S., 2007. The miniature pig: A useful large animal model for dental and orofacial research. *Oral Diseases* 13, 530–537.
- Wang, X., Mabrey, J., Agrawal, C., 1998. An interspecies comparison of bone fracture properties. *Bio-Medical Materials and Engineering* 8, 1–9.
- Westhauser, F., Senger, A., Reible, B., Moghaddam, A., 2017. In vivo models for the evaluation of the osteogenic potency of bone substitutes seeded with mesenchymal stem cells of human origin: A concise review. *Tissue Engineering Part C: Methods* 23, 881–888.
- Willie, B., Bloebaum, R., Bireley, W., Bachus, K., Hofmann, A., 2004. Determining relevance of a weightbearing ovine model for bone ingrowth assessment. *Journal of Biomedical Materials Research Part A* 69, 567–576.
- Yang, Z., Yuan, H., Tong, W., *et al.*, 1996. Osteogenesis in extraskeletally implanted porous calcium phosphate ceramics: Variability among different kinds of animals. *Biomaterials* 17, 2131–2137.
- Yin, P., Lv, H., Li, Y., *et al.*, 2017. Exosome-mediated genetic information transfer, a missing piece of osteoblast–osteoclast communication puzzle. *Frontiers in Endocrinology* 8, 336.
- Yiostalo, J., Bartosh, T., Coble, K., Prockop, D., 2012. Human mesenchymal stem/stromal cells cultured as spheroids are self-activated to produce prostaglandin E2 that directs stimulated macrophages into an anti-inflammatory phenotype. *Stem Cells* 30, 2283–2296.
- Yoshimura, Y., Kikuri, T., Hasegawa, T., *et al.*, 2017. How much medium do you use for cell culture? Medium volume influences mineralization and osteoclastogenesis in vitro. *Molecular Medicine Reports* 16, 429–434.
- Zhao, M.-D., Huang, J.-S., Zhang, X.-C., *et al.*, 2016. Construction of radial defect models in rabbits to determine the critical size defects. *Plos One* 11, e0146301.
- Zhu, S., Ehner, S., Rouß, M., *et al.*, 2018. From the clinical problem to the basic research – Co-culture models of osteoblasts and osteoclasts. *International Journal of Molecular Sciences* 19, 2284.

Zirconia Ceramics: Clinical and Biological Aspects in Dentistry

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Background

Fixed partial dentures (FPDs) produced from modern dental materials are used in dental medicine to restore anatomic form and function, and/or esthetics. Traditional metal-ceramic restorations have had acceptable success rates, but are limited by pertinent concerns such as tissue compatibility and esthetics. Successful emergence of 3 mol% yttria partially-stabilized tetragonal zirconia (3Y-TZP) bioceramics in orthopedics gained an immense interest in dentistry in the early 90s. Owing to 3Y-TZP's high esthetics, chemical inertness, exceptionally high strength and toughness for a ceramic material, it advocated the replacement of traditional porcelain veneered metal-ceramic FPDs. It followed that in the past three decades, there have been profound advances in the application of 3Y-TZP in restorative dentistry further expanding clinical indications of tooth-colored, all-ceramic systems to crowns and bridges, root posts and even implants (Piconi and Maccauro, 1999; Denry and Kelly, 2008).

3Y-TZP ceramics exhibit high flexural strength (900 – 1200 MPa), fracture toughness ($4 - 6 \text{ M Pam}^{-1}$), and a lower Young's modulus (210 GPa) compared to alumina (340 GPa) (Piconi and Maccauro, 1999). Therefore, it is suitable to serve as a core material and withstand high stresses produced in the posterior dentition, where masticatory forces are higher due to the masticatory muscle attachment.

3Y-TZP's high strength and fracture toughness are governed by the stress-induced tetragonal-to-monoclinic (*t-m*) transformation toughening mechanism, where under applied stress the metastable tetragonal phase (grains) transforms to monoclinic. This causes volumetric expansion and creates compressive stresses that oppose the tensile stress in the vicinity of a propagating crack tip (Fig. 1(a)) (Butler, 1985). Because of this toughening mechanism, the 3Y-TZP ceramic was labeled as “ceramic steel” (Garvie *et al.*, 1975; Gupta *et al.*, 1978). 3Y-TZP's mechanical properties are far superior to other dental (glass) ceramics, such as feldspathic porcelain, lithium disilicate, alumina, allowing it to be also used in high load-bearing areas.

Pure zirconia (ZrO_2), an oxide ceramic polymorphic system, exhibits three different crystal lattice types under atmospheric pressure. At temperatures higher than 2370°C , zirconia occupies cubic lattice. Between 1170°C and 2370°C , zirconia is tetragonal, and below 1170°C the lattice is monoclinic. Upon cooling, the *t-m* phase transition is accompanied by 3 – 5 vol% increase, which facilitates cracking of the sintered bulk. The spontaneous phase transformation can be avoided by modifying the composition with traces of other oxides, such as MgO, CaO and CeO_2 . Such doping strategy results in partial stabilization of the tetragonal phase at room temperature, and thus cracking upon cooling is prevented and the stress-induced transformation toughening installed (Hannink *et al.*, 2004). Generally, biomedical grade zirconia used in dentistry is doped with 3 mol% of yttria (Y_2O_3) and a small amount of alumina (0.25 wt%). Such 3Y-TZP ceramics are characterized by fine-grained microstructures (0.3–0.5 μm) (Fig. 1(b)), where inclusions of distinct alumina grains can be found in the matrix (Samodurova *et al.*, 2015b).

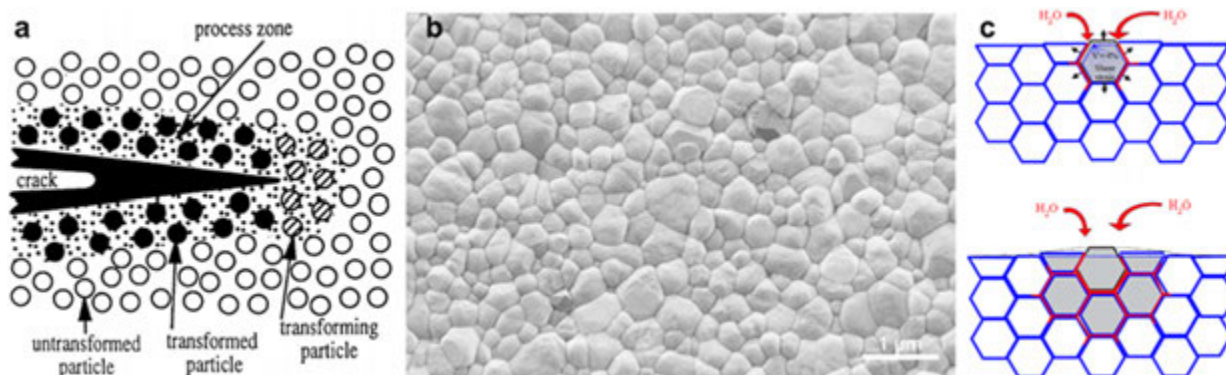


Fig. 1 (a) Schematics of stress-induced *t-m* transformation toughening around an advancing crack, where transforming tetragonal particles to monoclinic symmetry form a process zone exerting compressive strain. (b) SEM micrograph of polished and thermally etched surface of the 3Y-TZP sintered for 2 h at 1450°C . Darker faceted grains are alumina inclusions. (c) Schematics of the ageing process in a cross-section showing spontaneous nucleation and growth, stress-corrosion-type mechanism of *t-m* transformation, leading to microcracking and stresses to the neighboring grains. Reproduced from (a) Butler, E.P., 1985. Transformation-toughened zirconia ceramics. *Mater. Sci. Technol.* 1, 417–432. doi:10.1179/mst.1985.1.6.417, Copyright Taylor & Francis. (c) Chevalier, J., 2006. What future for zirconia as a biomaterial *Biomaterials* 27, 535–543. doi:https://doi.org/10.1016/j.biomaterials.2005.07.034, Copyright Elsevier.

3Y-TZP is pressure-less sintered at relatively low sintering temperatures (1350 – 1500°C) to produce full density ($\geq 99.5\%$). The addition of Y^{3+} replaces Zr^{4+} in the crystal lattice creating oxygen vacancies that maintain the tetragonal phase partially stable at room temperature after sintering (Chevalier *et al.*, 2009). A small amount of alumina is added to 3Y-TZP to prevent yttria segregation, which results in improved ageing resistance and reinforces grain boundaries (Matsui *et al.*, 2006; Samodurova *et al.*, 2015a).

However, the long-term stability of the 3Y-TZP ceramics is known to be susceptible to a superficial ageing phenomenon the so-called low-temperature degradation (LTD); a spontaneous *t-m* transformation of 3Y-TZP's surface in an aqueous environment at moderate temperature, including body temperature. At the onset of the present millennium, several hundreds of 3Y-TZP femoral heads failed in a short period following implantation, with the origin of the fracture indirectly associated with LTD (Haraguchi *et al.*, 2001). Since then, numerous studies have been performed to investigate the mechanisms and kinetics of LTD.

It was found out that the *t-m* transformation is temperature-dependent and diffusion-controlled, accompanied by extensive microcracking, and surface uplifting, which ultimately leads to strength degradation (Fig. 1(c)) (Chevalier, 2006). The LTD process was found out to be a grain-size dependent stress-corrosion-type mechanism starting at the 3Y-TZP's surface and proceeding into the bulk (Kosmač *et al.*, 2012; Hallmann *et al.*, 2012). It is sensitive to the differences in the starting materials and process additives (co-dopants) (Samodurova *et al.*, 2015a; Zhang *et al.*, 2016a; Bučevac *et al.*, 2017) and the materials' processing-related prehistory (grinding or sandblasting; Kosmač *et al.*, 1999; Chintapalli *et al.*, 2013; Cotič *et al.*, 2016). Moreover, some studies showed how the highly distorted tetragonal zirconia grains and pre-existing monoclinic zirconia in the ground and air-particle abraded surfaces hindered the *t-m* transformation during ageing (Kosmač *et al.*, 2008).

Déville and Chevalier established a relationship between the amount of the transformed monoclinic phase and the accelerated hydrothermal ageing time in an autoclave at 134°C in distilled water to estimate the equivalent ageing time under "in vivo" conditions based on the results obtained with retrieved 3Y-TZP femoral heads (Chevalier *et al.*, 2007; Chevalier and Gremillard, 2009). A postulation was made that one hour of ageing in vitro corresponds to about three years "in vivo". However, as stated above, 3Y-TZP ceramics may differ substantially in their fabrication method and properties, as well as in clinical conditions and it was later shown by Keuper *et al.* (2014) that such approximation of the ageing process to room temperature can result in important underestimation. However, at the moment, there are no obvious clinical indications that the LTD of 3Y-TZP used in dentistry would represent a severe concern.

In the beginning, the 3Y-TZP frameworks were produced by costly and time-consuming precise hard-milling of densely sintered and hot isostatically pressed 3Y-TZP blocks. Later, direct oversize milling of pre-sintered 3Y-TZP blanks has become increasingly popular in dentistry and is now the most common method in the fabrication of 3Y-TZP FPDs (Raigrodski, 2005). In this manufacturing technology, the die or a wax pattern is scanned, and/or enlarged restoration is digitally designed by computer software (CAD), and a pre-sintered ceramic blank is oversize-milled by computer-aided machining (CAM). The restoration is then sintered to full density. However, the process of milling of preformed zirconia blocks generates a lot of waste material that is environmentally unfriendly; therefore, new methods of zirconia fabrication have evolved recently.

Biomedical Grade Zirconia in Fixed and Removable Prosthodontics

Biomedical grade 3Y-TZP was initially used for the fabrication of orthodontic brackets (Keith *et al.*, 1994), root canal posts (Meyenberg *et al.*, 1995) and implant abutments (Glauser *et al.*, 2004). Afterwards, 3Y-TZP emerged as a strong and tough core material in all-ceramic FPDs. Nowadays, 3Y-TZP ceramics is a material of choice for the entire spectrum of fixed restorations, including inlays, onlays, single crowns, multi-unit bridges, and implant-supported restorations (Guess *et al.*, 2012). It may also successfully serve as an alternative option to implants and/or bridges of replacing missing lateral incisors in adolescents and young adults with a cantilevered resin-bonded fixed dental prosthesis (RBFDP) and thereby avoiding more aggressive treatment (Fig. 2).

In addition, several indications in removable prosthodontics exist, where 3Y-TZP ceramics is successfully implemented. There is a strong clinical evidence of double crown system, where primary crowns are milled from 3Y-TZP ceramics and secondary crowns galvano-formed in gold (Fig. 3(a)). This clinical protocol has been introduced by Weigl and Lauer (2000). The retention mechanism of the 3Y-TZP-galvano system is based primarily on the very precise manufacturing of both crowns. The template for the galvano-forming of the secondary crown is the primary ceramic crown itself. Consequently, a gap not exceeding 5 μm can be achieved. Retention of the system is therefore primarily based on capillary pressure and adhesion between the crowns. This way predictable and long-term stable clinical success can be achieved. Retention of the system also depends on the conical crowns' surface area and surface roughness of the materials. The proposed protocol includes intraoral bonding of the secondary galvano-crowns to the tertiary metal framework. This concept has also been extended to tooth-implant prosthetic rehabilitations (Fig. 3(a)), where custom made zirconia implant abutments serve as primary crowns (Brandt *et al.*, 2019).

Bar retained implant dentures are often designed in edentulous patients with head and neck cancer. This way, good denture retention and stability can be achieved. In the past, bars were cast from Co-Cr alloys. Currently they are milled from metal blocks in a CAD-CAM process. As there is a common trend to minimize metals in the oral cavity 3Y-TZP milled bars are indicated (Fig. 3(b)).

Bonding to Dental Zirconia Ceramics

The evolution of new generations of dental adhesives that promote a reliable bond between two chemically diverse materials, i.e., dentin or enamel and composite resin has enabled to replace conventional, retentive-based cementation techniques with adhesive

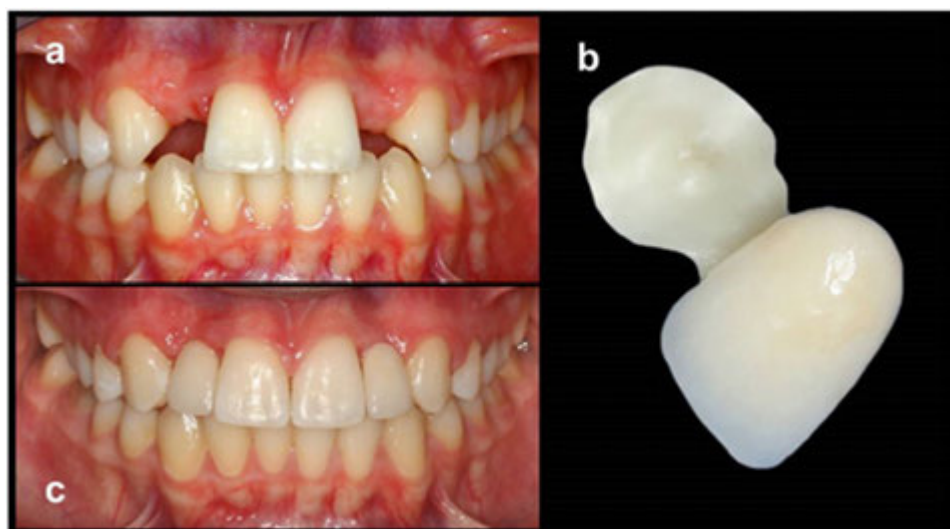


Fig. 2 A clinical case replacing lateral incisors resin-bonded fixed dental prosthesis (RBFDP): (a) before the prosthetic rehabilitation, (b) veneered zirconia dental prosthesis and (c) after the prosthetic rehabilitation.



Fig. 3 3Y-TZP ceramics applied in removable prosthodontics: (a) Primary telescopic crowns on abutment teeth and implants (lower left). Secondary crowns are galvanofomed via electrolytic gold deposition (upper left) and bonded to tertiary framework (lower right). (b) 3Y-TZP screw-retained CAD/CAM milled bar (left) in the edentulous lower jaw for the retention of implant-supported denture (lower right).

bonding procedures of FPDs. To achieve a durable bond between 3Y-TZP ceramics and bonding agent, several methods have been proposed. Numerous “in vitro” and “in vivo” studies have been conducted to resolve the durability and strength of the resin bond (Kern, 2015), since chemical methods such as acid-etching and silanization, that are successful in luting of silicate ceramics, proved to be ineffective to promote adhesion of composite luting agents to zirconia surface due to the high chemical inertness and the absence of siliceous phases in polycrystalline zirconia matrix. It followed the advent of employing surface roughening of zirconia by air-particle abrasion (APA) with alumina particles also called sandblasting (Fig. 4(a)), which enhances the mechanical interlocking, which is the most commonly used surface treatment (Shahin and Kern, 2010). APA parameters, such as alumina particles size (30–250 μm), blasting pressure (0.05 – 0.6 MPa) and blasting distance, have been studied immensely. The interchange of these parameters has led to a consensus that APA with 50–110 μm alumina particles at 0.25 MPa is effective in cleaning and roughening zirconia ceramics as it most likely removes contaminants from ceramic surface and exposes a fresh bonding surface. The APA could theoretically lead to mechanical degradation of zirconia ceramics by producing microcracks and subsurface damage. Many authors have questioned the use of aggressive treatments of zirconia; however, several studies on the other hand demonstrated that APA improved the mechanical strength of 3Y-TZP presumably via transformation toughening mechanism irrespective of the blasting pressure (Kosmac *et al.*, 1999; Aurélio *et al.*, 2016; Chintapalli *et al.*, 2014; Cotič *et al.*, 2017).

It is fundamental to combine APA with the use of chemical promoters, capable of improving adhesion. Primers contain organophosphate monomers, including 10-MDP (10-Methacryloyloxydecyl Dihydrogen Phosphate), present a terminal functional group with phosphoric acid, which reacts with zirconia and forms P-O-Zr bonds. The other end of the molecule exposes a vinyl

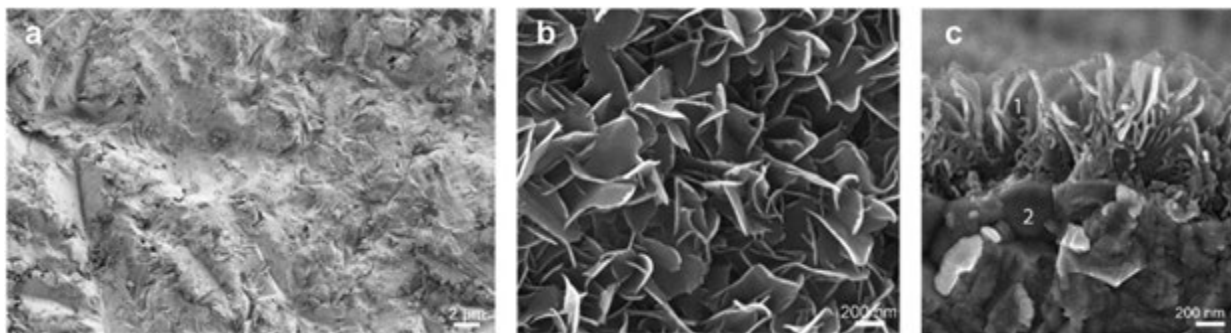


Fig. 4 SEM micrographs showing (a) APA modified 3Y-TZP surface; and nanostructured alumina coating deposited on the as-sintered 3Y-TZP surface: (b) coatings' topography; (c) cross-sectional view (1 – coating; 2–3Y-TZP substrate). Reproduced from (b, c) Malgaj, T., Kocjan, A., Jevnikar, P., 2020. The effect of firing protocols on the resin-bond strength to alumina-coated zirconia ceramics. *Adv. Appl. Ceram. Struct. Funct. Bioceram.* 119, 267–275, Copyright Taylor & Francis.

terminal group, which allows the copolymerization with the resin. Today 10-MDP-based cements and primers are used for this purpose. The low viscosity of 10-MDP primers favors penetration into surface micro-porosities and bond resistance over time. In the other hand, 10-MDP-based viscous cement can bind to zirconia but are not able to, alone, maintain stable long-term adhesion, which is more susceptible to hydrolysis (Russo *et al.*, 2019).

Among surface roughening techniques the APA using silica modified alumina particles (i.e., the so-called Rocatec system) has been developed not only to enhance the surface roughness of zirconia but also to provide free silica groups to form the bond with the silane coupling agent. Although this bond is according to thermodynamic calculations more resistant to hydrolysis than the bond between zirconia and 10-MDP (Xie *et al.*, 2016), the effectiveness of APA using silica modified alumina particles has been questioned (Kern, 2015).

An alternative solution to the adhesion problem has recently been proposed by a non-invasive functionalization of the zirconia surface, by applying a thin (200–400 nm) nanostructured alumina coating consisting of interlocked 2D lamellae or nanosheets exhibiting a large surface area by which bonding to the substrate is significantly improved. The coating shows a uniform thickness and good surface coverage (Fig. 4(b) and (c)). It is almost insensitive to thermocycling and has the potential of durable improvement of the adhesive bond between the coated core material and the dental cements by a factor of 2–4, depending on the surface roughness of the substrate, the dental cement and the firing protocol used (Jevnikar *et al.*, 2010, 2012; Malgaj *et al.*, 2020).

Delamination and Chipping of the Veneered Overlayer

Chipping and fracture of veneering porcelain are commonly reported in all-ceramic zirconia restorations, which is reportedly higher than the chipping rate of porcelain bonded to metal-ceramic restorations. This could be ascribed to the higher chemical inertness, less favorable wetting ability and considerably lower thermal diffusivity of 3Y-TZP ceramics, as compared to metals. The thermal expansion mismatch and cooling rate-induced tempering of zirconia framework and veneering porcelain contribute to the formation of high tensile subsurface residual stresses in layers of porcelain which may result in unstable crackings or chippings, that are presumably contact-induced (Swain, 2010). Minor chipping damages can be temporarily repaired (Özcan, 2015; Özcan *et al.*, 2013), but in most cases, the whole restoration has to be replaced. Other causes for failures of all-ceramic FPDs are debonding, i.e., loss of coherence between the restoration and the abutment tooth, fracture of the framework, and delamination of the veneering porcelain. The fracture is due to the locally exceeded stress concentration in the framework, while the debonding and delamination are associated with the chemical inertness of the core material. Also worth mentioning is the problem that not only dental clinicians but also the producers of the zirconia blanks are facing. This is the lack of relevant standards and recommendations regarding the physical and chemical properties of 3Y-TZP ceramics for dental applications, i.e., considering specific clinical conditions in the aggressive environment of the oral cavity.

Aside of the several unsuccessful attempts to overcome the chipping problem by hot pressing or CAD/CAM machining and subsequent joining with 3Y-TZP core, the community geared toward a more radical but practical solution, i.e., toward porcelain-free, monolithic zirconia crowns and bridges, despite the risk of higher wear of the opposing tooth enamel and the direct exposure of the ageing-susceptible zirconia surface to the aggressive wet environment of the oral cavity. Nevertheless, the introduction of this conceptual idea was largely accepted in the dental community leading to wide production and application of the monolithic or full-contour zirconia ceramics for FPDs.

Translucency

In the quest towards highly translucent but stronger than glass-ceramics, new generation zirconia grades have been developed and commercialized recently. Due to the improved esthetics, monolithic restorations with only a thin, few microns thick, glaze coating layer (in visible regions) can be realized, allowing a further reduction of the restoration thickness. Moreover, pre-sintered blocks

are both available as pre-shaded in several tonalities and multilayered with gradients of chroma and different degrees of translucency. The benefit of the so-called “monolithic/full-contour” restorations allow decreasing the risks of chipping, the prosthetic cost and production time.

Zirconia ceramics with increased translucency can be realized in several ways: (1) refining the microstructure using (a) wet shaping techniques of zirconia nanopowders (Liu *et al.*, 2016) and/or (b) advanced sintering strategies (Xiong *et al.*, 2014; Kocjan *et al.*, 2015) and specific sintering additives, (2) grain boundary (microstructural) engineering by co-doping to control dopant segregation (Zhang *et al.*, 2015) (3) increasing the amount of cubic phase that ultimately increases grain size that also possesses considerably lower optically anisotropy (birefringence) (Zhang and Lawn, 2018).

All these strategies can be found in different commercial zirconias with a claimed improved translucency. In particular, we may now find novel yttria fully-stabilized grades with a higher content of yttria. However, not only do these microstructural variations imply substantial improvements in the overall optical performance of zirconia, but they also inevitably introduce noticeable changes in its mechanical properties and long-term stability (Camposilvan *et al.*, 2018).

Elastic Modulus and Hardness Mismatch

3Y-TZP hardness (12–14 GPa) is ~50% lower than of alumina, which is a clear advantage over alumina in the adjustments of occlusal surfaces of FPDs by grinding, finishing or polishing. In addition, the importantly lower hardness of zirconia should also reflect in a less severe impact of occlusal wear of opposing teeth, where the average hardness of enamel was reported to be between 3.4 and 4.8 GPa (Cuy *et al.*, 2002; Willems *et al.*, 1993). Moreover, due to the ability of zirconia ceramics to be finely polished, the occlusal wear appears to be negligible. The observed wear is even less damaging than in the case of feldspathic porcelain, lithium disilicate ceramics and enamel to enamel attrition (Chong *et al.*, 2015; Lawson *et al.*, 2014; Passos *et al.*, 2014; Wang *et al.*, 2012; Zhang *et al.*, 2019b). Such a positive outcome might be related to the ability of quasi-plastic deformation under mechanical wear as a result of evolved subsurface shear stresses triggering the *t-m* phase transformation (Luthardt *et al.*, 2004).

Another advantage of zirconia in relation to alumina is that its elastic modulus is much lower than that of alumina (200 GPa versus 380 GPa), which implies lower elastic stresses between the natural dentine and the prosthetic work. Still, the elastic modulus of zirconia is considerably higher than natural dentin that is demonstrated with posts-cores in endodontically treated teeth with insufficient tooth structure. Zirconia posts were introduced to replace esthetically unpleasant metal posts (Meyenberg *et al.*, 1995). However, the high elastic modulus of zirconia posts causes stress to be transferred to the less rigid dentin, thereby resulting in vertical root fractures (Mannocci *et al.*, 1999). A significantly improved fracture resistance and predominantly favorable failure modes were manifested, when restoring teeth with a prefabricated zirconia post and core system with a wide, retentive coronal shape and when the root post space is designed with 1–2-mm deep internal plateau (Fig. 5) (Jovanovski *et al.*, 2019).

Biocompatibility

Over the years, the tissue compatibility of zirconia ceramics has been evaluated extensively “in vivo” and “in vitro”. There has been an abundance of in vitro tests performed on different physical forms of zirconia (e.g., powders and dense ceramics), that showed no local or systemic cytotoxic effects or adverse reactions associated with zirconia. The “in vivo” bone formation adjacent to zirconia and the inflammatory response to zirconia have been shown to be satisfactory. However, initial results frequently showed

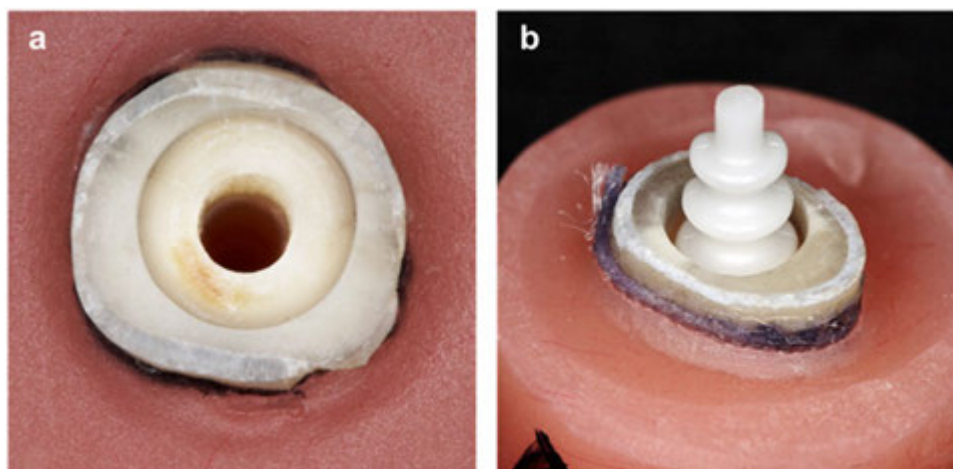


Fig. 5 (a) The internal plateau preparation in an extracted tooth mounted in resin and (b) after inserting the prefabricated zirconia post and core system in post space. Reproduced from (b) Jovanovski, S., Cotič, J., Kocjan, A., Oblak, Č., Jevnikar, P., 2019. Fracture resistance of endodontically treated maxillary incisors restored with zirconia posts: Effect of the internal plateau preparation. *Adv. Appl. Ceram.* 118, doi:10.1080/17436753.2018.1508625, Copyright Taylor & Francis.

the formation of connective tissue at the bone-ceramic interface before the implementation of surface roughening of zirconia implants improved bone-implant contact. Furthermore, microorganisms seem to adhere to zirconia to the same extent as to other materials. One can conclude that minor observed irritations may be attributed to mechanical irritation, e.g., from roughened surfaces. The mutagenic and cancerogenic *in vitro* tests on zirconia ceramics also showed the dearth of any similar reactions and no emergence of tumor cells (Piconi and Maccauro, 1999).

Zirconium is derived from Zircon (ZrSiO_4) or Baddeleyite. These minerals may contain a small amount of radioactive impurities. Thus, using zirconia in biomedical applications raised the question of the materials' safety. Zirconia-based medical devices are strictly regulated for radioactive decay (max. 0.2 Bq/g) by the ISO 13356 standard. The activity of uranium-radium and thorium radionuclides in different types of zirconia bioceramics was investigated by Porstendörfer *et al.* (1996). They showed that the estimated effective dose found was below the dose limit of 1 mSv/year. It was recently shown that the radioactive potential of zirconia dental ceramics is negligible compared to radioactive appliances in our environment (Bavbek *et al.*, 2014) obviously posing no risk to the patient.

Full-Contour Monolithic Zirconia and Minimally Invasive Dentistry

The development and commercialization of translucent zirconia dental ceramics allowed fabrication monolithic FPDs with innumerable advantages; these are the elimination of chipping risk, the satisfactory mechanical properties (compared to leucite and lithium disilicate glass-ceramics), the possibility of employing the CAD-CAM processing workflow (greater standardization and quality of results, with cost reduction), the possibility of manufacturing of thinner FPDs, and a more conservative dental preparation restricting within the principles of minimally invasive dentistry (Zhang and Lawn, 2018).

High-Translucency Zirconia (4Y, 5Y) Grades

Traditional partially-stabilized zirconia ceramics doped with 3 mol% yttria (3Y-TZP) have been shown to withstand the stresses superior to the highest biting forces. In the last few years, the progress in the manufacturing of zirconia ceramics with improved translucency and esthetic features have established new generations of high-, super- and ultra-translucent zirconia ceramics. This was mainly achieved by modifying the *t*- ZrO_2 matrix by adjusting the concentrations of minor elements, such as reducing the amount of alumina (Al_2O_3) and, more importantly, increasing the molar percentage (concentration) of yttria (Y_2O_3), up to 5 mol%, to the extent allowing its use in a monolithic form, e.g., single crowns, onlays, inlays, anterior cantilever resin-bonded bridges (Zhang and Lawn, 2018).

With that in mind, different zirconia generations have evolved historically. Zirconia materials can currently be divided into four types or generations according to their mechanical and optical properties (Güth *et al.*, 2019).

Biomedical grade 3Y-TZP

1st generation of dental zirconia is represented by the conventional biomedical grade 3Y-TZP. Since it is a birefringent material, the optical properties of 3Y-TZP are greatly influenced by the structure of the grain boundaries. Typically, the alumina content in this family of zirconia ceramics is around 0.25%, which is concentration high enough to facilitate the formation of isolated alumina grains in the 3Y-TZP matrix during sintering. As a consequence, light transmittance is hampered resulting in a high opacity and compromised visual appearance. Thus, 1st generation 3Y-TZP zirconia is not suitable material for monolithic use. In the past years, the main focus was to improve the optical properties, especially increasing the translucency.

Highly-translucent 3Y-TZP

A 2nd generation of highly-translucent zirconia ceramics was introduced around 2013 – a 3Y-TZP variant with lowered amount (~ 0.05 wt%) of alumina in the matrix. This way, the alumina grains do not form anymore in the ceramic matrix (Samodurova *et al.*, 2015b) resulting in a higher level of light transmission. The flexural strength remained high, and the *in-vitro* stability was sufficient allowing it to be predominantly used as a framework material for one- and multi-unit FDPs.

Ultra-translucent zirconia (stabilised with 5 mol% yttria)

The 3rd generation of dental zirconia ceramics was developed in 2015 labeled as ultra-translucent and is recommended for the production of single-tooth crowns and FDPs with up to three units in the anterior region. The increase of the yttria (Y_2O_3) content up to 5 mol% substantially increases the translucency (Fig. 6(a)), mainly because the resultant ceramic material with such an amount of yttria is closer to a more optically isotropic cubic symmetry form (or *t*- ZrO_2 with a much lowered tetragonality (Fujimori *et al.*, 2001)). The matrix grains are larger and less birefringent than the tetragonal grains; therefore, the light passes fewer boundaries that are also plan-parallel causing lower light scattering on passing through the material (Krell *et al.*, 2009). Besides a higher degree of translucency, the increase of the yttria content ultimately provides a genuinely LTD-resistant zirconia ceramics (Zhang *et al.*, 2016b).

The tremendously profitable improvements of gained by increasing the yttria content undoubtedly have a deleterious trade-off, i.e., they are mechanically weaker ceramic material due to the absence of the *t-m* transformation toughening (Fig. 6(b)). Compared

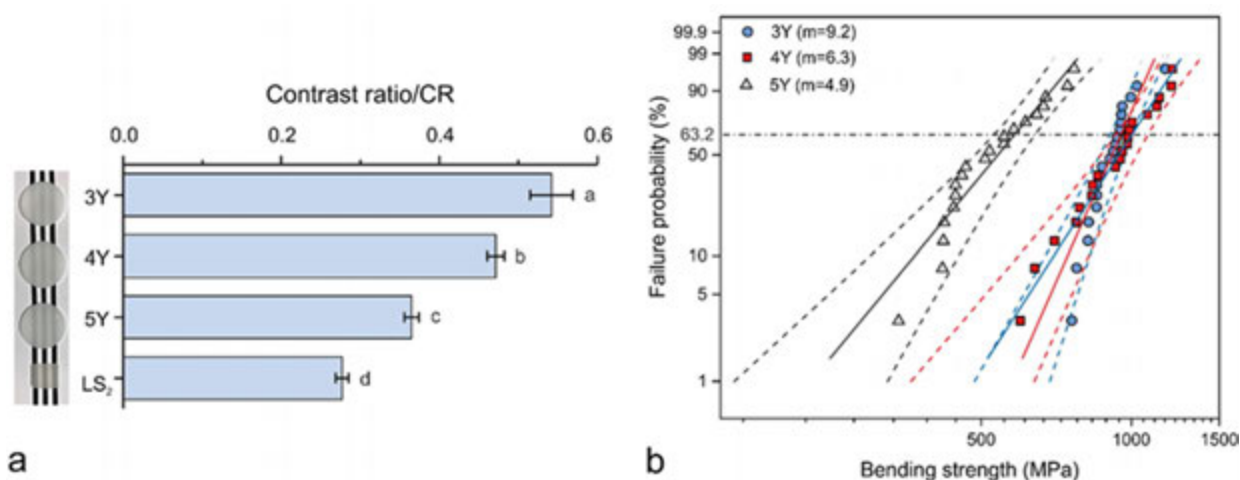


Fig. 6 (a) Comparison of translucency of various zirconia grades and lithium disilicate (LS2) ceramics in 0.5-mm thickness. (b) Weibull plots showing data for four-point bending strength of various grades of zirconia ceramics. Reproduced from (b) Zhang, F., Reveron, H., Spies, B.C., Van Meerbeek, B., Chevalier, J., 2019a. Trade-off between fracture resistance and translucency of zirconia and lithium-disilicate glass ceramics for monolithic restorations. *Acta Biomater.* 91, 24–34. doi:10.1016/j.actbio.2019.04.043, Copyright Elsevier.

to the lithium disilicate, the translucency of the 3rd zirconia generation is slightly lower, but the flexural strength and fracture toughness are higher (Zhang *et al.*, 2019a).

Super-translucent zirconia (stabilised with 4 mol% yttria)

Most recently, in 2017, the 4th generation of zirconia, known as super-translucent, was announced to increase the indication range for monolithic zirconia restorations, such as short-span multi-unit FDPs in the premolar region. Compared to the 3rd generation, the yttria content was reduced to 4 mol% (*t*-ZrO₂ polymorph), which led to an enhancement of the mechanical properties with a combined reduction in its optical properties. It is LTD resistant material owing to the absence of t-m process, whereas the improved strength and toughness in comparison to 5 mol% variant originate from the process of ferroelastic domain switching typically encountered in *t*-ZrO₂ (Hannink *et al.*, 2004; Virkar and Matsumoto, 1986; Mercer *et al.*, 2007).

Glazing and Staining

Milling of a presintered blank to full-contour has been established for monolithic zirconia restorations (Fig. 3(b)). In this way, the common use of a thick ceramic veneer layer can be avoided, but a thin stain and glaze coating layer still need to be applied to realize the overall appearance of monolithic crowns, inlays, onlays or veneers. Fine glass powder that may contain metal oxides as pigments is applied on zirconia surface and subsequently fired at temperatures between 550 and 900°C. The characteristic and smooth esthetic layer of overglaze is formed superficially on zirconia restoration. Glazing does appear to protect the first two zirconia generations against LTD in a humid oral environment (Oblak *et al.*, 2017).

However, it has been shown that glazed zirconia increases wear of antagonist teeth and also of restoration itself; the extent of wear of the antagonists was reported to be even higher than for the polished zirconia (Lawson *et al.*, 2014). Therefore, the occlusal surfaces of monolithic restorations in posterior regions should not be altered with glazing, unless esthetics is preeminent and that exposed, unglazed surfaces are carefully polished before use in order to reduce the wear of the enamel of the opposite teeth (Liu *et al.*, 2016).

Moreover, it was also shown that after long-term thermal and mechanical fatigue the glaze layer might represent the weakest link for crack initiation and propagation, which can dramatically affect the strength of FPDs. Studies have shown that the glazing significantly reduces the flexural strength of high translucent zirconia and that LTD decreased the flexural strength of glazed translucent (Nam and Park, 2018) and super-translucent zirconia (Lai *et al.*, 2017) indicating accumulating stress areas in the surface layers of the material. Furthermore, in a fractographic study of Oblak *et al.*, it was clearly indicated that the flaws and imperfections in the glaze layer or the glaze-zirconia interface depict the weakest spot of the glazed zirconia restorations where the initiation of the fracture presumably originates (Fig. 7) (Oblak *et al.*, 2017).

Self-Glazed Zirconia Ceramics

A new grade of self-glazed zirconia ceramics, based on 3Y-TZP system, with natural-looking, enamel-like surface finish has been recently developed to address the above-mentioned risks of glazing (Shen *et al.*, 2017). It requires no further need for veneering or glazing, thereby evading fragile interfaces (Fig. 8(a)). Moreover, beside rationalization, i.e., abolishing the need for glazing step

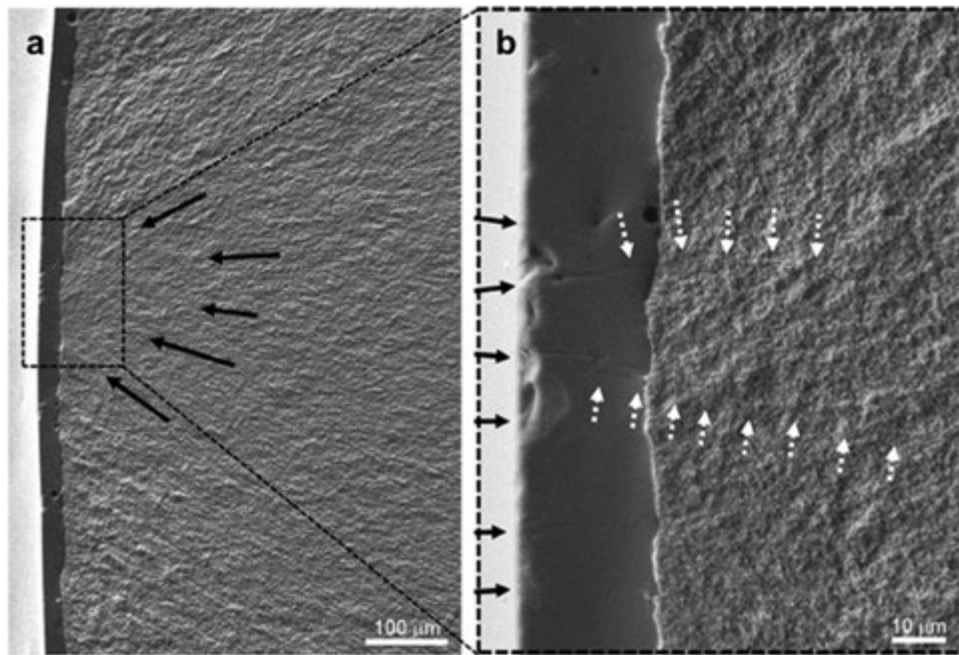


Fig. 7 SEM fractographic analysis of the monolithic 4-unit zirconia bridge overlaid with thin glaze layer after fracture in bending. (a) Black arrows are indicating on the formed coarse microstructural hackle lines running away from the fracture mirror. (b) Inset at from (a). Dotted white arrows are indicating on a series of wake hackles propagating from the entrapped bubbles in the glaze. Reproduced from (a) Oblak, C., Kocjan, A., Jevnikar, P., Kosmac, T., 2017. The effect of mechanical fatigue and accelerated ageing on fracture resistance of glazed monolithic zirconia dental bridges. *J. Eur. Ceram. Soc.* 37, 4415–4422. doi:10.1016/j.jeurceramsoc.2017.04.048, Copyright Elsevier.

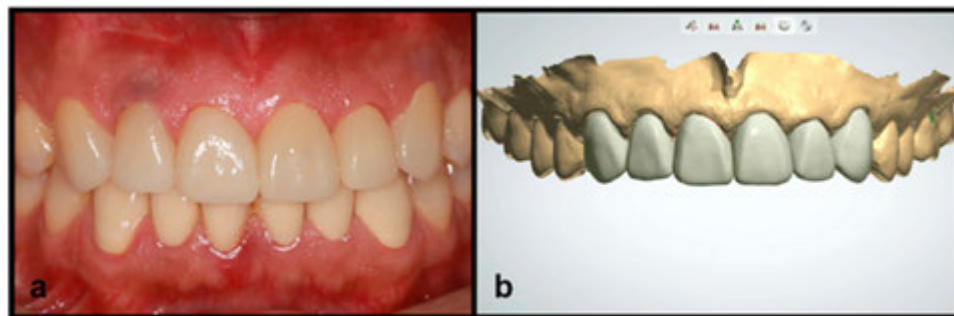


Fig. 8 (a) Intraoral view after the treatment with self-glazed zirconia crowns on the upper incisors and canines and (b) virtual digital design of the crowns. Reproduced from (b) Wu, Z., Shi, A., Liang, Q., *et al.*, 2020. Aesthetic restoration of anterior teeth with monolithic self-glazed zirconia crowns via a completely digital workflow: A clinical case report. *Adv. Appl. Ceram.* 119, 291–296. doi:10.1080/17436753.2019.1690847, Copyright Taylor & Francis.

that is done in a dental laboratory, the precision additive 3D gel deposition fabrication allows full digitalized reconstruction approach (**Fig. 8(b)**), since it can be applied with slightest clinical adjustment (Liu *et al.*, 2016).

The reliability of self-glaze zirconia material was shown comparatively strong to conventional zirconia materials in crown and bridge restorations (Zhang *et al.*, 2017). Different from the rougher CAD/CAM milled zirconia, the self-glazed zirconia has very smooth surfaces that prevent excessive wear of antagonist teeth, which is similar to the polished surface. The improved esthetic appearance of self-glazed zirconia ensures its potential for direct clinical uses (Liu *et al.*, 2016).

Zirconia Oral Implantology

Oral implants to replace lost teeth were a big step forward in oral rehabilitation. With oral implants, the patients' comfort can be increased with implant-supported/-retained fixed/removable prosthesis (Heydecke *et al.*, 2005). Titanium is considered to be the material of choice for the fabrication of oral implants (Howe *et al.*, 2019). However, due to certain reasons, e.g., patient request,

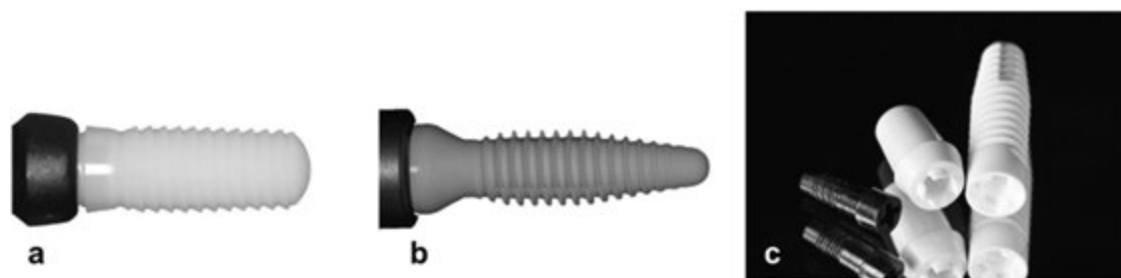


Fig. 9 (a) A Y-TZP one-piece implant (ceramic_implant, Vitaclinical, Bad Säckingen, Germany), (b) an ATZ one-piece implant (Ziraldent, Metoxit, Thayngen, Switzerland) and (c) an ATZ two-piece implant (Zeramex XT, Dentalpoint AG, Spreitenbach, Switzerland).

esthetic concerns, health issues like titanium hypersensitivity, and more, zirconia ceramic implants are also being used in oral implantology today (Balmer *et al.*, 2020; Kohal *et al.*, 2020).

Zirconia-Based Implant Materials

In the beginning of the ceramic implant era, alumina was applied as a substrate for implant fabrication (Schulte, 1981). However, this material was too weak to withstand oral function over a longer period of time (De Wijs *et al.*, 1994). Furthermore, bone apposition (i.e., osseointegration) onto that material was not predictable. In the search of a “better” tooth-color-like ceramic material, zirconia was evaluated. Today, the ceramic materials which are possibly to be used for the fabrication of oral implants are 3Y-TZP (Balmer *et al.*, 2018), ATZ (Spies *et al.*, 2015), Ce-TZP (Lopez-Pérez *et al.*, 2017) or composite ceramics (Altmann *et al.*, 2017). In clinical investigations (Pieralli *et al.*, 2017; Roehling *et al.*, 2018), the dominant zirconia material so far is 3Y-TZP (Fig. 9(a)) followed by ATZ (Fig. 9(b)). Composite materials such as ceria-stabilized zirconia–alumina–aluminate composite ceramics are in the experimental stage.

Implant Systems – One/Two-Piece

Initially, zirconia ceramic implants were designed as one-piece implants because of fabrication and stability reasons. Therefore, most of the clinical investigations published so far were evaluating one-piece zirconia implants. The advantages of the one-piece implants are their excellent stability (high fracture resistance), good short- to mid-term clinical performance, low marginal bone loss, no abutment screw loss and no microgap between abutment and implant body possibly serving as bacterial reservoir leading to marginal periimplant soft tissue inflammation. The disadvantages of the one-piece implants are found in their versatility. The adaptation of the abutment part to the clinical situation is only possible through grinding which in the end might lead to stability reduction (Fig. 10).

The correct prosthetic position can be problematic, especially in areas with an increased inclination of the alveolar ridge. The prosthetic reconstructions of one-piece implants are generally regarded as limited. Due to the mentioned shortcomings of one-piece implants, two-piece implants were developed (Fig. 9(c)). They present an improved prosthetic versatility with the application of angulated abutments if needed. The reconstructions are usually screw retained (gold alloy, titanium alloy, carbon-reinforced PEEK) and can therefore be removed for any reasons without destroying those (Fig. 11).

Implant Stability

An expressed concern with ceramic implants is their long-term stability. Therefore, it is of utmost importance to evaluate fracture resistance in-vitro before launching an implant product on the market. Numerous reports have been published on the in-vitro stability of one- and two-piece zirconia oral implants which have been evaluated in a systematic review by Bethke and coworkers (Bethke *et al.*, 2020). From the included and evaluated publications, the authors came to several conclusions: one-piece implants are obviously more stable than two-piece implants. Regarding the material, implants made from 3Y-TZP seem to be less stable than implants fabricated from ATZ. In a systematic review on clinical studies, Roehling *et al.* (2018) found regarding implant stability that only one out of 510 commercially available implants evaluated fractured. This translates into an overall fracture rate of 0.20% which is comparable to the fracture rate of titanium implants (0.18%) (Jung *et al.*, 2012).

One-piece implants with a diameter of 4 or more mm seem to be stable enough to survive at least 5 years of clinical function (Kohal *et al.*, 2020; Balmer *et al.*, 2020). From the in-vitro investigations, these implants survived long-term artificial chewing and it is anticipated that these implants also withstand long-term clinical load.

Zirconia ceramic implants made from 3Y-TZP are prone to LTD (see above) and show *t-m* transformation already in the as-delivered state or after hydrothermal ageing (Fig. 12). LTD was initially discussed to reduce the stability of zirconia. However, regarding zirconia ceramic implants that have been hydrothermally treated and have shown (superficial) transformation, no decrease in fracture stability (Sanon *et al.*, 2013; Spies *et al.*, 2018, 2017) could be observed.



Fig. 10 (a) An ATZ one-piece implant in the anterior upper region after adaptation to the prosthetic needs. (b) Implant reconstructed with an all-ceramic crown (Ziraldent, Metoxit, Thayngen, Switzerland).



Fig. 11 (a) A two-piece implant system in-situ. (b) The prosthetic reconstruction is screw-retained on the implant models (Zeramex XT, Dentalpoint AG, Spreitenbach, Switzerland).

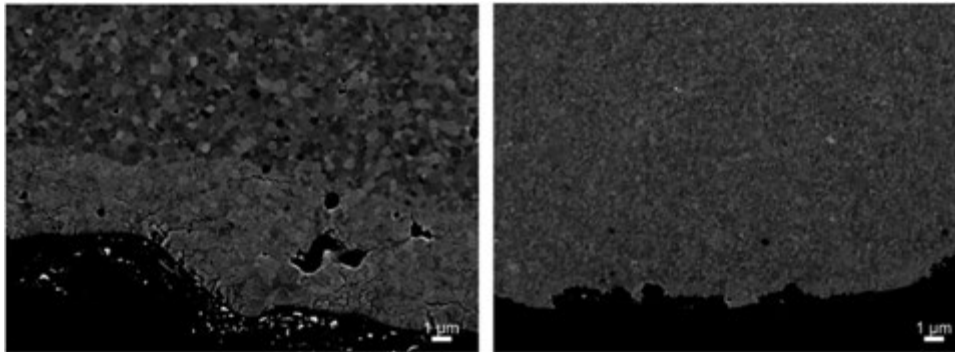


Fig. 12 (a) A 3Y-TZP implant that shows t-m transformation already in the as-delivered state. (b) A 3Y-TZP without a transformation zone when delivered.

Clinical Performance of Zirconia Oral Implants

Zirconia oral implants are evaluated in clinical investigations. The scientific interest in zirconia implants is reflected among else in the fact that many systematic reviews on this type of implant have been published ([Andreiotelli et al., 2009](#); [Vohra et al., 2015](#); [Haro Adanez et al., 2018](#); [Pieralli et al., 2017](#); [Roehling et al., 2018](#)). The more recent reviews concluded that commercially available implants show similar survival rates as titanium implants in short term with up to two to five years (one-year survival: 95%–98%). In addition, the marginal bone loss around zirconia oral implants is not different in comparison to titanium implants

for the same follow-up period (0.78–0.98 mm). It is noteworthy to state that most of the primary investigations were dealing with implants used for single crown or small bridge reconstructions. For larger reconstructions or removable prosthesis on zirconia implants no data is available and no information can be therefore given regarding survival rates.

The data for two-piece zirconia implants are considered as insufficient to date and therefore no conclusion on their (short- and mid-term) clinical behavior can be made.

Ce-TZP-Aluminate Pseudoplastic Ceramic Composite

Zirconia-based composites were developed to resist ageing (Reveron *et al.*, 2017; Palmero *et al.*, 2015). The laboratory investigations that have been performed were encouraging. Also, the biological testing with primary osteoblasts has shown positive results. Furthermore, in an animal model, it was shown that miniature implants made from one of those composites integrated well into rat femur (Altmann *et al.*, 2017). Additional preclinical research is necessary in order to be able to describe the mechanical, biological and clinical behavior of such ceramic composites.

Emerging Additive Manufacturing of Zirconia Dental Ceramics

Additive manufacturing (AM) or 3D printing of dental ceramics is a relatively new class of shaping technologies in which a zirconia part is directly generated from a digitally designed virtual 3D model by adding material layer upon layer, as opposed to subtractive manufacturing methodologies. Digital dentistry is reported to be one of the fastest-growing sectors of the AM technologies (Van Noort, 2012). Concerning dental materials that can be used in AM, polymers are the most studied and used ones, followed by metals. AM of ceramics is possible but issues with suitable surface finishing, mechanical properties and dimensional accuracy persist. However, compared to subtractive CAD/CAM machining, AM of ceramics reduces material waste and tooling stresses that are associated with the milling of ceramics. It also allows lower production costs compared to milling, faster production of customized dental pieces with complex details (e.g., intricate internal geometries and arbitrary angles), since they involve less manufacturing steps (Branco *et al.*, 2020). In most of the cases, AM of zirconia is used to obtain preliminary 3D structures in green state that are built from mixture powders with polymeric binder materials and need to be submitted to further steps of debinding and sintering.

The production of zirconia parts adopting different AM techniques has been the main focal point of some latter studies that investigated properties as density, porosity, surface roughness, microstructure, dimensional accuracy, morphology and mechanical behavior. It is possible to print zirconia components with mechanical properties close to milled zirconia (flexural strength 943 – 1154 MPa (Scheithauer *et al.*, 2015)), fracture toughness 3.9–6.7 MPa m^{1/2} (Branco *et al.*, 2020; Scheithauer *et al.*, 2015) and hardness 13.9 GPa (Xing *et al.*, 2017) and high dimensional stability (Osman *et al.*, 2017; Xing *et al.*, 2017). Overall, the preliminary results show that AM fabricated zirconia can be used in dental restorations such as ultra-thin occlusal veneers, with substantial advantages for processing (Branco *et al.*, 2020). However, besides the surface finish, the difficulties of the debinding process of the green part influence the consistency of the mechanical performance of 3D-printed zirconia.

Among many AM technologies available, the most promising remains to be VAT polymerization (Fig. 13), which can realize high precision and accuracy in the ranges of ten micrometers (Ioannidis *et al.*, 2020). VAT polymerization utilizes photopolymerization of a ceramic slurry to produce dense objects in a layer-by-layer fashion. Typical composition of ceramic suspension includes a monomer, photoinitiator, dispersants and solid ceramic loading of 40%–60% volume. As-printed green compacts are manufactured with a packing density of 55% theoretical density (TD), and it is possible to achieve densities exceeding 99% TD after sintering. The only restriction is imposed by the lengthy debinding step, that is diffusion-limited, thus depending on the thickness of the fabricated part. However, 3D printed zirconia may be regarded as a forthcoming material for the production of dental restorations.

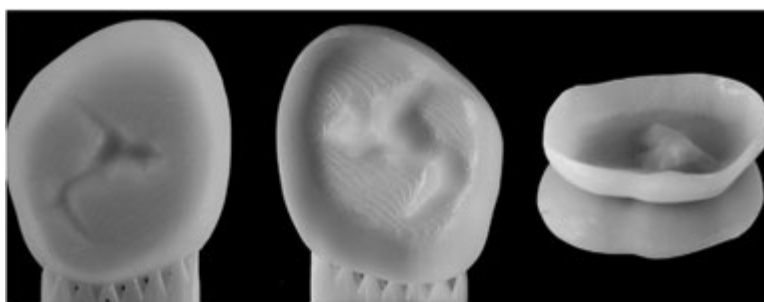


Fig. 13 3D-printed by VAT polymerization occlusal veneer before removing the support structures resulting from the printing process, viewing (from left to right) from occlusal, inner surface, and after having removed the supporting structure. Reproduced from (a) Ioannidis, A., Bomze, D., Hämmerle, C.H.F., *et al.*, 2020. Load-bearing capacity of CAD/CAM 3D-printed zirconia, CAD/CAM milled zirconia, and heat-pressed lithium disilicate ultra-thin occlusal veneers on molars. *Dent. Mater.* 36, e109–e116. doi:10.1016/j.dental.2020.01.016, Copyright Elsevier.

The Outlook of Zirconia Ceramics for Dentistry

Dentistry has since the last decade been undertaking a major change of the workflow from the traditional manual dependent to novel digital technology, where zirconia, especially the full-contour monolithic variant, has proved the ability to realize complete digital workflow. Successful digitalization, however, requires immediate addressing of several issues; (1) the development of digital manufacturing technologies beyond the state-of-the-art for the fabrication of net-shape zirconia FPDs. Preferably, with no or only scarce manual work involved not having any decisive role in the determination of the final quality of the fabricated FPD. With this restriction in mind, AM technologies appear to take over the subtractive type of manufacturing processes. (2) Overcoming big challenge of realization of the optical appearance of the natural teeth; as optical appearance is generated by many physical properties, such as color, translucency, opalescence and surface roughness. (3) The “bioactivation” of an otherwise bio-inert zirconia surface for oral implantology, where hierarchical, multiscale surface texturing has emerged as a promising strategy for enhanced soft and hard tissue integration. Other issues, such as improving mechanical reliability, chemical stability, optical translucency and bonding strength with teeth, all have already been successfully addressed, still, an endless journey of additional optimization is to be expected to further optimize zirconia's clinical and biological experience.

Conclusions

The large research of the 3Y-TZP's low-temperature degradation (LTD) process initiated at the onset of the present millennium was followed by the development of new generations of zirconia ceramics systems to address the demanding needs of advanced dental materials. Zirconia dental ceramics had ever since emerged from the oblivion masked by the dramatic failure of femoral heads to become a dental ceramics of choice in modern restorative dentistry. Nowadays it is expanding clinical indications of tooth-colored, metal-free all-ceramic systems from crowns and bridges, orthodontic brackets, root posts and even implants, but also allowing the minimally invasive dentistry.

The evolution from veneer-overlaid zirconia FPDs to full contour monolithic restorations has increased the need for more translucent and LTD resistant zirconia ceramics. The transition to yttria, fully-stabilised zirconias` however need to carefully balance between the conflicting demands of the increasing the translucency (and LTD resistance) at the expense of losing beneficial mechanical properties at the absence of *t-m* transformation mechanism depending on the perceived clinical indication.

The advent of additive manufacturing of dental ceramics has very high expectations. Still there are issues to be resolved before the wasteful but very effective FPDs fabrication by CAD/CAM technology can be replaced. Yet the idea of the possibility to fabricate hybrid multilayered zirconia FPDs in restorative dentistry, where the core layer would be composed of a tougher more opaque zirconia variant to provide mechanical integrity, while the outer layer from highly translucent one for the increased esthetics in the region of incisive to mimic dentin and enamel, respectively, is now firmly placed on the horizon.

References

- Altmann, B., Karygianni, L., Al-Ahmad, A., *et al.*, 2017. Assessment of novel long-lasting ceria-stabilized zirconia-based ceramics with different surface topographies as implant materials. *Adv. Funct. Mater.* 27, 1–14. doi:10.1002/adfm.201702512.
- Andriotelli, M., Wenz, H.J., Kohal, R.J., 2009. Are ceramic implants a viable alternative to titanium implants? A systematic literature review. *Clin. Oral Implants Res.* 20, 32–47. doi:10.1111/j.1600-0501.2009.01785.x.
- Aurélio, I.L., Marchionatti, A.M.E., Montagner, A.F., May, L.G., Soares, F.Z.M., 2016. Does air particle abrasion affect the flexural strength and phase transformation of Y-TZP? A systematic review and meta-analysis. *Dent. Mater.* 32, 827–845. doi:10.1016/j.dental.2016.03.021.
- Balmer, M., Spies, B.C., Vach, K., *et al.*, 2018. Three-year analysis of zirconia implants used for single-tooth replacement and three-unit fixed dental prostheses: A prospective multicenter study. *Clin. Oral Implants Res.* 29, 290–299. doi:10.1111/clr.13115.
- Balmer, M., Spies, B.C., Kohal, R.J., *et al.*, 2020. Zirconia implants restored with single crowns or fixed dental prostheses: 5-year results of a prospective cohort investigation. *Clin. Oral Implants Res.* 31, 452–462. doi:10.1111/clr.13581.
- Bavbek, A.B., Özcan, M., Eskitascioglu, G., 2014. Radioactive potential of zirconium-dioxide used for dental applications. *J. Appl. Biomater. Funct. Mater.* 12, 35–40. doi:10.5301/JABFM.2012.9341.
- Bethke, A., Pieralli, S., Kohal, R.J., *et al.*, 2020. Fracture resistance of zirconia oral implants in vitro: A systematic review and meta-analysis. *Materials* 13, 1–21. doi:10.3390/ma13030562.
- Branco, A., Silva, R., Santos, T., *et al.*, 2020. Suitability of 3D printed pieces of nanocrystalline zirconia for dental applications. *Dent. Mater.* 1–14. doi:10.1016/j.dental.2020.01.006.
- Brandt, S., Winter, A., Weigl, P., *et al.*, 2019. Conical zirconia telescoping into electroformed gold: A retrospective study of prostheses supported by teeth and/or implants. *Clin. Implant Dent. Relat. Res.* 21, 317–323. doi:10.1111/cid.12739.
- Bučevac, D., Kosmač, T., Kocjan, A., 2017. The influence of yttrium-segregation-dependent phase partitioning and residual stresses on the aging and fracture behaviour of 3Y-TZP ceramics. *Acta Biomater.* 62, 306–316. doi:10.1016/j.actbio.2017.08.014.
- Butler, E.P., 1985. Transformation-toughened zirconia ceramics. *Mater. Sci. Technol.* 1, 417–432. doi:10.1179/mst.1985.1.6.417.
- Composilvan, E., Leone, R., Gremillard, L., *et al.*, 2018. Aging resistance, mechanical properties and translucency of different yttria-stabilized zirconia ceramics for monolithic dental crown applications. *Dent. Mater.* 34, 879–890. doi:10.1016/j.dental.2018.03.006.
- Chevalier, J., 2006. What future for zirconia as a biomaterial? *Biomaterials* 27, 535–543. doi:10.1016/j.biomaterials.2005.07.034.
- Chevalier, J., Gremillard, L., 2009. Ceramics for medical applications: A picture for the next 20 years. *J. Eur. Ceram. Soc.* 29, 1245–1255. doi:10.1016/j.jeurceramsoc.2008.08.025.
- Chevalier, J., Gremillard, L., Deville, S., 2007. Low-temperature degradation of zirconia and implications for biomedical implants. *Annu. Rev. Mater. Res.* 37, 1–32. doi:10.1146/annurev.matsci.37.052506.084250.

- Chevalier, J., Gremillard, L., Virkar, A.V., Clarke, D.R., 2009. The tetragonal-monoclinic transformation in zirconia: Lessons learned and future trends. *J. Am. Ceram. Soc.* 92, 1901–1920. doi:10.1111/j.1551-2916.2009.03278.x.
- Chintapalli, R.K., Marro, F.G., Jimenez-Pique, E., Anglada, M., 2013. Phase transformation and subsurface damage in 3Y-TZP after sandblasting. *Dent. Mater.* 29, 566–572. doi:10.1016/j.dental.2013.03.005.
- Chintapalli, R.K., Mestra Rodriguez, A., Garcia Marro, F., Anglada, M., 2014. Effect of sandblasting and residual stress on strength of zirconia for restorative dentistry applications. *J. Mech. Behav. Biomed. Mater.* 29, 126–137. doi:10.1016/j.jmbbm.2013.09.004.
- Chong, B.J., Thangavel, A.K., Rolton, S.B., Guazzato, M., Klineberg, I.J., 2015. Clinical and laboratory surface finishing procedures for zirconia on opposing human enamel wear: A laboratory study. *J. Mech. Behav. Biomed. Mater.* 50, 93–103. doi:10.1016/j.jmbbm.2015.06.007.
- Cotič, J., Jevnikar, P., Kocjan, A., 2017. Ageing kinetics and strength of airborne-particle abraded 3Y-TZP ceramics. *Dent. Mater.* 33. doi:10.1016/j.dental.2017.04.014.
- Cotič, J., Jevnikar, P., Kocjan, A., Kosmač, T., 2016. Complexity of the relationships between the sintering-temperature-dependent grain size, airborne-particle abrasion, ageing and strength of 3Y-TZP ceramics. *Dent. Mater.* 32, 510–518. doi:10.1016/j.dental.2015.12.004.
- Cuy, J.L., Mann, A.B., Livi, K.J., Teaford, M.F., Weihs, T.P., 2002. Nanoindentation mapping of the mechanical properties of human molar tooth enamel. *Arch. Oral Biol.* 47, 281–291. doi:10.1016/S0003-9969(02)00006-7.
- De Wijs, F.L., Van Dongen, R.C., De Lange, G.L., De Putter, C., 1994. Front tooth replacement with Tübingen (Frialit) implants. *J. Oral Rehabil.* 21, 11–26.
- Denry, I., Kelly, J.R., 2008. State of the art of zirconia for dental applications. *Dent. Mater.* 24, 299–307. doi:10.1016/j.dental.2007.05.007.
- Fujimori, H., Yashima, M., Sasaki, S., *et al.*, 2001. Cubic-tetragonal phase change of yttria-doped hafnia solid solution: High-resolution X-ray diffraction and Raman scattering. *Chem. Phys. Lett.* 346, 217–223.
- Garvie, R., Hannink, R., Pascoe, R., 1975. Ceramic steel? *Nature* 258, 703–704.
- Glauser, R., Sailer, I., Wohlwend, A., *et al.*, 2004. Experimental zirconia abutments for implant-supported single-tooth restorations in esthetically demanding regions: 4-year results of a prospective clinical study. *Int. J. Prosthodont.* 17, 285–290.
- Guess, P.C., Att, W., Strub, J.R., 2012. Zirconia in fixed implant prosthodontics. *Clin. Implant Dent. Relat. Res.* 14, 633–645. doi:10.1111/j.1708-8208.2010.00317.x.
- Gupta, T.K., Lange, F.F., Bechtold, J.H., 1978. Effect of stress-induced phase transformation on the properties of polycrystalline zirconia containing metastable tetragonal phase. *J. Mater. Sci.* 13, 1464–1470. doi:10.1007/BF00553200.
- Güth, J.F., Stawarczyk, B., Edelhoff, D., Liebermann, A., 2019. Zirconia and its novel compositions: What do clinicians need to know? *Quintessence Int.* 50, 512–520. doi:10.3290/j.qi.a42653.
- Hallmann, L., Mehl, A., Ulmer, P., *et al.*, 2012. The influence of grain size on low-temperature degradation of dental zirconia. *J. Biomed. Mater. Res. - Part B Appl. Biomater.* 100 B, 447–456. doi:10.1002/jbm.b.31969.
- Hannink, R.H.J., Kelly, P.M., Muddle, B.C., 2004. Transformation toughening in zirconia-containing ceramics. *J. Am. Ceram. Soc.* 83, 461–487. doi:10.1111/j.1151-2916.2000.tb01221.x.
- Haraguchi, K., Sugano, N., Nishii, T., *et al.*, 2001. Phase transformation of a zirconia ceramic head after total hip arthroplasty. *J. Bone Jt. Surg. - Ser. B* 83, 996–1000. doi:10.1302/0301-620X.83B7.12122.
- Haro Adanez, M., Nishihara, H., Att, W., 2018. A systematic review and meta-analysis on the clinical outcome of zirconia implant-restoration complex. *J. Prosthodont. Res.* 62.
- Heydecke, G., Thomason, J.M., Lund, J.P., Feine, J.S., 2005. The impact of conventional and implant supported prostheses on social and sexual activities in edentulous adults: results from a randomized trial 2 months after treatment. *J. Dent.* 33, 649–657. doi:10.1016/j.jdent.2005.01.003.
- Howe, M.S., Keys, W., Richards, D., 2019. Long-term (10-year) dental implant survival: A systematic review and sensitivity meta-analysis. *J. Dent.* 84, 9–21. doi:10.1016/j.jdent.2019.03.008.
- Ioannidis, A., Bomze, D., Hämmerle, C.H.F., *et al.*, 2020. Load-bearing capacity of CAD/CAM 3D-printed zirconia, CAD/CAM milled zirconia, and heat-pressed lithium disilicate ultra-thin occlusal veneers on molars. *Dent. Mater.* 36, e109–e116. doi:10.1016/j.dental.2020.01.016.
- Jevnikar, P., Golobič, M., Kocjan, A., Kosmač, T., 2012. The effect of nano-structured alumina coating on the bond strength of resin-modified glass ionomer cements to zirconia ceramics. *J. Eur. Ceram. Soc.* 32, 2641–2645. doi:10.1016/j.jeurceramsoc.2012.03.037.
- Jevnikar, P., Krnel, K., Kocjan, A., Funduk, N., Kosmac, T., 2010. The effect of nano-structured alumina coating on resin-bond strength to zirconia ceramics. *Dent. Mater.* 26, 688–696. doi:10.1016/j.dental.2010.03.013.
- Jovanovski, S., Cotič, J., Kocjan, A., Oblak, Č., Jevnikar, P., 2019. Fracture resistance of endodontically treated maxillary incisors restored with zirconia posts: Effect of the internal plateau preparation. *Adv. Appl. Ceram.* 118. doi:10.1080/17436753.2018.1508625.
- Jung, R.E., Zembic, A., Pjetursson, B.E., Zwahlen, M., Thoma, D.S., 2012. Systematic review of the survival rate and the incidence of biological, technical, and aesthetic complications of single crowns on implants reported in longitudinal studies with a mean follow-up of 5 years. *Clin. Oral Implants Res.* 23, 2–21. doi:10.1111/j.1600-0501.2012.02547.x.
- Keith, O., Kusy, R.P., Whitley, J.Q., 1994. Zirconia brackets: An evaluation of morphology and coefficients of friction. *Am. J.* 106, 605–614. doi:10.1016/S0889-5406(94)70085-0.
- Kern, M., 2015. Bonding to oxide ceramics – Laboratory testing versus clinical outcome. *Dent. Mater.* 31, 8–14. doi:10.1016/j.dental.2014.06.007.
- Keuper, M., Berthold, C., Nickel, K.G., 2014. Long-time aging in 3 mol% yttria-stabilized tetragonal zirconia polycrystals at human body temperature. *Acta Biomater.* 10, 951–959. doi:10.1016/j.actbio.2013.09.033.
- Kocjan, A., Pouchly, V., Shen, Z., 2015. Processing of zirconia nanoceramics from a coarse powder. *J. Eur. Ceram. Soc.* 35, 1285–1295. doi:10.1016/j.jeurceramsoc.2014.10.022.
- Kohal, R.-J., Spies, B.C., Vach, K., Balmer, M., Pieralli, S., 2020. A prospective clinical cohort investigation on zirconia implants: 5-year results. *J. Clin. Med.* 9, 2585. doi:10.3390/jcm9082585.
- Kosmac, T., Oblak, Č., Jevnikar, P., Funduk, N., Marion, L., 1999. The effect of surface grinding and sandblasting on flexural strength and reliability of Y-TZP zirconia ceramic. *Dent. Mater.* 15, 426–433.
- Kosmač, T., Oblak, Č., Marion, L., 2008. The effects of dental grinding and sandblasting on ageing and fatigue behavior of dental zirconia (Y-TZP) ceramics. *J. Eur. Ceram. Soc.* 28, 1085–1090. doi:10.1016/j.jeurceramsoc.2007.09.013.
- Kosmač, T., Kocjan, A., Golobič, M., Jevnikar, P., 2012. Resin bond strength to alumina coated Ce-TZP/Al₂O₃ dental ceramic. *Key Eng. Mater.* 493–494, 632–636. doi:10.4028/www.scientific.net/KEM.493-494.632.
- Krell, A., Hutzler, T., Klimke, J., 2009. Transmission physics and consequences for materials selection, manufacturing, and applications. *J. Eur. Ceram. Soc.* 29, 207–221. doi:10.1016/j.jeurceramsoc.2008.03.025.
- Lai, X., Si, W., Jiang, D., *et al.*, 2017. Effects of small-grit grinding and glazing on mechanical behaviors and ageing resistance of a super-translucent dental zirconia. *J. Dent.* 66, 23–31. doi:10.1016/j.jdent.2017.09.003.
- Lawson, N.C., Janyavula, S., Syklawer, S., McLaren, E.A., Burgess, J.O., 2014. Wear of enamel opposing zirconia and lithium disilicate after adjustment, polishing and glazing. *J. Dent.* 42, 1586–1591. doi:10.1016/j.jdent.2014.09.008.
- Liu, Y., Wang, Y., Wang, D., *et al.*, 2016. Self-glazed zirconia reducing the wear to tooth enamel. *J. Eur. Ceram. Soc.* 36, 2889–2894. doi:10.1016/j.jeurceramsoc.2015.11.029.
- Lopez-Piriz, R., Fernández, A., Goyos-Ball, L., *et al.*, 2017. Performance of a new Al₂O₃/Ce-TZP ceramic nanocomposite dental implant: A pilot study in dogs. *Materials* 10. doi:10.3390/ma10060614.
- Luthardt, R.G., Holzhueter, M.S., Rudolph, H., Herold, V., Walter, M.H., 2004. CAD/CAM-machining effects on Y-TZP zirconia. *Dent. Mater.* 20, 655–662. doi:10.1016/j.dental.2003.08.007.

- Malgaj, T., Kocjan, A., Jevnikar, P., 2020. The effect of firing protocols on the resin-bond strength to alumina-coated zirconia ceramics. *Adv. Appl. Ceram. Struct. Funct. Bioceram.* 119, 267–275.
- Mannocci, F., Ferrari, M., Watson, T.F., 1999. Intermittent loading of teeth restored using quartz fiber, carbon-quartz fiber, and zirconium dioxide ceramic root canal posts. *J. Adhes. Dent.* 1, 153–158.
- Matsui, K., Ohmichi, N., Ohgai, M., Yoshida, H., Ikuhara, Y., 2006. Effect of alumina-doping on grain boundary segregation-induced phase transformation in yttria-stabilized tetragonal zirconia polycrystal. *J. Mater. Res.* 21, 2278–2289. doi:10.1557/JMR.2006.0274.
- Mercer, C., Williams, J.R., Clarke, D.R., Evans, A.G., 2007. On a ferroelastic mechanism governing the toughness of metastable tetragonal-prime (t') yttria-stabilized zirconia. *Proc. R. Soc. A Math. Phys. Eng. Sci.* 463, 1393–1408. doi:10.1098/rspa.2007.1829.
- Meyenberg, K.H., Luthy, H., Schärer, P., 1995. Zirconia posts: A new all-ceramic concept for nonvital abutment teeth. *J. Esthet. Restor. Dent.* 7, 73–80. doi:10.1111/j.1708-8240.1995.tb00565.x.
- Nam, M.G., Park, M.G., 2018. Changes in the flexural strength of translucent zirconia due to glazing and low-temperature degradation. *J. Prosthet. Dent.* 120 (969), e1–e6. doi:10.1016/j.prosdent.2018.07.017.
- Oblak, C., Kocjan, A., Jevnikar, P., Kosmac, T., 2017. The effect of mechanical fatigue and accelerated ageing on fracture resistance of glazed monolithic zirconia dental bridges. *J. Eur. Ceram. Soc.* 37, 4415–4422. doi:10.1016/j.jeurceramsoc.2017.04.048.
- Osman, R.B., van der Veen, A.J., Huijbers, D., Wismeijer, D., Alharbi, N., 2017. 3D-printing zirconia implants: A dream or a reality? An in-vitro study evaluating the dimensional accuracy, surface topography and mechanical properties of printed zirconia implant and discs. *J. Mech. Behav. Biomed. Mater.* 75, 521–528. doi:10.1016/j.jmbbm.2017.08.018.
- Özcan, M., 2015. Intraoral repair protocol for chipping or fracture of veneering ceramic in zirconia fixed dental prostheses. *J. Adhes. Dent.* 17, 189–190.
- Özcan, M., Valandro, L.F., Braga Pereira, S.M., *et al.*, 2013. Effect of surface conditioning modalities on the repair bond strength of resin composite to the zirconia core/veneering ceramic complex. *J. Adhes. Dent.* 15, 207–210.
- Palmero, P., Fornabaio, M., Montanaro, L., *et al.*, 2015. Towards long lasting zirconia-based composites for dental implants: Part I: Innovative synthesis, microstructural characterization and invitro stability. *Biomaterials* 50, 38–46. doi:10.1016/j.biomaterials.2015.01.018.
- Passos, S.P., Torrealba, Y., Major, P., *et al.*, 2014. In vitro wear behavior of zirconia opposing enamel: A systematic review. *J. Prosthodont.* 23, 593–601. doi:10.1111/jopr.12167.
- Piconi, C., Maccauro, G., 1999. Zirconia as a ceramic biomaterial. *Biomaterials* 20, 1–25.
- Pieralli, S., Kohal, R.J., Jung, R.E., Vach, K., Spies, B.C., 2017. Clinical outcomes of zirconia dental implants: A systematic review. *J. Dent. Res.* 96, 38–46. doi:10.1177/0022034516664043.
- Porstendörfer, J., Reineking, A., Willert, H.G., 1996. Radiation risk estimation based on activity measurements of zirconium oxide implants. *J. Biomed. Mater. Res.* 32, 663–667. doi:10.1002/(SICI)1097-4636(199612)32:4<663::AID-JBM20>3.0.CO;2-D.
- Raigrodski, A.J., 2005. All-ceramic full-coverage restorations: Concepts and guidelines for material selection. *Pract. Proced. Aesthet. Dent.* 17 (4), 249–256.
- Reveron, H., Fornabaio, M., Palmero, P., *et al.*, 2017. Towards long lasting zirconia-based composites for dental implants: Transformation induced plasticity and its consequence on ceramic reliability. *Acta Biomater.* 48, 423–432. doi:10.1016/j.actbio.2016.11.040.
- Roehling, S., Schlegel, K.A., Woelfler, H., Gahlert, M., 2018. Performance and outcome of zirconia dental implants in clinical studies: A meta-analysis. *Clin. Oral Implants Res.* 29, 135–153. doi:10.1111/clr.13352.
- Russo, D.S., Cinelli, F., Sarti, C., Giachetti, L., 2019. Adhesion to zirconia: A systematic review of current conditioning methods and bonding materials. *Dent. J.* 74, 1–19. doi:10.3390/dj7030074.
- Samodurova, A., Kocjan, A., Swain, M.V., Kosmač, T., 2015a. The combined effect of alumina and silica co-doping on the ageing resistance of 3Y-TZP bioceramics. *Acta Biomater.* 11, 477–487. doi:10.1016/j.actbio.2014.09.009.
- Samodurova, A., Vengust, D., Kocjan, A., Kosmač, T., 2015b. The sintering-temperature-related microstructure and phase assemblage of alumina-doped and alumina-silica-co-doped 3-mol%-yttria-stabilized tetragonal zirconia. *Scr. Mater.* 105, 50–53. doi:10.1016/j.scriptamat.2015.04.031.
- Sanon, C., Chevalier, J., Douillard, T., *et al.*, 2013. Low temperature degradation and reliability of one-piece ceramic oral implants with a porous surface. *Dent. Mater.* 29, 389–397. doi:10.1016/j.dental.2013.01.007.
- Scheithauer, U., Schwarzer, E., Richter, H.-J., Moritz, T., 2015. Thermoplastic 3D printing – An additive manufacturing method for producing dense ceramics. *Int. J. Appl. Ceram. Technol.* 12, 26–31. doi:10.1111/ijac.12306.
- Schulte, W., 1981. Das enossale Tübinger Implantat aus Al2O3 (Frialit). *Der Entwicklungsstand nach 6 Jahren. Zahnärztl. Mitt.* 71, 1114–1122.
- Shahin, R., Kern, M., 2010. Effect of air-abrasion on the retention of zirconia ceramic crowns luted with different cements before and after artificial aging. *Dent. Mater.* 26, 922–928. doi:10.1016/j.dental.2010.06.006.
- Shen, Z., Liu, L., Xu, X., *et al.*, 2017. Fractography of self-glazed zirconia with improved reliability. *J. Eur. Ceram. Soc.* 37, 4339–4345. doi:10.1016/j.jeurceramsoc.2017.03.008.
- Spies, B.C., Maass, M.E., Adolfsson, E., *et al.*, 2017. Long-term stability of an injection-molded zirconia bone-level implant: A testing protocol considering aging kinetics and dynamic fatigue. *Dent. Mater.* 33, 954–965. doi:10.1016/j.dental.2017.06.002.
- Spies, B.C., Fross, A., Adolfsson, E., *et al.*, 2018. Stability and aging resistance of a zirconia oral implant using a carbon fiber-reinforced screw for implant-abutment connection. *Dent. Mater.* 34, 1585–1595. doi:10.1016/j.dental.2018.08.290.
- Spies, B.C., Balmer, M., Patzelt, S.B., Vach, K., Kohal, R.J., 2015. Clinical and patient-reported outcomes of a zirconia oral implant: Three-year results of a prospective cohort investigation. *J. Dent. Res.* 94, 1385–1391.
- Swain, M.V., 2010. Unstable cracking (chipping) of veneering porcelain on all-ceramic dental crowns and fixed partial dentures. *Acta Biomater.* 5, 1668–1677. doi:10.1016/j.actbio.2008.12.016.
- Van Noort, R., 2012. The future of dental devices is digital. *Dent. Mater.* 28, 3–12. doi:10.1016/j.dental.2011.10.014.
- Virkar, A., Matsumoto, R., 1986. Ferroelastic domain switching as a toughening mechanism in tetragonal zirconia. *J. Am. Ceram. Soc.* 69, C-224–C-226.
- Vohra, F., Al-Kheraif, A.A., Ab Ghani, S.M., *et al.*, 2015. Crestal bone loss and periimplant inflammatory parameters around zirconia implants: A systematic review. *J. Prosthet. Dent.* 114, 351–357. doi:10.1016/j.prosdent.2015.03.016.
- Wang, L., Liu, Y., Si, W., *et al.*, 2012. Friction and wear behaviors of dental ceramics against natural tooth enamel. *J. Eur. Ceram. Soc.* 32, 2599–2606. doi:10.1016/j.jeurceramsoc.2012.03.021.
- Weigl, P., Lauer, H.C., 2000. Advanced biomaterials used for a new telescopic retainer for removable dentures. *J. Biomed. Mater. Res.* 53, 337–347. doi:10.1002/1097-4636(2000)53:4<337::aid-jbm7>3.0.co;2-7.
- Willems, G., Celis, J.P., Lambrechts, P., Braem, M., Vanherle, G., 1993. Hardness and Young's modulus determined by nanoindentation technique of filler particles of dental restorative materials compared with human enamel. *J. Biomed. Mater. Res.* 27, 747–755. doi:10.1002/jbm.820270607.
- Xie, H., Li, Q., Zhang, F., *et al.*, 2016. Comparison of resin bonding improvements to zirconia between one-bottle universal adhesives and tribochemical silica coating, which is better? *Dent. Mater.* 32, 403–411. doi:10.1016/j.dental.2015.12.014.
- Xing, H., Zou, B., Li, S., Fu, X., 2017. Study on surface quality, precision and mechanical properties of 3D printed ZrO₂ ceramic components by laser scanning stereolithography. *Ceram. Int.* 43, 16340–16347. doi:10.1016/j.ceramint.2017.09.007.
- Xiong, Y., Fu, Z., Pouchly, V., Maca, K., Shen, Z., 2014. Preparation of transparent 3Y-TZP nanoceramics with no low-temperature degradation. *J. Am. Ceram. Soc.* 97, 1402–1406. doi:10.1111/jace.12919.

- Zhang, F., Vanmeensel, K., Batuk, M., *et al.*, 2015. Highly-translucent, strong and aging-resistant 3Y-TZP ceramics for dental restoration by grain boundary segregation. *Acta Biomater.* 16, 215–222. doi:10.1016/j.actbio.2015.01.037.
- Zhang, F., Batuk, M., Hadermann, J., *et al.*, 2016a. Effect of cation dopant radius on the hydrothermal stability of tetragonal zirconia: Grain boundary segregation and oxygen vacancy annihilation. *Acta Mater* 106, 48–58. doi:10.1016/j.actamat.2015.12.051.
- Zhang, F., Inokoshi, M., Batuk, M., *et al.*, 2016b. Strength, toughness and aging stability of highly-translucent Y-TZP ceramics for dental restorations. *Dent. Mater.* 32, e327–e337. doi:10.1016/j.dental.2016.09.025.
- Zhang, F., Reveron, H., Spies, B.C., Van Meerbeek, B., Chevalier, J., 2019a. Trade-off between fracture resistance and translucency of zirconia and lithium-disilicate glass ceramics for monolithic restorations. *Acta Biomater.* 91, 24–34. doi:10.1016/j.actbio.2019.04.043.
- Zhang, F., Spies, B.C., Vleugels, J., *et al.*, 2019b. High-translucent yttria-stabilized zirconia ceramics are wear-resistant and antagonist-friendly. *Dent. Mater.* 35, 1776–1790. doi:10.1016/j.dental.2019.10.009.
- Zhang, Y., Lawn, B.R., 2018. Novel zirconia materials in dentistry. *J. Dent. Res.* 97, 140–147. doi:10.1177/0022034517737483.
- Zhang, Y., Han, J., Zheng, G., *et al.*, 2017. Fatigue behaviours of the zirconia dental restorations prepared by two manufacturing methods. *Adv. Appl. Ceram.* 116, 368–375. doi:10.1080/17436753.2017.1336365.

Subject Index

Note

This index is in letter-by-letter order, whereby hyphens and spaces within index headings are ignored in the alphabetization, and it is arranged in set-out style, with a maximum of three levels of heading.

Cross-reference terms in italics are general cross-references, or refer to subentry terms within the main entry (the main entry is not repeated to save space).

Location references refer to the volume number, in bold, followed by the page number.

Page numbers followed by “*f*” and “*t*” refer to figures and tables, respectively.

A

- Abbe diagram 2:660, 2:661*f*, 2:668, 2:671
- ab initio* molecular dynamics (AIMD) 1:454, 1:455, 1:467–468
- abrasives 2:406
 - application guidance 2:414
 - electro fused 2:407–410
 - minerals for 2:406–407
 - sintered abrasives 2:410–414
 - extrusion processes 2:411
 - sol-gel process 2:412
- absorbers 3:120
- absorbing cladding 3:120
- accelerating voltage 1:657
- acceptor doping 3:352
- achromatic lens 2:669–670
- acoustic impedance 3:394
- acrylamide (AM) 1:151–152
- acrylic acid 1:151–152
- acrylics 1:223
- actinides 2:776–777
- active metal brazing (AMB) 2:401–402
- additive-free LTCC (low temperature co-fired ceramics substrates) 3:444–445
- additive manufacturing (AM) 3:486–487, 1:382–384, 1:185, 2:375–377, 1:344–345, 3:662, 3:670–671, 3:665*t*, 1:225, 1:203, 1:203–204, 3:691–692, 1:109, 3:651–654, 3:655*t*
- bioprinting 3:654, 3:488–489
- direct AM technologies 1:213–214
 - material extrusion 1:214–216
 - material jetting 1:213–214
 - negative AM technologies
- direct energy deposition (DED) 1:383–384
- direct inkjet printing (DIP) 1:390
 - advantages and limitations of 1:390
- extrusion based methods 3:654
- feasibility of AM processing of monolithic ceramics
- fused deposition modeling 3:487
- future developments
- indirect AM technologies 1:207–209
- laminated object manufacturing (LOM) 1:212–213
- powder-based 3D printing 1:207–209
- inkjet 3D printing 3:654
- materials extrusion 1:388–390
 - ceramic material extrusion 1:388–390
- powder bed based techniques 1:386–388, 3:654
 - binder jetting 1:387–388
 - slurry based binder jetting 1:388
- powder bed fusion (PBF) 1:384
 - direct laser sintering (dLS) 1:384–385
 - direct powder bed fusion (PBF) 1:384
 - indirect powder bed fusion 1:385–386
 - powder-based indirect laser sintering (p-iLS) 1:385–386
- Selective Laser Sintering/Melting (SLS/SLM) process 3:487–488
- sheet lamination 1:388
- stereolithography 3:652, 3:486–487
- technologies, overview of 1:204–207
- 3D printing 3:488
- vat photopolymerization 1:393–394
- ADT *see* automated diffraction tomography (ADT)
- advanced ceramics, joining of 2:393
 - see also* technical ceramics
 - chemical methods 2:395–396
 - glass-to-metal bonding and sealing 2:397–399
- hybrid chemical processes 2:397
 - anodic bonding 2:397
 - gas–metal eutectic bonding 2:397
- joint design 2:404–405
- liquid phase methods 2:399–400
 - active metal brazing (AMB) 2:401–402
 - brazing of ceramics 2:402–403
 - fundamentals of wetting 2:400
 - inorganic “ceramic” adhesives 2:403–404
 - metallization 2:401
 - organic adhesives 2:400–401
 - sintered metal powder processing (SMPP) 2:401
- soldering and brazing 2:401
- soldering of ceramics 2:402
- mechanical methods 2:393–395
- thermomechanical processes 2:394–395
- solid phase methods 2:395–396
 - advantages and disadvantages of diffusion bonding 2:397
 - ceramic–ceramic diffusion bonding 2:395–396
 - ceramic–metal diffusion bonding 2:396
 - use of thin interlayers to enhance diffusion bonding 2:396–397
 - testing of ceramic-containing joints 2:404
- AEM *see* analytical electron microscopy (AEM)
- aerogel–glass transformation 2:691
- aerogels 2:692, 2:693
- aerosol-assisted vapor phase syntheses 1:69
- aerosol generation 1:70
- aerosol generator device 1:71–72
- aerosols 1:37
- aerospace 2:288–294
- AES *see* Auger electron spectroscopy (AES)
- agglomerants, use of 2:754
- AI *see* artificial intelligence (AI)
- AIM *see* aspherical ion model (AIM)
- AIMD *see ab initio* molecular dynamics (AIMD)
- AIP *see* Aluminum isopropoxide (AIP)
- air bubble inclusion 1:170–171
- air plasma spraying (APS) techniques 2:64
- Al₂O₃–SiC nanocomposites
 - high-temperature properties of 2:241
 - processing and microstructure of 2:240
 - room-temperature properties of 2:240–241
- Al₂O₃–SiO₂ binary glasses 2:505
- Al₂O₃–YAG 2:219–222
- Al₂O₃–ZrO₂ (Y₂O₃) 2:222–224
- albite 2:735
- Al bonding and coordination in M–Si–Al–O–N glasses 2:565–566
- alginate 3:686
- alkali aluminosilicate glasses 2:505–507

bone ash reinforced geopolymer composites 1:430–431

amorphous silicon (a-Si) thin films 3:64–65

amorphous tetrahedral semiconductors 1:530–531

amorphous tricalcium phosphate (am-TCP) 3:582

amorphous vanadium oxides thin films 3:64

amorphous ZIFs (a-ZIFs) 1:459, 1:461

amplified spontaneous emission (ASE) 3:120

amplifier fibers 2:686

amplitude contrast 1:587–589

AMs *see* amorphous materials (AMs)

am-TCP *see* amorphous tricalcium phosphate (am-TCP)

AN *see* aluminum nitrate (AN)

analytical electron microscopy (AEM) 1:600

anelasticity and mechanical spectroscopy 1:705–707

ankle joint replacements, oxide ceramics in 3:522

annealing and tempering, of glass 2:623

 annealing process 2:625

 annealing lehrs 2:625–626

 basic principles 2:625

 impact of annealing on glass properties 2:626–627

 quantification of the stresses 2:627

 taking advantage of thermal stresses 2:627–628

 stresses in glass 2:623–625

 non-thermal stresses 2:625

 thermal stresses 2:625

 thermal tempering glass 2:628–630

 commercial tempering processes 2:630

 viscosity versus temperature in glass 2:623

annealing point 2:651

annealing process 2:625

 annealing lehrs 2:625–626

 basic principles 2:625

 impact of annealing on glass properties 2:626–627

 quantification of stresses 2:627

 thermal stresses, taking advantage of 2:627–628

anode substrates and anodes 3:53–54

anode thin films, pulsed laser deposition (PLD) of 3:64–65

anodic bonding 2:397

antenna duplexer of portable telephones 3:379–380

antenna miniaturization 3:199

antiferroelectrics

 applications 3:291–293

 basic concepts of 3:288–290

antiphase boundaries (APBs) 3:220–221, 3:221–222, 1:596

AOS *see* Amorphous Oxide Semiconductors (AOS)

apatite 3:595

apatite-wollastonite (A/W) system 3:650

apatitic ceramics 3:575

 biological properties 3:578–581

 physicochemical characterization 3:578

 structure 3:575–576

 synthesis and processing routes 3:576–577

 nanocrystalline apatites 3:577–578

 well-crystallized apatites 3:576–577

apatitic tricalcium phosphate (ap-TCP) 3:582–583

APBs *see* antiphase boundaries (APBs)

APS *see* air plasma spraying (APS)

 techniques; ammonium persulfate (APS); amorphous phase separation (APS); atmospheric plasma spraying (APS)

ap-TCP *see* apatitic tricalcium phosphate (ap-TCP)

APTES *see* (3-aminopropyl)triethoxysilane (APTES)

APUs *see* Auxiliary Power Units (APUs)

aqueous environments, corrosion of ceramics in 1:921

 assessment methods 1:924*t*

 corundum ceramics 1:927–929

 silicon carbide ceramics 1:929–930

 silicon nitride ceramics 1:929

 zirconium dioxide ceramics 1:928–929

aqueous suspension, electrical characteristics of powders in 1:115–116

aramid family of fibers 2:307

Archimedean method 1:694

Arrhenius analysis 1:87–88

artificial intelligence (AI) 1:441

ASCB *see* Asymmetric Semi-Circular Bend specimen (ASCB)

ASE *see* amplified spontaneous emission (ASE)

AS glasses *see* aluminosilicate (AS) glasses

ASH-C *see* amorphous self-healed ceramics (ASH-C)

ASH-G composites *see* amorphous self-healed geopolymer (ASH-G) composites

a-Si thin films *see* amorphous silicon (a-Si) thin films

aspherical ion model (AIM) 1:487

aspheric lenses 2:672, 2:672*f*

associate species solution models 1:503–504

Asymmetric Semi-Circular Bend specimen (ASCB) 1:833

AT *see* aluminum titanate (AT)

atmospheric plasma spraying (APS) 3:732

atmospheric re-entry 2:361–363

 non-ablative thermal protection materials 2:363–364

 thermally insulative thermal protection materials 2:362–363

atomic packing density *see* Glass compactness

atomic scale heating 2:431

atomic switch/nano-ionics circuits 3:34–36

atomistic MD simulations, salient features of 1:483–484

atom ensembles 1:484

 classical and Ab initio calculations 1:483–484

ATZ *see* alumina-toughened zirconia (ATZ)

Auger electron spectroscopy (AES) 1:517

auger/screw extrusion 1:162–163

Aurivillius compounds 3:454

autografts 3:473–474, 3:647

automated diffraction tomography (ADT) 1:619, 1:618–619, 1:623–624, 1:623, 1:620*f*, 1:623*f*

Auxiliary Power Units (APUs) 3:57

average relaxation time 2:451

Avrami coefficient 2:459, 2:459*t*

A/W Cerabone glass-ceramic 3:740

A/W system *see* apatite-wollastonite (A/W) system

a-ZIFs *see* amorphous ZIFs (a-ZIFs)

B

B3B test *see* ball-on-three-balls (B3B) test

BA *see* bond angle (BA)

bactericides 1:107

BADs *see* bond-angle distributions (BADs)

BA-LIFT *see* Blaser Assisted Laser Induced Forward Transfer (BA-LIFT)

ball-on-ring (BOR) test 1:815–816

ball-on-three-balls (B3B) test 1:770

 for subcritical crack growth (SCCG) 1:815–816

BaO-SiO₂ system 2:473–474

barium calcium aluminosilicate (BCAS) 3:56–57

barium calcium magnesium aluminosilicate (BCMAS) 3:56–57

barium-magnesium-aluminum silicate (BMAS) 2:294

barium oxide (BaO) 2:655

barium strontium aluminosilicates (BSAS) 2:442

barium titanate 3:361–362

barium titanate-based ceramics 3:311

 crystal structure, nonstoichiometry and defect chemistry of 3:311–314

dielectric properties 3:322–326

 BaTiO₃-BaMO₃ solid solutions 3:325–326

 BaTiO₃-Bi(M)O₃ solid solutions 3:326–327

 dielectrics for energy storage 3:330

 microstructure control: core-shell grains 3:327–330

 phase transition engineering 3:323–326

 tunable dielectrics 3:330–331

foreign ions, incorporation of 3:315–317

homovalent substitution 3:320–321

 BaTiO₃-BaMO₃ solid solutions 3:321–322

 BaTiO₃-MTiO₃ solid solutions 3:320–321

piezoelectric properties 3:331–334

rare-earth ions, incorporation of 3:319–320

 incorporation site 3:320

size and scaling effects 3:334–338

transition metal ions, incorporation of 3:317–318

 dipolar defects, formation of 3:318–319

- barium titanate-based ceramics (*continued*)
 - stabilization of the hexagonal modification 3:317–318
 - valence state of transition metal ions in perovskite lattice 3:318
- basic multicellular unit (BMU) 3:803
- BaTiO₃-based ceramics 3:3–4
- Bauchy's potential 2:528
- Bayer process 2:32
- BCAS *see* barium calcium aluminosilicate (BCAS)
- BCMAS *see* barium calcium magnesium aluminosilicate (BCMAS)
- BCN *see* boron carbonitride (BCN)
- BCP *see* biphasic calcium phosphate (BCP)
- BDDGE *see* 1,4-butanediol diglycidyl ether (BDDGE)
- bend contours and thickness fringes 1:589
- bending losses 2:685–686
- beryllia 1:414
- beryllium silicate glasses 2:473
- beta-tricalcium phosphate (β -TCP) 3:608–609
- BGO 3:105
- BGs *see* bioactive glasses (BGs)
- BHJ *see* bulk heterojunction (BHJ)
- biaxial bending 1:756–757
- binary and ultraphosphate glasses 2:582–583
- binary oxides 1:414
 - beryllia 1:414
 - magnesia 1:414
 - zirconia 1:414–415
- binder(s) 1:190, 1:106
 - and plasticizers 1:106
- binder jetting (BJ) process 1:387–388, 1:109, 3:668–669, 1:208–209
 - applications 3:668–669
 - monolithic components 1:208
 - porous components 1:208
- binding liquid and paste characteristics 1:170
- bioactive and biodegradable polymer-based composites 3:674–675
 - bioactive ceramic phases 3:675–676
 - bioactive glasses 3:678–679
 - calcium phosphates 3:675–676
 - biodegradable polymer matrices 3:682–683
 - natural polymers 3:684–685
 - synthetic polymers 3:682–683
- current challenges 3:692–694
 - advantage of nanocomposites 3:694–695
 - properties of 3:692–694
- properties of 3:692–694
- scaffold fabrication techniques and state of the art 3:687–689
 - additive manufacturing (AM) 3:691–692
 - electrospinning 3:690–691
 - melt electrospinning writing 3:692
 - microsphere sintering 3:689
 - particulate leaching (PL) 3:689
 - solvent casting (SC) 3:689
 - supercritical CO₂ foaming 3:690
 - thermally induced phase separation (TIPS) 3:689–690
- bioactive bioceramics 3:650, 3:476–477
 - biphasic calcium phosphate (BCP) 3:478
 - calcium phosphate 3:476–477
 - calcium sulfate 3:479
 - CaP cements 3:479
 - doped CaP 3:478–479
 - hydroxyapatite (HA) 3:477–478
 - tricalcium phosphate (TCP) 3:478
- bioactive ceramic phases 3:675–676
- bioactive glasses 3:678–679
 - borate bioactive glasses 3:680
 - general characteristics 3:678–679
 - phosphate bioactive glasses 3:680–681
 - silicate bioactive glasses 3:679–680
- calcium phosphates 3:675–676
 - general characteristics 3:676
 - hydroxyapatite 3:676–677
 - tricalcium phosphates 3:677–678
- bioactive glass-ceramics for implant and bone tissue regeneration 2:716–717
- bioactive glasses (BGs) 3:678–679, 3:674, 3:675
 - based products and clinical applications 3:618–621
 - borate bioactive glasses 3:680
 - characteristics 3:678–679
 - doping elements, biological role of 3:618
 - genesis of 3:614–615
 - phosphate bioactive glasses 3:680–681
 - production processes and types of 3:615–616
 - melt-derived bioactive glasses 3:615–616
 - sol-gel bioactive glasses and hierarchical materials 3:617–618
 - silicate bioactive glasses 3:679–680
- bioactive glass powder 3:621
- bioactive phosphate glasses 2:583
- bioceramics 3:476, 3:458
 - bioactive bioceramics 3:476–477
 - biphasic calcium phosphate (BCP) 3:478
 - calcium phosphate 3:476–477
 - calcium sulfate 3:479
 - CaP cements 3:479
 - doped CaP 3:478–479
 - hydroxyapatite (HA) 3:477–478
 - tricalcium phosphate (TCP) 3:478
 - inert bioceramics 3:476
 - in organic-inorganic composites 3:650
- bioceramics, in regenerative medicine 3:601
 - future perspectives 3:610
 - methods for bioceramic synthesis 3:602–603
 - additive manufacturing of bioceramic scaffolds 3:608–609
 - bioactive nanoparticles 3:602–603
 - biomimetic functionalization of bioceramics, approaches for 3:603–605
 - injectable bioceramic pastes and cements 3:606–608
 - 3-D forming technologies 3:605–606
 - preclinical and clinical testing of bioceramics 3:609–610
- requirements for regenerative bioceramics 3:601–602
- bioceramics, mechanical properties of 3:772
 - cyclic fatigue 3:779–782
 - low temperature degradation 3:782–783
 - mechanical behavior 3:772
 - elastic behavior 3:772
 - hardness 3:772
 - mechanical strength 3:772–773
 - toughness 3:773–774
- microstructural toughening 3:774
 - grain (crack) bridging 3:774
 - transformation toughening 3:774–775
- subcritical crack growth 3:776–779
- zirconia-toughened ceramics (ZTC), mechanical properties of 3:775–776
- bioceramics, surface treatment of 3:701
 - chemical modifications 3:709
 - biofunctionalization 3:711
 - coating 3:709–711
 - self-assembly 3:711–713
 - ultraviolet light treatment 3:709
 - influential surface properties for biocompatibility 3:701
 - surface charge 3:701–702
 - surface chemistry 3:703–704
 - surface energy 3:701
 - surface topography 3:702–703
 - wettability 3:702
- physical modifications 3:704
 - chemical etching 3:705–706
 - laser treatment 3:708–709
 - machining and grinding 3:704
 - polishing 3:706–708
 - sandblasting 3:704–705
 - surface modification techniques 3:704
 - surface treatment perspectives 3:713–714
- bioceramics' biological characterization, in vitro cell culture models for 3:799–801
 - bone remodeling, immune cells involved in 3:806
 - bone remodeling cycle 3:803–806
 - co-culture models of osteoblastic and osteoclastic cells 3:804–806
 - multi-culture models 3:806
 - osteoblast and bone formation 3:800–801
 - osteoblastic cell cultures 3:801
 - osteoclasts and bone resorption 3:801–803
 - osteoclastic cell cultures 3:802–803
- bioceramics' biological characterization, in vivo models for 3:806–807
 - animal species 3:807
 - dogs 3:808
 - non-human primates (NHPs) 3:809
 - pigs 3:808
 - rabbits 3:807–808
 - rodent models 3:807
 - sheep and goat 3:808–809
 - ectopic bone formation, models of 3:809
 - intramuscular implantation 3:809–810
 - kidney capsule implantation 3:810
 - subcutaneous implantation 3:809
 - orthotopic bone formation, models of 3:810–812

- calvarial/mandibular bone defects 3:810–812
 segmental bone defects 3:812–813
 biocompatibility 3:473
 biodegradable polymer matrices 3:682–683
 natural polymers 3:684–685
 polyhydroxyalkanoates (PHA) 3:687
 polypeptides 3:684–685
 polysaccharides 3:685–687
 synthetic polymers 3:682–683
 biodegradable polyurethanes 3:683–684
 polypropylene fumarate (PPF) 3:683
 saturated poly- α -hydroxy esters 3:682–683
 biodegradable polymers 3:674
 biodegradable polyurethanes 3:683–684
 biofunctionalization 3:711
 bioglasses 3:479–480, 3:738–739
 bioinert bioceramics 3:649–650
 bio-inert ceramics
 current developments on 3:497–499
 new progresses on 3:494–495
 from alumina to plastic alumina-zirconia composites 3:494–495
 improved testing methods 3:497
 new implant designs 3:496
 towards pseudo-plastic ceramics 3:495–496
 biomedical grade 3Y-TZP 3:822
 biomedicine, phosphate glasses in 2:583
 biomineralization process 3:761
 biomolecular systems 1:465–466
 bio-inspired cements 1:467–468
 complex biomolecules 1:465–466
 interfaces of biomolecules and inorganic crystals 1:466–467
 biomolecules, immobilization of 3:722–723
 bioplotting 3:691–692
 bioprinting 3:654, 3:488–489
 4-D-Bioprinting 3:609
 bioreactive glasses 3:458
 bioresorbable bioceramics 3:650
 Bioverit implants 3:740
 biphasic calcium phosphate (BCP) 3:478, 3:572–573, 1:214–215, 3:586–588, 3:597, 3:676, 3:669
 bismuth, glasses based on 2:605
 bismuth chloride, glasses based on 2:598
 bismuth tribromide, glasses based on 2:600
 BJ process *see* binder jetting (BJ) process
 BL *see* bond length (BL)
 blade gap 1:191
 blade height 1:191
 Blaser Assited Laser Induced Forward Transfer (BA-LIFT) 3:598
 blue fired brown corundum 2:409–410
 BMAS *see* barium-magnesium-aluminum silicate (BMAS)
 BMH pair-wise potentials *see* Born-Mayer-Huggins (BMH) pair-wise potentials
 BMPs *see* bone morphogenetic proteins (BMPs)
 BMU *see* basic multicellular unit (BMU)
 BN *see* boron nitride (BN)
 BO *see* bridging oxygens (BO)
 Boltzmann distribution 3:133
 bond angle (BA) 1:454
 bond-angle distributions (BADs) 1:488
 bonded ferrites 3:214
 magnetic properties 3:214–215
 manufacturing process 3:214
 bonding and sealing, glass-ceramics for 2:713–715
 glass-ceramic-to-metal bonding 2:713–715
 joining for SiC-based materials 2:715–716
 sealants in solid oxide fuel cells 2:715
 bond length (BL) 1:454
 bond order (BO) values 1:442
 bone
 in ageing and disease 3:465–466
 bone hierarchical organization 3:461–462
 collagen 3:459
 composition 3:459
 fracture behavior 3:464–465
 mechanical behavior at tissue level in 3:463–464
 mechanical behavior of 3:462
 mineral 3:459–460
 natural and synthetic biomaterials that mimic 3:466–467
 non-collagenous proteins and cells 3:460–461
 as a remarkably strong and adaptive material 3:465
 structural mechanical behavior of 3:462–463
 bone cells, stimulating 3:718–719
 bone morphogenetic proteins (BMPs) 3:657, 3:474, 3:718
 bone regeneration with ceramics scaffold 3:646
 bone composition, structure, and mechanical properties 3:646
 bone implant materials 3:646–647
 alloplastic graft 3:647–648
 autograft 3:647
 scaffolds 3:647–648
 xenograft 3:647
 ceramics materials 3:648–650
 bioactive bioceramics 3:650
 bioceramics in organic-inorganic composites 3:650
 bioinert bioceramics 3:649–650
 bioresorbable bioceramics 3:650
 future directions 3:658–659
 scaffolds processing techniques 3:650–651
 additive manufacturing (AM) 3:651–654, 3:655t
 bioprinting 3:654
 conventional techniques 3:650–651
 extrusion based methods 3:654
 inkjet 3D printing 3:654
 powder bed-based methods 3:654
 stereolithography 3:652
 scaffolds which introduce stimulus 3:658
 scaffolds with particles 3:655–656
 scaffolds with therapeutics 3:656–657
 drug release scaffolds 3:657
 gene therapy 3:658
 growth factors 3:657
 hormones 3:657–658
 scaffolds with living cells 3:658
 scaffolds with polymers 3:658
 bone remodeling, immune cells involved in 3:806
 bone remodeling cycle 3:803–806
 multi-culture models 3:806
 osteoblastic and osteoclastic cells, co-culture models of 3:804–806
 bone replacement, substitutes for 3:473
 implants physical shape 3:482
 cements 3:482–483
 granules 3:482
 putties 3:483
 scaffolds manufacturing 3:484–485
 material composition 3:473–474
 comparison natural synthetic 3:481–482
 natural origin 3:473–474
 synthetic origin 3:476
 materials functionalization and drug delivery systems 3:489–491
 Bone Source 3:642
 bone tissue-biomaterial interaction 3:798–799
 bone tissue engineering
 customized bone graft substitutes and scaffolds for 3:664–666
 binder jetting 3:668–669
 material extrusion 3:667–668
 powder bed fusion 3:666–667
 vat polymerization 3:664–666
 mathematical models used in 3:750–751
 bone tissue systems biology approaches 3:752–753
 bone void filler applications 3:641
 premixed formulations 3:641
 borate and phosphate glasses 1:533–534
 borate bioactive glasses 3:680
 borate glasses 2:749
 borates 1:494–495
 boria (B_2O_3)-forming ceramics 2:442
 boride HTCCs (high temperature co-fired ceramic substrates) 3:443
 Born-Mayer-Huggins (BMH) pair-wise potentials 2:527
 borosilicate glass-ceramic materials 2:752
 borocarbides
 interplay between superconductivity and magnetism in $HoNi_2B_2C$ 3:167–170
 antiferromagnetic order in $HoNi_2B_2C$ 3:167–170
 multiband coexistence of superconductivity and magnetism in $HoNi_2B_2C$ 3:171–172
 reentrant and near-reentrant behavior 3:170–171
 non-magnetic borocarbides
 fermi surface in 3:164–166
 upper critical field for 3:166–167
 superconducting gap, symmetry of 3:163–164
 superconductivity and magnetism in 3:162–163
 boron carbide materials 2:421
 boron carbonitride (BCN) 1:22–23

- boron fibers 2:304, 2:309
 boron nitride (BN) 1:22–23
 boron trioxide 2:655
 borosilicate glasses 2:654–655, 2:534, 2:537, 2:535, 2:519, 2:520*t*, 2:656
 applications 2:532–533, 2:534*f*
 general aspects 2:532–533
 glass fibers and wools for insulation and reinforcement 2:534–535
 lighting, optics and display 2:535
 nuclear waste disposal 2:535–537
 thermal shock and chemical resistant glass vessels and containers 2:533–534
 biomedical and other applications 2:537
 characterizations 2:519–521
 boron anomaly 2:521–522
 cooling rate and temperature effect 2:522–523
 pressure effect 2:523–524
 short- and medium-range order structure 2:519–521
 structural heterogeneity and thermodynamic behaviors 2:524–526
 molecular dynamics (MD) simulations 2:526–527
 background 2:526–527
 boroxol rings and larger structural features 2:529
 development of empirical potentials for 2:527–528
 effect of cooling rate and system size on simulated glass structure and properties 2:528
 NMR spectra from 2:529
 short and medium range structure information 2:528–529
 physical properties, prediction of 2:529–531
 MD simulations, prediction from 2:531–532
 rigidity theory, prediction by 2:529–531
 borosilicates 1:494–495
 boroxol rings and larger structural features 2:529
 BOR test *see* ball-on-ring (BOR) test
 BO values *see* bond order (BO) values
 bovine spongiform encephalopathy (BSE) 3:475–476
 BPTT *see* brittle-to-plastic transition temperature (BPTT)
 Bragg angle 1:555
 Bragg's law 1:561, 1:592
 Brazilian test 1:754–755
 brazing of ceramics 2:402–403
 bridging oxygens (BO) 2:462, 2:454–455, 1:481, 2:484
 bridging stresses, determination of 1:786–789
 calculation of bridging stresses from experimental crack profiles 1:789–790
 multi-cutting compliance technique 1:789
 post-fracture tensile (PFT) test 1:789
 Raman and fluorescent spectroscopy, bridging stresses from 1:790
 Vickers cracks, calculation of bridges stresses from of COD in 1:790–791
 Bridgman method 2:216–218
 brittle compounds 1:913–914
 brittle-to-plastic transition temperature (BPTT) 2:194–195
 broadband transmission optical fibers 2:616–617
 broken ergodicity 2:454
 bromide glasses 2:598–600
 bismuth tribromide, glasses based on 2:600
 cadmium bromide, glasses based on 2:600
 ditellurium bromide glasses 2:600
 gallium(III) bromide, glasses based on 2:600
 lead(II) bromide, glasses based on 2:600
 zinc bromide, glasses based on 2:600
 bromides 1:420
 brushite cements 3:637–638
 factors affecting the setting reaction, paste stability and injectability 3:638
 Ca/P molar ratio 3:638
 mechanical injection device 3:639
 particle size 3:639–640
 pH and temperature 3:639
 powder/liquid ratio 3:638–639
 use of additives 3:638
 mechanical properties 3:640–641
 setting rate/reaction rate 3:637–638
 BSAS *see* barium strontium aluminosilicates (BSAS)
 BSE *see* bovine spongiform encephalopathy (BSE)
 bulk-active SMOX 3:131–132
 bulk heterojunction (BHJ) 3:12–13
 bulk lattice diffusion 1:237
 bulk liquid phase, chemistry in 1:27–28
 precipitation 1:30–31
 advantages, issues, applications 1:31
 process, overview of 1:30–31
 sol-gel synthesis 1:27–28
 advantages, issues, applications 1:28–30
 process, overview of 1:27–28
 bulk modulus 1:443
 bulk pyroelectric materials 3:142–144
 devices 3:144–145
 dielectric bolometer materials 3:144
 intrinsic pyroelectrics 3:142–144
 1,4-butanediol diglycidyl ether (BDDGE) 3:762–763
 Butler-Volmer equation 3:129
 Butterworth–van Dyke (BVD) model 3:232
 BVD model *see* Butterworth–van Dyke (BVD) model
- C**
- CAC *see* citric acid cycle (CAC)
 CACS *see* chemically assisted combustion synthesis (CACS)
 CAD *see* computer aided design (CAD)
 CAD-CAM systems *see* Computer-aided design/computer-aided manufacturing (CAD-CAM) systems
 cadmium, glasses based on 2:605
 cadmium bromide, glasses based on 2:600
 cadmium chloride, glasses based on 2:598
 cadmium iodide, glasses based on 2:601
 CA glasses *see* calcium aluminate (CA) glasses
 calcination and phase transformations 1:83
 decomposition reactions 1:83–86
 epitaxy 1:89–90
 phase separation 1:90–91
 seeding of ceramic reactions 1:88–89
 seeding strategy 1:90
 solid-state reactions 1:86–87
 transformation kinetics, analysis of 1:87–88
 calcium aluminate (CA) glasses 2:502, 2:502–503
 calcium deficient hydroxyapatite (CDHA) 3:626
 calcium fluoride 1:420, 3:119–120
 calcium oxide 2:655
 calcium phosphate 3:675–676, 3:595, 3:701, 3:601, 3:603, 3:675, 3:476, 3:646, 1:160, 3:476–477
 cements 3:479
 in the field of biomaterials 3:595–596
 general characteristics 3:676
 hydroxyapatite 3:676–677
 processing 3:597–598
 properties and applications 3:598–599
 synthesis 3:596–597
 tricalcium phosphates 3:677–678
 calcium phosphate based bioceramics (CPC) 3:737–738
 chemical functionalization routes of 3:719
 calcium phosphate bioceramic surfaces, chemical functionalization of 3:716
 biological activity of CPC functionalized 3:723
 biological events, molecules to stimulate 3:716–718
 adhesive proteins from ECM and derivatives 3:717–718
 bone cells, stimulating 3:718–719
 calcium phosphate based bioceramics (CPC), chemical functionalization routes of 3:719
 covalent immobilization, functionalization by 3:721–722
 biomolecules, immobilization of 3:722–723
 silanization 3:721–722
 cytokines, growth factors and 3:718
 endothelial cells, stimulating 3:719
in vitro evaluation 3:723–725
in vivo osteogenic and osteointegrative properties 3:725–726
 osteoimmunomodulation (OIM) 3:719, 3:726, 3:726–727
 substrate/protein interactions 3:719–721
 calcium phosphate cements (CPCs) 3:624, 3:632–634, 3:572–573, 3:606, 3:607*f*, 3:608*f*
 apatite and DCPD forming 3:636–637
 biodegradation/bioresorption of 3:633–634
 bone void filler applications 3:641
 premixed formulations 3:641

- brushite (DCPD) cements 3:637–638
 Ca/P molar ratio 3:638
 mechanical injection device 3:639
 mechanical properties 3:640–641
 particle size 3:639–640
 pH and temperature 3:639
 powder/liquid ratio 3:638–639
 setting rate/reaction rate 3:637–638
 use of additives 3:638
 chemistry of setting in 3:637
 critical assessment of current literature on 3:643
 characterization 3:643
 compressive strength 3:643
 immersion media 3:643
 existing products 3:641–642
 Bone Source 3:642
 drawbacks of 3:642–643
 HydroSet 3:642
 Mimix Bone Void Filler 3:642
 Norian CRS Bone Cement 3:641–642
 hydroxyapatite cement 3:637
 solubility of calcium phosphates in 3:634–636
 X-ray diffraction dicalcium phosphate dihydrate 3:631–632
 in vivo use of calcium phosphates 3:631–632
 calcium phosphate materials, suspension spraying of 3:745–746
 calcium phosphate salts 3:624–628
 dicalcium phosphate dihydrate (DCPD) 3:630
 NMR spectroscopy of 3:631
 hydroxyapatite 3:627–628
 NMR spectroscopy of 3:628
 X-ray diffraction of 3:628
 octacalcium phosphate (OCP) 3:628–629
 NMR spectroscopy of 3:629
 structure 3:630–631
 X-ray diffraction 3:629–630
 calcium silicate hydrate (C-S-H) cement crystals 1:445–446
 calcium sulfate 3:476, 3:479, 3:691–692
 calculation of phase diagram (CALPHAD) methodology 1:499–501, 1:498, 1:499, 1:439
 brief history of 1:498–499
 calculation software packages 1:508–509
 equilibrium and phase diagram, calculation of 1:508
 experimental data and ab initio calculation 1:500–501
 extrapolation of Gibbs energy to higher order systems 1:507–508
 optimization of parameters 1:507
 thermodynamic assessment of binary $\text{CaO-P}_2\text{O}_5$ system 1:509–511
 of $\text{ZrO}_2\text{-CaO-MgO}$ ternary system 1:511–514
 thermodynamic modeling 1:501
 associate species solution models 1:503–504
 compositional dependence of Gibbs free energy of multicomponent solution phases 1:502–503
 for ceramic systems 1:503
 ionic two-sublattice models for ionic liquids 1:505–507
 modified quasichemical model 1:504–505
 pressure dependence of Gibbs free energy 1:501–502
 random substitutional models 1:503
 sublattice models 1:505
 temperature dependence of Gibbs free energy 1:501
 calendring 1:139–140
 calorimetric glass transition 2:454
 CALPHAD methodology *see* calculation of phase diagram (CALPHAD) methodology
 Cambridge Crystallographic Data Center (CCDC) 1:441–442, 1:477
 cancellous 3:646
 cancellous allografts 3:474
 cantilever based piezoelectric energy harvester 3:407–409
 CaO-SiO_2 system 2:472–473
 capacitor discharge sintering (CDS) 1:291
 carbide HTCCs (high temperature co-fired ceramic substrates) 3:442–443
 carbides 1:410–412, 1:443–444
 diamond 1:411–412
 silicon carbide (SiC) 1:412–413
 carbonate and nitrate glasses 1:532–533
 Carbon Fiber Composite (CFC) heaters 1:274
 carbon fiber reinforced plastic (CFRP) composite 2:265
 carbon fiber reinforced polyetheretherketone (CFR-PEEK) 3:537
 carbon fibers 3:537, 2:304, 2:310–312, 2:311
 carbon in biomedical engineering 3:533
 applications
 carbon fibers 3:537
 cardiovascular applications 3:534–535
 hand and wrist implants 3:535–536
 orthopedic applications 3:535–536
 shoulder implants 3:536–537
 pyrolytic carbon
 biocompatibility of 3:534
 fabrication of 3:533
 mechanical properties of 3:533–534
 structure of 3:533
 carbon-matrix composites 2:353
 composite materials 2:353
 electromagnetic shielding effectiveness of 2:357–358
 fabrication of 2:355
 high-temperature resistance of 2:355–356
 mechanical behavior of 2:356
 multiscale 2:356–357
 reinforcement in 2:353–354
 self-monitoring 2:357
 self-powering 2:357
 thermal conductivity of 2:358
 carbon nanotube-reinforced ceramic composites 2:233–237
 carbon nanotubes (CNTs) 2:243, 1:903–904, 2:244–245, 2:245f, 3:682
 mechanical properties of CNTs- and graphene-containing ceramic matrix composites 2:252–255
 reinforced ceramic composites 1:903
 structure of CNTs- and graphene-containing ceramic matrix composites 2:249–252
 carborundum *see* silicon carbide (SiC)
 carcinogenesis 3:516
 Car-Parrinello MD (CPMD) simulations 1:484
 CAS *see* Covalent Amorphous Semiconductors (CAS)
 CaSR *see* cation-sensing receptor (CaSR)
 catalysts 2:380–381
 catalytic combustion gas sensors 3:126–127
 cathode 3:54–55
 cathode thin films, pulsed laser deposition (PLD) of 3:63–64
 cation field strength (CFS) 1:488, 2:455
 cation-sensing receptor (CaSR) 3:602–603
 cavitation 2:115
 c-axis-grown wafer material 3:95–96
 CBED *see* convergent beam electron diffraction (CBED)
 c-BN *see* cubic boron nitride (c-BN)
 CCC *see* critical cation concentration (CCC); critical coagulation concentration (CCC)
 CCDC *see* Cambridge Crystallographic Data Center (CCDC)
 CCR *see* critical cooling rates (CCR)
 CCRN model *see* Compensated Continuous Random Network (CCRN) model
 CDG *see* coral derived granules (CDG)
 CDHA *see* calcium deficient hydroxyapatite (CDHA)
 CDS *see* capacitor discharge sintering (CDS)
 cellular base stations, filters in 3:380
 cellular ceramics 1:346–348, 1:343–344
 cellulose 3:686
 celsian 2:55–56
 cement 1:445–446, 3:482–483
 Cemfil 2:679
 centrifugal casting 1:150
 ceramic based PENGs 3:409–412
 ceramic-based piezoelectric materials 3:394–396
 ceramic capacitors 3:386–387
 multilayer 3:387–389
 single-layer 3:386–387
 ceramic/carbon nanostructure composites 1:733
 contact damage resistance of 1:733–735
 friction and wear mechanisms in 1:738–741
 nanotubes/graphene 1:741–743
 tribological response of 1:735–738
 ceramic-ceramic diffusion bonding 2:395–396
 ceramic injection molding (CIM) 2:33, 2:271
 binder systems and debinding concepts 1:180–181
 feedstock and feedstock preparation, necessity of 1:179–180, 1:180f
 future process variants 1:184–185

- ceramic injection molding (CIM) (*continued*)
 hybridization of forming processes
 1:185
 materials and applications, examples of
 1:185
 micro in-mold labeling (MicroIML)
 1:185
 variothermal temperature control 1:185
 historical background 1:179
 initial powder 1:179
 injection molding process 1:181–183,
 1:181f
 processing chain 1:179, 1:179f
 process variants 1:183
 low-pressure injection molding (LP-
 CIM) 1:183
 micro ceramic injection molding
 (MicroCIM) 1:183–184
 ceramic magnetic materials 3:2–3
 ferrite ceramics at microwave frequencies
 3:3
 ferrite magnets 3:3
 ceramic materials 1:388–390
 see also total bond order density (TBOD)
 ceramic matrix composites (CMCs) 2:342,
 2:349, 2:758, 2:20–21, 2:22,
 2:246–248, 2:225, 2:317, 2:319f,
 2:277, 2:359, 2:360, 2:363–364,
 2:367, 2:369, 2:377, 1:733
 definition 2:317
 electrical conductivity of 2:256–257
 fibrous reinforcement 2:317–318
 manufacturing 2:323–324
 choice of manufacturing process with
 respect to required properties
 2:323–324
 gaseous route, fabrication by 2:324–326
 hybrid processing route or the use of the
 MI/RMI process 2:331–333
 liquid/semi-liquid route infiltration,
 fabrication by 2:326–329
 mechanical behavior 2:318
 definition of an interphase 2:318–319
 fiber/matrix interfacial shear stress
 2:322–323
 mechanical behavior under tensile
 loading 2:319–322
 non-linear behavior, origin of 2:318
 properties of constituents 2:318
 preparation of carbon nanotubes- and
 graphene-containing CMCs
 2:248–249
 with reinforcing phase 2:246–248
 tribological properties of 2:255–256
 ceramic matrix composites with roughly
 equiaxed reinforcements 2:227
 carbon nanotube-reinforced ceramic
 composites 2:233–237
 graphene-reinforced ceramic composites
 2:237–238
 particle- and platelet-reinforced
 composites 2:231–232
 reinforcement mechanisms in ceramics
 2:227
 crack bridging 2:227–228
 crack deflection 2:227
 microcracking 2:227
 transformation toughening 2:227
 whisker reinforcement 2:228
 whisker composites, properties of
 2:230–231
 creep behavior 2:231
 SiC(W) 2:230–231, 2:231
 zirconia-toughened composites,
 mechanical properties of 2:228–229
 creep and fatigue behaviors of zirconia-
 toughened composites 2:230
 effect of size and amount of zirconia
 particles on toughening 2:228–229
 effect of solute content and temperature
 2:229–230
 ceramic-metal diffusion bonding 2:396
 ceramic nanocomposites *see* Al₂O₃-SiC
 nanocomposites
 ceramic on-demand extrusion (CODE)
 1:389
 ceramic oxide fibers 2:316
 ceramic powders
 characterization of 1:517
 current static measures 1:517–519
 granular and powder batch flowability
 1:519–524
 powder batch permeability and
 compressibility 1:524–528
 low energy fabrication routes to
 1:433–435
 ceramics
 applications 1:822
 constrained transformation 1:818
 toughening mechanism 1:818–819
 transformation-toughened ceramics,
 microstructures and properties of
 1:819–821
 transformation toughening, theoretical
 understanding of 1:821–822
 ceramic sensors 3:2
 for industrial applications 3:2
 pyroelectric crystals, ceramics, and thin
 films for IR sensors 3:2
 ceramic sintering 3:226–228
 ceramic steel 3:514
 ceramic thermal control coatings for
 satellites 2:364–365
 ceramization 2:729
 Ceravital 2:716–717, 3:740
 ceria-tetragonal zirconia polycrystal (9Ce-
 TZP) 1:849
 cerium- and terbium-doped rare-earth
 silicon oxynitrides 3:84–85
 rare-earth-doped sialon materials 3:84–85
 cetyl trimethylammonium bromide (CTAB)
 1:9
 CFC heaters *see* Carbon Fiber Composite
 (CFC) heaters
 CFD programs *see* Computational Fluid
 Dynamics (CFD) programs
 CFF values *see* Compressive Fracture Force
 (CFF) values
 CFRP composite *see* carbon fiber reinforced
 plastic (CFRP) composite
 CFR-PEEK *see* carbon fiber reinforced
 polyetheretherketone (CFR-PEEK)
- CFS *see* cation field strength (CFS)
 chalcogenide crystals 1:446–450
 chalcogenide glasses (ChGs) 2:540–541,
 1:531–532, 2:445, 2:454
 for bulk media and fibers 2:541
 crystallization stability and
 compositional trends 2:541–543
 processing characteristics 2:541
 viscosity and temperature dependence
 2:543–545
 low-loss waveguides 2:547–548
 novel optical function and gradient
 properties 2:545–546
 bulk GRIN materials 2:546
 GRIN via spatially controlled nucleation
 and growth 2:545–546
 planar GRIN materials 2:546–547
 optical nonlinearity 2:548–550
 MWIR and LWIR supercontinuum
 generation 2:550–552
 nonlinear optical property
 measurements 2:548–550
 chalcogenides 1:419
 sulfides/selenides 1:419
 characterization of ceramics and glasses
 1:439, 1:439–440, 1:440
 charge-balanced SiO₂-MAl₂O₄ glasses 1:532
 charge compensator 2:462
 charge injection depth 3:401–402
 charge transfer (CT) 3:90, 3:91, 3:91f
 charge transfer band 2:654
 chemical bond 2:757
 chemical diffusion coefficient 3:23
 chemical etching 3:705–706, 1:647–648
 chemically assisted combustion synthesis
 (CACS) 1:54
 chemical processing 2:314, 3:452
 chemical solution deposition (CSD)
 3:145–146
 chemical strengthening 2:633–636
 ion-exchange, stress generation by
 2:636–639
 salt and glass, kinetics of the chemical
 reaction between 2:634–636
 chemical tempering methods 2:639–640
 molten salt-free chemical strengthening
 2:641–644
 electric field-assisted ion-exchange (EF-
 IE) 2:642–644
 engineered stress profiles 2:644
 using molten salt 2:639–640
 glass composition 2:639–640
 salt bath composition and impurities
 2:640–641
 temperature and time 2:640
 chemical vapor deposition (CVD) 2:357,
 1:419, 2:64, 2:80, 2:304, 2:245–246,
 2:155, 2:341, 2:146
 properties of ceramic fibers produced by
 2:310t
 SiC fiber made by 2:310f
 chemical vapor infiltration (CVI)
 2:324–326, 2:368
 chemo-mechanical polishing (CMP)
 approach 1:646
 chemoresistive gas sensors 3:130–131

- Cherns-Preston rules 1:596
 Chevron-Notched beam (CNB) method 1:766–767
 Chinese Script (CS) microstructure 2:216
 chitosan 1:109–110, 3:685–686
 chloride glasses 2:597–598
 bismuth chloride, glasses based on 2:598
 cadmium chloride, glasses based on 2:598
 lead(II) chloride, glasses based on 2:598
 TeX glasses 2:598
 thorium(IV) chloride, glasses based on 2:598
 zinc chloride, glasses based on 2:598
 chlorides 1:420
 chromatic dispersion 2:684
 chromium 2:771
 CIDP *see* coupled interface dissolution-precipitation model (CIDP)
 CIJ *see* continuous inkjet printing (CIJ)
 CIM *see* ceramic injection molding (CIM)
 CIPed blanks 3:562
 citric acid cycle (CAC) 3:682–683
 CK *see* cytokines (CK)
 Clausius-Mosotti equation 2:663
 clays 1:106
 cleaning 1:638
 CMCs *see* ceramic matrix composites (CMCs)
 CMEQ method *see* cycles for maximized energy output (CMEQ) method
 CMOS *see* complementary metal-oxide-semiconductor (CMOS)
 CMP approach *see* chemo-mechanical polishing (CMP) approach
 CMR *see* creep mismatch ratio (CMR)
 CN *see* coordination number (CN)
 CNB method *see* Chevron-Notched beam (CNB) method
 CNC machining *see* computer numerical control (CNC) machining
 CNTs *see* carbon nanotubes (CNTs)
 coal fly ash 2:723
 coating 3:709–711
 coating materials 1:420
 coaxial transmission line method 3:201, 3:202f
 Cobalt-Phosphate (Co-Pi) 3:571
 Coble creep 2:448
 CODE *see* ceramic on-demand extrusion (CODE)
 coefficient of friction (COF) 2:426
 coefficient of thermal expansion (CTE) 2:356, 3:53, 3:53–54, 3:54t, 2:540, 2:731, 2:191, 3:788–791, 2:254–255, 1:184, 2:521–522, 2:652
 measurement of 1:685–687
 co-extrusion 1:175
 COF *see* coefficient of friction (COF)
 cold isostatic pressing 1:138
 cold mounting 1:640–641
 cold sintered/upside down/room temperature ceramic substrates (CSCC) 3:447–449
 cold sintering 1:247, 1:320
 cold sintering and hydrothermal sintering 1:311
 cold sintering and hydrothermal sintering, comparison between 1:321
 comparison between 1:321
 current challenges and future outlook 1:321–323
 aging of as-sintered ceramics 1:324
 modeling for a better understanding of the involved mechanisms 1:323–324
 socio-economic and environmental impact 1:322–323
 TRL (technological readiness level), increase of 1:324
 experimental set up, design of 1:311–312
 cold sintering 1:312
 experimental conditions, overview of 1:312
 hydrothermal sintering 1:312
 sintering mechanisms 1:312–314
 chemical effects 1:314–316
 different pathways towards densification under solvent-assisted sintering processes 1:316–318
 mechanical-chemical effects 1:313–314
 solvents, role of 1:318–320
 sintering of ceramics and composites 1:320
 cold sintering 1:320
 hydrothermal sintering 1:320–321
 cold sintering process (CSP) 1:311, 1:314t, 1:320t, 3:437
 colloidal granulation 1:108
 colloidal processing 2:385–386, 1:108
 colloidal sols 2:282–283
 colloid casting processes 1:146
 centrifugal casting 1:150
 gel casting 1:150–152, 1:151f
 pressure casting 1:148–149, 1:148f
 slip casting 1:146–148
 vacuum casting 1:149–150, 1:149f
 color coordinate 3:89
 columbite process 1:90–91
 commercial fibers 2:315–316
 commercial glass 2:654
 commercial off-the-shelf (COTS) electronics 2:359
 commercial tempering processes 2:630
 compaction modeling 1:142–144
 compaction techniques 1:138
 calendering 1:139–140
 isostatic pressing 1:138
 uniaxial pressing 1:138–139
 Compensated Continuous Random Network (CCRN) model 2:498
 complementary metal-oxide-semiconductor (CMOS) 3:234
 complex aluminosilicate glasses 2:510–511
 complex biomolecules 1:465–466
 complex oxides 1:416–417
 garnets 1:417
 pyrochlores 1:417
 spinel 1:416–417
 composite LTCC (low temperature co-fired ceramics substrates) 3:445–446
 composite preparation, starting materials for 2:244
 carbon nanotubes 2:244–245
 graphene, multilayered graphene (MLG) 2:245–246
 silicon nitride 2:244
 composites 3:480–481
 definition of 2:243–244
 composition modification 1:359–362
 dopant elements addition to modify grain boundary energy 1:361–362
 extra small particles addition at grain boundaries 1:362–363
 compression mounting *see* hot mounting
 Compressive Fracture Force (CFF) values 2:407
 compressive strength 3:643
 compressive surface layers 2:100
 Computational Fluid Dynamics (CFD) programs 1:172
 computer aided design (CAD) 3:691
 Computer-aided design/computer-aided manufacturing (CAD-CAM) systems 3:508
 computer numerical control (CNC) machining 1:216, 1:223
 concretes 1:445–446
 conducting oxides 1:418
 conductive ceramics 1:930
 congruent dissolution 2:650–651
 constant displacement rate method 1:801
 constant loading test 1:800
 contact flattening 1:259–261
 contactless optical dilatometers 2:728
 continuous inkjet printing (CIJ) 1:390
 continuous random network (CRN) model 2:486, 1:454–455
 Continuous Stiffness Measurement (CSM) mode 1:751
 continuum micromechanics, homogenization of mechanical properties based on 3:751–752
 contrast transfer function 1:597
 controllable interfaces method 1:307
 controlled rate sintering 1:353–354
 conventional lens making, challenge from 2:660–663
 conventional molds 1:149
 convergent beam electron diffraction (CBED) 1:618, 1:594–595, 1:595
 cooperatively rearranging regions (CRR) 2:452
 Cooper pairs 3:163, 3:151
 coordination number (CN) 2:502–503
 copolymers acting as dispersant and binder 1:107
 coral derived granules (CDG) 3:475
 cordierite 2:51–52, 2:54
 Corning's Pyrex 2:534
 corrosion 1:932–933
 corrosion media 1:933
 corrosion of glass 1:932
 classification schemes 1:932t
 kinetics of 1:934–936
 molecular mechanism in aqueous media 1:938–939
 parameters influencing 1:936–937
 characteristics of corrosion medium 1:937

- corrosion of glass (*continued*)
 conditions of corrosion process
 1:937–938
 structure, composition, and corrosion of
 glass 1:939
 system glass-liquid, thermodynamic
 equilibrium in 1:933–934
cortical allografts 3:474–475
corundum ceramics 1:927–929
 silicon carbide ceramics 1:929–930
 silicon nitride ceramics 1:929
 zirconium dioxide ceramics 1:928–929
COTS electronics *see* commercial off-the-
 shelf (COTS) electronics
Coulomb's law 2:663
coulometric gas sensors 3:130
coupled interface dissolution-precipitation
 model (CIDP) 2:782
Covalent Amorphous Semiconductors
 (CAS) 3:243
covalent immobilization 3:720–721
 functionalization by 3:721–722
 biomolecules, immobilization of
 3:722–723
 silanization 3:721–722
CPC *see* calcium phosphate based
 bioceramics (CPC); calcium
 phosphate cements (CPCs)
CPMD simulations *see* Car–Parrinello MD
 (CPMD) simulations
crack bridging 2:227–228
crack deflection 2:227
crack growth, microstructure and
 environmental effects on 1:762–763
crack growth law 1:797
crack growth mechanisms during cycling
 loading 1:847–849
crack growth rate 1:800
 constant displacement rate method 1:801
 constant loading test 1:800
 load relaxation test 1:800–801
crack propagation 1:823–824, 1:880–882
 microstructural effects during mixed-mode
 fracture 1:837–838
 mixed-mode fracture criteria 1:824–828
 empirical criterion 1:832–833
 energy-based criteria 1:829–830
 maximum tangential strain (MTSN)
 criterion 1:828–829
 maximum tangential stress criterion
 1:826–828
 testing in mixed-mode fracture 1:833–837
creep 2:448
creep behavior of ceramic matrix
 composites 1:901–902
 long fiber reinforced composites
 1:904–906
 nanocomposites 1:902–903
 particle reinforced composites 1:901–902
 whisker, carbon nanotube, and graphene
 reinforced composites 1:903–904
creep behavior of ceramics
 deformation maps 1:895–896
 monolithic ceramics, creep of 1:895
 phenomenological aspects 1:891
 superplasticity 1:896–899
 applications of superplasticity
 1:899–901
 future trends in superplastic ceramics
 1:901
 GBS accommodated by diffusional flow
 of point defects 1:897–899
 solution-precipitation model 1:899
creep behavior of SiAlON ceramics
 2:133–135
creep mechanisms 1:891–893
 diffusional creep 1:893
 grain boundary sliding 1:893–894
 recovery creep 1:891–893
creep mismatch ratio (CMR) 1:904
creep rate 1:908
critical cation concentration (CCC) 1:66
critical coagulation concentration (CCC) 1:159
critical cooling rates (CCR) 2:541–542
critical current density 3:152–153
critical defect 1:704
critical length 2:280–281
critical size defects (CSDs) 3:810, 3:810–811,
 3:811, 3:811–812, 3:812, 3:813
CRN model *see* continuous random
 network (CRN) model
CRR *see* cooperatively rearranging regions
 (CRR)
crystal, defined 2:448–449
crystal defects, contrast of 1:589–591
crystal growth 3:103
crystalline materials 2:463
crystalline silicon 3:8–9
crystalline solid electrolytes 3:38
crystalline zeolitic imidazolate frameworks
 (c-ZIFs) 1:459
crystallization 3:616, 2:455–456
 crystal growth 2:456–458
 crystal nucleation 2:455–456
 defined 2:449
 overall 2:458–459
crystallization of glasses
 crystal growth 1:681–682
 nucleation 1:682
crystallographic phases 2:94
crystallography 2:218–219
crystal structure and supercell models
 1:441–442
CSD *see* chemical solution deposition
 (CSD); critical size defects (CSDs)
C-S-H cement crystals *see* calcium silicate
 hydrate (C-S-H) cement crystals
CS microstructure *see* Chinese Script (CS)
 microstructure
CSM mode *see* Continuous Stiffness
 Measurement (CSM) mode
CSP *see* cold sintering process (CSP)
C-sphere test 1:755–756
CSZ *see* cubic stabilized zirconia (CSZ)
CT *see* charge transfer (CT)
CTAB *see* cetyl trimethylammonium
 bromide (CTAB)
CTE *see* coefficient of thermal expansion
 (CTE)
cubic boron nitride (c-BN) 1:414
cubic crystals 1:912–913
 brittle compounds 1:913–914
 ductile compounds 1:912–913
cubic stabilized zirconia (CSZ) 1:928
Cu electrodes for ML actuators 3:433–434
cullet 2:487
Curie point 3:333
curie temperature 3:347
cuspidine 2:736
customized ceramic medical devices, design
 of 3:662
 bone tissue engineering, customized bone
 graft substitutes and scaffolds for
 3:664–666
 binder jetting 3:668–669
 material extrusion 3:667–668
 powder bed fusion 3:666–667
 vat polymerization 3:664–666
 dental applications 3:669–671
 digital manufacturing processes
 3:662–664
CV *see* cyclic voltammetry (CV)
CVD *see* chemical vapor deposition (CVD)
CVI *see* chemical vapor infiltration (CVI)
CWO Remarkable 3:108
cycles for maximized energy output
 (CMEQ) method 3:403–405
cyclic fatigue (*R*-ratio) and ceramic and
 glasses applications 1:852
cyclic fatigue 1:841
cyclic fatigue evaluation and *R*-ratio effect
 1:842–844
 fatigue crack growth rate (FCGR) curves
 1:844–847
 stress-cycles curves 1:842–844
cyclic fatigue phenomenon (*R*-ratio) and
 microstructural effect 1:849–852
cyclic voltammetry (CV) 3:69
cytokines (CK) 3:716–717
 growth factors and 3:718
c-ZIFs *see* crystalline zeolitic imidazolate
 frameworks (c-ZIFs)
Czochralski (Cz) method 3:105
- ## D
- damped precession 3:188–189
dark-field (DF) imaging 1:588–589
DB *see* diffusion bonding (DB)
DBM *see* demineralized bone matrix (DBM)
DCB method *see* double cantilever beam
 (DCB) method
DCC *see* direct coagulation casting (DCC)
d.c. hysteresis loss 3:219
DCPA *see* dicalcium phosphate anhydrous
 (DCPA)
DCPD *see* dicalcium phosphate dihydrate
 (DCPD)
“dead” magnetic interface layers 3:221–222
deairing time 1:191
Deborah number 2:453, 2:454
Debye frequency 1:858, 1:861
Debye-Hückel equation 1:154
Debye model 1:858
decomposition reactions 1:83–86
DED *see* direct energy deposition (DED)

- defect engineering 3:302
 defective oxides 3:372–373
 deficiency line 1:593
 deflocculant/dispersant, selection of 1:190
 deformable interfaces method 1:307
 deformation maps 1:895–896
 de Haas van Alphen (dHvA) effect 3:164, 3:165
 deionised water 3:643
 DEJ *see* dentin-enamel junction (DEJ)
 delayed failure 1:841
 DEM *see* discrete element method (DEM)
 demagnetization coefficients 3:192*t*, 3:193
 demagnetized samples, characterization of 3:201
 demineralized bone matrix (DBM) 3:474, 3:481–482, 3:475
 dendrite theory 2:756
 densification/consolidation 2:11
 hot pressing (HP) 2:11–14
 liquid phase sintering (LPS) 2:15–16
 microwave sintering (MW) 2:15
 non-sintering based techniques 2:16
 pressureless sintering 2:11
 spark plasma sintering (SPS) 2:14–15
 densification during liquid phase sintering 1:258–259
 contact flattening 1:259–261
 particle rearrangement 1:258–259
 pore filling 1:261
 densification methods 3:116–117
 hot forming 3:117
 pressure-assisted sintering 3:117
 pressureless sintering 3:117
 sintering aids 3:117–118
 sintering approaches 3:117
 vacuum sintering 3:116–117
 density functional perturbation theory (DFPT) 1:479
 density functional theory (DFT) 1:476, 1:10–11, 1:627, 1:484, 3:305, 1:441
 for piezoelectric ceramics 1:478–479
 piezoelectric charge tensor, calculation of 1:478–479
 voltage constants, derivation of 1:479
 dental ceramics 3:784, 3:785*t*
 fracture mechanisms 3:784–787
 slow crack growth (SCG) and fatigue 3:792–796
 strength and toughness of 3:787–791
 glass phase, ceramics with 3:787–791
 polycrystalline oxide ceramics and ceramic composites without glass phase 3:791–792
 dental restoration 2:718
 dental zirconia implants, ceramic coatings on 3:744–745
 dentin-enamel junction (DEJ) 3:501
 dentistry, new trends in ceramics for 3:501–502
 all-ceramic dental materials 3:502–504, 3:504–506
 functionally graded ceramics 3:506–508
 innovative manufacturing 3:508–509
 monolithic restorations 3:504–506
 dentistry, zirconia ceramics for 3:827–828
 deposited fibers 2:309–310
 detector configurations 1:552*f*
 deuterated triglycine fluoroberyllate (DTGFB) 3:142
 deuterated triglycine sulphate (DTGS) 3:142
 Deutsche Nanoschicht 3:181
 devitrifying sealing glasses 2:750
 DF imaging *see* dark-field (DF) imaging
 DFPT *see* density functional perturbation theory (DFPT)
 DFT *see* density functional theory (DFT)
 DGL *see* D-glucorono-6,3-lactone (DGL)
 D-glucorono-6,3-lactone (DGL) 1:159, 1:160
 diamond 1:411–412
 diamond cutting wheel for sectioning 1:636*f*
 dicalcium phosphate 3:737
 dicalcium phosphate anhydrous (DCPA) 3:624, 3:626, 3:572–573, 3:606
 dicalcium phosphate dihydrate (DCPD) 3:624, 3:626, 3:630, 3:606
 NMR spectroscopy of 3:631
 die, function of 1:163
 die filling 1:140, 1:140*f*
 dielectric antenna 3:383–386
 dielectric bolometers 3:144, 3:146, 3:141
 dielectric constant 3:347
 dielectric crystalline media 3:3
 dielectric heating 1:328–329
 microwaves and 1:327–328
 dielectric heating 1:328–329
 electromagnetic fields, propagation of 1:327–328
 penetration depth 1:329–330
 dielectric loss 3:376–378
 dielectric loss factor 3:347
 dielectric resonator 3:375
 applications 3:378–379
 antenna duplexer of portable telephones 3:379–380
 filters in cellular base stations 3:380
 high-temperature superconductivity, materials for 3:380–383
 millimeter wave applications 3:380
 dielectric loss 3:376–378
 dielectric properties 3:375–376
 material 3:375
 dielectric resonator-controlled local oscillator (DRO) 3:375
 dielectrics
 applications 3:291–293
 basic concepts of 3:281–282
 die pressing 1:139
 diesel injection valve 3:434
 diesel particulate filter (DPF) 1:635, 2:88
 differential scanning calorimetry (DSC) 2:452–453, 2:453, 1:677
 differential thermal analysis (DTA) 2:691
 and differential scanning calorimetry 1:676–677
 advanced DTA techniques 1:683
 crystal growth 1:681–682
 crystallization of glasses
 degradation, volatilization and melting 1:677–678
 glass transition temperature 1:678–680
 interpolation of other important glass properties from DTA/DSC data 1:680–681
 nucleation 1:682
 phase transformations, DTA/DSC analysis of 1:682–683
 diffraction conditions and diffracted intensity 1:560
 diffraction contrast 1:589
 diffraction peak shifts and broadening 1:561–562
 diffusional creep 1:893
 diffusion bonding (DB) 2:395
 advantages and disadvantages of 2:397
 ceramic–ceramic 2:395–396
 ceramic–metal 2:396
 use of thin interlayers to enhance 2:396–397
 Digital Image Correlation 1:748
 Digital Light Processing (DLP) 1:390, 1:390–391, 1:211
 digital manufacturing processes 3:662–664
 digital micro-mirror device (DMD) technology 1:390–391, 3:665
 dihedral angle effect 1:253–254
 (di)hydrogen phosphates 3:567–568
 4,5-dihydroxy-1,3-benzenedisulfonic acid 1:105–106
 dilation anomaly 2:637–638
 dilatometric softening point of glasses 1:685–687
 dilatometry 1:683–684, 2:691
 coefficient of thermal expansion (CTE), measurement of 1:685–687
 dilatometric softening point of glasses 1:685–687
 glass transition temperature 1:685–687
 phase transformation 1:685
 sintering, analysis of 1:684–685
 diopside 2:735
 diopside-based glass-ceramics 2:736
 DIP *see* direct inkjet printing (DIP); direct ink printing (DIP)
 dip coating 2:385–386
 dip coating deposition 2:699–700
 direct casting forming methods 1:108–109
 direct coagulation casting (DCC) 1:154, 1:154–155, 1:156–157, 3:563, 1:156
 advantages and limitations of 1:160
 coagulation by high valence counter-ions (DCC-HVCI) 1:159–160
 coagulation of suspensions by thermal decomposition of lactones 1:157–159
 electrical double layer 1:154–155
 fundamentals of the method 1:156–157
 stability of suspensions – DLVO theory 1:155–156
 directed laser deposition (DLD) 2:80
 direct energy deposition (DED) 1:383–384
 direct foaming method 3:606
 direct inkjet printing (DIP) 1:390
 advantages and limitations of 1:390

- direct inkjet printing (DIP) (*continued*)
 direct ink printing (DIP) 3:668
 direct ink writing (DIW) 1:214–216, 1:216,
 1:388–389, 1:214
 monolithic components 1:215
 porous components 1:214
 directionally-solidified eutectic (DSE) oxide
 ceramics 2:216, 2:220*t*
 crystallography 2:218–219
 mechanical properties 1:219–222
 Al₂O₃–YAG 2:219–222
 Al₂O₃–ZrO₂ (Y₂O₃) 2:222–224
 oxide eutectics 2:216
 microstructure 2:216
 preparation 2:216–218
 direct laser sintering (dLS) 1:384,
 1:384–385
 Direct Photo Shaping Large Area Maskless
 Photopolymerization (LAMP)
 1:390–391
 discrete element method (DEM) 1:143,
 1:144, 1:172
 disk replacement, oxide ceramics in 3:523
 dislocations in ceramic materials 1:911
 cubic crystals 1:912–913
 brittle compounds 1:913–914
 ductile compounds 1:912–913
 general features 1:911–912
 low symmetry crystals 1:914–915
 nitrides 1:916–917
 silicon carbide 1:915–916
 superconductors 1:917–918
 α -alumina 1:914–915
 disordered carbon-based materials 1:531
 disordered packing and lacunar model
 2:615–616
 dispersant and binder, copolymers acting as
 1:107
 dispersants 1:104–105, 1:119–122, 1:106
 electrostatic and electrosteric stabilization
 1:105–106
 selection of 1:190
 stabilization 1:105*t*
 steric stabilization 1:105
 dispersion 1:114–115
 parameters influencing the state of
 1:117–118
 polymerization 1:386
 various stages of 1:113
 ditellurium bromide glasses 2:600
 DIW *see* direct ink writing (DIW)
 DLD *see* directed laser deposition (DLD)
 DLP *see* Digital Light Processing (DLP)
 dLS *see* direct laser sintering (dLS)
 DLVO theory 1:155–156
 DMD technology *see* digital micro-mirror
 device (DMD) technology
 DMEM *see* Dulbecco's Modified Eagle's
 Medium (DMEM)
 doctor blade tape casting process
 1:189–190, 1:191–192, 1:189*f*
 batching and slip preparation 1:190
 materials selection 1:189–190
 slip conditioning and characterization
 1:190–191
 donor doping 3:352
 doped CaP 3:478–479
 doping elements, biological role of 3:618
 doping ion and conduction band states,
 absorption involving 3:89–90
 doping ion and valence band states,
 absorption involving 3:90–91
 double cantilever beam (DCB) method
 1:799, 1:801
 double plate lamination 1:193
 double torsion (DT) method 1:800*f*, 1:799
 crack growth rate 1:800
 constant displacement rate method
 1:801
 constant loading test 1:800
 load relaxation test 1:800–801
 specimen and loading configuration 1:799
 stress intensity factor 1:799–800
 DPF *see* diesel particulate filter (DPF)
 DRO *see* dielectric resonator-controlled
 local oscillator (DRO)
 droplet, chemistry in 1:35–36
 emulsion and microemulsion synthesis
 1:35–36
 advantages, issues, applications 1:36–37
 process, overview of 1:35–36
 spray-based syntheses 1:37–38
 advantages, issues, applications 1:38
 process, overview of 1:37–38
 drop on demand (DoD) approach 1:390
 drug delivery systems 3:489–491
 dry bag isostatic pressing 1:138
 dry pressing 2:384, 3:115
 DSC *see* differential scanning calorimetry
 (DSC)
 DSE oxide ceramics *see* directionally-
 solidified eutectic (DSE) oxide
 ceramics
 DSSCs *see* dye-sensitized solar cells (DSSCs)
 DTA *see* differential thermal analysis (DTA)
 DTGFB *see* deuterated triglycine
 fluoroberyllate (DTGFB)
 DTGS *see* deuterated triglycine sulphate
 (DTGS)
 DT method *see* double torsion (DT) method
 ductile compounds 1:912–913
 Dulbecco's Modified Eagle's Medium
 (DMEM) 3:800
 DVS measurements *see* dynamic vapor
 sorption (DVS) measurements
 dye-sensitized solar cells (DSSCs) 3:12, 3:13
 dynamic demagnetizing aspect 3:196–197
 dynamic vapor sorption (DVS)
 measurements 1:522
 Dyneema 2:308–309
- E**
- EAC *see* energy absorption (handling)
 capability (EAC)
 EAS *see* electrodeposit-assisted stripping (EAS)
 EBCs *see* environmental barrier coatings
 (EBCs)
 EBM *see* electron beam melting (EBM)
 ECM *see* extracellular matrix (ECM)
 ectopic bone formation, models of 3:809
 intramuscular implantation 3:809–810
 kidney capsule implantation 3:810
 subcutaneous implantation 3:809
 eddy current contribution 3:219
 eddy current loss 3:219
 EDFA *see* Erbium-Doped Fiber Amplifiers
 (EDFA)
 edge-defined film growth (EFG) method
 2:216–218
 edge tearing 1:174
 EDL *see* electrical double layer (EDL)
 EDM *see* electrical discharge machining
 (EDM); electro discharge machining
 (EDM)
 EDS *see* Electro-Discharge-Sintering (EDS);
 energy-dispersive X-ray spectroscopy
 (EDS)
 EDX *see* energy dispersive X-ray analysis
 (EDX)
 EELS *see* electron energy loss spectroscopy
 (EELS)
 EE multiplication *see* electronic excitations
 (EE) multiplication
 EFF *see* Extrusion Freeform Fabrication
 (EFF)
 effective medium approximations (EMA)
 3:299–300
 EFG method *see* edge-defined film growth
 (EFG) method
 EF-IE *see* electric field-assisted ion-exchange
 (EF-IE)
 EFTEM *see* energy filtered transmission
 electron microscopy (EFTEM)
 EGG *see* exaggerated grain growth (EGG)
 E-glass fiber 2:677, 2:309
 elastic and inelastic behavior of ceramics
 1:705
 anelasticity and mechanical spectroscopy
 1:705–707
 experimental data 1:707
 mechanical loss and toughness 1:714–717
 mechanical spectrometer 1:707
 silicon nitride, mechanical spectroscopy in
 1:713–714
 zirconia, mechanical spectroscopy of
 1:707–711
 grain size effect 1:711–713
 low temperature peak 1:707–711
 elastic constants, calculation of (case study)
 1:477–478
 finite differences 1:478
 strain controlled calculations 1:478
 elastic scattering 1:585–586
 elastin 3:467
 electrical applications of glass-ceramics
 2:718
 glass-ceramics dielectrics for high power
 capacitors 2:718–719
 insulators 2:718
 pyroelectric/piezoelectric glass-ceramics
 2:719
 solid state electrolytes for rechargeable
 batteries 2:719–720
 thermoelectric glass-ceramics 2:719
 electrical discharge machining (EDM) 2:195

- electrical double layer (EDL) 1:154
 electric current as a source of internal heating 1:286–288
 capacitor discharge sintering (CDS) 1:291
 flash sintering 1:286–288
 mechanism of flash sintering 1:288–289
 technical specification of the flash sintering apparatus 1:287–288
 spark plasma sintering (SPS)/field assisted sintering (FAST) 1:289–291
 technical aspects 1:289–291
 electric field-assisted ion-exchange (EF-IE) 2:642–644
 electric propulsion 2:369–370
 Ion and Hall thrusters 2:370
 Variable Specific-Impulse Magneto-Plasma (VASIMR) 2:370
 electrocatalysts 1:8
 electroceramics 3:1, 3:3, 3:295–296
 ceramic magnetic materials 3:2–3
 ferrite ceramics at microwave frequencies 3:3
 ferrite magnets 3:3
 ceramic sensors 3:2
 for industrial applications 3:2
 pyroelectric crystals, ceramics, and thin films for IR sensors 3:2
 dielectric/ferroelectric/piezoelectric/electrostrictive ceramic materials 3:3
 BaTiO₃-based ceramics 3:3–4
 dielectric, ferroelectric, antiferroelectric, relaxor, piezoelectric ceramics 3:3
 lead zirconate titanate (PZT) system 3:4
 multilayer ceramic actuators 3:4
 electronics and optoelectronics 3:1
 aluminum, gallium, and indium nitrides 3:1
 ceramics for laser technologies 3:2
 novel nitride phosphors 3:1–2
 phosphors 3:2
 scintillator crystals 3:2
 silicon carbide electronic devices 3:2
 energy conversion and storage 3:1
 ion conducting materials 3:1
 laser processing of energy storage materials 3:1
 photovoltaics 3:1
 solid oxide fuel cells 3:1
 functional properties of 3:299–301
 defects 3:302
 domain structure and switching properties of ferroelectric ceramics 3:303–308
 effective dielectric properties in inhomogeneous ceramics 3:299–301
 grain boundaries 3:302–303
 grain size effects 3:303
 microstructure evolution in 3:297–299
 sintering process 3:296–297, 3:297–299
 superconducting materials 3:2
 superconductors 3:2
 technologies that are relevant for several materials and applications 3:4
 functional ceramics through novel chemical approaches 3:4
 zinc oxide 3:3
 -based electronics and photonics 3:3
 latest trend of ZnO multilayer ceramic varistors 3:3
 varistor electrical properties: microstructural effects 3:3
 electrodeposit-assisted stripping (EAS) 3:8–9
 electro discharge machining (EDM) 2:19
 Electro-Discharge-Sintering (EDS) 1:286
 electrodynamics 2:658
 electromagnetic waves and their interaction with matter 2:658
 wave propagation
 in an ideal transparent refracting medium 2:659–660
 in vacuum 2:658–659
 in a weakly absorbing medium 2:660
 electro fused abrasives 2:407–410
 electrolysis of gaseous molecules 3:34
 electrolytes 3:52–53
 electrolytic etching 1:648
 electrolytic theory 2:756–757
 electromagnetic fields, propagation of 1:327–328
 electromagnetic shielding effectiveness of carbon-matrix composites 2:357–358
 electromechanical coupling factor 3:394, 3:347
 electromechanical resonance (EMR) 3:231
 electromotive force (EMF) 2:103
 electron beam melting (EBM) 1:384
 electron beam precession 1:618, 1:619f
 electron diffraction 1:591–596
 electron energy loss spectroscopy (EELS) 1:439–440, 1:579, 1:600, 1:443
 principles of 1:610–616
 electronic excitations (EE) multiplication 3:91
 electronics and optoelectronics 3:1
 aluminum, gallium, and indium nitrides 3:1
 ceramics for laser technologies 3:2
 novel nitride phosphors 3:1–2
 phosphors 3:2
 scintillator crystals 3:2
 silicon carbide electronic devices 3:2
 electronic structure and interatomic bonding 1:442
 electronic toll collector (ETC) system 3:383
 electron mobility 3:302
 electron paramagnetic resonance (EPR) 3:578
 electrophoretic deposition (EPD) 2:345–346, 2:283, 1:379–380, 2:700
 electrospinning 3:651, 3:485–486, 3:690–691
 electrostatic and electrosteric stabilization 1:105–106
 electrostatic repulsion, stabilization principle by 1:116
 electrostatic repulsion stabilization, parameters changing 1:116–117
 electrostriction 3:369
 microscopic explanation of 3:370–371
 electrostrictive ceramics
 application 3:369–370
 thermal expansion, Newnham's law, and materials 3:371–372
 defective oxides 3:372–373
 linear dielectrics and glasses ceramics 3:371–372
 perovskite ferroelectrics and relaxor ferroelectrics 3:372
 polymers 3:373
 electrostrictor 3:428–429, 3:430
 EMA *see* effective medium approximations (EMA)
 embryonic stem cells (ESCs) 3:801
 EMF *see* electromotive force (EMF)
 empirical criterion 1:832–833
 EMR *see* electromechanical resonance (EMR)
 EMRN model *see* extended modified random network (EMRN) model
 EMTSN *see* extended version of the maximum tangential strain (EMTSN)
 emulsion and microemulsion synthesis 1:35–36
 advantages, issues, applications 1:36–37
 process, overview of 1:35–36
 endothelial cells, stimulating 3:719
 energy absorption (handling) capability (EAC) 3:259
 energy-based criteria 1:829–830
 maximum energy release rate criterion 1:829–830
 strain-energy-density criterion 1:830–832
 energy conversion and storage 3:1
 ion conducting materials 3:1
 laser processing of energy storage materials 3:1
 photovoltaics 3:1
 solid oxide fuel cells 3:1
 energy dispersive X-ray analysis (EDX) 1:439–440, 1:658–659
 energy-dispersive X-ray spectroscopy (EDS) 1:579, 1:660, 1:600
 principles of 1:607–610
 energy filtered transmission electron microscopy (EFTEM) 1:610–616
 energy harvesting technologies 3:407–409
 applications 3:420–421
 magneto-mechano-electric generators 3:421–422
 piezo/triboelectric nanogenerators 3:420–421
 cantilever based piezoelectric energy harvester 3:407–409
 figure of merit for 3:397–398
 magneto-mechano-electric generator 3:418–420
 piezoelectric nanogenerator 3:409
 ceramic based PENGs 3:409–412
 polymer-based PENGs 3:412–413
 ZnO based PENGs 3:409
 selection of piezoelectric materials for 3:396–397
 triboelectric nanogenerator 3:413–416
 solid-liquid contact based TENGs 3:416–418
 solid-solid contact based TENGs 3:413–416
 environmental barrier coatings (EBCs) 2:64, 2:442

environmental scanning electron microscopy (ESEM) 1:658
 EPD *see* electrophoretic deposition (EPD)
 epitaxy 1:89–90
 EPR *see* electron paramagnetic resonance (EPR)
 Erbium-Doped Fiber Amplifiers (EDFA) 2:617–618
 ergodicity 2:449, 2:453–454
 ergodic state, defined 2:449
 erosion 2:428–429
 ESCs *see* embryonic stem cells (ESCs)
 ESEM *see* environmental scanning electron microscopy (ESEM)
 esthetic materials 2:723–725
 etching 1:646
 before 1:646
 methods 1:647
 chemical etching 1:647–648
 electrolytic etching 1:648
 less common etching methods 1:649
 plasma etching 1:648–649
 relief etching 1:647
 thermal etching 1:647
 removal of specimens from mounts 1:646–647
 ETC system *see* electronic toll collector (ETC) system
 ettringite, properties of 1:445–446, 1:451t
 Eu-doped alkaline-earth silicon nitrides and oxynitrides 3:85–86
 Eu-doped aluminum-oxynitrides with β -alumina and other structures 3:86
 eutectics 2:216, 2:218–219
 exaggerated grain growth (EGG) 1:239
 exciton 3:90, 3:90f, 3:91
 extended modified random network (EMRN) model 2:498, 2:499f
 extended version of the maximum tangential strain (EMTSN) 1:829
 extensive reactive sintering, glass-ceramics from 2:732–733
 direct sintering of glass-ceramics with engineered crystal phases 2:734–737
 direct sintering of waste-derived glass-ceramics 2:733–734
 glass-ceramics from the interaction between glass and reactive binders 2:737–739
 polymer-derived glass-ceramics 2:739–740
 sintered glass-ceramics from mixtures of glasses 2:732–733
 external electromagnetic field, heating by 1:291–292
 induction sintering 1:292
 microwave sintering 1:292
 perspectives 1:292–293
 selective laser sintering (SLS) 1:291–292
 extracellular matrix (ECM) 3:716, 3:716–717, 3:717f, 3:717, 3:465
 extrusion 1:162, 2:384–385, 3:654, 2:411
 co-extrusion 1:175
 die, function of 1:163
 extrusion defects 1:173–174
 edge tearing 1:174
 lamination 1:174

 particle re-orientation 1:174
 phase migration 1:174–175
 paste formulation 1:163
 basic formulation 1:163–164
 designing paste formulations 1:165–166
 manufacturing cycle 1:163
 mixing 1:166–167
 particle packing 1:164–165
 paste additives 1:167–168
 paste formulations, characterization of 1:168–170
 air bubble inclusion 1:170–171
 binding liquid and paste characteristics 1:170
 Liquid Phase Migration 1:170
 mathematical expressions, paste behavior in 1:171–172
 mixedness 1:171
 wall slip 1:170
 yield stress 1:170
 pressure generation 1:162
 auger/screw extrusion 1:162–163
 Piston extrusion 1:162
 solid free form fabrication 1:172–173
 extrusion defects 1:173–174
 edge tearing 1:174
 lamination 1:174
 particle re-orientation 1:174
 phase migration 1:174–175
 Extrusion Freeform Fabrication (EFF) 1:172, 1:173

F

face-centered cubic (FCC) materials 3:174–175
 Faraday's law 3:130
 FAST *see* field assisted sintering technique (FAST)
 Fast Firing 1:354
 Fast Fourier Transform (FFT) technique 1:604
 fast ion conductors 3:569–570
 fast sintering 1:354–355
 fatigue 1:841
 fatigue crack growth rate (FCGR) curves 1:844–847
 FBAR magnetoelectric antennas *see* film bulk acoustic resonator (FBAR) magnetoelectric antennas
 FB set *see* full basis (FB) set
 FCC materials *see* face-centered cubic (FCC) materials
 FCD *see* functional capillary density (FCD)
 FCGR curves *see* fatigue crack growth rate (FCGR) curves
 FDC *see* fused deposition of ceramics (FDC)
 FDM *see* fused deposition modeling (FDM)
 FDPs *see* fixed dental prostheses (FDPs)
 FEF *see* freeze-form extrusion fabrication (FEF)
 "feldspathoid" minerals 2:736
 FEM *see* finite element methods (FEM)
 ferrimagnetic materials 3:183
 hexaferrites 3:186–187
 hysteresis loops and magnetocrystalline anisotropy 3:183–186
 polycrystalline ferrites, basic properties of 3:183, 3:184f
 soft ferrites
 garnets ferrites 3:186
 spinel ferrites 3:186
 ferrimagnetic resonance frequency (FMR) 3:191
 ferrimagnetism 3:217
 ferrite ceramics at microwave frequencies 3:3
 ferrimagnetic materials 3:183
 garnets ferrites 3:186
 hexaferrites 3:186–187
 hysteresis loops and magnetocrystalline anisotropy 3:183–186
 polycrystalline ferrites, basic properties of 3:183, 3:184f
 spinel ferrites 3:186
 magnetic permeability in microwave range of frequencies 3:187–188
 damped precession 3:188–189
 dynamic demagnetizing aspect 3:196–197
 frequency dispersion of permeability spectrum 3:189–191
 modeling the dynamic permeability of polycrystalline ferrites 3:197
 shape-demagnetizing effects 3:191–196
 undamped precessions 3:187–188
 microwave characterization methods 3:200–201
 demagnetized samples, characterization of 3:201
 magnetized samples, characterization of 3:201–203
 microwave passive components using ferrites 3:197–198
 antenna miniaturization 3:199
 isolators and circulators 3:199–200
 microwave magnetic losses 3:198–199
 wave propagation in magnetized ferrimagnetic materials 3:197–198
 ferrite magnet materials 3:210–211
 bonded ferrites 3:214
 magnetic properties 3:214–215
 manufacturing process 3:214
 magnetic properties of ferrite magnets 3:210–211
 materials processing 3:211
 sintered hard ferrites 3:211–212
 anisotropic ferrites 3:213
 ceramic process 3:211–212
 isotropic ferrites 3:213
 properties of 3:212
 ferrite magnets 3:206, 3:3
 hexaferrite materials 3:209–210
 manufacture of 3:211f
 permanent magnets 3:206
 market 3:207–209
 materials 3:206
 properties 3:206–207
 ferrite permanent magnets, applications of 3:215

- ferrites
 applications 3:218–220
 new developments 3:220–222
 ferrite films 3:220–222
 life sciences applications 3:222–223
 properties 3:217–218
 resistivity of 3:219
 spinel-type lattice structure 3:217, 3:217f
 typical magnetic hysteresis loop 3:218, 3:218f
- ferroelectric ceramics, domain structure and switching properties of 3:303–308
- ferroelectrics 1:417–418
 applications 3:291–293
 basic concepts of 3:284–288
 complex-anion and other oxides 1:418
 conducting oxides 1:418
 perovskites 1:417–418
- ferrois 3:571
- ferromagnetic resonance (FMR) 3:228, 3:219–220
- FET *see* field effect transistor (FET)
- FFF *see* Fused Filament Fabrication (FFF)
- FFT technique *see* Fast Fourier Transform (FFT) technique
- FGF *see* fibroblast growth factors (FGF)
- FGM *see* functionally graded materials (FGM)
- fiber drawing 2:687–688, 2:677
- fiber fabrication 2:686
- fiber lasers 2:617–618
 optical amplification 2:617–618
- fiber-optic communication 2:617
- fiber spraying process 2:272–274
- fibroblast growth factors (FGF) 3:474
- fibronectin (FN) 3:460–461
- fibrous ceramics 1:346, 1:342–343
- fibrous reinforcement 2:317–318
- field assisted sintering technique (FAST) 1:358, 1:311, 1:289–291, 1:294
 see also spark plasma sintering (SPS)
- field effect transistor (FET) 3:139–140, 3:140
- field-orientational dependence of the density of states (FODOS) 3:164
- figure of merit (FOM) 3:402–405
- film bulk acoustic resonator (FBAR)
 magnetoelectric antennas 3:237–238
- finger joint replacements, oxide ceramics in 3:522–523
- finite element methods (FEM) 1:143, 3:260, 3:258–259, 3:464, 3:751, 3:300
- first sharp diffraction peak (FSDP) 2:468
- fixed dental prostheses (FDPs) 3:784
- fixed partial dentures (FPDs) 3:817
- flame spraying 2:64
- FLASH *see* flash sintering (FLASH)
- flash sintering (FLASH) 1:286–288,
 1:358–359, 1:246–247, 2:421, 1:286
 mechanism of flash sintering 1:288–289
 technical specification of the flash sintering apparatus 1:287–288
- flash sintering and other rapid sintering techniques 1:286
 electric current as a source of internal heating 1:286–288
 capacitor discharge sintering (CDS) 1:291
- flash sintering 1:286–288
 spark plasma sintering (SPS) or field assisted sintering (FAST) 1:289–291
 external electromagnetic field, heating by 1:291–292
 induction sintering 1:292
 microwave sintering 1:292
 perspectives 1:292–293
 selective laser sintering (SLS) 1:291–292
- flat color display 3:89
- Florine-19 NMR Spectra 1:542
- fluoride and chrollide ion conductors 3:26–28
- fluoride glasses 2:592, 1:534
 fluoroaluminates 2:594–595
 fluoroberyllates 2:592
 fluoroindates 2:595–596
 fluorozirconates 2:592–594
- fluoride phosphate glasses 2:586
- fluorides 1:419–420
 calcium fluoride 1:420
 magnesium fluoride 1:420
- fluorine 2:736
 effect on oxynitride glass formation 2:560–561
 effect on properties of oxynitride glasses 2:576
- fluoroaluminates 2:594–595
- fluoroberyllates 2:592
- fluorochloride glasses 2:603–604
- fluorohalide glasses 2:603
 fluorochloride glasses 2:603–604
 fluorozirconates, incorporation of halides in 2:603
 halides in fluoride glasses 2:604
- fluoroindates 2:595–596
- fluorophosphate (FP) glasses 2:586
- fluorozirconates 2:592–594, 1:534
 incorporation of halides in 2:603
- FN *see* fibronectin (FN)
- FODOS *see* field-orientational dependence of the density of states (FODOS)
- FOM *see* figure of merit (FOM)
- force fields 1:486
 accounting for polarization effects 1:487
 force fields accounting for polarization effects 1:487
 long-range Coulombic interactions 1:486
 short-range interactions 1:486–487
 three-body interatomic potentials 1:487
- Fourier transform infrared spectroscopy (FTIR) 1:542–543, 1:517, 2:561–562
- 45S5 Bioglass 1:490
- FPDs *see* fixed partial dentures (FPDs)
- FP glasses *see* fluorophosphate (FP) glasses
- fractal geometry 1:670–674
- fractographic procedures 1:664–666
 global residual stress 1:666
 local residual stress 1:666–667
 mixed mode fracture 1:668–670
 R-curve determination using quantitative fractography 1:667–668
 slow crack growth 1:667
- fracture mechanics of thermal shock 1:879–880
 crack propagation analysis 1:880–882
- transient thermal stresses 1:879–880
- fracture strength, determination of 1:751–752
 multiaxial tests used to determine tensile strength 1:754–755
 biaxial bending 1:756–757
 Brazilian test 1:754–755
 C-sphere test 1:755–756
 triaxial testing 1:757
- non-uniform tests 1:753–754
 bending/flexion test 1:754
- parameters influencing strength 1:758
 sample preparation, influence of 1:747
 test environment 1:758–759
- small scale testing, towards 1:757–758
- statistical analysis/size effect 1:759
- uniform tests 1:751–752
 uniaxial compression 1:752–753
 uniaxial tension 1:752
- fracture surfaces, general appearance of 1:662–663
 quantitative analysis 1:663–664
 sources of failure 1:662–663
- fracture toughness 1:823–824
 by indentation 1:725–730
- fracture toughness measurement 1:762
 basic principles 1:762
 linear elastic fracture mechanics 1:762
 microstructure and environmental effects on crack growth 1:762–763
 Chevron-Notched beam (CNB) method 1:766–767
- comparison of the standardized methods 1:767–768
 R-curves, standardized methods and 1:767–768
 sub-critical crack growth, standardized methods and 1:768–769
- indentation fracture resistance (IF-method) 1:771–772
- indentation strength (IS) method 1:771
- pre-cracks/notches, methods for introducing 1:769–770
- single-edge pre-cracked beam (SEPB) method 1:763–764
- single-edge V-notched (SEVNB) method 1:767
- specific specimen geometries/components, testing of 1:770
 balls, small disks and plates 1:770–771
 thin specimens, strips 1:770
- surface crack in flexure (SCF) method 1:764–766
- Franck-Condon shift 3:89, 3:91
- free volume (FV) 2:570
- freeze casting 3:651, 2:386, 1:195
 controlling the porous structure 1:198–201
 mechanical properties 1:201
 processing porous ceramic by 1:196–198
 working 1:195–196
- freeze-drying 3:485
- freeze-form extrusion fabrication (FEF) 1:389
- Frenkel defect 3:20–21
 schematic model of 3:22f
- Frenkel's model 1:266

- frequency dispersion of permeability spectrum 3:189–191
- friction 2:425–427
- FSDP *see* first sharp diffraction peak (FSDP)
- FSZ *see* fully stabilized zirconia (FSZ)
- FTIR *see* Fourier transform infrared spectroscopy (FTIR)
- full basis (FB) set 1:442
- full-contour monolithic zirconia and minimally invasive dentistry 3:822
- glazing and staining 3:823
- high-translucency zirconia (4Y, 5Y) grades 3:822
- biomedical grade 3Y-TZP 3:822
- highly-translucent 3Y-TZP 3:822
- super-translucent zirconia 3:823
- ultra-translucent zirconia 3:822–823
- self-glazed zirconia ceramics 3:823–824
- full width at half maximum (FWHM) 1:370, 1:369f
- fully stabilized zirconia (FSZ) 1:928
- functional capillary density (FCD) 3:726
- functional ceramics through novel chemical approaches 3:4
- chemical modification for porous and nano-structured TiO₂ thin films 3:452–453
- low-temperature processing of layer-structured perovskite thin films 3:453–455
- UV-processing of perovskite solid-solution thin films 3:455–456
- functional gradient materials 1:900–901
- functionally graded materials (FGM) 3:506–507, 2:345, 1:374–375, 1:302–303, 1:50
- additive manufacturing (AM) 1:382–384
- binder jetting 1:387–388
- direct energy deposition (DED) 1:383–384
- direct inkjet printing (DIP) 1:390
- materials extrusion 1:388–390
- powder bed fusion (PBF) 1:384
- sheet lamination 1:388
- slurry based binder jetting 1:388
- vat photopolymerization 1:393–394
- applications 1:391–393
- mechanical properties and applications 1:391–393
- medical implants 1:394–395
- thermal protection systems 1:393–394
- wear protection 1:391–393
- coating 1:382
- thermal spraying 1:382
- future outlook 1:395
- melt processing 1:382
- powder processing 1:378–381
- densification of FGM powder compacts 1:381–382
- shaping and consolidation processes for FGMs 1:378–381
- theoretical research 1:375–377
- fundamental absorption 3:91, 3:92
- fungicides 1:107
- fused deposition modeling (FDM) 1:217, 1:216, 3:487, 3:691–692
- fused deposition of ceramics (FDC) 3:487
- Fused Filament Fabrication (FFF) 1:185
- fused mullite 2:63
- FV *see* free volume (FV)
- FWHM *see* full width at half maximum (FWHM)
- ## G
- gadolinia-doped ceria (GDC) 3:713
- GAL *see* gluconic acid lactone (GAL)
- gallium(III) bromide, glasses based on 2:600
- gallium 3:1
- gallium nitride 3:75–76, 3:75t
- gallium phosphide (GaP) 1:414
- gang saw 1:193–194
- garnets 1:417, 3:118–119
- LuAG 3:119
- YAG 3:118–119
- garnets ferrites 3:186
- GASED criterion *see* generalized averaged strain energy density (GASED) criterion
- gas foaming 3:651, 3:485
- gas–metal eutectic bonding 2:397
- gasoline direct injection (GDI) systems 1:733
- gas phase reactions and other methods of synthesis 2:10–11
- gas pressure sintering (GPS) 2:111, 2:153, 2:173–174, 2:246–247
- gas sensors 3:125
- based on ion conducting metal oxides 3:127–130
- based on semiconducting metal oxides 3:130–132
- bulk-active SMOX 3:131–132
- surface-active SMOX 3:132–137
- gas separation 3:34
- Gatan Microscopy Suite 1:604
- GB *see* grain boundary (GB)
- GBS *see* grain boundary sliding (GBS)
- GCM *see* glass composite materials (GCM)
- GCs *see* glass-ceramics (GCs)
- GCS *see* gyroid cellular structures (GCS)
- GDA *see* glycerol diacetate (GDA)
- GDC *see* gadolinia-doped ceria (GDC)
- GDI systems *see* gasoline direct injection (GDI) systems
- gel
- defined 2:689
- synthesis 2:690–691
- gelatin 3:467
- gel casting 3:651, 2:385, 1:152, 1:150–152, 1:151f
- gelled fibers 2:677
- generalized averaged strain energy density (GASED) criterion 1:832
- generalized fracture toughness 1:829
- generalized maximum energy release rate criterion (GMERR) 1:830
- generalized MTS criterion (GMTS) 1:827
- generic spray pyrolysis set-up 1:71–72
- aerosol generator device 1:71–72
- powder traps 1:73
- pyrolysis set-up 1:72–73
- gene transfer technology 3:658
- geometry optimization 1:477
- geopolymer aerogels 1:429
- geopolymer composites 1:428–430
- amorphous self-healed geopolymer composites 1:430–431
- amorphous self-healed, basalt fiber-reinforced, geopolymer composites 1:431–432
- bone ash reinforced geopolymer composites 1:430–431
- porous geopolymers 1:428–430
- geopolymers and geopolymer-based composites 1:424
- geopolymer composites 1:428–430
- amorphous self-healed geopolymer composites 1:430–431
- porous geopolymers 1:428–430
- low energy fabrication routes to ceramic powders 1:433–435
- metakaolin-based, acid-activated geopolymers 1:425–426
- metakaolin-based, alkali-activated geopolymers 1:424–425
- metakaolin-based geopolymers versus alkali activated cements from slag and fly ash waste materials 1:426–428
- tailorable thermal expansion ceramics derived from metakaolin-based, alkali activated geopolymers 1:432–433
- GF *see* growth factors (GF)
- GFA *see* glass forming ability (GFA)
- GHGs *see* greenhouse gases (GHGs)
- Gibbs free energy
- compositional dependence of 1:502–503
- extrapolation to higher order systems 1:507–508
- pressure dependence of 1:501–502
- temperature dependence of 1:501
- GICs *see* glass-ionomer cements (GICs)
- Ginzburg-Landau theory of superconductivity 3:166
- glass and glass-ceramic matrix composites (GMCs and GCMCs) 2:277–278
- applications of 2:288–294
- aerospace 2:288–294
- biomaterials 2:296–297
- electronic substrates 2:297–299
- solid oxide fuel cells (SOFCs) 2:294–296, 2:295f
- structural applications 2:299–300
- composite constituents 2:278–279
- matrices 2:278–279
- reinforcements 2:279–280
- manufacturing techniques 2:281–282
- alternative fabrication methods 2:283–284
- colloidal sols 2:282–283
- electrophoretic deposition (EPD) 2:283
- polymer infiltration and pyrolysis (PIP) 2:283
- powder-bed-based technologies 2:283
- powder technology 2:281–282
- slurry infiltration and hot-pressing 2:282

- sol-gel method 2:282–283
- toughening mechanisms in 2:280–281
- glass and glass ceramics 2:445, 2:445–446, 2:446, 2:446–447, 2:447
- glass-ceramic materials for sealing 2:750–752
- aluminosilicate glass-ceramics 2:752
- boroaluminosilicate glass-ceramic materials 2:752
- phosphate glass-ceramic materials 2:752–753
- silicate glass-ceramics 2:752
- glass-ceramics (GCs) 2:279, 3:739–740, 2:445, 2:446, 2:709–710
- for bonding and sealing 2:713–715
- glass-ceramic-to-metal bonding 2:713–715
- joining for SiC-based materials 2:715–716
- solid oxide fuel cells (SOFC), sealants in 2:715
- dielectrics, for high power capacitors 2:718–719
- electrical applications 2:718
- glass-ceramics dielectrics for high power capacitors 2:718–719
- insulators 2:718
- pyroelectric/piezoelectric glass-ceramics 2:719
- solid state electrolytes for rechargeable batteries 2:719–720
- thermoelectric glass-ceramics 2:719
- esthetic materials 2:723–725
- exploiting thermomechanical properties 2:711–712
- high mechanical properties 2:712–713
- specific uses 2:713
- thermal-shock resistance 2:712
- very high temperature use 2:713
- from extensive reactive sintering 2:732–733
- direct sintering of glass-ceramics with engineered crystal phases 2:734–737
- direct sintering of waste-derived glass-ceramics 2:733–734
- glass-ceramics from the interaction between glass and reactive binders 2:737–739
- polymer-derived glass-ceramics 2:739–740
- sintered glass-ceramics from mixtures of glasses 2:732–733
- in the field of healthcare 2:716–717
- bioactive glass-ceramics for implant and bone tissue regeneration 2:716–717
- dental restoration 2:718
- hyperthermia treatments of cancerous tumors 2:717–718
- glass-ceramics from wastes 2:721–722
- radioactive product confinement 2:721–722
- toxic wastes disposal and recovery 2:722–723
- key points of the process 2:710–711
- machinable glass-ceramics 2:720
- chemical machining 2:720–721
- laser machining 2:721
- mechanical machining 2:720
- microstructure and synthesis 2:709–710, 2:710f
- glass-ceramics from sinter-crystallization 2:728–730
- main fields of application 2:729–730
- glass-ceramic joints 2:730–731
- sintered glass-ceramics for building applications 2:731–732
- sintered glass-ceramics in biomedical applications 2:729–730
- sinter-crystallization aided by chemical reactions 2:732
- glass-ceramic-to-metal bonding 2:713–715
- glass-ceramic wasteforms 2:782–785
- glass compactness 2:570
- glass composite materials (GCM) 2:782
- glass crystallization-related phenomena 2:456
- glass fibers 2:304, 2:309
- applications 2:679
- aerospace market 2:679
- automotive market 2:679
- biomaterial applications 2:680
- civil construction 2:679
- electrical/electronic market 2:680
- marine market 2:679
- sporting goods 2:679–680
- chemical compositions 2:677–678, 2:678t
- fabrication 2:676, 2:677f
- fractures 2:679
- properties 2:678–679, 2:678t
- for reinforcement of polymers 2:676–677
- sol-gel processing of 2:677
- structure 2:678
- glass forming ability (GFA) 1:459
- glass-ionomer cements (GICs) 3:650
- glass making, challenge from 2:667–668
- glass materials, properties of
- amorphous phase separation (APS) 2:648–650
- nucleation and growth 2:650
- spinodal decomposition 2:650
- chemical durability of glasses 2:650–651
- chemical reaction mechanism 2:650–651
- crystallization effect on chemical durability 2:651
- common glass systems 2:654
- aluminosilicate glass 2:654
- borosilicate glass 2:654–655
- lead glass 2:654
- soda-lime glass/commercial glass 2:654
- definition of glass 2:647
- effect of composition on glass properties 2:655
- alkali earth metal oxides 2:655
- alkali metal oxides 2:655
- boron trioxide (B_2O_3) 2:655
- property modifying oxides 2:655–656
- refining component 2:656
- silicon dioxide (SiO_2) 2:655
- electrical properties 2:652–653
- resistivity 2:653
- glass transition 2:647
- mechanical and thermal properties 2:651
- strength 2:651–652
- thermal expansion behavior 2:652
- viscosity 2:651
- optical properties 2:653–654
- absorption 2:654
- refraction of light 2:653–654
- random network model 2:647–648
- structure of glass 2:647–648
- glass matrix composites (GMCs) and glass-ceramic matrix composites (GCMCs), applications of 2:288–294
- aerospace 2:288–294
- biomaterials 2:296–297
- electronic substrates 2:297–299
- solid oxide fuel cells (SOFCs) 2:294–296, 2:295f
- structural applications 2:299–300
- glass phase, ceramics with 3:787–791
- glass reaction sintering as a new route to glass-making 2:740
- glass structure, molecular dynamics (MD) simulations of *see* molecular dynamics (MD) simulations
- glass-tissue interfacial bond 3:614–615
- glass-to-metal bonding and sealing 2:397–399
- “glass transition” range 2:450
- glass transition temperature 1:685–687, 2:647
- glassy and glass-ceramic solid electrolytes 3:38–39
- glassy state 2:449–451
- crystallization 2:455–456
- crystal growth 2:456–458
- crystal nucleation 2:455–456
- overall 2:458–459
- glass structure 2:454–455
- glass transition 2:452–454
- ergodicity 2:453–454
- relaxation 2:451–452
- gluconic acid lactone (GAL) 1:158
- glycerol diacetate (GDA) 1:160
- glycosaminoglycans 3:467
- GMCs and GCMCs *see* glass and glass-ceramic matrix composites (GMCs and GCMCs)
- GMERR *see* generalized maximum energy release rate criterion (GMERR)
- GMTS *see* generalized MTS criterion (GMTS)
- GNPs *see* graphene nanoplates (GNPs)
- GO *see* graphene oxide flakes (GO)
- Göbel mirror 1:552
- GPS *see* gas pressure sintering (GPS)
- G-quadruple DNA 1:465
- gradient index optical elements 2:693
- gradients in refractive index (GRIN)
- bulk GRIN materials 2:546
- planar GRIN materials 2:546–547
- via spatially controlled nucleation and growth 2:545–546
- grain anisotropy 2:105
- grain boundaries, extra small particles addition at 1:362–363
- grain boundary (GB) 3:255, 1:705

grain boundary diffusion 1:237
 grain boundary energy, dopant elements
 addition to modify 1:361–362
 grain boundary sliding (GBS) 1:901,
 1:893–894
 grain bridging, influence of 1:807
 grain growth during liquid phase sintering
 1:261–263
 granular and powder batch flowability
 1:519–524
 granulation 3:115, 1:136, 1:137*f*
 characteristics of 1:136–137
 granules 3:482
 granule stiffness 1:142
 graphene 2:245–246, 2:246*f*, 1:741–743
 graphene nanoplates (GNPs) 2:245–246
 graphene oxide flakes (GO) 2:245–246
 graphene-reinforced ceramic composites
 2:237–238
 graphene reinforced composites 1:903–904
 graphite, crystal structure of 2:354*f*
 greenhouse gases (GHGs) 3:5
 green laminates 1:193–194
 green machining of ceramics 1:222
 hybridization 1:224–225
 laser milling 1:224
 mechanical machining
 green ceramic characteristics 1:223
 green ceramic cutting process 1:222–223
 parameters 1:223–224
 Griffith criterion 3:773–774
 Griffith energy principle 1:825
 Griffith equation 2:315
 Griffith-Irwin energy 1:829
 Griffith's energy release theory 1:824–825
 GRIN *see* gradients in refractive index (GRIN)
 grinding 3:704, 1:641–642, 1:122
 abrasive systems for 1:644
 fine 1:645
 machine 1:642–644
 manual 1:642
 planar 1:645
 growth factors (GF) 3:716–717
 and cytokines 3:718
 gyroid cellular structures (GCS) 1:391
 gyromagnetic resonance linewidth 3:201

H

HA *see* hydroxyapatite (HA)
 HAADF *see* High Angle Annular Dark Field
 (HAADF)
 half width full maximum (HWHM) 1:612
 halide glasses 2:591
 applications and prospects 2:616
 broadband transmission optical fibers
 2:616–617
 fiber lasers 2:617–618
 supercontinuum sources 2:618
 UV optical components 2:616
 monocomponent glasses 2:591–592
 monohalide glasses 2:592
 bromide glasses 2:598–600
 chloride glasses 2:597–598
 fluoride glasses 2:592

fluorohalide glasses 2:603
 heavy halide glasses 2:604–605
 iodide glasses 2:600–601
 polyhalide glasses 2:601–603
 outstanding material, glass as 2:591
 physical properties 2:608
 chemical durability 2:613
 composition-property relationships 2:608
 devitrification 2:613
 electrical properties 2:612–613
 optical properties 2:608
 thermal properties 2:611
 quick historical survey 2:591
 structure 2:614–615
 disordered packing and lacunar model
 2:615–616
 local order 2:614–615
 network model 2:615
 halides 3:105–106
 hand and wrist implants 3:535–536
 hard coatings
 low-energy ion bombardment versus
 structure and mechanical properties
 of 2:432–435
 mixing processes, formation of
 nanocomposite hard coatings by
 2:433–435
 post-deposition annealing, formation of
 nanocomposite hard coatings by
 2:435–437
 physical vapor deposition (PVD) methods
 for the preparation of 2:430–431
 energy delivered to the growing film
 2:431
 mixing processes 2:431–432
 structure and property control in 2:430
 hard ferrites
 hexaferrites 3:186–187
 hardness tests 1:718–719
 hardness to modulus (H/E) ratio 2:226
 “hard” superconductors 3:152
 see also type 2 superconductors
 Hasselman Unified Theory 1:871–872
 crack instability, regions of 1:872–873
 degree of damage 1:873–874
 fracture onset, thermal requirement for
 1:872
 propagation of the cracks 1:873
 Haynes282 1:464–465
 HAZ *see* heat affected zone (HAZ)
 HB *see* hydrogen bonding (HB)
 HCA layer *see* hydroxycarbonate apatite
 (HCA) layer
 hDFs *see* human dermal fibroblasts (hDFs)
 HEA *see* high entropy alloys (HEA)
 healthcare, application of glass-ceramics in
 2:716–717
 bioactive glass-ceramics for implant and
 bone tissue regeneration 2:716–717
 dental restoration 2:718
 hyperthermia treatments of cancerous
 tumors 2:717–718
 heat affected zone (HAZ) 2:393
 heat capacity 1:857–858, 1:863
 Debye model 1:858
 example 1:858–859

high temperature limit of 1:857–858
 heat energy 1:857
 heavy halide glasses 2:604–605
 bismuth, glasses based on 2:605
 cadmium, glasses based on 2:605
 lead, glasses based on 2:605
 zinc, glasses based on 2:605
 HEC *see* high entropy carbides (HEC)
 Henderson-Hasselbalch equation 1:158
 Hertzian contact tests 1:734–735
 heterogeneous phases, chemistry between
 1:31–32
 molten salt synthesis 1:33–34
 advantages, issues, applications 1:34–35
 process, overview of 1:33–34
 solvothermal synthesis 1:31–32
 advantages, issues, applications 1:32–33
 process, overview of 1:31–32
 hexaferrite materials 3:209–210
 hexaferrites 3:186–187
 hexametaphosphate (HMP) 1:106
 Hg-free lamp 3:89
 High Angle Annular Dark Field (HAADF)
 1:601
 high-density plasma dry-etching techniques
 3:98
 high entropy alloys (HEA) 1:461–463,
 1:464
 high entropy carbides (HEC) 2:422
 high entropy ceramics 2:422
 Higher Order Laue Zones (HOLZ) 1:595
 high level radioactive waste (HLW) 2:722
 immobilization of 2:763–765
 vitrification of 2:765–767
 highly-translucent 3Y-TZP 3:822
 high-performance ceramics and ceramic
 composites 2:225, 2:225–226, 2:226
 high performance fibers
 carbon fibers 2:310–312
 comparison of organic fiber properties 2:308*t*
 deposited fibers 2:309–310
 fiber development 2:304
 glass fibers 2:309
 molecular composition of 2:305*t*
 organic fibers 2:304–309
 oxide fibers 2:312
 SiC based fibers 2:312–313
 high-power diode rectifier 3:101
 high-pressure nitrogen 1:908
 high refractive index, making glasses with
 2:663–664
 high resolution analytical electron
 microscopy of ceramics and glasses
 analytical electron microscopy (AEM)
 1:600
 electron energy loss spectroscopy (EELS),
 principles of 1:610–616
 energy dispersive X-ray (EDX)
 spectroscopy, principles of 1:607–610
 energy filtered transmission electron
 microscopy (EFTEM), principles of
 1:610–616
 high spatially and energy resolved EELS,
 applications of 1:612–616
 integrated differential phase contrast
 (iDPC) 1:605–607

- scanning transmission electron microscopy (STEM), principles of 1:600–607
- high-resolution imaging in TEM (HRTEM) 1:596–597
- High Strain Rate Superplasticity (HSRS) 1:901
- high-temperature characterization of glasses and melts 1:689–690
- density 1:693–694
- measurement methods 1:694
- Archimedean method 1:694
- characterization procedure for density data 1:695–696
- levitation methods 1:695
- sessile drop method 1:694–695
- surface tension 1:696–697
- interpretation of melt surface tension 1:699–700
- levitation technique 1:698–699
- MBP method 1:697–698
- measurement methods 1:696–697
- ring method 1:697
- viscosity 1:690–691
- characterization procedure of viscosity data 1:692–693
- levitation method 1:691–692
- measurement methods 1:690–691
- rotating cylinder method 1:690–691
- high temperature co-fired ceramic substrates (HTCC) 3:439–440, 3:437, 3:439*t*, 3:441*f*
- boride HTCCs 3:443
- carbide HTCCs 3:442–443
- nitride HTCCs 3:442
- oxide HTCCs 3:440–442
- High-Temperature Reusable Surface Insulation tile (HRSI) 2:362
- high-temperature superconducting (HTSC) cuprates 3:156–157
- high-temperature superconductivity, materials for 3:380–383
- high thermal conductivity ceramics 2:165
- aluminum nitride 2:169–172
- intrinsic thermal conductivities 2:165–168
- silicon carbide 2:168–169
- silicon nitride 2:172–174
- lattice oxygen, effect of 2:174–178
- microstructure, effect of 2:174
- rare-earth oxide additives, effect of 2:178
- high-translucency zirconia (4Y, 5Y) grades 3:822
- biomedical grade 3Y-TZP 3:822
- highly-translucent 3Y-TZP 3:822
- super-translucent zirconia 3:823
- ultra-translucent zirconia 3:822–823
- high velocity flame spraying (HVOF) 3:733
- high velocity suspension flame spraying (HVSFS) 3:733–734
- spraying of metal doped calcium phosphate materials 3:746–747
- high-voltage power device structures 3:98
- Hi-Nicalon fiber 2:313
- HIP *see* hot isostatic pressing (HIP)
- hip resurfacing, oxide ceramic 3:519
- HLW *see* high level radioactive waste (HLW)
- HMAM *see* hydroxymethylacrylamide (HMAM)
- HMP *see* hexametaphosphate (HMP)
- hMSCs *see* human mesenchymal stromal cells (hMSCs)
- hole-transporting layer (HTL) 3:13
- HOLZ *see* Higher Order Laue Zones (HOLZ)
- Hoogsteen hydrogen bonds 1:466, 1:467*f*
- Hooke's law 3:369, 1:856–857
- host-sensitized luminescence 3:91–92
- hot forming 3:117
- hot isostatic pressing (HIP) 1:357, 2:111, 2:155, 1:419, 1:273–277, 2:173–174, 1:385–386, 1:256, 1:908, 3:117
- hot mounting 1:640
- hot pressing (HP) 2:152–153, 1:270–271, 1:356–357, 2:111, 2:342, 2:173–174, 2:11–14, 3:226–228, 3:117, 1:267
- densification mechanisms during 1:271–273
- technology 1:270–271
- Houskeeper seal 2:398
- HP *see* hot pressing (HP)
- hPMSC *see* human placenta-derived mesenchymal stem cell (hPMSC)
- HRSI *see* High-Temperature Reusable Surface Insulation tile (HRSI)
- HRTEM *see* high-resolution imaging in TEM (HRTEM)
- HS *see* hydrothermal sintering (HS)
- HSRS *see* High Strain Rate Superplasticity (HSRS)
- HTCC *see* high temperature co-fired ceramic substrates (HTCC)
- HTL *see* hole-transporting layer (HTL)
- HTSC cuprates *see* high-temperature superconducting (HTSC) cuprates
- human dermal fibroblasts (hDFs) 3:580
- human mesenchymal stromal cells (hMSCs) 3:805
- human placenta-derived mesenchymal stem cell (hPMSC) 3:580
- human umbilical vein endothelial cells (HUVEC) 3:723
- humectants 1:107
- HUVEC *see* human umbilical vein endothelial cells (HUVEC)
- HVOF *see* high velocity flame spraying (HVOF)
- HVPE *see* hydride vapor-phase epitaxy (HVPE)
- HVSFS *see* high velocity suspension flame spraying (HVSFS)
- HWFM *see* half width full maximum (HWFM)
- hybrid chemical processes 2:397
- anodic bonding 2:397
- gas-metal eutectic bonding 2:397
- hybridization 3:432, 1:224–225
- hybrid SPS 1:308–309
- hydraulic systems 1:138
- hydride vapor-phase epitaxy (HVPE) 3:74
- hydrogen bonding (HB) 1:441, 1:443
- HydroSet 3:642
- hydrothermal and solvothermal processes 1:4–5
- hydrothermal hot pressing *see* hydrothermal sintering (HS)
- hydrothermal sintering (HS) 1:311, 1:314*t*, 1:320–321
- hydrothermal synthesis
- algorithm for 1:63*f*
- approaches for 1:62
- evaluation of the solubility-pH diagrams in aqueous system 1:64
- expected powder characteristics 1:62–63
- nature of the material 1:62
- surface and colloid chemistry of the material in aqueous media 1:63–64
- thermodynamics and kinetic variables 1:64
- general principles and equipment 1:61–62
- mechanisms 1:66
- modeling 1:66–67
- powder synthesis methods 1:59
- powder synthesis via hydrothermal method 1:64–65
- additives 1:66
- preparation of gels 1:65
- selection of precursors 1:64–65
- undesired species, removal of 1:65–66
- recent activities in 1:59–61
- stages of 1:65*f*
- hydrothermal synthesis tree 1:61*f*
- hydroxyapatite (HA) 1:478, 3:628, 3:627–628, 3:676–677, 3:475, 3:477–478, 3:626, 3:631–632, 3:608–609, 3:602*f*, 3:669, 3:466–467
- hydroxyapatite cement 3:637
- hydroxycarbonate apatite (HCA) layer 3:479, 2:583, 3:614, 2:729–730
- hydroxylaluminum diacetate 1:108–109
- hydroxymethylacrylamide (HMAM) 1:151–152
- hyperthermia treatments of cancerous tumors 2:717–718
- hysteresis loops and magnetocrystalline anisotropy 3:183–186
- I**
- IBAD process *see* Ion Beam Assisted Deposition (IBAD) process
- ICDD *see* International Center for Diffraction Data (ICDD)
- ICRH *see* ion cyclotron resonance heating (ICRH)
- iDPC *see* integrated differential phase contrast (iDPC)
- IDTs *see* Inter-Digitated Transducers (IDTs)
- IF *see* indentation fracture (IF)
- IGF *see* insulin growth factor (IGF)
- IGF models *see* intergranular glassy film (IGF) models
- ignition 1:41
- IME *see* In-mold Embossing (IME)
- IML *see* In-mold Labeling (IML)
- immersion 2:754

- immersion media 3:643
 impact ionization (I.I.) 3:14–15
 Inclined Substrate Deposition process 3:174
 Inconel740 1:464–465
 indentation fracture (IF) 2:233
 indentation fracture resistance (IF-method)
 1:771–772, 1:772
 indentation of ceramics 1:718
 fracture toughness by indentation
 1:725–730
 hardness tests 1:718–719
 nanoindentation 1:720–721
 degraded surfaces 1:725
 measuring single grains 1:723
 measuring the intrinsic properties of
 coatings 1:722–723
 nanoindentation of ceramics 1:721–722
 Oliver and Pharr method 1:720–721
 porosity 1:724
 statistical nanoindentation 1:723–724
 weak interfaces 1:724–725
 spherical contact 1:719–720
 indentation strength (IS) method 1:771
 indirect powder bed fusion 1:385–386
 powder-based indirect laser sintering (p-
 iLS) 1:385–386
 indium gallium nitride 3:77–78
 InGaN/GaN LEDs 3:80–81
 indium nitride 3:76, 3:75*t*, 3:1
 induction sintering 1:292
 industrial applications, ceramic sensors for
 3:125
 catalytic combustion gas sensors
 3:126–127
 definitions of gas sensors and
 characteristic properties 3:125–126
 ion conducting metal oxides, gas sensors
 based on 3:127–130
 semiconducting metal oxides, gas sensors
 based on 3:130–132
 bulk-active SMOX 3:131–132
 surface-active SMOX 3:132–137
 inert bioceramics 3:476
 infrared (IR) spectroscopy 1:530, 2:691
 injectable bioceramic pastes and cements
 3:606–608
 injection molding process 1:181–183,
 1:181*f*
 inkjet printing (IP) 1:213
 inkjet 3D printing 3:654
 In-mold Embossing (IME) 1:184
 In-mold Labeling (IML) 1:184
 innovative manufacturing 3:508–509
 innovative processing methods, organics for
 1:108
 additive manufacturing (AM) processes
 1:109
 colloidal granulation 1:108
 direct casting forming methods 1:108–109
 inorganic “ceramic” adhesives 2:403–404
 inorganic metabolic phases 3:759
 insulating glasses 1:454–456
 insulators 2:718
 insulin growth factor (IGF) 3:657
 integrated differential phase contrast (iDPC)
 1:605–607, 1:605
 interaction constant 1:597
 interatomic bonding 1:442
 intercalation hosts and ion exchangers
 3:570–571
 interconnect 3:55–56
 interdigital electrode 3:427*f*
 Inter-Digitated Transducers (IDTs) 3:248
 intergranular glassy film (IGF) models
 1:450–453, 1:454*f*
 intergranular particles 2:240
 intermediate band approach 3:15–16
 Intermediate eXperimental Vehicle (IXV)
 2:362
 intermediate-range structure (IRO) 2:463
 intermediate temperature solid oxide fuel
 cell (IT-SOFCs) 3:441–442
 internal interdigital electrode actuator,
 structure of 3:427*f*
 International Center for Diffraction Data
 (ICDD) 1:553
 International Simple Glass (ISG) 2:535–536
 intragranular domain walls 3:219–220
 intragranular particles 2:240
 intrinsic material property, challenge from
 2:664–665
 intrinsic pyroelectrics 3:142–144, 3:146
 intrinsic thermal conductivity 1:860–862,
 2:165–168
 examples 1:861–862, 1:862–863
 iodide glasses 2:600–601
 cadmium iodide, glasses based on 2:601
 lead(II) iodide, glasses based on 2:601
 zinc iodide, glasses based on 2:601
 iodides 1:420
 Ion and Hall thrusters 2:370
 Ion Beam Assisted Deposition (IBAD)
 process 3:174
 ion conducting materials 3:1
 ion conducting metal oxides, gas sensors
 based on 3:127–130
 ion conducting solids 3:31–32
 application examples 3:32–33
 atomic switch/nano-ionics circuits
 3:34–36
 electrolysis of gaseous molecules 3:34
 gas separation 3:34
 lithium ion batteries 3:33–34
 NaS battery 3:34
 sensors 3:33
 solid oxide fuel cell (SOFC) 3:34, 3:35*f*
 benefits of 3:32
 three fundamental functions applicable to
 devices 3:32
 ion cyclotron resonance heating (ICRH) 2:370
 ionic conduction, classification of solids
 with 3:17–18
 ionic conduction in solids 3:18–20, 3:17*t*,
 3:18*t*
 fundamental migration mechanism of
 ions in solid 3:18–20
 point-defect type 3:20–21
 sub-lattice liquid type 3:18–20
 theory of ionic conduction in solids
 3:21–23
 ionic conductor, typical examples of 3:23–24
 cation conductors 3:26
 fluoride and chrollide ion conductors
 3:26–28
 lithium ion conductors 3:24–25
 Mixed Ionic-Electronic Conductors
 (MIEC) 3:30–31
 oxide ion conductors 3:28–30
 proton (or hydride ion) conductors
 3:25–26
 silver and copper ion conductors 3:23–24
 sodium ion conductors 3:24
 ionic two-sublattice models for ionic liquids
 1:505–507
 Ion-Polaron Effect 2:585
 IP *see* inkjet printing (IP)
 IPG *see* iron phosphate glasses (IPG)
 IRO *see* intermediate-range structure (IRO)
 iron based superconductors 3:156
 iron phosphate glasses (IPG) 2:585
 iron selenide thin films 3:160
 IR spectroscopy *see* infrared (IR)
 spectroscopy
 Irwin’s stress intensity factor theory
 1:824–825
 ISG *see* International Simple Glass (ISG)
 IS method *see* indentation strength (IS)
 method
 isolators and circulators 3:199–200
 isostatic pressing 1:138
 isovalent doping 3:351–352
 IT-SOFCs *see* intermediate temperature solid
 oxide fuel cell (IT-SOFCs)
 IXV *see* Intermediate eXperimental Vehicle
 (IXV)
- ## J
- JMAK theory *see* Johnson-Melch-Avrami-
 Kolmogorov (JMAK) theory
 Johnson-Melch-Avrami-Kolmogorov (JMAK)
 theory 2:613, 2:458–459, 2:459
 joining spectrum 2:393*f*
 joint time-frequency analysis (JTFA)
 3:413–414
 JTFA *see* joint time-frequency analysis (JTFA)
- ## K
- K₂O-SiO₂ glasses 2:468
 KDP *see* potassium dihydrogen phosphate
 (KDP)
 kevlar 29 2:307
 Kieu’s potential 2:528
 Kikuchi line pairs 1:593–594
 Kissinger equation 1:87–88
 knee joint replacements, oxide ceramic
 3:519–522
 ceramic knee replacements, development
 of 3:520–522
 knee joints 3:742
 knife coating process *see* tape casting of
 ceramics
 Knoop hardness 2:406, 2:407*f*
 knuckle epitope 3:718

- Kohlrausch–William–Watts (KWW)
equation 2:451–452, 2:452, 2:453t
- Kossel cones 1:593
- Krebs cycle 3:674
- KTN films *see* potassium tantalate niobate (KTN) films
- KWW equation *see*
Kohlrausch–William–Watts (KWW)
equation
- L**
- LACBED *see* large angle convergent beam
electron diffraction (LACBED)
- lacunar model 2:615–616
- laminar flow 1:174
- laminated object manufacturing (LOM)
1:212–213, 1:388
- lamination process, tape casting and
1:192–194
- LAMP *see* Large Area Maskless
Photopolymerization (LAMP)
- Landau–Lifschitz–Gilbert (L–L–G) equation
3:188–189
- lanthanides 2:774–776
- large angle convergent beam electron
diffraction (LACBED) 1:595–596
- Large Area Maskless Photopolymerization
(LAMP) 1:390–391
- LASER *see* light amplification by stimulated
emission of radiation (LASER)
- laser cutting 1:193–194
- Laser Engineered Net Shaping *see* direct
energy deposition (DED)
- laser induced forward transfer (LIFT)
techniques 3:59–60, 3:60f
solid state electrolytes, laser printing of
3:60–61
thick film electrodes, laser printing of
3:59–60
ultracapacitors, laser printing of 3:61–62
- laser melting (LM) 1:384
- laser milling 1:224
- laser processing of energy storage materials
3:1, 3:59
challenging issues 3:70–71
laser induced forward transfer (LIFT)
techniques 3:59–60, 3:60f
solid state electrolytes, laser printing of
3:60–61
thick film electrodes, laser printing of
3:59–60
ultracapacitors, laser printing of
3:61–62
- laser surface modification (LSM) 3:67–69
thick film electrodes, laser drying of
3:69–70
thin film electrodes, laser annealing of
3:69
3D electrodes, laser structuring for
3:67–69
- pulsed laser deposition (PLD) techniques
3:62–64
of anode thin films 3:64–65
of cathode thin films 3:63–64
of solid electrolyte films 3:65–67
- laser sintering (LS) 1:384
- laser technologies, ceramics for 3:2,
3:110–111
applications, beyond the state of the art
3:120–121
calcium fluoride 1:420, 3:119–120
dopant concentration 3:110
garnets 3:118–119
LuAG 3:119
YAG 3:118–119
MgAl₂O₄ 3:120
non-gain-media ceramics for lasers 3:120
absorbers 3:120
magneto-optical materials 3:120
optical transparency 3:111–113
processing technologies 3:113–115
densification methods 3:116–117
powders 3:114–115
shaping 3:115
production conditions 3:110
sesquioxides 3:119
shaping flexibility 3:110
size 3:118–119
spatial control of composition 3:117
thermal properties 3:113
- laser treatment 3:708–709
- LAS GCs *see* lithium alumino-silicate (LAS)
GCs
- lateral nanowire integrated nanogenerator
(LNG) 3:399
- lattice defect 3:378
- lattice diffusion 1:237
- Laue condition 1:560
- layered carbides sulfides and nitrides
1:19–21
- layer-structured perovskite thin films
low-temperature processing of 3:453–455
- LCD *see* liquid crystal display (LCD)
- LDM *see* low-temperature deposition
manufacturing (LDM)
- lead(II) bromide, glasses based on 2:600
- lead(II) chloride, glasses based on 2:598
- lead(II) iodide, glasses based on 2:601
- lead-free piezoelectric ceramics 3:358
applications 3:362–363
barium titanate 3:361–362
environmental and health concerns 3:363
processing 3:362
sodium bismuth titanate 3:360–361
sodium potassium niobate 3:358–360
- lead-free piezoelectric materials 3:432–433
- lead glass 2:654
- lead-lanthanum zirconate-titanate (PLZT)
1:417–418
- lead-magnesium niobate-lead titanate
(PMN-PT) 1:417–418, 3:231
- lead oxide (PbO) 2:655
- lead scandium tantalate (PST) 3:146
- lead zirconate titanate (PZT) system 1:852,
3:426–427, 3:429, 3:432–433, 1:214,
3:231, 3:233, 3:345, 3:4, 1:478
crystal structure of Pb(Zr,Ti)O₃ 3:348–349
piezoelectric applications 3:345–347
piezoelectric phenomenon 3:345
piezoelectric properties 3:347, 3:351–352
- acceptor doping 3:352
curie temperature 3:347
dielectric constant 3:347
dielectric loss factor 3:347
donor doping 3:352
electromechanical coupling factor 3:347
influence of dopants and microstructure
on electrical properties of PZT 3:355
isovalent doping 3:351–352
mechanical quality factor 3:347–348
microstructure 3:353–355
multiple-valency additives 3:353
piezoelectric constants 3:348
valence compensation, substitutions
with 3:352–353
synthesis routes 3:349–351
- lead-zirconium niobate - lead titanate
(PZN-PT) 1:417–418
- LEDs *see* light emitting diodes (LEDs)
- LEFM *see* linear elastic fracture mechanics
(LEFM)
- levitation methods 1:695, 1:698–699
- Li₂O–Al₂O₃–SiO₂ (LAS) compounds 2:54–55
- Li₂O–SiO₂ glasses 2:466
- LIBs *see* lithium-ion secondary batteries (LIBs)
- Lifshitz–Slyozov–Wagner (LSW) theory 1:263
- LIFT techniques *see* laser induced forward
transfer (LIFT) techniques
- light amplification by stimulated emission
of radiation (LASER) 3:708–709
- light emitters 3:247–248
- light emitting diodes (LEDs) 3:99, 3:85
- light propagation 2:682–684
amplifier fibers 2:686
bending losses 2:685–686
materials effects 2:685
absorption 2:685
scattering 2:685
transmission bandwidth 2:683–684
- lignosulfonates 1:109
- linear dielectrics and glasses ceramics
3:371–372
- linear elastic fracture mechanics (LEFM)
1:825–826, 1:762
- linear network dilation coefficient (LNDC)
2:636
- linear-parabolic rate law 2:440
- linear thermal expansion coefficient 2:652
- LIPON *see* lithium phosphorous oxynitride
(LIPON)
- liquid, defined 2:448
- liquid crystal display (LCD) 2:535,
3:245–247
- Liquid Phase Maldistribution (LPM) 1:170
- liquid phase methods 2:399–400
active metal brazing (AMB) 2:401–402
brazing of ceramics 2:402–403
inorganic “ceramic” adhesives 2:403–404
metallization 2:401
organic adhesives 2:400–401
sintered metal powder processing (SMPP)
2:401
soldering and brazing 2:401
soldering of ceramics 2:402
wetting, fundamentals of 2:400
- Liquid Phase Migration 1:170

- liquid-phase-sintered SiC (LPS-SiC) 2:150, 1:930
- liquid phase sintering (LPS) 1:258, 1:239–244, 2:15–16
- densification during 1:258–259
- contact flattening 1:259–261
- particle rearrangement 1:258–259
- pore filling 1:261
- description of matter transport
- mechanisms 1:240–244
- general phenomena of 1:258
- grain growth during 1:261–263
- grain growth mechanisms 1:244–245
- liquid rocket engines (LRE) 2:367–369, 2:366
- liquid/semi-liquid route infiltration,
- fabrication by 2:326–329
- impregnation by an organic precursor of the matrix (PIP) 2:329–331
- slurry – infiltration/hot pressing sintering (SI/HPS) route 2:326–329
- lithium aluminosilicate (LAS) GCs 2:279
- lithium dioxide (Li_2O) 2:655
- lithium disilicate 2:736
- lithium ion batteries 3:33–34
- lithium ion conductors 3:24–25
- lithium-ion secondary batteries (LIBs) 3:38
- lithium phosphorous oxynitride (LIPON) 3:65–66
- L–L–G equation *see*
- Landau–Lifschitz–Gilbert (L–L–G) equation
- LM *see* laser melting (LM)
- LNDC *see* linear network dilation coefficient (LNDC)
- LNG *see* lateral nanowire integrated nanogenerator (LNG)
- load-bearing segmental bones, emerging technologies for regeneration of 3:763–766
- load relaxation test 1:800–801
- Loeb model 2:168
- “Loewenstein Al avoidance” rule 1:482
- LOM *see* laminated object manufacturing (LOM)
- long fiber reinforced composites 1:904–906
- long-range Coulombic interactions 1:486
- Lorentzian curve 3:201
- low dispersion, making glasses with 2:665–667
- low-loss ceramics in mobile
- communications 3:375
- ceramic capacitors 3:386–387
- multilayer 3:387–389
- single-layer 3:386–387
- ceramic substrates 3:383
- low-temperature co-fired ceramics (LTCC) 3:383
- low-temperature co-fired ceramics (LTCCs), multilayer devices using 3:383
- multichip module (MCM) 3:383
- dielectric antenna 3:383–386
- dielectric resonator 3:375
- applications 3:378–379
- dielectric loss 3:376–378
- dielectric properties 3:375–376
- dielectric resonator material 3:375
- low-pressure injection molding (LP-CIM) 1:183
- low symmetry crystals 1:914–915
- nitrides 1:916–917
- silicon carbide 1:915–916
- superconductors 1:917–918
- α -alumina 1:914–915
- low-temperature co-fired ceramics (LTCCs) 2:298–299, 3:383, 3:443–444, 3:437, 3:439*t*, 3:444*f*, 3:445*t*
- additive-free LTCC 3:444–445
- composite LTCC 3:445–446
- multilayer devices using 3:383
- recent advancement in LTCC substrates 3:446
- low temperature degradation (LTD) 3:504, 3:553, 3:540, 3:545, 2:98
- low-temperature deposition manufacturing (LDM) 3:487
- Low-Temperature Reusable Surface Insulation (LRSI) 2:362
- low-temperature superconductor 3:151
- low thermal expansion ceramic and glass-ceramic materials 2:47
- ceramic materials 2:49–51
- aluminum titanate (tialite) 2:52
- cordierite 2:51–52
- NZP materials 2:54
- silica 2:49–51
- zirconyl phosphate 2:53–54
- glass-ceramic materials 2:54
- celsian 2:55–56
- cordierite 2:54
- $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (LAS) compounds 2:54–55
- pollucite 2:55
- thermal expansion 2:47–49
- LP-CIM *see* low-pressure injection molding (LP-CIM)
- LPM *see* Liquid Phase Maldistribution (LPM)
- LPS *see* liquid phase sintering (LPS)
- LPS-SiC *see* liquid-phase-sintered SiC (LPS-SiC)
- LRE *see* liquid rocket engines (LRE)
- LRSI *see* Low-Temperature Reusable Surface Insulation (LRSI)
- LS *see* laser sintering (LS)
- LSM *see* laser surface modification (LSM)
- LSW theory *see* Lifshitz-Slyozov-Wagner (LSW) theory
- LTCCs *see* low-temperature co-fired ceramics (LTCCs)
- LTD *see* low temperature degradation (LTD)
- LuAG 3:119
- lubricants 1:107, 1:168, 1:138
- Lucalox 2:146
- luminescent materials 3:89, 3:92
- lutetia 1:416
- lutetium(III) oxide 3:119
- M**
- M5 fiber 2:308
- MA *see* mechanical alloying (MA)
- machinable glass-ceramics 2:720
- chemical machining 2:720–721
- laser machining 2:721
- mechanical machining 2:720
- machine learning (ML) 1:441
- machining 3:704
- Mach numbers 2:361
- MACOR (Corning) 2:720
- Macor glass ceramic (MGC) 1:670
- macrophage colony-stimulating factor (m -CSF) 3:801, 3:801–802
- macroscale, modeling ceramics at 1:475–476
- MAE *see* mixed alkali effect (MAE)
- MAEE *see* Mixed Alkaline Earth Effect (MAEE)
- Magellan International 2:308
- magnesia 1:414, 2:485
- magnesia–partial stabilized zirconia (Mg-PSZ) 1:849, 1:818, 1:822
- magnesium diboride 3:154–156
- magnesium fluoride 1:420
- magnesium microparticles 3:681
- magnesium oxide (MgO) 2:655, 1:160
- magnetic beads 3:222, 3:222–223
- magnetic permeability in microwave range of frequencies 3:187–188
- permeability tensor 3:187–188
- damped precession 3:188–189
- dynamic demagnetizing aspect 3:196–197
- frequency dispersion of permeability spectrum 3:189–191
- modeling the dynamic permeability of polycrystalline ferrites 3:197
- shape-demagnetizing effects 3:191–196
- undamped precessions 3:187–188
- magnetic scaffold to boost tissue regeneration 3:766–769
- magnetic superexchange interaction 3:217
- magnetized ferrimagnetic materials, wave propagation in 3:197–198
- magnetized samples, characterization of 3:201–203
- magnetoelectric (ME) coupling 3:225
- magnetoelectric (ME) effect 3:405–406
- magnetoelectric antennas 3:235–236
- film bulk acoustic resonator (FBAR) 3:237–238
- nano-plate resonator (NPR) 3:236–237
- magnetoelectric compositions in composites 3:226–228
- magnetoelectric filters 3:234–235
- magnetoelectric inductor 3:233–234
- magnetoelectric sensor 3:231–233
- magneto-mechano-electric (MME) effect 3:405–406, 3:418–420, 3:391
- applications 3:421–422
- figure of merit 3:406–407
- types of ME transducers 3:406
- magneto-optical materials 3:120
- magnetoresistive sensors 3:220–221
- magnetorheological finishing 2:672, 2:673*f*
- manufacture of ceramics 1:1
- MAP *see* mixed-anion phosphates (MAP)
- MAP model *see* Mauro–Allan–Potuzak (MAP) model

- Mask-Image-Projection-based Stereo-lithography (MIP-SL) 1:390–391
- MAS NMR analysis of ceramics and glasses
basics of MRI 1:539–540
fluorine-19 NMR spectra 1:542
fundamental effects in NMR 1:537–539
chemical shielding 1:538
J coupling 1:538
relaxation 1:538
origin of NMR spectroscopy 1:536–537
phosphorus-31 NMR spectra 1:541
silica-29 NMR 1:541
solid state MAS NMR 1:540
spectrometer 1:539
- material extrusion 3:667–668
applications 3:668
- materials effects 2:685
absorption 2:685
scattering 2:685
- materials extrusion 1:388–390
ceramic material extrusion 1:388–390
- materials functionalization 3:489–491
- mathematical modeling, tissue engineering
scaffold by means of *see* tissue engineering scaffold by means of mathematical modeling
- Mauro–Allan–Potuzak (MAP) model 2:452
- maximum bubble pressure (MBP) method 1:697–698
- maximum energy release rate (MERR)
criterion 1:829, 1:829–830
- maximum tangential strain (MTSN)
criterion 1:828–829
- maximum tangential stress (MTS) criterion 1:826, 1:826–828
- maximum tensile stress (MTS) 1:825, 1:669
- MAX phases 1:444–445
attractive properties of 2:190–191
corrosion resistance in liquid metals 2:191–193
fracture toughness and damage tolerance 2:190–191
machinability 2:195
oxidation resistance and crack healing 2:191
stability at elevated temperature 2:193–195
formation and dissociation mechanisms 2:189–190
historical overview 2:182
structure of $M_{n+1}AX_n$ phases 2:182–185
i-MAX phases 2:186
o-MAX phases 2:185–186
single-site and double-site solid solutions 2:185
solid solutions and ordered MAX phases 2:185
ternary MAX phases 2:182–185
synthesis methods 2:187–188
MAX phase bulk ceramics 2:188–189
MAX phase coatings 2:188
MAX phase powders 2:187–188
- Maxwell model 2:451
- Maxwell's displacement current 3:399–400
- Maxwell's equations 3:281
- MBAM *see* N,N'-methylenebisacrylamide (MBAM)
- MBE *see* molecular beam epitaxy (MBE)
- MBGs *see* mesoporous bioactive glasses (MBGs)
- MBP method *see* maximum bubble pressure (MBP) method
- MB set *see* minimal basis (MB) set
- MCFC *see* molten carbonate fuel cells (MCFC)
- MCM *see* multichip module (MCM)
- MCP *see* multiphase coexistence point (MCP)
- MCPA *see* monocalcium phosphate anhydrous (MCPA)
- MCPM *see* monocalcium phosphate monohydrate (MCPM)
- m-CSF *see* macrophage colony-stimulating factor (m-CSF)
- MCVD *see* modified chemical vapor deposition (MCVD)
- MDEM *see* meshed discrete element method (MDEM)
- MDS *see* molecular dynamic simulations (MDS)
- MD simulations *see* molecular dynamics (MD) simulations
- measurement methods 1:694
Archimedean method 1:694
characterization procedure for density data 1:695–696
levitation methods 1:695
sessile drop method 1:694–695
- mechanical alloying (MA) 2:189, 2:9
- mechanical breakage/comminution 1:113–114
- mechanical fatigue 1:841
- mechanical machining
green ceramic characteristics 1:223
green ceramic cutting process 1:222–223
parameters 1:223–224
- mechanical properties of ceramics and glasses 1:704
- mechanical quality factor 3:394, 3:347–348
- mechanical spectrometer 1:707
- mechanobiological stimuli, utilization of micromechanics for quantification of 3:753–754
- medium-range structure (MRO) 2:463
- ME effect *see* magnetoelectric (ME) effect
- MEG *see* multiple exciton generation (MEG)
- Meissner phase 3:152
- melt-derived bioactive glasses 3:615–616
bioactive and resorbable phosphate glasses 3:617
bioactive borate glasses 3:616–617
bioactive silicate glasses 3:616
- melt electrospinning writing (MEW) 3:692
- melt processing 1:382
- melt-quenching (MQ) 2:701
- melt-quench simulations 1:484–485
cooling rate 1:485–486
procedure 1:484–485
- MEMS *see* micro-electromechanical systems (MEMS)
- MERR criterion *see* maximum energy release rate (MERR) criterion
- mesenchymal stem cells (MSC) 3:580, 3:604, 3:723, 3:465, 3:800
- mesenchymal stromal cells (MSCs) 3:801
- MESFETs *see* Metal Semiconductor FETs (MESFETs)
- meshed discrete element method (MDEM) 1:143, 1:143–144
- mesoporosity 1:429, 1:108
- mesoporous bioactive glasses (MBGs) 3:618, 3:690
- mesoporous non-oxides 1:22–23
- metakaolin-based, acid-activated geopolymers 1:425–426
- metakaolin-based, alkali-activated geopolymers 1:424–425
- metakaolin-based geopolymers versus alkali activated cements 1:426–428
- Metal Insulator Semiconductor Field Effect Transistor (MISFET) 3:244–245
- metal-insulator–SiC (MIS) prototype gas sensor structures 3:99
- metallic biomaterials 3:466
- metallic dies 1:299–300
- metallic glasses (MGs) 1:456–457
vitreloy ($Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$) 1:457–459
 Zr_xCu_{1-x} and $Zr_xCu_yAl_z$ 1:456–457
- metallization 2:401
- metal-organic chemical vapor deposition (MOCVD) 3:145–146, 3:74
- metal-organic deposition (MOD) 3:145–146
- metal-organic frameworks (MOFs) glasses 1:459–461
- metal-oxide-semiconductor field effect transistors (MOSFETs) 3:98
- metal-oxide-semiconductor technology 3:98–99
- Metal Oxide Varistors (MOV) 3:254
- Metal Semiconductor FETs (MESFETs) 3:247
- metal–SiC 3:99
- metal supported SOFCs (MS-SOFCs) 3:53
- metastable immiscibility 2:648–650
- methoxy poly (ethylene glycol) monomethacrylate (MPEGMA) 1:151–152
- methyl cellulose 1:223
- N,N'-methylenebisacrylamide (MBAM) 1:151–152
- MEW *see* melt electrospinning writing (MEW)
- MgAl₂O₄ 3:120
- MGC *see* Macor glass ceramic (MGC)
- MGFE *see* Mixed Glass-Former Effect (MGFE)
- MgO–SiO₂ system 2:470–472
- MGs *see* metallic glasses (MGs)
- MgTiO₃ synthesis for multilayer capacitors type I (example) 1:125–126
influence of rheology on the synthesis of MgTiO₃ 1:127
stabilization tests by electrostatic repulsion of MgO/TiO₂ slurry 1:125–126
steric repulsion stabilization 1:126–127
- MHDS *see* multi-head deposition system (MHDS)

- micro ceramic injection molding (MicroCIM) 1:183–184
- MicroCIM *see* micro ceramic injection molding (MicroCIM)
- microcracking 2:227
- microcrack toughening 2:96
- micro-electromechanical systems (MEMS) 3:397–398, 3:98, 3:370, 3:59
- microemulsion techniques 1:6
- micro in-mold labeling (MicroIML) 1:185
- Micro-Mirror-Arrays (MMA) 1:211
- “micro-nano” composites 3:496
- micro-opto-electro-mechanical system (MOEMS) 1:390–391
- microporous materials 3:571
- microsphere sintering 3:689
- microstructural development, strategies to control 1:352–353
 - composition modification 1:359–362
 - dopant elements addition to modify grain boundary energy 1:361–362
 - extra small particles addition at grain boundaries 1:362–363
 - optimal sintering parameters, choice of 1:353–354
 - controlled rate sintering 1:353–354
 - fast sintering 1:354–355
 - two-step sintering (TSS) 1:355–356
 - powder characteristics, choice of 1:352–353
 - pressure and/or electric field assisted sintering 1:356–357
 - flash sintering (FLASH) 1:358–359
 - hot isostatic pressing (HIP) 1:357
 - hot pressing (HP) 1:356–357
 - spark plasma sintering (SPS) 1:357–358
- microstructural development during ceramic processing 1:350–352
- microstructural developments in ceramics 1:1
- microstructural effects during mixed-mode fracture 1:837–838
- microstructural examination 1:634–635
 - cleaning 1:638
 - etching 1:646
 - before 1:646
 - chemical etching 1:647–648
 - electrolytic etching 1:648
 - less common etching methods 1:649
 - plasma etching 1:648–649
 - relief etching 1:647
 - removal of specimens from mounts 1:646–647
 - thermal etching 1:647
- grinding 1:641–642
 - abrasive systems for 1:644
 - fine 1:645
 - machine 1:642–644
 - manual 1:642
 - planar 1:645
- material characteristics and properties affecting choice of techniques 1:635
- mounting 1:638
 - cold mounting 1:640–641
 - hot mounting 1:640
 - initial considerations 1:638
 - mounting in clamps 1:639–640
 - post mounting operations 1:641
 - pre-treatments including pre-impregnation 1:638–639
 - taper sectioning 1:639, 1:639f
- polishing 1:641–642, 1:645–646
 - machine 1:642–644
 - manual 1:642
- sectioning 1:635–636
 - coolants/lubricants 1:638
 - preferred sectioning speeds and loads 1:636
 - sample support 1:637–638
 - sectioning blade 1:636–637
 - selection of volume to be sampled 1:635–636
- micro-structured fibers 2:684
- microstructures 1:819–821
- Micro-Tubular Fuel Cells (MTFCs) 1:175
- microwave characterization methods 3:200–201
 - demagnetized samples, characterization of 3:201
 - magnetized samples, characterization of 3:201–203
- microwave generators 1:332
- microwave magnetic losses 3:198–199
- microwave passive components using ferrites 3:197–198
 - antenna miniaturization 3:199
 - isolators and circulators 3:199–200
 - magnetized ferrimagnetic materials, wave propagation in 3:197–198
- microwave magnetic losses 3:198–199
- microwave sintering (MS) 2:111, 2:15, 1:292, 1:247
- microwave sintering of ceramics 1:327, 1:336
 - densification enhancement and lowered sintering temperature 1:336–338
 - finer microstructures 1:338–339
- microwave heating of ceramics 1:333–334
 - dielectric properties of ceramics 1:333–334
 - direct heating, inverted gradient, thermal runaway 1:334–335
 - indirect and hybrid heating with susceptors 1:335–336
 - thermal insulators and casketing 1:336
- microwaves and dielectric heating 1:327–328
 - dielectric heating 1:328–329
 - electromagnetic fields, propagation of 1:327–328
 - penetration depth 1:329–330
 - non-thermal effects 1:339–340
 - successful way for sintering almost all ceramics 1:336
 - towards applications in ceramics production 1:340
- waveguides and applicators 1:330–331
 - microwave generators 1:332
 - multimode cavity 1:332
 - temperature control in MW heating 1:332–333
 - tunable single mode cavity 1:331–332
- MIEC *see* Mixed Ionic-Electronic Conductors (MIEC)
- millimeter wave applications 3:380
- Mimix Bone Void Filler 3:642
- minerals 3:572
- miniaturization 3:432
- minimal basis (MB) set 1:442
- MIP-SL *see* Mask-Image-Projection-based Stereolithography (MIP-SL)
- MISFET *see* Metal Insulator Semiconductor Field Effect Transistor (MISFET)
- mixed alkali effect (MAE) 2:462, 2:468–469, 1:455–456
- Mixed Alkaline Earth Effect (MAEE) 2:469
- mixed-anion phosphates (MAP) 3:568
- Mixed Glass-Former Effect (MGFE) 2:584
- Mixed Ionic-Electronic Conductors (MIEC) 3:17, 3:30–31
- mixed-mode fracture 1:824–828
 - empirical criterion 1:832–833
 - energy-based criteria 1:829–830
 - maximum energy release rate criterion 1:829–830
 - strain-energy-density criterion 1:830–832
 - maximum tangential strain (MTSN) criterion 1:828–829
 - maximum tangential stress criterion 1:826–828
 - microstructural effects during 1:837–838
 - testing in 1:833–837
- Mixed Modifier Effect (MME) 2:469
- mixedness 1:171
- mixed polaron-ion phosphate glasses 2:585
- ML *see* machine learning (ML)
- MLAs *see* multilayer actuators (MLAs)
- MLCCs *see* multilayer ceramic capacitors (MLCCs)
- MLC electrode development process *see* multilayer chip (MLC) electrode development process
- MLCP *see* multilayer ceramic packages (MLCP)
- MLCVs *see* multilayer ceramic varistors (MLCVs)
- MLG *see* multilayered graphene (MLG)
- MLG *see* multilayer graphene (MLG)
- MMA *see* Micro-Mirror-Arrays (MMA)
- MME *see* Mixed Modifier Effect (MME)
- MME effect *see* magneto-mechano-electric (MME) effect
- MMJ *see* Multi Material Jetting (MMJ)
- MNCs *see* mononuclear cells (MNCs)
- mobile communications, low-loss ceramics in 3:375
 - ceramic capacitors 3:386–387
 - multilayer 3:387–389
 - single-layer 3:386–387
 - ceramic substrates 3:383
 - low-temperature co-fired ceramics (LTCC) 3:383
 - low-temperature co-fired ceramics (LTCCs), multilayer devices using 3:383
 - multichip module (MCM) 3:383
 - dielectric antenna 3:383–386
 - dielectric resonator 3:375

- applications 3:378–379
- dielectric loss 3:376–378
- dielectric properties 3:375–376
- dielectric resonator material 3:375
- MOCVD *see* metal-organic chemical vapor deposition (MOCVD)
- MOD *see* metal-organic deposition (MOD)
- modelling of ceramics and glasses 1:439, 1:439–440, 1:440
- modified chemical vapor deposition (MCVD) 2:687
- modified Lely process 3:95–96
- modified quasichemical model 1:504–505
- modified random network (MRN) model 2:462–463, 2:486
- modifier cations, role of 2:566–567
- modifier oxides 2:557
- MOEMS *see* micro-opto-electro-mechanical system (MOEMS)
- MOFs glasses *see* metal-organic frameworks (MOFs) glasses
- mold 1:147
- molecular beam epitaxy (MBE) 3:221–222
- molecular dynamics (MD) simulations 2:526–527
 - background 2:526–527
- boroxol rings and larger structural features 2:529
- development of empirical potentials for 2:527–528
- NMR spectra from 2:529
- short and medium range structure information 2:528–529
- simulated glass structure and properties, effect of cooling rate and system size on 2:528
- molecular dynamics (MD) simulations of glass structure 1:481
- atomistic MD simulations, salient features of 1:483–484
 - atom ensembles 1:484
 - classical and Ab initio calculations 1:483–484
- force fields 1:486
 - force fields accounting for polarization effects 1:487
 - long-range Coulombic interactions 1:486
 - short-range interactions 1:486–487
 - three-body interatomic potentials 1:487
- melt-quench simulations 1:484–485
 - cooling rate 1:485–486
 - procedure 1:484–485
- modeling of various glass systems 1:488–490
 - aluminosilicates 1:492–494
 - borates and borosilicates 1:494–495
 - phosphates and phosphosilicates 1:490–492
 - silicates 1:488–490
- oxide-based glass structures 1:481–482
 - glass building blocks 1:481–482
 - structural order 1:482–483
- short-range structural parameters, evaluation of 1:487–488
- molecular dynamic simulations (MDS) 3:290–291
- molten carbonate fuel cells (MCFC) 2:758
- molten salt, chemical tempering using 2:639–640
 - glass composition 2:639–640
 - salt bath composition and impurities 2:640–641
 - temperature and time 2:640
- molten salt-free chemical strengthening 2:641–644
 - electric field-assisted ion-exchange (EF-IE) 2:642–644
 - engineered stress profiles 2:644
- molten salt synthesis 1:33–34
 - advantages, issues, applications 1:34–35
 - process, overview of 1:33–34
- molybdenum 2:771–773
- monocalcium phosphate anhydrous (MCPA) 3:626
- monocalcium phosphate monohydrate (MCPM) 3:625
- monoclinic 1:818
- monocomponent glasses 2:591–592
- monohalide glasses 2:592
 - bromide glasses 2:598–600
 - bismuth tribromide, glasses based on 2:600
 - cadmium bromide, glasses based on 2:600
 - ditellurium bromide glasses 2:600
 - gallium(III) bromide, glasses based on 2:600
 - lead(II) bromide, glasses based on 2:600
 - zinc bromide, glasses based on 2:600
- chloride glasses 2:597–598
 - bismuth chloride, glasses based on 2:598
 - cadmium chloride, glasses based on 2:598
 - lead(II) chloride, glasses based on 2:598
 - TeX glasses 2:598
 - thorium(IV) chloride, glasses based on 2:598
 - zinc chloride, glasses based on 2:598
- fluoride glasses 2:592
 - fluoroaluminates 2:594–595
 - fluoroberyllates 2:592
 - fluoroindates 2:595–596
 - fluorozirconates 2:592–594
- fluorohalide glasses 2:603
 - fluorochloride glasses 2:603–604
 - halides in fluoride glasses 2:604
 - incorporation of halides in fluorozirconates 2:603
- heavy halide glasses 2:604–605
 - bismuth, glasses based on 2:605
 - cadmium, glasses based on 2:605
 - lead, glasses based on 2:605
 - miscellaneous 2:605–608
 - zinc, glasses based on 2:605
- iodide glasses 2:600–601
 - cadmium iodide, glasses based on 2:601
 - lead(II) iodide, glasses based on 2:601
 - zinc iodide, glasses based on 2:601
- polyhalide glasses 2:601–603
- monolithic ceramics, creep of 1:895
- monolithic components 1:208
- monolithic mullite ceramics 2:71
- monolithic restorations 3:504–506
- mononuclear cells (MNCs) 3:580
- Monte Carlo simulations 1:653f, 1:815–816
- morphotropic phase boundary (MPB) 3:394–395, 3:287, 3:332–333
- MOSFETs *see* metal–oxide–semiconductor field effect transistors (MOSFETs)
- mounting 1:638
 - initial considerations 1:638
 - methods 1:639–640
 - cold mounting 1:640–641
 - hot mounting 1:640
 - mounting in clamps 1:639–640
 - post mounting operations 1:641
 - pre-treatments including pre-impregnation 1:638–639
 - taper sectioning 1:639, 1:639f
- mounting crack 1:640
- MOVs *see* Metal Oxide Varistors (MOVs)
- MPB *see* morphotropic phase boundary (MPB)
- MPEAs *see* multi-principle element alloys (MPEAs)
- MPEGMA *see* methoxy poly (ethylene glycol) monomethacrylate (MPEGMA)
- MQ *see* melt-quenching (MQ)
- MRN model *see* modified random network (MRN) model
- MRO *see* medium-range structure (MRO)
- MS *see* microwave sintering (MS)
- MSC *see* mesenchymal stem cells (MSC); mesenchymal stromal cells (MSCs)
- M-Si-Al-O-N systems, representation of 2:124–127
 - with α' -SiAlON 2:126–127
- MS-SOFCs *see* metal supported SOFCs (MS-SOFCs)
- MTFCs *see* Micro-Tubular Fuel Cells (MTFCs)
- MTS *see* maximum tensile stress (MTS)
- MTS criterion *see* maximum tangential stress (MTS) criterion
- MTSN criterion *see* maximum tangential strain (MTSN) criterion
- M-type hexagonal ferrites 3:209
- Mulliken population analysis scheme 1:442
- mullite 2:442
- mullite ceramics 2:59
 - advanced 2:69–71
 - monolithic mullite ceramics 2:71
 - mullite fibers 2:71–74
 - application and use of 2:66–68
 - phase diagram of mullite 2:59–60
 - processing of 2:62–64
 - chemical route 2:64
 - melting route 2:63
 - plasma processing and others 2:64
 - sintering route 2:63
- properties of 2:64–66
 - electrical and thermal properties 2:66
 - mechanical properties 2:64–66
 - optical properties 2:66
- structure and crystallography of mullite 2:60–62

- mullite ceramics (*continued*)
 traditional 2:67–68
 pottery and whitewares 2:67–68
 refractories 2:68–69
 mullite fibers 2:71–74
 mullite glass-ceramics 2:713
 Mullite-Zirconia based composites
 1:281–283
 multiaxial tests used to determine tensile
 strength 1:754–755
 biaxial bending 1:756–757
 Brazilian test 1:754–755
 C-sphere test 1:755–756
 triaxial testing 1:757
 multichip module (MCM) 3:383
 Multi-component Ceramic Injection
 Molding (multi-C-CIM) 1:184
 multi-culture models 3:806
 multi-cutting compliance technique 1:789
 multiferroic composites 3:225–226
 applications 3:231–233
 film bulk acoustic resonator (FBAR)
 magnetoelectric antennas 3:237–238
 magnetoelectric antennas 3:235–236
 magnetoelectric filters 3:234–235
 magnetoelectric inductor 3:233–234
 magnetoelectric sensor 3:231–233
 nano-plate resonator (NPR)
 magnetoelectric antennas 3:236–237
 challenges and opportunities 3:238
 characterization and modeling 3:228–231
 magnetoelectric compositions in
 composites 3:226–228
 multi-head deposition system (MHDS)
 3:487
 multijunction tandem cells 3:13–14
 multilayer actuators (MLAs) 3:426, 3:429*f*,
 3:430*f*, 3:432
 actuator materials 3:426–429
 applications of 3:430
 Europe 3:432
 Japan 3:430–432
 USA 3:430
 Cu electrodes for ML actuators 3:433–434
 diesel injection valve 3:434
 ML structures 3:426
 Pb-free piezoelectric materials 3:432–433
 reliability of 3:429–430
 trends in ceramic actuators 3:426
 multilayer ceramic actuators 3:4
 multilayer ceramic capacitors (MLCCs)
 3:311, 3:448–449, 3:387–389, 1:189,
 1:192–193
 multilayer ceramic packages (MLCP) 1:189
 multilayer ceramic varistors (MLCVs)
 cofired with internal electrodes of base
 metal 3:277–278
 enhancement of nonlinearity by
 increasing P-type carriers at grain
 boundaries 3:278–279
 MLCVs cofired with internal electrodes
 of base metal 3:279
 nonlinearity of SrCoO₃-doped ZnO
 varistors Co-fired with base metal
 3:277–278
 ultralow-capacitance MLCVs with a
 discharge cavity 3:275–277
 using SrCoO₃-doped ZnO varistors 3:275
 multilayer chip (MLC) electrode
 development process 3:439
 multilayered graphene (MLG) 2:245–246
 multilayer glass-ceramic/ceramic composite
 substrates
 cold sintered/upside down/room
 temperature ceramic substrates
 (CSCC) 3:447–449
 high temperature co-fired ceramic
 substrates (HTCC) 3:439–440, 3:437,
 3:439*t*, 3:441*f*
 boride HTCCs 3:443
 carbide HTCCs 3:442–443
 nitride HTCCs 3:442
 oxide HTCCs 3:440–442
 historical development 3:437
 low temperature co-fired ceramics
 substrates (LTCC) 3:443–444, 3:437,
 3:439*t*, 3:444*f*, 3:445*t*
 additive-free LTCC 3:444–445
 composite LTCC 3:445–446
 recent advancement in LTCC substrates
 3:446
 tape casting and post-processing
 3:437–439
 ultra-low temperature co-fired ceramic
 substrates (ULTCC) 3:446–447,
 3:437, 3:439*t*, 3:447*t*, 3:447*f*, 3:448*f*
 multilayer graphene (MLG) 2:246, 3:65
 Multi Material Jetting (MMJ) 1:185
 multimode cavity 1:332
 multimode fibers 2:683
 multimorph 3:426, 3:427*f*
 multiphase coexistence point (MCP)
 3:361–362
 multiple exciton generation (MEG) 3:14–15
 multiple-valency additives 3:353
 multi-principle element alloys (MPEAs)
 1:463
 multi-wall carbon nanotubes (MWCNTs)
 2:244–245, 2:245, 2:233
 MWCNTs *see* multi-wall carbon nanotubes
 (MWCNTs)
- N**
 Na₂O-SiO₂ glasses 2:466–468
 Nabarro–Herring creep 2:448
 (Na,K)NbO₃ (NKN) systems 3:432–433
 nano beam diffraction (NBD) *see* nano
 beam electron diffraction (NBED)
 nano beam electron diffraction (NBED) 1:618
 nanocomposite hard coatings, formation of
 by mixing processes 2:433–435
 by post-deposition annealing 2:435–437
 nanocomposite material, definition of
 2:243–244
 nanocomposite nanogenerators (NNG) 3:399
 nanocomposites 1:902–903, 1:420
 advantage of 3:694–695
 nanocrystalline TiO₂ films 3:452–453
 nano electron diffraction (NBED) *see* nano
 beam electron diffraction (NBED)
 nanoindentation 1:720–721
 of ceramics 1:721–722
 degraded surfaces 1:725
 measuring single grains 1:723
 measuring the intrinsic properties of
 coatings 1:722–723
 Oliver and Pharr method 1:720–721
 porosity 1:724
 statistical nanoindentation 1:723–724
 weak interfaces 1:724–725
 nano-plate resonator (NPR) magnetoelectric
 antennas 3:236–237
 nanoscale, modeling ceramics at 1:476
 density functional theory (DFT) 1:476
 density functional theory (DFT) for
 piezoelectric ceramics 1:478–479
 calculation of piezoelectric charge
 tensor 1:478–479
 derivation of voltage constants 1:479
 elastic constants, calculation of (case
 study) 1:477–478
 finite differences 1:478
 strain controlled calculations 1:478
 geometry optimization 1:477
 predicting material properties 1:476–477
 nanoscale ceramic composites
 high-temperature properties of Al₂O₃-SiC
 nanocomposites 2:241
 processing and microstructure of
 Al₂O₃-SiC nanocomposites 2:240
 room-temperature properties of Al₂O₃-SiC
 nanocomposites 2:240–241
 nanostructured bulk materials 1:302
 nanotubes 1:741–743
 NaS battery 3:34
 NASICON (NA Super Ionic CONductor)
 3:569, 3:570*f*
 Nasicon nanopowders 1:76–77
 natural glasses 2:448
 natural polymers 3:684–685
 polyhydroxyalkanoates (PHA) 3:687
 polypeptides 3:684–685
 polysaccharides 3:685–687
 NBED *see* nano beam electron diffraction
 (NBED)
 NBO *see* non-bridging oxygen (NBO)
 NBT *see* notched ball test (NBT)
 NCPs *see* non-collagenous proteins (NCPs)
 NCSERR *see* non-coplanar strain energy
 release rate (NCSERR)
 NDE *see* non-destructive evaluation
 techniques (NDE)
 nebulization techniques 1:70
 aerosol generation 1:70
 modelization 1:70–71
 necking 2:676
 negative temperature coefficient ceramics
 (example) 1:127–128
 characterization of ceramics made from
 reground calcined powders 1:130–134
 effects of grinding on densification 1:130
 grinding of calcinated YCr_{0.5}Mn_{0.5}O₃
 1:128–130

- influence of raw material grinding times on $\text{YCr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ calcinated powders 1:128
- mixing conditions of the oxides 1:128
- negative thermal expansion ceramics 3:572
- network forming 2:454–455
- Neumann's principle 3:393
- neutral glass 2:534
- Nextel 720 fiber 2:316
- NHS *see* N-hydroxysuccinimide (NHS)
- N-hydroxysuccinimide (NHS) 3:722–723
- Ni-based superalloys 1:463–465
- Nicalon fibers 2:313
- Nippon Carbon 2:313
- nitrate glasses 1:532–533
- nitride HTCCs (high temperature co-fired ceramic substrates) 3:442
- nitride phosphors 3:1–2
- Ce- and Tb-doped rare-earth silicon oxynitrides 3:84–85
- rare-earth-doped sialon materials 3:84–85
- Eu-doped alkaline-earth silicon nitrides and oxynitrides 3:85–86
- Eu-doped aluminum-oxynitrides with β -alumina and other structures 3:86
- nitrides 1:413, 1:916–917, 1:443–444
- aluminum nitride 1:413–414
- cubic boron nitride (c-BN) 1:414
- SiALON 1:413
- silicon nitride 1:413
- nitrogen
- effect on hardness and Young's modulus 2:570–571
- effect on thermal properties 2:571
- changes in viscosity with nitrogen content 2:571
- effect of nitrogen content on glass molar volume and fractional glass compactness 2:573
- variation of Tg with N content 2:571–573
- nitrogen content
- structural implications of 2:573
- variations in optical properties with 2:574
- NNG *see* nanocomposite nanogenerators (NNG)
- Nomex 2:307, 2:305t
- non-ablative thermal protection materials 2:363–364
- non-bridging oxygen (NBO) 2:651, 2:521, 2:765, 2:462, 1:532, 2:484, 2:454–455, 2:455
- non-cavitation 2:115
- non-collagenous proteins (NCPs) 3:459
- non-collagenous proteins and cells 3:460–461
- non-coplanar strain energy release rate (NCSERR) 1:669
- non-crystalline/amorphous ZIFs (a-ZIFs) 1:459, 1:461
- non-crystalline material, defined 2:449
- non-destructive evaluation techniques (NDE) 2:322
- non-equilibrium materials 1:303–304
- non-equilibrium thermodynamic state, defined 2:449
- non-gain-media ceramics for lasers 3:120
- absorbers 3:120
- magneto-optical materials 3:120
- nonlinear optical materials 3:571–572
- non-magnetic borocarbides
- fermi surface in 3:164–166
- upper critical field for 3:166–167
- non-oxide advanced ceramics, synthesis of 1:14–15
- see also* oxide ceramics, synthesis of
- emergent techniques 1:17–23
- layered carbides sulfides and nitrides 1:19–21
- mesoporous non-oxides 1:22–23
- solar cells 1:19
- supercapacitors 1:18
- thermoelectrics 1:18
- solid-state approach 1:15
- solution-based wet chemistry techniques 1:15–17
- non-oxide ceramics
- creep and creep rupture of 1:908, 1:908–909
- oxidation and corrosion of 2:440
- oxidation of other nonoxide ceramics 2:442
- oxidation of polymer-derived silicon-based ceramics 2:442
- oxidation of pure silica-forming materials in other oxidants 2:441
- oxidation of pure silica-forming materials in oxygen 2:440–441
- oxidation of silica-forming materials in impurity-containing environments 2:441
- oxidation of silicon-based composites 2:442
- passive oxidation of silica-forming ceramics 2:440–441
- refractory oxide coatings on silica-forming ceramics 2:442
- ultra-high temperature ceramics (UHTCs), oxidation of 2:442–443
- volatilization of silica-forming ceramics 2:441–442
- non-oxide ceramics as biomaterials
- silicon carbide 3:530–531
- silicon nitride 3:526
- fabrication techniques 3:530
- SiALONs 3:526–527
- silicon nitride as a biomedical material 3:527–528
- silicon nitride biomedical devices 3:528–529
- surface chemistry of, on biological interactions 3:529–530
- non-oxide CMCs 2:264–267
- non-oxide fiber reinforcements 2:267–269
- nonradiative dielectric waveguide (NRD) 3:376
- non-sintering based techniques 2:16
- Norian CRS Bone Cement 3:641–642
- notched ball test (NBT) 1:770
- novel processing approaches 2:386
- NPR magnetoelectric antennas *see* nanoplate resonator (NPR)
- magnetoelectric antennas
- NRD *see* nonradiative dielectric waveguide (NRD)
- nuclear waste immobilization, glasses and glass-ceramics for 2:762
- alkalis and alkaline-earths, incorporation of 2:770–771
- glass-ceramic wasteforms 2:782–785
- high level radioactive waste (HLW) immobilization of 2:763–765
- vitrification of 2:765–767
- lanthanides and actinides, incorporation of 2:773–776
- actinides, case of 2:776–777
- lanthanides, case of 2:774–776
- long-term behavior of nuclear glasses 2:777–778
- resistance of nuclear glasses against alteration in aqueous environment 2:778–782
- self-irradiation resistance of nuclear glasses 2:777–778
- nature of highly radioactive waste and need for their immobilization 2:762–763
- transition metals, incorporation of 2:771
- chromium, case of 2:771
- molybdenum, case of 2:771–773
- technetium, case of 2:771
- zirconium, case of 2:771
- nuclear wastes, phosphate glasses for immobilization of 2:586
- nucleation 1:682, 3:459–460
- N-vinyl pyrrolidone (NVP) 1:151–152
- NVP *see* N-vinyl pyrrolidone (NVP)
- nylon fibers 2:304, 2:304–306
- NZP materials 2:54

O

- OA *see* open area (OA) osteoarthritis (OA); oxyapatite (OA)
- OAT *see* oxyacetylene torches (OAT)
- OC *see* osteocalcin (OC)
- OCP *see* octacalcium phosphate (OCP)
- octacalcium phosphate (OCP) 3:628–629, 3:626
- NMR spectroscopy of 3:629
- ODF *see* orientation distribution function (ODF)
- OHA *see* oxyhydroxyapatite (OHA)
- OIM *see* osteoimmunomodulation (OIM)
- OLCAO method *see* orthogonalized linear combination of atomic orbitals (OLCAO) method
- Oliver and Pharr method 1:720–721, 1:750
- open area (OA) 1:228
- OPG *see* osteoprotegerin (OPG)
- OPT *see* oxypropylene torches (OPT)
- optical fibers 2:681
- fiber drawing 2:687–688
- fiber fabrication 2:686
- light propagation 2:682–684
- amplifier fibers 2:686
- bending losses 2:685–686

- optical fibers (*continued*)
 loss and gain mechanisms in optical fibers 2:684–685
 materials effects 2:685
 transmission bandwidth 2:683–684
 preform fabrication 2:686–687
 silica fibers 2:681–682
 optical filtering 3:241
 optical glass 2:658
 achromatic lens 2:669–670
 challenges from optical design 2:660
 Abbe diagram 2:660
 challenge from an intrinsic material property: dispersion 2:664–665
 challenge from conventional lens making 2:660–663
 glass making, challenge from 2:667–668
 high refractive index, making glasses with 2:663–664
 low dispersion, making glasses with 2:665–667
 optical glass families 2:668–669
 transmission 2:668
 electrodynamics 2:658
 electromagnetic waves and their interaction with matter 2:658
 wave propagation in an ideal transparent refracting medium 2:659–660
 wave propagation in a weakly absorbing medium 2:660
 wave propagation in vacuum 2:658–659
 new materials and technologies 2:671–672
 magnetorheological finishing 2:672, 2:673f
 optoceramics 2:672–674
 precision molding 2:672, 2:673f
 secondary axial color correction by selecting glasses with anomalous partial dispersion 2:670–671
 two element lens system, primary axial color correction by 2:669–670
 optical transparency 3:111–113
 optimal sintering parameters, choice of 1:353–354
 controlled rate sintering 1:353–354
 fast sintering 1:354–355
 two-step sintering (TSS) 1:355–356
 optoceramics 2:672–674
 organic additives in ceramic processing 1:103
 binders and plasticizers 1:106
 copolymers acting as dispersant and binder 1:107
 dispersants 1:104–105
 electrostatic and electrosteric stabilization 1:105–106
 steric stabilization 1:105
 formulation concepts for ceramic processing 1:103–104
 innovative processing methods, organics for 1:108
 additive manufacturing (AM) processes 1:109
 colloidal granulation 1:108
 direct casting forming methods 1:108–109
 low environmental impact formulations 1:109–110
 porous ceramics, organic templates for 1:107–108
 types of 1:104
 organic adhesives 2:400–401
 organic fibers 2:304–309
 organic solar cells (OSCs) 3:12
 orientation distribution function (ODF) 1:555
 ORR *see* oxygen reduction reaction (ORR)
 orthogonalized linear combination of atomic orbitals (OLCAO) method 1:442, 1:443, 1:464–465
 orthopedic applications, oxide ceramics in 3:517–519
 ankle joint replacements, oxide ceramics in 3:522
 disk replacement, oxide ceramics in 3:523
 finger joint replacements, oxide ceramics in 3:522–523
 hip resurfacing, oxide ceramic 3:519, 3:520f
 knee joint, oxide ceramic replacements 3:519–522
 ceramic knee replacements, development of 3:520–522
 shoulder joint replacement, oxide ceramics in 3:522
 total hip replacements, oxide ceramic in 3:517–519
 orthopedics, new trends in ceramics for bio-active ceramics, current developments on 3:497–499
 bio-inert ceramics, new progresses on 3:494–495
 from alumina to plastic alumina-zirconia composites 3:494–495
 improved testing methods 3:497
 new implant designs 3:496
 towards pseudo-plastic ceramics 3:495–496
 state of the art 3:493–494
 orthophosphates 3:567–568
 orthotopic bone formation, models of 3:810–812
 calvarial/mandibular bone defects 3:810–812
 segmental bone defects 3:812–813
 OSCAR *see* osteoclast membrane immunoreceptors osteoclast-associated receptor (OSCAR)
 OSCs *see* organic solar cells (OSCs)
 osteoarthritis (OA) 3:760
 osteoblast and bone formation 3:800–801
 osteoblastic cell cultures 3:801
 osteoblastic and osteoclastic cells, co-culture models of 3:804–806
 osteoblasts 3:753
 osteocalcin (OC) 3:460–461
 osteochondral regeneration, biomimetic scaffolds for 3:760–761
 osteoclast membrane immunoreceptors osteoclast-associated receptor (OSCAR) 3:801–802
 osteoclasts and bone resorption 3:801–803
 osteoclastic cell cultures 3:802–803
 osteocytes 3:753, 3:465
 osteoimmunomodulation (OIM) 3:719, 3:726, 3:726–727
 osteonectin 3:460–461
 osteoporosis 3:657–658, 3:465–466
 osteoprotegerin (OPG) 3:753
 Osterix 3:800
 Ostwald ripening theory 1:263, 2:178, 1:367–368
 outside vapor deposition (OVD) 2:687
 OVD *see* outside vapor deposition (OVD)
 OxGCs *see* oxyfluoride glass-ceramics (OxGCs)
 oxidation catalysts 3:571
 oxide-based glass structures 1:481–482, 1:481
 glass building blocks 1:481–482
 structural order 1:482–483
 oxide ceramics 3:476
 and non-oxide ceramics 2:1, 2:2
 oxide ceramics, synthesis of 1:2
see also non-oxide advanced ceramics, synthesis of
 chemical-based solution approaches 1:2–14
 colloidal precipitation 1:4
 emergent techniques 1:6–14
 biomaterials 1:11–14
 electrocatalysts 1:8
 supercapacitors 1:6
 hydrothermal and solvothermal processes 1:4–5
 intercalation and ion exchange 1:4
 microemulsion techniques 1:6
 Pechini process 1:5–6
 sol – gel method 1:3–4
 solid-state approach 1:2
 thermal decomposition of precursors 1:5
 topochemical methods 1:5
 oxide ceramics for biomedical applications 3:511–512
 alumina 3:512–513
 alumina biocompatibility 3:513
 chemical-physical and mechanical properties 3:513
 wear of alumina 3:513–514
 development 3:511–512
 orthopedic applications 3:517–519
 ankle joint replacements 3:522
 disk replacement 3:523
 finger joint replacements 3:522–523
 hip resurfacing 3:519
 knee joint replacements 3:519–522
 shoulder joint replacement 3:522
 total hip replacements 3:517–519
 zirconia 3:514–515
 alumina-zirconia composites 3:516–517
 chemical-physical and mechanical properties 3:514–515
 stability in zirconia ceramics 3:515–516
 zirconia biocompatibility 3:516
 oxide CMCs 2:267–269
 ceramic injection molding (CIM) 2:271
 fiber spraying process 2:272–274
 impregnation of short fiber preforms 2:271–272

non-oxide fiber reinforcements 2:267–269
oxide fiber reinforcement 2:269–271
oxide eutectics 2:216
 microstructure 2:216
 preparation 2:216–218
oxide fiber precursor chemistry 2:314
 basic aluminum salts 2:314
 polymeric aluminosilicates 2:314–315
oxide fiber reinforcement 2:269–271
oxide fibers 2:312
oxide glasses 2:454
oxide HTCCs (high temperature co-fired ceramic substrates) 3:440–442
oxide ion conductors 3:28–30
oxide reduction methods 2:9–10
oxides 1:414, 3:106–108, 3:740–741, 1:443–444
 binary oxides 1:414
 beryllia 1:414
 magnesia 1:414
 zirconia 1:414–415
 complex oxides 1:416–417
 garnets 1:417
 pyrochlores 1:417
 spinel 1:416–417
 ferroelectrics 1:417–418
 complex-anion and other oxides 1:418
 conducting oxides 1:418
 perovskites 1:417–418
 sesquioxides 1:415
 alumina 1:415
 lutetia 1:416
 scandia 1:416
 yttria 1:415–416
oxide solid electrolytes 3:45–47
oxyacetylene torches (OAT) 2:21
oxyapatite (OA) 3:738
oxyfluoride glass-ceramics (OxGCs) 2:701
oxygen and Qⁿ speciation, relationship between 2:463–465
oxygen ions 3:217
oxygen reduction reaction (ORR) 1:76
oxygen triclusters 2:462
oxyhydroxyapatite (OHA) 3:738
oxynitride glass 2:569, 2:556–557, 2:557
 crystallization of, to form glass-ceramics 2:576–577
 effect of fluorine on properties of 2:576
 effect of nitrogen on hardness and Young's modulus 2:570–571
 effect of nitrogen on thermal properties 2:571
 changes in viscosity with nitrogen content 2:571
 effect of nitrogen content on glass molar volume and fractional glass compactness 2:573
 variation of T_g with N content 2:571–573
effects of cation composition on properties of 2:574
 rare earth (RE) oxynitride glasses 2:574–575
 RE–Si–Mg–O–N glasses 2:575–576
 Y–Si–Al–O–N glasses 2:574
formation and structure 2:555

Al bonding and coordination in M–Si–Al–O–N glasses 2:565–566
early research on nitrogen solubility in commercial glasses 2:555–556
fluorine, effect of 2:560–561
FTIR spectroscopy 2:561–562
glass formation in oxynitride systems and their representation 2:557–561
modifier (M) cations, role of 2:566–567
Raman spectroscopy 2:563–565
Si-based oxynitride glasses, preparation of 2:556–557
silicates and aluminosilicates, substitution of nitrogen into 2:556
solid state magic angle spinning (MAS) nuclear magnetic resonance (NMR) 2:562–563
X-ray photoelectron spectroscopy 2:562
initial studies of effects of nitrogen on properties of 2:569–570
nitrogen content, structural implications of 2:573
potential applications for 2:577–578
structural considerations in relation to properties 2:570
subcritical crack growth (SCG) resistance of 2:573–574
variations in optical properties with nitrogen content 2:574
oxynitrides 1:418–419
 ALON 1:418–419
oxypropylene torches (OPT) 2:21

P

PA *see* polyamide (PA)
PAA *see* polyacrylic acid (PAA)
pair distribution functions (PDF) method 1:558–559
PAM *see* pressure-assisted microsyringe (PAM)
PAN fibers *see* polyacrylonitrile (PAN) fibers
para-aramids 2:307
parallel plate viscometry (PPV) 2:544
parathyroid hormone (PTH) 3:474
Paris law 1:845–846
Parker Solar Probe 2:362–363
Parker Space Probe 2:365
partial bond order (PBO) 1:465
partial bond order density (PBOD) 1:442, 1:445–446, 1:446, 1:444t, 1:447t
partially stabilized zirconia (PSZ) 3:514–515, 3:515, 2:228, 1:820
partial sintering 1:342
 of bioceramic powders 3:605
particle- and platelet-reinforced composites 2:231–232
particle rearrangement 1:258–259
particle reinforced composites 1:901–902
particle statistics 1:552
particulate leaching (PL) 3:689
paste formulation 1:163, 1:168–170
 basic formulation 1:163–164
 designing paste formulations 1:165–166
 particle size distribution 1:165–166
general characterization 1:168–170
 air bubble inclusion 1:170–171
 binding liquid and paste characteristics 1:170
 Liquid Phase Migration 1:170
 mixedness 1:171
 wall slip 1:170
 yield stress 1:170
manufacturing cycle 1:163
 requirements 1:163
mixing 1:166–167
particle packing 1:164–165
paste additives 1:167–168
paste behavior in mathematical expressions 1:171–172
patterned etching of SiC 3:98
Pauli exclusion principle 3:217–218
Pb, glasses based on 2:605
PBC theory *see* periodic bond chain (PBC) theory
PBF *see* powder bed fusion (PBF)
PBMCs *see* peripheral blood monocytes (PBMCs)
PBO *see* partial bond order (PBO); poly(*p*-phenylene benzobisoxazole) (PBO)
PBOD *see* partial bond order density (PBOD)
PBO fiber *see* *p*-phenylene benzobisoxazole (PBO) fiber
PBS *see* phosphate-buffered saline (PBS)
PBTCa *see* 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCa)
PCBs *see* printed circuit boards (PCBs)
PCEs *see* power conversion efficiencies (PCEs)
PCVD *see* plasma chemical vapor deposition (PCVD)
PDB *see* protein data bank (PDB)
PDCs *see* polymer-derived ceramics (PDCs)
PDF method *see* pair distribution functions (PDF) method
PDL *see* periodontal ligament (PDL)
PDLLA *see* poly (D, L-lactic) acid (PDLLA)
pDNA *see* plasmid DNA (pDNA)
Pechini process 1:5–6
pectin 3:686–687
PED *see* precessed electron diffraction patterns (PED); precision extruding deposition (PED)
PEEK *see* polyether ether ketone (PEEK)
PEG *see* polyethylene glycol (PEG)
PEHZ *see* poly(ethynyl)hafnizane (PEHZ)
PEI *see* polyethylene imine (PEI)
Pei chart 1:458
pellistors 3:127
PEMFC *see* proton-exchange membrane fuel cells (PEMFC)
PEN *see* polyethylenene naphthalate (PEN)
penetration depth 1:329–330, 3:152, 1:562–563
PEN fiber *see* polyethylenenaphthalate (PEN) fiber
PENGs *see* piezoelectric nanogenerators (PENGs)
PEO *see* poly(ethylene oxide) (PEO)
perfect glasses 2:627
perfluoroalkoxy (PFA) 3:416

- periodic bond chain (PBC) theory 2:131
 periodontal diseases, biomimetic scaffolds
 to treat 3:761–763
 periodontal ligament (PDL) 3:762–763
 periodontitis 3:762
 peripheral blood monocytes (PBMcs) 3:805
 permanent magnets 3:206
 market 3:207–209
 materials 3:206
 properties 3:206–207
 permeability tensor 3:187–188
 damped precession 3:188–189
 dynamic demagnetizing aspect 3:196–197
 frequency dispersion of permeability
 spectrum 3:189–191
 polycrystalline ferrites, modeling the
 dynamic permeability of 3:197
 shape-demagnetizing effects 3:191–196
 undamped precessions 3:187–188
 perovskite ferroelectrics 3:372
 perovskites 1:417–418
 perovskite solar cells (PeSCs) 3:12
 perovskite solid-solution thin films
 UV-processing of 3:455–456
 perovskite structure 3:348f
 PERV *see* porcine endogenous retrovirus
 (PERV)
 PeSCs *see* perovskite solar cells (PeSCs)
 PET *see* polyethylene terephthalate (PET)
 petriugic process 2:729
 PFA *see* perfluoroalkoxy (PFA)
 PFT test *see* post-fracture tensile (PFT) test
 PGA *see* poly glycolic acid (PGA)
 PGM technique *see* precision glass molding
 (PGM) technique
 PHA *see* polyhydroxyalkanoates (PHA);
 precipitated hydroxyapatite (PHA)
 phase distortion function 1:597
 phase inversion techniques 2:386
 phase migration 1:174–175
 phase object approximation 1:597
 phase separation 1:90–91
 phase transformation 1:685, 1:818
 PHB *see* poly-3-hydroxybutyrate (PHB);
 poly- β -hydroxybutyrate (PHB)
 phosphate anions 3:567–568
 mixed-anion phosphates (MAP) 3:568
 orthophosphates, (di)hydrogen
 phosphates 3:567–568
 polyphosphates 3:568
 pyrophosphates, diphosphates 3:568
 ultraphosphates 3:568
 phosphate bioactive glasses 3:680–681
 phosphate-buffered saline (PBS) 3:527
 phosphate glass-ceramic materials
 2:752–753
 phosphate glasses 2:749–750, 1:533–534,
 3:617
 basic structure of 2:581
 binary and ultraphosphate glasses
 2:582–583
 in biomedicine 2:583
 electrical and optical properties of
 2:583–584
 fluoride phosphate/fluorophosphate (FP)
 glasses 2:585–586
 for immobilization of nuclear wastes
 2:586
 ionic and electronic (polaronic)
 conductivity in 2:584–585
 mixed polaron-ion 2:585
 phosphate dosimeters 2:586
 rare-earth ion host matrices 2:585
 uses 2:580–581
 vitreous P_2O_5 ($v-P_2O_5$) 2:581–582
 phosphate materials 3:569–570
 biomaterials 3:572–573
 fast ion conductors 3:569–570
 ferroics 3:571
 intercalation hosts and ion exchangers
 3:570–571
 microporous materials 3:571
 minerals 3:572
 negative thermal expansion ceramics
 3:572
 nonlinear optical materials 3:571–572
 oxidation catalysts 3:571
 phosphors and laser materials 3:572
 phosphates 1:490–492, 3:567, 1:443–444
 anions 3:567–568
 mixed-anion phosphates (MAP) 3:568
 orthophosphates, (di)hydrogen
 phosphates 3:567–568
 polyphosphates 3:568
 pyrophosphates, diphosphates 3:568
 ultraphosphates 3:568
 characterization of 3:569
 materials 3:569–570
 biomaterials 3:572–573
 fast ion conductors 3:569–570
 ferroics 3:571
 intercalation hosts and ion exchangers
 3:570–571
 microporous materials 3:571
 minerals 3:572
 negative thermal expansion ceramics
 3:572
 nonlinear optical materials 3:571–572
 oxidation catalysts 3:571
 phosphors and laser materials 3:572
 solid phosphates, preparation of 3:568
 sol-gel methods 3:569
 solution and hydrothermal methods
 3:568
 thermal treatments and flux growth
 3:568–569
 vapor transport 3:569
 phosphides 1:414
 2-phosphonobutane-1,2,4-tricarboxylic acid
 (PBTCA) 1:105–106
 phosphor efficiency 3:89, 3:92
 phosphors 2:137, 3:2, 3:89
 doping ion and conduction band states,
 absorption involving 3:89–90
 doping ion and valence band states,
 absorption involving 3:90–91
 host-sensitized luminescence 3:91–92
 and laser materials 3:572
 rare earth center, excitations in 3:89
 Phosphorus-31 NMR Spectra 1:541–542,
 1:541
 phosphosilicates 1:490–492
 photocatalytic reaction 3:452
 photoluminescence (PL) 3:91–92, 3:91f
 photoluminescence excitation (PLE)
 3:91–92, 3:91f
 photon multiplication 3:91
 photovoltaics (PV) 3:1
 advanced inorganic materials 3:5
 crystalline silicon 3:8–9
 devices 3:5–7
 emerging materials and cells concepts
 3:14–15
 all-silicon tandem cells approach 3:16
 intermediate band approach 3:15–16
 multiple exciton generation (MEG)
 3:14–15
 figures of merit 3:7–8
 multijunction tandem cells 3:13–14
 thin films 3:9–10
 from amorphous to polycrystalline
 silicon films 3:9–10
 from organic to hybrid structures
 3:12–13
 thin-film CdTe, copper indium selenide,
 its alloys and related chalcopyrites
 3:10–12
 transparent contact oxides based
 contacts chalcopyrites 3:13
 phthalates 1:106
 pH value 1:118
 physical properties of ceramics and glasses
 1:704
 physical vapor deposition (PVD) 2:64,
 2:386
 for the preparation of hard coatings
 2:430–431
 energy delivered to the growing film 2:431
 mixing processes 2:431–432
 physiological-like solution (PLS) 3:643
 PI *see* polymer impregnation (PI)
 piezoelectric applications 3:345–347
 piezoelectric ceramics 3:293
 piezoelectric charge tensor, calculation of
 1:478–479
 piezoelectric constants 3:348
 piezoelectricity 3:391, 3:393–396
 energy harvesting
 figure of merit for 3:397–398
 selection of piezoelectric materials for
 3:396–397
 impedance matching 3:398
 piezoelectric nanogenerator 3:398–399
 geometrical configuration 3:399
 types of piezoelectric materials 3:394–396
 ceramic-based piezoelectric materials
 3:394–396
 piezoelectric single crystals 3:396
 polymer-based piezoelectric materials
 3:396
 textured piezoelectric ceramics 3:396
 piezoelectric material, working mechanism
 of 3:393f
 piezoelectric nanogenerators (PENGs)
 3:398–399, 3:409, 3:391, 3:420–421,
 3:399f
 ceramic based PENGs 3:409–412
 geometrical configuration 3:399

- polymer-based PENGs 3:412–413
 ZnO based PENGs 3:409
 piezoelectric phenomenon 3:345
 piezoelectric properties 3:347
 curie temperature 3:347
 dielectric constant 3:347
 dielectric loss factor 3:347
 electromechanical coupling factor 3:347
 mechanical quality factor 3:347–348
 piezoelectric constants 3:348
 piezoelectrics 3:426, 3:426–427
 applications 3:291–293
 basic concepts of 3:282–284
 piezoelectric single crystals 3:396
 piezoelectric strain constant 3:394
 piezoelectric transducers 3:370
 piezoelectric voltage constant 3:394
 piezo/triboelectric nanogenerators
 applications 3:420–421
 piezotronic effect 3:78–79
 PIM *see* polarized ion models (PIM)
 pin-on-three-balls (POB) technique
 1:815–816
 PIP *see* polymer infiltration and pyrolysis (PIP); precursor/polymer infiltration and pyrolysis (PIP)
 PIP joint of hand *see* proximal interphalangeal (PIP) joint of hand
 PISA *see* pyrolytic carbon interposition shoulder arthroplasty (PISA)
 piston extrusion 1:162
 PL *see* particulate leaching (PL); photoluminescence (PL)
 PLA *see* poly lactic acid (PLA)
 planetary mills 1:122–123
 plasma arc melting 2:144
 plasma chemical vapor deposition (PCVD) 2:687
 plasma etching 1:648–649
 plasmid DNA (pDNA) 1:11–14
 plastic flow 1:237
 plasticizers 1:106, 1:190, 1:168, 1:138
 platelet-rich plasma (PRP) 3:474
 PLE *see* photoluminescence excitation (PLE)
 PLGA *see* poly lactic-co-glycolide (PLGA)
 PLZT *see* lead-lanthanum zirconate-titanate (PLZT)
 PMAA *see* polymetacrylic acid (PMAA)
 PMMA *see* polymethyl methacrylate (PMMA)
 PMNCs *see* primary human polymorphonuclear cells (PMNCs)
 PMN-PT *see* lead-magnesium niobate-lead titanate (PMN-PT)
 PM processes *see* powder metallurgy (PM) processes
 PNRs *see* polar nanoregions (PNRs)
 POB technique *see* pin-on-three-balls (POB) technique
 point-defect type 3:20–21
 Poisson's ratio 1:829, 1:745, 1:747, 1:463, 1:443
 polarimeters 2:627
 polariscopes 2:627
 polarization 3:78
 polarized ion models (PIM) 1:487
 polar nanoregions (PNRs) 3:290
 Polder-Smit effect 3:196–197, 3:197f
 polishing 3:706–708, 1:641–642, 1:645–646
 machine 1:642–644
 manual 1:642
 pollucite 2:55
 poly{2,6-dimidazo [4.5-b:4'5-e] pyridinylene-1,4 (2,5-dihydroxy) phenylene} (PIPD) M5 2:305t
 poly-3-hydroxybutyrate (PHB) 3:687
 poly- β -hydroxybutyrate (PHB) 3:480
 poly(ϵ -caprolactone) 3:480
 polyacrylate adsorption 1:105
 polyacrylic acid (PAA) 1:120, 1:120–122, 1:122, 1:106, 3:412
 polyacrylonitrile (PAN) fibers 2:304, 2:310–311, 2:311f, 2:354
 polyamide (PA) 2:304, 2:304–306
 polyamide 6 (Nylon 6) 2:305t
 polyamide 6/6 (Nylon 6.6) 2:305t
 polycermet 1:320
 polycrystalline ferrites
 basic properties of 3:183, 3:184f
 modeling the dynamic permeability of 3:197
 polycrystalline oxide ceramics and ceramic composites without glass phase 3:791–792
 polycrystalline Si₃N₄ 2:110–112
 development of Si₃N₄ microstructure 2:111–112
 effect of rare-earth oxides on the microstructure development 2:112
 grain boundary phases 2:112
 self-reinforced microstructure 2:112–113
 textured microstructure 2:113
 functional properties 2:116
 biological properties 2:116
 thermal conductivity 2:116
 high temperature mechanical properties 2:114–115
 creep resistance 2:115–116
 oxidation resistance 2:114–115
 room temperature mechanical properties 2:113–114
 fracture toughness 2:114
 hardness 2:113–114
 strength 2:114
 polydimethylsiloxane (PDMS) 3:411, 3:411–412
 poly(D, L-lactic acid) (PDLLA) 3:743, 3:681–682
 tricalciumphosphate (TCP) coatings on 3:743–744
 polyelectrolytes 1:106
 polyester fibers 2:304–306
 polyether ether ketone (PEEK) 3:527–528
 poly(ethylene oxide) (PEO) 2:8
 polyethylene terephthalate (PET) 2:304–306
 polyethylene glycol (PEG) 1:223, 3:452
 polyethylene imine (PEI) 1:105
 polyethylenene naphthalate (PEN) 2:305t, 2:304–306
 polyethylene terephthalate (Polyester) 2:305t
 poly(ethynyl)hafnizane (PEHZ) 2:340
 poly glycolic acid (PGA) 3:480
 polyhalide glasses 2:601–603
 polyhydroxyalkanoates (PHA) 3:687
 poly lactic acid (PLA) 3:480
 poly lactic-co-glycolide (PLGA) 3:480
 polymer-based biocomposites 3:674
 polymer-based PENGs 3:412–413
 polymer-based piezoelectric materials 3:396
 polymer bead 3:651
 polymer-derived ceramics (PDCs) 1:93
 flow diagram for the processing of 1:94f
 microstructural feature of 1:97–99
 processability of preceramic polymers-functional 1:99–100
 various microstructures identified in 1:97f
 polymer-derived glass-ceramics 2:740
 polymer-derived silicon-based ceramics, oxidation of 2:442
 polymeric aluminosilicate 2:314–315
 polymeric binders 1:107
 polymeric-ceramic composites 3:598
 polymeric molds 1:149
 polymer impregnation (PI) 2:329
 polymer infiltration and pyrolysis (PIP) 2:283
 polymers 3:480, 3:373
 polymetacrylic acid (PMAA) 1:106
 polymethyl methacrylate (PMMA) 1:147, 3:742, 1:348, 3:606, 3:480, 3:684, 1:344
 poly(*m*-phenylenediamine-isophthalamide) 2:305t
 poly-paraphenylene/3,4-diphenylether ter-ephthalamide (Technora) 2:305t
 polypeptides 3:684–685
 polyphosphates 1:106, 3:568
 poly(*p*-phenylene benzobisoxazole) (PBO) 2:305t, 2:307
 poly(*p*-phenylene terephthalamide) 2:305t, 2:307
 poly(propyl)hafnizane (PPHZ) 2:340
 poly(propylene oxide) (PPO) 2:8
 polypropylene carbonates (PPC) 3:438
 polypropylene fumarate (PPF) 3:683, 3:692
 polysaccharides 3:685–687
 poly(sodium 4-styrenesulfonate) (PSS) 1:108
 polytetrafluoroethylene (PTFE) 3:518
 polyurethanes (PU) 3:683–684
 polyvinyl alcohol (PVA) 1:223, 1:106
 polyvinyl butyral (PVB) 3:438
 polyvinylidene difluoride (PVDF) 3:231
 polyvinylidene fluoride (PVDF) 3:396, 3:412–413, 3:142, 3:373
 chemical structure of 3:397f
 porcelain 3:503
 porcine endogenous retrovirus (PERV) 3:475–476
 pore entrapment 1:254–255
 pore filling 1:261
 porosity 1:724
 porous and nano-structured TiO₂ thin films
 chemical modification for 3:452–453
 porous ceramic catalysts 2:387
 catalysts carriers ceramic monoliths 2:387
 zeolite catalysis 2:387–388

- porous ceramic catalysts (*continued*)
- porous ceramics 2:380–381, 1:346
- advanced processing techniques 2:386
 - freeze casting 2:386
 - novel processing approaches 2:386
 - phase inversion techniques 2:386
 - physical vapor deposition (PVD) 2:386
 - templating 2:386
- catalysts 2:380–381
- ceramic membranes for liquid and gas separation 2:389
- performance requirements and characterization 2:389
 - relationship between processing, structure and performance layers 2:389–390
- colloidal processing 2:385–386
- dry pressing 2:384
- extrusion 2:384–385
- liquid and gas separation, ceramic membranes for 2:382–383
- organic templates for 1:107–108
- porous ceramic catalysts 2:387
- catalysts carriers ceramic monoliths 2:387
 - zeolite catalysis 2:387–388
- processing
- additive manufacturing (AM) 1:344–345
 - cellular ceramics 1:343–344
 - fibrous ceramics 1:342–343
 - partial sintering 1:342
- sintering of porous ceramics 2:386–387
- solid oxide cell (SOC) technology 2:388–389, 2:381–382
- structure – property relationships 2:388–389
- structure and properties of 1:346
- cellular ceramics 1:346–348
 - fibrous ceramics 1:346
- porous components 1:208
- porous geopolymers 1:428–430
- porous glasses 2:692
- porous silicon nitride-based ceramics 3:527
- position-sensitive detectors (PSDs) 1:553
- positive temperature coefficient of resistivity (PTCR) 3:311, 3:302
- post-fracture tensile (PFT) test 1:789
- potassium dihydrogen phosphate (KDP) 3:571
- potassium dioxide 2:655
- potassium niobate 3:455
- potassium tantalate 3:455
- potassium tantalate niobate (KTN) films 3:455
- potentiometric solid electrolyte gas sensors 3:129
- pottery 2:67–68
- powder-based 3D printing 1:207–209
- binder jetting (BJ) process 1:208–209
 - monolithic components 1:208
 - porous components 1:208
- powder bed fusion 1:209–211
- slurry-based BJ (S-BJ) and slurry-based SLS (S-SLS) 1:212
- vat photopolymerization 1:211–212
- powder-based indirect laser sintering (p-iLS) 1:385–386
- powder batch permeability and compressibility 1:524–528
- powder-bed-based technologies 2:283, 3:654
- powder bed fusion (PBF) 1:209–211, 3:608, 3:666–667, 1:384
- applications 3:667
 - direct laser sintering (dLS) 1:384–385
 - direct powder bed fusion (PBF) 1:384
 - indirect powder bed fusion 1:385–386
 - powder-based indirect laser sintering (p-iLS) 1:385–386
- powder characteristics, choice of 1:352–353
- powder-forming 3:485
- powder granulation 1:136
- characteristics of granules 1:136–137
 - organic additives 1:137–138
- powder metallurgy (PM) processes 1:378
- powder mixing and grinding processes for ceramics 1:112
- different shredders 1:122
 - dispersants 1:119–122
 - dispersion 1:114–115
 - various stages of 1:113
- electrical characteristics of powders in aqueous suspension 1:115–116
- grinding 1:122
- mechanical breakage/comminution 1:113–114
- MgTiO₃ synthesis for multilayer capacitors type I (example) 1:125–126
- influence of rheology on the synthesis of MgTiO₃ 1:127
 - stabilization tests by electrostatic repulsion of MgO/TiO₂ slurry 1:125–126
 - steric repulsion stabilization 1:126–127
- negative temperature coefficient ceramics (example) 1:127–128
- characterization of ceramics made from reground calcined powders 1:130–134
- effects of grinding on densification 1:130
 - grinding of calcinated YCr_{0.5}Mn_{0.5}O₃ 1:128–130
 - influence of raw material grinding times on YCr_{0.5}Mn_{0.5}O₃ calcinated powders 1:128
 - mixing conditions of the oxides 1:128
- parameters influencing the state of dispersion 1:117–118
- parameters that can change the electrostatic repulsion stabilization 1:116–117
- pH 1:118
- physical factors improving stabilization 1:115
- planetary mills 1:122–123
- shear-thickening grinding slurries 1:117
- slurries and pastes, properties of 1:112–113
- solid content 1:118–119
- stabilization 1:115
- by electrostatic repulsion 1:115
 - by steric repulsion 1:117
- stabilization principle by electrostatic repulsion 1:116
- temperature 1:119
- wetting 1:114
- powder pressing process 1:140
- compaction defects 1:142
 - compaction mechanisms 1:141
 - die filling 1:140, 1:140f
 - ejection 1:142
 - granule characteristics and compaction 1:141–142
 - powder compaction 1:140–141
- powder synthesis methods 1:59
- via hydrothermal method 1:64–65
 - additives 1:66
 - preparation of gels 1:65
 - selection of precursors 1:64–65
 - undesired species, removal of 1:65–66
- powder traps 1:73
- Powder X-ray Diffraction (PXRD) 1:542–543
- power conversion efficiencies (PCEs) 3:12
- power spectral density estimation (PSDE) 3:413–414
- PPC *see* polypropylene carbonates (PPC)
- PPF *see* polypropylene fumarate (PPF)
- p*-phenylene benzobisoxazole (PBO) fiber 2:308f
- p*-phenylene terephthalamide (PPTA) 2:307
- PPHZ *see* poly(propyl)hafnizane (PPHZ)
- PPO *see* poly(propylene oxide) (PPO)
- PPTA *see* *p*-phenylene terephthalamide (PPTA)
- PPV *see* parallel plate viscometry (PPV)
- preceramic polymers 1:93
- blended precursors 1:95–96
 - micro-/nanoscale, modification at 1:96–97
 - polymer-derived ceramics (PDCs) microstructural feature of 1:97–99
 - processability of preceramic polymers-functional 1:99–100
 - pre-formed polymers' reaction with low molecular weight species 1:95
 - synthesis of 1:93–95
 - thermo-chemical conversion into ceramics 1:97
- precessed electron diffraction patterns (PED) 1:618
- precipitated hydroxyapatite (PHA) 3:626
- precipitation 1:30–31
- advantages, issues, applications 1:31
 - process, overview of 1:30–31
- precision extruding deposition (PED) 3:487
- precision glass molding (PGM) technique 2:544–545, 2:540
- precision molding 2:672, 2:673f
- precursor/polymer infiltration and pyrolysis (PIP) 2:340–341
- predicting material properties 1:476–477
- predictive modeling of ceramic materials 1:475
- future of ceramics modeling 1:479
 - macroscale, modeling ceramics at 1:475–476
 - nanoscale, modeling ceramics at 1:476

- density functional theory (DFT) 1:476
 density functional theory (DFT) for piezoelectric ceramics 1:478–479
 elastic constants, calculation of (case study) 1:477–478
 geometry optimization 1:477
 predicting material properties 1:476–477
 preform fabrication 2:686–687
 pressure and/or electric field assisted sintering 1:356–357
 flash sintering (FLASH) 1:358–359
 hot isostatic pressing (HIP) 1:357
 hot pressing (HP) 1:356–357
 spark plasma sintering (SPS) 1:357–358
 pressure and/or plasma assisted sintering 1:245–246
 flash sintering (FLASH) 1:246–247
 spark plasma sintering (SPS) 1:246
 uniaxial and isostatic hot pressings 1:245–246
 pressure-assisted microsyringe (PAM) 3:487
 pressure-assisted sintering 3:117
 pressure casting process 1:148–149, 1:148f
 pressure generation 1:162
 auger/screw extrusion 1:162–163
 Piston extrusion 1:162
 pressureless sintering (PS) 2:111, 3:117, 2:11, 2:150–152
 pressurized water reactors (PWR) 2:762–763
 primary human polymorphonuclear cells (PMNCs) 3:580
 printed circuit boards (PCBs) 2:360–361
 processing techniques 2:216–218
 properties of ceramics and glasses 1:704
 property modifying oxides 2:655–656
 property testing of ceramics and glasses 1:704
 protective and contact coatings 3:56
 protective oxide, requirements for 2:440
 protein data bank (PDB) 1:441–442
 proton (or hydride ion) conductors 3:25–26
 proton-exchange membrane fuel cells (PEMFC) 1:76
 proximal interphalangeal (PIP) joint of hand 3:535
 PRP *see* platelet-rich plasma (PRP)
 PS *see* pressureless sintering (PS)
 PSDE *see* power spectral density estimation (PSDE)
 PSDs *see* position-sensitive detectors (PSDs)
 pseudobrookite, crystal structure of 2:77, 2:78f
 pseudobrookite-type oxides 2:77
 PSS *see* poly(sodium 4-styrenesulfonate) (PSS)
 PST *see* lead scandium tantalate (PST)
 PSZ *see* partially stabilized zirconia (PSZ)
 PTCR *see* positive temperature coefficient of resistivity (PTCR)
 PTFE *see* polytetrafluoroethylene (PTFE)
 PTH *see* parathyroid hormone (PTH)
 PU *see* polyurethanes (PU)
 Pugh's ratio 1:464–465
 pulsed electric current sintering (PECS) 1:382
 see also spark plasma sintering (SPS)
 pulsed laser deposition (PLD) techniques 3:59, 3:62–64, 3:145–146
 of anode thin films 3:64–65
 of cathode thin films 3:63–64
 of solid electrolyte films 3:65–67
 pulverization 2:754
 pure silica-forming materials, oxidation of 2:440–441, 2:441
 putties 3:483
 PV *see* photovoltaics (PV)
 PVA *see* polyvinyl alcohol (PVA)
 PVB *see* polyvinyl butyral (PVB)
 PVD *see* physical vapor deposition (PVD)
 PVDF *see* polyvinylidene difluoride (PVDF); polyvinylidene fluoride (PVDF)
 PWR *see* pressurized water reactors (PWR)
 PXRD *see* Powder X-ray Diffraction (PXRD)
 pyrochlores 1:417
 pyroelectric detector element 3:139f
 pyroelectric IR detectors 3:144
 and materials figures-of-merit 3:139–140
 pyroelectric materials, bulk 3:142–144
 devices 3:144–145
 dielectric bolometer materials 3:144
 intrinsic pyroelectrics 3:142–144
 pyroelectric material selection 3:140–142
 pyroelectric/piezoelectric glass-ceramics 2:719
 pyroelectric thin films 3:145–146
 devices 3:146–148
 dielectric bolometers 3:146
 intrinsic pyroelectrics 3:146
 pyrolysis 2:329
 pyrolysis set-up 1:72–73
 pyrolytic carbon
 biocompatibility of 3:534
 fabrication of 3:533
 mechanical properties of 3:533–534
 structure of 3:533
 pyrolytic carbon interposition implants 3:536
 pyrolytic carbon interposition shoulder arthroplasty (PISA) 3:536
 pyrophosphate crystal 1:443, 1:448f
 pyrophosphates, diphosphates 3:568
 PZN-PT *see* lead-zirconium niobate - lead titanate (PZN-PT)
 PZT system *see* lead zirconate titanate (PZT) system
- Q**
 QE *see* quantum efficiency (QE)
 quantitative fractography, R-curve determination using 1:667–668
 quantum efficiency (QE) 3:7
- R**
 RABiTS *see* Rolling Assisted Biaxially Textured Substrates process (RABiTS)
 radial-distribution function (RDF) 1:592
 radioactive product confinement 2:721–722
 radio frequency (RF) magnetron sputtering 3:145–146
 Radon transform 3:754
 Raman and fluorescent spectroscopy, bridging stresses from 1:790
 Raman spectroscopy 2:563–565, 1:517, 2:521, 1:530
 random network model (RNM) 1:490, 2:647–648, 2:647
 random solid solution model (RSSM) 1:464
 random substitutional models 1:503
 RANK *see* receptor activator of nuclear factor kappa beta (RANK)
 RANKL *see* receptor activator of nuclear factor kappa- β ligand (RANKL)
 Rapid Prototyping (RP) 1:203
 see also additive manufacturing (AM)
 rapid prototyping *see* additive manufacturing (AM)
 rare-earth (RE) aluminates 2:503
 rare-earth aluminosilicate glasses (RE-AS) 2:509–510, 2:566
 rare earth center, excitations in 3:89
 rare-earth-doped sialon materials 3:84–85
 rare-earth ion host matrices 2:585
 rare-earth ions, incorporation of 3:319–320
 incorporation site 3:320
 rare-earth oxides 1:908
 rare earth oxynitride glasses 2:574–575
 rare-earth transition-metal borocarbides (RTBC) 3:162
 rate controlled sintering (RCS) 1:684–685
 Rayleigh scattering 2:685
 rayon 2:304
 Rb₂O-SiO₂ and Cs₂O-SiO₂ glasses 2:468
 RBFDP *see* resin-bonded fixed dental prosthesis (RBFDP)
 RBSiC ceramics (reaction-bonded silicon carbide) 1:209, 1:210f
 RBSN *see* reaction-bonded silicon nitrides (RBSN)
 RCS *see* rate controlled sintering (RCS)
 R-curve 1:818–819, 1:819f, 3:774
 determination using quantitative fractography 1:667–668
 standardized methods and 1:767–768
 R-curve behavior of ceramics
 bridging stresses, determination of 1:786–789
 bridging stresses from Raman and fluorescent spectroscopy 1:790
 calculation of bridges stresses from of COD in Vickers cracks 1:790–791
 calculation of bridging stresses from experimental crack profiles 1:789–790
 multi-cutting compliance technique 1:789
 post-fracture tensile (PFT) test 1:789
 in ceramic laminates 1:791–794
 determination of bridging parameters from the K_R -curves 1:785–786
 determination of K_{Ic} and K_R -curves 1:780–781
 K_R -curves from strength measurements from indentation cracks 1:783–784

- R*-curve behavior of ceramics (*continued*)
 long cracks 1:780–781
 starting notch for the determination of fracture resistance 1:781–783
 effect of specimen geometry, crack size, and type of loading on the *R*-curve 1:786
 fracture mechanics, basic concepts on 1:775
 K_{IC} and *R*-curve behavior 1:775–776
 long and small cracks 1:786
 mechanisms responsible for *R*-curves 1:776
 domain switching in piezoelectric ceramics 1:778–780
 grain bridging 1:776
 microcrack zone and crack deflection and branching 1:780
 phase transformation toughening in zirconia ceramics 1:776–778
 and strength 1:791
 stress intensity factor from bridging interactions 1:784–785
- reaction-bonded SiC 2:154
 reaction-bonded silicon nitrides (RBSN) 2:105
 reaction sintering 1:278
 concept 1:278
 in the presence of transitory liquids 1:279–280
 processes and factors 1:279
 technical ceramics 1:280–281, 1:283–284
 Mullite-Zirconia based composites 1:281–283
 single-phase 1:280–281
 technological interest 1:278–279
- reaction sintering under isostatic pressure (RSIP) 2:740
 reactive ion etching (RIE) of SiC 3:98
 reactive melt infiltration (RMI) 2:341
 reactive nitrogen species (RNS) 3:529
 reactive oxygen species (ROS) 3:580
 reactive template grain growth (RTGG) method 3:395–396, 1:367, 1:370
- RE aluminates *see* rare-earth (RE) aluminates
 RE-AS *see* rare-earth aluminosilicate glasses (RE-AS)
 receptor activator of nuclear factor kappa beta (RANK) 3:753
 receptor activator of nuclear factor kappa- β ligand (RANKL) 3:801, 3:801–802, 3:753
 recovery creep 1:891–893
 recrystallized SiC 2:154–155
 RED *see* Rotation Electron Diffraction (RED)
 reduced graphene oxide (RGO) 2:238, 2:245–246
 reduced modulus 1:750
 refining component 2:656
 refractive index 2:659, 2:659*f*, 2:451–452, 2:452*f*
 effect of composition of glasses on 2:653–654
 refractories 2:68–69
 refractoriness 2:60
 refractory oxide coatings on silica-forming ceramics 2:442
 regenerative medicine, bioceramics for 3:758
see also bioceramics in regenerative medicine
 biomimetic approach 3:758–760
 future perspectives 3:769
 load-bearing segmental bones, emerging technologies for regeneration of 3:763–766
 magnetic scaffold to boost tissue regeneration 3:766–769
 multifunctional anatomical regions, hybrid scaffolds for the regeneration of 3:760–761
 osteochondral regeneration, biomimetic scaffolds for 3:760–761
 periodontal diseases, biomimetic scaffolds to treat 3:761–763
- reinforcement mechanisms in ceramics 2:227
 crack bridging 2:227–228
 crack deflection 2:227
 microcracking 2:227
 transformation toughening 2:227
 whisker reinforcement 2:228
- reinforcement of polymers, glass fibers for 2:676–677
 relaxation, defined 2:449
 relaxor ferroelectrics 3:372
 applications 3:291–293
 basic concepts of 3:290–291
 relief etching (polishing) 1:647
 “repair and regeneration” approach 3:674
 “replacement” strategy 3:674
 replica technique 3:606
 representative elementary volume (REV) 1:748
 representative volume element (RVE) 3:751
 residual loss 3:219
 resin-bonded fixed dental prosthesis (RBFDP) 3:818
 resonance absorptions 2:685
 resonance Raman spectroscopy 1:530
 resonant ultrasound spectroscopy (RUS) 1:747–748
 reusable surface insulation (RSI) 2:51
 REV *see* representative elementary volume (REV)
 RF electronics 3:99
 RF magnetron sputtering *see* radio frequency (RF) magnetron sputtering
 RGO *see* reduced graphene oxide (RGO)
 RIE of SiC *see* reactive ion etching (RIE) of SiC
 Rietveld method 1:563–564
 ring method 1:697
 RMI *see* reactive melt infiltration (RMI)
 RNM *see* random network model (RNM)
 RNS *see* reactive nitrogen species (RNS)
 robocasting (RB) method 3:668, 3:487
see also direct ink writing (DIW)
 Robocasting or Fused Deposition Modeling processes 1:109
 rocket engine components 2:366–367
 liquid rocket engines (LRE) 2:367–369
 solid rocket motor (SRM) nozzles 2:366–367
- Rolling Assisted Biaxially Textured Substrates process (RABITS) 1:367, 3:174–175
 for 2G high temperature superconductors 3:174, 3:182, 3:176*f*, 3:177*f*
 cuprate-based high temperature superconductors 3:174–175
 buffer layers 3:177–180
 metal substrate 3:176–177
 roll-to-roll manufacturing of RABITS-based 2G HTS wire 3:180–181
 roll-to-roll manufacturing of RABITS-based 2G HTS wire 3:180–181
 roll-to-roll processing 1:191
- ROS *see* reactive oxygen species (ROS)
 rotary screen printing 1:231, 1:232, 1:230*f*
 Rotation Electron Diffraction (RED) 1:619
 RPL (radiophotoluminescence) dosimeters 2:586
r-ratio 2:677
- R*-ratio and microstructure effects 1:841–842
 crack growth mechanisms during cycling loading 1:847–849
 cyclic fatigue (*R*-ratio) and ceramic and glasses applications 1:852
 cyclic fatigue evaluation and *R*-ratio effect 1:842–844
 fatigue crack growth rate (FCGR) curves 1:844–847
 stress-cycles curves 1:842–844
 cyclic fatigue phenomenon (*R*-ratio) and microstructural effect 1:849–852
- RSI *see* reusable surface insulation (RSI)
 RSIP *see* reaction sintering under isostatic pressure (RSIP)
 RSSM *see* random solid solution model (RSSM)
 RTBC *see* rare-earth transition-metal borocarbides (RTBC)
 RTGG method *see* reactive template grain growth (RTGG) method
 RTM (resin transfer molding) process 2:330
 Ruler-Bernoulli beam theorem 3:228–231
 RUS *see* resonant ultrasound spectroscopy (RUS)
 Rutherford backscattering spectroscopy (RBS) 1:517
 Rutherford scattering 1:585
 RVE *see* representative volume element (RVE)

S

- sacrificial bonds 3:460
 sacrificial fugitives 3:606
 sacrificial mold 3:651
 SAED *see* selected area electron diffraction (SAED)
 safety glass *see* Thermally tempered glass
 Saint Gobain Demarquest (SGD) 3:546–547
 sample controlled thermogravimetric analysis (SCTGA) 1:676

- sandblasting 3:704–705
sapphire 2:29, 3:74
 crystalline structure of 2:27f
saturable absorbers 3:120
saturated poly- α -hydroxy esters 3:682–683
SAXS analyses *see* small angle X-ray
 scattering (SAXS) analyses
SBF *see* simulated body fluid (SBF)
SC *see* solvent casting (SC)
scaffold fabrication techniques and state of
 the art 3:687–689
 additive manufacturing (AM) 3:691–692
 electrospinning 3:690–691
 melt electrospinning writing 3:692
 microsphere sintering 3:689
 particulate leaching (PL) 3:689
 solvent casting (SC) 3:689
 supercritical CO₂ foaming 3:690
 thermally induced phase separation (TIPS)
 3:689–690
scaffolds 3:647–648
 introducing stimulus 3:658
 with particles 3:655–656
 with therapeutics 3:656–657
 drug release scaffolds 3:657
 gene therapy 3:658
 growth factors 3:657
 hormones 3:657–658
 living cells, scaffolds with 3:658
 polymers, scaffolds with 3:658
scaffolds manufacturing 3:484–485
 additive manufacturing 3:486–487
 bioprinting 3:488–489
 fused deposition modeling 3:487
 Selective Laser Sintering/Melting (SLS/
 SLM) process 3:487–488
 stereolithography 3:486–487
 3D printing 3:488
 conventional techniques 3:484–485
 electrospinning 3:485–486
 freeze-drying 3:485
 gas foaming 3:485
 powder-forming 3:485
 sol-gel 3:485
 solvent-casting and particle leaching
 3:484–485
 thermally induced phase separation
 (TIPS) 3:485
scaffolds processing techniques 3:650–651
 additive manufacturing (AM) 3:651–654,
 3:655t
 bioprinting 3:654
 extrusion based methods 3:654
 inkjet 3D printing 3:654
 powder bed-based methods 3:654
 stereolithography 3:652
 conventional techniques 3:650–651
scandia 1:416
scandium oxide 3:119
scanning electron microscopy (SEM) for
 ceramics and glasses 1:651
 anatomy of 1:651–653
 factors affecting image resolution and
 apparent quality 1:656–657
 accelerating voltage 1:657
 environmental SEM 1:658
 objective aperture 1:657
 probe/beam current 1:656–657
 working distance 1:657
 interactions of electron beam with
 materials 1:653–656
X-ray analysis 1:658
 characterization of ceramic
 microstructures 1:661
 energy dispersive spectroscopy (EDS)
 1:660
 energy dispersive X-ray analysis 1:658–659
 information sources 1:661
 uses of 1:660–661
 wavelength dispersive spectrometry
 (WDS) 1:660
 wavelength dispersive X-ray analysis
 1:659–660
scanning transmission electron microscopy
 (STEM) 1:600–607
SCB *see* Semi-Circular Bend specimen (SCB)
SCCG *see* subcritical crack growth (SCCG)
SCD *see* supercritical drying (SCD)
SCF method *see* surface crack in flexure
 (SCF) method
Schottky approximation 3:133
Schottky defect 3:20–21
 schematic model of 3:22f
Schulze-Hardy rule 1:159
scintillator crystals (SCs) 3:103t, 3:2
 growth of 3:104–106
 halides 3:105–106
 oxides 3:106–108
 physical effect and construction of devices
 3:103–104
scintillator detector, principle of 3:104f
SCL *see* supercooled liquids (SCL)
screen-offset (SOS) printing 1:232, 1:231f
screen-offset curved-surface (SOS-CS)
 printing 1:232
screen-printing process 1:227–228, 1:228f,
 2:385
 alternative to 1:229–231
 chemical composition of 1:228–229
 history 1:227
 properties of 1:227–228
 screen mask 1:227–228
Screw Dislocation growth model 2:458
SCs *see* scintillator crystals (SCs)
SCS *see* solution combustion synthesis
 (SCS)
SCS-*n* 2:309–310
SCTGA *see* sample controlled
 thermogravimetric analysis (SCTGA)
SDAs *see* structure-directing agents (SDAs)
seal, adherence of 2:755–756
 applications 2:757–758
 conventional applications 2:757–758
 new applications 2:758–759
 mechanical bonding 2:756
 dendrite theory 2:756
 electrolytic theory 2:756–757
 mutual solubility and formation of
 intermediate compounds 2:757
 chemical bond 2:757
 thermodynamic approach 2:755–756
sealants in solid oxide fuel cells 2:715
sealing, glass materials for 2:749, 2:753
 borate glasses 2:749
 glasses based on other oxide glass formers
 2:750
 phosphate glasses 2:749–750
 silicate and borosilicate glasses 2:749
sealing glasses 2:748
 requirements for 2:746
 adherence 2:747
 chemical durability 2:747–748
 electrical resistance 2:748
 emission gases, control of 2:748
 flow temperature and viscosity 2:746
 thermal expansion coefficient
 2:746–747
sealing process 2:753
 application of glass 2:753–754
 agglomerants, use of 2:754
 glass injection 2:754
 immersion 2:754
 preform 2:754
 pulverization 2:754
 sedimentation 2:754
 tape process 2:754
 cleaning of the components 2:753
 previous treatments 2:753
 thermal treatment 2:754–755
sealings 3:56–57
secondary ion mass spectrometry (SIMS)
 1:517
sectioning 1:635–636
 coolants/lubricants 1:638
 preferred sectioning speeds and loads
 1:636
 sample support 1:637–638
 sectioning blade 1:636–637
 selection of volume to be sampled
 1:635–636
sedimentation 2:754
seeding of ceramic reactions 1:88–89
seeding strategy 1:90
selected area electron diffraction (SAED)
 2:432–433, 1:583, 1:595, 1:618,
 1:619, 1:622–623
selective laser sintering (SLS) 1:291–292,
 3:691–692
Selective Laser Sintering/Melting (SLS/SLM)
 process 3:487–488
selenides 1:419
self-assembly 3:711–713
“self-cleaning” SLS glass products 2:491
self-glazed zirconia ceramics 3:823–824
self-propagating high-temperature synthesis
 (SHS) 2:9, 1:40, 1:49, 1:40f, 1:43f,
 1:44f
 adiabatic temperature 1:45–46
 classification 1:44–45
 general approach 1:40–43
 modeling 1:45–46
 obtaining final products by structural
 transformation 1:43–44
 review of materials prepared using SHS
 methods 1:51–52
SHS state of the art 1:48–51
thermal explosion mode of 1:46–47, 1:46f
“thermal wave” modeling 1:47–48

- self-propagating high-temperature synthesis (SHS) (*continued*)
 used for ceramic materials technologies 1:52–53
 advantages of the SHS method for ceramics 1:52–53
 application of SHS methods in technological scale 1:56
 principles in the processing of ceramics using SHS 1:53–54
- SEM *see* scanning electron microscopy (SEM) for ceramics and glasses
- Semi-Circular Bend specimen (SCB) 1:833
- semiconducting metal oxides, gas sensors based on 3:130–132
 bulk-active SMOX 3:131–132
 surface-active SMOX 3:132–137
- SENB *see* singleedge notch beam (SENB)
- sensors 3:248–250, 3:33
- SEPB method *see* single-edge pre-cracked beam (SEPB) method
- SERR *see* strain energy release rate (SERR)
- Se–Se stretching 1:531
- sesquioxides 1:415
 alumina 1:415
 lutetia 1:416
 scandia 1:416
 yttria 1:415–416
- sesquioxides 3:119
- sessile drop method 1:694–695
- SEVNB *see* single-edge V-notch beam (SEVNB)
- SF-CMCs *see* short fiber ceramic matrix composites (SF-CMCs)
- SFE *see* stacking fault energy (SFE)
- SFF *see* solid freeform fabrication (SFF)
- SGD *see* Saint Gobain Demarquest (SGD)
- S-glass 2:309
- shape-demagnetizing effects 3:191–196
- shear modulus 1:443
- shear-thickening grinding slurries 1:117
- sheet lamination 1:388
- shell models 1:487
- SHM *see* structural health monitoring (SHM)
- shock wave (SW) technique 2:9
- short fiber ceramic matrix composites (SF-CMCs) 2:260
 mechanisms of short fiber reinforcement 2:260–262
 damage tolerance and extrinsic toughness 2:260–262
 debonding of fiber and matrix 2:262–263
 estimate composite strength 2:263–264
 estimate stiffness quantities 2:264
 load transfer between matrix and fiber 2:263
 non-oxide CMCs 2:264–267
 oxide CMCs 2:267–269
 ceramic injection molding (CIM) 2:271
 fiber spraying process 2:272–274
 non-oxide fiber reinforcements 2:267–269
 oxide fiber reinforcement 2:269–271
 short fiber preforms, impregnation of 2:271–272
- short fiber preforms, impregnation of 2:271–272
- short-range interactions 1:486–487
- short-range structural parameters, evaluation of 1:487–488
- Shottky defect 3:20–21
- shoulder implants 3:536–537
- shoulder joint replacement, oxide ceramics in 3:522
- shredders 1:122
- SHS *see* self-propagating high-temperature synthesis (SHS)
- Shubnikov phase 3:152
- Si–Al–O–N ceramics 2:128, 1:413
 applications of 2:137–139
 electrical properties of 2:137
 mechanical properties of 2:129–132
 optical properties of 2:136–137
 structure and phases of 2:128–129
 thermal properties of 2:132–133
 creep behavior 2:133–135
 oxidation behavior and chemical stability 2:135–136
 thermal conductivity 2:132–133
 thermal shock resistance 2:133
- Si–Al–O–N system 2:119, 2:119–120
 M–Si–Al–O–N systems, representation of 2:124–127
 with α' -SiAlON 2:126–127
 phases in 2:121–122
 polytypoids 2:122–124
 representation of 2:120–121
 research on 2:124
 X-phase 2:122
- Si-based oxynitride glasses, preparation of 2:556–557
- SIF *see* stress intensity factor (SIF)
- silanization 3:721–722
- silica 2:49–51, 2:484
- Silica-29 NMR 1:541
- silica-based glass 2:678
- silica fibers 2:681–682
- silica-forming ceramics
 passive oxidation of 2:440–441
 refractory oxide coatings on 2:442
 volatilization of 2:441–442
- silica-forming materials in impurity-containing environments, oxidation of 2:441
- silicate and aluminosilicate glasses 1:532
- silicate and borosilicate glasses 2:749
- silicate-based glasses 2:454–455
- silicate bioactive glasses 3:679–680
- silicate glass-ceramics 2:752
- silicate glasses 2:462–463
- silicates 1:488–490
- silicates and aluminosilicates, substitution of nitrogen into 2:556
- silica-water interaction 1:455–456
- silicon 1:532
- silicon-based composites, oxidation of 2:442
- silicon carbide (SiC) 2:168–169, 1:908–909, 3:530–531, 1:915–916, 2:150, 2:151f, 1:412–413, 3:74, 1:299–300, 1:305
 applications 2:160–161
- based fibers 2:312–313, 2:313t
 β -SiC 3:93
 creep rupture of 1:908–909
 electrical properties 2:157–159
 15R-SiC 3:93
 4H-SiC 3:93
 mechanical properties 2:155–157
 high-temperature strength 2:157
 room-temperature mechanical properties 2:155–157
 metallizations 3:97
 processing 2:150–152, 2:155
 gas pressure sintering 2:153
 hot pressing 2:152–153
 pressureless sintering 2:150–152
 reaction-bonded SiC 2:154
 recrystallized SiC 2:154–155
 spark plasma sintering (SPS) 2:153–154
 processing and creep of 1:908
 properties of major SiC polytypes 2:151t
 6H-SiC 3:93, 3:94f, 3:95–96
 solid-state sintering of 1:908
 structure 2:150
 thermal properties 2:159–160
 3C-SiC 3:93
 and wide band gap 3:99
- silicon carbide (SiC) electronic devices
 chemical vapor deposition (CVD) 3:96
 electronics benefits of 3:93–95
 fabrication 3:97
 contacts 3:97–98
 metal–oxide–semiconductor technology 3:98–99
 patterned doping by ion implantation 3:97
 patterned etching 3:98
 polytypes of SiC 3:93, 3:94t
 properties of SiC 3:93
 prototyping and production of 3:99
 high-power switching 3:100–101
 high-temperature devices and ICs 3:99–100
 optoelectronics and sensors 3:99
 RF electronics 3:99
- reactive ion etching (RIE) 3:98
- SiC crystal growth 3:95–97
 and wide band gap 3:99
- silicon carbide based ceramics 2:420–421
- silicon carbide ceramics 1:929–930
- silicon carbide electronic devices 3:2
- silicon carbide fibers 2:304, 2:309–310
- silicon dioxide 2:655, 2:314
- silicon infiltrated SiC ceramics (SiSiC) 1:930
- silicon nitride 2:109, 1:413, 2:172–174, 2:244, 2:244f, 2:119, 3:526, 3:528f
 biomedical devices 3:528–529
 as biomedical material 3:527–528
 creep rupture of 1:908–909
 fabrication techniques 3:530
 lattice oxygen, effect of 2:174–178
 mechanical spectroscopy in 1:713–714
 microstructure, effect of 2:174
 polycrystalline Si_3N_4 2:110–112
 development of Si_3N_4 microstructure 2:111–112

- properties of 2:113–114
- processing and creep of 1:908
- rare-earth oxide additives, effect of 2:178
- SiAlONs 3:526–527
- single crystals of 2:109
 - preparation 2:110
 - properties 2:109–110
 - structure 2:109
- surface chemistry of, on biological
 - interactions 3:529–530
- silicon nitride based ceramics 2:419–420
- silicon nitride-ceramics 1:929
 - crystal structures 2:105
 - mechanical properties 2:106–107
 - processing and microstructural development 2:105–106
 - toughening mechanisms 2:106
- silver and copper ion conductors 3:23–24
- SIMS *see* secondary ion mass spectrometry (SIMS)
- simulated body fluid (SBF) 3:643, 1:215, 3:800, 3:527
- single-crystal aluminum oxide 2:27–28
 - crystalline structure 2:27–28
 - elastic and mechanical properties 2:28–29
 - properties 2:29–30
 - thermal and functional properties 2:29
- single-edge notch beam (SENB) 2:233
- single-edge pre-cracked beam (SEPB)
 - method 1:763–764
- single-edge V-notch beam (SEVNB) 2:233, 3:501, 1:767
- single-layer (microchip) capacitor
 - 3:386–387
- single-stage to orbit (SSTO) spacecraft 2:361
- single-wall carbon nanotubes (SWCNTs)
 - 2:244–245, 2:245, 3:65, 2:233
- sinter-crystallization, glass-ceramics from
 - 2:728–730
 - main fields of application 2:729–730
 - glass-ceramic joints 2:730–731
 - sintered glass-ceramics for building applications 2:731–732
 - sintered glass-ceramics in biomedical applications 2:729–730
 - sinter-crystallization aided by chemical reactions 2:732
- sintered abrasives 2:410–414
 - extrusion processes 2:411
 - sol-gel process 2:412
- sintered glass-ceramics from mixtures of glasses 2:732–733
- sintered hard ferrites 3:211–212
 - anisotropic ferrites 3:213
 - high coercivity materials 3:213
 - high remanence materials 3:213
 - ceramic process 3:211–212
 - isotropic ferrites 3:213
 - properties of 3:212
 - chemical stability 3:212
 - dispersion of magnetic and mechanical values 3:212–213
 - quality coefficient 3:213
 - temperature coefficients 3:212
- sintered metal powder processing (SMPP)
 - 2:401
- sintered silicon nitrides (SSN) 2:105, 2:106
- sintering
 - see also* reaction sintering
 - analysis of 1:684–685
 - driving force for 1:249
 - of porous ceramics 2:386–387
 - stages 1:249
 - sintering aids 3:117–118, 1:908
 - sintering approaches 3:117
 - sintering mechanisms 1:312–314
 - chemical effects 1:314–316
 - different pathways towards densification under solvent-assisted sintering processes 1:316–318
 - mechanical-chemical effects 1:313–314
 - solvents, role of 1:318–320
 - cold sintering process (CSP), illustration in the case of 1:320
 - of hydrothermal and solvothermal sintering of amorphous SiO₂, illustration in the case 1:318–320
 - sintering models 1:265–266
 - sintering of ceramics 1:233, 1:320
 - alternative sintering techniques 1:247
 - cold sintering 1:247
 - microwave sintering 1:247
 - cold sintering 1:320
 - densification kinetics 1:245
 - general outline 1:233–235
 - hydrothermal sintering 1:320–321
 - liquid phase sintering 1:239–244
 - description of matter transport mechanisms 1:240–244
 - grain growth mechanisms 1:244–245
 - pressure and/or plasma assisted sintering 1:245–246
 - flash sintering (FLASH) 1:246–247
 - spark plasma sintering (SPS) 1:246
 - uniaxial and isostatic hot pressings 1:245–246
 - solid state sintering 1:235–238
 - description of matter transport mechanism 1:235–238
 - grain growth mechanisms (GG) 1:238–239
- sintering of reaction-bonded silicon nitride (SRBSN) 2:174, 3:526
- sintering process 3:296–297, 3:297–299
- sintering rate, factors affecting 1:266–267
- sintering-reaction-crystallization 2:732
- sintering route 2:63
- sintering under constraint 1:267–268
 - constitutive equation 1:267–268
 - practical applications 1:268
- SIS *see* slurry infiltration and sintering (SIS)
- SITs *see* static induction transistors (SITs)
- SL *see* stereolithography (SL)
- slip casting 1:146–148, 3:115
- slow crack growth (SCG) 2:39, 1:841, 3:494–495, 3:792–796
 - see also* subcritical crack growth (SCCG)
- SLS *see* selective laser sintering (SLS)
- SLS glasses *see* soda-lime-silica (SLS) glasses
- SLS/SLM process *see* Selective Laser Sintering/Melting (SLS/SLM) process
- slurries and pastes, properties of 1:112–113
- slurry based binder jetting 1:388
- slurry-based BJ (S-BJ) 1:212
- slurry-based SLS (S-SLS) 1:212
- slurry infiltration and hot-pressing 2:282
- slurry infiltration and sintering (SIS)
 - 2:342–343
 - continuous fibers, UHTCMCs with 2:343–344
 - short fibers, UHTCMCs with 2:342–343
- slurry – infiltration/hot pressing sintering (SI/HPS) route 2:326–329
- SM *see* subtractive machining (SM)
- Small Angle Neutron Scattering 2:691
- small angle X-ray scattering (SAXS) analyses
 - 2:526
- small-scale energy harvesting devices for smart electronics 3:391–392
 - energy harvesting technologies 3:407–409
 - applications 3:420–421
 - cantilever based piezoelectric energy harvester 3:407–409
 - magneto-mechano-electric generator 3:418–420
 - piezoelectric nanogenerator 3:409
 - triboelectric nanogenerator 3:413–416
- future challenges 3:422–423
- transduction mechanism 3:392–396
 - magneto-mechano-electric (MME) effect 3:405–406
 - piezoelectricity 3:393–396
 - triboelectricity 3:399–402
- SMDs *see* surface mount devices (SMDs)
- SMPP *see* sintered metal powder processing (SMPP)
- SMT *see* surface mount technology (SMT)
- Snoek's law 3:219–220
- SOCs *see* solid oxide cells (SOCs)
- soda-lime glass 2:654
- soda-lime-silica (SLS) glasses 2:483, 2:445, 2:454
 - chemical durability 2:491–492
 - commercial production of 2:486–488
 - compositions 2:483–486
 - mechanical properties 2:492–493
 - chemical tempering 2:493
 - sub-critical crack growth 2:493–494
 - thermal tempering 2:493
 - optical properties of 2:489–490
 - color 2:490
 - photoelasticity and stress birefringence 2:490–491
 - structure 2:486
 - viscosity-temperature behavior and SLS glass production 2:488–489
- sodium bismuth titanate 3:360–361
- sodium carbonate 1:106
- sodium hexametaphosphate (HMP) 1:106
- sodium ion conductors 3:24
- sodium metasilicate 1:106
- sodium orthosilicate 1:106
- sodium oxide 2:655
- sodium potassium niobate 3:358–360
- SOECs *see* solid oxide electrolysis cells (SOECs)
- SOFCs *see* solid oxide fuel cells (SOFCs)
- softening point 2:651

- soft ferrites
 - garnets ferrites 3:186
 - spinel ferrites 3:186
- soft-magnetic ferrites 3:217
- "soft" superconductors 3:151
- soft X-ray absorption spectroscopy 3:221–222
- solar cell cover glass 2:373
- solar cells 1:19
- solar cell technologies 3:241–242
- soldering and brazing 2:401
- soldering of ceramics 2:402
- sol-gel bioactive glasses and hierarchical materials 3:617–618
- sol-gel coating 2:695–697, 3:485
 - applications of 2:701, 2:698–699
 - biomaterials made by sol-gel 2:704–705
 - optical and photonics applications 2:701
 - porous coatings for sensors, biosensors and photo-catalysis 2:702–704
 - protective coatings 2:701–702
- colloidal and polymeric sol-gel routes 2:696f
- deposition methods for 2:699–700
 - dip coating deposition 2:699–700
 - electrophoretic deposition 2:700
 - spin coating deposition 2:700
 - spray coating 2:700–701
- physical-chemical basis of the process 2:697–698
- sol-gel chemistry mesostructure assembly 2:696f
- sol-gel method 1:3–4, 2:282–283, 2:412, 2:385, 2:314, 3:651, 1:27–28
 - advantages, issues, applications 1:28–30
 - of glass fibers 2:677
 - in glass technology 2:689
 - aerogel-glass transformation 2:691
 - characterization of gel-sintered glass and comparison with conventional glass 2:691–692
 - drying process 2:691
 - gel synthesis 2:690–691
 - porous glasses 2:692
 - principle of 2:689–690
 - process, overview of 1:27–28
- solid, defined 2:448
- solid content 1:118–119
- solid electrolyte films, pulsed laser deposition (PLD) of 3:65–67
- solid freeform fabrication (SFF) 1:203, 1:172–173
 - see also* Additive Manufacturing (AM)
- solid-liquid contact based TENGs 3:416–418
- solid oxide cells (SOCs) 2:381–382, 2:388–389
- solid oxide electrolysis cells (SOECs) 2:730–731, 2:381–382, 3:34
- solid oxide fuel cells (SOFCs) 2:360–361, 3:49, 3:50f, 3:51f, 3:34, 3:35f, 3:1, 3:441, 3:442f, 2:758, 2:88–89, 3:31, 2:730–731, 2:294–296, 2:295f, 2:381–382
 - description of the various types of 3:49–50
 - materials development and processing, progress in 3:52–53
 - anode substrates and anodes 3:53–54
 - cathode 3:54–55
 - electrolytes 3:52–53
 - interconnect 3:55–56
 - protective and contact coatings 3:56
 - sealings 3:56–57
 - remaining issues/technological hurdles to be solved 3:57
 - technological trends during the recent years 3:50–52
 - working principle 3:49
- solid phase methods 2:395–396
 - advantages and disadvantages of diffusion bonding 2:397
 - ceramic-ceramic diffusion bonding 2:395–396
 - ceramic-metal diffusion bonding 2:396
 - use of thin interlayers to enhance diffusion bonding 2:396–397
- solid phosphates, preparation of 3:568
- sol-gel methods 3:569
- solution and hydrothermal methods 3:568
- thermal treatments and flux growth 3:568–569
- vapor transport 3:569
- solid rocket motor (SRM) 2:366–367, 2:366
- solid-solid contact based TENGs 3:413–416
- solid state electrolytes
 - laser printing of 3:60–61
 - for rechargeable batteries 2:719–720
- solid-state lasers 3:110
- solid state magic angle spinning (MAS) nuclear magnetic resonance (NMR) 2:562–563, 1:540
- solid-state reactions 1:86–87
- solid state sintered SiC ceramics (SSiC) 1:930, 1:922f, 2:150
- solid state sintering 1:278, 1:235–238, 1:249
 - constraints, effects of 1:256
 - description of matter transport mechanism 1:235–238
 - dihedral angle effect 1:253–254
 - driving force for sintering 1:249
 - electric fields and currents, effects of 1:256
 - final stage 1:253
 - grain growth mechanisms (GG) 1:238–239
 - heating rate, effects of 1:255
 - initial stage 1:249–252
 - intermediate stage 1:252–253
 - mechanical pressure, effects of 1:255–256
 - pore entrapment 1:254–255
 - sintering stages 1:249
- solution-based wet chemistry techniques 1:15–17
- solution combustion synthesis (SCS) 2:64, 1:50–51
- solution-precipitation model 1:899
- solvent-based 3D printing 3:691–692
- solvent casting (SC) 3:689
- solvent-casting and particle leaching 3:484–485, 3:651
- solvothermal synthesis 1:31–32
 - advantages, issues, applications 1:32–33
 - process, overview of 1:31–32
- SOS-CS printing *see* screen-offset curved-surface (SOS-CS) printing
- SOS printing *see* screen-offset (SOS) printing
- space applications, ceramics in 2:359–360
 - additive manufacturing (AM) 2:375–377
 - application areas 2:360–361
 - design considerations 2:359–360
 - mirror substrates 2:372–373
 - solar cell cover glass 2:373
 - space environment 2:360
 - thermal management of spacecraft 2:361–363
 - atmospheric re-entry 2:361–363
 - ceramic thermal control coatings for satellites 2:364–365
 - tribological and wear applications 2:373–375
 - windows for spacecraft 2:370–372
- space propulsion applications 2:365–367
 - electric propulsion 2:369–370
 - Ion and Hall thrusters 2:370
 - VASIMR 2:370
 - rocket engine components 2:366–367
 - liquid rocket engines (LRE) 2:367–369
 - solid rocket motor (SRM) nozzles 2:366–367
- spark plasma sintering (SPS) 2:719, 1:357–358, 2:111, 2:153–154, 2:342, 2:421, 2:14–15, 2:247, 1:382, 3:117, 1:246, 1:256, 3:226–228, 1:286, 1:291, 1:289–291, 1:294, 1:295f
 - application, examples of 1:301–302
 - functionally graded materials (FGMs) 1:302–303
 - nanostructured bulk materials 1:302
 - non-equilibrium materials 1:303–304
 - experimental setup 1:294–295
 - experimental procedure 1:295
 - machine layout 1:294–295
 - temperature, current and stress distribution 1:295–297
 - tooling 1:297–300
 - general characteristics 1:294
 - innovative aspects and future evolutions 1:304–305
 - high and ultra-high pressures 1:304–305
 - hybrid heating 1:307–309
 - tooling optimization 1:305–307
 - microscopic mechanisms 1:300
 - applied electric fields 1:300–301
 - applied pressure 1:301
 - arc and plasma discharges 1:300
 - heating rates 1:301
- Specialty Materials Inc. 2:309–310
- specimen and loading configuration 1:799
- Spectra 2:308–309
- spectrometer 1:539
- speeds for casting 1:192
- spherical contact 1:719–720
- spheric and aspheric lenses 2:672f
- spin coating deposition 2:700
- spinel ferrites 3:186, 3:218

- “Spinelisation” reaction 1:280–281
 spinels 1:416–417
 spinel-type lattice structure 3:217, 3:217f
 SPION *see* superparamagnetic iron oxides NPs (SPION)
 spray-based syntheses 1:37–38
 advantages, issues, applications 1:38
 process, overview of 1:37–38
 spray coating 2:700–701
 spray pyrolysis processes 1:69, 1:72f
 SPS *see* spark plasma sintering (SPS);
 suspension plasma spaying (SPS)
 spun (slurry and sol-gel) ceramic fibers
 chemical processing 2:314
 heat treatment and fiber microstructure 2:315–316
 oxide fiber precursor chemistry 2:314
 basic aluminum salts 2:314
 polymeric aluminosilicate 2:314–315
 SRBSN *see* sintering of reaction-bonded silicon nitride (SRBSN)
 SRM *see* solid rocket motor (SRM)
 SSiC *see* solid state sintered SiC ceramics (SSiC)
 SSN *see* sintered silicon nitrides (SSN)
 SSTO spacecraft *see* single-stage to orbit (SSTO) spacecraft
 stabilization 1:115
 by electrostatic repulsion 1:115
 physical factors improving 1:115
 by steric repulsion 1:117
 stabilization principle by electrostatic repulsion 1:116
 stacking fault energy (SFE) 3:176
 stair stepping effect 1:211
 standardized methods
 and R-curves 1:767–768
 and sub-critical crack growth 1:768–769
 staple fibers 2:679
 starch 3:687
 static fatigue 1:841
 static induction transistors (SITs) 3:99
 STEM *see* scanning transmission electron microscopy (STEM)
 step bunching 3:96
 step-controlled epitaxy 3:96
 step index 2:682
 stereolithography (SL) 1:390, 3:652,
 3:486–487, 1:109, 1:211, 3:664–665,
 3:691–692
 steric repulsion, stabilization by 1:117
 steric stabilization 1:105
 Stokes shift 3:84
 strain-energy-density criterion 1:830–832
 strain energy release rate (SERR) 1:669
 strain point 2:651
 stress corrosion 1:841
 stress-cycles curves 1:842–844
 stresses in glass 2:623–625
 non-thermal stresses 2:625
 thermal stresses 2:625
 stress-induced transformation toughening 2:95–96
 stress intensity factor (SIF) 1:879,
 1:799–800, 1:818, 1:821–822,
 3:784–786, 1:668
 stress relaxation time 2:451
 stress-shielding 3:466
 strontium oxide (SrO) 2:655
 strontium silicate glasses 2:473
 structural and thermostructural ceramics 2:3
 applications 2:4–7
 classification and properties 2:3–4
 densification/consolidation 2:11
 hot pressing (HP) 2:11–14
 liquid phase sintering (LPS) 2:15–16
 microwave sintering (MW) 2:15
 non-sintering based techniques 2:16
 pressureless sintering 2:11
 spark plasma sintering (SPS) 2:14–15
 mechanical and physical properties 2:19
 microstructure 2:16–19
 synthesis 2:7–8
 chemical methods 2:7–8
 direct elemental reaction method 2:8–9
 gas phase reactions and other methods of synthesis 2:10–11
 mechanical alloying (MA) 2:9
 oxide reduction methods 2:9–10
 self-propagating high-temperature synthesis (SHS) 2:9
 shock wave (SW) technique 2:9
 thermal properties 2:19–21
 structural health monitoring (SHM) 3:421–422
 structure-directing agents (SDAs) 3:571
 stuffed derivatives of silica 2:736
 subcritical crack growth (SCCG) 1:811–812,
 1:763, 3:793–795
 ball-on-three-balls testing method for 1:815–816
 crack growth law 1:797
 double cantilever beam (DCB) method 1:801
 double torsion (DT) method 1:799, 1:800f
 constant displacement rate method 1:801
 constant loading test 1:800
 crack growth rate 1:800
 load relaxation test 1:800–801
 specimen and loading configuration 1:799
 stress intensity factor 1:799–800
 dynamic tests 1:802
 lifetimes prediction 1:797–799
 modeling in different environments 1:813–815
 oxynitride glasses, SCG resistance of 2:573–574
 slow crack growth, experimental evidence of 1:812
 biaxial strength, experimental evaluation of 1:812
 biaxial strength results in different environments 1:812–813
 reference material and geometry 1:812
 standardized methods and 1:768–769
 static tests 1:802
 standard procedure 1:802
 statistical analysis 1:802–804
 typical ν - K_I curves for glasses 1:804–806
 typical ν - K_I curves for polycrystalline ceramics 1:806
 effect of environment and temperature 1:806
 effect of phase transformation toughening 1:807–808
 grain bridging, influence of 1:807
 microstructural effects 1:806–807
 sub-lattice liquid type 3:18–20
 sublattice models 1:505
 sublimation etching 3:97
 substrate/protein interactions 3:719–721
 subtractive machining (SM) 3:662
 sulfides 1:419
 sulfide solid electrolytes 3:38
 crystalline solid electrolytes 3:38
 glassy and glass-ceramic solid electrolytes 3:38–39
 structural change of 75Li₂S-25P₂S₅ glass during annealing 3:42–45
 structure for Li₂S-P₂S₅ glassy system 3:39–42
 Young’s moduli of the sulfide glasses 3:45–47
 suolunite
 crystal structure of 1:445–446, 1:451f
 properties 1:451t
 supercapacitors 1:6, 1:18
 superconducting materials 3:2, 3:151,
 3:153–156
 compound YBa₂Cu₃O_{7-x} 3:157–159
 critical current density 3:152–153
 high-temperature superconducting (HTSC) cuprates 3:156–157
 iron based superconductors 3:156
 iron selenide thin films 3:160
 magnesium diboride 3:154–156
 1223 and 2223 type compounds 3:159–160
 type 1 superconductors 3:151–152, 3:152f
 type 2 superconductors 3:152, 3:152f, 3:153f
 superconductors 3:2, 1:917–918
 fermi surface in non-magnetic borocarbides 3:164–166
 interplay with magnetism in HoNi₂B₂C 3:167–170
 antiferromagnetic order in HoNi₂B₂C 3:167–170
 multiband coexistence of superconductivity and magnetism in HoNi₂B₂C 3:171–172
 reentrant and near-reentrant behavior 3:170–171
 and magnetism in borocarbides 3:162–163
 symmetry of superconducting gap 3:163–164
 upper critical field for non-magnetic borocarbides 3:166–167
 supercontinuum sources 2:618
 supercooled liquids (SCL) 2:449, 2:450, 2:445
 defined 2:448
 supercritical CO₂ foaming 3:690
 supercritical drying (SCD) 2:691
 superionic conductors 3:18–19
 superparamagnetic iron oxides NPs (SPION) 3:767

superplasticity 1:896–899
 applications of superplasticity 1:899–901
 future trends in superplastic ceramics 1:901
 GBS accommodated by diffusional flow of point defects 1:897–899
 solution-precipitation model 1:899
 super-translucent zirconia 3:823
 surface-active SMOX 3:132–137
 surface charge 3:701–702
 surface charge density 3:402
 surface chemistry 3:703–704
 surface crack in flexure (SCF) method 1:764–766
 surface diffusion 1:237
 surface energy 3:701
 surface functionalization for biomedical applications 3:732
 surface mount devices (SMDs) 3:386
 surface mount technology (SMT) 3:386
 surface tension 1:696–697
 interpretation of melt surface tension 1:699–700
 measurement methods 1:696–697
 levitation technique 1:698–699
 MBP method 1:697–698
 ring method 1:697
 surface topography 3:702–703
 surfactants 1:168
 Surge Arresters 3:254
 surge protection, varistors in 3:254
 suspension plasma spaying (SPS) 3:733–734
 SWCNTs *see* single-wall carbon nanotubes (SWCNTs)
 SW technique *see* shock wave (SW) technique
 Synroc ceramics 2:765
 synthetic polymers 3:467, 3:682–683
 biodegradable polyurethanes 3:683–684
 polypropylene fumarate (PPF) 3:683
 saturated poly- α -hydroxy esters 3:682–683
 system glass-liquid, thermodynamic equilibrium in 1:933–934

T

tailorable thermal expansion ceramics
 derived from metakaolin-based, alkali activated geopolymers 1:432–433
 tangential *T*-strain 1:829
 tape casting 3:115–116, 2:385
 and post-processing 3:437–439
 tape casting of ceramics 1:189
 doctor blade process 1:189–190, 1:191–192, 1:189f
 batching and slip preparation 1:190
 materials selection 1:189–190
 slip conditioning and characterization 1:190–191
 and lamination 1:192–194
 organic systems for 1:190t
 shaping 1:192
 tape process 2:754

taper sectioning 1:639, 1:639f
 TAS *see* triboelectric auditory sensor (TAS)
 TBC *see* thermal barrier coating (TBC)
 TBO *see* total bond order (TBO)
 TBOD *see* total bond order density (TBOD)
 TCO *see* transparent conducting oxide (TCO)
 TCP *see* tricalcium phosphate (TCP)
 TDI network *see* three-dimensional interpenetrating (TDI) network
 TDOS *see* total density of states (TDOS)
 TE *see* tissue engineering (TE)
 TEC *see* thermal expansion coefficient (TEC)
 TECD *see* triboelectric charge density (TECD)
 technetium 2:771
 technical ceramics 1:278
 technological readiness level (TRL) 1:324
 TEM *see* transmission electron microscopy (TEM)
 TEMED *see* tetramethylethylene diamine (TEMED)
 temperature 1:119
 temperature control in MW heating 1:332–333
 temperature-induced phase separation (TIPS) 1:386
 templated grain growth (TGG) 1:367, 1:367–368, 1:368, 1:370f
 templated grain growth of textured ceramics 1:367–368, 1:368–373
 templating 2:386
 TENG *see* triboelectric nanogenerator (TENG)
 ternary MgO–CaO–SiO₂ system 2:472
 testing in mixed-mode fracture 1:833–837
 tetracalcium phosphate (TTCP) 3:624, 3:627, 3:737, 3:572–573
 tetraethoxysilane 3:330
 tetraethylorthosilicate 1:425–426
 tetragonal 1:818
 tetragonal-monoclinic phase transformation 2:94–95
 tetragonal zirconia polycrystals (TZP) 1:820, 3:791–792
 tetramethylethylene diamine (TEMED) 1:151–152
 TeX glasses 2:598
 Textron 2:309–310
 textured piezoelectric ceramics 3:396
 TGA/TG *see* thermogravimetric analysis (TGA/TG)
 TGF *see* transforming growth factor (TGF)
 TGF-beta *see* transforming growth factor beta (TGF-beta)
 TGG *see* templated grain growth (TGG)
 TGS family *see* triglycine sulphate (TGS) family
 thaumasite, properties of 1:445–446, 1:451t
 thermal analysis techniques for technical ceramics and glasses
 differential thermal analysis (DTA) and differential scanning calorimetry 1:676–677
 advanced DTA techniques 1:683
 crystallization of glasses – crystal growth 1:681–682

crystallization of glasses – nucleation 1:682
 degradation, volatilization and melting 1:677–678
 DTA/DSC analysis of phase transformations 1:682–683
 glass transition temperature 1:678–680
 Interpolation of other important glass properties from DTA/DSC data 1:680–681
 dilatometry 1:683–684
 analysis of sintering 1:684–685
 coefficient of thermal expansion (CTE), measurement of 1:685–687
 dilatometric softening point of glasses 1:685–687
 glass transition temperature 1:685–687
 phase transformation 1:685
 thermogravimetric analysis 1:676
 thermal barrier coating (TBC) 1:394, 2:418, 2:64
 thermal conductivity 1:863–865, 3:113
 of carbon-matrix composites 2:358
 thermal etching 1:647
 thermal expansion 2:47–49
 thermal expansion coefficient (TEC) 2:47, 3:371
 thermal explosion 1:41
 thermal fatigue 1:883–886
 fundamental aspects 1:883–886
 microstructural effects 1:886–889
 thermally induced phase separation (TIPS) 3:485, 3:651, 3:689–690
 thermally insulative thermal protection materials 2:362–363
 thermally sprayed materials for biomedical applications 3:732
 bioglasses 3:738–739
 calcium phosphate based bioceramics 3:737–738
 classification of biomaterials used in thermal spray applications 3:735–737
 commercially available applications, examples of 3:741–742
 glass-ceramics 3:739–740
 involved substrates 3:741
 oxides 3:740–741
 research and development topics, examples of 3:742–744
 calcium phosphate materials, suspension spraying of 3:745–746
 dental zirconia implants, ceramic coatings on 3:744–745
 high velocity suspension flame spraying (HVSFS) spraying of metal doped calcium phosphate materials 3:746–747
 tricalciumphosphate (TCP) coatings on poly (D, L-lactic) acid (PDLLA) implants 3:743–744
 surface functionalization for biomedical applications 3:732
 thermal spraying (TS) process 3:732–735
 thermal spraying of biomaterials 3:735
 titanium 3:741

- thermally tempered glass 2:628–630
 commercial tempering processes 2:630
 thermal management of spacecraft
 2:361–363
 atmospheric re-entry 2:361–363
 non-ablative thermal protection
 materials 2:363–364
 thermally insulative thermal protection
 materials 2:362–363
 ceramic thermal control coatings for
 satellites 2:364–365
 thermal properties of ceramic materials
 1:855
 heat capacity 1:857–858
 Debye model 1:858
 example 1:858–859
 high temperature limit of 1:857–858
 intrinsic thermal conductivity 1:860–862
 examples 1:861–862, 1:862–863
 lattice vibrations 1:855–857
 microstructure, influence of 1:863
 heat capacity 1:863
 thermal conductivity 1:863–865
 thermal expansion 1:859–860
 thermal protection system (TPS) 2:360,
 2:361, 2:200
 of spacecraft 2:364
 thermal shock, fracture mechanics of
 1:879–880
 crack propagation analysis 1:880–882
 transient thermal stresses 1:879–880
 thermal shock behavior of ceramics 1:867
 energy balance criterion 1:870–871
 Hasselman Unified Theory 1:871–872
 crack instability, regions of 1:872–873
 degree of damage 1:873–874
 fracture onset, thermal requirement for
 1:872
 propagation of the cracks 1:874–876
 materials, selection of 1:874–876
 thermal stresses 1:867–868
 thermoelastic approach 1:870
 variation of the properties due to thermal
 shock 1:868–869
 thermal shock resistance, microstructural
 effects on 1:882–883
 thermal spraying (TS) process 3:732–735,
 1:382
 of biomaterials 3:735
 thermal stresses, taking advantage of
 2:627–628
 thermal tempering process 2:623,
 2:632–633
 thermal treatment of ceramics 1:233–235
 alternative sintering techniques 1:247
 cold sintering 1:247
 microwave sintering 1:247
 densification kinetics 1:245
 general outline 1:233–235
 liquid phase sintering 1:239–244
 description of matter transport
 mechanisms 1:240–244
 grain growth mechanisms 1:244–245
 pressure and/or plasma assisted sintering
 1:245–246
 flash sintering (FLASH) 1:246–247
 spark plasma sintering (SPS) 1:246
 uniaxial and isostatic hot pressings
 1:245–246
 solid state sintering 1:235–238
 description of matter transport
 mechanism 1:235–238
 grain growth mechanisms (GG)
 1:238–239
 thermodynamic modeling 1:501
 for ceramic systems 1:503
 associate species solution models
 1:503–504
 ionic two-sublattice models for ionic
 liquids 1:505–507
 modified quasichemical model
 1:504–505
 random substitutional models 1:503
 sublattice models 1:505
 Gibbs free energy
 compositional dependence of
 1:502–503
 pressure dependence of 1:501–502
 temperature dependence of 1:501
 thermoelectric glass-ceramics 2:719
 thermoelectrics 1:18
 thermogravimetric analysis (TGA/TG) 1:676
 thermogravimetry 2:691
 thermomechanical properties, applications
 of glass-ceramics exploiting
 2:711–712
 high mechanical properties 2:712–713
 specific uses 2:713
 thermal-shock resistance 2:712
 very high temperature use 2:713
 thermoplastic 3D printing (T3DP) 1:388
 thick film electrodes
 laser annealing of 3:69
 laser drying of 3:69–70
 laser printing of 3:59–60
 thin film PVs 3:9–10
 from amorphous to polycrystalline silicon
 films 3:9–10
 from organic to hybrid structures 3:12–13
 thin-film CdTe, copper indium selenide, its
 alloys and related chalcopyrites 3:10–12
 transparent contact oxides based contacts
 chalcopyrites 3:13
 thorium(IV) chloride, glasses based on
 2:598
 THR *see* Total Hip Replacement (THR)
 three-body interatomic potentials 1:487
 3DBiplotter system 3:487
 3D electrodes, laser structuring for 3:67–69
 three dimensional electron crystallography
 1:618
 automated diffraction tomography (ADT)
 1:623–624, 1:620f, 1:623f
 data processing and analysis 1:624–627
 diffuse scattering 1:629–630
 high pressure modification
 of LaPO_4 1:629
 of SnN_2O 1:627–629
 history 1:618–620
 illumination mode and imaging 1:622–623
 sample preparation and crystal selection
 1:620–622
 TEM set-up and data collection 1:623–624
 three-dimensional electron diffraction (3D-
 ED) 1:618
 3-D forming technologies 3:605–606
 three-dimensional interpenetrating (TDI)
 network 2:216
 three-dimensional printing (3DP) 3:668,
 3:488
see also additive manufacturing (AM)
 and selective laser treatment 2:283
 thrombospondin-2 (TSP2) 3:460–461
 throughput power 3:218–219
 TID *see* Total Iodizing Dose (TID)
 TiO_2 thin films 3:452
 TIPS *see* temperature-induced phase
 separation (TIPS); thermally induced
 phase separation (TIPS)
 tissue engineering (TE) 3:674, 3:467
 tissue engineering scaffold by means of
 mathematical modeling 3:750
 bone tissue engineering, survey on
 mathematical models used in
 3:750–751
 bone tissue systems biology approaches
 3:752–753
 continuum micromechanics,
 homogenization of mechanical
 properties based on 3:751–752
 mechanobiological stimuli, utilization of
 micromechanics for quantification of
 3:753–754
 modeling strategies 3:754–755
 X-ray physics-based analysis of CT data
 3:754
 titania 2:656
 titanium 3:741
 titanium-diboride based ceramics 2:421–422
 titanium dioxide 2:656, 3:681–682
 titanium oxide 3:681–682
 TKR *see* Total Knee Replacement (TKR)
 TMDs *see* transition metal dichalcogenides
 (TMDs)
 TMOs *see* transition metal oxides (TMOs)
 T–M phase transformation 3:541–542
 TM random alloys *see* transition metal (TM)
 random alloys
 TMR effect *see* tunnel magneto-resistance
 (TMR) effect
 t–m transformation temperature 1:818
 TNM model *see*
 Tool–Narayanaswamy–Moynihan
 (TNM) model
 Tool–Narayanaswamy–Moynihan (TNM)
 model 2:452
 topochemical methods 1:5
 torsion pendulum 1:707
 total bond order (TBO) 1:465
 total bond order density (TBOD) 1:441,
 1:444t, 1:447t
 application of 1:443–444
 calcium silicate hydrate (C–S–H) cement
 crystals 1:445–446
 chalcogenide crystals 1:446–450
 intergranular glassy film (IGF) models
 1:450–453, 1:454f
 MAX phases 1:444–445

- total bond order density (TBOD) (*continued*)
 oxides, nitrides, carbides and phosphates 1:443–444
 transition metal carbides 1:446
 biomolecular systems and their interfaces, extension to 1:465–466
 bio-inspired cements 1:467–468
 complex biomolecules 1:465–466
 interfaces of biomolecules and inorganic crystals 1:466–467
 glasses, application of TBOD to 1:453–456
 insulating glasses 1:454–456
 metallic glasses (MGs) 1:456–457
 metal-organic frameworks glasses 1:459–461
 methods and approach 1:441–442
 crystal structure and supercell models 1:441–442
 electronic structure and interatomic bonding 1:442
 physical properties calculation 1:442–443
 transition metal (TM) random alloys, extension to 1:461–463
 high entropy alloys (HEA) 1:461–463
 Ni-based superalloys 1:463–465
 total density of states (TDOS) 1:442
 total hip replacement (THR) 3:511, 3:518*f*, 3:493, 3:553
 oxide ceramic in 3:517–519
 Total Iodizing Dose (TID) 2:360
 Total Knee Replacement (TKR) 3:493, 3:512, 3:514, 3:520
 toxic wastes disposal and recovery 2:722–723
 Toyobo Company 2:307
 TPB *see* triple phase boundary (TPB)
 TPS *see* thermal protection system (TPS)
 traditional ceramics 1:103
 transduction mechanism 3:392–396
 fundamentals of magneto-mechano-electric (MME) effect 3:405–406
 figure of merit 3:406–407
 types of ME transducers 3:406
 piezoelectricity 3:393–396
 ceramic-based piezoelectric materials 3:394–396
 figure of merit for energy harvesting 3:397–398
 impedance matching 3:398
 piezoelectric nanogenerator 3:398–399
 piezoelectric single crystals 3:396
 polymer-based piezoelectric materials 3:396
 selection of piezoelectric materials for energy harvesting 3:396–397
 textured piezoelectric ceramics 3:396
 triboelectricity 3:399–402
 choice of materials for triboelectric harvesters 3:402
 figure of merit (FOM) 3:402–405
 parametric analysis 3:401–402
 transformable zirconia, toughening mechanism in 3:542–544
 transformation induced plasticity (TRIP) 1:818
 transformation kinetics, analysis of 1:87–88
 transformation-toughened ceramics, microstructures and properties of 1:819–821
 transformation-toughened zirconia 1:822
 transformation toughening 1:818, 1:819*f*, 2:227
 theoretical understanding of 1:821–822
 transforming growth factor (TGF) 3:657
 transforming growth factor beta (TGF-beta) 3:753
 transient thermal stresses 1:879–880
 transition aluminas 2:315
 transition metal (TM) random alloys 1:461–463
 high entropy alloys (HEA) 1:461–463
 Ni-based superalloys 1:463–465
 transition metal carbides 1:446
 transition metal dichalcogenides (TMDs) 1:19–21
 transition metal ions and other acceptors, incorporation of 3:317–318
 dipolar defects, formation of 3:318–319
 stabilization of the hexagonal modification 3:317–318
 valence state of transition metal ions in the perovskite lattice 3:318
 transition metal oxides (TMOs) 2:584, 2:580
 transition metals, incorporation of 2:771
 chromium, case of 2:771
 molybdenum, case of 2:771–773
 technetium, case of 2:771
 zirconium, case of 2:771
 transitory liquids, reaction sintering in the presence of 1:279–280
 transmission 2:668
 transmission bandwidth 2:683–684
 transmission electron microscopy (TEM) 1:578, 1:580*f*, 1:581*f*, 1:600, 2:432–433
 brief history 1:578–579
 components of TEM instrument 1:580–583
 lens systems 1:582–583
 electron diffraction 1:591–596
 high-resolution imaging 1:596–598
 image contrast in 1:584–586
 amplitude contrast 1:587–589
 bend contours and thickness fringes 1:589
 crystal defects, contrast of 1:589–591
 elastic scattering 1:585–586
 volume scattering 1:586–587
 resolution and lens aberrations 1:583–584
 sample preparation 1:579–580
 transmission loss 2:684
 transmission physics 1:399–401
 transparent ceramics 1:399, 1:404*t*, 1:405*t*–406, 1:408*t*
 applications 1:408–410
 carbides 1:410–412
 diamond 1:411–412
 silicon carbide (SiC) 1:412–413
 chalcogenides 1:419
 sulfides/selenides 1:419
 chlorides, bromides and iodides 1:420
 coating materials 1:420
 fluorides 1:419–420
 calcium fluoride 1:420
 magnesium fluoride 1:420
 microstructure of 1:409*f*
 nanocomposites 1:420
 nitrides 1:413
 aluminum nitride 1:413–414
 cubic boron nitride (c-BN) 1:414
 SiAlON 1:413
 silicon nitride 1:413
 oxides 1:414
 binary oxides 1:414
 complex oxides 1:416–417
 ferroelectrics 1:417–418
 sesquioxides 1:415
 oxynitrides 1:418–419
 ALON 1:418–419
 phosphides 1:414
 physical properties 1:401–403
 processing 1:403–408
 transmission physics 1:399–401
 transparent ceramics, processing technologies of 3:113–115
 densification methods 3:116–117
 hot forming 3:117
 pressure-assisted sintering 3:117
 pressureless sintering 3:117
 sintering aids 3:117–118
 sintering approaches 3:117
 vacuum sintering 3:116–117
 powders 3:114–115
 shaping 3:115
 dry pressing, granulation 3:115
 slip casting 3:115
 tape casting 3:115–116
 transparent conducting oxide (TCO) 3:13, 3:241, 3:9, 1:418
 transparent conductors 3:241
 transparent/flexible electronics 3:242–247
 TREM2 *see* triggering receptor expressed on myeloid cells 2 (TREM2)
 triaxial testing 1:757
 triboelectric auditory sensor (TAS) 3:413–414
 triboelectric charge density (TECD) 3:402
 strategies for improving 3:402
 triboelectricity 3:391, 3:399–402
 choice of materials for triboelectric harvesters 3:402
 figure of merit (FOM) 3:402–405
 parametric analysis 3:401–402
 charge injection depth 3:401–402
 surface charge density 3:402
 triboelectric charge density, strategies for improving 3:402
 triboelectric nanogenerator (TENG) 3:413–416, 3:391, 3:401, 3:415–416, 3:420–421, 3:400*f*
 solid-liquid contact based TENGs 3:416–418
 solid-solid contact based TENGs 3:413–416
 tricalcium phosphate (TCP) 3:478, 3:626, 3:581, 3:581*t*, 3:596, 3:677–678, 3:466–467

- biological properties 3:586
 in vitro cell tests on TCPs 3:586
 in vivo studies 3:586
 main physicochemical properties of TCP phases 3:584–585
 solubility 3:585
 surface properties of TCP 3:585–586
 TCP phases evolution in aqueous medium 3:585
 thermal stability of TCP phases 3:585
 structures 3:581–582
 TCP-ceramics processing 3:583–584
 cements 3:584
 coatings 3:584
 composites 3:584
 dense and macroporous ceramics 3:583–584
 TCP powders synthesis 3:582
 α - and β -TCP, synthesis of 3:583
 amorphous tricalcium phosphate (am-TCP), synthesis of 3:582
 apatitic tricalcium phosphate (ap-TCP), synthesis of 3:582–583
 tricalciumphosphate (TCP) coatings on poly (D, L-lactic) acid (PDLLA) implants 3:743–744
 triggering receptor expressed on myeloid cells 2 (TREM2) 3:801–802
 triglycine sulphate (TGS) family 3:142
 TRIP *see* transformation induced plasticity (TRIP)
 triple phase boundary (TPB) 3:54–55
 Tris buffer 3:643
 TRL *see* technological readiness level (TRL)
 true microstructure 1:634, 1:635
 TSP2 *see* thrombospondin-2 (TSP2)
 TS process *see* thermal spraying (TS) process
 TSS *see* two-step sintering (TSS)
 T-stress 1:825–826
 TTCP *see* tetracalcium phosphate (TTCP)
 tunable single mode cavity 1:331–332
 tungsten carbide 1:305
 tunnel magneto-resistance (TMR) effect 3:220–221
 two-dimensional superconductivity 3:156–157
 two-photon polymerization (2PP) 1:211
 two-step sintering (TSS) 1:355–356
 type 1 superconductors 3:151–152, 3:152f
 type 2 superconductors 3:152, 3:152f, 3:153f
 Tyranno fibers 2:313
 TZP *see* tetragonal zirconia polycrystals (TZP)
- U**
- UHMWPE *see* ultrahigh molecular weight polyethylene (UHMWPE)
 UHTC *see* ultra-high temperature ceramics (UHTC)
 UHTCMCs *see* ultra-high temperature ceramic matrix composites (UHTCMCs)
- ULTCC *see* ultra-low temperature co-fired ceramic substrates (ULTCC)
 ultracapacitors, laser printing of 3:61–62
 ultrahigh molecular weight polyethylene (UHMWPE) 3:553, 3:493, 3:518, 3:519, 3:476
 ultra-high temperature ceramic matrix composites (UHTCMCs) 2:340, 2:349, 2:225–226, 2:16, 2:20
 future prospects 2:349
 mechanical properties 2:346–348
 preparation via non-sintering routes 2:340–341
 chemical vapor deposition/infiltration (CVD or CVI) 2:341
 precursor/polymer infiltration and pyrolysis (PIP) 2:340–341
 reactive melt infiltration (RMI) 2:341
 preparation via sintering routes 2:341–343
 continuous fibers, UHTCMCs with 2:343–344
 short fibers, UHTCMCs with 2:342–343
 slurry infiltration and sintering (SIS) 2:342–343
 thermo-ablative performance 2:348–349
 variations in manufacture of 2:344–345
 electrophoretic deposition (EPD) 2:345–346
 functionally graded composites 2:344–345
 ultra-high temperature ceramics (UHTC) 3:443, 2:294
 oxidation of 2:442–443
 ultra-low temperature co-fired ceramic substrates (ULTCC) 3:446–447, 3:437, 3:439t, 3:447t, 3:447f, 3:448f
 ultraphosphate glass 2:582–583
 ultraphosphates 3:568
 ultrasonic imaging 3:292
 ultrasonic motor 3:426, 3:429–430, 3:431
 ultrasonic sprayed aerosol for ultrafine ceramic powder synthesis 1:69–70
 core-shell particles and advanced structures 1:79
 advanced morphology of particles obtained by spray pyrolysis 1:79–81
 porous particles 1:79
 generic spray pyrolysis set-up 1:71–72
 aerosol generator device 1:71–72
 powder traps 1:73
 pyrolysis set-up 1:72–73
 nanopowders size and composition, control of 1:75
 grain morphology control through precursor solution in laser spray pyrolysis 1:75–76
 nanopowders synthesis in GdCeO system 1:75
 nanopowders synthesis in SiCN system 1:77–79
 towards complex crystalline structures 1:76–77
 nebulization techniques 1:70
 aerosol generation 1:70
 modelization 1:70–71
 particles growth phenomena 1:73–75
- ultra-translucent zirconia 3:822–823
 ultraviolet light treatment 3:709
 undamped precessions 3:187–188
 uniaxial lamination 1:193
 uniaxial pressing 1:138–139
 unit cell indexing 1:554
 UV light-mediated photofunctionalization 3:709
 UV optical components 2:616
- V**
- VACNTs *see* vertically aligned carbon nanotubes (VACNTs)
 vacuum bag 1:193
 vacuum casting 1:150, 1:149–150, 1:149f
 vacuum de-airing 1:191
 vacuum sintering 3:116–117
 vacuum ultraviolet (VUV) excitation 3:89
 doping ion and conduction band states, absorption involving 3:89–90
 doping ion and valence band states, absorption involving 3:90–91
 host-sensitized luminescence 3:91–92
 rare earth center, excitations in 3:89
 valence compensation, substitutions with 3:352–353
 vanadium oxide thin films 3:64
 vapor transport 1:237
 variable pressure scanning electron microscopy (VPSEM) 1:658
 Variable Specific-Impulse Magneto-Plasma (VASIMR) 2:370
 varistors 3:241
 failure mechanisms of 3:263–266
 practical guidelines 3:266–269
 in surge protection 3:254
 zinc oxide 3:254–257
 varistors microstructure
 modeling of 3:260–263
 nonuniformity of 3:257–260
 vascular endothelial growth factor (VEGF) 3:719, 3:474
 VASIMR *see* Variable Specific-Impulse Magneto-Plasma (VASIMR)
 VASP *see* Vienna Ab initio simulation package (VASP)
 vat photopolymerization 1:393–394, 1:211–212
 vat polymerization 3:608, 3:664–666
 applications 3:665–666
 VBr *see* Vertical Bridgman (VBr)
 VCS *see* volume combustion synthesis (VCS)
 Vectran fiber 2:306–307, 2:305t
 VEGF *see* vascular endothelial growth factor (VEGF)
 Vertical Bridgman (VBr) 3:104
 vertically aligned carbon nanotubes (VACNTs) 1:6–7, 1:7–8, 1:7f, 1:8f
 vertical nanowire integrated nanogenerator (VNG) 3:399
 very large scale integration (VLSI) chips 3:145–146
 VFT method *see* Vogel-Fulcher-Tahmann (VFT) method

vibrating sample magnetometer (VSM) 3:228

vibrational spectroscopy

- amorphous tetrahedral semiconductors 1:530–531
- borate and phosphate glasses 1:533–534
- carbonate and nitrate glasses 1:532–533
- chalcogenide glasses 1:531–532
- fluoride glasses 1:534
- IR and Raman spectroscopy 1:530
- silicate and aluminosilicate glasses 1:532

Vickers cracks, calculation of bridges stresses from of COD in 1:790–791

Vickers indentations 1:728

Vickers test 1:718

Vienna Ab initio simulation package (VASP) 1:442, 1:464–465

viscosity 1:690–691

- characterization procedure of viscosity data 1:692–693
- defined 2:623
- measurement methods 1:690–691
- levitation method 1:691–692
- rotating cylinder method 1:690–691
- versus temperature in glass 2:623

viscous flow versus creep, defined 2:448

viscous sintering 1:265

- future directions 1:268
- sintering models 1:265–266
- sintering rate, factors affecting 1:266–267
- sintering under constraint 1:267–268
- constitutive equation 1:267–268
- practical applications 1:268

vitreloy 1:457–459

vitreous P_2O_5 (v- P_2O_5) 2:581–582

vittrification 2:535

VLSI chips *see* very large scale integration (VLSI) chips

VNG *see* vertical nanowire integrated nanogenerator (VNG)

Vogel-Fulcher-Tahmann (VFT) method 2:544

Voight-Reuss-Hill (VRH) polycrystals approximation 1:443

voltage constants, derivation of 1:479

volume combustion synthesis (VCS) 1:50

volume scattering 1:586–587

Voronoi network 3:260

VPSEM *see* variable pressure scanning electron microscopy (VPSEM)

VRH polycrystals approximation *see* Voight-Reuss-Hill (VRH) polycrystals approximation

VSM *see* vibrating sample magnetometer (VSM)

VUV excitation *see* vacuum ultraviolet (VUV) excitation

W

wall slip 1:170

waste of electrical and electronic equipment (WEEE) 3:358

wastes, glass-ceramics from 2:721–722

radioactive product confinement 2:721–722

toxic wastes disposal and recovery 2:722–723

WAT *see* Water Adsorption Test (WAT)

Water Adsorption Test (WAT) 1:165

waveguides and applicators 1:330–331

- microwave generators 1:332
- multimode cavity 1:332
- temperature control in MW heating 1:332–333
- tunable single mode cavity 1:331–332

wavelength dispersive spectrometry (WDS) 1:656–657, 1:660

wavelength dispersive X-ray analysis 1:659–660

wave propagation

- in an ideal transparent refracting medium 2:659–660
- in vacuum 2:658–659
- in a weakly absorbing medium 2:660

WAXS *see* wide-angle X-ray scattering (WAXS)

WDS *see* wavelength dispersive spectrometry (WDS)

weak matrix concept (WMC) 2:270–271

weak phase object approximation (WPOA) 1:597

wear 2:427–428

wear and erosion resistant ceramic coatings 2:425

- nanocomposite hard coatings, formation of
- by mixing processes 2:433–435
- by post-deposition annealing 2:435–437

physical vapor deposition (PVD) methods 2:430–431

- energy delivered to the growing film 2:431
- mixing processes 2:431–432

structure and property control in hard coatings 2:430

tribology 2:425–427

- erosion 2:428–429
- friction 2:425–427
- wear 2:427–428

wear reduction 2:429–430

wear and erosion resistant ceramic materials 2:416

- alumina based ceramics 2:418
- boron carbide materials 2:421
- ceramic materials and ceramic matrix composites, development of 2:416–418
- high entropy ceramics 2:422
- silicon carbide based ceramics 2:420–421
- silicon nitride based ceramics 2:419–420
- titanium-diboride based ceramics 2:421–422
- wear and erosion evaluation 2:416
- zirconia based ceramics 2:418–419

wear reduction 2:429–430

WEEE *see* waste of electrical and electronic equipment (WEEE)

Weibull modulus 3:772

Weibull plot 3:786–787

Weibull theory 1:811

Werthamer-Helfand-Hohenberg (WHH) behavior 3:167

wet bag route 1:138

wet-chemically prepared films 3:220

wet chemical routes, synthesis of ceramic powders by 1:27

- bulk liquid phase, chemistry in 1:27–28
- precipitation 1:30–31
- sol-gel synthesis 1:27–28

droplet, chemistry in 1:35–36

- emulsion and microemulsion synthesis 1:35–36
- spray-based syntheses 1:37–38

heterogeneous phases, chemistry between 1:31–32

- molten salt synthesis 1:33–34
- solvothermal synthesis 1:31–32

wettability 3:702

wetting 1:114, 2:400

WHH behavior *see* Werthamer-Helfand-Hohenberg (WHH) behavior

whisker 1:903–904, 2:231

whisker composites, properties of 2:230–231

- creep behavior 2:231
- SiC(W)
- alumina composites 2:230–231
- matrices composites 2:231

whisker reinforcement 2:228

whitewares 2:67–68

wide-angle X-ray scattering (WAXS) 2:468

WMC *see* weak matrix concept (WMC)

working point 2:651

WPOA *see* weak phase object approximation (WPOA)

wrist implants 3:535–536

X

XANES *see* X-ray absorption near edge spectroscopy (XANES)

XAS *see* X-ray absorption spectroscopy (XAS)

xenografts 3:475–476, 3:647

xerogels 2:692

XPS *see* X-ray photoelectron spectroscopy (XPS)

X-ray absorption near edge spectroscopy (XANES) 1:443

X-ray absorption spectroscopy (XAS) 3:221–222

X-ray analysis 1:658

- characterization of ceramic microstructures 1:661
- energy dispersive spectroscopy (EDS) 1:660
- energy dispersive X-ray analysis 1:658–659
- information sources 1:661
- uses of 1:660–661
- wavelength dispersive spectrometry (WDS) 1:660
- wavelength dispersive X-ray analysis 1:659–660

X-ray diffraction (XRD) 3:604, 3:629–630
 X-ray diffraction dicalcium phosphate dihydrate 3:631–632
 in vivo use of calcium phosphates 3:631–632
 X-ray diffraction of ceramics, case studies in 1:560
 cordierite honeycomb substrates, anisotropic thermal expansion behavior of 1:564–566
 characterization of phase transformations during reactive sintering 1:564–566
 characterization of textures in green and fired bodies 1:566–567
 characterization of thermal expansion behavior 1:567–569
 diffraction conditions and diffracted intensity 1:560
 diffraction peak shifts and broadening 1:561–562
 penetration depth of X-rays 1:562–563
 piezoelectric glass ceramics, development of 1:569–570
 characterization of thermal expansion of Sr-fresnoite crystals 1:573–575, 1:575–576
 investigation of crystallization of a glass-ceramic 1:570
 investigation of internal stresses due to thermal expansion mismatch 1:570–575
 investigation of preferential orientation 1:570
 investigation of the influence of barium substitutions 1:576
 Rietveld method 1:563–564
 X-ray diffractometer 1:560–561
 X-ray diffractometer 1:560–561
 X-ray photoelectron spectroscopy (XPS) 1:517, 2:562, 3:578
 X-ray physics-based analysis of CT data 3:754
 X-ray powder diffraction 1:549
 applications of 1:553
 crystallite size 1:555–556
 in situ analysis 1:556–557
 pair distribution functions (PDF) method 1:558–559
 phase identification 1:553
 preferred orientation 1:555
 profile fitting and rietveld analysis 1:556
 quantitative phase analysis 1:553–554
 refining accurate lattice parameters 1:554–555
 residual stress 1:556
 structure solution 1:557–558
 unit cell indexing 1:554
 instrumentation for 1:551–552
 modern X-ray detectors 1:552–553
 parallel-beam diffractometers 1:552
 traditional parafocusing instruments 1:551–552
 origins of 1:549–551
 X-rays Scattering 2:691
 XRD *see* X-ray diffraction (XRD)

Y

YAG fibers 2:316, 3:118–119
 yield stress 1:170
 YIG *see* yttrium iron garnets (YIG)
 YMCK *see* Yokohama Medical Ceramic Knee (YMCK)
 Yokohama Medical Ceramic Knee (YMCK) 3:512
 Young's modulus 1:771, 2:210–212, 1:723, 1:724, 3:228–231, 3:45–47, 1:745, 1:747, 1:749, 1:443, 2:83
 of sulfide glasses 3:45–47
 Young's modulus, determination of 1:745
 definition 1:745
 direct methods 1:748
 bending tests 1:749–750
 general considerations 1:748
 instrumented indentation 1:750–751
 sample size 1:748
 uniaxial compression tests 1:748–749
 uniaxial tension tests 1:748
 vibration methods 1:745–746
 forced vibration 1:747
 free and forced vibration 1:746–747
 impulse excitation method 1:747–748
 ultrasonic propagation 1:745–746
 YSZ *see* yttria-stabilized zirconia (YSZ)
 ytterbium 2:585
 yttria 1:415–416
 yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) 3:512, 3:553, 1:849, 1:822
 yttria-stabilized zirconia (YSZ) 3:540–541, 2:294, 1:160
 main features of 3:541–542
 optical properties of 3:548–549
 past, present and future of Y-TZP zirconia 3:549–551
 phase transformation by grinding 3:544–545
 T-M phase transformation 3:541–542
 transformable zirconia, toughening mechanism in 3:542–544
 zirconia-based biomedical implants 3:545–548
 yttrium iron garnets (YIG) 3:220
 Y-TZP *see* yttria-stabilized tetragonal zirconia polycrystal (Y-TZP)

Z

Zachariasen-Warren continuous random network model 2:486
 Zeeman splitting 1:536
 zeolite catalysis 2:387–388
 zeolites 1:544–545
 zeolitic imidazolate frameworks (ZIFs) 1:459
 Zero Order Laue Zone (ZOLZ) 1:592, 1:595
 ZIFs *see* zeolitic imidazolate frameworks (ZIFs)
 zinc, glasses based on 2:605
 zinc bromide, glasses based on 2:600

zinc chloride, glasses based on 2:598
 zinc iodide, glasses based on 2:601
 zinc oxide 3:3, 2:655
 -based compositions 3:302
 -based electronics and photonics 3:3
 future perspectives 3:250–251
 light emitters 3:247–248
 optical filtering 3:241
 sensors 3:248–250
 solar 3:241–242
 transparent conductors 3:241
 transparent/flexible electronics 3:242–247
 varistors 3:241
 varistors 3:254–257
 varistor electrical properties 3:3
 ZnO multilayer ceramic varistors, latest trend of 3:3
 zinc selenide 1:419
 zinc sulfide 1:419
 zirconia 3:441, 1:414–415, 3:511, 3:514–515
 alumina-zirconia composites 3:516–517
 biocompatibility 3:516
 chemical-physical and mechanical properties 3:514–515
 radioactive impurities 3:515
 mechanical spectroscopy of 1:707–711
 grain size effect 1:711–713
 low temperature peak 1:707–711
 stability in zirconia ceramics 3:515–516
 yttria-stabilized *see* yttria-stabilized zirconia (YSZ)
 zirconia ceramics 2:93–95, 2:418–419
 aging of 2:100
 applications of 2:102–103
 refractories 2:102–103
 zirconia electrolytes 2:103
 background 3:817–818
 biomedical grade zirconia in fixed and removable prosthodontics 3:818–820
 biocompatibility 3:821–822
 dental zirconia ceramics, bonding to 3:818–820
 elastic modulus and hardness mismatch 3:821
 translucency 3:820–821
 veneered overlayer, delamination and chipping of 3:820
 compressive surface layers 2:100
 for dentistry 3:827–828
 emerging additive manufacturing of zirconia dental ceramics 3:827
 full-contour monolithic zirconia and minimally invasive dentistry 3:822
 glazing and staining 3:823
 high-translucency zirconia (4Y, 5Y) grades 3:822
 self-glazed zirconia ceramics 3:823–824
 microcrack toughening 2:96
 phase relationships 2:96–97
 ZrO₂-CeO₂ 2:98–100
 ZrO₂-MgO 2:96–97
 ZrO₂-Y₂O₃ 2:97–98
 stress-induced transformation toughening 2:95–96

- zirconia ceramics (*continued*)
 synthesis of doped zirconia powders for
 ceramic processing 2:100–102
 tetragonal-monoclinic phase
 transformation 2:94–95
 zirconia ceramics (LTD), aging of 2:100
 zirconia oral implantology 3:824–825
 Ce-TZP-aluminate pseudoplastic
 ceramic composite 3:827
 clinical performance of zirconia oral
 implants 3:825–827
 implant stability 3:825
 implant systems 3:825
 zirconia-based implant materials 3:825
 zirconia toughened alumina (ZTA) 1:901,
 3:494, 2:26, 2:18, 3:516, 1:807–808,
 3:741, 3:553, 3:558–559
 manufacturing 3:559–564, 3:458
 reinforcement mechanisms 3:556–557
 microcracking 3:557
 residual stress 3:557–558
 third phases 3:558
 transformation toughening 3:557
 set of requirements and the resulting current
 standard ISO6474-2 3:558–559
 tailoring of the microstructure 3:554–556
 zirconia-toughened ceramics (ZTC) 1:820,
 3:774, 3:553, 3:558
 mechanical properties of 3:775–776,
 2:228–229
 creep and fatigue behaviors 2:230
 effect of size and amount of zirconia
 particles on toughening 2:228–229
 effect of solute content and temperature
 2:229–230
 zirconium 3:822, 2:771
 zirconium diboride 2:443
 zirconium dioxide ceramics 1:928–929,
 2:656
 zirconyl phosphate 2:53–54
 ZnO based PENGs 3:409
 ZnO multilayer ceramic varistors 3:272
 discovery of ZnO varistors, and issues of
 conventional materials 3:272–273
 MLCVs cofired with internal electrodes of
 base metal 3:277–278
 enhancement of nonlinearity by
 increasing P-type carriers at grain
 boundaries 3:278–279
 MLCVs cofired with internal electrodes
 of base metal 3:279
 nonlinearity of SrCoO₃-doped ZnO
 varistors co-fired with base metal
 3:277–278
 MLCVs using SrCoO₃-doped ZnO varistors
 3:275
 new varistor material, development
 direction of 3:273
 Bi/Pr-doped ZnO varistors,
 characteristics for grain boundaries in
 3:273
 effect of thermal properties of
 compositional materials on ESD
 stability 3:273–274
 novel low-voltage ZnO varistor material
 with ESD withstanding 3:274–275
 ultralow-capacitance MLCVs with a
 discharge cavity 3:275–277, 3:275f
 ZOLZ *see* Zero Order Laue Zone (ZOLZ)
 ZrB₂, HfB₂, OsB₂ and IrB₂ boride ceramics
 2:200
 nanoindentation of 2:207–210
 indentation strain behavior, elasticity
 and ductility indices of 2:210–212
 methodology 2:207–210
 processing of 2:200–202
 structure of 2:202–203
 crystal structure 2:203
 microstructure 2:203–207
 Z-scan 2:549–550
 ZTA *see* zirconia toughened alumina (ZTA)
 ZTC *see* zirconia-toughened ceramics (ZTC)
 Zyon *p*-phenylene benzobisoxazole fiber
 2:308f